Diffusion with dissolution and precipitation in a porous media approximation by a finite volume scheme

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ABSTRACT. *This paper study a finite volumes scheme for nonlinear diffusion and dissolution-precipitation equations with non homogeneous Dirichlet boundary conditions. The approximate solution is shown to converge to a weak solution which existence is thus proved. The chemical reaction is kinetics controlled. It involves two species in liquid phase and one species in solid phase. Some numerical tests are shown.*

RÉSUMÉ. *Cet article étudie un schéma volumes finis pour un système d'équations non linéaires de diffusion et de précipitation dissolution avec des conditions limites de type Dirichlet. On montre que la solution approchée converge vers une solution faible dont l'existence est ainsi prouvée. La réaction chimique est sous contrôle cinétique. Elle met en jeu deux espèces aqueuses et une espèce solide. Quelques tests numériques sont ensuite montrés.*

KEYWORDS: *diffusion, dissolution-precipitation, porous media, finite volumes, kinetics.*

MOTS-CLÉS : *diffusion, dissolution-precipitation, milieu poreux, volumes finis, cinétique.*

1. Introduction

In several countries, one plans to store radioactive waste in deep geological disposals. The French atomic energy commission, CEA, is interested in modelling the reactive transport coupling so as to figure nuclear safety and repository sites tightness. These computations affect the French nuclear waste agency, ANDRA, which is in charge of the repository. CEA and ANDRA have developped, in the context of the Alliances platform, a sequential iterative chemical/transport coupling. Recent developments, supported by a nonlinear conjugate gradient method, were carried out to improve the coupling efficiency [BMH 05]. The aim of Alliances is to produce a software platform for the simulation of nuclear waste repository [MDM 03]. The efficiency of such disposals relies on material barriers. For such a use, cement concrete offers the advantage of having a weak porosity. However, disposal safety relies on the durability of concrete, subjected to the attack of water, which dissolves the calcium included into the skeleton mineral constituants (the leaching phenomenon).

It is essential to forecast the evolution of the porosity and the permeability of the concrete since these properties increase with calcium leaching. Simple models of this phenomenon can be drawn. In such models, only one mineral species is taken into account. We consider that its dissolution or its precipitation obeys to a classical kinetic law. It is of interest to study the influence of the kinetics of dissolution (or precipitation) compared to the kinetics of diffusion which is slowed down by the tortuosity of the porous medium.

This work naturally follows those of [EGHDM 98] where an instantaneous and non-instantaneous dissolution of one mineral in one aqueous species is studied and approximated by a finite volume scheme. This model was broadly studied [EGHDM 98] [Pou 00], both in the instantaneous case (infinite value of kinetic constant) and the non-instantaneous case (finite value of kinetic constant). In these former works, precipitation is not considered, and therefore the sign of the mineral concentration time derivative is known (and negative), which allows uniform L^∞ estimates on the mineral concentration. Hence the singular limit problem may also be successfully handled in this case. In the present work, we shall consider the case of a mineral which can dissolve or precipitate in two aqueous species according to a kinetic law, which is for instance, the case of Portlandite $Ca(OH)_2$ in the process of concrete leaching:

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} \ + \ 2OH^- \tag{1}$$

More generally, we shall consider chemical reactions of the form $W \Leftrightarrow \alpha U + \beta V$, where α, β are the algebraic stoichiometric coefficients, W the mineral, U and V species in liquid phase. Let u (resp. v and w) be the concentrations of U (resp. V and W) in moles per volume of solution. We denote by Φ the porosity and by Φ_W the volume fraction of W. We assume that the aqueous species migrate into the saturated porous media Ω through the process of diffusion. Following [SL 94] 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 molecular diffusion and d the diffusion coefficient. The rates R_U, R_V and R_W are in moles per volume of porous media per time unit. The stoichiometry implies that

$$R_U = -\alpha R_W\,, R_V = -\beta R_W\,.$$

The closing equation concerning the porosity Φ is

$$\Phi = 1 - \Phi_W\,. \tag{5}$$

Assume that there are small relative variations of porosity Φ compared to relative variations of u, v and w

$$|\partial_t \Phi|/|\Phi| << |\partial_t u|/|u|\,,\, |\partial_t v|/|v|\,,\, |\partial_t w|/|w|\,. \tag{6}$$

