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KINETIC PROPERTIES OF NATURAL ZEOLITES OF CLINOPTILOLITE AND MORDENITE TYPES OBTAINED FROM THE DEPOSITS IN EAST AND CENTRAL SLOVAKIA

Sorption and ion exchange properties of natural clinoptilolite from the Nížný Hrabovec deposit and natural mordenite from Bartošova Lehôtka-Jastrabá deposit were investigated. Kinetics and thermodynamics of the process and the effects of ionic strength of NaCl on metal desorption were tested. Rate constants, equilibrium constants, diffusion coefficients as well as selectivity series for the cations tested in the model systems were estimated. Adsorption isotherms of the linearized and nondimensional shapes for the systems of clinoptilolite/metal solutions as well as the dependence of the selectivity coefficient upon the saturation degree of the solid phase were graphically presented. For a better description of the ion exchange reactions on zeolite, the thermodynamic quantities were assessed.

SYMBOLS AND ABBREVIATIONS

- a* – sorption capacity of zeolite with respect to ions investigated, mmol/g, mg/g,
c – concentration of the ions investigated in solution, mg/dm³, mmol/dm³,
D – diffusion coefficient, cm²/s,
*k*₁ – rate constant of surface ion diffusion, 1/s,
*k*₂ – rate constant of internal ion diffusion, 1/s,
K – equilibrium constant,
r – diameter of zeolite grains, cm,
X – mass fraction of the component investigated in liquid phase (concentration degree),
Y – mass fraction of the component investigated in solid phase (saturation degree).

1. INTRODUCTION

To evaluate the efficiency of sorption of metal cations and NH₄⁺ from various types of waters (specially from wastewaters discharged from the metallurgical industry) on natural

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zeolites, it is necessary to conduct a preliminary investigation of the basic kinetic properties of those materials.

The kinetics of the ion exchange for the system such as natural and modified zeolite-model solutions of metal cations and NH_4^+ as well as selectivity and adsorption capacity of the materials and the effect of temperature on the process were investigated in the present work.

Some thermodynamic variables of the system such as natural clinoptilolite-water solution of NH_4^+ ions and activation energy of the process were also determined.

2. MATERIALS AND METHODS

2.1. CHEMICAL AND MINERALOGICAL COMPOSITION OF ZEOLITE TUFFS

The clinoptilolite tuff occurs in the deposits Nižný Hrabovec in East Slovakia.

Semiquantitative composition of this tuff was determined by means of the RTG phase analysis (diffractometr Phillips: radiation CuK, voltage 40 kV, intensity 20 mA, Ni- filter, diaphragm 1,021) as follows [1]: clinoptilolite ca. 60%, cristobalite 20–25%, feldspars 10–15%, quartz ca. 5%.

Chemical composition of the clinoptilolite tuff:

SiO_2 – 70.06%,
 Al_2O_3 – 12.32%,
 Fe_2O_3 – 1.48%,
 CaO – 3.42%,
 MgO – 0.96%,
 TiO_2 – 0.71%,
 P_2O_5 – 0.05%,
 MnO – 0.02%,
 Na_2O – 0.68%,
 K_2O – 2.83%,
 $\text{SO}_3(\text{total})$ – 0.17%,
 H_2O – 8.19%.

The mordenite tuff originates from the site Bartošova Lehôtka–Jastrabá in Central Slovakia. Mineralogical composition of this tuff is as follows: mordenite ca. 40%, cristobalite, quartz, vulcanic glass ca. 30%, feldspars ca. 15%, mica ca. 6%, clays ca. 6%.

Chemical composition of the mordenite tuff:

SiO_2 – 70.04%,
 Al_2O_3 – 12.23%,
 Fe_2O_3 – 1.31%,
 CaO – 1.90%,
 MgO – 0.37%,
 TiO_2 – 0.12%,
 P_2O_5 – 0.02%,
 MnO – 0.03%,

Na₂O – 0.78%,
 K₂O – 3.43%,
 SO₃(total) – 0.03%,
 H₂O – 9.64%.

2.2. PREPARATION OF MODIFIED FORMS OF CLINOPTILOLITE

The samples of granular zeolite of the grain size ranging within 0.2–0.7 mm (about 10 g in 1 dm³ of the solution) were shaken in a shaker containing 10% salt solution (ammonia salt or salt of metal cations) for 3 days, followed by decantation of zeolites in distilled water. The decantation of zeolites in distilled water was considered as completed after reaching a minimum concentration of Cl⁻ ions in the washing water. The samples were then dried at 105°C up to constant weight.

