Assessment of Bentonite Characteristics in KBS3 Method – 14344

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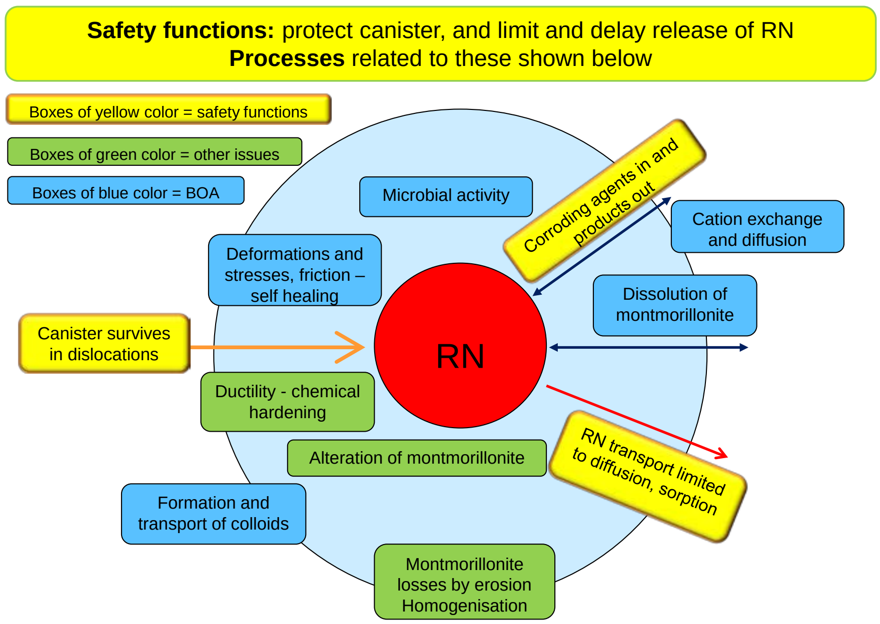
ABSTRACT
In the KBS-3 method, the reliable estimation of functioning of buffer and backfilling materials protecting the copper canister and spent fuel therein is a bottom line issue for safety. For that target, the regulator and scientific community must have enough know-how about the behavior and long-term functioning of these materials from the point of view of long-term safety. Our aim is to produce just that data and knowledge, the work being divided into three major topics. First, in the Thermal-Hydrological-Mechanical (THM) topic, the goal is to gain more understanding about coupled THM processes by applying both experimental methods and modeling; the experimental work is planned to be carried out on all levels from nano-scale (SAXS) via meso-scale (tomography, mineralogy) up to full scale (shear block). Second, in the Thermal-Hydrological-Chemical (THC) topic, the goal is to gain more understanding of these processes by applying both experimental methods and modeling; the experimental work is planned to be carried out on cation exchange, colloids, solubility of montmorillonite, and microbes in bentonite. Third, in the Thermal-Hydrological-Mechanical-Chemical-Biological (THMCB) topic, the goal is to gain more understanding of the full THMCB coupled processes, mainly by applying suitable modeling tools, especially Numerrin and COMSOL Multiphysics. Aalto University has studied shear phenomena between different backfill material interfaces. The Geological Survey of Finland (GTK) has developed mineralogical methods for characterization of bentonite. The University of Jyväskylä has successfully applied 3D X-ray tomography to study wetting of montmorillonite, and these results form the basis of their modeling work. The University of Helsinki (Radiochemistry) has developed methods for bentonite colloid measurements and has studied sorption of radionuclides onto those colloids. The University of Helsinki (Physics) has applied modern X-ray diffraction methods to study the nano-level structure of bentonite. Numerola Oy has applied their own mathematical methods, Numerrin, both to analyze 3D tomography data and to solve transport models based on that data. VTT Technical Research Centre of Finland has been successful in measuring the solubility of montmorillonite, applying chemical sensors in aqueous concentration measurements and studying microbial activity in bentonite. All these methods are directly applicable in studies of the bentonite buffer in a large application area, such as from dry to saturated bentonite, from initial state to post glacial conditions, and from compacted bentonite to dilute colloidal solutions.

