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A worksheet-based tool to implement reactive transport models in COMSOL Multiphysics

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SUPPLEMENTARY MATERIAL

EE4MGM <https://ars.els-cdn.com/content/image/1-s2.0-S0045653520333737-mmc1.zip>

Tutorial <https://ars.els-cdn.com/content/image/1-s2.0-S0045653520333737-mmc2.docx>

ABSTRACT

The increasing needs for modelling of reactive transport phenomena in different areas of environmental modelling have led to the development of many numerical codes. However, many of them suffer from a lack of flexibility, which hinders the adaptation of the codes to new problems. Moreover, in many cases, changes can be done by a very reduced group of people, and often by a single person, the main developer. Implementation platforms based on multiphysics modelling removes these barriers, although until now within that programming environments has been only possible the coupling of geochemical codes to transport equations using operator splitting techniques. This paper presents a tool (EE4MGM) in MS Excel worksheet for the edition and complete implementation of a reactive transport models in COMSOL. This provides greater flexibility and advantages in terms of numerical performance and computational effort. The tool, the organization of data input and the equation libraries obtained for the implementation in the multiphysics COMSOL environment are described. Besides, two examples of verification in one and two-dimensional domains, respectively, are presented. Their implementation in COMSOL can be done through the Excel file provided as supplementary material to this paper.

KEYWORDS

Multiphysics simulation; code editor; geochemical model; reactive transport; MS Excel; COMSOL

1. INTRODUCTION

In recent decades there has been a growing interest in the simulation of reactive transport to understand and simulate the different physical-chemical phenomena in environmental applications. Different studies have been developed in various areas of knowledge such as environmental engineering (Runkel, 2010; Bahadur et al., 2013; Wang et al., 2013; Tabelin et al., 2017; Lopez Vizcaino et al., 2018; Reiller and Descostes, 2020), material science (Moranville et al., 2004; Samson and Marchand, 2007; Tiruta-Barna, 2008; Yuan et al., 2013) or geosciences (Steefel et al., 2015; Ajayi and Gupta, 2019). However, reactive transport by itself does not describe the complete behaviour of porous media in real conditions. For this reason, in recent decades, an important effort in development of thermo-hydro-geochemical (THC) models (Zhang et al., 2012) and even thermo-hydro-mechanical and geochemical coupled (THMC) models (Zheng et al., 2010; Guimarães et al., 2013; Sedighi et al., 2016; Zheng et al., 2017) has been made. All these numerical tools arise from the need to consider the different physical-chemical phenomena that explain the complexity of the behaviour of porous media under different environmental and mechanical conditions. Usually, these tools are the result of the combination of different modules developed independently and which are coupled employing numerical interfaces specifically designed for that purpose (Saaltink et al., 2005; Juncosa et al., 2010). Generally, this coupling is made through the operator splitting approach (Carrayrou et al., 2004a). This technique allows to obtain accurate results as long as the successive time steps in which the transport equations and the geochemical equilibrium calculations are solved are sufficiently small. On the other hand, models have also been developed that integrate all phenomena (THMC) in a single calculation module. These models allow to solve at the same time the state variables of the transport and mechanical equations and those of the chemical reactions (monolithic approach). Both approaches

require an important effort in the implementation stage and a solid scientific knowledge ranging from numerical methods to geochemical and thermo-hydro-mechanical modelling of porous media, which makes the development and the use of these codes often remain in the academic field.

In contrast, due to their versatility, multi-physical codes (Keyes et al., 2013) are currently being presented as one of the most interesting alternatives within modelling in various fields. Since some of these codes are capable of working at the level of defining the coefficients of the partial differential equations (PDE), their solution is left to the work of symbolic algebra and the numerical algorithms included in the software (Farrell et al., 2013; McRae et al., 2016; Houston and Sime, 2018). This allows the end-user to model problems with many PDEs, even with important degrees of coupling between them, very quickly and efficiently as can be seen in many recent application examples (López-Vizcaíno et al., 2017; Navarro et al., 2019).

However, so far, the modelling of reactive transport in these multi-physical implementation platforms has only been done using the operator splitting approach. Most of these application examples (Wissmeier and Barry, 2011; Nardi et al., 2014; Nasir et al., 2014; Von Schenck et al., 2015; Azad et al., 2016; Jara et al., 2017; Guo et al., 2018; Kim et al., 2019) have been made on COMSOL Multiphysics (CM) software using its application programming interface (API) (COMSOL, 2018), although there are examples with other multi-physical codes (Damiani et al., 2020). A complete implementation in CM has not been done so far since the resolution of geochemical equilibrium systems is quite complex due to different factors. On the one hand, if the geochemical system is extensive enough, it requires the implementation of several balance equations, one for each master species minus one that is solved by applying the condition of electroneutrality

