Modeling microbially induced calcite precipitation

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Motivation

Increased use of the subsurface injecting or extracting fluids.

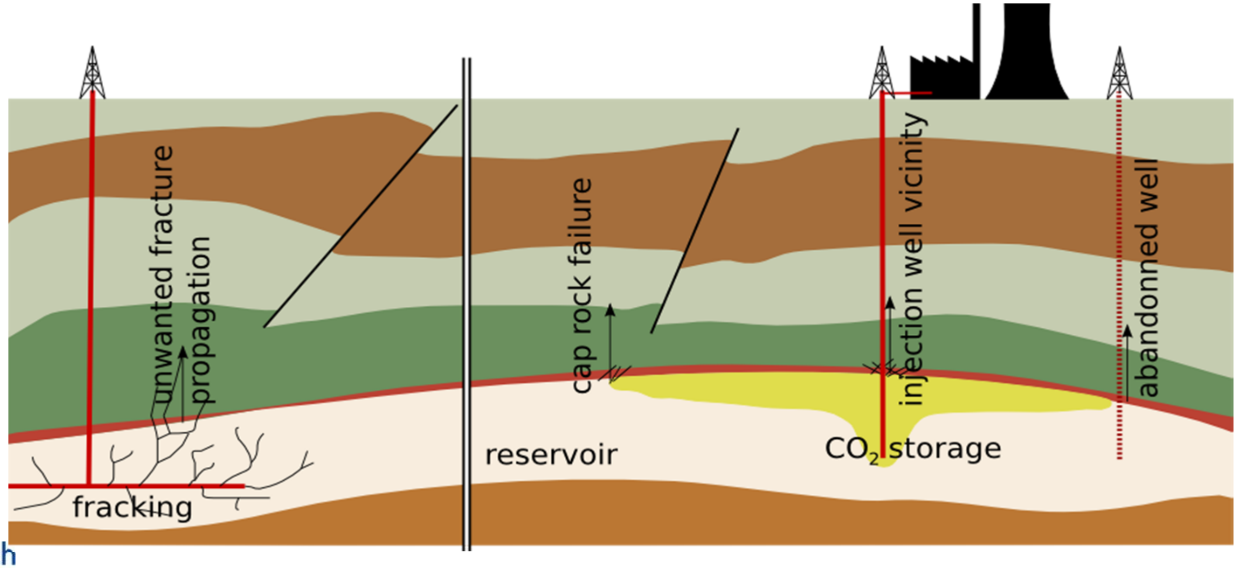
→ changing the chemistry of the pore water, which will re-equilibrate with the present minerals

→ need for reactive transport models

Exclusive and storage uses require separation.

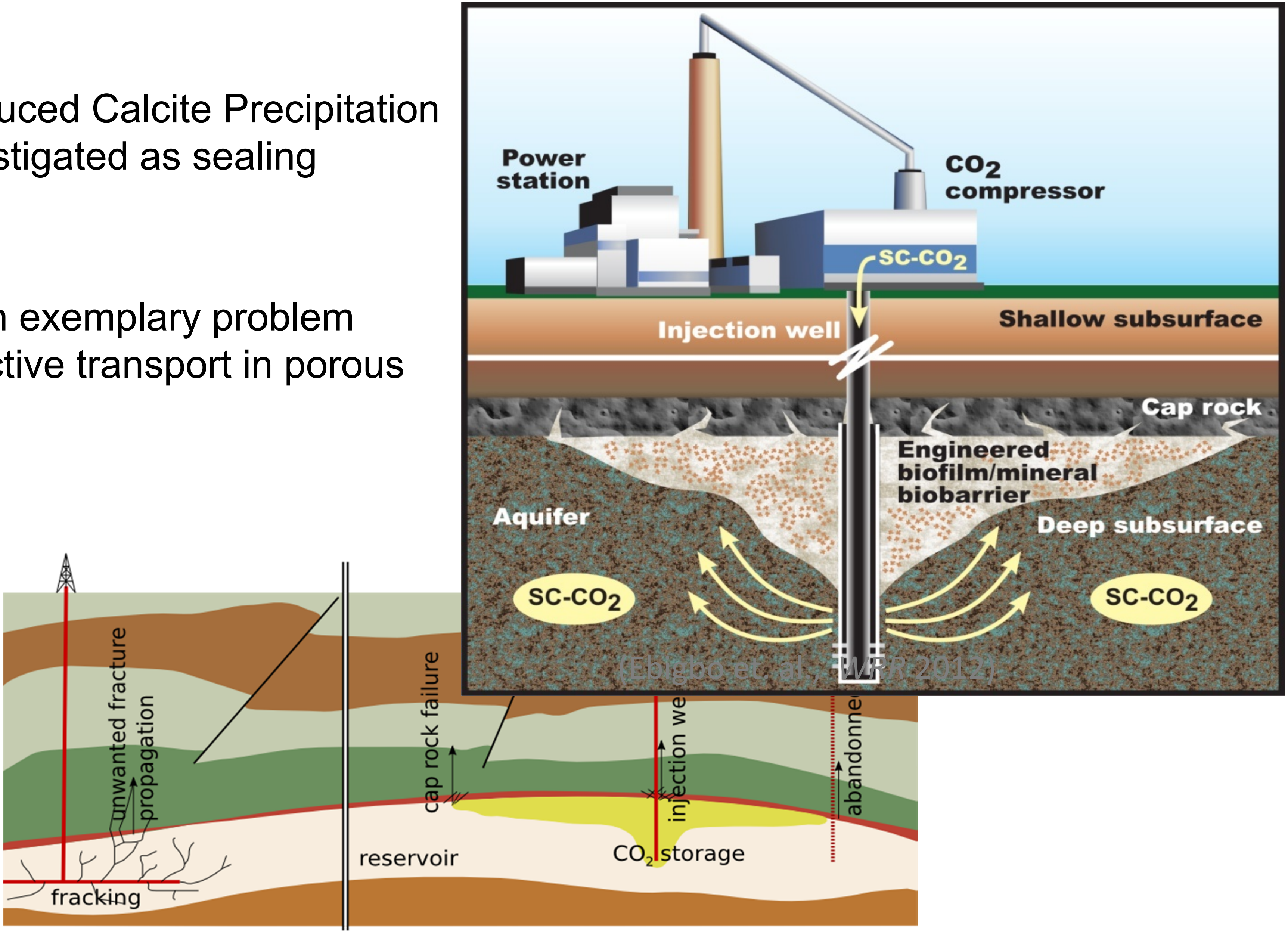
sealing of leakage pathways is important

→ sealing = mineral precipitation = reactive transport



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:

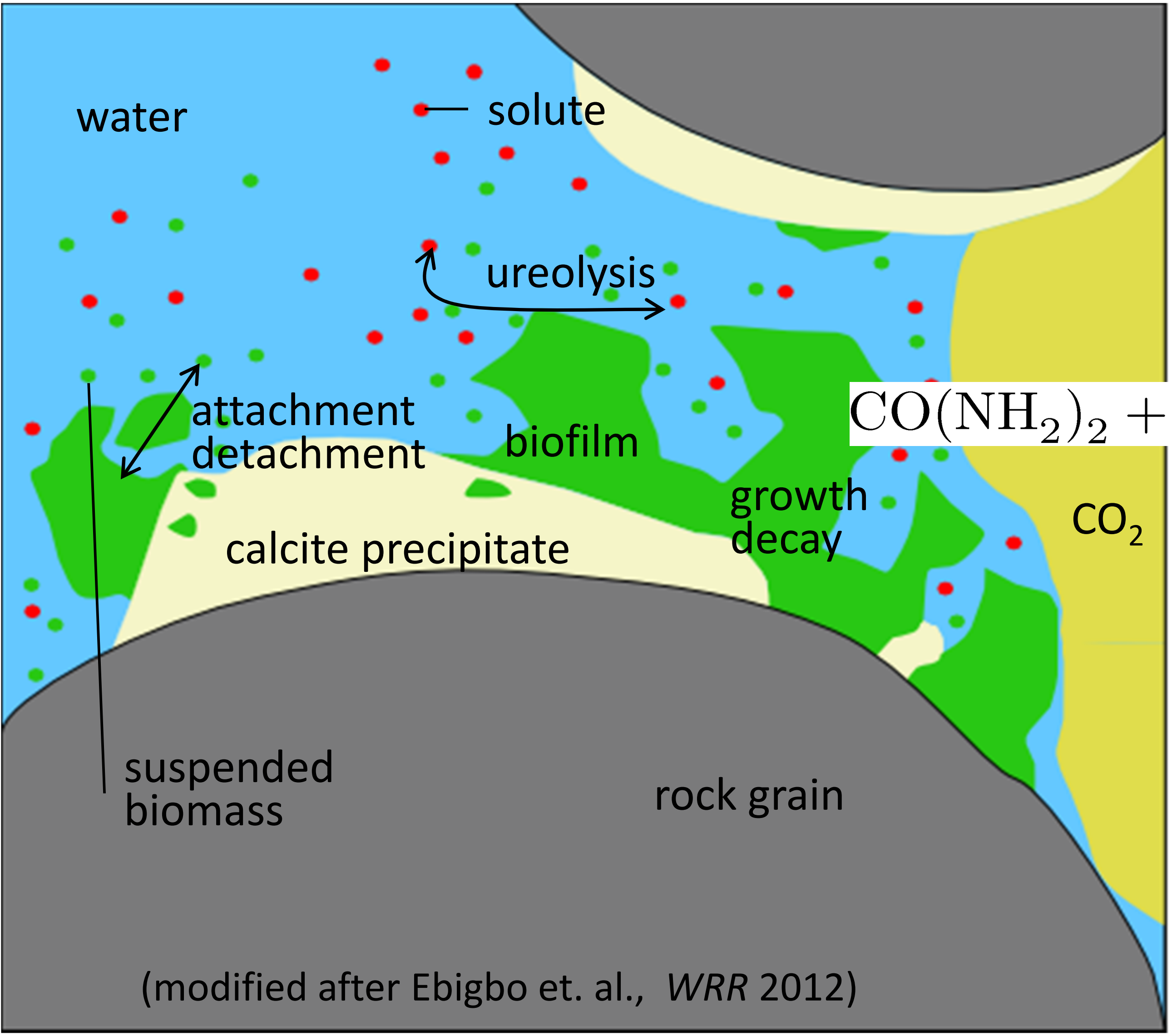
- Implementation of the experimentally observed kinetics of ureolysis by living *S. pasteurii*
- Recalibration of the model using inverse modeling
- Improvement of the description of the biofilm impact on permeability

Attachment experiments

Model efficiency: sequential approach

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

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

- Precipitation / dissolution of calcite

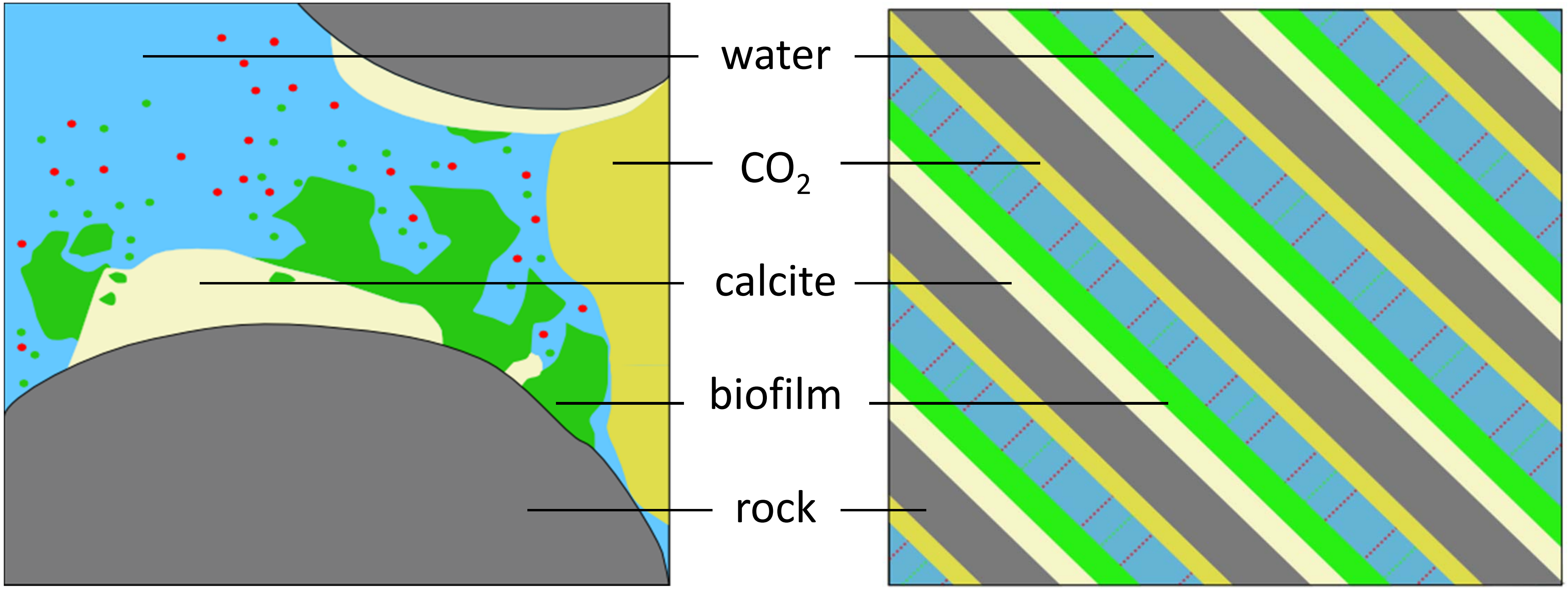
$$\mathrm{Ca}^{2+} + \mathrm{CO}_3^{2-} \longleftrightarrow \mathrm{CaCO}_3 \downarrow$$

- 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: Scale



water

CO_2

calcite

biofilm

rock

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

averaging

Pore scale → REV scale

Model concept: Important reactions

The bacterium *Sporosarcina pasteurii* produces the enzyme urease.
Urease catalyzes the hydrolysis of urea, which produces ammonia and leads to an increase in pH.

