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EVALUATION OF BASIC PROPERTIES OF INLAND AND CHINESE ZEOLITES FOR POTENTIAL REMOVAL OF IONIC COMPONENTS FROM LIQUID PHASE

Basic properties of inland and Chinese zeolites for some ionic species removal from simulated low-activity liquid waste have been studied. Domestic clinoptilolite originates from the industrial deposit Nižný Hrabovec, inland mordenite – from the East Slovakian locality of Byšta and Chinese clinoptilolite – from the south-eastern Hubei region. Physicochemical and mineralogical characteristics of the mineral samples were investigated using various techniques, i.e. X-ray powder diffraction, water vapour desorption, ion-exchange and chemical analysis. Concentrations of ions in aqueous solutions have been measured predominantly radiometrically (Ag^+ ions' concentration by atomic absorption spectrometry and by gravimetry). On the basis of the dimensionless ion-exchange isotherms plotted for the systems studied as well as on the basis of the calculated selectivity coefficients, the selectivity preference of zeolites has been concluded and the process has been described mathematically.

LIST OF SYMBOLS

- K – correction coefficient estimating the percentage content of zeolite ore,
- k – correlation coefficient obtained by regression analysis,
- a – amount adsorbed, $\text{mmol}\cdot\text{g}^{-1}$,
- c – equilibrium concentration in solution, $\text{mmol}\cdot\text{dm}^{-3}$,
- X – equivalent ionic fraction of ions in solution, dimensionless variable,
- Y – computed fractional ion-exchange capacity of zeolite occupied by the ions.

1. INTRODUCTION

Zeolites are aluminosilicates with a structure characterized by a reversible ion-exchange and hydration–dehydration capabilities. A three-dimensional framework of zeolites consists of a central silicon or substituted aluminium ion, which are coordinated by oxygen ions, giving the framework of a negative charge, balanced for electroneutrality by exchangeable cations. Owing to these capabilities as well as a large surface area and considerably lower cost than that of the synthetic counterparts, natu-

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rally occurring specimens (i.e. clinoptilolite, mordenite, erionite, phillipsite, chabazite, analcime, ferrierite, laumontite) have aroused a deep interest in world scientific community. Nevertheless, a rapid jump in the prices of raw materials places natural zeolites in an improving price-performance position compared to the synthetic ones.

In consequence of chemical and mineralogical variability of natural zeolites, adsorption and selectivity properties of various deposit zeolite species have not been generalized, but become a scope of the wide national research.

This paper presents fundamental measurements of the ion-exchange equilibria and investigation of qualitative and quantitative properties of three ore zeolites, using X-ray diffraction and water vapour desorption. The selectivity of domestic clinoptilolite with respect to Zn^{2+} and Ag^+ ions is presented as selectivity series in other papers. Almost all model solutions used were labelled with radioactive tracer and thus considered as a low-activity liquid waste.

2. EXPERIMENTAL

Inland clinoptilolite from the industrial deposit Nižný Hrabovec, mordenite from the locality of Byšta and Chinese clinoptilolite from the south-eastern Hubei were used in this research.

Active mineral contents of the tested zeolite tuffs were determined and verified by means of various techniques, e.g. X-ray powder diffraction, water vapour desorption and ion-exchange.

About 60% of Slovakian clinoptilolite and mordenite-bearing volcanic rocks and about 50% of Chinese ones were tested according to the above methods.

The chemical composition of the natural zeolites was determined by inductively coupled plasma spectrometer ICP 2070, Baird (USA). Mineralogical and chemical composition of inland clinoptilolite is described elsewhere [1]–[3].

Ammonium-saturated zeolite was prepared from 5 M solution of NH_4Cl and 10 g of zeolite which were mixed and boiled for a half an hour. Surface-adsorbed salt was removed by repeated decantation of samples in distilled water, resulting in disappearance of $AgCl$ precipitates, checked by $AgNO_3$ solution. The ammonium from zeolite was determined by distillation method; during distillation from solid phase ammonia was released due to addition of 30% $NaOH$ solution to 0.1 M H_2SO_4 and then analysed titrimetrically with 0.2 M $NaOH$ in the presence of methyl red.

