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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.

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. Kräutle [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. Kräutle [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:

$$A_j \rightleftharpoons \nu_{jw}\mathrm{H_2O}_l + \sum_{i=2}^{N_c} \nu_{ji} A_i, \quad j = 1, \dots, N_r, \tag{1}$$

where A_k denotes the label of species k, and ν_{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

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

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 γ_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]

$$\gamma_k = -\frac{A z_k^2 \sqrt{I}}{1 + B\dot{a}_k\sqrt{I}} + \dot{b}_k I, \qquad k = 2, \dots, N_c, N_c + 1, \dots, N_c + N_r, \tag{3}$$

where I is the ionic strength,

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

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 $T = 25$ °C [7]) and $\dot{a}_k$ and $\dot{b}_k$ 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

$$A_l \rightleftharpoons \nu_{lw}H_2O_l + \sum_{i=2}^{N_c} \nu_{li} A_i. \tag{5}$$

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

$$\mathrm{SI}_l = \frac{\prod_{i=2}^{N_c} a_i^{\nu_{li}}}{K_m}, \tag{6}$$

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. $\mathrm{SI}_l < 1$ and $n_l > 0$ the mineral is undersaturated and will dissolve.
2. $\mathrm{SI}_l < 1$ and $n_l = 0$ the mineral is undersaturated and will not precipitate.
3. $\mathrm{SI}_l > 1$ the mineral is oversaturated and will precipitate.
4. $\mathrm{SI}_l = 1$ 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]

$$n_l \geq 0, \quad -\log(\mathrm{SI}_l) \geq 0, \quad \text{and} \quad -n_l \log(\mathrm{SI}_l) = 0. \tag{7}$$

This condition states that either the mineral is present and at equilibrium ($n_l \geq 0$, and $\mathrm{SI}_l = 1$) or the mineral is not present, thus undersaturated ($n_l = 0$, and $\mathrm{SI}_l \leq 1$). 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. $\Omega = \log(\mathrm{SI}_l)$ 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

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

where $\overline{m}_w$ is the mass of water ($\mathrm{kg_w}$) and M_w is the molar mass of water. T_w is the so-called *Total concentration* (in mol). An explanation of the