

# COMSOL Multiphysics, TOUGHREACT and Numerrin Comparison in Some Modelling Tasks of Spent Nuclear Fuel Disposal

Aku Itälä<sup>1</sup>, Mika Laitinen<sup>2</sup>, Merja Tanhua-Tyrkkö<sup>1</sup>, Veli-Matti Pulkkanen<sup>1</sup> & Markus Olin<sup>1</sup>

<sup>1</sup>VTT Technical Research Centre of Finland, Espoo, Finland

<sup>2</sup>Numerola Oy, Jyväskylä, Finland

\*VTT, P.O. Box 1000, FI-02044 VTT, FINLAND, markus.olin@vtt.fi

**Abstract:** The bentonite barrier is an essential part of a safe spent fuel repository in granitic bedrock. In this work COMSOL Multiphysics®, TOUGHREACT and Numerrin are used and compared in modelling the saturation, cation-exchange and mass transport in compacted bentonite. Model comparison was not a straightforward task due different approaches in the model setup. Therefore, we tried to write down all the equations and via parameterisation of those equations to create model descriptions near each other.

**Keywords:** bentonite, nuclear waste, saturation, 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

- to minimize hydraulic conductivity near waste canisters,
- to maintain a beneficial chemical environment
- to delay or limit the waterborne mass flows, e.g. release of radionuclides and
- to limit the stresses acting on the canister.

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. This work includes modelling the initial saturation (wetting)

of the bentonite buffer, cation exchange between Na and Ca, and mass transport of Na, Ca and Cl.

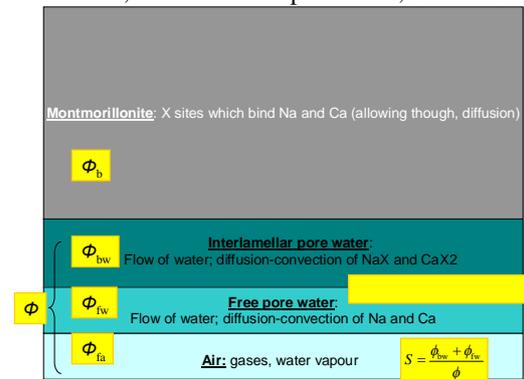


Figure 1. Basic concept.

## 2. Governing equations and available data

### 2.1 Components of bentonite

Compacted bentonite consists of dry bentonite (montmorillonite and accessory minerals), water, and air, which together fill all the available space (see Figure 1). Total mass of bentonite in volume  $V$  is therefore

$$\begin{aligned} M &= M_b + M_{bw} + M_{fw} + M_{fa} \\ &= \rho_b \phi_b V + \rho_w \phi_{bw} V + \rho_w \phi_{fw} V + \rho_a \phi_{fa} V \quad (1) \\ &\cong \left[ \rho_b \phi_b + \rho_w \phi_{bw} + \rho_w \frac{\chi}{1 - \chi} \phi_{bw} \right] V \end{aligned}$$

which gives for the density of the bentonite:

$$\rho \cong \phi_b \rho_b + \frac{\phi_{bw} \rho_w}{1 - \chi} \quad (2)$$

where

$M_i$  is the mass of dry bentonite (b), water bound on bentonite (bw), free water (fw) or air (fa)

$\rho_b$  is the specific dry density of bentonite ( $2760 \text{ kg m}^{-3}$ )

$\rho_w$  is the density of water; both bound on bentonite and free ( $\cong 1000 \text{ kg m}^{-3}$ ), though bound water may have higher density  
 $\rho_a$  density of air ( $\cong 1.3 \text{ kg m}^{-3}$ ) is very low

$\phi_i$  is the volume fraction of component  $i$ :

$$\sum_{i=b,bw,fw,fa} \phi_i = 1 = \phi_b + \phi$$

$\phi$  is the volume fraction of all fluids:

$$\phi = \phi_{bw} + \phi_{fw} + \phi_{fa}$$

$\chi$  is the ratio of volume fractions of free and total water volume:  $\gamma = \phi_{fw} / (\phi_{bw} + \phi_{fw})$

Mass of bentonite per total volume

$$\rho_d = M_b / V = (1 - \phi) \rho_b \quad (3)$$

is called the dry density.

