

## TREBALL FI DE CARRERA

### Títol

**Transport de soluts pel medi porós amb intercanvi catiònic**

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### Intensificació

**Hidrologia subterrània**

### Data

**Gener 2014**



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## **Agraïments**

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## Abstract

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Solute transport with cation exchange in groundwater is one of the predominant chemical processes existent in nature, with broad environmental implications. Presently, cation exchange is described by a series of non-linear coupled partial differential equations quite challenging to solve. Even so, this cation exchange mathematical description is not perfectly adjusted to the real behaviour observed in laboratory experiment. As an example, existing theory cannot account for the variations in concentration versus time curves observed for varying velocities. In order to find an explanation to the imbalance between the cation exchange mathematical description and reality, we have developed a new possible solution introducing an alternative to the description of transport in porous media, in particular the multirate mass transfer model.

This thesis is structured along the following lines of activity: after reviewing the existing cation exchange theories, a first computer code (in Matlab) is written. The theory of cation exchange coupled with multirate transport is developed, and finally the main features of a numerical solution to this coupled problem are proposed.





## Resum

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El transport de soluts amb intercanvi catiònic en aigües subterrànies és un dels processos químics predominants que existeixen a la natura, el qual comporta àmplies implicacions ambientals. Actualment, l'intercanvi catiònic és descrit per una sèrie d'equacions diferencials en derivades parcials no lineals difícils de resoldre. Tot i això, aquesta descripció matemàtica de l'intercanvi catiònic no s'ajusta perfectament al comportament real, observat als experiments de laboratori. A tall d'exemple, la teoria existent fins ara, no té en compte les variacions observades en la concentració en relació al temps per diferents velocitats. Per tal de trobar una explicació al desequilibri entre la descripció matemàtica d'intercanvi catiònic i la realitat, hem desenvolupat una nova solució possible introduint una alternativa a la descripció de transport en medis porosos, en particular el model de *multirate mass transfer*.

Aquesta tesi s'estructura al voltant de la següent línia de treball: després de revisar les teories existents d'intercanvi catiònic, s'escriu un primer codi d'ordinador (en Matlab). La teoria d'intercanvi catiònic juntament amb el *multirate mass transfer* es desenvolupa i, finalment, es proposen les característiques principals d'una solució numèrica per a aquest problema acoblat.



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## **1. Introduction**

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### **1.1. Motivation**

Cation exchange is a chemical process that may occur in a number of applications related to the flow of water through some porous media, whether natural or artificial. The easiest application to understand the process of cation exchange (CE) is domestic water softeners. Hard water charged of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  flows through an exchanger resin; this resin is capable of fixing these bivalent ions, releasing  $\text{Na}^+$  that stays in solution. While this is probably the most widely known application of cation exchange, other environmental and industrial applications in metallurgy, chemistry, petrochemistry, energy, as well as food and drink industries exist. In groundwater, cation exchange is one of the most common reactions it can occur since it is a very typical heterogeneous reaction involving water and rock interactions. This process is frequent because links between cations and minerals are weak and, for that, developing this exchange process is easy when other cations appear.

There are several physical theories to model this process, leading to a suite of governing non-linear partial differential equations. All of them have similar tendencies which allow being able to understand the cation exchange phenomenon properly. However, they are not able to properly fit existing experiments. Moreover, they pose a number of numerical challenges. The present work has the purpose to gather what it has been studied by now and to analyse it in a qualitative way.

This paper also introduces the multirate mass transfer (MRMT) in order to find a solution to the imbalance between existing theories of cation exchange and reality. This method is new and has never been tested.

### **1.2. Objectives**

The objectives, in a specific way, of the present work are threefold:

The first one is to gather the needed information about the cation exchange processes and driving equations; to define the main concepts and to study the existing methodologies for the solution of the equations. Here we also present a laboratory experiment to show the difficulties in the modelling process.

The second objective is to find a numerical solution for this set out problem. For that reason, a qualitative analyse is made. The idea is to prove the cation exchange theory results are slightly similar than reality and to see the changes in velocity are not properly considered in the cation exchange existing theory.

The third and last objective is to find a more approximate numerical solution to the previous defined one, introducing the concept of multirate mass transfer; developing its theory and adapting it with the existent cation exchange one. The point is, after this analysis, to be able to suggest another numerical solution in order to, in a future, find results that are closer to reality.

### **1.3. Layout**

The thesis is organized in 5 different concepts:

- A brief look at the solute transport processes in groundwater.
- A description of cation exchange related with solute transport.
- Two numerical resolutions of solute transport with cation exchange.
- A description of multi-rate mass transfer and its influence in cation exchange.
- A suggested numerical solution of the MRMT and CE theory.



## 2. Solute transport processes in groundwater

---

This section summarizes known concepts of solute transport of non-reactive substances, as an introduction to the concepts of heterogeneous reactions such as cation exchange (to be introduced in the following section).

### 2.1. Transport mechanisms

- **Advection:** process of dragging particles by the water. A solute is moved by the water with a real flux velocity  $v$ .

$$v = \frac{-q}{\emptyset} = \frac{-K}{\emptyset} \frac{\partial h}{\partial x} = \frac{-K \cdot \nabla h}{\emptyset} \quad (2.1)$$

Where:

$K$  is the permeability,

$\emptyset$  is the porosity,

$\nabla h$  is the hydraulic gradient,

and  $q$  is the specific flow.

As a consequence we can define a mass flux component :

$$\mathbf{J}_a = \mathbf{v}C\emptyset = \mathbf{q}C \quad (2.2)$$

With  $\mathbf{J}_a$  being the advection mass flux vector,  $\mathbf{v}$ ; the water velocity and  $C$ ; the solute concentration.

- **Molecular diffusion:** random molecular movement of the fluids due to concentration differences. The Fick law is used to model it.

$$\mathbf{J}_d = -\emptyset \mathbf{D}_d \tau \nabla C = -\emptyset \mathbf{D}_d^* \nabla C \quad (2.3)$$

Where:

$\mathbf{J}_d$  is the diffusion mass flux,

$\tau$  is the tortuosity,

$\mathbf{D}_d^* = D_d^* \mathbf{I}$  is the molecular diffusion tensor, assumed diagonal

and  $\nabla C$  is the concentration gradient.

- **Mechanical dispersion:** the velocity variation in space is caused by the pores geometry and their interconnections. An extension of second Fick's law is used to model this process.

$$\mathbf{J}_{md} = -\phi \mathbf{D}_m \nabla C \quad (2.4)$$

Where:

$\mathbf{J}_{md}$  is the mechanical dispersion mass flux.

$\mathbf{D}_m$  is the dispersivity tensor, potentially fully anisotropic.

- Hydrodynamic dispersion: the sum of the two processes: molecular diffusion + mechanical dispersion.

$$\mathbf{J}_h = \mathbf{J}_d + \mathbf{J}_{md} = -\phi (\mathbf{D}_d^* + \mathbf{D}_m) \nabla C = -\phi \mathbf{D} \nabla C \quad (2.5)$$

Where

$\mathbf{J}_h$  is the hydrodynamic dispersion mass flux.

$\mathbf{D}$  is the full dispersion tensor

All solutes experiment the previous three processes, but in the case of ionic elements, an additional process often occurs:

- **Adsorption:** solute fixation in the water limit layer of the solid surface. Depending on the solute attractive strength to the solid surface, this process can appear as different mechanisms: physical, electrostatic or by chemical bonding.

**Total mass flux:**

Is the sum of all mass fluxes previously defined:

$$\mathbf{J} = \mathbf{J}_a + \mathbf{J}_d + \mathbf{J}_{md} \quad (2.6)$$

## 2.2. Transport equation

### Continuity equation

Is the equation that results by applying mass conservation principles to the previously defined processes.

$$-\nabla \cdot \mathbf{J} + f = \frac{\partial(\phi C)}{\partial t} \quad (2.7)$$

$$\text{Where } \mathbf{J} = \mathbf{J}_a + \mathbf{J}_d + \mathbf{J}_{md} = \mathbf{q}C + (-\phi \mathbf{D}_d^* \nabla C) + (-\phi \mathbf{D}_m \nabla C) \quad (2.8)$$

The final resulting equation is:

$$-\nabla \cdot (\mathbf{q}C) + \nabla \cdot (-\phi \mathbf{D} \nabla C) + f = \frac{\partial(\phi C)}{\partial t} \quad (2.9)$$

Where:

$f$  is a sink/source term; corresponds either to the external mass income through the boundary or to other reaction-transfer processes,

The convective equation in the case of external recharge is:

$$-\nabla \cdot (\mathbf{q}C) + \nabla \cdot (-\phi \mathbf{D} \nabla C) + f - rC = \frac{\partial(\phi C)}{\partial t} \quad (2.10)$$

Where  $r$  comes from  $-\nabla \cdot \mathbf{q} + r = S \frac{\partial h}{\partial t} \approx \frac{\partial \phi}{\partial t}$ , water balance.

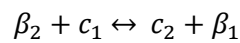
### 3. Solute transport involving cation exchange

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#### 3.1. Description

The first definition to add in this section is the cation exchange capacity (CEC), defined as the maximum quantity of cations a soil is capable of holding for exchange with the soil solution. CEC is used as an indicator of fertility, retention capacity of nutrients and protection capacity for the groundwater for cation contamination. It is expressed as centimol per Kg in SI or milliequivalent of hydrogen per 100g of dry soil. Actually the full definition involves the number of sites that are available for exchange, and thus the effect of the cation valence is significant.

The mass transfer of the cation exchange in pollutants can be described by a series of partial differential equations. To solve the system is mathematically challenging. Sanchez-Vila and Bolster (2009) propose a methodology to solve the exchange problem for two homovalent cations by employing the transport solution using the advection, dispersion and cation exchange factors. Consider two cations with equal valence and with a variable concentration in time. The complete set of equations can be found also in the same paper. Consider the following fully reversible reaction:



Where

$c_j (j = 1, 2)$  is the solute concentration [ $\text{mmolL}^{-3}$ ];

$\beta_j$  is the equivalent fraction of exchange cation [-];

The governing equations are then:

Two transport equations (mass balance) involving advection and dispersion terms but also including an additional term to account for the mass being released by the resin towards the flowing system:

$$\frac{\partial c_1}{\partial t} + \frac{\gamma}{z_1} \frac{\partial \beta_1}{\partial t} = -\mathbf{v}\nabla c_1 + \nabla(\mathbf{D}\nabla c_1) \quad (3.1)$$

$$\frac{\partial c_2}{\partial t} + \frac{\gamma}{z_2} \frac{\partial \beta_2}{\partial t} = -\mathbf{v}\nabla c_2 + \nabla(\mathbf{D}\nabla c_2) \quad (3.2)$$

Where:

$z_j$  is the valence for each solute;

$\mathbf{v}$  is the water velocity;

$\mathbf{D}$  is the dispersion tensor;

An additional definition has been included in these equations:

$$\gamma \stackrel{\text{def}}{=} CEC \frac{\rho_b}{\emptyset}$$

Where:

CEC is the cation exchange capacity [mmol/M];

$\rho_b$  is the bulk density [ML<sup>-3</sup>];

and  $\emptyset$  is the porosity.

