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Sorption of Cs^+ Ions from Seawater by a Nanostructured Aluminosilicate Sorbent

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Abstract—We have studied the Cs^+ sorption properties of a synthetic nanostructured X-ray amorphous $KAlSi_3O_8 \cdot 1.5H_2O$ potassium aluminosilicate (SPA) with a specific surface area of 105.0 m^2/g under static conditions in cesium carbonate solutions in seawater at Cs^+ concentrations from 0.05 to 23.07 mmol/L. The results demonstrate that, in this Cs^+ concentration range, the sorption capacity of the SPA reaches 0.45 mmol/g.

Keywords: synthetic potassium aluminosilicate, sorption, cesium ions, seawater

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INTRODUCTION

Rapid development of nuclear power engineering and industrial facilities for nuclear fuel and irradiated structural materials processing does not preclude possible accidents resulting in radioactive contamination of the environment. The disposal of long-lived nuclides (such as ^{137}Cs, ^{60}Co, and ^{90}Sr) is a serious problem from both the technological and environmental points of view.

To eliminate negative environmental impacts, more and more use is being made of inorganic sorbents that largely meet requirements on selectivity to individual radionuclides and possess mechanical strength, chemical stability, and radiation resistance [1].

Among the great diversity of inorganic sorbents that are used for cesium sorption, a special group is constituted by natural and synthetic silicates with various compositions and structures and related composite sorbents [2–7].

Borai et al. [2] investigated ^{134}Cs sorption from low-level liquid waste using natural and synthetic zeolites: natural clinoptilolite, synthetic and natural mordenites, and natural chabazite. Their results demonstrate that, at the highest cesium chloride concentration (0.1 M), natural clinoptilolite, natural chabazite, and natural and synthetic mordenites have sorption capacities of 1.27, 2.07, 1.93, and 1.67 mmol/g, respectively, that is, natural chabazite has the highest sorption capacity for cesium. In a study of the effect of Na^+ and K^+ ions on cesium ion sorption (pH 5, solid : liquid = 1 : 100), the degree of ^{134}Cs removal was shown to be reduced to a greater extent by the presence of K^+ ions in solution because potassium ions were involved in ion exchange processes.

For ^{137}Cs radionuclide sorption in the pH range from 3 to 10, Singh et al. [3] employed a synthetic sodium aluminosilicate with a specific surface area of 457.0 m^2/g, prepared by reacting sodium acetate, aluminum nitrate, and tetraethyl orthosilicate. Their results indicate that the degree of cesium removal increases with increasing pH, reaching 65.0% at pH 10.

According to Lee et al. [7], mesoporous geopolymers containing nanocrystalline zeolites are effective in removing Cs^+ ions from aqueous solutions. The maximum sorption capacity of mesoporous geopolymers was found to be 15.24 mg/g.

Researchers at the Institute of Chemistry, Far East Branch, Russian Academy of Sciences, investigated the Cs^+ sorption properties of nanostructured synthetic potassium aluminosilicates (SPAs) with Si/Al ratios from 1 to 5 and specific surface areas from 58.3 to 182.8 m^2/g [8–10]. The aluminosilicates studied were shown to range in maximum sorption capacity from 1.7 to 4.2 mmol/g. In choosing sorbents, one should have data on the effect of the ionic composition of the salt background on the sorption of particular ions from aqueous solutions. As shown in a study of the effect of nitrates ($NaNO_3$, KNO_3, and NH_4NO_3)

Table 1. Concentrations of chemical elements in the seawater

Element	Al	Ca	Fe	Ba	Cd	Cr	Mn	Pb	Sr
C, mg/L	0.31	339.51	0.07	0.02	0.04	0.03	0.02	0.05	6.28

on Cs^+ sorption, the effect is weakest in the case of sodium nitrate.

Knowledge of sorption parameters of nanostructured SPAs for cesium ion sorption from natural seawater containing different Cs^+ concentrations is of practical interest.

This paper presents a continuation of our research into the effect of salt background on the sorption properties of nanostructured synthetic $KAlSi_3O_8 \cdot 1.5H_2O$ for Cs^+ ions in solutions prepared using seawater.

EXPERIMENTAL

Cs^+ sorption experiments. As a sorbent, we used an SPA with a specific surface area of 105.0 m^2/g. The synthesis and properties of the sorbent were described elsewhere [8].

Seawater for the preparation of solutions with different Cs^+ concentrations was taken in the Sea of Japan in the water area of Amur Bay (Vladivostok) and passed through white ribbon filter paper. Cesium carbonate solutions with a particular concentration were prepared by dissolving a weighed amount of analytical-grade Cs_2CO_3 in an appropriate amount of seawater, whose composition is indicated in Table 1.

