

Studies on the Sorption Properties of Natural Mordenite-Containing Tuff with Respect to Cerium (III) Ions

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(Received December 5, 2008; revised April 16, 2009)

Abstract

Ion-exchange sorption of cerium (III) ions from aqueous solutions of sulphate by naturally occurring mordenite-containing tuff has been studied under static conditions. The extraction of cerium from dilute (<0.003 mol/L) solutions is established to occur to a quantitative extent. It has been noted that the increase in the solution concentration results in a decrease in the sorption capacity of tuff. Adsorption isotherms for cerium ions have been plotted as well as kinetic parameters of the sorption process have been determined.

Key words: mordenite-containing tuff, cerium, sorption capacity, sorption mechanisms

INTRODUCTION

Naturally occurring zeolites modified by the ions of rare-earth elements (REE), are promising from the standpoint of obtaining efficient stimulators for the regeneration therapy and biologically active preparations [1, 2]. Rare-earth elements are employed in the treatment of tuberculosis, tumors, and skin diseases. Lanthanum sulphate exhibits an anticoagulative action [3].

For obtaining pharmaceutical products basing on REE compounds it is appropriate to use a sorption technology, and to employ naturally occurring zeolites as sorbents those play the role of a prolonging REE carrier to increase their biological activity [1–3].

At the same time, an insufficient comprehension level for ion-exchange properties of natural zeolites with respect to REE ions restricts the possibilities of their application.

Earlier we have studied kinetics and equilibrium for the sorption of lanthanum, neodymium and samarium cations of mordenite-containing and clinoptilolite-containing tuff [1, 2]. For the sorption isotherm of REE ions we have revealed the presence of maxima caused by an interaction in the system zeolite–REE ions.

The influence of REE nature on the equilibrium and kinetics of sorption requires for deeper studying the laws of sorption in the system zeolite–REE ions. With this purpose, we have investigated the sorption processes on mordenite-containing tuff for cerium (III) ions depending on the concentration of solutions, the sorbent grain size and the mass ratio between solid and liquid phases.

EXPERIMENTAL

As a sorbent, we used mordenite-containing tuff taken from the Mukhor-Tala perlite-zeolite deposit with the following composition, mass %: SiO₂ 70.96, MgO 0.18, Al₂O₃ 11.97, CaO 0.92, Na₂O 2.38, K₂O 5.22. The ratio of Si/Al = 5.2 [1]. The content of zeolite in rock was determined by means of XRD analysis employing a PZL-2 portable zeolite laboratory [4] being amounted to 62 mass %.

In order to study the kinetics and equilibrium of the adsorption of cerium (III) ions, the mordenite-containing tuff was grinded then sampled the fraction with grain size of 0.25–0.5 and 1–2 mm in diameter using a sifter meth-

od, separated from dust, dried at a room temperature during 24 h and then a weighed sample portion was taken. The duration of drying was determined from the results of three control weighing procedures every 3 h during the drying.

The investigation of equilibrium was carried out under static conditions for $Ce_2(SO_4)_3$ aqueous solutions employing a constant mass method [5–7]. The content of cerium (III) ions was analyzed employing a photometric method with Arsenazo III notorious by a high sensitivity and selectivity [8]. The absorption capacity was calculated from the difference in the concentration of cerium (III) ions in the solution before and after sorption basing on the results of three parallel experiments, the relative determination error did not exceed 3%.

The kinetics of cerium ion absorption was studied using a limited volume method at the proportion between the solid (S) and liquid (L) phases equal 1 : 10 and 1 : 50 for the solutions of cerium (III) with the concentration value of 0.001–0.003 mol/L under continuous stirring. The contact time with the sorbent was varied from 5 min to 6 days. The influence of the sorbent grain size was investigated for sorbent grains of 0.25–0.5 and 1–2 mm in diameter.

The kinetic parameters were calculated from the curves of $Q - \tau$ of dependence (where Q is the amount of sorbed cerium (III) ions, mmol/g; τ is time, s) using the technique for the sorption on zeolites presented in monograph [9]. For the initial period of time when the sorption occurs on the surface of a sorbent and the process is controlled by the mechanism of external diffusion, the rate constant of external diffusion process R can be calculated according to the equation

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

Here C_s is the concentration of an ion in the solution, mol/L; K is the equilibrium distribution coefficient, mL/g.

