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Mathematical model of biofilm induced calcite precipitation

T. Zhang and I. Klapper

ABSTRACT

Microbially modulated carbonate precipitation is a fundamentally important phenomenon of both engineered and natural environments. In this paper, we propose a mixture model for biofilm induced calcite precipitation. The model consists of three phases – calcite, biofilm and solvent – which satisfy conservation of mass and momentum laws with addition of a free energy of mixing. The model also accounts for chemistry, mechanics, thermodynamics, fluid and electrodiffusion transport effects. Numerical simulations qualitatively capturing the dynamics of this process and revealing effects of kinetic parameters and external flow conditions are presented.

Key words | biofilm, calcite precipitation, mixture model, ureolysis

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INTRODUCTION

Microbially modulated carbonate precipitation is a fundamentally important phenomenon of natural and engineered environments which involves the interaction of biological, chemical, geological, and hydrological processes, and is important in controlling atmospheric and aqueous levels of carbon dioxide on a number of spatial and temporal scales (Riding & Liang 2005). In addition, calcite precipitation resulting from ureolysis catalyzed by bacteria has been suggested as a potential mechanism for geologic carbon sequestration (Mitchell *et al.* 2008) as well as a bioremediation strategy (Fujita *et al.* 2000) for aquifers in western USA, where ground water is contaminated with divalent metals (e.g. Pb^{2+} , Zn^{2+}).

There have been a number of experimental investigations of calcite precipitation induced by ureolytic bacteria (usually in bacterial biofilms), (e.g. Warren *et al.* 2001; Ferris *et al.* 2003; Mitchell & Ferris 2005), as well as a rich literature on mathematical modeling of biofilm growth and biofilm–flow interaction (Picioreanu *et al.* 1998; Eberl *et al.* 2001; Alpkvist & Klapper 2007) including both discrete and continuous models. Mathematical models for solute precipitation also exist, e.g. Xu & Meakin (2008). However, less attention has been devoted to the mathematical

modeling of biofilm induced calcite precipitation through ureolysis, in part due to the complex combination of physical, chemical, and biological processes involved. But, because of the difficulty in obtaining pointwise measurement of important quantities (pH value, chemical concentrations, etc.) experimentally, it would be helpful to construct a reliable mathematical model which can answer some of the important questions: how do biofilm communities interact with and alter their local physical and chemical environments? What are the influences of varying kinetic parameters (e.g. urea hydrolysis rate) on calcite precipitation? What are the differences between calcite precipitation in systems with and without external flow?

In this paper, we propose a versatile mixture model which accounts for the important physical, chemical and biological processes involved in biofilm induced calcite precipitation. In this model, the system as a whole consists of three phases – biofilm, calcite and solvent – each represented by its own volume fraction. These phases satisfy conservation of mass and momentum laws with addition of a free energy of mixing. In addition, each chemical species involved is treated as a solute in the solvent and represented by its own concentration governed by an advection–diffusion–reaction equation.

METHODS

We consider a rectangular domain in which are contained solvent, biofilm, dissolved urea, and calcium chloride. Urea hydrolysis is catalyzed by ureolytic bacteria; the subsequent carbonate species distribution leads to the formation of carbonate ions. In the presence of soluble calcium ions (originating from calcium chloride in our study), calcite (CaCO_3) precipitation occurs once its saturation state exceeds a critical level.