Then,

$$\partial_t(\Phi\, u) \simeq \Phi \partial_t u \quad , \quad \partial_t(\Phi\, v) \simeq \Phi \partial_t v \quad , \quad \partial_t(\Phi_W) \simeq V_W\, \Phi \partial_t w\,,$$

since $\Phi_W = V_W\, \Phi\, w$. From (6), Φ is constant. Let us introduce

$$\tilde{r}_U = R_U/\Phi\,, \tilde{r}_V = R_V/\Phi\,, \tilde{r}_W = R_W/\Phi\,.$$

Thus

$$\tilde{r}_U = -\alpha \tilde{r}_W \quad , \quad \tilde{r}_V = -\beta \tilde{r}_W\,. \tag{7}$$

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

$$\partial_t u + \nabla \cdot (d \nabla u) = \tilde{r}_U\,, \tag{8}$$

$$\partial_t v + \nabla \cdot (d \nabla v) = \tilde{r}_V\,, \tag{9}$$

$$\partial_t w = \tilde{r}_W\,. \tag{10}$$

It is pointed out that the strong assumption upon the porosity reduces the validity of this model to small variations of Φ_W (or w). The release of this assumption is the object of ongoing work.

The kinetics rate of precipitation or dissolution process could be under surface control, with a rate v^S, or diffusion control (v^D) depending on the slowest rate. On the whole, if the temperature is less than $300°C$, the overall reaction is controlled by surface processes since $v^S << v^D$ [MCF 94]. This is the case in geological disposals for storing nuclear waste. Indeed, the mean surface temperature ranges $12°C$ in France, the geothermal gradient is around $3°C$ for 100 m and the disposal stands at 500m depth. The nuclear waste package has a temperature lower than $100°C$. An easy computation leads to $127°C << 300°C$.

Therefore it is assumed that the overall reaction is under surface control. The popular chemical-affinity based rate laws used in this paper derives from Transition

State Theory and experimental approaches [AH 82], [SVC 90], [L 95] that can be resumed in [MCF 94]

$$\tilde{r}_W = \begin{cases} -k^{pH}_{dissol,W}\, S_{dissol,react}(w)\ (1 - Q/K) & \text{, if } Q/K < 1 \\ +k_{precip,W}\, S_{precip,react}(w)\ ((Q/K)^q - 1)^p & \text{, if } Q/K > 1 \end{cases}$$

where $S_{dissol,react}(w)$ (resp. $S_{precip,react}(w)$) is the dissolution (resp. precipitation) reactive surface that depends on the mineral concentration w, $k^{pH}_{dissol,W}$ the constant rate for dissolution depending on pH [MCF 94] and $k_{precip,W}$ the constant rate for precipitation. In the sequel, the pH dependance is omitted and $k^{pH}_{dissol,W}$ is denoted by $k_{dissol,W}$. The thermodynamic constant of the chemical reaction (1) is denoted by K and the activity products by Q. The positive parameters p and q depends on the minerals with $q \leq 1$ linked to the stoichiometry of mineral formation reaction [SVC 90]. Values of p are provided by theorical and experimental works and ranges in $[1, 2]$. In the sequel, $p = q = 1$.

For the sake of simplicity, the supersaturation threshold is omitted [MCF 94]. Nevertheless, the modelling of dissolution precipitation kinetics is still a matter of concern since the popular chemical-affinity based rate laws, derived from laboratory scale works, do not account for microscopic processes [L 95]. For instance, growth rates are strongly dependent upon dislocation structures observed at microscopic scale [TDDY 00].

In diluted solutions, the activity is akin to the concentration. Thus

$$Q = u^{\alpha}\, v^{\beta}\ ,$$

if $\alpha\, ,\, \beta > 0$. Several models of reactive surfaces can be found in the litterature [Maz 03] and references therein. Its evaluation is often crucial. We choose the nondifferentiable form

$$\begin{aligned} S_{dissol,react}(w) &= sign(w)^+\, S^0_{react} = \begin{cases} S^0_{react} & \text{if } w > 0 \\ 0 & \text{otherwise,} \end{cases} \\ S_{precip,react}(w) &= S^0_{react}, \end{aligned}$$

where S^0_{react} stands for an average reactive surface. Thus

$$\tilde{r}_W = \lambda \left(F_p(u,v)^+ - sign(w)^+\, F_d(u,v)^- \right), \tag{11}$$

with $\lambda = k_{precip,W}\ S^0_{react}$ and

$$F_p(u,v) = Q/K - 1, F_d(u,v) = (k_{dissol,W}/k_{precip,W})\,(Q/K - 1)\,.$$

The following notations were used :

$$\forall x \in \mathbb{R},\ x^+ = \max(0,x) \text{ and } x^- = \max(0,-x). \tag{12}$$

