EUROPEAN COMMISSION

Community research

BELBaR

(Contract Number: 295487)

DELIVERABLE (D-N°:5.3)

Summary of development of conceptual and mathematical models within BELBaR

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Reporting period: 01/03/2015 – 29/02/2016

Date of issue of this report: **28/04/2016**

Start date of project: **01/03/12** Duration: 48 Months

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research &Training Activities (2007-2011)		
Dissemination Level		
PU	Public	X

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Index

1 Understanding at the outset

1.1 Objectives

The objectives for WP5 were derived from the main aim of BELBaR that 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. The objective of development activities was to improve conceptual and the mathematical models used to predict mass loss of clay in dilute waters and clay colloids generation in special as well as clay colloids facilitated radionuclide transport. A target of validating advanced model(s) for the purposes of spent nuclear fuel disposal was set at the beginning.

With respect to the processes relevant to geological disposal the time scales are far too long in terms of experimental assessments regarding the time scales of industrial product development. For this reason validation was planned to be based on small-scale experiments committed in WP2-4. Such validation can be judged useable provided that scaling can be reasoned using sufficient understanding of processes and conditions relevant to application. The resulting overall understanding of clay mass loss in dilute waters was used in the safety assessment formulations in WP1.

To summarise, the work was planned and committed to

1) validate and advance models
    a. for predicting mass loss of clays in dilute waters and
    b. for clay colloids facilitated radionuclide transport
2) formulate data needs for other work packages, and
3) use of overall understanding in the safety assessment formulations in WP1.

1.2 Baseline conceptual and mathematical models used

1.2.1 System conceptualization

Currently the system is described in terms of solids content distribution within clay components and hydraulic and mechanical properties depending on it. Initial solids content distribution has been shown to meet the requirements (e.g. SKB 2011, TR 11-01) such that adequate swelling pressures and hydraulic conductivities are reached. The rate of change of porewater composition is limited by diffusional transport of porewater solutes to and from groundwater. Changes in porewater composition influence solids content and hydraulic and mechanical properties. For instance, a buffer in KBS-3 concept at this density has porosity around 37 %. If the bentonite is allowed to swell the density and the swelling pressures decreases. Further swelling decreases the volume fraction of bentonite and the swelling pressure becomes increasingly lower. Porewater composition of clays will change should there be changes in geochemical conditions in the repository.
Moreover, the solids lost from clay component are considered primarily as colloids fed into the groundwater in the fracture intersecting the part of repository in question. The transport of colloidal phases is usually described in terms of models based on the advection-dispersion equation (Sen and Khilar, 2006). The source terms embedded describe the interaction with the stationary phase either as equilibrium or as a non-equilibrium process.

1.2.2 Model of bentonite erosion (based on Koskinen et al. 2016)

Earlier studies discussed mostly physical erosion mechanisms and dispersion-flocculation behaviour of bentonite particles colloid formation by flowing groundwater (Grindrod et al. (1999), Kurosawa et al (1999), Verbeke et al. (1997), and Tanai and Matsumoto (2007)) whereas none of these studies addressed the details of chemical and surface chemical process in depth.

1.2.2.1 Conceptual aspects

Liu and Neretnieks (2006) seem to be the first to quantitatively address the role of chemistry that may influence the rate of colloid generation and the resulting erosion. Liu (2010) and Liu et al. (2009a) devised a dynamic model for pure smectite swelling and colloid release that accounts for competing attractive and repulsive forces between the smectite particles as well as on them by thermal movement (Brownian motion) and gravity. The model accounts for the influence of monovalent cations but not for divalent ions such as calcium. The model was validated by experiments of compacted smectite pellets swelling in distilled and low ionic strength waters and experiment on penetration through fine pore filters. The model was also used to derive a new method to determine the CCC, which gave about two orders of magnitude better results than the conventional DLVO model, (Liu 2011). The results agree well with observed values.

A gel viscosity model accounting for the influence of sodium concentration was devised based on published experimental results Liu (2011).

The dynamic model together with the viscosity model was used to simulate the rate of expansion of smectite into a fracture with flowing water. The expanding viscous gel can flow and release particles at the gel/sol/water interface. The gel/sol is carried downstream. The rate of loss of smectite and the distance to which the gel expands into the fracture was modelled for some cases relevant to the KBS-3 repository concept (Moreno et al. 2011). In this model the simultaneous diffusion of sodium from the buffer in the deposition hole towards and into the water seeping past the gel/sol/water interfaces also was accounted for. The phenomena accounted for are listed in the following.