Biofilm–calcite mechanics and thermodynamics

We generalize the one fluid, two phase (biomaterial and solvent) biofilm models of Klapper & Dockery (2006) and Zhang *et al.* (2008) to include a third phase, namely calcite, while retaining the biofilm–flow interactions and also adding solidification thermodynamics. A description of the system follows: we use notation Φ_c , Φ_b , and Φ_s for volume fractions of calcite, biofilm, and solvent respectively (satisfying $\Phi_c + \Phi_b + \Phi_s = 1$), $\mathbf{v}$ for mean velocity, p for pressure, and c for a limiting nutrient concentration in the solvent. For simplicity, we model calcite as an extremely viscous fluid, sufficiently viscous so that it does not deform significantly over the computation time. Also, we assume a sufficiently slow fluid time scale so that biofilm can be well approximated to be a viscous fluid (evidence indicates that biofilms are viscoelastic fluids with elastic relaxation times of approximately 20 min (Shaw *et al.* 2004) – hence on time scales much longer than 20 min, biofilms behave as viscous fluids). The system of governing equations, excluding chemical species equations, is then

$$\nabla \cdot \mathbf{v} = 0,$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot (\nu(\phi_c, \phi_b, \phi_s) \mathbf{D}) - \nabla p + \frac{\delta f}{\delta \phi_c} \nabla \phi_c + \frac{\delta f}{\delta \phi_b} \nabla \phi_b,$$

$$\frac{\partial}{\partial t}(\phi_s c) + \nabla \cdot (\phi_s c \mathbf{v} - \mathbf{D}_s \phi_s \nabla c) = -\phi_b \frac{Ac}{c_0 + c},$$

$$\frac{\partial \phi_c}{\partial t} + \nabla \cdot (\phi_c \mathbf{v}) = \nabla \cdot \left(\Lambda_c \phi_c \nabla \frac{\delta f}{\delta \phi_c} \right) + g_c(S),$$

$$\frac{\partial \phi_b}{\partial t} + \nabla \cdot (\phi_b \mathbf{v}) = \nabla \cdot \left(\Lambda_b \phi_b \nabla \frac{\delta f}{\delta \phi_b} \right) + \mu \phi_b \frac{c}{c_0 + c}.$$

where

$$v(\phi_c, \phi_b, \phi_s) = \phi_c \nu_c + \phi_b \nu_b + \phi_s \nu_s, \quad \rho = \phi_c \rho_c + \phi_b \rho_b + \phi_s \rho_s,$$

$$\mathbf{D} = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$$

and ν_c , ν_b , ν_s are viscosities of the calcite, biofilm and solvent, ρ_c , ρ_b , ρ_s are corresponding densities, and Λ_c and Λ_b are mobility parameters for calcite and biofilm. The first two equations are the Navier–Stokes equations with additional stress terms (the ones with f dependence) arising from chemical free energy-related stresses. The last three equations are mass conservation equations for limiting substrate, calcite, and biomaterial. The Flory–Huggins chemical free energy density of mixing f (Doi 1995) which includes mixing energy, transitional energy and energy due to mixing entropy is given by

$$f(\phi_c, \phi_b, \phi_s) = k_B T \left[\chi_b \phi_b \phi_s + \chi_c \phi_c (1 - \phi_c) + \frac{\Gamma_c}{2} \|\nabla \phi_c\|^2 + \frac{\Gamma_b}{2} \|\nabla \phi_b\|^2 + \frac{\Gamma_s}{2} \|\nabla \phi_s\|^2 + \frac{1}{N} \phi_b \ln \phi_b + \phi_s \ln \phi_s + \phi_c \ln \phi_c \right]. \quad (1)$$

where k_B is Boltzmann constant and T is absolute temperature. We focus discussion of parameters in (1) to the key parameter χ_c (see Zhang *et al.* (2008) for discussion of the others as well as parameters in the equations for Φ_b and c). The term $\chi_c \phi_c (1 - \phi_c)$ is the calcite mixing energy density: $\chi_c > 0$ indicates that this energy is positive so that calcite volume fraction close to 0 or 1 is energetically preferred (favoring phase decomposition). χ_c thus controls the rate of calcite phase accumulation. The source term $g_c(S)$ (in the governing equation for Φ_c) arises from calcite precipitation as a result of solvent chemistry, and is given by a widely used quadratic rate law (Zhang & Dawe 1998; Zuddas & Mucci 1998),

$$g_c(S) = \begin{cases} -C_{\text{vol}} k_p (S - 1)^2, & S \geq S_{\text{crit}} \\ 0, & S < S_{\text{crit}}, \end{cases}$$

where k_p is the calcite precipitation rate constant, C_{vol} is the inverse molar density of mineralized calcite (Marini 2007), and S is the calcite saturation state (defined later).