Hence $x = x^+ - x^-$ and $|x| = x^+ + x^-$.

$$sign(x) = \begin{cases} 1 & \text{if } x > 0 \\ 0 & \text{if } x = 0 \\ -1 & \text{if } x < 0. \end{cases} \tag{13}$$

Otherwise, if $\alpha > 0$ and $\beta < 0$, for instance

$$Ca(OH)_2 \, + \, 2H^+ \Leftrightarrow Ca^{2+} \, + \, 2H_2O \, ,$$

assuming that the activity of H_2O equals 1 then

$$Q = u^\alpha / v^{|\beta|} \, , (U = Ca^{2+}, \alpha = 1 \, ; V = H^+, \beta = -2).$$

We consider her a much more elementary kinetics law:

$$F_p(u,v) = u^\alpha/K - v^{|\beta|}, F_d(u,v) = (k_{dissol,W}/k_{precip,W}) \left(u^\alpha/K - v^{|\beta|} \right),$$

which allows us to perform the mathematical analysis of the discretization scheme.

These statements justify Assumptions 1 item (v). Hence we seek an approximation of a solution $(u,v,w) \; : \; \Omega \times (0,T) \to \mathbb{R}^3$ to the following adimensional problem which comes from (8)-(10),(7),(11) with the additional assumption $k_{dissol,W} = k_{precip,W}$ such that $F_d = F_p = F$:

$$\begin{aligned} u_t(x,t) - \Delta u(x,t) &= -\alpha \, w_t(x,t), && (14) \\ v_t(x,t) - \Delta v(x,t) &= -\beta \, w_t(x,t), && (15) \\ w_t(x,t) &= \lambda (F(u(x,t),v(x,t))^+ \\ & \quad -\text{sign}(w(x,t))^+ F(u(x,t),v(x,t))^-), && (16) \end{aligned}$$

$$(x,t) \in \Omega \times (0,T).$$

with the notations previously defined. The function F estimates the thermodynamical equilibrium gap :

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

We assume that u and v satisfy the following nonhomogeneous Dirichlet boundary conditions:

$$\begin{aligned} u(x,t) &= \bar{u}(x,t), \quad (x,t) \in \partial\Omega \times (0,T), && (17) \\ v(x,t) &= \bar{v}(x,t), \quad (x,t) \in \partial\Omega \times (0,T), && (18) \end{aligned}$$

and that u, v, w satisfy the initial conditions

$$u(x,0) = u_0(x), \quad x \in \Omega, \tag{19}$$

$$v(x,0) = v_0(x), \quad x \in \Omega, \tag{20}$$

$$w(x,0) = w_0(x), \quad x \in \Omega. \tag{21}$$

We suppose that the following assumptions and notations are used.

ASSUMPTION 1

(i) The domain Ω is an open bounded connex polygonal subset of $\mathbb{R}^N$, $N = 1, 2, 3$; we denote by $\partial\Omega$ its boundary. The problem is considered for a given duration $T > 0$.

(ii) The parameters $\alpha \in [0, +\infty)$, $\beta \in \mathbb{R}$, and $\lambda \in (0, +\infty)$ are given.

(iii) 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 $H^1(\Omega \times (0,T))$. Moreover, there exist three real numbers U_0, V_0 and W_0 such that

$$0 \le \bar{u}(x,t) \le U_0\,,\ 0 \le \bar{v}(x,t) \le V_0\,,\ \text{for a.e. } (x,t) \in \Omega \times (0,T),$$

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

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

where U_0, V_0 are defined above.

(v) 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 according to

- $F(u,v) = F(u,0)$ 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 $u, v \in (-\infty, 0)$.

We can now state the definition of a weak solution to Problem (14)-(21).

