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A NUMERICAL SCHEME FOR THE PORE-SCALE SIMULATION OF CRYSTAL DISSOLUTION AND PRECIPITATION IN POROUS MEDIA*

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Abstract. In this paper we analyze a numerical scheme for a dissolution and precipitation model in porous media. We focus here on the chemistry, which is modeled by a parabolic problem that is coupled through the boundary conditions to an ordinary differential inclusion defined on the boundary. We use a regularization approach for constructing a semi-implicit scheme that is stable and convergent. For dealing with the emerging time discrete nonlinear problems, we propose a simple fixed-point iterative procedure. The paper is concluded by numerical results.

Key words. dissolution, precipitation, porous media, convergence, linearization, coupled system, differential inclusion

AMS subject classifications. 65M12, 65N12, 35K57, 76S05

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1. Introduction. In this paper we consider a pore-scale model for the dissolution and precipitation of crystals in a porous medium. This model is studied in [7] and represents the pore-scale analogue of the macroscopic (core-scale) model proposed in [17]. The particularity of the model is in the description of the precipitation processes taking place on the surface of the grains Γ_G , involving a multivalued function. Models of similar type are analyzed in a homogenization context in [23, 5, 12, 13, 24].

Without going into details, we briefly recall the background of the model. A fluid in which cations and anions are dissolved occupies the pores of a porous medium. The boundary of the void space consists of two disjoint parts: the surface of the porous skeleton (the grains), named from now on the *internal boundary*, and the external part, which is the outer boundary of the domain. Under certain conditions, the ions transported by the fluid can precipitate and form a crystalline solid, which is attached to the internal boundary and thus is immobile. The reverse reaction of dissolution is also possible.

The model proposed in [7] consists of several components: the Stokes flow in the pores, the transport of dissolved ions by convection and diffusion, and dissolution/precipitation reactions on the surface of the porous skeleton (grains). It is assumed that the flow geometry as well as the fluid properties are not affected by

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the chemical processes. Therefore the flow component can be completely decoupled from the remaining part of the model. This situation appears, for example, if the crystal size is negligible when compared to the typical grain size or the pore scale. We mention [25] for a preliminary investigation of the case where dissolution and precipitation lead to changes in the pore space.

Another simplification follows by considering the total electric charge in the fluid. This is a linear combination of the concentrations of the ions and can be determined by solving a linear parabolic problem that depends only on the flow and not on the chemistry. Therefore once the fluid flow is determined, the total charge can be decoupled from the chemistry (see [6] for details).

Our main interest is focused on the chemistry, this being the challenging part of the model. Here we investigate an appropriate numerical scheme for the dissolution and precipitation component of the model in [7]. The present work is closely related to [11]. The numerical scheme proposed there also involves a special treatment of the diffusion on the grain boundary. The coupled system is solved by iterating between the equations in the pores and on the solid matrix.

Numerical methods for the macroscale equations modeling the dissolution and precipitation in porous media are considered in [1, 8, 9, 21, 22]. The time stepping is performed by various first order implicit schemes, and finite elements or finite volumes are employed for the spatial discretization. For the upscaled version of the present model, a numerical algorithm for computing traveling wave solutions is proposed in [17].

We denote the flow domain by $\Omega \subset \mathbb{R}^d$ ($d > 1$), which is assumed to be open, connected, and bounded. Further, the boundary $\partial\Omega$ is assumed to be Lipschitz continuous. It consists of two disjoint parts: an internal and an external one. The internal boundary Γ_G is the surface of the grains, and the external boundary Γ_D is the outer boundary of the domain. Let $\vec{\nu}$ denote the outer normal to $\partial\Omega$ and $T > 0$ be a fixed but arbitrarily chosen value of time. For X being Ω , Γ_G , or Γ_D , and any $0 < t \leq T$, we define

$$X^t = (0, t] \times X.$$

To simplify the presentation, we assume that the initial data are compatible in the sense of [6, 17]. Essentially this means that initially the system is in equilibrium. Moreover, the boundary data are assumed such that the total charge remains constant in time and space. In this way, and after an appropriate scaling, the model can be reduced to

$$(1.1) \quad \begin{cases} \partial_t u + \nabla \cdot (\vec{q}u - D\nabla u) = 0 & \text{in } \Omega^T, \\ -D\vec{\nu} \cdot \nabla u = \varepsilon \tilde{n} \partial_t v & \text{on } \Gamma_G^T, \\ u = 0 & \text{on } \Gamma_D^T, \\ u = u_I & \text{in } \Omega, \text{ for } t = 0, \end{cases}$$

for the ion transport and

$$(1.2) \quad \begin{cases} \partial_t v = D_a(r(u) - w) & \text{on } \Gamma_G^T, \\ w \in H(v) & \text{on } \Gamma_G^T, \\ v = v_I & \text{on } \Gamma_G, \text{ for } t = 0, \end{cases}$$

for the precipitation and dissolution. Here u denotes the cation concentration and is defined in the entire void space Ω , whereas v stands for the concentration of the

precipitate, which is defined only on the interior boundary Γ_G . These two concentrations, together with w modeling the actual value of the dissolution rate, are the unknown quantities.

In the above \vec{q} is the divergence-free fluid velocity, which is assumed to be known and to have a zero trace along the internal grain boundary Γ_G :

$$(1.3) \quad \vec{q} \in [H^1(\Omega)]^d, \quad \nabla \cdot \vec{q} = 0 \text{ in } \Omega, \quad \vec{q} = \vec{0} \text{ on } \Gamma_G.$$

By $H^1(\Omega)$ we mean the space of functions defined on Ω and having L^2 generalized derivatives. To avoid unnecessary technical complications we also assume that the fluid velocity \vec{q} is essentially bounded, $\vec{q} \in [L^\infty(\Omega)]^d$, and define

$$(1.4) \quad M_q = \|\vec{q}\|_{\infty, \Omega} < \infty.$$

For the Stokes model with homogeneous Dirichlet boundary conditions, the essential boundedness of \vec{q} holds if, for example, the domain is polygonal (see [16] or [20]).

The above equations are employing several functions, which are model-specific. Here we assume them to be given. By r we denote the precipitation rate. Assuming mass action kinetics, with $[\cdot]_+$ denoting the nonnegative cut,

$$(1.5) \quad [u]_+ = \begin{cases} 0 & \text{if } u < 0, \\ u & \text{if } u > 0, \end{cases}$$

the precipitation rate is defined by

$$(1.6) \quad r(u) = [u]_+^{\tilde{m}} [(\tilde{m}u - c)/\tilde{n}]_+^{\tilde{n}},$$

where \tilde{m} and \tilde{n} are the valences of the cation and the anion, respectively. As mentioned before, the total negative charge c is assumed to be known and constant in time and space. In a generalized framework, r satisfies the following:

- (A_r) (i) $r : \mathbb{R} \rightarrow [0, \infty)$ is locally Lipschitz in \mathbb{R} ;
(ii) there exists a unique $u_* \geq 0$, such that

$$r(u) = \begin{cases} 0 & \text{for } u \leq u_*, \\ \text{strictly increasing for } u > u_* & \text{with } r(\infty) = \infty. \end{cases}$$

Remark 1.1. In this setting, a unique u^* exists for which $r(u^*) = 1$. If $u = u^*$ for all t and x , then the system is in equilibrium: No precipitation or dissolution occurs, since the precipitation rate is balanced by the dissolution rate regardless of the presence or absence of crystals.

In (1.2₂), H stands for the Heaviside graph,

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

This implies that the dissolution rate is constant (scaled to 1) in the presence of crystals, i.e., for $v > 0$ somewhere on Γ_G . In the absence of crystals ($v = 0$), the overall rate is either zero, if $r(u) \leq 1$, or positive. In the first case we have $u < u^*$, and we speak about an undersaturated fluid since there are not sufficient ions for an effective

gain in the precipitate. This second situation is appearing in the oversaturated regime, when $u > u^*$. Then we take $w = 1$, and the overall rate is $r(u) - 1 > 0$. Following the detailed discussion in [6], this can be summarized as

$$(1.7) \quad w = \begin{cases} 0 & \text{if } v < 0, \\ \min\{r(u), 1\} & \text{if } v = 0, \\ 1 & \text{if } v > 0. \end{cases}$$

Finally, D in (1.1)–(1.2) denotes the diffusion coefficient. D_a represents the ratio of the characteristic precipitation/dissolution time scale and the characteristic transport time scale—the Damköhler number. Both D and D_a are assumed to be of moderate order $O(1)$. By ε we mean the ratio of the characteristic pore scale and the reference (macroscopic) length scale. In an appropriate scaling (see Remark 1.2 of [7]), this gives

$$(1.8) \quad \varepsilon \operatorname{meas}(\Gamma_G) \approx \operatorname{meas}(\Omega).$$

This balance is natural for a porous medium, where $\operatorname{meas}(\Gamma_G)$ denotes the total surface of the porous skeleton and $\operatorname{meas}(\Omega)$ the total void volume. Throughout this paper we keep the value of ε fixed. However, the convergence results are uniform with respect to ε and thus also for arbitrarily small values of ε .

The present setting is a simplification of the dissolution/precipitation model in [7]. However, the main difficulties that are associated with that model are still present here: The system (1.1)–(1.2) consists of a parabolic equation that is coupled through the boundary conditions to a differential inclusion defined on a lower-dimensional manifold. For ease of presentation we have considered here only the case of homogeneous Dirichlet boundary conditions on the external boundary Γ_D , but the results can be extended to more general cases. With $H^1_{0,\Gamma_D}(\Omega)$ being the subspace of $H^1(\Omega)$ functions having a zero trace on the external boundary Γ_D , for the initial data we assume the following:

(A_D) The initial data are assumed essentially bounded and nonnegative. Further, $u_I \in H^1_{0,\Gamma_D}(\Omega)$ and $v_I \in L^2(\Gamma_G)$.

Due to the occurrence of the multivalued dissolution rate, classical solutions do not exist, except for some particular cases. For defining a weak solution we consider the following sets:

$$\mathcal{U} := \{u \in L^2(0, T; H^1_{0,\Gamma_D}(\Omega)) : \partial_t u \in L^2(0, T; H^{-1}(\Omega))\},$$

$$\mathcal{V} := \{v \in H^1(0, T; L^2(\Gamma_G))\},$$

$$\mathcal{W} := \{w \in L^\infty(\Gamma_G^T), : 0 \leq w \leq 1\},$$

where by $H^{-1}(\Omega)$ we mean the dual of $H^1_{0,\Gamma_D}(\Omega)$. Here we have used standard notations in the functional analysis. In what follows $(\cdot, \cdot)_X$ stands for the usual scalar product in a Hilbert space X , or the duality pairing between H^{-1} and H^1 . With $t \in (0, T]$, by $(\cdot, \cdot)_{X^t}$ we mean the integration in time of $(\cdot, \cdot)_X$ on $(0, t)$.

