

**VILNIUS UNIVERSITY
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Justina Šapolaitė

**DYNAMICS OF RADIOACTIVE NUCLIDES IN HETEROGENEOUS
DISPERSIVE SYSTEMS**

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FIZIKOS INSTITUTAS**

Justina Šapolaitė

**RADIOAKTYVIŲJŲ NUKLIDŲ DINAMIKA HETEROGENINĖSE
DISPERSINĖSE SISTEMOSE**

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I. 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, 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 forced 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.

Performance assessment of radioactive waste disposal requires modelling of long-term migration of radionuclides through the engineered barriers and the geological environment. The chemical complexity of sorption–desorption processes is usually reduced to integrated parameter – distribution coefficients (K_d). There are a great number of publications on K_d determination, however, the existing data on K_d of radionuclides on different geological materials are for general understanding only and are not very useful for performance assessment since changes of the geological conditions result in variability of K_d values by two orders of magnitude. In order to obtain realistic sorption data sets for safety relevant radionuclides present in a cement/concrete based repository, preliminary studies were carried out. The development of sorption database for the near-surface repository was started with measurements of cesium, plutonium and americium K_d values. Samples of loam available at the Galilaukė site (Quaternary deposits) and Triassic clay from industrial Šaltiškiai quarry selected as a candidate for the engineered barrier of the Lithuanian near-surface repository were taken for laboratory investigations. Cs, Pu and Am K_d values were determined under a wide range of geochemical conditions. Changes in the geochemical conditions resulted in the variability of Cs, Pu and Am K_d values.

Kinetic sorption experiments indicated insignificant variation of sorption parameters depending on the chemical composition of groundwater and clay minerals.

Speciation studies showed the high content of exchangeable cesium up to 70% in experiments with high cesium concentrations. Results of kinetic tracer experiments and sequential extraction studies reveal differences in sorption mechanisms depending on the Cs concentration. Data obtained from sorption-desorption experiments were used to model sorption process by applying the kinetic 4-box model to describe the cation exchange processes at three sites of clay minerals with distinctly different selectivity. The obtained forward and backward exchange rate constants were used to calculate apparent equilibrium constants which ranged from 1 to 26 and the highest ones were found for reversible sites.

Oxidation–reduction reactions are of the top importance in the environmental chemistry. Plutonium redox chemistry is also complicated as speciation strongly affects its environmental behavior [1]. Many previous studies indicated transformation of Pu oxidation state through interactions with surfaces of Mn(IV) – bearing and iron oxide minerals [2, 3, 4]. Recent publications have shown that Pu oxidation states can also be strongly affected by natural organic substances [5, 6]. On the basis of lysimetric experiments with well-defined solid sources of Pu(III)(PuCl₃), Pu(IV)(Pu(NO₃)₄) and Pu(C₂O₄)₂, and Pu(VI)(PuO₂(NO₃)₂), it was concluded that Pu(III) may have a wide natural occurrence, especially in acidic environments [7]. Influence of biotic processes on transformation of redox speciation of radionuclides has also received considerable attention [8].

The main aim of doctoral dissertation

The aim of the work is to evaluate equilibrium and kinetic sorption parameters in heterogeneous systems as well as to investigate sorption mechanisms and processes responsible for radionuclide removal from liquid medium and retention by artificial and natural barriers.

The main tasks

The main tasks of the dissertation are:

1. To investigate the sorption ability of inorganic (titanium silicates and iron oxides) sorbents for Cs, Pu and Am elements and to evaluate their equilibrium and kinetic sorption parameters.

2. To investigate Cs, Pu and Am sorption dynamics to natural clay minerals and kinetics in a wide range of pH values under conditions maximally close to natural environment expected at radioactive waste repositories.
3. To evaluate the influence of Cs and other competing ion concentrations on the sorption and desorption process in heterogeneous systems: natural clay – groundwater.
4. To determine the sorption ability of minerals naturally present in clay coatings towards studied radionuclides.
5. To evaluate the oxidation reduction ability of natural clay and iron minerals using plutonium isotopes as an indicator.

Novelty

1. The sorption parameters of Cs, Pu and Am for newly synthesized inorganic sorbents (distribution coefficient (K_d), kinetic coefficients) have been evaluated. It has been determined that the magnetite/hematite composite is distinguished by better sorption ability towards plutonium isotopes as compared with pure magnetite. It is a promising sorbent for plutonium removal from contaminated solutions due to its better sorption parameters and because of application of magnetic methods in separation technologies.
2. It has been determined that the variation of sorption parameters (e.g., decrease in K_d values at high pH) in heterogeneous natural systems is complicated and does not correspond to the simplified laboratory experiments due to the effect of various factors.
3. Different Cs retention mechanisms by Šaltiškiai clay minerals have been determined for various Cs concentrations. At low concentration the illite minerals having high selectivity for Cs eliminate this element from various media but with the increase in its concentration and/or of competing ions the montmorillonite minerals of lower selectivity but larger sorption capacity take this role due to the lack of selective sorption places.
4. Iron and calcium minerals found in Šaltiškiai clay coatings play an important role in sorption of Am and Pu isotopes but the role of Mn minerals in retaining the actinides by this clay is negligible.

- Existing solvent extraction methods were applied and verified for Pu(III) determination in the liquid and solid phases of natural clay and goethite systems with 0.1 and 0.01 mol/L NaNO₃. The reductive ability of the Šaltiškiai clay and goethite as a natural component of its coatings has been determined using plutonium isotopes as an indicator of oxidation reduction reactions. Plutonium was found in the Pu(III) oxidation state which is important for the prediction of its sorption and migration behaviour.

Statements presented for defence

- It has been determined that titanium silicates synthesized using TiOSO₄ (Na₂Ti₂SiO₇·2H₂O) are the most suitable for Cs isotope removal from contaminated solutions. The best results for actinide elimination from liquid radioactive waste were obtained using iron oxides (magnetite - Fe₃O₄, goethite - α-FeOOH, hematite - α-Fe₂O₃).
- Complicated physical-chemical conditions, cement - concrete degradation and rainwater - cement water evolution in the heterogeneous environment of the cement - concrete based repository determine sorption behavior of radionuclides. Gradients of various ions released into solutions, changes in pH values and formation of various complexes have a great effect on the radionuclide sorption behavior in this multicomponent system. Such complicated systems must be analyzed as close as possible to natural ones to ensure reliable prediction.
- Different sorption dynamics, kinetics and selectivity towards Cs, Pu and Am radionuclides determine the existence of various sorption sites, their concentrations at the Šaltiškiai clay mineral surfaces as well as changes in the Pu oxidation state during its interaction with Šaltiškiai clay mineral components.

II. OBJECT OF THE STUDY AND USED METHODS

Synthesized sorbents (both titanium silicates and iron oxides) and natural clay minerals were used in sorption experiments. The BET surface area and pore volume of studied sorbents were determined using the nitrogen adsorption/desorption method at the liquid nitrogen temperature by means of a surface area analyzer NOVA 2200. The pore size distribution was determined according to the BJH method using the desorption

branch of the isotherms. The X-ray diffraction studies of the prepared Ti-Si 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 [9].

Samples of loam originated from the Galilaukė site (Galilaukė clay) and Triassic clay from industrial Šaltiškiai quarry (Šaltiškiai clay) selected as a candidate for the engineered barrier of the Lithuanian near-surface repository were taken for laboratory investigations. X-ray diffraction analyses show about 14% of montmorillonite in Šaltiškiai clay. The mineral composition of Šaltiškiai clay was estimated as follows: SiO_2 – 45.51%, Al_2O_3 – 13.49%, Fe_2O_3 – 5.17% MgO – 2.99%, CaO - 12.88%, Na_2O – 0.28%, K_2O – 5.02%, TiO_2 – 0.43%, total S – 0.16%, loss on ignition 13.95% [10]. Samples of the natural groundwater (GW) from well No 5 of the Galilaukė site and the synthetic rain water (SRW) (filtered through the 0.45 μm membrane filter) were put into contact with the solidified locally available Portland cement (from “Akmenės cementas”) to obtain the extracts of groundwater - cement water (GWCW) and synthetic rainwater - cement water (SRWCW) solutions. The particles of different sizes of solidified cement were used in the experiments. The chemical composition of rainwater, groundwater and the cement water solutions was determined by the AAS and the ion chromatography techniques (Table 1). The composition of rainwater was estimated taking into account the long-term studies performed in Lithuania [11].

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 ($\alpha\text{-FeOOH}$) and the trace amount of $\epsilon\text{-Fe}_2\text{O}_3$ mineral which is rare intermediate between maghemite and hematite was determined by Mössbauer spectrometry in Šaltiškiai clay [12].

Table 1. Chemical composition of solutions used in sorption experiments.

