10th April 2013

Numerical investigation of microbially induced calcite precipitation as leakage mitigation technology

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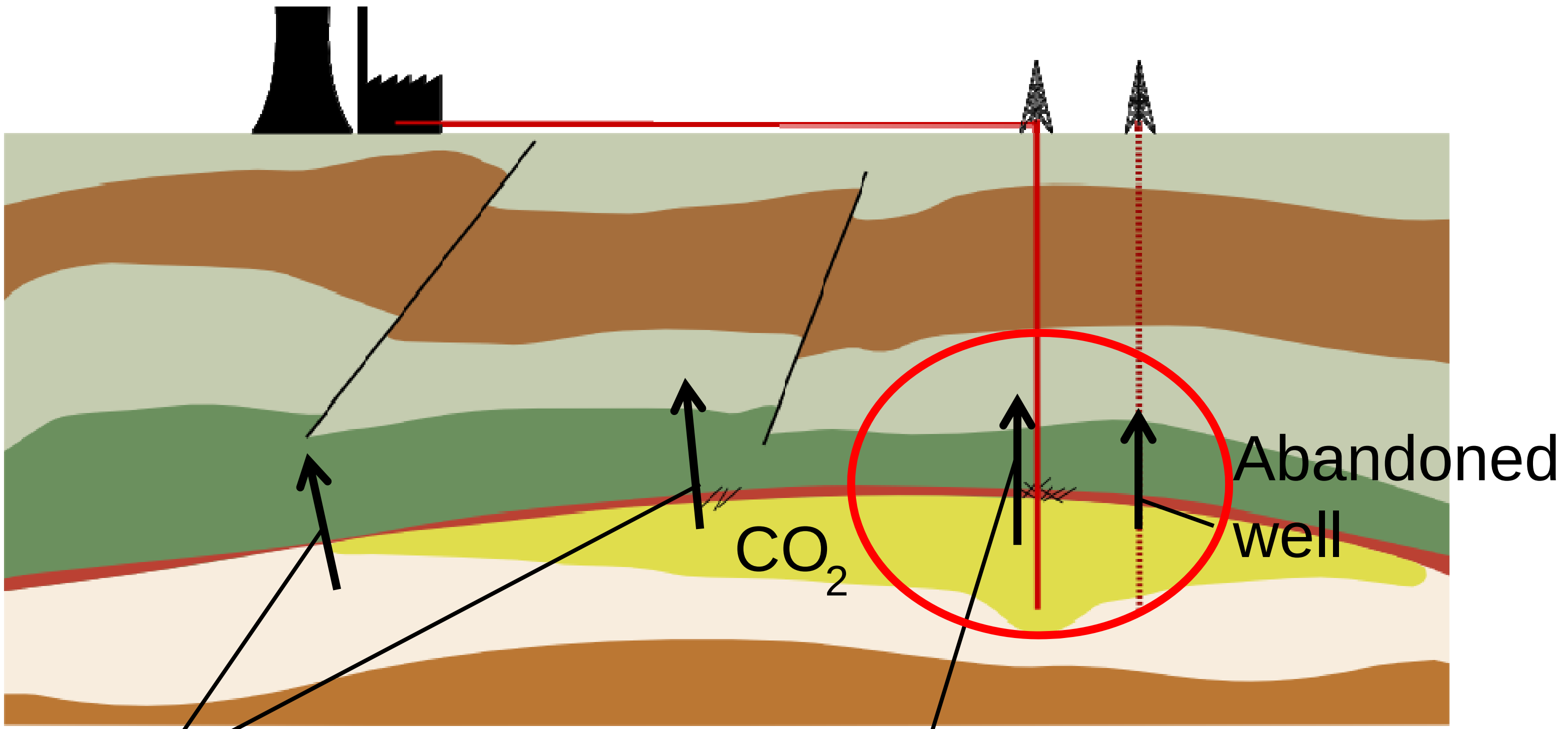
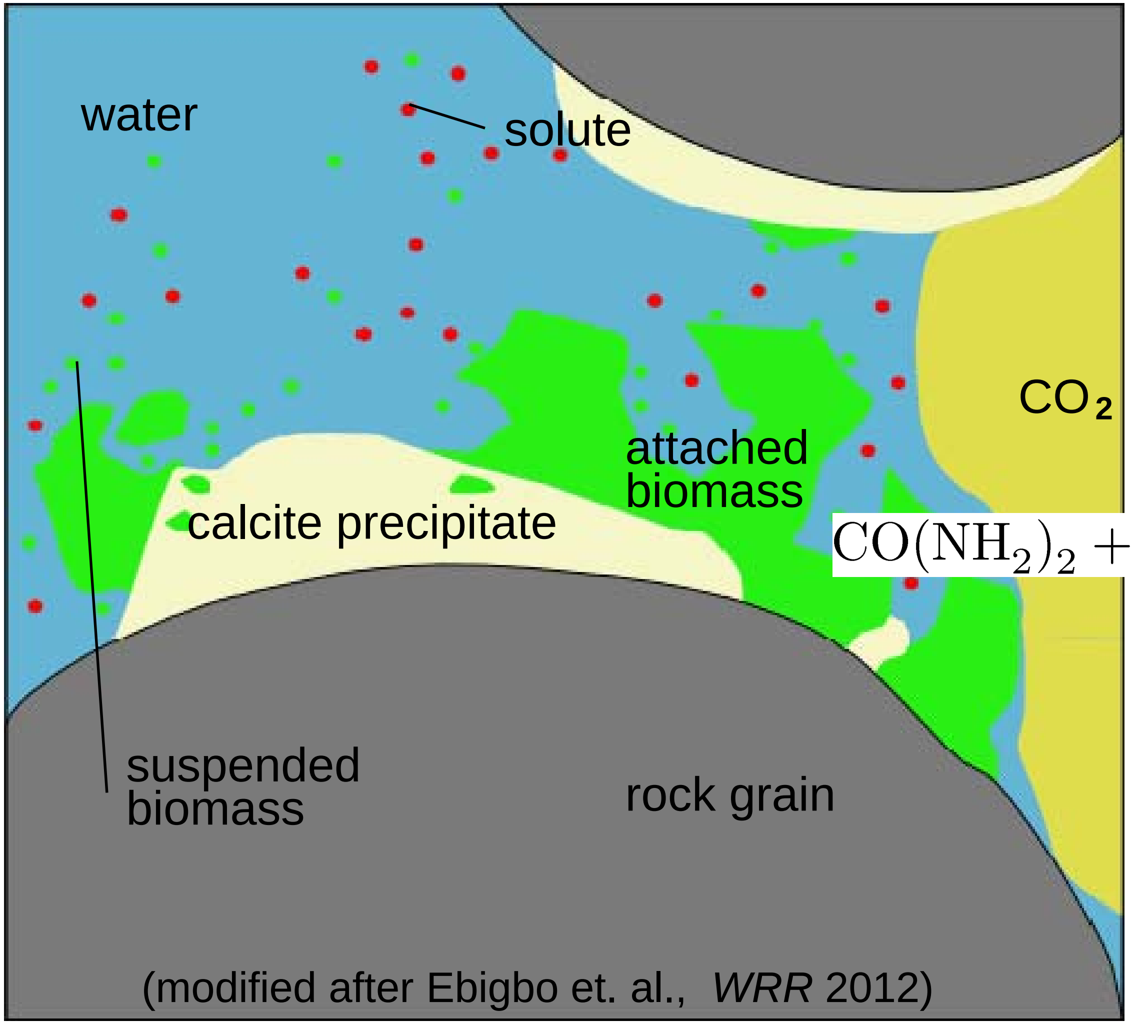
CCS – storage safety, CO_2 leakage



