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DIFFUSION WITH DISSOLUTION AND PRECIPITATION IN A POROUS MEDIUM: MATHEMATICAL ANALYSIS AND NUMERICAL APPROXIMATION OF A SIMPLIFIED MODEL *

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Abstract. Modeling the kinetics of a precipitation dissolution reaction occurring in a porous medium where diffusion also takes place leads to a system of two parabolic equations and one ordinary differential equation coupled with a stiff reaction term. This system is discretized by a finite volume scheme which is suitable for the approximation of the discontinuous reaction term of unknown sign. Discrete solutions are shown to exist and converge towards a weak solution of the continuous problem. Uniqueness is proved under a Lipschitz condition on the equilibrium gap function. Numerical tests are shown which prove the efficiency of the scheme.

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1. Introduction

Deep geological repositories are one of the most considered alternatives for the storage of long term radioactive waste. The numerical simulation of nuclear waste disposals needs to predict coupled thermo-hydro-mechanical and chemical (T-H-M-C) processes, involving phenomena such as heat generation and transport (due to radioactive decay of nuclear waste), infiltration of ground water (hydrological processes), swelling pressure of buffer material due to saturation (mechanical processes) and chemical evolution of buffer material and pore water (chemical processes). More precisely, the near field environment (that is the area constituted by the waste packages, the engineered barrier, and the disturbed geological medium) is characterized by its evolution with time in terms of water composition, pH, redox potential, mineral composition. Therefore, any modeling attempt of this zone should use reactive transport codes taking into account the combined effects of transport and chemical phenomena. In particular, it is important to focus on the stiff precipitation/dissolution fronts which are present due to the different media interactions (canister/engineering barrier/geological media). For example, the different cement-based materials of a repository are subject to chemical degradation like sulfate

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attack or leaching. These chemical attacks are mainly linked with dissolution/precipitation processes of the solid constituents of the cement matrix (portlandite, ettringite, gypsum) [2, 28].

To assess the safety of nuclear waste repositories, the French Atomic Energy Commission (CEA), the French Nuclear waste Agency (ANDRA) and the French Electricity Producer (EDF) are jointly developing the software platform Alliances [24, 27]. This offers the possibility of designing coupling algorithms for reactive transport simulations [27]. Mathematical and numerical models for reactive fluid flow systems have been developed in several papers, see *e.g.* [16, 31] for a survey. Different numerical algorithms are currently studied [4]; in order to get a good grasp of the behavior of these algorithms, simple models are drawn from the overall problem and studied for the analytical and numerical point of view. Hence, in this work, we shall focus our attention on the numerical approximation of the problem of the diffusion of chemical species transported by water, with a dissolution precipitation reaction.

We shall deal here with the simplified case of two chemical species in the liquid phase and one species in the solid phase. The modeling of the kinetics of the precipitation dissolution reaction and the diffusive transport is presented in Section 2 below; the model is written at the representative elementary volume scale (also called the Darcy scale) in several space dimensions, and yields a system of two parabolic equations and one ordinary differential equation that are coupled by a reaction term. This reaction rate is expressed by a general law (Eq. (20)), which models an elementary chemical reaction; in particular, it is only a discontinuous and monotonic function. The two aqueous species can be either on the same side of the reaction in which case $\alpha\beta > 0$, or on each side in which case $\alpha\beta < 0$, where α and β are the stoichiometric coefficients of the two aqueous species (see Eq. (1)). Both cases are addressed in the present work. In the first case, *i.e.* $\alpha\beta > 0$, the rate model used in this paper has the same properties as the one used in [18]. The latter model was justified by upscaling techniques in one space dimension [32]. In the case $\alpha\beta < 0$, we propose an extension of the kinetic law supported by the assumption of elementary reaction and the use of Transition State Theory [20].

Several papers have studied related diffusion-dissolution-precipitation problems at different scales. At the Darcy scale, a number of cases have already been investigated: in the case of the dissolution of one mineral coupled with the diffusion of one aqueous species (with no precipitation), existence and uniqueness have been proved both in the instantaneous (*i.e.* reaction rate tending to infinity) and in the non instantaneous case [8, 23, 29]. In the case of a first order kinetics, diffusion and dissolution with several minerals and aqueous species [21, 26] may be considered; with such a kinetics, the convergence of a finite element approximation towards weak solution was proved in [22]. At the pore scale, the papers [17, 32] study the case where a reaction between solid and liquid species occur at the interface of the grain; the intersticial flow is modeled by the Stokes equations; convection and diffusion are both considered in the conservation equations for the solutes. Precipitation-dissolution is considered in [32], while [17] deals with a sorption-like reaction. In [32], in the case $\alpha\beta > 0$ and in one space dimension, existence of a weak solution to the same problem as in the present paper (with additional convection) is proved by upscaling. In [17], existence of a weak solution for a quite general system (*i.e.* for any space dimension and for any number of aqueous and solid species) is proved by homogenization; however, in this latter work each aqueous species is assumed to react with one associated solid species, and therefore the resulting study does not encompass the problem presented here. Let us also mention that similar problems arise in population dynamics or biological models: see *e.g.* [3, 11, 15] and references therein. However, in all these studies, the reaction term is either more regular (C^1) than the reaction term considered here or has a determined sign. The existence of solutions of such systems is often obtained by the Legendre transformation or by Lyapunov techniques, which do not seem to easily adapt to our more complex reaction term.

The main goal of the present paper is to develop and study a numerical scheme to find approximate solutions to the above mentioned dissolution precipitation diffusion problem. We consider an implicit finite volume scheme on an admissible mesh [9]; the resulting discrete system is therefore nonlinear, and the existence of discrete solutions is proved by a topological degree argument. Using compactness theorems [9], we prove the convergence of approximate solutions (up to a subsequence) towards a weak solution. Some characterization of a weak solution, avoiding graph functions or inclusion equations, is used in order to deal with the discontinuity of the reaction term. This characterization is indeed the equation resulting from a passage to the limit in the numerical scheme; existence of a weak solution is then obtained by showing the equivalence of the resulting equation with the definition of a weak equation (Prop. 4.4). We also prove uniqueness of the weak solution under a Lipschitz condition on the equilibrium gap function and show some numerical tests. Let us note that existence in multiple dimensions, obtained here as a by-product of the convergence of the scheme, could also be obtained by regularization techniques, see [32], Remark 4.8.

This paper is organized as follows. In Section 2, the model is derived. In Section 3, we prove existence and uniqueness of the pure dissolution precipitation model (without diffusion), which amounts to a single differential equation. Then, a weak solution of the full coupled problem is characterized in Section 4. Section 5 is devoted to the proof of convergence of the finite volume scheme for the fully coupled system, which uses the previously mentioned characterization of a weak solution. This proof also relies on a convergence result for the implicit finite volume discretization of a linear parabolic equation with source term and non-homogeneous Dirichlet boundary conditions, which is given in the Appendix. Uniqueness is proved in Section 6. Numerical results are shown in Section 7. Conclusions and ongoing works are finally presented.

2. Derivation of the model

In this section, we derive the system of two parabolic partial differential equations coupled with an ordinary differential equation, which models a reactive transport system with one mineral species and two aqueous species which react according to a kinetic law. Let us consider chemical reactions of the form

$$W \Leftrightarrow \alpha U + \beta V, \tag{1}$$

where α, β are the algebraic stoichiometric coefficients, W the mineral, U and V the species in the liquid phase. Let u (resp. v and w) be the concentrations of U (resp. V and W) in moles per volume of solution. We assume that the aqueous species migrate into the saturated porous media Ω through a molecular diffusion process (no convection). We denote by Φ the porosity and by Φ_W the volume fraction of W. Following [31] and references therein, the mass conservation equation writes

$$\partial_t(\Phi\, u) - \nabla \cdot (D_m \nabla u) = R_U, \tag{2}$$

$$\partial_t(\Phi\, v) - \nabla \cdot (D_m \nabla v) = R_V, \tag{3}$$

$$\partial_t \Phi_W = V_W R_W, \tag{4}$$

where V_W is the molar volume of W, $D_m = \Phi\, d$ is the effective diffusion and d the pore diffusion coefficient. The relation between Φ_W and w is

$$\Phi_W = V_W \Phi w. \tag{5}$$

Remark 2.1 (Choice of the diffusion coefficient)**.** Note that the diffusion coefficients are chosen to be equal for both species U and V. There are two reasons for doing so: firstly, important differences in these coefficients would arise mainly at high concentrations, which is not the case of interest here. Secondly these coefficients are not precisely known, so that an average value should be considered. From a numerical point of view, the equality of the coefficients helps in formulating the system with respect to the total concentrations [4, 14, 16]. Moreover, the L^∞ estimate on the approximate solutions obtained in Proposition 5.3 in Section 5 below, which is crucial for the proof of convergence, also requires this assumption.

The reaction rates R_U, R_V and R_W are in moles per volume of porous media per time unit. The stoichiometry implies that $R_U = -\alpha R_W$ and $R_V = -\beta R_W$. In the sequel, we shall assume that there are small relative variations of Φ compared to relative variations of u, v and w and hence consider a constant Φ. Note that in doing so, we do not take into account the variation of Φ which may take place because of the precipitation reaction (this would yield a degenerate nonlinearity in the diffusion term). Let us then introduce $\tilde{r}_U = R_U/\Phi$, $\tilde{r}_V = R_V/\Phi$, and $\tilde{r}_W = R_W/\Phi$. Thus:

$$\tilde{r}_U = -\alpha \tilde{r}_W, \quad \tilde{r}_V = -\beta \tilde{r}_W. \tag{6}$$

Assuming that V_W and d are constant, the system (2)–(4) and (5) leads to

$$\partial_t u - \nabla \cdot (d\nabla u) = \tilde{r}_U, \tag{7}$$
$$\partial_t v - \nabla \cdot (d\nabla v) = \tilde{r}_V, \tag{8}$$
$$\partial_t w = \tilde{r}_W. \tag{9}$$

Let us now give the details of the derivation of the expression of $\tilde{r}_W$ from some kinetics theory.

Kinetic rate of a precipitation dissolution reaction

We first state some definitions and notations used in the study of the interaction between minerals and water [19]. We denote by Q the ion activity product derived from water analyses, and by K the thermodynamic constant of the overall reaction (1), the rate of which is $\tilde{r}_W$. The ratio $S = Q/K$ is called the saturation state, and $SI = \log(S)$ the saturation index. The extent of disequilibrium is then simply computed by the difference between S and 1 (or by the sign of SI) since at thermodynamic equilibrium, S equals 1. The ion activity product of reaction (1) is $Q = u^\alpha v^\beta$, assuming the activity of aqueous species is its concentration and the activity of a mineral is taken by definition to be one. Then, clearly

$$S = u^\alpha v^\beta / K. \tag{10}$$

Applying the mass action law, the equilibrium constant is

$$K = u_{\mathrm{eq}}^\alpha v_{\mathrm{eq}}^\beta, \tag{11}$$

where the subscript $_{\mathrm{eq}}$ refers to equilibrium concentrations. In the sequel $\alpha > 0$; the sign of β is either negative or positive, depending on whether the species V is a reactant ($\beta < 0$) or a product ($\beta > 0$). The following notations are introduced:

$$x^+ := \max(0, x) \text{ and } x^- := (-x)^+, \quad \mathrm{sign}(x) := \begin{cases} 1 & \text{if } x > 0, \\ 0 & \text{if } x = 0, \\ -1 & \text{if } x < 0, \end{cases} \qquad \text{for all } x \in \mathbb{R}, \tag{12}$$

so that $x = x^+ - x^-$ and $|x| = x^+ + x^-$. The net rate $\tilde{r}_W$ is governed by the balance between the rate of the forward (precipitation) and backward (dissolution) reactions that may be described respectively by

$$\alpha U + \beta^+ V \overset{K_+^\dagger}{\Longleftrightarrow} AC^\dagger \overset{\lambda_+}{\rightarrow} W + \beta^- V \tag{13}$$
$$W + \beta^- V \overset{K_-^\dagger}{\Longleftrightarrow} AC^\dagger \overset{\lambda_-}{\rightarrow} \alpha U + \beta^+ V \tag{14}$$

where $AC^\dagger$ is the activated complex, $K_+^\dagger$ and $K_-^\dagger$ are equilibrium constants and λ_+ and λ_- are rate coefficients that are constant under constant environmental conditions. The formulation of equations (13) and (14) is based on Transition State Theory [20]. This theory applies under the assumption that the dissolution and precipitation are the backward and forward cases of an elementary reaction, or at least their rates are controlled by the same elementary reaction. The rates R_+ and R_- of the forward and backward reactions are:

$$R_+ \;=\; \lambda_+ C_{AC^\dagger} = \lambda_+ \frac{K_+^\dagger}{\nu_{AC^\dagger}} u^\alpha v^{\beta^+} = \lambda'_+ u^\alpha v^{\beta^+} \tag{15}$$
$$R_- \;=\; \lambda_- C_{AC^\dagger} = \lambda_- \frac{K_-^\dagger}{\nu_{AC^\dagger}} v^{\beta^-} = \lambda'_- v^{\beta^-} \tag{16}$$

where $C_{AC^\dagger}$ and $\nu_{AC^\dagger}$ are the concentration and the activity coefficient of the activated complex and λ'_+ and λ'_- are rate coefficients defined by these two equations. Therefore, the net rate is the balance between the forward and backward rate

$$\tilde{r}_W = R_+ - R_- = \lambda'_+ u^\alpha v^{\beta^+} - \lambda'_- v^{\beta^-}. \tag{17}$$

According to the principle of detailed balancing [20], at equilibrium, the forward and backward rates must balance

$$\lambda'_+ u^\alpha_{\mathrm{eq}} v^{\beta^+}_{\mathrm{eq}} = \lambda'_- v^{\beta^-}_{\mathrm{eq}}.$$

Using equation (11),

$$\lambda'_- = \lambda'_+ u^\alpha_{\mathrm{eq}} v^{\beta^+ - \beta^-}_{\mathrm{eq}} = \lambda'_+ u^\alpha_{\mathrm{eq}} v^{\beta}_{\mathrm{eq}} = \lambda'_+ K.$$

Thus, by substituting in equation (17), we get

$$\tilde{r}_W = \lambda'_- \left(\frac{u^\alpha v^{\beta^+}}{K} - v^{\beta^-} \right), \tag{18}$$

or

$$\tilde{r}_W = \lambda'_- v^{\beta^-} \left(\frac{u^\alpha v^\beta}{K} - 1 \right) = \lambda\,(S-1) \tag{19}$$

with S the previously defined saturation state and $\lambda = \lambda'_+ v^{\beta^-}$.