	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
Groundwater GW1	94.8	8.29	59.0	6.90	25.0	40.4	473	7.81	-60.1	1.09
Groundwater- cement water GWCW	109	206	49.0	370	183	0.01	45.3	12.6	-335	8.04
Groundwater GW4	40.3	22.4	10.4	1.90	139	39.7	517	7.16	-71.7	0.86
Groundwater GW6	22.8	5.20	5.20	1.60	89.6	24.9	367	7.47	-69.8	0.54
Synthetic rainwater SRW	1.22	0.75	0.58	0.14	0.42	-	90.0	4.89	108	0.23
Synthetic rainwater- cement water SRWCW	2.90	345	22.6	545	96.8	0.03	53.6	11.6	-283	2.15

The laboratory batch method was applied to determine the distribution coefficient (K_d) values of Cs, Pu and Am radionuclides. The protocol of the standard method used at Pacific Northwest National Laboratory for measuring laboratory batch K_d values was applied [13].

The total concentrations of cesium in solutions were $2.30 \cdot 10^{-10} \text{ mol} \cdot \text{L}^{-1}$ and $6.80 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ (the solutions were labeled by ¹³⁴Cs). A mixture of Pu(IV) isotopes was used in sorption experiments. The oxidation state purity of Pu (IV) stock solution was analyzed by solvent extraction at pH 0.5 using $0.5 \text{ mol} \cdot \text{L}^{-1}$ thenoyl-trifluoro-acetone (TTA) as extractant. Typically $96 \pm 3 \%$ of the total plutonium was found in the tetravalent state. Starting concentrations of Pu(IV) and ²⁴¹Am were $1.10 \cdot 10^{-9}$ and $3.20 \cdot 10^{-11} \text{ mol} \cdot \text{L}^{-1}$, respectively.

¹³⁴Cs activities were measured with an intrinsic germanium detector (resolution 1.9 keV/1.33 MeV and efficiency 42 %). Plutonium and americium in the solution and the solid-phase were determined after radiochemical separation using the UTEVA and TRU (Eichrom Industries), and/or NdF₃ precipitation and activities were measured by alpha spectrometry. ²⁴²Pu and ²⁴³Am were used as tracers in the separation procedure. Precision of radionuclide measurements by gamma- alpha- spectrometry was: Cs $\leq 2\%$, Pu $\leq 5 \%$, Am $\leq 7 \%$.

The association of sorbed Cs, Pu and Am in geological material was determined using the sequential extraction procedure [14, 15]. Exchangeable and carbonate bound Cs was extracted using 1 mol·L⁻¹ NH₄C₂H₃O₂ pH 5 CH₃COOH extracting agent.

Oxidation state distribution analysis employs an ultrafiltration/solvent extraction technique. TTA, HDEHP and DBM were used as described in literature [6-8]. In experiments with Pu(IV) and natural clay a liquid-phase from solids was separated by centrifugation and Pu(III,IV), Pu(IV polymeric), Pu(V) and Pu(VI) were extracted from the aqueous-phase using TTA and HDEHP. Pu was desorbed from the solids with 3 mol·L⁻¹ HCl for 1 h. Solutions were filtered using 10 kD centrifugal filter devices (Amicon, Millipore). An aliquot of the filtrate was removed to determine oxidation state distribution by solvent extraction, and fractions of Pu(III,IV), Pu(V), Pu(VI) were separated using TTA and HDEHP as well as Pu(IV) extraction was performed in parallel by TTA from a pH 0 solution. In experiments with Pu(V) and goethite all samples were separated from solids by centrifugation followed by ultrafiltration prior to solvent extraction. Analysis of oxidation state distribution in the solid-phase was carried out using TTA and HDEHP solvent extraction as discussed above, whereas for analysis of the liquid-phase both TTA/HDEHP and DBM extraction techniques were applied. ²⁴¹Am(III), ²²⁸Th(IV), ²³⁷Np(V) and ²³²U(VI) as oxidation state analogs for Pu(III), (IV), (V) and (VI) as well as ²⁴²Pu(IV), ²³⁶Pu(III) were used to establish effective leaching conditions of Pu from the solid-phase, and to validate oxidation state analysis procedure.

III. EXPERIMENTAL RESULTS AND ANALYSIS

3.1. Sorption of Cs, Pu and Am to synthesized inorganic sorbents

Some studies were performed in order to determine the sorption ability of synthesized inorganic sorbents towards Cs, Pu and Am. The highest K_d values were found for the system groundwater - TiSi ion exchangers. Cs K_d for the inorganic sorbents and 0.1 mol·L⁻¹ NaNO₃ solutions varied from 40500 to 30 mL/g and decreased in the following order: TiSi 59(Cl)> TiSi 20(Cl)> TiSi 55(Cl)> TiSi 17(SO₄)> TiSi 30(SO₄)> TiSi 32(SO₄)> Clay > TiSi 57+58(Cl)> TiSi 82-1> TiSi 86-1>TiSi 84-3> TiSi 86-4> TiSi 82'-1> TiSi 84-4> TiSi 40> TiSi 82-3 > Magnetite. Pu K_d varied from 4600 to 200 mL/g and decreased in the following order: TiSi 17(SO₄)> TiSi 55(Cl)> Clay> TiSi 84-3> TiSi 30(SO₄)> TiSi 57+58(Cl)> TiSi 59(Cl)> TiSi 82-3> TiSi 86-4> TiSi 82'-1>

TiSi 40> TiSi 32(SO₄)> TiSi 82-1> TiSi 84-4> TiSi 86-1, whereas Am K_d ranged from 12000 to 50 mL/g and the following sequence was determined: Magnetite> Clay > TiSi 84-3> TiSi 84-4> TiSi 82-3> TiSi 82-1> TiSi 86-4> TiSi 57+58(Cl)>TiSi 32(SO₄).

Sorbent TiSi-17 showed the highest Pu K_d value for 0.1 mol·L⁻¹ NaNO₃ solution which is usually used to model fuel pond water with the 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 suggested that Am K_d values are quite close to the Pu ones. Studies of Am sorption are in progress.

Preliminary data on Pu sorption to iron minerals are presented. K_d values ranged from 4750 to 16260 mL/g and 9000 to 257620 mL/g for Am and Pu, respectively, and the found values were in the close range as determined for natural clay. An increase in the Pu K_d value by a factor of ~7 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.

3.2. Kinetics of Cs, Pu and Am sorption to synthesized inorganic sorbents

Data on Pu sorption kinetics have indicated that rather short time is required to reach equilibrium (Fig. 1). Equilibrium was reached after about 2 hours of sorption. Kinetic data were fitted to the pseudo-first-order kinetic model: $q_t = q_e(1 - e^{-k_{ad}t})$, where q_t and q_e are Pu concentrations (mol/g) at time t and equilibrium ones, respectively, as well as k_{ad} (min⁻¹) is the pseudo-first-order rate constants. It can be seen from the obtained parameters that iron oxide kinetic data fit well the pseudo-first-order equation, whereas TiSis data require additional analyses. Pu K_d equilibrium ranged from 2500 to 4130 mL/g for studied sorbents TiSi-17(SO₄), TiSi-32(SO₄), TiSi-55(Cl) and TiSi-59(Cl).

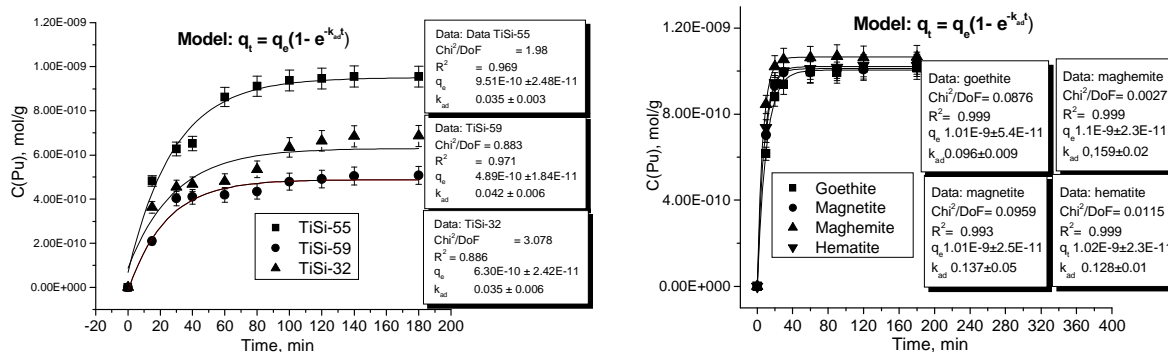


Fig. 1. Kinetics of Pu(IV) sorption to TiSi sorbents and Fe oxides (0.1 mol·L⁻¹ NaNO₃ solution, pH 6.08 – 7.02 ± 0.06, solid: liquid ratio 1: 1000 g/mL).