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

Mass balance equations

Mass balance equation for components in both phases:

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

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

Mass balance equation of components exclusively in the water phase:

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

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

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

$$
\begin{aligned}
&\text{Suspended biomass:} && q^{\mathrm{bio}} &&= r^{\mathrm{bio}}_{\mathrm{growth}} - r^{\mathrm{bio}}_{\mathrm{decay}} - r_{\mathrm{attach}} + r_{\mathrm{detach}} \\
&\text{Biofilm:} && q^{\mathrm{biofilm}} &&= r^{\mathrm{biofilm}}_{\mathrm{growth}} - r^{\mathrm{biofilm}}_{\mathrm{decay}} + r_{\mathrm{attach}} - r_{\mathrm{detach}}
\end{aligned}
$$

$$
\begin{aligned}
&\text{Growth:} && r^{\mathrm{bio}}_{\mathrm{growth}} &&= \mu \phi S_{\mathrm{w}} C^{\mathrm{bio}}_{\mathrm{w}} \\
& && r^{\mathrm{biofilm}}_{\mathrm{growth}} &&= \mu \phi_{\mathrm{biofilm}} \rho_{\mathrm{biofilm}} \\
&\text{Growth coefficient:} && \mu &&= \mu_{\mathrm{max}} Yield \frac{C^{\mathrm{substrate}}_{\mathrm{w}}}{K_{\mathrm{substrate}} + C^{\mathrm{substrate}}_{\mathrm{w}}} \cdot \frac{C^{\mathrm{O_2}}_{\mathrm{w}}}{K_{\mathrm{O_2}} + C^{\mathrm{O_2}}_{\mathrm{w}}} \\
&\text{Decay:} && r^{\mathrm{bio}}_{\mathrm{decay}} &&= k^{\mathrm{bio}}_{\mathrm{decay}} \phi S_{\mathrm{w}} C^{\mathrm{bio}}_{\mathrm{w}} \\
& && r^{\mathrm{biofilm}}_{\mathrm{decay}} &&= k^{\mathrm{biofilm}}_{\mathrm{decay}} \phi_{\mathrm{biofilm}} \rho_{\mathrm{biofilm}} \\
&\text{Attachment:} && r_{\mathrm{attach}} &&= \left(c_{\mathrm{a},1} \phi_{\mathrm{biofilm}} + c_{\mathrm{a},2}\right) C^{\mathrm{bio}}_{\mathrm{w}} \phi S_{\mathrm{w}} \\
&\text{Detachment:} && r_{\mathrm{detach}} &&= \left(c_{\mathrm{d},1} \left(\left| \nabla p_{\mathrm{w}} \right| \phi S_{\mathrm{w}} \right)^{0.58} + \mu \frac{\phi_{\mathrm{biofilm}}}{\phi_0 - \phi_{\mathrm{calcite}}} \right) \phi_{\mathrm{biofilm}} \rho_{\mathrm{biofilm}}
\end{aligned}
$$

Sources & sinks: Solutes and Calcite

$$
\begin{aligned}
&\text{Substrate:} && q^{\text{substrate}} &&= -\left(r^{\text{bio}}_{\text{growth}} + r^{\text{biofilm}}_{\text{growth}}\right)/Yield \\
&\text{Oxygen:} && q^{\text{O}_2} &&= -\left(r^{\text{bio}}_{\text{growth}} + r^{\text{biofilm}}_{\text{growth}}\right)\cdot(0.5/Yield) \\
&\text{Urea:} && q^{\text{urea}} &&= \boxed{-r^{\text{urea}} = f(\phi_{\text{biofilm}}, C^{\text{urea}}_{\text{w}}, \text{pH}, C^{\text{NH}_4}_{\text{w}})} \\
&\text{Total nitrogen:} && q^{\text{NH}_{\text{tot}}} &&= 2r^{\text{urea}} \\
&\text{Calcium:} && q^{\text{Ca}} &&= r_{\text{diss}} - r_{\text{precip}} = f(area, saturation\ state, \text{pH}) \\
&\text{Total carbon:} && q^{\text{C}_{\text{tot}}} &&= r^{\text{urea}} + r_{\text{diss}} - r_{\text{precip}}
\end{aligned}
$$

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

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Model efficiency: sequential approach

Summary and Outlook

Ureolysis

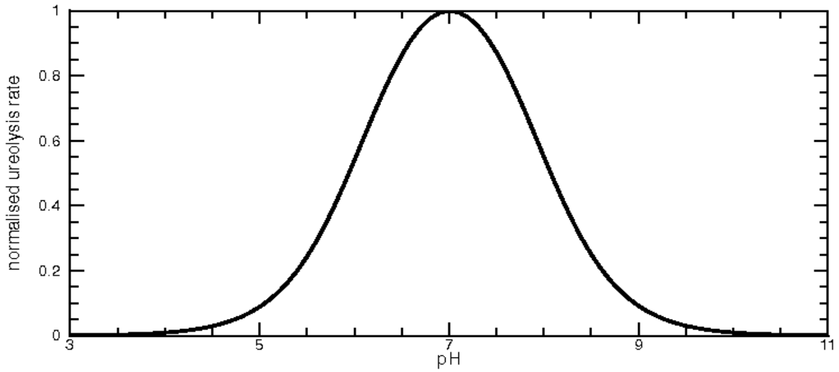
$$r_{\mathrm{urea}} = \overbrace{k_{\mathrm{urease}}}^{\text{activity of enzyme}} \underbrace{\frac{1}{1+\frac{m_{\mathrm{H}^+}}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{m_{\mathrm{H}^+}}}}_{\text{inactivation due to non-optimal pH}} \overbrace{k_{\mathrm{ub}}\left(\rho_{\mathrm{f}}\phi_{\mathrm{f}}\right)^{n_{\mathrm{ub}}}}^{\text{mass of enzyme}} \underbrace{\frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}}}_{\text{Michaelis-Menten term, urea dependency}} \overbrace{\frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}}^{\text{inhibition due to ammonium}}$$

rate of ureolysis (jack bean urease) as implemented in Ebigbo et al., *WRR* 2012 adapted from:
Fidaleo and Lavecchia, *Chem. Biochem. Eng. Q*. 17 (4) 2003

Ureolysis, pH

$$r_{\mathrm{urea}} = k_{\mathrm{urease}} \frac{1}{1+\frac{\mathrm{H}^+}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{\mathrm{H}^+}} k_{\mathrm{ub}} (\rho_{\mathrm{f}}\phi_{\mathrm{f}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}} \frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}$$

old



Adapted from:
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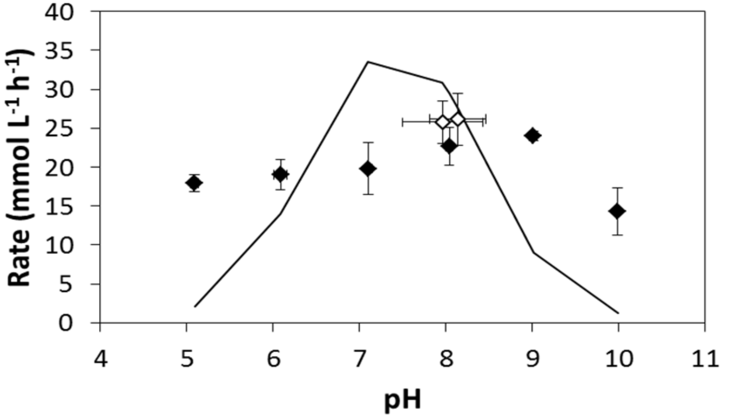
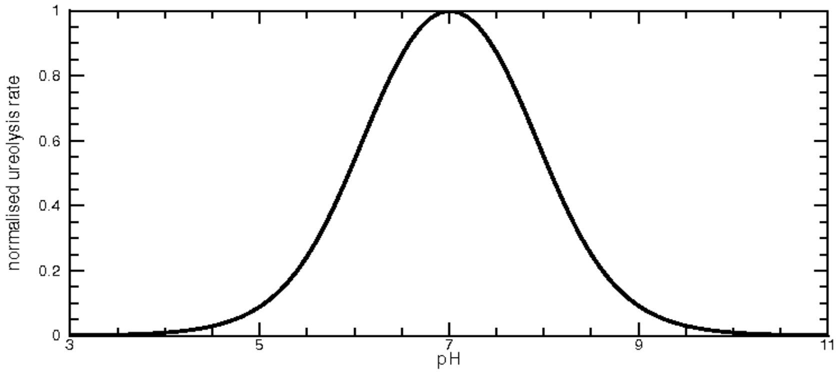


Ellen Lauchnor, CBE, personal communication, 2013:
Solid diamonds: rates at different pH at 83 mmol/l urea

Ureolysis, pH

$$r_{\mathrm{urea}} = k_{\mathrm{urease}} \frac{1}{1+\frac{\mathrm{H}^+}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{\mathrm{H}^+}} k_{\mathrm{ub}}(\rho_{\mathrm{f}}\phi_{\mathrm{f}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}} \frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}$$

old



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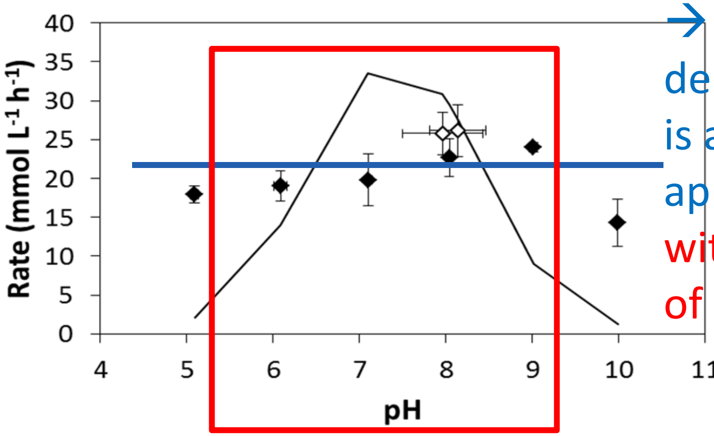

→ no pH dependency is a better approximation within the range of interest!

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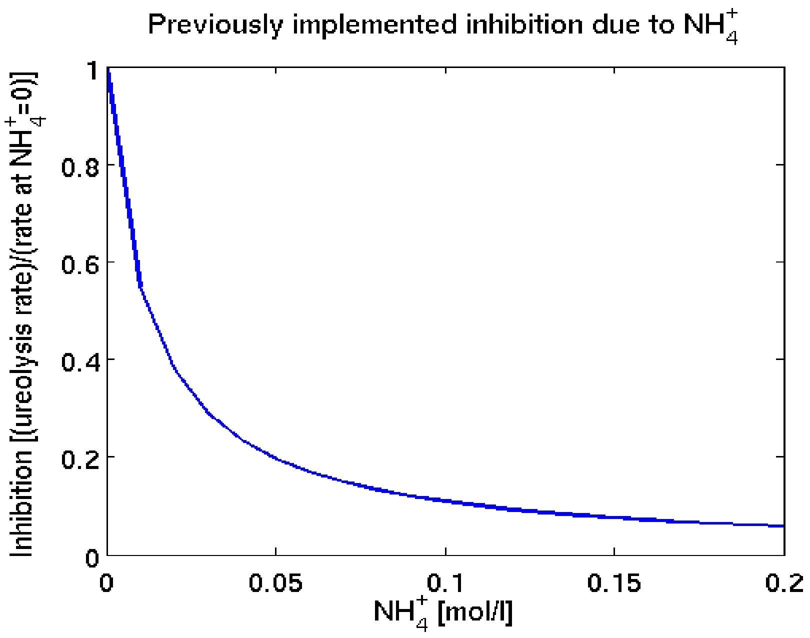
Solid diamonds: rates at different pH at 83 mmol/l urea

$$r_{\mathrm{urea}} = k_{\mathrm{urease}} \cancel{\frac{1}{1+\frac{\mathrm{H}^+}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{\mathrm{H}^+}}} k_{\mathrm{ub}}(\rho_{\mathrm{f}}\phi_{\mathrm{f}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}} \frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}$$

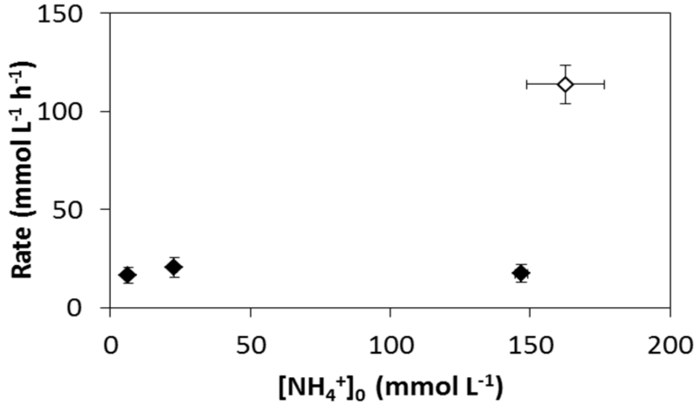
Ureolysis, inhibition due to ammonium

$$r_{\mathrm{urea}} = k_{\mathrm{urease}} \xcancel{\frac{1}{1+\frac{\mathrm{H}^+}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{\mathrm{H}^+}}} k_{\mathrm{ub}}(\rho_{\mathrm{f}}\phi_{\mathrm{f}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}} \frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}$$

old



new



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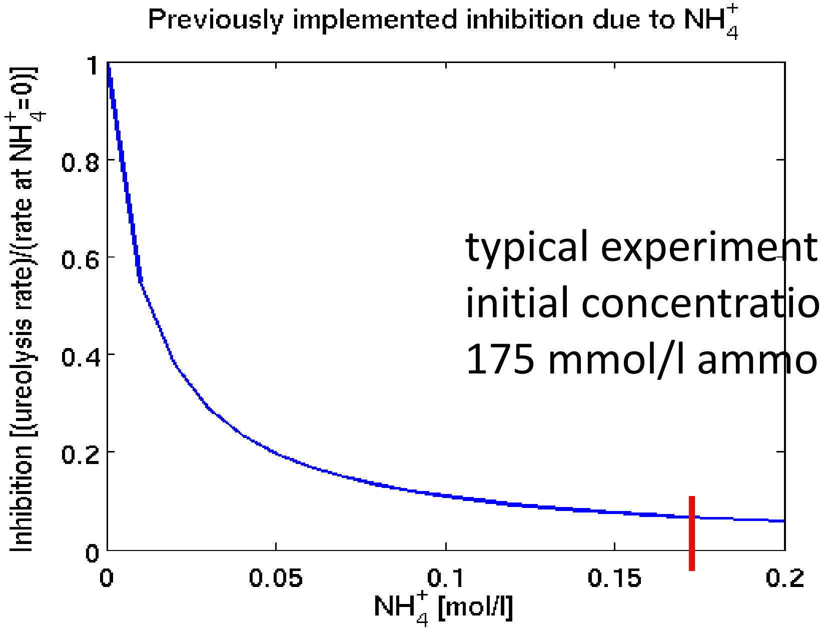
Ureolysis, inhibition due to ammonium

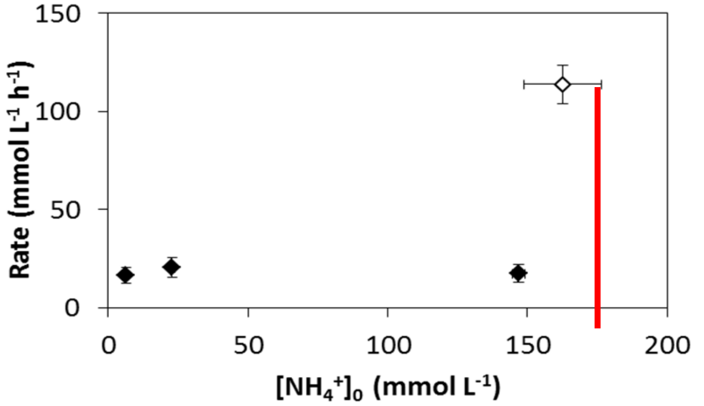
$$r_{\mathrm{urea}} = k_{\mathrm{urease}} \cancel{\frac{1}{1+\frac{\mathrm{H}^+}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{\mathrm{H}^+}}} k_{\mathrm{ub}} (\rho_{\mathrm{f}} \phi_{\mathrm{f}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}} \frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}$$

old



typical experiment
initial concentration:
175 mmol/l ammonium

new



Ellen Lauchnor, CBE, personal communication, 2013:
Solid diamonds: rates at different ammonium concentrations at 83 mmol/l urea

$$r_{\mathrm{urea}} = k_{\mathrm{urease}} \cancel{\frac{1}{1+\frac{\mathrm{H}^+}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{\mathrm{H}^+}}} k_{\mathrm{ub}} (\rho_{\mathrm{f}} \phi_{\mathrm{f}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}} \cancel{\frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}}$$

