

Sorption Process of Toxic Pollutions by Natural Zeolite as a Geochemical Barrier

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Abstract—The mathematical model describing strontium sorption by natural zeolite as a geochemical barrier in case of a variable flow rate and two-phase kinetics is defined. The criterion for the selection of the model is to fit the calculations results to a 10% interval of the mean-square deviation of the experimental data.

Keywords: sorption process, zeolite's barrier, toxic pollutions.

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INTRODUCTION

In many cases pollution from some technogenic object is spread together with underground water, and the prevention of the distribution of this pollution is an important ecological problem. One of the possible means of resolving this problem, in the case when the pollutant is toxic but its concentration is insignificant, is the creation of a cleaning barrier, which represents some layer—a trench located perpendicularly to the direction of the water's movement and filled with a sorbent. The water passes through the layer and the pollutants remain in the sorbent.

Obviously, in designing such a cleaning barrier, it is necessary, first, to know the hydrological conditions, that is, the mode, direction, and volume of water passing underground, and, second, having the characteristics of water movement, to be able to calculate the distribution process of the target pollutant on the sorption barrier.

In the work, the latter question has been studied. Mathematical modeling is a natural method for calculating the transfer dynamics of the target pollutant. A distinctive feature of the examined problem, in comparison, for example, with the problem of industrial water-preparation, is that the movement of water through a barrier is not constant and can change in wide ranges from high rates during high water in the spring to low rates, down to the termination of filtration entirely during a drought or in winter. Therefore, in a modeling problem, the selection of the model, as well as the sorbent parameters corresponding to it, is an important question.

As is well known, sorption dynamics can be described by various models which differ on account of a greater or smaller number of physical factors. Some of them are listed below: the presence of macro and micropores in a sorbent, the difference of the diffusion coefficients of ions in them, and the influence of sorption on a surface and in deep layers of the sorbent. Moreover, taking many factors into account does not result in an improvement of the model. The more the factors the more the unknown coefficients that need to be determined on experimental data before calculating the ecological process. An increase in the number of required parameters leads to instability in their definition and, as a consequence, to errors in the forecasting process in the essentially variable conditions of water movement.

Thus, the main and most difficult modeling problem is the inverse problem of establishing the functional structure of a model and the value of all its coefficients on the basis of experimental data. The model, on one hand, should have, whenever possible, a smaller number of parameters that need to be defined; on the other hand, with the same coefficients it needs to describe the experimental data received in various modes of water movement (with stoppages and without them), with various sizes of sorbent grains, and with various concentrations of the target component.

One of the well-known and extremely widespread natural sorbents is clinoptilolite. In the present work, the inverse problem specified above has been investigated on an example of strontium sorption on clinoptilolite from the model solution of natural drinking water. Such a problem arises at the real barrier designed

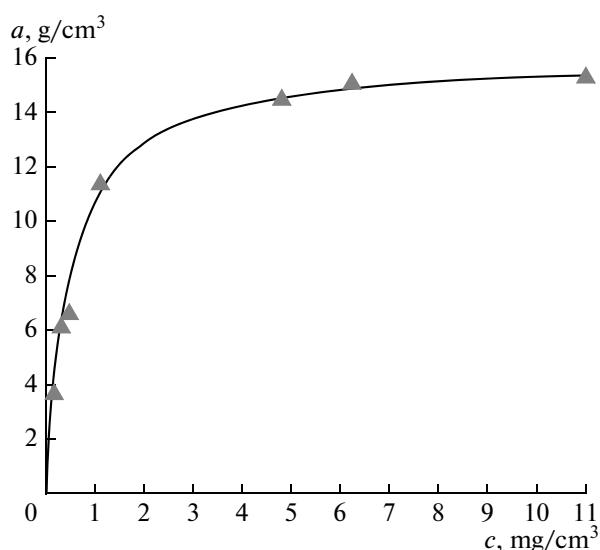


Fig. 1. Isotherm of strontium sorption.

to protect the Markha river against radioactive ions of caesium and strontium, of which the source is a technogenic object in Yakutia (the Kraton-3 object of an underground nuclear explosion (UNE)) [1, 2].

EXPERIMENTAL DATA

In the laboratory of sorption methods of the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, a series of experiments were conducted. First, the isotherm of strontium sorption on the investigated clinoptilolite from the model solution of natural water was determined. The isotherm is presented in Fig. 1 and expresses the association between the strontium concentration c in solution and its concentration a in a sorbent in conditions of equilibrium.

