Metals and Metalloids Removal from Mine Water Using Natural and Modified Heulandite

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***Abstract*—The paper represents the results of batch experiments on the extraction of As, Sb, Zn, and Cu from real acidic and alkaline drainage solutions using natural and modified MnO_2 heulandite $[AlSi_3O_8]_2 \times Ca(H_2O)_5$. It was found that the modified zeolite is effective for removal As and Sb, but it is necessary to take into account the possibility of Mn releasing into the solution after interaction with acid drainage. For Zn removing from acid drainage solutions, the modified zeolite is not suitable. Both samples of heulandite effectively remove arsenic from the acidic solution as opposed to the alkaline solution. Perhaps this is due to the presence in the acid solution of a large amount of iron and aluminum, which during neutralization form hydroxides, contributing to additional sorption of the elements.**

***Index Terms*—Batch experiment, drainage solution, modified zeolite, arsenic.**

I. INTRODUCTION

Wastes from mining and processing plants stored in the tailing ponds have a negative impact on the system “water reservoir - soil - plant and animal world – people”, so now studies are actively being carried out to neutralize ecological effect and recultivate of disturbed areas. Various methods are used to treat drainage water from metals and metalloids: ion exchange [1], electrochemical methods [2], membrane technologies [3], precipitation [4], [5].

Sorption extraction of metals from drainage solutions has become quite widespread due to high efficiency and the absence of secondary impurities. Correctly selected materials absorb metals from aqueous solutions practically to any residual concentrations [1], [6], [7]. In addition to environmental safety, natural sorbents (plant waste, coal, and zeolite) have economic benefits. In the world practice, the use of natural minerals as sorbents for water purification is encountered, but often such materials do not possess the necessary sorption properties and must be chemically and physically modified [8]. As a result of the modification, sorbents with a surface nature different from the original mineral are obtained, combining the useful properties of the natural material and modified sorbents. Despite the frequent practical use of sorption methods in the purification of drainage solutions, there are a number of problems in this area. The most significant are: insufficient sorption capacity of the used materials, lack of reliable, cheap, eco-friendly methods for regenerating sorbents and methods for further utilization of heavy metals [8], [9]. Previously, studies were conducted using a modified and natural zeolite to purify acid and neutral solutions. In the literature, the following transformations of zeolites occur to increase the extraction efficiency of metals and metalloids: iron (hydr) oxide modification [10], surface modification by surfactants [11]. The purpose of this work was to compare the extraction efficiency of As, Sb, Cu and Zn from real drainage solutions with modified MnO_2 heulandite and its natural analog. The effect of pH and the initial concentration of elements on the adsorption capacity of the zeolite was analyzed. The article presents the results of batch experiments on the treatment of subalkaline and acid drainage solutions from the Komsomolsk tailings impoundment and water from ponds on the surface of the Berikul mine tailings located in the village of Komsomolsk, Kemerovo region.

II. METHODS

Natural zeolite heulandite used in the experiments was extracted from a field in Western Siberia (OOO Sibir-Zeo). Prior to the experiments, a fraction of 0.5-0.25 mm of heulandite was isolated, washed with distilled water and dried at room temperature. The modification of the zeolite proceeded according to the following scheme [9]: 50 ml of 2.5 M $MnCl_2$ was added with 0.5 ml of 10M NaOH and 50 g of zeolite were added to the resulting solution by a magnetic stirrer. The resulting mixture was heated for 5 hours at 150 ℃, and then for 3 hours at 500℃. The modified zeolite was washed 3 times with distilled water and dried at room temperature. Photos of the natural and modified zeolites are shown in Fig. 1.

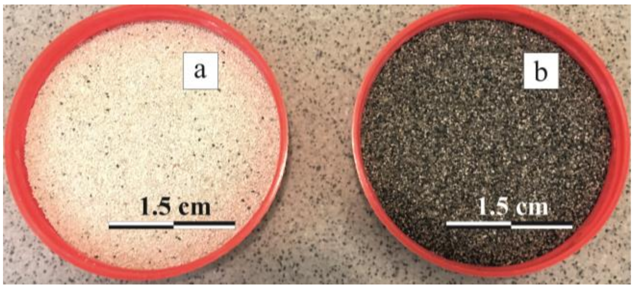

Fig. 1. Photographs of natural (a) and modified (b) zeolite used in the experiments.

