Máster en Ingeniería Matemática

Neutralization of Acid WasteWaters

Modeling Week

Group I:

SERGIO RUIZ

NEUTRALIZATION OF ACID WASTEWATERS

Intro

The system is described by the evolution of the overall ion concentration and the radii of the spheres (we consider water particles as small spheres). 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.

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.

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. 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. 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.

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. One of the possible options to the neutralization process involves the use of a basic chemical compound, such as sodium hydroxide, calcium hydroxide or calcium carbonate. 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.

Potential source of calcium carbonate waste are marble industries, paper industries, sugar industries, hatcheries and food processing factories, limestone and a lot more.

The chemical reactions occurring are the following:

$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + H_2O + CO_2$$
$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3$$
$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3$$
$$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO^{3-} + OH^-$$

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

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 $\phi_s = 1-\phi_l$. So, to keep notation simple, here and in the sequel ϕ represents the solid volume fraction and $(1-\phi)$ 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 (for the CaCO3 spheres) and for H+, obtaining to a system of two coupled equations.

The Model

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

If the liquid saturating the pores is an acid solution, we introduce:

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

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

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

We assume that the solid matrix is constituted by n families of $CaCO_3$ spheres with radii r^*_1, r^*_2, r^*_n, uniformly mixed, so that the total solid volume fraction is given by:

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

con i=1, 2, …, n, is the granulometric distribution.

We assume:

N^*_i, i = 1, 2, …, n, are given and constant in time. Moreover the spheres do not compact.

Of course each r^*_i, will depend on $\vec{x}^*, t^*$. We have:

$$\phi(\vec{x}^*, t^*) = 1 - \frac{4}{3}\pi \sum_{i=1}^{n} \left(r_i^*(\vec{x}^*, t^*)\right)^3 \mathcal{N}_i^*.$$

Introducing $\mathcal{N}^* = \sum_{i=1}^{n} \mathcal{N}_i^*$, the granulometric fractions $\mathcal{N}_i = \frac{\mathcal{N}_i^*}{\mathcal{N}^*}, \quad i = 1, 2, \ldots, n,$

and the dimensionless radii (r^* is a reference radius), $r_i = \frac{r_i^*}{r^*}, \quad i = 1, 2, \ldots, n,$ we have

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

In case n = 1 (just one family of spheres), we have $\phi = 1 - \frac{4}{3}\pi r^{*\,3}\mathcal{N}^* \quad \Leftrightarrow \quad r^* = \sqrt[3]{\frac{3}{4\pi\mathcal{N}^*}(1-\phi)}$.

The radius of the $CaCO_3$ spheres varies (decreases) in time because of the chemical reaction occurring on their surface. So, following an Eulerian formalism, the continuity equation for the molar concentration of H^+ is

$$\frac{\partial}{\partial t^*}\left(c^*_{ph}\,\phi\right) = -\nabla^* \cdot \left(c^*_{ph}\,\vec{q}^{\,*}\right) - \Gamma^*.$$

With:

- $\vec{q}^{\,*}$: liquid discharge, 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 cm3. Assuming a first order kinetics

$\Gamma^* = \gamma^*$ (total reaction surface per unit volume)$(c^*_{ph} - c^*_{ph,0})_+ =$

$$= 4\pi\gamma^*\mathcal{N}^*\left(\sum_{i=1}^{n}\mathcal{N}_i r_i^{*\,2}\right)\left(c^*_{ph} - c^*_{ph,o}\right)_+ ,$$

where γ^* is a constant usually referred as reaction rate [γ^*] = cm/s, $c^*_{ph,0}$ is the equilibrium concentration (the concentration at neutralization), and where $(\cdot)_+$ denotes the positive part. In general $c^*_{ph,0}$ depends on the reaction. Here we assume that $c^*_{ph,0}$ corresponds to pH = 7, $c^*_{ph,0} = 10^{-7}$ mol/ℓt.