Chemical kinetics

We use kinetics of calcite precipitation induced by bacterial urea hydrolysis as summarized by Equations

(2)–(5) below. Equation (2), the microbial source component, describes urea hydrolysis to ammonia and carbonic acid, a process catalyzed by the presence of ureolytic bacteria (with a rate approximately 10^{14} times

Parameters K_1 , K_2 , K_3 are known equilibrium reaction rate constants under prescribed conditions (pressure, temperature). Ca^{2+} is supplied by CaCl_2 . Altogether the various chemical species with concentrations S_i and valences z_i are

i	1	2	3	4	5	6	7	8	9	10
S_i	$[\text{CO}(\text{NH}_2)_2]$	$[\text{NH}_3]$	$[\text{H}_2\text{CO}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$	$[\text{HCO}_3^-]$	$[\text{CO}_3^{2-}]$	$[\text{Ca}^{2+}]$	$[\text{Cl}^-]$	$[\text{H}^+]$
z_i	0	0	0	+1	-1	-1	-2	+2	-1	+1

faster than the uncatalyzed rate (Benini *et al.* 1996)). Ureolysis simultaneously results in ammonium and carbonate production. Equations (3) and (4), the “fast local chemistry”, together with the water self-ionization condition $[\text{H}^+][\text{OH}^-] = K_w = 10^{-14} \text{ (mol L}^{-1})^2$ describe the ammonia-ammonium balance, the carbonate species distribution, as well as the pH. Shifting balance (via ureolytic input) leads to formation of carbonate ions (Equation (4)), which, in the presence of soluble calcium ions, precipitate as CaCO_3 . Equation (5) describes calcite precipitation when its saturation state exceeds a critical supersaturation. The equations involved in biofilm induced calcite precipitation are

(Urea hydrolysis) – – Slow

(pH increase) – – Fast

– – Fast

(calcite precipitation) – – Slow

Here (3) and (4) are fast reactions, and we can rewrite them in terms of H^+ as

The following species participate the fast reactions (6) (S_i , $i \in I_f = \{2, 3, 4, 5, 6, 7, 10\}$): $[\text{NH}_3]$, $[\text{H}_2\text{CO}_3]$, $[\text{NH}_4^+]$, $[\text{OH}^-]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, $[\text{H}^+]$. From (6) and the local conservation of total dissolved nitrogen (N_T) and carbon (C_T), we have

$$\frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}^+]} = K_3, \quad [\text{NH}_4^+] + [\text{NH}_3] = N_T \quad (7)$$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1, \quad \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2, \quad (8)$$

$$[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = C_T$$

In (7) and (8), N_T and C_T are known prior to equilibration of fast reactions (N_T and C_T vary according to mass transport as well as the slow reactions including urea hydrolysis and calcite precipitation). By solving (7) and (8), concentrations $[\text{NH}_3]$, $[\text{NH}_4^+]$, $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ can be written in terms of $[\text{H}^+]$ and other known constants. Then, by writing all species involved in fast reactions in terms of $[\text{H}^+]$, the charge neutrality constraint

$$\begin{aligned} &[\text{NH}_4^+] + [\text{H}^+] + 2[\text{Ca}^{2+}] - [\text{OH}^-] - [\text{HCO}_3^-] \\ &- 2[\text{CO}_3^{2-}] - [\text{Cl}^-] = 0 \end{aligned}$$

yields the following equation for $[\text{H}^+]$:

$$\begin{aligned} &\frac{N_T K_3 [\text{H}^+]}{1 + K_3 [\text{H}^+]} + [\text{H}^+] - \frac{K_w}{[\text{H}^+]} - \frac{C_T}{([\text{H}^+]/K_1) + 1 + (K_2/[\text{H}^+])} \\ &- \frac{2C_T}{([\text{H}^+]^2/K_1 K_2) + ([\text{H}^+]/K_2) + 1} \\ &= -2[\text{Ca}^{2+}] + [\text{Cl}^-] \end{aligned} \quad (9)$$

