USE OF CLAY MATERIALS IN THE CONSTRUCTION OF PROTECTIVE BARRIERS AT RADIATION HAZARDOUS FACILITIES

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The article discusses the types of mineral raw materials that can be used to manufacture clay barrier materials. The paper evaluates the characteristics of materials governing the performance of clay barriers: grain size, mineral and chemical composition, physical, mechanical (in dry state) and colloidal properties, stability in the environment. It considers the methods used to identify these characteristics and provides relevant examples.

Keywords: *bentonite, kaolin, barrier mixture, bulk density, moisture content, colloidality, moisture capacity, fluidity, deformation, internal friction, residual adhesion, specific surface area, clay colloids, physicochemical stability, climatic effect, radioactive waste.*

Implementation of the Federal Target Program Nuclear and Radiation Safety in 2016—2030 (FTP NRS-2) [1] prompts the need for an increased supply of clay materials for engineered safety barriers (ESB) construction at final radioactive waste (RW) disposal facilities: RW disposal facilities (RWDF) and radiation hazardous facilities upgraded to ensure long-term safety (CF RHF) (term referred to as conservation in Russia). In 2010, a research on the development of dry finely dispersed clay material for the construction of internal barriers during the decommissioning of industrial uranium-graphite reactors (PUGR) was launched. In 2015, PUGR EI-2 decommissioning at SCC site was completed in accordance with the entombment decommissioning option [2]. These efforts provided a foundation for the development of dry barrier mixtures for RWDF and CF RHF EBS based on natural clays. However, this project on clay material properties was focused on the barriers development considering only one type of facilities assuming considerable thickness and height of the barriers. These factors had a positive effect on the self-compaction and sorption capacity of the barrier materials. These studies also accounted for a shallow emplacement, in fact, within a near-surface formation limiting the influence of hydrogeological factors. The main challenge needed to be addressed at that time was to ensure the filling of voids having complex geometry with a barrier material ensuring the absence of any cavities. In this regard, the key focus was placed on the following main characteristics of the material: granulometric (microaggregate), mineral and chemical composition, bulk density, moisture capacity, colloidality, water permeability of low-density materials at a low hydraulic gradient, cation exchange capacity, and coefficients of radionuclide sorption distribution.

At present time, FTP NRS-2 specifies relevant plans with the construction efforts already launched to develop three near-surface RWDF for RW Class 3 and 4 in the vicinity of Novouralsk (the 1st section has been operating since 2015 [3]), Ozersk and Seversk, underground research laboratory in the Nizhnekansk rock mass near Zheleznogorsk and seven disposal facilities for PUGR, four of which are near-surface DF located at SCC sites and three DF are located in underground excavations at MCC site. Due to the variety of facility types, the number of factors and the range of physical and chemical parameters potentially affecting the barrier properties and the resistance of clay materials to external influences has ramped up.

Each facility type is characterized with some specific design features, siting conditions and is designed for various RW types with a specific radionuclide composition: all these factors should be also taken into account during barrier material development. Clay material resistance to degradation due to external influences associated with microbiological activity, radiolysis of pore and interlayer water leading to changes in the oxidation-reduction and acid-base characteristics of groundwater, as well as interaction with other components of natural-engineered system is viewed as a special research task being considered extremely important in terms of forecasting the long-term RWDF safety.

In addition to barrier material characteristics studied earlier, it appeared necessary to study the specific surface area, flow and deformation of dispersed materials in a dry state, deformation in a water-saturated state, parameters of pressure filtration under load, diffusion of components in a pore solution of compacted materials with an account taken of chemical and sorption interactions, the tendency of materials to form colloid in a water-saturated state, deformation of water-saturated materials during cyclic freezing-thawing and drying.

This paper focuses on the classification of natural clay and industrial clay materials being considered important for the development and operation of safety barriers at radiation hazardous facilities, mainly CF RHF and RW disposal facilities. It also discusses methods, equipment and results of studies dealing with these characteristics relevant for some of currently considered materials. The paper elaborates on the available concepts dealing with the ranges of these characteristics for barrier materials, as well as preliminary data on the composition of materials that can be used in the development of safety barriers taking into account their functional characteristics and stability under physical and chemical conditions suggesting the interaction with a natural-engineered system, radiation exposure and microbiological activity.

The problem discussed in this paper appears to be of great relevance, since the design development and installation of protective clay barriers at the facilities already being at the construction stage occurs in the absence of regulatory requirements for the applied materials [4]. At the same time, EBS safety demonstration is based on specific calculations dealing with the migration of radioactive contaminants [5, 6], for which barrier material properties are essential.

