Pore-scale Simulation of Carbonate Dissolution: the Impact of Rock Heterogeneity

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Objective

Develop a pore-scale particle tracking method capable of simulating rock-fluid reactions in carbonates:

- Evolution of petrophysical properties during reactive transport
- Physical basis for the decrease of average reaction rates in porous rocks

Applications - \( \text{CO}_2 \) injection (EOR or CCS) and diagenesis modeling
Introduction

Wormhole in a bioclastic limestone

Vialle et al., 2014

Uniform dissolution in an oolite,

Menke et al., 2015

- Acidic fluids flowing through carbonates react with the rock matrix, changing the petrophysical properties of the reservoir – 100’s of papers since the 1960’s.

- Dissolution patterns and average rates are the result of a complex interaction between transport and kinetic properties
Reaction rates in porous media are scale-dependent

Our focus:

Chemical, physical & geological heterogeneities from microns to kms

This work: physical heterogeneities at the micron-mm scale
Dissolution Behaviour Diagram (Daccord, Lenormand, Golfier…)

Compact

wormholes

Uniform

Heterogeneity ? Precise cutoffs ?

\[ Pe = \frac{\text{Advection}}{\text{Diffusion}} \]

\[ Pe. Da = \frac{\text{Reaction}}{\text{Diffusion}} \]
Outline

I. Model Description
   1. Flow & Transport
   2. Geochemical Model

II. Comparison with dynamic imaging data

III. Average reaction rates - Heterogeneity

IV. Concluding remarks
I – Model Description
Our approach:

• Lagrangian method based on a pore-scale streamline method to simulate evolution of petrophysical properties at in situ conditions

• Simulations done directly on the voxels of micro-CT images

• Model validated with 3D dynamic imaging data from a real carbonate
Flow and Transport Model

Navier-Stokes eq. solved directly on the image voxels with OpenFoam:

Particle displacements:

\[
\Delta \vec{X}_p = \Delta \vec{X}^{adv}_p(\vec{V}, \Delta t) + \Delta \vec{X}^{diff}_p
\]

Random walk

Semi-Analytical

SL tracing
Dissolution happens when solute particles (lack of \(\text{Ca}^{2+}\)) collide with the solid voxels (calcite).

**Geochemical Model**

**ADR eq. for the particle concentration:**

\[
\frac{\partial C}{\partial t} + \vec{V} \cdot \nabla C = D_m \nabla^2 C - [RC]
\]

Reaction at the interfaces

**In the particle-tracking approach:**

\[
\Delta \vec{X}_p = \Delta \vec{X}^{\text{adv}}_p(\vec{V}, \Delta t) + \Delta \vec{X}^{\text{diff}}_p
\]

Controls particle flux at the interfaces

Dissolution happens when solute particles (lack of \(\text{Ca}^{2+}\)) collide with the solid voxels (calcite).
We improve Pollock’s algorithm, to trace streamlines semi-analytically, respecting the no-slip boundary conditions at pore-solid walls.

No need to make the time-step small. More efficient than std. particle tracking methods. Very useful in high Peclet flows.

In a cubic lattice there are 64 possible types of pores:

- 1 – no solid boundaries
- 6 – one solid boundary
- 15 – two solids
- 20 – three solids
- 15 – four solids
- 6 – five solids
- 1 – six solids
Streamline tracing: non-Fickian behaviour in heterogeneous rocks

**Voxel Time-of-flight distributions**

- Modified Pollock
- Std. Pollock

**Breakthrough**

- Modified Pollock
- Std. Pollock

Modified Pollock algorithm – Semi-analytical streamlines, consistent with the no-slip boundary condition at the pore-solid interfaces.

Particularly useful in high Péclet conditions

Pereira Nunes et al., TiPM, 2015
Calcite Dissolution

Three reactions occurring in parallel at the grain surface:

- \[ \text{CaCO}_3(s) + H^+ \xrightarrow{k_1} \text{Ca}^{2+} + \text{HCO}_3^- \]
- \[ \text{CaCO}_3(s) + \text{H}_2\text{CO}_3 \xrightarrow{k_2} \text{Ca}^{2+} + 2\text{HCO}_3^- \]
- \[ \text{CaCO}_3(s) \xrightarrow{k_3} \text{Ca}^{2+} + \text{CO}_3^{2-} \]

With intrinsic rate - \( r = k_1 \alpha_H + k_2 \alpha_{\text{H}_2\text{CO}_3} + k_3 \)

\[ r = 0.00081 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \ @ 10\text{MPa} & 50\text{C} (\text{Peng et al., 2015}) \]

Local concentration of \( \text{Ca}^{2+} \) controls the reaction.
Surface-controlled dissolution in the particle approach

