Chemistry for Sustainable Development **21** (2013) 197–200

UDC 549.67

Studies on the Complex Sorption in the System Geotechnogenous Solutions–Zeolite Bearing Rocks

E. S. EPOVA, O. V. EREMIN, R. A. FILENKO and G. A. YURGENSON

Institute of Natural Resources, Ecology and Cryology, Siberian Branch of the Russian Academy of Sciences, Ul. Butina 26, Chita 672014 (Russia)

E-mail: apikur1@yandex.ru

(Received July 30, 2012)

Abstract

Experimental results are presented on studying the ionic mobility of metals in geotechnogenous solutions from an opencast mine of the Sherlovaya Gora tin-polymetallic deposit in the presence of zeolite-containing rocks taken from the Shivyrtuy deposit (Transbaikalia). A high sorption activity of zeolite-bearing rocks is revealed concerning almost all the metal ions in solution. Concentrating the large amounts of zinc, iron, manganese ions and other elements in the solid phase could be caused replacing the ions of sodium in the structure of clinoptilolite by the mentioned ions.

Key words: geotechnogenous solutions, zeolite-containing rocks, sorption, ion exchange

INTRODUCTION

Naturally occurring zeolites are a relatively new type of minerals, whose practical use began in the second half of the last century with the discovery of large-scale deposits in the United States, Russia, Japan and other countries.

According to the mineralogical classification, the zeolites represent a class of skeletal aluminosilicates of alkali and alkaline earth metals associated with water. The spatial structure of these compounds includes a plurality of pores and channels, wherein there could occur sorption and ion exchange, hydration and dehydration processes [1]. Such properties determine a widespread use of zeolites in industry, agriculture, medicine, in dealing with issues related to the protection of the environment, and others.

Despite a large number of naturally occurring zeolite minerals (so far they are registered to be over 50) [9], mainly more expensive synthetic analogs thereof are used.

In the Transbaikalian Territory there are about 80 % of the proven reserves of the naturally occurring zeolites of Russia. The main part of them is attached to the largest Shivyrtuy and Kholinsk deposits [4, 8], whose zeolite-bearing features are associated with the volcanic activity within the Jurassic-Early Cretaceous of the terrain development [7]. The zeolite-bearing rocks of these deposits are used in agriculture, veterinary medicine, building materials production, medicine [3, 6].

In the Transbaikalian Territory, there are a large number of flooded quarries such as the Sherlovaya Gora, Klyuchevskiy, and Bom-Gorkhon *etc.* [2]. The waters in such quarries or sumps, on the one hand, represent a potential environmental hazard, and on the other hand, might be of interest as natural-and-technogeneous concentrator of rare elements. For example, water in old sumps of the Bom-Gorkhon ore mine contains a great amount of rare earth elements (1.6 mg/L of La, 4 mg/L of Ce, 0.3 mg/L of Pr, 0.9 mg/L of Nd, 0.1 mg/L of Sm, 0.5 mg/L of U).

Zeolite materials are widely used for water treatment [3, 10, 11]. The purpose of this work

TABLE 1

Composition of the Shivyrtuy clinoptilolite tuffs, mass %

Samples	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5	BaO	SrO	H_2O
Sh	64.30	13.90	1.24	0.14	0.40	1.36	0.02	2.16	1.55	2.38	0.15	–	–	12.08
Sh1	62.20	13.40	1.43	–	0.38	1.07	0.12	2.03	1.90	2.45	0.12	0.16	0.24	14.50

Notes. 1. Sh – data from [5], Sh1 – experimental data of our work. 2. Dash – not determined.

consisted in studying the interaction between the zeolite-bearing rocks and geotechnogenous solutions.

MATERIALS AND METHODS

The Sherlovaya Gora tin ore deposit was discovered in 1930 being attached to an explosion tube, located in the western part of the Sherlovaya Gora ore-magmatic granite massif. In 1962, there was a processing plant commissioned with starting the production of basement ores using a pit method (quarrying). Since 1992, the quarrying was ceased with further forming a lake therein.