(Bethke, 2007). Furthermore, it is also required the implementation of the database of thermodynamic constants for each chemical reaction that defines the generation of the secondary species and the parameter for the calculation of the species activities. Besides, it should be noted that the entire implementation effort must also be repeated every time that a change is made to the geochemical system, by adding the new species and removing the ones that no longer exist. This implementation task is heavy and falls outside the main interests of the most common end-users. However, it may be of interest for the scientific community to test different conceptual models, formulations, or values of thermodynamic variables. In fields where knowledge of geochemical systems is advancing rapidly, such as in the geological storage of CO₂ (Akono et al., 2019; Derakhshan-Nejad et al., 2019) or in the storage of radioactive waste (Xiao et al., 2018; de Windt and Spycher, 2019), flexibility in the formulations and the proposal of new conceptual and numerical models are key aspects. On the other hand, the complete implementation in platforms as COMSOL, using a monolithic approach rather the operator splitting one, has an advantage in terms of computational time because the geochemical module does not have to be reset and the thermodynamic database has not to be read at each time step. Furthermore, the time required for data exchange between the transport and the chemical reaction modules disappears completely and potential errors in the management of transient boundary conditions and mass balance errors associated with the correct selection of the calculation time step are eliminated (Barry et al., 1997; Carrayrou et al., 2004b; Jacques et al., 2006).

In this context, and to facilitate the development of reactive transport models in COMSOL under a monolithic approach, this paper presents the Equation Editor for Multiphysics Geochemical Modelling (EE4MGM) application, developed in the friendly and well-known MS Excel spreadsheet environment. In this module, the sequence of the code

needed to implement reactive transport models in COMSOL can be developed automatically. Additionally, EE4MGM also allows, in a fast and very flexible way, to make the calculations associated to the chemical speciation in aqueous phase (Chemical Equilibrium Speciation, CES), resulting in a very useful tool for obtaining the initial and boundary conditions of the reactive transport simulations. Thanks to the capabilities of the EE4MGM tool, it has been possible to implement a reactive transport module entirely in COMSOL. To check the validity and quality of the tool, a verification exercise has been performed by analysing a synthetic case of seawater injection into a river water environment. For this purpose, reactive transport has been simulated in one- and two-dimensional domains and checked with PHREEQC (Parkhurst and Appelo, 2013) and PHAST (Parkhurst et al., 2010), respectively. In these cases, only equilibrium reactions in aqueous phase have been considered. The inclusion of heterogeneous reactions that involve two separate phases can easily be done in EE4MGM following the same procedure as for aqueous phase reactions (Steefel and Lasaga, 1994; Steefel et al., 2015). Processes that are not under chemical equilibrium conditions (kinetic processes) can simply be added thanks to COMSOL's versatility in the solution of ordinary and partial differential equations.

2. REACTIVE TRANSPORT: MATHEMATICAL FORMULATION

The implemented geochemical model consists of a total of I species, divided into S secondary species that can be generated from M ($=I-S$) master species. The total molal concentration of a master species m , C_m , which is usually a known initial condition for the speciation problem, is defined by the expression

$$C_m = \sum_{i=1}^I \alpha_{im} c_i \quad (1)$$

where the contribution of the m-th master species, in the formation of the i-th secondary species is given by the value of the stoichiometric coefficient α_{im} , positive, if it is a reactive, and negative if it is a product of the considered chemical reaction and where c_i denotes the molal concentration of the i-th secondary species. As an example, the water dissociation reaction ($\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$) is presented. In this case, H_2O and H^+ are master species and OH^- is the secondary species, therefore $\alpha_{\text{OH}^-, \text{H}_2\text{O}} = 1$ and $\alpha_{\text{OH}^-, \text{H}^+} = -1$. In the case of $\alpha_{m,m}$, i.e. the stoichiometric coefficient of a master species generated from itself is always 1. The molal concentration of the i-th secondary species is defined by the expression

$$c_i = \frac{a_i}{\gamma_i} \quad (2)$$

where a_i and γ_i are the activity and the activity coefficient of the i-th species. The value of a_i can be calculated from the mass action law equations of each equilibrium reaction by the expression

$$\log_{10}(a_i) = \log_{10}(K_{\text{eq},i}) + \sum_{m=1}^M \alpha_{im} \cdot \log_{10}(a_m) \quad (3)$$

where $K_{\text{eq},i}$ is the equilibrium constant of the formation reaction of the i-th secondary species from the combination of the m-th master species and where a_m is the activity of each master species. The activity of H_2O ($a_{\text{H}_2\text{O}}$) is calculated from the expression (Parkhurst and Appelo, 2013)

$$a_{\text{H}_2\text{O}} = 1 - 0.017 \sum_{i=1}^{I-\text{H}_2\text{O}} c_i \quad (4)$$

where the summation includes the concentrations of all the species except that of the water H_2O itself. The value of the concentration of Cl^- (c_{Cl^-}) is obtained following the electroneutrality principle using the expression

