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Bentonite stability, speciation and migration behaviour of some critical radionuclides

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Abstract The contribution is focused on chemical, geochemical and mineralogical research of bentonite stability with the aim to determine the effect of saturation medium composition and loading by heat on bentonite stability. The main part of the research is directed to the experimental results of bentonite and bentonite leachate samples obtained for the bentonite interaction under laboratory experiments. Computer-modeling methods were used to calculate equilibrium thermodynamic principles, the distributions of predominant aqueous species, and potential solubility controls for the environmentally important oxidation states of each investigated radioactive contaminants. The Eh–pH diagrams of individual chemical species of the tested radionuclides were calculated by the geochemical software tool Geochemist's Workbench that included the actual chemical compositions of the solid–liquid systems under the given experimental conditions. It was confirmed that smectites are transformed to more stable silicate phases, such as illite/smectite mixed layers, illite. The data obtained from the model calculations conform with experimental results. The effect of the variable aqueous phase composition on bentonite stability using Ca–Mg and Na–Ca bentonites for the experiments was studied. The synthetic granitic waters with the higher concentration of the K^+ and Mg^{2+} cations were applied for the study of bentonite stability.

Keywords Bentonite · Stability · Speciation · Critical radionuclides

Introduction

The most of geological concepts for the storage of radioactive waste are based on "multi-barrier" systems: the waste packaging, an engineered barrier incorporating bentonite material and a geological barrier. The stability of engineered barriers can be affected by long-term pressure and temperature gradients [1, 2].

The favourable behaviour of bentonites as a buffer is mainly influenced by the presence of montmorillonite, a member of the smectite-clay mineral family [3, 4]. Bentonite is included in buffer and backfill materials in the most high-level waste repository concepts [5]. Its low hydraulic conductivity, micro-porous structure, good sorption properties and plasticity make this material an effective barrier—protecting the canister and restricting the movement of radionuclides released from the waste packages after canister failure.

Stability of smectites (mineralogical, physical and chemical) represents the key factor of all concepts employing smectite-rich materials in the engineered barriers of nuclear waste repositories [6]. The physico-chemical properties of smectites deteriorate mainly due to the increase of temperature causing changes of crystal structural properties and gradual transformation of smectite to illite as documented in natural geological diagenesis [7].

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Geochemical research of bentonite samples was focused on set up of geochemical model of bentonite interaction with the aqueous environment under the experimental conditions with the aim to evaluate the bentonite stability of individual minerals that formed bentonite [8].

The aim of our research was the study of bentonite interaction with the aqueous media, long term stability of these systems and identification of potential bentonite transformation with respect to migration behavior of selected critical radionuclides.

In view of the nuclear waste management, the sorption studies of radionuclides on various materials is of great importance and significance in migration predicting of these nuclides in geological formations near the waste storage sites and also it is very important for evaluating feasibility of a particular natural material for the disposal of high level radioactive waste into the deep repository. Generally, any of processes at which dissolved substance is removed from the solution and bound on the solid phase surface, can be specified as a sorption. Radionuclides of ^{99}Tc and ^{129}I may exist in the various oxidation states in the dependence of the redox conditions of the aqueous environment [9]. Technetium exists in oxidation states from +7 to −1. In natural environments, the most stable oxidation states of technetium are +7 and +4 under oxidizing and reducing conditions, respectively. The −1, +5, and molecular I_2 [$I_2^0(aq)$] oxidation states are those most relevant for iodine in environmental systems. Iodine usually exists in fresh water in the −1 oxidation state as iodide (I^-), in alkaline and marine environments, iodine usually exists in the +5 oxidation state as iodate (IO_3^-).

Experimental

Solid and liquid phases

Bentonite materials taken from locality Rokle, 4 km from Kadan town, Czech Republic and from the dismantling process of the Mock-Up-Cz experiment were used as the solid phase in this work (detail information [10, 11]).

Synthetic granitic water was used as the liquid phase for the sorption experiments; its chemical composition is shown in Table 1 and composition of bentonites in Table 2.

Ion exchange capacities (both anion exchange capacity—AEC and cation exchange capacity—CEC) were determined by method [12].

Methods of mineralogical determination of composition of experimental material is described in [12]. Mineralogical study identified the transformation of original bentonite material as result of the bentonite interaction with the synthetic granitic water under the conditions used in the Mock-Up-Cz experiment [10, 11].