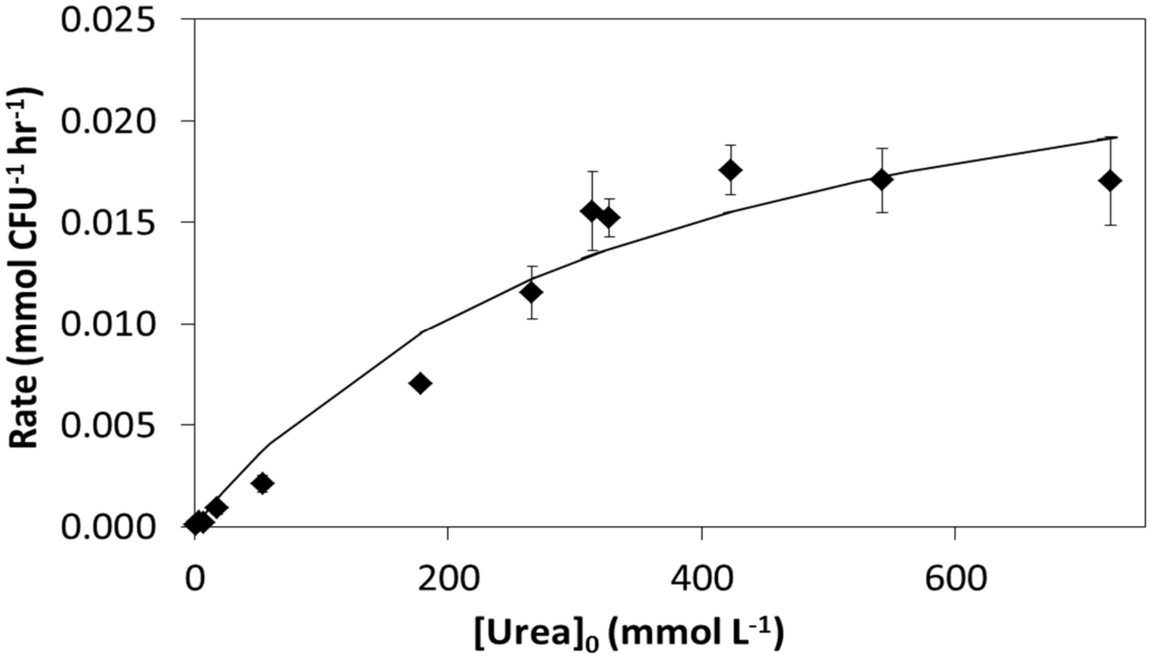
Ureolysis, simplification of the eqation

$$r_{\mathrm{urea}} = k_{\mathrm{urease}}\cancel{\frac{1}{1+\frac{\mathrm{H}^+}{K_{\mathrm{eu},1}}+\frac{K_{\mathrm{eu},2}}{\mathrm{H}^+}}}\,k_{\mathrm{ub}}(\rho_{\mathrm{f}}\phi_{\mathrm{f}})^{n_{\mathrm{ub}}}\frac{m_{\mathrm{urea}}}{K_{\mathrm{u}}+m_{\mathrm{urea}}}\cancel{\frac{K_{\mathrm{NH}_4^+}}{K_{\mathrm{NH}_4^+}+m_{\mathrm{NH}_4^+}}}$$

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

Fitted to experimental data, previously literature values.

Previously fitted parameter, Now literature values.



Ellen Lauchnor, personal communication, 2013:
Solid diamonds: rates at different urea concentrations

Ureolysis, simplification of the eqation

$$r_{\text{urea}} = \underset{41.67}{k_{\text{urease}}} \overset{1 \text{ to } 0.01}{\cancel{\frac{1}{1+\frac{\text{H}^+}{K_{\text{eu},1}}+\frac{K_{\text{eu},2}}{\text{H}^+}}}} \overset{0.11}{k_{\text{ub}}}(\rho_{\text{f}}\phi_{\text{f}})^{\overset{1.5}{n_{\text{ub}}}} \frac{m_{\text{urea}}}{\underset{0.017}{K_{\text{u}}}+m_{\text{urea}}} \overset{0.06 \text{ to } 0.01}{\cancel{\frac{K_{\text{NH}_4^+}}{K_{\text{NH}_4^+}+m_{\text{NH}_4^+}}}}$$

$$\downarrow$$

$$r_{\text{urea}} = \underset{706}{\underline{k_{\text{urease}}}} \overset{0.01}{\underline{k_{\text{ub}}}}(\rho_{\text{f}}\phi_{\text{f}})^{\overset{1.0}{\underline{n_{\text{ub}}}}} \frac{m_{\text{urea}}}{\underset{0.355}{\underline{K_{\text{u}}}}+m_{\text{urea}}}$$

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.

→ Need to recalibrate the updated model

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Attachment experiments

Model efficiency: sequential approach

Summary and Outlook

Refit: Fitting parameters

- 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}
- Equations containing the fitting parameters:

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

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

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

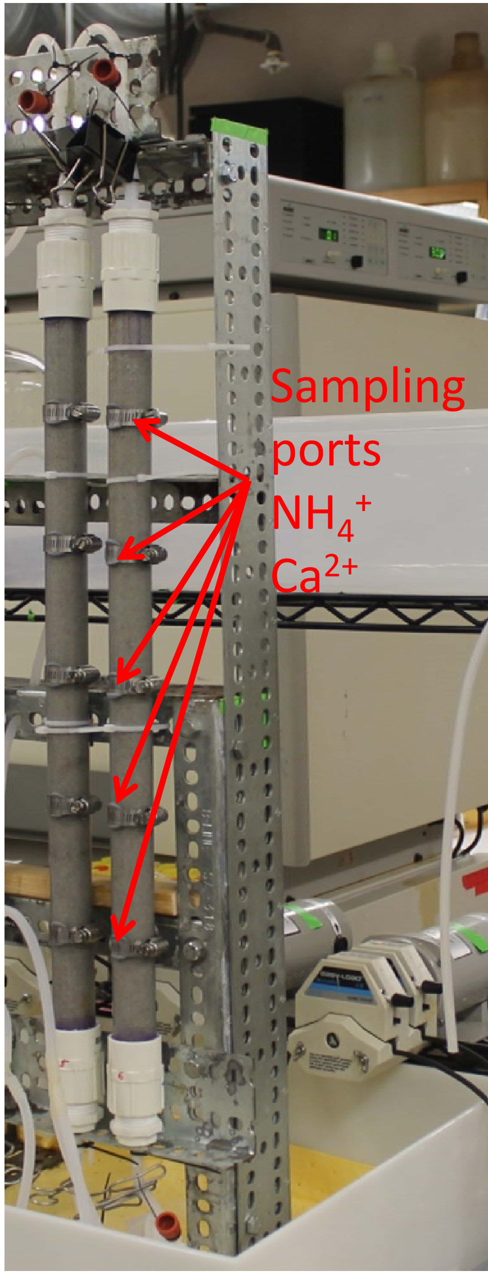
$$\underline{\phi} = \phi_0 - \phi_{\text{calcite}} - \underline{\phi_{\text{biofilm}}} \qquad K = K_0 \left(\frac{\underline{\phi} - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}}\right)^3$$

Recalibration: Experimental data used

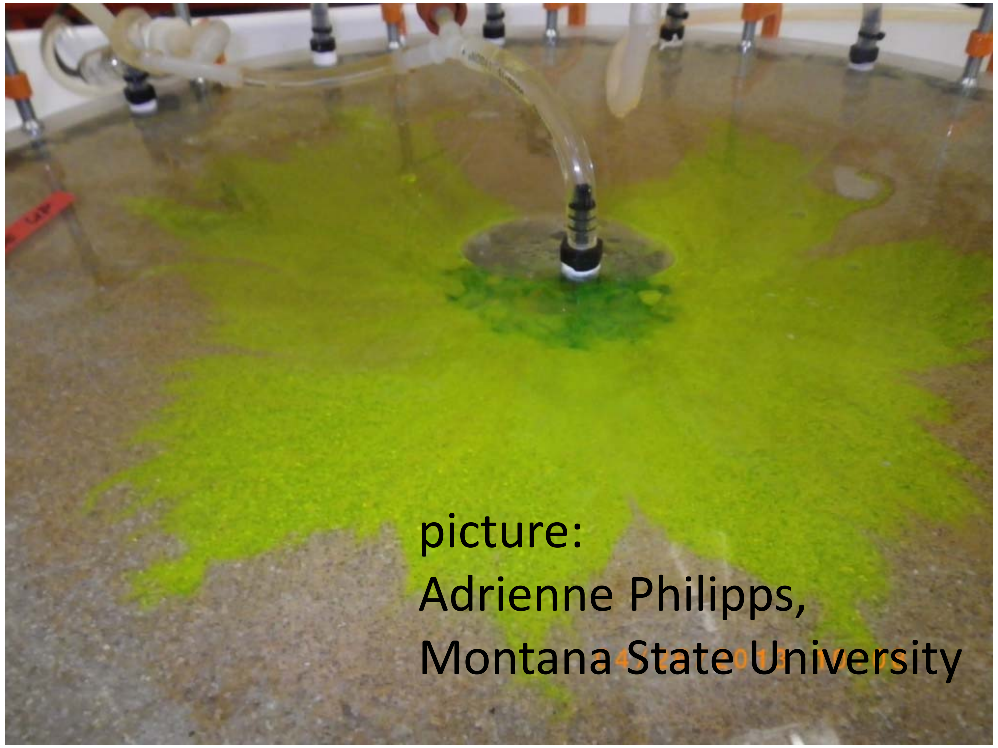
Different experiments:

- All experiments measured $CaCO_3$ at t_{end}
- Column 4, without measurement ports
- Column 8 and 9 with additional ports for NH_4^+ and Ca^{2+} measurements
- 2D radial flow → Bicycle Rim Reactor

Columns



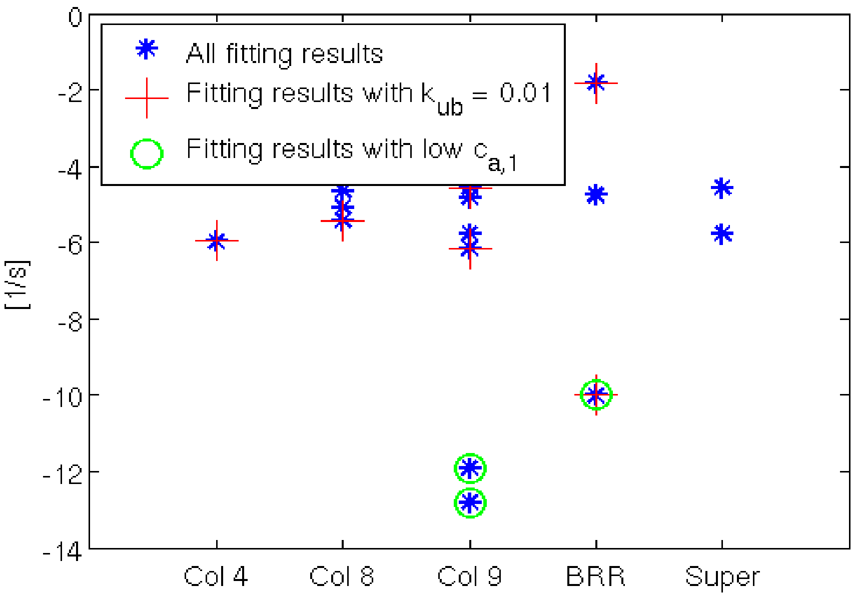
Bicycle Rim Reactor

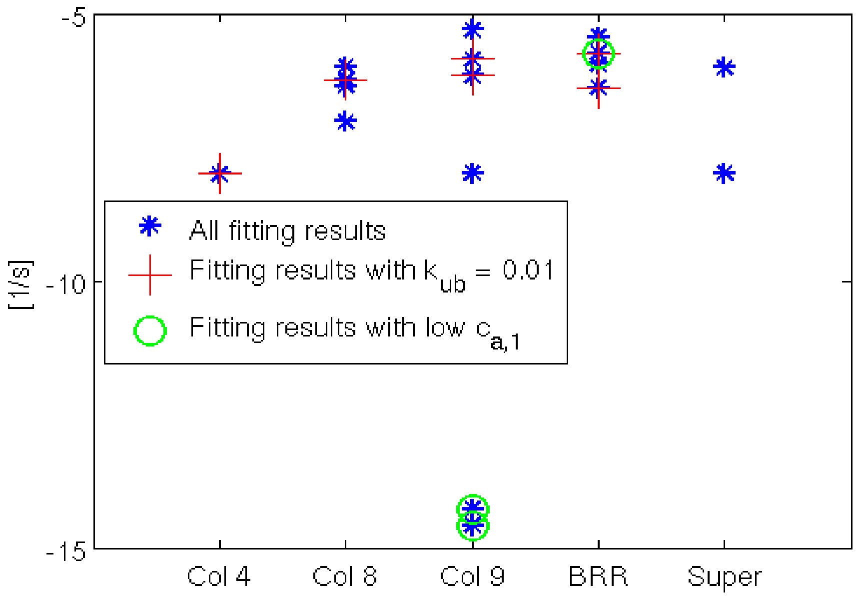

picture:
Adrienne Philipps,
Montana State University

International Research Training Group nupus

MONTANA STATE UNIVERSITY
Center for Biofilm Engineering

Recalibration results


Fitting Results for $\log(c_{a,1})$

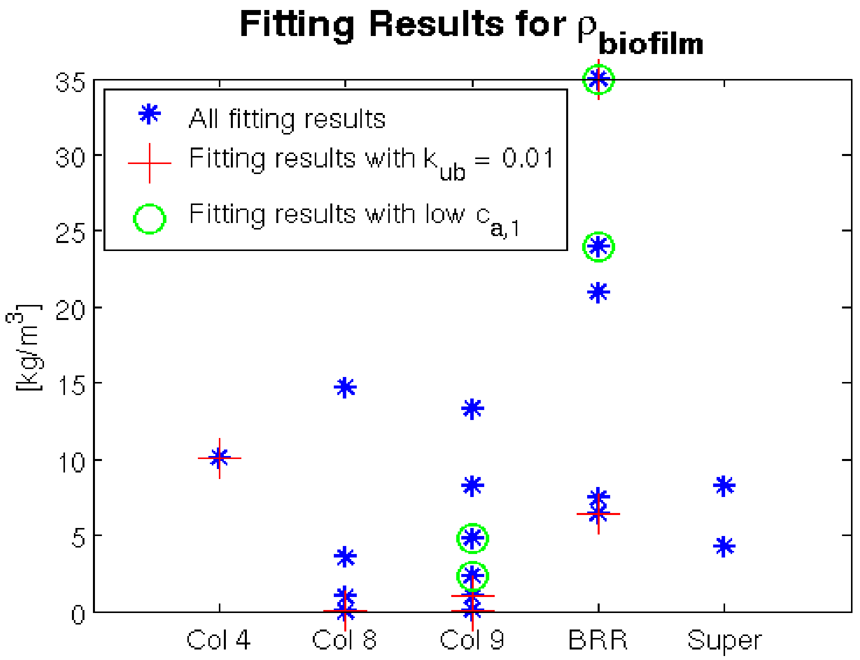

Fitting Results for $\log(c_{a,2})$

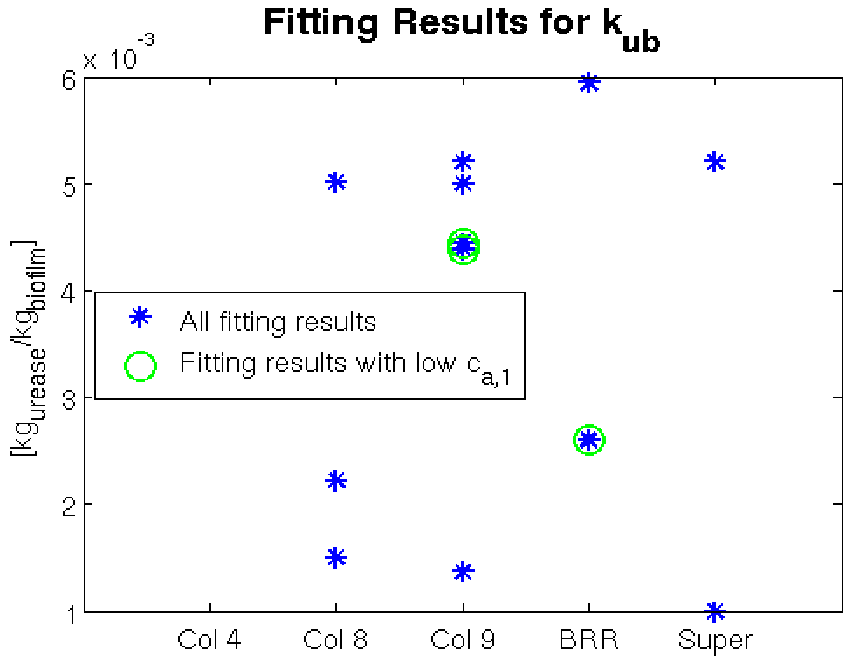
$$r_{\text{attach}} = \left(c_{\text{a},1}\phi_{\text{biofilm}} + c_{\text{a},2}\right) C_{\text{w}}^{\text{bio}}\phi S_{\text{w}}$$