The per cent content of clinoptilolite in the tuffs was determined according to standardized calorimetry method, which was based on temperature rise in distilled water medium after immersing a calcined zeolite sample. The per cent contents of active components in studied natural zeolites were calculated and referred to U.S. Hector clinoptilolite and theoretical maximum ion-exchange capacity of pure clinoptilolite.

The concentration of ions in aqueous solutions was measured by means of radioactive indicators, i.e. solutions were labelled with ^{65}Zn , ^{59}Fe , ^{60}Co , ^{137}Cs , ^{133}Ba and ana-

lysed using multichannel gamma spectrometer MCA EG & G, Berthold Ortec (USA) with scintillation detector.

Other alkaline, earth-alkaline and transition metal cations were analysed using atomic absorption spectrometry on Perkin-Elmer Apparatus (USA) with flame atomization. For high silver concentrations gravimetry by means of AgCl precipitation was chosen.

Chemicals used for the preparation of model solutions in deionized (D.I.) water were of analytical purity.

3. RESULTS AND DISCUSSION

Natural mordenite from the north-eastern site of Slovakia, near Byšta village, was recently found in a perlitized glassy margin of the rhyolite body. Mordenite enrichment of the body ranged from 40 to 60%.

Chemical and mineralogical composition of mordenite tuff (from the Byšta locality) is presented in table 1. The chemical formula of the crystallographical unit of the mineral tested was calculated based on published data and analyses of the exchanged cations [5].

Table 1

Chemical and mineralogical composition of mordenite tuff (Byšta)

Component	Content (% w/w)
SiO ₂	71.86
Al ₂ O ₃	12.92
Fe ₂ O ₃	1.38
TiO ₂	0.14
CaO	2.94
MgO	0.25
Na ₂ O	1.58
K ₂ O	2.64
Loss-on-ignition	6.35
Sum	100.05
Calculated crystallo-chemical formula	
(Ca _{1.7} Mg _{0.2} Na _{1.8} K _{2.3})(Al _{8.2} Si _{39.9} O ₉₆)·27.9 H ₂ O	
Mordenite	58
Volcanic glass	26
Cristobalite	9
Quartz	2
Plagioclase	5
Biotite	traces

Specific gravity of natural mordenite measured using micromeritics autopycnometer 1320 (Germany) equalled to $2.173 \text{ g}\cdot\text{cm}^{-3}$ and crushed bulk density of $1.927 \text{ g}\cdot\text{cm}^{-3}$ was determined.

X-ray diffraction patterns of the perlitized margin of rhyolite body (Byšta) and the identical ones of mordenite in geodes from the same body are shown in figure 1.

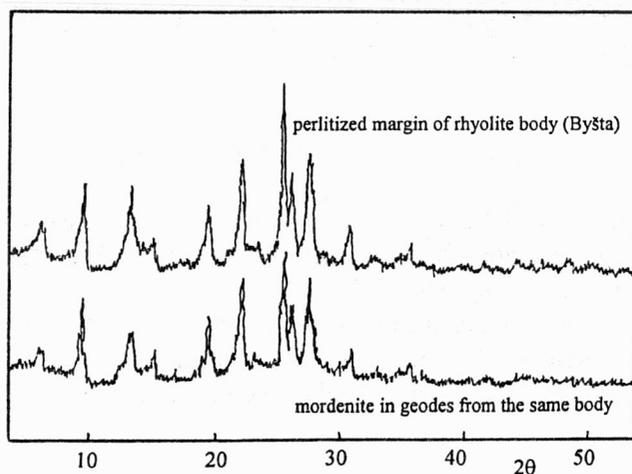


Fig. 1. X-ray diffraction patterns of the perlitized margin of rhyolite body (Byšta) and of mordenite in geodes from the same body