Table 1 Composition of saturation media

Component	Unit	
Mg^{2+}	mg/L	5.1
Ca^{2+}	mg/L	14.8
K^+	mg/L	108.3
Na^+	mg/L	5.5
SiO_2	mg/L	0.0
Cl^-	mg/L	42.5
SO_4^{2-}	mg/L	133.3
HCO_3^-	mg/L	11.8
TDS	mg/L	321.3

Table 2 Chemical composition of bentonites (in weight %)

Component	Mock-Up-Cz	Rokle
$-H_2O$	7.55	9.83
$+H_2O$	4.58	6.71
SiO_2	46.73	43.72
TiO_2	3.14	4.17
Al_2O_3	11.48	13.85
Fe_2O_3	10.02	14.47
FeO	0.21	0.11
MnO	0.16	0.14
CaO	4.54	2.66
MgO	2.33	2.13
K_2O	0.81	0.94
Na_2O	0.58	0.26
Li_2O	0.0040	0.0021
S	0.04	0.01
CO_2	2.5	0.25
P_2O_5	0.52	0.83
C	4.89	0.00
Total	100.08	100.08

Identification of the individual chemical species of radionuclides in the studied systems was determined by TLC with the radiometric detection and by capillary isotachophoresis with conductivity detection (cITP), which is detailed describe in our previous work [13].

β-activity of ^{99}Tc was measured with an SPF 35 plastic scintillation detector. 1 mL of aqueous phase was pipette on the Petri dish and dry under the IR lamp and afterwards was measured the β-activity of ^{99}Tc [9, 14]. The γ-activity of ^{134}Cs was measured in the aqueous phase in a similar way to the radionuclide ^{99}Tc, with a NaI(Tl) scintillation detector.

The γ-activity of ^{125}I was measured analogous in the aqueous phase as in the case of the radionuclide ^{99}Tc, this measurement is based on the pulse counts with scintillation detector NaI(Tl).

Sorption experiments

A static batch method was used for the sorption experiments [8, 9]. The mineralogical transformation and characterization of the solid phase by RTG diffraction, infrared spectroscopy and cation exchange capacity measurement were evaluated after the termination of these experiments. These mixtures were simultaneously applied for the sorption study of the selected radionuclides (^{134}Cs, ^{125}I and $^{99}TcO_4^-$) with the aim to evaluate the changes of sorption behaviour as the result of bentonite with synthetic granitic water interaction.

Geochemical modeling was performed with Geochemist's Workbench, Release 6 [14].

Results and discussion

Bentonite transformation and interaction of bentonite with the aqueous media

As first approximation of bentonite mixture transformation during Mock-Up-CZ experiment the simple thermodynamic model was build up. Mixture of Na-, K-, and Ca-montmorillonite series end members was used as substitution for original bentonite mixture. According to the chemical analysis of bentonite mixture the proportion of each end member of montmorillonite series is about Na:K:Ca = 45:40:15 molar %. The Fe-montmorillonite end member of montmorillonite series could not be included because no reliable thermodynamic data are available.

The mixture of end members of montmorillonite series was let to interact with granitic water in geochemical modeling program Geochemist's Workbench till the equilibrium with water solution was reached and reaction path was traced.

Two examples of outputs from modeling for temperatures 25 and 95 °C are given here. Mixture of 4.5 mmol of Na-montmorillonite, 4.0 mmol K-montmorillonite, and 1.5 mmol of Ca-montmorillonite was reacted with one kilogram of granitic water. From beginning (reaction progress 0.0) the corresponding amount of montmorillonite mixture is added in selected step to granitic water and equilibrium is calculated. Each step is repeated until full amount of reactants is added to solution (reaction progress 1.0). When in certain step the solution becomes oversaturated with respect to particular mineral, equivalent amount of this mineral is precipitated and solution is kept just saturated. Detailed interpretation of modeling outputs goes far behind the scope of this paper, nevertheless basic transformation scheme and its consequences can be stated here.

Right on the beginning granitic water solution becomes saturated with respect to gibbsite (aluminum hydroxide, not shown for clarity), and right after this is saturated with respect to Mg-montmorillonite and kaolinite (Fig. 1, upper row left). It means that all other members of montmorillonite series are dissolved and Mg-montmorillonite precipitates. At reaction progress about 0.1 the solution becomes oversaturated with respect to Ca-montmorillonite and from this point alkali metals montmorillonite members are transformed to Mg- and Ca-montmorillonite. From reaction progress about 0.45 this transformation goes only to Ca-montmorillonite. At the same point the solution is saturated with respect to K-montmorillonite. As a source of Ca serves calcite (calcium carbonate) which is present in bentonite mixture. From reaction progress about 0.92 becomes solution oversaturated with respect to the last montmorillonite end member (Na) and transformation of montmorillonite mixture used for modeling is finished. In the first part of reaction trace the transformation can be described by overall chemical reaction

$$\begin{aligned}&(\mathrm{Na,K,Ca})_{0.33}(\mathrm{Al,Mg})_2\mathrm{Si_4O_{10}(OH)_2}\\&\quad\rightarrow \mathrm{Mg_{0.5}Al_{1.67}Si_4O_{10}(OH)_2} + \mathrm{Na^+} + \mathrm{K^+} + \mathrm{Ca^{2+}}\end{aligned}$$

and in further steps as

$$\begin{aligned}&(\mathrm{Na,K,Ca})_{0.33}(\mathrm{Al,Mg})_2\mathrm{Si_4O_{10}(OH)_2}\\&\quad\rightarrow \mathrm{Ca_{0.165}(Mg,Al)_2Si_4O_{10}(OH)_2} + \mathrm{Na^+} + \mathrm{K^+}\end{aligned}$$

$$\begin{aligned}&(\mathrm{Na,K,Ca})_{0.33}(\mathrm{Al,Mg})_2\mathrm{Si_4O_{10}(OH)_2}\\&\quad\rightarrow (\mathrm{K,Ca})_{0.33}(\mathrm{Mg,Al})_2\mathrm{Si_4O_{10}(OH)_2} + \mathrm{Na^+}\end{aligned}$$

