

SYNTHESIS AND CHARACTERIZATION OF INORGANIC SORBENTS AND THEIR APPLICATION TO SORPTION OF RADIONUCLIDES

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Titanium silicates and iron oxides were synthesized. Their structural characteristics and sorption ability towards a number of radionuclides were studied using X-ray, Mössbauer, gamma, and alpha spectroscopy as well as the laboratory batch method. X-ray studies of synthesized titanium silicates revealed their amorphous structure. Mössbauer spectrometry showed typical spectra of nanocrystalline goethite, hematite, magnetite, and the mixture of hematite and magnetite. Approximate size of nanocrystalline minerals was determined and it was in the range from about 14 to 30 nm. Distribution coefficient (K_d) values obtained using the laboratory batch method ranged from 390 to 163000 ml/g for Sr, from 6 to 40470 ml/g for Cs, from 220 to 257000 ml/g for Pu, and from 50 to 16260 ml/g for Am.

Keywords: titanium silicates, iron oxides, sorption Cs, Sr, Pu, Am, distribution coefficient

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1. Introduction

Nowadays numerous studies have been performed in order to identify new waste forms and disposal strategies because of large quantity of high activity radioactive waste which requires treatment prior to final disposal or storage. The application of inorganic sorbents such as ferrites and crystalline silicotitanates is one of the alternative technologies which can reduce the costs associated with waste disposal and minimize the contamination risk of the environment during processing and disposal of the radioactive waste. This issue is an especially hot topic nowadays in Lithuania because of the decommissioning of the Ignalina Nuclear Power Plant. The necessity of a highly efficient treatment stimulated studies in this field. The application of selective inorganic materials for the removal of harmful radionuclides from the bulk waste solution can be one of the possible solutions, because they are distinguished for high efficiency, ionizing radiation resistance, their thermal stability, and compatibility with the final waste forms.

The application of such a technique will result in considerable reductions in the volumes of waste that require solidification prior to final disposal, as well

as in lower radioactive discharges from storage containers into the environment. New types of sorbents such as crystalline silicotitanates, tunnel type titanium silicates, transition metal hexacyanoferrates, etc., having high selectivity for various radionuclides, have recently been developed [1]. Crystalline silicotitanates have high selectivity for Cs^+ in solutions with high Na^+ concentrations, they are selective for Sr^{2+} and have low affinity for actinides. Substitution of Nb for Ti in the framework modified the selectivity towards Cs^+ and Sr^{2+} . The Nb substitution increases sorption capacity towards Cs^+ ions and decreases Sr^{2+} selectivity. This effect is attributed to higher coordination number, an increase in the unit cell volume and change in water/ Na^+ population [2]. Among challenging materials are sodium titanate ($\text{NaTi}_2\text{O}_5\text{H}$), titanium silicates with pharmacosiderite structure, sodium nonatitanate ($\text{Na}_4\text{Ti}_9\text{O}_{20}\cdot x\text{H}_2\text{O}$), and heteropolymetalates ($\text{M}_{12}[\text{Ti}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}]\cdot 16\text{H}_2\text{O}$, $\text{M} = \text{Na}, \text{K}$).

Titanium compounds, e. g. titanium silicates and titanium dioxide, which is also known to be an excellent sorbent for a number of radionuclides and possesses catalytic activity, are excellent oxidizing agents [3]. This ability can be applied to the oxidative destruction in waste management. For instance, the combined

treatment of spent decontamination solutions in the presence of titanium compounds could provide effective destruction of the complexing agents with release of radionuclides in a form suitable for sorption by the catalyst/sorbent [4].

Ferrites and a variety of iron-containing minerals such as akaganeite, ferrosilite, ferrihydrite, goethite, hematite, lepidocrocite, maghemite, and magnetite have been widely used as inorganic ion exchangers for the treatment of liquid wastes containing radioactive and hazardous metals [5, 6].

Ferrites possess the property of spontaneous magnetization, are crystalline materials soluble only in strong acid, and can be used for efficient separation by magnetic methods [7, 8]. For instance, natural magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), due to its ferromagnetic property, can be used not only as an adsorbent for removing toxic metals from solution, but also in the high gradient magnetic separation process for attracting and retaining paramagnetic nanoparticles, thus removing them from solution [4].

The aim of this study was a comparative assessment of possible application of various synthetic and natural sorptive materials in liquid waste treatment technologies to remove long-lived radionuclides Cs, Sr, Pu, and Am.