DEFINITION 1.1. A triple $(u, v, w) \in \mathcal{U} \times \mathcal{V} \times \mathcal{W}$ is called a weak solution of (1.1) and (1.2) if $\{u(0), v(0)\} = \{u_I, v_I\}$ and if

$$(1.9) \quad (\partial_t u, \varphi)_{\Omega^T} + D(\nabla u, \nabla \varphi)_{\Omega^T} - (\tilde{q}u, \nabla \varphi)_{\Omega^T} = -\varepsilon \tilde{n}(\partial_t v, \varphi)_{\Gamma_G^T},$$

$$(1.10) \quad (\partial_t v, \theta)_{\Gamma_G^T} = D_a(r(u) - w, \theta)_{\Gamma_G^T},$$

$$w \in H(v) \quad \text{a.e. in } \Gamma_G^T$$

for all $(\varphi, \theta) \in L^2(0, T; H^1_{0, \Gamma_D}(\Omega)) \times L^2(\Gamma_G^T)$.

In the above definition the initial condition should be understood in the sense of L^2 functions. This makes sense since $\mathcal{U} \subset C([0, T]; L^2(\Omega))$ and $\mathcal{V} \subset C([0, T]; L^2(\Gamma_G))$ (see, for example, [31] or [36]). The existence of a weak solution is proven in [7, Theorem 2.21]. Moreover, with

$$(1.11) \quad M_u := \max\{\|u_I\|_{\infty, \Omega}, u^*\},$$

$$(1.12) \quad M_v := \max\{\|v_I\|_{\infty, \Omega}, 1\}, \quad C_v := \frac{r(M_u)D_a}{M_v},$$

a weak solution satisfies

$$(1.13) \quad \begin{aligned} 0 \leq u \leq M_u \quad &\text{a.e. in } \Omega^T, \\ 0 \leq v(t, \cdot) \leq M_v e^{C_v t} \quad &\text{for all } t \in [0, T] \text{ and a.e. on } \Gamma_G, \\ 0 \leq w \leq 1 \quad &\text{a.e. on } \Gamma_G^T, \end{aligned}$$

and

$$(1.14) \quad \begin{aligned} \|u(t)\|_{\Omega}^2 + \|\nabla u\|_{\Omega^T}^2 + \|\partial_t u\|_{L^2(0, T; H^{-1}(\Omega))}^2 \\ + \varepsilon \|v(t)\|_{\Gamma_G}^2 + \varepsilon \|\partial_t v\|_{\Gamma_G^T}^2 \leq C \end{aligned}$$

for all $0 \leq t \leq T$. Here $C > 0$ is a constant not depending on u, v, w , or ε . The proof is based on regularization arguments and provides a solution for which, in addition, we have

$$w = r(u) \quad \text{a.e. in } \{v = 0\} \cap \Gamma_G^T.$$

This is in good agreement with the definition in (1.7).

Finally we mention that (1.1) and (1.2) have a unique weak solution, as proven in [26].

2. The time discrete numerical scheme. In this section we analyze a semi-implicit numerical scheme for the system (1.1)–(1.2). To overcome the difficulties that are due to the multivalued dissolution rate, we approximate the Heaviside graph by

$$(2.1) \quad H_{\delta}(v) := \begin{cases} 0 & \text{if } v \leq 0, \\ v/\delta & \text{if } v \in (0, \delta), \\ 1 & \text{if } v \geq \delta, \end{cases}$$

where $\delta > 0$ is a small regularization parameter.

Next we consider a time stepping that is implicit in u and explicit in v . Though possible here as well, an implicit discretization of v would involve an additional non-linearity in v without bringing any significant improvement of the results.

With $N \in \mathbb{N}$, $\tau = T/N$, and $t_n = n\tau$ ($n = 0, \dots, N$), the approximation pair (u^n, v^n) of $(u(t_n), v(t_n))$ is the solution of the following problem.

Problem P_{\delta}^n. Given u^{n-1} and v^{n-1} compute $u^n \in H^1_{0, \Gamma_D}(\Omega)$ and $v^n \in L^2(\Gamma_G)$ such that

$$(2.2) \quad \begin{aligned} (u^n - u^{n-1}, \phi)_{\Omega} + \tau D(\nabla u^n, \nabla \phi)_{\Omega} - \tau(\bar{q}u^n, \nabla \phi)_{\Omega} \\ + \varepsilon \tilde{n}(v^n - v^{n-1}, \phi)_{\Gamma_G} = 0, \end{aligned}$$

$$(2.3) \quad (v^n, \theta)_{\Gamma_G} = (v^{n-1}, \theta)_{\Gamma_G} + \tau D_a(r(u^n) - H_{\delta}(v^{n-1}), \theta)_{\Gamma_G}$$

for all $\phi \in H_{0,\Gamma_D}^1(\Omega)$ and $\theta \in L^2(\Gamma_G)$.

Here $n = 1, \dots, N$, while $u^0 = u_I$ and $v^0 = v_I$. For consistency with the original setting, in (2.3) we approximate the dissolution rate $w(t_n)$ by

$$(2.4) \quad w^n := H_\delta(v^n).$$

To simplify the notations, we have given up the subscript δ for the solution triple (u^n, v^n, w^n) .

Remark 2.1. As we will see later, for guaranteeing the stability of the scheme the regularization parameter δ should be chosen such that $\delta \geq \tau D_a$. This is the only restriction that is related to the explicit discretization of v . Further, the convergence result is obtained under the assumption that the ratio τ/δ approaches 0 as $\tau \searrow 0$. This happens, for example, if $\delta = O(\tau^\alpha)$, with some $\alpha \in (0, 1)$, which is consistent with the previous restriction. To simplify the presentation, from now on we assume $\delta = D_a\sqrt{\tau}$. Then the stability condition $\delta \geq \tau D_a$ is ensured whenever $\tau \leq 1$, which is a mild restriction.

Due to the explicit discretization of v , the ion transport equation in Problem P_δ^n can be decoupled from the time discrete precipitation/dissolution equation. Replacing the Γ_G -scalar product in (2.2) by the last term in (2.3), we end up with an elliptic problem having a nonlinear boundary condition on Γ_G . Specifically, given u^{n-1} and v^{n-1} , we seek for $u^n \in H_{0,\Gamma_D}^1(\Omega)$ such that

$$\begin{aligned} (u^n - u^{n-1}, \phi)_\Omega + \tau D(\nabla u^n, \nabla \phi)_\Omega - \tau(\tilde{q}u^n, \nabla \phi)_\Omega \\ + \tau \epsilon \tilde{n} D_a (r(u^n) - H_\delta(v^{n-1}), \theta)_{\Gamma_G} = 0 \end{aligned}$$

for all $\phi \in H_{0,\Gamma_D}^1(\Omega)$. Since r is monotone and Lipschitz, standard monotonicity methods provide the existence and uniqueness for the above problem (see, e.g., [34, Chapter 10]). Alternatively, a contraction argument is described in section 3. This writing is used there as the starting point for constructing a linear iterative scheme for solving Problem P_δ^n . The fixed-point approach proving the convergence of the iteration procedure discussed in section 3 can also be employed for the existence and uniqueness of a u^n solving the nonlinear problem above. Having u^n, v^n can be determined straightforwardly from (2.3). In this way we obtain the following.

LEMMA 2.2. *Problem P_δ^n has a unique solution pair (u^n, v^n) .*

2.1. Stability in L^∞ . All of the estimates in this section should be interpreted in the a.e. sense. As follows from (1.13), the concentrations u and v as well as the dissolution rate w are nonnegative and bounded. Here we prove similar results for the time discrete concentrations u^n and v^n . The bounds for w^n follow straightforwardly from (2.4).

LEMMA 2.3. *Assume $\tau \leq 1$ and that u^{n-1} and v^{n-1} are nonnegative. Then u^n and v^n are nonnegative as well.*

Proof. We start with the estimate in v^n . With $[\cdot]_-$ denoting the nonpositive cut (see also (1.5)), we test (2.3) with $\theta := [v^n]_-$ and obtain

$$\|[v^n]_-\|_{\Gamma_G}^2 = \tau D_a (r(u^n), [v^n]_-)_{\Gamma_G} + (v^{n-1} - \tau D_a H_\delta(v^{n-1}), [v^n]_-)_{\Gamma_G}.$$

In view of (A_r) , the first term on the right is nonpositive. Further, since $v^{n-1} \geq 0$ and $\delta = D_a\sqrt{\tau}$, by the construction of H_δ we have

$$v^{n-1} - \tau D_a H_\delta(v^{n-1}) \geq v^{n-1}(1 - \tau D_a/\delta) \geq 0$$

a.e. on Γ_G . Hence the second term on the right is nonpositive as well. This yields

$$\|[v^n]_-\|_{\Gamma_G}^2 \leq 0,$$

implying the assertion for v^n .

For proving that u^n is nonnegative we proceed in a similar manner. Testing (2.2) with $\phi := [u^n]_-$ gives

$$(2.5) \quad \begin{aligned} & \|[u^n]_-\|_{\Omega}^2 + \tau D \|\nabla [u^n]_-\|_{\Omega}^2 - \tau (\vec{q} u^n, \nabla [u^n]_-)_{\Omega} \\ & + \epsilon \tilde{n} (v^n - v^{n-1}, [u^n]_-)_{\Gamma_G} = (u^{n-1}, [u^n]_-)_{\Omega}. \end{aligned}$$

The first two terms in the above are nonnegative, whereas the third one vanishes. This follows from

$$\begin{aligned} (\vec{q} u^n, \nabla [u^n]_-)_{\Omega} &= \frac{1}{2} (\vec{q}, \nabla [u^n]_-^2)_{\Omega} \\ &= \frac{1}{2} (\vec{\nu} \cdot \vec{q}, [u^n]_-^2)_{\Gamma_D \cup \Gamma_G} - \frac{1}{2} (\nabla \cdot \vec{q}, [u^n]_-^2)_{\Omega} \end{aligned}$$

and the boundary conditions on $\partial\Omega$, since $\nabla \cdot \vec{q} = 0$ in Ω .

Further, since $[u^n]_- \leq 0$ a.e. and it belongs to $H_{0,\Gamma_D}^1(\Omega)$, its trace $[u^n]_-|_{\Gamma_G}$ is a nonpositive $L^2(\Gamma_G)$ function. Testing (2.3) with $[u^n]_-|_{\Gamma_G}$ gives

$$\begin{aligned} (v^n - v^{n-1}, [u^n]_-)_{\Gamma_G} &= \tau D_a (r(u^n) - H_{\delta}(v^{n-1}), [u^n]_-)_{\Gamma_G} \\ &= -\tau D_a (H_{\delta}(v^{n-1}), [u^n]_-)_{\Gamma_G} \geq 0, \end{aligned}$$

where we have used (A_r) and the positivity of H_{δ} .

