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Influence of pH and Ca²⁺ Ions on Chemical Composition and Sorption of ¹³⁷Cs by Cherkasy Bentonites (Ukraine)

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Вплив іонів Ca²⁺ на елементний склад та сорбційну здатність щодо ¹³⁷Cs черкаських бентонітів (Україна)

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Ключові слова: черкаський бентоніт; Na-модифікований бентоніт; сорбція; цезій; чорнобильська зона відчуження; інженерні бар'єри.

The safety of near-surface and deep radioactive waste storage facilities is based on a system of engineered and natural barriers. Significant degradation of the engineered barrier system composed of cemented waste matrixes covered by cement mixture, concrete compartments, and structures at the basement of the storage facility may cause radionuclide transfer from the facility to groundwater. Mixing of the cement and concrete with water leads to the formation of several various hydration products with subsequent leaching of Ca²⁺ ions and formation of hydroxyl ions (OH⁻), which affects the alkalinity of the water environment and the sorption properties of bentonite, as a component of the engineered barrier at the basement of near-surface facilities. The article presents the results of an experimental study of the influence of Ca²⁺ ion concentration and pH of the model solution (similar to groundwater composition at Vector Site in Chernobyl Exclusion Zone) on the elemental composition and sorption properties of natural (NB) and Na-modified (PBA-20) bentonites from the Cherkasy deposit concerning ¹³⁷Cs at the Solid : Solution ratio of 1 : 100. Geochemical modeling suggests that addition of CaCl₂ to test solution and resulting alkaline pH leads to precipitation of solids, mainly oxides, hydroxides, Fe oxyhydroxides (hematite, goethite, limonite), and Ca carbonates (calcite, aragonite, dolomite). Their role in Cs adsorption was evaluated. The concentration of structural elements (Si, Al) in bentonites practically does not change with Ca²⁺ ion concentration increase in the model solution, demonstrating the bentonite structure's stability under these conditions. At the same time, an increase in the Ca concentration and a decrease in the Na concentration was found in the ion exchange complex of the bentonites if compared to the initial natural bentonite. This results in the transformation of Na-modified bentonite from Na, Ca-form to Ca, Na-form. The total sorption capacity of NB and PBA-20 bentonite concerning Cs⁺ ions at increased concentrations of Ca²⁺ ions and pH of the solution slightly decreases, though retaining high values of the degree of absorption (> 90 %). The total adsorption of Cs⁺ ions on NB and PBA-20 bentonites from model groundwater with the addition of CaCl₂ from 16 to 960 mg/dm³ and increase of pH from 7.4 to 11.8 decreases with the increase in ionic strength, in particular, due to competition with Ca²⁺ and Na⁺ ions. NB and PBA-20 bentonites of the Cherkasy deposit remain a reliable component of the liner at the repository basement owing to their main functional property – high absorption capacity for ¹³⁷Cs, which is an important dose-forming radionuclide of short-lived low- and medium-level waste.

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Introduction

At present, radioactive waste (RAW) in Ukraine is stored in national storage facilities at the Industrial Complex “Vector” (IC “Vector”) in the Chornobyl Exclusion Zone (ChEZ). The IC “Vector” accepts various classes of RAW, including low- and intermediate-level waste with short-lived radionuclides (LILW-SL), from various enterprises generating waste and from interim waste storage facilities. Large volumes of accumulated radioactive waste require an extension of the already existing storage facilities and the construction of new ones (State Agency of Ukraine on Exclusion Zone Management, 2022).

The safety of such storage facilities is based on an engineered (EBS) and natural barrier system, and it determines the Waste Acceptance Criteria (WAC) for the disposal of radioactive waste at each facility. The WAC for near-surface disposal facilities for LL-ILW at IC “Vector” contains requirements on the rate of radionuclide leaching from a waste matrix (for example, cement) of immobilized LILW-SL by groundwater (Criteria for acceptance of radioactive waste for disposal, 2009), which would also affect the performance of other EBS components.

Most of the world’s concepts of near-surface and deep disposal facilities for radioactive waste consider bentonite clays as an underlying engineered barrier at the base of the storage facility or as compaction and backfill material (Canadian National Report for the Joint Convention on the Safety of Spent Fuel Management, 2020; Joint Convention on the Safety of Spent Fuel Management, 2020; Sweden’s seventh national report under the Joint Convention on the safety of spent fuel management, 2020; Shabalin et al., 2023). The isolating hydraulic and sorption properties of bentonite clays are much higher than those of other clay materials (Wilson, 2013).

In the absence of emergencies, only significant degradation of the EBS may cause radionuclide transfer from the facility with infiltration to groundwater. The RAW and EBS components at the base of the repository can encounter water due to leakage through the walls and basement of the compartments because of flooding (for example, with rising groundwater or/and perched water levels), as well as with atmospheric precipitations through insufficiently watertight engineered covering of the facility.

In the process of functioning (the post-closure institutional control period lasts for 300 years) of

near-surface RAW storage facilities, the bentonite barriers can be exposed to a strongly alkaline environment, and increased concentration of Ca²⁺ ions produced in the case of concrete-cement structures and cement matrices degradation. Under such conditions, the contact of bentonites with an aqueous environment can change the sorption properties of bentonites with respect to cations of radionuclides (Balmer et al., 2016).

