Crystal dissolution and precipitation in porous media: variable pore geometry and upscaled model

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Outline

- Introduction: crystals in porous media
- Model: free boundary problem
- Thin strip
  - Numerics: ALE method
  - Upscaling: limit of vanishing width
  - Traveling waves
- Perforated domain: upscaled model en numerics
- Conclusions and Open Problems
Flow through porous medium

porous medium, fully saturated

dissolved ions transported by the flow, e.g. sodium (\(Na^+\)) and chlorine (\(Cl^-\)) ions

crystals attached to the grain surface (porous matrix), e.g. sodium chloride (\(NaCl\))

precipitation/dissolution reaction on the grain surface

\[ M_{12} \rightleftharpoons n_1 M_1 + n_2 M_2 \]
Previous work: fixed pore geometry

Thickness of crystal layers negligible with respect to pore size: fixed pore geometry

Pore scale model equations: flow and concentrations one way coupled, flow can be solved for independent of concentrations.

Existence of solutions (Van Duijn and Pop, 2004), Uniqueness (Röger, Pop, v.N. 2006), Numerics (Devigne, Pop, Van Duijn, Clopeau, 2006)

Upscaling: averaging in thin strip (Van Duijn and Pop, 2004) Traveling waves for upscaled equations (Van Duijn and Knabner, 1997)

Open: rigorous upscaling and existence+uniqueness of macroscopic equations
Model equations

Flow:

\( q \) – fluid velocity (m/s)
\( p \) – pressure inside fluid (Pa)
\( \mu \) – dynamic viscosity (kg/(ms))

Stokes flow:

\[
\begin{align*}
\mu \Delta q &= \nabla p, \\
\nabla \cdot q &= 0.
\end{align*}
\]

in \( \Omega_t \) and \( q = K v_n \nu \), on \( \Gamma_t \),

with \( K = \frac{\rho_f - (n_1 + n_2) \rho_c}{\rho_f} \). (Using the assumption \( c_f + c_1 + c_2 \equiv \rho_f \))
Model equations

Ion concentration:

Precipitation, dissolution reaction:

\[ M_{12} \rightleftharpoons n_1 M_1 + n_2 M_2, \]

Mass conservation for ion concentrations \( c_i \) (mol/m\(^3\)) \((i = 1, 2)\): in fluid

\[
\frac{\partial}{\partial t} c_i + \nabla \cdot (q c_i - D \nabla c_i) = 0 \quad \text{for} \quad x \in \Omega_t \\
(n_i \rho - c_i) v_n = D \nu \cdot \nabla c_i \quad \text{for} \quad x \in \Gamma_t
\]
Dissolution and precipitation rate

Thickness of crystalline layer:
normal velocity of interface between crystals and fluid

\[ v_n = r_p - r_d, \]

1) Precipitation rate \( r_p \) (mol/m\(^2\)s):

\[ r_p = k_p r(c_1, c_2) = k_p [c_1]_{n_1} [c_2]_{n_2} \]

2) Dissolution rate \( r_d \) (mol/m\(^2\)s)

\[ r_d \in k_d H(d(x, \Gamma w)) \]

where \( H \) denotes the set-valued Heaviside graph

\[ H(u) = \begin{cases} 
\{0\}, & \text{if } u < 0, \\
[0, 1], & \text{if } u = 0, \\
\{1\}, & \text{if } u > 0. 
\end{cases} \]
2D Model: dimensionless equations

Denote $\epsilon := \frac{l}{L}, ...$
Assumptions: symmetry w.r.t. $y$-axis, $c_1 = c_2 = c_{ref}u^\epsilon$

\[
\begin{cases}
    u_t^\epsilon = \nabla \cdot (D \nabla u^\epsilon - q^\epsilon u^\epsilon), \\
    \epsilon^2 \mu \Delta q^\epsilon = \nabla p^\epsilon, \\
    \nabla \cdot q^\epsilon = 0, \\
    u^\epsilon, q^\epsilon \text{ and } p^\epsilon \text{ symmetric around } y = 0,
\end{cases}
\]

in $\Omega^\epsilon(t)$,

\[
\begin{cases}
    d_t^\epsilon = k(r(u^\epsilon) - w) \sqrt{1 + (\epsilon d_x^\epsilon)^2}, \\
    w \in H(d^\epsilon), \\
    \nu^\epsilon \cdot (D \nabla u^\epsilon - q^\epsilon u^\epsilon) = -\epsilon k(r(u^\epsilon) - w)(\rho - u^\epsilon), \\
    q^\epsilon = -\epsilon K k(r(u^\epsilon) - w) \nu^\epsilon,
\end{cases}
\]
on $\Gamma^\epsilon(t)$

where

$\Omega^\epsilon(t) := \{(x, y)|0 \leq x \leq 1, -\epsilon(1/2 - d^\epsilon(x, t)) \leq y \leq \epsilon(1/2 - d^\epsilon(x, t))\}$,

and where

$$
\nu^\epsilon = (\epsilon \partial_x d^\epsilon, -1)^T / \sqrt{1 + (\epsilon \partial_x d^\epsilon)^2},
$$
Existence!? (Uniqueness?)
1D model