2. Materials and methods

2.1. Synthesis of titanium silicates $\text{Na}_2\text{Ti}_2\text{SiO}_7\cdot 2\text{H}_2\text{O}$

The method of titanium silicates preparation (Ti:Si = 1:1) is based on precipitation of precursor from the $\text{TiO}_2\text{-SiO}_2\text{-Me}_2\text{O}$ alkaline solution followed by hydrothermal treatment (HT). The synthesis was performed under considerably soft conditions (under air pressure from 3–5 to 0.3–0.4 mPa and at 130–200 °C for 12–24 hours) in comparison with the well-known method by Poojary et al. [2]. Changes in the reaction conditions resulted in the product yield increase from 30 to 250–300 g/l of initial reagents. Titanium silicates were synthesized using cheap and available Ukrainian raw materials – alkali silicate (Na_2SiO_3), potassium/sodium methylsilicates $\text{CH}_3\text{Si}(\text{OH})_2\text{ONa/K}$, titanium tetrachloride (TiCl_4), and titanyl sulphate (TiOSO_4). Hydrogen peroxide was used as a complexing agent [9, 10].

2.2. Synthesis of titanium silicates $\text{Na}_2\text{TiSiO}_5\cdot n\text{H}_2\text{O}$

Synthesis of titanium silicates (Ti:Si = 1:1) was performed using the sol–gel method developed at the In-

stitute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine. This method is based on the sol–gel technologies and local technical titanyl sulfate, and organic complexions as stock-materials were used for the synthesis.

The initial reaction mixture contained solutions of technical 3.2 mol/l TiOSO_4 , 3.6 mol/l Na_2SiO_3 , and 4.5–5.0 mol/l NaOH or KOH (for adjustment of pH). Gel was prepared by fast and intensive mixing of stock solutions. After gel aging during one day, the hydrothermal treatment was performed in autoclaves under different conditions. Hydrothermally modified samples were thoroughly washed with water and then with ethanol for removing Na_2SO_4 and K_2SO_4 remaining in the system due to the specific sorption conditions. During the washing process, pH was controlled constantly. After that samples were dried at 120 °C for 4 hours.

2.3. Synthesis of iron oxides

Iron oxides synthesis was performed using methods described in publications with some modifications [11–13]. Magnetite (Fe_3O_4) was prepared by adding 1 M ammonia solution (NH_4OH) to 2 M FeCl_2 and 1 M FeCl_3 mixture (1:4). The temperature was kept at 90 °C. The synthesis was conducted under the N_2 atmosphere. Particles were separated by magnet and dried under the N_2 atmosphere.

Magnetite/hematite ($\text{Fe}_3\text{O}_4\text{-}\alpha\text{-Fe}_2\text{O}_3$) composite was prepared by adding 2 M FeCl_2 and FeCl_3 (1:2) to 1 M ammonia solution (NH_4OH), with vigorous stirring for 40 min under the N_2 atmosphere and at 50 °C temperature. Particles were separated by centrifugation and dried for 90 min under vacuum.

Goethite ($\alpha\text{-FeOOH}$) mineral was prepared by adding 5 M NaOH solution to 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution until pH was 12. The solution was stirred during 2 days at 60 °C temperature. The precipitate was washed and dialyzed in deionised water until the conductivity was stable at $10\ \mu\text{Scm}^{-1}$. Particles were separated and dried frozen.

Synthesis of hematite ($\alpha\text{-Fe}_2\text{O}_3$) was conducted under the N_2 atmosphere by mixing 0.5 M FeCl_2 solution with 2.1 M NaHCO_3 solution, well stirring until precipitate changed its colour to dark green. Then oxygen was introduced and the precipitate was washed until washings showed the presence of Cl ions. Suspension of hematite particles was separated from solution

Table 1. Structural and sorptive characteristics of titanium silicate samples synthesized using H₂O₂.

Ti:Si = 2:1		HT		pH of washings	V _s , cm ³ /g		S _{spec.} , m ² /g by argon
Sorbent	Form	t, °C	τ, hours		H ₂ O	C ₆ H ₆	
17	SO ₄	150	24	9.00	0.18	0.34	228
20	Cl	150	24	9.26	0.10	0.13	52
30	SO ₄	150	24	7.39	0.38	0.39	177
32	SO ₄	200	24	7.80	0.22	0.18	104
55	Cl	150	24	9.60	0.22	0.21	64
57+58	Cl	150*	24	8.20*	0.22*	0.22*	62
59	Cl	150	24	8.13	0.37	0.37	159

* average values, V_s is sorption volume of pores by water (H₂O), by benzene (C₆H₆).

