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Analysis and numerical computation of geochemical systems with kinetic precipitation and dissolution reactions involving several minerals

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Abstract

In this paper, we study underground media where chemical interactions involve aqueous and mineral species. In most kinetic models, a mineral species is involved in a single precipitation or dissolution reaction. In this work, we consider more general precipitation and dissolution kinetic reactions, which can include several minerals, which can each participate in several reactions. We propose a differential inclusion model, with reaction rates defined by set-valued functions, in order to ensure positive quantities of species. We also develop a regularized model, with reaction rates defined by regularized Heaviside functions and blendings if several minerals dissolve in the same reaction. We prove that the unique solution of this system of ODEs converges towards a solution of the differential inclusion model. We run numerical experiments by using a classical ODEs solver for computing the regularized solution. We get good numerical approximations of the quantities of species and the discontinuous reaction rates.

1 Introduction

Underground media provide both natural resources and potential sites for waste storage. The conflicting resource and storage objectives reveal a wide panel of chemical and biological interactions. Evolution is characterized by many complex processes, such as precipitation and dissolution with or without kinetics and ion exchanges involving evolution of pH and redox conditions. Risk assessment and resource management rely on numerical simulations at large scale. Relevant and efficient reactive transport models are

essential to assess the complexity of physical and chemical processes at large time and space scales [7, 13].

In this paper, we consider geochemical reactions involving minerals [17], [21], [23], [24], [20] and [25]. If reactions are sufficiently fast, they can be considered in a local equilibrium, mathematically modeled by algebraic nonlinear equations [12]. On the other hand, kinetic reactions are governed by mass balance equations, written as ordinary differential equations (ODEs), where the right-hand side involves stoichiometry of the geochemical system and reaction rates. These ODEs must take into account precipitation or dissolution of minerals. When a mineral participates in only one reaction, with only aqueous species, the kinetic rate can be described by a discontinuous function, a set-valued function, or a complementarity problem, [1], [4], [15], [16], [17], [18], [19] and [25]. These three models are equivalent under some conditions [16].

In some complex chemical systems, several minerals participate in the same kinetic reaction, or a mineral is involved in several reactions, [3], [15] and [21]. Reaction rates must be limited as previously when dissolving minerals disappear. However, the extension of the single mineral limiting process is far from straightforward when considering a chemical network of several mineral reactions. It becomes even more intricate if several minerals dissolve in the same reaction, but are still produced in other reactions.

In this paper, we propose a generalized model dealing with these cases. A key idea of this paper is to control reaction rates by set-valued functions, which limit the rate when dissolving minerals disappear. This results in a differential inclusion problem. In the analysis of differential inclusion systems, a first difficulty is to prove the existence of a solution, while a second difficulty is to provide a numerical method to solve the system. For geochemical systems with one mineral per reaction and one reaction per mineral, Filippov's theory [14] provides a strong theoretical basis for the study of such systems and allows the use of efficient custom even driven methods to solve the resulting system of ODEs [1]. Unfortunately, characterizing the set-valued functions for the systems considered in this paper is still an open question [9] [10] [8]. It is also possible to limit the derivatives of each mineral species in a projected dynamical system, which is another topic under consideration [11].

In this work, we overcome these difficulties using regularized reaction rates to obtain a regular system of ODEs. A second key idea is the choice of an appropriate blending function to uniquely define the regularized limiters. This leads to a unique solution of the regularized system for a given blending function. Then, we prove convergence of the regularized quantities of species and limiters towards a solution of the differential inclusion problem. Since the regularized system is easy to solve, it provides a numerical approximation of the desired result.

This paper is organized as follows. Section 2 is a general introduction to geochemical kinetics with aqueous and mineral species. Section 3 summarizes the state of the art in the case of one mineral per reaction and one reaction per mineral. In section 4, we discuss the discontinuous model applied to a single reaction between a solute and a mineral. Then section 5 is devoted to our general differential inclusion problem, with the corresponding regularized model. We prove convergence and existence results. In order to illustrate our model, we consider a system of two reactions where a mineral is a product of the first reaction and a reactant of the second one. A detailed analysis of convergence is given in section 6. Numerical experiments, developed in Matlab, show the efficiency of

regularization to get an approximate solution. In section 7, we propose several test cases, with either simple or complex geochemical systems. We conclude and discuss future work in last section.

2 Mathematical model of kinetic reactions

We consider a geochemical system with an aqueous phase and several mineral phases. The aqueous phase is composed of water and several diluted species whereas a mineral phase contains only one species. We do not consider source or sink terms. We assume that the pressure and temperature are constant during the reactions.

Kinetic reactions in this system are governed by reaction rates and conservation laws. Reactions are considered reversible, with forward and backward directions. The number of reactions is $N_r > 0$ and each reaction is noted $R_j, j = 1, \dots, N_r$. The number of aqueous species is $N_a > 0$ and each aqueous species is noted $A_i, i = 1, \dots, N_a$. The number of minerals is $N_p \geq 0$ and if $N_p > 0$, each mineral is noted $M_k, k = N_a + 1, \dots, N_a + N_p$. The stoichiometric matrix $S \in \mathbb{Z}^{(N_a+N_p) \times N_r}$ contains the coefficients of reactions.

We set an arbitrary forward direction of a reversible reaction R_j . Species on the left are called reactants and are associated to negative stoichiometric coefficients, whereas species on the right, called products, correspond to positive coefficients [20]. In reaction R_j , we denote by \mathcal{A}_i^- and \mathcal{M}_k^- the sets of aqueous and mineral reactants, by \mathcal{A}_i^+ and \mathcal{M}_k^+ the sets of aqueous and mineral products.

A reaction R_j is written

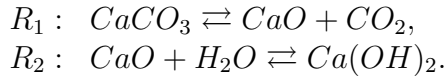
$$\sum_{i \in \mathcal{A}_j^-} |s_{ij}| A_i + \sum_{k \in \mathcal{M}_j^-} |s_{kj}| M_k \rightleftharpoons \sum_{i \in \mathcal{A}_j^+} |s_{ij}| A_i + \sum_{k \in \mathcal{M}_j^+} |s_{kj}| M_k. \quad (1)$$

In this paper, we only consider balanced chemical equations, with as many atoms on the reactants side than on the products side.

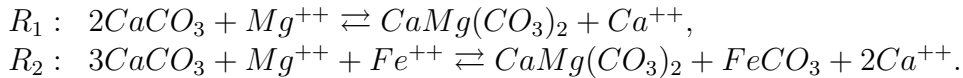
2.1 Examples of reactions with more than one mineral

We provide here three examples of geochemical reactions, where a mineral precipitates into another one.

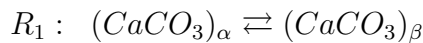
In the first example, calcite $CaCO_3$ is decarbonated to produce calcium oxide CaO which undergoes hydrolysis to form calcium hydroxide $Ca(OH)_2$:



In the second example, calcite either reacts with Magnesium ions to form dolomite $CaMg(CO_3)_2$ or with Magnesium and Iron ions to form siderite $FeCO_3$:



The last example is the phase transition of calcite into aragonite:



where α and β represent respectively the calcite and aragonite crystal forms of calcium carbonate.

2.2 Quantities of species and reaction rates

The unknowns in such a geochemical system are the number of moles of each species, grouped into a vector of functions $\mathbf{c} = (c_i)$, $i = 1, \dots, N_a + N_p$ of the time variable t with $t \geq 0$. We denote by $\mathbf{c}_a = (c_i)$, $i = 1, \dots, N_a$ the vector of quantities for aqueous species, and by $\mathbf{c}_p = (c_k)$, $k = N_a + 1, \dots, N_a + N_p$ the vector of mineral quantities. The quantities \mathbf{c} should satisfy a positivity constraint $\mathbf{c}(t) \geq 0$, $t \geq 0$. We also require that $\mathbf{c} \in (H^1(0, T))^{N_a + N_p}$ with $T > 0$.

In this paper, we propose a model of differential equations, which satisfy mass conservation laws and various invariants. The right-hand side uses reaction rates $\mathbf{r} = (r_j)$, functions in $L^2(0, T)$, based on mass action laws. Our objective is to define a model of reaction rates such that the differential system has a solution satisfying the requirements given above.

2.3 Conservation laws

Mass conservation laws are grouped into a system of differential equations:

$$\begin{cases} \frac{d\mathbf{c}(t)}{dt} = S\mathbf{r}(t), t \in (0, T) \\ \mathbf{c}(t) \geq 0, \\ \mathbf{c}(0) = \mathbf{c}_0, \end{cases} \quad (2)$$

where $\mathbf{c}_0 \geq 0$ is a given initial condition, and reaction rates \mathbf{r} are discontinuous functions, defined thanks to mass action laws and set-valued functions. We define a weak solution of system (2).

Definition 2.1. *Let $T > 0$, let $\mathbf{c} \in H^1(0, T)^{N_a + N_p}$. It is a weak solution of system (2) if $\mathbf{c} \geq 0$ and $\forall t \in [0, T]$,*

$$c_i(t) = c_{0,i} + \int_0^t (Sr)_i(s) ds, \quad i = 1, \dots, N_a + N_p.$$

It can be noted that this system implies invariants, which correspond to balance equations and conservative variables. Indeed, let Q be a basis of it, or equivalently a basis of the subspace orthogonal to the image of S . We get $Q^T S = S^T Q = 0$. Then, any solution of (2) satisfies $\forall t \geq 0, Q^T \mathbf{c}(t) = Q^T \mathbf{c}_0$. Functions $Q^T \mathbf{c}$ are thus constant in time and are conservative variables.

In particular, let \mathbf{q} be the vector of molar mass of species, which satisfies $\mathbf{q} > 0$. Since we assume that each equation is mass balanced, \mathbf{q} satisfies $S^T \mathbf{q} = 0$, so that total mass $\mathbf{q}^T \mathbf{c}$ is an invariant of the system. This vector provides an upper bound on the solutions of (2) using the following lemma:

Lemma 2.1. *Let \mathbf{q} be the vector of molar mass of species involved in the chemical system.*

If \mathbf{c} satisfies $\mathbf{c} \geq 0$ and $\mathbf{q}^T \mathbf{c} = \mathbf{q}^T \mathbf{c}_0$ then $\mathbf{c} \leq C$ with $C = \frac{1}{\min_k(q_k)} \mathbf{q}^T \mathbf{c}_0$.

Proof. Let $k \in \{1, \dots, N_a + N_p\}$. First, $\mathbf{q}^T \mathbf{c} = q_k c_k + \sum_{i \neq k} q_i c_i \geq q_k c_k$ since $c_i \geq 0$ and $q_i > 0$. Then $q_k c_k \leq \mathbf{q}^T \mathbf{c}_0$ and $c_k \leq \frac{1}{q_k} \mathbf{q}^T \mathbf{c}_0 \leq C$. □

Other notable invariants in usual chemical systems can be the charge balance or the total mass of each chemical element.

2.4 Maximal reaction rates

Reactions R_j involve a forward reaction, with reactants and products, and a backward reaction, where products become reactants and vice versa. Each direction has its own reaction rate, and the net rate is the difference between both. When a reaction involves only aqueous species, its rate is given by a mass action law, which is a function of species' activities [6]. When a pure phase exists, its activity is equal to 1; we extend it to 1 when the quantity of pure phase is zero. Various models of aqueous activities exist in the literature, see [5] for example. Throughout the paper, we make the following assumptions.

Assumption 2.1. *The activity a_i of a solute A_i is a C^1 function of \mathbf{c}_a which satisfies:*

$$\mathbf{c}_a \geq 0 \Rightarrow \mathbf{a}(\mathbf{c}_a) \geq 0$$

$$c_{a,i} \leq 0 \Rightarrow a_i(\mathbf{c}_a) = 0.$$

The forward reaction rate of reaction R_j is given by

$$\tau_{f,j} = k_{f,j} \prod_{i \in \mathcal{A}_j^-} \left(\frac{a_i}{K_i}\right)^{|s_{ij}|} \prod_{k \in \mathcal{M}_j^-} \left(\frac{1}{K_k}\right)^{|s_{kj}|}$$

and its backward reaction rate is

$$\tau_{b,j} = k_{b,j} \prod_{i \in \mathcal{A}_j^+} \left(\frac{a_i}{K_i}\right)^{|s_{ij}|} \prod_{k \in \mathcal{M}_j^+} \left(\frac{1}{K_k}\right)^{|s_{kj}|}$$

If \mathcal{A}_j^- is empty, the product $\prod_{i \in \mathcal{A}_j^-} \left(\frac{a_i}{K_i}\right)^{|s_{ij}|}$ is equal to 1. The same property applies to other subsets. The net reaction rate is the difference between forward and backward reaction rates:

$$\tau_j = \tau_{f,j} - \tau_{b,j}.$$

Finally, we will use the following formula, where constants are grouped together:

$$\tau_j(\mathbf{c}_a) = \alpha_j \prod_{i \in \mathcal{A}_j^-} a_i(\mathbf{c}_a)^{|s_{ij}|} - \beta_j \prod_{i \in \mathcal{A}_j^+} a_i(\mathbf{c}_a)^{|s_{ij}|}, j = 1, \dots, N_r. \quad (3)$$

where α_j and β_j are strictly positive constants.

Thermodynamic equilibrium of reaction R_j is obtained when forward and backward reactions are balanced, in other words when the net reaction rate is zero: $\tau_j = 0$. It corresponds to the mass action law for chemistry at equilibrium.

In our differential inclusion model, we control reaction rates r_j with τ_j being an upper bound (in absolute value). From now on, we call the vector $\boldsymbol{\tau}$ the maximal reaction rates.

2.5 Continuous model

We consider the continuous differential system with the vector $\boldsymbol{\tau}$ of maximal reaction rates:

$$\begin{cases} \frac{d\mathbf{c}(t)}{dt} = S\boldsymbol{\tau}(\mathbf{c}_a(t)), t \geq 0, \\ \mathbf{c}(0) = \mathbf{c}_0. \end{cases} \quad (4)$$

Proposition 2.1. *The geochemical system (4) has a unique solution satisfying $\mathbf{c} \in (H^1(0, +\infty))^{N_a+N_p}$.*

Proof. Thanks to Assumption 2.1, the maximal rate $\boldsymbol{\tau}$ is C^1 . Since the right-hand side is regular, we can apply Cauchy-Lipschitz theorem so that the system has a unique solution in $(0, +\infty)$. \square

In order to study the non-negativity of quantities c_i , we introduce the notion of essential non negativity [6].

