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End User Review Board Evaluation Report

Evaluation of the third 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 **third annual meeting** of the project, held in **Madrid, Spain, March 5-6, 2015**.

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 at SSM – The Swedish Radiation Safety Authority
and
Jarmo Lehikoinen, Senior Inspector, Nuclear Waste and Material Regulation, Nuclear Waste Safety Assessment – Radiation and Nuclear Safety Authority (STUK).

The third annual meeting of the project

The aims of the third annual meeting were to summarise the outcomes that had been achieved during the third year of the project, to continue to disseminate the previous findings and to get in-depth understanding of the related issues.

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 presentations covered most of the areas/topics that had been planned to study at the beginning of the project. It can be stated that new research methods have been introduced into the project, and new findings have been achieved during the third year of the project. The previous achievements both in mechanism studies and in experimental studies of bentonite erosion have also been updated. Moreover, the presentations during the third annual meeting are still problem-oriented and focus on applications of the research results to performance assessment in nuclear waste management, as was observed during the second annual meeting. In general, the End User Review Board has the opinion that this meeting has achieved its aims and was also a successful and fruitful meeting, as was the project's previous annual meetings. More detailed evaluation of the meeting's presentations is given below.

Summary of the presentations in the third 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

The presentation by **Bailey** was largely the same as that given by **Beard** at the first annual workshop in 2013 in that it presented the objectives of WP1, linkages between WPs at the start and end of the project, synthesis of issues for each WP, and a summary. Bailey also presented the four items to be addressed in the final state-of-the-art report: i) integration of information produced by other WPs with due consideration of answers to the issues identified for each WP; ii) examination of the extent to which other WP findings provide satisfactory answers to the needs identified at the project outset; iii) definition of "scenarios" for colloid issues, discussion of uncertainties in these "scenarios" and identification of model and data needs for their treatment; and iv) update of the state-of-art report to include justified recommendations for improved and updated treatment of colloids and related issues in relation to post-closure safety assessments, based on integrated project findings. Overall, WP1 is looking to understand where removal of current pessimistic assumptions regarding colloid behaviour can be justified in order to present a more realistic and confident safety case.

Characterisation

The presentation by **Eriksson** concerned the study of montmorillonite rheology through characterisation of its microscopic structure. The presentation started with reviewing of several important concepts discussed in the literature: phase diagram with regions of repulsive and attractive gel; formation of hierarchical agglomerate structures; lamellar structure with periodicities. The storage modulus was determined against the applied strain for 50/50 Na/Ca-montmorillonite in 1 mM NaCl

solution. The presentation finally discussed the dynamic response to strain and emphasised the importance of the effect of prolonged small shear stress.

The presentation by **Fernández** concerned the influence of the physico-chemical and crystallographic properties of clay minerals on erosion processes. The presentation outlined that the smectite particles in gels and suspensions are strongly influenced by swelling and decreases in dry density; by pore water and groundwater chemistry; by changes in cation compositions at the cation exchange sites, as well as by crystallochemistry of the clay minerals. The physical, mineralogical, surface and physico-chemical properties of the bentonite had been characterised. The texture, microstructure and crystallochemistry of the samples had also been characterised.

The studies of **Friedrich et al.** on bentonite hydration observed by wet-mode (environmental) scanning electron microscopy (ESEM) and atomic force microscopy (AFM) force measurements were presented. Some basic principles of ESEM and its advantage over the traditional high-vacuum SEM were discussed. The ESEM technique can be applied to characterise the compacted samples in hydration experiments. The ESEM-data can be correlated with water content in powered samples, and with X-ray diffraction data for hydrated textured samples. The hydration isotherms can also be determined. Some practical difficulties were encountered in characterisation of montmorillonite samples with AFM. Some kaolinite samples were characterised instead.