Relevant processes



- Two-phase multi-component transport
- Biomass
  - growth / decay
  - attachment / detachment
- Urea hydrolysis

$$CO(NH_2)_2 + 2\,H_2O \xrightarrow{\text{urease}} 2\,NH_3 + H_2CO_3$$

- Precipitation / dissolution of calcite

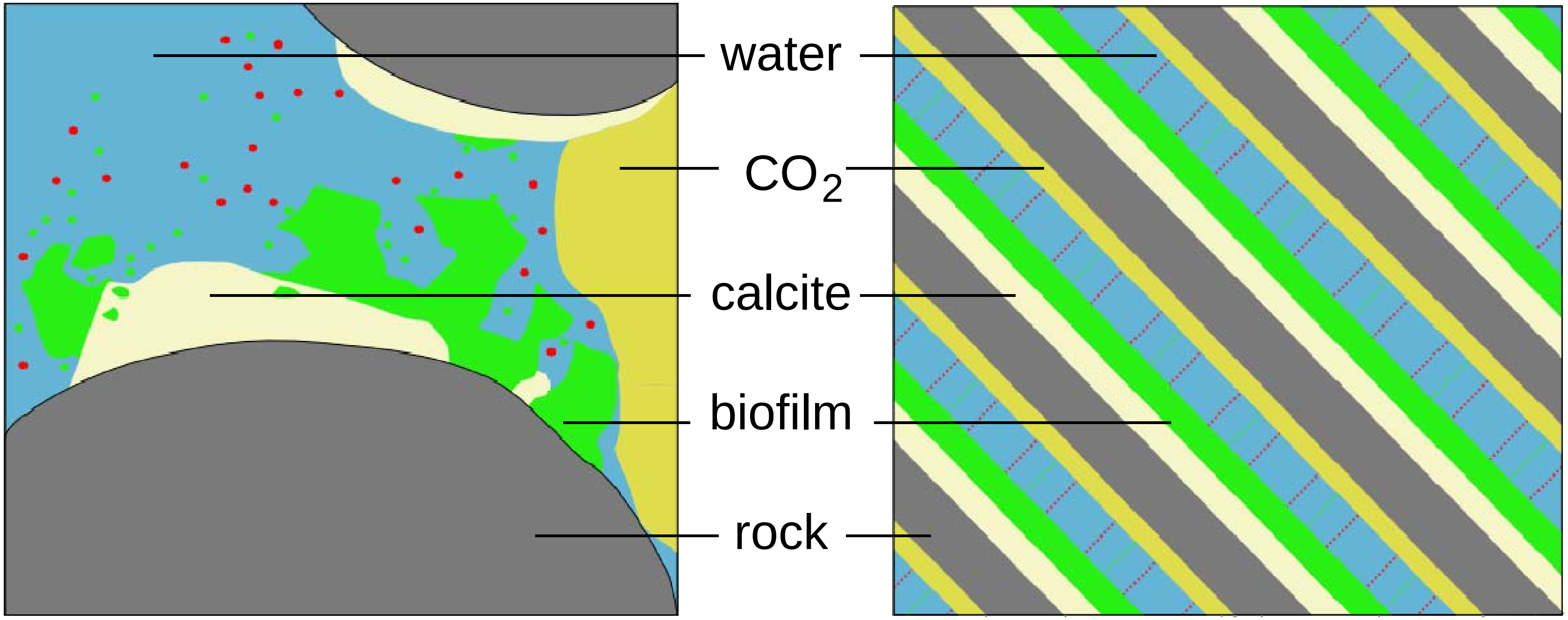
$$Ca^{2+} + CO_3^{2-} \longleftrightarrow CaCO_3 \downarrow$$

- Clogging

$$\phi = \phi_0 - \phi_f - \phi_c$$

$$K = K_0 \left(\frac{\phi - \phi_{crit}}{\phi_0 - \phi_{crit}} \right)^3$$

REV-scale model



(modified after Ebigbo et. al., *WRR* 2012)

averaging

Pore scale → REV scale

Phases, components, primary variables

2 fluid phases: Water and CO_2

2 solid phases: Calcite and biofilm

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

Component	Variable	Description
water	p_w	. . . . water phase pressure
total carbon	S_n or $x_\mathrm{w}^{\mathrm{C_{tot}}}$	$\mathrm{CO_2}$ saturation or mole frac. of tot. carbon in water
components	x_w^{κ}	. . . . mole fraction of component κ in water
solid phases	ϕ_λ	. . . . .volume fraction of solid phase λ

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:

$$\sum_\alpha \left\{ \frac{\partial}{\partial t} \left(\phi \varrho_\alpha x_\alpha^\kappa S_\alpha \right) + \nabla \cdot \left(\varrho_\alpha x_\alpha^\kappa \mathbf{v}_\alpha \right) - \nabla \cdot \left(\varrho_\alpha \mathbf{D}_{\alpha,\mathrm{pm}} \nabla x_\alpha^\kappa \right) \right\} = q^\kappa$$

$$\kappa \in \{\mathrm{w}, \mathrm{C}_{\mathrm{tot}}, \mathrm{O}_2\}\,; \alpha \in \{\mathrm{w}, \mathrm{n}\}$$

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

$$\frac{\partial}{\partial t} \left(\phi \varrho_\mathrm{w} x_\mathrm{w}^\kappa S_\mathrm{w} \right) + \nabla \cdot \left(\varrho_\mathrm{w} x_\mathrm{w}^\kappa \mathbf{v}_\mathrm{w} \right) - \nabla \cdot \left(\varrho_\mathrm{w} \mathbf{D}_{\mathrm{w,pm}} \nabla x_\mathrm{w}^\kappa \right) = q^\kappa$$

$$\kappa \in \{\mathrm{Na}, \mathrm{Cl}, \mathrm{Ca}, \mathrm{bio}, \mathrm{substrate}, \mathrm{N}_{\mathrm{tot}}, \mathrm{urea}\}$$

- Mass balance for the immobile components / solid phases:

$$\varrho_\lambda \frac{\partial \phi_\lambda}{\partial t} = q^\lambda \qquad \lambda \in \{\mathrm{biofilm}, \mathrm{calcite}\}$$

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: $$r^{\text{bio}}_{\text{growth}} = \mu \phi S_{\text{w}} C^{\text{bio}}_{\text{w}}$$

$$r^{\text{biofilm}}_{\text{growth}} = \mu \phi_{\text{biofilm}} \varrho_{\text{biofilm}}$$

Growth coefficient: $$\mu = \mu_{\text{max}} Yield \frac{C^{\text{substrate}}_{\text{w}}}{K_{\text{substrate}} + C^{\text{substrate}}_{\text{w}}} \cdot \frac{C^{\text{O}_2}_{\text{w}}}{K_{\text{O}_2} + C^{\text{O}_2}_{\text{w}}}$$

Decay: $$r^{\text{bio}}_{\text{decay}} = f(\text{pH}, C^{\text{bio}}_{\text{w}}, \phi, S_{\text{w}},)$$

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

Attachment: $$r_{\text{attach}} = f(C^{\text{bio}}_{\text{w}}, \phi, S_{\text{w}}, \phi_{\text{biofilm}})$$

Detachment: $$r_{\text{detach}} = f(\left|\nabla p_{\text{w}}\right|, \phi_{\text{biofilm}}, r^{\text{biofilm}}_{\text{growth}})$$

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^{urea}	$=$	$-r^{\text{urea}} = f(C_{\text{w}}^{\text{urea}}, \text{pH}, C_{\text{w}}^{\text{NH}_4})$
Total nitrogen:	$q^{\text{NH}_{\text{tot}}}$	$=$	$2r^{\text{urea}}$
Calcium:	q^{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^{calcite}	$=$	$r_{\text{precip}} - r_{\text{diss}}$