INTRODUCTION
In the KBS-3 concept, the reliable estimation of functioning of buffer and filling materials is a bottom line issue for safety. For that target, the regulator and scientific community must have enough know-how about the behavior and long-term functioning of these materials from the point of view of long-term safety. The aim in our BOA project (Assessment of Bentonite Characteristics) is just to produce that data and knowledge.

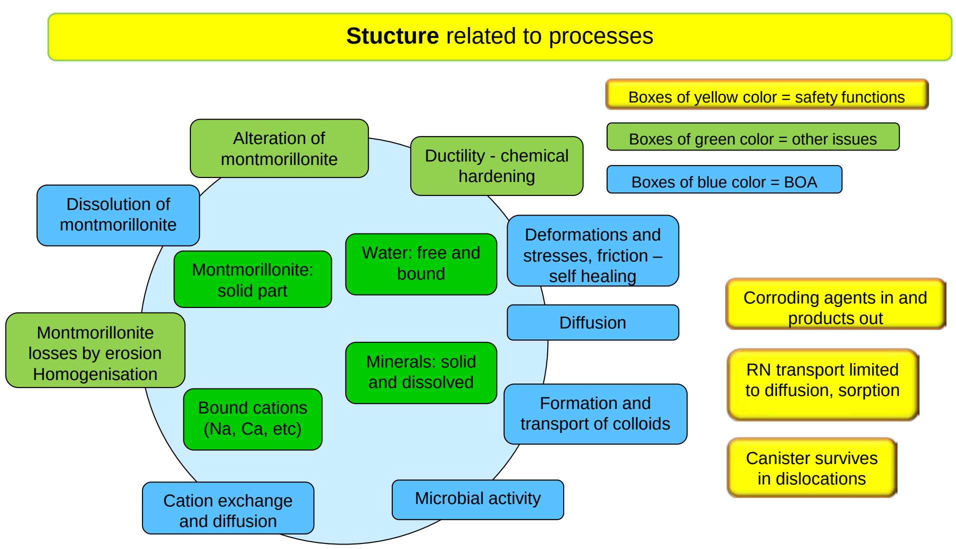
The bentonite buffer is one of the most essential components in the KBS-3 concept:

- it limits the mass flow to and from the copper canister
  - to prevent corrosion and
  - in the case of canister failure, it retards transport of radionuclides to bed rock
- it protects the canister in the case of large dislocations of bed rock.

The most important safety functions and the related processes in our studies are shown in Fig. 1a, while the microstructure components coupled to those processes are sketched in Fig. 1b. Therefore, any evaluation of the safety of final disposal is heavily dependent on proper understanding of the bentonite buffer: installation, pre-saturation conditions, and long-term safety.



a)



b)

Fig. 1. Top: Safety functions and related processes in the bentonite buffer. Those of a blue color are studied in our project. Bottom: the safety function processes and their coupling to the structure.

The general aim of our project is to develop and extend know-how related to the coupled behavior of buffer and backfilling materials. This know-how is divided into three topic areas:

1. Thermal-Hydrological-Mechanical (THM)
    a. The goal is to gain more understanding by applying experimental methods and modeling.
    b. The experimental work is planned to be carried out on all levels from nano-scale (SAXS) via meso-scale (tomography, mineralogy) up to full scale (shear block).
    c. The modeling aims to apply the experimental results of BOA and scientific literature.
2. Thermal-Hydrological-Chemical (THC), colloids and microbes
    a. The goal is to gain more understanding by applying experimental methods and modeling.
    b. The experimental work is planned to be carried out on cation exchange, ion selective electrodes, colloids, solubility of montmorillonite, and microbes in bentonite.
    c. The modeling aims to apply both the experimental results of BOA and good practices from scientific literature. The scope here is mainly in cation-exchange and solubility studies.
3. Thermal-Hydrological-Mechanical-Chemical-Biological (THMCB)
    a. The goal is to gain more understanding, mainly by applying suitable modeling tools.
    b. The overall long-term target of the BOA project, the THMCB model, is included here.

