The sorption behavior of Cs+ ion on clay minerals and zeolite in radioactive waste management: sorption kinetics and thermodynamics

B. Yıldız · H. N. Erten · M. Kış

Abstract In this work, Cs^+ ion sorption on some clays and zeolite were investigated. ^{137}Cs was used as a tracer. Activities were measured with a NaI crystal gamma counter. The particle size distribution was determined by a laser sizer. Surface area of the particles were determined by BET (Brunauer, Emmett and Teller method). Structure analysis was made by using X-ray diffraction. The chemical compositions of the solid samples were determined using a ICAP-OE spectrometer. Kinetic and thermodynamic parameters were determined. Due to very high uptake results; clay and zeolite can be proposed as a good sorbents in waste management considerations.

Keywords Clay · Bentonite · Zeolite · Radioactive waste

Introduction

Nuclear wastes are one of the most important environmental problems of facing the world. Many countries must address the disposal of very large quantities of waste

Now M. Kış is retired.

B. Yıldız (✉) · M. Kış
Department of Chemistry, Faculty of Science, Hacettepe University, Beytepe, Ankara, Turkey
e-mail: yberna73@gmail.com

H. N. Erten
Department of Chemistry, Faculty of Science, Bilkent University, Bilkent, 06533 Ankara, Turkey

Present Address:
B. Yıldız
Turkish Atomic Energy Authority (TAEK), Sarayköy Nuclear Research and Training Center, Ankara, Turkey

containing long-lived natural radionuclides. Geological formations that contain clay minerals are used as repository for the radioactive wastes. They act as as natural barriers against their leakage. The use of clays is chosen because of their low permeability, good adsorption/ion exchange characteristics, and wide availability [1, 2]. Bentonite has recently attracted increasing attention as a backfilling (buffer) material [3]. Fission products ^{137}Cs and ^{90}Sr are hazardous radionuclides with considerable lifetime and they should be stored in geologic formations. When radioactive wastes are disposed in a geologic repository, they interact with groundwater. While radionuclides are transported along migration pathways in underground, they may be adsorbed onto rock surfaces [4].

Ebina et al. studied the sorption behavior of caesium ions onto smectites [5]. Plecas et al. investigated leaching behavior and diffusivities of ^{137}Cs and ^{60}Co at different leach rates [6]. They found that by adding 1–5% bentonite into cement-based formulations, only 1–2% of initial radionuclides leach into the environment after 245 days. They could predict percentage of leaching during next 300 years (10 halflives of ^{137}Cs). In the paper of Sakr et al. Portland cement was mixed with kaolinite, clay and epoxy polymer at different ratios to immobilize radioactive waste ions [7]. Singh et al. modified the surface of the zeolite using n-octadecyltrichlorosilane for extraction of Cs^+ and Sr^{2+} from aqueous to organic phase [8].

Kaya and Durukan utilized bentonite-embedded zeolite as clay liner [9]. Chmielewská-Horvátová studied the removal of ^{137}Cs and ^{134}Ba radionuclides from aqueous solutions by means of natural clinoptilolite and mordenite [10]. Elizondo et al. studied the effects of solution pH and particle size on the removal of ^{137}Cs and ^{90}Sr by natural zeolite (clinoptilolite) from liquid radioactive wastes and observed that natural zeolite is an effective filter for the

radionuclides from a liquid radioactive waste solution having a pH value of 8 [11]. Jeong investigated sorption characteristics of the ^{137}Cs and ^{90}Sr onto kaolinite and showed in most of the experiments Cs^{+} is preferentially adsorbed onto kaolinite in comparison to Sr^{2+} [4]. Tsai et al. also examined sorption and diffusion behaviors of Cs^{+} and Sr^{2+} ions on compacted bentonite [12]. In the literature, there are research about ^{137}Cs sorption behaviours by using a lot of different sorbents at varying chemical structures like titanosilicate [13], aluminum pillared montmorillonite [14], TiSi sorbents [15], sediment [16], soil [17], nickel ferrocyanide [18], and hydrous silica [19], granite [20].
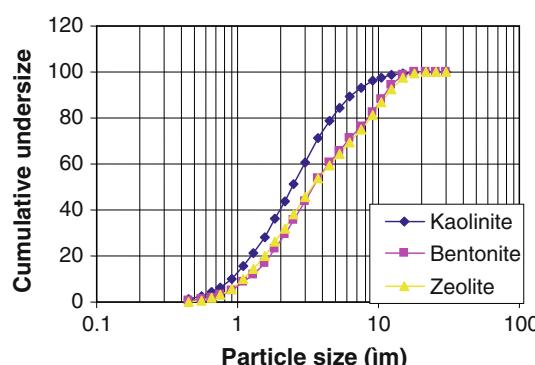
In the scope of this study, the sorption behaviour of Cs^{+} ion on some natural clay minerals and zeolite from Turkey were investigated. The effect of shaking time, concentration, and the temperature on sorption were investigated. Isotherm parameters as well as kinetic and thermodynamic parameters were determined.

Experimental

In this study natural inorganic sorbents used in the experimental studies were kaolinite from Bozhöyük (Bilecik), bentonite from Çankırı and zeolite from Bigadiç (Balıkesir) Turkey. The samples were reduced in size using a jaw crusher, roll crusher and grinded by ring mill. Then finer fractions in the samples were separated by an air separator (Alpin). The size distributions of the samples were determined by a Sympatec laser sizer. The particle size of particles used in experiments were all under 15 μm (Fig. 1).

Figure 1 shows that kaolinite has the finest, and zeolite and the bentonite have nearly the same particle size distribution.

Figure 2 shows the X-ray diffraction patterns of solid samples used in sorption experiments.