Assessment of the quality of the natural zeolites according to calorimetry method was as follows: 10 g tuff of grain-size approaching 0.2 mm after 1 hour calcination at $400 \text{ }^\circ\text{C}$ was immersed in 100 cm^3 of distilled water ($T = 20 \text{ }^\circ\text{C}$) and the temperature gradient Δt of reversible rehydration of samples was recorded. The method was standardized on the basis of numerous serial trials, which consisted in altering the experimental conditions and utilizing various natural clinoptilolite samples with known percentage content of active component (Hector-California, Castle Creek-Idaho, Buckhorn-New Mexico) [4]. Thus, the correction coefficient (K) for percentage content estimation in the tuff studied was calculated by dividing the known percentage content of standard (U.S. Hector clinoptilite) and its equivalent Δt . As arithmetic mean value of 26 was determined, the following equation for evaluating the quality of minerals was employed (table 2):

$$X(\%) = 26\Delta t.$$

Synthetic mordenite (100%) was used for estimating correction coefficient by mordenite tuff characterization.

Figure 2 shows typical X-ray diffraction patterns of both Slovakian and Chinese clinoptilolites which differ mainly in the peak intensities and in not enough significant variabilities of mineral composition (cristobalite, quartz, feldspar).

Table 2

Selected physicochemical properties of studied zeolites

Zeolite	Ion-exchange capacities (mol·kg ⁻¹)				Temperature gradient by rehydration	Mineral content (%)
	NH ₄ ⁺	Zn ²⁺	Ag ⁺	Fe ³⁺		
Mordenite (Byšta)		0.353	1.452		2.750	58
Clinoptilolite (Nižný Hrabovec)	1.394	0.435	1.230	0.026	2.400	60
Chinese clinoptilolite	1.100			0.020	1.800	47

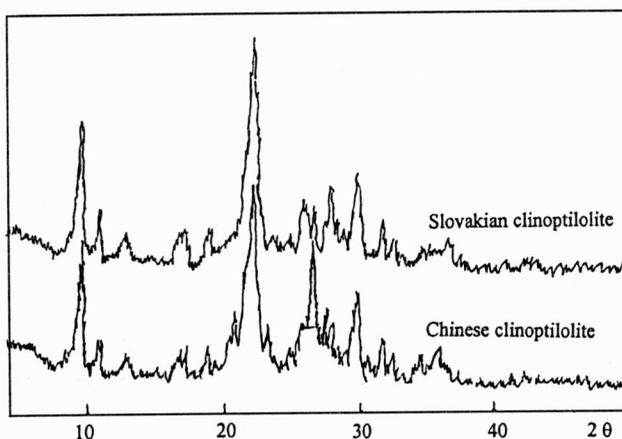


Fig. 2. X-ray diffraction patterns of both Slovakian and Chinese clinoptilolites

Chinese clinoptilolite was qualitatively characterized by maximum ion-exchange capacity (for ammonium ions), amount of reversely exchanged cations and temperature gradient based on rehydration measurements.

The process described in experimental part allowed us to determine the maximum ion-exchange capacity of the tuff. In solution applied the concentrations of the counter-ions (Ca, Mg, Na, K) were analyzed.

Assuming that the ion-exchange capacity of the clinoptilolite tested was found to be 1.1 mol·kg⁻¹, the percentage content of active mineral in Chinese zeolite rock was calculated according to the following formula:

$$X(\%) = \frac{1.1 \cdot 100}{2.35} = 46.8.$$

The value of 2.35 means maximum ion-exchange capacity of pure clinoptilolite, which is equivalent to chemically analysed aluminium content [6], [7]. This value is in good agreement with the results obtained by means of another methods (calorimetry, reverse cation-exchange analysis, tables 2 and 3).

