A Free Boundary Problem for CaCO$_3$ Neutralization of Acid Waters

Lorenzo Fusi, Angiolo Farina, Mario Primicerio, 
Università degli Studi di Firenze 
Dipartimento di Matematica “Ulisse Dini” 
Viale Morgagni 67/A, I-50134 Firenze, Italy

Abstract

In this paper we propose a mathematical model for the reaction kinetics of CaCO$_3$ in an acid solution. In particular we study the system in planar geometry showing that the problem is a free boundary problem with an intrinsic multi-scale structure. We rescale the problem and show how the equations simplify according to the specific scale considered. We present also a result that allows to calculate the diffusivity coefficient from experimental measurements of pH.

1 Introduction

Environmental pollution due to acid mine drainage is probably the most critical problem in mining industry. This phenomenon occurs naturally as part of the weathering process of rocks but is enhanced by mining activities, especially within rocks containing an abundance of sulfide minerals (see [10]).

Though many options are available for remediation purposes, the main being the ones based on chemical reactions neutralizing the acid water. A typical approach to the neutralization process is the so-called lime neutralization, which basically consists in the addition of lime to the acid water in order to raise the pH (so that dissolved heavy metals can precipitate).

Limestone is a cheap neutralizing agent (mainly formed by calcium carbonate, CaCO$_3$ ) that is particularly useful when available in crushed or pulverized form (because of the large available reaction surface). The neutralization process can be described as the one in which excess of CaCO$_3$ (w.r.t. the stoichiometric amount) results in an increase of the pH to an equilibrium value, providing also a granular network capable of retaining precipitates.

In this paper we propose a mathematical model which describes the evolution of the process described above. First, we derive a mathematical model for the acid water CaCO$_3$ chemical reaction occurring at the interface between the solid and the liquid acid solution. The model is developed in a general 3D setting (section 2), assuming a chemical reaction of the first order. Once the main physical quantities are defined (such the concentration of ions H$^+$ or, equivalently, the solution pH) we write a mass balance equation between CaCO$_3$ and the acid solution as well as a convection diffusion equation for H$^+$ concentration. Actually, the mathematical problems turns out to be a free boundary problem
since, due to the chemical reaction, the surface separating the liquid phase from the solid evolves in time.

Then we focus on a one-dimensional setting (section 3), considering a slab filled by an acid solution and neglecting convection. The left part of the slab is a CaCO$_3$ layer whose surface is exposed to the acid solution. The surface location (a priori unknown) evolves in time. We do not focus on the well posedness of the mathematical problem (since an abundant literature is already existent) but we analyze the qualitative behavior of the solution. The problem is multi-scale in both time and space and the nondimensional formulation of the problem puts in evidence the existence of three time scales having precise physical meaning. Depending on which time scale we are interested in, we may simplify the problem so that pieces of information concerning the space-time behavior of the solution can be easily obtained. In particular, according to the value of $\theta$, which is the ratio between the diffusive characteristic time and the reaction characteristic time, defined by formula (3.7), two scenarios are possible. The latters are analyzed in detail in section 4.

Focussing on the longest time scale (section 5) we are able to derive a formula for estimating $D^*$, i.e. the H$^+$ ions diffusivity in the acid solution. In particular, measuring the rate at which the acid solution neutralizes (i.e. the pH growth rate) we may infer the value of $D^*$. Of course, such a experimental measurements have to be operated when the asymptotic regime is fully developed. This occurs on a time scale, which we explicitly estimate.

2 Derivation of the model

We assume that the system is constituted by a given domain $\Omega \subset \mathbb{R}^3$, such that

$$\Omega = \Omega_l(t^*) + \Omega_s(t^*),$$

where $\Omega_l(t)$ is the volume occupied by acid water and $\Omega_s(t^*)$ is the volume occupied by the solid reacting material (for instance CaCO$_3$). The surface separating the liquid and solid regions is denoted with $\Sigma(t^*)$, and it is supposed to be evolving with time, but its evolution it is a priori unknown. $\Sigma$ is thus a free boundary. In particular, we assume that the surface $\Sigma$ is represented by $S(\vec{x}^*, t^*) = 0$ (with $S$ sufficiently smooth), so that its normal (pointing toward the liquid region $\Omega_l$) is given by

$$\vec{n}_\Sigma = \frac{\nabla^* S}{|\nabla^* S|}$$

(2.1)

We also introduce $\Gamma_l = \overline{\Omega}_l \cap \partial \Omega$ and $\Gamma_s = \overline{\Omega}_s \cap \partial \Omega$.