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

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

Recalibration results


Fitting Results for ρ_{biofilm}


Fitting Results for k_{ub}

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

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

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

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

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Summary and Outlook

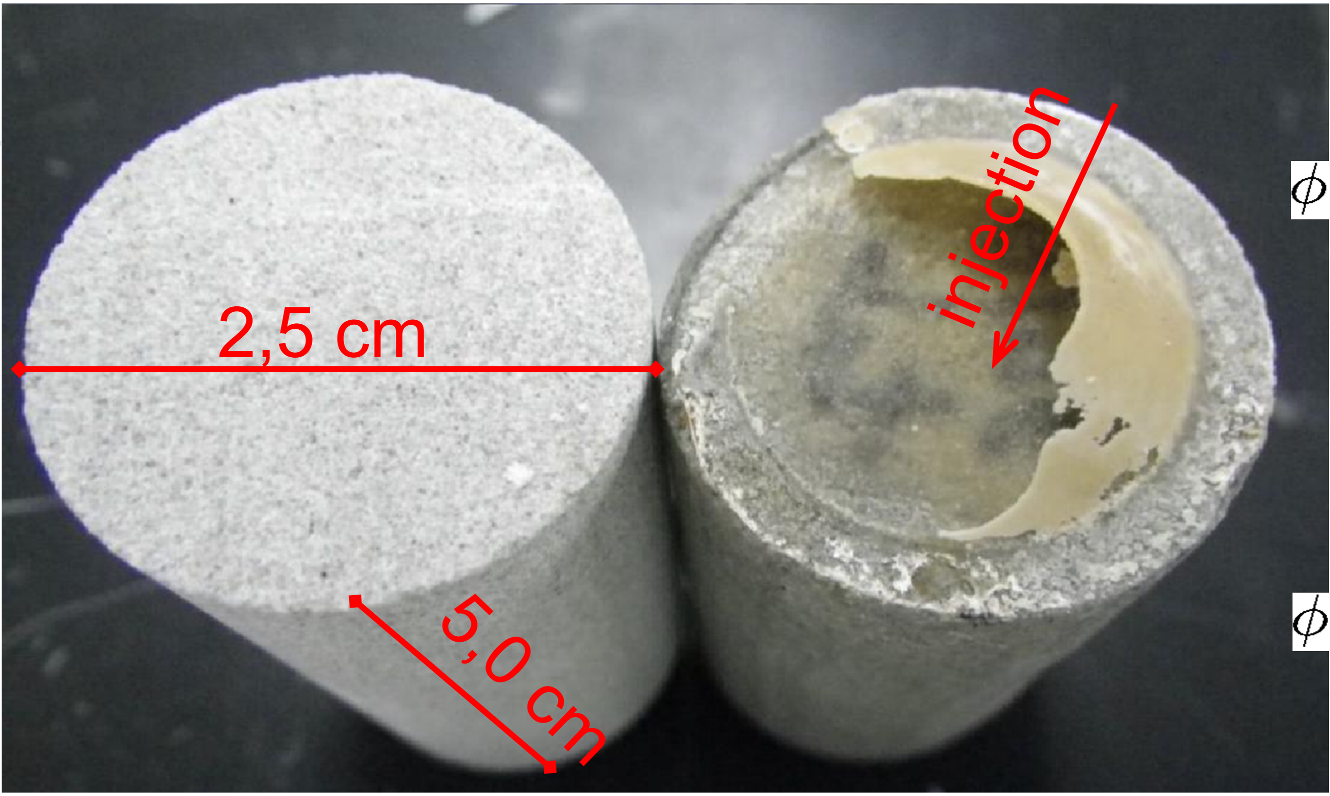
Permeability: High-pressure core experiments

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

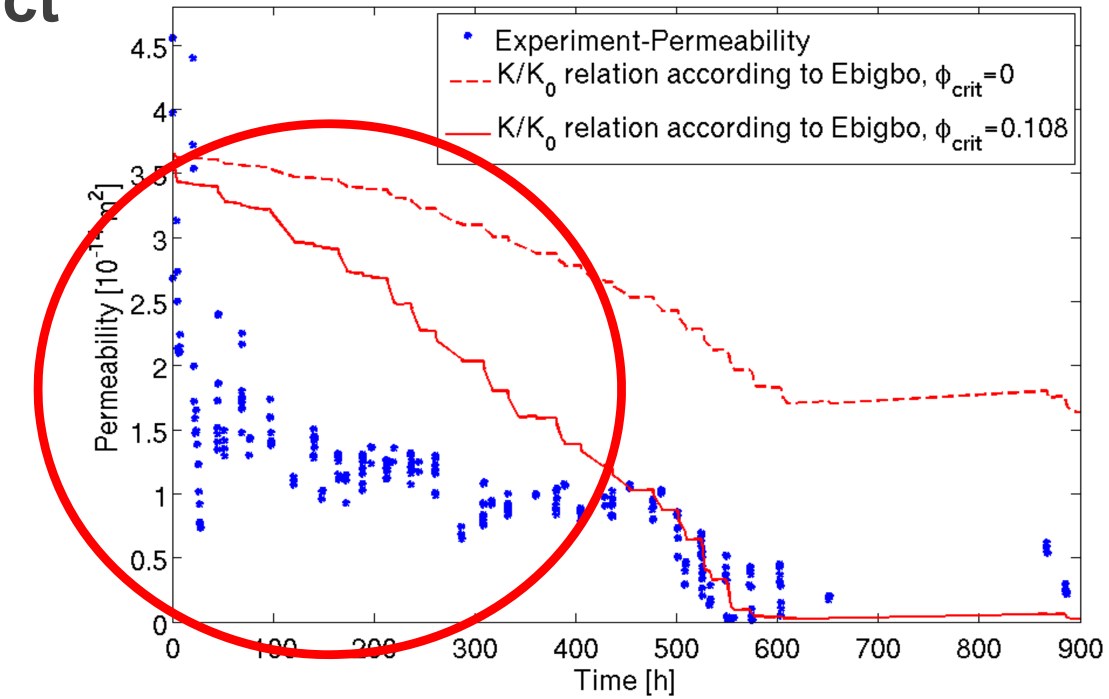
$\phi = 0.138$

$\phi_{\text{calcite}} = 0.031$

$K =$
$1.0 \cdot 10^{-15}\text{m}^2$

before after
biomineralization

Permeability: Biofilm impact



- Changes in porosity

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

- Changes in permeability

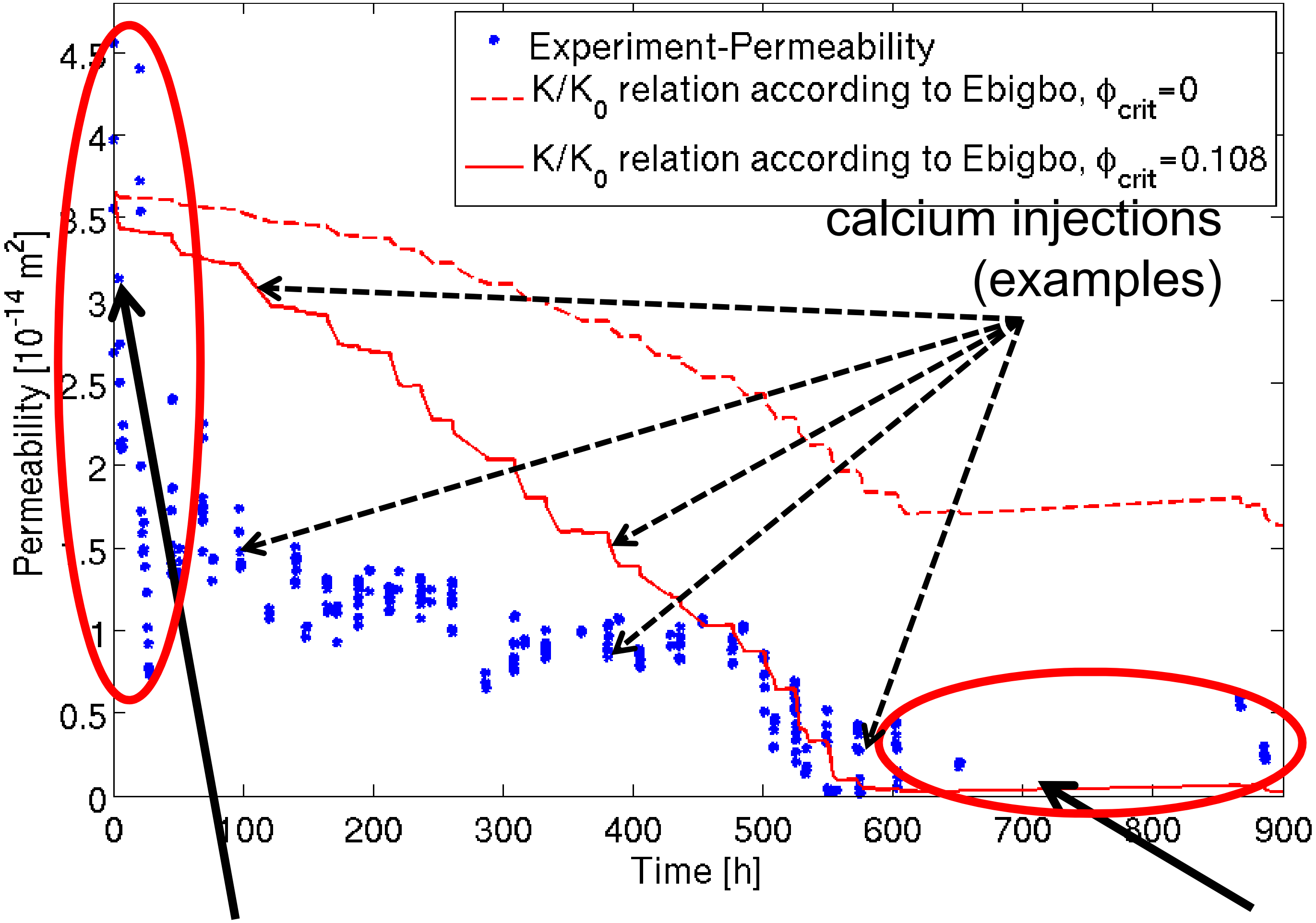
$$K = K_0 \left(\frac{\phi-\phi_{\text{crit}}}{\phi_0-\phi_{\text{crit}}}\right)^3 \ \text{Kozeny-Carman type relation}$$

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



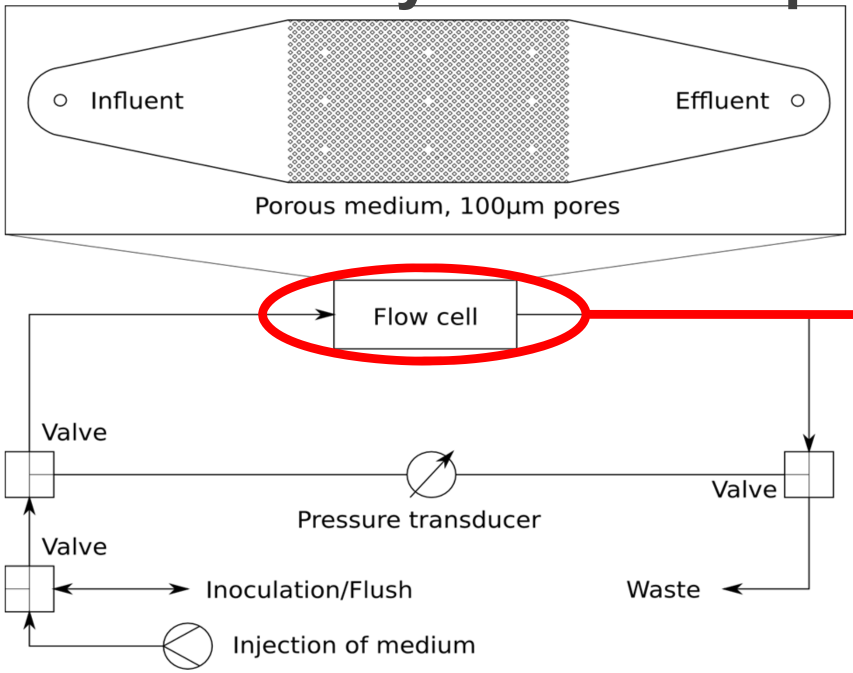
calcium injections (examples)

