

**Problem 1.**

- (a) Assume a brine contains 0.05 M Na<sup>+</sup>, 0.02 M Ca<sup>2+</sup> and 0.03 M SO<sub>4</sub><sup>2-</sup>.  
 - Calculate the ionic strength of the solution.  
 - Calculate the activity coefficients.  
 - What is the ion activity product of anhydrite CaSO<sub>4</sub> (s)?

Relevant equations are:

$$I = 1/2 \sum_i m_i Z_i^2, \quad \log \gamma_i = -Az_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right), \quad A = 0.51$$

(Answer) -

$$I = 1/2 \sum_i m_i Z_i^2 = 1/2(0.05 \cdot 1^2 + 0.02 \cdot 2^2 + 0.03 \cdot 2^2) = 1/2(0.05 + 0.08 + 0.12) = 0.125$$

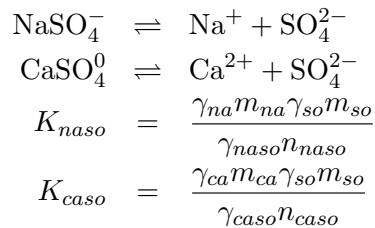
$$\log \gamma_i = -Az_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) = -0.51z_i^2 \left( \frac{\sqrt{0.125}}{1 + \sqrt{0.125}} - 0.3 \cdot 0.125 \right) = -0.114z_i^2$$

$$\gamma_{na} = 10^{-0.114} = 0.77, \quad \gamma_{ca} = \gamma_{so} = 10^{-0.114 \cdot 2^2} = 0.35$$

$$IAP = \gamma_{ca} m_{ca} \gamma_{so} m_{so} = 0.35 \cdot 0.02 \cdot 0.35 \cdot 0.03 = 7.35 \cdot 10^{-5}$$

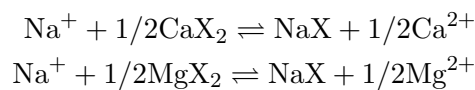
- (b) For the same brine, assume formation of the complexes NaSO<sub>4</sub><sup>-</sup> CaSO<sub>4</sub><sup>0</sup>.  
 - Describe the relevant dissociation reaction for these complexes and corresponding equilibrium equations.  
 - Write mass balance equations for the species Na<sup>+</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>.

(Answer) -



$$\begin{aligned} C_{na} &= m_{na} + n_{naso} \\ C_{ca} &= m_{ca} + n_{caso} \\ C_{so} &= m_{so} + n_{caso} + n_{naso} \end{aligned}$$

- (c) The reactions for ion exchange of Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> are given as follows



- Use the law of mass action to write equilibrium conditions for this system.
- Define, in words and mathematically, the mass balance condition for the surface activities.

Assume  $\gamma_i = 1$  and the solution contains 0.1 M  $\text{Na}^+$ , 0.02M  $\text{Ca}^{2+}$  and 0.03 M  $\text{Mg}^{2+}$ . Also assume  $K_{naca} = 0.4$  and  $K_{namg} = 0.5$ .

- Use the 3 equations to determine the surface composition.

(Answer) -

$$K_{naca} = \frac{\beta_{na} \gamma_{ca}^{0.5} m_{ca}^{0.5}}{\beta_{ca}^{0.5} \gamma_{na} m_{na}}$$

$$K_{namg} = \frac{\beta_{na} \gamma_{mg}^{0.5} m_{mg}^{0.5}}{\beta_{mg}^{0.5} \gamma_{na} m_{na}}$$

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$$\beta_{na} + \beta_{ca} + \beta_{mg} = 1$$

The activities are given by equivalent fractions or molar fractions and must therefore add to 1.

- Using  $\gamma = 1$  we get:

$$\beta_{ca} = \beta_{na}^2 \frac{m_{ca}}{m_{na}^2 K_{naca}^2}$$

$$\beta_{mg} = \beta_{na}^2 \frac{m_{mg}}{m_{na}^2 K_{namg}^2}$$

$$\beta_{na} + \beta_{na}^2 \frac{m_{ca}}{m_{na}^2 K_{naca}^2} + \beta_{na}^2 \frac{m_{mg}}{m_{na}^2 K_{namg}^2} = 1$$

$$\beta_{na}^2 \left( \frac{m_{ca}}{m_{na}^2 K_{naca}^2} + \frac{m_{mg}}{m_{na}^2 K_{namg}^2} \right) + \beta_{na} - 1 = 0$$

$$\beta_{na}^2 \left( \frac{0.02}{0.1^2 \cdot 0.4^2} + \frac{0.03}{0.1^2 \cdot 0.5^2} \right) + \beta_{na} - 1 = 0$$

$$\beta_{na}^2 \cdot 24.5 + \beta_{na} - 1 = 0$$

$$\beta_{na} = \frac{1}{2 \cdot 24.5} (-1 + \sqrt{1 - 4 \cdot 24.5 \cdot (-1)}) = 0.183$$

$$\beta_{ca} = \beta_{na}^2 \frac{m_{ca}}{m_{na}^2 K_{naca}^2} = 0.187^2 \frac{0.02}{0.1^2 \cdot 0.4^2} = 0.419$$

$$\beta_{mg} = \beta_{na}^2 \frac{m_{mg}}{m_{na}^2 K_{namg}^2} = 0.187^2 \frac{0.03}{0.1^2 \cdot 0.5^2} = 0.402$$

