

Sulphide induced stress corrosion cracking of copper

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Business from technology

BACKGROUND-1

In 2007 a Japanese research group reported that copper is susceptible to stress corrosion cracking in sea water with sulphides, with minimum tested $[S^{2-}] = 70 \text{ mg/l}$.

Sulphides may come to contact with the copper canister surface through three different processes:

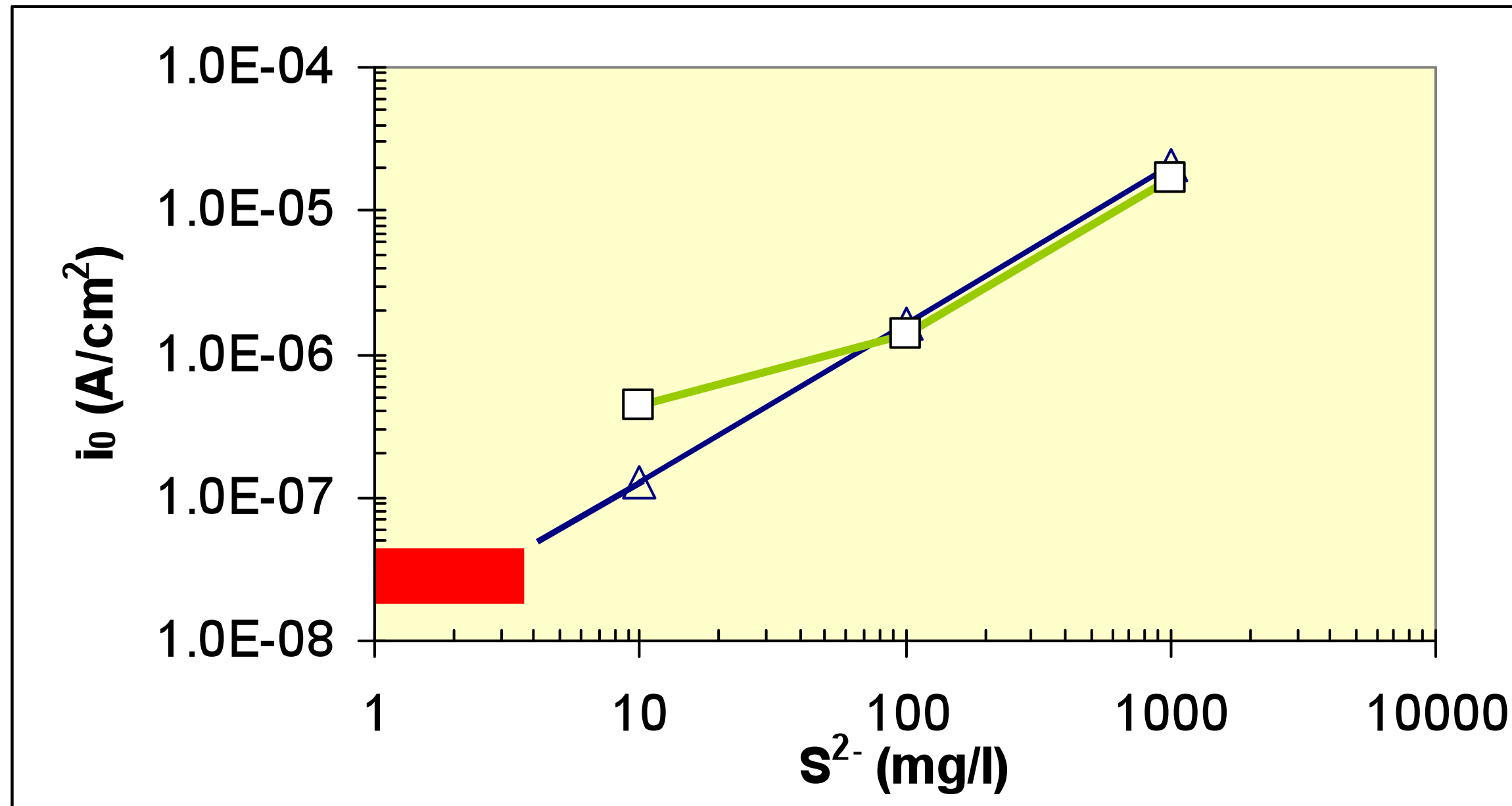
- 1) transport via groundwater flow (typically $[S^{2-}] = 1\text{-}3 \text{ mg/l}$),
- 2) production at the bentonite/rock interface via sulphate reducing bacteria (SRB) and further transport (unknown $[S^{2-}]$) and
- 3) through SRB activity within bentonite (e.g. pyrite reduction), $[S^{2-}]$ depending on bentonite density.

BACKGROUND-2

A project was started at VTT in 2009 within the KYT2010 research programme to further study this area. The goals of the project are:

- Evaluate the maximum sulphide concentration which can form at the bentonite/rock interface because of SRB activity.
- Develop a diffusion model and make a quantitative estimate of the sulphide concentration reaching the surface of the copper canister in three different scenarios.
- Develop an experimental arrangement for SCC tests in sulphide containing groundwater.
- Determine experimentally the minimum concentration of sulphide in groundwater which can cause SCC in pure copper (CuOFP).

