Organomineral sorbents based on clinoptilolite-containing tuffs
2.* Study of ion-exchange and technological properties of organomineral sorbents

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The anion-exchange properties of a new organomineral sorbent obtained by modification of clinoptilolite-containing tuffs by polyhexamethyleneguanidine have been studied after different periods of storage (time after synthesis) and numbers of "sorption—regeneration" cycles. The sorbent can be used as a cation- and an anion-exchanger simultaneously. Selectivity coefficients (exchange constants) for F^-, SO_4^{2-}, and HPO_4^{2-} ions *vs.* Cl^- ions on modified clinoptilolite-containing tuffs have been determined. The modification improves the mechanical properties of clinoptilolite tuffs.

Key words: clinoptilolite-containing tuff, organomineral sorbent; "sorption—regeneration" cycle; anion-exchange properties, selectivity coefficients.

Previously[1] we reported the preparation of a new organomineral anion-exchanger based on clinoptilolite-containing tuff (CT) and a water-soluble polymer, polyhexamethyleneguanidine (metacide (MC)), and some of its properties were considered. In the present work the results of further testing using known methods for studying ion-exchange sorbents[2] are presented. The anion-exchange capacity of the modified CT was studied at different times after the moment of synthesis and for different numbers of "sorption—regeneration" cycles. Ion-exchange equilibrium constants were determined for certain anions, and data were obtained that characterize the cation-exchange capacity of samples in addition to the anion-exchange capacity. The mechanical properties of the modified CT were characterized.

Experimental

Bromide, fluoride, chloride, sulfate, and phosphate ions were chosen for studying the anion-exchange properties of modified CT. The method of radioactive indicators was used for the determination of Br^- ions, while Cl^-, SO_4^{2-}, and HPO_4^{2-} ions were determined by ion chromatography.[3] The cation-exchange capacity of the modified CT was evaluated by the sorption of NH_4^+. The concentration of the latter was determined by titration with formaline.[4] The mechanical properties of the sorbent were studied by the previously described procedure.[5]

One of the modified samples prepared by the treatment of CT from the Tedzami deposit with a granulation of 0.5—1.0 mm with 33 % MC solution (ECH/MC = 0.2, where EHC was epichlorohydrin) was used for the study. The ion-exchange capacities of this sample in Br^- were determined under dynamic conditions after 3 weeks, 3.5 months, 4.5 months, and 1.5 years, as well as the dependence of the ion-exchange capacity on the number of "sorption—regeneration" cycles. The results are presented in Tables 1—5.

Table 1. Dependence of the anion-exchange capacity of modified CT on the number of "sorption—regeneration" cycles and on the time elapsed after synthesis

Time after synthesis /months	Cycle number	Capacity/meq. mL^{-1}	
		Sorption	Desorption
0.75	1	0.26	0.31
0.75	2	0.30	0.22
0.75	3	0.26	0.17
3.5	1	0.17	0.15
3.5	3	0.12	0.12
3.5	6	0.13	0.14
4.5	1	0.16	0.17
4.5	4	0.16	0.23
18.0	1	0.21	—
18.0	3	—	0.19

Note. In the range of change in the exchange capacity from 0.12 to 0.30 meq. mL^{-1}, the determination error (Δx) was ±0.02 meq. mL^{-1}, standard deviation, S_r = 0.3 at the confidence probability, P = 0.95, and n = 26.

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* For part 1, see Ref. 1.

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Table 2. Concentration equilibrium constants (*K*) of the exchange of fluoride, phosphate, and sulfate ions for the chloride ion on modified clinoptilolite (according to the data of frontal dynamics)

Anions	$K = \frac{a_i^{1/z}\cdot c_j}{c_i^{1/z}\cdot a_j}$ *
F^-	0.29
HPO_4^{2-}	1.70
SO_4^{2-}	3.20

* Here z is the charge of an exchanged ion; a_i, a_j (meq. mL^{-1}) are concentrations of ions in the sorbent phase, c_i, c_j (meq. mL^{-1}) are concentrations of ions in solution.

Results and Discussion

The data in Table 1 show that the capacities in anions of a given modified sample are almost unchanged from cycle to cycle.