**Problem 2.**

- (a) Brine is injected into a system with velocity  $v_w$ , and it carries a species with concentration  $c$  which adsorbs at amount  $q(c)$  at a given concentration  $c$ . This system can be described by the partial differential equation:

$$\partial_t c = -v \partial_x c - \partial_t q(c)$$

- Show that for continuous solutions the speed  $v_c$  of a given concentration  $c$  is given as

$$v_c = v_w \frac{1}{1 + dq/dc}$$

Assume  $v_w = 1$  m/d and the length of the system is 1 m.

- The adsorption term is given as  $q = c^{0.5}$ . What type of adsorption isotherm is this? What other types do you know?
- The initial concentration is  $c = 1$  and the injected concentration is  $c = 4$ , Plot the concentration profile  $c(x)$  after 1 d.
- Assume that the initial concentration is  $c = 4$  and the injected concentration is  $c = 1$ . Plot the concentration profile  $c(x)$  after 1 d.

- (Answer) - A species not adsorbing has speed given by  $v$ . By accounting for adsorption we see that

$$\partial_t(c + q(c)) = (1 + dq/dc)\partial_t c = -v\partial_x c$$

such that a concentration gets an equivalent speed

$$\partial_t c = -\frac{v}{(1 + dq/dc)} \partial_x c$$

- When  $q$  is of the form  $q = Kc^n$  it is called a Freundlich isotherm. Another type is the Langmuir isotherm  $q = q_{max} \frac{rc}{1+rc}$ .
- After 1 day the water has travelled  $x_w = 1$ m. We calculate  $dq/dc$  for different concentrations.  $dq/dc = \frac{0.5}{c^{0.5}}$ . The position for a continuous solution is  $x_c = \frac{x_w}{1+dq/dc}$ .

$$c = 1 : \quad dq/dc = 0.50, \quad x_c = 0.67$$

$$c = 2 : \quad dq/dc = 0.35, \quad x_c = 0.74$$

$$c = 3 : \quad dq/dc = 0.29, \quad x_c = 0.78$$

$$c = 4 : \quad dq/dc = 0.25, \quad x_c = 0.80$$

The lowest concentrations are slowed down the most. If a low concentration is injected it represents the continuous solution. If a high concentration is injected a jump is formed. The jump has position given by:

$$x_f = \frac{x_w}{1 + \frac{q_4 - q_1}{4 - 1}} = \frac{1}{1 + \frac{2 - 1}{4 - 1}} = 0.75$$

- (b) Assume we inject a brine into a rock that can adsorb one of the components in the brine.
- Which mathematical model can be used to describe the system?
  - Show mathematically how we can use measurements of the concentration at the