The equation can be rewritten as

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

where

$$c = \frac{c^*_{ph}}{c^*_{ph,ref}}, \qquad \delta = \frac{c^*_{ph,o}}{c^*_{ph,ref}},$$

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

If only one family is present (namely n = 1), we may express Γ^* in terms of ϕ. Indeed, we have: $\Gamma^* = \gamma^*\sqrt[3]{36\pi\mathcal{N}^*}\,(1-\phi)^{2/3}\left(c^*_{ph} - c^*_{ph,o}\right)_+$.

Concerning $\vec{q}^{\,*}$, we assume that it is given and constant. In general, if boundary pressure is given, an additional equation should be written representing mass conservation of the liquid coupled with Darcy's law:

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

where $K^*(\phi)$ is the medium hydraulic conductivity (whose dependence on ϕ should be prescribed through an experimental law) and P^* is the liquid pressure.

<u>One dimension case</u>

We consider a cylinder whose length is L^*. The axial coordinate is denoted by x^*. The discharge is prescribed, $\vec{q}^{\,*} = q_o^*\,\vec{e}_x$ with q_0^* given constant. We introduce

$$t = \frac{t^*}{t^*_{ref}},\; x = \frac{x^*}{L^*}$$

where t^*_{ref} is a reference time that has 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 $c_A^* = \sup_{t\,\geq 0} c^*_{ph,in}(t)$. We take

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

which corresponds to a strongly acid solution. 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).
- $t^*_{reac} = \left(4\pi\gamma^*\mathcal{N}^* r^{*\,2}\right)^{-1}$, characteristic reaction time, namely the H^+ reaction time.

We can write the continuity equation and the consumption equation as follows:

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

As initial conditions we take $r_i(x, 0) = r_{i,\,o}(x)$, i = 1, 2, ... , n, and $c(x, 0) = c_o(x)$, while the only boundary condition is the one for c, $c(0, t) = c_{in}(t)$.
We assume the compatibility condition $co(0)=c_{in}$ (0). Of course, by definition, the inlet H^+ ions concentration c^*_{in} does not exceed the reference concentration (the inlet pH is always not smaller than pH_A), so that $0 < c_{in}(t) \leq 1$ for all times. Concerning δ, we get $\delta = 10^{-5}$, because, as mentioned, $c^*_{ph,\,0} = 10^{-7}$ mol/ℓt. Finally, concerning the initial porosity, we have

$$\phi_o(x) = 1 - \frac{4}{3}\pi r^{*\,3}\mathcal{N}^* \sum_{i=1}^{\mathfrak{n}} r^3_{i\,o}\,\mathcal{N}_{.i}$$

We define

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

and we evaluate them using the values

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

We have

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

So that

$$\theta \sim 10^{-2}, \qquad \varepsilon \sim 10^{-3}$$

And

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

.

We write

$$\theta = \hat{\theta}\varepsilon, \quad \text{with} \quad \hat{\theta} = \mathcal{O}(10).$$

<u>Two time scale approach</u>

We select t^*_{CaCO3} as reference time setting $t^*_{ref} = t^*_{CaCO3}$ meaning that we are interested in analyzing the lifetime of the cartridge. So, the system can be rewritten as:

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

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

$$\tau = \frac{t}{\varepsilon}.$$

Actually, there is also the convective time scale θ which can be considered simply multiplying the time scale τ by a factor θ. Next, we look for c, ϕ, of the form c (x, t) = C (x, t/ε, t), r_i (x, t) = R_i (x, t/ε, t), i = 1, 2…n. Thus, we have:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial t} + \frac{1}{\varepsilon}\frac{\partial}{\partial \tau}.$$

We introduce the asymptotic expansion for the unknowns C, R_i

$f = f^{(0)} + \varepsilon f^{(1)} + \varepsilon^2 f^{(2)} + \dots$.