Total porosity  $\phi$ , and dry and specific densities are conveniently coupled by

$$\phi = 1 - \rho_d / \rho_b \quad (4)$$

Saturation  $S$  is written as

$$S = \frac{\phi_{bw} + \phi_{fw}}{\phi} = \frac{1}{1 - \chi} \frac{\phi_{bw}}{\phi} \quad (5)$$

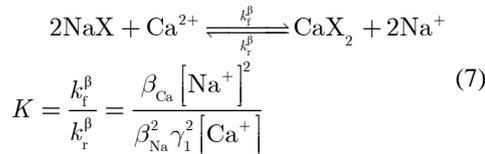
Cation exchange capacity  $CEC$  (eq/kg) is the fixed charge content (negatively charged sites  $X$  occupied by cations) of the solid bentonite. Concentration of  $CEC$  per bound water volume is given by

$$c_X = \frac{M_{CEC}}{\phi_{bw} V} = \frac{CEC \cdot \phi_b \rho_b V}{\phi_{bw} V} = \frac{\phi_b}{\phi_{bw}} CEC \cdot \rho_b \quad (6)$$

Any other quantity given as content (moles per kilogram of bentonite) will be transformed similarly to concentration per bound water.

## 2.2 Cation exchange reactions

The chemical model is simple: sodium (Na), calcium (Ca), chloride (Cl) and cation exchange site (X).  $\text{Na}^+$  and  $\text{Ca}^{2+}$  form complexes  $\text{NaX}$  and  $\text{CaX}_2$  with  $X^-$ :



Where  $[\cdot]$  denotes the molar concentration (mol/L),  $K$  is the selectivity constant,  $\beta_i$  is the

equivalent fraction of cation  $i$ , and  $\gamma_z$  is the activity coefficient for ion of charge  $z$ , which are calculated for example by Davies equation [Appelo and Postma, 2007]

$$I = \frac{1}{2} \left( [\text{Na}^+] + 4[\text{Ca}^{2+}] + [\text{Cl}^-] \right)$$

$$\lg \gamma_1 = 0.51 \cdot \left[ \sqrt{I} / (1 + \sqrt{I}) - 0.3I \right] \quad (8)$$

$$\lg \gamma_z = z^2 \lg \gamma_1 \rightarrow \gamma_2 = \gamma_1^2 = \gamma_1^4$$

where  $I$  is the stoichiometric ionic strength.

For implementation in the COMSOL or Numerrin, the cation exchange reaction is reformulated for aqueous concentrations, which are the applied variables in transport equations instead of equivalents fractions ( $\beta_i = z_i c_{\text{Xi}} / c_X$ )

$$\frac{\phi_{bw}}{\phi_b} \frac{\alpha \gamma_0^2 K_{\text{NaCa}}}{2 \rho_b CEC} = \frac{c_{\text{CaX}_2} c_{\text{Na}}^2}{c_{\text{NaX}}^2 c_{\text{Ca}}} \quad (9)$$

where  $\alpha$  is the unit transform coefficient ( $1000 \text{ L/m}^3$ ), which transforms from molar units to  $\text{mol/m}^3$ .

The total mass of each element is conserved.

$$\begin{aligned} \overline{c_{\text{Na}}} &= \phi_{fw} c_{\text{Na}} + \phi_{bw} c_{\text{NaX}} \\ \overline{c_{\text{Ca}}} &= \phi_{fw} c_{\text{Ca}} + \phi_{bw} c_{\text{CaX}_2} \\ \overline{c_{\text{Cl}}} &= \phi_{fw} c_{\text{Cl}} \end{aligned} \quad (10)$$

where  $\overline{c_i}$  is the total concentration of element  $i$ .

