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EVOLUTION OF BENTONITES IN THE PRESENCE OF Ca²⁺ IONS IN A CONTACT SOLUTION AND SORPTION CAPACITY OF BENTONITES FOR ¹³⁷Cs AND ⁹⁰Sr

The article presents the results of an experimental modelling of the influence of Ca²⁺ ion concentration and pH of a model solution on the elemental composition and sorption capacity of natural (NB) and sodium-modified (SMB-20) bentonites from the Cherkasy deposit for ¹³⁷Cs and ⁹⁰Sr. The processes of the Cs and Sr sorption from multicomponent solutions with different pH, Eh and salt composition depend on the insoluble or sparingly soluble compounds precipitated on the bentonite surface. Based on the computer simulation data, it was found that small amounts of sediments, mainly oxides, hydroxides, Fe oxyhydroxides (hematite, goethite, limonite), and Ca carbonates (calcite, aragonite, dolomite) were present in the model solution with alkaline pH after adding CaCl₂ solutions. Oxides and hydrated oxides of Fe, and calcium carbonates play an important role in the Cs and Sr sorption processes on bentonites. They can concurrently sorb radionuclides and block the sorption centres in montmorillonites. The concentration of the main structural elements (Si, Al) in the bentonites practically does not change with the increased pH and Ca²⁺ ion concentration in the model solution compared to the initial samples of NB and SMB-20, which indicates their structural stability. At the same time, an increase in the calcium concentration and a decrease in the sodium concentration were found in the ion-exchange complex of montmorillonite — the main bentonite mineral if compared to the initial samples. This can eventually lead to the transformation of SMB-20 bentonite from Na, Ca form to Ca, Na form. The ¹³⁷Cs and ⁹⁰Sr sorption on NB is shown to proceed more effectively, compared to SMB-20 in conditions of the increased pH and Ca²⁺ ion concentration. The results of this research may justify the bentonite clay application as a component of the isolating engineered barriers of radioactive waste disposal facilities.

Keywords: sorption, strontium, caesium, bentonite, engineered barriers, near-surface radioactive waste storage.

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Introduction. A significant amount of short lived low- and intermediate-level waste (SL LLW/ILW) from various sources has been accumulated in Ukraine. This waste is submitted for the disposal in the currently operating and being under construction near-surface disposal facilities at the "Vektor" industrial complex (IC "Vektor") in the Chornobyl Exclusion Zone (ChEZ). During the operational and post-closure institutional control phases, the safety of a near-surface disposal facility is based on the engineered barrier system (EBS). To ensure safe disposal of radioactive waste, the Waste Acceptance Criteria (WAC) are established for the near-surface disposal facilities. The IC "Vektor's" WAC specify requirements concerning the leaching rate of radionuclides from SL LLW/ILW matrices (for example, cement-based) by the infiltration and ground water at the IC "Vektor" sites (WAC, 2009; Regulatory document 1.037: 2013, 2013). This water would also affect the performance of other EBS components, and contact with the pore water in the concrete constructions.

To prevent the radionuclide migration from a near-surface disposal facility located on highly permeable rock (for example, sandy soil), construction of an isolating lining mainly made of concrete and a natural sorbent, usually bentonite clay, underneath the facility is envisaged by most concepts accepted by different countries (Shabalin, Lavrynenko and Mitsiuk, 2023). Bentonite clays have superior barrier properties compared to other natural sorbents such as kaolinite, silicate minerals, aluminum oxides, organic substances and hydroxyapatite due to a peculiar layered structure of the main rock-forming component — montmorillonite (Sellin and Leupin, 2014; Wang et al., 2023).

The physical-mechanical and chemical properties of montmorillonite change under the influence of highly alkaline solutions (with the pH range from 12.5—13.5 to 10—10.5) formed due to a gradual leaching of portlandite from the cement and concrete of the EBS (Sato et al., 2004; Ochs, Mallants and Wang, 2016). The interaction of the concrete and bentonite EBS components can cause the redistribution of the interlayer ions and change in bentonite mineral composition (Proceedings of International Workshop, 2004; Alonso et al., 2017). As reported in (Kaufhold and Dohrmann, 2011; Anh

et al., 2017), the Na cation exchange sites (NaX) in the original (unaltered) montmorillonite will become Ca exchange sites (CaX_2) in $\text{Ca}(\text{OH})_2$ solutions (Na/Ca molar ratio about 2.4, 24 and 23.3) after adding CaCl_2 solutions. At the same time, a decrease in the cation-exchange capacity of bentonite was reported in the above researches. Significant changes were observed in the basal reflections of the X-ray diffraction (XRD) patterns of montmorillonite. Increased interplanar distances (d_{001}) were observed in some samples and increased intensity in others. The relative intensities of quartz display the dissolution of quartz in some samples. At the same time, the changes in the intensity of quartz were not observed in other samples. The dissolution of montmorillonite was not observed, and the leaching of structural elements was quite insignificant, which indicates the high structural stability of montmorillonite.

^{137}Cs and ^{90}Sr radionuclides are important fission products (ICRU Report 92, 2015). Based on the results of radiogeohydrological studies of the groundwater in the near field of the ChEZ radioactive waste disposal facilities, ^{90}Sr is considered to be one of the most mobile water migrants (Shevchenko et al., 2023).

The aim of this work is to identify the patterns of ^{137}Cs and ^{90}Sr sorption on the Cherkasy bentonites in conditions simulating the EBS concrete degradation in order to determine the possibility of use of these bentonites as an EBS component in near-surface disposal facilities.

Materials and Methods. Bentonite Characterization. In our study, we used powdered natural bentonite (NB) and industrial sodium modified bentonite (SMB-20) from the Cherkasy deposit (layer II) which were earlier described in (Shabalin et al., 2022a). The NB from the Cherkasy deposit is calcium-magnesium. After industrial treatment of NB with soda solution, an increase of alkaline smectite content was observed indicating the high degree of Ca and Mg replacement with Na in the natural exchange complex of bentonite, which is confirmed by the chemical analysis data (Shabalin et al., 2022a).

