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PHASE FORMATION PROCESSES IN STEEL – BENTONITE INTERFACE IN THE CONDITIONS OF RADIOACTIVE WASTE GEOLOGICAL REPOSITORY EVOLUTION

The review work presents the analysis of up to date publications, including original ones, devoted to studying of nano-sized mineral phase formation processes on the interface surface of a bentonite buffer, mineral composition of which contains montmorillonite (70-90 mass%), and a steel container in the conditions of radioactive waste geological repository. Probable changes of mineralogical, geomechanical and hydraulic properties of bentonite during evolution of geological disposal have been considered. It is expected that ferric saponite, berthierine or chlorite may be formed as a result of phase transformations of the buffer material. It has been demonstrated that saponitization of the buffer will not significantly decrease its isolation properties due to ability of saponite to swell and similarity of its physicochemical properties to montmorillonite, while montmorillonite illitization may cause buffer insulating properties loss. Characterization of the germinal structures of Green Rust and Fe-ferrhydrite which can be formed on the surface of a steel container under geological disposal conditions, and contribute to radionuclides fixation on the steel-bentonite interface is presented. It is emphasized that it is necessary to carry out complex experimental researches, which will allow prediction of bentonite buffer long-term stability in geological repository conditions, taking into account mineralogical-geochemical processes caused by corrosion of steel containers. A change of physicochemical conditions, mineralogical, geomechanical and hydraulic properties of the bentonite during geological disposal facilities operation and closure which can lead to decrease of buffer insulating properties is considered. Particular attention need to be paid for the analysis of the processes, taking place on the bentonite buffer – steel container interface. It has been shown that formation on the surface of old germinal structures of Green Rust and ferrhydrite and their phase transformations into sorption-active phases of ferrum oxyhydroxides and oxides can become an additional mechanism for fixation of mobile forms of radionuclides and transfer them to a less mobile and toxic state by means of reduction. During contact of the ground-water saturated bentonite buffer with the steel surface, mineralogical changes of the bentonite are directed to processes of saponitization and beidelitization. While saponitization is not critical to buffer isolating properties because of the ability of saponite to swell, partial or complete formation of beidelite substantially worsens them. One of the main processes that can become critical for the bentonite isolation properties is illitization of montmorillonite, the rate of which depends on temperature, chemical composition of the aqueous medium (pH and alkaline cation concentration, especially K⁺), degree of bentonite saturation with water, and the ratio between dispersion phase and dispersion medium. While a predictive estimate shows impossibility of buffer illitization due to low temperature, the use of external building materials, in particular, cements may shift the balance and lead to transformation of the bentonite to illite. The article emphasizes the necessity of carrying out complex experimental researches that will allow to predict the long-term stability of the bentonite buffer in the conditions of geological repository existence, taking into account mineralogical-geochemical processes caused by corrosion of steel containers.

Key words: bentonite, steel corrosion, steel-bentonite interface, phase bentonite changes, illitization, Green Rust, ferrhydrite

Introduction

Today, the optimal prototypes for geological storage facilities (GS) that are planned to be located in crystalline rocks of Chernobyl exclusion zone or adjacent regions of Ukraine [34] 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 use of multiple barriers in the disposal systems that perform protective functions over different time periods. Standard design of storage facilities foresees the follow-

ing barriers: matrix with HLW, metal canister for the matrix, clay buffer between the canister and the containing rock, filler for main tunnels and other underground workings (the backfill) - engineering barriers system (EBS), containing rock and geological environment as a whole that separate EBS from the biosphere. The canister is one of the EBS most important elements, which is usually made of iron alloys (carbon steel, cast iron, stainless steel) [37].

The 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 engineering barriers system (EBS) and to prevent access of groundwater [9].

In the conceptual decisions of many 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. It contains up to of 75% Na-montmorillonite, 15% quartz, 5-8% feldspar, 1% carbonate, 0.3% pyrite, 0.4% C org. There are numerous deposits of bentonite clays on the territory of Ukraine in Cherkaska, Vinnytska, Zakarpatska, Chernivetska and other oblasts. Chemical and mineral composition, crystallochemical features and ion-exchange properties are studied for samples of some repositories [8].

Steel packaging provides isolation of radionuclides from groundwater flow for one thousand years, bentonite buffer may increase this period, at least by one order of magnitude [20]. At the same time the isolating properties of the bentonite buffer in multibarrier disposal system can change over time and negatively affect the safety of the GR [49]. It is distinguished three stages in evolution of the GR: 1. early aerobic (with presence of oxygen) phase (100-200 years, stage of waste placing in the disposal and some period after its closure); 2. transition from aerobic to anaerobic phase (up to 1000 years) and 3. long-term anaerobic phase (more than 10,000 years) [26]. Saturation of the repository with water may occur in both transitional and long-term anaerobic phase and depends on groundwater filtration rate.

