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End User Review Board Evaluation Report

Evaluation of the first annual meeting of the project

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Introduction

The EU-project BELBaR - *Bentonite Erosion, effects on the long term performance of the engineered Barrier and Radionuclide transport*, was launched in March 2012. The main aim of the project is to increase the knowledge of the processes that control clay colloid stability, generation and ability to transport radionuclides. The overall purpose of the project is to suggest treatment of the issues in long-term safety/performance assessment. This report evaluates the outcome of the **first annual meeting** of the project, held at **Helsinki University, Helsinki, Finland, March 5-7, 2013**.

Partners include national radioactive waste management organisations (WMOs) from a number of countries, research institutes, universities and commercial organisations working in the radioactive waste disposal field. The Collaborative Project is based on the desire to improve the long-term safety assessments for repository concepts that combine a clay Engineered Barrier System (EBS) with a fractured rock. The formation and stability of colloids from the EBS may have a direct impact of assessed risk from the repository in two aspects:

– Generation of colloids may degrade the engineered barrier
– Colloid transport of radionuclides may reduce the efficiency of the natural barrier.

An increased understanding of processes will have an effect on the outcome of future assessments.

The main aim of BELBaR is to reduce the uncertainties in the description of the effect of clay colloids on the long term performance of the engineered barrier and on radionuclide transport. This is done by:

– Improving the understanding on when bentonite colloids are unstable.
– Improving the quantitative models for erosion on the bentonite barrier for the cases when the colloids are stable
– Improving the understanding of how radionuclides attach to clay colloids.

To meet the main aim a number of experimental and modelling activities are undertaken within the project. Those, and the initial results, are described in the presentations of the first annual meeting.

Key issues in BELBaR are interaction, communication and cooperation, and the annual meetings have an important function in this aspect.

The End User Review Board consists of
Jinsong Liu, Analyst, The Swedish Radiation Safety Authority (SSM)
and
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The first annual meeting of the project

The BELBaR-project held its first annual meeting at Helsinki University, Helsinki, Finland, on March 5-7, 2013. The aims of the workshop were to disseminate the initial findings as well as to establish a network of specialists from various areas of the world and with a range of expertise relevant to the project.

In addition to the project's participating partners, several other institutions have also attended the meeting. They are ESPCI Paris Tech from France, Lund University from Sweden, Helsinki University from Finland, Amphos21 from Spain, and Numerola Oy from Finland.

The 24 presentations during the meeting covered a wide range of research areas related to bentonite chemical erosion: montmorillonite colloid properties and stability; mechanism of bentonite erosion; colloid characterisation; rheology of montmorillonite/bentonite; radionuclide transport mediated by colloids; experimental studies in laboratory and at field site; numerical modelling of the erosion processes; etc.

In this deliverable the merits and usefulness of the results presented during the meeting are evaluated from the end-user (here, regulatory) point of view. The End User Review Board has the opinion that the annual meeting has well-defined aims, has succeeded in attracting a relatively large number of participants not formally involved in the project. The presentations made during the meeting are of high scientific quality and reflect the most recent research status in the respective areas. The presentations will benefit the nuclear management programs using bentonite as a buffering material. The meeting has been successful and fruitful. More detailed evaluation of the meeting's presentations are given below.

Summary of the presentations in the first annual meeting of the project

The following is a summary of the presentations during the meeting. The presentations are grouped into the following topics: general, characterisation, process study and mechanism understanding, colloid mobility and radionuclide sorption (ir)reversibility, as well as modelling.

General

Beard's presentation on the treatment of colloids and related issues in the safety case, based on D1.2, summarized the current treatment of colloidal issues in performance assessment (PA) for the three national radioactive waste management organisations participating in the BELBaR project. The presentation also identified limitations of the current treatment, discussed the need for additional colloid studies in PA context, and identified relevance of and expected benefit from WPs 2-5.