There is a need to know bentonite behavior in many different conditions:

- compacted dry bentonite, which starts to wet and swell, under effects from the temperature gradient
- fully saturated bentonite in the planned density window, reacting with the groundwater
- colloid formation of bentonite and the transport of these colloids, possibly carrying radionuclides – in the case of very dilute post-glacial groundwater penetrating into the repository
- bentonite altered by pre-saturation erosion
- microbial activity in the bentonite – which determines the microbial life

Processes to be investigated:

- cation exchange, which changes the properties of montmorillonite rather quickly
- solubility, which is usually a slow process compared to cation exchange, but the impact is much bigger
- wetting, which is still demanding to model
- swelling, which is also an essential part of wetting in free volume cases
- swelling pressure development, which is also an essential part of wetting in closed volume cases
- colloids, which may be released in post-glacial conditions – possibly contaminated by radionuclides
- microbial activity, which is the single most important issue in setting a lower limit to the dry density of the buffer

Microstructure studies will concentrate on

- thickness of the interlamellar space and correlations to neighboring spaces
- pore size distribution of free water
- fractions of bound and free water
- water activity and microbial activity

METHODS AND RESULTS

Block Shear Experiments (Aalto University)

One of the key aspects in ensuring the safety of the KBS-3V is that the saturated density of the buffer should be maintained within a narrow range of 1 950 kg/m^3 to 2 050 kg/m^3 [1]. The interface shear resistance data helps to predict the swelling of the buffer accurately, which enables the backfill components to be designed accordingly [2, 3, 4]. The interface shear behavior of backfill materials is crucial only during the early stages of saturation (i.e., when the interfaces exist) (Fig. 2). On the other hand, the internal shear of backfill materials becomes vital in the long term. Therefore, it is safe to assume that the early stages of saturation are the worst-case-scenario, because the dry backfill is more prone to deformation due to the presence of interfaces that have relatively lower shear resistance compared to the internal shear resistance of the entire backfill when it is saturated.