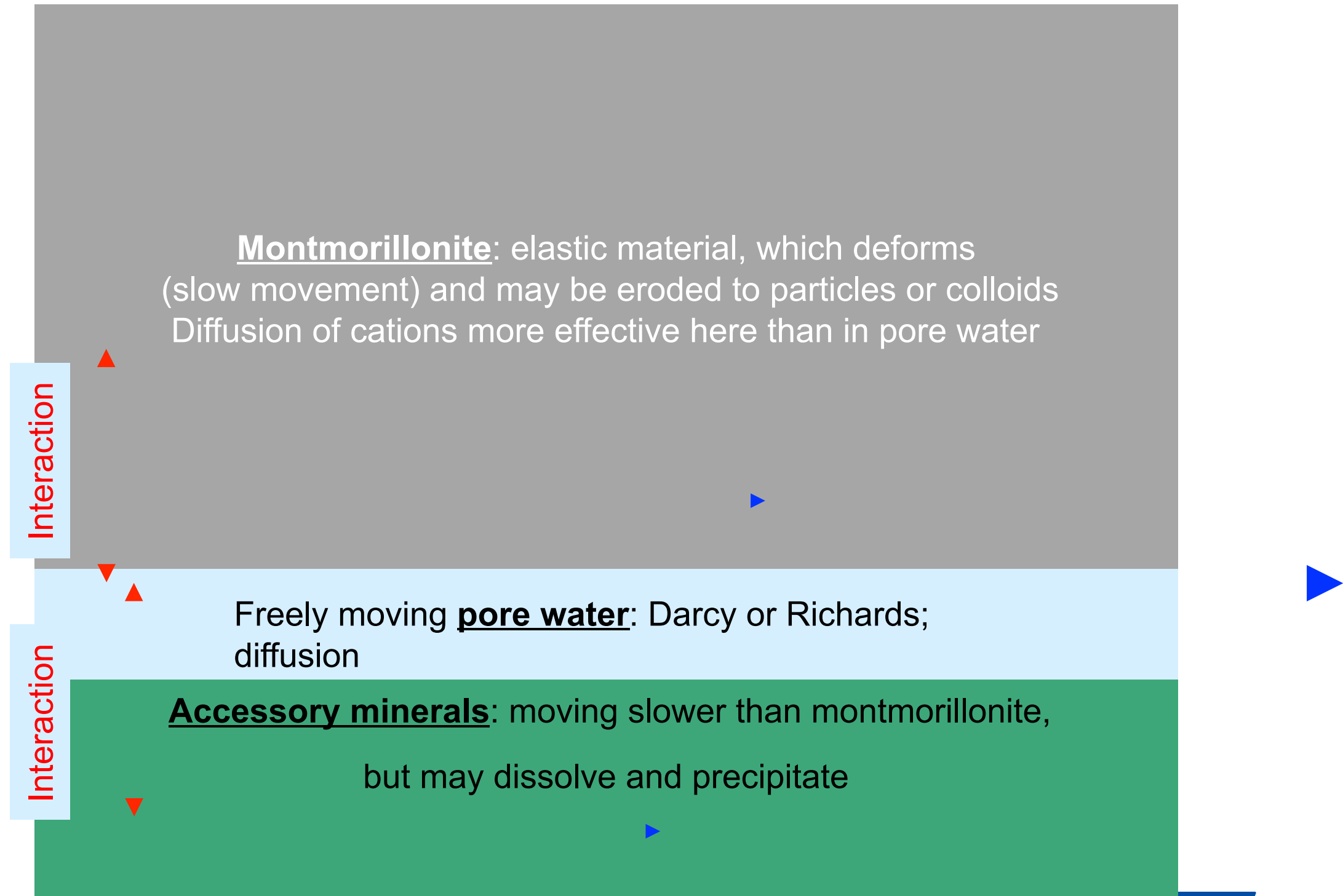
BACKGROUND-3



Exchange current density as a function of sulphide concentration.
Triangles = Tafel data, squares = EIS data. The red bar marks the exchange current density measured without sulphide.

DIFFUSION MODEL CONCEPT

- All components are transporting: either directly or indirectly
- Time scales are very different for the important processes



