

**VILNIUS UNIVERSITY
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CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY**

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**SORPTION OF CESIUM, AMERICIUM AND PLUTONIUM RADIONUCLIDES
ON SYNTHETIC AND NATURAL SORBENTS**

Summary of doctoral dissertation
Physical sciences, Physics (02P)

Vilnius 2015

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Summary of the dissertation was sent on 27th November, 2015.

The dissertation is available at the libraries of Vilnius University and State Research Institute Center for Physical Sciences and Technology.

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FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

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SINTETINIŲ IR NATŪRALIŲ SORBENTŲ TYRIMAS**

Daktaro disertacijos santrauka
Fiziniai mokslai, fizika (02P)

Vilnius 2015

Disertacija rengta 2008 – 2015 metais VMTI Fizinių ir technologijos mokslų centre, Vilnius, Lietuva.

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Disertacija bus ginama viešame Fizikos mokslo krypties (02 P) tarybos posėdyje 2015 m. gruodžio mėn. 29 d. 10 val. VMTI Fizinių ir technologijos mokslų centre, Fizikos instituto salėje.

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Disertacijos santrauka išsiuntinėta 2015 m. lapkričio mėn. 27 d.

Disertaciją galima peržiūrėti Vilniaus universiteto ir VMTI Fizinių ir technologijos mokslų centro bibliotekose.

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INTRODUCTION

Radionuclides such as ^{137}Cs , $^{239,240}\text{Pu}$ and ^{241}Am are originated as global fallout, as discharges from nuclear industry, as well as releases into the environment after various accidents. The Baltic Sea is one of the seas that have been contaminated by radionuclides to a great extent after the Chernobyl accident (Egorov *et al.*, 1999). These radionuclides are hazardous to human health and must be isolated from the environment using reliable disposal systems such as highly efficient synthetic and natural sorbents.

Natural inorganic sorbent clay is a locally available low cost material which is often used for engineered barriers. Natural clays can retard migration of radionuclides from a repository of radioactive wastes as components of the engineered and natural barriers. An important characteristic of the retardation is the reaction kinetics of radionuclides with clays. While the kinetics of the sorption was quite frequently studied (Helal *et al.*, 1998), very little information on the time dependence of radionuclide bonding to natural clays is available.

The most important components which are on the natural clay mineral surface affecting sorption of radionuclides are iron oxides and organic substances (Povinec *et al.*, 2003; Egorov *et al.*, 1999). One of the available technique for analysis of radionuclide speciation at the low environmental level (in clays and bottom sediments) is a sequential extraction (Miller *et al.*, 1986). The results of sequential extraction can provide useful information about environmental behavior of radionuclides. This method estimates association of radionuclides with components of environmental samples such as carbonate minerals, Fe/Mn oxides and organic substances.

In this work the sorption kinetics of Cs(I), Pu(IV) and Am(III) radionuclides on synthetic and natural sorbents have been studied. The aim of the study was investigation of radionuclide speciation distribution in the clay minerals during the long-term experiments (361 days). The investigation of ^{137}Cs , $^{239,240}\text{Pu}$ and ^{241}Am radionuclide speciation in bottom sediments gives important information about their bioavailability and sorption behavior.

Aim of the study

The main aim of this study is to evaluate the Cs(I), Pu(IV) and Am(III) radionuclides sorption kinetics and determine the sorption parameters of synthetic and natural sorbents.

Tasks of the study:

1. To investigate ability of synthetic inorganic sorbents (titanium silicate and iron oxide) to adsorb Cs(I), Pu(IV) and Am(III) as well as compare their sorption parameters with natural sorbents.
2. To investigate ability of natural sorbents to adsorb Cs(I), Pu(IV) and Am(III) also evaluate their sorption kinetics parameters; To investigate variations of solid-phase speciation of Cs(I), Pu(IV) and Am(III) radionuclides in the long-term (361 days) experiment using the sequential extraction method.
3. To prove the presence of organic substances in clay and bottom sediment samples using the FT-IR, ^1H , ^{13}C NMR spectroscopy.
4. To evaluate the impact of suspended particulate matter on the dispersion of Cs(I), Pu(IV) and Am(III) radionuclides in the Baltic Sea coastal zone.

Scientific novelty

The long-term (361 days) experiment results revealed Pu(IV) transformation of geochemical forms in solid phase of clay minerals from amorphous iron oxides to crystalline structure oxides and insoluble Ca humates with low mobility in the environment. For Am(III) such transformation is not happening.

Practical importance

The performed work is closely related to the radioactive waste repository under construction in the Lithuanian territory, where the Saltiskiai clay as an artificial barrier of natural clay it is planned to use. At present there is a lack of information and research on the behavior of radioactive elements in the repository environment. In order to evaluate the radionuclide migration, sorption parameters and their distribution during a long time interval, the comprehensive investigations have been done. In this work we present the physical and chemical properties of analyzed elements, sorption parameters, kinetics calculations and experiment data of the radionuclide long-term behavior (361 days). The above mentioned studies can be used in modeling the radionuclide dispersion in natural barriers.

Defended statements:

1. Cs isotopes are best removed using titanium silicates, synthesized on TiOSO_4 ($\text{Na}_2\text{Ti}_2\text{SiO}_7 \cdot 2\text{H}_2\text{O}$) basis. To remove actinides the best sorbents are iron oxides (magnetite - Fe_3O_4 , goethite - $\alpha\text{-FeOOH}$, hematite - $\alpha\text{-Fe}_2\text{O}_3$).
2. The greatest quantity of Am(III) in clay samples was found in the exchangeable and carbonate forms. The greatest amount of Pu(IV) was found to be bound to amorphous oxides and organic compounds.
3. The kinetics of Pu(IV) and Am(III) sorption kinetics on natural clay minerals are controlled by diffusion in the inert layer (ID) control process. The exception is only in the case of Pu(IV) sorption to clay 7 when sorption was controlled by the chemical reaction (CR) control process.
4. It has been determined that particles of 0.2-5.0 μm in size are responsible for transport of Cs(I), Pu(IV) and Am(III) radionuclides.

Approbation

Results of the research, which are presented in the thesis, were published in 5 scientific journals and in 8 presentations at international and national scientific conferences.

Publications on the subject of the dissertation

The results were presented in 5 publications:

1. Lujanienė, G., Garnaga, G., Remeikaitė-Nikienė, N., Jokšas, K., Garbaras, A., Skipitytė, R., Barisevičiūtė, R., Šilobritienė, B., Stankevičius, A., Kulakauskaitė, I., Ščiglo, T.: Cs, Am and Pu isotopes as tracers of sedimentation processes in the Curonian Lagoon–Baltic Sea system, *J. Radioanal. Nucl. Chem.*, 296, p. 787-792, 2013.
2. Lujanienė, G., Beneš, P., Štamberg, K., Ščiglo, T.: Kinetics of plutonium and americium sorption to natural clay, *J. Environ. Radioactivity.*, 108, p. 41-49, 2012.
3. Lujanienė, G., Beneš, P., Štamberg, K., Šapolaitė, J., Vopalka, D., Radžiūtė, E., Ščiglo, T.: Effect of natural clay components on sorption of Cs, Pu and Am by the clay, *J. Radioanal. Nucl. Chem.*, 286, p. 353-359, 2010.
4. Ščiglo, T., Lujanienė, G., Šapolaitė, J., Radžiūtė, E.: Effect of natural organic substances on Pu and Am migration in the environment. Radiation interaction with material and its use in technologies, ISSN 1822-508X, p. 197-200, 2010.
5. Lujanienė, G., Meleshevych, S., Kanibolotsky, V., Šapolaitė, J., Strelko, V., Remeikis, V., Oleksienko, O., Ribokaitė, K., Ščiglo, T.: Application of inorganic sorbents for removal of Cs, Sr, Pu and Am from contaminated solutions, *J. Radioanal. Nucl. Chem.*, 282., p. 787-791, 2009.

Presentations at the conferences:

1. Lujanienė, G., Garnaga, G., Remeikaitė-Nikienė, N., Jokšas, K., Garbaras, A., Skipitytė, R., Ščiglo, T., Barisevičiūtė, R., Valiulis, D., Šilobritienė, B.: ^{137}Cs , $^{239,240}\text{Pu}$, ^{241}Am behavior in the Baltic Sea - Curonian Lagoon system, MARC IX: Ninth international conference on methods and applications of radioanalytical chemistry, abstracts, Kailua-Kona, p. 88, 2012.

2. Lujanienė, G., Garnaga, G., Jokšas, K., Garbaras, A., Skipitytė, R., Ščiglo, T., Barisevičiūtė, R., Šilobritienė, B., Radžiūtė, E., Lagunavičienė, L.: ^{137}Cs , $^{239,240}\text{Pu}$, ^{241}Am and trace elements behaviour in the Baltic Sea - effect of organic substances. International symposium on isotopes in hydrology, marine ecosystems, and climate change studies, abstracts, Monaco, p. 223, 2011.
3. Lujanienė, G., Beneš, P., Štamberg, K., Šapolaitė, J., Radžiūtė, E., Ščiglo, T.: A comparative study of Pu and Am migration capability in clay and soil matrixes. Environmental radioactivity - new frontiers and developments, abstracts, Rome, p. 101, 2010.
4. Lujanienė, G., Meleshevych, S., Radžiūtė, E., Strelko, V., Oleksienko, O., Šapolaitė, J., Ščiglo, T.: Removal of Cs, Sr, Pu and Am from contaminated solutions under laboratory and real conditions. Environmental radioactivity - new frontiers and developments, abstracts, Rome, p. 88-89, 2010.
5. Lujanienė, G., Beneš, P., Štamberg, K., Radžiūtė, E., Jokšas, K., Šilobritienė, B., Ščiglo, T.: Pu, Am and Cs sorption behaviour in the Baltic Sea /Environmental radioactivity - new frontiers and developments, abstracts, Rome p. 42, 2010.
6. Ščiglo, T., Lujanienė, G.: Humuso ir fulvo rūgščių poveikis Pu ir Am elgsenai dugno nuosėdose. 1-oji Fizinių ir technologijos mokslų centro doktorantų ir jaunųjų mokslininkų konferencija FizTeCh, Vilnius, p. 34, 2010.
7. Lujanienė, G., Šapolaitė, J., Strelko, V., Oleksienko, O., Ščiglo, T., Meleshevych, S., Kanibolotsky, V.: Removal of Cs, Sr, Pu and Am from contaminated solutions by inorganic sorbents, 16th Radiochemical conference, Marianske Lazne, p. 110, 2010.
8. Lujanienė, G., Šapolaitė, J., Ščiglo, T.: Study of Pu(IV) and Am(III) sorption to clay minerals, 4th international conference in the series of Asia-Pacific Symposium on Radiochemistry, abstracts, Napa, p. 238, 2009.

The author's contribution:

1. Participation in the sample collection process in Saltiskiai and the Baltic Sea.
2. Organization of the Pu(IV) and Am(III) radionuclide long-term (361 days) experiments.
3. Separation of the solid-phase speciation in clay and bottom sediments using the sequential extraction method.
4. Separation of the humic substances from clay and bottom sediment samples using the FT-IR, ^1H , ^{13}C NMR spectroscopy method to prove the presence of organic substances in the samples.
5. Publication of the research results in scientific journals and their presentation at the conferences

Outline of the thesis

The thesis consists of introduction, two chapters, main results and conclusions, references. The research object and research methodology are described in the first chapter. The main radionuclide sorption parameters, chemical composition of the clay minerals, bottom sediments, long-term experiments and radionuclide migration in the Baltic Sea are presented and discussed in the second chapter of the thesis. At the end of this dissertation the main results, conclusions and the list of references are presented.