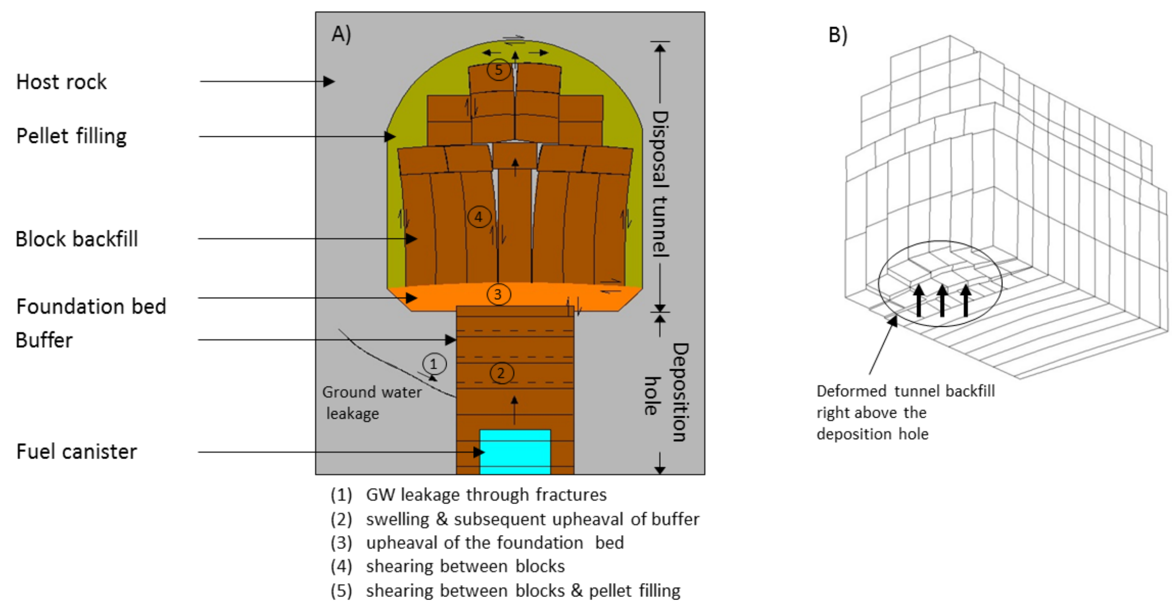


Fig. 2. (A) Schematic of KBS-3V disposal tunnel backfill and possible shear planes as a result of the swelling of the buffer, (B) 3-D view of the upheaval of the backfill caused by the swelling of the buffer [4].

Different tunnel backfill materials, such as Friedland clay blocks (FCB), Cebogel QSE bentonite pellets (CQSEP), and granulated bentonite (GB), were tested [5, 6]. Two different types of direct shear box apparatus (300 mm x 300 mm, and 60 mm x 60 mm) were used to test typical backfill interfaces such as FCB-FCB, FCB-CQSEP, and FCB-GB. The FCB surface was also tested with several host rock surface profiles. All the tests were carried out at room temperature (22±1°C), except for the temperature dependent tests, and a constant shear-deformation rate of 0.5 mm/s was used.

Geological Survey of Finland (GTK)

GTK has studied bentonite materials from VTT's bentonite tests. The mineralogy of the bentonites was studied using a scanning electron microscope, SEM (JEOL JSM5900LV equipped with an EDS analyzer), and with an electron probe micro-analyzer, EPMA (Cameca SX100). SEM feature analyses were performed in a high-vacuum with carbon-coated epoxy embedded samples. SEM feature analyses give not only the chemical composition of the analyzed particles, but also the number of different mineral particles, at high accuracy. Samples were also studied in more detail with the EPMA, to get the exact chemical composition of the clay matrix and accessory minerals.

All bentonites, as well as purified bentonites, include accessory minerals. The number and the quality of the mineral phases can vary remarkably, depending on the bentonite source. Therefore, it is important to know the quality of the bentonite material, before any chemical experiments, and whether there are accessory minerals present that can affect the test results.

The aim of the mineralogical studies is also to find out whether the bentonite mineralogy changes if external conditions change, or whether new mineral phases appear in changed environmental circumstances. In our studies, we have found that copper used in a copper canister can be mobilized in an oxygen environment and from secondary mineral phases, cuprite and malachite.

University of Helsinki (Laboratory of Radiochemistry) - Colloids

The potential relevance of colloids for radionuclide transport is highly dependent on the colloid formation, the stability of colloids in different chemical environments, and their interaction with radionuclides [7]. Colloids can be produced from degraded Engineered Barrier System (EBS) materials such as the bentonite clay buffer, bentonite–crushed rock back-fill, the copper–iron container, and grouting materials, as well as from uranium fuel itself. The main colloid source is the bentonite buffer; as a result of erosion, bentonite mass loss occurs via colloid formation. Radionuclides diffused and retarded in the buffer could be released directly into the groundwater flow. The knowledge and understanding about bentonite erosion in colloidal form can be utilized in the estimation performance of the bentonite barrier. The possibility of a future post-glacial phase when the infiltration of fresh, glacial meltwater dilutes the groundwater, implies that dilute groundwater conditions cannot be excluded and the influence of bentonite and other colloids has to be taken into consideration. The objective of this subtask is to determine the release and stability of inorganic colloids, to study bentonite erosion, and to study radionuclide sorption on bentonite colloids.

The release and stability of inorganic colloids from MX-80 type bentonite powder and compacted bentonite is followed. NaCl and $CaCl_2$ electrolyte solutions, Allard (low salinity granitic reference groundwater) and diluted OLSO (Olkiluoto reference groundwater) of different ionic strengths, are used to determine the effect of salinity. The colloidal particle fraction is separated by filtration, and the pH, particle size distribution, zeta potential, colloidal particle concentration, and morphology are determined. Radionuclide sorption on MX-80 bentonite powder and bentonite colloids as a function of pH and ionic strength is studied using Sr-85, Cs-134, Eu-152, Np-235, and/or other relevant radionuclides and NaCl and $CaCl_2$ solutions, as well as Allard and OLSO reference groundwater.

