

PERFORMANCE OF CLAY MATERIALS CONSTITUTING TO SAFETY BARRIERS IN RADIATION HAZARDOUS FACILITIES

Martynov K. V.¹, Zakharova E. V.¹, Dorofeev A. N.², Zubkov A. A.³, Prishchep A. A.⁴

¹Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

²State Corporation "Rosatom", Moscow, Russia

³Joint stock company "Siberian Chemical Combine", Seversk, Tomsk Region, Russia

⁴SIVER LLC, Berezovka, Krasnoyarsk Territory, Russia

Article received on September 17, 2020

The paper elaborates on the characteristics of clays and clay materials governing functional properties (performance) of clay barriers. It considers methods applied to identify these characteristics with relevant examples provided. Certain criteria were proposed to select the required and sufficient numerical values of these characteristics (requirements) considered appropriate for the barrier materials. The paper discusses operating and envisaged test installations designed for mock-up and field tests of clay barrier materials.

Keywords: radioactive waste, clay materials, safety barriers, compression and filtration tests, deformation, capillary suction, swelling pressure, hydraulic conductivity, cation exchange capacity, sorption distribution coefficient, sorption capacity coefficient, effective diffusion coefficient, underground research laboratory, mock-up and field experiments.

Introduction

This article is a continuation of a previously published study [1] exploring the main characteristics of natural clays and industrial clay-based materials being considered important for the development and operation of engineered safety barriers (EBS) for radioactive waste disposal facilities (RWDF) and radiation hazardous facilities (RHF) upgraded to ensure long-term safe storage configuration (term referred to as conservation in Russian literature sources). The previous study also evaluated the process characteristics of clay-based barrier materials, their ability to form colloidal particles, as well as their stability during the interaction with a natural-technogenic system.

Now let us consider the performance characteristics governing the anti-filtration and anti-migration properties of clay-based safety barriers: deformation and strength parameters in a water-saturated state; capillary absorption; swelling pressure; cation exchange capacity; radionuclide sorption distribution coefficients; water filtration coefficient; gas filtration coefficient in water-saturated material; effective pore diffusion coefficients of radionuclides.

The ranges in which the performance characteristics set for the barrier materials can vary should be identified to develop appropriate regulatory requirements governing the use of clay-based

materials during EBS development. These will be set based on physical and chemical conditions in the considered facility, thus, allowing the development of some general principles for the decision-making on the required and sufficient values of the performance characteristics.

Model experimental studies are considered of a fundamental importance for the refinement of various barrier material characteristics under actual setup. They not only provide initial data for numerical predictive calculations of radionuclide migration in a natural-engineered system, which is essential for RHF safety demonstration, but also allow for the verification of relevant models and software applied in such calculations. Below are described some of already available and planned experimental stands developed for model mock-up and field tests of clay barrier materials in the underground research laboratory (URL) constructed in the Nizhnekanskiy rock mass (NKM).

Performance characteristics of clay barrier materials

Performance of clay-based safety barriers is governed by three processes: groundwater filtration (compression-filtration properties), pore diffusion of components dissolved in the groundwater (diffusion properties), sorption retention of radionuclides on the minerals of the clay-based barrier materials (sorption properties).

Pressure filtration of liquid and gas, deformation in a water-saturated state under load, capillary suction, swelling pressure (compression-filtration properties)

Compression and filtration parameters are responsible for the performance of clay-based barriers under given operational conditions. They reflect the waterproofing and stabilization characteristics of clay materials during their saturation with water. Considering this group of parameters, the following are considered of primary importance: permeability (filtration coefficient), compaction coefficient (compression curve), capillary pressure (suction), swelling pressure.

Provisions of GOST 25584-2016 Interstate Standard. Soils. Methods for the Laboratory-based Identification of Filtration Coefficients are used to determine the filtration coefficients. For the first time, the current version of this GOST includes a description of a compression-filtration device considered as the only acceptable equipment that can be applied to study clay soils of low-permeability. Automated testing complex (AIK) ASIS developed by OOO Research and Production Enterprise Geotek (Penza) can be considered as an example of such equipment (Figure 1) designed for compression

and filtration tests of unconsolidated samples in a water-saturated state allowing the measurement of one-dimensional deformation under a load of up to 12.5 MPa and pore pressure control of up to 2 MPa.

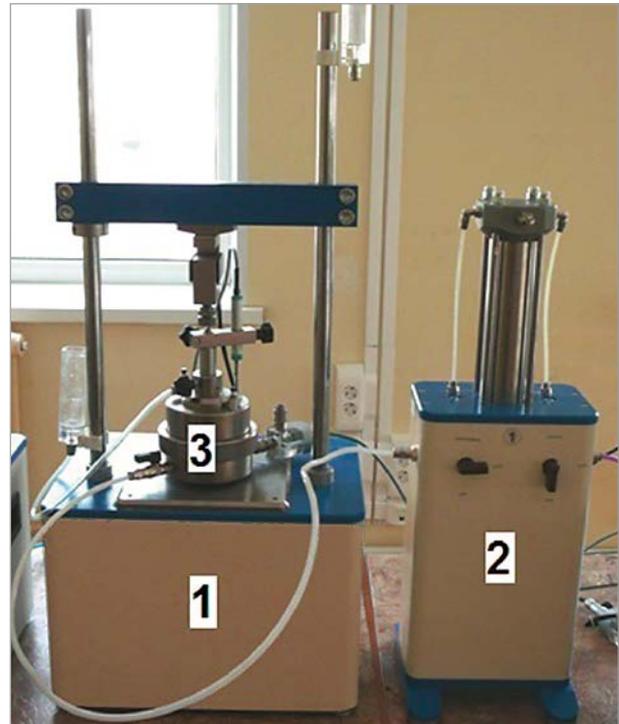


Figure 1. The main units of AIK ASIS:

1 – axial loading device, 2 – blower, 3 – filtration odometer

AIK ASIS allows high accuracy measurements of the liquid volume filtered through a standard size sample (diameter – 71.5 mm, height – 20.5 mm) placed into an odometer ring and the axial deformation of the sample under controlled pressure. To describe the filtration parameters, a series of experiments is performed accounting for various loads and pressures selected intentionally to cover the range of the considered parameters [2]. Depending on the load and pressure, one experiment in such a series can last several weeks or even months in case of low-permeability materials (Figure 2a).

The volume V (cm³) of the liquid filtered during time t (s) is used to calculate the Darcy volumetric filtration rate (m/s) under a stationary mode (Figure 2a):

$$v = V / (t \cdot S),$$

where S is the cross-sectional area of the sample (cm²). The filtration coefficient (m/s) is calculated based on the Darcy velocity:

$$K_f = (v \cdot L \cdot \rho_l) / \Delta P_1,$$

where L is the sample thickness (cm), ρ_l is the liquid density (being equal to 1 g/cm³ under normal

