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Characterizations of Solutions in Geochemistry: Existence, Uniqueness and Precipitation Diagram

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Abstract

In this paper, we study the properties of a geochemical model involving aqueous and precipitation-dissolution reactions at a local equilibrium. By reformulating the model as an equivalent optimization problem, we prove existence and uniqueness of a solution. It is classical in thermodynamic to compute diagrams representing the phases of the system. We introduce here the new precipitation diagram that describes the mineral speciation in function of the parameters of the system. Using the polynomial structure of the problem, we provide characterizations and an algorithm to compute the precipitation diagram. Numerical computations on some examples illustrate this approach.

Keywords: geochemistry, existence, uniqueness, precipitation diagram, modeling, polynomial system, convex optimization, precipitation-dissolution reaction

1. Introduction

Many environmental studies rely on modeling geochemical reactions such as aquifer contamination, underground waste disposal, remediation. In some of these applications the reactions can be assumed to be fast compared with their environment and so the reactions are considered in a local equilibrium. In this latter case, the model involves non-linear algebraic equations

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[2]. Here, we focus on aqueous and precipitation-dissolution reactions so only liquid and mineral species are involved. Many applications consider geochemical reactions coupled with hydrodynamic processes as in reactive transport model [19]. It is therefore of great interest to get a deep knowledge of the geochemical properties and to solve efficiently the algebraic equations.

We consider here an approach based on the definition of primary and secondary aqueous species, which are related by mass action laws [28]. Regarding the minerals, their appearance or disappearance is governed by saturation thresholds. The mathematical model is completed by mass balance equations, with so-called totals which are given data of the system.

In order to solve the non-linear equations resulting from the geochemical model, the main challenge is to find out which minerals are precipitated and which ones are dissolved, in other words to check whether saturation thresholds are active or not. Some numerical algorithms are based on a combinatorial approach [1, 3, 24]. Because the system can be formulated as a non-linear complementarity problem [7], numerical solving algorithms are frequently based on semi-smooth Newton methods [14, 16] or interior-point methods [25]. However, existence and uniqueness of solutions have been rarely studied from a theoretical point of view. One of our motivations in this paper is to bridge this gap between theory and practice.

Complementarity problems have been extremely popular in the field of Optimization Theory and have been extensively studied, [11] and references therein. Many first-order optimality conditions of a minimization problem with inequality constraints can be casted as a complementarity problem. In this paper, we prove, in the other way round, that the geochemical model can be viewed as first-order optimality conditions. As far as we know, this formulation is totally new. We define an objective function based on the mass balance equation and constraints based on the saturation thresholds.

In order to to so, we have to use logarithmic variables for the aqueous species, thus to assume that the variables are strictly positive. This usage of logarithms is quite common in the literature, see for example [9, 20, 15, 5]. In this paper, we carefully analyze the mathematical model and prove that it is equivalent to a reduced system with only strictly positive aqueous variables. To the best of our knowledge, we did not find any such theoretical justification of logarithms in the literature.

Under some assumptions on the stoichiometry, we can prove that the geochemical system is solution of a minimization problem with constraints. Then, thanks to results of Optimization Theory, it becomes easy to assess

the uniqueness of a solution. We also characterize the set of data $\mathcal{T}$ such that there exists a solution. Therefore, we can associate the totals in $\mathcal{T}$ to a unique geochemical system.

As we already pointed out, one motivation is to characterize the set of precipitated minerals and the complement set of dissolved minerals. We introduce the concept of precipitation diagram. More precisely, we build a partition of the set $\mathcal{T}$ such that each subset is associated to a geochemical system with a given set of precipitated minerals.

We propose to build precipitation diagrams thanks to symbolic computations. This approach provides a graphical view of the conditions under which some minerals can precipitate. With numerical values of given totals, the symbolic approach can compute the solution, although this is not the main objective. Moreover, the diagram can be used in the context of reactive transport models, for example to provide an initial guess of non-linear algorithms or to find out in which subset are the totals. Then the complementary problem could be replaced by an easier system of equations, which can be solved by a classical Newton's method.

We developed a software in Maple and used it for several test cases. These experiments show that precipitation diagrams are quite complex, even for simple examples. We also point out that the CPU and memory requirements are reasonable.

The paper is organized as follows: in Section 2, we describe the geochemical model and show that it can be reduced to equations with strictly positive variables, justifying the use of logarithmic unknowns. We introduce an elementary example of geochemical systems as a common thread throughout the paper. Then, in Section 3, we define the equivalent optimization problem and prove uniqueness of the solution along with preliminary results of existence. We provide an example where existence is conditioned by the parameters. Based on these theoretical outputs, we introduce in Section 4 our new concept of a precipitation diagram. Finally, our numerical experiments of Section 5 illustrate the complexity of these diagrams and the information they provide.

2. A Model for Geochemistry

In this section, we describe a mathematical model for geochemistry, which has already been used in the context of reactive transport, see [9, 26, 10].

We consider a species/components model frequently used in geochemistry modelling as in [2] or [27].

We consider here aqueous and precipitation-dissolution reactions, so that species can be in solution or minerals. For the sake of simplicity, we do not include reactions with fixed species other than minerals.

We first describe the mathematical model, then we show that we can consider aqueous species with positive concentrations. Therefore we can introduce an equivalent model with logarithms. Using logarithmic variables is classical in the reactive transport literature, see [26] and references therein.

2.1. Mass action laws and mass balance equation

We make several classical assumptions to define the mathematical model. First, we assume an ideal solution, a constant fluid density and a water saturated media. Second, a precipitation-dissolution reaction involves only one mineral.