These changes in transformation mechanism have of course impact on the water solution composition. In the first part of transformation the ratio of Ca/Mg increases as well ratio of alkali to alkaline earth metals. Those ratios are dependent not only on the transformation progress but also on temperature. At 95 °C the mechanism of montmorillonite mixture transformation is in principle the same, but Na-montmorillonite series member becomes more stable compare to K-montmorillonite end member (Fig. 1, lower row left). New mineral—illite $\mathrm{KAl_2(Si,Al)_4O_{10}(OH)_2}$—is formed in the second part of reaction progress according to reaction scheme

$$\begin{aligned}&\mathrm{K_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2} + \mathrm{Ca^{2+}}\\&\quad\rightarrow \mathrm{KAl_2(Si,Al)_4O_{10}(OH)_2} + \mathrm{Ca_{0.165}(Mg,Al)_2Si_4O_{10}(OH)_2}\end{aligned}$$

Different stability of montmorillonite series end members and changes in transformation mechanism of montmorillonite mixture naturally affect the resulted metals ratios in water solution. First results of geochemical modeling of bentonite mixture transformation are in good agreement with experimental results and proved that geochemical modeling can be used for detailed study of transformation mechanism.

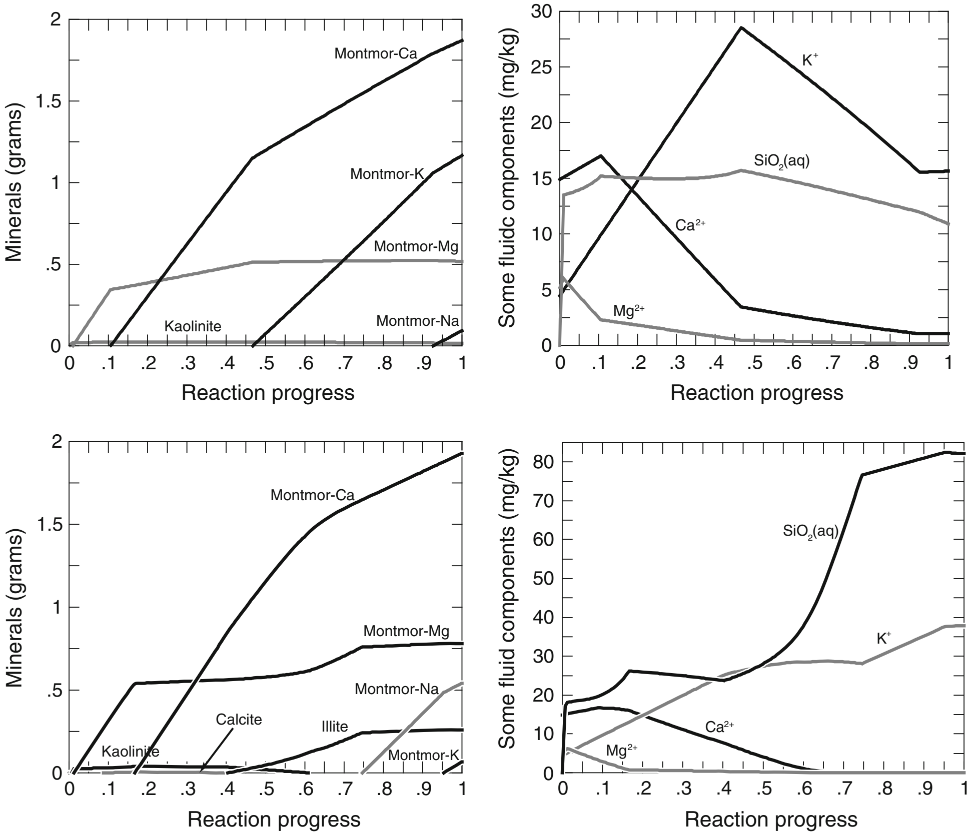

Fig. 1 Outputs from modeling of montmorillonite mixture interaction with granitic water at 25 (*upper row*) and 85 °C (*bottom row*). More detailed explanation is given in text

Transformation of bentonite mixture with addition of calcite and pyrite

As reactants there were used following minerals: calcium montmorillonite contained in GWB database as $Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$, potassium montmorillonite ($K_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2$), and sodium montmorillonite ($Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2$) (Fig. 2). Relative proportion of montmorillonites were derived from silicate analyses of bentonite from Rokle locality. Mixture was transformed in granitic water at 25 and 85 °C, respectively. To make the model as close as possible to reality pyrite and calcite were added in proportions as were found in bentonite mixture.

