Motivation

Increased use of the subsurface injecting or extracting fluids.

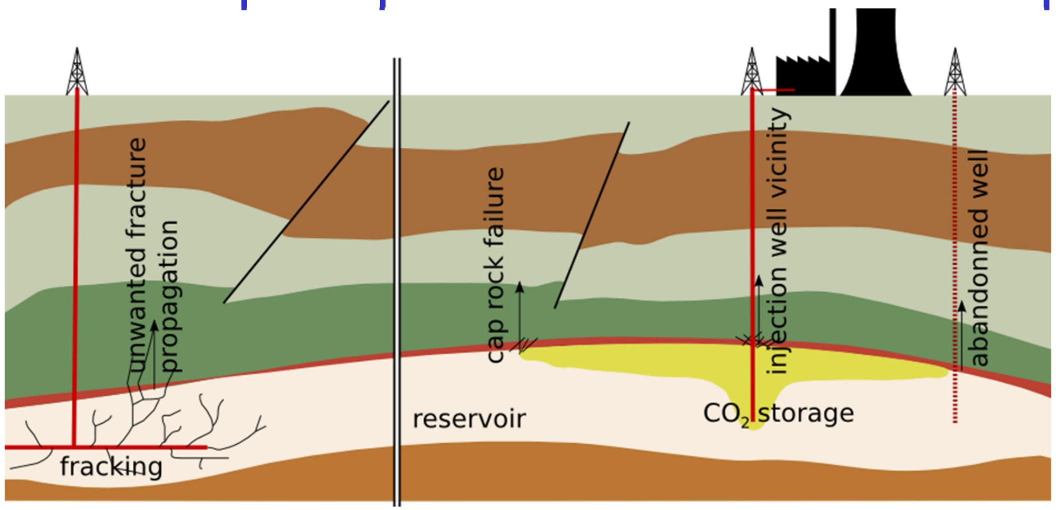
→ changing the chemistry of the pore water, which will re-equilibrate with the present minerals

→ need for reactive transport models

Exclusive and storage uses require separation.

→ sealing of leakage pathways is important

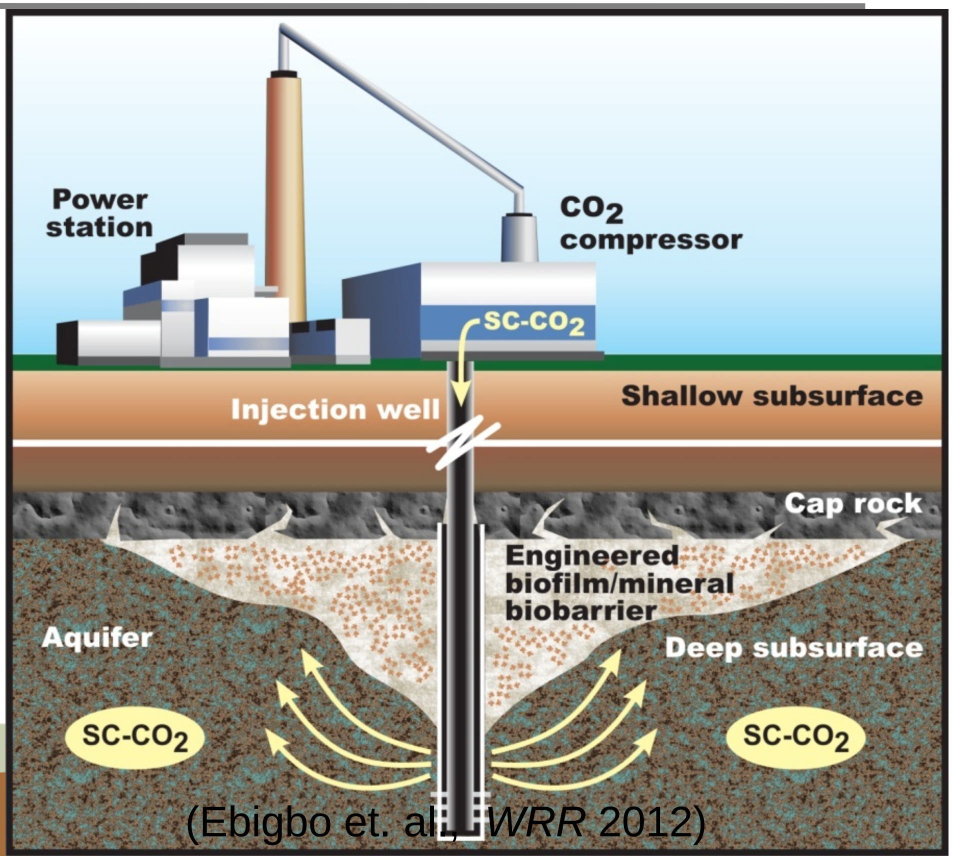
→ sealing = mineral precipitation = reactive transport



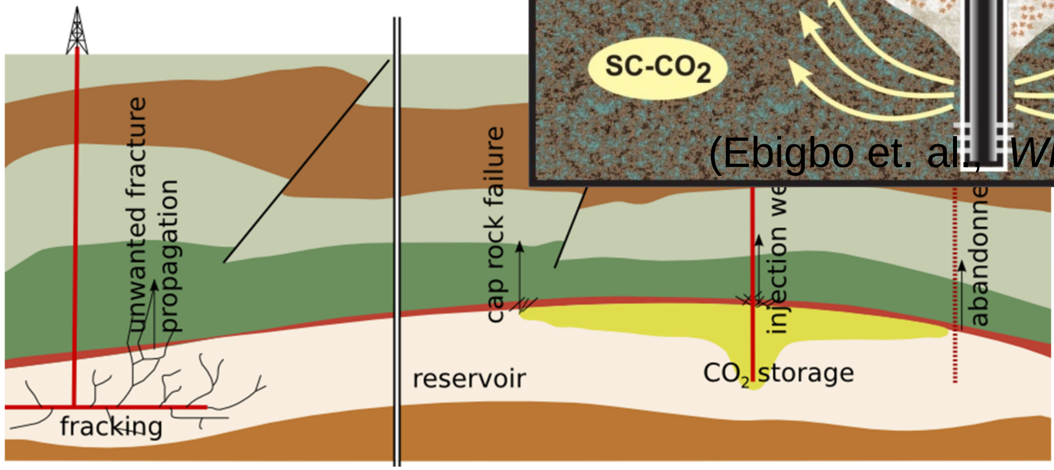
Motivation

Microbially Induced Calcite Precipitation (MICP) is investigated as sealing technology.

It is used as an exemplary problem setting for reactive transport in porous media.