Sorption kinetics is an important parameter of sorbents reflecting their efficiency and cost. Kinetics data for four sorbents are presented in Fig. 2. Better sorption parameters were found for sorbents TiSi-112 and TiSi-100a when 90% of C_s was removed in the first 10 minutes. It can be explained by their structure. C_s kinetics data of sample TiSi-55(Cl) indicated that there is limitation on C_s ion diffusion into the mesoporous sorbent matrix. Studies of plutonium sorption kinetics indicated faster plutonium sorption to iron oxides in comparison to TiSi.

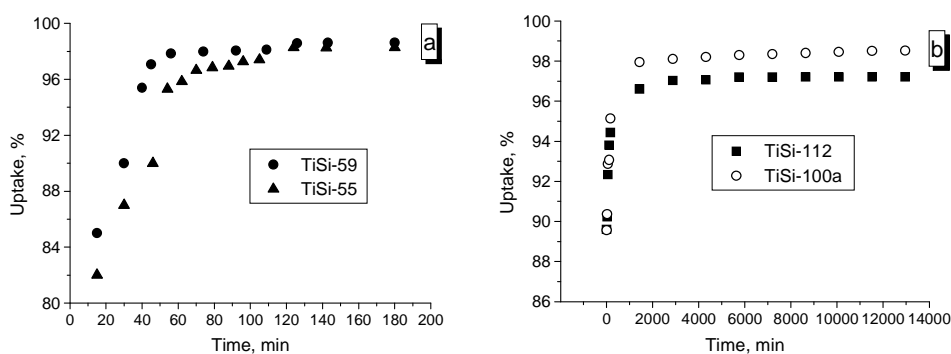


Fig. 2. Kinetics of Cs sorption to TiSi sorbents (0.1 mol·L⁻¹ NaNO₃ solution, pH 5.6 – 6.2 ± 0.1, solid: liquid ratio 1: 1000 g/mL).

3.3. K_d values of clay samples towards Cs, Pu and Am

To obtain cesium K_d values for the natural clay based on soil material originated from the Galilaukė site (Galilaukė clay) and montmorillonite clay (Šaltiškiai clay) selected as a candidate for the engineered barrier of the Lithuanian near-surface repository, SRW, GW, SRWCW and GWCW solutions were used (Table 1). K_d values

are in good agreement with presented ones in various publications and ranged from 9700 to 450 mL/g. The highest values were detected for natural groundwater. The Šaltiškiai clay exhibited the high retention capacity towards cesium. During interaction of precipitation and groundwater with cement and concrete the leached NaOH, KOH and later Ca(OH)₂ result in increase of pH (up to 10-13) and concentrations of K⁺, Na⁺, Ca²⁺, NH₄⁺ ions in the surrounding solution. The retardation of Cs can be decreased by competition with the dissolved cations. The low K_d values were expected under alkaline conditions (pH 11-13), however, comparatively low K_d values determined in experiments using SRW indicated that acid rainwater can affect the cesium retention. K_d values as a function of pH and ionic strength of contact solutions are presented in Fig. 3.

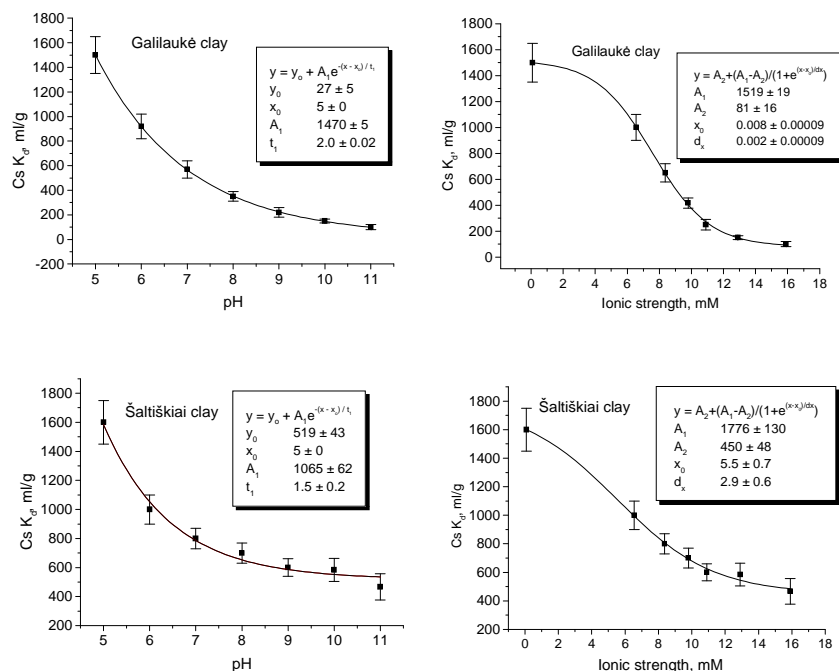


Fig. 3. Variations of Cs K_d values depending on pH and ionic strength of SRWCW solutions.

It was supposed that the pH and the chemical composition of rain and groundwater can vary under natural conditions depending on their contact time with cement material and/or different dissolution. Two sorption experiments were conducted. These studies showed the gradual decrease in Cs K_d values due to an increase in concentration of K⁺, Na⁺, Ca²⁺, NH₄⁺ in aqueous phase. Desorption experiments indicated that from 25 to 37% of reversibly sorbed cesium can be released to the surrounding solution during the

first week of the sorption experiment. The amount of desorbed cesium correlated with concentration of K^+ in initial solutions used in the sorption experiments. It seems that K^+ ions can compete with Cs for the FES and in such a manner can reduce the portion of irreversibly sorbed cesium.

The retardation factor (R_f) is the ratio of the pore-water velocity (v_p , cm/hr) to the contaminant velocity (v_c , cm/hr): $R_f = v_p / v_c$. Retardation factors of Cs (for rainwater experiment) versus the pH values and the concentration of K^+ , NH_4^+ ions which are able to compete with Cs for FES are plotted in Fig. 4. The values of Cs R_f decrease exponentially with an increase in the pH values and the concentration of NH_4^+ (for Šaltiškiai clay). In other cases the more complicated decrease which corresponds to the Sigmoidal (Boltzman) fit was observed.

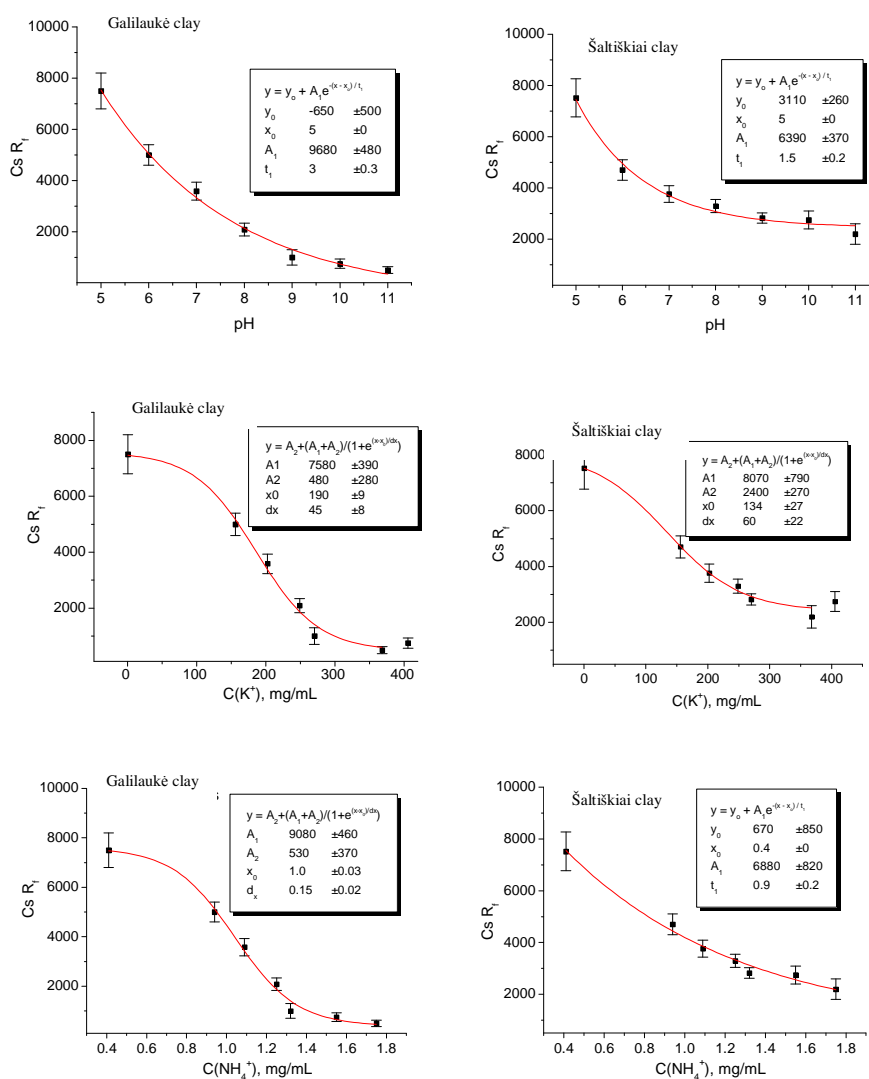


Fig. 4. $Cs R_f$ value variations depending on different chemical composition of rainwater-cement solutions.

