

PHYSICAL CHEMISTRY
OF SURFACE PHENOMENA

Sorption of Cesium Ions by Nanostructured Calcium Aluminosilicates

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Received November 17, 2015

Abstract—Data on the sorption properties of synthetic calcium aluminosilicates (CASes) with Al : Si ratios of 2 : 2, 2 : 6, and 2 : 10, fabricated within the multicomponent system $\text{CaCl}_2\text{--AlCl}_3\text{--KOH--SiO}_2\text{--H}_2\text{O}$, are presented. Isotherms of the sorption of Cs^+ ions from aqueous solutions with Cs^+ concentrations of 0.2 to 6.0 mmol L⁻¹ are analyzed. The CAS maximum sorption capacity and the Langmuir constants are determined. Kinetic data are obtained, and the energy of cation-exchange activation upon the sorption of Cs^+ ions is determined. The effect of a salt background (1% KCl + 6% NaCl) has on the values of distribution coefficient (K_d) and the degree of Cs^+ ion removal is established.

Keywords: synthetic calcium aluminosilicate, sorption, cesium ions, sorption capacity, sorption kinetics

DOI: 10.1134/S0036024416100125

INTRODUCTION

Long-lived ¹³⁴Cs and ¹³⁷Cs isotopes with half-lives of 2.06 and 30 years, respectively, are among the most hazardous radionuclides found widely in natural objects. Radioactive contamination by cesium radioisotopes occurs as a result of nuclear tests and nuclear power plant accidents, and in industries specializing in the treatment and disposal of radioactive waste. The year 1950, when radioactive wastes with a total ¹³⁷Cs activity of around 12.4×10^{15} Bq were dumped from the Mayak Chemical Plant into the Techa River in the southern Ural Mountains, can be considered the starting point for counting major accidents at nuclear industry facilities. In 1957, radionuclides with a total activity of 0.2×10^{15} Bq (¹³⁷Cs) were emitted into the atmosphere in the same region as a result of a thermal explosion at a radioactive waste storage facility, while 46×10^{12} Bq were emitted in Windscale (Great Britain) because of a reactor fire accident [1]. In the accidents at the Chernobyl and Fukushima-1 nuclear power plants, the share of radioactive contamination attributable to ¹³⁷Cs isotopes was a total activity of more than 500×10^{15} Bq. In addition, ¹³⁷Cs radioisotopes are sources of contamination for territories where underground nuclear tests for military and “peaceful” purposes are performed.

Cesium is a very active chemical element; it is found in water predominantly in the ionic form and is easily accumulated in plants, while its accumulation in animal or human organisms results in radiation damage and sickness. An effective way of removing cesium radioisotopes from the environment is to bind it into

water-insoluble compounds. Despite the versatility of the available sorbents used in the sorption and extraction of cesium radionuclides from solutions by dynamic and static means, the search for and study of new sorption materials and ways of increasing their sorption capacity, improving their kinetic characteristics, and increasing the distribution coefficient of the radionuclides to be removed are now under way. One group of sorbents in which researchers are especially interested is natural, synthetic, and modified aluminosilicates [2–13].

Since aluminosilicates are characterized by changes in their structure and properties depending on the nature of the cations and the ratio of Al to Si and crystallization water in their composition under specific conditions of synthesis, the study of the effect the above parameters have on their functional properties is not only of scientific interest but of practical interest as well. We should note that most authors study natural or synthetic aluminosilicates of specific compositions. There are relatively few works devoted to the detailed examination of a multicomponent system used to obtain such compounds, particularly the effect the Al : Si ratio has on a compound’s physicochemical properties.

