# Modeling porous medium modification through induced calcite precipitation

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#### **Micro Abstract**

Induced calcite precipitation is an emerging technology to alter properties of porous media. It results in a decrease in porosity and permeability as well as an increase in mechanical strength. For a reliable prediction of these changes, numerical modeling is the method of choice, as the involved processes are strongly coupled. Validated to experimental data, such numerical models are useful tools in the upscaling from laboratory to field-scale applications.

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## Introduction

Fluid storage in the subsurface is important to reduce climate change (sequestration of supercritical  $CO_2$ ) or for energy storage (CH<sub>4</sub>, H<sub>2</sub>) to cope with the intermittent, unpredictable production of renewable sources like wind and solar. However, the fluids have the potential to leak through damaged cap rocks or wellbores. Methods to remediate these problems include the induction of calcium carbonate precipitation (ICP). The engineered precipitation of calcium carbonate has been demonstrated to have immense potential to seal such leakage pathways which depends on both reducing the cap-rock permeability to sufficiently low values as well as increasing its mechanical strength to withstand the high pressures close to the injection well.

Currently, most applications of ICP rely on urea hydrolysis by microbes to promote precipitation within the porous media. However, precipitation may also be induced by injection of extracted or plant-based sources of urease or at elevated temperatures. The applicability of a certain method of ICP is largely determined by the depth below ground surface and the local geothermal gradient. Microbially induced calcium carbonate precipitation (MICP) relies on the activity of living bacterial cells, which only thrive within a limited temperature range. This temperature range may include the shallow subsurface, where  $CH_4$  or natural gas may be stored, but is lower than the temperatures commonly present at depths suitable for  $CO_2$  storage. As a consequence, other ICP technologies such as enzymatically induced calcium carbonate precipitation (EICP) or thermally induced calcium carbonate precipitation (TICP) have to be developed and demonstrated in the field. Regardless of the precipitation-inducing process, the overall ICP reaction equation is:

$$\operatorname{CO}(\operatorname{NH}_2)_2 + 2\operatorname{H}_2\operatorname{O} + \operatorname{Ca}^{2+} \longrightarrow 2\operatorname{NH}_4^+ + \operatorname{CaCO}_3 \downarrow .$$
 (1)

Using MICP, it has been shown that both a significant decrease in permeability and an increase in mechanical strength can be achieved. E.g. in [13], the permeability of a sample is reduced by four orders of magnitude and the fracturing well bore pressure increased by a factor of more than three. And in [14], it was observed that already during the first day, the shear modulus of sand increased by a factor of seven due to microbially induced precipitation. Other studies observe similar behavior, e.g. [1,12]. Even successful field demonstrations have been completed [3,11].

## 1 Model concept

As the models are intended for the use in predicting the leakage mitigation for subsurface gas storage, it accounts for two-phase flow. Additionally, a variety of different components and are necessary to describe ICP, the specific number of components being dependent on the precipitation-inducing process. Common components for all ICP models are water (w), gas (n), inorganic carbon (C<sup>tot</sup>), calcium (Ca), chloride (Cl), sodium (Na), and urea (u) as well as the solid phase calcite (c). The TICP model considers no additional components, the EICP model has additionally the enzyme urease (e) in mobile and immobilized form and ammonium (a), and the MICP model additionally accounts for biomass (b) as the solid phase biofilm and as suspended biomass, ammonium (a), as well as substrate (s) and oxygen (o) necessary for biomass growth. All models are implemented in the open-source simulator DuMu<sup>X</sup> [5].

The primary variables solved are the aqueous-phase pressure  $p_w$ , mole fractions  $x_w^{\kappa}$  of each component  $\kappa$  in the water phase, temperature T, and, for the solid phases, biofilm and calcium carbonate in case of MICP and exclusively calcium carbonate for EICP and TICP, volume fractions  $\phi_{\varphi}$ . All calcium carbonate is assumed to precipitate as calcite, since experimental investigations confirmed by XRD measurements that calcite is the predominant form of calcium carbonate occurring, at least under MICP conditions [8, 10, 12]. For EICP and TICP, this assumption will have to be revised with increasing availability of experimental data.

