Diffusion experiments in laboratory and Diffusion simulations in time domain

Matrix diffusion workshop
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- Matrix diffusion measurements in water phase based on solute conductivity measurements
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- Time Domain Diffusion (TDD) simulation
He gas through diffusion measurements

- Measurements are done as through diffusion measurements using helium as tracer and nitrogen as carrier gas.
- 5 ml of helium is injected into a chamber facing the sample. Measuring chamber (at opposite face) is continuously flushed by nitrogen (~zero concentration of He), and He flux is determined by continuously measuring the He contents of nitrogen.
- Diffusion equation can be solved analytically with the corresponding initial and boundary conditions, and the measured breakthrough curve is fitted by its solution:

\[
\frac{\dot{m}}{m_0} = 2D_a h^2 \sum_{n=0}^{\infty} \frac{\alpha_n \exp(-D_a \alpha_n^2 t)}{\sin(l \alpha_n)(l(\alpha_n^2 + h^2) + h)}
\]

where \(\alpha_n\) are the roots of

\[
\alpha \tan(l \alpha) = h
\]

and

\[
h = \frac{A \varepsilon}{V}
\]
He gas through diffusion measurements

Advantages:
- Fast compared to measurements in water phase
- Relatively simple measurements
- Samples are preserved uncontaminated

The measurement setup has been used since ’90s when selecting the place for disposal of nuclear waste

Now the setup has been rebuilt and slightly modified

The results may be converted to water phase and for other elements using a conversion factor.
- For example chloride in water phase (at 25 °C):

\[ D_a^{Cl} = \frac{D_{H_2O}^{Cl}}{D_{N_2}^{He}} D_a^{He} \approx 2.9 \times 10^{-5} D_a^{He} \]

Same setup can be used to measure permeability
He gas through diffusion measurements

- We have recently measured diffusion coefficients, e.g., for:

**Grimsel granodiorite**

- \( D_e = 2.6 \times 10^{-6} \text{ m}^2/\text{s} \); porosity = 0.7 %

**Samples from Olkiluoto**

- \( D_e = 4.8 \times 10^{-10} \text{ m}^2/\text{s} \); porosity = 0.7 %
Matrix diffusion experiments in water phase

- In order to validate developed models and their features we constructed a simple measurement setup.
- We introduce a pulse of potassium chlorine in a flow channel with porous wall.
- Migration of K⁺ and Cl⁻ ions are observed with conductivity measurement.
- Here we were mainly interested about input and breakthrough curves.
Matrix diffusion experiments in water phase:

Effect of matrix with finite depth

- Experimental breakthrough curves fitted by the mathematic model
- Effect of matrix finite depth was studied using various flow rates (Q)
  - Fast Q: Case of infinite matrix
  - Intermediate Q: A hump appears next to the primary peak
  - Slow Q: These two peaks unite
- Excellent agreement between the measurements and the mathematic model was found.
Matrix diffusion experiments in water phase: Contaminated matrix

- Experimental breakthrough curves fitted by a model with arbitrary input and initial tracer concentrations
- Excellent agreement between the measurements and the mathematic model was found
- The resulting breakthrough curve can be divided into two parts
  - Initially contaminated matrix
  - Input concentration
Matrix diffusion experiments in gas phase:

- Measurement setup similar than in through diffusion measurements
- A pulse of helium introduced in nitrogen flow
  - Advection and longitudinal diffusion in flow channel
  - Matrix diffusion in rock sample
- Preliminary results:
  - Matrix diffusion observed
  - Not yet analyzed

![Breakthrough curve](image)

- ONK-PP323
- Flow rate: 5 cm³/min
- Flow velocity: 0.16 cm/s

Flow with tracer pulse

Tracer flow rate measurement
Time Domain Diffusion (TDD) simulations

- Fast particle tracking method which allows simulation of diffusion in heterogeneous materials when the local porosities and diffusivities are known.

- Each particle is forced to hop out of a pixel after a randomly chosen time to one of the neighboring pixels.

- Transition probabilities and hopping times depend on local porosity and diffusivity.

\[ P_{ij} = \frac{b_{ij}}{\sum_j b_{ij}} ; t_{ij} = -\frac{\varepsilon_i V_i}{\sum_j b_{ij}} ; b_{ij} = \frac{A_{ij}(\varepsilon D)_{ij}}{L_{ij}} \]

- Forcing the particle to hop makes this method faster than the conventional random walk methods.
TDD simulations: Preparing geometries

- **Homogeneous sample**
  - Uniform diffusion coefficient and porosity
  - Possible to construct geometries and conditions as in the measurement

- **Tomographic reconstructions**
  - Diffusion coefficients and porosities of different components has to be determined
  - Possible to simulate diffusion in more realistic medium
TDD simulations: Applications

- Predict and analyze results of various diffusion experiments
- Study an effect of material heterogeneity and anisotropy on diffusion processes
- Plans to include sorption into the TDD code has already been made

Through diffusion exp. - Analysis

Out-diffusion diffusion exp. - Analysis

In-diffusion – homog. vs heterog.
References

Thank you, for your attention!