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



Outline

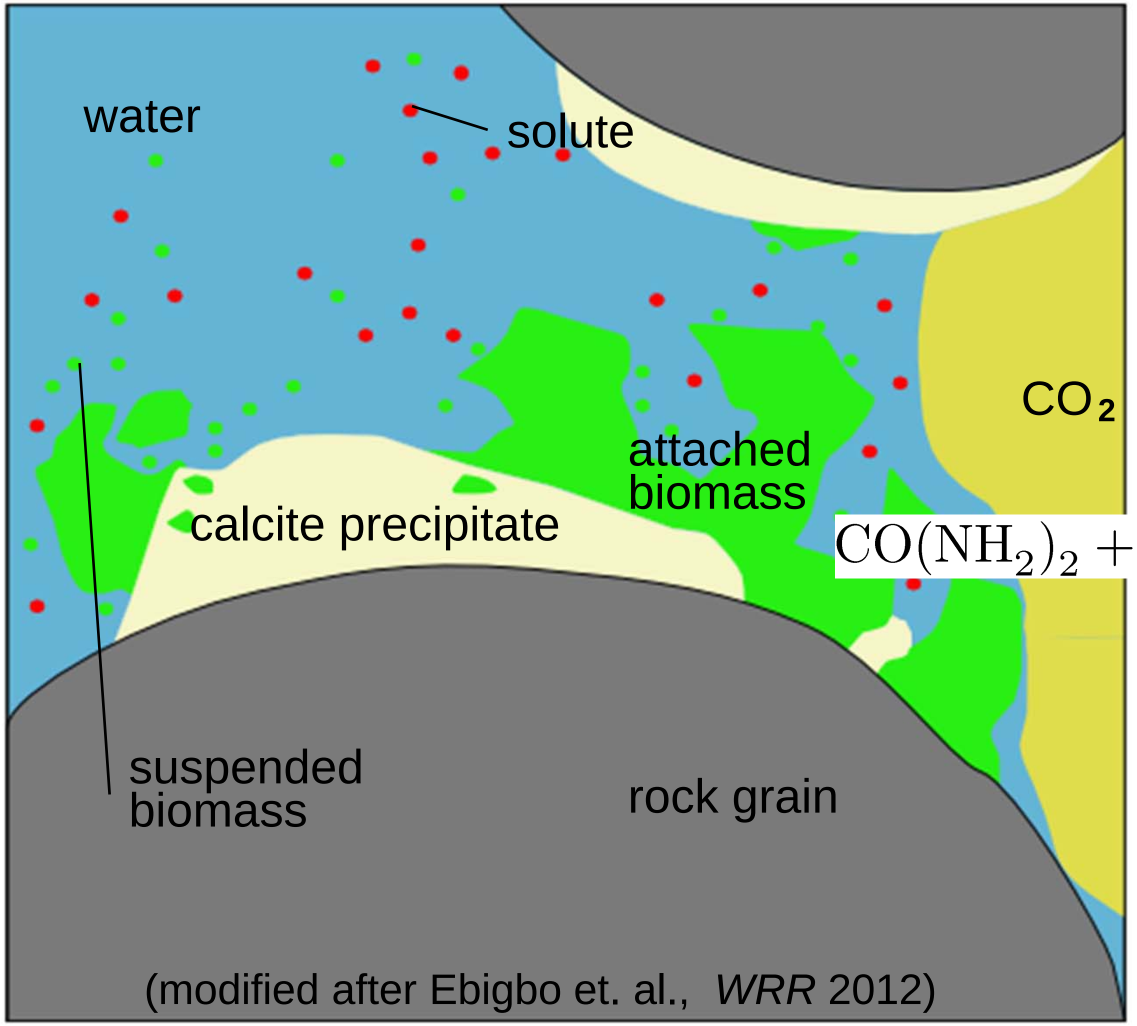
Model concept

Improvement of the numerical model for MICP:

- Implementation of the experimentally observed kinetics of ureolysis by living *S. pasteurii*
- Improvement of the description of the biofilm impact on permeability

Summary and Outlook

Model concept: Relevant processes



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

- 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

$$\phi = \phi_0 - \phi_{\text{biofilm}} - \phi_{\text{calcite}}$$

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

Model concept: important reactions

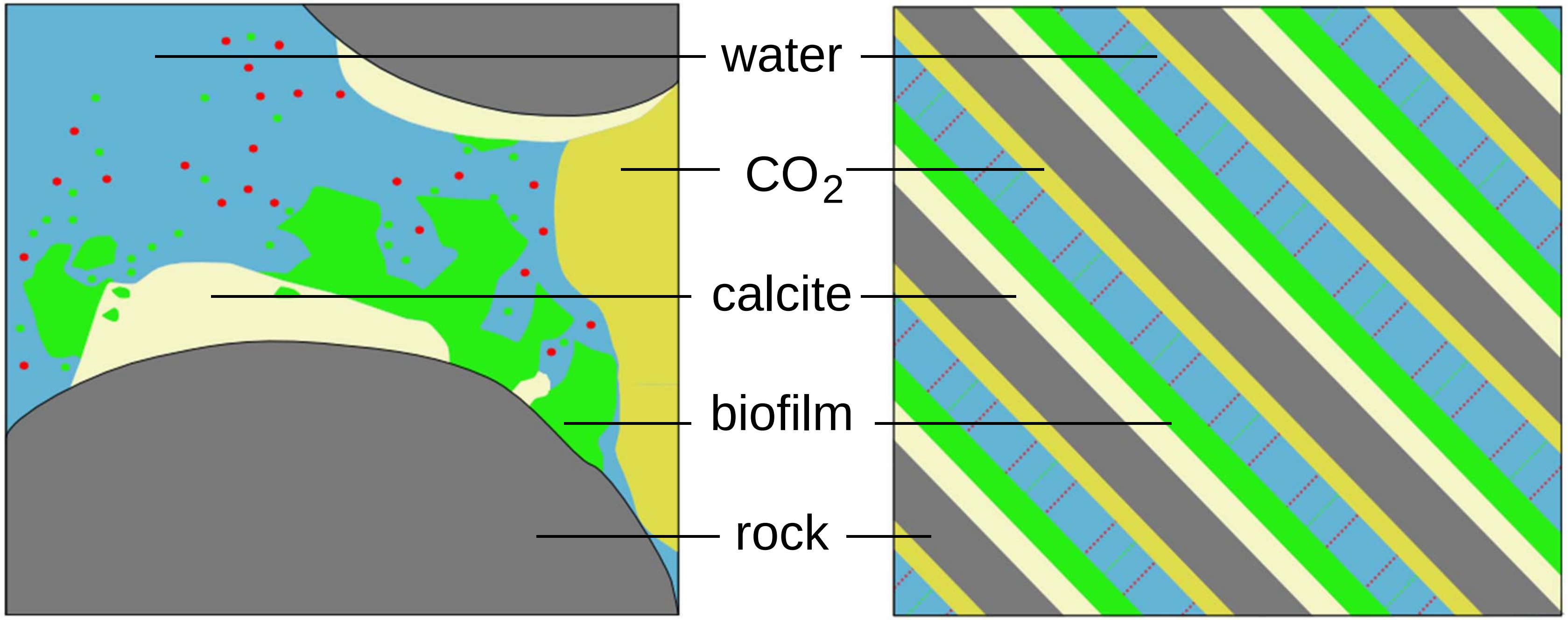
- Bacteria *Sporosarcina pasteurii* produce the enzyme urease.