With an increase in the contact time, the amount of absorbed ions is determined by the exchange rate inside a grain of a sorbent. The effective diffusion coefficient (D) and the rate constant internal diffusion process (B) describing an internal diffusion mechanism were calculated according to the equations deduced for spherical particles:

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

TABLE 1

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

Parameters	Solution concentration, mol/L		
	0.001 ^a	0.002 ^b	0.003 ^c
τ_∞ , min	1553	1682	1624
$dQ/d\tau$, 10^{-5} mmol/(g · s)	5.7	4.4	4.8
K , mL/g	50.1	40.8	57.2
R , 10^4 s ⁻¹	4.7	4.3	4.9
D , 10^8 cm ² /s	4.3	3.5	3.8
B , 10^4 s ⁻¹	8.5	7.9	8.2

^a $d = 0.25-0.5$ mm, S : L = 1 : 50.

^b $d = 1-2$ mm, S : L = 1 : 10.

^c $d = 1-2$ mm, S : L = 1 : 50.

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

Here F is the absorption level for cerium (III) ions; r is the average radius of sorbent grains, cm.

RESULTS AND DISCUSSION

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

Figure 1 demonstrates equilibrium curves for cerium (III) ions for the sorption from the solutions of cerium sulphate on naturally occurring zeolite obtained for different grain size

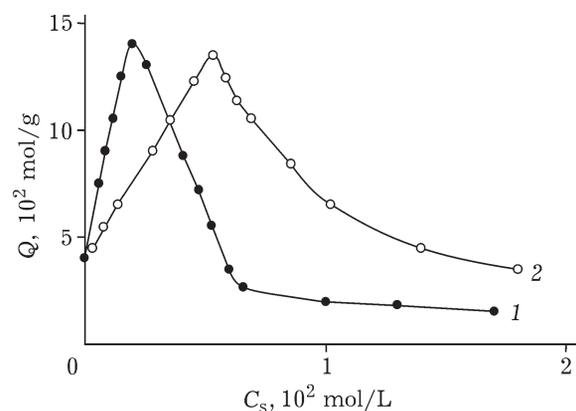


Fig. 1. Isothermal curves for the sorption of cerium from cerium sulphate solutions for grains with various size d and different ratio between solid and liquid phases (S : L): 1 - $d = 0.25-0.5$ mm, S : L = 1 : 50; 2 - $d = 1-2$ mm, S : L = 1 : 10.

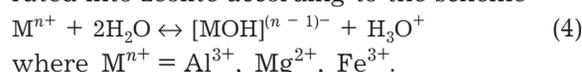
(~0.25–0.5 and 1–2 mm), at a mass ratio between the solid and liquid phases equal to 1 : 50 and 1 : 10. The equilibrium curves are of similar shape and reflecting certain regularity in the character of interaction between cerium ions and the phase of zeolite. The isotherms exhibit an extremum, which, to all appearance, could be caused by the formation of intermediate species in the solution with respect to those the sorbent demonstrates an increased selectivity [8]. Such processes as hydration, hydrolysis, polymerization and complex formation are inherent in the condition of cerium (III) aqueous solutions.

In neutral and acidic aqueous solutions, the ions cerium exist in the form of aqua complexes such as $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$ and hydroxo-aqua complexes $[\text{Ce}(\text{H}_2\text{O})_n\text{OH}]^{2+}$, where $n = 5-8$ [10, 11].

For the solutions of cerium sulphate, the formation has been also registered for such complexes as $[\text{Ce}(\text{SO}_4)_n]^{3-2n}$, where $n = 1-3$. At a low concentration of sulphate ions (<0.03 mol/L), prevail such cations as $[\text{CeSO}_4]^+$ are observed to prevail [12] though anionic complexes could be formed under these conditions, too [13].

The process of the absorption of cerium (III) ions is accompanied by a decrease in the solution pH by 0.5–0.8 units. In order to establish the cause of this decrease we have conducted control experiments where the mordenite-containing tuff was flooded with distilled water. With the contact duration amounting to 28–32 h, the experiments demonstrated a decrease in pH by 0.5–0.8 units irrespective of cerium ion absorption, resulting from the exchange between Na^+ and H^+ ions those are present within zeolites [8]. Hence, acidifying the solution of sorbate occurs as the result of ion exchange between ions present within zeolite, being by no means connected with changing the composition of the complex cerium (III) ion under sorption.

The reduction of pH value in the contact between mordenite and distilled water could be caused also due to the hydrolysis of aluminium (III), magnesium (II), iron (III) cations incorporated into zeolite according to the scheme



The acidity of cerium (III) sulphate solutions of with the concentration of 0.003 and 0.001 mol/L amounts to pH 6.5 and 6.2, respectively.

