



BELBaR D1.3

FIRST WORKSHOP

March 5-7, 2013

Collection of abstracts
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BELBaR first Workshop

The EC project BELBaR (Bentonite Erosion: effects on the Long term performance of the engineered Barrier and Radionuclide Transport) is arranging an open workshop at Helsinki University March 5-7 2013. The aim of the workshop is:

- Dissemination of initial findings
- Establish a network of specialists from various areas of the world and with a range of expertise relevant to the project.

The format of the workshop is based on presentations of work relevant to the topics of the BELBaR project. The presentations will be followed by topical discussion forums the last day. The workshop is open to scientists from outside and within the BELBaR project. Anyone working in the field is encouraged to participate.

At this stage, the plan is to publish the presentations on the BELBaR website (www.belbar.eu), but not to make formal proceedings.

Please send confirm your participation to Patrik Sellin (patrik.sellin@skb.se) and Pirko Hölttä (pirkko.holtt@helsinki.fi) before January 20, 2013.

Also indicate whether or not you intend to give a presentation, as well as the title of the presentation. One page abstracts should be submitted by February 20.

Preliminary agenda:

Tuesday March 5:

- 13:00 Welcome, Introduction and background (Patrik Sellin/Christian Nyström, SKB)
13:15 Colloidal stability: the reverse problem (Bernard Cabane, ESPCI ParisTech)
14:20 Treatment of Colloids and related issues in the safety case (Rebecca Beard, NDA)
14:55 Basic properties and coagulation of clay dispersions by inorganic cations: Czech Rokle bentonite (Radek Cervinka, UJV Rez)
15:15 Montmorillonite colloid size heterogeneity - Impact on stability in solution and radionuclide sorption (Karin Knapp Norrfors, KTH)
15:35 Coffee
16:00 Finnish Research Programme on Nuclear Waste Management (KYT) in brief (Kari Rasilainen, VTT)
16:20 SAXS Studies and Monte Carlo Simulations of Montmorillonite in Mixed Electrolyte Solutions (Bo Jönsson, Lund University)
16:40 Erosion / destabilisation of compacted FEBEX bentonite with glacial melt type water under quasi-stagnant flow conditions (Muriel Bouby, KIT)
17:00 Bentonite colloid studies (Pirkko Hölttä, Helsinki University)
17:20 End of Day 1

~19:00 Dinner

Wednesday March 6:

- 9:00 Visit to laboratories at Helsinki University
11:00 Coffee
11:20 Geochemical modelling of bentonite stability and colloidal generation at the buffer/groundwater interface (Jordi Bruno, Amphos21)
11:40 Summary of CIEMAT experimental results in BELBAR (Tiziana Miassana, Ciemat)

- 12:00 Radionuclide transport results with an assumed erosion of bentonite (Henrik Nordman, VTT)
- 12:20 Lunch
- 13:30 Application of combined optical coherence tomography and rheometry to montmorillonite dispersions (Rasmus Eriksson, B+Tech)
- 13:50 Rheology in montmorillonite/bentonite (Magnus Hedström, Clay Technology)
- 14:10 Micro-scale reactive transport modeling in natural single fractures from Äspö, Sweden (Florian Huber, KIT)
- 14:30 Coffee
- 14:50 Prediction of swelling pressures of different types of bentonite in dilute solutions (Longcheng Liu, KTH)
- 15:10 Swelling bentonite in a narrow channel. Modeling and experiments (Markku Kataja, JYU)
- 15:30 Hydromechanical Model for Bentonite Based on X-ray Tomography Experiments (Mika Laitinen, Numerola Oy)
- 15:50 Reversibility in Radionuclide/Bentonite Ternary Systems (Nick Bryan, University of Manchester)
- 16:10 Microstructural studies of bentonite and modelling of erosion experiments (Veli-Matti Pulkkanen, VTT)
- 16:30 Modelling smectite erosion- testing model simplifications (Ivars Neretnieks, KTH)
- 16:50 Bentonite erosion by dilute waters in initially saturated bentonite – some implementations of Neretnieks’ model (Markus Olin, VTT)
- 17:10 End of Day 2

Thursday March 7:

- 9:00 Testing of sorption and desorption behavior of radionuclides in column with crushed granite: determination of system behavior without colloid presence (Katerina Videnska, UJV Rez)
- 9:20 The latest results on colloid associated radionuclide mobility from the CFM project, Grimsel (Switzerland) (Thorsten Schäfer, KIT)
- 9:40 Erosion behaviour of different compacted bentonites (Ursula Alonso, Ciemat)
- 10:00 Behaviour of montmorillonite at low ionic strength (Emilie Hansen, Clay Technology)
- 10:20 Update on the Artificial Fracture Testing at B+Tech (Tim Schatz, B+Tech)
- 10:40 Coffee
- 11:00 Topical discussions (suggestions):
- 1) *How to perform and interpret bentonite erosion tests in artificial fractures*
 - 2) *Clay Colloids and geochemistry – what is the relation?*
 - 3) *Predictive modelling tools – the way forward*
 - 4) *Sorption irreversibility*
 - 5) *Mechanisms of retention/filtration of clay colloids in rocks*
- 12:00 Lunch
- 13:00 Summary from topical discussion
- 13:45 Workshop summary
- 14:00 End of workshop

Colloidal stability: the reverse problem

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Abstract

This work deals with the spontaneous redispersion of aggregated colloidal particles. Aqueous dispersions of colloidal alumina particles have been submitted to processes where the dispersion was aggregated, dried, and then redispersed in water. The aim was to find out when spontaneous redispersion would take place. To obtain reproducible results, standard protocols were designed (i) for preparing the surface state of the particles (bare surfaces with monovalent counterions, or else surfaces that have been covered with small molecule ligands), and for generating controlled interparticle contacts; and (ii) for measuring the amount of redispersed material. The results show that there are thresholds, determined by amount of surface water and by the pH of redispersion, where all the powder goes from the aggregated state to the dispersed state. In all cases, redispersion was produced by an increase in the ionic pressure due to the counterions, after immersion of the powder in water at the appropriate pH. In all cases, the pH that produced the appropriate ionic pressure was 5-6 pH units away from the isoelectric point of the surfaces. This was related to the fact that the surfaces were, in all cases, separated by a thin water film, which had a constant thickness (8 Å) set by the strength of binding of water to the alumina surfaces. However, for surfaces that had been covered with high amounts of macromolecular ligands, the minimum separation of surfaces was increased, and redispersion could be obtained at a pH that was closer to the isoelectric point. These phenomena can be accounted for, quantitatively, through a calculation of the balance of surface forces, including van der Waals attractions, hydration forces, and ionic pressures.

References

- Redispersion of alumina particles in water. S. Desset, O. Spalla, B. Cabane. *Langmuir* 16 (2000) 10495
- From powders to dispersions in water: effect of adsorbed molecules on the redispersion of alumina particles. S. Desset, O. Spalla, P. Lixon, B. Cabane. *Langmuir*, 17 (2001) 6408
- Competition between ligands for Al₂O₃ in aqueous solution. S. Desset-Brethes, B. Cabane, O. Spalla. *J. Phys. Chem. A* 116 (2012) 6511-6518

Treatment of colloids and related issues in the safety case

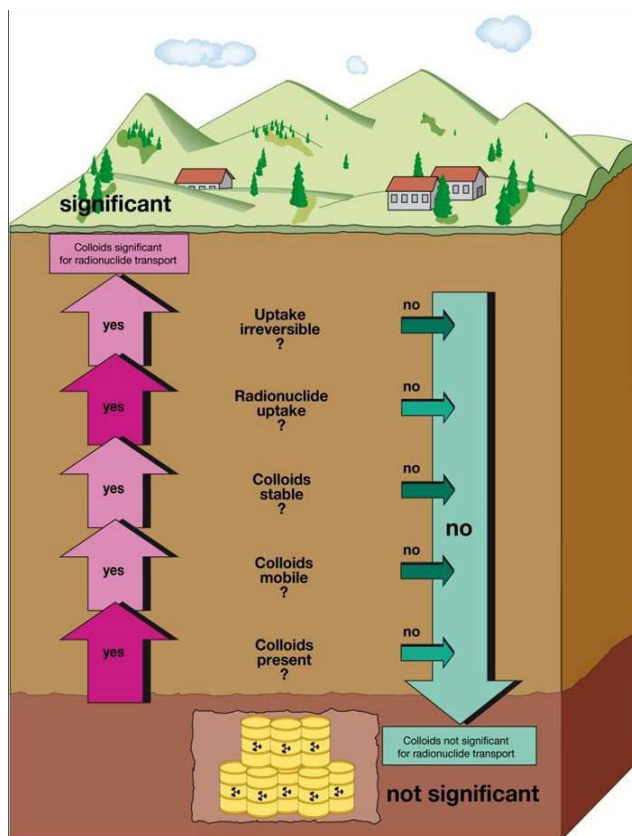
Rebecca Beard, NDA RWMD

This presentation summarises the current state-of-the-art treatment of colloidal issues in performance assessment (PA) for the participating national radioactive waste management organisations. The presentation is based on the first deliverable from work package (WP) 1, state-of-the-art report on the treatment of colloids and related issues in the long term safety case¹.