OBJECT AND RESEARCH METHODOLOGY

In the first part of this section we will describe the places where the samples were collected and evaluate the chemical and physical properties of the clay and the bottom sediments. We will also look at the synthetic inorganic sorbents. We will show the humic and fulvic acid separation method and present the details of investigations materials and procedure of extraction and separation of radionuclides.

1.1. Object of investigation

1.1.1. The clay samples collection places

For the study the clay samples were collected in the Saltiskiai. The origin, locations, physical and chemical description of the clays are also listed in the (Table 1.1). Samples were collected in such a way that contamination with environment was minimized. The raw samples were placed in polyethene bags and tied up.

1.1.2. The bottom sediments sample collection places

The investigation was based on sampling performed at 9 stations located in the Baltic sea. Suspended particulate matter and bottom sediments BS samples were collected during sampling campaigns in 1997-2012. The bottom sediments in the Baltic Sea were collected with a Van Veen grab. Suspended particulate matter was collected in situ by filtering water (400–1.000 L) through 1, 5 and 25 μm Sediment Filter Cartridges (US Filter Plymouth Products), as well as by 0.2 μm and 0.45 μm membrane filtration. Site description, sampling and sample preparation details are given in publications (Lujanienė *et al.*, 2006 a; 2010).

1.1.3. Synthetic inorganic sorbents

The titanium silicate synthesis developed at the Institute for Sorption and Problems of Endoecology of the National Academy of Sciences of Ukraine is based on the use of local technical titanyl sulfate and organic complexions as stock-materials for the synthesis.

1.2. Sample characterization

1.2.1. Natural clay characterization

The composition of the clay shown in (Table 1.1) (Ecofirma, 2004). The clay can be characterized as micro-aggregates of clay particles cemented by limonite $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$.

Table 1.1. Clay composition (Ecofirma, 2004)

Clay (fraction of <1 μm)		
Montmorillonite minerals	Illite minerals	Chlorite minerals
64%	24%	12%
Chemical composition		
Silicon dioxide SiO_2		45.51%
Aluminium oxide Al_2O_3		13.50%
Iron(III) oxide Fe_2O_3		5.17%
Magnesium oxide MgO		3.00%
Calcium oxide CaO		12.88%
Sodium oxide Na_2O		0.28%
Potassium oxide K_2O		5.02%
Titanium dioxide TiO_2		0.43%
Total sulfur S		0.16%
Loss on ignition		13.96%

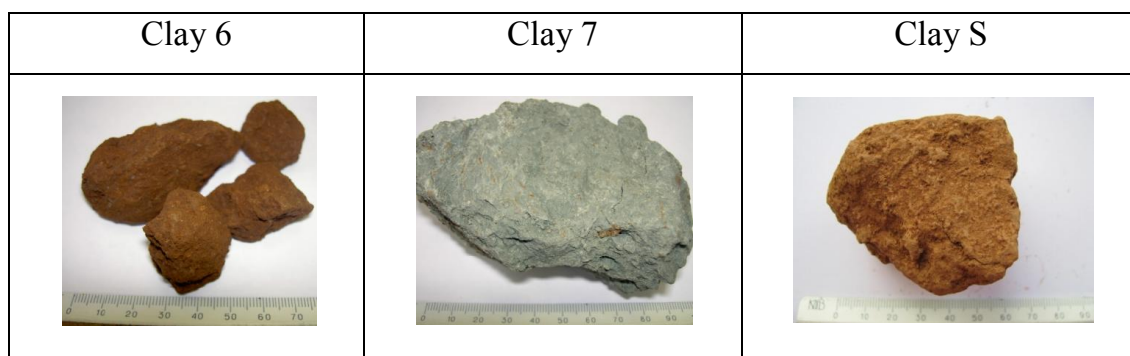


Fig. 1.1. The pictures of Saltiskiai clays (clay 6, clay 7 and clay S)

The chemical composition and the selected physical and chemical properties of the clay samples (Fig. 1.1) used in this study are characterized in (Table 1.2). Iron speciation in the clay minerals and their leaching during the SE procedures were investigated by means of the Mössbauer spectroscopy (Lujanienė *et al.*, 2007). The obtained data revealed the presence of Fe^{2+} , lepidocrocite ($\gamma\text{-FeOOH}$), siderite FeCO_3 , Fe hydroxides ($\text{Fe}(\text{OH})_3$), ferrihydrite ($\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$),

goethite (α -FeOOH) and the trace amount of ϵ -Fe₂O₃ mineral which is a rare intermediate between maghemite and hematite (Lujanienė *et al.*, 2006 a, b).

Table 1.2. Selected physical and chemical properties of the Saltiskiai clay samples (clay S, clay 6 and clay 7)

Parameter	Clay S	Clay 6	Clay 7
pH	7.98 ± 0.01	8.18 ± 0.01	8.05 ± 0.01
Total organic carbon ^a , %	0.034 ± 0.001	0.035 ± 0.001	0.062 ± 0.002
CaCO ₃ ^b , %	19.8 ± 0.3	19.3 ± 0.3	34.0 ± 0.5
Iron minerals ^c , FeCO ₃ / α -Fe ₂ O ₃ / α -FeOOH, %	1.6 ± 0.1/2.3 ± 0.1/0.10 ± 0.02	n.d./3.0±0.1/0.3 ± 0.02	n.d/ n.d/ n.d
Surface area (BET) ^d , m ² · g ⁻¹	64 ± 0.1	65 ± 0.1	65 ± 0.1
Total Fe, %	6.1 ± 0.1	6.3 ± 0.1	3.4 ± 0.1
Dithionite extractable Fe ^e , mg · kg ⁻¹	6500 ± 300	12700 ± 500	780 ± 20
Oxalate extractable Fe ^e , mg · kg ⁻¹	3400 ± 200	1050 ± 40	1.3 ± 0.1
Dithionite extractable Mn ^e , mg · kg ⁻¹	45 ± 2	73 ± 2	21 ± 1
Oxalate extractable Mn ^e , mg · kg ⁻¹	40 ± 2	29 ± 1	35 ± 2
n.d. - not detectable ^a LECO CS-125 ^b X-ray diffraction ^c Mössbauer spectroscopy ^d Surface area analyzer NOVA 2200 ^e Sequential extraction, ICP-MS			

1.2.2. The separation of humic substances from the clay samples

The separation method of humic substances from clays minerals is described by (Hansel *et al.*, 2008). The experiment was done with different compounds of clays (clay S, clay 6 and clay 7). Non-polar and polar compounds were extracted from the surface of clay parts. Non-polar wax fraction was extracted with chloroform and polar wax fraction was extracted with methanol:KOH mixture. An undried clay was extracted in a vial for 8 h with solvent in ratio 20 g clay (dry wt):20 mL CHCl₃. After, the mixture was centrifuged 20 minutes at 8000 rpm/min and then the solvent was leaved to evaporate. Then to the clay sample was added methanol:KOH (1 mol/L KOH in 96% methanol solution) in ratio 20 g clay:40 mL methanol:KOH. The mixture was heated 30 min at 70°C and mixing every 10 min. After cooling and centrifuged the soil residue was further

extracted 8 h with 40 mL methanol:chloroform (1:1), and chloroform (2 · 40 mL). The combined extracts were acidified to pH 1.0 with 12 mol/L HCl, and then 20 mL of solvent extracted distilled water was added. The released compounds were recovered in the chloroform phase, and two more extractions with chloroform (20 mL) were performed. Extracts were combined and leaved to evaporate.

1.2.3. The FT-IR spectra of humic substances

These preliminary results confirmed the presence of natural organic substances on the clay particles surface. It was found that humic substances isolated from all three clay samples were similar. Typical FT-IR spectrum of humic acids isolated from clay samples are shown in (Fig. 1.2). FT-IR spectra were recorded with Spectrum BX II, Perkin Elmer in the wave-number range of 500 - 3700 cm^{-1} . A sample was prepared by pressing pellets containing 0.1 or 0.2 mg clay in 100 mg KBr.

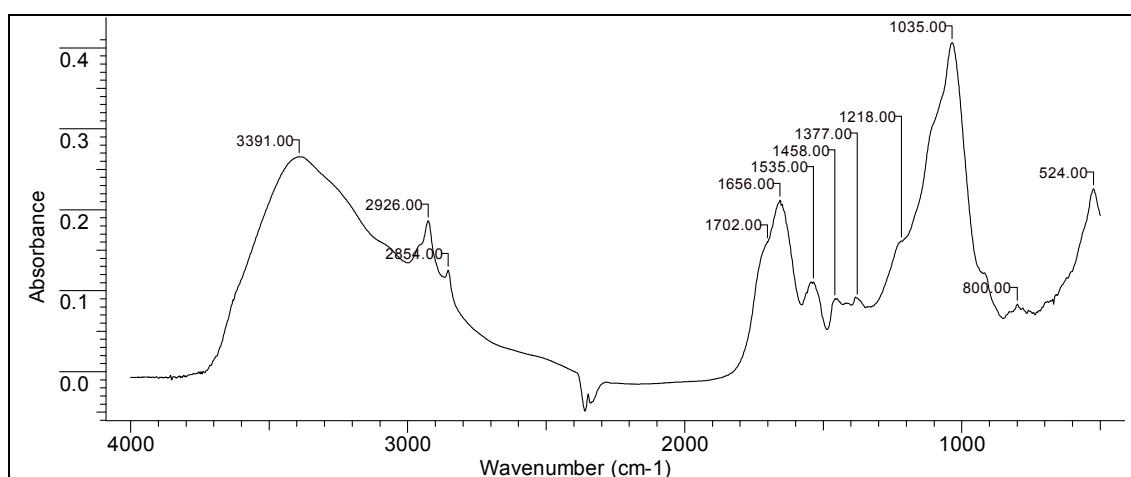


Fig. 1.2. FT-IR spectrum of humic substances

The FT-IR spectrum (Fig. 1.2) display characteristic bands of CH_2 , CH_3 , aliphatic groups 2926 cm^{-1} , 2854 cm^{-1} , 1458 cm^{-1} . A wide band at $3500 - 3300 \text{ cm}^{-1}$ show us O-H or N-H groups. A small band at 1702 cm^{-1} show us C=O groups of aldehydes, ketones, carboxylic acids, esters and the small peak at 1656 cm^{-1} of mostly aromatic C=C. The peak at 1218 cm^{-1} might have arisen from the -C-O groups of alcohols, ethers, carboxylic acids, esters. Carbohydrate and aliphatic alcohol were also observed by the presence of a strong signal at 1035 cm^{-1} .

A careful analysis of the FT-IR spectra data shows that the humic substances have aromaticity and carbohydrate content. It is known that their major functional groups include carboxylic, phenolic, carbonyl, hydroxyl, amine, amide and aliphatic moieties. The similar results of humic substances identification was obtained by (Stevenson *et al.*, 1971; Meissla *et al.*, 2007).

1.2.4. Bottom sediments characterization

In all bottom sediments fractions we found organic compounds (Table 1.3), the ranges is from 0.4% to 7.4%. The highest concentration of organic compounds we found in station R7. Iron concentration is from 1.1% to 0.9%. Calcium content reflects what the bottom sediments may be carbonaceous matter. In all 8 stations, their content is similar - about 3-4%.

Table 1.3. Selected chemical properties of the bottom sediment samples.