Types of clay raw materials for barrier construction

Both natural clays and industrially processed natural clay raw materials can be used as barrier materials. Clay processing can be divided into the following types: drying, grinding, enrichment, mixing, modification, pressing. Drying is necessary to produce dispersed materials, since the natural moisture content in natural clays accounts for some 25—35 wt%. Depending on the mineral clay composition its drying temperature can account for some 150—400 °C. Clay is grinded in vortex mills which allows to address various issues. Firstly, to separate coarse-clastic fractions (sand, gravel) formed by non-clay minerals: quartz, feldspars, plagioclases. Secondly, it provides raw material dispersion reducing granulometric (micro-aggregate) content. High degree of grinding also causes mechanical activation of the product. Raw material enrichment with fine fractions (dust, clay particles) and, accordingly, with clay minerals is provided using gravity separation in flange separators. Mixing is applied both to obtain clay materials with a polymineral composition and clay-sand or clay-gravel mixtures. In the first case, mixing is done at the initial stage of the processing cycle, in the second — at the final stage in mixing drums. Modification (activation) with soda, sodium phosphate and other reagents is mainly applied to bentonite raw materials to increase the colloidal capacity and moisture capacity of clay powders, increasing the quality of drilling fluids. Modification also affects sorption properties and swelling capacity of bentonite materials. The final industrial processing product can be both dispersed material and granular products of various shapes and sizes and pressed products: grains, granules, pellets, bricks, shaped products.

Processing of raw materials implemented in laboratories and large-scale production facilities can proceed in different ways. Therefore, to validate the composition and properties of the product, pilot tests are performed and the quality of the product

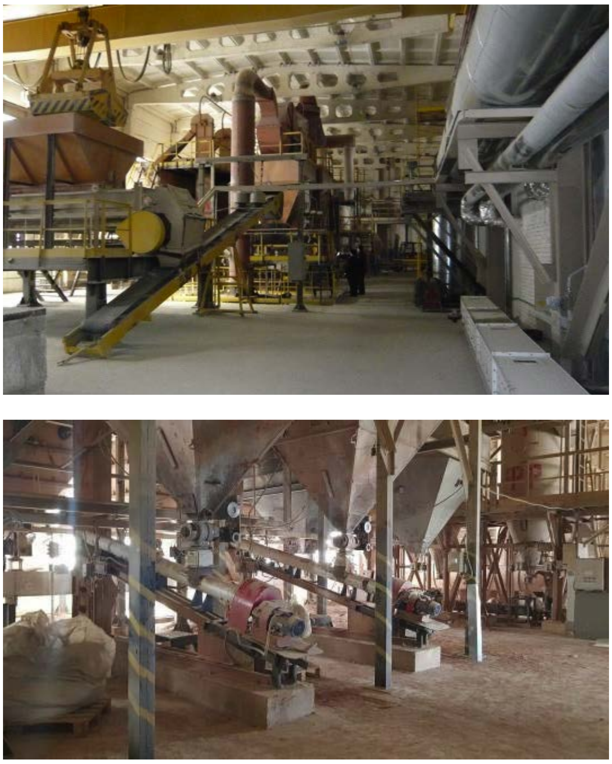


Figure 1. Production line for dispersed mixtures: GDE enrichment unit at the top, bins with emptying systems at the bottom

from all received batches is monitored. In the drying — grinding mode, grinding and drying equipment (GDE) that was used in the production of barrier mixture for PUGR EI-2 (Figure 1) has a capacity of 1.8—2.6 t/hour (considering the feedstock). It was used to test three feedstock materials: bentonite from the 10th Khutor deposit (Khakassia), kaolin from the Kampanovsk deposit (Krasnoyarsk Territory) and a mixture of these clays with a mass ratio of 30 : 70 (SKB). Based on 20 tests with each one involving 1 ton of material, the distribution of products between bins and bag filters (Figure 2) associated with the categorization by particle size distribution and bulk density was calculated.

A small amount of all tested materials was found in bag filters having a fraction of less than 0.1 mm. Crushed kaolin was evenly distributed between the bins, which indicates its homogeneous fractional composition. Bentonite was crushed unevenly: the greater part (48 wt %) had a low bulk density and a finer micro-aggregate composition and was collected in bin No. 3. In case of clay mixture grinding, the amount of bentonite in the products of joint grinding increased starting from bin No. 1, where it appeared to be less than in the initial mixture, to bin No. 3, where its amount has increased.

Mineral composition accounts for the main feature allowing scientific and applied categorization of clay materials and clay raw materials

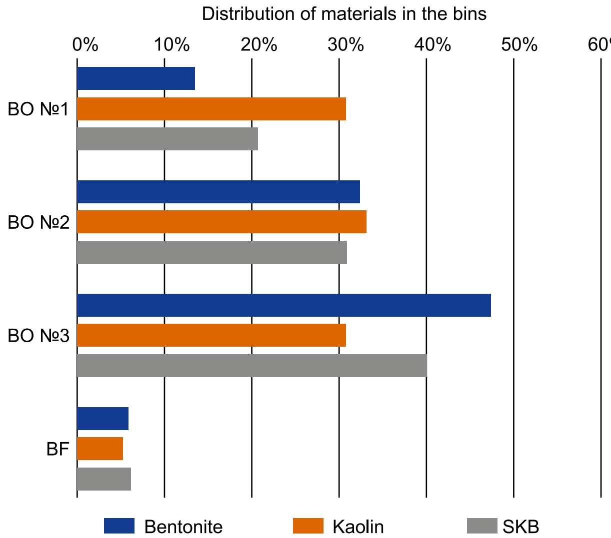


Figure 2. Mass distribution of materials in bins (BO) and bag filters (FR) in GDE tests under drying – grinding categorization mode

indicating the main barrier properties of clays: filtration, diffusion and sorption characteristics. Basically, two types of clays form industrial deposits: bentonite clays (bentonites) mainly consisting of montmorillonite and kaolin clays (kaolins) with a predominant content of kaolinite in their mineral composition. The latter can also include deposits of refractory and high-melting clays, polymineral clays (containing illite, chlorite, smectites), but with a predominance of kaolinite in the clay fraction.