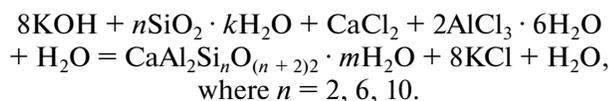
An important applied aspect of this work is that the initial compounds used in the synthesis of calcium aluminosilicates (e.g., calcium chloride and amorphous silica) are often contained in different technogenic wastes. From this viewpoint, detailed study of the relationship between the ratio of the initial components during synthesis and the physicochemical properties of the resulting compounds allows us to optimize

the functional properties of the final product. The aim of this work was to study the composition, structure, morphology, and sorption properties of calcium aluminosilicates (CASEs) obtained at different Al : Si ratios (2 : 2, 2 : 6, and 2 : 10) in the multicomponent system $\text{CaCl}_2\text{--AlCl}_3\text{--KOH--SiO}_2\text{--H}_2\text{O}$ with respect to Cs^+ ions from aqueous solutions of cesium carbonate with and without a salt background (1% KCl + 6% NaCl).

EXPERIMENTAL

Synthesis of Calcium Aluminosilicates

The following reagents were used as initial substances in synthesizing calcium aluminosilicates with preset Al : Si ratios of 2 : 2, 2 : 6, and 2 : 10: calcium chloride (CaCl_2), aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), and silicon dioxide ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) of chemically pure grade and potassium hydroxide (KOH) of analytical grade. The initial components were taken in the stoichiometric ratio (relative to the assumed composition of the water-free final product) needed to produce aluminosilicates with compositions $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot m\text{H}_2\text{O}$ (I); $\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot m\text{H}_2\text{O}$ (II); and $\text{CaAl}_2\text{Si}_{10}\text{O}_{24} \cdot m\text{H}_2\text{O}$ (III) according to the chemical reaction



A sample of potassium hydroxide was dissolved in distilled water, and the resulting solution was heated to 85–95°C. We added a calculated amount of silicon hydroxide and the mixture was held under constant stirring until it was completely dissolved (solution 1). Solutions of CaCl_2 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were prepared separately and then mixed with solution 1. During mixing, the solution was stirred intensively, and the temperature was maintained within the range 85–95°C. The resulting chemical reaction yielded a bulky white precipitate. It should be noted that the compaction of the precipitate after synthesis was slowed considerably as the content of SiO_2 in the initial system grew. The resulting precipitates were washed with hot distilled water until there was a negative reaction to the chloride ions in the wash water. Precipitates were separated through a white ribbon filter paper on a Buchner funnel using a water-jet pump. The washed precipitates were dried at 105–110°C in a drying oven over 3 days and stored in a desiccator filled with prepared silica gel.

Chemical Modification of Calcium Aluminosilicates

All of the aluminosilicates were characterized by chemical modifications associated with cation-exchange during their synthesis and their subsequent treatment in melts of salt solutions at different temperatures. In the multicomponent system under study

($\text{CaCl}_2\text{--AlCl}_3\text{--KOH--SiO}_2\text{--H}_2\text{O}$), salts of polysilicic acid with the preset KOH/SiO_2 ratio were obtained and subsequently mixed with solutions of calcium and aluminum chlorides. The exchange of cations in the system resulted in the establishment of a thermodynamic equilibrium due to a change of the Gibbs free energy equal to the difference between the energies of cations interacting with the negatively charged lattice of the formed aluminosilicate and the energies of their hydration in solution and in aluminosilicate [14].

Cs⁺ Ion Sorption Experiments

Our cesium salt solution was prepared by dissolving a sample of analytical grade Cs_2CO_3 in distilled water. A series of initial aqueous solutions with Cs^+ ion concentrations in the range 0.2–6.0 mmol L⁻¹ were prepared from the obtained stock solution with a Cs^+ concentration 54.5 mmol L⁻¹. The sorption of Cs^+ ions was conducted under static conditions at a solid to liquid phase ratio (S : L) of 1 : 1000 and a temperature of 20°C over 3 h. To study the effect the salt background had on the sorption of cesium ions, the prepared sorbent samples mixed with aqueous solutions of Cs^+ with and without the salt background (1% KCl + 6% NaCl, both of chemically pure grade) were stirred for 3 h. Experiments were performed at different solid : liquid phase ratios (1 : 40; 1 : 100; 1 : 400; 1 : 1000, and 1 : 2000). Stirring was done with a magnetic stirrer. The solution was separated from the solid phase through a white ribbon filter, and the concentrations of cesium and potassium in the filtrate were determined. A control solution was made in each series of experiments; distilled water with the sorbent was used as a reference solution.