- Urease catalyses the hydrolysis of urea, which produces ammonia and leads to a pH increase.

$CO(NH_2)_2 + 2\,H_2O \xrightarrow{\text{urease}} 2\,NH_3 + H_2CO_3$	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 due to ureolysis will drive the precipitation of calcite.

Model concept: Scale



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

averaging

Pore scale → REV scale

Mass balance equations

Mass balance equation for components in both phases:

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

$$\kappa \in \{\mathrm{w}, \mathrm{C_{tot}}, \mathrm{O_2}\}\,;\, \alpha \in \{\mathrm{w}, \mathrm{n}\}$$

Mass balance equation of components exclusively in the water phase:

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

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

Mass balance for the immobile components / solid phases:

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

Sources & sinks: Biomass

Suspended biomass: $q^{\text{bio}} = r_{\text{growth}}^{\text{bio}} - r_{\text{decay}}^{\text{bio}} - r_{\text{attach}} + r_{\text{detach}}$

Biofilm: $q^{\text{biofilm}} = r_{\text{growth}}^{\text{biofilm}} - r_{\text{decay}}^{\text{biofilm}} + r_{\text{attach}} - r_{\text{detach}}$

Growth:

$$r_{\text{growth}}^{\text{bio}} = \mu \phi S_{\text{w}} C_{\text{w}}^{\text{bio}}$$
$$r_{\text{growth}}^{\text{biofilm}} = \mu \phi_{\text{biofilm}} \rho_{\text{biofilm}}$$

Growth coefficient:

$$\mu = \mu_{\text{max}} Yield \frac{C_{\text{w}}^{\text{substrate}}}{K_{\text{substrate}} + C_{\text{w}}^{\text{substrate}}} \cdot \frac{C_{\text{w}}^{O_2}}{K_{O_2} + C_{\text{w}}^{O_2}}$$

Decay:

$$r_{\text{decay}}^{\text{bio}} = k_{\text{decay}}^{\text{bio}} \phi S_{\text{w}} C_{\text{w}}^{\text{bio}}$$
$$r_{\text{decay}}^{\text{biofilm}} = k_{\text{decay}}^{\text{biofilm}} \phi_{\text{biofilm}} \rho_{\text{biofilm}}$$

Attachment:

$$r_{\text{attach}} = \left(c_{\text{a},1} \phi_{\text{biofilm}} + c_{\text{a},2}\right) C_{\text{w}}^{\text{bio}} \phi S_{\text{w}}$$

Detachment:

$$r_{\text{detach}} = \left(c_{\text{d},1} \left(\left|\nabla p_{\text{w}}\right| \phi S_{\text{w}}\right)^{0.58} + \mu \frac{\phi_{\text{biofilm}}}{\phi_0 - \phi_{\text{calcite}}}\right) \phi_{\text{biofilm}} \rho_{\text{biofilm}}$$

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}	$=$	$-r^{\text{urea}} = f(\phi_{\text{biofilm}}, C^{\text{urea}}_{\text{w}}, \text{pH}, C^{\text{NH}_4}_{\text{w}})$
Total nitrogen:	$q^{\text{NH}_{\text{tot}}}$	$=$	$2r^{\text{urea}}$
Calcium:	q^{Ca}	$=$	$r_{\text{diss}} - r_{\text{precip}} = f(area, saturation\ state, \text{pH})$
Total carbon:	$q^{\text{C}_{\text{tot}}}$	$=$	$r^{\text{urea}} + r_{\text{diss}} - r_{\text{precip}}$

Calcite:	q^{calcite}	$=$	$r_{\text{precip}} - r_{\text{diss}} = f(area, saturation\ state, \text{pH})$

Outline

Model concept

Improvement of the numerical model for MICP:

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- Improvement of the description of the biofilm impact on permeability

Summary and Outlook

Ureolysis, simplified equation

$$r_{\text{urea}} = k_{\text{urease}} \frac{1}{1+\frac{H^+}{K_{\text{eu},1}}+\frac{K_{\text{eu},2}}{H^+}} k_{\text{ub}}(\rho_f \phi_f)^{n_{\text{ub}}} \frac{m_{\text{urea}}}{K_u + m_{\text{urea}}} \frac{K_{NH_4^+}}{K_{NH_4^+} + m_{NH_4^+}}$$

41.67 — 1 to 0.01 — 0.11 — 1.5 — 0.017 — 0.06 to 0.01

$$r_{\text{urea}} = k_{\text{urease}} k_{\text{ub}}(\rho_f \phi_f)^{n_{\text{ub}}} \frac{m_{\text{urea}}}{K_u + m_{\text{urea}}}$$

706 — 0.01 — 1.0 — 0.355

New rate according to Lauchnor et al. at MSU

Fitted to experimental data, previously literature values.

Previously fitted parameter, Now literature values.

- Removing pH dependency and inhibition term results in an increase of the calculated rate of ureolysis by a factor of 16 to 10000.
- The experimentally determined k_{urease} increases the calculated rate even more.

→ the model needs to be refitted

Refitting

- Refit done using inverse modelling with iTOUGH2
- 3 (4) fitting parameters:
  - biofilm density ρ_{biofilm}
  - attachment coefficients $c_{\text{a},1}$, $c_{\text{a},2}$
  - (urease to biomass ratio k_{ub})

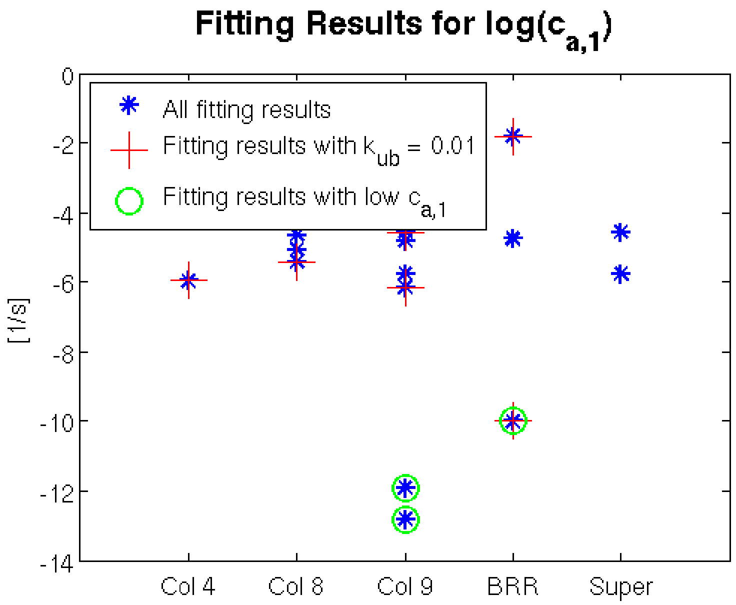
$$r_{\text{urea}} = k_{\text{urease}}\, \underline{k_{\text{ub}}} (\underline{\rho_{\text{biofilm}}}\,\underline{\phi_{\text{biofilm}}})^{n_{\text{ub}}} \frac{m_{\text{urea}}}{K_{\text{u}} + m_{\text{urea}}}$$