2.3. ANALYTICAL METHODS AND EXPERIMENTAL

Concentration of ammonia was determined according to the Nessler method, concentration of metals in solutions, by atomic absorption spectrophotometry (Perkin-Elmer apparatus and flame technique).

Selectivity properties of the chosen zeolite types were compared under static conditions in isomolar acid water solutions of inorganic metallic salts.

Model solutions of ammonia ions have been prepared from ammonium chloride (p.a.) in distilled water.

The concentration of the ions tested in water solutions was 10⁻³ mol/dm³.

The bath (static) experiments were carried out as follows: Each of 100 cm³ samples of the model solution in the 250 cm³ Erlenmeyer flask was mixed with 1g of the dried zeolite tuff by means of horizontal shaker. After 2.5 h the concentration of the ions did not change significantly. Thereupon the suspension was filtered and ion concentrations in the solution and zeolite were determined.

Simultaneously the effect of NaCl concentration on desorption of metal cations from zeolite was investigated under static equilibrium conditions.

3. RESULTS AND DISCUSSION

3.1. KINETIC AND THERMODYNAMIC PROPERTIES OF THE MODEL SYSTEMS: ZEOLITES-WATER SOLUTIONS

The process of ion exchange on zeolite in the time range from t_0 to t_∞ can be described by two mechanisms, i.e. surface diffusion and internal diffusion.

The rate constant of the surface diffusion of ions investigated through the sorbent may be evaluated on the basis of the following equation [2]:

$$k_1 = \frac{da/dt}{cK}$$

where da/dt is the adsorption rate of ions. It can be evaluated graphically using the tangent formed by the gradient line issuing from the beginning of the coordinates $a-t$ (fig. 1).

As the contact time is prolonged, the degree of ion exchange increases and finally the sorption changes to internal ion exchange enabled by diffusion. In the given case the diffusion coefficient (D) and the rate constant (k_2) may be obtained according to the following equations [3]:

$$\frac{a}{a_{\max}} = \frac{6}{r} \left(\frac{Dt}{\pi} \right)^{1/2}, \quad (2)$$

$$D = \frac{\pi r^2}{36} \tan^2 \alpha, \quad (3)$$

$$k_2 = \frac{\pi^2 D}{r^2}. \quad (4)$$

Kinetic characteristics of the ion exchange process in the clinoptilolite/water solutions of NH_4^+ , Pb^{2+} , Cu^{2+} , Zn^{2+} system and the analogous system with mordenite are presented in table 1 and in fig. 1.

Table 1

Kinetic characteristics of the ion exchange process for the systems consisting of clinoptilolite (C) or mordenite (M) and 0.001 M water solutions of NH_4^+ , Pb^{2+} , Cu^{2+} , Zn^{2+} ions

Ion exchange system	External diffusion			Internal diffusion		
	Degree of exchange (%)	da/dt (mmol/gs)	K^*	k_1 (1/s)	D (cm^2/s)	k_2 (1/s)
C/ NH_4^+	61.7	$5.5 \cdot 10^{-5}$	413.6	$2.39 \cdot 10^{-4}$	$2.21 \cdot 10^{-7}$	$1.07 \cdot 10^{-3}$
M/ NH_4^+	50.0	$4.4 \cdot 10^{-5}$	321.3	$2.18 \cdot 10^{-4}$	$1.14 \cdot 10^{-7}$	$7.05 \cdot 10^{-4}$
C/ Cu^{2+}	60.4	$2.7 \cdot 10^{-5}$	68.5	$5.00 \cdot 10^{-4}$	$1.93 \cdot 10^{-7}$	$9.39 \cdot 10^{-4}$
M/ Cu^{2+}	55.5	$2.2 \cdot 10^{-5}$	52.3	$4.90 \cdot 10^{-4}$	$1.52 \cdot 10^{-7}$	$9.30 \cdot 10^{-4}$
C/ Zn^{2+}	50.0	$1.4 \cdot 10^{-5}$	46.3	$4.30 \cdot 10^{-4}$	$9.70 \cdot 10^{-8}$	$4.70 \cdot 10^{-4}$
M/ Zn^{2+}	55.0	$1.2 \cdot 10^{-5}$	33.9	$5.00 \cdot 10^{-4}$	$8.70 \cdot 10^{-8}$	$5.30 \cdot 10^{-4}$
C/ Pb^{2+}	60.0	$6.3 \cdot 10^{-5}$	793.2	$1.56 \cdot 10^{-4}$	$2.40 \cdot 10^{-7}$	$1.16 \cdot 10^{-3}$
M/ Pb^{2+}	48.2	$3.0 \cdot 10^{-5}$	109.4	$3.39 \cdot 10^{-4}$	$8.90 \cdot 10^{-8}$	$5.48 \cdot 10^{-4}$

* $K = a_{\text{eq}}/c_{\text{eq}}$.