Disposal of Radioactive Waste

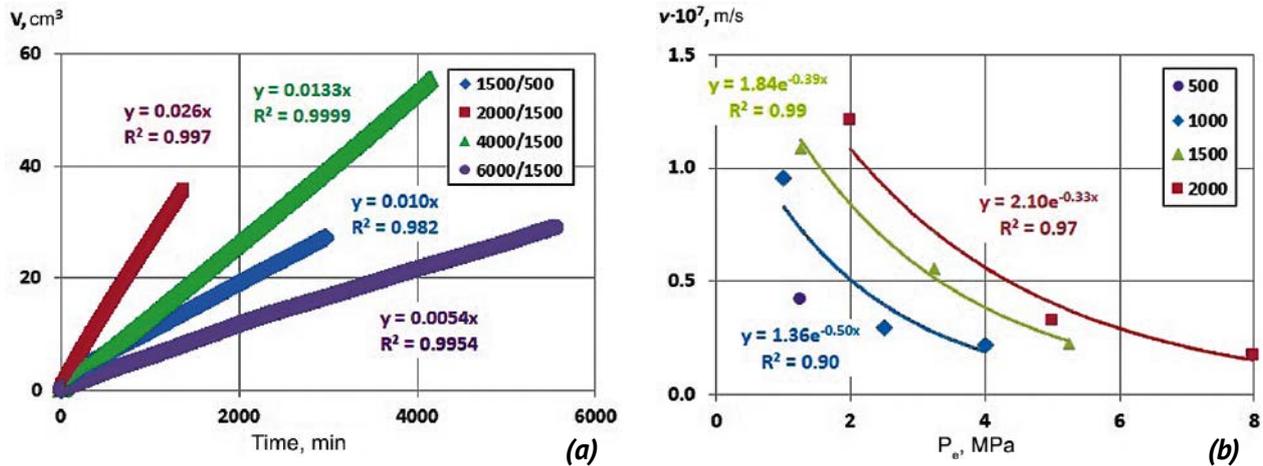


Figure 2. Dependence between the volume of water filtered through a sample and the time accounting for various P_j/P_i ratios, kPa (a) and the dependence between the Darcy velocity and the effective pressure accounting for various values of P_e , kPa (b) derived for a mixture of 30 wt.% bentonite and 70 wt.% kaolin according to [2]

conditions), ΔP_i is the pore pressure drop in the sample.

The calculated filtration characteristics of water-saturated materials can be presented as an effective pressure function (Terzaghi pressure) (MPa):

$$P_e = P_s - P_i/2,$$

where P_s is the pressure acting on the sample skeleton, P_i is the pressure in the compressor (Figures 2b, 3a). The compression characteristic, namely, the linear deformation (ΔL , mm) of the sample measured throughout the mass of the skeleton considering the moisture level previously measured according to GOST 5180-2015 was recalculated in ρ_s (g/cm³) – the density of the sample skeleton. Thus, material filtration coefficient depending on the skeleton density could be introduced, which appeared to be more visual and convenient for practical use (Figure 3b). The results shown in Figure 3

demonstrate that filtration coefficient for bentonite is approximately an order of magnitude lower than the one for kaolin. Whereas, the mixture of materials has somewhat average filtration properties with its skeleton density being similar to kaolin.

Every year, more and more experimental data on the filtration of aqueous solutions through clay materials and publications on this topic appear abroad, although these are mainly focused on bentonites [3–5]. Unfortunately, this is still not the case of Russian research on mineral raw materials [6, 7]. Meanwhile, characteristics describing some individual clay raw materials or materials produced based on it account for the main value of such data.

Gas filtration in clay barrier materials is viewed as no less important subject of research than the liquid one. Although one order less of publications can be found on the former one which is due the complexity of gas filtration modeling process and not due to its lower relevance. Gas generation under

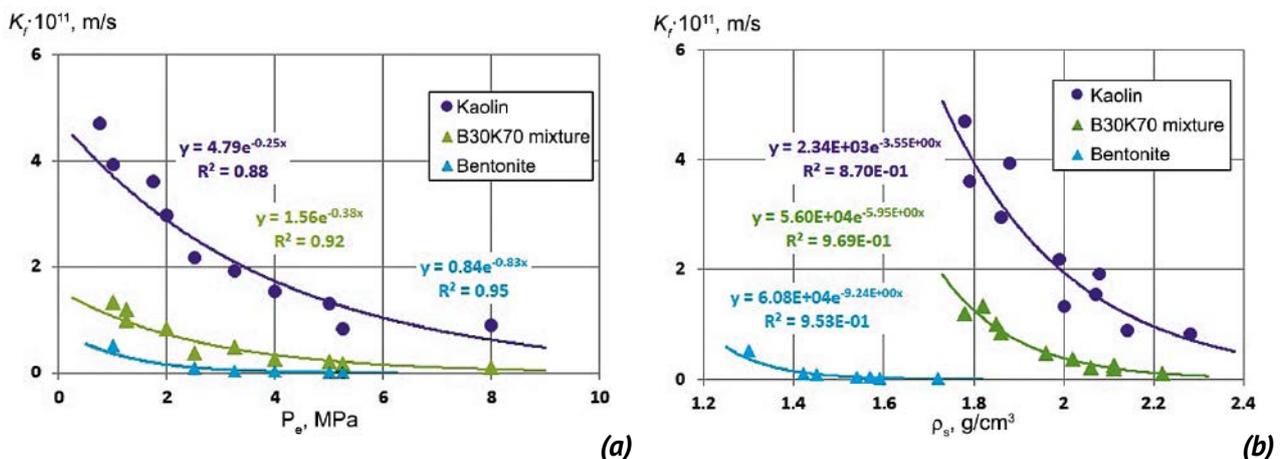


Figure 3. Dependence between filtration coefficients identified for various clay-based materials and the effective pressure (a) / density of the skeleton (b) according to [2]

RWDF conditions may be triggered by metal corrosion, water radiolysis, microbiological activity. Gas pressure increases when it gets accumulated inside an enclosed space. To prevent the destruction of RWDF structures, including the safety barriers, the gas should be able to escape the system.

In a water-saturated clay barrier, all pore channels are filled with liquid. To displace it, gas pressure should overcome the capillary one, which in case of clay materials, as discussed below, exceeds the plastic deformation pressure. Thus, the gas pressure acting on the barrier does not displace the liquid from the pores, but on the contrary tightens the barrier, which further reduces its permeability. The stresses will continue to grow and the only way they can be relieved is a breaching (local structure destruction) of the barrier. In this case, the gas pressure drops sharply, its load on the barrier disappears, whereas ruptured barrier "self-heals" due to the plasticity of clay materials. This process is impulsive, cyclical and does not lend itself to any laboratory scaling; it can be adequately reproduced only under actual conditions. This description can be illustrated by some experiments involving water-saturated bentonite [8] that allowed to calculate the critical break down pressure for the samples.

A simplified option is most commonly used in gas permeability experiments focused on clay material behavior: gas filtration under pressure through a sample not being completely saturated with water, in which, stationary gas filtration is possible due to the availability of liquid-free pore channels which are commonly the largest ones. In this case, gas permeability is considered as a fraction of the total permeability minus the porosity blocked by the liquid [9]. Nevertheless, the gas permeability appears to be several orders of magnitude higher than the liquid one partly due to the phenomenon of gas slippage (the Klinkenberg effect) and other

deviations from the Darcy's law. However, this is mainly explained by the fact that in undersaturated samples, swelling (in case of smectites) and capillary effects do not manifest themselves to the full extent, which is reflected in the porosity structure.

As it comes to barrier characteristics, clay material deformation in a water-saturated loaded state is seen as an important characteristic not so much because of its ability to reflect the stabilizing properties of barrier materials, but by being dependent on two most important compression parameters: capillary pressure and swelling pressure of the material. Thus, due to capillary suction, clay materials can become saturated with water even if the hydraulic gradient is absent. Another very important effect of capillary pressure that has been already noted above is its action against gas filtration. Clay material swelling causes alterations in the porosity structure and decreases the material permeability.