Remark 2.2. From (10), if $\beta < 0$ and $v = 0$, then $S = +\infty$, but $\tilde{r}_W$ is still bounded since $\lambda = \lambda'_- v^{\beta^-} = 0$.

In order to take into account the fact that mineral dissolution stops once the mineral has disappeared, the rate of dissolution precipitation of a mineral W in the reaction (1), stated in equation (18), is changed in

$$\tilde{r}_W = \lambda \left(F(u,v)^+ - \mathrm{sign}^+(w)\, F(u,v)^- \right), \tag{20}$$

where

$$F(u,v) = u^\alpha v^{\beta^+}/K - v^{\beta^-}, \tag{21}$$

and λ'_- is replaced by λ for simplicity of notation. Finally, assuming constant environmental conditions, λ is taken to be constant.

The derivation of the rate (19) was performed in [13] for the overall reaction

$$\mathrm{SiO_2(quartz)} + 2\mathrm{H_2O} \longleftrightarrow \mathrm{H_4SiO_4}, \tag{22}$$

which corresponds to the case $\beta < 0$. The precipitation of Quartz is a key factor in promoting the smectite-illite transition [13].

Another example, which fits the case $\beta > 0$ is the process of Portlandite leaching:

$$\mathrm{Ca(OH)_2} \leftrightarrow \mathrm{Ca^{2+}} + 2\mathrm{OH^-}. \tag{23}$$

Finally, let us recall that our model was obtained assuming that the overall reaction is an elementary reaction. In the general case, the overall reaction can be considered as a sequence of elementary reactions. The rate of the overall reaction depends on the rates of the individual elementary reactions and how these take place, either in series or in parallel. In practice however, most of the rate laws devised for mineral dissolution and precipitation are more empirical than theoretical, since the reaction mechanism is unknown. The determination of rates is a topic for intensive research within the geochemical community, see [1, 20, 25] and references therein, since a general theory of surface dissolution/precipitation mechanisms is still lacking to satisfactorily relate observations of mineral surfaces and concentrations of dissolved components [25].

The complete model

Equations (6), (7)–(9), (20) may be rewritten as:

$$u_t(x,t) - \Delta u(x,t) = -\alpha\, w_t(x,t), \tag{24}$$
$$v_t(x,t) - \Delta v(x,t) = -\beta\, w_t(x,t), \tag{25}$$
$$w_t(x,t) = \lambda\left(F(u(x,t),v(x,t))^+ - \mathrm{sign}^+(w(x,t))F(u(x,t),v(x,t))^-\right) \tag{26}$$

for $(x,t) \in \Omega \times (0,T)$ where Ω is the physical domain of study, *i.e.* an open bounded connected convex polygonal subset of $\mathbb{R}^N$, $N = 1,2,3$, $(0,T)$ is the time interval, $\alpha > 0$, $\beta \in \mathbb{R}$, λ a constant rate coefficient and F is a function that represents the thermodynamical equilibrium gap, that is:

$$\begin{cases} F > 0: & \text{the mineral precipitates} \\ F = 0: & \text{chemical equilibrium exists} \\ F < 0: & \text{the mineral dissolves as soon as the mineral exists.} \end{cases}$$

Remark 2.3 (other choice of mathematical unknowns)**.** The electroneutrality assumption implicitly involves an additional linear relation between the two solutes. One could therefore consider only one of the solutes concentration (say u) as an unknown, and determine the second one (say v) by stating that the total negative charge $z := \beta u - \alpha v$ is a conserved quantity. The rate equation (20) is then replaced by $\hat{r}(u,z,w) := \tilde{r}_W(u^+, (\frac{\beta u - z}{\alpha})^+, w)$. This latter modification is used in [32] with $\tilde{r}_W$ defined by (20) and (21). This modification consists in a truncation of the rate equation, which also occurs in Assumption 4.2 below when stating the properties of a generalized F function (which encompasses (21)).

We shall introduce in Section 4 below some boundary and initial conditions for the system (24)–(26); we shall then approximate the resulting system by a finite volume scheme, and show the existence of a solution by a passage to the limit in the scheme. This result uses an original characterization of a weak solution; for the sake of clarity, we first introduce this characterization for the sole ordinary differential equation on w obtained when assuming that the concentrations u and v are given data.

3. The pure dissolution precipitation model

If one assumes, in the above model, u and v to be given data, then the model becomes an ordinary differential equation, which reads:

$$w'(t) = G(t, w(t)), \qquad t \in (0,T) \tag{27}$$
$$w(0) = w_0, \tag{28}$$

with

$$G(t, w(t)) = F^+(t) - \mathrm{sign}^+(w(t))F^-(t), \tag{29}$$

using notations (12). For the pure dissolution model precipitation model we assume the following:

Assumption 3.1. *Let* $w_0 \in \mathbb{R}_+$ *and* $F \in L^2(0,T)$.

Let us note that the Cauchy-Lipschitz framework does not apply here, since G is not continuous. In fact, for a general discontinuous function G, the problem (27)–(28) is ill-posed, as can be easily seen with, for instance, $G(w) = 0$ if $w \le 0$ and $G(w) = 1$ if $w > 0$. However, for the particular function G defined by (29), problem (27)–(28) admits a unique solution, in a sense which we now give.

Definition 3.2. Under Assumption 3.1, w is a weak solution of (27)–(28) if

$$\begin{aligned} & w \in H^1(0,T), \\ & w(0) = w_0, \\ & \int_0^T \phi(t)\ (w'(t) - G(t,w(t)))\,\mathrm{d}t = 0,\ \forall \phi \in C_c^\infty(0,T). \end{aligned} \tag{30}$$

Note that thanks to Assumption (3.1), $G(\cdot, w(\cdot)) \in L^2((0,T))$, and therefore all the integrals in (30) above make sense. Let us then state that the problem (27)–(28) is well posed:

Theorem 3.3. *Under Assumption* 3.1*, there exists a unique weak solution of the Cauchy problem* (27)–(28) *in the sense of Definition* 3.2*.*

Proof. Let us start by proving the uniqueness of the solutions. Let $w_1 \in H^1(0,T)$ and $w_2 \in H^1(0,T)$ be two weak solutions of (27)–(28) in the sense of Definition 3.2. Then the weak derivatives w_1' and w_2' are functions of $L^2(0,T)$ which both satisfy (27). Performing the difference of these two equations, multiplying by $w_1 - w_2$ and noting that the function $x \mapsto \mathrm{sign}^+(x)$ is nondecreasing leads to:

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}(w_1 - w_2)^2 = \left(\mathrm{sign}^+(w_1) - \mathrm{sign}^+(w_2)\right)(w_1 - w_2)\left(-F^-\right) \le 0.$$

This proves that $w_1 = w_2$.

The existence of a solution to (30) is proven by constructing a sequence of functions using an Euler type scheme. Let $\Delta t > 0$ be the time step, and let $\mathcal{T} = (t_n)_{n=0,\dots,N} \subset [0,T]$ be a discretization of $[0,T]$ defined by:

$$\begin{aligned} & t_0 = 0, \\ & t_{n+1} = t_n + \Delta t, \qquad \text{for all } n \le N-1, \\ & t_N \le T. \end{aligned}$$

Let $(w^{(n)})_{n\in\mathbb{N}} \subset \mathbb{R}$ be defined by

$$\begin{cases} w^{(0)} = w_0, \\ w^{(n+1)} = \left(w^{(n)} + \int_{t_n}^{t_{n+1}} F(s)\mathrm{d}s\right)^+. \end{cases} \tag{31}$$

Note that by definition, $w^{(n)} \ge 0$ for all $n \in \mathbb{N}$. Let $\hat{w}_\tau$ and $\hat{F}_\tau$ be the two piecewise constant functions defined by

$$\hat{w}_\tau(t) = w^{(n+1)},\ \forall t \in (t_n, t_{n+1}], \tag{32}$$

and

$$\hat{F}_\tau(t) = \frac{1}{t_{n+1} - t_n}\int_{t_n}^{t_{n+1}} F(s)\mathrm{d}s,\ \forall t \in (t_n, t_{n+1}], \tag{33}$$

and let $w_{\mathcal{T}}$ be the continuous piecewise linear function defined by

$$\begin{cases} w_{\mathcal{T}}(t) = w^{(n+1)} + \frac{w^{(n+1)} - w^{(n)}}{\Delta t}(t - t_{n+1}),\ \forall t \in (t_n, t_{n+1}], \\ w_{\mathcal{T}}(0) = w^{(0)}. \end{cases} \tag{34}$$

Let us first show that:

$$\left(w_{\mathcal{T}}'(t) - \hat{F}_\tau(t)\right)\left(\hat{w}_\tau(t) + \hat{F}_\tau^+(t)\right) = 0 \text{ for a.e. } t \in (0,T). \tag{35}$$

Indeed, let $t \in \{ (t_n, t_{n+1}]$, such that $w^{(n+1)} = 0\}$, then $\hat{w}_\tau(t) = w^{(n+1)} = 0$; furthermore, from equations (31) and (33), we get that $\hat{F}_\tau(t) \le 0$ so $\hat{F}^+_\tau(t) = 0$; hence (35) is true for such a t. Let us now consider the case where $t \in \{(t_n, t_{n+1}]$, with $w^{(n+1)} > 0\}$. From equation (31), we get

$$\hat{F}_\tau(t) = \frac{w^{(n)} - w^{(n+1)}}{t_n - t_{n+1}} = w'_\tau(t);$$

and again, (35) is true for such a t.

Now, thanks to the fact that $w^{(n)} \ge 0$ for all $n \in \mathbb{N}$, simple calculations then yield that

$$0 \le w^{(n)} \le w_0 + \sqrt{T}\|F\|_{L^2((0,T))} \text{ for all } n \in \mathbb{N},$$

and that

$$\int_{t_n}^{t_{n+1}} (w'_{\mathcal{T}}(t))^2 \mathrm{d}t \le \int_{t_n}^{t_{n+1}} (F(s))^2 \mathrm{d}s, \ \forall n \in \mathbb{N};$$

therefore

$$\|w'_{\mathcal{T}}\|_{L^2((0,T))} \le \|F\|_{L^2((0,T))}.$$

Hence the functions $w_{\mathcal{T}}$ and $w'_{\mathcal{T}}$ are bounded in $L^2((0,T)))$ uniformly with respect to $\mathcal{T}$. Let $(\mathcal{T}_p)_{p\in\mathbb{N}}$ be a sequence of discretizations of $[0,T]$ with vanishing step size, (*i.e.* $(\Delta t)_p$ tends to 0 as p tends $+\infty$), and let $(w_{\mathcal{T}_p})_{p\in\mathbb{N}}$ and $(\hat{w}_{\mathcal{T}_p})_{p\in\mathbb{N}}$ be the associated functions defined by (31) and (32). We have just shown that $(w_{\mathcal{T}_p})_{p\in\mathbb{N}}$ is bounded in $H^1(0,T)$, and therefore, by Rellich's theorem, there exists a subsequence still denoted $(w_{\mathcal{T}_p})_{p\in\mathbb{N}}$ of $\mathcal{T}$ and a function $w \in L^2(0,T)$ such that $w_{\mathcal{T}_p}$ converges to w in $L^2(0,T)$ as p tends $+\infty$, and such that $w'_{\mathcal{T}_p}$ tends to w' weakly in $L^2(0,T)$ as p tends $+\infty$. We then remark that $\hat{F}_{\mathcal{T}_p}$ tends to F in $L^2(0,T)$ and $\|w_{\mathcal{T}_p} - \hat{w}_{\mathcal{T}_p}\|_{L^2(0,T)}$ tends to 0 as p tends to infinity. Hence, since the function $(.)^+$ is continuous, we may pass to the limit as Δt tends to 0 in (35). We thus get that

$$\big(w(t) + F^+(t)\big)\ (w'(t) - F(t)) = 0.$$

Since $w(t) \ge 0$ for all $t \in (0,T)$, we conclude from Proposition 3.4 given below that w satisfies (30), which concludes the proof. $\square$

