

Mineral stability of Fe-rich bentonite in the Mock-Up-CZ experiment

IGOR STRÍČEK¹, VLADIMÍR ŠUCHA¹, PETER UHLÍK¹, JANA MADEJOVÁ² and IGOR GALKO³

¹Department of Geology of Mineral Deposits, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republic; stricek@fns.uniba.sk

²Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovak Republic; jana.madejova@savba.sk

³G55 s.r.o., Bakossova 8, 974 01 Banská Bystrica, Slovak Republic; g55@g55.sk

(Manuscript received September 4, 2008; accepted in revised form December 18, 2008)

Abstract: Bentonite is a basic component of most concepts of multibarrier systems in underground radioactive waste repositories. It is important to determine the bentonite stability under the conditions close to the future real situation. The paper brings the detailed mineral and structural analyses of smectites from the bentonitic material exposed to the long term Mock-Up-CZ experiment. The compacted barrier blocks and residual filling contained 85 % of bentonite from the Rokle deposit, 10 % of quartz sand and 5 % of graphite. They were exposed to temperatures of up to 90 °C for almost 4 years. Quantitative mineral analyses, crystal size distributions, FTIR spectra, as well as cation exchange capacity and layer charge density show high mineral stability of the Rokle bentonite under the conditions of Mock-Up-CZ experiment. Small changes in the crystal sizes and slight change in the layer charge as a consequence of the experimental alteration could be linked to the hydration and the variation of the geochemical environment of the experiment.

Key words: Mock-Up experiment, long-term bentonite stability, bentonite barrier, Rokle bentonite, Fe-rich montmorillonite.

Introduction

The decaying power from the spent fuel in the high level waste canisters will increase temperature and initially give rise to a thermal gradient over the bentonite buffer by which original water will be redistributed parallel to an uptake of water from the surrounding rock. A number of laboratory test series, made by different research groups, have resulted in various buffer alteration models. The most popular are large laboratory and in-situ tests, done by radioactive waste management agencies such as: ANDRA (France; Delay et al. 2007); ENRESA (Spain; EUR, ENRESA 2005), NAGRA (Switzerland; Villar et al. 2005); ONDRAF/NIRAS (Belgium; ONDRAF/NIRAS 2001); SKB (Sweden; Karnland et al. 2000) in Europe, and many others in the world. The main objective of these studies is to identify the processes occurring in the Mock-Up tests during the heating and water saturation of bentonites. The quantitative analyses of the changes are instrumental for understanding the nature and potential consequences for future repositories. The Belgian Mock-Up experiment OPHELIE (Verstricht & Dereeper 2002, 2003), and Spanish experiment FEBEX (EUR 2000; 2005) are very good examples of large scale projects based on several heating tests simulating the conditions of a radioactive waste repository, and reproducing the thermo-hydro-mechanical processes that could eventually occur in the repositories using the bentonitic barriers.

A similar experiment — Mock-Up-CZ was built by the team of the Czech University of Technology in Prague (Pacovský 2004; Pacovský et al. 2007). The main aim was to test the stability of the local bentonite buffer material for the even-

tual construction of the repository. In this paper we bring the results of detailed mineral and structural analyses of smectites from the bentonitic material used for the experiment.

Materials and methods

The material used for this study is part of an experimental barrier exposed to the experimental conditions of a large physical model Mock-Up-CZ (Pacovský 2004). This experiment simulated the vertical placement of a container with radioactive waste according to the Swedish KBS-3 system. The model consisted of a barrier of bentonite blocks and the heater. Bentonite barrier was closed in a steel tank with a cylinder diameter 800 mm and height 2230 mm and wall thickness of 8 mm. The top and bottom covers were made of 50 mm thick steel. These individual components were connected using 16 bolts. The compacted blocks ($\rho_d = 1700 \text{ kg/m}^3$) and filling of residual free space contained 85 % of bentonite (from the Rokle deposit), 10 % of quartz sand and 5 % of graphite (from the conditioning plant at Netolice) (Pacovský et al. 1998, 2007). The model was saturated with synthetic granitic water (Svoboda & Vašíček 2009). The maximum temperature reached in bentonite buffer was 90 °C. Temperature, swelling pressure and hydration measurements were taken continuously from inside the bentonite barrier throughout the entire duration of the experiment, a period of 3 years and 9 months.

