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Máster Universitario
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con COMSOL Multiphysics

Master Thesis

Reactive transport at pore-scale with consideration of evolving geometry: applications to geosciences

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Summary

This Master Thesis will show the evolution of the biphasic system (L-S) where a calcite pellet is deformed in the presence of an acid current (rich in H^+). The model is built with COMSOL Multiphysics® v.6.0, a CFD (Computational Fluid Dynamics) commercial software that can couple different modules to make a more solid simulation. In this simulation the modules used are: Chemical Engineering, Deformed Geometry, Chemistry module, Surface Reactions, Transport of Diluted Species, Laminar Flow and Secondary Current Distribution.

The model consists of two components, the first one in 0 dimensions which is used to establish the chemistry of the system with the dissociation of the calcite (main reaction) and the equilibrium of the most relevant species. The second component includes the rest of the modules mentioned, the multiphysics coupling and the geometry that consists of a semicircle that represents the surface of the pellet and a rectangle that represents the fluid where the particle rests and where the acid current is added. Both components have time dependent studies.

The results of the model are represented by 1D graphics and 2D images that show the concentration of species and the deformation caused by the inlet current of protons. The results of the first component show the distribution of the different species in the equilibrium and its variation until reaching the stationary state. The results of the second component are obtained in progressive steps; firstly, the system is solved without the modules of Transport of Diluted Species and Flux of fluids and a very high reaction rate to make sure the model is working properly, that there is deformation on the pellet and to compare the concentration of the chemical species with Phreeqc, a chemical solver software. Once these results are validated, the complete model is solved with all the modules coupled and the final model shows how the surface of the pellet is reduced by the inflow of the acid current.



Introduction

The deformation that takes place in minerals and rocks is caused by several phenomena such as sedimentation, erosion by wind or water, heating, cooling, pressure, or chemical reactions. The last one is very important because it is continuously taking place due to the multiple chemical elements found at the geosphere and the atmosphere. Different types of reactions such as equilibrium or irreversible reactions keep modifying, for example, the structure of caves. The study of geochemical processes has evolved throughout the years in order to keep exploring and exploiting of surface and underground resources. The creation of conceptual and numeric models in porous media has improved the performance of many sectors such as mining industry or hydraulic engineering. These processes have been studied throughout the time to learn about them and try to control them to apply them to new technological advances. One of the most famous and developed application of this process is the carbon dioxide capture and storage (CCS) [1].

This upcoming technology may be one of the most promising measures for mitigating the anthropogenic greenhouse gas emissions. Some of the mechanisms of geological CO₂ storage include structural and stratigraphic trapping or dissolution trapping which must consider mineral precipitation or deformation due to chemical reactions. Mineralization and deformation phenomena have been studied by indirect measurements over a wide range of chemical compositions, under different storage conditions and the results show that geochemical reactions among CO₂, water and rock minerals have impact on calcite (CaCO₃) growth rate [2]. The fact that these processes take place at pore scale makes them extremely difficult to study and require complex experiments to get exact results.

The development of Computational Fluid Dynamics (CFD) software technology has led to the creation of mathematical models that can simulate the geochemical systems that take place in mineralization by solving the equations which define the physical phenomena that take place. As it involves several physical events such as fluid flows, species transport or deformation and there are many agents that can affect the model such as temperature, pressure, or pH, it is important to establish the limits of the model which include: the geometry studied, the reaction/s that take place and if their type (equilibrium, reversible...), the chemical elements involved,

the fluid used as solvent, etc. A common practice is to combine CFDs with other software to make a more accurate model by using a scanned geometry of, for example, a real sandstone as the domain [2] or couple a chemical solver which solves the mass balances and reactions that take place in the system and sends that values to the CFD to keep solving the model [3][4].

Numerical models that couple the effects of flow, transport and chemical reactions are called reactive transport models (RTM). They are essential tools for investigating fluid-rock reactions [5]. Fluid flow in natural porous media is mainly governed by flow, transport and chemical reactions. The treatment of these processes has traditionally been done using the continuum scale approach, where it is assumed that all the phases of the media coexist at each point in space. This leads to volume-averaging properties like porosity, permeability and mineral surface area within the porous media. This assumption might not be true because the inherent heterogeneity of a natural medium dictates the irregular distribution of these properties. In contrast, each physical point within the medium is occupied either by the fluid or solid phase in a pore scale model and variables like reaction rate can be measured directly [4]. Some studies have studied numerical modelling using true pore geometries [6] or tried to obtain the order of the reaction rate or de kinetic coefficient [7].

