

UDC 549.67:547.59

## Sorption of Europium (III) Ions by Natural Mordenite-Containing Tuff

N. M. KOZHEVNIKOVA

*Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Ulan Ude, Russia*

*E-mail: nicas@binm.bscnet.ru*

(Received March 15, 2016; revised May 19, 2017)

### Abstract

Natural zeolites modified by REE (rare earth element) ions are promising to obtain efficient regenerative stimulants and biologically active drugs. Rare earth elements are used upon treatment of tuberculosis, tumours, skin diseases, and REE of cerium subgroup have anticoagulative action. Europium introduced into the zeolite matrix exerts neuroprotective effects. It is considered reasonable to use potassium channel blockers with the aim of reducing ischemic brain damage. Lanthanum, cerium, praseodymium, and europium ions in biological systems substitute calcium ions block their entrance into cells exerting inhibitory effects on the development of calcium-induced cascade of pathologic reactions in cerebral ischemia [4]. Sorption technology allows increasing biological activity of natural zeolites that act as a prolonging carrier of REE ions. Equilibrium and sorption kinetics of europium (III) ions from sulphate solutions by natural mordenite-containing tuff were studied. The kinetic parameters of the sorption process were defined; adsorption isotherms of europium ions were constructed. It was determined that both external and internal diffusion were the rate-limiting step; europium was completely extracted from diluted solutions ( $<0.0025$  mol/L).

**Key words:** natural mordenite-containing tuff, europium ions, sulphate solutions, adsorption of europium ions, sorption isotherms, kinetic regularities

### INTRODUCTION

Natural zeolites are used as sorbents in chemical technology, hydrometallurgy, industrial ecology, agriculture, and medicine [1]. Natural zeolites modified by REE (rare earth element) ions are promising to obtain efficient regenerative stimulants and biologically active drugs [1, 2]. Rare earth elements are used upon treatment of tuberculosis, tumours, skin diseases, and REE of cerium subgroup have anticoagulative action. Europium introduced into the zeolite matrix exerts neuroprotective effects [3, 4]. It is considered reasonable to use potassium channel blockers with the aim of reducing ischemic brain damage. Lanthanum, cerium, praseodymium, and europium ions in biological systems replace cal-

cium ions; block their entrance into cells exerting inhibitory effects on the development of calcium-induced cascade of pathologic reactions in cerebral ischemia [4]. Sorption technology allows increasing biological activity of natural zeolites that act as a prolonging carrier of REE ions.

Sorbents based on natural zeolites are used in various areas of molecular biology, medicine, biochemistry, chemical technology, hydrometallurgy, industrial ecology, and agriculture. The use of natural zeolites as sorbents to isolate, separate and purify biologically active substances, immobilize ferments opens up great practical opportunities [1–4].

The efficiency of ion-exchange systems is largely defined by their kinetic properties [1, 4]. Natural zeolites modified with REE ions are

promising to obtain efficient regenerative stimulants and biologically active drugs [1, 3].

The insufficient knowledge about ion-exchange properties of natural zeolites in relation to REE ions limits the possibility of their use.

Earlier [1, 4], sorption of lanthanum, cerium, neodymium, samarium, praseodymium ions by mordenite and clinoptilolite tuff was studied by us. However, the data on sorption of europium ions by natural mordenite-containing tuff required to assess the effect of the nature of REE on equilibrium and sorption kinetics were not found in literature. For this purpose, sorption of europium (III) ions from sulphate solutions by mordenite-containing tuff was studied by us depending on solution concentration, sizes of sorbent grains and the mass ratio of solid and liquid phases.

