Universität Stuttgart

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CENTER FOR BIOFILM ENGINEERING

Enzymatically induced calcite precipitation: model development and experiments

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Interpore German Chapter 2021

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What is Induced Calcium Carbonate Precipitation (ICP)?

- Microbially (MICP) → Established models (Uni Stuttgart and others)
- **Enzymatically (EICP) → New model**
- Thermally (TICP) → New model

$$CO(NH_2)_2 + 2H_2O \xrightarrow{ureolysi} 2NH_4^+ + CO_3^{2-}$$

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

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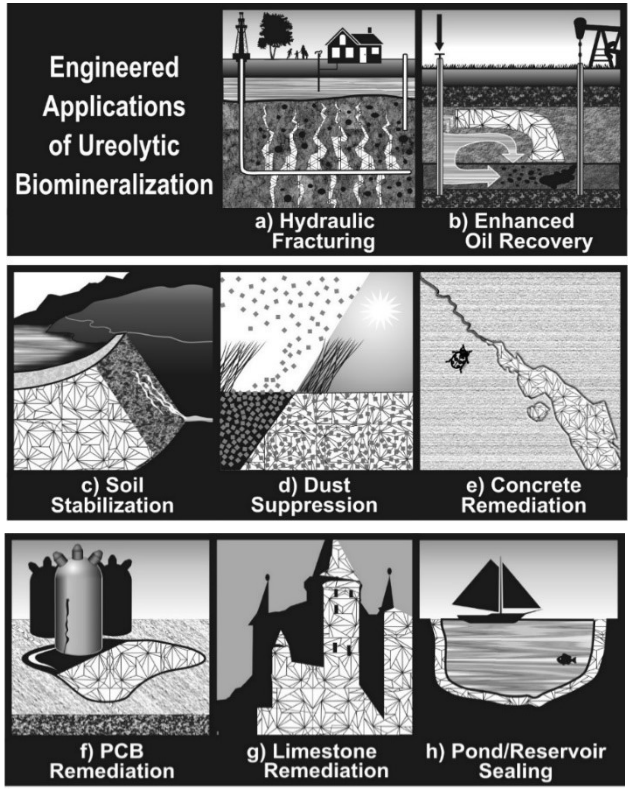
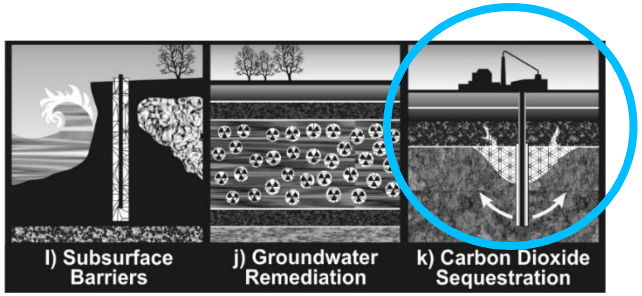
Why investigate ICP?