Assumptions:
- 1 component: $v := c_1 = c_2$, $n_1 = n_2$
- no flow: $q = 0$
- 1D

\[
\begin{cases}
\partial_t v = \partial_{xx} v, & \text{for } x \in (0, h(t)), \\
\partial_x v = 0, & \text{for } x = 0, \\
\partial_x v = (\rho - v)h'(t), & \text{for } x = h(t), \\
h'(t) = D_a(w(t) - r(v)), & \text{for } x = h(t), \\
w(t) \in H(1 - h(t)).
\end{cases}
\]

Theorem. *There exists a unique, positive and bounded solution.*

2D: existence and uniqueness are open
Thin strip

Ratio of width and length small: \( \epsilon := \frac{l}{L} \)

- Simulations: ALE method

- What happens if we let \( \epsilon \rightarrow 0 \)?
  Upscaling
2D Simulations: deformed mesh

ALE (arbitrary Lagrangian-Eulerian) method: spatial frame vs. reference frame

Coordinates

\[ x = x(X, Y, t), \quad y = y(X, Y, t) \]

Solve

\[ \dot{x} = u(X, Y, t), \quad \dot{y} = v(X, Y, t), \]

with

\[ \Delta_{(X,Y)} u = 0, \quad \Delta_{(X,Y)} v = 0, \quad \text{on } \Omega_{(X,Y)} \quad \text{and} \quad \begin{pmatrix} u \\ v \end{pmatrix} = \nu n \quad \text{on } \Gamma_{(X,Y)}. \]
2D Simulation: dissolution in strip

(Loading striptrav2.avi)
Thin strip: upscaling

Formal asymptotics for $\epsilon \to 0$

Assume

$$u^\epsilon(x, y, t) = u_0(x, \frac{y}{\epsilon}, t) + \epsilon u_1(x, \frac{y}{\epsilon}, t) + \epsilon^2(...),$$

$$q^\epsilon(x, y, t) = q_0(x, \frac{y}{\epsilon}, t) + \epsilon q_1(x, \frac{y}{\epsilon}, t) + \epsilon^2(...),$$

$$p^\epsilon(x, y, t) = p_0(x, \frac{y}{\epsilon}, t) + \epsilon p_1(x, \frac{y}{\epsilon}, t) + \epsilon^2(...),$$

$$d^\epsilon(x, t) = d_0(x, t) + \epsilon d_1(x, t) + \epsilon^2(...).$$

The vertical coordinate of the variables $u_i(x, z, t)$, $q_i(x, z, t)$ and $p^\epsilon(x, z, t)$ are rescaled. They are defined on

$$\Omega(t) := \{(x, z)|0 \leq x \leq 1, -1/2 + d^\epsilon \leq z \leq 1/2 - d^\epsilon\}.$$
Formal asymptotics

Substituting the asymptotic expansions, integrating along the \( z \)-coordinate, and retaining only terms independent of \( \epsilon \), yields

\[
\begin{aligned}
\partial_t((1 - 2d_0)u_0 + 2\rho d_0) &= \partial_x(D(1 - 2d_0)\partial_x u_0 - \bar{q}u_0), \\
\partial_x\bar{q} - 2K\partial_t d_0 &= 0, \\
\partial_t d_0 &\in k(r(u_0) - H(d_0)),
\end{aligned}
\]

where

\[
\bar{q}(x, t) = \int_{-1/2+d_0(x,t)}^{1/2-d_0(x,t)} q_0^{(1)}(x, z, t) \, dz.
\]
Profiles of both 2-D and effective model, for $t = 20$ and $t = 40$.
Thin line: solution of the effective model
Dashed line: 2-D model with $\epsilon = 0.1$
Dots: 2-D model with $\epsilon = 0.01$
Thin strip: traveling wave

Non-negative traveling wave solutions:
\( u = u(\eta), \ d = d(\eta) \) and \( q = q(\eta) \) with \( \eta = x - at \), and \( d < 1/2 \), satisfying

\[
\begin{align*}
-\alpha((1 - 2d)u + 2\rho d)' - ((1 - 2d)Du' - qu)' &= 0, \\
-\alpha d' &\in k(r(u) - H(d)), \\
q' + 2\alpha K d' &= 0,
\end{align*}
\]

in \( \mathbb{R} \).

and boundary conditions

\begin{align*}
 u(-\infty) &= u^*, & u(\infty) &= u_*, \\
 d(-\infty) &= d^*, & d(\infty) &= d_*, \\
 q(-\infty) &= q^*,
\end{align*}

where \( 0 \leq u^*, u_*, q^* \) and \( 0 \leq d^*, d_* < 1/2 \).
Thin strip: traveling wave (2)

\[ \begin{align*}
I & \quad \begin{cases} 
    d^* > 0, & d^* = 0 \\
    u_* = u_s, & 0 \leq u^* < u_s
\end{cases} \quad \text{(dissolution wave)} \\
II & \quad \begin{cases} 
    d^* > 0, & d_* = 0 \\
    u^* = u_s, & 0 \leq u_* < u_s
\end{cases} \quad \text{(precipitation wave)}
\end{align*} \]

Theorem. No traveling wave exists with boundary conditions from class II.