Station	TOC,%	Fe,%	Ca,%
Nida, 65, 6B, 5, 9, KJ-1, KJ-3, 1, R7	0.4 - 7.4	0.9 - 1.1	3 - 4

1.2.5. The separation of humic substances from the bottom sediment samples

The separation method of humic substances from clays minerals is described in (Swift *et al.*, 1996). The experiment was done with different compounds of bottom sediments. Bottom sediments were extracted with 0.5 mol/L NaOH at 1:10 solid to solution (mass/volume) ratio under N₂ for 8 hours. The suspension was then centrifuged at 8000 rpm for 20 min, the supernatant was acidified with 6 mol/L HCl to pH 1.0 and suspension was allowed to stand overnight. Precipitated humic acids was separated from fulvic acid by centrifugation at 8000 rpm for 20 min. Obtained HA precipitate was redissolved in 0.1 mol/L KOH, under N₂. Solid KCl was added to attain 0.3 mol/L (K⁺) and then suspension was centrifuged at high speed to remove suspended solids. The HA was reprecipitated with 6 mol/L HCl to pH 1.0. Precipitated humic acids were separated from fulvic acid by centrifugation at 8000 rpm for 20 min. The separated fulvic acid was dialyzed to separate dialyzed fulvic acid and non-dialyzed fulvic acids. Then dialyzed fractions were evaporated and dried. FT-IR spectra were recorded with Spectrum BX II, Perkin Elmer in the wavenumber range of 500 - 3700 cm⁻¹. A sample preparation of

pressed pellets containing 0.1 or 0.2 mg bottom sediments in 100 mg KBr. ^1H , ^{13}C NMR spectra were recorded at 300 MHz Varian Inova spectrometer. For nuclear magnetic resonance spectra, solutions were prepared by dissolving 30 mg sample in 1 mL CDCl_3 .

1.2.6. The FT-IR spectra of humic substances

All bottom sediments fraction from Baltic See and Curonian Lagoon were characterized by a combination of method FT-IR spectrometry (Fig. 1.3). These preliminary results confirmed the presence of organic substances in bottom sediments samples and showed that most probably they are humic and fulvic acids.

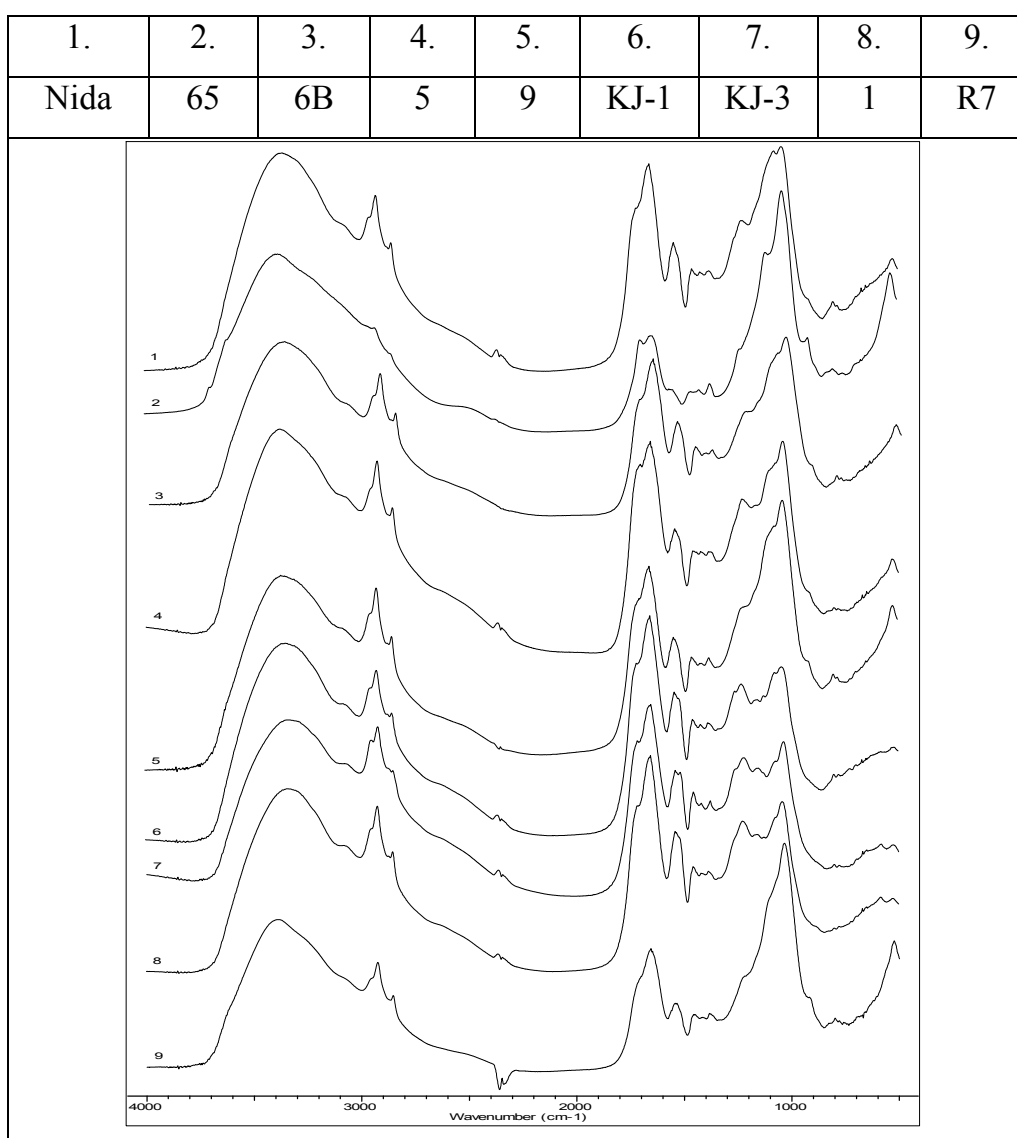


Fig. 1.3. FT-IR spectra of humic substances in Baltic See and Curonian Lagoon

The characteristic absorption bands typical of humic substances are observed in all FT-IR spectra. The sample spectra (Fig. 1.3) display characteristic bands of CH_2 , CH_3 ,

aliphatic groups 2930 - 2920 cm^{-1} , 2860 - 2850 cm^{-1} , 1458 cm^{-1} . A wide band at 3500 – 3300 cm^{-1} show us O-H or N-H groups. A small band at 1720 - 1680 cm^{-1} show us C=O groups of aldehydes, ketones, carboxylic acids, esters. In the spectral region of 1625 - 1610 cm^{-1} sorption indicated the presence of aromatic C=C and carbonyl groups and quinones. The peak at 1470 - 1370 cm^{-1} might have arisen from the –C-O groups of alcohols, ethers, carboxylic acids, esters. Sorption at 1080 cm^{-1} shows OH deformation or C-O stretch of phenol and alcohol OH groups, and at 1040 cm^{-1} indicates C-O stretch of polysaccharide components.

1.3. Sorption experiments

Synthesised sorbents, both titanium silicates and iron oxides, as well as natural clay minerals with 14% of montmorillonite were used in sorption experiments. The laboratory batch method was applied to determine the distribution coefficient values of Cs, Pu and Am radionuclides (background electrolyte 0.1 mol/L Na^+) at the 1:100 and 1:1.000 g/mL liquid:solid. The total concentrations of caesium in solutions were $2.30 \cdot 10^{-10}$ mol/L and $6.80 \cdot 10^{-5}$ (the solutions were labelled by ^{134}Cs). A mixture of Pu(IV) isotopes ($^{238,239, 240, 241}\text{Pu}$ prepared from highly contaminated Chernobyl soil) was used in sorption experiments (Lujanienė *et al.*, 2002). Starting concentrations of Pu(IV) and Am(III) were $1.10 \cdot 10^{-9}$ mol/L and $3.20 \cdot 10^{-11}$ mol/L, respectively. Sorption was studied using natural groundwater of the following composition in (Table 1.4).

Table 1.4. Natural groundwater composition.

Natural groundwater									
SO_4^{2-} , mg/l	Cl^- , mg/l	Na^+ , mg/l	K^+ , mg/l	Ca^{2+} , mg/l	Mg^{2+} , mg/l	HCO_3^- , mg/l	pH	Eh, mV	χ , mS/cm
40.3	22.4	10.4	1.90	139.0	39.7	517.0	7.16	-71.7	0.86
χ - conductivity; Eh – redox potential;									

1.4. Sequential extraction analysis

The bonding of sorbed Pu and Am in the solid phase was determined using SE procedures with the following fractions and extractants (solid : extractant ratios):

Table 1.5. Extraction protocol for sea sediment Miller method (Miller *et al.*, 1986)

Fr.	Reagent	Fraction
F1	0.44 mol/L CH ₃ COOH + 0.1 mol/L Ca(NO ₃) ₂ (1:20)	Exchangeable and carbonate bound - the most available and mobile fraction
F2	0.1 mol/L Na ₄ P ₂ O ₇ (1:100)	bound to organic matter
F3	0.175 mol/L (NH ₄) ₂ C ₂ O ₄ + 0.1 mol/L oxalic acid H ₂ C ₂ O ₄ , pH 3 (1:75)	bound to amorphous oxides
F4	Na ₂ S ₂ O ₄ sodium dithionite in 0.15 mol/L C ₆ H ₇ NaO ₇ sodium citrate - 0.05 citric acid buffer (1:45)	bound to crystalline oxides
F5	Concentrated HCl and HNO ₃ (3:1 v/v) (1:20)	bound to minerals

Centrifugation at 3000 rpm and filtration through 0.20 mm membrane filters were applied for the separation of solid phase after the extraction. The efficiency of iron oxide extractions from samples was corroborated by Fe concentration measurements in the repeatedly extracted fractions. In this method (Table 1.5) (Miller *et al.*, 1986) the exchangeable and carbonate fractions were extracted together. The exchangeable fraction of actinides is known to be rather small, usually it does not exceed a few percent and it is therefore difficult to measure (Lujanienė *et al.*, 2009 a). Another problem is quantitative separation from the carbonate fraction, especially in solids containing high concentrations of carbonates since a pH close to neutral values leads to re-adsorption whereas its shift to acidic values causes dissolution of carbonates. These effects can lead to high uncertainties. The predominating Am and Pu association with clays S, 6 and 7 was first tested by extraction with 0.1 M MgCl₂ (method by Outola *et al.*, 2009). It was found that exchangeable fractions of Am and Pu varied within 1-2% after the short time contact and decreased when the contact time increased. Moreover, a possible sorption of Am and Pu to Mn oxides was checked by adding an extra step for the extraction of Mn oxides. However, the fraction bound to Mn oxides was found to be very small ($\leq 1\%$) and thus this step was finally excluded. The method described above has been most frequently used for actinide speciation analyses due to the suitable pH and complexing ability of extraction solutions. It enables extraction of organic compounds before that of iron oxides and it well corresponds with the recent studies of the SE techniques (Petersen *et al.*, 2008; Schultz *et al.*, 1998; Lucey *et al.*, 2007; Lujanienė *et al.*, 2002).

Reagent and bottom sediment ratio is 12 g sediment (dry wt) : 180 ml solvent. The undried sea bottom sediments were extracted 1 h with the first reagent in the 250 ml centrifuge bottle. After, the mixture was centrifuged 20 minutes at 7000 rpm/min and vacuum filtrated at 0.2 μm , then the solvent was leaved to evaporate. A similar approach was followed for each of the five fractions. In the first fraction (Table 1.6) the sea sediment was mixed with MgCl_2 to extract relatively soluble species of elements that may be displaced from the solid phase by cation exchange. In the second fraction, ammonium acetate was used to attack easily acid soluble mineral phase. In the third fraction, species that were associated with reducible metal (Fe) oxides and oxyhydroxides were expected to be released. In the fourth fraction, hydrogen peroxide was used as a strong oxidizing agent to release elements associated with organic matter in the sediment. In the last fraction, nitric acid was used to dissolve all the most resistant phases.