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

1. Characterization of primary nanoscale structures of corrosive origin

The primary mineral phases formed on steels surface during the corrosion process are Fe(II)-Fe(III) layered double hydroxides (Green Rust) and ferrihydrite (Fh). The main factors that determine the chemical composition and structure of germinal phase are the anionic component of dispersion medium, presence of Fe (II) or Fe (III) aqua hydroxyl forms and the reduction-oxidation conditions of particles formation.

1.1. Fe(II)-Fe(III) layered double hydroxides (LDH) structure, their formation mechanism and phase transformations.

Fe(II)-Fe(III) LDH structure consists of hydroxide layers formed by $\text{Fe}^{\text{II-III}}(\text{OH})_6$ octahedra. In the interlayer space there are located water molecules and anions, which are coordinated with the hydroxide layers, which provide compensation of Fe^{3+} charge and gives electro-

neutrality to entire structure of the mineral. Depending on the coordination of the anions in the interlayer, Fe(II)-Fe(III), layered double hydroxides (LDH) are referred to the first or second type, which is reflected in their crystallochemical properties: the ability to gradually change $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations ratio in the Green Rust- I structure and permanency of this ratio in Green Rust-II structure [44]. Thus, the typical representative of Fe(II)-Fe(III) LDH of the first type, which can be formed by steel surface contacting with groundwater, is the hydroxycarbonate Green Rust- (CO_3^{2-}) with crystallochemical formula $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{CO}_3 \cdot 2\text{H}_2\text{O}$, and of the second type - hydroxysulphate Green Rust- (SO_4^{2-}) , crystallochemical formula of which is $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4 \cdot \sim 8\text{H}_2\text{O}$ [46].

Green Rust- (CO_3^{2-}) formation can occur by several mechanisms: 1. by chemical interaction of aqua-hydroxy forms of ferrum (II) and oxygen-containing carbon compounds under oxidative conditions [47], 2. by their reaction with pre-deposited $\text{Fe}(\text{OH})_3$ or 3. by solid phase reaction between $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ in presence of oxygen-containing carbon compounds. At the same time, the formation of structures Fe(II)-Fe(III) LDH can occur with participation of so-called "green complexes", formation of which is associated with hydrolysis and polymerization of aqua hydroxy forms of Fe (II) and Fe (III) and their flow into reaction zone [1]. Formation of Green Rust phases occurs topotactically without destroying the mineral structure during oxidation of natural amakinite $\text{Fe}(\text{OH})_2$ in the presence of Fe^{2+} and of SO_4^{2-} or CO_3^{2-} anions [2].

Investigation of Fe(II)-Fe(III) LDH formation kinetics on the steel surface of showed [30] that the relative quantity of Green Rust phase does not remain constant and, depending on chemical composition of the dispersion medium and reducing- oxidation conditions on steel-dispersive medium interface, may increase or decrease due to the phase transformation of GR into other ferric oxygen-containing mineral phases - ferrihydrite, ferric oxyhydroxides or magnetite. The main criteria that determine the course of Green Rust phase transformations are the reduction- oxidation potential (ROP) of the system, dispersion medium chemical composition and pH, temperature, presence of microorganisms.

«Green Rust – ferrihydrite» system (Green Rust – Fh)

Studying of ferrihydrite formation process during $\text{Fe}(\text{OH})_2$ water suspension oxidation in presence of HCO_3^- anions (pH 7,5–9,0), shows that Fh is a transitional product between Green Rust- (CO_3^{2-}) and goethite $\square\text{-FeOOH}$ phases [15]. Green Rust- (Cl^-) transformation to ferrihydrite can be a result of Fe(II) hydrated cations and Green Rust itself rapid oxidation [18].

At the same time, restoration of ferrihydrite and mixed forms of oxidized Green Rust-Fe(III) to Fe^{2+} cations is possible in natural systems [16].

«Green Rust – goethite» system

Formation of α -FeOOH goethite during oxidation of Fe(II)-Fe(III) DLH with dissolved oxygen was investigated for the mineral phases Green Rust-(SO_4^{2-}), Green Rust-(Cl^-) [18], Green Rust-(CO_3^{2-}) [55]. The mechanism of such a transformation goes through stages of Green Rust dissolution and subsequent deposition of well-ordered iron (III) oxyhydroxides structures [7]. At the same time, it was shown in [11] that 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 iron (III) hydroxide.

