Chapter 2
Development of the Nano-mineral Phases at the Steel-Bentonite Interface in Time of the Evolution of Geological Repository for Radioactive Waste

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2.1 Introduction

Today, the optimal prototypes for geological storage (GS) facilities (GS) that are planned to be located in crystalline rocks of Chernobyl Exclusion Zone or adjacent regions of Ukraine are geological repositories (GR) of high-level waste (HLW) and spent nuclear fuel (SNF) that are situated in Precambrian crystalline rocks (granites) of Sweden and Finland [34]. The GR safety concept is based on the usage of multiple barriers in the disposal systems that perform protective functions over different time periods. Standard design of the storage facilities foresees the following barriers: matrix with HLW, metal canister for the matrix, clay buffer between the canister and the containing rock, and filler for main tunnels and other underground workings (the backfill) – engineered barrier system (EBS) – including the host rock in contact with or near the EBS and the environment as a whole that separates EBS from the geosphere and biosphere. The canisters relate to the most important elements of EBS, which are usually made of iron alloys (carbon steel, cast iron, stainless steel, etc.) [37]. A main function of the clay buffer is to isolate the waste container from the environment due to its high ability to retain radionuclides in the engineered barrier system (EBS) and to prevent entry of groundwaters [9].

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O. Fesenko, L. Yatsenko (eds.), *Nanocomposites, Nanostructures, and Their Applications*, Springer Proceedings in Physics 221,
https://doi.org/10.1007/978-3-030-17759-1_2

In the conceptual decisions of a number of GR, clay buffer material is considered to be natural bentonite (montmorillonite clay) of the MX-80 grade produced in states of Wyoming and North Dakota (USA), as well as pure sodium or calcium forms of montmorillonite. Its composition contains up to of 75% Na-montmorillonite, 15% quartz, 5–8% feldspar, 1% carbonate, 0.3% pyrite, and 0.4% C org. Numerous bentonite clay deposits are situated in Ukraine, namely, in Cherkaska, Vinnytska, Zakarpatska, and Chernivetska Oblasts and other parts of the country. Chemical and mineral composition, crystallochemical features, and ion-exchange properties have been studied for samples of some repositories [8].

Steel packaging provides radionuclide isolation from groundwater flow for one thousand years, but bentonite buffer may increase this period, at least by one order of magnitude [20, 41]. At the same time, the isolating properties of the bentonite buffer in a multibarrier disposal system can change over time and negatively affect the safety of the GR [49]. Three stages in GR evolution are distinguished:

1. Early aerobic (with the presence of oxygen) phase (100–200 years; the stage where waste is disposed of into storage facilities and some period after its closure)
2. Transition from aerobic to anaerobic phase (up to 1000 years)
3. Long-term anaerobic phase (more than 10,000 years) [26]

   Saturation of the water repository may occur in both phases (transitional and long-term anaerobic), and it depends on the rate of groundwater filtration.

The aim of the review is to analyze the phase transformation of bentonite clay at the steel-bentonite interface in the radioactive waste geological repository system and to evaluate the impact of newly formed mineral phases of corrosive and geochemical origin on the isolating properties of bentonite buffer and the long-term safety of the GR as well.

2.2 Characterization of Primary Nanoscale Structures of Corrosive Origin

The primary mineral phases formed on the steel surface during the corrosion process are Fe(II)-Fe(III) layered double hydroxides (Fe(II)-Fe(III) LDH of Green Rust) and ferrihydrite (Fh). The main factors that determine the chemical composition and structure of such primary particles are the anionic composition of dispersion medium, the presence of ferric or ferrous aqua hydroxyl forms, and the reductive-oxidative conditions in the system.

2.2.1 Fe(II)-Fe(III) Layered Double Hydroxide (LDH) Structures, the Mechanism of Their Formation and Their Phase Transformations

Fe(II)-Fe(III) LDH structure consists of hydroxide layers formed by $Fe^{II\text{-}III}(OH)_6$ octahedrons. Water molecules and anions that are coordinated by the hydroxide layers, which provide the compensation of ferric charge in the crystal lattice and give electroneutrality to the entire structure of the mineral, are located in the interlayer space of Green Rust. Depending on the kind of coordinated anions in the interlayer space, Fe(II)-Fe (III) LDH are referred to the first or second types, which determine their crystallochemical properties: the ability to gradually change Fe^{2+}/Fe^{3+} cation ratio in the Green Rust I lattice and constancy of this ratio in the Green Rust II structure [44]. Thus, the typical Fe(II)-Fe (III) LDH which can be formed when the steel surface is in contact with groundwater is the hydroxycarbonate Green Rust-(CO_3^{2-}). Its crystallochemical formula can be written as $Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3{\bullet}nH_2O$, where $n = 2$ or 3. The sample of Fe(II)-Fe(III) LDH which corresponded to the second type is hydroxysulfate Green Rust-(SO_4^{2-}). Its crystallochemical formula is written as $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4{\sim}8H_2O$ [46].

