Numerical investigation of microbially induced calcite precipitation as leakage mitigation technology

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CCS – storage safety, CO$_2$ leakage

- Abandoned well
- CO$_2$
- Cap rock failure
- Injection well vicinity
Relevant processes

- Two-phase multi-component transport
- Biomass
  - growth / decay
  - attachment / detachment
- Urea hydrolysis
  \[
  \text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{urease}} 2\text{NH}_3 + \text{H}_2\text{CO}_3
  \]
- Precipitation / dissolution of calcite
  \[
  \text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3 \downarrow
  \]
- Clogging
  \[
  \phi = \phi_0 - \phi_f - \phi_c
  \\
  K = K_0 \left( \frac{\phi - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}} \right)^3
  \]

(modified after Ebigbo et. al., *WRR* 2012)
REV-scale model

(modified after Ebigbo et al., WRR 2012)
2 fluid phases: Water and CO₂

2 solid phases: Calcite and biofilm

10 mobile components: Water, total carbon, sodium, chloride, calcium, biomass, substrate, oxygen, total nitrogen, urea

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<th>Component</th>
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<tr>
<td>components</td>
<td>$x_{w}^{\kappa}$</td>
<td>mole fraction of component $\kappa$ in water</td>
</tr>
<tr>
<td>solid phases</td>
<td>$\phi_{\lambda}$</td>
<td>volume fraction of solid phase $\lambda$</td>
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The variable for total carbon depends on the phase presence.
In case of both phases present, it is the non-wetting phase saturation,
if only water phase is present, it is the mole fraction of total carbon in water.
Mass balance equations

- Mass balance equation for components in both phases:

\[
\sum_{\alpha} \left\{ \frac{\partial}{\partial t} \left( \phi \rho_{\alpha} x_{\alpha}^{\kappa} S_{\alpha} \right) + \nabla \cdot \left( \rho_{\alpha} x_{\alpha}^{\kappa} \mathbf{v}_{\alpha} \right) - \nabla \cdot \left( \rho_{\alpha} D_{\alpha,pm} \nabla x_{\alpha}^{\kappa} \right) \right\} = q^{\kappa}
\]

\( \kappa \in \{w, C_{tot}, O_2\}; \alpha \in \{w, n\} \)

- Mass balance equation of components exclusively in the water phase:

\[
\frac{\partial}{\partial t} \left( \phi \rho_{w} x_{w}^{\kappa} S_{w} \right) + \nabla \cdot \left( \rho_{w} x_{w}^{\kappa} \mathbf{v}_{w} \right) - \nabla \cdot \left( \rho_{w} D_{w,pm} \nabla x_{w}^{\kappa} \right) = q^{\kappa}
\]

\( \kappa \in \{Na, Cl, Ca, bio, substrate, N_{tot}, urea\} \)

- Mass balance for the immobile components / solid phases:

\[
\rho_{\lambda} \frac{\partial \phi_{\lambda}}{\partial t} = q^{\lambda} \quad \lambda \in \{biofilm, calcite\}
\]
Sources & sinks: Biomass

Suspended biomass: \( q^{\text{bio}} = r^{\text{bio}}_{\text{growth}} - r^{\text{bio}}_{\text{decay}} - r_{\text{attach}} + r_{\text{detach}} \)

Biofilm: \( q^{\text{biofilm}} = r^{\text{biofilm}}_{\text{growth}} - r^{\text{biofilm}}_{\text{decay}} + r_{\text{attach}} - r_{\text{detach}} \)

Growth: \( r^{\text{bio}}_{\text{growth}} = \mu \phi S_w C^{\text{bio}}_w \)

\( r^{\text{biofilm}}_{\text{growth}} = \mu \phi^{\text{biofilm}} q^{\text{biofilm}} \)

Growth coefficient: \( \mu = \mu_{\text{max}} \frac{Yield}{K_{\text{substrate}} + C^{\text{substrate}}_w} \cdot \frac{C^{\text{O}_2}_w}{K_{\text{O}_2} + C^{\text{O}_2}_w} \)

Decay: \( r^{\text{bio}}_{\text{decay}} = f(\text{pH, } C^{\text{bio}}_w, \phi, S_w, ) \)

\( r^{\text{biofilm}}_{\text{decay}} = f(\text{calcite precipitation, } \phi^{\text{biofilm}}) \)

Attachment: \( r_{\text{attach}} = f(C^{\text{bio}}_w, \phi, S_w, \phi^{\text{biofilm}}) \)