This work consists of a model of the deformation of a calcite particle (CaCO₃) caused by the flow of a current containing H⁺, a similar experiment to the one done by Apoorv Jyoti and Ralf R.Haese [4]. Calcite is chosen as the chemical system to study because it's a common mineral and, as mentioned before, it's present at geological CO₂ storage. It is a very slow reaction that takes place during months and even years but when adding acid to it, it dissolves much faster. So, the objectives of this work are:

- 1° Simulate the equilibrium of calcite with the most relevant species.
- 2° Simulate the chemical system of in the domain and verify its correct.
- 3° Simulate the deformation of the calcite pellet in presence of an acid current.

Materials and methods

The model is built up with the software COMSOL Multiphysics. As it is a complex model, it is made up of two components:

-**Component 1**: zero dimensions using the Chemical Engineering module.

-**Component 2**: two dimensions using the Deformed Geometry module, Chemistry module, Surface Reactions module, Transport of Diluted Species, Laminar Flow module and Secondary Current Distribution. In this component, three

Table 1: Reactions considered in the model and their constants.

Reaction name	Reaction equation	Equilibrium constant (K)	Kinetic constant (k)
Calcite dissociation	$\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	10E-8.48 (mol ² /L ²)	1E-8 (mol/m ² ·s)
Carbonic Acid	$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$	10E-7.329	-
Bicarbonate	$\text{H}_2\text{CO}_3 \leftrightarrow 2\text{H}^+ + \text{CO}_3^{2-}$	10E-10.681	-
Water equilibrium	$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	1E-8	-

In this component 1, as it is of 0D there is no need to mesh, and a temporal study is used for 250 days with a time step of 1 so a stationary state is reached. It takes so much time because is a slow process and the constant is the order of E-8. Once the chemical system is completed and is logic, using the tool Generate Space-Depended Model, the second component is created (**Figure 1**). This generates a 2D component with the Chemistry module coupled, a Surface Reaction module, a Transport of Diluted Species module and a Laminar Flow module. In this case, no heat transfer is studied. The component 2 ensembles the chemistry of the system with the transport of species, the convection of the fluid and the deformation of the pellet. It is formed by a 2D geometry that consists of a rectangle with 0.05 cm of with and 0.025 cm of height and a semicircle in the middle bottom width a radius of 0.01 cm which is subtracted. The final geometry is shown in **Figure 2**. The rectangle represents the aqueous system and the semicircle the calcite particle that deforms. It is considered symmetry on the blue contours in order to reduce the computation time. The materials used are water in all the domain as all the species are diluted and CaCO₃ on the boundary of the semicircle as it represents a pellet of this material. The mesh used is a physics-controlled mesh with

multiphysic couplings are used: Deforming Electrode Boundary, Nondeforming Boundary and Reacting Flow, Diluted Species.

The first component in 0D is used to establish the chemical system of the model. The studied mineral is calcite (CaCO₃) and the reactions considered are shown in **Table 1** with their respective kinetic or equilibrium constants. As the calcite dissociation is very slow, the rest of the reactions are considered to reach equilibrium.

fine element size (1.12 E-5 maximum, 5 E-7 minimum) and two boundary layers at the contours shown in **Figure 3**. Boundary layers are used when simulating fluid flow because it's important to detail the behavior of the fluid near the walls.

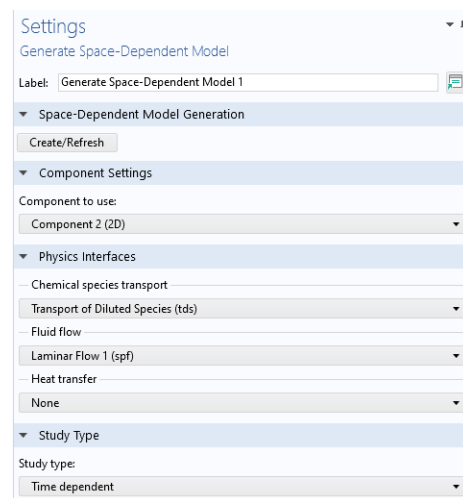


Figure 1: Creation of the second component with the tool Generate Space-Depended Model

