Isolating Properties of a Bentonite Buffer in Conditions of an Underground Repository for High-Level Radioactive Wastes

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Abstract—The use of a bentonite buffer as an engineered barrier is specified in many contemporary designs of deep-seated underground repositories for high-level radioactive wastes (HLW). Briquettes of compacted bentonite are placed between a canister with HLW and rock. The thickness of the bentonite buffer is from 0.3 to 1.3 m. The isolating properties of bentonite are manifested in its low water permeability, swelling, plasticity, high sorption capacity, and high montmorillonite content (more than 60%). When saturated with water, bentonite swells and seals fissures in host rocks. In order to provide maximal durability of canisters and minimal solubility of HLW, the composition of bentonites is specifically selected to ensure reducing low-alkaline properties of pore waters. Due to low water permeability, radionuclides can migrate through the buffer only by diffusion. If a canister ensures the isolation of radionuclides from groundwater for 1000 years, a bentonite buffer increases this term by at least one order of magnitude. Only poorly sorbed long-lived radionuclides (^{14}C, ^{129}I, ^{79}Se, ^{135}Cs, and ^{99}Tc) can overcome a bentonite buffer, and only thousands of years after the failure of canisters. By the time of such failure, all short- and mid-lived radionuclides (^{137}Cs and ^{90}Sr) will decay, and 98% of HLW radioactivity will be caused by actinides. The bentonite buffer is capable of retaining these most environmentally hazardous radionuclides for a virtually unlimited period. The transfer of radioisotopes in colloidal form through the buffer is completely excluded due to the very fine size of pores in bentonite and the lack of open channels. In underground repositories of vitrified HLW, ^{79}Se and ^{135}Cs can overcome a bentonite buffer only after 10000 years, and ^{99}Tc, only after 300000 years. The isotope ^{135}Cs is the main contributor to contamination of the biosphere. In this case, the radiation dose received by a human will not exceed 10^{-3} of the dose obtained from background radiation. In repositories of spent nuclear fuel, ^{14}C, ^{36}Cl, and ^{129}I, which are absent in vitrified HLW, will be the first to penetrate into groundwater through the bentonite buffer. However, their contribution to the radiation dose cannot exceed a few hundredth fractions of the background radiation. It would be reasonable to conclude that the use of this barrier allows us to ensure the reliable isolation of the most hazardous radionuclides (actinides) for the required period. The illitization of montmorillonite is the main process that can deteriorate the isolating properties of bentonite. The rate of this process depends on temperature and the potassium concentration in groundwater. The analysis of experimental and geological–geochemical data on the conditions of formation of clay minerals shows that, during the time when bentonite is undergoing the impact of a temperature up to 250°C, the amount of newly formed illite layers will be insignificant and will not influence the isolating properties of the buffer. This is all the more valid for the temperature of 100°C provided for in designs of underground HLW repositories in most countries. The isolating properties of bentonite could be considerably improved by introducing additives that decrease the solubility of HLW in pore water and improve bentonite sorption properties. The addition of iron filings or shavings increases the reducing capacity and heat conductivity of the buffer; the addition of vivianite decreases the solubility of HLW solidified into alumophosphate glass; and the addition of weathered basic rocks enriched with leucoxene and iron hydroxides improves sorption properties. The high technological and economic efficiency of the bentonite buffer allows us to consider this buffer as the main engineered barrier reliably ensuring the safety of underground HLW repositories.

INTRODUCTION

A bentonite buffer as an engineered barrier preventing radionuclide release is used for the isolation of HLW from the biosphere in deep-seated underground repositories. The buffer is placed between canisters with wastes and host rock for

(a) limiting the access of groundwater to the HLW;

(b) providing efficient sorption of radionuclides after the corrosion of the container with HLW;

(c) sealing the nearest open fissures in host rocks in the case of buffer swelling;

(d) facilitating heat transfer from the HLW into the surrounding geological medium;

(e) lessening the destructive impact of tectonic processes on HLW packings.

In accordance with these functions, the isolating properties of the buffer are defined as its water perme-

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ability, capacity for sorption of radionuclides, ability to increase in volume during saturation with water (swelling), heat conductivity, and plasticity. The bentonite buffer is considered as the most important engineered barrier in virtually all contemporary designs that provide for HLW isolation in underground repositories located below the groundwater level (Brookins, 1984; Chapman and McKinley, 1988; Krauskopf, 1988[1]). If corrosion-proof canisters provide for radionuclide isolation from groundwater for 1000 years, the bentonite buffer increases this term by at least one order of magnitude.

At present, a great number of experiments have been carried out on the study of the isolating properties of the bentonite buffer, including long-term (over several years) experiments in underground laboratories, as well as experiments under conditions simulating processes developing in underground HLW repositories. These studies were intended to obtain information on the following issues:

(a) the influence of a bentonite buffer on the corrosion resistance of a metallic canister and HLW;

(b) the dependence of water permeability on bentonite density;

(c) the sorption properties of bentonites in relation to radionuclides;

(d) the determination of coefficients of diffusion of various radioisotopes through water-saturated bentonite;

(e) the heat conductivity of bentonite and ways of increasing it;

(f) the influence of radiation, elevated temperature, and compositions of aqueous solutions on the isolating properties of bentonite.

In the Russian literature, the problem of the use of buffer materials as engineered barriers was practically not considered. In our paper, we tried to fill this gap insofar as possible, briefly describing the study of this problem on the whole. At present, the solution to the problem of the influence of the long-term thermal impact of HLW on the isolating properties of the bentonite buffer is least developed. It is hardly possible to solve this problem on the basis of short-term experiments, due to the low rate of reactions of mineral formation. The results of studies of natural processes operating within the range of temperatures typical of the nearest field of an HLW repository are more reliable. We accumulated a considerable amount of relevant data during study of argillitization within a wide range of physicochemical conditions, as well as the study of the transformations of clayey rocks during exogenous–epigenetic, hydrothermal, and metamorphic processes. On the basis of these data, we tried to answer the question of whether montmorillonite will conserve its properties in the temperature field of an underground HLW repository. Various additives to the buffer composition decrease the solubility of HLW in the pore water of bentonite, improve its sorption properties, and elevate its heat conductivity and reducing and neutralizing

capacities. This paper examines the problem of improving the isolating properties of a bentonite buffer.

BENTONITE AND ITS ISOLATING PROPERTIES

The idea to use clay minerals as engineered barriers is based on their low water permeability, their plasticity, and their ability to best retain radionuclides during the filtration of contaminated groundwater. Radionuclides are retained in rocks for various reasons, including the following: (1) the attraction of ions by residual charges on the surfaces of minerals; (2) the replacement of sorbed ions on surfaces by new ions; (3) the replacement of ions incorporated in the mineral structure by ions contained in the solution; and (4) the formation of difficultly soluble chemical compounds.

All these phenomena are classified under the general term "sorption." During the movement of groundwater through rocks, a considerable fraction of sorbed particles can be again transferred into the solution and again sorbed at a considerable distance from the source. As a result, the contaminating components move more slowly than the water flow. The retardation factor R_f shows how many times lower the rate of transfer of a certain chemical element is than the flow rate. This factor depends on the geochemical properties of elements, sorption properties of rocks, compositions and properties of water solutions, temperature, concentration of radionuclides, and so on. Of all rock varieties, clays are characterized by the maximal R_f value (Table 1).

Table 1 shows maximal R_f values that can be used for an approximate estimation of this factor, as these values characterize real hydrogeochemical conditions of the geological environment of underground repositories (low-mineralized groundwater with reducing low-alkaline properties). The lowest R_f are typical of conditions of elevated solubility of radionuclides artificially created during experiments.