Results : Sulphide diffusion

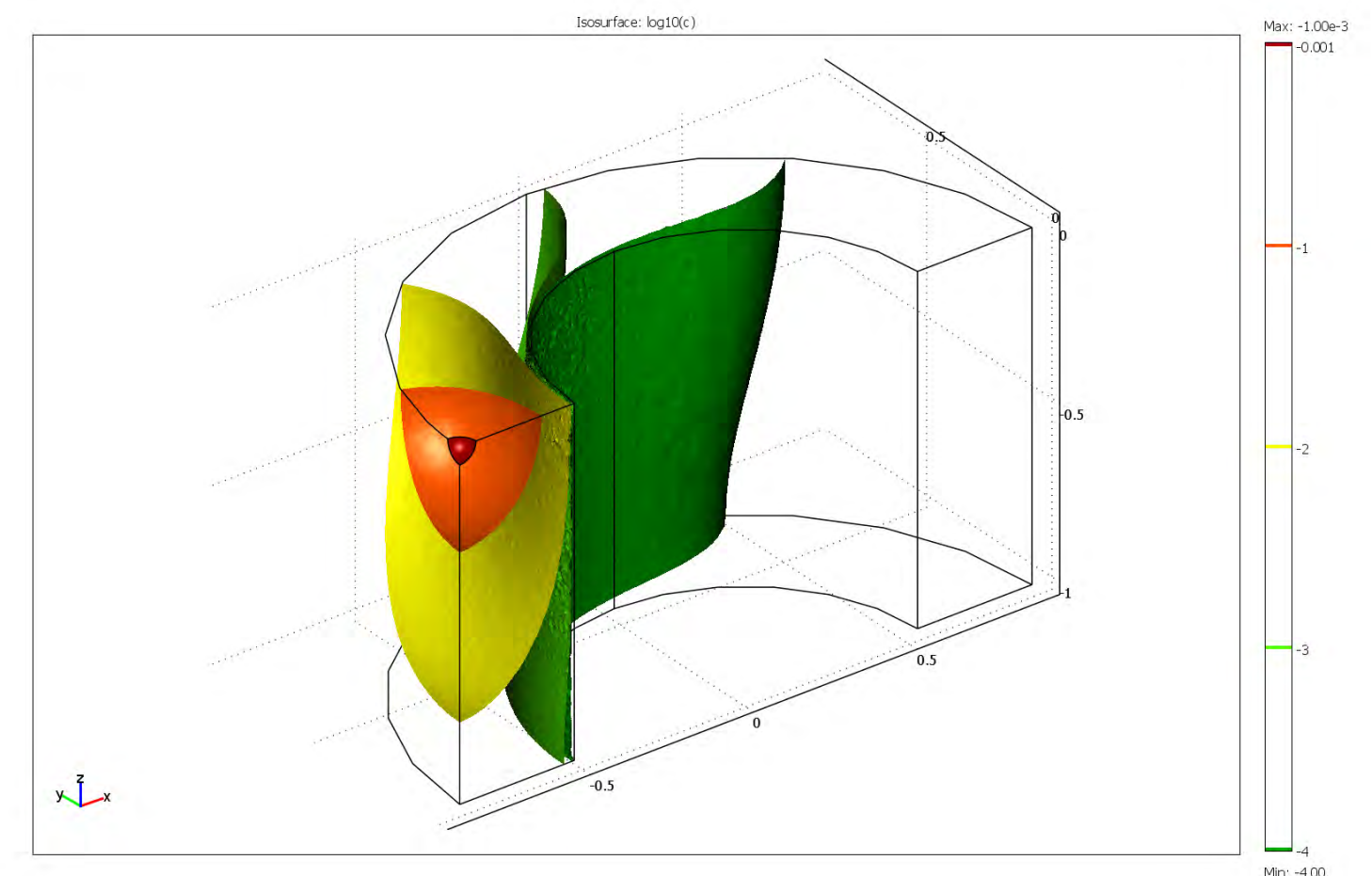
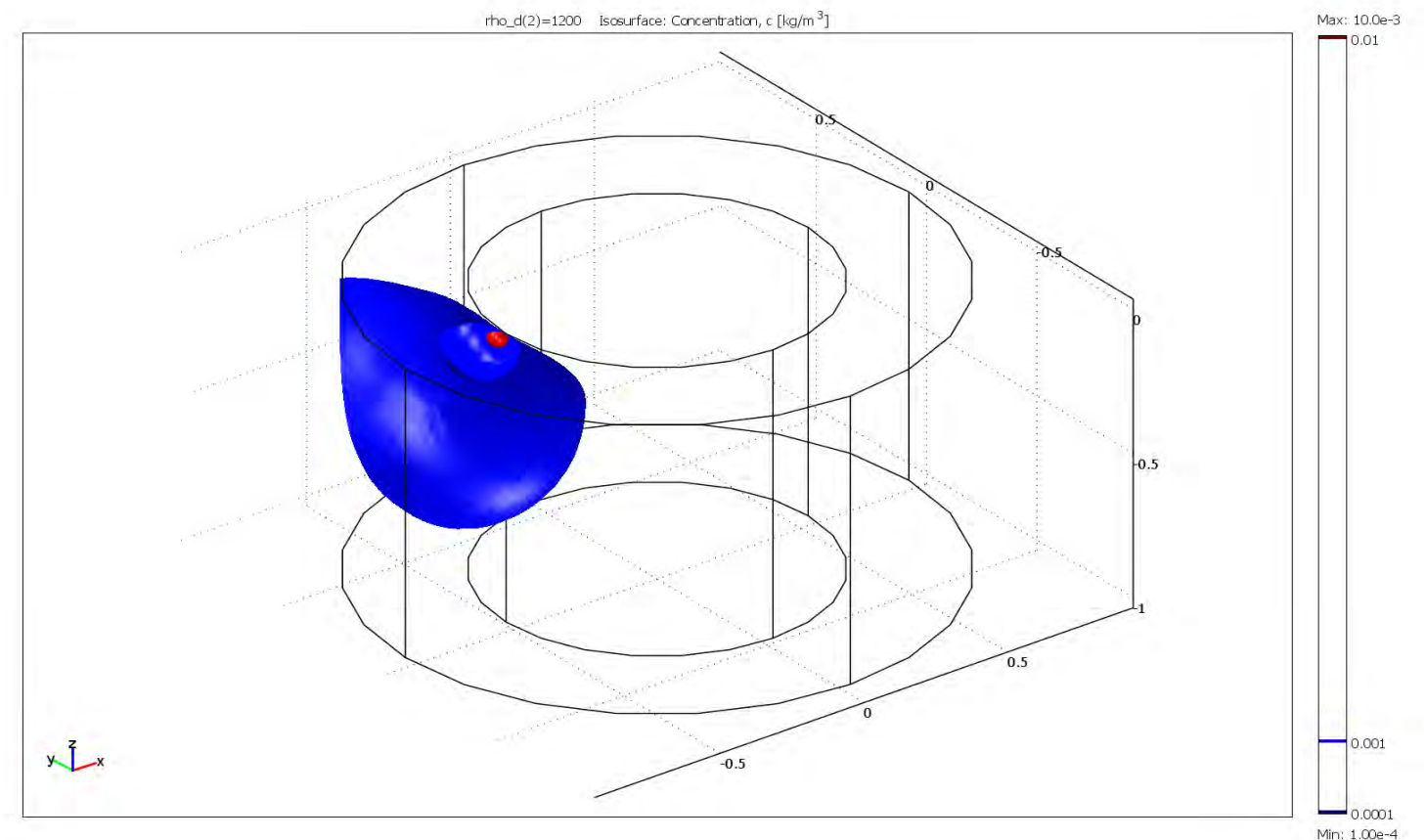
- Diffusion flux in bentonite for anions is given by Fick's first law
- Effective diffusivity D_e is a product of the anion exclusion correction v , the porosity Φ , the geometric factor G and diffusivity in free water D_w
- Ochs & Talerico (2004) give experimental fitting as a function density
- Preliminary relative concentration iso-surfaces for case S1 (top) and S2 to (below)

$$j = -D_e \frac{\partial c_w}{\partial x} = -v\phi G D_w \frac{\partial c_w}{\partial x}$$

$$D_e = D_e^0 \left[b_3 \left(\frac{\rho_d}{\rho_0} \right)^3 + b_2 \left(\frac{\rho_d}{\rho_0} \right)^2 + b_1 \frac{\rho_d}{\rho_0} + b_0 \right]$$