The Rokle bentonite deposit is part of an accumulation of argillized volcanoclastic rocks in the Tertiary stratovolcanic complex of the Doupovské hory Mountains. The main mineral phase — Fe-rich montmorillonite was produced by the al-

teration of basaltic ash in a stagnant, lacustrine environment. Biotite was apparently stable during the alteration of the hyaloclasts. Anatase and possible accessory heulandite-clinoptilolite were also formed in small amounts. Goethite is the youngest oxidation product in some parts of the bentonite. Minute fragments of sodium-rich plagioclase, potassium feldspar, quartz, and muscovite are ubiquitous accessories of the original hyaloclasts. Together with kaolinite, they formed from the underlying fresh or kaolinized orthogneiss (Konta 1986; Hradil et al. 2004).

A series of samples were taken from three different distances with regard to the position of the block in the experimental vessel: close to the heater (T), from the block centre (C), close to the hydration system (O) and the last one from the hand-compacted mixture (N). Samples were also divided in vertical orientation into upper part (V), central part (C), and bottom part (S) with regard to their position in the block (Fig. 1).

Mineral and crystallochemical changes after the experiment were tested by the following techniques:

The XRD analyses of oriented (clay fraction) and random specimens (bulk fraction) were carried out using a Philips PW 1710 (CuK α radiation with graphite monochromator) diffractometer.

Samples for quantitative analyses were milled in a McCrone Micronizing Mill with internal standard ZnO to <20 μm size. The XRD data were converted into wt. % minerals using the RockJock software (Eberl 2003). The program fits the sum of stored XRD patterns of standard, pure minerals and amorphous phases (the calculated pattern) to the measured pattern by varying the fraction of each standard pattern, by using the Solver function in Microsoft Excel to minimize the degree of fit parameter between the calculated and measured pattern. Data were normalized to 100 % at the end of analysis.

XRD patterns with longer exposure times were used for calculations of particle crystal thicknesses using the Bertaut-Warren-Averbach (BWA) technique of Drits et al. (1998) implemented in the MudMaster program (Eberl et al. 1996).

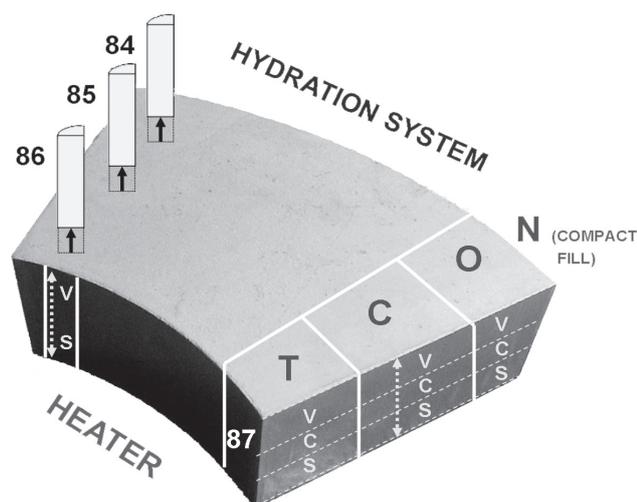


Fig. 1. Position of samples in the compacted block. The distance between the heater and the hydration system was 210 mm.

MudMaster is a program used to calculate crystal thickness from the interference function, which is extracted from intensities of basal XRD reflections by dividing them by the Lorentz-polarization and structure factors. The measurements of the smectite crystal thickness were performed on 001 reflections, recorded for clay samples saturated with ethylene glycol.

The FTIR (Fourier Transform Infrared) spectra were obtained using a Nicolet Magna 750 spectrometer. The KBr pressed pellets technique (1 mg of sample and 200 mg of KBr) was used for the transmission measurements.

The determination method of the CEC (cation exchange capacity) is based on the complete exchange of the naturally occurring cations against a copper triethylenetetramine complex [Cu (trien)]²⁺ (Meier & Kahr 1999). Smectite samples (80, 100 and 120 mg) were added to 50 ml distilled water and 10 ml solution of [Cu (trien)]²⁺. The suspensions were dispersed by an ultrasonic treatment. After 5 min, the suspension was centrifuged. The supernatant solution was separated and the concentration of the Cu(II) complex was determined by spectrophotometry (Cary 100, Varian). A standard deviation of the measurements is 4 % (Ammann et al. 2005).