Finally, the term on the right in (2.5) is nonpositive, since $u^{n-1} \geq 0$. In this way we obtain $[u^n]_- = 0$ a.e. in Ω , implying the result. \square

Now we turn our attention to the upper bounds for u^n and v^n . First, with M_u defined in (1.11) we have the following.

LEMMA 2.4. *If $u^{n-1} \leq M_u$, then the same holds for u^n .*

Proof. We test (2.2) with $\phi := [u^n - M_u]_+$, the nonnegative part of $u^n - M_u$. This gives

$$\begin{aligned} & \|[u^n - M_u]_+\|_{\Omega}^2 + \tau D \|\nabla [u^n - M_u]_+\|_{\Omega}^2 - \tau (\vec{q} u^n, \nabla [u^n - M_u]_+)_{\Omega} \\ & = (u^{n-1} - M_u, [u^n - M_u]_+)_{\Omega} - \epsilon \tilde{n} (v^n - v^{n-1}, [u^n - M_u]_+)_{\Gamma_G}. \end{aligned}$$

Arguing as in the proof of Lemma 2.3, we first observe that the convection term vanishes. Further, since $u^{n-1} \leq M_u$, the first term on the right is nonpositive. Finally, for the last term we have

$$(v^n - v^{n-1}, [u^n - M_u]_+)_{\Gamma_G} = \tau D_a (r(u^n) - H_{\delta}(v^{n-1}), [u^n - M_u]_+)_{\Gamma_G}.$$

By the definition of M_u , whenever $u^n \geq M_u$ we have $r(u^n) \geq 1 \geq H_{\delta}(v^{n-1})$. This implies the positivity of the above scalar product. We are therefore left with

$$\|[u^n - M_u]_+\|_{\Omega}^2 + \tau D \|\nabla [u^n - M_u]_+\|_{\Omega}^2 \leq 0,$$

implying that $u^n \leq M_u$. \square

Remark 2.5. Since for the initial data we assume $0 \leq u_I \leq M_u$ and $0 \leq v_I$, Lemmas 2.3 and 2.4 show that $0 \leq u^n \leq M_u$ and $0 \leq v^n$ for all $n = 0, \dots, N$.

Upper estimates for v^n can be obtained as for u^n .

LEMMA 2.6. *With M_v and C_v defined in (1.12), assume that $v^{n-1} \leq M_v e^{C_v(n-1)\tau}$. Then $v^n \leq M_v e^{C_v n\tau}$.*

Proof. Testing (2.3) with $\theta := [v^n - M_v e^{C_v n\tau}]_+$ gives

$$(2.6) \quad \begin{aligned} \|[v^n - M_v e^{C_v n\tau}]_+\|_{\Gamma_G}^2 &= (v^{n-1} - M_v e^{C_v(n-1)\tau}, [v^n - M_v e^{C_v n\tau}]_+)_{\Gamma_G} \\ &\quad + M_v (e^{C_v(n-1)\tau} - e^{C_v n\tau}, [v^n - M_v e^{C_v n\tau}]_+)_{\Gamma_G} \\ &\quad + \tau D_a (r(u^n) - H_\delta(v^{n-1}), [v^n - M_v e^{C_v n\tau}]_+)_{\Gamma_G}. \end{aligned}$$

We denote the terms on the right by I_1 , I_2 , and I_3 . We first notice that the assumption on v^{n-1} implies $I_1 \leq 0$. Further, since $0 \leq u^n \leq M_u$, $H_\delta(v^{n-1}) \geq 0$, and due to the monotonicity of r we obtain

$$I_3 \leq \tau D_a (r(M_u), [v^n - M_v e^{C_v n\tau}]_+)_{\Gamma_G}.$$

Recalling (1.12), this gives

$$I_2 + I_3 \leq M_v (\tau C_v + e^{C_v(n-1)\tau} (1 - e^{\tau C_v}), [v^n - M_v e^{C_v n\tau}]_+)_{\Gamma_G} \leq 0.$$

Here we have used the elementary inequality $e^x \geq 1 + x$, as well as $e^{C_v(n-1)\tau} \geq 1$. In this way (2.6) becomes

$$\|[v^n - M_v e^{C_v n\tau}]_+\|_{\Gamma_G}^2 \leq 0,$$

implying the upper bounds for v^n . \square

Remark 2.7. As before, since $v_I \leq M_v$, it follows that $v^n \leq M_v e^{C_v n\tau}$ for all $n = 1, \dots, N$.

Remark 2.8. The essential bounds provided by Lemmas 2.3, 2.4, and 2.6 are uniform in δ , whereas τ appears only in the upper bounds for v^n . But for any $0 \leq n \leq N$ one has $n\tau = t_n \leq T$, and we have $v^n \leq M_v e^{C_v t_n} \leq M_v e^{C_v T}$, which is τ -independent as well.

2.2. A priori estimates. We continue the analysis of the numerical scheme (2.2)–(2.3) by giving some energy estimates for the sequence of time discrete concentrations $\{(u^n, v^n), n = 0, \dots, N\}$. We start with the estimates in v , which are depending on $\text{meas}(\Gamma_G)$.

LEMMA 2.9. *For any $n \geq 1$ we have*

$$(2.7) \quad \|v^n - v^{n-1}\|_{\Gamma_G} \leq \tau D_a r(M_u) \text{meas}(\Gamma_G)^{1/2} \quad \text{and}$$

$$(2.8) \quad \|v^n\|_{\Gamma_G} \leq \|v_I\|_{\Gamma_G} + n\tau D_a r(M_u) \text{meas}(\Gamma_G)^{1/2}.$$

Proof. Testing (2.3) with $\theta := [v^n - v^{n-1}] \in L^2(\Gamma_G)$ and applying Cauchy’s inequality gives

$$(2.9) \quad \|v^n - v^{n-1}\|_{\Gamma_G}^2 \leq \tau D_a \|r(u^n) - H_\delta(v^{n-1})\|_{\Gamma_G} \|v^n - v^{n-1}\|_{\Gamma_G}.$$

The essential bounds on u^n and v^n , together with the assumptions on r and H_δ , imply $-1 \leq r(u^n) - H_\delta(v^{n-1}) \leq r(M_u)$. By (1.11) we have $r(M_u) \geq 1$, implying the first estimates.

In a similar manner, by taking $\theta := v^n \in L^2(\Gamma_G)$ in (2.3) and applying the Cauchy inequality we obtain

$$(2.10) \quad \|v^n\|_{\Gamma_G}^2 \leq \|v^{n-1}\|_{\Gamma_G} \|v^n\|_{\Gamma_G} + \tau D_a r(M_u) \text{meas}(\Gamma_G)^{1/2} \|v^n\|_{\Gamma_G}.$$

By dividing by $\|v^n\|_{\Gamma_G}$ and applying the inequality backward we immediately obtain the estimate (2.8). \square

Remark 2.10. Notice that the estimates in Lemma 2.9 are δ -independent. Next, for $n \leq N$, the term on the right in (2.8) is bounded uniformly in τ as well. Finally, due to (1.8) we can replace $\text{meas}(\Gamma_G)$ by C/ϵ , where C does not depend on δ , τ , or ϵ .

Now we proceed by the estimates for u .

LEMMA 2.11. *Assume $\tau \leq \tau_0$, with $\tau_0 > 0$ a fixed value that will be given below. For the time discrete solute concentrations we have*

$$(2.11) \quad \tau \sum_{n=1}^N \|\nabla u^n\|_{\Omega}^2 \leq C,$$

$$(2.12) \quad \sum_{n=1}^N \|u^n - u^{n-1}\|_{\Omega}^2 \leq C\sqrt{\tau},$$

$$(2.13) \quad \tau \sum_{n=1}^N \|\nabla(u^n - u^{n-1})\|_{\Omega}^2 \leq C\sqrt{\tau},$$

$$(2.14) \quad \sum_{n=1}^N \|u^n - u^{n-1}\|_{\Gamma_G}^2 \leq C.$$

Here C is a constant that does not depend on δ and τ .

Proof. We start by testing (2.2) with $\phi = u^n$. This gives

$$(2.15) \quad (u^n - u^{n-1}, u^n)_{\Omega} + \tau D \|\nabla u^n\|_{\Omega}^2 + \tau (\tilde{q}u^n, \nabla u^n)_{\Omega} + \epsilon \tilde{n}(v^n - v^{n-1}, u^n)_{\Gamma_G} = 0.$$

We denote the terms on the right by T_1, \dots, T_4 . We have

$$T_1 = \frac{1}{2} (\|u^n\|_{\Omega}^2 - \|u^{n-1}\|_{\Omega}^2 + \|u^n - u^{n-1}\|_{\Omega}^2).$$

Furthermore, T_2 is nonnegative, and T_3 vanishes as argued in the proof of Lemma 2.3.

Before estimating the last term we notice the existence of positive constants C_1 and C_2 such that

$$(2.16) \quad \|\varphi\|_{\Gamma_G}^2 \leq C_1 \|\varphi\|_{\Omega}^2 + C_2 \|\varphi\|_{\Omega} \|\nabla \varphi\|_{\Omega}$$

for all $\varphi \in H_{0,\Gamma_D}^1(\Omega)$. This can be obtained by following the proof of the trace theorem (e.g., see [10, Theorem 1.5.1.10]). By the inequality of means

$$(2.17) \quad ab \leq \frac{1}{4\rho} a^2 + \rho b^2 \quad \text{for all } a, b, \text{ and } \rho > 0,$$

we get

$$(2.18) \quad \|\varphi\|_{\Gamma_G}^2 \leq \left(C_1 + \frac{C_2^2}{4\rho} \right) \|\varphi\|_{\Omega}^2 + \rho \|\nabla \varphi\|_{\Omega}^2.$$

Here $\rho > 0$ can be taken arbitrarily small.