3.4. Kinetics of Cs and Pu sorption to clay minerals

Data of sorption experiments using the clay sample No 6 and groundwater samples GW4 and GW6 (Data: 6_4 and 6_6) as well as the clay sample No 7 and groundwater samples GW4 and GW6 (Data: 7_4 and 7_6) are presented in Fig. 5. Very fast adsorption of Cs to clay minerals was observed in all four cases with residence time of Cs in the aqueous phase of about one day.

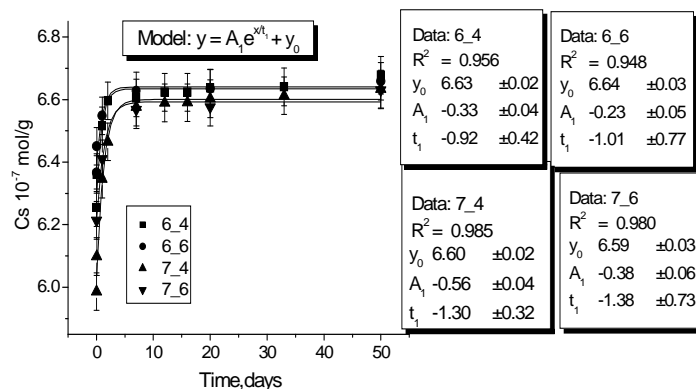


Fig. 5. Cs⁺ adsorption on clay minerals (Šaltiškiai clay samples No 6 and No 7 groundwater samples No 4 and 6) as a function of time ($C(\text{Cs}) = 6.80 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$).

3.5. The association of Cs with geological material

Sequential extraction experiments pointed out the small amount of irreversibly sorbed Cs in the residual fraction (Fig. 6).

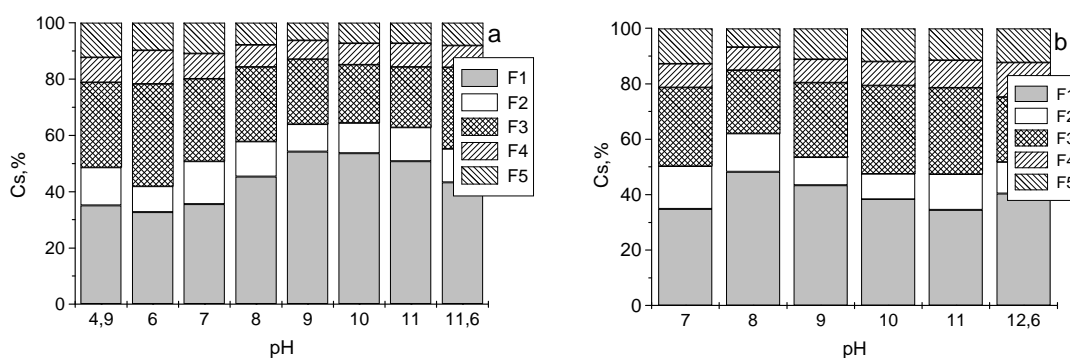


Fig. 6. Fraction distribution of Cs as function of pH after 10 days contact (a) Šaltiškiai clay-SRWCW and b) Šaltiškiai clay- GWCW), F1 exchangeable and bound to carbonates, F2 reducible, F3 bound to organic matter, F4, F5 residual.

The decrease in the Cs amount associated with the mentioned fractions was observed

after 45 days of sorption (Fig. 7).

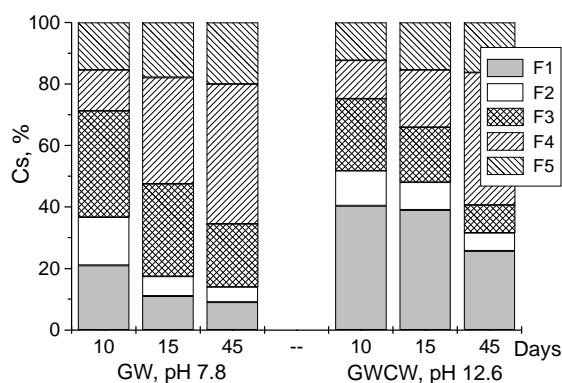


Fig. 7. Fraction distribution of Cs as function of time, Šaltiskiai clay-GW and GWCW, F1 exchangeable and bound to carbonates, F2 reducible, F3 bound to organic matter, F4, F5 residual.

Sequential extraction studies indicated that variations of cesium concentrations in the groundwater affected the partitioning of Cs to clay. The main differences deal with an amount of cesium sorbed to sites from which it can be easily desorbed (exchangeable fraction) and to sites from which it cannot be desorbed (acid soluble and residual fraction). Average values of Cs in both fractions in experiments with low and high concentrations are presented in Fig. 8. The decrease in the Cs amount in exchangeable fraction (exchangeable (2)) and the decrease in the Cs amount in residual fraction (residue (2)) were determined in experiments with low Cs concentrations, while no changes (exchangeable (1) and residue (1)) were observed in experiments with high concentrations. It can be explained by sorption of cesium to sites of different affinity. Generally, FES of micas and illites act as the high affinity sites, while basal and interlamellar regions of expansible layer silicates such as smectites act as lower selectivity sites. The studied clay consists mainly of smectite type minerals with the small amount of illite. Thus, the selective sorption sites of FES were available for Cs at illite and were capable to bind Cs at trace concentrations. In experiments with high Cs concentrations, almost all cesium was sorbed to smectite on sites of lower selectivity.

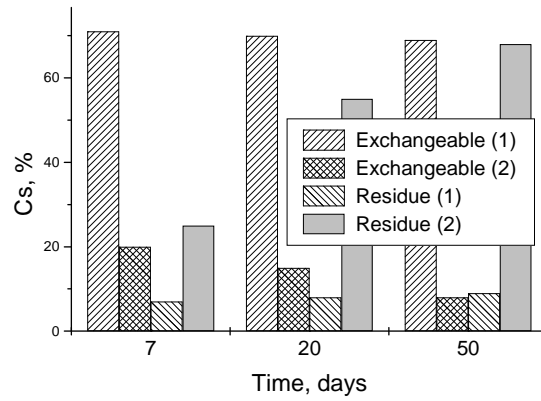
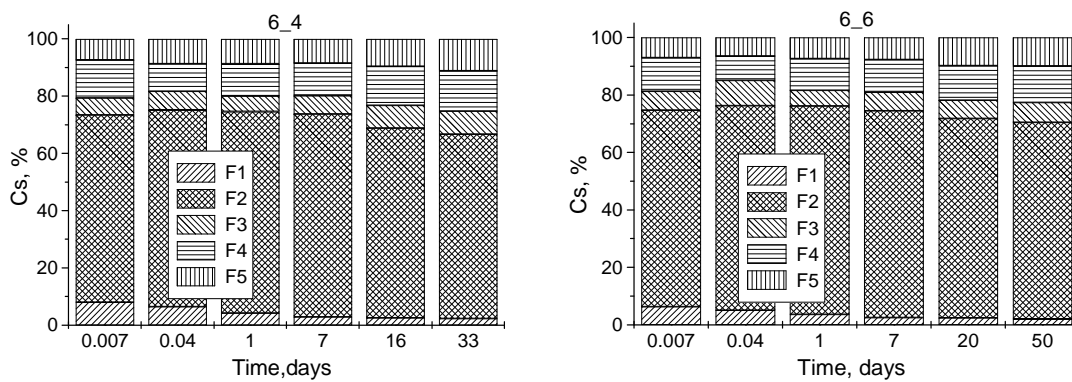


Fig. 8. Fraction distribution of Cs in Šaltiškiai clay (average data) as a function of time (exchangeable (1) and residue (1) with $C(Cs) = 6.80 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ and exchangeable (2) and residue (2) with $Cs C(Cs) = 2.30 \cdot 10^{-10} \text{ mol} \cdot \text{L}^{-1}$).

Data obtained from sorption-desorption experiments were used to model the sorption process. The kinetic 4-box model was used (Fig. 10) to describe the cation exchange processes on three sites of different selectivity. The sorption sites can be defined on the basis of sequential extraction data (Fig. 9).