When evaluating the strength of structures being in contact with the clay barrier, the swelling pressure should be accounted for. Depending on the density of the material skeleton, it can be calculated based on a decompression curve (P_{DVM}), whereas in the first approximation (without taking into account internal friction) the capillary pressure (suction) can be calculated as the difference between the compression curves in a dry (P_{KSM}) and water-saturated (P_{KVM}) state accounting for swelling pressure correction:

$$P_{VS} = P_{KSM} - P_{KVM} + P_{DVM}$$

Figure 4 provides an example of how the compression characteristics of a natural bentonite clay powder can be calculated based on some AIK ASIS test results [10]. Compression curve shifts which is clearly seen when the material is saturated with water. The decompression curve for water-saturated bentonite shows swelling at a load pressure

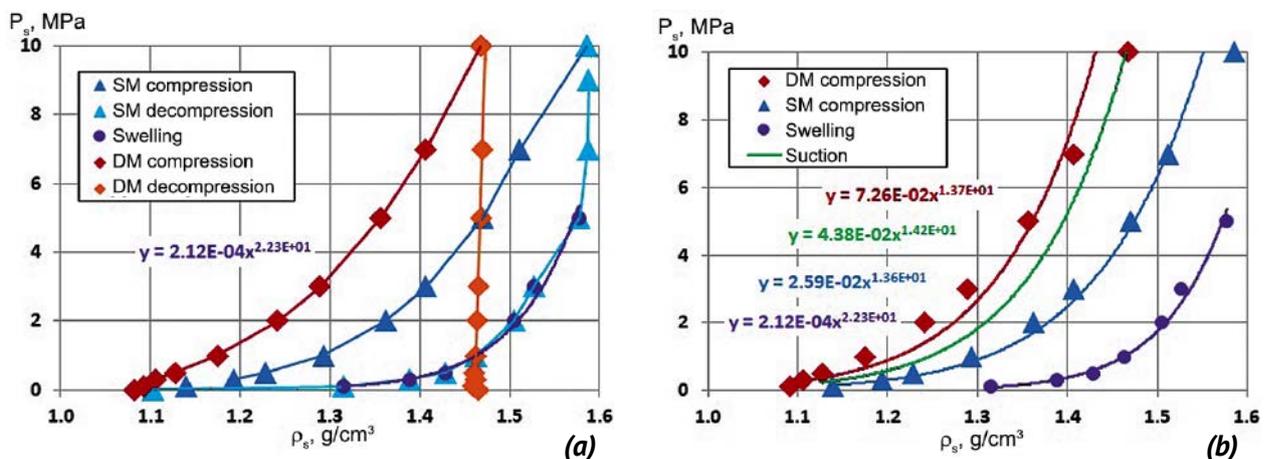


Figure 4. Experimental data on the compression characteristics of bentonite clay powder (a); corresponding approximating curves and mathematical expressions (b) describing them according to [10]

Disposal of Radioactive Waste

below 5 MPa, in contrast to complete deformation-free decompression of a dry material (Figure 4a). The swelling pressure first becomes noticeable when the dry density of the material reaches the level of 1.3 g/cm³ and grows rapidly above the level of 1.5 g/cm³.

The calculated capillary pressure (suction) curve lies above the compression one (Figure 4b). If this is true, then under the gas pressure acting on the water-saturated bentonite, its deformation will increase the skeleton density, but the pore water will remain in the pores due to capillary forces. High capillary suction pressure even at low density of the bentonite skeleton indicates the inevitability of bentonite barrier saturation with water upon its contact with the aquifer even if the pressure head is absent.

Cation exchange capacity (CEC), radionuclide sorption distribution coefficients, sorption capacity (sorption properties)

Clay materials are effective, durable, and affordable sorbents. Different clay minerals are characterized with different mechanisms of sorption interaction with radionuclides. Therefore, there is a certain selectivity in relation to different radionuclides. Polymineral mixtures containing a complex of clay minerals (montmorillonite, kaolinite, chlorite, vermiculite, micas and hydromicas) interact with radionuclides by several parallel or sequential mechanisms, which significantly increases the reliability of clay safety barriers as regards their anti-migration properties.

Cation exchange capacity (CEC) is most commonly used as a sorption property indicator for clay-based materials, which characterizes the ability of the rock to absorb cations due to the exchange mechanism and is expressed in mg equivalents from the sum of exchangeable cations that can be replaced by cations of a different type per 100 g of a dry material. Normally, CEC level is growing

along with the increasing clay fraction in the rock, the degree of clay particle dispersion (since they both affect the specific surface) and also depending on the composition of clay minerals in the series: kaolinite — chlorite — illite — vermiculite — montmorillonite. This indicator can be calculated using several methods based on different material properties, therefore, resulting in different absolute values.

Effective provisions of GOST 21283-93 Bentonite Clay for Fine and Building Ceramics. Methods Used to Calculate the Adsorption Index and the Cation Exchange Capacity should be applied in CEC calculations. These provisions recommend the application of organic dyes: methylene blue and methyl violet. Obviously, adsorption of these molecules by clay materials is not quite adequate to the one of radionuclides from aqueous solutions. A method providing for CEC identification based on the adsorption of a bivalent copper triethylenetetramine complex [Cu (Trien)]²⁺ [11] (CEC_m) is considered as much more akin to the mechanism of radionuclide sorption on clays. Alternatively, CEC can be calculated as the sum of exchangeable bases contained in the sample, which is commonly used in soil research [12] (CEC_o). Table 1 summarizes the results obtained for some natural clay materials using these methods.

CEC application as a sorption property indicator is challenged by the fact that none of the methods used for its identification fully reflects the sorption characteristics of the material, therefore CEC is viewed as an indirect indicator. To characterize sorption processes being somewhat different as regards the sorption mechanisms involved, another generalized indicator is applied, namely, the inter-phase distribution coefficient, which is equal to the ratio between the amount of the radionuclide absorbed on the solid phase and its equilibrium content in the solution:

Table 1. Specific surface area and CEC calculated for some natural clay materials

Indicator	Material (deposit)			
	Bentonite (10th Khutor)	Bentonite (Kamalinskoe)	Kaolin (Kampanovskoe)	Kaolin (Kantatskoe)
Specific surface, m ² /g	33	51–59	15	42
CEC _m , mEq/100 g	68–88	29–58	8–15	19–28
Content of exchange cations, mEq/100 g				
Ca ²⁺	27.9	24.39	6.13	15.72
Mg ²⁺	14.8	6.51	0.76	4.16
K ⁺	0.32	0.48	0.20	0.24
Na ⁺	16.4	0.56	2.95	0.77
CEC _o	59.4	31.9	10.0	20.9

Table 2. Coefficients of radionuclide sorption distribution (cm^3/g) for some natural clay materials

Radionuclide	Material (deposit)			
	Bentonite (10th Khutor)	Bentonite (Kamalinskoe)	Kaolin (Kampanovskoe)	Kaolin (Kantatskoe)
^{60}Co	$(3.0-4.9)\cdot 10^2$	$(1.2-1.8)\cdot 10^2$	$(6.0-6.9)\cdot 10$	$(7.3-8.7)\cdot 10$
^{90}Sr	$(3.3-5.3)\cdot 10^2$	$(1.3-2.2)\cdot 10^2$	$(6.2-7.9)\cdot 10$	$(7.2-8.9)\cdot 10$
^{137}Cs	$(6.2-7.1)\cdot 10^3$	$(2.1-3.9)\cdot 10^3$	$(1.9-4.1)\cdot 10^3$	$(3.8-5.4)\cdot 10^3$
^{233}U	$(3.4-5.6)\cdot 10$	$(7.2-8.1)\cdot 10^2$	$(6.1-6.8)\cdot 10$	$(7.0-7.8)\cdot 10$
^{237}Np	$(2.6-4.3)\cdot 10^2$	$(1.9-2.9)\cdot 10^2$	$(7.5-9.8)\cdot 10$	$(4.6-8.0)\cdot 10^2$
^{239}Pu	$(2.0-4.0)\cdot 10^3$	$(1.2-2.0)\cdot 10^4$	$(8.2-9.9)\cdot 10^3$	$(8.2-9.0)\cdot 10^3$
^{241}Am	$(5.1-7.8)\cdot 10^3$	$(1.7-2.4)\cdot 10^4$	$(7.5-8.4)\cdot 10^3$	$(7.7-8.4)\cdot 10^3$

$$K_d = a_s/a_1 = V_1 \cdot (a_0 - a_1)/(a_1 \cdot m_s),$$

where a_s is the ultimate specific activity on the sorbent (Bq/g), a_0 and a_1 stand for the initial and ultimate specific activities in the solution (Bq/cm^3), V_1 is the solution volume (cm^3), m_s is the mass of the sorbent (g).

