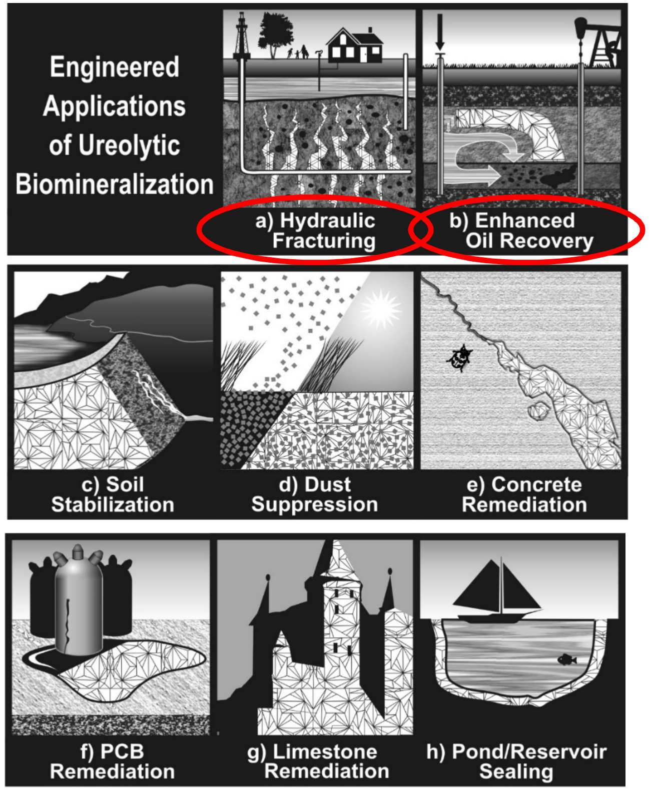
University of Stuttgart
Institute for Modelling Hydraulic and Environmental Systems
Department of Hydromechanics and Modelling of Hydrosystems

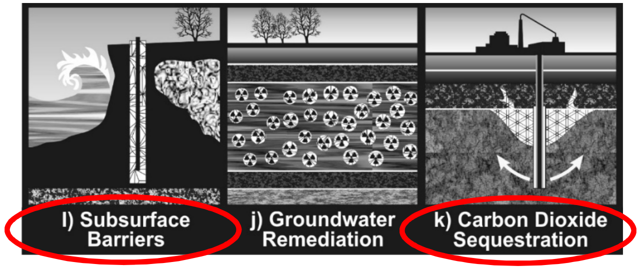
New models for biomineralization processes

NUPUS Meeting 2016

Johannes Hommel

Why investigate e.g. biomineralization?





In the context of this presentation mainly:
wellbore integrity remediation in gas storage, oil production, hydraulic fracking

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

Outline

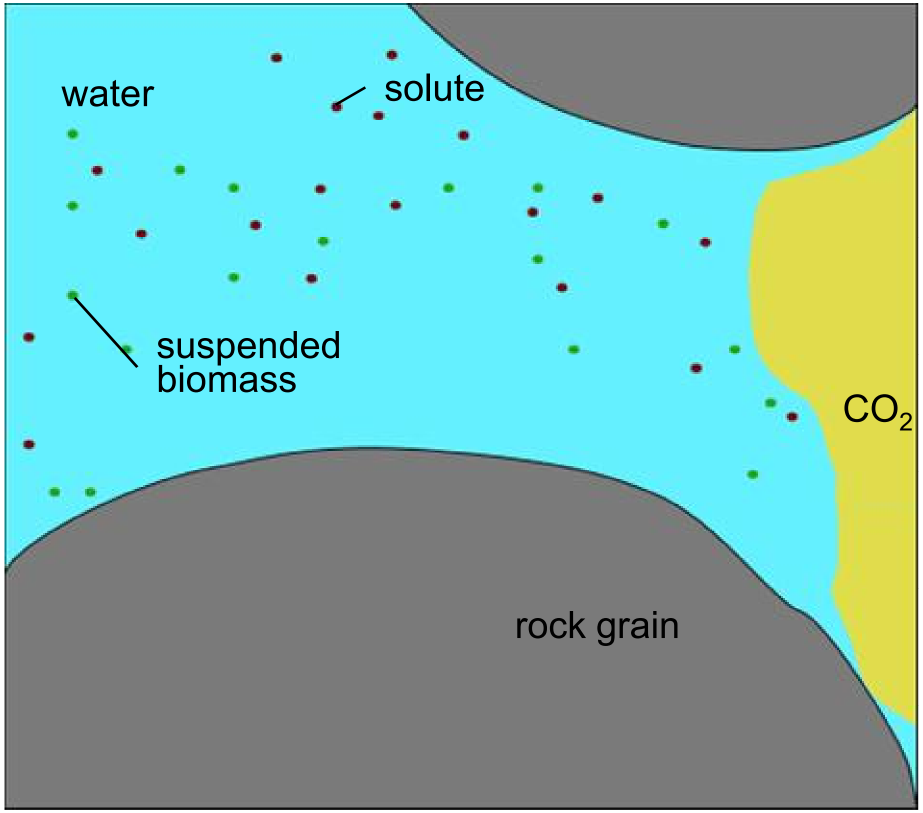
- Motivation

- **Microbially induced calcite precipitation (MICP)**
  - **MICP (model) concept**
  - Successful field-scale application and limitations

- New biomineralization processes:
  - Enzymatically induced calcite precipitation (EICP)
  - Thermally induced calcite precipitation (TICP)