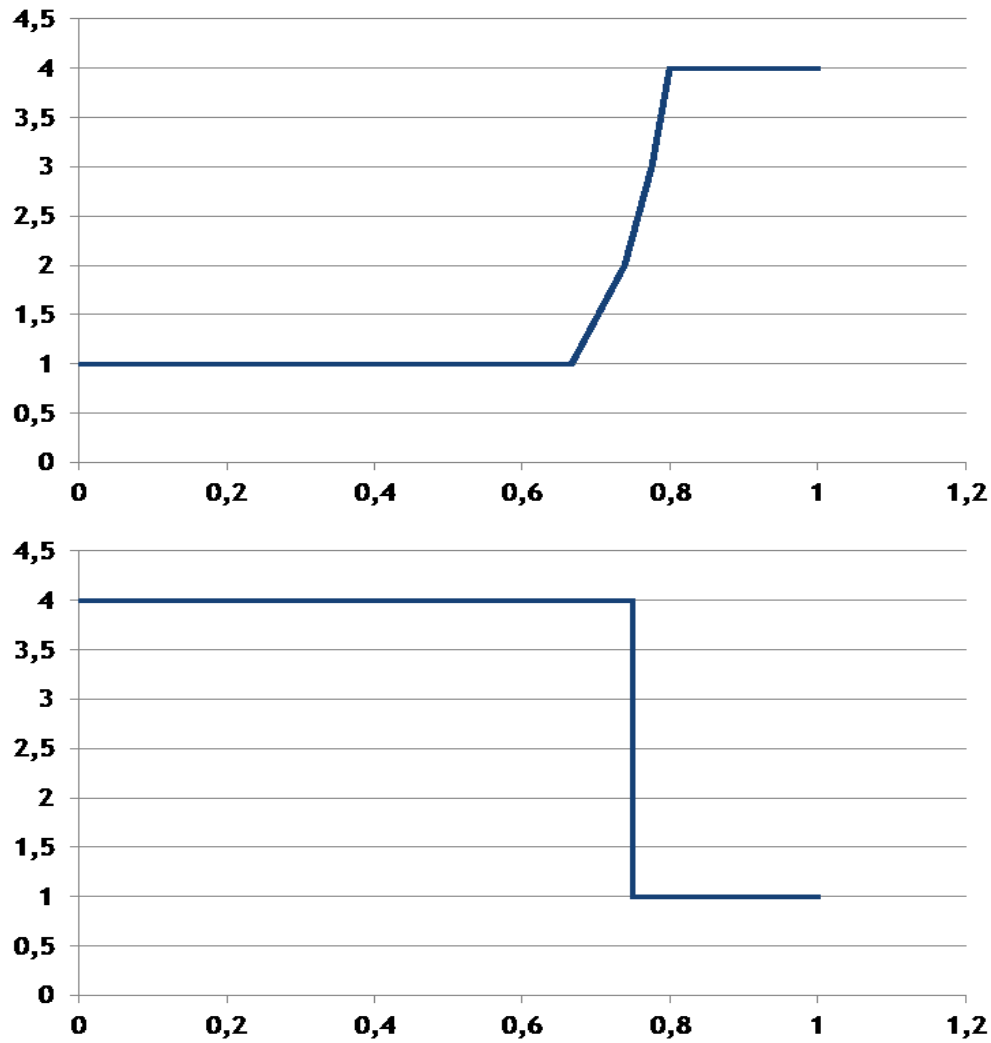


FIGURE 1. Concentration distributions for problem 2a.

- outlet of the sample vs time to measure how many moles are adsorbed by the rock.
- Explain how an adsorption isotherm can be produced from experimental measurements. There are several ways to do this.
  - How can a tracer-adsorption system be used to interpret wettability in chalk?

(Answer) - We should include mechanisms such as advection, dispersion, diffusion and adsorption. This can be written by the following equation for sorbing agents

$$\partial_t(c + q(c)) = -v_w \partial_x c + D \partial_{xx} c$$

and

$$\partial_t c = -v_w \partial_x c + D \partial_{xx} c$$

for tracers.

- The moles entering the system are given by  $\int_{t_1}^{t_2} Av_w c(x=0, t) dt$ , The moles produced are given by  $\int_{t_1}^{t_2} Av_w c(x=L, t) dt$ . If we inject a tracer and sorbing agent at the same concentrations we will inject the same amounts, but produce less of the sorbing agent. The sorbed amount in moles is then given by  $\int_{t_1}^{t_2} Av_w (c_{tracer} - c_{sorbant})(x=L, t) dt$ .

- By the described procedure we can measure the amount of moles adsorbing at a given concentration and normalize by volume or mass of rock. By using different concentrations we produce different  $q(c)$  for different  $c$ . It is also possible to match the sorbant profile of the experiments by adjusting the assumed isotherm. Notably only the concentration range between the injected and initial should be the valid range of the isotherm.

- If more of the surface is wetted by oil, less of the component should be able to adsorb on the surface. The wettability should therefore be related to the amount of adsorption.

- (c) The equation for a system with advection, dispersion and adsorption can be described as

$$\partial_t(c + q(c)) = -v_w \partial_x c + D \partial_{xx} c$$

where  $D$  is dispersion coefficient. Assuming a fixed concentration  $c_0$  at the inlet boundary and a uniform initial concentration  $c_i$ : If there is no adsorption  $q(c) = 0$  the concentration  $c(x, t)$  is given by

$$c(x, t) = c_i + \frac{c_0 - c_i}{2} \left[ \operatorname{erfc}\left(\frac{x - vt}{\sqrt{4Dt}}\right) + \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x + vt}{\sqrt{4Dt}}\right) \right]$$

- Using this result, derive an analytical expression for the solution of (1) in the case where  $q(c) = k \cdot c$  (a linear adsorption isotherm).

- Find the analytical solution if there is no advection or adsorption.

- Assume  $c_0 = 10$ ,  $c_i = 0$  and  $D = 10^{-9}$ . Calculate the position of the concentration  $c = 5$  after 5 hrs (still assuming no advection).