The Green Rust-(CO_3^{2-}) formation occurs through several mechanisms: (1) chemical interaction of ferrous aqua hydroxyl forms and oxygen-containing carbonate species under oxidative conditions [47], (2) their interaction with pre-deposited ferric hydroxide, and (3) solid-state interaction of ferrous and ferric hydroxides in the presence of oxygen-containing carbonates species. At the same time, the formation of Fe(II)-Fe(III) LDH structures can occur via coagulation of so-called green complexes and is associated with hydrolysis and polymerization of ferric and ferrous aqua hydroxyl forms in the reaction area near the steel surface [1]. Green Rust phase formation occurs via topotactic transformation without oxidative destruction of a natural amakinite $Fe(OH)_2$ in the presence of ferrous cations and SO_4^{2-} or CO_3^{2-} anions [2].

Kinetic regularities of Fe(II)-Fe(III) LDH formation on the steel surface was reported in the work of [30]. According to obtained data, the relative quantity of Green Rust phase did not stand constant. It depended on chemical composition of the dispersion medium and reductive-oxidative conditions at the interface between the steel surface and dispersion medium. Hence, it may increase or decrease due to the phase transformation of Green Rust into other ferric oxygen-containing mineral phases: ferrihydrite, ferric oxyhydroxides, or magnetite. The main criteria which determined the process of Green Rust transformations are the redox potential (ROP) of the system, the chemical composition of the dispersion medium, the pH value, temperature, and, probably, the presence of various microorganisms.

2.2.1.1 "Green Rust-Ferrihydrite" System (Green Rust-Fh)

The study of the process of ferrihydrite formation via oxidation of ferrous hydroxide water suspension in the presence of HCO_3^- anions (in the range of the pH value from 7.5 to 9) shows that Fh is a transitional product between Green Rust-(CO_3^{2-}) and goethite α-FeOOH [15]. Phase transformation of Green Rust-(Cl^-) into ferrihydrite may be estimated as a result of ferrous hydrated cations and Green Rust itself fast oxidation [18].

At the same time, the transformation of ferrihydrite as well as mixed oxidized forms of Fe(III)-Green Rust into ferrous cations is possible in natural systems [16].

2.2.1.2 "Green Rust-Goethite" System

Formation of α-FeOOH goethite during oxidation of Fe(II)-Fe(III) LDH by dissolved oxygen was shown for the mineral phases of Green Rust-(SO_4^{2-}), Green Rust-(Cl^-) [18], and Green Rust-(CO_3^{2-}) [55]. The mechanism of such transformation went through the stages of Green Rust dissolution and re-precipitation accompanied by subsequent deposition of well-ordered ferric oxyhydroxide structures [7]. At the same time, Green Rust-(CO_3^{2-}) of corrosive origin turns into α-FeOOH goethite in 0.1 M solution of $NaHCO_3$ without intermediate formation of the ferric hydroxide [11].

Growth of redox potential from (−0.45) to (−0.3) V [55] is observed in the solution when Fe(II)-Fe(III) LDH phase was transformed into goethite α-FeOOH (pH value ~9.5). Usually, the formations of goethite particles lead to decrease in the pH value of the dispersion medium.

2.2.1.3 "Green Rust-Akaganeite" System

According to published data, the determinative condition for the transformation of Green Rust into akaganeite β-FeOOH is the relatively high concentration of dissolved ferrous and chloride species [36].

2.2.1.4 "Green Rust-Lepidocrocite" System

The formation of lepidocrocite γ-FeOOH under the slow oxidation of Green Rust (pH ~ 7.0) occurs in two stages [40]. The first stage gives place to partial oxidation of ferrous cations in the Fe(II)-Fe(III) LDH structure, hydrolysis, and re-precipitation of ferric cations into poorly crystalline hydrated ferrihydrite phase. Here, Fh can quickly react with ferrous cations and turn into Green Rust again. The reaction order of the secondary formation of Green Rust is limited by the deposition of Fh and concentration of ferrous cations. Re-precipitation of lepidocrocite particles occurs at the second stage.