## EXPERIMENTAL

Tuff from the Mukhor-Talin perlite-zeolite deposit of the following composition was used as a sorbent (%): SiO<sub>2</sub> 70.96, MgO 0.18, Al<sub>2</sub>O<sub>3</sub> 11.97, CaO 0.92, Na<sub>2</sub>O 2.38, K<sub>2</sub>O 5.22. A Si/Al ratio is 5.2. The zeolite content in the rock was determined by X-ray diffraction analysis using PCL-2 [5] and amounted to 62–64 mass %. To determine the optimum conditions of modification of zeolite with europium (III) ions their absorption by mordenite-containing tuff was examined.

To study the kinetics and equilibrium of adsorption of europium (III) ions mordenite-containing tuff was crushed, a fraction of seeds with a diameter of 0.25–0.5 and 1–2 mm was selected, separated from dust, dried at room temperature for 24 h and sample weight was selected. Drying time (24 h) was selected using triple check weighing in each 3 h of drying.

The equilibrium was studied under static conditions in aqueous solutions of Eu<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> by constant mass method [6, 7]. The content of europium (III) ions was analysed by the photometric method with the use of arsenazo III distinguished by high sensitivity and selectivity [8]. KFK-3 spectrophotometer was used for measurements. The residual concentration of europium ions in the exchange solution was defined by the optical density of europium complexes with arsenazo III at  $\lambda$  of 640 nm, 5 cm cuvette length. The

amount of absorbed europium was calculated by the difference of europium (III) concentrations in a solution before and after sorption from the results of three parallel experiments, the relative determination error did not exceed 3 %.

The kinetics of absorption of europium ions was studied by the limited volume method at the ratios of solid (S) and liquid (L) phases of 1 : 10 and 1 : 50 from europium (III) sulphate solutions with concentrations of 0.001–0.003 mol/L while constant stirring. The contact time of sorbent with solution was changed from 5 min to 6 days. The effect of sorbent grain size was studied for sorbent grains with a diameter of 0.25–0.5, 1–2 mm.

Kinetic parameters were calculated from  $Q - \tau$  curves ( $Q$  is the amount of sorbed europium (III) ions, mmol/g;  $\tau$  is time, s) by the method given in monography [9] for sorption on zeolites. The rate constant of external diffusion mechanism ( $R$ ) is calculated by the equation

$$R = dQ/d\tau(1/cK) \quad (1)$$

where  $c$  is the concentration of ions in solution (mol/L);  $K$  is the equilibrium distribution coefficient (mL/g).

With increase in contact time, the amount of absorbed ions is defined by the exchange rate inside a sorbent grain. Effective diffusion coefficient ( $D$ ) and the rate constant of internal diffusion process ( $B$ ) characterizing the internal diffusion mechanism were calculated by equations derived for spherical particles:

$$F = Q_\tau/Q_\infty = (6/r)\sqrt{Dr}/\pi \quad (2)$$

$$B = \pi^2 D/r^2 \quad (3)$$

where  $F$  is the degree of absorption of europium (III) ions;  $r$  is the average radius of sorbent grains (cm).

TABLE 1

Kinetic parameters of sorption of europium (III) ions from sulphate solutions by natural mordenite-containing tuff

Parameters	Solution concentration, mol/L		
	0.001*	0.002**	0.003**
$\tau_\infty$ , min	1569	1692	1623
$dQ/d\tau$ , 10 <sup>5</sup> mmol/(g · s)	5.7	4.2	4.9
$K$ , mL/g	47.7	39.8	55.6
$R$ , 10 <sup>4</sup> s <sup>-1</sup>	4.7	4.6	5.3
$D$ , 10 <sup>8</sup> cm <sup>2</sup> /s	4.8	3.7	3.6
$B$ , 10 <sup>4</sup> s <sup>-1</sup>	8.8	7.9	8.5

\*  $d = 0.25-0.5$  mm, S/L = 1 : 50.

\*\*  $d = 1-2$  mm, S/L = 1 : 10.