1. Gel/sol behaviour and expansion
   - When the water in contact with the clay contains dissolved salts in a concentration above the CCC the clay particles swell only up to a certain volume fraction. At this point the gel is cohesive and will not release particles spontaneously. In the gel the main forces acting on the particles that were considered were gravitation, buoyancy, diffusion, electrical diffuse double layer repulsive forces (DDL) and van der Waals (vdW) attractive forces. Particle movement caused by these forces are balanced by friction against the water. Friction of the gel, containing only montmorillonite particles and water, against the fracture walls was unknown but in this connection assumed not to influence or limit gel expansion.
2. Ion exchange and influence of calcium and other divalent ions
   - The above description of gel/sol behaviour applies best to smectites in which monovalent ions such as sodium dominate in the different water pools (hereafter referred to as porewater) around the montmorillonite stacks and sheets. During swelling the individual sheets tend to separate and the colloid particles consist of one sheet. CCC is then in the range 20-100 mM wherea the CCC for calcium smectite is 2-4 mM (Birgersson et al 2009). The stacks repel each other with forces comparable to those for the individual sheets in sodium-dominated systems. Ion exchange equilibria between different water pools in porewater are expected to strongly impact on the gel/sol properties. For instance, the cations in the diffuse layer are mobile and may dominate the rate of cation diffusion in the gel (Neretnieks et al. 2009). This wasn't accounted for in many modelling studies of ion exchange in bentonite buffers.
3. Friction in fractures
   - Friction of the incompressible gel, containing only smectite particles and water, against the fracture walls was not assumed to hinder smectite particle migration from a closed volume into a fracture in this connection.

1.2.2.2 Governing parameters

The water composition strongly influences the DDL forces but has a very weak or negligible influence on the other forces. The viscosity of the dilute gel increases with decreasing ionic strength. The CCC determines when the smectite particles can be released to the water in the form of colloids or when they still will be held together by the attractive vdW forces. When ionic strength is below the CCC in the porewater and in the water seeping in the fractures the gel is always expansive and its rate of expansion will not be limited by the rate of leaching of CCC determining ions. The rate of expansion will then only be limited by the friction forces between the water and the particles in the gel/sol.

A further potential factor to limit expansion and mass loss is a gradual build-up of a layer of accessory minerals enrichment at the gel-groundwater interface thereby possibly inducing a structure that gets increasingly more efficient in filtering montmorillonite colloids. This way *the accessory minerals composition and contents* has at least a thinkable effect.

The viscous and viscoelastic deformation (commonly referred to as rheological behaviour) of clay-water suspensions is delicate with respect to microstructural details and is not understood in sufficient details. Nevertheless, there are some effects that are generally agreed on qualitatively and sometimes also quantitatively. Due to its direct influence on the electroviscous effect and the thickness of stacks, layer charge and charge heterogeneity is expected to strongly affect the rheological properties of smectite suspensions. This includes aspects of charge magnitude (i.e. layer charge) and charge localization (i.e. charge distribution). The movement of the individual particles is affected by the presence of neighbours as long as they do not have space enough to rotate freely. Onsager (1949) introduced the concept of co-volume where the basic idea is that the particles have volume in which to rotate freely without touching neighbouring spheres at low volume fractions. At higher volume fractions the rotation is hindered and this strongly influences the behaviour of the gel/sol. The co-volume plays a central role in the models used for the *viscosity of dilute gel/sols*. The idea is that a suspension containing spherical particles is more viscous than the mere fluid without particles. For coin-like particles the co-volume is the volume of a sphere within which the particle could rotate in. Liu (2011) extended the idea by to the radius of the coin adding some fraction *m* of the thickness of the diffuse double layer. The diffuse layer extends further in low ionic strength waters and the viscosity will therefore tend to increase with decreasing ionic strength.

The effect of gravitational forces is due to the density difference between the solids and the liquid comprising the suspension. A further contribution to particle movement due to gravity rises from the viscous friction between a particle and the fluid surrounding it and it is comparable to the *viscosity of the fluid* and the *size or the gyration radius of the particle*.

Random diffusive movement of particles is driven by thermal agitation (i.e. *temperature*) and the *differences in particle concentrations.*

The van der Waals forces between the solid particles in suspension depend on geometrical details of microstructure like the *inter-particle distances* and the *thickness of the plate-like particles* that are directly proportional to *dry density*.

The DDL forces depend on *layer charge*, *charge distribution* and *charge heterogeneity*. If smectite particles come so near that the double diffuse layers overlap considerably strong repulsive forces develop. This is the reason for the strong swelling pressures found in wet compact bentonite. A measure of the distance can be assessed from the Debye length that suggests that the repulsion force drops off exponentially with particle distance.

1.2.2.3 Numerical implementation by KTH

The numerical implementation was based on solving a time-dependent mass balance that takes into account body forces, diffusive and advective fluxes and forces between the particles as described above. To simulate these processes the mass balance must be coupled to and solved simultaneously with the sodium diffusion, the model for viscosity and the model describing the flow of gel/sol and water in the fracture. The problem formulation is 2-dimensional and dircretisation of partial differential equations is committed using finite element formulation.

1.2.2.4 Numerical implementation by VTT

During the course of VTT validating the KTH model with small-scale experimental data some discrepancies were met. To overcome the related consequences some functional simplifications for relative viscosity were made and the resulting functions were implemented numerically. The resulting approximate set of equations was verified against the original implementation.

1.2.3 Model of transport of bentonite colloids in a fracture

1.2.3.1 Conceptual models

In the literature the interaction of the colloidal phase and the contaminant in the dissolved phase is most often considered as equilibrium. Another step in the model development was to implement the influence of reversible and irreversible radionuclide sorption processes showing that slow desorption kinetics of the contaminant from the colloid is a essential prerequisite in order for nanoparticle-facilitated contaminant transport to become significant. Colloids/ nanoparticles interaction with the stationary phase is customarily implemented via correlation equations to calculate the theoretical single-collector efficiencies , either classical or with the more recently published Tufenkji and Elimelech correlation.