The presentation will:

- Describe the current treatments of colloid issues in PA for Posiva, SKB and NDA RWMD;
- Identify limitations of the current treatment;
- Discuss needs for additional studies of colloidal issues, and PA relevance;
- Identify relevance of and expected benefit from BELBaR WPs 2-5 work.

Figure 1 The colloid ladder illustrating that if one rung of the ladder can be removed, colloids can be shown to be a minimal risk factor to the PA



Through the work being undertaken in the BELBaR project, progress will be made against the issues noted in the presentation. The state-of-the-art report will be updated at the end of the BELBaR project to reflect the projects progress – the revised version of the report will clearly demonstrate how the BELBaR project has been of significant benefit to the national programmes that are participating in it with regard to the treatment of colloids in performance assessment.

¹ Rebecca Beard, David Roberts, Patrik Sellin, Kari Koskinen and Lucy Bailey (ed.), *state-of-the-art report on the treatment of colloids and related issues in the long term safety case*, October 2012

BASIC PROPERTIES AND COAGULATION OF CLAY DISPERSIONS BY INORGANIC CATIONS: CZECH ROKLE BENTONITE

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Naturally, the Rokle bentonite (Rokle deposit, Tertiary neovolcanic area, NW Bohemia) is Ca-Mg bentonite representing by a complex mixture of (Ca,Mg)-Fe-rich montmorillonite, micas, kaolinite and other mineral admixtures (mainly Ca, Mg, Fe carbonates, feldspars and iron oxides). The bentonite is processed on the production line (grinding, homogenization) and the final commercial product (partly Na-activated) is denoted as Bentonite 75 (B75). In the last decade, the chemical variability of natural and commercial Rokle bentonite is quite stable, major differences are in the mineralogical composition and swelling minerals content. The amount of swelling minerals (mainly montmorillonite) varies from ~ 50 to ~ 75 wt. %, similarly as a cation exchange capacity (CEC) ~ 50 to ~ 75 meq/100g for both natural and commercial bentonites.

The experimental works started with purification of B75. At first the carbonates were removed by sodium acetate-acetic acid buffer, followed by iron removal using sodium dithionite in acetic acid buffer and washed by NaCl. Clay fraction < 2 μm were obtained by sedimentation in enough amount of distilled water. Next step was transfer to homoionic Na^+ form by treatment with NaCl and washing with distilled water. Dialysis as a last step was performed until the conductivity of solution was > 10 $\mu\text{S}/\text{cm}$. The final product was air dried or lyophilised.

The bentonite colloids stability was investigated for the purified B75 present in sodium form. The critical coagulation concentration (CCC) of univalent cations (Na^+ , K^+) and divalent cations (Ca^{2+} , Mg^{2+}) were determined in the series of test-tube coagulation tests for one bentonite suspension concentration (bentonite in distilled water: 0.5% w/w, pH = 7.3) and different electrolyte (NaCl, KCl, CaCl_2 and MgCl_2) concentrations. The visual inspection was performed after more than 48 hours and later. For more precision the inspection using laser light beam was used (see Fig. 1).

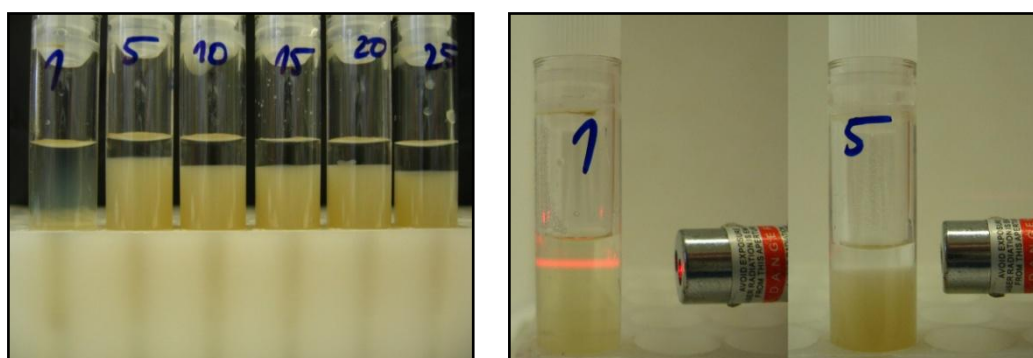


Fig. 1. Left: Coagulation of B75 suspension (0.5 % w/w) in KCl solution of various concentrations (1-25 mmol/l). CCC identified between 1-5 mmol/l KCl. Right: Identification of colloids presence using laser light beam, B75 suspension (0.5 % w/w) in KCl solution (1 mmol/l, left; 5 mmol/l, right). All photos were taken after 14 days of sedimentation.

The obtained CCC for individual cations and bentonite suspension concentration 0.5% w/w are summarised in Tab. 1. For Na⁺ the CCC was found to be in the range 6-7 mmol/l. The CCC for K⁺ was found to be slightly shifted to lower concentrations and lies in the concentration interval 4-5 mmol/l. The CCC for divalent cations decrease into the range 1.5-1.75 mmol/l for Ca²⁺ and 1-2.5 mmol/l for Mg²⁺.

Tab.1: Comparison of obtained CCC values with appropriate concentrations in synthetic granitic water (SGW) representing ground water in granitic environment and liquid phase for further experiments.

Component	Concentration in SGW		CCC for selected cations	
	mg/l	mmol/l	mg/l	mmol/l
Na	10.642	0.463	138-161	6-7
K	1.8	0.046	157-196	4-5
Ca	27.001	0.674	60-70	1.5-1.75
Mg	6.405	0.264	24-61	1-2.5
F	0.2	0.011		
Cl	42.403	1.196		
SO ₄	27.704	0.288		
HCO ₃	30.412	0.498		
NO ₃	6.3	0.102		

Comparison of obtained CCC of selected uni and divalent cations for the 0.5% w/w suspension of B75 in simple electrolytes were found to be significantly higher than the concentrations of appropriate cations in the SGW. In the case of univalent cations, the observed CCC are more than one order of magnitude higher than the appropriate concentration in groundwater. In the case of calcium and magnesium, the CCC was found to be only approx. three times higher than the concentration in groundwater. This finding is important for future experimental work, because the concentration of Ca and Mg in the solution may be influenced by the presence of calcite and gypsum present in bentonite or rock material. It has to be noted here that presented results are valid for the purified B75 converted to sodium form.

Further experiments will focus on variations in coagulation experiments (w/w ratio of bentonite dispersions, materials: natural Rogle bentonite, MX-80) and on organic complexing agents (e.g. humic substances).

Montmorillonite colloid size heterogeneity

- Impact on stability in suspension and radionuclide sorption

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In contact with dilute melt water, the bentonite has the potential to release montmorillonite colloids which can be transported away from the buffer. In the case of large mass loss, the buffer functionality will be endangered. In the case of an early canister failure, the transport of radionuclides (RNs) out from the canister may be enhanced if the RNs are sorbed and transported with mobile montmorillonite colloids. During transport in bedrock fractures, the colloids may be separated according to their size. Therefore, the size distribution of the montmorillonite colloids and their stability are parameters which are important for predicting RN transport. Currently, conceptual models of RN and colloid transport are used in safety assessments for estimating the RN transport with colloids. These models include transport of RNs in solution and attached to colloids in a laminar ground water flow, however, no sorption kinetics or size dependent sorption and transport of the montmorillonite colloids are included. Are mass-normalized sorption coefficients (K_D) for RNs valid for quantifying RN-montmorillonite interactions? The ratio is given for the whole size distribution of colloids, and does not take in account the exposed surface area of colloids in solution. In modeling, transport of RNs may be under- or overestimated since the K_D -values are not representative if only the smaller colloids are transported and not the larger ones, or vice versa [1]. Therefore, we examine in this work the effect of the montmorillonite colloid size on their stability, on their radionuclide sorption capacity and on the sorption reversibility.