Biofilm inoculation

Biofilm decay during one week starvation period

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

Permeability: Biofilm impact



Influent

Effluent

Porous medium, 100µm pores

Flow cell

Valve

Pressure transducer

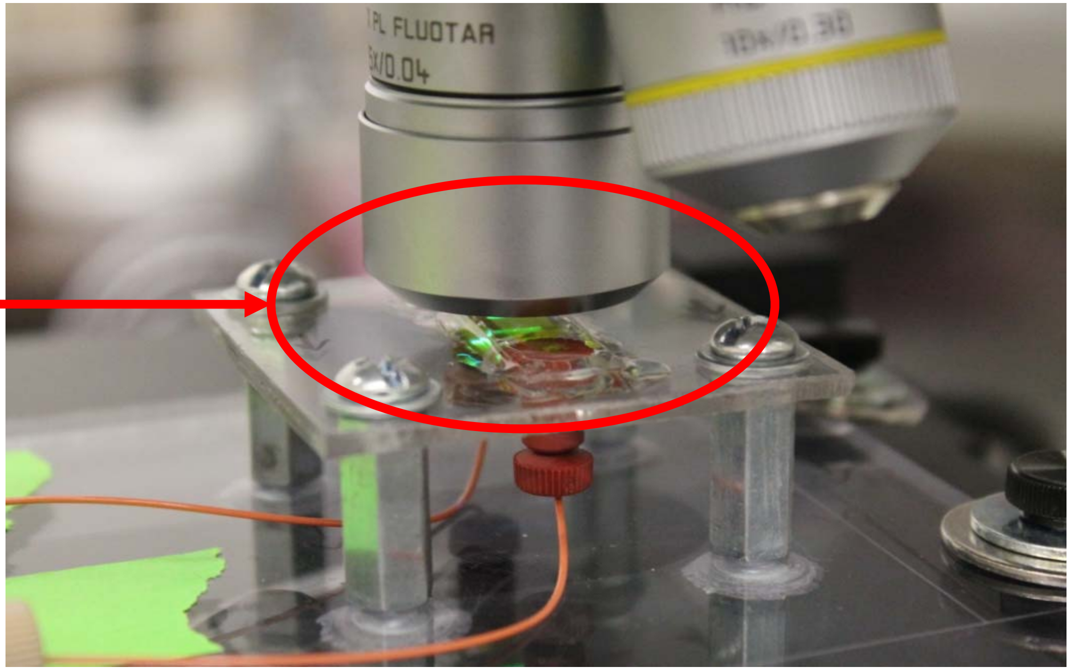
Valve

Valve

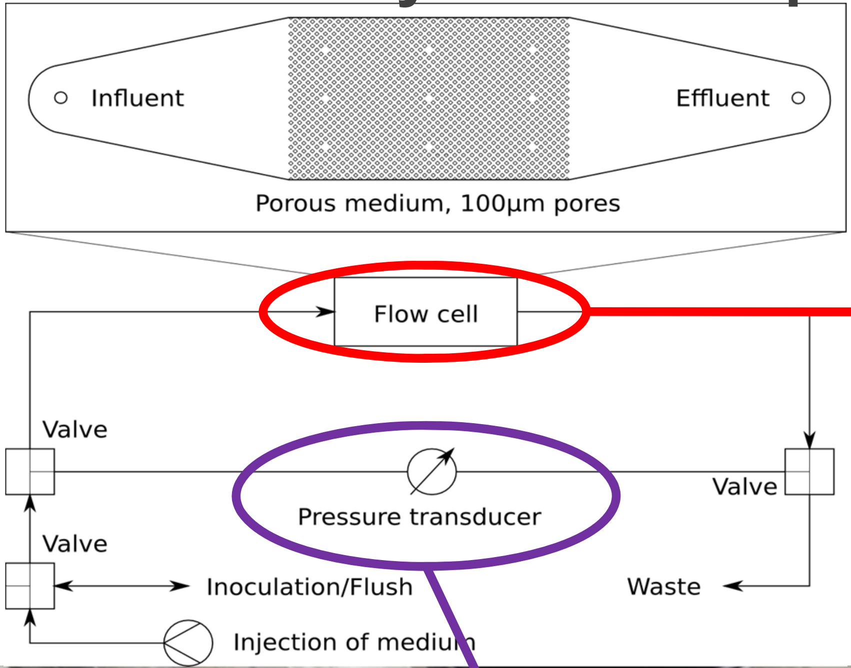
Inoculation/Flush

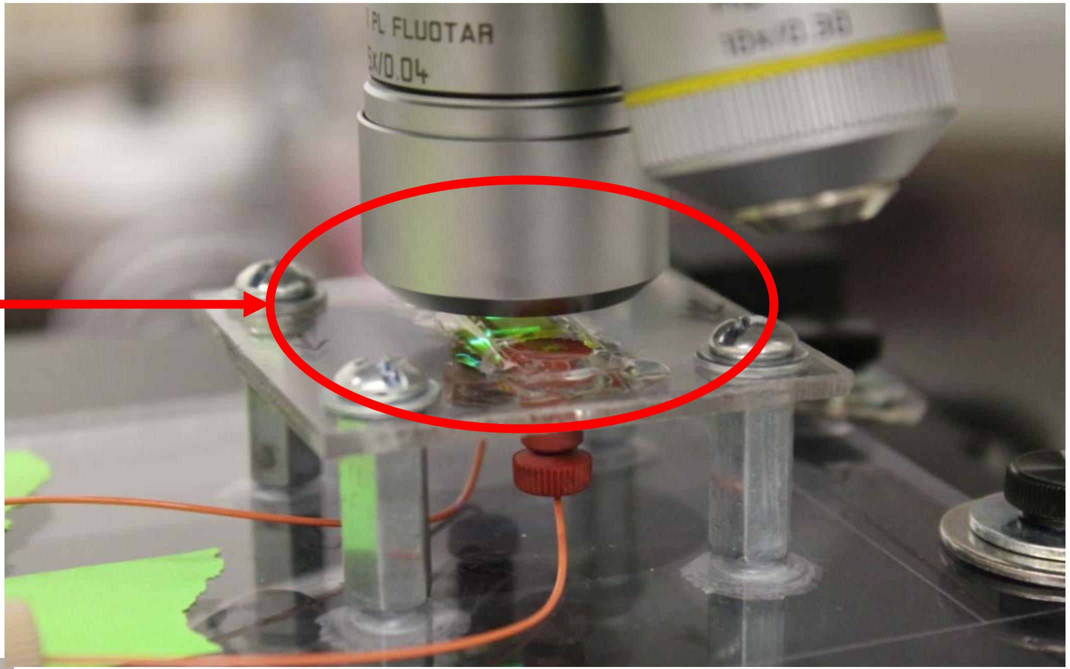
Waste

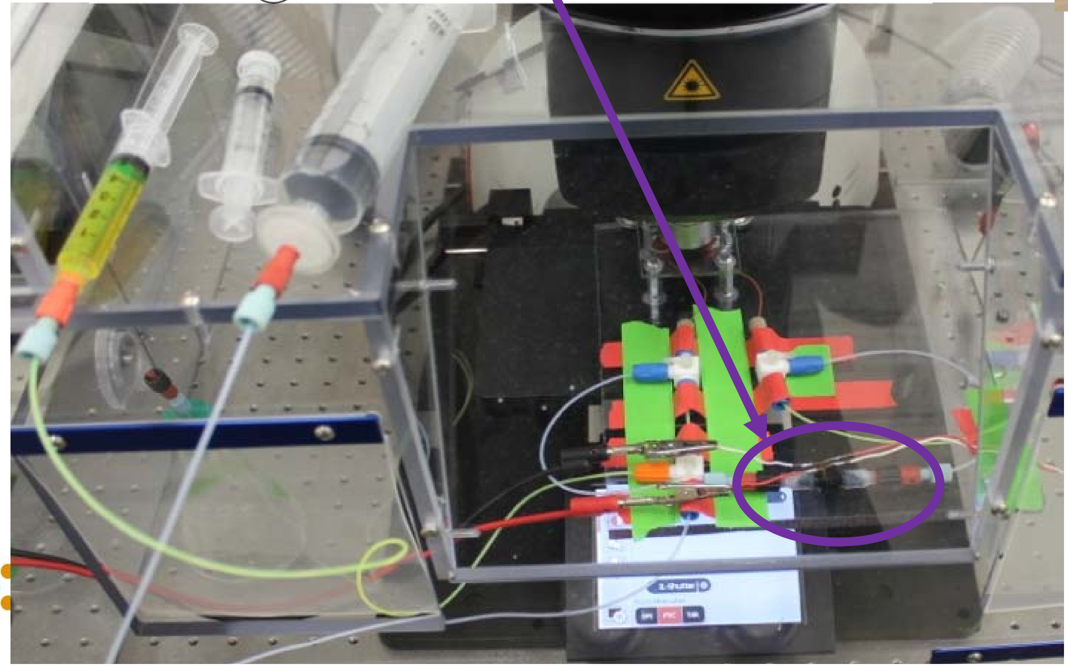
Injection of medium



Permeability: Biofilm impact

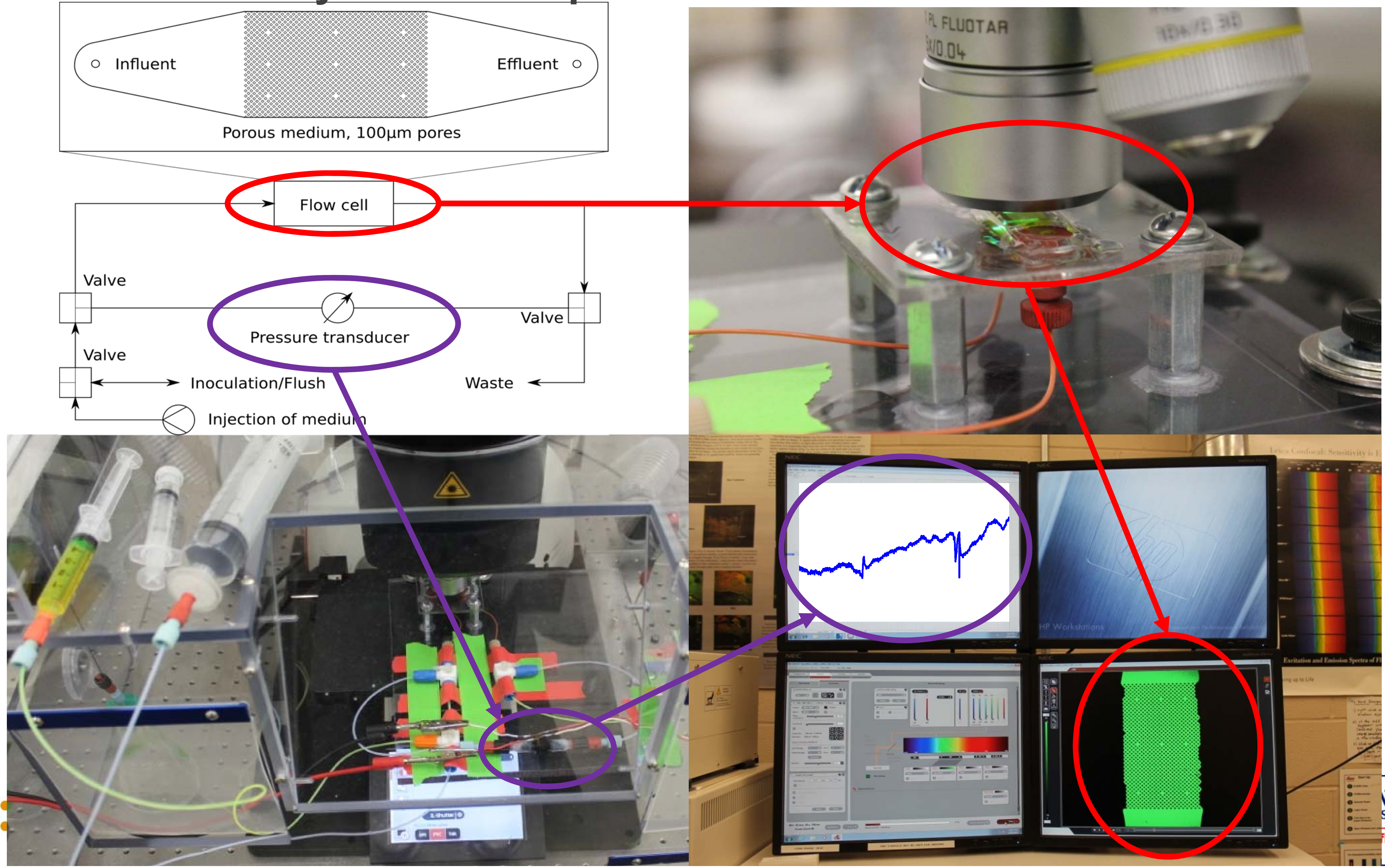






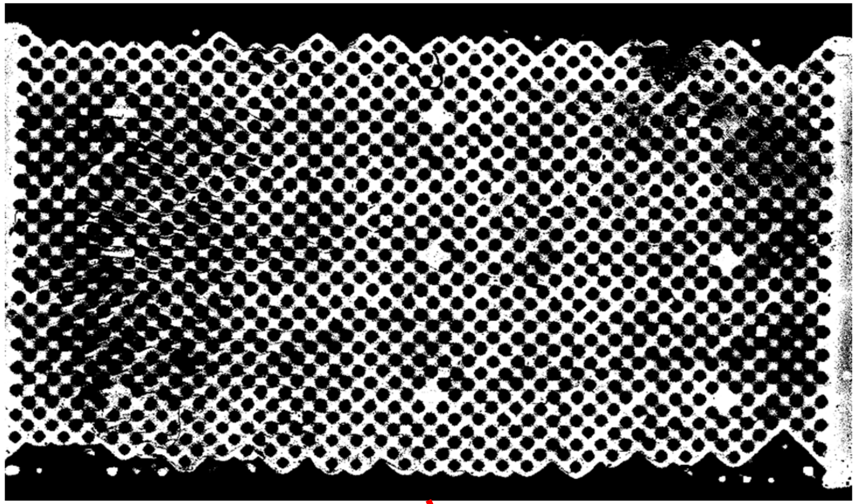
MONTANA STATE UNIVERSITY
Center for Biofilm Engineering

