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## Features of kinetics of $\text{Sr}^{2+}$ sorption from surface drinking water on clinoptilolites from Russian and Bulgarian deposits

### ABSTRACT

The kinetics of  $\text{Sr}^{2+}$  ion-exchange process on  $\text{NH}_4^+$ - forms of clinoptilolites from deposits in Russia and Bulgaria on the sample of the surface drinking water was investigated in detail. It was shown, that the kinetic process on clinoptilolite includes 3 stages. The obtained data are the initial one for the development of a mathematical model of the dynamic ion-exchange process on  $\text{NH}_4^+$ -form of clinoptilolites from diluted solutions that makes possible to generate the computer program and thereupon to calculate the break-through curves of  $\text{Sr}^{2+}$  sorption on  $\text{NH}_4^+$ - clinoptilolite for different dynamic conditions.

**Keywords:** clinoptilolite,  $\text{Sr}^{2+}$  ion-exchange, kinetics, the surface drinking water, mathematical model.

### 1. INTRODUCTION

Natural clinoptilolites (CPT) are characterized by high selectivity for a number of ions, including  $\text{Sr}^{2+}$ , and are used in purification of the natural surface and ground waters from the radioactive and stable  $\text{Sr}^{2+}$  [1-3]. In recent years, many papers were published, showing that the natural zeolites - clinoptilolite-containing tuffs can be used in natural conditions as a permeable reactive barrier (PRB) [4-8]. The scale of ion-exchange processes taking place in geochemical barriers and at variety of the environmental conditions (ground water concentration, contact time of CPT with solution, etc.) determine the necessity of their mathematical modeling. Hypothetically, the ion exchange process on CPT is described by 2 kinetic stages - relatively fast stage and slower one [9]. Therefore, it is necessary to investigate all ion-exchange kinetic stages in detail. Earlier we proposed a mathematical model of sorption dynamics, which takes into account both kinetic stages and makes possible to determine the corresponding coefficients [10,11]. The model was based on the experimental break through curves of  $\text{Sr}^{2+}$  on CPT from Khonguruu deposit (Yakutiya), obtained for natural solutions of different composition in a continuous mode and with the periodic interruptions.

However, the dynamic experiments permit to obtain the effective kinetic coefficients only. Therefore in the present study the kinetic experiments were carried out in accordance with known method of the "thin layer" [12]. 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.

Earlier we have studied  $\text{Sr}^{2+}$  sorption kinetics on Na-CPT (Khonguruu deposit, Russia) from the surface drinking water ( $C_{\text{Sr}^{2+}} = 0.18-0.20$  mg/L) using the "thin layer" method [13]. The experiment duration was more than 7 monthes. It was noticed, that the first stage of ion-exchange process is described by the particle diffusion kinetics, then ion-exchange process slows down, and by that moment only 30% of  $\text{Sr}^{2+}$  equilibrium capacity was realized. The aim of this study was to carry on (or prolong) detailed investigation of the  $\text{Sr}^{2+}$  sorption kinetics from surface drinking water containing increased  $\text{Sr}^{2+}$  concentration ( $C_{\text{Sr}^{2+}} = 3$  mg/L), using  $\text{NH}_4^+$ -forms of CPT from three different deposits - Khonguruu and Kholinskoye (Russia) and Beli Plast (Bulgaria) as a basis for further mathematical modeling of the dynamic process.

### 2. MATERIALS AND METHODS

- The obtaining  $\text{NH}_4^+$ -form CPT - 2 g of CPT was submerged in 250 ml of 1N  $\text{NH}_4\text{Cl}$ . The mixture was heated for 2-3 hours in water bath,

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and then shaken for 5 hr on Shuttel apparatus. Then, the NH<sub>4</sub>Cl solution was decanted from the tuffs and the sample was again placed in 250 ml of 1N NH<sub>4</sub>Cl. This procedure was repeated three times. The tuff was filtered on regular filter paper, rinsed with 500 ml distilled water to remove excess

salts, and dried to a constant weight at 100-105°C [14].

