Studying the Kinetics and Equilibrium of Praseodymium (III) Sorption by Naturally Occurring Mordenite-Containing Tuff

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Abstract

Kinetic laws inherent in the sorption of praseodymium (III) ions from sulphate solutions on mordenite containing tuff. Kinetic parameters for the sorption process were determined, and constructed absorption isotherms for praseodymium ions were obtained. It has been established that the rate-determining stage is presented both by external and internal diffusion. From dilute solutions (<0.002 mol/L) praseodymium can be extracted to a complete extent.

Key words: naturally occurring mordenite-containing tuff, praseodymium, kinetics, equilibrium

INTRODUCTION

Naturally occurring zeolites modified by ions of rare earth elements (REE) are used in the development of efficient regeneration therapy stimulators as well as the preparations of anti-coagulant action, in the treatment of tuberculosis, tumours, skin diseases [1, 2]. Lanthanum, cerium, praseodymium being introduced into zeolite matrix exhibit a neuroprotective activity [3]. In order to reduce ischemic brain damage it is considered application of calcium blockers to be appropriate. In biological systems the ions of lanthanum, cerium, and praseodymium substitute calcium ions to inhibit supply thereof into cells, exerting an inhibitory effect on the development of the calcium-induced cascade of pathological reactions in cerebral ischemia [4].

In order to solve technological tasks connected with the preparation of pharmaceuticals based on rare earth compounds, it is appropriate to use a sorption technology, using naturally occurring zeolites as sorbents with in-creased biological activity those play the role of a prolonging REE carrier [1–4].

Studying the sorption kinetics allows determining the rate of achieving the equilibrium, the maximum exchange capacity level of the zeolite for a specific composition of solution, the mechanism of sorption. The influence of REE nature upon the sorption kinetics and equilibrium requires a more detailed study of the laws inherent in the sorption within the system zeolite-REE ions. With this purpose, we studied the processes of the sorption of praseodymium (III) by mordenite-containing tuff depending on the concentration of solutions, the sorbent grain size and the mass ratio between the solid and the liquid phases.

EXPERIMENTAL

As a sorbent we used mordenite-containing tuff taken from the Mukhor-Tala perlite and zeolite deposit with the following composition (mass %): SiO_2 70.96, MgO 0.18, Al_2O_3 11.97, CaO

0.92, Na_2O 2.38, K_2O 5.22; Si/Al ratio = 5.2. The zeolite content in the rock was determined by means of XRD structure analysis with the help of PCL-2 [5] to be equal to 62–64 mass %.

In order to study the kinetics and equilibrium for the sorption of praseodymium (III) ions by mordenite-containing tuff the latter was grinded in a MC 23200 planetary mill (Siemens) equipped with agate balls. Using the method of sieving we selected fractions with a grain diameter ranging within 0.25–0.5 mm and 1–2 mm, with further separating from the dust drying then at a room temperature during 24 h to take a weighed sample portion. The drying time was chosen basing on three checks weighing in every 3 h of drying.

The investigation of the kinetics and equilibrium was carried out under static conditions for $Pr_2(SO_4)_3$ aqueous solutions [6, 7]. The content of praseodymium (III) ions was analyzed using a photometric method with Arsenazo III, which method is highly sensitive and selective [8]. The sorption capacity was calculated from the difference in the concentrations of praseodymium (III) ions in the solution before and after sorption basing on the results of three parallel experiments, the relative error did not exceed 3 %.

The kinetics of praseodymium ion absorption was studied using a limited volume technique at the ratio values between the solid (S) and the liquid (L) phases S/L equal to 1 : 10 and 1 : 50, for praseodymium (III) sulphate solutions, with the concentration ranging within 0.001-0.003 mol/L under permanent stirring [6, 7]. The contact time between the solution and the sorbent was varied within the range from 5 min to 6 days. The effect of grain size was investigated for the sorbent grains with the diameter ranging within 0.25–0.5 mm and 1–2 mm.

The kinetic parameters were calculated basing on $Q - \tau$ curves (Q is the amount of praseodymium (III) ions absorbed, mmol/g; τ is the time, s) according to the procedure described for the adsorption on zeolites [9]. For the initial period of time, when the sorption takes place on the surface of the sorbent and the process is controlled by an external diffusion mechanism, the rate constant of the an external diffusion (R) can be calculated using the following equation:

$$R = \mathrm{d}Q/\mathrm{d}\tau(1/CK) \qquad (1)$$

where C is the ion concentration in solution, mol/L; K is the equilibrium distribution coefficient, mL/g.

With increasing the contact time, the amount of ions absorbed is determined by the exchange rate within the sorbent grain. The effective diffusion coefficient (D) and the rate constant of the internal diffusion process (B), those characterize the internal diffusion mechanism, were calculated using the equations derived for spherical particles:

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

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

where F is the absorption level for praseodymium (III) ions; r is the mean radius of the sorbent grains, cm.