Table 1.6. Extraction protocol for botttom sediments (Outola *et al.*, 2009)

Fraction	Reagent	pH	Temp. (°C)	Conc.(M)	Time (h)
FI - exchangeable	MgCl_2	4.5	25	0.1	1
FII - carbonates	NH_4Ac in 25% HAc	4.0	50	1	2
FIII - oxides	$\text{NH}_2\text{OH-HCl}$ in 25 % HAc	2.0	70	0.1	6
FIV - organic substances	30 % H_2O_2 in 0.02 M HNO_3	1.5	70		3
FV - residue	HNO_3	1.0	90	4	4

1.5. Radionuclide activity measurement

Preparation of samples for electrodeposition

The fraction with the separated and purified radionuclides is evaporated to dryness. The remaining solid residue is dissolved in a few ml of 15M HNO_3 and evaporated to dryness. The same is done with H_2O_2 30%, 15M HNO_3 , HClO_4 and twice with 15M HNO_3 . The aim is to eliminate fraction of organic compounds that can disturb electrodeposition.

Electrochemical deposition of the sample

The dry residue was dissolved in a few ml of 0,4M HCl/4,0% $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and transported into an electrolytic cell. Cathode is a polished stainless steel disc and an anode is platinum wire. Electrolysis is done for 2 hours at the high current densities. In these conditions all radionuclides in solution tightly and efficiently deposited on the cathode electro coating form. The cathode is washed with distilled water and acetone mixture and dried. The activity of steel disc is explored with α -spectrometer.

Alpha - activity

The radionuclides α -activity are measured with Alpha Quattro spectrometer which consists of four independent measuring chambers with passivated implanted planar silicon ions detectors, 450 mm² active area. From the α -spectra line width was determined and calculated the activity. ²⁴²Pu and ²⁴³Am used as internal standards. To treat, analyze Pu and Am isotopes activity and to calculate their ratio we used the computer program Mecaplus. Measurement accuracy < 10%.

Gamma-ray measurement

¹³⁷Cs activities were measured with intrinsic germanium HPGe detector (resolution 1,9 keV/1,33 MeV and relative efficiency 42%). Measuring time is depending of the activity samples. Calibration of the system is carried out using different density and geometry calibration sources, prepared from the standard solutions (Amersham, UK), which corresponded to the measured specimen geometry and density. Analytical exactitude tested in interlaboratory studies organized by the Riso National Laboratory (Denmark). ¹³⁷Cs gamma spectrometer measurement uncertainty $\leq 3\%$ Cs sorption on the walls of the centrifuge cup was less than 2%.

2. RESULTS AND DISCUSSION

2.1. Sorption of radionuclides on synthetic inorganic sorbents

The main aim of this study is to evaluate the Cs(I), Pu(IV) and Am(III) radionuclides sorption kinetics and determine the sorption parameters of synthetic and natural sorbents. The sorption ability of synthetic inorganic sorbents towards Cs(I), Pu(IV) and Am(III) was tested using the laboratory batch method. The obtained results are expressed as distribution coefficients. The results help us to better understand Cs(I), Pu(IV) and Am(III) radionuclides sorption on natural clay minerals.

2.1.1. Typical isotherm of adsorption-desorption N₂ for TiSi samples

The specific surface area estimated using the BET method, the description of surface area you can see in Table (2.1). It was observe that using Cl⁻ and SO₄²⁻ ions in titanium silicates synthesis, the average pore radius in the presence of sulfate ion increased from 5.7 to 7.8 nm (Lujanienė *et al.*, 2009 a). X-ray investigations of synthesised by different techniques (precipitation and sol-gel methods) showed their amorphous structure. Nitrogen adsorption-desorption isotherms belong to type IV in the IUPAC classification. S-shaped character indicates the mesoporous structure of synthesised TiSi samples.

Table 2.1. The surface area description of titanium silicates

Surface area (BET method)	120 - 726 m ² /g
Total volume of pores	0.20 – 0.90 cm ³ /g
Volume of micropores	0.02 – 0.09 m ³ /g
Pores radii	2.5 – 15.5 nm
Pores radii of SO ₄ ²⁻	5.7 – 7.8 nm

The sorption ability of synthesised inorganic sorbents towards Cs, Pu and Am from natural groundwater, 0.1 mol/L NaNO₃ solutions, and fuel pond water. The highest K_d values, you can see below, were found for the system groundwater - TiSi ion exchangers. The data obtained indicated that Cs K_d for the TiSi sorbents and 0.1 mol/L NaNO₃ solutions varied from 30 to 4.1 · 10⁴ mL/g whereas Pu K_d varied from 2 · 10² to 4.6 · 10³ mL/g. Comparably high K_d values found for TiSi-17(SO₄) and TiSi-55(Cl) are promising

for particular separations, and it is probably an indication that amorphous TiSi can act as exchangers towards a wide range of cations with dissimilar sizes and charge. On the other hand, the highest Pu K_d value found for sorbent TiSi-17(SO₄) in 0.1 mol/L NaNO₃ solution can be explained by an effect of the methyl groups introduced into the Ti silicate structure using the potassium methyl silicon and the hydrogen peroxide as complexation during the synthesis procedure. The presence of these groups provided formation of sorbent with a mesoporous structure, appropriate for sorption of large size ions.

2.1.2. Pu sorption kinetics to TiSi and Fe oxides

Data on the Pu(IV) sorption kinetics (Fig. 2.2) have indicated that a rather short time period is required to reach equilibrium. Equilibrium was reached after about 2 h of sorption. Kinetic data were fitted to the pseudo-first-order kinetic model:

$$q_t = q_e(1 - e^{-k_{ad}t}) \quad (2.1)$$

where q_t and q_e are Pu concentrations (mol/g) at time t and equilibrium, respectively as well as k_{ad} (min⁻¹) is the pseudo-first-order rate constant. It can be seen from the obtained parameters that the iron oxide kinetic data fit well the pseudo-first-order equation, whereas the TiSi's data require additional analyses. Pu K_d equilibrium (Fig. 2.1) ranged from $2.5 \cdot 10^3$ to $4.1 \cdot 10^3$ mL/g for studied sorbents TiSi-17(SO₄), TiSi-55(Cl) and TiSi-59(Cl).

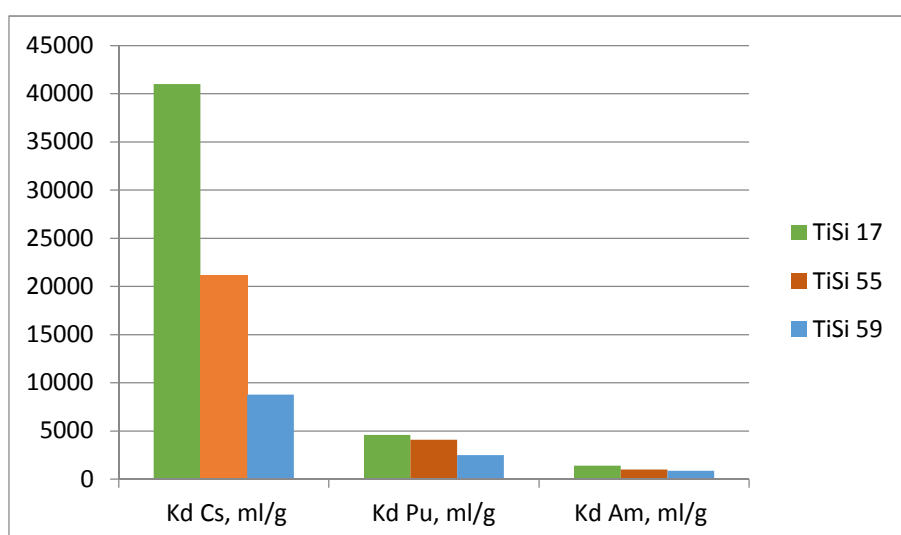


Fig. 2.1. Cs(I), Pu(IV) and Am(III) radionuclides K_d values in the system titanium silicates - 0.1 mol/L NaNO₃, pH 6.08 – 7.02 ± 0.06

It should be noted that TiSi are porous materials with pore size distribution from 0.8 to 1.5 nm and their sorption ability towards studied radionuclides depends on their structural parameters. In addition, modification of methods used for preparation of TiSi gives opportunities to change their microstructure and porosity.

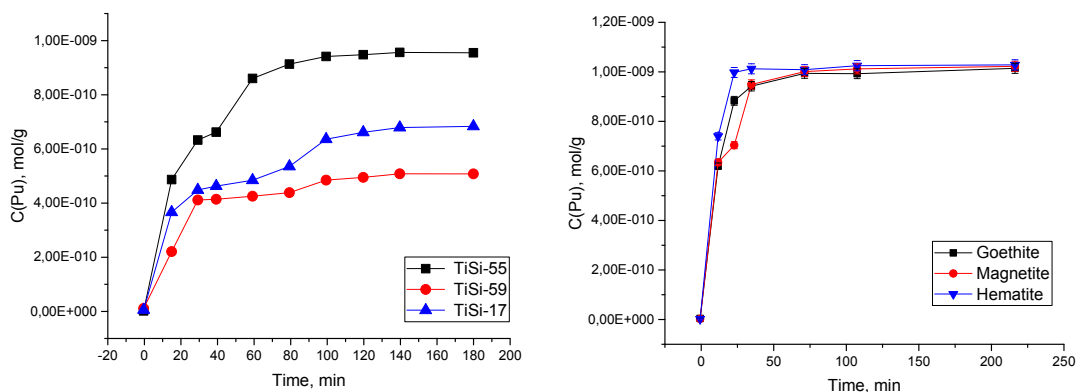


Fig. 2.2. Kinetics of Pu(IV) sorption to TiSi and Fe oxides sorbents (0,1 mol/l NaNO₃ solution, pH 6.08–7.02 ±0.06, solid : liquid ratio 1: 1,000 g/mL)

Am(III) K_d values ranged from $4.8 \cdot 10^3$ to $1.6 \cdot 10^4$ mL/g, while K_d varied from $9.0 \cdot 10^3$ to $2.6 \cdot 10^5$ mL/g for Pu(IV) in the system iron minerals — natural groundwater (Fig. 2.3). The obtained values were in a close range as determined for natural clay (Lujanienė G et al. 2006 b and 2007).

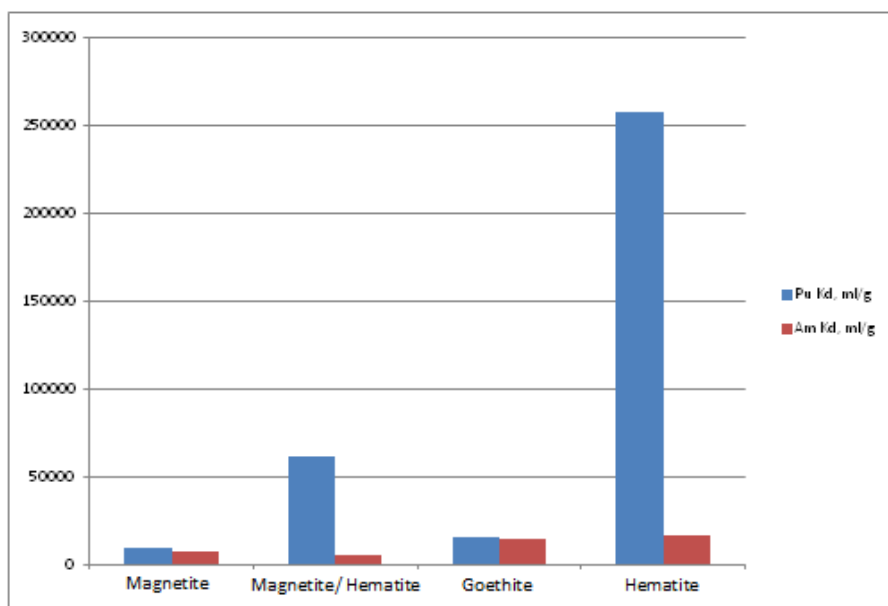


Fig. 2.3. Am(III) and Pu(IV) radionuclides K_d values in the system iron minerals - natural groundwater

An increase in the Pu K_d value by a factor of 6.8 was found for magnetite/hematite composite in comparison with the value for pure magnetite, and lower by a factor of 4 in comparison with the K_d value obtained for pure hematite. Nevertheless, synthesised magnetite/hematite composites possess magnetic properties and comparatively a high sorption ability towards Pu. Therefore, they can be used for separations. Studies of plutonium sorption kinetics indicated a faster plutonium sorption to iron oxides in comparison to TiSi.