Table 2. Parameters of porous structure of titanium silicate synthesized using the sol–gel method.

Ti:Si = 1:1*		HT		Washing		pH	Calcination		V _s , cm ³ /g		S _{spec.} , m ² /g by argon
Sorbent	t, °C	τ, hours	H ₂ O	Ethanol	t, °C		τ, hours	H ₂ O	C ₆ H ₆		
40**	200	6	+	–	11.5	–	–	0.21	0.16	237	
82–1	150	6	+	+	9.2	–	–	0.47	0.68	726	
82'–1	150	6	+	–	9.7	–	–	0.18	1.10	64	
82–3	150	6	+	+	9.9	400	10	–	–	145	
84–3	150	6	+	+	9.9	400	2	0.19	0.46	191	
84–4	150	6	+	+	9.9	400	10	–	–	189	
86–1	150	6	+	+	10.4	–	–	0.23	0.71	251	
86–4	150	6	+	+	10.4	400	10	–	–	189	

* in all feedstock solutions anion was present, ** in Na form. All other samples are of Na, K form.

by centrifugation, dried for several days at 90 °C and then aged for 5 hours at 500 °C.

2.4. Physical and chemical analysis of prepared samples

The BET surface area of TiSi sorbents was measured by the chromatographic method of argon thermal desorption [14].

The pore volume V_s of titanium-containing materials was determined using a standard technique – the desiccator method (sorption of benzene and water vapours) [14].

The X-ray diffraction studies of the prepared TiSi sorbents were conducted with an automated diffractometer (DRON–4–07) using Ni-filtered Cu K_α radiation.

Synthesized iron oxides were characterized using Mössbauer spectroscopy. The samples were prepared using ≈50 mg of synthesized material and mixing it with a small amount of MgO powder. Then the material was placed into a special holder and used for measurements. The thickness of samples was ≈17 mg/cm² of studied material.

The Mössbauer spectra of the samples were recorded using the Mössbauer spectrometer operating in transmission geometry in a constant acceleration mode. The

source of ⁵⁷Co in Rh matrix was used. For the description of Mössbauer spectra, separate subspectra (doublets and sextets) and hyperfine field *B* distributions were applied.

Synthesized sorbents, both titanium silicates and iron oxides, as well as natural clay minerals (6 and 7) with 14% of montmorillonite were used in sorption experiments. The laboratory batch method was applied to determine the distribution coefficient (*K*_d) values of Cs, Sr, Pu, and Am radionuclides.

¹³⁷Cs activities were measured with an intrinsic germanium detector (resolution 1.9 keV/ 1.33 MeV and the relative efficiency of 42%). Pu (IV) was used in the sorption experiment. Details of experiments are described in the previous publications [15, 16]. Solids were separated from liquid by centrifugation for 20 minutes at 10000 g. Plutonium and americium were determined after radiochemical separation using the UTEVA and TRU resins (Eichrom Industries) and precipitation with NdF₃, then activities of Pu and Am were measured by alpha spectrometry. ²⁴²Pu and ²⁴³Am were used as tracers in the separation procedure. Sr was measured using atomic absorption spectrometry. *K*_d values for sorption of Cs, Sr, Am, and Pu were determined from three replicates.

3. Results and discussions

3.1. Identification and characterization of prepared samples

Structural and sorptive characteristics of titanium silicates having the chemical formula $\text{Na}_2\text{Ti}_2\text{SiO}_7 \cdot 2\text{H}_2\text{O}$ are shown in Table 1. It has been found that synthesis of titanium silicates using TiOSO_4 (sorbents TiSi-17, TiSi-30) in comparison with titanium silicates, the synthesis of which was based on TiCl_4 as feedstock (sorbents TiSi-20, TiSi-32, TiSi-55, TiSi-(57+58), TiSi-59), leads to the change in characteristics of the porous structure (sorptive volumes V_s measured by benzene and water are increased). It should be noted that an introduction of methyl group (synthesis was carried out using potassium methylsilicate) to the titanium silicate structure (e. g. TiSi-17 sorbent prepared by a traditional technique using the hydrogen peroxide as a complexing agent) results in the formation of mesoporous products which are important for the sorption of big size ions.