Proposition 3.4 (characterization of the weak solution)**.** *Under Assumption* 3.1*, a function w is a weak solution of the Cauchy problem* (27)–(28) *if and only if:*

$$w \in H^1(0,T), \ \textit{and } w(0) = w_0,$$

$$(w(t) + F^+(t))\,(w'(t) - F(t)) = 0 \textit{ for a.e. } t \in (0,T), \tag{36}$$

$$w(t) \ge 0 \textit{ for all } t \in (0,T). \tag{37}$$

Proof. ($\Leftarrow$) Let $w \in H^1(0,T)$ such that $w(0) = w_0$, satisfying (36) and (37). Then w is such that:

$$\begin{array}{l} w(t) \ge 0, \forall t \in (0,T) \\ (w'(t) = F(t)) \quad \text{or} \quad (w(t) = 0 \text{ and } \quad F(t) \le 0) \quad \text{ for a.e. } t. \end{array}$$

Let $A = \{t \in (0,T)$ such that $w(t) = 0$ and $F(t) \le 0\}$ and its complementary set $A^c = \{t$ s.t. $w(t) > 0$ or $F(t) > 0\}$. Hence

$$G(t, w(t)) = \left\{ \begin{array}{l} 0 \text{ if } t \in A, \\ F(t) \text{ if } t \in A^c. \end{array}\right.$$

Therefore, if $\phi \in C_c^\infty(0,T)$, one has:

$$\int_0^T \phi(t)\{w'(t) - G(t,w(t))\}\mathrm{d}t = \int_A \phi(t)w'(t)\mathrm{d}t + \int_{A^c} \phi(t)\{w'(t) - F(t)\}\mathrm{d}t.$$

By Stampacchia's theorem [30], on A we have $w' = 0$, yielding $\int_A \phi(t)w'(t)\mathrm{d}t = 0$. In addition, for a.e. $t \in A^c$ we have $w'(t) = F(t)$, implying $\int_{A^c} \phi(t)\{w'(t) - F(t)\}\mathrm{d}t = 0$. This concludes the proof of the first implication.

($\Rightarrow$) Conversely, let us now assume that $w \in H^1(0,T)$ is a weak solution to (27)–(28), *i.e.* satisfying (30). Let us first notice that if $t \in \mathbb{R}_+$ is such that $w(t) = 0$, then $w'(t) = G(t,0) = F^+(t) \geq 0$. Since $w_0 \geq 0$, the function w is therefore nonnegative. Let us then prove that w satisfies (36). Notice that for almost every t,

$$\begin{aligned} w'(t) - F(t) &= G(t,w(t)) - F^+(t) + F^-(t) \\ &= \left(1 - \mathrm{sign}^+(w(t))\right)\, F^-(t). \end{aligned}$$

Thus, since $F^+ F^- = 0$,

$$\int_0^T \phi(t)\,(w(t) + F^+(t))\,(w'(t) - F(t))\mathrm{d}t = \int_0^T \phi(t)\,w(t)\,\left(1 - \mathrm{sign}^+(w(t))\right)\,F^-(t)\mathrm{d}t,\ \forall \phi \in C_c^\infty(0,T).$$

Furthermore, if $w(t) = 0$ then $\phi(t)\,w(t)\,\left(1 - \mathrm{sign}^+(w(t))\right)\,F^-(t) = 0$ and if $w > 0$, $\left(1 - \mathrm{sign}^+(w(t))\right) = 0$. Hence

$$\int_0^T \phi(t)\,w(t)\,\left(1 - \mathrm{sign}^+(w(t))\right)\,F^-(t)\mathrm{d}t = 0,$$

which concludes the proof. □

4. The continuous problem

Assumption 4.1.

(i) *Let Ω be an open bounded convex connected polygonal subset of $\mathbb{R}^N$, $N = 1,2,3$, $\partial\Omega$ its boundary, and let $T > 0$. Set $Q_T = \Omega \times (0,T)$.*

(ii) *Let $\alpha \in [0,+\infty)$, $\beta \in \mathbb{R}$, and $\lambda \in (0,+\infty)$ be the given parameters of the chemical reaction.*

Note that the assumption that Ω is polygonal is considered here for simplicity (for the definition and convergence of the finite volume scheme), and could be relaxed.

We now consider the full system (24)–(26), for $(x,t) \in Q_T$, with the following nonhomogeneous Dirichlet boundary conditions and initial conditions:

$$\begin{cases} u(x,t) = \bar{u}(x,t), & (x,t) \in Q_T, \\ v(x,t) = \bar{v}(x,t), & (x,t) \in Q_T, \end{cases} \tag{38}$$

$$\begin{cases} u(x,0) = u_0(x), & x \in \Omega, \\ v(x,0) = v_0(x), & x \in \Omega, \\ w(x,0) = w_0(x), & x \in \Omega, \end{cases} \tag{39}$$

and under the following (realistic) assumptions on the data:

Assumption 4.2.

(i) *The boundary values $\bar{u}$, $\bar{v}$ are the traces on $\partial\Omega \times (0,T)$ of respectively two functions, again denoted by $\bar{u}$, $\bar{v}$, which belong to $H^1(Q_T)$. Moreover, there exist three real numbers U_0, V_0 and W_0 such that*

$$0 \leq \bar{u}(x,t) \leq U_0,\ 0 \leq \bar{v}(x,t) \leq V_0,\ \textit{for a.e. } (x,t) \in Q_T,$$

(ii) *The initial data u_0, v_0 and $w_0 \in L^\infty(\Omega)$ are such that there exists W_0 with*

$$0 \le u_0(x) \le U_0,\ 0 \le v_0(x) \le V_0,\ 0 \le w_0(x) \le W_0, \ \textit{for a.e. } x \in \Omega,$$

where U_0, V_0 are defined above.

(iii) *The function F is a given continuous function on $[0, +\infty)^2$, such that*
- *if $\beta > 0$, then for all $(u, v) \in [0, +\infty)^2$, $F(u, v)$ is increasing with u and v, and the inequalities $F(0, v) \le 0$, $F(u, 0) \le 0$ and $F(0, 0) \le 0$ hold;*
- *if $\beta < 0$, then for all $(u, v) \in [0, +\infty)^2$, $F(u, v)$ is increasing with u and decreasing with v, and the inequalities $F(0, v) \le 0$, $F(u, 0) \ge 0$ hold (which implies $F(0, 0) = 0$).*

The function F is then prolonged so that
- *$F(u, v) = F(u, 0)$ for all $u \in [0, +\infty)$ and $v \in (-\infty, 0)$,*
- *$F(u, v) = F(0, v)$ for all $v \in [0, +\infty)$ and $u \in (-\infty, 0)$,*
- *$F(u, v) = F(0, 0)$ for all $u, v \in (-\infty, 0)$.*

Definition 4.3 (weak solution)**.** Under Assumptions 4.1 and 4.2, (u, v, w) is a weak solution to problem (24)–(26), (38)–(39) if

$$(u - \bar{u}, v - \bar{v}) \in \left\{L^\infty(Q_T) \cap L^2(0, T; H_0^1(\Omega))\right\}^2 \ \text{and} \ w \in L^\infty(Q_T), \tag{40}$$

$$\int_{Q_T} (u(x,t) + \alpha w(x,t))\, \psi_t(x,t)\, \mathrm{d}x\, \mathrm{d}t - \int_{Q_T} \nabla u(x,t) \cdot \nabla \psi(x,t)\, \mathrm{d}x\, \mathrm{d}t + \int_\Omega (u_0(x) + \alpha w_0(x))\ \psi(x,0)\, \mathrm{d}x = 0, \tag{41}$$

$$\int_{Q_T} (v(x,t) + \beta w(x,t))\, \psi_t(x,t)\, \mathrm{d}x\, \mathrm{d}t - \int_{Q_T} \nabla v(x,t) \cdot \nabla \psi(x,t)\, \mathrm{d}x\, \mathrm{d}t + \int_\Omega (v_0(x) + \beta w_0(x))\ \psi(x,0)\, \mathrm{d}x = 0, \tag{42}$$

$$\int_{Q_T} w(x,t)\psi_t(x,t)\, \mathrm{d}x\, \mathrm{d}t + \lambda \int_{Q_T} \left\{F(u(x,t), v(x,t))^+ \mathrm{sign}^+(w(x,t)) F(u(x,t), v(x,t))^-\right\} \psi(x,t)\, \mathrm{d}x\, \mathrm{d}t + \int_\Omega w_0(x)\, \psi(x,0)\, \mathrm{d}x = 0, \tag{43}$$

for all $\psi \in C^\infty(\Omega \times [0, T))$.

Similarly to the case of the pure dissolution precipitation model stated in Section 3, let us give the following characterization of a weak solution.

Proposition 4.4. *Under Assumptions* 4.1 *and* 4.2*, (u, v, w) is a weak solution to problem* (24)–(26), (38)–(39) *(that is a solution to* (40)–(43)*) if and only if the relations* (40)–(42) *hold in addition to*

$$w_t \in L^2(Q_T) \tag{44}$$

$$w(x,0) = w_0(x), \quad \textit{for a.e. } x \in \Omega \tag{45}$$

$$w(x,t) \ge 0, \quad \textit{for a.e. } (x,t) \in Q_T \tag{46}$$

$$\int_{Q_T} \psi(x,t) \left[\left(w(x,t) + F(u(x,t), v(x,t))^+\right) (w_t(x,t) - \lambda F(u(x,t), v(x,t)))\right] \mathrm{d}x\, \mathrm{d}t = 0, \ \textit{for all } \psi \in C_c^\infty(Q_T). \tag{47}$$

Remark 4.5. The above result gives a characterization of a solution to (40)–(43). Existence of such a weak solution is proven in Theorem 5.6 by passing to the limit on a finite volume scheme, leading to this formulation. Uniqueness is proven under a Lipschitz condition on F in Theorem 6.3.

Proof. The proof of this result closely follows that of Proposition 3.4.
($\Leftarrow$) Let $A = \{(x,t) \in Q_T$ such that $w(x,t) = 0$ and $F(u(x,t), v(x,t)) \leq 0\}$ and its complementary set $A^c = \{(x,t)$ s.t. $w(x,t) > 0$ or $F(u(x,t), v(x,t)) > 0\}$. Hence,

$$F(u,v)^+ - \mathrm{sign}^+(w) F(u,v)^- = \begin{cases} 0 \text{ if } (x,t) \in A, \\ F(u,v) \text{ if } (x,t) \in A^c. \end{cases}$$

As in the proof of Proposition 3.4, we use Stampacchia's theorem [30] which states that $\nabla g = 0$ and $g_t = 0$ on the set $\{g = 0\}$ for every $g \in H^1(Q_T)$, and obtain:

$$\int_{Q_T} \left(w_t(x,t) - \lambda(F(u,v)^+ - \mathrm{sign}^+(w)F(u,v)^-)\right)\psi(x,t)\,\mathrm{d}x\,\mathrm{d}t = 0, \text{ for all } \psi \in C^\infty(\Omega \times [0,T)).$$

($\Rightarrow$) Conversely, assume that (u,v,w) is a weak solution to problem (24)–(26), (38)–(39). Then equations (40)–(42) hold, and equation (43) is still valid if the test function ψ is chosen in $C_c^\infty(Q_T) \subset C^\infty(\Omega \times [0,T))$. Green's formula leads to:

$$-\int_{Q_T} w_t(x,t)\psi(x,t)\,\mathrm{d}x\,\mathrm{d}t + \lambda \int_{Q_T} \left\{F(u(x,t),v(x,t))^+ - \mathrm{sign}^+(w(x,t))F(u(x,t),v(x,t))^-\right\}\psi(x,t)\,\mathrm{d}x\,\mathrm{d}t = 0,$$

for all $\psi \in C_c^\infty(Q_T)$. Since $C_c^\infty(Q_T)$ is densely contained in $L^2(Q_T)$, and by Assumption 4.2, F is uniformly bounded, this immediately implies (44). Furthermore, testing in (43) by a regularization of the Heaviside-type function $1 - H(t)$ we immediately obtain (45).