Then, a series of dynamic experiments was conducted. For this purpose, a model solution of natural water containing strontium was passed at a fixed rate through a column filled with clinoptilolite of a certain granulation. Periodically, the strontium concentration was measured on its exit from the column. The conditions of the experiments are presented in Table 1.

During experiments Nos. 1, 2, 9, and 10, the rate of the passage of the solution through the sorbent layer was changed, as shown in Table 2. This is related to the modeling of two operating modes of the barrier: the filtering of the solution through a barrier, then its interruption for a certain time interval, followed by the subsequent renewal of the filtering process. In other experiments, the rate of the solution flow through a sorbent was kept constant.

MODELING RESULTS

We studied a number of models of differing complexity and within the limits of these models the results of the calculations were compared with the specified experiments. We considered that a root-mean-square relative error of the experimental data caused by the variability of a medium should not exceed 10%. It was established that the best result, in terms of the problem stated above, is attained if the process is described on the basis of the mathematical model representing a sorbent as a biporous (dual-zoned) medium. According to this model, the sorbent has a zone that is easily available for sorption, which includes macro and mesopores on which the diffusion of matter inside grain occurs, and walls surrounding the pores on which sorption occurs. The time of the sorption of ions from the internal pore solution on the walls sur-

Table 1. Experimental data

	Exp1	Exp2	Exp3	Exp4	Exp5	Exp6	Exp7	Exp8	Exp9	Exp10
Sorbent mass, g	5	5	2	3	1	1	10	10	10	5
Sorbent length, cm	8.5	8.5	3.36	5	1.68	1.68	5	1.73	4.2	4.45
Sorbent cross-sectional area, cm ²	0.7	0.7	0.7	0.7	0.7	0.7	2.23	6.8	2.77	1.25
Radius of sorbent grain, mm	0.5	0.5	0.275	0.5	0.3	0.3	0.5	0.55	0.7	0.4
Linear rate of the solution through a sorbent layer at the start of the experiment, cm/s	0.11	0.09	0.106	0.116	0.012	0.021	0.0037	0.0014	0.039	0.064
Strontium concentration in the initial solution, mg/l	6	6	6	3.6	7	6	6	6	9.99	7.75
Duration of the experiment, h	37	821	9	9.5	184	103	1012	256	1240	243
Sorbent porosity	0.3	0.3	0.36	0.36	0.4	0.42	0.3	0.4	0.4	0.4

Table 2. Dependence of flow rate on time

Exp1		Exp2		Exp10	
v , cm/s	t , s	v , cm/s	t , s	v , cm/s	t , s
0.11	$0 < t < 25260$	0.09	$0 < t < 1320$	0.064	$0 < t < 4320$
0	$25260 < t < 111400$	0	$1320 < t < 865200$	0	$4320 < t < 868400$
0.11	$111400 < t < 132000$	0.097	$865200 < t < 866800$	0.066	$868400 < t < 873500$
Expr9		0	$866800 < t < 1560000$	0	$873500 < t < 1653000$
v , cm/s	t , s	0.27	$1560000 < t < 1563000$	0.06	$1653000 < t < 1680000$
0.013	$0 < t < 47400$	0	$1563000 < t < 2168000$		
0	$47400 < t < 4464000$	0.1	$2168000 < t < 2174000$		
0.003	$4464000 < t < 4500000$	0	$2174000 < t < 2952000$		
		0.095	$2952000 < t < 3000000$		

rounding it is much shorter than the characteristic time of the whole process. Therefore, we consider that the liquid and sorbing phases are in local equilibrium. Further, for brevity, we refer to the whole easily available zone as macropores. Since the concentration of the solution is insignificant, and the basic quantity of the component inside the grain is in a sorbing state, we describe the local aggregate concentration of both component phases in the macropores by the unified parameter $a(t, x, r)$, mg/cm³. Here, t is the time, s; r is the radial coordinate in grain, cm; and x is the coordinate along the sorption column, cm. Besides macropores, in the grain there is a hard-to-reach zone uniting the micropores and areas adjoining them. Let us designate the total local concentration in this zone as $b(t, x, r)$. A diffusive exchange occurs between the zones. We obtain a mathematical model including the following ratios:

$$\varepsilon \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = \beta(\phi(\bar{a}) - c), \quad (1)$$

$$\frac{\partial a}{\partial t} = D\Delta a + \frac{\gamma}{F_a}(b - a), \quad (2)$$