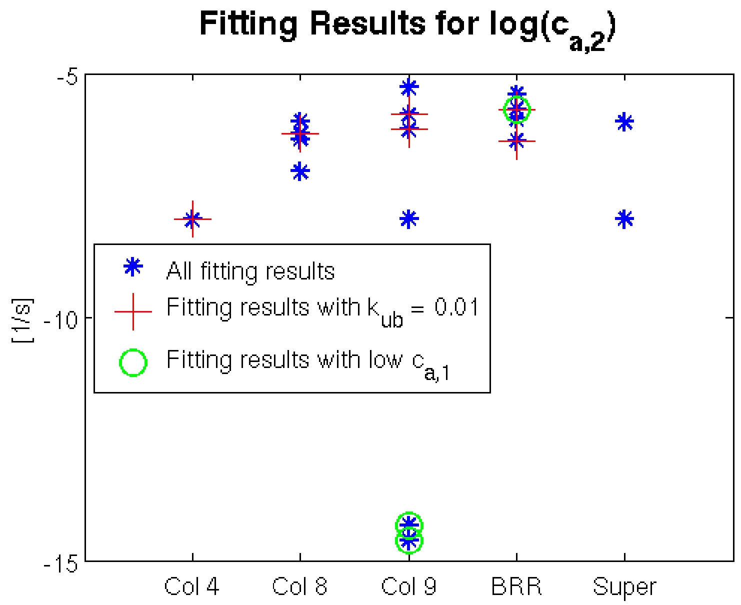
$$r_{\text{attach}} = \left(\underline{c_{\text{a},1}}\,\underline{\phi_{\text{biofilm}}} + \underline{c_{\text{a},2}}\right) C_{\text{w}}^{\text{bio}} \phi S_{\text{w}}$$

$$r_{\text{detach}} = \left(c_{\text{d},1} \left(|\nabla p_{\text{w}}|\, \phi S_{\text{w}}\right)^{0.58} + \mu \frac{\underline{\phi_{\text{biofilm}}}}{\phi_0 - \phi_{\text{calcite}}}\right) \underline{\phi_{\text{biofilm}}}\,\underline{\rho_{\text{biofilm}}}$$

$$\underline{\phi} = \phi_0 - \phi_{\text{calcite}} - \underline{\phi_{\text{biofilm}}} \qquad K = K_0 \left(\frac{\underline{\phi} - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}}\right)^3$$

Recalibration results



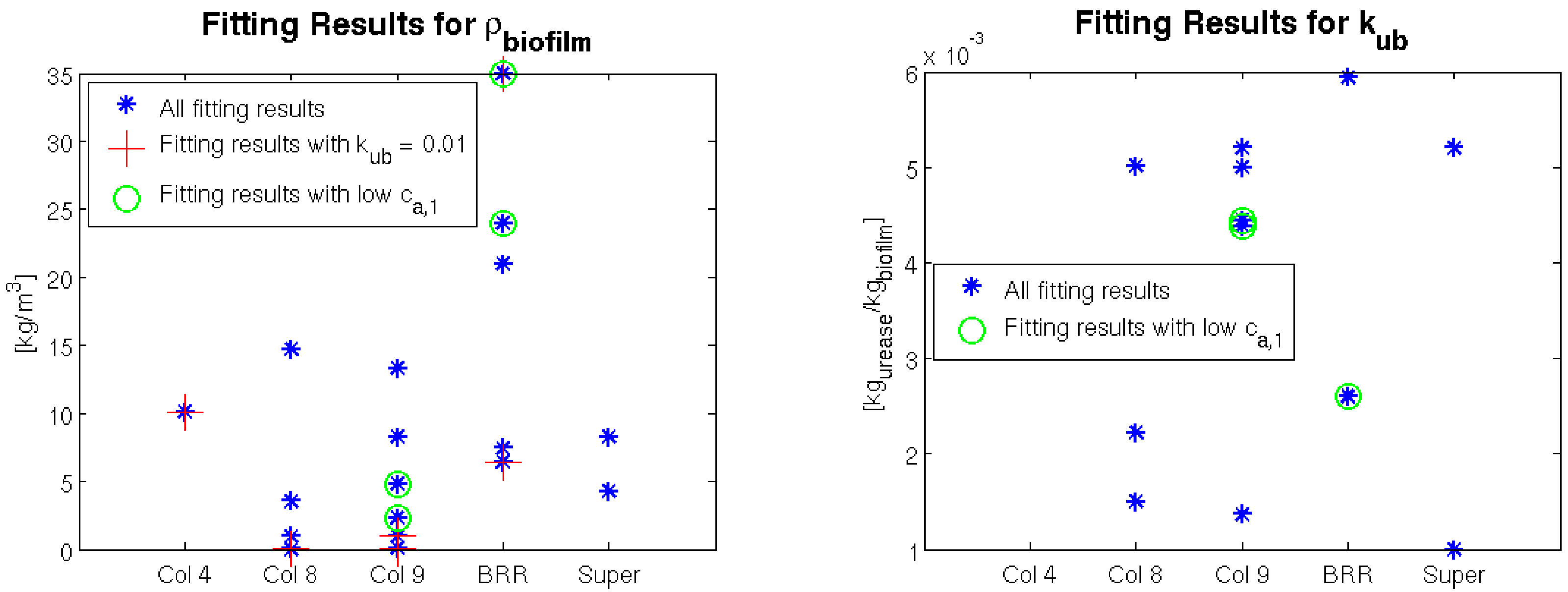


$$r_{\text{attach}} = \left(c_{a,1}\phi_{\text{biofilm}} + c_{a,2}\right) C_{\text{w}}^{\text{bio}}\phi S_{\text{w}}$$

$$r_{\text{detach}} = \left(c_{d,1}\left(|\nabla p_{\text{w}}|\,\phi S_{\text{w}}\right)^{0.58} + \mu\frac{\phi_{\text{biofilm}}}{\phi_0 - \phi_{\text{calcite}}}\right)\phi_{\text{biofilm}}\rho_{\text{biofilm}}$$

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

Recalibration results



$$r_{\text{urea}} = k_{\text{urease}}\, k_{\text{ub}} (\rho_{\text{biofilm}} \phi_{\text{biofilm}})^{n_{\text{ub}}} \frac{m_{\text{urea}}}{K_{\text{u}} + m_{\text{urea}}}$$

$$r_{\text{detach}} = \left(c_{\text{d},1} \left(|\nabla p_{\text{w}}| \, \phi S_{\text{w}} \right)^{0.58} + \mu \frac{\phi_{\text{biofilm}}}{\phi_0 - \phi_{\text{calcite}}} \right) \phi_{\text{biofilm}} \rho_{\text{biofilm}}$$