$$c_{\text{Cl}^-} = -\frac{1}{z_{\text{Cl}^-}} \sum_{i=1}^{I-\text{Cl}^-} z_i c_i \quad (5)$$

where z_i denotes the electrical charge of i-th species and the summation extends to all species except Cl^- . On the other hand, the activity coefficient, γ_i , has been estimated using the WATEQ Debye-Hückel approach by the expression

$$\log_{10}(\gamma_i) = \frac{-A \cdot z_i^2 \cdot \sqrt{I_s}}{1 + a_i^o \cdot B \cdot \sqrt{I_s}} + B^o \cdot \sqrt{I_s} \quad (6)$$

where A , B and B^o are fitting parameters that depend on the temperature and can be obtained using the expressions

$$A = 1.086 \cdot 10^{-10} \cdot T^4 - 4.297 \cdot 10^{-8} \cdot T^3 + 9.806 \cdot 10^{-6} \cdot T^2 + 4.032 \cdot 10^{-4} \cdot T + 4.946 \cdot 10^{-1} \quad (7)$$

$$B = 4.899 \cdot 10^{-12} \cdot T^4 - 2.570 \cdot 10^{-9} \cdot T^3 + 6.689 \cdot 10^{-7} \cdot T^2 + 1.223 \cdot 10^{-4} \cdot T + 3.253 \cdot 10^{-1} \quad (8)$$

$$B^o = -3.208 \cdot 10^{-11} \cdot T^4 + 1.276 \cdot 10^{-8} \cdot T^3 - 1.974 \cdot 10^{-6} \cdot T^2 + 1.856 \cdot 10^{-4} \cdot T + 3.741 \cdot 10^{-2} \quad (9)$$

where a_i^o is the hardcore diameter (Å) of the i-th species and I_s is the ionic strength. Drummond parameterization has been used for the species H_2CO_3^* , using the following equation (Drummond, 1981)

$$\log_{10}(\gamma_{\text{H}_2\text{CO}_3}) = \left[C + F(T - 273.15) + \frac{G}{(T - 273.15)} \right] I_s - [E - H(T - 273.15)] \left(\frac{I_s}{1 + I_s} \right) \quad (10)$$

where T is the temperature expressed in Celsius degrees, and C , F , G , E and H are the parameters corresponding to Drummond's approach, which are collected in Table 1.

Table 1. Parameters of Drummond's approach (Drummond, 1981).

Parameter	Value
C	-1.0312
F	1.2806×10^{-3}
G	255.9
E	0.4445
H	-1.606×10^{-3}

The ionic strength, I_s , is calculated by the expression

$$I_s = \frac{1}{2} \sum_{i=1}^I c_i z_i^2 \quad (11)$$

For the chemical speciation, a system of non-linear equations must be solved, consisting of $M-2$ equations of the type defined in the expression Eq. (1) corresponding to the calculation of the total concentration of all master species except Cl^- and H_2O . The unknowns are the decimal logarithms of the activities of these $M-2$ species considered. Also, three additional equations must be solved, Eqs. (4), (5) and (11), whose unknowns are the decimal logarithm of water activity, the molal concentration of Cl^- and the ionic strength. To solve this system, the Newton-Raphson method has been used, through the free add-in module OPTIMIZ to solve systems of non-linear equation in the MS Excel environment (Foxes, 2004).

Additionally, $M-2$ total mass balance equations are formulated for the master species (except for Cl^- and H_2O)

$$\frac{\partial m_m}{\partial t} + \nabla \cdot \mathbf{l}_m = R_m \quad (12)$$

where m_m is the total mass of the m-th master species per unit total volume, $\mathbf{l}_m$ is its total molar flux which is defined as the sum of the contributions of the advective transport and the Fickian diffusion and R_m is the sink/source term that involves the rate of production or consumption of the m-th master species. Advective flow is defined by the equation

$$\mathbf{l}_m^{\text{adv}} = \rho_w C_m \mathbf{q}_m^{\text{adv}} \quad (13)$$

where ρ_w is the water density and $\mathbf{q}_m^{\text{adv}}$ is the advection velocity of m-th master species. Diffusive flow is defined by the following expression

$$\mathbf{l}_m^{\text{dif}} = -\rho_w \sum_{i=1}^I D_i^e \alpha_{im} \nabla c_i \quad (14)$$

where D_i^e is the effective diffusion coefficient of the i-th species, which is determined by the following expression, according to (Mattson et al., 2002)

$$D_i^e = \phi Sr \tau D_i^o \quad (15)$$

where ϕ is the porosity, Sr is the degree of saturation of the soil, τ is the tortuosity of the medium and D_i^o is the binary diffusion coefficient in water of the i-th species.