$$\frac{\partial b}{\partial t} = \frac{\gamma}{F_b}(a - b), \quad (3)$$

$$\beta(c - \phi(\bar{a})) = \pi \frac{D}{r} \frac{\partial \bar{a}}{\partial r} \text{ at } r = R, \quad (4)$$

$$\frac{\partial a}{\partial r} = \frac{\partial b}{\partial r} = 0 \text{ at } r = 0, \quad (5)$$

$$a = b = c = 0 \text{ at } t = 0, \quad c = c_0, \quad x = 0, \quad (6)$$

$$\beta = 4.86 \times 10^{-4} \left(\frac{1 - \varepsilon}{\varepsilon d} \right)^{1.53} p v^{0.47} \frac{1}{s}. \quad (7)$$

For the case of the exchange $\text{Sr}^{2+} - \text{Na}^+$ coefficient $p = 6.32$, and in the general case $p = (z_1/\lambda_1 + z_2/\lambda_2)^{-2/3}$, where λ_1 and λ_2 are the electroconductivity of the exchanged ions, cm²/ohm, and z_1 and z_2 are their charges.

The following definitions refer to (1)–(7):

β is the external diffusion kinetic coefficient describing the rate of the ion supply to the surface of the sorbent, 1/s;

γ is the kinetic coefficient of the mass transfer in micropores, 1/s;

$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{R} \frac{\partial}{\partial r}$ is the Laplace operator in a radial-symmetric case;

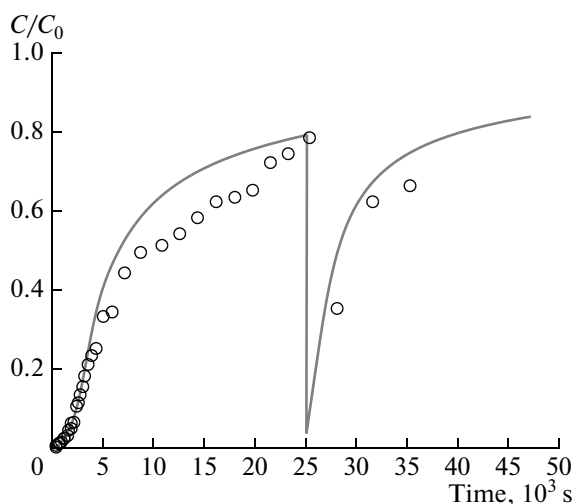


Fig. 2. Output concentration curve of strontium in experiment 1.

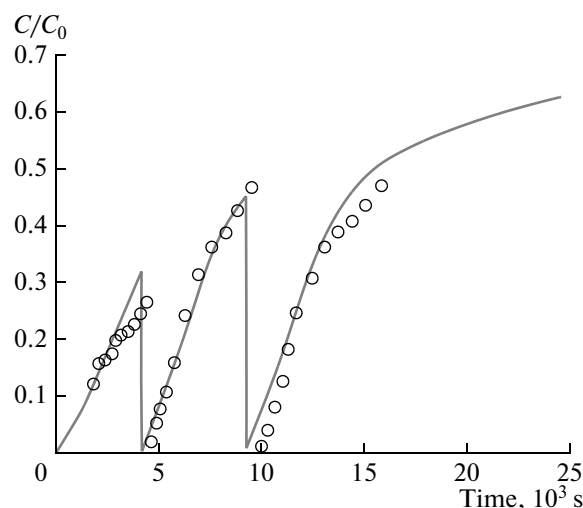


Fig. 3. Output concentration curve of strontium in experiment 10.

ε is the porosity of the column;

$v(t)$ is the linear rate of the solution in the column, cm/s;

$\phi(a)$ is a function, inverse to the sorption isotherm introduced in Fig. 1;

$a(t, x, r)$ is the strontium concentration in the micropores of the sorbent, mg/cm³;

$\bar{a}(t, x) = a(t, x, R)$ is the strontium concentration a on the surface of a grain, mg/cm³;

$b(t, x)$ is the strontium concentration in the micropores of the sorbent, mg/cm³;

$c(t, x)$ is the strontium concentration in the solution in the column, mg/cm³;

$c_0(t)$ is the strontium concentration on the input in the column at $x = 0$, mg/cm³;

d is the diameter of the sorbent grain, cm;

D is the coefficient of strontium diffusion in sorbent macropores, cm²/s;

e_p is the share of the volume of the macropores relative to the total volume of the sorbent granule;

$F_a = (1 - \varepsilon)e_p$ is the share of the volume of the sorbent's macropores relative to the total column volume;

$F_b = (1 - \varepsilon)(1 - e_p)$ is the share of the volume of the sorbent's micropores relative to the total column volume;

r is the radial coordinate inside the grain, cm;

R is the radius of the sorbent grain, cm;

t is the time, s;

x is the longitudinal coordinate along the sorption column, cm.