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The elemental composition of the zeolite was studied by the ICP-MS method in the analytical centre “Plasma” (Tomsk) using the ELAN DRC-E mass spectrometer of PerkinElmer Instruments LLS (Certificate of Attestation, 2010) and the XRF method (analyst Yu. P. Kolmogorov). An electronic scanning microscope (SEM LEO 1430 VP) with an energy dispersive attachment (EDS (Oxford) spectrometer) was used to determine locations on the surface of sorbents that concentrate metals and metalloids and to study the morphology of the zeolite. Determination of the phase composition of the zeolite was carried out by X-ray diffraction analysis on a DRON 4 diffractometer with monochromatic CuKα radiation (Research Center of IGM SB RAS, analyst N.A. Pal’chik, Ph.D). Samples of natural and modified zeolite before and after the experiments were investigated by IR spectroscopy to identify the functional groups involved in the sorption of the elements under consideration. Fourier transform infrared (FT-IR) spectra were recorded on a Specord 75 IR two-beam spectrophotometer in the wave number range from 400 to 4000 cm^{-1} with a tablet of spectrally pure KBr in the comparison channel. Samples were prepared by the method of pressing tablets with KBr. Also IR spectra were recorded in the range from 370 to 4000 cm^{-1} on the Brotier VERTEX 70 FT-IR Fourier spectrometer in the absorption mode with a spectral resolution of 2 cm^{-1}. To process the spectra, the software package OPUS (the Research Center of IGM SB RAS, analyst T.N. Moroz, Ph.D.) was used. To study the sorption and ion-exchange properties of zeolites, batch experiments were carried out: samples of zeolite (in grams) 5, 1.6, 1, 0.4, 0.1, 0.04, was transferred to a flask containing 20 mL of solution (Table 1), mixed and filtered through a 0.45 μm membrane filter. 10 ml of samples were taken to determine the contents of As, Sb, Cu, and Zn by the AAS method using the SOLAAR spectrometer, M6 series (IGM SB RAS Research Center, analyst N.V. Androsova). The other part of the sample was used to measure pH, Eh, EC.

TABLE I: PHYSICO-CHEMICAL PARAMETERS AND CONCENTRATIONS (MG/L) OF SOME ELEMENTS IN THE DRAINAGE SOLUTIONS.

	KOM	BER	MPC
pH	8.1	2.5	
Eh [mV]	400	734	
As	0.22	0.60	0.01
Sb	0.75	0.0058	0.005
Zn	0.53	9.0	1
Cu	0.0093	1.9	1

Note: KOM – water from Komsomolsk tailings impoundment; BER – water from ponds on the surface of the Berikul mine tailings; MPC according to the normative document [12].

III. RESULTS AND DISCUSSION

By composition, the used zeolite belongs to the subfamily of high-silica zeolites. FT-IR spectra of natural and modified zeolites are shown in Fig. 2 and 3.

The observed absorption bands in the FT-IR spectrum of the zeolite refer to the internal vibrations of Si-O-Si, Si-O-Al bonds in SiO_4 and AlO_4 tetrahedra and characterize zeolite-heulandite [13], [14]. An intense band of an antisymmetric stretching vibration of Si-O-Si of about 1058 cm^{-1} with arms ~ 1140 cm^{-1}, 1200 cm^{-1} was registered. The exact position of this band depends on the ratio nSi/nAl in the crystalline framework [15]. The band of the symmetric valence vibration of ~ 794 cm^{-1} Si-O- (Si, Al = T), double 4 and 6-ring ~ 722, 605 cm^{-1} and the deformation vibration of the T-O bond ~ 470 cm^{-1} was registered. The 3421 cm^{-1} band in the valence vibration region of OH bonds refers to loosely bound water molecules in the zeolite framework. The FT-IR spectrum of the modified zeolite is practically unchanged, the shift of the stretching vibration band of the Si-O bond from 1058 to 1066 cm^{-1} is observed in the spectrum of the modified sample (Fig. 3a) and the shift to 3446 cm^{-1} and broadening of the stretching vibration band $(H_2O)Me(H_2O)$ connections (Fig. 3b). The FT-IR spectrum of the zeolite after the experiments remains practically unchanged, which indicates the preservation of short-range order in the structure of the zeolite, with the exception of the spectrum in the valence vibration region of OH bonds, which is due to redistribution of the $(H_2O)Me(H_2O)$ bonds in the zeolite framework.

