Modelling the transport of water and ions tracers in a micrometric clay sample

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Introduction

- **Clay minerals**: highly abundant natural materials
- **Interfacial properties**

  ➔ Many environmental and engineering applications

For example: barrier materials for long-term isolation of high-level radioactive waste (ANDRA)
Introduction

• Complex multi-scale structure

Montmorillonite: \((\text{Si}_8)(\text{Al}_{3.25}\text{Mg}_{0.75})\text{O}_{20}\text{(OH)}_4\text{Na}_{0.75})\)
Introduction

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Compacted clays: essentially nano/microporosity
Introduction

• Complex multi-scale structure
• Mainly diffusive transport:
  – Water
  – Ions (Na\(^+\), Ca\(^{2+}\), Cl\(^-\), Cs\(^+\), I\(^-\)…)

Micrometric model of porous medium

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Introduction
Model
BD Simulations
Results
Conclusion
Introduction

- Complex multi-scale structure
- Mainly diffusive transport
- Different behavior according to charge

Water: complete and rapid exchange

Cations: diffusion through IP + IL

Anions: partial exclusion from IL
Introduction

- Complex multi-scale structure
- Mainly diffusive transport
- Different behavior according to charge

Macroscopic description taking into account all parameters?
Introduction

Our idea:

- Brownian Dynamics
- Model with two environments with different diffusion coefficients

$D_0 \neq D_p$
Model

Structure

- Cylindrical platelets (p) overlapping each other
- $R = 250\text{nm}$
- $20$ layers $\Rightarrow h = 20 \times \Delta L$

$\Delta L$ depends on the compaction / dry density $\rho_b$
Amount of water in IL varies according to compaction:

- 1W
- 2W
- 3W
- 40Å

The interlayer distance isn’t unique for all particles!

Model

Dimensions of the platelets

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<table>
<thead>
<tr>
<th>0% 3W</th>
<th>0% 2W</th>
<th>0% 1W</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% 40 Å</td>
<td>100% 3W</td>
<td>100% 2W</td>
</tr>
<tr>
<td>3W + 40 Å</td>
<td>2W + 3W</td>
<td>1W + 2W</td>
</tr>
<tr>
<td>0.6 kg L⁻¹</td>
<td>1.35 kg L⁻¹</td>
<td>1.7 kg L⁻¹</td>
</tr>
</tbody>
</table>


Micrometric model of porous medium

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Introduction

Model
- Structure
- Dimensions of the platelets
- Generating samples
- Results

BD Simulations

Results

Conclusion
Model

Dimensions of the platelets

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The interlayer distance isn’t unique for all particles!

How to arrange the cylinders?

The platelets are allowed to overlap each other:
- High densities
- Accounts for the flexibility of the particles

Two configurations

Random
- Positions & orientations chosen randomly

Gay-Berne (GB)
- Positions & orientations determined by MD simulations

What does it look like?

Random

GB

GB VS random configurations
What does it look like?

Random

GB

GB VS random configurations
- More realistic orientations
What does it look like?

Random

GB

GB VS random configurations
- More realistic orientations
- Lower tortuosity
What does it look like?

Random

GB

GB VS random configurations
- More realistic orientations
  - Lower tortuosity
- Better interparticle pores connectivity
Brownian Dynamics Simulations

Method

• Solution of diffusion equation (3D):

\[ C(r,t) = \frac{1}{(4\pi D_t)^{3/2}} \exp \left( \frac{-r^2}{4D_t t} \right) \]

• 3D displacements: chosen from the Gaussian distribution

\[ p_i = \frac{1}{(4\pi D_i t)^{3/2}} \exp \left( \frac{d^2}{4D_i t} \right) \]
Brownian Dynamics Simulations

Method

- Crossing from one platelet to another: always accepted
- Crossing from one environment to another:
  - **Basal surface**: tracer bounces back
  - **Lateral surface**: acceptance probability

\[
\begin{align*}
    p_{acc}^{i\rightarrow j} &= \min\left\{ 1; \frac{c_j}{c_i} \times \left( \frac{D_i}{D_j} \right)^{3/2} \times \exp\left( \frac{d^2}{4D_j t} + \frac{d^2}{4D_i t} \right) \right\} \\
    \text{If rejected: tracer bounces back}
\end{align*}
\]

Input parameters: \( c_p, c_0, D_p, D_0 \)
Brownian Dynamics Simulations
Concentrations

Water:

– Concentration inside IL pores equal to concentration inside IP pores
– Some fraction of the platelet is solid:

\[ c_p = c_0 \times \frac{L}{L_{dry}} \]
Brownian Dynamics Simulations

Concentrations

**Ions**: Excess of cations inside IL pores + Anions partially excluded

- Solution of Poisson-Boltzmann equation \( \Rightarrow \frac{c_{\text{int}}}{c_0} \)
- Concentration in nW-platelet:

\[
c_p^{nW} = c_{\text{int}}^{nW} \times \frac{L_{nW}}{L_{\text{dry}}} \]

- (nW + mW)-Platelet:

\[
c_p = \frac{c_p^{nW} x_{nW} \left( \frac{L_{nW}}{L_{\text{dry}}} \right) + c_p^{mW} x_{mW} \left( \frac{L_{mW}}{L_{\text{dry}}} \right)}{L}
\]
Brownian Dynamics Simulations

Diffusion coefficients in IL pores:

- **Water**: QENS experiments (1W, 2W) + MD simulations (3W)

- **Ions**: MD simulations (1W, 2W, 3W)
  - Bourg, I.C and Sposito, G. *Environmental Science and Technology*, 2010

- **40Å /Interparticle pore**: literature

Diffusion coefficient in platelets:

\[ D_p = \left[ \frac{D_{nW} x_{nW} \left( \frac{L_{nW}}{L_{dry}} \right) + D_{mW} x_{mW} \left( \frac{L_{mW}}{L_{dry}} \right)}{x_{nW} \left( \frac{L_{nW}}{L_{dry}} \right) + x_{mW} \left( \frac{L_{mW}}{L_{dry}} \right)} \right] \]
Brownian Dynamics Simulations

Evaluating the diffusion coefficient

- Trajectories of $5 \times 10^{10}$ ps (time step: 10 ps)
- Diffusion coefficients obtained from MSD curves

$$\text{MSD}(\tau) = 6D_a \tau$$
Similar trends for experiments and simulations
Overestimation for GB configuration
Results

Water

- Similar trends for experiments and simulations
- Overestimation for GB configuration
Results

Cations : Na⁺

Trends fairly similar but overestimation
Cations diffuse through platelets ➔ too high connectivity?
Results

Anions: Cl$^-$

Good agreement with experimental values
**Cl\textsuperscript{-}**: strong salinity-dependence

- Anions don’t solely travel in the IP pores

**Na\textsuperscript{+}**: salinity has little impact

- Cations diffuse primarily through the platelets
Conclusions

Advantages:
- Rather simple model
- Accounts for realistic features such as flexibility of the particles and orientations
- Allows to investigate self-diffusion of ionic and water tracers on scales of micrometers and milliseconds
- Predicts most features of water, Na\(^+\) and Cl\(^-\) diffusion in compacted clays

But...

Our model overestimates the diffusion coefficients, especially for Na\(^+\)

How to improve our model?
By tuning the probability to cross from one particle to another and increasing the interparticle pores connectivity
Thank you for your attention!