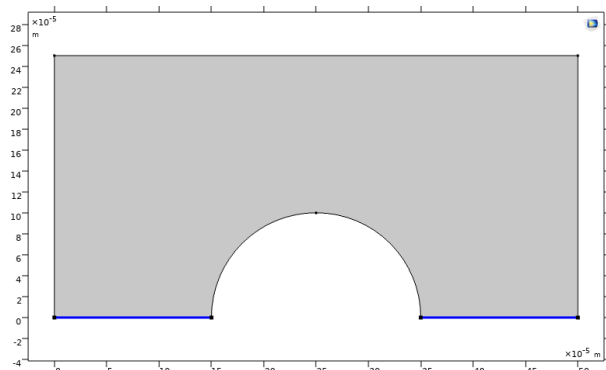


Figure 2: Final geometry constructed for the model with the symmetry axes on blue

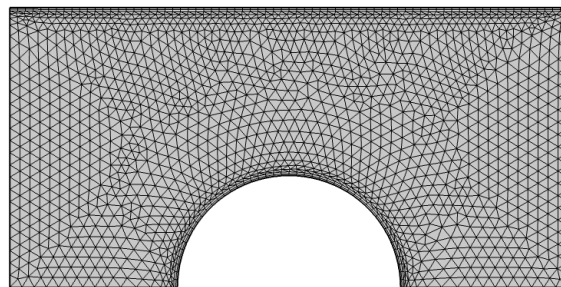


Figure 3: Physics controlled-meshing of the geometry of component 2

Theory

In component 1, the reactor is a Batch type with a volume of 1 m³. The temperature of the system is of 300 K. When the reactions are introduced, the species used are created and the rate constants are established. As the CaCO₃ is a pellet, it is considered a surface species with a constant concentration of 0.1 mol/m² assuming its size doesn't reduce much until reaching the equilibrium and the water as a solvent because it

is the fluid where the reaction takes place. The initial value of each species is calculated with the equations shown in the **Table 2**. The concentration of [H⁺] and [OH⁻] depend on the pH which is 4 at the beginning and [Ca²⁺] and [CO₃²⁻] are considered very small but not 0 to make the convergence easier.

Table 2: Initial value calculation for the different species involved for a pH = 4

Species	Initial value calculation	Initial value (mol/m ³)
H ⁺	10E-pH	0.1
OH ⁻	K _w /[H ⁺]	1 E-20
Ca ²⁺	1E-20	1 E-7
CO ₃ ²⁻	1E-20	1 E-20
HCO ₃ ⁻	[H ⁺] · [CO ₃ ²⁻]/10E-7.329	2.133 E-14
H ₂ CO ₃	[H ⁺] ² · [CO ₃ ²⁻]/10E-10.681	4.797 E-12
H ₂ O	-	1/18

As the reaction of calcite dissociation is very slow, it is considered irreversible, so it solves the equation (1) for each species where r_j is the reaction rate. The different reaction rates of the different reactions are shown in the **Table 3**. The rest of the reactions are equilibriums, so the equation (2) is calculated where K_{eq} is the equilibrium expression and K_{eq0} the equilibrium constant. C_{ref} is a parameter of 1 mol/m³ to make the units match. For the equilibrium reactions, the

reaction rate is the default by COMSOL but in the calcite dissociation depends on the dissociation kinetic constant (kf_{CaCO3}) and the distance to the equilibrium.

$$R_j = \sum_j v_{ij} r_j \quad (1)$$

$$K_{eq} = K_{eq0} \quad (2)$$

Table 3: Reaction rates definition for each reaction in the component 1.

Reaction	Reaction rate
Calcite dissociation	$k_f_{CaCO3} \cdot (1 - (re.c_Ca_2p \cdot re.c_CO3_2m / K_{eq_CaCO3}))$
Carbonic Acid	$re.c_H_1p \cdot re.c_CO3_2m \cdot 1[m^3/mol] / re.c_HCO3_1m \cdot re.Keq0_2$
Bicarbonate	$re.c_CO3_2 \cdot (re.c_H_1p \cdot 1[m^3/mol])^2 / re.c_H2CO3 \cdot re.Keq0_4$
Water equilibrium	$re.c_OH_1m \cdot re.c_H_1p \cdot re.Keq0_3$