According to the granulometric composition analysis, 80—85% of NB is composed of 0.5—1.0 μm fractions which have the highest sorption capacity. Based on the analysis data, montmorillonite consists of 70—75% by weight of bento-

nite, quartz — 20–25% by weight, feldspars and calcite — $\leq 5\%$ by weight. Based on the averaged chemical composition data, the crystal chemical formulae were calculated for air-dry NB — $((\text{Al}_{3.14}\text{Fe}_{0.50}^{3+}\text{Mg}_{0.30}\text{Ti}_{0.03})_{3.97}[\text{Al}_{0.20}\text{Si}_{7.80}]_{8.00}(\text{Na}_{0.03}\text{K}_{0.03}\text{Ca}_{0.19})_{0.25} \cdot 2.6 \times \text{H}_2\text{O})$ and for SMB-20 — $((\text{Al}_{3.17}\text{Fe}_{0.49}^{3+}\text{Mg}_{0.30})_{3.96}[\text{Al}_{0.18}\text{Si}_{7.82}]_{8.00}(\text{Na}_{0.25}\text{K}_{0.03}\text{Ca}_{0.08})_{0.37} \cdot 2.6 \times \text{H}_2\text{O})$. The total cation exchange capacity of NB is 77.6 and SMB-20 — 152 meq/100 g of dry clay. According to the exchangeable cation composition, NB is an alkaline-earth bentonite containing mainly calcium cations. Whereas SMB-20 is an alkaline bentonite with predominant content of sodium cations in the exchange complex.

X-Ray Diffractometry (XRD). The phase composition was studied using a Shimadzu XRD-6000 diffractometer (a discrete mode, step size — 0.02 degrees, step time — 1 s, scan interval — 5–70 degrees (2θ)) with a copper anode ($\text{Cu}_{\text{K}\alpha} = 1.54178 \text{ \AA}$). The scans were obtained at tube voltage — 35 kV, current — 30 mA. The qualitative analysis was performed using Crystallographica Search-Match program with the ICDD PDF-2 international databases. Semiquantitative analysis was performed using the Rietveld method with Siroquant software.

Scanning Electronic Microscopy with Energy Dispersive Spectrometry (SEM, EDS). The chemical composition of bentonite surfaces 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 $6 \times 10^{-10} \text{ A}$ 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.

Chemical Composition of the Solution. The chemical composition of the model solution contacting with bentonite was calculated based on the analysis of the ChEZ groundwater (Regulatory document 1.037:2013, 2013) and the composition of the simulated concrete

pore water (Savage, Noy and Mihara, 2002) (Table 1).

For the batch-experiments, 50 ml aliquots of the solution were taken for each sample. The samples were mixed intensively. Then the CaCl_2 solution was added to the samples to reach Ca^{2+} concentration equal to 160 mg/dm^3 ($4 \times 10^{-4} \text{ mol/l}$), 320 mg/dm^3 ($8 \times 10^{-4} \text{ mol/l}$), 640 mg/dm^3 ($1.6 \times 10^{-3} \text{ mol/l}$) and 960 mg/dm^3 ($2.4 \times 10^{-3} \text{ mol/l}$) taking into account the significant amount of cement and concrete in the near-surface modular SL LLW/ILW storage facilities (Shestopalov, 1999). The mass ratio bentonite:solution was 1:100, the contact time — 14 days at room temperature. Then, the bentonite was separated from the solutions by decantation and washed with double distilled water using a vacuum filter. After that, it was air-dried at room temperature.

γ -spectrometry. To measure the Cs sorption degree (S, %) we used ^{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 was $3.13 \times 10^4 \text{ Bq/dm}^3$. ^{137}Cs activity was measured using the semiconductor γ -spectrometer "ATOLL-1 M" (Ukraine) with CsI-crystals. The relative measurement error of 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 measurement error of ^{137}Cs activity in the initial solution (high activity) was 1%. The measurement error of ^{137}Cs activity in the solutions after sorption (low activity) was within 3.8–20.3% depending on the amount of radioactivity.

β -spectrometry. To measure the Sr sorption degree (S, %) we used ^{90}Sr isotope ($t_{1/2} = 28.79$ years) in the solution form with radionuclide purity of more than 99.5%. The activity of the

Table 1. Composition of the model solution

Ions	Concentration, mg/dm^3 (mol/l)	Ions	Concentration, mg/dm^3 (mol/l)
Na^+	31.2 (1.36×10^{-3})	Cl^-	42.4 (1.19×10^{-3})
Ca^{2+}	16.0 (4×10^{-4})	SO_4^{2-}	27.2 (2.83×10^{-4})
K^+	3.3 (8.46×10^{-5})	HCO_3^-	68.9 (2.38×10^{-3})
Fe^{2+}	1.0 (1.79×10^{-5})	NO_3^-	5.7 (1.9×10^{-4})
Mg^{2+}	4.8 (1.98×10^{-4})	Mineralization	201.5
Cs^+	1.0 (7.52×10^{-6})		

initial solution was 6.75×10^3 Bq/dm³. ⁹⁰Sr activity was measured using the semiconductor β -spectrometer "SEB-01/70" (Ukraine). The relative measurement error of 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 measurement error of ⁹⁰Sr activity in the initial solution (high activity) was 1.9%. The measurement error of the ⁹⁰Sr activity in the solutions after sorption (low activity) was within 4.8–23.1% depending on the amount of activity.

Potentiometry. The acid-alkaline index (pH) was measured at 25 °C after a short-term exposure (24 hours for ¹³⁷Cs-bearing solutions and 14 days for ⁹⁰Sr-bearing solutions) in a glass vessel. The solution pH was adjusted with 0.1 M HCl. The pH values of the solutions were taken as reference values. The relative error was $\pm 0.3\%$.

Experimental procedure. Powdered bentonite was mixed with the model solution and kept at room temperature for 24 hours. Then, it was filtered through a microporous Capron membrane filter (0.2 μ m pore size) and washed with double distilled water using a Buchner funnel vacuum pump and a Bunsen flask. Then, it was air-dried at room temperature. The residual activity of the filtrate and the final pH values were measured.