A lot of laboratory studies of cement (concrete) – bentonite systems showed that extended chemical reactions between the pore water and concrete-cement hydration products lead to partial dissolution of the formed solid phases and leaching of Na⁺ and K⁺ ions at the initial stage and later of Ca²⁺ from cement (concrete) with the formation of hydroxyl ions (OH⁻). These processes increase the alkalinity of the water environment, starting from pH 11–12, and affect the stability of bentonites and their physical and chemical properties (Pusch et al., 2003; Karnland et al., 2007; Kaufhold and Dohrmann, 2011; Anh et al., 2017; Liu et al., 2018).

One of the mechanisms affecting the sorption properties of bentonites is self-compaction due to precipitation and co-precipitation caused by the composition, pH and/or redox potential Eh of the contact water due to filling pore spaces with degradation products.

Consequently, determining the elemental composition and sorption properties of bentonites in case of degradation of the cement-concrete EBS components of a near-surface RAW storage facility is a fundamental area of research related to radioactive waste disposal.

The maximum specific activity of radionuclides in wastes disposed of in near-surface facilities can reach 3.7×10^7 Bq/kg (Management of radioactive waste, 2018). The radionuclide composition of waste buried in surface / near-surface repositories is quite diverse and includes ¹³⁷Cs, ¹³⁴Cs, ⁹⁰Sr, ⁶⁰Co, ⁵⁴Mn, ²³⁹Pu, ²⁴¹Am, and several short-lived radionuclides. The ¹³⁷Cs represent one of the most environmentally hazardous components of radioactive waste stored in near-surface repositories due to the long half-life of this radionuclide and the high yield during the uranium fuel fission in reactors in Ukraine.

The article aims to assess the influence of Ca²⁺ ion concentration in model solution (similar to the composition of groundwater at the “Vector” Site in the Chornobyl Exclusion Zone) on the elemental composition and sorption properties of the Cher-

kasy bentonites for ^{137}Cs in case of degradation of cement-concrete engineered barriers in a near-surface radioactive waste storage facility.

While this study is focused on ^{137}Cs , it is interesting to conduct similar studies for other radionuclides such as ^{90}Sr , ^{60}Co , and other radioactive constituents present in RAW.

Materials and Methods

Bentonite Characterization. We used powdered natural (NB) and industrial sodium modified (PBA-20) Cherkasy bentonite. The characteristics of the bentonites are presented in previous authors' articles (Shabalin et al., 2018; Shabalin et al., 2022).

Bentonite clays of the Cherkasy deposit (Dashukivka area, II layer) consist mainly of low-dispersed fractions: the 0.005–0.001 mm fraction makes 86–87.5 wt. %. Natural bentonite predominantly comprises smectite (Ca-montmorillonite) – 70–75 wt. % and quartz – 20–25 wt. %. The accessory minerals are calcite (3–5 %), kaolinite (3–5 %), mica (5 %) and feldspar (3 %). SiO_2 contained in quartz, cristobalite, and silica, which is confirmed by plasma atomic emission spectrometry data. The composition of exchangeable cations is as follows (mg-equiv/100 g): Na^+ – 2.6; Ca^{2+} – 41.3; Mg^{2+} – 32.6; K^+ – 1.2; the total amount of exchangeable cations is 77.6.

The chemical composition of bentonites was studied by scanning electron microscopy (SEM) in combination with roentgen energy dispersion spectroscopy (EDS) using a scanning electron microscope JSM-6700F, equipped with an energy dispersion system for microanalysis JED-2300 (JEOL, Japan). SEM images and the chemical composition of the samples were obtained at an accelerating voltage of 15 kV, a probe current of 6×10^{-10} Å, and a probe diameter of 1 to 2 μm . Pure metals, minerals, oxides, and fluorides were used as standards. The relative error (%) was as follows: SiO_2 – 0.87; Al_2O_3 – 0.75; $\text{FeO}+\text{Fe}_2\text{O}_3$ – 0.35; MgO – 0.22; CaO – 0.36; Na_2O – 0.23; K_2O – 0.49.

Mineral composition of sediments. The composition of sediments (precipitated solids) in the model solution under the experimental conditions was simulated using the program Modeling with USGS PHREEQC (PHREEQC Software), which analyses the chemical composition, pH, and Eh of multicomponent solutions.

Solution Chemistry. The initial composition of the model solution was like the composition of groundwater at the Vector Site in the Chernobyl Exclusion Zone and is given in Table 1 (Shestopalov, 1999).