The sorption capacity (A_s , mmol g⁻¹) of the studied samples was calculated according to the formula

$$A_s = \frac{(C_{\text{init}} - C_{\text{eq}})V}{m}, \quad (1)$$

where C_{init} is the initial concentration of Cs^+ in the solution, mmol L⁻¹; C_{eq} is the concentration of equilibrium ions in the solution, mmol L⁻¹; V is the volume of the solution, L; and m is the weight of the sorbent, g. The degree to which the Cs^+ ions were removed from the solution was calculated according to the formula

$$\alpha = \frac{(C_{\text{init}} - C_{\text{eq}})}{C_{\text{init}}} \times 100\%. \quad (2)$$

The distribution coefficient (K_d , mL g⁻¹) was determined as

$$K_d = \frac{(C_{\text{init}} - C_{\text{eq}})V}{C_{\text{eq}}m}. \quad (3)$$

CAS samples with a Al : Si ratios of 2 : 10 were used in our kinetic experiments. Sorbent samples were placed

into a series of test tubes, into which an aqueous solution of cesium salt with a Cs^+ ion concentration of 19 mmol L^{-1} at a liquid/solid phase ratio (S : L) of 1 : 1000 was added and stirred using a magnetic stirrer for 1, 5, 10, 20, and 60 min (filtration time was not taken into account) under thermostatic conditions at 20, 40, and 60°C . At certain intervals, the solution was separated from the solid phase through a white ribbon filter, and the concentration of Cs^+ ions was determined.

Methods of Analysis

Energy-dispersive X-ray fluorescence on an EDX-800HS spectrometer (Shimadzu, Japan) was employed to determine the elemental composition of our CAS. Samples for analysis were ground in an agate mortar with finely dispersed Teflon powder (weight ratio, 2 : 1) and placed into a mold 20 mm in diameter. Each pellet was compacted for 2 min at a pressure of 5000 kg. Measurement time was 200 s; the source of excitation was an X-ray tube equipped with a rhodium anode. Our analysis was performed with no allowance for light elements using the spectrometer's software. The relative error of determination was no greater than $\pm 2\%$.

The content of the crystallization (zeolite) water in the resulting calcium aluminosilicates was determined from the difference between the weight of a sample, dried to a constant value at 110°C and then annealed at 900°C .

The samples' X-ray diffraction images were recorded using a D8 ADVANCE automatic diffractometer (Bruker, Germany) with sample rotation in $\text{CuK}\alpha$ -radiation. X-ray diffraction analysis (XRD) was performed using the EVA search program with the PDF-2 database. The samples' IR spectra were recorded in the range of $400\text{--}4000 \text{ cm}^{-1}$ using a Shimadzu FTIR Prestige-21 Fourier spectrometer at room temperature. Samples for recording were ground to a finely dispersed state in an agate mortar and deposited, in the form of a suspension in Vaseline, on a KRS-5 substrate. The specific surface areas of our CAS samples was determined by means of low-temperature nitrogen sorption using a Sorbtometer-M device (Russia).

Studies of the samples' morphological characteristics and elemental composition in local volumes were performed using a Hitachi S5500 high-resolution scanning electron microscope equipped with an accessory for transmission microscopy and a Thermo Scientific energy-dispersive spectrometer. The content of Cs^+ and K^+ ions in the filtrates upon sorption was determined via atomic absorption using a Solaar 6 M double-beam spectrometer (Thermo, United States) on analytical lines 852.1 and 766.5 nm, respectively. The detection limit of Cs^+ ions in aqueous solutions is $0.01 \mu\text{g mL}^{-1}$; the same value for potassium is

$0.002 \mu\text{g mL}^{-1}$. The concentration of hydrogen ions in all our experiments was determined using a Multitest IPL-102 pH-meter/ion-meter (Russia) equipped with an ESK-10601/7 glass electrode standardized on buffer solutions.