During oxidation of Green Rust, magnetite as an intermediate phase may be included into Green Rust crystal lattice. Further oxidation of the system involves the destruction of both mineral phases and the following precipitation of needlelike γ-FeOOH particles. Transformation of natural fougerite into lepidocrocite when the last was contacting with dispersion medium in the presence of high quantities of carbonates, aluminum aquaforms, and silicate species was shown in [52].

2.2.1.5 “Green Rust-Feroxyhyte” System

A mixture of weakly crystallized ferrihydrite and feroxyhyte (ferric Green Rust) structures was obtained during phase transformation of Green Rust-(CO_3^{2-}) of corrosive origin under oxidation conditions of the system [11].

2.2.1.6 “Green Rust-Magnetite” System

Formation of Fe_3O_4 magnetite in aqueous suspension of Green Rust is also associated with dissolution and re-precipitation of the unstable structures Fe(II)-Fe(III) LDH [21]. At the pH value 9 and the ferrous/ferric ratio 0.5 and 1, the formation of hexagonal particles of GR(SO_4^{2-}) lasts ~ 6 min, and then they quickly transform into magnetite. At the same time, Green Rust-(SO_4^{2-}) phase remains stable when the pH value decreases to 7. Moreover, when the ferrous/ferric ratio equals 0.5, the magnetite phase is not formed. Decrease of pH < 7 leads to dissolution of Green Rust structure and saturation of the dispersion medium with ferrous cations. In time ferrous species are gradually oxidized and precipitated as the ferric oxyhydroxide phases [31].

The main results of modern studies related to Green Rust synthesis under laboratory conditions, its structure, properties, as well as its formation in the natural environment and interaction with various chemical species are summarized in the review papers [5, 6]. So, the formation of Green Rust structures on the steel and iron surfaces, due to its strong reductive properties, sorption, and chemical activity in respect to high toxically chemical elements and compounds, together with the ability to phase transformation accompanied by involvement of different cations, may be an important additional contribution to fixation of radionuclides in case of the steel vessel usage in geological repository of radioactive waste.

2.2.2 *Phase Transformation of Ferrihydrite*

Ferrihydrite (Fh) is another primary mineral phase that can be formed on the steel surface via the corrosion process. It belongs to the Fe(III) (oxy)hydroxysalt group and is closely connected to the iron oxides by supergene phase formation processes [39]. Synonyms of ferrihydrite are “hydrated oxide of ferric iron” (HFeO), "amorphous hydroxide of ferric iron," "colloidal hydroxide of ferric iron," and "$Fe(OH)_3$."

So, ferrihydrite as a metastable ferrous-hydroxide phase is easily transformed into more stable disperse minerals, such as goethite and hematite [12]. The main factors influencing the chemical mechanisms of the ferrihydrite formation and the composition of the transformation products are chemical composition and pH value of the dispersion medium, temperature, reductive-oxidative conditions, etc. [10]. Because the phase transformation of ferrihydrite into goethite belongs to the typical processes in natural systems, it is extensively covered in the literature sources.

The main mechanism for such a transformation is dissolution/re-precipitation that is catalyzed by ferrous cations of aqueous medium [50]. Dissolution of ferrihydrite and its precipitation into α-FeOOH in the presence of ferrous cations completes under standard conditions within 24 h, while ferrihydrite remains stable for a long time when the solution is free of ferrous cations. Taking into account that solubility of Fh (10^{-39}) is higher than solubility of its transformation products – α-FeOOH (10^{-41}) and α-Fe_2O_3 (10^{-43}) – their formation via dissolution-re-precipitation mechanism is quite expectable.

In general, two- and six-line ferrihydrites are formed by hydrolysis of ferric cations and polymerization of their dimeric species $Fe_2(OH)_4^{4+}$ at $pH < 4.1$, whereas the most favorable conditions for Fh transformation are pH values 4 and 12, when corresponding complexes $Fe(OH)_2^{+}$ and $Fe(OH)_4^{-}$ are formed in the water medium. According to other data, the optimal conditions for ferrihydrite transformation into goethite correspond to $pH = 9$ and $T \sim 40$ °C, where the polymerization of ferric hydroxocomplexes may occur [17].