Clays vary in mineral and chemical composition and, thus, in the properties that define their applicability as buffer materials. According to the combination of properties, bentonite clays are the most promising for this purpose.

Bentonites are finely dispersed clays with a high degree of swelling. The ability of clays to swell is defined by the presence of minerals of the montmorillonite group. If montmorillonite minerals make up 60% of a clay, it is designated a bentonite; if less than 60%, it is attributed to bentonite-like clays (Kirsanov, 1984). The largest bentonite deposits were formed as a result of the transformation of volcanic glasses and tuffs during their interaction with seawater. On a lesser scale, bentonites are formed by the interaction of hydrothermal solutions with rocks or during weathering under conditions of elevated alkalinity.

Minerals of the montmorillonite group are characterized by the following general formula: $[(Ca_{0.5},Na)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O]$. In

Table 1. Factors of the retardation (R_f) of radionuclides in rocks (Krauskopf, 1988_2)

Elements	Granite	Basalt	Salt	Clay
Sr	20–4000	50–3000	10–50	100–100000
Cs	20–100000	200–100000	40–100	200–100000
I	1	1	1	1
Tc	1–40	1–100	1–10	1–40
U	20–500	50–500	20–100	50–2000
Np	10–500	10–200	10–200	40–1000
Pu	20–2000	20–10000	40–4000	50–100000
Am	500–10000	100–1000	200–2000	500–100000

addition, bentonite often contains hydromicas; mixed-layer minerals (such as mica–montmorillonite, kaolinite–montmorillonite, etc.); kaolinite; sepiolite; palygorskite; quartz; and Fe, Mn, and Ti oxides and hydroxides. Quantitative mineral and chemical compositions and the corresponding properties of bentonite vary. In many experiments in other countries, MX-80 bentonite extracted from deposits in Wyoming and South Dakota is used. This bentonite contains about 75% Na montmorillonite, 15% quartz, 5–8% feldspar, 1.4% carbonate, 0.3% pyrite, and 0.4% C_{org}. The presence of C_{org} underlies the reducing properties of porous solutions.

The low permeability of bentonite is the most important factor preventing the penetration of radionuclides into groundwater. For pure bentonite, this value is within 10^{-13}–10^{-14} m/s, whereas, for bentonite consisting of the most finely dispersed particles, obtained by the centrifuging method, the water permeability is 10^{-16} m/s (Conca *et al.*, 1993). These data testify that the migration of dissolved components in bentonite sat-urated with water is possible only by diffusion. The low rate of this process prevents any release of radionuclides in dissolved form. Thus, the penetration of radionuclides through bentonite in colloidal form is virtually impossible. This is related to the fact that the size of the cross sections in bentonite channels through which water filters varies widely. This ensures reliable fixation of even the nanoparticles, the size of which does not exceed a few nanometers (Fig. 1).

Cation exchange ability is a very valuable property of minerals of the montmorillonite group (including bentonite). During interaction with an aqueous solution, these minerals can change their compositions, absorbing certain cations and releasing others. According to the composition of exchange cations, bentonites are subdivided into alkaline, in which Na is the principal component, and calc-alkaline, in which the cations are mostly represented by Ca and Mg. In natural conditions, the exchange cation composition of bentonite can change with time. Most often, under the attack of
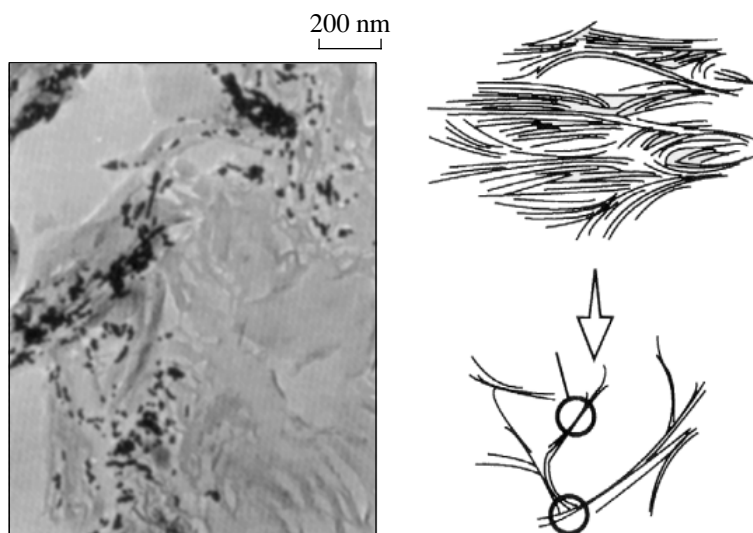

Fig. 1. TEM image of a mixture of 50% of bentonite and quartz sand after experiments on the filtration of distilled water containing colloidal gold (Kurosawa *et al.*, 1997). The density of the dry mixture is 1.8 t/m³. Bentonite, gray; colloidal gold, black. Right: scheme of the microstructure explaining the retardation of colloidal particles in narrowings between scales of montmorillonite.

groundwater, alkaline bentonites are partly or completely transformed into calc–alkaline bentonites. The maximal plasticity, swelling, and cation exchange capacity are typical of bentonites with the highest content of Na montmorillonite. The Na_2O content in alkaline bentonites exceeds 2 wt %. The treatment of bentonites by solutions under artificial conditions can improve their properties by the replacement of exchange cations. Thus, calc–alkaline bentonite treated with Na solution transforms into alkaline bentonite, with its inherent characteristics. The exchange capacity of bentonites reaches 90 mg-equiv/100 g. About 80% of the exchange capacity is related to replacements in the crystal structure. The cation exchange ability of bentonites is especially important for the immobilization of the ^{137}Cs and ^{90}Sr radioisotopes, with which the main environmental hazard of HLW during the first one hundred years of their storage is associated. However, this property of montmorillonite does not noticeably influence the retardation of actinides. Studies of rocks and minerals by fission track radiography persuasively showed that montmorillonite could not be attributed to active sorbents of uranium (Omel'yanenko *et al.*, 1983). This element is much more actively sorbed by Fe, Ti, and Mn oxides and hydroxides and organic matter, as well as by products of altered minerals containing Fe and Ti (chlorites, leucoxene, trioctahedral hydromicas, and others). These minerals should sorb all other actinides efficiently. Thus, with respect to their sorption properties relative to actinides, montmorillonite clays with high contents of the above minerals are greatly preferable to montmorillonite bentonites. Such minerals are contained in great amounts in weathering crusts developed on basic rocks.