Variables of the problem are the concentrations of species denoted by $c \in \mathbb{R}_+^{N_c}$, $\alpha \in \mathbb{R}_+^{N_\alpha}$ and $p \in \mathbb{R}_+^{N_p}$ respectively for the primary aqueous components, the secondary aqueous species and the minerals. All of them are non-negative quantities.

The law of mass action is directly used to model chemical equilibrium instead of Gibbs energy minimization, both methods are similar conceptually [28]. Assumptions made earlier imply that the activity of aqueous components are equal to their molar concentrations.

Aqueous reactions can be described through a Morel table [23]. Without loss of generality, the stoichiometric coefficients can be chosen as integers. Let $S \in \mathbb{Z}^{N_\alpha \times N_c}$ be the stoichiometric matrix for aqueous reactions associated to the positive constants of reaction $\kappa_c \in \mathbb{R}^{N_c}, \kappa_c > 0$. The laws of mass action for each aqueous reaction are written

$$\alpha_i(c) = \kappa_{ci} \prod_{k=1}^{N_c} c_k^{S_{ik}}, \ \forall i = 1, ..., N_\alpha \ .$$

Precipitation-dissolution reactions cannot be treated in the same way, since the activity of a mineral is constant. Those are heterogeneous reactions, which are represented with a matrix $E \in \mathbb{Z}^{N_p \times N_c}$ of integer stoichiometric coefficients and a vector of solubility products denoted by $\kappa_p \in \mathbb{R}^{N_p}$ with $\kappa_p > 0$. Appearance and disappearance of the mineral $i, i = 1, \ldots, N_p$, are

governed by a saturation threshold $\gamma_i(c)$ defined by

$$\gamma_i(c) = \prod_{k=1}^{N_c} c_k^{E_{ik}}.$$

So, there are two possible cases, either the fluid is under-saturated and there is no mineral,

$$p_i = 0,\ \kappa_{pi} - \gamma_i(c) > 0,\ \forall i = 1, ..., N_p,$$

either the fluid is saturated and the mineral is present,

$$p_i \geq 0,\ \kappa_{pi} - \gamma_i(c) = 0,\ \forall i = 1, ..., N_p.$$

By convention we use a strict inequality in the under-saturated case to avoid any confusion. This kind of equilibrium problems are well-known in optimization theory under the name of complementarity problem, [7]. It may be reformulated as

$$p \geq 0,\ \kappa_p - \gamma(c) \geq 0,\ p^T(\kappa_p - \gamma(c)) = 0.$$

The model is completed by a mass balance equation, written for each primary aqueous component. Let $T \in \mathbb{R}^{N_c}$ be the vector of total concentrations, which is given data in the context of a closed geochemical system. The mass balance equations are then written

$$T = c + S^T\alpha(c) + E^T p.$$

Finally, combining these three equations gives the geochemical model :

$$\begin{array}{l} c + S^T\alpha(c) + E^T p - T = 0, \\ p^T(\kappa_p - \gamma(c)) = 0, \\ c \geq 0,\ p \geq 0,\ \kappa_p \geq \gamma(c). \end{array} \tag{1}$$

This system is a closed system of $(N_c + N_p)$ equations with inequality constraints. With our assumptions, all the expressions are polynomials. This observation will be used in section 4.3.

2.2. A logarithmic model

The stoichiometric coefficients can be zero, strictly positive or strictly negative.

When a stoichiometric coefficient S_{ik} is zero, the component c_k does not participate in the reaction involving the secondary species $\alpha_i(c)$. Similarly, it does not participate in the reaction with the mineral p_i if $E_{ik} = 0$. A particular case arises when all the coefficients associated to a component are zero, which does not react with any other species. Such a component is called a tracer.

Another particular case is a component such that all coefficients S_{ik} and E_{ik} are non-negative. If the associated total is zero, it means that this component is absent, as well as the secondary species and minerals associated.

The remaining case is when at least a stoichiometric coefficient S_{ik} or E_{ik} is negative. Then the factor $c_k^{S_{ik}}$ and $c_k^{E_{ik}}$ are defined only if $c_i > 0$, as well as the secondary species $\alpha_i(c)$ and the saturation thresholds γ_i. Thus the constraint $c_i \geq 0$ must be replaced by $c_i > 0$ in that case.

We sum up these remarks in a proposition:

Proposition 2.1. *For an aqueous tracer k with $S_{ik} = E_{ik} = 0$, the concentration is given by $c_k = T_k$ and the component can be removed from the system.*

For an aqueous component c_k with non-negative coefficients $S_{ik} \geq 0, E_{ik} \geq 0$, three cases can be considered: if $T_k < 0$, the model has no solution; if $T_k = 0$, then $c_k = 0, S_{ik}\alpha_i(c) = 0, E_{ik}p_i = 0$; if $T_k > 0$, then $c_k > 0$.

For an aqueous component c_k with a negative coefficient $S_{ik} < 0$ or $E_{ik} < 0$ for some i, the concentration must be positive: $c_k > 0$.

Thus any tracer or component associated to non-negative coefficients and to a given null total can be removed from the system. Moreover, the secondary species or minerals associated to this component can also be removed from the model. Indeed, the reactions involving a primary component with a zero concentration can be removed from the system.

Thus it is possible to define a reduced model where all the concentrations c_k of the primary components are positive.

Proposition 2.2. *Model (1) is equivalent to a reduced model where:*

- *There is no tracer: $\forall k, \exists i, S_{ik} \neq 0$ or $E_{ik} \neq 0$.*
- *All the components are reactive: $c_k > 0$.*

- *All the secondary species are reactive:* $\alpha_i(c) > 0, i = 1, \ldots, N_\alpha$.
- *All the saturation thresholds are non-zero:* $\gamma_i(c) > 0, i = 1, \ldots, N_p$.