As follows from Fig. 3 the presence of calcite and pyrite causes transformation of more amount of montmorillonite compare to the case where calcite and pyrite are not present in the mixture. Solution is supersaturated with respect to calcium montmorillonite. Concentration of sodium does not exceed values needed for supersaturation with respect to sodium montmorillonite despite of fact that their concentration increases and that they are not consumed by any other mineral formed. Potassium ions are binded to illite formed a solution cannot be supersatureted with respect to potassium montmorillonite. Iron released during the course of reaction is binded into nontronite formed.

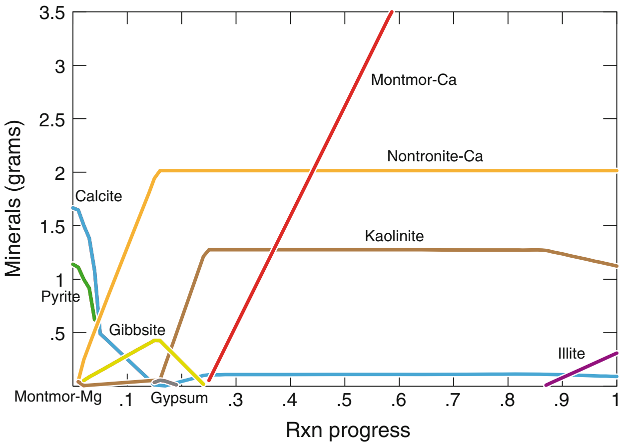

Fig. 2 Transformation of montmorillonite mixture with minor admixtures at 25 °C

As a result of transformation at given conditions 3,010 µmol (1.09 g) of calcium montmorillonite, 7,560 µmol (2.81 g) of potassium montmorillonite, and 8,400 µmol (3.08 g) sodium montmorillonite are dissolved.

Increasing temperature to 95 °C at the same content of calcite and pyrite causes markedly higher advance in transformation of montmorillonite (Fig. 3).

Presence of pyrite and calcite has pronounced influence on pH values, too. Overall, the lower values are reached compare

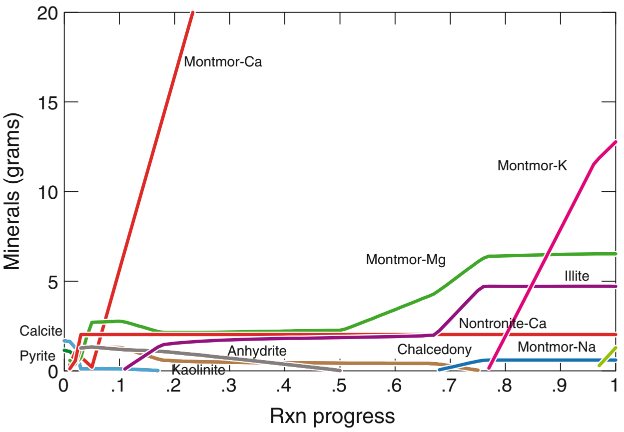

Fig. 3 Transformation of montmorillonite mixture at presence of pyrite and calcite at 85 °C

to model without pyrite and calcite. At 25 °C the final value of pH is 7.7, at 95 °C is final pH only 6.97 (here we need to mention that neutral pH at this temperature is only 6.2).

Concentrations of main cations were subtracted from text output and their ratios were calculated. As ratio were used Na^+/K^+ and Ca^{2+}/Mg^{2+}. During the reaction course the ratios remain nearly the same. At 25 °C is at step 100 equals ratio of Na/K 1.5, for step 75 before illite is formed it is 1.46. Ratio for Ca/Mg is for step 100 and 75 the same (9.6). For temperature 95 °C is situation similar. Ratio Na/K is at step 75 (before potassium montmorillonite appeared) 1.2 and on the end of reaction path this ratio increases to 2.4. For ration Ca/Mg is characteristic value about 6.6 in all steps.

First results of bentonite transformation modeling including appropriate amount of pyrite and calcite confirm basic mechanism given above. Iron released by gradual pyrite oxidation is fully participating on transformation and is bind into another product of transformation—into calcium nontronite $Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$. Calcium nontronite is formed because excess amount of calcium is released by parallel dissolution of calcite. This transformation can be expressed by equation

$$\begin{aligned}&\text{Ca-montmorillonite} + 4.68H_2O + 2\ Fe^{3+}\\&\quad\rightarrow 5.34\ H^+ + \text{Ca-nontronite} + 0.33Mg^{2+}\\&\qquad + 1.34\text{gibbsite} + 0.33\ SiO_2(aq)\end{aligned}$$

Overall transformation correspond to the following reaction mechanism

$$\begin{aligned}&\text{Ca-montmorillonite} + 8.089\text{calcite} + 6.1\ H_2O\\&+ 8.174\ O_2(aq) + 2.18\text{pyrite}\\&\quad\rightarrow 8.074\ Ca^{2+} + 0.33Mg^{2+} + 1.31\text{gibbsite}\\&\quad+ 1.09\ \text{Ca-nontronite} + 4.36\ SO_4^{2-} + 8.089HCO_3^-\end{aligned}$$

At the same time the modeling shows that as for influence on bentonite mixture stability the amount of pyrite and composition of granitic water (and in more common composition of underground water) is much more important than composition of montmorillonite in bentonite mixture.

