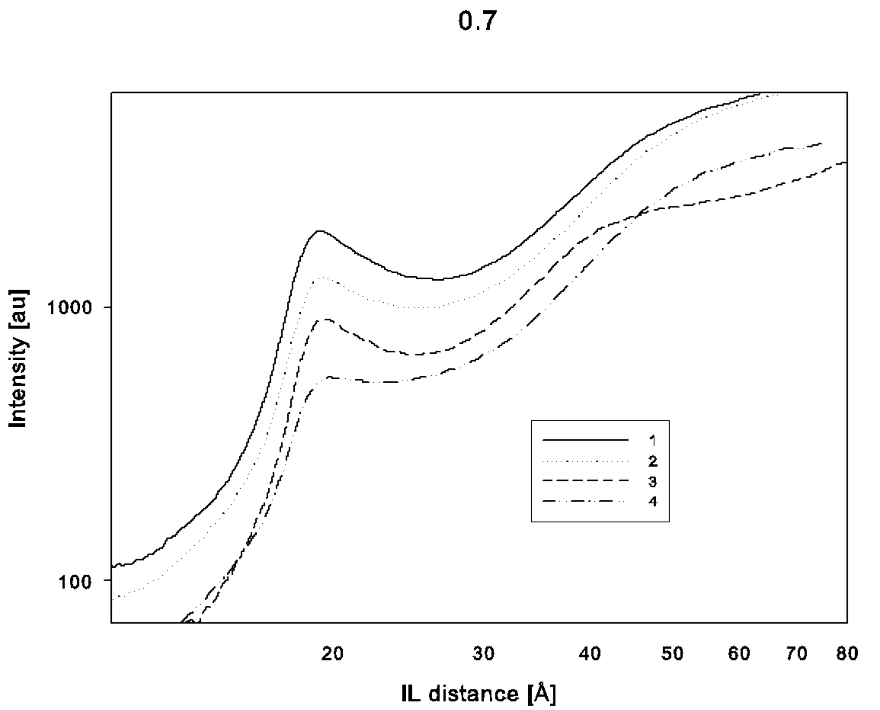
Experiments and modelling & some conclusions from VTT's work

BELBaR workshop 2015, Karlsruhe
Veli-Matti Pulkkanen, Michał Matusewicz & Markus Olin

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement n°295487, the BELBaR project.

CONTENT

- Experimental work
  - Effect of sample preparation
- Modelling
  - New approach
  - Scaling results
- General conclusions
  - Binding together models, experiments and real systems
- Final reporting



Experiments by Michal Matusewicz: Effect of sample preparation

Effects of sample preparation

- Many properties of the MX-80 clay are estimated in the small scale laboratory experiments
  - There are publications in the literature reporting the influence of sample preparation, e.g. ageing or saturation method, on the structure
  - We tested the influence of four different ways of compaction and water saturation on the bentonite structure
- As received MX-80 bentonite (CetCo, UK) was used in this research
- Water saturated samples were investigated at four target dry densities: 0.7, 1.0, 1.3 and 1.5 g/cm^3

Sample preparations tested

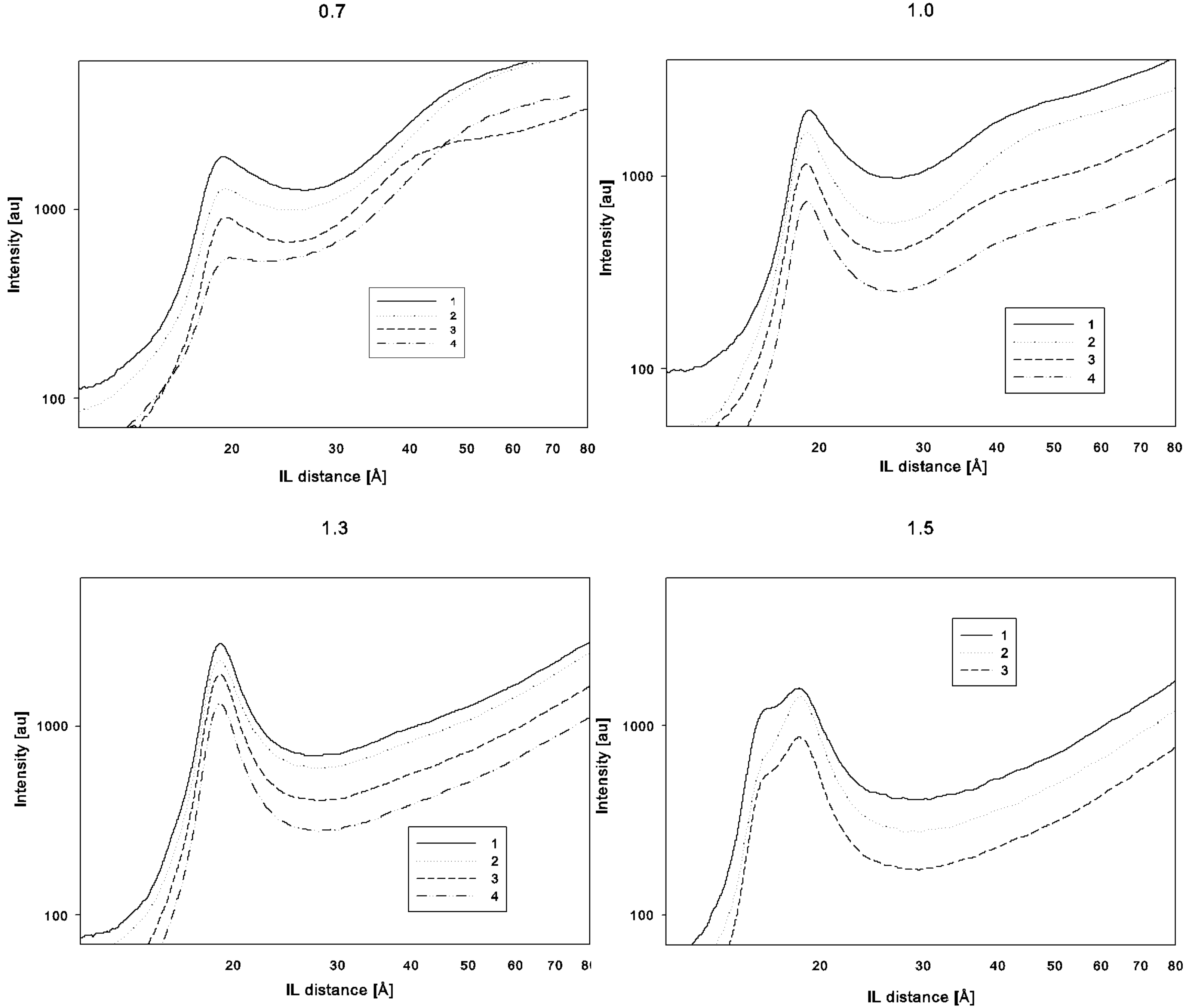
1. Air-dry clay is compacted to the target density if required and saturated with Milli-Q water in confined volume
2. Air-dry clay is compacted to approximately 1.8 g/cm^3, saturated with Milli-Q water and let to swell to the target density
3. Air-dry clay is compacted to approximately 1.8 g/cm^3, saturated with 0.1M NaCl solution and let to swell to the target density
4. Milli-Q water saturated clay at 1.6 g/cm^3, dry density is let to swell to the target density.
   - Cylindrical samples (2 cm in diameter, 1 cm high) were placed in stainless steel equilibration cells.
   - Contact with water or salt solution was ensured through sinters confining the bases of the pellet. Samples were compacted uniaxially directly to the equilibration cells.
   - Equilibration time of the samples was around 45-55 days.