With $M := \varepsilon \tilde{n} D_a r(M_u) \text{meas}(\Gamma_G)^{1/2}$, we use (2.7) to estimate T_4 :

$$|T_4| \leq \tau M \|u^n\|_{\Gamma_G} \leq \frac{\tau M^2}{4} + \tau \|u^n\|_{\Gamma_G}^2.$$

Now we use (2.18) with $\rho = D/2$ and obtain

$$|T_4| \leq \frac{\tau M^2}{4} + \tau \left(C_1 + \frac{C_2^2}{2D} \right) \|u^n\|_{\Omega}^2 + \frac{\tau D}{2} \|\nabla u^n\|_{\Omega}^2.$$

Using the estimates above into (2.15), summing for $n = 1, \dots, N$, and multiplying the result by 2 yields

$$\|u^N\|_{\Omega}^2 + \sum_{n=1}^N \|u^n - u^{n-1}\|_{\Omega}^2 + \tau D \sum_{n=1}^N \|\nabla u^n\|_{\Omega}^2 \leq \|u_I\|_{\Omega}^2 + \frac{TM^2}{2} + C,$$

where $C = T(C_1 + C_2^2/(2D))M_u^2 \text{meas}(\Omega)$. This estimate follows by the essential bounds on u^n . An alternative proof can be given based on the discrete Gronwall lemma. In this way we have proven (2.11). Notice that we have also obtained

$$\sum_{n=1}^N \|u^n - u^{n-1}\|_{\Omega}^2 \leq C,$$

which is not as good as (2.12).

To proceed with (2.12) and (2.13) we notice that, since $u_I \in H_{0,\Gamma_D}^1$, $u^n - u^{n-1}$ is a H_{0,Γ_D}^1 function for all $n \geq 1$. Testing (2.2) with $u^n - u^{n-1}$ gives

$$(2.19) \quad \|u^n - u^{n-1}\|_{\Omega}^2 + \tau D (\nabla u^n, \nabla (u^n - u^{n-1}))_{\Omega} - \tau (\tilde{q} u^n, \nabla (u^n - u^{n-1}))_{\Omega} + \varepsilon \tilde{n} (v^n - v^{n-1}, u^n - u^{n-1})_{\Omega} = 0.$$

Denoting the terms in the above by I_1, \dots, I_4 , we have

$$I_2 = \frac{\tau D}{2} (\|\nabla u^n\|_{\Omega}^2 - \|\nabla u^{n-1}\|_{\Omega}^2 + \|\nabla (u^n - u^{n-1})\|_{\Omega}^2).$$

Recalling (1.4), the inequality of means gives

$$\begin{aligned} |I_3| &= \tau (\nabla \cdot (\tilde{q} u^n), u^n - u^{n-1})_{\Omega} \leq \tau M_q \|\nabla u^n\|_{\Omega} \|u^n - u^{n-1}\|_{\Omega} \\ &\leq \frac{1}{2} \|u^n - u^{n-1}\|_{\Omega}^2 + \frac{\tau^2 M_q^2}{2} \|\nabla u^n\|_{\Omega}^2. \end{aligned}$$

With M defined above, for I_4 we use the estimate (2.7) and obtain

$$|I_4| \leq \varepsilon \tilde{n} \|v^n - v^{n-1}\|_{\Gamma_G} \|u^n - u^{n-1}\|_{\Gamma_G} \leq \frac{(\tau M)^2}{4\mu_1} + \mu_1 \|u^n - u^{n-1}\|_{\Gamma_G}^2,$$

where $\mu_1 > 0$ will be chosen below. Now we can take $\rho = \tau D/(4\mu_1)$ into (2.18) to obtain

$$|I_4| \leq \frac{(\tau M)^2}{4\mu_1} + \mu_1 \left(C_1 + \frac{\mu_1 C_2^2}{\tau D} \right) \|u^n - u^{n-1}\|_{\Omega}^2 + \frac{\tau D}{4} \|\nabla (u^n - u^{n-1})\|_{\Omega}^2.$$

Using the above estimates into (2.19), taking $\mu_1 = \sqrt{\tau D}/(2C_2)$, multiplying the result by 2, and summing up for $n = 1, \dots, N$, (2.11) gives

$$\begin{aligned} & \left(\frac{1}{2} - \frac{C_1\sqrt{\tau D}}{C_2} \right) \sum_{n=1}^N \|u^n - u^{n-1}\|_{\Omega}^2 + \frac{\tau D}{2} \sum_{n=1}^N \|\nabla(u^n - u^{n-1})\|_{\Omega}^2 \\ & \leq \tau D \|\nabla u_I\|_{\Omega}^2 + \frac{TM^2C_2}{\sqrt{D}}\tau^{1/2} + \tau C. \end{aligned}$$

For $\tau_0 := C_2^2/(16C_1^2D)$ and $\tau \leq \tau_0$, since $u_I \in H^1_{0,\Gamma_D}$, the inequality above immediately implies (2.12) and (2.13).

Finally, using (2.18) with $\rho = \tau^{1/2}$, (2.14) is a direct consequence of (2.12) and (2.13). \square

Remark 2.12. As in Remark 2.10, if the medium is ϵ -periodic, the constant C in Lemma 2.11 does not depend on ϵ . To see this we recall (1.8), and Lemma 3 of [12], saying that there exists a constant $C > 0$, independent of ϵ , such that

$$\epsilon \|\varphi\|_{\Gamma_G}^2 \leq C (\|\varphi\|_{\Omega}^2 + \epsilon^2 \|\nabla \varphi\|_{\Omega}^2)$$

for all $\varphi \in H^1(\Omega)$. Then the boundary term in (2.19) yields a constant C which does not depend on ϵ as well.

2.3. Convergence. In this part we proceed by proving the convergence of the numerical scheme defined in (2.2)–(2.3) to a weak solution of the system (1.1)–(1.2), as given in Definition 1.1. The multivalued dissolution rate hinders us in obtaining useful error estimates. Therefore convergence will be achieved by compactness arguments. In doing so we mainly follow the ideas in [7].

By considering the sequence of time discrete triples $\{(u^n, v^n, w^n), n = 1, \dots, N\}$ solving Problem P_{δ}^n , where w^n is defined in (2.4), we construct an approximation of the solution of (1.1) and (1.2) for all times $t \in [0, T]$. Specifically, define for any $n = 1, \dots, N$ and $t \in (t_{n-1}, t_n]$

$$(2.20) \quad Z^{\tau}(t) := z^n \frac{(t - t_{n-1})}{\tau} + z^{n-1} \frac{(t_n - t)}{\tau},$$

where (z, Z) stands for (u, U) or (v, V) , and define

$$(2.21) \quad W^{\tau}(t) := H_{\delta}(V^{\tau}(t)).$$

Notice that U_{τ} , V_{τ} , and W_{τ} depend not only on τ but also on the regularization parameter δ .

For the time continuous triple $\{U^{\tau}, V^{\tau}, W^{\tau}\}$ we can use the uniform L^{∞} bounds, as well as the a priori estimates in Lemmas 2.9 and 2.11, to derive δ -independent estimates that are similar to those for the solution defined in Definition 1.1 (see [7]).

LEMMA 2.13. *Assume $\delta \geq \tau D_a$. Then for $(U^{\tau}, V^{\tau}, W^{\tau})$ we have*

$$(2.22) \quad 0 \leq U^{\tau} \leq M_u \quad \text{a.e. in } \Omega^T,$$

$$(2.23) \quad 0 \leq V^{\tau} \leq M_v e^{CT}, \quad 0 \leq W^{\tau} \leq 1 \quad \text{a.e. in } \Gamma_G^T,$$

$$(2.24) \quad \|U^{\tau}(t)\|_{\Omega} + \|V^{\tau}(t)\|_{\Gamma_G}^2 \leq C \quad \text{for all } 0 \leq t \leq T,$$

$$(2.25) \quad \|\partial_t U^{\tau}\|_{L^2(0,T;H^{-1}(\Omega))}^2 + \|\nabla U^{\tau}\|_{\Omega^T}^2 + \|\partial_t V^{\tau}\|_{\Gamma_G^T}^2 \leq C.$$

Here $C > 0$ is a constant that does not depend on τ or δ .

Proof. The essential bounds in (2.22) and (2.23) are a direct consequence of Lemmas 2.3, 2.4, and 2.6 and (2.4). The same holds for (2.24), for which we employ the stability estimates in Lemmas 2.9 and 2.11.

To proceed with the gradient estimates in (2.25) we notice that

$$\begin{aligned} \int_0^T \|\nabla U^\tau(t)\|_\Omega^2 dt &\leq 2 \sum_{n=1}^N \tau \|\nabla u^{n-1}\|_\Omega^2 \\ &\quad + \int_{t_{n-1}}^{t_n} 2 \frac{(t - t_{n-1})^2}{\tau^2} \|\nabla(u^n - u^{n-1})\|_\Omega^2 dt \\ &\leq 2\tau \sum_{n=1}^N \|\nabla u^{n-1}\|_\Omega^2 + \frac{2\tau}{3} \sum_{n=1}^N \|\nabla(u^n - u^{n-1})\|_\Omega^2 \leq C. \end{aligned}$$

Here we have used the estimate in (2.11) and (2.13).

The estimate on $\partial_t V^\tau$ follows by (2.7):

$$\int_0^T \|\partial_t V^\tau(t)\|_{\Gamma_G}^2 dt = \sum_{n=1}^N \int_{t_{n-1}}^{t_n} \left\| \frac{v^n - v^{n-1}}{\tau} \right\|_{\Gamma_G}^2 dt \leq CN\tau = CT.$$

Finally, for estimating $\partial_t U^\tau$ we notice that

$$(\partial_t U^\tau(t), \phi) = \left(\frac{u^n - u^{n-1}}{\tau}, \phi \right)$$

for all $\phi \in H_{0,\Gamma_D}^1(\Omega)$ and all $t \in (t_{n-1}, t_n]$. By (2.2) this gives

$$\begin{aligned} |(\partial_t U^\tau, \phi)| &\leq D \|\nabla u^n\|_\Omega \|\nabla \phi\|_\Omega + M_q \|\nabla u^n\|_\Omega \|\phi\|_\Omega \\ &\quad + \frac{\epsilon \tilde{n}}{\tau} \|v^n - v^{n-1}\|_{\Gamma_G} \|\phi\|_{\Gamma_G}. \end{aligned}$$

By using the trace theorem we obtain

$$\begin{aligned} (2.26) \quad |(\partial_t U^\tau, \phi)| &\leq (D + M_q) \|\nabla u^n\|_\Omega \|\phi\|_{H^1(\Omega)} \\ &\quad + C(\Omega) \frac{\epsilon \tilde{n}}{\tau} \|v^n - v^{n-1}\|_{\Gamma_G} \|\phi\|_{H^1(\Omega)} \end{aligned}$$

for any $\phi \in H_{0,\Gamma_D}^1(\Omega)$. This implies that

$$(2.27) \quad \|\partial_t U^\tau(t)\|_{H^{-1}(\Omega)} \leq C \left(\|\nabla u^n\|_\Omega + \frac{\epsilon \tilde{n}}{\tau} \|v^n - v^{n-1}\|_{\Gamma_G} \right)$$

for all $t \in (t_{n-1}, t_n]$, and the remaining part is a direct consequence of the L^∞ and stability estimates. \square

Remark 2.14. For an ϵ -periodic medium, the estimates in Lemma 2.13 can be made ϵ -independent. This follows from Remarks 2.10 and 2.12. In this case the estimates (2.24) and (2.25) become

$$\begin{aligned} \|U^\tau(t)\|_\Omega + \|\partial_t U^\tau\|_{L^2(0,T;H^{-1}(\Omega))}^2 + \|\nabla U^\tau\|_{\Omega T}^2 \\ + \epsilon \left(\|V^\tau(t)\|_{\Gamma_G}^2 + \|\partial_t V^\tau\|_{\Gamma_G}^2 \right) \leq C \end{aligned}$$

for all $0 \leq t \leq T$, where C does not depend on τ , δ , or ε .