Results calculations. The degree of sorption (S , %) was calculated from the data obtained on the residual activity of the radionuclide in the solution:

$$S = \frac{C_0 - C}{C_0} \times 100,$$

where C_0 is the initial concentration of the radionuclide in the solution, Bq/ml; C — the equilibrium concentration of the radionuclide in the solution, Bq/ml.

The coefficient of interphase distribution (K_d , ml/g) is equal to the ratio of the amount of the radionuclide sorbed on the bentonite to its content in the solution:

$$K_d = \frac{N}{C} = \left(\frac{C_0 - C}{C} \right) \times \left(\frac{V}{m} \right),$$

where N — mass of sorbed radionuclide, g/g of sorbent; C — concentration in the solution after sorption, g/dm³; C_0 — initial concentration in the solution, g/dm³; V — the volume of the liquid phase, ml; m — mass, g.

Results and Discussion. The physical-chemical characteristics of bentonites, primarily sorption, are determined by the montmorillonite content in bentonite and the montmorillonite structural features. At the same time, the sorption characteristics of the EBS bentonite components are due to the geological and geochemical conditions in the near field of the disposal facilities and the mechanism of binding of radionuclides within the montmorillonite structure.

Montmorillonite belongs to the group of dioctahedral smectites. The main element of smectites is a 2:1 layer structure consisting of two tetrahedral sheets containing Si, Al, and Fe³⁺ cations and an octahedral sheet located between them and occupied by Al, Mg, and Fe²⁺ cations. Isomorphic substitutions in the structure cause the appearance of a negative charge of the octahedral and tetrahedral sheets, which is compensated by exchangeable hydrated cations (for example, Na⁺, K⁺, Ca²⁺, etc.) in the interlayer space. In addition, the aluminol and silanol groups on the surface of the particles are available for the cation sorption. Binding with these groups goes via the complexation mechanism of sorption. Interaction with water may lead to the formation of hydration shells around the exchangeable cations causing intracrystalline swelling. The hydration ability of Na-montmorillonites is very strong (Wilson, 2013).

The SEM images (Fig. 1) show that the natural morphology of bentonite particles is preserved during the sodium modification of the NB at high pH and Ca²⁺ ion concentration, which confirms the resistance of its structure to alkaline effects. A distinctly layered structure of montmorillonite is visible in the images.

So, the Cs and Sr sorption in short-term experiments is not associated with the disintegration of the structure and significant dissolution of montmorillonite, which is consistent with the previously published results (Sato et al., 2004; Anh et al., 2017) regarding the contact interaction of natural and alkali-modified bentonites from various deposits with Portland cement in an aqueous environment.

At the same time, in case of long-term experiments and based on the mathematical modelling, changes in the bentonite mineral composition and an increase in the leaching of

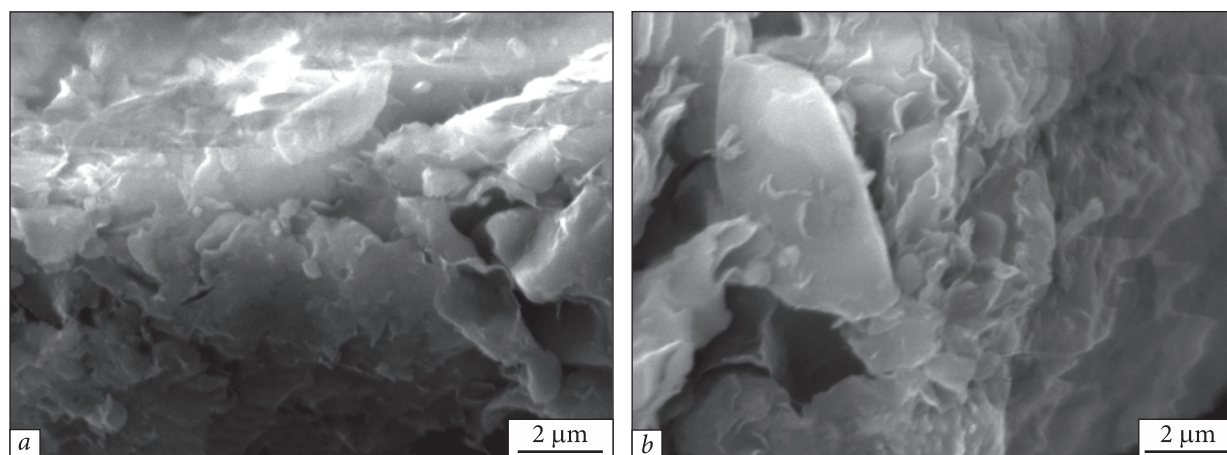


Fig. 1. Suspension of NB (a) and SMB-20 (b) from the Cherkasy deposit (II layer). pH = 11.8; Ca^{2+} ion concentration — 960 mg/dm³ (Shabalin et al., 2022a)

Table 2. Average chemical composition of the bentonite surface (based on the EDS data)*

Oxides	SiO ₂	Al ₂ O ₃	FeO + Fe ₂ O ₃	MgO	MnO	CaO	Na ₂ O	K ₂ O	Total
NB	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
SMB-20	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

* Average values of 10 measurements with an area of 0.25 mm²: 1 — NB with the addition of 960 mg/dm³ of Ca^{2+} into the model solution with pH = 11.8; 2 — SMB-20 with the addition of 960 mg/dm³ of Ca^{2+} into the model solution with pH = 11.8; ND — not detected.

montmorillonite with its possible transformation into other minerals are predicted (Kaufhold et al., 2018; Sánchez et al., 2006; Pusch et al., 2003).

In our experiments, 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 content in the interlayer ion exchange complex compared to the original bentonites is explained by leaching of Na⁺ from the interlayer space of montmorillonite (Table 2). The decrease in the quartz concentration (Table 2, sample 1) can occur due to the quartz amorphization and dissolution in the solution with high pH.

