Review of Studies of Clay Minerals as Significant Component of Potential Host Rocks or Engineering Barriers for Radioactive Waste Disposals Performed at Comenius University in Bratislava

Uhlík Peter[1*], Stríček Igor[2], Šucha Vladimír[1], Čaplovičová Mária[1]

[1] Department of Geology of Mineral Deposits, Faculty of Natural Sciences, Comenius University in Bratislava, (SK)
[2] Department of Geotechnics, Faculty of Civil Engineering, Slovak University of Technology in Bratislava, (SK)

* Corresponding author: uhlik@fns.uniba.sk

Introduction

About 50 % of electric power is produced by nuclear power plants in Slovakia. In spite of the significant production of nuclear waste, Slovakia has not defined basic strategy of radioactive-waste isolation. However, some pilot projects and studies have been carried out. Five areas were determined as prospective sites for construction of deep geological repository (DGR). Two of them are situated in the south of Slovakia. Szecseny schlier (mixture of siltstones and claystones) of Lučenec Formation (Egerian) is one of the most prospective host rocks from lithological, structural and spatial perspective (Matejovic et al., 2006). Besides the investigation of potential host rock for DGR the studies of bentonite properties as important part of engineering barriers for radioactive waste disposals were performed (Galamboš et al., 2011). Detailed mineral and structural analyses of smectites from the bentonitic material exposed to laboratory Mock-Up test were realised (Stríček et al., 2009, Stríček, 2010). Particular interest has been focused on interaction between Fe and smectites (Osacký et al., 2009, 2010). Other field of interest is investigation of sorption of Cs and Sr on natural and modified bentonites, including irradiation (Galamboš et al., 2009a, b). Purpose of this work is to present a short review of other studies done by our group with partial focusing to interaction of organic dye (Rhodamine 6G) with smectite that is connected with changes of layer charge after treatment; possibilities to measure preferential orientation of clays after compaction by TEM and to effort to use X-ray microtomography for inner structure of sediments.

1 Gamma-irradiation effects on smectite properties

Irradiation effects on a smectite stability is one of important phenomena that is or should be interesting for safety managements of radioactive waste disposals. Therefore, two of Slovak bentonites were tested by gamma-irradiation. Samples were irradiated in dry state (JC; drying at 105°C, 24 hours), hydrated state (JB; saturated by water vapour, 24 hours) and in hydrated state with 10 % admixture of powder Fe at Slovak Technical University, using ^{60}Co source with medium dose input of 0.21 kGy/h. Maximal total absorbed dose was 1.5 MGy.

The mineralogical composition and the crystal structure of the samples were investigated by X-ray diffraction and infrared spectroscopy. The cation exchange capacity was determined using the complexes of copper (II) ion (Meier & Kahr, 1999), layer charge by the Rhodamine 6G technique: water and Rhodamine 6G solution (10^{-5} mol dm^{-3}) were added with stirring to obtain R6G-clay dispersions with final R6G and clay concentrations of $5x10^{-6}$ mol dm^{-3} and $5x10^{-2}$ g dm^{-3}, respectively. The visible spectra of R6G-clay dispersions were recorded using a UV-vis spectrophotometer (Varian Cary 100) (Bujdák et al., 2003; Czimerová et al., 2006; Šucha et al., 2009).
Mineral composition as well as the structure of the main mineral - smectite seems to be stable even under at the highest gamma-irradiation doses that were applied. Practically only one very moderate change was observed for hydrated sample after irradiation by Rhodamine 6G technique (Fig. 1). Small increase of negative intensity of absorption peak of monomers (~ 500 nm) points out decreasing of charge. If the spectra of dry and saturated samples without irradiation are compared there is also increase of area of absorbance band that relate to lower charge for dry sample (Figure 1).

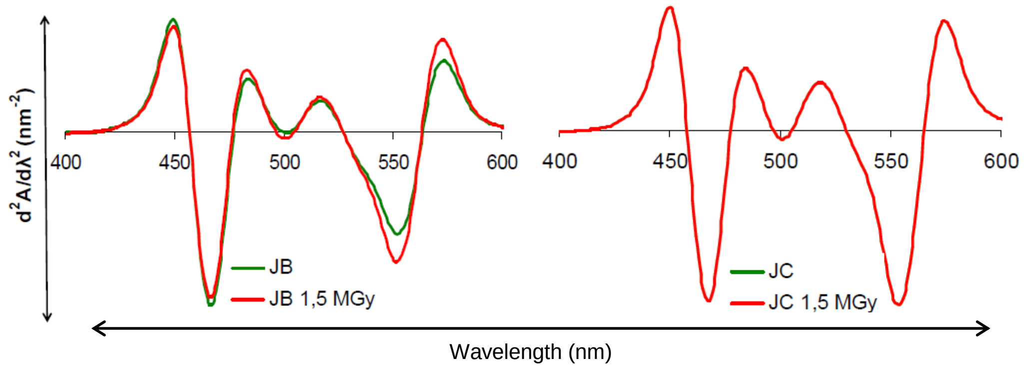

Figure 1. Second-derivate spectra of Rhodamine 6G (band position of H-aggregates: 460-470 nm– higher layer density; H-dimers: ~ 500 nm; monomers: 535-570 nm– lower layer density) measured 24 h after mixing the dye solution with the clays before and after irradiation.