2.3 The Study of Corrosion Processes on the Surface of Steel Containers

Much of the world canisters for vitrified HLW are made of steel containing <0.3 wt.% carbon, where Mn, Si, Cu, Cr, Ni, Mo, W, V, and Zr may also be present among additional chemical components. The guaranteed lifetime of such kind of canisters is determined within 1000 years, and the main destructive process for them may be corrosion [27]. The main reasons for the corrosion of steel are its chemical composition; the physical-chemical conditions in the geological repositories, such as temperature; oxidation potential; alkalinity and mineralization of groundwater; and the presence of bentonite buffer and other structural materials in the repository system, in particular, cement [9].

Oxidizing conditions in the RW repository will be kept several hundred years at the stage of waste deposition and some period after repository closure. After that, the repository will be characterized by anaerobic reduction regime, set as a result of reactions in EBS. Generally speaking, aerobic corrosion has very limited significance for analyzing multilayer container behavior, because it takes place during the relatively short operational stage of the repository and some period after its closure. During this time, only the outer packaging can be damaged. After all oxygen has been used in the ESB reduction-oxidation reactions, anaerobic corrosion of the container in a water-saturated environment starts to play the main role. These conditions are corresponded by two types of steel container corrosion that change its properties, which can cause deterioration of metal functions and the whole barrier system. Also, corrosion can be divided into general and local and crevice corrosion. General corrosion occurs throughout the surface and at a constant speed. In aqueous media, this is an electrochemical process having at least one oxidation reaction: $(M^{X+}, xe^-) \rightarrow (M^{X+}) + x(e^-)$ and cathode reduction: $Ox^{q+} + x(e^-) \rightarrow Red^{(q\text{-}x)+}$, where Ox and Red are oxidized and reduced forms of elements. Under aerobic conditions, cathode reaction runs according to the scheme:

$$O_2 + 2H_2O + 4e^- \rightarrow 4O,$$

while as in anaerobic conditions, it occurs with hydrogen formation:

$$H_2O + e^- \rightarrow 0.5H_2 + OH^-.$$

Thickness of metal would decrease in time, if corrosion products are soluble in water, or the surface iron oxide layer is formed. In other cases, the overall thickness does not change. In the first case, active corrosion process is accompanied by transfer of charges and matter, and in the second one, passive corrosion process leads to the appearance of dense protective film of newly formed mineral phases. So, at the near-neutral pH values, the formation of protective layer is an important aspect of steel corrosion in water solutions.

Generally, the protective layer on the steel surface can affect SNF container corrosion process in a different way:

- To limit transfer of outer matter and reagents to corroding surface and, correspondingly, corrosion products from corroding surface
- To protect the steel surface against the following dissolution (if the film has no conductive properties)
- To change anode and cathode areas and their ratio (if the film is conductive enough to maintain electrochemical reactions)

Among effects listed above, surface protection and limitation of matter transport to the surface and from it may be called. In both cases, we achieve decrease of corrosion process, as it was proved by experimental work, including obtained in underground research laboratories.

Numerous works were devoted to the study of carbon steel behavior under conditions of GR. Long-term experiments (6000 h) under conditions simulating HLW disposal facility of clays showed that the rate of steel destruction in water at $T = 90$ °C is less than 10^{-3} cm per year [13], whereas by the contact of seawater (at $T = 80$ °C) with steel under aggressive conditions, it is slightly higher – $2{\cdot}10^{-3}$ cm per year [48].

In the first decades after the repository closure and its filling with water under aerobic stage, the process of local container corrosion with microfracture formation under the influence of current will dominate. In the ongoing anaerobic stage, the main degradation reasons will be general container corrosion and its destruction due to the appearance and action of hydrogen [37]. Usually, carbon steel has high corrosion rate (0.06 mm/year) within the aerobic stage when it is contacting with water having 2.5 g per liter mineralization that is achieved in the presence of Na^+, Ca^{2+}, Cl^-, $SO_4{}^{2-}$, and sulfuric and carbonic acids. Herein, the corrosion rate is increased by 30–50 percent when the temperature increases from 30 to 50 °C [59].

The rate of corrosion of low carbon steel in 1 M NaCl solution in the pH range from 8.4 to 11 is independent of alkalinity. It decreases from 30 μm/h, at the beginning of the experiment, to 1–3 μm/h after 4600 h of the contact of steel with the solution. Under anaerobic conditions, the rate of corrosion becomes less than 5 μm/h after 300–600 h of contact of the steel surface with water that equilibrated with bentonite [43].