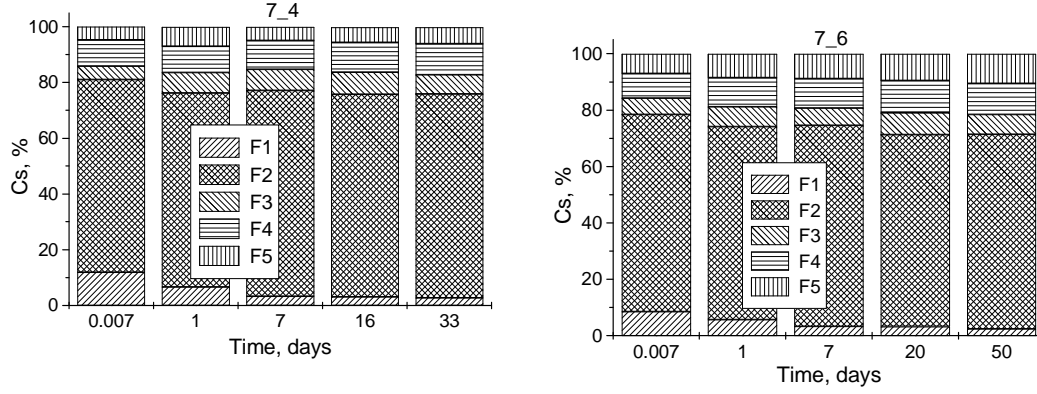
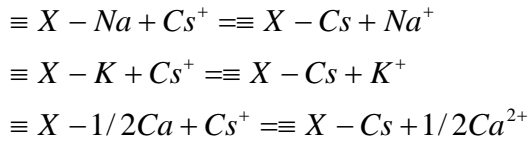


Fig. 9. Fraction distribution of Cs (Šaltiškiai clay samples No 6 and No 7 groundwater samples No 4 and 6) as a function of time. F1 – groundwater, F2 - exchangeable and bound to carbonates, F3 reducible, F4 bound to organic matter, F5 residual ($C(Cs) = 6,80 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$).

The main Cs^+ exchange reactions in the multicomponent system can be expected as follows:



The cation exchange of Cs^+ to layer silicates and soils is usually represented by a mass action equation of the following form:

$$Cs_{(aq)}^+ + \frac{1}{u} AX(i)_u = CsX(i) + \frac{1}{u} A_{(aq)}^{u+} \quad (1)$$

where u is the valence of ionic species A ; $AX(i)_u$ and $CsX(i)$ are the exchanger phase species of A^{u+} and Cs^+ ; and $Cs_{(aq)}^+$ and $A_{(aq)}^{u+}$ are aqueous species. The Cs distribution coefficient K_d is defined as:

$$K_d = \frac{[CsX(i)]}{[Cs_{(aq)}^+]} \quad (2)$$

The rate of exchange of Cs^+ is:

$$\frac{d[Cs_{(aq)}^+]}{dt} = -k_1 [Cs_{(aq)}^+] [AX(i)_u]_u^1 + k_{-1} [A_{(aq)}^{u+}]_u^1 [CsX(i)] \quad (3)$$

assuming a first order reaction kinetics and at a steady state or equilibrium:

$$K_{ap} = \frac{k_1}{k_{-1}} = \frac{[A_{(aq)}^{u+}]^u [CsX(i)]}{[Cs_{aq}^+][AX(i)_u]^u} \quad (4)$$

where K_{ap} is the apparent equilibrium constant; k_1 and k_{-1} are forward and backward reaction rate constants, respectively; $Cs_{(aq)}^+$ is the concentration of cesium in the aqueous phase (mol/ml) and $CsX(i)$ is the concentration of adsorbed cesium on the exchange site (i) (mol/g).

The Cs sorbed to the first type of sorption sites (box 2, concentration of radionuclide C_2) can be defined as reversibly sorbed Cs to clay, the amount of which was determined as the exchangeable fraction of the first step of sequential extraction (F2, Fig. 9). The Cs sorbed to the second type of sorption sites (box 3, concentration of radionuclide C_3) can be characterized as slowly reversible Cs, the release of which into solution is strongly dependent on oxidation-reduction processes in the system. The slowly reversible Cs was determined as Cs amount extracted during the sequential extraction analyses (the F3 and F4 fractions of which usually contain radionuclides bound to oxides and organic matter, respectively) (Fig. 9). The Cs sorbed to the third type of sorption sites (box 4, concentration of radionuclide C_4) can be described as partly or/and fully irreversibly sorbed Cs, the amount of which was estimated as the residual fraction of the sequential extraction (F5, Fig. 9). The definition of sorption sites is quite conditional because of heterogeneous origin of the natural geological material containing the various sorption sites of different selectivity. The sorption sites were defined on the basis of desorption capabilities and on the general knowledge about sorption of cesium to clay minerals.

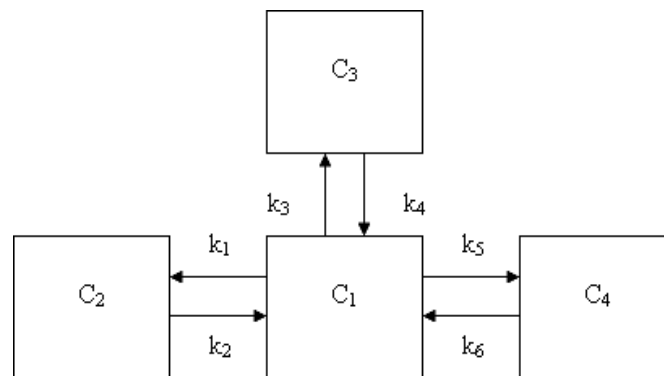


Fig. 10. Schematic representation of the kinetic 4-box model.

The kinetic equations of 4-box model are:

$$\frac{dC_1}{dt} = -k_1C_1 + k_2C_2 - k_3C_1 + k_4C_3 - k_5C_1 + k_6C_4 \quad (5)$$

$$\frac{dC_2}{dt} = k_1C_1 - k_2C_2 \quad (6)$$

$$\frac{dC_3}{dt} = k_3C_1 - k_4C_3 \quad (7)$$

$$\frac{dC_4}{dt} = k_5C_1 - k_6C_4 \quad (8)$$

where C_1 is the concentration of the radionuclide in solution, C_2 is the concentration of reversibly sorbed Cs, C_3 is the concentration of slowly reversible Cs, C_4 is the concentration of irreversibly sorbed Cs and $k_1 - k_6$ are forward and backward exchange rate constants.

Table 2. Apparent equilibrium constants for Cs sorbed to reversible (1), slowly reversible (2) and irreversible (3) sites.

Site	Clay No6, GW4	Clay No6, GW6	Clay No7, GW4	Clay No7, GW4
1	18.6	26.4	18.2	23.4
2	5.3	6.7	4.5	6.1
3	2.6	3.0	1.3	3.1

We tried to describe complicated Cs sorption processes to the natural clay minerals which include sorption on reversible sorption sites and frayed edge sites as well as sorption sites containing iron and organic matter coatings (slowly reversible sites). The kinetic equations of the 4-box model were integrated and fitted to experimental results obtained from the kinetic tracer experiment using the least square procedure. The set of kinetic equations was integrated applying the Bader and Deuflhard method [16] which allows obtaining high accuracy even for stiff integral equations. The obtained forward and backward exchange rate constants were used to calculate apparent equilibrium constants which are presented in Table 2. The apparent equilibrium constants ranged from 1 to 26, and the highest ones were found for reversible sites. The reversible fraction indicates the possible radionuclide release into surrounding solution and, hence, the amount of cesium available for transport. Thus, knowledge about the apparent

equilibrium constants is important since the K_d values are very complicated functions of many parameters.

3.6. The association of Pu and Am with geological material

The sorption behavior of plutonium isotopes was studied using a sequential extraction method for better understanding their binding to geological material (Fig. 11). Large amounts of plutonium (from 10 to 62 %) were found to be associated with the reducible fraction (F2) and it decreased with an increase in pH. Pu removed with this fraction is usually interpreted as Pu bound with Fe and Mn (hydr)oxides. Pu K_d values correlated ($R=0.88$) with the amount of Pu associated with Fe/Mn oxides measured in reducible fraction of sequential extraction (Fig. 11, A and C).

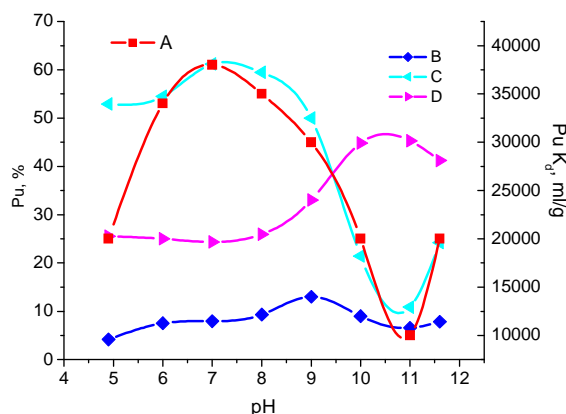


Fig. 11. Variations of plutonium K_d values (A) and percentage of sorbed Pu to various geochemical phases (B – carbonate, C – Fe/Mn oxide, D – residue) depending on pH of solutions.

