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Mathematical Physics — *Mathematical model for calcium carbonate acid mine drainage reaction: a multiple time scale approach*, by LORENZO FUSI*, ALESSANDRO MONTI, ANGIOLO FARINA and MARIO PRIMICERIO, communicated on 10 May 2013.

ABSTRACT. — In this paper we present a mathematical model for the flow of an acid solution through a reacting porous medium. The solid matrix is supposed to be formed by families of spheres with different radii and the fluid is supposed to saturate the pores. The system is described by the evolution of the overall ion concentration and the radii of the spheres. The structure of the mathematical problem is multi-scale in time and for each time-scale different simplified problems can be obtained. We give some analytical results and display some numerical simulations to show the behavior of the solutions. The main practical application of this model is the flow of acid solution through neutralizing cartridges in which solid particles of $CaCO_3$ are used to neutralize a given flow of an acid mine drainage.

KEY WORDS: Reaction kinetics, multi-scale problem, acid mine drainage, neutralization.

MATHEMATICS SUBJECT CLASSIFICATION: 92E20, 80E30, 76S05.

1. INTRODUCTION

Acid mine drainage (AMD) and Acid rock drainage (ARD) represent a serious environmental hazard all around the world, especially since they can cause long term damages to waterways and biodiversity. AMD is mainly originated by the exposition of sulfide ores, chiefly iron pyrite, to water and oxygen and it usually refers to the generation of acidic streams from abandoned mines (see [15] and [6]).

Once a mine site begins to produce acid mine drainage, it will continue to release acidic waters, even long after the mine plant has ended its activity. For example acid mine drainage continues to emanate from mines in Europe established during the Roman Empire prior to 467 BC, [6]. The consequences of AMD can be tremendous for aquatic life, the first one to come into contact with the acidic outflow. The extinction of entire fish population has been repeatedly reported, but the danger occurs also for plants and animals living along the acid stream, [14]. The impact on human health can also be very high, on account of the AMD capability to leach metals from mine ore, thus making these metals bioavailable. Among the most dangerous leached metals there are lead (toxic,

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poisonous and potentially cancerous), antimony (toxic and poisonous) and cadmium (known carcinogen).

Although the prevention of acid mine drainage formation would be the best option, it is certainly not feasible in the vast majority of the locations where the phenomenon is found. As a consequence, in such cases suitable processes to collect and treat acid waters must be set up, in order to avoid environmental pollution.

Many different options are suitable for AMD remediation purposes, the main being the ones based on chemical reactions and/or the exploitation of biological mechanism to neutralize and remove metals from the solution, [1], [7], [3], [13]. One of the possible approach to the neutralization process involves the use of a basic chemical compound, such as sodium hydroxide, calcium hydroxide or calcium carbonate, [2]. The process basically consists in the addition of a base to the acidic water or in the flow of the acid solution through a basic bulk, in order to raise the pH of the solution. The process triggers the oxidation and precipitation of the dissolved heavy metals as hydroxides too. In this context any carbon carbonate waste is an ideal neutralizing agent since it is cheap, mainly formed by calcium carbonate $CaCO_3$, and it can be particularly effective when available in crushed or pulverized form, because of the large accessible reaction surface, [19]. Potential source of calcium carbonate waste are marble industries (such as the Carrara marble district in Tuscan), paper industries (black liquor), sugar industries, hatcheries and food processing factories (for instance in Europe, approximately $1.5 \cdot 10^5$ Tons of eggshells are sent each year to landfills), limestone and a lot more.

In a previous article [11] we have analyzed the erosion of a marble slab caused by a strongly acidic solution, which, in turn, gradually raises its pH just as there is no H^+ supply from the outside. The present paper is focussed on the neutralization of AMD (deriving from pyrite, FeS_2, waste) during its flow through a porous medium made up of marble powder. The AMD's that we are considering are the result of several chemical reactions which occur between FeS_2, H_2O, oxygen and other compounds. The AMD neutralization process occurs during the flow through a cartridge containing marble dust. We model the cartridge as a porous medium constituted by calcium carbonate spheres. The chemical reactions occurring between the spheres and the acid solution are the following

$$\begin{aligned} &CaCO_{3(s)} + 2H^+ \leftrightarrow Ca^{2+} + H_2O + CO_2 \\ &CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3 \\ &CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3 \\ &CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO^{3-} + OH^- \end{aligned} \tag{1.1}$$

The final effect is a pH increase until an equilibrium value is reached, the equilibrium being function of the chemical and physical environmental parameters (e.g. temperature, pH initial value, CO_2 partial pressure, and so on).

In the sequel we present a model for reactions (1.1) that occur during acid solution flow through cartridges used in experimental tests (see Fig. 1).

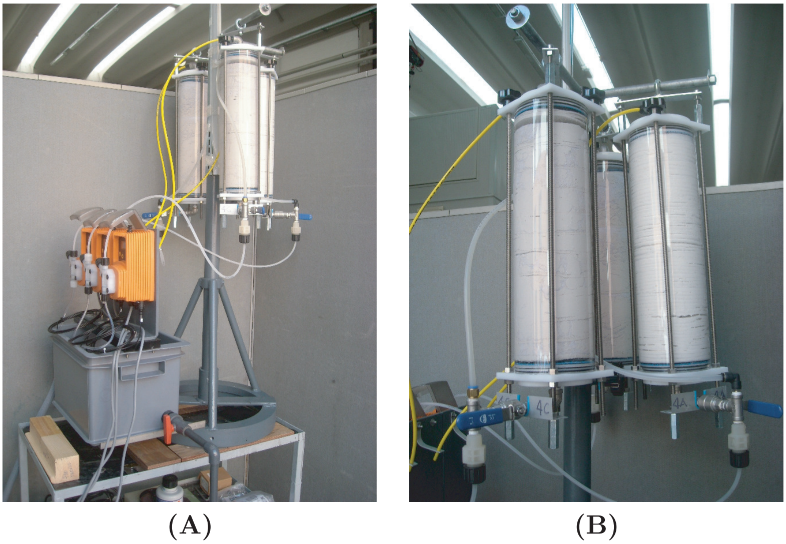
(A) (B)

Figure 1. Experimental cartridge. (**A**) Reactive system overview, the three shown cartridges differ in calcium carbonate/inert fibres ratio. The reactive cartridges works with an acid water upflow. (**B**) The calcium carbonate is in the form of powder, with a granulometric distribution in the range 1–60 micron. The polymeric inert fibers are present in three different forms, high density disks, low density disks and whiskers. Disks are regularly alternated with calcium carbonate, while whiskers are homogeneously distributed in the $CaCO_3$ matrix.

The aim of the model, as well as of the experimental tests, is to give qualitative and quantitative information that can be useful in designing systems of reactive cartridges to be used for treating acid waste-water of mining plants. This study, has been developed within the C.R.E.A. project (Sistema di Cartucce Reattive per gli Effluenti Acidi di Miniera), funded by the Tuscan Regional Government (POR FESR 2007–2013 Activity 1.1, Line A and B), whose goal is improving the performances of the cartridges for mining plants waste water.

The model is developed in the following way. We consider the basic R.E.V., ΔV^* (representing volume element of the cartridge to be modeled), occupied by solid spheres (in case of marble dust cartridge, the spheres diameter ranges between 1 and 60 μm) and by acid water. In the context of mixture theory (see, e.g., [18] and [5]) we define the solid, ϕ_s, and liquid, ϕ_l, volume fractions supposing that at each point liquid and solid phases co-exist. Assuming saturation we write $\phi_l = 1 - \phi_s$. So, to keep notation simple, here and in the sequel $(1 - \phi)$ represents the solid volume fraction and ϕ the porosity, or liquid volume fraction. Once the main physical quantity are defined (such as the concentration of ions H^+ or, equivalently, the solution pH), we write the mass balances for solid skeleton (i.e. for the $CaCO_3$ spheres) and for H^+, obtaining a system of two coupled equations.

