Cs AND Pu MIGRATION THROUGH ENGINEERED AND NATURAL BARRIERS [*]

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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 the changes of the geological conditions result in a 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 some preliminary studies were carried out. The development of sorption database for the near-surface repository was started with measurements of cesium and plutonium 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 Lithuanian near-surface repository were taken for laboratory investigations. Several experiments were performed in order to determine the chemical composition of cement water which could originate from infiltration of precipitation and from contact of groundwater with concrete. More than 100 batch sorption experiments were conducted with two clay samples. Cs and Pu K_d values were determined under a wide range of geochemical conditions. Changes in the geochemical conditions resulted in the variability of Cs and Pu K_d values.

Keywords: Cs, Pu, distribution coefficients (K_d), clay, surface repository, radioactive waste

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1. Introduction

The fate and transport of dissolved contaminants in the geological environment to a great extent are determined by radionuclide interactions with mineral surfaces. The retardation of radionuclides depends on geochemical processes which include aqueous speciation, redox and interface reactions, precipitation and dissolution of minerals as well as colloids. Changes in geochemical conditions (mineral and solution composition, pH, Eh, and temperature) can considerably affect the behaviour of different radionuclides. To assess migration of radioactive contaminants in the repository environment it is essential to identify important geochemical processes affecting the contaminant transport.

The retardation and engineering extraction of cesium are difficult problems. For sorbing the radionuclides such as Cs, long time is required to reach steady state conditions and its sorption–desorption behaviour in clay minerals is complicated [1, 2].

Cesium is one of the most important artificial radionuclides that has been introduced into the environment through nuclear weapons testing and the nuclear accident in Chernobyl in 1986; its inventories in radioactive waste are significant as well. The half-life of ^{137}Cs is 30.2 years and it is obvious that its migration to human accessible environment must be limited for only a few decades. The long-term isolation must be demonstrated where releases of ^{135}Cs (half-life is $2.3 \cdot 10^6$ years) from the high-level radioactive wastes are possible in addition to ^{137}Cs. Harmful effects of cesium on animate nature are evident taking into account its properties: unlimited solubility, potential mobility, and high bioavailability. Cs exists in the environment in +1 oxidation state, the formation of organic and inorganic complexes has negligible effect on cesium speciation, and the dominant aqueous species in groundwater is the uncomplexed Cs$^+$ ion. The sorption–desorption pro-

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cesses of radiocesium on various minerals have been the subject of many recent studies [3, 4]. The selective adsorption of Cs by mica-like minerals, such as illite {(K,H$_3$O)(Al,Mg,Fe)$_2$(Si,Al)$_4$O$_{10}$[(OH)$_2$,H$_2$O]}, has been attributed to the large ionic radius, uncomplexing nature, and especially to its low hydration energy. Although cations with similar charges and ionic radii are expected to compete with cesium, the sequence of sorption ability of alkali elements Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$ is in good agreement with the sequence of effective ionic radii of alkali elements and the sequence of single ion hydration enthalpies of alkali elements [5]. In the clay mineral muscovite, a fixed negative charge arises primarily from isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet comprising the siloxane site. In illite mineral with composition very close to that of muscovite, isomorphic substitution of Al^{3+} for Si^{4+} and partly of Fe^{2+} and Mg^{2+} for Al^{3+} enhances the stability of the Cs$^+$–siloxane surface complex. Strongly sorbed Cs$^+$ on fraered edge sites (FES), external basalt sites, or within the interlayer exists as an inner-sphere, dehydrated surface complex, which is usually much more stable than outer-sphere complexes [6]. Cesium sorbed to outersphere complexes can be easily desorbed and is distinguished for higher mobility in the environment, while inner-sphere sorption complexes can limit the Cs transport and bioavailability. In smectites, the isomorphous substitution in both tetrahedral and octahedral layers generates weak negative charges of the sheets thus leading to the formation of a structural feature and resulting in wide ranges of cation exchange capacity, selectivity, and swelling properties. Water and cations (H$^+$, Na$^+$, Ca^{2+}, Mg^{2+}) can easily penetrate into the smectite interlayer and participate in exchange processes and, for example, from a species like beidellite the sorbed cation can easily be ion-exchanged by the other cations. However, the existence of electrostatically stable sorption site for a cation with ionic size small enough to enter the hole was established for montmorillonite [7].