→ reduce flow → **leakage mitigation**

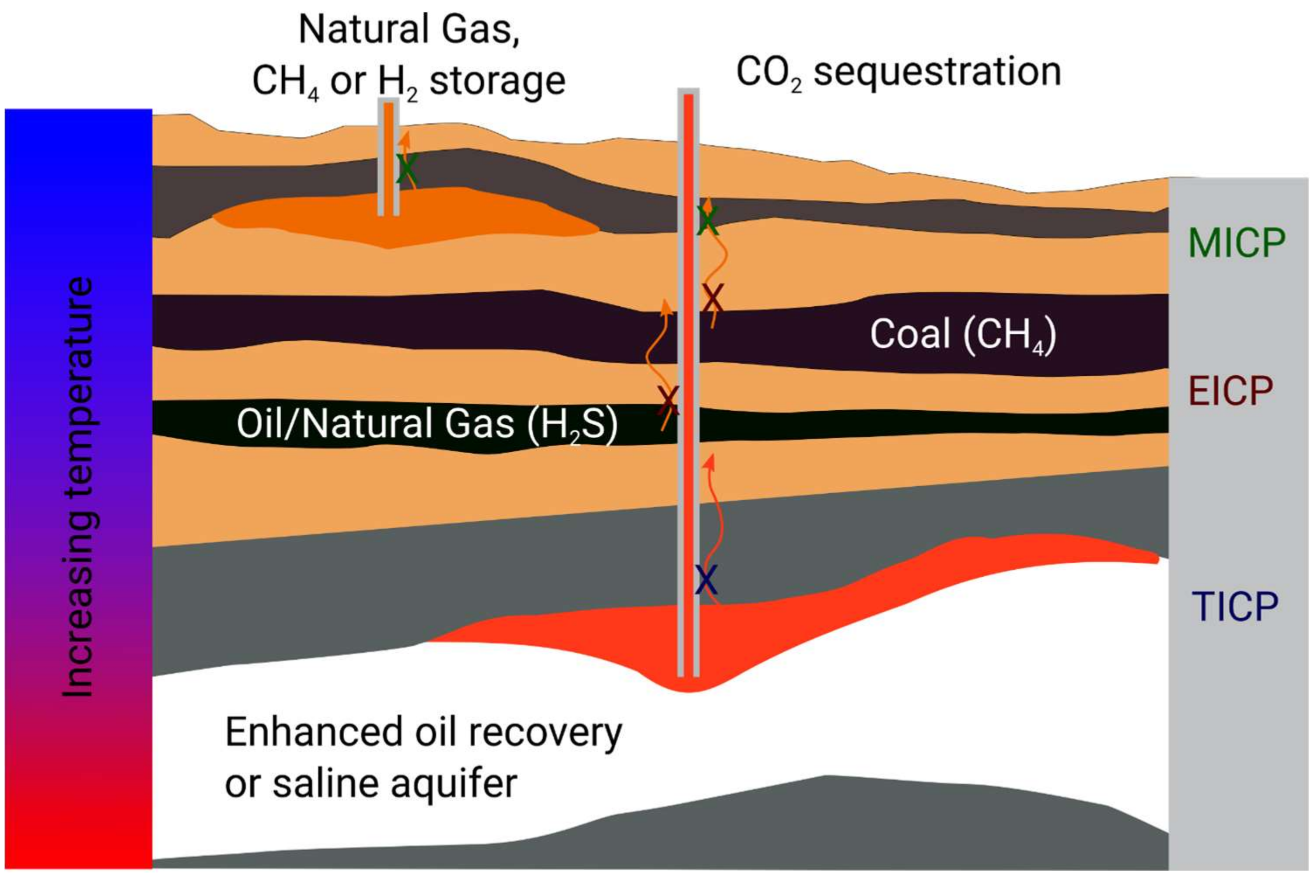
→ (increase mechanical strength)

Figures from:
Phillips et al. 2013
Engineered applications of ureolytic biomineralization: A review.

Why not use only MICP?

40 - 50°C

80 - 100°C



Summarized History of (M)ICP Model Development

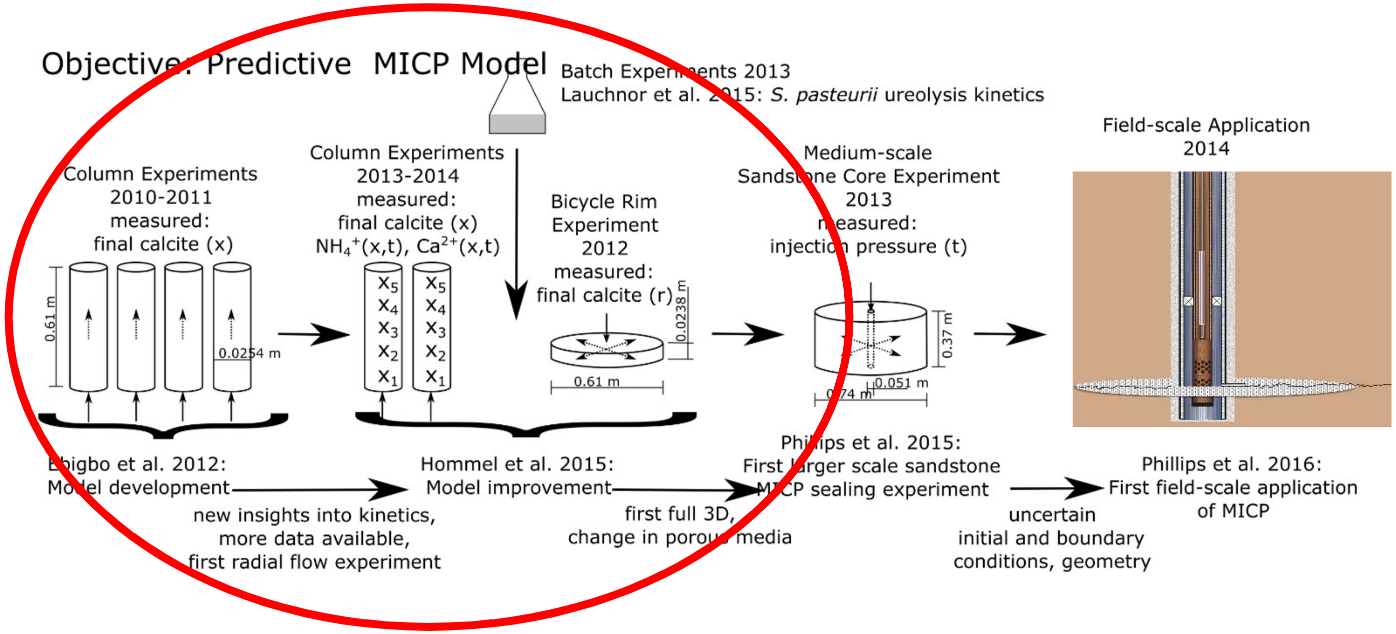


Figure from:
Cunningham et al. 2019. Field-scale modeling of microbially induced calcite precipitation. *Computational Geosciences*, doi: 10.1007/s10596-018-9797-6