The overwhelming majority of studies published abroad over the past decade and focused on clay barrier materials addresses swelling smectite (montmorillonite) clays — bentonites. This is reflected in the content of reviews published, namely, journal articles, chapters of monographs, technical reports [7—10]. It may seem that no alternative to bentonite is available as a barrier material. This conclusion is actively promoted in some scientific and technical [11] and popular scientific [12] publications. However, this is not quite true. Firstly, foreign developments on the use of bentonites are focused on underground disposal of high-level waste and spent nuclear fuel (SNF). This area is of high relevance, but in terms of the required material amounts it is not the largest, whereas, in terms of practical implementation, it addresses a very distant perspective both in Russia and abroad. As for the low- and intermediate-level waste, clay barrier materials are either not used in foreign practice or are applied in a mixture with cement, sand, gravel. Moreover, often these are not even bentonites, but locally-produced mostly kaolin or polymineral raw materials [13]. In this respect, the above practice suggesting the development of protective barriers at such facilities in Russia seems to be ahead of foreign experience, at least according to open sources. Even the Russian adherents of bentonite materials admit the validity of this remark [14].

Secondly, bentonite itself is a controversial material. Bentonite clays actually possess some unique properties, which in some conditions can be considered as their undeniable advantage, and in others – as no less important disadvantage. Thus, the ability of bentonites to swell when saturated with water is a very useful property when it comes to the shrinkage resistance of clay materials during capillary or pressure saturation of barriers. However, excessive swelling pressure can lead to additional loads on the structural elements of RWDF and RW packaging up to their deformation and destruction. The risks associated with such scenario are partly offset by high fluidity (low strength) of water-saturated bentonite causing barrier material movement into free cavities (spreading) resulting in a decreased matrix density and, consequently, in a decreased swelling pressure. Due to this, the barrier can become thinner locally up to complete wedging out in some areas, if external pressure is exerted on it by rocks, RWDF structures, RW packages, etc. Such depletion can result in much more dangerous consequences than simply failure to fulfill the stabilization function, since it causes deterioration of the main functional barrier characteristics: resistance to water filtration and radionuclide migration.

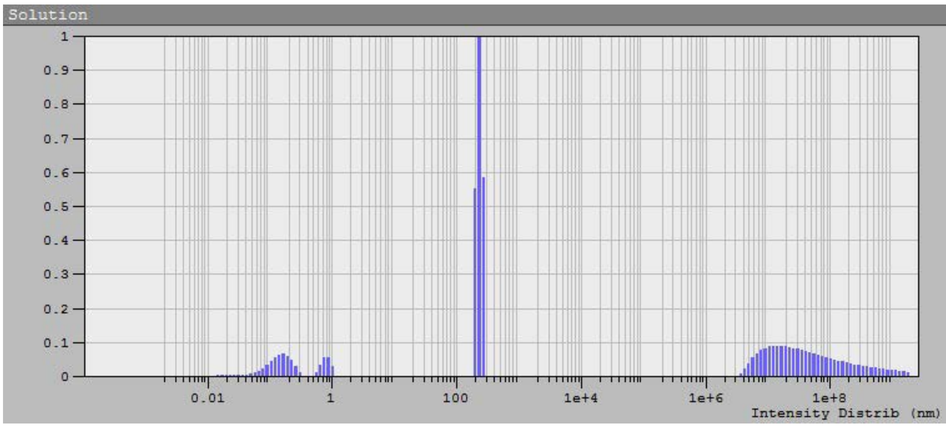
In case of temperature increase and decrease in the groundwater level, high moisture capacity of bentonite clays along with water exchange and temperature mode cyclicity can cause barrier material drying accompanied by its shrinkage with the formation of open contraction cracks. With temperature inversion and a change in the water mode, such cracks can turn into salvo filtration channels until the bentonite swells again and the continuity of the barrier is restored. An attempt was made to simulate filtration under laboratory conditions with cyclic temperature mode. However, due to short duration of the experiments, the effect of temperature fluctuations on bentonite permeability still remained quite unclear [15]. Nevertheless, this study showed the need of drawing particular attention to this problem.

At negative temperatures, freezing of free pore water in bentonite accompanied by an increase in its volume and high crystallization pressure of ice, can lead to an increase in the volume of the barrier, which, after temperature inversion and ice melting, will cause the formation of cracks and parietal fractures, ultimately resulting in salvo filtration as shown in previous example. The likelihood of such an evolution is also admitted by foreign supporters of bentonite. However, they expect that the temperature in deep underground disposal facilities, even in northern countries (Sweden, Finland), will not fall below the critical value for bentonite pore water (–6 °C, [10]). However, this assumption was not justified under the forecasts covering geochronologically significant periods. According to paleoclimatic reconstructions, 18,000—20,000 years ago during the Sartan glaciation, the freezing depth of rocks in the Krasnoyarsk region amounted to 600 m [16].