Different colloid characterization methods will be applied and tested. Colloidal particle size distribution is determined by applying photon correlation spectroscopy, and zeta potential by applying dynamic electrophoretic mobility (Malvern Zetasizer Nano ZS). Colloid concentration will be determined using a standard series made from MX-80 bentonite and a derived count rate obtained from PCS measurements, as well as by using the Al content of montmorillonite analyzed using ICP-MS. The other available methods to be applied are asymmetrical flow field-flow fractionation (AsFlFFF), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), XRD, and SAXS, in co-operation with the University of Helsinki, Department of Physics.

University of Helsinki (Department of Physics) – Microstructure

In the topic, studies are carried out on the nanostructure of bentonite and purified montmorillonite. The main method is X-ray scattering (small-angle X-ray scattering SAXS, and wide-angle X-ray scattering WAXS/XRD), which is an excellent tool to get averaged information on the stacking and structure of clay platelets in samples of about one cubic millimeter in size. X-ray microtomography is also utilized in combination with SAXS (or XRD) in order to relate the macroscopic and microscopic structures and their orientation.

The parameters to be determined in SAXS studies include the distribution of interlamellar distances and water layer thicknesses, the number of clay platelets in the stacks, and the fraction of delaminated discs. X-ray scattering intensities or density profiles of the clay stacks may be computed from the coordinate sets and compared to the experimental data.

Combined in-situ SAXS and microtomography studies on drying or wetting clay will be continued. Tactoid reorientation along with the forming microcracks will be determined. This affects water mobility and is of interest from the point of view of buffer properties of bentonite. More samples will be measured to complete the study and to write a publication. SAXS/XRD studies on aged bentonite are also planned for determining structural changes in the clay during storage. SAXS studies on clay colloids are being carried out in co-operation with the University of Helsinki, Laboratory of Radiochemistry. Information is obtained on montmorillonite platelet stacking in colloidal samples.

University of Jyväskylä

During the present project, experimental methods for a detailed study of the wetting/swelling process, based on X-ray microtomography, have been developed at the University of Jyväskylä tomography laboratory. This novel technique allows direct non-intrusive 3D monitoring of the wetting process, and simultaneous measurement of the 3D deformation field induced by swelling. The primary objective is to provide the necessary experimental data for finding the relevant material parameters and for validating the predicted results of hydromechanical models. In addition to the hydromechanical properties, the tomographic data provides very useful information on the transport mechanisms of water in compacted, swelling bentonite (Fig. 3).