A variable called pH is created for a later representation of the pH in the system. The expression is shown in the equation (3).

$$pH = -\log_{10}(re.c_H_1p / C_{ref} / 1000) \quad (3)$$

In component 2, two variables are created and are shown in the equations (4) and (5). The equation (4) represents the reaction rate of the calcite dissolution and the equation (4) the distance to the equilibrium of calcite. A function step is created and shown in the **Figure 4** and an average function is created in all the domain. The variable r_{CaCO_3} is the negative of the reaction rate of the chemistry module to use it in other modules and Q_{CaCO_3} is the distance to the calcite equilibrium.

$$r_{CaCO_3} = -chem.r_1 \quad (4)$$

$$Q_{CaCO_3} = chem.c_Ca_2p \cdot chem.c_CO3_2m / K_{eq_CaCO_3} \quad (5)$$

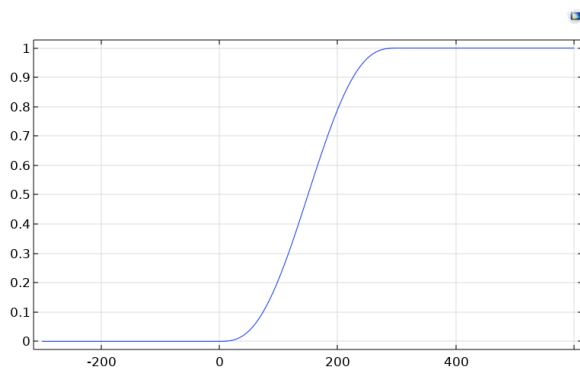


Figure 4: Function step 1 created in component 2.

The Deformed Geometry module applies as a deforming domain in all the domain. The Chemistry module and the

Surface Reaction module are generated as mentioned before so they are automatically set but for the second one where the pellet boundaries are selected and the surface material ($CaCO_3$) is established.

The Transport of Diluted Species is generated but it needs some more configuration such as the activation of convection as transport system and couple it with the velocity field of the Laminar Flow module. Diffusion coefficients are taken from the chemistry module. Initial values and reactions are already set and coupled to the chemistry module. A contour condition of symmetry is set at the lower boundaries as shown in **Figure 2**. Additionally, an inflow on the left and an outflow on the right are set. The inflow concentration of the species is the same as the initial values to simplify the calculation. The convection is coupled to the Laminar Flow. In this module, another symmetry condition is set and an inlet and outlet condition are established on the respective boundaries. The inlet velocity is 0.1 cm/min multiplied by the function step 1 to make easier the convergence by letting some time to the flux to develop.

Finally, the Secondary Current Distribution module is added and two electrode surface conditions are set. The first one on the pellet contours with a non-faradaic reaction which is the variable r_{CaCO_3} . In the dissolving-depositing species, the density and molar mass of $CaCO_3$ are set. The second electrode surface is set on the top boundary but with no reaction this time. Is important to establish 0 stoichiometric coefficient on both electro reaction conditions so that no electrochemical reaction takes place. This module is used because it is more detailed and specific with boundary deformation in chemical reactions than the Deforming Geometry module by itself.

Results and discussion

The most relevant results of the work are represented in 1D graphs and images of the resulting model. As there are 2 components, they are solved in 2 different studies and so, different groups of solution. On firsthand, the solution of the first component is shown in **Figure 5**. It can be appreciated that H^+ concentration decreases till 0 because its present in 3 of the reactions involved while on the other hand, Ca^{2+}

accumulates in the system. There is more carbonic acid than bicarbonate because equilibrium constant is three orders lower so at the beginning bicarbonate forms and then it disappears. On **Figure 6**, the evolution of the pH in the system is represented and, as it is expected, it grows due to the consumption of H^+ and the appearance of OH^- .

