Using COMSOL for the Transport Modelling of Some Special Cases in a Bentonite Buffer in a Final Repository for Spent Nuclear Fuel

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Abstract: The bentonite barrier is an essential part of a safe spent fuel repository in granitic bedrock. In this work COMSOL Multiphysics® is used in modelling the thermal (T), hydrological (H), mechanical (M) and chemical (C) phenomena and processes taking place in a bentonite buffer. Special interest lies in systems in which the density of bentonite or bentonite pore water varies. Typically, variation occurs during the erosion and wetting stage of bentonite. The reason for developing COMSOL models for this purpose is the lack of commercially available software, which typically covers either THC or THM models; M and C are not modelled together.

Keywords: bentonite, nuclear waste, density, diffusion, Darcy's law

1. Introduction

The basic option in Finnish spent nuclear fuel management is deep geological disposal. The next milestone will be the construction licence application for the underground disposal facility at Olkiluoto that Posiva Oy is planning to submit to the Finnish Government in 2012.

Many phenomena and processes have to be understood when considering the safety of the engineering barrier system (EBS) of the spent fuel repository**.** In this work the main interest is in the bentonite buffer part of the EBS. Its main functions in terms of different process classes are (Olin et al., 2008)

o to minimize hydraulic conductivity near waste canisters (hydraulic processes (H)),
o to maintain a beneficial chemical environment (chemical (C) and thermal (T) processes),
o to delay or limit the waterborne mass flows, e.g. release of radionuclides (CH) and
o to limit the stresses acting on the canister (mechanical processes (M)).

Typically, mass transport in the bentonite buffer occurs only by molecular diffusion, but in some special cases, like during initial wetting and post-glacial erosion, convection may be an important transport mechanism. During wetting the main problem lies in the proper and accurate calculation of the variably saturated flow field under temperature gradient. On the other hand, in glacial erosion, the interest lies in the modelling of changing bentonite density conditions, and the formation and release of colloids.

This work includes modelling the initial saturation (wetting and swelling) of the bentonite buffer, transport of (bacterial) sulphide after post-glacial erosion has decreased the density of the bentonite buffer, and glacial erosion lab experiments. Our work in using COMSOL in the field of radionuclide transport is described by Pulkkanen (2009), but all the above processes also affect radionuclide transport.

2. Governing equations and available data

2.1 Coupling between saturated density, porosity and cation exchange capacity

Compacted bentonite consists of dry bentonite and water, which together fill all the available space. Density of the bentonite itself or specific dry density is denoted by ρ_s (2 760 kg m^{-3}) and water by ρ_w (1 000 kg m^{-3}). Total mass of bentonite in volume V is therefore

$$M = M_b + M_w = (1-\phi)V\rho_s + \phi V \rho_w \quad (1)$$

which gives the density of the compacted bentonite:

$$\rho = \frac{M}{V} = (1-\phi)\rho_s + \phi\rho_w \quad (2)$$

Mass of bentonite per total volume

$$\rho_d = \frac{M_s}{V} = (1-\phi)\rho_s \qquad (3)$$

is called the dry density. Porosity and dry and specific densities are conveniently coupled by

$$\phi = \frac{\rho_s - \rho}{\rho_s - \rho_w} = \frac{\rho - \rho_d}{\rho_w} = 1 - \frac{\rho_d}{\rho_s} \qquad (4)$$

Cation exchange capacity CEC (eq/kg) is the fixed charge content (negatively charged sites occupied by cations) of the solid. Concentration of CEC per pore volume is given by

$$c_{CEC} = CEC \times \rho_d \frac{1-\phi}{\phi} \qquad (5)$$

2.2 Cation exchange and aqueous reactions

We started the chemical modelling of bentonite-water with this system: sodium (Na), calcium (Ca), chloride (Cl) and cation exchange site (X). Na^+ and Ca^{2+} form surface complexes NaX and CaX_2 with X^-, and aqueous complexes NaCl(aq) and $CaCl^+$ with Cl^-:

$$
\begin{cases}
2NaX + Ca^{2+} = CaX_2 + 2Na^+ & \lg K_{NaCa} = -0.20 \\[2mm]
K_{NaCa} = \dfrac{\beta_{Ca}\left[Na^+\right]^2}{\beta_{Na}^2 \gamma_0^2 \left[Ca^+\right]} & K_{NaCa} = 0.62 \\[2mm]
NaCl(aq) = Na^+ + Cl^- & \lg K_{NaCl} = 0.78 \\[2mm]
K_{NaCl} = \dfrac{\gamma_0^2 \left[Na^+\right]\left[Cl^-\right]}{\left[NaCl(aq)\right]} & K_{NaCl} = 6.0 \\[2mm]
CaCl^+ = Ca^{2+} + Cl^- & \lg K_{CaCl} = 0.79 \\[2mm]
K_{CaCl} = \dfrac{\gamma_0^4 \left[Ca^{2+}\right]\left[Cl^-\right]}{\left[CaCl^+\right]} & K_{CaCl} = 5.0
\end{cases} \qquad (6)
$$

