P-1.2-09

Investigation and mathematical modeling of Sr^{2+} ion-exchange kinetics from surface drinking water on natural clinoptilolite

V.A.Nikashina[1], M.G.Tokmachev[2], I.B.Serova[1], T.G.Kuzmina[1], I.A.Roschina[1], .A.Tikhonov[2]
[1] *Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow, Russia*
nikashina_v@mail.ru
[2] *Department of Physics, Moscow State University, Moscow, Russia*

Keywords: natural clinoptilolite, ion-exchange, kinetic coefficients, mathematical model, surface water

Introduction

As is known, the natural clinoptilolite (CLT) is characterized by high selectivity for a number of ions, including Sr^{2+}, and can be used in the natural conditions as a permeable reactive barrier [1-2]. The scale of ion-exchange processes taking place in geochemical barriers and a variety of the environmental conditions (the ground water concentration, the contact time of CLT and solution, etc.) stipulate the necessity of their mathematical modeling. Ion exchange process on the CLT is described by 2 kinetic stages (relatively fast and much slower), due to structural features of CLT. [3].

Earlier we proposed a mathematical model of sorption dynamics, which takes into account both kinetic stages and makes possible to determine the corresponding coefficients [4,5]. The model was based on the experimental breakthrough curves of Sr^{2+} on CLT from Khonguruu deposit (Yakutiya), obtained for natural solutions of different composition in a continuous mode and with the periodic interruptions.

However, the dynamic experiments can get effective kinetic coefficients only. The aim of the present study was to carry out the kinetic experiments in accordance with well-known method of the "thin layer" [6]. Such experiments with dilute solutions (which composition is similar to the composition of surface drinking water) clarify the character of the kinetic dependences of the sorption process and the contribution of each kinetic stage to the process.

Experimental

The tap water was used as the initial solution. Its composition was as follows, (mg/l): (42.0-50.0) Ca^{+}+ (6.9-9.8) Mg^{2+} + (4.0-6.0) K^{+} + (6.5-10.5) Na^{+} + (0.18-0.20) Sr^{2+}. Natural clinoptilolite was from Khonguruu deposit (Yakutiya), in Na-form. The chemical composition Na-CLT was the following, (%): SiO_2-68.27; Al_2O_3 -11.55; TiO_2 -0.32; Fe_2O_3 -0.65; MnO- 0.006; MgO -0.50; CaO - 0.05; Na_2O – 7.17; K_2O – 0.82; LOI – 10.50; total – 99.83. The average percentage of CLT in the tuff varied from 83% to 91 % depending on fractional composition.

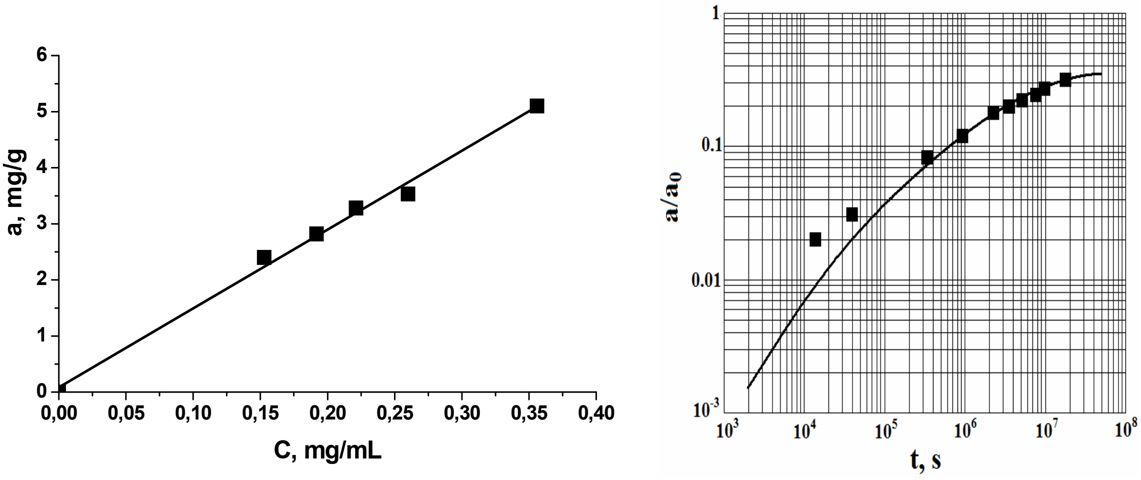
The ion- exchange isotherm of Sr^{2+} on the Na-form of CLT from this solution has been determined and the corresponding distribution coefficient of Sr^{2+} (K_d) was calculated [7]. The contact time solution and CLT was 7 months. The results obtained are presented in Figures 1(a).

