On-Going Bentonite Pore Water Studies by NMR and SAXS

Torbjörn Carlsson [1*], Arto Muurinen [1], Andrew Root [2]

[1] VTT Technical Research Centre of Finland (FIN)
[2] MagSol (FIN)

* Corresponding author: torbjorn.carlsson@vtt.fi

Abstract

Compacted water-saturated MX-80 bentonite is presently being studied by SAXS and NMR in order to quantify the major pore water phases in the bentonite. The SAXS and NMR measurements gave very similar results indicating that the porewater is mainly distributed between two major phases (interlayer and non-interlayer water) and also indicate how these phases depend on the bentonite dry density.

Introduction

The repository

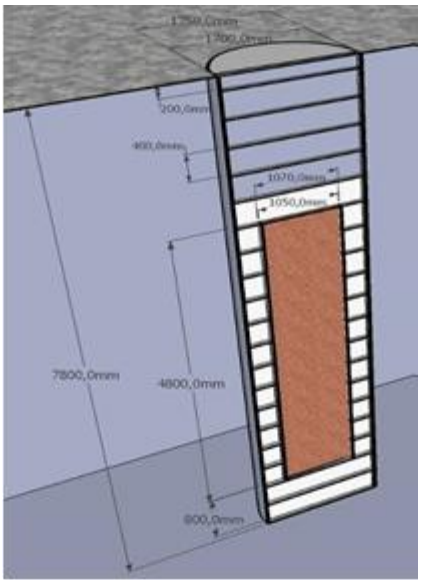

Figure 1. Conceptual image of a filled deposition hole (Posiva 2010).

The planned Finnish repository for spent nuclear fuel is based on the well-known KBS-3 concept. This means that the nuclear waste is contained in iron/copper canisters placed at a depth of 400-500 m in solid bedrock. Each canister is located in a deposition hole, which contains compacted bentonite as a buffer between the rock and the canister (Figure 1).

The pore water

One of the safety functions of bentonite is to hinder radionuclide transport in case of canister failure. In the long-term, the bentonite is expected to be completely water-saturated and possible radionuclide transport through the bentonite is thought to occur in the pore water. Understanding and modelling of the behaviour of bentonite require, inter alia, data on how the pore water is distributed between different phases under various conditions. The pore water is mainly found to be distributed between two phases, which in the following are denoted 'interlayer water' and 'non-interlayer water'. These terms refer to the water located in the pore space between montmorillonite unit layers and to the water filling the remaining part of the total pore space, respectively.

Rationale for the study

The state of water in various clay/water systems has been studied for several decades. Examples of early studies are the development of a structural model of water in contact with a montmorillonite surface (Forslind 1948), the work on the nature and properties of water in montmorillonite (Low 1979), and the development of a general microstructural model for water-saturated bentonite (Pusch et al. 1990). These, as well as numerous other early studies, improved the understanding of how water is organised in saturated bentonite. Subsequent recent research benefits from the development of new techniques, access to more advanced computers and analytical software, etc., and can therefore improve our knowledge further. Recent studies have shown, for example, the number of water phases in compacted saturated Kunigel-V1 bentonite (59.3 wt% montmorillonite) by ^{1}H NMR (Ohkubo et al. 2008) and provided quantitative 3D-characterisations of the bentonite pore structure by FIB-nanotomography combined with high pressure freezing (Holzer et al. 2010).

The use of more than one analytical method is advantageous, since the combined results from different methods might, at least ideally, add more to the understanding of the bentonite microstructure, than results based on one method alone. This is why a series of parallel bentonite studies, one of which is the present one, is being carried out at VTT. This paper presents the results of SAXS and ^{1}H NMR experiments/measurements performed in order to quantify the relative proportions of different water phases in saturated MX-80 bentonite. Briefly, the objective of the ongoing work is to determine the number of water phases and also to quantify their relative amounts in saturated MX-80 under the experimental conditions considered.