The system is studied in a one dimensional setting where all the main variables depend on the longitudinal coordinate (the cartridge is modelled as a cylinder) and on time only. This assumption is reasonable since transport occurs only along the longitudinal direction and diffusion does not play a significant role in the system (see Remark 3).

The dimensionless formulation of the problem (obtained rescaling with the typical experimental data) puts in evidence the existence of three time scales (see section 3): (i) t^*_{reac}, the H^+ reaction characteristic time (the shortest); (ii) t^*_{conv}, the convective characteristic time; and (iii) $t^*_{\mathrm{CaCo}_3}$, the characteristic time for the reduction of the spheres (the longest). We thus adopt a multiple time scale approach, that allows to obtain the solution (within a known accuracy) at each particular time scale.

In particular, focussing on the reaction and transport time scales, we prove that the problem admits an explicit solution which, as physically expected, shows that the CaCO_3 consumption is negligible. The problem in the longest time scale (i.e. the one characterizing the solid depletion) cannot be explicitly solved. We however prove global existence and uniqueness.

Numerical simulations have been developed to validate our model. In particular we have compared the simulations with some simple experiments performed using acid waste waters collected on the field of Abbadia San Salvatore (Mount Amiata, Tuscany), within the context of CREA project. In such experiments some strongly acid AMDs (pH ~ 2) were pumped through the neutralizing cartridge at a fixed rate ($\sim 5\ m/s$), see Fig. 1. The evolution of pH at the outlet was then monitored (along with temperature, salinity, conductivity and other physical parameters) and the efficiency of the cartridge (duration of its neutralizing effect) was assessed. The experiments have shown that the time needed to rise the pH to circumneutral values (pH $\sim$ 5–6) is of the order of 15/30 *sec* and that the cartridge is completely exhausted after approximately one month. Looking at the simulations (Fig. 2, 5, 6) we see that they are in agreement with the experimental results.

2. DEFINITIONS AND BASIC ASSUMPTIONS

The aim of this section is to model the dynamics of the solid-liquid mixture whose constituents are subject to a chemical reaction.

We consider a portion of a porous medium whose volume is[1] ΔV^*. The quantity $\int_{\Delta V^*} \phi(\vec{x}^*, t^*) d^3x^*$ provides the volume of the liquid within ΔV^*. Because of saturation, the volume of the solid contained in ΔV^* is

$$\Delta V_s^* = \int_{\Delta V^*} [1 - \phi(\vec{x}^*, t^*)] d^3x^*.$$

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[1] Throughout this paper the superscript "*" means that the quantity has physical dimension.

If the liquid saturating the pores is an acid solution (e.g. hydrochloric acid), we introduce

$$c^*_{ph} = \frac{\text{number of moles of H}^+ \text{ ions dissolved into the water}}{\text{volume occupied by water} = \Delta V^*_{\mathrm{H_2O}}},$$
$$[c^*_{ph}] = mol/\ell t.$$

The concentration of H^+ ions can be also expressed in terms of pH, where

$$\mathrm{pH} = -\log_{10}\left(\frac{c^*_{ph}}{1\ mol/\ell t}\right). \tag{2.1}$$

We assume that the solid matrix is constituted by $\mathfrak{n}$ families of $CaCO_3$ spheres with radii $r^*_1, r^*_2, \dots, r^*_{\mathfrak{n}}$, uniformly mixed, so that the total solid volume fraction is given by $1 - \phi = \frac{4}{3}\pi \sum_{i=1}^{\mathfrak{n}} r_i^{*3} \mathcal{N}_i^*$, where $\mathcal{N}_i^*$, $i = 1, 2, \dots, \mathfrak{n}$, is the granulometric distribution per unit volume, namely

$$\mathcal{N}_i^* = \text{number of spheres, per unit volume, whose radius is } r_i^*,$$
$$[\mathcal{N}_i^*] = 1/cm^3.$$

We assume[2]:

A1. $\mathcal{N}_i^*$, $i = 1, 2, \dots, \mathfrak{n}$, are given and constant in time. In particular, such an assumption means that the spheres do not compact.

We have

$$\phi = 1 - \frac{4}{3}\pi \sum_{i=1}^{\mathfrak{n}} r_i^{*3} \mathcal{N}_i^*.$$

Of course, the spheres radii are uniform in space at the beginning of the process. But, due to the chemical reaction occurring on the spheres surface, the radii decrease according to the local (and generally non-uniform) concentration of H^+. So, spheres belonging to the same i^{th} family (i.e. whose initial radius is r_i^*), will have, at time t^*, different radius according to their spatial location. In this sense, we write $r_i^* = r_i^*(\vec{x}^*, t^*)$, acknowledging that the index i simply denotes the spheres family (i.e. the initial spheres radius). This fact will be clarified also in Remark 7.

Introducing $\mathcal{N}^* = \sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i^*$, the granulometric fractions

$$\mathcal{N}_i = \frac{\mathcal{N}_i^*}{\mathcal{N}^*}, \quad i = 1, 2, \dots, \mathfrak{n},$$

---

[2] If compactification would be allowed, ϕ could be, in principle, remain unchanged even though r_i, $i = 1, 2, \dots, \mathfrak{n}$, are reducing.

and the dimensionless radii (r^* is a reference radius),

$$r_i = \frac{r_i^*}{r^*}, \quad i = 1, 2, \ldots, \mathfrak{n},$$

we have

$$\phi = 1 - \frac{4}{3}\pi r^{*3}\mathcal{N}^* \sum_{i=1}^{\mathfrak{n}} r_i^3 \mathcal{N}_i. \tag{2.2}$$

Remark 1. *In case* $\mathfrak{n} = 1$ (*i.e. just one family of spheres*), *we have*

$$\phi = 1 - \frac{4}{3}\pi r^{*3}\mathcal{N}^* \quad \Leftrightarrow \quad r^* = \sqrt[3]{\frac{3}{4\pi\mathcal{N}^*}(1-\phi)}. \tag{2.3}$$

Following an Eulerian formalism, the continuity equation for the molar concentration of H^+ is

$$\frac{\partial}{\partial t^*}(c_{ph}^*\phi) = -\nabla^* \cdot (c_{ph}^*\vec{q}^*) - \Gamma^*, \tag{2.4}$$

with:

- $\vec{q}^*$: liquid discharge, i.e. volume of solution passing through the unit surface in the unit time, $[\vec{q}^*] = cm/s$.
- Γ^*: number of moles of H^+ consumed in the unit time per unit volume of the porous medium as an effect of the chemical reaction, $[\Gamma^*] = mol/s\ cm^3$. Assuming a first order kinetics (see [17], [4])

$$\begin{aligned}\Gamma^* &= \gamma^*(\text{total reaction surface per unit volume})(c_{ph}^* - c_{ph,o}^*)_+ \\ &= 4\pi\gamma^*\mathcal{N}^*\Big(\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i r_i^{*2}\Big)(c_{ph}^* - c_{ph,o}^*)_+,\end{aligned}$$

  where γ^* is a constant usually referred as reaction rate $[\gamma^*] = cm/s$, $c_{ph,o}^*$ is the equilibrium concentration (i.e. the concentration at neutralization), and where $(\cdot)_+$ denotes the positive part. In general $c_{ph,o}^*$ depends on the reaction. Here we assume that $c_{ph,o}^*$ corresponds to pH $= 7$, i.e. $c_{ph,o}^* = 10^{-7}\ mol/\ell t$.

Equation (2.4) can be rewritten as

$$\frac{\partial(c\phi)}{\partial t^*} + \nabla^* \cdot (c\vec{q}^*) = -4\pi\gamma^*\mathcal{N}^* r^{*2}\Big(\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i r_i^2\Big)(c-\delta)_+, \tag{2.5}$$

where

$$c = \frac{c^*_{ph}}{c^*_{ph,ref}}, \quad \delta = \frac{c^*_{ph,o}}{c^*_{ph,ref}}, \tag{2.6}$$

with $c^*_{ph,ref}$ reference concentration (to be selected) and r^* is the characteristic radius.