The kinetic experiments have been carried out in the column with diameter of 5 cm and height of 10 cm. The tap water was fed to the column from bottom to top. The filtration flow rate of solution was 1500-1800 ml/min (~1.5 cm/s). The sorbent is "fluidized" that provided the condition of constant concentration of ions at the CLT grains surface during the experiment. The water supply regularly suspended for a short time (2-3 minutes) in order to take CLT aliquot for analysis. The selected CLT aliquots were washed with a large amount of distilled water, dried and analyzed. The chemical composition of CLT and of CLT aliquots taken from kinetic experiments were determined by the X-ray fluorescence spectrometry method (PW-1600 system, Rh-anode, 50 kV, 40 μA).

The results of kinetic experiments are depicted in Fig. 1(b).

Results and Discussion

As shown in Fig.1 (a), Sr^{2+} isotherm is linear and the distribution coefficient of Sr^{2+} is about $1.5*10^4$ [ml/g]. For treatment of kinetic experiments we used two-stage model of sorption kinetics, which was earlier described by us in [4, 5]. It makes us possible to determine values of diffusion coefficient of the first kinetic stage and the kinetic coefficient of the second kinetic stage (conventionally - in macro and in micro pores). As you can see in Fig. 1 (b), the calculated curve fits well to experimental data if $D=10^{-15}$ m^2/s and $\gamma \le 10^{-9}\ s^{-1}$.



(a) (b)

Fig.1 (a) Sr^{2+} sorption isotherm on CLT Khonguruu (Na-form) from tap water;
(b) Sr^{2+} sorption kinetics on CLT Khonguruu (Na-form) from tap water.
(■-■) - experimental data, (—) - calculated results.

The comparison of kinetics coefficients values obtained from the dynamic breakthrough curves and from the kinetics experiments in ”thin layer” indicates, that the partical diffusion coefficients values are distinguished in 10 times (the first stage), that is probably stipulated by low Sr^{2+} concentration in the initial solution (0.2 mg/l), the determined value of kinetic coefficient $\gamma \le 10^{-9}\ s^{-1}$ (the second stage) remains the same.

Conclusions

The results obtained confirm the applicability of the suggested model.

References

[1] Park J., Lee S., Lee J. & Lee C. (2002**)**. *Journal of Hazardous Materials*, **95**, 1-2, 65-79.
[2] Rabideau A.J., Van Benschoten J., Patel A. & Bandilla K. (2005) *J. of Contaminant Hydrology* **79**, 1-2, 1-24.
[3] Thompson P.W.& Tassopulos M.A.(1986) *Zeolites*, **6**, 1, 12-20.
[4] Tokmachev M.G., Tikhonov N.A.,et.al (2010) Mathematical Models and Computer Simulations **2**, 6, 733.
[5] Nikashina V. A., Serova I. B.,. Kats E. M,. Tikhonov N. A, Tокmachev M. G.&Novgorodov P.G.(2011) Clay Minerals, **46**, 233- 240
[6] Boyd G.E.,Adamson A.W. & Meyers L.S. (1947) J.Am.Chem.Soc. **69,** 2836
[7] Nikashina, V.A.,Galkina, N.K.& Senyavin , M.M. (1977), *Russian Institute of Scientific and Technical Information*, Moscow, Article No.3668, 44 pp.(in Russian)