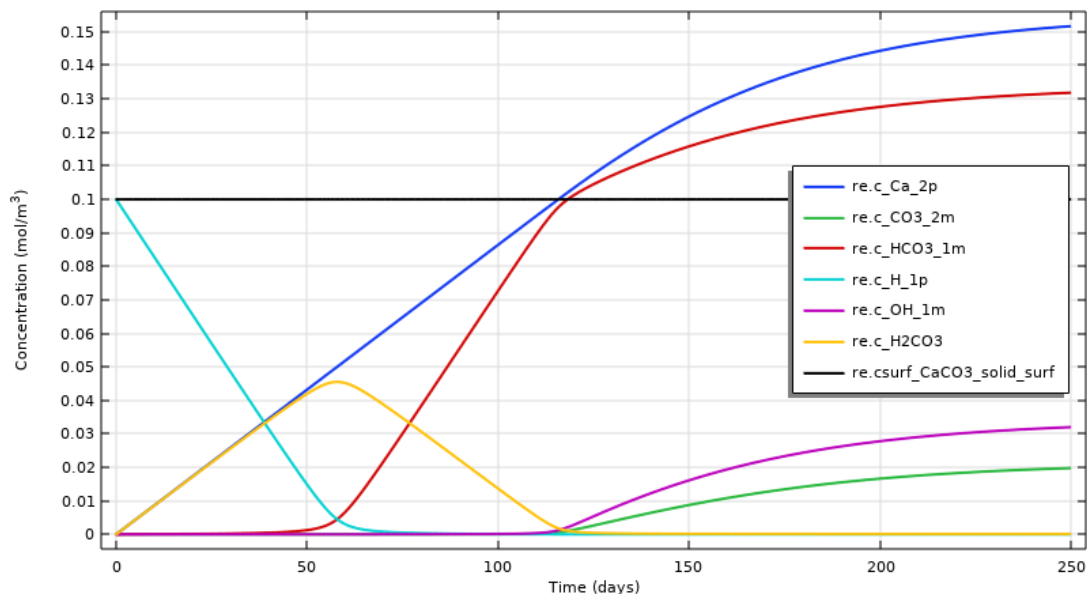


Figure 5: Representation of the chemical system and evolution of the concentration of the different species involved until reaching the calcite equilibrium in water calculated by the component 1 of the model.

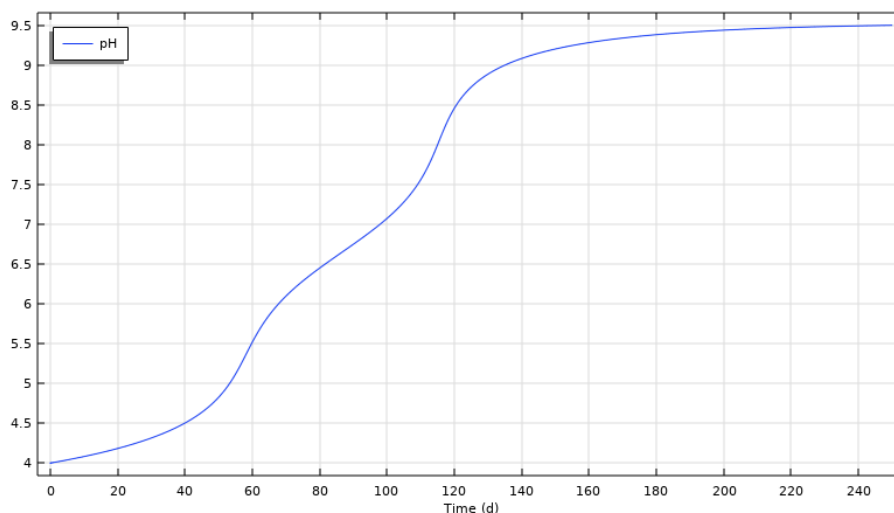


Figure 6: Evolution of the pH in the chemical system until reaching the calcite equilibrium in water calculated by the component 1 of the model.

The solution of the second component is divided in two parts. First, the system was solved without the laminar Flow Module and the inflow of species, only the chemical reactions and the deformation of the pellet in the built geometry. Also, on the Non-faradic reaction node, the reaction rate is multiplied by 1e5 to make a result observation to see if the

model is working correctly. To check the chemical system, the average function created is used to measure the Ca^{2+} , CO_3^{2-} , HCO_3^- and H_2CO_3 average concentrations (Figure 7) and compare them with a simulation of a calcite equilibrium in Phreeqc, a chemical simulator shown in Figure 8.