Similar development of the current EICP (and TICP) model, starting at lab-scale with column and batch kinetics experiments

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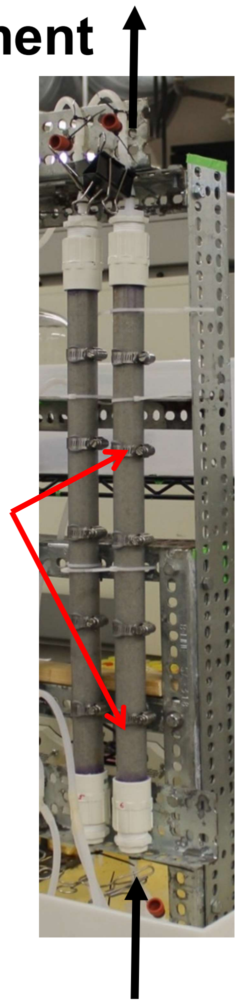
EICP experiments used for model development

- Kinetics batch experiments at 20-80°C at various concentrations

- Calibration and validation to EICP column experiments at 60°C:
  - 3 days, pulsed injection of 5 g/l crude enzyme, followed by 20g/l urea and 13.3 g/l calcium every 2h
  - Concentrations measured at 10.16 and 40.64 cm over time after each injection
  - Final calcite measured over length

Samp-ling ports

Urea Ca^{2+}



61 cm,
2,4 cm diam.
sand filled

40.64 cm

10.16 cm

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Balance Equations

- Mass balance equation of components

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

- Mass balance for the immobile components / solid phases:

$$\frac{\partial}{\partial t} \left(\rho_\varphi \phi_\varphi \right) = q^\varphi$$

- Energy balance:

$$\frac{\partial}{\partial t} \left(\left(1 - \phi_0 \right) \rho_\mathrm{s} c_\mathrm{s} T \right) + \sum_{\varphi} \left[\frac{\partial}{\partial t} \left(\phi_\varphi \rho_\varphi c_\varphi T \right) \right] + \sum_{\alpha} \left[\frac{\partial}{\partial t} \left(\phi \rho_\alpha u_\alpha S_\alpha \right) - \nabla \cdot \left(\rho_\alpha h_\alpha \mathbf{v}_\alpha \right) \right] - \nabla \cdot \left(\lambda_\mathrm{pm} \nabla T \right) = q^\mathrm{h}$$

Sources & Sinks: Ureolysis and Precipitation

$$
\begin{aligned}
&\text{Urea:} && q^{\mathrm{urea}} &&= -r_{\mathrm{urea}} \\
&\text{Total nitrogen:} && q^{\mathrm{NH_{tot}}} &&= 2r_{\mathrm{urea}} \\
&\text{Calcium:} && q^{\mathrm{Ca^{2+}}} &&= r_{\mathrm{diss}} - r_{\mathrm{precip}} \\
&\text{Total carbon:} && q^{\mathrm{C_{tot}}} &&= r_{\mathrm{urea}} + r_{\mathrm{diss}} - r_{\mathrm{precip}} \\
&\text{Calcite:} && q^{\mathrm{c}} &&= r_{\mathrm{precip}} - r_{\mathrm{diss}}
\end{aligned}
$$

$$
\begin{aligned}
&\text{Precipitation rate} && r_{\mathrm{precip}} &&= f\left(A_{\mathrm{interface}},\ \Omega = \frac{[\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]}{K_{\mathrm{sp}}},\ T\right) \\
&\text{Dissolution rate} && r_{\mathrm{diss}} &&= f\left(A_{\mathrm{interface}},\ \Omega = \frac{[\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]}{K_{\mathrm{sp}}},\ \mathrm{pH},\ T\right) \\
&\text{Ureolysis rate} && r_{\mathrm{urea}} &&= k_{\mathrm{u}}^{\mathrm{e}}(C_{\mathrm{w}}^{\mathrm{e}} + \phi^{\mathrm{e}}\rho^{\mathrm{e}})C_{\mathrm{w}}^{\mathrm{urea}} S_{\mathrm{w}}\phi
\end{aligned}
$$

$$
k_{\mathrm{u}}^{\mathrm{e}} = c_{\mathrm{u}}^{\mathrm{e}} \cdot e^{\left(\frac{c_{\mathrm{u,T}}^{\mathrm{e}}}{T}\right)}
$$

