EUROPEAN COMMISSION

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BELBaR

(Contract Number: 295487)

DELIVERABLE (D-N°:2.6)

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Reporting period: 01/06/13 – 31/05/14

Date of issue of this report: **01/06/2014**

Start date of project: **01/03/12** Duration: 48 Months

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research &Training Activities (2007-2011)		
Dissemination Level		
PU	Public	x
RE	Restricted to a group specified by the partners of the BELBaR project	
CO	Confidential, only for partners of the BELBaR project	

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1 Background and Objectives

The objective of the Work Package 2 in the BELBaR project is to understand the mechanisms of bentonite erosion.

This report summarizes the work done in KIT-CN/INE, University of Jyväskylä and VTT Technical Research Centre of Finland during the reporting period from the 1st of June 2013 to 31st of May 2014.

The objective of KIT-CN/INE has been to study the swelling behaviour of compacted bentonite and to characterize the mineral composition and structure of the gel layer of swollen bentonite and the detaching colloids.

The main contribution of University of Jyväskylä (JyU) within this Work Package is to apply X-ray tomographic techniques for studying wetting and expansion of bentonite in narrow fractures or tubes. The primary objective is to gain direct experimental data for identifying the basic physical mechanisms of water transport and swelling of bentonite, and to provide data for model validation.

The contribution of VTT is investigation of the structure of compacted, water saturated clay samples as a function of dry density and water salinity. The purpose of the research is mainly to characterize the initial state of the system before the erosion process begins.

2 Summary

At KIT-CN/INE the erosion and swelling behaviour of the FEBEX bentonite has been investigated. Therefore erosion experiments were conducted in a custom-made flow through cell. During the experiment a halo of eroded material has been formed, which was investigated with X-ray diffractometry, electron microscopic and infrared spectroscopic methods. In this report preliminary results of this study are discussed.

At the University of Jyväskylä, an experimental method based on X-ray imaging has been developed for studying transport of water and the resulting swelling of bentonite. To this end, an X-ray tomographic scanner is used in sequential X-ray imaging of one-dimensional wetting-swelling process in a narrow tube. The expansion history of the swelling bentonite is found by an image correlation method, which allows direct monitoring of temporal evolution of displacement and solid density of the bentonite. In addition, the final state water content is measured gravimetrically from a fast-frozen and sectioned sample.

Since the beginning of the BELBaR project three types of samples were analysed by VTT: MX-80 bentonite, homoionic sodium and calcium montmorillonite obtained by purification of the MX-80 bentonite. Characterization was performed using a set of analytical methods: small-angle x-ray scattering (SAXS), nuclear magnetic resonance (NMR), ion exclusion measurement (IE) and transmission electron microscopy (TEM).

This is a report of an ongoing work containing a few preliminary results.

3 Results

3.1 Analysis and characterization of the bentonite gel and colloids obtained in erosion tests (KIT-CN/INE)

To study the swelling behaviour of compacted bentonite and to characterize the gel layer an erosion test was conducted using the custom-designed flow through cell with an outer diameter of 18 cm and the aperture of 1 mm. For the test a compacted FEBEX bentonite ring (inner diameter: 4 cm, outer diameter 8 cm, height: 2.5 cm) was used which was provided by CIEMAT (initial density: 1650 kg/m^3). Grimsel groundwater was used with initial flow velocity $v_{init.} = 10^{-5}$ m/s.

During the experiment a “halo”-like structure of eroded material was formed within the 1 mm aperture. The bentonite did not expand anymore after 40 days and had a final diameter of 2 – 2.5 cm. The experiment was stopped and the eroded material was sampled along a traverse from the outermost part (gel layer) to the bentonite ring, in total eight samples were taken (Fig. 1).