Sorption experiments were carried out under static conditions at solid : liquid = 1 : 40 and $t = 20°C$, using cesium carbonate solutions in seawater with different initial Cs^+ concentrations in the range from 0.05 to 23.07 mmol/L. The solutions were stirred in a laboratory shaker for 3 h. Next, they were separated from the sorbent by filtration (blue ribbon filter paper) and Cs^+ concentration in the solutions was determined. For comparison, we used Termoksid-35 sorbent, which is employed in the nuclear industry for removing cesium radionuclides from liquid radioactive waste and aqueous process media.

In a control experiment, weighed amounts of the sorbents under study were placed in tubes filled with seawater, which was then stirred in parallel with the samples under study.

The sorption capacity (A_s, mmol/g) of the samples under study was evaluated as

$$A_s = \frac{(C_0 - C_{eq})}{m} V, \qquad (1)$$

where C_0 (mmol/L) is the initial Cs^+ concentration in solution, C_{eq} (mmol/L) is the equilibrium Cs^+ concentration in solution, V (L) is the volume of the solution, and m (g) is the mass of the sorbent.

The degree of Cs^+ removal (α, %) was evaluated as

$$\alpha = \frac{(C_0 - C_{eq})}{C_0} \times 100\%. \qquad (2)$$

Characterization techniques. X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer (Germany) with CuK_α radiation.

The elemental composition of the samples was determined by energy dispersive X-ray fluorescence analysis using a Shimadzu EDX-800HS spectrometer system (Japan). Analysis was carried out with no allowance for light elements, using software supplied with the spectrometer. The relative error of determination was within ±2%.

The thermal behavior of the sorbent was studied in an argon atmosphere at a heating rate of 10°C/min in the temperature range 20–850°C using a Netzsch STA 449 C Jupiter simultaneous thermal analysis system (Germany).

The specific surface area of the SPA was determined by low-temperature nitrogen adsorption measurements with a Sorbtometr-M instrument (Russia).

IR absorption spectra of samples prepared as Vaseline mulls were measured in the range 400–2000 cm^{-1} on a Shimadzu FTIR Prestige-21 Fourier transform IR spectrophotometer (Japan).

The morphological characteristics and elemental composition of the samples were determined on a Hitachi S-5500 high-resolution scanning electron microscope (SEM) (Japan) equipped with a scanning transmission electron microscopy accessory and Thermo Scientific energy dispersive X-ray spectrometer system. The presence of cesium in the samples after sorption was ascertained on the Hitachi S-5500. The samples were first washed with distilled water and dried at 100°C.

The concentrations of chemical elements in the seawater was determined by inductively coupled plasma atomic emission spectroscopy on an iCAP 6500 Duo atomic emission spectrometer (Thermo Electron Scientific, the United States).

In all of our experiments, the concentration of hydrogen ions was monitored by a Mul'titest IPL-102 pH meter/ion-selective meter (Russia) with an EDK-10601/7 glass electrode, calibrated using buffer solutions.

The concentration of Cs^+ ions in solution was determined by atomic absorption on a SOLAAR M6 double-beam spectrometer (Thermo, the United States) using an 852.1 nm analytical line. The detection limit for Cs^+ ions in aqueous solutions was 0.01 μg/mL, with a relative uncertainty of ±15%.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the SPA sorbent shows a smooth, broad peak typical of an amorphous phase, with an average interplanar spacing of 3.8209 Å (Fig. 1).

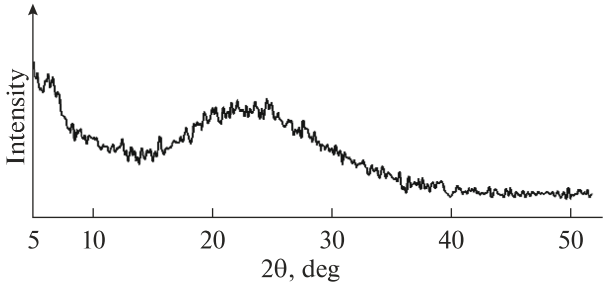

Fig. 1. X-ray diffraction pattern of the SPA sorbent.

According to quantitative X-ray fluorescence analysis data, the overall composition of the amorphous sample is $KAlSi_3O_8$. With allowance for thermal analysis data, the chemical composition of the sorbent is $KAlSi_3O_8 \cdot 1.5H_2O$ (under the assumption that 50% of the weight loss during heating to 850°C is accounted for by the removal of sorbed water below 150°C).