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

Outline

Model concept

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Summary and Outlook

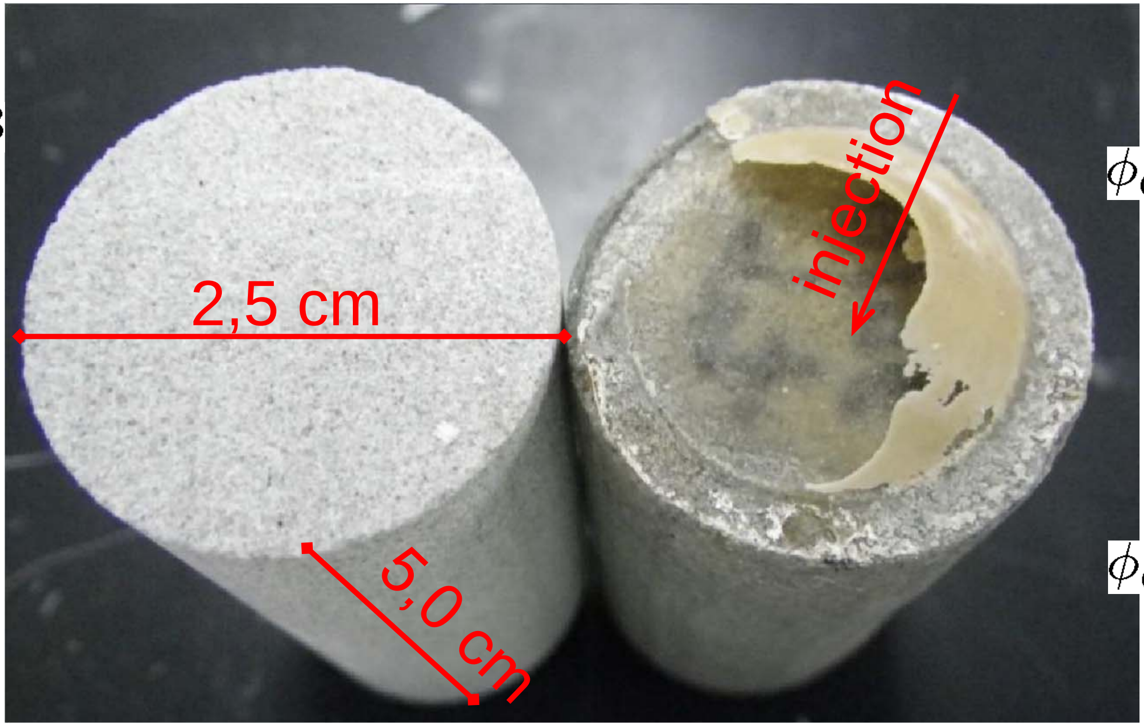
Permeability: High-pressure core experiments

Sandstone core used for the high pressure core experiment

$\phi = \phi_0 = 0.18$

$\phi_{\text{calcite}} = 0.0$

$K = K_0$
$3.7 \cdot 10^{-14} \text{m}^2$



Experiment
$\phi = 0.137$
$\phi_{\text{calcite}} = 0.037$
$K =$
$2.3 \cdot 10^{-15} \text{m}^2$

Simulation
$\phi = 0.138$
$\phi_{\text{calcite}} = 0.031$
$K =$
$1.0 \cdot 10^{-15} \text{m}^2$