USE OF A BENTONITE BUFFER AS AN ENGINEERED BARRIER IN UNDERGROUND HLW REPOSITORIES

Prepared as dry briquettes, bentonite is placed between walls of rock and HLW packages. The latter can contain both spent nuclear fuel (SNF) and vitrified HLW (Figs. 2, 3). With time, under the attack of groundwater penetrating along fractures in the rock, bentonite swells, increases in volume, and seals voids and fractures. The higher the density of the bentonite in a dry state, the higher the pressure during swelling. The bentonite density is calculated to achieve a pressure growth on swelling sufficient for sealing fractures but unable to cause destruction of host rocks and HLW packages. The time required for swelling depends on the bentonite properties, water permeability of the rock, and temperature. Modeling showed that this process could occur over less than 100 years to more than 1000 years (Andrews *et al.*, 1986). In various designs of repositories of the shaft type, the thickness of the bentonite buffer varies from 0.3 to 1.3 m, whereas, in borehole repositories, it is considerably smaller.
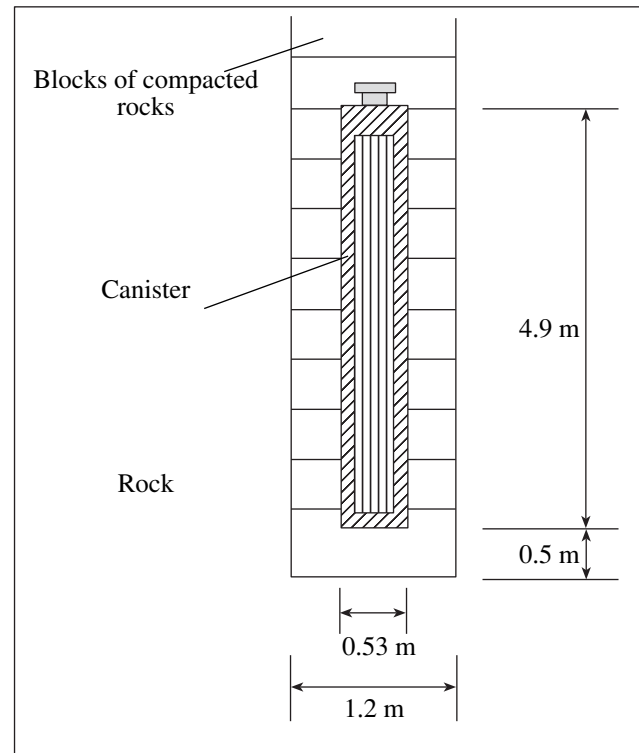

Fig. 2. Scheme of the placement of a bentonite buffer and a canister containing SNF in the vertical cell of an underground working in granites (Luhmann *et al.*, 2000). The distance between cells is 10 m.

On the whole, bentonites comply with the requirements for buffer materials. An obvious disadvantage of bentonites is their low heat conductivity. For increasing the heat conductivity, bentonite is mixed with quartz sand or rock rubble, although this results in a certain deterioration of other properties, in particular, in an increase in water permeability. Nevertheless, even at a high content of quartz sand, the water permeability of bentonite remains at a rather low level. Thus, with a mixture composed of 15 wt % of bentonite and 85 wt % of quartz, the water permeability of the buffer mixture lies within 5×10^{-11} m/s (Esaki *et al.*, 1997). At these values, diffusion becomes the main mechanism of transfer of radionuclides. That swelling is the main cause of such a low water permeability is evidenced by that fact that this value is 10^{-7} m/s for a mixture of nonswelling kaolinite with sand in the same proportion.

The corrosion rate of canisters and the intensity of radionuclide leaching from HLW depend on the compositions and properties of aqueous solutions acting on the radionuclides. Groundwater penetrating bentonite gradually changes composition, approaching conditions of equilibrium with the buffer minerals. Therefore, the solutions used in experiments on the assessment of the corrosion rate of canisters and HLW should be (1) solutions produced by long-term interaction between groundwater and bentonite or (2) model pore
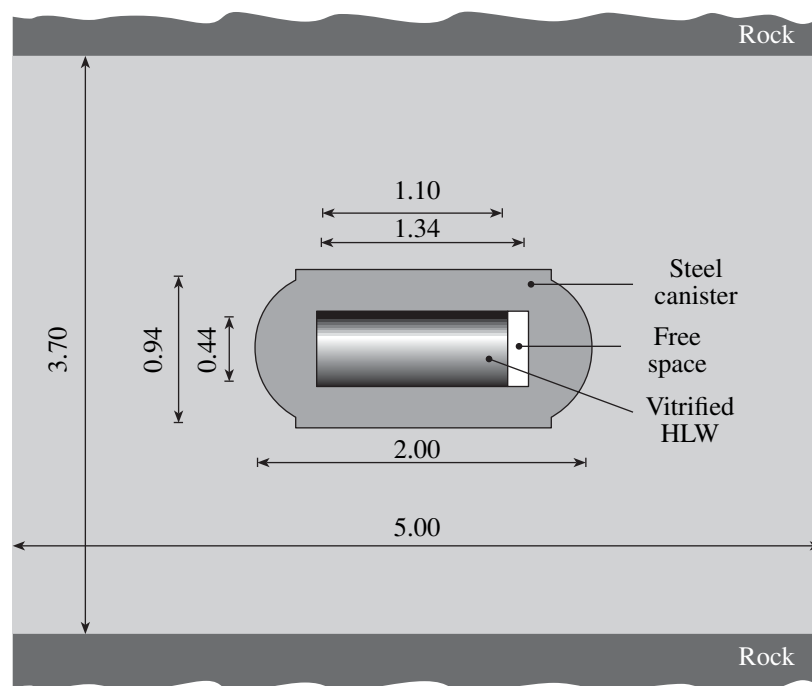
Fig. 3. Scheme of the placement of a canister containing vitrified HLW and a bentonite buffer in a horizontal working in gneisses (NAGRA, 1994). The interval of the working for the placement of one canister is 5 m.

solutions with compositions and properties determined by modeling of equilibrium conditions of groundwater with bentonite. The final composition of pore solutions depends on both the composition of the bentonite and of the groundwater. As an example, Table 2 shows the compositions of aqueous solutions in equilibrium with MX-80 bentonite used for the estimation of radionu-

clide release in studies on a repository for vitrified HLW in crystalline rocks in northern Switzerland (NAGRA, 1994). The values shown in Table 2 were obtained taking into account experimental data and thermodynamic calculations for low- and high-salinity groundwater.

In general, in comparison with groundwater of crystalline massifs, the pore solutions have elevated Na^+, SO_4^{2-}, CO_3^{2-}, and F^- concentrations and lower Ca^{2+} concentrations. Depending on the bentonite composition, the equilibrium pH value ranges from 8 to 10 (*The Scientific* …, 1995). The Eh value of the pore solutions depends on the material of the canister and the compositions of additives initially contained in bentonite or specially added for decreasing Eh.

It is assumed that the failure of canisters will take place not earlier than within 1000 years after their disposal in a repository. By this time, all short- and mid-lived radionuclides (^{137}Cs and ^{90}Sr) will have decayed and 98% of HLW will be associated with actinides. The radioactivity of vitrified HLW will be defined by Am and, to a lesser extent, Pu, whereas SNF radioactivity will be determined by Pu and Am. Of other radionuclides, ^{99}Tc and ^{237}Np will contribute considerably to the radioactivity of HLW and SNF. The intensity of release of the above radionuclides is limited by their solubility, which is rather low under reducing conditions. The analysis of experimental data on the solubility of HLW in pore solutions of bentonite showed that the maximal Pu and Am concentrations could reach 10^{-6} M/l. In this case, the colloidal form is strongly

Table 2. Properties of porous waters formed as a result of interaction of groundwater with bentonite

Parameters and components, mM/l	Low-salinity waters	High-salinity waters
T, °C	50	50
pH	8.97	8.49
Eh, mV	−396	−367
Na^+	78	240
K^+	0.17	0.57
Ca^+	0.011	0.055
Mg^{2+}	0.067	0.48
HCO_3^-	52	18
Cl^-	3	187
F^-	0.70	0.19
SO_4^{2-}	4.5	16
Al^{3+}	0.1	0.036
Si_{tot}	0.26	0.19

dominant, whereas the concentration of the dissolved species does not exceed 10^{-8} M/l.