Characterisation

Vejsadů and Červinka's presentation on basic properties and coagulation of clay dispersions by inorganic cations started with a description of the bentonite deposit in Czech Republic. The content of swelling minerals and the cation exchange capacity (CEC) of the Rokle bentonite were specifically outlined. The bentonite purification processes were discussed. **F**inally some experimental results of the coagulation of clay dispersions by inorganic cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were shown. The main conclusions of this presentation are: in the case of univalent cations, the observed critical coagulation concentration (CCC) is more than one order of magnitude higher than the appropriate concentration in the synthetic granitic water (SGW). In the case of calcium and magnesium, the CCC was found to be only approximately two times higher than the concentration in groundwater.

Jönsson's presentation dealt with studies of montmorillonite in mixed salt solutions with small-angle X-ray scattering (SAXS) technique and Monte Carlo method. Two types of montmorillonite were studied: MX-80 and an Iraqi bentonite (IQ-WB) dominated by Ca^{2+} cations. The following aspects had been investigated: swelling and swelling reversibility; ion-ion interaction in divalent bentonite; tactoid kinetics and platelets size; counter-ion competition; as well as Monte Carlo simulations. The main conclusions of the studies are, *inter alia*, that divalent counter-ions lead to tactoid formation; the tactoid formation is fast and the tactoids grow with platelets size; composition of the bulk solution is an important factor for tactoid formation; and the Poisson-Boltzmann equation is not valid for divalent ions.

Eriksson et al. presented preliminary results for using combined optical coherence tomography (OTC) and rheometry to study montmorillonite dispersion. The fundamental principles for rheological measurements were believed to be that the elastic modulus of bentonite samples is directly proportional to their network strength. The radial velocity profile of bentonite suspensions flowing in a capillary tube can be obtained by OCT imaging technique, and the viscosity of the suspensions locally anywhere along the flow field can be calculated. Some future collaboration works were outlined.

Hedström and Nilsson presented rheology of montmorillonite/bentonite system. Several non-Newtonian viscosity models were outlined. Previous studies of viscosity of clay suspensions were reviewed, including some of the results obtained by the authors themselves.

The presentation of **Pulkkanen et al.** consisted of two parts: microstructural studies and modelling of erosion experiments. The methods used in the experimental studies were small-angle X-ray scattering (SAXS), nuclear magnetic resonance (NMR) and transmission electron microscopy (TEM) and anion exclusion. The first step was to get the methods work for compacted bentonite. Some preliminary experimental results were also obtained. Modelling efforts had been planned to couple the mechanical and wetting processes, as well as the effect of salinity.

Process study and mechanism understanding

Rasilainen andTanhua-Tyrkkö presented in brief the Finnish research program on nuclear waste management. The program is based on the Finnish Nuclear Energy Act (99/1987) to enhance the authorities scientific and technique expertise, and is funded by the State Nuclear Waste Management Fund (VYR). The basic aim is to produce high quality research results to be used by Finnish nuclear authorities.

The presentation of **Bouby et al.** was about the erosion/destabilisation of compacted FEBEX bentonite with glacial melt water under quasi-stagnant flow conditions. Colloid generation experiments were carried out. Two different set-ups were used: erosion on one side of a compacted clay pellet, and radial design with erosion of all the external ring surfaces. Gel layer and bentonite plug were characterised by post-mortem analysis. The erosion rates determined from the experiments were below the model predictions.

Bruno raised several questions after reviewing the recent achievements in colloid formation research, such as whether our understanding of bentonite colloidal generation under diffusive regimes is complete, whether water is the only reagent that will have an enhancing effect on colloidal generation, and if montmorillonite is stable in water or not. The author then outlined several issues that may be our future focus for the research, including the role montmorillonite dissolution/alteration plays in colloidal generation, as well as how to link the previously developed geochemical models to colloidal generation.