Low permeability of water-saturated compacted bentonite (below 10^{-19}—10^{-20} m^2), which is envisaged by the Swedish KBS-3 concept [8, 9], prevents not only the filtration of underground water, but also the one of gases that can be produced due to corrosion, microbiological activity and radioactive exposure. Paradoxically at the same time, gas permeability in the KBS-3 concept is stated under mandatory requirements for the bentonite barrier. Gas generation (primarily hydrogen) during water radiolysis in the bentonite barrier body can cause increased pressure on the barrier up to levels exceeding its strength characteristics resulting in its destruction.

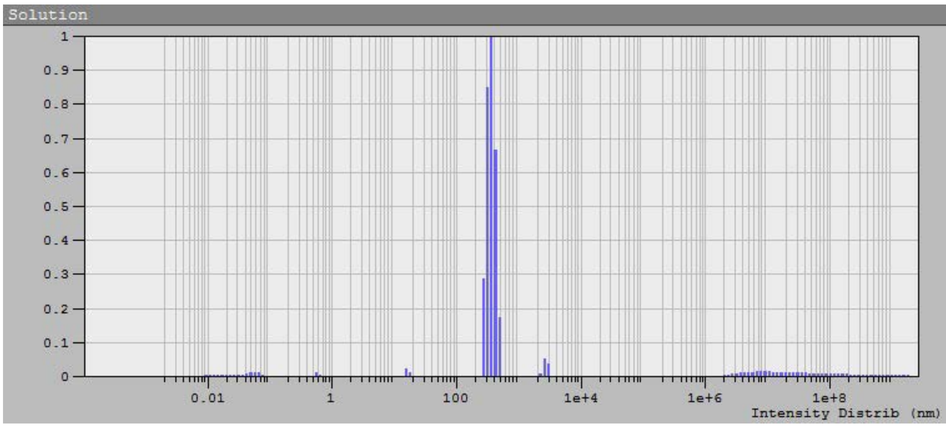
High sorption capacity of bentonite with respect to many radionuclides, which is seen as one of its main advantages over other barrier materials, can also produce some negative effects since bentonite tend to form colloids and suspended particles. Under certain conditions, stability of such particles in solutions (groundwater) can be quite high: in this case they start carrying the absorbed radionuclides acting as a "vehicle". Colloidal and suspended particles have increased mobility resulting in advective migration of radionuclides with filtering fractured or stratal groundwater.

This effect was demonstrated experimentally, namely, in the study of solutions by dynamic light scattering method using a particle size analyzer Photocor Compact-S manufactured by JSC Photocor (Moscow) (Figure 3). It was shown that during model groundwater interaction with the Khakass bentonite at a temperature of 25 °C, the colloidal particles in the solution were unstable. Average value of the scattering intensity being proportional to the particle concentration accounted for 25 thousand imp./s, which only doubled the values for distilled water (10—12 thousand imp./s). In the presence of aluminophosphate model glass with RW simulators being similar in their elemental composition to the glass produced by FSUE PA Mayak, stable 300 nm particles were formed in the leach. Moreover, the scattering intensity exceeded by 50 times the values suggested for solutions available in the



Peak No	Area, %	Mean value, nm	St. dev
1	0.153	0.134	0.051
2	0.025	1.184	0.204
3	0.436	233.0	45.38
4	0.386	1.4×10^7	3.5×10^7

Total intensity – 25,000 imp./sec



Peak No	Area, %	Mean value, nm	St. dev
1	0.003	0.052	0.014
2	0.006	14.09	3.854
3	0.933	334.9	107.2
4	0.027	2,576	732.7
5	0.031	9.1×10^6	4.4×10^6

Total intensity – 580,000 imp./sec.

Figure 3. Particle size distribution in solutions following the interaction of model groundwater with Khakass bentonite without (above) and in the presence (below) of aluminophosphate glass at a temperature of 25 °C according to dynamic light scattering data

glass-free system. Elemental composition of leachates was evaluated based on inductively coupled plasma mass spectrometry: it was shown that these were aluminosilicate particles with an increased content of rare earth elements, i. e. clay colloidal particles with radionuclide imitators sorbed on them, the so-called pseudocolloids.

Third, in terms of resistance to physical and chemical external impacts, bentonites are significantly inferior to kaolin clays due to the ratio between thermodynamic characteristics of montmorillonite and kaolinite. As regards the resistance to microbiological impacts, it seems reasonable to expect the same ratio due to bentonite saturation with components serving as "nutrients" for bacteria (non-silicate iron, sulfur, phosphorus, organic compounds).