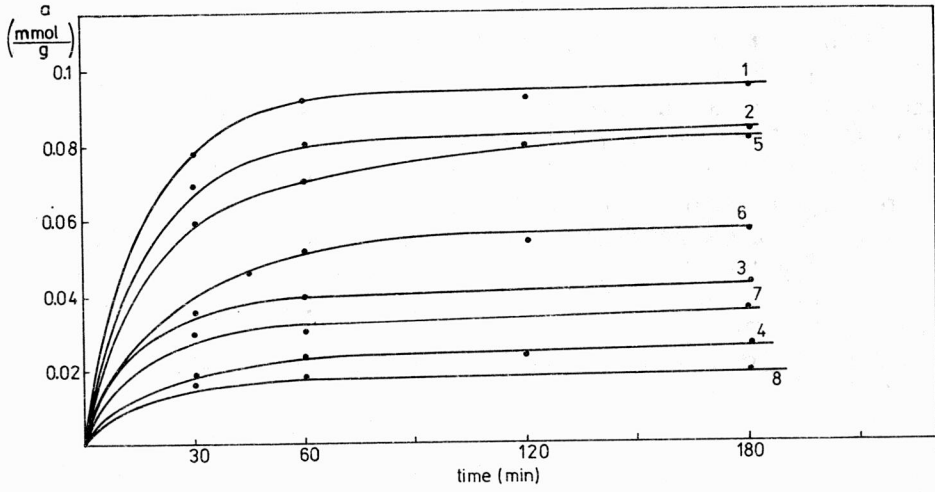


Fig. 1. Kinetics of ion exchange in the following systems: natural clinoptilolite (NC)/water solutions of Pb^{2+} ions (1), NC/ NH_4^+ ions (2), NC/ Cu^{2+} ions (3), NC/ Zn^{2+} ions (4), natural mordenite (NM)/water solution of NH_4^+ ions (5), NM/ Pb^{2+} ions (6), NM/ Cu^{2+} ions (7), NM/ Zn^{2+} ions (8)

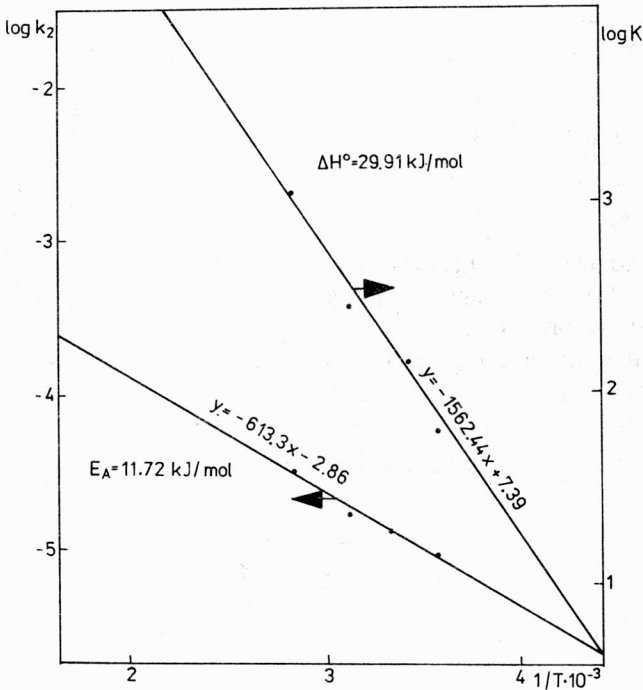


Fig. 2. Logarithmic dependence of the rate and equilibrium constants upon temperature in the system consisting of natural clinoptilolite and water solution of NH_4^+ ions

On the basis of values obtained, the following conclusions may be drawn:

1. The capacity of zeolite tuffs to cations investigated is correlated with the equilibrium constant according to the following selectivity series: $\text{Pb} > \text{NH}_4 > \text{Cu} > \text{Zn}$ (clinoptilolite), $\text{NH}_4 > \text{Pb} > \text{Cu} > \text{Zn}$ (mordenite).