Fig. 1 Particle size distribution curves of the samples used in the sorption experiments

The BET surface area (Quantachrome, Monosorb) of the samples used in the sorption studies were determined as (28.85 ± 2.75), (40.16 ± 0.18), (25.23 ± 2.47) m[2]/g. for kaolinite, bentonite and zeolite, respectively.

The chemical compositions of the solid samples were determined using ICAP-OE spectrometer and the results are given in Table 1. According to Chmielewská, mass percent of SiO_2 in clinoptilolite type zeolite is 67.16% [10]. In the Table 1 our result is 67.22% SiO_2.

The radioactive tracer used in the experiments, [137]Cs ($t_{1/2}$ = 30.15 years) was in 0.1 M HCl form with a radionuclide purity of >99.5%.

The synthetic ground water was prepared using Merck grade salts. The anion and cation concentrations in the synthetic groundwater are given in Table 2.

Radiotracer experiments

30 mg samples of sorbents were weighed in polypropylene centrifuge tubes. Three milliliters of groundwater was added onto each sample and the suspension was ultrasonicated for 5 min in a Bandalin sonicator. The samples were then shaken with ground water for one day in a Agitator D-3 (Model 500).

After pretreatment, the phases were separated by centrifugation (Sigma centrifuge) at 13,500 rpm for 10 min. The clear liquid was decanted and wet solid at the bottom of the tubes was weighed. The difference in the weights, ΔW_{pt}, is the amount of liquid remaining in the tube after pretreatment. Then 3 mL of radiotracer solutions of chosen concentrations were added to each centrifuge tube. The batch method was used; clay as solid phase and radioactive solution as the mobile phase.

The tubes were taken out of the shaker after predetermined sorption times, centrifuged at a rate of 13,500 rpm for 10 min. One milliliter of supernatant solution was then transferred into polypropylene counting tubes. A γ-counting system with NaI(Tl) crystal was used for the counting of gamma radiation from the ^{137}Cs tracer.
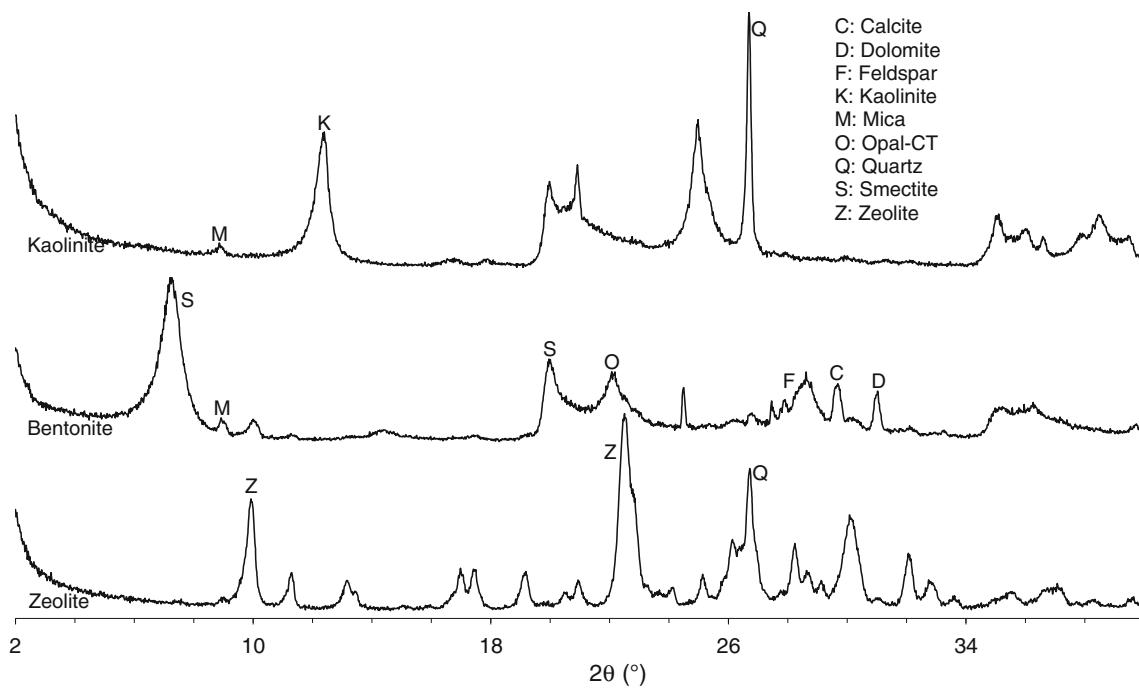
The distribution ratio

The experimental data in sorption are expressed in terms of the distribution ratio, R_D, defined as the ratio of sorbate concentration on solid phase to its concentration in liquid phase.

The distribution ratio is defined by

$$R_{D,ad} = \frac{[Cs]_{s,ad}}{[Cs]_{ad}} \tag{1}$$

where, $[Cs]_{s,ad}$ is the concentration of Cs^{+} in the solid phase after sorption, $[Cs]_{ad}$ is the concentration of Cs^{+} in the solution after sorption.

