

MULTICOMPONENT REACTIVE TRANSPORT MODELING IN A 1D COLUMN

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Summary. Transport of reactive species, like most geochemical phenomena of interest in Earth science, is characterized by a combination of physical and chemical processes¹. In a recent work², an exact analytical expression to describe the space-time evolution of reaction rates associated with a multicomponent reactive transport problem in presence of both kinetic and equilibrium chemical reactions was developed. The resulting expressions are then solved numerically by means of an implicit predictor-corrector approach relying on a forward finite difference and central finite difference approximation respectively for time and space, to simulate the dissolution of calcite in the presence of precipitating gypsum. Here we present an experimental study, which allowed us to acquire information for the accuracy assessment of the ADE model coupled with the reaction rates expressions. A PVC column was packed with porous media using a wet method, which provided great reproducibility; was saturated with water in equilibrium with respect to calcite and gypsum. Water oversaturated with respect to calcite is continuously introduced in the system at the inlet causing calcite to precipitate. Even the application example simplifies the calcite-gypsum system by assuming only carbonate in solution, thus neglecting the species bicarbonate and carbonic acid which are dominant in natural solutions, and that ionic strength typically does not vary much in space and time, the time evolution of carbonate is well represented by the model, meanwhile the calcium and sulfate concentrations are not accurate due to the lack of gypsum into the column.

1. INTRODUCTION

Chemical reactions may affect the fate of pollutants and the properties of the host porous medium. However, the conditions for the reactions to occur, their location, and often their rate, are largely controlled by transport³ which is what motivates analyses of reactive transport. Modeling multicomponent reactive transport problems requires specifying: (i) a set of mass balance equations, one for each species being transported, and (ii) a second set of equations describing the reactions amongst species. Mass balance of each individual species is expressed by a solute transport equation with a source term to account for all the reactions participated by each individual species. The transport equation itself can be written according to different conceptual models.

A crucial element on the reactive transport analysis is the estimation of space-time distributions of the reaction rates. First, they allow to identify the magnitude and position of the maximum local rates, which may have significant impacts on the hydraulic properties; secondly, identifying the extension of the domain fraction that contributes to the observed process and finally, providing information about the rate evolution towards the equilibrium².

Chemical reactions can be classified into two broad groups, depending on whether a characteristic reaction time is much smaller than the time scales associated with other mass-transfer processes (e.g., advection, diffusion, dispersion). In the presence of “sufficiently fast” reactions the assumption of local chemical equilibrium can be considered appropriate. This is the case for most aqueous reactions. On the other hand, reactions involving minerals and aqueous species are often better described as kinetic, that is, “insufficiently fast”^{e.g., 4}. Whenever reactions with different characteristic times occur simultaneously, the solution of the associated multicomponent system becomes mathematically complex due to the presence of non-linear processes⁴⁻⁶.

In a recent work² developed an exact analytical expression to describe the space-time evolution of reaction rates associated with a multicomponent reactive transport problem in presence of both kinetic and equilibrium chemical reactions. The resulting expressions are then solved numerically to simulate the dissolution of calcite in the presence of precipitating gypsum.

This paper describes the development and installation of a physical model whose main objective is to provide reliable experimental data to evaluate the theoretical model presented in reactive transport². To accomplish this, it is necessary to design an experiment to ensure physical and chemical reproducibility for determining the hydrodynamic parameters of a conservative tracer transport and studying the spatial and temporal variation of concentrations of species in the study of reactive transport. Finally, we compare experimental with obtained data by using the expressions of the reaction rates for the ADRE transport model (Advection-Dispersion-Reaction).

The document is divided into three sections. Section 2 describes the most relevant theoretical foundations, starting with chemical concepts, followed by the description of transport phenomena, which are eventually coupled to present the reaction rates of a multicomponent reactive transport model. Section 3 presents the experimental design which describes the materials used to construct the model, methods of analysis used to determine concentrations of chemical species studied, and describes the activities carried out for optimal experimental construction of the experimental model. Section 4 presents the evaluation of the theoretical model, which includes a description of the restrictions of the theoretical model, the final assembly of the physico-chemical model, and comparison of theoretical model results with information obtained experimentally.

2. THEORETICAL FRAMEWORK

Modeling reactive transport involves describing mass balances of species and reactions among species. The basic equations, an ADRE formulation, and the strategy adopted to solve them, are described below.