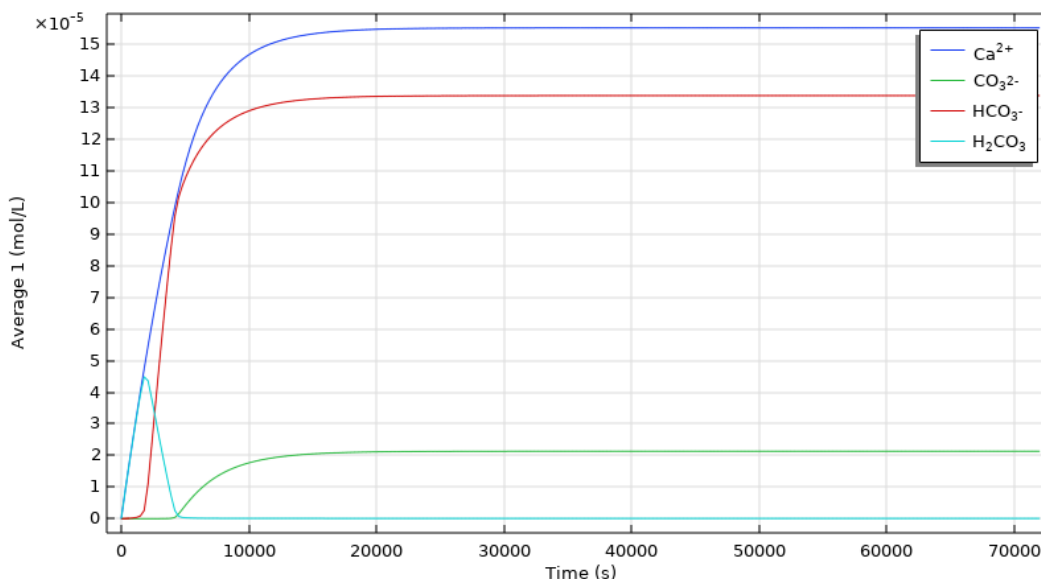


Figure 7: Average concentration of the species in the system using the average function calculated by the component 2 of the model.

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-----Description of solution-----
                                pH = 9.557      Charge balance
                                pe = -3.887     Adjusted to redox equilibrium
-----Distribution of species-----

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Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm ³ /mol
OH-	3.747e-05	3.652e-05	-4.426	-4.438	-0.011	-4.12
H+	2.842e-10	2.772e-10	-9.546	-9.557	-0.011	0.00
H2O	5.551e+01	1.000e+00	1.744	-0.000	0.000	18.07
C(-4)	8.939e-29					
CH4	8.939e-29	8.940e-29	-28.049	-28.049	0.000	35.46
C(4)	1.681e-04					
HCO3-	1.371e-04	1.337e-04	-3.863	-3.874	-0.011	24.67
CO3-2	2.505e-05	2.262e-05	-4.601	-4.646	-0.044	-5.31
CaCO3	5.562e-06	5.563e-06	-5.255	-5.255	0.000	-14.60
CaHCO3+	2.562e-07	2.497e-07	-6.591	-6.603	-0.011	9.66
CO2	8.330e-08	8.331e-08	-7.079	-7.079	0.000	34.43
(CO2) 2	1.274e-16	1.274e-16	-15.895	-15.895	0.000	68.87
Ca	1.681e-04					
Ca+2	1.622e-04	1.464e-04	-3.790	-3.834	-0.044	-18.17

Figure 8: Value of the species involved in a calcite equilibrium calculated with Phreeqc.

As the values of concentration and pH values are very similar for both simulations it can be assumed that the chemical system of the model is correct. With this first simulation, results of deformation are obtained and are shown in **Figure 9** after including a mirror 2D dataset to show the

complete particle. The figure represents the system at two different times where the deformation and reduction of the surface of the pellet can be seen. The represented species is CO_3^{2-} and, as mentioned in the **Figures 5** and **7**, its stationary concentration is 0.02 mol/m^3 .