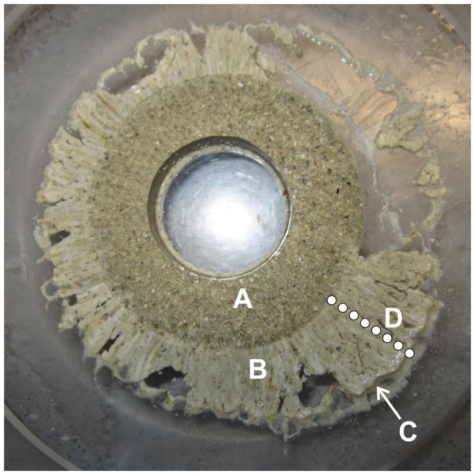

Figure 1. Halo of eroded material around the bentonite ring. (A) dark material, compacted bentonite ring, (B) eroded material, (C) gel layer, (D) sample locations for XRD measurements.

3.1.1 X-ray diffractometer analysis and scanning electron micrographs of the gel layer

An X-ray diffractometric analysis of the gel layer shows that not only clay minerals like montmorillonite and traces of illite are eroded, but also feldspars (orthoclase, plagioclase) and quartz particles migrate far into the outer parts of the erosion halo (Fig. 2a), while carbonates like calcite and dolomite where only detected in the inner halo parts (Fig.2b).

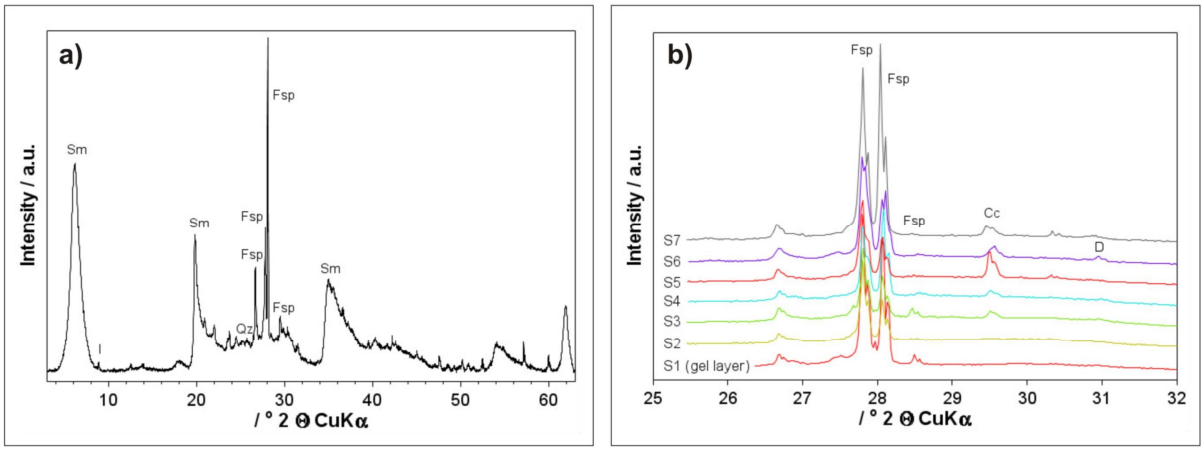

Figure 2. X-ray diffractogramms of halo samples. a) XRD pattern of the gel layer showing peaks of smectite, feldspars and traces of illite and quartz. b) patterns of the samples S1 (gel layer) to S7 (contact to ring) showing peaks in the range from 25 – 32° 2Θ. Carbonates can be detected close to the compacted ring, but not in the gel layer.

Furthermore, scanning electron micrographs show strongly agglomerated clay material and unexpectedly large sizes for feldspar and quartz grains, lying in the range of 10 – 50 µm even in the gel layer (Fig. 3).

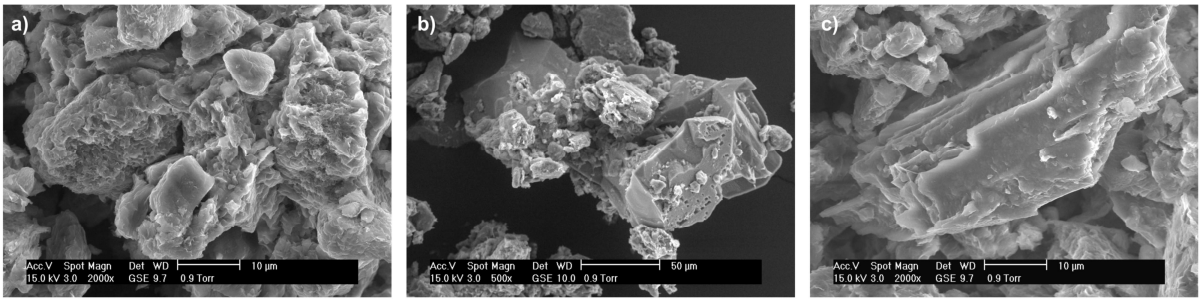

Figure 3. Scanning electron micrographs of particles in the gel layer. a) agglomerates with typical smectite morphology, b) large quartz grain, c) feldspar grain.

