

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?

Answer. Ion exchange:

- The middle concentration of chloride breaks through after 1 PV has been injected. Mg is retained and is produced later. Since the adsorption process is only transient, after a while the injected concentrations are produced. Ca is accumulated in the brine and transported out. There is only Mg in the injected brine, no Ca, and therefore the brine will continue to desorb Ca and lose Mg until the capacity is filled by Mg.
- At increased CEC we see more adsorption and desorption. The Mg is more delayed and more Ca is produced.
- At lower K it takes higher concentrations of Mg to give the same adsorption. The result is a slower adsorption / desorption process.

Dissolution processes:

- This is not a transient process, but a steady-state process where a dynamic equilibrium between transport and reaction processes develops. The concentration profiles along the core stabilizes after some time. A stable production of Ca and stable retention of Mg is observed.
- At higher reaction rates we see more dissolution and precipitation, but not more than the equilibrium composition. The greatest changes happen near the inlet where the brine is most reactive. The concentrations also stabilize closer to the inlet.
- At lower rates the brine has more time inside the core to react and the chemical effects are seen more clearly. There are strong similarities in the observed behaviour between reducing the injection rate and increasing the reaction rate.

Combined effects:

- A peak in the Ca effluent profile can be observed due to ion exchange. Stable production of Ca and retention of Mg is observed due to dissolution and precipitation. The ion exchange effects are most visible in the beginning.
- Dissolution of calcite along the core produces Ca to the brine which balance the amount of Ca that can desorb from the surface. Since there is a stable dissolution, there is also a finite amount that will desorb from the surface.
- Slower injection gives more dissolution and precipitation effects. Higher Ca concentrations and lower Mg concentrations are then obtained in the core which leads to less desorption of Ca from the surface and less adsorption of Mg.

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).

Answer. Concentrations:

$$C_{na} = 0.04 \cdot 1 = 0.04 \text{ mol/L} \quad (1)$$

$$C_{cl} = 0.04 \cdot 1 + 0.01 \cdot 2 = 0.06 \text{ mol/L} \quad (2)$$

$$C_{ca} = 0.01 \cdot 1 = 0.01 \text{ mol/L} \quad (3)$$

Ionic strength:

$$I = 1/2(0.04 \cdot 1^2 + 0.06 \cdot (-1)^2 + 0.01 \cdot (+2)^2) = 1/2(0.04 + 0.06 + 0.04) = 0.07 \quad (4)$$

Activity coefficients:

$$\log \gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) = -0.51z_i^2 \left(\frac{\sqrt{0.07}}{1 + \sqrt{0.07}} - 0.3 \cdot 0.07 \right) \quad (5)$$

$$= -0.096z_i^2 \quad (6)$$

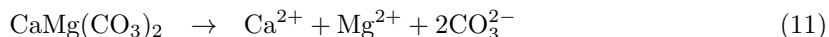
$$\log \gamma_{na} = \log \gamma_{cl} = -0.096 \cdot 1^2 = -0.096 \quad (7)$$

$$\gamma_{na} = \gamma_{cl} = 0.80 \quad (8)$$

$$\log \gamma_{ca} = -0.096 \cdot 2^2 = -0.384 \quad (9)$$

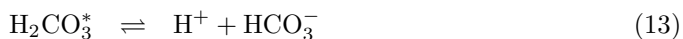
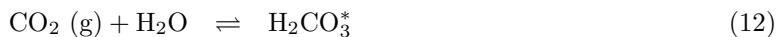
$$\gamma_{ca} = 0.413 \quad (10)$$

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

$$m_{ca}z_{ca} + m_{mg}z_{mg} + m_{hco3}z_{hco3} = 0 \quad (15)$$

Answer.