3. TOOL DESCRIPTION

The EE4MGM tool is composed of several worksheets that allow conducting different tasks in the conception and implementation of geochemical models in COMSOL, the multiphysics platform selected for this work. The EE4MGM tool is provided as

Supplementary Material. The capabilities and methods of use of worksheet are described in the following sections.

3.1. CES module

In the worksheet CES (Chemical Equilibrium Speciation) a geochemical speciation module for homogeneous reactions (in aqueous phase) has been implemented. The different blocks of the CES module are described below

3.1.1. Nomenclature

This block shows a list of the variables that appear in the module along with a brief description of their meaning.

3.1.2. Input - Chemical System

The selected geochemical system (species and chemical reactions involved) must be defined by the user in this block. This block is divided into 4 sections. In the section "Chemical Formula", the species considered in the geochemical system are specified, differentiated between master (yellow background) and secondary species (orange background). The section "Chemical Formula for EE4MGM" is used to define the nomenclature used for each species, both in the module for solving chemical speciation (CES) and in the worksheets that compose the code editor (EE4MGM). The name of all species-specific variables is automatically linked to this section. Therefore, to update the nomenclature, it would be enough to modify the corresponding cell in this block. In the section "Reactions" the chemical reactions of the formation of the i -th secondary species are shown. This information is very useful as it will help the user to identify α_{im} in each

case. Finally, the section " z_i " must be completed by the user with the value of the electric charge for the i -th species.

To adapt this block to any chemical system it would be enough to add and/or remove as many species as necessary and complete the information required in the four sections described above.

3.1.3. Testing Module

The purpose of this block is to check that the input variables z_i and α_{im} have been entered correctly in the CES module. For this task, a control variable, $z_{i, \text{calc}}$, has been defined that relates to the previous ones, employing the expression

$$z_{i, \text{calc}} = \sum_{m=1}^m \alpha_{im} z_m \quad (16)$$

The "Species Charge Test" section automatically indicates the ionic nature of the species (anion, cation or neutral) by highlighting the corresponding cell in green, if the input of variables is correct ($z_i = z_{i, \text{calc}}$) and in red if it's wrong. This utility facilitates the identification of any possible mistake in the inputs quickly and visually.

Additionally, a sub-block is shown for checking the electro-neutrality condition.

3.1.4. Matrix of α_{im}

In this block, the stoichiometry coefficient matrix of the m -th master species involved in the formation of the i -th secondary species is defined. These values must be entered by the user with extreme caution since both the CES module and the EE4MGM editor use these values. The matrix is composed of I rows and M columns, so its size will depend

on the chemical system evaluated, being very easy the process of adaptation to any geochemical system (add and/or remove so many rows and/or columns).

Additionally, this block shows the variables $\log_{10}(a_m)$ and z_m , linked to the precedent cells, so they should not be modified in this block.

3.1.5. Chemical Speciation

In this block, the formulation detailed in Section 2 for the chemical speciation of the geochemical system has been implemented. The block is divided into two sub-blocks, the first for the calculation of concentration, activity and activity coefficients of all species ("calculation of concentration of the i-th species") and the second, as a database, which contains all the parameters needed for the calculation of activity coefficients using the selected approach (WATEQ Debye-Hückel formulation). Both blocks are fully automated so the only inputs the user has to provide are the values of $\log_{10}(K_{eq,i})$ and a_i^o

3.1.6. Total concentration of master species

In this block, the calculations involved in the estimation the total concentration of the m-th master species (C_m) have been programmed using Eq. (1). This block does not require any user input.

3.1.7. Nonlinear System of Equations

This block shows the system of non-linear equations required to solve the chemical speciation problem. As commented previously, the system is formed by $M-2$ equations corresponding to each master species (except for Cl^- and H_2O) and three additional ones corresponding to the water activity, the molal concentration of Cl^- and the ionic strength. In this block, three sections can be differentiated: (i) Algebraic equations, where a

schematic description of the equation to be solved is shown, (ii) Right-hand side (RHS) term, which shows the calculated value of the corresponding equation, and (iii) Left-hand side (LHS) term, intended to enter the values of the total concentrations of master species of the system (text in red). The input of the values of the logarithm of water activity, the molal concentration of Cl^- and the ionic strength (text in black) are not required.

3.1.8. Computational Block

This block is the source of information needed by the module for solving the system of non-linear equations (Foxes, 2004). It is composed by three sections, the first one (blue background) shows the name of the unknowns, the second section (yellow background) includes the numerical values of these unknowns (before solving the speciation problem, the user must provide some initial values). Finally, the third section (green background) shows the error obtained after the solution of each equation.

3.2. EE4MGM module

The Equation Editor for Multiphysics Geochemical Modelling (EE4MGM) module aims to provide the modeller with the set of functions to be defined in COMSOL for the simulation of the reactive transport problem. It consists of several worksheets to distinguish the type of variable to be edited, and thus facilitate the creation of the libraries for the implementation in a multiphysics platform, as described below.