Plutonium comprises only small part of total activities even in spent fuel, however, the toxic effect of ^{239}Pu (half-life is 24400 years) will be dominant for thousands of years after the decay of short-lived fission products. Plutonium can exist in 4 oxidation states under the conditions and the pH typically present in the natural environment. Plutonium exhibits a complicated redox behaviour that permits transformation of one oxidation state into another. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas, under reducing conditions, Pu(III) and Pu(IV) would exist [8]. Dissolved plutonium forms the strong hydroxy-carbonate-mixed ligand complexes, therefore, its adsorption and mobility can be strongly affected by these complex species. Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium–organic complexes can control adsorption and mobility of plutonium in the environment. Plutonium can adsorb on different geological materials from low to extremely high affinities, with K_d values typically ranging over 4 orders of magnitude (from 11 to 330000 ml/g) [9]. The changes in oxidation state of plutonium considerably affect its mobility in the environment. The environmental mobility of Pu(IV) is from 2 to 3 orders of magnitude lower than the mobility of Pu(V) or Pu(VI). Pu(III) due to its negative potential at higher pH can be readily oxidized by water at even neutral pH levels [10, 11]. Therefore, it is supposed that plutonium exists in +4, +5, and +6 oxidation states in natural environment at low pH values. Disproportionation reactions have negligible effect on the plutonium oxidation state in natural systems with typically low concentrations [11]. However, interactions with various minerals (e. g., goethite (α-FeOOH), manganite (Mn(III)O$_2$H), hausmannite (Mn(II/III)$_3$O$_4$), pyrolusite (β-Mn(IV)O$_2$), and birnessite (δ-Mn(IV)O$_2$) with different redox potentials can change the plutonium sorption characteristics by either oxidizing or reducing the sorbed species [12–16]. In addition, the interaction with the bacteria can cause changes in the oxidation state of plutonium under environmental conditions [17, 18]. The published material provides much useful information on the mobility of plutonium, but some of these publications are contradictory, especially regarding the oxidation state and speciation of plutonium at low pH values, and also the data obtained from the experiments conducted without the determination of the oxidation state of plutonium. Thus, further studies related to the behaviour of plutonium in different environments under controlled oxidation state are required.

2. Methods

The chemical composition of groundwater and the cement water solutions was determined. Samples of the natural groundwater (GW) from the 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

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

	Type of solution			
	GW	GWCW	SRW	SRWCW
SO_4^{2-}, mg/l	94.76	109.52	1.22	2.90
NO_3^-, mg/l	<0.4	2.16	0.71	4.40
Cl^-, mg/l	8.29	20.68	0.75	345.78
F^-, mg/l	0.08	0.32	–	0.32
NH_4^+, mg/l	0.50	3.00	0.41	2.26
Na^+, mg/l	59.00	49.00	0.58	22.57
K^+, mg/l	6.90	370.00	0.14	545.02
Ca^{2+}, mg/l	25.00	183.20	0.42	96.82
Mg^{2+}, mg/l	40.39	0.01	–	0.03
Al^{3+}, mg/l	0.018	0.01	–	0.64
Si, mg/l	3.26	0.24	–	0.50
pH	7.81	12.61	4.89	11.61
U, mV	-60.1	-335.0	108.5	-283.0
χ, mS/cm	1.09	8.04	0.23	2.15

extracts of groundwater – cement water (GWCW) and synthetic rainwater – cement water (SRWCW) solutions (Table 1). The particles of different sizes of solidified cement were used in the experiments. The chemical composition of the extracts was determined by the atomic absorption spectrometry and the ion chromatography techniques (Table 1). The composition of rainwater was estimated taking into account the long-term studies performed in Lithuania [19].

The laboratory batch method was used for the determination of K_d values. The protocol of the standard method used at Pacific Northwest National Laboratory for measuring laboratory batch K_d values was applied [9].

The tests were performed under atmosphere conditions at 25 °C. The sample was disaggregated by an ultrasonic method. The total concentration of cesium in solutions was $2.30 \cdot 10^{-10}$ mol/l and the solutions were labeled by ^{134}Cs. The ^{134}Cs activities were measured with an intrinsic germanium detector (resolution 1.9 keV/1.33 MeV and relative efficiency 42%). Measuring time varied according to sample activities. An efficiency calibration of the system was performed using calibration sources (prepared from a solution supplied by Amersham, UK) of different densities and geometry that were close to measured samples. Accuracy and precision of analysis were tested in intercomparison runs, organized by the Riso National Laboratory, Denmark. Precision of ^{134}Cs measurements by gamma spectrometry was ≤3%. The sorption of cesium on centrifuge bottle walls was detected to be less than 2%.