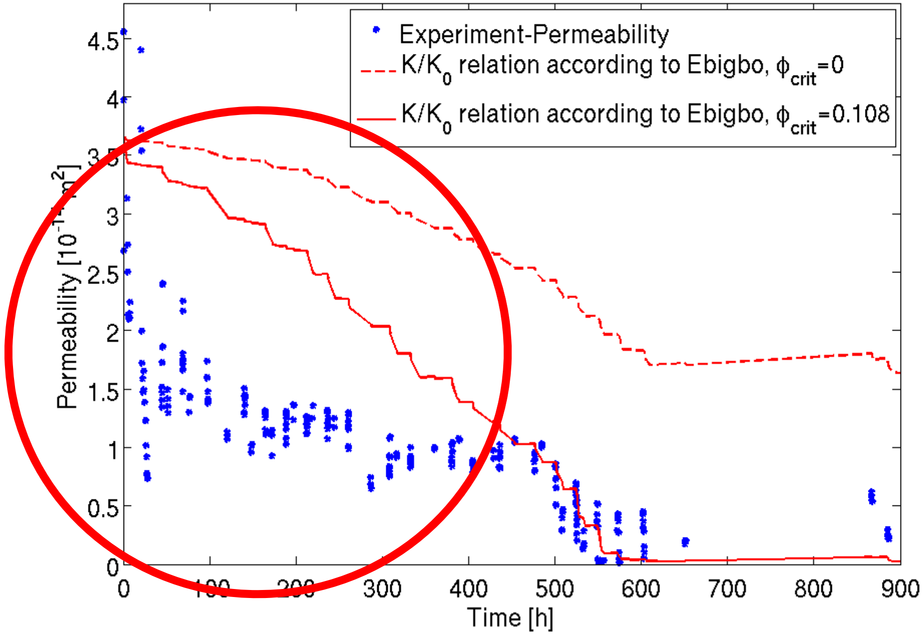
before after
biomineralization

Permeability: Biofilm impact

- Changes in porosity

$$\phi = \phi_0 - \phi_{\text{calcite}} - \phi_{\text{biofilm}}$$

- Changes in permeability



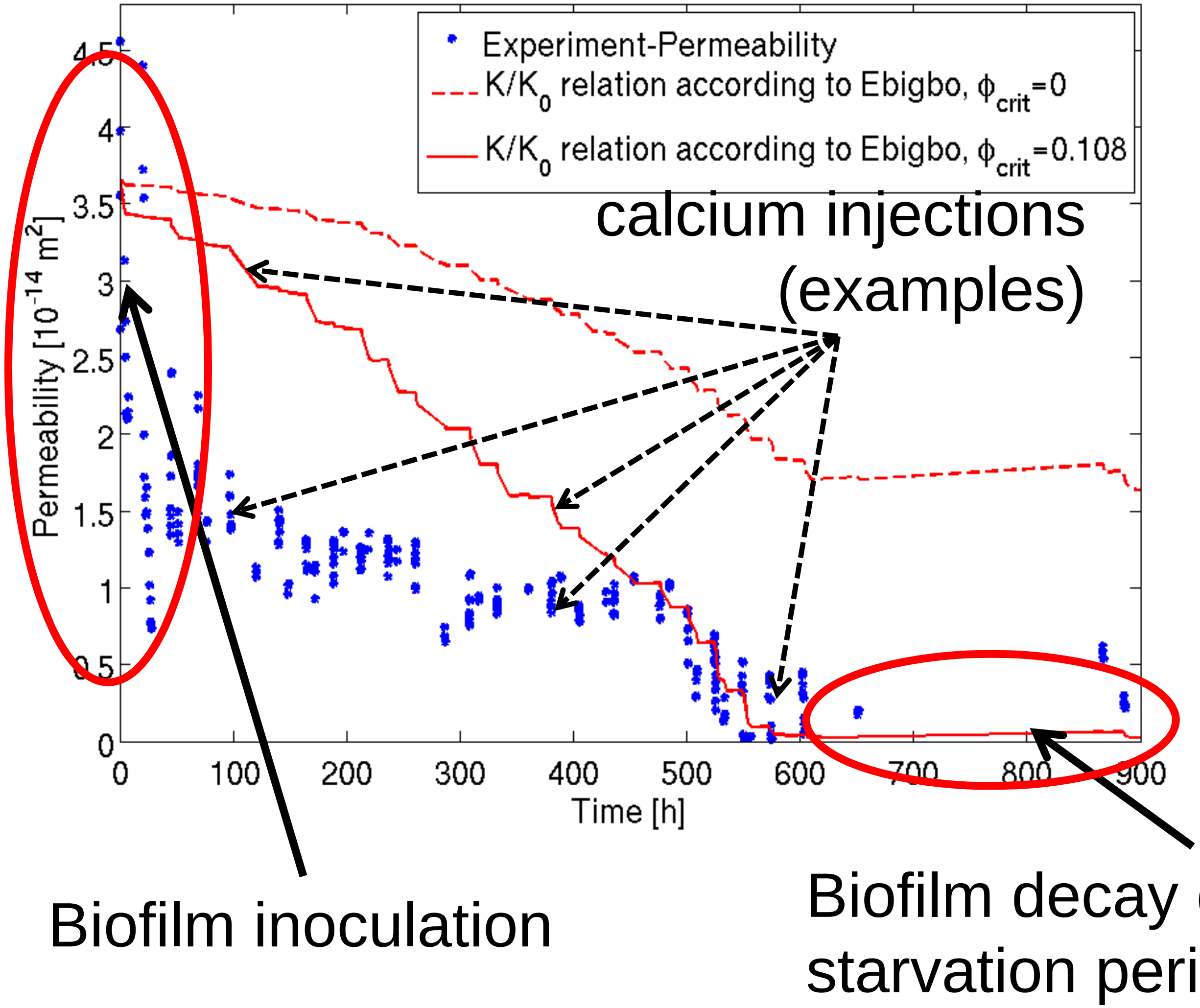
$$K = K_0 \left(\frac{\phi - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}}\right)^3 \text{ Kozeny-Carman type relation}$$

Is there a better description?

$$K = K_0 \left(\frac{\phi - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}}\right)^n \cdot S\left(\phi,\ \phi_{\text{calcite}},\ \phi_{\text{biofilm}},\ \ldots\right)$$

→ Measurements of both porosity and permeability needed

Permeability: Biofilm impact



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

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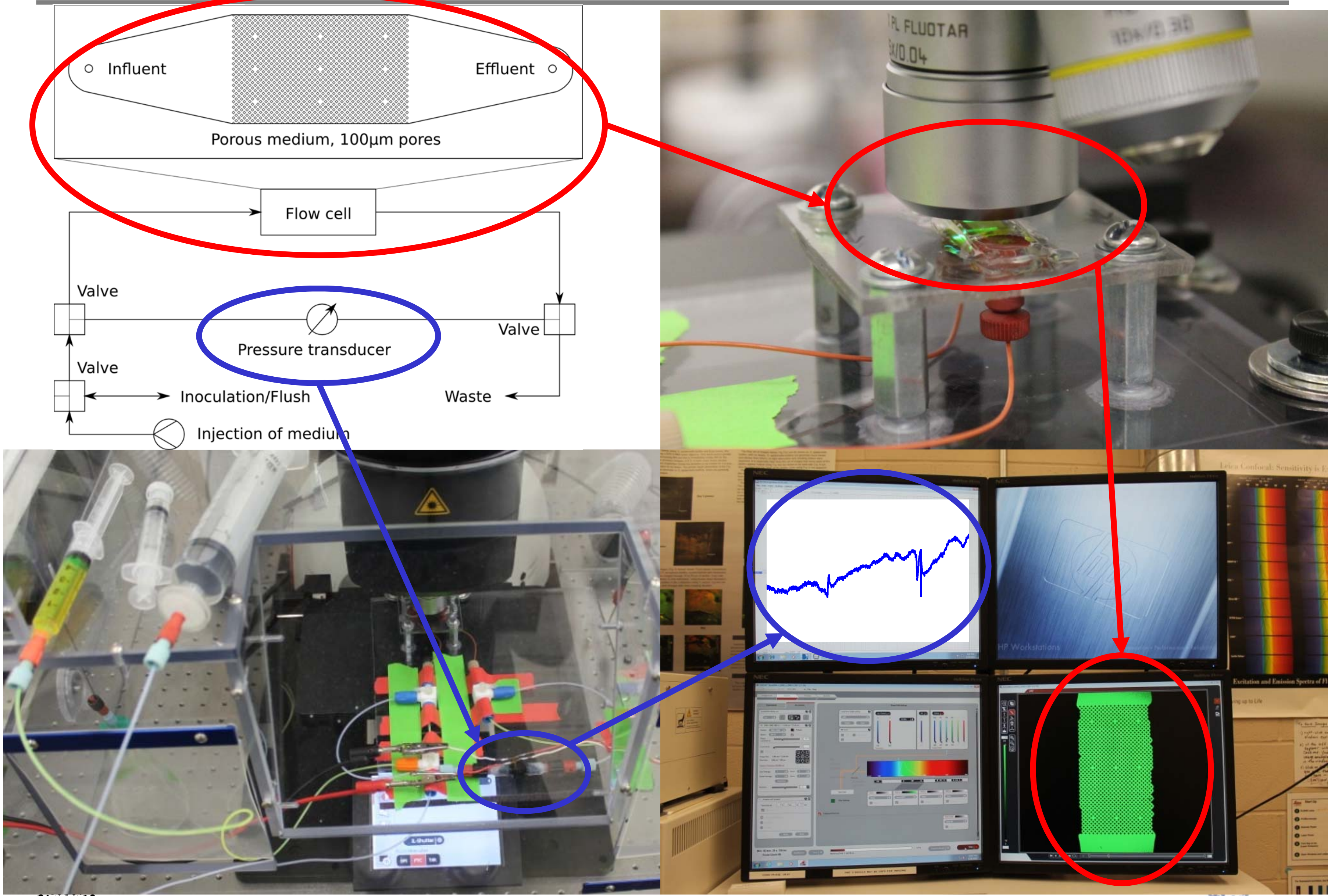
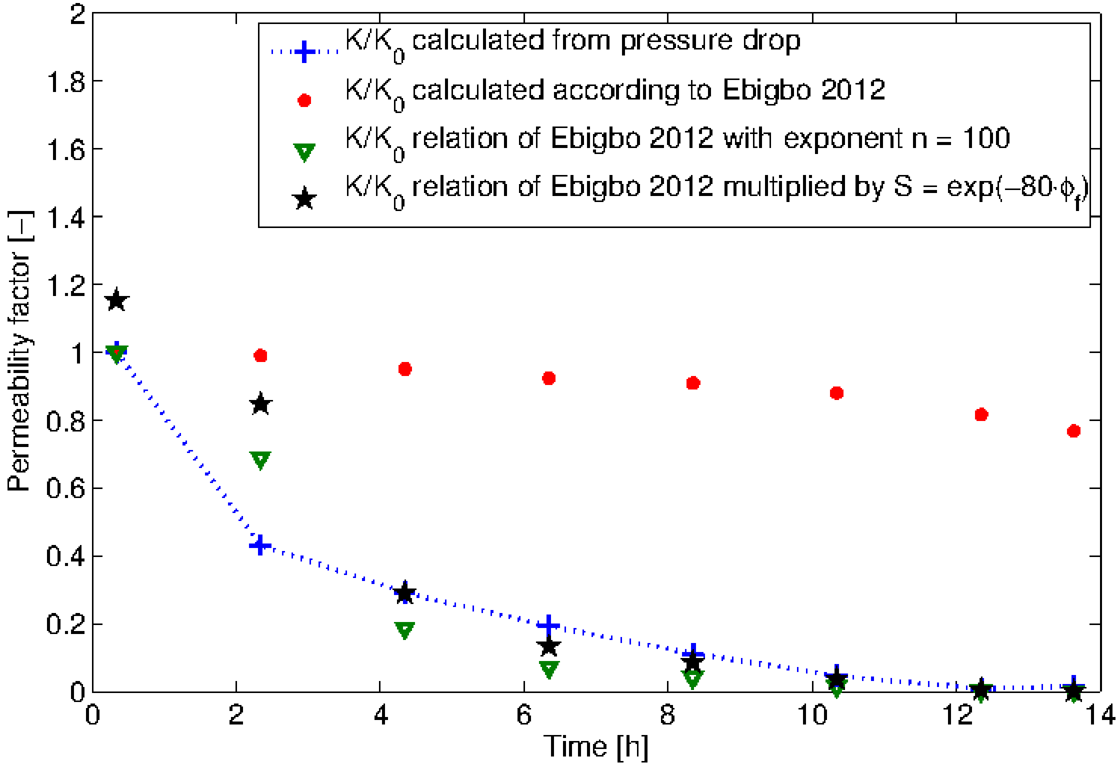
Permeability: Biofilm impact