DEFINITION 1.1 (Weak solution to Problem (14)-(21))

Under Assumption 1, we say that (u,v,w) is a weak solution to Problem (14)-(21) if

$$u-\bar{u}\in L^\infty(\Omega\times(0,T))\cap L^2(0,T;H_0^1(\Omega))\,, \quad (22)$$

$$\int_{\Omega\times(0,T)}(u(x,t)+\alpha w(x,t))\,\Psi_t(x,t)\,\mathrm{d}x\mathrm{d}t-\int_{\Omega\times(0,T)}\nabla u(x,t)\cdot\nabla\Psi(x,t)\,\mathrm{d}x\mathrm{d}t$$

$$+\int_\Omega(u_0(x)+\alpha w_0(x))\;\Psi(x,0)\,\mathrm{d}x=0\qquad\forall\Psi\in C^\infty(\Omega\times[0,T))\,, \quad (23)$$

$$v-\bar{v}\in L^\infty(\Omega\times(0,T))\cap L^2(0,T;H_0^1(\Omega))\,, \quad (24)$$

$$\int_{\Omega\times(0,T)}(v(x,t)+\beta w(x,t))\,\Psi_t(x,t)\,\mathrm{d}x\mathrm{d}t-\int_{\Omega\times(0,T)}\nabla v(x,t)\cdot\nabla\Psi(x,t)\,\mathrm{d}x\mathrm{d}t$$

$$+\int_\Omega(v_0(x)+\beta w_0(x))\;\Psi(x,0)\,\mathrm{d}x=0\qquad\forall\Psi\in C^\infty(\Omega\times[0,T))\,, \quad (25)$$

$$w\in L^\infty(\Omega\times(0,T)) \quad (26)$$

$$\int_{\Omega\times(0,T)}w(x,t)\Psi_t(x,t)\,\mathrm{d}x\mathrm{d}t+\lambda\int_{\Omega\times(0,T)}\left(\begin{array}{l}F(u(x,t),v(x,t))^+-\\ \mathrm{sign}(w(x,t))^+F(u(x,t),v(x,t))^-\end{array}\right)\Psi(x,t)\,\mathrm{d}x\mathrm{d}t$$

$$+\int_\Omega w_0(x)\,\Psi(x,0)\,\mathrm{d}x=0\qquad\forall\Psi\in C^\infty(\Omega\times[0,T)). \quad (27)$$

We then have the following characterization of a weak solution [BEHM].

PROPOSITION 1.2 Under Assumption 1, (u,v,w) is a weak solution to Problem (14)-(21) if and only if the relations (22)-(25) hold in addition to

$$w\in L^\infty(\Omega\times(0,T))\text{ and }w_t\in L^2(\Omega\times(0,T)) \quad (28)$$

$$w(x,0)=w_0(x),\quad\text{for a.e. }x\in\Omega \quad (29)$$

$$\int_{\Omega\times(0,T)}\Psi(x,t)\left(\begin{array}{l}(w(x,t)+F(u(x,t),v(x,t))^+)\times\\ (w_t(x,t)-\lambda F(u(x,t),v(x,t)))\end{array}\right)\mathrm{d}x\,\mathrm{d}t=0,\;\forall\psi\in C_c^\infty(\Omega\times(0,T)). \quad (30)$$

2. Study of the finite volume scheme

Under Assumption 1, we now turn to the discretization of problem (14)–(21). Let $\mathcal{M}$ be an admissible finite volume mesh, in the sense of Definition 9.1 page 762 in [EGH 00]. In the case of triangular meshes, this definition implies that the triangulation complies with the Delaunay condition. We present in Figure 1 two control volumes K and L, as well as their “centers” x_K and x_L. The straight line (x_K,x_L) is orthogonal to the interface $K|L$. We denote by $\mathcal{E}_K^{\mathrm{ext}}$ the edges of the control volume K, located on $\partial\Omega$. Let $\Delta t>0$ denote the time step. We then say that $\mathcal{D}$, the family of all the discrete parameters $\mathcal{M}$, $\mathcal{E}$, $(x_K)_{K\in\mathcal{M}}$, Δt, is an admissible discretization

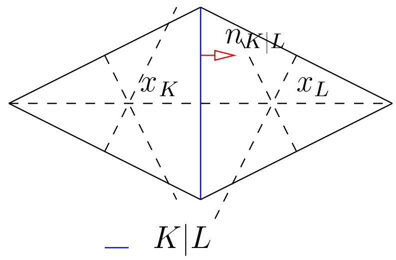

Figure 1. *Example of two control volumes*

of $\Omega \times (0,T)$. We then define by $\mathrm{size}(\mathcal{D})$ the maximum value between the diameters of the elements of $\mathcal{M}$ and Δt, and we define $\mathrm{regul}(\mathcal{D})$, which is the minimum of the ratios between the distance from x_K to any edge of K and the diameter of K, for all $K \in \mathcal{M}$. The initial condition are discretized by:

$$\begin{array}{l} u_K^0 = \frac{1}{\mathrm{m}(K)} \int_K u_0(x)\,\mathrm{d}x\,, \\ v_K^0 = \frac{1}{\mathrm{m}(K)} \int_K v_0(x)\,\mathrm{d}x\,, \\ w_K^0 = \frac{1}{\mathrm{m}(K)} \int_K w_0(x)\,\mathrm{d}x \quad \forall K \in \mathcal{M}. \end{array} \tag{31}$$