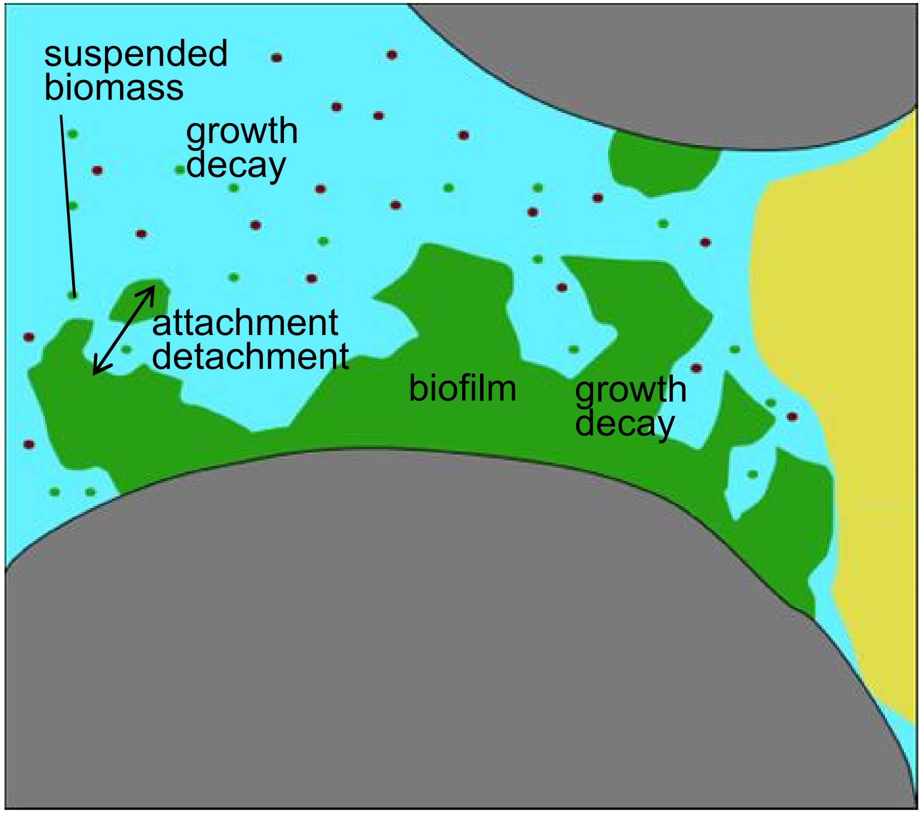
- Summary

MICP model concept: Relevant processes



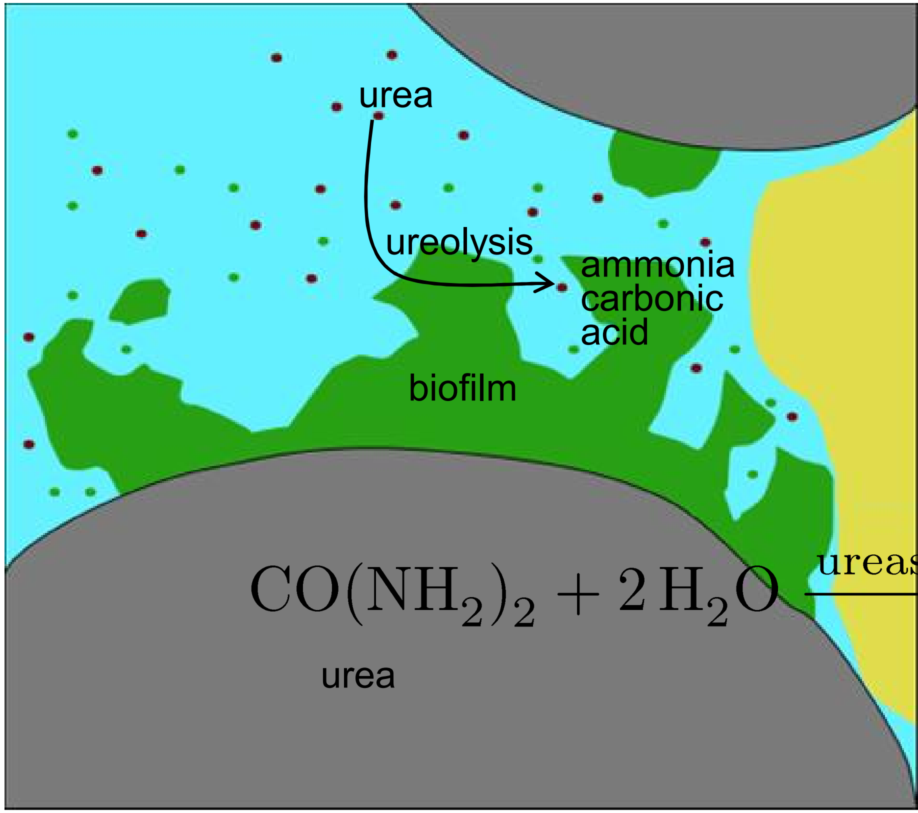
- Two-phase, multi-component transport

MICP model concept: Relevant processes



- Biomass (*S. pasteurii*)
  - growth / decay
  - attachment / detachment

MICP model concept: Relevant processes

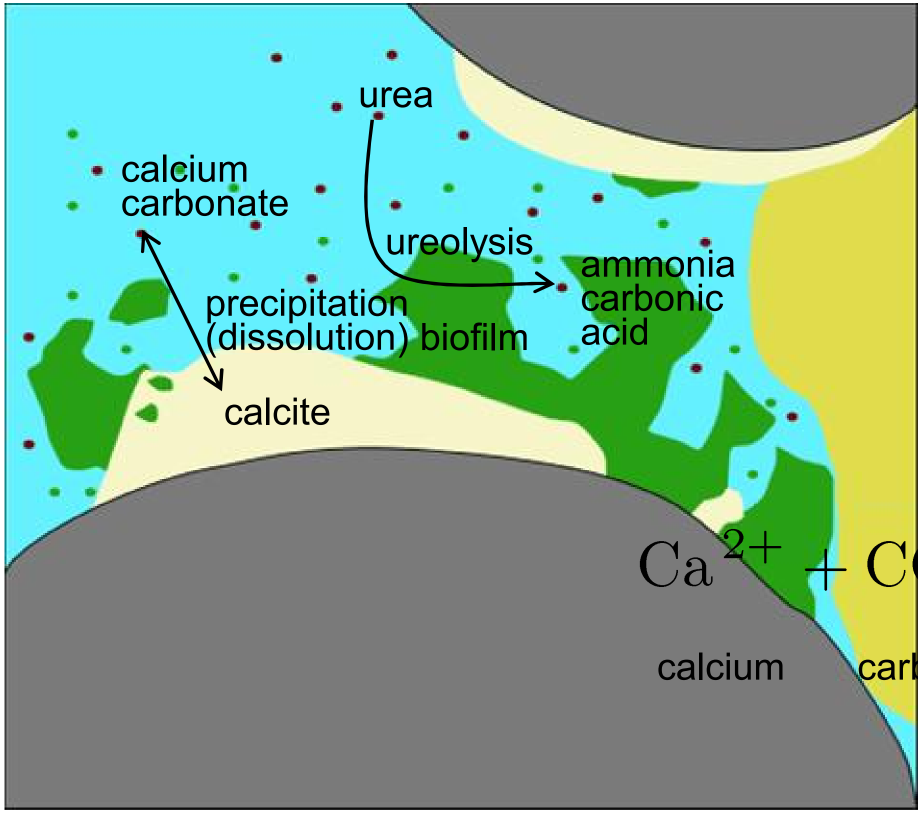


- Urea hydrolysis *(Lauchnor et al. 2015 batch experiment kinetics)*

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

urea — ammonia — carbonic acid

MICP model concept: Relevant processes

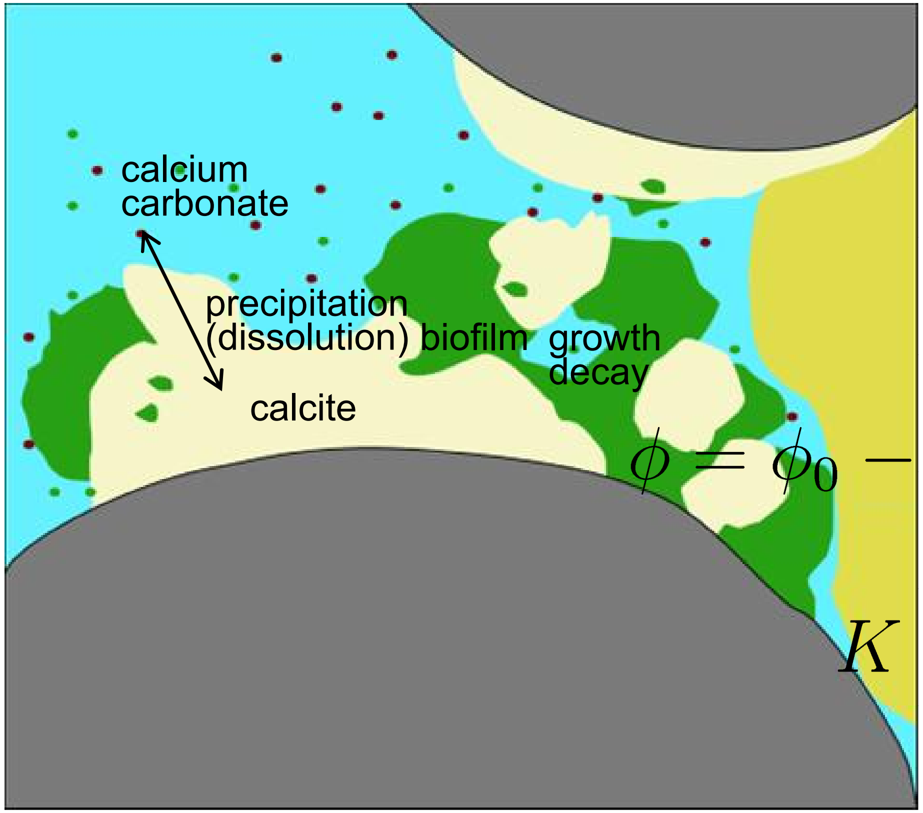


- Precipitation and dissolution of calcite

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

calcium carbonate calcite

MICP model concept: Relevant processes

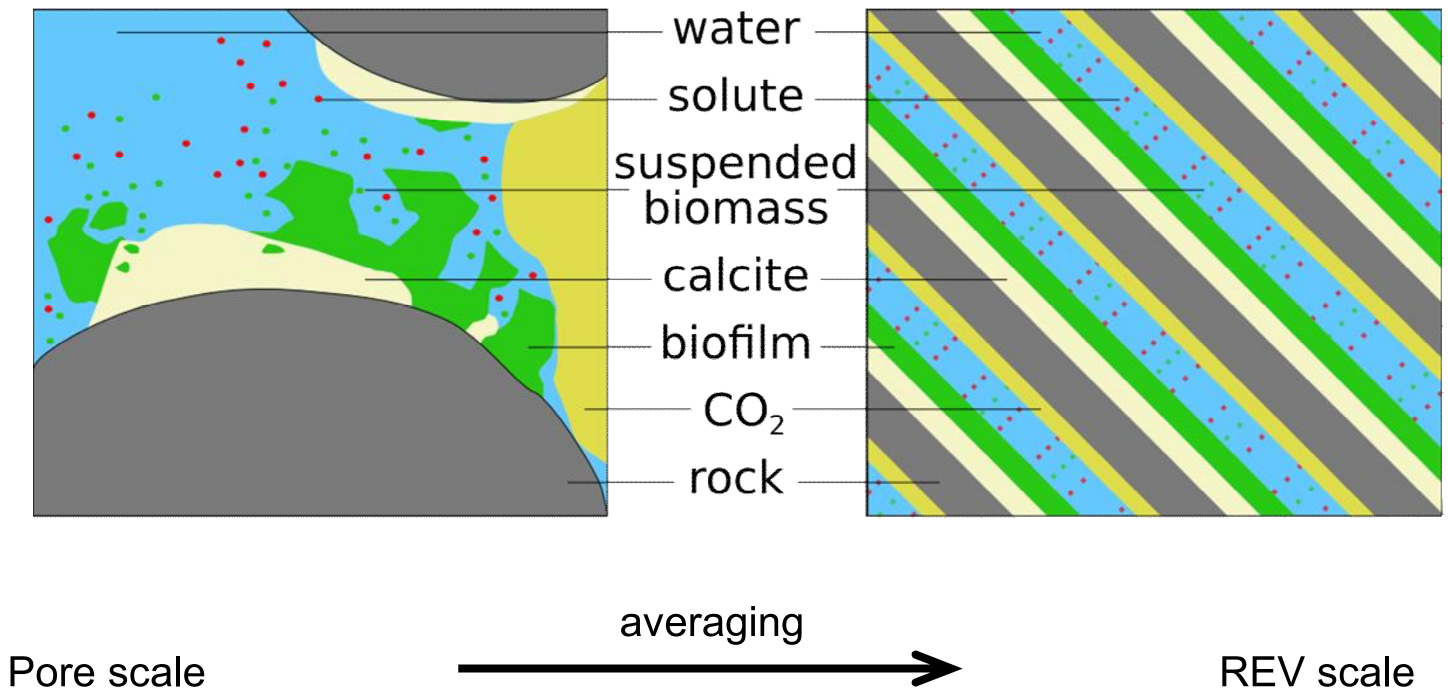


- Clogging: Reduction of porosity and permeability

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

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

Model concept: Scale