Growth of redox potential from (-0,45) to (-0,3) V [55] is observed in the solution during phase transformation of Fe(II)-Fe(III) DLH to goethite \square -FeOOH (pH value ~9.5). Formation of goethite particles is accompanied by a decrease in the pH of the dispersion medium.

«Green Rust – akaganeite» system

The main condition of Green Rust transformation to akaganeite \square -FeOOH is Fe(II) and Cl^- increased concentrations [36].

«Green Rust – lepidocrocite» system

The formation of lepidocrocite \square -FeOOH during slow oxidation of Green Rust (pH ~ 7.0) occurs in two stages [40]. The first stage is connected to partial oxidation of Fe^{2+} in DLH structure, hydrolysis and redeposition of Fe^{3+} cations in poorly crystallized hydrated ferrihydrite phase. Here, Fh can quickly react with Fe^{2+} cations and turn into Green Rust again. Secondary formation of Green Rust reaction order is limited by the deposition of Fh and concentration of Fe^{2+} . Redeposition of lepidocrocite particles occurs at the second stage.

During Green Rust oxidation, a magnetite as an intermediate phase may be formed, which then that forms a part of Green Rust structure or replaces its structural elements. Further oxidation of the system goes with both mineral phases destruction and γ -FeOOH needle-like particles precipitation. Transformation of natural foigherite into lepidocrocite during its contact with dispersion medium, containing high quantities of carbonates, aluminum aqua form and silicates, is illustrated in [52].

«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].

«Green Rust – magnetite» system

Formation of Fe_3O_4 magnetite in aqueous suspension of Green Rust is also associated with dissolution and redeposition of Fe(II)-Fe(III) LDH unstable structures [21]. At pH = 9 and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio 0.5 and 1, the for-

mation of hexagonal particles of $\text{GR}(\text{SO}_4^{2-})$ lasts ~ 6 minutes, then they turn into magnetite. At the same time, Green Rust-(SO_4^{2-}) phase remains stable when pH decrease to 7 with $\text{Fe}^{2+} / \text{Fe}^{3+}$ ratio = 0.5 - magnetite does not form. Decreasing pH <7 leads to dissolution of Green Rust structure and dispersion medium saturation with Fe^{2+} cations, which are gradually oxidized with iron oxyhydroxides phase deposition [31].

The main results of modern studies of laboratory synthesis methods, structure, Fe(II)-Fe(III) LDH properties, their formation in the natural environment and interaction with components of various nature are covered in the review papers [5, 6]. Formation of Green Rust on steel and iron surfaces, which is characterized by strong reduction properties, chemical activity to a series of chemical elements and compounds, and the ability for phase transformation with involvement of different cations, may be an important additional contribution to radionuclides fixation in case of steel vessels usage in GR of radioactive waste.

2.2 Phase transformation of ferrihydrite

Another primary phase that can originate on the steel surface during the corrosion process is ferrihydrite (Fh), which belongs to the Fe(III) oxy-hydroxy salts group and is closely related to the iron oxides [39]. Synonyms of ferrihydrite are "hydrated oxide of trivalent iron" (HFeO), "amorphous hydroxide of trivalent iron", "colloidal hydroxide of trivalent iron" and " $\text{Fe}(\text{OH})_3$ ".

Ferrihydrite belongs to ferrous-hydroxide metastable phases and is easily converted into more stable minerals, in particular, goethite and hematite [12]. The main factors influencing the mechanisms and products of ferrihydrite phase transformations are chemical composition and pH of the dispersion medium, temperature, redox conditions [10]. Because of that the transformation of ferrihydrite to goethite is a typical process in natural systems, it is extensively covered in the literature. The main mechanism for such a transformation is dissolution/redeposition, which is catalyzed by presence of Fe^{2+} cations in aqueous medium [50]. Under standard conditions, Fh to \square -FeOOH transformation in the presence of Fe^{2+} ends over 24 h. with complete dissolution of the ferrihydrite, while in the absence of Fe^{2+} cations, ferrihydrite remains stable for a long time. Considering that solubility of Fh (10^{-39}) is higher than solubility of its transformation products - \square -FeOOH (10^{-41}) and \square - Fe_2O_3 (10^{-43}), this mechanism is quite probable. Formation of all types of Fh occurs at hydrolysis of Fe^{3+} by polymerization of $\text{Fe}_2(\text{OH})_4^{4+}$, while the most favorable conditions for Fh transformation are at pH ~4 and pH ~12 due to formation of $\text{Fe}(\text{OH})_2^+$ complexes and, respectively, $\text{Fe}(\text{OH})_4^-$. According to other data, the optimal conditions for ferrihydrite transformation to goethite correspond to pH = 9 and

$T \sim 40\text{ }^{\circ}\text{C}$, where polymerization of Fe (III) hydroxocomplexes occurs [17].