Characteristics of porous structure of titanium silicates synthesized by the sol-gel method are presented in Table 2. An increase in the sorptive volume measured by benzene for the mixed Na, K samples indicates their mesoporous nature. An additional water-ethanol treatment of mixed Na, K titanium-containing xerogels by washing samples till pH of the solution reached 9.2–10.4 resulted in the significant enhancement of the surface area ($S_{\text{spec.}}$) up to 251–726 m^2/g (e. g. sorbent TiSi-82-1) in comparison with sample TiSi-40 (surface area of 237 m^2/g). The calcination of hydrothermally modified sorbents TiSi-82-3, TiSi-84-3, TiSi-84-4, TiSi-86-4 revealed their high structural stability. However, it has been found that the stability tests and heating of samples up to 400 °C lead to some decrease in the surface area due to reconfiguration processes. Thus, changes in synthesis conditions, the chemical and hydrothermal treatment of titanium silicates can have an essential effect on their structural and sorption characteristics. This is important when considering the possible practical application of the titanium silicates for the extraction of toxicants of different origin.

X-ray investigations of titanium silicates synthesized by different techniques (precipitation and sol-gel methods) evidenced their amorphous structure.

The paramagnetic part of the Mössbauer spectrum of the goethite sample (Fig. 1(a)) is described using doublet (Table 3). For the description of antiferromagnetic part of the spectrum the distribution of hyperfine field

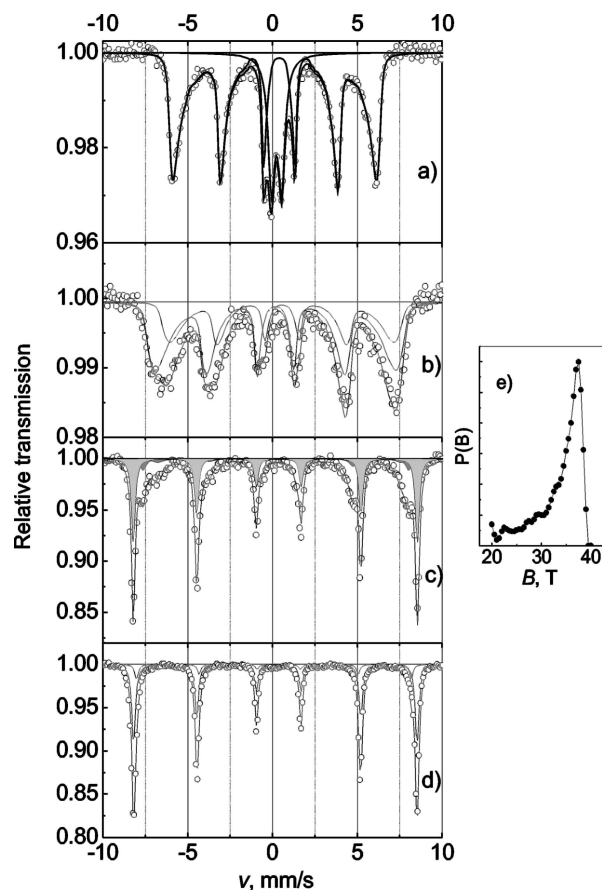


Fig. 1. Mössbauer spectra of (a) goethite ($\alpha\text{-FeOOH}$), (b) nanocrystalline magnetite (Fe_3O_4), (c) composite of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4), and (d) hematite ($\alpha\text{-Fe}_2\text{O}_3$) samples. (e) Antiferromagnetic part of goethite ($\alpha\text{-FeOOH}$) is described using hyperfine field distribution.

$P(B)$ is used. In this case, the spectrum is expressed by the sum of sextets:

$$f(v) = \sum_i P(B_i) f_s(B_i, v), \quad (1)$$

where the hyperfine field B of sextets i and $i + 1$ differs by $\Delta B = 0.5$ T.

The broadening of Mössbauer lines (decrease in hyperfine fields compared with the static hyperfine field $B \approx 38$ T specific to goethite) indicates the influence of the superparamagnetic relaxation of the magnetic moment due to small sizes of crystallites. The paramagnetic part (doublet) is a consequence of the superparamagnetism due to even smaller particles. The Mössbauer spectrum of the sample is typical of nanocrystalline goethite [17]. The determination of the sizes of particles of goethite on the basis of Mössbauer data may be only very approximate, especially because of the lack of knowledge of magnetic anisotropy values for this material. In this case, the average size of

Table 3. Description of Mössbauer spectra presented in Fig. 1.