Where [·] denote the molar concentration (mol/L), K is the equilibrium constant or selectivity (for cation exchange reactions), β is the equivalent fraction of cations and γ_0 is the activity coefficient of monovalent ions. Many more complexes and ions are typically handled in more chemically oriented modelling. For implementation in the Chemical Reaction Engineering Lab (CREL), the cation exchange reaction is reformulated for aqueous concentrations

$$
\begin{cases}
\beta_i = z_i \dfrac{c_{Xi}}{c_{CEC}} = \dfrac{z_i \phi}{CEC \times \rho_s} c_{Xi} \\[3mm]
\dfrac{K_{NaCa}}{2c_{CEC}} = \dfrac{c_{CaX2}\left[Na^+\right]^2}{c_{Na}^2 \gamma_0^2 \left[Ca^+\right]} \\[3mm]
c_{NaX} + 2c_{CaX2} = c_{CEC}
\end{cases} \qquad (7)
$$

where the last equation stands for charge equilibrium in solid phase. The activity coefficient is given by

$$
\begin{cases}
\lg \gamma_0 = -0.51 \times \left(\dfrac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \\[3mm]
I = \dfrac{1}{2}\left(\left[Na^+\right] + 4\left[Ca^{2+}\right] + \left[CaCl^+\right] + \left[Cl^-\right] \right)
\end{cases} \qquad (8)
$$

where I is the stoichiometric ionic strength.

The total mass of each element is conserved and the charge balance must be kept in the aqueous phase as well.

$$
\begin{cases}
c_{Na} = \left[Na^+\right] + \left[NaCl(aq)\right] + c_{NaX} \\[2mm]
c_{Ca} = \left[Ca^+\right] + \left[CaCl^+\right] + c_{CaX2} \\[2mm]
c_{Cl} = \left[Cl^-\right] + \left[NaCl(aq)\right] + \left[CaCl^+\right] \\[2mm]
\left[Na^+\right] + 2\left[Ca^{2+}\right] + \left[CaCl^+\right] = \left[Cl^-\right]
\end{cases} \qquad (9)
$$

Altogether, the chemical systems are defined by three chemical reactions and their non-linear mass-action laws, three mass balance equations, two charge balance equations and an activity coefficient model.

2.3 Momentum transport

The water flow problems in the study are modelled with the Earth Science Module, because variably saturated systems are essential when modelling wetting. The problem solving consists of finding pressure $p=p(x,t)$ such that

$$\begin{cases} \left[\dfrac{C}{\rho_{\mathrm f} g} + Se \times S\right]\dfrac{\partial p}{\partial t} = \nabla \cdot \left(\dfrac{\kappa_{\mathrm s}}{\mu} k_{\mathrm r}\left(\nabla p - \rho \mathbf{g}\right)\right) \\ \text{in } \Omega_{flow} = \{\text{buffer, rock}\} \\ p = 0 \\ \text{on } \partial\Omega_{inlet} = \{\text{inlet boundary}\} \\ \mathbf{n}\cdot\left(-\dfrac{\kappa}{\mu}k_{\mathrm r}\nabla p\right) = 0 \\ \text{elsewhere on } \partial\Omega\,(\text{no flux}) \end{cases} \qquad (10)$$

where C is the specific capacity, Se is the effective saturation, S is the storage coefficient, $\kappa_{\mathrm s}$ is the intrinsic permeability, $k_{\mathrm r}$ is the relative permeability, $\rho_{\mathrm f}$ is the fluid density, g is the gravitational acceleration and μ is the viscosity of water. The velocity field $\mathbf{u}(\mathbf{x},t)$ (to be used in conduction and convection) is then derived from Richards's law: $\mathbf{u} = -\dfrac{\kappa_{\mathrm s}}{\mu}k_{\mathrm r}\left(\nabla p - \rho\mathbf{g}\right)$.

