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STUDY OF THE SELECTIVITY OF DIFFERENT TYPES OF ZEOLITES TOWARDS SOME NON-FERROUS METALS[*]

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SUMMARY

The selective properties of zeolites of types A, X and Y towards some non-ferrous metals (copper, nickel, zinc and cobalt) have been investigated. The values of the isotherms of sorption-exchange capacity of the zeolites have been defined, and thermodynamic equilibrium constants are calculated.

INTRODUCTION

Selectivity is one of the most important properties of ion exchangers; it makes possible the separation and concentration of ions, and is widely used in solving practical problems.

The selectivity of an ion exchanger towards ions of equal charge is characterized by the values of the equilibrium coefficients. The greater the difference between the values of these coefficients, the more effective is the process of ion-exchange separation. In most instances, ion-exchange processes are carried out under dynamic conditions, in which the kinetic parameters of the sorbent play a considerable part. Thus, the kinetic parameters must be taken into consideration when selectivity is investigated. These characteristics are both necessary and sufficient for further calculations on the ion-exchange processes under dynamic conditions[1].

This work deals with the selective properties of zeolites, many of which are known to display selectivity even towards similar ions. For example, the separation of calcium from strontium, and rubidium from caesium, can be accomplished on zeolites[2,3]. Also, zeolites are characterized by their high selectivity towards silver ions[4]. Because of this property, we decided to study the selectivity of various types of zeolites towards certain non-ferrous metals.

For this work, we used zeolites of types A, X and Y, the characteristics of which are shown in Table I.

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TABLE I

PHYSICAL PROPERTIES OF THE ZEOLITES

Zeolite type	Ratio of SiO_2 to Al_2O_3	Channel dimensions $(Å)$
A	. 1.8	4.0
X	2.7	9.0
Y	4.7	8–10

TABLE II

EXCHANGE CAPACITIES OF ZEOLITES TOWARDS METAL IONS

Ion	Exchange capacity (mequiv./g)		
	X	Y	A
Cu^{2+}	4.0	3.6	5.2
Zn^{2+}	4.0	3.6	4.0
Co^{2+}	3.6	2.8	3.6
Ni^{2+}	3.2	2.8	3.6
Na^+	5.0	4.0	4.0

RESULTS AND DISCUSSION

The exchange capacity of each zeolite, its stability to the acid used for regeneration and its specific weight were determined by known methods[5]; the exchange capacities are shown in Table II.

It can be seen from Table II that the A-type zeolite displays the greatest exchange capacity to copper (5.2 mequiv./g) and is characterized by the greatest difference in its exchange capacity towards the other non-ferrous metals. For instance, its capacity towards nickel is only just over half that towards copper. The capacities of the X- and Y-type zeolites towards the ions investigated were approximately the same; in this respect, the A-type zeolite is of special interest.

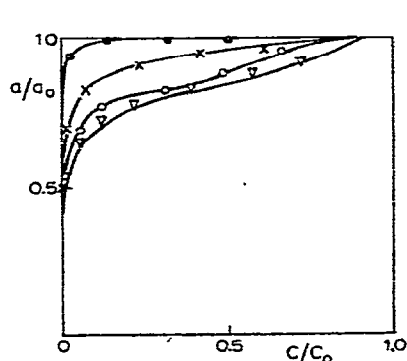The exchange equivalence of the sorbed ions towards ammonium ions was

Fig. 1. Sorption isotherms of ions of non-ferrous metals on A-type zeolite: a/a_0 and c/c_0 are the equivalent cation fractions in the zeolite and the solution, respectively. ●, Cu^{2+}; ×, Zn^{2+}; ○, Co^{2+}; △, Ni^{2+}.
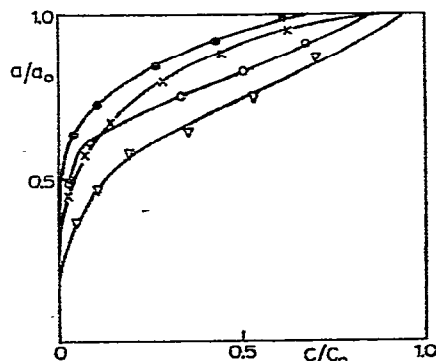
Fig. 2. Sorption isotherms of ions of non-ferrous metals on X-type zeolite. Symbols as in Fig. 1.

studied; each of the sorbed ions was completely eluted by ammonium ions, *i.e.*, true ion exchange took place.