2 Effect of bentonite compaction on the orientation of smectite particles

An important function of bentonite as a buffer material in a geological disposal of high-level radioactive waste is to inhibit groundwater flow and to retard the movement of radio nuclides in the region between the waste forms and surrounding rocks. It is well known from other studies that the diffusion of radio nuclides in bentonite is a function of various pore structural properties or parameters, such as porosity, dry density of bentonite, additives to bentonite, initial bentonite grain size, etc. Most of these parameters are directly connected to smectite particle orientation which may be influenced significantly during bentonite processing and compacting. Therefore study was focused on the role of compaction on the orientation of smectite particles and/or aggregates. Two different compaction techniques were applied to two Slovak bentonites. They were milled to the fractions < 250, 45 and 15 µm. A standard uniaxial technique along with an isostatic technique with pressure up to 300 MPa were used. The bentonites were compacted to dry density between 1.6 g/cm^3 and 1.9 g/cm^3. Oriented pieces were carefully sampled from pressed samples. The effect of the clay particle orientation was tested directly by transmission electron microscopy (JEOL JEM-2000 FX) of ultra thin sections observed at magnifications of 4000 – 8000x. TEM images were processed in graphical program ImageJ, used also for determination of optical porosimetry (Janega, Durmeková, 2004). Partical orientation was determined by using rose diagram software Rose (Figure 2).
Dependence of preferential orientation of particles on the compaction technique were not confirmed. The preferential orientations of smectite particles, perpendicularly to uniaxial pressure, were determined only sometimes. Randomly oriented particles were observed with same frequency as oriented.

Contradictory results were detected also for samples pressed by isostatic technique. Part of TEM images show randomly oriented and part preferred oriented samples. We assume that these phenomena could be caused by mineral and predominately partical size inhomogeneity of bentonites. Partial orientation of clay particles were observed around aggregates or larger mineral grains in bentonites pressed by both technique. The aggregates were composed of randomly oriented fine particles. Such observation allows possibility that the TEM image could represent just one large aggregate with original random orientation. Used technique is also suitable for calculation of interparticle and pore space. The technique is time consuming and involves special attention for selection of TEM images without artificial defects resulted from sample preparation.

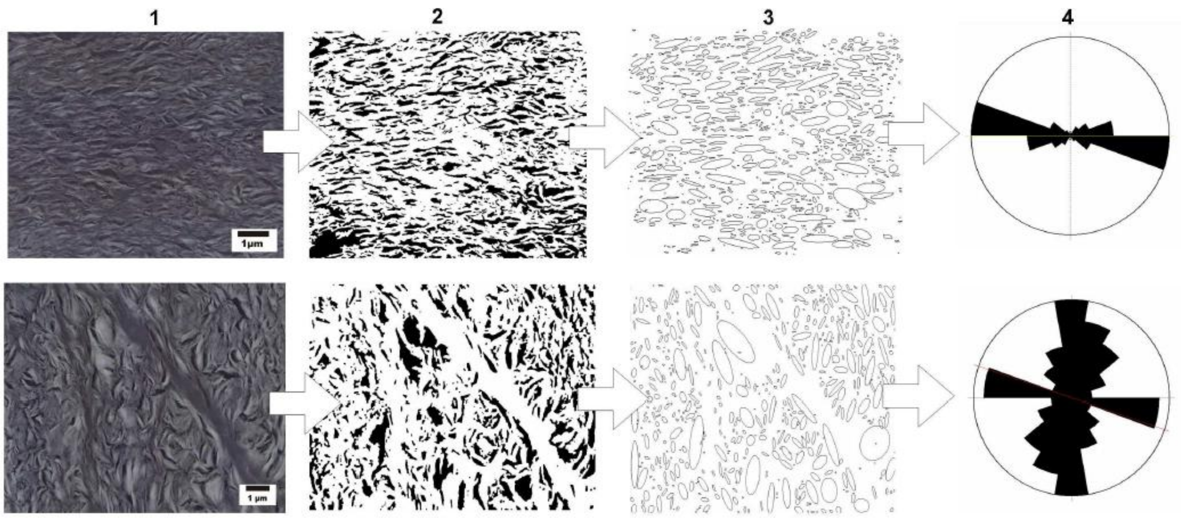

Figure 2. Example of preferential orientation (A-bentonite J, fraction <45□m, uniaxial stress) and random orientation of particles (B- bentonite J, fraction <250□m, isostatic stress) at the TEM images (1). 2- binary pictures (black area represent solid particles), 3-solid particles transformed to elipses, 4- rose diagram.