Definition 2.2. *Let f be a function from \mathbb{R}^{N_a} to \mathbb{R}^{N_a} . It is essentially non-negative if, for any $k = 1, \dots, N_a$,*

$$c_i \geq 0, i = 1, \dots, N_a \text{ and } c_k = 0 \Rightarrow f_k(c) \geq 0.$$

Since the reaction rates τ_j depend only on the quantities \mathbf{c}_a of aqueous species, we can define a function f from \mathbb{R}^{N_a} to \mathbb{R}^{N_a} by

$$f_k(\mathbf{c}_a) = (S\boldsymbol{\tau}(\mathbf{c}_a))_k, k = 1, \dots, N_a. \quad (5)$$

Proposition 2.2. *The function f defined by (5) is locally Lipschitz continuous and essentially non negative.*

Proof. Since $\boldsymbol{\tau}$ is regular, f is at least locally Lipschitz continuous.

Let $\mathbf{c}_a \geq 0$ with $c_k = 0$ for some k . Then $\mathbf{a}(\mathbf{c}_a) \geq 0$ and $a_k(c_k) = 0$.

If $s_{kj} > 0$ then $A_k \in \mathcal{A}_j^+$ and $\tau_j(\mathbf{c}_a) \geq 0$ thus $s_{kj}\tau_j \geq 0$.

If $s_{kj} < 0$ then $A_k \in \mathcal{A}_j^-$ and $\tau_j(\mathbf{c}_a) \leq 0$ thus $s_{kj}\tau_j \geq 0$.

Finally, $f_k(\mathbf{c}_a) = \sum_{j: s_{kj} \neq 0} s_{kj}\tau_j(\mathbf{c}_a) \geq 0$. \square

Thanks to this property, we prove that the quantities of all aqueous species remain positive.

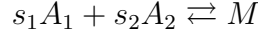
Proposition 2.3. *If $\mathbf{c}_0 \geq 0$ then the unique solution \mathbf{c} of system (4) satisfies $\mathbf{c}_a \geq 0$.*

Proof. Let us consider the system of ODE with only the first N_a equations, in other words with the function f , which is essentially non negative and locally Lipschitz continuous by Proposition 2.2. By using Theorem 1 in [6], we get the result wanted. \square

Denoting by \mathbf{c} the solution of (4), it may exist a mineral M_k , $N_a + 1 \leq k \leq N_a + N_p$ and a time t^* such that $c_k(t^*) < 0$. Mathematical models aim at limiting reaction rates \mathbf{r} so that the solution of (2) is non-negative. We first consider a specific case, well studied in the literature.

3 State of the art: one mineral in one reaction

Here, we consider the particular case of two aqueous species A_1 and A_2 which precipitate into a mineral M :



with $s_1 > 0, s_2 > 0$. An example is the precipitation and dissolution of calcite: $Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3$. Such kinetic models have been studied by several authors [1, 4, 16]. Since the system of three equations has two invariants, it is sufficient to consider the equation for c_M :

$$\frac{dc_M}{dt} = r.$$

The maximal reaction rate given by (3) is

$$\tau = \alpha a_1^{s_1} a_2^{s_2} - \beta,$$

where a_1, a_2 are activities of aqueous species A_1, A_2 . It seems natural to choose $r = \tau$ as long as c_M is not fully dissolved ($c_M > 0$). Different choices of r appear in the literature when $c_M = 0$. With a discontinuous model, r is such that the reaction stops as soon as the mineral is fully dissolved [4]. With a set-valued model, r belongs to a given set [16]; moreover, the value at $c_M = 0$ can be specified [1]. A third model is based on a complementarity problem [16]. Under some assumptions, the three models are equivalent in the sense that they have the same unique weak solution [16].

3.1 Discontinuous model

Let us introduce the positive part $\tau^+(\mathbf{c}_a)$ and the negative part $\tau^-(\mathbf{c}_a)$ of the continuous reaction rate so that

$$\tau(\mathbf{c}_a) = \tau^+(\mathbf{c}_a) - \tau^-(\mathbf{c}_a).$$

If $\tau(\mathbf{c}_a) > 0$ then $\tau(\mathbf{c}_a) = \tau^+(\mathbf{c}_a)$ and the product mineral M precipitates. There is no need to limit the reaction. On the other hand, if $\tau(\mathbf{c}_a) < 0$ then $\tau(\mathbf{c}_a) = \tau^-(\mathbf{c}_a)$ and the product mineral M dissolves. The reaction rate r must be limited in order to ensure the positivity of c_p : it is defined by multiplying the negative part of τ by a control function.

$$r(\mathbf{c}) = \tau^+(\mathbf{c}_a) - H(c_M)\tau^-(\mathbf{c}_a), \quad (6)$$

where H is the Heaviside function defined in $[0, +\infty[$ by

$$\begin{cases} \text{if } x > 0 \text{ then } H(x) = 1, \\ \text{if } x = 0 \text{ then } H(x) = 0. \end{cases}$$

It can be noted that the Heaviside function H thus the reaction rate r can be defined for negative values: $H(x) = 0$ if $x < 0$. Clearly, the reaction stops ($r = 0$) when M is fully dissolved and continues at the maximal rate ($r = \tau$) otherwise. In other words, the choice (6) satisfies the following requirements:

$$\begin{cases} \text{if } c_M > 0 \text{ or } \tau \geq 0 \text{ then } r = \tau, \\ \text{if } c_M = 0 \text{ and } \tau \leq 0 \text{ then } r = 0. \end{cases} \quad (7)$$

The kinetic model (2) is then a system of differential equations, where the reaction rate is a piecewise discontinuous function. It has a unique weak solution [4].

3.2 Set-valued model

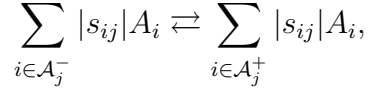
The set-valued model does not specify the value of r with total dissolution. The idea is to limit the backward reaction rate β by a set-valued function:

$$r = \alpha a_1^{s_1} a_2^{s_2} - w_M \beta,$$

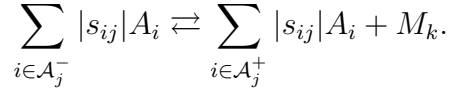
where $w_M \in W(c_M)$ with

$$\begin{aligned} W(u) &= \{1\} & \text{if } u > 0, \\ &= [0, 1] & \text{if } u = 0, \\ &= \{0\} & \text{if } u < 0. \end{aligned} \tag{8}$$

Thus, $r = \tau$ as long as $c_M > 0$ and $\tau \leq r \leq \alpha a_1^{s_1} a_2^{s_2}$. When $c_M = 0$, the value of w_M can be chosen such that $r = 0$ [1]. This model can be extended to a set of aqueous and mineral reactions, provided that a mineral reaction contains exactly one mineral which participates only in this reaction of precipitation and dissolution [16]. Therefore an aqueous reaction R_j is written



whereas a mineral reaction R_j involving the mineral M_k is written



It can be noted that it is more restrictive than general reactions (1) considered in this paper.

Let R_j be a reaction with mineral M_k , with τ_j defined by (3). Then the set-valued model for reaction rate r_j is written

$$r_j = \alpha_j \prod_{i \in \mathcal{A}_j^-} a_i(\mathbf{c}_a)^{|s_{ij}|} - w_k \beta_j \prod_{i \in \mathcal{A}_j^+} a_i(\mathbf{c}_a)^{|s_{ij}|},$$

where $w_k \in W(c_k)$ with the set-valued function W defined by (8).

Under some assumptions, the reactive transport model coupling advection-diffusion with the geochemical system has a unique weak solution [16]. The proof uses a regularized chemical system where the set-valued function W is replaced by a regularized Heaviside function.

3.3 Complementarity model

Here, the value of r when $c_M = 0$ is not given, but the function r is defined by the following complementarity problem:

$$c_M(r - \tau) = 0, \quad c_M \geq 0, \quad r \geq \tau.$$

Then system (2) with r defined above has a unique weak solution [16].

4 Discontinuous solution of system $A \rightleftharpoons M$

In order to illustrate the appearance and disappearance of a pure phase, we study a very simple model with one reaction involving one aqueous species and one mineral: $A \rightleftharpoons M$.

System (2) is then written, with $\mathbf{c} = (c_A, c_M)$:

$$\begin{cases} \frac{dc_A(t)}{dt} = -r(t), \\ \frac{dc_M(t)}{dt} = +r(t), \\ c_A(t) \geq 0, c_M(t) \geq 0, \\ c_A(0) = c_{A,0}, c_M(0) = c_{M,0}. \end{cases} \quad (9)$$

The conservative variable is $(c_A + c_M)$, since $Q = (1, 1)^T$. Here, we choose a simple activity model with $a(c_A) = c_A$, so that the mass action law (3) becomes $\tau(c_A) = \alpha c_A - \beta$, which we rewrite (with $\alpha = 1$ and $\beta = K$)

$$\tau(c_A) = c_A - K,$$

where K is a strictly positive constant.

The continuous problem (4) with the reaction rate $\tau(c_A)$ has a unique solution:

$$\begin{cases} c_A^*(t) = K + \tau_0 \exp(-t), t \geq 0, \\ c_M^*(t) = c_{M,0} + \tau_0(1 - \exp(-t)), t \geq 0. \end{cases} \quad (10)$$

where $\tau_0 = c_{A,0} - K$. Thus $\tau(t) = \tau_0 \exp(-t)$ and $c_A^*(t) > 0, t > 0$.

If $\tau_0 = 0$, then $\tau(t) = 0$ and $r(t) = 0$, thus the system is at equilibrium at any time. From now on, we assume that $\tau_0 \neq 0$.

The discontinuous reaction rate (6) becomes here:

$$r(c_A, c_M) = \tau^+(c_A) - H(c_M)\tau^-(c_A). \quad (11)$$

The discontinuous model (9) with reaction rate (11) has a unique weak solution, satisfying definition 2.1. In what follows, we compute this solution, in the three situations depicted in Figure 1.

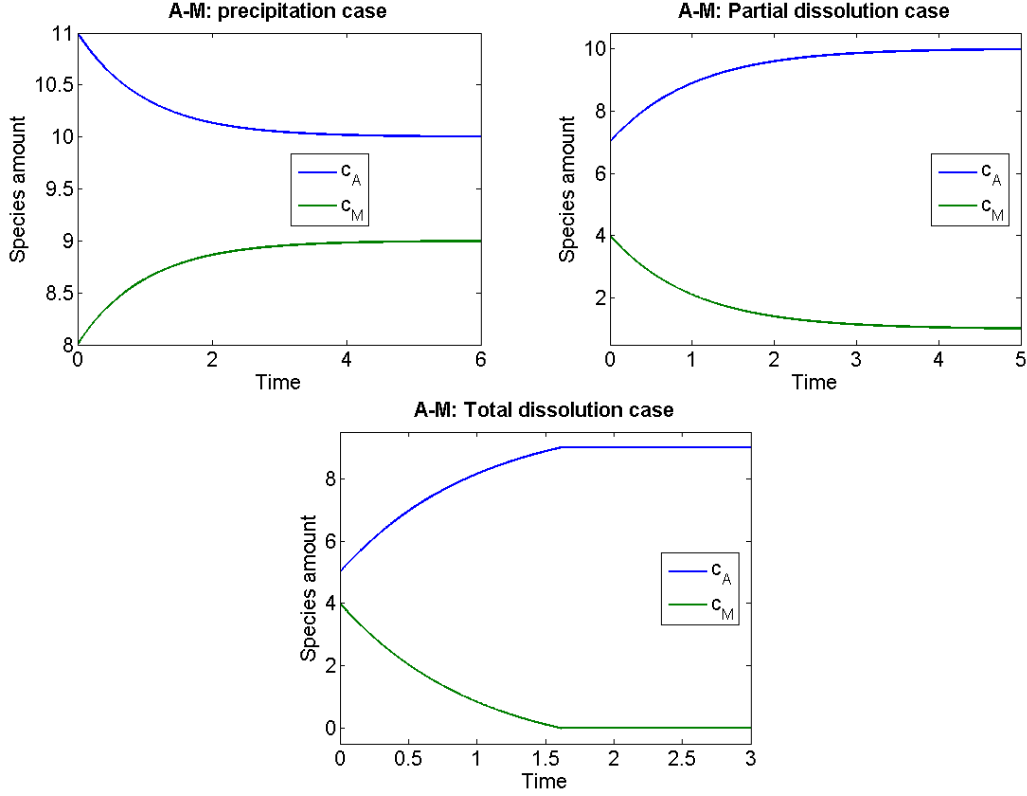


Figure 1: Quantities of solute c_A and mineral c_M for reaction $A \rightleftharpoons M$ with $K = 10$. Top left: precipitation with $c_{A,0} = 11, c_{M,0} = 8$. Top right: partial dissolution with $c_{A,0} = 7, c_{M,0} = 4$. Bottom: full dissolution with $c_{A,0} = 5, c_{M,0} = 4$.

4.1 Precipitation

If $\tau_0 > 0$, then $\forall t > 0, c_A^*(t) > 0, c_M^*(t) > 0, \tau(t) > 0$. The solute precipitates but does not disappear and the quantity of mineral increases. Here, c^* is the weak solution of system (9) and formula (11) gives $r = \tau$.

4.2 Partial dissolution

If $-c_{M,0} \leq \tau_0 < 0$, then $\forall t > 0, c_A^*(t) > 0, c_M^*(t) > 0$. The mineral dissolves but does not disappear and the quantity of solute increases. Here too, c^* is the weak solution of system (9) and $r = \tau$.

4.3 Full dissolution

If $\tau_0 < -c_{M,0}$, then $c_M^*(t_M) = 0$ where $t_M \geq 0$ is given by

$$t_M = \log\left(\frac{\tau_0}{\tau_0 + c_{M,0}}\right) \quad (12)$$

The mineral is fully dissolved. Let (c_A, c_M) be defined by:

$$\begin{cases} c_A(t) = c_A^*(t), t \leq t_M, \\ c_M(t) = c_M^*(t), t \leq t_M, \\ c_A(t) = c_{A,0} + c_{M,0}, t \geq t_M, \\ c_M(t) = 0, t \geq t_M, \end{cases}$$

It is the weak solution of (9) with $r = H(c_M)\tau$.