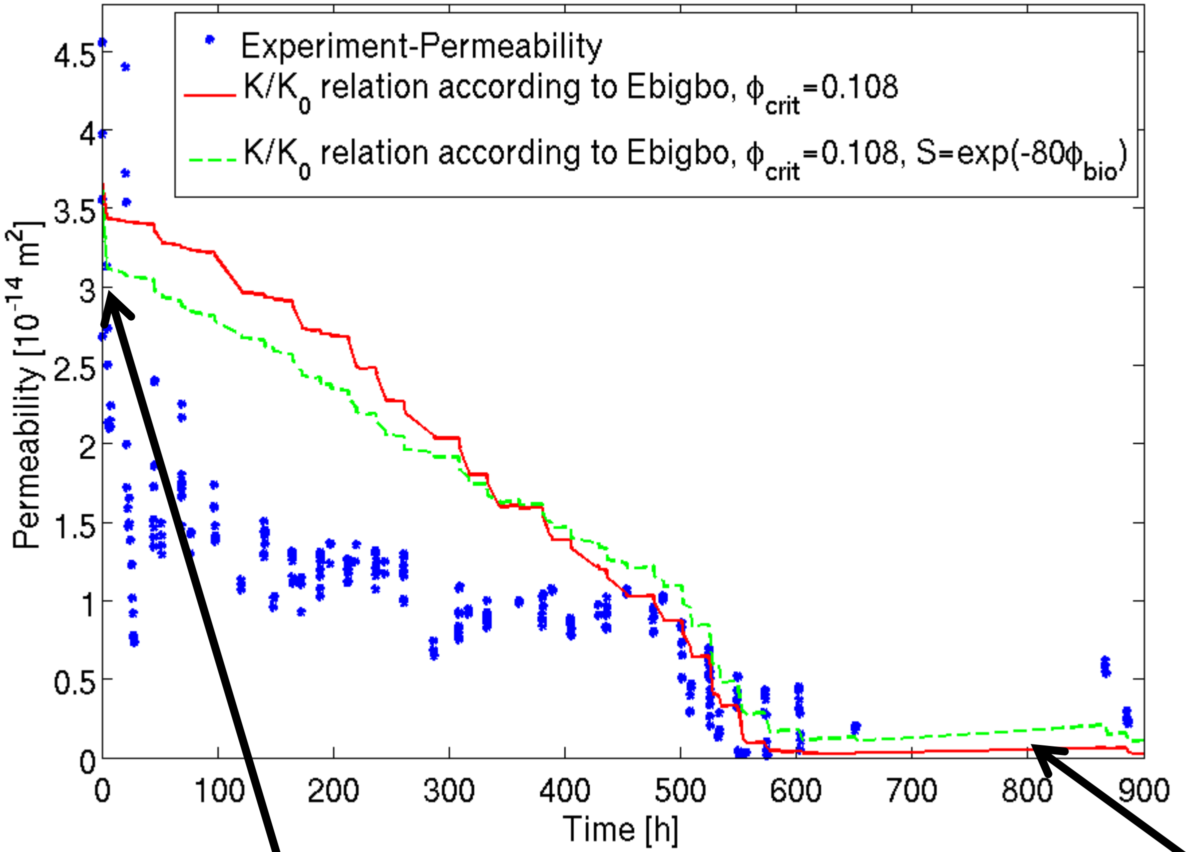
Permeability: Biofilm impact, updated relation



Extension of the previously used Kozeny-Carman by a shape factor *S* or an increased exponent *n* fit the observed permeability reduction.

$$K = K_0 \left(\frac{\phi - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}}\right)^n \cdot S\left(\phi,\ \phi_{\text{calcite}},\ \phi_{\text{biofilm}},\ \ldots\right)$$

Permeability: Biofilm impact, updated relation



Biofilm inoculation

Biofilm decay during one week starvation period

Extension of the previously used Kozeny-Carman by a shape factor

$$S = e^{-80\phi_{\text{biofilm}}}$$

improves modeled permeabilities.

More experiments have to be conducted to further improve it.