MIGRATION OF RADIONUCLIDES THROUGH BENTONITE BUFFERS

The possibility of the migration of radionuclides through bentonite buffers to groundwater is a key problem in assessment of the safety level of an HLW repository. Therefore, the results of estimates of the time needed for radionuclides to penetrate to groundwater through the bentonite buffer are of great interest. In analyzing this problem, we proceed from the premise that, in any case, reducing properties of pore solutions are ensured. This can be accomplished by selecting a bentonite of appropriate composition or by adding reducers to the bentonite. Many experimental and theoretical studies have been devoted to the diffusion through bentonite. The main results of these studies are reviewed below.

As was noted above, due to the very fine size of pores in bentonite and the lack of pervasive channels, colloidal particles cannot penetrate through a bentonite buffer. As a proof of this, let us consider the results of representative experiments performed by Japanese researchers (Kurosawa *et al.*, 1997). In the experiments, a compacted Na bentonite and mixtures of Na bentonite with quartz sand were used. The sand content was 30, 40, and 50 wt %; the grain size, 0.92–1.18 mm. The material was pressed into discs with a diameter of 50 mm and a height of 5 mm. The density of bentonite and its mixture with sand was from 1000 to 1800 kg/m³. Prior the experiment, the mixture was saturated with distilled water or a 0.5 M NaCl solution simulating seawater. Nanoparticles of gold 15–50 nm size was used for experiments. Gold is an exceptionally favorable element for studying the migration of colloidal particles, as it is virtually not sorbed by bentonite. Tracing solutions with gold colloids were prepared on the basis of distilled water and 0.5 M NaCl solution. The experiments lasted 135 days. The results of experiments with distilled water and NaCl solution turned out to be similar. All colloidal particles were retained by bentonite (Fig. 4), and the main mass of colloidal particles was accumulated in the subsurface zone of the discs. Only a small amount of colloidal particles penetrated through a relatively loose mixture of bentonite with 50 wt % of sand with a density of 1000 kg/m³. However, colloidal particles failed to penetrate through the mixture of the same density containing 40 wt % of sand. The authors believe that the retention of colloidal particles was defined by the particulars of bentonite structure, namely, by the presence of fine pores (Fig. 1). Bentonite also contains larger pores, but the lack of links between them does not allow colloidal particles to penetrate through the buffer. It was concluded that, in the presence of a bentonite buffer, the release of radionuclides from HLW into groundwater is impossible. Therefore, in analyzing the diffusion mass transfer of
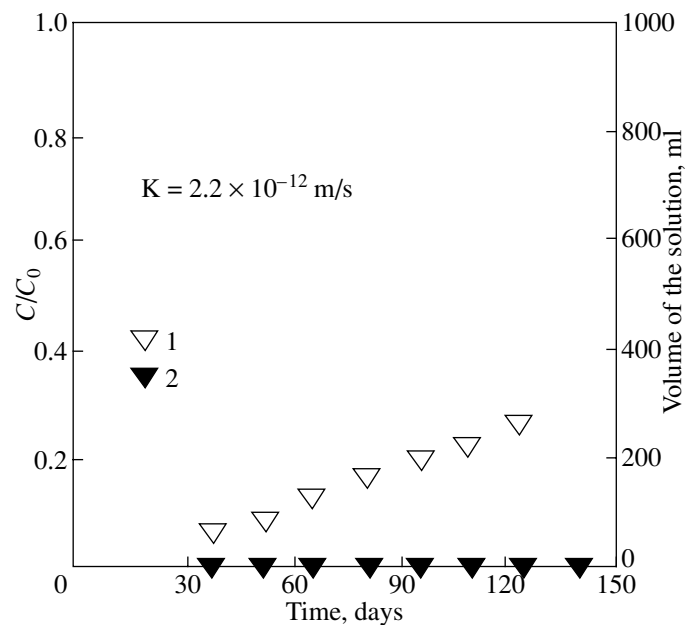

Fig. 4. Results of experiments on the filtration of distilled water containing colloidal gold through a 50% mixture of bentonite and quartz sand with density of 1.8 t/m³ in a dry state (Kurosawa *et al.*, 1997). 1. Volume of the solution penetrating through bentonite; 2. Fraction of colloidal particles contained in the solution. Concentrations of colloidal particles in the initial and penetrating solutions C_0 and C; K. Permeability.

radionuclides through bentonite, it is necessary to take into account only the dissolved form of the radionuclides. Real and conservative estimates of the concentrations of dissolved Pu, Am, and Np in pore solutions at the boundary with bentonite range from 10^{-8} to 10^{-6} M/l, and of Tc, from 10^{-7} to 10^{-5} M/l. The concentrations of such long-lived and highly mobile radionuclides as ^{135}Cs, ^{14}C, and ^{129}I can be very high.

Sorption is the most important factor limiting the transfer of radionuclides in dissolved form through the buffer. Many experimental studies have been devoted to determining the sorption properties of bentonites. In spite of the considerable scatter of the values obtained, related to the various conditions of the experiments, we hold that, taking into account the compositions and properties of pore solutions of bentonites, the distribution coefficients (K_d) for actinides should be defined by values exceeding 1000 ml/g, and for Cs and Tc, from tens to several hundreds of ml/g. For example, a report of the Swiss National Cooperative for the Disposal of Radioactive Wastes (NAGRA, 1994) devoted to assessment of the safety of a repository of vitrified HLW in crystalline rocks defines the following K_d (ml/g): 5000 for Pu, 5000 for Am, 5000 for Np, 100 for Tc, and 10 for Cs. These values are based on the aggregate of available experimental data. They are accepted as conservative estimates for which the probability of an error in the direction of an increase is virtually excluded.

Experiments on the diffusion of actinides through buffers show that their migration in dissolved form can proceed very slowly. Thus, experiments on ^{238}Pu diffusion through bentonite with a density of 1 g/cm^3 in a dry state showed that, after the interaction of bentonite with a solution containing 10^{-7} M/l Pu at 90°C, its concentration in the pore solution after 375 days at a depth of 3 mm amounted only to 10^{-10} M/l (Tsukamoto *et al.*, 1995). These results demonstrate that 1000 years are required for a concentration of 10^{-12} M/l to be attained in the pore solution at a distance of 15 cm from the zone of contact with radioactive glass, whereas 1000 years are needed for this concentration to be reached at a distance of 55 cm. This suggests that any release of actinides into groundwater can be prevented for at least 10 000 years with the aid of a bentonite buffer.

Experimental studies show that, for ^{229}Th, $^{241, 243}$Am, and $^{239, 240}$Pu, a time of 30 half-life periods of these radioisotopes is required to overcome a bentonite buffer with a thickness of 1 m (Torstenfelt *et al.*, 1982). Taking K_d values of about 2000 ml/g, Nowak (1980) established that the time required for the penetration of ^{237}Np through a bentonite buffer with a thickness of 30 cm is 10 000–100 000 years, whereas, for other actinides, this time is considerably longer.

According to the estimation of Nilsson *et al.* (1993), for penetration through a buffer to groundwater, radionuclides require such a long time that the concentration of even long-lived actinides should fall to a very low level due to their decay. For example, the concentration of ^{239}Pu and ^{243}Am migrating into groundwater will be too low to noticeably influence its radioactivity.

There are numerous data in the literature on the dependence of K_d of various radionuclides on the density of bentonite, the content of montmorillonite in bentonite, the Eh value, the presence or absence of products of corrosion of steel containers, and so on. All these data agree with the conclusion that, independently of the form of waste, a bentonite buffer in a reduced medium is a practically insurmountable barrier for the migration of actinides and other sorbed radionuclides from HLW repositories into the geological environment.