According to other data [37], at moderate temperatures in anaerobic conditions, corrosion of carbon steel occurs at a rate of the first microns per year. Thereat, radiation does not significantly influence the rate of corrosion, and it can lead to slight increase or even decrease the corrosion process, but under large radiation loads a negative accelerating effect on the destruction of steel becomes more evident.

Stainless steel is more stable in comparison to carbon steel. Its average corrosion rate under hypothetical RW repository conditions is estimated at 0.01 μm/h, expected corrosion is 31.8 mm per 1000 years. So, the real values of the corrosion rate are 2–20 mm in 10,000 years [60].

For Belgian HLV repository situated in Boom clay formation, the corrosion rates of stainless steel lies in the range from 0.003 to 0.15 μm/h [35]. Its total corrosion in water equilibrated with cement is 0.03–0.5 μm/year in aerobic medium and 0.001–0.01 μm/year under anaerobic conditions. Corrosion of steel slows down during the time when the pH of water medium grows, but it increases when temperature, oxidation potential, and water mineralization rise.

As it was shown in the works [25, 54], the rate of anaerobic corrosion of steel during first tens of hours reached 70 μm/h, and next it decreased up to the first microns per year due to the formation of a protective layer consisting of corrosion products – iron oxides (magnetite, maghemite) and carbonates (siderite $FeCO_3$). Whereas the increase in pH value of water led to reduction of the rate of corrosion of steel and hydrogen generation by two orders of magnitude – from several dozens to one tens of liters per square meter per year – irradiation caused its increase [45]. Temperature accelerated the formation of protective layer on the steel surface in contact with 0.1 M ($HCO_3{}^- + CO_3{}^{2-}$) solution [19].

A corrosion layer formed by the similar structures was obtained in an 8-month experiment by the contact of steel and argillites at 90 °C under anaerobic conditions [13]. External dense layer of iron carbonate ($FeCO_3$) corrosion products and an internal interchange layer of iron oxides and silicates can be highlighted.

The corrosion rate of steel in contact with water medium in the presence of bentonite was decreased over time, reaching stationary state of 1–3 microns per year. Such result was achieved under experimental conditions after hundreds of hours when the steel surface was placed into bentonite suspension or water equilibrated with bentonite, as well as after one thousand hours in contact of the steel with compacted bentonite. The increase in the pH value suppressed the steel corrosion because the poorly soluble ferric hydroxide phases were formed on the surface of the steel container.

Thus, the corrosion rate is strongly dependent on the physical-chemical properties of the metal and the determinative environmental factors (Eh-pH value, temperature, the chemical composition and total mineralization of groundwater, etc.), together with processes taking place in the EBS, for instance, the formation of iron oxide and hydroxide particles in the corrosion layer.

At the aerobic stage (in the presence of oxygen) following waste disposal into storage facilities, corrosion of steel slows down in time due to increase in the pH value, but if the temperature, oxidation potential, and water mineralization grow, the corrosion rate would increase. So, the main criteria in reducing corrosion rate at this stage are the formation of protective iron oxide layer on the steel surface, high pH values in contact with bentonite, and when the temperature is growing.

At the beginning of the anaerobic period, a previously formed film consisting of a porous layer of ferric-ferrous corrosion products (magnetite or other spinel ferrite phases) may be present on the steel surface. Such structures will have the same effect on the corrosion process as a porous film formed in anaerobic corrosion. Also, if the main protective function of spinel ferrite film is to block the surface only, the appearance of primary porous film under anaerobic conditions would not be important. However, if the corrosion layer limits the matter transfer in the direction to and from the steel surface, the thickness of the previously formed ferric oxyhydroxide film would be important for the following overall thickness of the film, and, thus, it determines the rate of corrosion.

2.4 The Phase Transformation of Bentonite Clays at the Steel-Bentonite Interface Under Conditions of Geological Repository

Bentonite belongs to montmorillonite clays that are characterized by high sorption capacity, plastic property, and swelling when they are saturated by water. The specificity of montmorillonite structure lies in the presence of a three-layer package including tetrahedron-octahedron-tetrahedron. The bonding between all the packages is weak, and water can penetrate into this interlayer space causing strong swelling of the mineral. Its capacity of cation exchange reaches 80–120 mg-eq per 100 g. Montmorillonite content in bentonite reaches 55–95%, and hydromica, chlorite, kaolinite, and quartz are present in their composition as additional minerals.