3.1.2 Analysis of colloids in the water outside the gel layer

About 5 mm outside of the gel layer a small amount of suspension was sampled and freeze dried. The electron microscopic investigation (SEM/EDX) revealed only salts (NaCl and $CaSO_4$) and small traces of Si and K in this sample, reflecting the composition of the Grimsel GW (Fig. 4a). Clay particles could not be detected. In contrast samples of colloidal suspensions taken during the erosion tests contained remarkable amounts of fine grained smectite particles (Fig. 4b).

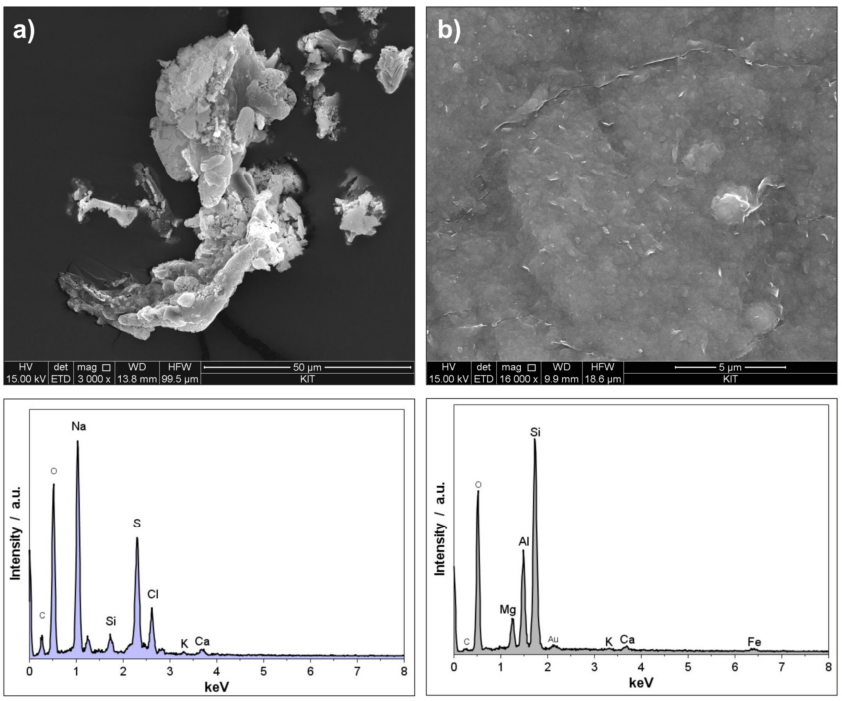

Figure 4. Scanning electron micrographs of colloidal phases. a) salt particles of suspension close to the gel layer. EDX-analysis shows NaCl and $CaSO_4$. b) thin film of smectite particles from colloidal suspensions taken during the erosion experiment (on filter).

3.2 X-ray imaging method for measuring wetting and swelling of bentonite in a narrow channel (JyU)

The development of an experimental method for monitoring water transport and free swelling of bentonite has been continued. The purpose is to produce direct experimental time-series data on transport and swelling processes in laboratory conditions. The results will be made available for use in model validation. The method is based on a differential 4D X-ray imaging of one-dimensional wetting-swelling process in a vertical tube. The evolution of strain and the local dry density of the swelling bentonite are found by image correlation techniques based on small metallic tracer particles doped in the initially dry bentonite.