Studies on assessing the safety of underground repositories of vitrified HLW in which the use of a bentonite buffer is envisioned show that relatively poorly sorbed long-lived radionuclides can penetrate into groundwater only after 10 000 years. ^{79}Se will be the first to penetrate the bentonite buffer, then ^{135}Cs. ^{99}Tc could penetrate to groundwater only 300 000 years after the closure of the repository (NAGRA, 1994). The main contributor to the contamination of the biosphere will be the ^{135}Cs isotope, and the share of radiation related to it will amount to no more than 10^{-3} of the background radiation.

In SNF repositories, volatile highly mobile radionuclides (^{14}C, ^{36}Cl, and ^{129}I) that are absent in vitrified HLW will be the first to penetrate to groundwater through a bentonite buffer. However, their contribution to the dose of irradiation received by a human cannot exceed a few hundredths of the background radiation. In descending order of significance, the main contribution to the contamination of the biosphere will be made by the following radionuclides: ^{14}C, ^{135}Cs, ^{129}I, ^{36}Cl, and ^{79}Se (Luhmann *et al.*, 2000). The contribution of other radionuclides is negligibly small. It can be concluded that, if the bentonite buffer retains its protective properties, this barrier will provide reliable isolation of the most hazardous radionuclides (actinides) for the required period. Therefore, it is important to analyze to what extent and for how long a bentonite buffer can preserve its properties under the conditions of a repository.

THERMAL IMPACT OF HLW ON BUFFER MATERIALS

From the moment of HLW disposal in underground workings until the failure of canisters, HLW will be isolated from the impact of aqueous solutions. According to the standards accepted in most countries, the corrosion stability of canisters should ensure the isolation of HLW for a period of no less than 1000 years. During this time, the bentonite buffer will be subjected to the impact of groundwater at elevated temperatures. The question arises of whether bentonite will lose its isolating properties by the time of the canister failure. Numerous studies devoted to this problem are analyzed below.

Temperature of the Bentonite Buffer and the Duration of the Thermal Impact

It is well known that the lower the temperature, the easier it is to insure the safety of a repository. A decrease in temperature can be attained by (1) increasing the time of SNF storage before vitrification; (2) decreasing the content of radionuclides in canisters containing HLW; (3) increasing the time of HLW storage in subsurface temporary sites; (4) increasing the distance between canisters with HLW in underground workings.

The use of any of these ways of decreasing temperature inevitably increases expenditures. In most countries, the maximal admissible temperature in the nearest field of an HLW repository is 100°C; in the United States, 250°C. In Russia, the problem of the maximal admissible temperature at an HLW repository has not been solved. Taking into account the quantity of HLW to be buried, we may assume that the economic factor will be decisive in solving this problem. In this connection, a decision to limit the temperature to 250°C in the nearest field of repositories is very probable (Laverov *et al.*, 2001).

In the literature, there are examples of calculation of the temperature regime within the nearest field of HLW repositories that allow us to estimate the duration of thermal impact on the buffer material. These examples show that several decades are required for the maximal
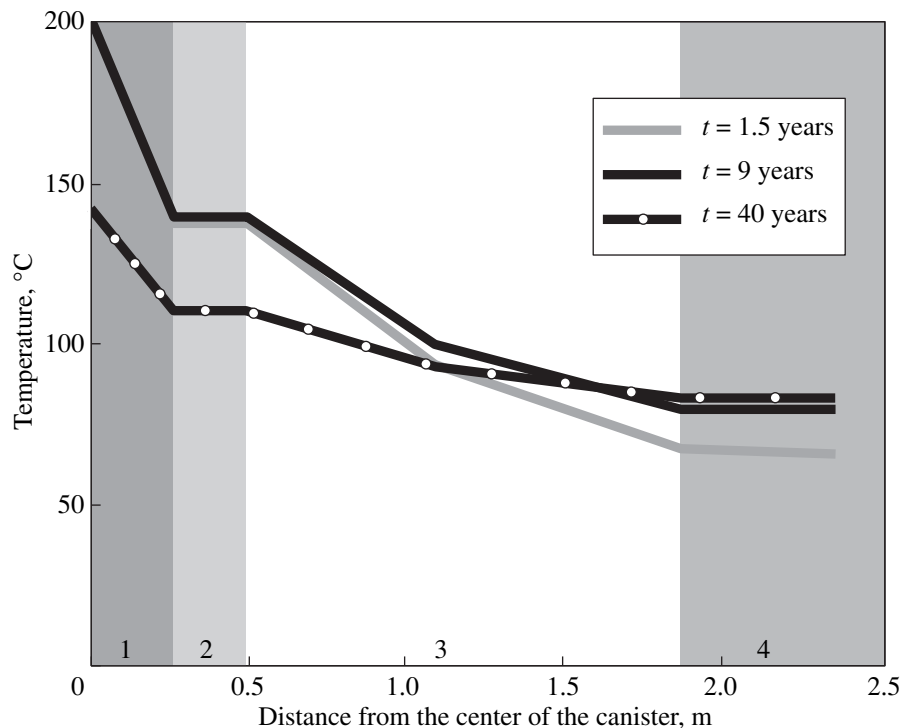
Fig. 5. Distribution of temperature near a canister with vitrified wastes 1.5, 9, and 40 years after the burial (NAGRA, 1994). 1. Vitrified HLW; 2. Steel canister; 3. Bentonite buffer; 4. Rock.

temperature at the boundary of the buffer with the rock to be attained (Fig. 5). The temperature will be maintained at this level for a few decades and then will gradually decrease. On the whole, the buffer will be subjected to an elevated temperature for several hundred years. In general, the thermal impact may have the following consequences: (1) a redistribution of pore water in bentonite corresponding to the temperature gradient; (2) an increase in porosity and water permeability; (3) an increase in the concentration of salts and their deposition near HLW; (4) a change in the chemical and mineral composition of bentonite and its thermal destruction. The most important experiments in the study of thermal impact on the bentonite buffer are characterized below.

Water Redistribution

At present, representative experiments on the distribution of water in bentonite exposed to thermal impact have been conducted. The scheme of laboratory experiments is as follows. A heater simulating a canister with HLW is placed in the central part of a cylindrical hole drilled in a granite block. The space between the heater and the granite is filled with water-saturated bentonite or a mixture of bentonite with sand. After prolonged heating, the temperatures on the heater walls, in various parts of the buffer mixture, and in the granite, as well as the moisture content of bentonite, are measured. The experiments, lasting 2000 hours, were conducted at a

temperature at the surface of the heater of 110°C (Selvadurai and Onofrei, 1993). A mixture of equal amounts of bentonite and sand with a density of 2 g/cm^3 was used. At the end of the experiment, the temperature at the contact of the buffer with granite was 70°C; in the peripheral part of the granite block with a thickness of 90 cm, 62°C. The moisture content increased by 30% in the central part of the buffer but decreased by 10% in the peripheral part. The total moisture loss was 3.2%. There was no noticeable cracking in the buffer.

Similar results were obtained in experiments conducted according to the same scheme but under different conditions (Pusch and Karnland, 1993). Here, a water-saturated Na bentonite with a density of 1.83 g/cm^3 in a dry state was used. After heating for 10 months, the buffer temperature was 80°C at the boundary with the heater and 32°C in the external part. Correspondingly, the water contents were 7.5% and 19%. The ability of montmorillonite to swell deteriorated. This was related to the deposition of silica along the margins of montmorillonite scales, which prevented penetration of water.

The most important and long-term experiment under conditions maximally close to those of HLW repositories was performed in Grimsel (Switzerland). A horizontal working in granite with a diameter of 2.28 m and a length of 70 m was filled in the interval from 53 m to the end of working (70 m) with bentonite with a density of 1.7 g/cm^3 in a dry state and a total mass of 115.7 tons. The water content in bentonite was 14%.

