

# CRYSTAL DISSOLUTION AND PRECIPITATION IN POROUS MEDIA: THE CASE OF FIXED GEOMETRY

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## ABSTRACT

We propose a pore scale model for dissolution and precipitation in porous media. Here we assume that the crystals are small when compared to the solid grains, thus the geometry of the pores and of the solid grains does not change.

## 1. THE MODEL

We consider a pore scale model for crystal dissolution and precipitation in a porous medium. A fluid in which cations ( $M_1$ ) and anions ( $M_2$ ) are dissolved is occupying the pores of the medium. Under certain conditions that will be described later,  $n$  particles of  $M_1$ , and  $m$  particles of  $M_2$  can precipitate in the form of one particle of a crystalline solid  $M_{12}$ . This process is encountered at the surface of the solid grains; the precipitate is attached to the surface of the grains and thus immobile. The reverse reaction of dissolution is also possible:



In what follows we denote by  $\tilde{\Omega}$  the void space in the porous medium. This is a subset in the  $d$ -dimensional space ( $d > 1$ ). The boundary of  $\tilde{\Omega}$  is consisting of two parts. The surface between the fluid and the porous matrix (grains) is the interior part of the boundary of the void space, which is denoted by  $(\tilde{\Gamma}_G)$ . The outer boundary of the medium is the external part of the boundary.

In this paper we assume that the size of crystalline particles is small when compared to the grains. Therefore the flow geometry, as well as the fluid density and viscosity ( $\tilde{\mu}$ , given) are not affected by the reactions, and the chemistry does not interfere with the fluid flow. Denoting the fluid velocity by  $\tilde{q}$  and the fluid pressure by  $\tilde{p}$ , we assume that the flow is described by the Stokes equations:

$$\left. \begin{aligned} \tilde{\mu} \Delta \tilde{q} &= \nabla \tilde{p}, \\ \nabla \cdot \tilde{q} &= 0, \end{aligned} \right\} \text{ in } \tilde{\Omega}. \tag{2}$$

Along the internal grain boundary we assume a no-slip condition, implying

$$\tilde{q} = \vec{0} \quad \text{along } \tilde{\Gamma}_G. \tag{3}$$

We denote by  $c_i$  be the volumetric molar concentration of  $M_i$  in  $\tilde{\Omega}$  and by  $c_{12}$  the surface molar concentration of  $M_{12}$  on  $\tilde{\Gamma}_G$ . Further we assume that both types of ions have the

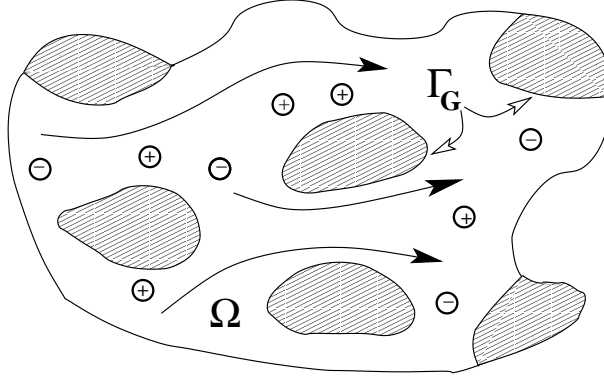


FIGURE 1. Flow domain with grains.

same diffusion coefficient  $\tilde{D} > 0$ . For  $M_i$  ( $i = 1, 2$ ) we have

$$\partial_t c_i + \nabla \cdot (\tilde{q} c_i - \tilde{D} \nabla c_i) = 0, \quad \text{in } \tilde{\Omega}. \quad (4)$$

On the surface of the grains  $\tilde{\Gamma}_G$  the flux of  $c_i$  is proportional to the changes in the crystalline concentration  $c_{12}$ . Recalling (3) we have

$$\partial_t c_{12} = -\frac{1}{n} \tilde{D} \tilde{\nu} \cdot \nabla c_1 = -\frac{1}{m} \tilde{D} \tilde{\nu} \cdot \nabla c_2 \quad \text{on } \tilde{\Gamma}_G, \quad (5)$$

where  $\tilde{\nu}$  denotes the normal unit vector pointing into the grains.

Another equation for the precipitate concentration  $c_{12}$  is given by the the description of the precipitation and dissolution processes:

$$\partial_t c_{12} = r_p - r_d \quad \text{on } \tilde{\Gamma}_G.$$

Here  $r_p$  denotes the precipitation rate expressed by

$$r_p = k_p r(c_1, c_2),$$

where  $k_p$  is a positive rate constant and  $r$  a rate function depending on  $c_1$  and  $c_2$ . A typical example is mass action kinetics leading to

$$r(c_1, c_2) = c_1^n c_2^m. \quad (6)$$

For the mathematical rigor, in the unphysical situation of having negative values for  $c_1$  or  $c_2$ , one should take their positive cut in the above. In this way, the mathematical analysis can guarantee that the concentrations remain positive (see [van Duijn, Pop, 2004]).

