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End User Review Board Evaluation Report

Evaluation of the second 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 **second annual meeting** of the project, held at **Meiringen, Switzerland, June 17-18, 2014.**

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
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and

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The second annual meeting of the project

The aims of the annual meeting were the same as of the project's first annual meeting, i.e., to disseminate the initial findings and 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, the meeting had an invited speech given by Daniel Grolimund from Paul Scherrer Institute, Switzerland, and other participants not being partners of the project, such as University of Strathclyde from UK, Helsinki University from Finland, Helmholtz Zentrum Dresden Rossendorf, Institute of Resource Ecology from Germany.

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 roughly the same areas/topics as the first annual meeting, but have been characterised with more in-depth insights of the erosion issue. For example the invited speech entitled "colloid mobilisation and colloid facilitated transport in natural porous media: phenomena and modelling" has given a critical review of the researches of colloid stability and mobility. Recent achievements both in mechanism studies and in experimental studies of bentonite erosion have been updated. Moreover, the presentations during the second annual meeting have also been more problem-oriented and focus more on the application of the research results to final disposal of nuclear waste. In general, the End User Review Board has the opinion that this meeting has achieved its aims and was as successful and fruitful as the first annual meeting. More detailed evaluation of the meeting's presentations is given below.

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

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

Characterisation

In **Matusewicz et al.**'s presentation the characterisation results of pore structure and interlamellar distance were discussed. The techniques used in characterisation were transmission electron microscope (TEM) imaging, small-angle X-ray scattering (SAXS), nuclear magnetic resonance (NMR). The main conclusions are: with lower density the amount of large pores increase; interlamellar distance changes between dry density of 1.5-1.3 g/cm^3; one can probably distinguish water in the interlamellar pores from that on the clay surface; and sample preparation has an influence on the structure, but it is unclear whether it also influences erosion.

In the presentation by **Friedrich et al.** their work on erosion experiments and characterization of eroded material was updated. During the setup of the flow-through experiments, swelling pressure was measured and the samples mineralogical compositions were analysed. During the experiment, the erosion halo and the eroded colloidal material were characterised. Hydration of cation exchanged FEBEX-bentonite had also been dealt with.

Process study and mechanism understanding

Eriksson and Schatz gave a progress update on their rheological studies. The aims of the study were to relate the strength of montmorillonite gels to the shear forces exerted on them by the flowing water, and to study the rheological properties of montmorillonite suspensions in order to gain new knowledge of the microstructural ordering and dynamics. Some general observations were also given: most samples up to 1 vol-% exhibit a nearly Newtonian behaviour; Ca-montmorillonite has a lower tendency to form volume-spanning gel-like structure, but it forms stronger individual flocs, as compared to Na-montmorillonite; edge-face interactions seem to be important for the build-up of a network structure. Moreover, the studies concluded that there is a small likelihood of particle detachment from gels due to expected shear forces.

Hedström and Hansen first gave a historical overview of the erosion problem in the Swedish waste management program. Several important concepts, such as erosion phase diagram of montmorillonite, attractive gel, ion-ion interaction and no erosion of Ca-montmorillonite, were reviewed. Their experiments of erosion in artificial fractures were presented and the results were compared with those from other similar experiments in the BELBaR project. Some of the observations were: attractive gel has sufficiently high yield strength and will not be eroded, but sol will; without formation of gel erosion rates may be high; hysteresis had been observed when coming from higher to lower salinity of the water and the effect gives lower erosion rates. It had also been concluded that including edge-faces forces is crucial in understanding the erosion process and in mixed Ca/Na system critical coagulation concentration (CCC) is not quantitatively defined.

Schatz gave an update on artificial fracture experiments at B+Tech. The issues studied in the experiments included the effect of fracture slope, of montmorillonite composition, of fracture surface roughness on erosion, as well as application of optical coherence tomography (OCT) and magnetic resonance imaging (MRI) in the studies. The large fracture system had also been investigated. The status of artificial fracture benchmark tests was also presented. Most of the experiments were still on-going.

The presentation by **Reid** focused on understanding the role of accessory minerals in mitigation of bentonite erosion. At very high flow rates (10^5 m/yr) the experimental erosion rate could be as two orders of magnitude higher than that of model prediction. It was proposed that the erosion exhibits a cyclic nature. Some of the reasons for cyclic erosion were outlined.