The boundary conditions are discretized by

$$\begin{array}{l} \bar{u}_\sigma^{n+1} = \frac{1}{\mathrm{m}(\sigma)\Delta t} \int_{n\Delta t}^{(n+1)\Delta t} \int_\sigma \bar{u}(x,t)\,\mathrm{d}\gamma(x)\mathrm{d}t, \\ \bar{v}_\sigma^{n+1} = \frac{1}{\mathrm{m}(\sigma)\Delta t} \int_{n\Delta t}^{(n+1)\Delta t} \int_\sigma \bar{v}(x,t)\,\mathrm{d}\gamma(x)\mathrm{d}t, \quad \forall \sigma \in \mathcal{E},\ \sigma \subset \partial\Omega,\ \forall n \in \mathbb{N}. \end{array} \tag{32}$$

The scheme is then defined by

$$\mathrm{m}(K)\frac{u_K^{n+1} - u_K^n}{\Delta t} - \sum_{L \in N(K)} T_{KL}\,(u_L^{n+1} - u_K^{n+1}) - \sum_{\sigma \in \mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{u}_\sigma^{n+1} - u_K^{n+1}) = -\alpha\,\mathrm{m}(K)\frac{w_K^{n+1} - w_K^n}{\Delta t}, \tag{33}$$

$$\mathrm{m}(K)\frac{v_K^{n+1} - v_K^n}{\Delta t} - \sum_{L \in N(K)} T_{KL}\,(v_L^{n+1} - v_K^{n+1}) - \sum_{\sigma \in \mathcal{E}_K^{\mathrm{ext}}} T_\sigma\,(\bar{v}_\sigma^{n+1} - v_K^{n+1}) = -\beta\,\mathrm{m}(K)\frac{w_K^{n+1} - w_K^n}{\Delta t}, \tag{34}$$

$$w_K^{n+1} = \left(w_K^n + \Delta t \lambda F(u_K^{n+1}, v_K^{n+1})\right)^+, \tag{35}$$

$$\forall K \in \mathcal{M}, \qquad \forall n \in \mathbb{N},$$

where T_{KL} denotes the ratio of the length of interface $K|L$ over the distance between x_L and x_K. We then define

$$u_{\mathcal{D}}(x,t) = u_K^{n+1},\ v_{\mathcal{D}}(x,t) = v_K^{n+1},\ w_{\mathcal{D}}(x,t) = w_K^{n+1},\ \text{ for a.e. } (x,t) \in K \times (n\Delta t, (n+1)\Delta t),\ \forall K \in \mathcal{M}, \tag{36}$$

$$\forall n \in \mathbb{N}.$$

REMARK 2.1
From the relation (35), 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

$$w_K^{n+1} - w_K^n = \Delta t \lambda \, \theta_K^{n+1} \, F(u_K^{n+1}, v_K^{n+1}) \, . \tag{37}$$

We then have the following property.

PROPOSITION 2.1 ($L^\infty(\Omega \times (0,T))$ ESTIMATE ON THE APPROXIMATE SOLUTION)

Under Assumption 1, let $\mathcal{D}$ be an admissible dicretization of $\Omega \times (0,T)$. Let $\mu \in [0,\lambda]$ and let $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ satisfy (31), (32), (33), (34), (35) replacing λ by μ, and (37). Then there exist (U,V,W), only depending on T, α, β, λ, F, U_0, V_0 and W_0, such that

$$0 \le u_\mathcal{D}(x,t) \le U, \quad 0 \le v_\mathcal{D}(x,t) \le V, \quad 0 \le w_\mathcal{D}(x,t) \le W, \text{ for a.e. } (x,t) \in \Omega \times (0,T). \tag{38}$$

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 1, 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 $u_K^{n+1} = \min_{L \in \mathcal{M}} u_L^{n+1}$. Reasonning by contradiction, let us assume that $u_K^{n+1} < 0$. From the scheme (33) and using (37), we get