RESULTS AND DISCUSSION

The results obtained are presented in Table 1. Studying the equilibrium for the sorption of praseodymium ions on mordenite-containing tuff within a wide concentration range (10^{-5}–10^{-2} mol/L) allowed us to reveal changes in the initial and final parts of the equilibrium curves.

Figure 1 demonstrates equilibrium curves for praseodymium (III) ions in praseodymium sulphate solutions on the naturally occurring mordenite-containing tuff obtained for different sized grains times (~0.25–0.5 and 1–2 mm) at the mass ratio of the solid and liquid phases equal to 1 : 50 and 1 : 10. The equilibrium curves are similar in view and reflect certain

TABLE 1

Kinetic parameters for the sorption of praseodymium (III) ions from sulphate solutions by naturally occurring mordenite-containing tuff

Parameters	Solution concentration, mol/L		
	0.001^a	0.002^b	0.003^c
τ_∞, min	1568	1691	1621
$\mathrm{d}Q/\mathrm{d}\tau$, 10^5 mmol/(g · s)	5.6	4.3	4.8
K, mL/g	47.4	39.6	55.8
R, 10^4 s^{-1}	4.8	4.5	5.2
D, 10^8 cm^2/s	4.8	3.7	3.6
B, 10^4 s^{-1}	8.7	7.8	8.6

$^a d$ = 0.25–0.5 mm, S/L = 1 : 50.

$^{b, c} d$ = 1–2 mm, S/L = 1 : 10.

regularity in the character of interaction between praseodymium ions and the phase of zeolite. The isotherms demonstrate an extremum to appear, which could be caused by the formation of intermediate products in the solution, whereto the sorbent exhibit an increased selectivity level [9]. Hydration, hydrolysis, polymerization and complexation processes are inherent in aqueous solutions of praseodymium (III).

In neutral and acidic aqueous solutions the praseodymium ions are present in the form of aqua complexes such as $[Pr(H_2O)_n]^{3+}$ and aqua hydroxo complexes such as $[Pr(H_2O)_nOH]^{2+}$, where $n = 5-8$ [10, 11].

Cerium sulphate solution exhibited also the formation of complexes such as $[Pr(SO_4)_n]^{3-2n}$, where $n = 1-3$. At a low concentration of sulphate ions (<0.03 mol/L), $[PrSO_4]^+$ cations are prevailing [12], although under these conditions anionic complexes could be formed, too [13].

The absorption of praseodymium (III) ions is accompanied by a decrease in acidity of the solution by $0.5-0.8$ pH units. To elucidate the reasons for this phenomenon we performed control experiments wherein the mordenite-containing tuff was filled with distilled water. During the contact time ranging within $28-32$ h in the experiments, the pH value decreased by $0.6-0.8$ units, this occurred regardless of the absorption of cerium ions as a result of exchanging between the ions Na^+ and H^+ present in zeolites [9]. Reducing the pH value in the course of contacting the mordenite-containing tuff with distilled water could occur also due to the hydrolyzing the cations of aluminum (III), magnesium (II) and iron (III), included in the structure of zeolite according to the scheme $M^{n+} + 2H_2O \leftrightarrow [MOH]^{(n-1)-} + H_3O^+$

$M^{n+} = Al^{3+}, Mg^{2+}, Fe^{3+}$ (4)
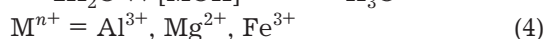
The acidity of the solutions with a concentration of praseodymium (III) sulphate equal to 0.003 and 0.001 mol/L corresponded to pH 6.4 and pH 6.1, respectively.

With increasing the concentration of the solution up to the extreme point the sorption of praseodymium (III) aqua hydroxo complexes, since these complexes have a higher ion charge and an increased zeolite selectivity level exhibited with respect to them. The size of "windows" and cavities inherent in the zeolite rang-
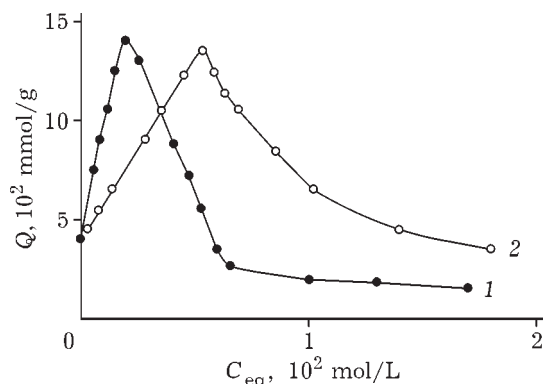

Fig. 1. Sorption isotherm for praseodymium from praseodymium sulphate solutions (Q is the amount of praseodymium (III) ions absorbed, C_{eq} is the equilibrium concentration of Pr(III) in the solution): $1 - d = 0.25-0.5$ mm, S/L = 1 : 50; $2 - d = 1-2$ mm, S/L = 1 : 10.

es within $5-7$ Å, which is significantly larger than the size of aqua and aqua hydroxo complexes. The proposed mechanism of exchange sorption via the substitution of Na^+, K^+, H^+ by Pr^{3+} ions confirms the data presented in [11].

