BELBaR

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Progress Report on the analysis and characterization of the bentonite gel and colloids obtained in erosion tests

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1 Objectives and Background

The purpose of the microstructural studies of bentonite and montmorillonite at VTT is describing of the structure of compacted, water saturated bentonite clay at different densities and in different salinity conditions. Knowing the initial state of the system is essential to understand the mechanism of the bentonite erosion. Also, observations about the microstructure when bentonite swells from a solid material towards gel will give insight into the erosion mechanism.

The main contribution of Universtiy of Jyväskylä (JyU) within Work Package 2 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 in, and swelling of bentonite, and to provide data for model validation. In addition, a phenomenological expansion model, developed mainly within another project, will be applied in describing the wetting/swelling process studied in the experimental part and analysing their results.

This is a status report of an on-going work, with a few preliminary results.

2 Summary

During last 15 months calcium and sodium montmorillonite samples at four densities within the range of 0.5-1.5 g/cm^3 were investigated. There were two groups of samples: equilibrated with deionized water or with 0.1M perchlorate solution. A set of analytical methods was used: small-angle x-ray scattering (SAXS), nuclear magnetic resonance (NMR), ion exclusion measurement (IE) and transmission electron microscopy (TEM). Detailed description of the methods can be found in our publication in Clay Minerals [1]. We obtain quantification of the fraction of interlamellar porosity in the total porosity of the system and estimation of the mean size of the clay stacks.

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 to produce an X-ray image sequence of a one-dimensional wetting-swelling process in a narrow channel. The expansion history of the swelling bentonite is found by an image correlation method, which allows direct monitoring the temporal evolution of displacement, solid density and water content distributions in the bentonite.

A general phenomenological swelling model is being developed within a parallel project devoted to experimental research and modelling of the bentonite buffer behaviour[1]. In this work, a one-dimensional version of the model is considered and applied in wetting and swelling of bentonite in the channel geometry used in the experimental part. The model is based on combining experimental data on elasto-plastic properties and swelling behaviour to construct a consistent hydromechanical material model for bentonite swelling in constrained conditions.

3 Results

3.1 Qualitative imaging

TEM imaging gives an opportunity to have an intuitive view on the structure of compacted, water saturated clay. In Fig. 1 one can distinguish clay stacks (darker areas) and areas with lower clay content (brighter colours).

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[1] Assessment of bentonite characteristics (BOA), Part of the Finnish Research Programme on Nuclear Waste Management, KYT 2014.

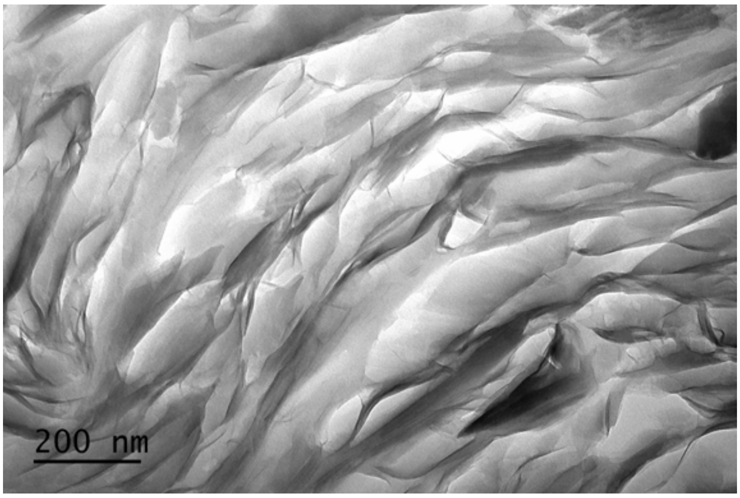

Figure 1. TEM micrograph of Na-montmorillonte at dry density of 1.1 g/cm^3. Thickness of the section is 90 nm.

3.2 Interlamellar part of total porosity

A Figure showing total and interlamellar porosity change with the dry density can be found in Matusewicz et al. [1] (Fig. 3). A clear increase of interlamellar porosity with increasing clay density is seen. Simultaneously the total porosity is decreasing, what means a significant decrease of pore volume between clay aggregates.

3.3 Mean stack size

An attempt was made to calculate the average size of the clay stack. Two different approaches have been used. One was based on modelling of SAXS results[2], other on the amount of perchlorate ions present in the sample. Results for Ca-montmorillonite samples are presented in Fig. 2. Modelling SAXS data according to the currently used model [2] showed no visible change in stack size for different samples. High increase trend in dense samples observed in the IE estimation is probably an overestimation caused by general decrease of pore sizes at high density samples.