Test methods

- The samples for SAXS measurements
  - were probed with stainless steel cylindrical cutter 4 mm in diameter and cut into 0.3 mm slices.
  - Slices were closed in metal rings sealed tightly with thin plastic film to prevent drying during the measurement.
  - All the sample preparation was carried out in a chamber with controlled relative humidity of around 80%.
- The X-rays were generated with X-ray tube with Cu-anode (PANalytica, Almelo, the Netherlands).
  - The X-ray beam was collimated and monochromated to Cu-Kα radiation (1.54 Å) using a Montel-multilayer mirror.
  - The scattered X-rays were recorded using a Bruker Hi-Star area detector.

Results

- The differences between the samples were much more pronounced in case of the 0.7 and 1.0 g/cm^3 samples than for the denser samples. Differences practically disappeared for 1.3 g/cm^3 samples and minor ones appeared between 1.5 g/cm^3 samples.
- The variations can be seen both for the 001 peak, suggesting different size of the montmorillonite stacks and inter-lamellar distances, as well as in the Porod region, suggesting different arrangement of clay particles.
- However, it is difficult to find a general trend connecting the sample preparation procedures with obtained X-ray scattering curves.

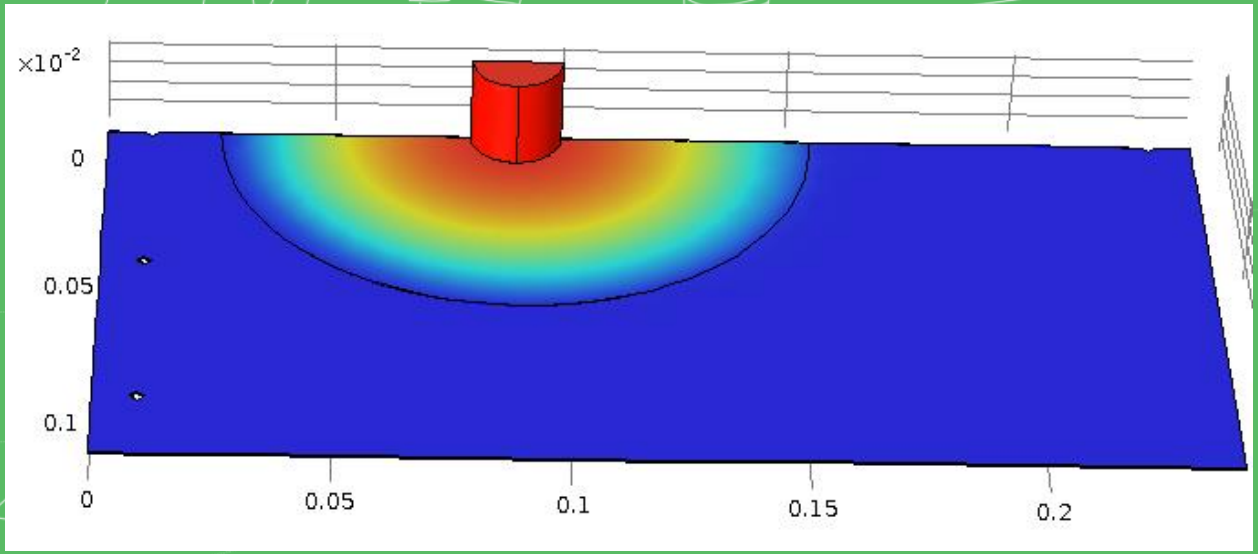


Scattering curves from the clay samples grouped by density. Numbers in legends refer to the sample preparation ways as described in the Materials and Methods part.

CONCLUSIONS Experiments

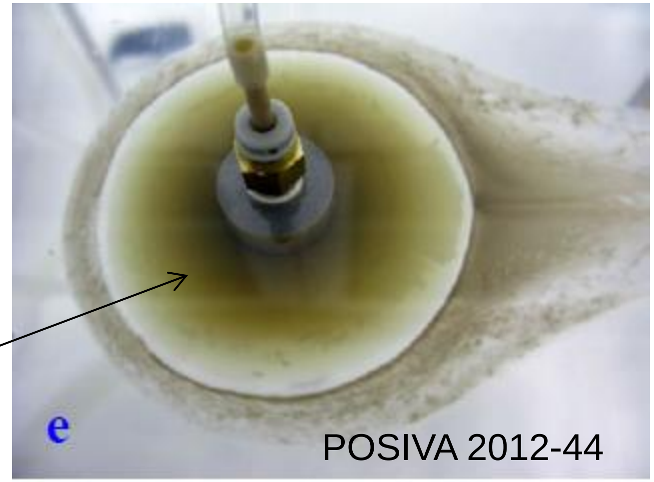
- It has been shown that different treatment of the bentonite samples can lead to different structural features, which can possibly influence properties of bentonite, e.g. in diffusion experiments.
- However, further systematic research is needed to link and characterize the relation between different preparation procedures and resulting differences in the clay structure.

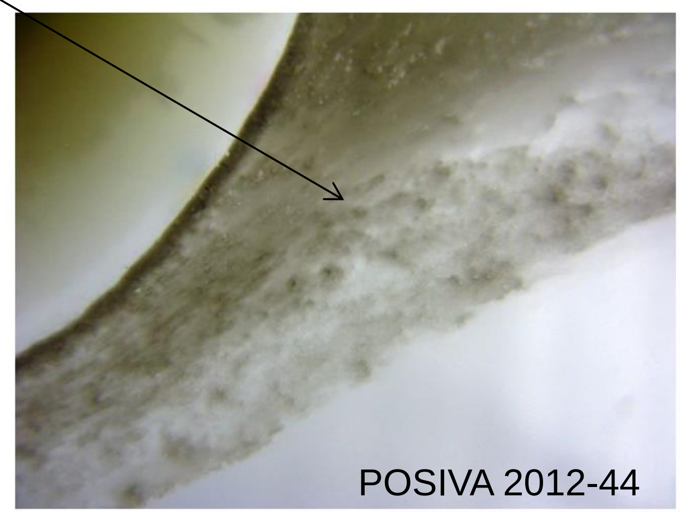
Modelling by Veli-Matti Pulkkanen: New ideas