γ -spectrometry. The isotope indicator used in the experiments was ^{137}Cs isotope ($t_{1/2} = 30.15$ years) in the solution form with radionuclide purity of more than 99.5 %. The activity of the initial solution

Table 1. Initial composition of model solution simulating the ChEZ groundwater

Ions	Na^+	Ca^{2+}	K^+	Fe^{2+}	Mg^{2+}	Cs^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	Mineralization
Concentration, mg/dm ³	31.2	16.0	3.3	1.0	4.8	1.0	42.4	27.2	68.9	5.7	201.5

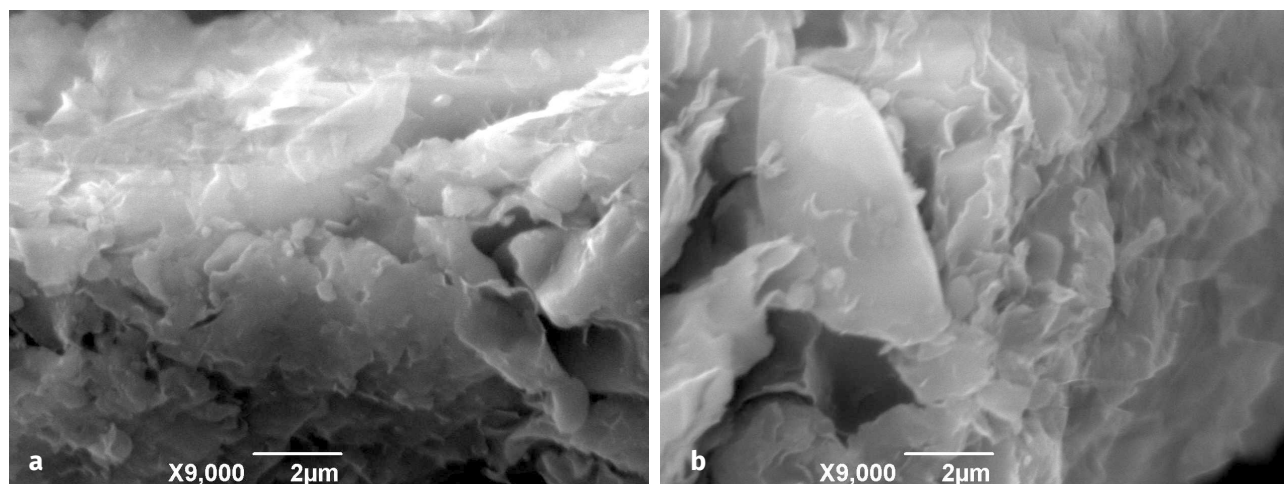


Fig. 1. Suspension of natural (a) and Na-modified (b) bentonite of the Cherkasy deposit (Dashukivka site, II layer). pH 11.8; Ca^{2+} ion concentration – 960 mg/dm³

was 3.13×10^4 Bq/dm³. ¹³⁷Cs activity was measured using the semiconductor γ -spectrometer "ATOLL-1M" (Ukraine) with CsI-crystals. The relative error of measuring the radionuclide activity by semiconductor detectors depends on the sample activity and the measurement time (set by the operator). The sample measurement time was 60 minutes. The error ¹³⁷Cs activity measuring in the initial solution (high activity) was 1 %. The error of measuring the ¹³⁷Cs activity in the solutions after sorption (low activity) was within 3.2–21.8 % depending on the amount of activity.

Potentiometry. The pH of the solution was measured with a potentiometer (pH meter) "IT pH-150" (Russian Federation) with an appropriate electrode. The relative measurement error is ± 0.1 unit.

Experimental procedure. For the batch experiments, 50 ml aliquots of the solution were taken for each sample. Then CaCl₂ solution was added to the samples to reach Ca²⁺ concentration equal to 160 mg/dm³ (4×10^{-4} mol/L), 320 mg/dm³ (8×10^{-4} mol/L), 640 mg/dm³ (1.6×10^{-3} mol/L) and 960 mg/dm³ (2.4×10^{-3} mol/L) taking into account the significant amount of cement and concrete in the total mass of near-surface modular LILW-SL storage facilities (Industrial..., 2003).

NaOH (0.1 M) was added to the samples to achieve pH₀ of the solutions 9.5 and 11.8 (± 0.05 –0.1). Powdered bentonite was added to the solution in a ratio of 1 : 100 (0.5 g of bentonite per 50 ml of model solution). After 24 hours, the mixture was filtered through a microporous Capron membrane filter (0.2 μ m pore size) using a Buchner funnel vacuum pump and a Bunsen flask. The residual activity of the filtrate and the final pH values were measured. Each experiment was repeated three times, and the average value was used. The maximum experimental error was 0.5 %. The accuracy of determination of the degree of sorption of ¹³⁷Cs on bentonites and of respective K_d values was calculated considering both experimental and analytical errors.

Results and Discussion

The results of experiments of the ¹³⁷Cs adsorption on natural and soda-modified bentonite are shown in Figs. 1, 2 and Table 2. SEM images (see Fig. 1) show that the natural morphology of bentonite particles is preserved during sodium modification, which confirms the resistance of its structure to alkaline effects (Shabalin et al., 2022). So, the cesium adsorption cannot be related to the decomposition of the structure and dissolution of bentonite. Similar results on the contact interaction between natural and alkali-modified bentonites from various deposits and Portland cement in an aqueous environment are reported in the publications of (Sato et al., 2003; Anh et al., 2017; Morozov et al., 2022).