Having the τ and δ uniform estimates in Lemma 2.13, we can proceed by sending τ and δ to 0. For any $\tau > 0$ and $\delta = \sqrt{\tau}D_a \geq \tau D_a$ we have $(U^\tau, V^\tau, W^\tau) \in \mathcal{U} \times \mathcal{V} \times L^\infty(\Gamma_G^T)$. Obviously $\tau \searrow 0$ implies the same for δ , as well as for the ratio τ/δ . Compactness arguments give the existence of a triple $(u, v, w) \in \mathcal{U} \times \mathcal{V} \times L^\infty(\Gamma_G^T)$ and a subsequence $\tau \searrow 0$ such that

- (a) $U^\tau \rightharpoonup u$ weakly in $L^2((0, T); H_{0, \Gamma_D}^1(\Omega))$,
- (b) $\partial_t U^\tau \rightharpoonup \partial_t u$ weakly in $L^2((0, T); H^{-1}(\Omega))$,
- (c) $V^\tau \rightharpoonup v$ weakly in $L^2((0, T); L^2(\Gamma_G))$,
- (d) $\partial_t V^\tau \rightharpoonup \partial_t v$ weakly in $L^2((0, T); L^2(\Gamma_G))$,
- (e) $W^\tau \rightharpoonup w$ weak star in $L^\infty(\Gamma_G^T)$.

It remains to show that the limit triple (u, v, w) solves (1.1)–(1.2) weakly. By the uniqueness of the solution, this would actually imply that, along any sequence $\tau \searrow 0$, the approximating triple (U^τ, V^τ, W^τ) converges to (u, v, w) . This result is proven in the following.

THEOREM 2.15. *The limit triple (u, v, w) is the weak solution of (1.1)–(1.2) in the sense of Definition 1.1. Moreover, for the dissolution rate we have*

$$w = r(u) \quad \text{a.e. in } \{v = 0\} \cap \Gamma_G^T,$$

meaning that w satisfies (1.7).

Proof. By the weak convergence, all of the estimates stated in Lemma 2.13 hold for the limit triple (u, v, w) . Furthermore, for any $t \in (t_{n-1}, t_n]$, by (2.2) we have

$$\begin{aligned} (2.28) \quad & (\partial_t U^\tau(t), \phi)_\Omega + D(\nabla U^\tau(t), \nabla \phi)_\Omega \\ & + (\nabla \cdot (\vec{q} U^\tau(t)), \phi)_\Omega + \varepsilon \tilde{n}(\partial_t V^\tau(t), \phi)_{\Gamma_G} \\ & = D(\nabla(U^\tau(t) - u^n), \nabla \phi)_\Omega + (\nabla \cdot (\vec{q}(U^\tau(t) - u^n)), \phi)_\Omega \end{aligned}$$

for all $\phi \in H_{0, \Gamma_D}^1(\Omega)$. Denoting the terms on the right by $I_1(t)$ and $I_2(t)$, taking $\phi \in L^2(0, T; H_{0, \Gamma_D}^1(\Omega))$, and integrating (2.28) in time gives

$$\begin{aligned} (2.29) \quad & (\partial_t U^\tau, \phi)_{\Omega^T} + D(\nabla U^\tau, \nabla \phi)_{\Omega^T} \\ & + (\nabla \cdot (\vec{q} U^\tau), \phi)_{\Omega^T} + \varepsilon \tilde{n}(\partial_t V^\tau, \phi)_{\Gamma_G^T} \\ & = \sum_{n=1}^N \int_{t_{n-1}}^{t_n} I_1(t) + I_2(t) dt. \end{aligned}$$

The definition (2.20) of U^τ implies for almost all $0 \leq t \leq T$

$$(2.30) \quad |I_1(t)| \leq D \frac{t_n - t}{\tau} \|\nabla(u^n - u^{n-1})\|_\Omega \|\nabla \phi\|_\Omega$$

and

$$(2.31) \quad |I_2(t)| \leq M_q \frac{t_n - t}{\tau} \|u^n - u^{n-1}\|_\Omega \|\nabla \phi\|_\Omega.$$

In (2.31) we have integrated by parts and used the essential bounds (1.4) on \vec{q} . Now

we can proceed by estimating the terms on the right in (2.29). For I_1 we get

$$\begin{aligned} \left| \sum_{n=1}^N \int_{t_{n-1}}^{t_n} I_1(t) dt \right| &\leq \sum_{n=1}^N \int_{t_{n-1}}^{t_n} \frac{t_n - t}{\tau} D \|\nabla(u^n - u^{n-1})\|_{\Omega} \|\nabla\phi(t)\|_{\Omega} dt \\ &\leq \sum_{n=1}^N \left(\frac{\tau}{3} D^2 \|\nabla(u^n - u^{n-1})\|_{\Omega}^2 \right)^{\frac{1}{2}} \left(\int_{t_{n-1}}^{t_n} \|\nabla\phi(t)\|_{\Omega}^2 dt \right)^{\frac{1}{2}} \\ &\leq \frac{1}{2\sqrt{3}} \tau^{\frac{1}{4}} \int_0^T \|\nabla\phi(t)\|_{\Omega}^2 dt + \frac{\tau^{\frac{3}{4}}}{2\sqrt{3}} \sum_{n=1}^N D^2 \|\nabla(u^n - u^{n-1})\|_{\Omega}^2 \\ &\leq \frac{1}{2\sqrt{3}} \left(\int_0^T \|\nabla\phi(t)\|_{\Omega}^2 dt + C \right) \tau^{\frac{1}{4}}. \end{aligned}$$

In the above we have used the inequality of means (2.17) with $\rho = \tau^{1/4}$, as well as the estimates (2.12) and (2.13). In a similar manner, for I_2 we get

$$\left| \sum_{n=1}^N \int_{t_{n-1}}^{t_n} I_2(t) dt \right| \leq \left(\frac{1}{2\sqrt{3}} \int_0^T \|\nabla\phi(t)\|_{\Omega}^2 dt + C\tau^{\frac{1}{2}} \right) \tau^{\frac{1}{4}}.$$

Letting $\tau \searrow 0$, the weak convergence of U^τ and V^τ as well as the estimates above imply that u and v satisfy (1.9).

For the dissolution-precipitation equation (1.10) we start by analyzing the behavior of U^τ on Γ_G^T . The a priori estimates, together with Lemma 9 and Corollary 4 of [31], imply

$$U^\tau \rightarrow u \quad \text{strongly in} \quad C([0, T]; H^{-s}(\Omega)) \cap L^2(0, T; H^s(\Omega))$$

for any $s \in (0, 1)$. Then the trace theorem (see, for example, Satz 8.7 of [36]) gives

$$U^\tau \rightarrow u \quad \text{strongly in} \quad L^2(\Gamma_G^T).$$

Taking into account the Lipschitz continuity of r , this yields

$$r(U^\tau) \rightarrow r(u) \quad \text{strongly in} \quad L^2(\Gamma_G^T).$$

Further we proceed as for (1.9). For any $t_{n-1} < t \leq t_n$ and $\theta \in L^2(\Gamma_G)$ we rewrite (2.3) as

$$\begin{aligned} (2.32) \quad (\partial_t V^\tau(t), \theta)_{\Gamma_G} &= D_a(r(U^\tau(t)) - W^\tau(t), \theta)_{\Gamma_G} \\ &\quad + D_a(r(u^n) - r(U^\tau(t)), \theta)_{\Gamma_G} \\ &\quad + D_a(W^\tau(t) - H_\delta(v^{n-1}), \theta)_{\Gamma_G}. \end{aligned}$$

Denoting the last two terms on the right by $I_3(t)$ and $I_4(t)$, with $\theta \in L^2(\Gamma_G^T)$, we integrate (2.32) in time and obtain

$$\begin{aligned} (2.33) \quad (\partial_t V^\tau, \theta)_{\Gamma_G^T} &= D_a(r(U^\tau) - W^\tau, \theta)_{\Gamma_G^T} \\ &\quad + \sum_{n=1}^N \int_{t_{n-1}}^{t_n} I_3(t) + I_4(t) dt. \end{aligned}$$

For almost all $0 \leq t \leq T$, since r and H_δ are Lipschitz, we use the definition of V^τ and W^τ in (2.20) and (2.21) to obtain

$$(2.34) \quad |I_3(t)| \leq D_a L_r \frac{(t_n - t)}{\tau} \|u^n - u^{n-1}\|_{\Gamma_G} \|\theta\|_{\Gamma_G}$$

and

$$(2.35) \quad |I_4(t)| \leq \frac{D_a}{\delta} \frac{(t_n - t)}{\tau} \|v^n - v^{n-1}\|_{\Gamma_G} \|\theta\|_{\Gamma_G},$$

respectively. Using the estimate in (2.14), the first sum in (2.33) is bounded by

$$\begin{aligned} \left| \sum_{n=1}^N \int_{t_{n-1}}^{t_n} I_3(t) dt \right| &\leq D_a L_r \sum_{n=1}^N \int_{t_{n-1}}^{t_n} \frac{t_n - t}{\tau} \|u^n - u^{n-1}\|_{\Gamma_G} \|\theta(t)\|_{\Gamma_G} dt \\ &\leq D_a L_r \sum_{n=1}^N \left(\frac{\tau}{3} \|u^n - u^{n-1}\|_{\Gamma_G}^2 \right)^{\frac{1}{2}} \left(\int_{t_{n-1}}^{t_n} \|\theta(t)\|_{\Gamma_G}^2 dt \right)^{\frac{1}{2}} \\ &\leq \frac{D_a L_r}{2\sqrt{3}} \left(\|\theta\|_{\Gamma_G^T}^2 + \sum_{n=1}^N \|u^n - u^{n-1}\|_{\Gamma_G}^2 \right) \tau^{\frac{1}{2}} \\ &\leq \frac{D_a L_r}{2\sqrt{3}} \left(\|\theta\|_{\Gamma_G^T}^2 + C \right) \tau^{\frac{1}{2}}. \end{aligned}$$