We denote by $c^*(\vec{x}^*, t^*)$ the molar concentration ([c$^*$] = mol/vol) of the H$^+$ ions. The dynamics of $c^*$ is governed by the following equation

$$\frac{\partial c^*}{\partial t^*} + q^* \cdot \nabla^* c^* = D^* \Delta^* c^*, \quad \vec{x}^* \in \Omega_l(t^*), \quad t^* \geq 0,$$

(2.2)

where:

1Throughout this paper the superscript "" means that the quantity has physical dimension.
• $\vec{q}^* (\vec{x}^*, t)$ is the convective flux ($[\vec{q}^*] = \text{length/time}$). We assume mechanical incompressibility of the liquid phase and hence $\nabla^* \cdot \vec{q}^* = 0$;

• $D^*$ is the diffusivity coefficient assumed to be constant ($[D^*] = \text{length}^2/\text{time}$).

The boundary $\Gamma_l$ is impermeable to water and to ions so that

$$\nabla^* c^* \cdot \vec{n}_l = 0, \quad \vec{q}^* \cdot \vec{n}_l = 0, \quad \vec{x}^* \in \Gamma_l, \quad t^* \geq 0,$$

where $\vec{n}_l$ is the outward unit normal to $\Gamma_l$.

The chemical reaction occurs on $\Sigma$ and it is described by the so-called “velocity” of the reaction $v^*$ ($[v^*] = \text{mol/time} \cdot \text{length}^2$), which represents the rate, per unit surface, at which the $\text{H}^+$ ions are neutralized on $\Sigma$. Hence, assuming a reaction of the first order we have

$$\int_{\Sigma} v^* d\sigma^* = -k^* \int_{\Sigma} \left( c^* - c_o^* \right)_+ d\sigma^*,$$

where:

• $k^*$ is the chemical reaction rate constant ($[k^*] = \text{length/time}$).

• $c_o^*$ is the “neutral concentration”, i.e. the concentration at which the solution is neutralized ($[c_o^*] = \text{mol/vol}$).

• $(\cdot)_+$ denotes the positive part.

Of course, by standard mass conservation arguments, $\int_{\Sigma} v^* d\sigma^*$ equals also the rate at which the solid material (namely CaCO$_3$) is consumed. Therefore we can also write

$$\int_{\Sigma} v^* d\sigma^* = \frac{d}{dt^*} \left[ \int_{\Omega(t^*)} \rho^* d^3 \vec{x}^* \right],$$

where $\rho^*$ is the molar density (assumed to be uniform and constant) of the solid reacting material ($[\rho^*] = \text{mol/vol}$). Hence introducing $w^*$, the normal velocity of the surface $\Sigma$, we have

$$\int_{\Sigma} v^* d\sigma^* = \frac{d}{dt^*} \left[ \int_{\Omega(t^*)} \rho^* d^3 \vec{x}^* \right] = \rho^* \int_{\Sigma} w^* d\sigma^*.$$  \hspace{1cm} (2.5)

Obviously

$$w^* = -\frac{1}{|\nabla^* S|} \frac{\partial S}{\partial t^*},$$  \hspace{1cm} (2.6)

\textsuperscript{2}The stoichiometric coefficient of the reaction is taken to be 1. This means that one mole of $\text{H}^+$ is reacting with one mole of CaCO$_3$. Of course, depending on the particular acid solution considered, the coefficient may have a different value. For instance when considering HCl we have 2 moles of $\text{H}^+$ reacting with one mole of CaCO$_3$, and hence the coefficient is 2.

\textsuperscript{3}$w^* > 0$ means a growing solid phase.
and hence, (2.4), (2.6) and (2.5) yield
\[
\frac{\rho^*}{|\nabla^* S|} \frac{\partial S}{\partial t^*} = k^* (c^*|_{\Sigma} - c^*_o)_+, \tag{2.7}
\]
which is the evolution equation of $\Sigma$.