2. In the prevailing part of the cations investigated the degree of exchange as a result of external diffusion amounts to $\geq 50\%$.

3. The diffusion coefficient and the rate constant of the internal diffusion decrease in the case of clinoptilolite tuff according to the following selectivity series: $\text{Pb} > \text{NH}_4 > \text{Cu} > \text{Zn}$. In the case of mordenite tuff, an expressive change in copper position occurred, $\text{Cu} > \text{NH}_4 > \text{Pb} > \text{Zn}$.

The rate constant of the internal diffusion increases with temperature elevation (table 2).

Table 2

Thermodynamic parameters of the ion exchange in the system
of natural clinoptilolite/0.001 mol water solution of NH_4^+ ions

T (°C)	$1/T$ (K^{-1})	k_2 (s^{-1})	K_T	ΔG^0 (kJ mol^{-1})	ΔS^0 ($\text{kJ mol}^{-1}\text{K}^{-1}$)
7	$3.5 \cdot 10^{-3}$	$0.9 \cdot 10^{-5}$	63.9	-9.67	-0.07
20	$3.4 \cdot 10^{-3}$	$1.21 \cdot 10^{-5}$	150	-12.19	-0.06
45	$3.1 \cdot 10^{-3}$	$1.36 \cdot 10^{-5}$	284.6	-14.93	-0.04
75	$2.8 \cdot 10^{-3}$	$2.9 \cdot 10^{-5}$	1150	-20.37	-0.02

Interpreting the results it is necessary to consider the heterogeneous character of both the material formed by crystal aggregation and accompanying minerals. These materials do not sorb the above-mentioned ions in the same manner as zeolites do (chiefly mordenite tuff, the active component content of which does not reach 40%).

For the better description of the ion exchange reactions on zeolite, the thermodynamic quantities (standard enthalpy, free energy, standard entropy) were assessed as well as the activation energy of the clinoptilolite/water solution of NH_4^+ ions system (table 2, fig. 2).

If evaluations concern highly diluted solutions (10^{-3} mol of NH_4Cl), the difference between the value of the activity of the respective component and the ion concentration was neglected, and therefore the equilibrium constant K corresponds to the thermodynamic equilibrium constant K_T [3], [4]:

$$\frac{d \ln K_T}{dT} = \frac{\Delta H^0}{RT^2} \quad (5)$$

$$\Delta G^0 = -RT \ln K_T, \quad (6)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}. \quad (7)$$

As can be seen from fig. 2, the value of the standard enthalpy of the ion exchange reaction on zeolite is low, thus it may be concluded that such a reaction is not a typical chemisorption reaction.

3.2. METAL ADSORPTION ON CLINOPTILOLITE

Due to a high content of the active component in the clinoptilolite tuff, sorption and selective abilities of this zeolite with respect to other metals (Hg, Pd, Cd, Co, Ni) were investigated.

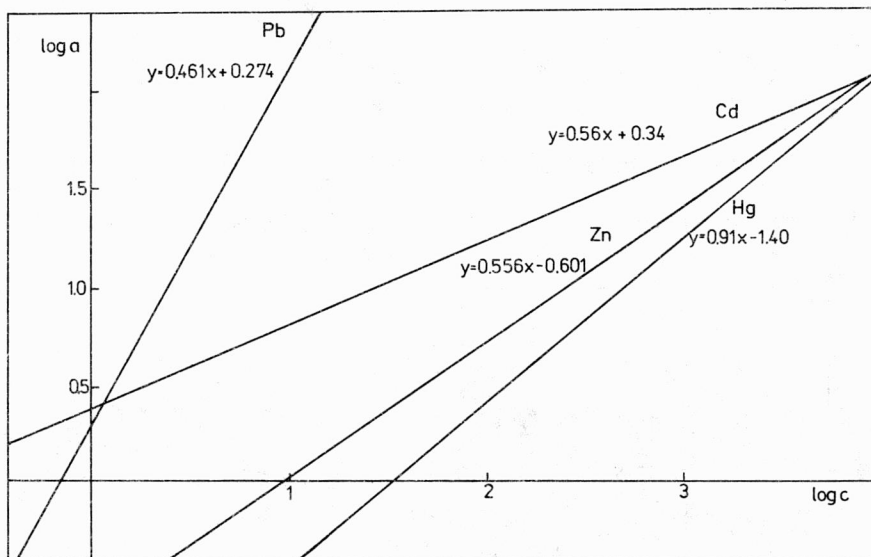


Fig. 3. Linearized shapes of adsorption isotherms of the systems consisting of clinoptilolite and metal solutions

The relationships obtained were expressed by Freundlich isotherm (fig. 3), the empirical constants of which ($a = kc^{1/n}$) increased with the increasing adsorption capacity of the sorbent.