Sorption experiments aiming to identify the K_d values are usually carried out under static conditions, which seems quite reasonable given the negligibly low filtration rates of solutions flowing through clay barriers. Clay material properties are evaluated according to the following procedure: calculated is the kinetics of the interaction process, equilibrium distribution coefficients, and the strength of radionuclide fixation.

Table 2 presents sorption distribution coefficients for fission products and actinides accounting for the same conditions and different samples allowing to compare their sorption properties.

The K_d values presented in the table were calculated given a solid and liquid phase ratio of 1 : 20, a room temperature and a contact time of 168 hours (pseudo-equilibrium state). The composition of the simulated ground water was as follows (mg/l): Ca^{2+} – 52.1; Mg^{2+} – 24.3; Na^+ – 69.0; HCO_3^- – 288.2; SO_4^{2-} – 17.1 and Cl^- – 71.6; and $\text{pH}=7.3$. A slightly higher increase in the K_d values has been observed in case of an increased interaction time.

Following sorption, interaction of these samples with model radionuclide-free reservoir water resulted in the desorption of cesium, plutonium and americium of no more than 5%, the one of uranium and neptunium of 10% with the maximum desorption observed for strontium – up to 20–25%. Tessier selective desorption method is commonly used to determine the fixation strength and the speciation of radionuclides sorbed by clay samples [13]. The method suggests that the radionuclides sorbed by clays change over into a liquid phase during staged treatment with solutions of various compositions.

Standard experimental methods used to calculate sorption distribution coefficients are focused on the process occurring in dispersed systems with a low ratio of solid to liquid phases (S : L). Under real conditions, these processes occur in a pore solution of a compacted material at a S : L ratio being several orders of magnitude higher. Therefore, it appears essential to estimate the degree of this influence, thus, allowing to predict the behavior of radionuclides in actual barriers based on K_d values calculated using the standard methods.

Radionuclide sorption capacity is considered as another important parameter characterizing the barrier properties of clay materials. It can be calculated based on the sorption distribution coefficient and the specific activity of the radionuclide contained in a solution (a_1). Based on these characteristics, it is easy to calculate the mass of the barrier material (M_t) required for the retardation of the total radionuclide activity (A_t) contained in the RWDF:

$$M_t = A_t / (K_d \cdot a_1).$$

In practice, the application of a dimensionless parameter called the coefficient of sorption capacity appears to be more convenient [14]:

$$\alpha = K_d \cdot \rho_s + 1.$$

It characterizes a barrier made of a material with a skeleton density ρ_s and is associated with the diffusion characteristics discussed below. The volume of the barrier required for the sorption retardation of the entire radionuclide activity in the RWDF can be expressed as follows:

$$V_s = M_s / \rho_s = A_s / (\alpha \cdot a_1).$$

Diffusion of radionuclides in a pore solution (diffusion properties)

Under the design mode of safety barrier operation, diffusion in a pore solution is considered as the main mechanism providing radionuclide migration outside the barrier. Until the barrier reaches its full

Disposal of Radioactive Waste

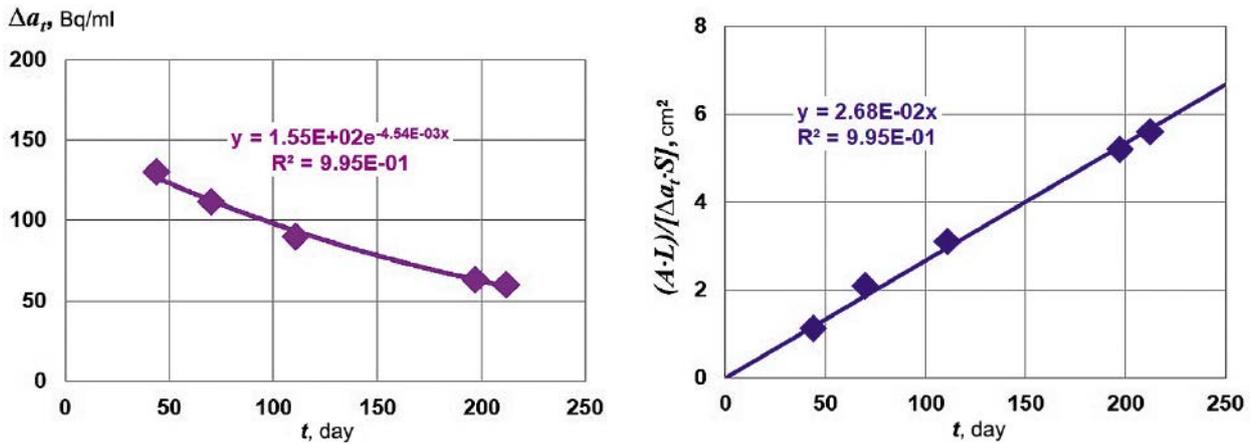


Figure 5. NTO Diffusion through a sample of mixed clay material K70B30 inside an experimental cell (see explanations above)

sorption capacity, nonstationary diffusion is characterized by a visible or true diffusion coefficient (D_a , cm²/s) specified for a radionuclide in a barrier material. Then, if the capacity of the barrier appears to be insufficient to absorb the entire activity of the radionuclide, its release beyond the barrier will occur at a constant rate (stationary diffusion) depending on the effective coefficient of pore diffusion (D_e , cm²/s). The ratio of the diffusion coefficients is expressed precisely through the sorption capacity coefficient:

$$D_e/D_a = \alpha.$$

In case of non-absorbable radionuclides: $\alpha = 1$, the true diffusion coefficient becomes equal to the effective one, sorption retardation is absent, diffusion is stationary. At the same time, in case of absorbable radionuclides, the true and effective diffusion coefficients may differ from each other by several orders of magnitude. The same is the case of sorption distribution coefficients. With the exception of insignificant details, the described model of diffusion-sorption interaction [14] coincides with the one adopted in foreign literature sources [15]. It is the sorption on the pore surface and not the pore diffusion of radionuclides that is essential for radionuclide retardation. According to the recommendations of [16], effective pore diffusion coefficients for radionuclide cations can be assumed as being of the same order of magnitude, while the differences in K_d and, accordingly, D_a values may amount to six orders of magnitude.

Experimental methods allowing to investigate diffusion processes in dense clay samples are quite diverse [17]. The main approaches (techniques, equipment) implemented in this area are similar to those applied in case of crystalline rocks [14]. Only the experimental cell used to study reach-through diffusion [18] has required some minor

modifications introduced to the container designs allowing it to hold a clay sample. Figure 5 shows the results of diffusion experiments with tritiated water (NTO) flowing through a sample of mixed K70B30 material (70 wt% kaolin and 30 wt% bentonite, $\rho_s = 1.78$ g/cm³): alterations in the specific activity of tritium in the experimental cell considered as a term source (Δa_t , Bq/ml) are shown on the left, whereas on the right, one can find the specific increment of tritium's total activity (A , Bq) in the receiver depending on the experiment duration (t). Effective self-diffusion coefficient for water with respect to tritium can be defined as:

$$D_e^{NTO} = (A \cdot L) / (\Delta a_t \cdot S \cdot t),$$

where L is the sample thickness, cm; S is the sample area, cm². For the studied sample, this coefficient amounted to $3.1 \cdot 10^{-7}$ cm²/s.

Nevertheless, diffusion method is considered as the only source of exhaustive information when it comes to independent calculations performed to identify the main diffusion-sorption parameters (D_e and α) of absorbable radionuclides. In this case, it is useful to compare the sorption parameters (α or K_d) with the results of sorption experiments in low-density systems. Unfortunately, this method still cannot be applied to study strongly sorbed ($K_d > 10^5$ cm³/g) radionuclides due to insufficient length of the experiments. In the latter case, non-stationary direct diffusion method can be implemented. Furthermore, to process the experimental data, either the distribution coefficients from sorption experiments implying the use of same materials or concentration profiles of the radionuclides in the solid phase can be studied. This approach requires extremely delicate experimental study. However, in case of loose clay materials it can be implemented much easier than in case of consolidated crystalline rocks.

