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REVISITING THE KAZAKHSTAN NATURAL SORBENTS MODIFICATION

Kazakhstan ranks second in the world in natural uranium reserves and a leading position in its production. Hydrometallurgical processing of uranium raw materials results in a significant amount of liquid technogenic wastes containing radionuclides. Sorption cleaning methods for these wastes are the most effective ones. However, the high cost of synthetic sorbents and the low sorption capacity of natural ones is a deterrent to their use. So, to increase the sorption capacity of natural sorbents by their modification is an urgent problem.

In this paper, a method to modify Kazakhstani natural zeolite was proposed by us and previously not investigated. Also the data of physicochemical studies of the initial raw material and the modified product was given and the increase in the natural sorbent specific surface in the modification process was demonstrated.

Key words: zeolite, modification, activation, raw material, Kazakhstan

INTRODUCTION

A significant amount of liquid technogenic wastes - waste solutions are produced in the course of hydrometallurgical processing of uranium-containing raw materials.

Industrial products and wastes from the uranium industry contain rare earth elements and radionuclides [1]. The sorption, precipitation and membrane process-based methods are used most often to extract radionuclides thereof. The choice of one or another method depends on the chemical and radionuclide composition of liquid radioactive waste (LRW) and is determined under the state of the radionuclides in the solution. The use of sorption methods is one of the most effective methods to clean objects contaminated with radionuclides and, in particular, water. Today, sorption purification methods using synthetic and natural sorbents are the most common and effective, and they have no alternatives in many cases.

The disadvantage of synthetic sorbents is their high cost, and that of natural ones is low exchange capacity. In order to increase the sorption properties, natural materials used for cleaning solutions undergo different modifications. At the same time, there are no actual methods to obtain modified sorbents that would be well-proven in the uranium sorption process. So, the problem to obtain modified sorbents based on natural raw materials remains relevant for the nuclear industry.

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METHODS OF ANALYSIS

The elemental and phase compositions of natural zeolites were determined tith the help of X-ray fluorescence and X-ray phase analyzes using Venus 200 X-ray fluorescence wave dispersion spectrometer made by PANalytical and a D8 Advance diffractometer made by Bruker (Cu –K$_\alpha$ radiation).

The quantitative uranium content in solutions before and after sorption with the help of an Optima 8000DV inductively coupled plasma (ICP) atomic emission spectrometer was determined.

RESULTS AND ITS DISCUSSION

Zeolites are widely used among inorganic ion exchangers. In their turn, in terms of practical importance, first of all, high-silica zeolite - clinoptilolite – can be distinguished among zeolites due to its high sorption properties and selectivity.

Natural zeolite-containing minerals are subject to close attention of researchers because they are much cheaper materials compared with synthetic zeolites.

At the same time, the demand for natural sorbents imposes the need to study the possibility to use mineral raw materials produced in newly discovered and little-studied deposits in order to develop the conditions for their modification and subsequent targeted use.

The zeolites produced in the Shankhayskoye field with 80 % composed of sodium-type clinoptilolite are the most thoroughly investigated among the Kazakhstani ones. The mineralogical and chemical composition of the averaged sample of natural zeolites previ-

ously unexplored originated from northern Kazakhstan was studied (the Kusmurynskoye deposit).

Table 1 presents the zeolite elemental composition under X-ray fluorescence analysis.

Table 1 **The original natural zeolite elemental composition / wt. %**

Components	Content
SiO_2	62,2
Al_2O_3	13,4
Fe_2O_3	5,9
Na_2O	1,6
CaO	5,3
K_2O	6,5
MgO	2,2
P_2O_5	0,4
MnO	0,2
TiO_2	0,5
SiO_2/Al_2O_3	1,8
Others	4,6

As specified in the table, the ratio of the main components - SiO_2/Al_2O_3 cations is 4,6 confirming the aggressive substances and high temperatures resistance of the zeolite studied.

The phase composition is represented by clinoptilolite, quartz, albite, diopside, hematite, lomonite, ernite. The results of the phase analysis confirm the prevalence of clinoptilolite and quartz in the zeolite composition, and those of mineralogical analysis - calcium-form clinoptilolite.

Thermogravimetric studies (TG, DTA, DTG) supplemented the zeolite phase composition information with the presence of a small amount of harmotome and chabazite.

Thus, the Northern Kazakhstan zeolites to be studied belong to the calcium-form zeolite less studied and not typical for the Kazakhstani zeolite raw materials studied (Figure 1).