Mass balance equations

- Mass balance equation for components in both phases:

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

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

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

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

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

$$\kappa \in \{\mathrm{Na},\ \mathrm{Cl},\ \mathrm{Ca},\ \mathrm{susp.\ biomass},\ \mathrm{substrate},\ \mathrm{urea},\ \mathrm{NH_{tot}}\}$$

Mass balance equations

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$$\kappa \in \{\mathrm{Na},\ \mathrm{Cl},\ \mathrm{Ca},\ \mathrm{susp.\ biomass},\ \mathrm{substrate},\ \mathrm{urea},\ \mathrm{NH_{tot}}\}$$

- Mass balance for the immobile components / solid phases:

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

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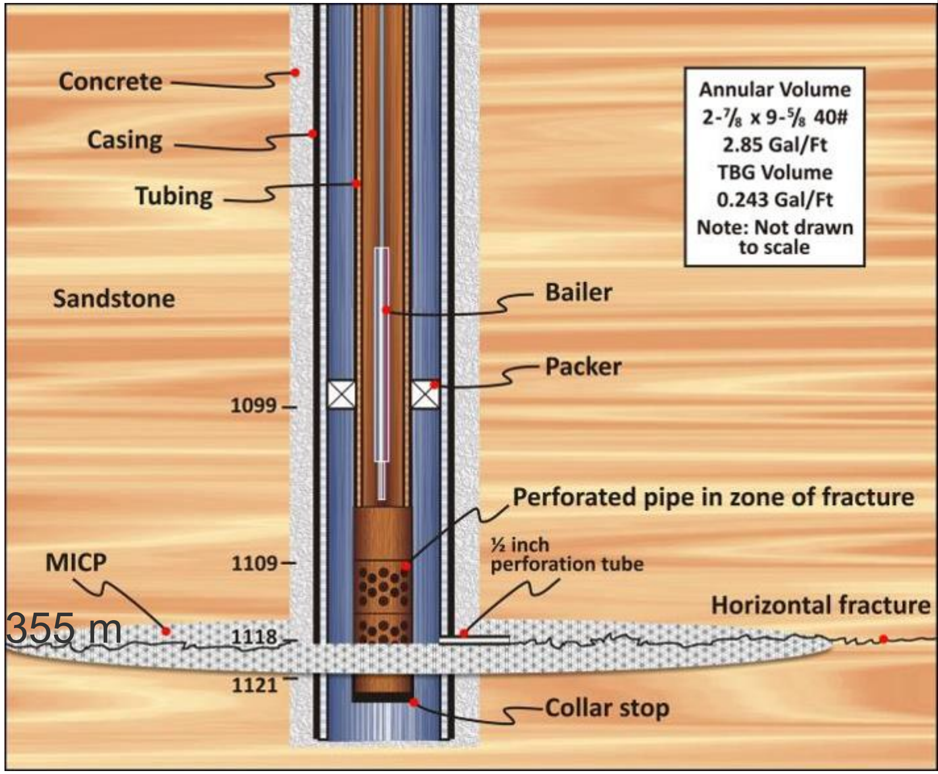
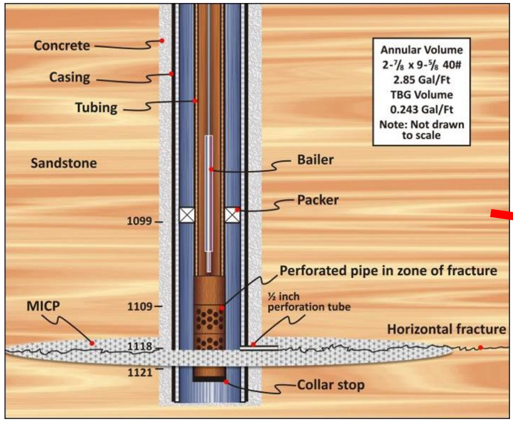
Field-scale applications of MICP