Detachment: \( r_{\text{detach}} = f(|\nabla p_w|, \phi^{\text{biofilm}}, r^{\text{biofilm}}_{\text{growth}}) \)
Sources & sinks: Solutes

Substrate: 
\[ q_{\text{substrate}} = -(r_{\text{bio} \text{growth}} + r_{\text{biofilm} \text{growth}})/Yield \]

Oxygen: 
\[ q^{O_2} = -(r_{\text{bio} \text{growth}} + r_{\text{biofilm} \text{growth}}) \cdot (0.5/Yield) \]

Urea: 
\[ q^{\text{urea}} = -r^{\text{urea}} = f(C^{\text{urea}}_w, \text{pH}, C^{\text{NH}_4}_w) \]

Total nitrogen: 
\[ q^{\text{NH}_{\text{tot}}} = 2r^{\text{urea}} \]

Calcium: 
\[ q^{\text{Ca}} = r_{\text{diss}} - r_{\text{precip}} \]

Total carbon: 
\[ q^{\text{C}_{\text{tot}}} = r^{\text{urea}} + r_{\text{diss}} - r_{\text{precip}} \]

Calcite: 
\[ q^{\text{calcite}} = r_{\text{precip}} - r_{\text{diss}} \]
High-pressure core experiments

Berea sandstone core used for the high pressure core experiment

\[
\phi = \phi_0 = 0.18
\]

\[
\phi_c = 0
\]

\[
K = K_0 = 3 \cdot 10^{-14} \text{m}^2
\]

Experiment
\[
\phi = 0.137
\]
\[
\phi_c = 0.037
\]
\[
K = 2.3 \cdot 10^{-15} \text{m}^2
\]

Simulation
\[
\phi = 0.114
\]
\[
\phi_c = 0.030
\]
\[
K = 6.0 \cdot 10^{-15} \text{m}^2
\]
Results: High-pressure core experiments

- In general good agreement between experiment and simulation.
- At the end and the beginning the experiment is not matched by the simulation.
Results: High-pressure core experiments

- Kozeny-Carman relation does not represent effects of biofilm on permeability.
- The effect of calcite precipitation is pictured quite well.

**Graph:**
- **Permeability** [10^{-14} m²]
- **Time** [h]
- **Biofilm inoculation**
- **Biofilm decay during one week starvation period**
- **Calcium injections (examples)**

**Legend:**
- **Experiment – Permeability**
- **Simulation – Permeability**
Future work: Large and field-scale application

Challenges:
- few information
- heterogeneous and anisotropic media
- 3-D radial flow
- large scale vs. necessity of fine discretization

Phillips et al., *Environmental Science & Tech.* 2012
Outlook

- Validation of two-phase model.
- High-pressure experiments with supercritical carbon dioxide.
- Validation of the model for inhomogeneous media.
- Use the model as a predictive tool to design field scale application.
- Improve the implementation of clogging with respect to biofilm presence.
Thank you for your attention!

Numerical implementation:

**DuMuX** (DUNE for Multi-\{Phase, Scale, Component, Physics, ...\})
- Based on DUNE (Distributed and Unified Numerics Environment)
- Modular numerical simulator

For further information see: [http://dumux.org/](http://dumux.org/) or:

Thank you for your attention!
Motivation – Injection-Well Vicinity

- corrosion of well cement
- high injection pressure → cause fracture
  → leakage of CO2

(Ebigbo et. al., AWR 2010)

→ interested in investigating the use of biofilms which are capable of causing calcite precipitation
Model concept

- What kind of a model do we need?

(Ebigbo et. al., AWR 2010; Phillips et al., Environmental Science & Tech. 2012)
Model concept

- What kind of a model do we need?
- Two-phase multi-component flow model
- Including relevant bio-chemical processes

(Ebigo et. al., *AWR* 2010; Phillips et al., *Environmental Science & Tech.* 2012)
**List of Components / Primary Variables**

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<tr>
<td>susp. biomass</td>
<td>$x_{w}^{b}$</td>
<td>...... mole fraction of suspended biomass in water</td>
</tr>
<tr>
<td>biofilm</td>
<td>$\phi_f$</td>
<td>volume fraction of biofilm</td>
</tr>
<tr>
<td>substrate</td>
<td>$x_{w}^{s}$</td>
<td>...... mole fraction of substrate in water</td>
</tr>
<tr>
<td>oxygen</td>
<td>$x_{w}^{O_2}$</td>
<td>...... mole fraction of oxygen in water</td>
</tr>
<tr>
<td>urea</td>
<td>$x_{w}^{u}$</td>
<td>...... mole fraction of urea in water</td>
</tr>
<tr>
<td>total nitrogen</td>
<td>$x_{w}^{N_{tot}}$</td>
<td>...... mole fraction of total nitrogen in water</td>
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<td>$\phi_c$</td>
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<td>$x_{w}^{Ca}$</td>
<td>...... mole fraction of calcium in water</td>
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<td>...... mole fraction of chloride in water</td>
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<td>$x_{w}^{Na}$</td>
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In total 2 fluid phases, 2 solid phases and 10 mobile components