Sample	Constituent	S , %	B , T	δ , mm/s	Δ , mm/s	D , nm
(a)	Antiferromagnetic goethite	79	20–38	0.37	-0.27	≈ 20 –30
	Paramagnetic goethite	21	0	0.34	0.59	
(b)	Magnetite subspectrum A	65	0–49.3	0.29	–	≈ 14
	Magnetite subspectrum B	35	0–46.0	0.67	–	
(c)	Hematite	58	51.9	0.38	-0.2	≥ 30
	Magnetite subspectrum A	22	48.5	0.31	–	
	Magnetite subspectrum B	20	44.7	0.54	–	
(d)	Hematite 1 subspectrum	82	51.8	0.38	-0.2	
	Hematite 2 subspectrum	8	50.8	0.38	-0.2	

S is relative area of subspectrum attributed to the constituent of the sample, B is hyperfine field, δ is isomer shift (relative to α -Fe), Δ is quadrupole splitting, D is size of particles (crystallites). For hyperfine field distribution, the range of B is indicated.

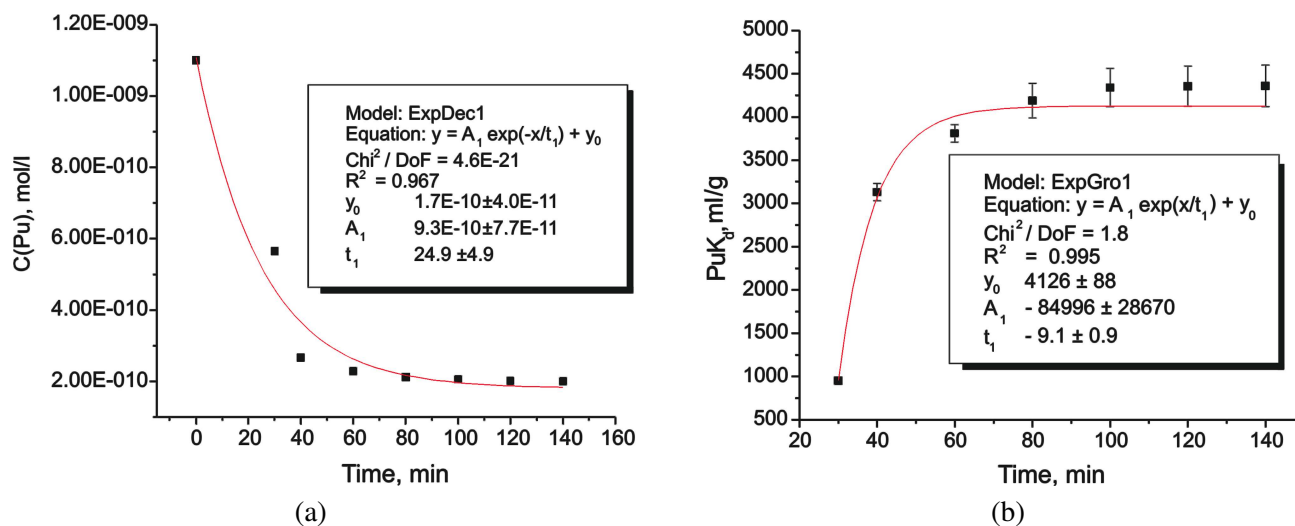
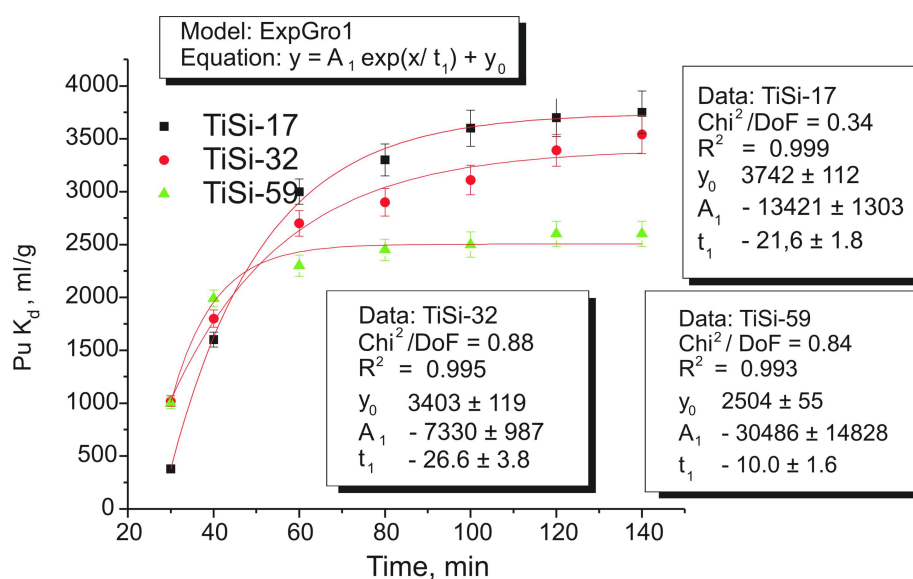
Fig. 2. Pu concentration in contact solution (0.1 M NaNO_3) and Pu K_d as a function of time (sorbent TiSi 55).Fig. 3. Pu K_d s as functions of time.