In addition, one can prove that $w(x,t) \geq 0$ a.e in $\Omega \times [0,T)$ if w is a weak solution. Indeed,

$$\frac{1}{2}({w^-}^2)_t = -\lambda F(u,v)^+ w^- + \lambda\,\mathrm{sign}^+(w)F(u,v)^- w^- = -\lambda F(u,v)^+ w^- \leq 0.$$

Thus $w(x,t)^- = 0$ a.e in $\Omega \times [0,T)$ and then $w = w^+$ and (46) holds. Then as in the proof of Proposition 3.4, we proved equation (47). □

5. Study of the finite volume scheme for the coupled problem

Definition 5.1 (admissible discretization)**.** Let $\mathcal{M}$ be an admissible finite volume mesh in the sense of [9], Definition 9.1, p. 762, that is a set of convex polygonal subsets of Ω satisfying usual geometrical and non intersecting conditions, together with the so-called "orthogonality condition", which states that there exists a family of points $(x_K)_{K\in\mathcal{M}}$ such that any interface $K|L$ neighbouring the control volumes K and L is orthogonal to the line segment (x_K, x_L), see 1. We denote by $\mathcal{E}$ the set of edges (or faces in 3D) the mesh, and by $\Delta t > 0$ the time step. We define by $\mathcal{D} = (\mathcal{M}, \mathcal{E}, (x_K)_{K\in\mathcal{M}}, \Delta t)$ an admissible discretization of Q_T. We then define by size($\mathcal{D}$) as the maximum value among the diameters of the elements of $\mathcal{M}$ and Δt, and we define regul($\mathcal{D}$) as the minimum, for all $K \in \mathcal{M}$, of the ratio between the distance from x_K to any edge of K and the diameter of K. We also set the following notations:
$\mathcal{E}_K^{\mathrm{ext}}$ is the set of edges (or faces in 3D) of the control volume K, located on $\partial\Omega$.
$\mathrm{m}(K)$ is the measure of the control volume K and $\mathrm{m}(\sigma)$ that of any edge σ.
$N(K)$ is the set of control volume having one common edge with K ($N(K) \subset \mathcal{M}$),
d_{KL} (resp. $d_{K\sigma}$) is the Euclidean distance between x_K and x_L (resp. x_K and σ),
$T_{KL} := \frac{\mathrm{m}(K)}{d_{KL}}$ (resp. $T_\sigma := \frac{\mathrm{m}(\sigma)}{d_{K\sigma}}$) is the transmissivity of an internal (resp. external) edge.

Note that the above meshes include triangles and rectangles in 2D, tetrahedra and parallelepipeds in 3D, and Voronoï meshes in any space dimensions, see [9] for more details.

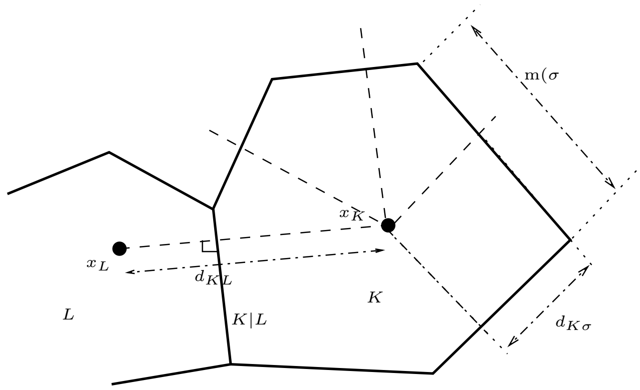

FIGURE 1. Notations for the finite volume mesh.

Let us now give the discretization of problem (24)–(26), (38)–(39) by the finite volume scheme. The initial condition is discretized by

$$u_K^0 = \frac{1}{\mathrm{m}(K)} \int_K u_0(x)\,\mathrm{d}x,\ v_K^0 = \frac{1}{\mathrm{m}(K)} \int_K v_0(x)\,\mathrm{d}x \text{ and } w_K^0 = \frac{1}{\mathrm{m}(K)} \int_K w_0(x)\,\mathrm{d}x, \tag{48}$$

for all $K \in \mathcal{M}$. The boundary conditions are discretized by

$$\bar{u}_\sigma^{n+1} = \frac{1}{\mathrm{m}(\sigma)\Delta t} \int_{n\Delta t}^{(n+1)\Delta t} \int_\sigma \bar{u}(x,t)\,\mathrm{d}\gamma(x)\mathrm{d}t \text{ and } \bar{v}_\sigma^{n+1} = \frac{1}{\mathrm{m}(\sigma)\Delta t} \int_{n\Delta t}^{(n+1)\Delta t} \int_\sigma \bar{v}(x,t)\,\mathrm{d}\gamma(x)\mathrm{d}t, \tag{49}$$

for all $\sigma \in \mathcal{E}, \sigma \subset \partial\Omega$ and for all $n \in \mathbb{N}$. The balance equations are obtained from equations (24)–(26) by integrating on each control volume K, which are then discretized by:

$$\mathrm{m}(K)\frac{u_K^{n+1} - u_K^n}{\Delta t} - \sum_{L \in N(K)} T_{KL}\,(u_L^{n+1} - u_K^{n+1}) - \sum_{\sigma \in \mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_\sigma^{n+1} - u_K^{n+1}) = -\alpha\,\mathrm{m}(K)\frac{w_K^{n+1} - w_K^n}{\Delta t}, \tag{50}$$

$$\mathrm{m}(K)\frac{v_K^{n+1} - v_K^n}{\Delta t} - \sum_{L \in N(K)} T_{KL}\,(v_L^{n+1} - v_K^{n+1}) - \sum_{\sigma \in \mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{v}_\sigma^{n+1} - v_K^{n+1}) = -\beta\,\mathrm{m}(K)\frac{w_K^{n+1} - w_K^n}{\Delta t}, \tag{51}$$

$$w_K^{n+1} = \left(w_K^n + \Delta t \lambda F(u_K^{n+1}, v_K^{n+1})\right)^+, \tag{52}$$

for all $K \in \mathcal{M}$ and $n \in \mathbb{N}$. If there exists $(u_K^n, v_K^n, w_K^n)_{K \in \mathcal{M}, n \in \mathbb{N}}$ solution to (48)–(52) (existence is proven in Cor. 5.5), we may then define

$$u_\mathcal{D}(x,t) = u_K^{n+1},\ v_\mathcal{D}(x,t) = v_K^{n+1},\ w_\mathcal{D}(x,t) = w_K^{n+1},\ \text{ for a.e. } (x,t) \in K \times (n\Delta t, (n+1)\Delta t), \tag{53}$$

for all $K \in \mathcal{M}$ and $n \in \mathbb{N}$.

Remark 5.2. From the relation (52), one can prove that, for all $K \in \mathcal{M}$ and $n \in \mathbb{N}$, there exists $\theta_K^{n+1} \in (0,1)$ such that

$$w_K^{n+1} - w_K^n = \Delta t \lambda\, \theta_K^{n+1}\, F(u_K^{n+1}, v_K^{n+1}). \tag{54}$$

We then have the following property.

Proposition 5.3 ($L^\infty(Q_T)$ estimate on the approximate solution)**.** *Under Assumptions* 4.1 *and* 4.2*, let $\mathcal{D}$ be an admissible discretization of Q_T. Let $\mu \in [0,\lambda]$ and let $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ satisfying* (48)–(52) *with λ being replaced by μ, and* (53)*. Then there exist (U,V,W), only depending on T, α, β, λ, F, U_0, V_0 and W_0, such that*

$$0 \le u_\mathcal{D}(x,t) \le U, \quad 0 \le v_\mathcal{D}(x,t) \le V, \quad 0 \le w_\mathcal{D}(x,t) \le W, \quad \textit{for a.e. } (x,t) \in Q_T. \tag{55}$$

Remark 5.4. The above statement is written with $\mu \in [0,\lambda]$ instead of λ, in order to obtain an estimate for a family of problems, as needed for the use of the topological degree in the proof of Corollary 5.5.

Proof. Let us first prove by induction the positiveness of u_K^n, v_K^n and w_K^n for all $n \in \mathbb{N}$. Using Assumption 4.2, we have for all $K \in \mathcal{M}$, $0 \le u_K^0 \le U_0$, $0 \le v_K^0 \le V_0$, $0 \le w_K^0 \le W_0$. Let us assume that, for a given $n \in \mathbb{N}$, for all $K \in \mathcal{M}$, $0 \le u_K^n$, $0 \le v_K^n$, $0 \le w_K^n$. Let K be a control volume such that $u_K^{n+1} = \min_{L\in\mathcal{M}} u_L^{n+1}$. Reasoning by contradiction, let us assume that $u_K^{n+1} < 0$. From the scheme (50) and using (54), we get

$$u_K^{n+1} = u_K^n + \frac{\Delta t}{\mathrm{m}(K)} \left(\sum_{L\in N(K)} T_{KL}\,(u_L^{n+1} - u_K^{n+1}) + \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_\sigma^{n+1} - u_K^{n+1}) \right) - \alpha\mu\,\theta_K^{n+1}\,F(u_K^{n+1}, v_K^{n+1}).$$

From Assumption 4.2 (iii), we get that $F(u_K^{n+1}, v_K^{n+1}) = F(0, v_K^{n+1}) \le 0$, which implies the right hand side of the above equation is a sum of nonnegative terms. Therefore we get $u_K^{n+1} \ge 0$. The lower bounds of v_K^{n+1} follow in a similar manner. Let us now obtain the existence of an upper bound. We first consider the case $\beta < 0$. In this case, let $z_K^n = \alpha v_K^n - \beta u_K^n$ for all $K \in \mathcal{M}$ and $n \in \mathbb{N}$, and let $\bar{z}_\sigma^{n+1} = \alpha\bar{v}_\sigma^{n+1} - \beta\bar{u}_\sigma^{n+1}$ for all $\sigma \in \mathcal{E}$, $\sigma \subset \partial\Omega$. We then get, from (50) and (51):

$$z_K^{n+1} = z_K^n + \frac{\Delta t}{\mathrm{m}(K)} \left(\sum_{L\in N(K)} T_{KL}\,(z_L^{n+1} - z_K^{n+1}) - \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{z}_\sigma^{n+1} - z_K^{n+1}) \right).$$

We then classically get that the maximum value z_K^{n+1} is lower than that of the values z_K^0 and $\bar{z}_\sigma^{n+1}$, which implies that $\alpha v_K^n - \beta u_K^n \le \alpha U_0 - \beta V_0$, and therefore $v_K^n \le V := (\alpha U_0 - \beta V_0)/\alpha$ and $u_K^n \le U := (\alpha U_0 - \beta V_0)/(-\beta)$. We now consider the case $\beta > 0$. Let us denote by U_n, V_n, W_n an upper bound for respectively u_K^n, v_K^n, w_K^n for all $K \in \mathcal{M}$. Let $K \in \mathcal{M}$ be such that $u_K^{n+1} = \max(\max_{L\in\mathcal{M}} u_L^{n+1},\ \max_{\sigma\in\mathcal{E}_L^{\mathrm{ext}},\ L\in\mathcal{M}} \bar{u}_\sigma^{n+1})$. If $u_K^{n+1} > U_0$, then, from (50), we get

$$u_K^{n+1} \le U_n - \alpha\Delta t\mu F(u_K^{n+1}, v_K^{n+1}) \le U_n - \alpha\Delta t\mu F(0,0),$$

thanks to the monotonicity properties of F in the case $\beta > 0$. We thus set $U_{n+1} = U_n - \alpha\Delta t\mu F(0,0)$, and similarly $V_{n+1} = V_n - \beta\Delta t\mu F(0,0)$. We thus set $U = U_0 - \alpha T\lambda F(0,0)$, and $V = V_0 - \beta T\lambda F(0,0)$.

In both cases, using the fact that the function F is continuous, it admits the maximum value $\bar{F}$ on $[0,U] \times [0,V]$. We then get that $w_K^{n+1} \le W_0 + \mu T\bar{F} \le W := W_0 + \lambda T\bar{F}$. We remark that in all cases, U, V, W do not depend on μ. □

We can then deduce the following corollary.

Corollary 5.5 (existence of a discrete solution)**.** *Under Assumptions* 4.1 and 4.2*, let $\mathcal{D}$ be an admissible discretization of Q_T. Then there exists at least one triplet $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ satisfying* (48)–(53) *such that* (55) *holds, with (U,V,W) only depending on T, α, β, λ, F, U_0, V_0 and W_0.*

Proof. This corollary is proved using Brouwer's topological degree argument (see *e.g.* [5], p. 47 for a general presentation and [6, 7] for its use in the setting of discretized nonlinear partial differential equations).