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

From Assumption (1).(v), 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 $u_K^{n+1} \ge 0$. Similarly, let K be a control volume such that $v_K^{n+1} = \min_{L \in \mathcal{M}} v_L^{n+1}$. Let us again assume that $v_K^{n+1} < 0$. We have

$$\begin{aligned} v_K^{n+1} \quad &= \quad \frac{\Delta t}{\mathrm{m}(K)} \left(\sum_{L \in N(K)} T_{KL} \, (v_L^{n+1} - v_K^{n+1}) + \sum_{\sigma \in \mathcal{E}_K^{\mathrm{ext}}} T_\sigma \, (\bar{v}_\sigma^{n+1} - v_K^{n+1}) \right) \\ &\quad + v_K^n - \beta\mu \, \theta_K^{n+1} \, F(u_K^{n+1}, v_K^{n+1}). \end{aligned}$$

From Assumption (1).(v), we get in this case that $\beta F(u_K^{n+1}, v_K^{n+1}) = \beta F(u_K^{n+1}, 0) \le 0$, which gives again a contradiction. Thus $v_K^{n+1} \ge 0$. The positiveness of w_K^{n+1} immediately results from (35). Let us now obtain the existence of an upper bound. We first consider the case $\beta < 0$. In this case, then we denote, for all $K \in \mathcal{M}$ and

$n \in \mathbb{N}$, $z_K^n = \alpha v_K^n - \beta u_K^n$, and $\bar{z}_\sigma^{n+1} = \alpha \bar{v}_\sigma^{n+1} - \beta \bar{u}_\sigma^{n+1}$ for all $\sigma \in \mathcal{E}$. We then get, from (33) and (34):

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

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 $\alpha v_K^n - \beta u_K^n \leq \alpha U_0 - \beta V_0$, and therefore $v_K^n \leq V := (\alpha U_0 - \beta V_0)/\alpha$ and $u_K^n \leq U := (\alpha U_0 - \beta V_0)/(-\beta)$. 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 $u_K^{n+1} = \max_{L \in \mathcal{M}} u_L^{n+1}$. If $u_K^{n+1} > U_0$, then, from (33), we get

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

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 $w_K^{n+1} \leq W_0 + \mu T \bar{F} \leq W := W_0 + \lambda T \bar{F}$. We remark that in all cases, U, V, W do not depend on μ. $\square$

We can then deduce the following corollary.

COROLLARY 2.2 (EXISTENCE OF A DISCRETE SOLUTION)

Under Assumption 1, let $\mathcal{D}$ be an admissible dicretization of $\Omega \times (0,T)$. Then there exists at least one $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ satisfying (31), (32), (33), (34), (35) and (37) such that (38) holds, with (U,V,W), only depending on T, α, β, λ, F, U_0, V_0 and W_0.

This corollary is proven using the topological degree method (see [EGH 00]). For a complete proof, refer to [BEHM].

THEOREM 2.3 (CONVERGENCE OF THE FINITE VOLUME SCHEME)

Under Assumption 1, let $\mathcal{D}$ be an admissible dicretization of $\Omega \times (0,T)$. Let $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ be a solution of (31), (32), (33), (34), (35) and (37). Then $(u_\mathcal{D}, v_\mathcal{D}, w_\mathcal{D})$ converges in $L^2(\Omega \times (0,T))$ to (u,v,w), a weak solution of Problem ((14)-(21)) in the sense of Definition 1.1, as $\mathrm{size}(\mathcal{D})$ tends to 0 while $\mathrm{regul}(\mathcal{D})$ 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 2.1, 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 on the dicretization. Thus, from this sequence, one can extract a subsequence and a function f such that the functions $f_{\mathcal{D}}$ 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 $L^2(\Omega \times (0,T))$ to f. Then, using the tools developped in [EGH 00], one may show [BEHM] the strong convergence in $L^2(\Omega \times (0,T))$ 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 $L^\infty(\Omega \times (0,T))$). Let us prove that $w_{\mathcal{D}}$ also strongly converges in $L^2(\Omega \times (0,T))$. Let $\xi \in \mathbb{R}^N$ and Ω_ξ be defined by $\Omega_\xi = \{x \in \Omega$ 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 (35),

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

We then get

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

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

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

thus producing

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

Integrating the above equation on Ω_ξ, we obtain

$$\begin{aligned}\int_{\Omega_\xi} (w_{\mathcal{D}}^n(x) \quad - \quad & w_{\mathcal{D}}^n(x+\xi))^2 \mathrm{d}x \leq 2 \int_{\Omega_\xi} (w_{\mathcal{D}}^0(x) - w_{\mathcal{D}}^0(x+\xi))^2 \mathrm{d}x \\ & + 2T\lambda \sum_{p=1}^{n} \Delta t \int_{\Omega_\xi} (F_{\mathcal{D}}^p(x) - F_{\mathcal{D}}^p(x+\xi))^2 \mathrm{d}x.\end{aligned}$$