- The chemical composition of initial clinoptilolite-containing tuffs and theirs NH<sub>4</sub><sup>+</sup> forms was determined by X-ray fluorescence spectrometer Axios Advanced PANanalytical, the Netherlands. These data are presented in Table 1.

Table 1 - Chemical composition of clinoptilolite-containing tuffs in natural and NH<sub>4</sub><sup>+</sup> -forms (wt. %).

Deposit	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	MnO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	Sr	LOI*	Total
Beli Plast - natural	66.58	10.74	1.37	3.32	3.13	0.15	0.08	0.28	0.043	0.27	0.043	13.84	99.84
Beli Plast - NH <sub>4</sub>	70,81	10,47	0,83	0,64	0,01	<0.01	0,13	0,15	0,042	0,27	0,005	16,64	99.99
Kholinskoye - natural	67.95	12.92	1.897	4.597	1.58	0.398	0.096	0.893	0.04	0.183	0.01	9.36	99.92
Kholinskoye - NH <sub>4</sub>	71.68	12.64	1.04	2.137	0.041	0.222	0.083	0.873	0.046	0.207	0.008	10.86	99.83
Khongururu - natural	67.51	11.74	1.14	1.56	3.05	1.08	0.032	0.686	0.034	0.25	0.196	12.61	99.88
Khongururu - NH <sub>4</sub>	73.90	10.82	0.27	0.73	0.19	0.31	0.022	0.86	0.037	0.16	0.004	13,06	100.36

\*LOI- loss on ignition

- Phase composition of clinoptilolite-containing of tuffs was determined by powder XRD and is presented on the Table 2.

Table 2. Phase composition of clinoptilolite-containing of tuffs and TCEC.

Deposit	CPT (wt.%)	Other minerals	TCEC, meq/g
Khongururu (Russia)	80,0	quartz, feldspars, mica	1.85
Kholinskoye (Russia)	60,0	crystalite, quartz.	1.41
Beli Plast (Bulgaria)	82,0	celadonite, plagioclase, quartz, montmorillonite	1.90

- The total cation-exchange capacity (TCEC) of the tuffs was calculated as a difference in Na, K, Ca, and Mg ions content in the natural and the NH<sub>4</sub>-form of CPT and is presented in Table 2.

- The grain size of the used CPT was, (mm): Khongururu -0.6+0.3; Beli Plast and Kholinskoye - 0.5+0.25;

- The crystallite size of CPT was determined by XRD profile fitting analysis of 020 diffraction line and was the following, (nm): Khongururu ~ 50; Beli Plast ~ 33; Kholinskoye ~ 25;

- The composition of surface drinking water is (mg/L): (42.0-50.0) Ca<sup>2+</sup>; (6.9-9.8) Mg<sup>2+</sup>; (4.0-6.0) K<sup>+</sup>; (6.5-10.5) Na<sup>+</sup>; (2.8-3.0) Sr<sup>2+</sup>. The water analysis was carried out by AAS or ICAP-9000.

- The ion-exchange isotherms of Sr<sup>2+</sup> on NH<sub>4</sub>-forms of CPT from this water were determined. CLT mass was 0.2 g. Sr initial concentration in solution is varied between 3.5 mg/L and 15 mg/L. V/m =400, where V- the volume of solution, ml; m- CPT mass, g; the contact time of solution and CPT

was 3 months [14,15]. The obtained data are presented on the Fig.1.

The kinetic experiments were carried out in a column with diameter of 5 cm and height of 10 cm, divided on two sections by a mesh (Fig. 2). CPT content in each section was 1.5 g. The water was passed through the column from bottom to top. The filtration flow rate of the solution was 1500-1800 ml/min (~1.5 cm/s). The sorbent was "fluidized" that provided a constant concentration of ions at the surface of CPT grains. The solution was supplied at a constant flow rate with short interruption for 3-5 min for sample collection (0.1-0.15 g of wet CPT) for analysis. The interval between interruptions was 2 hours at beginning of the experiment, then interval was gradually increased to 4, 8, 12, 24 hours and so on. The selected samples of CPT were washed with distilled water, dried 1-1.5 hour at 110° and then analyzed. The chemical composition of CPT portions taken from the kinetic experiments was determined by X-ray fluorescence spectrometer Axios Advanced PANanalytical, the Netherlands.