Specifying the requirements for the characteristics of clay-based materials used in the safety barriers

As noted in [1], regulatory requirements regarding the characteristics of barrier materials, namely, their list and values have not been developed yet. Design development and construction takes place simultaneously with scientific and technical research, and sometimes, when no other alternative exists, the former ones have to outstrip them. However, thanks to the accumulated knowledge on the construction of clay-based safety barriers, scientific and technical support of these efforts, information on global trends, certain practice regarding the requirements for clay barrier materials has been established, which, provided its further development and scientific justification, can become a basis for future regulations.

Not all of the indicators contained in the requirements for clay barrier materials that should be met by existing facilities [19] are considered worth to be included into the normative list. Thus, colloidity and water absorption referred to in GOST 28177-89 Forming Bentonite Clays do not reflect any performance or operational characteristic of barrier materials. The same applies to bulk chemical composition, which, in contrast to the mineral one, is considered as an indirect characteristic. It seems advisable that the list of regulatory requirements would include the indicators being immediately responsible for the performance and operational properties of the barrier material, namely:

- mineral composition: main minerals and standards limiting the content of harmful impurities (carbonates, sulfides, organic substances);
- share of clay fraction in the mixture and the granulometric composition of clastic fractions;
- moisture, bulk density and operational characteristics (fluidity for dry dispersed materials, deformation and strength parameters of the material in dry and water-saturated state);
- specific surface area and cation exchange capacity (CEC);
- sorption distribution coefficients (K_d) for different radionuclides (Sr, Co, Cs, U, Pu, Am and others, depending on RW class and type) taking into account physical and chemical setup at a particular facility;
- as regards barrier material skeleton density specified in the designs: water filtration coefficient (K_f); gas filtration coefficient in water-saturated material; sorption capacity of the material as regards different radionuclides; effective diffusion coefficients (water self-diffusion coefficient at least) taking into account physical and chemical setup

at a particular facility, capillary absorption, swelling pressure;

- ability of the material to form colloidal particles, their migration and sorption properties in relation to different radionuclides;
- stability under the interaction with a natural-engineered system, including radiation exposure, temperature exposure in cycles of water saturation – freezing – thawing – drying.

Appropriate methods and equipment should be developed to specify some of the above characteristics, for example, gas filtration in pore fluid, colloidal properties, climatic cyclic temperature effects. Probably, the proposed list can be expanded, but not all of the characteristics may be required in case of a particular type of facility. Specific lists of characteristics along with the methods applied for their identification should be regulated based on RW type and class. It should be noted that numerical values of the characteristics can vary quite significantly depending on the facility in question, namely its design features, natural and climatic conditions and the geological structure of the site, physical and chemical environmental conditions. Some recent examples discussed in [19] demonstrate the differences in these indicators when it comes to RW DF holding similar RW classes (3–4), but being different in their designs and the type of RW disposed of there, namely Novouralsk RWDF and PUGR AD. Therefore, numerical values should be calculated under each individual project and presented in the designs developed for the facility.

Main functional characteristics of barrier materials (sorption distribution, filtration, diffusion coefficients) should be calculated based on physical and chemical conditions being specific for the considered RWDF site (specific activities of radionuclides leached from RW matrix found in the groundwater, hydraulic gradients, gradients of radionuclide concentrations in the pore solution of a clay barrier) with the latter ones along with the normalized characteristics of clay materials governing the migration of radionuclides. The characteristics of structural RWDF materials and the surrounding rocks should be also taken into account. For example, experimental data shows that at a room temperature and an effective pressure of 15 MPa, the permeability of non-fractured gneisses and amphibolites similar to those enclosing NKM DDF RW, is no less than 10–18 m² [20]. This value corresponds to a filtration coefficient for water of 10–11 m/s. Obviously, there is no need to strive for filtration coefficients in clay barriers that would be significantly lower than those of the host rocks, in which groundwater circulates not through the pores, but through the cracks with the filtration coefficient of more than 10⁻⁹ m/s [21].

Disposal of Radioactive Waste

Model experiments aimed to confirm the barrier properties of clay materials

Mockup and full-scale long-term experiments should address two problems. Firstly, they must validate the laboratory-measured characteristics of materials subject to a complex action of external parameters under a scale similar to an actual facility; secondly, the results of these experiments can be used to verify the mathematical models describing facility evolution. Industrially produced batches of clay barrier materials are recommended for such model experiments.

Based on model experiments, the reliability of safety demonstration for the designed facilities can be qualitatively increased. These can be divided into mock-up tests focused on engineered component of the facility, namely, at validating its performance, and field tests with the natural environment playing a decisive role. For both cases, experimental stands are developed: these are both tested in research centers and subject to in-situ testing, for example, in underground research laboratories. A great number of publications devoted to full-scale and model long-term experiments can be found in foreign literature sources requiring a special review [22, 23].

The experience gained during the development of barriers for Russian facilities (PUGR EI 2 at SCC

site in 2013–2015, internal safety barriers of a disposal facility for non-retrievable RW at MCC site in 2017–2020, 1st section of NO RAO's Novouralsk RWDF for RW Class 3–4 in 2018–2020) showed that the quality of industrially produced clay material batches should be verified based on full-scale models simulating actual setup at RW disposal and non-retrievable RW disposal facilities. In 2019, several experimental stands were developed by SCC, mock-up testing was launched for a pilot batch of a clay barrier mixture produced by PIK Group (Krasnoyarsk). These are briefly described below.

Studying the self-compaction of a bulk barrier material

In a dry state, barrier material is characterized by low density commonly ranging from 0.9 to 1.1 g/cm³. When the barrier is backfilled, its self-compaction is expected to reach a level of 0.2 g/(cm³·MPa). A model was constructed to study barrier material self-compaction (Figure 6): it involved a pipe insulated from moisture with an internal diameter of 180 mm. From the side the pipe was perforated to allow the installation of strain gauges. Sensor pitch accounted for 500 mm.

Shrinkage of the backfilled barrier material was measured at its upper edge once per day. When the shrinkage process was deemed to be completed, samples were taken from the holes of the pipe