Sequential and direct centrifugations have been used to separate and isolate montmorillonite colloidal fractions, originating from unpurified MX-80 bentonite. The separation was performed after a first equilibration and sedimentation step in carbonated synthetic groundwater with low ionic strength. Eight colloidal clay suspensions were obtained with various size distributions, which were characterized by PCS and AsFIFFF/UV-Vis/LLS/ICP-MS. The ion and colloid concentrations in all suspensions have been measured by IC and ICP-OES, and the mineral phase composition was checked by XRD. Stability studies at pH 7 and 8 and different ionic strengths (0.01 M- 3M) with the electrolytes NaCl, CaCl₂, MgCl₂ were performed according to the experimental protocol described in [2], from which the stability ratios (W) were calculated after monitoring the initial agglomeration rate by PCS measurements. Sorption, sorption reversibility and desorption tests were performed using ²³³U, ²³⁸U, ²⁴²Pu, ²³²Th, ⁹⁹Tc, ²³⁷Np and ¹⁵²Eu [3] on the various montmorillonite colloidal suspensions and followed over time. Sorption reversibility was tested by varying the chemical composition of the suspensions by decreasing the pH or increasing the ionic strength, or by adding fulvic acids (FA) or fracture filling material (FFM) as competing ligands and mineral surface.

A summary of the results achieved so far is presented in the presentation.

[1] A.S. Madden, M.F. Hochella, T.P. Luxton, Insights for size-dependent reactivity of hematite nanomineral surfaces through Cu²⁺ sorption, *Geochim. Cosmochim. Acta*, 70 (2006) 4095-4104.

[2] R. Kretzschmar, H. Holthoff, H. Sticher, Influence of pH and Humic Acid on Coagulation Kinetics of Kaolinite: A Dynamic Light Scattering Study, *Journal of Colloid and Interface Science*, 202 (1998) 95-103.

[3] S. Wold, Sorption of prioritized elements on montmorillonite colloids and their potential to transport radionuclides, SKB internal report TR-10-20, (2010).

FINNISH RESEARCH PROGRAMME ON NUCLEAR WASTE MANAGEMENT (KYT) IN BRIEF,

by Kari Rasilainen and Merja Tanhua-Tyrkkö, VTT Technical Research Centre of Finland

ABSTRACT

Finnish Research Programme on Nuclear Waste Management (KYT2014) extends from 2011 to 2014. It is the current member in a chain of coordinated public research programmes in Finland that started in 1989. Public research programmes aim to serve the research needs of Finnish authorities.

The research work in KYT2014 is based on annual calls for project proposals. The calls usually refer to the Framework programme of KYT2014 (defining the general contents and structure of KYT2014) and to the annual guidance of the Steering Group (defining the up-to-date research needs). Project proposals are assessed by the three Support Groups, and the proposals receiving funding form the annual ensemble of projects. Assessment criteria are defined by the Steering Group, and research needs is considered as the main criterion when project proposals are assessed.

Overall research topics within KYT2014 are shown in Fig. 1. Buffer and backfill materials is the subtopic that provides our link to the BELBaR project. The coordinated projects mentioned in Fig. 1 are an effort to focus collaboration between individual research groups and to get rid of overly fragmented small projects. Research topic Other safety related studies covers topics like Nuclide migration, Microbiology, Concrete, and Biosphere. In 2013 KYT2014 includes 32 research projects of which 28 are on safety research.

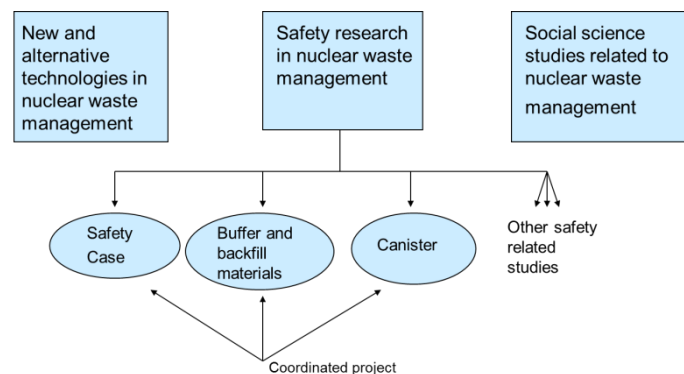


Fig. 1. KYT2014 research topics. Coordinated projects are actually small research programs of many years' standing (<http://kyt2014.vtt.fi/eng/index.htm>).

The annual funding of the research programme is around 1.7 M€, it is mainly provided by the State Nuclear Waste Management Fund (VYR). Individual research organisations provide also own funding in their projects, in 2013 about 1 M€ altogether. In 2013 the planned total funding is thus around 2.7 M€.

In order to be sure that the research programme is on track, the Ministry of Employment and the Economy (formerly Ministry of Trade and Industry) has organised repeated international reviews of the public research programmes. KYT2014 was reviewed in 2012, the review has not yet been reported. Its predecessor KYT2010 was reviewed 2007 and its results were carefully utilised in the planning of KYT2014.

SAXS Studies and Monte Carlo Simulations of Montmorillonite in Mixed Electrolyte Solutions

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Aqueous dispersions of Ca montmorillonite contain small clusters of clay platelets, often named "tactoids". In these tactoids the platelets are arranged parallel to each other with a constant spacing of 1 nm. We have used small angle X-ray scattering (SAXS) to determine the average number of platelets per tactoid, $\langle N \rangle$. We found that this number depends on the platelet size, with larger platelets yielding larger tactoids. For a dispersion in equilibrium with a mixed electrolyte solution, the tactoid size also depends on the ratio of divalent to monovalent cations in the reservoir.

Divalent counterions are strongly favored in this competition and will accumulate in the tactoids. In dispersions of pure montmorillonite, that are equilibrated with a mixture of Na^+ and Ca^{2+} cations, the Na^+ cations initially cause a repulsion between the platelets, but the divalent ions rapidly replace the monovalent ones and lead to the formation of tactoids; typically within less than one hour based on the divalent to monovalent ratio. This cation exchange as well as tactoid formation can be semi-quantitatively predicted from Monte Carlo simulations.

Erosion / destabilisation of compacted FEBEX bentonite with glacial melt type water under quasi-stagnant flow conditions

Muriel Bouby, Stephanie Heck, Florian Huber, Thorsten Schäfer

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In most repository designs, compacted bentonite is planned to be used as a buffer material. In contact with glacial melt water, the bentonite has the potential to release montmorillonite colloids which can be transported away from the buffer. In the case of a large mass loss, the buffer functionality will be endangered. The idea is to show under which conditions compacted bentonite is able to produce colloidal particles free to move which may thus mobilize strong sorbing radionuclides. In this work we study the erosion processes in compacted bentonite by using two different set-ups.

In the first one [1], raw FEBEX bentonite was compacted in pellets (1.6 g.cm^{-3}) and placed in reactors to perform erosion/destabilisation experiments at $\sim 3 \text{ }\mu\text{l/min}$ (quasi-stagnant conditions) using a carbonated synthetic water at low ionic strength. In this preliminary study run over one month, the evolution of the water chemistry and the amount of colloids released were registered. A sorption test was performed with a cocktail of radioelements in order to check the behaviour of the colloids produced in comparison to suspended colloidal material by using the Asymmetrical Flow Field Flow Fractionation (AsFFFF) coupled to an ICP-MS.

The second set-up is a radial one (mock-up of a cylindrical deposition borehole) with a defined artificial fracture aperture (Plexiglas design, aperture 1mm). It is used to obtain erosion rates as a function of the flow velocity. In these experiments the low ionic strength natural ground water (comparable to glacial melt water [2]) from the Grimsel Test Site is currently used. The formation of a gel layer was monitored as well as the chemical water composition evolution. The formation of colloids was detected by using the Laser Induced Breakdown Detection (LIBD) showing the formation of a bimodal size distribution with colloids ranging from 15-500 nm and a significant part in the 15-25 nm range not detectable by laser light scattering techniques. The conceptual idea is to compare via normalization to the contact surface area the results obtained with the SKB erosion model from Moreno et al. [3]. A first comparison indicates, that the erosion rates determined from the laboratory experiments are considerably below the model predictions for a bentonite backfill or buffer material.

The first results obtained will be presented in addition to the new developments concerning compacted bentonite labelling.

[1]: Seher, H. Influence of colloids on the migration of radionuclides, PhD thesis, University of Heidelberg, Faculty of Chemistry and Earth Sciences.

[2]: Bath, A. Infiltration of dilute groundwaters and resulting groundwater compositions at repository depth. (2011) SSM Report, SSM 2011:22.

[3]: Moreno, L. et al. Modelling of erosion of bentonite gel by gel/sol flow (2010) SKB Technical Report TR-10-64

Bentonite colloid studies

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Colloids produced from the degraded bentonite buffer may effect on the migration of radionuclides and colloid-facilitated transport may be significant to the long-term performance of a spent nuclear fuel repository. 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. The effect of colloids on radionuclide transport is studied in KYT2014/BOA programme and in BELBaR WP3. The study is divided into subtasks: release and stability of colloids, radionuclide sorption, colloid/rock interaction and the effect of colloids on radionuclide transport. The results achieved so far are presented.