2. Steel containers corrosion investigation

In most countries, canisters for vitrified HLW are made of steel containing <0.3% wt. carbon, Mn, Si, Cu, Cr, Ni, Mo, W, V, Zr may also be present. The guaranteed lifetime of such a canister is about 1,000 years, and corrosion is the main destructive process [27]. Main factors, affecting steel corrosion are its composition, temperature, oxidation potential, alkalinity and mineralization of groundwater, as well as presence of bentonite buffer and other structural materials, in particular cement, in repository system [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 of multilayer container behavior, because it is present during 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. Corrosion can be divided into general and local, and the latter - on hole corrosion and crevice corrosion. General corrosion occurs throughout the surface and at 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: $Ox^{q+} + x(e^-) \rightarrow Red^{(q-x)+}$, where Ox and Red are oxidized and restored element forms. In aerobic conditions, cathode reaction occurs according to the scheme: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, and in anaerobic conditions - with hydrogen formation: $H_2O + e^- \rightarrow 0.5H_2 + OH^-$. Thickness of metal wall decreases with time, if corrosion products are soluble in water, or corrosion products layer is formed, remaining the overall thickness - if not. First case is active corrosion with charge and matter transfer, and second case is passive corrosion with protective film formation from newly formed compounds. Films formation is an important aspect of steel corrosion process in solutions with close to neutral pH.

Surface films can affect SNF container steel corrosion process in different way:

- Limiting matter reagents transfer to corroding surface and corrosion products from corroding surface;

- Surface blocking from further dissolution (if the film is not conducting);
- Changing anode and cathode surfaces and their ratio (if the film is conductive enough to maintain electrochemical reactions).

Surface blocking and matter transport limiting to and from the surface are the most important possible effects among listed above. Both of these effects lead to corrosion decrease over time, which is proved by experimental work, including in underground research laboratories.

Numerous works are devoted to the study of carbon steel behavior in conditions of GR. Long experiments (6000 h) in conditions simulating HLW disposal facility of in clays showed that the rate of steel destruction in water at $90\text{ }^{\circ}\text{C}$ is less than 10^{-3} cm per year [13] and in aggressive conditions of seawater contact ($80\text{ }^{\circ}\text{C}$) it is slightly higher - 2×10^{-3} cm/year [48].

First decades after the repository closure and its filling with water in aerobic stage it will dominate the process of local container corrosion with microfractures formation under the influence of current. In the ongoing, anaerobic stage, the main degradation reasons will be general container corrosion and its destruction due to appearance and action of hydrogen [37].

Carbon steel has high corrosion rate (0.06 mm/yr) during aerobic stage in water with a 2.5 g/l mineralization (main cations are Na^+ and Ca^{2+} , anions - Cl^- , SO_4^{2-} sulfate and carbonic acid), which increases by 30-50 percent with temperature increase from 30 to 50 Celsius degrees [59]. The rate of corrosion of low carbon steel in 1 M NaCl solution at pH range 8.4-11 is independent of pH and decreases from 30 $\mu\text{m/h}$ at the experiments beginning to 1-3 $\mu\text{m/h}$ after 4600 hours of interaction. In anaerobic conditions, the rate of corrosion becomes less than 5 $\mu\text{m/h}$ after 300-600 hours of steel contact with water that equilibrated with bentonite [43].

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

Stainless steel is more stable than carbon steel. Its average corrosion rate under hypothetical RW repository conditions is estimated at 0.01 $\mu\text{m/h}$, expected corrosion is 31.8 mm per 1,000 years, realistic values of the corrosion rate are 2-20 mm in 10,000 years [60].

Stainless steel corrosion rates are in the range from 0.003 to 0.15 $\mu\text{m/h}$ for Belgian HLV repository in Boom clay formation [35]. Its total corrosion in water equilibrated with cement is 0.03-0.5 $\mu\text{m/year}$ in aerobic medium and 0.001-0.01 $\mu\text{m/year}$ in anaerobic conditions.

Corrosion of steel slows down with time and pH of water increase, but increases with temperature growth, increase of oxidizing potential and increase of water mineralization.