The presentation of **Kataja et al.** dealt with measurement of water transport and swelling of bentonite clay using X-ray tomography and imaging. The aims were to develop experimental methods based on X-ray imaging that can be used to gain detailed information on water transport and swelling dynamics of bentonite, as well as to produce detailed and well characterised data on wetting/swelling processes and thereby to support modelling of bentonite erosion. The techniques X-ray tomography was used to measure wetting and swelling of bentonite in a closed volume, to analyse water content based on different images between wet and dry sample, to characterise free welling of bentonite in a channel, and to study evolution of bentonite density and water content in a channel. Some of conclusions are that the method yields detailed time-series data on solid phase displacement field, solid phase density field and liquid phase density field. The results are useful especially in validation of models.

Process study and mechanism understanding

Rinderknecht et al. presented their experimental work on bentonite erosion with an artificial fracture setup, updated the benchmark test for stagnant phase, as well as their experimental work with double-side reactor setup. In the experiments with artificial fracture setup, the swelling pressure was measured, the pH was monitored, colloid in the effluent was determined and the gel layer and the halo were characterised with electron microscopy. In the experiments with double-side reactor setup, the pH, the flowrates, the evolution of compositions of ions (Na^+, Ca^{2+}, SO_4^{2-} and Cl^-) and major elements (Si, Al, Fe Mg), the colloid size and the sorption behaviour of the eroded material were all determined.

In **Alonso et al.**'s presentation the erosion experiments at CIEMAT was updated. In the benchmark test, Nanocor®, a purified Na-montmorillonite, and FEBEX Ca- or Mg-bentonite were compared. Phase 1 of the experiment was carried at stagnant conditions. Phase 2 of experiment dealt with low flow conditions (10^{-6} m/s). In Phase 3 high flow conditions were implemented (10^{-4} m/s). For the analysis of the eroded material, analytical techniques of photon correlation spectrometry for determining concentration and particle size, turbidity analyses for determining concentration were used. Final post mortem analyses were also made for the extruded mass to check mass balance. The main observations of the benchmark tests were: extrusion behaviour of natural FEBEX is comparable with that of purified Nanocor (Na-bentonite) only at low flow rate. At high flow rate the erosion of FELEX is slower. Moreover, it was observed that the colloidal particles with size less than 1 µm are mobilised. The results of static experiments can be summarised as follows: colloid erosion is related to

clay smectite content. Some clays and oxides affect bentonite colloid stability and inhibit bentonite erosion.

Schatz presented the work of design, implementation and evaluation of an artificial fracture database for the BELBaR project and some benchmark test results. The database will be based on joint analysis from the BELBaR project, followed by comparative analysis. The metadata will be related to raw data of different categories: sample (including material type, initial density and water content, initial sample size); solution (chemistry, flow rate, duration of flow regime); environment (extrusion space, fracture aperture, fracture orientation); results (extrusion distance, mass loss) and other information. The benchmark tests were carried in an experimental setup with 0.1 mm fracture aperture and 1 mM NaCl solution. The results were that rate of mass loss during high-flow period was nearly an order of magnitude lower than those observed under similarly dilute conditions in 1 mm aperture fracture.

Svensson presented studies of crystalline swelling of montmorillonite with divalent interlayer cations at high water to solid ratio. The study had focused on the swelling properties of three montmorillonites with divalent interlayer cations with free access to water (Wyoming, Milos and Kutch). The swelling was studied using synchrotron X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS). The purpose was to investigate the effects from temperature, type of interlayer cation, salt concentration and type of montmorillonite on the basal spacing. Two regions of swelling for smectite were proposed: crystalline swelling with one to four layers of water, and osmotic swelling caused by delamination of the tactoids into smaller tactoids or even into single platelets. The crystalline swelling is of relevance to the bentonite buffer saturation and the osmotic swelling is of relevance to its chemical erosion. Different forces are relevant for crystalline swelling and osmotic swelling, but in both cases, type of smectite, type of interlayer cation and salt content are relevant. New phenomena were observed for some samples of the Ca-Woyming montmorillonite upon cooling: it expands prior to ice formation, and was dehydrated after ice formation. As osmotic swelling leads to increase entropy, while crystalline swelling does the opposite, osmotic swelling increases at higher temperature, while crystalline swelling decreases (contraction). With the addition of salt the freezing point drops. The layer charge was found to be non-uniformly distributed in the bentonites, and the layer charge has an impact to osmotic swelling. The heterogeneous distribution of layer charge is of interest when it comes to release of colloids.