The release and stability of inorganic colloids have been determined in the batch dispersion experiments. Powdered MX-80 type bentonite was added to diluted OLSO reference groundwater, sodium chloride and calcium chloride electrolyte solutions whose ionic strengths were adjusted between 0.001–0.1 M. The colloidal particle fraction was separated by filtration and the pH, particle size distribution, particle concentration and zeta potential were determined applying the photon correlation spectroscopy and the dynamic electrophoretic mobility (Malvern Zetasizer Nano ZS). Colloid concentration was determined using a standard series made from MX-80 bentonite and a count rate obtained PCS measurements as well as using the Al content of montmorillonite analysed using ICP-MS. Sr-85 and Eu-152 sorption on MX-80 bentonite powder and bentonite colloids in NaCl and CaCl₂ solutions and OLSO water was studied as a function of ionic strength. Colloid mobility and colloid/rock interaction and the effect of colloids on radionuclide migration have been studied in crushed rock columns from Kuru Grey granite and strongly altered tonalite and in fracture columns using Cl-36, I-125, Sr-85 and Eu-152 as the tracers. Transport experiments in a natural fracture (0.9 m x 0.9 m) in Kuru Grey granite block will start in the near future.

The release and stability of bentonite colloids have been followed for three years. The stability strongly depends on the ionic strength of the solution and the valence of the cation. Colloids are smaller and more stable in monovalent (Na⁺) than in divalent (Ca²⁺) and dominated solutions. The zeta potential was approximately -40 mV at 0.005 M ionic strength and increased to -10 mV at ionic strength 0.07 M. After 2.5 years, cumulative particle concentration of bentonite colloids in 0.001 M OLSO reference groundwater was around 20 g/L, the colloid concentration was very low when the ionic strength was higher than 0.01 M. The stability of bentonite colloids in diluted OLSO and electrolyte solutions did not change substantially.

At current conditions in Olkiluoto, the ionic strength of the groundwater is around 0.5 M and the colloids released from the bentonite barrier are aggregated and unstable do not have an influence on the migration of radionuclides. However, knowledge and understanding of bentonite erosion in colloidal form can be utilized in the estimation performance of the bentonite barrier. The possibility of a future glacial period and subsequent post-glacial phase when the infiltration of fresh, glacial melt water dilutes groundwater, implies that dilute groundwater conditions cannot be excluded and the influence of bentonite and other colloids has to take into consideration.

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Geochemical modelling of bentonite stability and colloidal generation at the buffer/groundwater interface

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The generation and stability of colloidal bentonite under certain deglaciation conditions pose some challenges to the long-term performance of the EBS system within the KBS3 concept. Most of the work has been mainly concerned to the potential stability of bentonite colloids once they are generated and the subsequent radionuclide migration effects. We believe that there is a need to approach the mechanisms of bentonite colloidal generation from a dual mechanical and hydrochemical perspective. This will be helpful to ascertain the conditions that trigger colloidal generation and therefore it will be possible to integrate the process under current geochemical models for bentonite stability.

There are two main mechanisms affecting the mechanical stability of the bentonite buffer, one is the decrease in dry density due to variations in the chemical stability of montmorillonite, and the second related to colloid formation as a result from changes in cation distribution in the CEC and water flow conditions at the bentonite/groundwater interface. However, there is a link between both processes that has not been fully investigated so far. Chemical instability can promote the dissolution of montmorillonite, resulting in a decrease of dry density and enhancing diffusive transport from the interface deeper into the bentonite buffer. This can result in a larger volume of bentonite able to change the cation distribution of the CEC and, therefore, with the potential to generate colloids. Moreover, mineralogical changes of clay minerals in bentonite (i.e. transformation of montmorillonite into saponite) will modify the properties of the CEC, by changing the total CEC and/or modifying the affinity for certain cations (bivalent vs. monovalent). These changes in the CEC could affect the capability of colloid formation under certain groundwater chemical conditions in comparison to what we can expect for a montmorillonite-rich bentonite.

To evaluate the long-term chemical stability of clay minerals in the bentonite it is essential to conduct models that can link the chemical stability of the clay minerals with changes in the CEC. These models should take advantage of the large amount of present-day data generated from different experiments on clay stability (i.e. kinetic dissolution experiments and clay-water interaction experiments that lead to mineral changes) and experiments devoted to colloid formation from different clay minerals under different chemical boundary conditions. The objective of our presentation will be to discuss this approach within the Belbar forum to gain some insights from the experiences of the project in order to guide future developments of the proposed geochemical model.

Summary of CIEMAT experimental results in BELBAR: First Year.

Tiziana Missana, Ursula Alonso, Miguel García-Gutiérrez, Ana Maria Fernández, Manuel Mingarro

CIEMAT activities in the BELBAR Project are related with all the experimental Work Packages: WP 2 (Bentonite Erosion); WP 3 (Radionuclides and host rock interactions); WP 4 (Colloid stability).

In WP 2 the focus is on the understanding of the main mechanisms of clay particles erosion based on factors identified as relevant as: 1) the physico-chemical characteristics of the bentonite; 2) Groundwater chemistry and clay-water interactions; 3) Water velocity and characteristics extrusion paths.

The physico-chemical characterization of five different bentonites, with the objective of analyzing different properties affecting the clays colloidal behavior, was carried out. Additionally, new generation tests were done to compare the generation behavior of different bentonite (FEBEX, MX-80 and Mylos) under the same experimental conditions (Alonso et al., this Workshop)

Additionally, new erosion tests in artificial fracture (180 μm) in 20x20 methacrylate cells, with the same experimental configuration used by other institutions were started with the FEBEX clay and using simple electrolytes: $1 \cdot 10^{-3}$ M NaClO_4 and CaCl_2 .

In WP 3, the focus is on bentonite colloids interaction processes with the rock surface (filtration) and radionuclide transport (Cs) in the presence of bentonite colloids under different chemical conditions.

The transport of bentonite colloid in fracture with two different aqueous solution of low ionic strength ($I \approx 1 \cdot 10^{-3}$ M), the first one mono-cationic (Na) and the second bi-cationic (Na and Ca), showed that the small quantity of calcium significantly affected the recovery behavior. Whereas in the case of mono-cationic aqueous solution colloids were completely recovered, a large quantity of bentonite colloids was retained in the fracture in the case of the bi-cationic solution. Furthermore, in the sodium solution, the size of the colloid eluted was very similar to the initial one, but in presence of calcium, colloids eluted presented a significantly larger size than the initial.

Cesium migration (with and without bentonite colloids) in a granite fracture, under the Grimsel and Äspö conditions, was compared. In the Grimsel case, the transport was significantly different in the presence or absence of colloids, being the cesium breakthrough curves were very similar in the Äspö case.

In WP 4, the coagulation/re-suspension behavior of different clays following a chemical change was analyzed. Some preliminary studies were carried out to understand the aggregation/disaggregation kinetics. Preliminary studies (performed at different ionic strengths) seem to indicate that colloids, once aggregated, cannot be completely disaggregated as to reach their initial size, at least within the considered experimental time frame.

Radionuclide transport results with an assumed erosion of bentonite

Henrik Nordman

ABSTRACT

The Posivas Safety Case is still partly in progress. In this presentation are presented generic features of potential bentonite erosion and colloidal release of radionuclides from a KBS3-V repository.

Erosion of bentonite

In an assumed generic case chemical erosion of the buffer and backfill takes place due to low ionic strength water penetrating to repository depth, e.g. in association with glacial retreat (chemical erosion). Significant buffer erosion is considered unlikely, but cannot currently be excluded in at least some of the deposition holes. The degraded buffer has a reduced capacity to retain radionuclides released subsequent to canister failure. Bentonite erosion may also act as a source of bentonite colloids. These can sorb radionuclides and transport them relatively rapidly into the geosphere.

Modelling assumptions

When a canister fails, water is assumed to have immediate access to the fuel. Advective conditions are assumed in a ring of partly eroded bentonite extending radially 35 cm from the canister wall to the wall of the deposition hole and extending vertically above and below the rock fracture plane, with a total vertical height also of 35 cm (See Figure 1.) The defect height in canister is also 35 cm. Radionuclides are assumed to be well mixed both in the void space in the canister interior and in the 35 cm × 35 cm eroded bentonite ring. The eroded amount of bentonite is replaced from bentonite both above and below. The assumptions include several 333 year long glacial water cycles with high flow to geosphere and an enhanced release of radionuclides during the cycle as colloids. The release rate from near field as colloids is as in equation 1 in GoldSim model.

$$J = \text{NUCINV} \cdot \text{flowselect} \cdot \text{collrate} \cdot Q_F / 848.0 \quad , \quad (1)$$

NUCINV is the nuclide inventory in the advective volume
848.0 is the mass of bentonite in the advective volume (848 kg)
collrate is the colloid concentration in water during the cycle (kg/m³)
Q_F is the high flow rate to geosphere from advective volume (m³/yr)
flowselect is a variable which is switched to value 1 during the glacial cycle.