All of the above examples indicate that for multi-factor systems a trade-off approach is usually needed to be applied in engineering solutions. Given the uncertainties in the evolution of events occurring in a complex multi-parameter system, application of only one raw material type for barrier material production, namely bentonite, notwithstanding the unique individual properties it possesses, can result in some negative consequences. To prevent such consequences and ensure the disposal safety, a system of engineered barriers should be developed specifically for each facility using barrier materials of different composition balanced in their characteristics taking into account the design features of a particular facility, siting conditions and radioactive waste composition.

Main characteristics of clay barrier materials

There are two types of requirements for clay barrier materials. The first one can be designated as engineering requirements mainly associated with mechanical characteristics of materials governing the engineering flowchart for barrier fabrication and their mechanical stability. For bulk materials, this accounts for high fluidity needed to fill the cavities having complex geometry and self-compaction ability in a dry state, which, among other things, stabilizes the backfilling. As the barrier materials are saturated with water due to hydraulic pressure or capillary suction, the deformation (compression) characteristics of materials in a water-saturated state, including swelling, start to play into mechanical stability. However, the strength parameters are viewed as most important characteristics of barrier mechanical stability, especially in a water-saturated state. In case of unconsolidated plastically deformable materials, these are the angle of internal friction (φ) and specific adhesion (*c*) according to Mohr — Coulomb failure criterion:

$$\tau = P_m \cdot \mathrm{tg}\,\varphi + c,$$

where τ is the shear stress (pressure), P_m stands for the effective normal stress (pressure). The fluidity function (*ff*) mentioned above can be presented as follows:

$$ff = \mathrm{ctg}\,\varphi.$$

The second type of requirements can be denoted as functional: these are relevant to anti-filtration and anti-migration properties of barrier materials due to low water permeability, low diffusion of radionuclides in pore solution when filtration is absent, high sorption capacity, low desorption of radionuclides when physical and chemical parameters alter, chemical and radionuclide composition of the pore solution. Moreover, there is a number of requirements affecting the state of barriers during operation, particularly at the early stage, when various radiation effects are sizable. These include the requirements for thermophysical properties: thermal conductivity and heat capacity of dry and water-saturated materials considered important for barriers surrounding the packages with heat-generating RW.

Main characteristics governing engineering properties of clay barrier materials and their performance are as follows:

- granulometric, mineral and chemical composition;
- bulk density, moisture content, colloidity, moisture capacity, specific surface (physical properties);
- flow characteristics and deformation of dispersed materials in a dry state (mechanical properties);
- formation and migration of clay colloids (colloidal properties);
- physical and chemical stability during the interaction with natural and technogenic systems (evolutionary properties);
- permeability and deformation in a water-saturated state under load, capillary suction, swelling pressure (compression-filtration properties);
- cation exchange capacity, radionuclide sorption distribution coefficients, sorption capacity (sorption properties);
- diffusion of radionuclides in pore solution (diffusion properties).

This article is focused only on the main characteristics governing the engineering properties of barrier materials indicated in the first five paragraphs.

Granulometric, mineral and chemical composition

Granulometric and micro-aggregate composition is viewed as an important characteristic influencing the engineering properties of clay materials: fluidity, bulk density, self-compacting, as well as reflecting the amount of clastic (non-clay) fractions governing material performance. Despite its apparent simplicity, as in fact we are dealing with the evaluation of particle sizes or aggregate sizes, its results oftentimes depend on the evaluation method. Of various evaluation methods, the standard ones (GOST 12536-2014 Soils. Laboratory Methods for the Evaluation of Granulometric (Grain) and Microaggregate Composition) are the most routine ones: sieve (particle size exceeding 0.05 mm) and sedimentation (0.001—0.1 mm). The latter one was expanded as regards the range of identified minimum dimensions (up to 0.01 μm) and automated using centrifugation with photometric or X-ray registration. Laser diffraction is considered as the most versatile standardized method allowing to evaluate the particle sizes (small-angle or static light scattering). GOST R 8.777-2011 Disperse Composition of Aerosols and Suspensions. Particle Size Identification by Laser Radiation Diffraction specifies the required range of 0.2—1000 μm for this method. Smaller particles (0.001—5 μm), but only those present in liquid media, can be analyzed by dynamic light scattering method.

A huge number of methods is available to identify mineral composition being a characteristic governing all properties of clay materials [17, 18]. In many cases, sample preparation process significantly affects the representativeness of the estimated results. Mineral analysis methods are not supported by GOSTs. X-ray diffraction quantitative phase analysis can be assumed as a basic method. This mature method has a high degree of automation both as regards the measurement procedure and the result interpretation [19, 20]. Despite insufficient locality when it comes to evaluating individual clay mineral crystals, X-ray microanalysis using energy dispersive spectrometers fitted with scanning electron microscopes is considered as a highly effective method that can be applied to specify mineral composition of clays and elemental composition of clay minerals [21]. Total elemental composition can be evaluated using any suitable spectral method with X-ray fluorescence analysis being considered as most sensitive and accurate in this regard also allowing to identify the content of impurities. However, during bulk chemical analysis, it's also important to keep in sight of organic clay components.

Bulk density, moisture, moisture capacity, colloidality, specific surface area (physical properties)

Appropriate requirements regulate the identification of the majority of physical characteristics, for example, GOST 28177-89 Forming Bentonite Clays.