Plutonium for tracer experiments was prepared by the separation of plutonium isotopes from the highly contaminated Chernobyl soil. Three cycles of the ion exchange and the extraction chromatography were used to purify plutonium. The prepared plutonium tracer was standardized using ICP-MS and alpha spectrometry.

Pu(IV) 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 M thenoyltrifluoroacetone (TTA) as extractant [20]. Typically 96±3% of the total plutonium was found in the tetravalent state. In addition, oxidation state analyses were preformed in the GW and the GWCW solution samples after 20 hours. The redox speciation of plutonium was studied using TTA and di(2-ethylhexyl)orthophosphoric acid (HDEHP) as extractants [21, 22].

To determine K_d values each clay sample was prepared by adding 1.0 g of studied clay to a pre-weighed, acid washed polypropylene centrifuge tube. The GW and GWCW solutions of different dilutions, the pH of which ranged from 5 to 13, were passed through 0.45 μm pore size filters. A 10 ml aliquot of these solutions was added to the respective tubes. The samples were then placed on an end-over-end shaker and the solutions were changed every other day until the pH remained stable over the desirable range. The empty blank tubes containing no clay were also prepared to evaluate adsorption of the plutonium to the tube walls. From 1 to 12% of Pu(IV) was found adsorbed to the tube walls for samples containing geological materials. The initial concentration of Pu(IV) was adjusted by this fraction.

The blank and sample tubes are centrifuged for twenty minutes at 10,000 g. After the pH remained stable for 48 hours (±0.1 pH units), Pu(IV) spike was added for a final concentration of $\sum Pu = 1.11 \cdot 10^{-9}$ mol/l. Solids were separated from liquid by centrifugation after 10-day contact. Plutonium quantties in the solution and the geological material were determined after radiochemical separations based on the extraction chromatography. The UTEVA and TRU columns from Eichrom Industries were used and activities were measured by alpha spectrometry. ^{242}Pu was used as tracer in the separation procedure. K_d values of Cs and Pu were determined from three replicates.