Červinka, J. Gondolli studied the coagulation behaviour of clay dispersions in the presence of various cations, anions and organic matter. The aims were to investigate the colloid stability in dilute clay suspension during transport in the far field, and to extrapolate the results of the dilute systems to much more dense systems. The following issues were studied: coagulation of clay dispersions by inorganic cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) as well as effect of anions and effect of humic acid. Coagulation kinetics was studied. Some of the conclusions of the studies were that colloid particles are not stable in the synthetic groundwater, and humic acid significantly increases the colloid stability.

Colloid mobility and radionuclide sorption (ir)reversibility

In their presentation, **Grolimund et al.** gave a general description of the phenomena and modelling associated with colloid-facilitated transport of contaminants in natural porous media. Empirically, the colloid release rate was found to obey a power law as a function of ionic strength and the relative sodium saturation in a binary Na-Ca-system. The power-law dependence of ionic strength could be regarded as a potential indication of colloidal instability. The concentration of released particles was found to depend on the cation and co-ion in the system and on the presence of a complexing agent.

While the pore-water velocity and the type and concentration of cation (Na or Ca) affected the colloidal particle deposition rate, the particle concentration did not. The experimental results and model calculations considered in the presentation demonstrated the potential importance of *in-situ* mobilized colloidal particles as a predominant factor in contaminant transport in natural subsurface systems.

In the presentation by **Missana et al.**, the disaggregation of sodium montmorillonite was shown to be partly irreversible. While the aggregation process was very rapid, the disaggregation rate largely depended on the initial experimental conditions. Aggregation-disaggregation hysteresis was observed in mildly saline electrolyte systems. Dilute electrolyte systems, such as deionized water, promoted disaggregation of clay colloids. Also, the disaggregation rate was higher in more diluted suspensions.

Hölttä et al. studied the radionuclide and bentonite colloid interaction by the means of batch sorption and column experiments. The distribution coefficient of Sr-85 and Eu-152 on bentonite colloids was found to decrease with the ionic strength. The experimental results supported the previous findings on the influence of ionic strength and Ca^{2+} concentration on the sorption of Sr-85 and Eu-152 onto bentonite colloids. Bentonite colloids were observed to have an influence on the transport of Sr-85 and Eu-152 in the granite crushed rock and tonalite fracture columns. The transport of bentonite colloids was affected primarily by colloid size but also by water flow rate and column type. The potential of colloids to mediate the transport of Sr-85 was particularly clear in the fracture column. The sorption of Np-237 on bentonite colloids and montmorillonite was found to obey a linear isotherm.

Videnská and Červinka studied the transport of strontium through crushed granite in the presence of bentonite colloids by dynamic column experiments under aerobic conditions. The sorption of Sr-85 on granite was lower in a synthetic ground water than in deionized water due to increased ion competition for sorption sites on granite surface. The micaceous minerals in granite were not the dominant sink for Sr-85. In dynamic experiments with crushed granite, bentonite colloids were found to behave similarly to a non-sorbing conservative tracer, H-3. The transport of Sr-85 through the column in a synthetic ground water was significantly faster than in deionized water. In the presence of Sr-85, the transport of bentonite colloids through the column was slightly slower than in the absence of Sr-85. Sr was found to preferably sorb on granite to bentonite colloids and be transported through the column in deionized water faster in the presence of bentonite colloids than in their absence.

Bryan and Sherriff. presented results from sequential ultrafiltration of radionuclide and bentonite colloid mixtures (size fractionation) and experimental dissociation kinetics for bulk and colloidal bentonite. Evidence was found for slow release of Eu(III) from the bulk bentonite and an increase in the amount of 'non-exchangeable' Eu(III) with pre-equilibration time. However, all systems studied tended towards equilibrium. The dissociation rate of Eu from bentonite did not depend upon pre-equilibration time. After practically instantaneous removal of 50–60 % of clay bound material, no consistent variation in dissociation rate with equilibration time was observed. Evidence for slow release of Eu(III) from the bentonite colloids was also observed. The dissociation kinetics was simpler for bentonite colloids than for the bulk bentonite and the dissociation rate of Eu from bentonite appeared independent of the pre-equilibrium time. The dissociation rate was about one order of magnitude higher for the bentonite colloids than the bulk bentonite. A mean rate constant of around $9 \cdot 10^{-7}$ s^{-1} was considered representative of Eu(III) dissociation from bentonite colloids. This value can be used to obtain improved conceptual and mathematical colloid-mediated radionuclide transport models (WP5). In both bulk and colloidal bentonite systems, there was no 'irreversible' up-take despite slow dissociation from bentonite. The authors also discussed uncertainties in the dissociation kinetics of tetravalent radionuclides.