Results preview

It is self evident that assuming of the 35 cm x 35 cm eroded bentonite ring with advective conditions increase the release rate of radionuclides as normally the transport mechanism is only diffusion in the ring. Also the increase of flow rate during the 333 years cycle and the release of nuclides as colloids of course increase additionally the release rate.

Application of Combined Optical Coherence Tomography and Rheometry to Montmorillonite Dispersions

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Abstract

During recent years, optical coherence tomography (OCT) has attracted considerable interest as a visualization tool when combined with conventional rheometry [1,2]. Compared to other imaging techniques, OCT offers several advantages. It is able to probe very small volumes (in the picoliter range) and can probe deeper into samples (including opaque samples) than many other velocimetry techniques. It has a wide range of probing time scales and is sensitive to much faster time scales in sheared fluids than techniques based on CCD read out times or beam scanning speeds.

The main advantage of directly imaging fluids under shear is the possibility to obtain *in situ* velocity profiles of these fluids. It is thus possible to measure the local velocity of the fluid anywhere along the flow field and observe phenomena such as wall slip and shear banding. Using capillary tube flow geometry [2], it is possible to calculate the local viscosity of a fluid along the flow field using the *in situ* velocity profile and the pressure drop along the capillary tube. This opens up the possibility to more accurately determine viscosities of fluids with non-linear velocity profiles.

Preliminary results using capillary tubes indicate that montmorillonite sols have fairly ideal velocity profiles at low solids content and fairly low ($< \sim 300 \text{ s}^{-1}$) shear rates. The next step is to systematically study the structure and rheological properties of montmorillonite dispersions near the sol/gel transition zone in order to gain information about these systems at conditions that are potentially erosive. A state-of-the-art rheometer combined with an OCT instrument will be used for this purpose.

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RHEOLOGY OF MONTMORILLONITE/BENTONITE SYSTEMS

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Compacted bentonite with high montmorillonite content has been proposed as buffer material surrounding canisters containing spent nuclear fuel in several concepts for final repositories.

Montmorillonite, which is the main constituent in bentonite, has an exceptional affinity for water which results in the build-up of a swelling pressure when bentonite (with access to water) is placed in a confined volume. There may be fractures intersecting the deposition hole and at those fractures the bentonite is not restricted but can continue to swell until equilibrium or steady state is reached.

Apart from an understanding of the swelling process, knowledge of rheological properties of bentonite is of importance for the modelling and the prediction of the behaviour of a bentonite buffer during the operational time of a repository for spent nuclear fuel. The viscosity of bentonite/montmorillonite suspensions is a quantity needed to predict the velocity field outside a deposition hole where the seeping groundwater comes in contact with the extruded bentonite. The bentonite may also behave as a gel rather than a liquid, and knowledge of the yield strength will tell if such a gel can withstand the shearing forces from the seeping water.

The aim of this presentation is to provide suggestions regarding what systems to study with regard to montmorillonite/bentonite volume fraction (or concentration), cation composition (in particular the Ca/Na content) and ionic strength of the water in equilibrium with the montmorillonite/bentonite. Bentonite may be highly thixotropic and it is found that the handling and preparation influence the outcome from rheological measurement [1, 2]. It is therefore important to also consider these aspects when using rheological data for modelling.

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Micro-scale reactive transport modeling in a natural single fracture from Äspö, Sweden

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Laboratory radionuclide migration experiments have been conducted on a fractured drill core from the Hard Rock Laboratory in Äspö, Sweden under Grimsel groundwater conditions to simulate the effect of glacial melt water intrusion. Migration experiments show an immobility of ²³³U(VI) and bentonite colloid associated radionuclides (²⁴²Pu(IV), ²⁴³Am(III), ²³²Th(IV)) whereas ⁹⁹Tc(VII) behaves like the conservative tracer. ²³⁷Np(V) shows a retarded breakthrough and a pronounced tailing. Furthermore, 3D computational fluid dynamics (CFD; FLUENT (Ansys)) simulations have been carried out to model the fluid flow and experimental conservative tracer (Tritium, HTO) transport on basis of computed tomography data of the drill core. CFD simulation shows a heterogeneous flow field in the fracture as function of the complex fracture geometry. Solute transport simulation of HTO cannot predict accurately the experimental data but shows a pronounced tailing of the tracer in line with the experiments (Huber et al., 2012).

Reactive transport simulations using a 1D stream-tube approach called FASTREACT (Trinchero et al., 2011) which is coupled to PhreeqC are carried out at the moment to model the ²³⁷Np(V) experimental breakthrough curves. Two approaches have been tested to derive particle travel time distribution (reflecting the flow field heterogeneities) needed by FASTREACT, namely (i) Lagrangian particle tracking simulations on the 3D flow field using FLUENT and (ii) fitting of a probability density function to the experimental tracer breakthrough curve. Several conceptual geochemical models with increasing complexity ranging from simple Kd simulations, first order reversible kinetic simulations up to surface complexation models using up to three mineral phases have been tested. The parameter estimation code PEST was coupled to FASTREACT/PhreeqC to obtain best fit parameters of e.g. the total reactive surface area.

Preliminary results of the reactive transport modeling will be presented.

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Prediction of swelling pressures of different types of bentonite in dilute solutions

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Abstract

A mechanistic model is developed to predict the swelling pressure of fully saturated, bentonite-based materials in distilled water or dilute saline solutions over a large range of final dry densities of bentonite. It is essentially a combination of the thermodynamic model and the diffuse double-layer model that account for crystalline swelling and osmotic swelling, respectively, in addition to taking into consideration the demixing of exchangeable cations and the disintegration of the montmorillonite particles into small stacks of unit layers upon water uptake.

Comparison of the model predictions with a great number of experimental results of swelling pressures of different types of bentonites and bentonite-aggregate mixtures in both distilled water and saline solutions suggests that the model works excellently in the cases tested. It is found that the water chemistry, the montmorillonite content, the type and amount of exchangeable cations in the interlayers are important in determining the extent to which the montmorillonite particles are delaminated and hence the swelling behavior of saturated, bentonite-based materials.

In addition, the applicability of the model in predicting the water retention curves of unsaturated bentonites is also tested. The results show that the predicted curves are in good agreement with the measured data and that the montmorillonite particles are more difficult to disintegrate into small pieces in the case of unsaturated bentonites than would otherwise be possible.

Swelling bentonite in a narrow channel. Modeling and experiments

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A phenomenological swelling model of bentonite including finite deformations and plasticity is considered. The model is based on availability of a definite set of experimental data on elasto-plastic and free swelling behaviour of partially saturated bentonite in a sufficiently large range of water content and effective strain. The experimental procedures for obtaining the required data is presented, or projected. The model is first formulated in one-dimensional case and applied in swelling of bentonite in a narrow channel. A full three-dimensional generalization of the model is also presented.

Hydromechanical Model for Bentonite Based on X-ray Tomography Experiments

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Numerola Oy (Ltd.)

This presentation concentrates on a formulation and numerical implementation of a three-dimensional hydromechanical model for bentonite. The work is based on a phenomenological model formulated by Markku Kataja and the purpose of the model is to describe simultaneous moisture transport and deformation of bentonite. In this model bentonite is described as a multiphase continuum where a change in a moisture distribution induces a new mechanical equilibrium state. The mechanical behavior is governed by an elastoplastic material law depending on the moisture content of bentonite.

The model is grounded on X-ray tomography experiments and the model parameters will be fitted to the tomography experiments. A numerical model is implemented with an in-house software at Numerola Oy.

In this presentation the mathematical formulation is first reviewed and then the numerical and algorithmic aspects are discussed. Finally, a preliminary comparison of a numerical solution and a wetting-swelling tomography measurement is shown.

Reversibility in Radionuclide/Bentonite Ternary Systems

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The effect of humic acid (HA) on U(VI) sorption on bentonite has been studied in batch experiments at room temperature at a ²³⁷U(VI) concentration of 10⁻¹⁰ M and HA concentration of 100 mg·L⁻¹. The distribution of U(VI) between the liquid and solid phase was studied as a function of pH and ionic strength, both in the absence and presence of HA. The uranyl sorption on bentonite is dependent on pH and the presence of humics. In the absence of HA an enhancement in the uptake with increasing pH was observed, and a sharp sorption edge was found between pH 3.2 and 4.2. The presence of HA slightly increases uranium(VI) sorption at low pH and curtails it at moderate pH, compared to the absence of HA. In the basic pH range for both the presence and absence of HA the sorption of uranium is significantly reduced, which could be attributed to the formation of soluble uranyl carbonate complexes. Most importantly, it was found that the effect of the addition order was negligible, and there was no evidence for slow dissociation or (pseudo-)irreversible binding to the bentonite for uranyl(VI).