The UV-Vis spectra of the R6G/clay dispersion were measured using the same spectrophotometer. The final concentration and loading of the dye solution in the dispersions were always 1×10^{-6} M and $0.05 \text{ mol} \cdot \text{g}^{-1}$ of clay, respectively. Visible spectra were measured 1 min after mixing the clay dispersions with the solution of R6G. The prepared R6G/clay dispersions were then shaken for 24 hours to achieve equilibrium in the systems. Another series of spectra for aged dispersions was taken. The spectra of the clay dispersions without dye, related to light scattering from solid particles, were subtracted from the spectra of the dye/clay dispersions in order to obtain the pure spectra of the dye species. Second derivative spectroscopy was used for a better resolution of the individual bands in dye absorption spectra, for the estimation of the peaks' position of arisen forms of the dye, and for the comparison of the amounts of the species reaction systems.

All analyses (except quantitative mineral analyses) were made with <2 μm fractions separated from bulk samples by sedimentation in distilled water. Prior to fractionation, the samples were dispersed in an ultrasonic bath and subsequently treated with sodium acetate buffer, hydrogen peroxide and sodium dithionite (partially modified Jackson 1975 in Šucha et al. 1991). Excess soluble salts were removed by centrifugation followed by dialysis.

Results and discussion

Bulk analysis

Smectite is the main mineral phase in all samples according to the quantitative XRD analyses with contents varying between 42 and 46 % as determined by the RockJock software (Table 1). The quartz content is between 16 and 22 %, volcanic glass up to 9 %, calcite 8 %, and graphite 4 %. Other accessory minerals (up to 5 %) were biotite, muscovite,

Table 1: Quantitative mineral composition of samples.

%	smectite	quartz	biotite	muscovite	kaolinite	illite	calcite	graphite	volcanic glass	feldspar	goethite	SUM %
BUFFER MATERIAL	46	16	4	4	4	2	6	4	9	3	2	100
87 TS	45	20	2	4	4	2	8	4	6	3	2	100
87 TV	44	19	3	3	5	3	8	3	7	3	2	100
87 OS	43	19	4	3	5	2	7	3	9	2	3	100
87 OV	42	19	3	4	5	2	8	3	9	3	2	100
87 NS	46	17	4	4	5	3	6	2	8	3	2	100
84 S	45	21	3	4	4	1	7	2	7	3	3	100
85 S	43	22	3	2	4	3	8	3	6	4	2	100

kaolinite, illite, goethite and in some samples traces of the anatase were detected. Vejsada et al. (2005) identified variable amounts of possibly vermiculite in the Rokle bentonite as a product of biotite alteration. No vermiculite was detected in the present study which can be explained by the high heterogeneity of the material in the deposit. The quantitative mineralogical composition of the experimentally altered bentonite material is stable and does not show any variability. It is almost identical with the original buffer material used for the experiment. This means that no significant modifications occurred in the bentonite during the experiment (Fig. 2). The presence of neoformed calcium sulphate described in other studies (Humbeek et al. 2005; Karnland & Birgersson 2006; Vinšová et al. 2008) was not confirmed in the samples examined in this paper. The precipitation of calcium sulphate in the Mock-Up-CZ test could be the result of dissolution of pyrite (trace amount in Rokle bentonite; Vinšová et al. 2008) or presence of Ca^{2+} and SO_4^{2-} in synthetic

granitic water. The amount of gypsum is probably so small that it is under the detection limit of the techniques used in this study.