3. Results and discussion

To obtain cesium K_d values for the natural clay based on soil material originated from the Galilaukė site (Galilaukė clay) and smectite clay material (Šaltiškiai clay) selected as a candidate for the engineered
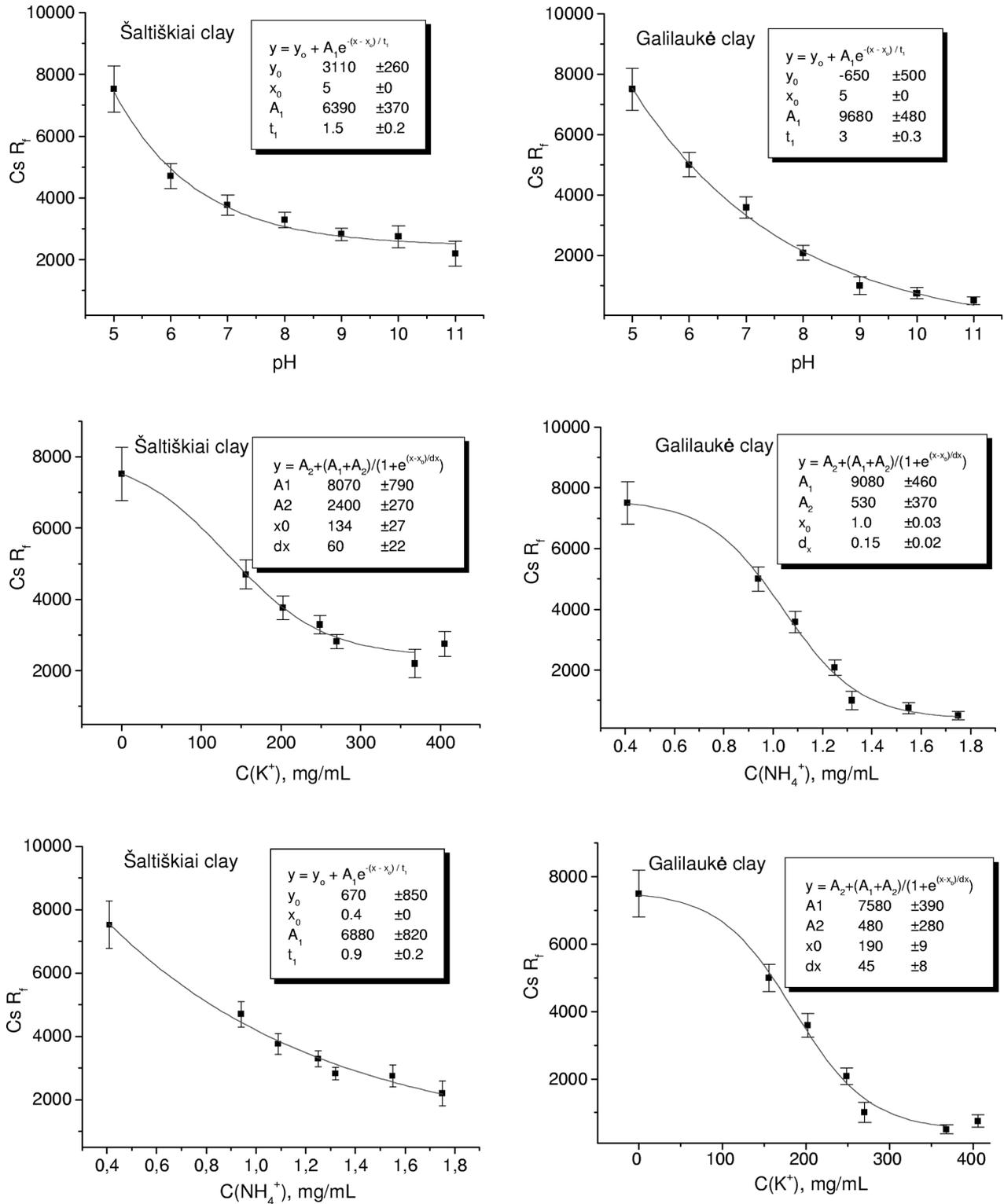
Fig. 1. Cs R_f values variations depending on different chemical composition of rainwater – cement solutions.

Table 2. Cesium and plutonium distribution coefficients.

| Type of used solution | Distribution coefficients, K_d, ml/g | | | |
| | Galilaukė clay | | Šaltiškiai clay | |
	Cs	Pu	Cs	Pu
SRW	1500±110	140000±11000	1600±100	20000±1700
GW	9700±900	120000±9000	8400±800	15000±1200
SRWCW	1100±70	140000±10000	1400±800	20000±1600
GWCW	450±30	80000±6000	500±40	21000±1700

barrier of the Lithuanian near-surface repository, SRW, GW, SRWCW, and GWCW solutions were used (Table 1). The average values obtained from three replicates are presented in Table 2. K_d values are in good agreement with ones presented in various publications and ranged from 10000 to 100 ml/g. The highest values were detected for natural groundwater. The Šaltiškiai clay exhibited a retention capacity towards cesium. 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. Sorption as a function of pH and chemical composition of contact solutions was studied. It was supposed that the pH and the chemical composition of rain and groundwater can vary in natural conditions depending on their contact time with cement material and/or different dissolution. Two sorption experiments were conducted. These studies showed the decrease in Cs K_d values with the increase in the pH of aqueous phase. The variation in pH values can affect the retention of cesium ions by clay minerals due to competition reactions and because of a partial dissolution of clay. The effect of pH on the sorption process is very well known, however, a certain degree of clay dissolution is possible and the stability of clay is a function of pH [23]. It should be noted that the stability of clay during the experiment was not controlled. Moreover, the degradation of cement results not only in the pH increase but also in the release of K^+, Na^+, Ca^{2+}, NH_4^+ ions into solution. All of them can displace Cs from different sorption sites and affect a retardation of Cs. Retardation factors for unsaturated conditions were calculated using obtained K_d values and clay properties [24]. The retardation factor is the empirical parameter commonly used in transport models to describe the chemical interaction between the contaminant and geological materials. Depending on the conditions under which the contaminant moves and interacts with the geological material, the retardation factor can correlate with the distribution coefficient in different ways. Different formulations of the retardation factor have been proposed [25, 26]. The retardation factor (R_f) is the ratio of the pore-water velocity (v_p, cm/h) to the contaminant velocity (v_c, cm/h): $R_f = v_p/v_c$. 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. 1. 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 the other cases a more complicated decrease that corresponds to the sigmoidal (Boltzmann) fit was observed. Desorption experiments show that from 25 to 37% of reversibly sorbed cesium can be released to the surrounding solution. The released fraction increased in desorption experiments with samples in which the higher concentrations of K^+ ions were used in sorption experiments. It seems that K^+ ions can block the FES and in such a manner can reduce the portion of irreversibly sorbed cesium.