Remark 2. *If only one family is present (namely* $\mathfrak{n} = 1$*), we may express* Γ^* *in terms of* ϕ*. Indeed, from* (2.3)*, we have*

$$\Gamma^* = \gamma^* \sqrt[3]{36\pi\mathcal{N}^*}(1-\phi)^{2/3}(c^*_{ph} - c^*_{ph,o})_+. \tag{2.7}$$

Remark 3. *More generally, in writing* (2.4) *we should take into account also of the* H^+ *Fickian diffusion. However, estimating the Péclet number* $\mathsf{Pe} = L^*q^*/D^*$*, with* D^* *diffusivity of the* H^+ *ions, we find (using typical values, i.e.* $D^* = 10^{-4}$ cm^2/s*, and* $L^* = 40$ cm*,* $q^* = 0.15$ cm/s*, see Table* 1) $1/\mathsf{Pe} = \mathcal{O}(10^{-5})$*. The diffusion can be safely neglected.*

Now we have to write an evolution equation for r_i. To this aim we take into account the stoichiometric coefficients of reaction and introduce:

- $\mathfrak{S}$, number of moles of H^+ that react with one mole of $CaCO_3$ per the unit time (stoichiometric coefficient).
- $\mathfrak{M}^*_{CaCO_3}$, $CaCO_3$ molar mass ($\mathfrak{M}^*_{CaCO_3} \approx 100$ gr/mol).
- $\rho^*_{CaCO_3}$, $CaCO_3$ density (2.7 gr/cm^3).

Each sphere of (dimensionless) radius r_i is exposed to the acid solution whose (dimensionless) molar concentration of H^+ is c. Thus the number of $CaCO_3$ moles that are removed form the surface of a sphere per unit time is $4\pi\mathfrak{S}\gamma^* c^*_{ph,ref} r_i^{*2}(c-\delta)$. The corresponding reduction in volume (per unit time) is

$$4\pi \frac{\mathfrak{M}^*_{CaCO_3}}{\rho^*_{CaCO_3}} \mathfrak{S}\gamma^* c^*_{ph,ref} r_i^{*2}(c-\delta)_+.$$

Hence the rate at which r_i decreases is given by

$$\frac{\partial r_i}{\partial t^*} = -\frac{\mathfrak{M}^*_{CaCO_3}}{r^*\rho^*_{CaCO_3}} \mathfrak{S}\gamma^* c^*_{ph,ref}(c-\delta)_+. \tag{2.8}$$

Remark 4. *When* $\mathfrak{n} = 1$*, exploiting* (2.7) *we may write explicitly the variation in time of* ϕ

$$\frac{\partial \phi}{\partial t^*} = \mathfrak{S} c^*_{ph,ref} \frac{\mathfrak{M}^*_{CaCO_3}}{\rho^*_{CaCO_3}} (\gamma^* \sqrt[3]{36\pi\mathcal{N}^*})(1-\phi)^{2/3}(c-\delta)_+. \tag{2.9}$$

To close the model we assume $\vec{q}^* = \vec{q}_o^*$ uniform and constant. This hypothesis can be relaxed, for instance, when the inlet and outlet pressure are prescribed as described in the following

REMARK 5. *When pressure at the boundary of the system is given (i.e. in case of pressure driven flow), we may link $\vec{q}^*$ to the fluid pressure P^* by means of an empiric law (see e.g.* [9], [10], [8]). *For instance, considering Darcy's law*

$$\vec{q}^* = -\frac{K^*(\phi)}{\mu^*}\nabla^* P^*,$$

with K^* being the medium permeability and μ^* the fluid viscosity, we get

$$\frac{\partial(\rho_l^*\phi)}{\partial t^*} - \nabla^* \cdot \Big(\frac{\rho_l^* K^*(\phi)}{\mu^*}\nabla^* P^*\Big) = 0,$$

to which we must add the boundary conditions: $P^*|_{inlet} = P^*_{in}$, and $P^*|_{outlet} = P^*_{out}$.

3. A ONE-DIMENSIONAL CASE

We consider a cylinder whose length is L^*. We assume azimuthal symmetry and that there is no dependence on the radial coordinate of the cylinder. The axial coordinate is denoted by x^*. The flow occurs along x^*, so that $\vec{q}^* = q_o^*\vec{e}_x$, where q_o^* is the given inlet discharge (constant in time and space). We introduce $x = \dfrac{x^*}{L^*}$, $t = \dfrac{t^*}{t^*_{ref}}$, with t^*_{ref} reference time (still to be selected). Next we set $c^*_{ph,ref} = c^*_A$, where c^*_A is the supremum of the inlet H^+ concentration $c^*_{ph,in}$, namely

$$c^*_A = \sup_{t\geq 0} c^*_{ph,in}(t). \tag{3.1}$$

This means that the reference concentration is taken as the one we have at the inlet corresponding to the lowest pH. In particular, we take

$$c^*_A = 10^{-2}\ mol/\ell t, \quad \Leftrightarrow \quad \mathrm{pH}_A = -\log_{10}\Big(\frac{c^*_A}{1\ mol/\ell t}\Big) = 2,$$

i.e. a strongly acid solution. Recalling (2.1), we also have $c = 10^{2-\mathrm{pH}}$.

We also define the following quantities:

- $t^*_{conv} = \dfrac{L^*}{q_o^*}$, characteristic convective time.
- $t^*_{\mathrm{CaCO_3}} = \dfrac{\rho^*_{\mathrm{CaCO_3}} r^*}{\mathfrak{S} c^*_A \mathfrak{M}^*_{\mathrm{CaCO_3}} \gamma^*}$, characteristic time for the $CaCO_3$ consumption (when the solution is strongly acid).
- $t^*_{reac} = (4\pi\gamma^*\mathcal{N}^* r^{*2})^{-1}$, characteristic reaction time, namely the H^+ reaction time.

The continuity equations (2.5) and the consumption rate equation (2.8) can be rewritten as follows

$$
(3.2)\qquad \begin{cases} \dfrac{1}{t^*_{ref}}\dfrac{\partial(c\phi)}{\partial t}+\dfrac{1}{t^*_{conv}}\dfrac{\partial(c)}{\partial x}=-\dfrac{1}{t^*_{reac}}\Big(\displaystyle\sum_{i=1}^{\mathfrak{n}}\mathcal{N}_i r_i^2\Big)(c-\delta)_+, & \mathrm{H}^+ \text{ ions},\\[2ex] \dfrac{1}{t^*_{ref}}\dfrac{\partial r_i}{\partial t}=-\dfrac{1}{t^*_{\mathrm{CaCO_3}}}(c-\delta)_+, \quad i=1,2,\dots,\mathfrak{n}, & \mathrm{CaCO_3}, \end{cases}
$$

with ϕ given by (2.2).

System (3.2) has to be supplemented with two boundary conditions: one for the flow $q|_{x=0}=1$, and one for the H^+ concentration, i.e. $c|_{x=0}=c_{in}(t)$. Of course, by definition (3.1), c^*_{in} does not exceed the reference concentration (the inlet pH is always not smaller than pH_A), so that $0<c_{in}(t)\le 1$. We also assume a compatibility condition: $c_o(0)=c_{in}(0)$, where $c_o(x)$ denotes the initial (dimensionless) concentration

$$
(3.3)\qquad c(x,0)=c_o(x).
$$

Concerning δ, from $(2.6)_2$, we get $\delta=10^{-5}$, because, as mentioned, $c^*_{ph,o}=10^{-7}\ mol/\ell t$.