Next, we have to write the boundary condition for $c^*$ on $\Sigma$. The latter, essentially, is a “sink” surface, so that the classical Rankine-Hugoniot condition \[4\] gives
\[
[c^*(\vec{q}^* \cdot \vec{n}_\Sigma - w^*) - D^* \nabla^* c^* \cdot \vec{n}_\Sigma]_{\Sigma} = v^*.	ag{2.8}
\]
Finally we consider the following initial data
\[
c^*(x^*, 0) = c^*_m(\vec{x}^*), \quad S(\vec{x}^*, t^*) = S^*_o(\vec{x}^*).	ag{2.9}
\]
The free boundary problem, considering $\vec{q}^*$ known, is thus given by (2.2), (2.3), (2.7), (2.8), and (2.9).

3 One dimensional model

In this section we write the problem in a one-dimensional setting. The domain $\Omega$ is constituted by a slab $[0, L^*]$. The region $[0, s^*(t^*)]$ is $\Omega_s$, i.e. the part occupied by the solid and $\Omega_t = [s^*(t^*), L^*]$. The interface $\Sigma$ separating the acid water from the solid is $S(x^*, t^*) = x^* - s^*(t^*) = 0$, yielding $w^* = s^*$. We consider a static situation so that $\vec{q}^* = 0$. Following (2.2) we can write $c^*_{t^*} = D^* c^*_{x^*, t^*}$, while (2.3) gives $c^*_x(L^*, t^*) = 0$. From (2.7) we obtain
\[
\rho^* s^* = -k^*(c^*(s^*, t^*) - c^*_o)_+.
\]
Concerning (2.8), we first observe that, exploiting (2.5), it can be rewritten as $-D^* \nabla^* c^*|_{\Sigma} \vec{n}_\Sigma = (\rho^* + c^*|_{\Sigma}) w^*$, provided $\vec{q}^* = 0$. We thus get
\[
[\rho^* + c^*(s^*, t^*)] s^* = -D^* c^*_{x}(s^*, t^*).
\]
Therefore, in the 1D case, the free boundary problem becomes
\[
\begin{cases}
  c^*_{t^*} - D^* c^*_{x^*, t^*} = 0, & s^* < x^* < L^*, \quad t^* > 0 \\
  c^*(x^*, 0) = c^*_m(x^*), & s^*_o < x^* < L^* \\
  c^*_x(L^*, t^*) = 0, & t^* > 0, \\
  \rho^* s^* = -k^*(c^*(s^*, t^*) - c^*_o)_+, & t^* > 0 \\
  [\rho^* + c^*(s^*, t^*)] s^* = -D^* c^*_{x^*}(s^*, t^*), & t^* > 0, \\
  s^*(0) = s^*_o, & 0 < s^*_o < 1.
\end{cases}
\tag{3.1}
\]
Before studying problem (3.1) we rescale the variables to obtain a non dimensional formulation. For this purpose we define $c^*_A > 0$ as the molar concentration corresponding to a strong acid solution (e.g. $c^*_A = 10^{-1}$ mol/l), and introduce the characteristic times
\[
t^*_D = \frac{L^*}{D^*}, \quad t^*_R = \frac{L^*}{k^*}, \quad t^*_E = \frac{L^* \rho^*}{k^* c^*_A},
\tag{3.2}
\]
representing the diffusive characteristic time, the reaction characteristic time and the erosion time scale, respectively. We also introduce the non dimensional parameters

\[
\lambda = \frac{\rho^*}{c_A^*} = \frac{t_E^*}{t_R^*}, \quad \delta = \frac{c_o^*}{c_A^*}.
\]  

(3.3)

When considering CaCO₃ in an acid solution typical values are

\[
\rho^* = 2.7 \times 10^{-2} \text{ mol/ℓt}, \quad c_o^* \sim 10^{-7} \text{ mol/ℓt}
\]  