Peggy Dirckx, MSU

Adrienne Phillips, Al Cunningham, MSU

Field-scale modeling



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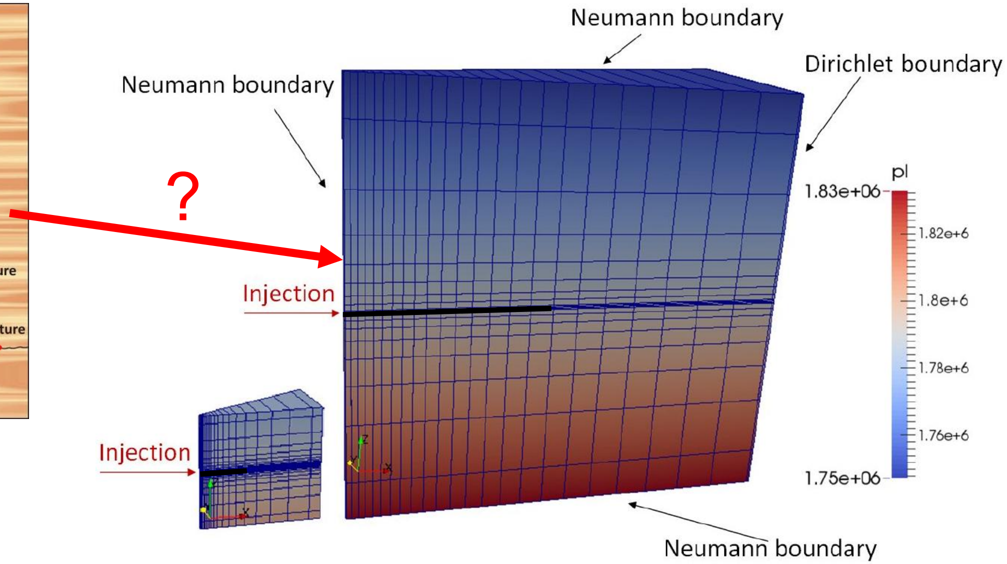
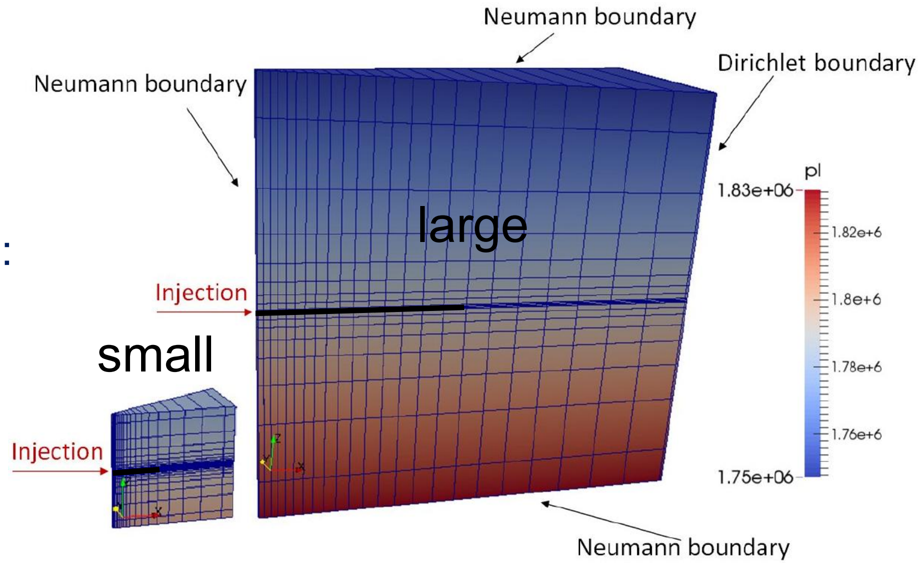


- First challenge:
- Use the limited information to set up a simplified but still realistic simulation domain.

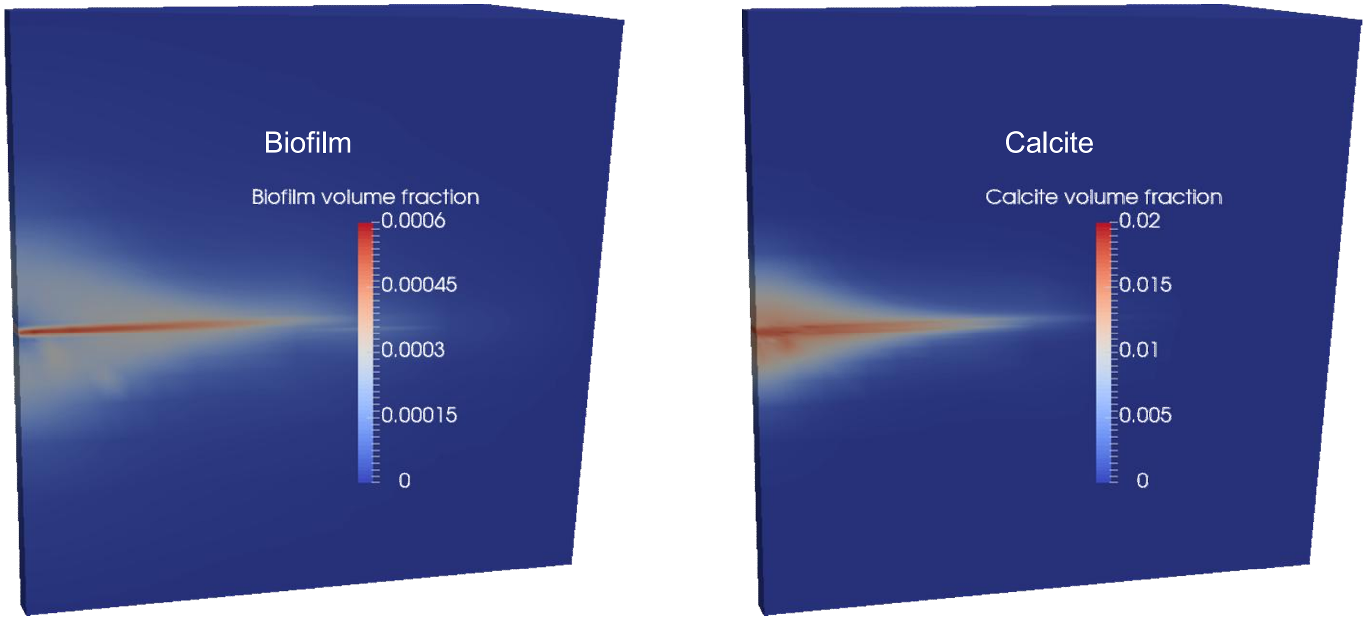
Field-scale modeling

- 2 simulation domains:
  - small
  - large

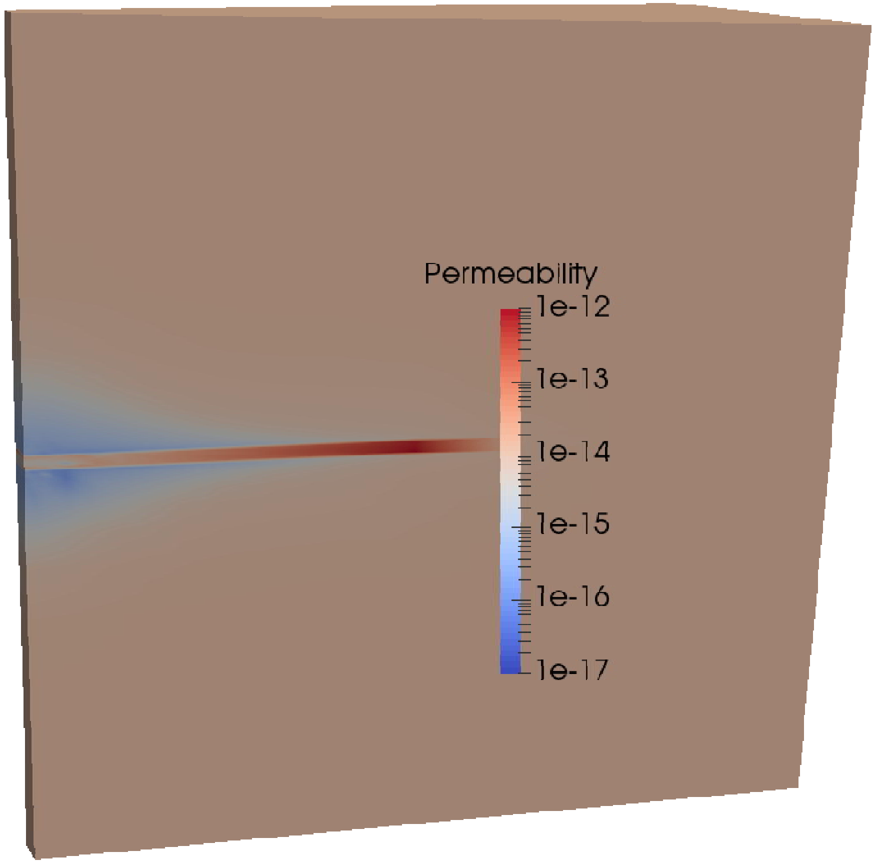


- 3 different injection strategies:
  - simple: few but long injections
  - ideal: many short injections, proved to be the „best“ injection strategy
  - real: the actual injection strategy from the field test

Field-scale modeling: Results



Field-scale modeling: Results



The ideal injection strategy predicted plugging after 24 Calcium rich injections,

25 were done in the field.

