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Kinetics of Sr^{2+} sorption on clinoptilolite-containing tuffs of different deposits from the surface drinking water

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Previously Sr^{2+}ion-exchange isotherms were obtained from the surface drinking water and the corresponding Sr^{2+} distribution coefficients (Kd) were calculated for linear part of the isotherms of the studied CLT. The comparative kinetic data of Sr^{2+} ion-exchange sorption on NH_4^+- forms of the clinoptilolite-containing tuffs from deposits of Russia and Bulgaria on the sample of the surface drinking water was investigated in detail with the known method of the "thin layer". It was shown, that the kinetic process of the Sr-sorption on the clinoptilolite- containing tuffs is characterized with the features and includes 3 stages. The first stage is described with the particle diffusion law, the second stage –a slowing down, the ion-exchange process reaches a plateau, then an increase of Sr^{2+} sorption is observed again. The particle diffusion coefficients of Sr^{2+} describing the first stage of the sorption process on CLT of different deposits were calculated. The obtained data are the initial one for the development of a mathematical model of the dynamic ion-exchange process on NH_4^+-form of the clinoptilolite- containing tuffs from the surface drinking waters, that makes possible to generate the computer program and thereupon to calculate the break-through curves of Sr^{2+} sorption on NH_4^+- clinoptilolite- containing tuffs for the different dynamic conditions, including the sorption dynamic conditions on the permeable reactive barrier.

Keywords: the clinoptilolite-containing tuff, Sr^{2+}ion-exchange, kinetics, the surface drinking water, the mathematical model, permeable reactive barrier.

Кинетика сорбции Sr^{2+} на клиноптилолит-содержащих туфах различных месторождений из поверхностной питьевой воды

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Цель исследования – изучить в деталях все особенности кинетики сорбции Sr^{2+} на клиноптилолитсодержащих туфах различных месторождений из разбавленных растворов - поверхностной питьевой воды. Предварительно были получены ионообменные изотермы Sr^{2+}из поверхностной питьевой воды на изучаемых клиноптилолит-содержащих туфах (КЛТ) и по линейному участку изотермы рассчитаны соответствующие коэффициенты распределения (Kd) Sr^{2+}. Сравнительные кинетические данные ионообменной сорбции Sr^{2+} на NH_4^+ форме клиноптилолитсодержащих туфов месторождений России и Болгарии из поверхностной питьевой воды были изучены известным методом «тонкого слоя». Было показано, что кинетический процесс сорбции Sr^{2+} на NH_4^+ форме КЛТ разных месторождений характеризуется тремя этапами. Первый этап сорбции описывается законом внутренней диффузии, 2-ой этап происходит замедление процесса и выход на плато, затем (3-ий этап) вновь наблюдается увеличение сорбции Sr^{2+} и достигается равновесие. Были рассчитаны коэффициенты внутренней диффузии Sr^{2+} на трех различных КЛТ, описывающие первый этап сорбции. Полученные данные являются исходным и для разработки математической модели динамических ионообменных процессов $\mathbf{Sr^{2+}}$ на NH_4^+ форме КЛТ из поверхностной питьевой воды, что дает возможность создать компьютерную программу и на этой основе осуществить расчет выходных кривых Sr^{2+} на NH_4^+ форме КЛТ для различных динамических условий (скорость фильтрации, зернение КЛТ и т.д.), включая условия, реализуемые в проницаемых геохимических барьерах.

Ключевые слова. Клиноптилолит-содержащие туфы, ионный обмен Sr^{2+}, кинетика, поверхностная питьевая вода, математическая модель, проницаемые геохимические барьеры.