Presented geochemical model of bentonite transformation cannot involve all aspect of real behaviour of bentonite—its mineralogical composition was simplified and at this stage it is not possible to include different rate particular minerals. Nevertheless model behaviour is in good agreement with experimentally observed trends. From this point of view is presented geochemical model quite reliable and can serve as effective tool for experimental data analysis, deeper study of transformation mechanism at assumed conditions and as one of few tools for assessment of long term bentonite stability.

Speciation of selected radionuclides

The occurrence of various technetium and iodine species was expected in the dependence of the reaction mixture composition (namely the effect of Fe compounds on $^{99}TcO_4{}^-$ sorption). Suitable analytical methods enable to determinate of technetium and iodine chemical species, which play significant role for the uptake mechanism.

TLC with radiometric detection identified insoluble TcO_2 and mobile $TcO_4{}^-$ anion. CE with DAD detection is supplement method to TLC; its advantage is possible separation of technetium mobile forms with different electrophoretic mobility.

Insoluble TcO_2 could not be to analyse by CE. $^{99}TcO_4{}^-$ anion was separated for the reverse polarity of voltage; its maximum absorbance was for $\lambda = 242$ nm. Two peaks for $\lambda_{max} = 200$ nm were separated approximately for 4 and 10 min corresponded with systematic peaks obtained from synthetic granitic water. No peak for the other technetium mobile forms in various oxidation states was obtained for the reverse and normal polarity of voltage. Only peak of pertechnetate anion was presented in measured electrophoregrams of tested supernatant solutions (bentonite systems with Fe compounds).

Fe compounds in the various oxidation states (Fe: 0, 2+, 3+) did not have a significant influence on the iodine valence state. Iodide anion was the major species of iodine in studied bentonite systems. Isotachophoretic zone corresponding to iodide anion was only observed in measured supernatant solutions after the $^{125}I^-$ sorption.

Calculation of Eh versus pH diagrams of technetium and iodine species

The Eh versus pH behaviour of technetium and iodine species in the aqueous environment has been summarized in the predominance diagrams of Fig. 4a, b. Data used to construct the Eh versus pH diagrams were based on the experimentally determined chemical composition of solid–liquid systems. Eh–pH diagrams of individual chemical species of tested radionuclides were calculated by geochemical software tool Geochemist's Workbench including real composition of the solid–liquid systems under the experimental conditions.

The solid lines represent the equilibrium between TcO_3(s); $TcO_2 \cdot H_2O$(am); TcO_4^-; Tc_3O_4(s); Tc_2S_7(s); TcS_2(s); TcOH(s) solution species. The calculated technetium and iodine species in Eh–pH diagrams corresponded with the species experimentally determined by suitable analytical methods. Time of $^{99}TcO_4^-$ anion reduction strongly depends on the initial $^{99}TcO_4^-$ anion concentration. Therefore, $^{99}TcO_4^-$ anion was not reduced to the lower valence state, without the presence of compounds with reductive properties [e.g. Fe(0), Fe(2+)], for 2 months. Tc (VII) in the form of pertechnetate anion represents major species of technetium in studied bentonite–Fe_2O_3 and bentonite–Fe_3O_4 aqueous systems, under the anaerobic conditions with Eh (SHE) < −150 mV. Iodide anion forms stable species in these selected studied bentonite systems with Fe compounds in different valence states (Fig. 4c).