RESULTS AND DISCUSSION

Characterizing the Synthesized Calcium Aluminosilicates (CASes)

As was mentioned above, the initial reagent compositions in the $\text{CaCl}_2\text{--AlCl}_3\text{--KOH--SiO}_2\text{--H}_2\text{O}$ system were taken in the stoichiometric ratio calculated for producing the corresponding calcium aluminosilicates: $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot m\text{H}_2\text{O}$ (I); $\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot m\text{H}_2\text{O}$ (II), and $\text{CaAl}_2\text{Si}_{10}\text{O}_{24} \cdot m\text{H}_2\text{O}$ (III). Quantitative determination of the elemental compositions of the obtained samples showed the following elemental contents in the resulting CASes, wt % (mol):

CAS(I): Si, 31.4 (1.12); Al, 9.3 (1.08); Ca, 22.5 (0.56); K, 16.8 (0.43);

CAS(II): Si, 61.2 (2.18); Al, 20.0 (0.74); Ca, 5.8 (0.14); K, 13.0 (0.33);

CAS(III): Si, 63.1 (2.25); Al, 12.7 (0.47); Ca, 8.2 (0.2); K, 16.0 (0.41).

As follows from the obtained data, the Al : Si ratios in the samples correspond to the preset ones (2 : 2, 2 : 6, and 2 : 10), but total amount of calcium and potassium cations (their total charge) indicates that the compositions of calcium aluminosilicates are not monophasic. They could contain aluminosilicates and calcium and aluminum silicates. The presence of crystallization water was established for the CAS compositions: CAS(I), 3 H_2O molecules; CAS(II) and CAS(III), 4 H_2O molecules each.

According to the data from X-ray diffraction analysis, only X-ray amorphous phases were present in the compositions of the produced CASes. As can be seen from the X-ray images, interplanar distance d (E) for aluminosilicates changes in the order $\text{I} < \text{II} < \text{III}$ ($3.2200 < 3.5344 < 3.5432 \text{ nm}$). The latter is indirectly corroborated by formation of compounds with different parameters of the crystal lattice that depend on the Al : Si ratio. Peaks attributed to aluminum oxide and aluminum silicate (Al_2SiO_5) were registered on samples' X-ray diffraction images upon annealing at 920°C for 4 h against the background of an amorphous peak in the $15^\circ\text{--}35^\circ$ range of angles. The peaks attributed to the crystalline phase ($\text{CaAl}_2\text{Si}_2\text{O}_8$) of the triclinic modification (unit cell parameters $a = 8.173$, $b = 12.869$, $c = 14.165$, $\alpha = 93.113^\circ$, $\beta = 115.913^\circ$, $\gamma = 91.261^\circ$) and those attributed to the mullite phase ($\text{Al}_{2.4}\text{Si}_{0.6}\text{O}_{4.8}$) of the orthorhombic modification (unit cell parameters $a = 7.583$, $b = 7.681$, $c = 2.6854$, $\alpha = \beta = \gamma = 90^\circ$) were registered on the X-ray diffraction

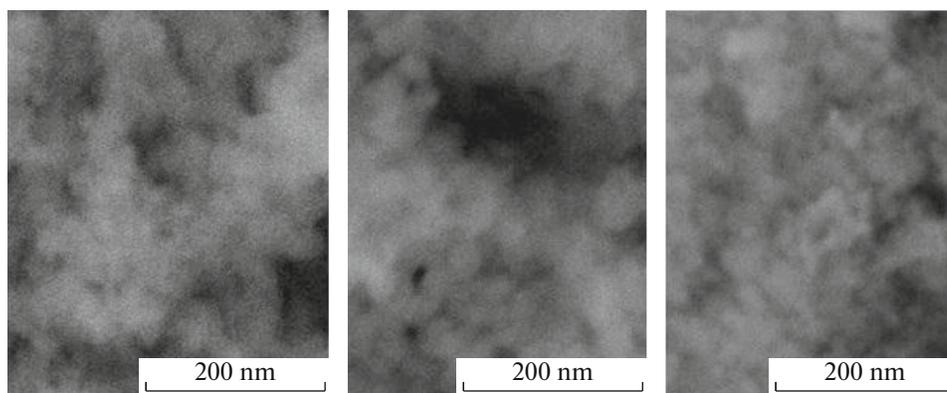


Fig. 1. Images of microparticles of CAS samples, obtained via scanning electron microscopy with an accessory for transmission electron microscopy.

images within 5–6 h after the samples were annealed at 1100°.