For the dissolution rate  $r_d$  we follow the detailed discussion in [Knabner et al., 1995]. This is assumed constant ( $k_d > 0$ ) in the presence of crystal, i. e. for  $c_{12} > 0$  somewhere on  $\tilde{\Gamma}_G$ . Further, in the absence of crystal and in the undersaturated regime, i. e.  $c_1$  and  $c_2$  are such that

$$r(c_1, c_2) \leq k_d/k_p,$$

the overall rate  $r_p - r_d$  is zero. This is obtained by considering the set-valued expression

$$r_d(c_{12}) \in k_d H(c_{12}),$$

where  $H$  denotes the Heaviside graph,

$$H(u) = \begin{cases} 0, & \text{if } u < 0, \\ [0, 1], & \text{if } u = 0, \\ 1, & \text{if } u > 0. \end{cases}$$

In the oversaturated regime ( $r(c_1, c_2) > \frac{k_d}{k_p}$ ) somewhere on  $\tilde{\Gamma}_G$ , we have  $r_d(c_{12}) = 1$  and precipitation ( $\partial_t c_{12} > 0$ ) will occur at such points. In the undersaturated regime, when the concentrations  $c_1$  and  $c_2$  are such that

$$r(c_1, c_2) < \frac{k_d}{k_p} \quad \text{somewhere on } \tilde{\Gamma}_G,$$

we can distinguish two cases. In the presence of the precipitate ( $c_{12} > 0$ ) at some grain boundary location we have  $\partial_t c_{12} < 0$  at such points, and dissolution will occur. In the absence of crystals ( $c_{12} = 0$ ) we set

$$r_d = \frac{k_p}{k_d} r(c_1, c_2) < 1,$$

implying  $\partial_t c_{12} = 0$ . This discussion can be comprised in the crystalline solid the equation

$$\partial_t c_{12} \in k_d \left( \frac{k_p}{k_d} r(c_1, c_2) - H(c_{12}) \right) \quad \text{on } \tilde{\Gamma}_G. \quad (7)$$

**1.1. Dimensionless form.** Since the chemistry does not affect the flow, the fluid velocity  $\tilde{q}$  and fluid pressure  $\tilde{p}$  can be determined in the first instance, without knowing the concentrations  $c_1$ ,  $c_2$  and  $c_{12}$ . This is the first simplification in the model. The second one is induced by the assumption that the diffusion coefficient for both ions are the same. By this we can eliminate one ion from the system. To do so we define the total negative charge

$$\tilde{c} = mc_1 - nc_2. \quad (8)$$

Recalling (4) and (5), we immediately get

$$\partial_t \tilde{c} + \nabla \cdot (\tilde{q}\tilde{c} - \tilde{D}\nabla\tilde{c}) = 0 \quad \text{in } \tilde{\Omega},$$

and

$$\tilde{D}\vec{\nu} \cdot \nabla\tilde{c} = 0 \quad \text{on } \tilde{\Gamma}_G.$$

Clearly, once  $\tilde{q}$  is known, the charge  $\tilde{c}$  can be determined by solving a linear parabolic problem, and without knowing the ion and precipitate concentrations. Knowing  $\tilde{c}$  and, say,  $c_1$ , the remaining concentration can be determined straightforwardly from (8). In this way the chemistry can be modeled in terms of the concentrations  $c_1$  and  $c_{12}$ .

For bringing the model to a dimensionless form we let  $\hat{c}_1$  and  $\hat{c}_{12}$  be characteristic values for the concentrations of cation  $c_1$ , respectively of the precipitate  $c_{12}$ . Further,  $Q$ ,  $P$  and  $L$  stand for the characteristic values for flow, pressure and distance. In this framework,

three time scales can be identified:

$$\begin{aligned}
T_L &:= \frac{L}{Q}, & \text{the characteristic transport time scale,} \\
T_D &:= \frac{L^2}{D}, & \text{the characteristic diffusion time scale,} \\
T_C &:= \frac{\hat{c}_{12}}{k_d}, & \text{the characteristic reaction time scale.}
\end{aligned} \tag{9}$$

Associated to these time scales one can define

$$P_e := \frac{T_L}{T_D}, \quad \text{and} \quad D_a := \frac{T_L}{T_C}, \tag{10}$$

the *Peclet*, respectively *Damköhler* numbers.