We now sum (39) over $n = 1, \ldots, N_{\Delta t}$. This gives

$$\begin{aligned}\sum_{n=0}^{N_{\Delta t}} \Delta t \int_{\Omega_\xi} (w_{\mathcal{D}}^n(x) - w_{\mathcal{D}}^n(x+\xi))^2 \mathrm{d}x \leq \quad & 2 \sum_{n=0}^{N_{\Delta t}} \Delta t \int_{\Omega_\xi} (w_{\mathcal{D}}^0(x) - w_{\mathcal{D}}^0(x+\xi))^2 \mathrm{d}x \\ & + \sum_{n=0}^{N_{\Delta t}} 2T\lambda \sum_{p=1}^{n} \Delta t \int_{\Omega_\xi} (F_{\mathcal{D}}^p(x) - F_{\mathcal{D}}^p(x+\xi))^2 \mathrm{d}x,\end{aligned} \tag{39}$$

and therefore

$$\int_0^T \int_{\Omega_\xi} (w_{\mathcal{D}}^n(x,t) - w_{\mathcal{D}}^n(x+\xi,t))^2 \mathrm{d}x\mathrm{d}t \leq \quad 2T \int_{\Omega_\xi} (w_{\mathcal{D}}^0(x) - w_{\mathcal{D}}^0(x+\xi))^2 \mathrm{d}x$$
$$+2T^2\lambda \int_0^T \int_{\Omega_\xi} (F_{\mathcal{D}}(x,t) - F_{\mathcal{D}}(x+\xi,t))^2 \mathrm{d}x\mathrm{d}t. \tag{40}$$

This implies that the space translates of $w_{\mathcal{D}}$ uniformly tend to 0. Since, from (35), we easily get that the time translates of $w_{\mathcal{D}}$ also uniformly tend to 0, a simple prolongement by 0 and the L^∞ bound on $w_{\mathcal{D}}$ are sufficient to apply Kolmogorov's theorem. We thus get that we can extract a subsequence such that $w_{\mathcal{D}}$ strongly converges. We now remark that

$$\left(w_K^{n+1} + (F(u_K^{n+1}, v_K^{n+1}))^+\right) \left(\frac{w_K^{n+1} - w_K^n}{\Delta t} - \lambda F(u_K^{n+1}, v_K^{n+1})\right) = 0, \quad \forall K \in \mathcal{M}, \forall n \in \mathbb{N},$$

since, either $\frac{w_K^{n+1} - w_K^n}{\Delta t} = \lambda F(u_K^{n+1}, v_K^{n+1})$, either $\frac{w_K^{n+1} - w_K^n}{\Delta t} \neq \lambda F(u_K^{n+1}, v_K^{n+1})$, which implies that $w_K^{n+1} = 0$ and $F(u_K^{n+1}, v_K^{n+1}) \leq 0$. Let $\Psi \in C^\infty(\Omega \times [0,T))$. We multiply the above equation by $\Psi(x_K, n\Delta t)$. we get

$$\sum_{n=0}^{N_{\Delta t}} \Delta t \sum_{K \in \mathcal{M}} \Psi(x_K, n\Delta t) \left(w_K^{n+1} + (F(u_K^{n+1}, v_K^{n+1}))^+\right) \left(\frac{w_K^{n+1} - w_K^n}{\Delta t} - \lambda F(u_K^{n+1}, v_K^{n+1})\right) = 0.$$

It is then possible to pass to the limit on the above subsequence, 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 application of Proposition 1.2 suffices to conclude the proof of the convergence.
□

3. Numerical tests

For instance, we consider the simplified chemical reaction

$$Portlandite(Ca(OH)_2) \Leftrightarrow 2\, OH^- \,+\, Ca^{2+} \quad K\,.$$

The parameters value

$$\lambda = 10^6\,,\; K = 10^{-3}\,.$$

We denote by $u = [OH^-]$, $v = [Ca^{2+}]$ and $w = [(Ca(OH)_2)]$. We consider $\alpha = 2$, $\beta = 1$. The diffusion values 0.5 m^2 year^{-1}. The porous media is a square

$\Omega = (0,1) \times (0,1)$ (m^2). Here are the initial conditions $u_0 = 0$, $v_0 = 0$, $w_0 = 0$ and the boundary conditions are :

$$\text{Dirichlet Conditions} \quad : \quad \begin{cases} u = 1\,,\, v = 0 & \text{if } y \in [0.2, 0.32], \\ u = 0\,,\, v = 1 & \text{if } x \in [0.2, 0.32], \end{cases}$$

Homogeneous Neumann Conditions : elsewhere.

