

KINETICS OF Cs SORPTION TO CLAY MINERALS

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Preliminary data of kinetic sorption experiments are presented. Batch sorption experiments with the aim of estimation of distribution coefficient (K_d) values were conducted using natural clay minerals from the Šaltiškiai quarry and two sets of solutions with different caesium concentrations ($C(\text{Cs}) = 2.30 \cdot 10^{-10}$ mol/l and $C(\text{Cs}) = 6.80 \cdot 10^{-5}$ mol/l). 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 (up to 70%) of exchangeable caesium in experiments with high caesium concentrations. Results of kinetic tracer experiments and sequential extraction studies revealed 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 on 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.

Keywords: Cs, distribution coefficients (K_d), apparent equilibrium constants (K_{ap}), clay minerals, radioactive waste

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1. Introduction

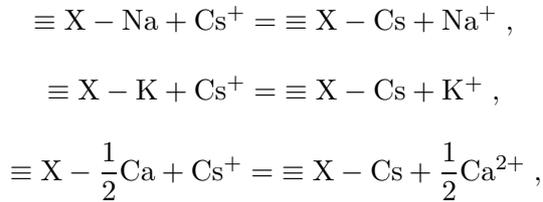
The development of nuclear energy resulted in accumulation of radioactive waste of different activity in various countries, including Lithuania. The isolation of such waste for a long period of time requires the reliable engineered and natural barrier systems where migration of radionuclides should be retarded through different physical and chemical processes. An understanding of geochemical processes affecting the contaminant transport is necessary for assessment of migration of radioactive contaminants in the repository environment. One of the most important issues of this is sorption to clay minerals.

The retardation and engineering extraction of caesium are difficult problems. For sorbing the radionuclides such as Cs, a long time is required to reach steady-state conditions, and its sorption–desorption behaviour in clay minerals is complicated [1, 2]. The formation of organic and inorganic complexes has negligible effect on caesium speciation and the dominant aqueous species in groundwater is the uncomplexed Cs^+ ion. It is now generally recognized that Cs^+ is strongly and selectively sorbed by the phyllosilicate fraction of soils, sediments, and suspended particles,

and this selective adsorption of Cs by mica-like minerals, such as illite $\{(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,\text{H}_2\text{O}]\}$, can considerably reduce the toxic caesium effect in the natural environment [3]. Recently a few studies have indicated that even highly contaminated organic soils, such as peats, contain trace amounts of illite, which should be sufficient to immobilize the trace amounts of Cs present even in very contaminated soils. It has also been found that the humic substances decrease the adsorption of Cs on clays [4, 5]. Along with humic substances, the polysaccharides and proteins are the most important organic macromolecules in soils, where they can affect various adsorption sites in different ways, by preventing the clay layer collapse at frayed edge sites, and they can inhibit Cs sorption to clay minerals by modifying the properties of regular exchange sites [6]. The major sorbents are found to be the layer-type silicates that bind Cs either through electrostatic associations of hydrated Cs with anionic surfaces within the basal plane and dissociated edge hydroxyl groups forming outer-sphere complexes or through electronic bonding at the frayed edge sites (FES), external basal sites, or within the interlayer forming inner-sphere complexes [7]. The high affinity FES are supposed to constitute only a small

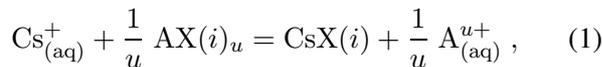
proportion ($\sim 10^{-8}$ mol/kg) of the total ones [8]. Caesium adsorption by layer-type silicates has been often described as a cation exchange process on two or more sites with distinctly different selectivity [9–11].

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



where $\equiv \text{X}$ denotes surface sites on the clay minerals.