The implementation of physical and chemical heterogeneity is essential in describing nanoparticle transport and retention. In the EU IP-FUNMIG project a twofold approach was used to tackle the issue of colloid transport, namely (a) programming an object oriented code (CHEPROO, CHEmical PRocesses Object-Oriented) that is capable to simulate complex hydrobiogeochemical processes and is open to include more complex chemical systems as e.g. solid solutions, nanoparticle transport without loss in the handling of simple problems (Bea *et al.*, 2009) and (b) to characterize and monitor by integrating the analytical tools available within the FUNMIG consortium to a maximum extend the heterogeneity of natural systems observed in nanoparticle transport experiments. The methods included *inter alia* µCT (computer tomography) to characterize the fracture geometry (Enzmann and Kersten, 2006), C-14 PMMA impregnation (Kelokaski et al., 2006; Leskinen et al., 2007; Sardini et al., 2006; Voutilainen et al., 2009) and application of positron-emission-tomography (PET) to direct visualisation of the solute transport and nanoparticle transport in this natural rock fracture (Kulenkampff *et al.*, 2008). Based on the geometrical data available a comparison between experimental determined colloid breakthrough curves and computational fluid dynamics (CFD) modelling of colloid migration in a stationary flow field using this real 3D geometrical information was made (Huber et al., 2012). Simplified fracture geometry assumption as e.g. parallel plate models using the average fracture aperture were not capable to simulate appropriate the colloid breakthrough behaviour.

1.2.3.2 Numerical implementation

The implementation of a nanoparticle transport code was not completed within FUNMIG, but recently a Lagrangian particle tracking model (PTM) was proposed for predicting colloid/nanoparticle transport near a rough surface by embedding protruding spherical asperities in a planar surface (Kemps and Bhattacharjee, 2009). In summary, the model results show that asperities protruding from the planar surface can act as additional collectors, either directly or indirectly through changing the flow field. All the observations made in this study indicate that physical surface heterogeneity has a far reaching influence on particle deposition and it is important to accurately determine the flowfield near roughness features in nanoparticle deposition models in order to reliable predict deposition efficiencies or deposit morphologies.

2 The development process

2.1 Incremental modifications and advances

To gain more in depth insight into the rate determining mechanisms the work was focussed on instabilities of the numerical implementation.

At KTH finer grids were tested as well as simplified equations together with simplifications assuming a) steady state, b) solids concentration gradient in the direction of the flow as being much smaller than that in the cross-stream direction to it (i.e. omitted), c) cross-stream velocity being much smaller than that in the streamwise direction (i.e. omitted) and d) diffusive mass loss at the outer rim. The result was an ordinary differential equation instead of a set of partial differential equations. When comparing the results the erosion rate was some 5 % smaller in the simplified methods when compare to the full method. Moreover, the assuming anisotropic hydraulic conductivity in the fracture resulted roughly in a further 10 % reduction erosion rate.

Different simplifications of the same approach were experimented with at VTT. When assuming "erosion zone" at the outer rim such that solids volume fraction remains between 1 and 10 %, the comparison to the solids penetration distance observed in small-scale experiments indicated qualitatively different dominant processes. Moreover, different fits for diffusivities as function of solids content were experimented without major advances that is illustrated in Figure 1.

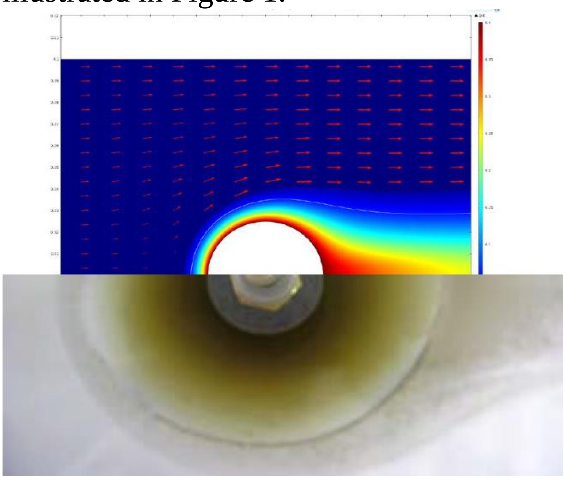

Figure 1. *A typical numerically simulated solids content compared to experimentally observed in a small-scale setup.*

These experiments led to consider a concept for a simpler model that could be used for scaling purposes by assuming only the size of the system (e.g. diameter of an excavation filled with clay). This model was calibrated with the KTH's computer simulations and at least seemed to reproduce the experimental results of small-scale tests. A key suggestion of this simplified model is that the erosion rate increases with square root of the system size thus suggesting e.g. that erosion rate in KBS-3 buffer is approximately nine (9) times larger than in the small-scale tests committed (1.7 m vs. 0.02 m).