Continuity equation (normalized  $\beta$ ):

$$\beta_1 + \beta_2 = 1 \tag{3.3}$$

indicating that all sites are always fully occupied.

Equilibrium equation:

$$K_{12} = \left(\frac{\beta_1}{c_1}\right)^{\frac{1}{z_1}} \left(\frac{c_2}{\beta_2}\right)^{\frac{1}{z_2}} \tag{3.4}$$

Where:

$K_{12}$  is an experimentally determined constant;

## **3.2. Lab experiment**

### **3.2.1. Description**

Considering the transport processes combined with the cation exchange theory, a lab experiment was done at the hydrogeology lab in UPC. From the simplest setting, a standard exchanger and a commercial resin, as much regular as possible, were used. The model of the resin is: Lewatit MonoPlus S 108 – LanXess. This was done in a column with controlled conditions. The characteristics of the synthetic resin were the following ones:

- Tridimensional macromolecular net, irregular chain of hydrocarbons with groups of  $SO_3^-$ , see figure 3.1.
- Crosslinked polystyrene matrix.
- Hydrophobic matrix, hydrophilic ionic group.
- Gel type beads
- Constant exchange capacity.
- Elastic matrix and expansible when solvent adsorption.
- Black-brown appearance.

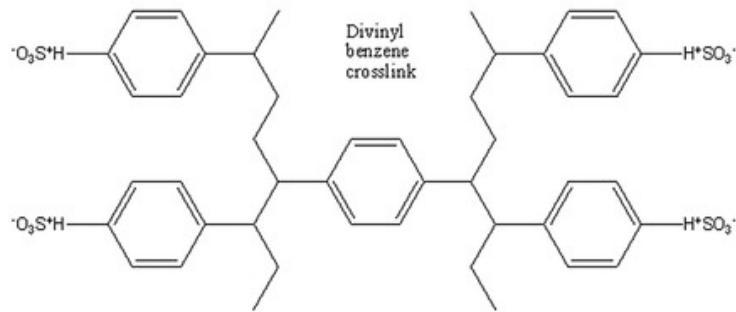


Figure 3.1: Resin's molecular structure.

Table 3.1: Physical and chemical properties of the resin Lewatit MonoPlus S 108 – LanXess

Physical and chemical properties	Metric units	Value
Uniformity coefficient	-	1.05 (+/- 0.05)
Mean bed size	mm	0.62 (+/- 0.05)
Bulk density (+/- 5%)	g/l	840
Density	approx.. g/ml	1.30
Water retention	wt. %	41 – 46
Total capacity	min. eq/l	2.2
Volume change $Na^+ \rightarrow H^+$	max. vol %	10
Stability at pH-range	-	0 – 14
Storability of the product	max. years	2
Storability temperature range	°C	-20 - 40

Table 3.1 shows the fabric characteristics of the used resin with its metric units. The uniformity coefficient, the mean bead size and the total capacity are values subjected to continuous monitoring.

As shown in figure 3.2, the system was set up by a circuit which begins with the experimental solution connecting with the column of resin. This solution goes through the column; there is a progressive exchange of the cations from the base to the top, for where the concentration is modified by the new cations. After this step, the final solution goes through the electrodes measuring pH and CE. Those electrodes are connected with a datalogger with which the results are registered.

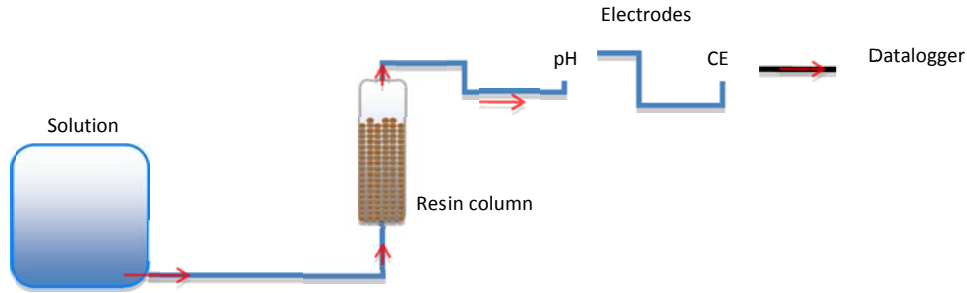
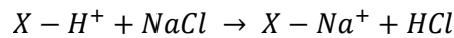


Figure 3.2: Simplified lab system.

This lab experiment was based on the following cation exchange reaction:



This is a reversible reaction but it was studied with the indicated direction. It is an exchange reaction 1 to 1 (both cations are monovalent). Water with NaCl flows through the resin containing  $H^+$  bonds. The resin fixes  $Na^+$  and releases  $H^+$ . As compared to the input water, the resulting outflow displays a higher concentration of  $H^+$ , decreasing the pH, with a lower  $Na^+$  concentration.

With time, the resin becomes  $Na^+$  saturated, becoming incapable to get more sodium. In cases like this which have an important paper in environmental implications, like water decontamination; the way to proceed is introducing water with protons to begin again the cycle.

In this process, contrast indicators of CE were used as holding parameters.

This experiment was done eleven times, each one in a different day. The initial conditions for the experiment were:

- $[NaCl]_{initial} = 1gr/l = 1.711 \times 10^{-2} mol/l$
- $pH_{initial} = 5.6$
- $[H^+]_{initial} = 2.512 \times 10^{-6} mol/l$

### 3.2.2. Results

Figure 3.3 is an example of one of the experiments done, chosen to explain the global results. This is an experiment made with H<sub>2</sub>O going through a [H<sup>+</sup>] charged resin. The incoming solution is changed by a saline solution with a concentration of 1 gr/l. Because of this change, [H<sup>+</sup>] begins to be liberated causing a big drop of the pH. These results become constant with time until the resin is saturated of the saline solution and the liberation of [H<sup>+</sup>] is declining again to a new equilibrium state. This equilibrium means that the incoming solution is equal to the outgoing one. The final equilibrium, and the resin proportion replaced, depends on the saline solution concentration and on its involving cations selectivity.

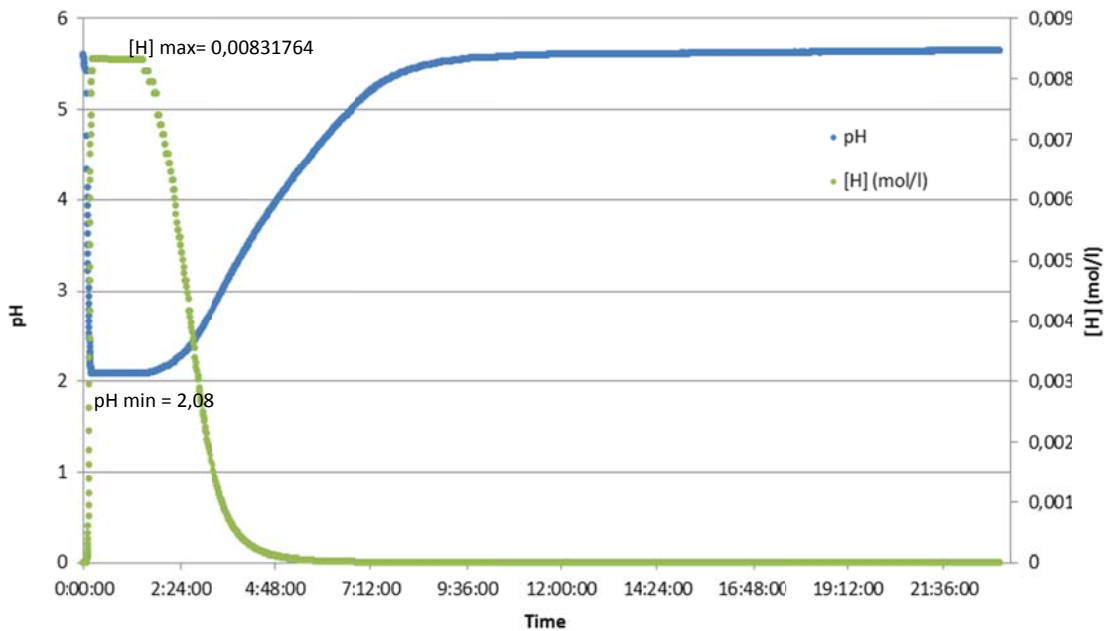


Figure 3.3: Variation of the pH and the [H<sup>+</sup>] with time. Theoretical flux velocity = 1.8mm/min, pH<sub>initial</sub>=5.6, [H<sup>+</sup>]<sub>initial</sub>=2.512x10<sup>-6</sup> mol/l and [NaCl]<sub>initial</sub>=1gr/l. Day 11.

The CE values are used to determine when the reaction reaches the equilibrium in an easier way than with the pH results. This particular system remains in equilibrium after the 7 first hours (see figure 3.4).



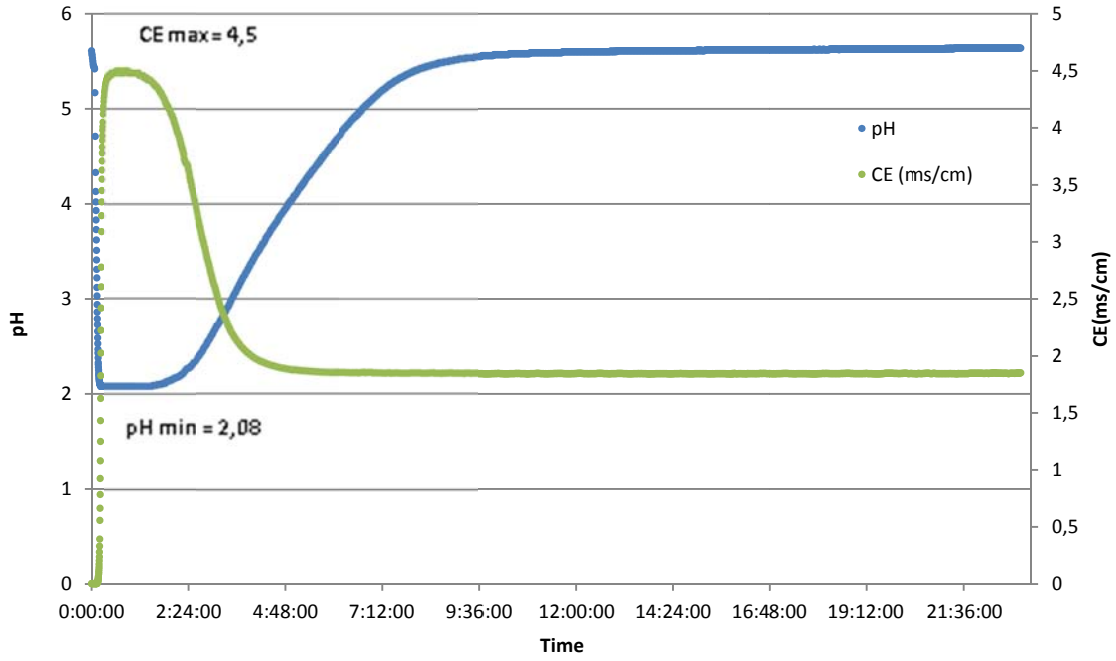


Figure 3.4: Variation of the pH and the CE with time. Theoretical flux velocity = 1.8mm/min,  $pH_{initial}=5.6$ ,  $[H^+]_{initial}=2.512 \times 10^{-6}$  mol/l and  $[NaCl]_{initial}=1$ gr/l. Day 11.

