



# A speciation solver for cement paste modeling and the semismooth Newton method



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## ABSTRACT

The mineral assemblage of a cement paste may vary considerably with its environment. In addition, the water content of a cement paste is relatively low and the ionic strength of the interstitial solution is often high. These conditions are extreme conditions with respect to the common assumptions made in speciation problem. Furthermore the common trial and error algorithm to find the phase assemblage does not provide any guarantee of convergence. We propose a speciation solver based on a semismooth Newton method adapted to the thermodynamic modeling of cement paste. The strong theoretical properties associated with these methods offer practical advantages. Results of numerical experiments indicate that the algorithm is reliable, robust, and efficient.

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## 1. Introduction

To mitigate the environmental impact of the cement industry, cement manufacturers add by-products of other industries (such as fly-ash, blast-furnace slag, pozzolanic materials, ...) into their products [1]. The sustainability goal may be achieved only if one can predict the long term properties of the concrete and mortars made with these binders. However predicting these properties is a challenging task. Lab experiments cannot fairly represent the condition of a 50–100 year process. In addition, these materials are used, or intended for use, in many extreme conditions such as deep oil well casing [2], nuclear waste storage [3], or thinner and taller structures. Reactive transport modeling is a simulation tool to predict these long-term properties [4,5]. Reactive transport is a well-established framework to solve problems where chemical reactions and transport phenomena are coupled. However many difficulties remain. They can be modeling questions (transport coefficient predictions, phases and composition of the phases, ...) or numerical issues (how to couple models, how to obtain a reliable answer, ...). In this work we focus on the numerical issues associated with the speciation problem which addresses the issue of finding the equilibrium state of a chemical system. This problem is at the core of the reactive transport framework [6,7]. However, its application to cement science is not straightforward since cement paste presents three particularities. First, water is not in huge excess as commonly assumed [8]. Then, the ionic strength is usually high and the non-ideality of the solution has to be taken into account [1]. Finally, the cement paste

may contain many minerals and the phase assemblage varies greatly with the formulation of the cement [9,10]. The mineral problem is commonly solved by a trial and error process to determine the minerals present in the system [7,11]. This procedure is unsatisfactory since there is no guarantee of its success. S. Krättele [12] proposed to solve this problem using the mathematics of the complementarity problems. Following this approach, we propose a speciation solver based on a semismooth Newton method to solve the mixed complementarity problem. Our work differs from the previous study of S. Krättele [12] on two main points: the water conservation equation and the non-ideality of the solution are considered. Several solving strategies are presented and compared. This paper is the opportunity to present to the cement community the complementarity problem and the semismooth Newton method. These two mathematical tools have been recently developed and may be used in many different settings [13]. For instance, Marchand et al. used it to take into account the appearance or disappearance of the gas phase in a multiphase flow [14].

The first section of this paper describes the speciation model. Then we discuss different strategies to solve this problem and explain our algorithm based on the semismooth Newton method. The last section presents some numerical results based on thermodynamical modeling of cement. We show that the semismooth approach is justified and performs well.

## 2. The speciation problem

### 2.1. A purely aqueous system

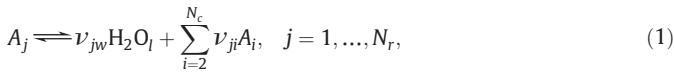
Given an initial composition of a system, a speciation solver finds the composition at equilibrium. Two main schools exist to solve this

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problem (for an historical review see [7]). The stoichiometric approach is based on the equilibrium constant [11,15,16], and the non-stoichiometric approach minimizes the Gibbs free-energy [17–20]. These two approaches are theoretically equivalent [21] since the equilibrium constants are an expression of the minimum of the Gibbs free energy for a given reaction. However, each formulation and implementation may have its own feature. In this work, we focus on the stoichiometric method. This choice was made because the extension of the stoichiometric method to reactive transport is straightforward and well established [6,22]. Moreover it is considered faster [19] and easier to implement [7]. The higher flexibility usually provided by the non-stoichiometric approach [19,20] is not required in this study since we focus on a very specific system: a saturated cement paste. However the complementarity approach may be transferable to the other method since the same phase selection problem may occur depending on the formulation.

We first consider a solution without minerals to introduce the general framework and the notations. Let  $N_s$  denote the number of aqueous species in equilibrium in an aqueous solution. The equilibrium state is defined with respect to  $N_r$  linearly independent chemical reactions [6, 23]. These reactions determine a set of  $N_c = N_s - N_r$  independent components called the basis. By convention, water, the solvent, is the first component of this basis. This assumes that liquid water is always present in the chemical system. This is not a restriction since it is also a modeling assumption for reactive transport in concrete. At the exception of fire or oven drying, most of the durability model always assumes an aqueous solution. It is required for the heterogeneous precipitation/dissolution of solid phases and oxidation of the reinforcement bars [9]. The other components of the basis are also taken as real aqueous species since it is easier to obtain meaningful physical result [7]. The chemical reactions can be written as the decomposition of the remaining  $N_r$  species over the basis:



where  $A_k$  denotes the label of species  $k$ , and  $\nu_{ji}$  is the stoichiometric coefficient of component  $i$  for reaction  $j$ . These stoichiometric coefficients can be negative and the corresponding component is thus a reactant. A system written in this form is said to be in the canonical form [6]. The components are chosen to be real species instead of the element as it is commonly done in the field. It is important, especially for reactive transport, to keep the mathematical problem close to the physical problem in order to easily detect any incoherence.