Density variation in bentonite is assumed to change the saturated permeability, k (Bear, 1972)

$$k = k_0 \frac{(1-\phi_0)^2}{(1-\phi)^2}\left(\frac{\phi}{\phi_0}\right)^3 = k_0\left(\frac{\rho_0}{\rho_{\mathrm d}}\right)^2\left(\frac{\rho_{\mathrm s}-\rho_{\mathrm d}}{\rho_{\mathrm s}-\rho_0}\right)^3$$

where subscript 0 stands for the reference state.

2.4 Heat transport

Heat transport by conduction must be included in the model, because in many cases there is a heat source of some kind in the system. The temperature field, $T(\mathbf{x},t)$, obeys the equations

$$\begin{cases} C_{\mathrm{eq}}\dfrac{\partial T}{\partial t} = \nabla\cdot\left(K_{\mathrm{eq}}\nabla T - C_{\mathrm L}\mathbf{u}T\right) \\ \text{in } \Omega \\ T = T_0 \\ \text{on } \partial\Omega_{inlet}\ (\text{actually outlet for heat}) \\ \mathbf{n}\cdot\left(-K_{\mathrm{eq}}\nabla T + C_{\mathrm L}\mathbf{u}T\right) = N_0(t) \\ \text{on } \partial\Omega_{copper}\ (\text{copper surface is heated}) \\ \mathbf{n}\cdot\left(-K_{\mathrm{eq}}\nabla T + C_{\mathrm L}\mathbf{u}T\right) = 0 \\ \text{elsewhere on } \partial\Omega\ (\text{no flux}) \end{cases} \qquad (11)$$

where C_{eq} denotes the effective volumetric heat capacity, K_{eq} is the effective thermal conductivity, and $C_{\mathrm L}$ is the volumetric heat capacity of the moving fluid.

2.5 Mass transport by molecular diffusion

The mass transport problem is: find $c=c(\mathbf{x},t)$ such that

$$\begin{cases} \dfrac{\partial}{\partial t}(\phi c) = \nabla\cdot\left(\phi G D_{\mathrm p}\nabla c - \mathbf{u}c\right) \\ \text{in } \Omega \\ c = c_0(t) \\ \text{on } \partial\Omega_{inlet} \\ \mathbf{n}\cdot\left(-D_e\nabla c + \mathbf{u}c\right) = 0 \\ \text{elsewhere on } \partial\Omega\ (\text{no flux}) \end{cases} \qquad (12)$$

Diffusion in porous media is often described by modified Fickian laws of diffusion. Instead of Fick's first law, the diffusion flux j is given in the form

$$j = -D_{\mathrm e}\frac{\partial c_{\mathrm w}}{\partial x} = -\nu\phi G D_{\mathrm w}\frac{\partial c_{\mathrm w}}{\partial x} \qquad (13)$$

where $D_{\mathrm e}$ (m^2/s) is called effective diffusivity even though it is strictly speaking a mass transport coefficient (directly comparable to heat conductivity), c_w is the free concentration per pore volume, G is the geometric factor, which takes account of the longer diffusion path in a porous medium compared to free space, $D_{\mathrm w}$ is the diffusivity in free water, and ν takes account of either surface diffusion (cations) or anion exclusion (anions).

For Fick's second law, a storage factor α, usually called capacity factor, is needed. In an ideal case without any sorption

$$\alpha = \phi \qquad (14)$$

but if some sorption occurs or there is interaction between species and pore walls (typically electrostatic) a more useful definition is

$$\alpha = \nu\phi + (1-\phi)K_d\rho \qquad (15)$$

where $K_{\mathrm d}$ is the sorption distribution coefficient

$$K_{\mathrm{d}} = \frac{c_s}{c_w} \qquad (16)$$

where c_{s} is the content (amount per unit mass) of the studied element in solid phase. For anion diffusion, K_{d} is typically set to zero, but an alternative way is to fix it to some suitable negative value and then set $\nu = 1$, in order to avoid double calculation of anion exclusion.

Fick's second law is derived by putting Eq. (13) into a continuity equation:

$$\frac{\partial c}{\partial t} = \alpha \frac{\partial c_{\mathrm{w}}}{\partial t} = D_{\mathrm{e}} \frac{\partial^2 c_{\mathrm{w}}}{\partial x^2} \qquad (17)$$

or

$$\frac{\partial c}{\partial t} = D_{\mathrm{a}} \frac{\partial^2 c}{\partial x^2} \qquad (18)$$

where any relevant concentration (in the case of our linear system) can be used and where

$$D_{\mathrm{a}} = \frac{D_{\mathrm{e}}}{\alpha} \qquad (19)$$

is the apparent diffusivity, which is now the real diffusion constant as can be seen from Eq. (17).