The IR spectrum of the SPA sample (Fig. 2) contains a strong absorption band in the range 850–1100 cm^{-1}, due to Si–O–Si and Al–O–Al stretching vibrations. The low-frequency bands in the range 450–600 cm^{-1} arise from Si–O–Si and Al–O–Si bending vibrations. The band around 1653 cm^{-1}, δ(O–H), indicates that the sample contains bound water [11].

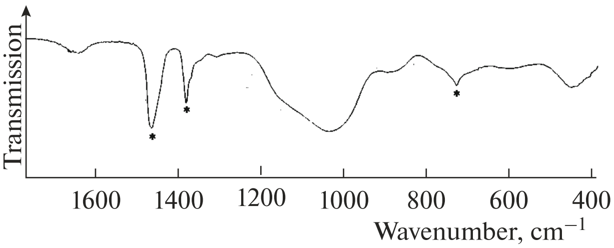

Fig. 2. IR absorption spectrum of the SPA sorbent. The asterisks mark the absorption bands of Vaseline.

Figure 3 shows SEM images illustrating the morphology of the SPA sorbent. No sputter deposition of the sample was performed.

As seen in Fig. 3, the sample has the form of an agglomerate of nanoparticles 15–20 nm in size, with pores of roughly the same size in between. The nanoparticles form associates ~100–250 nm in size. Between the associates, there are pores ranging in size up to ~50–100 nm. The structure of the sample is similar to that of coral sponge.

Figure 4 illustrates the effect of the initial Cs^+ concentration in seawater on the sorption capacity of the SPA and Termoksid-35 sorbents. It follows from these data that, at low Cs^+ concentrations in solution (below 6.0 mmol/L), the Termoksid-35 sorbent ensures better purification of the solution (up to 98.7%) than does the SPA sorbent (below 82.0%). As the Cs^+ concentration in solution is raised to above 6.0 mmol/L, the degree of solution purification by the SPA sorbent becomes higher than that by the Termoksid-35 sorbent. It is seen from these data that, at Cs^+ concentrations in seawater above 10.0 mmol/L, the sorption capacity of the SPA is as high as 0.45 mmol/g and that of the Termoksid-35 sorbent is 0.24 mmol/g. These sorption capacities and the degrees of Cs^+ removal from seawater by the SPA and Termoksid-35 sorbents can be accounted for in terms of both their different specific surface areas and their stability in the aqueous media under consideration, differing in pH. With increasing initial Cs^+ concentration, the pH of the solutions rises to 9.2–10.0. At these solution pH values, the decrease in the sorption capacity of the Termoksid-35 sorbent is due to its instability in alkaline media, whereas the SPA is stable in a wide range of pH values [9].

The sorption capacity of the SPA as a function of Cs^+ concentration in solution can be described by the Langmuir equation:

$$A_s = A_{max} K C_{eq} \frac{1}{1 + K C_{eq}},$$

where K (L/mmol) is the Langmuir constant and A_{max} (mmol/g) is the maximum sorption capacity. The Langmuir constant K evaluated from experimental data is 0.089 L/mmol, and the maximum sorption capacity A_{max} is 1.0 mmol/g.

Figure 5 shows an SEM image of SPA nanoparticles after Cs^+ sorption from solutions with a Cs^+ concentration of 23.07 mmol/L. In zone 1 in Fig. 5, we determined the total concentrations of cesium and the constituent elements of the sorbent. Figure 6 shows the X-ray spectrum of the constituent elements