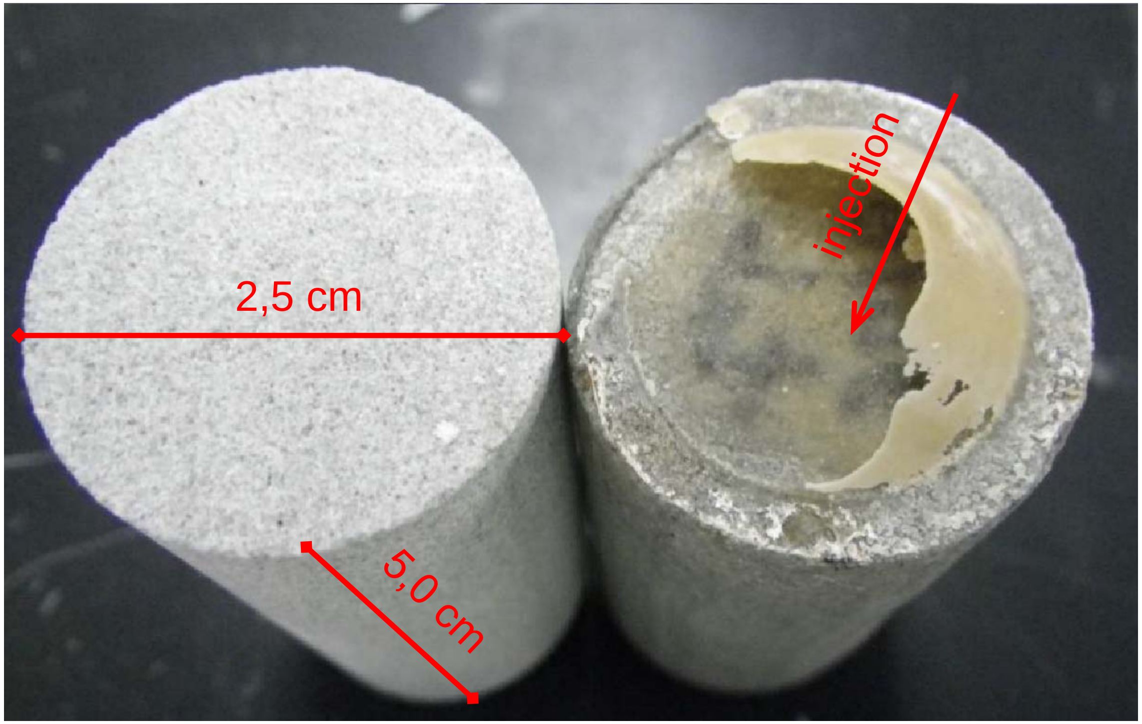
High-pressure core experiments

Berea sandstone core used for the high pressure core experiment

$\phi = \phi_0 = 0.18$

$\phi_c = 0$

$K = K_0 =$
$3 \cdot 10^{-14} \mathrm{m}^2$



Experiment

$\phi = 0.137$

$\phi_c = 0.037$

$K =$
$2.3 \cdot 10^{-15} \mathrm{m}^2$

Simulation

$\phi = 0.114$

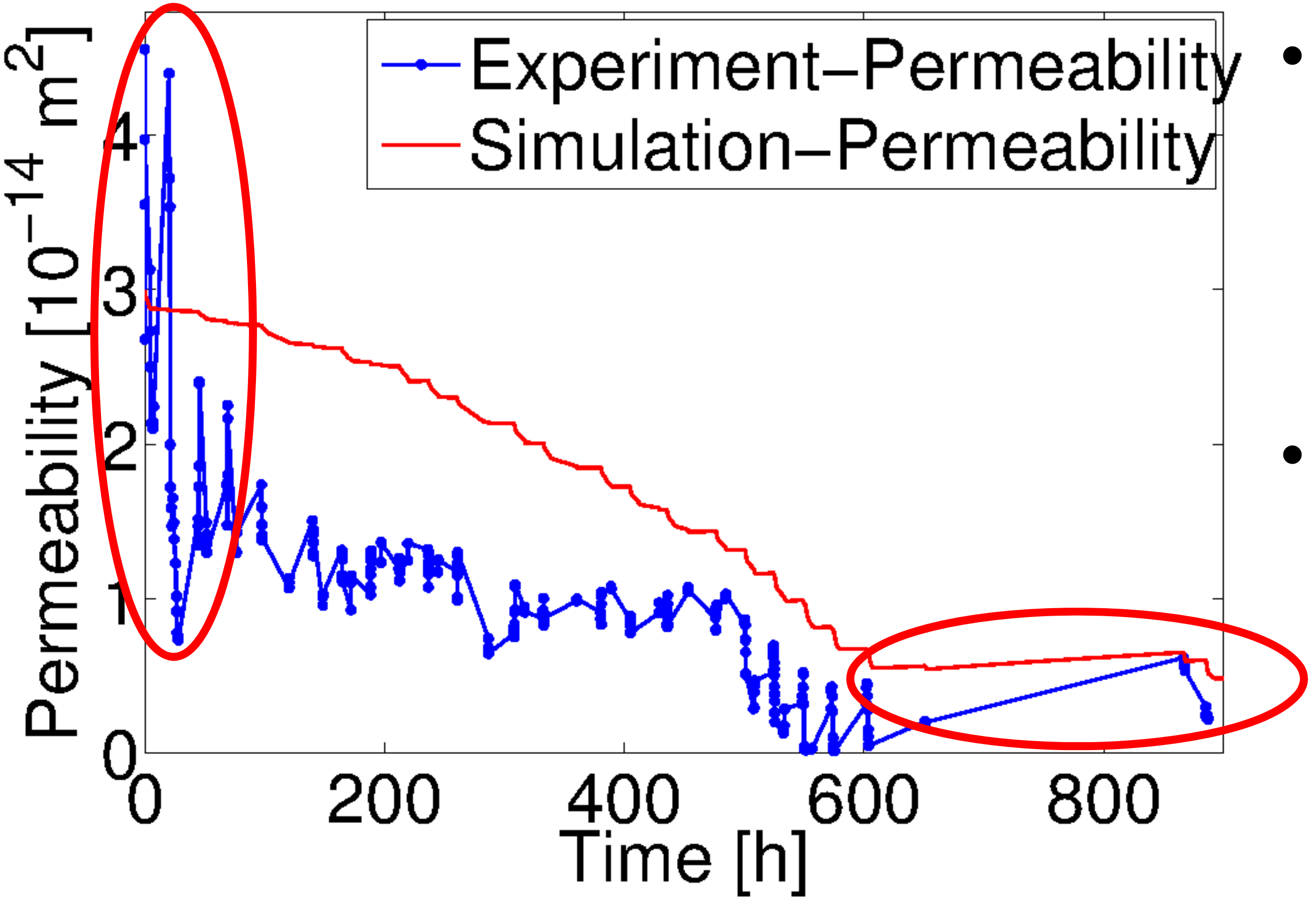
$\phi_c = 0.030$

$K =$
$6.0 \cdot 10^{-15} \mathrm{m}^2$

before after

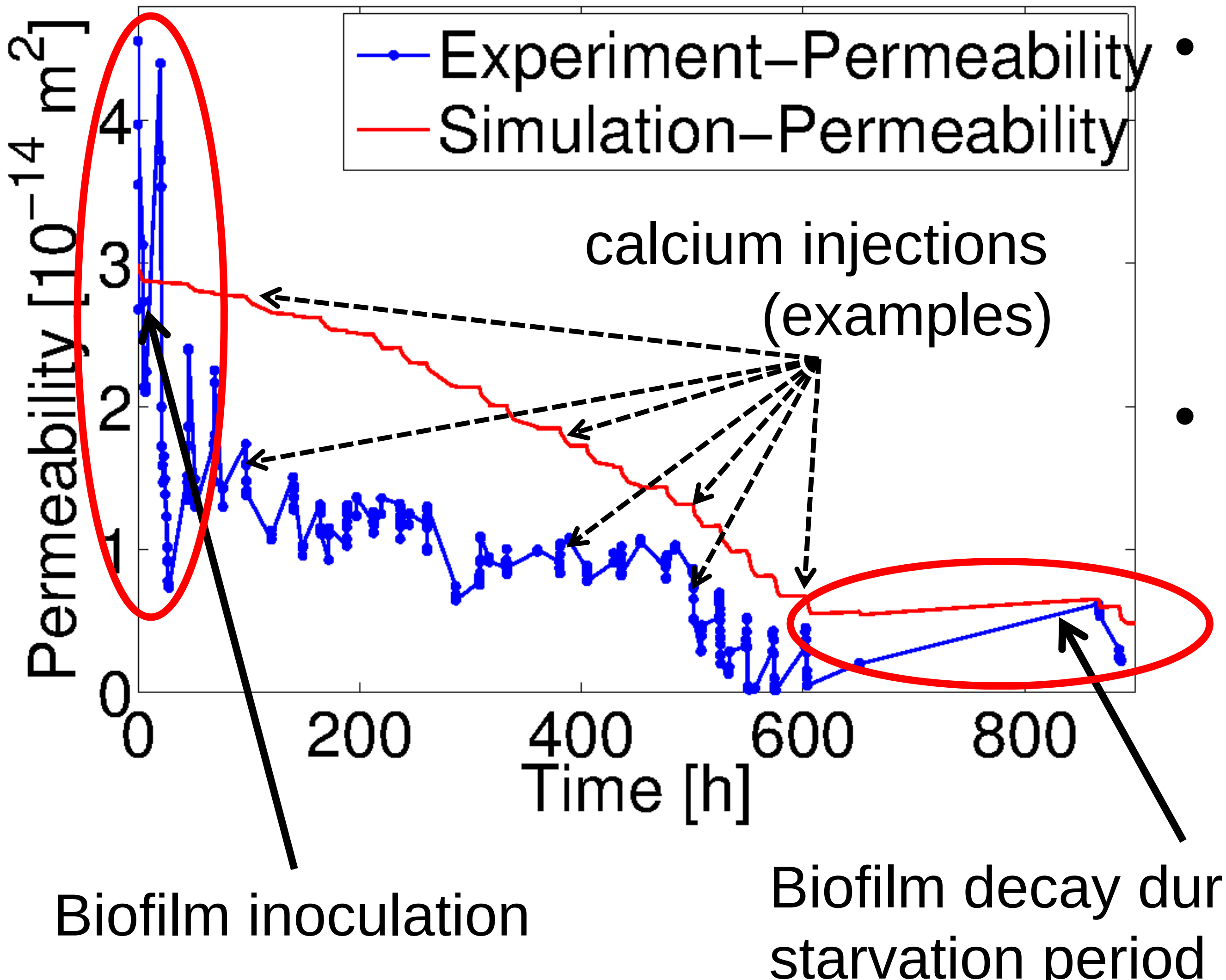
biomineralization

Results: High-pressure core experiments



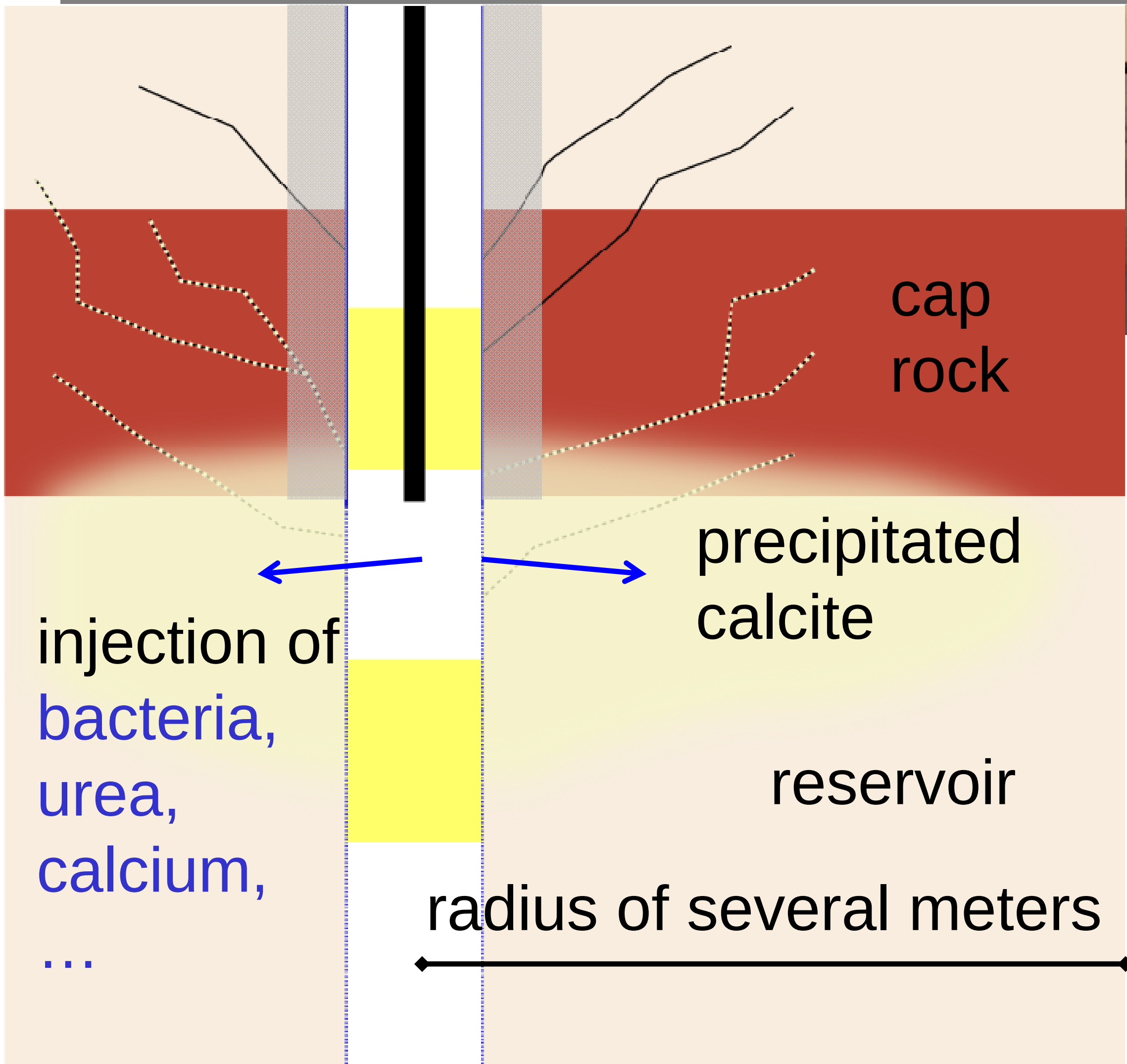
- In general good agreement between experiment and simulation
- At the end and the beginning the experiment is not matched by the simulation

