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A model for calcium carbonate neutralization in the presence of armoring

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ABSTRACT

In this paper we present a mathematical model for the reaction between calcium carbonate ($CaCO_3$) and a solution containing sulfuric acid (H_2SO_4). We assume that Ca^{2+} ions (liberated on the reaction surface) react with SO_4^{2-} ions to form solid gypsum crystals ($CaSO_4$) which, in turn, may accumulate on the reaction surface, hindering the neutralizing process (armoring). We suppose that neutralization is governed by a first order reaction, with the reaction rate depending on the superficial density of solid $CaSO_4$. We prove that the problem is multiscale in time and study the problem in fast time scale (order of hours), showing numerical and analytical results. In particular we determine the conditions that guarantee complete neutralization.

1. Introduction

The problem of acid mine drainage (AMD) treatment is certainly one of the most challenging and critical in mining industry, since it encompasses a series of complex phenomena that may lead to dramatic pollution problems, [1]. Among the various processes occurring in a treatment plant, neutralization is surely one of the most significant, since it allows to buffer the waste effluent to a pH which is not environmentally-threatening. Limestone (i.e. $CaCO_3$) is definitely the least expensive neutralizing agent and it is widely used for this purpose (especially in pulverized form), even if some concerns are expressed about its relatively slow reaction rates and possible coating (armoring) of the limestone surface by solid precipitates. A predictive model that evaluates and quantifies the efficiency of a neutralizing system (accounting for phenomena like precipitation and armoring) is undoubtedly a useful tool for designing neutralizing devices (e.g. cartridges).

To this aim, in the last few years, we have developed a series of mathematical models that describe the evolution of a neutralizing system and where the neutralizing agent is calcium carbonate (see [2–4]). These models have been proposed for different geometrical settings and both in static and dynamical regimes. In this paper we propose a mathematical model for the neutralization of a sulfuric acid solution (H_2SO_4) by means of marble ($CaCO_3$). Differently from some previous papers on this topic, here we also take into account the so-called "armoring" phenomenon, i.e. the formation of an insoluble precipitate (calcium sulfate, $CaSO_4$) that settles (because of gravity) on the reacting surface, hindering the neutralization process. The armoring phenomenon is indeed a very challenging one, since it involves many parameters such as solubility

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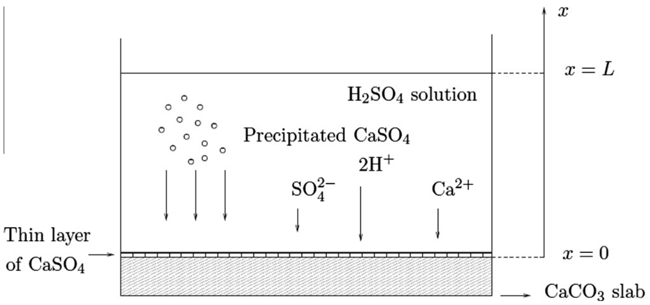

Fig. 1. Sketch of the system.

product constant (K_{ps}), ions diffusivity, chemical environment and interactions between the insoluble formed species. The armoring can be due to many chemical species among which there are iron hydroxides and oxyhydroxides, metal hydroxides in general (Aluminium et al.) and insoluble salts (see [5]). The formation mechanisms are multiple, depending on the precipitating chemical species and environmental conditions and may include different states as gels, colloids et al. After the first crystal/molecule is formed, the species can evolve in different ways, some of which bring to dispersions that do not affect the neutralization process, while others generate a precipitate that coat the other chemical species present inside the system, making them incapable to react. The precipitation times can be various, ranging from seconds to day or even weeks and they mainly depend on ions concentrations, solubility product and on whether the solution is stirred or not. The present work focuses on calcium sulfate ($CaSO_4$) chiefly because of the high concentration of calcium and sulfates that can be found in the acid mine drainage to which the present model is aimed. We stress also that this is the simplest species to model, especially for what concerns the parameters required by the model, that are unavailable for more complex compounds like oxyhydroxides (i.e. lepidocrocite, feroxyhyte, goethite et al.)

The sulfuric acid H_2SO_4 – which is dissociated in SO_4^{2-} and $2H^+$ – reacts with $CaCO_3$ liberating Ca^{2+} ions in the solution. The latter in turn react with available SO_4^{2-} ions to form solid $CaSO_4$ (calcium sulfate). The precipitation rate depends on the solubility product of the calcium ions Ca^{2+} and sulfate ions SO_4^{2-} and in particular on how this product deviates from the equilibrium value K_{ps}.

The problem is proposed in a simple 1-D geometry and in a static setting (see Fig. 1), assuming that the precipitate motion is driven only by gravity whereas the motion of the ions is driven only by diffusion. We suppose that the incoming flux of $2H^+$ and SO_4^{2-} ions at the "top" free surface $x = L$ is proportional to the concentrations of such ions at $x = L$ (Robin boundary condition). We also assume that the only source of Ca^{2+} ions is at $x = 0$ (where they are produced by the reaction between H_2SO_4 and $CaCO_3$).

We suppose that the thickness of the "coating" layer is by far smaller than the other characteristic lengths of the system so that we can neglect the problem of its growth (i.e. a free boundary problem). Further we assume that the consumption of the marble slab occurs on a time scale which is substantially larger than those of the other phenomena and therefore we neglect this phenomenon as well. Finally we suppose that the neutralization reaction rate γ depends on the superficial density $\mathcal{S}$ of precipitated calcium sulfate deposited on the reacting surface (armoring) and we postulate the existence of a threshold beyond which neutralization ceases. In particular we suppose that γ is a decreasing function of $\mathcal{S}$, since an increase of the precipitated $CaSO_4$ on the reacting surface entails less efficiency in the neutralizing process.

We demonstrate that the system is multi-scale in time and space and we see that there exists a "fast" time scale in which all the diffusive phenomena can be safely neglected. This time scale is characterized by the presence of "thin" boundary layers outside which the variables can be considered spatially homogeneous (bulk). We prove that in the bulk the system reduces to a nonlinear system of differential equations whose solution depends on the efficiency of the armoring phenomenon (parameter Υ) and on the rate at which ions H^+ and SO_4^{2-} are provided on the free surface (parameter ω). In particular we study the case in which the solution is slowly stirred.

We solve the problem numerically and we determine the "critical" values for Υ, ω for which armoring/neutralization is activated/inhibited.

2. The physical model

Assume to have a beaker filled with a solution of H_2SO_4 (sulfuric acid) and assume that a slab of $CaCO_3$ (marble) is placed horizontally inside the beaker as depicted in Fig. 1. In a neighborhood of the marble surface the following reaction[1] occurs

$$CaCO_3 + 2H^+ + SO_4^{2-} \rightleftharpoons Ca^{2+} + SO_4^{2-} + H_2O + CO_2. \tag{1}$$

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[1] Sulfuric Acid is written considering its ionic dissociation.