The comparison difference between the different implementations of the KTH model and small-scale experiments sparked another line of development at VTT. This system of

equations comprised of coupled elasto-plastic model to capture the essence of clay swelling in fracture, wetting model to capture vapour diffusion and migration of liquid water (to be compared to the results from X-ray tomography) and a then currently open way capture the effects of groundwater salinity on wetting and swelling rates, swelling stresses, porewater composition and cohesivity/erodability of bentonite.
A mechanistic model to predict swelling pressure was proposed by KTH. Although the predictions agreed well with experiments a major shortcoming of the model was that it assumed a single number of montmorillonite flakes in a stack whereas the results of the SAXS data of VTT indicated stacking number varying between 1 and 14.
Although the approach for assessing transport of bentonite colloids in fractures was selected as one assuming only established theory (i.e. Navier-Stokes equations for laminar flows with fairly straightforward boundary conditions) and simplifications derived from this approach, the comparison differences with experimentally produced breakthrough curves were too large to consider the understanding to be validated. Examples of these differences are reproduced in Figure 2.

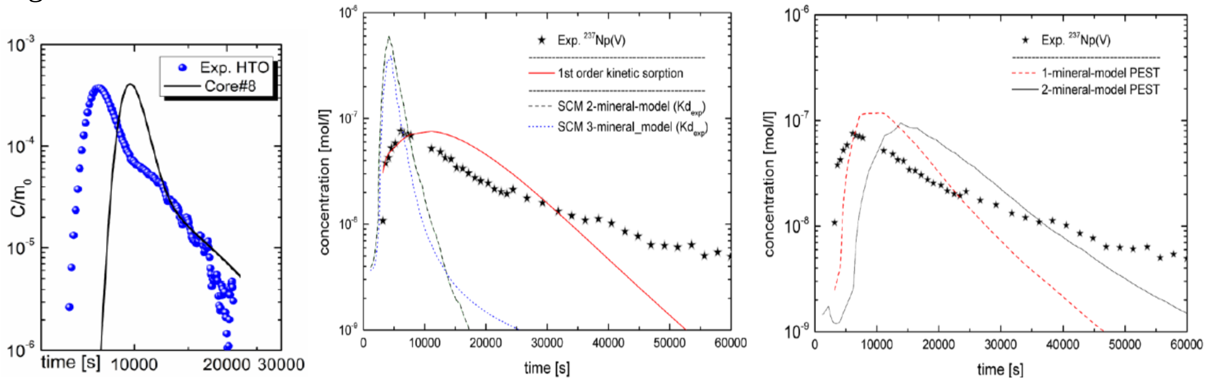

Figure 2. *A numerically simulated breakthrough curves compared to experimental ones.*

2.2 Benchmark to capture essence of dominating phenomena

To advance conceptual understanding and to justify dominating processes and parameters and benchmark case was formulated. Objective was to perform tests and compare results from computer simulations to these results to address the shortcomings recognised when trying to validate the currently existing mathematical models. The details of the benchmark case were agreed in a workshop organised in November 2013 in Tuusula, Finland. It was decided to focus on tabletop sized setup to get data on swelling of clay into a slow filled with stagnant fresh water. The results generated by various groups on experiments and computer simulations were to be compared and discussed in forthcoming workshops. At this time new conceptual models have been developed taking into account swelling and floc formation in more details.
The aspects raised in the discussions were

- selection of most important processes,
- the way to account accessory minerals,
- are flocs to be considered,
- is hysteresis effect to be considered and
- will the effect of gravity be included.

A summary of the discussions is presented in Table 1.

Table 1. *Summary of the discussion before agreeing on the definition of the benchmark. The aspects circulated with red were highlighted in the discussions.*

	PROCESSES	ACCESSORY MINERALS	FLOCS	HYSTERESIS	GRAVITY
GROUP 1	Swelling into fracture • measure details in the front • different apertures • in non-"sol forming" conditions • in "sol forming" conditions	Maybe not ... just montmorillonite alone at this stage	Aren't they of part of buffer system?	Range of densities in which gel is table	Not doable

GROUP 2	• There are plenty of data available
	  • Rate of expansion
	  • Erosion rate
	• => FOCUS on swelling
	  • Maybe not in great details
		What is this actually about?
		• To include this we'd need to understand it better
			Not sufficiently well understood to be included into benchmarks	Data needed	Potentially important

GROUP 3	• Keep it limited • Expansion -> rate • (erosion -> rate) • 2bv~0.1 mm • NaMt • Tabletop • Low salinity 1 mM NaCl • No flow • -> Experiment -> upscaling the geometry • Expansion -> erosion -> geometry upscaling	Not to be considered in benchmarks	This is conceptual uncertainty -> This is question for modellers!	Not to be considered in benchmarks -> premature	We have too little data for benchmark -> premature

In this connection it is worthwhile to pay attention to a single detail that although the observed effects of gravity suggested that it should be addressed, it was considered that it would still be premature to do so.

2.3 Validation of incremental modifications and bigger changes

At KTH model development yielded a "two-region model" in which a rim area is discretised in far higher resolution than the rest of the domain and in addition the bulk of the domain is assessed by solving a set of partial differential equations while the behaviour at the rim is evaluated by an ordinary differential equation. A comparison of the results of the "full model" and the "two-region model" is presented in Tables 2 and 3.

