

# A study on dissolution induced pore-shape evolution in calcite system

Priyanka Agrawal<sup>\*1</sup>, Amir Raoof<sup>1</sup>, Oleg Iliev<sup>2</sup> and Mariette Wolthers<sup>1</sup>

<sup>1</sup> Department of Earth Sciences-Geochemistry, Faculty of Geosciences, Utrecht University, The Netherlands <sup>2</sup>Fraunhofer ITWM, Kaiserslautern, Germany

Pe < 1; Diffusion dominated flow regime; Da-I > 0.1

# **INTRODUCTION AND AIM**

- The aim of this study is to simulate dissolution in carbonate rock systems in response to the injection of CO<sub>2</sub> -rich fluid under high pressure.
- In addition to the solution saturation state, dissolution rate is controlled by the fluid injection rate, mineral surface roughness, pH, temperature, and solution impurity.
- In dissolution experiments, pore sizes as well as pore connectivity and shape are observed to change. Such pore scale modifications contribute to the evolution of rock macroscopic properties including its porosity and permeability values. Still, these changes are difficult to capture with (pore scale) simulations
- The aim of the current work is to develop pore-scale

### **SIMULATION RESULTS**

### IMPACT OF THE FLOW RATE: pore wall dissolves more uniformly in advection dominated flow regimes.



Figure 1: Simulation results under two different flow regimes, after injection of around 3000 pore volumes, to show dissolution induced pore shape changes, the distribution of the pH field inside the pore space and calcite dissolution rate along the lateral walls of the pore. The black cylinder within the profiles indicates the size of the pore at t=0s, the coloured regions around the cylinder indicate zones dissolved during reaction.

Pe > 1; Advection dominated flow regime; Da-I < 0.1



5.3

relations for pore-shape and conductivity change with dissolution.

### THERMODYNAMICS AND KINETICS

The model is fully coupled, re-equilibrating the  $H_2O-CO_2$ -CaCO<sub>3</sub> system at every iteration.

Reversible reaction at the surface of pore •  $Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3$   $R_{calcite} = (k_1a_{H+} + k_2a_{CO2(aq)} + k_3)* \{1-[(a_{Ca}^{2+}*a_{CO3}^{2-})/K_{eq}]^{0.67}\}$ (Plummer et.al., 1978)

Dissolution rate [mol m<sup>-2</sup> s<sup>-1</sup>]
Rate constants

- Equilibrium constant
- : Activity of species *i*

# **FLUID FLOW**

R<sub>calcite</sub>

 $\mathsf{K}_{\mathsf{eq}}$ 

a

k<sub>1</sub>, k<sub>2</sub>, k<sub>3</sub>

To solve fluid flow in a single pore (under low Reynolds number and Incompressible fluid)

#### **Stokes Equation**

• Conservation of momentum:

$$\rho \frac{\partial \mathbf{u}}{\partial \mathbf{t}} + \nabla \mathbf{.} \mathbf{p} = \mu(\Delta \mathbf{u})$$

• Conservation of mass:

# IMPACT OF INFLOW ACIDITY: Pore wall dissolves more uniformly in the case of less acidic fluid injection.



#### Pe >> 1; pH 3.9; Da-I < 0.1;



Figure 2: Simulation results for two reaction regimes, after injection of around 8000 pore volumes, to show dissolution induced pore shapes, the distribution of the pH field inside the pore space and calcite dissolution rate along the lateral walls of the pore. The black cylinder within the profiles indicates the size of the pore at t=0s, the coloured regions around the cylinder indicate zones dissolved during reaction.

# FLOW EXPERIMENTS WITH CALCITE CRYSTAL



u : fluid velocity, p : fluid pressure,  $\rho$  : fluid density  $\mu$  : fluid viscosity

**Boundary Conditions:** 

- Inlet: Constant flow rate
- Outlet: Constant pressure

# **SPECIES TRANSPORT**

Advection-Diffusion-Reaction controlled transport

 $\frac{\partial ci}{\partial t} + \nabla (-Di \nabla ci) + u \nabla ci = Ri$ 

u : fluid velocity,  $c_i$ ,  $D_i$ ,  $R_i$  : concentration, diffusion coefficient and reaction term of species i

Initial conditions inside the pore:

- Calcite saturated water with pH = 9.99
- Surface concentration of calcite = 2.71 mol/m<sup>2</sup>

Boundary Conditions:

• Inflow: Water equilibrated to different level of pCO<sub>2</sub>

# **MOVING BOUNDARY**

Normal velocity of the wall-fluid interface, due to dissolution of the calcite:

$$V_n = R_{calcite} * MV$$



Figure 3: Results from the microscopic experiments conducted to observe changes in the shape of the channel drilled through a calcite crystal, after a number of dissolution rounds through injection of 0.01M HCl acid with two flow rates. The measured pH of outflow solution is 3.1 (High flow rate experiment) vs 8.4 (Low flow rate experiment), confirming the trend we see in the simulations (FIG 1).



V<sub>n</sub> : Normal velocity of the pore wall [m/s] MV : Molar volume of calcite [m<sup>3</sup>/mol]

### **FUTURE WORK**



- <sup>2</sup>To test the influence of solution stoichiometry in terms of the  $Ca^{2+}$  vs  $CO_3^{2-}$  ions over the pore shape.
- <sup>3</sup>To implement the conductance vs pore volume relations in the pore network model.

### REFERENCES

- 1. Plummer, L. N., T. M. L. Wigley, and D. L. Parkhurst (1978), The kinetics of calcite dissolution in CO2– water systems at 5 degree C to 60 degree C and 0.0 to 1.0 atm CO2, Am. J. Sci., 278, 179–216.
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- 3. Raoof, A., Nick, H. M., Hassanizadeh, S. M., & Spiers, C. J. (2013). PoreFlow: A complex pore-network model for simulation of reactive transport in variably saturated porous media. *Computers & Geosciences*, *61*, 160-174.

Figure 4 : Pore shape spectrum across different flow and reaction regimes

Figure 5: Pressure drop profile along the pore length

#### 9.0 - Pe = 320 8.0 - Pe = 32 7.0 -Pe = 3.2 6.0 — Pe = 0.32 0 5.0 4.0 3.0 2.0 1.0 2.5 1.5 2.0 3.0 1.0 V/Vo

Figure 6 : Normalized conductance of the pore vs Normalized volume of the pore across different flow regimes.

### **CONCLUSION**

- This reactive transport model of calcite dissolution at a single pore scale shows the effect of flow rate and the acid strength of the injecting solution on the pore shape evolution.
- High injection rate or fluids with low acid strength, yields more uniform pore shapes and larger increase in conductance.

The implication of shape over the pressure drop profile, and consequently the conductance-pore volume relationship, is significant. Therefore, the assumption of a well-mixed system at the pore scale, needs screening through such pore scale work.