Batch experiments have also been performed for ternary systems of ¹⁵²Eu(III), bentonite and humic acid and also ¹⁵²Eu(III), bentonite and EDTA. The Eu(III) concentration was 7.9 10⁻¹⁰ M and the pH was in the range of 6.0 – 7.0. In the absence of a competing ligand, there was evidence for some slow uptake in a two stage process, with initial rapid sorption of Eu(III), followed by slower uptake of a much smaller fraction. In the humic acid ternary system, it was found that on a timescale of several months, there were important kinetic effects in the interactions between: bentonite and humic acid; bentonite and Eu(III); humic acid and Eu(III). A kinetic model was developed to interpret the uptake of Eu(III) and humic acid by the bentonite. In a separate series of experiments, the reversibility of Eu(III) binding was tested by allowing Eu(III) to sorb to bentonite (50 g/l) for times in the range of 1 – 65 days. EDTA was added to the pre-equilibrated Eu bentonite mixtures at a concentration (0.01 M) that was sufficient to suppress sorption in a system where EDTA is present prior to the contact of Eu(III) with bentonite. It was found that some fraction of the sorbed Eu was released by the bentonite instantaneously, but that a significant fraction remained bound. With time, the amount of Eu(III) remaining bound to the bentonite reduced, with a dissociation rate constant of approximately 3.8 x 10⁻⁷ s⁻¹. However, after an EDTA contact time of approximately 100 days, the amount of Eu(III) remaining bound to the bentonite was within error of that when EDTA was present prior to contact (4.5% ± 0.6). It was found that the amount of slowly dissociating Eu increased with increasing Eu(III)/bentonite pre-equilibration time.

Although slow dissociation from bentonite has been observed in the case of Eu(III), no ‘irreversible’ uptake of either Eu(III) or uranyl(VI) by bentonite has been observed so far.

Microstructural studies of bentonite and modelling of erosion experiments

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Since bentonite is thought to erode as colloids in dilute water, it is necessary to study the solid bentonite turning into a gel on the scale of the eroding particles, that is, on the scale that bentonite breaks down in erosion. Such microstructural studies have been started by using two methods, namely SAXS (small angle x-ray scattering) and NMR (nuclear magnetic resonance), for which the development of sample preparation techniques and measurement procedures have been begun earlier in Finnish Programme on Nuclear Waste Management (KYT) and continued in BELBaR.

The first step in the microstructural studies has been preparation and measurement of the reference samples: MX-80 bentonite, purified Ca-montmorillonite and purified Na-montmorillonite compacted to four different dry densities (0.7, 1.0, 1.3, and 1.6 g/cm³). The most important outcome of this stage has been finding that SAXS and NMR can actually be used to study the microstructure of bentonite with certain procedures and careful sample preparation. The results with both the methods agree fairly well and suggest that the total porosity of bentonite can be divided into so-called interlayer and external porosities, the ratio of which (interlayer porosity/external porosity) increases when the dry density increases. A detailed comparison of the Ca- and Na-montmorillonites will be done when the results for Na-montmorillonite are ready. At the next step, the same methods and materials as at the first step will be used, but the samples will be prepared in a slightly different way. Instead of compacting the samples directly to the target dry densities (0.7, 1.0, 1.3, and 1.6 g/cm³), they will be compacted to the emplacement density of a bentonite buffer (1.8 g/cm³) and then let swell to the target density. The goal is simply to see the microstructural differences between the reference and the swollen samples at the same dry densities.

In addition to the constant density samples, monitoring the microstructural changes with SAXS while bentonite swells has been planned. When preparing the samples, the slit erosion experiments done e.g. at B+Tech will be mimicked but in a way that the samples still fit to the SAXS device. Other methods, such as XRD (X-ray diffraction), may also be tried on the swelling bentonite samples, if they are found useful.

Comparison of modelling results to experimental ones truly testing the validity of a model concept, the ultimate goal in WP5 is to develop the ability to model the bentonite erosion slit experiments that have been done e.g. at B+Tech. The slit experiments are not only experiments on erosion in dilute water but combined wetting-swelling-erosion experiments what makes modelling challenging. The approach to modelling is to break the experimentally observed phenomena into pieces that fit the theoretical framework, move forward piece by piece and finally put the pieces together to form the complete model.

Large deformations of bentonite are observed in slit experiments, thus the mechanical model that sets the geometry should also include them. According to experiments done e.g. at University of Jyväskylä (JyU), the mechanical material model of solid bentonite should be an elasto-plastic model, in which the elastic parameters and plastic model depend on the dry density and water content of bentonite. When the density of bentonite drops and bentonite turns into a gel, other mechanical models (including e.g. viscous effects) may become

relevant. The current view of the wetting part of the model includes wetting by water vapour (sorption of it on bentonite pore surfaces) and by liquid water according the classical soil mechanical formulations. The view is based on observations from the swelling stress experiments where the time development of the swelling stress often includes two components: a quickly developing short spike and a slow but dominating part. Also, the tomography experiments at JyU support the division of wetting to fast and slow components. The working hypothesis on swelling is that it is caused by the tendency of water to move into the interlayer space due to the imbalance in the cation composition in the interlayer space and in the external pore space. As experiments show, this tendency depends on the interlayer cation type and chemical composition of the pore water. For erosion, the working hypothesis is the following: when cations diffuse out from the external pores of bentonite due to dilute water, there is no restriction for water to move into the interlayers expanding them until bentonite breaks into eroding pieces.

Data need for model development is considerable not only from the experiments done in BELBaR but also from experiments done earlier at e.g. Claytech, B+Tech and University of Jyväskylä.

MODELLING SMECTITE EROSION - TESTING MODEL SIMPLIFICATIONS

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The bentonite erosion model was developed to estimate the loss of smectite from bentonite used as buffer and backfill in the Swedish KBS-3 repository concept. It was used in SR-Site calculations by SKB and in the modelling of the performance of the Finnish repository at Onkalo. The model is based on the dynamic force balance model and gel/sol viscosity models described in Neretnieks et al (2009). The swelling of the smectite in the bentonite clay into the fractures with seeping water and the further transport as gel/sol with the water seeping in the fractures is influenced by the pore water concentration of primarily mono- and divalent cations.

The system of equations to solve is quite nonlinear and sometimes difficult to solve numerically because of the mutual influence of the evolving chemistry in the gel/sol, the forces acting on the smectite particles and the viscosity of the gel/sol, which determines how it can flow. The numerical difficulties have led us to explore which mechanisms have a dominating impact on the erosion and how simplifications could be made that will lead to more transparent, faster and stable calculations.

It is found that the water chemistry has the largest influence in the outer regions of the gel/sol and that the water composition in the approaching groundwater essentially determines the smectite properties in the region where the gel sol flows with the water. This allows the chemical transport model to be decoupled from the smectite expansion model, which eliminates the need for continuous coupling of the migration of ions in the expanding gel between the seeping water and interior of bentonite bulk.

It was also found the flow of the gel/sol occurs in a thin rim where the smectite volume fraction changes from a few percent by volume to essentially smectite free water. This has led us to explore if it is possible to decouple the swelling of the gel/sol in the region where it expands by the swelling forces from the thin rim where it swells and flows.

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Bentonite erosion by dilute waters – some implementations of Neretnieks' model

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One scenario of interest for the long-term safety assessment of a spent nuclear fuel repository involves the loss of bentonite buffer material through contact with dilute groundwater at a transmissive fracture interface (SKB 2011, Posiva 2012a). The scenario is based on the stable colloids at low ionic strength:

- the cohesive forces of bentonite decrease in low-salinity conditions, and colloids start to dominate and are able to leave the gel-like bentonite on the groundwater bentonite boundary;
- after colloid formation, groundwater may carry away the only just released clay colloids;
- low-salinity events are most probable during post-glacial conditions, when also pressure gradients are high, causing elevated flow velocity, which may enhance colloidal transport.

Therefore, it is very important from the point of view of repository safety assessment to be able to estimate how much bentonite may be lost during a post-glacial event, when the groundwater salinity and velocity, as well as the duration of the event are known or assumed.

The results in the issue so far may be divided into modelling attempts and experimental work. The modelling has been based on two main guidelines: external (Birgersson et al., 2009) and internal friction models (Neretnieks et al., 2009). However, these models have not been validated for erosion, probably due to lack of suitable laboratory data. The latter approach is more ambitious due to lack of fitting parameters, though the internal friction model itself may be varied. The internal friction model has proven to be time-consuming to solve numerically. This work indicates that experiments carried out by Schatz et al. (2012) differ significantly from the predictions obtained from Neretnieks' model. We present our numerical modelling results based on a set of simplifications of the original model (Olin, 2012). In addition, there are some suggestions given to the model of Neretnieks. The numerical modelling is performed by COMSOL Multiphysics. The original equations in Neretnieks et al. (2009) model include several nested function calls, whereas in this work it was chosen to apply numerical functions in COMSOL Multiphysics instead of implementing the functions directly. In this approach, the values of functions are given over a mesh and COMSOL interpolates and extrapolates the function values needed (BESW_D implementation). All the functions were tested in Matlab and Maple before implementing them into COMSOL. In addition, we fitted the original highly nonlinear diffusivity of smectite to a relatively simple analytical function (BESW_S). Typical results from the model calculations differ from experiments by higher erosion rate and a clear bentonite wake: an observation is that in the model calculations there is not so much bentonite upstream migration, while in downstream a clear wake has formed. This is in clear contrast to the almost circular montmorillonite extrusion in the experiment.