Fig. 2 X-ray diffractograms of the samples used in sorption studies

Table 1 The chemical analyses of the samples used in the sorption studies

Sample	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	MgO (%)	CaO (%)	Na$_2$O (%)	K$_2$O (%)	TiO$_2$ (%)	P$_2$O$_5$ (%)	MnO (%)	Cr$_2$O$_3$ (%)
Bentonite	60.47	17.08	3.39	2.11	2.29	2.36	0.68	0.30	0.11	0.07	<0.001
Zeolite	67.22	11.00	0.80	1.19	3.32	0.17	1.51	0.07	0.03	0.01	0.001
Kaolinite	49.81	31.23	1.56	0.65	0.21	0.10	1.04	1.02	0.09	0.01	0.018

Table 2 The chemical composition of the ground water

Anion	Concentration (meq/mL)	Cation	Concentration (meq/mL)
HCO$_3^-$	0.50	Na$^+$	0.50
NO$_3^-$	4.20	K$^+$	0.05
Cl$^-$	0.26	Ca^{2+}	0.26
SO$_4^{2-}$	0.79	Mg^{2+}	4.94

Total equivalent values of cations and anions is equal to 5.75 meq/L and is equal to each other. For prepare the ground water NaHCO$_3$, KNO$_3$, CaCl$_2$, MgSO$_4$·7H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O salts used

The concentration of Cs$^+$ in the solid after sorption is given by

$$[Cs]_{s,ad} = \frac{V \cdot [Cs]^o - [Cs]_{ad} \cdot (V + \Delta W_{pt})}{W_s} \quad (2)$$

Since at the beginning of sorption V mL of solution with an initial caesium concentration $[Cs]^o$ was added and at the end of sorption step $(V + \Delta W_{pt})$ mL of solution with concentration $[Cs]_{ad}$ was present. Here ΔW_{pt} is the amount of liquid remaining in the tube after pretreatment and decantation.

R_D can be expressed in terms of activity.

The adsorption distribution ratio, $R_{D,ad}$, was calculated from the measured activities before and after shaking using the following relations;

$$[Cs]_{ad} = \frac{A_{l,ad}}{A^o} \cdot [Cs]^o \quad (3)$$

Substituting Eqs. 2 and 3 into Eq. 1 leads to;

$$R_{D,ad} = \frac{V \cdot A^o - A_{l,ad} \cdot (V + \Delta W_{pt})}{A_{l,ad} \cdot W_s} \quad (4)$$

where A^o is the initial activity of 1 mL of solution, $A_{l,ad}$ is the count rate of 1 mL of solution after sorption, W_s is the weight of solid material (g), V is the volume of solution (mL), and ΔW_{pt} is the amount of liquid remaining in the tube after pretreatment, before sorption.

The unit of the distribution ratio, $R_{D,ad}$ is mL g^{-1}.

For desorption experiments, after centrifuging 3 mL of ground water were added into the tubes. They were shaken for various predetermined times and centrifuged. One milliliter of ground water from these tubes were counted. The distribution ratio of desorption, R_{de},

$$R_{de} = \frac{[Cs]_{s,de}}{[Cs]_{de}} \qquad (5)$$

$[Cs]_{s,de}$ is the concentration of Cs^+ in the solid phase after desorption, $[Cs]_{de}$ is the concentration of Cs^+ in the solution after desorption.

$$[Cs]_{de} = \frac{A_{l,de}}{A^o} \cdot [Cs]^o \qquad (6)$$

The distribution ratio of desorption, R_{de}, was calculated from the following relation;

$$R_{D,de} = \frac{V \cdot A^o - A_{l,ad} \cdot (V + \Delta W_{pt} - \Delta W_{ad}) - A_{l,de} \cdot (V + \Delta W_{ad})}{A_{l,de} \cdot W_s} \qquad (7)$$

where ΔW_{ad} is the the amount of liquid remaining in the tube after adsorption and decantation, $A_{l,de}$ is the count rate of 1 mL of solution after desorption.

The rest of the terms in Eq. 7 have been defined earlier.

Thermodynamic calculations

Sorption behaviour was studied as a function of temperature. The dependence of distribution ratios on temperature was investigated. The relationship between R_D and Gibbs free energy change in sorption is shown below;

$$\Delta G^o = -RT \ln R_d \qquad (8)$$

Gibbs free energy change can also be written in terms of enthalpy change, ΔH^o, and the entropy change, ΔS^o, as given below:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (9)$$

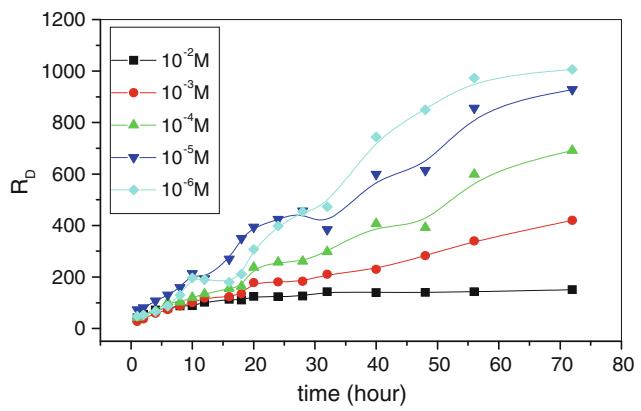Combining Eqs. 8 and 9 the following expression is obtained:

$$\ln R_D = \frac{-\Delta H^o}{R} \times \frac{1}{T} + \frac{\Delta S^o}{R} \qquad (10)$$

By plotting $\ln R_D$ versus $1/T$, it is possible to determine enthalpy ΔH^o of sorption from the slope and entropy ΔS^o of sorption from the intercept of the linear fits.
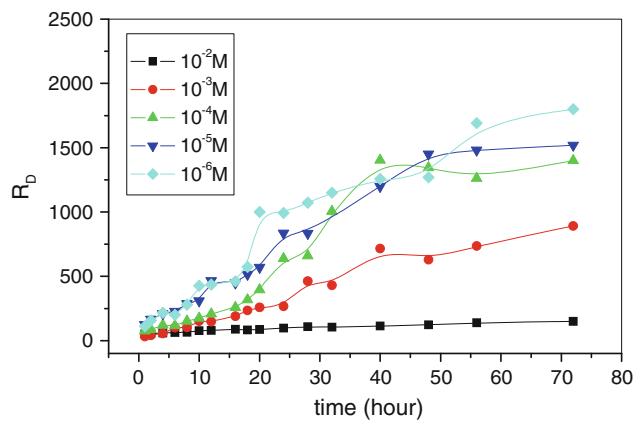
Results