3.2.1. EE4MGM speciation

The first sheet is called "EE4MGM Speciation". The libraries needed for the calculation of the molal concentration (c_i) of each species can be obtained from that sheet. This requires the use of the stoichiometric coefficient matrix defined in the CES module. Next, there are different blocks aimed at obtaining the required libraries for the implementation.

All the equation editing blocks have the same structure. First, it shows the generic name of the variable, a brief description, the root of the nomenclature used in the multiphysics code and then the list of variables (first column) and equations required for its calculation (second column) using the nomenclature defined in EE4MGM. In Table 2, a sample of the c_i library is presented.

Table 2. Example of a library of for an equation edited with EE4MGM

Variable	C_i / m
Description	Molal concentration of the i-th species
EE4MGM variable	c_
c_Cl	c_Cl_LHS
c_H2O	a_H2O/ac_DH_H2O
c_H	a_H/ac_DH_H
c_CO3	a_CO3/ac_DH_CO3
c_i	a_i/ac_DH_i
...	...

The following libraries are available in the worksheet "EE4MGM Speciation": (i) a database of the equilibrium constants of the formation reaction of the i-th species, $K_{eq,i}$, (information linked to the CES module), (ii) the activities of the i-th species, a_i , using the Eq. (3), (iii) the electric charge of i-th species, z_i , (information linked to the CES module), (iv) parameters of WATEQ Debye-Hückel approach, (v) the activity coefficients of the i-th species, γ_i , using the Eqs. (6) and (10) and (vi) the molal concentration of the i-th species, c_i , by the Eq. (2). It is important to highlight that this worksheet is fully automated, since the information for its correct operation is provided from the CES module, and no additional input is required from the user.

3.2.2. *EE4MGM Total concentrations*

The worksheet "EE4MGM Total concentrations" is intended to create the code for the calculation of the total concentration of each master species, C_m (RHS term of algebraic equations defined in CES module). This is done using functions such as those defined in the Eq. (1). In case of a modification of the geochemical system, the incorporation or removal of blocks of calculation from the worksheet will be required, depending on the number of master species. Regarding the methodology of use, this module also does not require any user input for the correct operation of the worksheet.

3.2.3. *EE4MGM Implicit Variables*

This worksheet aims to define the code for the calculation of the activity of water (a_{H_2O}), the molal concentration of Cl^- (c_{Cl^-}) and the ionic strength (I_s), by the Eqs. (4), (5) y (11) respectively. As with the worksheets described above, no additional information is required from the user. If the geochemical model were to be modified, only the number of summands involved in the functions contemplated by the Eqs. (4), (5) and (11) would have to be adapted

3.2.4. *EE4MGM Transport*

The last worksheet, "EE4MGM transport", is focused on editing the equations that define the transport of the species of the geochemical system. From this worksheet, you can obtain the libraries of the binary diffusion coefficients (provided by the user), the effective diffusion coefficients calculated by Eq. (15), as well as the sum term corresponding to the diffusive flow through the Eq. (14). Regarding this last term, and intending to simplify the code editor, this worksheet presents greater interactivity on the user's side. The modeller must indicate which is the m-th master species for which the code for the

calculation of the diffusive flow is to be obtained. Furthermore, the selection of the direction (x, y or z) in which this flow will be evaluated (the module is prepared to obtain codes applicable to three-dimensional domains). To do this, the user only must select the master species using the labels shown on the worksheet itself and the direction of the vector component (cell Axis). On the other hand, it is necessary to indicate that to provide greater flexibility to the code editing module, the advective velocity, $\mathbf{q}_m^{adv}$, will entirely be defined by the user.

3.3 Implementation methodology

Once the code has been generated in the EE4MGM editor, the procedure for creating libraries that can be imported into COMSOL is very fast and systematic. The procedure to be followed by the user is illustrated in Figure 1. Firstly, the libraries are copied from the Excel environment, pasted into a text file, and then imported into COMSOL.

As a summary, Table 3 shows the libraries that can be obtained with the EE4MGM editor.