Table 2. *Loss of smecite for ion concentration 0.1 mM for different water velocities in 0.1 mm aperture fracture. The y-component of the velocity is accounted for (Neretnieks et al. (2015a)).*

Water velocity m/s	*Mass eroded at rim at 10 000 years, kg. Old*	*Penetration depth, S, of rim at SS m Old*	*Mass eroded at rim at 10 000 years, kg.*	*Mass lost from deposition hole at 10 000 years, kg.*	*Penetration depth S of rim at 10 000 years m*
10^{-7}	*43*	*7.0*	*7.6*	*140*	*34.2*
10^{-6}	*117*	*2.1*	*22*	*148*	*32.0*
10^{-5}	*292*	*0.5*	*144*	*172*	*14.7*

Table 3. *Loss of smecite for different ion concentrations in 0.1 mm aperture fracture. Water velocity 10^{-5} m/s. The y-component of the velocity is accounted for (Neretnieks et al. (2015a)).*

Concentration cion mM	*Mass eroded at rim at 10 000 years, kg.*	*Mass lost from deposition hole at 10 000 years, kg.*	*Mass in fracture at 10 000 years, kg.*	*Penetration depth of rim at 10 000 years m*
0.1	*144*	*172*	*28*	*14.7*
1	*63*	*148*	*85*	*27.0*
10	*59*	*146*	*87*	*24.3*

It is seen in Table 2 that there are considerable differences between the old and the new results; when comparing the results obtained with the earlier "full resolution model" mass loss rate is smaller by a factor from 1.5 to 5 while the reduction in mass loss rate yields a larger penetration depth by a factor of 5 and up to 30. It may further be noted that the mass in the fracture could be large when water velocities are low.

Although the columns *"Mass lost from deposition hole at 10 000 years, kg.*" in Tables 2 and 3 suggest that the *total loss* from the source is not very sensitive to the water velocity or the ion concentration the specific mass loss rate "mass loss [g/(m^2 a)]"-row in Table 4 suggests almost linear dependence of mass loss rate on flow velocity.

Table 4. *Specific mass loss rate as function of groundwater velocity.*

velocity [m/s]	**1E-07**	**1E-06**	**1E-05**
velocity [m/a]	*3*	*32*	*315*
Mass lost [kg]	140	148	172
Eroded mass [kg]	7,6	22	144
penetration depth [m]	34,2	32	14,7
time [a]	10000	10000	10000
mass loss [g/(m^2 a)]	**34**	**107**	**1 471**

This insensitivity was indicated in the small-scale experiments and in Section 3.1.2 in D1.1. However, the comparison error to small-scale experimental data is far from satisfactory. This difference is depicted in Figure 3.

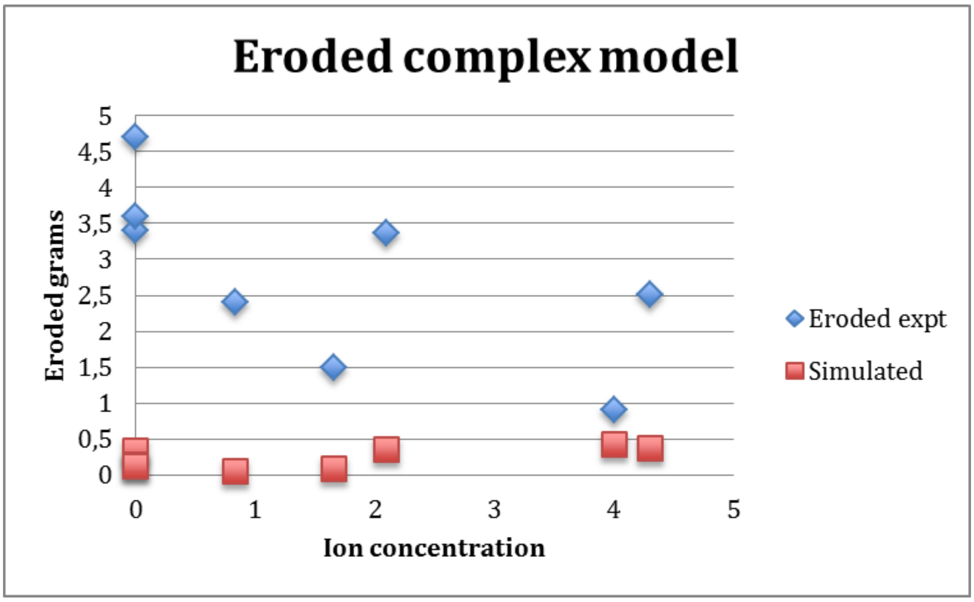

Figure 3. *Eroded mass as function of ion concentration mM from experiments and simulations with variable ϕ_R.(Neretnieks et al. (2015b))*

When assuming a specific volume fraction at the rim that the triggers the release of smectite particles by diffusion (from the gel to the flowing water) ϕ_R=0.015 as an input in the "two-region model" the match with the small-scale experimental results is very good. This is presented in Figure 4.