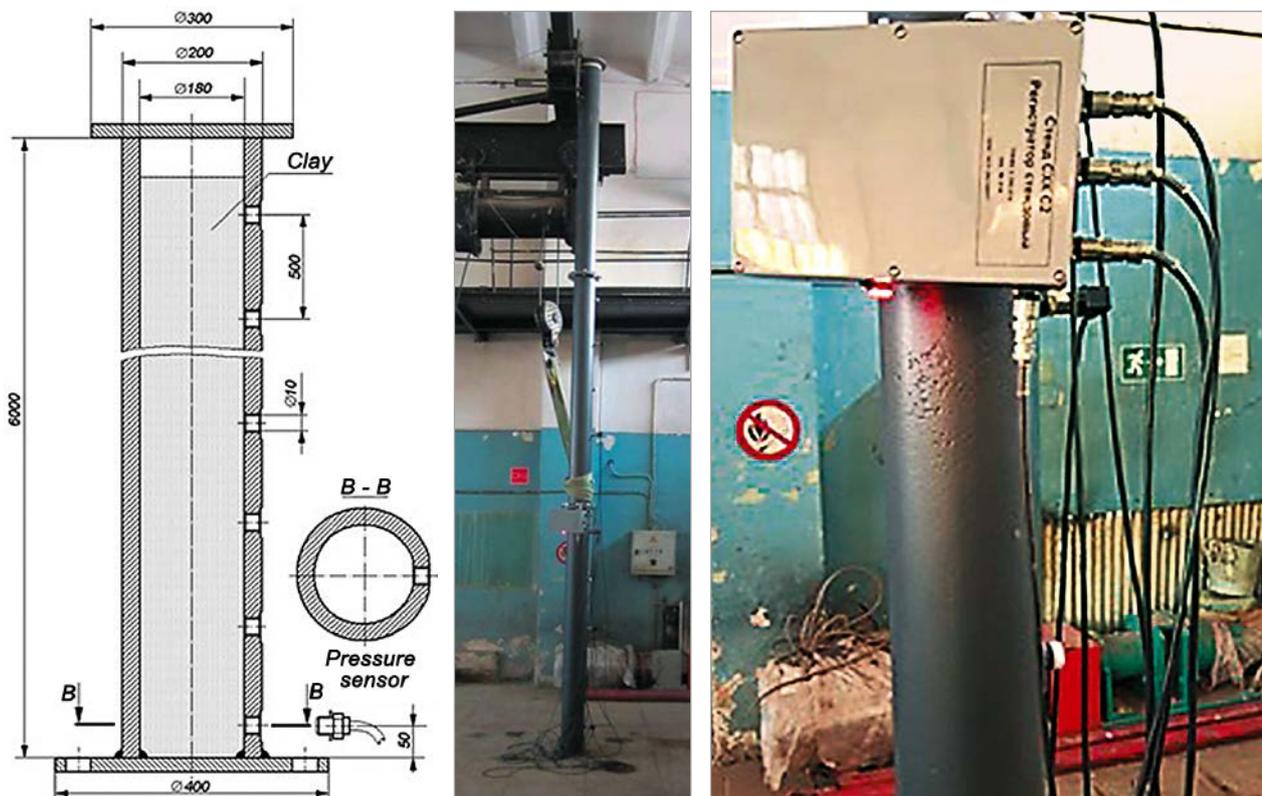


Figure 6. Outline design and appearance of the stand developed to study the self-compaction of bulk barrier material

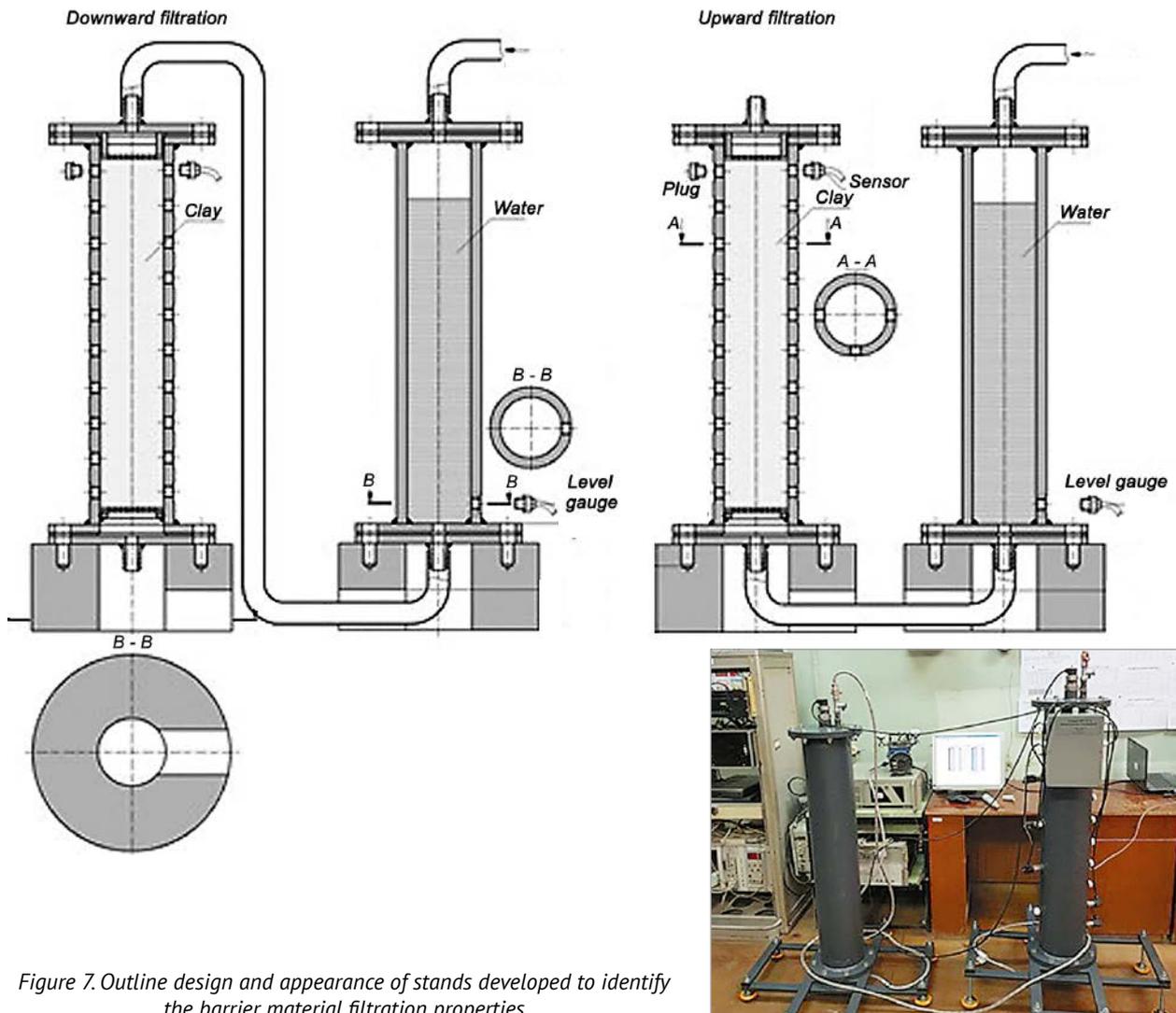


Figure 7. Outline design and appearance of stands developed to identify the barrier material filtration properties

along its height to measure the density, porosity and filtration coefficient of the self-compacted barrier material.

Studying water filtration in a barrier material

Two mockup stands were used for model experiments focused on water filtration through barrier material (Figure 7):

- with water supply from the bottom (simulated was the water inflow through the bottom of a near-surface RWDF);
- with water supply from above (simulated was the water inflow through the overlapping screen of a near-surface RWDF).

During these experiments, water is injected under pressure through a layer of barrier material poured into a steel pipe. Water is supplied to the column under nitrogen pressure up to 10 kg/cm², thus, providing constant hydraulic gradient of up to $I=100$ at a column length of 1 m. Measuring tools of the following types are installed into the column openings:

- sensors monitoring the swelling pressure of clay material;
- sensors monitoring pH levels during the water flow through the barrier material;
- electrical conductivity sensors to monitor the advance of the filtering water front.

At the first stage of the experiment (water saturation of the dry barrier material and establishment of a stationary filtration mode), the hydrogeochemical composition of model water should correspond to the one of the groundwater flows in the near-surface horizons of the SCC site. When the stationary state is established, water containing some 1 g/l of NaCl will start being supplied to determine the filtration coefficient of the saturated barrier material by conductometric method.

Primary results of the described model experiments are expected by the end of 2020. The layouts of the full-scale experiments to be implemented in NKM URL are currently being discussed with the general designs and layout of experimental installations being developed [24]. Development

Disposal of Radioactive Waste

and testing of stands intended for full-scale model experiments should be completed by 2026 by the time when URL construction is expected to be according to the strategy approved for DDF RW development [25]. A multipurpose MiG experiment is proposed for a comprehensive study of RW Class 1 and 2 matrix interaction with clay barrier materials and groundwater.