Here $[Ca^{2+}]$ and $[Cl^-]$ are known from the slow reactions. Solving (9), we then obtain $[H^+]$ and subsequently the concentration of all species involved in fast reactions.

Next we describe the slow processes including convection, diffusion (due to concentration gradients and to the electric potential gradient) and slow chemical reactions. These processes affect all S_i , $1 \leq i \leq 10$. The governing equations are

$$\frac{\partial S_i}{\partial t} + \nabla \cdot (S_i \mathbf{v}) = \nabla \cdot (D_i \nabla S_i + a z_i S_i \nabla \zeta) + R_i, \quad (10)$$

$$1 \leq i \leq 10$$

where D_i is the diffusion coefficient of species i , a is a unit-related constant, ζ is the electric potential (discussed later), and R_i is the slow chemical reaction term for the species i . For $S_1 = [CO(NH_2)_2]$, since it is the reactant of ureolysis, we have

$$R_1 = -k_{urea} \cdot \Phi_b \cdot S_1$$

where k_{urea} is the urea hydrolysis rate coefficient. The presence of Φ_b reflects that ureolysis occurs in the biofilm. For $S_2 = [NH_3]$, $S_3 = [H_2CO_3]$, since they are the products of ureolysis, we have $R_2 = -2R_1$, $R_3 = -R_1$ where the factor 2 reflects that one mole of urea produces two moles of ammonia. For $S_4 = [NH_4^+]$, $S_5 = [OH^-]$, $S_6 = [HCO_3^-]$, $S_9 = [Cl^-]$, and $S_{10} = [H^+]$, we have $R_4 = R_5 = R_6 = R_9 = R_{10} = 0$ since they don't participate in slow reactions. For $S_7 = [CO_3^{2-}]$, $S_8 = [Ca^{2+}]$, since they are reactants of calcite precipitation, we have

$$R_7 = R_8 = \begin{cases} -k_p(S-1)^2, & S \geq S_{crit} \\ 0, & S < S_{crit} \end{cases}, \quad S = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{SO}}$$

where K_{SO} is the equilibrium calcite solubility product, S is the calcite saturation state, k_p is the calcite precipitation rate constant and S_{crit} is some critical supersaturation.

Electrochemistry

Since different ion species generally have different diffusivities, diffusion in ionic systems leads to charge separation which in turn leads to generation of an electric field.

Conversely, electric field affects ionic transport – faster diffusing ionic species tend to be “retarded” and slower ones “accelerated” (Robinson & Stokes 1959). Furthermore, local ionic species concentrations determine local pH, which controls mineral precipitation. Thus we include the predicted ionic spatial gradient-induced electric field in our model.

We compute the electric field so as to enforce charge neutrality (this idea is very much analogous to choosing fluid pressure so as to enforce divergence free velocity in the case of incompressible fluids). Thus, requiring $\sum_i z_i R_i = 0$ (charge conservation) and $\sum_i z_i S_i = 0$ (charge neutrality) pointwise, then multiplying equations (10) by z_i and summing over i results in the following Poisson equation for the electric potential ζ :

$$\nabla \cdot \left(\sum_{i \in I_E} z_i^2 S_i \nabla \zeta \right) = -\frac{1}{a} \nabla \cdot \left(\sum_{i \in I_E} z_i D_i \nabla S_i \right) \quad (11)$$