Sources & Sinks: EICP, enzyme

$$
\begin{aligned}
\text{Enzyme, mobile:} \quad q^{\mathrm{e,mob}} &= -r^{\mathrm{e,mob}}_{\mathrm{inactiv}} - r^{\mathrm{e}}_{\mathrm{attach}} + r^{\mathrm{e}}_{\mathrm{detach}} \\
\text{Enzyme, imm.:} \quad q^{\mathrm{e,imm.}} &= -r^{\mathrm{e,imm.}}_{\mathrm{inactiv}} + r^{\mathrm{e}}_{\mathrm{attach}} - r^{\mathrm{e}}_{\mathrm{detach}}
\end{aligned}
$$

$$
\begin{aligned}
\text{Inactivation:} \quad r^{\mathrm{e,mob}}_{\mathrm{inactiv}} &= k_{\mathrm{ia}} \cdot \phi S_{\mathrm{w}} C^{\mathrm{e}}_{\mathrm{w}}; \\
\text{Inactivation:} \quad r^{\mathrm{e,imm}}_{\mathrm{inactiv}} &= k_{\mathrm{ia}} \cdot \rho_{\mathrm{e}} \phi_{\mathrm{e,imm}};
\end{aligned}
$$

$$k_{\mathrm{ia}} = c_{\mathrm{ia}} \cdot e^{\left(\frac{c_{\mathrm{ia,T}}}{T}\right)}$$

$$
\begin{aligned}
\text{Attachment:} \quad r^{\mathrm{e}}_{\mathrm{attach}} &= c_{\mathrm{a}} \cdot \phi S_{\mathrm{w}} C^{\mathrm{e}}_{\mathrm{w}} \\
\text{Detachment:} \quad r^{\mathrm{e}}_{\mathrm{detach}} &= c_{\mathrm{d}} \cdot \rho_{\mathrm{e}} \phi_{\mathrm{e,imm}}
\end{aligned}
$$

Supplementary Equations

- Updating permeability and porosity

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

- Capillary pressure and relative permeability according to Brooks & Corey

$$p_{\mathrm{c}} = p_{\mathrm{d}} S_{\mathrm{e}}^{-\frac{1}{\lambda}}, \; S_{\mathrm{e}} = \frac{S_{\mathrm{w}} - S_{\mathrm{w,r}}}{1 - S_{\mathrm{w,r}}}$$

$$k_{\mathrm{r,w}} = S_{\mathrm{e}}^{\frac{2+3\lambda}{\lambda}}, \; k_{\mathrm{r,n}} = (1 - S_{\mathrm{e}})^2 \left(1 - S_{\mathrm{e}}^{\frac{2+\lambda}{\lambda}}\right)$$

- Elektroneutrality condition for the chemical system:

$0 = \sum_{\kappa} m_{\mathrm{w}}^{\kappa} z^{\kappa}$ and H^+-dependent dissociation reactions

EICP experiments used for model development

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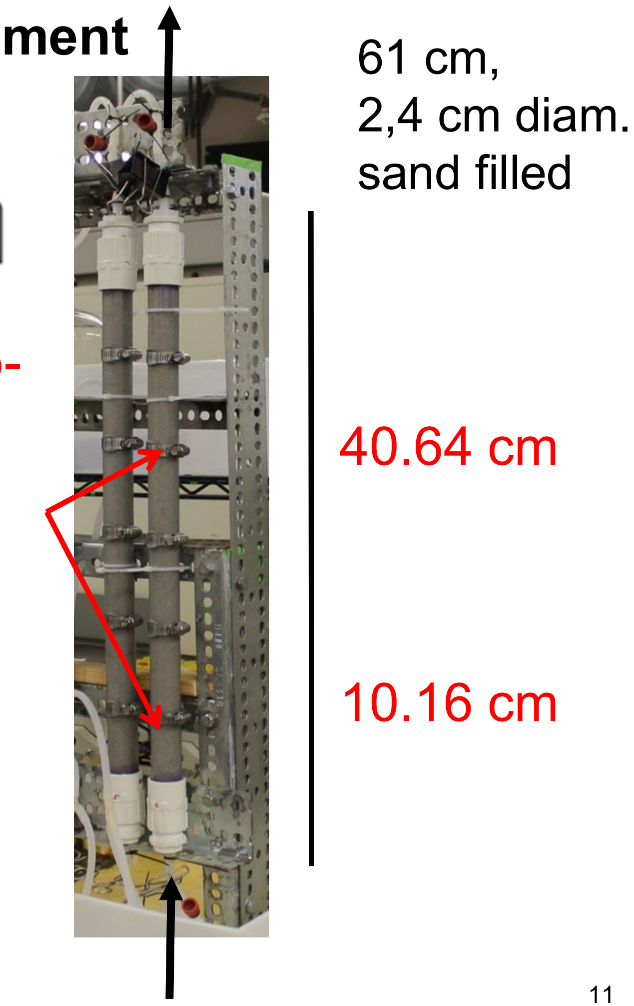