Clay fraction analyses

Since the smectite is the most important and the most sensitive component of the buffer material, we focused our interest more closely on the clay fraction ($<2 \mu\text{m}$) which is largely dominated by smectite. Crystallochemical characteristic was determined by the FTIR. The spectrum of original unaffected buffer material and the spectra of samples after the experiment are very similar (Fig. 3). The OH deformation bands at 917 cm^{-1} (AlAlOH) and near 880 cm^{-1} (AlFeOH) show significant substitution of octahedral Al by Fe. Other features in the spectrum, common to all dioctahedral montmorillonites, include a complex Si-O stretching band at 1039 cm^{-1} and Si-O-Al and Si-O-Si deformations at 526 cm^{-1}

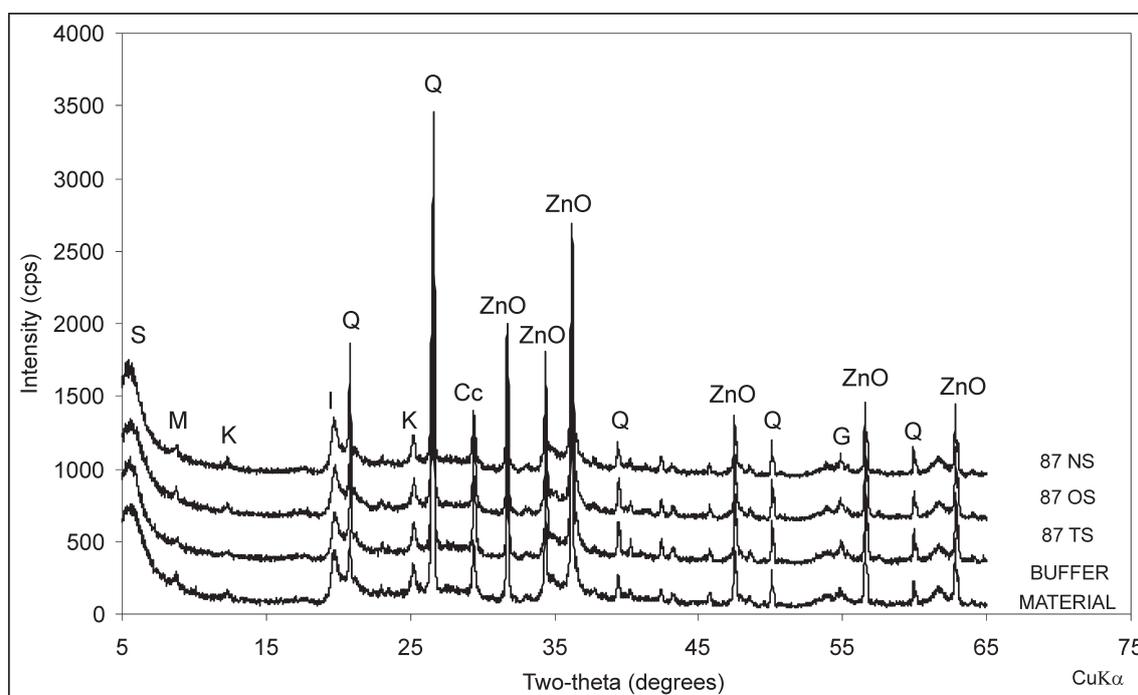


Fig. 2. XRD patterns of unoriented specimens with inner standard ZnO. (S — smectite, M — mica, K — kaolinite, I — clays, Q — quartz, Cc — calcite, G — graphite).

and 470 cm^{-1} respectively. The band at 802 cm^{-1} indicates the presence of an amorphous silica admixture. The weak diagnostic bands of kaolinite at 3696 and 698 cm^{-1} and the quartz doublet at 802 and 780 cm^{-1} were also determined in the IR spectra. No changes in the intensities or positions of the characteristic OH and Si-O bands of montmorillonites can be recognized in the IR spectra of the samples taken from different parts of the compacted block (Fig. 3). Thus the IR spectroscopy confirms the crystallochemical stability of the bentonite Rokle upon the selected experimental conditions.

The stability of smectite crystals (coherently diffracting 1 nm thick 2:1 layers) was determined using XRD based BWA technique. This technique is able to detect the mean thickness of the crystals and the distribution of their sizes. The distribution (Fig. 4) is almost the same for all the measured sample and is of an asymptotic shape. The shape of the distribution is a good parameter to test the differences in the origin or evolution of the samples (Eberl et al. 1998; Šucha et al. 2001; Honty et al. 2004). The similar shape of the crystal distribution in the studied set of samples indicates the environment with no or little influence on the system. However some differences were detected in the mean crystal sizes (Fig. 5). There is a systematic decrease of the mean thickness towards the edge of the experimental vessel where the source of hydration is situated. We suspect that the intensive hydration may have a slight impact on the number of coherently diffracting smectite layers. Water content rises gradually from 15 % near the centre of experimental vessel to 40 % close to the hydration system. The swelling phenomenon in highly compacted smectite clay was studied by Saiyouri et al. (2000). They found that a slight decrease in the thickness of the smectite crystals can be attributed to a partial splitting of them, probably caused by swelling under high pressure conditions. This could easily be the case of the Mock-Up-CZ.

