Fluid Flow, Solute Mixing and Precipitation In Porous Media

Idaho National Laboratory
George D. Redden
Yoshiko Fujita

Pacific Northwest National Laboratory
Yi-Lin Fang
T.D. Scheibe
A.M. Tartakovsky

University of Idaho
Mikala Beig
Joanna Taylor
Robert W. Smith

U.S. Geological Survey
Michael M. Reddy

Argonne National Laboratory
Shelly Kelly

Support from the U.S. Department of Energy, Environmental Remediation Sciences Program, under contracts DE-AC07-05ID14517 and DE-AC06-76RLO 1830
Theme:

Reactant Mixing → Precipitation → Modification of Permeability or Flow Paths → Prediction and Control of Subsurface Processes
Mixing: Dispersion vs. Diffusion

- **Diffusion**
  - Molecular-scale mixing $\rightarrow$ precipitation
  $$\text{Flux} = -D_{\text{diff}}(\nabla C)$$

- **Dispersion**
  - Macroscopic volume-averaged concentration
  $$\text{Flux} = \Theta D_{\text{disp}}(\nabla C)$$
Issues and challenges:

• Evolution of the spatial distribution of properties and processes

• Volume averaging of properties and processes in systems characterized by mixing zones (at all scales). For example:

  How should volume-averaged concentration be used to predict reaction rates?

  Averaged concentrations may exist only in mixing zones, which can be small and transient.
Issues and challenges:

• Hysteresis

Precipitation path  
(advection > diffusion)  

Dissolution path  
(diffusion > advection)
Precipitation

- Mineral precipitation
- Biomass growth
- Biofilm formation
- Colloid filtration
Impact:

- Fate and transport, sequestration
- Field-scale kinetics vs. laboratory kinetics
- Understanding the evolution of subsurface properties (MNA)
- Developing amendment introduction strategies
- Understanding “Rapid” engineered events
Flagship experiment:

- Hypotheses
  - Precipitation can be induced in the mixing zone between solutions containing reactive substrate (intuitively obvious, but interested in possible deviation of flow paths)
  - Permeability of a mixing zone where mineral precipitation occurs does not go to zero. (If it did, both sides of the mixing zone would be undersaturated)
Premodeling using Smoothed Particle Hydrodynamics: Parallel flow with mixing and precipitation
Experimental approach: Parallel flow, mixing and precipitation at a solution-solution interface, “2-D”
Tracer test showing fluid-fluid interface and mixing

Blue dye  Red dye
Tracer test showing fluid-fluid interface and mixing
Tracer test showing fluid-fluid interface and mixing
Tracer test showing fluid-fluid interface and mixing
Tracer test showing fluid-fluid interface and mixing
Tracer test showing fluid-fluid interface and mixing
Tracer test showing fluid-fluid interface and mixing

Blue dye

Red dye
Tracer test showing fluid-fluid interface and mixing

Blue dye

Red dye
Tracer test showing fluid-fluid interface and mixing

Blue dye

Red dye
Tracer test showing fluid-fluid interface and mixing

Blue dye  Red dye
Tracer test showing fluid-fluid interface and mixing (second attempt)
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow $\sim$ 1cm/min

$\sim$0.5mm silica sand
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

Darcy Flow $\sim$ 1cm/min

50mM CaCl$_2$

$\sim$0.5mm silica sand

60 cm
Propagation of calcium carbonate

60 cm

~0.5mm silica sand

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow ~ 1cm/min
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

$\sim$0.5mm silica sand

50mM CaCl$_2$

Darcy Flow $\sim$ 1cm/min
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow ~ 1cm/min

~0.5mm silica sand

60 cm
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

Darcy Flow $\sim$ 1cm/min

50mM CaCl$_2$

$\sim$0.5mm silica sand

60 cm
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

Darcy Flow ~ 1cm/min

50mM CaCl$_2$

~0.5mm silica sand

60 cm
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

60 cm

~0.5mm silica sand

50mM CaCl$_2$

Darcy Flow $\sim$ 1cm/min
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow ~ 1cm/min

~0.5mm silica sand
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

Darcy Flow ~ 1cm/min

50mM CaCl$_2$

~0.5mm silica sand

60 cm
Propagation of calcium carbonate

60 cm

50mM Na₂CO₃

50mM CaCl₂

~0.5mm silica sand

Darcy Flow ~ 1cm/min
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

Darcy Flow ~ 1cm/min

60 cm ~0.5mm silica sand

50mM CaCl$_2$
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow ~ 1cm/min

~0.5mm silica sand
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow $\sim$ 1cm/min

$\sim$0.5mm silica sand
Propagation of calcium carbonate

50mM \( \text{Na}_2\text{CO}_3 \)

50mM \( \text{CaCl}_2 \)

Darcy Flow \( \sim 1\text{cm/min} \)

\sim 0.5\text{mm} \text{ silica sand}
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