Modeling the interaction of RW matrices and clay barriers under deep geological disposal conditions (MiG experiment)

The MiG experiment seeks to test the performance characteristics of the main EBS materials used for RW Class 1&2 disposal (RW matrices and materials of clay-based safety barriers in the presence of RW packaging materials) on a scale of an industrial model under real conditions and long-term exposure. Under this experiment, model phosphate glass similar to the glass produced by PA Mayak fitted with mockup radionuclides and/or radionuclide tracers is proposed as a radionuclide source term (RW matrix). Other types of RW Class 1&2 matrices and their packaging can be also tested in this experiment, when more complete information about them is obtained.

During the experiment, physical and chemical parameters similar to those expected under real disposal conditions will be simulated and monitored: increased temperature of the RW matrix simulating heat generation due to radioactive decay and increased pressure of the liquid phase simulating the pressure of fractured pore groundwater at the disposal depth. Furthermore, pressure acting on the solid phase will be measured during the experiment, namely, the one prompted by the preliminary compaction and the swelling pressure of clay materials, as well as the changes in the volume of solid phases due to phase transformations (dissolution, precipitation, transformation). Solid materials are going to be studied following the completion of the experiment: matrix, clay, packing RW materials, host rocks at the clay interface. The plans suggest that the experiment will last no more than 5 years.

An experimental bench (800×2000 mm) is planned to be developed and constructed for this experiment involving (Figure 8): a steel perforated container with model glass or other RW matrix (1), a heater (2), a clay-based barrier material (3), an injection system also providing pressure measurements and liquid sampling (4), strain gauge pressure sensors (5), thermocouples (6), cover (7), thermal insulation (8).

Experiments provide both for vertical and horizontal arrangement of the experimental stand. To accommodate the stand, a 2,000 mm-deep excavation

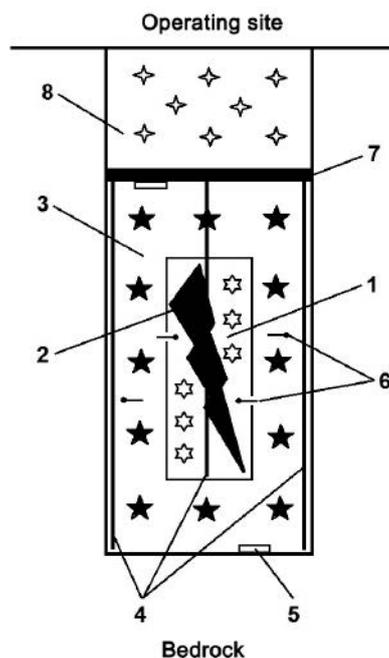


Figure 8. Layout of a stand proposed for MiG field experiment (see the discussion above)

of 800 mm in its diameter should be drilled in a monolithic block of rocks containing neither cracks, veins nor alteration zones.

This experiment is seeking to provide an integral assessment for the protective characteristic of the studied materials and their individual properties: the rate of RW matrix degradation, changes in the radionuclide and macro-component composition of groundwater due to radionuclide leaching from RW matrices, filtration and diffusion-sorption characteristics of clay barriers, etc. Corrosive properties and the degradation of steel and concrete RW packages, filtration coefficient of the enclosing rocks, thermophysical properties of barrier materials in dry and water-saturated state can be also estimated along the way. The considered parameters will be evaluated both during the experiment and according to its final result which is considered essential.

Conclusion

Mixed materials are characterized with more versatile properties compared to mono-mineral ones, which may appear to be beneficial under complex natural and engineered RW disposal systems. Poly-mineral clays not being commonly developed on an industrial scale (local raw materials) may be considered as a good analogue of mixed materials used in the development of clay-based safety barriers for radiation hazardous facilities. The application of mineral additives is recommended to improve some individual characteristics of mixtures and poly-mineral raw materials.

Potential applicability of clay materials in safety barrier construction should be validated based on the numerical values of their performance characteristics set corresponding to the skeleton density specified in the designs. The list of these characteristics includes: deformation and strength parameters of the material in a water-saturated state; cation exchange capacity; sorption distribution coefficients for radionuclides taking into account physical and chemical conditions at a particular facility; water filtration coefficient; gas filtration coefficient in water-saturated material; effective pore diffusion coefficients of radionuclides; capillary absorption; swelling pressure.

The list of barrier characteristics should be specified based on the specific type of facility, in particular, its design, site, RW type and class. Physical and chemical characteristics of the facility (specific activities of radionuclides leached from the RW matrix into the groundwater, hydraulic gradients, gradients of radionuclide concentrations in the pore solution of the clay barrier) should be considered as a basis for numerical calculations of the main parameters governing the system performance (sorption distribution, filtration, diffusion coefficients). Structural materials characteristics, namely, those of the facility itself and the bedrock should be also taken into account.

In addition to laboratory tests, long-term model experiments both performed using mock-ups simulating the conditions at a particular facility and involving field-studies under URL conditions are required to test the industrially produced clay barrier materials.

Acknowledgments

The study was supported by the Ministry of Science and Higher Education of the Russian Federation.

References

1. Martynov K. V., Zakharova E. V., Dorofeev A. N., Zubkov A. A., Prishchep A. A. Use of Clay Materials in the Construction of Protective Barriers at Radiation Hazardous Facilities. *Radioaktivnye otkhody – Radioactive Waste*, 2020, no. 3 (12), pp. 39–53. DOI: 10.25283/2587-9707-2020-3-39-53.
2. Martynov K. V., Zharkova V. O., Zakharova E. V. Fil'tratsiya vody cherez glinyanye bar'ery bezopasnosti PZRO [Filtration of Water Through Clay Safety Barriers of DFRW]. *Trudy Vserossiyskogo yezhegodnogo seminara po eksperimental'noy mineralogii, petrologii i geokhimii* [Proceedings of Russian Annual Seminar on Experimental Mineralogy, Petrology and Geochemistry]. Moscow, 2018, April 18–19. Pp. 425–428. URL: <http://www.geokhi.ru/rasempg/Shared Documents/2018/Труды ВЕСЭМПГ-2018.pdf> (accessed 17.06.2020).
3. Wang Q., Tang A. M., Cui Y.-J., Delage P., Barnichon J.-D., Ye W.-M. The effects of technological voids on the hydro-mechanical behaviour of compacted bentonite–sand mixture. *Soils and Foundations*, 2013, vol. 53, no. 2, pp. 232–245.
4. Zhu C.-M., Ye W.-M., Chen Y.-G., Chen B., Cui Y.-J. Influence of salt solutions on the swelling pressure and hydraulic conductivity of compacted GMZ01 bentonite. *Engineering Geology*, 2013, vol. 166, pp. 74–80.
5. Horpibulsuk S., Yangsukkaseam N., Chinkulkijniwat A., Du Y. J. Compressibility and permeability of Bangkok clay compared with kaolinite and bentonite. *Applied Clay Science*, 2011, vol. 52, no. 1–2, pp. 150–159.
6. Martynov K. V., Zharkova V. O., Zakharova E. V. Fil'tratsionnye svoystva glinistykh bar'ernykh materialov [Filtration Properties of Clay Barrier Materials]. *Institut fizicheskoy khimii i elektrokhimii im. A. N. Frumkina RAN – 90 let*. [Frumkin Institute of Physical Chemistry and Electrochemistry Russian Academy of Sciences – 90 years]. Moscow, IPCE RAS Publ., 2019. Pp. 174–175.
7. Martynov K. V., Zharkova V. O., Zakharova E. V. Kompessionnye i fil'tratsionnye svoystva bar'ernykh materialov [Compression and filtration properties of barrier materials]. *VI Rossiyskaya Shkola po glinistym mineralam Argilla Studium-2019 i IV Rossiyskoye Soveshchaniye po glinam i glinistym mineralam GLINY-2019* [Clays and Clay Minerals: VI Russian School of Clay Minerals Argilla Studium – 2019 and IV Russian Meeting on Clays and Clay Minerals CLAY – 2019. Proceedings]. Moscow, IGEM RAS Publ., 2019. P. 265–268.
8. Xu L., Ye W. M., Ye B. Gas breakthrough in saturated compacted GaoMiaoZi (GMZ) bentonite under rigid boundary conditions. *Canadian Geotechnical Journal*, 2017, vol. 54, no. 8, pp. 1139–1149.
9. Carbonell B., Villar M. V., Martín P. L., Gutiérrez-Álvarez C. Gas transport in compacted bentonite after 18 years under barrier conditions. *Geomechanics for Energy and the Environment*, 2019, vol. 17, pp. 66–74.
10. Martynov K. V., Zharkova V. O., Zakharova E. V. Opredeleniye davleniya nabukhaniya i kapillyarnogo vsasyvaniya glinistykh materialov dlya bar'yerov bezopasnosti [Evaluation of Swelling Pressure and Capillary Suction for Clay Materials Constituting to Safety Barriers]. *Trudy Vserossiyskogo yezhegodnogo seminara po eksperimental'noy mineralogii, petrologii i geokhimii* [Proceedings of Russian Annual Seminar on Experimental Mineralogy, Petrology and Geochemistry]. Moscow, 2019 April 16–17. Moscow,