Two heaters 4.54 m long with a diameter of 0.90 m were placed in the central part of the bentonite buffer. The distance between the heaters along the axis of the working was 1.02 m. The thickness of bentonite located between the heater and walls of the working was 69 cm. A total of 620 gages were mounted into the heat generator, buffer, and host rocks. The readings of these gages enabled monitoring of the temperature, water content, gas generation, and other parameters. The proposed term of the experiment was three years. Within 53 days after switching on of the heaters, the temperature on their surfaces reached 100°C. Within 140 days after the beginning of the experiment, a gradient of the water concentration in bentonite with a clear decrease from the periphery to the center was established (Fuentes-Cantillana *et al.*, 1998). Thus, the experimental data testify to a redistribution of water in the buffer in correspondence with the temperature gradient. As a result, salts accumulated. In the hot part of the buffer, the evaporation of water, its supersaturation with salt, and salt deposition took place (Allen and Wood, 1988). In the external part of the buffer, vapor condensed, and new portions of water penetrated into the hot part of the buffer. Chlorides and sulfates were established as newly formed salts.

Hydraulic Permeability of Bentonite

With the increasing temperature, the hydraulic permeability of bentonite increases. Thus, with a temperature increase from 20°C to 130°C, the hydraulic permeability of Na montmorillonite with densities of 1.78 and 1.96 g/cm^3 changed, correspondingly, from 10^{-12} to $10^{-11.8}$ m/s and from $10^{-12.8}$ to $10^{-12.0}$ m/s (Nilsson *et al.*, 1993). According to other data, the hydraulic permeability of bentonite increased threefold with a temperature increase from 20°C to 80°C (Cho *et al.*, 1998). On the whole, the increase in hydraulic permeability, redistribution of water, and salt deposition did not lead to cardinal deterioration of the isolating properties of bentonite.

Changes in Chemical and Mineral Composition of Bentonite

In the conditions of an HLW repository, dry bentonite prior to its saturation with water is subjected to thermal impact. This period can continue for several decades and even for hundreds of years. Therefore, experiments with both dry bentonite and bentonite saturated with a pore solution are of interest for researchers. It is known that the effect of temperature on dry montmorillonite in the range up to 200°C leads to a loss of interlayer water, which is easily restored with the saturation of montmorillonite with water (Deer *et al.*, 1962). The water loss is reversible at higher temperature. This is confirmed by experiments showing that bentonite kept for 340 days at a temperature of 370°C retains its swelling ability (Allen *et al.*, 1984). At the same time, at a temperature of 440°C, irreversible water loss took place. The results of experiments show that thermal impact up to 250°C prior to saturation with water does not lead to a noticeable loss of the ability of bentonite to swell. Considerably more substantial transformations of bentonite at this temperature take place in water-saturated bentonite. A partial replacement of Na by Ca and Mg is most typical. This process is accompanied by an insignificant decrease in plasticity (Chapman and Savage, 1984). In case of interaction with alkaline solutions, but in the absence of K in these solutions, montmorillonite is stable up to 300°C, but at temperatures higher than 300°C, it is replaced by paragonite and albite (Hemley *et al.*, 1961). In basic rocks enriched with Mg, chlorite is formed after montmorillonite. In case of attack of acid solutions on montmorillonite impoverished in K, montmorillonite is replaced by kaolinite and, at temperatures exceeding 200°C, by pyrophyllite. Upon an elevated temperature and the presence of K in solutions, montmorillonite is subjected to illitization with the formation of a mixed-layer illite–montmorillonite phase and, finally, illite. The quantitative ratios of montmorillonite and illite sheets in the mixed-layer minerals characterize the intensity of the transformation. Strong illitization of montmorillonite leads to the loss of the isolating properties of bentonite. Therefore, for assessing the reliability of a bentonite buffer, it is important, first of all, to analyze the probability of changes in its protective properties under the influence of illitization.

Illitization of Montmorillonite

Illitization of montmorillonite is a widespread process. It takes place as a result of hydrothermal and metamorphic transformations of sedimentary rocks. All researchers agree that, at pH values typical of groundwater of crystalline massifs and in thermal conditions of underground HLW repositories, illitization is the most realistic process of the transformation of the buffer. However, the question of whether the rate of this process is sufficient for substantial illitization of montmorillonite within 300–500 years (the time necessary for a considerable decrease in HLW temperature) remains open. Let us consider available experimental and geological–geochemical data.

Experimental Data

Experimental data convincingly show that the main factors influencing the equilibrium conditions in the montmorillonite–illite system are the temperature, K concentration, and pH of the solution. The growth of these parameters is favorable for the formation of illite after montmorillonite. The presence of other cations along with K retards the illitization (Eberl, 1978). It was established on the basis of experiments at 270°C and 350°C that the presence of Na, Ca, and Mg retards the reaction of illite formation in the proportion 1 : 10 : 30 (Roberson and Lahann, 1981). Taking these data into
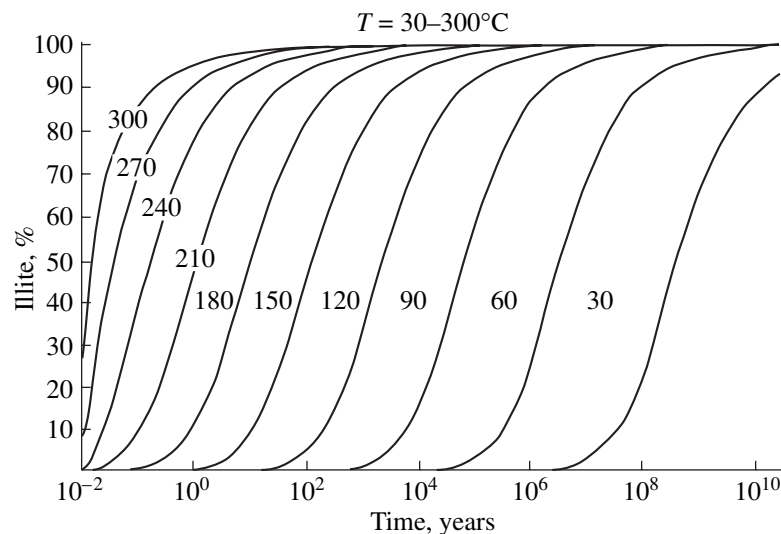
Fig. 6. Calculated diagram characterizing the dependence of the degree of illitization of montmorillonite on temperature and the duration of the thermal impact (Pytte, 1982). The K^+ concentration taken in the calculations corresponds to conditions of albite–microcline equilibrium; activation energy, 27 kcal/mol.

account, we may assume that, all other conditions being equal, the illitization of bentonite in basic rocks (for example, basalts) will be much slower than in granites.

Many experiments have been devoted to the rate of illitization. In experiments lasting 341 days on the interaction of bentonite with a solution whose composition corresponded to fracture water in basalts at a temperature of 300°C, a newly formed illite could not be established (Allen and Wood, 1988). However, in experiments lasting 379 days at the same temperature, the transformation of montmorillonite into a mixed-layer illite–montmorillonite phase with more than 65% of illite sheets was established. The results of experiments suggest that, in experiments at 300°C over a shorter period and at much lower temperatures, illitization also took place. However, the amount of newly formed illite turned out to be insufficient to be established by X-ray diffraction.