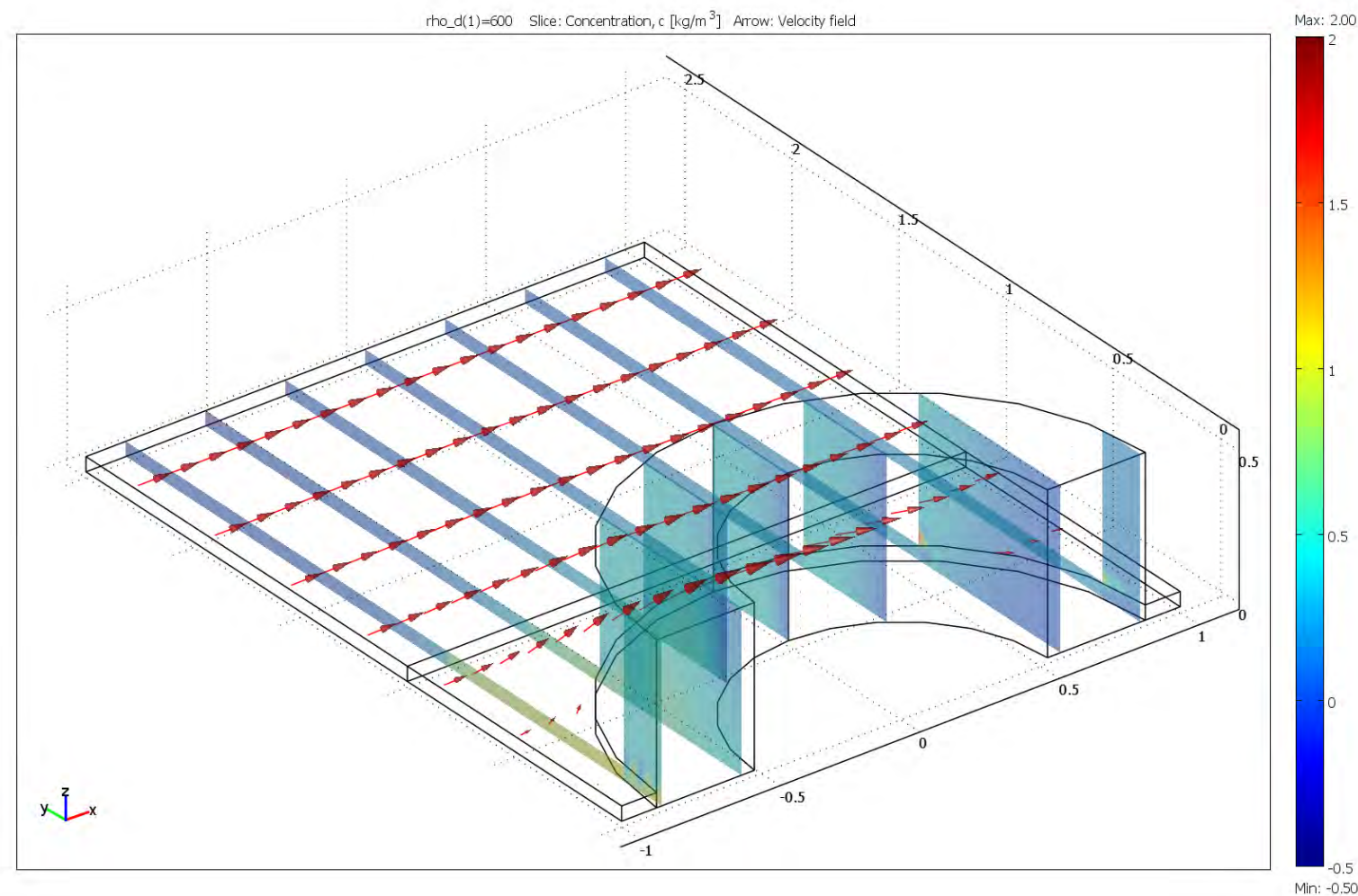
$$\begin{cases} b_0 = 16.167 & D_e^0 = 1 \cdot 10^{-11} \text{ m}^2/\text{s} \\ b_1 = -30.962 & \rho_0 = 1590 \text{ kg/m}^3 \\ b_2 = 20.553 \\ b_3 = -4.7609 \end{cases}$$

Ochs, M., Talerico, C. Data and uncertainty assessment. Migration parameters for the bentonite buffer in the KBS-3 concept. SKB TR-04-18 (2004)



Results : diffusion+advection

- Diffusion-advection equation
- Flow velocity from Darcy's law – water conductivity depends on bentonite density
- Top: geometry, flow velocity arrows, and concentration surfaces
- Down: concentration profile, 1 m near the canister, density varies



$$\nabla \cdot (\phi G D_p \nabla c - \mathbf{u}c) = 0 \quad \text{in } \Omega$$

$$c = c_0 \quad \text{on } \partial\Omega_{\text{inlet}}$$

$$c = 0 \quad \text{on } \partial\Omega_{\text{copper}}$$

$$\mathbf{n} \cdot (-D_e \nabla c + \mathbf{u}c) = 0 \quad \text{elsewhere on } \partial\Omega \text{ (no flux)}$$

Initial results!
Still numerical Problems!

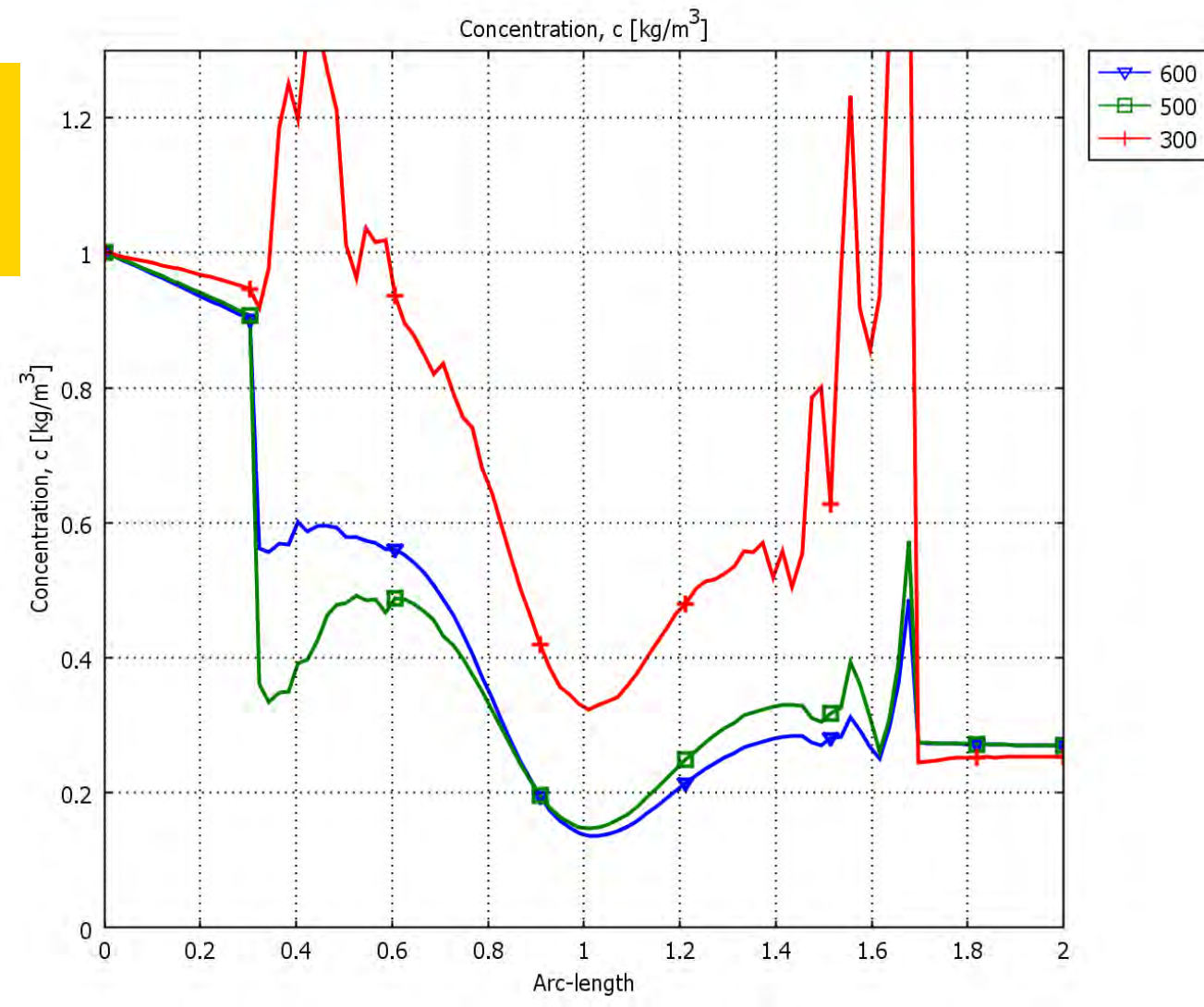
$$\nabla \cdot (k(\rho_d)(\nabla p - \rho \mathbf{g})) = 0 \quad \text{in } \Omega_{\text{flow}} = \{\text{bentonite, rock}\}$$