Ochs & Talerico (2004) recommend a value of 0.4 for ν in the case of chloride, so that the capacity factor for chloride is

$$\alpha = \nu\phi = \nu\left(1 - \frac{\rho_{\mathrm{d}}}{\rho_{\mathrm{s}}}\right) = 0.4 \times \left(1 - \frac{\rho_{\mathrm{d}}}{2760 \ \mathrm{kg/m^3}}\right) (20)$$

Ochs & Talerico (2004) also give D_{e} as a 3rd order polynomial function of dry density, which is given below in numerically more stable form

$$D_{\mathrm{e}} = D_{\mathrm{e}}^{0}\left[b_3\left(\frac{\rho_{\mathrm{d}}}{\rho_0}\right)^3 + b_2\left(\frac{\rho_{\mathrm{d}}}{\rho_0}\right)^2 + b_1\frac{\rho_{\mathrm{d}}}{\rho_0} + b_0\right]$$

$$\begin{cases} b_0 = 16.167 & D_{\mathrm{e}}^{0} = 1 \cdot 10^{-11} \ \mathrm{m^2/s} \\ b_1 = -30.962 & \rho_0 = 1590 \ \mathrm{kg/m^3} \\ b_2 = 20.553 \\ b_3 = -4.7609 \end{cases} \qquad (21)$$

3. Use of COMSOL Multiphysics: applied modules and some applications

The major advantages of COMSOL, over some other computer programs, are the possibility to handle complicated geometrical structures, advanced and flexible mesh generation, and options in solvers, and therefore, the possibility to test how the chosen numerical methods affect the solutions. It is critical to have close to full control of the solution procedure, since the reliability of solutions is very important in nuclear waste applications due to the difficulties in direct long-term experimental testing.

3.1 Applied modules

CREL was applied to chemical modelling and some attempts were made to export models created in CREL into COMSOL for transport modelling. The main module for transport modelling was the Earth Science Module, which makes it easier to model a partially saturated porous medium compared to, for example, the Chemical Engineering Module.

3.2 Chemical erosion

The goal in chemical erosion studies is to understand the processes and estimate the magnitude of the bentonite mass due to erosion. Chemical erosion is a problem especially during post-glacial periods (the first is predicted to occur about 100 000 years after the closing of the repository), when very low salinity groundwater may intrude into the final repository. Bentonite is not very stable in low salinity conditions, in which the cation exchange sites may be occupied by monovalent ions (Na or K). The first task is to calculate the evolution of the bentonite buffer over the 100 000-year period to obtain a realistic initial state for the post-glacial period. The next task is to calculate the kinetics of colloid formation and the capacity of groundwater flow to transport away these released colloidal particles.

A simplified COMSOL model about the chemical equilibrium is already implemented in CREL, but its conversion into COMSOL is still underway. On the other hand, COMSOL enables the calculation of diffusion transport without chemical reactions in realistic geometries.

Modelling of the colloid formation and transport has just started. Our goal is to compare the results gained with TOUGHREACT, which are chemically more detailed but done only in 1D-geometry, to COMSOL results.

3.3 Corrosive sulphide diffusion

Bacterial activity near a bentonite buffer in a deposition hole may produce sulphide ions (most typical species HS^- with far lower occurrence of S^{2-}), which can cause corrosion of the copper canister if transported near the canister surface. In most conditions diffusion through the bentonite is the only transport mechanism, but in certain extreme cases the buffer density is so low that groundwater can flow through the buffer, at least to a certain extent.

The goal is to develop a diffusion and advection model for sulphide ion transport to the surface of the copper canister. The main variables considered are diffusion distance, diffusion coefficient as a function of bentonite dry density, sulphide concentration at the source and the dimensions of the source.

The scenarios considered are as follows:

S1. Source inside: sulphide is produced by bacterial activity in the bentonite buffer itself: concentration is low.
S2. Source at the bentonite-rock boundary: a bacterial population living at the interface between the rock and bentonite produces sulphide: concentration is high.
S3. Bentonite density low – otherwise like S2
S4. Advective conditions – otherwise like S3
S5. Aggressive conditions – otherwise like S4

All scenarios are already implemented in COMSOL, but thus far the results are only relative due to the lack of data on real concentration levels.