Equation (1) describes the transfer of matter on the column; Eq. (2) describes the change of concentration in the macropores; Eq. (3) describes the hard-to-reach zone including micropores and areas adjoining them; Eqs. (4)–(6) describe the boundary and initial conditions; Eq. (7) describes the expression for the external diffusion coefficient [3]. In formula (4), coefficient $R/[3(1 - \varepsilon)]$ appears as a result of accounting for the surface area of sorbent grains falling on the unit of the length of the sorption column.

The parameters ε , v , R , $F_a(\varepsilon, e_p)$, and $F_b(\varepsilon, e_p)$, as well as function $\phi(a)$, are known. Thus, in the model the unknown values which were defined from the experiment were D , γ , and e_p .

The comparison of the results of the calculation and experiment are presented in Figs. 2 and 3. The typical output curves are shown, where the experimental data on the strontium concentration during various moments in time are shown exiting the sorbent in the form of circles. The continuous line represents the calculated curve.

On the Ot axis, the time during which the solution moved, i.e., $v > 0$ is set on the graphs. The periods when the solution did not move conform to the same abscissa t . Thus, when $v = 0$, the graph of concentration changes is compressed on the Ot axis and represents the vertical segments. For example, in Fig. 1 the

curve shown on the graph after time $t = 25\,260$ s conforms to the output data received at $t > 111\,400$ s (see Table 2).

As can be seen from Figs. 2 and 3, on the first stage of filtering, the usual output curve of strontium was received. Further on attaining a certain, predetermined time point (on the first graph, this is 25 260 s), the filtering of the solution was stopped, i.e., we modeled a drought or a winter period. Moreover, inside the sorbent, matter was redistributed from the edges to the center of the grain, which is reflected in the output curve of strontium after a break in filtering.

As a result of the conducted calculations, it was established that the output curves obtained in all ten experiments are described within the limits of the model (1)–(7), with the error specified above ($\leq 10\%$), at $D = 2 \times 10^{-10}$ cm²/s, $\gamma = 7 \times 10^{-6}$ 1/s, and $e_p = 30\%$. Thereby, highly satisfactory conformity of the calculation and experiment has been obtained. In the best case (experiment 4), the standard deviation of the calculations from the experimental data was 5%.

At the same time, any further model simplifications (1)–(7) by ignoring the action of any factor lead to a significant growth of modeling error. Thus, we consider that the examined model conforms in complexity with the experimental material and can calculate the ecological process within the limits of this model.

Modeling has shown that for the break in the period of filtering water through the barrier ($v = 0$), the strontium diffused mostly from the grain surface and from the macropores in the sorbent's micropores. This, in turn, means that due to the great exchange capacity of the internal sorbent zones and at small concentrations of the toxic component, the barrier can effectively clean the water even after ten years. The calculation shows that a protective sorption layer with a width of 2 m and a diameter of the sorbent grain of 0.4 mm, for maximal flow rates of $v = 0.02$ cm/s and concentrations $c = 0.1$ mg/l, is capable of providing the ecological safety of the river Markha for a period of 20 years.

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REFERENCES

1. K. I. Mikulenko, A. I. Chomchoev, and S. P. Gotovtsev, *Geological-Geographical Conditions of the Underground Nuclear Explosions at Sakha (Yakutia) Republic and Their Aftermaths* (Izd-vo YaNTs SO RAN, Yakutsk, 2006), pp. 65–73 [in Russian].
2. V. I. Sergeev, A. V. Savenko, and T. G. Shimko, "Theory and Practice of Creating the Artificial Geochemical Barriers for Preventing the Environmental Pollution by Fuel-Energy Plants Wastes," in *Proc. Sci.-Appl. Conf. "Ecological Aspects of Power Strategy as a Factor of Russian Sustainable Development"* (Noosfera, Moscow, 2000), pp. 84–86 [in Russian].
3. E. V. Venitsianov and R. N. Rubinshtein, *Sorption Dynamics from Liquid Mediums* (Nauka, Moscow, 1983) [in Russian].