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

Future work: Large and field-scale application



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

Challenges:

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

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:

DuMu$^{\mathbf{X}}$ (**DU**NE for **Mu**lti-{Phase, Scale, Component, Physics, ...})

- Based on DUNE (Distributed and Unified Numerics Environment)
- Modular numerical simulator

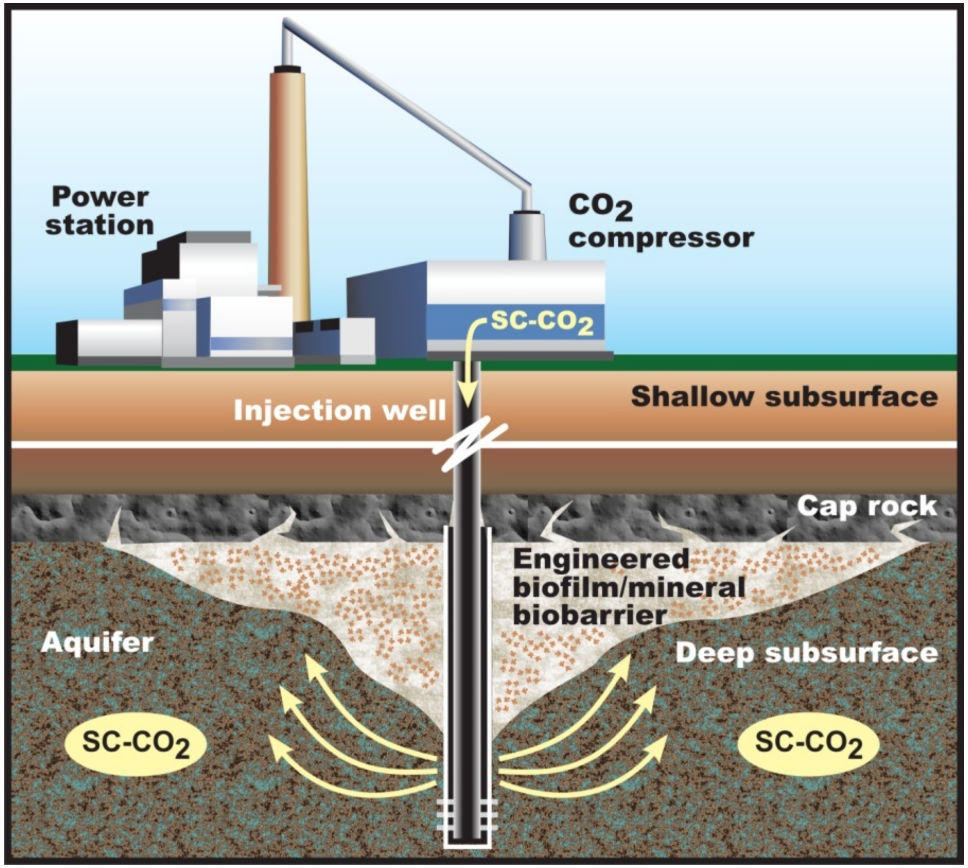
For further information see: http://dumux.org/ or:

Flemisch et. al; DuMux: DUNE for Multi-{Phase, Component, Scale, Physics, ...} Flow and Transport in Porous Media. *Advances in Water Resources* , 2011.