Similar results were obtained in the experiments with bentonites saturated with CaCl₂ solutions (Kaufhold and Dohrmann, 2011).

Since the interlayer distance can expand, montmorillonite has the ability for intra-crystalline ion exchange sorption. At the same time, its basal interplanar distance along the c axis (d_{001}) depends on the nature of the exchangeable cations and the structure of the sorbed sub-

stances. So, the change in the montmorillonite interplanar distance as a result of sorption and ion exchange can be studied by the X-ray diffraction method (Fusova, 2009; Qui et al., 2020). Fig. 2 shows the diffraction patterns of the original air-dry samples of NB and SMB-20 and their changes due to the ion-exchange substitution in the interlayer space after treatment with CaCl₂ solutions. The NB clay minerals (Fig. 2, curve 1) are represented by montmorillonite and quartz, calcite and feldspar impurities. According to the calculations based on X-ray diffraction analysis (XRD) data using the Rietveld method, the size of the primary particles of quartz is 49.2 nm, calcite — 68.6 nm, and smectite — 23.4 nm. After Cs and Sr sorption from the model solution (pH = 11.8, Ca^{2+} — 960 mg/dm³), NB contains montmorillonite, quartz, and calcite (Fig. 2, curve 2). The size of the particles is the following: quartz — 44.7 nm, montmorillonite — 34.8 nm. This may indicate an insignificant decrease in the quartz and montmorillonite content compared to the original NB. The clay minerals in the original SMB-20

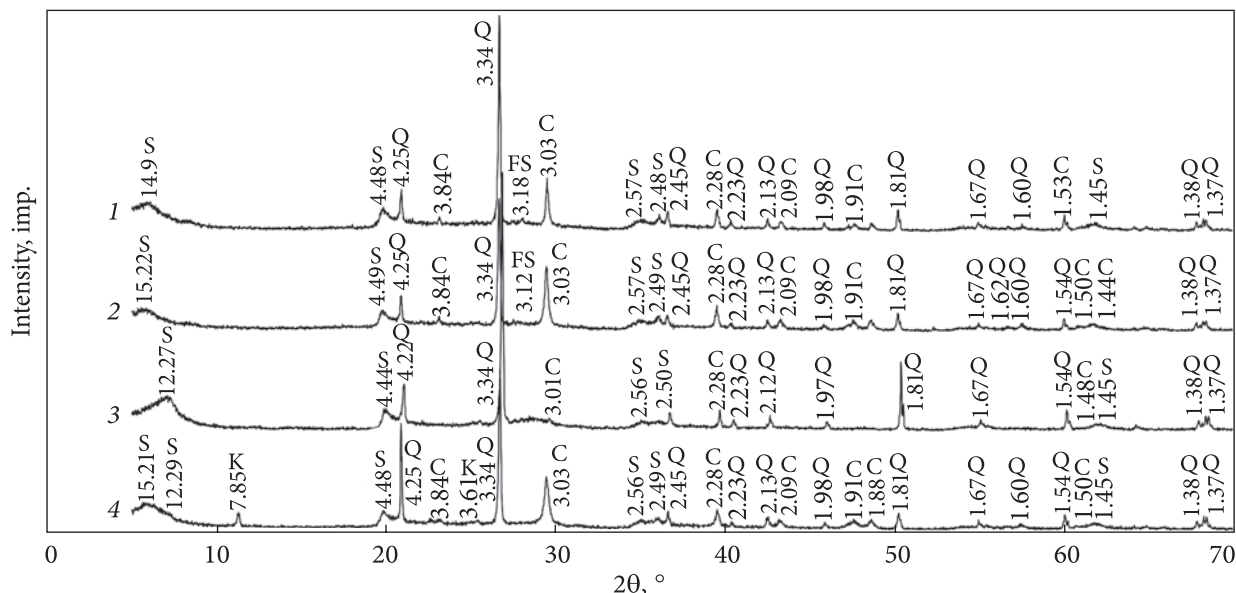


Fig. 2. Diffraction patterns of air-dry samples: NB from the Cherkasy deposit (Dashukivka site, II layer) (1); NB after sorption from the model solution ($\text{pH} = 11.8$, $\text{Ca}^{2+} - 960 \text{ mg/dm}^3$) (2); original SNB-20 (3); SMB-20 after sorption from the model solution ($\text{pH} = 11.8$, $\text{Ca}^{2+} - 960 \text{ mg/dm}^3$) (4). S — smectite (montmorillonite), Q — quartz, FS — feldspar, C — calcite, K — kaolinite

sample (Fig. 2, curve 3) are presented predominantly by montmorillonite. The sample contains quartz, the interplanar distances of which are slightly shifted towards smaller angles compared to the original NB and NB treated with the solution. The calcite content is at the detection limit of the spectrometer. The size of the primary quartz particles is 46.9 nm. After Cs and Sr sorption from the model solution ($\text{pH} = 11.8$, $\text{Ca}^{2+} - 960 \text{ mg/dm}^3$), the SMB-20 sample contains montmorillonite, quartz and calcite with a number of characteristic peaks similar to those in the samples 1 and 2, and kaolinite (Fig. 2, curve 4). According to the calculation, the size of primary particles is the following: quartz — 53.5 nm, calcite — 31.5 nm, kaolinite — 48.1 nm, smectite — 29.1 nm. From the obtained data, it can be assumed that compared to the original samples of NB contacting with the model water, an increase in the quartz and calcite content, and a decrease in the montmorillonite content is observed for the SMB-20 samples.