At the same time, the composition of the interlayer ion exchange complex of bentonites, which is mainly determined by the surrounding equilibrium solution, changes. An increase in Ca and a decrease in Na concentrations in the interlayer ion exchange complex compared to the original bentonites is explained by the ion exchange of Na⁺ in the montmorillonite structure. An increase in the mass fraction of CaO in the chemical composition of bentonite after contact with solutions containing high concentrations of Ca²⁺ is an important indicator of its competitive sorption, which leads to a decrease in the sorption properties of bentonite concerning ¹³⁷Cs. Moreover, the mass fraction of CaO increases twice for natural bentonite – from 5.33 to 11.64 %, for Na-modified bentonite three times – from 2.27 to 6.75 %. Similar results were obtained in experiments with bentonites saturated with CaCl₂ solutions (Kaufhold and Dohrmann, 2011). Minor variations in the composition of Al and Fe can be explained by the partial dissolution of these elements on the wedge-shaped edge areas of the montmorillonite layers and partly by the relative error of the used method. The decrease in the concentration of quartz (see Table 2) occurs due to quartz amorphization and its dissolution in the solution with an excess of Ca(OH)₂ from a highly alkaline pH.

Table 2. Average chemical composition of bentonites (based on energy dispersion spectroscopy data – EDS)*

Oxides	SiO ₂	Al ₂ O ₃	FeO+Fe ₂ O ₃	MgO	MnO	CaO	Na ₂ O	K ₂ O	Total
Natural bent.	65.85	17.56	6.89	2.78	ND	5.33	0.9	0.71	100.01
1	61.13	16.26	8.00	2.13	ND	11.64	0.21	0.63	100.00
Na-mod. bent.	66.17	16.51	4.21	1.61	0.33	2.27	8.49	0.4	99.99
2	65.6	15.32	7.71	1.25	ND	6.75	3.04	0.33	100.00

*Note. Average values of 10 measurements with an area of 0.25 mm²; 1 – natural bentonite with the addition of Ca²⁺ in a model solution – 960 mg/dm³, pH 11.8; 2 – bentonite PBA-20 with the addition of Ca²⁺ in a model solution – 960 mg/dm³, pH 11.8; ND – not detected.

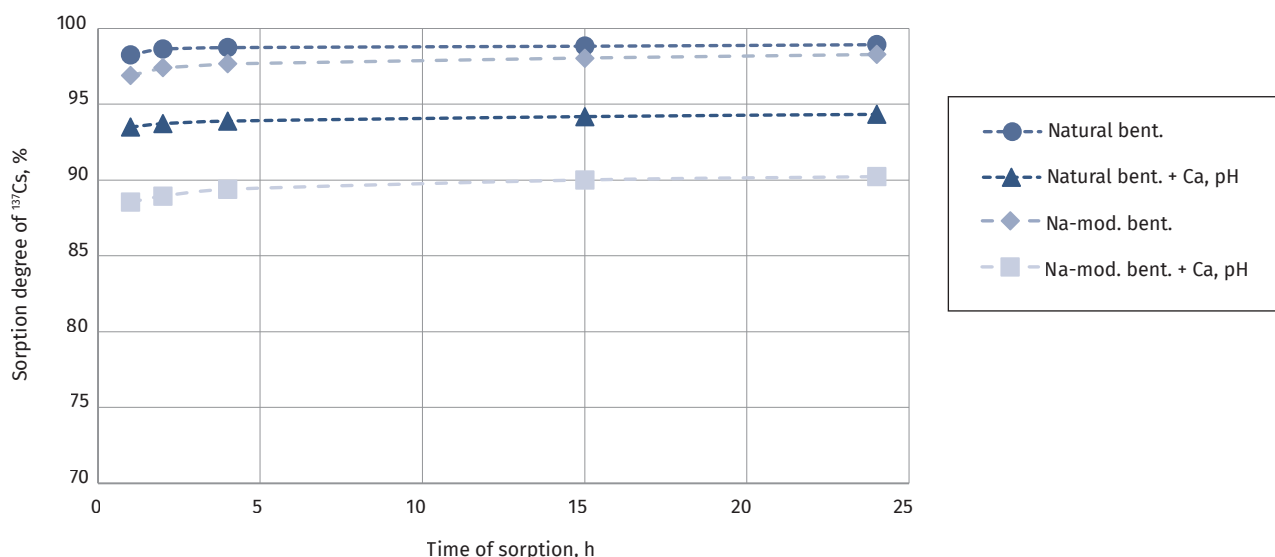


Fig. 2. Kinetics of ^{137}Cs adsorption on natural (NB) and Na-modified (PBA-20) Cherkasy deposit bentonites from a model solution in the presence of Ca^{2+} (960 mg/dm^3) and pH_0 11.8

Adsorption of Cs on bentonite in the presence of Ca^{2+} (960 mg/dm^3) and pH_0 11.8 is relatively fast, and the equilibrium is established in 14–15 hours (see Fig. 2). In NB and PBA-20 clays, the pH of the equilibrium solutions slightly differed from the pH_0 of the initial solutions. It is explained by the different buffering capacities of the clays and deprotonation of the edge structural units of montmorillonite ($=\text{SOH} \leftrightarrow =\text{SO}^- + \text{H}^+$). Similar dependencies concerning the contact interaction between natural bentonites from different deposits and Portland cement are reported in international comprehensive studies (Disposal-Engineered..., 2004; Geological..., 2016).