Genetically the largest deposits of bentonite are formed via decomposition of volcanic ash and tuffs under subaqueous conditions [4, 23].

The transformation of bentonite buffer at the initial stage of GR evolution depends on the degree of its saturation by water: first, dehydration due to bentonite heating in the presence of radioactive waste and, second, rehydration due to the penetration of groundwater into the GR. When bentonite is saturated with groundwater, it swells and fills empty spaces between the buffer, canister of waste, and rock cracks near to the buffer.

Mineral composition of bentonite clays and their isolating properties can change due to the influence of high temperature, chemical composition of groundwater, products of dissolution of the radioactive waste, related microbiological processes, and chemical composition of corroded canisters, which are made of steel or other materials. Complex influence of these factors and the possible synergistic effect cannot be predicted. Chemical and physical-chemical evolution of the buffer is regulated by thermodynamic conditions in GR system that contributes to form and transform new nanosized minerals and is closely related to the quantitative ratios of the dispersed phase and the dispersion medium (solution) [29]. Duration of thermal, hydrodynamic, and mechanical processes can be determined from several hundred to 1000 years, but mineralogical-geochemical reactions caused by corrosion of canisters or products of destruction of structural and associated materials will occur during the entire time of GR evolution.

Temperature is one of the key factors that affect the rate and degree of transformation of smectite (montmorillonite) mineral phase. At the same time, it is well known that at the beginning of evolution, the temperature in GR will be relatively low (<150 °C), moreover it is predicted the trend to its steady decrease. According to the prognosis [33], the maximum expected temperature in GR will be 45.5 °C within 1000 years, and after 10,000 years 20.5 °C. Consequently, it is likely that chemical composition of the water environment will control bentonite buffer evolution with respect to transformations of the mineral phases [51].

It can be assumed that the chemical composition of porous water in bentonite buffer should be influenced by diffusion of ferric/ferrous aqua hydroxyl forms, obtained during canister corrosion, and other compounds that went from containing rock. At the same time, bentonite is characterized by high acid-alkaline buffer capacity that is provided by protonation-deprotonation of surface hydroxyl groups. As a result, the chemical composition of bentonite porous water will remain stable for very long time [14], and it is almost similar to the composition of groundwater in contact with it [38]. Moreover, if bentonite contacts with groundwater from granites located in GR, the buffer sorption capacity and clay's ability to cation exchange practically would not decrease. So, it should promote sorption retardation of individual forms of radionuclides.

Probably, Na-form of montmorillonite will be changed to its calcium form during evolution of the geological repository, but to date, there has been no experimental evaluation of the actual speed and extent of these changes. It is expected that the transformation of bentonite into its Ca-dominating composition will contribute to long-term stability of the buffer, since calcium-containing smectite is characterized by high water-holding (isolating) properties, high sorption capacity, and resistance to dissolution when it is in contact with strongly alkaline groundwaters. Natural bentonites (MX-80, Cherkaskii) contain not only Ca^{2+} and Na^{+} cations but also cations Mg^{2+} and K^{+}, which have low effect on the cation exchange process; therefore, it is almost impossible to achieve mono-cation composition of bentonite buffer under the GR conditions.

One of the important questions concerning the phase transformation of bentonite and, consequently, changes in its physical and chemical properties, are processes of interaction buffer with corrosion products of steel container. When bentonite buffer is saturated with groundwater and contacted with steel surface, mineralogical changes of bentonite can occur by two ways of saponitization and/or beidellitization according to the following scheme, low-charged montmorillonite → high-charged beidellite + saponite + quartz [32, 56], and or illitization [53].

Saponitization does not critically influence the isolating properties of the buffer, because newly formed saponite, likes bentonite, is capable of swelling, and, so, it can be used as a buffer material too; however, the formation of beidellite may critically affect the isolating properties of the buffer.