The results from Pu sorption kinetics experiments showed us that sorption on iron oxides is more better than sorption on titanium silicate (Fig. 2.3).

2.1.3. Cs sorption kinetics to TiSi

Cs sorption kinetics data for four sorbents are presented by (Lujanienè *et al.*, 2009). Sorption kinetics is an important parameter of sorbents reflecting their efficiency and cost. The sorption of cesium on titanium silicates occurs in the first 10 min after the 90% of Cs was removed. These better sorption parameters can be explained by their structure. Cs kinetics data of sample TiSi-55(Cl) indicated that there is a limitation on Cs ion diffusion into the mesoporous sorbent matrix.

The study of TiSi showed close sorbtion ability towards studied radionuclides, whereas they were synthesised under mild conditions using cheaper materials. It should be noted that modification of methods used for preparation of TiSi gives great opportunities to change their microstructure and porosity.

The results from (Section 2.1) radionuclides sorption on synthetic inorganic sorbents showed us that the highest sorption ability towards studied radionuclides showed titanium silicates synthesized using $TiOSO_4$. The highest Pu K_d values and better Pu sorption kinetics were found for synthetic iron oxides. The results from Pu sorption kinetics experiments showed us that sorption on iron oxides is more better than sorption on titanium silicate (Fig. 2.2).

2.2. Sorption of radionuclides on natural clay sorbents

Kinetics of Pu(IV) and Am(III) sorption from natural groundwater to three types of clays (clay 6, 7, S) were studied in this section. For sorption kinetics study we use six different control processes. In addition to kinetics of the sorption elements, we investigate the radionuclides distribution in the clay geological forms during the long-term experiments (361 days).

2.2.1. The study of radionuclides Pu(IV) and Am(III) sorption kinetics on clays samples

The kinetics of sorption from natural groundwater was studied on clay S, clay 6 and clay 7 with different content and composition of reactive compounds in their coatings in (Table 1.2). The main differences were observed in carbonate and iron minerals in coatings of the clays studied. Siderite (FeCO_3) was not found in clays 6 and 7, and iron oxides were below the detection limit of Mössbauer spectroscopy in clay 7 coatings mainly composed of CaCO_3 . The largest amount of hematite was found in clay 6 and a high content of dithionite extractable iron proved the presence of mainly crystalline iron oxides in the coatings of this clay. Experimental data obtained from six kinetic sorption experiments and the results of their modeling are presented in (Fig. 2.4).

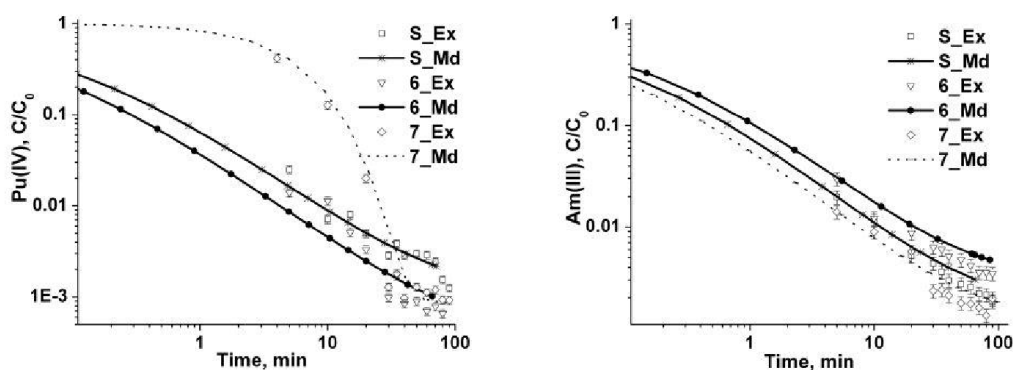


Fig. 2.4. Pu(IV) (experiments Pu 6, Pu 7, Pu S) and Am(III) (experiments Am 6, Am 7, Am S) sorption kinetics to three natural clays from groundwater as a function of contact time ((Ex - experimental data, Md – calculated data) Md = ID in all cases except for Pu 7 experiment where Md = CR)

The data was evaluated by fitting with six different types of kinetic models (Beneš *et al.*, 1994) derived for the following six control processes: mass transfer (DM), film diffusion (FD), diffusion in the inert layer (ID), diffusion in the reacted layer (RLD), chemical reaction (CR) and gel diffusion (GD). The differential model equations describing these control processes are summarized in (Table 2.2).

Table 2.2. Sorption kinetics equations (Beneš *et al.*, 1994)

Sorption kinetics equations		
Control process		Differential equation
Mass transfer	DM	$dq/dt = K_{DM} \times (q^* - q)$
Film diffusion	FD	$dq/dt = K_{FD} \times (C - C^*)$ $K_{FD} = 3 \times D/(\delta \times R \times h_s)$
Diffusion in the inert layer	ID	$dq/dt = K_{ID} \times (C - C^0)/\{[1 - (q/q^*)]^{-1/3} - 1\}$ $K_{ID} = 3 \times D/(R^2 \times h_s)$
Diffusion in the reacted layer	RLD	$dq/dt = K_{RLD} \times (q^* - q)/\{[1 - (q/q^*)]^{-1/3} - 1\}$ $K_{RLD} = 3 \times D/(R^2 \times h_s)$
Chemical reaction	CR	$dq/dt = K_{CR} \times r_{CR} \times [1 - (q/q^*)]^{2/3}$ $K_{CR} = 3/(R \times h_s)$ $r_{CR} = k_{CR} \times (C - C^*)$
Gel diffusion	GD	$dq/dt = K_{GD} \times [(q^* - q_0)^2 - (q - q_0)^2]/(q - q_0)$ $K_{GD} = D \times \pi^2/(2 \times R^2)$
C	Concentration of the component in the solution at time t ;	
C^*	Equilibrium concentration of the component in the solution corresponding to the concentration of the component in solid phase at time t (see Eq. 2.2);	
q	Concentration of the component in the solid phase at time t ;	
q^*	Equilibrium concentration of the component in the solid phase corresponding to the concentration of the component in the liquid phase at time t (see Eq. 2.2);	
q_0	Starting concentration of the component in the solid phase (in our case $q_0 = 0$);	
t	Time;	
D	Diffusion coefficient of the component;	
K_{DM}	Mass transfer coefficient;	
K_{FD}	Kinetic coefficients;	
K_{RLD}	Kinetic coefficients;	
K_{CR}	Kinetic coefficients;	
K_{GD}	Kinetic coefficients;	
K_{ID}	Kinetic coefficients;	
k_{CR}	Rate constant of the chemical reaction;	
r_{CR}	Rate of the chemical reaction;	
R	Mean radius of the solid particle;	
h_s	Specific mass of the solid;	
d	Thickness of the liquid film on the surface of the solid particle	

The control process used are designed for the description of mass transfer processes and non-catalytic heterogeneous reactions between the solid and liquid phase and represent, especially in the case of ID, RLD and CR, a combination of the Fick's diffusion equation with chemical kinetic relation. The other three control process DM, FD and GD are based on the Fick's equation and are best suited for two phase systems as liquid-liquid extraction (DM, so called two-film or double-film control process) or ion exchange (FD, GD). The main limitation of all these control process consists in their "one-component" character since they do not explicitly consider the possible influence of the "second" component, e.g. of the exchanged or reacted product. On the other hand, their application enables identification of the corresponding control process, i.e. the slowest process, on the basis of which the significance of individual system parameters can be judged. From this point of view it is useful to take into consideration the relations for the kinetic coefficients (see K_{FD} , K_{ID} , K_{RLD} , K_{CR} and K_{GD} in Table 2.2).

It is evident that:

- (i) the stirring or shaking rate is important only in the case of the film diffusion (FD) control process, because the thickness of the surface liquid film is inversely proportional to this parameter.
- (ii) the rate of sorption controlled by processes like ID, RLD and GD is inversely proportional to the quadrate of the mean radius of the solid particle and directly proportional to the diffusion coefficient.
- (iii) the rate of sorption controlled by chemical reaction (CR) is inversely proportional to the mean radius of the particle and directly proportional to the rate coefficient of given reaction.

Each model consists of a set of kinetic (see Table 2.2), equilibrium (2.2) and balance (2.3) equations:

$$\text{Equilibrium } (K_d) \quad q^* = K_d \cdot C \text{ or } C^* = \frac{q}{K_d} \quad (2.2)$$

$$\text{Balance (general form)} \quad q = \frac{V}{m} \cdot (C_0 - C) + q_0 \quad (2.3)$$

V/m - liquid-to-solid ratio

C_0 - starting concentration of the component in the solution

K_d - distribution coefficient

The fitting of experimental data proceeded by means of nonlinear regression procedure in an iteration cycle from which it was possible to determine the K_{DM} , K_{FD} , K_{ID} , K_{RLD} , K_{CR} and K_{GD} values. As a fitting criterion, reflecting the agreement between the calculated and experimental values, the WSOS/DF (Weighted Sum of Squares divided by the Degrees of Freedom) quantity was calculated (Herbelin *et al.*, 1996). Generally, the agreement is acceptable if $0.1 \leq \text{WSOS/DF} \leq 20$.

The values of WSOS/DF obtained in the course of fitting procedures for all six experiments, using the model equations mentioned above, are summarized in (Table 2.3). Qualified evaluation of the data suggests that diffusion in the inert layer is the control process in the sorption experiments Pu 6, Pu S, Am 6, Am 7 and Am S, since the best fits, the lowest values of WSOS/DF, were obtained with the ID kinetic model. Only in the case of experiment Pu 7 the 1st order reversible chemical reaction (CR) was found as the control process. Although the slightly lower value of WSOS/DF was found for the control process DM in the latter case, in our opinion the chemical reaction better corresponds to the nature of the studied system (a composition and structure of the clay). Similar reasoning also applies for the experiment Am 7 where the same values of WSOS/DF were found for control processes ID and GD. None of the experiments can be well described by the model of film diffusion (FD). Thus the studied kinetics was not significantly affected by the rate of shaking used.