Phillips et al. , *Environmental Science & Tech.* 2012
Thank you for your attention!

Supplementary slides

Motivation – Injection-Well Vicinity



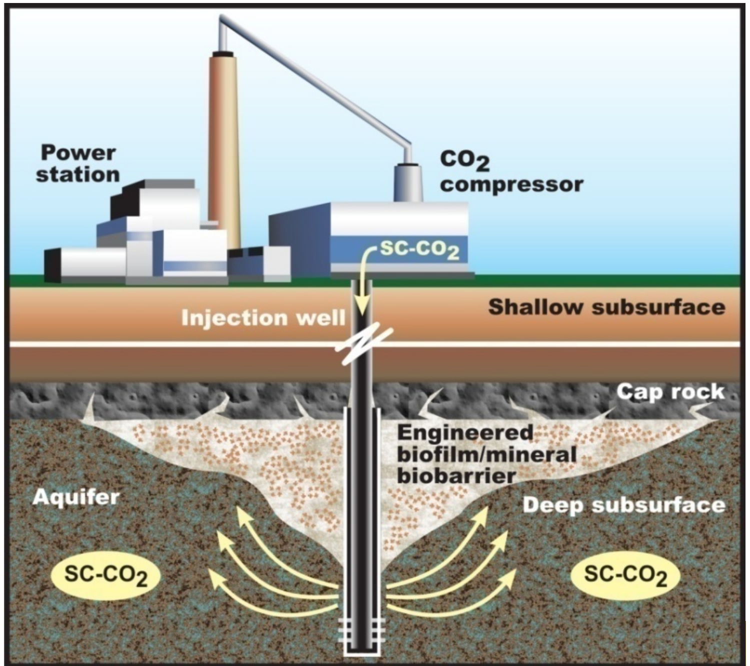
- corrosion of well cement
- high injection pressure
  → cause fracture

→ leakage of CO2

(Ebigbo et. al., *AWR* 2010)

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

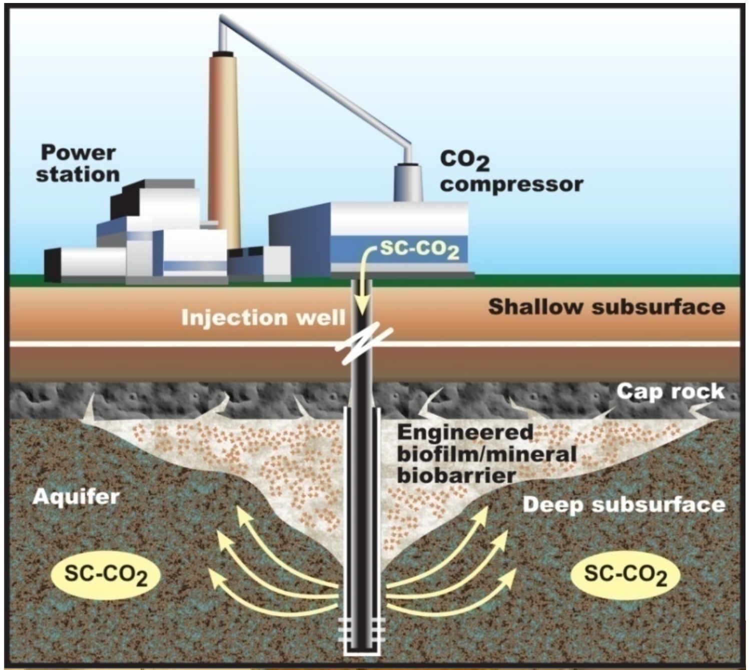
Model concept



- 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

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

List of Components / Primary Variables

Component	Variable	Description
water	p_w	.... water phase pressure
total carbon	S_n / $x_\mathrm{w}^{\mathrm{C_{tot}}}$	CO_2 saturation / mole frac. of tot. carbon in water
susp. biomass	x_w^b	......mole fraction of suspended biomass in water
biofilm	ϕ_f	.... volume fraction of biofilm
substrate	x_w^s	................mole fraction of substrate in water
oxygen	$x_\mathrm{w}^{\mathrm{O_2}}$	.... mole fraction of oxygen in water
urea	x_w^u	.....................mole fraction of urea in water
total nitrogen	$x_\mathrm{w}^{\mathrm{N_{tot}}}$	..........mole fraction of total nitrogen in water
calcite	ϕ_c	.........................volume fraction of calcite
calcium	$x_\mathrm{w}^{\mathrm{Ca}}$	..................mole fraction of calcium in water
chloride	$x_\mathrm{w}^{\mathrm{Cl}}$	.... mole fraction of chloride in water
sodium	$x_\mathrm{w}^{\mathrm{Na}}$	..................mole fraction of sodium in water

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**

$CO(NH_2)_2 + 2\,H_2O \xrightarrow{urease} 2\,NH_3 + H_2CO_3$	ureolysis
$H_2CO_3 \longleftrightarrow HCO_3^- + H^+$	dissociation of carbonic acid
$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+$	dissociation of bicarbonate ion
$2\,NH_4^+ \longleftrightarrow 2\,NH_3 + 2\,H^+$	dissociation of ammonia
$Ca^{2+} + CO_3^{2-} \longleftrightarrow CaCO_3 \downarrow$	calcite precipitation/dissolution

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

Rate of Urea Hydrolysis

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

ν_{max} ... maximum reaction rate

k_{ub} ... amount of urease per bulk volume

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

$K_{\mathrm{EU},i}$ ... dissociation constants for enzyme–urea complex

Adapted from:

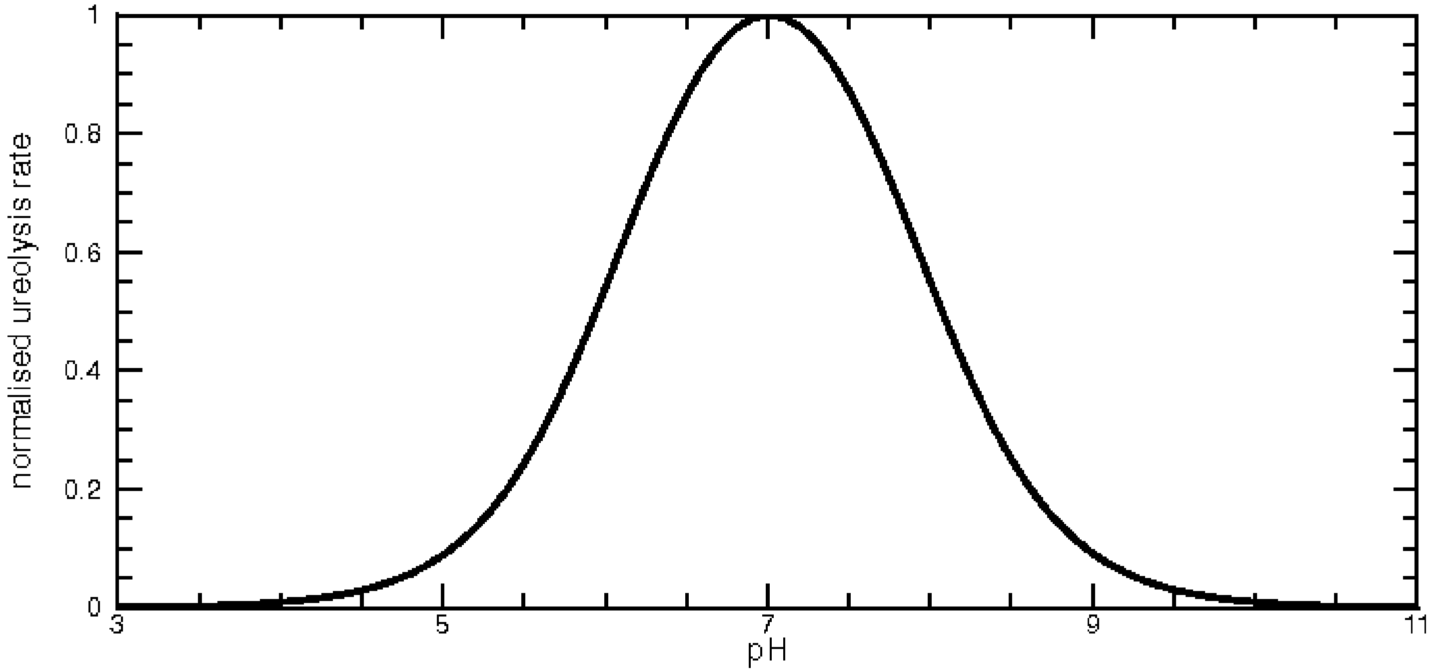
Fidaleo and Lavecchia, *Chem. Biochem. Eng. Q*. 17 (4) 2003