3.4 Water saturation of compacted bentonite

Water saturation of compacted bentonite is actually a very complicated process, during which chemical reactions take place, bentonite swells and forms swelling pressure, bentonite deforms and its porosity undergoes both qualitative and quantitative changes.

In many cases, and especially in chemical or THC modelling of bentonite, a simplified approach is adopted, using the well-known van Genuchten (1980) parameterisation for partially saturated bentonite.

Our goal is to compare the COMSOL results to results from TOUGH2 (Pruess *et al.,* 1999) and Numerrin[1]. The first one is a well-known computer code for solving fully and partially saturated flow problems and the latter is a general-purpose numerical solver that is easily adaptable to many partial differential equation based problems.

A good solution for saturation problems will enable better transport calculations due to more stable and realistic velocity fields. In the beginning, only verification calculations are done, because no suitable data is currently available for validation calculations.

3.5 Saturation stage erosion of bentonite

During or just after the installation of bentonite buffer around the copper canister in the deposition hole, several processes may impair the planned saturation of bentonite. Ideally, the bentonite buffer saturates, swells and deforms such that it fills the deposition hole homogeneously.

Two closely related processes are piping and erosion: formation of pipes through the bentonite buffer and water flow along these pipes transporting away bentonite mass. A 1D-model, at a level enabling comparison to experimental results, has been proposed to describe this complicated set of processes. Mathematically it is given by two equations

$$\frac{\partial c}{\partial t} - \frac{Q(t)}{\pi R(z,t)^2}\frac{\partial c}{\partial z} + 2\frac{c(z,t)}{R(z,t)}\frac{\partial R}{\partial t} = 2\frac{\sigma(z,t)}{R(z,t)} + 2\frac{G(z,t)}{R(z,t)} \tag{22}$$

and

$$\frac{\partial R}{\partial t} = \frac{\sigma(z,t)}{\rho_p} + \frac{G(z,t)}{\rho_p} - v_B(t)\frac{R(t)}{R_0} \tag{23}$$

where c is the eroding mass concentration, Q is the volumetric flow rate in the channel (pipe), R

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is the radius of the channel, sigma is the erosion rate, G is the gravitational settling term, ρ is the density of eroded bentonite particles and v_B is the local swelling velocity.

Implementation of these equations into COMSOL will be straightforward once enough suitable experimental data is available for their parameters.

4. Results

4.1 Chemical erosion

The sensitivity of the bentonite buffer to chemical erosion depends on the fraction of sodium in the cation exchanger mineral montmorillonite. The more sodium, the higher is the risk of chemical erosion, which occurs when very dilute groundwaters are in contact with bentonite. We have implemented a cation exchanger model in CREL, as given in Eqs. (1-9); our aim is to export the model into COMSOL for transport calculation. In Figure 1 the sodium and calcium equivalent fractions in solid phase are sketched as a function of the equivalent fraction of calcium in groundwater.

4.2 Corrosive sulphide diffusion

Scenarios S1 and S2 (see section 3.3) have already been calculated and some of the results are shown in Figure 2. Other scenarios are still under construction.
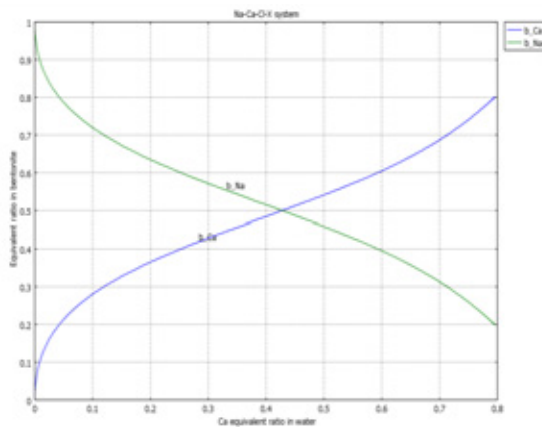

Figure 2. Concentration isosurfaces (0.01, 0.001 and 0.0001 times the surface concentration on the source) and diffusion flux onto the copper canister (relative scale). 1/100 concentration is observed very close to the source and the flux onto the copper canister decreases rapidly as the distance from the source increases.

4.3 Water saturation of compacted bentonite

Some effective bentonite saturation results from our calculations are shown in Figure 3. These problems are not numerically very stable – more research is clearly needed.