Rescaling the length with  $L$  and the time with  $T_L$  and setting

$$\begin{aligned}
u &:= \frac{c_1}{\hat{c}_1}, & v &:= \frac{c_{12}}{\hat{c}_{12}}, & c &:= \frac{\tilde{c}}{\hat{c}_1}, & \vec{q} &:= \frac{\tilde{q}}{Q}, & p &:= \frac{\tilde{p}}{P}, \\
\mu &:= \frac{\tilde{\mu}Q}{PL}, & D &:= \frac{1}{P_e}, & \varepsilon &:= \frac{\hat{c}_{12}}{L\hat{c}_1}, \\
r(u, c) &:= \frac{k_p}{k_d} r(\hat{c}_1 u, \hat{c}_1 \frac{mu-c}{n}),
\end{aligned}$$

the equations in the scaled domain  $\Omega$  become

$$\begin{cases} \mu \Delta \vec{q} = \nabla p, \\ \nabla \cdot \vec{q} = 0, \\ \partial_t c + \nabla \cdot (\vec{q}c - D\nabla c) = 0, \\ \partial_t u + \nabla \cdot (\vec{q}u - D\nabla u) = 0. \end{cases} \tag{11}$$

On the scaled interior boundary  $\Gamma_G$  we have

$$\begin{cases} \vec{q} = \vec{0}, \\ \vec{\nu} \cdot \nabla c = 0, \\ -D\vec{\nu} \cdot \nabla u = \varepsilon n \partial_t v, \\ \partial_t v = D_a(r(u, c) - w), \\ w \in H(v). \end{cases} \tag{12}$$

Notice that in the above  $w$  plays the role of the scaled dissolution rate  $r_d/k_d$ . All these equations are defined for the time  $0 < t < T$ , where  $T$  is a maximal time. Further, the above model is completed by initial and external boundary conditions.

**Remark 1.1.** *When choosing the characteristic values  $\hat{c}_1$  and  $\hat{c}_{12}$  one can assume that for these values the system contains about the same number of moles for both the precipitate and the solutes. This assumption can be expressed as*

$$\hat{c}_{12} \cdot \text{meas}(\tilde{\Gamma}_G) \approx \hat{c}_1 \cdot \text{meas}(\tilde{\Omega}), \tag{13}$$

for which the definition of  $\varepsilon$  gives

$$\varepsilon L \text{meas}(\Gamma_G) \approx \text{meas}(\Omega).$$

In other words,  $\varepsilon$  can also be seen as the ratio of two length scales: the characteristic pore scale length  $\text{meas}(\Omega)/\text{meas}(\Gamma_G)$  and the problem related scale  $L$ . In a porous medium,

(13) is natural, since  $\text{meas}(\Gamma_G)$  denotes the total surface of the porous matrix and  $\text{meas}(\Omega)$  the total void volume. If the medium is periodic,  $\text{meas}(\Omega)/\text{meas}(\Gamma_G)$  is of order  $1/\varepsilon$ . As  $\varepsilon \searrow 0$ , the total internal surface goes to infinity. In this case, a blow up in the total amount of precipitate is avoided by the presence of  $\varepsilon$  in the boundary flux in (12<sub>3</sub>) (see for example [Hornung, 1997]).

## 2. RESULTS

A rigorous analysis of the model proposed in the previous section can be found in [van Duijn, Pop, 2004], where the existence of a solution has been proven for general domains. This result is completed by the analysis for a simplified geometry, a strip. This case is similar to a pore, where the lateral walls represent the grain boundary. Then the occurrence of dissolution and precipitation fronts is studied. Specifically, two characteristic situations are considered:

Dissolution fronts. Assuming that initially the system is in equilibrium, and that crystals are present and uniformly distributed everywhere on the side walls, we inject an undersaturated fluid at the inlet. In this case a dissolution front occurs after a *waiting time* that can be computed explicitly.

Precipitation fronts. Assuming that initially there is no precipitate on the side walls and the fluid is undersaturated, injecting an oversaturated fluid at the inlet leads to an instantaneous occurrence of a precipitation front.

Further, as the ratio between the thickness of the strip and its length approaches 0, the cross-section average of  $u$ , together with the precipitate concentration  $v$  and the dissolution rate  $w$  converge to the solution of the upscaled one-dimensional transport-reaction model introduced in [Knabner et al., 1995],

$$\begin{cases} \partial_t(U + nV) + Q\partial_x U &= D\partial_{x^2}^2 U, \\ \partial_t V &= D_a(r(U) - W), \\ W &\in H(V). \end{cases}$$

Here  $Q$  is the cross-section average of the Poiseuille velocity.