Each reaction is accompanied by a law of mass action which expresses the equilibrium condition

$$K_j = \frac{\prod_{i=2}^{N_c} a_i^{\nu_{ji}}}{a_j}, \quad j = 1, \dots, N_r, \quad (2)$$

where  $a_k$  is the activity coefficient for species  $k$ . As commonly assumed, the activity of water is 1.0. For aqueous species,  $a_k = \gamma_k m_k$ , where  $m_k$  is the molality (mol/kg w) and  $\gamma_k$  is the activity coefficient, which represents the effect of the non-ideality of the solution. It is given by an extended Debye Hückel law [1,24]

$$\gamma_k = -\frac{Az_k^2\sqrt{I}}{1 + B\bar{a}_k\sqrt{I}} + \bar{b}_k I, \quad k = 2, \dots, N_c, N_c + 1, \dots, N_c + N_r, \quad (3)$$

where  $I$  is the ionic strength,

$$I = \sum_{k=2}^{N_c+N_r} m_k z_k^2. \quad (4)$$

The ionic strength is a measure of an equivalent concentration of charge in the system.  $A$  and  $B$  are constants for a given temperature ( $A = 0.5092$  and  $B = 0.3823$  at  $T = 25^\circ\text{C}$  [7]) and  $\bar{a}_k$  and  $\bar{b}_k$  are defined species-wise by the database [24].

## 2.2. Minerals

The minerals are handled differently since they may or may not be present in the system, depending on their saturation state. Let's consider a mineral  $A_l$  and its mole number  $n_l$ . Its dissolution follows this reaction



Only the primary aqueous species appears in this expression because the canonical form is used [6]. The saturation state of the mineral is defined as

$$SI_l = \frac{\prod_{i=2}^{N_c} a_i^{\nu_{li}}}{K_m}, \quad (6)$$

where  $K_m$  is the equilibrium constant for decomposition of the mineral over the basis (Reaction (5)). If needed, the modeler may add the contribution of the water activity or the mineral activities (to model solid solutions) to the saturation index [7,25]. Four distinct situations are possible

1.  $SI_l < 1$  and  $n_l > 0$  the mineral is undersaturated and will dissolve.
2.  $SI_l < 1$  and  $n_l = 0$  the mineral is undersaturated and will not precipitate.
3.  $SI_l > 1$  the mineral is oversaturated and will precipitate.
4.  $SI_l = 1$  the mineral is at equilibrium with the solution.

Only cases 2 and 4 are at equilibrium. Let  $n_l$  denote the mole number of the mineral  $l$ . These two situations may be summarized as a complementarity condition [12,13]

$$n_l \geq 0, \quad -\log(SI_l) \geq 0, \quad \text{and} \quad -n_l \log(SI_l) = 0. \quad (7)$$

This condition states that either the mineral is present and at equilibrium ( $n_l \geq 0$ , and  $SI_l = 1$ ) or the mineral is not present, thus undersaturated ( $n_l = 0$ , and  $SI_l \leq 1$ ). If  $N_{min}$  minerals are allowed to precipitate in the system, one has  $N_r + N_{min}$  equilibrium conditions. The remaining  $N_c$  equations are given by the mass conservation. The logarithm version of the condition has been chosen for numerical reasons. Unless explicitly mentioned, the logarithm is the logarithm base ten as commonly used in aqueous chemistry problems.  $\Omega = \log(SI_l)$  is commonly called the saturation index in the literature.

## 2.3. Mass conservation

The mass conservation equations constrain the quantity of each component throughout the computation [7,11]. The conservation equation for water is

$$T_w = \bar{m}_w \left( \frac{1}{M_w} + \sum_{j=1}^{N_r} \nu_{jw} m_j \right) + \sum_{l=1}^{N_{min}} \nu_{lw} n_l, \quad (8)$$

where  $\bar{m}_w$  is the mass of water (kg<sub>w</sub>) and  $M_w$  is the molar mass of water.  $T_w$  is the so-called *Total concentration* (in mol). An explanation of the

physical meaning of the total concentration is given by Bethke [7]. In a similar fashion, the conservation of each aqueous component is defined as

$$T_i = \bar{m}_w \left( m_i + \sum_{j=1}^{N_r} \nu_{ji} m_j \right) + \sum_{l=1}^{N_{min}} \nu_{li} n_l, \quad i = 2, \dots, N_c. \quad (9)$$

These equations are similar to the ones presented by Bethke [7] with the difference that the minerals are not included in the basis. Therefore, they must be added to the mass conservation equations as secondary species.

It is possible to solve the  $N_c$  equations under the  $N_r + N_{min}$  equilibrium constraints. Another possibility is to note that  $m_j$  may be obtained from the law of mass actions (Eq. (2)) and substituted in the conservation equations. This operation reduces the system to  $N_c$  equations under  $N_{min}$  equilibrium constraints. From our experience, this reduction does not strongly perturb the convergence properties. However it may reduce the number of variables by a large amount, especially for systems with a large number of components where many complexes can coexist. This operation destroys the sparsity of the resulting matrix. However, the rows and columns corresponding to the components are already almost dense for arbitrary systems, since all species are expressed as functions of the components.

The reduction proposed in the previous paragraph is only valid if we consider fixed activity coefficient when solving the system or if we add the activity coefficients as variables. The ionic strength and activity equations are usually not included directly in the system (see for instance [7,26]). In this approach the activity coefficients are computed using fixed-point iterations. The downside is that we reduce the rate of convergence near the solution. In the two examples of Section 5, the rate of convergence is only linear in average instead of the quadratic rate obtained when we consider an ideal solution. However including these equations in the linear system will at least double the size of the Jacobian, multiplying by eight the factorization time. Moreover, computing the entries corresponding to these variables is computationally expensive. Since the main difficulty is to obtain the solid phase assemblage, this “slow” rate of convergence only means a few cheap iterations more. These considerations are also discussed by Bethke [7, pg. 64–66]. When considering reactive transport in cement paste, it should also be noted that other parameters such as kinetics law or transport parameters obtained through upscaling may also be computed through fixed-point iterations therefore this theoretically slow algorithm may in practice be very efficient.