The mechanism of cation adsorption on montmorillonite is complex and has yet to be determined. One of the reasons why it is difficult to study this mechanism is that sorption occurs on a small area that cannot be observed even with the latest experimental equipment (Okumura et al., 2018). Generally, the sorption mechanism is explained by the specific characteristics of the structure and heterogeneity of the montmorillonite surface (Proceedings..., 2004).

According to the X-ray structure analysis data, the main mechanism of Cs^+ ion adsorption on montmorillonites is the ion exchange mechanism of interaction on flat surfaces of bentonite, which does not depend on the pH of the solution (Belousov et al., 2019). Still, it decreases with an increase in the ionic strength of solutions at low and high pH (Priadko et al., 2020).

Another mechanism of Cs^+ ion adsorption is sorption at the expanded edge regions of montmorillonite layers. It was found (Osipov and Sokolov, 2013) that ions with low hydration energy (Cs^+ , Rb^+ , K^+ , NH_4^+) can comparatively easily lose their hydration shell and penetrating the wedge-shaped edge areas of montmorillonite layers, formed fixed forms ($=\text{SOH} + \text{R}^+ \leftrightarrow =\text{SOR} + \text{H}^+$, S = edge area, $\text{R} = \text{Cs}^+$, Rb^+ , K^+ , NH_4^+). Such sites are extremely highly selective towards Cs^+ ions compared to other singly charged cations and depend on the pH of the solution. Such adsorption centers may fix Cs^+ by the chemisorption process due to deprotonation. This bond is stronger than the electrostatic interaction of Cs^+ ions with flat surfaces in the form of exchangeable cations. The centers are more selective; they are initially filled with Cs^+ ions, significantly contributing to total sorption (Anderson et al., 1998).

The data we obtained from this study suggest that the total adsorption of Cs^+ ions on NB and PBA-20 from model groundwater solutions after adding CaCl_2 solution from 16 mg/dm^3 to 960 mg/dm^3 and an increase in pH_0 – from 7.4 to 11.8 decreases with an increase in ionic strength also due to competition with Ca^{2+} and Na^+ ions. But it retains high values ($> 90\%$) (Fig. 3). Thus, the degree of Cs adsorption (%) on natural bentonite at pH_0 7.4 with the increase in Ca^{2+} ion concentration from 16 to 960 mg/dm^3 decreases from 97.7 ± 1.0 to 88.2 ± 1.3 , at pH_0 9.5 – from 98.4 ± 0.9 to 90.2 ± 1.0 , at pH_0 11.8 – from 99.4 ± 0.9 to 91.2 ± 1.0 . For PBA-20 bentonite at pH_0 7.4 and the concentration of Ca^{2+} ions 16 mg/dm^3 , the degree of

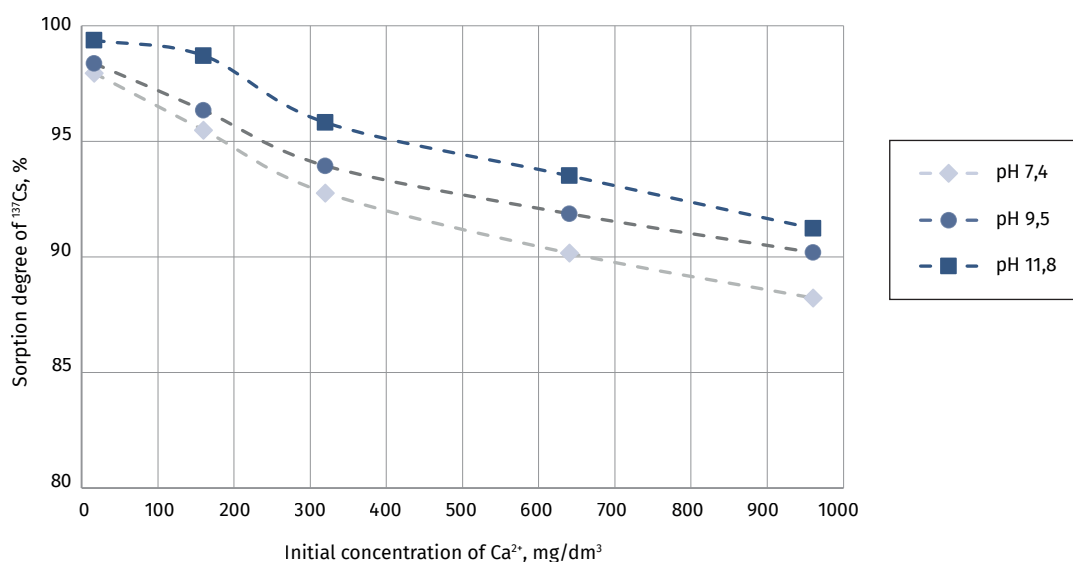


Fig. 3. Dependence of the degree of ¹³⁷Cs adsorption on natural bentonite from the Cherkasy deposit on the concentration of Ca²⁺ ions and pH₀ of the model solution