Permeability: Biofilm impact

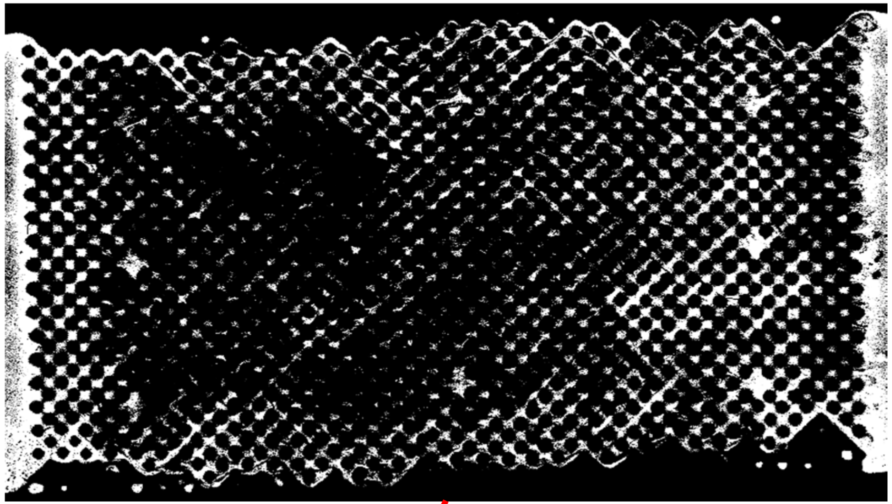


Permeability: Biofilm impact

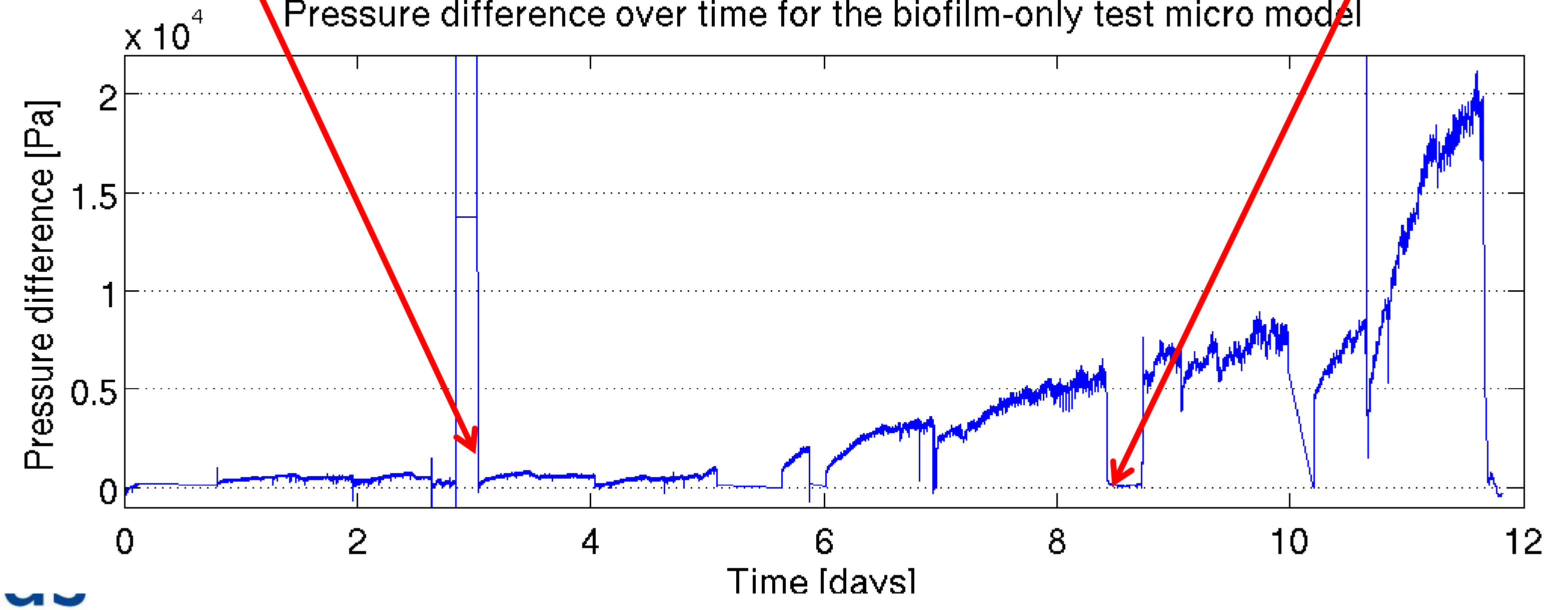
Porosity after 3 days



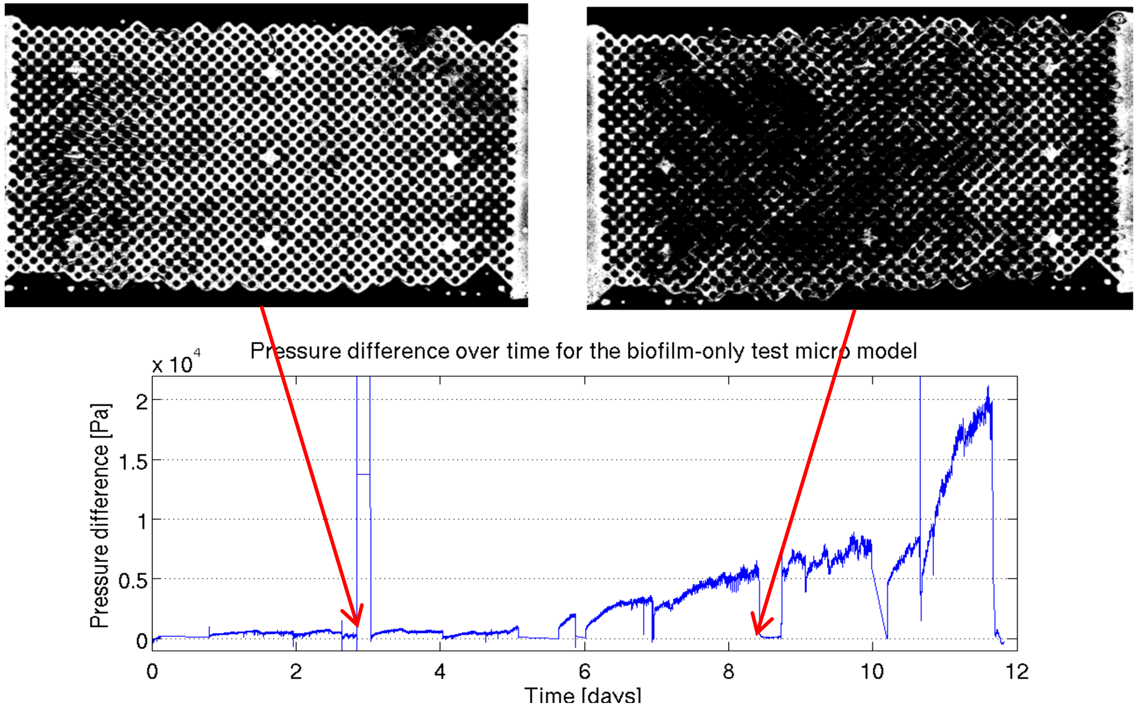
Porosity after 8 days



Pressure difference over time for the biofilm-only test micro model



Permeability: Biofilm impact



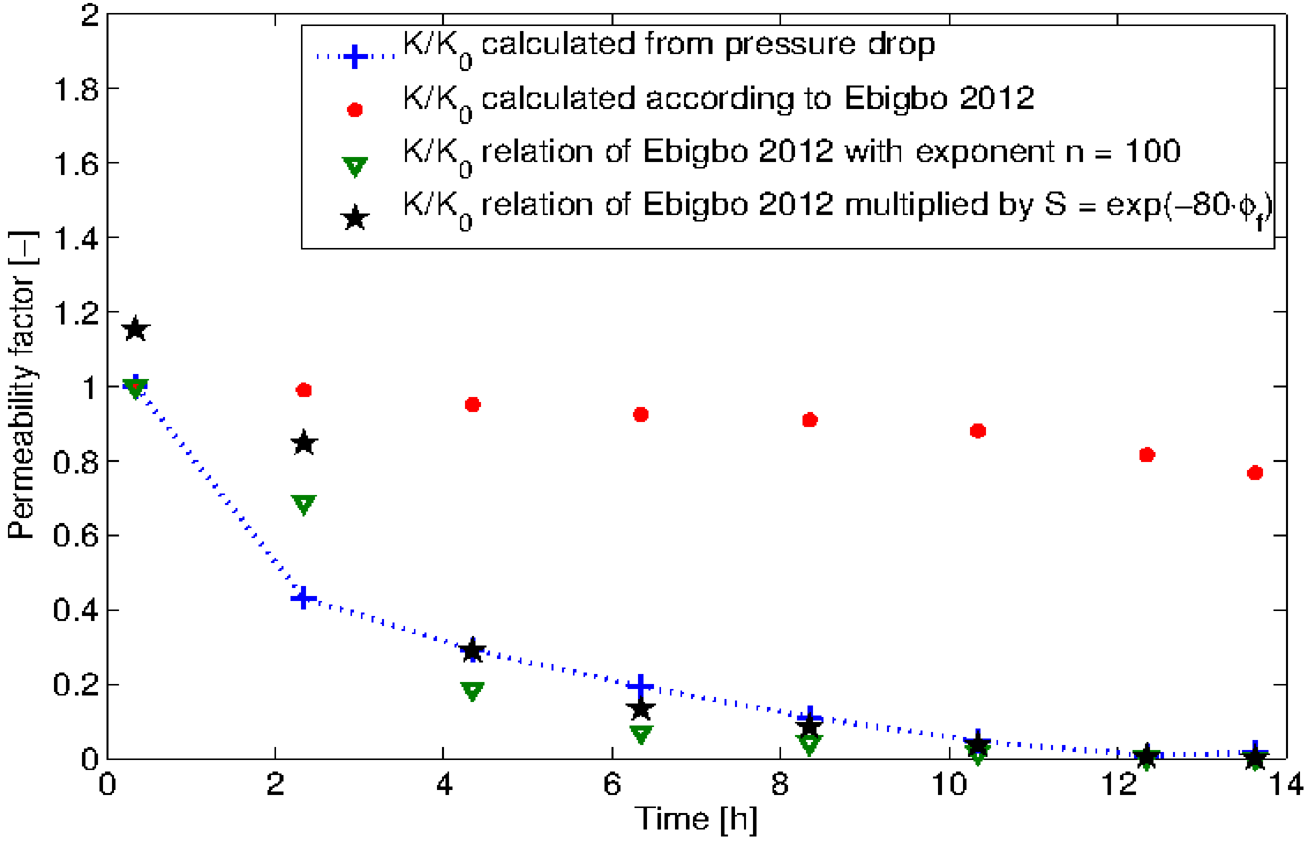
Idea:
Extend the previously used Kozeny-Carman by a shape factor S, that describes the effects of the change in pore geometry due to biomineralization on permeability

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

Using pressure and volume measurements at each time at which the flow cell was imaged, S can be calculated using:

$$S(\phi_{\mathrm{c}}(t), \phi_{\mathrm{f}}(t)) = \frac{-QL\mu}{A\Delta p(t)(\phi(\phi_{\mathrm{c}}(t), \phi_{\mathrm{f}}(t)) - \phi_{\mathrm{crit}})^3}$$

Permeability: Biofilm impact, updated relation



Both an extension of the previously used Kozeny-Carman by a shape factor

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

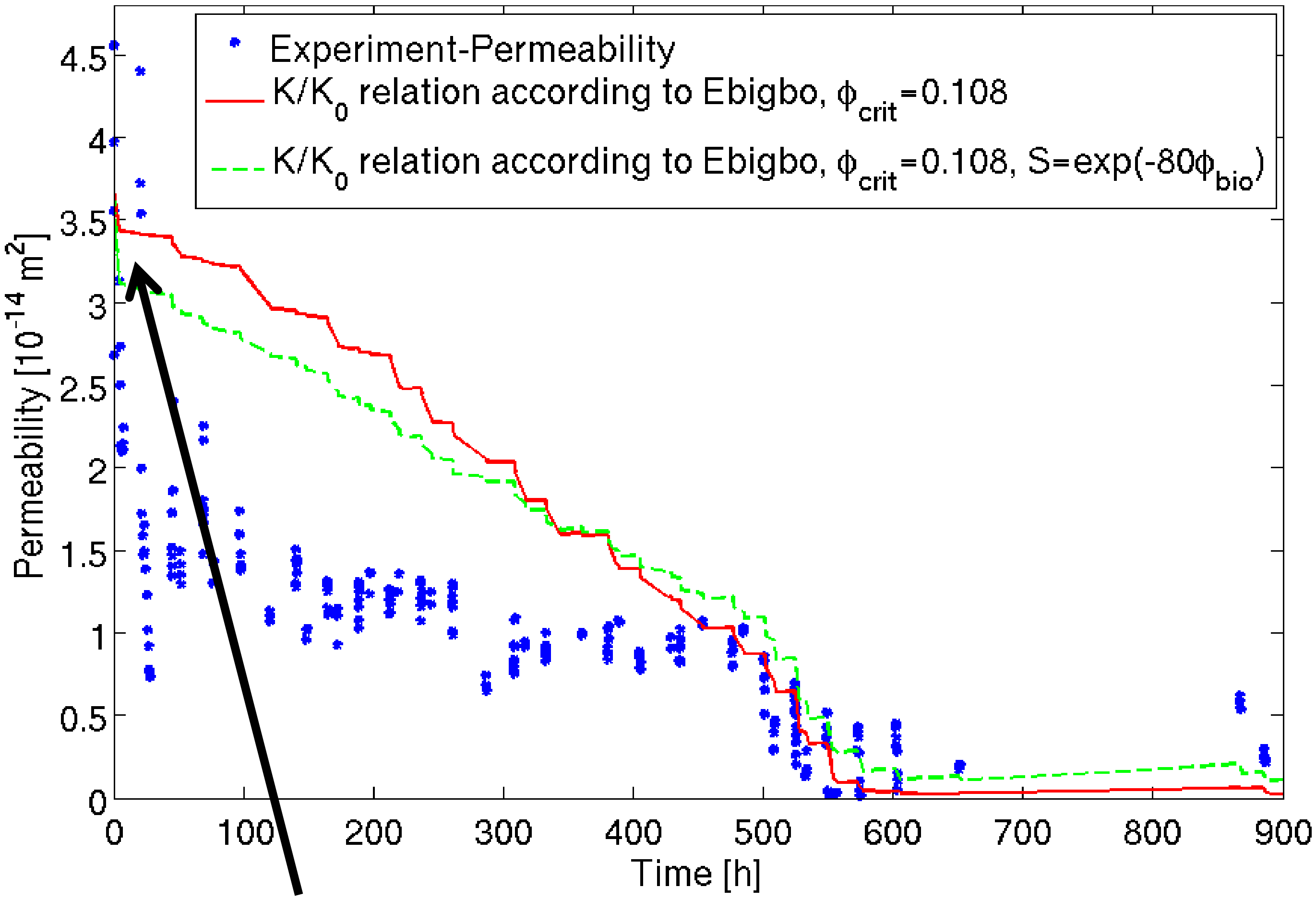
or an increased exponent

$$n = 100$$

fit the observed permeability reduction.

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

Permeability: Biofilm impact, updated relation



Biofilm inoculation

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

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

improves modeled permeabilities.

More experiments have to be conducted to further improve it.

Permeability: Biofilm impact, updated relation

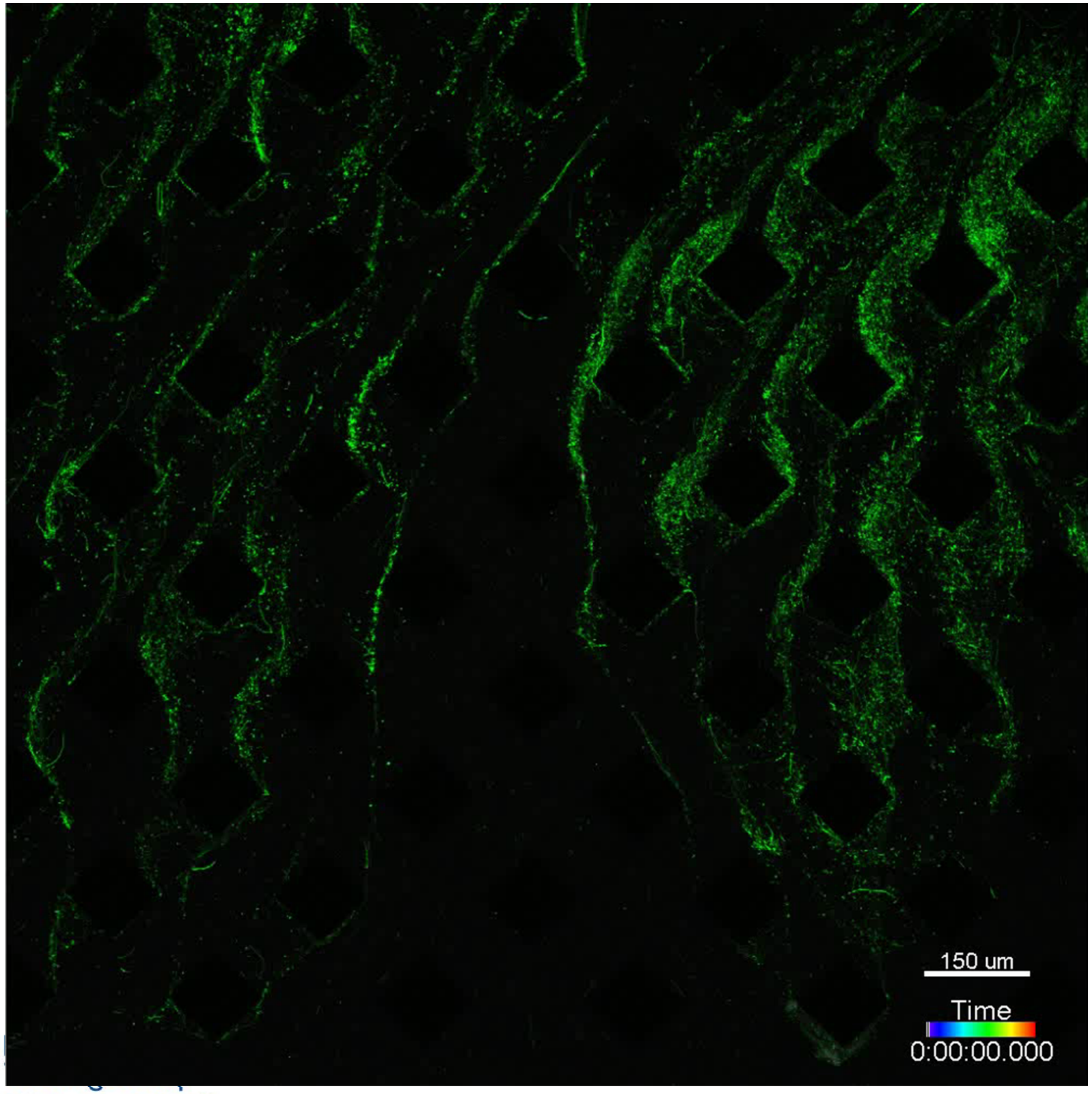
Difficulties:

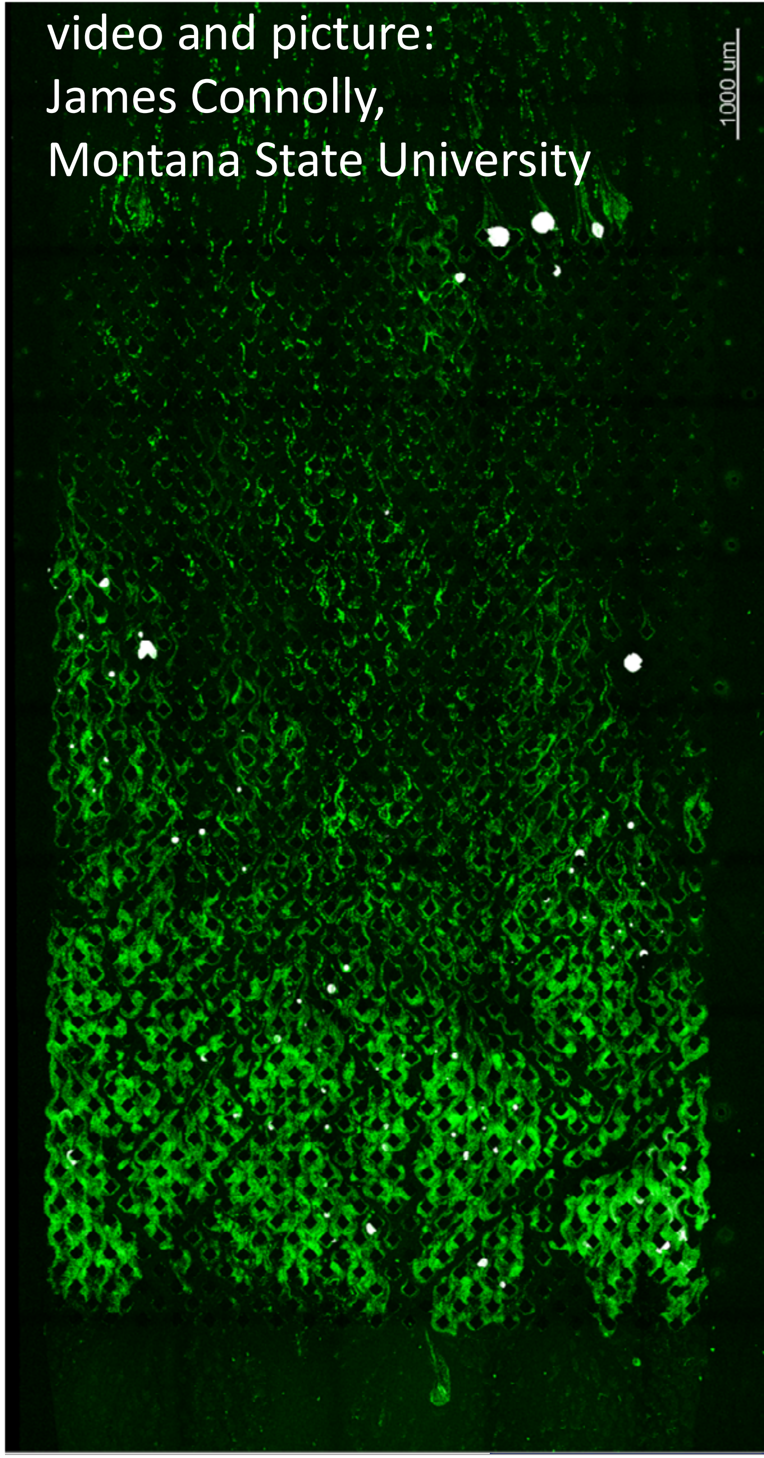
- The experimental measurements do not cover the needed rage of porosities, especially, there are no measurement for low porosities < 0.5.
- The pressure difference increases quickly during the experiments, exceeding the calibration range.

  → few experiments with a porosity change > 0.1.
- Only the fluorescent cells can be imaged.

  → possible error in the measured biofilm volume
- 2D, homogeneous flow cell experiments, but heterogeneous, 3D reality

Calcite precipitation within the flow cell





video and picture:
James Connolly,
Montana State University

Outline

Model concept

Improvement of the numerical model for MICP:

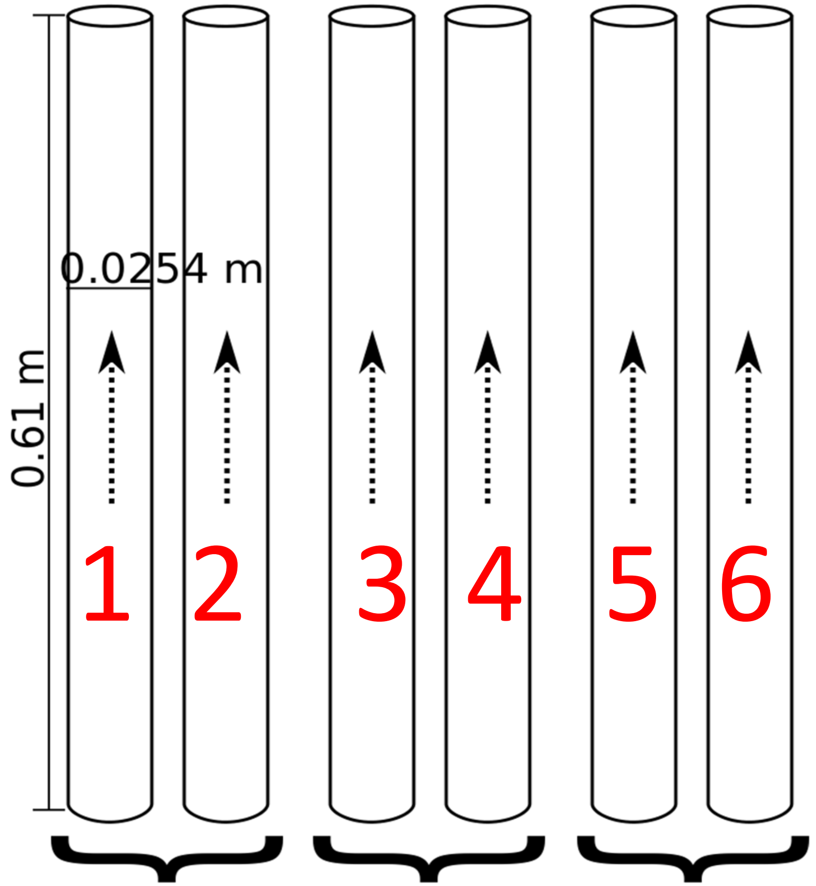
- Implementation of the experimentally observed kinetics of ureolysis by living *S. pasteurii*
- Recalibration of the model using inverse modeling
- Improvement of the description of the biofilm impact on permeability

Attachment experiments

Model efficiency: sequential approach

Summary and Outlook

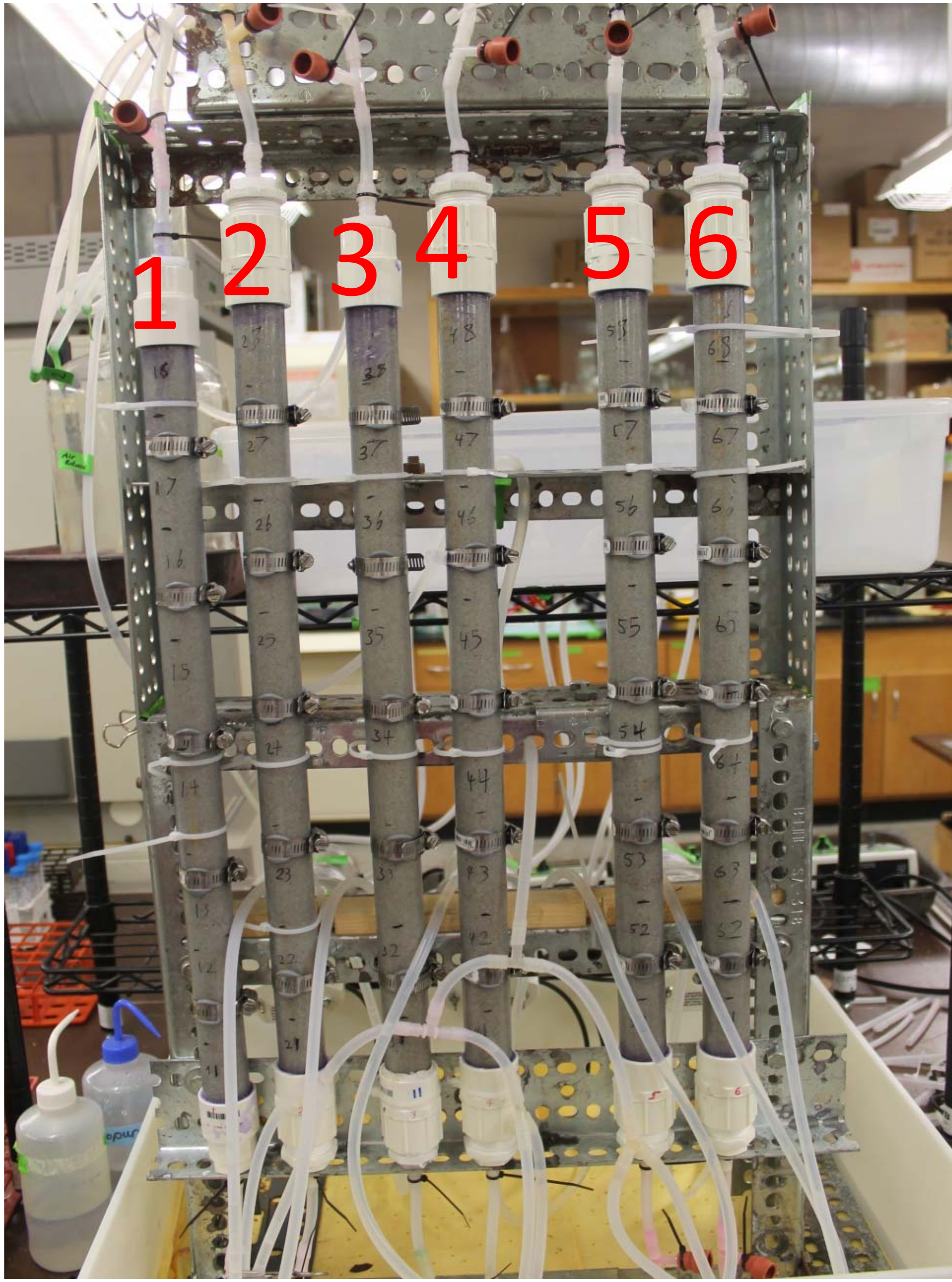
Attachment experiments - setup



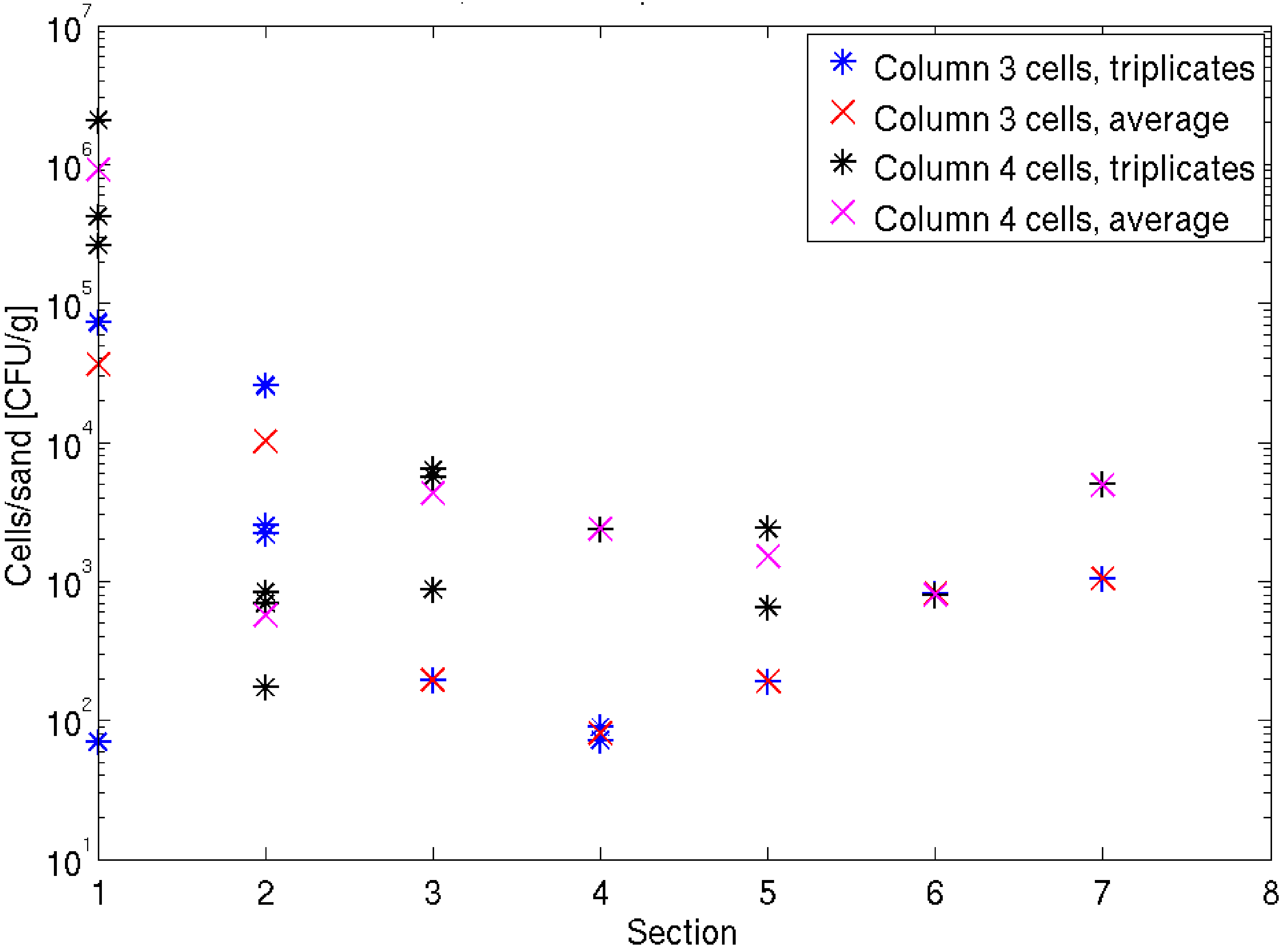
inoc.
+ rinse

inoc.
+ 8h
+ rinse

inoc.
+ 8h
+ 18h growth
+ rinse



Column 3 and 4 (inoc. + 8h batch + rinse)



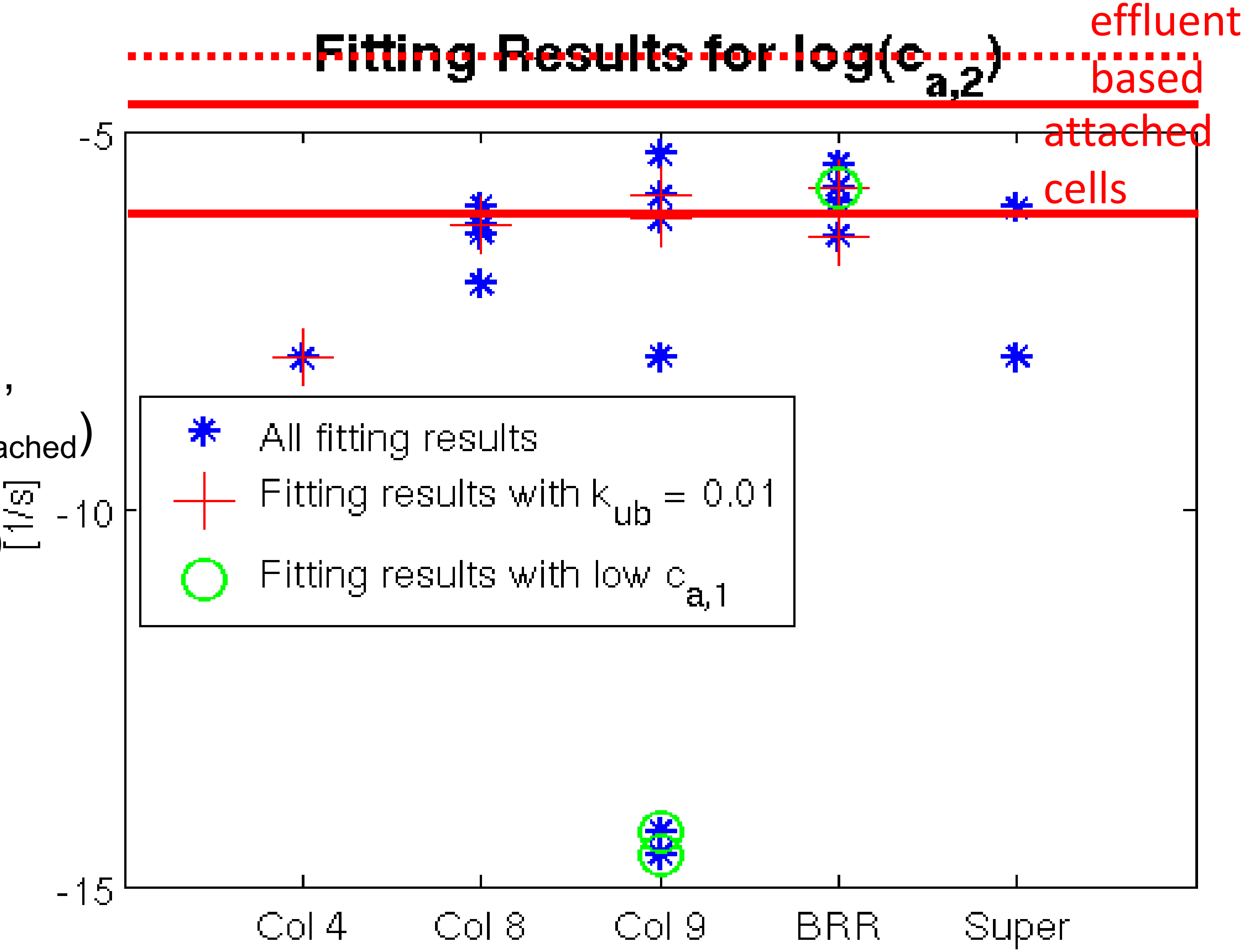
Attachment coefficient

	Effluent based $c_{a,2}$ (overestimates attachment) $c_{a,2} = \frac{\text{cells}_{\text{in}} - \text{cells}_{\text{out}}}{time}$ **[CFU/s] / [1/s]**	**$c_{a,2}$ fitted to cells in the column [1/s]**	**$c_{a,2}$ fitted to cells in the column, but $c_{a,2}$= 0 for v=0 [1/s]**	**Time for attachment [h]**
1	1600000 /1.67 10^{-4}	-		0
2	1316667 / 1.37 10^{-4}	1.45779 10^{-5}	2.18561 10^{-5}	0
3	1116667 / 1.16319 10^{-4}	1.24678 10^{-6}	2.11147 10^{-5}	8
4	433333 / 4.51 10^{-5}	2.75281 10^{-5}	4.29265 10^{-4}	8