Figure 5 shows the table-top X-ray tomographic scanner used in the experiments. The insert shows an aluminium test tube into which the purified bentonite[1] with tracer particles is compacted. The channel bottom is made of a porous material to allow air escape as water intrudes the sample from above. The test channel is placed in the scanner, connected to a wetting tube and sealed to prevent drying by evaporation. The first X-ray image is taken of the air dry sample (water content ~8%). An amount of synthetic ground water (Allard pH 7) is added in the tube on top of the dry bentonite, and the wetting/swelling process is monitored by imaging sequences for several days. Figure 6 shows examples of X-ray images taken at different times during the wetting process. Examples of dry density profiles of bentonite, obtained using the displacement data from X-ray images, are shown in Figure 7.

The distribution of water content at the end of experiment is found by rapidly freezing the partially wetted samples in liquid nitrogen, slicing the samples in small segments, and finding the water content and dry density of each of the segments separately by a straightforward weighing-drying procedure. In addition to providing direct experimental information on the

[1] Producer: MP Biomedicals, LLC, California, USA.

wetting/swelling process related to erosion in narrow fractures, the results can be used to obtain necessary material properties for swelling models.

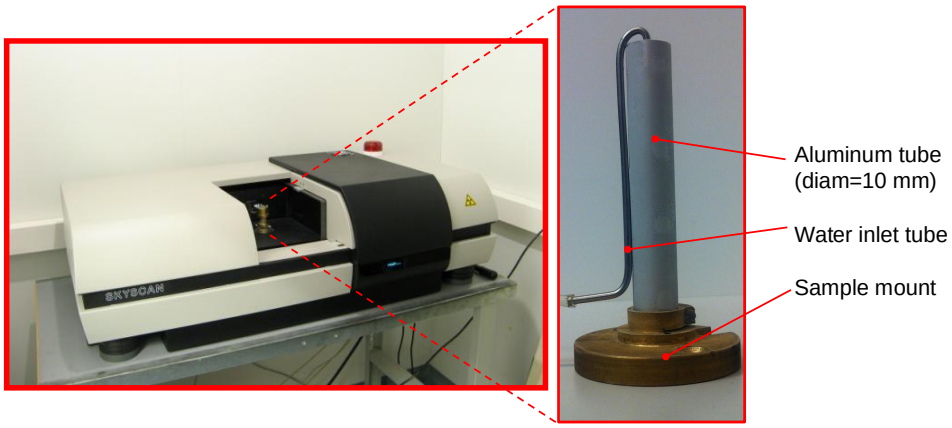

Figure 5. X-ray tomographic scanner (SkyScan 1072) used in monitoring the wetting process. The insert shows an aluminum sample holder tube that contains compacted purified bentonite.

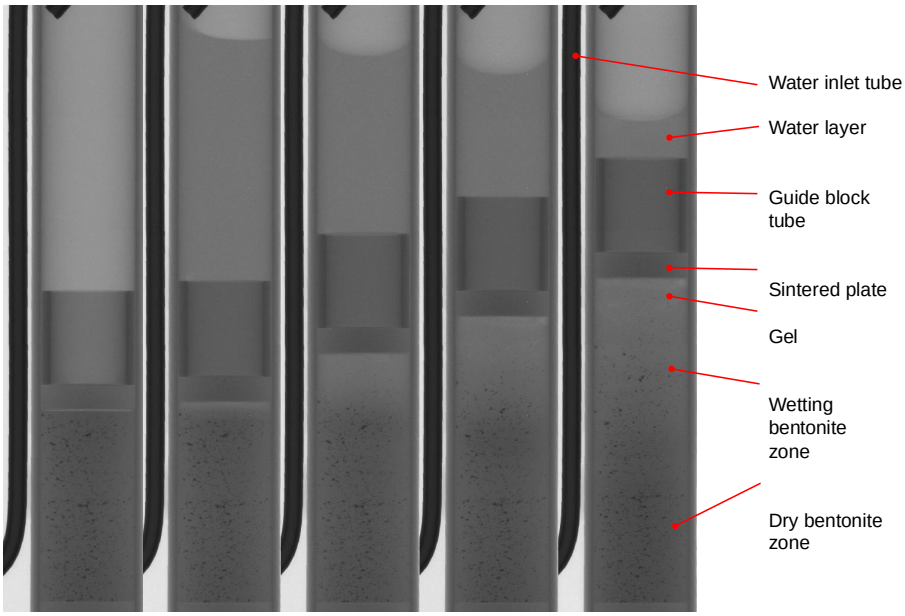

Figure 6. A series of X-ray images of purified bentonite wetting in an aluminum tube. The leftmost image shows the dry compacted bentonite before adding water in the tube. The next image shows the contents of the tube shortly after inserting water. The rest of the images show the wetting/swelling process at later times. Dark and light shades of gray indicate dense and less dense material, respectively. The motion of the tracer particles (dark dots) and the gray-scale values at wet bentonite region can provide information on the local bentonite density and water content.