Cs adsorption is 98.2 ± 0.9 , at pH₀ 11.8 and the concentration of Ca²⁺ ions 960 mg/dm³ it decreases to 90.2 ± 1.0 %. Accordingly, the calculated phase distribution coefficients of ¹³⁷Cs (K_d) adsorbed on natural bentonite at pH₀ 7.4 and Ca²⁺ ion concentration 16 mg/dm³ in the model groundwater solution increases. In contrast, with an increase in pH and Ca²⁺ ion concentration, it decreases (Table 3), which fully corresponds to the conclusions from the data on the ¹³⁷Cs sorption degree. Earlier, it was shown (Shabalin et al., 2022) that at neutral pH (6.1) and the concentration of Na⁺ ions from 6.1 to 61 mg/dm³ and Ca²⁺ ions from 16 to 60 mg/dm³, the values of adsorption degree remain high enough – at least 80 % for both types of bentonite. The difference in the adsorption degree values is within 10 %. Similar dependencies are reported by (Hong et al., 2016), i.e., K_d of bentonite increases with the increase in pH and decreases with the increase in ionic strength of the contact solution.

In (Nakano et al., 2003) the energy of Cs⁺ ion adsorption on Na-bentonite was measured. It was found that montmorillonite has at least two types of sorption centers for Cs⁺ cations. It was also observed that bentonite MX 80 (Wyoming, USA) treated with cesium chloride solution, contains sorption centers in the interlayer spaces and extended edge areas of bentonite layers (Bostick et al., 2002). Thus, we can conclude that the adsorption of Cs⁺ ions on bentonites occurs mainly via two mechanisms. The main sorption mechanism is the fixation of Cs⁺ on flat surfaces due to ion exchange. Increasing pH to alkaline values strengthens the pH-dependent positions on the wedge-shaped edge areas of montmorillonite layers, on which Cs⁺ ions can be fixed more firmly. In (Makarov et al., 2017), it was published that the adsorption of various cations on alkaline and alkaline earth bentonites does not affect the nature of the distribution of the main active centers but changes their ratio in the alkaline regions of pH values.

Table 3. Distribution coefficients (K_d) of ¹³⁷Cs adsorption on natural bentonite of the Cherkasy deposit from a model solution depending on pH and concentration of Ca²⁺ ions

Concentration of Ca ²⁺ , mg/dm ³	16	160	320	640	960
pH₀	7.4				
K_d (¹³⁷ Cs), ml/g	4800 ± 60	2120 ± 40	1280 ± 30	920 ± 30	750 ± 30
pH₀	9.5				
K_d (¹³⁷ Cs), ml/g	6030 ± 70	2630 ± 40	1550 ± 30	1130 ± 30	920 ± 30
pH₀	11.8				
K_d (¹³⁷ Cs), ml/g	16000 ± 130	7660 ± 80	2290 ± 40	1440 ± 30	1040 ± 30

Adsorption of Cs⁺ cations on montmorillonites is accompanied by competitive interaction with Na⁺, Ca²⁺, Mg²⁺, and K⁺ cations at alkaline pH values. In NB and PBA-20 bentonites, Na⁺ and Ca²⁺ ions usually co-exist in the interlayer space as compensatory ions. In montmorillonite, the mobility of Na⁺ is always much higher than that of Ca²⁺ due to the difference in their hydration shells and hydration energy (Ca²⁺ > Na⁺ > Cs⁺). Based on the contact time of aqueous solutions with hydration complexes of Na⁺ and Ca²⁺, the complexes with Ca²⁺ are more stable than with Na⁺. In montmorillonites with a high Ca²⁺/Na⁺ ratio, a clearly expressed inhibitory impact of Ca²⁺ hydrate complexes on Na⁺ mobility was found (Ferrage et al., 2007). Thus, the sorption of Cs⁺ on the basal surfaces is blocked by excess Ca²⁺ cations, which are well-adsorbed on these sites. In other words, the sorption properties of bentonite concerning ¹³⁷Cs can be limited owing to the partial blocking of the sorption centers by Ca²⁺ ions on the interlayer and the basal and edge surfaces (Zhang et al., 2014). This is also observed from the results of our experiments.

The processes of ¹³⁷Cs adsorption (as well as other radionuclides) from multicomponent solutions with different pH, Eh, and salt composition values also depend on the precipitated insoluble or sparingly soluble compounds on the bentonite surface. According to our computer simulations data, in model groundwater with the addition of CaCl₂ solutions and alkaline pH, small amounts of sediments, mainly oxides, hydroxides, oxyhydroxides of Fe (hematite, goethite, limonite) and Ca carbonates (calcite, aragonite, dolomite) were present (Fig. 4). Insoluble Fe compounds play an important role in Cs adsorption processes on bentonites (Shabalín et al., 2022). At the same time, they block adsorption centers predominantly on the basal surface of montmorillonite though partially adsorbing Cs. Adsorption of these compounds is non-selective, the bonds are weaker than in montmorillonite. High Cs adsorption values indicate (see Fig. 2, 3; Table 3) that the formed insoluble / sparingly soluble compounds on the surface of bentonites do not block the interlayer surface of montmorillonite but are formed mainly on the basal surface, chips, and surface defects of the mineral grains. Taking into account the obtained results of ¹³⁷Cs adsorption on both types of bentonites, it can be assumed that PBA-20 bentonite gets more compacted with pore collapse due to precipitation of insoluble / sparingly soluble compounds on the surface than the natural sample, which requires additional research.