Table 3

Chemical composition of the Chinese clinoptilolite (in % w/w)

Component	Original (before ion exchange) (%) (1)	After ion exchange (%) (2)	Calculated according to original SiO ₂ content (%) (3)	Composition difference (%) (1)-(3)	Exchangeable cations content (mol·kg ⁻¹)	Calculated clinoptilolite content (%)
SiO ₂	73.570	76.130	73.570			
Al ₂ O ₃	11.840	12.280	11.870			
Fe ₂ O ₃	1.250	1.050	1.010			
TiO ₂	0.083	0.087	0.084			
CaO	2.440	0.380	0.370	2.070	0.738 Ca	
MgO	0.630	0.290	0.280	0.350	0.174 Mg	
Na ₂ O	0.570	0.490	0.470	0.100	0.032 Na	
K ₂ O	4.340	3.190	3.080	1.260	0.267 K	
Loss-on-ignition	5.230	6.220	6.010			
Sum	99.953	100.117			1.211	51.500

The results of the adsorption equilibrium studies for the systems: natural and Na-modified forms of domestic zeolites–aqueous solutions of AgNO₃ and Zn(NO₃)₂·6H₂O are plotted in figures 3–5.

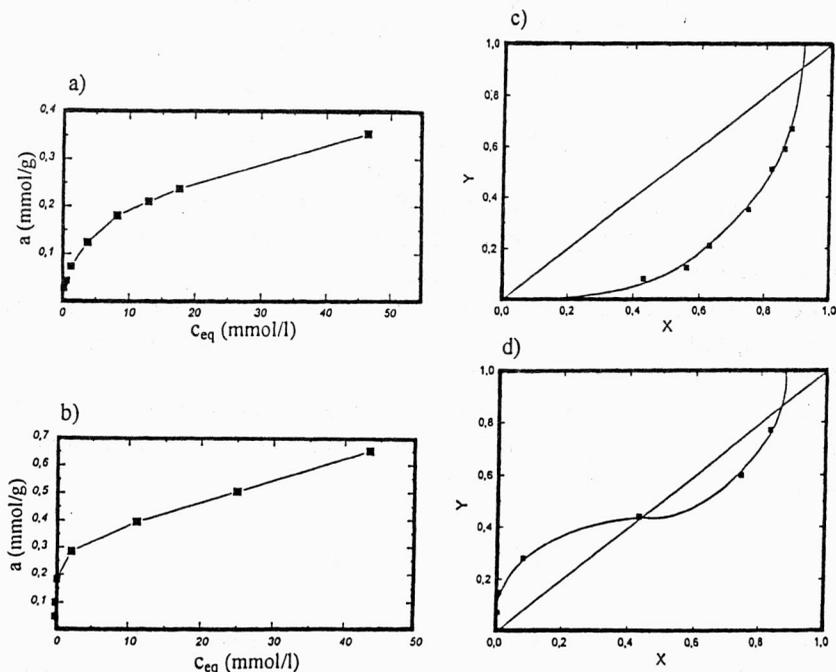


Fig. 3. Ion-exchange isotherms of Slovakian clinoptilolite/aqueous solution of Zn²⁺ ions: a) natural, b) Na-form, c) dimensionless for natural, d) dimensionless for Na-form