The tin-polymetallic ore species of the mentioned deposit are characterized by a complicated mineral composition with a substantial portion of the oxidized varieties of sulphides. For the experiments, we used water taken from the quarry lake, which water exhibited the following macrocomponential composition (mg/L): SO_4^{2-} 3625.5, HCO_3^- 200.7, Cl^- 5.2, Ca^{2+} 420.1, Mg^{2+} 220.0, Zn^{2+} 515.6, Mn^{2+} 100.0, Al^{3+} 33.5, Na^+ 30.9, Fe^{3+} 10.7, K^+ 4.6, Cu^{2+} 3.6, Cd^{2+} 3.2, Ni^{2+} 3.2, Sr^{2+} 1.9.

Preparation of tuffs

Samples of zeolite-bearing rocks were taken from a quarry of the Shivyrtuy deposit. The rocks are presented by volcanic-sedimentary tuff species consisting of clinoptilolite (90 %) and montmorillonite (20 %) with cryptocrystalline mineralization [4, 5].

The results of chemical analysis are presented in Table 1. The water content was determined using a thermogravimetric method with the help of a STA 449 F1 Jupiter thermal analyzer.

The samples tuffs were sieved after grinding, washed with distilled water and dried. For the experiments we used use the tuff fractions of 1–2 and 2–3 mm in diameter.

Steady-state experiments

The samples of tuffs sizing 2–3 mm in diameter with the mass of 5 g were placed in a solution (50 mL) within a sealed vessel for 7 days. The solution was then filtered and ana-

TABLE 2

Concentration of macro- and microcomponents in the initial solution and in the solution after the interaction with tuff, mg/L

Solution components	Solution	
	Initial	After interaction with tuff
Macrocomponents		
Zn	515.6	290.0
Ca	420.0	300.0
Mg	220.0	177.5
Mn	100.0	63.8
Al	33.5	14.6
Na	30.9	463.3
Fe	10.7	0.4
K	4.6	11.3
Cu	3.6	1.6
Ni	3.2	2.2
Cd	3.2	1.7
Sr	1.9	2.7
Microcomponents		
Co	900	620
Y	600	210
Pb	360	50
Be	180	79
Ba	10	60
La	20	40
Ag	11	5
Sc	6	2

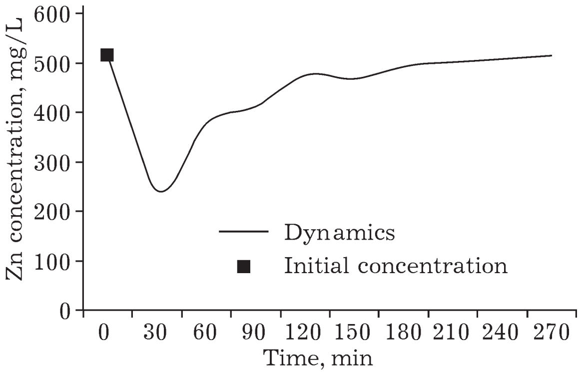

Fig. 1. Dynamics of zinc concentration in the solution in the course of filtering through the tuff.

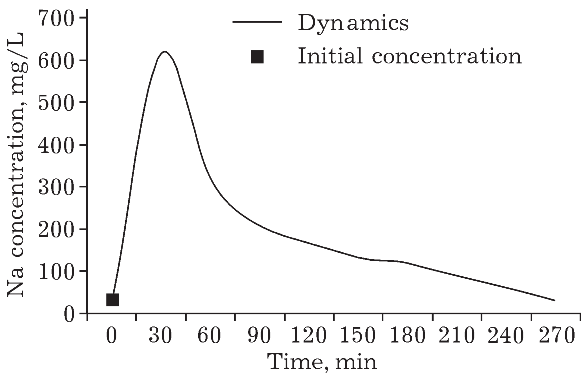

Fig. 2. Dynamics of sodium concentration in the solution in the course of filtering through the tuff.

lyzed for 31 chemical elements. Table 2 demonstrates the content of the components in the solutions.

Dynamic experiments

The samples of tuffs sizing 2–3 mm in diameter with the mass of 5 g were placed in a plastic vessel with a capacity of 5 mL. Using a Peristaltic Pump Type pp1-05 pumping unit (Poland), a geotechnogenous solution (300 mL) was supplied thereto with a constant rate equal to 1.5 mL/min. From the solution flown through, there was 30 mL of the filtrate taken for chemical analysis.

The sorption dynamics for zinc ions is demonstrated in Fig. 1.

