

Universität Stuttgart



CENTER FOI

BIOFILN

ENGINEER



Johannes Hommel

Interpore German Chapter 2021



What is Induced Calcium Carbonate Precipitation (ICP)?

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

$$CO(NH_2)_2 + 2H_2O \xrightarrow{ureolysi} 2NH_4^+ + CO_3^{2-}$$
$$CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3 \downarrow$$



Why investigate ICP?





- → reduce flow → leakage mitigation
- \rightarrow (increase mechanical strength)

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











Summarized History of (M)ICP Model Development

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



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

Sampling ports Urea Ca²⁺ 61 cm, 2,4 cm diam. sand filled

40.64 cm

10.16 cm



Balance Equations

• Mass balance equation of components

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

• Mass balance for the immobile components / solid phases:

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

• Energy balance:

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



Sources & Sinks: Ureolysis and Precipitation





Sources & Sinks: EICP, enzyme

Enzyme, mobile:
$$q^{e, \text{mob}} = -r^{e, \text{mob}}_{\text{inactiv}} - r^{e}_{\text{attach}} + r^{e}_{\text{detach}}$$

Enzyme, imm.: $q^{e, \text{imm.}} = -r^{e, \text{imm.}}_{\text{inactiv}} + r^{e}_{\text{attach}} - r^{e}_{\text{detach}}$

Inactivation:
$$r_{\text{inactiv}}^{\text{e,mob}} = k_{\text{ia}} \cdot \phi S_{\text{w}} C_{\text{w}}^{\text{e}};$$

Inactivation: $r_{\text{inactiv}}^{\text{e,imm}} = k_{\text{ia}} \cdot \rho_{\text{e}} \phi_{\text{e,imm}};$
 $k_{\text{ia}} = c_{\text{ia}} \cdot e^{\left(\frac{c_{\text{ia},\text{T}}}{T}\right)}$

Attachment:
$$r_{attach}^{e}$$
= $c_{a} \cdot \phi S_{w} C_{w}^{e}$ Detachment: r_{detach}^{e} = $c_{d} \cdot \rho_{e} \phi_{e,imm}$



Supplementary Equations

• Updating permeability and porosity

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

 Capillary pressure and relative permeability according to Brooks & Corey

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

• 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

- Kinetics batch experiments at 20-80°C
- Calibration and validation to FICP 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

Ca²⁺

61 cm, 2,4 cm diam. sand filled

40.64 cm

10.16 cm





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)





Thank you!



Johannes Hommel

e-mail <u>Johannes.hommel@iws.uni-stuttgart.de</u> phone +49 (0) 711 685-64600 fax

University of Stuttgart

Institute for Modelling Hydraulic and Environmental Systems Department of Hydromechanics and Modelling of Hydrosystems Pfaffenwaldring 61, D-70569 Stuttgart, Germany

DuMu^X All simulations conducted with DuMu^X <u>www.dumux.org</u>



Support of the German Research Foundation is gratefully acknowledged.





Sources & Sinks: Ureolysis, for EICP

• MICP $r_{\text{urea}}^{\text{MICP}} = k_{\text{u}}^{\text{m}} k_{\text{u,biofilm}} (\rho_{\text{biofilm}} \phi_{\text{biofilm}}) \frac{m_{\text{urea}}}{K_{\text{u}} + m_{\text{urea}}}$ • EICP $r_{\text{urea}}^{\text{EICP}} = k_{\text{u}}^{\text{e}} (C_{\text{w}}^{\text{e}} + \phi^{\text{e}} \rho^{\text{e}}) C_{\text{w}}^{\text{urea}} S_{\text{w}} \phi$ $k_{\text{u}}^{\text{e}} = c_{\text{u}}^{\text{e}} \cdot e^{(\frac{c_{\text{u},\text{T}}}{T})}$

TICP

$$r_{\text{urea}}^{\text{TICP}} = k_{\text{u}}^{\text{t}} C_{\text{w}}^{\text{urea}} S_{\text{w}} \phi$$
$$k_{\text{u}}^{\text{t}} = c_{\text{u}}^{\text{t}} \cdot e^{(\frac{c_{\text{u},\text{T}}^{\text{t}}}{T})}$$



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*, <u>https://doi.org/10.3390/app10134</u> 538



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?







Results: EICP model validation second column

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





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

Summary

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