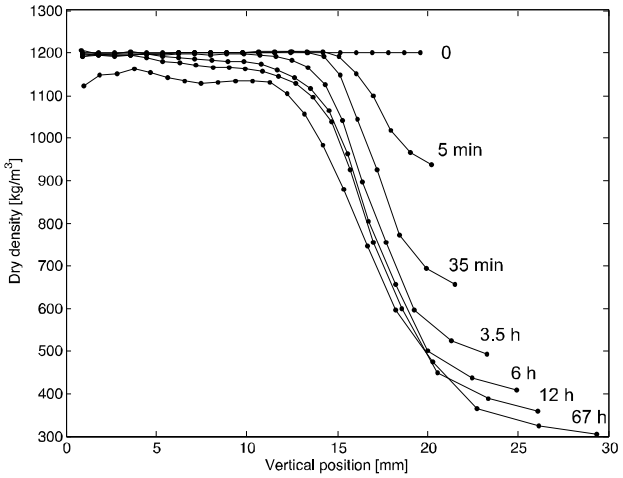

Figure 7. Evolution of bentonite dry density of in a free swelling experiment. The density values have been calculated based on the known initial density (1200 kg/m^3) and the displacement data obtained by correlating X-ray images shown in Figure 6.

3.3 Microstructure of compacted bentonite (VTT)

During the reporting period, the investigation of the microstructure was performed mainly on MX-80 bentonite samples. Characterization was carried out using a set of analytical methods: small-angle x-ray scattering (SAXS), nuclear magnetic resonance (NMR), ion exclusion measurement (IE) and transmission electron microscopy (TEM). Detailed description of the sample preparation and the characterization methods can be found in literature [1].

3.3.1 Qualitative imaging

TEM images give a qualitative view of the structure of compacted clay. In the micrographs (Figures 7 and 8) one can see two-dimensional shadowgraph of 90 nm thick section.

Figure 7 compares purified sodium bentonite with MX-80 bentonite. It is seen that at the micrometre scale the arrangement of clay aggregates in both samples is clearly different.

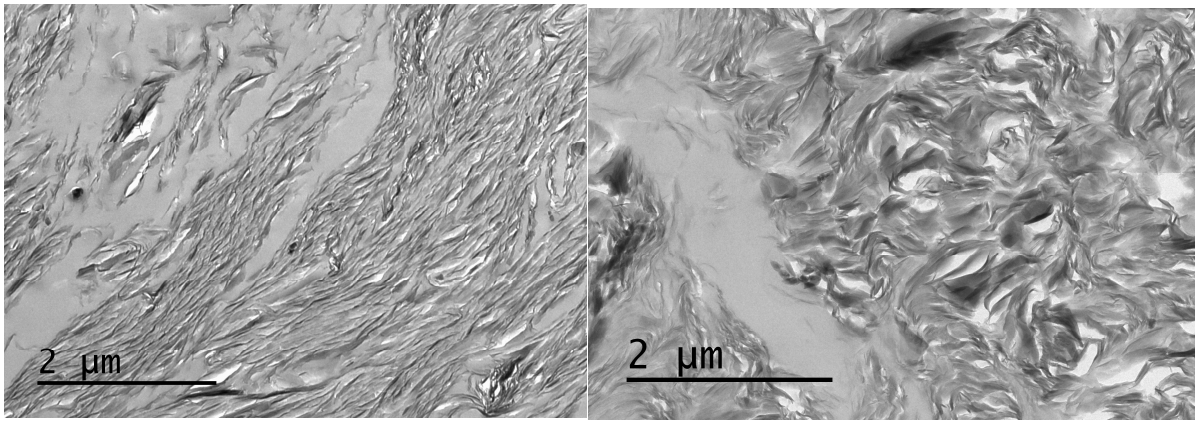

Figure 8. Micrograph of purified sodium bentonite (left) and MX-80 bentonite (right) at the dry density of 0.7 g/cm^3. A difference of clay stacking is visible in the micrometer scale.