The real injection strategy was slightly less efficient.

MICP: Challenges and limitations

- Large amounts of the bacterium *Sporosarcina pasteurii* have to be grown before the application and might be difficult to store.

- The bacterium *Sporosarcina pasteurii* producing the enzyme urease survives up to temperatures of 40-50°C.

- At greater depths, which are relevant for e.g. CO_2 storage, the temperature is usually higher than 50°C.

- → Need for more temperature stable technologies

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EICP and TICP model concept: Ureolysis and reactions

The bacterium *Sporosarcina pasteurii* produces the enzyme urease.

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

EICP and TICP model concept: Ureolysis and reactions

Urease is injected or thermal ureolysis occurs

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

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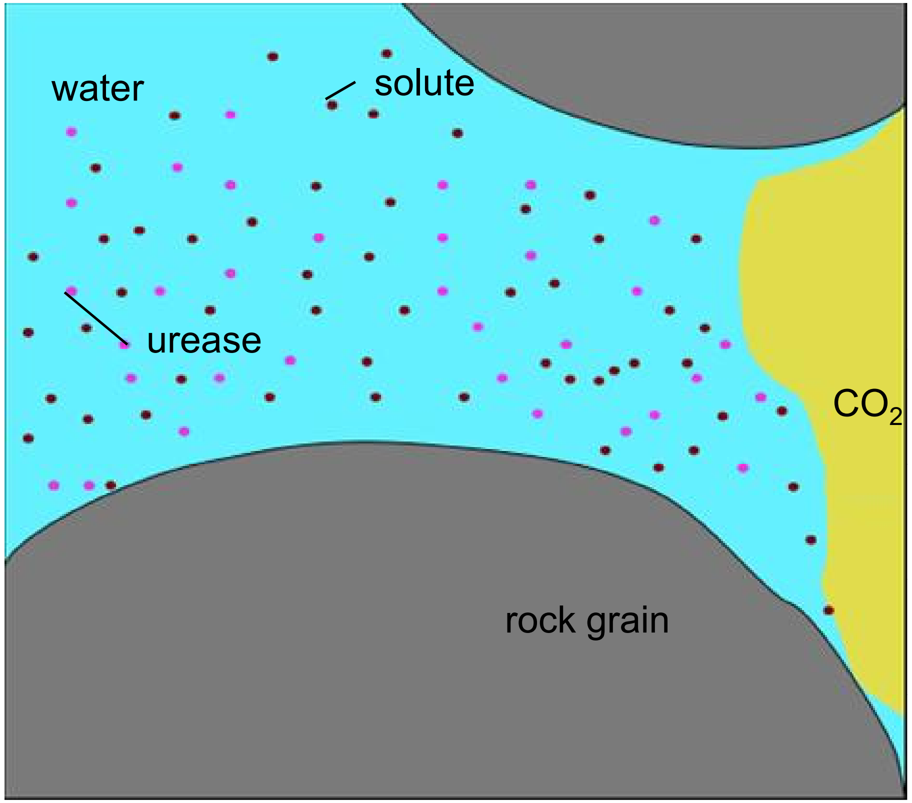
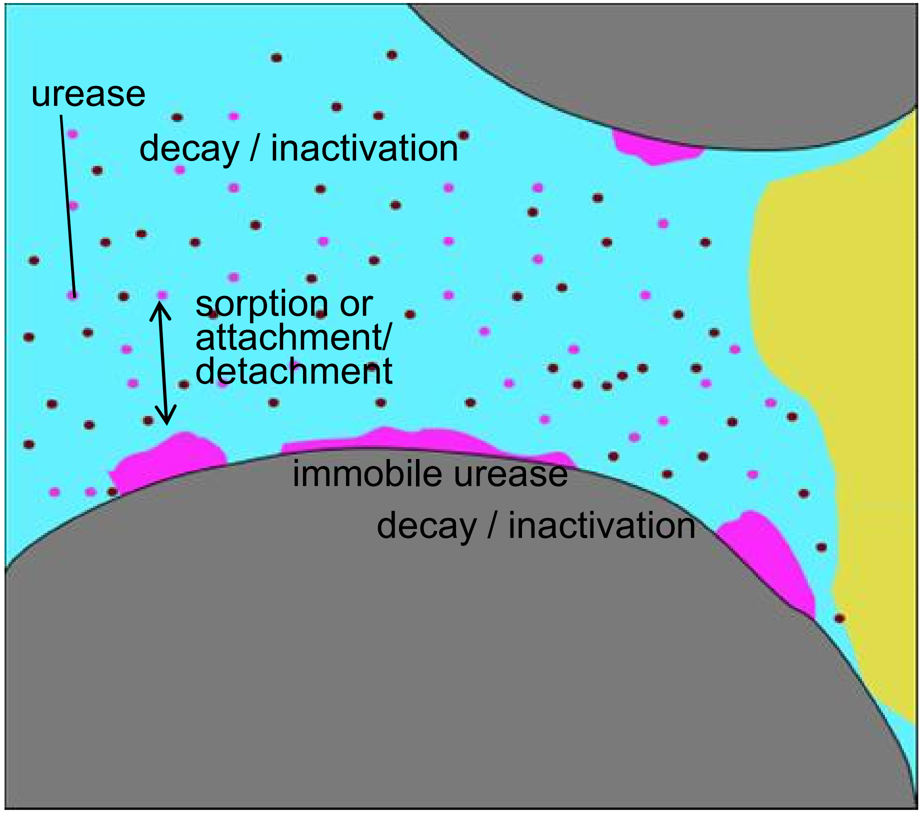
EICP model concept: Relevant processes



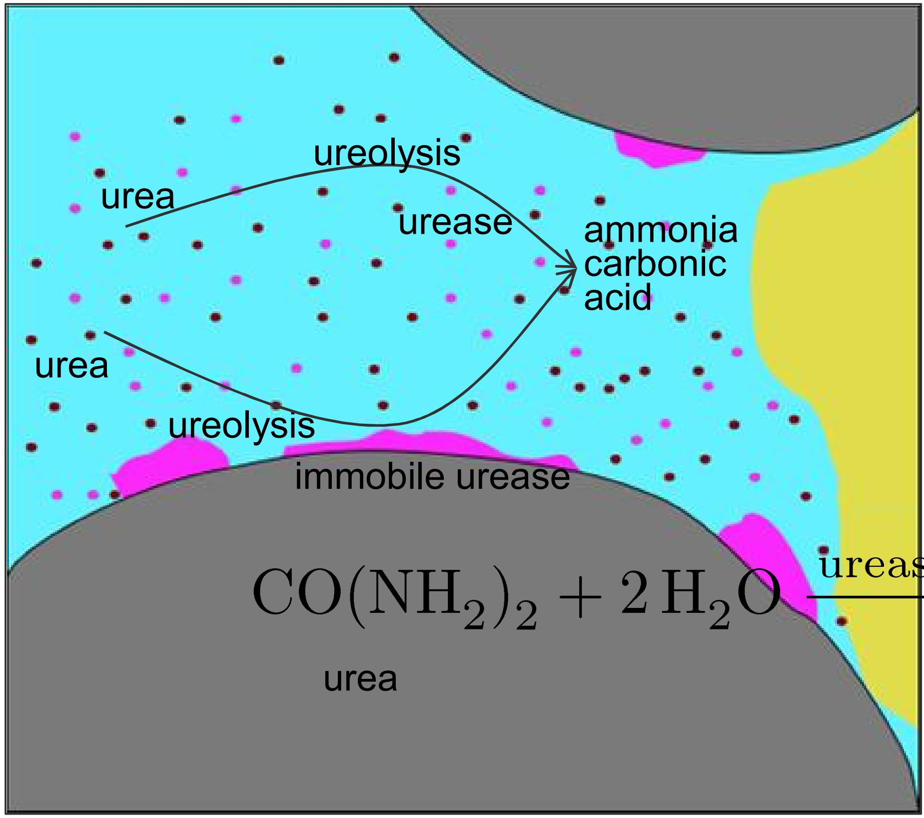
- Two-phase, multi-component transport

EICP model concept: Relevant processes



- Urease transport and immobilization:
  - *Attachment-detachment*
  - *Inactivation of suspended and immobile urease: temperature and precipitation*