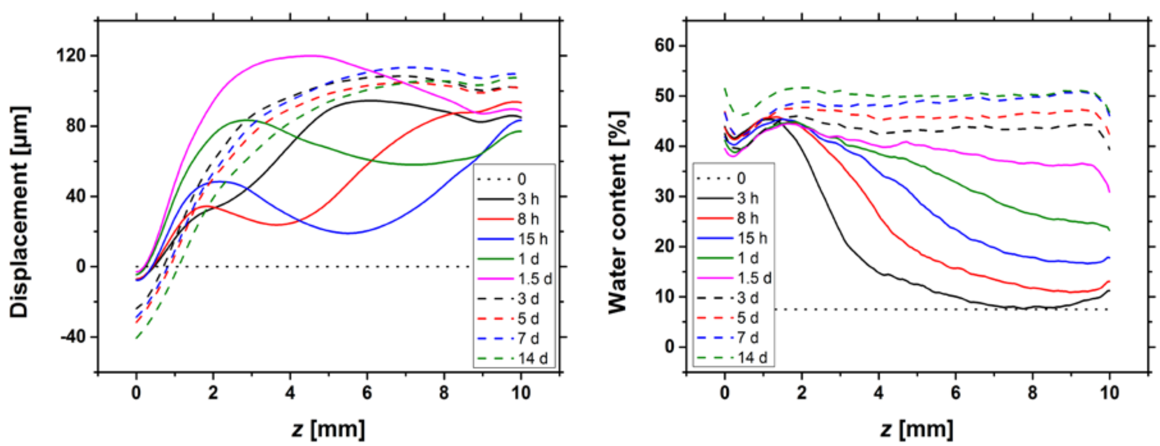


Fig. 3. Axial displacement and water content profiles in a one-dimensional wetting experiment at various times during the total wetting time of 14 days.

During the present project, a phenomenological hydromechanical model including swelling and finite plastic deformations has been developed at the University of Jyväskylä. The present version of the model is a generalization of a conventional hypo-elastic scheme based on an assumption that a certain minimum set of data from odeometric and swelling experiments, defining the behavior of the 'effective' quantities, is available. In order to provide the necessary data, dedicated experimental devices have been constructed and tested, and systematic experiments have been carried out for the same purified bentonite material as used in the X-ray tomographic studies. However, the experimental data available for the particular bentonite material used here is still insufficient, especially concerning the relevant range of moisture content.

The main objectives of this task are:

- to carry out an extensive set of small-scale odeometric measurements, including one-dimensional restrained compression and hydrostatic compression of bentonite samples, over an extended range of moisture levels.
- to carry out the necessary one-dimensional free-swelling experiments.
- to extend the present phenomenological hydromechanical model to a full three-dimensional case and implement that model numerically (in collaboration with Numerola Oy).
- to validate the model using the data from X-ray tomographic experiments for one-dimensional, three dimensional cylindrically symmetric, and fully three dimensional cases.

Numerola Oy

The role of Numerola Oy (Ltd.) in the BOA project is to combine the advances in bentonite modeling into a software tool that can be used to simulate the behavior of a bentonite buffer. To fully model the bentonite buffer, a coupled thermal, hydrological, mechanical, chemical, and biological model is needed, which is known as a THMCB model.

THMC-model implementation at Numerola is based on an elastoplastic hydromechanical model developed at the University of Jyväskylä, a chemical transport model including the exchange of five ions developed in collaboration with VTT, a hydrological model for transport of two moisture components (water vapor and liquid water) based on the ideas of Klaus-Peter Kröhn [8], and a heat conduction equation. Microbial activity is not yet taken into account.

These models are implemented using the in-house code of Numerola, which enables flexible model development, easy coupling of multiphysical models, and an efficient numerical solution. The models are solved with time-dependent finite element and control volume finite element methods, yielding values of solution variables on a finite element grid representing the geometry of a bentonite block.

The primary solution variables are solid material velocity, liquid water and water vapor densities, temperature, and concentrations of three ions. The solution methods are implemented for fully three-dimensional cases as well as for cylindrical symmetric and one-dimensional simplifications. When beneficial, the models are solved simultaneously as a system of coupled equations, but so far the interactions of the different phenomena are only partly modeled.

Currently, the THMC software is used to simulate various experiments in order to validate the models and to identify the model parameters. Fig. 4 shows a comparison of X-ray tomography measurements and simulations in a wetting experiment conducted at the University of Jyväskylä.