The cation exchange of Cs^+ to layer silicates and soils is usually represented by a mass action equation of the following form [12, 13]:



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

$$K_d = \frac{[\text{CsX}(i)]}{[\text{Cs}_{(\text{aq})}^+]}. \quad (2)$$

The rate of exchange of Cs^+ is

$$\begin{aligned} \frac{d[\text{Cs}_{(\text{aq})}^+]}{dt} &= -k_1[\text{Cs}_{(\text{aq})}^+][\text{AX}(i)_u]^{1/u} \\ &\quad + k_{-1}[\text{A}_{(\text{aq})}^{u+}]^{1/u}[\text{CsX}(i)], \end{aligned} \quad (3)$$

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

$$K_{ap} = \frac{k_1}{k_{-1}} = \frac{[\text{A}_{(\text{aq})}^{u+}]^{1/u}[\text{CsX}(i)]}{[\text{Cs}_{(\text{aq})}^+][\text{AX}(i)_u]^{1/u}}, \quad (4)$$

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

The aim of this study was to determine the caesium sorption parameters to clay minerals and to investigate the sorption mechanism under different conditions.

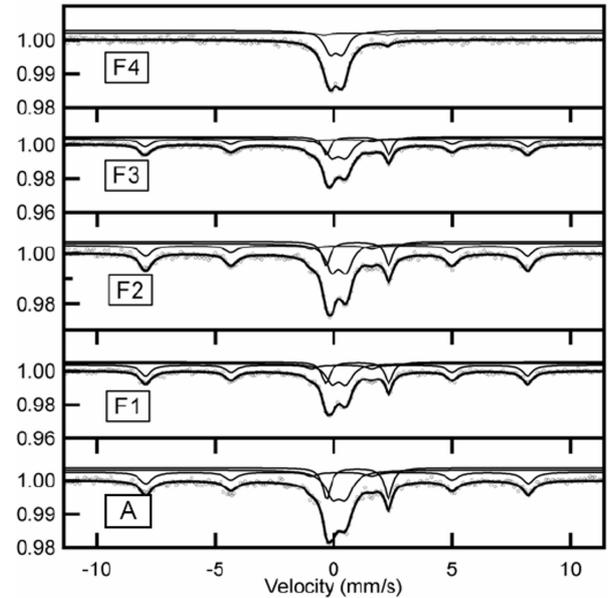


Fig. 1. Room-temperature Mössbauer spectra of the Šaltiškiai clay (sample No. 6): the initial A and after four steps of sequential extraction of iron minerals, F1 (exchangeable and bound to carbonates), F2 (reducible), F3 (bound to organic matter), F4 (*aqua regia*).

2. Methods

Samples of Triassic clay from a site mined for industrial exploitation known as the Šaltiškiai (North Lithuania) quarry were taken for laboratory investigations. X-ray diffraction analyses indicated the presence of about 14% of montmorillonite in the Triassic clay. The analysis of $< 1 \mu\text{m}$ size particles showed the high content of smectite group minerals (from 56 to 71%), illite (about 20%), and chlorite minerals (from 1 to 9%) in the fraction of smaller than $1 \mu\text{m}$ particles of the Šaltiškiai clay. The chemical composition of the Šaltiškiai clay was estimated as follows: SiO_2 made 45.51%, Al_2O_3 13.50%, Fe_2O_3 5.17%, MgO 3.00%, CaO 12.88%, Na_2O 0.28%, K_2O 5.02%, TiO_2 0.43%, total S 0.16%, the loss on ignition was 13.96% [14]. The grain size composition of the Triassic clay is characterized by microaggregates of clay particles which are cemented by limonite $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$. The mixture of iron oxide minerals is characteristic of limonite. 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 were determined by Mössbauer spectrometry in the Šaltiškiai clay [15].

The Mössbauer spectra were measured at room temperature using a constant acceleration method in transmission geometry. For the Mössbauer studies, the $^{57}\text{Co}(\text{Rh})$ source was used. The thickness of samples was approximately 100 mg/cm^3 of clay. Isomer shifts are given relative to $\alpha\text{-Fe}$.

Two samples from the Šaltiškiai quarry were selected for sorption experiments. In samples No. 6 and 7 a different amount of iron oxides and carbonates was determined. Data of Mössbauer spectra of the initial sample No. 6 and after four steps of sequential extraction are presented in Fig. 1. Significant changes in Mössbauer spectra were observed after the step *F4 (aqua regia)* and after extraction using citrate-bicarbonate-ditionite (CBD). In both cases hematite ($\alpha\text{-Fe}_2\text{O}_3$) was removed, and the sextet associated with it was not observed. In sample No. 7 only a trace amount of iron oxides was found, while a large amount of CaCO_3 was determined using X-ray diffraction and atomic absorption spectrometry (AAS) in combination with sequential extraction.

