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Sorption of Cesium Radionuclides onto Semicrystalline Alkali Metal Silicotitanates

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Abstract—Sorption of microamounts of ^{137}Cs from solutions of various compositions onto semicrystalline alkali metal silicotitanates (TiSi) was studied. The pore structure analysis showed that the TiSi samples formed under the conditions of the experiments had bimodal nanoporosity characterized by the presence of ultramicropores (r ~0.4–1.0 nm) and transport mesopores (r ~2.5–30 nm). Potentiometric titration showed that TiSi contained acidic protonogenic groups with pK_a ~1.5–2.5, suggesting the possibility of ion-exchange sorption of alkali metal cations from acid solutions. A study of the ^{137}Cs distribution coefficient on TiSi as a function of the concentrations of sodium, potassium, and ammonium nitrates showed that the cations can be ranked in the following order with respect to the effect on the cesium sorption: $Na^+ < K^+ < NH_4^+$. As demonstrated by experiments on the ^{137}Cs removal from simulated bottom residue of nuclear power plants and on treatment of liquid radioactive waste from the Shelter Object of the Chernobyl NPP, semicrystalline alkali metal silicotitanates exhibit high sorption ability and selectivity with respect to ^{137}Cs and can be used for removing cesium from multicomponent salt solutions.

Keywords: sorption, silicotitanates, cesium radionuclides

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Inorganic sorbents and ion exchangers occupy today the leading position among materials used for selective recovery of the majority of radionuclides from multicomponent salt solutions [1–3]. Particular place has been occupied in the past 10–15 years by crystalline titanium and zirconium silicate materials (TiSi, ZrSi), which exhibit high selectivity in sorption of cesium and strontium radionuclides [4–6]. Large-scale tests of crystalline titanium silicates in removal of cesium radionuclides from liquid radioactive wastes accumulated in Savannah River (USA) have been reported [5].

Crystalline silicotitanates, as a rule, are prepared by hydrolysis and alkali treatment of mixtures of organic derivatives (alkoxides) or salts of titanium and silicon [4]:

$$Ti(OR)_4 + Si(OR)_4 + MOH + H_2O \rightarrow M_xTi_ySi_zO_m{\cdot}nH_2O, \quad (1)$$

$$TiCl_4 + Na_2SiO_3 + MOH + H_2O \rightarrow M_xTi_ySi_zO_m{\cdot}nH_2O, \quad (2)$$

where R is an organic substituent and M is an alkali metal ion.

The voluminous amorphous precipitates formed in the process are subsequently subjected to hard hydrothermal treatment (180–200°C, several days) at high pH values. The layered or framework sodium forms of crystalline silicotitanates, e.g., $Na_2Ti_2O_3(SiO_4)$, are converted to the H form by acid treatment and are used for selective recovery of radionuclides of cesium, strontium, and also uranium [6].

Despite the attractiveness of crystalline silicotitanates as a new class of materials selectively taking up radionuclides from multicomponent solutions, they find only limited use in the radiochemical practice be-

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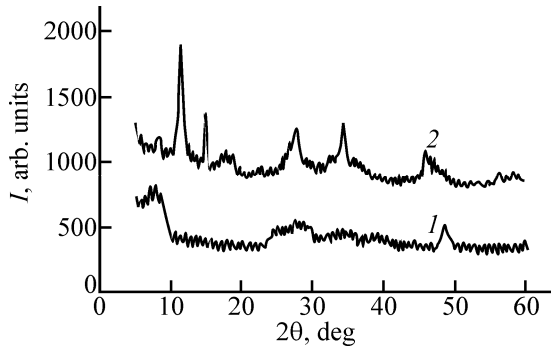

Fig. 1. Diffraction patterns of silicotitanate samples after hydrothermal treatment for 6 h at (*1*) 120 and (*2*) 150°C. Curve *2* is shifted along the ordinate by 500 units.

cause of difficult synthesis. The most power-consuming and expensive step is hydrothermal treatment at temperatures of 200°C and higher for 7–30 days [4, 6]. It has been reported recently that the poorly crystallized samples prepared under milder conditions also exhibit quite acceptable selectivity [7]. The procedure for preparing such materials was described previously in a Ukrainian patent [8].

This study deals with the sorption of microamounts of ^{137}Cs from model solutions of various compositions onto semicrystalline alkali metal silicotitanates synthesized at the Institute for Sorption and Problems of Endoecology (ISPE) of the National Academy of Sciences of Ukraine (Kyiv). The results of testing these sorbents for treatment of liquid radioactive waste from the Shelter Object of Chernobyl NPP are also reported.