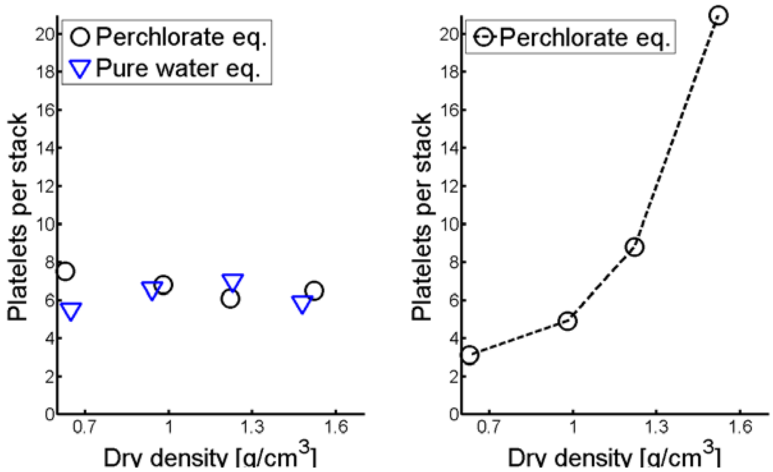

Figure 2. Comparison of stack size estimation in Ca-montmorillonite obtained by modelling of SAXS results (left) and by perchlorate exclusion estimation (right).

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[2] Modelling made at Helsinki University by Kari Pirkkalainen.

3.4 X-ray imaging method for measuring wetting and swelling of bentonite in a narrow channel.

An experimental method for direct monitoring of water transport in bentonite and the resulting free expansion is being developed. The method is based on using an X-ray tomographic scanner in producing an X-ray image sequence during a one-dimensional wetting-swelling process in a narrow channel. The expansion history of the swelling bentonite is found by doping the initial dry bentonite material with metallic tracer particles and using image correlation techniques to compute the local displacement of the bentonite phase at each instant of time. The measured displacements also allow computing the local dry density of bentonite, given that the initial dry density is known. The distribution of water content at each instant of time during the wetting process is found by utilizing the X-ray image gray-scale values that depend on the local X-ray attenuation strength of the bentonite-water mixture. The necessary calibration between the gray-scale value, dry bentonite density and water content is to be obtained 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.

Figure 3 shows the table-top X-ray tomographic scanner used in the experiments. The insert shows a test channel with a partially wetted bentonite sample. The experiment is done by first mixing a small amount of metallic tracer in a known amount of dry bentonite, and compacting the sample on the bottom of the channel in a certain initial dry density. The channel bottom is made of a porous material to allow air escape as water intrudes the sample from above. The test channel is then placed in the scanner, connected to a wetting tubing and sealed to prevent drying by evaporation. After a proper warm-up time, the first X-ray image of the dry sample is taken. An amount of water is then added in the channel on top of the dry bentonite, and the imaging sequence is initated. The wetting is allowed to continue typically for about 2-4 days during which 500-1000 X-ray images are taken, first at intervals of a few minutes and later, as the wetting process gets slower, at intevals of a few tens of minutes. Figure 4 shows a few examples of X-ray images taken at different times during the wetting process. The total wetting time is seleceted such that an observable water content profile remains in the sample after the experiment.