The grain size and the mass ratio between the solid and liquid phases affect the position of maxima on the isotherms (see Fig. 1). The maximum exchange capacity level (ECL) on the grains with $d = 0.25-0.5$ mm and S/L = 1 : 50 (see Fig. 1, curve 1) is shifted to lower equilibrium concentration values, whereas increasing the grain size ($d = 1-2$ mm), and S/L = 1 : 10
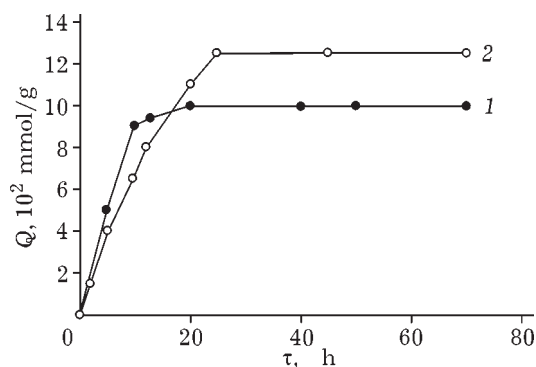

Fig. 2. Kinetic curves for the sorption of praseodymium (III) from praseodymium (III) sulphate aqueous solutions by mordenite-containing tuff: 1 − praseodymium (III) sulphate concentration, in 0.001 mol/L solution, $d = 0.25-0.5$ mm, S/L = 1 : 50; 2 − that in 0.003 mol/L solution, $d = 1-2$ mm, S/L = 1 : 10.
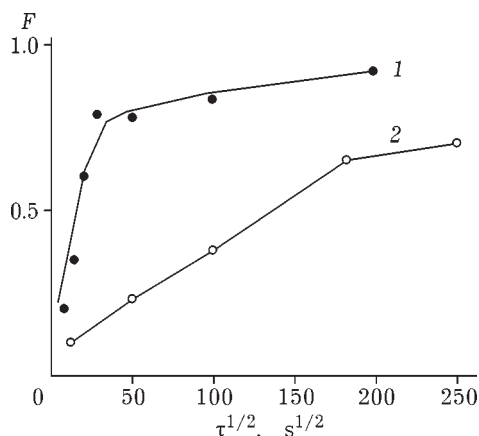
Fig. 3. Exchange level (F) depending on time τ: *1* − praseodymium (III) sulphate concentration in 0.005 mol/L solution, d = 0.25−0.5 mm, S/L = 1 : 50 ; *2* − that in 0.05 mol/L solution, d = 1−2 mm, S/L = 1 : 10.

the maximum of ECL is located at higher concentration values (curve *2*).

So, small tuff grains exhibit a maximum ECL equal to 0.151 mmol/g, is attained at lower reagent consumption.

The kinetic curves for the absorption of praseodymium (III) ions are similar in shape (Fig. 2).

A linear dependence of the filling level for the zeolite phase F on the time τ (Fig. 3) confirms a relatively high contribution of an internal diffusion sorption mechanism [6, 9].

Kinetic parameters indicate the fact that the absorption rate for praseodymium (III) ions depends on the grain size of mordenite-containing tuff and on the concentration of the solution (see Table 1). Decreasing the sorbent grain size results in increasing the surface, which promotes increasing the absorption rate dQ/dτ according to an external diffusion mechanism.

With increasing the concentration of praseodymium (III) sulphate solutions one can observe reducing the time of reaching the equilibrium state τ_∞, and increasing the rate constants of external (R) and internal diffusion (B) processes, the distribution coefficient (K), as well as the values of the effective diffusion coefficient (D). The R and B constants are of the same order of magnitude, which confirms the hypothesis concerning the mixed mechanism of praseodymium (III) ion sorption by mordenite-containing tuff.

CONCLUSION

It has been found that the rate of the sorption of praseodymium (III) on mordenite-containing tuff depends on the grain size, solution concentration, S/L ratio, being controlled both by external and internal diffusion.

The sorption isotherms inherent in the system praseodymium (III) ions-mordenite-containing tuff are characterized by the presence of a maximum, which could be connected with a complicated nature of interaction in the system praseodymium sulphate solution-zeolite. Increasing concentration of the aqueous solution results in changing the selectively of the mordenite-containing tuff with respect to praseodymium (III) ions, with reducing the sorption capacity thereof.

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