Alonso et al. presented their studies of erosion behaviour of different compacted bentonites. The aims were to identify the most relevant parameters affecting bentonite erosion so such to obtain qualitative and quantitative information of erosion rate. Both diffusive and flow conditions were considered for both compacted and confined clay samples. A wide range of water/clay experimental conditions were employed and the possibility of scenario evolution through chemical or physical changes were studied. Some of the conclusions are: maximum eroded mass was measured from Na-bentonites, at higher clay compaction density and in Ca-free electrolytes of low ionic strength; FEBEX bentonite with a 30% Na behaves similar to Na-bentonite and the erosion behaviour of the natural raw clays (FEBEX, Mylos and MX-80) seems to be related to their contents of smectite.

Hansen and Hedström studied the behaviour of montmorillonite at low ionic strength. A Na-montmorillonite phase diagram was first presented. Several laboratory observations were shown to illustrate the features of the phase diagram. Free swelling of Wyoming Na-montmorillonite and of Wyoming 50/50 (Na/Ca) montmorillonite in an artificial fracture was demonstrated. Water flow was applied in the fracture following the swelling test. The main conclusion was that erosion appears to be highly dependent on the salinity of the water and the flow rate.

Schatz and Kanerva gave an update of the artificial fracture testing program at B+Tech. Some experimental work done before the BELBaR project was first reviewed. An erosion threshold seems to exist: erosion was not observed for Na-montmorillonite against contact solution compositions from 171 mM to 8.6 mM NaCl solutions or for 50/50 Ca/Na-montmorillonite against 8.6 mM NaCl solution; but erosion was observed for both Na-Montmorillonite and 50/50 Ca/Na-Montmorillonite in contact with solutions of compositions less than 4.3 mM of NaCl. It has also been observed that not all system erode equally. For Na-Montmorillonite or 50/50 Ca/Na-Montmorillonite against deionised water (DI) or groundwater (GW) at the same flow rate, the average mass loss rates were nearly identical (2%), but were faster in the sloped case compared to the horizontal case by almost exactly a factor of 2. The results also indicated that the accessory phases (from within bentonite) remain behind and form layers at the solid/solution interface after the montmorillonite in the bentonite was eroded, but no apparent attenuation of the erosion of montmorillonite was observed in the tests for a fracture aperture of 1 mm. Smaller apertures will be tested in the future.

Colloid mobility and radionuclide sorption (ir)reversibility

The presentation by **Norrfors et al.** examined the effect of the montmorillonite colloid size on their stability, on their radionuclide sorption capacity and on the sorption reversibility. No difference in stability was observed for the different size fractions of montmorillonite colloids considered in the study. A number of radionuclides were considered in the sorption studies (U-233, U-238, Pu-242, Th-232, Tc-99, Np-237 and Eu-152). Ongoing activities included sorption reversibility investigations as a function of suspension pH and ionic strength and also by adding fulvic acids and fracture-fill material as competing ligands and mineral surface, respectively, and interpretation of the results from the sorption and sorption reversibility studies with a computational model.

The presentation by **Hölttä et al.** considered the release and stability of bentonite colloids, radionuclide (Sr-85 and Eu-152) sorption, colloid-rock interaction and the effect of colloids on the radionuclide transport. In a three-year experiment, the stability of bentonite colloids was found to strongly depend on the solution ionic strength and the cation charge. The zeta potential increased from around -40 mV at 5 mM to -10 mV at 70 mM. The colloid concentration was very low with ionic strengths exceeding 10 mM. The experimental time did not have a discernible effect on colloidal stability.

In the presentation by **Missana et al.**, the focus was on bentonite colloid interaction with rock surface (filtration) and colloid-mediated radionuclide (Cs-137) transport under different chemical conditions. A small quantity of calcium in the influent used in the experiments to investigate the transport of bentonite colloids in fracture was found to significantly decrease the colloid recovery and to increase the size of colloids eluted. Under the Grimsel conditions which promote colloid stability, the transport of Cs was significantly different in the presence or absence of colloids while the Cs breakthrough curves were very similar under the Äspö conditions, which promote colloid instability, irrespective of colloids.