EXPERIMENTAL

Samples of semicrystalline titanium silicate were synthesized from $TiOSO_4$ and Na_2SiO_3 solutions by the procedure described in [8]. Hydrothermal treatment of the working mixture was performed for 6 h at 150°C. After the treatment completion, the samples were washed with water and dried in air at 110°C. The resulting silicotitanate (TiSi) samples are white amorphous powders.

The sorption characteristics of the samples were determined with sorption of microamounts of ^{137}Cs as example. The experiments were performed in the batch mode by stirring a weighed portion of the sorbent with a solution aliquot for 48 h. After that, the liquid and solid phases were separated by filtration through a blue band paper filter. The specific activity of ^{137}Cs in the filtrate was determined, and the distribution coefficient (K_d) of ^{137}Cs was calculated by formula (3):

$$K_d = [(A_0 - A_e)/A_e](V_L/m_S), \quad (3)$$

where A_0 and A_e are the initial and equilibrium specific activities of ^{137}Cs, respectively, Bq L^{-1}; V_L is the liquid phase volume, cm^3; and m_S is the sorbent weight, g.

The specific activity of ^{137}Cs in solutions was determined by the direct radiometric method using an NRG-603 two-channel γ-ray analyzer (Tesla, Czechia).

The kinetics of the ^{137}Cs sorption onto TiSi was studied by the following procedure: A 600 cm^3 temperature-controlled beaker was charged with 500 cm^3 of a solution with pH 6.0, containing 0.1 M $NaNO_3$ and ~10^5 Bq L^{-1} ^{137}Cs. After that, a weighed portion (0.500 g) of the air-dry sorbent with the particle size of 0.05–0.10 mm was added with vigorous stirring. Solution samples (3 cm^3) were taken at definite time intervals. The samples were filtered through a blue band paper filter, and the specific activity of ^{137}Cs in the filtrate was determined.

X-ray diffraction analysis of the samples was performed with a DRON-4-07 device (CuK_α radiation). The pore structure was studied by low-temperature adsorption–desorption of nitrogen with a Quantachrom Nova 2200 device. The specific surface area of the samples was calculated by the Brunauer–Emmett–Teller (BET) equation. The curves of the pore distribution with respect to effective radii were calculated from the desorption branch of the nitrogen adsorption–desorption isotherms using the Barrett–Joyner–Halenda (BJH) method and the density functional theory (DFT). The micropore volume was evaluated using the Dubinin–Radushkevich theory ($V_{DR,micro}$) and DFT. The boundary sorption pore volume (V_s) was determined at the relative pressure of nitrogen (P/P_0) close to 1.

Potentiometric titration of the samples was performed with an I-500 ion meter by the procedure described in [9].

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of silicotitanate samples prepared by hydrothermal treatment (HTT) for 6 h at 120 and 150°C. As can be seen, only X-ray amorphous material is formed at 120°C, whereas at the treatment temperature of 150°C well-

defined reflections of the silicotitanate crystal structure, corresponding to the general formula $X_2Ti_2O_3 \cdot (SiO_4) \cdot 2H_2O$ [10], where X = Na, H, appear in the X-ray diffraction pattern.

All the subsequent experiments were performed using silicotitanate samples (TiSi) after HTT for 6 h at 150°C.

A study of the pore structure of TiSi samples shows that the samples formed under these conditions are microporous and are characterized by the type I adsorption isotherm (Fig. 2). The curve steeply ascends at low relative pressures, at which ultra- and micropores are filled. The shape of the hysteresis loop at P/P_0 ~1 is indicative of capillary condensation occurring in this portion of the isotherm, i.e., of filling of large-diameter pores. Hence, this sample is characterized by bimodal nanoporosity, i.e., by the presence of ultramicropores of radius ~0.4–1.0 nm and transport mesopores with a broad radius distribution in the range ~2.5–30 nm. This fact means that the ion-exchange sorption of cations on this TiSi sample will not involve noticeable transport (kinetic) limitations [11].

To evaluate the acid–base properties of TiSi, we performed potentiometric titration of the hydrogen forms of the samples with 0.1 M HCl and MOH solutions against the background of 0.1 M MCl, where M = Li, Na, K, Cs, Rb. The titration curves obtained are shown in Fig. 3.