Table 2.3. Fitting of experimental data by six sorption kinetics control process - values of WSOS/DF

Experiment	Control process					
	DM	FD	ID	RLD	CR	GD
Pu 6	52.2	96.2	14.9	38.8	97.5	39.5
Pu 7	10.4	33.0	38.1	36.1	13.8	36.3
Pu S	45.8	52.1	7.4	21.8	52.4	25.6
Am 6	1.4E +4	22.6	3.2	3.6	31.7	8.6
Am 7	41.4	1.2E+5	6.9	9.6	112.0	6.9
Am S	46.3	78.6	1.7	12.7	102.0	9.01

The fitting of experimental data with the chosen models is demonstrated in (Fig. 2.4) in the form of model curves. The small deviations of the experimental points from model curves, especially near the equilibrium (see the experiments Pu 6 and Am 6, 7 and S), can be explained by uncertainty of the measurement and modeling in this region. Characteristic parameters of the sorption kinetics obtained from the model curves are presented in (Table 2.4). Similar kinetic curves and parameters were obtained for all the clay samples, except for Pu(IV) sorption to clay 7 observed in the experiment Pu 7 which was slower. This dissimilarity, as well as the different control process found in this case, can be explained by the chemical composition of surface coatings in clay 7, the large amount of carbonates, the small amount of iron oxides and the slightly higher amount of total organic carbon - TOC (Table 2.2).

The approximate halftime of sorption values presented in (Table 2.3) demonstrate high sorption rates of Pu and Am under given conditions. All the data can be useful for modeling Pu and Am migration through a barrier made of the studied clays. In such a case, the models and kinetic coefficients corresponding to the best type of control process have to be used.

Table 2.4. Results of modeling of sorption kinetics of Pu(IV) and Am(III) on clay 6, clay 7 and clay S from natural groundwater

Exper. No.	C_0 - starting concentration in solution [mol/L]	Control process	Sorption kinetics coefficients [min ⁻¹]	$T_{S1/2}$ [min]	K_d [mL/g]	WSOS /DF
Pu 6	$1.10 \cdot 10^{-9}$	ID	$(3.30 \pm 0.05) \cdot 10^{-2}$	<2	$23.5 \cdot 10^3$	14.9
Pu 7	$1.10 \cdot 10^{-9}$	CR	2.31 ± 1.41	≈ 4	$11.4 \cdot 10^3$	13.8
Pu S	$1.10 \cdot 10^{-9}$	ID	$(4.80 \pm 0.01) \cdot 10^{-2}$	<2	$8.39 \cdot 10^3$	7.41
Am 6	$3.20 \cdot 10^{-11}$	ID	$(6.89 \pm 0.02) \cdot 10^{-2}$	<2	$3.01 \cdot 10^3$	3.22
Am 7	$3.20 \cdot 10^{-11}$	ID	$(6.1 \pm 1.2) \cdot 10^{-2}$	<2	$7.83 \cdot 10^3$	6.93
Am S	$3.20 \cdot 10^{-11}$	ID	$(1.42 \pm 0.53) \cdot 10^{-2}$	<2	$5.7 \cdot 10^3$	1.67

Higher K_d values were determined for sorption of Pu(IV) than those of Am(III) (Table 2.4) but no clear dependence of the Pu K_d values and kinetic coefficients K_{ID} for Am(III) and Pu(IV) on the mineral composition of the clays can be deduced. The highest Pu(IV) K_d value was found for clay 6 which has the highest content of crystalline Fe oxides and mineral hematite. However, the order of Pu(IV) K_d values (6 clay > 7 clay > S clay) disagree with the change in the content of both amorphous (S clay > 6 clay > 7 clay) and crystalline (6 clay > S clay > 7 clay) Fe oxides. The sequence of Am(III) K_d values (7 clay > S clay > 6 clay) corresponds to the carbonate content in the clay mineral coatings. Sorption of Am(III) on S clay, which has almost the same content of CaCO_3 as 6 clay, may be enhanced by the presence of FeCO_3 . Apparently, Pu(IV) can be sorbed to various sorption sites on the clay surface whereas Am(III) sorption is restricted to the carbonate sorption sites.

2.2.2. Radionuclide sorption changes on clays minerals geochemical phases during long-term experiment

In order to examine the effect of the contact time between clay and sorption solution on the nature of bonding of Am and Pu to the clays, a sequential extraction analysis of the bonding was carried out as a function of the time. The results shown in (Fig. 2.5 and 2.6) indicate variations in the bonding of Pu with time which is different for the different clay samples. This variation can be due to a redistribution of Pu among the unchanged geochemical phases of the clays and due to changes of the phases with the increasing contact time.

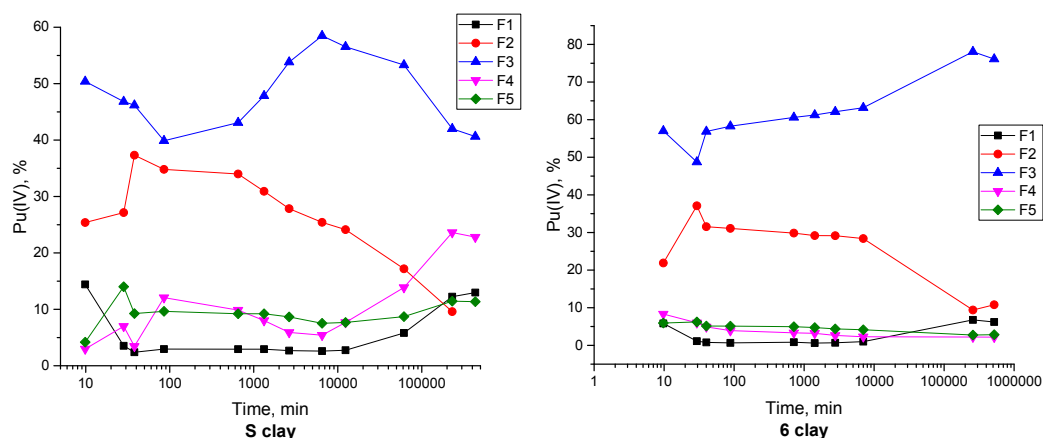


Fig. 2.5. Distribution of different binding forms of Pu sorbed on clays S and 6 as a function of sorption time (F1 - exchangeable and carbonate bound; F2 - in organic

matter; F3 - in amorphous iron oxides; F4 - in crystalline iron oxides; F5 - in the residue). Sorption from groundwater GW.

The distribution of Pu(IV) among various bonding forms is very similar in the different clays at the beginning of sorption but as the contact time increases the proportions of the prevailing fractions (F3) and (F2) change in a different way. A greater similarity exists between clays 6 and S, particularly if the sums of amorphous (F3) and crystalline (F4) oxides are compared. Obviously, the structure of Fe oxides can affect the mechanism and probably also the kinetics of the sorption process. For instance, the increase of the part of Pu(IV) associated with crystalline oxides in time, apparently at the expense of that bonded to amorphous oxides in clay S, can be explained by crystallization of part of the amorphous oxides during longer contact with the solution. Clay S has the highest concentration of amorphous oxides (Table 2.2, oxalate extractable Fe).

The similar results published (Stumm *et al.*, 1996). They are observed a formation of goethite and hematite in aqueous ferrihydrite suspension after it had been stored for three years at 24 °C. The increase in the hematite/goethite ratio took place after 441 days of storage, particularly at pH 7-8. According to our previous study (Lujanienė G *et al.*, 2006 c) the content of Pu in the crystalline oxide fraction corresponds to plutonium bonding to hematite. Fe minerals lepidocrocite, siderite, Fe hydroxides, ferrihydrite, hematite, goethite and Fe(II) were identified in S clay samples using Mössbauer spectroscopy. It was supposed that the time changes observed in the plutonium bonding in this case could be related to changes in the iron species. Among the species identified in the S clay coatings, siderite (FeCO₃) is the most unstable under the given experimental conditions. Also the thermodynamic stability of ferrihydrite is questionable, and thus the proportion of iron species in the mixture can be shifted presumably toward the formation of nanocrystalline goethite and hematite during a long-term experiment (Stumm *et al.*, 1996). A possible mechanism is the hydration of mineral surfaces and the reductive dissolution of ferric minerals via electron transfer from ferrous-iron-bearing minerals (such as siderite, chlorite, biotite, vermiculite, and montmorillonite), with subsequent oxidation of ferrous ions in the liquid phase and formation of secondary minerals containing ferric iron. These minerals can further change, for instance by transformation

of ferrihydrite and lepidocrocite to more stable Fe oxides (e.g. goethite or hematite) as it was observed elsewhere (Hansel *et al.*, 2005; Pedersen *et al.*, 2005; Zänker *et al.*, 2006). Therewith the mineral siderite found in the coatings of clay S can play an important role in the transformation of ferrihydrite to crystalline Fe oxide species. Catalytic transformation of ferrihydrite to lepidocrocite, goethite and hematite induced by the trace concentration of Fe(II) at a room temperature in the pH range of 5-9 was observed. The transformation rate, amount and ratio of formed species were found to be a function of the initial pH, temperature and ionic media (Lujanienė *et al.*, 2007, 2010). The (Das *et al.*, 2011) reported that 10% conversion of ferrihydrite to hematite should take about 3 years (rate constant of $9.02 \cdot 10^{-6} \text{ h}^{-1}$) and 100% conversion should take about 90 years under conditions of pH 10 and 1-2 °C. The rate of ferrihydrite transformation should be faster under unoxic condition in the presence of Fe(II). These findings are in good agreement with our results and are important for the prediction of Pu(IV) migration in the environment.

Different timing of Pu(IV) partitioning among the geochemical phases was found for clay 7 where a gradual decrease in Pu(IV) bonding to amorphous oxides accompanied by an increase in its association with organic matter was observed (Fig. 2.6).

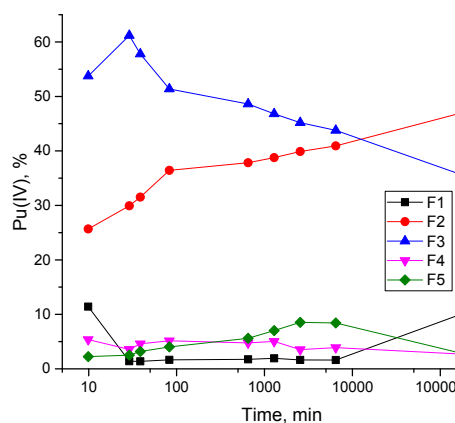


Fig. 2.6. Distribution of different binding forms of Pu sorbed on clays S and 6 as a function of sorption time (F1 - exchangeable and carbonate bound; F2 - in organic matter; F3 - in amorphous iron oxides; F4 - in crystalline iron oxides; F5 - in the residue). Sorption from groundwater GW.

This can be explained by the different chemical composition of coatings of the clay sample (Table 1.2). It should be noted that a slightly higher amount of organic

substances (humic and fulvic acids) was found in this sample. The substances probably compete with the other geochemical phases for Pu in the absence of iron minerals in the particle coatings. Presumably the variation in mineralogical composition of the clay coatings and their different transformation pathways during the long-term experiment resulted in structural changes of particle surfaces and in their reactivity in the groundwater mineral interface (Macášek *et al.*, 1999). For instance, the organic substances (humic and fulvic acids) found on the surface of this clay and possibly present in the groundwater can form insoluble Ca humates which can bind Pu isotopes.

A small but evident increase of the exchangeable and carbonate bound Pu(IV) was found for all the studied clays during long contact times (Figure 2.5 and 2.6). This increase can be most probably explained by the formation of a carbonate layer on the surface of clays during the long-term experiments, which competes with other components of the clays during Pu sorption. The similar results published (Zavarin *et al.*, 2005), the K_d values for Pu(IV) sorption on solid carbonates are rather low, 0.06-1.1 L/g for calcite, the sorption on the carbonate layer can proceed after the reduction of Pu(IV) to Pu(III) by ferrous-iron-bearing minerals. (Lujanienė *et al.*, 2009b) was observed reduction in the clay - 0.1 mol/L NaNO₃ suspensions even in short-term experiments. Sorption behavior of Pu(III) should be close to that of Am(III). This explanation seems to be supported by the results of sequential extraction of bottom sediment samples from the Bornholm Deep of the Baltic Sea (Pawlukowska, 2010) where about 80% of plutonium was found to be associated with carbonates. This is in agreement with our results on Pu oxidation state distribution in the sequential extraction fractions indicating that a large portion of Pu (up to 76%) in the carbonate fraction was present as Pu(III) (Lujanienė *et al.*, 2012).