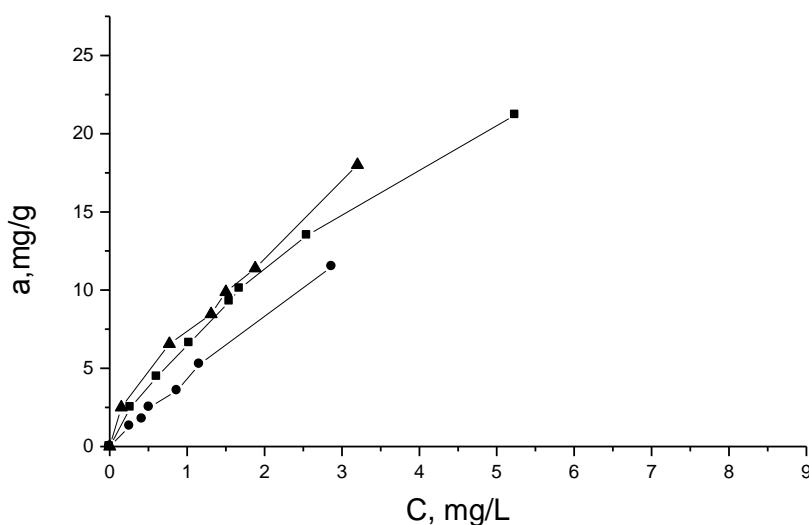


Figure 1 -  $\text{Sr}^{2+}$  ion-exchange isotherms for CPT's Kholinskoye (●-●-●), Khonguruu (■-■-■) and Beli Plast (▲-▲-▲) from surface drinking water.

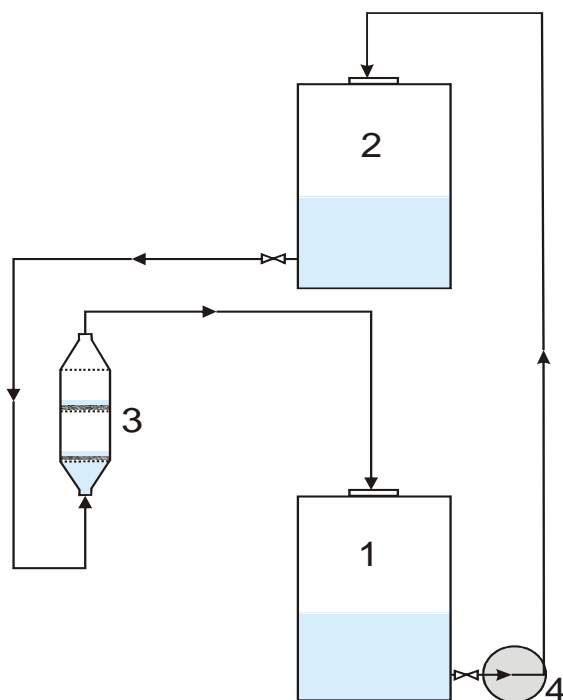


Figure 2 - Experimental scheme of "kinetics in thin layer". 1, 2 - the tanks; 3 - the column; 4 - pump. The tank capacity is 120 L. The studied solution volume is 90 L.

### 3. RESULTS AND DISCUSSION

The obtained  $\text{Sr}^{2+}$  ion-exchange isotherms are presented on the Fig. 1. As shown in Figure 1, the  $\text{Sr}^{2+}$  isotherms are linear practically for all studied CPT to  $\text{Sr}^{2+}$  concentration in equilibrium solution near 3 mg/L. The corresponding  $\text{Sr}^{2+}$  distribution coefficients ( $K_d$ ) were calculated for linear part of the isotherms of the studied CPT, and their values were the following, (ml/g):  $6.0 \cdot 10^3$ ;  $5.38 \cdot 10^3$  and

$4.4 \cdot 10^3$  for Beli Plast, Khonguruu, Kholinskoye deposits respectively.