However, the gas (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>) or non-wetting-phase saturation ( $S_n$ ) is used as primary variable instead of the mole fraction of gas in water  $x_w^n$  whenever both fluid phases are present within the same control volume [2]. All reactive and mass-transfer processes are incorporated in the mass balance equations for the components (2) and solid phases (3) by component-specific source and sink terms:

$$\sum_{\alpha} \left[ \frac{\partial}{\partial t} \left( \phi \rho_{\alpha, \, \text{mol}} x_{\alpha}^{\kappa} S_{\alpha} \right) + \nabla \cdot \left( \rho_{\alpha, \, \text{mol}} x_{\alpha}^{\kappa} \mathbf{v}_{\alpha} \right) - \nabla \cdot \left( \rho_{\alpha, \, \text{mol}} \mathbf{D}_{\text{pm}, \alpha}^{\kappa} \nabla x_{\alpha}^{\kappa} \right) \right] = q^{\kappa}, \, \alpha \in \{n; w\}$$
(2)

Here, t is time,  $\phi$  porosity,  $\rho_{\alpha, \text{mol}}$ ,  $S_{\alpha}$ , and  $\mathbf{v}_{\alpha}$  the molar density, saturation and the velocity of phase  $\alpha$  respectively,  $x_{\alpha}^{\kappa}$  the mole fraction of component  $\kappa$  in phase  $\alpha$ .  $\mathbf{D}_{\text{pm},\alpha}$  is the dispersion tensor of phase  $\alpha$  in the porous medium, and  $q^{\kappa}$  is the source term of component  $\kappa$  due to biochemical reactions. However, all components except water and the gas are assumed to be restricted to the water phase.

The mass balances for the solid phases, calcite, and biofilm for MICP or immobilized urease for EICP, contain only a storage and source term since they are immobile:

$$\frac{\partial}{\partial t} \left( \phi_{\varphi} \rho_{\varphi} \right) = q^{\varphi}, \ \varphi \in \{ \mathbf{c}; \mathbf{b}; \mathbf{e} \}$$
(3)

Here,  $\phi_{\varphi}$  and  $\rho_{\varphi}$  are volume fraction and mass density of the solid phase  $\varphi$ , and  $q^{\varphi}$  is the source term of phase  $\varphi$  due to biochemical reactions. The sources and sinks due to reactions  $q^{\kappa}$  and  $q^{\varphi}$  are specific to the components. For MICP, the source terms include microbial growth, decay, attachment and detachment, the consumption of oxygen and nutrients by biomass growth, ureolysis, as well as the precipitation and dissolution of calcite. All these processes and the associated rate equations are discussed in detail in [4,6]. For TICP, the number of processes is reduced to only the central reactions of ICP, see Equation (1): ureolysis, which is the driving force of the overall reaction, and calcite precipitation and dissolution. In EICP, the temperature-dependent inactivation of enzyme has to be considered in addition to the processes of TICP. For the sake of brevity, only the most important rate equations, those for ureolysis and calcite precipitation, are discussed here. Rate equations for the other processes are given in [6]. The

ureolysis rate  $r_{\text{urea}}$  is specific for each ICP method and the ureolysis rate equations are developed based on data from kinetics experiments, e.g. for MICP [7]. For TICP,  $r_{\text{urea,t}}$  is assumed to be dependent only on the temperature and the concentration of urea:

$$r_{\rm urea,t} = k_{\rm t} c_{\rm w}^{\rm u} \tag{4}$$

where  $k_{\rm t}$  is the temperature-dependent rate constant for thermal uncellasis and  $c_{\rm w}^{\rm u}$  is the waterphase concentration of uncertain of enzyme  $c^{\rm e,e}$ :

$$r_{\rm urea,e} = k_{\rm e} c^{\rm e,e} c^{\rm u}_{\rm w} \tag{5}$$

where  $k_{\rm e}$  is the rate constant for enzymatic ureolysis depending on temperature and pH. Note that  $c^{\rm e,e}$  is a not only the concentration of enzyme in the water phase, but also includes eventually immobilized enzyme attached to the solid matrix and is calculated per total volume of the porous media:  $c^{\rm e} = c_{\rm w}^{\rm e} \phi S_{\rm w} + \phi_{\rm e} \rho_{\rm e}$ . For MICP, the reaction rate  $r_{\rm urea,m}$  was found to have a Michaelis-Menten type kinetic [7]:

$$r_{\rm urea,m} = k_{\rm m} c^{\rm e,m} \frac{c_{\rm w}^{\rm u}}{K_{\rm u} + c_{\rm w}^{\rm u}} \tag{6}$$