EICP model concept: Relevant processes

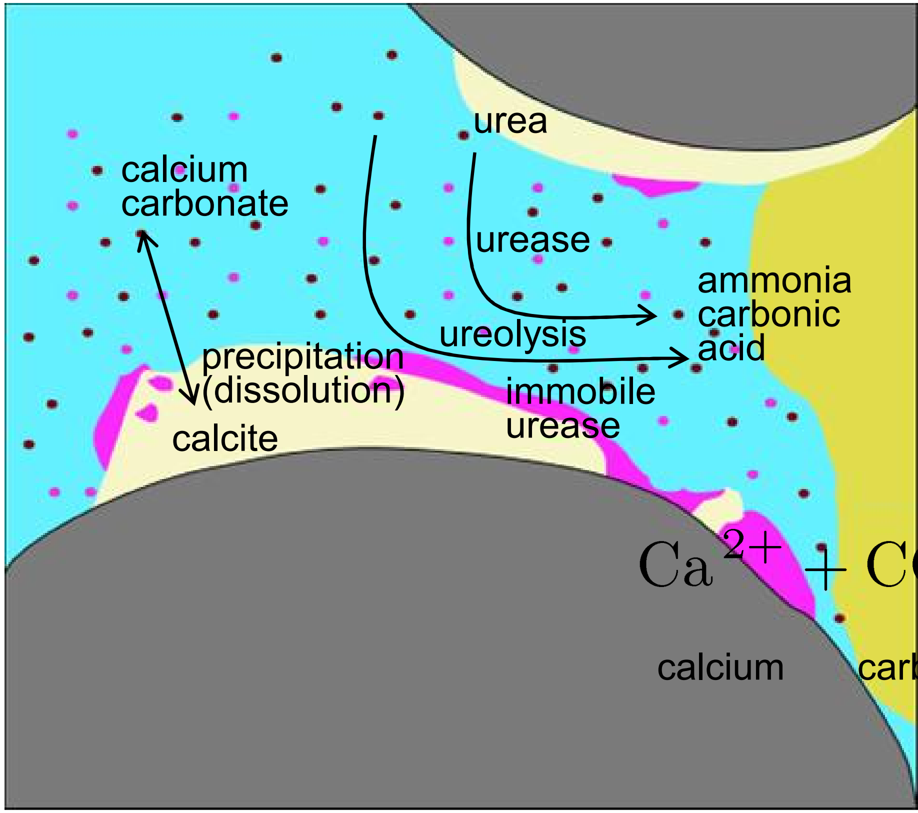


$$CO(NH_2)_2 + 2\,H_2O \xrightarrow{\text{urease}} 2\,NH_3 + H_2CO_3$$

urea — ammonia — carbonic acid

- Urea hydrolysis
  - *Exp. 1st order kinetics*

EICP model concept: Relevant processes

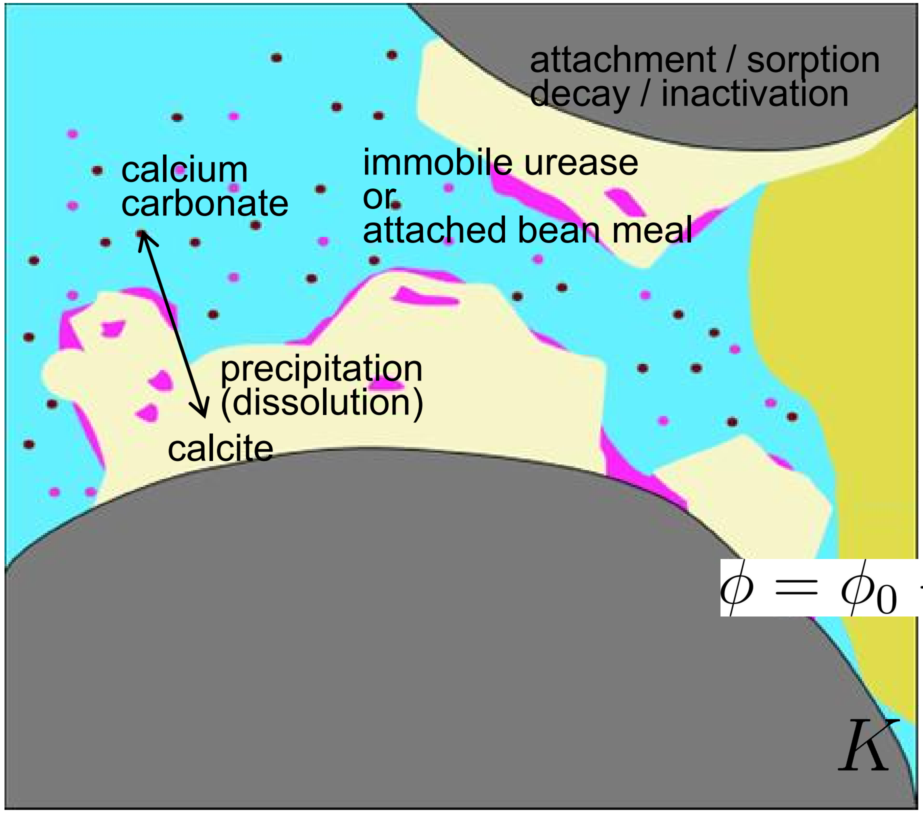


- Precipitation and dissolution of calcite
  - *Kinetics valid at higher temperatures*

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

calcium　　carbonate　　calcite

EICP model concept: Relevant processes



- Clogging: Reduction of porosity and permeability
  - *Attachment / detachment*

$$\phi = \phi_0 - \phi_{\mathrm{im.\,urease}} - \phi_{\mathrm{calcite}}$$

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

EICP compared to MICP

- The enzyme urease is surprisingly temperature stable.
- Temperature limit is approximately 80°C, but at 70-80°C rapid enzyme inactivation. The optimum temperature is 60°C.
- Urease can be stored more easily than living cells.
- Urease can be obtained from plants, e.g. jack beans or soy beans.