As can be seen, the TiSi sample contains acidic protonogenic groups with pK ~1.5–2.5, suggesting the possibility of the ion-exchange sorption of alkali metal ions from acid solutions. The TiSi sample exhibits the highest selectivity to the K^+, Rb^+, and Cs^+ ions. We believe that the increased affinity of TiSi for these ions is due to the presence of ultramicropores in the sorbent matrix with the diameter comparable with the size of the heavy alkali meal cations. We noted similar effect previously [11] for ion exchangers based on zirconium phosphate. We concluded that the strength of binding of large single-charge cations in ultramicropores of size comparable with the cation size is determined by the mechanisms typical of complexation of these cations with crown ethers [12].

To determine the sorption-selective characteristics of silicotitanates, we performed experiments on sorption of microamounts of ^{137}Cs from model solutions of various compositions.

The ^{137}Cs sorption from 0.1 and 1.0 M $NaNO_3$ solutions with pH 6.0 was studied in batch experiments at S : L = 1 : 400 and contact time of 48 h. To obtain comparative characteristics of TiSi samples, the experiments on the ^{137}Cs sorption under similar conditions were also performed with sorbents traditionally used in radiochemical practice as selective sorbents for radiocesium: FNS-10, granulated ferrocyanide sorbent based on nickel potassium ferrocyanide applied by the sorption method onto silica gel, TU (Technical Specification) 2641-003-51255813–2007; Termoxid-35, spherically granulated sorbent based on nickel potassium ferrocyanide on zirconium hydroxide as inorganic support, TU 6200-305-12342266–98; natural clinoptilolite of the Shivertuinskoe deposit (Chita oblast). The results are given in Table 1.

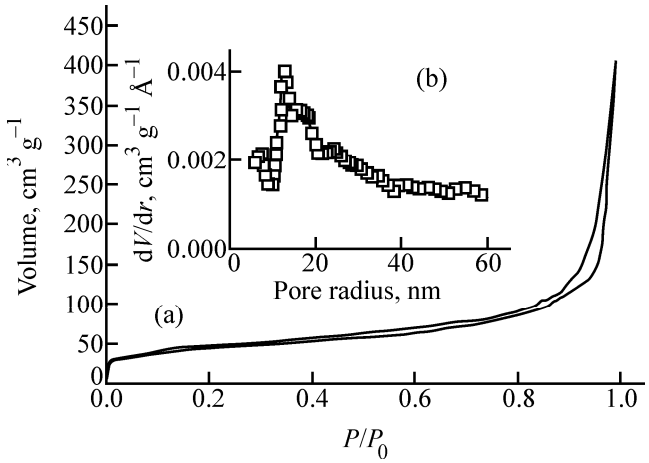

Fig. 2. (a) Isotherms of nitrogen adsorption–desorption on silicotitanate prepared by hydrothermal treatment at 150°C for 6 h; (b) distribution of the pore volume with respect to effective radii, calculated by DFT.

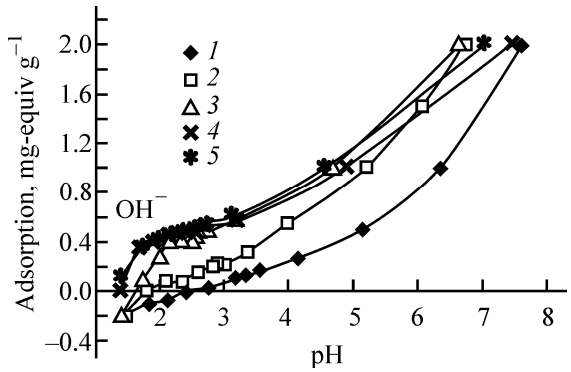

Fig. 3. Curves of pH-metric titration of the hydrogen form of TiSi with 0.1 M HCl and MOH solutions. Supporting electrolyte 0.1 M MCl. M: (*1*) Li, (*2*) Na, (*3*) K, (*4*) Cs, and (*5*) Rb.

Table 1. Distribution coefficients (K_d) of ^{137}Cs from $NaNO_3$ solutions on various sorbents

Sorbent	K_d, cm^3 g^{-1}, at indicated $NaNO_3$ concentration, M	
	0.1	1.0
TiSi	$(1.7 \pm 0.3) \times 10^5$	$(6.2 \pm 0.6) \times 10^4$
FNS-10	$(8.4 \pm 0.6) \times 10^4$	$(7.3 \pm 0.7) \times 10^4$
Termoxid-35	$(8.0 \pm 0.7) \times 10^4$	$(3.5 \pm 0.3) \times 10^4$
Clinoptilolite	$(2.5 \pm 0.2) \times 10^3$	620 ± 30

Table 2. Parameters of the approximating dependence $\log K_d = A \log C + B$ (A and B are constants, R is the correlation coefficient)

System	A	B	R
Cs–Na	–0.84	5.256	0.970
Cs–K	–1.15	3.007	0.997
Cs–NH_4	–1.18	1.467	0.995

The results presented in Table 1 show that semicrystalline silicotitanate (TiSi sample) in its sorption-selective characteristics with respect to ^{137}Cs is comparable with ferrocyanide sorbents exhibiting high selectivity to cesium ions [13].