2.1. Kinetics of geochemical processes

Dissolution of minerals that form the porous environment represents the destruction of the bonds of the crystal structure in the surface of minerals and the subsequent increase in the mass of water. Precipitation is the opposite process. To understand water-rock interaction in a quantitative way is necessary to measure the velocity of dissolution or precipitation. Hence, a slow dissolution process compared to the speed of the flow will barely increase the mass of the solution.

According to Samper et al.⁷, assuming that precipitation reactions have a symmetrical behavior when compared to those of dissolution, it is possible to express the dissolving rate of the mineral, r_m , as:

$$r_m = \sigma_m k_m (\Omega_m^\theta - 1)^p, \quad (1)$$

here k_m is the experimental equilibrium constant, σ_m is its specific reactive surface; Ω_m is the ratio between the ion product activity and the equilibrium constant. The parameters θ and p have to be determined with experiments and are usually assumed as 1⁷. The term inside parentheses decreases the reaction rates in a non linear way as the solution reaches equilibrium.

2.2. Mass transfer

For a conservative solute, the space-time distribution of the concentration is controlled by (i) the movement in the direction of the flow (advection) and (ii) by the longitudinal and transversal mix phenomena that allow the increase in the size of the contaminated area and the decrease in the maximum concentrations (dispersion). The transport equation obtained from the mass continuity condition in an elemental volume can be expressed as:

$$L(\mathbf{c}) = -\mathbf{q}\nabla\mathbf{c} + \nabla(\mathbf{D}\nabla\mathbf{c}), \quad (2)$$

where $L(\mathbf{c})$ is the transport operator, ∇ is divergence, \mathbf{D} is the dispersion tensor that involves both molecular diffusion and mechanical dispersion, \mathbf{c} is the concentration, ϕ is the porosity and \mathbf{q} Darcy's flow.

2.3. Coupling chemical with transport

The dissolved species are transported along the liquid phase and can experience chemical interactions with other dissolved chemical species (homogeneous reactions). The solid species include the mineral phases (precipitates), the exchanged species (from the change complex) and the absorbed species. These species are not transported and only take part in geochemical processes⁷.

In equilibrium aqueous systems, the reactive transport system of solutes is reduced to reactive transport system of components as long as the dispersion and diffusion coefficients are the same for all the aqueous species. In these conditions the transport equations can be written in terms of the total component concentrations, c_i . From the mass conservation principle, transport equations of the chemical equations can be expressed as:

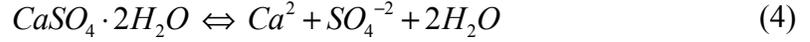
$$\frac{\partial \mathbf{c}}{\partial t} = \mathbf{M}L(\mathbf{c}) + \mathbf{S}'_e \mathbf{r}_e + \mathbf{S}'_k \mathbf{r}_k(\mathbf{c}), \quad (3)$$

where \mathbf{M} is the diagonal matrix whose terms are 1 for mobile species and 0 for the rest, \mathbf{S}'_e is the stoichiometric transpose matrix of the reactions in equilibrium, where every row

represents a reaction, S'_k is the stoichiometric transpose matrix of the kinetic reactions, r_e and r_k are vectors for the rates of equilibrium and kinetic reactions respectively.

2.4. Chemical system

The dissolved species are transported along the liquid phase and can experience chemical interactions with other dissolved chemical



The system considers that reaction (4) to occur in equilibrium at all points in the domain. On the other hand and the reaction (5) is consider a “slow reaction”. The system involves the precipitation/dissolution of two minerals $B_4^{(s)}$ and $B_5^{(s)}$ in presence of three aqueous species B_1 , B_2 and B_3 , one of them participating in both reactions (common ion effect).