Variations of Pu speciation in clay under different sorption conditions were explained by Pu redox speciation found in groundwater and cement-water solutions and different iron oxide (α -FeOOH and α -Fe₂O₃) coatings were identified by Mössbauer spectrometry in the initial samples and after different steps of sequential extraction. The amount of leached Fe and Mn from the studied samples was determined by AAS. Comparatively similar amount of Mn found in all fractions can be interpreted as a trace amount of Mn oxides distributed almost equally between other minerals. Mn-oxides

were not identified by the X-ray diffraction analysis due to the small amount present and could not be taken into account in the explanation of the Pu sorption mechanism.

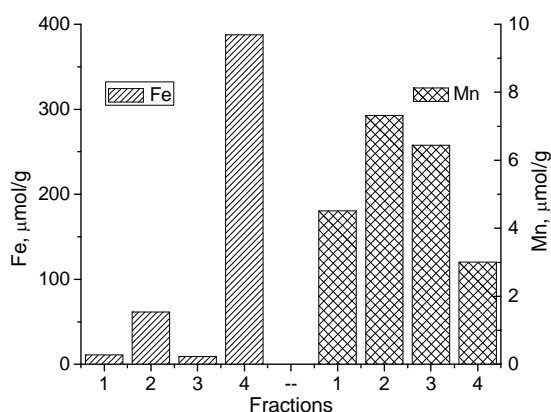


Fig. 12. Fe and Mn ($\mu\text{mol/g}$) leached during the extraction procedure (F1 exchangeable and bound to carbonates, F2 reducible, F3 bound to organic matter, F4 residue).

Rather different behaviour of Am was observed, up to 40% of Am was found in exchangeable and carbonate bound fractions. We suppose that sorption to carbonate minerals, coprecipitation and incorporation into calcite are responsible for higher Am K_d values in comparison with that of Pu K_d .

3.7. Plutonium oxidation state distribution in natural systems

Sorption and desorption tests using Am(III), Np(V) and U(VI) as oxidation state analogs for Pu(III), (V) and (VI) were conducted to determine appropriate condition to remove Pu from the solid-phase. Results indicated that Pu can be quantitatively desorbed (up to 96 ± 6 %) from solids, they are in good agreement with data obtained in different laboratories using Pu oxidation state analogs and sequential extraction procedures [16, 17]. Additional experiments performed using $^{242}\text{Pu(IV)}$, $^{236}\text{Pu(III)}$ indicated that Pu(III) and Pu(IV) remain stable during the desorption procedure using $3 \text{ mol}\cdot\text{L}^{-1}$ HCl.

Pu(IV) oxidation state distribution in the system of natural clay ($0.1 \text{ mol}\cdot\text{L}^{-1}$ NaNO_3 after 7-day contact time) is shown in Fig. 13.

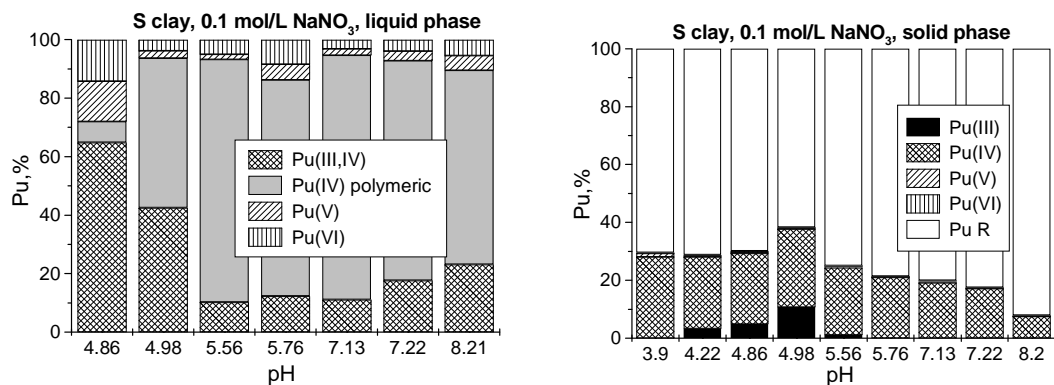


Fig. 13. Dependence of Pu oxidation state distribution on pH in the liquid-phase (L), the solid-phase (S) and the residue (R) of natural clay - $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaNO}_3$ system, $[\text{Clay}] = 64.2 \text{ m}^2/\text{L}$, initial $[\text{Pu}] = 1.10 \cdot 10^{-10} \text{ mol}\cdot\text{L}^{-1}$.

It can be seen (Fig. 13) that comparatively high content (up to 75%) of Pu(III, IV) was observed at pH 4.86 – 4.98, while polymeric species of Pu(IV) were found to be the dominant ones at pH 5.76 – 8.21 in the liquid-phase. The formation of $\text{Pu}(\text{OH})^{3+}$ and $\text{Pu}(\text{OH})_4^0$ species may explain this distribution [18].

Analyses of Pu oxidation state determination in the solid-phase (Fig. 13) were performed after the desorption step using $3 \text{ mol}\cdot\text{L}^{-1} \text{ HCl}$, and Pu(III, IV), Pu(V) and Pu(VI) as well as Pu(IV) at pH= 0 were analyzed in parallel. The content of Pu(III) was calculated from the reaction balance. Pu(III) was not found in the system at pH (5.76 - 8.2), while 4.9% and 10.7% of Pu(III) were found at pH 4.86 ± 0.11 and 4.98 ± 0.08 , respectively. Iron-bearing minerals such as montmorillonite, siderite, goethite and hematite determined in the studied clay to a great extent account for 10.7 % of Pu(III) in solids, because these minerals possess a reductive capacity and can cause the abiotic reductive transformation of plutonium [19]. It should be noted that adsorption experiments with clay and $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ NaNO}_3$, where oxidation state distribution analyses were performed using the DBM extraction procedure, also evidenced the presence of Pu(III) in the system. The observed high stability of Pu(IV) in the system may be attributed to two factors: a rapid adsorption to solids, and a strong hydrolysis at near-neutral and high pH.

Sorption behavior of plutonium in natural clay systems can be affected by a variety of reactions, including surface complexation, oxidation and reduction. Since iron oxides

and minerals found in Triassic clay coatings could alter the plutonium redox speciation in a different way, experiments were conducted with pure phases, and as the first approach with synthetic goethite and $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ NaNO}_3$ (at $\text{pH} = 4.89\text{-}5.01$).

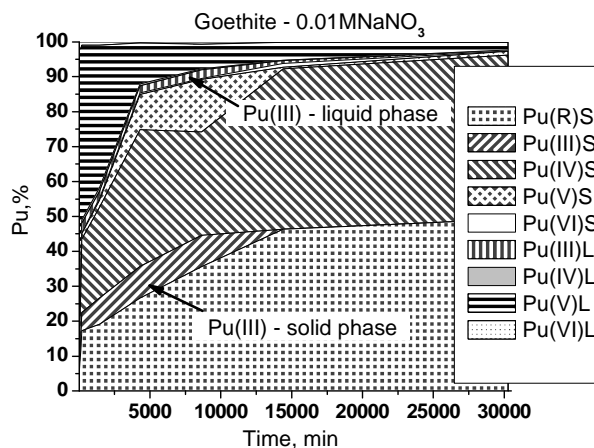


Fig. 14. Pu oxidation state distribution in the liquid-phase (L), the solid-phase (S) and the residue (R) of synthetic goethite - 0.01M NaNO₃ system, $[\alpha\text{-FeOOH}] = 172 \text{ m}^2/\text{L}$, $\text{pH} = 4.89\text{-}5.01$, initial $[\text{Pu}] = 2.50 \cdot 10^{-11} \text{ mol}\cdot\text{L}^{-1}$.

The oxidation state transformation of Pu(V) over time in the liquid- and solid-phase for the system containing Pu(V) is presented in Fig. 14. The obtained data revealed the complicated oxidation-reduction behaviour of Pu(V) in the system. It seems that Pu(V) after adsorption was reduced to Pu(IV), while a small portion reduced to Pu(III) was later oxidized to Pu(IV). Furthermore, a higher amount of Pu(III) was found in the solid-phase (up to 15%) in comparison with the liquid-phase, where it varied from 1 to 3%. It should be noted that the reduction of Pu(IV) to Pu(III) in the natural clay - $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaNO}_3$ system was expected because of rather high content of siderite determined in the studied clay coatings. Probably a long contact time and oxidation of Pu(III) in the system resulted in the low concentrations of Pu(III) measured in the solid-phase. However, Pu(III) concentrations found in the goethite solids after sorption are rather surprising and require additional studies, whereas minor concentrations of Pu(III) in the aqueous-phase are probably due to the absence of any ligand capable of stabilizing it in the system. We suppose that Pu(III) was quantitatively desorbed from the goethite solid since the amount of ^{241}Am found in the residue after the desorption step did not exceed 5%, however, the Pu amount in the residue has been increasing with contact time (Fig. 15).