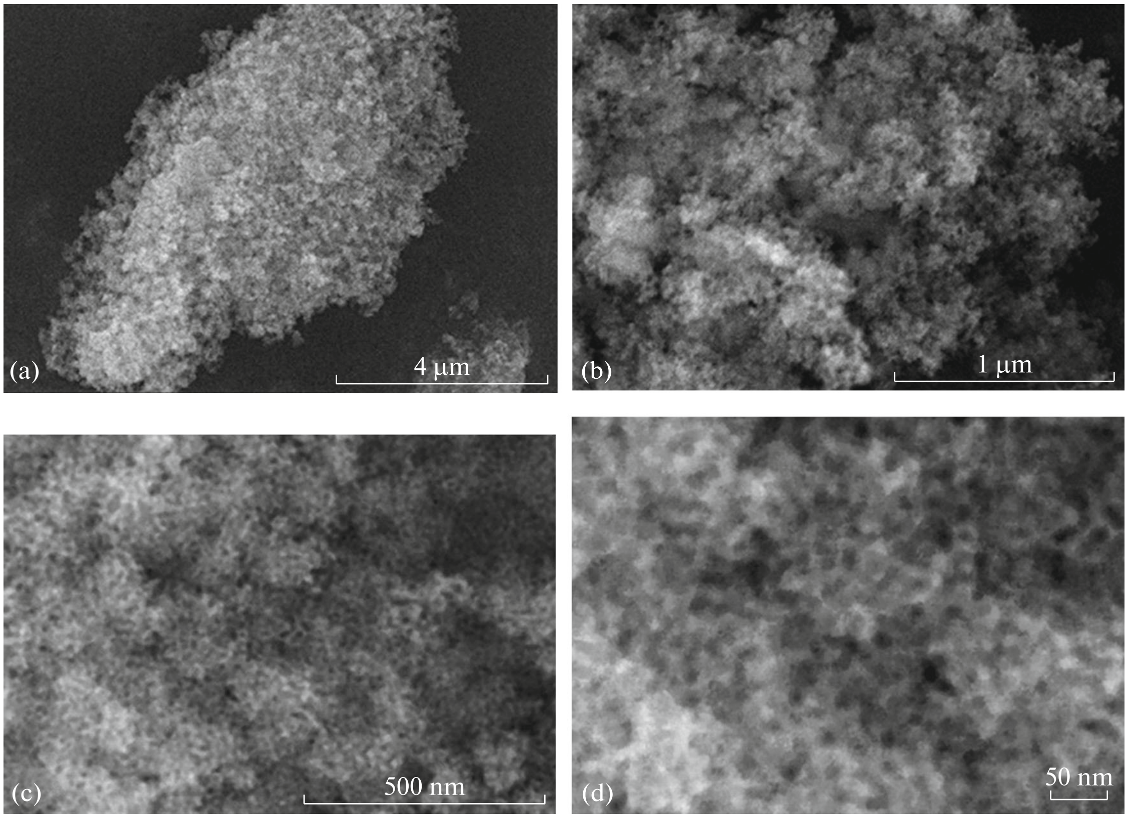

Fig. 3. SEM images of the SPA sorbent at different magnifications.

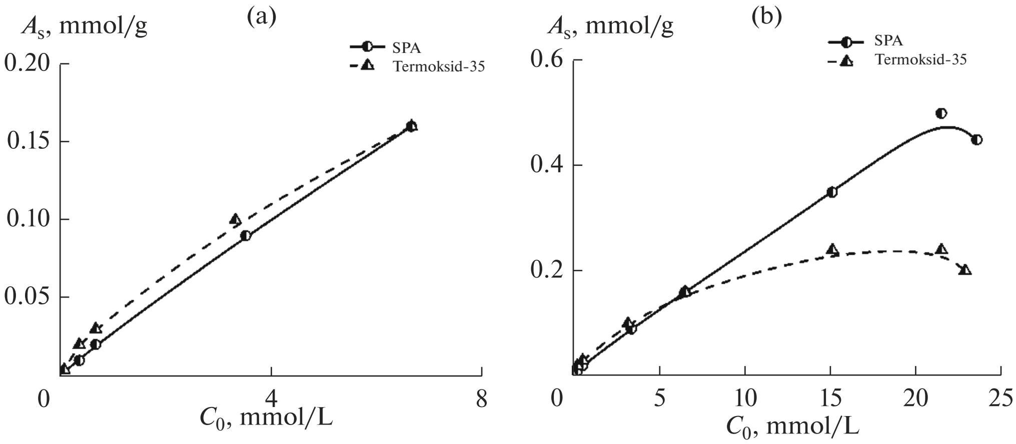

Fig. 4. Sorption capacity A_s of the SPA and Termoksid-35 sorbents in seawater at Cs^+ concentrations in solution (a) below 6.0 and (b) up to 23.07 mmol/L.

obtained on the Hitachi S-5500 scanning electron microscope using an energy dispersive X-ray spectrometer system.

According to the data obtained with the energy dispersive spectrometer system, the cesium content is 3.5 wt %, in agreement with the atomic absorption data on the sorption capacity of this SPA sample.