Systematic changes in CEC values were observed neither among the Mock-Up-CZ samples, nor in comparison with the initial sample (Fig. 6). All differences can be assigned to the error of the CEC determination (Ammann et al. 2005) and to the small variations in smectite content.

The molecular aggregation of cationic dyes on the surface of smectites should be able to distinguish the changes in the layer charge density (Bujdák et al. 2003; Czi-

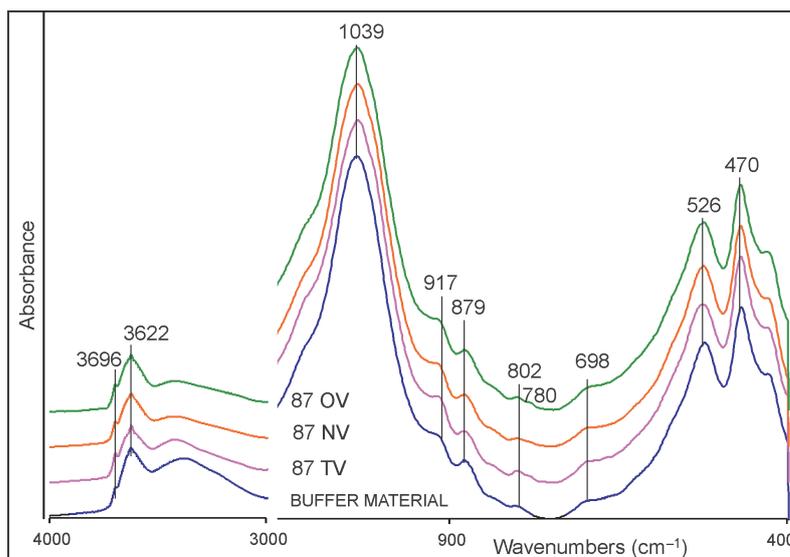


Fig. 3. FTIR spectra of samples.

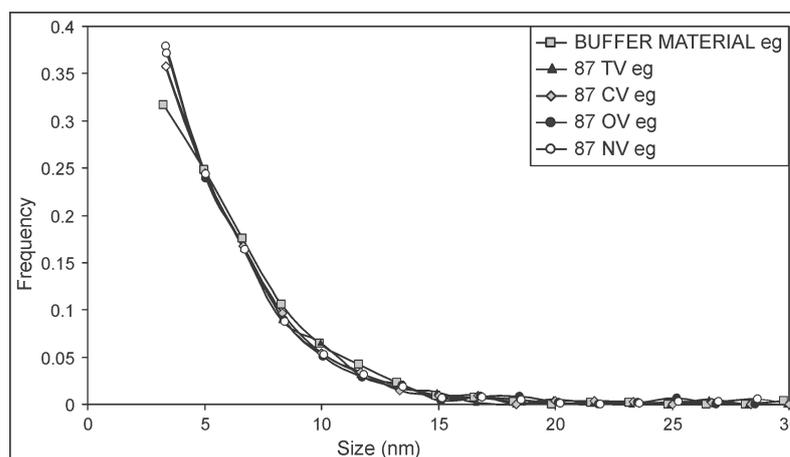


Fig. 4. Particle thickness distribution of smectite crystals.