It is very well known that the chemical behaviour of plutonium in the environment is primarily defined by its oxidation state. Due to variations of the chemical properties for each oxidation state, the reactions of each oxidation state should be taken into account in conceptual models. Plutonium is able to exist in five different oxidation states as the oxy/hydroxy ions $Pu(III)^{3+}$, $Pu(IV)^{4+}$, $Pu(V)O_2^+$, $Pu(VI)O_2^{2+}$, and $Pu(VII)O_4^{-1}$. PuO_4^- is not considered to be a stable species in the natural environment. In moderate pH or oxic groundwater, Pu(III) is rapidly oxidized to Pu(IV) [11].

Plutonium Pu(IV), Pu(V), Pu(VI) oxidation state analysis was performed on the aqueous phase of the lowest pH GWCW solution used in the sorption experiments and the GW sample from Galilaukė site. Our preliminary results of plutonium redox speciation are presented in Fig. 2. It can be seen that Pu(IV) was still the dominant species in the GWCW solution (pH 12.6) and there was no evidence of Pu(VI) in the GWCW and in the GW samples after twenty hours. About 50% of the Pu(VI) spiked was found in the pentavalent oxidation state in the GW samples. Although thermodynamic calculations indicate the Pu(V)
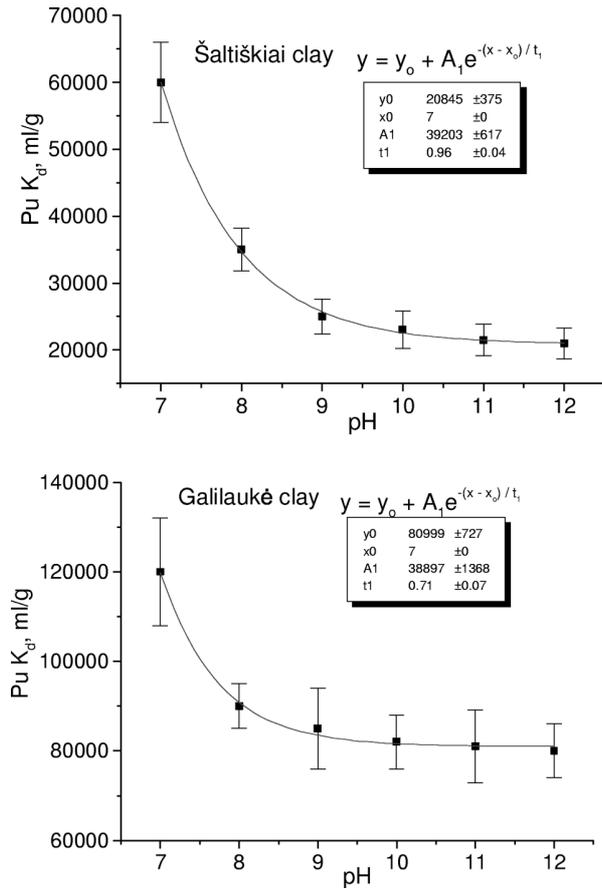
Fig. 2. Plutonium K_d values depending on pH in groundwater – cement solutions.

Fig. 3. Redox speciation of Pu in groundwater (pH 7.8) and groundwater – cement water (pH 12.6) after 20 hours.

PuO_2^+, and $PuCO_3^+$. Differences in the Pu speciation and changes in the chemical composition of aqueous phase resulted in the variation of Pu K_d values (Fig. 3). The exponential decrease in the Pu K_d values with the increase in the pH of aqueous phase was found for both clays (Fig. 3). Strong sorption (higher K_d values) of Pu to the Galilaukė clay can possibly be attributed to the mineralogical composition of clays.