5 A differential inclusion model for general geochemical systems

In this section, we consider the general geochemical system described in section 2. We develop an original new model based on a differential inclusion [14]. In this model, each reaction rate r_j is equal to τ_j if the quantities of dissolving minerals are strictly positive, and must be controlled if one mineral is fully dissolved. It is important to note that these controls may depend on the vector \mathbf{c}_p of all mineral quantities. As in the discontinuous model, we limit the positive and negative parts of τ_j . A dissolving mineral M_k in reaction R_j is such that $s_{kj}\tau_j < 0$. For example, if $\tau_j > 0$, then $\tau_j^+ = \tau_j$ and $\tau_j^- = 0$; reactant minerals dissolve, so that the limiter takes into account reactant minerals. On the other hand, if $\tau_j < 0$, the limiter is based on dissolving product minerals. As in the set-valued model, limiters belong to set-valued functions.

Our objective is to define reaction rates \mathbf{r} in order to ensure a non-negative solution. We propose a model where reaction rates r_j are governed by maximal reaction rates τ_j in the following way:

$$\forall j = 1, \dots, N_r, |r_j| \leq |\tau_j| \text{ and } r_j\tau_j \geq 0. \quad (13)$$

For any $j \in \{1, \dots, N_r\}$, we introduce set-valued functions U_j and V_j of variables $\mathbf{c}_p \in (\mathbb{R}^+)^{N_p}$. Then we introduce two control functions $u_j, v_j \in L^\infty(0, T)$ in order to define the reaction rates.

Definition 5.1. *The set-valued functions $U_j, j = 1, \dots, N_r$ are defined in $[0, +\infty)^{N_p}$ by:*

$$\begin{aligned} U_j(\mathbf{c}_p) &= \{1\} \text{ if } \forall k \in \mathcal{M}_j^-, c_k > 0, \text{ or } \mathcal{M}_j^- = \emptyset, \\ &= [0, 1] \text{ else.} \end{aligned}$$

The set-valued functions $V_j, j = 1, \dots, N_r$ are defined in $[0, +\infty)^{N_p}$ by:

$$\begin{aligned} V_j(\mathbf{c}_p) &= \{1\} \text{ if } \forall k \in \mathcal{M}_j^+, c_k > 0, \text{ or } \mathcal{M}_j^+ = \emptyset, \\ &= [0, 1] \text{ else.} \end{aligned}$$

For general geochemical systems, we can now define our model of reaction rates.

Definition 5.2. *Let $T > 0$ and $\mathbf{c} \in (H^1(0, T))^{N_a+N_p}$ such that $\mathbf{c}(t) \geq 0, 0 \leq t \leq T$. Reaction rates \mathbf{r} are defined by*

$$r_j = u_j\tau_j^+(\mathbf{c}) - v_j\tau_j^-(\mathbf{c}), j = 1, \dots, N_r, \quad (14)$$

where $u_j, v_j \in L^\infty(0, T)$ and $u_j(t) \in U_j(\mathbf{c}_p(t)), v_j(t) \in V_j(\mathbf{c}_p(t)), 0 < t < T$.

Clearly, the vector of reaction rates \mathbf{r} satisfies (13). The reaction rate r_j , $j = 1, \dots, N_r$ is equal to the maximal value τ_j if all the dissolving minerals are present. If, for example, $\tau_j > 0$ and a reactant mineral is fully dissolved, then $0 \leq r_j \leq \tau_j$. The reaction is not stopped but it may continue at a limited rate.

The problem to solve is then a differential inclusion system [14]:
find $\mathbf{c} \in (H^1(0, T))^{N_a + N_p}$, $\mathbf{u} \in (L^\infty(0, T))^{N_r}$, $\mathbf{v} \in (L^\infty(0, T))^{N_r}$ such that

$$\begin{cases} \frac{d\mathbf{c}(t)}{dt} = S\mathbf{r}(t), t \in (0, T), \\ \mathbf{c}(t) \geq 0, t \in (0, T), \\ \mathbf{c}(0) = \mathbf{c}_0, \\ u_j(t) \in U_j(\mathbf{c}_p(t)), v_j(t) \in V_j(\mathbf{c}_p(t)), t \in (0, T), \\ r_j = u_j\tau_j^+(\mathbf{c}_a) - v_j\tau_j^-(\mathbf{c}_a), j = 1, \dots, N_r, \end{cases} \quad (15)$$

where $\mathbf{c}_0 \geq 0$ is a given initial condition, τ is defined by (3), U_j and V_j are introduced in Definition 5.1.

We are now faced to the two issues stated in the introduction: prove existence of a solution and compute it. Here, we introduce a regularization method, as in [16].

5.1 Regularized model

Our regularized model is controlled by a parameter ϵ , with a continuous reaction rate. We get a system of stiff ODEs and prove that it has a unique non negative solution. Then we prove that the differential inclusion (15) has a weak solution, limit of a convergent sequence of regularized functions. Moreover, the regularized problem can be solved by a classical ODE solver and provides a numerical method to approximate a solution of the discontinuous system.

Let us first define a regularized Heaviside function H_ϵ :

$$\begin{cases} \text{if } x \geq \epsilon \text{ then } H_\epsilon(x) = 1, \\ \text{if } 0 \leq x \leq \epsilon \text{ then } H_\epsilon(x) = \gamma(x/\epsilon), \\ \text{if } x = 0 \text{ then } H_\epsilon(x) = 0, \end{cases} \quad (16)$$

where γ is an increasing Lipschitz continuous function defined in the interval $[0, 1]$ such that $\gamma(0) = 0$ and $\gamma(1) = 1$, so that the function H_ϵ is Lipschitz continuous and bounded. For example, we can choose $\gamma(x) = x$.

We can now define regularized reaction rates. Let us first consider a reaction, where only one mineral M_k participates. If it is a reactant, then $u_{j,\epsilon}(\mathbf{c}) = H_\epsilon(c_k)$ and $v_{j,\epsilon}(\mathbf{c}) = 1$. On the other hand, if it is a product, then $u_{j,\epsilon}(\mathbf{c}) = 1$ and $v_{j,\epsilon}(\mathbf{c}) = H_\epsilon(c_k)$. Then either $r_j = \tau_j$ or $r_j = H_\epsilon(c_k)\tau_j$.

It becomes more difficult in a general case with a set of reacting minerals, since we have to deal with several potential dissolutions. In this case, we define the reaction limiter by using a blending of the regularized Heaviside functions. Let us consider a reaction R_j with $\tau_j > 0$ such that reactant minerals dissolve. We limit τ_j^+ by a blending function, as introduced in [2], which is equal to 0 as soon as one of the reactant minerals is fully dissolved and is equal to 1 as long as all of them are present in sufficient quantity. Similarly, we limit τ_j^- by a blending function applied to product minerals. Examples of such blendings are the minimum and the product functions. For the sake of simplicity, we choose the min function in what follows.

Definition 5.3. For general geochemical systems, the regularized reaction rates are defined by

$$r_{j,\epsilon}(\mathbf{c}) = u_{j,\epsilon}(\mathbf{c})\tau_j^+(\mathbf{c}) - v_{j,\epsilon}(\mathbf{c})\tau_j^-(\mathbf{c}), \quad (17)$$

where $u_{j,\epsilon}$ and $v_{j,\epsilon}$ are defined by

$$\begin{cases} \text{if } \mathcal{M}_j^- = \emptyset, \text{ then } u_{j,\epsilon}(\mathbf{c}) = 1, \text{ else } u_{j,\epsilon}(\mathbf{c}) = \min_{k \in \mathcal{M}_j^-} (H_\epsilon(c_k)), \\ \text{if } \mathcal{M}_j^+ = \emptyset, \text{ then } v_{j,\epsilon}(\mathbf{c}) = 1, \text{ else } v_{j,\epsilon}(\mathbf{c}) = \min_{k \in \mathcal{M}_j^+} (H_\epsilon(c_k)). \end{cases} \quad (18)$$

It can be noted that these regularized reaction rates satisfy the requirements (13). Now, we define a regularized system of kinetic reactions:

$$\begin{cases} \frac{d\mathbf{c}(t)}{dt} = S\mathbf{r}_\epsilon(\mathbf{c}(t)), t \geq 0, \\ \mathbf{c}(0) = \mathbf{c}_0. \end{cases} \quad (19)$$

It is easy to show that the regularized system (19) has a unique solution.

Lemma 5.1. The function r_ϵ is locally Lipschitz continuous.

Proof. The functions $u_{j,\epsilon}$ and $v_{j,\epsilon}$ are bounded and Lipschitz continuous. The function τ is C^1 and locally bounded. Therefore the function r_ϵ is locally Lipschitz continuous. \square

Proposition 5.1. For any $T > 0$, system (19) with non-negative initial condition \mathbf{c}_0 , has a unique maximal solution \mathbf{c}_ϵ in $[0, T[$.

Proof. We apply Cauchy-Lipschitz theorem. \square

Now, in order to prove the non negativity of the solution, we start by showing that the right-hand side is essentially non negative.

Lemma 5.2. The function f defined by $f(\mathbf{c}) = S\mathbf{r}_\epsilon(\mathbf{c})$ is locally Lipschitz continuous and essentially non negative.

Proof. By using Lemma 5.1 and linearity, f is locally Lipschitz continuous. Let \mathbf{c} a vector of species quantities such that $\mathbf{c} \geq 0$.

First, let $A_k, 1 \leq k \leq N_a$ be an aqueous species such that $c_k = 0$ for some $k \in \{1, \dots, N_a\}$. We proved in Proposition 2.2 that $s_{kj}\tau_j \geq 0$, so using 13, $s_{kj}r_{j,\epsilon} \geq 0$ and $(Sr_\epsilon)_k \geq 0$.

Second, let $M_k, N_a + 1 \leq k \leq N_a + N_p$ be a mineral such that $c_k = 0$. If M_k is a reactant of reaction R_j , then $s_{kj} < 0$; since $c_k = 0$ we get $u_{j,\epsilon} = 0$ and $r_{j,\epsilon} \leq 0$. On the contrary, if M_k is a product of reaction R_j , then $s_{kj} > 0$; since $c_k = 0$ we get $v_{j,\epsilon} = 0$ and $r_{j,\epsilon} \geq 0$. Finally $(Sr_{j,\epsilon})_k \geq 0$. \square

Proposition 5.2. If $\mathbf{c}_0 \geq 0$ then the solution of system (19) satisfies $\mathbf{c}_\epsilon \geq 0$ in the maximal interval.

Proof. As in Proposition 2.3, it is a direct consequence of Lemmas 5.1 and 5.2. \square

5.2 Convergence of the regularized solutions

In this section, we prove convergence of the regularized solutions, towards a non-negative and bounded weak solution of the differential inclusion problem. Recall that the vector \mathbf{q} of molar mass satisfies $\mathbf{q} > 0$ and $S^T \mathbf{q} = 0$. Using Lemma 2.1, we prove that the regularized solution is bounded and can be defined in $[0, +\infty[$:

Proposition 5.3. *Let \mathbf{q} be the vector of molar mass. System (19) has a unique solution \mathbf{c}_ϵ in $[0, +\infty[$ which satisfies*

$$0 \leq \mathbf{c}_\epsilon \leq C,$$

where C is defined in Lemma 2.1.

Proof. Let \mathbf{c}_ϵ be the maximal solution of (19). Since $S^T \mathbf{q} = 0$, it satisfies $\mathbf{q}^T \mathbf{c}_\epsilon = \mathbf{q}^T \mathbf{c}_0$. Thanks to Proposition 5.2, it also satisfies $\mathbf{c}_\epsilon \geq 0$. Thus, using Lemma 2.1, it also satisfies $\mathbf{c}_\epsilon \leq C$. So, the maximal interval of the non-negative solution is $[0, +\infty[$. \square

It also implies that the sequence \mathbf{c}_ϵ converges.

Theorem 5.1. *Let $T > 0$. The sequence \mathbf{c}_ϵ converges strongly in $C^0(0, T, \mathbb{R}^{(N_a+N_p)})$. Any limit \mathbf{c} of a subsequence satisfies $0 \leq \mathbf{c} \leq C$.*

Also for any $j = 1, \dots, N_r$, subsequences of the regularized controls $u_{j,\epsilon}(\mathbf{c}_\epsilon)$ and $v_{j,\epsilon}(\mathbf{c}_\epsilon)$ converge weakly- $$ in $L^\infty(0, T, \mathbb{R}^{N_r})$ towards respectively u_j and v_j which satisfy $0 \leq u_j \leq 1$ and $0 \leq v_j \leq 1$. Moreover, for any $j = 1, \dots, N_r$ and any $0 < t < T$, limits $\mathbf{c}, \mathbf{u}, \mathbf{v}$ defined above satisfy $u_j(t) \in U_j(\mathbf{c}_p(t))$ and $v_j(t) \in V_j(\mathbf{c}_p(t))$.*

Proof. Let \mathbf{c}_ϵ be the solution of (19) in $[0, +\infty[$. Since $0 \leq \mathbf{c}_\epsilon \leq C$, the norms $\|\mathbf{c}_\epsilon\|_{L^2(0,T)}$ and $\|Sr_\epsilon(\mathbf{c}_\epsilon)\|_{L^2(0,T)}$ are bounded, thus $\|\mathbf{c}_\epsilon\|_{H^1(0,T)}$ is also bounded.

By compact injection of $H^1(0, T)$ in $C^0(0, T)$, a subsequence of \mathbf{c}_ϵ converges in $C^0(0, T)$ and the limit \mathbf{c} is bounded below by 0 and above by C .

Let $1 \leq j \leq N_r$.

Since $0 \leq u_{j,\epsilon}(\mathbf{c}_\epsilon) \leq 1$, a subsequence of $u_{j,\epsilon}(\mathbf{c}_\epsilon)$ converges weakly- $*$ in $L^\infty(0, T)$ and the limit u_j is bounded below by 0 and above by 1. The result is similar for v_j . Thus $\forall j = 1, \dots, N_r$, the control satisfies $u_j \in L^\infty(0, T)$ and $0 \leq u_j(t) \leq 1$, $0 < t < T$.