Conclusions

In our study of the influence of the Ca²⁺ ion concentration (from 16 to 960 mg/dm³) and pH (from 7.4 to 11.8) of the model solution (similar to the composition of groundwater at the Vector Site in the Chernobyl exclusion zone) on the elemental composition and adsorption properties of natural (NB) and Na-modified (PBA-20) bentonites from the Cherkasy deposit concerning ¹³⁷Cs, in case of failure of the components of the water-proofing liner and degraded concrete constructions of the engineered barrier system of a near-surface RAW storage facility we obtained the following results:

1. Based on geochemical modeling, adding CaCl₂ to test solutions with alkaline pH, the precipitated solids are formed mainly in the form of iron oxides, hydroxides, oxyhydroxides (hematite, goethite, limonite), and calcium carbonates (calcite, aragonite, dolomite), which considerably impact Cs adsorption processes.
2. The concentration of montmorillonite's main structural elements (Si, Al) (the dominating mineral of bentonite) practically does not change with increased Ca²⁺ ion concentration and pH of the model solution, demonstrating the bentonite structure stability. At the same time, the concentration of Ca increases and Na decreases in the ion exchange complex of bentonites. Thereby PBA-20 bentonite transforms from a Na, Ca-form into Ca, Na-form.
3. Increased concentrations of Ca²⁺ ions in the model solution and alkaline pH reduce the efficiency of Cs adsorption on bentonites. The total adsorption of Cs⁺ on natural and modified (soda) bentonites from model solutions with the addition of CaCl₂ from 16 to 960 mg/dm³ and an increase in pH value from 7.4 to 11.8 decreases with an increase in ionic strength. This occurs due to competition with Ca²⁺ and Na⁺ ions. Despite the above, the values of adsorption remain high (> 90 % at solid : liquid ratio of 1 : 100). So, the degree of Cs adsorption (%) on natural bentonite at pH₀ 7.4 with an increase in Ca²⁺ ion concentration from 16 to 960 mg/dm³ decreases from 97.7 ± 1.0 to 88.2 ± 1.3, at pH₀ 9.5 – from 98.4 ± 0.9 to 90.2 ± 1.0, at pH₀ 11.8 – from 99.4 ± 0.9 to 91.2 ± 1.0. For PBA-20 bentonite at pH₀ 7.4 and Ca²⁺ ion concentration 16 mg/dm³, the degree of Cs adsorption is 98.2 ± 0.9 %, at pH₀ 11.8 and Ca²⁺ ion concentration 960 mg/dm³, it decreases to 90.2 ± 1.0 %. Thus, the calculated phase distribution coefficients (K_d) of ¹³⁷Cs adsorption on