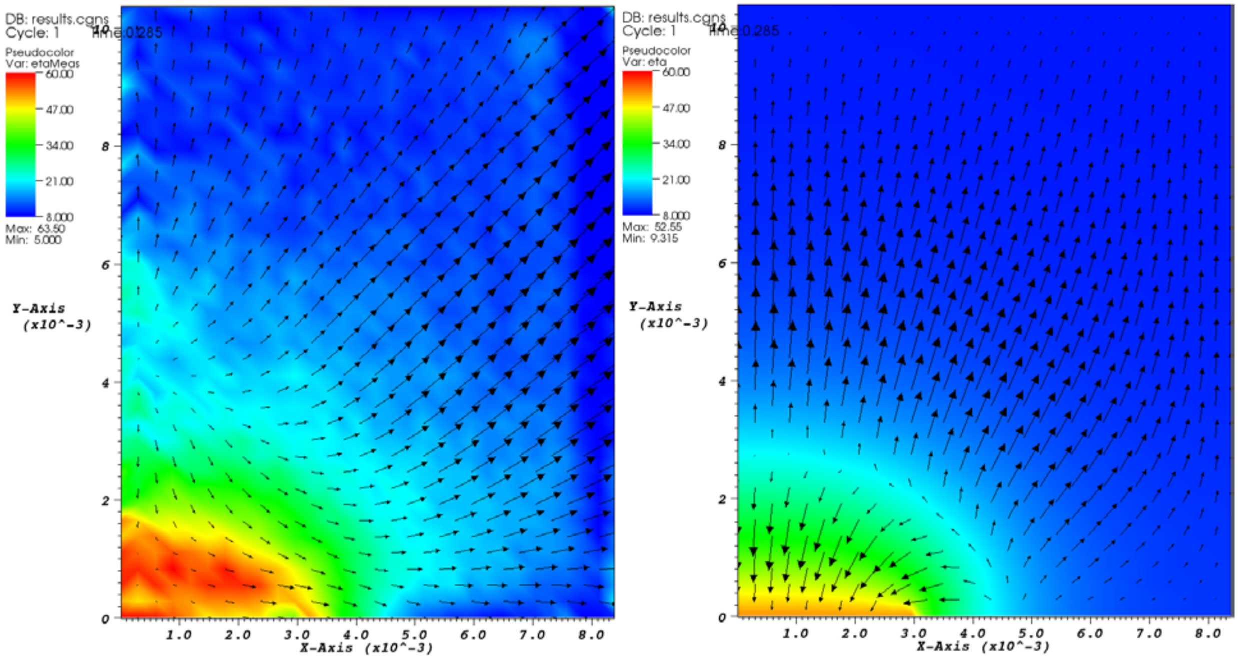


Fig. 4. Water content and displacement vectors at one time step, in an experiment where a cylindrical bentonite block is wetted from below causing swelling of bentonite. (A) shows measured values in a cylinder crosscut and (B) shows the corresponding simulated values. These are very preliminary comparisons with the mechanical model, still lacking fittings for some of its parameters.

VTT Technical Research Centre of Finland
The aims of this research are to study the temperature dependence of the ion exchange selectivity of the montmorillonite, to develop a method for measuring the main ions in the porewater of compacted bentonite, to study the solubility of montmorillonite, and to evaluate microbial activity in bentonite.

Many of the performance targets of the bentonite buffer in the KBS-3 concept are coupled to processes that occur in the water-saturated bentonite. The water in compacted bentonite (porewater) exists in interlamellar pores and non-interlamellar pores. The ion compositions of these two water types have a great effect on the processes of swelling, ion exchange, dissolution-precipitation, and transport of ions through to clay. The porewater composition can be determined by squeezing the water out from the bentonite, but unfortunately this method includes many sources of errors. For example, different water types will be mixed, some of the accessory minerals will dissolve, and cation exchange between these two water types will exist. The ion-selective electrodes can measure directly the ion activity in non-interlamellar water, but unfortunately commercial electrodes cannot stand the bentonite swelling pressure.

VTT has succeeded in developing a method of measuring H^+ and Cl^- ions directly in the compacted bentonite using ion selective electrodes [9, 10, 11]. The electrodes for measuring Na^+, Ca^{2+}, and $SO4^{2-}$ ions have been developed and tested [11]. In any case, the electrodes were unstable during long-term measurements (two weeks), which will be needed for determining the ion content inside the compacted bentonite. The stability of the electrodes can be improved by using liquid junctions between the membrane and conductor wire, instead of solid junctions. The liquid junction was tested for the Na electrode and the calibration results were promising.