Background

- Model parts
  - Swelling of bentonite from solid to gel
  - Breakdown to colloids (or larger particles) and transport of them





Model concept

- Water flow in the fracture
  - No flow through the gel
  - Water can flow through the colloid mass (Brinkman flow)

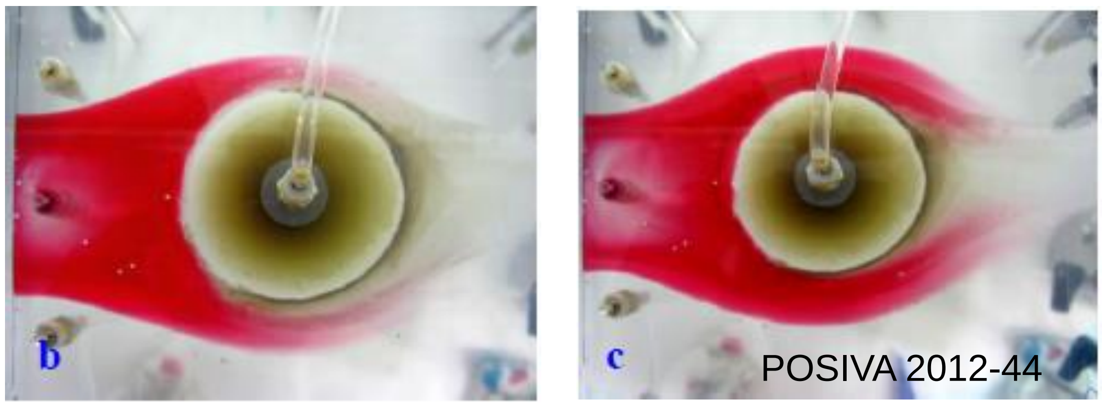
- Diffusion of NaCl (or other salts) from bentonite

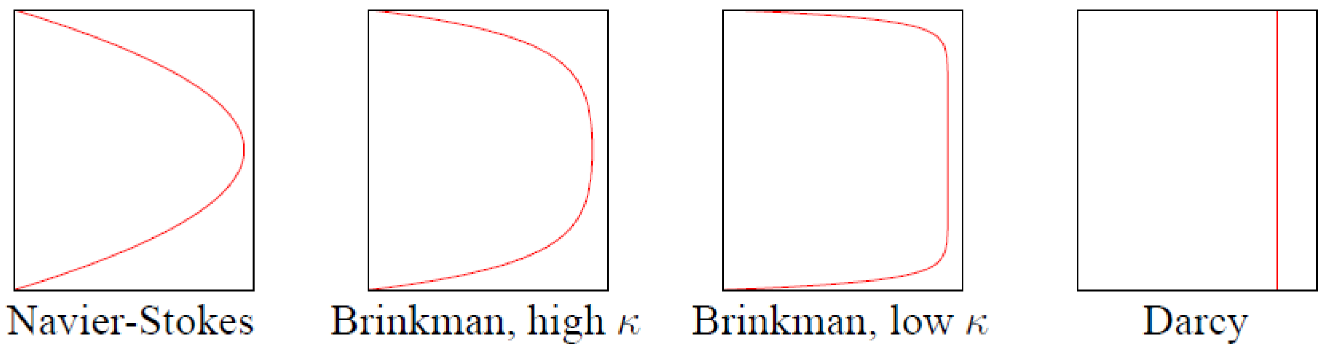
- Na concentration < CCC in bentonite
  - Structure breaks down: from gel to mobile colloids

- Initial state: bentonite (solid-gel) density distribution
  - From experiments or from swelling modelling
  - No swelling of bentonite modelled

Model components

- Flow of water
  - Stokes-Brinkman equations: Stokes + effect of porosity
  - 3D flow profile



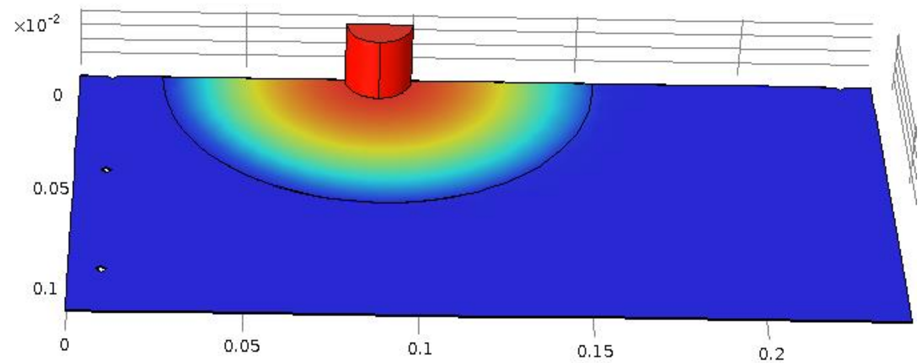


Model components

- Movement of Na
  - Diffusion + advection
  - Diffusion coefficient from “Neretnieks’ model”

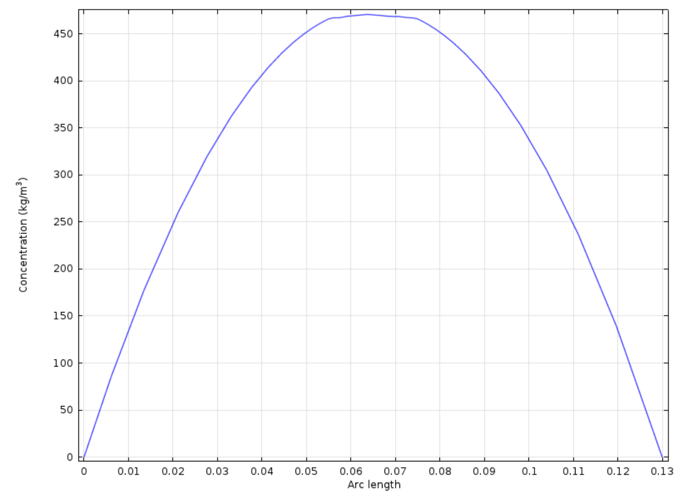
- Movement of colloids
  - Diffusion + advection
  - Mobility depends on Na concentration

Demonstration 1



- Geometry
  - Artificial fracture (POSIVA 2012-44)
  - 1 mm aperture
  - Bentonite sample: diameter 2cm, height 2.1 cm

- Initial state
  - Non-saline water in bentonite (no Na in model)
    - Colloids mobile
  - Parabolic bentonite density distribution
    - 6 g of bentonite in cylinder
    - 3 g of bentonite in the fracture (radius 6.5 cm)