In the above we have used the inequality of means (2.17) with $\rho = \tau^{1/2}$. Similarly, for the last sum in (2.33), by (2.7) we get

$$\begin{aligned} \left| \sum_{n=1}^N \int_{t_{n-1}}^{t_n} I_4(t) dt \right| &\leq \frac{D_a}{\delta} \sum_{n=1}^N \int_{t_{n-1}}^{t_n} \frac{t_n - t}{\tau} \|v^n - v^{n-1}\|_{\Gamma_G} \|\theta(t)\|_{\Gamma_G} dt \\ &\leq \frac{D_a}{\delta} \sum_{n=1}^N \left(\frac{\tau}{3} \|v^n - v^{n-1}\|_{\Gamma_G}^2 \right)^{\frac{1}{2}} \left(\int_{t_{n-1}}^{t_n} \|\theta(t)\|_{\Gamma_G}^2 dt \right)^{\frac{1}{2}} \\ &\leq \frac{1}{2\sqrt{3}} \left(\tau D_a^2 \|\theta\|_{\Gamma_G^T}^2 + \sum_{n=1}^N \|v^n - v^{n-1}\|_{\Gamma_G}^2 \right) \frac{1}{\delta} \\ &\leq \frac{D_a^2}{2\sqrt{3}} \left(\|\theta\|_{\Gamma_G^T}^2 + r(M_u)^2 \text{meas}(\Gamma_G) \right) \frac{\tau}{\delta}. \end{aligned}$$

We now let $\tau \searrow 0$. Since $\delta = \sqrt{\tau} D_a$, the above estimates together with the weak convergence of $\partial_t V^\tau$, the strong convergence of $r(U^\tau)$, and the weak-star convergence of W^τ imply that u , v , and w satisfy (1.10₁).

It remains only to show that the dissolution rate satisfies (1.10₂). To this aim we improve the previously stated weak $L^2(\Gamma_G^T)$ convergence of V^τ to a strong one, implying also a pointwise convergence a.e. This is done by employing the Riesz–Fréchet–Kolmogorov compactness criterion, requiring estimates on translations in time and space.

We first notice that V^τ is bounded uniformly in $L^2(\Gamma_G^T)$. Moreover, by (2.7) it immediately follows that, as $h \searrow 0$, the time translations of V^τ converge to 0 in $L^2(\Gamma_G^{T-h})$, and the convergence is uniform with respect to τ . So we only have

to consider estimates for translations in space. To avoid an excess of technicalities, these are proven in a simplified setting: Decomposing $x \in \mathbb{R}^n$ into $x = (y, x_n)$, with $y \in \mathbb{R}^{n-1}$, we assume Γ_G to be open and bounded in the hyperplane $\{x_n = 0\}$. The proof for general (compact and Lipschitz) boundaries follows similarly and involves a finite number of homeomorphisms, mapping Ω locally inside the half-space $\{x_n > 0\}$.

Given a $\zeta \in \mathbb{R}^{n-1}$, we consider an arbitrary $\gamma \subset \Gamma_G$ such that $y + \zeta \in \Omega$ for any $y \in \gamma$. With Δ_ζ denoting the translation operator

$$\Delta_\zeta f(y) = f(y) - f(y + \zeta)$$

and fixing a $t \in (t_{n-1}, t_n]$ ($0 < n \leq N$) and a $y \in \gamma$, by (2.20) we get

$$\Delta_\zeta V^\tau(t, y) = \Delta_\zeta v^{n-1}(y) + (t - t_{n-1})D_a [\Delta_\zeta r(u^n)(y, x_n) - \Delta_\zeta H_\delta(v^{n-1})(y)].$$

Since $\delta = \sqrt{\tau}D_a$ and because r is Lipschitz continuous, this yields

$$|\Delta_\zeta V^\tau(t, y)| \leq |\Delta_\zeta v^{n-1}(y)| + D_a L_r (t - t_{n-1}) |\Delta_\zeta u^n(y)|.$$

Continuing the argument for $t = t_{n-1}, \dots, t_1$ we obtain

$$|\Delta_\zeta V^\tau(t, y)| \leq |\Delta_\zeta v_I(y)| + \tau D_a L_r \sum_{p=1}^n |\Delta_\zeta u^p(y)|.$$

Since $n\tau \leq T$, standard arithmetic inequalities as well as integration over γ yield

$$\|\Delta_\zeta V^\tau(t, \cdot)\|_{L^2(\gamma)}^2 \leq 2\|\Delta_\zeta v_I\|_{L^2(\gamma)}^2 + 2\tau T D_a^2 L_r^2 \sum_{p=1}^N \|\Delta_\zeta u^p\|_{L^2(\gamma)}^2.$$

With \bar{U}^τ denoting the piecewise constant time interpolation of the time discrete approximations $\{u^n, n = 1, \dots, N\}$,

$$\bar{U}^\tau(t) = u^n \quad \text{whenever} \quad t_{n-1} < t \leq t_n,$$

the inequality above becomes

$$(2.36) \quad \|\Delta_\zeta V^\tau(t, \cdot)\|_{L^2(\gamma)}^2 \leq 2\|\Delta_\zeta v_I\|_{L^2(\gamma)}^2 + 2TD_a^2 L_r^2 \|\Delta_\zeta \bar{U}^\tau\|_{L^2(\gamma^\tau)}^2.$$

Since v_I is L^2 , the first term on the right vanishes as $|\zeta| \rightarrow 0$. It remains only to deal with the last term. In doing so we notice that

$$(\bar{U}^\tau - U^\tau)(t) = \frac{t_n - t}{\tau} (u^n - u^{n-1}).$$

By the estimates in (2.14), this gives

$$\|\bar{U}^\tau - U^\tau\|_{L^2(\Gamma_G^\tau)}^2 = \sum_{n=1}^N \int_{t_{n-1}}^{t_n} \frac{(t_n - t)^2}{\tau^2} \|u^n - u^{n-1}\|_{L^2(\Gamma_G)}^2 dt \leq C\tau.$$

Since $U^\tau \rightarrow u$ strongly in $L^2(\Gamma_G^T)$ along a sequence $\tau \searrow 0$, the same follows for \bar{U}^τ . Therefore the last term in (2.36) approaches 0 uniformly with respect to τ (see also Corollary IV.26 in [2] and its converse).

Once the strong $L^2(\Gamma_G^T)$ convergence $V^\tau \rightarrow v$ is proven, we can proceed as follows. For almost every pair $(t, x) \in \Gamma_G^T$ we have either $v(t, x) > 0$ or $v(t, x) = 0$. In the first case and with $\mu := v(t, x)/2 > 0$, the pointwise convergence of V^τ to v yields the existence of a $\tau_\mu > 0$ so that $V^\tau(t, x) > \mu$ for all $\tau < \tau_\mu$. Then for any $\tau \leq \min\{\tau_\mu, (\mu/D_a)^2\}$ we have $W^\tau(t, x) = 1$, implying $w(t, x) = 1$. For the second case we let $S_0 = \{v = 0\}$. Since $\partial_t v \in L^2(\Gamma_G^T)$, it follows that $\partial_t v = 0$ a.e. in the interior of S_0 , and therefore $w = r(u)$ with $0 \leq w \leq 1$ there. \square

Remark 2.16. Notice that in the proof of Theorem 2.15 we have improved the convergence of V^τ stated before. Specifically, we have shown that $V^\tau \rightarrow v$ not only weakly but also strongly in $L^2((0, T); L^2(\Gamma_G))$.

Remark 2.17. Besides the convergence of the numerical scheme, Theorem 2.15 also provides an alternative existence proof for a weak solution of (1.1)–(1.2). In [7] this is obtained by fixed-point arguments, whereas here the solution is the limit of a time discrete approximating sequence.

Remark 2.18. In this section we have considered only the time discretization of the system (1.1)–(1.2). For performing the numerical calculations that are presented in section 5, we have employed piecewise linear finite elements on Ω , whereas the crystal concentration is determined at the nodes located on Γ_G . Since the solutions of the time discrete problems are sufficiently regular, the convergence of the fully discrete scheme can be proven by standard techniques (see, e.g., [35]). In the case of convection-dominated regimes, numerical instabilities may occur as the result of the lacking maximum principle for the standard finite element method discretization. Such situations require appropriate stabilization techniques, as proposed, for example, in the book [14] or more recent works [3, 15, 19].

3. A fixed-point iteration for the time discrete problems. In this section we analyze a linear iteration scheme for solving the nonlinear time discrete Problem P_δ^n . The nonlinearity appears in the boundary condition (2.3). Numerical experiments based on a Newton-type iteration led to instabilities in the form of negative concentrations or to a precipitation in the undersaturated regime ($u \leq u^*$). Moreover, there is no guarantee of convergence, unless the time stepping is not small enough. Here we discuss an alternative fixed-point approach that provides stable results. Moreover, the scheme converges linearly in H^1 , regardless of the initial iteration or of the parameters ε , τ , and δ .

Assume u^{n-1} and v^{n-1} to be given and to satisfy the bounds in Lemmas 2.3, 2.4, and 2.6. To construct the iteration scheme we proceed as discussed in the beginning of section 2 and decouple the ion transport equation from the dissolution/precipitation equation on the boundary. Using (2.3), (2.2) can be rewritten as

$$(3.1) \quad \begin{aligned} (u^n - u^{n-1}, \phi)_\Omega + \tau D(\nabla u^n, \nabla \phi)_\Omega - \tau(\vec{q}u^n, \nabla \phi)_\Omega \\ + \tau \varepsilon \tilde{n} D_a(r(u^n) - H_\delta(v^{n-1}), \theta)_{\Gamma_G} = 0 \end{aligned}$$

for all $\phi \in H_{0, \Gamma_D}^1(\Omega)$. This is a scalar elliptic equation with nonlinear boundary conditions on Γ_G . We first construct a sequence $\{u^{n,i}, i \geq 0\}$ approximating the solution u^n of (3.1). Once this is computed, we use (2.3) for determining v^n directly.

Let L_r be the Lipschitz constant of the precipitation rate r on the interval $[0, M_u]$. With

$$(3.2) \quad \mathcal{K} := \{u \in H_{0, \Gamma_D}^1(\Omega) / 0 \leq u \leq M_u \text{ a.e. in } \Omega\},$$

and for a given $u^{n,i-1} \in \mathcal{K}$, we define $u^{n,i}$ as the solution of the linear elliptic equation

$$\begin{aligned}
 (3.3) \quad & (u^{n,i} - u^{n-1}, \phi)_\Omega + \tau D(\nabla u^{n,i}, \nabla \phi)_\Omega - \tau(\vec{q}u^{n,i}, \nabla \phi)_\Omega \\
 & = \tau \epsilon \tilde{n} D_a L_r(u^{n,i-1} - u^{n,i}, \phi)_{\Gamma_G} \\
 & \quad - \tau \epsilon \tilde{n} D_a(r(u^{n,i-1}) - H_\delta(v^{n-1}), \theta)_{\Gamma_G}
 \end{aligned}$$

for all $\phi \in H^1_{0,\Gamma_D}(\Omega)$. The starting point of the iteration can be chosen arbitrarily in \mathcal{K} . However, a good initial guess is $u^{n,0} = u^{n-1}$.