The system consists, then, of five reacting species. According to Molins et al.⁸, any chemical system can be represented by means of the stoichiometric matrix S that can be divided in two matrices, S_e and S_k , containing the equilibrium and kinetic reactions. In this particular problem this leads to:

$$S = \begin{pmatrix} S_e \\ S_k \end{pmatrix} = \left(\begin{array}{ccc|cc} SO_4^{-2} & CO_3^{2-} & Ca^{2+} & CaCO_3 & CaSO_4 \cdot 2H_2O \\ 1 & 0 & 1 & 0 & -1 \\ 0 & 1 & 1 & -1 & 0 \end{array} \right) \quad (6)$$

Sanchez-Vila et al.² use the classification of Molins et al.⁸ to distinguish the different species involved in the chemical system, which leads to the particular ordering of columns adopted: (i) secondary aqueous species involved in the equilibrium reaction, SO_4^{-2} , (ii) primary kinetic aqueous species, CO_3^{2-} , (iii) general primary aqueous species, Ca^{2+} , (iv) kinetic mineral, $CaCO_3$, and (v) constant activity species, $CaSO_4 \cdot 2H_2O$.

2.5. Restrictions

The theoretical model and the analytical expressions presented in Sanchez-Vila et al.² part from many assumptions that do not represent natural behavior as is presented in our environment.

In their application example, Sanchez-Vila et al.² simplify the calcite-gypsum system even further by assuming: i) only CO_3^{2-} in solution, thus neglecting the species HCO_3^- and H_2CO_3 which are dominant in natural solutions and thus in practical applications. ii) that ionic strength typically does not vary much in space and time, although the majority of hydrochemical problems is related to salinization changes associated with fresh-salt water movement, pollution, or waste-management; iii) ion association in solution is absent.

Due to the lack of practical application of the example described in Sanchez-Vila et al.², it was necessary to change the chemical system. As at high pH the dominant carbonate specie is CO_3^{2-} , and the precipitation of calcite at that pH is much easier to obtain. It was

set up the chemical system on the other way around, which implied the dissolution of gypsum in presence of precipitating calcite.

3. MATERIALS AND METHODS

3.1. Solutions

A conservative solution (Sodium Chloride) and three potentially reactive solutions (Calcium Carbonate, Sulphate Carbonate and Sodium Carbonate) were used in the experiments. After weighing the salts and mixing with deionized water, solutions were equilibrated with ambient air.

3.2. Column

After having chosen silicate sand for packing the column, three packing methods were evaluated to ensure reproducibility of the experiment: i) 2 mm of dry sand was deposited into the column and rammed with a metallic tool, ii) 2 mm of dry sand were deposited while stirring and iii) the sand were deposited into a column full of water while stirring, (References). Bulk density was sampled eight times for each method and statistical analysis was performed, and it was determined that the better packing method for was the wet method.

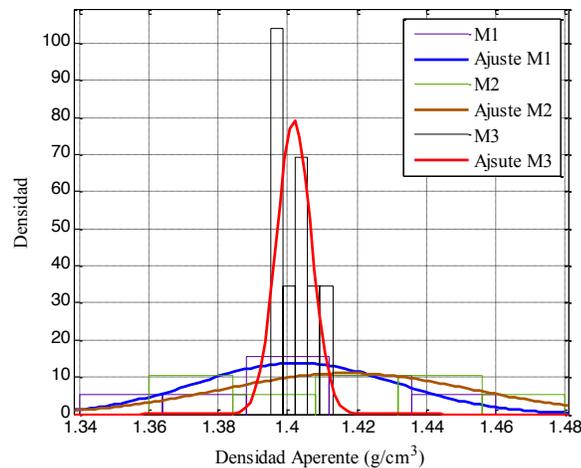


Figure 1: Normal fit for the sampling of bulk density for three packing methods

Avoiding undesirable preferential flows by giving roughness to the wall were considered. Sand was stuck to the column wall using silicone. The column was packed in a three inches PVC pipe and 30 cm long. Three sampling port were located at 1,5, 15 and 28,5 cm from the top of the column to get de sample. After evaluating different shapes and configurations for the samplers, it was design a sample that ensured i) the sample was rapidly extracted from the column, ii) the size did not disturb the porous media, and iii) the material was not extracted.

3.3. CO₂ capture

Due to the interaction of the system with carbon dioxide, it was necessary to evaluate the CO₂ capture by the water exposed to environmental conditions. Five liters of water in a plastic bowl open to environment conditions were disposed. The temporal evolution of

acidity due CO_2 was measured hour after hour for the first six hours and later at 12, 24, 48 and 96 hours.

3.4. Analytical method

Calcium concentration was measured using a complexometry titration method. Sulphate and chloride concentrations were measured using ionic chromatography, and carbonate concentration were measured by an acid-base titration.