$$p = P_0 \quad \text{on } \partial\Omega_{\text{inlet}} = \{\text{inlet boundary}\}$$

$$p = 0 \quad \text{on } \partial\Omega_{\text{outlet}} = \{\text{outlet boundary}\}$$

$$\mathbf{n} \cdot \left(-\frac{\mathbf{\kappa}}{\mu} k_r \nabla p \right) = 0 \quad \text{elsewhere on } \partial\Omega \text{ (no flux)}$$

$$k(\rho_d) = k_0 \frac{(1 - \phi_0)^2}{(1 - \phi)^2} \left(\frac{\phi}{\phi_0} \right)^3 = k_0 \left(\frac{\rho_0}{\rho_d} \right)^2 \left(\frac{\rho_s - \rho_d}{\rho_s - \rho_0} \right)^3$$

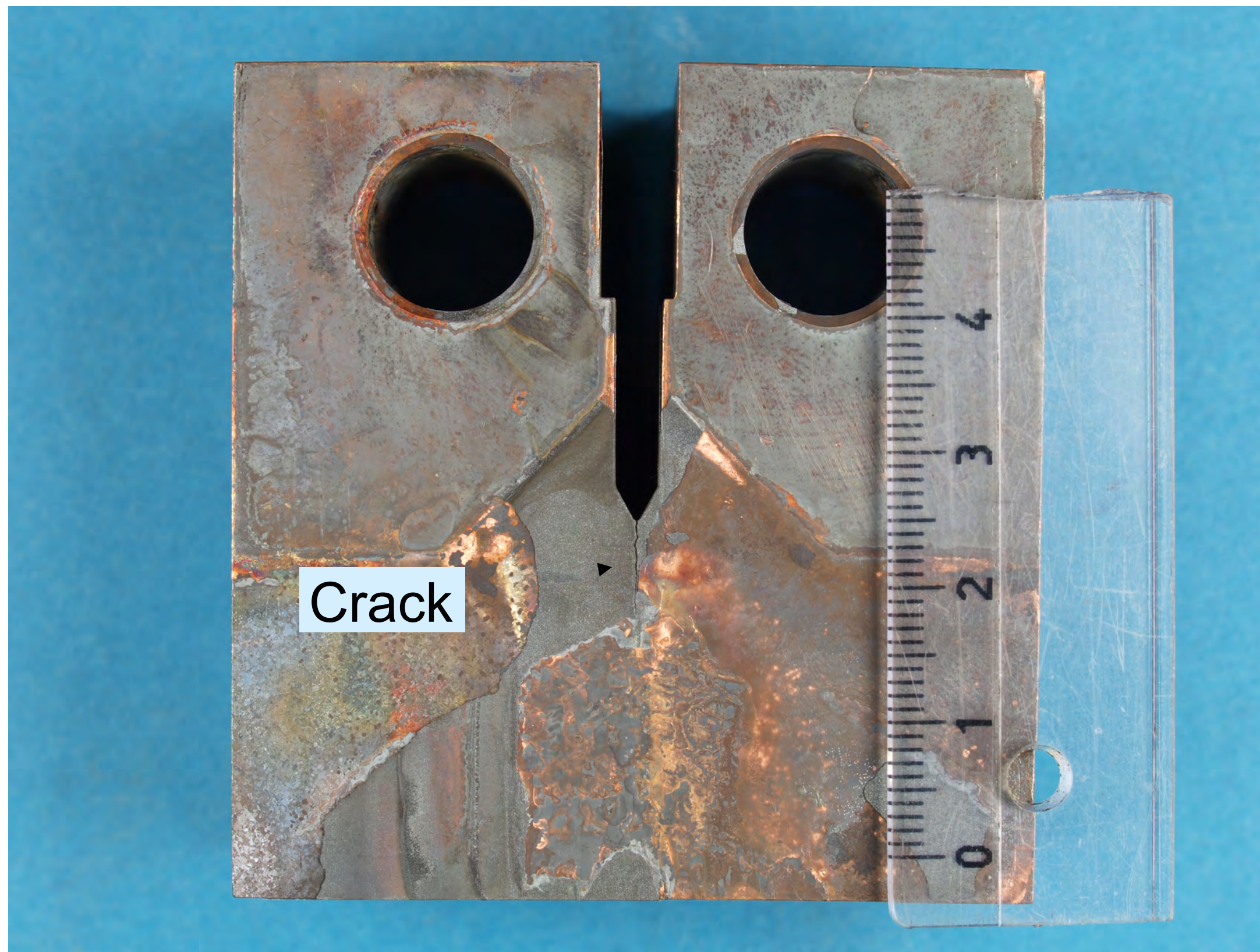


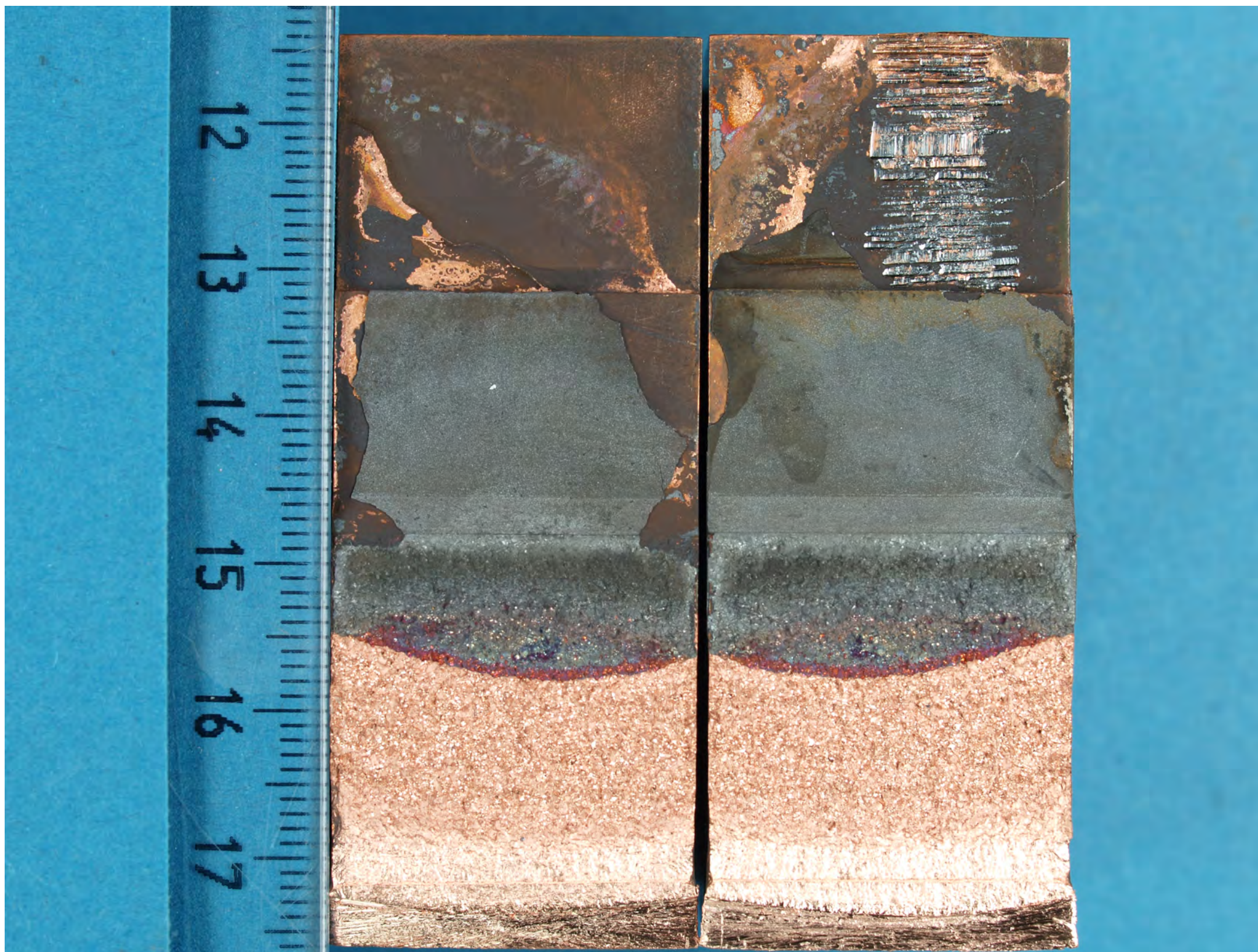
SULPHIDE FROM SRB

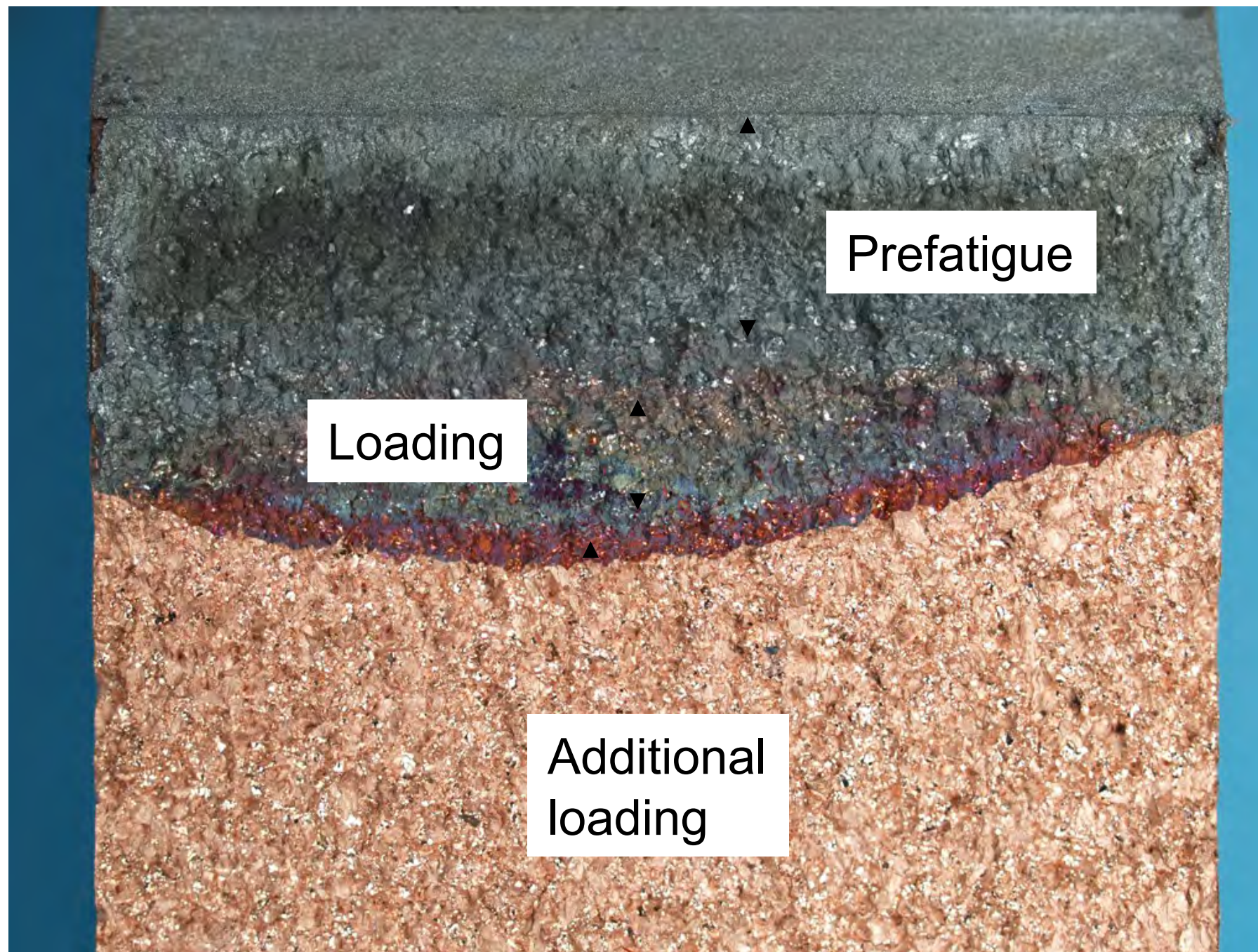
- Literature survey underway
- Preliminary result: SRB can produce $[S^{2-}] = 400...450$ mg/l.
- The size of SRB population depends on available nutrition.