Numerical procedure

The governing equations are solved by a finite difference method. In particular, the coupled momentum transport equation and the continuity equation are solved by a velocity corrected projection scheme (Guermond *et al.* 2006). The advection–reaction–diffusion equations for Φ_c , Φ_b , Φ_s , c , S_i are solved by a Crank–Nicolson scheme in which the resulting system of algebraic equations is solved by a GMRES iterative method (Saad & Schultz 1986). The computational steps are:

- (1) Initialize Φ_c , Φ_b , Φ_s , c , $\mathbf{v}$, S_i , $1 \leq i \leq 10$.
- (2) Calculate total dissolved Nitrogen N_T and Carbon C_T .
- (3) Solve Equation (9) to obtain $[H^+]$ and S_i , $i \in I_f$ after fast reactions.
- (4) Solve Equation (11) to obtain the electric potential ζ .
- (5) Solve the equations for $\mathbf{v}$, Φ_c , Φ_b , c .
- (6) Solve the slow process Equations (10) to obtain S_i , $1 \leq i \leq 10$ after slow process.
- (7) Update time $t = t + \Delta t$ and go to step 2.

The important parameters values used in the simulation are provided in Table 1. The parameter values related to

Table 1 | Parameter values used in the simulation

Symbol	Parameter	Value	Unit	Symbol	Value
χ_c	Calcite mixing parameter	$10^{16} - 10^{17}$	Dimensionless	D_1	1.38×10^{-9}
ν_c	Dynamic viscosity of calcite	5×10^2	$\text{kg m}^{-1} \text{s}^{-1}$	D_2	2.14×10^{-9}
ν_b	Dynamic viscosity of biofilm	4	$\text{kg m}^{-1} \text{s}^{-1}$	D_3	1.92×10^{-9}
ν_s	Dynamic viscosity of solvent	1.002×10^{-5}	$\text{kg m}^{-1} \text{s}^{-1}$	D_4	1.96×10^{-9}
k_{urea}	Ureolysis rate coefficient	0.04–0.2	day^{-1}	D_5	5.28×10^{-9}
k_p	Calcite precipitation rate	0.2	$\text{mmol L}^{-1} \text{day}^{-1}$	D_6	1.18×10^{-9}
K_{SO}	Equilibrium solubility product	3.8×10^{-9}	$[\text{mol/L}]^2$	D_7	0.92×10^{-9}
S_{crit}	Critical supersaturation	50	Dimensionless	D_8	0.79×10^{-9}
C_{vol}	Calcite inverse molar density	32.05	L/mol	D_9	2.03×10^{-9}
T	Temperature	293.15	Kelvin	D_{10}	9.31×10^{-9}
a	Unit constant for electric field	1	$\text{kg}^{-1} \text{s}$	K_1	$10^{-6.35}$
ρ_c	Calcite density	2.71×10^3	kg m^3	K_2	$10^{-10.33}$
ρ_b	Biofilm density	1×10^3	kg m^3	K_3	$10^{9.25}$

ureolysis and calcite precipitation are taken from Ferris *et al.* (2003), and D_i , K_1 , K_2 , K_3 are taken from (CRC 2008), where D_i has unit $\text{m}^2 \text{s}^{-1}$, K_1 , K_2 has unit mol L^{-1} , and K_3 has unit $\text{mol}^{-1} \text{L}$.

RESULTS AND DISCUSSION

Calcite precipitation without external flow

We consider a two dimensional system with a rectangular domain of size 1 mm by 4 mm (Figure 1, between the

horizontal blue lines). Initially it consists of randomly attached biofilm colonies and dissolved urea and calcium chloride with concentration 6 and 2 mmol L^{-1} respectively. In this first example, we assume that there is no externally driven flow so the velocity is zero on the entire domain boundary. Figure 1(a) shows the initial contours of Φ_b (biofilm volume fraction). Figure 1(b) shows contours of Φ_b after 4.5 days. They show little change since the growth of biofilm is slow and there is little effect from the bulk fluid flow (and gravity is not included in the fluid equation). The contours of the calcite saturation state S at $t = 4.5 \text{ d}$ are shown in Figure 1(c), and we observe that the peaks of

Figure 1 | A 2D simulation of biofilm induced calcite precipitation without external flow. $k_{\text{urea}} = 0.2 \text{ day}^{-1}$, $\chi_c = 10^{17}$. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.