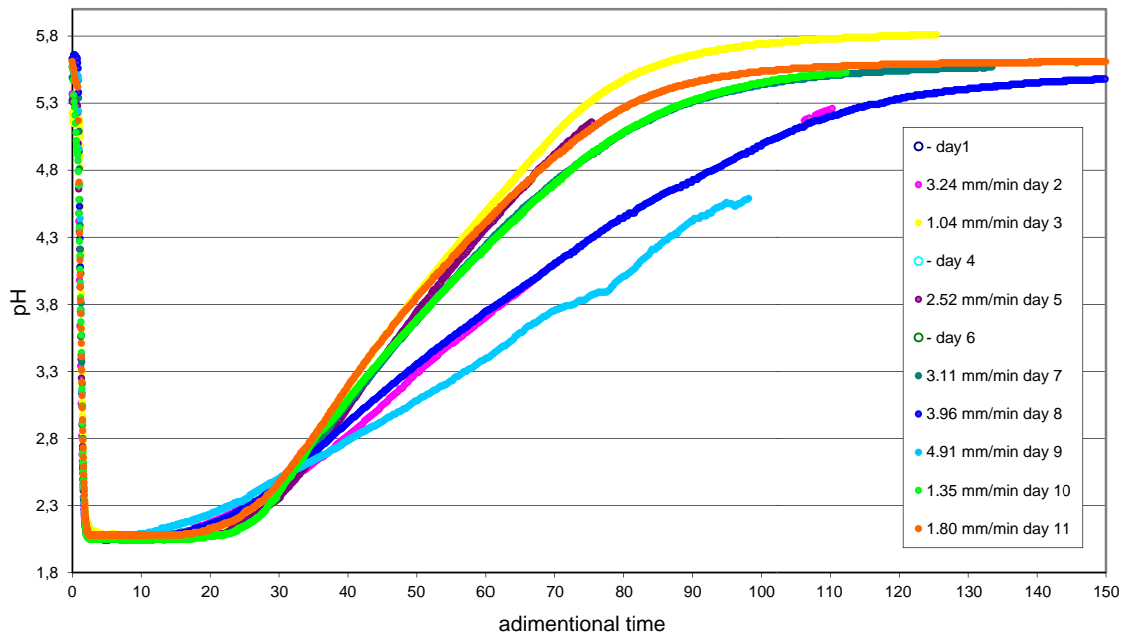


Figure 3.5: pH vs adimentional time for different velocities.

Figure 3.5 introduces another concept. Changes in the velocity affect the variation of the pH with time. Each system has a different velocity and for this reason, each of them has a different behaviour. Notice that this concept is not included in the cation exchange process, which establishes that changes in velocity do not affect the behaviour of the concentrations.

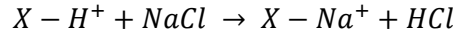
For that, a new theory appears considering the results change with different velocities. This theory is based on the introduction of the multi-rate mass transfer concept (MRMT) in the cation exchange approach/proposal which takes in consideration two different velocities, one in a mobile zone and the other in an immobile zone. The corresponding equations will be presented later in this work.

## 4. Cation exchange numerical solution with standard finite differences

### 4.1. Resolution

A combination of transport equations and cation exchange process is solved in this section to evaluate it qualitatively.

The previous defined equations of cation exchange are solved with the parameters of the reaction already presented in the lab experiment section. Notice that this is an exchange reaction 1 to 1 and for monovalent cations ( $z_1=z_2=1$ ).

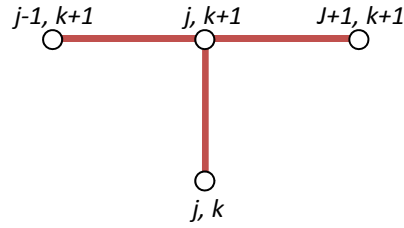


To solve the system of four equations and four unknown variables, the implicit method of finite differences is used.

a. 
$$\frac{\partial C}{\partial t} = \frac{C_j^{k+1} - C_j^k}{\Delta t}$$

b. 
$$\frac{\partial C}{\partial x} = \frac{C_{j+1}^{k+1} - C_{j-1}^{k+1}}{2\Delta x}$$

c. 
$$\frac{\partial^2 C}{\partial x^2} = \frac{C_{j+1}^{k+1} - 2C_j^{k+1} + C_{j-1}^{k+1}}{(\Delta x)^2}$$



Combining a, b and c with the equations 3.1, 3.2, 3.3 and 3.4

$$\frac{C_{1j}^{k+1} - C_{1j}^k}{\Delta t} + \gamma \frac{\beta_{1j}^{k+1} - \beta_{1j}^k}{\Delta t} = -v \frac{C_{1j+1}^{k+1} - C_{1j-1}^{k+1}}{2\Delta x} + D \frac{C_{1j+1}^{k+1} - 2C_{1j}^{k+1} + C_{1j-1}^{k+1}}{(\Delta x)^2} \quad (4.1)$$

$$\frac{C_{2j}^{k+1} - C_{2j}^k}{\Delta t} + \gamma \frac{\beta_{2j}^{k+1} - \beta_{2j}^k}{\Delta t} = -v \frac{C_{2j+1}^{k+1} - C_{2j-1}^{k+1}}{2\Delta x} + D \frac{C_{2j+1}^{k+1} - 2C_{2j}^{k+1} + C_{2j-1}^{k+1}}{(\Delta x)^2} \quad (4.2)$$

$$\beta_{1j}^{k+1} + \beta_{2j}^{k+1} = 1 \quad (4.3)$$

$$K_{12} = \frac{\beta_{1j}^{k+1} C_{2j}^{k+1}}{C_{1j}^{k+1} \beta_{2j}^{k+1}} \quad (4.4)$$

The equations are ordered having as a result:  $\mathbf{Ax}^{k+1} = \mathbf{b}^k$ , in this way the matrix  $\mathbf{A}$  remains constant. The final equations are:

$$-\left(\frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2}\right) C_{1j-1}^{k+1} + \left(1 + \frac{2D\Delta t}{(\Delta x)^2}\right) C_{1j}^{k+1} + \left(\frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2}\right) C_{1j+1}^{k+1} + \gamma\beta_{1j}^{k+1} = C_{1j}^k + \gamma\beta_{1j}^k \quad (4.5)$$

$$-\left(\frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2}\right) C_{2j-1}^{k+1} + \left(1 + \frac{2D\Delta t}{(\Delta x)^2}\right) C_{2j}^{k+1} + \left(\frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2}\right) C_{2j+1}^{k+1} + \gamma\beta_{2j}^{k+1} = C_{2j}^k + \gamma\beta_{2j}^k \quad (4.6)$$

$$\beta_{1j}^{k+1} + \beta_{2j}^{k+1} = 1 \quad (4.7)$$

$$\beta_{2j}^{k+1} = \frac{\beta_{1j}^k C_{2j}^k}{C_{1j}^k K_{12}} \quad (4.8)$$

Notice that 4.8 is slightly different from 4.4. The latter was a non-linear equation; while here it has been “linearized” supposing concentrations vary very little with time.

R, S and T are defined as:

$$R \stackrel{\text{def}}{=} -\left(\frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2}\right) \rightarrow (i, i-1)$$

$$S \stackrel{\text{def}}{=} \left(1 + \frac{2D\Delta t}{(\Delta x)^2}\right) \rightarrow (i, i)$$

$$T \stackrel{\text{def}}{=} \left(\frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2}\right) \rightarrow (i, i+1)$$

Initial conditions:

$$pH_{inicial} = 5.6$$

$$C_2' = [H^+] = 10^{-pH} = 2.512 * 10^{-6}$$

$$\beta_1' = 0.99$$

$$\beta_2' = 0.01$$

$$C_1' = \beta_1' C_2' / (K_{12} \beta_2')$$

Boundary conditions:

- Left boundary conditions:

$$C_{10} = 1.711 * 10^{-2} \text{ mol/l} = C_{1i=1}$$

$$C_{20} = 2.512 * 10^{-6} \text{ mol/l} = C_{2i=1}$$

$$\beta_{20} = 1 / (1 + K_{12} C_{10} / C_{20}) = \beta_{2i=1}$$

$$\beta_{10} = 1 - \beta_{20} = \beta_{1i=1}$$

- Right boundary conditions (Neumann):

$$-\left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2}\right) C_{i-1}^{k+1} + \left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2} + 1\right) C_i^{k+1} = C_i^k$$

$$\text{Where: } R_o \stackrel{\text{def}}{=} -\left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2}\right) \text{ and } S_o \stackrel{\text{def}}{=} \left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2} + 1\right)$$

Once the equations are defined as well as the initial and boundary conditions, they have been programmed with Matlab to obtain the problem solution  $\mathbf{A}\mathbf{c}^{k+1} = \mathbf{b}^k$ . The following system is representative of this solution.