The Pb, NH_4 , Zn in the selectivity series is also expressed by the nondimensional isotherms for monoionic clinoptilolite (fig. 4).

The proper result requires strictly defined conditions. Creation of such conditions requires modification the polyionic natural material to obtain the monoionic one. Therefore we pretreated the natural forms of clinoptilolite (containing Ca^{2+} , Na^+ , Mg^{2+} , K^+ ions) to obtain monoionic form of clinoptilolite (containing Na^+ only).

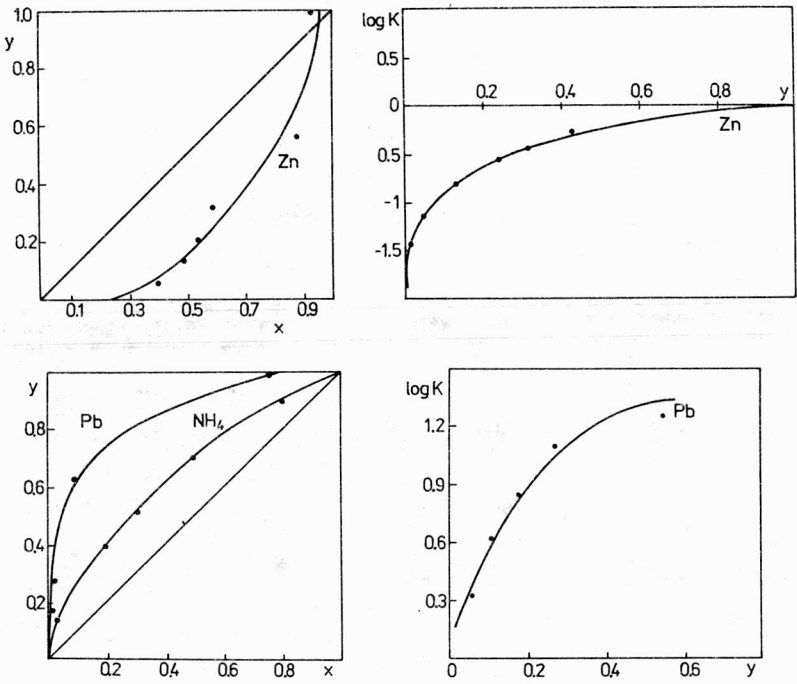


Fig. 4. Nondimensional isotherms of the ion exchange and the dependence of the selectivity upon the saturation degree of the solid phase

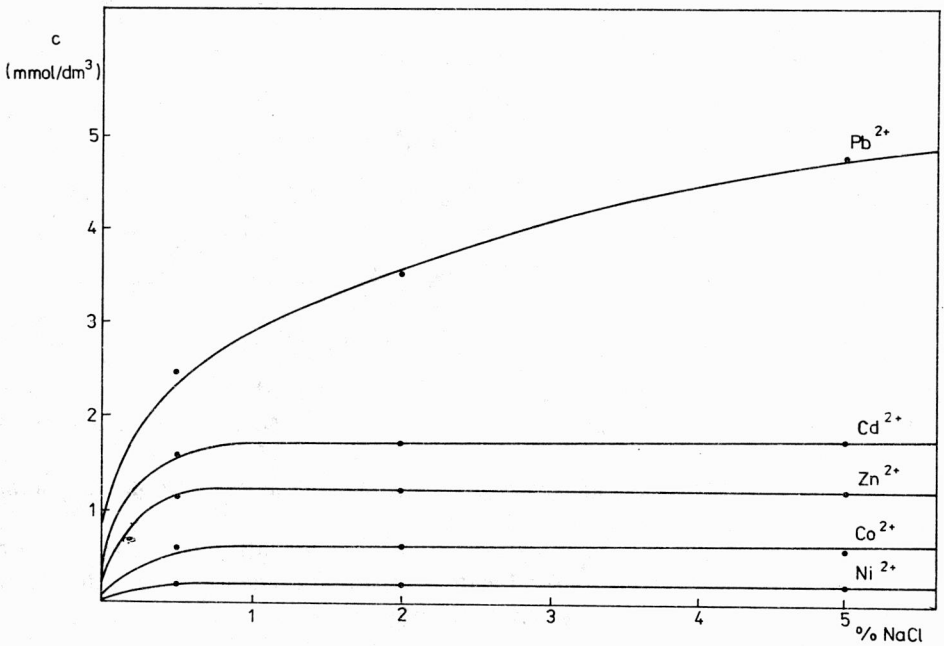


Fig. 5. Effect of NaCl concentration on metal cation desorption from zeolite

Using the mass action law, we can express the selectivity coefficient as:

$$K = \frac{Y(1 - X)}{X(1 - Y)} \quad (8)$$

The course of the straight line in fig. 4, close to ion exchange isotherms, is in agreement with the change of selectivity described by the isotherms.

Investigation of selectivity properties of the Slovak natural clinoptilolite shows that the industrial exploitation of this material is promising, first of all because of its capacity for removing lead and ammonia from polluted waters.

In order to enable the continuous process of such a removal, we test a clinoptilolite regeneration. The improvement of adsorption capacity of clinoptilolite for industrial purposes is carried out mainly in dynamic regime using 0.5–5% solution of sodium chloride.

In laboratory experiments, the regeneration of clinoptilolite was performed under conditions of static desorption.

The desorption of metal cations from the clinoptilolite into the NaCl solutions is shown in fig. 5. It can be seen that except for Pb^{2+} ions the increasing concentration of the regeneration solution does not influence the desorption of Cd^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} ions. Decreasing of cation desorption is in firm agreement with the selectivity series developed [5].

The results obtained correlate with significantly lower ion exchange capacity of clinoptilolite (in relation to the ions mentioned), i.e. with the lower efficiency of ion desorption into regeneration solutions.

4. CONCLUSIONS

Kinetic parameters (table 1) prove that ion exchange systems are mainly characterized by the adsorption process such as external diffusion.

Thermodynamic constants (table 2) show that the exothermic adsorption process cannot be considered as a typical chemisorption reaction. First of all its character is physical and thus the electrostatic interactions are decisive.

Clinoptilolite and mordenite are highly selective in respect to the Pb^{2+} and NH_4^+ ions. These statements are supported graphically by isotherms and kinetic curves.

On the basis of the results obtained it can be stated that the use of natural clinoptilolite in industrial water treatment is more promising than the use of natural mordenite.

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WŁASNOŚCI KINETYCZNE NATURALNYCH ZEOLITÓW TYPU KLILOPTYLOLIT I MORDENIT POCHODZĄCYCH ZE ŻŁÓŻ WE WSCHODNIEJ I CENTRALNEJ SŁOWACJI

Zbadano właściwości sorpcyjne i jonowymienne naturalnego klinoptylolitu pochodzącego ze złóż Nižný Hrabovec i naturalnego mordenitu ze złóż Bartošova Lehôtka–Jastrabá. Określono kinetykę i termodynamikę procesu oraz wpływ siły jonowej NaCl na desorpcję metali. Wyznaczono stałe szybkości reakcji, stałe równowagi, współczynniki dyfuzji oraz szeregi selektywności badanych kationów w układach modelowych. Przedstawiono graficznie zlinearyzowane i bezwymiarowe izotermy adsorpcji oraz zależność współczynnika selektywności od stopnia nasycenia fazy stałej. Aby lepiej opisać reakcje jonowymienne na zeolicie, określono wielkości termodynamiczne.

КИНЕТИЧЕСКИЕ СВОЙСТВА НАТУРАЛЬНЫХ ЦЕОЛИТОВ ТИПА КЛИНОПТИЛОЛИТ И МОРДЕНИТ, ПРОИСХОДЯЩИХ ИЗ МЕСТОРОЖДЕНИЙ В ВОСТОЧНОЙ И ЦЕНТРАЛЬНОЙ СЛОВАКИИ

Исследованы сорбционные и ионообменные свойства натурального клиноптилолита, происходящего из месторождений Нижни Храбовец и натурального мordenита из месторождений Бартошова Лехотка–Ястраба. Определены кинетика и термодинамика процесса, а также влияние ионной силы NaCl на десорбцию металлов. Определены постоянные скорости реакций, постоянные равновесия, коэффициенты диффузии, а также ряды селективности исследуемых катионов в модельных системах. Представлены графически линеаризованные и безразмерные изотермы абсорбции, а также зависимость коэффициента селективности от степени насыщения постоянной фазы. Для лучшего описания ионообменных реакций на цеолите определены термодинамические величины.