Natural groundwater (GW) and synthetic rainwater (SRW) were used in experiments. The chemical composition of GW and SRW samples is presented in Table 1. The composition of rainwater was estimated taking into account the long-term studies performed in Lithuania [16].

The laboratory batch method was used for the determination of K_d values. The protocol of the standard method used at the Pacific Northwest National Laboratory (USA) for measuring laboratory batch K_d values was applied [17]. Two sets of solutions were prepared for batch experiments. The tests were performed under atmospheric conditions at 25°C . The sample was disaggregated by an ultrasonic method. The total concentrations of caesium in solutions were $2.30 \cdot 10^{-10} \text{ mol/l}$ and $6.80 \cdot 10^{-5} \text{ mol/l}$ (the solutions were labelled by ^{134}Cs). The sorption of caesium on centrifuge bottle walls was detected to be less than 2%. ^{134}Cs activities were measured with an intrinsic germanium detector (resolution $1.9 \text{ keV} / 1.33 \text{ MeV}$ and the relative efficiency 42%). Duration of measurement 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 Risø National Laboratory, Denmark. The uncertainty of ^{134}Cs measurements by gamma spectrometry was $\leq 3\%$.

The association of sorbed Cs in the studied geological material was determined using the sequential extraction procedure [18,19]. Exchangeable and carbonate bound Cs was extracted using 1 mol/l $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, pH 5, CH_3COOH extracting agent.

3. Results and discussion

Data of sorption experiments using the clay sample No. 6 and groundwater samples GW4 and GW6 (data: C6, GW4 and C6, GW6) as well as the clay sample No. 7 and groundwater samples GW4 and GW6 (data: C7, GW4 and C7, GW6) are presented in Fig. 2. 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. Cs K_d values as functions of time are presented in Fig. 3. The determined K_d values ranged from 80 to 470 ml/g . Insignificantly higher values were found for clay No. 6. Higher Cs K_d values were expected in experiments using the groundwater sample GW6 with lower concentrations of major ions (Table 1). However, even slightly higher K_d values were observed in experiments with the clay No. 6 and the groundwater GW4 (data: C6, GW4, Fig. 3). It can be explained taking into account the different adsorption selectivity of Cs in a multicomponent $\text{Cs}^+ - \text{Ca}^{2+} - \text{Na}^+ - \text{K}^+$ system. The changes in chemical composition of groundwater are mainly related to an increase in concentrations of Ca^{2+} and Na^+ . The concentration of K^+ in both samples was found to be almost the same, whereas the selectivity coefficients of Cs for mentioned ions can differ more than 10 times. The highest coefficients were determined for $\text{Cs}^+ - \text{Ca}^{2+}$ and the lowest for $\text{Cs}^+ - \text{K}^+$ exchange. In addition, an increase in selectivity coefficients with

Table 1. Physical parameters and major ion concentrations in groundwater solutions used in sorption experiments.

Type of solution	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	U, mV	χ , mS/cm
GW4	40.3	22.4	10.4	1.9	139	39.7	517	7.16	-71.7	0.863
GW6	22.8	5.2	5.2	1.6	89.6	24.9	367	7.47	-69.8	0.535
SRW	1.22	0.75	0.58	0.14	0.42	-	90.0	4.89	108.5	0.23