The results of the kinetic experiments are presented on Figure 3-6. As shown from Figure 3, the initial stage of  $\text{Sr}^{2+}$  kinetic dependence (from experiment beginning to time of  $t=5-6 \cdot 10^4$ s) is described by the particle diffusion law for all three CPT. The  $\text{Sr}^{2+}$  particle diffusion coefficients of the studied CPT ( $D_{\text{Sr}^{2+}}$ ) were calculated by fitting experimental and theoretical kinetic dependences [12,14].

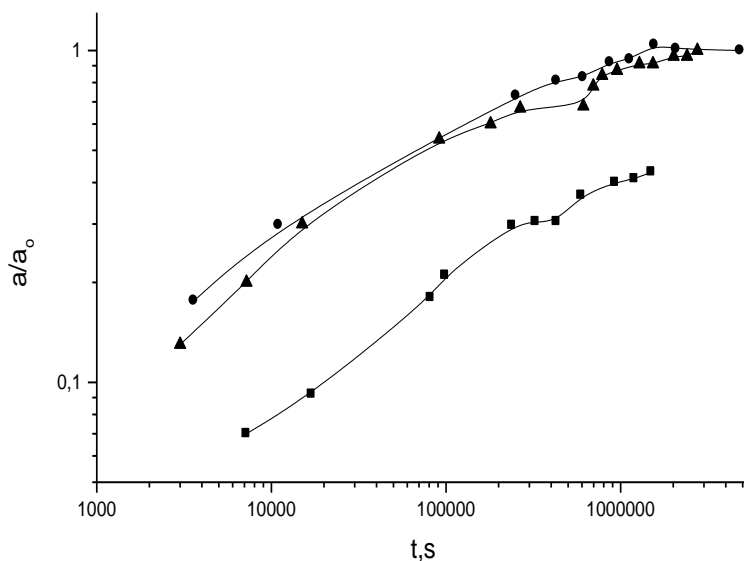


Figure 3 - Sr<sup>2+</sup> sorption kinetics on NH<sub>4</sub><sup>+</sup>-CPT's of different deposits from the surface drinking water (method "thin layer"). Khonguruu (■--■), Beli Plast (-▲-▲-), Kholinskoye deposit (-●-●-).

Calculated D<sub>Sr<sup>2+</sup></sub> of Kholinskoye, Beli Plast and Khonguruu CPT in NH<sub>4</sub><sup>+</sup> form are the following, (cm<sup>2</sup>/s): 2.8·10<sup>-10</sup>; 2.3·10<sup>-10</sup>; 3.6·10<sup>-11</sup>, respectively, i.e. Kholinskoye CPT is characterized the highest value of the particle diffusion coefficient compared to others investigated CLT. Presumably this is due to smaller size of the Kholinskoye crystallite. Further, a slowing down the ion-exchange process occurs on all studied CPT. The process reaches a

plateau in the time interval of 2.5·10<sup>5</sup>- 5·10<sup>5</sup>s, but then an increase of Sr<sup>2+</sup> sorption is observed again. It should be noted, that as shown from Figure 4-6, the K<sup>+</sup> sorption is decreased simultaneously with the Sr<sup>2+</sup> sorption increase on this stage. It could be assumed that Sr<sup>2+</sup> begins to occupy the K<sup>+</sup> sites in the channels of CPT structure. But this assumption requires special structural investigations.