On the basis of the assumption that the ratio of K^+/Na^+ activities in a solution is controlled by the solubility of microcline and albite, an assessment of the illitization rate of montmorillonite clays at contacts with basalts was made (Pytte, 1982). Experimental data and field observations showed that, at 90°C, approximately 10% of illite forms within 10 000 years and 90% of illite within 10 m.y. Similar contents of illite could be attained within 10 and 100 000 years at 150°C and within 30 days and 1000 years at 210°C (Fig. 6). The above results show that the transformation of montmorillonite in the basalt–bentonite–water system at elevated temperatures is expressed in an increase in Ca and Mg contents at the expense of Na, partial illitization, and chloritization. The presence of potassium feldspar in bentonite increases the illitization rate.

The estimation of the illitization rate was made according to a design for the burial of vitrified HLW in a crystalline massif by specialists of NAGRA (1994) in Switzerland. Bentonite with a density of 1650–1750 kg/m³ in a dry state was taken as a buffer. The water permeability taken in calculations for water-saturated bentonite was 10^{-16} m/s. The calculations showed that the maximal temperature at the contact of HLW with the buffer will reach 150°C and will then decrease, falling after 50 years to 100°C (Fig. 5). According to the prognosis, during this time, the reverse dehydration of montmorillonite and the formation of fractures will take place. After the saturation of bentonite, the water content in montmorillonite will be restored and the fractures healed. The montmorillonite swelling will decrease insignificantly due to the deposition of silica scales along the margins of the montmorillonite. It was shown that, during the period of elevated temperatures, no substantial illitization at the existing K concentrations in groundwater (4.2–8.5 mg/l) can take place. Even at upon an increase in the water permeability of bentonite by two orders of magnitude and the transfer of all available K from the solution into illite, the complete illitization of montmorillonite would require more than one million years.

Geological–Geochemical Data

Geological–geochemical data on the conditions of formation of montmorillonite, illite, and other layered silicates were accumulated in study of processes of hydrothermal argillitization and epigenesis and metagenesis of sedimentary rocks. The high stability of montmorillonite at low temperatures is doubtless. Thus, in bentonites that were subjected to temperatures lower than 50°C over tens of millions of years, no evidence for

the transformation of montmorillonite was found even upon careful study (Perry and Hower, 1970).

It was established that montmorillonite is formed in both exogenous and hydrothermal conditions in almost neutral medium at temperatures lower than 200°C. At the same temperatures in more acid medium, kaolinite is formed instead of montmorillonite. Under the attack of moderately acid solutions on rocks, kaolinite mainly forms in the internal zones of metasomatic rocks and montmorillonite, in the external zones. High basicity of host rocks is favorable for the formation of montmorillonite instead of kaolinite. Like montmorillonite, kaolinite is formed in exogenous and hydrothermal conditions. As hydrothermal argillisites are an important prospecting feature for various types of ore mineralization, some studies were carried out on the elaboration of criteria for separation of hydrothermal argillisites from linear weathering crusts (Andreeva *et al.*, 1982, 1984). The most important result of these studies was the conclusion that mixed-layer illite–montmorillonites, hydromicas, and sericites are not formed in weathering crusts. However, if these minerals are present in initial rocks, they show high resistance to weathering and often are preserved as relicts.

Temperature conditions of the formation of mixed-layer illite–montmorillonites can be assessed on the basis of studies of mineral formation in areas of thermal activity in regions of active volcanism. It was established that illite–montmorillonites are formed at temperatures of not lower than 110°C. The following sequence of minerals was established with temperature growth: montmorillonite $\longrightarrow$ ordered mixed-layer mica–montmorillonite containing 55% of illite $\longrightarrow$ mica–montmorillonite containing 70–80% of illite $\longrightarrow$ light potassium mica. The replacement of montmorillonite by mixed-layer minerals takes place at 110–130°C, whereas mica is formed at temperatures higher than 230°C.

Mixed-layer minerals of the mica–montmorillonite type are also formed under conditions of regional epigenesis of sedimentary montmorillonite-bearing rocks. As a result of subsidence of sediments, montmorillonite becomes involved in processes that are close to hydrothermal. In this case, montmorillonite is transformed into hydromica through a number of mixed-layer minerals with various quantitative ratios between illite and montmorillonite sheets. The formation of mixed-layer mica– montmorillonite minerals is also possible in metamorphosed Precambrian weathering crusts subjected to the same transformations that take place during deep-seated epigenesis of sediments. In hydrothermal argillisites, mixed-layer mica– montmorillonites are widespread and commonly contain 50–70% of illite layers. The results of natural observations testify to a considerable influence of K on the mineral compositions of argillisites. Under similar temperature conditions, montmorillonite or illite–montmorillonite are often formed in rocks poor in K, whereas rocks rich in

K contain hydromica. This regularity is especially noticeable in argillitization zones cutting rocks of various initial compositions (Omel'yanenko, 1978). In this respect, basic rocks rich in Ca and Mg are preferable as a hosting medium for HLW repositories.

As to the problem of HLW disposal, the most important result of observations is the fact that, below a temperature of 110°C, the illitization of montmorillonite does not take place even if the interaction with solutions is not limited in time. Therefore, we may completely exclude the possibility of illitization of bentonite in repositories with temperatures below 110°C. At higher temperatures, especially in a medium rich in K (for example, in granites), the illitization of bentonite is inevitable. However, the degree of the illitization during the time when bentonite is subjected to elevated temperatures is an open question. In this connection, data on the rate of bentonite illitization in a medium rich in K are of great interest.

Data presented by Pusch and Karnland (1988) testify to a very low illitization rate at temperatures below 150°C. On the island of Gotland, Ordovician bentonites with a thickness of 0.3 m lie at a depth of 500 m. They were subjected to heating at 110–120°C over millions of years. However, they preserved their plasticity and contain 25% of montmorillonite. These data testify that, under natural conditions, the illitization is slower than that predicted by calculation (Fig. 6). The authors explain this by suggesting that the calculated data characterize the maximal illitization rate with the presence of K in solutions. However, in real conditions, K diffusion in bentonite proceeds very slowly, which considerably retards the illitization.

In Sweden, Paleozoic sedimentary rocks with bentonite beds intruded by basalts were studied (Brusewitz, 1986). In the contact halo, with a thickness up to 100 m, thin beds of bentonite with a thickness up to 10 cm were illitized, with the illite content reaching 50–70%. In a 2-m thick bed, zoning is expressed in a gradual decrease of the share of illite layers in the mixed-layer minerals from the bed margins to its center. It is suggested that the illitization took place as a result of K diffusion into bentonite from sedimentary rocks containing potassic feldspar and mica. Due to the low rate of K diffusion, the central parts of the relatively thick bentonite beds were not subjected to illitization. The depth of K penetration did not exceed 1 m over the period of 36 m.y. during which the illitization took place.

Interpreting these data as applied to conditions of HLW storage, we may conclude that, even in a medium rich in K at temperatures up to 250°C, the probability of intensive illitization is very insignificant due to the very low rate of this process. Due to the decay of short- and long-lived radionuclides, a temperature of the bentonite buffer of 100°C can be sustained for a period of no more than 100–200 years. The combination of experimental and geological data does not allow us to suppose

that any substantial illitization could occur during this time. However, for an unambiguous conclusion to be drawn, it is necessary to carry out long-term experiments in an underground laboratory in conditions simulating the environment of future HLW repositories.