(3.4)

which yields \( \lambda \approx 2.7 \times 10^3 \) and \( \delta \sim 10^{-6} \). Introducing then the following non dimensional quantities

\[
c = \frac{c^*}{c_A^*}, \quad c_{in} = \frac{c_{in}^*}{c_A^*}, \quad t = \frac{t^*}{t_D^*}, \quad x = \frac{x^*}{L^*}, \quad s = \frac{s^*}{L^*}, \quad s_o = \frac{s_o^*}{L^*};
\]  

(3.5)

the non-dimensional version of (3.1) becomes

\[
\begin{align*}
\frac{c_t - c_{xx}}{c_A^*} & = 0, & s < x < 1, & t > 0 \\
c(x, 0) & = c_{in}(x), & s_o < x < 1 \\
c_x(1, t) & = 0, & t > 0, \\
\lambda \dot{s} & = -\theta [c(s, t) - \delta], & t > 0 \\
[\lambda + c(s, t)] \dot{s} & = -c_x(s, t), & t > 0, \\
s(0) & = s_o, & 0 < s_o < 1,
\end{align*}
\]  

(3.6)

where

\[
\theta = \frac{t_D^*}{t_R^*} = \frac{L^* k^*}{D^*}.
\]  

(3.7)

### 3.1 Integral formulation and stationary solution

We integrate equation (3.6) over \( D_t = (s, 1) \times (0, t) \), by means of Green formulas, and we get

\[
s(t) - s_o = \frac{1}{\lambda} \left[ \int_{s(t)}^{1} c(x, t) dx - \int_{s_o}^{1} c_{in}(x) dx \right].
\]  

(3.8)

We can prove the following

**Theorem 1** If the asymptotic solution of system (3.6) exists, it is given by \( c(x, t) \equiv \delta \) and \( \theta \)

**Proof.** Let us assume for a moment that a classical solution of (3.6) exists for all times. Then the stationary concentration is clearly \( c = \delta \). Moreover suppose that the function \( s(t) \) is differentiable. From the integral formulation we see that

\[
\lim_{t \to \infty} s(t) \neq -\infty.
\]
Indeed if (by absurd) we had that \( \lim_{t \to \infty} s(t) = -\infty \), then from (3.8)
\[
-\infty - s_o = \frac{1}{\lambda} \lim_{t \to \infty} \int_0^1 c^\prime dx - \frac{1}{\lambda} \int_{s_o}^1 c_{in} dx > \frac{1}{\lambda} \delta \lim_{t \to \infty} (1 - s) - \frac{1}{\lambda} \int_{s_o}^1 c_{in} dx = +\infty,
\]
which is an obvious contradiction.

\[\square\]

Therefore there can be only two situations:

1. \(-\infty < \lim_{t \to \infty} s(t) = s_\infty \leq 0\).
2. \(0 < \lim_{t \to \infty} s(t) = s_\infty \leq s_o\).

Since \(c(x, t)\) is bounded and tends to \(\delta\) as \(t \to \infty\) we have from (3.8)
\[
s_\infty - s_o = \frac{1}{\lambda} \int_{s_\infty}^1 \delta - \frac{1}{\lambda} \int_{s_o}^1 c_{in} dx,
\]
which after some algebra becomes
\[
s_\infty = \frac{\lambda s_o + \delta - \int_{s_o}^1 c_{in} dx}{\lambda + \delta}.
\]

Clearly,

1. \(s_\infty \leq 0 \iff \lambda s_o + \delta \leq \int_{s_o}^1 c_{in} dx\), 
\hspace{1cm} (3.9)
2. \(s_\infty > 0 \iff \lambda s_o + \delta > \int_{s_o}^1 c_{in} dx\).
\hspace{1cm} (3.10)

### 3.2 Mathematical analysis of the one dimensional problem

First we notice that the free boundary problem (3.6) does not belong to the broad class of nonlinear free boundary problems studied in [8]. However, considering the transformation
\[
u(x, t) = \lambda(x - s(t)) + \int_{s(t)}^x c(\eta, t) d\eta,
\]
problem (3.6) becomes of Stefan-type
\[
\begin{align*}
u_t - u_{yy} &= 0, & s(t) < x < 1, & t > 0, \\
u(x, 0) &= u_{in}(x), & s_o < x < 1, \\
u(1, t) &= u_{in}(1), & t > 0, \\
u(s, t) &= 0, & t > 0, \\
\lambda s' &= -\theta [u_x(s, t) - \lambda - \delta], & t > 0, \\
s(0) &= s_o, & 0 < s_o < 1,
\end{align*}
\]
where \( u_m(x) = \lambda (x - s_o) + \int_{s_o}^x c_{\infty}(\eta) d\eta \). Problem (3.11) has the same structure as the problem arising from a model for sorption of solvents into glassy polymers first presented in [2]. A series of papers devoted to the analysis of this problem with various boundary conditions have been proposed, see [7], [5], [6], [1]. In particular, following the papers cited above it is easy to see that, under specific assumptions on the data, problem (3.11) admits a unique classical solution. We also have the following