Experimental

The material consisted of water-saturated compacted MX-80 bentonite (from American Colloid Company). The dry density ranged from 0.7 to 1.6 g/cm^3. The temperature of the samples was 25 ˚C. The ^{1}H NMR measurements were carried out using a Chemagnetics CMX Infinity 270 MHz spectrometer. A CPMG pulse sequence was used with a very short (22µs) refocusing delay, τ, and acted as a spin locking pulse. This effectively measured the relaxation in the rotating frame, referred to as $T_{1\rho}$, with a spin locking field of $1/2\tau$. The relative amounts of the water phases were determined by peak-o-mat, a data analysis and curve fitting program suitable for fitting of discrete exponential decays (Kristukat 2008).

The SAXS measurements were made by a Bruker MICROSTAR microfocus rotating anode X-ray source with Montel Optics. Details on the SAXS measurements are found in Muurinen (2009).

Results

The results from the SAXS measurements are shown in Figure 2, where scattering data are plotted vs. basal space for four water-saturated MX-80 samples. The graphs differ with regard to both the positions of the diffraction peak, and the slopes seen at higher basal space values. The curves were analysed in accordance with procedures described elsewhere (Muurinen 2009 and references therein). The results indicate the presence of two different clay/water fractions in the samples; a ‘soft fraction’ and a ‘dense fraction’. By combining the information from SAXS measurements with chloride exclusion data, it was possible to evaluate the pore sizes in each fraction.

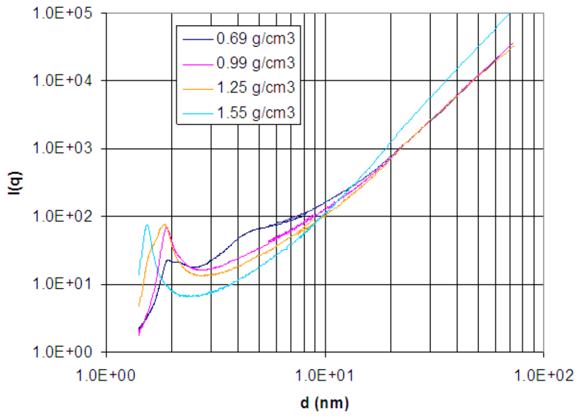

Figure 2. SAXS scattering data as a function of the basal space for the MX-80 samples (Muurinen 2009).

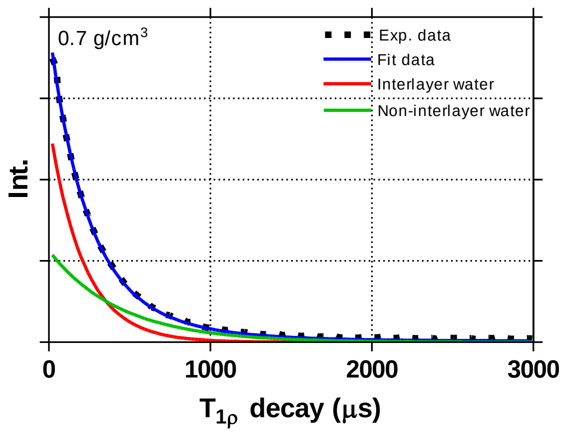

Figure 3. NMR $T_{1\rho}$ decay curves indicating the presence of two water phases, interpreted as 'interlayer water' (red graph) and 'non-interlayer water' (green graph)[3].