Inserting the above expansions in the dimensionless system, we obtain initial-boundary value problems at successive order of ε. Here we consider only the leading order (the zero order), neglecting convergence issues.

Stationary solution

We observe that, ϕ = 1 entails r_i = 0, i = 1, 2 . . . n. So, if ϕ (x, t) is analytic, then for every x ∈ [0, 1], $\partial^n \phi/\partial t^n = 0$, when ϕ = 1, ∀ n ∈ N.

This means that if at some point x and at some time t^* we have ϕ (x^*, t^*) = 1, then ϕ (x^*, t) = 1 for all $t \geq t^*$. Once the solid fraction has disappeared, it can never be formed again!

The stationary solution is given by the solution of

$$\frac{\partial c}{\partial x} = 0, \qquad c(0) = c_{in}$$

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

(i) ϕ = 1 is reached in a finite time (possibly depending on x).

(ii) ϕ = 1 is reached in an infinite time.

Suppose that $\phi|_{x=0}$ becomes 1 in a finite time t^* at x = 0. Then, we can introduce t_i, i = 1, 2, … n, such that

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

We thus estimate t^*, setting t^* = max i=1, 2, …, n $\{t_i\}$.

Zero order approximation

We can rewrite de system in terms of C:

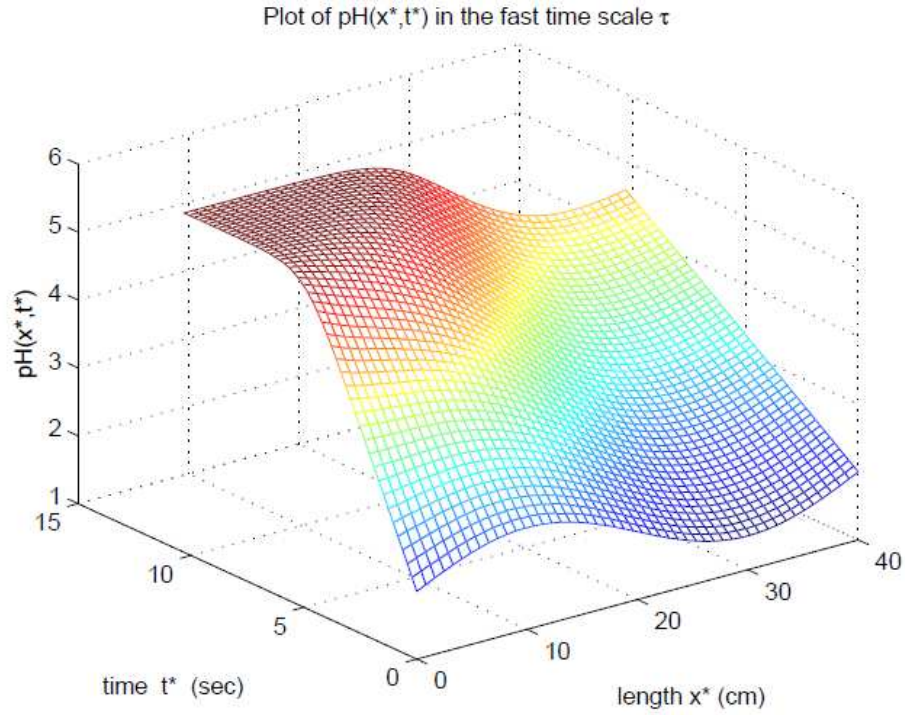
$$\begin{cases} \dfrac{\partial (C\phi)}{\partial t} + \dfrac{1}{\varepsilon}\dfrac{\partial (C\phi)}{\partial \tau} + \dfrac{1}{\hat{\theta}_\varepsilon}\dfrac{\partial C}{\partial x} = -\dfrac{1}{\varepsilon}\left(\displaystyle\sum_{i=1}^{n} \mathcal{N}_i r_i^2\right)(C-\delta)_+ \\ \dfrac{\partial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