Let $(u_K^n, v_K^n, w_K^n)_{K\in\mathcal{M}}$ be given. For all $\mu \in [0,\lambda]$, the mapping $\mathcal{F}(\cdot,\mu) : (u_K, v_K, w_K)_{K\in\mathcal{M}} \mapsto \mathcal{F}((u_K, v_K, w_K)_{K\in\mathcal{M}}, \mu) = (U_K^{(\mu)}, V_K^{(\mu)}, W_K^{(\mu)})_{K\in\mathcal{M}}$ defined by

$$U_K^{(\mu)} = \mathrm{m}(K)\frac{u_K - u_K^n}{\Delta t} - \sum_{L\in N(K)} T_{KL}\,(u_L - u_K) - \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_\sigma^{n+1} - u_K) + \alpha\,\mathrm{m}(K)\frac{w_K - w_K^n}{\Delta t}, \tag{56}$$

$$V_K^{(\mu)} = \mathrm{m}(K)\frac{v_K - v_K^n}{\Delta t} - \sum_{L\in N(K)} T_{KL}\,(v_L - v_K) - \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{v}_\sigma^{n+1} - v_K) + \beta\,\mathrm{m}(K)\frac{w_K - w_K^n}{\Delta t}, \tag{57}$$

$$W_K^{(\mu)} = w_K - (w_K^n + \Delta t \mu F(u_K, v_K))^+, \tag{58}$$

for all $K \in \mathcal{M}$ and $n \in \mathbb{N}$ is continuous from $\mathbb{R}^{\mathrm{card}(\mathcal{M})}$ to $\mathbb{R}^{\mathrm{card}(\mathcal{M})}$. We seek the existence of a solution to the system of equations $\mathcal{F}((u_K, v_K, w_K)_{K\in\mathcal{M}}, \lambda) = 0$. From the estimates of Proposition 5.3, we get that the topological degree $d(\mathcal{F}(\cdot,\mu), B_{R+1}, 0)$ is well defined for any $\mu \in [0,\lambda]$ and for a given $R > 0$ (where B_R denotes the open ball of $\mathbb{R}^{\mathrm{card}(\mathcal{M})}$ with center 0 and radius R). Since $\mathcal{F}(\cdot,0)$ is affine and invertible for $\mu = 0$, we have that $d(\mathcal{F}(\cdot,0), B_{R+1}, 0) \neq 0$. Hence we get that $d(\mathcal{F}(\cdot,\lambda), B_{R+1}, 0) \neq 0$, which proves the existence of $(u_K^{n+1}, v_K^{n+1}, w_K^{n+1})$ solution to (50)–(52). A simple induction concludes the proof. □

Theorem 5.6 (convergence of the finite volume scheme)**.** *Under Assumptions* 4.1 *and* 4.2*, let* $\mathcal{D}$ *be an admissible discretization of* Q_T*. Let* $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ *be defined by* (53)*. Then, there exists* (u, v, w)*, a weak solution of problem* (24)–(26), (38)–(39) *in the sense of Definition* 4.3*, such that the sequence* $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ *converges, up to a subsequence, in* $L^2(Q_T)$ *to* (u, v, w) *as* size$(\mathcal{D})$ *tends to 0 while* regul$(\mathcal{D})$ *remains bounded by below.*

Proof. We consider a sequence of discretizations, the size of which tends to 0 whereas the regularity factor remains bounded by below. From Proposition 5.3, we get that $\frac{w_K^{n+1} - w_K^n}{\Delta t} = \lambda\,\theta_K^{n+1}\,F(u_K^{n+1}, v_K^{n+1})$ is bounded independently of the discretization. Thus, from this sequence, one can extract a subsequence and a function f such that the sequence of functions $f_\mathcal{D}$ (omitting the sequence's index) defined by the values $f_K^{n+1} = \lambda\,\theta_K^{n+1}\,F(u_K^{n+1}, v_K^{n+1})$ weakly converges in $L^2(Q_T)$ to f. We can then apply Theorem 9.2, giving the strong convergence in $L^2(Q_T)$ of $u_\mathcal{D}$ and $v_\mathcal{D}$, also implying the convergence of $F_\mathcal{D} = F(u_\mathcal{D}, v_\mathcal{D})$ (which is bounded in $L^\infty(Q_T)$). Let us prove that $w_\mathcal{D}$ also strongly converges in $L^2(Q_T)$. Let $\xi \in \mathbb{R}^N$ and Ω_ξ be defined by $\Omega_\xi = \{x \in \Omega \text{ such that, } [x, x+\xi] \subset \Omega\}$. Let $(x,t) \in \Omega_\xi \times (0,T)$ be given. We denote by $K \in \mathcal{M}$ and $L \in \mathcal{M}$ the control volumes such that $x \in K$ and $x + \xi \in L$ (these control volumes exist for a.e. $x \in \Omega_\xi$). We then have $w_\mathcal{D}(x,t) - w_\mathcal{D}(x+\xi,t) = w_K^n - w_L^n$, and therefore, using (52),

$$|w_K^n - w_L^n| \le |w_K^{n-1} - w_L^{n-1}| + \Delta t\lambda |F(u_K^n, v_K^n) - F(u_L^n, v_L^n)|.$$

We then get

$$|w_K^n - w_L^n| \le |w_K^0 - w_L^0| + \Delta t\lambda \sum_{p=1}^{n} \left(|F(u_K^p, v_K^p) - F(u_L^p, v_L^p)|\right).$$

Using the Cauchy-Schwarz inequality and $(a+b)^2 \le 2a^2 + 2b^2$, we get

$$|w_K^n - w_L^n|^2 \le 2|w_K^0 - w_L^0|^2 + 2\Delta t^2\lambda^2 \left(\sum_{p=1}^{n} |F(u_K^p, v_K^p) - F(u_L^p, v_L^p)|\right)^2,$$

thus producing

$$|w_K^n - w_L^n|^2 \le 2|w_K^0 - w_L^0|^2 + 2(n\Delta t)\lambda^2 \sum_{p=1}^{n} \Delta t |F(u_K^p, v_K^p) - F(u_L^p, v_L^p)|^2.$$

Integrating the above equation on Ω_ξ, we obtain

$$\int_{\Omega_\xi}(w^n_{\mathcal{D}}(x)-w^n_{\mathcal{D}}(x+\xi))^2\mathrm{d}x \le 2\int_{\Omega_\xi}(w^0_{\mathcal{D}}(x)-w^0_{\mathcal{D}}(x+\xi))^2\mathrm{d}x + 2T\lambda^2\sum_{p=1}^{n}\Delta t\int_{\Omega_\xi}(F^p_{\mathcal{D}}(x)-F^p_{\mathcal{D}}(x+\xi))^2\mathrm{d}x. \quad (59)$$

We now multiply (59) by Δt and sum the resulting for $n=1,\dots,N_{\Delta t}$

$$\begin{aligned}\sum_{n=0}^{N_{\Delta t}}\Delta t\int_{\Omega_\xi}(w^n_{\mathcal{D}}(x)-w^n_{\mathcal{D}}(x+\xi))^2\mathrm{d}x \ \le\ & 2\sum_{n=0}^{N_{\Delta t}}\Delta t\int_{\Omega_\xi}(w^0_{\mathcal{D}}(x)-w^0_{\mathcal{D}}(x+\xi))^2\mathrm{d}x \\ &+ 2T\lambda^2\sum_{n=0}^{N_{\Delta t}}\Delta t\sum_{p=1}^{n}\Delta t\int_{\Omega_\xi}(F^p_{\mathcal{D}}(x)-F^p_{\mathcal{D}}(x+\xi))^2\mathrm{d}x,\end{aligned} \quad (60)$$

and therefore

$$\begin{aligned}\int_0^T\int_{\Omega_\xi}(w^n_{\mathcal{D}}(x,t)-w^n_{\mathcal{D}}(x+\xi,t))^2\mathrm{d}x\,\mathrm{d}t \ \le\ & 2T\textstyle\int_{\Omega_\xi}(w^0_{\mathcal{D}}(x)-w^0_{\mathcal{D}}(x+\xi))^2\mathrm{d}x \\ &+ 2T^2\lambda^2\displaystyle\int_0^T\int_{\Omega_\xi}(F_{\mathcal{D}}(x,t)-F_{\mathcal{D}}(x+\xi,t))^2\mathrm{d}x\,\mathrm{d}t.\end{aligned} \quad (61)$$

This implies that the space translates of $w_{\mathcal{D}}$ uniformly tend to 0. Since, from (52), we easily get that the time translates of $w_{\mathcal{D}}$ also uniformly tend to 0, a simple lift by 0 and the L^∞ bound on $w_{\mathcal{D}}$ are sufficient to apply the Fréchet-Kolmogorov compactness theorem. Hence we may extract a subsequence such that $w_{\mathcal{D}}$ converges in $L^2(Q_T)$. We now remark that

$$\left(w^{n+1}_K+(F(u^{n+1}_K,v^{n+1}_K))^+\right)\left(\frac{w^{n+1}_K-w^n_K}{\Delta t}-\lambda F(u^{n+1}_K,v^{n+1}_K)\right)=0,\quad \forall K\in\mathcal{M},\ \forall n\in\mathbb{N},$$

since, either $\frac{w^{n+1}_K-w^n_K}{\Delta t}=\lambda F(u^{n+1}_K,v^{n+1}_K)$, or $\frac{w^{n+1}_K-w^n_K}{\Delta t}\ne\lambda F(u^{n+1}_K,v^{n+1}_K)$ in which case $w^{n+1}_K=0$ and $F(u^{n+1}_K,v^{n+1}_K)\le 0$. Let $\psi\in C^\infty(\Omega\times[0,T))$. We multiply the above equation by $\psi(x_K,n\Delta t)$ and sum over $K\in\mathcal{M}$ and $n\in\{0,\dots,N_{\Delta t}\}$. We get

$$\sum_{n=0}^{N_{\Delta t}}\Delta t\sum_{K\in\mathcal{M}}\psi(x_K,n\Delta t)\left(w^{n+1}_K+(F(u^{n+1}_K,v^{n+1}_K))^+\right)\left(\frac{w^{n+1}_K-w^n_K}{\Delta t}-\lambda F(u^{n+1}_K,v^{n+1}_K)\right)=0.$$

It is then possible to pass to the limit in this latter equality, since we have a product of strongly and weakly converging functions. We thus get

$$\int_0^T\int_\Omega\psi(x,t)\left(w(x,t)+(F(u(x,t),v(x,t)))^+\right)(w_t(x,t)-\lambda F(u(x,t),v(x,t)))\,\mathrm{d}x\,\mathrm{d}t=0.$$

The proof is then concluded by Proposition 4.4. □

6. Uniqueness of solutions of the fully coupled problem

This section is devoted to the proof of uniqueness of a solution to (40)–(43) in the case of a Lipschitz function F. Note that if the function F is under the form (21), then it is a Lipschitz function if $\alpha\ge 1$ and $|\beta|\ge 1$. Let us begin with the two following technical lemmas.

Lemma 6.1. *Let Ω be a bounded polygonal and convex subset of $\mathbb{R}^N$, $N = 1, 2, 3$ and $\beta \in \mathbb{R}^*$. Let $u_0, w_0 \in L^\infty(\Omega)$ and $\bar{u}$ be the trace on $\partial\Omega \times (0, T)$ of a function of $H^1(Q_T)$, still denoted by $\bar{u}$. Let (u_1, w_1) and (u_2, w_2) be two pairs of weak solution with the same initial and boundary conditions of the following problem:*

$$\left\{\begin{array}{l} u - \bar{u} \in L^\infty(Q_T) \cap L^2(0, T; H_0^1(\Omega)),\ w \in L^\infty(Q_T) \\ \displaystyle\int_{Q_T} (u(x,t) + \beta w(x,t))\, \psi_t(x,t)\, \mathrm{d}x\, \mathrm{d}t - \int_{Q_T} \nabla u(x,t) \cdot \nabla\psi(x,t)\, \mathrm{d}x\, \mathrm{d}t \\ \qquad\qquad \displaystyle + \int_\Omega (u_0(x) + \beta w_0(x))\ \psi(x,0)\, \mathrm{d}x = 0,\ \forall \psi \in C_c^\infty(\Omega \times [0,T)) \\ u(x,t) = \bar{u}(x,t) \textit{ for all } (x,t) \in \partial\Omega \times (0,T), \\ u(x,0) = u_0(x) \textit{ and } w(x,0) = w_0(x) \textit{ for all } x \in \Omega. \end{array}\right. \tag{62}$$

Then

$$\|u_1 - u_2\|_{L^2(0,t;L^2(\Omega))} \le |\beta|\, \|w_1 - w_2\|_{L^2(0,t;L^2(\Omega))},\ \textit{for all } t \in (0,T). \tag{63}$$

Proof. We consider the following test function:

$$\psi^{(t)}(x,s) = \left\{\begin{array}{ll} 0 & \text{if } t \le s \le T \\ \int_s^t (u_1 - u_2)(x,\theta)\, \mathrm{d}\theta & \text{if } 0 \le s \le t, \end{array}\right.$$

for all $t \in (0,T)$. One can check that $\psi^{(t)} \in \{\psi \in H^1(Q_T),\ \psi(.,T) = 0, \psi(x,t) = 0 \text{ for a.e. } x \in \partial\Omega\}$. Hence, by density, $\psi^{(t)}$ is the limit of a sequence of functions of $C_c^\infty(\Omega \times [0,T))$. Substracting the weak formulation of w_1 with that of w_2, using $\psi_s^{(t)}(x,s) = -(u_1 - u_2)(x,s)$ if $s < t$ and 0 if $s \ge t$ and $\partial_s \nabla\psi^{(t)}(x,s) = -\nabla(u_1 - u_2)(x,s)$ if $s < t$ then

$$\int_{Q_t} \left\{-(u_1 - u_2)^2 + \beta(w_1 - w_2)(u_1 - u_2)\right\} = \frac{1}{2} \int_\Omega |\nabla\psi^{(t)}(x,0)|^2 \mathrm{d}x,$$

with $Q_t := \Omega \times (0,t)$. Equation (63) is then obtained by the Cauchy-Schwarz inequality. □

Lemma 6.2. *Let $T > 0$ and let Ω be a bounded subset of $\mathbb{R}^N$. Then the following problem:*

$$\left\{\begin{array}{ll} \partial_t w(x,t) = F(x,t)^+ - \mathrm{sign}^+(w(x,t)) F(x,t)^- & (x,t) \in Q_T, \\ w(x,0) = w_0(x) & x \in \Omega, \end{array}\right. \tag{64}$$

has a unique weak solution in $L^\infty(Q_T)$ with $w_t \in L^2(Q_T)$ if $F \in L^2(Q_T)$ and $w_0 \in L^\infty(\Omega; \mathbb{R}^+)$. Furthermore, if we consider two weak solutions w_1 and w_2 of problem (64) with resp. $F = F_1$ and $F = F_2$, and the same initial conditions, we have:

$$\|(w_1 - w_2)(.,t)\|_{L^2(\Omega)} \le 2\sqrt{t} \|F_1 - F_2\|_{L^2(0,t;L^2(\Omega))}\,. \tag{65}$$

Proof. Let us first note that the existence and uniqueness of a weak solution of problem (64) is an easy extension of Theorem 3.3, Section 3.