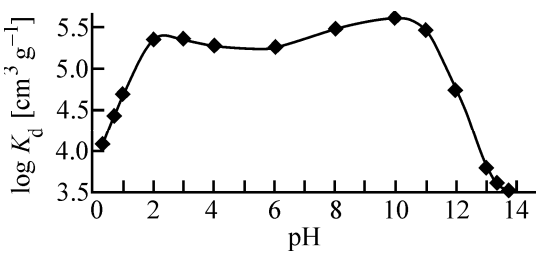

Fig. 4. pH dependence of the distribution coefficient (K_d) of ^{137}Cs on silicotitanate from 1 M $NaNO_3$ solution.

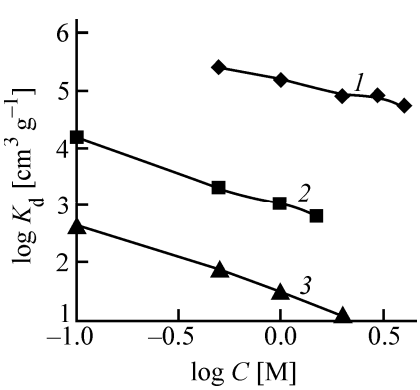

Fig. 5. Distribution coefficient (K_d) of ^{137}Cs on sililcotitanate as a function of the concentration of (*1*) sodium, (*2*) potassium, and (*3*) ammonium nitrates.

Experiments on studying the pH dependence of K_d of ^{137}Cs on silicotitanate were performed with model solutions of $NaNO_3 + HNO_3$ and $NaNO_3 + NaOH$ mixtures with constant ionic strength (1 M) at S : L = 1 : 400 and contact time of 48 h. The results are presented in Fig. 4. They show that the cesium sorption onto silicotitanate is the most efficient at pH in the range 2–10.

Experiments on studying how K_d of ^{137}Cs on TiSi depends on the concentration of sodium, potassium, and ammonium nitrates were performed from solutions with pH 6.0 at the ratio S : L = 1 : 400 and contact time of 48 h. The results are shown in Fig. 5.

As seen from Fig. 5, the log–log plots of K_d of ^{137}Cs vs. concentration of alkali metal nitrates are straight lines. The parameters of the approximating equation $\log K_d = A \log C + B$, where A and B are constants, were calculated by the least-squares treatment of the dependences obtained. The results are given in Table 2.

The slope (parameter A) for all the systems is close to unity, suggesting the ion-exchange mechanism of the cesium sorption. From the parameter B, we calculated the corresponding exchange constants (K_{ex}) by Eq. (4) [14]:

$$\log K_{ex} = B - \log Q, \quad (4)$$

where Q is the total capacity of the sorbent, mmol g^{-1}.

At Q = 1.5 mmol g^{-1}, K_{ex} for the ion combinations Cs^+–Na^+, Cs^+–K^+, and Cs^+–NH_4^+ is 1.2×10^5, 677, and 19.6, respectively. These results indicate that the cations can be ranked in the following order with respect to the effect that they exert on the cesium sorption onto silicotitanates: $Na^+ < K^+ < NH_4^+$.

In the kinetic study of the ^{137}Cs sorption onto TiSi, we calculated from the analysis results the degree of attainment of the equilibrium (F) at time τ by Eq. (5):

$$F(\tau) = A_\tau / A_\infty, \quad (5)$$

where A_τ and A_∞ are the specific activities of the given radionuclide in the sorbent at time τ and at complete saturation, respectively, Bq g^{-1}.

The quantity A_∞ was determined after continuous stirring of the mixture for 3 days. The dependence of F on τ is shown Fig. 6.

Our results show that the sorption equilibrium is

attained within 2–3 min after introducing the sorbent into the solution.