In contrast to plutonium, only small variations in the bonding of Am(III) to the studied clays with time were found and after a short contact time, nearly all Am(III) was found in the exchangeable and carbonate bound fraction (Fig. 2.7). This reflects the negligible role of Fe oxides in Am sorption and small changes which may occur in the clay-solution system. The results obviously indicate the ion exchange of Am at various sorption sites and its bonding to calcite present in the system. This interpretation is supported by data obtained from TRLFS Cm(III) and EXAFS Am(III) investigations which showed outer-sphere sorption of trivalent actinides onto a smectite surface and the

formation of inner-sphere complexes with an increase of pH (Stumpf *et al.*, 2006). In addition, studies of Am(III) and Cm(III) interaction with mineral calcite by TRLFS indicated the formation of two different Am(III), Cm(III)/calcite species: one - bonded onto the calcite surface and the second - incorporated into the calcite lattice via substitution of Ca(II) for Am(III) (Stumpf *et al.*, 2004).

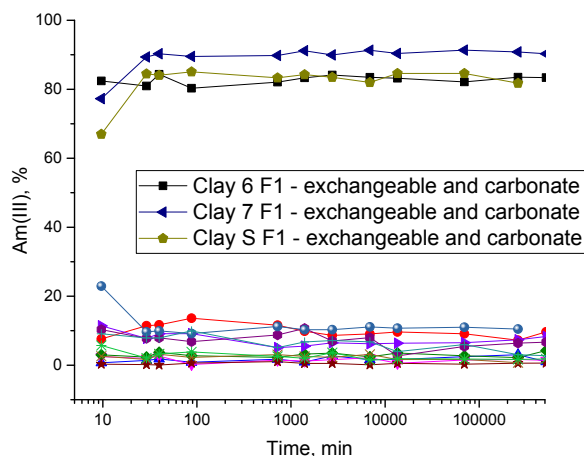


Fig. 2.7. Distribution of different binding forms of Am sorbed on three natural clays as a function of sorption time (F1 - exchangeable and carbonate bound; F2 - in organic matter; F3 - in amorphous iron oxides; F4 - in crystalline iron oxides; F5 - in the residue. Sorption from groundwater GW.

The study of radionuclides sorption kinetics has indicated that sorption was controlled by two different control process. Higher K_d values were determined for sorption of Pu(IV) than of Am(III). The similar sorption kinetics of Pu(IV) and Am(III) showed a different bonding to clay particle coatings. It was found that Pu(IV) was predominantly associated with amorphous and crystalline Fe oxides as well as natural organic matter sites on the clays, whereas in the case of Am(III) the exchangeable and carbonate sites played the principal role. Thus, from the data obtained in this study, from published data related to the field observations (Lujanienė *et al.*, 2002; Lusa *et al.*, 2009) and from laboratory experiments (Lujanienė *et al.*, 2007, 2010) we may conclude that the exchangeable and carbonate bound Am(III) has displayed a faster migration and greater bioavailability in the environment. The obtained sorption parameters can be used for modeling Pu(IV) and Am(III) migration in clay materials.

2.3. Cs, Am and Pu radionuclides distribution in the Curonian Lagoon and Baltic Sea system

^{137}Cs , ^{241}Am and $^{239,240}\text{Pu}$ isotopes were analyzed in seawater, bottom sediments and suspended particulate matter samples collected in the Baltic Sea during 2008–2011. The particle size distribution and sequential extraction studies were carried out with the aim to better understand the association of radionuclides with particles and their bonding patterns in the bottom sediments.

2.3.1. Activities of Cs, Pu and Am in the Curonian Lagoon and Baltic Sea system

The location of monitoring stations you can see in (Fig. 1.2) provides a reflection of the major impact of the Nemunas River and the Curonian Lagoon discharges as well as dumping and the overall level of pollution of the Baltic Sea. Seasonal investigations indicated that the area is characterized by variable loading with suspended particulate matter (SPM): from <2.0 to 304.0 mg/L in the Curonian Lagoon and from <2.0 to 18.5 mg/L in the Baltic Sea and that mean concentrations in the lagoon area tended to be approximately 3 times higher in comparison with those measured in the Baltic Sea (Lujanienė *et al.*, 2010). Total organic carbon (TOC) in bottom sediments (BS) samples ranged from $0.22 \pm 0.04\%$ to $12.6 \pm 0.4\%$ (mean value $2.7 \pm 0.1\%$, $n = 31$), while TOC in SPM varied from $8.6 \pm 0.3\%$ to $21.3 \pm 0.6\%$ (mean value $13.6 \pm 0.1\%$, $n = 10$) and higher values were observed in the Curonian Lagoon. In the Baltic Sea the highest TOC values were found in the bottom sediments collected in the accumulation zone located at the wash of the Nemunas River (sampling stations R7, 9, 12A).

Activities of Cs, Pu and Am measured in 1997–2012 are summarized in (Table 2.5). Wide ranges in the ^{137}Cs activities are due to its removal from the water column over a long observation period, different sampling station locations, seasonal variations, peculiarities of transport and resuspension. Association of ^{137}Cs with SPM and BS and its sorption to suspended solids have been described in previous publications by (Lujanienė *et al.*, 2012).

Table 2.5. Ranges of ^{137}Cs , $^{239,240}\text{Pu}$, ^{241}Am activities in the Baltic Sea and Curonian Lagoon samples. Baltic sea sample (a), Curonian Lagoon samples (b)

Sample type	^{137}Cs (Bq/L, Bq/kg)	$^{239,240}\text{Pu}$ (Bq/L, Bq/kg)	^{241}Am , (Bq/L, Bq/kg)
Open sea waters ^a	0.014-0.12	-	-
Near shore waters ^a	0.037-0.12	$2-4 \cdot 10^{-5}$	-
Suspended particles ^a	50-370	0.16-8	0.13-1.9
Suspended particles ^b	20-250	-	-
Bottom sediments ^a	2-588	0.03-7.5	0.001-2.2
Open waters ^b	1.1-26.4	-	-
Bottom sediments ^b	0.4-208	-	-

Results obtained from the laboratory kinetic tracer experiments with the bottom sediments derived from the Baltic Sea showed variations in kinetic coefficients from $3.11 \cdot 10^{-2}$ to $9.9 \cdot 10^{-2} \text{ min}^{-1}$ and in K_d values from $1.02 \cdot 10^2$ to $1.02 \cdot 10^3 \text{ ml/L}$, the latter decreased with a decrease in the particle size and an increase in clay mica minerals in samples. These data were used to study Cs sorption mechanisms in the Baltic seawater and it was found that the modeled data best conformed to the mechanism of ion diffusion through the inert layer on the surface of the sediment particles (Lujanienė *et al.*, 2006 a).

The measured Pu and Am activities in seawater, suspended particulate matter and bottom sediments samples (Table 2.5) are in agreement with results published for the Polish economical zone (Struminiska-Parulska *et al.*, 2012 and Skwarzec *et al.*, 2011). The highest actinide activities were detected in the BS collected in the accumulation zone (sampling stations R7, 9, 12A).

2.3.2. Association of ^{137}Cs , $^{239,240}\text{Pu}$ and ^{241}Am with particles of various sizes in bottom sediments

A limited number of samples analyzed concerning the size of particles carrying ^{241}Am and $^{239,240}\text{Pu}$ showed that they were associated with particles of similar sizes as that of ^{137}Cs both in bottom sediments ($n = 5$) and suspended particulate matter ($n = 3$) (Fig. 2.8). ^{137}Cs was bound to fine particles of $0.2-1.0 \mu\text{m}$ and $1.0-4.0 \mu\text{m}$ ($n = 20$) while the highest activities (from 120 ± 10 to $1450 \pm 140 \text{ Bq/kg}$) were found in the fraction of $0.2-1.0 \mu\text{m}$ of bottom sediments. Although a comparatively good correlation of ^{137}Cs activities with TOC ($r = 0.75$) and clay minerals ($r = 0.95$) was observed based on the

sequential and mineral composition studies, it was concluded that ^{137}Cs was mainly adsorbed on clay particles in the SPM and BS (Lujanienė *et al.*, 2010). $^{239,240}\text{Pu}$ ($r = 0.98$, $n = 31$) and ^{241}Am ($r = 0.96$, $n = 23$) activities correlated well with TOC in bottom sediments. Correlation of Pu and Am with TOC in suspended particulate matter was estimated for samples collected in the Baltic Sea in October 2001 when high water volumes were filtrated in situ through 1 μm filters. $^{239,240}\text{Pu}$ and ^{241}Am behavior was found to be rather different as compared to that of ^{137}Cs (Lujanienė *et al.*, 2010).

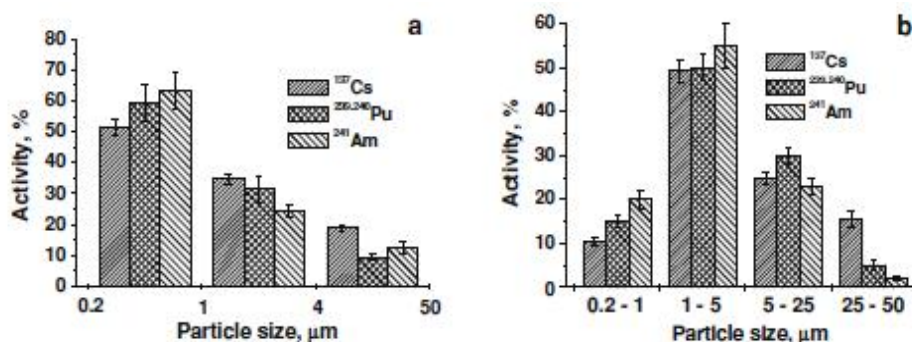


Fig. 2.8. Association of ^{137}Cs , $^{239,240}\text{Pu}$ and ^{241}Am with particles of various sizes (a) in bottom sediments (station R7, $n = 5$), (b) suspended matter ($n = 3$) in the Baltic Sea

Weak correlation ($r = 0.53$, $n = 5$) of actinides with particulate organic carbon (POC) and weak negative correlation ($r = -0.50$, $n = 5$) with dissolved organic carbon DOC were found while they well correlated with the POC/DOC ratio ($r = 0.89$, $n = 5$). It seems that competitive reactions with organic matter (humic substances) present in seawater and SPM could affect association of actinides.

2.3.3. The distribution ^{137}Cs , $^{239,240}\text{Pu}$ and ^{241}Am of the Baltic Sea bottom sediments in sequential extraction fractions

The characterize the bonding of radionuclides, bottom sediments from R7 site (selected as representative of the radiological monitoring in the Lithuanian economical zone, $55^{\circ}36.6' - 20^{\circ}20'$, depth 77 m) were analyzed by sequential extraction and alkaline extraction. The BS from sampling station R7 were characterized as mud silty fine grained (Fe, 1.1 % (including Fe(II) 21 %), TOC 7.4 %, clay 12.0 %, illite 20.0 %, calcite 15.0 %).