The results of caesium ion sorption on bentonite, kaolinite and zeolite
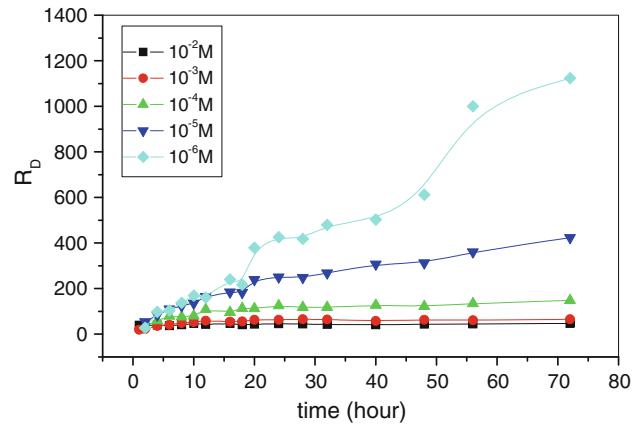
The sorption behaviour of Cs^+ ion on bentonite, zeolite and kaolinite as a function of sorption time for different initial concentrations are shown in Figs. 3, 4 and 5. It is observed

Fig. 3 Cs^+ uptake on bentonite at 5 °C. The effect of cation concentration on sorption

Fig. 4 Cs^+ uptake on zeolite at 5 °C. The effect of cation concentration on sorption

Fig. 5 Cs^+ uptake on kaolinite at 5 °C. The effect of cation concentration on sorption

that in all cases, equilibrium is reached in about 2 days. The sorption experiments were carried out at 5 °C.

In further experiments under equilibrium conditions the shaking time was taken 2 days.

The enthalpy of hydration, ΔH_{hyd}, of an ion is the amount of energy released when one mole of the ion dissolves in a large amount of water forming an infinite dilute solution. In the process, $M_{(aq)}^{z+}$ represents ions surrounded by water molecules and dispersed in the solution. Cs$^+$ is in group 1A. Its ionic radius, r_{ion} is 1.67 (Å). Its enthalpy of hydration, ΔH_{hyd} is -276 (kJ/mol). Cs$^+$ ion has a large ionic size. Its hydration energy is rather low. Thus Cs$^+$ ion is more likely to be adsorbed rather than be hydrated.

The kinetic results of the sorption behaviour of Cs$^+$ onto bentonite, zeolite and kaolinite at 5 °C are shown in Figs. 3, 4, and 5 respectively.

Clay minerals are arranged in groups according to the type of silicate layer present (1:1 or 2:1). The rock in which these smectite minerals are usually dominant is bentonite. Smectite (montmorillonite) is composed of units consisting of two silica tetrahedral sheets with a central alumina octahedral sheet (2:1). The lattice has an unbalanced charge because of substitution of alumina for silica in the tetrahedral sheet and iron and magnesium for alumina in the octahedral sheet. As a clay layer is a combination of sheets, there is an interlayer space between two layers in montmorillonite. Therefore, usually the layers are charged and cations have to be present in the interlayer space to counterbalance this charge, in order to constitute a neutral compound. Montmorillonite layers are bonded to each other weakly; by means of van der Waals bonds. Both interlayer and surface adsorption takes place with Cs$^+$ sorption.

Zeolites are crystalline, hydrated aluminosilicates. Their three-dimensional, polyanionic networks are built of SiO$_4$ and AlO$_4$ tetrahedra linked through oxygen atoms. Depending on the structure type, they contain regular channels or interlinked voids whose diameters are in the micropore range. The size of Cs$^+$ ion is suitable for these channels. Therefore sorption order of Cs$^+$ ion is zeolite > bentonite > kaolinite.

The structure of kaolinite consists of a single silica tetrahedral sheet and a single alumina octahedral (1:1) layer. There are no cations in the interlayer space [21, 22]. On kaolinite, only surface bondings of cations occur. In Fig. 5 it is seen rapid increase in sorption, so Cs$^+$ ions adsorbed in short time. Surface adsorption of Cs$^+$ ions on kaolinite occurs.

Loading curves of Cs$^+$ ion adsorption on the three minerals are presented in Fig. 6. It is observed that the R_D values slightly decrease with initial concentration until $\sim 10^{-2}$ M for bentonite and zeolite.

This is due to the fact that the available sorption sites have not be saturated until a concentration of 10^{-2} M. In the case of kaolinite the decrease of R_D values with initial concentration starts at very low initial concentrations
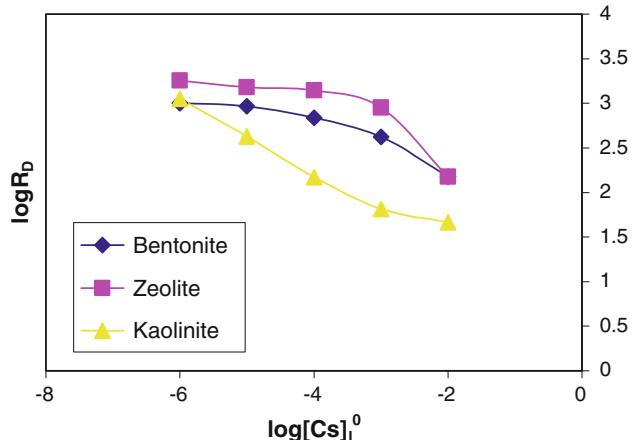

Fig. 6 Loading curves of Cs$^+$ on bentonite, zeolite and kaolinite

showing poor adsorption of Cs$^+$ ions on kaolinite as compared to bentonite and zeolite.