**Theorem 2** Any classical solution \((c, s)\) is such that

\[
\delta < c(x, t) \leq \sup_{x \in [s_o, 1]} c_m(x).
\]

The proof is based on the parabolic version of Hopf’s lemma (see [9]) and maximum principle.

### 4 Quantitative analysis

In this section we focus on a quantitative analysis of problem (3.1), showing that the problem has a multi-scale structure in both time and space. We will study the qualitative behaviors of \(c\) and \(s\) corresponding to different values of the main physical parameters \(D^*\) (diffusivity of ions \(H^+\) in the aqueous solution) and \(k^*\) (chemical reaction rate constant). Depending on the values of such parameters and on the selected spatial and temporal scale, problem (3.1) may significantly simplify.

Let us go back to problem (3.1) and rescale it with generic characteristic time and spatial scales

\[
x^* = x_{\text{ref}} x, \quad t^* = t_{\text{ref}} t, \quad s^* = s_{\text{ref}} s.
\]

We get

\[
\begin{cases}
c_t - \left( t_{\text{ref}} D^* \right) \frac{x_{\text{ref}}^2}{x_{\text{ref}}^*} c_{xx} = 0, & \frac{s_{\text{ref}}^*}{x_{\text{ref}}^*} < x < \frac{L^*}{x_{\text{ref}}^*}, \quad t > 0 \\
c(x, 0) = c_m(x), & s_{\text{ref}}^* < x < \frac{L^*}{x_{\text{ref}}^*} \\
c_x \left( \frac{L^*}{x_{\text{ref}}^*}, t \right) = 0, & t > 0 \\
\dot{s} = -\frac{1}{\lambda} \left( \frac{k^* t_{\text{ref}}^*}{s_{\text{ref}}^*} \right) (c(s, t) - \delta), & t > 0 \\
[\lambda + c(s, t)] \dot{s} = -\left( \frac{D^* t_{\text{ref}}^*}{x_{\text{ref}}^* s_{\text{ref}}^*} \right) c_x(s, t), & t > 0, \\
s(0) = s_o, & 0 < s_o < \frac{L^*}{x_{\text{ref}}^*}.
\end{cases}
\]

In the forthcoming sections we will study problem (4.2) for various combinations of the reference scales \(x_{\text{ref}}^*\) and \(t_{\text{ref}}^*\).
4.1 Large diffusivity

We begin by assuming a “large” value for the diffusivity coefficient $D^*$. This corresponds to the case in which diffusion occurs on a temporal scale which is much smaller than the reaction time, namely $t_D^* \ll t_R^*$, and so, recalling (3.7),

$$\theta \ll 1.$$ 

Assuming an increasing concentration profile, we expect that near the boundary $x = s$ the concentration is initially increasing, since ions are supplied at a rate which is faster than the reaction rate. We first investigate the evolution of the system in the diffusive time scale (i.e. the fastest). Considering the scalings (3.5), we get

$$\begin{align*}
&c_t - c_{xx} = 0, \quad s < x < 1, \quad t > 0 \\
&c(x, 0) = c_{in}(x), \quad s_o < x < 1 \\
&c_x(1, t) = 0, \quad t > 0, \\
&s = 0, \quad t > 0 \\
&c_x(s, t) = 0, \quad t > 0, \\
&s(0) = s_o, \quad 0 < s_o < 1.
\end{align*}$$

Exploiting the maximum principle it is easy to check that $0 \leq c_x(x, t) \leq \sup_{[s_o, 1]} c_{in}'(x)$. Therefore $c_x$ is bounded in this time scale and no boundary layer can be formed at the boundaries $x = s$ and $x = 1$.