Outline

Model concept

Improvement of the numerical model for MICP:

- Implementation of the experimentally observed kinetics of ureolysis by living *S. pasteurii*
- Improvement of the description of the biofilm impact on permeability

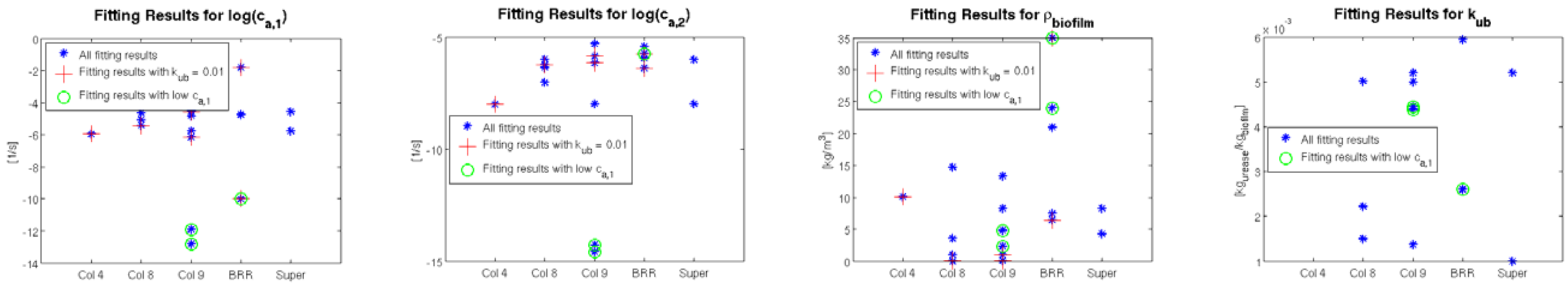
Summary and Outlook

Summary and Outlook

- Updated the ureolysis kinetics according to the experimentally observed
  Lauchnor et al. at MSU, not yet published.

$$r_{\mathrm{urea}} = k_{\mathrm{urease}}\, k_{\mathrm{ub}} (\rho_{\mathrm{biofilm}} \phi_{\mathrm{biofilm}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}} + m_{\mathrm{urea}}}$$

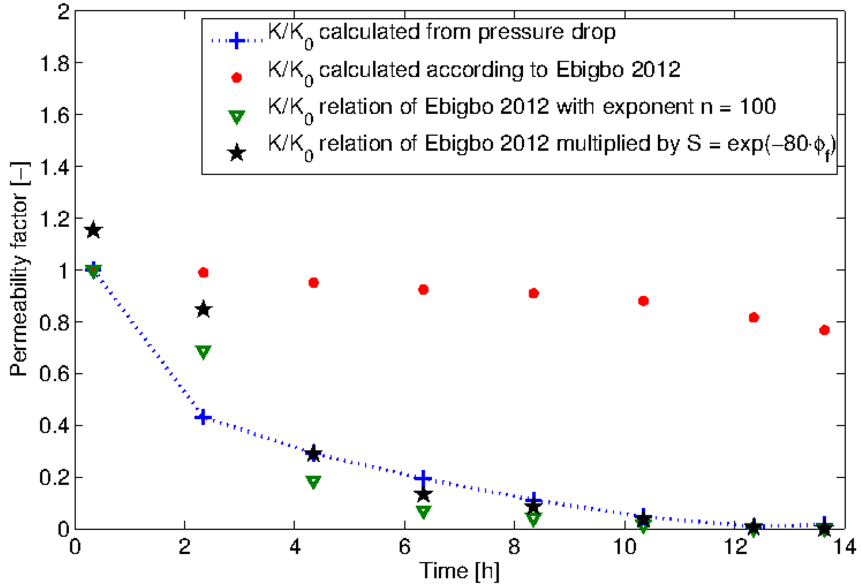
- Recalibrated the numerical model against different experiments.



Summary and Outlook

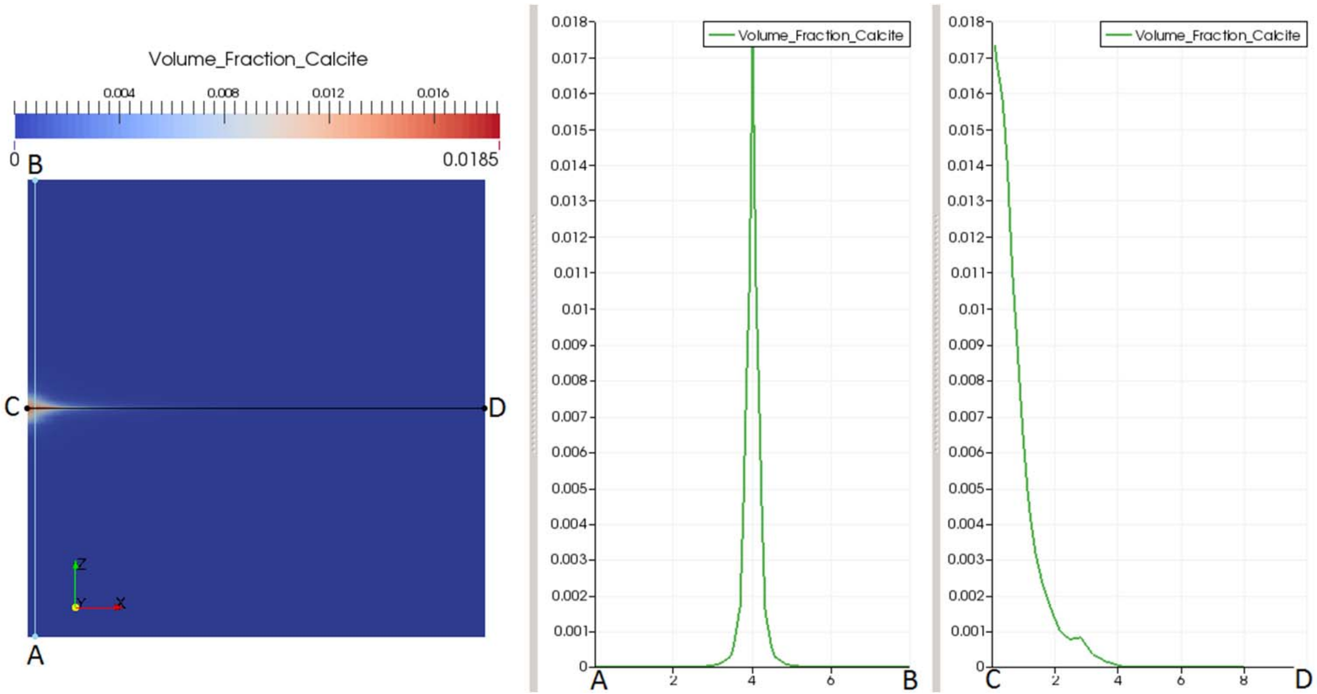
- Derived and implemented an improved porosity-permeability relation (started based on first experiment, waiting for experimental replicates).

$$K \approx K_0 \left(\frac{\phi - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}}\right)^3 \cdot e^{-80\phi_{\text{biofilm}}}$$



Summary and Outlook

- Showed that the model is able to produce reasonable results on field-scale, see previous presentation by A. Cunningham.



- Further investigation of the possible increases in efficiency using sequential calculation of transport and chemical reactions to increase the feasibility of field-scale simulations.

Thank you for your attention!

All simulations were done using DuMu^{x}