From now on, we consider such a reduced model, where the number of primary components is still denoted by N_c and the positivity constraint is now $c > 0$:

$$\begin{cases} c + S^T\alpha(c) + E^T p - T = 0, \\ p^T(\kappa_p - \gamma(c)) = 0, \\ c > 0,\ p \geq 0,\ \kappa_p \geq \gamma(c). \end{cases} \tag{2}$$

Finally, we can introduce logarithmic variables and define an equivalent model.

Proposition 2.3. *Model 2 is equivalent to the complementarity problem*

$$\begin{cases} \exp(x) + S^T \exp(\log(\kappa_c) + Sx) + E^T p - T = 0, \\ p^T(Ex - \log(\kappa_p)) = 0, \\ p \geq 0, Ex \leq \log(\kappa_p), \end{cases} \tag{3}$$

where $x = \log(c)$.

It can be noted that some conditions on T are necessary to ensure the existence of a solution.

Proposition 2.4. *If a primary component k has only non negative stoichiometric coefficients and if $T_k \leq 0$, then system (2) has no solution.*

Proof. If the stoichiometric coefficients associated to the primary component k are non-negative, the corresponding total mass $(\exp(x) + S^T \exp(\log(\kappa_c) + Sx) + E^T p)_k$ is strictly positive. Thus, if there exists a solution, the total T_k satisfies $T_k > 0$. □

2.3. Example with two salts: sodium chloride and potassium chloride

We conclude this section by giving a first example of a geochemical system, in order to illustrate and highlight some characteristics. Chemistry reactions are only precipitation-dissolution in order to simplify the presentation. Therefore, there are as many reactions as minerals and the system is defined by the stoichiometric matrix E and the solubility products κ.

This first example, with two salts, considers precipitation of sodium chloride $NaCl$ and potassium chloride KCl, involving the three aqueous components, sodium ion Na^+, potassium ion K^+, chloride ion Cl^-, [] The two reactions, along with the solubility products, are summed up in the following table:

Mineral	Reaction	κ
$NaCl$	$NaCl \rightleftarrows Na^+ + Cl^-$	37.5837
KCl	$KCl \rightleftarrows K^+ + Cl^-$	7.6208

The stoichiometric matrix of this system is :

$$E = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix},$$

which is of full rank N_p.

Since all the coefficients are positive, the data T must satisfy $T > 0$.

3. Equivalence with an Optimization Problem

In this section, we prove that the geochemical system (3) is equivalent to a minimization problem with inequality constraints. Indeed, we show that the complementarity equations are optimality conditions of an optimization problem. This result is the keystone for studying existence and uniqueness of solutions of the geochemical model. Another approach could use variational analysis tools, for instance from [11].

3.1. Objective function and inequality constraints

We first define the objective function of the optimization problem by

$$f(x) = e_{N_c}^T \exp(x) + e_{N_\alpha}^T \exp(\log(\kappa_c) + Sx) - T^T x,\ x \in \mathbb{R}^{N_c}, \tag{4}$$

where e_n is the vector of dimension n whose components are 1.

The function f is C^∞ in $\mathbb{R}^{N_c}$ with a gradient given by

$$\nabla f(x) = \exp(x) + S^T \exp(\log(\kappa_c) + Sx) - T,$$

and a Hessian matrix given by

$$\nabla^2 f(x) = \mathcal{D}\left(\exp(x)\right) + S^T \mathcal{D}\left(\exp(\log(\kappa_c) + Sx)\right) S,$$

where $\mathcal{D}(y)$ denotes a diagonal matrix with the elements of y on the diagonal.

Then we define inequality constraints by introduction the feasible set:

$$\mathcal{F} = \{x \in \mathbb{R}^{N_c},\ g(x) \leq 0\},$$

where $g(x) = Ex - \log(\kappa_p)$. Clearly, the feasible set is convex.

Finally, we introduce the convex minimization problem

$$\min_{x \in \mathcal{F}} f(x). \tag{5}$$

3.2. Uniqueness of a solution

We are now able to prove the equivalence between the model (3) and the minimization problem (5). Indeed, the complementarity problem is nothing else than the Karush-Kuhn-Tucker (KKT) optimality conditions [17]. Uniqueness of a solution immediately follows.

We first show that the objective function is strictly convex:

Lemma 3.1. *If $N_c \leq N_\alpha$ and if the matrix S is of full rank N_c, then the Hessian matrix is symmetric positive definite for any x and the function f is strictly convex in $\mathbb{R}^{N_c}$.*

Proof. The elements of the diagonal matrices in the Hessian matrix are positive. Since the matrix S is of full rank, any matrix of the form $S^T DS$, where D is a diagonal matrix with positive elements, is symmetric positive definite (spd). Thus the matrix $\nabla^2 f(x)$ is also spd. □

From this lemma, and using the linearity of the constraints, it becomes easy to prove that the equations (3) are the KKT conditions of the minimization problem (5) and to prove the uniqueness of a solution.

Theorem 3.1. *Assuming that the matrix S is of rank N_c, and that the feasible set is non-empty, equations (3) are equivalent to solve the minimization problem (5). Moreover, if the minimization problem has a solution x, it is unique.*

Proof. We first note that any x satisfies a linear constraint qualification. Since the feasible set is non-empty convex and a linear constraint qualification is satisfied everywhere, the KKT conditions are necessary and sufficient. Using the gradient of f and the Jacobian E^T of g, it appears that these KKT conditions are exactly equations (3). Thus, x is a solution of (5) if and only if there exists a Lagrange multiplier $p \in \mathbb{R}^{N_p}$ such that x and p are solutions of (3).