3 Lučenec Formation (Western Carpathian) – potential site for deep repository of nuclear waste

The mineral composition of Szecseny schlier was studied. XRD quantitative analysis of selected siltstones from several drill cores demonstrated their homogeneity. Major mineral phase is quartz that together with feldspars comprises half of the mineral composition. Carbonates (calcite, dolomite ± Fe carbonate) and phyllosilicates comprise approximately a quarter of siltstones composition each. The homogeneity of clay fraction was also confirmed. The presence of clay minerals is practically the same without regard to the depth of studied samples (22 to 870 m) and boreholes location. Major clay mineral is illite-smectite (75-85 % of smectite interlayers). It comprises about 60-65 % of clay fraction. Determined mineral homogeneousness of studied sediments and presence of expanding clays are next positive features of Szecseny schlier as potential geological site for nuclear waste disposal. Previous works pointed out to high dry bulk density (2.2 g/cm^3) and low porosity (14 to 20%) which relates to it. Preliminary measurements of hydraulic conductivity performed on remolded samples (i.e., samples made by recomposing and compacting samples to their *in situ* density) yield values as low as 10^{-10}m/s and even 10^{-10} m/s (Matejovic et al., 2006). An application of X-ray microtomography (David et al., 2007; Hain et al., 2011) to Szecseny schlier is testing as a possibility to determine properties of inner structure (porosity, pore size) by nondestructive three-dimensional method.

Acknowledgement

Support by Slovak grant agency (VEGA) 1/0219/10 is appreciated.

References

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. *AppliedClay Sci.* 34, 2—13.

David C., Robion P.. Menendez B. (2007) Anisotropy of elastic, magnetic and microstructural properties of the Callovo-Oxfordian argillite. 1983 Annual Meeting of the Southwestern Psychological Assoc., San Antonio, Physics and Chemistry of the Earth**,** 32**,** 1-7, 145-153.

Galamboš M., Kufčáková J., Rajec P. (2009a) Sorption of strontium on Slovak bentonites. J Radioanal Nucl Chem 281(3): 347–357

Galamboš M., Kufčáková J., Rajec P. (2009b) Adsorption of cesium on domestic bentonites. J Radioanal Nucl Chem 281(3): 485–492

Galamboš M., Rosskopfova O., Kufčáková J., Rajec P.(2011) Utilization of Slovak bentonites in deposition of high-level radioactive waste and spent nuclear fuel. J Radioanal Nucl Chem 288 (3), 765-777

Hain, M. Nosko, M. Simančík, F. Dvorák, T. Florek, R. X-ray microtomography and its use for non-destructive characterisation of materials. In *MEASUREMENT 2011 : Proceedings of the 8th International Conference on Measurement.* Editors: J. Maňka, V. Witkovský, M. Tyšler, I. Frollo. Bratislava : Institute of Measurement Science SAS, 2011. 123-126.

Matejovic I., Hok J., Madaras J., Slaninka I. and Pritrsky J., (2006). Status of the Deep Geological Disposal Program in the Slovak Republic. In Witherspoon P. A. and Bodvarsson G.S., ed.: Geological Challenges in Radioactive Waste Isolation. Fouth Worldwide Review, Report LBNL – 59808, 173-189.

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.

Janega, A., Durmeková, T.(2004) Application of optical porosimetry in engineering and environmental geology. *Geológia a životné prostredie,* Štátny geologický ústav D. Štúra, 45-47, (in Slovak).

Osacký M, Honty M, Madejová J., Bakas T., Šucha V (2009) Experimental interactions of Slovak bentonites with metallic iron. Geologica Carpathica 60(6):535–543

Osacký M., Šucha V, Czimerová J., Madejová J (2010) Reaction of smectites with iron in a nitrogen atmosphere at 75 _C. Appl Clay Sci 50(2):237–244.

Stríček I. (2010) Bentonite mineral stability in barrier conditions. PhD thesis. Comenius University in Bratislava, 117p.

Stríček I, Šucha V, Uhlík P, Madejová J, Galko I. (2009) Mineral stability of Fe-rich bentonite in the Mock-Up-CZ experiment. Geologica Carpathica 60(5):431–436

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.