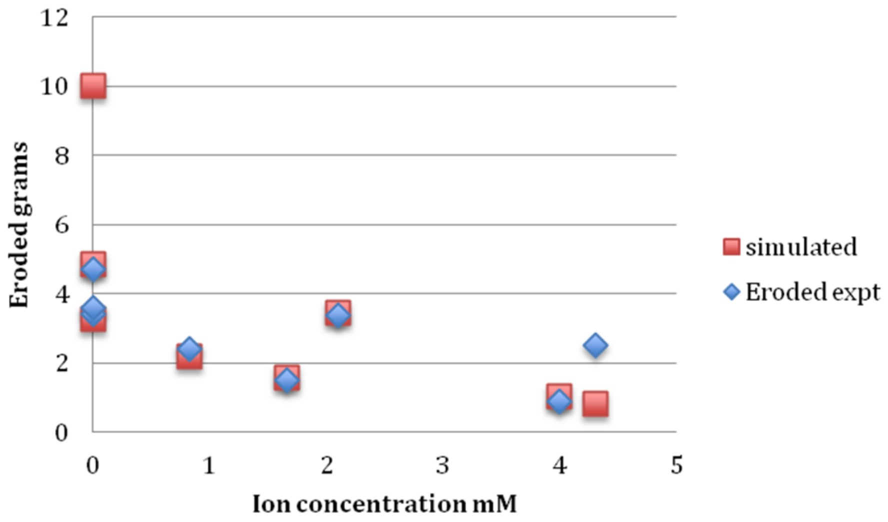

Figure 4. *Eroded mass as function of ion concentration mM from experiments and simulations with ϕ_R=0.015. (Neretnieks et al. (2015b))*

It was suggested that the colloids released from the rim would get in touch with each other and form flocs. An illustration of this is given in Figure 5.

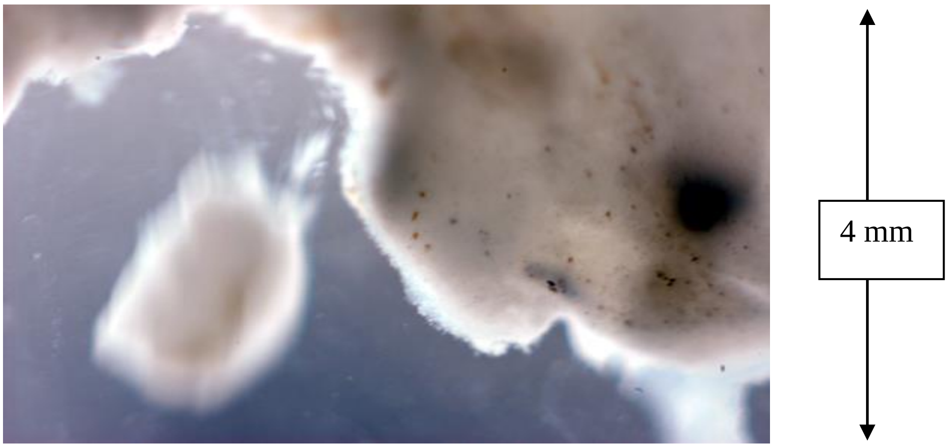

Figure 5. *An enlarged detail of the hanging gel. The whole picture is 4 mm high. Large and small black particles are clearly seen. (Neretnieks (2015))*

Nevertheless, such a good match with experimental results suggests the model to capture the dominating processes while scaling remains to be addressed in this connection.
When assessing the potential consequent migration of flocs in a fracture the following was concluded.
The smectite loss from a deposition hole by smectite agglomerates/flocs pulled by gravity is restrained by the rate of agglomerate transport in the fracture. In fractures smaller that 0.1 mm it is found to be less than 10-100 g/a from a deposition hole in a KBS-3 type repository that is intersected by a semi-vertical fracture. This is of the same order of magnitude as the loss by erosion in horizontal fractures, presented in Tables 2 and 3.
Shearing of agglomerates from the gel/water interface has at least theoretical potential to contribute to the release from the gel/water interface at very high seepage velocities. Based on the viscosity measurements committed Eriksson & Schatz (2013)) the resistance of the gel to deformation even at low solids volume fractions remains far higher than the potential shear forces induced by the flow at the gel/water interface.
All the simulations described above consider only purified smectites. These contain negligible amounts of larger non-smectite particles normally present in natural bentonites, which typically contain tens of percent of detritus material. It is expected that this material will be carried along by the expanding bentonite but will be released and left behind when the gel turns to sol. The detritus can then clog the narrower passages in the variable aperture fracture and it is expected that a filter will develop in the fracture that will prevent agglomerates or even individual smectite particles to pass. It was experimentally shown that a few mm thick detritus filter is sufficient to stop smectite transport, Richards and Neretnieks (2000). However this has as yet not been experimentally demonstrated to form in actual fractures.

2.4 Scaling aspects

When estimating the system scaling with respect to the size of the source ("R") by solving the simplified full resolution model (as referred to in Section 2.1) the mass loss rates presented in Figure 6a ("Flux") are obtained in which the penetration depths are as presented in Figure 6b ("L").