Now, let $0 < t < T$. We want to show that $u_j(t) \in U_j(\mathbf{c}_p(t))$. In other words, we want to show that if $\mathcal{M}_j^- \neq \emptyset$ and if $\forall k \in \mathcal{M}_j^-$, $c_k(t) > 0$, then $u_j(t) = 1$. Since \mathbf{c} is continuous, there exists an interval I containing t such that $\forall s \in I, \forall k \in \mathcal{M}_j^-$, $c_k(s) > 0$. Since a subsequence of \mathbf{c}_ϵ converges towards \mathbf{c} in $C^0(0, T)$, the same property is true for ϵ sufficiently small: $\forall s \in I, \forall k \in \mathcal{M}_j^-$, $c_{k,\epsilon}(s) > 0$. Consequently, $\forall s \in I, u_{j,\epsilon}(\mathbf{c}_\epsilon)(s) = 1$. Since $u_{j,\epsilon}(\mathbf{c}_\epsilon)$ is a constant function of time in I , it converges towards 1 and $u_j(t) = 1$. This concludes the proof. \square

Now, we can prove the existence of a weak solution of system (15).

Theorem 5.2. *Let $T > 0$ and \mathbf{c} a limit of \mathbf{c}_ϵ in $C^0(0, T, \mathbb{R}^{(N_a+N_p)})$. Let \mathbf{u} and \mathbf{v} weakly- $*$ limits of a subsequence of $\mathbf{u}_\epsilon(\mathbf{c}_\epsilon)$ and $\mathbf{v}_\epsilon(\mathbf{c}_\epsilon)$ in $L^\infty(0, T, \mathbb{R}^{N_r})$. Then $(\mathbf{c}, \mathbf{u}, \mathbf{v})$ is a weak solution of system (15).*

Proof. First, the limits u_j and v_j satisfy the requirements of definition 5.2. Also, $\mathbf{c}(0) = \mathbf{c}_0$ and $\mathbf{c} \geq 0$. Since \mathbf{c}_ϵ weakly converges towards \mathbf{c} in $H^1(0, T)$, $\forall \phi \in (\mathcal{C}_c^\infty(0, T))$,

$$\lim_{\epsilon \rightarrow 0} \int_0^T \left(\frac{d\mathbf{c}_\epsilon(s)}{dt} - \frac{d\mathbf{c}(s)}{dt} \right) \phi(s) ds = 0. \quad (20)$$

Thanks to Lemma 5.1, $u_{j,\epsilon}, u_j \in L^\infty(0, T)$ and $\|u_{j,\epsilon}\|_\infty \leq 1$. Also, since τ_j and $\mathbf{c}_\epsilon, \mathbf{c}$ are continuous, $\tau_j^+(\mathbf{c}), \tau_j^+(\mathbf{c}_\epsilon) \in L^1(0, T)$.

Let us decompose $r_{j,\epsilon} - r_j$ in the following way:

$$\begin{aligned} r_{j,\epsilon} - r_j &= u_{j,\epsilon}(\mathbf{c}_\epsilon)(\tau_j^+(\mathbf{c}_\epsilon) - \tau_j^+(\mathbf{c})), \\ &+ (u_{j,\epsilon}(\mathbf{c}_\epsilon) - u_j)\tau_j^+(\mathbf{c}), \\ &- v_{j,\epsilon}(\mathbf{c}_\epsilon)(\tau_j^-(\mathbf{c}_\epsilon) - \tau_j^-(\mathbf{c})), \\ &- (v_{j,\epsilon}(\mathbf{c}_\epsilon) - v_j)\tau_j^-(\mathbf{c}). \end{aligned}$$

Then $\forall \phi \in \mathcal{C}_c^\infty(0, T)$,

$$\begin{aligned} \left| \int_0^T (r_{j,\epsilon}(\mathbf{c}_\epsilon(s)) - r_j(s, \mathbf{c}(s))) \phi(s) ds \right| &\leq \| \tau_j^+(\mathbf{c}_\epsilon) - \tau_j^+(\mathbf{c}) \|_{L^1(0, T)} \| \phi \|_{L^\infty(0, T)} \\ &+ \left| \int_0^T (u_{j,\epsilon}(\mathbf{c}_\epsilon(s)) - u_j(s)) \tau_j^+(\mathbf{c}(s)) \phi(s) ds \right| \\ &+ \| \tau_j^-(\mathbf{c}_\epsilon) - \tau_j^-(\mathbf{c}) \|_{L^1(0, T)} \| \phi \|_{L^\infty(0, T)} \\ &+ \left| \int_0^T (v_{j,\epsilon}(\mathbf{c}_\epsilon(s)) - v_j(s)) \tau_j^-(\mathbf{c}(s)) \phi(s) ds \right|. \end{aligned}$$

Since \mathbf{c}_ϵ converges towards \mathbf{c} in $C^0(0, T)$ and τ_j is continuous, we get $\lim_{\epsilon \rightarrow 0} \| \tau_j^+(\mathbf{c}_\epsilon) - \tau_j^+(\mathbf{c}) \|_{L^1(0, T)} = 0$. Since a subsequence of $u_{j,\epsilon}(\mathbf{c}_\epsilon)$ weakly-* converges to u_j in $L^\infty(0, T)$ and $\tau_j^+(\mathbf{c}) \phi \in L^1(0, T)$, we also obtain $\lim_{\epsilon \rightarrow 0} \int_0^T (u_{j,\epsilon}(\mathbf{c}_\epsilon) - u_j) \tau_j^+(\mathbf{c}) \phi ds = 0$. Similar results apply to v_j and τ_j^- .

So, $\forall \phi \in \mathcal{C}_c^\infty(0, T)$,

$$\lim_{\epsilon \rightarrow 0} \int_0^T (Sr_\epsilon(\mathbf{c}_\epsilon(s)) - Sr(s, \mathbf{c}(s))) \phi(s) ds = 0. \quad (21)$$

Using both weak convergence results (20) and (21), we conclude that $\mathbf{c}, \mathbf{u}, \mathbf{v}$ are a weak solution of system (15). □

6 Test case with a mineral involved in two reactions

The system we consider here is a set of two reactions with a mineral which participates in both reactions. This system is similar to the two reactions between calcite, calcium oxide and calcium hydroxide described in Section 2.1. Other species are also minerals in order to get constant reaction rates, so that reactions are written $M_1 \rightleftharpoons M_2$ and $M_2 \rightleftharpoons M_3$.

The objective is to analyze reaction rates after dissolution of one or several minerals. We can expect that the first reaction stops if M_1 dissolves completely, as for the reference example. Similarly, the second reaction stops if M_3 is fully dissolved. But the case where

M_2 precipitates in the first reaction and dissolves in the second one is more complex. We analyze below the different situations and compute the limit of the regularized solution.

The two maximal reaction rates defined by the mass action laws (3) are $\tau = (\tau_1, \tau_2)$. System (15) becomes

$$\begin{cases} \frac{dc_1}{dt} = -r_1, \\ \frac{dc_2}{dt} = r_1 - r_2, \\ \frac{dc_3}{dt} = r_2, \\ c(0) = c_0, \\ c \geq 0, \end{cases} \quad (22)$$

with $r_1 = u_1\tau_1^+ - v_1\tau_1^-$ and $r_2 = u_2\tau_2^+ - v_2\tau_2^-$.

The kernel of S^T is of dimension 1 and $q = (1, 1, 1)^T$ is a basis vector satisfying $q > 0$. The conservative variable (up to a constant) is $c_1 + c_2 + c_3$ so that it is possible to consider only two equations out of the three in (22).

The unique solution c^* of the continuous model (4) is a linear function of time:

$$\begin{cases} c_1^*(t) = c_{1,0} - \tau_1 t, \\ c_2^*(t) = c_{2,0} + (\tau_1 - \tau_2)t, \\ c_3^*(t) = c_{3,0} + \tau_2 t. \end{cases}$$

It is easy to compute the first times $t_i^* \geq 0$ when the quantities c_i^* are zero (and then negative):

$$\begin{cases} \text{If } \tau_1 > 0 \text{ then } t_1^* = \frac{c_{1,0}}{\tau_1}, \\ \text{If } \tau_2 - \tau_1 > 0 \text{ then } t_2^* = \frac{c_{2,0}}{\tau_2 - \tau_1}, \\ \text{If } \tau_2 < 0 \text{ then } t_3^* = -\frac{c_{3,0}}{\tau_2}. \end{cases} \quad (23)$$

Let $c_{\epsilon,i}^*$ be the solution of the regularized system (19), where the function γ is identity. Since there is only one dissolving mineral in each reaction, there is no blending in the regularized model. In other words, the regularized functions are $H_\epsilon(c_k)$, where c_k is the dissolving mineral. We analyze convergence in different cases and show stronger results than Theorem 5.2. Indeed, for almost any $t > 0$, the regularized controls $u_\epsilon(c_\epsilon(t))$ and $v_\epsilon(c_\epsilon(t))$ converge towards discontinuous functions $u(c(t))$ and $v(c(t))$.

6.1 Dissolution of M_1 and M_3

Here, we assume that $\tau_1 > 0$ and $\tau_2 < 0$, that $c_{1,0} > 0$ and $c_{3,0} > 0$. The pure phase M_1 dissolves and produces M_2 while M_3 dissolves and produces M_2 . The regularized reaction rates are given by

$$\begin{cases} r_{1,\epsilon} = H_\epsilon(c_1)\tau_1, \\ r_{2,\epsilon} = H_\epsilon(c_3)\tau_2. \end{cases} \quad (24)$$

The regularized solutions are easy to compute in that case, since the first and third equations are independent.

Taking ϵ sufficiently small, let $t_{1,\epsilon} = \frac{c_{1,0} - \epsilon}{\tau_1}$ so that $0 < t_{1,\epsilon} < t_1^*$ and $\lim t_{1,\epsilon} = t_1^*$. The solution $c_{1,\epsilon}$ is then

$$\begin{cases} c_{1,\epsilon}(t) = c_{1,0} - \tau_1 t = c_1^*(t), & t \leq t_{1,\epsilon}, \\ c_{1,\epsilon}(t) = \epsilon \exp\left(-\frac{\tau_1}{\epsilon}(t - t_{1,\epsilon})\right), & t \geq t_{1,\epsilon}, \end{cases}$$

and the regularized control is

$$\begin{cases} H_\epsilon(c_{1,\epsilon}(t)) = 1, & t \leq t_{1,\epsilon}, \\ H_\epsilon(c_{1,\epsilon}(t)) = \exp\left(-\frac{\tau_1}{\epsilon}(t - t_{1,\epsilon})\right), & t \geq t_{1,\epsilon}. \end{cases}$$

It is easy to verify that $\forall t \geq 0, \lim_{\epsilon \rightarrow 0} c_{1,\epsilon}(t) = c_1(t)$ where c_1 is defined by

$$\begin{cases} c_1(t) = c_{1,0} - \tau_1 t = c_1^*(t), & t \leq t_1^*, \\ c_1(t) = 0, & t \geq t_1^*. \end{cases}$$

Also, the control converges: $\forall t \geq 0, t \neq t_1^* \lim_{\epsilon \rightarrow 0} H_\epsilon(c_{1,\epsilon}(t)) = H(c_1(t))$.

Clearly, results are the same for the variable c_3 and c_2 is deduced from the conservative quantity. Thus c is solution of (22) where

$$r_1 = H(c_1)\tau_1, \quad r_2 = H(c_3)\tau_2.$$

Figure 2 illustrates this case. Mineral M_2 precipitates at rate $(\tau_1 - \tau_2)$ until M_3 is fully dissolved, then reaction R_2 stops and M_2 precipitates at rate τ_1 until M_1 is fully dissolved and reaction R_1 stops.

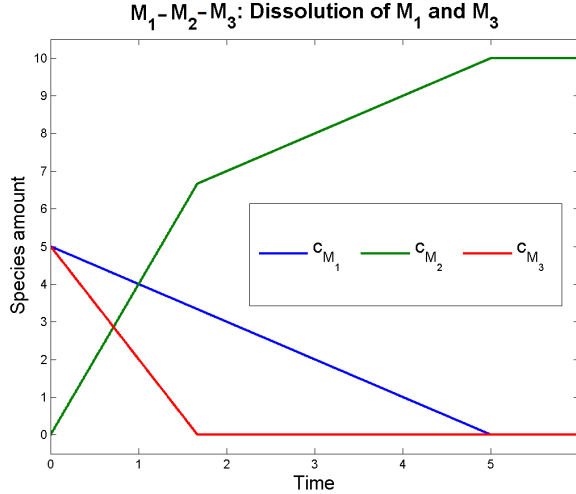


Figure 2: Reactions $M_1 \rightleftharpoons M_2$ and $M_2 \rightleftharpoons M_3$ with maximal rates $\tau_1 = 1, \tau_2 = -3$ and initial conditions $c_{1,0} = 5, c_{2,0} = 0, c_{3,0} = 5$.

6.2 Dissolution of M_2

Here, we assume that $\tau_1 < 0$ and $\tau_2 > 0$ and $c_{2,0} > 0$. The pure phase M_2 dissolves and produces M_1 and M_3 . The regularized reactions rates are given by

$$\begin{cases} r_{1,\epsilon} = H_\epsilon(c_2)\tau_1, \\ r_{2,\epsilon} = H_\epsilon(c_2)\tau_2. \end{cases} \quad (25)$$

In that case, the second equation is independent and similar to the previous case. In the same way as $t_{1,\epsilon}$, we define, with $0 < \epsilon < c_{2,0}$, $t_{2,\epsilon} = \frac{c_{2,0} - \epsilon}{\tau_2 - \tau_1}$ so that $0 < t_{2,\epsilon} < t_2^*$ and $t_{2,\epsilon}$ converges to t_2^* . Thus the quantity $c_{2,\epsilon}$ converges for all $t \geq 0$ towards c_2 defined as c_1 above (with $(\tau_2 - \tau_1)$ instead of τ_1), and the control $H_\epsilon(c_{2,\epsilon}(t))$ converges towards $H(c_2(t))$ for $t \neq t_2^*$.