Darcy Flow $\sim$ 1cm/min

50mM CaCl$_2$

60 cm

$\sim$0.5mm silica sand
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow ~ 1cm/min

~0.5mm silica sand

INL Idaho National Laboratory
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow $\sim$ 1cm/min

60 cm

$\sim$0.5mm silica sand
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

50mM CaCl$_2$

Darcy Flow ~ 1cm/min

~0.5mm silica sand

60 cm
Propagation of calcium carbonate

$50 \text{mM Na}_2\text{CO}_3$

$50 \text{mM CaCl}_2$

Darcy Flow $\sim 1\text{cm/min}$

$60 \text{cm}$

$\sim 0.5\text{mm silica sand}$
Propagation of calcium carbonate

50mM Na$_2$CO$_3$

Darcy Flow ~ 1cm/min

50mM CaCl$_2$

~0.5mm silica sand

60 cm
Propagation of calcium carbonate (second attempt)

And Biofilms…?
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Tracer test following precipitation
Impact on permeability

Before carbonate precipitation

After carbonate precipitation:
Average permeability decreased by ~ 100
100mM Na$_2$CO$_3$, 1 cm/min

Sample Position: 2.5 cm

5 µm

100mM CaCl$_2$, pH ~7, 1 cm/min

Sample Position: 45 cm

20 µm

20 µm

10 µm

SEM images
Plans:

- Precipitation Kinetics
  - Extend outside conventional conditions
  - Ion ratios
  - Correlation to Sr uptake and speciation

- 2-D flow experiments
  - Full characterization
  - Propagation of precipitates in physically heterogeneous systems
    - Low permeability inclusions
    - High permeability flow paths
  - Propagation of precipitates in chemically heterogeneous systems
    - Calcite seeds
    - Clay on sand

- SPH and continuum-scale model refinement
Precipitation Kinetics
(see A.E. Nielsen (1983))

- \( R = k'(\Omega - 1) \) \textit{Adsorption (linear)}
- \( R = k''(\Omega - 1)^2 \) \textit{Spiral growth (parabolic)}
- \( R = [k_{ex} \Omega^{7/6}(\Omega - 1)^{2/3}(\ln \Omega)^{1/6}] \exp(-K_{ex}/\ln \Omega) \) \textit{Surface nucleation}
  \[ \sim (\Omega - 1)^{5/6} \exp(-K_{ex}/\ln \Omega) \]
  \[ \sim \exp(-K_{ex}/\ln \Omega) \]
- \( R = k'''(\Omega - 1)^n \) …Practical

Where:

ks are rate constants
\[ \Omega = \frac{\Pi(a_i^\nu)}{K_{sp}} \] (saturation ratio)
\( a_i^\nu \) is the activity of component i with stoichiometry \( \nu \)
\( K_{sp} \) = solubility product

- Also, Ostwald Ripening, Ostwald Step Rule
- Colloid filtration? Biomass growth?
Precipitation Kinetics

Precipitation Kinetics and Sr\textsuperscript{2+} sequestration: Experimental Approach

- **Goals:**
  - Test growth rate functions – apply in models
  - Test influence of ion ratios and modifiers
  - Morphologies, modes, products – interpretive
  - Sr\textsuperscript{2+} uptake and speciation

- **Method - constant composition**
  - *Batch reactors*
  - *Seeding* – to confine the role of homogeneous nucleation
  - *Stirring* - maintain uniform concentrations and reduce the influence of diffusive transport to surface layers.
  - *Maintain chemical composition* (as opposed to “free drift”) - to prolong the state of supersaturation.
Precipitation Kinetics: Relevant to Field?

• Will these relationships help predict what happens in the field?
  – Subsurface mixing zones are not stirred reactors. Diffusion will influence precipitation kinetics and, subsequently, distributions of saturation states.
  – Relative rate at which solutes are replenished or consumed – can result in non-stoichiometric, varying ion ratios

• \( R = k_f(Ca^{2+})^p(CO_3^{2-})^q - k_b \)  
Pre-modeling: 
Simulating pore-scale precipitation using 
Smoothed Particle Hydrodynamics

• Lagrangian, gridless, particle-based 
• Used to establish a basis for parameters and 
  conceptual basis for continuum approach

  • Continuity: \[ \frac{d\rho}{dt} = \rho \nabla \cdot \mathbf{v} \]
  
  • Conservation of momentum:
    \[ \frac{d\mathbf{v}}{dt} = \frac{1}{\rho} \nabla P + \mu \nabla^2 \mathbf{v} + \mathbf{F}^{ext} \]

  • Diffusion/reaction:
    \[ \frac{dC^A}{dt} = D^A \nabla^2 C^A - k_{AB} C^A C^B \]
    \[ \frac{dC^B}{dt} = D^B \nabla^2 C^B - k_{AB} C^A C^B \]
    \[ \frac{dC^C}{dt} = D^C \nabla^2 C^C + k^{AB} C^A C^B \]

