

## **Use of ion-exchange composites based on natural zeolites for cleaning of water solutions with purpose to create environmentally safe technologies**

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### **Abstract**

This work is devoted to the development of methods of a controlled synthesis, the study of properties and the application of ion-exchange composites on the basis of cheap natural zeolites with the structure of clinoptilolite, but having better characteristics in comparison with them. By modifying chemical structure of natural zeolites of two deposits by the ion exchange method sodium, calcium, magnesium, ammonium and hydrogenous forms with different degree of exchange cation replacement were synthesized. The comparative characteristic of sorption properties of ion-exchange derivatives of natural zeolites and their initial forms is received. Prospects for use of a number of cation-replaced forms of clinoptilolites have been shown as regards the extraction of cesium and strontium from water solutions.

Keywords: zeolites, synthesis, radioactive elements, sorption, cleaning

### **1. Introduction**

In many cases creation of the effective systems for the cleaning of water solutions, polluted with radioactive elements and heavy metals, for example, realization of extraction processes of radionuclides from wastes, deactivation and cleaning of waste waters, water preparation, is connected with necessity of use of sorption materials with given properties. Sorption processes have the advantages over other methods (for example, evaporation and precipitation) as they are more effective at large volumes of solution, do not bring about difficulties, caused by corrosion of the equipment and in majority of cases provide additional clearing of corrosive impurities and products of division.

It is well known that aluminosilicate molecular sieves (synthetic and natural zeolites) are considered the best sorbents which are used in technological processes of division and deep clearing of liquid and gas mixtures due to their chemical nature and particularities of their porous structure. Large stocks of natural zeolites in many

countries of the world (in Japan, on the territory of the former USSR, in the USA, in Eastern and South-Eastern Europe), their low prime cost and possibility of using them without preliminary enrichment together with their unique ion exchange and adsorption properties provide considerably more ample opportunities of their practical application in comparison with synthetic zeolites.

As ion exchange and adsorption properties of zeolites, as well as of other sorbents, are largely determined by the chemical condition of their surface, development of the methods of directed synthesis of zeolites of various chemical structure is especially urgent and topical. One of the effective ways in this direction is modifying the chemical structure of zeolites by the ion exchange methods. Inculcation of new cations into a zeolite can greatly change its stability, adsorption characteristics, including selectivity and other important physical properties.

This work is devoted to the development of the methods of directed synthesis, the study of properties and the application of ion-exchange materials on the basis of cheap natural zeolites with the structure of clinoptilolite, but processing higher characteristics in comparison with them. The choice of clinoptilolite from basic minerals of zeolite rocks (clinoptilolite, erionite and mordenite) was caused by higher maximum exchange capacity and greater prevalence. It has bigger acid resistance, higher chemical and radiating stability, high thermostability.

During fulfilment of the work there were used natural clinoptilolites of two effusion-sedimental deposits (Dzegvi and Tedzami – Georgia) with molar properties accordingly:  $\text{SiO}_2 : \text{Al}_2\text{O}_3 = 8,53$  and  $7,15$ ;  $(\text{Na}_2\text{O} + \text{K}_2\text{O}) : \text{Al}_2\text{O}_3 = 0,47$  and  $0,44$ . Clinoptilolites-containing tufas of these deposits are characterized by high (90-95 % mas.) contents of clinoptilolite, therefore these rocks can be considered raw material for receiving sorbents, not requiring preliminary enrichment. The high mechanical solidity of this mineral allows to exclude the stage of sorbent granulation. As a result cost of the natural clinoptilolite, which includes expenses on extraction milling and scattering is much less than the cost of synthetic zeolites.

Clinoptilolites have also a number of essential advantages before natural clay sorbents (montmorillonite, vermiculite) – higher acid resistance, stability of alkalis and also mechanical solidity. Existing data on ion-exchange properties of clinoptilolites show that these zeolites can be used for extraction of ions of heavy metals from water solutions, radionuclides of cesium and strontium. And capacity of clinoptilolite on cesium, for example, is almost 30 times as high as that one ion-exchange resins [1-3]. In this connection the use of ionites on the basis of clinoptilolite-containing tufas as filtering material at water preparation represents great interest.

## **2.Experimental**

With the purpose of creation effective ways water cleaning of decreasing contents of harmful microimpurity up to the extreme allowable concentration (including rather toxic and long-living radioactive elements – cesium-137 and strontium-90) sodium,

ammonium, magnesium, calcium and hydrogenous ion-exchange derivatives of clinoptilolites of the given deposits with a different degree of exchange cation replacement were synthesized.

Synthesis of the first four ion-exchange forms has been carried out at room temperature in static conditions according to the technique, described in work [4]. Solutions of NaCl, NH<sub>4</sub>Cl, MgCl<sub>2</sub> and CaCl<sub>2</sub> were used as modifying solutions. Synthesis of hydrogenous forms of clinoptilolites was carried out in two ways: by annealing their NH<sub>4</sub>-forms at 400°C during 8 hours and by direct processing of the initial clinoptilolites by solutions HCl [5].