- The effluent based attachment coefficients overestimate attachment due to the measurement method, which allows only to count active cells.
- Observed that the fitted attachment coefficient seems to be dependent on the time available for attachment, which is not physical. → further investigation
- Parameter estimation: range from 3.2 10^{-7} to 10^{-5}, experiment: 1.2 10^{-6} to 4.3 10^{-4}

Attachment: Summary and comparison to fitting results

- Experimentally verified the fitted attachment coefficient $c_{a,2}$.
- Fitted and experimental values agree.
- Effluent based experimental values overestimate attachment (≈30% of cells not detected, →Cells_{in} - $\text{Cells}_{out} \neq \text{Cells}_{attached}$)
- Plate count (measurement) related uncertainty.



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Mass balances split into transport and reaction only

- Mass balance, fully implicit:

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

- Mass balance, transport only:

$$\sum_\alpha \frac{\partial}{\partial t}(\phi \rho_\alpha x_\alpha^\kappa S_\alpha) + \nabla \cdot (\rho_\alpha x_\alpha^\kappa \mathbf{v}_\alpha) - \nabla \cdot (\rho_\alpha \mathbf{D}_\alpha \nabla x_\alpha^\kappa) = 0$$

→ **No reactive sources in the transport subproblem**

- Mass balance, reaction only:

$$\sum_\alpha \frac{\partial}{\partial t}(\phi \rho_\alpha x_\alpha^\kappa S_\alpha) = q^\kappa$$

→ **Only local information is needed in the reaction subproblem**

Mass balances split into transport and reaction only

- Mass balance of solid phases, fully implicit:

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

- Mass balance of solid phases, transport only:

$$\rho_\lambda \frac{\partial \phi_\lambda}{\partial t} = 0$$

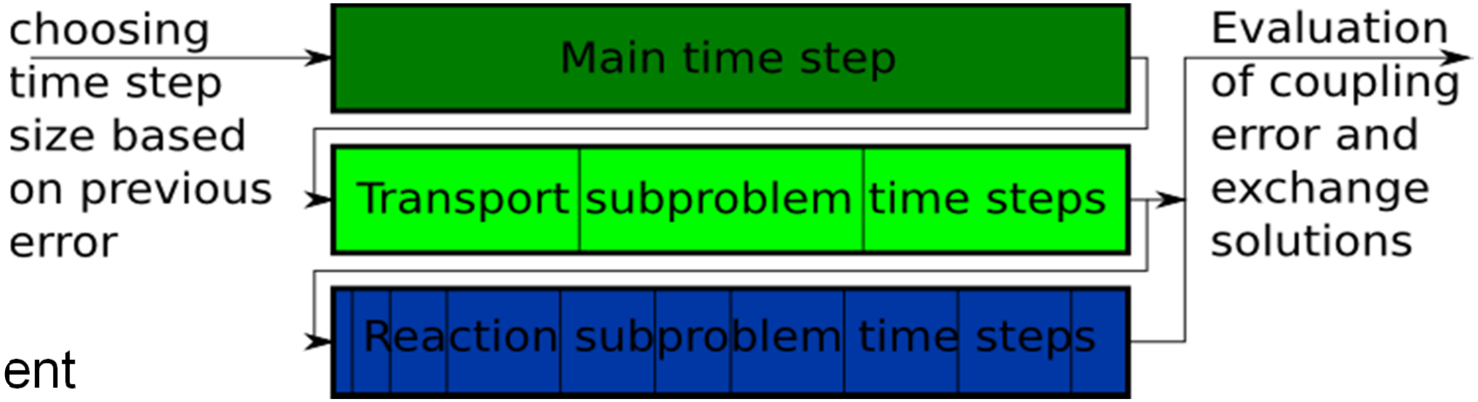
→ Solid phases disappear in the transport subproblem

- Mass balance of solid phases, reaction only:

$$\rho_\lambda \frac{\partial \phi_\lambda}{\partial t} = q^\lambda$$

Sequential approach used

- Implemented a sequential non-iterative coupling scheme.



choosing time step size based on previous error

Main time step

Transport subproblem time steps

Reaction subproblem time steps

Evaluation of coupling error and exchange solutions

- Advantages:
  - easy to implement
  - suitable for large scale
  - suitable for advection dominated systems like the vicinity of an injection well
- Disadvantages:
  - time step size constraints (main time step) or increasing error due to sequential calculation

Sequential approach: Preliminary results

- The transport-only subproblem does not need to resolve time step contraints resulting from the non-linear chemical reaction rates.

Table: Comparison of CPU times for a reduced model (only $CaCO_3$ dissolution)

	Fully implicit (FI)	**Seq., tol. decoupl. error 10^{-3}**	**Seq., tol. decoupl. error 10^{-4}**	**Seq., tol. decoupl. error 10^{-5}**
CPU time [s]	9500	240	900	9500
„Quality“ of results		much worse than FI	sufficiently close to FI	identical to FI

$$error = \frac{2|PV_r - PV_t|}{PV_r + PV_t}$$

→ Significant speedup, dependent on tolerated “decoupling error”, discretization, …

- The solid phases disappear in the transport-only subproblem, reducing the number of unknowns per node from 12 to 10.

→ Additional CPU-time reduction of 15% ≈ 2/12

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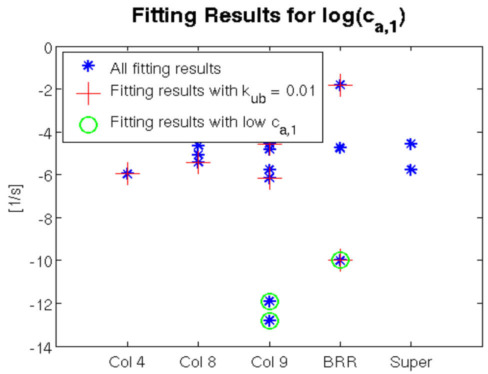
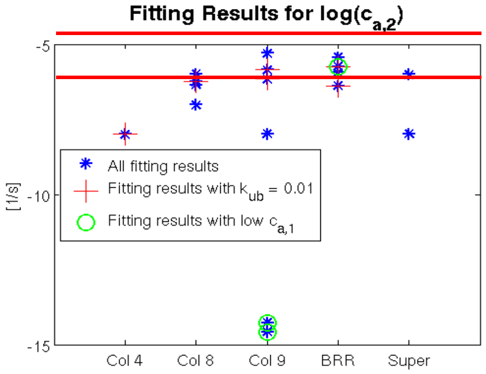
Summary

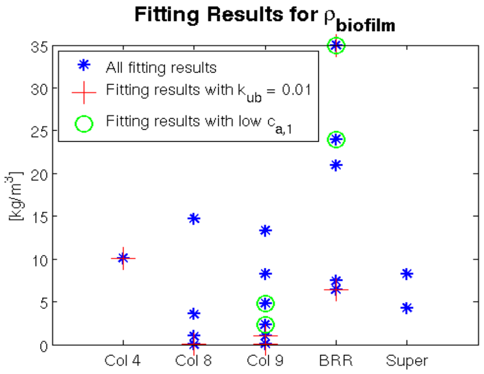
- Updated the ureolysis kinetics according to the experimentally observed, Lauchnor et al. at MSU.

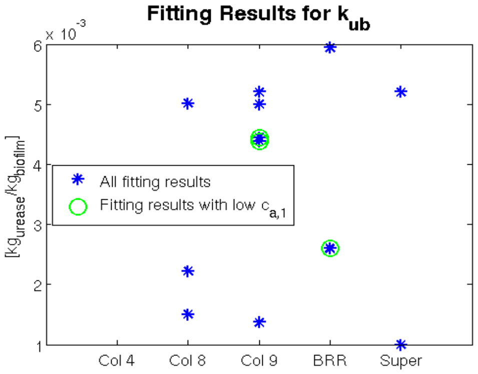
$$r_{\mathrm{urea}} = k_{\mathrm{urease}}\, k_{\mathrm{ub}} (\rho_{\mathrm{biofilm}} \phi_{\mathrm{biofilm}})^{n_{\mathrm{ub}}} \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}} + m_{\mathrm{urea}}}$$

- Recalibrated the numerical model against different experiments.







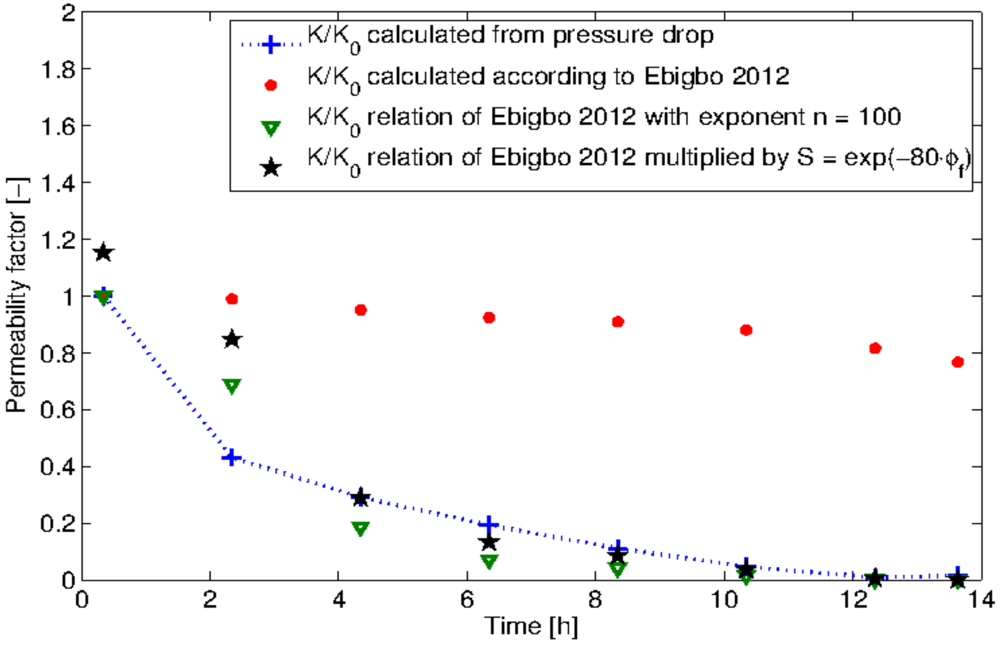


- Experimentally investigated the attachment.

Summary

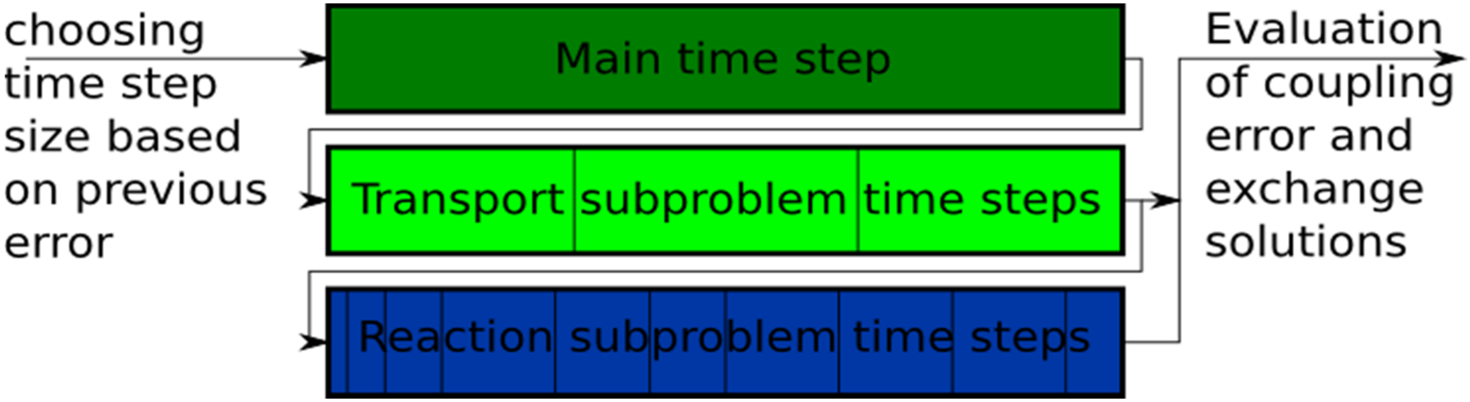
- Derived and implemented an improved porosity-permeability relation (done based on first experiment, waiting for more experimental data).

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



Summary

- Implemented a sequential method to reduce the CPU time.



- Neglecting the unnecessary solid phases in the transport subproblem results in an additional speedup.

Outlook

- Not shown: model applied on field-scale.

→ very time consuming, run times of up to 1.5 months for a 22,5° x 10m x 10m domain with some 1000 nodes.

This motivates the two points of focus for further research:

- Further investigation of the possible increases in efficiency using the implemented sequential calculation of transport and chemical reactions to increase the feasibility of field-scale simulations.
- Investigation of possible model simplifications to develop an “engineering” model with sufficient accuracy.

Thank you for your attention!

All simulations were
done using DuMu^x

Key papers / further information

A. Ebigbo, A.J. Philipps, R. Gerlach, R. Helmig, A.B. Cunningham, H. Class, L.H. Spangler: **Darcy-scale modeling of microbially induced carbonate mineral precipitation in sand columns**. Water Resources Research, 2012 (48)WO7519.

A.J. Philipps, R. Gerlach, E. Lauchnor, A.C. Mitchell, A.B. Cunningham, L.H. Spangler: **Engineered applications of ureolytic biomineralization: a review**. Biofouling, 2013 (29)715-733

J. Hommel, E. Lauchnor, A.J. Philipps, R. Gerlach, A.B. Cunningham, R. Helmig, A. Ebigbo, H. Class: **A revised model for microbially induced calcite precipitation – improvements and new insights based on recent experiments**. Submitted to Water Resources Research, October 2014