Figure 1. Procedure to import library equation from EE4MGM to COMSOL

356 Table 3. Library of equations edited with EE4MGM

Library	Description	EE4MGM variable	EE4MGM worksheet
$\log_{10}(K_{eq,i})$	Logarithm of the equilibrium constant	LK_	EE4MGM speciation
$\log_{10}(a_i)$	Logarithm of activity of the i-th species	L_a_	
z_i	Electric charge of the i-th species	z_	
a_i	Activity of the i-th species	a_	
a_i^o	Hard core diameter of the i-th species/ A	ai_DH_	
$\log_{10}(\gamma_i)$	Logarithm of activity coefficient of the i-th species	L_ac_DH_	
γ_i	Activity coefficient of the i-th species	ac_DH_	
c_i	Molal concentration of the i-th species	c_	
C_m	Total concentration of the m-th master species	T_m_RHS	EE4MGM Total concentrations
a_{H_2O}	Activity of H2O	L_a_H2O_RHS	EE4MGM Total concentrations
I_s	Ionic strength	IS_RHS	
c_{Cl^-}	Free chloride concentration	c_Cl_RHS	
D_i^o	Binary Diffusion coefficient	Dc_	EE4MGM Transport
D_i^e	Effective diffusion coefficient	EDc_	
$I_{m,x}^{dif}$	Diffusive flux in the x-axis of the m-th master species	Ldif_m_x	
$I_{m,y}^{dif}$	Diffusive flux in the y-axis of the m-th master species	Ldif_m_y	
$I_{m,z}^{dif}$	Diffusive flux in the z-axis of the m-th master species	Ldif_m_z	
$q_{m,x}^{adv}$	Advective velocity in the x-axis of the m-th master species	qw_x	
$q_{m,y}^{adv}$	Advective velocity in the y-axis of the m-th master species	qw_y	
$q_{m,z}^{adv}$	Advective velocity in the z-axis of the m-th master species	qw_z	
$I_{m,x}$	Total flux in the x-axis of the m-th master species	L_m_x	
$I_{m,y}$	Total flux in the y-axis of the m-th master species	L_m_y	
$I_{m,z}$	Total flux in the z-axis of the m-th master species	L_m_z	

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358 4. INSPECTION CASE

359 To check the reliability of the presented modules (CES and EE4MGM), a reactive
360 transport model has been developed in COMSOL using the code generated in the
361 EE4MGM editor and using the CES module for the calculation of the initial and boundary
362 conditions. The model implemented in COMSOL has been verified against a well-known

reactive transport software, PHREEQC, for one-dimensional transport cases and the PHAST extension for the simulation of two or three-dimensional cases. The verification case studied corresponds to a synthetic problem of seawater injection in river water both in one- and two-dimensional domains.

4.1. Modelled configuration

A one-dimensional domain of 0.5 m and a two-dimensional domain of rectangular geometry with an area of 0.125 m² (height 0.25 m and length 0.5 m) have been proposed for the modelling (Figure 2). The point of injection of seawater was at the left side of the one-dimensional domain ($x = 0$) and at an inner point of the two-dimensional domain located at $x = 0.15$ m and $y = 0.125$ m (see Figure 2). Table 4 presents the geochemical system composed of 12 master species and 39 secondary species. The equilibrium reactions, their thermodynamic constants and the physicochemical properties of each species are also shown in Table 4 (Giffaut et al., 2014). A common binary diffusion coefficient in water was employed for all species (1.157×10^{-7} m² s⁻¹).

Table 4. Thermodynamic properties of the modelled geochemical system.

Master species			
Species	Reaction	Log ₁₀ (K _{eq,i}) (25°C)	a_i^0 (Å)
Cl ⁻	-	0.00	3.6
H ₂ O	-	0.00	3.4
H ⁺	-	0.00	4.1
CO ₃ ²⁻	-	0.00	4.7
SO ₄ ²⁻	-	0.00	4.7
H ₂ PO ₄ ⁻	-	0.00	3.6
NH ₄ ⁺	-	0.00	4.1
Ca ²⁺	-	0.00	5.7
Mg ²⁺	-	0.00	5.7
Na ⁺	-	0.00	4.1
K ⁺	-	0.00	4.1
Secondary species			