Uniqueness of x is ensured by the strict convexity of f [18]. □

If we further assume that the matrix E is of rank N_p, the Lagrange multiplier is also unique.

Corollary 3.1. *Assuming that the matrix S is of rank N_c and the matrix E is of rank N_p, and the feasible set is non-empty, the Lagrange multiplier p is unique.*

Proof. The gradients of the inequality constraints are the lines of the matrix E and are linearly independent if E is of rank N_p. Thus, any x satisfies a linear independence constraint qualification (LICQ), so that if there is a solution, then the Lagrange multiplier p is unique. [18]. □

Consequently, Corollary 3.1 guarantees uniqueness of the solution of the geochemical system (3).

3.3. Existence of a solution

In Proposition 2.4, we have shown that, with positive stoichiometric coefficients, the existence of a solution requires that $T > 0$. Now, we prove that, for any full rank stoichiometric matrices, there exists a solution of (5), provided that $T > 0$.

Theorem 3.2. *Assuming that the matrix S is of rank N_c and the matrix E is of rank N_p, and that $T > 0$, the geochemical model (2) has a unique solution.*

Proof. Let $F(x) = e_{N_c}^T \exp(x) - T^T x, x \in \mathbb{R}^{N_c}$, clearly $\forall x \in \mathbb{R}^{N_c}, f(x) > F(x)$. Now, $\forall k = 1, \ldots, N_c, \lim_{x_k \to +\infty}(\exp(x_k) - T_k x_k) = +\infty$; since, by assumption $T_k > 0$, we also have $\forall k = 1, \ldots, N_c, \lim_{x_k \to -\infty}(\exp(x_k) - T_k x_k) = +\infty$. Thus the function F is coercive, in other words $\lim_{\|x\| \to +\infty} F(x) = +\infty$, and the function f is also coercive.

This property ensures the existence of a solution of the minimization problem. □

We denote by $\mathcal{T}$ the set of totals T such as the problem has a solution. This set is then easy to define when all the stoichiometric coefficients are positive.

Corollary 3.2. *Assuming that the matrix S is of rank N_c with $S \geq 0$, the matrix E is of rank N_p with $E \geq 0$, the geochemical model (2) has a solution if and only if $T > 0$: $\mathcal{T} = \{T \in \mathbb{R}^{N_c},\ T > 0\}$*

Proof. The result follows from Proposition 2.4 and Theorem 3.2. □

However, in the general case, it seems quite challenging to find the set $\mathcal{T}$, as illustrated by the following example.

3.4. Example with two minerals: calcite and gypsum

We point out here an example where one of the stoichiometric coefficient is negative. The two reactions involve 2 minerals, calcite $CaCO_3$ and gypsum $CaSO_4$, with 3 aqueous components, hydrogen ion H^+, calcium ion Ca^{2+}, sulfate ion $SO4^{2-}$, along with water and carbon dioxide, considered in excess.

Mineral	Reaction	κ
$CaCO_3$	$CaCO_3 + 2H^+ \rightleftarrows Ca^{2+} + CO_{2(aq)} + H_20$	10^9
$CaSO_4$	$CaSO_4 \rightleftarrows Ca^{2+} + SO_4^{2-}$	$4\ 10^{-5}$

The stoichiometric matrix E is given by

$$E = \begin{pmatrix} -2 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix},$$

which is of rank N_p.

The following result provides necessary and sufficient conditions on T to get a solution.

Proposition 3.1. *The set $\mathcal{T}$ is given by*

$$\mathcal{T} = \{(T_1, T_2, T_3) \in \mathbb{R}^3,\ T_2 > 0,\ T_3 > 0,\ T_1 + 2T_2 > 0\}.$$

Proof. Mass balance equations and positivity constraints imply the necessary conditions $T_2 > 0$, $T_3 > 0$ and $T_1 + 2T_2 > 0$.

Now, we show that they are sufficient.

Recall that $f(x) = \exp(x_1) + \exp(x_2) + \exp(x_3) - T_1x_1 - T_2x_2 - T_3x_3$, and that $g_1(x) = -2x_1 + x_2 - \log(\kappa_1)$, $g_2(x) = x_2 + x_3 - \log(\kappa_2)$.

The function $\exp(x_3) - T_3x_3$ is coercive since $T_3 > 0$.

If x_1 is finite or $x_1 \to +\infty$, then $\lim_{|x_2| \to +\infty} f(x) = +\infty$.

Now, since $g_1(x) \leq 0$ we have $-x_2 \geq -2x_1 - \log(\kappa_1)$ thus, since $T_2 > 0$, also $-T_2x_2 \geq -2T_2x_1 - T_2\log(\kappa_1)$ and finally $f(x) \geq \exp(x_1) + \exp(x_2) + \exp(x_3) - T_3x_3 - (T_1 + 2T_2)x_1 - T_2\log(\kappa_1)$.

Since $T_1 + 2T_2 > 0$, for any (x_2, x_3), we get $\lim_{x_1 \to -\infty} f(x) = +\infty$.

We conclude that the function f is coercive and that the minimization problem has a solution.

□

4. Precipitation Diagram

Throughout this section, we assume that the matrices S and E are of full rank. Then, for any $T \in \mathcal{T}$, there is a unique solution of the chemical model, which is the speciation of the geochemical system associated with the data T. It gives the positive concentrations of the primary components (the unknown c or $x = \log(c)$) and the non-negative quantities of the minerals (the Lagrange multiplier p).

Now, we propose to characterize this speciation by the presence or lack of each mineral. Then, the objective is to find the subset of totals T which lead to a speciation with a given subset of precipitated minerals. We build a partition of $\mathcal{T}$ into so-called mineral states, associated to subsets of minerals. This partition defines a diagram, in the same spirit as thermodynamical diagrams [6, 8].