Introduction

Natural clinoptilolites – the clinoptilolite-containing tuffs (CLT) are characterized by the high selectivity for a number of ions, including Sr^{2+}, and are used in purification of the natural surface and ground water from the radioactive and stable Sr^{2+} [1-3]. In recent years, many the 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 the ion-exchange processes taking place in the geochemical barriers and at variety of the environmental conditions (ground water concentration, contact time of CLT with solution, etc.) determine the necessity of their mathematical modeling. Hypothetically, the ion exchange process on CLT 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 breakthrough curves of Sr^{2+} on CLT from Khonguruu deposit (Yakutiya), obtained for the natural solutions of the 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 the known most correct method of the «thin layer»[12]. Such experiments with dilute solutions, which composition is similar to the composition of the 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 Sr^{2+} sorption kinetics on Na-CLT (Khonguruu deposit , Russia) from the surface drinking water ($C_{Sr}{}^{2+}$ = 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 the ion-exchange process is described by the particle diffusion kinetics, then ion-exchange process slows down , and by that moment only 30% of Sr^{2+} equilibrium capacity was realized. The aim of this study was to carry on (or prolong) detailed investigation of the Sr^{2+} sorption kinetics from surface drinking water containing increased Sr^{2+} concentration ($C_{Sr}{}^{2+}$ = 3 mg/L), using $NH^+{}_4$-forms of CLT from three different deposits – Khonguruu and Kholinskoye (Russia) and Beli Plast (Bulgaria) as a basis for further mathematical modeling of the dynamic process.

Experimental

The obtaining NH_4^+ -form CLT – 2 g of CLT was submerged in 250 ml of 1N NH_4Cl. The mixture was heated for 2-3 hours in water bath, and then shaken for 5 hr on Shuttel apparatus. Then, the NH_4Cl solution was decanted from from the tuffs and the sample was again placed in 250 ml of 1N NH_4Cl. 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_4^+ 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_4^+-forms (wt.%).

Deposit	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	MnO	Fe_2O_3	P_2O_5	TiO_2	Sr	LOI*
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
Beli Plast-NH4	70.81	10.47	0.83	0.64	0.01	<0.01	0.13	0.15	0.042	0.27	0.005	16.64
Kholinskoye -natural	67.95	12.92	1.897	4.597	1.58	0.398	0.096	0.89	0.04	0.18	0.01	9.36
Kholinskoye-NH4	71.68	12.64	1.04	2.137	0.04	0.222	0.083	0.87	0.046	0.21	0.008	10.86
Khonguruu--natural	67.51	11.74	1.14	1.56	3.05	1.08	0.032	0.68	0.034	0.25	0.196	12.61
Khonguruu-NH4	73.90	10.82	0.27	0.73	0.19	0.31	0.022	0.86	0.037	0.16	0.004	13.06

*LOI- loss on ignition

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

- 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_4-form of CLT and is presented in Table 2.

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

Deposit	CLT(wt.%)	Other minerals	TCEC, meq/g
Khonguruu (Russia)	80.0	quartz, feldspars, mica	1.85
Kholinskoye (Russia)	60.0	cristobalite, quartz.	1.41
Beli Plast (Bulgaria)	82.0	celadonite, plagioclase, quartz, montmorillonite	1.90

-The ion- exchange isotherms of Sr^{2+} on NH_4- 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-CLT mass, g; The contact time of solution and CLT was 3 months [14,15]. The obtained data are presented on the Fig.1.

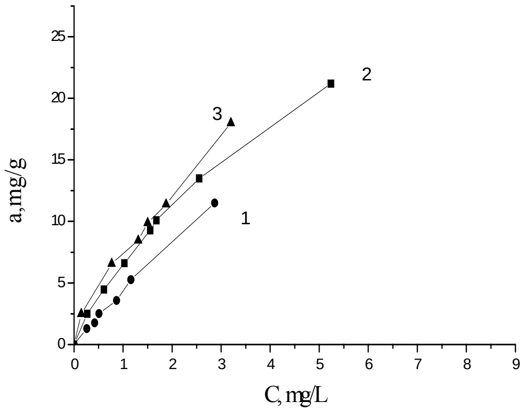

Fig. 1. Sr^{2+} ion-exchange isotherms for CLT's Kholinskoye (1 -●-●-), Khonguruu (2-■--■) and Beli Plast (3-▲-▲) from surface drinking water.