We can insert the expansion introduced before, getting (at the zero order):

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

We thus conclude that $R^{(0)}_i = r^{(0)}_i$ i=1, 2, …, n so:

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



We got:

$$C^{(0)}(x,t_o,\tau)=\delta+[C(x,t_o,0)-\delta]\exp\left\{-\left[\sum_{i=1}^{n}\mathcal{N}_i\left(r_i^{(0)}(x,t_o)\right)^2\right]\frac{\tau}{\phi^{(0)}(x,t_o)}\right\}$$

Since n=1, this equation has the form:

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

Or, in terms of pH,

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

Now, we consider the characteristics originating from the boundary x=0, namely

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

Then, we can estimate the "transit time" T_{tr}, the time needed for the water to reach the outlet, namely

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

Considering now t=0, we have

$$\tau = \hat{\theta} \int_{\xi}^{x} \phi_o(s)\, ds, \qquad 0 < \xi < 1, \quad \xi < x < 1,$$

$$c^{(0)} = \delta + (c_o(\xi) - \delta) \exp\left\{ -\hat{\theta} \int_{\xi}^{x} \sum_{i=1}^{n} \mathcal{N}_i r_{i,\,o}^2(s)\, ds \right\} \qquad 0 < \xi < 1, \quad \xi < x < 1,$$

Well posedeness of the mathematical problem

We will omite the "$^{(0)}$" to have a lighter notation. We will consider the following system:

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

We got a pair of functions (c(x,t), ϕ(x, t)) which will be a solution of the problem for some T>0 and if the following conditions hold true:

1. c(x, t), ϕ(x, t) in C1 (Ω_T).
2. δ < c(x, t) ≤ 1, and 0 < ϕ(x, t) ≤ 1 for all (x, t) in Ω_T.
3. ϕ(x, 0) = ϕ_0(x), and c(0, t) = c_{in}(t), with $\sup_{t\geq 0} |c_{in}(t)| \leq 1$.
4. c(x, t) and ϕ(x, t) fulfill the system for all (x, t) in Ω_T.

Introducing:

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

system can be rewritten as:

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

Where

$$u_{in} = c_{in} - \delta, \text{ and } \psi_o = (1-\phi_o)^{1/3}.$$

Suppose that ϕ_0(x) and c_{in}(t) satisfy the hypotheses of the solutions (c(x,t), ϕ(x, t)) and

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

Where

$$B = \sup_{t\geq 0} |u_{in}(t)|.$$

Then, for 0 < t ≤ T, there exists one and only one solution (u, ψ) in the sense of the last 4 conditions defined before.

Numerical solutions of the system

We will present some numerical results for the system presented. We will write the system in terms of pH:

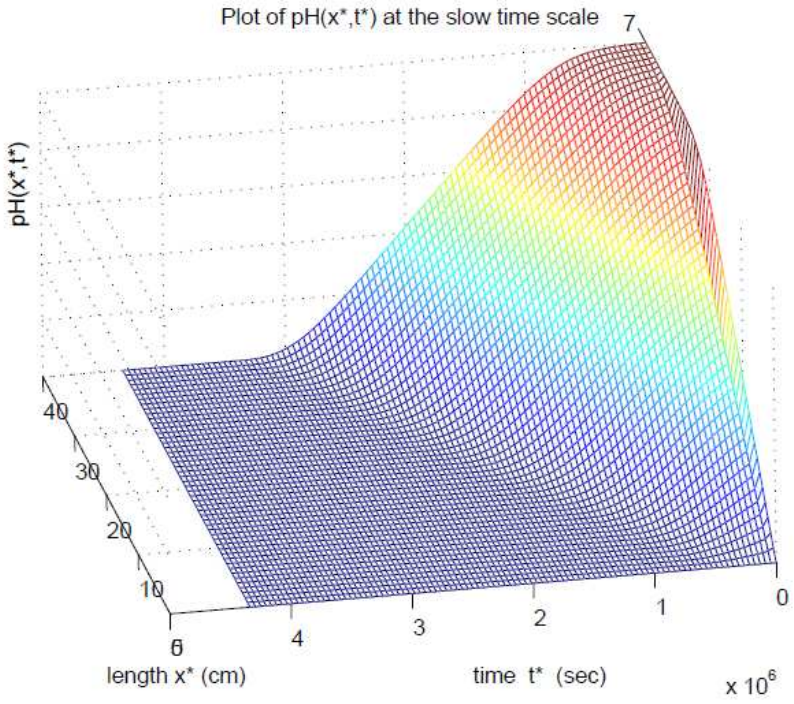
$$\begin{cases} \dfrac{\partial \mathrm{pH}}{\partial x} = \dfrac{\hat{\theta}}{\ln 10}\,(1-\phi)^{2/3}\left(1-10^{\mathrm{pH}-\mathrm{pH}_o}\right), \\ \dfrac{\partial \phi}{\partial t} = 10^{\mathrm{pH}_A}\,(1-\phi)^{2/3}\left(10^{-\mathrm{pH}}-10^{-\mathrm{pH}_o}\right). \end{cases}$$

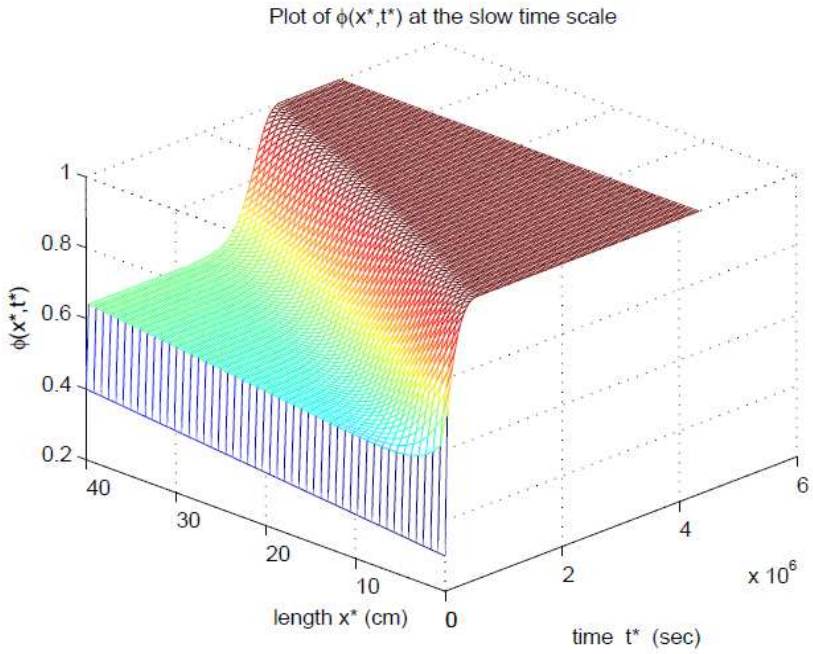
To solve numerically, a forward explicit mode has been used, namely

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

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

So, in the next figures, we see the behavior of pH and ϕ, considering $pH_{in}(t)=2$, $\phi_0(x)=0.3+0.1x$, $pH_0=7$.





PRACTICE WITH MATLAB

We made several simulations with Matlab, depending on the time scale, as we show:

Reaction time scale:

$\partial\phi/\partial t - \ln 10.(\partial pH/\partial t) - (t^*_{reac}/t^*_{conv}).\ln(10\partial pH/\partial x) = -(1-\phi)^{2/3}$

$\partial\phi/\partial t = (t^*_{reac}/t^*_{CaCO3}).(1-\phi)^{2/3}.10^{2-pH}$ ⟶ $\phi=\phi_0(x)$