The IR spectra of the CASes under study were characterized by the presence of intense absorption bands in the range of 850–1100 cm^{-1} . These were attributed in [15, 16] to stretching vibrations of Si–O–Si and Al–O–Al bonds, while the low-frequency bands in the range of 450–600 cm^{-1} were attributed to the bending vibrations of Si–O–Si and Al–O–Si bonds. Along with the increased Si : Al ratio in aluminosilicates, the maximum of the absorption peak [7] attributed to Si–O stretching vibrations shifted to the high-frequency range: CAS(I), 1010.7 cm^{-1} ; CAS(II), 1056.99 cm^{-1} ; CAS(III), 1064.71 cm^{-1} . This shift could be due to an increase in the energy of the lattice of calcium aluminosilicate as the Si : Al ratio grew [17]. The presence of water in the CASes was corroborated by the fairly intense absorption peak in the frequency range of 3000–3800 cm^{-1} characteristic of stretching vibrations with the participation of hydrogen atoms

[16]. The absorption bands around 1600 cm^{-1} were caused by water bending vibrations.

The specific surface areas of the CAS samples under study (I, II, III), determined via multipoint BET, were 83 ± 5.0 ; 90 ± 5.0 ; and $121 \pm 5.0 \text{ m}^2 \text{ g}^{-1}$, respectively; i.e., an increase in the specific surface areas of the synthesized compounds was observed as the Si : Al ratio grew.

According to the data obtained using the high-resolution scanning electron microscope (Fig. 1), the samples' morphological features were similar to those established for synthetic potassium aluminosilicate [10, 13]. They were all nanostructured formations and had multilevel porous structures with pore sizes of up to hundreds of nanometers and unit sizes of up to tens of nanometers.

Cesium Ion Sorption

Figure 2 shows isotherms of Cs^+ ion sorption for samples CAS(I), CAS(II), and CAS(III).

The maximum sorption capacities A_{max} within the measurement errors were 1.05, 0.95, and 1.1 mmol g^{-1} , respectively. The Langmuir constant (K_L) for the presented isotherms was calculated from the dependence of sample sorption capacity A_s on the initial concentration of cesium (C_{init}) according to the procedure described in [10]:

$$K_L = V_0 / (C_{\text{init}}V_0 - A_s m),$$

where C_{init} was determined from the graphic dependence of A_s on the preset concentration when $A_s = A_{\text{max}}$; V_0 is the volume of the solution, L; and m is the weight of the sorbent, g. The Langmuir constant (K_L) for the presented isotherms was 6.66 L mmol^{-1} . The maximum sorption capacity (A_{max}) for all the samples with allowance for measurement errors was taken to be equal to 1.03 mmol g^{-1} . For CAS(I), CAS(II), and CAS(III), the dependence of the sorption capacity (A_s) on the equilibrium concentration (C_{eq}) was

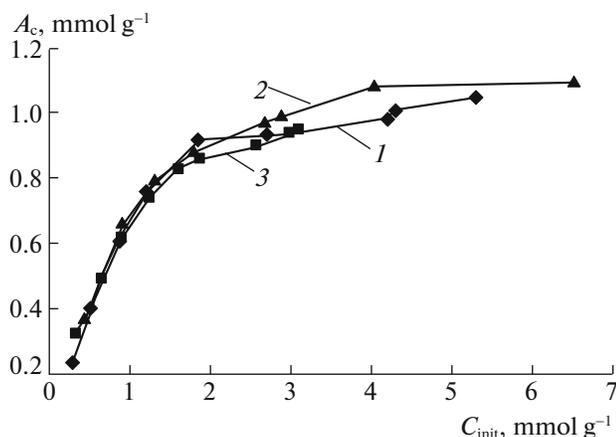


Fig. 2. Isotherms of the sorption of Cs^+ ions by synthetic aluminosilicate: (1) CAS(I), (2) CAS(II), (3) CAS(III).

described by the Langmuir equation $A_s = 6.66A_{\max}C_{\text{eq}}/(1 + 6.66C_{\text{eq}})$.