Figure 2 | Simulation of biofilm induced calcite precipitation without external flow with different parameter values. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.

S coincide closely with the biofilm colonies. This is expected since ureolysis is catalyzed by biofilm, thus the chemical reaction rate and the concentration of CO_3^{2-} is higher in the region occupied by biofilm. We remark that the region where S takes high values is broader than the biofilm region due to the diffusion of CO_3^{2-} . Figure 1(d) shows the contour of Φ_c (calcite volume fraction) at $t = 4.5$ d, indicating that calcite precipitation happens in the biofilm region, and that calcite phase accumulation (the red region) mainly occurs near the biofilm–solvent interface.

Then we illustrate the effect of certain parameters on the prediction of the model. Figure 2(a) shows the contour of Φ_c at $t = 4.5$ d with only one parameter change: ureolysis rate $k_{\text{urea}} = 0.04 \text{ day}^{-1}$ (the value in the previous computation was 0.2). We observe that calcite precipitation still occurs in the same region, but to a lesser degree due to

smaller value of k_{urea} , illustrating the importance of ureolysis rate (which depends on temperature) as a key kinetic parameter in controlling the calcite precipitation rate. Figure 2(b) shows the result of a different single parameter change: calcite mixing parameter $\chi_c = 10^{16}$ (the value in the previous computation was 10^{17}). We observe that due to the smaller value of χ_c , calcite contours are smoother and less calcite phase accumulation (red region) has occurred, illustrating that χ_c is also an important parameter in controlling calcite phase accumulation rate.

Calcite precipitation with external flow

Now we consider a system of same size with biofilm colonies attached to the top and bottom boundaries of the domain (Figure 3(a)). An external flow with velocity

Figure 3 | A 2D simulation of biofilm induced calcite precipitation with external flow of 10^{-3} m/s . $k_{\text{urea}} = 0.2 \text{ day}^{-1}$, $\chi_c = 10^{17}$. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.

1 mm s^{-1} carrying dissolved urea and calcium chloride with concentration 6 and 2 mmol L^{-1} enters the domain from the left boundary and effluent leaves the domain from the right boundary, and the velocity at the top and bottom boundaries is zero. Figure 3(b) shows the contours of Φ_b at $t = 4.5\text{ d}$. We observe that under shear stress from the external flow, biofilm is significantly stretched in the downstream direction. Figure 3(c) shows the contours of S at $t = 4.5\text{ d}$. It again shows that the peaks of S coincide with the biofilm region, and that S takes high values in a broader region than the biofilm due to both advection and diffusion of CO_3^{2-} . Figure 3(d) shows contours of Φ_c at $t = 4.5\text{ d}$. We again observe that calcite phase accumulation mainly occurs in the biofilm–solvent interface. In addition, since the external flow keeps transporting in new carbonate and calcium, more calcite precipitates out than the previous case, nearly forming a shell between biofilm and solvent. This simulation indicates external flow can significantly change the dynamics of calcite precipitation.

CONCLUSION

We have proposed a versatile mixture model for biofilm induced calcite precipitation through ureolysis. This type of process has potential application in, for example, geologic carbon sequestration and bioremediation of polluted water. The mixture model is based on conservation of mass and momentum with addition of a free energy of mixing, and treats the mechanics, thermodynamics, chemistry, and electrodiffusion involved in the process. 2D numerical simulations qualitatively reveal essential temporal and spatial features of biofilm induced calcite precipitation, as well as identification of key parameters and effects of external flow.

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