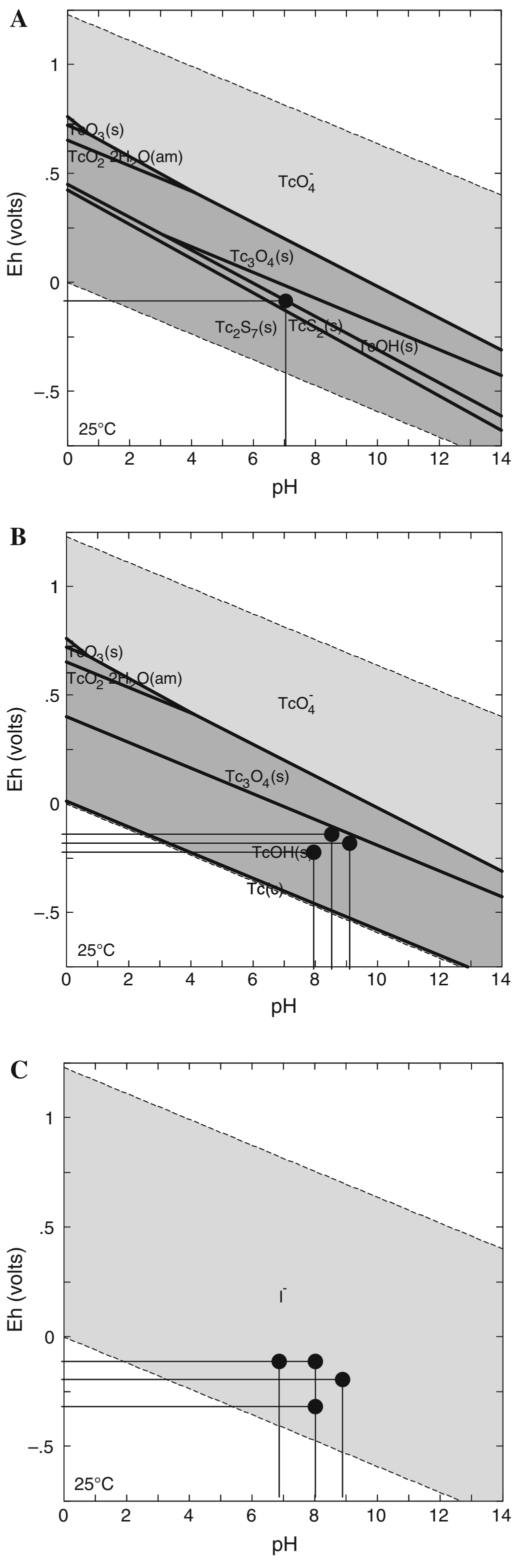

Fig. 4 Eh versus pH predominance diagrams for **a**, **b** technetium and **c** iodine aqueous environments. **a** $^{99}TcO_4^-$ sorption on bentonite–$FeSO_4$. **b** $^{99}TcO_4^-$ sorption on bentonite–Fe; bentonite–Fe_3O_4; bentonite–Fe_2O_3. **c** $^{125}I^-$ sorption on bentonite–Fe; bentonite–Fe_3O_4; bentonite–Fe_2O_3; bentonite–$FeSO_4$

Reflection of stability bentonites on migration characteristics of selected radionuclides

Ion exchange capacity

Ion exchange capacity of bentonite is a fundamental parameter in evaluating the uptake of the aqueous phase components. It was found that determined values of CEC were not changed in the dependence on time interaction in the experiments [15]. The values of ion exchange capacity corresponding with the values for the original material for Rokle and Mock-Up-Cz (CEC = 63.2 ± 9.5 mmol/100 g and AEC = 2.6 ± 0.4 mmol/100 g), for. Febex (81.4 ± 9.7 mmol/100 g and AEC = 3.6 ± 0.4 mmol/100 g).

It can be concluded that long term loading bentonite material with moisture, temperature and pressure gradients did not markedly influenced ion exchange properties of this material and the changes are only in the interval of the uncertainty determination of the ion exchange properties.

Isolated newly formed mineral phases (illite, montmorillonite) and mixed layer structure (illite-montmorillonite) from the 2 selected layers of bentonite buffer in the experimental container were applied for the determination of the cation exchange capacity (CEC). The CEC values of isolated mineral phases illite and mixed layer structure illite–montmorillonite decreased approximately 50%

Table 3 Cation exchange capacities of newly formed minerals

	CEC (mmol/100 g)
Illite	28.0 ± 5.6
Montmorillonite	71.8 ± 14.4
Illite–smectite	37.5 ± 7.5
Unloaded bentonite material	63.2 ± 9.5

(Table 3). This fact could play important role for the sorption of cationic forms of radionuclides.

But newly formed minerals domains (beidellite, illite, illite–montmorillonite; about first weight percent) presented in the bentonite material in the low amount have no significant influence on the changes of chemical properties of bentonite material. Beidellite belongs to the same smectite clay family as montmorillonite, therefore has the similar chemical properties as montmorillonite and did not caused any changes in chemical properties of studied materials. These results play a dominant role for the evaluation of radionuclides migration on bentonite especially cationic forms of radionuclides, when ion exchange of cationic species (e.g. Cs^+, Sr^{2+}) on the bentonite surface sites (layer site) is major mechanism.

Sorption study

Sorption includes ion exchange, complex formation on the surface of sorbent, specific adsorption, physical sorption and other mechanisms. From the group of more than 40 critical radionuclides, we selected 2 representative radionuclides from the category with a notional maximum migration only—ion form radionuclides as cesium (^{137}Cs) and one radionuclide representing a group changing a valence state (^{99}Tc) and by this, a chemical composition, which can be seen in marked changes of sorption characteristics in dependence on aerobic and anaerobic conditions of the aqueous environment [16]. Mobile form of technetium representing pertechnetate anion TcO_4^- and sparingly soluble $TcO_2 \cdot nH_2O$ are the stable forms of technetium under aerobic and anaerobic conditions of the aqueous phase environment. Sorption mechanisms of cesium cation and pertechnetate anion on the bentonite material including studies of technetium chemical forms were studied in detailed in our previous papers [8, 16].