Nordman presented results from a generic analysis of radionuclide transport affected by bentonite buffer erosion. Subject to the assumptions made in the analysis (e.g., advective conditions in the buffer), the release rate of radionuclides was clearly higher than without bentonite erosion. Also, increased water flow rate during a glacial cycle and colloid-mediated radionuclide transport were stated to increase the release rate.

Sherriff et al. studied the sorption of uranyl on bentonite as a function of pH and ionic strength both in the absence and presence of humic acid (HA). The sorption was found to depend on the pH and the presence of HA. HA increased uranyl sorption at low pH and limited it at moderate pH in comparison to the absence of HA. The reduced sorption of uranyl in the basic pH range for both the absence and presence of HA was hypothesized to result from the formation of soluble uranyl complexes. No evidence for slow dissociation or (pseudo-)irreversible binding of uranyl on bentonite was found. The batch experiments for ternary systems of Eu-152, bentonite and ligand (HA or EDTA) showed slow uptake of Eu following the initially rapid sorption in the absence of a competing ligand. For the HA ternary system, important kinetic effects were found in some of the binary sub-systems. The authors developed their kinetic model further to interpret the uptake of Eu and HA by the bentonite (WP5). Although slow dissociation from bentonite has been observed in the case of Eu, no irreversible uptake of either Eu or uranyl on bentonite was observed.

Videnská et al. studied the sorption and desorption of radioactive (H-3, Cl-36, Sr-85 and Cs-137) and stable (selenate and selenite) tracers in columns of crushed granite and fracture infill in the presence of a synthetic ground water. H-3 and Cl-36 were observed to behave like conservative tracers without any sorption. Consequently, H-3 was considered as a suitable tracer to determine transport parameters of the system. Co-ion exclusion was observed for Cl-36. Selenite showed completely different sorption behaviour from selenate, which behaved like a conservative tracer. The transport of Sr-85 was found significantly retarded in comparison to other tracers. Fracture infill was found to retard the transport of non-conservative tracer more than crushed granite.

Schäfer et al.'s presentation reported on the progress of work concerning the colloid transport under near-natural hydraulic conditions at the Grimsel Test Site (GTS). Montmorillonite colloids, a conservative tracer and a number of radioisotopes (Na-22, Ba-133, Cs-137, Th-232, Np-237, Pu-242 and Am-243) were injected into a rock fracture in the MI shear zone of the GTS. All injected radionuclides, including the strongly sorbing tri- and tetravalent actinides, were detected in the effluent. The data clearly showed the mobility of bentonite-derived montmorillonite colloids under near-natural flow conditions in the shear zone.

Modelling

Liu presented the mechanistic model development for prediction of swelling pressures of different types of bentonite in dilute solutions. The swelling mechanisms were first outlined: crystalline (interlayer) swelling; osmotic (interparticle) swelling; breakup of particles; demixing of exchangeable cations; co-volume swelling as well as Brownian swelling. Based on the outlined mechanisms a model was developed and benchmark tested. The model predictions were in agreement with experimental results.

Kataja et al. presented both experiments and phenomenological model of bentonite swelling in a narrow channel. The aim was to construct a hydromechanical model that include finite deformation, plasticity and swelling that is based on direct experimental data and that will be experimentally validated. Material properties such as P-wave modulus, yield stress, free swelling strain were experimentally obtained. A hydromechanical model was then developed by assuming that the bentonite has local homogeneity, is an elasto-plastic material. The water transport was assumed to be simple diffusion, and the swelling process was assumed to be quasistationary. **Laitinen** presented some model validation results by applying the model numerically. Some preliminary results were obtained.