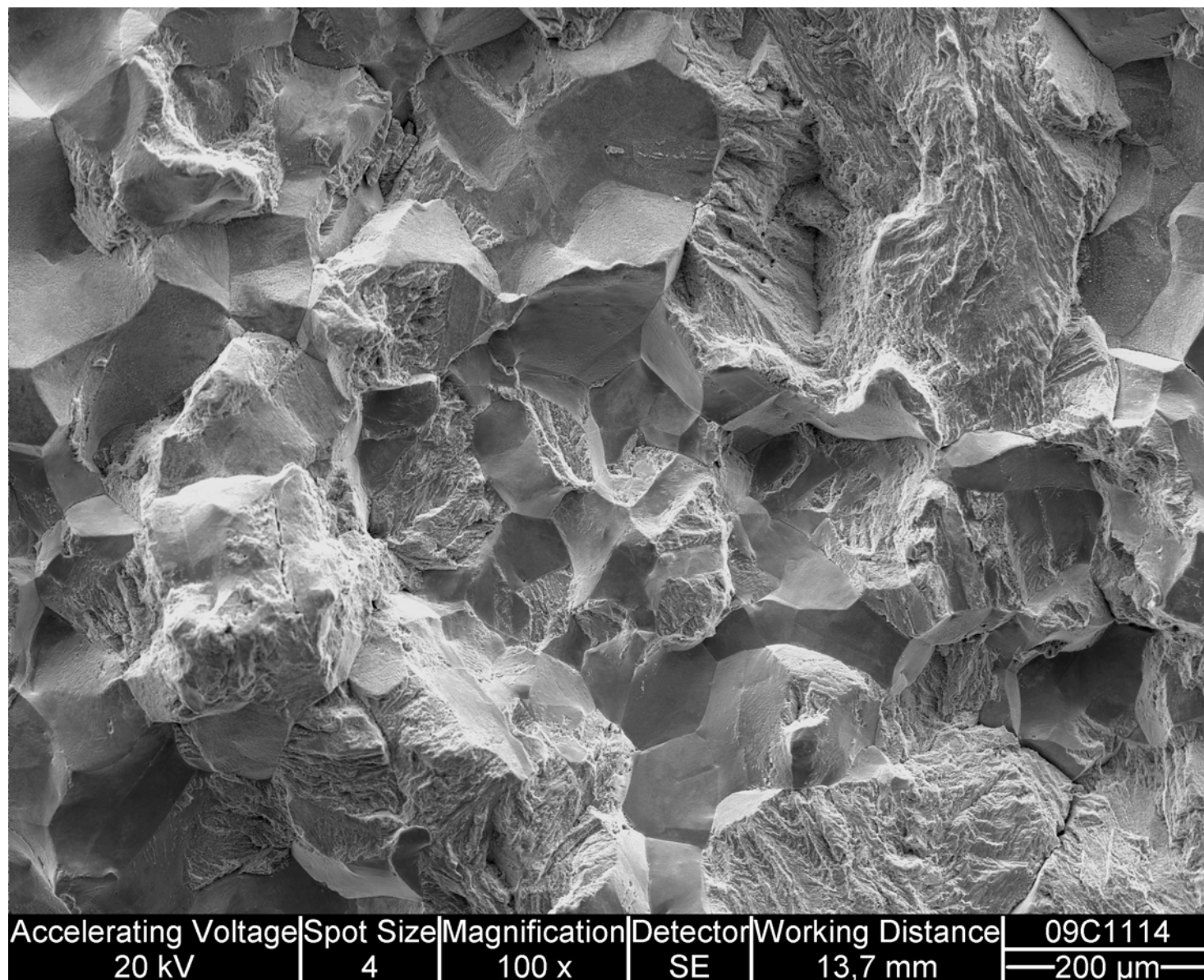
EXPERIMENTAL DETERMINATION OF MINIMUM [S²⁻]

- Experimental arrangement developed
- Test pieces 25 mm thick copper, Compact Tension geometry to simulate the stress/strain state of canister (plain strain).
- Test pieces with precrack to simulate defects.
- First test with [S²⁻] = 100 mg/l performed.