A study of the acid stability of the zeolites showed that each began to disintegrate at pH 3 or less (the Y-type zeolite at pH less than 2.8), and this limited their use. For instance, it was impossible to study the sorption of iron by these zeolites, as iron is completely precipitated as hydroxide at pH values above 3.

As the Y-type zeolite differed little from the X-type, further investigation was continued only with the A and X types.

In order to determine the selectivity of the sodium forms of these zeolites towards copper, zinc, nickel and cobalt, the sorption isotherms of these ions were obtained under static condition according to accepted methods, and the values of the equilibrium coefficients were calculated. The isotherms are shown in Figs. 1 and 2, from which it can be seen that the sodium form of the A-type zeolite has a very great affinity towards copper (the isotherm is nearly right-angled) and a comparatively great affinity towards zinc, over the entire concentration interval studied. The sorption isotherms of cobalt and nickel are sigmoid in character; the isotherms of these ions on the sodium forms of the X-type zeolites are also sigmoid.

The selectivities of the zeolites differs according to the concentration of ions in the solution. Calculated from these data, the equilibrium coefficients of the ions tested towards sodium ions depend on the degree of filling in the zeolite. The nature of this dependence is shown in Fig. 3 for both A- and X-type zeolites.

The thermodynamic equilibrium constants (K'') of the investigated ions were calculated from the equilibrium coefficients (K) and the equivalent cation fractions in the zeolites (M_{AZ} and M_{BZ}) from the equation[6]

$$\log K'' = \log K + a \cdot \frac{M_{AZ} - 0.5\,M_{BZ}}{M_{AZ} + 0.5\,M_{BZ}}$$

The results are shown in Table III.

It is clear from Table III that the selectivity towards copper is several times as large as that towards nickel and cobalt. This suggests the possibility of effective
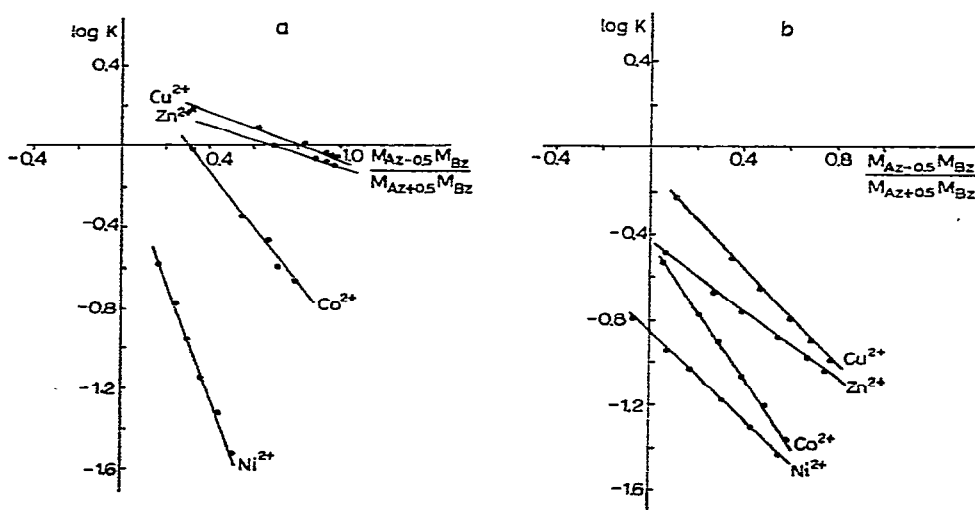

Fig. 3. Dependence of equilibrium coefficients on the degree of the filling for (a) A-type zeolite, and (b) X-type zeolite.