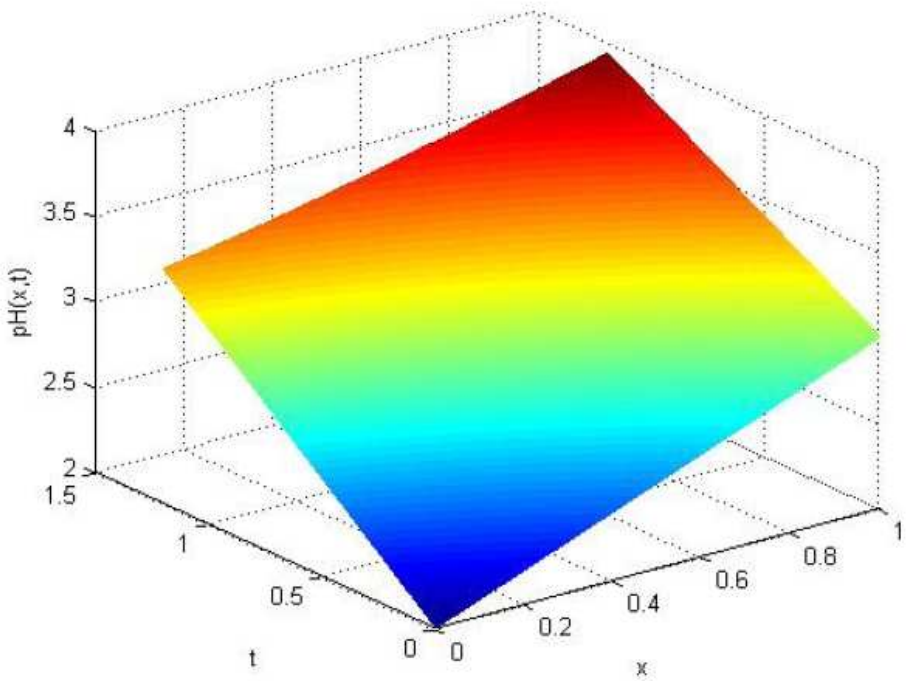
Initial and boundary conditions:

$\phi(x, 0)=\phi_0(x)$
$pH(x, 0)=pH_0(x)$

Solution: Reaction time scale

$pH(x, t)=pH_0(x)+(1/\ln 10).(1-\phi_0(x))^{2/3}/\phi_0(x)$, $t\approx O(1)$

Plot: Reaction time scale



Convective time scale:

$\partial\phi/\partial t - \ln 10.(\partial pH/\partial t) - \ln 10.(\partial pH/\partial x) = -t^*_{conv}/t^*_{reac}(1-\phi)^{2/3}$

$\partial\phi/\partial t = (t^*_{conv}/t^*_{CaCO3}).(1-\phi)^{2/3}.10^{2-pH}$ ⟶ $\phi=\phi_0(x)$

Initial and boundary conditions:

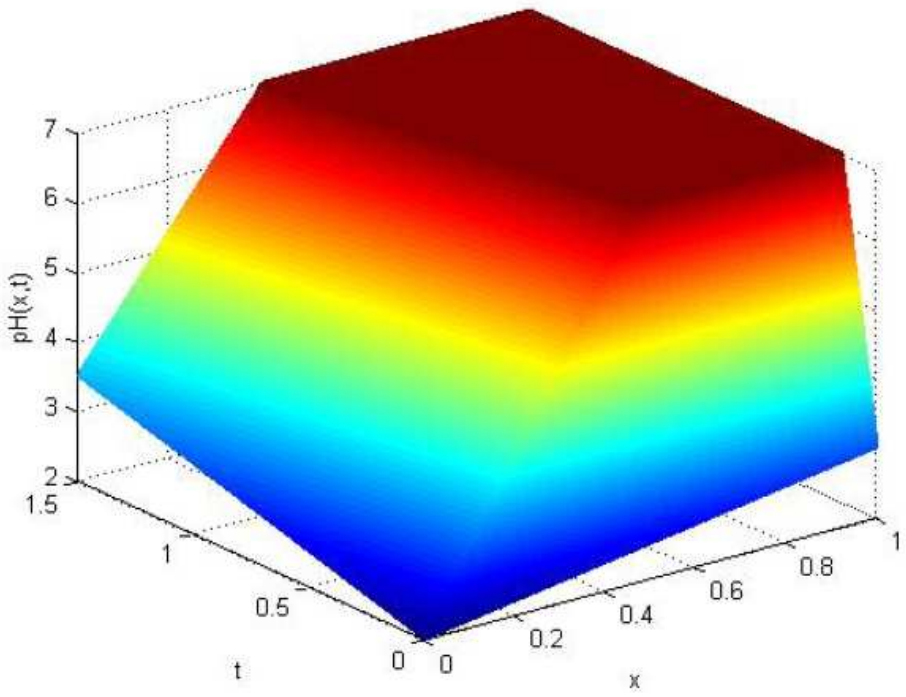
$\phi(x, 0)=\phi_0(x)$
$pH(x, 0)=pH_0(x)$
$pH(0, t)=pH_{in}(t)$

Solution: Convection time scale

$pH(x, t)=pH^{ext}_0(x-t/\phi_0)+ t^*_{conv}/t^*_{reac}.(1- \phi_0(x))^{2/3}/ \ln 10\phi_0(x),$ $t\approx O(1)$

$$pH^{ext}_0(u)= \begin{cases} pH_0(u) & u>0 \\ pH_{in}(-\phi_0 u)+t^*_{conv}/t^*_{reac}.(1- \phi_0(x))^{2/3}/ \ln 10\phi_0(x) & u<0 \end{cases}$$

Plot: Convection time scale



Consumption time scale:

$(t^*_{conv}/t^*_{CaCO3}).[(\partial\phi/\partial t - \ln 10.(\partial pH/\partial t)] - \ln 10.(\partial pH/\partial x) = -t^*_{conv}/t^*_{reac}(1-\phi)^{2/3}$

$\partial\phi/\partial t = (1-\phi)^{2/3}.10^{2-pH}$

Initial and boundary conditions:

$\phi(x, 0) = \phi_0(x)$
$pH(x, 0) = pH_0(x)$
$pH(0, t) = pH_{in}(t)$

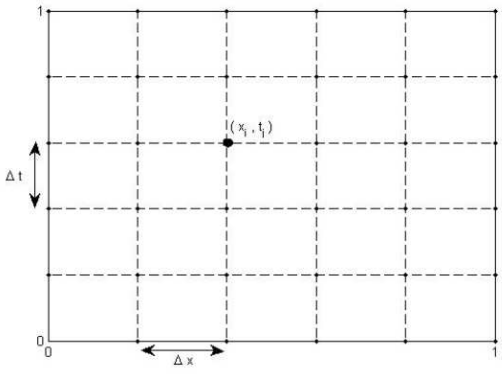
Finite difference scheme:

$pH^j_i \approx pH(x_i, t_j)$, $\phi^j_i = \phi(x_i, t_j)$

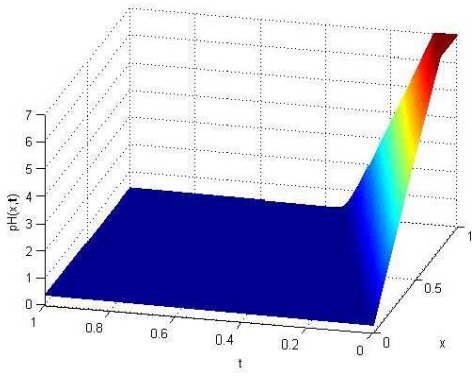
$(pH^j_{i+1} - pH^j_i)/\Delta x = t^*_{conv}/t^*_{reac}.(1/\ln 10).(1-\phi^j_i)^{2/3}$