It is slightly more complicated to compute the solution $c_{1,\epsilon}$:

$$\begin{cases} c_{1,\epsilon}(t) = c_{1,0} - \tau_1 t = c_1^*(t), & t \leq t_{2,\epsilon}, \\ c_{1,\epsilon}(t) = -\epsilon \frac{\tau_1}{\tau_2 - \tau_1} (1 - \exp(-\frac{\tau_2 - \tau_1}{\epsilon}(t - t_{2,\epsilon}))) + c_1^*(t_{2,\epsilon}), & t \geq t_{2,\epsilon}. \end{cases}$$

Therefore, for all $t \geq 0$, the regularized solution converges towards c_1 defined by

$$\begin{cases} c_1(t) = c_{1,0} - \tau_1 t = c_1^*(t), & t \leq t_2^*, \\ c_1(t) = c_1^*(t_2^*), & t \geq t_2^*. \end{cases}$$

The third quantity c_3 is obtained thanks to the conservation law. The limit \mathbf{c} is solution of (22) where reaction rates are the discontinuous functions

$$r_1 = H(c_2)\tau_1, \quad r_2 = H(c_2)\tau_2.$$

As illustrated in Figure 3, minerals M_1 and M_3 precipitate until M_2 is fully dissolved and both reactions R_1 and R_2 stop.

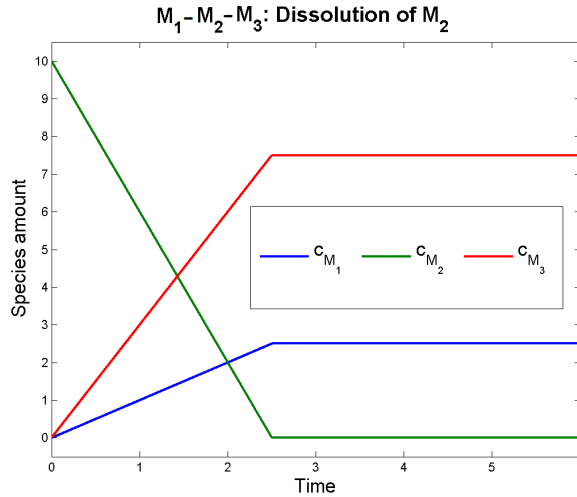


Figure 3: Reactions $M_1 \rightleftharpoons M_2$ and $M_2 \rightleftharpoons M_3$ with maximal rates $\tau_1 = -1$, $\tau_2 = 3$ and initial conditions $c_{1,0} = c_{3,0} = 0$, $c_{2,0} = 10$.

6.3 Dissolution of M_1 then M_2

Here, we assume that $\tau_2 > 0$ and $\tau_1 > 0$, also $c_{1,0} > 0$ and $c_{2,0} > 0$; moreover, if $\tau_2 > \tau_1$, we assume that $t_1^* < t_2^*$. In these conditions, the mineral M_1 dissolves and produces M_2 while M_2 dissolves and produces M_3 . As previously, the regularized solution $c_{1,\epsilon}$ converges towards c_1 defined above.

With these assumptions and with ϵ sufficiently small, $c_{2,\epsilon}^*(t) \geq \epsilon$ for $t \leq t_{1,\epsilon}$. As long as $c_{2,\epsilon}(t) \geq \epsilon$, it is given by

$$\begin{cases} c_{2,\epsilon}(t) = c_{2,0} - (\tau_2 - \tau_1)t = c_2^*(t), & t \leq t_{1,\epsilon}, \\ c_{2,\epsilon}(t) = \epsilon(1 - \exp(-\frac{\tau_1}{\epsilon}(t - t_{1,\epsilon}))) - \tau_2(t - t_{1,\epsilon}) + c_2^*(t_{1,\epsilon}), & t \geq t_{1,\epsilon}. \end{cases}$$

Since $c_{2,\epsilon}(t_{1,\epsilon}) \geq \epsilon$ and $\lim_{t \rightarrow +\infty} c_{2,\epsilon}(t) = -\infty$, by continuity, there exists $\hat{t}_{2,\epsilon} \geq t_{1,\epsilon}$ such that $c_{2,\epsilon}(\hat{t}_{2,\epsilon}) = \epsilon$. Then, for $t \geq \hat{t}_{2,\epsilon}$ the equation becomes

$$\frac{dc_2}{dt} = \frac{c_1}{\epsilon}\tau_1 - \frac{c_2}{\epsilon}\tau_2, \quad t \geq \hat{t}_{2,\epsilon}$$

with $c_2(\hat{t}_{2,\epsilon}) = \epsilon$. The solution is

$$c_{2,\epsilon}(t) = \epsilon(a \exp(-\frac{\tau_1}{\epsilon}(t - t_{1,\epsilon})) + (1 - ab_\epsilon) \exp(-\frac{\tau_2}{\epsilon}(t - \hat{t}_{2,\epsilon})))$$

where $a = \frac{\tau_1}{\tau_2 - \tau_1}$ and $b_\epsilon = \exp(-\frac{\tau_1}{\epsilon}(\hat{t}_{2,\epsilon} - t_{1,\epsilon}))$.

Finally, the regularized quantity $c_{2,\epsilon}$ satisfies the equation

$$\begin{cases} c_{2,\epsilon}(t) = c_{2,0} - (\tau_2 - \tau_1)t = c_2^*(t), & t \leq t_{1,\epsilon}, \\ c_{2,\epsilon}(t) = \epsilon(1 - \exp(-\frac{\tau_1}{\epsilon}(t - t_{1,\epsilon}))) - \tau_2(t - t_{1,\epsilon}) + c_2^*(t_{1,\epsilon}), & t_{1,\epsilon} \leq t \leq \hat{t}_{2,\epsilon}, \\ c_{2,\epsilon}(t) = \epsilon(a \exp(-\frac{\tau_1}{\epsilon}(t - t_{1,\epsilon})) + (1 - ab_\epsilon) \exp(-\frac{\tau_2}{\epsilon}(t - \hat{t}_{2,\epsilon}))) & t \geq \hat{t}_{2,\epsilon}. \end{cases}$$

Let us now analyze the convergence of $\hat{t}_{2,\epsilon}$ and $c_{2,\epsilon}(t)$ when ϵ tends towards 0.

The equality $c_{2,\epsilon}(\hat{t}_{2,\epsilon}) = \epsilon$ can be rewritten

$$-\epsilon \exp(-\frac{\tau_1}{\epsilon}(\hat{t}_{2,\epsilon} - t_{1,\epsilon})) - \tau_2(\hat{t}_{2,\epsilon} - t_{1,\epsilon}) + c_2^*(t_{1,\epsilon}) = 0.$$

Since $\hat{t}_{2,\epsilon} \geq t_{1,\epsilon}$, it implies that $\hat{t}_{2,\epsilon}$ has a limit which we denote by \hat{t}_2 , and which satisfies

$$\tau_2(\hat{t}_2 - t_1^*) = c_2^*(t_1^*) = 0.$$

Then $\forall t \geq 0$, $\lim_{\epsilon \rightarrow 0} c_{2,\epsilon}(t) = c_2(t)$ given by

$$\begin{cases} c_2(t) = c_2^*(t), & t \geq t_1^*, \\ c_2(t) = -\tau_2(t - t_1^*) + c_2^*(t_1^*), & t_1^* \leq t \leq \hat{t}_2, \\ c_2(t) = 0, & t \geq \hat{t}_2. \end{cases}$$

Moreover, $\forall t \geq 0$, $t \neq t_1^*$, $t \neq \hat{t}_2$, $\lim_{\epsilon \rightarrow 0} H_\epsilon(c_{2,\epsilon}(t)) = H(c_2(t))$.

Finally, \mathbf{c} is solution of the discontinuous system (22) with

$$r_1 = H(c_1)\tau_1, \quad r_2 = H(c_2)\tau_2.$$

In Figure 4 where $\tau_1 > \tau_2$, mineral M_1 dissolves at rate τ_1 and mineral M_2 precipitates at rate $\tau_1 - \tau_2$, then reaction R_1 stops and M_2 dissolves at rate τ_2 until reaction R_2 stops.

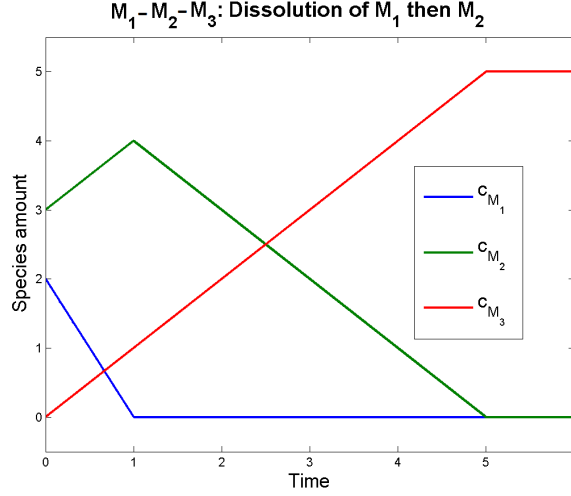


Figure 4: Reactions $M_1 \rightleftharpoons M_2$ and $M_2 \rightleftharpoons M_3$ with maximal rates $\tau_1 = 2, \tau_2 = 1$ and initial conditions $c_{1,0} = 2, c_{2,0} = 3, c_{3,0} = 0$.

6.4 Dissolution of M_2 then M_1

Up to now, the regularized Heaviside functions converged towards the Heaviside function and reactions stopped when a mineral was fully dissolved. This case is more remarkable as it illustrates the capacity of the regularized model to continue the reactions although M_2 is fully dissolved.

We assume that $\tau_2 > \tau_1 > 0$ and $t_2^* < t_1^*$ so that, for ϵ sufficiently small, $0 < t_{2,\epsilon} \leq t_{1,\epsilon}$. The second regularized equation is

$$\frac{dc_2}{dt} = H_\epsilon(c_1)\tau_1 - H_\epsilon(c_2)\tau_2,$$

so that the regularized solution $c_{2,\epsilon}$ satisfies

$$\left\{ \begin{array}{ll} c_{2,\epsilon}(t) = c_{2,0} - (\tau_2 - \tau_1)t = c_2^*(t), & t \leq t_{2,\epsilon}, \\ c_{2,\epsilon}(t) = \frac{\epsilon}{\tau_2}(\tau_1 + (\tau_2 - \tau_1) \exp(-\frac{\tau_2}{\epsilon}(t - t_{2,\epsilon}))), & t_{2,\epsilon} \leq t \leq t_{1,\epsilon}, \\ c_{2,\epsilon}(t) = \epsilon \left(\frac{\tau_2 - \tau_1}{\tau_2} \exp(-\frac{\tau_2}{\epsilon}(t - t_{2,\epsilon})) - \frac{\tau_1^2}{\tau_2(\tau_2 - \tau_1)} \exp(-\frac{\tau_2}{\epsilon}(t - t_{1,\epsilon})) \right) + \frac{\tau_1}{\tau_2 - \tau_1} \exp(-\frac{\tau_1}{\epsilon}(t - t_{1,\epsilon})), & t \geq t_{1,\epsilon}. \end{array} \right.$$

Thus the regularized solution $c_{2,\epsilon}$ converges, for all $t \geq 0$, towards c_2 defined by

$$\left\{ \begin{array}{ll} c_2(t) = c_{2,0} - (\tau_2 - \tau_1)t = c_2^*(t), & t \leq t_2^*, \\ c_2(t) = 0, & t \geq t_2^*. \end{array} \right.$$

Also, the regularized control $H_\epsilon(c_{2,\epsilon})$ has a special limit, for any $t \geq 0$, $t \neq t_1^*$, $t \neq t_2^*$:

$$\lim_{\epsilon \rightarrow 0} H_\epsilon(c_{2,\epsilon}(t)) = H(c_2(t)) + H(c_1(t))\delta(c_2(t))\frac{\tau_1}{\tau_2},$$

where $\delta(x)$ is the Dirac function at point x . The limit c of the regularized solution satisfies the discontinuous differential equations (22) with

$$r_1 = H(c_1)\tau_1, \quad r_2 = H(c_2)\tau_2 + H(c_1)\delta(c_2)\tau_1.$$

Mineral M_3 precipitates at rate τ_2 until M_2 is fully dissolved. Then, reaction R_2 does not stop but continues at rate τ_1 , so that M_2 remains fully dissolved, until M_1 is fully dissolved. In some sense, the two reactions are replaced by the unique reaction $M_1 \rightarrow M_3$ at rate τ_1 . This behaviour is shown in Figure 5.

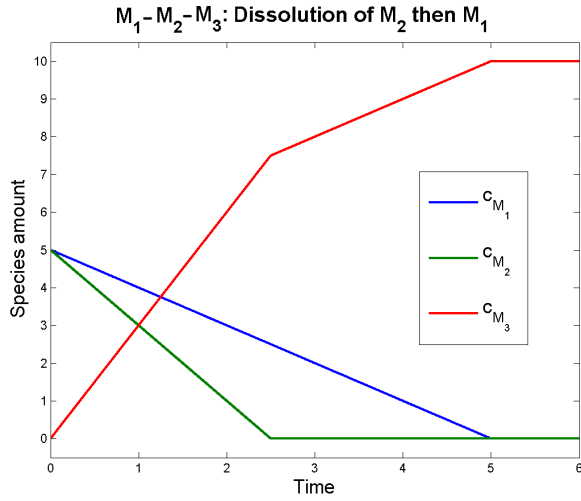


Figure 5: Reactions $M_1 \rightleftharpoons M_2$ and $M_2 \rightleftharpoons M_3$ with maximal rates $\tau_1 = 1$, $\tau_2 = 3$ and initial conditions $c_{1,0} = 5$, $c_{2,0} = 5$, $c_{3,0} = 0$.

6.5 Summary of test case $M_1 - M_2 - M_3$

The other cases can be easily deduced from the four cases considered above. Finally, the regularized solution converges towards c which is solution of a discontinuous differential system. Moreover, the regularized controls converge, except at a finite number of discontinuity points, to the discontinuous ones.