As noted by Brassard and Bodurtha [27], and Carayrou et al. [26] the aqueous speciation problem is quite difficult to solve and even starting guess close to the solution may fail to provide a solution. It has been observed [27] that the method performs better when the starting point contains a high surplus of mass. It was also verified in most cases with our code. However this choice is not favorable to the activity problem since the ionic strength will be too high and will modify too much the reactivity of the species. In order to increase the robustness of our code, these secondary variables are only solved once the residuals are sufficiently small. In practice, the threshold has been fixed arbitrarily to the number of component in the basis and is crossed after a few iterations.

Another issue is the choice of the main variables. The molalities may vary over several orders of magnitude and must remain positive. Therefore the logarithms of the molalities are used as the main variables  $x_i = \log_{10} m_i$ ,  $i = 2, \dots, N_c$  [11]. This choice is especially important since our approach fixes the basis at the beginning of the computation, so the components may be, or may become, species in minority in the system. Such a situation should be avoided when possible [11], but it should not be an insurmountable obstacle for finding a solution. Detection of an ill-

conditioned Jacobian and scaling are some methods to prevent these problems [28–30].

The system presented in this section (Eqs. (8), (9), (2) and (7)) is a Mixed Complementarity Problem (MiCP) [13]. It is a constrained mathematical system. Therefore it cannot be solved by the common Newton method. The next section presents some of the algorithms developed to solve these problems.

### 3. Mixed complementarity problem

A MiCP is defined as follows [13]: Given  $G(u, v) : \mathbb{R}^n \times \mathbb{R}^m \rightarrow \mathbb{R}^n$ , and  $H(u, v) : \mathbb{R}^n \times \mathbb{R}^m \rightarrow \mathbb{R}^m$ , find  $(u^*, v^*) \in \mathbb{R}^n \times \mathbb{R}^m$  such that

$$\begin{aligned} G(u^*, v^*) &= 0, \\ 0 \leq v^* \perp H(u^*, v^*) &\geq 0. \end{aligned} \quad (10)$$

In our case  $u = \{\bar{m}_w, x_{i,i=2,\dots,N_c}\}$ ,  $v = \{n_{l,l=1,\dots,N_{min}}\}$ ,  $G$  are the mass conservation equations and the components of  $H$  are the saturation indexes  $H_l = -\log(S_l)$ . It is important to note that  $H$  does not depend on the set  $v$  (the mineral numbers of moles), but only on the concentration of aqueous components. It introduces some numerical difficulties.

#### 3.1. Active set methods

This class of algorithms is designed to search the active set of constraints ( $\{v_i | H_i(u^*, v^*) = 0\}$ ) and solve the resulting unconstrained system. The traditional approach to solve the speciation problem is an active set approach with a twist [6,7,11]. The mass conservation equations are linear with respect to the amount of minerals. By including the active set of minerals in the basis, the corresponding linear equation may be removed from the set of non-linear equations to be solved by the “expensive” Newton method. An algorithm to find the active set of minerals by trial and error is described in the book of C. Bethke [7]. This method presents some advantages, the number of variables is reduced, the Gibb's phase rule is explicitly enforced and a traditional Newton method can be used. This idea has been applied successfully in many codes [11,16]. However, some major drawbacks exist. First the set of equations is changed at each solid phase assemblage. No mathematical proof of convergence exists for such a system and it introduces some instabilities. Then, in cement paste, some minerals may have very similar composition (for example the jennite and tobermorite models for C–S–H which only differs by the calcium to silica ratio [9,31]) and it may be difficult for the algorithm to find the correct active set. This is even more important when one does not have a good starting point. The lack of mathematical proof of convergence may seem irrelevant due to the successful applications of this type of algorithm. However, there is no safeguard against special cases and there are no theorems to help the development of more efficient algorithms.

#### 3.2. Interior-point method

Interior point algorithms are a class of methods to solve constrained problems. They have the particularities that the problem stays feasible at each iteration [32,33]. Like the Newton method two flavors exist: the optimization method [32] and the constrained system of equation solver [13]. An interior point method was successfully adapted to the speciation problem by F. Saaf [34] and LOQO, a nonconvex nonlinear interior-point solver [35], solves ideal systems with and without minerals. However, these methods have a major drawback: the complementarity conditions are handled by adding slack variables. First, it increases the size of the system. In concrete application many minerals may be taken into account; therefore the inflation of the system may be significant (see Table 1). But more importantly, the slack variables make warmstarting more difficult. A warmstart is the use of a previous solution in a slightly perturbed system. Since reactive transport contains many similar problems, warmstarting offers an important gain in

**Table 1**  
Number of main variables for each method. The examples correspond to the two simulations presented in Section 5.  $N_{min,i}$  is the number of minerals present in the system at equilibrium. The activity coefficients are considered fixed. If they are not fixed,  $N_c + N_r + 1$  equations must be added to the system.

					A priori selection	Active set	C-function	Interior point
Theory	$N_c$	$N_r$	$N_{min}$	$N_{min,i}$	$N_c - N_{min,i}$	$N_c + N_{min,i}$	$N_c + N_{min}$	$N_c + 2N_{min}$
Example 1	5	10	5	2	3	7	10	15
Example 2	7	21	14	5	2	12	21	35

efficiency and stability. This point will be proved in the last section. If some warmstarting methods exist for the interior-point method [36, 37], their application is not straightforward. Thus, we chose to implement the method presented in the next paragraph.