Matrix  $\mathbf{A}$   $\times$  vector  $\mathbf{c}^{k+1}$ :

$$\begin{array}{l}
 (1) \quad 1 \quad 0 \quad 0 \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad 0 \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad C1(i=1) \\
 (2) \quad R \quad S \quad T \quad \ddots \quad \vdots \quad \vdots \quad \dots \quad \dots \quad \dots \quad \vdots \quad 0 \quad \gamma \quad \ddots \quad \vdots \quad \vdots \quad \dots \quad \dots \quad \dots \quad \vdots \quad \vdots \\
 \vdots \quad 0 \quad \ddots \quad \ddots \quad \ddots \quad 0 \quad \vdots \quad \vdots \quad \vdots \quad \ddots \quad \ddots \quad \ddots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\
 (TN-1) \quad \vdots \quad \ddots \quad R \quad S \quad T \quad \vdots \quad \vdots \quad \vdots \quad \ddots \quad \gamma \quad 0 \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\
 (TN) \quad 0 \quad \dots \quad 0 \quad Ro \quad So \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad 0 \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad C1(i=TN) \\
 (TN+1) \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 1 \quad 0 \quad 0 \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad 0 \quad \dots \quad \dots \quad 0 \quad C2(i=TN+1) \\
 (TN+2) \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad R \quad S \quad T \quad \ddots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad 0 \quad \gamma \quad \ddots \quad \vdots \quad \vdots \quad \vdots \\
 \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad 0 \quad \ddots \quad \ddots \quad \ddots \quad 0 \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \ddots \quad \ddots \quad \ddots \quad \vdots \quad \vdots \quad \vdots \\
 (2TN-1) \quad \vdots \quad \vdots \quad \vdots \quad \ddots \quad R \quad S \quad T \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \ddots \quad \gamma \quad 0 \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\
 (2TN) \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad 0 \quad Ro \quad So \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad 0 \quad 0 \quad C2(i=2TN) \\
 (2TN+1) \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 1 \quad 0 \quad \dots \quad \dots \quad 0 \quad 0 \quad 0 \quad \dots \quad \dots \quad 0 \quad \beta1(i=2TN+1) \\
 (2TN+2) \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad 0 \quad \ddots \quad \ddots \quad \vdots \quad \vdots \quad 0 \quad 1 \quad \ddots \quad \vdots \quad \vdots \\
 \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \ddots \quad \ddots \quad \ddots \quad \vdots \quad \vdots \quad \ddots \quad \ddots \quad \ddots \quad \vdots \quad \vdots \\
 (3TN-1) \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad 0 \quad \ddots \quad \ddots \quad 0 \quad \vdots \quad \ddots \quad \ddots \quad 0 \quad \vdots \\
 (3TN) \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad 0 \quad 1 \quad 0 \quad \dots \quad \dots \quad 0 \quad 1 \quad \beta1(i=3TN) \\
 (3TN+1) \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 1 \quad 0 \quad \dots \quad \dots \quad 0 \quad \beta2(i=3TN+1) \\
 (3TN+2) \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad 0 \quad \ddots \quad \ddots \quad \vdots \quad \vdots \\
 \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \ddots \quad \ddots \quad \ddots \quad \vdots \quad \vdots \\
 (4TN-1) \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad 0 \quad \ddots \quad \ddots \quad 0 \quad \vdots \\
 (4TN) \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad \dots \quad 0 \quad 0 \quad \dots \quad \dots \quad 0 \quad 1 \quad \beta2(i=4TN)
 \end{array}$$

This is a matrix composed by 4TNx4TN multiplied by its unknowns, where TN is the total number of nodes and it goes from  $i=1$  to  $i=TN$ . The column in the left shows the number of rows and their positions, those numbers are the same for every column, which are not written. So the matrix has 4TN equations and 4TN unknowns ( $C1(i), C2(i), \beta1(i)$  and  $\beta2(i)$ ). For that, it involves 4 rows  $\times$  4 columns of different submatrices each of them referred to one unknown. The vector  $\mathbf{b}^k$ , written below is the result of the product  $\mathbf{A}\mathbf{c}^{k+1}$ .

Vector  $\mathbf{b}^k$ :

$$\begin{array}{c}
 C1o \\
 C1(i = 2) + \gamma\beta1(i = 2) \\
 \vdots \\
 C1(i = TN - 1) + \gamma\beta1(i = TN - 1) \\
 C1(i = TN) \\
 C2o \\
 C2(i = TN + 2) + \gamma\beta2(i = TN + 2) \\
 \vdots \\
 C2(i = 2TN - 1) + \gamma\beta2(i = 2TN - 1) \\
 C2(i = 2TN) \\
 \beta1o \\
 1 \\
 \vdots \\
 \vdots \\
 1 \\
 \beta2o \\
 \beta1(i = 3TN + 2) \cdot C2(i = 3TN + 2) / (K12 \cdot C1(i = 3TN + 2)) \\
 \vdots \\
 \beta1(i = 4TN - 1) \cdot C2(i = 4TN - 1) / (K12 \cdot C1(i = 4TN - 1)) \\
 \beta1(i = 4TN) \cdot C2(i = 4TN) / (K12 \cdot C1(i = 4TN))
 \end{array}$$

Each boundary condition is applied to every first and last line of each submatrix. That is:

- The left boundary conditions are applied in the rows  $1, TN+1, 2TN+1$  and  $3TN+1$  of the whole matrix:

Row  $1$ , column  $1 \rightarrow C1^{k+1} = C1o_{(constant)}$ , so that  $A_{(1,1)} = 1$ , and  $b_{(1)}^k = C1o$ .

Row  $TN+1$ , column  $TN+1 \rightarrow C2^{k+1} = C2o_{(constant)}$ , so that  $A_{(TN+1,TN+1)} = 1$  and  $b_{(TN+1)}^k = C2o$ .

Row  $2TN+1$ , column  $2TN+1 \rightarrow \beta1^{k+1} = \beta1o_{(constant)}$ , so that  $A_{(2TN+1,2TN+1)} = 1$  and  $b_{(2TN+1)}^k = \beta1o$ .

Row  $3TN+1$ , column  $3TN+1 \rightarrow \beta2^{k+1} = \beta2o_{(constant)}$ , so that  $A_{(3TN+1,3TN+1)} = 1$  and  $b_{(3TN+1)}^k = \beta2o$ .

- The right boundary conditions are applied in the rows  $TN$  and  $2TN$  of the whole matrix:

Row  $TN \rightarrow R_o C1_{(TN,TN-1)}^{k+1} + S_o C1_{(TN,TN)}^{k+1} = C1_{(TN,1)}^k$ , so that  $A_{(TN,TN-1)} = R_o$ ,  $A_{(TN,TN)} = S_o$  and  $b_{(TN)}^k = C1_{(TN,1)}^k$ .

Row  $2TN \rightarrow R_o C2_{(2TN,2TN-1)}^{k+1} + S_o C2_{(2TN,2TN)}^{k+1} = C2_{(2TN,1)}^k$ , so that  $A_{(2TN,2TN-1)} = R_o$ ,  $A_{(2TN,2TN)} = S_o$  and  $b_{(2TN)}^k = C2_{(2TN,1)}^k$ .

Notice that in the rows  $3TN$  and  $4TN$  no right boundary conditions are applied, indicating mass continuity.

## 4.2. Results

The solution of this numerical problem is programmed in Matlab (see annex 1). Once the code is written, the following step is to evaluate the results and how they change with the variation of parameters. The ones used for the modelling are presented in table 4.1.

Table 4.1: Used values for the different parameters involved in the solution of the full system of equations.

Velocity	1.8 mm/min
Dispersion coefficient	0.0001
Length of domain	1 dm
Time	15h
Reaction rate coefficient ( $K_{12}$ )	0.2
Cation exchange capacity	$10^{-5}$ mol/g
Porosity	0.2
Bulk density	840 g/dm <sup>3</sup>
$\gamma' = \text{CEC} \cdot \text{bulk density} / \text{porosity}$	0.042
$\gamma$	0.0003
Total nodes	101
Total time	3010
$\Delta x$	0.01
$\Delta t$	0.2991

In the table 4.1 it is shown that in the numerical model we had to use a value of  $\gamma$  that is extremely low, and that it does not correspond to the one based on data for the resin supplied by the provider. The problem is just numerical since the non-linearities result in a divergent problem when  $\gamma'$  exceeds 0.0003 in order to work with a convergent problem.

Figure 4.1 shows the results of the four concentrations at the last node as a function of time. Notice that the ones for the flowing concentrations are equal to the ones that would be recorded at the outlet.

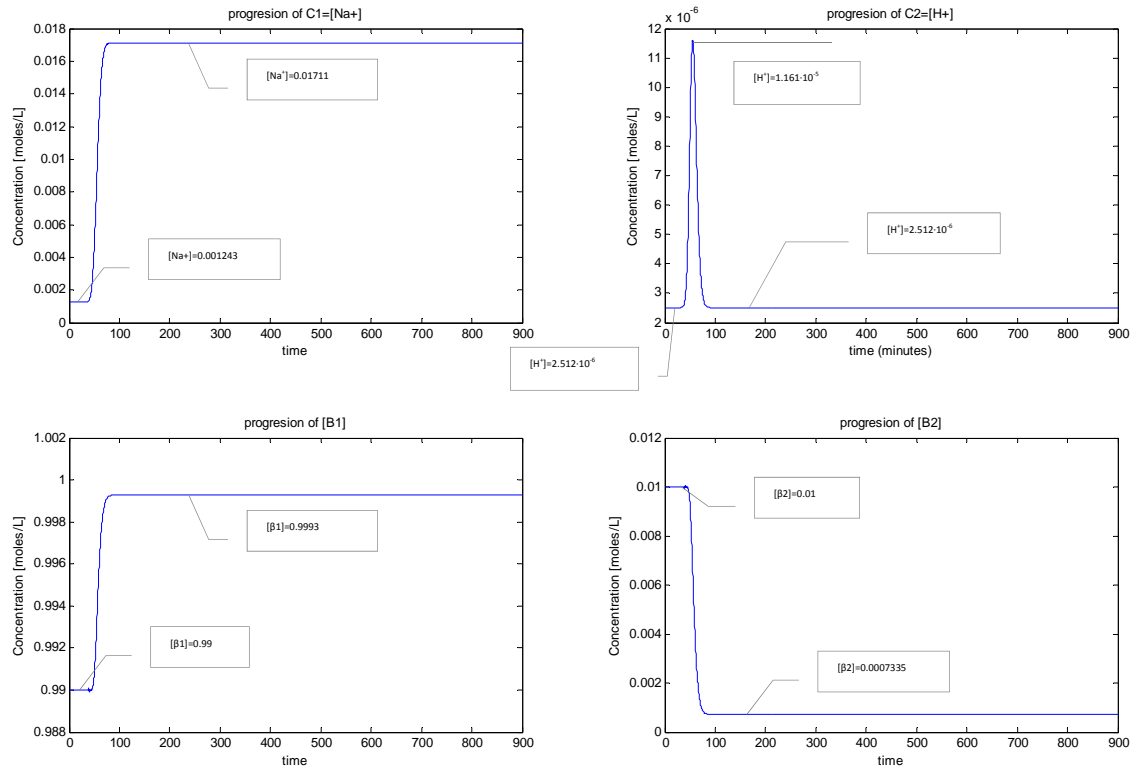


Figure 4.1: Variation of the concentration of Na+, H+,  $\beta_1$  and  $\beta_2$  with time [min] in the last node.