Mayordomo et al. presented their studies of destabilisation of bentonite colloids by addition of alumina nanoparticles. Since alumina nanoparticles have high specific surface area, are ubiquitous in environment and interact with inorganic colloids, it is worth studying their interaction with bentonite colloids. The main conclusions of the studies were that addition of alumina nanoparticles destabilises bentonite colloids, even at low alumina proportions at pH less than 9; and hetero-aggregation is higher at low pH values and at higher ionic strengths.

Červinka and Gondolli studied coagulation behaviour of clay dispersions in simple electrolytes and its consequences for the possible real groundwater. Series of test-tube tests were carried out with a variety of electrolytes. The presence of colloids was confirmed more precisely by photon cross correlation spectroscopy (PCCS). The main conclusions are: The critical coagulation concentration (CCC) of univalent alkaline metal cations lies in the range of 2 to 5 mmol/l and their effect on coagulation is similar; there is no significant effect by varying anions at given conditions; the presence of humic acid significantly increases the colloidal stability in case of NaCl electrolyte. In case of $CaCl_2$ electrolyte there is only a minor effect.

The title of **Cuevas**' presentation is clay erosion in safety assessment in deep geological repositories. The presentation reviewed a wide variety of studies of stability of different soil aggregates in the literature. Some conclusions in the literature were outlined, such as, small amounts of Al or Fe oxides improve flocculation of clay systems; in soils of mixed mineralogy (illite, smectite, kaolinite**),** the

removal of amorphous and crystalline oxides increases the clay dispersivity; removal of organic matter decreased clay dispersivity.

Colloid mobility and radionuclide sorption (ir)reversibility

The objectives of the work by **Hölttä et al.** included determination of the release and stability of bentonite colloids in different groundwater conditions, determination of the radionuclide sorption on bentonite colloids and montmorillonite, and studies of colloid-radionuclide and colloid-rock interaction in dynamic conditions. The stability of bentonite colloids was found to strongly depend on the ionic strength and cation charge. For example, the particle concentration dropped to zero when the ionic strength of the diluted Olkiluoto ground water increased from 5 mM to 10 mM. The colloid dispersion has shown remarkable long-term stability in low salinity conditions. Slow agitation was found to promote colloid formation significantly, especially in the systems that included a divalent cation. The pH and ionic strength had a great influence on the chemical form of the radionuclides, especially actinides, and thus on their adsorption behaviour. The bentonite colloid recovery in crushed-rock and drill-core column experiments was low, and affected by water flow rate, column type and colloid size. The sorption of Np-237 on various colloids was found to follow linear isotherms.

The focus in the presentation by **Huber et al.** was on colloid/particle transport in synthetic fractures (modelling of flow cell experiments) made of granite or acrylic glass. Fairly good fit between the model and experimental results for the breakthrough of a conservative tracer and latex colloids in the granite fracture was obtained.

Modelling

The presentation of **Pulkkanen and Olin** dealt with swelling mechanisms in artificial fracture experiments. After arguing that swelling into fractures is an important process for determining bentonite erosion, the studies focused on the swelling process and distinguished influences of "bound water" and "free water" in the pores of the bentonite on erosion. The studies went further to model diffusion of the bound water, diffusion of salt and interchange of water. The mechanical part of the model included an elastic model, von Mises perfect plasticity, as well as volume change induced by bound water. The main conclusions are: the initial swelling effects seem to be significant in the artificial fracture experiments. The presentation suggested that, when interpreting results, the swelling effects should be separated to get the correct erosion rates.

Moreno et al. applied their models for bentonite erosion to model Schats et al.'s experiments. The model was the modified two-zone model, the gel zone and the rim zone. The two-zone concept was adapted based on the experimental observations from the experiments of Schatz et al.: In general, there is a sharp rim separated the expanding gel from water and expansion was radially symmetric. There were some deviations from the experimental results and the simulated results based on the original two-zone model. The two-zoon model was then modified by assuming that the sol viscosity as that of water, and the volume fraction at the rim was independent of ion concentration. After modification, the modelling and the experimental results agreed well. At the end of the presentation, the importance of sedimentation of flocs by gravity was discussed.