## WAYS OF IMPROVING THE ISOLATING PROPERTIES OF BENTONITE

In general, a long-term fixation of radionuclides in a limited volume of a geological medium can be provided with the aid of physical and (or) chemical isolation (Laverov *et al.*, 2001). The low water permeability of bentonite and the swelling-related ability to heal fractures are favorable for physical isolation. However, the possibilities of improving physical isolation by using finely dispersed bentonite and increasing the degree of its compactness are limited. Quartz sand added to bentonite for increasing the heat conductivity of the buffer inevitably increases water permeability, whereas the necessity of limiting the pressure of bentonite on rocks and containers with HLW limits the degree of bentonite compactness. Geochemical isolation of HLW presents considerably larger possibilities for increasing conditions of isolation.

Geochemical isolation can be provided at the expense of a low solubility of radionuclides in bentonite pore water and good sorption properties of bentonite. Changing the composition of bentonite and its pore water, we can decrease the solubility of HLW-bearing matrices, diminish the equilibrium concentration of radionuclides in pore water, and improve sorption properties of the buffer relative to certain radionuclides. The optimal composition of additives strongly depends on specific features of HLW. At present, SNF and solidified HLW with borosilicate and alumophosphate glasses used as immobilization matrices are subject to long-term disposal. In the future, crystalline ceramics of various compositions will most likely be used as matrices for certain groups of long-lived HLW (for example, actinides). Possible ways of improving the isolating properties of bentonite buffers for various forms of HLW are considered below.

The main factor in safe underground storage of SNF is the reducing medium (Laverov *et al.*, 2003). This is related to the fact that 95–98% of SNF consists of uraninite (UO_2), which serves as an immobilization matrix for all other radionuclides. As, in reducing conditions, groundwater (including pore water in bentonite) is saturated relative to uranium, uraninite interacting with such water preserves stability. However, unlike for natural uraninite, the possibility of creating reducing conditions in the radiation field of SNF is not clearly evident. Under the effect of radiation, radiolysis of pore waters can take place, with local oxidation conditions arising. If Fe (II) minerals are present, the oxidizers should be the first to be consumed for the oxidation:

$$2FeO + H_2O_2 \longleftrightarrow Fe_2O_3 + H_2O. \qquad (1)$$

The rate of movement of the oxidation front toward the SNF will directly depend on the Fe (II) content in bentonite. With the propagation of the oxidation front and the exhaustion of the reducers in bentonite, conditions favoring the dissolution of uraninite become dominating according to the following reaction:

$$UO_2 + H_2O_2 \longleftrightarrow UO_2^{2+} + 2OH^-. \qquad (2)$$
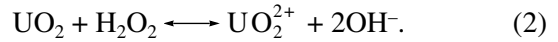
The realization of this reaction leads to the release of all the radionuclides contained in the SNF. It is possible to prevent the dissolution of uraninite by increasing the reducing capacity of bentonite at the expense of various additives. Ferrous pyroxenes, amphiboles, chlorites, phosphates of bivalent Fe (vivianite) and others can be used as such additives. However, the simplest and most efficient way to solve this problem would be addition of Fe particles (steel or pig iron) to bentonite as filings, shavings, or shot. Their oxidation should prompt the creation of a reduced medium according to the following reaction:

$$2Fe + 3H_2O \longleftrightarrow Fe_2O_3 + 3H_2. \qquad (3)$$
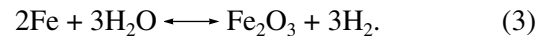
The use of such additives also allows us to increase the heat conductivity of bentonite and completely exclude quartz sand. The ways of improving the isolating properties of bentonite for vitrified HLW differ. The solubility of alumophosphate and borosilicate glasses used as conserving HLW matrices, unlike that of uraninite, does not depend on redox conditions. The main factors defining the corrosion intensity of radioactive glasses are temperature, pH, and the compositions of pore solutions. According to experiments, the rate of dissolution of alumophosphate glasses at a temperature of 120°C is 20 times higher than at 70°C (Zotov *et al.*, 1996). It is evident that the later canisters with vitrified HLW are destroyed, the lesser the intensity of the release of radionuclides into pore waters. As for the composition and properties of pore solutions of the bentonite buffer, their moderate alkaline composition and elevated Na concentrations undoubtedly favor a low solubility of vitrified HLW. With the aim of further decreasing the rate of dissolution of alumophosphate glasses, vivianite powder [$Fe_3(P_2O_8) \cdot 8H_2O$] can be added to increase the P concentration in the pore solution. In addition, the reducing capacity of bentonite increases on account of vivianite. The presence of vivianite will counteract radiolysis and the release outside the bentonite buffer of radionuclides possessing variable valency and an elevated migration ability in oxidizing conditions (Np, Tc, and Se).

During interaction of groundwater with borosilicate glasses, the incongruent leaching of elements takes place. Here, boron and sodium have an elevated rate of leaching. In this case, the porosity of glasses increases, which fosters an increase in the area of their interaction with water and the release of radionuclides. As noted above, an elevated Na concentration in the pore solution is favors the corrosion resistance of glasses. The effect of this factor can be enhanced owing to elevated

B concentrations by adding Na borate, for example, borax [$Na_2B_4O_7 \cdot 4H_2O$] to bentonite.

The possibilities for improving the sorption properties of bentonite by using various additives are very great. Experience in studying specific features of the U distribution by fission track radiography shows that, in the presence of a water solution, uranium is actively redistributed in rocks, accumulating in sorbent minerals. Such minerals include leucoxene, formed after Ti-bearing minerals; Fe oxides and hydroxides; and organic matter. Even if the content of these minerals does not exceed 1%, they contain the main mass of uranium. The lower the content of sorbent minerals in the rock, the higher the U concentration in these minerals. It can be supposed that other actinides and Tc will behave in the similar way. Weathering crusts on basic rocks are characterized by a high concentration of sorbent minerals. Products of weathering of basic rocks always contain large amounts of finely dispersed leucoxene and Fe hydroxides, retaining the main mass of uranium. Studying the possibilities of the use of weathering crusts for purification of contaminated groundwater, we tried to assess the sorption properties of secondary minerals in extensively weathered volcanic rocks (Omelianenko *et al.*, 1995). The studies showed that the sorption properties of weathering crusts on volcanic rocks are very good and are characterized by a wide range of values. For Cs and Sr, these properties are defined by the contents of such secondary minerals as montmorillonite, chlorite–vermiculite, and chlorite–montmorillonite; for uranium, Fe and Ti hydroxides. By adding extensively weathered basic rocks to bentonite, we can considerably improve the sorption properties of buffers without deteriorating other characteristics. The ideas presented on ways of improving the isolating properties of a bentonite buffer undoubtedly require further development and experimental confirmation.

CONCLUSIONS

1. In underground HLW repositories, an engineered barrier such as a bentonite buffer is capable of retarding the input of highly mobile radionuclides into groundwater for several thousand years and completely ensuring the isolation of actinides, the components most hazardous for the environment.

2. The most important properties of bentonites are their low water permeability and ability to heal water-conducting fractures and protect volumes with HLW from the impact of tectonic movements.

3. The isolating properties of bentonite can be considerably improved by introducing additives increasing its reducing and sorption capacities and fostering a decrease in HLW solubility.

4. The illitization of montmorillonite is the only process that can lead to a loss of the high isolating properties of bentonite. The most important factors influencing the rate of the illitization are temperature and potassium concentration in pore solutions.

5. On the basis of experimental data and natural observations, we established that, within the range of conditions of HLW repositories, the illitization cannot significantly influence the isolating properties of the bentonite buffer.

6. Taking into account the technological simplicity and economic efficiency of the bentonite buffer, it would be reasonable to specify the use of bentonite in all designs of underground HLW repositories. Enhanced safety of these repositories can be attained, first of all, by increasing the thickness of the bentonite buffer and introducing additives improving the reducing and sorption properties of the buffer.

ACKNOWLEDGMENTS

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