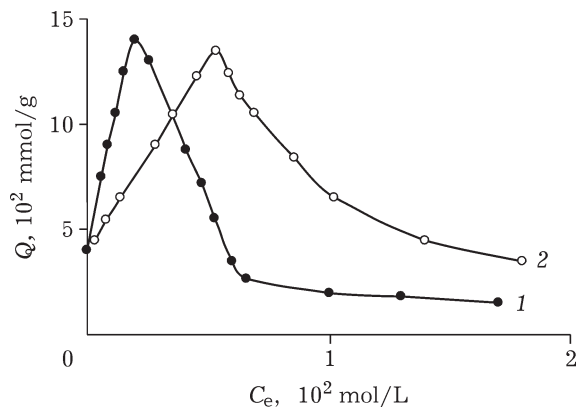


Fig. 1. Sorption isotherm of europium from europium sulphate solutions ( $Q$  is the amount of sorbed europium (III) ions, mol/g;  $C_e$  is the equilibrium concentration of Eu(III) in solution, mol/L): 1 -  $d = 0.25-0.5$  mm,  $S/L = 1 : 50$ ; 2 -  $d = 1-2$  mm,  $S/L = 1 : 10$ .

The received results are presented in Table 1. The study on equilibrium of sorption of praseodymium ions on mordenite-containing tuff in a wide concentration range ( $10^{-5}$ – $10^{-2}$  mol/L) allowed revealing changes in the initial and final portions of equilibrium curves.

Figure 1 presents equilibrium curves of europium (III) from europium sulphate solutions on natural mordenite-containing tuff obtained for different-sized grains (0.25–0.5 and 1–2 mm) at mass ratios of solid and liquid phases  $S/L$  of 1 : 50 and 1 : 10.

Equilibrium curves have similar forms and reflect certain regularity in the nature of the interaction of europium ions with the zeolite phase. The appearance of the extremum is observed on the isotherms, which may be due to the formation in solution of intermediates, to which the sorbent exhibits increased selectivity [8]. The state of aqueous solutions of europium (III) is characterized by the processes of hydration, hydrolysis, polymerization and complexation.

Europium ions in neutral and acid aqueous solutions are found as aqua complexes  $[\text{Eu}(\text{H}_2\text{O})_n]^{3+}$  and hydroxy aqua complexes  $[\text{Eu}(\text{H}_2\text{O})_n\text{OH}]^{2+}$ , where  $n = 5-8$  [10, 11].

The formation of complexes with the composition  $[\text{Eu}(\text{SO}_4)_n]^{3-2n}$  was also registered in europium sulphate solutions, where  $n = 1-3$ . Cations  $[\text{EuSO}_4]^+$  [12], prevail at low concentrations of sulphate ions ( $<0.03$  mol/L), though anion complexes can also be formed [13].

The process of absorption of europium (III) ions is accompanied by a decrease in the pH

value of a solution by 0.5–0.8 units. With the aim of clarifying the cause of the pH decrease check experiments were carried out, where mordenite-containing tuff was poured with distilled water. A decrease in the pH value by 0.6–0.8 units was noted in the experiments during the contact time of 28–32 h, regardless of absorption of europium ions resulting from the exchange between  $\text{Na}^+$  and  $\text{H}^+$  ions that are present in zeolites [9]. A decrease in the pH value upon contact of mordenite-containing tuff with distilled water is also possible due to hydrolysis of aluminum (III), magnesium (II), and iron (III) cations comprising zeolite by scheme

$$\text{M}^{n+} + 2\text{H}_2\text{O} \rightarrow [\text{MOH}]^{(n-1)+} + \text{H}_3\text{O}^+ \quad (4)$$

where  $\text{M}^{n+} = \text{Al}^{3+}, \text{Mg}^{2+}, \text{Fe}^{3+}$ .

A change in the pH value does not affect absorption of europium (III) ions for 0.003 and 0.001 mol/L solutions of europium (III) sulphate with pH 6.5 and 6.2, respectively.