Theorem 6.1. *The limit c of the regularized solution c_ϵ is solution of system (22) where the reaction rates are discontinuous functions defined by:*

$$\begin{cases} r_1 = H(c_1)\tau_1^+ - H(c_2)\tau_1^- - \delta(c_2)H(c_3)\tau_2^-, \\ r_2 = H(c_2)\tau_2^+ + \delta(c_2)H(c_1)\tau_1^+ - H(c_3)\tau_2^-. \end{cases} \quad (26)$$

Moreover, the regularized limiters $u_\epsilon(c_\epsilon)$ and $v_\epsilon(c_\epsilon)$ strongly converge, up to a subsequence, in $L^p(0, T)$, $p \in [1, \infty[$.

Proof. Existence is proved above by construction. We proved in all cases that $u_\epsilon(c_\epsilon)$ converges almost everywhere to u in $[0, T]$. Thanks to the dominated convergence theorem applied to $|u_\epsilon(c_\epsilon(t)) - u(t)|^p$, we get strong convergence in L^p . \square

We observe, in all cases of this example, that when a mineral disappears at a given time, then it remains fully dissolved afterwards. In other words, if $c_i(t^*) = 0$ then $c_i(t) = 0, t \geq t^*$ so that $\frac{dc_i}{dt} = 0, t > t^*$. Finally, the reaction rates satisfy $(Sr)_i = 0, t > t^*$. For example, when c_2 becomes fully dissolved, then $r_2 = r_1$. This result is a so-called sliding mode of differential inclusion problems [14].

7 Numerical experiments

In this section we describe and discuss the results of five numerical experiments done with synthetic geochemical systems. The first one is the reference example $A \rightleftharpoons M$ defined in Section 4. The second one, with two reactions $M_1 \rightleftharpoons M_2$ and $M_2 \rightleftharpoons M_3$, is analyzed in Section 6. Then we replace M_1 and M_3 by aqueous species A_1 and A_3 in the third test case. In order to introduce competition between two reactions dissolving M_2 , we add a third reaction $M_2 \rightleftharpoons A_4$ in the fourth test case. These four examples do not require blending in the regularized model, in contrary to the last one, which involves two reactant minerals in the same reaction.

7.1 Numerical context

We have developed a Matlab code for solving the regularized ODE (19), where we vary the value of the regularizing parameter ϵ in order to analyze numerical convergence. We have implemented several regularizing functions defined in (16), namely a linear function, an exponential smoothing, and a polynomial one. We show results with the linear function, other results were similar. For the last test case, we implemented two types of blending: the min function defined in (18), and the prod function defined below:

$$\begin{cases} \text{if } \mathcal{M}_j^- = \emptyset, \text{ then } u_{j,\epsilon}(\mathbf{c}) = 1, \text{ else } u_{j,\epsilon}(\mathbf{c}) = \prod_{k \in \mathcal{M}_j^-} (H_\epsilon(c_k)), \\ \text{if } \mathcal{M}_j^+ = \emptyset, \text{ then } v_{j,\epsilon}(\mathbf{c}) = 1, \text{ else } v_{j,\epsilon}(\mathbf{c}) = \prod_{k \in \mathcal{M}_j^+} (H_\epsilon(c_k)). \end{cases} \quad (27)$$

The maximal reaction rates are implemented in a Matlab function, using data of the physical model, mainly stoichiometry and constants in (3). In our tests, the activity of a mineral species is equal to 1 and the activity of an aqueous species is equal to the molar fraction:

$$a_i(\mathbf{c}_a) = \frac{c_i}{c_{\text{H}_2\text{O}} + \sum_{l=1}^{N_a} c_{a,l}}, \quad (28)$$

where $c_{\text{H}_2\text{O}}$ is the quantity of water. This definition assumes that the coefficient of activity is equal to 1. Moreover, we consider a dilute solution such that $c_{\text{H}_2\text{O}}$ is constant.

We used the Matlab solver ode15s which implements an implicit scheme with variable order in order to solve stiff differential equations (see [22] and Matlab documentation for

ode15s). An adaptive time step uses tolerance options *RelTolSolver* and *AbsTolSolver*, both taken as the default value 10^{-6} . The Jacobian matrix of the nonlinear right-hand side is computed by a finite difference method. The time interval $[0, T]$ and the initial condition $\mathbf{c}_0 \geq 0$ are parameters.

We define a set of discrete times in $[0, T]$: $t_k = k dt$, $k = 0, \dots, N_f$ with $t_{N_f} = T$ and $dt = \frac{T}{N_f}$ where dt is an external time step. We get as output of ode15s a set of discrete values $\mathbf{c}_\epsilon(t_k)$, where $\mathbf{c}_\epsilon(t_k)$ is a vector of size $N_a + N_p$.

In the first two tests, we know the limit \mathbf{c} of the regularized model, exact solution of the differential inclusion model. Therefore we can compute a discrete error for each species i :

$$e_{c_i}(t_k) = |c_i(t_k) - c_{\epsilon,i}(t_k)|, \quad k = 0, \dots, N_f,$$

and a global error:

$$e_c(t_k) = \sum_{i=1}^{N_a+N_p} e_{c_i}(t_k). \quad (29)$$

We also analyze the errors in the limiting discontinuous functions $u_{\epsilon,j}$ and $v_{\epsilon,j}$ for each reaction R_j . In the first two tests, the number N_l of discontinuity points is finite and the corresponding times t_l^* , $l = 1, \dots, N_l$, are known. As above, we compute discrete errors for each reaction R_j :

$$\begin{cases} e_{u_j}(t_k) = |u_j(t_k) - u_{\epsilon,j}(t_k)|, & k = 0, \dots, N_f, \\ e_{v_j}(t_k) = |v_j(t_k) - v_{\epsilon,j}(t_k)|, & k = 0, \dots, N_f, \end{cases}$$

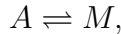
and global errors:

$$\begin{cases} e_u(t_k) = \sum_{j=1}^{N_r} e_{u_j}(t_k), \\ e_v(t_k) = \sum_{j=1}^{N_r} e_{v_j}(t_k). \end{cases} \quad (30)$$

Then we compute discrete L^p -norms with $p = 1, 2, \infty$. We also define a discrete error at times t_k outside $[t_l^* - \delta, t_l^* + \delta]$, $\forall l = 1, \dots, N_l$, where $\delta > 0$. Then we compute the discrete L^∞ norm out of the jumps defined by these intervals.

7.2 Reference example $A - M$, total dissolution

This test case corresponds to the reference example of Section 4:



with A a solute in the water phase and M a mineral. We consider the total dissolution case, as in Section 4.3, with data given in table 1. The activity of A is defined by (28) and the reaction rate by (3), so that

$$a(c_A) := \frac{c_A}{c_A + c_{\text{H}_2\text{O}}} \quad \text{and} \quad \tau(c_A) := \alpha a(c_A) - \beta.$$

Since there is only one mineral product in the chemical reaction, the limiter is $v_\epsilon = H_\epsilon(c_{M,\epsilon})$.

Reaction	$A \rightleftharpoons M$
S	$\begin{pmatrix} -1 \\ 1 \end{pmatrix}$
(α, β)	$(2, 2)$
$c_{\text{H}_2\text{O}}$	2
c_0	$(0.2 \ 0.6)$

Table 1: Test case $A - M$: physical parameters

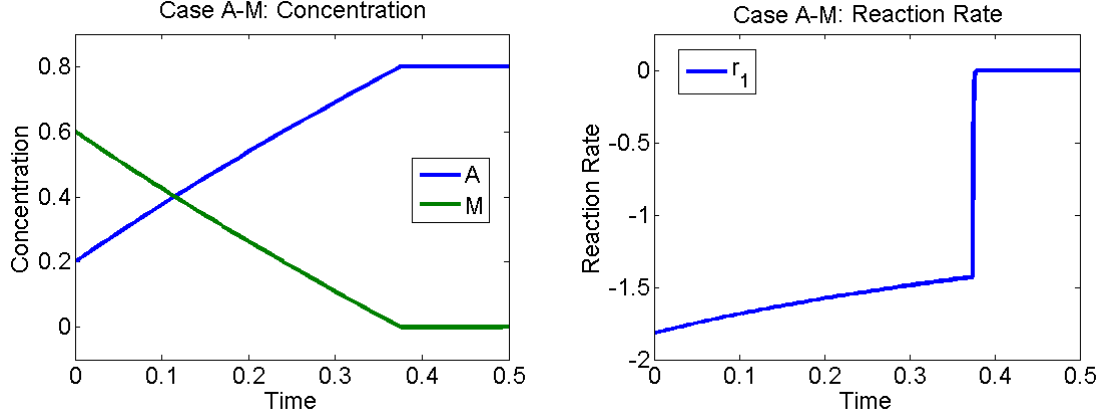


Figure 6: Case $A - M$ with dissolution of M . Results with $\epsilon = 0.001$.

Figure 6 shows the regularized solution and the reaction rate computed with $\epsilon = 0.001$. We observe that the limit of the regularized quantities is the discontinuous solution of Section 3. Physical data are such that the mineral is fully dissolved at time t^* and for $t \geq t^*$, the quantity of mineral c_M remains equal to 0. The reaction stops: $r = \tau$ until time t^* then $r = 0$.

Now we run the regularized model for a decreasing sequence of parameters ϵ and compute errors. We choose $T = 0.5$, $dt = \frac{T}{10^4} = 5 \times 10^{-5}$ and $\delta = 0.1$. We observe in Figure 7 that errors are localized around the discontinuity. As expected, when ϵ tends towards 0, the error e_c converges towards 0 at any time, and the error e_u converges towards 0 except at the time t^* of discontinuity.

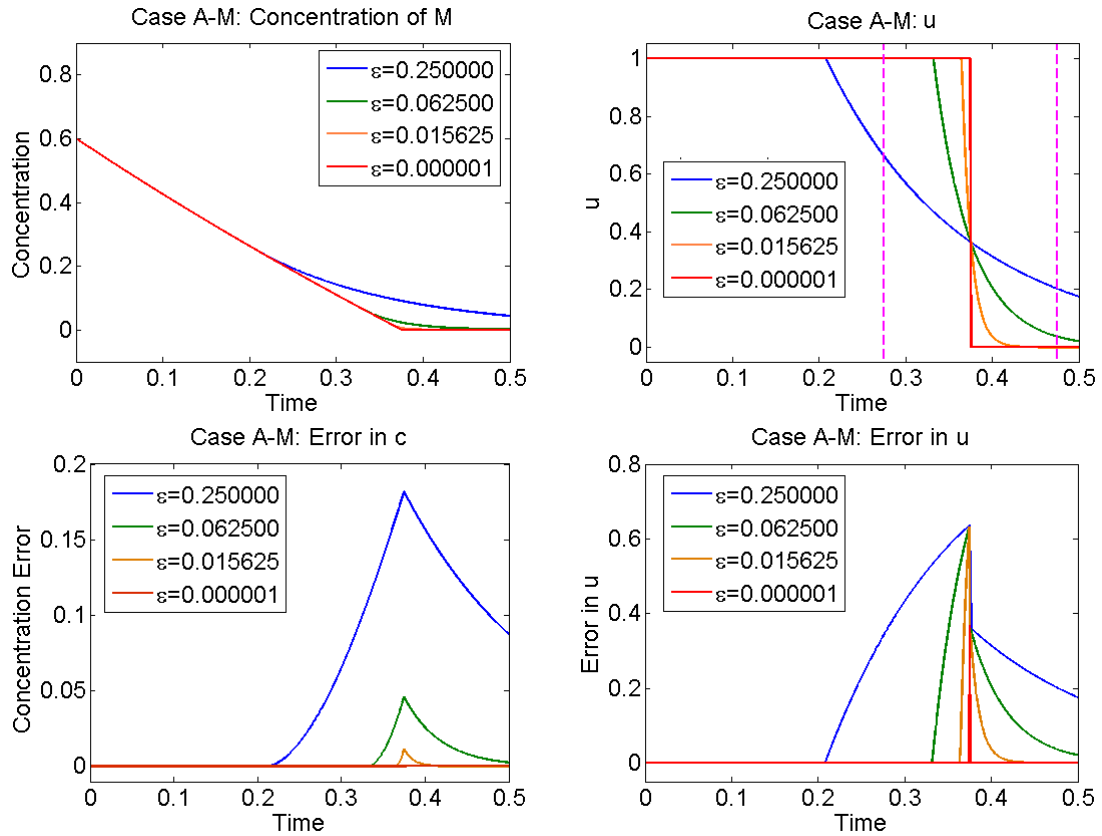


Figure 7: Case $A - M$ with dissolution of M . Results and errors for different values of ϵ . Top: Quantity of mineral (left) and function u (right). Bottom: error e_c (left) and error e_u (right). The interval $[t^* - \delta, t^* + \delta]$ is represented in pink.

In Figure 8, we plot L^1 and L^∞ norms of errors e_c and e_u in function of the parameter ϵ . As proved in Lemma 5.1, the error e_c converges in both norms whereas the error e_u converges only in L^1 norm. Nevertheless, for this test case, the error e_u converges numerically in the L^∞ norm, out of jumps.