We define

$$
(3.4)\qquad \theta=\frac{t^*_{conv}}{t^*_{\mathrm{CaCO_3}}},\quad \text{and}\quad \varepsilon=\frac{t^*_{reac}}{t^*_{\mathrm{CaCO_3}}}.
$$

Concerning the cartridges used in the experimental tests (see Fig. 1 and Table 1 we have

$$
(3.5)\qquad t^*_{reac}\sim 10\ s,\quad t^*_{conv}\sim 10^2\ s,\quad t^*_{\mathrm{CaCO_3}}\sim 10^4\ s,
$$

so that

$$
(3.6)\qquad \theta\sim 10^{-2},\quad \varepsilon\sim 10^{-3},
$$

and

$$
\hat{\theta}=\frac{\theta}{\varepsilon}\sim 10.
$$

We thus write

$$
(3.7)\qquad \theta=\hat{\theta}\varepsilon,\quad \text{with } \hat{\theta}=\mathcal{O}(1).
$$

Table 1. Typical values of the parameters.

L^*	q_o^*	$\mathfrak{S}$	$\mathcal{N}^*$	γ^*
40 *cm*	0.15 *cm*/*s*	1	$10^9\ cm^{-3}$	$2\cdot 10^{-5}\ cm/s$

REMARK 6. *We notice that the value of* $\mathcal{N}^*$ *in Table* 1 *has been obtained through granulometric analysis on the marble powder contained in the cartridge, whereas the rate constant* γ *has been determined through an experimental procedure described in* [12]. *Both experiments have been performed within the context of CREA project.*

3.1. Two time scales approach

We select the consumption characteristic time $t^*_{\mathrm{CaCO_3}}$ as reference time setting $t^*_{ref} = t^*_{\mathrm{CaCO_3}}$. We indeed are interested in analyzing the lifetime of the cartridge. Hence, because of (3.4) and (3.7), system (3.2) can be rewritten as

$$
(3.8) \qquad \begin{cases} \dfrac{\partial(c\phi)}{\partial t} + \dfrac{1}{\hat{\theta}\varepsilon}\dfrac{\partial(c)}{\partial x} = -\dfrac{1}{\varepsilon}\Big(\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i r_i^2\Big)(c-\delta)_+, & \mathrm{H}^+ \text{ ions,} \\ \dfrac{\partial r_i}{\partial t} = -(c-\delta)_+, \quad i = 1, 2, \ldots, \mathfrak{n}, & \mathrm{CaCO_3} \text{ spheres,} \end{cases}
$$

with ϕ given in terms of the r_i's by formula (2.2).

The system possess two natural time scales. The slower, represented by t, is the one of the $\mathrm{CaCO_3}$ spheres consumption (in presence of a strongly acid solution). Then we have the fast time scale (the reaction time scale) given by

$$
(3.9) \qquad \tau = \frac{t}{\varepsilon}.
$$

In such a time scale $\tau = \mathcal{O}(1)$ implies $t = \mathcal{O}(\varepsilon)$, and $t = \mathcal{O}(1)$ implies $\tau = \mathcal{O}(\varepsilon^{-1})$. Actually, there is also the convective time scale θ which can be considered simply multiplying the time scale τ by a factor $\hat{\theta}$.

Next, we look for c, r_i, ϕ, and q, of the form $c(x,t) = C(x, t/\varepsilon, t)$, $r_i(x,t) = R_i(x, t/\varepsilon, t)$, $i = 1, 2 \ldots \mathfrak{n}$ and $\phi = \Phi(x, t/\varepsilon, t)$. Thus, because of (3.9), we have $\dfrac{d}{dt} = \dfrac{\partial}{\partial t} + \dfrac{1}{\varepsilon}\dfrac{\partial}{\partial \tau}$.

Concerning the data, we assume:

A2. $c_{in} = c_{in}(t)$, i.e. the inlet H^+ concentration does not vary in time intervals whose amplitude is $\mathcal{O}(\varepsilon)$.

We then introduce the asymptotic expansion for the unknowns C, R_i

$$
(3.10) \qquad f = f^{(0)} + \varepsilon f^{(1)} + \varepsilon^2 f^{(2)} + \cdots.
$$

Inserting the above expansions in the dimensionless system (3.8), we obtain initial-boundary value problems at successive order of ε. Here we consider only the leading order (i.e. the zero order), neglecting convergence issues and $\mathcal{O}(\varepsilon)$ corrections as well.

3.1.1. Stationary solution. Let us go back to problem (3.8). First of all we observe that, because of assumption **A1** and (2.2), $\phi = 1$ entails $r_i = 0$, $i = 1, 2 \dots \mathfrak{n}$. So, if $\phi(x,t)$ is analytic, then for every $x \in [0,1]$, $\dfrac{\partial^n \phi}{\partial t^n} = 0$, when $\phi = 1$, $\forall n \in \mathbb{N}$. This means that if at some point $\bar{x}$ and at some time $\bar{t}$ we have $\phi(\bar{x}, \bar{t}) = 1$, then $\phi(\bar{x}, t) = 1$ for all $t \geq \bar{t}$. Once the solid fraction has disappeared, it can never be formed again!

The stationary solution of problem (3.8) is given $q = 1$, and by the solution of

$$\frac{\partial c}{\partial x} = 0, \quad c(0) = c_{in}, \tag{3.11}$$

that is $c_\infty(x) = c_{in} > 1$, and $\phi_\infty(x) = 1$ (spheres completely consumed). Two different situations may arise:

(i) $\phi = 1$ is reached in a finite time.
(ii) $\phi = 1$ is reached in an infinite time.

Suppose that $\phi|_{x=0}$ becomes 1 in a finite time $\hat{t}$ at $x = 0$. Then, from $(3.8)_2$, we can introduce $\hat{t}_i$, $i = 1, 2, \dots, \mathfrak{n}$, representing the time at which the particles of radius r_i disappear at location $x = 0$. We have

$$r_i(0) - \int_0^{\hat{t}_i} (c_{in}(t) - \delta)_+ \, dt = 0,$$

so that

$$\hat{t} = \max_{i=1,2,\dots,\mathfrak{n}} \{\hat{t}_i\}.$$

In case $x \in (0,1]$ the time $\hat{t}(x)$ can be found only numerically.

3.2. Zero order approximation

System (3.8) can be rewritten in terms of C

$$\begin{cases} \dfrac{\partial (C\phi)}{\partial t} + \dfrac{1}{\varepsilon} \dfrac{\partial (C\phi)}{\partial \tau} + \dfrac{1}{\hat{\theta}\varepsilon} \dfrac{\partial (C)}{\partial x} = -\dfrac{1}{\varepsilon} \Big(\displaystyle\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i R_i^2 \Big) (C - \delta)_+, \\ \dfrac{\partial R_i}{\partial t} + \dfrac{1}{\varepsilon} \dfrac{\partial R_i}{\partial \tau} = -(C - \delta)_+. \end{cases} \tag{3.12}$$

We use expansion (3.10) into $(3.12)_2$ getting (at the zero order)

$$\frac{\partial R_i^{(0)}}{\partial \tau} = 0, \quad i = 1, 2, \dots, \mathfrak{n}, \quad \Rightarrow \quad R_i^{(0)} = R_i^{(0)}(x,t).$$

Therefore $R_i^{(0)} = r_i^{(0)}(x,t)$ (i.e. no dependence on τ) and

$$\frac{\partial R_i^{(0)}}{\partial t} = \frac{dR_i^{(0)}}{dt}. \tag{3.13}$$

Since

$$\varepsilon \frac{d}{dt} = \varepsilon \frac{\partial}{\partial t} + \frac{\partial}{\partial \tau} \quad \Rightarrow \quad \frac{dR_i^{(0)}}{dt} = \frac{\partial R_i^{(0)}}{\partial t} + \frac{\partial R_i^{(1)}}{\partial \tau}.$$