Species	Reaction	Log ₁₀ (K _{eq,i}) (25°C)	a _i ⁰ (Å)
OH ⁻	H ₂ O=H ⁺ +OH ⁻	-14.00	3.6
HCO ₃ ⁻	HCO ₃ ⁻	10.33	3.6
H ₂ CO ₃ [*]	2H ⁺ +CO ₃ ²⁻ =H ₂ CO ₃ [*]	16.68	3.4
HSO ₄ ⁻	2H ⁺ +SO ₄ ²⁻ =HSO ₄ ⁻	1.98	3.6
PO ₄ ⁻³	H ₂ PO ₄ ⁻ =2H ⁺ +PO ₄ ⁻³	-19.56	6.7
HPO ₄ ⁻²	H ₂ PO ₄ ⁻ =H ⁺ +HPO ₄ ⁻²	-7.21	4.7
H ₃ PO ₄	H ⁺ +H ₂ PO ₄ ⁻ =H ₃ PO ₄	2.14	3.4
NH ₄ ⁺	NH ₄ ⁺ =H ⁺ +NH ₃	-9.23	3.4
CaHCO ₃ ⁺	Ca ²⁺ +H ⁺ +CO ₃ ²⁻ =CaHCO ₃ ⁺	11.43	4.1
CaCO ₃	Ca ²⁺ +CO ₃ ²⁻ =CaCO ₃	3.22	3.4
CaSO ₄	Ca ²⁺ +SO ₄ ²⁻ =CaSO ₄	2.31	3.4
CaPO ₄ ⁻	Ca ²⁺ +H ₂ PO ₄ ⁻ =2H ⁺ +CaPO ₄ ⁻	-13.10	3.6
CaHPO ₄	Ca ²⁺ +H ₂ PO ₄ ⁻ =H ⁺ +CaHPO ₄	-4.47	3.4
CaH ₂ PO ₄ ⁺	Ca ²⁺ +H ₂ PO ₄ ⁻ =CaH ₂ PO ₄ ⁺	1.41	4.1
CaOH ⁺	Ca ²⁺ +H ₂ O=H ⁺ +CaOH ⁺	-12.78	4.1
MgHCO ₃ ⁺	Mg ²⁺ +H ⁺ +CO ₃ ²⁻ =MgHCO ₃ ⁺	11.37	4.1
MgCO ₃	Mg ²⁺ +CO ₃ ²⁻ =MgCO ₃	2.98	3.4
MgSO ₄	Mg ²⁺ +SO ₄ ²⁻ =MgSO ₄	2.23	3.4
MgPO ₄ ⁻	Mg ²⁺ +H ₂ PO ₄ ⁻ =2H ⁺ +MgPO ₄ ⁻	-14.71	3.6
OH ⁻	Mg ²⁺ +H ₂ PO ₄ ⁻ =H ⁺ +MgHPO ₄	-4.30	3.4
MgH ₂ PO ₄ ⁺	Mg ²⁺ +H ₂ PO ₄ ⁻ =MgH ₂ PO ₄ ⁺	1.17	4.1
MgOH ⁺	Mg ²⁺ +H ₂ O=H ⁺ +MgOH ⁺	-11.68	4.1
NaHCO ₃	Na ⁺ +H ⁺ +CO ₃ ²⁻ =NaHCO ₃	10.08	3.4
NaCO ₃	Na ⁺ +CO ₃ ²⁻ =NaCO ₃	1.27	3.6
NaPO ₄ ⁻²	Na ⁺ +H ₂ PO ₄ ⁻ =2H ⁺ +NaPO ₄ ⁻²	-18.07	4.7
NaSO ₄ ⁻	Na ⁺ +SO ₄ ²⁻ =NaSO ₄ ⁻	0.94	3.6
NaHPO ₄ ⁻	Na ⁺ +H ₂ PO ₄ ⁻ =H ⁺ +NaHPO ₄ ⁻	-6.34	3.6
NaH ₂ PO ₄	Na ⁺ +H ₂ PO ₄ ⁻ =NaH ₂ PO ₄	0.41	3.4
NaOH	Na ⁺ +H ₂ O=H ⁺ +NaOH	-14.75	3.4
KPO ₄ ⁻²	K ⁺ +H ₂ PO ₄ ⁻ =2H ⁺ +KPO ₄ ⁻²	-18.26	4.7
KSO ₄ ⁻	Na ⁺ +SO ₄ ²⁻ =NaSO ₄ ⁻	0.88	3.6
KHPO ₄ ⁻	K ⁺ +H ₂ PO ₄ ⁻ =H ⁺ +KHPO ₄ ⁻	-6.40	3.6
KOH	K ⁺ +H ₂ O=H ⁺ +KOH	-14.46	3.4
MgCl ⁺	Mg ²⁺ +Cl ⁻ =MgCl ⁺	0.35	4.1
CaCl ⁺	Ca ²⁺ +Cl ⁻ =CaCl ⁺	-0.29	4.1
KCl	K ⁺ +Cl ⁻ =KCl	-0.50	3.4
NaCl	Na ⁺ +Cl ⁻ =NaCl	-0.50	3.4
CaCl ₂	Ca ²⁺ +2Cl ⁻ =CaCl ₂	-0.64	3.4

379 The chemical compositions of the river and seawater are presented in Table 5 (data
 380 adapted from (Hem, 1985)).

381 Table 5. Chemical composition of the river and seawater.

Master Species	Seawater (mol kg ^{w-1}) Inflow condition	River water (mol kg ^{w-1}) Initial condition
<i>pH</i>	8.27	7.09
<i>I_s</i>	5.85×10^{-1}	1.73×10^{-3}
Cl ⁻	5.25×10^{-1}	2.90×10^{-4}
H ⁺	2.07×10^{-3}	9.92×10^{-4}
CO ₃ ²⁻	2.31×10^{-3}	8.67×10^{-4}
SO ₄ ²⁻	2.74×10^{-2}	8.59×10^{-5}
H ₂ PO ₄ ^{-*}	9.04×10^{-7}	-
NH ₄ ⁺ *	8.10×10^{-6}	-
Ca ²⁺	9.96×10^{-3}	3.34×10^{-4}
Mg ²⁺	5.41×10^{-2}	1.38×10^{-4}
Na ⁺	4.45×10^{-1}	2.24×10^{-4}
K ⁺	9.71×10^{-3}	3.33×10^{-5}

382 *the concentration of phosphorous and nitrogen species is negligible and therefore it is not considered in the simulation exercises

383
 384 Figure 2. Conceptual model and boundary conditions applied. (a) 1D and (b) 2D
 385 domains.