The charge balance must be kept in the bound and free aqueous phase

$$\begin{aligned} c_X &= c_{\text{NaX}} + 2c_{\text{CaX}_2} \\ c_{\text{Cl}} &= c_{\text{Na}} + 2c_{\text{Ca}} \end{aligned} \quad (11)$$

## 2.3 Chemical kinetics

For the reaction (8) it is possible to write forward and reverse rates

$$R_f = \alpha k_f \gamma_1^4 [\text{NaX}]^2 [\text{Ca}] = \frac{k_f \gamma_1^4 \phi_{bw}^2 c_{\text{NaX}}^2 c_{\text{Ca}}}{\alpha^2 \phi_{fw}^2} \quad (12)$$

and

$$R_r = \alpha k_r \gamma_1^2 [\text{CaX}_2] [\text{Na}]^2 = \frac{k_r \gamma_1^2 \phi_{bw} c_{\text{CaX}_2} c_{\text{Na}}^2}{\alpha^2 \phi_{fw}} \quad (13)$$

which give for total reaction rate  $R = R_f - R_r$ , which, at equilibrium, is zero:

$$\gamma_0^2 \frac{k_f}{k_r} \frac{\phi_{bw}}{\phi_{fw}} = \frac{c_{\text{CaX}_2} c_{\text{Na}}^2}{c_{\text{NaX}}^2 c_{\text{Ca}}} \quad (14)$$

and comparison by Eq. (10) gives

$$K^r = \frac{k_f \phi_b}{k_r \phi_{fw}} \frac{2\rho_b CEC}{\alpha} \quad (15)$$

for kinetics based selectivity.

## 2.4 Momentum transport

The problem solving of the water flow problems in the study consists of finding pressure  $p=p(\mathbf{x},t)$  such that satisfies (within given boundary and initial conditions)

$$\left[ \frac{C}{\rho_f g} + S\alpha \right] \frac{\partial p}{\partial t} = \nabla \cdot \left( \frac{\kappa_s}{\mu} k_r (\nabla p - \rho \mathbf{g}) \right) \quad (16)$$

where  $C$  is the specific capacity,  $S$  is the effective saturation,  $\alpha$  is the storage coefficient,  $\kappa_s$  is the intrinsic permeability,  $k_r$  is the relative permeability,  $\rho_f$  is the fluid density,  $\mathbf{g}$  is the gravitational acceleration and  $\mu$  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:

$$\mathbf{u} = -\frac{\kappa_s}{\mu} k_r (\nabla p - \rho \mathbf{g}) \quad (17)$$

In our present work the well known and much applied van Genuchten approach has been used [van Genuchten, 1980]. First, the saturation is given as a function of pressure (negative when  $S < 1$ )

$$S(p) = \left[ 1 + \left| \frac{p}{p_0} \right|^{\frac{1}{1-\lambda}} \right]^{-\lambda} \quad (18)$$

from which  $C$  is obtained by differentiation respect to  $p$

$$\begin{aligned} C(p) &= g\rho_f \phi \frac{\partial S}{\partial p} \\ &= \frac{g\rho_f}{p_0} \frac{\lambda}{1-\lambda} \phi \left| \frac{p}{p_0} \right|^{\frac{\lambda}{1-\lambda}} \left[ 1 + \left| \frac{p}{p_0} \right|^{\frac{1}{1-\lambda}} \right]^{-\lambda-1} \end{aligned} \quad (19)$$

The  $k_r$  is given as a function of pressure

$$k_r = \left[ 1 + \left| \frac{p}{p_0} \right|^{\frac{1}{1-\lambda}} \right]^{-\lambda/2} \left[ 1 - \left( 1 - \left[ 1 + \left| \frac{p}{p_0} \right|^{\frac{1}{1-\lambda}} \right]^{-1} \right)^\lambda \right]^2 \quad (20)$$