4. Conclusions

Cs K_d values ranged from 10000 to 100 ml/g. The retention capability of the clays was significantly reduced due to the impact of alkaline Portland cement. The highest values were detected for natural groundwater. K_d values of Pu ranged from 15000 to 21000 ml/g. The exponential decrease in the Pu K_d values with the increase in the pH of aqueous phase was found for both clays. Results of determination of plutonium redox speciation indicated that Pu(IV) was still the dominant species in the GWCW solution (pH 12.6) and there was no evidence of Pu(VI) in the GWCW and in the GW samples after twenty hours. About 50% of the Pu(VI) spiked was found in the pentavalent oxidation state in the GW samples.

as the most stable species under environmental conditions [11], this result is rather unexpected. It can possibly be attributed to the plutonium oxidation by pyrolusite (β-Mn(IV)O$_2$) and/or birnessite (δ-Mn(IV)O$_2$) colloids usually present in solutions [15, 27]. MnO$_2$ colloids could be present in the GWCW solutions since they were prepared using the same groundwater. Although a decrease in the concentration of hydrogen ion favours the oxidation reaction since more binding sites on the negatively charged surface of manganese dioxide are available, but increasing the pH values also enhances the influence of the hydrolysis reactions of Pu(IV) and the formation of Pu(OH)$_4^0$ stabilizes the tetravalent state. The negligible amount of Pu(IV) hydroxide polymers found in the both studied solutions can hardly be attributed to the formation of intrinsic colloids because of the low concentration of plutonium ($\sum \mathrm{Pu} = 1.11 \cdot 10^{-9}$ mol/l) used in the sorption experiments. However, this result can be explained by association of Pu(IV) with various pseudocolloids commonly present in natural waters. According to our studies and published data [28, 29] the possible Pu species in the aqueous phases were estimated as follows: Pu(OH)$_4^0$,
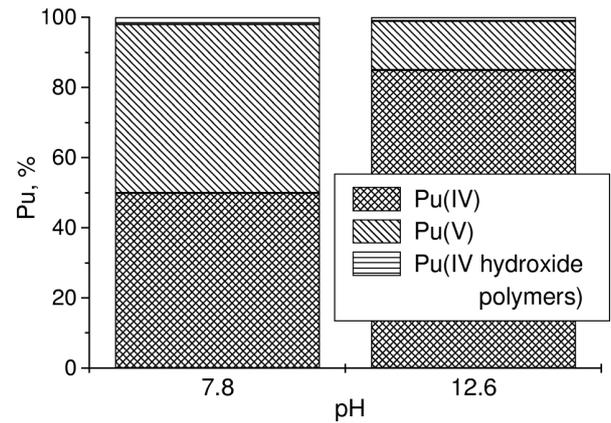
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Cs IR Pu MIGRACIJA PRO DIRBTINIUS IR GAMTINIUS BARJERUS

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Santrauka

Analizuojant radioaktyviųjų atliekų tvarkymo saugą, reikalingas ilgalaikis radionuklidų migracijos pro dirbtinius barjerus bei geologinės aplinkos modeliavimas. Sudėtingų cheminių gerties–atvirkštinės gerties vyksmų aprašymas dažniausiai supaprastinamas panaudojant integruotą parametrą – pasiskirstymo koeficientą (K_d). Daugelyje duomenų bazių pateikiama informacija apie radionuklidų K_d vertes skirtingose geologinėse aplinkose. Tačiau ta 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 gerties betono saugykloje parametrus, preliminariai tirta Cs ir Pu migracija. Pradėtas tų elementų gerties duomenų bazės kūrimas. Laboratoriniams tyrimams buvo paimti molių, parinktų paviršinės saugyklos Lietuvoje dirbtiniams barjerams, pavyzdžiai iš Galilaukės aikštelės (moreninis priemolis) ir pramoninio Šaltiškių karjero (triaso molis). Buvo atlikta keletas eksperimentų, siekiant nustatyti betono vandens, atsirandančio kritulių prasiskverbimo ir gruntinio vandens sąlyčio su betonu atvejais, cheminę sudėtį. Atlikta daugiau nei 100 gerties eksperimentų, naudojant dviejų molių pavyzdžius. Cs ir Pu K_d vertės buvo nustatytos plačiame geocheminių sąlygų intervale. Geocheminių sąlygų pokyčiai įtakojo Cs ir Pu K_d verčių kintamumą.