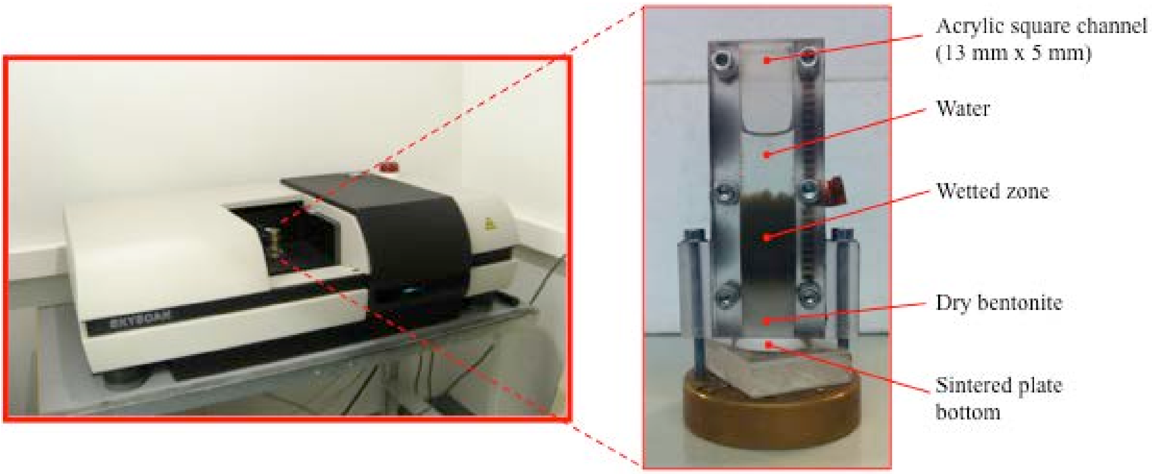

Figure 3. X-ray tomographic scanner (SkyScan 1072) used in monitoring the wetting process. The insert shows a rectangular acrylic sample holder (channel) with partially wetted compacted bentonite sample after 24 hours wetting period.

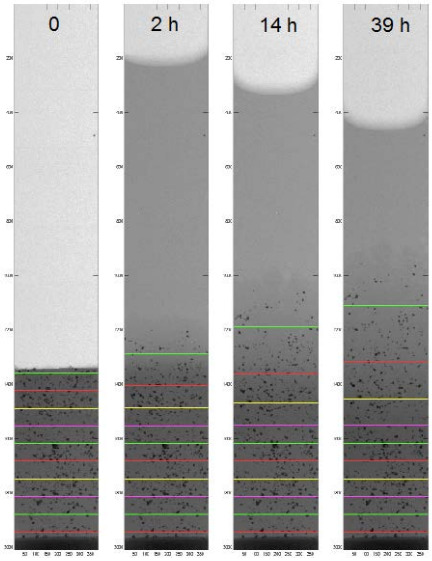

Figure 4. X-ray images of bentonite wetting in a narrow channel. The leftmost image shows the dry compacted bentonite in its initial state. The rest of the images show the wetting/swelling process at times indicated. The horizontal colored lines show the deformation of the bentonite as computed by image correlation method utilizing the metallic marker particles (dark spots). The gray-scale values at wet bentonite region provide information on the local water content.

In addition to providing direct experimental information on the wetting/swelling process related to erosion in narrow fractures, the results can be used to obtain the free swelling data necessary for the general phenomenological swelling model developed in a separate project, and in validating the one-dimensional swelling model (see below).

3.5 One-dimensional phenomenological swelling model.

In this project, a one-dimensional version of the general phenomenological swelling model, primarily developed in another project (BOA/KYT2014), is applied in describing wetting and swelling of bentonite in narrow channels in direct connection with experimental conditions discussed above. The model is based on combining experimental data on elasto-plastic properties and swelling behaviour to construct a consistent hydromechanical material model for bentonite swelling in constrained conditions. The overall model includes transport of water in the bentonite, generation of swelling stress, friction at channel wall and the geometrical constraints set by the channel shape.

3.5.1 Governing equations

Consider a long straight channel along the positive x -axis as shown in Fig. 5. The channel is closed at $x = 0$, and has a constant cross-section with area A and circumference l. At initial time $t = 0$, the part of the channel with $0 \leq x \leq L$ is filled with bentonite at constant dry density ρ_0 and initial water content. The channel is connected to an infinite source of water such that the portion of the channel not occupied by bentonite is always filled with water at constant pressure p_W. As time evolves, water is transported into the bentonite inducing swelling. The resulting motion of the bentonite is opposed by friction τ between the bentonite and channel wall and the pressure force applied by water on the bentonite-water interface.

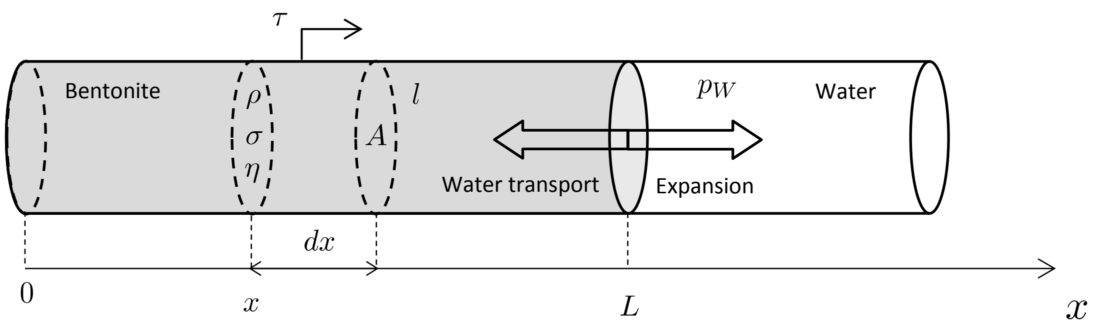

Figure 5. Set-up of the one-dimensional mixture model of bentonite swelling in a channel