General specifications. Nevertheless, some particular aspects related to their measurement and interpretation should be clarified. Not as strange as it sounds with respect to physical quantities, in case of clay materials there is an element of uncertainty when it comes to their assessment according to GOST standards. The bulk density depends on the way in which the measuring container is filled. Maximum water absorption which is identified as a measure of moisture capacity "by eye" according to meniscus mobility seems to be very subjective.

The objectivity of estimates associated with physical characteristics largely depends on the laboratory equipment provided for their measurement. The better the measurement method is justified and the more accurate the measuring equipment is used, the more objective the result is. A case in point is the method used to determine the specific surface area of materials by low-temperature nitrogen adsorption suggesting the adsorption curve processing according to the Brunauer — Emmett — Teller (BET) equation which is specified in GOST 23401-90 Metal Powders. Catalysts and Carriers. Specific Surface Evaluation. This method is widely used to evaluate clay materials. To identify the bulk density, more objective estimates (as those proposed according to GOST 9758-2012 Porous Inorganic Fillers for Construction Work. Test Methods) can be obtained using the curves showing the dependency between material densities and the applied loads derived based on evaluations performed using flow analyzer and compression instruments presented below.

Flow characteristics and deformation of dispersed materials (mechanical properties)

Flow and compaction characteristics of dry dispersed materials are essential when it comes to clay barrier installation by backfilling method, especially in cases when the cavities subject to backfilling have a complex geometry (a case in point is the construction of an internal barrier at PUGR EI-2). The flow parameters and their measurement methods are not standardized, but physically they correspond to shear tests performed to determine the strength parameters of the Mohr — Coulomb equation: angle of internal friction and specific cohesion. Therefore, relevant estimations can be guided by GOST 12248-2010 requirements Interstate Standard. Soils. Laboratory Methods for Strength and Deformability Characteristics.

The dry flow and compaction of particulate clay materials can be measured with powder flow analyzers such as the Brookfield PFTTM (Figure 4) at axial loads of up to 25 kPa for flow and 100 kPa for compaction. The diagram presenting the function for the measured flow shows the lines separating the areas intended for qualitative material characterization: $ff > 10$ — free flowing, $4 < ff \leqslant 10$ — easy flowing, $2 < ff \leqslant 4$ — viscous, $1 < ff \leqslant 2$ — very viscous, $ff < 1$ — not fluid. Dispersed materials designed for backfilling should be easy and free flowing. From

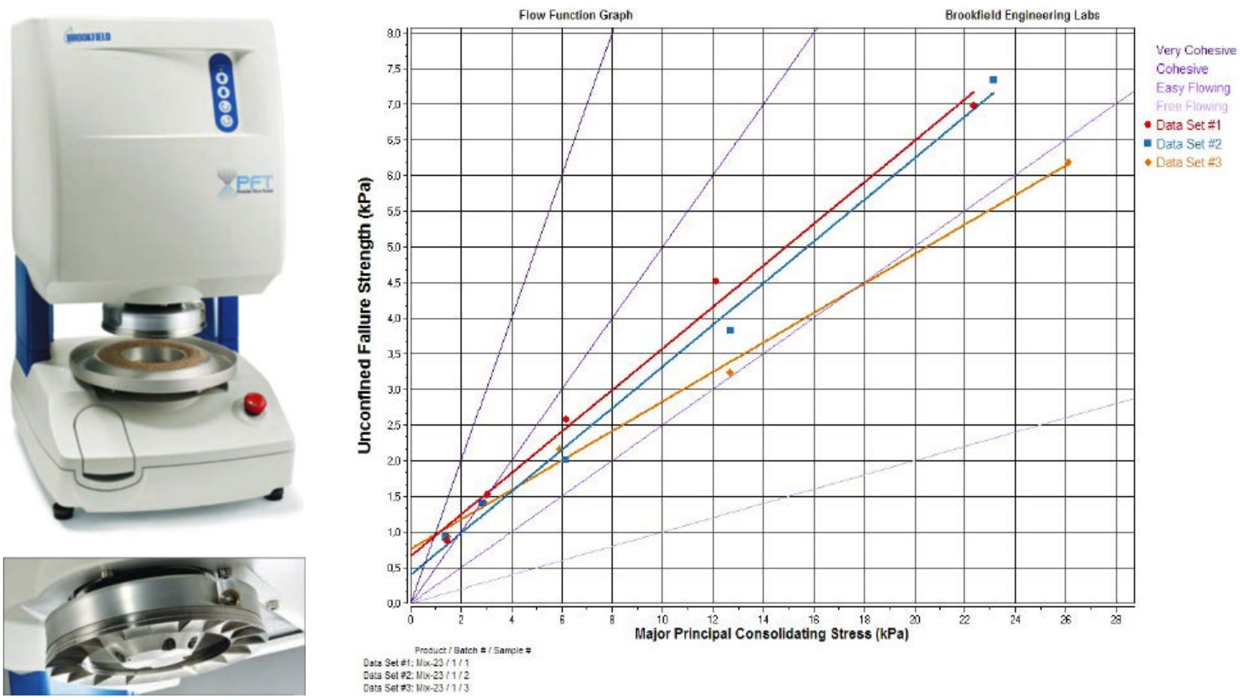


Figure 4. Brookfield PFTTM Dry Powder Flow Analyzer, blade cover for flow tests and measurement results for bentonite and kaolin mixtures with the following kaolin content: No. 1—50, No. 2—75, No. 3 — 85 wt.%

those presented in Figure 4, this requirement is met only by mixture No. 3 consisting of kaolin (85 wt.%) and bentonite (15 wt.%).