### 3.3. Equation based reformulation

Our approach, following the work of S Krättele [12], uses a C-function to reformulate the problem into an unconstrained problem. A C-function has the following property [13]

$$\phi(a, b) = 0 \Leftrightarrow a \geq 0, b \geq 0, \text{ and } ab = 0. \quad (11)$$

The right hand side is the complementarity condition. Thus, C-functions allow us to reformulate this constraint as a single equation and remove the need for slack variables. Two C-functions are used in this work. The min function  $\phi_{min}(a, b) = \min(a, b)$ , also used by S. Krättele, and the penalized Fischer–Burmeister function, first introduced by Chen, Chen and Kanzow [38]

$$\phi_{CCK} = \lambda \left( \sqrt{a^2 + b^2} - a - b \right) - (1 - \lambda) a_+ b_+ \quad (12)$$

where  $k_+ = \max(0, k)$ . The well-known Fischer–Burmeister function ( $\phi_{FB}$ ) can be retrieved when  $\lambda = 1$  but it has weaker theoretical, and practical properties [30,38]. The best value of  $\lambda$  is problem dependent. A value of 0.8 seems to be a good compromise in many cases for our problem. With this function, the residual is decreased when the number of moles is positive and the mineral is supersaturated. The effect of this function is thus to keep the system in the feasible domain and thus stabilize the algorithm, similar to the strategy of an interior point method. The min function may be seen as an active set approach and can be used to reduce the number of equations, since inactive degrees of freedom are trivial to evaluate [12,39]. These two functions are not differentiable everywhere, therefore the traditional Newton method cannot be used. However, this obstacle may be overcome by using a semismooth Newton method [13,40]. The next section presents the algorithms used to solve the speciation problem.

## 4. Algorithm

### 4.1. Smooth Newton method

The traditional Newton method solves a system of non-linear equations by solving iteratively the following linear system

$$J(x^k) \cdot d = -R(x^k) \quad (13)$$

$$x^{k+1} = x^k + d$$

where  $R$  are the residuals and  $J$  is the Jacobian matrix,  $J_{ij} = \frac{\partial R_i}{\partial x_j}$  [28,41]. Using the Jacobian requires that the residuals are differentiable everywhere. However, the development of the mathematical theories of nonsmooth functions and the generalized Jacobian allow us to adapt the Newton method to nonsmooth functions [13,42]. We present here the algorithm to solve the MiCP as presented in Eq. (10). Although the algorithm looks unusual, it is backed up by many mathematical results. For extensive details, we direct the reader to the book of Facchinei and Pang and the references therein [13].

### 4.2. Semismooth Newton system

The residual at iteration  $k + 1$  is approximated by the following model

$$M^{k+1} = \theta(u^k, v^k) + A^k d = 0, \quad (14)$$

where  $A^k$  is an element of the generalized Jacobian and  $\theta(u, v)$  are the semismooth residuals, using the C-function reformulation :

$$\theta_p(u, v) = \begin{pmatrix} G(u, v) \\ \phi_p(v, H(u, v)) \end{pmatrix}, \quad (15)$$

where  $\phi_p(a, b)$  stands for the chosen C-function. The element of the generalized Jacobian for  $\phi_{CCK}$ , and  $\phi_{FB}$  is selected according the algorithm given by Chen, Chen and Kanzow [38,43]. The Jacobian for  $\phi_{min}$  is the traditional Jacobian when only the rows and columns of active degrees of freedom ( $\bar{m}_w, \{x_i | i = 2, \dots, N_c\}$ , and  $\{n_i | n_i > 0\}$ ) are kept. In the case where  $n_i = 0 = \log(SI_i)$ , the degree of freedom is considered active. In that case, at each iteration, the reformulation is smooth, and the common Newton method can be used to solve the system. However, very poor performance was observed with the standard Newton or a mixed scheme, where the min function is used for the search direction and the Fischer–Burmeister for the linesearch, as presented by Luca et al. [40]. Better performance was obtained when the same algorithm as the  $\phi_{CCK}$  reformulation was used. We believe that the reason for this behavior is that it provides better protection against stationary points and ill-conditioned Jacobians. This algorithm is presented in the following paragraph.

The min function reformulation only keeps the active equations. If the equations are smooth and well-conditioned, the perturbation is small and traditional methods may be used [13]. However the reformulations using  $\phi_{CCK}$  and  $\phi_{FB}$  introduce stronger perturbations. The reformulated equations are only strongly semismooth. In order to ensure convergence, the following descent condition must be respected by the update [13,30]

$$\nabla \theta_{CCK}^T d \leq -\rho \|\nabla \theta_{CCK}\|^p. \quad (16)$$

If the condition is not respected then a gradient step is taken,

$$d = -\nabla \theta_{CCK}, \quad (17)$$

where  $\rho > 0$  and  $p > 2$ . This step is the steepest descent direction. However, we observed that taking a full gradient step is often a poor choice in our system. The following strategy, described by Facchinei and Pang [13, p. 834], has been adopted instead. It mixes the Newton solution with the gradient step, by perturbing the linear system:

$$(q\eta \nabla \theta_{CCK}(u, v) + \theta_{CCK}(u, v)) + (q\eta \mathbf{I} + A^k) d = 0, \quad (18)$$

where  $\eta$  is a positive constant,  $\mathbf{I}$  is the identity matrix, and  $q \in \mathbb{N}$ . The system is solved for increasing  $q$  until the following descent conditions are respected

$$\begin{aligned} \nabla\theta_{\text{CCK}}(u^k, v^k)^T d^k &\leq -c_1 \min\left(\|\nabla\theta_{\text{CCK}}(u^k, v^k)\|^2, \|\nabla\theta_{\text{CCK}}(u^k, v^k)\|^3\right), \\ \nabla\theta_{\text{CCK}}(u^k, v^k)^T d^k &\leq -c_2 \min\left(\|d^k\|^2, \|d^k\|^3\right), \end{aligned} \tag{19}$$

where  $0 < c_1, c_2 < 1$ . As noted by Facchinei and Pang,  $q = 0$  is equivalent to the initial system and when  $q$  tends to infinity, the update is a gradient step. Therefore, after a certain number of factorization, the gradient step may be taken directly to avoid unnecessary work. However, the gradient step is a poor choice in our system because it usually strongly decreases the amount of water in the system, which is an error difficult to repair in the following steps. From Eqs. (8) and (9), by setting  $\bar{m}_w = 0$  and by adjusting  $n_l$  one can obtain a zero, but this is not a physical answer and this solution must be avoided. It is consistent with the fact that we always assume that liquid water is present in our system and the formulation of our problem (see Section 2). One way to avoid being attracted by this solution is to set the initial amount of water to be relatively high, and the initial amount of minerals to be zero. Another mitigation technique is to limit the maximum step length ( $\|d\|$ ) that the algorithm can take [28]. It limits the error made in such steps and facilitates the recovery.