On the other hand, if we look for the solution in a much larger time scale (the reaction or the erosion time scale) we have to select $t_{ref}^* = t_R^* \gg t_D^*$, while keeping the other scalings reported in (3.5). Problem (4.2) essentially becomes

$$\begin{align*}
&c_{xx} = 0, \quad s < x < 1, \quad t > 0 \\
&c(x, 0) = c_{in}(x), \quad s_o < x < 1 \\
&c_x(1, t) = 0, \quad t > 0, \\
&s = -\frac{1}{\lambda}(c - \delta), \quad t > 0 \\
&c_x(s, t) = 0, \quad t > 0, \\
&s(0) = s_o, \quad 0 < s_o < 1.
\end{align*}$$

Equations (4.3)$_1$, (4.3)$_3$ entail $c(x, t) = f(t)$ and so (4.3)$_4$ gives $\dot{s}(t) = -\lambda(f(t) - \delta)$. This means that, after an initial transient in which diffusion plays a major role, the concentration profile is homogeneous in space and decreases towards the asymptotic value $\delta$ in an infinite time. Monitoring the H$^+$ concentration time evolution does not provide any information on the diffusivity $D^*$.

4 Referring to (4.1), we essentially consider $x_{ref}^* = s_{ref}^* = L^*$. 

8
4.2 Large chemical reaction rate constant

In this section we study the qualitative behavior of the solution for large values of $k^*$, i.e. for $t^*_R \ll t^*_D$, thus yielding $\theta \gg 1$. Now the reaction rate is much faster than diffusion. In such a case, in the vicinity of $x = s$, a thin boundary layer is formed. In this region the concentration decreases steeply towards the value $c = \delta$, while in the bulk no significant change from the initial profile occurs. We thus expect the existence of two different spatial scales: $h^*$, the one of the boundary layer, and $L^*$. Of course, $h^* \ll L^*$.

We begin by studying the problem in the spatial scale $L^*$, which is the one of the slab, and we consider $x^*_ref = s^*_ref = L^*$ in (4.1) and set $^5 t^*_ref = t^*_R$. Problem (4.2) can be simplified as follows

\[
\begin{cases}
  c_t = 0, & s < x < 1, \quad t > 0, \\
  c(x, 0) = c_{in}(x), & s_o < x < 1, \\
  c_x(1, t) = 0, & t > 0, \\
  \dot{s} = 0, & t > 0, \\
  c(s, t) = \delta, & t > 0, \\
  s(0) = s_o, & 0 < s_o < 1.
\end{cases}
\]

(4.4)

With this scaling the initial profile does not change with time (as expected), since diffusion is slower than reaction.

Next we focus on the boundary layer whose width is $d^* = \gamma(t) h^*$, where $h^*$ gives the order of magnitude and $\gamma$ is the dimensionless thickness\(^6\) which is, in general, evolving in time. Of course, both, $\gamma$ and $h^*$, are unknown at this stage.

For estimating $h^*$ we proceed as follows: the width of the boundary layer is such that diffusion time scale and reaction time scale, evaluated on $h^*$, are of the same order, namely

\[
\frac{h^*}{D^*} = O(1).
\]

This occurs because reaction and diffusion in the boundary layer take place in the same time scale. We thus assume

\[
h^* = \frac{D^*}{k^*},
\]

(4.5)

and, referring to (4.1), set $x^*_ref = h^*$, $s^*_ref = L^*$, and $t^*_ref = t^*_R$. It easy to check that, the assumption

\[^5\]In practice, we consider the scalings (3.5), except for $t$, which we rescale with $t^*_R$.

\[^6\]We have to remark that our hypothesis is verified provided $\gamma = O(1)$.
$t^*_R \ll t^*_D$, together with (4.5) implies $h^*/L^* \ll 1$. Problem (4.2) becomes\(^7\)
\[
\begin{aligned}
c_{xx} &= 0, & s < x, & t > 0, \\
\dot{s} &= -\frac{1}{\lambda}(c(s, t) - \delta), & t > 0, \\
[\lambda + c(s, t)]\dot{s} &= -c_x(s, t), & t > 0, \\
s(0) &= s_o, & 0 < s_o < 1.
\end{aligned}
\]
(4.6)