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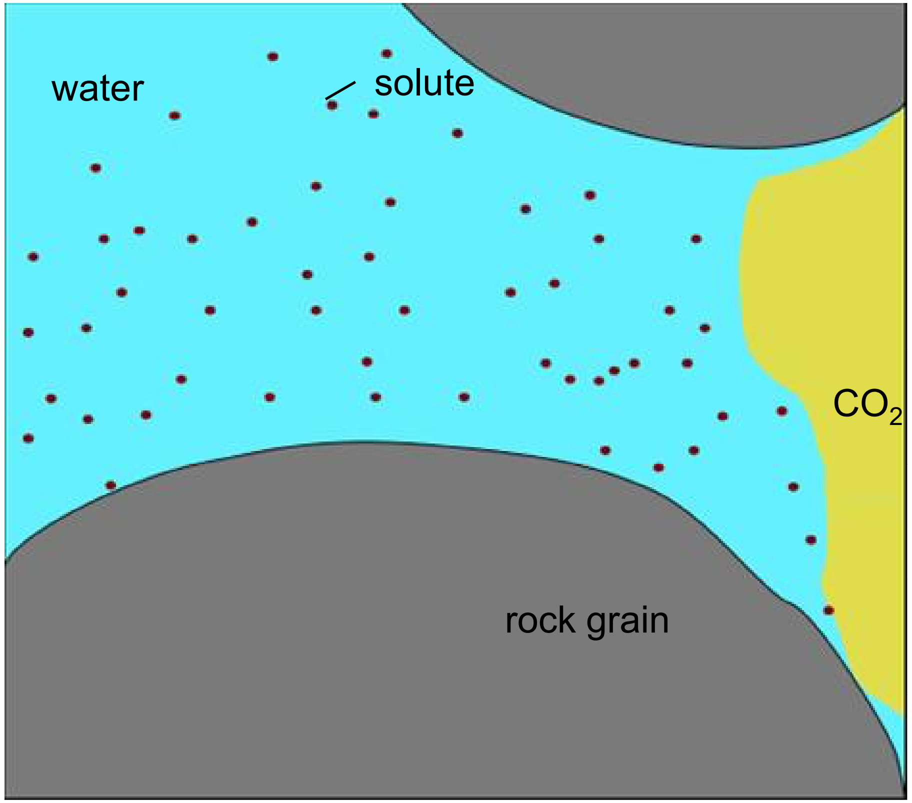
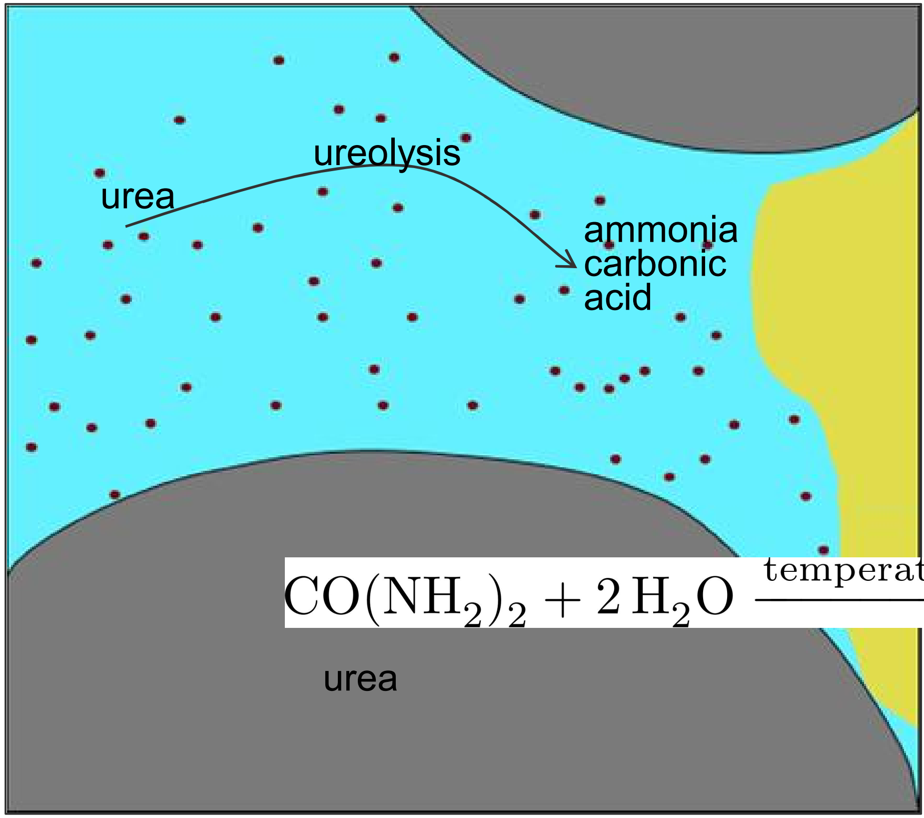
TICP model concept: Relevant processes



- Two-phase, multi-component transport

TICP model concept: Relevant processes

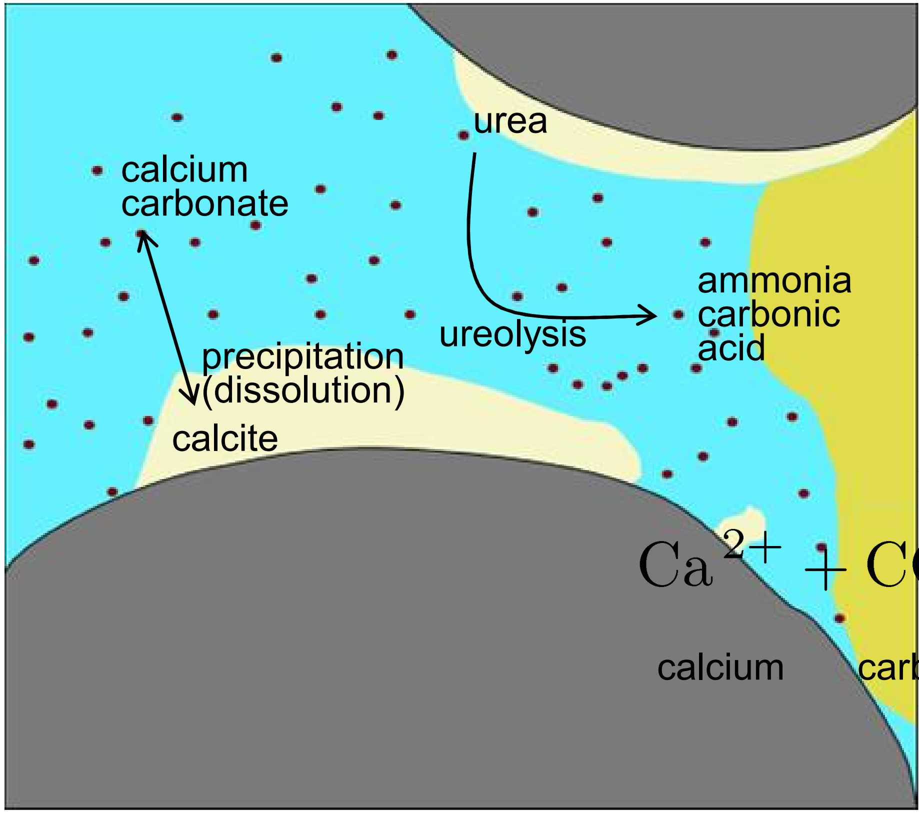


- Urea hydrolysis
  - *Temperature-induced ureolysis kinetics*

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

urea — ammonia — carbonic acid

TICP model concept: Relevant processes



- Precipitation and dissolution of calcite
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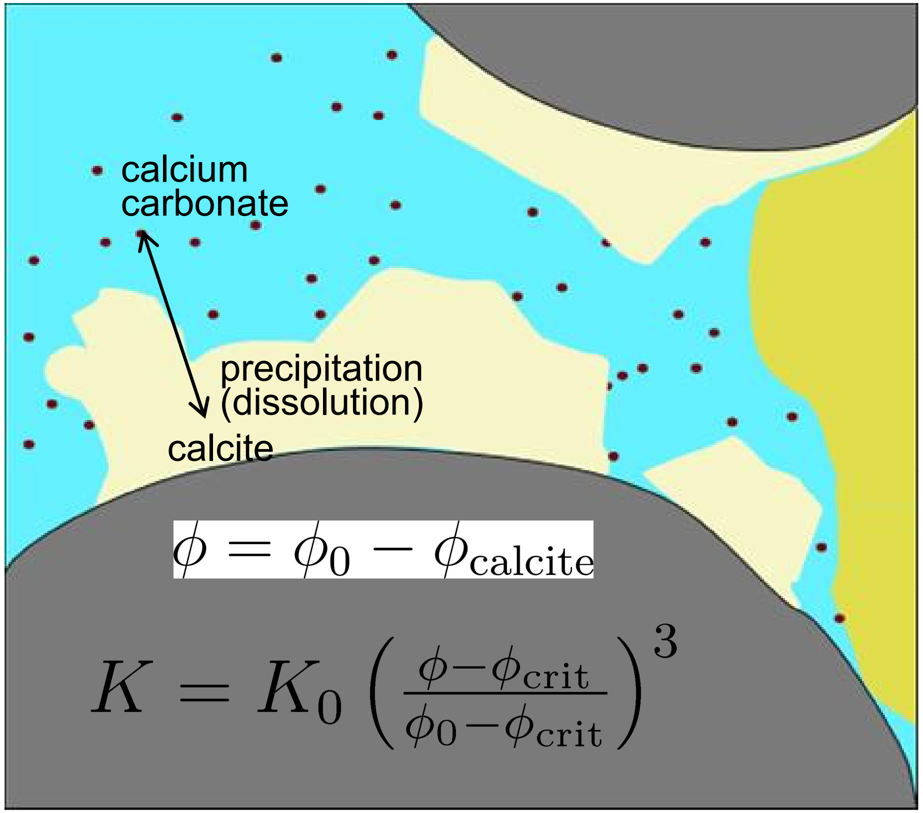
$$Ca^{2+} + CO_3^{2-} \longleftrightarrow CaCO_3 \downarrow$$

calcium carbonate calcite

TICP model concept: Relevant processes



- Clogging: Reduction of porosity and permeability
  - *Still calcite the dominant mineral?*

  → At least temporally aragonite.
  - *Effects of aragonite and higher temperatures on crystal distribution → poro.-perm. relation?*

TICP compared to MICP and EICP

- Higher temperatures >100°C provide sufficient activation energy to hydrolyze urea without catalyst, below 100°C only low reaction rate.