A solid voxel dissolves when the cumulative flux of particles > \( N_{hits} \):

\[
N_{hits}(\vec{r}) = \frac{\sqrt{6}}{4} \frac{D_m}{\Delta t} \frac{C(\vec{r})N_{mol}}{\vec{r}}
\]

- \( r \) – intrinsic reaction rate → From batch reactors
- \( D_m \) – diffusion coefficient
- \( \Delta t \) – time step
- \( C(r) \) – particle concentration
- \( N_{mol} \) – moles of calcite in each solid voxel
Surface-controlled dissolution of a semi-infinite rod

Rod dissolved by a fluid with cte. concentration of reactants.
II – Comparison with dynamic imaging data
Dynamic imaging experiment – H. Menke @ 11:25

- *Ketton oolite core flooded with CO$_2$-equilibrated brine @ 10MPa / 50C*
- *Porosity and permeability increasing*
- *Péclet $\approx 2300$, Damköhler $\approx 10^{-5}$*
- *Uniform dissolution regime*
Pe \gg 1 \\
Pe Da \ll 1

Experimental Conditions

\[ \text{Pe} = \frac{\text{Advection}}{\text{Diffusion}} \]
Dissolution after 50 min. of flow

\[
\text{Péclet} = \frac{[\text{Advection}]}{[\text{Diffusion}]} \gg 1
\]

\[
\text{Pe. Da} = \frac{[\text{Reaction}]}{[\text{Diffusion}]} \ll 1
\]
Slice-averaged porosity

Experimental Simulation

50min.

1

2

t0

Flow

Slice number
Time-lapse images - perpendicular to flow

Experimental

17 min.

33 min.

50 min.

Simulation

3.4 mm.
Time-lapse images – parallel to flow
Porosity and permeability after flow and reaction

*Permeability increase: wider throats and a reduction in tortuosity (1.5 → 1.3)*
Average dissolution rates – \( r^{\text{avg}} = \frac{\Delta \phi V n}{\Delta t S_A} \)

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>( \Delta \phi )</th>
<th>( k^{\text{avg}} ) ([10^{-4} \text{ mol.m}^{-2}.\text{s}^{-1}])</th>
<th>( \Delta \phi )</th>
<th>( k^{\text{avg}} ) ([10^{-4} \text{ mol.m}^{-2}.\text{s}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-17</td>
<td>0.029</td>
<td>0.87</td>
<td>0.023</td>
<td>0.79</td>
</tr>
<tr>
<td>17-33</td>
<td>0.023</td>
<td>0.76</td>
<td>0.027</td>
<td>0.97</td>
</tr>
<tr>
<td>33-50</td>
<td>0.020</td>
<td>0.62</td>
<td>0.026</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Compare with the batch rate: \( r = 8.1 \times 10^{-4} \text{ mol.m}^{-2}.\text{s}^{-1} \) (Peng et al., 2015)

Average rates 10 times smaller due to transport limitations – no chemical/surface heterogeneity in the model.
III – Average Reaction Rates & Flow Rate
Estaillades

Ketton

Beadpack

$650^3$ voxels

$500^3$ voxels

$500^3$ voxels
Hydraulic Tortuosity -

\[
T = \frac{\langle \text{Length Streamlines} \rangle}{\text{Sample Length}}
\]

**Estaillades**

\[T = 1.78\]

**Ketton**

\[T = 1.54\]

**Beadpack**

\[T = 1.25\]
Average Rates – $r^{\text{eff}} = \frac{\Delta \phi V n}{\Delta t S_A}$

The average rate depends on the rock heterogeneity and on the flow rate.
Solute transport to the grains surface is controlled by the velocity field
Dissolution after 1000 PV / Pe 100
Dissolution after 1000 PV / Pe 10 & Pe 100
Dissolution after 1000 PV / Pe 10 & Pe 100
IV – Future work
Dissolution Behaviour Diagram

Pe. Da = \frac{[\text{Reaction}]}{[\text{Diffusion}]} \rightarrow \text{Increasing reaction rate}

Péclet = \frac{[\text{Advection}]}{[\text{Diffusion}]} \rightarrow \text{Increasing flow rate}
Particle trajectories in the pore space

Particles travel longer distances when the Péclet is higher, thus moving the dissolution front away from the inlet face.
For the same amount of fluid, different permeabilities.
Conclusions

• We have presented a particle tracking method to simulate carbonate dissolution at the pore-scale

• The method was validated using dynamic image data – carbonate dissolution in CO$_2$-saturated brine - without any fitting parameters

• Based on a very efficient streamline tracing method – Modified Pollock algorithm

• We predict a decrease of one order of magnitude in the average dissolution rates due to transport limitations only

• Easily modifiable to incorporate deposition and different flow regimes
Acknowledgments

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END