From the second of (3.12) we have

$$\frac{\partial R_i^{(0)}}{\partial t} + \frac{\partial R_i^{(1)}}{\partial \tau} = -(C^{(0)} - \delta)_+ = \frac{dR_i^{(0)}}{dt}, \tag{3.14}$$

implying

$$\frac{\partial R_i^{(0)}}{\partial t} = -(C^{(0)} - \delta)_+.$$

We notice that (3.13) and (3.14) yield $\dfrac{\partial R_i^{(1)}}{\partial \tau} = 0$. In conclusion we get

$$\begin{cases} \phi^{(0)} \dfrac{\partial C^{(0)}}{\partial \tau} + \dfrac{1}{\hat{\theta}} \dfrac{\partial C^{(0)}}{\partial x} = -\Big(\displaystyle\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i r_i^{(0)2} \Big) (C^{(0)} - \delta)_+, \\ \dfrac{\partial r_i^{(0)}}{\partial t} = -(C^{(0)} - \delta)_+. \end{cases} \tag{3.15}$$

Remark 7. *System* (3.15) *puts in evidence an important property of the spheres radii: they may depend on the location x. Indeed, since* $C^{(0)}$ *depends on x,* $(3.15)_2$ *entails that spheres belonging to the same family* (*i.e. whose initial radius is the same*) *at the same time t may have different radii according to their location. We conclude therefore that* $r_i = r_i(x,t)$, *while* $r_i|_{t=0}$, $i = 1, 2, \ldots, \mathfrak{n}$, *are uniform in x.*

Now, if we neglect the term $1/\hat{\theta}$ (recall $1/\hat{\theta} \sim 4 \cdot 10^{-2}$), the solution of (3.15), when t_o is an "initial" time, is[3]

$$\begin{aligned} C^{(0)}(x, t_o, \tau) = \delta + [C(x, t_o, 0) - \delta] \\ \cdot \exp\left\{ -\left[\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i (r_i^{(0)}(x, t_o))^2 \right] \frac{\tau}{\phi^{(0)}(x, t_o)} \right\}, \quad \tau > 0. \end{aligned} \tag{3.16}$$

---

[3] We remark that (3.16) holds true up to $\tau = \mathcal{O}(1)$.

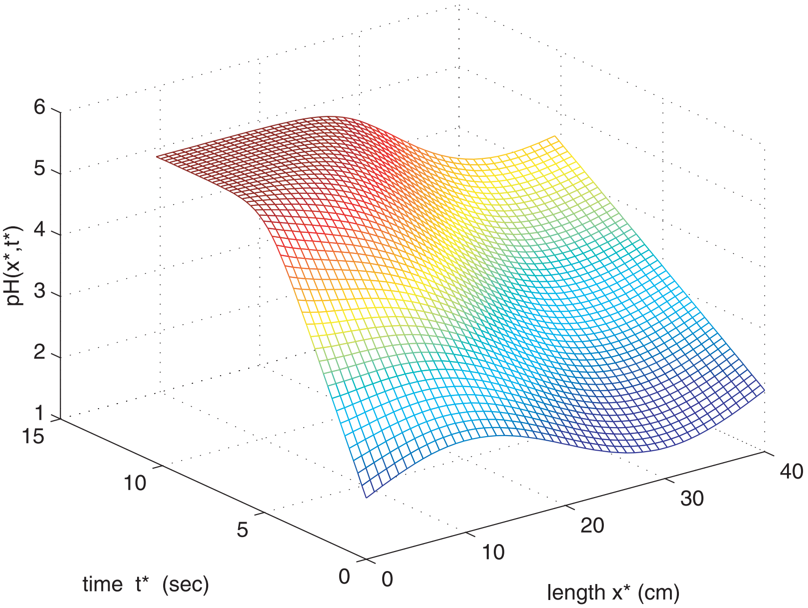

Figure 2. 3D—Plot of the function $pH(x^*, t^*)$ in the fast time scale.

EXAMPLE 1. *In Fig.* 2 *we have shown the space-time behavior of* pH *obtained considering* $\mathrm{n} = 1$, $t_o = 0$ (*so that* $C(x, t_o, 0) = c_o(x)$, *and* $\phi(x, 0) = \phi_o(x)$), *with*

$$c_o(x) = -\log_{10}\left[2 + \frac{1}{2}\sin(2\pi x)\right], \quad \text{and} \quad \phi_o(x) = \frac{1}{20} + \frac{1}{10}x. \tag{3.17}$$

Since $\mathrm{n} = 1$ (3.16) *has the form*

$$C^{(0)}(x, t_o, \tau) = \delta + [C(x, t_o, 0) - \delta] \cdot \exp\left\{-(1 - \phi^{(0)}(x, t_o))^{2/3}\frac{\tau}{\phi^{(0)}(x, t_o)}\right\}, \tag{3.18}$$

or, in terms of pH,

$$\mathrm{pH} = \mathrm{pH}_A - \log_{10}\left\{\delta + [C(x, t_o, 0) - \delta] \cdot \exp\left[-(1 - \phi^{(0)}(x, t_o))^{2/3}\frac{\tau}{\phi^{(0)}(x, t_o)}\right]\right\}.$$

Actually, (3.16) gives the H^+ concentration (within an $\mathcal{O}(\theta)$ accuracy) in the fastest time scale, i.e. the reaction time scale. Accordingly, in such a time scale, the H^+ convection is neglected. Hence, in such approximation, the system is treated as a "closed system", not considering the continuous supply of H^+ ions through the inlet $x = 0$. The dynamics of an isolated (namely closed) system in the long time scale (the $CaCO_3$ consumption time scale) is analyzed in Appendix A.

To take into account the H^+ influx (a fundamental feature of the system), we have to keep the $1/\hat{\theta}$ term in equation $(3.15)_1$, stretching the τ time scale, i.e. considering, for the time variable τ, intervals whose amplitude is $\mathcal{O}(\hat{\theta})$. In such a case $(3.15)_1$ becomes a first order semilinear PDE

$$\hat{\theta}\phi^{(0)}(x,t)\frac{\partial C^{(0)}}{\partial \tau} + \frac{\partial C^{(0)}}{\partial x} = -\hat{\theta}\Big(\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i r_i^{(0)2}\Big)(C^{(0)} - \delta), \tag{3.19}$$

which can be integrated exploiting the method of the characteristics. So we we consider the characteristics originating from the boundary $x = 0$, namely

$$\tau(x) = \zeta + \hat{\theta}\int_0^x \phi^{(0)}(s,t)\,ds, \tag{3.20}$$

and integrate (3.19) along it. Since c_{in} does not vary in the τ scale (recall assumption **A2**), we have

$$C^{(0)}(x,t) = \delta + (c_{in}(t) - \delta)\cdot \exp\left\{-\hat{\theta}\int_0^x \left[\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i (r_i^{(0)}(s,t))^2\right] ds\right\}. \tag{3.21}$$

The above formula shows an interesting feature: $C^{(0)}$ does not depend on τ. The reason is due to the fact that c_{in} does not present significative fluctuations in the short time scale (assumption **A2**). Therefore we replace $C^{(0)}$ with $c^{(0)}$, and remark that $c^{(0)}$ is essentially the solution of the following Cauchy problem

$$\begin{cases} \dfrac{\partial c^{(0)}}{\partial x} = -\hat{\theta}\left[\displaystyle\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i (r_i^{(0)}(x,t))^2\right](c^{(0)} - \delta), & 0 < x < 1, \\ c^{(0)}|_{x=0} = c_{in}(t). \end{cases} \tag{3.22}$$

Of course, in case $c_{in} = c_{in}(t, t/\varepsilon)$, then $C^{(0)}$ would present an explicit dependence on τ, and (3.22) would not hold true.