Similar results have been reported in recent papers. In the article of M. Galambos et al. the adsorption of Cs on the samples of bentonites was studied through radioisotope of ^{137}Cs at laboratory temperature. Adsorption parameters were determined after mixing in 0.05 g of adsorbent with 5 mL of water phase by batch method and measuring of radioactivity. Natural samples of bentonite were at disposal in grain size with average diameters 15 μm. Adsorption experiments were realized using the Cs-concentration range 1×10^{-5} to 5×10^{-2} mol L^{-1} solutions prepared from cesium chloride. They indicated that the adsorption process was fast, maximum distribution ratio K_d, adsorption capacity were nearly reached within 1 min from the beginning of contact of solid and liquid phase. The comparable values of R were reached in a time interval of 1–480 min. A period of 2 h was chosen for the further adsorption experiments. In the adsorption experiments carried out on the bentonite and montmorillonite samples, the highest K_d and R was observed at the lowest Cs-concentrations in the solution (1×10^{-5} mol L^{-1}). The highest value of K_d (3163 mL g^{-1}, type J15). Their distribution ratio results are for 1×10^{-2} M Cs 103 mL g^{-1}, for 1×10^{-3} M Cs 684 mL g^{-1}, for 1×10^{-4} M Cs 1810 mL g^{-1}, for 1×10^{-5} M Cs 3163 mL g^{-1} [23]. Their concentration effect experiments were evaluated as in our experiments. We also obtained higher distribution ratios with lower Cs concentrations similarly. Our concentration interval is between 1×10^{-2} and 1×10^{-6}. Our results also indicate that distribution ratio increases as concentration decreases. In another paper of M. Galambos the results show that equilibrium is reached almost instantaneously after mixing. Adsorption kinetics plots were presented as K_d mL g^{-1} versus t(min) up to 480 min. They expressed that almost ''instantaneous'' capture of the

cesium ions on the bentonite can be explained by adsorption and ions exchange on the surface for the cesium ions. Cs distribution coefficients K_d [mL g^{-1}] for Kopernica bentonites, type BK15, at grain size of 15 μm, are for 1×10^{-1} M Cs 9 mL g^{-1}, for 1×10^{-2} M Cs 166 mL g^{-1}, for 1×10^{-3} M Cs 261 mL g^{-1}, for 1×10^{-4} M Cs 295 mL g^{-1} [24].

Adsorption parameters of Cs on different type bentonite samples are presented in [25]. For example, type J45, bentonite at grain size of 45 μm, for 1×10^{-2} M Cs ion 130 mL g^{-1}, for 1×10^{-3} M Cs 785 mL g^{-1}, for 1×10^{-4} M Cs 1644 mL g^{-1}, for 1×10^{-5} M Cs 3426 mL g^{-1}. They concluded that the basic adsorption mechanism is used cation exchange, by this reason diversity of adsorption values between individual samples could be due to different cation exchange capacity, different mineralogical structure and difference in surface area of individual samples. The surface area of samples are directly proportional to particle size. In our experiments, size is under 15 μm and temperature is 5 °C for different initial concentration of Cs ion. In a recent research, the Šaltiškiai clay exhibited a high retention capacity towards cesium. K_d values ranged from 450 to 9700 mL g^{-1} for Cs [26].

A clinoptilolite-rich tuff and zeolite were used for cesium exchange reaction in the paper of P. Rajec and K. Domianova. In this article the grain size of zeolite samples is <1 mm; in the ion exchange experiments 0.5 g of the samples were mixed with 20 mL 1×10^{-3} M CsCl solution 10, 20, 40, 80 min for contact of the phases. Distribution coefficient value of cesium for clinoptilolite zeolite K_d(Cs), as 1923.28 mL g^{-1} [27].
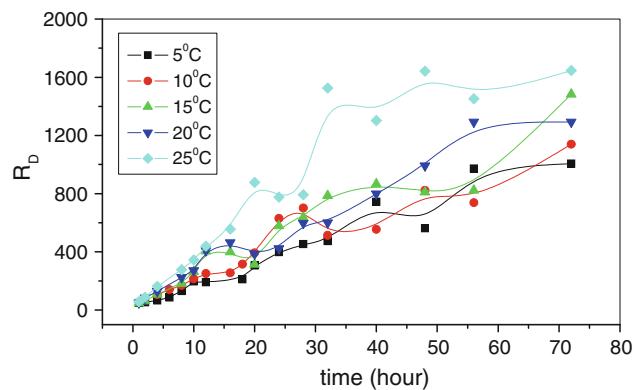
In the litareture, a sorption ability of titanium silicates (TiSi) and iron oxides towards Cs, Sr, Pu and Am was tested using the laboratory batch method. The obtained results are expressed as distribution coefficients (K_d). The K_d values ranged from 6 to 4.1×10^4 mL g^{-1} for Cs [15].

In the article of Chmielewska, mordenite and clinoptilolite samples of the grain size between 0.250 and 0.315 mm were chosen as sorbent material for the interaction mechanisms of ^{137}Cs. They indicated as the kinetics of Cs adsorption onto zeolites did not prove show a significant difference (20 min and 60 min in favour of mordenite) [10].
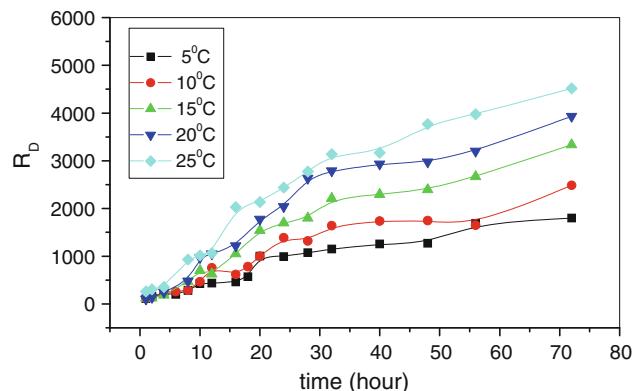
The effect of temperature on Cs$^+$ ion sorption