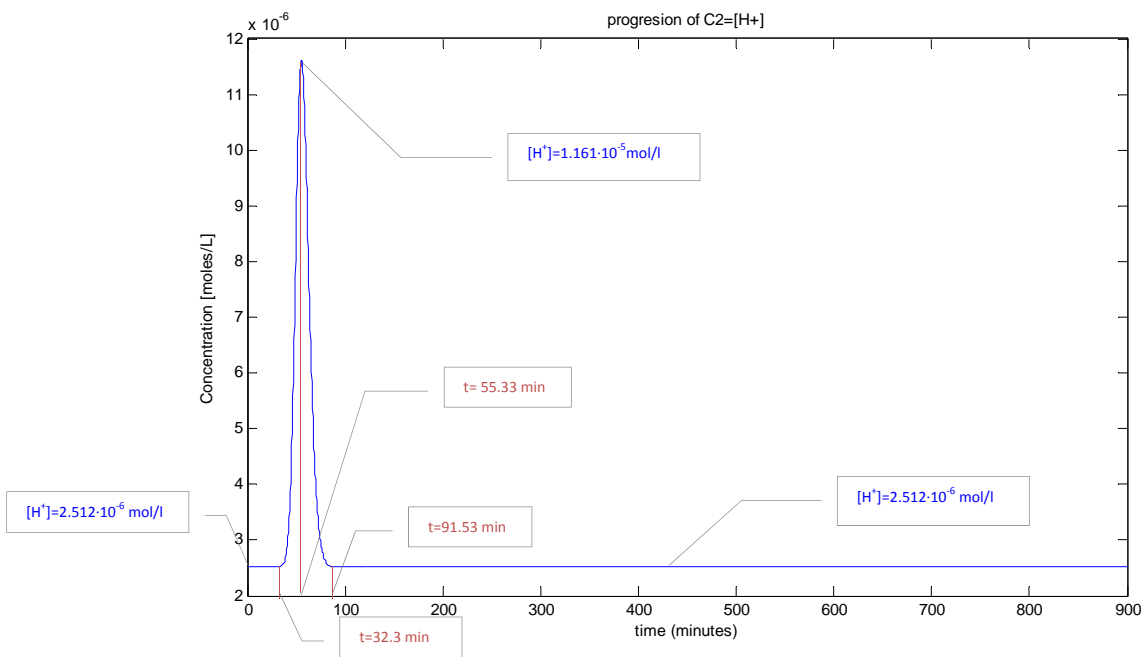


Figure 4.2: Variation of  $[H^+]$  with time in the last node.



Figure 4.2 shows just the behaviour of the concentration of  $H^+$  with the time in the last node to be able to evaluate the result.

The considered value of  $\gamma$  has been found in order to have a problem which converges. The tendency of the curve is the same than the one expected. The concentration of  $H^+$  is  $2.51 \cdot 10^{-6}$  mol/l at the beginning and it begins to grow after 29.9 minutes. It reaches its top in the minute 55.3 with a value of  $1.16 \cdot 10^{-5}$ . It means also that the pH decreases. After this peak, it drops until becoming stable in the minute 95.9 (1h36min) with the same value than the beginning  $2.51 \cdot 10^{-6}$  mol/l.

## 5. Cation exchange numerical solution with operator splitting

### 5.1. Operator splitting concept

The same problem is now solved with **operator splitting techniques**. This method is used to try to solve convergence problems that have appeared with the previous model. This is a strategy which consists in decomposing PDEs (partial differential equations), whose systems are difficult to handle, into simpler subproblems in order to treat them individually using specialized numerical algorithms.

### 5.2. Resolution

The advection-dispersion equations are a first subproblem (from equation 3.1 and 3.2):

$$\frac{\partial c_1}{\partial t} = -\mathbf{v}\nabla c_1 + \nabla(\mathbf{D}\nabla c_1) \quad (5.1)$$

$$\frac{\partial c_2}{\partial t} = -\mathbf{v}\nabla c_2 + \nabla(\mathbf{D}\nabla c_2) \quad (5.2)$$

Using the implicit method and the operator splitting:

$$\frac{C_{1j}^{k+1/2} - C_{1j}^k}{\Delta t} = -v \frac{C_{1j+1}^{k+1/2} - C_{1j-1}^{k+1/2}}{2\Delta x} + D \frac{C_{1j+1}^{k+1/2} - 2C_{1j}^{k+1/2} + C_{1j-1}^{k+1/2}}{(\Delta x)^2} \quad (5.3)$$

$$\frac{C_{2j}^{k+1/2} - C_{2j}^k}{\Delta t} = -v \frac{C_{2j+1}^{k+1/2} - C_{2j-1}^{k+1/2}}{2\Delta x} + D \frac{C_{2j+1}^{k+1/2} - 2C_{2j}^{k+1/2} + C_{2j-1}^{k+1/2}}{(\Delta x)^2} \quad (5.4)$$

Operating with the equations 5.3 and 5.4 and using  $\mathbf{A}\mathbf{c}^{k+1/2} = \mathbf{b}^k$  as a problem solution, the final system of 2 equations and 2 unknowns is:

$$-\left(\frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2}\right) C_{1j-1}^{k+1/2} + \left(1 + \frac{2D\Delta t}{(\Delta x)^2}\right) C_{1j}^{k+1/2} + \left(\frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2}\right) C_{1j+1}^{k+1/2} = C_{1j}^k \quad (5.5)$$

$$-\left(\frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2}\right) C_{2j-1}^{k+1/2} + \left(1 + \frac{2D\Delta t}{(\Delta x)^2}\right) C_{2j}^{k+1/2} + \left(\frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2}\right) C_{2j+1}^{k+1/2} = C_{2j}^k \quad (5.6)$$

The cation exchange concept is now considered. The equations used are the 3.3th and 3.4th previously defined. Using the implicit method and the operator splitting the second subproblem is presented:

$$\beta_{1j}^{k+1/2} = \frac{K_{12}C_{1j}^{k+1/2}}{K_{12}C_{1j}^{k+1/2} + C_{2j}^{k+1/2}} \quad (5.7)$$

$$\beta_{2j}^{k+1/2} = 1 - \beta_{1j}^{k+1/2} \quad (5.8)$$

The next step is to hitch both subproblems using part of the equations number 3.1 and 3.2:

$$\frac{\partial c_1}{\partial t} = -\gamma \frac{\partial \beta_1}{\partial t} \quad (5.9)$$

$$\frac{\partial c_2}{\partial t} = -\gamma \frac{\partial \beta_2}{\partial t} \quad (5.10)$$

Exchanging derivatives by increments:

$$\frac{C_{1j}^{k+1} - C_{1j}^{k+1/2}}{\Delta t} = -\gamma \frac{\beta_{1j}^{k+1/2} - \beta_{1j}^k}{\Delta t} \quad (5.11)$$

$$\frac{C_{2j}^{k+1} - C_{2j}^{k+1/2}}{\Delta t} = -\gamma \frac{\beta_{2j}^{k+1/2} - \beta_{2j}^k}{\Delta t} \quad (5.12)$$

And finally:

$$C_{1j}^{k+1} = C_{1j}^{k+1/2} - \gamma(\beta_{1j}^{k+1/2} - \beta_{1j}^k) \quad (5.13)$$

$$C_{2j}^{k+1} = C_{2j}^{k+1/2} - \gamma(\beta_{2j}^{k+1/2} - \beta_{2j}^k) \quad (5.14)$$

R, S and T are defined as:

$$R \stackrel{\text{def}}{=} -\left(\frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2}\right) \rightarrow (i,i-1)$$

$$S \stackrel{\text{def}}{=} \left(1 + \frac{2D\Delta t}{(\Delta x)^2}\right) \rightarrow (i,i)$$

$$T \stackrel{\text{def}}{=} \left(\frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2}\right) \rightarrow (i,i+1)$$

Initial conditions:

$$pH_{\text{initial}} = 5.6$$

$$C_{2j}' = [H^+] = 10^{-pH} = 2.512 * 10^{-6}$$

$$\beta_{1j}' = 0.99$$

$$\beta_2' = 0.01$$

$$C_1' = \beta_1' C_2' / (K_{12} \beta_2')$$

Boundary conditions:

- Left boundary conditions:

$$C_{10} = 1.711 * 10^{-2} \text{ mol/l} = C_{1i=1}$$

$$C_{20} = 2.512 * 10^{-6} \text{ mol/l} = C_{2i=1}$$

- Right boundary conditions (Neumann):

$$-\left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2}\right) C_{i-1}^{k+1/2} + \left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2} + 1\right) C_i^{k+1/2} = C_i^k$$

$$\text{Where: } R_o \stackrel{\text{def}}{=} -\left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2}\right) \text{ and } S_o \stackrel{\text{def}}{=} \left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2} + 1\right)$$

### 5.3. Results

The results obtained by this method are found modelling it with Matlab (see annex 2). Unfortunately the behaviour of the variation of the concentration of each specie with time is slightly similar than the one appeared with the finite differences resolution. All the parameters are the same than with finite differences. This means a numerical problem keeps existing in order to be able to increase the parameter  $\gamma$ . The way to proceed, to have the tools to match the results as the reality, would be with a more sophisticated numerical method.

In any case, solving the theory of cation exchange with transport equations with operator splitting is also possible and effective for low values of  $\gamma$ .

## **6. MRMT (Multiple-Rate Mass Transfer) model**

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### **6.1. Introduction to MRMT**

In general, the multirate mass transfer between mobile and immobile contaminant zones correspond to small-scale variation in the aquifer properties. These properties involve the following aspects (Haggerty and Gorelick, 1995):

- The types of minerals and their spatial distribution;
- the geometry, the chemical and mineralogical composition of coatings on the aquifer particles surface;
- the volume, the size and the geometry of the macro or microporosity of the aquifer particles and of their aggregates;
- the external and internal geometry of the low permeability materials and its proportions;
- the hydraulic conductivity variations inside the aquifer;
- and the chemical composition of the water and the contaminant.

There are definitely many media properties which can influence mass transfer. However, the existing models just had into account one small-scale transfer process. For that reason a model predicting a mass transfer process in heterogeneous and complex aquifers was unlikely.

### **6.2. Conceptual model**

Villermaux [1981] described the mass transfer between a mobile zone and different immobile zones with properties variations, and it is coupled with the transport model of advection-dispersion for a solute. Haggerty and Gorelick [1995] expanded this model to a subsurface transport modelling of the contaminant and the equivalence to the diffusion models of mass transfer in a reduced way was showed. The total mass transfer in the system can be any combination either of the first order transfer reaction, or of the diffusion of the spheres, cylinders and layers.

The figure 6.1a (extracted from Haggerty and Gorelick, 1995) shows a multi-mass transfer process in a porous medium. At the grain scale, on the right site of the figure, a dissolve compound being able to be situated in stagnant water zones (site-pockets) or in stagnant

zones around the grains is shown. Fractures and pores inside particles are also the cause of the slow diffusion. Moreover, the component might be adsorbed to any mineral surfaces and mineral coatings.

The figure 6.1b represents the multi-mas transfer model in which all the parameters of figure 8a are modelled by multirate equations. At the grain scale it is shown how the inside and outside grain diffusion is modelled by spherical diffusion and how the surface sorption reactions are modelled by a first order linear equation.