The zeolite structure specificity resulting in its properties makes it an attractive and promising material for sorption processes, but its low sorption capacity is an obstacle to its widespread use. Due to it, the task to improve the sorption properties of natural ion-exchange materials, or their modification, comes to prominence.

There are different methods to change the structural features of natural sorbents enabling to improve their properties. However, a common disadvantage of the methods described is the complexity of the performance, high cost and use of scarce reagents.

There is limited data on uranium sorption by modified zeolites in the scientific literature. Basically, the modification principles include coating the zeolite surface with hydroxides of metal [2, 3], such as iron, zinc and copper.

The sorption capacity of zeolites increases, and the possibility to use them in the uranium recovery technology and LRW disposal is growing in this case. However, these methods are difficult to implement, and therefore, the new modified reagents search and the development of new modification methods remain urgent problems.

Modification, as a rule, results in phase and sometimes structural changes of natural sorbents. Phase changes are also observed when natural sorbents are processed with chemical reagents, such as acids, alkalis, and salts. These changes are not as dramatic as in the methods specified above but they have a positive effect on the sorption capacity of sorbents [4, 5].

It should be noted that there is quite extensive information about the sorption properties of zeolite minerals with respect to ^{137}Cs and ^{90}Sr isotopes in the scientific literature; moreover, the greatest exchange capacity for these components is typical for natural calcium-form clinoptilolite [5]. But such information is limited for uranium.

During the research the activation process of aluminosilicates with acids, alkalis, and salts, and carried out ex-
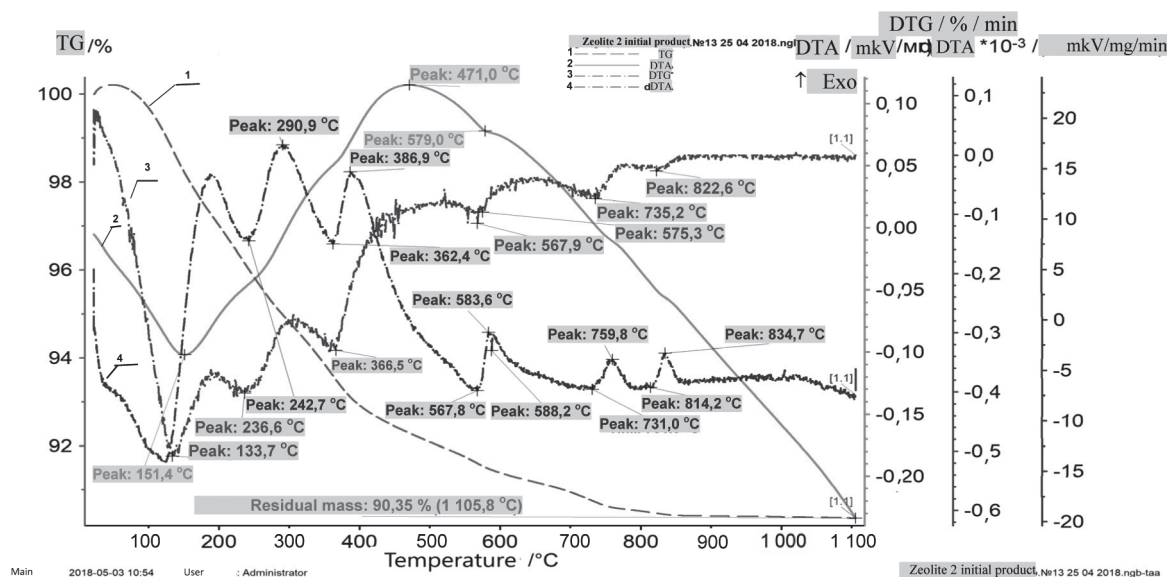

Figure 1 Zeolite Thermogram

Table 2 **Results of X-Ray fluorescence analysis of zeolite samples after activation**