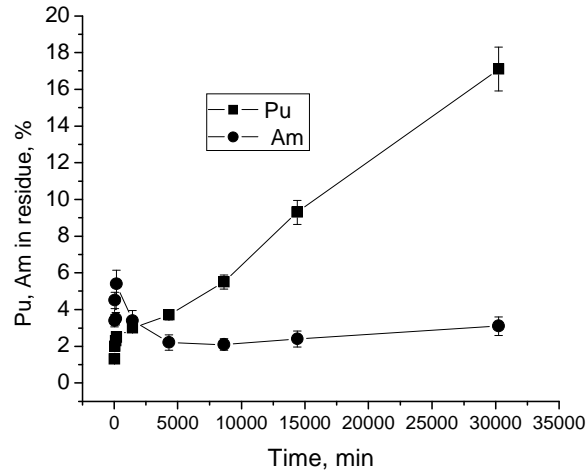


Fig. 15. Content of Pu and Am in the goethite residue after desorption.

This strong bonding to the solids can be explained by the Pu sorption to crystalline iron oxides present in the clay coatings, which was studied in kinetic sorption experiments followed by sequential extraction and Mössbauer spectroscopy. The slightly different adsorption/reduction patterns observed in this work when compared with tests performed by other researchers [8] are perhaps due to different experimental conditions and Pu concentrations used in experiments.

CONCLUSIONS

1. Extensive analyses of inorganic sorbent applications for removal of radionuclides from liquid radioactive waste have indicated that titanium silicates ($\text{Na}_2\text{Ti}_2\text{SiO}_7 \cdot 2\text{H}_2\text{O}$) synthesized using TiOSO_4 have the best sorption ability towards Cs isotopes (K_d varied from $6 \cdot 10^4$ to $4.1 \cdot 10^4 \text{ mL g}^{-1}$).
2. The largest Pu K_d values ($9 \cdot 10^3 - 6.2 \cdot 10^4 \text{ mL g}^{-1}$) and better sorption kinetics (kinetic coefficients varied from 0.096 ± 0.009 to $0.156 \pm 0.020 \text{ min}^{-1}$) were determined for synthesized iron oxides. An increase in Pu K_d values by a factor ~ 7 found in sorption experiments using the magnetite/hematite composite in comparison with the pure hematite implies that this sorbent is promising for Pu removal from contaminated solutions.
3. It has been found that gradients of competitive ion concentrations and variations in pH values can interfere Cs, Am and Pu retention by engineered barriers made from Šaltiškiai clay (Cs, Pu, Am K_d values ranged from 450 to $9.7 \cdot 10^3$, from $15 \cdot 10^3$ to $21 \cdot 10^3$ and from $15 \cdot 10^3$ to $8 \cdot 10^4 \text{ mL g}^{-1}$, respectively)
4. It has been found that different sorption mechanisms are responsible for Cs sorption by Šaltiškiai clay at low and high concentrations. Illite minerals can provide an effective immobilization of Cs at its low concentrations.
5. The similar geochemical partitioning of Cs, Am, Pu was found for Šaltiškiai clay No 6 and No 7 as well as groundwater samples GV4 ir GV6 (Cs, Pu, Am K_d values ranged from $5.27 \cdot 10^2$ to $6.35 \cdot 10^2$, from $1.62 \cdot 10^4$ to $9.40 \cdot 10^4$, from $1.88 \cdot 10^4$ to $4.38 \cdot 10^4 \text{ mL g}^{-1}$, respectively, Cs, Pu, Am kinetic coefficients varied from $4.55 \cdot 10^{-3}$ to $5.74 \cdot 10^{-3}$, from $6.96 \cdot 10^{-3}$ to $3.94 \cdot 10^{-2}$, from $3.29 \cdot 10^{-3}$ to $2.14 \cdot 10^{-2} \text{ min}^{-1}$, respectively). The highest equilibrium constants (from 18.2 to 26.4) were determined for exchangeable sorption sites for Šaltiškiai clay.
6. It has been found that plutonium isotopes are strongly bound to iron oxides naturally present in the clay mineral coatings of Šaltiškiai clay, K_d values obtained for the sorption of Pu on the clay well correlate (correlation coefficient $R= 0.88$) with the part of Pu found in sequential extraction fractions corresponding to the sum of iron hydroxides ($\text{Fe}(\text{OH})_3$), goethite ($\alpha\text{-FeOOH}$) and siderite (FeCO_3).
7. Solvent extraction techniques were verified with respect to determination of Pu(III) in the liquid- and solid-phase. Pu(III) was desorbed quantitatively from the solids, no

oxidation of Pu(III) and Pu(IV) was observed during desorption procedure. The reduction of Pu(IV) by natural clay containing iron-bearing minerals in the pH range from 4.22 to 4.98 was found, however, no reduction was detected at the near-neutral and high pH. In the kinetic sorption experiment with goethite - $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ suspensions, Pu(V) was mainly reduced to Pu(IV), and a small portion of Pu(III) found at the beginning in the solids (up to 15%) was later oxidized to Pu(IV).

The List of Original Publications by the Author

Publication on the Subject of the Dissertation

1. G. Lujanienė, S. Motiejūnas, J. Šapolaitė and Ž. Kamarauskas. Cs and Pu migration through engineered and natural barriers, *Lithuanian J. Phys.*, 45 (2005) 273.
2. G. Lujanienė, J. Šapolaitė, A. Amulevičius, K. Mažeika and S. Motiejūnas. Retention of cesium, plutonium and americium by engineered and natural barriers, *Czech. J. Phys.*, 56 (2006) 103.
3. G. Lujanienė, K. Mažeika, J. Šapolaitė, A. Amulevičius, and S. Motiejūnas. Kinetics of Cs sorption to clay minerals, *Lithuanian J. Phys.*, 46 (3) (2006) 375.
4. J. Šapolaitė, G. Lujanienė, A. Amulevičius, K. Mažeika and S. Motiejūnas. Study of sorption of cesium, plutonium and americium on clay minerals, *Radiation Interaction with Material and its use in Technologies 2006*, Kaunas, Lietuva (2006) 261.
5. G. Lujanienė, S. Motiejūnas, J. Šapolaitė. Sorption of Cs, Pu, Am on clay minerals. *J. Radioanal. Nucl. Chem.*, 274 (4) (2007) 345.
6. G. Lujanienė, S. Meleshevych, V. Kanibolotsky, K. Mažeika, V. Strelko, V. Remeikis, V. Kalenchuk, and J. Šapolaitė. Synthesis and characterization of inorganic sorbents and their application to sorption of radionuclides. *Lithuanian Journal of Physics*, 48 (1) (2008) 107.
7. G. Lujanienė, P. Beneš, K. Štamberg, K. Mažeika, D. Vopalka and J. Šapolaitė. Study of Iron Oxide Coating Effects on Cs, Pu and Am Sorption to Clays, *Seventh International Conference on Nuclear and Radiochemistry*, Budapest, Hungary (2008) 1.
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9. G. Lujanienė, S. Meleshevych, V. Kanibolotsky, J. Šapolaitė, V. Strelko, V. Remeikis, O. Oleksienko, K. Ribokaitė, T. Ščiglo. Application of inorganic sorbents for removal of Cs, Sr, Pu and Am from contaminated solutions, *J. Radioanal. Nucl. Chem.* (2009) (in press).

10. G. Lujanienė, J. Šapolaitė, E. Radžiūtė, V. Aninkevičius. Plutonium oxidation state distribution determination in natural clay and goethite, *J. Radioanal. Nucl. Chem.* (2009) (in press).

Approbation of the Results in Conferences

1. G. Lujanienė, S. Motiejūnas, J. Šapolaitė, Cs, Pu ir Am migracija pro dirbtinius ir gamtinius barjerus, 36-oji Lietuvos nacionalinė fizikos konferencija, Vilnius, Lietuva, birželio 16-18 d., 2005.
2. G. Lujanienė, S. Motiejūnas, J. Šapolaitė and Ž. Kamarauskas, Sorption of Cs, Pu and Am on clay minerals, The international Conference on Application of Radionuclides in Chemical, Environmental and Biological Sciences, Kolkata, India, 23-27 January, 2006.
3. G. Lujanienė, S. Motiejūnas, J. Šapolaitė and Ž. Kamarauskas, Retention of caesium, plutonium and americium by engineered and natural barriers, 15th Radiochemical Conference, Marianske Lazne, Czech Republic, 23-28 April, 2006.
4. G. Lujanienė, J. Šapolaitė, A. Amulevičius, S. Motiejūnas, Study of sorption of cesium, plutonium and americium on clay minerals, International Symposium, „In-situ Nuclear Metrology as a tool for Radioecology“, Kusadasi, Turkey, 6-8 September, 2006.
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8. J. Šapolaitė, G. Lujanienė, Plutonio oksidacijos laipsnio nustatymo metodai įvairios matricos skysčiuose, 37-oji Lietuvos nacionalinė fizikos konferencija, Vilnius, Lietuva, birželio 11-13 d. 2007 m.