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TESTING OF SORPTION AND DESORPTION BEHAVIOR OF RADIONUCLIDES IN COLUMN WITH CRUSHED GRANITE: DETERMINATION OF SYSTEM BEHAVIOR WITHOUT COLLOID PRESENCE

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The sorption and desorption of radionuclides were studied in columns of crushed granite and fracture infill of various grain size. These experiments represent an introduction providing information about the transport of radionuclides through crushed granite material of different composition in order to determine the start-up behaviour of the system without colloid presence. The aim of experiments was to study and compare tracer behavior passing through column filled crushed granite. The experiments studying migration of colloids through crushed granite material in presence of radionuclides will follow.

Column experiments allow determination of transport parameters such as the retardation and distribution coefficients (R and K_d), Peclet number and hydrodynamic dispersion coefficient under dynamic conditions. Those are determined by fitting the experimental breakthrough curves using regression procedures based on the erfc-function, assuming a non-linear reversible equilibrium sorption/desorption isotherm.

The radioactive (^3H , ^{36}Cl , $^{85}\text{Sr}^{2+}$, $^{137}\text{Cs}^+$) and stable (SeO_3^{2-} , SeO_4^{2-}) tracers and two type of crystalline rock materials were investigated (pure granite, coded as PDM1-1 and fracture filling materials, coded as PDM1-2). Synthetic granitic water (SGW) was used.

The breakthrough curves showed that behavior of ^3H and ^{36}Cl is different in comparison with other tracers, both displaying behaviour of conservative tracers without any sorption. For this reason tritium is also very suitable to determination of transport parameters. The anionic exclusion was observed in case of ^{36}Cl in granite PDM 1-1. The selenate (Se(VI)) showed similar behavior as ^{36}Cl and ^3H . The sorption of ^{85}Sr is significantly higher than sorption of ^3H and ^{36}Cl , but also the values of K_d and R showed differences on different granite material. The presence of fracture infill minerals (chlorite) significantly increased sorption of ^{85}Sr in comparison with pure granite. On the other hand selenite (Se(IV)) showed completely different sorption behavior. The sorption of selenite was observed on the both type of granitic rock. The values of R and K_d showed influence of granitic size and granite composition on selenite sorption.

The scale of different radionuclide breakthrough scale from the experiments presented can be used for further colloid experiments as a pattern for the system of crushed granite material column without colloid presence.

The experimental and theoretical breakthrough curves are displayed in Fig. 1.

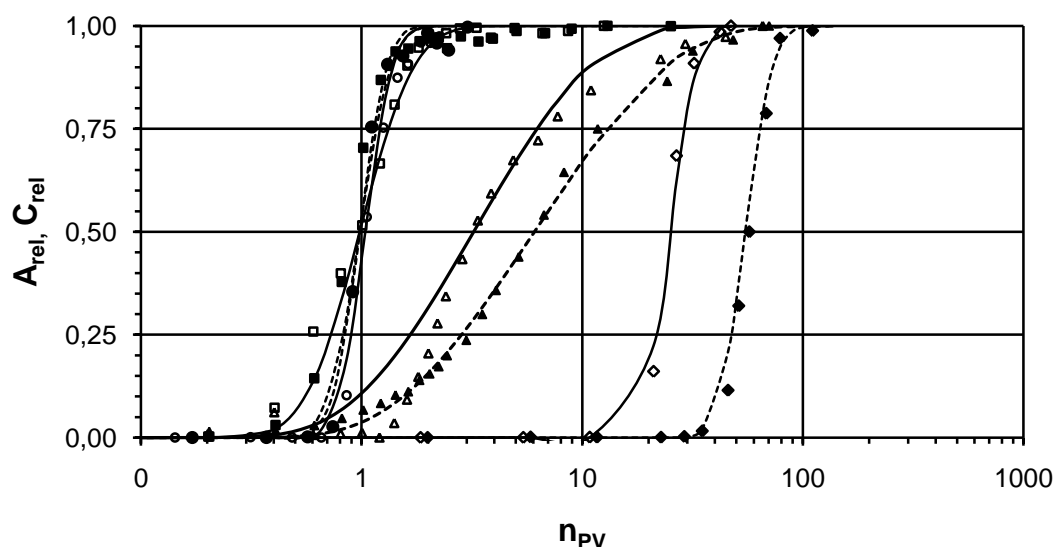


Fig. 1. Theoretical breakthrough curves (solid line, resp. dashed line) and experimental breakthrough curves of transport: $^3\text{H}^+$ (\circ , \bullet), Se^{IV} (Δ , \blacktriangle), Se^{VI} (\square , \blacksquare) a $^{85}\text{Sr}^{2+}$ (\diamond , \blacklozenge) in crushed granite (blank symbols) and in fracture infill materials (dark symbols) with grain size 0.125 – 0.63 mm in synthetic granitic water.

Reference:

Videnská, K., Palágyi, Š., Štamberg, K., Vodičková, H., Havlová, V. (2013) EFFECT OF GRAIN SIZE ON THE SORPTION AND DESORPTION OF ^{90}Sr AND ^{137}Cs IN COLUMNS OF CRUSHED GRANITE AND FRACTURE INFILL FROM GRANITIC WATER UNDER DYNAMIC CONDITIONS. *Journal of Radioanalytical and Nuclear Chemistry*, DOI : 10.1007/s10967-013-2429-7.

The latest results on colloid associated radionuclide mobility from the CFM project, Grimsel (Switzerland)

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The influence of colloidal/nano-scale phases on the radionuclide (RNs) solubility and migration behaviour is still one of the uncertainties in repository safety assessment [1]. In our work, we aim 1) to identify the presence and the formation of relevant colloids in repository specific areas, 2) to determine their stability as a function of geochemical parameters, 3) to elucidate the thermodynamics and kinetics of the colloid interaction with radionuclides, 4) to perform laboratory and field experiments to quantify the colloid mobility and their interaction with surfaces. The final goal is to state on the relevance of the nanoparticles (NPs) / colloids for the radionuclides migration in natural geochemical conditions. In this contribution we report on the progress concerning the colloid migration under near natural hydraulic conditions at the Grimsel Test Site.

Within the Colloid Formation and Migration (CFM) project at the Grimsel Test Site (GTS Switzerland) [2] a huge geo-technical effort was taken to isolate hydraulically a shear-zone from the artificially introduced hydraulic gradient due to the tunnel construction. The construction is a combination of polymer resin impregnation of the tunnel surface and a steel torus to seal the tunnel surface. The steel tube with reinforcement rings is sealed at both ends with rubber based hydraulic “donut” packers and the annulus between resin and steel ring is filled and pressurized with water to counteract the hydrostatic pressure of the water conducting feature giving mechanical support to the resin. Natural outflow points of the MI shearzone were localized prior to the construction and sealed by surface packers. This design gives the opportunity to regulate outflow and thereby adjust the flow velocity in the fracture.

After optimization of the experimental setup and injection procedure through a number of conservative tracer tests using fluorescence dyes and so-called “homologue” tracer tests performed by injecting a suspension of Febex bentonite colloids associated Eu, Tb, Hf in addition to the conservative tracer a license was granted in January 2012 by the Swiss regulator (BAG) to perform the first radionuclide tracer test under these low-flow conditions. The injection cocktail of 2.25L volume was prepared at INE and transferred to GTS. A total colloid concentration of 101.4 ± 2.5 mg/L montmorillonite clay colloids were used, whereas 8.9 ± 0.4 mg/L were present as synthetic montmorillonite with structural incorporated Ni. For details on the structural characterization of the Ni- montmorillonite phyllosilicate, see [3]. Beside the colloids and the conservative tracer Amino-G (1646 ± 8 ppb) the radioisotopes ²²Na, ¹³³Ba, ¹³⁷Cs, ²³²Th, ²³⁷Np, ²⁴²Pu and ²⁴³Am were injected. The trivalent and tetravalent actinides were quantitatively associated with the colloids present as well as Cs, whereas Np(V) and Na are not bentonite colloid bound.

The injection of the radionuclide bentonite colloid cocktail was performed through borehole CFM 06.002-i2 into the MI shearzone and the water extracted under a constant flow rate of approx. 25mL/min from the “Pinkel” surface packer (dipole distance 6.08m). The tracer cocktail was recirculated in the injection loop to monitor the fluorescence decrease of the conservative tracer (Amino-G) and therefore providing an injection function for consequent transport modeling. For on-site colloid analysis a mobile Laser- Induced Breakdown Detection (LIBD) system similar to the one used in the CRR experiments [4] was transferred

to Grimsel and installed in-line at the “Pinkel” outlet to directly monitor the mobile colloid fraction throughout the experiment.