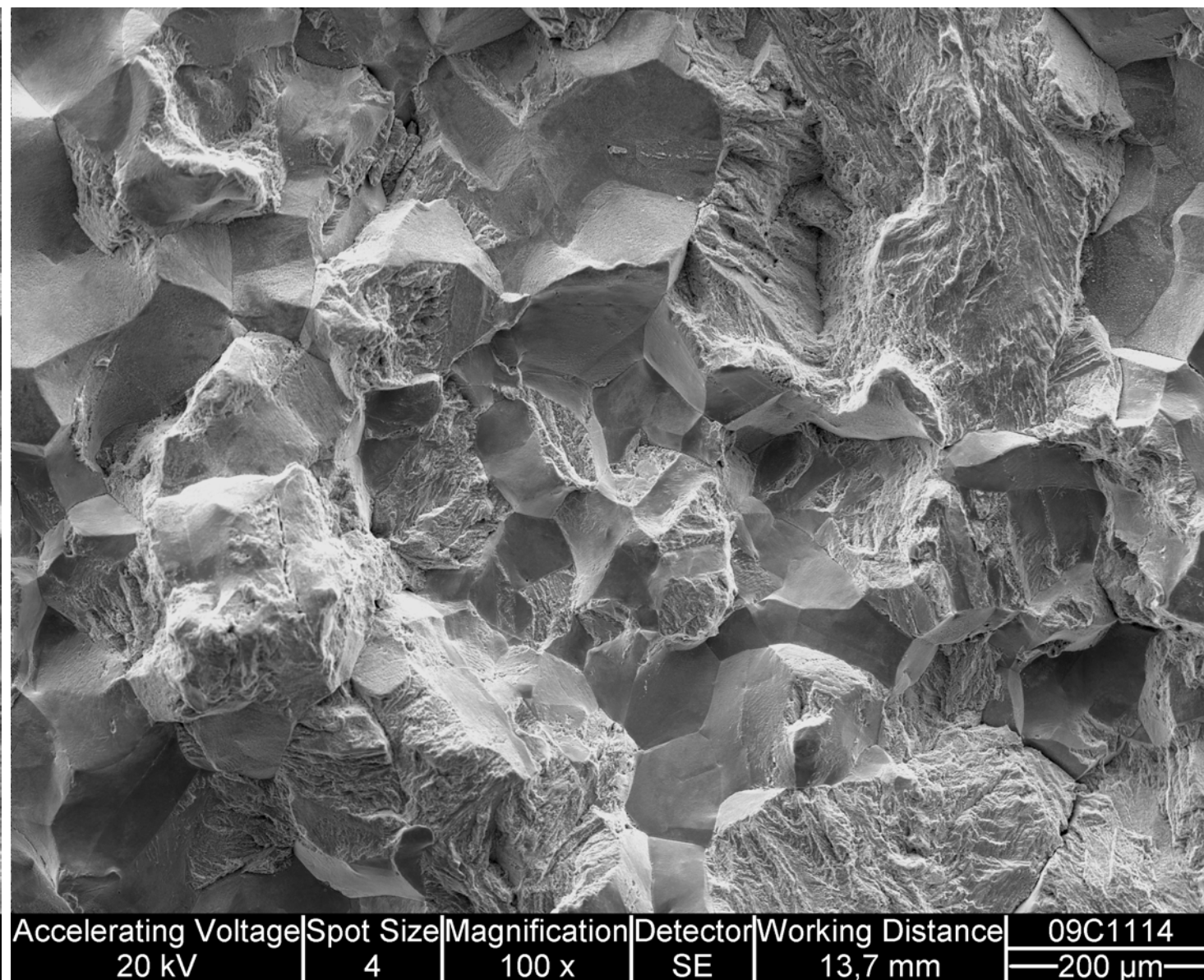








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CONCLUSIONS

Work in progress.

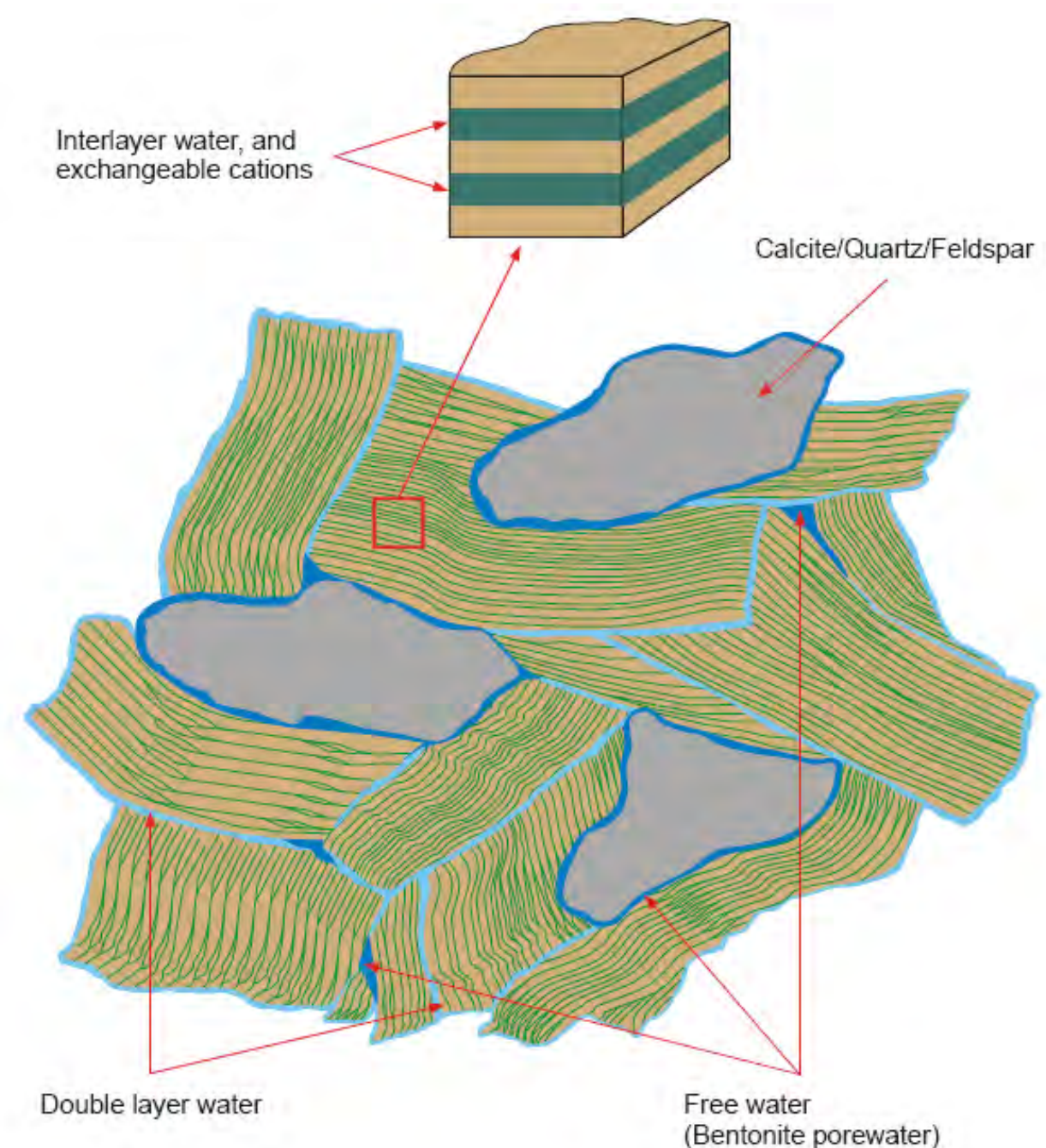


VTT creates business from technology



BENTONITE

- Bentonite is a swelling clay, which beneficial properties (for waste disposal) lie mainly on its main component **montmorillonite**
- Montmorillonite is a cation exchanger (Na, K, Ca, Mg):
 - e.g. one Ca ion can be taken out by putting to Na ions in
 - Charge of cations is compensated by negative layers very near each other
- Bentonite swells due to water wanting to go between lamellae, where the salinity is higher, and due to forces between charged (but ...) surfaces



TRANSPORT MODELLING OF BENTONITE

1. Bentonite reacts by water coming into contact with it by cation exchange, surface reactions and mineral precipitation/dissolution
2. Mass transport in bentonite takes place by convection and in high density by diffusion
3. On the other hand bentonite swells during wetting and in closed space produces swelling pressure
4. During swelling bentonite deforms and the mass is re-distributed
5. In many cases all this takes place under temperature gradient
 - Topics 521 = THC modelling (Thermo-Hydro-Chemical)
 - Topics 534 = THM modelling (Thermo-Hydro-Mechanical)
 - THC models are often developed by chemists and hydrologists
 - THM models are quite often developed by physicists and mathematicians
 - How to do all that by COMSOL?