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Results: EICP model calibratio

- Calibration to experiment:
- First port (10.16 cm)

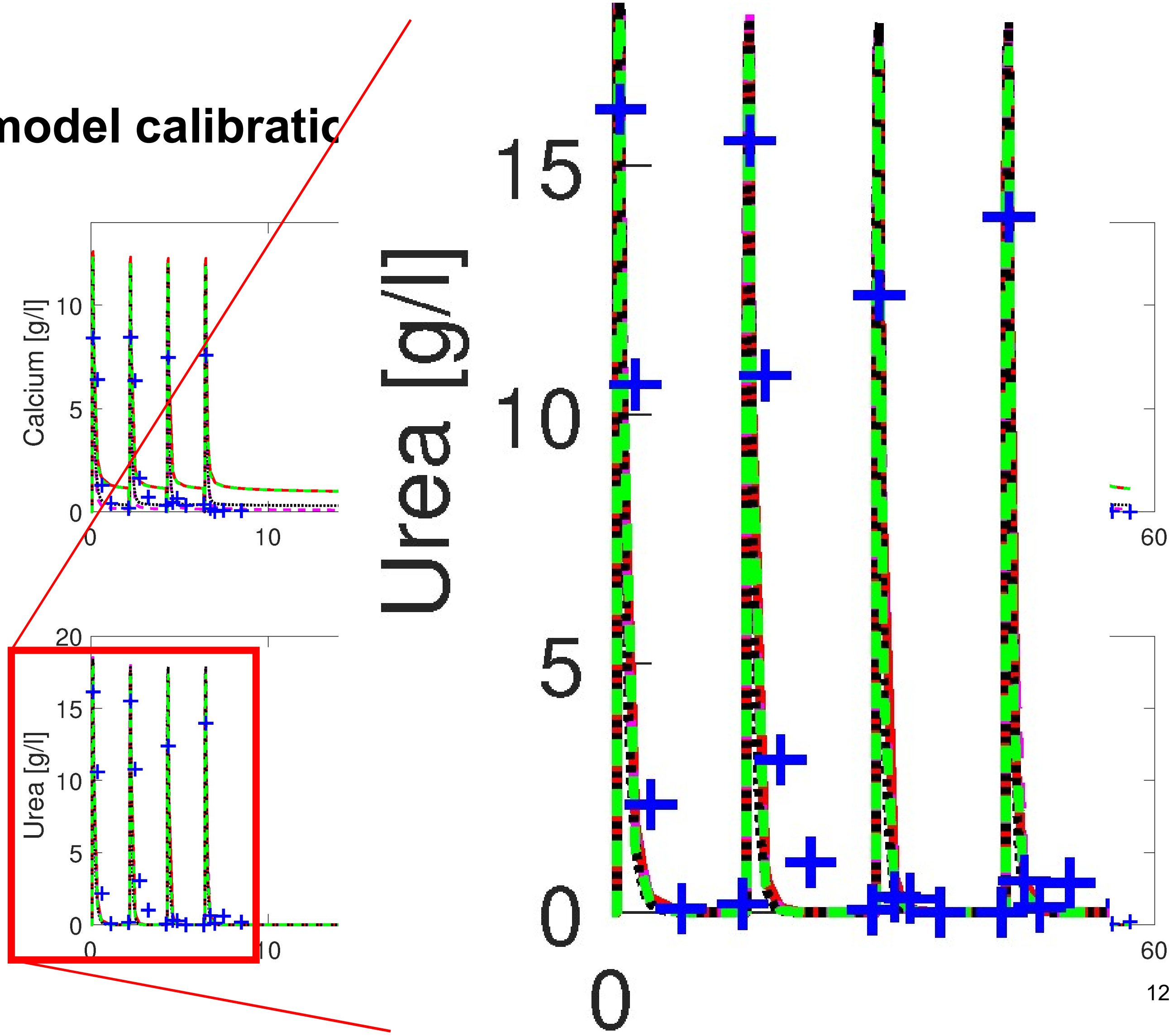

Figure from:
Hommel et al. 2020. A Numerical Model for Enzymatically Induced Calcium Carbonate Precipitation. *Applied Sciences*, https://doi.org/10.3390/app10134538