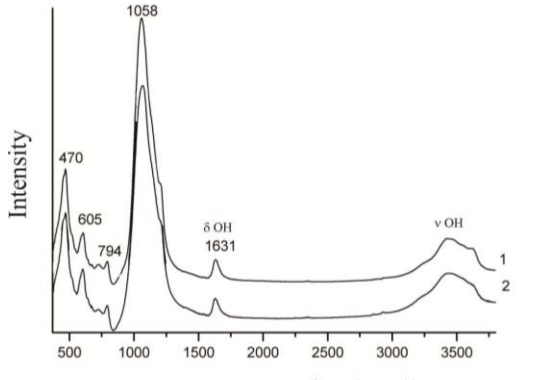

Fig. 2. FT-IR spectra of zeolites in the range from 400 to 3800 cm^{-1}. Zeolite (1), zeolite after an experiment with “BER” solution (2).

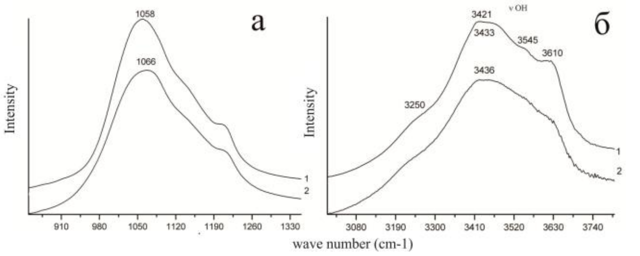

Fig. 3. Fragments of the FT-IR spectra of the zeolite in the region of stretching vibrations: (a) OH groups: zeolite (1), modified zeolite (2); (b) Si, Al-O groups: zeolite (1), modified zeolite (2).

When the zeolite interacts with an alkaline solution with an initial pH of 8.1 and an As the content of 0.22 mg/l, Sb 0.75, the pH value decreases to slightly acidic values. For modified zeolite, noticeable changes in pH values begin with a water/rock = 50, for a natural zeolite at a W:R ratio = 20. To remove As and Sb from water from Komsomolsk tailings impoundment, the modified zeolite is more efficient (Fig. 4). The natural zeolite also showed a good result and sorbed 39% of As and 76% of Sb from the solution at a ratio of W:R = 4. By modified zeolite 93% - As and 53% - Sb were sorbed and 27% As and 29% Sb were sorbed by its natural analog, respectively, at a ratio of W:R = 20.

A batch experiment on the interaction of an acid Berikul solution with a natural and modified zeolite was carried out under the same conditions as the experiment with water from Komsomolsk tailings impoundment. Modified and natural heulandite increased the pH of the acid drainage solution (BER) from 2.5 to 4.5 at a ratio (W:R) = 4:1. The modified zeolite proved to be ineffective for removal Zn from water from ponds on the surface of the Berikul mine tailings only 8% of Zn was sorbed with a minimum W:R ratio.

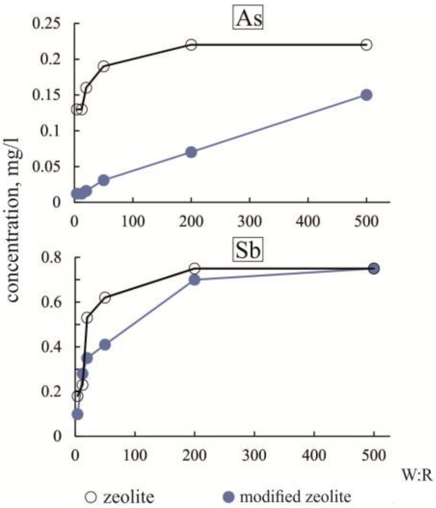

Fig. 4. Change in element concentrations during experiment on interaction of water from Komsomolsk tailings impoundment with a modified/natural zeolite.