Theorem. For any set of boundary conditions from class I, there exists a traveling wave (unique up to a shift).
Traveling wave: wave speed comparison

\[ a(\alpha) = \frac{u_s - u^*}{2d_*(\rho - \alpha u_s(1 - K)) + u_s - u^*q^*}. \]

\( \alpha = 0 \): fixed geometry (v.Duijn and Knabner 1997)
\( \alpha = 1 \): variable geometry

\( a(\alpha) \) increasing in \( \alpha \)

\[ a_{fix} = \frac{1}{2}q^*, \quad a_{var} = \frac{2}{3}q^*. \]
Perforated Domain

Level set function $S$ such that $\Gamma = \{S = 0\}$.
Evolution of $\Gamma$ given by

$$S_t + |\nabla S| v_n = S_t - \frac{1}{\rho_c} (k_p r(c_1, c_2) - k_d w(x)) |\nabla S| = 0$$

Expand $S^\varepsilon$
Upscaled equations

\[
\begin{cases}
\partial_t S_0(x, y, t) - f(u_0(x, t), y)|\nabla_y S_0(x, y, t)| = 0 & \text{for } y \in [0, 1]^2, \\
\partial_t(|Y_0(x, t)|u_0) = \nabla_x \cdot (A(x, t)\nabla_x u_0) + |\Gamma_0(x, t)|f(u_0)\rho & \text{for } x \in \Omega \\
\bar{q} = -\frac{1}{\mu}K(x, t)\nabla_x p_0 & \text{for } x \in \Omega \\
\nabla_x \cdot \bar{q} = |\Gamma_0(x, t)|K f(u_0) & \text{for } x \in \Omega
\end{cases}
\]

where

\[f(u_0(x, t), y) = k(u_0^2 - H_\delta(\text{dist}(y, \Gamma)))\]

\[Y_0(x, t) = \{S_0 < 0\}\]

\[\Gamma_0 = \{S_0 = 0\}\]

(Hard step: interchange $\nabla_x$ and integration

\[|Y_0(x, t)|\partial_t u_0 = \int_{Y_0(x, t)} \nabla_y \cdot (\nabla_y u_2 + \nabla_x u_1 - q_1 u_0 - q_0 u_1) \, dy\]

\[+ \int_{Y_0(x, t)} \nabla_x \cdot (\nabla_y u_1 + \nabla_x u_0 - q_0 u_0) \, dy\]

\]
where the tensors $\mathcal{A} = (a_{ij})_{i,j}$ and $\mathcal{K} = (k_{ij})_{i,j}$ are given by

$$a_{ij} = \int_{Y_0(x,t)} \delta_{ij} + \partial_y v_j \, dy,$$

where $v_j$ solves the cell-problem

$$\begin{cases}
\Delta_y v_j = 0 & y \in Y_0(x,t) \\
\nu_0 \nabla_y v_j = -e_j & y \in \Gamma_0(x,t)
\end{cases}$$

periodicity in $y$,

and

$$k_{ij} = \int_{Y_0(x,t)} w_{ji} \, dy,$$

where the vector $w_j$ with components $w_{ji}$ solves the cell-problem

$$\begin{cases}
\Delta_y w_j = \nabla_y \pi_j + e_j & y \in Y_0(x,t) \\
\nabla_y \cdot w_j = 0 & y \in Y_0(x,t) \\
w_j = 0 & y \in \Gamma_0(x,t)
\end{cases}$$

(1)

with $\pi_j$ the corresponding pressure, respectively.
Simplification: circular grains

\[
\begin{aligned}
\partial_t R(x, t) &= f(u_0, R(x, t)) := k(u_0^2 - H\delta(R - R_{\text{min}})) \\
\partial_t ((1 - \pi R^2)u_0) &= \nabla_x \cdot (A(R)\nabla_x u_0 - \bar{q}u_0) + 2\pi R f(u_0, R) \rho \\
\bar{q} &= -\frac{1}{\mu} K(R) \nabla_x p_0 \\
\nabla_x \cdot \bar{q} &= 2\pi R K f(u_0)
\end{aligned}
\] for \( x \in \Omega \)
Circular grains: computations

No flow, only diffusion, $\epsilon = 0.01$. 

![Graphs showing diffusion pattern over time and space.](image-url)
Perforated domain: upscaled vs. original equations

Profiles of both 2-D and effective model, for \( t = 10 \) and \( t = 40 \).
Thin black line: 2-D model with \( \epsilon = 0.01 \)
Red dots: effective model
Conclusions

* Existence and uniqueness for 1D equations describing crystal precipitation and dissolution

* Simulations tool for 1D and 2D cases (can be extended to 3D and to more complex geometries)

* Formal derivation of upscaled equations for thin strip and perforated domain

* Existence of traveling wave solutions of upscaled equations
Open problems

* Existence and uniqueness for microscale model in 2D/3D?

* Rigorous upscaling?

* Blocking of strip \((d = 1/2)\)?

* Stability of dissolution fronts?