The conservative tracer Amino-G was recovered quantitatively both by on site inline and off-site fluorescence detection. Analysis of the weakly sorbing tracers by α -spectrometry performed by PSI-LES and INE showed very good conformity and revealed recoveries for ^{22}Na , ^{137}Cs and ^{133}Ba of 64%, 10% and 1%, respectively. LIBD determined recovery was quantified to be ~66%, whereas for the structural components Al and Ni detected by high resolution HR-ICP-MS up to sample 60 (integration until 11.4 days) a recovery of 33-38% was quantified. The Al/Ni ratio in the injection cocktail was determined to be 21.6 and an average ratio of 20.4 ± 0.5 was found over the samples analyzed given clear evidence that a mobilization of Al containing phases as an additional colloid source from the fracture can be excluded. Based on a number of colloid migration experiments performed in the MI shearzone a colloid attachment/filtration rate can be estimated, which is considerably lower than the value of $2 \cdot 10^{-2}$ estimated by filtration theory in [5]. All injected radionuclides including the strong sorbing tri- and tetravalent actinides could be detected in the eluent. The data of Run 12-02 obtained so far clearly show the mobility of bentonite derived montmorillonite colloids under near-natural flow conditions in the MI shearzone of the Grimsel Test Site [6]. The experimental data will be discussed in detail in the presentation.

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Erosion behaviour of different compacted bentonites

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A generalized description of bentonite colloid generation processes requires the analysis of the main clay physico-chemical properties and clay/water interactions affecting erosion rates. An experimental cell in which compacted and confined clay tablets are immersed in 200 mL of selected electrolyte was used to evaluate colloid generation under stagnant/diffusive conditions. Clay hydration and colloid releases take place through two steel filters placed on both sides of the clay tablet. Colloid concentration and size distribution were periodically determined in the electrolyte by Photon Correlation Spectrometry.

During first essays, the effects of clay compaction density and clay main exchangeable cation (with homoionised Na or Ca bentonite) were analyzed, in several electrolytes at different ionic strength and with variable Na or Ca content. Higher generation was measured from Na-bentonites, at higher clay compaction density and in Ca-free electrolytes of low ionic strength. At present, the colloid generation behavior of three natural bentonites, Mx-80 from USA, FEBEX from Spain, and Mylos from Greece, was compared. Mx-80 is a Na-bentonite with a 88% smectite content, FEBEX bentonite is a Ca-Mg bentonite with a 98% smectite content and Mylos is as well a Ca-Mg bentonite with a nominal 79% of smectite. Cation exchange capacity and main exchangeable cations were determined in the three clays with the aim of explaining generation masses.

Results showed comparable colloid generation behavior from FEBEX and Mx.80 bentonites, while lower generation masses were measured from Mylos clay. The erosion behavior of the natural raw clays can be explained considering their content in swelleable smectite.

BEHAVIOUR OF MONTMORILLONITE AT LOW IONIC STRENGTH

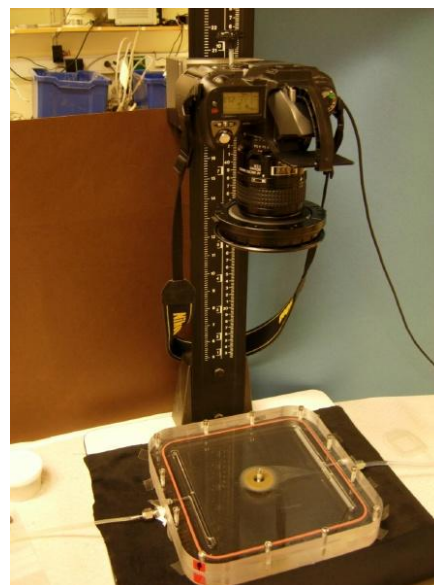
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In the Swedish KBS-3 concept for a geological deep storage, spent nuclear fuel will be placed in copper canisters surrounded by a buffer consisting of bentonite with high montmorillonite content. Montmorillonite has great affinity for water, which causes a swelling pressure to build up in the confined space of the storage in the presence of water. If there are fractures intercepting the deposition hole, there is nothing to mechanically stop the bentonite from continuing swelling until an equilibrium is reached. At present day conditions, bentonite at the swelling front will coagulate as the ground water is rather saline, thus hindering unlimited swelling. However, repository operational time may include one, or several, glaciations. As post-glacial melting water is expected to be very dilute, it is not unlikely that for a period of time the ground water may have very low salinity. It has been noticed that in contact with water of low salinity, bentonite may swell extensively and turn into a sol at the swelling front. The sol, a liquid colloidal state of dispersed clay particles, can easily be removed by flowing water. As significant loss of bentonite may compromise buffer function, we have studied the behaviour of montmorillonite at low ionic strength.

Initial studies of montmorillonite phase diagrams were performed in order to facilitate predictions of what type of behaviour, or colloidal phase (sol, gel), that can be expected at certain clay concentrations and levels of salinity.

Compacted montmorillonite clay was then allowed to swell out into an artificial fracture (picture). The swelling behaviour of clay in both deionised water and solutions with varying salt content was studied, as well as the behaviour of the clay during flow of an external solution. Our attention is now focused on the erosion of clay during flow. Recent work involves measuring the erosion depending on factors such as flow velocity and salinity. Also the influence of the composition of counterions in the montmorillonite as well as the composition of ions in the external solution is currently under investigation, as the ion composition has previously been shown to strongly affect the sol formation ability of clay.^{1,2,3}



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UPDATE ON THE ARTIFICIAL FRACTURE TESTING PROGRAM AT B+TECH

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Experiments probing buffer erosion in fracture environments under flow-through conditions relative to buffer composition, groundwater composition, flow velocity, accessory minerals, and fracture geometry are ongoing at B+Tech (see Figure 1).

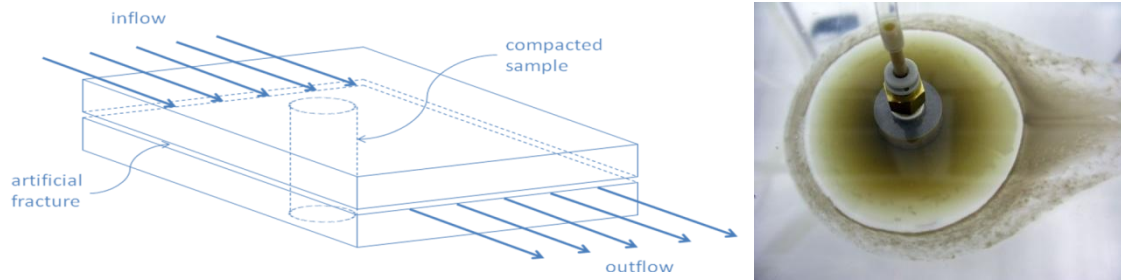


Figure 1. Schematic representation of the flow-through, artificial fracture test system (left) and characteristic overhead image of an actual test (right).

Results to be presented and discussed at the BELBaR 1st Workshop include:

- The effect of salinity gradient elution and switching between ionic strengths above and below the threshold limit on erosion.
- The effect of flow velocity (in the range between 10^{-6} and 10^{-3} m/s) on erosion.
- The effect of fracture aperture (comparing results at apertures of 1 and 0.1 mm) on erosion.
- The effect of fracture geometry (horizontal vs 45° down-sloping fracture planes) on erosion.

Additionally, a series of results from laboratory tests performed in order to examine whether the erosion of bentonite material through contact with dilute groundwater at a transmissive fracture interface could intrinsically result in 1) the formation of an accessory mineral filter bed and cake and/or 2) filter caking of montmorillonite itself will be presented and discussed. In these tests bentonite buffer material was simulated by using mixtures (75/25 weight percent ratio) of purified sodium montmorillonite and various additives serving as accessory mineral proxies (kaolin, quartz sand, chromatographic silica). The resulting mixtures were compacted into dense sample tablets with effective montmorillonite dry densities of ~ 1.6 g/cm³. The fracture erosion tests were performed using a Grimsel groundwater simulant (relative to Na⁺ and Ca²⁺ concentration only) contact solution at an average flow rate of 0.09 ml/min through the system.

The tests were designed to lead to the development of erosive conditions (i.e., sodium montmorillonite against a dilute solution) and, in every case, the formation of an accessory mineral bed layer near the extrusion/erosion interface was observed. Moreover, these layers grew progressively in thickness over the course of the tests. These results provide evidence that, following erosive loss of colloidal montmorillonite through contact with dilute groundwater at a transmissive fracture interface, accessory phases (within bentonite) remain behind and form bed layers.