The stress state of the bentonite is specified by the axial compressive stress σ. The bentonite is considered as an elasto-plastic material for which the current material properties depend on dry density ρ and on water content $\eta = \rho_W/\rho$, where ρ_W is the partial density of water. In addition, the material properties may depend on the history of straining as volumetric plastic deformations can occur due to mean stress increased by constrained swelling and external forces. Furthermore, we assume a quasi-stationary expansion process where the time evolution of the system is induced by transport of water into the bentonite. The relaxation time of the system to reach mechanical equilibrium for each given moisture distribution is assumed small as compared to time scales of the moisture transport, the detailed mechanism of which is to be specified later. At each instant of time, the bentonite column is thus assumed to be in mechanical equilibrium. Given the water transport mechanism, the problem is then to solve the change of the equilibrium configuration corresponding to the small change in moisture content.

In general, the transport of water in bentonite can be a very complicated process [3]. Here, we consider rather simple conditions plausible in the laboratory swelling experiments described in the previous section, where e.g. the fluid pressure is small. Consequently, water transport from free water zone into the bentonite is described here qualitatively by a one-dimensional diffusion equation of the form

$$\frac{d}{dx}\rho_W = \frac{d}{dx}\left(D\frac{d}{dx}\rho_W\right), \qquad (1)$$

where ρ_W is the partial density of water and D is the effective diffusion coefficient. Where necessary, this simple transport model can be replaced by a more comprehensive one such as that those discussed e.g. by Kröhn [3].

The force balance equation of an infinitesimal bentonite element of length dx (see Fig. 5) is given by

$$-Ad\sigma + \tau l dx = 0. \qquad (2)$$

The wall friction is assumed to be of the form

$$\tau = s\,\min\left\{\frac{A}{l}\left|\frac{d\sigma}{dx}\right|, \tau_C\right\}, \qquad (3)$$

where $s = \text{sign}\left(\frac{d\sigma}{dx}\right)$, $\tau_C = \mu\sigma_\perp$ is the slip wall stress, μ is the friction coefficient, $\sigma_\perp = \frac{\nu}{1-\nu}\sigma$ is the transverse normal stress and ν is the Poisson ratio. It follows from Eqns (1) and (2) that $\left|\frac{d\sigma}{dx}\right| \leq \frac{l}{A}\tau_C$. The balance equation (2) can be fulfilled with two possible conditions, the slip condition and no-slip condition. The no-slip condition is characterized by the relation

$$-\frac{l}{A}\tau_C < \frac{d\sigma}{dx} < \frac{l}{A}\tau_C \qquad (4)$$

in which case the balance equation (1) is identically fulfilled. In the slip case $\left|\frac{d\sigma}{dx}\right| = \frac{l}{A}\tau_C$ the balance equation is of the form

$$\frac{d\sigma}{dx} = s\frac{l}{A}\tau_C = s\frac{l\mu\nu}{A(1-\nu)}\sigma\,. \qquad (5)$$

3.5.2 Material properties and swelling model

We take the wet bentonite to be elasto-plastic material with well defined elastic domain and yield behaviour, and choose the strain measure to be $\epsilon = \rho/\rho_r$, where ρ is the partial density of the solid phase and ρ_r is a reference density. An example of the measured stress-strain behaviour of bentonite in uniaxial constrained compression experiment at various values of water content η is shown in Fig. 6 a). For simplicity, the actual measured behaviour is replaced by a qualitative behaviour, where the elastic domain is assumed to be linear with the slopes of elastic curves fitted using the reloading part of the data (see Fig. 6 b). In what follows, we thus assume that the elastic coefficient (P-wave modulus) M and the yield stress σ_Y are measured as functions of the effective plastic strain ϵ_p (see definition in Fig. 6 b) and water content η in a suffciently large domain of these parameters. In principle, we also need similar experimental information on Poisson ratio ν and the friction factor μ. Lacking such information at this point, we have to assume these quantities constant left as free parameters of the model.