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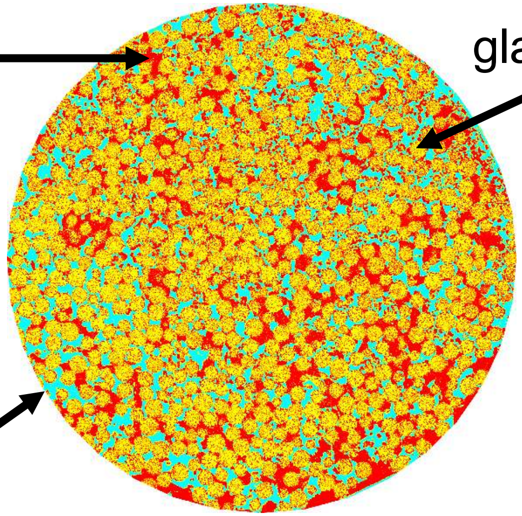
Summary and Outlook

- Developed a numerical model for EICP

- Next steps:
  - Closer investigation of effect of EICP on hydraulic properties (permeability, p_c-S_w, …)
  - Experiments in the Porous Media Lab at Stuttgart (collab. with SFB1313)

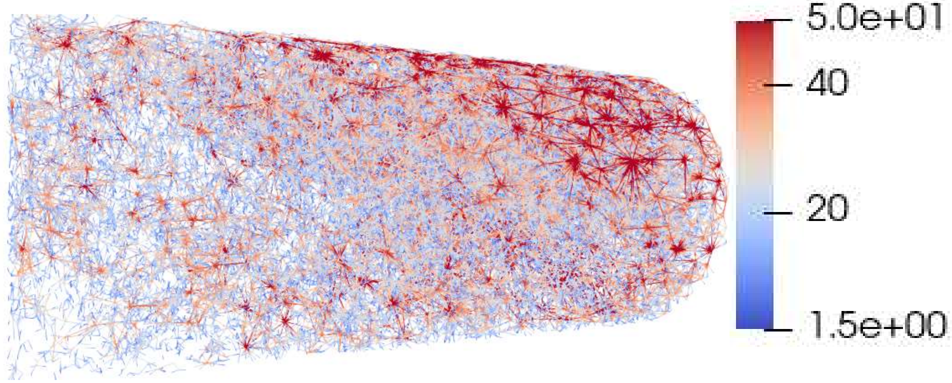
calcite

glass beads



pores

Generated PN: pore diameter [µm]



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Thank you!

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DuMu^X All simulations conducted with DuMu^X www.dumux.org

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DFG

Sources & Sinks: Ureolysis, for EICP

- MICP

$$r_{\mathrm{urea}}^{\mathrm{MICP}} = k_{\mathrm{u}}^{\mathrm{m}}\, k_{\mathrm{u,biofilm}} \left(\rho_{\mathrm{biofilm}} \phi_{\mathrm{biofilm}}\right) \frac{m_{\mathrm{urea}}}{K_{\mathrm{u}} + m_{\mathrm{urea}}}$$

- EICP

$$r_{\mathrm{urea}}^{\mathrm{EICP}} = k_{\mathrm{u}}^{\mathrm{e}} (C_{\mathrm{w}}^{\mathrm{e}} + \phi^{\mathrm{e}} \rho^{\mathrm{e}}) C_{\mathrm{w}}^{\mathrm{urea}} S_{\mathrm{w}} \phi$$

$$k_{\mathrm{u}}^{\mathrm{e}} = c_{\mathrm{u}}^{\mathrm{e}} \cdot e^{\left(\frac{c_{\mathrm{u,T}}^{\mathrm{e}}}{T}\right)}$$

- TICP

$$r_{\mathrm{urea}}^{\mathrm{TICP}} = k_{\mathrm{u}}^{\mathrm{t}} C_{\mathrm{w}}^{\mathrm{urea}} S_{\mathrm{w}} \phi$$

$$k_{\mathrm{u}}^{\mathrm{t}} = c_{\mathrm{u}}^{\mathrm{t}} \cdot e^{\left(\frac{c_{\mathrm{u,T}}^{\mathrm{t}}}{T}\right)}$$

Results: EICP model calibration

- Calibration to experiment:

- Second port (40.64 cm)