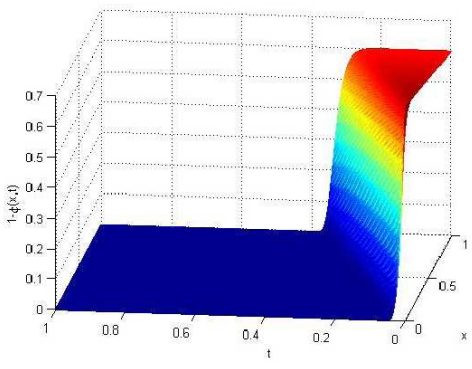
$10^{pHji}(\phi^{j+1}_i - \phi^j_i)/\Delta t = 100.(1-\phi^j_i)^{2/3}$

Finite difference grid:



Plot: Convection time scale





Advanced model:

In practice, we know ΔP^*, not q^*. By Darcy's law: $q^*-(k^*/\mu^*)(\partial p^*/\partial x^*)$
where k^* is permeability, μ^* is viscosity and p^* is pressure.

If k^*, μ^* constant, then because of incompressibility we have $q^*_{x^*} = 0$.

$$\partial^2 p^*/\partial x^{*2}=0 \quad \leftrightarrow \quad \partial^2 p^*/\partial x^*=\Delta p^*(t^*)/L^*$$

If Δp^* is constant, then $q^*$is constant and our model is consistent with Darcy's law.

Really:

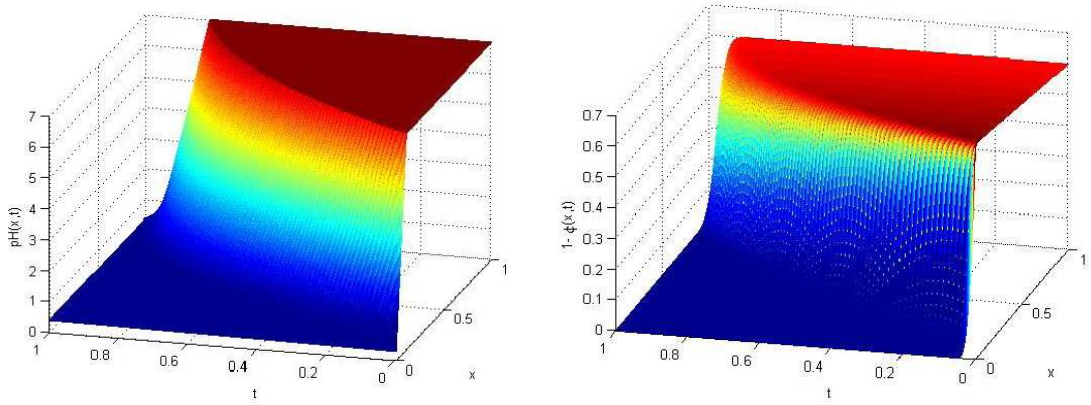
$\phi=0 \Longrightarrow k^*=0$, no permeability
ϕ increasing $\Longrightarrow k^*$, increasing

Use some correlation $k^*(\phi)=k(\phi)\, k^*_{ref}$

$$(1/t^*_{ref}).\partial\phi/\partial t+(\Delta p/t^*_{conv})(\partial c/\partial x)(\int_0^1 k^{-1}(\phi)dx)^{-1}=-1/t^*_{reac}(1-\phi)^{2/3}.c$$

$$(1/t^*_{ref}).\partial\phi/\partial t=1/t^*_{CaCO3}(1-\phi)^{2/3}.c$$

Plot: Advanced model



Conclusions

1. We know the behaviour of the system in the relevant time scales.
2. We can determine the lifetime of the cartridges using a basic or an advanced model.
3. We could develop a more precise study of $K^*(\phi)$ using experimental data based on Δp^* and K^* instead of q^*.