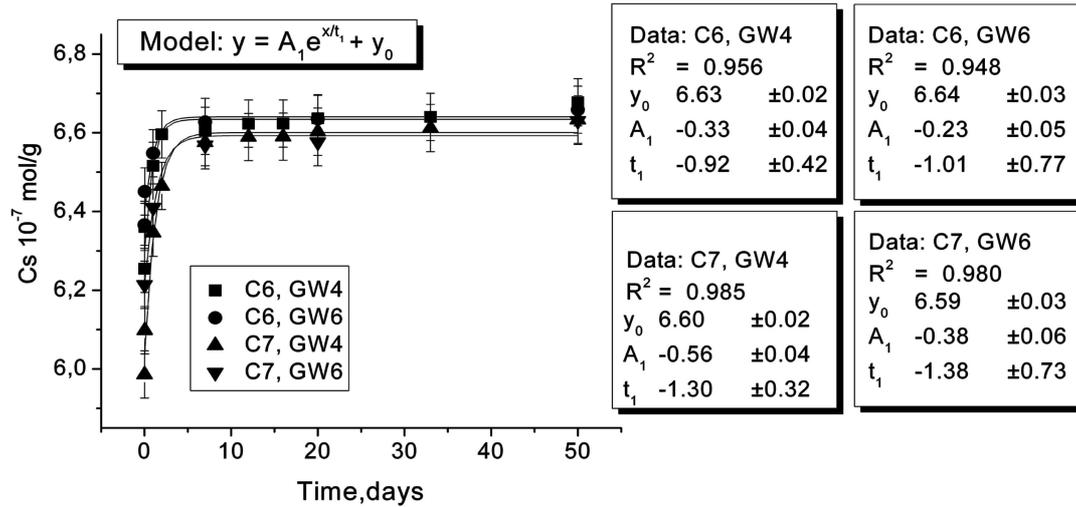


Fig. 2. Cs^+ adsorption on clay minerals (Šaltiškiai clay samples No. 6 and 7, groundwater samples No. 4 and 6) as a function of time ($C(\text{Cs}) = 6.80 \cdot 10^{-5}$ mol/l).

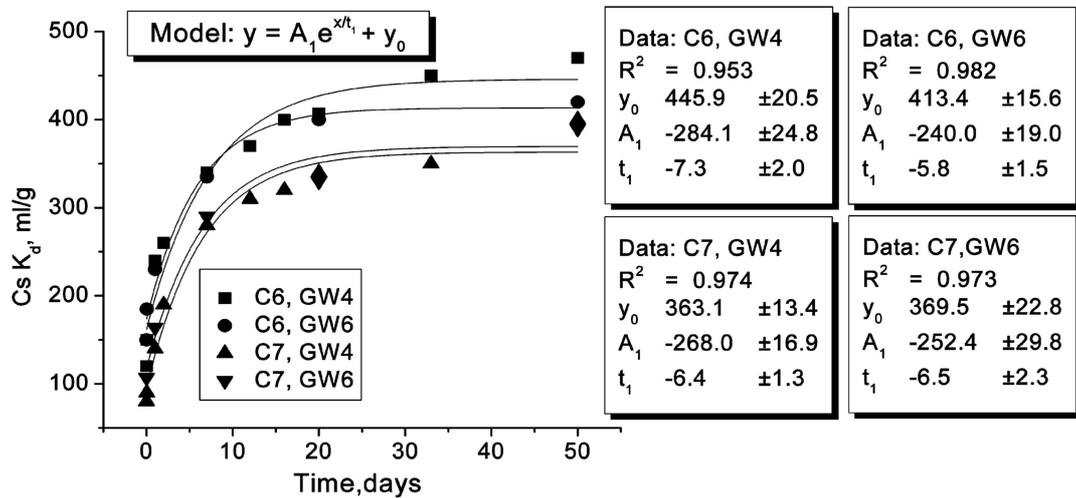


Fig. 3. $\text{Cs } K_d$ values as a function of time (Šaltiškiai clay samples No. 6 and 7, groundwater samples No. 4 and 6, $C(\text{Cs}) = 6.80 \cdot 10^{-5}$ mol/l).

increasing the electrolyte concentration indicated that the Cs exchange processes were nonideal for $\text{Cs}^+ - \text{Na}^+$ and $\text{Cs}^+ - \text{K}^+$ exchange systems [10]. Sequential extraction studies showed rather similar Cs partitioning to various geochemical phases (Fig. 4). Cs was mainly found in the exchangeable and bound to carbonate fraction of clay minerals (up to 70%) and this large amount can be considered as reversibly sorbed caesium (F2, Fig. 4). It should be noted that only insignificant variations were observed on the time scale of the study from 10 min to 50 days. Thus, sorption experiments and data obtained from sequential extraction studies indicated fast sorption processes, high reversibility, and almost full equilibrium in the system after 50 days of sorption experiments with the high caesium concentration ($C(\text{Cs}) = 6.80 \cdot 10^{-5}$ mol/l). Contrary to these findings the slow sorption process and large variations in

the Cs sorption reversibility are characteristic of Cs behaviour in the natural environment [20, 21]. However, K_d concept, usually used as a simplified approach to the complex sorption–desorption processes, is by definition restricted to instantaneous equilibrium and full reversibility.