Name		O	K	Al	Si	Fe	S	Na	Mg	P	Ca
Initial Content/ %		47,12	0,61	6,58	21,51	3,02	0,004	1,46	1,35	0,05	2,23
2 N HCl	Content after acti-vation, %	50,58	0,85	4,57	27,88	3,84	0,006	1,27	1,04	0,01	1,03
1,7N HCl		50,68	0,89	4,69	26,89	3,70	0,005	1,17	1,11	0,008	1,223
1N HCl		48,7	0,82	5,38	23,9	3,62	0,01	1,25	1,23	0,01	1,49
2N NH$_4$Cl		43,51	0,76	6,41	21,02	3,35	0,004	1,29	1,28	0,06	2,33
1.7 N NH$_4$Cl		47,64	0,78	6,92	22,27	3,54	0,004	1,42	1,41	0,07	2,64
1 N NH$_4$Cl		48,78	0,82	6,89	22,76	3,47	0,004	1,40	1,37	0,07	2,64
1.7 N HCl when boiled		46,01	0,85	5,03	25,62	3,29	0,004	1,23	0,70	0,02	1,44
3 N HCl		49,05	0,88	3,54	27,39	3,31	0,004	0,91	0,79	0,008	0,75
6 N HCl		49,9	0,84	3,09	29,1	3,06	0,01	0,89	0,72	0,01	0,58
2 N NaOH		47,59	0,80	6,41	21,16	3,22	0,005	2,10	1,28	0,063	2,90
4 N NaOH		45,76	0,74	6,31	20,59	3,14	0,003	2,16	1,26	0,05	2,73
6 N NaOH		48,08	0,79	6,58	21,98	3,46	0,004	2,51	1,31	0,07	3,14

periments to sorb uranium from technological solutions with activated materials in a static mode was studied.

The activation was carried out as follows. Transfer 5 g zeolite sample into a beaker, pour 50 ml HCl, NH4Cl or NaOH solution with a certain concentration and keep at room temperature within two days. Then filter it, dry at 400 ° C and analyze. Activate the sample with 1,75 N HCl solution boiling it within 30 minutes.

Tabular data (Table 2) confirm that after activation with hydrochloric acid under the normal conditions, the aluminum content is reduced by 30,6 %, that of magnesium – 22,8 %, calcium – 53,95 %, the silicon content increases by 29,6 %, that of iron – by 27,4 %, at elevated temperatures – respectively, Al – 23,5 %, Mg – 48,11 %, Ca – 35,23 %, Si – 19 %, Fe – 8,9 %.

When activated with sodium hydroxide, the aluminum content decreases by 2,7 %, calcium one increases by 41,02 %, the content of iron and silicon practically does not change. Processing a zeolite sample with ammonium chloride results in the iron content increase by 14,6 %, on average, and the content of silicon and calcium changes slightly.

Thus, it follows from the above results that the highest degree of decationization and dealumination was achieved when the zeolite was activated with hydrochloric acid. With acid activation, the decation and dealumination processes proceed simultaneously. This is evidenced by an increase in the silica content with a simultaneous decrease in the alumina content.

The increase in silicate modulus observed in this case indicates phase transformations, which is confirmed by X-ray diffraction studies. According to the author [6], an increase in the silicate module indicates the appearance of active centers, which, in his opinion, can contribute to an increase in the sorption capacity of the zeolite. According the X-ray phase analysis of a sample of zeolite after acid activation we can see that phase transforma-

tions occurred during the activation process: the content of cliniptilolite, albite, diopside, erinite and hematite decreased. The transformation of lomontite almost took place. New components have appeared: sodium silicate, calcium silicate carbonate, and terranovite. The quartz content is almost unchanged. When zeolite is activated with hydrochloric acid of a higher concentration, there is decrease in the content of hematite, diopside and clinoptilolite that is destroyed and transformed, the content of sodium silicate and calcium silicate carbonate increases, a new phase - microcline - appears.

Brunauer, Emmett and Taylor studies have shown that the specific surface area increases, and the average pore diameter decreases (Table 3) during the zeolite activation process contributing to sorption capacity increase. At the same time, the zeolite specific surface area increases by 1,5 times after activation.

It should be noted that a similar pattern is observed in the uranium sorption with activated zeolite, i.e. the sorption degree increases by 1,5 times, on average.

Table 3 **Properties of natural zeolites before and after activation**

Name	Zeolite No.1 (initial)	Zeolite No.1 (after activation)
Specific surface area S_{BET} / m^2	31,70	47,55
Actual pore volume Σ_{act}, / ml/g	0,0685	0,0677
Average pore diameter D_{av}, / Å	43,6337	31,7014
Mechanical strength / kgf/cm^2	35 - 40	35 - 40

CONCLUSION

Thus, based on the studies conducted, as well as the authors' results [3] can be assumed that processing the

zeolite-containing rock with acid solutions under different conditions results in the specific surface increase and the average pore diameter decrease contributing to increase in the sorption capacity due to more active access of adsorbent molecules to the active centers of the sorbent, i.e. samples of various decationation and dealumination degrees can be obtained with the sorption capacity higher than that of the initial ones depending on the conditions of the acid processing of zeolites - the change in the acid concentration, its nature, and the temperature of the process.

Acknowledgements

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