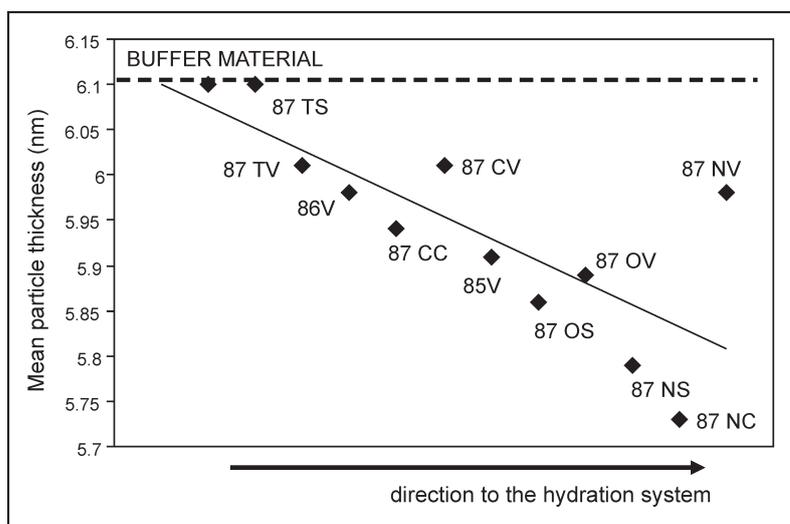


Fig. 5. Mean thickness of smectite particles.

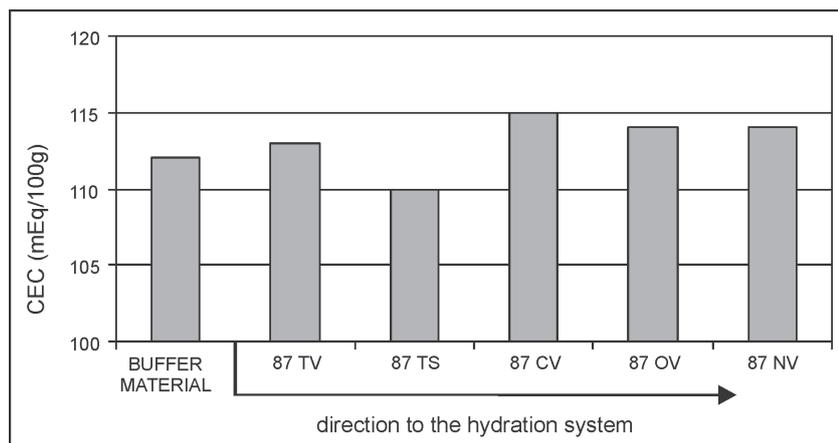


Fig. 6. Cation exchange capacity of <2 μm fraction.

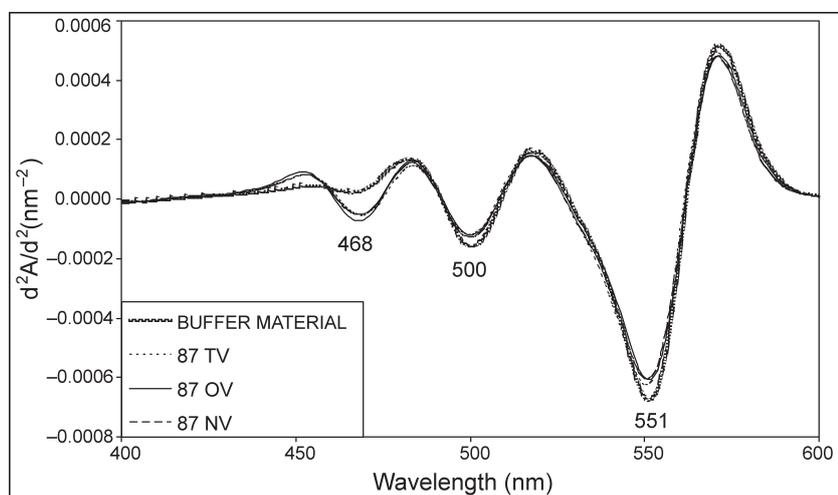


Fig. 7. Second-derivative spectra calculated from the absorption spectra of R6G/clay systems measured 24 hours after mixing the components.

merová et al. 2006). Šucha et al. (2009) demonstrated the relation between Rhodamine 6G (R6G) spectra and low/high charge smectites. According to these findings the bands at about 551 nm could be assigned to the monomers related to low charge smectites and the band at 468 nm to H-aggregates which are formed at the sites with the high layer charge density. Overall it seems that the original smectite represented here by the buffer material is of low layer charge. The R6G spectra changed slightly during the Mock-Up test. The intensity of the band related to H-aggregates increased and the band of monomers decreased as demonstrated by Fig. 7. Taking into account the findings referred to above, this would mean a very small increase in the layer charge during the test.