Considering that mineralogical studies of loaded bentonite material applied in this experiment identified transformation of original bentonite under the occurrence of the newly forming minerals domains it could be expected that these mineral phases will be affected sorption properties of radionuclides in comparison with sorption on original bentonite. Table 4 summarises the values of distribution coefficients of ^{134}Cs and ^{99}Tc on bentonite and the basic parameters describing the compositions of the aqueous phase during the sorption study, which have a significant influence on the sorption process of these radionuclides particularly technetium, where different chemical forms of technetium (TcO_4^-, $TcO_2 \cdot nH_2O$) are formed in the dependence of redox conditions of the aqueous environment).

The uptake mechanism of Cs on bentonite is ion exchange of Cs^+ cation on the surface sites of bentonite. The presence of the newly formed minerals domains (namely mixing structure illite-montmorillonite that has different chemical properties than montmorillonite, beidellite has very similar properties as montmorillonite) that are contained in the loaded material in low amount (about first weight percent) and were formed as a result of bentonite interaction with synthetic water under the conditions used in this experiment, did not caused significant changes of distribution coefficients (K_D) in comparison with the K_D values for the original bentonite material ($K_D \cong 330$ L/kg). Obtained results of Cs sorption are closely related with the knowledge of ion exchange properties of these materials because any markedly changes of CEC were not confirmed.

The values obtained for the distribution coefficient K_D for ^{99}Tc in the studied solid–liquid phase systems were lower than 1 L/kg. As well as what is known from the values of ion exchange capacity obtained for the tested

Table 4 K_D values of ^{99}Tc and ^{125}I for the sorption on bentonite mixtures with selected Fe compounds

Solid phase	pH	Eh (SHE) (mV)	K_D ^{99}Tc (mL g^{-1})	Tc valence state	K_D ^{123}I (mL g^{-1})	I valence state
Bentonite + Fe from degradation procedure	7.9 ± 0.1	−142 ± 7	1620 ± 210	TcO_2	0.7 ± 0.1	I^-
Bentonite + Fe	8.0 ± 0.1	−370 ± 19	4500 ± 550	TcO_2	1.5 ± 0.3	I^-
Bentonite + Fe_2O_3	8.5 ± 0.2	−190 ± 10	0.9 ± 0.2	TcO_4^-	0.7 ± 0.2	I^-
Bentonite + Fe_3O_4	9.1 ± 0.2	−200 ± 10	1.0 ± 0.2	TcO_4^-	0.6 ± 0.1	I^-
Bentonite + $FeSO_4$	6.8 ± 0.1	−140 ± 7	56.4 ± 7.3	TcO_2, TcO_4^-	3.3 ± 0.4	I^-
Unload bentonite	8.3 ± 0.1	435 ± 25	0.68 ± 0.12	TcO_4^-	0.2 ± 0.1	I^-

Experimental conditions: $c0(^{99}TcO_4^-) = 8 \times 10^{-5}$ mol L^{-1}, $c0(^{125}I) = 3.3 \times 10^{-11}$ mol L^{-1}, bentonite:Fe compounds ratio 10:1 [kg/L], time of sorption −2 months samples, this material has an excellent sorption ability for cationic forms of contaminants, while on the other hand a poor affinity for anionic forms. This is due to the basic properties of bentonite, where montmorillonite is a dominant mineral (with a high cation exchange ability for aqueous ions) you can see that obtained K_D values for Cs^+ are 2 orders higher than for $^{99}TcO_4^-$.

We assumed that in the loaded backfill material of the Mock-Up-Cz experiment, iron compounds in various oxidation states would be present (corrosion products of the container, minerals that formed bentonite contained Fe^{2+} ions, pyrite). Also, those suitable minor compounds in the tested geological material would influence changes in technetium oxidation state, enabling the subsequent formation of insoluble forms of technetium ($TcO_2 \cdot nH_2O$). A sorption study of the pertechnetate anion onto bentonite mixtures with various ratios of solid to liquid phase in the range 2:1–10:1 (*V*/*m*) over 3 months did not confirmed an increase in distribution coefficients ($K_D < 1$ L/kg). It was found that this material did not contained sufficient levels of compounds with reductive properties to enable the reductive precipitation of the pertechnetate anion. Changes in the oxidation state of technetium were not observed in these mixtures, the pertechnetate anion was the dominant species and the obtained low values of K_D correspond to low anion exchange capacity of bentonite.