where  $k_{\rm m}$  is the rate constant for microbial ureolysis,  $K_{\rm u}$  is the half saturation constant, and  $c^{\rm e,m} = R_{\rm e,b}\phi_{\rm b}\rho_{\rm b}$  is the total concentration of enzyme calculated using the ratio of enzyme per biomass  $R_{\rm e,b}$  and the biomass in the solid phase biofilm  $\phi_{\rm b}\rho_{\rm b}$ . In all models, the calcite precipitation rate  $r_{\rm prec}$  is dependent on the saturation state  $\Omega$  which is a function of the calcium and carbonate concentrations and activities, which themselves depend on the temperature and the water phase composition [4, 6]:

$$r_{\rm prec} = k_{\rm prec} A_{\rm sw} \left(\Omega - 1\right)^{n_{\rm prec}} \tag{7}$$

where  $k_{\text{prec}}$  and  $n_{\text{prec}}$  are rate parameters and  $A_{\text{sw}}$  is the surface area between water and solids [4,6].

Assuming local thermal equilibrium, the energy balance equation can be written as:

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

$$(8)$$

where  $\rho_{\rm s}$ ,  $\rho_{\varphi}$ , and  $\rho_{\alpha}$  are the mass densities of the unreactive solid,  $(1 - \phi_0)$ , the solid phases  $\varphi$ , and the fluid phase  $\alpha$ .  $c_{\rm s}$  and  $c_{\varphi}$  are the heat capacities of the respective solids,  $u_{\alpha}$  and  $h_{\alpha}$  are the specific internal energy and enthalpy of the fluids  $\alpha$ , and  $\lambda_{\rm pm}$  is the effective, averaged heat conductivity of the overall porous medium, which depends on the solid volume fractions and the fluid staturations.

Among the supplementary equations, one of the most important is the relation for updating the permeability with respect to the accumulation of additional solids in the pore space. In the model, the reduction of permeability is calculated based on the reduction of porosity according to a Verma-Pruess type relation [15]:

$$\frac{K}{K_0} = \left(\frac{\phi - \phi_{\rm crit}}{\phi_0 - \phi_{\rm crit}}\right)^3 \tag{9}$$

where  $K_0$  is the initial permeability,  $\phi_{\text{crit}}$  the critical porosity, a porous-medium specific parameter at which the permeability is zero, and  $\phi_0$  is the initial porosity. The porosity  $\phi$  decreases as the volume fractions of solid phases increase:

$$\phi = \phi_0 - \sum \phi_{\varphi} \tag{10}$$

## 1.1 Current model limitations

All ICP models presented here have some limitations in common, especially regarding the proposed application of ICP as a gas leakage mitigation technology. First, while they are all designed being able to account for two-phase flow, the impact of ICP on the parameters relevant for two-phase flow has been neglected up to now. One first attempt to include a dependency of the two-phase flow properties on mineralization could be the use of the so-called Leverett scaling [9], which relates the capillary-pressure-saturation relation to the porosity and permeability of the porous medium, properties, which are already adapted in the present model concepts. Second, while at least MICP has been shown to also increase the mechanical strength of a porous medium, e.g. [1,11–14], the current model concept does not yet include geomechanics and assumes a rigid porous medium, without deformation. Also for this, a fairly straightforward solution is to combine the model predictions of the calcium carbonate distribution and the relation between calcium carbonate content from e.g. [14] to estimate the increase in mechanical strength resulting from ICP with minimal change to the current model concepts.

# Conclusions

The presented model concept for modeling MICP has proven to be successful in predicting experimental results, these being the distribution of precipitated calcium carbonate along column experiments [4, 6] and the concentrations of relevant components along the column over time [6]. But also the number of calcium-rich injections and the reduction in permeability for a field-test were estimated surprisingly well [3, 11].

This model concept is generalized to include other processes inducing the precipitation of calcium carbonate, resulting in similar models for EICP and TICP. Once these models have been calibrated and validated, they will help to design field test in the same way as the MICP model was used to prepare for the MICP field test [3,11]. Some of the current model concept limitations are discussed and solutions to reduce the limitations proposed. However, rigorous experimental studies are necessary before calibration and validation, before these model concept extensions can be regarded reliable and used predictively.

#### References

- [1] T. H. Barkouki, B. C. Martinez, B. M. Mortensen, T. S. Weathers, J. D. De Jong, T. R. Ginn, N. F. Spycher, R. W. Smith, and Y. Fujita. Forward and inverse bio-geochemical modeling of microbially induced calcite precipitation in half-meter column experiments. *Transport in Porous Media*, 90(1):23–39, Aug. 2011.
- [2] H. Class and R. Helmig. Numerical simulation of non-isothermal multiphase multicomponent processes in porous media. 2. Applications for the injection of steam and air. 25:551–564, 2002.