Schäfer et al. presented new results from and the current status of the CFM project at the Grimsel Test Site (GTS). They described the suitability of the MI shear zone in the GTS for high-recovery low gradient radionuclide-colloid transport tests, and the adequacy and robustness of the sealing system for the CFM Long-term In-situ Test. In the *in-situ* radionuclide tracer tests, bentonite and montmorillonite colloids, a conservative tracer and a number of radioisotopes (Na-22, Ba-133, Cs-137, Th-232, U-233, Np-237, Am-243, Pu-242) were considered. All injected radionuclides, including the strongly sorbing tri- and tetravalent actinides, could be detected in the effluent. The radionuclide recovery was found to be lower for trivalent actinides than for tetravalent actinides. Also, slow long-term release of Pu was observed. The data showed the mobility of bentonite-derived montmorillonite colloids under the near-natural flow conditions in the MI shear zone. The dissociation rates of Th-232, Am-243 and Pu-242 reported in the presentation may, in part, be used to estimate an upper bound for colloid-mediated transport (WP5).

Zänker et al.'s presentation dealt with the role actinide(IV)-silica colloids may have in colloid-facilitated transport of radionuclides. According to the authors, the formation of An(IV)-silica colloids cannot be ruled out as several formation mechanisms are seen to be conceivable. On the basis of long-term stability of An(IV)-silica colloids in laboratory conditions, it was hypothesized that they might be stable in repository near-field conditions as well. The transport of An(IV)-silica colloids through clay-based barriers and in the repository far-field could not be ruled out either based on the results from laboratory studies. The question of chemical stability of An(IV)-silica colloids when they leave the near-field of a repository remains largely unanswered.

Modelling

Pulkkanen and Olin presented both baseline erosion model results and the update on model development. In the baseline modelling scaling estimate from the model was obtained. The results showed that the effect of different salinities in the models seems low. As for the shape of the gel, the model results do not match those from experiment. The model was difficult to solve as steep gradient had been built in the model. The further development of the model had the objective to build a model that includes the phenomena in slit erosion experiments: swelling by wetting and salinity change; erosion mechanism and transform from solid to gel, to sol, and then to eroding colloidal particles that were carried away by the flowing water. The model consists of the energy conservation part, the mechanical part, the breakdown mechanism, swelling by wetting, swelling by lowering the water salinity.

The presentation by **Huber et al.** described the status update of their modelling work. The effect of natural fracture geometry on bentonite erosion was studied by 3D computational flow dynamics simulations. The most comprehensive and frequently applied model for buffer erosion by Neretnieks had been implemented in 2D in the finite element code.

Neretnieks et al.'s presentation described the 2-stage model for bentonite swelling and erosion. The previous model was based on finite element method (FEM) and had much too low resolution in the rim zone where the dramatic changes occur. A new model was needed to resolve the rim zone. The new model was a two-region model: the inner region of smectite the does not flow but can expand by a diffusion-like process; a sudden jump from the inner, non-flow region to the rim region that flows with increasing velocity of the flowing water as the viscosity of the region drops. Some impact of the modelling outcomes on performance assessment were outlined: smectite loss from deposition hole at lower flowrates dominated by intrusion far into fracture; only extremely high flowrates that may cause loss by erosion need to be considered; and Smectite will invade even the finest fractures and generate a strong diffusion barrier to decrease solute transport to and from the canister. The model had not

included the processes such as loss by gravity pulling of aggregates and fate of detritus material in the bentonite.

Yang et al. presented theoretical studies with density functional theory (DFT) on Ca/Na montmorillonite structure, forces and swelling properties. The theory was based on the most popular methods: hypernetted chain approximation, modified Gouy-Chapman theory and density functional theory. Compared with the conventional Poisson-Boltzmann approach the DFT considers the direction correlation function. Results of the theoretical simulations were compared with Monte Carlo data and the agreement was well.