Analysis of the diffraction patterns shows that the nature of the exchangeable cation significantly affects the position of the first basal reflection 001 on the scale of $2\theta^\circ$ — angles and, accordingly, the interlayer expansion of montmorillonite. In the original (natural) NB sample, montmorillonite has an interplanar distance of

$d_{001} = 14.90 \text{ \AA}$, which indicates the presence of two molecular layers of water in the interlayer space of the mineral (Erdey-Gruz, 1976). Substitution of exchangeable Ca^{2+} cations of montmorillonite in the NB sample with Na^+ cations (Fig. 2, curve 3) leads to a shift of the basal reflection to smaller $2\theta^\circ$ — angles and a decrease in d_{001} to 12.27 $\text{\AA}$. This indicates that the air-dry SMB-20 is characterized by the presence of a hydrated phase, which contains one layer of water in the interlayer space. Treatment of the NB and SMB-20 samples with CaCl_2 solutions ($\text{pH} = 11.8$) is accompanied by a shift of the basal reflection towards higher Bragg $2\theta^\circ$ — angles and an increase in the interplanar distance d_{001} to 15.22 $\text{\AA}$ (Fig. 2, curve 3) and 15.21 $\text{\AA}$ (Fig. 2, curve 4), respectively, confirming the well-known fact that Na^+ ions are most easily displaced from the exchange positions of the interlayer space with other cations.

The interplanar distance d_{001} is probably associated with the ion exchange and specific sorption of hydroxyl cations with different degrees of polymerization, which is caused not only by the difference in the size and structure of the complexes, but also by their various orientation in the interlayer space of montmorillonite.

Bentonites are characterized by the efficient sorption capacity for most radionuclides. This

results from a peculiar layered structure of montmorillonite. A specific feature of montmorillonite is the chemical and energetic heterogeneity of its surface caused by structural defects and presence of different functional groups which are active sorption centers (Yang et al., 2019).

The mechanism of the cation sorption on montmorillonite is complex and has not been completely investigated due to the physical heterogeneity of the surface. The nanosized sorption sites have different sorption capacity, which is difficult to be determined even by the advanced instruments (Okumura, 2018). The total surface area of montmorillonite is very large ($7.5 \times 10^5 \text{ m}^2/\text{kg}$) due to its layered structure. The specific area of the basal and crystal edge surfaces is an order of magnitude smaller ($3 \times 10^4 \text{ m}^2/\text{kg}$) (Bradbury and Baeyens, 2002). The compensating cations are present predominantly in the interlayer space and account for up to 80% of the total cation exchange capacity. The cation exchange capacity is not sensitive to the solution pH. Though, it decreases as the ionic strength increases at both low and high pH.

The cation exchange on the basal surface occurs due to the formation of bonds of a tetrahedral sheet of montmorillonite (Kim and Kirkpatrick, 1997). At the same time, the sorption sites of Cs^+ ions on the basal surface of montmorillonite are blocked by excess Ca^{2+} cations, which are well-adsorbed on these sites. For Sr, under the optimal pH conditions, along with the sorption on the basal surface of montmorillonite, a chemisorption process is possible with the formation of various compounds ($-\text{SiOSr}^+$ or $\text{Si-Sr}(\text{OH})^+$, etc.) (Bondarenko, Kononenko and Koliabina, 2014).

Another mechanism of the Cs^+ ion sorption is the sorption on the exchange sites of the edge surfaces of montmorillonite, which contain weakly acidic hydroxyl (silanol Si-OH) and amphoteric (aluminol Al-OH) groups that may be formed during the splitting of the mineral and participate in the ion exchange. Such sites are responsible for about 20% of the total cation exchange capacity (Stewart and Hossner, 2001). Under their influence the concentrations of neutral, protonated and deprotonated centres ($=\text{SOH}$, $=\text{SOH}^-$, $=\text{SO}^-$) change with pH. It was reported (Wilson, 2013), that the ions with low

hydration energy (Cs^+ , Rb^+ , K^+ , NH_4^+) can relatively easily lose their hydration shell and, reaching the edges, form fixed forms ($=\text{SOH} + \text{R}^+ \leftrightarrow =\text{SOR} + \text{H}^+$, where $\text{S} = \text{edges}$, $\text{R} = \text{Cs}^+$, Rb^+ , K^+ , NH_4^+). Such exchange sites are extremely highly selective for Cs^+ ions compared to other monovalent cations and are sensitive to the pH of the contact solution. Access to these sites of the larger hydrated Ca^{2+} cations is impossible.

Analysis of the published results (Kaufhold and Dohrmann, 2011; Zhang et al., 2022) allows to speculate that the absorbed Sr^{2+} ions are predominantly present in the interlayer space and on the expanded edge regions of montmorillonite (according to the international classification — frayed edge sites (FES) replacing cations of the exchange complex (Essington, 2004). In contrast, Cs^+ ions are adsorbed on the basal surfaces (regular exchange sites (RES), which is confirmed by the results of the molecular dynamics simulations. The sorption energy on the sorption centres increases in the following order: basal surface > interlayer surface of hydrated sheets > edge surface (Okumura et al., 2018).

A necessary criterion for the evaluation of the physical-mechanical properties of the sorption material is the kinetics of sorption, i. e. dependence of the radionuclide sorption in the sorbent — solution system on the contact time. This parameter allows determining the effective time of the efficient ^{137}Cs and ^{90}Sr removal from water environments. The dependence of the degree of ^{137}Cs and ^{90}Sr sorption from the adsorbent solutions on the contact time of the solid and liquid phases is given in Fig. 3, a, 4, a.

The obtained experimental data indicate that the sorption is fastest in the early period of the contact. The shape of the kinetic curve shows that the ^{137}Cs sorption rate increases during the first hours of the process. Then, it sharply decreases, and the curve reaches the maximum sorption level.