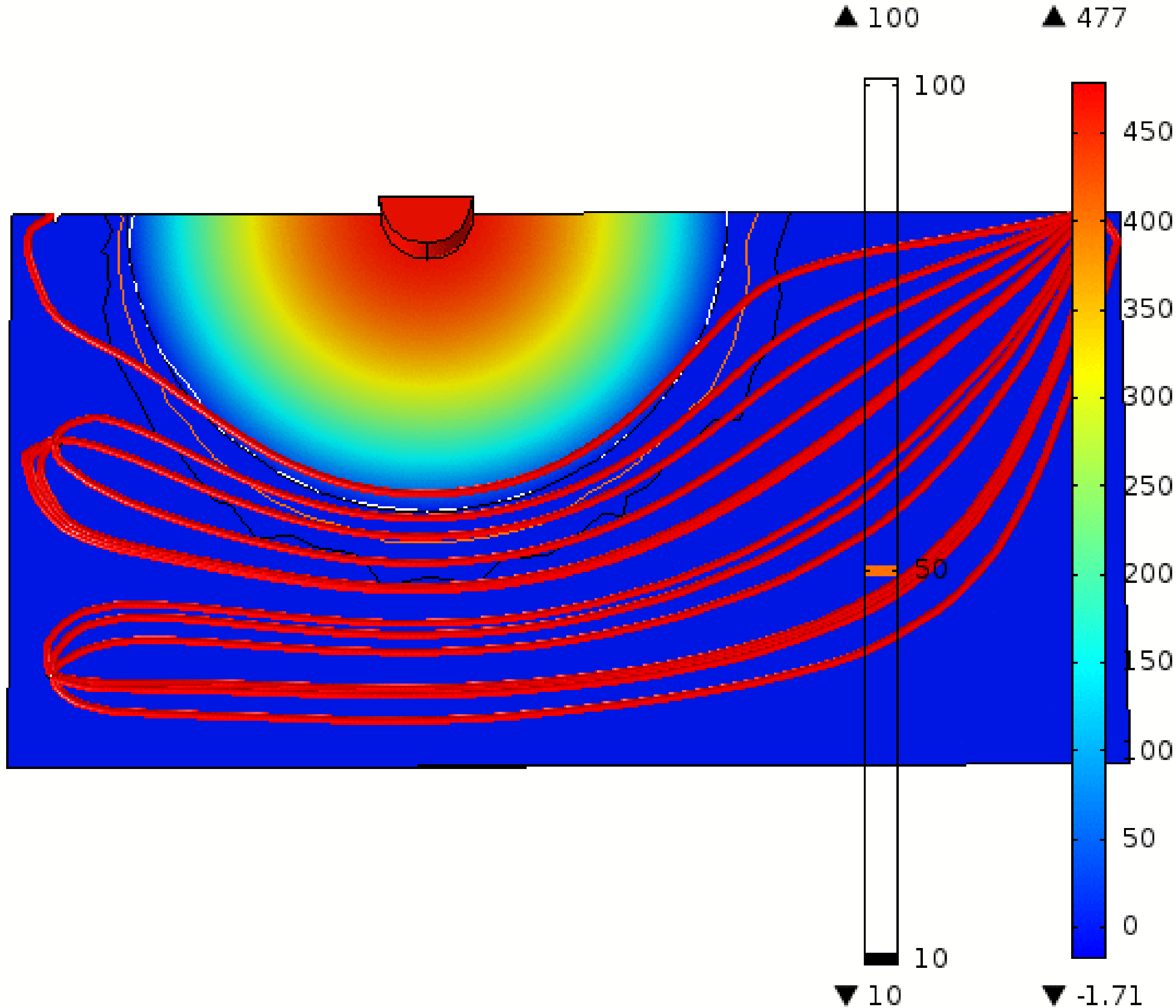


Demonstration 2

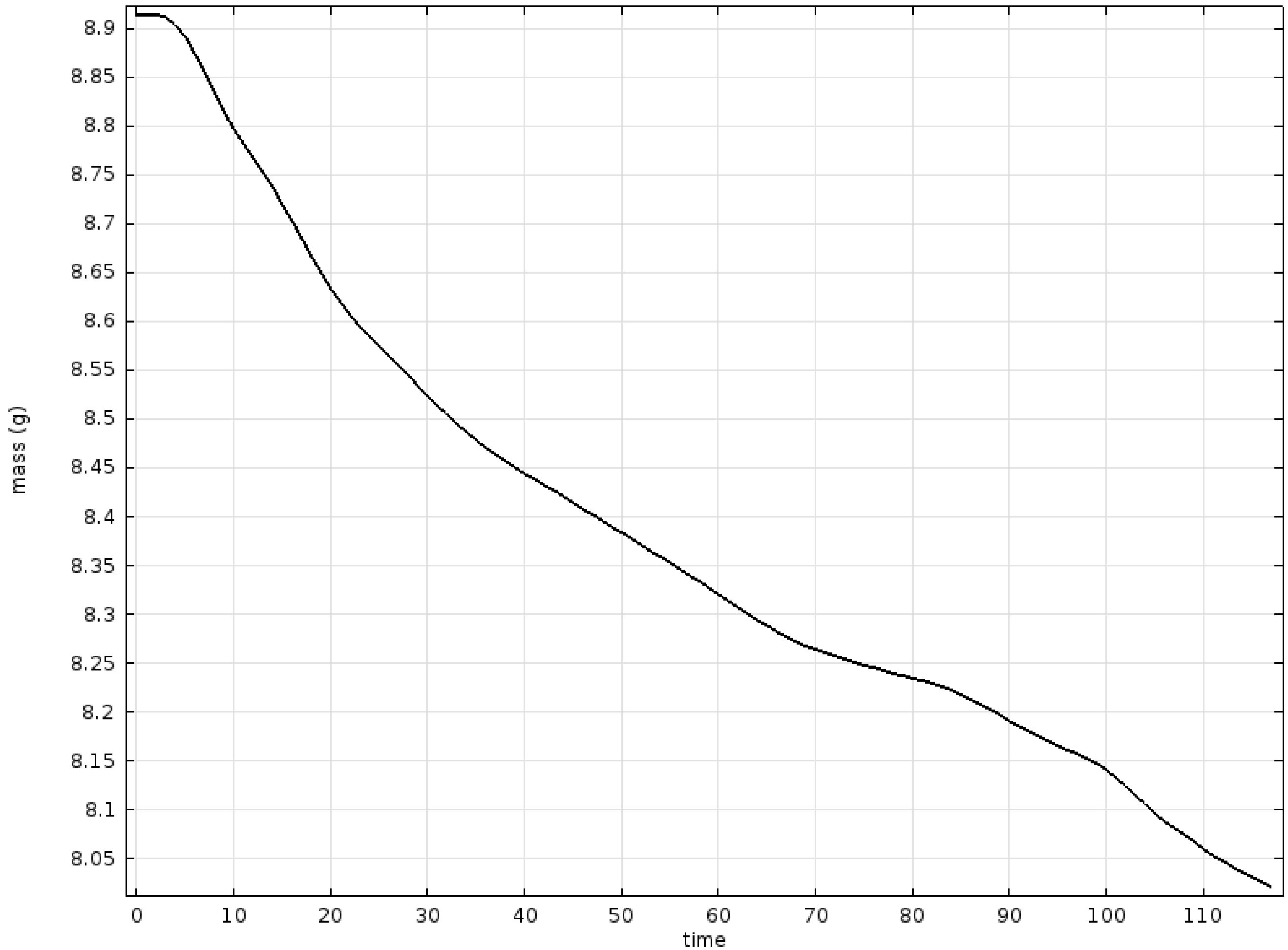
- Geometry
  - Same as in demonstration 1

- Initial state
  - Saline water in bentonite (0.2 mol/l)
    - Colloids become mobile when $c < 0.05$ mol/l
  - Parabolic density distribution of bentonite
    - 6 g of bentonite in cylinder
    - 3 g of bentonite in the fracture (radius 6.5 cm)

Demonstration 2: preliminary results



Demonstration 2: preliminary results



Conclusions

- The concept and just the very first results presented

- Improvement of quality of the solution
  - Moving boundary is now available
  - Better spatial resolution (= denser mesh)

- Parameters need to be updated

- The hoped final outcome: erosion rate estimates in different conditions (CCC varied, etc.)