Let w_1 and w_2 be two weak solutions of (64) with resp. $F = F_1$ and $F = F_2$. Since the function $x \mapsto \mathrm{sign}^+(x)$ is increasing and the functions $x \mapsto x^+$, and $x \mapsto x^-$ are Lipschitz, multiplying by $w_1 - w_2$ we immediately obtain:

$$\begin{aligned} \frac{1}{2}\partial_t \left(w_1 - w_2\right)^2 &= (w_1 - w_2)\left(F_1^+ - F_2^+\right) + F_2^-\left(w_1 - w_2\right)\left(\mathrm{sign}^+(w_2)\right. \\ &\qquad \left. - \mathrm{sign}^+(w_1)\right) + (w_1 - w_2)\left(F_2^- - F_1^-\right)\mathrm{sign}^+(w_1), \\ &\le (w_1 - w_2)\left(F_1^+ - F_2^+\right) + \mathrm{sign}^+(w_1)\left(w_1 - w_2\right)\left(F_2^- - F_1^-\right) \\ &\le |w_1 - w_2| \left(|F_1^+ - F_2^+| + |F_1^- - F_2^-|\right) \\ &\le 2\,|w_1 - w_2|\,|F_1 - F_2|,\ \text{ since } a^i - b^i \le |a - b|,\ i = +, -. \end{aligned}$$

Now by a space integration of the above relation combined with the Cauchy-Schwarz inequality, we have

$$\begin{aligned}\frac{1}{2}\partial_t\|(w_1-w_2)(.,t)\|^2_{L^2(\Omega)} &\leq 2\|(w_1-w_2)(.,t)\|_{L^2(\Omega)}\|(F_1-F_2)(.,t)\|_{L^2(\Omega)}\\ \partial_t\|(w_1-w_2)(.,t)\|_{L^2(\Omega)} &\leq 2\|(F_1-F_2)(.,t)\|_{L^2(\Omega)}.\end{aligned}$$

We conclude the proof by a direct integration in time. □

Theorem 6.3. *Under Assumptions* 4.1 *and* 4.2*, we furthermore assume that $F(u,v)$ is a Lipschitz function. Let (u_1,v_1,w_1) and (u_2,v_2,w_2) be weak solutions of problem* (24)-(39) *with the same initial and boundary conditions. Then, for all $T>0$,*

$$u_1=u_2,\ v_1=v_2,\ w_1=w_2 \quad a.e \text{ in } Q_T.$$

Proof. Let $T>0$, and let L_u and L_v be the Lipschitz constants of F which depend on α, β, $\|u\|_{L^\infty(Q_T)}$, $\|v\|_{L^\infty(Q_T)}$. Then:

$$\|F(u_1,v_1)(.,s)-F(u_2,v_2)(.,s)\|_{L^2(\Omega)} \leq L_u\|(u_1-u_2)(.,s)\|_{L^2(\Omega)} + L_v\|(v_1-v_2)(.,s)\|_{L^2(\Omega)}\,. \tag{66}$$

Setting $F_1=F(u_1,v_1)$ and $F_2=F(u_2,v_2)$, we get from Lemma 6.2 that

$$\|(w_1-w_2)(.,t)\|_{L^2(\Omega)} \leq 2\lambda\sqrt{t}\,\|F_1-F_2\|_{L^2(0,t;L^2(\Omega))}.$$

Therefore, since $t\leq T$, using equation (66) and Lemma 6.1 with $\{(u_1,w_1),(u_2,w_2)\}$ and $\{(v_1,w_1),(v_2,w_2)\}$, we get:

$$\|(w_1-w_2)(.,t)\|^2_{L^2(\Omega)} \leq C\int_0^t \|(w_1-w_2)(.,s)\|^2_{L^2(\Omega)}\,\mathrm{d}s,$$

with $C:=8\lambda^2 T\,\left(L_u^2\alpha^2+L_v^2\beta^2\right)$. Gronwall's lemma leads to the result. □

7. Numerical tests

In this section, we perform different numerical tests in order to test the efficiency of the approximation scheme. In particular, we wish to tackle some critical issues such as the behavior of the scheme for infinite kinetics compared with equilibrium approaches, dissolution fronts or coprecipitation (that is simultaneous precipitation of more than one substance).

These fronts have motivated several works. Dissolution and precipitation fronts are shown to exist at the pore scale for $\lambda<+\infty$ [32], Section 3 for some special initial and boundary data. Existence of dissolution front for $\lambda=+\infty$ is proved in [8,29] at the Darcy scale for one aqueous species model. It is also known that travelling waves exist if the charge distribution is constant and if dissolution is considered [18].

It is difficult to construct an analytical solution to problem (24)–(26), (38)–(39) in the general case. However, an asymptotic study in the one dimensional case yields an exact formal solution for $\lambda=+\infty$. We shall compare the numerical solutions obtained for large values of λ to this asymptotic solution. We then perform some 2D simulations with reactions such as (23) or (22). Indeed, these reactions occur in a system more complex than the one considered here.

In the different computations, a Newton algorithm is used to solve the discrete problems (50)–(52). The code is a matlab script, run on a PC (1 GHz, 750 MoRAM). The algebra toolbox of matlab was used for linear solvers. A direct method (Gaussian elimination) was chosen.

7.1. **Asymptotic study in 1D**

We consider here the dissolution of a mineral along a one dimensional ($N = 1$) domain $\Omega = (0,1)$. At time 0, the mineral is present in the whole domain and the boundary conditions are undersaturated with this mineral. This case may represent the dissolution of cement by clay water. We consider the following data: $\alpha = \beta = 1$, $K = 10^{-2}$, $d = 1\ \mathrm{m}^2 \cdot \mathrm{year}^{-1}$, $u_0 = 0$, $v_0 = 0$ and $w_0 = 5$ (in mol·m^{-3}), with the following boundary conditions:

$$\begin{array}{rcl} \text{Homogeneous Dirichlet Conditions in } x = 0 & : & u = 0,\ v = 0 \text{ (in mol}\cdot\text{m}^{-3}), \\ \text{Homogeneous Neumann Conditions in } x = 1 & : & u_x = 0,\ v_x = 0. \end{array}$$

In this one-dimensional case, assuming the existence of self similar solutions to problems (24)–(26), (38)–(39), an asymptotic study yields a formal analytical solution, passing to the limit as $\lambda \to +\infty$ (recall that the bounds of Prop. 5.3 depends on λ, hence the adjective "formal").

$$\text{For all } x \in (0, \zeta_0\sqrt{t}), \qquad \left\{ \begin{array}{l} u(x,t) = \sqrt{K}\ \mathrm{erf}(x/2\sqrt{t})\ /\ \mathrm{erf}(\zeta_0/2) \\ v(x,t) = \sqrt{K}\ \mathrm{erf}(x/2\sqrt{t})\ /\ \mathrm{erf}(\zeta_0/2) \\ w(x,t) = 0 \end{array} \right.$$

$$\text{for all } x \in (\zeta_0\sqrt{t}, +\infty), \qquad \left\{ \begin{array}{l} u(x,t) = \sqrt{K} \\ v(x,t) = \sqrt{K} \\ w(x,t) = w_0, \end{array} \right.$$

(recall that $\mathrm{erf}(z) = \int_0^z \mathrm{e}^{-s^2} \mathrm{d}s$), with ζ_0 defined by:

$$\sqrt{K} = \zeta_0\, w_0\, \mathrm{e}^{+\frac{\zeta_0^2}{4}}\, \mathrm{erf}(\zeta_0/2) := g(\zeta_0). \tag{67}$$

Note that the equation for the equilibrium is:

$$\left\{ \begin{array}{l} K = u(x,t)v(x,t) \\ w(x,t) \geq 0 \end{array} \right. \quad \text{or} \quad \left\{ \begin{array}{l} K < u(x,t)v(x,t) \\ w(x,t) = 0 \end{array} \right. \quad \text{for all } (x,t) \in Q_T.$$

A numerical resolution of equation (67) leads to $\zeta_0^{anal} = 0.1994$. This asymptotic analytical solution will be compared with approximate solutions obtained for increasing values of λ. This comparison is indeed useful in order to observe the behavior of the scheme for infinite kinetics.

The value of ζ_0^{num} is obtained by performing a numerical simulation on a large time interval. For instance, a simulation with $T = 30$ years is shown in Figure 2. The value of ζ_0 is determined by the intersection of the free boundary (between mineral and solution) and the border of the domain $(0,1)$. In Figure 2, this is the case at time $t^* = 24.645$ years. Hence, since $\zeta_0\sqrt{t^*} = 1$ we obtain the following approximate value of ζ_0: $\zeta_0^{num} = \frac{1}{\sqrt{t^*}} \simeq 0.2014$. Thus, the relative error between the asymptotic value and the value obtained by the scheme for $\lambda = 10^{10}$ is $\frac{0.2014-0.1994}{0.1994} = 0.9\%$.

In Figure 3, we can observe that the dissolution front becomes stiffer as λ increases.

The absolute error for the concentration of mineral is depicted in Figure 4. We can observe a good accuracy. Particularly, the localization of the front is accurate. Hence, numerically, we observe a convergence of discrete solutions when $\lambda \to +\infty$ even if theoretically it has not been proved.

Note that the determination of asymptotic solutions such as studied here may be quite useful in order to determine some characteristic times of the chemistry-transport coupling process (precipitation front evolution for example). Indeed, an automatic time step evolution algorithm may be constructed by remarking that the front is located at: $x_f(t) = \zeta_0\sqrt{t}$, moves at a speed: $v_f(t) = \zeta_0/2\sqrt{t}$. Given $\Delta t^{(i)}$ a time step, $\Delta x^{(i)}$ a mesh size, $t^{(i)}$ and $x_f(t^{(i)})$ an instant and the corresponding front position at time step i, we can compute $\Delta t^{(i+1)}$ such that the front at $t^{(i+1)} = t^{(i)} + \Delta t^{(i+1)}$ is moving at most by one mesh element.

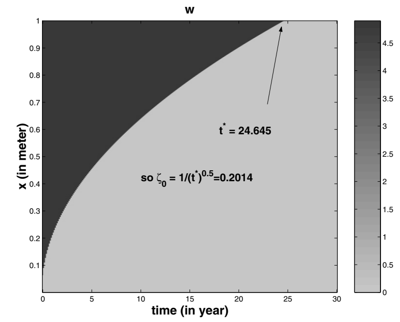

FIGURE 2. Numerical computation of ζ_0. w with $\lambda = 10^{10}$ and $T = 30$ years; computations with 3000 volume controls.

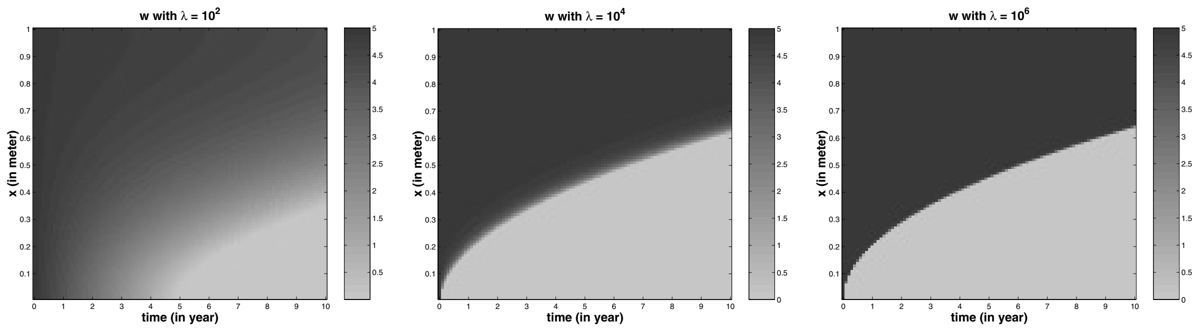

FIGURE 3. A dissolution case and $T = 10$ years. Left: w with $\lambda = 10^2$; center: w with $\lambda = 10^4$; right: w with $\lambda = 10^6$. Computations with 300 volume controls.