Thermodynamic calculations suggest processes of montmorillonite dissolution and precipitation of ferric-/ferrous-enriched minerals under conditions of the GR. The most probable products of montmorillonite transformation are ferrum smectites (e.g., Fe-saponite), berthierine, or chlorite, which was confirmed experimentally [58]. At the same time, the transformation of montmorillonite in contact with the steel surface at $T > 50$ °C remains controversial, and the obtained results are contradictory. Most of them were reported according to the French Radioactive Waste Management Program [32]. Thus, as it was shown in some experiments, the newly formed iron-oxide phases were not detected at $T = 80$ °C; in others, only corrosion products, magnetite, hematite, and goethite, were found; in the third, berthierine, nontronite, and saponite were found. Formation of chlorite and saponite, which corresponds to smectite characterized by high ferrum content, was reported at temperatures 250–300 °C. But the general conclusion regarding the processes of bentonite transformation in GR conditions in contact with the steel surface is that under the isothermal conditions the ratio of dispersed phase/dispersion medium is in the inverse correlation, depending on the change of mineralogical composition of the bentonite buffer. In particular, according to [24], the reductive ability of bentonite to swell due to its interaction with the container metal (iron) remains limited in space to several centimeters over a long period of time. The main source of the ferrum is newly formed siderite particles and ferrous cations from porous water of unchanged buffer.

According to the results of the long-lasting (8.2–10 years) experimental modeling of the phase transformation of MX-80 bentonite in contact with iron (cast iron) placed in a copper container, diffusion front of ferric/ferrous species into bentonite does not exceed 7–8 mm from iron surface [28]. Saturation of the initial solution (0.5 M NaCl) with Mg^{2+}, Ca^{2+}, and ${SO_4}^{2-}$ ions resulted in increase of solution alkalinity up to 8 and formation of the following mineral phases on the bentonite surface: gypsum, quartz, aragonite, and hematite. At the same time, bentonite in contact with cast iron was cemented to a certain extent due to increase of the content of illite fraction.

Converted montmorillonite was characterized by decrease in the ability to swell and swelling pressure, but its hydraulic conductivity practically was not changed. In general, ferrum was incorporated into the montmorillonite structure, whereas the silicon oxide is released from it. The amount of exchanged iron in the bentonite structure was increasing in direction to the cast iron. The redox conditions in external solution and porous water were strongly reducing within 8.6 years. The gas phases contained H_2, which probably evolved as a result of the corrosion of cast iron cylinders, and CO_2, which source had been the calcite dissolution.

At the same time, as it has been shown in serial IAEA tests, the transformation of bentonite occurred more intensively when the iron to clay ratio and pH value of dispersion medium were simultaneously increasing. Montmorillonite in contact with steel lost its swelling ability and turned into another clay containing phases of serpentine and berthierine when it was kept in 0.3–0.6 M NaCl solutions and, partly, in 0.1 M $NaHCO_3$ solution. Silicon oxide was released as a result of montmorillonite transformation.

In samples that were kept in distilled water and in 0.05 M solution of sulfate in distilled water solution, a montmorillonite fraction was isolated that contained magnetite and pyrite admixtures. In general, the montmorillonite component of bentonite MX-80 after 8–10 years of contact with iron practically did not change. There was also no evidence of complete montmorillonite transformation into non-swelling mineral. But if the pH value and content of ionized iron at the iron-bentonite interface are increased, such transformation would be accelerated.

Taking into account the presence of K^+ cations in the granite groundwater (mainly because of feldspars presence in granites), which have the largest energy of absorption by montmorillonite in comparison to other cations [3], the illitization of bentonite buffer can become a real threat to the safety of the storage facility. The gradual transformation of montmorillonite into illite takes place by replacing interlayer Na^+ or Ca^{2+} cations with K^+. At that, the mixed layers of illite/montmorillonite are formed as a result of illitization process. In this case, pure illite does not have the ability to swell, and for the mixed illite-montmorillonite layer, such ability is significantly limited. In addition, gradual changes in the mineralogical characteristics and physical-chemical properties of the buffer, such as the specific surface area, cation exchange properties, hydraulic conductivity, etc., have been observed.

At the same time, kinetics of the transformation of montmorillonite into illite, performed for KBS-3-type repository conditions [42], has proved practical impossibility illitization process because of low temperature in the repository. At temperatures below 100 °C, the rate of bentonite transformation will be small and will not lead to loss of buffer's isolating properties during the period when the buffer should perform safety functions. However, taking into account that the process of montmorillonite into illite transformation is also influenced by many other factors, such as the degree of bentonite saturation with water or ratio of dispersed phase to dispersion medium, pH value, and concentration of alkaline cations (in particular,

K^+), evaluation of illitization process probability should be carried out separately for each GR site.