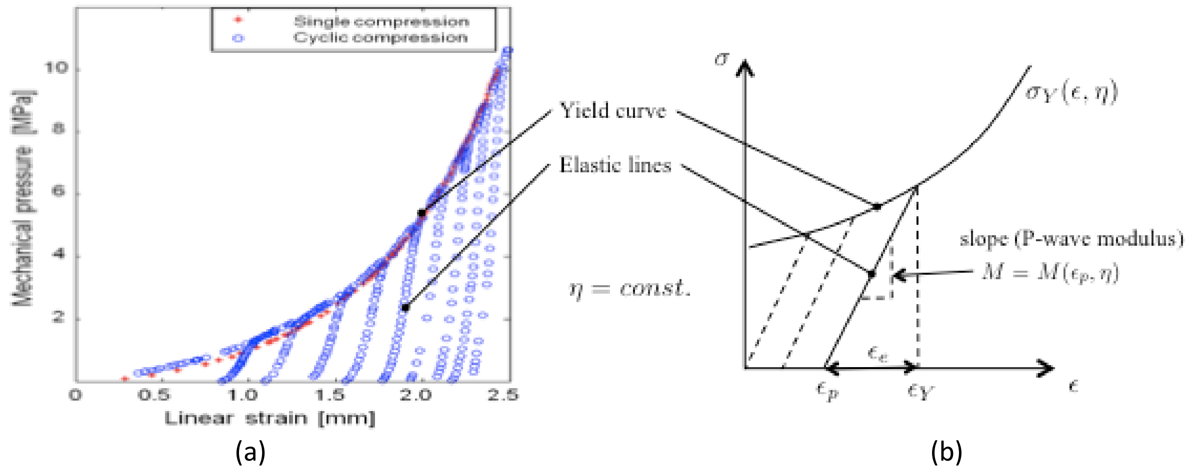

Figure 6. a) Experimental result of a uniaxial compression test of bentonite in a fixed water content η (result of the BOA project). b) Simplified behaviour assuming linear elasticity and uniquely defined yield point. Also shown are definitions of various elasto-plastic parameters used in the model.

In order to include generation of swelling pressure in the model, we assume that the strain change induced by swelling at zero pressure in a uniaxial swelling is measured for a suffciently large range of water content and initial dry density. A possible technique for performing such an experiment utilizing X-ray imaging is described in Section 3.4. Taken that the wall friction in the acrylic channel shown in Fig. 3 b) can be neglected, the x-ray images such as those shown in Fig. 4 can be calibrated to yield the necessary free swelling information.

Assuming that the necessary data from uniaxial compression experiment and from uniaxial free swelling experiments indeed is available, we seek to construct the phenomenological swelling model based on combining this experimental information in a consistent manner. To this end, we make the fundamental assumption that in its final state, the system obeys the prescribed experimental stress-strain relation of the material at constant water content (i.e., the set of curves such as the one illustrated in Fig. 6 b), irrespective of the path taken by the system between the initial and final state of water content. Notice that, irrespective of this conjecture, the stress state may still depend on the straining history of the system. The phenomenological swelling model is now established by considering the change of stress along a particular three-step path between the initial and final states.

1. Elastic expansion from initial state to zero stress at constant water content
2. Wetting and free swelling to new water content at zero stress
3. Compression (possibly plastic) to final stress at constant water content

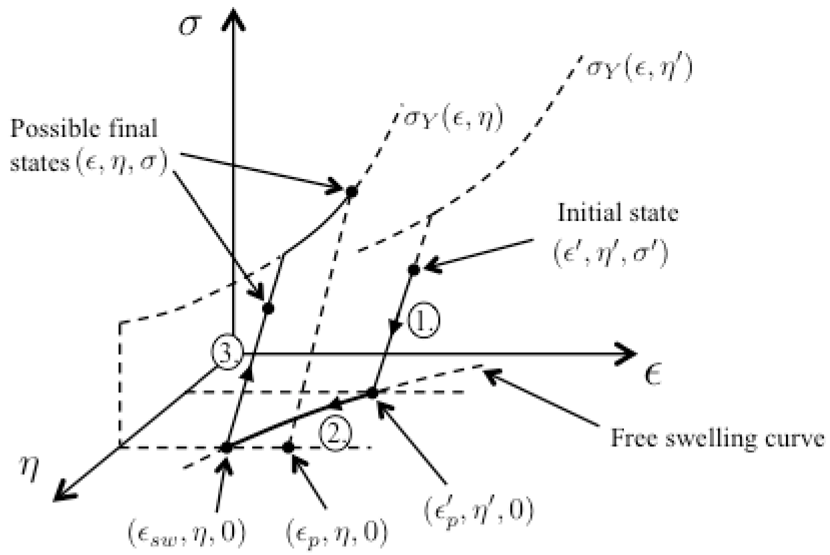

Figure 7. Construction of swelling stress within the one-dimensional phenomenological swelling model

