

PET565 PART B: EXERCISE SET 5

GOALS

- Become familiar with reactive chemistry in porous media through working with an example case where MgCl₂ is injected into chalk.
- Review important concepts by solving exercises

IMPORTANT NOTES

A code for solving the MgCl₂ case is implemented in Matlab which accounts for advection, dispersion, ion exchange and dissolution and precipitation of minerals. The code is run by opening and running the file 'main_GC_model.m'.

1. EXERCISES

1.1. Consider the MgCl₂ injection model implemented in Matlab.

Let the calcite concentration be given as $\rho_c^0 = 1000$. The initial composition is $C_{ca}^0 = 0.001$ with $C_{mg}^0, \beta_{ca}^0, \beta_{mg}^0$ defined to be in reactive equilibrium. The injected composition is $C_{ca}^{inj} = 0$, $C_{mg}^{inj} = 20$ and $C_{cl}^{inj} = 40$. All concentrations are measured in mmol/L. In all cases let $k_2 = 0.5k_1$. Use N=50 cells.

First, assume there are no dissolution / precipitation reactions by setting $k_1 = 10^{-6}$, while $CEC = 15$ meq/L, $K = 0.3$ (where $K = \frac{\beta_{mg}C_{ca}}{\beta_{ca}C_{mg}}$). Let the injection rate be $q = 1$ PV/d.

- Plot the time and spatial distributions of the concentration variables during the injection of 2 pore volumes (2d). What is the characteristic behaviour of the tracer (Cl), sorbant (Mg) and desorbant (Ca)? Why is the surface composition containing only Mg and no Ca after flooding?
- Increase the CEC to 30 meq / L. What is the effect?
- Let CEC = 15, but change K to 0.1. What is the effect?

Next, assume there are no ion exchange reactions by setting $CEC = 10^{-4}$, while the the reaction rate constant $k_1 = 0.1$.

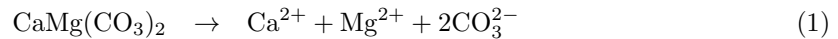
- Plot the ion concentration profiles along the core and with time during the first 4 pore volumes (4d). What is the difference between this process and the ion exchange process?
- Increase the rate constant to $k_1 = 1$ and then $k_1 = 10$. What happens to the effluent profiles? What happens to the mineral distributions?
- Let $k_1 = 0.1$, but reduce the injection rate to 0.1 PV/d and consider the profiles along the core after 40 d (4 PV). What is observed compared to the reference case ($q = 1$ PV/d and $k_1 = 0.1$)?

Finally, include both effects by setting $CEC = 15$ meq/L, $K = 0.3$ and $k_1 = 0.1$. Let the rate be $q=1$ PV/d.

- Plot the effluent profiles and spatial distributions during injection in 4 d (4 PV). What is similar and different compared to the previous cases? Describe the dynamic equilibrium state that develops inside the core.
- Why is there still Ca left on the rock surface after the system has reached a steady state?
- Reduce the rate to $q = 0.1$ PV/d and consider the effluent profiles during 40 d (4 PV). Is the amount of Ca on the surface at steady state the same in this case?

1.2. Assume a solution contains 0.04 mol/L NaCl and 0.01 mol/L CaCl₂. Calculate the concentrations C_i of aqueous species Na⁺, Cl⁻, Ca²⁺, the ionic strength I , and the activity coefficients γ_i (using Davies).

1.3. Consider a system where distilled water (no ions initially) is equilibrated with dolomite $\text{CaMg}(\text{CO}_3)_2$ (s) according to the reaction:



where the solubility product $K_{dol} = 10^{-16.7}$

- Calculate how many moles dolomite per L that can be dissolved. Assume $\gamma_i = 1$.
- Further assume that the brine is in contact with atmospheric CO_2 having partial pressure $P_{co2} = 10^{-3.5}$. Carbon interaction is described by the following reactions:



where the equilibrium constants are respectively $K_H = 10^{-1.5}$, $K_1 = 10^{-6.3}$, $K_2 = 10^{-10.3}$. How does the atmospheric interaction affect the dissolution of dolomite?

Hint: HCO_3^- dominates the carbon content. Assume charge balance in the brine is given by

$$m_{ca}z_{ca} + m_{mg}z_{mg} + m_{hco3}z_{hco3} = 0 \quad (5)$$

1.4. Seawater contains mainly the species Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} and carbon. Assume that it is possible to form aqueous complexes such as CaSO_4^0 , MgSO_4^0 and NaSO_4^- .

- Write the 3 relevant reactions for formation of the 3 complexes.
- Formulate 3 equilibrium equations for these reactions.
- Express 4 mass balances for Ca^{2+} , Mg^{2+} , Na^+ and SO_4^{2-} that relate total concentrations C_i , concentrations of free species m_i and concentrations of complexes n_{ij} .

1.5. Assume a species adsorbs according to $q(c) = c^{0.5}$ and brine is injected. Assume advection and adsorption are the dominant mechanisms. Calculate the concentration profile $c(x)$ when the injected water has moved $x_w = 10$ m if

- the initial concentration is $c_i = 1$ and the injected concentration is $c^{inj} = 4$.
- the initial concentration is $c_i = 4$ and the injected concentration is $c^{inj} = 1$.