The Figure 8 shows micrographs of two MX-80 samples of the same density but equilibrated with water or saline solution. In this case one cannot distinguish significant differences between the samples basing on the TEM imaging.

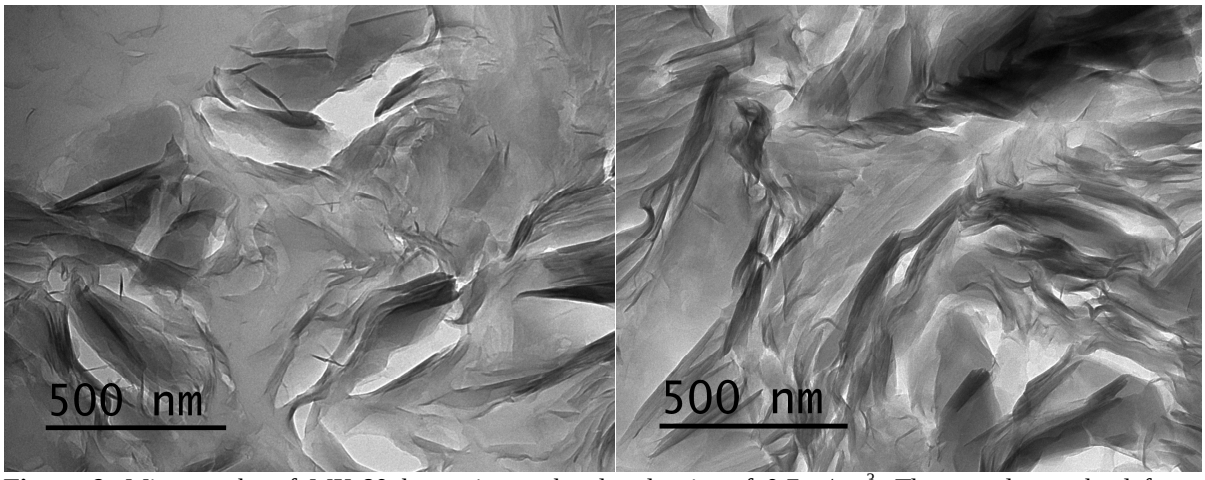

Figure 9. Micrographs of MX-80 bentonite at the dry density of 0.7 g/cm^3. The sample on the left was equilibrated with deionized water, whereas the sample on the right was equilibrated with 0.1 molar sodium perchlorate solution.

3.3.2 Porosity structure

Porosity of the water saturated bentonite was investigated basing on SAXS, ion exclusion and NMR data. NMR results require further work before publishing.