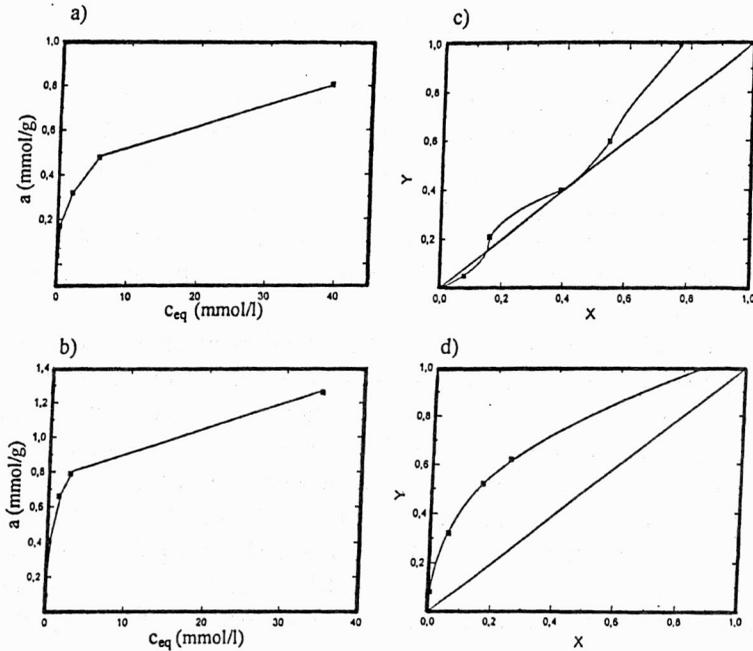


Fig. 4. Ion-exchange isotherms of Slovakian clinoptilolite/ aqueous solutions of Ag^+ ions: a) natural, b) Na-form, c) dimensionless for natural, d) dimensionless for Na-form

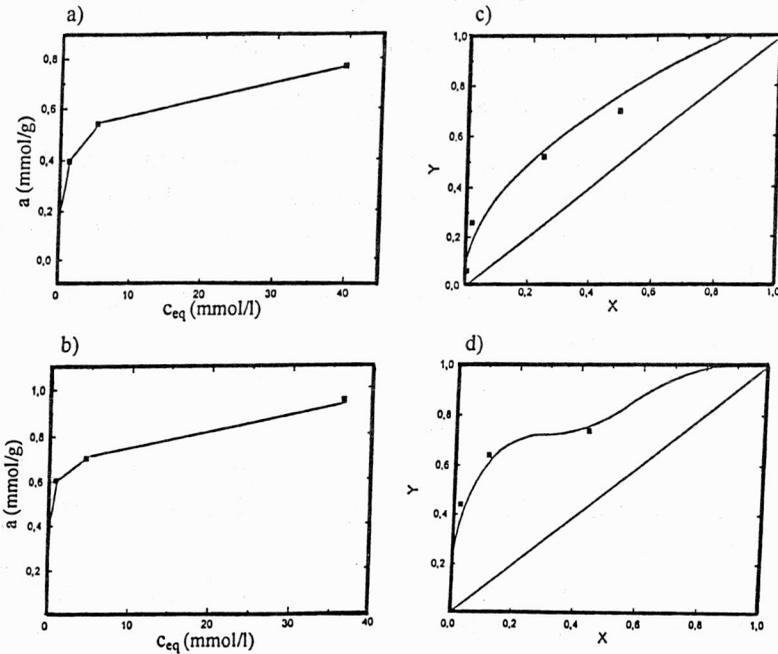


Fig. 5. Ion-exchange isotherms of Slovakian mordenite/ aqueous solution of Ag^+ ions: a) natural, b) Na-form, c) dimensionless for natural, d) dimensionless for Na-form

Predominantly, the Freundlich isotherm was feasible to describe the sorption process on zeolites [6], [8].

Slovakian clinoptilolite/aqueous solution of Fe^{3+} ions $a = 0.0173 \cdot c^{1/15.4083}$

Slovakian clinoptilolite/aqueous solution of NH_4^+ ions $a = 1.1166 \cdot c^{1/2.7397}$

Slovakian clinoptilolite/aqueous solution of Zn^{2+} ions $a = 0.0613 \cdot c^{1/2.0953}$

Slovakian clinoptilolite/aqueous solution of Ag^+ ions $a = 0.2360 \cdot c^{1/2.510}$

Slovakian mordenite/aqueous solution of Ag^+ ions $a = 0.3780 \cdot c^{1/3.530}$

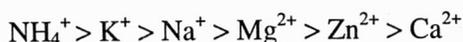
Maximum adsorption capacities of zeolites were computed on the basis of the above isotherm equations.

Except for the adsorption isotherms plotted the dimensionless isotherms represent the selectivity preference of tuff for the ions. The selectivity preference can be estimated based on the curve shape (convex, concave, inflexion point, diagonal).