In sorption experiments performed using the Šaltiškiai clay and using groundwater with low caesium concentrations ($C(\text{Cs}) = 2.30 \cdot 10^{-10}$ mol/l), which were close to that usually found in the natural environment, Cs K_d values ranged from 7000 to 10000 ml/g [22]. The lowest Cs K_d values were found in experiments with synthetic rainwater (Table 1), however, an increase in Cs K_d values was observed during 45 days (Fig. 5). Sequential extraction studies indicated that variations of caesium concentrations in the groundwater affected the partitioning of Cs to clay

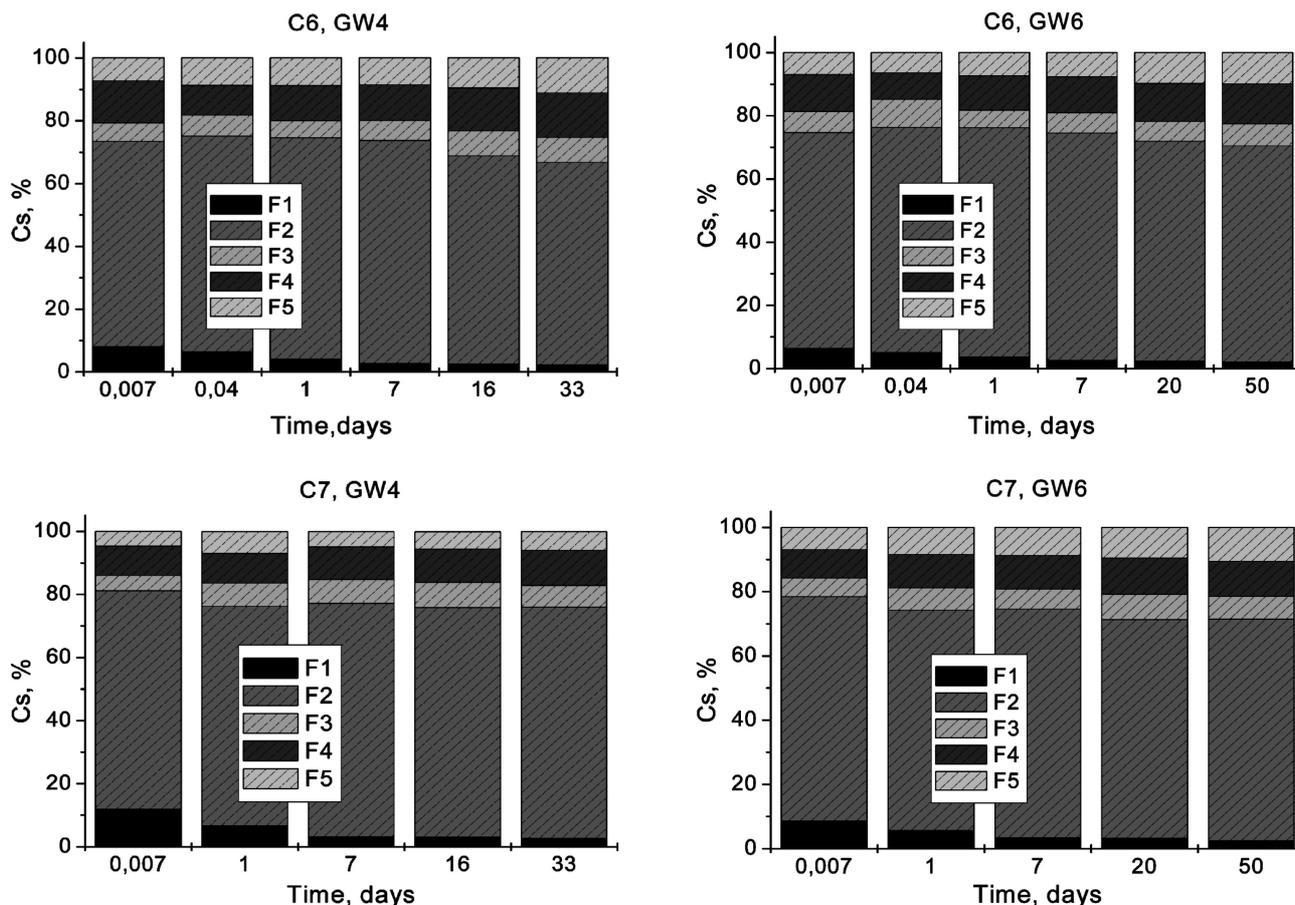


Fig. 4. Fraction distribution of Cs (Šaltiškiai clay samples No. 6 and 7, groundwater samples No. 4 and 6) as a function of time. *F1* is in groundwater, *F2* is exchangeable and bound to carbonates, *F3* is reducible, *F4* is bound to organic matter, *F5* is residual ($C(Cs) = 6.80 \cdot 10^{-5}$ mol/l).

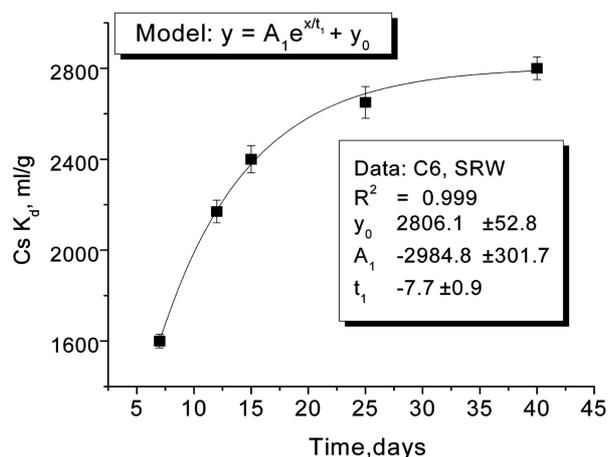


Fig. 5. $Cs K_d$ values as a function of time (Šaltiškiai clay sample No. 6 and synthetic rainwater (SRW), $C(Cs) = 2.30 \cdot 10^{-10}$ mol/l).