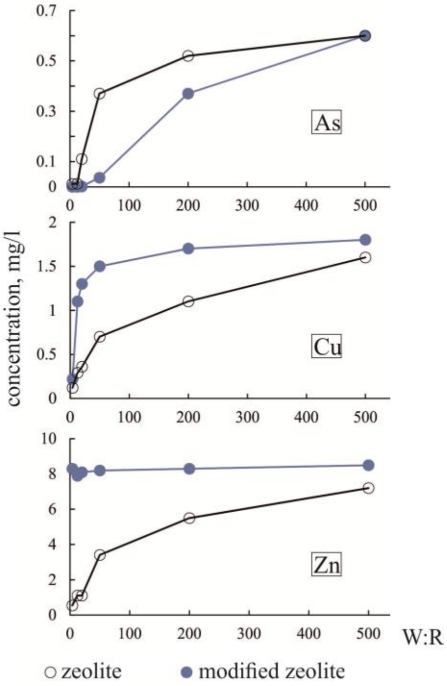

Fig. 5. Change in element concentrations during the experiments on interaction of water from ponds on the surface of the Berikul mine tailings with a modified/natural zeolite.

The content of Cu in the solution was significantly decreased in comparison with the initial solution only at the ratio water: rock =12.5. However, the modified zeolite sorbed As to a level below the detection limit (0.001 mg/l) at a ratio of W:R = 20, while the natural zeolite sorbed 82% at a given W:R ratio (Fig. 5).

In the course of the experiment, as the ratio of W:R decreases, the element species in solutions change. The pH-Eh diagrams show changes in the species for Al and Fe (Fig. 6). It is evident that in the course of the experiment it is possible to form iron and aluminum hydroxides, which are capable to sorb metals and metalloids from solutions.

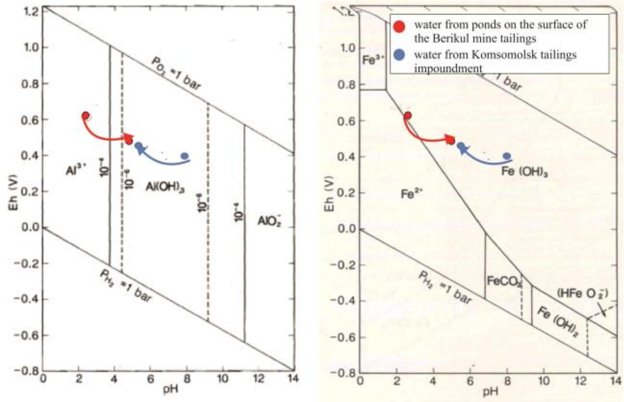

Fig. 6. pH-Eh diagrams modified from [16]. The arrows indicate the change in the physico-chemical parameters of solutions during the experiments.

The following processes are important during the removal of elements from the solution: ion exchange, adsorption, and sorption on newly formed iron and aluminum hydroxides.

IV. CONCLUSION

Modified MnO_2 zeolite can be used to remove As, Sb, Cu from drainage water (for both alkaline and acid solutions) but consider the possibility of releasing Mn (hazard class 3) into the solution. Optimum water:rock ratios for the modified and natural zeolite is 20-50. Since such proportions achieve significant percentages of deposition of the elements. Also, the maximum contents of metals and metalloids for natural zeolite were 12 μg -As, 6.5 μg/g -Sb, 60 μg -Cu, 280 μg -Zn per g of material and for the modified: As - 28 μg/g, Sb - 17 μg/g, Cu - 20 μg/g, Zn - 40 μg/g. Thus, to treat drainage water from metals, it is worth choosing a natural mineral, and to extract metalloids from the solution, a modified one. In an acid solution, arsenic sorption is better for both natural and for modified zeolite, in contrast to the alkaline solution. Perhaps this is due to the neutralization reaction and the formation of iron hydroxide capable of sorbing the elements from the solution.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Conceptualization, N.A.; methodology, N. Yu., S. B., N. A., A.D.; investigation, N. A., O. S., A. E., T. K..; resources, N. A.; writing-review and editing, S. B., N. Yu., N. A.; visualization, O. S., N. A., N. Yu.; supervision, N. A.; project administration, N. A.; funding acquisition, N. A. All authors had approved the final version.