In the works [25, 54] it has been shown that steel anaerobic corrosion rate during first tens of hours reaches 70 $\mu\text{m/h}$ (70 MKM/yr.) and then decreases to the first microns per year due to formation of protective layer consisting of steel corrosion products – oxides (magnetite, maghemite) and carbonates (siderite, FeCO_3) of iron (Fig. 1). With pH of water increasing, the rate of steel corrosion and hydrogen generation are reduced by two orders of magnitude - from several dozens to one tens of liters per square meter per year, but irradiation leads to its increase [45]. Temperature accelerates formation of protective layer on the steel surface, which in reducing conditions ($E_h -300 \text{ mV}$) at 90 °C and pH 8 starts to form during one hour of steel and 0.1 M ($\text{HCO}_3^- + \text{CO}_3^{2-}$) solution contact [19].

A similar structure of the corrosion layer was reported in an eight-month experiment on steel and argillites interaction at 90 °C under anaerobic conditions [13]. There can be highlighted external dense layer of iron carbonate (FeCO_3) corrosion products and an internal inter-change layer of iron oxides and silicates. In the presence of bentonite, it is reported a drop in of steel corrosion rate in water over time, reaching stationary regime of 1-3 microns/year, already after hundreds of hours in experiments with bentonite suspension or with water in equilibrium with bentonite or after one thousand hours in contact with compacted bentonite. Solution pH increase suppresses steel corrosion as a result of poorly soluble Fe^{2+} hydroxides the container surface.

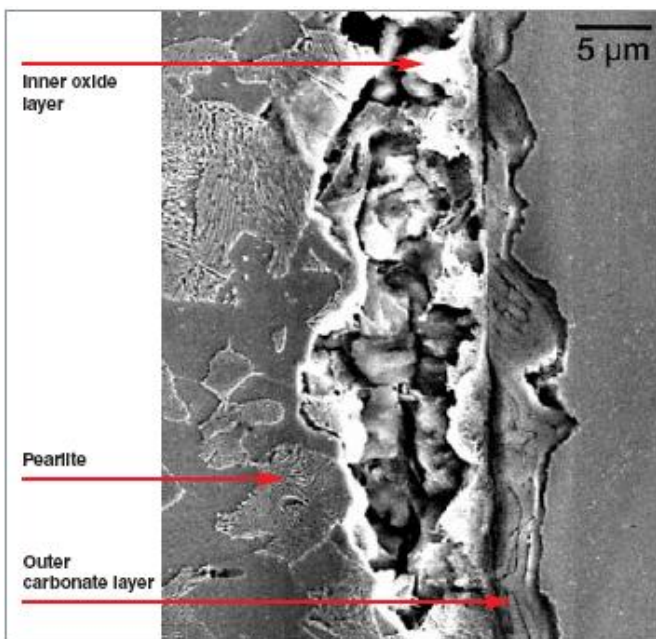
Thus, corrosion rate depends on the properties of the metal, various environmental factors (E_h -pH, temperature, composition and total mineralization of groundwater, etc.) and associated processes in the EBS, for example, formation of corrosion products films. In the aerobic stage (with oxygen presence) after waste placing into storage facilities, corrosion of steel slows down over time and with pH increase, but accelerates with temperature growth, increasing of oxidation potential and water mineralization. In this stage, formation of a protective film plays main role in reducing of corrosion rate, especially at high pH values in contact with bentonite and temperature growth.

At the beginning of the anaerobic period, a previously formed film consisting of a porous layer of Fe (II) corrosion products (and possibly Fe_3O_4) may be present. This previously formed film will have the same effect on the corrosion process as a porous film formed in anaerobic corrosion. If the main function of this film is to block the surface, then the formation of primary corrosion products film under anaerobic conditions, ignoring the

effect of the previously existing film will not matter. However, if the corrosion products film main effect is to limit the matter transfer in the direction to and from the surface, then ignoring the previously existing film will lead to underestimation of the overall thickness of the film and, thus, the rate of corrosion.

Рис. 1. Будова шару продуктів корозії на контакті низьковуглецевої сталі і водонасиченої пасти з глини після 550 г при 90 °C у анаеробних умовах [13]

Fig. 1. SEM cross-sectional view of a low-alloy steel corroded in a clay paste at 90 °C after 550 h under anaerobic conditions [13]



3. Bentonite clays transformation processes in steel container – bentonite system in geological repository conditions

Bentonite is a montmorillonite clay, which has high sorption capacity, plasticity and swelling when saturated with water. The specificity of montmorillonite structure is the presence of a three-layer package of the tetrahedron-octahedron-tetrahedron. The bonding between all the packages is weak and water can penetrate into this space, which causes strong swelling of the mineral. Its cation exchange capacity reaches 80-120 mg-eq per 100 g. Montmorillonite content reaches 55-95% in bentonite, other minerals are represented by hydromica, chlorite, kaolinite, and quartz. The largest deposits of bentonite are formed during decomposition of volcanic ash and tuffs in underwater conditions [4.23].