Table 4. Sr, Cs, Pu, and Am K_d s for titanium silicates and minerals used in this study.

Sorbent, No.	*Sr K_d , ml/g	**Cs K_d , ml/g	**Pu K_d , ml/g	**Am K_d , ml/g
TiSi 17	19500±7200	15860±550	4590±110	
TiSi 20	12000±4300	24180±700		
TiSi 30	197000±7500	12570±340	2870±60	
TiSi 32	220000±7300	8750±230	1240±30	270±20
TiSi 40(s)	2630±150	310±10	1500±40	
TiSi 55	163000±7500	21160±520	4030±100	
TiSi 57+58	17100±9800	7270±140	2730±70	905±50
TiSi 59	163000±7200	40470±1100	2590±60	
TiSi 82-1	5580±230	1460±30	570±30	2900±100
TiSi 82'-1	1910±110	470±15	1550±70	
TiSi 82-3	1800±100	200±10	2530±100	3300±120
TiSi 84-3	3020±130	640±25	3570±120	5670±300
TiSi 84-4	1960±90	460±20	400±20	4050 ± 200
TiSi 86-1	2550±120	1180±60	290±10	
TiSi 86-4	1830±90	550±20	2430±100	1480±60
PSiZr	920±50	144±20	220±10	110±10
Zr ₃ (PO ₄) ₄	1210±70	381±15	1520±60	1030±40
ZrO ₂	1150±50	6±0.5	2640±110	
TiP 1.0	3300±130	1790±70	2080±80	1790±70
TiP 1.5	2040±100	1589±50	2350±55	470±20
TiP 2.0	3100±170	2100±60	1960±60	50±5
MgFe(OH) _x ·nH ₂ O	12250±700	725±20	4025±120	7940±300
Clay 6	290±10	7860±100	3570±100	11160±560
Clay 7	390±25	7528±130	2470±60	6070±300
Magnetite	1150±50	30±1	1450±50	11670±520

* Sr K_d values for natural groundwater; ** Cs, Pu, and Am K_d values for 0.1 M NaNO₃ solution.

particles D (Table 3) is evaluated by analogy with the results of Ref. [17].

Magnetite has two sublattices which are reflected in the Mössbauer spectrum and are described by separate subspectra. The subspectra of bulk magnetite are fitted to sextets with different static hyperfine fields B and isomer shifts δ . The Mössbauer spectrum of nanocrystalline magnetite is also described by two separate subspectra (Fig. 1(b)), but these are broadened, and therefore are expressed by hyperfine field distributions. The spectra lines become broadened because of small sizes of particles in nanocrystalline magnetite when the superparamagnetic relaxation of the magnetic moment occurs. The Mössbauer spectrum of nanocrystalline magnetite is fitted using two distributions of the hyperfine field and the relation between the particle size D and the hyperfine field B . The size D is considered to be distributed according to the lognormal law. A detailed description of the used method is presented in Ref. [18].

The Mössbauer spectrum of the third sample (Fig. 1(c)) is fitted using three sextets. The most intensive one which covers $\approx 58\%$ of the spectrum area is caused by hematite. The second and third subspectra are characteristic of magnetite. Slightly smaller hyperfine fields for these subspectra compared with the static

ones indicate the presence of small particles in the sample.

The Mössbauer spectrum of the fourth sample (Fig. 1(d)) is fitted using two sextets with parameters which are typical of hematite. The second sextet of a much smaller area compared with the first one is needed to improve the fitting quality. It has a slightly smaller value of the hyperfine field than that of the first one and also indicates the effect of superparamagnetism of small particles.