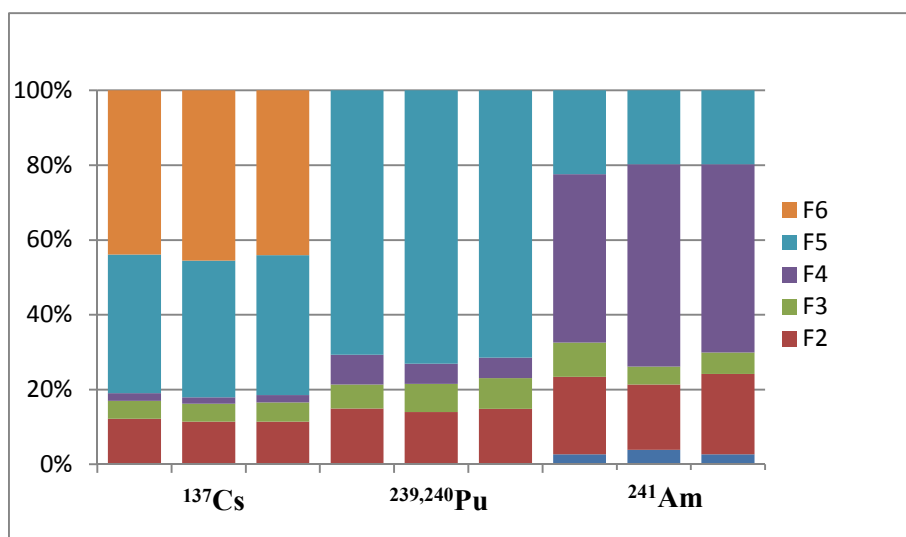


Fig. 2.9. Speciation of Cs, $^{239,240}\text{Pu}$ and ^{241}Am in bottom sediments samples (1–70 g, 2–100 g, 3–90 g, collected at station R7),(F1-exchangeable (0.1 mol/L MgCl_2), F2-carbonates (1 mol/L NH_4Ac in 25 % HAc), F3-oxides (0.04 mol/L $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25 % CH_3COOH), F4-organic substances (30 % H_2O_2 at pH 2 (HNO_3), F5– residue (4 mol/L HNO_3), F6–residue);

The ^{137}Cs distribution typical of the Baltic Sea bottom sediments in sequential extraction fractions was found (extracted with 4 mol/L HNO_3 ($37.0 \pm 3\%$) and in residue determined by gamma spectrometry ($45.0 \pm 4\%$) (Figure 3.9). This is an indication of its strong bonding to the bottom sediments including sorption to interlayer sites of the clay minerals. A small portion of ^{137}Cs determined in carbonate fractions ($11.0 \pm 1\%$) can be attributed to the coatings on clay minerals and/or desorption of Cs from the frayed edge sites by NH_4^+ ions present in the extraction solutions. It can be seen that the largest amount of Pu was also associated with residue. Small portions of Pu were associated with oxides ($8.0 \pm 0.7\%$), OM ($6.0 \pm 0.5\%$) and carbonates ($14.0 \pm 1\%$). Different distribution of ^{241}Am among SE fractions as compared to that of ^{137}Cs and $^{239,240}\text{Pu}$ was found (Fig. 2.9).

Data on ^{137}Cs , $^{239,240}\text{Pu}$ and ^{241}Am bonding to humic substances corroborated the results obtained by sequential extraction (Fig. 2.10). Cs and Pu isotopes were mostly associated with the residue containing clay particles, humins and inorganic compounds, while $53.0 \pm 5\%$ of Am was distributed among humic and fulvic acids. The large portion of Am bound to carbonates, fulvic acids and especially to dialysable fulvic acids indicated its

higher potential to migrate. Thus, both ^{137}Cs and $^{239,240}\text{Pu}$ bonding to bottom sediments can be considered as a strong while ^{241}Am bonding can be characterized as weaker and ^{241}Am should be more mobile in the marine environment.

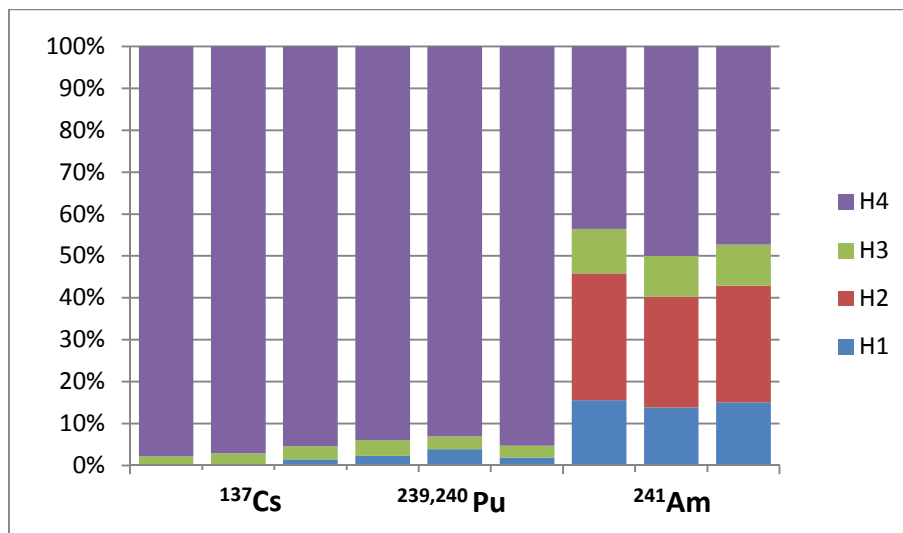


Fig. 2.10. Distribution of radionuclides in organic matter fraction. H1-humic acids (extracted with 0.5 mol/L NaOH, precipitated by HCl at pH = 1), H2-fulvic acids (supernatant after precipitation and dialyzes), H3- dialyzable fulvic acids (capable to diffuse through the 5 kD membrane), H4-residue.

The study of radionuclides Cs, Am and Pu distribution in the Curonian Lagoon–Baltic Sea system showed that activities of ^{137}Cs in bottom sediments varied from 2.1 to 588 Bq/kg. High correlation of ^{137}Cs activities with total organic carbon (TOC) in bottom sediments ($r = 0.75$) and with clay minerals ($r = 0.95$). $^{239,240}\text{Pu}$ activities in bottom sediments varied from 0.03 to 7.5 Bq/kg. High correlation with total organic carbon TOC was found for $^{239,240}\text{Pu}$ ($r = 0.98$) as well as for ^{241}Am ($r = 0.96$).

CONCLUSIONS

1. The obtained results show that for removal of Cs the best are titanium silicates that synthesized on TiOSO_4 ($\text{Na}_2\text{Ti}_2\text{SiO}_7 \cdot 2\text{H}_2\text{O}$) basis. For the actinide removal it is better to use iron oxides (magnetite - Fe_3O_4 , goethite - $\alpha\text{-FeOOH}$, hematite - $\alpha\text{-Fe}_2\text{O}_3$). Magnetite showed better sorption ability to americium. Plutonium showed 6.8 times higher sorption capacity to the magnetite / hematite mixture compared to pure magnetite.
2. The obtained results show that Pu and Am sorption kinetics on natural clay substances is controlled by diffusion in the inert layer of the solid phase (ID) control process. The exception is the only in the case of the Pu sorption to clay 7 when sorption is controlled by chemical reaction (CR) control process. The difference is due to higher concentration of carbonate minerals in clay 7. The sorption half-time of <2 min for ID kinetic and <4 min for CR kinetics. Data of Pu(IV) and Am(III) sorption on clay materials obtained during the long-term (361 days, 5-520000 min) experiment indicated that exchangeable and carbonate species of Am(III) are formed in the first 50 minutes. Pu(IV) was associated with amorphous oxides and natural organic matter.
3. The activity of ^{137}Cs , ^{241}Am , ^{240}Pu ranged from 2.1 Bq / kg to 588 Bq / kg in the Baltic sea sediments, respectively and correlated with TOC ($r = 0,75$). The presence of organic matter in bottom sediments was confirmed by FT-IR, ^1H and ^{13}C NMR spectra.
4. Iron oxides, organic compounds and clay minerals are responsible for strong bonding of Cs and Pu radionuclides with bottom sediments. Interaction of Am(III) with bottom sediments is weaker and ^{241}Am should be more mobile in the marine environment.

SANTRAUKA

Disertacijoje yra nagrinėjami Cs(I), Pu(IV) ir Am(III) radionuklidų sorbcijos kinetikos procesai ant sintetinių (geležies oksidų ir titano silikatų) ir natūralių sorbentų (Šaltiškių molio), taip pat yra tiriamas ^{137}Cs , $^{239,240}\text{Pu}$ ir ^{241}Am radionuklidų pasiskirstymas dugno nuosėdų ir suspenduotų kietųjų dalelių mėginiuose. Svarbiausi junginiai esantys natūralaus molio mineralų paviršiuje, turinčių įtakos radionuklidų sorbcijai, yra geležies oksidai, karbonatai ir organinės medžiagos. Gamtinės organinės medžiagos (humuso medžiagos), esančios molio ir dugno nuosėdų sudėtyje, gali paveikti sorbcijos procesus. Humuso medžiagos atlieka svarbų vaidmenį radionuklidų migracijai aplinkoje. Norint geriau suprasti radionuklidų elgseną natūralioje aplinkoje, šiame darbe atliktas tiriamųjų radionuklidų Pu(IV) ir Am(III) sorbcijos eksperimentas ant natūralaus molio mineralų geologinių formų laiko intervale (361 dienos).

Gauti rezultatai rodo, kad Cs izotopai geriausiai pašalinami naudojant titano silikatus. Aktinoidų pašalinimui geriausiai tinka geležies oksidai (magnetitas - Fe_3O_4 , getitas - $\alpha\text{-FeOOH}$, hematitas - $\alpha\text{-Fe}_2\text{O}_3$). Magnetitas geriausiai sorbuoja američių. Plutonis turi 6,8 kartų didesnę sorbcinę gebą magnetito/hematito mišiniui lyginant su grynu magnetitu.

Nustatyta, kad Pu(IV) ir Am(III) sorbcijos kinetika ant natūralaus molio medžiagų yra kontroliuojama difuzijos kietosios fazės inertiniuose sluoksniuose (ID) vyksmų. Išimtį sudaro tik Pu sorbcijos atvejis molyje 7, kai sorbcija yra kontroliuojama cheminės reakcijos (CR) vyksmo. Skirtumas atsiranda dėl molyje 7 esančios didesnės karbonatinių mineralų koncentracijos. Pu(IV) ir Am(III) sorbcijos eksperimentas ant molio medžiagų laiko intervale (361 dienos, 5-520000 min) parodė, kad Am (III) sorbcija vyksta per pirmąsias 50 min. pakaitinėje ir karbonatinėje frakcijose. Pu(IV) sorbcija vyksta amorfinių oksidų ir organinių junginių frakcijoje.

Nustatėme, kad ^{137}Cs , $^{239,240}\text{Pu}$ ir ^{241}Am aktyvumai Baltijos jūros dugno nuosėdose kito atitinkamai nuo 2,1 Bq/kg iki 588 Bq/kg, koreliacijos koeficientas su TOC yra $r = 0,75$. Organinių medžiagų buvimą dugno nuosėdose patvirtino FT-IR, ^1H ir ^{13}C BMR spektrai. Gauti rezultatai rodo, kad ^{137}Cs ir $^{239,240}\text{Pu}$ radionuklidų sąveika su dugno nuosėdomis stipri dėl dugno nuosėdų sudėtyje esančių geležies oksidų, organinių junginių ir molio mineralų. Tuo tarpu ^{241}Am sąveika su dugno nuosėdomis yra silpnesnė ir dėl to galima teigti, kad ^{241}Am turėtų būti judresnis jūrinėje aplinkoje.

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