Figure 1. Na-Ca-Cl-X system calculated in CREL: sodium and calcium equivalent fractions vary non-linearly as a function of the calcium equivalent fraction in aqueous phase.
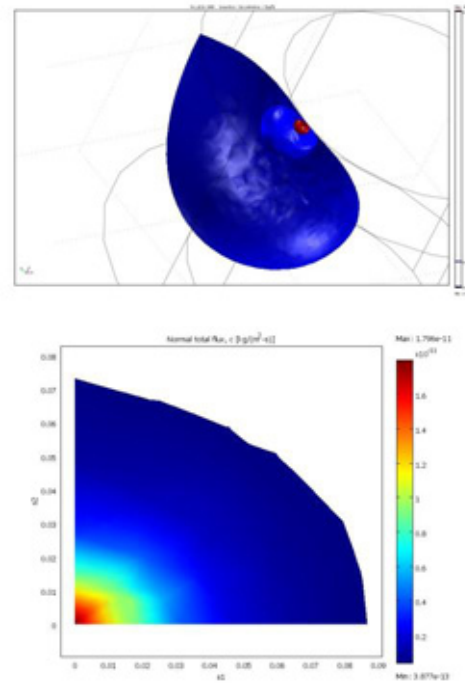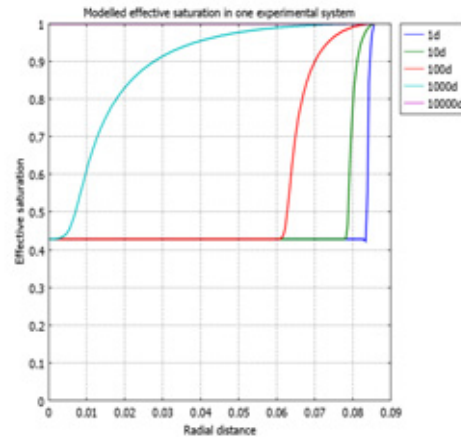

Figure 3. Saturation of bentonite modelled by van Genuchten equations. The effective saturation front has surprisingly steep gradients.

4.4 Saturation state erosion of bentonite

The saturation state erosion of bentonite takes place by separate but connected processes: piping and erosion. As the work on this subject is still ongoing, Figure 4 provides only a sketch of piping and erosion processes.

5. Discussion and conclusions

COMSOL appeared to be a flexible tool in implementing our model of bentonite, when the bentonite-water ratio varies either due to different erosion processes or during wetting. Our first results have already shown how difficult it is to get accurate and stable solutions for variably saturated bentonite buffers. We are also working to add chemical reactions, probably with COMSOL Reaction Engineering Lab, into COMSOL transport modules. These reactions are essential in many nuclear waste related problems.

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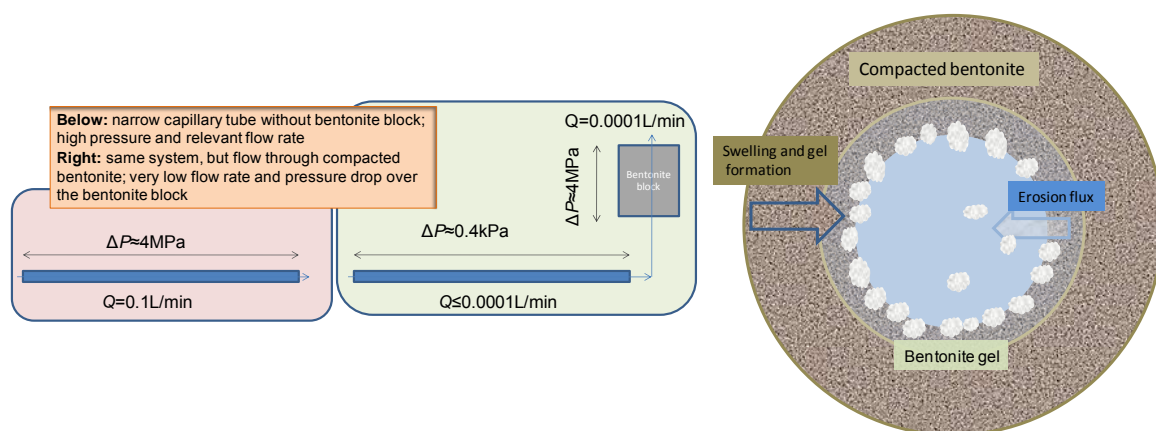
7. Acknowledgements

Figure 4. Simple system description of piping and erosion. Two extreme cases: (leftmost) bentonite causes no flow resistance at all and (right) almost all flow resistance takes place over the bentonite block (piping is possible). In the right figure, a model of one erosion channel is shown in detail.