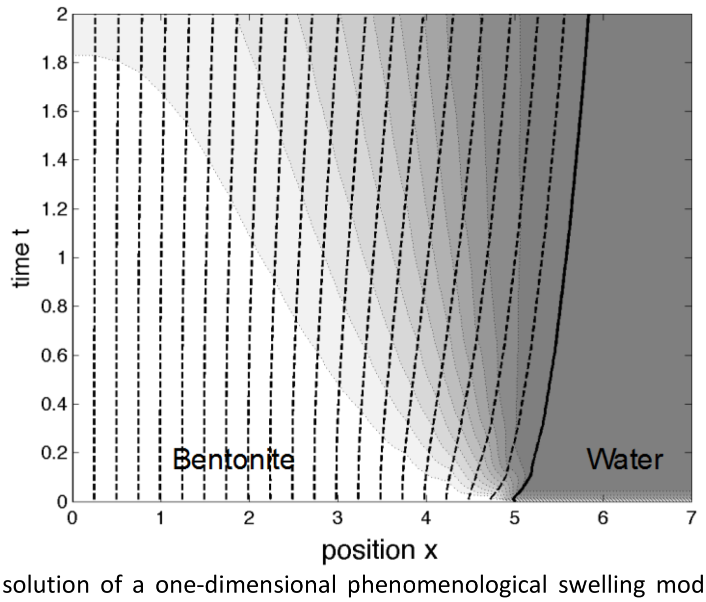

Figure 8. Numerical solution of a one-dimensional phenomenological swelling model (position and time in arbitrary units). The dashed lines show the pathlines of the swelling bentonite. The solid line is the boundary between wet bentonite and water. Water transport takes place by diffusion from right to left. The resulting water content distribution is shown as gray-scale color, darker shade indicating higher water content.

Without even presenting the detailed algorithm in algebraic form here, it is clear that the procedure described above and illustrated in Fig. 7, indeed leads to a definite model for generation of swelling stress in a uniaxial wetting geometry. Furthermore, it appears that the model can be generalised to an arbitrary three-dimensional case. The validity of the model remains to be tested experimentally.

Figure 8 shows a preliminary example of a numerical solution of wetting bentonite in a narrow channel according to the one-dimensional phenomenological swelling model described above. Here, uniaxial compression data produced by the BOA project and a synthetic free swelling data qualitatively consistent with the preliminary results from X-ray imaging experiments for purified bentonite was used. These results will be compared with data from experiments based on X-ray imaging as discussed in the previous section.

4 Conclusions and Next Steps

A relation between sample density and the amount of interlamellar pores is observed and fraction of interlamellar porosity can be estimated. Work has been done so far with calcium montmorillonite samples, there is on-going work with sodium montmorillonite. Investigation of MX-80 samples is planned later this year.

A second set of samples is planned to be prepared slightly differently than the first set, in which the samples have been (or will be) compacted directly to the target density. The second samples will be compacted near to the emplacement density of the bentonite buffers and let swell to the target densities of the experiment. Comparing the two sets, the changes in the microstructure caused by swelling can be analysed.

Another activity at the early stage is designing of the device that would enable SAXS measurements of clay extruding into a capillary. The experiment will follow the slit erosion experiments done by other partners in BELBaR but the sample size is restricted by the SAXS device.

Methods based on X-ray imaging techniques is being developed in order to study transport of water and swelling of bentonite in a 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 modeling of bentonite buffer behaviour and erosion process. A one-dimensional version of a general phenomenological swelling model, developed within a parallel project, is considered and applied in describing the wetting/swelling process of bentonite in the narrow channel geometry used in the experimental part. The model requires experimental data on elasto-plastic and swelling behaviour of bentonite in e.g. one-dimensional constrained straining conditions and within a sufficiently large range of dry density and water content values.

During the rest of the year 2013 the experimental method for monitoring wetting and swelling of bentonite in narrow channels using X-ray imaging techniques will be completed. Especially, the calibration of X-ray image gray scale and displacement field with the water content will be established. A systematic set of experiments will then be carried out in order to provide the free swelling data necessary for the one-dimensional phenomenological swelling model. 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.

References

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