3.5. 1D Column configuration

The experimental model configuration was formed by a peristaltic pump, which controlled the flow rate at the outlet of the column. The flow rate was 1,2 L/s. A storage tank with capacity of 600 mL was installed at the inlet, assuring saturation conditions for the porous media.

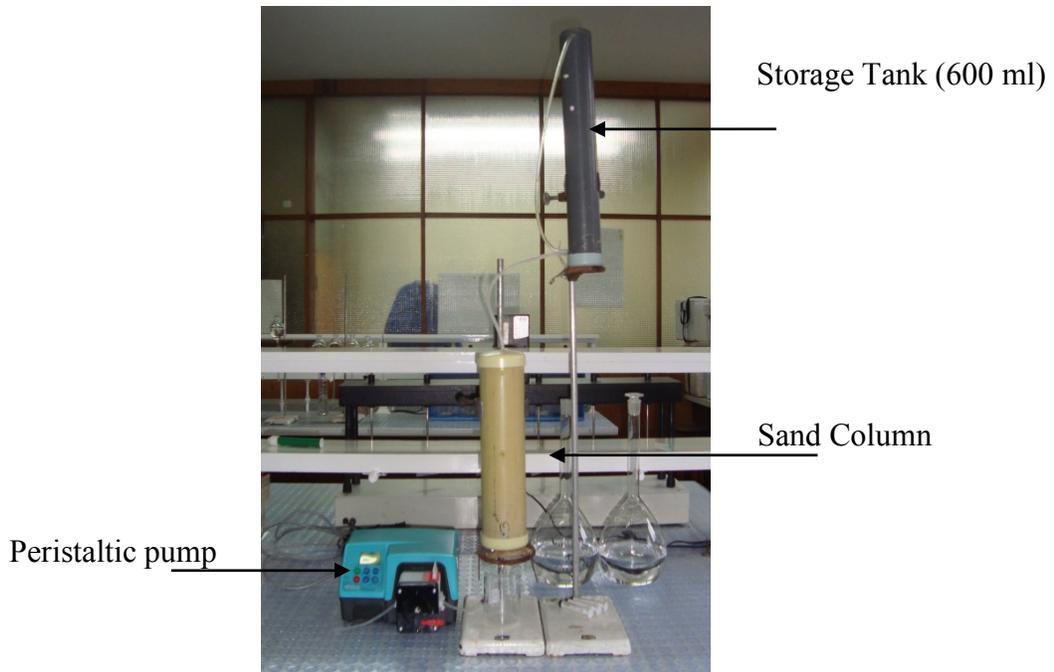


Figure 2: Experimental set up

4. RESULTS AND DISCUSSION

4.1. Conservative transport

Conservative transport experiments were run to determine hydrodynamic parameters transport. A solution of sodium chloride and sodium sulphate was continuously introduced into the sand column in place of the resident water. The CXTFIT code⁹ was used to solve the inverse problem by fitting mathematical solutions of theoretical transport models, based upon the advection-dispersion equation (ADE) to experimental results. This approach allows parameters in the transport models to be quantified.

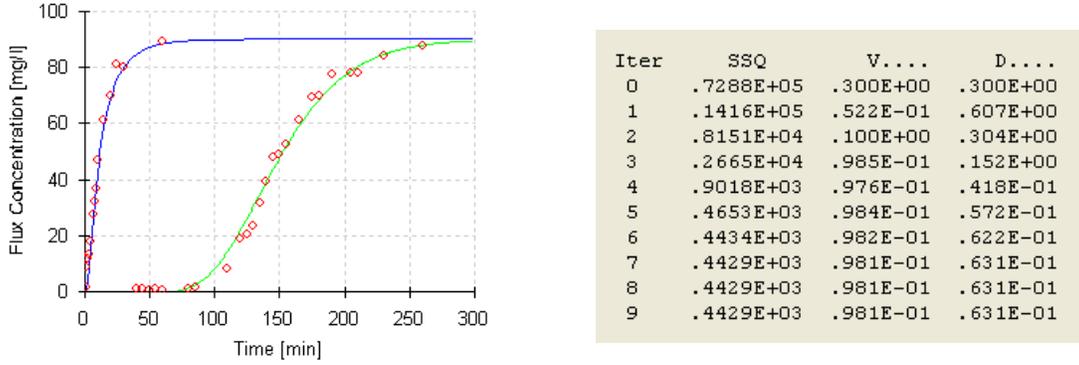


Figure 3: Breakthrough curves for conservative displacement experiment.