Table 2 summarizes data on the removal of Cs^+ ions by the SPA and Termoksid-35 sorbents from solutions with low Cs^+ concentration (0.103 mmol/L) at differ-

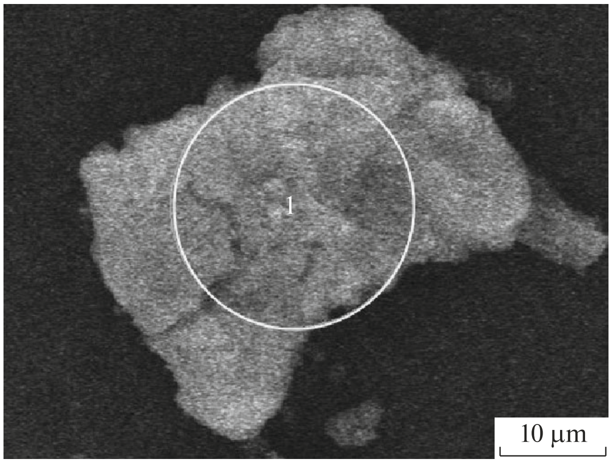

Fig. 5. SEM image of nanoparticles in one of the SPA samples after Cs^+ sorption from solutions with a Cs^+ concentration of 23.07 mmol/L.

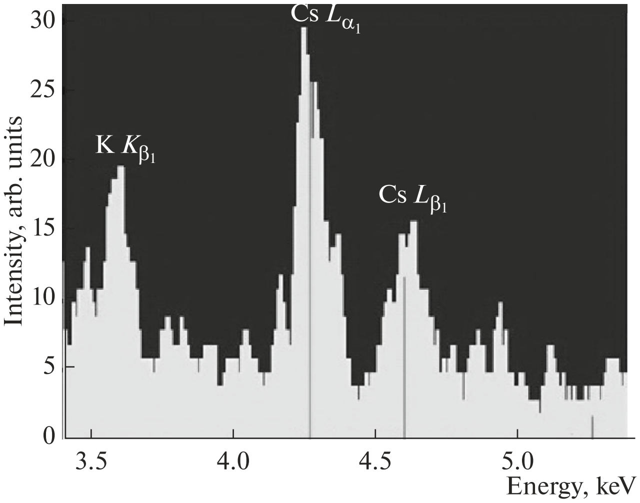

Fig. 6. X-ray spectrum of the constituent elements in the composition of the SPA sorbent (Fig. 5, zone 1).

ent solid–liquid ratios. The sorbents were in contact with the solutions for 72 h at 20°C. The pH of the starting (sorbent-free) solution was 7.31.

It follows from the present data that the SPA is most effective in removing Cs^+ ions from seawater under static conditions at Cs^+ concentrations above 6.0 mmol/L. Sorbents based on nanostructured SPAs typically have high sorption capacity, which exceeds that of Termoksid-35, a well-known sorbent, by almost a factor of 2. At lower Cs^+ concentrations in solution, Termoksid-35, which has a higher Cs^+ selectivity, is more effective. It is worth noting that the complex ionic composition of seawater reduces the maximum cesium ion sorption capacity of $KAlSi_3O_8 \cdot 1.5H_2O$ from 3.7 [8] to 0.45 mmol/g.

CONCLUSIONS

We have studied the Cs^+ sorption properties of a synthetic nanostructured X-ray amorphous $KAlSi_3O_8 \cdot 1.5H_2O$ potassium aluminosilicate with a specific surface area of 105.0 m^2/g in cesium carbonate solutions in seawater at Cs^+ concentrations from 0.05 to 23.07 mmol/L (solid : liquid = 1 : 40, 3 h, 20°C).

The results demonstrate that, at low Cs^+ concentrations in solution (below 6.0 mmol/L), the Termoksid-35 sorbent ensures better purification of the solution (up to 98.7%) than does the SPA sorbent (below 82.0%). As the Cs^+ concentration in solution is raised to above 6.0 mmol/L, the degree of solution purification by the SPA sorbent is higher than that by the Termoksid-35 sorbent.

The complex ionic composition of seawater has been shown to reduce the maximum cesium ion sorption capacity of $KAlSi_3O_8 \cdot 1.5H_2O$ from 3.7 to 0.45 mmol/g. The Langmuir constant K calculated for the SPA is

Table 2. Degrees of Cs^+ removal by the SPA and Termoksid-35 sorbents at different solid : liquid ratios

Sorbent	Solid : liquid	C_{eq}, mmol/L	pH after sorption	α, %
SPA	1 : 40	0.009	6.5	91.3
	1 : 400	0.07	8.5	32.0
	1 : 1000	0.0823	9.0	20.1
Termoksid-35	1 : 40	0.0006	7.5	99.4
	1 : 400	0.0014	7.5	98.6
	1 : 1000	0.008	8.5	92.2

0.089 L/mmol, and its calculated maximum sorption capacity $A_{\max}$ is 1.0 mmol/g. Termoksid-35 ensures higher degrees of Cs^+ removal at various solid : liquid ratios.

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