The variable for the total carbon depends on the phase presence. In case of both phases present, it is the non-wetting phase saturation, if only water phase is present, it is the mole fraction of total carbon in water.
Biomineralisation: Reactions

- bacteria *Sporosarcina pasteurii* produce the enzyme urease

- urease catalyses the hydrolysis of urea, which produces ammonia and leads to a pH increase → drives the precipitation of calcite

\[

cO_{(NH_2)_2} + 2H_2O \xrightarrow{\text{urease}} 2NH_3 + H_2CO_3
\]

\[
H_2CO_3 \leftrightarrow HCO_3^- + H^+
\]

dissociation of carbonic acid

\[
HCO_3^- \leftrightarrow CO_3^{2-} + H^+
\]

dissociation of bicarbonate ion

\[
2NH_4^+ \leftrightarrow 2NH_3 + 2H^+
\]

dissociation of ammonia

\[
Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \downarrow
\]

calcite precipitation/dissolution

→ in the presence of calcium ions, the rise in pH will drive the precipitation of calcite.
Rate of Urea Hydrolysis

\[ q^u = -\nu_{\text{max}} \cdot \frac{m_{\text{urea}}}{(K_M + m_{\text{urea}}) \left(1 + \frac{m_{\text{NH}_4^+}}{K_P}\right)} k_{\text{ub}} \left[ \text{mol}_{\text{urea}} \right] \left[ \text{m}^3 \cdot \text{s} \right] \]

\[ \nu_{\text{max}} \ldots \text{maximum reaction rate} \]

\[ k_{\text{ub}} \ldots \text{amount of urease per bulk volume} \]

\[ \nu_{\text{max}} = \frac{k}{1 + \frac{m_{\text{H}^+}}{K_{\text{EU},1}} + \frac{K_{\text{EU},2}}{m_{\text{H}^+}} \left[ \text{mol}_{\text{urea}} \right] \left[ \text{g}_{\text{urease}} \cdot \text{s} \right]} \]

\[ K_{\text{EU},i} \ldots \text{dissociation constants for enzyme–urea complex} \]

Adapted from:

Rate of Urea Hydrolysis

\[ q^u = -\nu_{\text{max}} \cdot \frac{m_{\text{urea}}}{(K_M + m_{\text{urea}}) \left(1 + \frac{m_{\text{NH}_4^+}}{K_P}\right)} k_{\text{ub}} \quad \text{[mol}_{\text{urea}} \text{m}^{-3} \cdot \text{s}^{-1}] \]

\( \nu_{\text{max}} \) ... maximum reaction rate
\( k_{\text{ub}} \) ... amount of urease per bulk volume

**Calcite Precipitation / Dissolution**

\[ r_{\text{prec}} = k_{\text{prec}} A_{\text{sw}} (\Omega - 1)^{n_p} \quad \text{for} \quad \Omega \geq 1 \quad \rightarrow \quad \text{precipitation occurs} \]

\[ r_{\text{diss}} = (k_{\text{diss}, 1}[H^+] + k_{\text{diss}, 2}) A_{\text{cw}} (1 - \Omega)^{n_d} \quad \text{for} \quad \Omega < 1 \quad \rightarrow \quad \text{dissolution occurs} \]

\[ \Omega = \frac{m_{\text{Ca}^{2+}} m_{\text{CO}_3^{2-}}}{K^* (I)} = \frac{\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} + \gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}}}{K_{sp}} \quad \ldots \text{saturation state} \]

\[ A_{\text{sw}} \ldots \text{specific interfacial surface between solid and water phases} \]

\[ A_{\text{cw}} \ldots \text{specific interfacial surface between calcite and water phases} \]

\[ \rightarrow \text{rate of precipitation or dissolution is dependent on the distance from equilibrium} \]
From the activity coefficients, one can calculate the apparent solubility product

\[ \Omega = \frac{\gamma_{\text{Ca}^2+}m_{\text{Ca}^2+}\gamma_{\text{CO}_3^{2-}}m_{\text{CO}_3^{2-}}}{K_{\text{sp}}} \]

\[ K_{\text{sp}}^* = \frac{K_{\text{sp}}}{\gamma_{\text{Ca}^2+}\gamma_{\text{CO}_3^{2-}}} \]