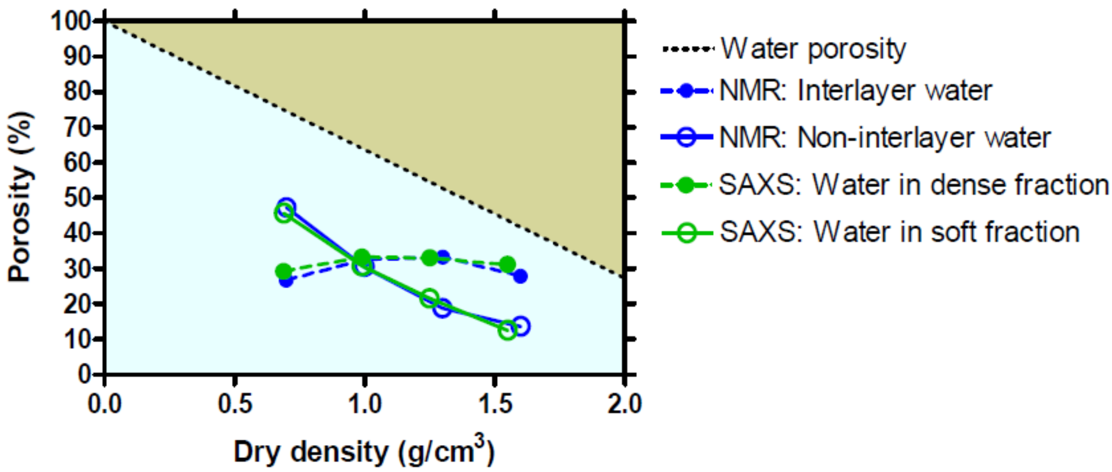

Figure 4. SAXS- and NMR-data suggest for a given dry density the same relative amounts of interlayer and non-interlayer water in compacted water-saturated MX-80.

The results from the $T_{1\rho}$ relaxation measurements indicate the presence of two major pore water phases in the MX-80 samples, which were interpreted as being 'interlayer water' and 'non-interlayer water'. A typical example of a $T_{1\rho}$-decay and its two associated discrete exponentials is seen in Figure 3.

The combined results from the SAXS and the NMR measurements are presented in Figure 4, which shows the relative amounts of the different water phases as a function of the dry density. The two methods are seen to give very similar results; the way water is found by SAXS to be distributed between a soft and a dense fraction is almost identical to the way water is found by NMR to be distributed between a non-interlayer and an interlayer phase. This way of combining the results by different methods, seems to provide more reliable data, than using a single method alone.

Conclusions

The results from the SAXS and NMR studies at VTT indicate the same thing:

- The pore water in water-saturated compacted (ρ_{dry} = 0.7-1.6 g/cm^3) bentonite is divided into two main phases: interlayer water and non-interlayer water.
- The amounts of these pore water phases can be determined quantitatively with the above methods.

Acknowledgement

This work has been sponsored by Posiva Oy.

References

Carlsson, T., Root, A. (2011). NMR study of water in MX-80 bentonite and in Na- and Ca-montmorillonite. (Unpublished study for Posiva Oy). Denna ref har nr 3 i texten.

Forslind, E. (1948). The clay-water system I – crystal structure and water adsorption on clay minerals. Bulletin No. 11, Swedish Cement and Concrete Research Institute, Royal Institute of Technology, Stockholm.

Holzer, L., Münch, B., Rizzi, M., Wepf, R., Marschall, P., Graule, T. (2010). 3D-microstructure analysis of hydrated bentonite with cryo-stabilized pore water. Applied Clay Science 47, 330-342.

Kristukat, C. (2008). Peak-o-mat. https://sourceforge.net/project/showfiles.php?group_id=67624.

Low, P.F. (1979). Nature and properties of water in montmorillonite-water systems. Soil Science Society of America Journal, 43, 651-658.

Muurinen, A. (2009). Studies on the Chemical Conditions and Microstructure in the Reference Bentonites of Alternative Buffer Materials Project (ABM) in Äspö. Posiva WR 2009-42, Posiva Oy. Denna ref har nr 2 i texten.

Ohkubo, T., Kikuchi, H., Yamaguchi, M. (2008). An approach of NMR relaxometri for understanding water in saturated compacted bentonite. Physics and Chemistry of the Earth, 33, S169-S176.

Posiva (2010). TKS-2009 Nuclear Waste Management at Olkiluoto and Loviisa Power Plants Review of Current Status and Future Plans for 2010-2012, Posiva Oy. Denna ref har nr 1 i texten.

Pusch, R., Karnland, O., Hökmark, H. (1990). GMM – A general microstructural model for qualitative and quantitative studies of smectite clays. SKB TR-90-43. SKB, Stockholm.