TABLE III

THERMODYNAMIC EQUILIBRIUM CONSTANTS OF METALS TOWARDS THE SODIUM
FORMS OF X- AND A-TYPE ZEOLITES

Ion	Zeolite type	
	A	X
Cu^{2+}	12.0	0.78
Zn^{2+}	2.93	0.36
Co^{2+}	2.64	0.35
Ni^{2+}	0.70	0.14

separation of copper from nickel with an A-type zeolite, or the concentration of copper
from a solution containing sodium ions. In this respect, the concentration of copper
(initially 2 g/l) from a solution of pH 4 and 0.7 N in sodium sulphate wasstudied.

To characterize this system, the sorption isotherm of copper and the break-
through curves were studied. Fig. 4 shows that the selectivity of the A-type zeolite
towards copper is so great that, despite the high concentration of sodium in the
solution, the isotherm is convex and, under certain conditions (an adequate time of
contact), the full ion-exchange capacity of the zeolite can be attained. This is illustra-
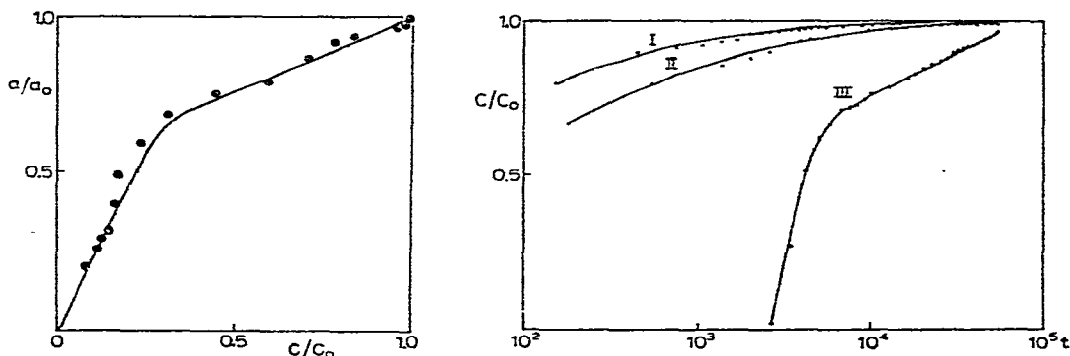ted by the break-through curves shown in Fig. 5.

Fig. 4. Sorption isotherm of copper ions in a solution, 0.7 N in Na_2SO_4, on the A-type zeolite.
Fig. 5. Break-through curves of copper ions from 0.7 N Na_2SO_4 on the A-type zeolite at various
flow-rates: (I) 3 ml/min; (II) 1 ml/min; (III) 0.08 ml/min. t in sec.

Further study of the process (kinetic data) should make it possible to calcu-
late the extent of copper concentration under dynamic conditions.

REFERENCES

1 M. M. Senjavin, R. N. Rubinstein, E. V. Venisianov, N. K. Galkina, I. V. Komarova and V. A.
  Nikashina, *Osnovi Rascheta i Optimisazii Ionoobmennih Prozessov*, Nauka, Moscow, 1972.
2 V. A. Nikashina E. Yu. Zaborskaya, E. M. Mahalov and R. N. Rubinstein, *Radiokhimiya*, 16
  (1974) 753.
3 N. F. Chelishchev, *Ionoobmennie Svoistva Mineralov*, Nauka, Moscow, 1973, p. 43.
4 V. A. Fedorov, *Ionoobmennie Svoistva Sinteticheskikh Zeolitov Tipa A i X*, Kand. Diss., Moscow,
  1964.
5 K. M. Saldadze, A. B. Pashkov and B. C. Titov, *Ionoobmennie Vysokomolekulyarnie Soedineniya*,
  Nauka, Moscow, 1960.
6 G. M. Panchenkov, A. M. Tolmachev and V. A. Fedorov, *Zhurn. Fiz. Khim.*, 37 (1963) 456.