Exploiting (3.20), we can estimate the "transit time" T_{tr}, i.e. the time needed for the water to reach the outlet, namely

$$T_{tr} = \hat{\theta}\int_0^1 \phi^{(0)}(s,t)\,ds.$$

As expected $T_{tr} = \mathcal{O}(\hat{\theta})$ and depends on the spatial average (evaluated at time t) of the medium porosity.

Actually, referring to Fig. 3, we realize that (3.21) gives the evolution of H^+ concentration in the $\mathcal{D}_{in}$ domain, but we have to consider also the domain $\mathcal{D}_o$,

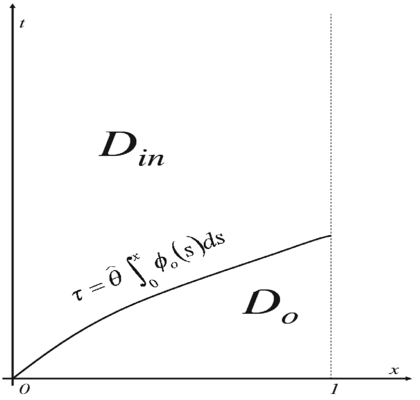

Figure 3. Domains $\mathscr{D}_{in}$ and $\mathscr{D}_o$.

where the characteristics "originate" form the x axis. Therefore, considering $t = 0$, we have

$$
(3.23)\qquad
\begin{aligned}
&\tau = \hat{\theta}\int_{\xi}^{x} \phi_o(s)\,ds,\\
&c^{(0)} = \delta + (c_o(\xi) - \delta)\exp\left\{-\hat{\theta}\int_{\xi}^{x}\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i r_{i,o}^2(s)\,ds\right\},
\end{aligned}
$$

for

$$0 < \xi < 1, \quad \xi < x < 1,$$

where ξ denotes the abscissa of the starting point of the characteristic line, ϕ_o is the initial porosity, and $r_{io} = r_i|_{t=0}$, $i = 1, 2, \ldots, \mathfrak{n}$. Of course, (3.23) gives the evolution in the initial transient (whose length is $\mathcal{O}(\hat{\theta})$), which will be disregarded when considering the overall dynamics.

Example 2. *We consider the initial transient, with* τ *ranging between* 0 *and* $\mathcal{O}(\hat{\theta})$, *i.e.* $0 < t < \hat{\theta}\varepsilon$, *and, as in Example* 1, $\mathfrak{n} = 1$. *Next we assume* $\phi_o(x) = \phi_o = const. \in (0, 1)$. *Since* r *and* ϕ *are linked by* (2.3), *we obtain*

$$
(3.24)\quad c^{(0)} = \begin{cases}
\delta + (c_{in} - \delta)\exp\{-\hat{\theta}(1-\phi_o)^{2/3}x\} \quad \text{for } 0 < x < 1\\
\hat{\theta}\phi_o x < \tau < \hat{\theta}(1 + \phi_o x) \quad \text{for } 0 < x < 1,\ \hat{\theta}\phi_o x < \tau < \hat{\theta}(1 + \phi_o x)\\
\delta + (c_o(\xi) - \delta)\exp\{-\hat{\theta}(1-\phi_o)^{2/3}(x - \xi)\}\\
\qquad \text{for } 0 < \zeta < 1,\ \xi < x < 1\\
0 < \tau < \hat{\theta}\phi_o x \quad \text{for } 0 < \zeta < 1,\ \xi < x < 1,\ 0 < \tau < \hat{\theta}\phi_o x,
\end{cases}
$$

Figure 4 *shows a plot of pH* (*within an* $\mathcal{O}(\varepsilon)$ *tolerance*) *derived from* (3.24), *when* c_o *is given by* $(3.17)_1$, $c_{in} = -\log_{10} 2$ (*constant in time*), *and* $\phi_o = 0.7$.

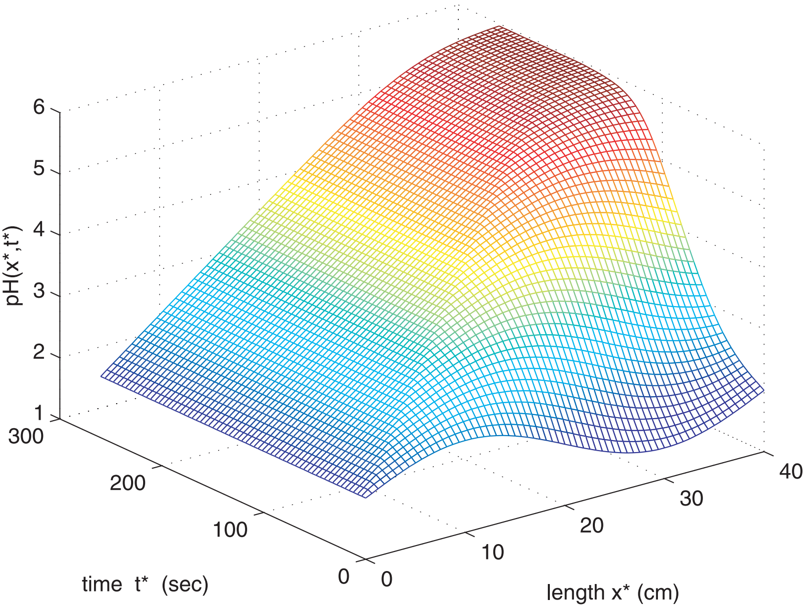

Figure 4. 3D—Plot of the function $pH(x^*, t^*)$ in the intermediate time scale.

We now focus on the $CaCO_3$ consumption time scale (slow). We can solve (formally) equation $(3.15)_2$, getting

$$r_i^{(0)}(x,t) = \left[r_i|_{t=0} - \int_0^t (c^{(0)}(x,\zeta) - \delta)_+ \, d\zeta \right]_+, \quad i = 1, 2, \ldots, \mathfrak{n}. \tag{3.25}$$

where we take the positive part $[\cdot]_+$, since $0 \le r_i$, always. At this point we can plug (3.25) into (3.21) (or vice-versa) to obtain a nonlinear integral equation for c (or for ϕ), i.e.

$$\begin{aligned} c^{(0)}(x,t) &= \delta + (c_{in}(t) - \delta) \\ &\quad \cdot \exp\left\{ -\hat{\theta} \int_0^x \left[\sum_{i=1}^{\mathfrak{n}} \mathcal{N}_i^2 \left(r_{io}(s) - \int_0^t (c^{(0)}(s,\zeta) - \delta)_+ \, d\zeta \right)_+^2 \right] ds \right\}. \end{aligned} \tag{3.26}$$

REMARK 8. *In case* $\mathfrak{n} = 1$, *in place of* (3.26) *we obtain the following integral equation*

$$\begin{aligned} c^{(0)}(x,t) &= \delta + (c_{in}(t) - \delta) \\ &\quad \cdot \exp\left\{ -\hat{\theta} \int_0^x \left[(1 - \phi_o(y))^{1/3} - \frac{1}{3} \int_0^t [c^{(0)}(y,\zeta) - \delta] \, d\zeta \right]^2 dy \right\}. \end{aligned} \tag{3.27}$$

3.3. *Well posedeness of the mathematical problem*

Here and in the sequel we omit the "${}^{(0)}$" to have a lighter notation. Next, we study the case $\mathfrak{n} = 1$, i.e. equation (3.27). Minor changes allow to extend the results we are going to show to the case $\mathfrak{n} > 1$. We consider the following system (easily derivable from $(3.15)_1$ when $\mathfrak{n} = 1$)

$$\begin{cases} \dfrac{\partial c}{\partial x} = -\hat{\theta}(1 - \phi(x,t))^{2/3}(c - \delta), \quad 0 < x < 1,\, 0 < t, \\ \dfrac{\partial \phi}{\partial t} = (1 - \phi)^{2/3}(c - \delta), \quad 0 < x < 1,\, 0 < t, \\ c|_{x=0} = c_{in}(t), \quad \phi|_{t=0} = \phi_o(x), \end{cases} \tag{3.28}$$

from which equation (3.27) derives.