RESULTS AND DISCUSSION

From Table 2, one can see that almost all of the elements analyzed are involved in the ion exchange process, replacing the sodium and potassium in the zeolite structure. To an insignificant extent, the processes involve barium and strontium moving from the zeolite into the solution.

In the course of dynamic experiments during 4–5 h of filtration, there occurs saturation with respect to all the metal ions. The sorption capacity in the course of filtration amounted to 5.8 mg/g of tuff for zinc ions, 1.2 mg/g of tuff for manganese ions and 0.5 mg/g of tuff for iron ions. In the course of filtration, there occurred a removal of sodium ions from the structure of zeolites in the amounts of 15.1 mg/g of the rock (Fig. 2).

According the results of the investigations performed, the Shivyrtuy zeolite-containing rocks represent good material for the sorption of metals from geotechnogenous solutions.

One of important applied consequence of the results obtained, alongside with a possible purification of geotechnogenous waste waters formed in opencast mines consists in a prospect of extracting useful components from these waters. For example, the estimates of the zinc content in the water of the lake in the Sherlovaya Gora opencast mine amounts to 1400 t, those of yttrium content amounting to 1.5 t, those of silver content being of 30 kg and those of scandium content being of 15 kg. In this connection, one of the important tasks for further research should consist in studying the species of zinc, scandium, yttrium, and silver occurring in the zeolite sieves, as well as studying the possibility of profitable isolation thereof.

CONCLUSION

1. Potentiality has been revealed for the absorption of toxic elements (Zn, Pb, Cr, Cd, Ni, Co, Be, Y, Ag, Sc) by clinoptilolite tuff from geotechnogenous solutions, which allows developing a technology for the purification of water from these environmentally hazardous elements.

2. The extraction of alkali (K, Na) metals from the clinoptilolite tuff into a man-caused water reservoir could promote softening thereof to further use it for technical purposes.

3. The large-scale reserves clinoptilolite tuffs of the Shivyrtuy deposit as well as the zeolites (heulandite, mordenite, chabazite) of other

deposits known in Transbaikalia in the case of revealing high sorption properties thereof could become an important raw material for purifying of geotechnogenous waste waters and for extracting and utilizing toxic chemical elements.

REFERENCES

1 Breck D., Zeolite Molecular Sieves, Wiley, New York, 1974.
2 Yurgenson G. A., Chechetkin V. S., Askokov V. M., Sinitsa S. M., Ptitsyn A. B., Geologicheskiye Issledovaniya i Gorno-Promyshlenny Kompleks Zabaikalya: Istoriya, Sovremennoye Sostoyaniye, Problemy, Perspektivy Razvitiya. K 300-letiyu Osnovaniya Prikaza Rudokopnykh Del, Nauka, Novosibirsk, 1999.
3 Zonkhoeva E. L., *Bezopasnost' Zhiznedeyatelnosti*, 6 (2010) 36.
4 Pavlenko Yu. V., Tseolitovye Mestorozhdeniya Vostochnogo Zabaikalya, Izd-vo ChitGU, Chita, 2000.
5 Pavlenko Yu. V., Beletskiy I A., Seretkin Yu. V., *Geologiya i Geofizika*, 7 (1989) 116.
6 Panichev L. M., Bogomolov N. I., Bgatov N. P., Silkin S. P., Gul'kov A. N., Izd-vo DVGTU, Vladivostok, 2004.
7 Gordienko I. V., Zhamoytsina L. G., Zonkhoeva E. L., Leonov V. E., Semushin V. N., Tselitonosnost' Bazaltov Zabaikalya, Nauka, 1989.
8 Yurgenson G. A., Mineralnoye Syrye Zabaikalya (School Book), part II: Nemetallicheskoye Syrye, book 1: Toplivno-Energeticheskoye, Gorno-Khimicheskoye i Gorno-Tekhnicheskoye Syrye, Poisk, Chita, 2009.
9 Bakakin V. V., Seryotkin Yu. V., *J. Struc. Chem.*, 50 (2009) 116.
10 Motsi T., Rowson N. A., Simmons M. J. H., *Int. J. Mineral Proc.*, 101 (2011) 42.
11 Wang S., Peng Y., *Chem. Eng. J.*, 156 (2010) 11.