The maximum degree of ^{137}Cs sorption from the solutions is reached in the first 4 hours. A NB sample adsorbs up to $98.5 \pm 1.3\%$ of ^{137}Cs , and SMB-20 sample — $90.0 \pm 1.2\%$ of ^{137}Cs . In other words, the effective time for reaching the maximum ^{137}Cs sorption on the sorbents does not exceed 4 hours, then the system comes to equilibrium and the content of ^{137}Cs in the

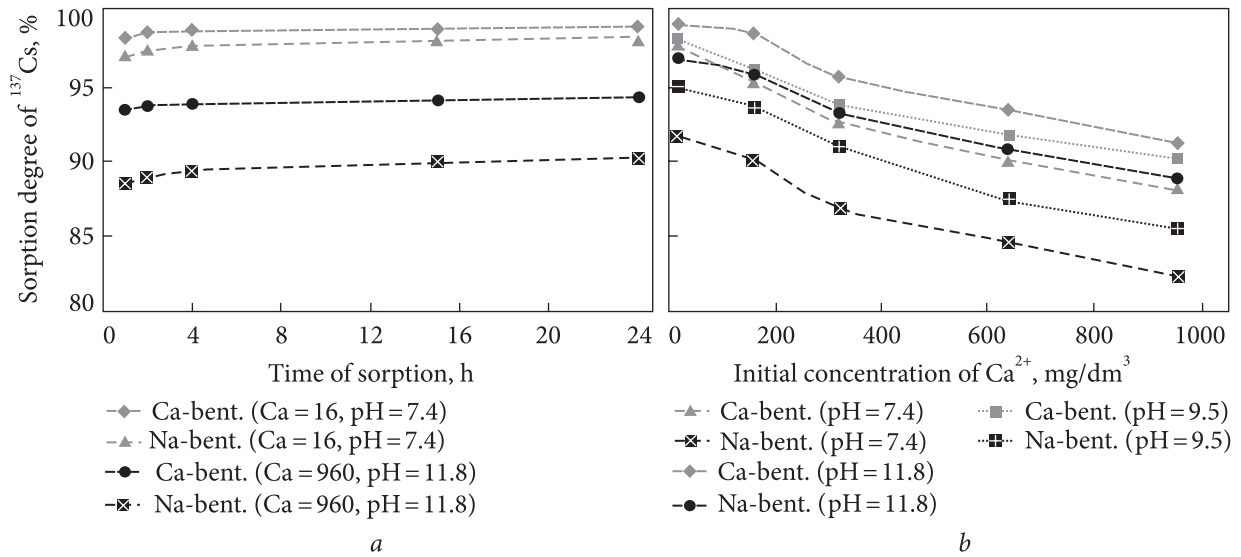


Fig. 3. Kinetics of ^{137}Cs sorption on NB and SMB-20 Cherkasy bentonites from the model solution with the Ca^{2+} concentration 960 mg/dm³ and pH = 11.8 (a); Dependence of the degree of ^{137}Cs sorption on NB and SMB-20 Cherkasy bentonite on the Ca^{2+} ion concentration and pH of the model solution (b). The sorption degree was measured after 14 days

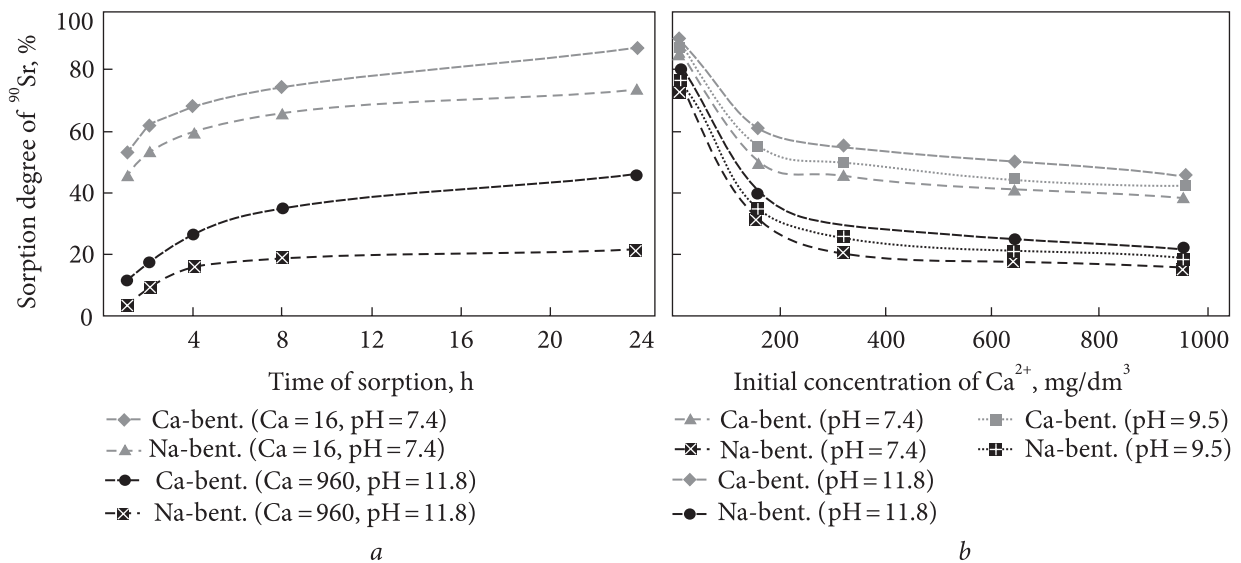


Fig. 4. Kinetics of ^{90}Sr sorption on NB and SMB-20 Cherkasy bentonites from the model solution with the Ca^{2+} concentration 960 mg/dm³ and pH = 11.8 (a); Dependence of the degree of ^{90}Sr sorption on NB and SMB-20 Cherkasy bentonites on the Ca^{2+} ion concentration and pH of the model solution (b). The sorption degree was measured after 14 days

solution practically does not change. For ^{90}Sr , the maximum sorption degree is reached in 14 hours and makes $90.5 \pm 1.2\%$. Then it slightly increases to $91 \pm 1.0\%$, which is consistent with the published data (Shabalin et al., 2022a).