Compression devices can be used to determine clay material deformation parameters in a dry state at a higher axial load. The load that these axial loading devices can provide is much higher than that of the flow analyzer and can be up to 50 kN, which corresponds to a pressure of 12.5 MPa acting on a sample of 40 cm^2 in a standard odometer, and even more. These values more than overlap the range of self-compaction loads. Therefore, the data obtained from such devices can be used not only to simulate compaction during barrier design development, but also to calculate the compression parameters during its operation under water saturation.

Formation and migration of clay colloids (colloidal properties)

Interaction of clay materials with water and aqueous solutions may result in the formation of clay particles of a colloidal size (less than 1 micron) even if external or flow-through filtration of the liquid through the safety barrier causing clay material erosion and suffusion is absent. Just similar to macroparticles of clay minerals, colloids actively sorb radionuclides on their surfaces resulting in pseudo-colloidal forms. Being characterized with high strength of radionuclide capture and mobility (mobility), the pseudocolloids themselves are characterized by low sorption capacity to rocks which enhances their migration in the natural environment.

Stability of colloidal particles in aqueous solutions, and hence their concentration and the activity of the radionuclides sorbed on them depend on the physical and chemical conditions of the environment. A case in point is a dependence for bentonite colloids provided above (Figure 3). Thus, experimental study of clay colloids is mainly focused on their stability in groundwater given the presence of structural materials and rocks under RWDF conditions. A number of factors are known that contribute to the coagulation of clay colloidal particles: an increase in the temperature and ionic strength of a solution (addition of an electrolyte), sharp decrease or increase in pH, presence of magnesium, calcium, iron in the solution, effects of various types of radiation. In turn, stability of clay colloids is promoted by organic (high-molecular) compounds and phosphate ions.

The number and size of colloidal particles in aqueous solutions can be measured by the microfiltration and dynamic light scattering (photon correlation spectroscopy) methods. The former one enables chemical and radiometric analyzes of filtrates and filters allowing to determine the composition of colloidal particles and the distribution of radionuclides between colloids and the solution. This method was used to study the migration of uranium colloids in groundwater of Streltsovsk ore field deposits [22]. Dynamic light scattering method allows to determine the diffusion coefficient of particles based on the relaxation time of fluctuations in the intensity of scattered light arising as a result of the Brownian motion of dispersed particles. The particle size (hydrodynamic radius, r) is calculated based on the Stokes — Einstein equation relating it to the diffusion coefficient (D) and dynamic viscosity of the liquid (η):

$$D = (k_B T)/(6\pi\eta r),$$

where k_B is the Boltzmann constant, T is the absolute temperature. The particle size of bentonite colloids for the case given above accounts for 330 ± 110 nm. This size corresponds to the diffusion coefficient of particles in water $(6 \pm 2)\cdot 10^{-9}$ cm^2/s at a room temperature, which is four orders of magnitude lower than the water self-diffusion coefficient identified based on tests for tritium under same conditions ($2.4\cdot 10^{-5}$ cm^2/s). Therefore, one can hardly expect quantitative diffusion of clay colloidal particles of this size even in water saturated macro-fractures of rocks, especially in their pore solution and in compacted clay materials.

Convective transfer (advection) of clay colloids by groundwater filtering along cracks is another matter since the sedimentation rate (v) of a solid particle in a stationary liquid can be calculated based on the Stokes equation:

$$v = \frac{2gr^2(\rho_s - \rho_l)}{9\eta},$$

where ρ_s and ρ_l are the densities of solid and liquid phases, g is the gravitational constant.

For the above-mentioned bentonite colloids with $r = 330$ nm, the sedimentation rate in water at room temperature amounts to $3\cdot 10^{-7}$ m/s. Thus, an ascending groundwater flow moving at a higher speed can carry such colloidal particles to the surface. Hydrogeological conditions within the Yenisei section of the Nizhnekansk rock mass referring to the depths envisaged for the construction of a deep RWDF for RW Class 1 and 2 are susceptible of rocks with filtration coefficients (K_f) amounting to 10^{-4}—10^{-2} m/day [16]. Extended fractured zones considered as main filtration channels are characterized with maximum K_f values. Porosity of rocks (ε) in such zones does not exceed 0.005. Maximum head gradient ($\Delta H/L$) that can be expected within the groundwater discharge area accounts for 0.4 km/4 km = 0.1. Given matrix porosity, the equation for the filtration coefficient allows to estimate the average groundwater flow rate:

$$v = K_f \cdot (\Delta H / L) / \varepsilon.$$

For an average K_f value of 10 m/day, the flow rate will be approximately equal to $2 \cdot 10^{-7}$ m/s, which is comparable to the sedimentation rate of bentonite colloids. This means that even such relatively large radionuclide pseudo-colloids can be transported by fractured groundwater and together with them discharged onto the surface causing biosphere contamination.

