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Research paper

Determination of pore water composition during long term interaction of bentonite substrates with water media: Comparative study

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ABSTRACT

Knowledge of pore water composition is crucial information in research of long-term stability of bentonite and is also crucial for any stability predictions based on geochemical modeling. This paper reports validation results of two frequently used extraction methods — centrifugation and leaching. Three types of bentonite materials were used in our study. The first one was the Czech raw bentonite from the Rokle deposit. The second type of bentonite was “Mock-Up-Cz”, which is a mixture of bentonite material from the Rokle deposit with finely ground quartz and graphite powder. The third type of material was the FEBEX bentonite obtained from the Cortijo de Archidona deposit. All the bentonite samples were placed into pressure vessels and interacted with natural water during a one-year experiment. Free water, obtained during these interactions, was used as a comparative pore water composition for both of the extraction methods. The high water content in saturated bentonite, reaching about 50 m%, allowed the use of both methods. Concentrations of Mg^{2+}, Ca^{2+}, K^{+} and Na^{+} in water were determined. Centrifugation could be generally considered as a more suitable method because of the smaller differences between free water composition and concentrations obtained from extracted pore water compared to the leaching method. However, actual differences will depend on the type of bentonite and on the composition of the water media. In some cases, the leaching method yields better results. Leaching usually leads to higher concentrations of alkali metals and lower concentrations of alkaline earth metals. This indicates that bentonite substrates are sensitive to the change of external conditions and quickly interact with the water media.

1. Introduction

As montmorillonite-rich clays, bentonites are considered as a good buffer and engineered barrier for long time repositories of high-level radioactive waste disposal. Their required features are high plasticity, high swelling capacity and low hydraulic conductivity.

The desired material properties of bentonites are dependent on the amount of smectite minerals in the bulk material, on the smectite species and on the exchangeable cations in the interlayer position. Also, interlayering of smectites with another clay mineral, illite, is common in bentonites (Carlson, 2004).

The knowledge of pore water composition plays a crucial role in the understanding of processes that take place during bentonite barrier interaction with water, in geochemical modeling of its transformation etc. Pore water composition influences many geochemical processes in compacted bentonite, such as adsorption on mineral surfaces, new mineral phases formation, transport of the radionuclides, etc. According to Wersin (2003), the aqueous phase in compacted bentonites is commonly regarded as “free water”. Data about pore water chemistry of compacted bentonite with water content at about 23 m% are rarely found; the extraction method may significantly influence the pore water composition. That is why the selection of an appropriate extraction laboratory method is so important (Fernández et al., 2004). There are several possibilities for pore water extraction, such as squeezing, centrifugation or leaching, but all these methods may influence pore water chemistry. Comprehensive comparison of pore water extraction laboratory methods was done by Sacchi et al. (2001) and Di Bonito (2005). Squeezing at high pressures may produce experimental artifacts and is not feasible for the extraction of pore water from bentonites with water content below 20 m% (Cuevas et al., 1997). On the other hand, leaching may cause dissolution of highly soluble salts and cation exchange reactions, especially at high liquid to solid ratio. Centrifugation and filtration methods are prone to artifacts resulting from sample oxidation (de Craen et al., 2004), temperature variations and contamination from colloidal particulate matter passing through filters (Angelidis, 1997). The analyses of pore water samples extracted by uniaxial or triaxial compression and by ultracentrifugation methods

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from adjacent core samples are generally in agreement, within the analytical error of 10% to 15% (Yang et al., 2003).

This paper focuses on usability validation of two extraction methods — centrifugation and leaching tests. Both methods were chosen since they are frequently used in laboratories and represent low-cost and easily available methods. The main advantage of our validation procedure was that we obtained data from a long term experiment where bentonite substrate interacted with natural water, and non-affected free water could be used as a comparative pore water composition for both extraction methods. Thus, this free water served for comparison with chemical composition of water obtained from two types of extraction experiments. Three types of bentonite were used in the experiment: raw Czech bentonite from the Rokle deposit, the “Mock-Up-Cz” bentonite (mixture of the Czech bentonite from the Rokle deposit, quartz and graphite, long term thermally loaded) and the FEBEX bentonite.

Long-term investigation of the stability of three types of bentonite during interactions with natural water provided sufficient data to assess the validity of water chemical composition in contact with the bentonite. The aim of this study is not to develop a standard method for chemical composition determination of the water in contact with bentonite or evaluation of bentonite transformation processes. The main purpose of the paper is to alert the observed differences in the obtained composition of the water, which is caused by the different extraction methodology and depends on the type of bentonite and particular cation.