REFERENCES

[1] S. E. Bailey, T. J. Olin, R. M. Bricka, and D. D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water research*, vol. 33, no. 11, pp. 2469-2479, August 1999.

[2] O. P. Saeva, N. V. Yurkevich, and V. G. Kabannik, "The electrochemical remediation of acid drainage," presented at the 13th International Conference on Water-Rock Interaction, Guanajuato, Mexico, August 16-20, 2010.

[3] H. Al-Zoubi, A. Rieger, P. Steinberger, W. Pelz, R. Haseneder, and G. Härtel, "Optimization study for treatment of acid mine drainage using membrane technology," *Separation Science and Technology*, vol. 45, no. 14, pp. 2004-2016, September 2010.

[4] N. V. Yurkevich, O. P. Saeva, and N. A. Pal'chik, "Arsenic mobility in two mine tailings drainage systems and its removal from solution by natural geochemical barriers," *Applied Geochemistry*, vol. 27, no. 11, pp. 2260-2270, November 2012.

[5] N. Abrosimova, O. Saeva, N. Yurkevich, and S. Bortnikova, "Treatment of neutral mine waters from metals and metalloids," presented at the 17th International Multidisciplinary Scientific GeoConference SGEM, Albena, Bulgaria, 29 June-5 July, 2017.

[6] M. Makarova, N. Abrosimova, E. Rybkina, R. Fiaizullina, and I. Nikolaeva, "Experimental investigation of sorption of microelements from mine drainage on zeolite and clay," presented at the 17th International Multidisciplinary Scientific GeoConference SGEM, Albena, Bulgaria, 29 June-5 July, 2017.

[7] R. Fiaizullina, M. Makarova, and N. Abrosimova, "The possibility of wastewater treatment of heavy metals by natural sorbents," presented at the 17th International Multidisciplinary Scientific GeoConference SGEM, Albena, Bulgaria, 29 June-5 July, 2017.

[8] E. S. Klimova and M. V. Byzaeva, *Natural Sorbents and Complexones in Wastewater Treatment*, Ulyanovsk, Russia: UlSTU, 2011, pp. 80-83.

[9] L. M. Camacho, R. P. Ramona, and S. Deng, "Arsenic removal from groundwater by MnO_2-modified natural clinoptilolite zeolite," *Journal of Hazardous Materials*, vol. 189, no. 1, pp. 286-293, May 2011.

[10] P. M. Nekhunguni, N. T. Tavengwa, and H. Tutu, "Investigation of as (V) removal from acid mine drainage by iron (hydr) oxide modified zeolite," *Journal of environmental management*, vol. 197, pp. 550-558, July 2017.

[11] M. E. Jiménez-Castañeda and D. I. Medina, "Use of surfactant-modified eolites and clays for the removal of heavy metals from water," *Water*, vol. 9, no. 4, p. 235, March 2017.

[12] *Maximum Permissible Concentration (MPC) of Chemical Substances in the Water of Drinking and Cultural-Domestic Water Objects*, RMH, Russian Ministry of Health, Moscow, Russia, HN 2.1.5.1315-03.

[13] H. Moenke, *Mineralspektren*, Berlin: Akademie-Verlag, 1962, p. 234

[14] J. A. Gadsden, *Infrared Spectra of Minerals and Related Inorganic Compounds*, Butterworths, 1975, p. 277.

[15] M. Ostrooumov, P. Cappelletti, and R. Gennaro, "Mineralogical study of zeolite from New Mexican deposits (Cuitzeo area, Michoacan, Mexico)," *Applied Clay Science*, vol. 55, pp. 27-35, January 2012.

[16] D. G. Brookins, *Eh-pH Diagrams for Geochemistry*, Springer-Verlag Berlin Heidelberg, 1988, p. 45.

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