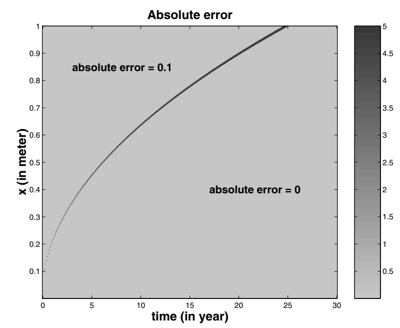

FIGURE 4. Comparison between the numerical and analytical solution. Absolute error for w with $\lambda = 10^{10}$ for the numerical solution; computations with 3000 volume controls; $T = 30$ years.

7.2. **A two dimensional precipitation or dissolution case**

Let us now turn to some two-dimensional numerical tests, both in the case of precipitation and dissolution. These tests are related with some experiments developed currently at CEA for the validation of the Alliances platform. Since, the specific conditions of this experiments are not yet determined we work here with generic values for physical coefficients.

For the precipitation case, the aim is to inject at two different points two aqueous species constitutive of a mineral and to observe the behavior of the mineral pattern formation when the two plumes reach each other. For the dissolution case, an initial amount of mineral is located in the middle of the media and the boundary condition are undersaturated with the mineral.

For these two simulations, we observe a good behavior of the numerical scheme: the monotony of the aqueous party is satisfied, and there is no oscillation on the mineral zone.

• For the precipitation case, we consider $\alpha = 2$, $\beta = 1$, $\lambda = 10^6$ $(\mathrm{m}^3{\cdot}\mathrm{mol}^{-1})^3{\cdot}\mathrm{year}^{-1}$, $T = 20$ years, $K = 10^{-3}$, $d = 0.5$ $\mathrm{m}^2{\cdot}\mathrm{year}^{-1}$, $\Omega = (0,1)\times(0,1)$, $u_0 = 0$, $v_0 = 0$, $w_0 = 0$ (in $\mathrm{mol}{\cdot}\mathrm{m}^{-3}$) with:

$$\begin{array}{rcl} \text{Dirichlet Conditions} & : & \left\{\begin{array}{ll} u = 1,\ v = 0 & \text{if } y \in [0.68, 0.8] \text{ and } x = 1 \text{ (in mol}{\cdot}\text{m}^{-3}) \\ u = 0,\ v = 1 & \text{if } x \in [0.2, 0.32] \text{ and } y = 1, \text{ (in mol}{\cdot}\text{m}^{-3}) \end{array}\right. \\ \text{Homogeneous Neumann Conditions} & : & \text{elsewhere.} \end{array}$$

In this case, we choose

$$F(u,v) = \left\{\begin{array}{ll} u^2 v - K, & \text{if } u, v \geq 0 \\ -K, & \text{elsewhere.} \end{array}\right.$$

In Figure 5, we observe the formation of a connex mineral zone with no oscillation. We remark that the migration of u and v is slowed down because of the precipitation of w. Our model allows w to precipitate; however in the present model, there is no constraint on the upper bound of w; in a more more realistic model, a variable porosity needs to be introduced in order to account that once the mineral has blocked the pores, no diffusion should then take place.

• For the dissolution case, we consider $\alpha = 1$, $\beta = -1$, $\lambda = 10^6$ $\mathrm{m}^3{\cdot}\mathrm{year}^{-1}{\cdot}\mathrm{mol}^{-1}$, $T = 35$ years, $K = 10^{-3}$, $d = 0.5$ $\mathrm{m}^2{\cdot}\mathrm{year}^{-1}$, $\Omega = (0,1)\times(0,1)$, $u_0 = 0$, $v_0 = 0$, $w_0 = 2$ (in $\mathrm{mol}{\cdot}\mathrm{m}^{-3}$) on $[0.36, 0.44]$ and 0 elsewhere with:

$$\begin{array}{rcl} \text{Dirichlet Conditions} & : & \left\{\begin{array}{ll} u = 0,\ v = 0 & \text{if } y \in [0.68, 0.8] \text{ and } x = 1, \text{ (in mol}{\cdot}\text{m}^{-3}) \\ u = 0,\ v = 1 & \text{if } x \in [0.2, 0.32] \text{ and } y = 0, \text{ (in mol}{\cdot}\text{m}^{-3}) \end{array}\right. \\ \text{Homogeneous Neumann Conditions} & : & \text{elsewhere.} \end{array}$$

In this case, we choose

$$F(u,v) = \left\{\begin{array}{ll} u - K\,v & \text{if } u, v \geq 0 \\ -K\,v & \text{if } v \geq 0 \text{ and } u < 0 \\ u & \text{if } u \geq 0 \text{ and } v < 0 \\ 0 & \text{elsewhere.} \end{array}\right.$$

In Figure 6, we observe that the dissolution starts when v reaches the boundary of the mineral. A satisfying qualitative behavior is observed: the dissolution front follows a regular pattern of concentrically edges around the initial mineral core.

8. Conclusion

In this paper, we studied a model of precipitation-dissolution in a porous media. The chemical reaction, under kinetics control, involves one mineral species and two aqueous species, these latter being transported by diffusion. The model consists in two coupled parabolic equations and a nonlinear differential equation with non continuous nonlinearity.

We proved that there exists a classical weak solution by studying the convergence of approximate finite volume solutions. Furthermore, under an additional Lipschitz condition, we prove uniqueness of the weak solution. Numerical simulations validate this scheme, in particular by comparing an asymptotic solution with the numerical solutions obtained for large values of the kinetics coefficient λ.

Next step in our work will be to study the case of a variable porosity. Indeed, the precipitation reaction influences the porosity, and in fact, there may exist zones where porosity vanishes. Such a model yields nonlinear

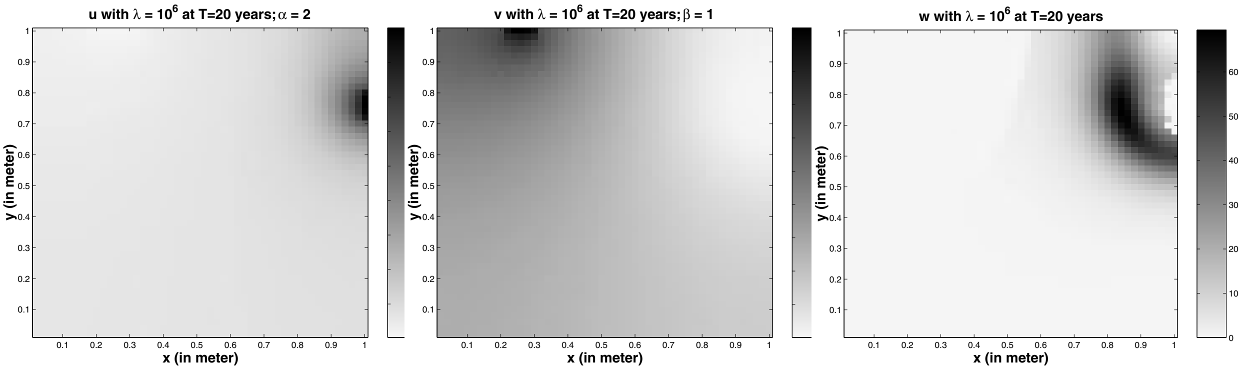

FIGURE 5. A precipitation case. u, v and w at $t = 20$ years and $\lambda = 10^6$. Computations with 250 volume controls.

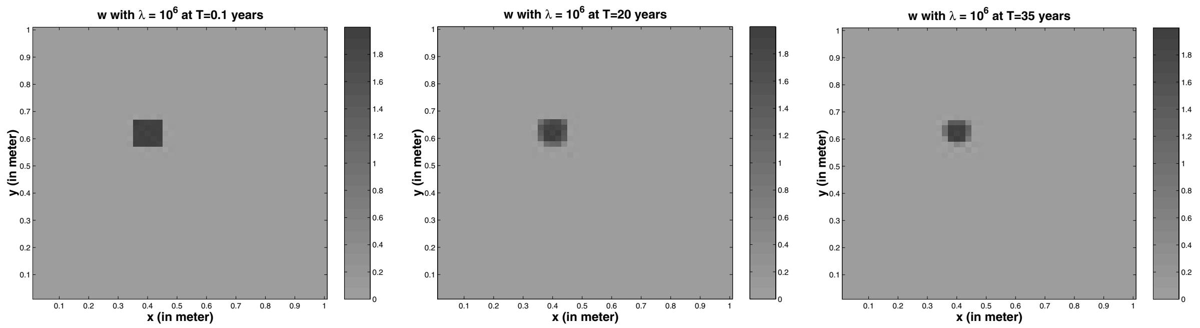

FIGURE 6. A dissolution case. w at $t = 0.1$, 10, 20, 35 years and $\lambda = 10^6$. Computations with 250 volume controls.

parabolic equations, such as the one studied in [12]. Future work will be devoted to developing the model and studying it with the techniques of [12] to obtain existence of the solutions and convergence of the scheme.

Furthermore, a more complete numerical study is currently being performed by comparing different algorithms [4] to solve the nonlinear system provided by the discrete problem studied in this paper.

9. Appendix

The proof of convergence of the finite volume scheme of Section 5 is based upon a convergence result in the linear case, which we now state. Let us consider the following assumptions:

Assumption 9.1. *Under Assumption* 4.1 (i), *we furthermore assume that:*

(ii) *Let* $f \in L^2(Q_T)$.
(iii) *Let* $\bar{u}$ *be the trace on* $\partial\Omega \times (0,T)$ *of some function, again denoted by* $\bar{u}$ *which belongs to* $H^1(Q_T)$.
(iv) *Let* $u_0 \in L^2(\Omega)$.

Let u be the (unique) weak solution of the problem

$$u_t(x,t) - \Delta u(x,t) = f(x,t), \quad (x,t) \in Q_T \tag{68}$$

$$u(x,t) = \bar{u}(x,t), \quad (x,t) \in \partial\Omega \times (0,T), \tag{69}$$

$$u(x,0) = u_0(x), \quad x \in \Omega, \tag{70}$$

in the sense that it satisfies

$$u - \bar{u} \in L^2(0,T;H_0^1(\Omega)), \quad (71)$$

$$\int_{Q_T} u(x,t)\psi_t(x,t)\,\mathrm{d}x\,\mathrm{d}t - \int_{Q_T} \nabla u(x,t)\cdot\nabla\psi(x,t)\,\mathrm{d}x\,\mathrm{d}t + \int_\Omega u_0(x)\,\psi(x,0)\,\mathrm{d}x + \int_{Q_T} f(x,t)\psi(x,t)\,\mathrm{d}x\,\mathrm{d}t = 0, \quad (72)$$

for all $\psi \in C^\infty(\Omega \times [0,T))$. We consider the following scheme. For any $K \in \mathcal{M}$, let u_K^0 be defined by (48). For any boundary edge $\sigma \in \mathcal{E} \subset \partial\Omega$ and for any $n \in \mathbb{N}$, let $\bar{u}_\sigma^{n+1}$ be defined by (49). The balance equation is obtained from equation (68) by integrating on each control volume K, which is then discretized by:

$$\mathrm{m}(K)\frac{u_K^{n+1} - u_K^n}{\Delta t} - \sum_{L\in N(K)} T_{KL}\,(u_L^{n+1} - u_K^{n+1}) - \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_\sigma^{n+1} - u_K^{n+1}) = \mathrm{m}(K) f_K^{n+1}, \quad (73)$$

for all $K \in \mathcal{M}$ and $n \in \mathbb{N}$. We then define the functions $u_\mathcal{D}$ and $f_\mathcal{D}$ by

$$u_\mathcal{D}(x,t) = u_K^{n+1}, \quad \text{for a.e. } (x,t) \in K \times (n\Delta t, (n+1)\Delta t), \quad (74)$$

$$f_\mathcal{D}(x,t) = f_K^{n+1}, \quad \text{for a.e. } (x,t) \in K \times (n\Delta t, (n+1)\Delta t), \quad (75)$$

for all $K \in \mathcal{M}$ and $n \in \mathbb{N}$. We can now state the following result:

Theorem 9.2 (convergence of the finite volume scheme)**.** *Under Assumption* 9.1*, let $\mathcal{D}$ be an admissible discretization of Q_T in the sense of Definition* 5.1*. Let $(f_K^{n+1})_{K\in\mathcal{M},n\in\mathbb{N}}$ be given, for all admissible discretization, such that the function $f_\mathcal{D}$, defined by* (75)*, weakly converges in $L^2(Q_T)$ to the function f as* size($\mathcal{D}$) *tends to* 0*. Then the function $u_\mathcal{D}$, defined by* (74) *and the scheme* (48), (49) *and* (73)*, converges in $L^2(Q_T)$ to u, the unique weak solution of problem* ((68)-(69)-(70)) *in the sense of* (72)*, as* size($\mathcal{D}$) *tends to* 0 *while* regul($\mathcal{D}$) *remains bounded by below.*