Since the gradient step is a poor search direction, crashing techniques [30,44] fail to provide a better starting point. Typical parameters are  $\eta \sim 100$ ,  $c_1 = c_2 = 10^{-4}$  and  $m \leq 4$ . The mitigation strategy is not always necessary and has been deactivated to solve the first problem of Section 5.

Since our system is dense and small, a dense rank revealing QR factorization is used to solve the linear system (Eq. (18)) [45]. The QR factorization was chosen since it is considered more stable and accurate than the LU decomposition [45]. Furthermore special treatments may be easily applied to the QR factorization in order to detect and treat a singular or poorly conditioned Jacobian [28,41]. To avoid an ill-conditioned problem we estimate the condition number of the matrix [28]. The algorithm used is the one designed by W. Hager [46]. If the condition number is too big, then we increase  $m$  and start another factorization. Scaling the Jacobian may be a way to avoid a condition number that is too high. The matrix scaling proposed by Munson et al. [30] has been implemented. This scaling is important for a purely aqueous system where the Jacobian is ill-defined in a large region [26,27]. Our experiments also tell us that scaling should be enabled when the min C-function is used but is optional in most cases for the penalized Fischer–Burmeister function.

### 4.3. Linesearch

Newton methods are only locally convergent, that is they require a good enough starting point. To enlarge their domain of convergence global methods have been invented [28,47]. The global methods are designed to force the minimization of a merit function. The algorithm uses the following common merit function [30]

$$\Psi(u, v) = \frac{1}{2}\theta(u, v)^T\theta(u, v). \tag{20}$$

The merit function may have stationary points that are not solutions of our system [13, pg. 797], therefore a nonmonotonic linesearch is used to avoid such points [30]. The algorithm used is based on algorithm 3.5 by Nocedal and Wright [47] with the exception of the condition to accept a step. We decompose the update as  $d = [\Delta u \ \Delta v]$ . The following modified Wolfe condition is used as the driving force of the linesearch

$$\Psi(u^k + t\Delta u, v^k + t\Delta v) \leq \xi^k - \sigma t \nabla\theta(u^k, v^k)^T [\Delta u \ \Delta v] \tag{21}$$

where  $t$  is the parameter of the linesearch,  $\sigma$  is a positive constant, and  $\xi^k$  is a reference value, that is a previous value of the merit function which is greater or equal to the actual value. With this choice, the algorithm accepts longer steps, making it more difficult to get stuck in a stationary point [30]. The basis of this idea is that eventually the full Newton step will be accepted [13, Theorem 9.1.29] therefore the linesearch does not change the convergence properties close to a solution, like for the smooth Newton method. When a gradient step has been taken,  $\xi^k$  is multiplied by 100 to get out of the troubling region. The nonmonotonic linesearch is crucial for convergence, especially when the min C-function is used. This linesearch using interpolation has been preferred to the more simple halving process commonly used in the literature [13,40] since it has proved to be more robust and to require less evaluation of the residuals.

We end this section by summarizing the algorithm for the reformulation using  $\phi_{\text{CCK}}$ . Many variations exist in the literature [13,30,38,40]; this one has proved to work well on our problem. SpecMiCP is the name of the code implementing this algorithm. We would like to end this section by noting that numerical optimization is an art. The choices made in this section have proved to work well with the specific problems presented in this paper. They may not be adaptable to other formulations.

### Algorithm. Semismooth Newton algorithm

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while (k = 0; k < max_iter; ++k) do
    Compute and reformulate the residuals  $\theta_{\text{CCK}}(u, v)$ 
    Check convergence, stop if a solution has been found
    Select  $A^k \in \partial\theta_{\text{CCK}}(u, v)$  ▷ Select an element of the generalized Jacobian
    for (q = 0; q < max_q; ++q) do
        solve (18) ▷ If it cannot be solved, continue
        if (19) then
            break;
        end if
    end for
    if system not solved then
         $d^k \leftarrow -\nabla\theta_{\text{CCK}}(u, v)$ 
    end if
    linesearch : given  $\xi^k$ , find t such that (21) holds
    update :  $u^{k+1} = u^k + t\Delta u, v^{k+1} = v^k + t\Delta v$ 
end while

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## 5. Numerical results

In this section, the cement notations are used. In particular, C is lime CaO, A stands for  $\text{Al}_2\text{O}_3$ ,  $\bar{\text{C}}$  for  $\text{CO}_2$ , H for  $\text{H}_2\text{O}$ , and S for  $\text{SiO}_2$  [9]. The simulations presented in this section have been designed to be close to a real simulation for a cement paste while providing good insight on the respective performance of the different strategies presented in the previous section. For more information about the thermodynamic modeling of cementitious material, we refer the reader to the review paper by Damidot et al. [10]. The simulations were run with both my software and PHREEQC [16]. PHREEQC was chosen for the comparison since it is one of the more robust and fastest speciation solvers available. The times of execution are also compared. They should only be taken as rough comparison since PHREEQC is more powerful, for example it also computes the state of oxidation of the solution. Moreover Eigen, the modern linear algebra library used in our code [45], takes full advantage of the features of the CPU. However, the large factor (x10–x15) in favor of our code shows that this method is very efficient, the main reason being that it very rarely fails. All experiments were run on a laptop (Intel i7-3612QM CPU) and the numbers of execution were adjusted so

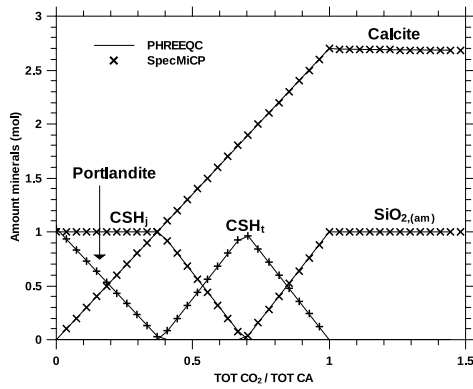
that the total time exceeds 2 min. The two following examples highlight the main features of the algorithm described in Sections 3 and 4.