Bentonite buffer transformations at the initial stage GR evolution depend on the degree of its saturation with water: first – dehydration, which is caused by bentonite heating with the heat of radioactive waste, and then – rehydration, due to the penetration of groundwater in the GR. When bentonite is saturated with groundwater, it

swells and fills empty spaces between the buffer and waste canister and rocks cracks near to the buffer.

Mineral composition and bentonite isolating properties can change under the influence of high temperature, chemical composition of groundwater, products of waste dissolution and package material corrosion, which is made of steel or other material, as well as related microbiological processes. Combined effect of these factors and the possible synergistic effect are difficult to predict. Chemical and physico-chemical evolution of the buffer are regulated by thermodynamic conditions in GR system, which contribute to formation and transformation of new nanosized minerals, and is closely related to the quantitative ratios of the disperse phase and the dispersion medium (solution) [29]. Thermal, hydrodynamic and mechanical processes can last from several hundred to 1000 years, and mineralogeochemical reactions caused by corrosion of canisters or products of destruction of structural and associated materials will occur during all time of GR evolution.

Temperature is one of the key factors that affect the rate and degree of smectite (montmorillonite) phase transformation. At the same time, it is known that at the evolution beginning, the temperature in GR will be relatively low (<150 °C), with steady decrease trend. According to the prognosis [33], the maximum expected temperature in GR will be 45.5 °C in 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 phase transformations of the mineral phases [51].

It can be assumed that the *porous water chemical composition* in bentonite buffer should be influenced by diffusion of iron water hydroxy forms, formed during canister corrosion, as well as other compounds introduced from containing rock. At the same time, bentonite is characterized by high acid-alkaline buffer capacity, which is provided by surface hydroxyl groups protonation-deprotonation, as a result of which the chemical composition of bentonite porous water will remain stable for very long time [14] and is almost the same as the composition of groundwater in contacting it [38]. Moreover, when contacting bentonite with groundwater of granites where GR is located in, the buffer sorption capacity and clay's ability to cation exchange are practically do not decrease, which will promote sorption retardation of individual forms of radionuclides.

It is possible that, Na-form of montmorillonite will be changed by its calcium form during the geological repository evolution, but to date there has been no experimental evaluation of the actual speed and extend of these changes. It can be predicted that the bentonites transformation 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 ground waters. Natural bentonites (MX-80, Cherkaskii) contain not only Ca^{2+} and Na^+ cations, but also cations Mg^{2+} and K^+ , which has low effect on cation exchange process, therefore, it is almost impossible to achieve mono-cation composition of bentonite buffer in the GR conditions.

Important questions concerning the phase transformation of bentonite and, consequently, changes in its physical and chemical properties, are processes of *buffer interaction with corrosion products* of steel container. When contacting groundwater saturated with bentonite buffer with steel surface, mineralogical changes of bentonite can occur in two ways: saponitization and/or beidellitization according to the scheme: low-charged montmorillonite \rightarrow high-charged beidellite + saponite + quartz [32, 56] and/or ilitization [53]. While saponitization is not critical to the isolating properties of the buffer due to the fact that saponite, like bentonite, is swelling-capable and can be used as a buffer material itself, the formation of beidellite critically affects the isolating properties of the buffer.

Thermodynamic calculations suggest processes of montmorillonite dissolution and iron enriched minerals precipitation in the conditions of the GR. The most probable products of montmorillonite transformation are iron smectites (for example, Fe-saponite), berthierine or chlorite, which has been confirmed experimentally [58]. At the same time, the transformation of montmorillonite in contact with iron at temperatures > 50 °C remains controversial, and the results obtained are contradictory. Most of them were obtained from the French Radioactive Waste Management Program [32]. Thus, at $T = 80$ °C, in some experiments, the newly formed iron-oxide phases were not detected; in others, only corrosion products - magnetite, hematite, goethite were found, in the third – it was reported the presence of berthierine, nootronite, saponite. At temperatures of 250-300 °C, it is reported the formation of chlorite and saponite, that is, smectite with high Fe content. But 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 disperse phase/dispersion medium are in the inverse-correlation dependence to mineralogical buffer changes.