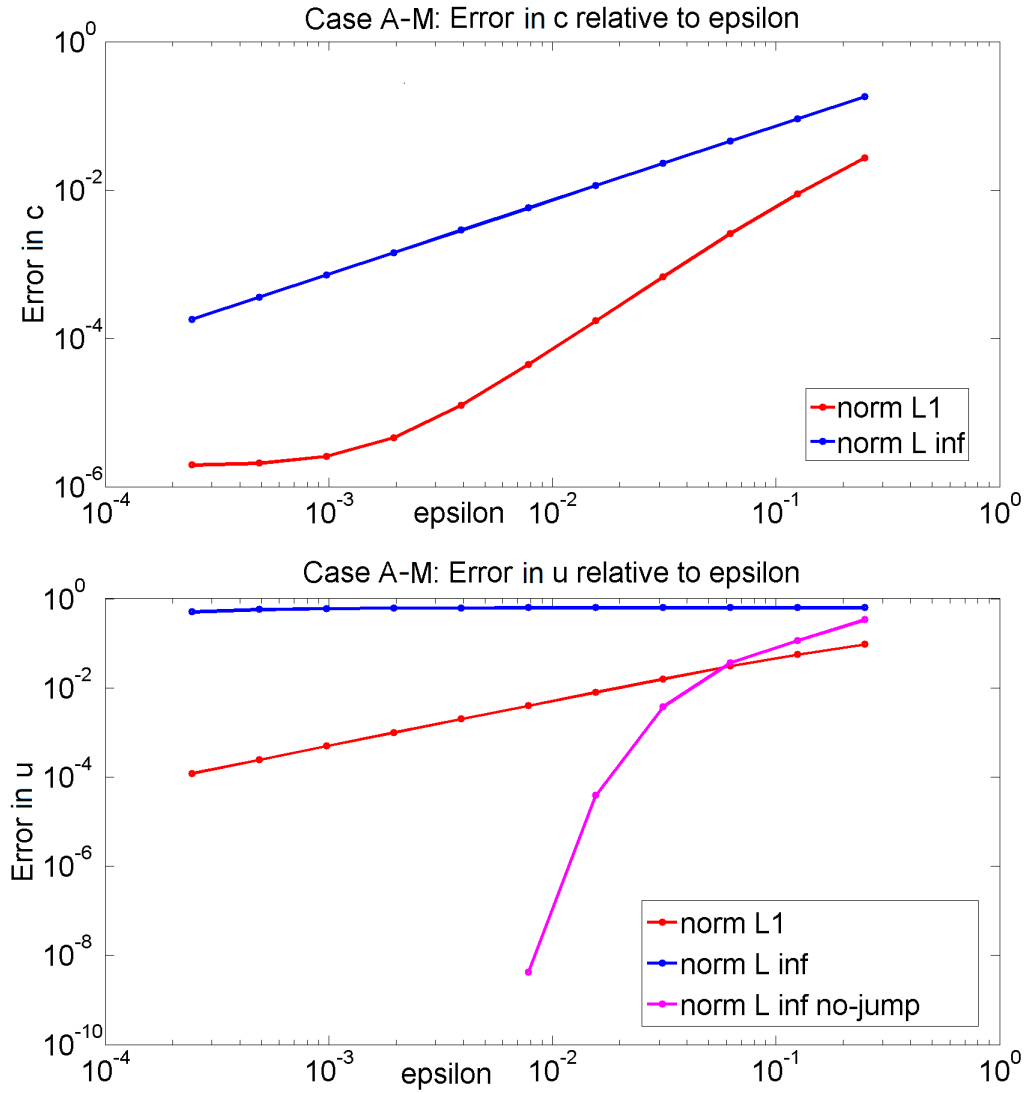
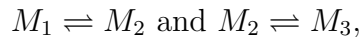


Figure 8: Numerical convergence for the case $A - M$ with dissolution of M .

7.3 Test case $M_1 - M_2 - M_3$

Now, we investigate the case where one mineral participates in two reactions, as a reactant in one of them and a product in the other. The geochemical system is described in Section 6:



where M_1 , M_2 and M_3 are three pure phase minerals, so that activities are equal to 1 and maximal reaction rates τ_1 and τ_2 are constant. We consider the case of Section 6.4, where the mineral M_2 precipitates in the first reaction and is dissolved in the second one. Table 2 provides a summary of physical data.

Reactions	$R_1 : M_1 \rightleftharpoons M_2$ $R_2 : M_2 \rightleftharpoons M_3$
S	$\begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix}$
(τ_1, τ_2)	$(1, 4)$
c_0	$(1, 0.6, 0.4)$

Table 2: Test case $M_1 - M_2 - M_3$: physical parameters

When we apply solver ode15s directly to the discontinuous system (26), with various values of ϵ , the solver gives either a false result or no result at all. This failure highlights the need for a numerical regularization.

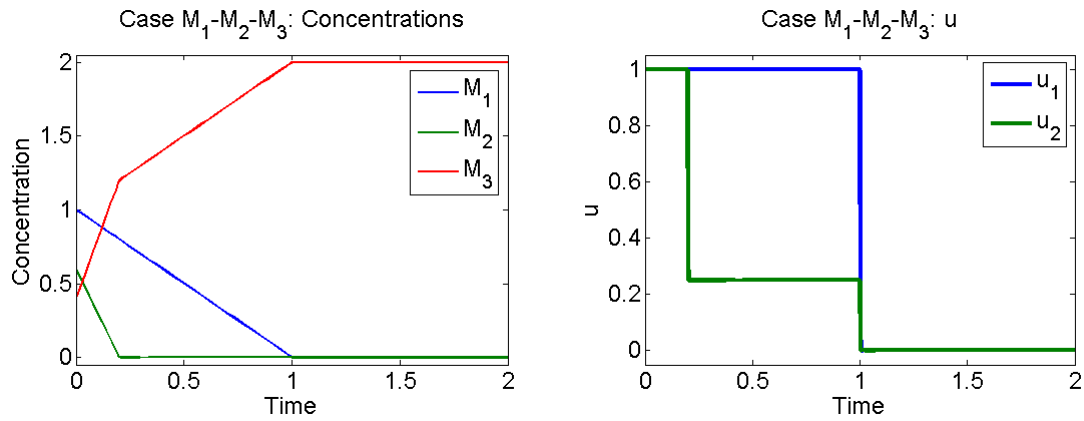


Figure 9: Case $M_1 - M_2 - M_3$ with dissolution of M_2 then M_1 . Results with $\epsilon = 0.001$.

Figure 9 shows the regularized solution and both limiters obtained with $\epsilon = 0.001$. Qualitatively, the quantities computed are close to the discontinuous ones given in Section 6.4.

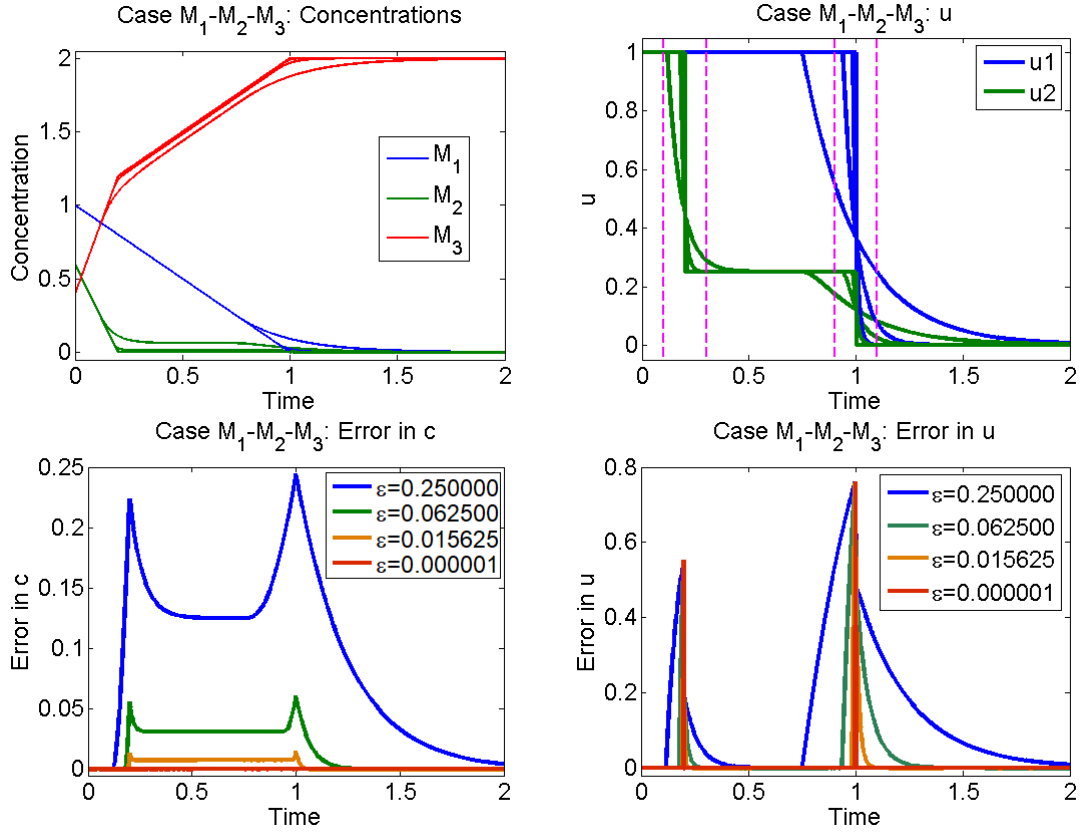


Figure 10: Case $M_1 - M_2 - M_3$ with dissolution of M_2 then M_1 . Results and errors for different values of ϵ . Top: quantities (left) and controls u (right). Bottom: errors e_c (left) and e_u (right). Both intervals $[t^* - \delta, t^* + \delta]$ are represented in pink.

In order to justify this observation, we analyze numerical convergence for a decreasing sequence of ϵ . We choose $T = 2$, $dt = \frac{2}{10^4} = 2 \times 10^{-4}$ and $\delta = 0.1$, as defined in Section 7. In Figure 10, we plot the regularized quantities (c_1, c_2, c_3) and controls (u_1, u_2) , as well as the errors e_c and e_u , in function of ϵ . We observe, as proved in Theorem 5.2, that the quantities c_ϵ converge strongly towards c in \mathcal{C}^0 , with an error e_c maximal around the times of discontinuity. Also, the controls $H_\epsilon(c_1)$ and $H_\epsilon(c_2)$ converge at any time except those of discontinuity towards respectively $H(c_1)$ and $H(c_2) + \delta(c_2)H(c_1)\frac{\tau_1}{\tau_2}$, as expected from Section 6.4.

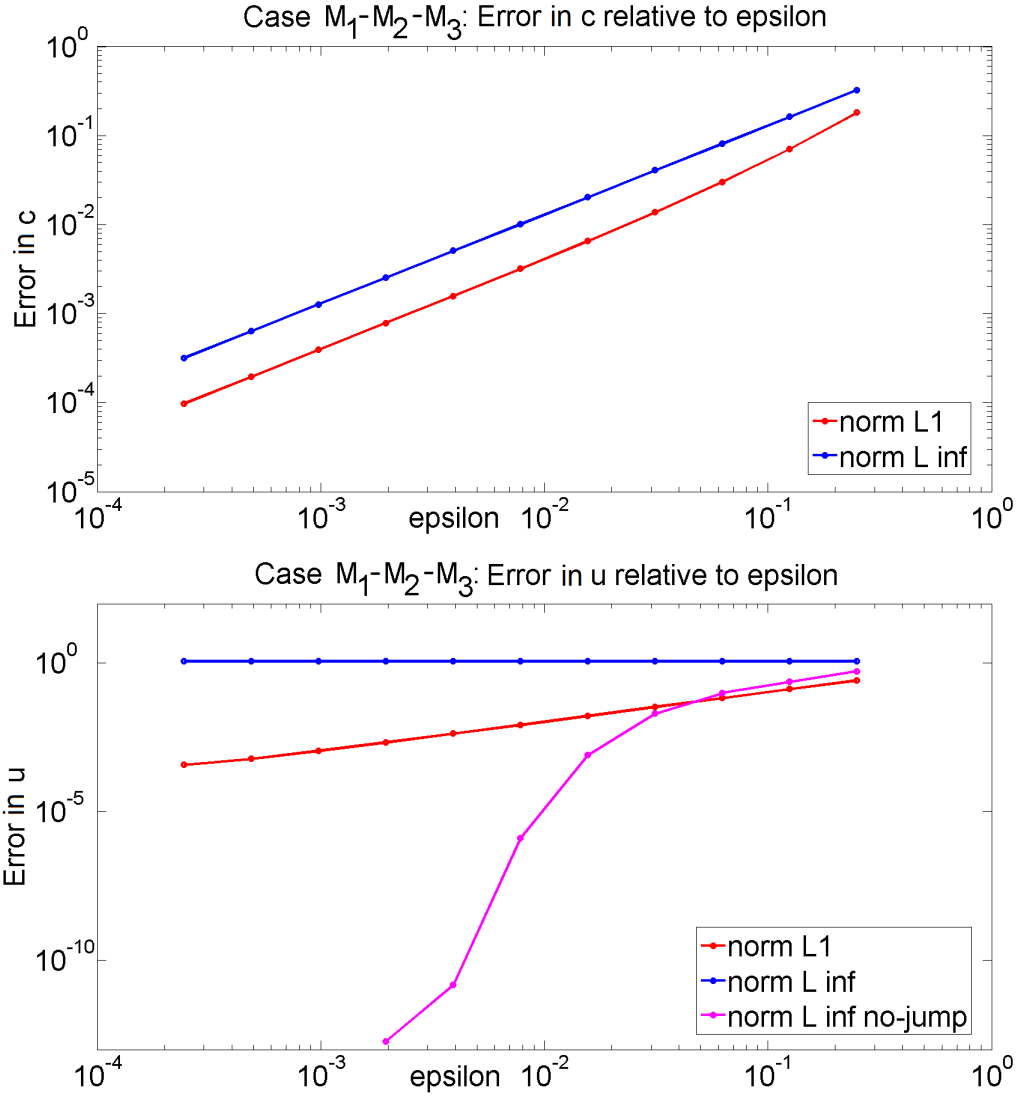


Figure 11: Numerical convergence for the case $M_1 - M_2 - M_3$ in dissolution of M_2 then M_1 .

Figure 11 represents the norms of the errors in the quantities e_c and in the controls e_u . Numerically, the rate of convergence of e_c is almost 1 for both norms L^1 and L^∞ . In Theorem 5.1, we proved strong convergence of e_u in L^1 norm. Numerically, the L^1 -norm of e_u converges with a rate almost equal to 1. Also, we observe a fast convergence of e_u in the L^∞ norm, out of jumps.

7.4 Test case $A_1 - M_2 - A_3$

This test case is very similar to the previous one, except that species M_1 and M_3 are replaced by aqueous species A_1 and A_3 :



where A_1 and A_3 are aqueous species and M_2 a pure phase mineral. Physical data, given in Table 3, are such that mineral M_2 precipitates in the first reaction and dissolves in the

second one. Activities of water solute A_1 and A_3 are given by (28) and maximal reaction rates by (3). They are non constant functions of \mathbf{c}_a :

$$a_i(\mathbf{c}_a) = \frac{c_{A_i}}{c_{A_1} + c_{A_3} + c_{\text{H}_2\text{O}}}, \quad i = 1 \text{ or } 3,$$

$$\tau_1(\mathbf{c}_a) = \alpha_1 a_1(\mathbf{c}_a) - \beta_1 \text{ and } \tau_2(\mathbf{c}_a) = \alpha_2 - \beta_2 a_3(\mathbf{c}_a)$$

Here the first reaction is not limited so that $r_1 = \tau_1$, whereas $r_{2,\epsilon} = H_\epsilon(c_{2,\epsilon})$.