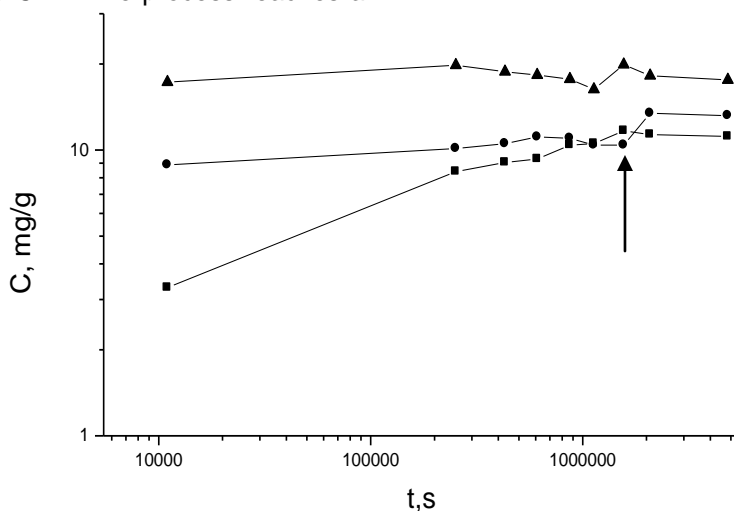


Figure 4 - Sorption kinetics of Sr<sup>2+</sup> (■--■), Ca<sup>2+</sup> (-▲-▲-), K<sup>+</sup> (-●-●-) on NH<sub>4</sub><sup>+</sup> CPT of Kholinskoye deposit from surface drinking water. → means the interruption of filtration process on 70 days. The last point on the Figure was obtained in 32 days of the following solution filtration.

For CPT from Kholinskoye deposit (Figure 4) the kinetic experimental data confirm that the process of strontium sorption reaches the equilibrium after 23-25 contact days of CPT with the studied solution, because even after 70 days of "rest" (the solution filtering is interrupted), the subsequent re-start of the sorption process in the

course of 32 days doesn't shows any significant change in the Sr-sorption. As shown from Fig. 5, after 23 contact days of CPT from Beli Plast deposit with solution and 14 days of "rest" and the subsequent re-start of the solution filtration in the course of 4 days we observed a small increase in the Sr-sorption again.

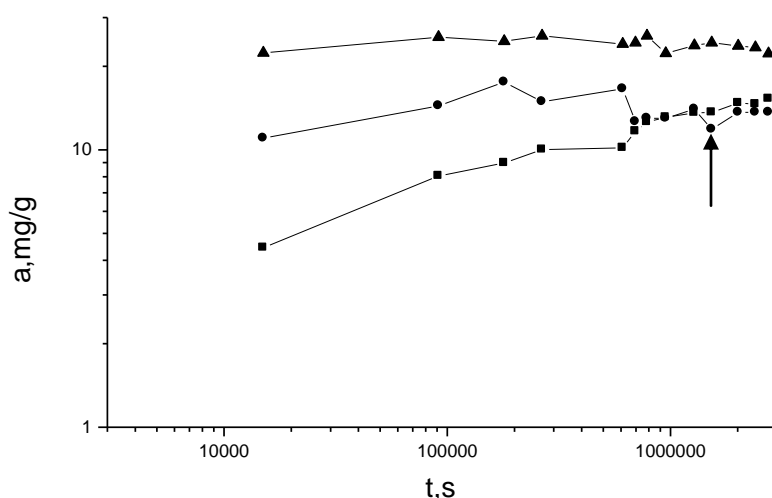


Figure 5 - Sorption kinetics of  $Sr^{2+}$  (■-■),  $Ca^{2+}$  (-▲-▲-),  $K^+$  (-●-●-) on  $NH_4^+$ -CPT of Beli Plast deposit (Bulgaria) from surface drinking water. → means the interruption of filtration process on 14 days.

As shown from Figure 6, the ion-exchange kinetics for Khonguruu CPT is much slower; however we observed the increase in the Sr-sorption after a plateau also. Possible explanations

for the above specificities and differences in the sorption behavior of the studied CPT may be found in the different crystallite sizes, structural defects and so on, which we intend to clarify later.