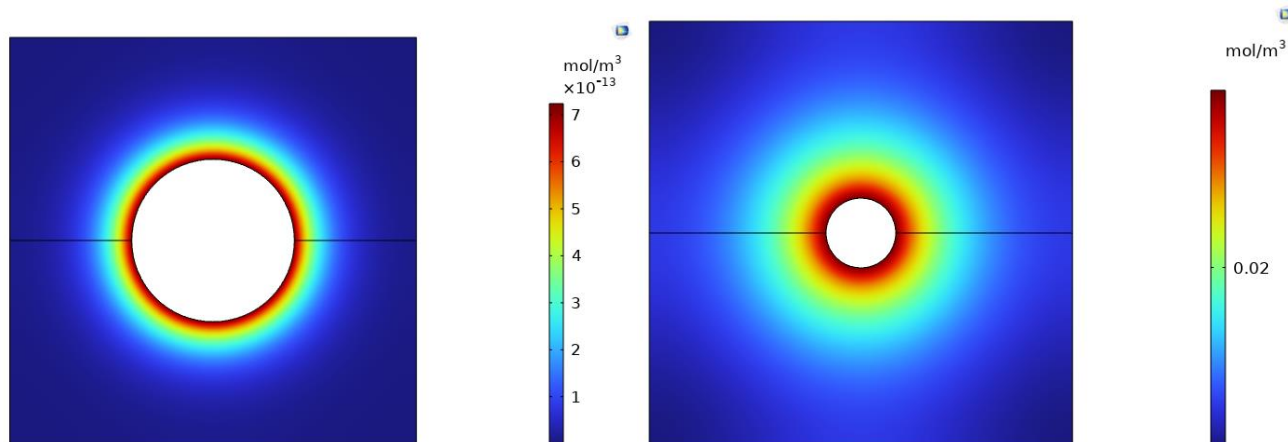


Figure 9: Evolution of the deformation of the surface of the pellet and the concentration of CO_3^{2-} in the system at time 0 mins (left) and 120 min (right) calculated by the component 2 of the model.

Now, the simulation is run with the Laminar Flow module and the inlet flow of species to get the final model and the results. In this case, three different times are represented in the **Figure 10** to show the evolution of the system in detail. In this case, an inlet flow of acid current (pH = 3 to make

convergence easier) is entering from the left side of the geometry so the concentration of H^+ in the system always keeps in the value of 1 mol/m^3 . There is less deformation in the pellet because in this case the reaction rate isn't modified and it only depends on the acid inlet.

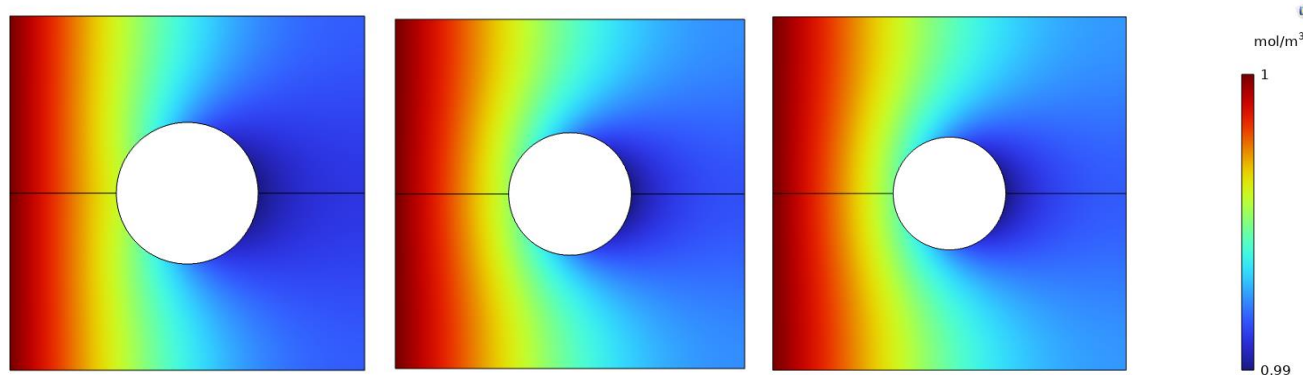


Figure 10: Evolution of the deformation of the surface of the pellet and the concentration of H^+ in the system at time 0 hours (left), 990 hours (middle) and 1200 hours (right) calculated by the component 2 of the model.



Conclusions

In this Master Thesis it has been built a model that shows the deformation of a pellet of calcite (CaCO_3) due to a current of protons (H^+) with COMSOL Multiphysics®. The main objectives have been achieved by establishing the chemical system of the equilibrium of the different species with the modules of Chemical Engineering, Chemistry and Surface Reaction while the fluid flow and transport of species has been simulated with the modules of Transport of diluted Species and Laminar Flow and the deformation of the pellet with the module of Secondary Current Distribution. Some possible continuations or extensions of this work could be to apply the model to a different geometry and use a more specific diffusion coefficient of each species.

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