Proof. There are only two differences with the proof given in [10], done in the more complex case of the Richards equation. The first one is due to the fact that we do not use an L^∞ estimate on the discrete unknown, and the second one is due to the presence of a right hand side in the parabolic equation. We first recall the method used to obtain a discrete version of an $L^2(0,T;H_0^1(\Omega))$ estimate. Indeed, for a given admissible discretization $\mathcal{D}$, the system of equations (48), (49), (73) uniquely defines the family of values $(u_K^{n+1})_{K\in\mathcal{M},n\in\mathbb{N}}$ (see [9]). For all $s \in \mathbb{R}$, let us define $[s]$ as the integer such that $[s] \le s < [s]+1$. We assume, without loss of generality, that $\Delta t < T$, and we define $N_{\Delta t} = [T/\Delta t]$. We prolong $\bar{u}$ such that $\bar{u} \in H^1(\Omega \times (0,T'))$, for all $T' > 0$ (this can be achieved by symmetry and periodicity). Defining

$$\bar{u}_K^{n+1} = \frac{1}{\mathrm{m}(K)\Delta t}\int_{n\Delta t}^{(n+1)\Delta t}\int_K \bar{u}(x,t)\,\mathrm{d}x\,\mathrm{d}t,\ \forall K \in \mathcal{M},\ \sigma \subset \partial\Omega,\ \forall n \in \mathbb{N},$$

and, denoting by $\bar{u}(\cdot,0)$ the trace of $\bar{u}$ on $\Omega \times \{0\}$, defining

$$\bar{u}_K^0 = \frac{1}{\mathrm{m}(K)}\int_K \bar{u}(x,0)\,\mathrm{d}x,\ \forall K \in \mathcal{M},$$

we set $\widehat{u}_K^{n+1} = u_K^{n+1} - \bar{u}_K^{n+1}$, we multiply (73) by $\Delta t\widehat{u}_K^{n+1}$, and we sum the result on $K \in \mathcal{M}$ and on $n = 0,\ldots,N_{\Delta t}$. We then denote by $\widehat{u}_\mathcal{D}$ and $\bar{u}_\mathcal{D}$ the functions respectively defined from the values $\widehat{u}_K^{n+1}$ and $\bar{u}_K^{n+1}$ in a similar way as (74). We thus get $T_1 + T_2 = T_3$ with

$$T_1 = \sum_{n=0}^{N_{\Delta t}}\sum_{K\in\mathcal{M}} \mathrm{m}(K)(u_K^{n+1} - u_K^n)\widehat{u}_K^{n+1},$$

$$T_2 = -\sum_{n=0}^{N_{\Delta t}} \Delta t \sum_{K\in\mathcal{M}} \widehat{u}_K^{n+1} \left(\sum_{L\in N(K)} T_{KL}\,(u_L^{n+1} - u_K^{n+1}) + \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_\sigma^{n+1} - u_K^{n+1}) \right)$$

and

$$T_3 = \sum_{n=0}^{N_{\Delta t}} \Delta t \sum_{K\in\mathcal{M}} \mathrm{m}(K) f_K^{n+1} \widehat{u}_K^{n+1}.$$

We first remark that $T_1 = T_4 + T_5$ with

$$\begin{aligned} T_4 &= \sum_{n=0}^{N_{\Delta t}} \sum_{K\in\mathcal{M}} \mathrm{m}(K)(\widehat{u}_K^{n+1} - \widehat{u}_K^n)\widehat{u}_K^{n+1} \\ &= \frac{1}{2}\sum_{K\in\mathcal{M}} \mathrm{m}(K)(\hat{u}_K^{N_{\Delta t}})^2 + \frac{1}{2}\sum_{n=0}^{N_{\Delta t}} \sum_{K\in\mathcal{M}} \mathrm{m}(K)(\widehat{u}_K^{n+1} - \widehat{u}_K^n)^2 - \frac{1}{2}\sum_{K\in\mathcal{M}} \mathrm{m}(K)(\hat{u}_K^0)^2, \end{aligned}$$

and

$$T_5 = \sum_{n=0}^{N_{\Delta t}} \sum_{K\in\mathcal{M}} \mathrm{m}(K)(\bar{u}_K^{n+1} - \bar{u}_K^n)\widehat{u}_K^{n+1}.$$

We define

$$T_6 = \sum_{n=0}^{N_{\Delta t}} \Delta t \left(\sum_{K|L\in\mathcal{E}^{\mathrm{int}}} T_{KL}(\widehat{u}_L^{n+1} - \widehat{u}_K^{n+1})^2 + \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\widehat{u}_K^{n+1})^2 \right).$$

As a consequence of the discrete Poincaré inequality $\|\widehat{u}_{\mathcal{D}}\|^2_{L^2(Q_T)} \le \mathrm{diam}(\Omega)^2 T_6$ (see [9], Lem. 9.1, p. 765) and to the Young inequality $ab \le \frac{a^2}{2c} + \frac{b^2 c}{2}$, we get $T_5 \ge -\frac{1}{4}T_6 - \mathrm{diam}(\Omega)^2 T_7$, with

$$T_7 = \sum_{n=0}^{N_{\Delta t}} \Delta t \sum_{K\in\mathcal{M}} \mathrm{m}(K) \left(\frac{\bar{u}_K^{n+1} - \bar{u}_K^n}{\Delta t} \right)^2.$$

We remark that we have

$$\bar{u}_K^1 - \bar{u}_K^0 = \frac{1}{\mathrm{m}(K)\Delta t} \int_0^{\Delta t} \int_K \int_0^t \bar{u}_t(x,s)\mathrm{d}s\,\mathrm{d}x\,\mathrm{d}t$$

and, for all $n \ge 1$,

$$\bar{u}_K^{n+1} - \bar{u}_K^n = \frac{1}{\mathrm{m}(K)\Delta t} \int_{(n-1)\Delta t}^{n\Delta t} \int_K \int_0^{\Delta t} \bar{u}_t(x,t+s)\mathrm{d}s\,\mathrm{d}x\,\mathrm{d}t.$$

Thanks to the fact that $u \in H^1(\Omega\times(0,2T))$ and to the Cauchy-Schwarz inequality, we therefore get the existence of C_1, which only depends on Ω, T and $\bar{u}$, such that $T_7 \le C_1$. We then remark that $T_2 = T_6 + T_8$ with

$$T_8 = \sum_{n=0}^{N_{\Delta t}} \Delta t \left(\sum_{K|L\in\mathcal{E}^{\mathrm{int}}} T_{KL}(\widehat{u}_L^{n+1} - \widehat{u}_K^{n+1})(\bar{u}_L^{n+1} - \bar{u}_K^{n+1}) + \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_K^{n+1} - \bar{u}_\sigma^{n+1})\widehat{u}_K^{n+1} \right).$$

Again applying the Young inequality, we get $T_8 \ge -\frac{1}{4}T_6 - T_9$, with

$$T_9 = \sum_{n=0}^{N_{\Delta t}} \Delta t \left(\sum_{K|L\in\mathcal{E}^{\mathrm{int}}} T_{KL}(\bar{u}_L^{n+1} - \bar{u}_K^{n+1})^2 + \sum_{\sigma\in\mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_K^{n+1} - \bar{u}_\sigma^{n+1})^2 \right).$$

Using the inequality (9.38) of [9], Lemma 9.4, p. 776, we get that there exists C_2 , which only depends on Ω, T, $\bar{u}$ and $\mathrm{regul}(\mathcal{D})$ (the regularity properties of the mesh are then explicitly used), such that

$$T_9 \le C_2 \, \|\bar{u}\|^2_{L^2(0,2T;H^1(\Omega))}.$$

The weak convergence of $f_{\mathcal{D}}$ yields the existence of an upper bound C_3 for $\|f_{\mathcal{D}}\|_{L^2(\Omega\times(0,T))}$ that does not depend on the discretization $\mathcal{D}$. This gives

$$T_3 \le C_3 \, \|\widehat{u}_{\mathcal{D}}\|_{L^2(Q_T)}.$$

Using once more the discrete Poincaré inequality on $\widehat{u}_{\mathcal{D}}$ and the Young inequality, we get

$$T_3 \le \frac{1}{4} T_6 + \mathrm{diam}(\Omega)^2 {C_3}^2.$$

Gathering the above results yields the existence of C_4 , which only depends on Ω, T, u_0, $\bar{u}$ and $\mathrm{regul}(\mathcal{D})$, such that

$$\sum_{K\in\mathcal{M}} \mathrm{m}(K)(\hat{u}_K^{N_{\Delta t}})^2 \le C_4 \tag{76}$$

and

$$T_6 \le C_4 \, . \tag{77}$$

Prolonging by 0 the function $\widehat{u}_{\mathcal{D}}$ on $(\mathbb{R}^N \times \mathbb{R}) \setminus (Q_T)$, the discrete $L^2(0,T;H_0^1(\Omega))$ estimate (77) suffices to provide an $L^2(Q_T)$ estimate on the space translates of $\widehat{u}_{\mathcal{D}}$, that is on the functions defined for all $\eta \in \mathbb{R}^N$ and for a.e. $(x,t) \in \mathbb{R}^N \times \mathbb{R}$ by $(x,t) \mapsto \widehat{u}_{\mathcal{D}}(x+\eta,t) - \widehat{u}_{\mathcal{D}}(x,t)$ (see [9], Lem. 9.3, p. 770). Estimate (77) is then used to derive an estimate on the time translates in a similar way as in [10], Section 4.2: that is we look, for any $\tau \in (0,T)$, for a bound of $T_{10}(\tau)$, defined for all $\tau \in (0,T)$ by

$$T_{10}(\tau) = \int_0^{T-\tau} \int_\Omega (\widehat{u}_{\mathcal{D}}(x,t+\tau) - \widehat{u}_{\mathcal{D}}(x,t))^2 \mathrm{d}x \, \mathrm{d}t.$$

Using the relation

$$\widehat{u}_{\mathcal{D}}(x,t+\tau) - \widehat{u}_{\mathcal{D}}(x,t) = \sum_{n=0}^{N_{\Delta t}} (\hat{u}_K^{[t/\Delta t]+n+1} - \hat{u}_K^{[t/\Delta t]+n}) \chi(n,t,t+\tau),$$

(where $[x]$ denotes the integer part of a real number x) with $\chi(n,t_1,t_2) = 1$ if $t_1 \le n\Delta t < t_2$ and 0 otherwise, and using the scheme (73), we get, in addition to terms that are similar to those resulting in the estimate of the left hand side of (4.72) p. 1521 of [10], the term T_{11} defined by

$$T_{11} = \int_0^{T-\tau} \sum_{n=0}^{N_{\Delta t}} \Delta t \sum_{K\in\mathcal{M}} f_K^{n+1} \chi(n,t,t+\tau)(\hat{u}_K^{[(t+\tau)/\Delta t]} - \hat{u}_K^{[t/\Delta t]}) \mathrm{d}t.$$

Thanks to the bound C_3 , to the Young inequality and to Lemma 4.6 of [10], we get that there exists C_5 , which only depends on Ω, T, u_0, $\bar{u}$ and $\mathrm{regul}(\mathcal{D})$, such that

$$T_{11} \le \tau C_5 \, .$$

Hence we get the existence of C_6 such that $T_{10}(\tau) \le \tau C_6$. Using this inequality and the $L^\infty(0,T;L^2(\Omega))$ estimate (76), we obtain that $\int_{\mathbb{R}} \int_{\mathbb{R}^N} (\widehat{u}_{\mathcal{D}}(x,t+\tau) - \widehat{u}_{\mathcal{D}}(x,t))^2 \mathrm{d}x \, \mathrm{d}t$ uniformly converges to 0 with τ.

These space and time translate estimates are then sufficient to obtain compactness properties on $\widehat{u}_{\mathcal{D}}$, and therefore also on $u_{\mathcal{D}}$ since it is easy to see that $\bar{u}_{\mathcal{D}}$ strongly converges. Then for any test function $\psi \in$

$C^\infty(\Omega \times [0,T))$, we multiply the scheme (73) by $\Delta t \psi(x_K,(n+1)\Delta t)$ and sum the result on $K \in \mathcal{M}$ and on $n = 0,\dots,N_{\Delta t}$. The only new term, compared to the proof of [10], is the right hand side T_{12} defined by

$$T_{12} = \sum_{n=0}^{N_{\Delta t}} \Delta t \sum_{K\in\mathcal{M}} \mathrm{m}(K) f_K^{n+1} \psi(x_K,(n+1)\Delta t),$$

which clearly converges to $\int_0^T \int_\Omega f(x,t)\psi(x,t)\mathrm{d}x\,\mathrm{d}t$. This concludes the proof of Theorem 9.2. □

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