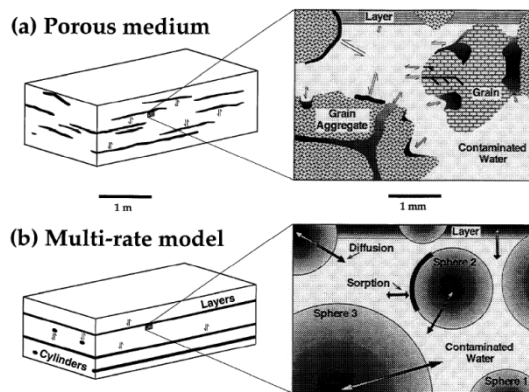


Figure 6.1: a. Illustration of a porous medium with heterogeneous mass transfer processes. b. Illustration of a multirate mass transfer model describing various mass transfer processes. (Haggerty and Gorelick, 1995)

### 6.3. Mathematical model

Transport equation for a non-conservative solute  $C_1$  (1D) involves advection-dispersion with an additional term to account for transfer between the mobile and the immobile phases described in Figure 6.1:

$$\frac{\partial C_1}{\partial t} = -v \frac{\partial C_1}{\partial x} + D \frac{\partial^2 C_1}{\partial x^2} + \mathcal{L} \quad (6.1)$$

Where  $\mathcal{L}$  is the non-conservative part

$D$  is the dispersion tensor [ $L^2/T$ ]

$v$  is the velocity [ $L/T$ ]

$C_1$  is the solute concentration.

The solute concentration depends on space and time  $C_1(x, t)$ . The concentration of a single point  $x$  is divided into two; a mobile  $C_{1m}$  and an immobile  $C_{1im}$  part. This concept can be explained like this:

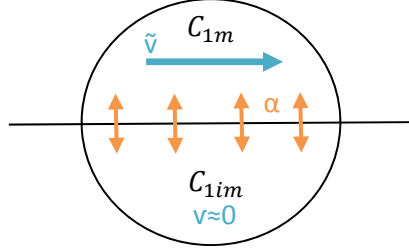


Figure 6.2: Diagram of the division of the concentration of a single point in a solute, with exchange between phases.

In figure 6.2, the velocity of the mobile zone is much higher than the one in the immobile zone. For this reason the velocity in the immobile part is supposed to be zero for practical purposes. The units of the  $\alpha$  factor (mass transfer coefficient) are  $t^{-1}$  so, if it is related with a distance it ends to be a velocity. This factor depends on the concentration, which at the same time it will depend on the porosity, for both zones. That is, if the concentration of the mobile zone is higher than the one in the immobile zone, a velocity of concentration transfer will exist from the immobile to the mobile zone.

It is established that:  $\phi_T C_1 = \phi_m C_{1m} + \phi_{im} C_{1im}$  and  $\phi_T = \phi_m + \phi_{im}$

Once the concept is explained the non-conservative part of the equation is completed in the following way:

Multirate solute transport equation:

$$\frac{\partial c_m}{\partial t} + \sum_{j=1}^N \beta_j \frac{\partial (c_{im})_j}{\partial t} = \mathcal{L}(c_m) \quad (6.2)$$

Mass transfer equation:

$$\frac{\partial (c_{im})_j}{\partial t} = \alpha_j [c_m - (c_{im})_j], \quad j = 1, 2, \dots, N \quad (6.3)$$

Where:  $\alpha_j = \alpha'_j / (R_{im})_j$

The relationship between the total contaminant mass in the mobile and the immobile zone is:

$$\sum_{j=1}^N \beta_j = \sum_{j=1}^N \frac{(R_{im})_j (\phi_{im})_j}{R_m \phi_m} = \beta \quad (6.4)$$

The retardation factor for the mobile zone:  $R_m = 1 + \frac{\rho_b K_{a,m} f_m}{\phi_m}$

The retardation factor for the immobile zone:  $R_{im} = 1 + \frac{\rho_b K_{(a,im)_j} (f_m)_j}{(\phi_{im})_j}$

In this case it is known that the retardation factors  $R_m$  and  $R_{im}$  are 1, so  $\sum_{j=1}^N \frac{(\phi_{im})_j}{\phi_m} = \beta$

Where:

$\mathcal{L}$  is the non-conservative part.

$\phi$  is the porosity.

$C_1$  is the solute concentration [M/L<sup>3</sup>].

The subscripts  $m$  and  $im$  correspond to the mobile and immobile zone.

$\beta$  is the total capacity of all the immobile zones together.

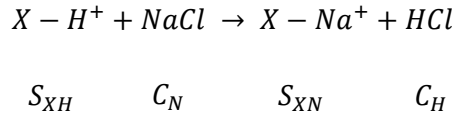


## 7. Combination MRMT with cation exchange in transport processes

### 7.1. Resolution

In this section a method based in finite differences is exposed in order to be able to model the problem of MRMT + cation exchange using Matlab. Combining the cation exchange model with the MRMT the final system of equations involves up to 10 equations.

We start with a new notation. In this case,  $\beta = \frac{SX}{CEC}$ .  $\beta$  was normalized.



The ten equations that must be solved together are:

$$\frac{\partial C_{Hm}}{\partial t} + \beta \frac{\partial C_{Him}}{\partial t} = -v \frac{\partial C_{Hm}}{\partial x} + D \frac{\partial^2 C_{Hm}}{\partial x^2} + r_m \quad (7.1)$$

$$\frac{\partial C_{Nm}}{\partial t} + \beta \frac{\partial C_{Nim}}{\partial t} = -v \frac{\partial C_{Nm}}{\partial x} + D \frac{\partial^2 C_{Nm}}{\partial x^2} - r_m \quad (7.2)$$

$$\frac{\partial C_{Him}}{\partial t} = \alpha(C_{Hm} - C_{Him}) + r_{im} \quad (7.3)$$

$$\frac{\partial C_{Nim}}{\partial t} = \alpha(C_{Nm} - C_{Nim}) - r_{im} \quad (7.4)$$

$$K = \frac{C_{Hm} S_{XNm}}{C_{Nm} S_{XHm}} \quad (7.5)$$

$$K = \frac{C_{Him} S_{XNim}}{C_{Nim} S_{XHim}} \quad (7.6)$$

$$r_m = -\frac{\partial S_{XHm}}{\partial t} \quad (7.7)$$

$$r_{im} = -\frac{\partial S_{XHim}}{\partial t} \quad (7.8)$$

$$S_{XHm} + S_{XNm} = CEC_m \quad (7.9)$$

$$S_{XHim} + S_{XNim} = CEC_{im} \quad (7.10)$$

From those 10 equations with 10 unknown variables; two are partial differential equations, four; ordinary differential equations and four equilibrium equations. The solution is really challenging.

The first idea is to operate mathematically and reduce them to 6 equations with 6 unknown variables:

Combining equations 7.1 and 7.7:

$$\frac{\partial C_{Hm}}{\partial t} + \beta \frac{\partial C_{Him}}{\partial t} = -v \frac{\partial C_{Hm}}{\partial x} + D \frac{\partial^2 C_{Hm}}{\partial x^2} - \frac{\partial S_{XHm}}{\partial t} \quad (7.11)$$

Combining equations 7.2 and 7.7:

$$\frac{\partial C_{Nm}}{\partial t} + \beta \frac{\partial C_{Nim}}{\partial t} = -v \frac{\partial C_{Nm}}{\partial x} + D \frac{\partial^2 C_{Nm}}{\partial x^2} + \frac{\partial S_{XHm}}{\partial t} \quad (7.12)$$

Combining equations 7.3 and 7.8:

$$\frac{\partial C_{Him}}{\partial t} = \alpha(C_{Hm} - C_{Him}) - \frac{\partial S_{XHim}}{\partial t} \quad (7.13)$$

Combining equations 7.4 and 7.8:

$$\frac{\partial C_{Nim}}{\partial t} = \alpha(C_{Nm} - C_{Nim}) + \frac{\partial S_{XHim}}{\partial t} \quad (7.14)$$

Combining equations 7.5 and 7.9:

$$K = \frac{C_{Hm}(CE C_m S_{XHm})}{C_{Nm} S_{XHm}} \quad (7.15)$$

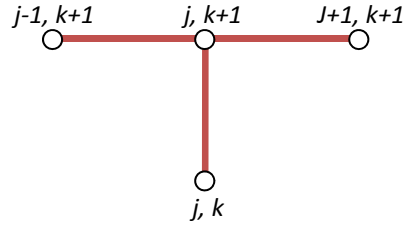
Combining equations 7.6 and 7.10:

$$K = \frac{C_{Him}(CE C_{im} S_{XHim})}{C_{Nim} S_{XHim}} \quad (7.16)$$

Once these six equations are fully solved, the remaining four unknowns are directly obtained by explicit expressions.

The implicit method of finite differences is used to solve this system of 6 equations and 6 unknown variables. In the same way than before:

- a.  $\frac{\partial C}{\partial t} = \frac{C_j^{k+1} - C_j^k}{\Delta t}$
- b.  $\frac{\partial C}{\partial x} = \frac{C_{j+1}^{k+1} - C_{j-1}^{k+1}}{2\Delta x}$
- c.  $\frac{\partial^2 C}{\partial x^2} = \frac{C_{j+1}^{k+1} - 2C_j^{k+1} + C_{j-1}^{k+1}}{(\Delta x)^2}$



Replacing a, b and c to the equations 7.11 to 7.16:

$$\frac{C_{Hmj}^{k+1} - C_{Hmj}^k}{\Delta t} + \beta \frac{C_{Himj}^{k+1} - C_{Himj}^k}{\Delta t} = -v \frac{C_{Hmj+1}^{k+1} - C_{Hmj-1}^{k+1}}{2\Delta x} + D \frac{C_{Hmj+1}^{k+1} - 2C_{Hmj}^{k+1} + C_{Hmj-1}^{k+1}}{(\Delta x)^2} - \frac{S_{XHmj}^{k+1} - S_{XHmj}^k}{\Delta t} \quad (7.17)$$

$$\frac{C_{Nmj}^{k+1} - C_{Nmj}^k}{\Delta t} + \beta \frac{C_{Nimj}^{k+1} - C_{Nimj}^k}{\Delta t} = -v \frac{C_{Nmj+1}^{k+1} - C_{Nmj-1}^{k+1}}{2\Delta x} + D \frac{C_{Nmj+1}^{k+1} - 2C_{Nmj}^{k+1} + C_{Nmj-1}^{k+1}}{(\Delta x)^2} - \frac{S_{XHmj}^{k+1} - S_{XHmj}^k}{\Delta t} \quad (7.18)$$

$$\frac{C_{Himj}^{k+1} - C_{Himj}^k}{\Delta t} = \alpha (C_{Hmj}^{k+1} - C_{Hmj}^k) - \left( \frac{S_{XHimj}^{k+1} - S_{XHimj}^k}{\Delta t} \right) \quad (7.19)$$

$$\frac{C_{Nimj}^{k+1} - C_{Nimj}^k}{\Delta t} = \alpha (C_{Nmj}^{k+1} - C_{Nmj}^k) + \frac{S_{XHimj}^{k+1} - S_{XHimj}^k}{\Delta t} \quad (7.20)$$

$$K = \frac{C_{Hmj}^k (CEC_m - S_{XHmj}^{k+1})}{C_{Nmj}^k S_{XHmj}^{k+1}} \quad (7.21)$$

$$K = \frac{C_{Himj}^k (CEC_{im} - S_{XHimj}^{k+1})}{C_{Nimj}^k S_{XHimj}^{k+1}} \quad (7.22)$$