Plan for the rest of BELBaR

- Development of the swelling model (solid and gel) continues
  - Veli-Matti Pulkkanen is at Aalto University from August to December

- Breakdown & colloid transport
  - Merja Tanhua-Tyrkkö and Markus Olin try to develop model approach suitable for COMSOL modelling

Trial functions

$$D_{\mathrm{F}}(\phi,c) = D_{\mathrm{F}}^{\mathrm{l}} \cdot \left(\frac{D_{\mathrm{F}}^{\mathrm{h}}}{D_{\mathrm{F}}^{\mathrm{l}}}\right)^{\alpha(\phi,c)} + D_{\mathrm{F}}^{\mathrm{c}}$$

$$\alpha = \alpha(\phi,c) = \left(1 + \left(\frac{\ln\phi}{\ln\phi_{\mathrm{critical}}}\right)^{n}\right)^{-1}$$

$$\phi = 1, \alpha = 1$$

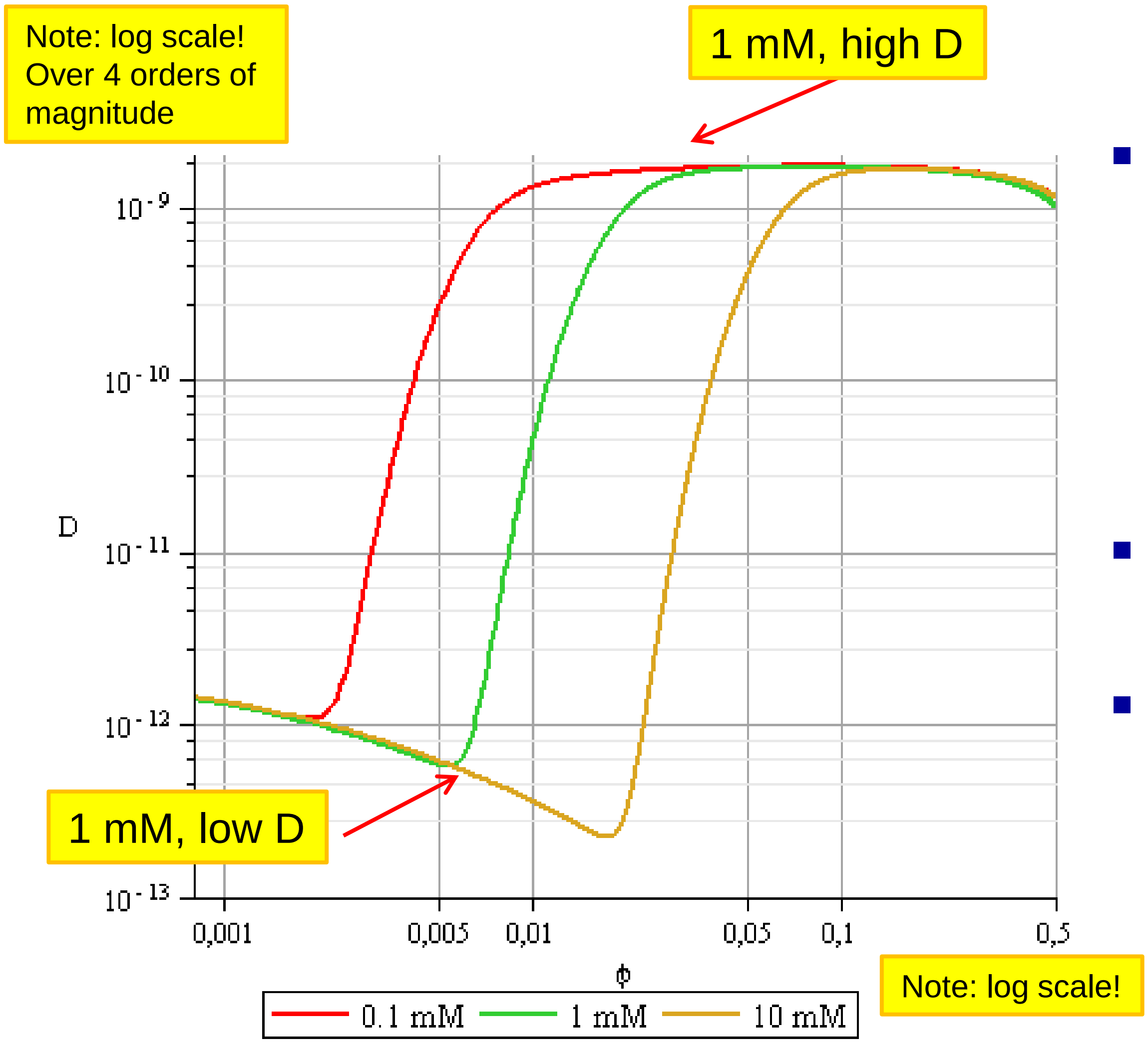
$$\phi \to 0, \alpha \to 0$$

$$\phi_{\mathrm{turning}} = Ac^{b} \cong 0.01\sqrt{c}$$

$$\alpha = \alpha(\phi,c) = \left(1 + \left(\frac{\ln\phi}{\ln A + b\ln c}\right)^{n}\right)^{-1}$$

Modelling by Markus Olin: Scaling results

Bentonite expands by non-linear "diffusion"