5.1. Carbonation of a simplified cement paste

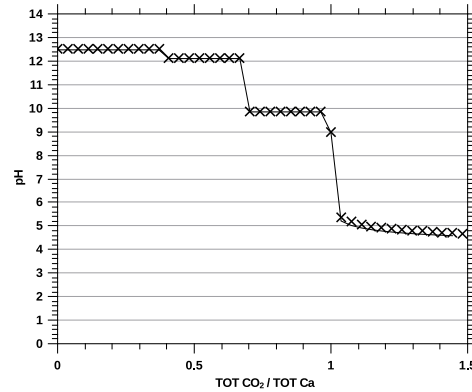
Carbonation is the ingress of carbon dioxide into the porous cement paste. It is a major damaging process for cementitious materials [4,9]. The main phases in a healthy cement paste are Portlandite (CH) and a C–S–H gel. These minerals are unstable at the low pH induced by the carbonation and will dissolve. Calcite (CC) will precipitate. The first numerical experiment consists in dissolving 0.7mol (159.6g) of C<sub>3</sub>S and 0.3mol (51.7g) of C<sub>2</sub>S in 0.106g of water. It corresponds to a water to cement ratio (w/c) of 0.5. Complete hydration is assumed. The remaining amount of water after hydration is 0.050g. 0.1mol of H<sub>2</sub>CO<sub>3</sub> is added at each timestep until a total of 4.0mol is reached. This is a simple system with only 5 components: H<sub>2</sub>O, HO<sup>-</sup>, Ca<sup>2+</sup>, SiO(OH)<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>. The solid phases included in the computations are: Portlandite,

calcite, silica gel and two stoichiometries of C–S–H gel: Ca/Si = 1.67 (C–S–H<sub>j</sub>), and Ca/Si = 0.83 (C–S–H<sub>t</sub>).

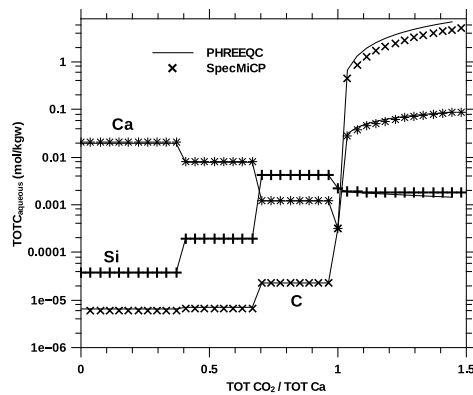
Results are presented in Fig. 1. The abscissa (TOT CO<sub>2</sub>/TOT Ca) represents the ratio of the total amount of carbon dioxide added in the system to the buffering capacity of the system. The buffering capacity is governed by the total amount of calcite that can be formed. When this ratio is bigger than one, the cement paste is entirely carbonated. The answers obtained are very similar with those given by PHREEQC. The only visible differences are in the total concentration of aqueous species. These differences disappear when more water are added in the system. Therefore, they are probably due to discrepancies in the ionic strength model. Nevertheless, these differences are smaller than the uncertainties on the parameters [1]. Moreover, when the buffering capacity is exceeded, the simulation is non-physical since the concentration of carbon dioxide in the aqueous solution is very high, and it will probably evaporate to the atmosphere. However, this is still a well-defined mathematical problem and the software should be able to provide an answer.



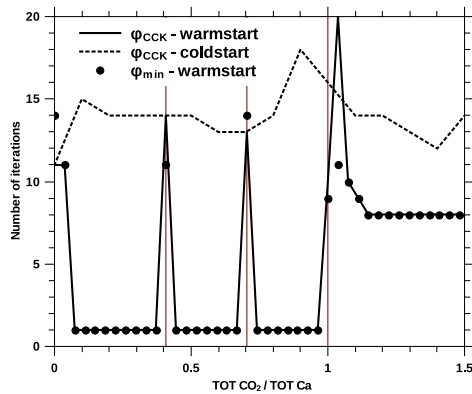
(a) Comparison with PHREEQC - minerals



(b) Comparison with PHREEQC - pH



(c) Comparison with PHREEQC - total concentration of aqueous species



(d) Number of iterations - comparison between coldstart/warmstart and C-functions. Vertical lines indicate a change in the active set of minerals. More iterations are expected at these points.

Fig. 1. Thermodynamic modeling of the carbonation of a CaO–SiO<sub>2</sub>–H<sub>2</sub>O system.

Typically our code solves the problem in less than 4ms. PHREEQC takes 71 to run the same simulation. This factor of 17 may be partially explained by the fact that warnings indicate that PHREEQC must restart the simulation at 3 points whereas our code solves directly each sub-problem. Failing is very expensive since the failure must be detected, which means many iterations for nothing, and the problem restarted from scratch.

Eqs. (8) and (9) form almost a linear system in the mass of water and the mole numbers of solid phases, when the Gibbs degree of freedom is zero, i.e. when the saturation conditions of the solid phases dictate the composition of the aqueous solution. Therefore, when the solid assemblage is not changed and there are 3 solid phases, and the solution of the previous step is available, the problem is linear and should be solved in only one step. In Fig. 1d we can observe that this is the case in our code. It mitigates the effect of the fixed-activity during a Newton iteration.