A literature survey to search for suitable compositions of filling solution for each ion-selective membrane will be carried out. Suitable membranes and electrodes for sodium, calcium, chloride, and sulfate will be manufactured at VTT (Table I). The electrodes will be calibrated in solution and tested in compacted Na and Ca montmorillonites. After sufficient stability has been reached according to long-term calibrations and test measurements, the electrodes can be used in cation exchange and diffusion experiments.

TABLE I. Ion selective membranes and test matrixes

Ion	Material	Structure	References, e.g.	Test matrix
Na^+	$Na_3Zr_2Si_2PO_{12}$	Homogeneous	[12]	Na montmorillonite
Ca^{2+}	CaF_2 + La(Eu)F_3	Homo-/heterogeneous (thermo or coating)	[13] [14] (patent)	Ca montmorillonite
Cl^-	AgCl	Homogeneous	[15]	Ca montmorillonite
SO_4^{2-}	Ag_2S, PbS, $PbSO_4$, Cu_2S	Homogeneous	[16]	Na montmorillonite

The cationic form affects many essential properties of montmorillonite. In the KBS-3 concept, the maximum temperature limit has been decided as 90°C. The thermal period when spent fuel is supplying heat may last for thousands of years. Thus, for the long-term modeling of the chemical processes in the buffer, the cation-exchange selectivity coefficients have to be known at different temperatures. However, the selectivities for montmorillonite have mostly been studied at room temperature. In this work, the cation-exchange selectivity coefficients and cation-exchange isotherms are determined in batch experiments for montmorillonite at three different temperatures (25, 50, and 75°C). Five different ratios of $NaClO_4/Ca(ClO_4)_2$ are used in the experimental solutions. After equilibration, the solution and montmorillonite are separated and both are analyzed to get the desired exchange parameters. The experiments are modeled with a computational model (PHREEQC), which is capable of taking into account the physicochemical processes that take place in the experiment.

The aim of the dissolution study is to gain a better understanding of the behavior of montmorillonite in different groundwater compositions, considering the dissolution rate and possible alteration of the structure. The behavior of bentonite in alternating groundwater conditions is an important part of the safety assessment of a nuclear waste repository. The favorable properties of bentonite for nuclear waste disposal, such as a high swelling capacity and high cation exchange capacity, are greatly based on the properties of bentonite's main mineral component, montmorillonite. However, many of the studies have concentrated on bentonite that also contains accessory minerals, complicating the interpretation of the analyzed data. The results gained so far are mainly reported in [17, 18].

A long-term bentonite experiment, which was started during 1997, has been studied: the capsules containing bentonite and copper have been opened anaerobically and the cultivation of sulfate-reducing microorganisms has been done at several elevated temperatures. In order to visualize the copper bentonite interfaces and tentative growth of microorganisms or biofilm formation, we have used SEM scanning electron microscopy for the samples. In addition, RNA and DNA extractions were done. The bioinformatics and phylogenetic analysis, as well as identification of the microorganisms which have grown on the culture media, have been studied.

CONCLUSIONS

Our work is an example of a coordinated domestic project, which is, however, collaborating with several international projects such as EU BELBaR. Bentonite has appeared difficult to understand in the context of spent fuel disposal by the KBS3 method. However, we have obtained good results by applying several methods in studying the properties of montmorillonite.

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ACKNOWLEDGEMENTS

The research leading to these results has received funding from the Finnish Research Programme on Nuclear Waste Management (KYT) 2011-2014 [19]. BOA, assessment of bentonite characteristics, is a coordinated project in the KYT2014 research program. The BOA project consortium is formed by VTT Technical Research Centre of Finland (VTT), the Geological Survey of Finland (GTK), the University of Jyväskylä (JyU), the University of Helsinki (Laboratory of Radiochemistry, HYRL, and Department of Physics, HYFL), Aalto University (Aalto), and Numerola Oy. Special thanks go to Gowthaman Sinnathamby, Aku Itälä, Emmi Myllykylä, Joonas Järvinen, Merja Tanhua-Tyrkkö, and Merja Itävaara.