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 $k2 = 0.5k1$. Use N=50 cells.

First, assume there are no dissolution / precipitation reactions by setting $k1 = 10^{-6}$, 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 $CaCl_2$. Calculate the concentrations C_i of aqueous species Na^+, Cl^-, Ca^{2+}, 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 $CaMg(CO_3)_2$ (s) according to the reaction:

$$CaMg(CO_3)_2 \quad \rightarrow \quad Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \tag{1}$$

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:

$$CO_2\ (g) + H_2O \quad \rightleftharpoons \quad H_2CO_3^* \tag{2}$$

$$H_2CO_3^* \quad \rightleftharpoons \quad H^+ + HCO_3^- \tag{3}$$

$$HCO_3^- \quad \rightleftharpoons \quad H^+ + CO_3^{2-} \tag{4}$$

  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

$$m_{ca} z_{ca} + m_{mg} z_{mg} + m_{hco3} z_{hco3} = 0 \tag{5}$$

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 $c^{inj} = 1$.