The values of distribution coefficients (K_d) at different S : L ratios and the degrees of Cs^+ ion removal from solutions with and without the salt background (1% KCl + 6% NaCl) at a concentration of Cs^+ ions in solution of $\sim 0.3 \text{ mmol L}^{-1}$ are shown in Table 1.

As can be seen from Table 1, the maximum degree of Cs^+ ion removal by CAS from solutions not containing the salt background is more than 99%, while the K_d value at S : L = 1 : 400 for CAS(III) is $2.2 \times 10^4 \text{ mL g}^{-1}$. The presence of the salt background (1% KCl + 6% NaCl) affects the sorption characteristics of the aluminosilicates under study through reduction of their sorption capacity, distribution coefficient, and degree of removal (Table 1).

Kinetic Characteristics of CAS(III) Sorbent

Figure 3 shows the dependences of the sorption capacity of CAS(III) with respect to Cs^+ ions at different temperatures on the sorption time.

As can be seen from our experiments, a rise in the solution temperature affects the value of the maximum sorption capacity: A_{\max} grows from 0.63 mmol g^{-1} at 20°C to 0.85 mmol g^{-1} at 60°C . As was found from the obtained kinetic dependences, the time needed to attain equilibrium thermodynamic values of Cs^+ ion concentrations under static conditions was no longer than several minutes. The dependences of changes in the sorption capacity over time were analyzed using the Kolmogorov–Erofeev equation

$$\alpha = 1 - [\exp(-kt^n)], \quad (\text{I})$$

where α is the degree of completeness of the cation exchange reaction during sorption; k is a constant characterizing the reaction rate; t is the sorption time; and n is the reaction order. After finding the double logarithm of Eq. (I), the experimental data were presented in the form of the dependence (Fig. 4)

$$\ln(-\ln(1 - \alpha)) = \ln k + n \ln t. \quad (\text{II})$$

The dependences shown in Fig. 4 are described by linear equations $y = 0.0396x + 0.479$ with correlation coefficient $R^2 = 0.9989$ (for 60°C); $y = 0.0239x + 0.1835$ with $R^2 = 0.935$ (for 40°C); and $y = 0.0223x - 0.141$ with $R^2 = 0.8813$ (for 20°C). For the analyzed temperature range, the order of the reaction of Cs^+ ion sorption is much lower than 1, which is characteristic of reactions controlled by diffusion processes. Based on the $\ln k$ values found from the temperature dependences (Fig. 4), according to the Arrhenius equation in the logarithmic form

$$\ln k = \ln A + Q/RT, \quad (\text{III})$$

where Q is the activation energy; R is the gas constant ($8.3144 \text{ J mol}^{-1}$); and T is the temperature, the activation energy of the sorption process was determined

Table 1. Distribution coefficients (K_d) at different S : L ratios and the degree of Cs^+ ion removal by CAS from solutions without and with a salt background (1% KCl + 6% NaCl)

No.	m , g	S : L	c_1 , mmol L^{-1}	K_d , mL g^{-1}	α , %
Sorbent CAS(I)					
Without salt background, $c = 0.219$					
1	0.5011	1 : 40	0.006	1427	97
2	0.2008	1 : 100	0.0133	1539	94
3	0.0502	1 : 400	0.058	1098	74
4	0.0200	1 : 1000	0.112	948	49
Salt background, $c = 0.266$					
5	0.5038	1 : 40	0.205	12	23
6	0.2028	1 : 100	0.23	12	14
7	0.0509	1 : 400	0.255	16	4
8	0.0207	1 : 1000	0.262	13	2
9	0.0100	1 : 2000	0.262	28	0.4
Sorbent CAS(II)					
Without salt background, $c = 0.251$					
1	0.5012	1 : 40	0.0015	6719	99.4
2	0.2029	1 : 100	0.0033	7497	98.7
3	0.0500	1 : 400	0.0074	13225	97
4	0.0212	1 : 1000	0.0233	9215	91
5	0.0100	1 : 2000	0.0516	7728	79
Salt background, $c = 0.251$					
6	0.5000	1 : 40	0.113	49	55
7	0.2002	1 : 100	0.173	45	49
8	0.0503	1 : 400	0.223	50	10
9	0.0218	1 : 1000	0.232	75	7
10	0.0109	1 : 2000	0.240	86	4
Sorbent CAS(III)					
Without salt background, $c = 0.346$					
1	0.5000	1 : 40	0.00145	9528	99.6
2	0.2000	1 : 100	0.0018	19380	99.5
3	0.0500	1 : 400	0.006	22810	98.3
4	0.0212	1 : 1000	0.017	18097	95.1
5	0.012	1 : 2000	0.0346	14988	90
Salt background, $c = 0.251$					
6	0.5000	1 : 40	0.092	69.2	63
7	0.2000	1 : 100	0.162	55	35.5
8	0.0500	1 : 400	0.214	70	15
9	0.0210	1 : 1000	0.245	25	2.3
10	0.0100	1 : 2000	0.248	24	1.2