Comparing the above to (3.1), disregarding the superscripts $i - 1$ and i , the only difference is in the appearance of the first term on the right in (3.3). In the case of convergence, this term vanishes, so $u^{n,i}$ approaches u^n . Before making this sentence more precise we mention that the above construction is common in the analysis of nonlinear elliptic problems, in particular when sub- or supersolutions are sought (see, e.g., [34, p. 96]). In [29], this approach is placed in a fixed-point context, for approximating the solution of an elliptic problem with a nonlinear and possibly unbounded source term (see also [37]). The same ideas are followed in [32, 28], where similar schemes are considered for the implicit discretization of a degenerate (fast diffusion) problem in both conformal and mixed formulation. We also mention here [33] for a related work on nonlinear elliptic equations.

Since (3.3) defines a fixed-point iteration, only a linear convergence rate is to be expected. This drawback is compensated by the stability of the approximation sequence, as well as its guaranteed convergence. These statements are made precise below.

LEMMA 3.1. *Assume $0 \leq u^{n,i-1} \leq M_u$ a.e. on Ω . Then $u^{n,i}$ solving (3.3) satisfies the same bounds.*

Proof. This can be shown by following the ideas used in proving Lemmas 2.3 and 2.4. We omit the details here. \square

Starting the iteration with $u^{n,0} \in \mathcal{K}$, a straightforward mathematical induction argument shows the stability of the entire sequence $\{u^{n,i}, i \geq 0\}$. To prove the convergence of the scheme we let

$$(3.4) \quad e^{n,i} := u^n - u^{n,i}$$

denote the error at iteration i and define the H^1 -equivalent norm

$$(3.5) \quad |||f|||^2 := \|f\|_\Omega^2 + \tau D \|\nabla f\|_\Omega^2 + \zeta \|f\|_{\Gamma_G}^2.$$

Here f is any function in $H^1_{0,\Gamma_D}(\Omega)$, and the constant $\zeta > 0$ is defined as

$$(3.6) \quad \zeta := \frac{\tau}{2} \epsilon \tilde{n} D_a L_r.$$

Notice that if τ is reasonably small, $\zeta < 1$.

The lemma below shows that the iteration error defined in (3.4) is a contraction in the norm (3.5).

LEMMA 3.2. *For $\tau < 2/(\epsilon \tilde{n} D_a L_r)$, an i -independent constant $0 < \gamma < 1$ exists such that*

$$|||e^{n,i}|||^2 \leq \gamma |||e^{n,i-1}|||^2,$$

provided $u^{n,i-1}$ satisfies the bounds in Lemma 3.1.

Proof. With ζ given above, we start by adding $2\zeta(u^n, \phi)_{\Gamma_G}$ on both sides of (2.2). Subtracting (3.3) from the resulting equation gives

$$\begin{aligned} & (e^{n,i}, \phi)_{\Omega} + \tau D (\nabla e^{n,i}, \nabla \phi)_{\Omega} - \tau (qe^{n,i}, \nabla \phi)_{\Omega} + 2\zeta (e^{n,i}, \phi)_{\Gamma_G} \\ & = 2\zeta (e^{n,i-1}, \phi)_{\Gamma_G} + \tau \epsilon \tilde{n} D_a (r(u^n) - r(u^{n,i-1}), \phi)_{\Gamma_G}. \end{aligned}$$

Since $\nabla \cdot q = 0$ and $e^{n,i}$ has a zero trace on Γ_D , taking $\phi = e^{n,i}$ into the above yields

$$\begin{aligned} & \|e^{n,i}\|_{\Omega}^2 + \tau D \|\nabla e^{n,i}\|_{\Omega}^2 + 2\zeta \|e^{n,i}\|_{\Gamma_G}^2 \\ & \leq \tau \epsilon \tilde{n} D_a \|L_r e^{n,i-1} - (r(u^n) - r(u^{n,i-1}))\|_{\Gamma_G} \|e^{n,i}\|_{\Gamma_G} \\ & \leq 2\zeta \|e^{n,i-1}\|_{\Gamma_G} \|e^{n,i}\|_{\Gamma_G}. \end{aligned}$$

We then immediately get

$$(3.7) \quad |||e^{n,i}|||^2 \leq \zeta \|e^{n,i-1}\|_{\Gamma_G}^2 = \zeta(1 - \alpha) \|e^{n,i-1}\|_{\Gamma_G}^2 + \zeta \alpha \|e^{n,i-1}\|_{\Gamma_G}^2,$$

where $|||\cdot|||$ is introduced in (3.5) and α is an arbitrary constant in $(0, 1)$ to be chosen below.

Using the trace estimate (2.16) and the inequality of means, for any $\beta > 0$ we have

$$\|e^{n,i-1}\|_{\Gamma_G}^2 \leq \left(C_1 + \frac{C_2^2}{4\beta}\right) \|e^{n,i-1}\|_{\Omega}^2 + \beta \|\nabla e^{n,i-1}\|_{\Omega}^2.$$

By using this in (3.7) and taking $\alpha \in (0, 1)$, $\beta > 0$, and $\gamma > 0$ satisfying the constraints

$$(3.8) \quad \begin{aligned} \zeta \alpha \left(C_1 + \frac{C_2^2}{4\beta}\right) & \leq \gamma, \\ \zeta \alpha \beta & \leq \tau D \gamma, \\ \zeta(1 - \alpha) & \leq \gamma, \end{aligned}$$

we obtain

$$(3.9) \quad \begin{aligned} |||e^{n,i}|||^2 & \leq (1 - \alpha) \zeta \|e^{n,i-1}\|_{\Gamma_G}^2 + \alpha \beta \zeta \|\nabla e^{n,i-1}\|_{\Omega}^2 \\ & + \alpha \zeta \left(C_1 + \frac{C_2^2}{4\beta}\right) \|e^{n,i-1}\|_{\Omega}^2 \leq \gamma |||e^{n,i-1}|||^2. \end{aligned}$$

With

$$\beta = \frac{\tau D}{2} \left(C_1 + \sqrt{C_1^2 + \frac{C_2^2}{\tau D}}\right) \quad \text{and} \quad \alpha = \left(1 + \frac{C_1}{2} + \frac{1}{2} \sqrt{C_1^2 + \frac{C_2^2}{\tau D}}\right)^{-1},$$

the restrictions on α and β are fulfilled. Further, this choice also gives identical lower bounds for γ in (3.8), for which we can now take

$$(3.10) \quad \gamma = \zeta \left(C_1 + \sqrt{C_1^2 + \frac{C_2^2}{\tau D}}\right) \left(2 + C_1 + \sqrt{C_1^2 + \frac{C_2^2}{\tau D}}\right)^{-1}.$$

By the assumptions on τ we have $\gamma < 1$, and hence the iteration error is contractive in the norm defined in (3.5). \square

Remark 3.3. The iteration (3.3) defines an operator $\mathcal{T} : \mathcal{K} \rightarrow \mathcal{K}$. Following the steps in the proof of Lemma 3.2, we can show that \mathcal{T} is a contraction with respect to the norm defined in (3.5). Therefore \mathcal{T} has a unique fixed point, yielding the existence and uniqueness of a solution for the nonlinear equation (3.1). This immediately implies the existence and uniqueness of a solution for Problem P_δ^n , as stated in Lemma 2.2.

Lemma 3.2 implies the linear convergence in H^1 of the iteration sequence $\{u^{n,i}, i \geq 0\}$. Moreover, its limit is the solution u^n of (3.1).

THEOREM 3.4. *With $u^{n,0} \in H_{0,\Gamma_D}^1(\Omega)$ bounded essentially by 0 and M_u , if $\tau < 2/(\epsilon\tilde{n}D_aL_r)$, the iteration (3.3) is convergent. Specifically, for all $i > 0$ we have*

$$\| \|e^{n,i}\| \|^2 \leq \gamma^i \| \|e^{n,0}\| \|^2.$$

Remark 3.5. The contraction constant γ in the above is bounded from above by $\zeta = \tau\epsilon\tilde{n}D_aL_r/2$. Notice that the first term in the H^1 -equivalent norm in (3.5) does not depend on τ . As $\tau \searrow 0$, γ approaches 0, implying a fast convergence of the iteration at least in the L^2 sense. In the numerical computations presented in the following section, 3–4 iterations were enough for obtaining a good numerical approximation of the time discrete solution.

As stated in Theorem 3.4, convergence is achieved as $i \rightarrow \infty$. In practice we stop this procedure after a finite (small) number of iterations. This means that at each time step we are adding an iteration error to the time discrete approximation. This error depends on the number of iterations performed per time step, as well as on the initial iteration error. As mentioned before, the solution at the previous time step can be used for initiating the iteration. In the remaining part of this section we show that by this choice the total error is vanishing as $\tau \searrow 0$.

To make this statement rigorous we assume that i iterations are performed at each time step n . The computed solution $\tilde{u}^n = u^{n,i}$ will be only an approximation of u^n , the solution of (3.1). Let now \tilde{e}^n denote the error at the time step n :

$$\tilde{e}^n := u^n - \tilde{u}^n.$$

Based on the stability estimates in Lemma 2.11, we can estimate the total error that is accumulated in the numerical approximation of the time discrete sequence $\{u^n, n = 1, \dots, N\}$.

LEMMA 3.6. *Assume that, for each $n = 1, \dots, N$, i iterations (3.3) are performed by starting with $u^{n,0} = \tilde{u}^{n-1} = u^{n-1,i}$. We have*

$$\sum_{n=1}^N \| \|\tilde{e}^n\| \| \leq C \frac{\gamma^{i/2}}{\tau^{1/4}}.$$

Remark 3.7. Since $\gamma = O(\tau)$, the total error vanishes as $\tau \searrow 0$.