In order to obtain ion-exchange equilibrium constants for various anions we studied the frontal dynamics of sorption of a mixture of ions on the OH^- form of the sorbent. The initial concentrations of F^-, Cl^-, HPO_4^{2-}, and SO_4^{2-} ions in the solution were $7.1 \cdot 10^{-4}$, $1.1 \cdot 10^{-3}$, $2.1 \cdot 10^{-3}$, and $1.1 \cdot 10^{-3}$ g-eq. L^{-1}, respectively, and pH 6.9. After the end of the experiment and after washing the sorbent layer with water, the sorbent was regenerated by a 0.05 *N* KOH solution, and the anion concentration was determined in the regenerate. The breackthrough curves for the anions studied and the change in pH of the solution during the filtration of the mixture of anions through the modified clinoptilolite are presented in Fig. 1, and the regeneration curves are presented in Fig. 2. The values of the concentration equilibrium constants for the exchange of ions for Cl^- were calculated from the corresponding values of equilibrium concentrations of anions in the sorbent and in the solution (see Table 2).

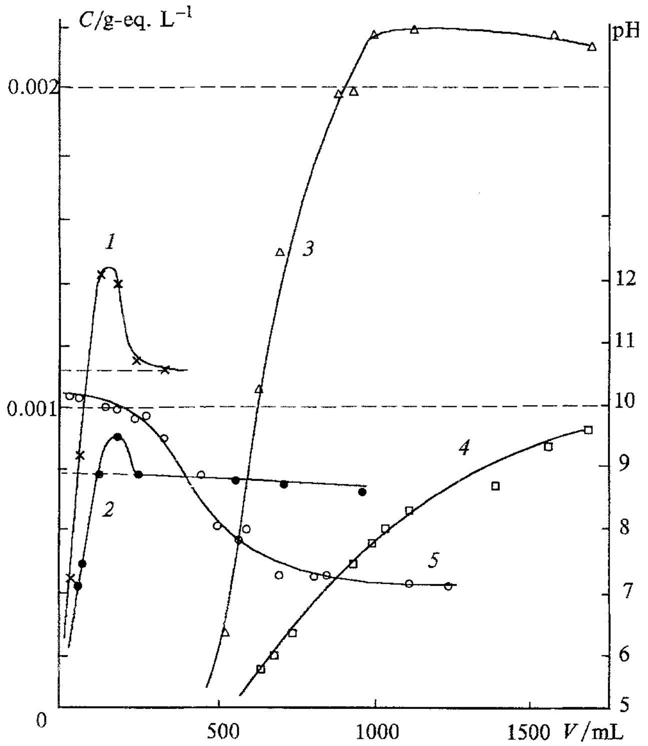

Fig. 1. Breackthrough curves of Cl^- (*1*), F^- (*2*), HPO_4^{2-} (*3*), and SO_4^{2-} (*4*) ions from their mixtures on a modified CT and the change in pH of the solution (*5*). Granulation of the air-dry sorbent is 0.5—1.0 mm, the height of the loading layer is 12.2 cm, the loading volume is 10 mL, and the flow rate is 0.8 mL min^{-1}.