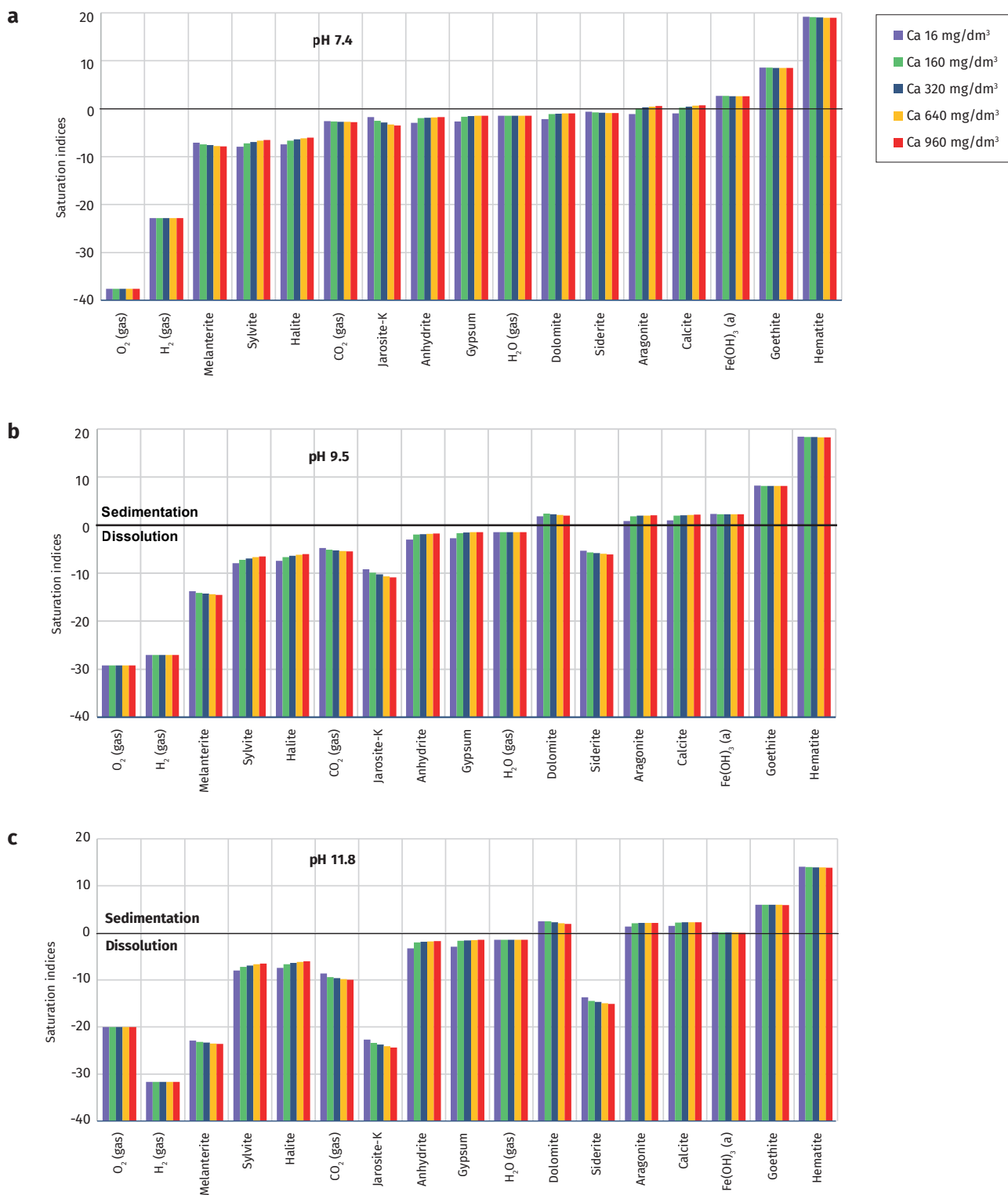


Fig. 4. Phase composition of model solutions with the addition of excess Ca²⁺ (Modelling with PHREEQC software)

NB increase at pH₀ 7.4 and Ca²⁺ ion concentration 16 mg/dm³ in the model pore water solution, while with an increase of pH and Ca²⁺ ion concentration, the K₀ values decrease.

4. Natural and modified (PBA-20) Cherkasy bentonites, in case of failure of the water-retaining barrier components and degradation of the engineered barrier systems in a near-surface ra-

dioactive waste storage facility, remain a reliable component of the isolating liner at the basement of the facility, retaining its main functional property – high values of adsorption concerning the important dose-forming radionuclide ¹³⁷Cs which is present in short-lived low- and medium-level waste, contributing to the safety of storage facilities safe for population and environment.

Безпека приповерхневих сховищ радіоактивних відходів ґрунтується на системі інженерних і природних бар'єрів. Значна деградація інженерної бар'єрної системи, що складається з цементованих матриць відходів, покритих цементною сумішшю, бетонних відсіків і конструкцій у підвалі сховища, може спричинити перенесення радіонуклідів зі сховища з інфільтрацією в ґрунтові води. Змішування цементу і бетону з водою призводить до утворення низки різних продуктів гідратації з подальшим вилугуванням іонів Ca^{2+} та утворенням гідроксильних іонів (OH^-), що впливає на лужність водного середовища і сорбційні властивості бентонітів як компонентів протиміграційного бар'єру в основі приповерхневих сховищ. У статті наведено результати експериментального дослідження впливу концентрації іонів Ca^{2+} та величини рН модельного розчину (аналогічного складу підземних вод майданчика «Вектор» у Чорнобильській зоні відчуження) на елементний склад і сорбційні властивості природного (ПБ) і Na-модифікованого (ПБА-20) бентонітів Черкаського родовища щодо ^{137}Cs у співвідношенні тверда речовина : розчин як 1 : 100. Геохімічне моделювання показує, що додавання CaCl_2 до модельного розчину та кінцеве лужне рН призводять до осадження твердих речовин, головним чином оксидів, гідроксидів, оксигідроксидів Fe (гематит, гетит, лимоніт), карбонатів Ca (кальцит, арагоніт, доломіт). Оцінено їх роль в адсорбції Cs. Концентрація структурних елементів (Si, Al) в бентонітах практично не змінюється при збільшенні концентрації іонів Ca^{2+} в модельному розчині, що свідчить про стабільність структури бентоніту в цих умовах. При цьому в іонообмінному комплексі бентонітів виявлено збільшення концентрації Ca та зменшення концентрації Na у порівнянні з вихідним природним бентонітом. Це призводить до перетворення Na-модифікованого бентоніту з Na, Ca-форми в Ca, Na-форми. Сумарна сорбційна здатність бентонітів ПБ та ПБА-20 щодо іонів Cs^+ при підвищеній концентрації іонів Ca^{2+} та рН розчину дещо знижується, але зберігає високі значення ступеня абсорбції (> 90 %). Сумарна адсорбція іонів Cs^+ бентонітами ПБ та ПБА-20 з модельного розчину підземних вод із додаванням CaCl_2 від 16 до 960 мг/дм³ та підвищенням рН₀ від 7,4 до 11,8 зменшується зі збільшенням іонної сили, зокрема за рахунок конкуренції з іонами Ca^{2+} та Na^+ . Бентоніти ПБ та ПБА-20 Черкаського родовища залишаються надійним компонентом футеровки фундаменту сховища завдяки основній функціональній властивості – високій поглинальній здатності щодо ^{137}Cs , який є важливим дозоутворюючим радіонуклідом короткоживучих низько- та середньоактивних відходів.

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