Nerietnieks and Moreno presented a smectite erosion model with some testing of model simplification. The main competing mechanisms considered in the model are swelling by a diffusion-like process in the seeping water, and great increase of gel/sol viscosity with volume fraction. The model was used to predict some experimental tests and good agreement was achieved. Literature data of dependence of gel/sol viscosity on volume fraction were reviewed, compared and selected for the modelling purposes. Numerical difficulties were encountered and some of the model's underlying mathematical equations were carefully simplified to overcome the difficulties. **Olin** implemented Neretniek's model to predict some experimental results made by Schatz et al. It was found that both the extrusion distance and shape differ, but not much.

Evaluation of presentations by the End-User Review Board

General

Deliverable 1.2 underlying Beard's presentation is a useful, and necessary, contribution to the project in that it clarifies the roles each WP has and presents the current position of the three national radioactive waste management organisations regarding bentonite erosion and colloid-mediated radionuclide transport as well as the working hypotheses (or assumptions) to be tested during the course of the BELBaR project.

Characterisation

The End User Review Board considers it positive that the project has started characterising bentonite colloid using relatively advanced analytical methods, such as small-angle X-ray scattering (SAXS), optical coherence tomography (OTC), nuclear magnetic resonance (NMR) and transmission electron microscopy (TEM). The Board has the opinion that detailed and accurate characterisation of bentonite colloid is an important step for comprehensive and in-depth understanding of the erosion processes. The board considers it also positive that a large variety of bentonite has been or is planned to be characterised. It is judged that, the project has a good start in this respect and it is expected more useful results will be obtained in the following years of the project.

Process study and mechanism understanding

Regarding the process study and mechanism understanding, the End User Review Board considers that the project has a very good start. The processes studied and the mechanisms investigated by the project are highly relevant for the performance assessment to handle the bentonite erosion issue. It is positive that the project studied the processes of gel/sol formation from compacted bentonite in contact with diluted water; the effect of cations' valence (mono- or divalent) on colloid formation; the effect of water flow conditions on clay erosion; as well as the erosion attenuation role played by accessary minerals that are left behind after erosion of montmorillonite. The parameters involved in the studies are also well chosen. The finding of the studies that bentonite erode faster in sloped fractures than in horizontal fractures has a direct impact on the performance assessment, as in nature fracture systems in granitic bedrocks, some fractures are deemed to be sloped. The End User Review Board can state that the process and mechanism studies are of high scientific quality and reflect the most recent research status in the areas. The studies will benefit performance assessment in nuclear management programs that use bentonite as a buffering material.

Colloid mobility and radionuclide sorption (ir)reversibility

Given that only the first year of the project has passed, WP3 already shows good progress towards meeting its objectives. While the stability of bentonite colloids was found to strongly depend on the solution ionic strength and the cation charge, it was independent of their size. This result regarding the effect of ionic strength and cation charge is in line with previous findings. However, the result regarding the effect of colloid size is anticipated to simplify safety analyses when considering the colloid-mediated transport of radionuclides. The remarkable "long-term" colloid stability in laboratory conditions may have the potential to translate into colloid stability in actual repository conditions, too. The experimental observation that a low concentration of soluble calcium significantly decreased the colloid recovery and increased the size of colloids recovered in laboratory conditions is consistent with the observations made regarding colloid stability in corresponding chemical conditions. Under *in-situ* conditions promoting colloid stability, the mobility of montmorillonite colloids derived from bentonite was clearly established and the transport of radionuclides was found to be affected by the presence of colloids. These findings point to the importance of considering colloid-mediated transport of radionuclides in a safety case. Also, the observed reversible uptake on bentonite of the radionuclides studied is hypothesized to have implications for the way such uptake is considered in safety-analysis calculations with colloid-mediated radionuclide transport.

Modelling

It is considered to be a good beginning that the project started by validating and improving some of the existing models. It can also be stated that the modelling group of the project has maintained a good dialogue with the groups that characterise the colloid and study the mechanisms and processes of erosion. It is also considered to be positive that some of the models have been applied to model the preliminary experimental results and predictions have been compared with the experimental observations. It is also considered to be positive that some hydromechanical models have been developed during the first year of the project.