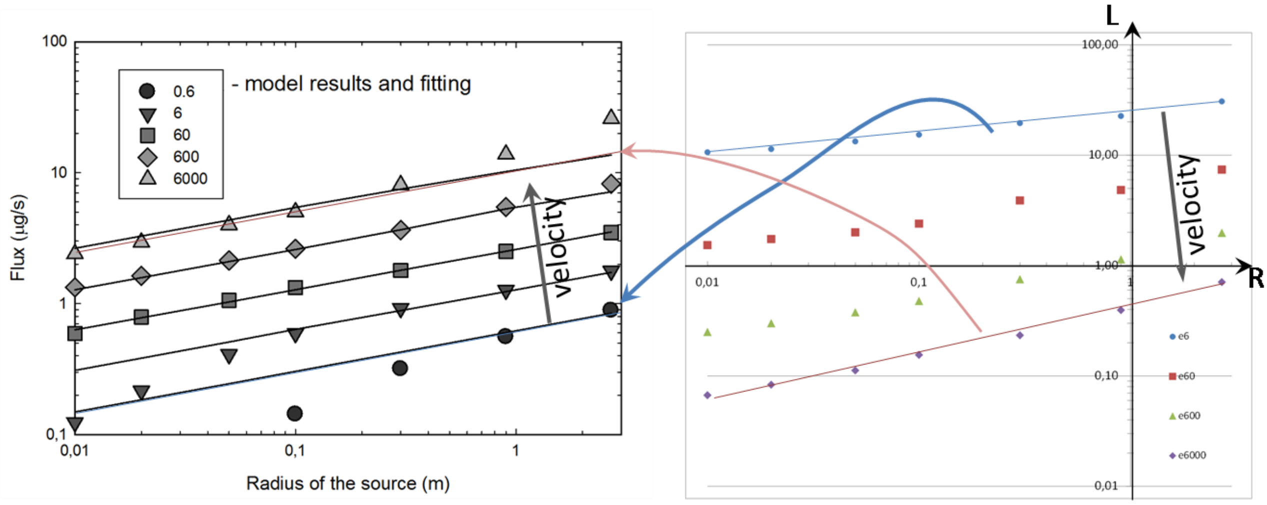

Figure 6. *a) Mass loss rate ("*Flux*") as function of radius of the source and velocity of the water flowing in fracture in metres per year (m/a) and b) penetration depth, L, in metres as function of the radius of the source and velocity of the water flowing in fracture.The bullets are results from computer simulations and the straight lines are mathematical fits. (1* µg/s = *31.5* g/a) *(Olin 2015)*

According to these simulations clay mass would be lost the closer to the source the higher the water velocity. The slope in the mathematical fits presented in Figures 6 is 0.31 (i.e. $Flux=0.73\cdot(v\cdot R)^{0.31}$) suggesting relevant dependence of mass loss rate on velocity. However, there are no evidences for or against clay penetrating tens of metres into fractures.

3 The resulting recommendations

The objectives set for the work were to

1. validate and advance the conceptual and mathematical models,
2. formulate data needs from other BELBaR work packages, and
3. use the overall increased understanding in the safety assessment formulations in WP1.

Regarding validation and advancing the models, sufficient confidence was obtained to predict clay mass loss rate in laboratory scales using numerical simulations whereas mass loss rate predictions repository relevant scales remain to be assessed using analytically derived expressions for bounding estimates. According to the bounding estimates referred to, the agglomerate/floc migration rate in fracture is the mass loss rate determining feature (Neretnieks (2015)).

The reasoning of dominant processes was succeeded considering agglomerate migration but was based only on expert judgement for clay swelling and gravity. Moreover, data needs specifications to assess the relative importance of clay swelling and gravity were raised but only when it was too late to commit experiments within BELBaR.

As to conclude it can be stated that a new bounding estimate is proposed to be used in the safety cases to assess clay mass loss rates; loss of clay at the clay-water interface is limited by migration of newly formed clay agglomerates in fractures. This estimate can be obtained with far lesser efforts and uncertainties than used in the previous safety cases.

References

Bea, S.A., Carrera, J., Ayora, C., Batlle, F., Saaltink, M.W., 2009. CHEPROO: A Fortran 90 object-oriented module to solve chemical processes in Earth Science models. Computers & Geosciences, 35(6): 1098-1112.

Birgersson M., Börgesson L., Hedström M., Karnland O., Nilsson U., 2009, Bentonite erosion, Final Report from Clay Technology, Swedish Nuclear Fuel and Waste management Co., SKB TR-09-34

Enzmann, F., Kersten, M., 2006. X-ray computed micro tomography (μ-XRT) results of a granitic drill core. In: Reiller, P., Buckau, G., Kienzler, B., Duro, L. (Eds.), 1st Annual workshop Proceedings of IP FUNMIG, report CEA R-6122. Commissariat a l'energie atomique (CEA), Gif sur Yvette (France), pp. 211-215.

Eriksson R, Schatz T. (2013): The Sol/Gel Interface in Bentonite Erosion, Poster at 8th EC Conference on the Management of Radioactive Waste, Vilnius, Lithuania, October 14th – 16th, 2013.

Grindrod, P., Peletier, M., Takase, H., 1999. Mechanical interaction between swelling compacted clay and fractured rock, and the leaching of clay colloids. Eng. Geol. 54, 159–165.