m is the weight of the sorbent; c and c_1 are the concentrations of Cs^+ ions in solution before and after sorption, mmol L^{-1} ; and α is the degree of Cs^+ ion removal.

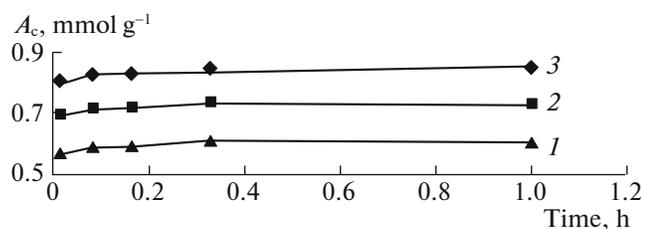


Fig. 3. Kinetic curves of sorption of Cs^+ ions by the CAS(III) sorbent at different temperatures: (1) 20, (2) 40, (3) 60°C.

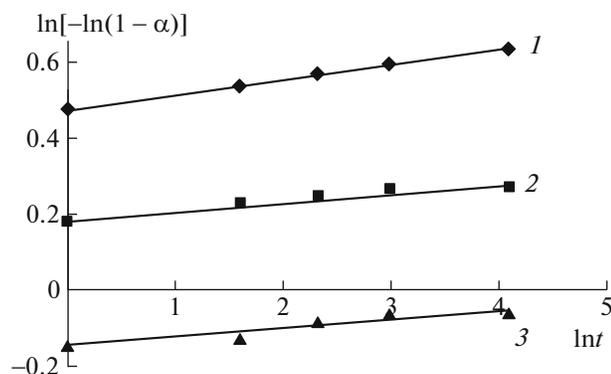


Fig. 4. Logarithmic dependences of the completeness of the cation-exchange reaction $\ln[-\ln(1-\alpha)]$ on time ($\ln t$) upon the sorption of Cs^+ ions by the CAS(III) sorbent at different temperatures: (1) 60, (2) 40, (3) 20°C.

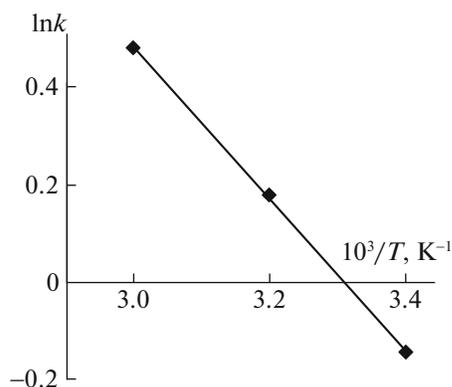


Fig. 5. Dependence of the logarithm of the constant of the reaction of sorption ($\ln k$) on the inverse temperature.

graphically from the $\ln k$ dependence on the inverse absolute temperature ($1/T$) (Fig. 5), which is described by the linear equation $y = -1.55x + 5.1333$ with regression coefficient $R^2 = 0.9997$.

The activation energy of the sorption process, calculated from the experimental data, was 12.89 kJ mol⁻¹. This is a fairly low value; such processes are characterized by slight changes in the rate of the cationic

exchange reaction along with changes in temperature, as was corroborated experimentally.