The mathematical analysis in [van Duijn, Pop, 2004] is continued in [Pop et al., 2005] (see also [Devigne, 2006]) with the numerical analysis of an approximation scheme for the chemistry components of the model. All the results mentioned above are obtained assuming that the time scales defined in (9) have the same order of magnitude. This means that both  $P_e$  and  $D_a$  are moderate, of order 1. For a model involving a linear chemistry, the case when  $P_e$  is large is analyzed in [Mikelić et al., 2005]. There the convergence to an effective model as  $\varepsilon \searrow 0$  is rigorously proven.

**2.1. Numerical results.** We conclude this presentation with numerical examples obtained in the undersaturated regime. For more examples we refer to [Devigne, 2006]. We have used the following parameters and rate function:

$$D = 0.25, D_a = 5, \varepsilon = 1, m = n = 1.0, \text{ and } r(u, c) = \frac{10}{9}[u]_+[u - 0.1]_+.$$

With this choice, the equilibrium situation is achieved for the value  $u^* = 1.0$  of the cation concentration  $u$ . Further, the precipitation rate is strictly positive only whenever  $u > u_* = 0.1$ .

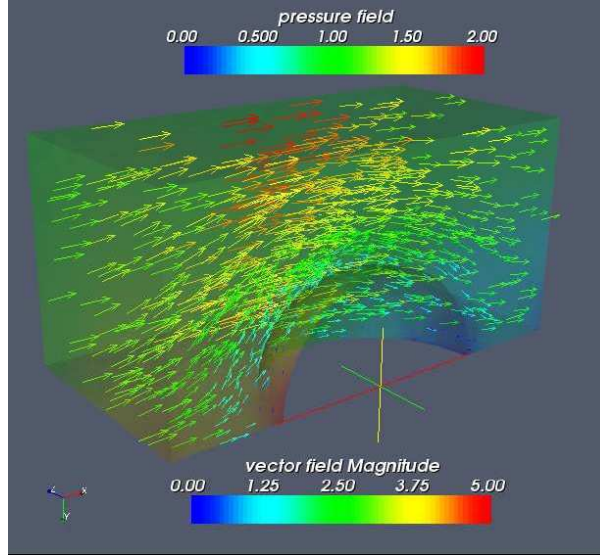


FIGURE 2. The velocity field  $\vec{q}$  and the pressure  $p$

The computational domain is a reference cell  $\Omega$ , where the cube  $(-1, 1)^3$  is including a spherical grain of radius  $R = 0.5$  centered in the origin. Then the external part of the boundary is the outer surface of the cube, while the grain boundary  $\Gamma_G$  is the interior sphere. We define the left and right sides of the cube as the in- and outflow boundaries. For symmetry reasons, the computations are restricted to the upper and back part of the domain.

The numerical results below are obtained assuming that the initial data are compatible (see [Knabner et al., 1995]), and that the total charge is constant in time and space. This is also the framework of the analysis in [Pop et al., 2005]. Then the simulations are performed in two steps: first we determine the fluid velocity  $\vec{q}$  by solving the Stokes system. To this aim we have applied the bubble stabilized finite element method proposed in [Russo, 1996]. In Figure 2 we present the computed velocity  $\vec{q}$  and pressure  $p$  for  $\mu = 0.01$  and with zero normal flow on the lateral and upper part of the boundary. The velocity at the in- and outlet is  $\vec{q} = (3, 0, 0)$ .

Once  $\vec{q}$  is known, we proceed by approximating  $u$  and  $v$ , the concentration of the cation, respectively of the precipitate. To this aim we approximate  $H$  by

$$H_\delta(v) := \begin{cases} 0, & \text{if } v \leq 0, \\ v/\delta, & \text{if } v \in (0, \delta), \\ 1, & \text{if } v \geq \delta, \end{cases} \quad (14)$$

where  $\delta > 0$  is a small regularization parameter. Next we consider a time stepping that is implicit in  $u$  and explicit in  $v$ . With  $N \in \mathbb{N}$ ,  $\tau = T/N$ , and  $t_k = k\tau$ , the approximation