Detailed investigations of the thermal transformation of bentonite into illite were performed for various samples in a wide range of physical and chemical conditions. So, the results of the study of illitization in the natural systems have proved [22] that montmorillonite can be existed in stable state for more than one million years at temperatures below $T = 100$ °C. The authors of the work [22] have concluded that noticeable illitization at temperatures of 100–130 °C will not occur even for 10 years. The review paper [57] that is devoted to the study of bentonite stability at $T < 100$ °C, assumed that the transformation of smectite into illite depends on temperature, time, and concentration of K^+ in porous water. At the same time, it was reported that in wet conditions at $T = 120$ °C, no significant changes in hydraulic and mechanical properties were detected for bentonite, whereas noticeable effects of cementation and possible illitization were observed only at $T > 150$ °C. In dry conditions, montmorillonite (bentonite) remains stable up to $T = 300$ °C.

According to prognostic estimates made for the state of Olkiluoto geological repository (Finland) [29], the processes of illitization and cementation of bentonite buffer by silicon dioxide or iron oxides are unlikely due to the current and expected natural conditions (composition and localization of groundwater and possible temperature changes). However, the usage of external materials in the construction of repository, similar to cement-based fillings, can lead to the release of K^+ and SiO^{2-} and increase pH > 13, which also can accelerate cementation/illitization processes and may start other phase transformations such as saponitization and/or beidellitization. In particular, it is believed that the formation of zeolites occurs even at a pH < 11. It is expected that initial leaching products in the repository will have the pH value ~ 10.5–11.5, but further redistribution of the substance under such conditions is not determined.

Thus, in spite of the prognostic estimation that does not show the destructive influence of the container shell on the physical and chemical properties of the buffer within 105 years, the phase transformation processes at the steel-bentonite interface should be taken into account when calculating the isolating characteristics of the buffer material. In particular the potential impact of ferrous aquaforms on the sorption centers of bentonite should also be considered during GR creation. But preliminary experimental results indicate that front of the ferrum transfer from the container surface will not penetrate deeply into the buffer for a long time. On the contrary, the corrosion process zone and formation of highly dispersed and sorption-active particles of ferric/ferrous hydroxides and oxides can play the role of effective sorbents and reducing agents (in the case of formation of Fe(II)-Fe(III) LDH and magnetite). This role helps to receive redox conditions aqua(hydroxo) forms of uranium (VI), plutonium, technetium, and selenium.

2.5 Conclusion

1. Bentonite clay that is usually used as a buffer material in the design of geological repository of radioactive waste can change its mineralogical-geochemical, geomechanical, and hydraulic properties under conditions of the repository evolution because of the influence of a number of factors that can significantly decrease the insulating properties of the buffer. Special attention is needed in the analysis of processes that take place at the interface between bentonite buffer and the surface of steel container. According to thermodynamic calculations, the most probable products of the mineralogical transformations in the disposal facility will be ferrum smectite (Fe-saponite), berthierine, or chlorite.
2. Due to the contact of bentonite buffer saturated by groundwater and the steel surface, mineralogical changes of bentonite can be directed to saponitization, beidellitization, or illitization. Whereas saponitization is not critical for buffer's isolating properties because of the saponite's ability to swell, the formation of beidellite may lead to critical decrease in insulating properties of the buffer.
3. One of the main processes that can become critical for bentonite's isolating properties is the illitization of montmorillonite. Its rate depends on temperature, chemical composition of the aqueous medium (pH value and concentration of alkaline cation, especially K^+), degree of bentonite saturation with water, and the ratio between dispersed phase and dispersion medium. While a preliminary estimate shows impossibility of buffer illitization due to low temperature, the usage of external building materials, in particular, cements, may shift the balance and causes transformation of bentonite into illite.
4. Preliminary studies have shown that diffusion of the ferrum-containing components into bentonite is limited to a few centimeters for a long time. Moreover, the formation of the primary ferrum-bearing structures such as Green Rust and ferrihydrite on the steel surface and their transformations into the sorption-active oxyhydroxides and oxides can become an additional mechanism for the fixation of radionuclide's mobile forms and their reduction into less mobile and toxic state.
5. In order to predict the long-term stability of the bentonite buffer and assess the safety of the storage facility, taking into account mineralogical-geochemical processes caused by corrosion of the container, and the possible transformation of bentonite buffer under conditions of the geological repository, the integral experimental research should be introduced into the future concept and program of creation of a geological repository in Ukraine. One of the important aspects of such study should be to analyze the phase formation processes at the steel-bentonite interface and to determine the effect of newly formed nanosized structures on the process of radionuclide migration and isolating properties of buffer material as well.

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