Our data on the values of the sorption capacity depending on the sorption time were also interpreted according to pseudo-first and pseudo-second orders. According to Lagergren's model, the kinetic model of the rate of a reaction of the pseudo-first order is described in the linear integral form by the equation

$$\log(A_e - A_t) = \log A_e - (k_1 t)/2.303, \quad (\text{IV})$$

where A_{eq} and A_t are the values of sorption in the equilibrium state and at moment t , respectively; k_1 is the apparent constant of the pseudo-first order rate (min⁻¹). The kinetic model of the pseudo-second order is

$$1/A_t = 1/A_e - 1/k_2 A_e^2 t, \quad (\text{V})$$

where k_2 is the constant of the sorption rate for the pseudo-second order model.

The dependence of the rate constant logarithm determined according to the model of the pseudo-first order ($\ln k_1$) on the inverse absolute temperature served as a basis for determining the activation energy of sorption: 10.39 kJ mol⁻¹, which is close to the one found using the Kolmogorov-Erofeev kinetic model for topochemical processes. The apparent pseudo-rate constants (k_1 and k_2) and the respective squares of correlation coefficients R^2 , which indicate the validity of associating them with the pseudo-first and pseudo-second order kinetic models, are shown in Table 2.

As can be seen from the data of Table 2, the sorption process within the analyzed time period is best described by the pseudo-first order model, as is indicated by respective correlation coefficients.

CONCLUSIONS

The sorption properties of X-ray amorphous nanostructured calcium aluminosilicates with Al : Si ratios of 2 : 2, 2 : 6, and 2 : 10 were investigated. The maximum sorption capacities of CAS(I), CAS(II), and CAS(III) with respect to Cs^+ ions were, within the limits of experimental error, 1.05, 0.95, and 1.1 mmol g⁻¹, respectively. It was established that in the aluminosilicates obtained in the system $\text{CaCl}_2\text{-AlCl}_3\text{-KOH-SiO}_2\text{-H}_2\text{O}$, the Al : Si ratio corresponded to the one preset during synthesis, but the total charge of calcium and potassium cations and their charge ratios changed, depending on the experimental conditions. Aluminosilicates of complex composition must be considered products of chemical modification during synthesis and their interaction with solutions containing salts of alkali metals.

The maximum degree of Cs^+ ion removal by CAS (for all of the considered Al : Si ratios) from solutions with no salt background was 95.0–99.0%, while the K_d value at S : L = 1 : 400 for CAS(III) lies in the range of

Table 2. Results from interpreting the kinetic curves of Cs⁺ ion sorption by sorbent CAS(II) using chemical kinetic models

T, °C	Pseudo-first order		Pseudo-second order	
	$k_1 \times 10^2$, min ⁻¹	R ²	k_2 , g mmol ⁻¹ min ⁻¹	R ²
20	12.3	0.9937	37.5	0.7048
40	12.3	0.9937	34.3	0.7493
60	8.2	0.982	22.8	0.8529

2.2×10^4 mL g⁻¹. A salt background (1% KCl + 6% NaCl) affected the sorption characteristics of the aluminosilicates under study by reducing their sorption capacities, distribution coefficients, and degrees of removal. CAS can be recommended for the effective removal of cesium ions from aqueous solutions with low salt backgrounds under static conditions.

Nanostructured aluminosilicates are characterized by high rates of cationic exchange under conditions of static sorption (no longer than a few minutes), a result of the low energy of process activation (~ 10 – 13 kJ mol⁻¹) and sample morphology. For natural aluminosilicate-based sorbents, this parameter varies from several hours to a few days. The studied calcium aluminosilicates can be recommended not only for removing cesium from different aqueous solutions, but for the rapid detoxification of living organisms as well.

ACKNOWLEDGMENTS

This work was supported by grants from the Far Eastern Basic Research Program of the Russian Academy of Sciences (FEBRAS) (project nos. 15-I-3-017 and 15-II-3-015) and by the Ministry of Science and Education of the Russian Federation (government regulation no. 218, April 9, 2010; contract no. 02.G25.31.0166, December 1, 2015).

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Translated by D. Marinin