In this case, we choose

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

On the Figure 2, we observe the different concentrations at times $t_0 = 0.1$ and $t_1 = 5$. The diffusion of u and v is slowed down because of the precipitation of w. Our model allow w to precipitate, nevertheless there is no constraint on the upper bound of w. Indeed w is always increasing. To be more realistic, the model should take into account the variation of porosity due to precipitation, which would lead to a slowing down of the diffusion of species in areas where a mineral precipitates.

4. Future works

Ongoing research concerns the singular limit problem ($\lambda \to +\infty$), for which a formal asymptotic study is considered. It consists in searching self-similar solutions such as in [HHP 96][ADDN 04] and solving a free boundary problem. We also plan on improving the model, taking into account the evolution of the porosity. Indeed, it is clear that the porosity should depend on the mineral concentration and strongly impacts the diffusion phenomena. The goal will be to obtain L^∞ estimates which do not depend on the kinetics parameter λ. In particular, the key point is to obtain L^∞ boundedness for the mineral concentration.

Aknowledgment This work was supported by GDR MOMAS.

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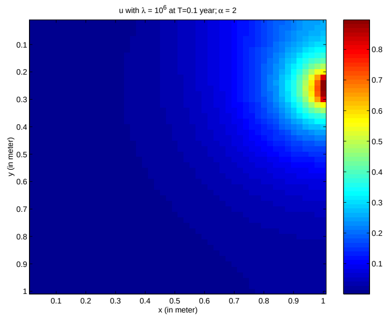
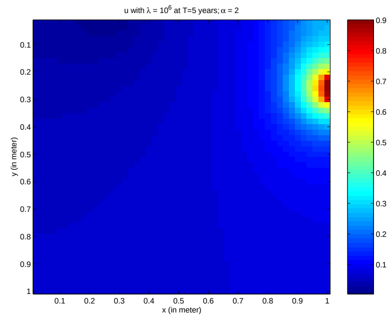
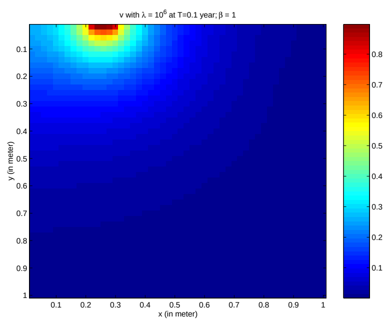


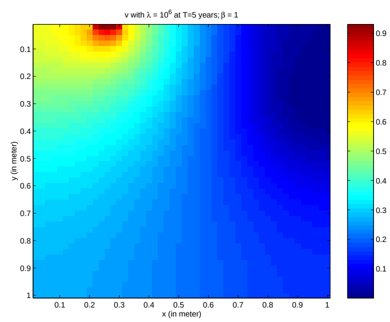
(a) OH^- à t_0



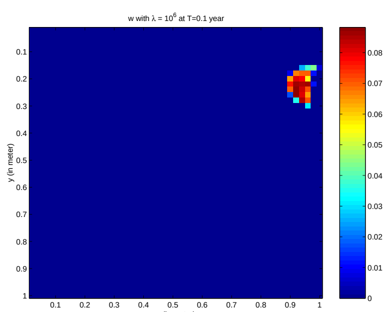
(b) OH^- à $t_1 > t_0$



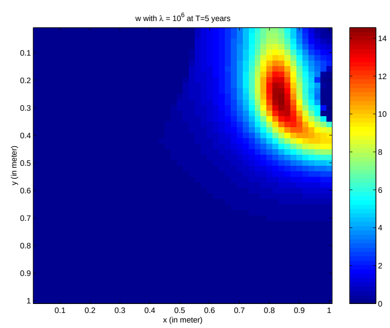
(c) Ca^{2+} à t_0



(d) Ca^{2+} à $t_1 > t_0$



(e) Portlandite à t_0



(f) Portlandite à $t_1 > t_0$

Figure 2. *Portlandite coprecipitation*