To evaluate the kinetic characteristics of the sorbent, we calculated the internal diffusion coefficient ($\bar{D}$) of the radionuclide into the sorbent granule and the half-exchange time ($\tau_{0.5}$) by formulas (6) and (7), respectively:

$$F = (6/r_0)(\bar{D}\tau/\pi)^{1/2} \text{ at } F < 0.4, \quad (6)$$

$$\tau_{0.5} = 0.03r_0^2/\bar{D}, \quad (7)$$

where r_0 is the mean granule radius, m, and τ is the sorption time, s.

The calculation was performed by the least-squares treatment of the initial portion of the kinetic curve in the F–$\tau^{1/2}$ coordinates. In the calculations, the mean granule radius was taken equal to 2.5×10^{-5} m.

The calculated values of $\bar{D}$ and $\tau_{0.5}$ are ~2×10^{-12} m^2 s^{-1} and ~10 s, respectively.

To evaluate the possibility of using the synthesized silicotitanates for applied purposes, we performed experiments on the ^{137}Cs sorption onto TiSi from a model solution simulating the bottom residue from an NPP with an RBMK reactor (high-power channel reactor) of the following composition, g dm^{-3}: $NaNO_3$ 300, KNO_3 42, NaOH 4.0; pH 13. Prior to the experiment, the solution was spiked with ^{137}Cs to the activity concentration of approximately 10^5 Bq dm^{-3}. The values of K_d of ^{137}Cs from the bottom residue on TiSi and Termoxid-35 sorbents and on phenol–resorcinol resin (PRS) synthesized at ZAO Aksion-RDM (Perm, Russia) are given below.

Sorbent	TiSi	PRS	Termoxid-35
K_d of ^{137}Cs, cm^3 g^{-1}	203 ± 5	1200 ± 30	(4.6 ± 0.5) × 10^4

Our results show that, among the sorbents studied, Termoxid-35 shows the highest performance in cesium sorption from the model solution simulating the NPP bottom residue. Relatively low K_d of ^{137}Cs on the silicotitanate are associated with the negative effect of the present ions, especially potassium, and with the high pH value.

Silicotitanates were also tested as materials for removing ^{137}Cs from real liquid radioactive waste (LRW) of the 4th unit of the Shelter Object of the Chernobyl NPP. This kind of LRW is a complex salt-containing substance containing a colloidal solution of

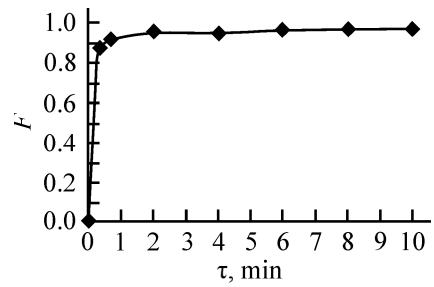

Fig. 6. Degree of attainment of the equilibrium (F) in sorption of ^{137}Cs onto silicotitanate as a function of time τ.

siloxane–acrylate emulsions used in dust suppression measures. The LRW of the following salt composition, mg-equiv dm^{-3}, was used in the tests: K^+ + Na^+ 12.3, Ca^{2+} 0.91, Mg^{2+} 1.03, PO_4^{3-} 0.03, Cl^- 1.07, SO_4^{2-} 0.27, CO_3^{2-} 4.67, HCO_3^- 8.2; total mineralization 1.23 g dm^{-3}; pH 8.7. Radionuclide composition: ^{137}Cs 5.8 × 10^7, ^{90}Sr 1.5 × 10^6, ∑Pu 1.8 × 10^3, ^{241}Am 9.0 × 10^3 Bq dm^{-3}; ∑U = 7.8 mg dm^{-3}. Because a part of the radionuclides are contained in the colloidal constituent of LRW, preventing the sorption, we performed coagulation of the colloidal solution prior to sorption of the radionuclides onto TiSi. Coagulation was performed by adding sodium phosphates to pH 4–7 to obtain a voluminous, well compactable precipitate. After the precipitate separation, the silicotitanate was added to the filtrate for the ^{137}Cs sorption. In addition, a sorbent of titanium phosphate type can be formed in this system. Such sorbents exhibit high sorption capacity, including that for ^{137}Cs. The results obtained (activity concentration of ^{137}Cs in LRW, Bq dm^{-3}) are given below.

Initial LRW	After coagulation	After sorption
5.8 × 10^7	1.4 × 10^5	<150

Thus, semicrystalline alkali metal silicotitanates exhibit high sorption-selective characteristics with respect to ^{137}Cs and can be used for removing ^{137}Cs from multicomponent salt solutions.

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