- No extra catalyst (bacteria, enzyme) needed.

- Probably more difficult to control in applications, because there is no catalyst!

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- **Summary**

Summary and outlook

- Implemented two additional mineralization models (EICP and TICP).

- Main differences are the number of components and the reaction rate kinetics.

- Added non-isothermal capabilities to all mineralization models.

- TODO:
  - Calibrate and validate both EICP and TICP models.

Resulting models and questions

	MICP	EICP	TICP
Common primary variables	**7**: water, CO_2 (C_{total}), sodium, chloride, calcium, urea, calcite		
Specific primary variables	**5**: substrate, oxygen, NH_{total}, suspended biomass, biofilm	**4** (2): urease susp./imm., non urease JBM susp./imm., (NH_{total} for FL kinetics, temperature for NI)	**0** (1): temperature for NI)
Ureolysis kinetics	Lauchnor et al. 2015	1st order from experiments	From experiments or literature
Solid phases	biofilm, calcite	calcite, (attached enzyme and bean meal)	calcite
Open questions	temperature dependence of microbial processes	Kinetics (ureolysis and precipitation), urease transport, bean meal vs. pure enzyme temperature dependence	Kinetics (ureolysis and precipitation) temperature dependence

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Thank you!

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Key papers / further information

- A. Ebigbo, A.J. Phillips, 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, doi:10.1029/2011WR011714

- E.G. Lauchnor, D.M. Topp, A.E. Parker, R. Gerlach: **Whole cell kinetics of ureolysis by *Sporosarcina pasteurii***. *Journal of Applied Microbiology*, 2015 (118) 1321-1332, doi:10.1111/jam.12804

- A.J. Phillips, E.G. Lauchnor, J. Eldring, R. Espositos, A.C. Mitchell, R. Gerlach, A.B. Cunningham, L.H. Spangler: **Potential CO_2 leakage leduction through biofilm-induced calcium carbonate precipitation**. *Environmental Science & Technology*, 2013 (47) 142-149, doi:10.1021/es301294q

- A.J. Phillips, R. Gerlach, E.G. Lauchnor, A.C. Mitchell, A.B. Cunningham, L.H. Spangler: **Engineered applications of ureolytic biomineralization: a review**. *Biofouling*, 2013 (29) 715-733, doi:10.1080/08927014.2013.796550

Papers / further information

- J. Hommel, E.G. Lauchnor, R. Gerlach, A.B. Cunningham, A. Ebigbo, R. Helmig, H. Class: **Investigating the influence of the initial biomass distribution and the injection strategies on biofilm-mediated calcite precipitation in porous media**. *Transport in Porous Media*, 2015, doi:10.1007/s11242-015-0617-3

- J. Hommel, E.G. Lauchnor, A.J. Phillips, 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**. *Water Resources Research*, 2015 (51) 3695-3715, doi:10.1002/2014WR016503

- J. Hommel, A.B. Cunningham, R. Helmig, A. Ebigbo, H. Class: **Numerical investigation of microbially induced calcite precipitation as a leakage mitigation technology**. *Energy Procedia*, 2013 (40C) 392-397, doi:10.1016/j.egypro.2013.08.045

Sources & sinks: Solutes and Calcite

$$
\begin{aligned}
&\text{Urea:} & q^{\text{urea}} &= -r_{\text{urea}} \\
&\text{Total nitrogen:} & q^{\text{NH}_{\text{tot}}} &= 2r_{\text{urea}} \\
\\
&\text{Calcium:} & q^{\text{Ca}^{2+}} &= r_{\text{diss}} - r_{\text{precip}} \\
&\text{Total carbon:} & q^{\text{C}_{\text{tot}}} &= r_{\text{urea}} + r_{\text{diss}} - r_{\text{precip}} \\
&\text{Calcite:} & q^{\text{c}} &= r_{\text{precip}} - r_{\text{diss}} \\
\\
&\text{Substrate:} & q^{\text{substrate}} &= -\left(r^{\text{bio}}_{\text{growth}} + r^{\text{biofilm}}_{\text{growth}}\right)/Yield \\
&\text{Oxygen:} & q^{\text{O}_2} &= -\left(r^{\text{bio}}_{\text{growth}} + r^{\text{biofilm}}_{\text{growth}}\right) \cdot 0.5/Yield
\end{aligned}
$$

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\\
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&\text{Oxygen:} & q^{\text{O}_2} &= -\left(r_{\text{growth}}^{\text{bio}} + r_{\text{growth}}^{\text{biofilm}}\right)\cdot 0.5/Yield \\
\\
&\text{Ureolysis rate} & r_{\text{urea}} &= f\left(\phi_{\text{biofilm}},\ \text{pH},\ C_{\text{w}}^{\text{urea}};\ C_{\text{w}}^{\text{NH}_4^+}\right) \\
\\
&\text{Precipitation rate} & r_{\text{precip}} &= f\left(A_{\text{interface}},\ \Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}}\right) \\
&\text{Dissolution rate} & r_{\text{diss}} &= f\left(A_{\text{interface}},\ \Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}},\ \text{pH}\right)
\end{aligned}
$$

Sources & sinks: Biomass

$$\text{Susp. biomass:} \qquad q^{\text{bio}} = r^{\text{bio}}_{\text{growth}} - r^{\text{bio}}_{\text{decay}} - r^{\text{bio}}_{\text{attach}} + r^{\text{bio}}_{\text{detach}}$$

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

Sources & sinks: Biomass

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\end{aligned}
$$

$$
\begin{aligned}
\text{Growth:} \quad r^{\text{bio}}_{\text{growth}} &= \mu \cdot \phi S_{\text{w}} C^{\text{bio}}_{\text{w}} \\
r^{\text{biofilm}}_{\text{growth}} &= \mu \cdot \phi_{\text{biofilm}} \rho_{\text{biofilm}} \\
\mu &= \mu_{\max} \cdot \frac{C^{\text{substrate}}_{\text{w}}}{K_{\text{substrate}} C^{\text{substrate}}_{\text{w}}} \cdot \frac{C^{\text{O}_2}_{\text{w}}}{K_{\text{O}_2} C^{\text{O}_2}_{\text{w}}}
\end{aligned}
$$

$$
\begin{aligned}
\text{Decay:} \quad r^{\text{bio}}_{\text{decay}} &= k^{\text{bio}}_{\text{decay}} \cdot \phi S_{\text{w}} C^{\text{bio}}_{\text{w}};\ k^{\text{bio}}_{\text{decay}} = f(\text{pH}) \\
r^{\text{biofilm}}_{\text{decay}} &= k^{\text{biofilm}}_{\text{decay}} \cdot \phi_{\text{biofilm}} \rho_{\text{biofilm}};\ k^{\text{biofilm}}_{\text{decay}} = f(r_{\text{precip}})
\end{aligned}
$$

$$
\begin{aligned}
\text{Attachment:} \quad r_{\text{attach}} &= \left(c_{\text{a},1} \phi_{\text{biofilm}} + c_{\text{a},1}\right) \cdot \phi S_{\text{w}} C^{\text{bio}}_{\text{w}} \\
\text{Detachment:} \quad r_{\text{detach}} &= \left(c_{\text{d},1} \left(|\nabla p_{\text{w}}| \phi S_{\text{w}}\right)^{0.58} + \mu \frac{\phi_{\text{biofilm}}}{\phi_0 - \phi_{\text{calcite}}}\right) \cdot \phi_{\text{biofilm}} \rho_{\text{biofilm}}
\end{aligned}
$$