Evaluation of presentations by the End-User Review Board

Characterisation

The End User Review Board considers it positive that more extensive and in-depth characterisation of the clay colloid system has been achieved since the project's first annual meeting. The pore structure, the interlamellar distance, the properties of the interlamellar water, as well as the properties of the erosion halo has all been characterised. The End Use Review Board has the opinion that these characterisations will provide the modelling group a wide range variety of information to support the model development and to validate the models. This in turn will enrich the toolkits for the performance assessment.

Process study and mechanism understanding

The process study and mechanism understanding had become more problem-oriented with focus on applications in performance assessment since the project's first annual meeting. The studies of the rheological properties of gels have provided relatively quantitative information concerning when a gel's cohesion is so strong that it will in practice not be eroded by the flowing water at a certain velocity. This information is judged to be of great importance for both the modelling and for the performance assessment. In the artificial fracture experiments, focus had been on the influences of several other parameters on erosion, in addition to flowrate and water salinity. These other parameters were fracture slope, fracture roughness and fracture size. All of these parameters are judged to be highly relevant for performance assessment. It had been observed that for bentonite that forms large stacks of montmorillonite platelets, gravitational effects on erosion are significant in sloped fractures. The End User Review Board would especially like to point out that this observation is of great importance for performance assessment and need to be paid further attention. In most of the performance modelling, Na-montmorillonite that erodes relatively faster compared to Ca-montmorillonite in horizontal fractures is selected to conservatively represent erosion of all types of montmorillonite. Ca-montmorillonite, however, is known to relatively readily form large stacks and may erode faster in sloped fractures. In this sense, the selection of Na-montmorillonite as a representative montmorillonite in performance assessment might be less conservative. Also from this perspective, it is judged that the study of the coagulation behaviour presented during this annual meeting becomes important.

Colloid mobility and radionuclide sorption (ir)reversibility

In one of the presentations not only cations and complexing agents but also anions were found to influence the release of colloidal particles. In a safety case, the role played by anions may thus be an additional complicating factor in considerations of colloid release from clay-based barriers. The presentation demonstrated the potentially predominant role of *in-situ* mobilized colloid particles in

contaminant transport in natural subsurface systems; the End-User Review Board acknowledge the implications this may have for a safety case. The rate of the partly irreversible disaggregation of montmorillonite was higher in more diluted suspensions and a function of the initial experimental conditions. The latter observation calls for a careful consideration of the role experimental conditions may have in disaggregation kinetics of clay particles and, in particular, of the role the experimental results may have in arguing for colloid stability. The previous findings of the influence of ionic strength and soluble calcium concentration on the sorption of strontium and europium onto bentonite colloids were supported and, hence, revisiting a safety case in this respect may not be necessary. Bentonite colloids were found to increase the transfer of strontium and europium in dynamic column experiments, an observation that cannot be dismissed in a safety case. The finding that the transport of bentonite colloids through a column was slightly slower in the presence of strontium than in its absence reveals the combined effect of radionuclides and colloids on the transport of both of them. Evidence for slow release of europium from bentonite was observed; the dissociation rate was an order of magnitude higher from bentonite colloids than from bulk bentonite. Despite slow dissociation from bentonite, no irreversible up-take was stated to occur, which indicates non-significant colloid-mediated transport of europium. The rate of dissociation from bentonite colloids determined for europium, thorium, americium and plutonium can be used to obtain improved models of colloid-mediated radionuclide transport, and to constrain the radiological risk posed by such transport. Under *in-situ* conditions that promote colloid stability, clear evidence for the mobility of bentonite-derived montmorillonite colloids under the near-natural flow conditions was established. Also, all injected radionuclides, including the strongly sorbing tri- and tetravalent actinides, were detected in the effluent. These results support the conception that the phenomenon of colloid-mediated radionuclide transport in natural conditions is real and needs to be accounted for in a safety case. To this end, the largely unanswered question of chemical stability of actinide(IV)-silica colloids could call for revisiting the relative contribution different types of colloid may have in mediating radionuclide transport.

Modelling

It can obviously be seen that the both improvement of existing models and development of new models had been in progress since the last annual meeting of the project. The model improvement focused mainly on overcoming some numerical difficulties and extending the application areas of the models. These endeavours are judged to be necessary for providing reliable and user-friendly models to performance assessment. The density functional theory approach is judged to be innovative and will pave new ways for modelling the erosion processes.