The observation of Vinšová et al. (2008) indicating illitization and beidelitization of smectite in some local parts of the Mock-Up-CZ experimental column, were not confirmed even using extremely detailed mineralogical examination. Unfortunately no analytical evidence is available in Vinšová et al. (2008) to support the observations and to compare with our data.

Conclusions

The detailed analyses of the bentonite based material used in the Mock-Up-CZ revealed stability of the mineral composition and the crystallochemical characteristics of smectite which is the main barrier component. We can conclude that no deterioration of the smectite's stability occurred during the experiment. No recrystallizations have been observed inside the buffer block, nor in the backfill material. A slight decrease in the crystal sizes could be assigned to the impact of hydration and the slight change in the layer charge could be due to change of geochemical environment inside the experiment. High iron content smectite is very sensitive to such a change.

According to the obtained data the mineral stability of the Rokle bentonite can be ensured over a long period of time if the conditions are similar to those of the Mock-Up-CZ experiment.

Acknowledgments: We thank the Centre of Experimental Geotechnics (CEG), Faculty of Civil Engineering, CTU for providing us with the samples, Dr. Adriana Czimerová, Institute of Inorganic Chemistry, Slovak Academy of Sciences for R6G spectra analyses and Dr. Ľubica Puškelová, Geological Institute, Slovak Academy of Sciences for XRD analyses. Financial support from the Slovak Grant Agency VEGA (Project 1/3072/06) is acknowledged.

References

- Amman L., Bergaya F. & Lagaly G. 2005: Determination of the cation exchange capacity of clays with copper complexes revisited. *Clay Miner.* 40, 441–453.
- Bujdák J., Iyi N., Kaneko Y., Czimerová A. & Sasai R. 2003: Molecular arrangement of rhodamine 6G cations in the films of layered silicates: the effect of the layer charge. *Physical Chemistry Chemical Physics* 5, 4680–4685.
- Czimerová A., Bujdák J. & Dohrmann R. 2006: Traditional and novel methods for estimating the layer charge of smectites. *Applied Clay Sci.* 34, 2–13.
- Delay J., Vinsot A., Krieguer J.M., Rebours H. & Armand G. 2007: Making of the underground scientific experimental programme at the Meuse/Haute-Marne underground research laboratory, North Eastern France. *Physics and Chemistry of the Earth* 32, 2–18.
- Drits V.A., Eberl D.D. & Šrodoň J. 1998: XRD measurement of mean thickness, thickness distribution and strain for illite and illite/smectite crystallites by the Bertaut-Warren-Averbach technique. *Clays and Clay Miner.* 46, 461–475.