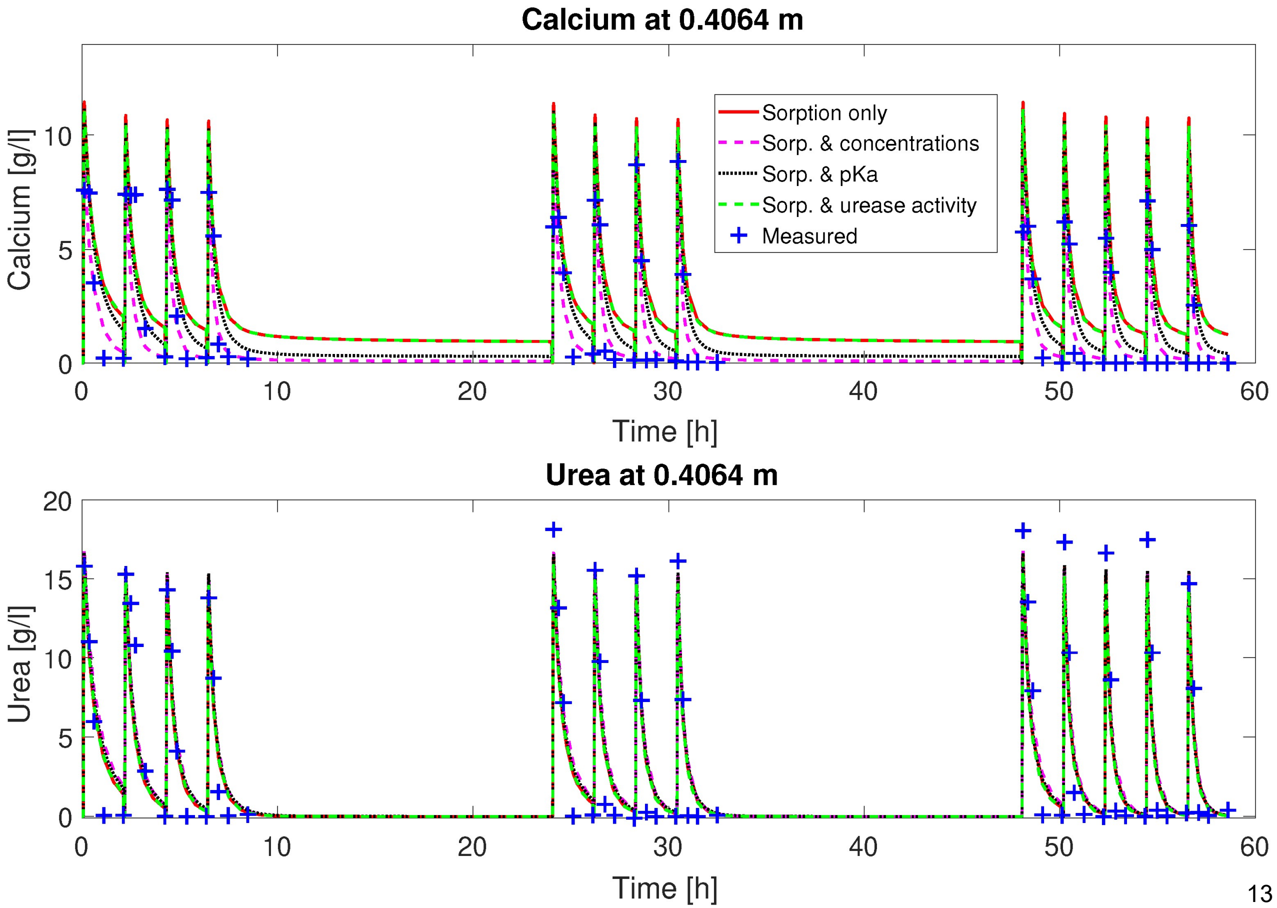

Figure from:
Hommel et al. 2020. A Numerical Model for Enzymatically Induced Calcium Carbonate Precipitation. *Applied Sciences*, https://doi.org/10.3390/app10134538