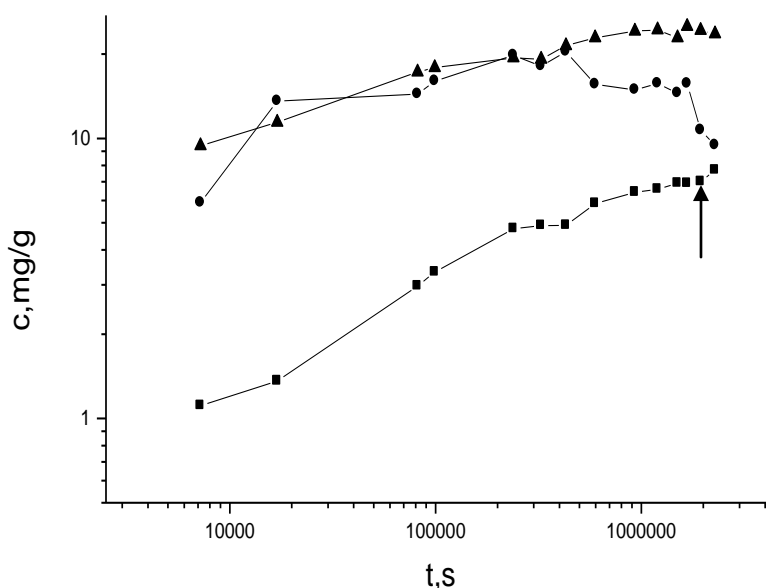


Figure 6 - Sorption kinetics of  $Sr^{2+}$  (■-■),  $Ca^{2+}$  (-▲-▲-),  $K^+$  (-●-●-) on  $NH_4^+$ -CPT of Khonguruu deposit (Yakutiya, Russian) from surface drinking water. → means the interruption of filtration process on 27 days.

#### 4. CONCLUSION

The kinetics of  $Sr^{2+}$  ion-exchange process on CPT of different deposits from surface drinking water was investigated in detail. It was shown, that the kinetic process on CPT includes 3 stages: a) the first stage - the particle diffusion process described by the particle diffusion coefficient, b) the second stage- the sorption process is slowing down and is described by the fitting kinetic

coefficient [14], and c) the third stage - secondary increase of  $Sr^{2+}$  sorption, which ends after reaching true equilibrium.

The particle diffusion coefficients of  $Sr^{2+}$  describing the first stage of the sorption process on CPT of different deposits were calculated.

The obtained data are the initial data for the development of the final mathematical model of the dynamic ion-exchange process on  $NH_4^+$ -form of

CLT from diluted solutions that makes possible to generate the appropriate computer program and then to calculate the break-through curves of  $\text{Sr}^{2+}$  - sorption for different dynamic conditions.

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## IZVOD

### KARAKTERISTIKE KINETIKE SORPCIJE $\text{Sr}^{2+}$ IZ POVRŠINSKIH PIJAČIH VODA NA KLINOPTILOLITU IZ RUSKIH I BUGARSKIH LEŽIŠTA

*U radu je ispitivana kinetika procesa jonske izmene  $\text{Sr}^{2+}$  na  $\text{NH}_4^+$ -formama klinoptilolita iz ležišta u Rusiji i Bugarskoj. Eksperimenti su rađeni sa realnim uzorkom površinske vode za piće. Pokazano je da kinetika procesa jonske izmene  $\text{Sr}^{2+}$  na klinoptilolitu uključuje tri stupnja. Dobijeni rezultati su neophodni za razvijanje matematičkog modela koji bi opisao proces jonske izmene, iz razblaženih rastvora, na  $\text{NH}_4^+$ -formama klinoptilolita u dinamičkim uslovima. Model bi bio osnova da se napravi kompjuterski program koji bi omogućio proračune krivih proboja za adsorpciju  $\text{Sr}^{2+}$  na  $\text{NH}_4^+$ -klinoptilolitu pri različitim dinamičkim uslovima.*

**Ključne reči:** klinoptilolit,  $\text{Sr}^{2+}$  jon-razmena, kinetika, površine vode za piće, matematički model.

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