Figures 7, 8 and 9 show the variation of the distribution ratio R_D values as a function of sorption time at five different temperatures (5, 10, 15, 20 and 25 °C). In these experiments the chosen Cs ion concentration is 1×10^{-6} M.
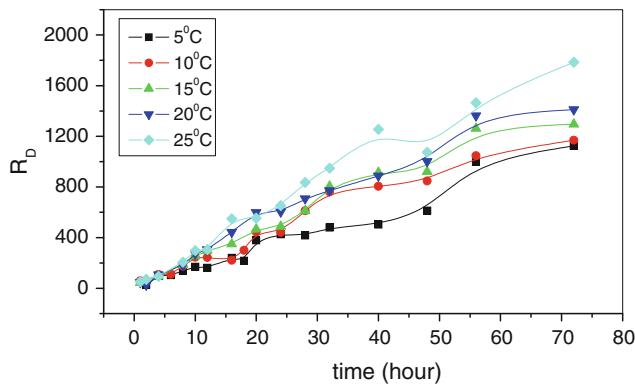
In all cases it is observed that increase in temperature leads to higher sorption. The curves are not monotonous,

Fig. 7 Cs$^+$ uptake on bentonite at constant cation concentration (1×10^{-6} M). The effect of temperature on sorption

Fig. 8 Cs$^+$ uptake on zeolite at constant cation concentration (1×10^{-6} M). The effect of temperature on sorption

Fig. 9 Cs$^+$ uptake on kaolinite at constant cation concentration (1×10^{-6} M). The effect of temperature on sorption

indicating some structure in the sorption process i.e. different sorption sites.

The equilibrium temperature data were used in exahating the thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o by using the Eqs. 8–10. The results for bentonite, zeolite and kaolinite are given in Table 3. The corresponding plot used in obtaining these results is shown in Fig. 10.

Table 3 Thermodynamic parameters for the sorption of Cs$^+$ ions on bentonite, kaolinite and zeolite

T (K)	ΔG^{o} (kJ/mol)			ΔH^{o} (kJ/mol)			ΔS^{o} (J/mol K)		
	Kaolinite	Zeolite	Bentonite	Kaolinite	Zeolite	Bentonite	Kaolinite	Zeolite	Bentonite
278	−16.24	−17.32	−15.98	17.71	31.79	15.33	122	177	113
283	−16.62	−18.39	−16.56						
288	−17.16	−19.42	−17.48						
293	−17.67	−20.16	−17.45						
298	−18.77	−20.85	−18.35						

Fig. 10 Loading curve as a function of temperature. Log R_{D} versus $1/T$ plot in the sorption of Cs$^+$ on zeolite. The initial cation concentration is 1×10^{-6} M

The negative values of ΔH^{o} in all cases reflect the spontaneity of the sorption process. The values are well below those associated with chemical bond formation, indicating the physical nature of the sorption process.

The enthalpy change ΔH^{o} following sorption is positive in all cases indicating the endothermic nature of sorption, that is the removal of Cs$^+$ is enhanced as the temperature rises. The entropy changes ΔS^{o} of the system accompanying the adsorption of Cs$^+$ ions on bentonite, zeolite and kaolinite are positive in all cases indicating that more disorder is generated following sorption.
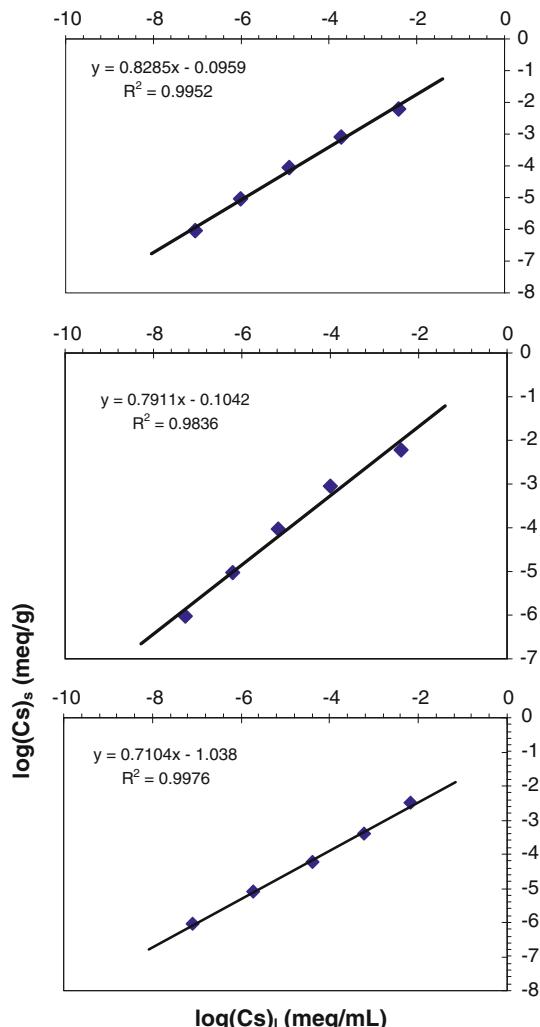
Freundlich isotherm