It is possible to define all these by  $S$  also

$$\begin{cases} p(S) = -p_0 \left[ S^{-1/\lambda} - 1 \right]^{1-\lambda} \\ k_r(S) = \sqrt{S} \left[ 1 - \left( 1 - S^{1/\lambda} \right)^\lambda \right]^2 \\ C(S) = \frac{g\rho_f \phi}{p_0} \frac{\lambda}{1-\lambda} S^{1/\lambda} \left( 1 - S^{1/\lambda} \right)^\lambda \end{cases} \quad (21)$$

And finally, it is possible handle the problem as a diffusion of saturation, where diffusivity is given by

$$\begin{aligned} D_\omega(S) &= p_0 \frac{\kappa_s}{\eta \phi} \frac{1-\lambda}{\lambda} \\ &\times S^{-1/\lambda - 1/2} \left[ S^{-1/\lambda} - 1 \right]^{-\lambda} \left[ 1 - \left( 1 - S^{1/\lambda} \right)^\lambda \right]^2 \end{aligned} \quad (22)$$

## 2.4 Mass transport by molecular diffusion

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

$$\frac{\partial}{\partial t} (\phi_j c_i) = \nabla \cdot (\mathbf{j}_{ij} - \mathbf{u} c_i) + R_{ij} \quad (23)$$

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

$$\mathbf{j}_{ij} = -\phi_j G(\phi_j, S) D_j \nabla c_i \quad (24)$$

where  $i$  denotes the species;  $j = bw$  or  $fw$  for bound and free water species, respectively;  $G$  is the geometric factor, which takes account of the longer diffusion path in a porous medium compared to free space, and may depend both on volume fraction and saturation. Free and bound water diffusion constants have traditionally been named pore ( $D_p$ ) and surface diffusion [Rasmuson & Neretnieks, 1983] constants ( $D_s$ ), respectively.

It is clarifying to write out the complete set of transport equations

$$\begin{aligned} \partial_t (\phi_{fw} c_{Cl}) &= \nabla \cdot \left[ (\phi_{fw} D_p \nabla - \mathbf{u}_f) c_{Cl} \right] \\ \partial_t (\phi_{fw} c_{Na}) &= \nabla \cdot \left[ (\phi_{fw} D_p \nabla - \mathbf{u}_f) c_{Na} \right] + 2R \\ \partial_t (\phi_{bw} c_{NaX}) &= \nabla \cdot \left[ (\phi_{bw} D_s \nabla - \mathbf{u}_b) c_{NaX} \right] - 2R \\ \partial_t (\phi_{fw} c_{Ca}) &= \nabla \cdot \left[ (\phi_{fw} D_p \nabla - \mathbf{u}_f) c_{Ca} \right] - R \\ \partial_t (\phi_{bw} c_{CaX}) &= \nabla \cdot \left[ (\phi_{bw} D_s \nabla - \mathbf{u}_b) c_{CaX} \right] + R \end{aligned} \quad (25)$$

### 3. Case studies for comparison of COMSOL Multiphysics, TOUGHREACT and Numerrin

#### 3.1 Review of codes applied

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.

PetraSim [Thunderhead engineering, 2005] is a user interface which is an interactive pre/post-processor for TOUGH2, T2VOC, TMVOC, TOUGHREACT, TOUGH-Fx/HYDRATE and TETRAD simulators. PetraSim helps users to develop models and view result of models based on (TOUGH2) nonisothermal flows of multicomponent/-phase fluids in one, two, and three-dimensional porous and fractured media. T2VOC and TMVOC include three-phase flows of water, air and volatile organic chemicals. The TOUGHREACT adds chemical reactions to TOUGH2 and the TOUGH-Fx/HYDRATE the capability to represent methane hydrates. PetraSim is also a capable tool for simulating the final repository but the code has also many problems and the user manual is concise. In addition it lacks the tools to construct realistic and modern geometries.

Numerrin is mathematical modelling software developed at Numerola Oy.

In Numerrin, mathematical models are written in modelling language which gives the user full control of the models and numerical methods.