Remark 9. *Equations* $(3.28)_1$ *and* $(3.28)_2$ *admit a traveling wave solution. Indeed, setting* $u = c - \delta$, $\psi = 1 - \phi$, *and looking for a solution of the form*

$$u = u(\xi) \quad \textit{and} \quad \psi = \psi(\xi), \quad \textit{with } \xi = x - \upsilon t,$$

where υ *is the wave speed, we obtain*

$$\begin{cases} u' = -\hat{\theta}\psi^{2/3}u, \\ \upsilon\psi' = \psi^{2/3}u, \end{cases} \Rightarrow \quad (u + \hat{\theta}\upsilon\psi)' = 0, \quad \Rightarrow \quad u + \hat{\theta}\upsilon\psi = const. \tag{3.29}$$

which allows to find υ, *imposing proper "boundary conditions" for* $\xi \to \pm\infty$. *Indeed considering:* $\psi(-\infty) = 0$, (*absence of solid*), $u(-\infty) = 1$, (*strongly acid solution*), *and* $u(+\infty) = 0$, (*negligible* H^+ *concentration*) *and* $\psi(+\infty) = \bar{\psi}$, $0 < \bar{\psi} < 1$, *with, e.g.,* $\bar{\psi} = \int_0^1 (1 - \phi_o(x))\,dx$, *we have*

$$1 = \hat{\theta}\upsilon\bar{\psi}, \quad \Rightarrow \quad \upsilon = \frac{1}{\hat{\theta}\bar{\psi}}.$$

We thus retrieve that the transit time is $\mathcal{O}(\hat{\theta})$.

The equation for ψ *can be found differentiating* $(3.29)_2$, *that is*

$$\psi'' = -\hat{\theta}\psi^{2/3}\psi' + \frac{2}{3}\frac{(\psi')^2}{\psi}.$$

Definition 1. *Given a smooth set of data* $\phi_o(x)$, $c_{in}(t)$ *with* $0 < \phi_o(x) < 1$ *and* $\delta < c_{in}(t) \leq 1$, *a pair of functions* $(c(x,t), \phi(x,t))$ *is called a solution to problem* (3.28) *in the domain* $\Omega_T = [0,1] \times [0,T]$, *for some* $T > 0$, *if the following conditions hold true:*

1. *$c(x,t), \phi(x,t) \in C^1(\Omega_T)$.*
2. *$\delta < c(x,t) \leq 1$, and $0 < \phi(x,t) \leq 1$ for all $(x,t) \in \overline{\Omega}_T$.*
3. *$\phi(x,0) = \phi_o(x)$, and $c(0,t) = c_{in}(t)$, with $\sup_{t\geq 0}|c_{in}(t)| \leq 1$.*
4. *$c(x,t)$ and $\phi(x,t)$ fulfill (3.28) for all $(x,t) \in \overline{\Omega}_T$.*

Introducing

$$u = c - \delta, \quad \text{and} \quad \psi = (1-\phi)^{1/3},$$

system (3.28) can be rewritten as

$$\begin{cases} \dfrac{\partial u}{\partial x} = -\hat{\theta}\psi^2 u, & 0 < x < 1,\, 0 < t, \\ \dfrac{\partial \psi}{\partial t} = -u, & 0 < x < 1,\, 0 < t, \\ u|_{x=0} = u_{in}(t), \quad \psi|_{t=0} = \psi_o(x), \end{cases} \tag{3.30}$$

where $u_{in} = c_{in} - \delta$, and $\psi_o = (1-\phi_o)^{1/3}$. We state the following result.

Theorem 1. *Suppose that $\phi_o(x)$ and $c_{in}(t)$ satisfy the hypotheses of definition 1, and*

$$T < \frac{1}{2\hat{\theta}B\|\psi_o\|}, \tag{3.31}$$

where $B = \sup_{t\geq 0}|u_{in}(t)|$. Then, for $0 < t \leq T$, there exists one and only one solution (u,ψ) in the sense of definition 1.

Proof. Let us define the set Σ_T, whose elements are continuous functions $v(x,t)$ such that $0 \leq v \leq 1-\delta$, and $v(0,t) = u_{in}(t)$. Next, we take $v \in \Sigma_T$, and, exploiting $(3.30)_2$, we set

$$\psi(x,t) = \left[\psi_o(x) - \int_0^t v(x,s)\,ds\right]_+. \tag{3.32}$$

Clearly ψ is $C^1(\Omega_T)$ and fulfills properties 2 and 3 of definition 1. Then, considering $(3.30)_1$, we define

$$u(x,t) = u_{in}(t)\exp\left\{-\hat{\theta}\int_0^x \left[\psi_o(x) - \int_0^t v(x,s)\,ds\right]^2 dx\right\}.$$

Clearly $u \in C^1(\Omega_T)$, and $u \in \Sigma_T$. We thus have a mapping, $u = \mathscr{L}v$, from Σ_T into Σ_T.

We now show that $\mathscr{L}$ is a contraction. Banach's theorem (see [16]) entails the existence of one and only fixed point $v = \mathscr{L}v$. So the pair (v,ψ), with ψ is given by (3.32), is the unique solution to (3.30).

So, if v_1, v_2 both belong to Σ_T, and $u_1 = \mathscr{L}v_1$, $u_2 = \mathscr{L}v_2$, we get

$$\begin{aligned}|u_1 - u_2| &\leq u_{in}(t)\hat{\theta}\left| \int_0^x \left[\left(\psi_o(x) - \int_0^t v_1(x,s)\, ds \right)^2 \right.\right. \\ &\qquad \left.\left. - \left(\psi_o(x) - \int_0^t v_2(x,s)\, ds \right)^2 \right] dx \right| \\ &\leq u_{in}(t)\hat{\theta} \int_0^x \left| 2\psi_o - \int_0^t (v_1(x,s) + v_2(x,s))\, ds \right| dxt \|v_1 - v_2\|.\end{aligned}$$

Hence, if T fulfills (3.31) the theorem is proved. □

So far we have proved the local existence and uniqueness. Actually we can show that this solution exists and is unique for all $T > 0$. Indeed, take a sequence $\{T_n\}_{n\in\mathbb{N}}$ such that

$$T_o = \frac{1}{1+\varepsilon} \frac{1}{2\|\psi_o\| B\hat{\theta}},$$
$$T_1 = \frac{1}{1+\varepsilon} \frac{1}{2\|\psi(x, T_o)\| B\hat{\theta}},$$

up to

$$T_j = \frac{1}{1+\varepsilon} \frac{1}{2\|\psi(x, T_{j-1})\| B\hat{\theta}}.$$

Then in each time interval $[T_{j-1}, T_j]$, by virtue of Theorem 1, there exists a unique solution. Considering now $\sum_{j\geq 0} T_j$, we have

$$\sum_{j\geq 0} T_j = \frac{1}{2\hat{\theta}(1+\varepsilon)B} \left(\sum_{j\geq 0} \frac{1}{\|\psi(x, T_{j-1})\|} \right).$$

But $1/\|\psi(x, T_{j-1})\| \geq 1$, for all j. Hence $\sum_{j\geq 0} T_j = \infty$, and so the solution can be extended for all times. We thus have proved the following results.

THEOREM 2. *Suppose that $\phi_o(x)$ and $c_{in}(t)$ satisfy the hypotheses of definition* 1. *Then for every $T > 0$, there exist, in the sense of definition* 1, *a unique solution (c, ϕ) to problem* (3.28).