The equations are written in the following way in order to have a final result like  $\mathbf{A}\mathbf{c}^k = \mathbf{b}^k$ , for that, the matrix  $\mathbf{A}$  remains constant. The final equations are:

$$\left( \frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2} \right) C_{Hmj+1}^{k+1} - \left( \frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2} \right) C_{Hmj-1}^{k+1} + \left( 1 + \frac{2D\Delta t}{(\Delta x)^2} \right) C_{Hmj}^{k+1} + \beta C_{Himj}^{k+1} + S_{XHmj}^{k+1} = \beta C_{Himj}^k + S_{XHmj}^k + C_{Hmj}^k \quad (7.23)$$

$$\left( \frac{v\Delta t}{2\Delta x} - \frac{D\Delta t}{(\Delta x)^2} \right) C_{Nmj+1}^{k+1} - \left( \frac{v\Delta t}{2\Delta x} + \frac{D\Delta t}{(\Delta x)^2} \right) C_{Nmj-1}^{k+1} + \left( 1 + \frac{2D\Delta t}{(\Delta x)^2} \right) C_{Nmj}^{k+1} + \beta C_{Nimj}^{k+1} + S_{XHmj}^{k+1} = \beta C_{Nimj}^k + C_{Nmj}^k + S_{XHmj}^k \quad (7.24)$$

$$(1 + \alpha\Delta t)C_{Himj}^{k+1} - \alpha\Delta t C_{Hmj}^{k+1} + S_{XHimj}^{k+1} = C_{Himj}^k + S_{XHimj}^k \quad (7.25)$$

$$(1 + \alpha\Delta t)C_{Nimj}^{k+1} - \alpha\Delta t C_{Nmj}^{k+1} - S_{XHimj}^{k+1} = C_{Nimj}^k - S_{XHimj}^k \quad (7.26)$$

$$S_{HXmj}^{k+1} = \frac{C_{Hmj}^k CEC_m}{C_{Hmj}^k + KC_{Nmj}^k} \quad (7.27)$$

$$S_{HXimj}^{k+1} = \frac{C_{Himj}^k CEC_{im}}{C_{Himj}^k + KC_{Nimj}^k} \quad (7.28)$$

Initial conditions:

$$pH_{initial} = 5.6$$

$$C_{Hm}' = [H^+] = 10^{-pH} = 2.512 * 10^{-6}$$

$$C_{Him}' = C_{Hm}'$$

$$S_{XHm}' = \beta_{1(CE)} * CEC_m = 0.01 * CEC_m$$

$$S_{XHim}' = S_{XHm}'$$

$$C_{Nm}' = C_{Hm}' * (CEC_m - S_{XHm}') / (K * S_{XHm}')$$

$$C_{Nim}' = C_{Nm}'$$

Boundary conditions:

- Left boundary conditions:

$$C_{Hmo} = [H^+] = 10^{-pH} = 2.512 * 10^{-6}$$

$$C_{Himo} = C_{Hmo}$$

$$C_{Nmo} = 0.01711$$

$$C_{Nimo} = C_{Nmo}$$

$$S_{XHmo} = C_{Hmo} * CEC_m / (C_{Hmo} + K * C_{Nmo})$$

$$S_{XHimo} = S_{XHmo}$$

- Right boundary conditions (Neumann):

$$-\left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2}\right) C_{i-1}^{k+1/2} + \left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2} + 1\right) C_i^{k+1/2} = C_i^k$$

$$\text{Where: } R_o \stackrel{\text{def}}{=} -\left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2}\right) \text{ and } S_o \stackrel{\text{def}}{=} \left(\frac{V\Delta t}{\Delta x} + \frac{D\Delta t}{\Delta x^2} + 1\right)$$

The problem could be modelled by using Matlab in this way:  $\mathbf{Ac}^{k+1} = \mathbf{b}^k$ . The solution would appear solving the system in the next page.

(1)	1	0	0	...	0	0	...	...	...	0	0	0	...	...	...	0	0	0	...	...	0	0	...	...	...	0	$CHm(i = 1)$	
(2)	R	S	T	...	:	:	...	...	...	:	0	$\beta$	...	...	...	:	0	1	...	...	:	:	...	...	...	:	:	
⋮	0	...	...	...	0	:	...	...	...	:	...	...	...	...	...	:	...	...	...	...	:	...	...	...	...	:	:	
(TN-1)	⋮	...	R	S	T	:	...	...	...	:	...	...	$\beta$	0	:	...	...	...	...	...	:	...	...	1	0	:	:	
(TN)	0	...	0	$R_0$	$S_0$	0	...	...	...	0	0	...	...	...	0	0	0	...	...	...	0	0	...	...	...	0	$CHm(i = TN)$	
(TN+1)	0	...	...	...	0	1	0	0	...	0	0	...	...	...	0	0	0	...	...	...	0	0	0	...	...	0	$CNm(i = TN + 1)$	
(TN+2)	⋮	...	...	...	:	R	S	T	...	:	:	...	...	...	:	0	$\beta$	...	...	...	:	0	-1	...	...	:	:	
⋮	⋮	...	...	...	:	0	...	...	...	:	...	...	...	...	:	...	...	...	...	...	:	...	...	...	...	:	:	
(2TN-1)	⋮	...	...	...	:	:	R	S	T	:	...	...	...	...	:	...	...	$\beta$	0	...	...	...	-1	0	:	:	:	
(2TN)	0	...	...	...	0	0	...	0	$R_0$	$S_0$	0	...	...	...	0	0	...	...	...	0	0	0	...	...	...	0	$CNm(i = 2TN)$	
(2TN+1)	0	0	...	...	0	0	...	...	...	0	1	0	...	...	0	0	...	...	...	0	0	...	...	...	0	0	$CHm(i = 2TN + 1)$	
(2TN+2)	0	$-\alpha\Delta t$	...	...	:	:	...	...	...	:	0	$(1 + \alpha\Delta t)$	...	...	:	...	...	...	...	:	...	...	0	1	...	:	:	
⋮	⋮	...	...	...	:	:	...	...	...	:	...	...	...	...	:	...	...	...	...	...	:	...	...	...	...	:	:	
(3TN-1)	⋮	...	...	...	0	:	...	...	...	:	0	...	...	...	:	...	...	...	...	...	:	...	...	...	1	0	:	
(3TN)	0	...	...	0	$-\alpha\Delta t$	0	...	...	...	0	0	...	...	0	$(1 + \alpha\Delta t)$	0	...	...	...	0	0	...	...	...	0	0	1	$CHm(i = 3TN)$
(3TN+1)	0	...	...	...	0	0	0	...	...	0	0	...	...	...	0	1	0	...	...	...	0	0	...	...	...	0	$CNm(i = 3TN + 1)$	
(3TN+2)	⋮	...	...	...	:	0	$-\alpha\Delta t$	...	...	:	:	...	...	...	:	0	$(1 + \alpha\Delta t)$	...	...	...	:	...	...	0	-1	...	:	
⋮	⋮	...	...	...	:	:	...	...	...	:	...	...	...	...	:	...	...	...	...	...	:	...	...	...	...	:	:	
(4TN-1)	⋮	...	...	...	:	:	...	...	...	:	0	...	...	...	:	0	...	...	$(1 + \alpha\Delta t)$	0	:	...	...	...	...	:	:	
(4TN)	0	...	...	...	0	0	...	...	0	$-\alpha\Delta t$	0	...	...	...	0	0	...	...	...	0	$(1 + \alpha\Delta t)$	0	...	...	...	0	-1	$CNm(i = 4TN)$
(4TN+1)	0	...	...	...	0	0	...	...	...	0	0	...	...	...	0	0	...	...	...	0	1	0	...	...	...	0	$SXHm(i = 4TN + 1)$	
(4TN+2)	⋮	...	...	...	:	:	...	...	...	:	:	...	...	...	:	...	...	...	...	...	:	0	1	...	...	:	:	
⋮	⋮	...	...	...	:	:	...	...	...	:	...	...	...	...	:	...	...	...	...	...	:	...	...	...	...	:	:	
(5TN-1)	⋮	...	...	...	:	:	...	...	...	:	:	...	...	...	:	0	...	...	...	...	:	...	...	0	:	:	:	
(5TN)	0	...	...	...	0	0	...	...	...	0	0	...	...	...	0	0	...	...	...	0	0	...	...	0	1	0	$SXHm(i = 5TN)$	
(5TN+1)	0	...	...	...	0	0	...	...	...	0	0	...	...	...	0	0	...	...	...	0	0	...	...	0	1	0	$SXHm(i = 5TN + 1)$	
(5TN+2)	⋮	...	...	...	:	:	...	...	...	:	:	...	...	...	:	...	...	...	...	...	:	...	...	0	1	...	:	
⋮	⋮	...	...	...	:	:	...	...	...	:	...	...	...	...	:	...	...	...	...	...	:	...	...	...	...	:	:	
(6TN-1)	⋮	...	...	...	:	:	...	...	...	:	:	...	...	...	:	...	...	...	...	...	:	...	...	0	...	...	:	
(6TN)	0	...	...	...	0	0	...	...	...	0	0	...	...	...	0	0	...	...	...	...	0	0	...	...	...	0	1	$SXHm(i = 6TN)$

This is a matrix composed by  $6TN \times 6TN$  multiplied by its unknowns, where  $TN$  is the total number of nodes and it goes from  $i=1$  to  $i=TN$ . The column in the left shows the number of rows and their position, those numbers are the same for every column, which are not written.

So the matrix has  $6TN$  equations and  $6TN$  unknowns:

$(CHm_{(i)}, CNm_{(i)}, CHim_{(i)}, CNim_{(i)}, SXHm_{(i)}$  and  $SXHim_{(i)})$ . For that, it involves 6 rows x 6 columns of different submatrices each of them referred to one unknown. The vector  $\mathbf{b}^k$ , written below is the result of the product  $\mathbf{A}\mathbf{c}^{k+1}$ .

Vector  $\mathbf{b}^k$ :

$$\begin{aligned}
 & CHmo \\
 & CHm(2) + \beta CHim(2) + SXHm(2) \\
 & \vdots \\
 & CHm(TN - 1) + \beta CHim(TN - 1) + SXHm(TN - 1) \\
 & CHm(TN) \\
 & CNmo \\
 & CNm(TN + 2) + \beta CNim(TN + 2) - SXHm(TN + 2) \\
 & \vdots \\
 & CNm(2TN - 1) + \beta CNim(2TN - 1) - SXHm(2TN - 1) \\
 & CNm(2TN) \\
 & CHimo \\
 & CHim(2TN + 2) + SXHim(2TN + 2) \\
 & \vdots \\
 & CHim(3TN - 1) + SXHim(3TN - 1) \\
 & CHim(3TN) + SXHim(3TN) \\
 & CNimo \\
 & CNim(3TN + 2) + SXHim(3TN + 2) \\
 & \vdots \\
 & CNim(4TN - 1) + SXHim(4TN - 1) \\
 & CNim(4TN) + SXHim(4TN) \\
 & SXHmo \\
 & (CECmCHm(4TN + 2)) / (CHm(4TN + 2) + KCNm(4TN + 2)) \\
 & \vdots \\
 & (CECmCHm(5TN - 1)) / (CHm(5TN - 1) + KCNm(5TN - 1)) \\
 & (CECmCHm(5TN)) / (CHm(5TN) + KCNm(5TN)) \\
 & SXHimo \\
 & (CECimCHim(5TN + 2)) / (CHim(5TN + 2) + KCNim(5TN + 2)) \\
 & \vdots \\
 & (CECimCHim(6TN - 1)) / (CHim(6TN - 1) + KCNim(6TN - 1)) \\
 & (CECimCHim(6TN)) / (CHim(6TN) + KCNim(6TN))
 \end{aligned}$$

Each boundary condition is applied to every first and last line of each submatrix. That is:

- The left boundary conditions are applied in the rows  $1, TN+1, 2TN+1, 3TN+1, 4TN+1$  and  $5TN+1$  of the whole matrix:

Row  $1$ , column  $1 \rightarrow CHm^{k+1} = CHmo_{(constant)}$ , so that  $A_{(1,1)} = 1$ , and  $b_{(1)}^k = CHmo$ .