Sorption of europium (III) aqua- and hydrocomplexes happens with the increase in solution concentration to an extremum point, since they have a higher ionic charge and increased selectivity of zeolite toward them. The size of the windows and cavities of studied zeolite is 5–7 Å, which is much larger than that of aqua and hydroxocomplexes. The proposed mechanism of exchange sorption by substitution of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}^+$  by  $\text{Eu}^{3+}$  is confirmed by the data of [7].

The grain size and the mass ratio of solid and liquid phases affect the position of the maximum on isotherms (see Fig. 1). The maximum

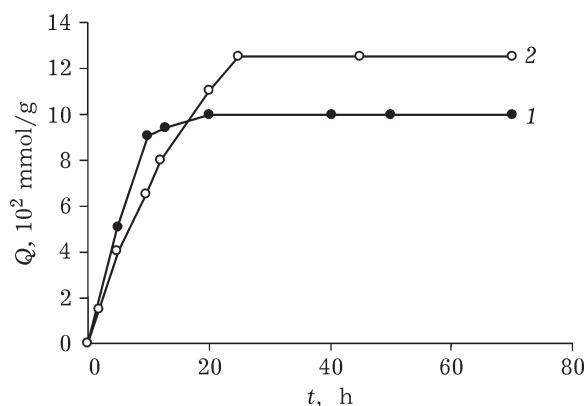


Fig. 2. Kinetic curves of sorption of europium (III) from aqueous solutions of europium (III) sulphate by mordenite-containing tuff ( $Q$  is the amount of sorbed of europium (III) ions, mol/L;  $\tau$  is sorption time, h): 1 - 0.001 mol/L,  $d = 0.25-0.5$  mm,  $S/L = 1 : 50$ ; 2 - 0.003 mol/L,  $d = 1-2$  mm,  $S/L = 1 : 10$ .

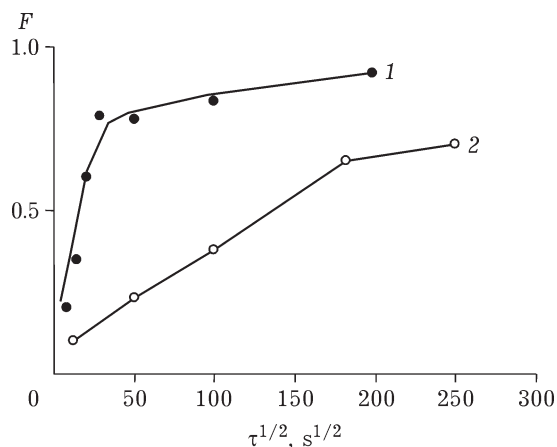


Fig. 3. Degree of exchange ( $F$ ) vs. time ( $\tau$ ): 1 – 0.005 mol/L,  $d = 0.25\text{--}0.5$  mm,  $S/L = 1 : 50$ ; 2 – 0.01 mol/L,  $d = 1\text{--}2$  mm,  $S/L = 1 : 10$ .

of exchange capacity (EC) for the grains with  $d = 0.25\text{--}0.5$  mm and  $S/L = 1 : 50$  (see Fig. 1, curve 1) is shifted to the region of lower equilibrium concentrations, and with increasing grain size ( $d = 1\text{--}2$  mm) and the ratio  $S/L = 1 : 10$  the maximum of EC is found in the area of higher concentrations (curve 2).

Thus, the maximum EC of  $0.153 \mu\text{mol/g}$  on fine tuff grains is reached upon lower reagent consumption.

Kinetic curves of absorption of europium (III) ions have similar forms (Fig. 2).

A linear dependence of the filling degree of ( $F$ ) zeolite on time  $\tau$  ( $F - \sqrt{\tau}$ ) (Fig. 3) confirms high contribution of the intradiffusion mechanism of sorption [7, 10].

From the data of Table 1 it follows that the dependence of absorption rate of europium (III) ions depends of the grain size of mordenite-containing tuff and solution concentration. A decrease in sorbent grain size leads to surface increase, which contributes to an increase in adsorption rate  $dQ/d\tau$  according to the mechanism of external diffusion.