- (Answer) - The left hand term can be written as

$$\partial_t(c + kc) = (1 + k) \partial_t c$$

such that the full equation can be written

$$\partial_t c = -\frac{v_w}{1+k} \partial_x c + \frac{D}{1+k} \partial_{xx} c$$

We can then replace the parameters  $v_w, D$  by  $\frac{v_w}{1+k}, \frac{D}{1+k}$  in the analytical solution when including adsorption.

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$$c(x, t) = c_i + (c_0 - c_i) \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right)$$

- We solve for  $x$ :

$$c = c_i + (c_0 - c_i) \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right)$$

$$x = \operatorname{erfc}^{-1}\left(\frac{c - c_i}{c_0 - c_i}\right) \sqrt{4Dt} = \operatorname{erfc}^{-1}\left(\frac{5 - 0}{10 - 0}\right) \sqrt{4 \cdot 10^{-9} \cdot 5 \cdot 3.6 \cdot 10^3}$$

$$x = \operatorname{erfc}^{-1}(0.5) \sqrt{7.20 \cdot 10^{-5}} = 0.47 \cdot 8.49 \cdot 10^{-3} \text{ m} = 4.0 \text{ mm}$$

(d) Assume a solution of  $\text{MgCl}_2$  is injected into a chalk core (made of calcite  $\text{CaCO}_3$ ). This task will be used to represent that system mathematically.

- Assuming  $\text{CaCO}_3$  can dissolve and  $\text{MgCO}_3$  can precipitate. Write dissolution reactions for both minerals.

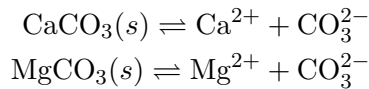
- Also, simplify into 1 reaction by assuming dissolution of one mineral results in precipitation of the other mineral. Suggest a reaction rate expression for dissolution of calcite in this reaction. What are the units?

- Assume ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can adsorb on the surface via ion exchange. Write the corresponding reaction and equilibrium condition.

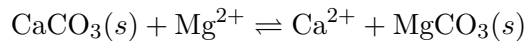
- Assume  $\text{Cl}^-$  behaves like a tracer. What does this mean?

- Write transport equations for the aqueous species  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , the adsorbing cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and the minerals  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . Describe the mechanisms and variables you include and how the transport and distribution of the different species are related.

(Answer) -



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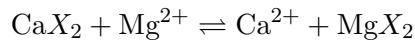


A rate expression can be given as

$$\dot{r} = k_1 C_{ca} - k_2 C_{mg}$$

If it is treated as a pure source term this will have the units of mol/liter/s.  $k_1, k_2$  will have units 1/s, while the concentrations are in mol/L.

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Equilibrium is given by

$$K = \frac{\gamma_{ca} m_{ca} \beta_{mg}}{\gamma_{mg} m_{mg} \beta_{ca}}$$

- It means chloride is assumed to not react chemically and can be described by transport mechanisms only (advection, dispersion, diffusion).

z	erfc(z)	z	erfc(z)	z	erfc(z)
0	0.0000	0.5	0.5205	1	0.8427
0.05	0.0564	0.55	0.5633	1.05	0.8624
0.1	0.1125	0.6	0.6039	1.1	0.8802
0.15	0.1680	0.65	0.6420	1.15	0.8961
0.2	0.2227	0.7	0.6778	1.2	0.9103
0.25	0.2763	0.75	0.7112	1.25	0.9229
0.3	0.3286	0.8	0.7421	1.3	0.9340
0.35	0.3794	0.85	0.7707	1.35	0.9438
0.4	0.4284	0.9	0.7969	1.4	0.9523
0.45	0.4755	0.95	0.8209	1.45	0.9597

FIGURE 2. Complementary error function table.

$$\begin{aligned}
\partial_t(C_{cl}) &= -v\partial_x C_{cl} + D\partial_{xx} C_{cl} \\
\partial_t(C_{ca} + \rho_{ca}^s) &= -v\partial_x C_{ca} + D\partial_{xx} C_{ca} + \dot{r} \\
\partial_t(C_{mg} + \rho_{mg}^s) &= -v\partial_x C_{mg} + D\partial_{xx} C_{mg} - \dot{r} \\
\partial_t \rho_c &= -\dot{r} \\
\partial_t \rho_m &= \dot{r}
\end{aligned}$$

Chloride is represented as a tracer, while calcium and magnesium are affected by precipitation /dissolution and ion exchange. The concentrations on the surface are given such that  $\rho_{ca}^s Z_{ca} + \rho_{mg}^s Z_{mg} = CEC$  is constant and the exchange equilibrium condition is fixed. The rate expression for dissolution and precipitation appears in the different equations to make sure that a species leaving one phase appears in another.  $\rho, \rho^s$  are moles per liter in mineral phase or surface with reference to the pore volume (for consistency with brine concentrations).