In particular, according to [24], the reduction of the 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 Fe^{2+} cations in porous water of unchanged buffer. According to the results of the long-lasting (8.2-10 years)

experimental modeling of MX-80 bentonite transformations in contact with iron (cast iron) placed in a copper container, it is shown [28] that the diffusion front of iron into bentonite is 7-8 mm from iron surface. Saturation of the initial solution (0.5 M NaCl) with Mg^{2+} , Ca^{2+} and SO_4^{2-} ions resulted in solution alkalinity increase to 8 and formation of mineral phases of gypsum, quartz, aragonite and hematite on the surface of the bentonite. At the same time, bentonite in contact with cast iron was cemented to a certain extent due to illite fraction content increase. Converted montmorillonite have been characterized by decrease in the ability to swell and swelling pressure, but its hydraulic conductivity practically did not change. In general, it was found that ferrum was incorporated into the structure of montmorillonite, and silicon oxide - released from it. The increase in amount of exchange iron in the bentonite occurred in the direction to cast iron. After 8,6 years, the redox conditions in external solution and porous water were strongly reducing. The gas phase contained H_2 , which was probably released due to cast-iron cylinders corrosion, and CO_2 , the source of which could be the calcite dissolution.

At the same time, with iron/clay ratio increase and pH value increase, the transformation of bentonite occurs more intensively, which have been shown in serial IAEA tests. In samples that were kept in 0.3-0.6 M NaCl solutions and, partly, in 0.1 M $NaHCO_3$ solution montmorillonite have lost its swelling ability and turned into another clay containing phases of serpentine and berthierine in the contact zone with steel. Silica 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 such a transformation can be accelerated by increasing ionized iron content on the bentonite container interface and increasing of aqueous medium pH.

Taking into account the presence in the granite groundwater of K^+ cations (mainly because of feldspars presence in granites) that have the largest, compared with other cations, energy of absorption by montmorillonite [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 happens because substitution of interlayer cations Na^+ or Ca^{2+} on K^+ . As a result of illitization, mixed layers of illite/montmorillonite are formed. In this case, pure illite does not have the ability to swell, and for the mixed later illite-montmorillonite, this ability is limited. Additionally, a gradual change in the mineralogical characteristics and

physical-chemical properties of the buffer, such as the specific surface, cation exchange properties, hydraulic conductivity, etc., are observed.

At the same time, kinetics simulations montmorillonite to illite transformation, 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 insignificant and will not lead to buffer isolation properties loss during the period when the buffer should perform safety functions. However, taking into account that montmorillonite to illite transformation process is also influenced by a number of other factors, such as the degree of bentonite saturation with water or disperse phase/solution ratio, pH value, concentration of alkaline cations (in particular, K^+), evaluation of illitization process probability should be carried out separately for each GR site.

Detailed studies of temperature of bentonite to illite transformation were performed for samples of different nature in wide range of physical and chemical conditions. Thus, the results of study of illitization in natural conditions have proved [22] that montmorillonite exists in stable state for more than 1 million years at temperatures below 100 °C. The authors of the work [22] have concluded that noticeable illitization at temperatures of 100-130 °C will not occur even for ten years. In a review paper [57], which is devoted to the study of bentonite stability at temperatures <100 °C, it is 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 in bentonite, and noticeable effects of cementation and possible illitization were observed only at temperatures > 150 °C. In dry conditions, montmorillonite (bentonite) remains stable to temperature up to 300 °C.

Prognosis estimates of the state of Olkiluoto geological repository (Finland) [29] testify that illitization and cementation (by silicon dioxide or iron oxides) of bentonite buffer are unlikely due to the current and expected natural conditions (composition and localization of groundwater and possible temperature changes). However, the use of external materials and repository structures, such as cement-based fillings, can lead to the release of K^+ and SiO_2 and increase $pH > 13$, which can accelerate of cementation/illitization processes, and also contribute to other transformations such as saponitization and/or beidelitisation. In particular, it is believed that zeolite formation occurs even at a pH of <11. It is expected that initial leaching products in the repository will have $pH \sim 10.5-11.5$, but further redistribution of the substance under such conditions is not determined.

Thus, in spite of the prognostic estimation, according to which significant harmful influence of the container shell on the physical and chemical properties of the buffer is not expected for 105 years, the processes of phase transformations on bentonite - steel interface should be taken into account when calculating the isolating characteristics of the buffer material. An important issue that should also be considered during GR creation is the potential impact of Fe^{2+} on the sorption centers of bentonite. But preliminary experimental results indicate that front of the ferrum transfer from the container surface will not penetrate deeply into buffer for a long time. On the contrary, the zone of corrosion process and formation of highly dispersed and sorption-active particles with iron-hydroxide and iron-oxide composition can play the role of effective sorbents and reducing agents (in the case of formation of Fe (II)-Fe(III) DLH and magnetite) for redox conditions sensitive aqua (hydroxo) forms of uranium (VI), plutonium, technetium and selenium.