The software can solve partial differential equations in complex geometries and the examples in this article were solved with control volume finite element method

#### 3.2 Geometry and boundary condition

Three one-dimensional modelling cases were performed with all these modelling codes. The

basis of all these modelling cases was a water reservoir in contact with 10cm long bentonite column, while the other end was closed.

#### 3.3 Saturation

The first case was a modelling of saturation in bentonite by van Genuchten approach; all parameters are listed in Table 1. The initial water saturation  $S$  in bentonite was selected to be 0.4.

**Table 1. The van Genuchten and some other parameters used in this comparison are representative for bentonite.**

Parameter	Value
$\lambda$	0.3
$p_0$	9.23 MPa
$P_{max}$	76 MPa
$\eta$	0.001 Pa s
$\kappa$	$6.4 \cdot 10^{-21} \text{ m}^2$
$D_p$	$10^{-10} \text{ m}^2/\text{s}$
$D_s$	$1 \cdot 10^{-12} \text{ m}^2/\text{s}$
$\chi$	0.05
$CEC$	0.8 eq/kg

**Table 2. The initial water composition in bentonite is calculated by using equations from [Tournassat, et al., 2007], with equivalent fractions 0.8 and 0.2 for NaX and CaX<sub>2</sub>, respectively; and the composition of water in contact with bentonite**

Ion	[mmol/L]	[mmol/L]
[Na <sup>+</sup> ]	1.00e-3	100
[Ca <sup>2+</sup> ]	1.22e-10	50
[Cl <sup>-</sup> ]	1.00e-3	200

#### 3.4 Chemical reactions and diffusion

The modelling case was a case where bentonite is fully saturated (i.e.  $S=1$ ) but cation exchange in bentonite is happening. The system consisted only of Na-Ca exchange where selectivity constant was as noted in equation d.

The equivalent fractions for NaX and CaX<sub>2</sub> were 0.8 and 0.2, respectively. These equivalent fraction leads to an assumption of initial bentonite pore water composition, see Table 2. The initial pore water composition in bentonite is calculated according to equations in [Tournassat, et al., 2007]. The composition of water in water reservoir is given in Table 2.

Kinetic constants for reaction (7) were set to  $k_f = 950 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$  accordingly Tang & Sparks (1993) and  $k_r = 2.0 \text{ E}5 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ , though the

latter one modified so that the selectivity given in Eq. (1) will be get when Eq. (15) is applied.

### 3.5 Reactive transport model: both saturation and chemistry

The third case “combines” the two cases above, the saturation and cation exchange in bentonite. The initial saturation is 0.4 as in modelling case 1. The initial porewater composition and the water composition in water reservoir are those mentioned in Table 3.

## 4. Results

### 4.1 Saturation

The results of comparison for bentonite wetting (saturation, pressure and velocity) are given in Figs. 2-4. As can be seen the Numerrin and COMSOL results are near each other, but, to our surprise, the TOUGHREACT result are remarkably different; we are working with these results to find out the reason of differences.

### 4.2 Chemical model

Chemical model is much more complicated to compare between the chosen models, because there are some basic differences in the modelling approach. The results for diffusion look similar, but the chemical reaction part still need more work before realistic comparison is relevant.

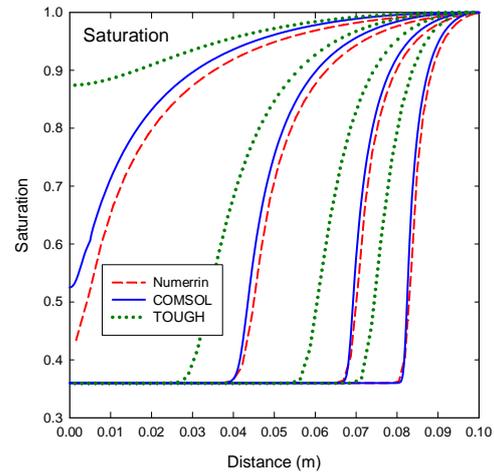
### 4.3 Reactive transport model: both saturation and chemistry

It is even more difficult to compare chemical reaction during wetting and we are still working with these problems.