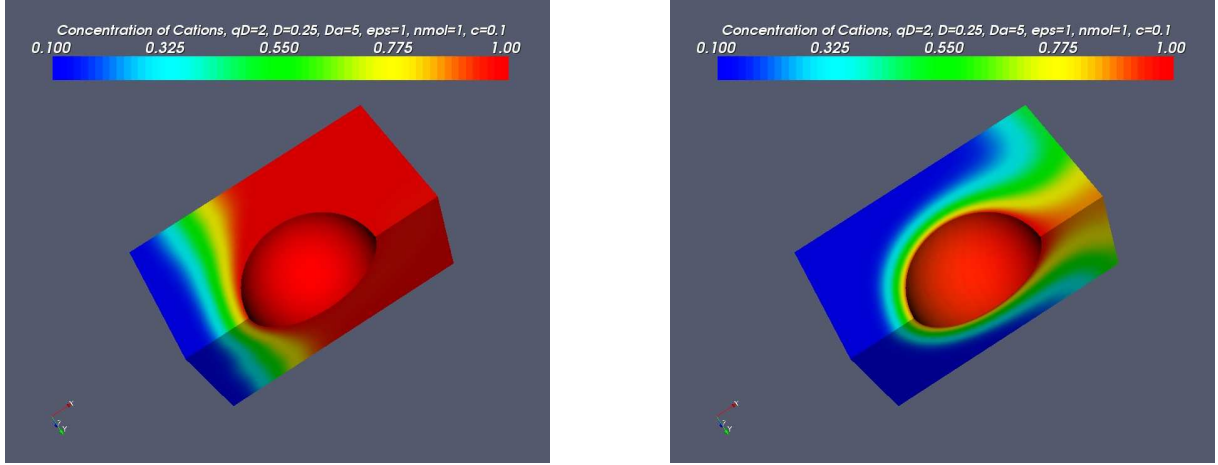


FIGURE 3. Concentration of the cation at  $t = 0.12$  (left) and  $t = 0.18$  (right)

$(u^k, v^k)$  of  $(u(t_k), v(t_k))$  is the solution of the following time discrete set of equations:

$$\left\{ \begin{array}{ll} u^k + \tau \nabla \cdot (\vec{q} u^k - D \nabla u^k) = u^{k-1}, & \text{in } \Omega, \\ -\tau D \vec{\nu} \cdot \nabla u^k = \epsilon n (v^k - v^{k-1}), & \text{on } \Gamma_G, \\ v^k = v^{k-1} + \tau D_a (r(u^k) - H_\delta(v^{k-1})), & \text{on } \Gamma_G. \end{array} \right. \quad (15)$$

Here  $k = 1, \dots, N$ , while  $u^0$  and  $v^0$  are given by the initial conditions. For completeness we define

$$w^k := H_\delta(v^k). \quad (16)$$

In the present computations we took  $\delta = \tau = 10^{-4}$ . For the spatial discretization we have employed piecewise linear finite elements. All the computations are implemented in the research software *SciFEM* (Scilab Finite Element Method, see [Devigne, 2006]) The convergence of the numerical scheme is proven [Pop et al., 2005], where also a stable and convergent linearization for the time discrete system (15) is proposed.

The initial concentrations are  $u_I = u^* = 1.0$  and  $v_I = 0.1$ , so the system is initially in equilibrium. This situation is perturbed by taking  $u = u_* = 0.1$  at the inlet. For the remaining of the exterior boundary we assume a zero normal flow. In this case, as follows from the analysis in [van Duijn, Pop, 2004], only dissolution is possible. This is confirmed by the results presented in the figures 3 and 4. Moreover, as can be seen in Figure 4, a dissolution front is encountered on the grain boundary, moving in the flow direction. This observation completes the analytical results obtained for the simplified geometry of a strip.

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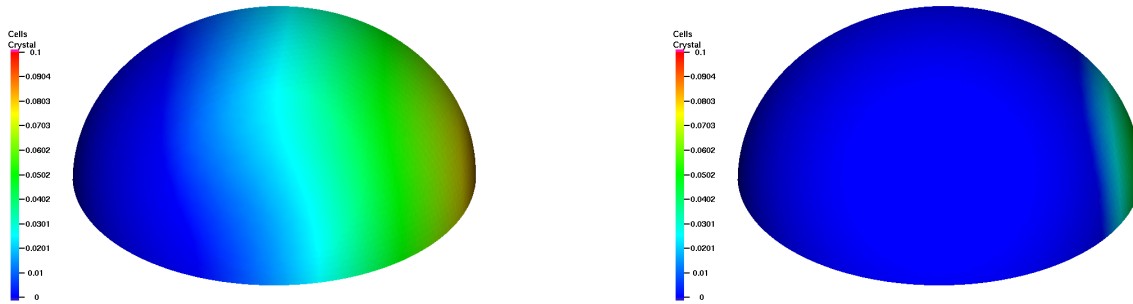


FIGURE 4. Concentration of the precipitate at  $t = 0.12$  (left) and  $t = 0.18$  (right)

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