Row  $TN+1$ , column  $TN+1 \rightarrow CNm^{k+1} = CNmo_{(constant)}$ , so that  $A_{(TN+1,TN+1)} = 1$  and  $b_{(TN+1)}^k = CNmo$ .

Row  $2TN+1$ , column  $2TN+1 \rightarrow CHim^{k+1} = CHimo_{(constant)}$ , so that  $A_{(2TN+1,2TN+1)} = 1$  and  $b_{(2TN+1)}^k = CHimo$ .

Row  $3TN+1$ , column  $3TN+1 \rightarrow CNim^{k+1} = CNimo_{(constant)}$ , so that  $A_{(3TN+1,3TN+1)} = 1$  and  $b_{(3TN+1)}^k = CNimo$ .

Row  $4TN+1$ , column  $4TN+1 \rightarrow SXHm^{k+1} = SXHmo_{(constant)}$ , so that  $A_{(3TN+1,3TN+1)} = 1$  and  $b_{(3TN+1)}^k = SXHmo$ .

Row  $5TN+1$ , column  $5TN+1 \rightarrow SXHim^{k+1} = SXHimo_{(constant)}$ , so that  $A_{(3TN+1,3TN+1)} = 1$  and  $b_{(3TN+1)}^k = SXHimo$ .

- The right boundary conditions are applied in the rows  $TN$  and  $2TN$  of the whole matrix:

Row  $TN \rightarrow R_o CHm_{(TN,TN-1)}^{k+1} + S_o CHm_{(TN,TN)}^{k+1} = C1_{(TN,1)}^k$ , so that  $A_{(TN,TN-1)} = R_o$ ,  $A_{(TN,TN)} = S_o$  and  $b_{(TN)}^k = CHm_{(TN,1)}^k$ .

Row  $2TN \rightarrow R_o CNm_{(2TN,2TN-1)}^{k+1} + S_o CNm_{(2TN,2TN)}^{k+1} = CNm_{(2TN,1)}^k$ , so that  $A_{(2TN,2TN-1)} = R_o$ ,  $A_{(2TN,2TN)} = S_o$  and  $b_{(2TN)}^k = CNm_{(2TN,1)}^k$ .

Notice that in the rows  $3TN, 4TN, 5TN$  and  $6TN$  no right boundary conditions are applied, indicating mass continuity.



## 8. Discussion

The numerical solutions found for the cation exchange problem, have given an effective qualitative analysis using a really small  $\gamma$  value. Using either finite differences or operator splitting, not only has a resolution for the existing theory of cation exchange been proved, but also a graphical response to this. The real behaviour of a  $\text{Na}^+$  charged water going through a  $\text{H}^+$  charged resin involves a cation exchange process. This effect makes the pH of the solute decreasing rapidly during the initial times and then it increases until reaching again the initial value, see figure 8.1. This is the behaviour which has been observed in a qualitative way in this paper.

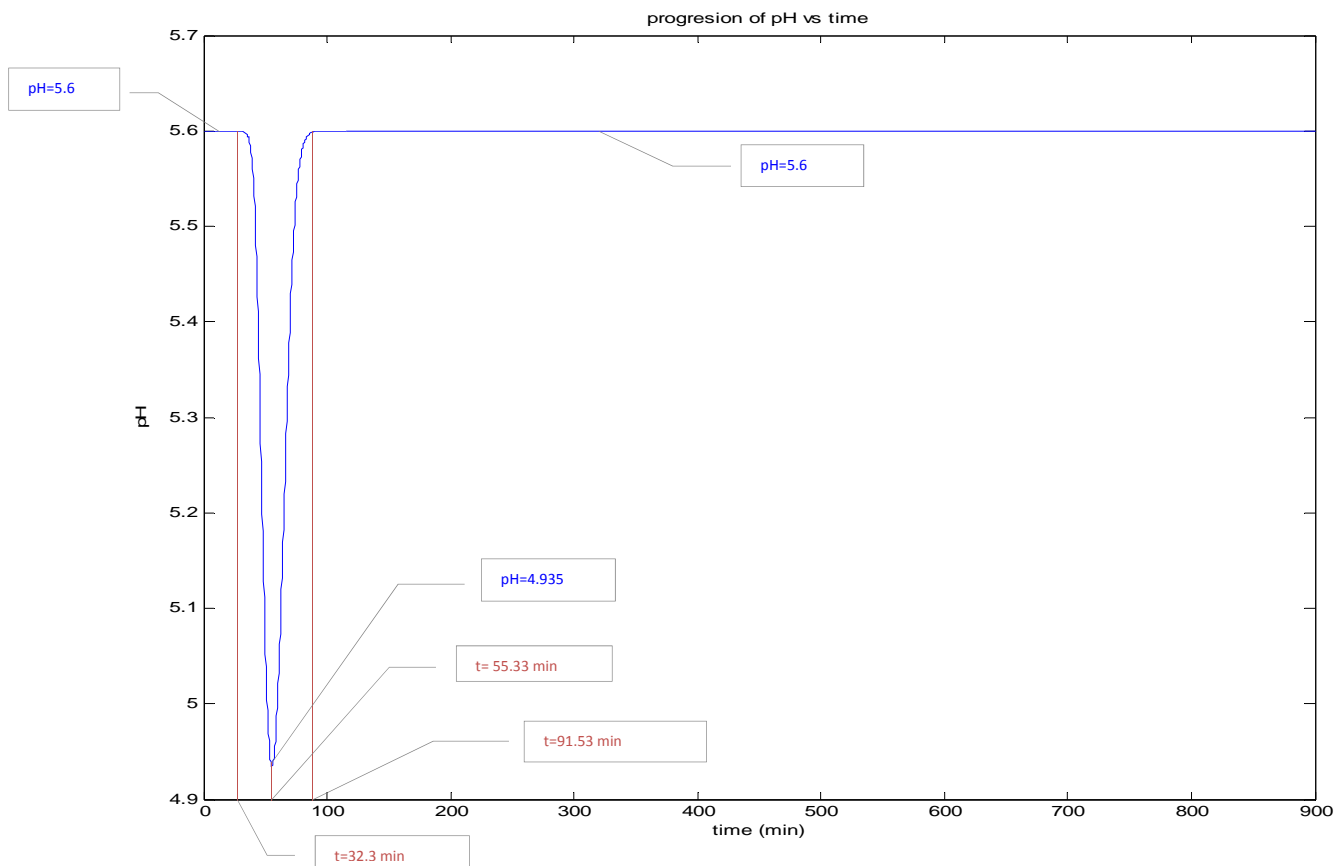


Figure 8.1: Variation of pH with time in the last node.

However, and as it has been said in several occasions, the two different solutions have been found using a different  $\gamma$  than real cases.

Using standard finite differences, the fact that this  $\gamma$  has to be lower than the real one to converge is because the equilibrium equation (eq.3.4) previously defined, which is non-linear,

$$K_{12} = \left(\frac{\beta_1}{c_1}\right)^{\frac{1}{z_1}} \left(\frac{c_2}{\beta_2}\right)^{\frac{1}{z_2}}, \text{ is solved considering it as a lineal equation (eq.4.8) } \rightarrow \beta_{2j}^{k+1} = \frac{\beta_{1j}^k c_{2j}^k}{c_{1j}^k K_{12}},$$

assuming its small concentrations would not give numerical problems.

Using operator splitting, developing this step  $\gamma(\beta_{nj}^{k+1/2} - \beta_{nj}^k)$  in the equations number 5.13 and 5.14,  $C_{nj}^{k+1} = C_{nj}^{k+1/2} - \gamma(\beta_{nj}^{k+1/2} - \beta_{nj}^k)$ , makes the same effect than with standard finite differences.

More sophisticated numerical methods would be adequate to solve those problems for increasing the value of  $\gamma$ , whose definition is  $\gamma \stackrel{\text{def}}{=} CEC \frac{\rho_b}{\phi}$ .

It is important to point out that the cation exchange capacity (CEC) is difficult to calculate because it involves some experimental work under very detailed chemical setup and experimental conditions.

For the introduction of the MRMT concept, a possible numerical solution has been found in a similar way than with just the cation exchange. All the steps needed are exposed in the paper. It has been solved using finite differences. The code of it with Matlab will have a similar format than the one made without MRMT. The result of this new approach would give an exact behaviour of the variation of the pH compared with real cases.

## 9. Conclusions

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In this thesis a deep analysis of solute transport with cation exchange was done. Based on previous theories, a gathering of the existing information was possible. A lab experiment was explained in order to extend the knowledge of the matter. After this analysis a different behaviour was seen. Changes of velocities in the experiment made a different behaviour of it, which it was not contemplated in the process of cation exchange. This aspect could be the reason why all the theories presented by now are unable to describe the exact behaviour of this process.

Once this big part was established the qualitative analysis of this information began. For that, two different numerical solutions were exposed; one done by finite differences and the other with operator splitting. Those two possible solutions were done in order to notice a different result. Contrary to this premise, both of them gave almost the same values. However, the results were the expected. When a  $\text{Na}^+$  charged solution passes through a resin whose function is to exchange cations, the solution becomes charged of  $\text{H}^+$ . At the initial times, the pH of the flowing water decreases rapidly until reaching a minimum; after that it increases until reaching chemical equilibrium, with a chemical signature that involves the same values than the original water present in the experimental column. This is the behaviour that appears in real cases and it is also the behaviour that could be modelled in both of the proposed numerical solutions.

After that, the concept of multirate mass transfer was introduced. The point was to develop a new proposal in order to figure out how to match the problem of the variation of the concentrations changing velocities, found in the experiment, with the cation exchange problem. Multirate mass transfer was studied and described, as well as its influence with the solute transport with cation exchange problem formulated before. For that, a possible numerical solution methodology was proposed. This solution would make, for future studies, that the behaviour of the pH observed could be totally described with a mathematical explanation.

## 10. References and bibliography

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