The Freundlich isotherm is generally used for non-linear dependence of sorption on adsorbate concentration. The formulation is:

$$\log[C]_s = \log k + n \log[C]_l \qquad (11)$$

where $[C]_s$ is the amount of ionic species adsorbed on the solid matrix at equilibrium (meq/g), $[C]_l$ is the concentration of the cation in solution at equilibrium (meq/mL), k and n are Freundlich constants.
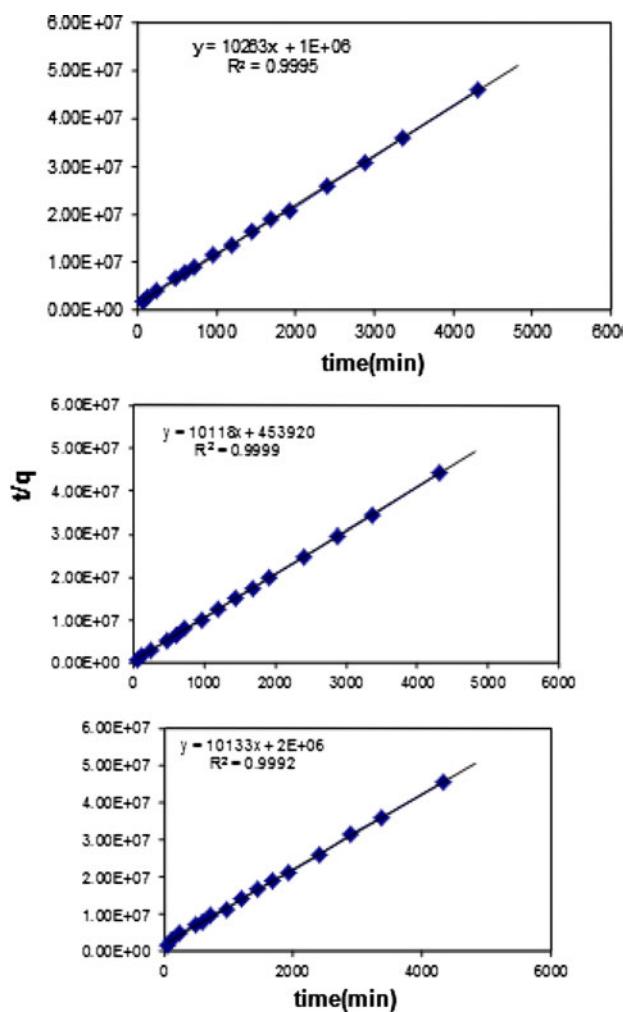
The isotherm plots of the sorption data at a temperature of 5 °C for the sorption of Cs$^+$ ion on bentonite, zeolite and kaolinite are shown in Fig. 11. The corresponding values of the parameters n and k obtained from these linear fits to the

Fig. 11 a Freundlich isotherm of Cs$^+$ sorption on bentonite. **b** Freundlich isotherm of Cs$^+$ sorption on zeolite. **c** Freundlich isotherm of Cs$^+$ sorption on kaolinite

data are given in Table 4. The n values in all cases ($n < 1$) indicate that the sorption process is nonlinear. Comparing k values; it may be said that bentonite and zeolite have about the same affinity for Cs$^+$ ion while that of kalinite is much lower. A result which is in line with the loading curves (Fig. 6).

Table 4 Freundlich isotherm constants for the sorption of Cs^+ ions on bentonite, kaolinite and zeolite

Bentonite		Zeolite		Kaolinite	
n	k	n	k	n	k
0.8285	0.8019	0.7911	0.7867	0.7104	0.0916

Table 5 The calculated parameters of the pseudo second order kinetic model for the sorption of Cs^+ ions on bentonite, kaolinite and zeolite. (1×10^{-6} M ion concentration, sorption at 25 °C)

System	q_e (mmol/g)	k_2 (g/mmol min)	R^2
Cs-bentonite	9.74×10^{-5}	105.4	0.9995
Cs-zeolite	9.88×10^{-5}	225.7	0.9999
Cs-kaolinite	9.87×10^{-5}	51.3	0.9992

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k^2(q_e - q)^2 \tag{12}$$

where q and q_e are the amounts of sorbed Cs^+ per gram of sorbent at any time t and at equilibrium, respectively. The constant k_2 is the rate constant. Integrating and linearizing the above equation, it takes the form;

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{13}$$

A plot of t/q against time t should give a straight line with slope $1/q_e$ and intercept $1/(k_2 q_e^2)$. Using such plots the values of q_e and k_2 were determined is shown in Fig. 12. The corresponding results are given in Table 5. It is seen that the fastest sorption rate is observed in the sorption of Cs^+ ion on zeolite. This is in line with higher sorption capacity of zeolite as was observed in the isotherm studies. In the literature, kinetics of ^{137}Cs adsorption on granite and rate order of sorption process was investigated [20]. They indicated as the sorption on granite can be expressed by a pseudo first order reaction model.

Fig. 12 Pseudo second-order kinetic modelling for **a** caesium–bentonite system, **b** caesium–zeolite system, **c** caesium–kaolinite system. Sorption was carried out at 25 °C and 1×10^{-6} M ion concentration

Desorption

Desorption studies following adsorption was conducted to check the reversibility of the sorption of Cs-ions on bentonite, zeolite and kaolinite. In all cases there was no significant activity above the background indicating that the sorption process was irreversible. These minerals can thus be used as backfill materials in geological repositories for the storage of ^{137}Cs containing radioactive wastes.

In a recent paper, sorption isotherms for cesium in two types of bentonite were plotted [28]. The cesium concentrations were in the range 10^{-2}–10^{-7} mol/dm³. According to their results Freundlich isotherm is fitting to the sorption.