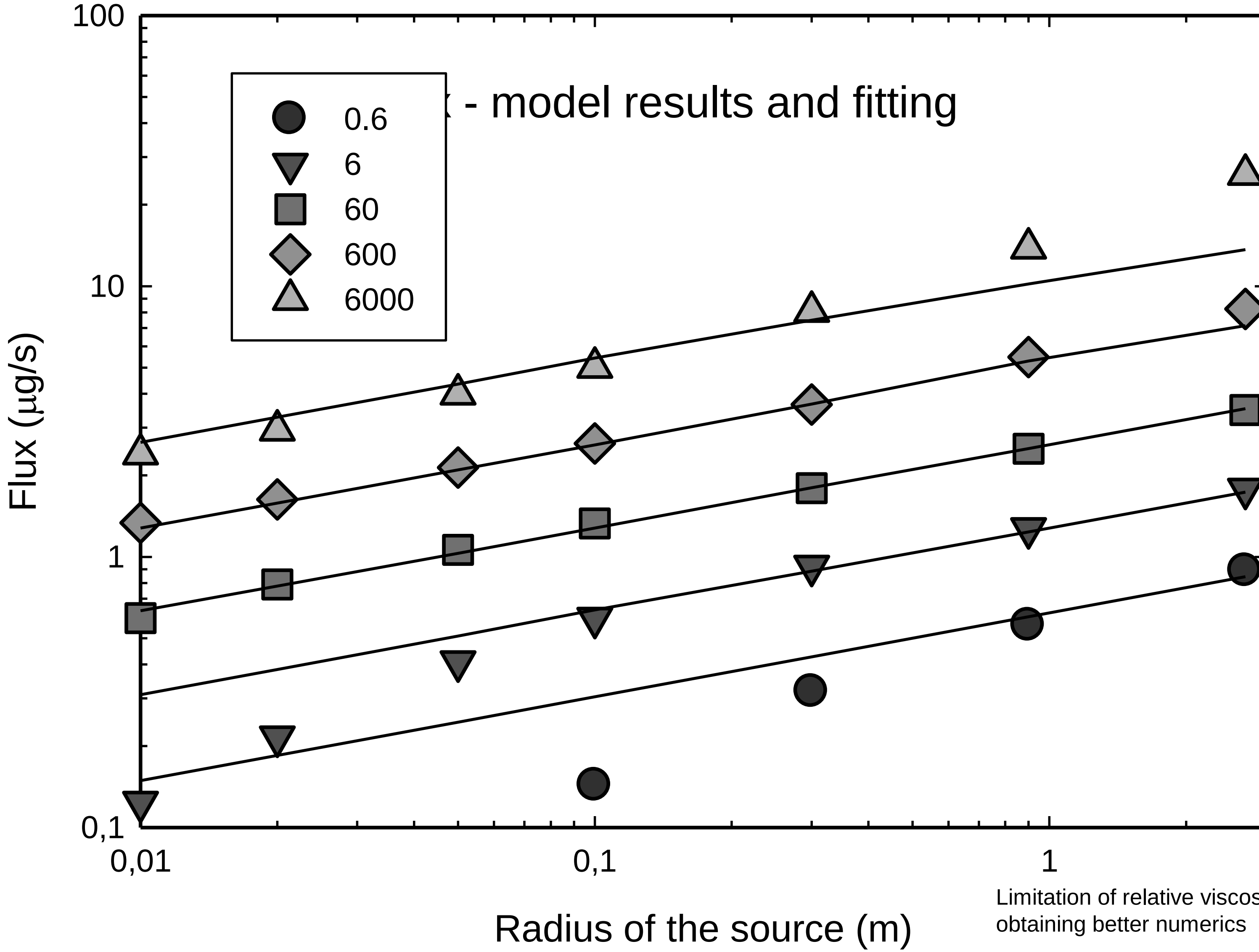
- Non-linear: diffusivity of bentonite depends on volume fraction of bentonite (or montmorillonite), ϕ
- At 1 mM solution
  1. High diffusivity (like ions in free water) above $\phi \approx 0.040$
  2. Low (more than three orders of magnitude, like colloids) diffusivity below $\phi \approx 0.006$
- By decreasing salinity dropdown changes to lower values of ϕ
- However, at low ϕ values groundwater flow starts to be an important transport mechanism → erosion of bentonite

Observables and parameter space

- Observables:
  - Flux (or flux density), Q, and
  - Penetration depth, L
- Parameters
  - Boundary value, φ_b
  - Salinity, c,
  - Geometry, radius R
  - Diffusivities, D
  - Velocity, v
- Simple dimensional analysis (Péclet number = Pe)
  - $Q=Q(\varphi_b,c,R,D,v)=Q_0\times F(R\times v/D)\times G(\varphi,c)\approx F(Pe)$
- Computed by varying R and v, and in some cases c

Q as a function of *R* and *v*: $Q=0.73\times(v\times R)^{0.31}$

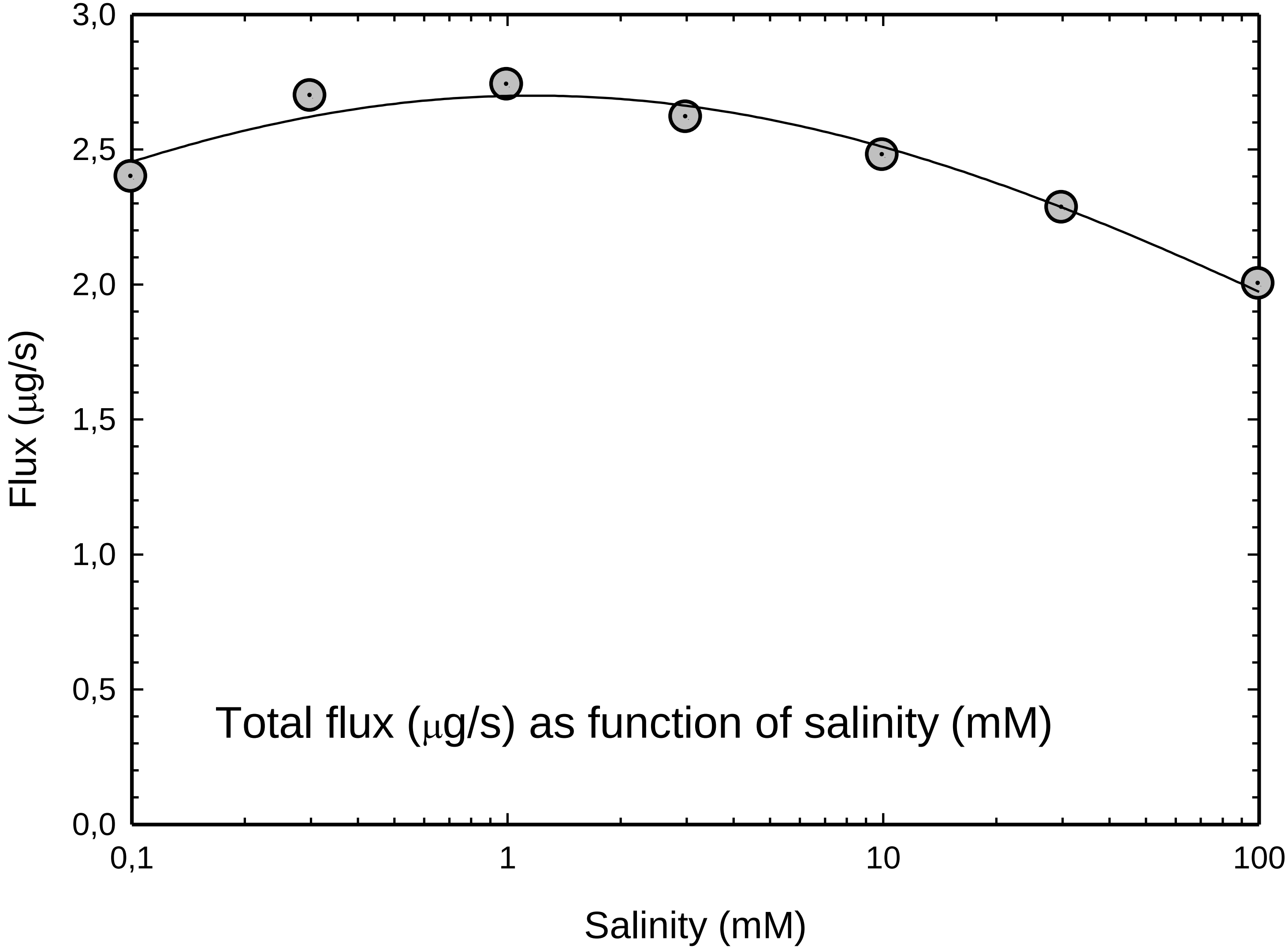
- Fitting deviates at high and low velocity