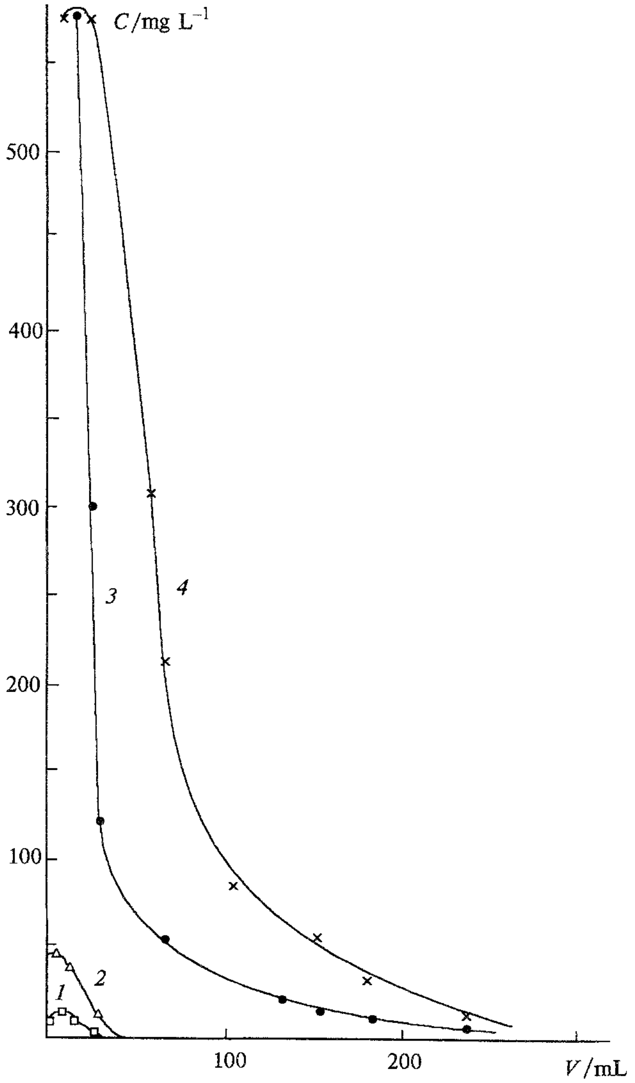

Fig. 2. Breackthrough curves of the regeneration (0.05 *N* KOH) for modified CT saturated with a sum of anions for F^- (*1*), Cl^- (*2*), HPO_4^{2-} (*3*), and SO_4^{2-} (*4*) ions. Flow rate is 1.1 mL min^{-1}.

Table 3. Cation-exchange capacity of natural and modified samples of clinoptilolite-containing tuffs from the Tedzami and Kholinskoe deposits (duration of contact is 5 days, V/m = 50, 0.1 $N\,NH_4Cl$)

Clinoptilolite (deposit)	Exchange capacity with respect to NH_4^+ /meq. mL^{-1}*	
	Sorption	Regeneration
Natural (Tedzami)	1.10	0.93
Modified (Tedzami)	0.98	0.75
Natural (Kholinskoe)	0.78	0.80
Modified (Kholinskoe)	0.98	0.58

* Sorbents were regenerated with a 2 N NaCl solution.

Table 4. Cation-exchange and anion-exchange capacities of the modified CT according to the data on sorption and regeneration

Ions	Exchange capacity/meq. mL^{-1}		
	Sorption	Regeneration	
		q = 5	q = 30
SO_4^{2-}	0.19	0.12	—
NH_4^+	0.67	0.32	0.50

* Here q is the number of volumes of 1 N NaCl per 1 volume of the sorbent.

Table 5. Mechanical properties of natural and modified CT

Clinoptilolite	Abradability (%)	Grinding resistance (%)
Modified	0.02	1.7
Natural	6.83	4.89

As can be seen from the presented data, the modified CT is most selective to SO_4^{2-} ions. It is known that CT are cation-exchangers with a fairly high capacity and selectivity to such ions as Cs^+, K^+, NH_4^+, Sr^{2+}, *etc.* The cation-exchange capacity was determined for several modified sorbents under dynamic and static conditions. The results of the determination of the exchange capacity of modified clinoptilolites from the Tedzami (Georgia) and Kholinskoe (Russia, Eastern Siberia) deposits with respect to the NH_4^+ ion under static conditions from a 0.1 $N\,NH_4Cl$ solution are presented in Table 3.

The data in Table 3 show that the cation-exchange capacities of the initial and modified CT differ only slightly, which allows us to propose that after modification CT simultaneously manifest both cation-exchange and anion-exchange properties.

In order to check this assumption, a 0.01 N $(NH_4)_2SO_4$ solution was filtered through a layer of the modified clinoptilolite-containing tuff in the Cl^- form, and the breackthrough curves were plotted with respect to both NH_4^+ and SO_4^{2-} ions. When the breackthrough curves had been obtained, the sorbent was regenerated and the content of SO_4^{2-} and NH_4^+ in the regenerate were determined. The results obtained are presented in Table 4.

It can be seen from the data in Table 4 that the modified CT sorbs both NH_4^+ and SO_4^{2-} simultaneously. Its subsequent treatment with a NaCl solution results in the simultaneous removal of these ions from the sorbent, and SO_4^{2-} is desorbed by a lower volume of regenerating solution than NH_4^+.

It was also of interest to study the mechanical strength of the modified clinoptilolite. The comparative results on abradability and grinding resistance of the initial natural clinoptilolite and its modified form are presented in Table 5.

As can be seen from the data presented in Table 5, the modified CT possesses noticeably improved strength characteristics, which is of substantial significance for its industrial use.

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