Rate of Urea Hydrolysis

$$q^{\mathrm{u}} = -\nu_{\mathrm{max}} \cdot \frac{m_{\mathrm{urea}}}{(K_{\mathrm{M}} + m_{\mathrm{urea}})\left(1 + \frac{m_{\mathrm{NH}_4^+}}{K_{\mathrm{P}}}\right)} k_{\mathrm{ub}} \qquad \left[\frac{\mathrm{mol}_{\mathrm{urea}}}{\mathrm{m}^3 \cdot \mathrm{s}}\right]$$

ν_{max} . . . maximum reaction rate

k_{ub} . . . amount of urease per bulk volume



Fidaleo and Lavecchia, *Chem. Biochem. Eng. Q*. 17 (4) 2003

Calcite Precipitation / Dissolution

$$r_{\mathsf{prec}} = k_{\mathsf{prec}} A_{\mathsf{sw}} (\Omega - 1)^{n_{\mathsf{p}}} \quad \text{for } \Omega \geq 1$$

→ precipitation occurs

$$r_{\mathsf{diss}} = (k_{\mathsf{diss,1}}[\mathrm{H}^+] + k_{\mathsf{diss,2}}) A_{\mathsf{cw}} (1 - \Omega)^{n_{\mathsf{d}}} \quad \text{for } \Omega < 1$$

→ dissolution occurs

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

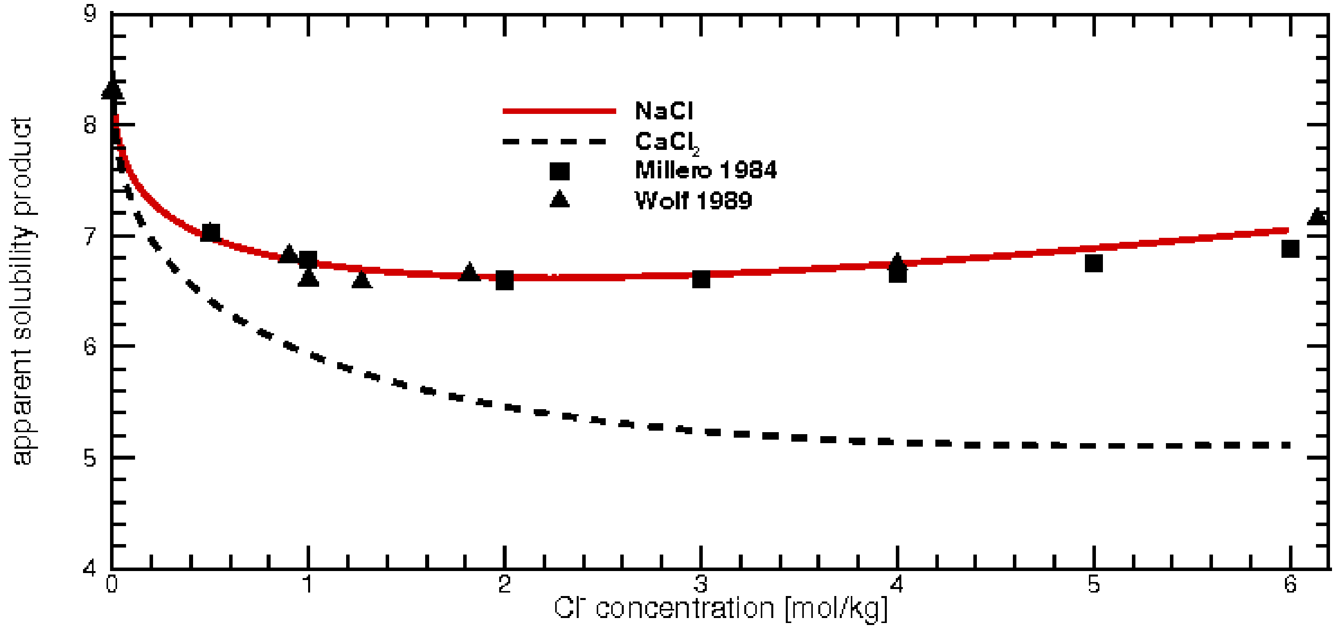
A_{sw} ...specific interfacial surface between solid and water phases
A_{cw} ...specific interfacial surface between calcite and water phases

→ rate of precipitation or dissolution is dependent on the distance from equilibrium

Solubility Product

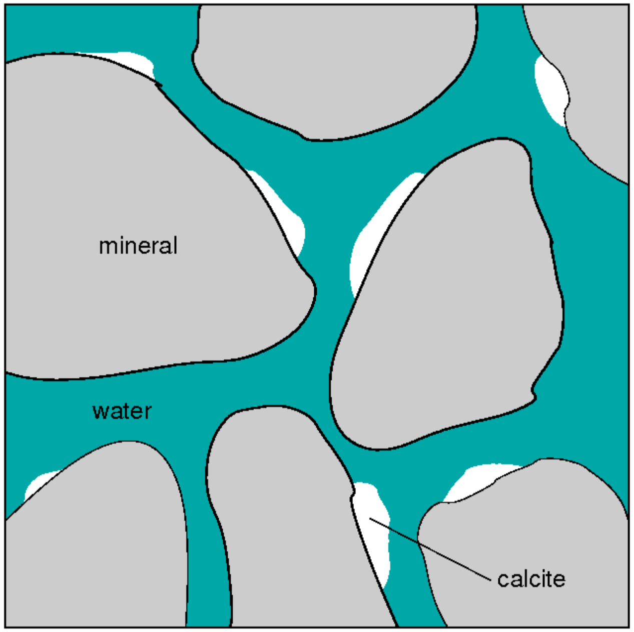
From the activity coefficients,
one can calculate the apparent solubility product

$$\Omega = \frac{\gamma_{Ca^{2+}} m_{Ca^{2+}} \gamma_{CO_3^{2-}} m_{CO_3^{2-}}}{K_{sp}}; \quad K_{sp}^* = \frac{K_{sp}}{\gamma_{Ca^{2+}} \gamma_{CO_3^{2-}}}$$

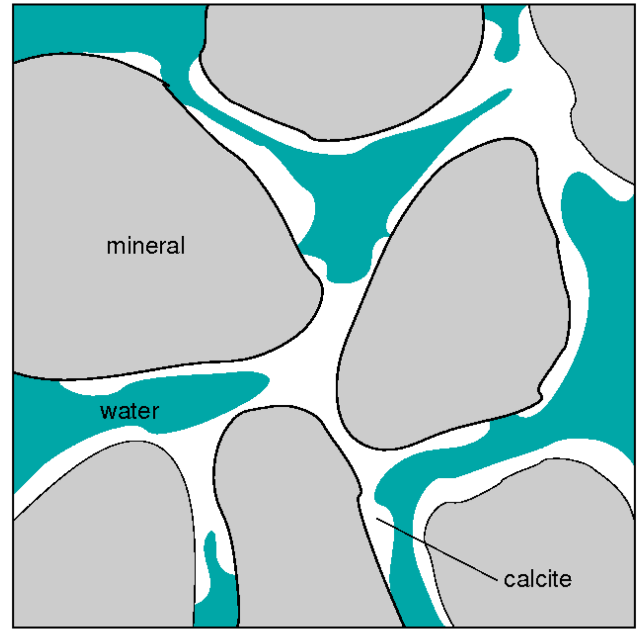


Negative logarithm of apparent solubility product K_{sp}^* in NaCl and $CaCl_2$ solutions.