Limitation of relative viscosity, 700 or 45 000, for obtaining better numerics

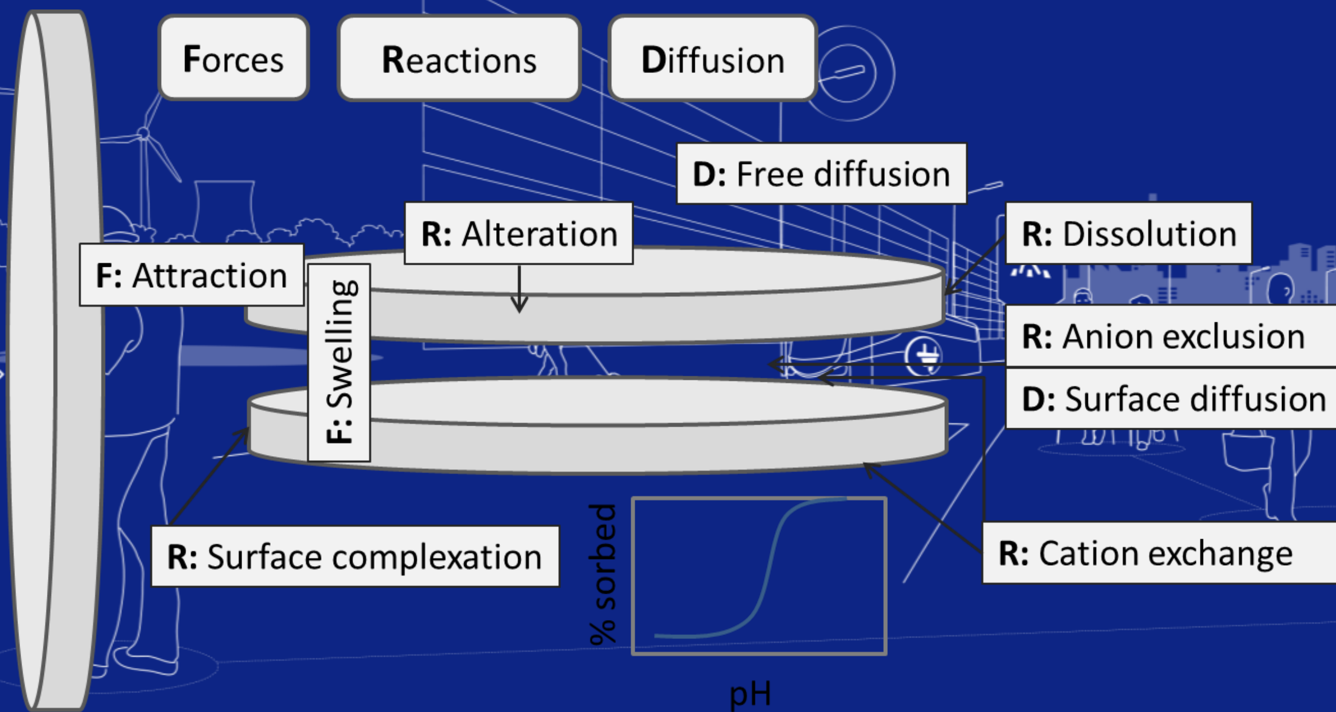
Almost no salinity effects

- *R* = 0.01 m, *v* = 6 000 m/a



Conclusions

- At least for VTT, the solution of Neretnieks' original model is still hard task
- If analytical formula applied, the modelling is possible at constant salinity
- Simple analysis show that model predicts "erosion" even in saline conditions
- Moving boundary solvers with dense grid on the interface hopefully available for this model, too