Conclusions

1. Bentonite clay, which is used as a buffer material in design of geological repository of radioactive waste, over repository evolution conditions under the influence of a number of factors, can change its mineralogical-geochemical, geomechanical and hydraulic properties, which can lead to decrease in buffer insulating properties. Particular attention needs to be paid to the analysis of processes that take place at the interface between bentonite buffer and the steel container. According to thermodynamic calculations, the most probable reaction products in the disposal facility will be ferrous smectite (Fe-saponite), berthierine or chlorite.

2. During the contact of groundwater saturated bentonite buffer with steel surface, mineralogical changes of bentonite can be directed by saponitization, beidelitization or illitization. While saponitization is not critical for buffer isolating properties because of the ability of saponite to swell, formation of beidelite essentially worsens the buffer insulation properties.

3. One of the main processes that can become critical for bentonite isolation properties is the illitization of montmorillonite, the rate of which depends on temperature, chemical composition of the aqueous medium (pH and alkaline cation concentration, especially K^+), degree of bentonite saturation with water, and the ratio between dispersion phase and dispersion medium. While a predictive estimate shows impossibility of buffer illitization due to low temperature, the use of external building materials, in particular, cements may shift the balance and lead to transformation of bentonite to illite.

4. Previous studies have shown that the diffusion of ferrum-containing components into bentonite is limited to a few centimeters in space for a long time. Formation of Green Rust embryonic structures and ferrihydrite on

the steel surface and their phase transformations into the sorption-active oxyhydroxides and ferrous oxides phases can become an additional mechanism for radionuclides mobile forms fixation and transferring them to less mobile and toxic state by reduction.

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 in the conditions of the geological repository, integral experimental research should be introduced into the future concept and program of creating a geological repository in Ukraine. One of the points of such a study should be to analyze the processes of phase formation on steel - bentonite interface and to determine the effect of newly formed nanosized phases on their isolating properties radionuclide migration.

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ПРОЦЕСИ ФАЗОУТВОРЕННЯ НА ПОВЕРХНІ РОЗДІЛУ СТАЛЬ – БЕНТОНІТ В УМОВАХ ЕВОЛЮЦІЇ ГЕОЛОГІЧНОГО СХОВИЩА РАДІОАКТИВНИХ ВІДХОДІВ

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В оглядовій роботі проведено аналіз сучасних публікацій, у т.ч. авторських, присвячених дослідженню процесів формування нанорозмірних мінеральних фаз на поверхні розділу бентонітового буферу, мінеральний склад якого містить переважно монтморилоніт (70-90мас.%), і сталевий контейнер в умовах геологічного сховища радіоактивних відходів. Розглянуто зміни фізико-хімічних умов, мінералогічних, геомеханічних і гідравлічних властивостей бентоніту під час експлуатації і закриття геологічного сховища, що можуть призвести до зниження ізолюючих властивостей буфера. Особливої уваги потребує аналіз процесів, які відбуватимуться на границі розділу бентонітового буферу та сталевий контейнер. Показано, що формування на поверхні сталі зародкових структур Green Rust і феригідриту та їх фазові перетворення на сорбційно-активні фази оксигідроксидів та оксидів феруму може стати додатковим механізмом фіксації мобільних форм радіонуклідів та переведення їх в менш мобільний та токсичний стан шляхом відновлення. При контакті насиченого ґрунтовими водами бентонітового буферу з поверхнею сталі мінералогічні зміни бентоніту спрямовані на процеси сапонізації і бейделітизації. В той час, як сапонізація не є критичною для ізолюючих властивостей буферу внаслідок здатності сапоніту до набухання, а часткове або повне утворення бейделіту суттєво погіршує ізоляційні властивості буфера. Одним із головних процесів, який може стати критичним для ізоляційних властивостей бентоніту, є літізація монтморилоніту, швидкість якої залежить від температури, хімічного складу водного середовища (значення рН та концентрації лужних катіонів, особливо, K⁺), ступеня насиченості бентоніту водою та співвідношення дисперсної фази та дисперсійного середовища. В той час, як прогнозна оцінка свідчить про неможливість літізації буфера внаслідок недостатньої температури на поверхні бентоніту, використання сторонніх будівельних матеріалів, зокрема, цементів, може зсунути рівновагу та призвести до перетворення бентоніту на літ. В статті підкреслено необхідність проведення комплексних експериментальних досліджень, які дадуть змогу спрогнозувати довгострокову стабільність бентонітового буфера в умовах існування геологічного сховища з урахуванням мінералого-геохімічних процесів, викликаних корозією сталевий контейнера.

Ключові слова: бентоніт, корозія сталі, поверхня розділу сталь-бентоніт, фазові перетворення бентоніту, літізація, GreenRust, феригідрит