- [3] A. B. Cunningham, A. J. Phillips, E. Troyer, E. G. Lauchnor, R. Hiebert, R. Gerlach, and L. H. Spangler. Wellbore leakage mitigation using engineered biomineralization. *Energy Proceedia*, 63:4612–4619, 2014.
- [4] A. Ebigbo, A. J. Phillips, R. Gerlach, R. Helmig, A. B. Cunningham, H. Class, and L. H. Spangler. Darcy-scale modeling of microbially induced carbonate mineral precipitation in sand columns. *Water Resourc. Res.*, 48(7):W07519, July 2012.
- [5] B. Flemisch, M. Darcis, K. Erbertseder, B. Faigle, A. Lauser, K. Mosthaf, S. Müthing, P. Nuske, A. Tatomir, M. Wolff, and R. Helmig. DUMUX: DUNE for multi-{Phase, Component, Scale, Physics,...} flow and transport in porous media. *Adv. Water Resour.*, 34(9):1102–1112, 2011.
- [6] J. Hommel, E. G. Lauchnor, A. J. Phillips, R. Gerlach, A. B. Cunningham, R. Helmig, A. Ebigbo, and H. Class. A revised model for microbially induced calcite precipitation - improvements and new insights based on recent experiments. *Water Resourc. Res.*, 51:3695–3715, 2015.
- [7] E. Lauchnor, D. Topp, A. Parker, and R. Gerlach. Whole cell kinetics of ureolysis by Sporosarcina pasteurii. *Journal of Applied Microbiology*, 118(6):1321–1332, 2015.
- [8] E. G. Lauchnor, L. N. Schultz, S. Bugni, A. C. Mitchell, A. B. Cunningham, and R. Gerlach. Bacterially Induced Calcium Carbonate Precipitation and Strontium Co-Precipitation in a Porous Media Flow System. *Environmental Science & Technology*, 47(3):1557–1564, 2013.
- [9] M. Leverett. Capillary behaviour in porous solids. Transactions of the AIME, 142:159–172, 1941.
- [10] A. C. Mitchell, A. J. Phillips, L. Schultz, S. Parks, L. H. Spangler, A. B. Cunningham, and R. Gerlach. Microbial CaCO<sub>3</sub> mineral formation and stability in an experimentally simulated high pressure saline aquifer with supercritical CO<sub>2</sub>. *International Journal of Greenhouse Gas Control*, 15:86–96, July 2013.
- [11] A. J. Phillips, A. B. Cunningham, R. Gerlach, R. Hiebert, C. Hwang, B. P. Lomans, J. Westrich, C. Mantilla, J. Kirksey, R. Esposito, and L. Spangler. Fracture Sealing with Microbially-Induced Calcium Carbonate Precipitation: A Field Study. *Environmental Science & Technology*, 50:4111–4117, 2016.
- [12] A. J. Phillips, J. Eldring, R. Hiebert, E. Lauchnor, A. C. Mitchell, A. B. Cunningham, L. Spangler, and R. Gerlach. Design of a meso-scale high pressure vessel for the laboratory examination of biogeochemical subsurface processes. *Journal of Petroleum Science and Engineering*, 126:55–62, 2015.
- [13] A. J. Phillips, E. G. Lauchnor, J. J. Eldring, R. Esposito, A. C. Mitchell, R. Gerlach, A. B. Cunningham, and L. H. Spangler. Potential CO<sub>2</sub> leakage reduction through biofilm-induced calcium carbonate precipitation. *Environmental Science & Technology*, 47:142–149, Aug. 2013.
- [14] L. A. van Paassen, R. Ghose, T. J. M. van der Linden, W. R. L. van der Star, and M. C. M. van Loosdrecht. Quantifying Biomediated Ground Improvement by Ureolysis: Large-Scale Biogrout Experiment. Journal of Geotechnical and Geoenvironmental Engineering, 136(12):1721–1728, 2010.
- [15] A. Verma and K. Pruess. Thermohydrological conditions and silica redistribution near highlevel nuclear wastes emplaced in saturated geological formations. *Journal of Geophysical Research: Solid Earth*, 93(B2):1159–1173, 1988.