4.2. Reactive transport

Once transport parameters were determined, the column was flushed with water assuring the conservative solution to be washed. The column was saturated with water in equilibrium with respect to calcite and gypsum, the initial concentration are shown in Table 1.

Specie	Concentration (mg/L)
Sulphate SO_4^{2-}	1400
Calcium Ca^{2+}	300
Carbonate CO_3^{2-}	0

Table 1 : initial concentration for the saturated solution

A solution of sodium carbonate, which concentration was 4100 mg/L, was continuously introduced in the column. The time evolution of aqueous concentrations was determined at the mid sampling port located in the column.

4.3. Numerical modeling

The analysis is performed upon introducing dimensionless space–time coordinates and state variables. Table reports the key dimensionless variables of interest, indicated as primed quantities. The solution of the reactive transport problem involves solving the non-linear PDE that is solved by means of an implicit predictor-corrector approach relying on a forward finite difference and central finite difference approximation respectively for time and space.

Having determined the parameter transport for the column, an optimization process was performed to determine the Da number, which picks the reaction process in the model. The best fit, was got using $Da = 0,1$, that permitted to obtain $Sk_0 = 1,26 \times 10^{-9}$ mol/g–s, which is an order of magnitude higher than the presented in Ayora et al.¹⁰ (2.1×10^{-8} mol/g–s). Nevertheless, as k_0 is an experimental constant, it is possible to conclude that this value is the particular constant for our experiment.

Figure 4 shows the temporal evolution of carbonate and calcium at the midpoint of the column.

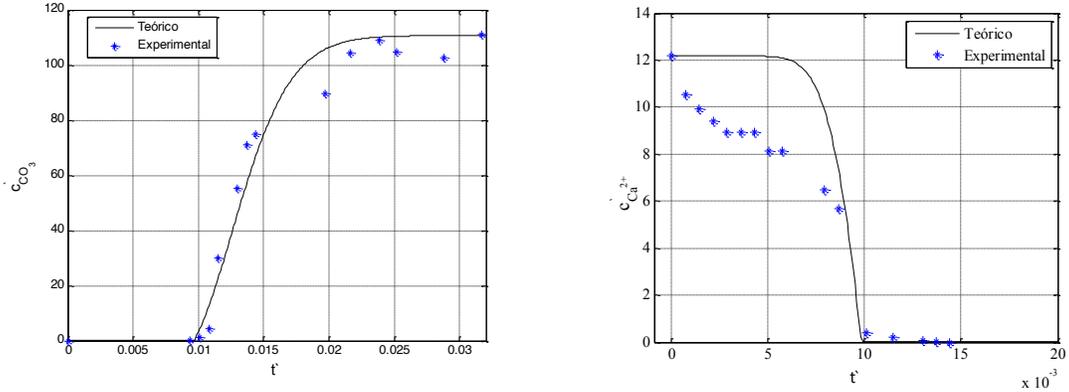


Figure 4: Temporal evolution of carbonate and calcium at the midpoint of the column.

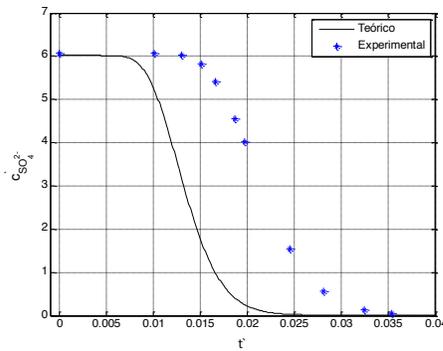


Figure 5: Temporal evolution of sulfate at the midpoint of the column

The model efficiency was evaluated using the Nash-Sutcliffe coefficient, broadly used for evaluating hydrological predicting models, and defined as:

$$E = 1 - \frac{\sum_{t=1}^t (X_{obs} - \bar{X}_m)^2}{\sum_{t=1}^t (X_{obs} - \bar{X}_{obs})^2} \quad (7)$$

here X_{obs} is the observed data and X_m is the data from the theoretical model. Coefficient obtained for Carbonate, Calcium and Sulfate, was 0.999, 0.553, -0,201, respectively

5. REFERENCES

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