This diagram can be formally defined by using the notions of strongly active or weakly active constraints. We first give some definitions based on the optimization problem, then propose a procedure to compute the diagram using symbolic calculus.

4.1. Definitions

For $T \in \mathcal{T}$, we denote by $(x(T), p(T))$ the unique solution of the minimization problem (5) with the data T. We characterize the geochemical system by the minerals, introducing the subset $M(T) \subset \{1, 2, \ldots, N_p\}$ of precipitated minerals and its complement $\bar{M}(T)$ of dissolved minerals, defined by

$$M(T) = \{i, p_i(T) > 0\},\ \bar{M}(T) = \{j, p_j(T) = 0\}.$$

Vice versa, let I be a subset of $\{1, 2, \ldots, N_p\}$ and $\bar{I}$ its complement set. We call a mineral state associated to I the subset of $\mathcal{T}$ such that, for any T in this subset, $M(T) = I$.

Therefore, there are 2^{N_p} mineral states.

Definition 4.1. *A mineral state associated to a subset I of $\{1, 2, \ldots, N_p\}$ is defined by*

$$\mathcal{M}_I = \{T \in \mathcal{T},\ \forall i \in I : p_i(T) > 0 \text{ and } g_i(x(T)) = 0\},$$

where $(x(T), p(T))$ is the solution of (5) with the data T. In other words, the constraints with indexes in the subset I are strongly active. Moreover, the indexes j in the complement set $\bar{I}$ satisfy $p_j(T) = 0$ and $g_j(x(T)) \leq 0$.

The mineral states are interfaced by what we call state boundaries, which are obtained by adding or removing a mineral which is dissolved and still at saturation. Therefore, each mineral state is associated to N_p boundaries and there are $N_P 2^{N_p-1}$ interfaces (since each of them is defined by one given mineral and a subset of the other $N_p - 1$ minerals).

Definition 4.2. *A state boundary of the mineral state associated to I and $j \notin I$ is defined by*

$$\{T \in \mathcal{T},\ \forall i \in I : p_i(T) > 0 \text{ and } g_i(x(T)) = 0,\ p_j(T) = g_j(x(T)) = 0\}.$$

A state boundary of the mineral state associated to I and $j \in I$ is defined by

$$\{T \in \mathcal{T},\ \forall i \in I, i \neq j : p_i(T) > 0 \text{ and } g_i(x(T)) = 0,\ p_j(T) = g_j(x(T)) = 0\}.$$

In other words, the constraint of index j is weakly active and those of other indexes in I are strongly active.

The intersection of boundaries is a special state where all minerals are dissolved and still at saturation. We call it the critical state.

Definition 4.3. *The critical state is the subset $\mathcal{C}$ defined by*

$$\mathcal{C} = \{T \in \mathcal{T},\ \forall i \in \{1, 2, \ldots, N_p\} : p_i(T) = g_i(x(T)) = 0\}$$

In other words, all constraints of the critical state are weakly active.

These definitions build a partition of the space $\mathcal{T}$ into 2^{N_p} mineral states, which we call a precipitation diagram.

Definition 4.4. *A precipitation diagram defines a partition of $\mathcal{T}$ into 2^{N_p} subsets $\mathcal{M}_I$ corresponding to the subsets I, bounded by the algebraic curves corresponding to the state boundaries.*

4.2. Example with two salts: sodium chloride and potassium chloride

Let us illustrate these definitions by the example with two salts of section 2.3. Here, all the totals must be strictly positive to ensure a unique solution.

We further assume that the species satisfy electrical neutrality. Using the charge of each ion, the balance equation can be written $c_1 + c_2 - c_3 = 0$, thus $c_3 = c_1 + c_2$ can be eliminated from the equations.

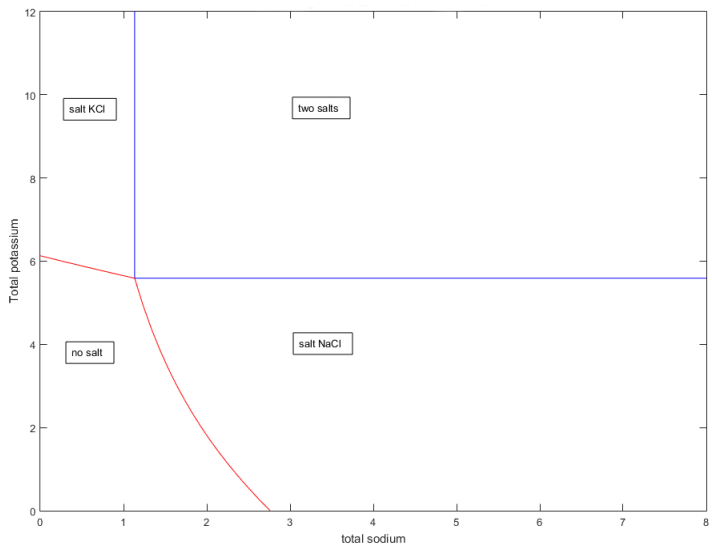

Figure 1: Precipitation diagram with the two salts $NaCl, KCl$.

By combining the mass balance equations, we also get the property $T_1 + T_2 - T_3 = 0$, thus we can restrict the study to only two parameters T_1, T_2.

The 2D precipitation diagram, with $T_1 > 0$ and $T_2 > 0$, is shown in Figure 1.