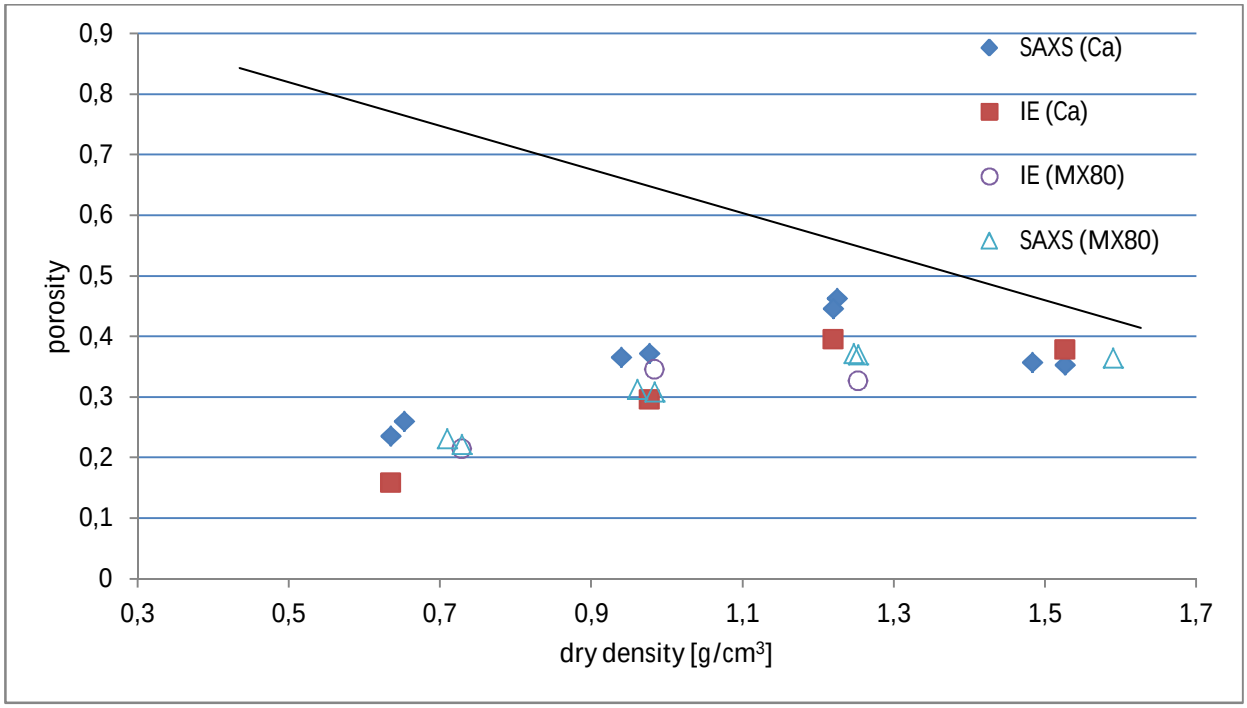

Figure 10. Plot comparing interlamellar porosity of Ca-montmorillonite (filled symbols) and MX80 bentonite (filled symbols) at different densities. Solid line represents the total theoretical porosity of the samples.

In the Figure 10 the estimation of the interlamellar porosity of calcium montmorillonite and MX80 bentonite samples is shown. The estimation was based either on SAXS or Ion Exclusion calculations. For all the samples the proportion of interlamellar volume in the total porosity is rising with increasing density. For the densities between 0.7 and 1.3 g/cm^3 Ca-montmorillonite samples seem to have slightly higher proportion of the interlamellar porosity. It may be caused by smaller swelling tendency of calcium clay and therefore larger stacks at lower density than in the case of, predominantly sodium, MX80 bentonite.

4 Conclusions and Next Steps

At the University of Jyväskylä, methods based on X-ray imaging techniques are being developed in order to study transport of water and swelling of bentonite in narrow channels. The primary objective of this work is to provide experimental methods and image analysis tools that can be used to gain detailed information on water transport and swelling dynamics of bentonite, and thereby to support modelling of bentonite buffer behaviour and erosion process. At the moment, measurement of local swelling rate, material displacement and the dry density of bentonite in one-dimensional swelling conditions are possible. The on-going work aims at providing calibration of the grayscale image information to facilitate direct monitoring of also the local water content. It has become evident that this will involve development of new dynamic flat field correction method of the X-ray images in order to compensate for errors arising from inhomogeneous X-ray beam and instabilities present in the device. After this stage, a systematic set of experiments will be carried out in order to provide the free swelling data set for validation of swelling models. At a later time, the experiments and associated modelling will be done in the context of more complicated fracture geometries and conditions relevant to erosion processes. This work will be carried out in close cooperation with the other project parties.

At VTT a set of complimentary methods is being used to characterize water saturated samples of different clays at different densities. MX-80 bentonite in as delivered state and purified to homoionic sodium and calcium forms has been investigated. Full interpretation of the results and comparison of the materials at different condition is ongoing.

5 References

[1] M. Matusewicz, V. Liljeström, K. Pirkkalainen, J.P. Suurinen, A. Root, A. Muurinen, R. Serimaa, M. Olin, "Microstructural investigation of calcium montmorillonite". Clay Minerals 48, no. 2 (2013): 267-276