Kinetic results

The results of the kinetic studies was analyzed using a pseudo second order rate equation [29–32]. This equation may be expressed as;

References

1. Shahwan T, Sayan S, Erten HN, Black L, Hallam KR, Allen GC (2000) Surface spectroscopic studies of Cs^+, Ba^{2+} sorption on chlorite-illite mixed clay. Radiochim Acta 88:681–686
2. Missana T, Adell A (2000) On the applicability of DLVO theory to the prediction of clay colloids stability. J Colloid Interface Sci 230:150–156
3. Xu YF, Sun D, Yao Y (2004) Surface fractal dimension of bentonite and its application to determination of swelling properties. Chaos Solitons Fractals 19(2):347–356

4. Jeong CH (2001) Mineralogical and hydrochemical effects on adsorption removal of cesium-137 and strontium-90 by kaolinite. J Environ Sci Heal A 36(6):1089–1099

5. Ebina T, Iwasaki T, Onodera Y, Chatterjee A (1999) A comparative study of DFT and XPS with reference to the adsorption of caesium ions in smectites. Comp Mater Sci 14(1–4):254–260

6. Plecas I, Pavlovic R, Pavlovic S (2004) Leaching behaviour of ^{60}Co and ^{137}Cs from spent ion exchange resins in cement-bentonite clay matrix. J Nucl Mater 327:171–174

7. Sakr K, Sayed MS, Hafez MB (2003) Immobilization of radioactive waste in mixture of cement, clay and polymer. J Radioanal Nucl Chem 256(2):179–184

8. Singh R, Dutta PK (1999) Use of surface-modified zeolite Y for extraction of metal ions from aqueous to organic phase. Micropor Mesopor Mater 32:29–35

9. Kaya A, Durukan S (2004) Utilization of bentonite-embedded zeolite as clay liner. Appl Clay Sci 25:83–91

10. Chmielewská-Horvátová E (1998) The interaction mechanisms between aqueous solutions of ^{137}Cs and ^{134}Ba radionuclides and local natural zeolites for an dectivation scenario. J Radioanal Nucl Chem 227(1–2):151–155

11. Elizondo NV, Ballesteros E, Kharisov BI (2000) Cleaning of liquid radioactive wastes using natural zeolites. Appl Radiat Isot 52:27–30

12. Tsai S-C, Ouyang S, Hsu C-N (2001) Sortion and diffusion behaviour of Cs and Sr on Jih-Hising bentonite. Appl Radiat Isot 54:209–215

13. Pavel CC, Popa K, Bilba N, Cecal A, Cozma D, Pui A (2003) The sorption of some radiocations on microporous titanosilicate ETS-10. J Radioanal Nucl Chem 258(2):243–248

14. Karamanis DT, Aslanoglou XA, Assimakopoulos PA, Gangas NH (1999) Characterization of an aluminum pillared montmorillonite with cation exchange properties. J Radioanal Nucl Chem 242(1):3–9

15. Lujaniene G, Meleshevych S, Kanibolotskyy V, Sapolaite J, Strelko V, Remeikis V, Oleksienko O, Ribokaite K, Sciglo T (2009) Application of inorganic sorbents for removal of Cs, Sr, Pu and Am from contaminated solutions. J Radioanal Nucl Chem 282:787–791

16. Ioannides KG, Mertzimekis TJ, Karamanis DT, Stamoulis KC, Kırıkopoulos I (1996) Radiocesium sorption-desorption processse in lake sediments. J Radioanal Nucl Chem 208(2):549–557

17. Man CK, Chu PY (2004) Experimental and modelling studies of radiocesium retention in soils. J Radioanal Nucl Chem 262(2):339–344

18. Orechovska J, Rajec P (1999) Sorption of cesium on composite sorbents based on nickel ferrocyanide. J Radioanal Nucl Chem 242(2):387–390

19. Pathak PN, Chopin GR (2006) Kinetic and thermodynamic studies of cesium(I) sorption of hdrous silica. J Radioanal Nucl Chem 270(2):299–305

20. Tsai S-C, Wang T-H, Wei Y-Y, Yeh W-C, Jan Y-L, Teng S-P (2008) Kinetics of Cs adsorption/desorption on granite by a pseudo first order reaction model. J Radioanal Nucl Chem 275(3):555–562

21. Konan KL, Peyratout C, Bonnet J-P, Smith A, Jacquet A, Magnoux P, Ayrault P (2007) Surface properties of kaolin and illite suspensions in concentrated calcium hydroxide medium. J Colloid Interface Sci 307(1):101–108

22. Salles F, Henry M, Douillard J-M (2006) Determination of the surface energy of kaolinite and serpentine using PACHA formalism—comparison with immersion experiments. J Colloid Interface Sci 303:617–626

23. Galambos M, Paucova V, Kufcakova J, Rosskopfova O, Rajec P, Adamcova R (2010) Cesium sorption on bentonites and montmorillonite K10. J Radioanal Nucl Chem 284:55–64

24. Galambos M, Kufcakova J, Rosskopfova O, Rajec P (2010) Adsorption of cesium and strontium on natrified bentonites. J Radioanal Nucl Chem 283:803–813

25. Galambos M, Kufcakova J, Rajec P (2009) Adsorption of cesium on domestic bentonites. J Radioanal Nucl Chem 281:485–492

26. Lujaniene G, Motiejunas S, Šapolaite J (2007) Sorption of Cs, Pu and Am on clay minerals. J Radioanal Nucl Chem 274(2):345–353

27. Rajec P, Domianova K (2008) Cesium exchange reaction on natural and modified clinoptilolite zeolites. J Radioanal Nucl Chem 275(3):503–508

28. Vokal A, Vopalka D, Vecernık P (2010) An approach for acquiring data for description of diffusion in safety assessment of radioactive waste repositories. J Radioanal Nucl Chem 286(3):751–757

29. El-Kamash AM, Zaki AA, El Geleel MA (2005) Modelling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. J Hazard Mater B127:211–220

30. El-Kamash AM, El-Gammal B, El-Sayed AA (2007) Preparation and evaluation of cerium(IV) tungstate powder as inorganic exchanger in sorption of cobalt and europium ions from aqueous solutions. J Hazard Mater 141:719–728

31. Ho YS, Ng JCY, McKay G (2000) Kinetics of pollutant sorption by biosorbents: review. Sep Purif Method 29:189–232

32. Lin S-H, Juang R-S (2002) Heavy metal removal from water by sorption using surfactant-modified montmorillonite. J Hazard Mater B92:315–326