Table 2 and Fig. 1d give insight into the choice of the C-function. The three reformulations perform very similarly with a slight advantage for the  $\phi_{min}$  reformulation. We note that the lower number of variables in the linear system of the min reformulation is not significant and most of the difference may be attributed to the fewer iterations. However, when the solution of the previous step is not used as initial guess, the  $\phi_{min}$  reformulation is only able to provide a solution for the first few points but fail afterwards while the two other methods succeed.

What happens if the water to cement ratio is reduced? Our tests show that our solver is able to solve the problem until  $w/c \leq 0.3$ , which consumes all the water in the system. For lower  $w/c$  a model taking into account the relative humidity will be necessary [48]. As the water to cement ratio is reduced, the convergence is slower for the first few points, especially for the min formulation.

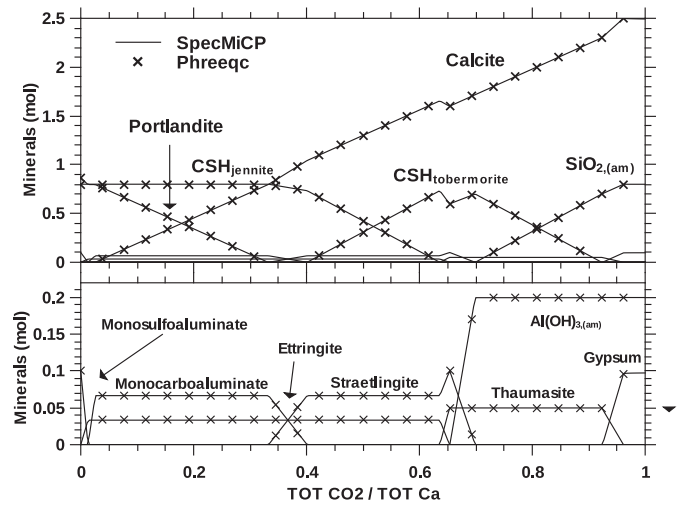
### 5.2. Simulation with aluminum and sulfates

A cement paste also contains aluminum and sulfate phases [9,31]. In this section we consider the carbonation of a cement paste made from the complete hydration of the following initial compounds:  $C_3S$  (0.6),  $C_2S$  (0.2),  $C_3A$  (0.1) and gypsum (0.1); the water to cement ratio is 0.8. The solid phases taken into account are: Portlandite, C–S–H<sub>j</sub>, C–S–H<sub>t</sub>, amorphous silica gel, calcite, amorphous aluminum oxide gel, monosulfoaluminate, monocarboaluminate, ettringite, gypsum, thaumasite, and hemicarboaluminate, and tricarboaluminate. The two last phases are not expected to precipitate and are only included to complicate the problem. Their compositions are described in Appendix A.

This system is more difficult since the algorithm has to choose between more minerals  $N_{min} = 14$  and some of them may have large stoichiometric coefficients. The high  $w/c$  ratio was chosen to simulate complete hydration and to obtain convergence with the  $\phi_{min}$  reformulation and PHREEQC. A lower  $w/c$  may be chosen without difficulty for the penalized Fischer–Burmeister reformulation. The evolution of the phases with the addition of carbonic acid is presented in Fig. 2. Compared to the previous simulation, the same trend is observed although some perturbations are visible due to the additional component. We

**Table 2**  
Thermodynamic modeling of the carbonation of a CaO–SiO<sub>2</sub>–H<sub>2</sub>O system – comparison of the C-function.

	Number of iterations		CPU time (ms)	
$\phi_{CCK}$	5.09		3.52	
$\phi_{CCK}$ coldstart	16.88	+232%	9.82	+179%
$\phi_{FB}$	5.17	+1.5%	3.55	<1%
$\phi_{FB}$ coldstart	16.93	+233%	10.1	+187%
$\phi_{min}$	4.58	–10%	3.29	–6.5%
$\phi_{min}$ coldstart	Failure			
PHREEQC			71	x19



**Fig. 2.** Carbonation of the cement paste with aluminum. The bottom layer is a magnification of the top layer over the phases that contain aluminum and sulfate ions.

note that the Gibbs phase rule is respected even though we didn't specify it explicitly in the algorithm. The consistent thermodynamic data are sufficient to enforce it with this formulation of the problem. The empirical rules as explained by Bethke [7] are not necessary here.

Results of simulations are presented in Table 3. The most efficient strategy is to use the penalized Fischer–Burmeister function. It is always successful and performs quite well. For comparison, PHREEQC is at least fifteen times slower to solve the same problem, and has to restart the computation many times. The number of factorizations is close to the number of iterations which means that the descent conditions (Eq. (19)) are almost always satisfied, allowing good performance. Some failures are detected if only one factorization per step is allowed. Therefore, the strategy adopted is working.

$\phi_{min}$  and  $\phi_{FB}$  fail in most cases, due to divergence, non-physical answers or stationary points. To allow convergence a restart strategy

**Table 3**

Carbonation of a cement paste with aluminum.  $\Delta H_2CO_3$  represents the increment of  $H_2CO_3$  added in the system at each step until a total of 2.5. mol.