Researchers are extremely concerned with radionuclides transport by clay colloids: both experimenters [23] and theorists developing mathematical models of colloidal transport. Among the latter, a significant contribution was made by Russian scientists [24]. However, to validate the reliability of the results, all models require reliable parameters that can be derived from experiments. In addition, numerical models must be verified based on correctly performed model experiments. Therefore, particular focus should be placed on the experimental data, including those concerning sorption distribution of radionuclides between the solution and clay colloids.

Stability during the interaction with natural and technogenic systems (evolutionary properties), experimental and numerical simulation

Designs of clay protective barriers shall consider that over long-term operation under the impacts produced by external environment and RW, structure, composition and, consequently, properties of barrier materials may evolve. Such influence associated with RW and structural materials of the RWDF (technosphere) may manifest itself as radioactive exposure, heat load, chemical impacts; as for external environment (geosphere) these factors involve physical (temperature and water cut fluctuations), chemical and mechanical (tectonic) impacts. All these long-term processes prompt the evolution of the natural-technogenic RWDF system in general and of its individual components, including clay barriers.

RW-induced radiation impacts produced on clay materials are viewed as an integral feature specific to all facilities being under consideration. Structure of main clay minerals can be characterized as radiationally stable (when exposed to low- and medium-energy particles, amorphization of the structure is not observed up to an absorbed dose of 10^9 Gy [25]), whereas radiolysis of water contained in the pore space and the interlayer of smectite minerals, is already manifested at minimum absorbed doses. Radiolysis of pore and interlayer water not only results in hydrogen generation [26], which in itself is of concern for RWDF design development, but also affects the parameters of montmorillonite crystal structure: along hydrogen generation basal distances tend to get bigger. Still, a clear picture of potential impacts produced on functional characteristics of bentonite materials is missing. To date, this matter appears to be of a key concern when it comes to the application of clay materials for RWDF safety barrier construction.

Temperature effects (RW and the environment) and changes in the water saturation of clay materials (both due to temperature fluctuations and changes in the flow mode) should be considered together, since they are interrelated. Provisions of GOST 30491-2012 Mixtures of Organic Minerals and Soils Reinforced with Organic Binders for Road and Airfield Construction are applied with respect to artificial soils. According to above GOST, soil frost resistance depends on the number of freeze-thaw cycles leading to a limited change in the axial compression strength of the considered samples. For barrier clay materials, compressive strength characteristics are not considered essential. Therefore, this standard falls short of fully conforming to the task associated with the characterization of barrier clays, but some methodological techniques can be borrowed from it. GOST 12248-2010 discusses a method that can be used to study linear and volumetric shrinkage of soils due to their drying. This method cannot be considered as a generic one but can be nevertheless used to assess the quality of barrier clay materials. However, some of the requirements provided in this GOST, for example, those concerning the absence of cracks in dried samples, are not seen as realistic in case of considerably swelling clays. All these facts indicate that existing techniques should be adapted to their specific application in case of such particular materials as clays and their mixtures.

Chemical interaction of clay materials with the external environment can be studied experimentally, nevertheless, having certain limitations. Thus, trends in the evolution of chemical composition and pH of solutions being in contact with clay samples can still be established under laboratory conditions, whereas changes in the clay minerals themselves over the actual time available during the experiments are practically invisible given not excessively high temperatures and not excessively aggressive nature of the simulated environment [27]. Even ultra-long field [28] and laboratory [29] model experiments do not allow making unambiguous conclusions about the clay materials evolution, namely in terms of their mineral composition. In this case, numerical thermodynamic modeling allowing to predict the outcomes of even very slow processes that cannot be detected by experimental methods within the actually available time can help in addressing this issue providing long-term forecasts covering a timeframe of tens and hundreds of thousands of years [30].

Conclusion

Various industrially mined types of clays can be used as natural mineral raw materials for the production of clay barrier materials: bentonite, kaolin, their mixtures, as well as locally produced polymineral raw materials. Industrial processing of clay raw materials (drying, grinding, enrichment, mixing, modification, compaction) can change its mineral composition. This must be taken into account in the decision making on the selection of certain processing methods.

To validate the feasibility of clay materials application in the construction of safety barriers at radiation hazardous facilities, their characteristics influencing the engineering properties should be investigated: mineral and particle size distribution; moisture, bulk density for dispersed or matrix density for molded materials; deformation and strength parameters of material in a dry state; specific surface area and ability of the material to form colloidal particles, as well as their migration and sorption properties with respect to radionuclides.

To ensure that the clay barriers can maintain their initial properties over the entire timeframe while radiation risks remain in place, it is necessary to demonstrate the required level of physical, chemical, radiation and microbiological stability of the barrier materials in the natural and technogenic environment under RW disposal conditions (RWDF or CF RHF).

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