The above equations hold only if the dimensionless variable $x$ ranges between 0 and $\gamma(t)$, which is $O(1)$. From (4.6) we get
\[
c(x, t) = \dot{s}[\lambda s - \lambda - \delta](x - s) + (\delta - \lambda \dot{s}),
\]
and
\[
c_x(x, t) = c_x(s, t) = \dot{s}[\lambda s - \lambda - \delta],
\]
(4.7)
where $s$ is still unknown. To determine $s(t)$ we must impose mass balance between the bulk (which we recall does not change its initial status) and the boundary layer, namely (using dimensionless variables)
\[
\frac{d}{dt} \left[ \int_{s+\gamma}^{1} c_{in}(x)dx \right] = -c_x(s, t),
\]
(4.8)
where $c_x(s, t)$ is given by (4.7). Clearly concentration must be continuous at the interface between the boundary layer and the bulk. Therefore we set $c_{in}(s + \gamma) = c(s + \gamma, t)$. The latter together with (4.8) yield
\[
\begin{aligned}
\dot{s}[\lambda s - \lambda - \delta]\gamma + (\delta - \lambda \dot{s}) &= c_{in}(s + \gamma), & s(0) &= s_o, \\
\dot{s}[\lambda s - \lambda - \delta] &= (\dot{s} + \gamma)c_{in}(s + \gamma), & \gamma(0) &= 0.
\end{aligned}
\]
which is a system of nonlinear differential equations. As an example to illustrate the evolution of the boundary layer we assume that $\delta \approx 0$ and\(^8\) $c_{in} = 1$. We get
\[
\begin{aligned}
\lambda \gamma \dot{s}^2 - \dot{s}(\lambda \gamma + 1) - 1 &= 0, & s(0) &= s_o, \\
\dot{\gamma} &= \lambda \dot{s}^2 - (\lambda + 1)\dot{s}, & \gamma(0) &= 0.
\end{aligned}
\]
(4.9)
From (4.9)\(_1\) we see that
\[
\dot{s} = \frac{\lambda(\gamma + 1) - \sqrt{\lambda^2(\gamma + 1)^2 + 4\gamma\lambda}}{2\lambda\gamma},
\]
(4.10)
where we have taken the minus sign in front of the square root because $s$ has to be decreasing (an increasing $s$ has no physical meaning). If we plug (4.10) into (4.9)\(_2\), we obtain
\[
\dot{\gamma} = \mathcal{F}(\gamma) = \frac{(\gamma - \lambda)\sqrt{\lambda^2(\gamma + 1)^2 + 4\gamma\lambda + \lambda^2 + \gamma\lambda^2 + \gamma\lambda - \lambda\gamma^2}}{2\lambda\gamma^2}, & \gamma(0) &= 0.
\]
\(^7\)Because of the approximation we are taking, the condition on $x^* = L^*$ and the initial condition are clearly neglected.
\(^8\) $c_{in} = 1$ means that the solution is initially strongly acid.
which is a degenerate nonlinear ODE for $\gamma$. Actually we see that $\dot{\gamma}$ is bounded when $\gamma \to 0$ (we can prove it by means of Hôpital’s rule) and that $\dot{s}(0) = -\frac{1}{\lambda}, \dot{\gamma}(0) = 1 + \frac{2}{\lambda}$.

The evolution of both $\gamma(t), s(t)$ and $c$ are displayed in Fig 1 and 2.

![Figure 1: Free boundaries $x^* = s^*$ and $x^* = s^* + \gamma^*$.](image1)

![Figure 2: Non-dimensional concentration profile.](image2)