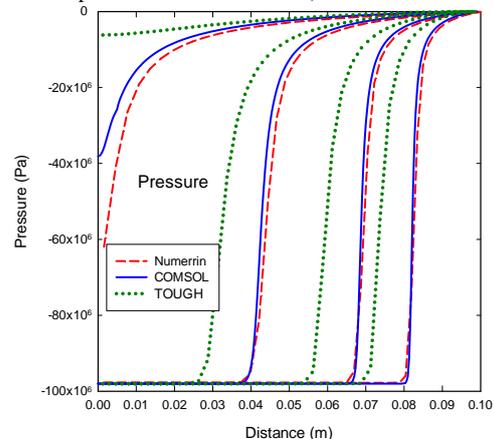
## 5. Discussion and conclusions

Model comparison between the applied three computing systems (COMSOL, TOUGHREACT and Numerrin) is not a straightforward task due different approaches in the model setup. Therefore, we have tried to write down all the equations and via parameterisation of those equations to create model descriptions that are at least near each other.

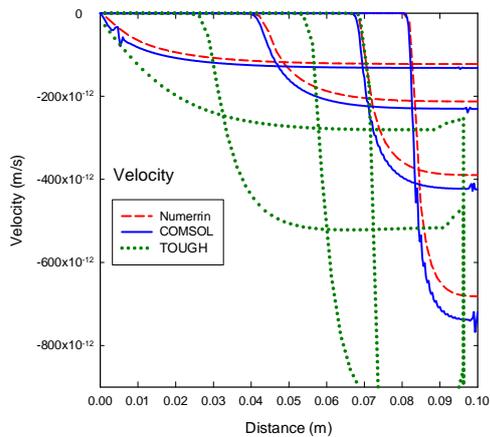
Some differences were already observed for the simplest system: wetting of bentonite by van Genuchten approach. The two are cases appeared to be much more difficult and our work on them continues.



**Figure 2.** Numerrin, COMSOL, and TOUGHREACT results (0.1, 0.3, 1 and 3 years, left most set of plots represents the earliest time) for saturation.



**Figure 3.** Numerrin, COMSOL, and TOUGHREACT results (plots like in Fig. 2) for pressure.



**Figure 4.** Numerin, COMSOL, and TOUGREACT results (plots like in Fig. 2) for velocity.

## 6. References

- Appelo, C.A.J. & Postma D. 2007. *Geochemistry, groundwater and pollution*. 2<sup>nd</sup> edition, Amsterdam, the Netherlands, 2007, 649 p.
- Bear, J. 1972. *Dynamics of Fluid in Porous Media*. Dover Publications, Inc. New York. (1972)
- Rasmuson A. & Neretnieks I. 1983. *Surface migration in sorption processes*. Stockholm, SKBF/KBS, Report 83-37. 54 p.

Tang L. & Sparks D.L. 1993. Cation-exchange kinetics on montmorillonite using pressure-jump relaxation. *Soil. Sci. Soc. Am. J.* 57. Pp. 42-46.

Thunderhead Engineering. 2008., *PetraSim user manual*, Manhattan 2008, 96 p.

Tournassat, C., Gailhanou, H., Crouzet, C., Braibant, G., Gautier, A., Lassin, A., Blanc, P., & Gaucher, E.G. 2007., Two cation exchange models for direct and inverse modelling of solution major cation composition in equilibrium with illite surfaces. *Geochimica et Cosmochimica Acta* 71 (5). (2007) Ppp 1098-1114.

van Genuchten, M. A. 1980. Closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal* 44. (1980), Ppp. 892-898.

## 7. Acknowledgements

The authors thank KYT2010 Research Programme and VTT for financing the studies reported here. We are also grateful to Mr. Jarmo Lehtikoinen for his comments and our many interesting discussions.