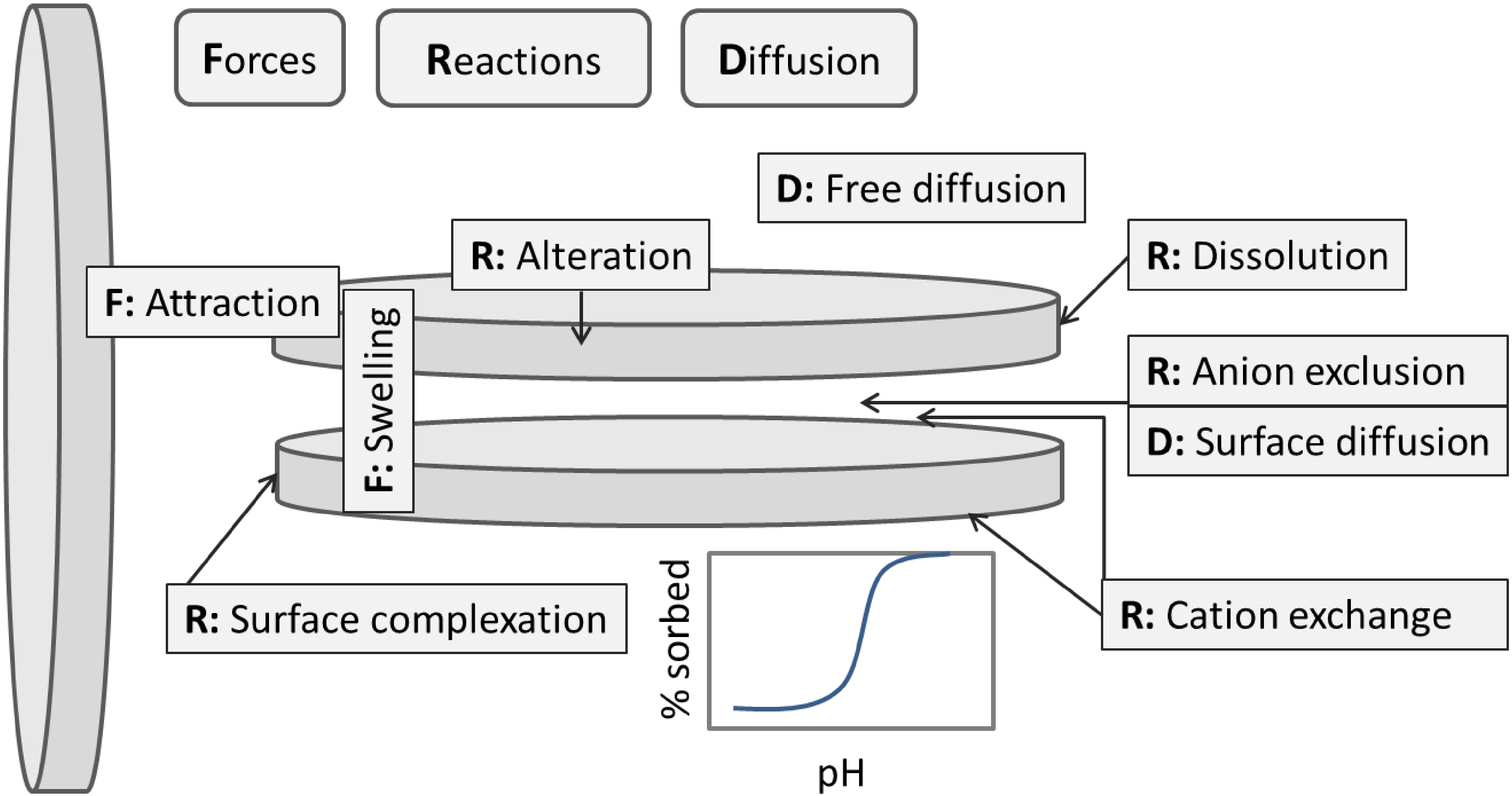
CONCLUSIONS and FINAL REPORTING

CONCLUSIONS

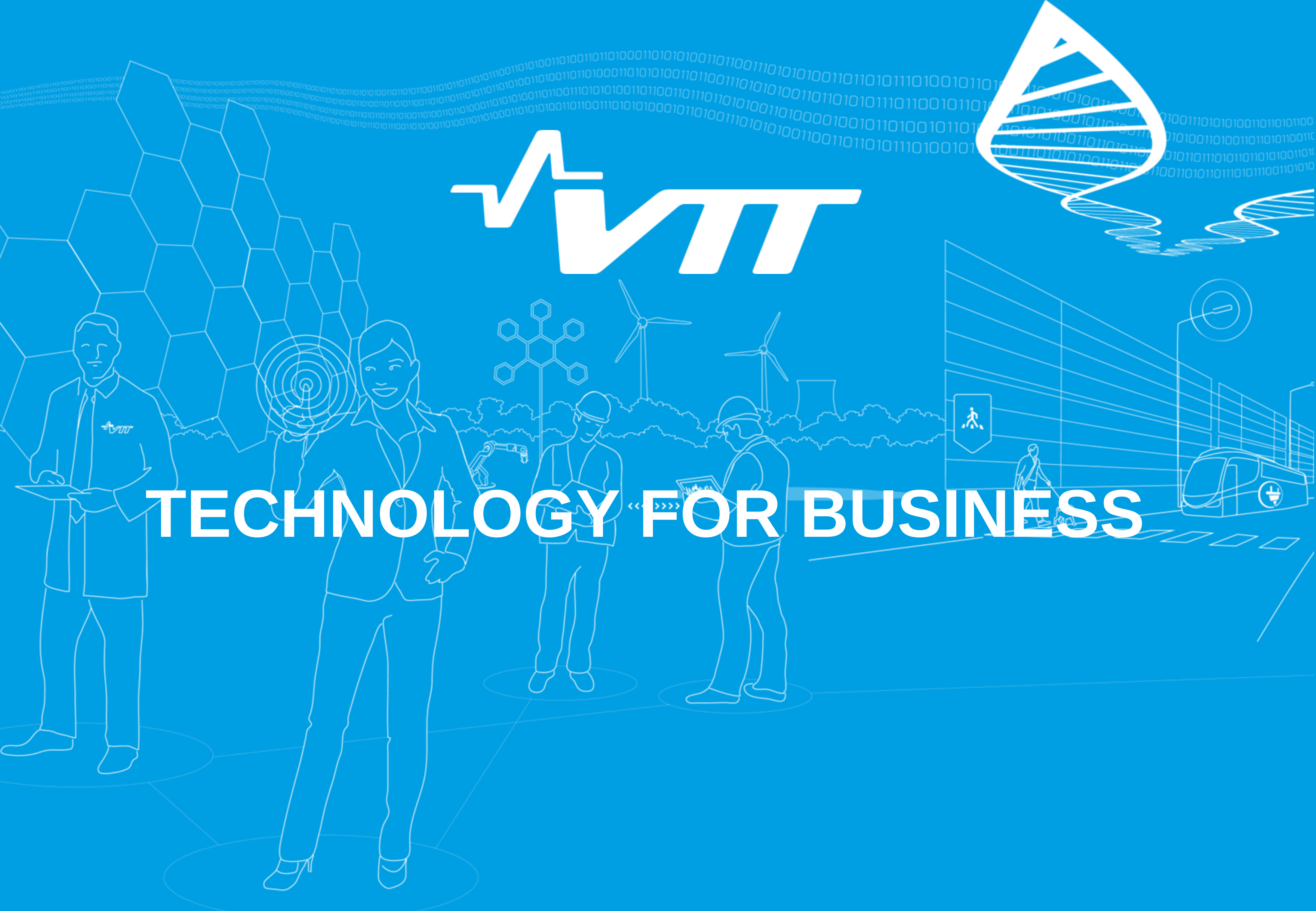
- Models, experiments and real systems: Differences between
  - models and experiments
    - Initial swelling in experiments even when the samples are totally wetted
    - Some model for swelling needed to take care of that
  - models and real systems
    - Scaling possible, if the model describes reality, but how to obtain that good models
  - experiments and real systems
    - In reality bentonite is very old, when erosion starts
    - Scaling difficulties both spatial and temporal

FINAL REPORTING COMMENTS

- Formulate the issues important for long-term safety assessment
  - Scaling of experimental results to real conditions
- Identify main uncertainties related to colloids in safety assessment
  - Which processes are really happening in repository's future?
- Bentonite erosion and production of colloids (WP2)
  - Colloid formation on interface between bentonite and water – colloidal diffusion is pretty slow and therefore water flow may have very important role: detailed know-how of water flowing in just colloid formation state is still lacking
- Improvements to models (WP5)
  - Some advances have been done
  - VTT's new COMSOL model is a simplified concept including moving boundaries



Forces
Reactions
Diffusion
D: Free diffusion
R: Alteration
R: Dissolution
F: Attraction
F: Swelling
R: Anion exclusion
D: Surface diffusion
R: Surface complexation
R: Cation exchange
% sorbed
pH


TECHNOLOGY FOR BUSINESS