Physical chemical properties of synthesized sorbents and their initial forms have been investigated through methods of X-ray structure analysis, derivatography, IR-spectroscopy and chemical analysis. On the basis of the complete chemical analysis of zeolites and study of their interaction with water-brine solutions the maximum exchange capacity of clinoptilolites of both deposits Dzegvi and Tedzami was experimentally established. The exchange capacity values accordingly were equal 2,83 and 3,39 mequ/g.

To predict the superficial adsorption interactions for obtaining sorbents with the given properties and the target-oriented performance of sorptions processes taking into account Lewis's and Brensted's theory, the investigation of the origin of distribution of acid-base centers and their concentration on the surface of synthesized sorbents has been done with the help of an indicator method.

The comparative characteristics of adsorption properties of synthesized ion-exchange derivatives of natural zeolites and their initial forms at cesium and strontium sorption from water solutions in dynamical conditions are received. Experiments on extraction of these elements were carried out with the use of  $1 \cdot 10^{-4} - 2 \cdot 10^{-2}$  N solutions of strontium chloride and cesium nitrate. Samples of clinoptilolites (initial and modified forms) with the fraction 0,25-0,50 mm were loaded into glass columns with the internal diameter of 16 mm, the height of a seam was 65 mm. Model solutions were passed through a column with sorbent with the line speed of 10 mm/min. With the help of the collector of fractions DOMBIFRAC D-003 the continuous automatic selection of the filtrate samples was carried out, and sorbed elements definition was made.

### **3.Results and discussion**

It is established that in all cases the prepared ion-exchange derivatives preserve their crystal structure.

Obtained values of sorption capacity of synthesized ion-exchange derivatives of natural zeolites and their initial forms on cesium and strontium till 10 per cent skip in sorption from 0.02 N solutions given in Table 1.

Table 1. Dynamical exchange capacity of synthesized ion-exchange derivatives of natural zeolites and their initial forms on cesium and strontium

Zeolite form	Dynamical capacity (till 10 per cent skip), mequ/g	
	Cesium	Strontium
Dzegvi Clinoptilolite, Cl. (Dz)	0,79	0,41
Na- Cl. (Dz)	0,83	0,43
NH <sub>4</sub> - Cl. (Dz)	0,86	0,47
H- Cl. (Dz)	0,70	0,34
Mg- Cl. (Dz)	1,04	0,56
Ca- Cl. (Dz)	1,26	0,68
Tedzami Clinoptilolite, Cl. (T)	0,72	0,39
Na- Cl. (T)	0,75	0,42
NH <sub>4</sub> - Cl. (T)	0,76	0,45
H- Cl. (T)	0,61	0,32
Mg- Cl. (T)	0,98	0,56
Ca- Cl. (T)	1,18	0,65

The chemical analysis of sorbents after each experiment has shown that strontium and cesium enter into clinoptilolite mainly to the place of calcium and magnesium (about 90% from the quantity of the sorbed cations), less (about 10%) to the place of sodium and practically do not exchange for potassium. The process of sorption is characterized by equivalence.

These researches have shown that cation modifying considerably changes sorption properties of clinoptilolites of the given deposits. The received results are well agreed with the results from the work [3]. So, sodium, ammonium, magnesium and calcium forms are characterized by higher meanings of exchange capacity in relation to cesium and strontium than initial natural clinoptilolites. Decationizing, that is reception of hydrogenous forms, reduces a little this parameter. Ion-exchange sorption of strontium and cesium ions from solutions, which are in contact with clinoptilolites, is based on replacement mainly of calcium, magnesium and sodium. The greatest exchange capacity on Cs and Sr is characteristic for ion-exchange forms of clinoptilolites with the high contents of calcium.

In the case of using solutions with the concentration  $1 \cdot 10^{-4}$  N after going through 350 column volumes the process was stopped and cesium and strontium skip was not found. Degree of extraction was 100 per cent.

The received results allow to make the conclusion about prospects on use of a number of cation-replaced forms of clinoptilolites of given deposits for cesium and strontium extraction from water solutions at low concentrations of these elements.

Even a small increase of exchange capacity of natural zeolite on cesium and strontium increases considerably the volume of the solution, which is being cleaned and has passed through the sorbent up to the same gap. Taking into consideration the fact that clinoptilolite has sharp selectivity in relation to cesium and strontium in the field of small concentration of these elements it becomes possible to extract trace quantities of these harmful substances from large volumes of cleared water at technologically and economically favourable alignment of solid and liquid phases.

## CONCLUSIONS

On the basis of the fulfilled researches it has become possible to make practical recommendations for replacement of natural clinoptilolites on their ion-exchange derivatives in various ion exchange technologies.

In connection with huge scales of such branches as water preparation, clearing of turnaround and waste waters with the help of cheap natural zeolites can greatly provide the growing industrial needs of ion-exchange materials. Besides that natural zeolites can be widely used in processes not dealing with sorbent regeneration because of their low cost.

In view of a high radiation stability and resistance to leaching, the synthesized ion exchangers represent also practical interest for providing safety to the environment in the event of their land disposal after use.

It is also necessary to take into account ample opportunities of simultaneous multitarget use of natural zeolites not only as ionites but also as adsorbents and filtering materials in various technological processes and environmental protection measures.

## References

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