Huber, F. et al., 2012. Natural micro-scale heterogeneity induced solute and nanoparticle retardation in fractured crystalline rock. Journal of Contaminant Hydrology, 133: 40-52.

Kelokaski, M., Siitari-Kauppi, M., Sardini, P., Mori, A., Hellmuth, K.H., 2006. Characterisation of pore space geometry by C-14-PMMA impregnation - development work for in situ studies. Journal of Geochemical Exploration, 90(1-2): 45-52.

Kemps, J.A.L., Bhattacharjee, S., 2009. Particle Tracking Model for Colloid Transport near Planar Surfaces Covered with Spherical Asperities. Langmuir, 25(12): 6887-6897.

Koskinen K . (ed.), Neretnieks I., Moreno L., Liu L., Olin M., Pulkkanen V-M., Schaefer T., Huber F. (2012): Description of Conceptual Models and the Related Mathematical Models to Support Treatment of Colloids Related Issues in the Safety Case, BELBaR D5.1.

Kulenkampff, J., Grundig, M., Richter, M., Enzmann, F., 2008. Evaluation of positron-emission-tomography for visualisation of migration processes in geomaterials. Physics and Chemistry of the Earth, 33(14-16): 937-942.

Kurosawa, S., Kato, H., Ueta, S., Yokoyama, K., Fujihara, H., 1999, Erosion properties and dispersion-flocculation behavior of bentonite particles. Mater. Res. Soc. Symp. Proc. 556, 679–686.

Leskinen, A. et al., 2007. Determination of granites' mineral specific porosities by PMMA method and FESEM/EDAX. Scientific Basis for Nuclear Waste Management XXX, 985: 599-604.

Liu, L., Moreno, L., Neretnieks, I., 2009a. A Dynamic force balance model for colloidal expansion and its DLVO-based application. Langmuir 25 (2), 679–687.

Liu L., 2010. Permeability and expansibility of sodium bentonite in dilute solutions. Colloids Surf. A: Physicochem. Eng. Aspects 358 (1–3), 68–78.

Liu L., 2011, A model for the viscosity of dilute smectite gels, Physics and chemistry of the earth, 36, p 1792-1798

Liu J., Neretnieks I., 2006, Physical and chemical stability of the bentonite buffer, Swedish Nuclear Fuel and Waste management Co., SKB report R-06-103

Moreno L., Neretnieks I., Liu L., 2011, Erosion of sodium bentonite by flow and colloid diffusion, Physics and chemistry of the earth, 36, p 1600-1606

Neretnieks I. (2015): Release and sedimentation of smectite agglomerates from bentonite gel/sol, KTH memorandum for BELBaR, August 2015.

Neretnieks, I., Liu, L., Moreno, L., 2009. Mechanisms and Models for Bentonite Erosion. Swedish Nuclear Fuel and Waste management Co., Swedish Nuclear Fuel and Waste management Co., SKB TR-09-35

Neretnieks I., Moreno L., Liu L. (2015a): Bentonite expansion and erosion- Development of a two-region model, KTH memorandum for BELBaR, August 2015.

Neretnieks I., Moreno L., Liu L. (2015b): Evaluation of some erosion experiments by the two-region model, KTH memorandum for BELBaR, August 2015.

Olin M. (2015): Some scaling results by simplified Neretnieks' model, Presentation at BELBaR Workshop, 20.-21.4.2015 Vantaa, Finland.

Richards T., Neretnieks I., 2010, Filtering of clay colloids in bentonite detritus material. Chem. Eng. Technol., 33, No 8, 1303-1310

Sardini, P., Siitari-Kauppi, M., Beaufort, D., Hellmuth, K.H., 2006. On the connected porosity of mineral aggregates in crystalline rocks. American Mineralogist, 91(7): 1069-1080.

Sen, T.K., Khilar, K.C., 2006. Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media. Advances in Colloid and Interface Science, 119(2-3): 71-96.

Tanai, K., Matsumoto, K. 2007: A study on extrusion behavior of buffer material into fractures using X-ray CT method, Proc. 3rd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement.

Tufenkji, N., Elimelech, M., 2004a. Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. Environmental Science & Technology, 38(2): 529-536.

Tufenkji, N., Elimelech, M., 2004b. Deviation from the classical colloid filtration theory in the presence of repulsive DLVO interactions. Langmuir, 20(25): 10818-10828.

Tufenkji, N., Elimelech, M., 2005. Breakdown of colloid filtration theory: Role of the secondary energy minimum and surface charge heterogeneities. Langmuir, 21(3): 841-852.

Verbeke, J., Ahn, J., Chambré P. L., 1997, Long-Term Behaviour of Buffer Materials in Geologic Repositories for High-Level Wastes, Report University of California at Berkeley UCB-NE-4220 (1997).

Voutilainen, M., Lamminmaki, S., Timonen, J., Siitari-Kauppi, M., Breitner, D., 2009. Physical Rock Matrix Characterization: Structural and Mineralogical Heterogeneities in Granite. Scientific Basis for Nuclear Waste Management Xxxii, 1124: 555-560.