Surface Areas



$$a_{\mathsf{c}}\phi_{\mathsf{c}} < A_{\mathsf{sw}}(\phi)$$



$$a_{\mathsf{c}}\phi_{\mathsf{c}} > A_{\mathsf{sw}}(\phi)$$

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

$$A_{\mathsf{cw}} = \min(A_{\mathsf{sw}}, a_{\mathsf{c}}\phi_{\mathsf{c}})$$

(Ebigbo et. al., *WRR* 2012)

a_{c} ... specific surface area of calcite grains

Supplementary equations

- Changes in porosity

$$\phi = \phi_0 - \phi_\mathrm{f} - \phi_\mathrm{c}$$

- Changes in permeability

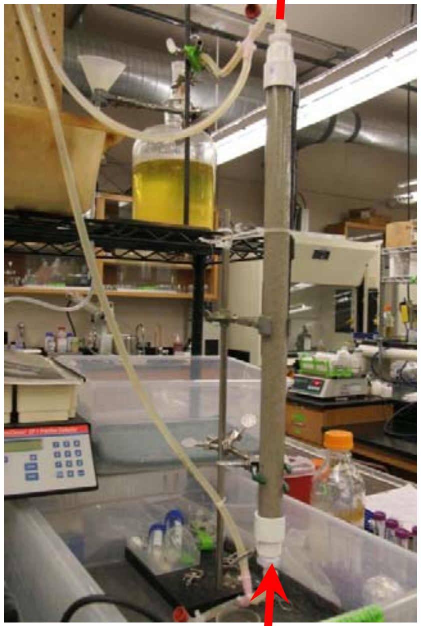
$$K = K_0 \left(\frac{\phi - \phi_\mathrm{crit}}{\phi_0 - \phi_\mathrm{crit}} \right)^3 \ldots Kozeny - Carman - type\ relation$$