3.2. Sorption of radionuclides

Some studies were performed in order to determine the sorption ability of synthesized inorganic sorbents towards Sr, Cs, Pu, and Am (Table 4).

Sorbent TiSi-17 showed the highest Pu K_d value for 1 M NaNO₃ solution which is usually used to model fuel pond water with pH of about 7. The obtained highest K_d value can be explained by the methyl group introduction into the Ti silicate structure. As was mentioned above, sorbent TiSi-17 was synthesized using the potassium methyl silicon and the hydrogen peroxide as complexon. Thus, the formation of sorbents with a mesoporous structure suitable for sorption of large size ions was expected. Preliminary data have

Table 5. Pu and Am K_d s for synthetic iron oxides and natural groundwater.

Sorbent	Pu K_d , ml/g	Am K_d , ml/g
Magnetite	9000±400	6760±300
Magnetite/hematite	61500±3000	4750±200
Goethite	15670±600	14530±700
Hematite	257620±10000	16260±800

suggested that Am K_d values are quite close to the Pu ones. Studies of Am sorption are in progress.

Data on Pu sorption kinetics have indicated that rather short time is required to reach equilibrium (Figs. 2 and 3). Equilibrium was reached after about 2 hours of sorption. Data were fitted by the first order kinetic equation to obtain Pu K_d equilibrium which ranged from 2500 to 4130 ml/g for studied sorbents TiSi-17, TiSi-32, TiSi-55, and TiSi-59.

Preliminary data on Pu sorption to iron minerals are presented in Table 5. K_d values ranged from 4750 to 16260 ml/g and 9000 to 257620 ml/g for Am and Pu, respectively, and the determined values were in a close range as determined for natural clay [15, 16]. An increase in the Pu K_d value by a factor of 6.8 was found for magnetite/hematite composite in comparison with that for pure magnetite. Thus, synthesized magnetite/hematite composites possess magnetic properties and better sorption ability towards Pu.

4. Conclusions

Synthesized inorganic sorbents are extremely chemically stable and have exclusive selectivity towards radiostrontium as well as radiocesium even in solutions with high Na^+ , Ca^{2+} , and Mg^{2+} concentrations.

Data on Pu sorption kinetics have indicated that rather short time is required to reach equilibrium. Equilibrium was reached after about 2 hours of sorption.

The synthesized magnetite/hematite composite showed magnetic properties and better sorption ability towards Pu in comparison with the pure magnetite.

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NEORGANINIŲ SORBENTŲ SINTEZĖ IR APIBŪDINIMAS BEI JŲ TAIKYMAS RADIOAKTYVIŲJŲ NUKLIDŲ SORBCIJAI

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Santrauka

Susintetinti titano silikatai ir geležies oksidai. Naudojant Rentgeno, Mesbauerio, gama ir alfa spektroskopiją bei laboratorinės sorbcijos metodu buvo tiriamos gautų neorganinių sorbentų struktūrinės charakteristikos ir cezio, stroncio, plutonio ir americio sorbcijos geba. Rentgeno spektroskopijos metodu tiriant susintetintą titano silikatą, nustatyta jo amorfinė struktūra. Pritaikius Mesbauerio spektrometriją gauti būdingi nanokristalinio getito, hematito, magnetito bei hematito ir magnetito mišinio spektrai. Buvo įvertintas nanokristalinių mineralų dydis, kuris kito nuo 14 iki 30 nm. Pa-

siskirstymo koeficiento (K_d) vertės, gautos laboratorinės sorbcijos metodu, kito nuo 390 iki 163000 ml/g Sr, nuo 6 iki 40470 ml/g Cs, nuo 220 iki 257000 ml/g Pu ir nuo 50 iki 16260 ml/g Am.

Susintetinti neorganiniai sorbentai yra labai chemiškai stabilūs ir ypatingai atrankiai sorbuoja radiostronciją bei radioceziją, net ir didelių Na^+ , Ca^{2+} ir Mg^{2+} koncentracijų tirpaluose. Pu sorbcijos kinetikos eksperimentų metu pastebėta, kad reikia palyginti trumpo laiko pusiausvyrai pasiekti (2 val. nuo sorbcijos pradžios). Ištyrus susintetintą magnetito ir hematito mišinį parodyta, kad šio mišinio Pu sorbcijos geba geresnė, nei gryno magnetito.