- Let m be dissolved moles per liter. We have $m = m_{ca} = m_{mg} = 2m_{co3}$.

$$K_{dol} = [\text{Ca}^{2+}][\text{Mg}^{2+}][\text{CO}_3^{2-}]^2 = m_{ca}m_{mg}m_{co3}^2 = m \cdot m \cdot (1/2m)^2 = 1/4m^4 \quad (16)$$

$$m = (4K_{dol})^{1/4} = 9.45 \cdot 10^{-5} \text{ mol / L} \quad (17)$$

- Let m be dissolved moles per liter. We have $m = m_{ca} = m_{mg}$. EQ equations (with $\gamma = 1$):

$$K_H = \frac{m_{h2co3}}{P_{co2}} \quad (18)$$

$$K_1 = \frac{m_h m_{hco}}{m_{h2co3}} \quad (19)$$

$$K_2 = \frac{m_h m_{co3}}{m_{hco3}} \quad (20)$$

Solve with respect to m_{co3} :

$$m_{co3} = K_2 m_{hco3}^2 / (K_1 K_H P_{co2}) \quad (21)$$

From the charge balance we further have

$$2m_{ca} + 2m_{mg} - m_{hco3} = 0 \quad (22)$$

or

$$m_{hco3} = 2m_{ca} + 2m_{mg} = 4m \quad (23)$$

such that

$$m_{co3} = K_2 (4m)^2 / (K_1 K_H P_{co2}) \quad (24)$$

$$K_{dol} = [\text{Ca}^{2+}][\text{Mg}^{2+}][\text{CO}_3^{2-}]^2 \quad (25)$$

$$= m_{ca}m_{mg}m_{co3}^2 = m \cdot m \cdot \left(K_2 (4m)^2 / (K_1 K_H P_{co2}) \right)^2 \quad (26)$$

$$= m^6 \left(\frac{16K_2}{K_1 K_H P_{co2}} \right)^2 \quad (27)$$

$$m = \left[K_{dol} \left(\frac{K_1 K_H P_{co2}}{16K_2} \right)^2 \right]^{1/6} = \left[10^{-16.7} \left(\frac{10^{-6.3} \cdot 10^{-1.5} \cdot 10^{-3.5}}{16 \cdot 10^{-10.3}} \right)^2 \right]^{1/6} \quad (28)$$

$$= 3.03 \cdot 10^{-4} \text{ mol/L} \quad (29)$$

The presence of atmospheric carbon has increased the solubility of dolomite by a factor of 3.2.

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} .

Answer. Reactions:



Equilibrium equations:

$$K_{caso} = \frac{[\text{CaSO}_4^0]}{[\text{Ca}^{2+}][\text{SO}_4^{2-}]} = \frac{\gamma_{\text{CaSO}_4^0}}{\gamma_{\text{Ca}^{2+}}\gamma_{\text{SO}_4^{2-}}} \frac{n_{\text{CaSO}_4^0}}{m_{\text{Ca}^{2+}}m_{\text{SO}_4^{2-}}} \quad (33)$$

$$K_{mgso} = \frac{[\text{MgSO}_4^0]}{[\text{Mg}^{2+}][\text{SO}_4^{2-}]} = \frac{\gamma_{\text{MgSO}_4^0}}{\gamma_{\text{Mg}^{2+}}\gamma_{\text{SO}_4^{2-}}} \frac{n_{\text{MgSO}_4^0}}{m_{\text{Mg}^{2+}}m_{\text{SO}_4^{2-}}} \quad (34)$$

$$K_{naso} = \frac{[\text{NaSO}_4^-]}{[\text{Na}^+][\text{SO}_4^{2-}]} = \frac{\gamma_{\text{NaSO}_4^-}}{\gamma_{\text{Na}^+}\gamma_{\text{SO}_4^{2-}}} \frac{n_{\text{NaSO}_4^-}}{m_{\text{Na}^+}m_{\text{SO}_4^{2-}}} \quad (35)$$

Mass balance equations:

$$C_{\text{Ca}^{2+}} = m_{\text{Ca}^{2+}} + n_{\text{CaSO}_4^0} \quad (36)$$

$$C_{\text{Mg}^{2+}} = m_{\text{Mg}^{2+}} + n_{\text{MgSO}_4^0} \quad (37)$$

$$C_{\text{Na}^+} = m_{\text{Na}^+} + n_{\text{NaSO}_4^-} \quad (38)$$

$$C_{\text{SO}_4^{2-}} = m_{\text{SO}_4^{2-}} + n_{\text{CaSO}_4^0} + n_{\text{MgSO}_4^0} + n_{\text{NaSO}_4^-} \quad (39)$$

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 $c^{inj} = 1$.