In each diagram, the ordinate axis Y represents the computed fractional ion-exchange capacity of zeolite occupied by the individual metal ions, and the abscissa X depicts the equivalent fraction of metal ions in the solution at steady state.

Figures 3, 4, 5 prove that the natural mordenite (Byšta) possesses a higher selectivity with regard to Ag^+ ions than the clinoptilolite (Nižný Hrabovec) and that this clinoptilolite after exchange its cations for Na^+ increases its selectivity preference for Zn^{2+} ions.

With respect to the previous, much broader selectivity studies [2] domestic clinoptilolite exhibits the following selectivity sequence:



With the purpose of ordering this sequence of cations, numerous laboratory tests were performed as well as some kinetic and thermodynamic data (i.e. thermodynamic equilibrium constants, selectivity coefficients, diffusion coefficients) were calculated to verify above results [2], [6], [7].

The above selectivity order corresponds to the calculated selectivity and diffusion coefficient-tailored selectivity order

$$K = \frac{Y(1-X)}{X(1-y)} \sim \frac{a}{c}$$

While the thermodynamic equilibrium constant approached the selectivity coefficient, the data can be arranged in the following descending order, where $K \sim a/c$ is the selectivity coefficient:

Ion	Cs^+	Ag^+	Pb^{2+}	Ba^{2+}	NH_4^+	Co^{2+}	Zn^{2+}	Cu^{2+}	Fe^{3+}
K	4281.8	942.4	793.2	486.9	413.6	96.8	77.7	68.5	9.41

The above approximation was done using 1 mmol/dm^3 of model solutions; the setting of concentration values was chosen instead of activities and activity coefficients.

In this paper, the measurements of clinoptilolite selectivity with regard to Ag^+ and Zn^{2+} components supplement the selectivity series of the inland mineral and thus contribute to technical characteristics of natural cation exchanger which can be applied in treatment processes.

4. CONCLUSIONS

The present paper allows us to draw the following conclusions:

- Inland clinoptilolite from the industrial ore Nižný Hrabovec, natural mordenite from recently explored rhyolite body (in Slovakia, near Byšta) and Chinese clinoptilolite were characterized using X-ray powder diffraction, ion exchange and calorimetry.
- Assessment of the quality of all natural zeolites tested was carried out in respect of the U.S. Hector clinoptilolite, generally considered as standard clinoptilolite [7].
- Predominantly, the Freundlich isotherm was feasible to describe mathematically the sorption process on zeolites.
- Excellent coincidence of cations in their selectivity sequence in the Slovakian clinoptilolite was achieved by several methods of examination (fit of ion-exchange isotherm in dimensionless form, calculation of selectivity coefficient values, batch experiments for selectivity influence in the presence of competing cations verified by some earlier work).

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SŁOWACKIE I CHIŃSKIE ZEOLITY W POTENCJALNYM USUWANIU JONÓW
SKŁADNIKÓW JONOWYCH Z FAZY CIEKLEJ

Zbadano podstawowe właściwości słowackich i chińskich zeolitów w zastosowaniu do usuwania jonów z płynnych ścieków o niskiej aktywności. Słowackie klinoptilolity pochodziły ze złoża w Niżnym

Hrabowcu, mordenity – z Byszty (wschodnia Słowacja), a chińskie klinoptilolity – z południowo-zachodniej prowincji Hubei. Fizykochemiczne i mineralogiczne właściwości próbek powyższych minerałów zbadano, stosując różne metody (np. rentgenograficzną dyfrakcję proszkową, desorpcję pary wodnej, wymianę jonową i analizę chemiczną). Stężenia jonów w roztworach wodnych zmierzono radiometrycznie (stężenie jonów srebra spektrograficznie i grawimetrycznie). Korzystając z bezwymiarowych izoterm wymiany jonowej i obliczonych współczynników selektywności, określono selektywność zeolitów i matematycznie opisano proces.