$\Delta H_2CO_3$ (mol)	Method	Iterations	Factorizations	CPU time (ms)	Time per step (ms)	
0.1	$\phi_{CCK}$	Success	6.3	6.92 (+9.8%)	7.4	0.28
	$\phi_{CCK}$ coldstart	Success	34.8	43.5 (+20.0%)	38.2	1.47
	$\phi_{min}, \phi_{FB}$	Failure				
	$\phi_{min}$	Success	20.57	28.61 (+39.1%)	15.7	0.6
	$\phi_{CCK}$ restart					
	$\phi_{FB}-\phi_{CCK}$ restart	Success	9.61	12.09 (+25.8%)	10.5	0.4
0.05	PHREEQC			117.0	4.5	
	$\phi_{CCK}$	Success	4.45	4.98 (+11.9%)	9.8	0.19
	$\phi_{min}, \phi_{FB}$	Failure				
	$\phi_{min}$	Success	13.5	17.9 (+32.5%)	31.9	0.63
	$\phi_{CCK}$ restart					
	$\phi_{FB}-\phi_{CCK}$ restart	Success	5.66	6.98 (+23.3%)	13.12	0.26
0.01	PHREEQC			226	4.43	
	$\phi_{CCK}$	Success	2.04	2.28 (+11.8%)	22.7	0.09
	$\phi_{min}, \phi_{FB}$	Failure				
	$\phi_{min}$	Failure				
	$\phi_{CCK}$ restart					
	$\phi_{FB}-\phi_{CCK}$ restart	Success	2.23	2.66 (+19.3%)	26.3	0.10
0.005	PHREEQC			984	3.92	
	$\phi_{CCK}$	Success	1.46	1.54 (+5.4%)	32.6	0.07
0.001	$\phi_{CCK}$	Success	1.14	1.17 (+2.6%)	136	0.05

was designed. If the computation fails, it is restarted using a corrected starting point and the  $\phi_{CCK}$  reformulation. This strategy allows convergence for large steps almost everywhere. The effect of the reduction of the number of variables provided by the  $\phi_{min}$  reformulation is not visible since it fails many times. It is better to use robust algorithms even if they are slower in theory. The main problem with the  $\phi_{min}$  reformulation is that it is more likely to be attracted by a stationary point and even the mitigation strategies described in Section 4 are not sufficient to avoid the problem. Although these strategies can be tweaked to solve each problem individually, we did not find a single strategy which provides convergence for all problems.

The ratio (number of factorizations)/(number of iterations) is a measure of how well a computation is going. It is very high with the  $\phi_{FB}$  and  $\phi_{min}$  reformulations. In fact, this ratio is very high (almost  $\times 4$ ) for only a few points where the algorithm is failing. Early detection of this anomaly may be possible but it is more rewarding to directly use the  $\phi_{CCK}$  reformulation. The penalized Fischer–Burmeister C-function is always able to get the correct answer. In fact, it was still converging for  $w/c = 0.5$ , which left almost no water in the system in the first steps. In every case, our implementation outperforms PHREEQC, therefore the higher number of variables and the work required for the reformulation are not a major obstacle.

We can also observe that our algorithm scales much better than PHREEQC with the decrease of the step increment. This is important to keep in mind for reactive transport. In cement paste, the mean pore size is small and as a result effective transport properties (diffusion coefficient, permeability, ...) are small [49]. In consequence, increments will probably be small to respect both the transport and the chemical reaction kinetics. Therefore the speciation solver will become the limiting step. A non-splitting scheme may be better in terms of performance since it allows longer timesteps, thus higher increments [12,22]. An advantage of the C-function reformulation for reactive transport is that the basis is constant through the computation, and only composed of aqueous species. Therefore, the transport basis and chemistry basis can be chosen to be the same. It removes the need of the procedure described by Huet et al. [5] to adapt the output of each module.

## 6. Conclusion

The present work is dedicated to the development of a reliable, robust and efficient speciation solver. Using the mathematical theories of mixed complementary problems and semismooth Newton methods, we propose an algorithm which has a good performance for cement paste applications, when the water content is low and the non-ideality important. The particularity of the algorithm is to find the active set of minerals without using the common trial and error procedure. The strong theoretical properties of the algorithm offer practical advantages. The extra work required in the semismooth method is more than compensated by the efficiency and the robustness of the method. The reformulation using the penalized Fischer–Burmeister function provides the best performance. This fact has been verified on the two examples presented in this article and many more we have run. The results are consistent with PHREEQC but our implementation is at least ten times faster. We note that processes such as hydration or carbonation are nonequilibrium processes and their modeling requires the study of the kinetics of dissolution and precipitation of minerals. Future work will include the extension of the algorithm to take into account these kinetics, the presence of a gas phase, as well as the construction of a reactive transport framework based upon this speciation solver.

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## Appendix A. Thermodynamic data

The simulations use the Cemdata '07 [31,50] database in addition to the NAGRA/PSI database [24]. The main solid phases are listed below. The equilibrium constants are computed with the following basis:  $H_2O$ ,  $HO^-$ ,  $Ca^{2+}$ ,  $SiO(OH)_3^-$ ,  $CO_3^{2-}$ ,  $Al(OH)_4^-$ , and  $SO_4^{2-}$ . This is the basis used in the simulations. The last two species are only included for the second example.

Label	Composition	$\log_{10}K$	reference
Portlandite	$Ca(OH)_2$	−5.1995	[24]
CSH, jennite	$C_{1.67}SH_{2.1}$	−13.17	[31]
CSH, tobermorite	$C_{0.83}SH_{1.3}$	−8.0	[31]
SiO <sub>2</sub> , (am)	SiO <sub>2</sub>	1.476	[31]
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	−44.9	[31,50]
Tricarboaluminate	$Ca_6Al_2(CO_3)_3(OH)_{12} \cdot 26H_2O$	−46.5	[31,50]
Thaumasite	$Ca_6(SiO_3)_2(SO_4)_2(CO_3)_2 \cdot 30H_2O$	−49.4	[51]
Monosulfoaluminate	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$	−29.6	[31,50]
Monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12} \cdot 5H_2O$	−31.47	[31,50]
Hemicarboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13} \cdot 5.5H_2O$	−29.13	[31,50]
Straetlingite	$Ca_2Al_2SiO_2(OH)_{10} \cdot 3H_2O$	−19.70	[31,50]
Al(OH) <sub>3</sub> , (am)	Al(OH) <sub>3</sub>	0.24	[31]
Gypsum	$CaSO_4 \cdot 2H_2O$	−4.5809	[24]
Calcite	CaCO <sub>3</sub>	1.8490	[24]

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