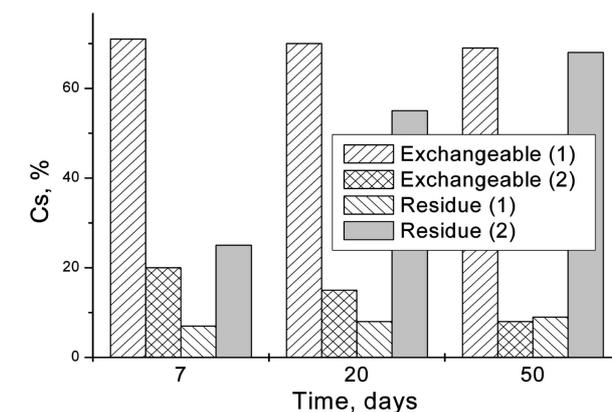


Fig. 6. Fraction distribution of Cs in Šaltiškiai clay (average data) as a function of time (exchangeable (1) and residue (1) with $C(Cs) = 6.80 \cdot 10^{-5}$ mol/l and exchangeable (2) and residue (2) with $C(Cs) = 2.30 \cdot 10^{-10}$ mol/l).

[23]. The main differences deal with an amount of caesium 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 exper-

iments with low and high concentrations are presented in Fig. 6. 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,

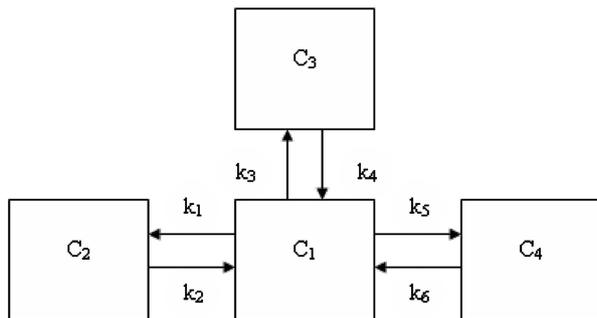


Fig. 7. Schematic representation of the kinetic 4-box model.

while no changes (exchangeable (1) and residue (1)) were observed in experiments with the high concentrations. It can be explained by sorption of caesium 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 a small amount of illite. Thus, the selective sorption sites of FES were available for Cs at illite and were capable of binding Cs at trace concentrations. In experiments with high Cs concentrations, almost all caesium was sorbed to smectite on sites of lower selectivity.