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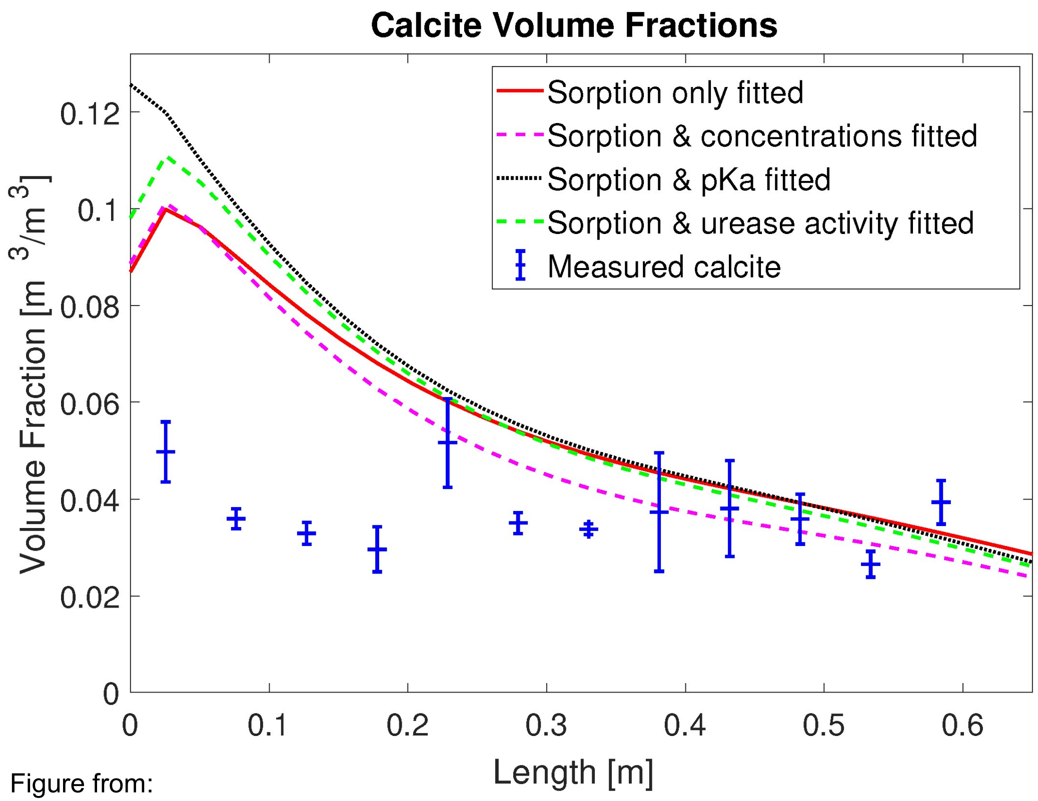
Results: EICP model validation

- Final calcite over column length
- Not used for calibration!
- Good fit for outlet half, inlet half overestimated
- → maybe some unaccounted process?



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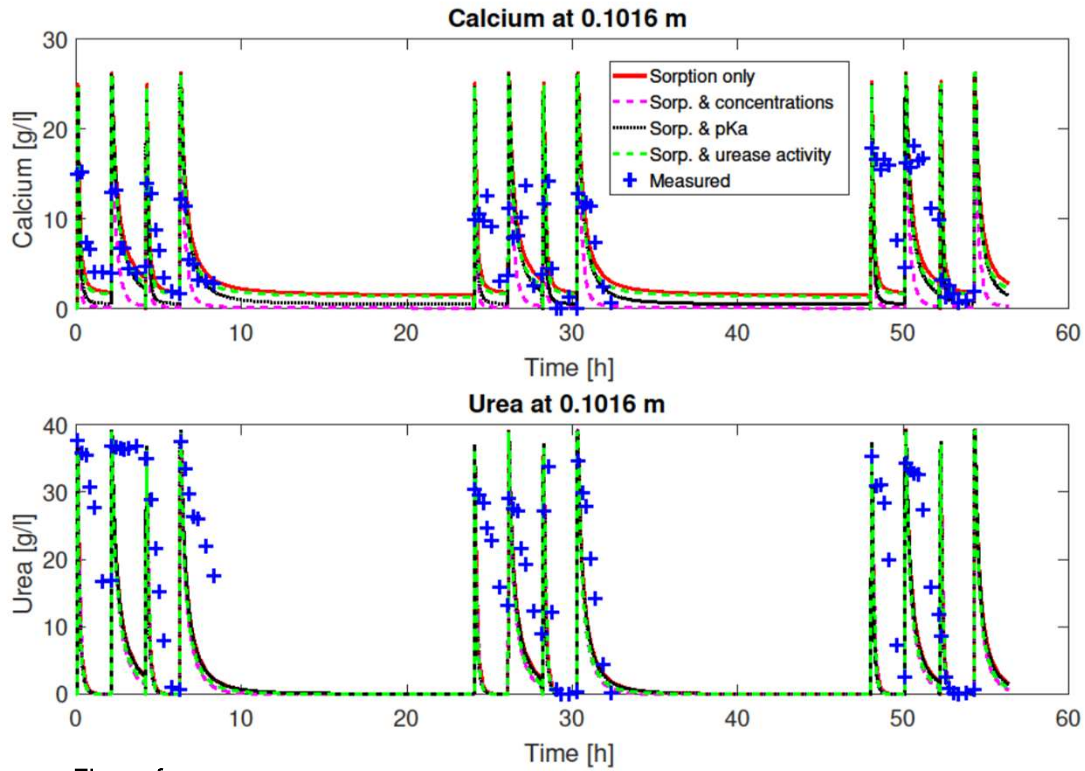
Results: EICP model validation second column

- Validation to second column experiment
- Doubled concentrations
- First port (10.16 cm)
- Not used for calibration!



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Summary

- Concentrations are matched quite well, urea and calcium are consumed very fast.
- Calcite precipitation overestimated in the inlet half. → maybe some additional process?