Reactions	$R_1 : A_1 \rightleftharpoons M_2$ $R_2 : M_2 \rightleftharpoons A_3$
S	$\begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix}$
(α_1, β_1)	(30, 3)
(α_2, β_2)	(4.5, 18.75)
c_0	(2, 5, 0)
$c_{\text{H}_2\text{O}}$	20

Table 3: Test case $A_1 - M_2 - A_3$: physical parameters

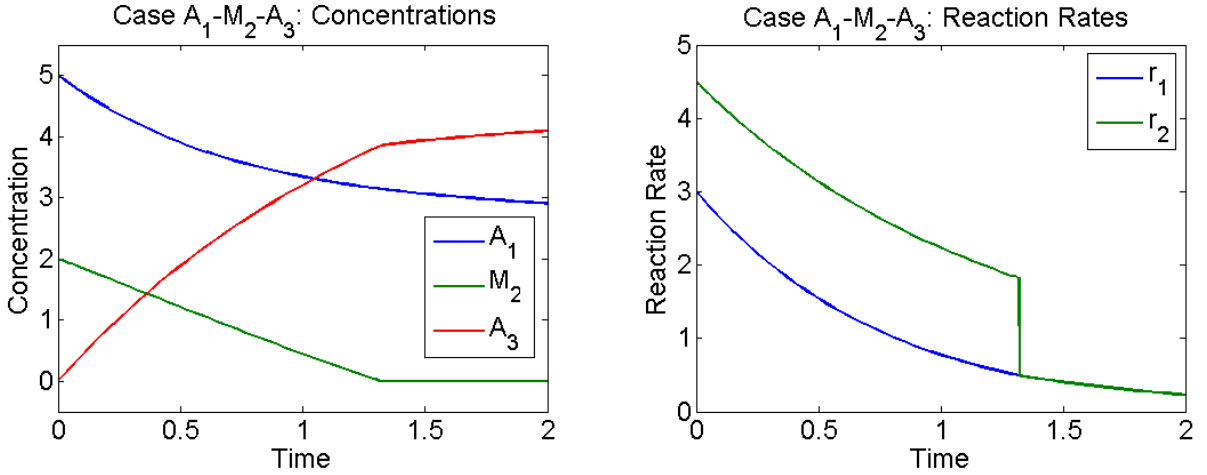
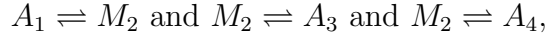


Figure 12: Case $A_1 - M_2 - A_3$ with total dissolution of M_2 . Results with $\epsilon = 0.001$.

Figure 12 shows the regularized solution and reaction rates computed with $\epsilon = 0.001$. We get a good approximation of the limit, solution of the discontinuous equations (15). We observe, like in the previous examples, that once the mineral M_2 is fully dissolved, it remains so. Thus the derivative dc_2/dt is equal to 0, in other words $r_2 = \tau_1$, meaning that $H_\epsilon(c_{2,\epsilon})$ converges towards $H(c_2) + \delta(c_2) \frac{\tau_1}{\tau_2}$, as in the previous example.

7.5 Test case with competition $A_1 - M_2 - A_3$ and $M_2 - A_4$

In this test case, we still consider the two reactions of the previous example and add a reaction of dissolution:



where M_2 is a pure phase mineral, A_1 , A_3 and A_4 are species in aqueous phase. Physical data are such that M_2 gets fully dissolved at a time of discontinuity t^* , see Table 4. The first reaction is not limited thus $r_1 = \tau_1$ whereas $r_2 = u_2(c_2)\tau_2$ and $r_3 = u_3(c_2)\tau_3$, with $u_2 = u_3 = 1$ if $c_2 > 0$. The activity of water solute \mathbf{c}_a is given by (28) and maximal reaction rates by (3):

$$a_i(\mathbf{c}_a) = \frac{c_{A_i}}{c_{A_1} + c_{A_3} + c_{A_4} + c_{\text{H}_2\text{O}}}, \quad i = 1, 3 \text{ or } 4,$$

$$\tau_1(\mathbf{c}_a) = \alpha_1 a_1(\mathbf{c}_a) - \beta_1, \quad \tau_2(\mathbf{c}_a) = \alpha_2 - \beta_2 a_3(\mathbf{c}_a) \text{ and } \tau_3(\mathbf{c}_a) = \alpha_3 - \beta_3 a_4(\mathbf{c}_a).$$

Reactions	$R_1 : A_1 \rightleftharpoons M_2$ $R_2 : M_2 \rightleftharpoons A_3$ $R_3 : M_2 \rightleftharpoons A_4$
S	$\begin{pmatrix} -1 & 0 & 0 \\ 1 & -1 & -1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
(α_1, β_1)	(30, 3)
(α_2, β_2)	(4.5, 18.75)
(α_3, β_3)	(4.5, 45)
c_0	(5, 2, 0, 0)
$c_{\text{H}_2\text{O}}$	20

Table 4: Test case with competition: physical parameters

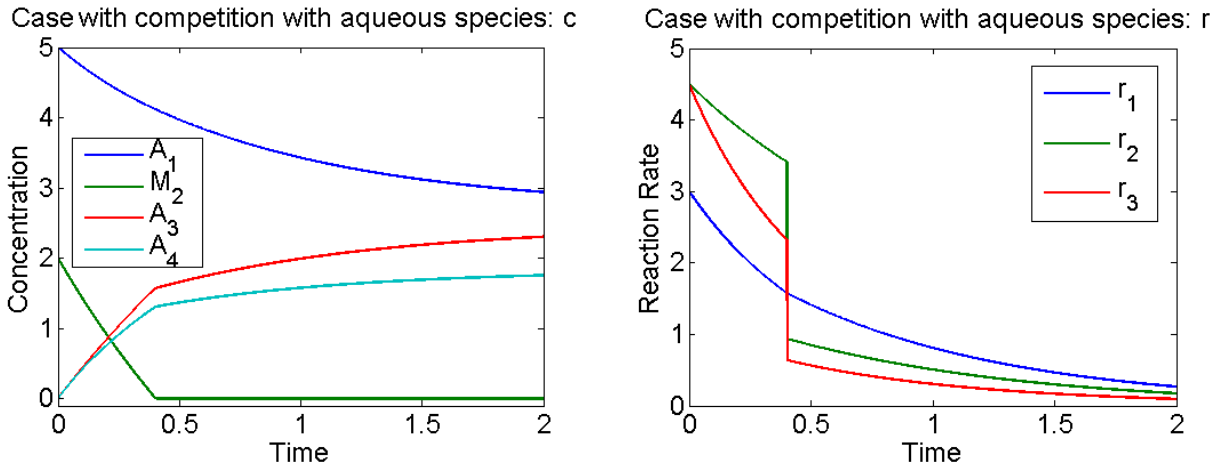
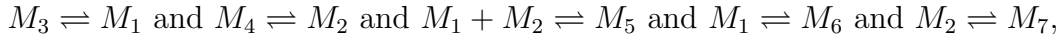


Figure 13: Case Competition with aqueous species. Results with $\epsilon = 0.001$.

The regularized limiters are $u_{2,\epsilon} = u_{3,\epsilon} = H_\epsilon(c_{2,\epsilon})$ thus, at convergence, $u_2 = u_3$. Figure 13 shows the regularized solution and reaction rates computed with $\epsilon = 0.001$. We get an approximation of the discontinuous solution. Again, we observe that once M_2 is dissolved at time t^* , the quantity c_2 remains equal to 0. Thus $dc_2/dt = 0$ for $t > t^*$, in other words $r_2 + r_3 = r_1$, so that $u_2 = u_3 = \frac{\tau_1}{\tau_2 + \tau_3}$. In some sense, the rate r_1 is evenly distributed between r_2 and r_3 , as if A_1 produces A_3 and A_4 .

7.6 Test case with blending

Up to now, there was only one dissolving mineral in a kinetic reaction. We investigate cases where at least two minerals dissolve in the same reaction, so that our regularized model requires using a blending function. We consider the following example:



where M_i , $i = 1, \dots, 7$, are pure phase minerals, so that maximal reaction rates are constant. Table 5 contains a summary of physical parameters.

Reactions	$R_1 : M_3 \rightleftharpoons M_1$ $R_2 : M_4 \rightleftharpoons M_2$ $R_3 : M_1 + M_2 \rightleftharpoons M_5$ $R_4 : M_1 \rightleftharpoons M_6$ $R_5 : M_2 \rightleftharpoons M_7$
S	$\begin{pmatrix} 1 & 0 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & -1 \\ -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$
τ	(0.5, 0.7, 1, 1, 1)
c_0	(0.2, 0.1, 2, 2, 2, 2, 2)

Table 5: Test case with blending: physical parameters

We use two blendings in the regularized model, the min function as in (18) and the prod function as in (27). As long as M_1 and M_4 are not fully dissolved, $u_{1,\epsilon} = u_{2,\epsilon} = 1$. Since $u_{3,\epsilon} = \min(u_{4,\epsilon}(c_{1,\epsilon}), u_{5,\epsilon}(c_{2,\epsilon}))$, at convergence $u_3 = \min(u_4, u_5)$ (similarly with prod).

In Figure 14, we plot the controls $u_{j,\epsilon}$ obtained with the two blendings, when $\epsilon=0.001$. As expected, we observe convergence except at times of discontinuity. Under these conditions, M_1 and M_4 are not yet fully dissolved so that $u_1 = u_2 = 1$, whereas M_2 is first fully dissolved, followed by M_1 . Again, after dissolution of a mineral, its time derivative is equal to 0. This observation gives rise to equations satisfied by the controls u_4 and u_5 . Between both dissolutions, $u_4 = 1$ and $r_2 = r_3 + r_5$, yielding $u_5 = \frac{\tau_2}{\tau_3 + \tau_5} = 0.35$. After

dissolution of the two minerals, $r_1 = r_3 + r_4$ and $r_2 = r_3 + r_5$. With the min blending, we get $\min(u_4, u_5) = u_4$, so that $u_4 = \frac{\tau_1}{\tau_3 + \tau_4}$ and $u_5 = \frac{\tau_2 - \tau_3 u_4}{\tau_5}$. Numerical values are

$$u_4 = 0.25, u_5 = 0.45, u_3 = \min(u_4, u_5) = 0.25. \quad (31)$$

With the prod blending, numerical values become

$$u_4 = \frac{\sqrt{\frac{43}{2}} - 3}{5} \simeq 0.32736, u_5 = \frac{\sqrt{\frac{43}{2}} - 2}{5} \simeq 0.52736, u_3 = u_4 u_5 \simeq 0.1726. \quad (32)$$

Consequently, the discontinuous reaction rates are different and the quantities c are also different with these two blendings. For example, $\frac{dc_6}{dt} = u_4$, $\frac{dc_7}{dt} = u_5$.

So, we observe that the regularized limiters and quantities depend on the blending, as well as their limits. Thus the choice of the blending has a direct impact on the differential inclusion problem. In a future work, we plan to compare in more details the different blendings.

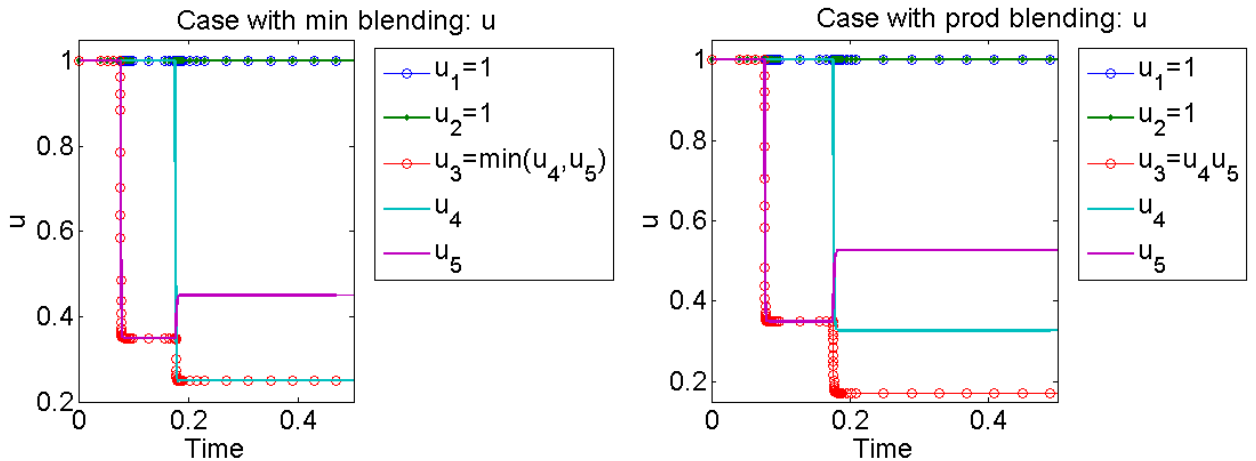


Figure 14: Case with two different blendings. Results with $\epsilon = 0.001$.

8 Discussion and conclusion

In this paper, we consider general precipitation dissolution reactions, where minerals can interact with other minerals and participate in several reactions. We propose a differential inclusion model with reaction rates defined by set-valued functions. Indeed, when a mineral is dissolved, reactions can stop or continue more slowly, thanks to limiting functions taking value in the interval $[0, 1]$. We prove existence of a continuous and positive solution to this problem by regularizing the reaction rates. This regularized model allows us also to compute numerical approximations of a discontinuous solution. In our tests, we observe that once a mineral is dissolved, it remains so, at least during a time interval. This provides equations to get unique values of the limiting functions and the discontinuous reaction rates. We plan to further analyze this sliding mode, in order

to characterize the set-valued functions in the differential inclusion problem. We also plan to study whether the limit of the regularized solution is the unique solution of the differential inclusion problem. When blending is required, regularized reaction rates as well as discontinuous ones depend on the choice of blending. We plan to compare these different models from a chemical point of view. In our differential inclusion model, the geochemical system is closed, with no external source term. Also, geochemical interactions are often coupled with transport processes such as dispersion or conduction. Future work will aim at adding source terms and at studying reactive transport models with these kinetic reactions.

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