- GEOKHI RAS, 2019, pp. 387–390. URL: <http://www.geokhi.ru/rasempg/SharedDocuments/2019/ТрудыБЕСЭМИП-2019.pdf> (accessed 17.06.2020).
11. Meier L. P., Kahr G. Determination of the cation exchange capacity (CEC) of clay minerals using the complexes of copper(II) ion with triethylenetetramine and tetraethylenepentamine. *Clays and Clay Minerals*, 1999, vol. 47, no. 3, pp. 386–388.
 12. Orlov D. S. *Khimiya pochv* [Soil Chemistry]. Moscow, Moscow State University Publ., 1992. 400 p.
 13. Tessier A., Campbell P. G. C., Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 1979, vol. 51, no. 7, pp. 844–851.
 14. Martynov K. V., Konevnik Yu. V., Zakharova E. V. Bar'ernye svoystva kristallicheskikh gornyx porod pri migratsii radionuklidov [Barrier Properties of Crystalline Rocks in Radionuclide Migration]. *Radiokhimiya — Radiochemistry*, 2017, vol. 59, no. 4, pp. 371–378.
 15. Tachia Y., Yotsujia K., Suyamaa T., Ochs M. Integrated sorption and diffusion model for bentonite. Part 2: porewater chemistry, sorption and diffusion modeling in compacted systems. *Journal of Nuclear Science and Technology*, 2014, vol. 51, no. 10, pp. 1191–1204.
 16. Ochs M., Talerico C. SR-Can. Data and uncertainty assessment. Migration parameters for the bentonite buffer in the KBS-3 concept. *Technical Report TR-04-18*. Stockholm, 2004. 155 p.
 17. Garcia-Gutierrez M., Cormenzana J. L., Misana T. et al. Overview of laboratory methods employed for obtaining diffusion coefficients in FEBEX compacted bentonite. *J. Iber. Geol.*, 2006, vol. 32, no. 1, pp. 37–53.
 18. Martynov K. V., Konstantinova L. I., Konevnik Yu. V., Proshin I. M., Zakharova E. V. Tritium diffusion through pore solution of crystal rocks (gneiss, lamprophyre). *Experiment in Geosciences*, 2014, vol. 20, no. 1, pp. 94–97.
 19. Zakharova E. V., Martynov K. V. Trebovaniya k bar'ernym glinistym materialam dlya zakhroneniya i konservatsii radiatsionno opasnykh ob"ektov [Requirements to Barrier Clay Materials Applied to Entomb and Backfill Radiation Hazardous Facilities]. *Gliny i glinistyye mineraly: VI Rossiyskaya Shkola po glinistym mineralam Argilla Studium — 2019 i IV Rossiyskoye Soveshchaniye po glinam i glinistym mineralam GLINY — 2019. Materialy dokladov* [Clays and Clay Minerals: VI Russian School of Clay Minerals Argilla Studium — 2019 and IV Russian Meeting on Clays and Clay Minerals CLAY — 2019. Proceedings. Moscow, IGEM RAS Publ., 2019. Pp. 257–259.
 20. Shmonov V. M., Vitovtova V. M., Zharikov A. V. *Flyuidnaya pronitsaemost' porod zemnoi kory* [Fluid Permeability of Crustal Rocks]. Moscow, Nauchnyi mir Publ., 2002. 216 p.
 21. Kochkin B. T., Malkovskiy V. I., Yudinsev S. V. *Nauchnye osnovy otsenki bezopasnosti geologicheskoy izolyatsii dolgozhivushchikh radioaktivnykh otkhodov (Yeniseyskiy proyekt)* [Scientific Basis for the Safety Assessment of Geological Disposal of Long-lived Radioactive Waste (Yenisei Project)]. Moscow, IGEM RAN Publ., 2017. — 384 p.
 22. Dixon D., Chandler N., Graham J., and Gray M. N. Two large-scale sealing tests conducted at Atomic Energy of Canada's underground research laboratory: the buffer-container experiment and the isothermal test. *Can. Geotech. J.*, 2002, vol. 39, pp. 503–518.
 23. Fernández A. M., Villar M. V. Geochemical behaviour of a bentonite barrier in the laboratory after up to 8 years of heating and hydration. *Applied Geochemistry*, 2010, vol. 25, no. 6, pp. 809–824.
 24. Abramov A. A., Bolshov L. A., Dorofeev A. N., Igin I. M., Kazakov K. S., Krasilnikov V. Y., Linge I. I., Trokhov N. N., Utkin S. S. Podzemnaya issledovatel'skaya laboratoriya v Nizhnekanskom massive: ehvolyutsionnaya prorabotka oblika [Underground Research Laboratory in the Nizhnekanskiy Massif: Evolutionary Design Study]. *Radioaktivnye otkhody — Radioactive Waste*, 2020, no. 1 (10), pp. 9–21. DOI: 10.25283/2587-9707-2020-1-9-21.
 25. Strategiya sozdaniya punkta glubinnogo zakhroneniya radioaktivnykh otkhodov [Strategy for the development of RW deep disposal facility]. *Radioaktivnye otkhody — Radioactive Waste*, 2018, no. 2 (3), pp. 114–120.

Information about the authors

Martynov Konstantin Valentinovich, PhD., leading researcher, Frumkin Institute of Physical Chemistry and Electrochemistry Russian Academy of Sciences (31, Leninsky prosp., Moscow, 119071, Russia), e-mail: mark0s@mail.ru.

Zakharova Elena Vasilievna, PhD., head of laboratory, Frumkin Institute of Physical Chemistry and Electrochemistry Russian Academy of Sciences (31, Leninsky prosp., Moscow, 119071, Russia), e-mail: zakharova@ipc.rssi.ru.

Dorofeev Aleksander Nikolaevich, PhD, Head of the Project Office on the Development of a Unified Radioactive Waste Management System, State Corporation “Rosatom” (24, Bolshaya Ordynka st., Moscow, 119017, Russia), e-mail: ANDorofeev@rosatom.ru.

Zubkov Andrey Aleksandrovich, PhD, Head of laboratory, Joint stock company “Siberian Chemical Combine” (1, Kurchatov st., Seversk, Tomsk Region, 636039, Russia), e-mail: SHK@seversk.tomsknet.ru.

Prishchep Alexander Alexandrovich, Development Director, SIVER LLC (2D, Polevaya st., Berezovka, Berezovsky District, Krasnoyarsk Territory, 662521, Russia), e-mail: aa.prishchep@gmail.com.

Bibliographic description

Martynov K. V., Zakharova E. V., Dorofeev A. N., Zubkov A. A., Prishchep A. A. Performance of Clay Materials Constituting to Safety Barriers in Radiation Hazardous Facilities. *Radioactive Waste*, 2020, no. 4 (13), pp. 42–57. (In Russian). DOI: 10.25283/2587-9707-2020-4-42-57.