2. Methods

2.1. Experiment and material

The long term experiment was performed at the Centre of Experimental Geotechnics (CEG) at the Faculty of Civil Engineering Czech Technical University (CTU) in Prague, Czech Republic. Three types of materials were used. The first one was Czech raw bentonite from the Rokle deposit situated in the northern part of the Czech Republic (Carlson, 2004; Carlson and Keto, 2006; Pusch et al., 2007). The second type of bentonite was the “Mock-Up-Cz”, which is a mixture of material from the Rokle deposit with 10% of finely ground quartz (of “Provodin” origin) and 5% of graphite powder (processing plant at “Netolice”), loaded during the Mock-Up-Cz experiment (Kolaříková et al., 2010; Pusch et al., 2007). Bentonites were used in a ground non-activated state. The third type of material was the FEBEX bentonite from the Cortijo de Archidona deposit, situated in the area of Serrata de Níjar (Almería, Spain). The montmorillonite content is higher than 90% (92 ± 3 m%), from which 10–15% is illite as montmorillonite–illite mixed layers. Besides, the bentonite contains variable quantities of quartz (2 ± 1 -m%), plagioclase (2 ± 1 m%), K-feldspar, calcite and opal-CT (cristobalite–tridymite, 2 ± 1 -m%). The major exchangeable cations are Ca^{2+} (38%), Mg^{2+} (28%), Na^{+} (23%) and K^{+} (2%) (Lloret and Villar, 2007).

All the bentonite samples were homogenized and dried out at the beginning of the experiment. The chemical composition of bentonite substrates is given in Table 1. For recalculated chemical analysis to normative mineral composition see Table 2.

Prepared bentonites were placed in pressure vessels and were in contact with natural water collected from the drills in the Josef Underground Educational Facility (Pacovský et al., 2007). The composition of this water is given in Table 3 The Josef gallery was excavated as part of the exploration of the Psí hory gold-bearing district which is located mainly in the proterozoic Jílovské belt, in rocks of more than 600 Ma old. These rocks were subsequently penetrated by Central Bohemian Pluton granitoid rocks during the Variscan orogenesis (Morávek and Litochleb, 2002).

The ratio of solid to liquid was 4 kg of bentonite to 3 L of natural water. Initial water content in all bentonite samples was ±10. High content of natural water was used for faster saturation of bentonites during loading test and for obtaining sufficient amount of water at the end of experiment.

Table 1
Chemical composition of bentonite substrates used for experiments (given in mass%).

Bentonite	Mock-Up-CZ	FEBEX	Rokle
Component	m%	m%	m%
$-H_2O$	7.55	6.13	9.83
$+H_2O$	4.58	6.73	6.71
SiO_2	46.73	56.46	43.72
TiO_2	3.14	0.28	4.17
Al_2O_3	11.48	17.54	13.85
Fe_2O_3	10.02	3.07	14.47
FeO	0.21	0.20	0.11
MnO	0.16	0.04	0.14
CaO	4.54	1.54	2.66
MgO	2.33	4.78	2.13
K_2O	0.81	1.00	0.94
Na_2O	0.58	1.25	0.26
Li_2O	0.0040	0.0132	0.0021
S	0.04	0.02	0.01
CO_2	2.5	0.25	0.25
P_2O_5	0.52	0.00	0.83
C	4.89	0.00	0.00
Total	100.08	99.30	100.08

This dispersion was enclosed in a pressure vessel and heated to 95 °C. Temperature of 95 °C was used to simulate the effect of radioactive waste container onto bentonite material (Svoboda and Vašíček, 2010). It is supposed that spent fuel cell will be deposited into bentonite barrier when temperature drops below the boiling point of water (100 °C). Closed vessels were used to avoid water excessive evaporation during the thermal loading.

Two runs of long term pressure vessel experiments were performed. The first one lasted for six months and the second one for twelve months. The pressure vessels were controlled in regular monthly intervals, bentonite substrates were carefully mixed with water and when needed, distilled water was added to reach the original mixture volume. It is obvious that the dispersion was in contact with atmosphere all the time during the experiment.

At the end of the experiments, the layer of free water equilibrated with bentonite remained above the bentonite substrate (Fig. 1).

The volume of 1 L of free water was sampled, placed into plastic bottles and stored in a refrigerator at 4 °C. The free water above bentonite substrate was clear — no filtration procedure was necessary.

The basic presumption is that free water above the saturated bentonite is in equilibrium with the bentonite and has the same composition as pore water inside the saturated bentonite (Fig. 2).

2.2. Extraction techniques

After sampling 1 L of the free water for analysis, 2 L of water remained in vessel, partly as free clear phase above bentonite, and partly in the form of bentonite dispersion. Thus, the water content in all

Table 2
Chemical analysis recalculated to normative mineral composition (given in mass%).

Mineral	Mock-Up-Cz	FEBEX	Rokle
Calcite	6.77	0.60	0.66
Mt–Ca	5.78	4.70	2.63
Mt–K	24.42	26.89	0.00
Mt–Na	25.88	50.30	11.39
Nontronite–Ca	34.17	9.82	47.27
Saponite–Ca	2.88	7.65	5.35
Illite	0.00	0.00	15.50
Kaolinite	0.00	0.00	17.17
Pyrite	0.09	0.04	0.02
Total	100.00	100.00	100.00