

Practical 3: Solubility, Sorption and Ion Exchange Equilibria Applied to Soil and Groundwater

The goal of this practical is to use solubility and surface complexation calculations to predict the aqueous concentrations of a toxic metal (Pb) in water equilibrated with a contaminated soil. As with earlier practicals, the strategy you should use is to write out the equilibrium expressions and take the p-function of both sides to get a set of simple linear equations that you can solve.

1. A soil contains 50 ppm Pb (Atomic mass = 207.2) as PbSO_4 (anglesite). The porosity of the soil is 15 % and the density of the soil is 2.65 g/cm^3 . For the problems below, use the table of equilibrium constants:

Reaction	pK
$\text{PbSO}_4 = \text{Pb}^{2+} + \text{SO}_4^{-2}$	7.8
$\text{PbCO}_3 = \text{Pb}^{2+} + \text{CO}_3^{-2}$	13.1
$\text{CaSO}_4 = \text{Ca}^{2+} + \text{SO}_4^{-2}$	4.4
$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{-2}$	8.5
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{-2}$	10.33
$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$	1.46
$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^{-}$	6.35

- (a) Calculate the concentration of Pb in a solution that saturates the solution in pore space of the soil. Assume that only anglesite is present. Does the amount of anglesite in the soil matter? Assume charge balance requires $[\text{Pb}^{2+}] = [\text{SO}_4^{-2}]$.
- (b) Now assume that the soil also contains 1 wt. % CaSO_4 (anhydrite). What does the charge balance condition require? Does the amount of anhydrite matter? Calculate the concentration of Pb in the porewater.
- (c) Now assume that the soil also contains 1 wt % CaCO_3 . Will PbSO_4 dissolve to precipitate PbCO_3 ? Calculate the solubility of Pb if the pH of the soil is 8 and is in equilibrium with the atmosphere so that $P_{\text{CO}_2} = 10^{-3.5}$

(d) Now include the effect of sorption on FeOOH (5 wt. %) in the soil at pH 8. The surface area of the FeOOH is 30 m²/g and there are 3 >FeOH sites/nm². (note: >FeOH means a surface site). Relevant equilibria are

Reaction	pK
>FeOH + H ⁺ = >FeOH ₂ ⁺	-9.2
>FeOH + Pb ⁺² = >FeOHPb ⁺²	-4.65

First, calculate the maximum sorption capacity of the goethite. Then assume, as a first approximation, that essentially all of the Pb sorbs to the goethite to get a value for {>FeOHPb⁺²}. Now, calculate the resulting concentration of dissolved Pb that would be in equilibrium with a goethite with that value of {>FeOHPb⁺²}. Note that you have {>FeOH}/{>FeOH₂⁺} = 10^{-pK_a}10^{-pH} and also {>FeOH} + {>FeOH₂⁺} + {>FeOHPb} = 1.

e) If you understand all this, do it again for the soil at pH = 6.

2. Water from the Bath Hot Springs (pH = 6.65) has the following chemical analysis:

	mol/kg	pC
HCO ₃ ⁻	3.147 x 10 ⁻³	
Ba	1.75 x 10 ⁻⁷	
Ca	9.52 x 10 ⁻³	
Cl	8.09 x 10 ⁻³	
Fe ⁺²	1.77 x 10 ⁻⁵	
K	4.45 x 10 ⁻⁴	
Mg	2.18 x 10 ⁻³	
Mn	1.24 x 10 ⁻⁶	
Na	7.96 x 10 ⁻³	
SO ₄	1.08 x 10 ⁻²	
Si	3.43 x 10 ⁻⁴	
Sr	6.73 x 10 ⁻⁵	

What minerals has this water equilibrated with? To find out, calculate the **saturation index** (log (Q/K) = pK-pQ) of each candidate mineral. The quantity Q is the observed "ion activity product" of a mineral. For example, the Q for KCl (sylvite) in the above analysis is [K][Cl] = (4.45x10⁻⁴)(8.09x10⁻³)= 3.6 x10⁻⁶. You need the following equilibria:

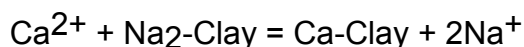
Equilibrium	pK	pQ
CaCO ₃ = Ca ²⁺ + CO ₃ ⁻²	8.48	
CO ₃ ⁻ + H ⁺ = HCO ₃ ⁻	-10.33	
MgSO ₄ ·7H ₂ O = Mg ²⁺ + SO ₄ ⁻² + 7H ₂ O	1.96	

$\text{BaSO}_4 = \text{Ba}^{+2} + \text{SO}_4^{-2}$	9.98	
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{-2} + 2\text{H}_2\text{O}$	4.85	
SiO_2 (quartz) + $2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	4.0	
SiO_2 (amorphous) + $2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	3.0	
$\text{FeCO}_3 = \text{Fe}^{2+} + \text{CO}_3^{-2}$	10.6	
$\text{Mg}_2\text{Si}_3\text{O}_7 \cdot 5\text{OH} \cdot 3\text{H}_2\text{O}$ (sepiolite) + $0.5\text{H}_2\text{O} + 4\text{H}^+ = 2\text{Mg}^{+2} + 3\text{H}_4\text{SiO}_4$	-15.91	
$\text{CaMg}(\text{CO}_3)_2$ (dolomite) = $\text{Ca}^{+2} + \text{Mg}^{+2} + 2\text{CO}_3^{-2}$	17.0	

When the saturation index > 0 , ($pQ < pK$) then the mineral will want to precipitate out; when $SI = 0$ ($pQ = pK$) the solution is in equilibrium with that mineral; when $SI < 0$ ($pQ > pK$), the mineral will dissolve in the solution. Because of analytical error and kinetics, you can assume that if $pQ = pK \pm 0.4$ then the solution is saturated in that mineral. Assume now that all of the iron oxidizes when reaching the surface. Will $\text{Fe}(\text{OH})_3$ precipitate out and make a rusty mess at Bath Spa? You need the following equilibria: (Hint: work out the dominant Fe dissolved complex (e.g. Fe^{3+} , $\text{Fe}(\text{OH})_2^+$ or $\text{Fe}(\text{OH})_3^0$ at pH 6.65 and the equilibrium expression for $\text{Fe}(\text{OH})_3$ (ferrihydrite) dissolving to give that complex.

$\text{Fe}(\text{OH})_3$ (ferrihydrite) + $3\text{H}^+ = \text{Fe}^{+3} + 3\text{H}_2\text{O}$	-4.9
$\text{Fe}^{+3} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	5.7
$\text{Fe}^{+3} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3^0 + 3\text{H}^+$	13.6

3. Consider the ion exchange reaction



with

$$K_s = \frac{N_{\text{Ca}} [\text{Na}]^2}{N_{\text{Na}}^2 [\text{Ca}]} = 2.35$$

a) Calculate the equivalent fraction of exchange sites occupied by Ca if $[\text{Na}] = 0.1 \text{ M}$ and $[\text{Ca}] = 0.1 \text{ M}$ assuming activities = concentrations.

b) Do the same as in a) but when the soil solution is diluted by a factor of 100. What is the effect of dilution on the Na content of the clay?

4. Consider the uptake of Cs⁺ by a Ca⁺² clay: In terms of Cation Exchange capacity (CEC), we can write:

$$N_{Cs} = \frac{M_{Cs}}{CEC}; \quad N_{Ca} = \frac{M_{Ca}/2}{CEC} = \frac{CEC - M_{Cs}}{CEC}$$

where M_{Cs} is the number of mmoles of Cs per kg/clay

$$K_s = \frac{(M_{Cs}/CEC)^2 [Ca^{2+}]}{\left(\frac{CEC - M_{Cs}}{CEC}\right) [Cs^+]^2} = 2.35$$

Supposing a clay had a cation exchange capacity of 200 mmoles/kg. Calculate the K_d for Cs between clay and the soil solution with $[Ca] = 0.001$ and $[Cs] = 0.001$ M. What assumptions have to be made before you can use this K_d in a contaminant-transport model?