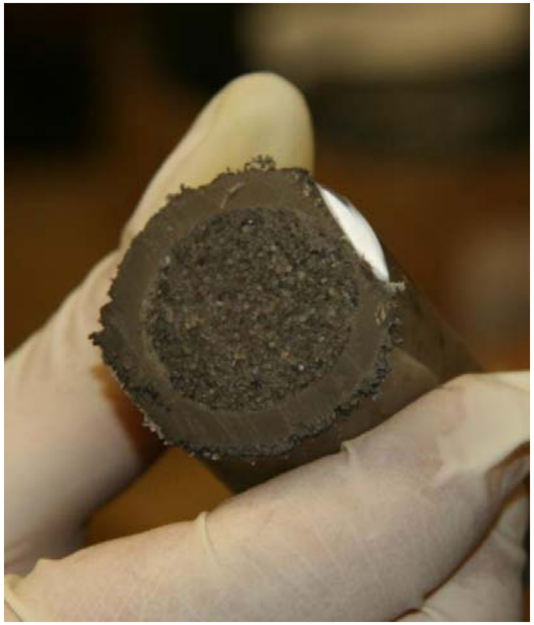
- Charge balance

$$\sum_i z_i m_i = 0$$

Column Experiments

NH_4Cl

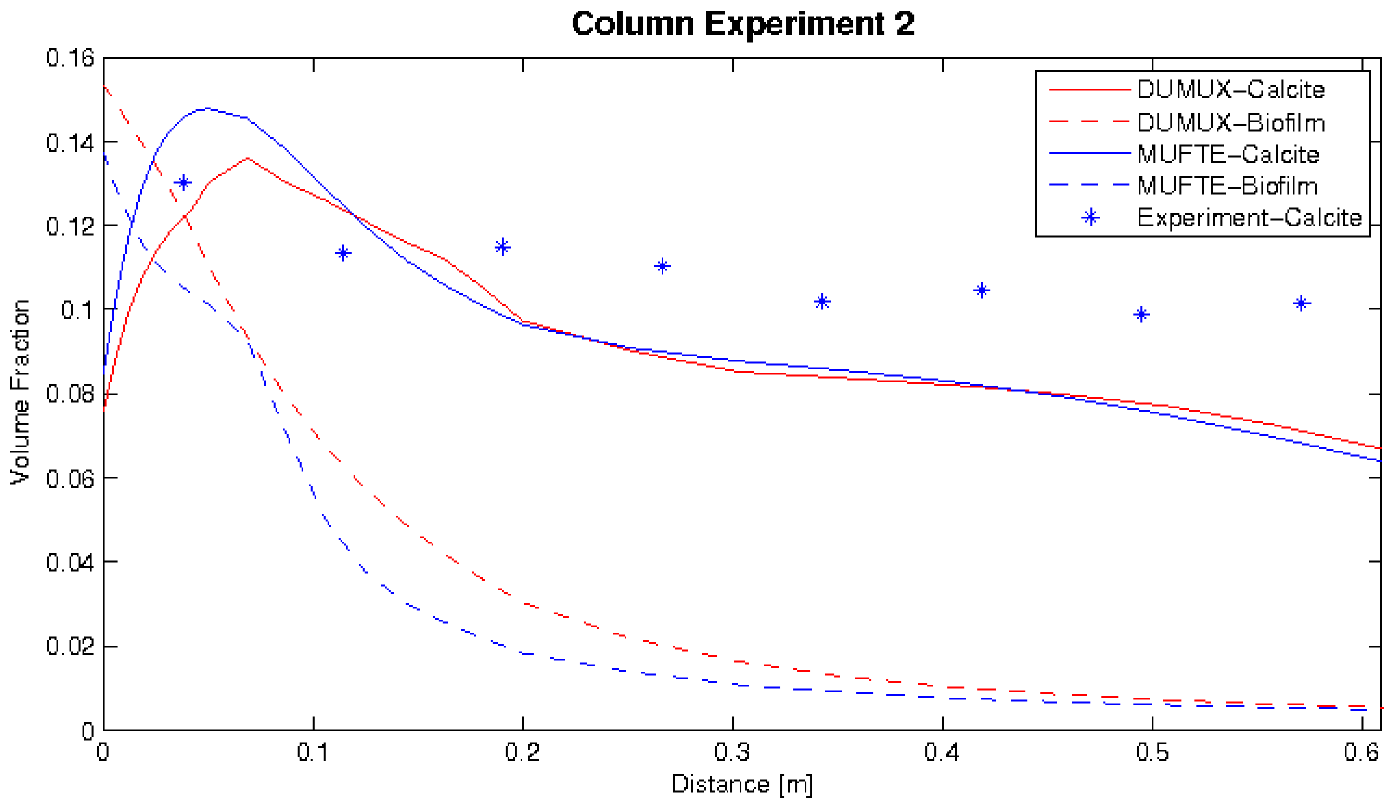




$CaCl_2$, urea, substrate

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

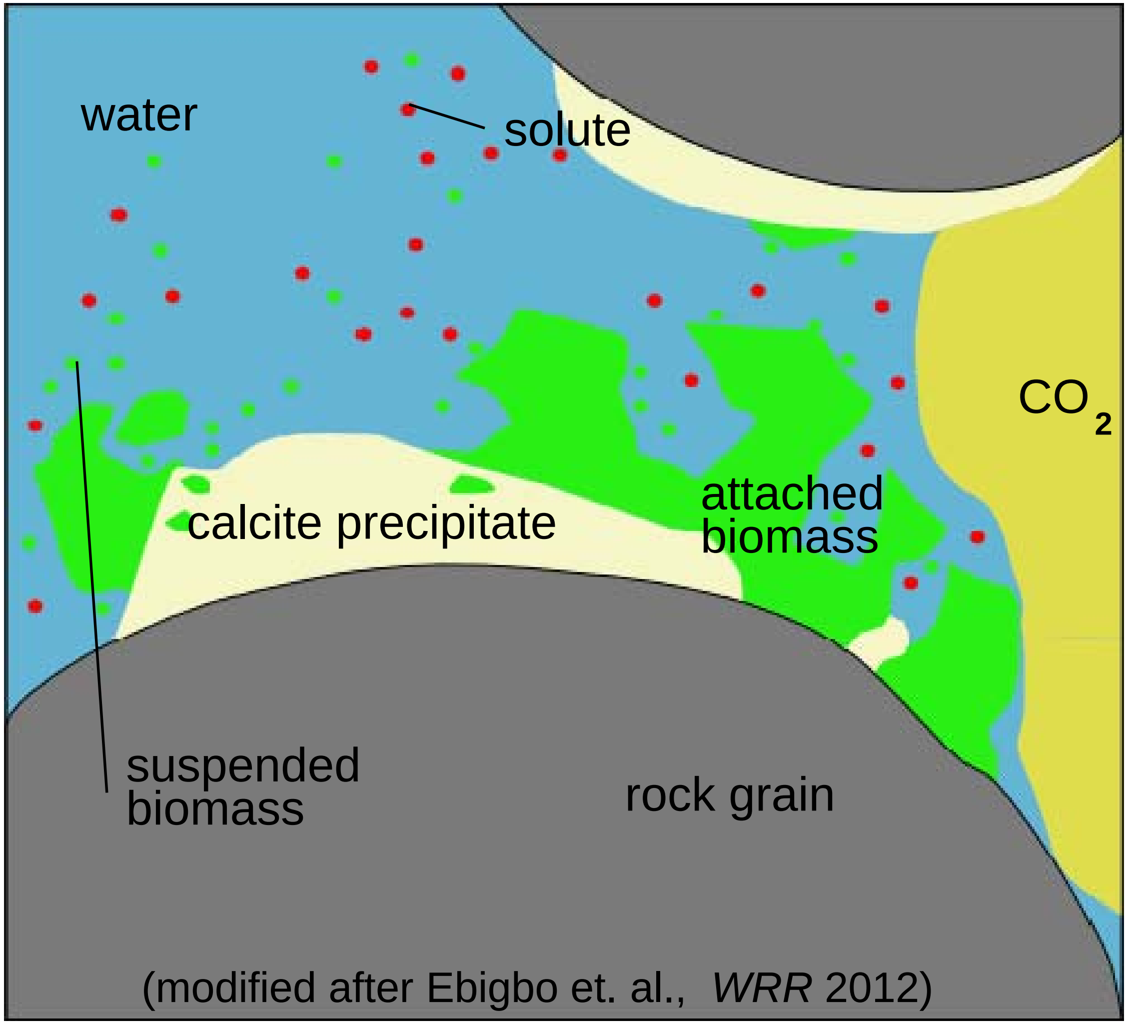
Montana State University

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

Sources & sinks: Biomass

Suspended biomass: $q^{\mathrm{b}} = r_{\mathrm{g}}^{\mathrm{b}} - r_{\mathrm{dc}}^{\mathrm{b}} - r_{\mathrm{a}} + r_{\mathrm{d}}$

Biofilm: $q^{\mathrm{f}} = r_{\mathrm{g}}^{\mathrm{f}} - r_{\mathrm{dc}}^{\mathrm{f}} + r_{\mathrm{a}} - r_{\mathrm{d}}$

Growth term:

$$r_{\mathrm{g}}^{\mathrm{b}} = \mu \phi S_{\mathrm{w}} C_{\mathrm{w}}^{\mathrm{b}}$$

$$r_{\mathrm{g}}^{\mathrm{f}} = \mu \phi_{\mathrm{f}} \varrho_{\mathrm{f}}$$

Growth coefficient:

$$\mu = k_{\mu} Y \frac{C_{\mathrm{w}}^{\mathrm{substrate}}}{K_{\mathrm{substrate}} + C_{\mathrm{w}}^{\mathrm{substrate}}} \cdot \frac{C_{\mathrm{w}}^{\mathrm{O_2}}}{K_{\mathrm{O_2}} + C_{\mathrm{w}}^{\mathrm{O_2}}}$$

Decay term:

$$r_{\mathrm{dc}}^{\mathrm{b}} = b^{\mathrm{b}} \phi S_{\mathrm{w}} C_{\mathrm{w}}^{\mathrm{b}}$$

$$r_{\mathrm{dc}}^{\mathrm{f}} = b^{\mathrm{f}} \phi_{\mathrm{f}} \varrho_{\mathrm{f}}$$

Attachment term: $r_{\mathrm{a}} = k_{\mathrm{a}} \phi S_{\mathrm{w}} C_{\mathrm{w}}^{\mathrm{b}}$

Detachment term: $r_{\mathrm{d}} = k_{\mathrm{d}} \phi_{\mathrm{f}} \varrho_{\mathrm{f}}$

Sources / Sinks: Biomass

$$q^{\mathrm{b}} = r_{\mathrm{g}}^{\mathrm{b}} - r_{\mathrm{b}}^{\mathrm{b}} - r_{\mathrm{a}} + r_{\mathrm{d}}$$
$$q^{\mathrm{f}} = r_{\mathrm{g}}^{\mathrm{f}} - r_{\mathrm{b}}^{\mathrm{f}} + r_{\mathrm{a}} - r_{\mathrm{d}}$$

Growth term:

$$r_{\mathrm{g}}^{\mathrm{b}} = \mu \phi S_{\mathrm{w}} C_{\mathrm{w}}^{\mathrm{b}}$$
$$r_{\mathrm{g}}^{\mathrm{f}} = \mu \phi_{\mathrm{f}} \varrho_{\mathrm{f}}$$

Growth coefficient:

$$\mu = k_{\mu} Y \frac{C_{\mathrm{w}}^{\mathrm{s}}}{K_{\mathrm{s}} + C_{\mathrm{w}}^{\mathrm{s}}} \cdot \frac{C_{\mathrm{w}}^{\mathrm{e}}}{K_{\mathrm{e}} + C_{\mathrm{w}}^{\mathrm{e}}}$$

Decay term:

$$r_{\mathrm{b}}^{\mathrm{b}} = b^{\mathrm{b}} \phi S_{\mathrm{w}} C_{\mathrm{w}}^{\mathrm{b}}$$
$$r_{\mathrm{b}}^{\mathrm{f}} = b^{\mathrm{f}} \phi_{\mathrm{f}} \varrho_{\mathrm{f}}$$

Attachment term: $r_{\mathrm{a}} = k_{\mathrm{a}} \phi S_{\mathrm{w}} C_{\mathrm{w}}^{\mathrm{b}}$

Detachment term: $r_{\mathrm{d}} = k_{\mathrm{d}} \phi_{\mathrm{f}} \varrho_{\mathrm{f}}$

Sources / Sinks: Solutes

Substrate:	q^{s}	$=$	$-(r_{\mathsf{g}}^{\mathsf{b}} + r_{\mathsf{g}}^{\mathsf{f}})/Y$
Electron acceptor:	q^{e}	$=$	$-(r_{\mathsf{g}}^{\mathsf{b}} + r_{\mathsf{g}}^{\mathsf{f}}) \cdot (R/Y)$
Urea:	q^{u}	$=$	$f(C_{\mathsf{w}}^{\mathsf{u}}, \mathsf{pH}, C_{\mathsf{w}}^{\mathsf{a}})$
Ammonium/ammonia:	q^{a}	$=$	$f(q^{\mathsf{u}})$
Calcium:	q^{Ca}	$=$	$r_{\mathsf{diss}} - r_{\mathsf{prec}}$
Calcite:	q^{c}	$=$	$r_{\mathsf{prec}} - r_{\mathsf{diss}}$