Data obtained from sorption–desorption experiments were used to model the sorption process. The kinetic 4-box model was used (Fig. 7) 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. 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 (F_2 , Fig. 4). 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 a Cs amount extracted during the sequential extraction analyses (the F_3 and F_4 fractions which usually contain radionuclides bound to oxides and organic matter, respectively) (Fig. 4). 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 (F_5 , Fig. 4). The definition of sorption sites is quite relative because of heterogeneous origin of the natural geological material containing the various sorption sites of different selec-

tivity. The sorption sites were defined on the basis of desorption capabilities and on the general knowledge about sorption of caesium to clay minerals. The kinetic equations of the 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.

We tried to describe complicated Cs sorption processes on the natural clay minerals that 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 the experimental results obtained from the kinetic tracer experiment using the least-squares procedure. The set of kinetic equations has been integrated applying the Bader and Deuflhard method [24], which allows obtaining high accuracy even for stiff integral equations. The obtained forward and backward exchange rate constants have been used to calculate apparent equilibrium constants which are presented in Table 2. The apparent equilibrium constants range from 1 to 26 and the highest ones are found for reversible sites. A high Cs content in the reversible fraction indicates the possible radionuclide release into surrounding solution and, hence, the amount of caesium available for transport. Thus, the knowledge about the apparent equilibrium constants is important since the K_d values are very complicated functions of many parameters.

4. Conclusions

Very fast adsorption of Cs to clay minerals was observed under studied conditions with residence time of

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

Site	Clay No. 6, GW4	Clay No. 6, GW6	Clay No. 7, GW4	Clay No. 7, GW6
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

Cs of about one day in the aqueous phase. The determined K_d values ranged from 80 to 470 ml/g.

The sequential extraction investigation indicated rather similar Cs partitioning to various geochemical phases of both clays in the experiments with different groundwater samples. Cs was mainly found in the exchangeable and bound to carbonate fraction of clay minerals (up to 70%).

The estimated apparent equilibrium constants ranged from 1 to 26 and the highest ones were found for reversible sites.

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Cs GERTIES MOLIO MINERALAIS KINETIKA

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Santrauka

Pateikti parengtiniai gerties kinetikos eksperimentinių tyrimų rezultatai. Naudojant natūralaus molio ėminius iš Šaltiškių karjero (šiaurės Lietuva) ir dviejų skirtingų cezio koncentracijų ($C(\text{Cs}) = 2,30 \cdot 10^{-10}$ mol/l ir $C(\text{Cs}) = 6,80 \cdot 10^{-5}$ mol/l) tirpalus, buvo eksperimentiškai tirta gertis Cs pasiskirstymo koeficientams (K_d) įvertinti. Iš tų tyrimų rezultatų paaiškėjo, kad priklausomai nuo grunto vandens ir molio mineralų cheminės sudėties gerties parametrai kinta nežymiai. Eksperimentuojant su didelėmis cezio koncentracijomis, buvo aptiktas didelis (iki 70%) pakaitinio cezio kiekis.

Kineticos eksperimentų ir nuoseklos ekstrakcijos tyrimų rezultatai atskleidė gerties mechanizmų skirtumų priklausomybę nuo Cs koncentracijos. Rezultatai, gauti iš gerties–atvirkštinės gerties eksperimentų, buvo naudojami gerties vyksmams modeliuoti, taikant kinetinį keturių dėžučių modelį, atvaizduojantį katijonų mainų vyksmus trijose molio mineralų gerties vietose, kur gerai išreikšti atrankumo skirtumai. Surastos gerties reakcijų spartos konstantos buvo naudojamos apskaičiuojant pusiausvyros konstantas, kurios kito nuo 1 iki 26. Didžiausios jų vertės gautos mineralų grįžtamios gerties vietose.