As can be seen from Fig. 3, b, the degree of ^{137}Cs sorption (S, %) from weakly alkaline (pH = 7.4) and low-salt model solutions (with Ca^{2+} concentration not exceeding 16 mg/dm³) is

over 95–98% for NB and about $90 \pm 1.3\%$ for SMB-20. However, the difference in sorption values is within 5–10%. With an increase in the Ca^{2+} cation concentration (ionic strength) from 160 to 900 mg/dm³ and pH from 7.4 to 11.8, the degree of ^{137}Cs sorption on bentonites decreases to $85 \pm 1.5\%$. Though, the sorption degree values remain quite high — over 80%. At the same time, the sorption degree on NB is 5–8% higher

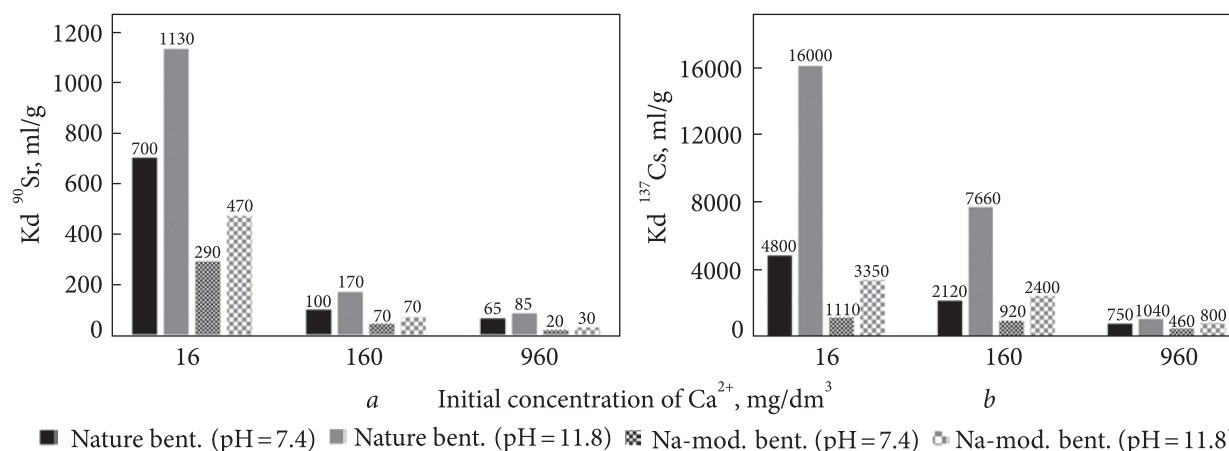


Fig. 5. Distribution coefficients (K_d) of ^{137}Cs (a) and ^{90}Sr (b) sorption on NB from the Cherkasy deposit from the model solution depending on pH and Ca^{2+} ion concentration

than on SMB-20. Under these conditions the cation exchange of Na for Ca takes place in the interlayer space of SMB-20.

The results of a study of the sorption at the solid : liquid phase ratio of 1 : 100 are reported in (Kulyeshova et al., 2014). The pH of the solutions was 7.2—8.0, and the exposure time — 24 hours. The sorption capacity of SMB-20 from the Cherkasy deposit was about 85%, which is consistent with our data.

With an increase in the Ca^{2+} ion concentration and pH in the model solution (ionic strength), the degree of ^{90}Sr sorption decreases sharply (Fig. 4, b). The values of ^{90}Sr sorption on NB were 35—40% lower than of ^{137}Cs sorption under similar conditions. For SMB-20, they were 50—60% lower.

The worser sorption of Sr compared to caesium can be explained by the low selectivity of bentonites for ^{90}Sr and its competition with other cations present in the model solution and interaction with carbonate ions.

Similar dependences of the ^{90}Sr sorption degree on the presence of Ca^{2+} ions in the solution were previously considered in (Kobets, Demchenko and Pshynko, 2007). The authors observed a sharp decrease in ^{90}Sr sorption with an increase in Ca^{2+} concentration up to 100 mg/dm^3 and inhibition of sorption at the concentration of 300 mg/dm^3 . This is caused by the competitive sorption of Ca^{2+} on sorption sites on the basal surface.

The concentration of Cs and Sr in the solution is also one of the important parameters that must be taken into account when choosing the

optimal conditions for radionuclide sorption. As published in the work (Semenkova et al., 2021), the degree of ^{137}Cs sorption from an aqueous solution was 96.8% at caesium concentration of 1 g/dm^3 . A further increase in the ^{137}Cs concentration to 4 g/dm^3 and more leads to a slight increase in the sorption degree. The degree of ^{137}Cs sorption during 1 hour, with the caesium concentration 4 g/dm^3 and pH = 6.5 was about 98%.

The sorption of radionuclides depends on the concentration of competing cations in the aqueous solution (ionic strength, mineralization) over a wide range of pH values.

It was shown earlier in the publication of Dyer, Chow and Umar (2000), that the selectivity of the alkaline and alkaline earth cation sorption on montmorillonite decreases in the order $\text{Cs}^+ \gg \text{K}^+ \gg \text{Na}^+ \gg \text{NH}_4^+ \gg \text{Ca}^{2+} \gg \text{Sr}^{2+} \gg \text{Mg}^{2+}$. Sorption of Cs^+ and Sr^{2+} is accompanied by the competitive interaction with Na^+ , Ca^{2+} , Mg^{2+} and K^+ cations at pH over 6.5. For all studied montmorillonites, the mobility of Na^+ is much higher than that of Ca^{2+} due to their different hydrate shells and hydration energy ($\text{Ca}^{2+} \gg \text{Na}^+ \gg \text{Cs}^+$). Depending on the water residence time in the typical hydrated Na^+ and Ca^{2+} complexes, the hydrated complexes of Ca^{2+} are more stable than those of Na^+ . In montmorillonites with a high $\text{Ca}^{2+} / \text{Na}^+$ ratio, clearly pronounced inhibitory effects of the hydrated Ca^{2+} complexes on Na^+ mobility are reported in (Ferrage et al., 2007). So, the Cs^+ and Sr^{2+} sorption can be limited by the partial blocking of the sorption centres by

Ca^{2+} ions both in the interlayer space and on the basal and edge surfaces, as can be seen from the results of our experiments.