Newly minerals domains that were formed by transformation of original bentonite (about first few weight percent) have similar properties as bentonite material and thus they do not contribute to the significant changes of chemical stability. This fact confirmed results of the ion exchange properties of this loaded bentonite material, when the changes of CEC and AEC values for the tested samples from the various locations in the experimental container (different vertical and horizontal distances) were changed only in the interval uncertainty of the determination ion exchange properties. Due to the fact that markedly changes of ion exchanges properties of bentonite material were not identified and only small amount of original bentonite material was transformed to new phyllosilicates that is why that determined distribution coefficients of cesium cation and pertechnetate anion on the loaded material have similar values in comparison with the values for the original bentonite.

Conclusion

- Geochemical modeling proved that bentonite mixture in principle formed by Na–K–Ca–Fe montmorillonite is transformed to Ca–Mg montmorillonite. Only small part of original material is transformed to kaolinite and at highest temperatures to illite.
- Stability of bentonite mixture is mainly determined by amount of pyrite present. Another important influence is caused by interacting water.
- The long-term loading of composite bentonite samples did not have a significant influence on the ion exchange properties (AEC and CEC) of bentonite material. The ion exchange properties of bentonite material play important role for the sorption on bentonite. The CEC values of isolated mineral domains as illite and mixed layer structure illite-montmorillonite decreased approximately 50% and this fact plays important role for the sorption of cationic forms of radionuclides.
- Lower values of illite CEC caused the decrease of sorption yield of radionuclide $^{134}Cs^+$ about 10%. Fractional transformation of original bentonite buffer material (<1% of original bentonite buffer was transformed) did not have a significant influence on the changes of cesium cation, pertechnetate and iodide anions sorption behaviour on composite bentonite samples.

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References

1. Allan C, Figure J, Nuttall K (1997) How to cope with the hazards of nuclear fuel waste. Nucl Eng Design 176:51–66
2. Bucher F, Műller-Vonmoos M (1989) Bentonite as a containment barrier for the disposal of highly radioactive wastes. Appl Clay Sci 4:157–177
3. Elzea J, Murray HH (1994) Bentonite. In: Carr DD (ed) Industrial minerals and rocks. Society for Mining, Metallurgy, and Exploration, Littleton, pp 233–246
4. Mazurek M, Pearson JF, Volckaert G, Bock H (2003) Features, events and processes evaluation catalogue for argillaceous media. OECD, NEA 4437, Moulineaux, France
5. Galamboš M, Paučová V, Kufčáková J, Rosskopfová O, Rajec P, Adamcová R (2010) Xcesium sorption on bentonites and montmorillonite K10. J Radioanal Nucl Chem 284:55–64
6. Pusch R (1998) Transport of radionuclides in smectite clay. In: Parker A, Rae JE (eds) Environmental interactions of clays. Springer, Berlin, pp 7–35
7. Pytte AM, Reynolds RC (1989) The thermal transformation of smectite to illite. In: Naesser ND, McCulloh TH (eds) Thermal history of sedimentary basins: methods and case history. Springer Verlag, New York, pp 133–140
8. Vinšová H, Jedináková-Křížová V, Kolaříková I, Adamcová J, Přikryl R, Zeman J (2008) The influence of temperature and hydration on the sorption properties of bentonite. J Environ Radioact 99:415–425
9. Vinšová H, Jedináková-Křížová V, Ožanová M (2009) Interaction of ^{99}Tc onto bentonite and influence of Fe(II) and Ca, Mg ion exchange in its interlayers. J Radioanal Nucl Chem 281:75–78

10. Svoboda J, Vašíček R (2010) Preliminary geotechnical results from the Mock-Up-CZ experiment. Appl Clay Sci 47:139–146
11. Pacovský J, Svoboda J, Zapletal L (2007) Saturation development in the bentonite barrier of the Mock-Up-CZ geotechnical experiment. In: Aranyossy JF (ed) Clay in natural and engineered barriers for radioactive waste confinement—Part 2. Phys Chem Earth A/B/C 32(8–14):767–779
12. Borden D, Giese RF (2001) Baseline studies of the clay mineral society source clays: cation exchange capacity measurements by the ammonia-electrode method. Clays Clay Miner 49:444–445
13. Kolaříková I, Švandová J, Přikryl R, Vinšová H, Jedináková-Křížová V, Zeman J (2010) Mineralogical changes in bentonite barrier within Mock-Up-CZ experiment. Appl Clay Sci 47:10–15
14. Bethke CM (1996) The geochemist's workbench®, GWB essentials guide. p 76
15. Vašíček R, Křížová V, Zeman J, Švandová J, Přikryl R (2010) Long term stability of the buffer material: Rokle, Mock Up-CZ and FEBEX bentonite. Appl Clay Sci (in press)
16. Vinšová H, Večerník P, Jedináková-Křížová V (2006) Sorption characteristics of ^{99}Tc on bentonite materials with different additives under anaerobic conditions. Radiochim Acta 94:435–440