The space is divided into four states, with four boundaries. The critical set is the point $(T_{1,c}\, T_{2,c})$:

$$\begin{aligned} T_{1,c} &= \kappa_1/\sqrt{\kappa_1 + \kappa_2}, \\ T_{2,c} &= \kappa_2/\sqrt{\kappa_1 + \kappa_2}. \end{aligned}$$

The four state boundaries are:

$$\begin{aligned} T_1 &= T_{1,c}, \\ T_2 &= T_{2,c}, \\ T_1(T_1 + T_2) &= \kappa_1, \\ T_2(T_1 + T_2) &= \kappa_2. \end{aligned}$$

Here, it is easy to compute by hand the solutions and to characterize the diagram. However, for more complex geochemical systems, the task becomes tricky.

4.3. Computing a precipitation diagram

We propose to follow a combinatorial approach exploring the 2^{N_p} mineral states and using symbolic computations. This framework is tractable for a moderate number of minerals, say a dozen. A by-product of this procedure will be to get a symbolic expression of the solution (c, p), but the main objective is to build the precipitation diagram.

We come back to the non-logarithmic system (2). Because we consider integer stoichiometric coefficients, equations are polynomial equalities and inequalities, which define semi-algebraic sets. Therefore solving means finding solutions depending on algebraic numbers, which are roots of univariate polynomials.

In order to simplify the symbolic computations, we can take advantage of some invariants, such as the charge balance described for the example with two salts.

4.4. Invariants with conservative variables

We still assume that the matrix E is of full rank N_p. Then the QR factorization of the matrix E^T yields an orthogonal matrix $(Q_1, Q_2) \in \mathbb{R}^{N_c \times N_c}$ and a non-singular triangular matrix $R \in \mathbb{R}^{N_p \times N_p}$ such that

$$E^T = (Q_1,\ Q_2) \begin{pmatrix} R \\ 0 \end{pmatrix} = Q_1 R.$$

It can be noted that $EQ_1 = R^T$ and $EQ_2 = 0$. It follows that p can be written as

$$np(c) = R^{-1} Q_1^T (T - c - S^T \alpha(c)). \tag{6}$$

Also, the variables $Q_2^T c$ are decoupled from minerals thanks to the relation

$$Q_2^T T = Q_2^T (c + S^T \alpha(c)). \tag{7}$$

Finally, these simplifications lead to a model involving only the N_c variables c:

$$\begin{cases} Q_2^T (c + S^T \alpha(c)) = Q_2^T T, \\ p(c)^T (\kappa_p - \gamma(c)) = 0, \\ c > 0,\ p(c) \geq 0,\ \kappa_p \geq \gamma(c). \end{cases} \tag{8}$$

The quantities $Q_2^T c$ are called conservative variables, because they are often related to some balance equation. In many cases, these equations can

be used to eliminate some unknowns, in order to simplify the precipitation diagram.

An example is the charge balance, when the primary components are ions. The corresponding vector q in Q_2 represents the charges of these ions. In order to ensure electrical neutrality, it is common to require that $q^T T = 0$. This invariant can be used to remove a parameter T_k and to eliminate the unknown c_k.

4.5. Symbolic computations

Let $I \subset \{1, 2, \ldots, N_p\}$ be a given mineral state and let $T \in \mathcal{T}$ be a parameter of the symbolic procedure. Then $T \in \mathcal{M}_I$ if and only if $(c(T), p(T))$ satisfies:

$$\begin{cases} Q_2^T(c + S^T\alpha(c)) - Q_2^T T = 0, \\ \gamma_i(c) = \kappa_{pi}, \forall i \in I, \\ p_i(c) = 0, \forall i \in \bar{I}, \\ c > 0, \\ p_i(c) > 0, \forall i \in I, \\ \gamma_i(c) \leq \kappa_{pi}, \forall i \in \bar{I}, \end{cases} \tag{9}$$

where $p(c)$ is given by (6).

We recall that this system can usually be simplified by using conservative variables and balance equations.

In this form, it is a set of N_c polynomial equations with N_c positivity constraints, and N_p polynomial inequalities. We first solve the N_c polynomial equations and get solutions in terms of algebraic numbers, which are function of T. We keep only those such that $c > 0$. Then, we check the polynomial inequalities with these algebraic numbers and get an implicit description of the state boundaries in function of T.

Several methods exist to compute a triangulation of a polynomial system, probably the most used one is to compute Gröbner bases [13]. This tool is in general useful as it also determines if the system is inconsistent and if it has a finite or infinite number of solutions. The oldest and most well-known method to compute such a base is the Buchberger's algorithm [4], but more recent and efficient methods were developed, for instance Faugère's F4 and F5 algorithms [12]. Computation of a Gröbner basis requires in the worst case $d^{2^{O(n)}}$ operations where d is an upper bound on the degrees of the polynomials and n the number of variables. Nowadays, most of the computer

algebra systems contain routines to do so. So we do not get into the details of these computations.

5. Numerical Experiments

In this section, we show numerical results with three examples. Precipitation diagrams were computed with a code developed in Maple^{TM}, implementing the symbolic procedure described above.

These diagrams are computed only once for a given geochemical system. Nevertheless, time and memory requirements could be high, regarding the number of mineral states and boundaries. We provide CPU and memory measurements for the last example, with 64 states.