3.4. Numerical solution of (3.28)

In this section we present some numerical results for problem (3.28). We write the system in terms of pH,

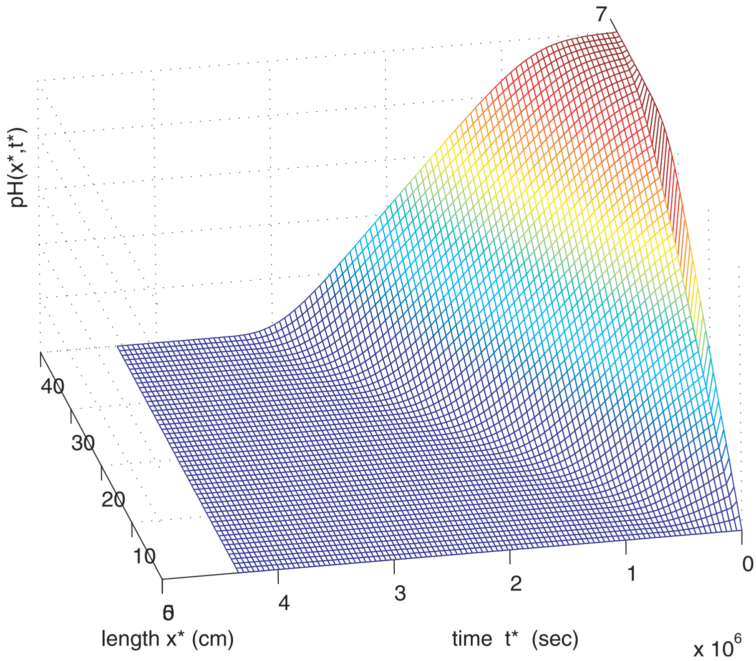

Figure 5. 3D—Plot of the function $pH(x^*, t^*)$ in the slow time scale.

$$\left\{\begin{aligned} \frac{\partial \mathrm{pH}}{\partial x} &= \frac{\hat{\theta}}{\ln 10}(1-\phi)^{2/3}\left(1-10^{\mathrm{pH}-\mathrm{pH}_o}\right), \\ \frac{\partial \phi}{\partial t} &= 10^{\mathrm{pH}_A}(1-\phi)^{2/3}\left(10^{-\mathrm{pH}}-10^{-\mathrm{pH}_o}\right). \end{aligned}\right. \tag{3.33}$$

To solve numerically (3.33) we have used the forward (in space) explicit method, namely

$$\frac{\mathrm{pH}^{i+1,j}-\mathrm{pH}^{i,j}}{\Delta x} = \frac{\hat{\theta}}{\ln 10}\left(1-\phi^{i,j}\right)^{2/3}\left(1-10^{\mathrm{pH}^{i,j}-\mathrm{pH}_o}\right)$$

$$\left(1-\phi^{i,j}\right)^{2/3} = \left[\left(1-\phi_o^i\right)^{1/3} - \frac{10^{\mathrm{pH}_A}}{3}\int_0^{t^j}\left[10^{(x^i,\zeta)}-10^{\mathrm{pH}_o}\right]d\zeta\right]_+^2.$$

In Fig. 5 and Fig. 6 we have plotted the behavior of pH and ϕ considering

$$\mathrm{pH}_{in}(t) = 2, \quad \phi_o(x) = 0.3 + 0.1x, \quad \mathrm{pH}_o = 7.$$

A. Appendix

If convection is absent (i.e. the system is closed), we drop the term $1/\hat{\theta}$ in equation $(3.15)_1$. In such a case, to find the solution in the $t^*_{\mathrm{CaCO}_3}$ time scale, we pro-

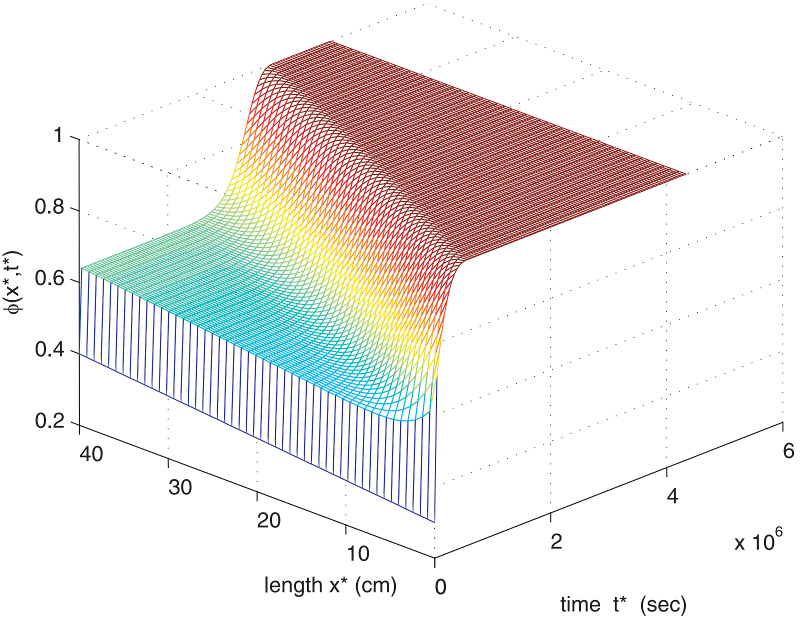

Figure 6. 3D—Plot of the function $\phi(x^*, t^*)$ in the slow time scale.

ceed as follows: we divide $[0, 1]$ in $N = 1/\varepsilon$, intervals whose amplitude is ε, setting $t_o = 0$, $t_1 = 1/\varepsilon$, $t_2 = 2/\varepsilon, \ldots$. Starting form $t_o = 0$, we apply formula (3.18) since, for the sake of simplicity, we consider $n = 1$. We thus get

$$C^{(0)}(x, 0, 1/\varepsilon) = \delta + [c_o(x) - \delta] \exp\left\{ -\frac{(1 - \phi^{(0)}(x, 0))^{2/3}}{\phi^{(0)}(x, 0)} \frac{1}{\varepsilon} \right\},$$

$$\begin{aligned} C^{(0)}(x, 1/\varepsilon, 2/\varepsilon) &= \delta + [C^{(0)}(x, 0, 1/\varepsilon) - \delta] \exp\left\{ -\frac{(1 - \phi^{(0)}(x, 1/\varepsilon))^{2/3}}{\phi^{(0)}(x, 1/\varepsilon)} \frac{1}{\varepsilon} \right\} \\ &= \delta + [c_o(x) - \delta] \exp\left\{ -\frac{(1 - \phi^{(0)}(x, 0))^{2/3}}{\phi^{(0)}(x, 0)} \frac{1}{\varepsilon} \right. \\ &\qquad \left. - \frac{(1 - \phi^{(0)}(x, 1/\varepsilon))^{2/3}}{\phi^{(0)}(x, 1/\varepsilon)} \frac{1}{\varepsilon} \right\}, \end{aligned}$$

so that

$$C^{(0)}(x, (N-1)/\varepsilon, N/\varepsilon) = +[c_o(x) - \delta] \exp\left\{ -\sum_{n=0}^{N} \frac{(1 - \phi^{(0)}(x, t_n))^{2/3}}{\phi^{(0)}(x, t_n)} \frac{1}{\varepsilon} \right\},$$

which we approximate as follows

$$c^{(0)}(x,t) = \delta + [c_o(x) - \delta]\exp\left\{-\int_0^t \frac{(1-\phi^{(0)}(x,\eta))^{2/3}}{\phi^{(0)}(x,\eta)}d\eta\right\}. \tag{A.1}$$

Plugging (A.1) into (3.25) we obtain an nonlinear integral for $\phi^{(0)}$, i.e.

$$\phi^{(0)}(x,t) = 1 - \Bigg[(1-\phi_o(x))^{1/3} - \frac{1}{3}(c_o(x)-\delta) \cdot \int_0^t \exp\left\{-\int_0^\zeta \frac{(1-\phi^{(0)}(x,\eta))^{2/3}}{\phi^{(0)}(x,\eta)}d\eta\right\}d\zeta\Bigg]_+^{1/3}. \tag{A.2}$$

Clearly this equation can be solved only numerically.

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