• Precipitation of A and B via \( C_{\text{intermediate}} \)
Hypothetical intermediate:
\[ A + B = C_{\text{intermediate}} \]
\[ C_{\text{intermediate}} = C_{\text{solid}}, \text{ driven by } (C - C_{eq}) \]

Irreversible formation of \( C_{\text{intermediate}} \):
\[ \frac{dC^A}{dt} = D_A \nabla^2 C^A - k_{AB} C^A C^B \]

Irreversible formation of \( C_{\text{intermediate}} \):
• Initial Saturation index

• Saturation index during precipitation

• Steady-state condition at solution-solution interface
  – Preservation of less stable solid phases
  – Co-existence of multiple phases

• Flow variations
  – Velocities and ratios
  – Changing map of Damköhler (reaction rate vs. advection), and Peclet (advection vs. diffusion) numbers
Continuum-scale simulation: mixing
Mixing without and with precipitation
Presentations, Publications:


Connections:

- Field Investigations of Microbially Facilitated Calcite Precipitation for Immobilization of Strontium-90 and Other Trace Metals in the Subsurface
  - University of Idaho; Robert W. Smith, PI

- Hybrid Numerical Methods for Multiscale Simulations of Subsurface Biogeochemical Processes
  - PNNL; Tim Scheibe, PI

- Collaboration opportunities for:
  - Microbial characterization methods
  - Geotechnical properties
Parallel flow: mixing and precipitation at a solution-solution interface, 3-D, X-ray tomography

CaCl$_2$  NaHCO$_3$

6 cm

Calcium carbonate  Inner perimeter of column
Injection of a supersaturated solution
Propagation of calcium carbonate

\[ \text{Darcy Flow} \approx 1 \text{cm/min} \]
Application: nested dipole application

Fluid A
Fluid B
Fluid B
Fluid A

Reaction Zone
Example 1: *In situ* generation and mixing of reactants and geophysical monitoring

- **Application:** Formation of calcium carbonate and co-precipitation (immobilization) of strontium

- **Reactions (simplified):**

  \[
  (\text{NH}_2)_2\text{CO} + 3\text{H}_2\text{O} \xrightarrow{\text{urease}} \text{HCO}_3^- + 2\text{NH}_4^+ + \text{OH}^- \\
  \text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3(\text{s}) + \text{H}^+ \\
  \text{HCO}_3^- + \text{Ca}^{2+} + \text{Sr}^{2+} \rightarrow (\text{Ca,Sr})\text{CO}_3(\text{s}) + \text{H}^+
  \]

- **Equilibrium constant:**

  \[
  K_{sp \text{ calcite}} = (\text{Ca}^{2+})(\text{CO}_3^{2-}) \approx 10^{-8.4}
  \]

- **An abiotic analog to a microbially mediated process**
Questions:

• Impact of flow rate
  – Location of precipitation
  – Efficiency of reaction = f(mixing)

• Impact of permeability reduction
  – Constant flow
  – Constant gradient
Ultimate Modeling Objective

 Prefer a macroscopic continuum scale description
  – Practical
  – Can simulate larger systems

 Perform pore-scale modeling to:
  – Validate continuum approach
  – Provide basis for empirical or effective parameters used in continuum approach

  → Reduce level of detail as much as possible
Continuum model

\[ A + B = C_{\text{solid}} \]

Continuity: \[ \frac{d \rho}{dt} = \rho \nabla \cdot \mathbf{v} \]

- Conservation of momentum:
  \[ \frac{d \mathbf{v}}{dt} = -\frac{1}{\rho} \nabla P + \mu \rho \nabla^2 \mathbf{v} + \mathbf{F}^{\text{ext}} \]

- Diffusion/reaction:
  \[ \frac{d C^A}{dt} = D_A \nabla^2 C^A - k_{AB} C^A C^B \]
  \[ \frac{d C^B}{dt} = D_B \nabla^2 C^B - k_{AB} C^A C^B \]
  \[ \frac{d C^C}{dt} = D_C \nabla^2 C^C + k^{AB} C^A C^B \]
Supersaturation and velocity profiles

$t = 1000$  
$t = 3000$  
$t = 6000$

$t=1000$  
$t=6000$
Impact of Peclet number (advection/diffusion)

Pe = 0.9

t = 1000  

Pe = 2.8

t = 3000  

Pe = 0.9

t = 6000  

Pe = 2.8

Pe = 0.9

t = 3000  

Pe = 2.8

INL Idaho National Laboratory
3. Find x.

Here it is
After explaining to a student through various lessons and examples that:

\[
\lim_{x \to 8} \frac{1}{x-8} = \infty
\]

I tried to check if she really understood that, so I gave a different example. This was the result:

\[
\lim_{x \to 5} \frac{1}{x-5} = \infty
\]

- anon