**Negative logarithm of apparent solubility product** $K_{\text{sp}}^*$ **in NaCl and CaCl$_2$ solutions.**
Surface Areas

\[ a_c \phi_c < A_{sw}(\phi) \]

\[ A_{sw} = A_{sw,0} \left( \frac{\phi}{\phi_0} \right)^{\frac{2}{3}} \]

\[ A_{cw} = \min(A_{sw}, a_c \phi_c) \]

(Ebigbo et. al., WRR 2012)

\[ a_c \ldots \text{specific surface area of calcite grains} \]
Supplementary equations

- Changes in porosity
  \[ \phi = \phi_0 - \phi_f - \phi_c \]

- Changes in permeability
  \[ K = K_0 \left( \frac{\phi-\phi_{\text{crit}}}{\phi_0-\phi_{\text{crit}}} \right)^3 \ldots \text{Kozeny – Carman – type relation} \]

- Charge balance
  \[ \sum_i z_i m_i = 0 \]
Column Experiments

NH₄Cl

CaCl₂, urea, substrate

Calcite is quantified at the end of the experiments
Results: Column Experiments

(MUFTE-distributions and Experimental data from Ebigbo et. al., WRR 2012)
Future work: Large rock core experiments

- The fully implicit model
  - is computationally too expensive
  - and sensitive to boundary conditions or the inclusion of the high permeability region = fracture

→ New concept:
Decoupling flow and transport calculation to get rid of those constraints
Future Test case: High-Pressure Experiments

DOE FOA 250

“Innovative Technologies in Geologic Carbon Sequestration”

Center for Biofilm Engineering
Montana State University
Old slides
Outline

- Motivation
- Model concept
- Numerical implementation
- Simulation results
- Final remarks
Relevant Processes

- Two-phase multi-component transport
- Biomass
  - growth / decay
  - attachment / detachment
- Urea hydrolysis
- Precipitation / dissolution of calcite
- Clogging

(modified after Ebigbo et. al., WRR 2012)
Sources & sinks: Biomass

Suspended biomass:
\[ q^b = r^b_g - r^b_{dc} - r_a + r_d \]

Biofilm:
\[ q^f = r^f_g - r^f_{dc} + r_a - r_d \]

Growth term:
\[ r^b_g = \mu \phi S_w C^b_w \]
\[ r^f_g = \mu \phi_f \varrho_f \]

Growth coefficient:
\[ \mu = \frac{k_{\mu} Y}{K_{\text{substrate}} + C^\text{substrate}_w} \frac{C^O_2_w}{K_{O_2} + C^O_2_w} \]

Décay term:
\[ r^b_{dc} = b^b \phi S_w C^b_w \]
\[ r^f_{dc} = b^f \phi_f \varrho_f \]

Attachment term:
\[ r_a = k_a \phi S_w C^b_w \]

Detachment term:
\[ r_d = k_d \phi_f \varrho_f \]
Sources / Sinks: Biomass

\[ q^b = r^b_g - r^b_b - r_a + r_d \]
\[ q^f = r^f_g - r^f_b + r_a - r_d \]

Growth term:
\[ r^b_g = \mu \phi S_w C^b_w \]
\[ r^f_g = \mu \phi_f \theta_f \]

Growth coefficient:
\[ \mu = k_\mu Y \frac{C^s_w}{K_s + C^s_w} \cdot \frac{C^e_w}{K_e + C^e_w} \]

Decay term:
\[ r^b_b = b^b \phi S_w C^b_w \]
\[ r^f_b = b^f \phi_f \theta_f \]

Attachment term:
\[ r_a = k_a \phi S_w C^b_w \]

Detachment term:
\[ r_d = k_d \phi_f \theta_f \]
Sources / Sinks: Solutes

Substrate: \[ q^s = -\frac{(r^b_g + r^f_g)}{Y} \]

Electron acceptor: \[ q^e = -\frac{(r^b_g + r^f_g)}{(R/Y)} \]

Urea: \[ q^u = f(C_w^u, \text{pH}, C_w^a) \]

Ammonium/ammonia: \[ q^a = f(q^u) \]

Calcium: \[ q^{Ca} = r_{\text{diss}} - r_{\text{prec}} \]

Calcite: \[ q^c = r_{\text{prec}} - r_{\text{diss}} \]