Answer. Assuming adsorption (by isotherm) and advection are the only mechanisms, we can apply the retardation model. We calculate

$$\frac{dq}{dc} = \frac{1}{2c^{0.5}} \quad R = 1 + dq/dc \quad x_c = \frac{1}{R_c} x_{H_2O} \quad (40)$$

For different concentrations we can calculate:

c	$R = 1 + dq/dc$	$x_c = x_w/R_c$
1	1.5	6.67
2.5	1.32	7.57
4	1.25	8

If the concentrations are not overlapping this provides the solution. In the situation that a front / jump develops we calculate the speed using

$$R_{jump} = 1 + \frac{\Delta q}{\Delta c} = 1 + \frac{q(4) - q(1)}{4 - 1} = 1 + \frac{4^{0.5} - 1^{0.5}}{4 - 1} = 1.33 \quad (41)$$

The different results are shown in Figures 1-3.

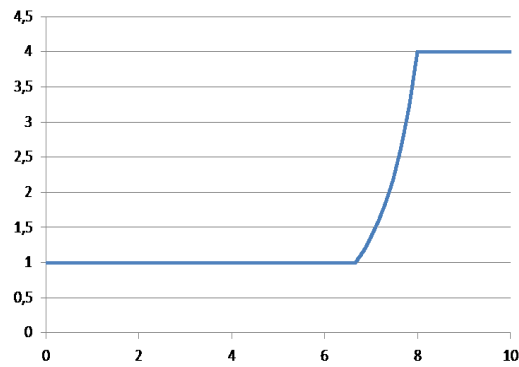


FIGURE 1. Plot of concentration c against position x after water has reached $x = 10\text{m}$. Initial concentration is 4 and injected concentration is 1. Since high concentrations travel faster this solution results in a broadening front where $x_c = x_{H_2O}/R_c$.

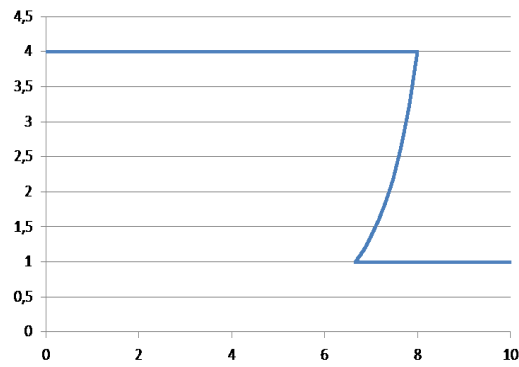


FIGURE 2. Plot of concentration c against position x after water has reached $x = 10\text{m}$. Initial concentration is 1 and injected concentration is 4. Since high concentrations travel faster they will catch up with each other. The drawn solution is unphysical.

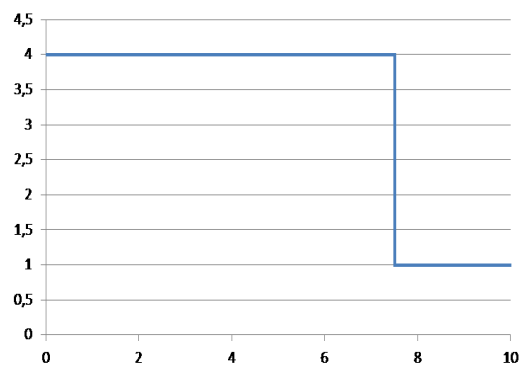


FIGURE 3. Plot of concentration c against position x after water has reached $x = 10\text{m}$. Initial concentration is 1 and injected concentration is 4. The front solution is drawn.