Evaluation of presentations by the End-User Review Board

General

In addition to presenting the objectives of WP1, linkages between WPs at the start and end of the project, synthesis of issues for each WP and a summary, the project also presented the four items to be addressed in the final state-of-the-art report (D1.4) where integration of information and assessment of meeting the objectives will be done. While the project is looking to understand where removal of current pessimistic assumptions regarding colloid behaviour can be justified in order to present a more realistic and confident safety case, it would also be of interest to learn if any new knowledge has emerged during the project that can give rise to new uncertainties in bentonite erosion and colloid-mediated transport of radionuclides and that should be taken into consideration in a safety case.

Characterisation

Concerning characterisation of the bentonite colloid systems, one presentation has tried to bring in new insights to the project by reviewing some of the issues at the research front related to bentonite erosion. The End User Review Board is positive that many new concepts and understandings have been introduced into the project. It is also a merit that, in other presentations, the microstructural and crystallochemical properties that are closed related to the erosion behaviour have been characterised, and more new techniques have been employed in the characterisation work of the project, such as ESEM, AFM, X-ray tomography and imaging, as well as photon correlation spectroscopy. A variety of unique information concerning the erosion behaviour has been obtained by the newly employed techniques. The results are useful especially in validation of models.

Process study and mechanism understanding

The End User Review Board has the opinion that the process study and mechanism understanding in the project have made a good progress since the last annual meeting. It is positive that many of the studies have gone more in-depth and started to achieve some of the project's initial objectives. The studies of influences of solution chemistry on erosion have been extended to include the influences of anions and other major elements. The influences of flow rate on erosion have been studied at rates that become more representative to the performance assessment conditions. Even more types of different bentonite have been studied. Both the stagnant condition experiments studying the swelling and wetting processes, and the flow condition experiments studying the erosion behaviour have been going on well during the third year of the project. More valuable results have also been obtained from these experiments. The End User Review Board would like to state that the following findings are uniquely achieved by this project and are of great importance for performance assessment and further attention need to be paid to them: the erosion rate is dependent on clay smectite content; alumna nanoparticles and humic acid influence the colloid stability. To distinguish between crystalline swelling and osmotic swelling, as well as to interpret the temperature dependence at different types of swelling by thermodynamics (entropy), are innovative approaches for understanding of the erosion processes. The observation that the the layer charge is non-uniformly distributed is of importance when studying the release of colloids.

Colloid mobility and radionuclide sorption (ir)reversibility

Unlike the previous annual meetings, the fairly low number of presentations connected to WP3 on the BELBaR webpage somewhat complicates forming a coherent view of the progress made in WP3[1] since the second annual meeting. The cut-off ionic strength for bentonite colloid stability was found to lie between 5 mM and 10 mM for a diluted ground water. This range can be iteratively narrowed for a better estimate of a cut-off ionic strength for colloid stability. An interesting experimental finding, which was unforeseen to the End-User Review Board, concerns the ability of agitation to significantly promote colloid formation especially in systems that included a divalent cation. More support for the low colloid recovery in dynamic column experiments was also found. A fairly good fit between model and experimental results for the breakthrough of a conservative tracer and colloids lends credence in the models' ability to quantify the risk posed by colloid-mediated transport of radionuclides.

Modelling

The End User Review Board has the opinion that, in the modelling approaches, more emphases had been put on the modelling's application to performance assessment. Moreover, including "bound water" diffusion in the model seems to be an innovative approach. The application of the two-zone model to predict and compare with experimental results is judged to be a progress of the project endeavour in right direction. The modification and improvement of the model after comparison with experimental results can be considered as an important approach for developing reliable and robust models. The End User Review Board has the same opinion as some of the project participants that sedimentation of flocs by gravity is an important process that need further study in the project.

[1] However, this "concern" was found unjustified on the basis of reporting in WP3. The deliverables in WP3 were outside the scope of this review.