- Eberl D.D. 2003: User's guide to Rockjock — a program for determining quantitative mineralogy from powder X-ray diffraction data. *U.S. Geological Survey, Open-File Report* 3-78, 40.
- Eberl D.D., Drits V., Šrodoň J. & Nüesch R. 1996: MUDMASTER: a program for calculating crystallite size distributions and strain from the shapes of X-ray diffraction peaks. *U.S. Geological Survey, Boulder, Open-File Report*.
- Eberl D.D., Drits V.A. & Šrodoň J. 1998: Deducing growth mechanisms for minerals from the shapes of crystal size distributions. *Amer. J. Sci.* 298, 499–533.
- EUR 19147 EN 2000: Full-scale engineered barriers experiment for a deep geological repository for high-active waste in crystalline host rock — Phase I (FEBEX project). *European Commission, Nuclear Science and Technology, Project Report*.
- EUR, ENRESA 2005: Full-scale engineered barriers experiment for a deep geological repository for high-active waste in crystalline host rock — Phase II (FEBEX project). *European Commission, Nuclear Science and Technology, Project Report*.
- Honty M., Uhlík P., Šucha V., Čaplovičová M., Franců J., Clauer N. & Biroň A. 2004: Smectite-to-illite alteration in salt bearing bentonites (The East Slovak Basin). *Clays and Clay Miner.* 52, 5, 533–551.
- Hradil D., Grygar T., Hrušková M., Bezdička P., Lang K., Schneeweiss O. & Chvátal M. 2004: Green earth pigment from Kadaň region, Czech Republic: use of rare Fe-rich smectite. *Clays and Clay Miner.* 52, 767–778.
- Humbbeck H.V., Verstricht J. & Gatabin C. 2005: The Mock-Up OPHELIE: A large scale backfill test for HLW disposal. International Meeting, *Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, Abstracts*, France.
- Jackson M.L. 1975: Soil chemical analysis — advanced course. *Published by the author*, Madison, Wisconsin, 1–386.
- Karnland O. & Birgersson M. 2006: Montmorillonite stability. With special respect to KBS-3 conditions. *SKB Technical Report*, TR-06-11.
- Karnland O., Sandén T., Johannesson L.E., Eriksen T.E., Jansson M., Wold S., Pedersen K., Motamedi M. & Rosborg B. 2000: Long term test of buffer material. *Final report on the pilot parcels*. SKB TR 00-22.
- Konta J. 1986: Textural variation and composition of bentonite derived from basaltic ash. *Clays and Clay Miner.* 34, 3, 257–265.
- Meier L.P. & Kahr G. 1999: Determination of the Cation Exchange Capacity of clay minerals based on the Complexes of the Copper(II) ion with Triethylenetetramine and Tetraethylenepentamine. *Clays and Clay Miner.* 47, 3, 386–388.
- ONDRAF/NIRAS 2001: SAFIR 2 — *Safety Assessment and Feasibility Interim Report* 2. NIROND 2001-06 E.
- Pacovský J. 1998: Research on bentonite barriers in underground repository of nuclear waste. *Proceedings of the International Symposium on Problematic Soils*, Sendai, 615–618.
- Pacovský J. 2004: The use of the Mock-Up-CZ physical model for the design of a geotechnical barrier for a deep repository. In: *Proceedings of the Fifteenth Southeast Asian Geotechnical Conference*, SEAGS, Pathumthani, Thailand, 669–680.
- Pacovský J., Svoboda J. & Zapletal L. 2007: Saturation development in the bentonite barrier of the Mock-Up-CZ geotechnical experiment. *Physics and Chemistry of the Earth* 32, 767–779.
- Saiyouri N., Hicher P.Y. & Tessier D. 2000: Microstructural approach and transfer water modelling in highly compacted unsaturated swelling clays. *Mech. Cohes.-Frict. Mater.* 5, 41–60.
- Svoboda J. & Vašíček R. 2009: Preliminary geotechnical results from the Mock-Up-CZ experiment. *Applied Clay Sci.* doi:10.1016/j.clay.2008.12.012. in print.
- Šucha V., Šrodoň J., Zatkalíková V. & Franců J. 1991: Mixed layer mineral of illite/smectite type: separation, identification, use. *Miner. Slovaca* 23, 267–274 (in Slovak with English abstract).
- Šucha V., Šrodoň J., Clauer N., Elsass F., Eberl D.D., Kraus I. & Madejová J. 2001: Weathering of smectite and illite-smectite under temperate climatic conditions. *Clay Miner.* 36, 403–419.
- Šucha V., Czimerová A. & Bujdák J. 2009: Surface properties of illite-smectite minerals detected by interactions with Rhodamine 6G dye. *Clays and Clay Miner.* 57, 361–370.
- Vejsada J., Hradil D., Řanda Z., Jelínek E. & Štulík K. 2005: Adsorption of cesium on Czech smectite-rich clays — a comparative study. *Applied Clay Sci.* 30, 1, 53–66.
- Verstricht J. & Dereeper B. 2002: The Mock-Up OPHELIE a large scale backfill test for HLW disposal. International Meeting, *Clays in Natural and Engineered Barriers for Radioactive Waste Confinement, Abstracts*, Reims, France.
- Verstricht J. & Dereeper B. 2003: The OPHELIE Mock-Up experiment First step in the demonstration of the feasibility of HLW disposal. *Abstr. in WM'03 Conference*, Tucson, AZ.
- Villar M.V., García-Sineriz J.L., Bárcena I. & Lloret A. 2005: State of the bentonite barrier after five years operation of an in situ test simulating a high level radioactive waste repository. *Engng. Geol.* 80, 175–198.
- Vinšová H., Jedináková-Křížová V., Kolaříková I., Adamcová J., Příkryl R. & Zeman J. 2008: The influence of temperature and hydration on the sorption properties of bentonite. *J. Environmental Radioactivity* 99, 2, 415–425.