5.1. Three salts: sodium chloride, potassium chloride, and carnallite

We consider here an example with 3 minerals, sodium chloride $NaCl$, potassium chloride KCl and carnallite $KMgCl_3$, reacting with 4 aqueous components, sodium ion Na^+, potassium ion K^+, magnesium ion Mg^{2+} and chloride ion CL^-. The three reactions and the solubility products are given in the following table:

Mineral	Reaction	κ
$NaCl$	$NaCl \rightleftarrows Na^+ + Cl^-$	37.5837
KCl	$KCl \rightleftarrows K^+ + Cl^-$	7.6208
$KMgCl_3$	$KMgCl3 \rightleftarrows K^+ + Mg^{2+} + 3Cl^-$	2.1380e+04

The stoichiometric matrix E of this system is given by

$$E = \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 \\ 0 & 1 & 1 & 3 \end{pmatrix}.$$

Since the matrix E is of full rank N_p and all the coefficients are positive, the set of parameters T with a unique solution is given by

$$\mathcal{T} = \{T \in \mathbb{R}^{N_c},\ T > 0\}.$$

The kernel of E has one vector q defined by the charges of ions: $q = (1,\ 1,\ 2,\ -1)^T$. Thus the charge balance is a conservative variable and electrical neutrality requires that $T_1 + T_2 + 2T_3 = T_4$. As described above, we use electrical neutrality to remove the total T_4 and the concentration c_4 of

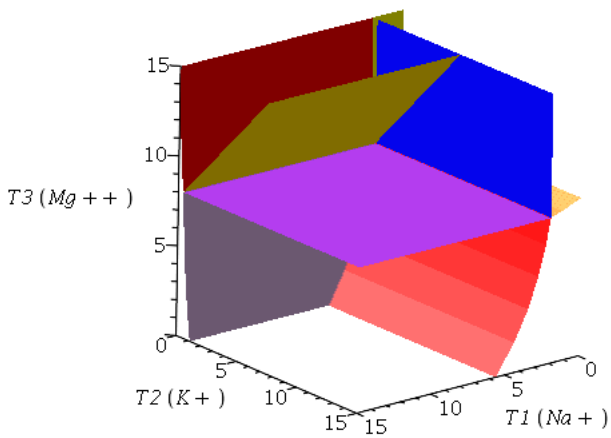

Figure 2: Precipitation diagram with the three salts $NaCl, KCl, KMgCl_3$.

chloride ion. The 3D precipitation diagram, with $T_i > 0$, $i = 1, 2, 3$, is shown in Figure 2.

There is only one critical point $(T_{1,c}\ T_{2,c},\ T_{3,c})$. The state with three minerals precipitated is bounded by the three hyperplanes:

$$\begin{aligned} T_1 &= T_{1,c}, \\ T_2 &= T_{2,c} + T_3 - T_{3,c}, \\ T_3 &= T_{3,c}. \end{aligned}$$

More details can be found in [21].

5.2. Two minerals: calcite and gypsum

This example was already described in section 3.4.

Here too, the matrix Q_2 has one vector which is defined by the charge of ions. Electrical neutrality allows to remove the total T_3 and the concentration c_3 of sulfate ion.

The 2D precipitation diagram of a similar system, with constants $\kappa_1 = 1$ and $\kappa_2 = 1.5$, is shown in Figure 3.

The critical set is the point $(T_{1,c}\ T_{2,c})$ where $T_{1,c}$ is the unique positive solution of $\kappa_1 y^3(1/2 + \kappa_1 y) - \kappa_2 = 0$ and $T_{2,c} = \kappa_1 T_{1,c}^2$. The four state

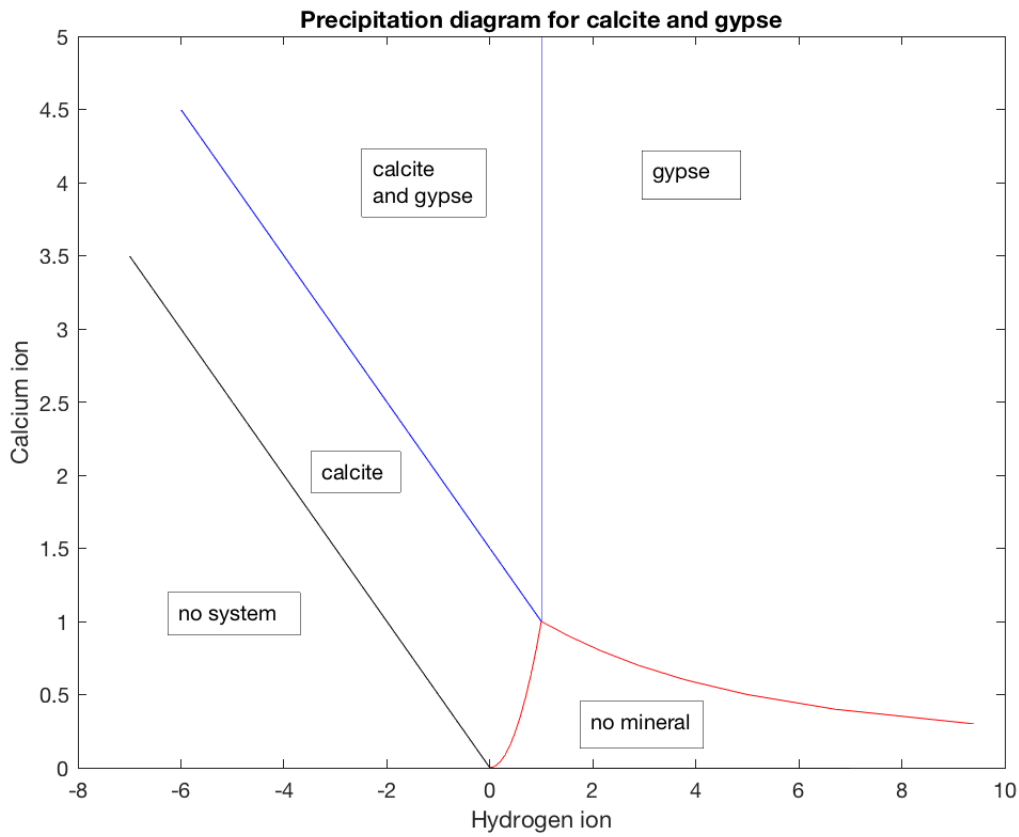

Figure 3: Precipitation diagram with a system similar to calcite and gypsum (using constants 1 and 1.5).