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

- The crystallite size of CLT was determined by XRD profile fitting analysis of 020 diffraction line and is as follows, (nm): Khonguruu ~ 50 ; Beli Plast ~ 33; Kholinskoye ~ 25; This analyses were performed by the specialized software WINFIT– a program designed for line-profile analysis and crystallite size determinations performed on single peaks and based FWHM and integral breadths of XRD diffraction lines [16].

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

-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). CLT 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 CLT 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 CLT 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.

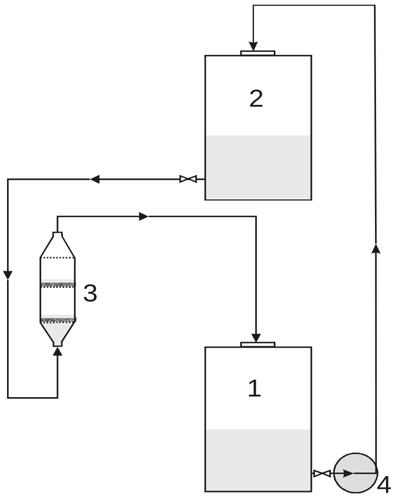

Fig. 2. Experiment scheme of «kinetics in thin layer». 1, 2- the tanks; 3 – the column; 4- pump. The tank capacity is 120 L. The studied solution volume is 90 L.

Results and discussion

The obtained Sr^{2+}ion-exchange isotherms are presented on the Fig. 1. As shown in Figure 1, the Sr^{2+} isotherms are linear practically for all studied CLT to Sr^{2+} concentration in equilibrium solution near 3 mg/L. The corresponding Sr^{2+} distribution coefficients (Kd) were calculated for linear part of the isotherms of the studied CLT , and their values were the following, (ml/g) : $6.0.10^3$; $5.38.10^3$ and $4.4.10^3$ for Beli Plast , Khonguruu, Kholinskoye deposits respectively.

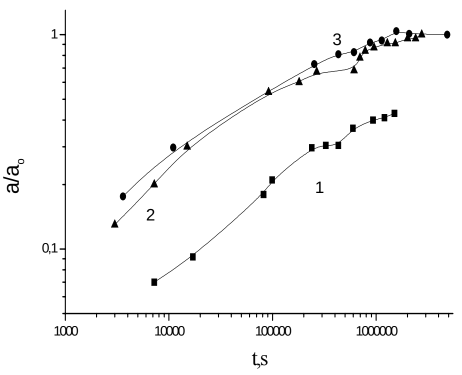

Fig. 3. Sr^{2+} sorption kinetics on NH_4^+-CLT's of different deposits from the surface drinking water (method «thin layer»). Khonguruu (1- ■--■), Beli Plast (2-▲-▲-), Kholinskoye deposit (3-●-●-)

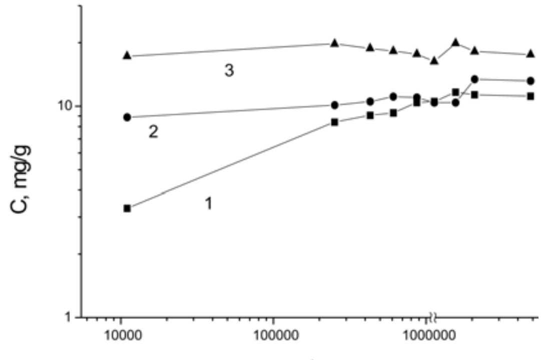

Fig. 4. Sorption kinetics of Sr^{2+} (1-■--■), K^+ (2-●-●-), Ca^{2+} (3-▲-▲-) on NH4- CLT of Kholinskoye deposite from surface drinking water . ≀≀- means the interruption of filtration process on 70 days. The last points on the Figure was obtained in 32 days of the following solution filtration.