The initial chemical condition in the two cases corresponds with the chemical composition of the river water (See Table 5). The initial hydraulic condition fixed was a liquid pressure equal to atmospheric pressure, P_{atm} , (100 kPa). The boundary conditions applied in the one-dimensional case were: (i) a Dirichlet boundary condition corresponding with the chemical composition of the seawater (See Table 5) was imposed at the left boundary of the domain (inflow point) and (ii) at the other boundary (outflow point), a Cauchy boundary condition to simulate a free flux was selected. The boundary conditions applied in the two-dimensional case were: (i) a Dirichlet boundary condition corresponding with the chemical composition of the river water (See Table 5) was imposed at the left and right sides of the domain, (ii) a Dirichlet condition corresponding with the chemical composition of the seawater (See Table 5) was imposed in the inflow point and (iii) a Neumann boundary condition of no flux was selected in the top and bottom sides. In addition, in both cases, a constant advective velocity of 10 cm day^{-1} was employed in the simulations.

The discretization selected in the one-dimensional domain was 100 equal-size Lagrange linear elements for the model in COMSOL and 100 cells for the PHREEQC model. In the case of the two-dimensional domain, an irregular triangular mesh (denser around the injection point) with of 4248 Lagrange linear elements was used in the COMSOL model and, in the PHAST model, a grid of 5000 cells (50 in the y-axis and 100 in the x-axis) was selected.

4.2. Simulation and verification processes

4.2.1. One-dimensional case

A simulation of 2 days was carried out. In this case, the code generated by the EE4MGM and implemented in COMSOL to simulate the chemical speciation and the reactive transport carried out by advective and diffusive processes have been verified with the well-known software PHREEQC (Parkhurst and Appelo, 2013). Figure 3 presents the spatial distribution of the total concentration of the representative master species at different times. As it can be noted, the concentration profiles obtained with the COMSOL model present a good agreement with the results obtained with PHREEQC. Besides, to check more exhaustively the chemical speciation, the concentration profiles of selected secondary species (NaCO_3^- , CaSO_4 , KOH and MgCl^+) have been analysed in Figure 4. It can be observed that the results obtained in the profiles of the secondary species also show a good agreement with the results obtained with the reference software. Finally, the pH profiles, which are more sensitive to changes in chemical speciation, have been analysed (Figure 5). As before, the fitting obtained is very satisfactory. The small discrepancies observed are since PHREEQC has implemented a much more extensive geochemical database than the one contemplated in COMSOL, and consequently includes some other chemical reactions of minor importance in which protons are involved and that are not included in the COMSOL model. However, it can be noted how the COMSOL model perfectly simulates the temporal and spatial evolution of this variable since, although the geochemical model is more limited, it includes the most important reactions in this type of problem.

431

432 Figure 3. Spatial distribution at different observation times of master species: (a) Na⁺,

433 (b) Cl⁻, (c) Ca²⁺, (d) Mg²⁺, (e) CO₃²⁻ and (f) SO₄²⁻.

Figure 4. Spatial distribution at different observation times of secondary species: (a) NaCO₃⁻, (b) CaSO₄, (c) KOH and (d) MgCl⁺.

Figure 5. Spatial distribution at different observation times of pH.

4.2.1. Two-dimensional case

In the 1-D verification case, the chemical speciation and transport have been checked in detail. As mentioned above, the EE4MGM code editor is also designed to generate the code for reactive transport modelling in higher dimensional domains. For this reason, an additional verification case applied to a two-dimensional domain was advisable. For this purpose, a simulation of 5 days has been carried out using as reference code PHAST (Parkhurst et al., 2010). To check the results obtained with the COMSOL model, two characteristic variables of the simulated problem have been selected, the pH (variable particularly sensitive to any variation in chemical speciation, Figure 6) and the total chloride concentration (a variable that experiences a great change in its magnitude in the case of an injection of seawater, Figure 7). The fitting obtained in both variables was also very satisfactory.

451

452 Figure 6. Spatial distribution of pH at different times: (a) 24 h, (b) 60 h and (c) 120 h.

453 COMSOL (solid line), PHAST (dotted line).

expressions have been included in an easily editable format, adaptable to any type of geochemical system.

The verification of the EE4MGM editor has been carried out for both one and two-dimensional domains, with excellent results, even in complex systems with many species and equilibrium reactions like the one presented. The results obtained for the total mass of the system's master species, for secondary species and the *pH* show the capabilities of the proposed tool.

SUPPLEMENTARY MATERIAL

The EE4MGM tool is provided as Supplementary Material (xlsm file).

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