## 5 Determining diffusivity from experimental results

Let us still assume that the diffusive time scale is larger than the reaction time scale, i.e. $t^*_D \gg t^*_R$ and $\theta \gg 1$. At the same time we require $t^*_D \ll \lambda t^*_R = t^*_E$, where, recalling (3.2) and (3.3), $t^*_E$ represents the erosion time scale, i.e. the characteristic time of depletion of the slab. Of course this assumption is reasonable, since if this was not the case, then diffusion would be playing a major role after the slab has completely depleted, which is absurd. In conclusion we have

$$1 \ll \frac{t^*_D}{t^*_R} \ll \lambda, \quad \Rightarrow \quad \frac{t^*_D}{\lambda t^*_R} \ll 1 \quad (5.1)$$
Next, we consider problem (4.2) setting $s_{\text{ref}}^* = L^*$, $t_{\text{ref}}^* = t_D^*$, and not specifying the spatial scale. Neglecting $\delta$ (recall that typically $\delta \sim 10^{-6}$) and exploiting (5.1), we get

$$
\begin{align*}
&c_t \left( \frac{x_{\text{ref}}^*}{L^*} \right) - c_{xx} = 0, \quad s_{\text{ref}}^* < x < \frac{L^*}{x_{\text{ref}}^*}, \quad t > 0 \\
c(x, 0) = c_{\text{in}}(x), \quad s_{\text{ref}}^* < x < \frac{L^*}{x_{\text{ref}}^*} \\
&c_x \left( \frac{L^*}{x_{\text{ref}}^*} \right) = 0, \quad t > 0, \\
\dot{s} = 0, \quad x = s, \quad t > 0 \\
c = -\frac{D^*}{x_{\text{ref}}^* L^*} c_x, \quad x = s, \quad t > 0, \\
s(0) = s_o, \quad 0 < s_o < \frac{L^*}{x_{\text{ref}}^*}.
\end{align*}
$$

(5.2)

Now we set $x_{\text{ref}}^* = h^*$, with $h^*$ given by (4.5). This corresponds to focus on the boundary layer spatial scale. Recalling that $h^*/L^* \ll 1$, problem (5.2) becomes

$$
\begin{align*}
&c_{xx} = 0, \\
&\dot{s} = 0, \\
&c = -c_x, \quad x = s, \\
&s(0) = s_o,
\end{align*}
$$

(5.3)

whose solution is $c(x, t) = -f(t)(x - s_o) + f(t)$, with $f(t)$ unknown and $s = s_o$.

Next, considering the bulk, i.e. $x \geq s + h$, we can safely assume that the bulk concentration is spatially homogeneous since we are in a time scale sufficiently larger than $t_D^*$ (see the previous section). Thus we set $c = \bar{c}(t)$ for $x \geq s + h$. We then impose continuity of the concentration and the usual mass balance, namely

$$
\begin{align*}
&f(t)(1 - h) = \bar{c}, \\
&\frac{d\bar{c}}{dt} = -f(t),
\end{align*}
$$

which yields

$$
\bar{c}(t) = \bar{c}(t_o) \frac{1}{1 - h} \exp \left\{ -\frac{t - t_o}{1 - h} \right\},
$$

where $t_o$ is a dimensionless initial time falling in the range of the characteristic time selected. Neglecting $h$ and going back to dimensional variables, we have

$$
\frac{\bar{c}^*(t^*)}{\bar{c}_A^*} = \frac{\bar{c}^*(t_o^*)}{\bar{c}_A^*} \exp \left\{ -\frac{t^* - t_o^*}{t_D^*} \right\}.
$$

(5.4)
Recalling the definition of pH

\[ \overline{\text{pH}}(t^*) = -\log_{10} \left( \frac{\bar{c}^*(t^*)}{c_A^*} \right), \]

and the definition of \( t_D^* \), it is easy to show that (5.4) implies

\[ D^* = \Theta (t^*, t_o^*) \cdot \ln 10 \cdot L^*^2, \quad \text{with} \quad \Theta (t^*, t_o^*) = \frac{\overline{\text{pH}}(t^*) - \overline{\text{pH}}(t_o^*)}{t^* - t_o^*}. \]

Hence, to determine the diffusivity coefficient it is sufficient to know the slope \( \Theta \) of the pH-plot in a time interval \((t_o^*, t^*)\), with \( t_o^* \) sufficiently larger than \( t_R^* \), where the dependence of pH on time is linear.

As an example we have used the data of [3] where \( \Theta = \mathcal{O}(10^{-8} \text{ s}) \), so that with \( L^* = 20 \text{ cm} \) we get \( D^* \approx 10^{-6} \text{ cm}^2/\text{s} \).

References