The processes of the Cs and Sr sorption from multicomponent solutions with different pH, Eh and salt composition are determined by the precipitated insoluble or sparingly soluble compounds on the surface of bentonites. According to the computer simulation data, trace amounts of sediments, mainly Fe oxides, hydroxides, oxyhydroxides (hematite, goethite, limonite), and Ca carbonates (calcite, aragonite, dolomite) were present in the model solution after adding CaCl_2 solutions. Hydrated iron oxides and calcium carbonates play an important role in the Cs and Sr sorption processes on bentonites (Shabalin et al., 2022b). This is also confirmed by the thermodynamic modeling of isomorphic binding of Sr in natural sand-clay rocks, taking into account its inclusion in the composition of the solid $\text{Ca}(\text{Sr})\text{CO}_3$ solution with alkaline $\text{pH} \geq 9$ (Synnysyn et al., 2006). At the same time, the surface sorption of carbonates is non-selective and the bonds are weaker than in montmorillonite.

Durability (reliability) of the EBS performance is an important indicator of the disposal facilities' safety. Long-run laboratory simulations do not lead to the unambiguous conclusion concerning the evolution of the mineralogical composition of clay materials. The numerical thermodynamic simulation can predict the results of very slow processes that cannot be studied by the experimental methods.

The calculated interphase distribution coefficients (K_d , ml/g) confirming the Cs and Sr sorption patterns on the studied bentonites are given in Fig. 5.

Thus, the presented results show that the highly alkaline solutions with an increased Ca^{2+} ion concentration decrease significantly the sorption capacity of the NB and SMB-20 Cherka-sy bentonites for Cs and Sr. The NB is more effective sorbent than SMB-20.

Conclusions. The data we obtained from this study suggest that:

1. Precipitates, mainly Fe oxides, hydroxides, oxyhydroxides (hematite, goethite, limonite), and Ca carbonates (calcite, aragonite, dolomite),

which play an important role in the bentonite sorption, are formed in the model solution with the addition of CaCl_2 solutions and alkaline pH. They can concurrently sorb radionuclides and block the sorption centres in montmorillonites.

2. The concentration of the main structural elements (Si, Al) of montmorillonite (the dominating mineral of bentonite) practically does not change with increased Ca^{2+} ion concentration and pH of the model solution demonstrating the bentonite structure stability. At the same time, in the ion exchange complex of bentonites, the concentration of Ca increases and Na decreases. As a result, SMB-20 can transform from a Na, Ca-form into Ca, Na-form.

3. Both types of bentonites are quite effective in removal of ^{137}Cs from aqueous solutions. The presence of competing ions in the aqueous medium does not significantly affect the ^{137}Cs sorption on bentonites. It is shown that the ^{137}Cs ion sorption on NB and SMB-20 slightly decreases with an increase in CaCl_2 concentration from 16 to 960 mg/dm³ (increase in the ionic strength) and increase in pH from 7.4 to 11.8. Though, the sorption degree values remain quite high — not less than $85\text{--}90 \pm 1.0\%$. At the same time, the sorption degree for NB is $5\text{--}8\%$ higher than for SMB-20.

4. The sorption degree for Sr sharply decreases under similar conditions. The ^{90}Sr sorption degree values for NB are $35\text{--}40 \pm 3.0\%$ and for SMB-20 — $50\text{--}60 \pm 2.5\%$ lower than those for ^{137}Cs under the similar conditions. NB will more reliably isolate caesium and strontium in short-lived low- and intermediate-level radioactive waste disposal facilities, ensuring safety for population and the environment. Considering the obtained results on ^{137}Cs and ^{90}Sr sorption on both types of bentonites, it can be assumed that SMB-20 gets more compacted with pore collapse due to precipitation of insoluble or sparingly soluble compounds on the surface than NB.

5. The results of this study can be used as a grounding for bentonite clay application as an isolating waterproof liner in radioactive waste disposal facilities.

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ТРАНСФОРМАЦІЯ БЕНТОНІТІВ ЗА НАЯВНОСТІ ІОНІВ Ca^{2+}

В КОНТАКТНОМУ РОЗЧИНІ ТА ЇХНІ СОРБЦІЙНІ ВЛАСТИВОСТІ ДО ^{137}Cs і ^{90}Sr

Наведено результати експериментального моделювання впливу концентрації іонів Ca^{2+} і рН модельних розчинів на елементний склад і сорбційні властивості щодо ^{137}Cs і ^{90}Sr зразків природного (ПБ) і промислово модифікованого содою (ПБА-20) бентонітів Черкаського родовища. Процеси сорбції Cs і Sr із багатоконпонентних розчинів з різними рН, Eh та сольовим складом залежать від осаджених нерозчинних або малорозчинних сполук на поверхні бентонітів. За результатами комп'ютерного моделювання визначено, що в модельних розчинах із додаванням розчинів CaCl_2 з високолузним рН є незначна кількість осадів, переважно оксидів, гідроксидів, оксигідроксидів Fe (гематит, гетит, лімоніт), а також карбонатів Ca (кальцит, арагоніт, доломіт). Оксиди і гідратовані оксиди Fe та карбонати Ca відіграють важливу роль у процесах сорбції Cs і Sr на бентонітах і можуть одночасно сорбувати радіонукліди і блокувати їхні центри сорбції в монтморилонітах. Концентрація основних структурних елементів (Si, Al) у бентонітах зі збільшенням концентрації іонів Ca^{2+} в модельному розчині і рН практично не змінюється порівняно з вихідними зразками ПБ і ПБА-20, що вказує на їхню структурну стабільність. Водночас у іонообмінному комплексі міжшарового простору монтморилоніту як основного мінералу бентонітів виявлено збільшення концентрації Ca і зменшення Na порівняно з вихідними зразками, що може поступово призводити до перетворення бентоніту ПБА-20 з Na-Ca-форми в Ca-Na. Показано, що сорбція ^{137}Cs і ^{90}Sr на ПБ відбувається ефективніше, ніж на ПБА-20, за підвищеної концентрації іонів Ca^{2+} і збільшення рН. Результати досліджень можуть слугувати основою під час застосування бентонітової глини як протиміграційного і протифільтраційного бар'єра для певного об'єкта захоронення радіоактивних відходів.

Ключові слова: сорбція, стронцій, цезій, бентоніт, інженерні бар'єри, приповерхневі сховища радіоактивних відходів.