Upon an increase in the concentration of europium (III) sulphate solutions, time to achieve equilibrium condition ( $\tau_{\infty}$ ), is reduced, rate constants of the processes of external ( $R$ ) and internal ( $B$ ) diffusion, and effective diffusion coefficient ( $D$ ) increase. Constants  $R$  and  $B$  have the same order, which is confirmed by a mixed

mechanism of sorption of europium (III) ions by mordenite-containing tuff.

## CONCLUSION

Sorption isotherms of europium (III) ions by mordenite-containing tuff are characterized by the presence of the maximum, which is related to the complex nature of the interaction in the system of europium sulphate solution and zeolite. A change in selectivity of mordenite-containing tuff in relation to europium (III) ions and a decrease in its sorption capacity are observed with an increase in aqueous solution concentration.

Sorption rate of europium (III) ions on mordenite-containing tuff depends on the grain size, solution concentration,  $L/S$  ratio and is controlled by mixed mechanism of sorption.

## REFERENCES

- Aleksandrova T. E., Maksarov V. S., Ubashev I. O., Kozhevnikova N. M., *Sib. Med. Zh.*, 4 (2001) 65.
- Kozhevnikova N. M., Ubashev I. O., Mitypov B. B., *Khim. Ust. Razv.*, 9, 2 (2001) 207.
- Polyntseva L. V., Ubashev I. O., Kozhevnikova N. M., Aleksandrova T. E., Strubina V. N., *Sib. Med. Zh.*, 3 (2003) 54.
- Gulyaev S. M., Ubashev I. O., Kozhevnikova N. M., *Vestn. Buryat. Gos. Un-ta*, 2 (2007) 86.
- Belitskiy I. A., Drobot I. V., Valueva G. P., *Opyt Ekspressnogo Opredeleniya Soderzhaniya Tseolitov v Gornykh Porodakh s Ispolzovaniyem Portativnykh Tseolitnykh Laboratoriy PTsL-1 i PTsL-2*, Nauka, Novosibirsk, 1979.
- Kokotov Yu. A., Zolotarev P. P., El'kin G. E., *Teoreticheskiye Osnovy Ionnoy Obmena: Slozhnyye Ionnoobmennyye Sistemy*, Khimiya, Leningrad, 1986.
- Tunitskiy N. N., Kaminskiy V. A., Timashev S. F., *Metody Fiziko-Khimicheskoy Kinetiki*, Khimiya, Moscow, 1973.
- Jeffery P. G., *Chemical Methods of Rock Analysis*, Pergamon Press, New York, 1970.
- Chelishchev N. F., Volodin V. F., Kryukov V. L., *Ionoobmennyye Svoystva Prirodnykh Vysokokremnistykh Tseolitov*, Nauka, Moscow, 1988.
- Komissarov L. N., Pushkina G. Ya., Shatskiy V. M., Znamenskaya A. S., Dolgikh V. A., Suponitskiy Yu. L., Shakhno I. V., Pokrovskiy A. N., Chizhov S. M., Bal'kina T. I., Belova I. D., Belov V. V., Kuz'mina T. I., Savelieva M. V., *Soyedineniya Redkozemel'nykh Elementov. Sulfaty, Selenaty, Telluraty, Khromaty (Khimiya Redkikh Elementov)*, Nauka, Moscow, 1986.
- Yatsemirskiy K. B., Kostromina N. A., Sheka Z. A., *Khimiya Kompleksnykh Soyedineniy Redkozemel'nykh Elementov*, Nauk. Dumka, Kiev, 1966.
- Spedding F. H., Jappe S., *J. Am. Chem. Soc.*, 5 (1954) 882.
- Secine T., *J. Inorg. Nucl. Chem.*, 7 (1964) 1463.