9. G. Lujanienė, K. Mažeika, J. Šapolaitė, A. Amulevičius, Cs, Pu ir Am sorbcijos mechanizmų molio mineraluose tyrimai, 37-oji Lietuvos nacionalinė fizikos konferencija, Vilnius, Lietuva, birželio 11-13 d. 2007 m.
10. G. Lujanienė, K. Mažeika, J. Šapolaitė, A. Amulevičius, Ž. Kamarauskas. Kinetics of Cs, Pu and Am sorption to clay minerals. Migration 2007: 11th international conference on the chemistry and migration behaviour of actinides and fission products in the geosphere, München, Germany, 26-31 August 2007.
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12. J. Šapolaitė, G. Lujanienė, K. Mažeika and A. Amulevičius, Kinetics of Cs sorption to clay minerals, Radiation Interaction with Material and its use in Technologies 2008, Kaunas, Lietuva, rugsėjo 24-27 d., 2008 m.
13. G. Lujanienė, K. Mažeika, and J. Šapolaitė, Study of Cs, Pu and Am Sorption Kinetics to Clay Minerals, 4th International Symposium on In Situ Nuclear Metrology as a tool for radioecology, 13-16 October 2008, Rabat Morocco.
14. G. Lujanienė, S. Meleshevych, V. Kanibolotsky, K. Mažeika, V. Strelko, V. Remeikis, V. Kalenchuk, and J. Šapolaitė. Application of inorganic sorbents for removal of Cs, Sr, Pu and Am from contaminated solutions, Eighth International Conference on Methods and Applications of Radioanalytical Chemistry, Hawaii, USA, balandžio 5-10, 2009.
15. G. Lujanienė, J. Šapolaitė, K. Mažeika, K. Jokšas and B. Šilobritienė. Recent Developments in Cs, Pu and Am, Sorption Studies in Natural Systems, Eighth International Conference on Methods and Applications of Radioanalytical Chemistry, Hawaii, USA, balandžio 5-10, 2009.

CURRICULUM VITAE

Justina Šapolaitė was born in Vilnius, Lithuania in 1980. She graduated from Žemyna gymnasium in 1998; in 1998-2002 she studied at Vilnius University, Department of Chemical Sciences and graduated with BA and MA Diploma Degree in Chemical Sciences in 2002 and 2004, respectively. From 2005 to 2009 postgraduate studies at the Institute of Physics for a Doctoral degree. Since 2004 she has been working at the Institute of Physics.

SANTRAUKA

Antropogeniniai radionuklidai, tokie kaip ^{137}Cs , ^{90}Sr , $^{239,240}\text{Pu}$ ir ^{241}Am , patekę į aplinką su branduolinės pramonės nuotėkomis bei po įvairių avarių, šiuo metu sulaukė didelio mokslinės visuomenės dėmesio. Atlikti tyrimai parodė, kad būtina tobulinti efektyvius bei ekonomiškus vandens valymo metodus ir, tokiu būdu, apsaugoti aplinką nuo žalingo šių atliekų poveikio. Buvo ištirti titano silikatai susintetinti Ukrainos Sorbcijos ir endoekologijos problemų institute bei geležies oksidai susintetinti ir apibūdinti, naudojant Mesbauerio spektroskopiją Fizikos institute. Titano silikatų ir geležies oksidų sorbcinė geba nustatyta Cs, Pu ir Am. Didžiausios Pu K_d vertės ir geresnė Pu sorbcijos kinetika nustatyta sintetiniams geležies oksidams. Magnetito/hematito mišinio K_d vertės didesnės ~7 kartus, lyginant su grynu magnetitu, leidžia teigti, kad sorbentas efektyvus Pu pašalinimui ir yra perspektyvus jo atskyrimui iš radioaktyviosiomis atliekomis užterštų tirpalų.

Radioaktyviųjų atliekų tvarkymo saugos analizė reikalauja ilgalaikės radionuklidų migracijos pro dirbtinius barjerus bei geologinės aplinkos modeliavimo. Sudėtingų cheminių sorbcijos-desorbcijos vyksmų aprašymas dažniausiai supaprastinamas, panaudojant integruotą parametą – pasiskirstymo koeficientą (K_d). Daugelyje duomenų bazių pateikiama informacija apie radionuklidų K_d vertes skirtingose geologinėse aplinkose. Tačiau ši informacija paprastai būna labai bendro pobūdžio ir mažai tinka saugos analizei, nes, kintant geologinėms sąlygoms, K_d vertės dažnai pakinta net dviem eilėmis. Siekiant nustatyti realius aktualių radiacinės saugos požiūriu radionuklidų sorbcijos betono saugykloje parametrus, atlikti Cs, Pu Am migracijos tyrimai. Laboratoriniams tyrimams buvo paimti molių, parinktų paviršinės saugyklos Lietuvoje dirbtiniams barjerams, ėminiai iš Galilaukės aikštelės (moreninis priemolis) ir pramoninio Šaltiškių karjero (triaso molis).

Cs K_d vertės kito nuo 400 iki 9700 ml/g. Molių sulaikymo geba žymiai sumažėja po kontakto su šarminiu Portlando cementu ir esant didelėms cezio koncentracijoms. Pu K_d vertės kito nuo $15 \cdot 10^3$ iki $21 \cdot 10^3$ ml/g, o Am – nuo $15 \cdot 10^3$ iki $8 \cdot 10^4$ ml/g. Didžiausios K_d vertės nustatytos, esant pH 6-8. Esant dideliems pH, Pu(IV) sorbuojasi ant hematito. Eksponentinis Pu K_d verčių mažėjimas, didėjant vandeninės fazės pH, buvo nustatytas Galilaukės ir Šaltiškių molių gruntinio vandens sistemose.

Platus Cs K_d verčių intervalas aiškinamas konkuruojančių K^+ , Na^+ , Ca^{2+} , NH_4^+ ir H^+ jonų reakcijomis su Cs^+ dėl sorbcijos vietų ant ilito ir smektito mineralų. Be to, Cs sorbcija, esant didelėms Cs koncentracijoms ($6,80 \cdot 10^{-5}$ mol/l), sumažėjo (K_d vertės iki 500) dėl mažos atrankių sorbcijos vietų talpos ilito minerale. Tačiau ilito mineralas gali labai efektyviai negrįžtamai imobilizuoti Cs, esant mažoms jo koncentracijoms.

Nuosekliosios ekstrakcijos eksperimentai parodė, kad Cs beveik vienodai pasiskirstęs įvairiose geocheminėse frakcijose, naudojant Šaltiškių molį Nr. 6 ir Nr. 7 bei gruntinius vandenius GV4 ir GV6. Cs daugiausiai buvo aptikta pakaitinėje ir susijusioje su karbonatais frakcijoje (iki 70%). Tariamosios pusiausvyros konstantos kito nuo 1 iki 26, o didžiausios nustatytos grįžtamoms molio mineralų vietoms.

Ištirta, kad didelis Pu kiekis, iki 62 %, buvo susijęs su redukuota frakcija ir mažėjo priklausomai nuo pH.

Plutonio oksidacijos laipsnių nustatymo rezultatai parodė, kad Pu(IV) dominavo GVCV tirpale (pH 12,6), o Pu(VI) GVCV ir GV tirpaluose nebuvo stebėtas po 20 valandų. Apie 50% pradinio Pu(VI) buvo rasta penkiavalentiniame būvyje GV mėginiuose.

Nustatytas Pu oksidacijos laipsnių kitimas natūralių molių sistemose su 0,1 ir 0,01 mol/l $NaNO_3$ skystoje ir kietoje fazėje. Skystoje fazėje iki pH 5 dominuoja Pu(III, IV), nedidelė jo dalis oksiduota į Pu(V) ir Pu(VI), kai $pH > 5$, dominuoja Pu(IV) polimerinė forma. Kietoje fazėje dalis Pu(IV) redukuojama į Pu(III) dėl Fe(II) buvimo mineraluose: daugiausia 10,7 %, kai pH 4,98.

Atliekant eksperimentus sistemoje getitas - 0,01 mol/l $NaNO_3$ Pu(V) didžiausias kiekis nustatytas skystoje fazėje. Jo mažėjimas vyksta dėl jo sorbcijos ir redukcijos ant getito dalelių. Didžiausia valentinių formų kaita stebėta kietoje fazėje. Pradžioje stebimas Pu(V), laike stebėta jo redukcija į Pu(IV), o laikui bėgant, dominuojanti forma tampa Pu(IV).

Vykdamas Pu(IV) ir Am(III) desorbcijos eksperimentus, pastebėta, kad Pu(IV) desorbuojamas kiekybiškai, Am(III) beveik visas pereina į tirpalą.

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