Proof. With $u^{n,0} = \tilde{u}^{n-1}$, the initial error at the time step n is given by

$$e^{n,0} = u^n - \tilde{u}^{n-1} = u^n - u^{n-1} + \tilde{e}^{n-1}.$$

By Theorem 3.4 the error at the time step n can be estimated as

$$\| \|\tilde{e}^n\| \| \leq \gamma^{i/2} \| \|e^{n,0}\| \| \leq \gamma^{i/2} (\| \|u^n - u^{n-1}\| \| + \| \|\tilde{e}^{n-1}\| \|).$$

Repeating this estimates inductively for $n = 1, \dots, N$, since $\tilde{e}^0 = 0$ we obtain

$$(3.11) \quad |||\tilde{e}^n||| \leq \sum_{k=1}^n \gamma^{(n+1-k)i/2} |||u^k - u^{k-1}|||.$$

Adding the above for $n = 1$ up to N gives

$$\sum_{n=1}^N |||\tilde{e}^n||| \leq \frac{\gamma^{i/2}}{1 - \gamma^{i/2}} \sum_{k=1}^N \left(1 - \gamma^{(N+1-k)i/2}\right) |||u^k - u^{k-1}|||.$$

By the definition of γ in (3.10), if τ is small enough, the fraction in the above can be bounded by $C\gamma^{i/2}$ for some constant $C > 0$. Now the proof can be completed straightforwardly by applying the stability estimates in Lemma 2.11. \square

4. Numerical results. In this section we present some numerical simulations obtained for the undersaturated regime, when only dissolution is possible. Extensive numerical results for both dissolution and precipitation, and for high or low Damköhler numbers, will be presented in a forthcoming paper. All of the computations are implemented in the research software *SciFEM* (Scilab finite element method [38]; see also [4]).

Here we consider a two-dimensional domain Ω , obtained by removing the disc $B_R(0,0)$ of radius $R = 1/4$ and centered in the origin from the square $(-1/2, 1/2)^2$. The impermeable grain is represented by the disc, and flow takes place around the grain, from the left boundary to the right one. The present experiments are similar to those presented in [7], where a simple geometry—a two-dimensional strip—has been considered. There the occurrence of a dissolution front has been investigated both analytically and numerically. After a waiting time t^* , the front started moving in the flow direction. As we will see below, the present computations reveal similar features.

We have used the following parameters and rate function:

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

This gives $u_* = 0.1$ and $u^* = 1.0$. The initial and (external) boundary conditions are

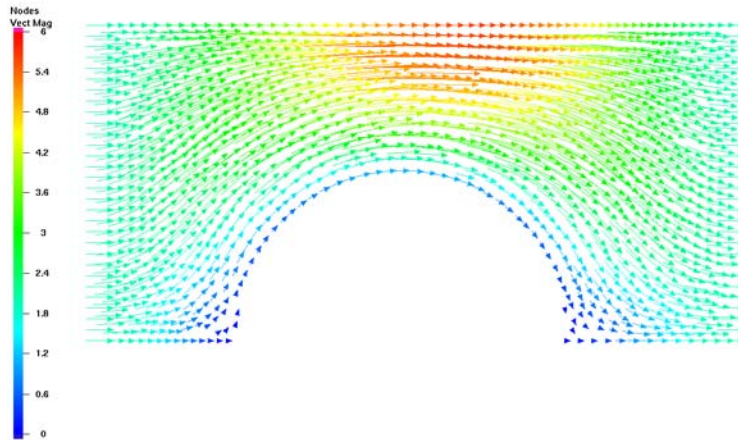
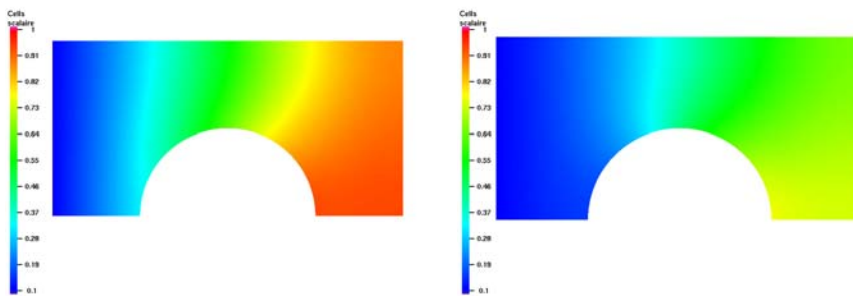
$$\begin{aligned} v_I &= 0.1 && \text{on } \Gamma_G, \\ u_I &= 1.0 && \text{in } \Omega, \\ u &= u_* && \text{if } x = -1/2, t > 0, \\ \partial_\nu u &= 0 && \text{on } \partial\Omega \setminus \{\Gamma_G \cup \{x = -1/2\}\}. \end{aligned}$$

With the data above, the system is initially in equilibrium: No precipitation or dissolution is taking place. This equilibrium is perturbed by injecting an undersaturated fluid at the inflow boundary $x = -1/2$. We start with a uniformly distributed layer of precipitate. As resulting from the L^∞ estimates, only dissolution is possible.

The fluid velocity \vec{q} is determined by solving numerically the Stokes system

$$\begin{cases} \mu \Delta \vec{q} = \nabla p & \text{in } \Omega, \\ \nabla \cdot \vec{q} = 0 & \text{in } \Omega, \end{cases}$$

where $\mu = 0.01$. At both the in- and outflow boundaries $x = \pm 1/2$ we take $\vec{q} = (2, 0)$. On the upper and lower boundaries $y = \pm 1/2$ we take $q_y = 0$, and $\partial_y q_x = 0$. For

FIG. 1. The computed velocity field \bar{q} .FIG. 2. Concentration of the cation u at $t_1 = 0.1$ (left) and $t_2 = 0.2$ (right).

symmetry reasons, the computations are restricted to the upper half of the domain. The numerical approximation of \bar{q} is obtained by employing the bubble stabilized finite element method proposed in [30] (see also [18]). The computed velocity field is presented in Figure 1.

For computing the cation concentration u and the precipitate concentration v we have applied the scheme (2.2)–(2.3) with a fixed time step $\tau = 10^{-4}$ and the regularization parameter $\delta = 10^{-4}$. As mentioned in the appendix of [6] (see also Theorem 2.15), we set $w = \min\{r(u), 1\}$ whenever $v = 0$. The emerging nonlinear time discrete problems are solved by the linearization (3.3), with $u^{n,0} = u^{n-1}$. The procedure is stopped once the maximal difference between two successive iterations is reduced below 10^{-3} . In our experiments 3–4 iterates were sufficient to fulfill this stopping criterion. We have used piecewise linear finite elements for the spatial discretization of the time discrete problems in Ω . The crystal concentration is determined at the corresponding nodes on Γ_G . In this specific example the Peclet number is moderate, so no special stabilizing techniques were needed.

The computations are performed up to $T = 0.4$. Figure 2 displays the cation

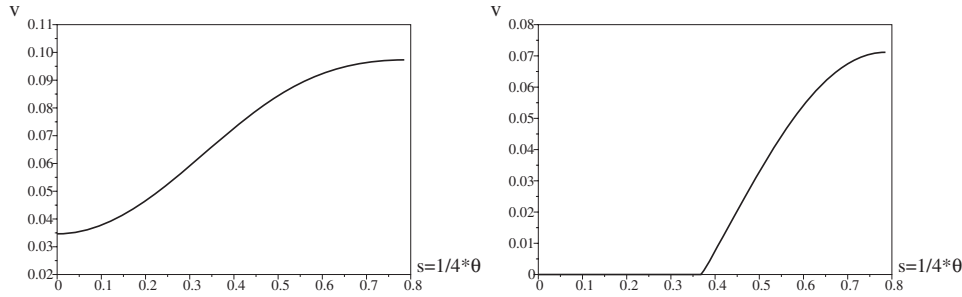


FIG. 3. Concentration of the precipitate v at $t_1 = 0.1$ (left) and $t_2 = 0.2$ (right) as a function of the arc length.

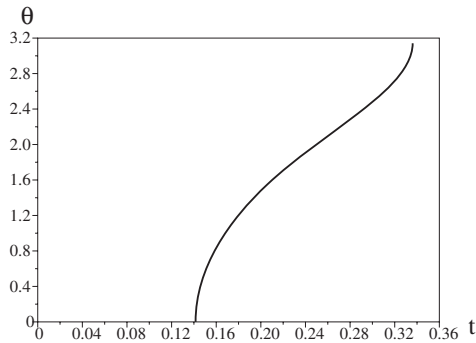


FIG. 4. The position of the dissolution front as a function of time: At $t^* \approx 0.1415$ precipitate is present everywhere on the grain boundary; after $\tilde{t} \approx 0.3359$ the entire precipitate has been dissolved.

concentration u at two different times $t_1 = 0.1$ and $t_2 = 0.2$. As expected, u is higher at the outflow than at the inflow and stays bounded by u_* and u^* . This excludes the possibility of precipitation. Moreover, the amount of cations is decreasing in time. Figure 3 displays the precipitate concentration v as a function of the arc length $s = R\theta$. Here $R = 1/4$, while θ is the angle between the radii through the leftmost point $(-R, 0)$ through the location of interest on Γ_G . Notice that v is monotone with respect to s . A major difference can be noticed in the v profiles for $t_1 = 0.1$ and $t_2 = 0.2$. In the former case we have $v > 0$ for any s , and thus precipitate is present everywhere. For t_2 we identify two different regions on Γ_G . In the left one the precipitate has been completely dissolved, whereas crystals can be found everywhere in the region on the right. This shows the occurrence of a dissolution front, located at the free boundary separating the two regions on Γ_G . At t_2 the dissolution front is located close to $(0, R)$, the upper point of Γ_G .

The evolution of the dissolution front is presented in Figure 4, where the angle θ is given as a function of time. Up to $t^* \approx 0.1415$, the precipitate is present everywhere on the grain surface Γ_G . For any time between t^* and $\tilde{t} \approx 0.3359$ the dissolution front moves towards the rightmost point on Γ_G , $(R, 0)$. After \tilde{t} the entire precipitate has been dissolved. Notice the fast movement of the free boundary as t is greater than but close to the waiting time t^* . This is due to the fact that the grain boundary Γ_G is nearly transversal to the flow. Since the inflow boundary conditions for u and \vec{q} are constant, a minimal variation of u in the vertical direction can be expected. This implies a similar behavior for v if s (or θ) is close to 0, and therefore the complete dissolution along this region occurs nearly simultaneously.

5. Conclusion. We have analyzed a numerical scheme for the time discretization of (1.1)–(1.2). This is a simplification of the pore-scale model for crystal dissolution and precipitation in porous media. The main difficulties associated with the model, a parabolic problem that is coupled through the boundary to a differential inclusion, are still present in this setting.

The numerical scheme is implicit in u and explicit in v . A regularization step is employed for dealing with the multivalued dissolution rate. We prove the stability of the scheme in both L^∞ as well as energy norms. Further, compactness arguments are used for showing that the scheme is convergent.

A fixed-point iteration is proposed for solving the nonlinear time discrete problems. This linearization is stable and converges linearly, regardless of the discretization parameters and the starting point.

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