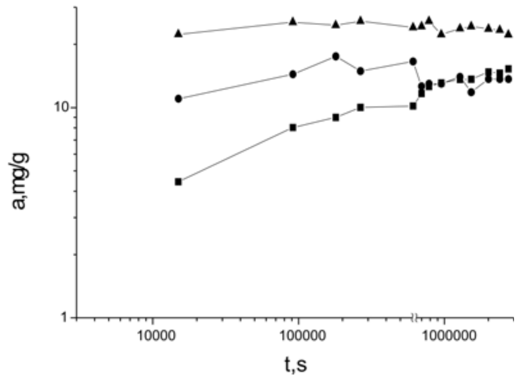

Fig. 5. Sorption kinetics of Sr^{2+} (1- ■—■), K^+ (2-●-●-), Ca^{2+} (3-▲-▲-), on NH_4^+- CLT of Beli Plast deposite (Bulgaria) from surface drinking water. ≀≀- means the interruption of filtration process on 14 days

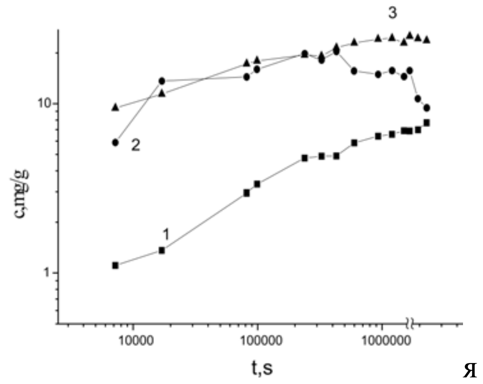

Fig. 6. Sorption kinetics of Sr^{2+}(1- ■--■), K^+ (2-●-●-),Ca^{2+} (3 -▲-▲-) on NH_4^+- CLT of Khonguruu deposite (Yakutiya, Russian) from surface drinking water. ≀≀- means the interruption of filtration process on 27 days

The results of the kinetic experiments are presented on Figure 3-6. As shown from Figure 3, the initial stage of Sr^{2+} kinetic dependence (from experiment beginning to time of $t=5\text{-}6 \cdot 10^4$s) is described by the particle diffusion law for all three CLT. The Sr^{2+} particle diffusion coefficients of the studied CLT ($D_{Sr}{}^{2+}$) were calculated by fitting experimental and theoretical kinetic dependences [12,14]. Calculated $D_{Sr}{}^{2+}$ of Kholinskoye, Beli Plast and Khonguruu CPT in NH_4^+- form are the following, (cm^2/s): $2.8 \cdot 10^{-10}$; $2.3 \cdot 10^{-10}$; $3.6 \cdot 10^{-11}$, respectively, i.e. Kholinskoye CLT 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 $2.5 \cdot 10^5$- $5 \cdot 10^5$s, but then an increase of Sr^{2+} sorption is observed again. It should be noted, that as shown from Figure 4-6, the K^+ sorption is decreased simultaneously with the Sr^{2+} sorption increase on this stage. It could be assumed that Sr^{2+} begins to occupy the K^+ sites

Nikashina et al. / **С**орбционные и хроматографические процессы. 2017. Т. 17. № 6

in the channels of CLT structure. But this assumption requires special structural investigations.

For CLT 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 CLT 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 CLT 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. As shown from Figure 6 , the ion-exchange kinetics for Khonguruu CLT 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 CLT may be found in the different crystallite sizes , structural defects and so on, which we intend to clarify later.

Conclusion

The kinetics of Sr^{2+} ion-exchange process on CLT of different deposits from surface drinking water was investigated in detail. It was shown, that the kinetic process on CLT includes 3 stages: a) the first stage - the particle diffusion process is 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 CLT 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 Sr^{2+} -sorption for different dynamic conditions.

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