boundaries are given by

$$
\begin{aligned}
&T_1 = T_{1,c},\\
&T_2 = T_{2,c} + 1/2(T_{1,c} - T_1),\\
&T_2 = \kappa_1 T_1^2,\\
&T_2(1/2T_1 + T_2) = \kappa_2.
\end{aligned}
$$

5.3. Acid mine drain

We now give an example coming from the literature of acid mine drain, [22]. An acid mine drain (AMD) is an acid mineral solution which appears

in some kind of mines or in the context of waste storage. The presence of AMD leads to acidification of the water and appearance of sulphuric acid (H_2SO_4). Figure 4 gives the various species in the initial porous media. We are interested in the precipitation-dissolution reactions of Figure 5. The solubility products come from the database MINTEQ/A2.

Table 1
Initial background, as well as AMD source and non-source (natural recharge water) concentrations at surface for the conceptual model based on the tailings source at the Nickel Rim mine, Ontario Canada (Walter et al., 1994b).

Component	Initial background conc.[a] (mol/L)	Source conc. (mol/L)	Non-source conc. (mol/L)
Ca^{2+}	5.2e-03	1.08e-02	6.9e-03
Mg^{2+}	1.5e-03	9.69e-04	1.9e-03
Na^{+}	1.3e-03	1.39e-03	1.3e-03
K^{+}	6.6e-05	8.14e-04	6.7e-05
Cl^{-}	1.0e-03	1.58e-02	1.0e-03
CO_3^{2-}	2.4e-06	4.92e-04	3.9e-03
SO_4^{2-}	5.3e-03	5.00e-02	7.5e-03
Mn^{2+}	2.9e-05	7.84e-03	4.7e-05
$H_4SiO_4^0$	1.9e-03	2.08e-03	1.9e-03
Fe^{2+}	3.6e-05	3.06e-02	5.4e-05
Fe^{3+}	8.7e-17	2.00e-07	2.3e-08
Al^{3+}	6.6e-13	4.30e-03	1.3e-07
pH	7.2	4	7.0

[a] Small differences with Walter et al. (1994b) due to equilibration with modified background mineralogy.

Figure 4: Chemical species in the Acid Mine Drain test case from [22].

Table 2
Stoichiometric reactions and equilibrium constants K_k of all minerals in the DFN and EPM simulations (after Mayer et al., 2002; Molson et al., 2008).

Mineral	Reaction	Log K_k
Calcite	$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}$	−8.5
Siderite	$FeCO_3 \Leftrightarrow Fe^{2+} + CO_3^{2-}$	−10.5
Gibbsite	$Al(OH)_3 + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O$	8.1
Gypsum	$CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	−4.6
Ferrihydrite	$Fe(OH)_3 + 3H^+ \Leftrightarrow Fe^{3+} + 3H_2O$	4.9
Quartz	$SiO_2\,(am) + 2H_2O \Leftrightarrow 3H_4SiO_4$	−2.7

Figure 5: Mineral reactions and constants in the Acid Mine Drain test case from [22].

In order to simplify the chemistry, we consider only the minerals and the primary species. So, we get a stoichiometric matrix E with three independent systems.

$$\begin{pmatrix} E & c_{H_4SiO_4} & c_{H^+} & c_{Fe^{3+}} & c_{Al^{3+}} & c_{Ca^{2+}} & c_{SO_4^{2-}} & c_{Fe^{2+}} & c_{CO_3^{2-}} \\ p_{quartz} & 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ p_{gibbsite} & 0 & -3 & 0 & 1 & 0 & 0 & 0 & 0 \\ p_{ferrihydrite} & 0 & -3 & 1 & 0 & 0 & 0 & 0 & 0 \\ p_{calcite} & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ p_{siderite} & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ p_{gypsum} & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \end{pmatrix}.$$

Even if solving polynomial equations is simplified, there are still a high number of states ($2^6 = 64$) to explore. In the Table below, we provide the time and memory required for the different steps of computations.

Steps	Time (in seconds)	Memory (in MB)
Loading function library	0.96	33.93
Generation of the reduced chemical system	< 1	< 1
Computation of every phase	2.14	16.00
Total	3.18	49.93

We observe that our symbolic software was able to compute the precipitation diagram quite quickly, with low memory requirements. The time and memory required to load the library of functions used in the computation are here to make a comparison point. Since the generation of the reduced chemical system involves only very simple operations, it requires almost no time and memory. Computing each mineral state with its boundaries out of 64 subsets is the most expensive step, as expected.

Conclusion and Perspectives

The study presented in this article shows some of the main characteristics of the geochemical equations considering aqueous and precipitation-dissolution reactions. In particular, we showed that under mild classical assumptions the geochemical system has at most one solution. Existence of the solution is discussed through a clear characterization, although we did not get a general result that gives a condition on the parameters of the system. Both results use a reformulation of the geochemical equations as a minimization problem.

Then, we introduced the precipitation diagram that describes the various possibles states of the reaction in terms of the parameters of the system. We

gave some characterization of this diagram and described a procedure to compute it based on the polynomial structure of the problem. Numerical results using a code developed in Maple illustrated some examples of precipitation diagram and showed that the whole computation is actually reasonable in time and memory.

Reactive transport is one of the main application that uses the geochemical model. It is clear that the computation of a precipitation diagram can not be included in a full code for this application since in this case the nonlinear equation has to be solved millions of time. However, it can be very useful in describing the chemical reactions and so it can be used to find a good initial point for a numerical code or to compute the exact solution in a verification process. These extensions to reactive transport and applications of the precipitation diagram are left for further research.

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