With increasing the concentration of the solution up to the point of extremum, the sorption of cerium (III) aqua and hydroxo complexes is observed to occur, since these complexes have a higher ionic charge and thus an increased selectivity of zeolite with respect to them. The sizes of “windows” and cavities of the zeolite under investigation are equal to 5–7 Å, which to a considerable extent exceeds the size of aqua and hydroxo-aqua complexes. The hypothetical mechanism of exchange sorption by the substitution of $\text{Na}^+, \text{K}^+, \text{H}^+$ ions by Ce^{3+} ions is in a good agreement with the data from [7].

The grain size and the mass ratio for solid and liquid phases affect the position of the maximum on the isotherms (see Fig. 1). The maximum of exchange capacity (EC) for the grains with $d = 0.25-0.5$ mm and $S : L = 1 : 50$ (curve 1) is shifted towards the region of lower equilibrium concentration. Increasing the grain size ($d = 1-2$ mm) and $S : L = 1 : 10$ results in the EC maximum shifting towards the region of higher concentrations (curve 2).

Thus, for fine tuff grains, the maximal EC value (0.125 mmol/g) can be reached at lower reagent consumption.

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

The linear time dependence observed for the filling level (F) of the zeolite phase $\tau (F - \sqrt{\tau})$ (Fig. 3) confirms the assumption concerning a high enough contribution of an external diffusion mechanism for sorption [7, 10].

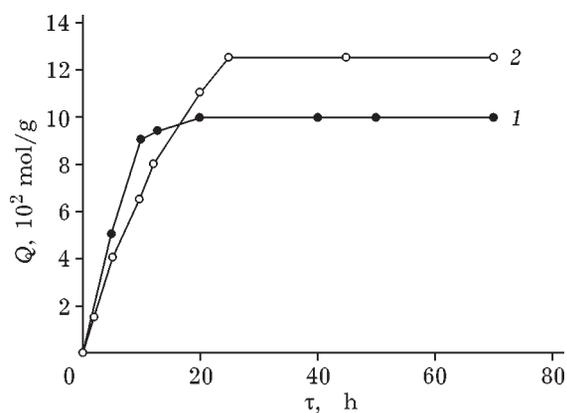


Fig. 2. Kinetic curves for the sorption of cerium (III) from aqueous solutions of cerium (III) sulphate by mordenite-containing tuff: 1 - $C = 0.001$ mol/L, $d = 0.2505$ mm, $S : L = 1 : 50$; 2 - $C = 0.003$ mol/L, $d = 1-2$ mm, $S : L = 1 : 10$.

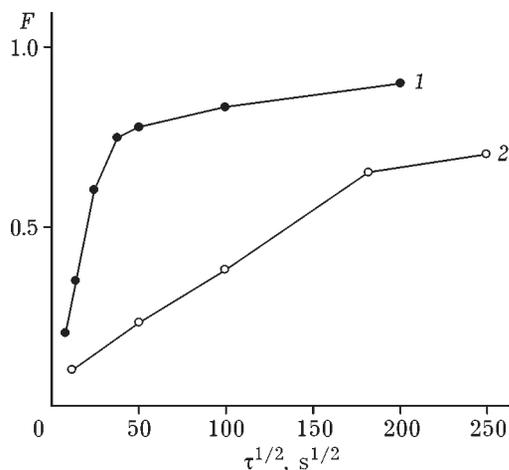


Fig. 3. Exchange level (F) depending on sorption time (τ):
 1 - $C = 0.005$ mol/L, $d = 0.25-0.5$ mm, $S : L = 1 : 50$;
 2 - $C = 0.01$ mol/L, $d = 1-2$ mm, $S : L = 1 : 10$.

The kinetic parameters presented in Table 1 indicate the absorption rate of cerium (III) ions to be dependent on the grain size of mordenite-containing tuff and on the solution concentration. The reduction of the sorbent grain size results in an increase in the surface area and thereby in the increase in the rate of absorption $dQ/d\tau$ according to the mechanism of external diffusion. With the increase in the concentration of cerium (III) sulphate solutions, the time of reaching the equilibrium state τ_{∞} is reduced; an increase in the rate constants for external diffusion (R) and internal diffusion (B) processes, in the distribution coefficient (K), as well as in the effective diffusion coefficient (D) is observed. The constants R and b are of the same order of magnitude, which can serve as a confirmation of the mixed mechanism for the sorption of cerium (III) ions by mordenite-containing tuff.

CONCLUSION

Sorption isotherms for cerium (III) ions by mordenite-containing tuff are characterized by the presence of a maximum, which is caused by a complicated character of interaction. With the increase in the concentration of aqueous solution, there is changing the selectivity of mordenite-containing tuff with respect to cerium (III) ions as well as decreasing its sorption capacity observed.

The sorption rate of cerium (III) ions onto mordenite-containing tuff depends on grain size, the concentration of solution, $S : L$ ratio being controlled by a mixed mechanism of sorption.

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