

### SOLUTIONS for Practical 3: Solubility and Sorption 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.

1. A soil contains 50 ppm Pb (Atomic mass = 207.2) as  $\text{PbSO}_4$  (anglesite). The porosity of the soil is 15 % and the density of the soil is  $2.65 \text{ g/cm}^3$ . 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
$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{CO}_3^{-2}$	6.35

- (a) Calculate the concentration of Pb in a solution that saturates the 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. %  $\text{CaSO}_4$  (anhydrite). What does the charge balance condition require? Does the amount of anhydrite matter?
- (c) Now assume that the soil also contains 1 wt %  $\text{CaCO}_3$ . Will  $\text{PbSO}_4$  dissolve to precipitate  $\text{PbCO}_3$ ? 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  $\text{FeOOH}$  (5 wt. %) in the soil. The surface area of the  $\text{FeOOH}$  is  $30 \text{ m}^2/\text{g}$  and there are 3  $>\text{FeOH}$  sites/ $\text{nm}^2$ . (note:  $>\text{FeOH}$  means a surface site). Relevant equilibria are

Reaction	pK
$>\text{FeOH} + \text{H}^+ = >\text{FeOH}_2^+$	-9.2
$>\text{FeOH} + \text{Pb}^{+2} = >\text{FeOHPb}^{+2}$	-11.0**

\*\*Note: I just made this pK up; don't use it for a real problem!

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

**Solution:**

(a) If only anglesite is present, then  $pPb + pSO_4 = 7.8$ . If  $[Pb]=[SO_4]$ , then  $pPb = pSO_4$  so that  $pPb = 3.9$ .

(b) If anglesite and anhydrite are present, we have:

$$pPb + pSO_4 = 7.8$$

$$pCa + pSO_4 = 4.4$$

By charge balance  $[Ca] + [Pb] = [SO_4]$ . But  $CaSO_4$  is much more soluble than  $PbSO_4$ . Hence,  $[Ca] = [SO_4]$  so that  $pCa \approx pSO_4$ . Hence,  $pSO_4 = 2.2$  and  $pPb = 5.6$ .

(c) Now, if  $CaCO_3$  is present, we have the following equilibria:

$$pH_2CO_3 - pP_{CO_2} = 1.46 \text{ or } pH_2CO_3 = 4.96$$

$$pHCO_3^- + pH - pH_2CO_3 = 6.35 \text{ or } pHCO_3^- = 3.31 \text{ (at pH=8)}$$

$$pH + pCO_3 - pHCO_3^- = 10.33 \text{ or } pCO_3 = 5.64$$

If cerussite ( $PbCO_3$ ) is present then  $pPb + pCO_3 = 13.1$ . Hence,  $pPb = 7.46$ . This is much smaller than if  $PbSO_4 + CaSO_4$  were present. Hence, if we add calcite, we will dissolve  $PbSO_4$  and precipitate  $PbCO_3$ .

(d) The sorption capacity of the  $FeOOH$  is

$$\frac{0.05 \text{ g } FeOOH}{\text{g Soil}} \times \frac{30 \text{ m}^2}{\text{g } FeOOH} \times \frac{3 \text{ sites}}{\text{nm}^2} \times \frac{10^{18} \text{ nm}^2}{\text{m}^2} \times \frac{1 \text{ mole}}{6.023 \times 10^{23}} = \frac{7.5 \times 10^{-6} \text{ moles } > FeOH}{\text{g Soil}}$$

$$\frac{7.5 \times 10^{-6} \text{ moles } > FeOH}{\text{g Soil}} \times \frac{2.6 \text{ g}}{\text{cm}^3 \text{ soil}} \times \frac{1 \text{ cm}^3 \text{ soil}}{0.15 \text{ cm}^3 \text{ water}} \times \frac{1000 \text{ cm}^3 \text{ water}}{\text{kg}} = \frac{0.129 \text{ moles } > FeOH}{\text{kg water}}$$

Given the surface complexation equilibria, we have

$$pK_a = p\{\text{FeOH}_2^+\} - p\{\text{FeOH}\} - \text{pH}$$

$$pK_s = p\{\text{FeOHPb}\} - p\{\text{FeOH}\} - \text{pPb}$$

at pH 8,  $p\{\text{FeOH}_2^+\} \approx 0$  and, hence,  $p\{\text{FeOH}\} \approx 1.2$ .

Most of the Pb will be adsorbed so that,  $p\{\text{FeOHPb}\} = p([\text{Pb}]_{\text{tot}}/\text{Stot})$

Now the total amount of Pb is

$$\frac{50\text{mgPb}}{\text{kgSoil}} \times \frac{2.6\text{gsoil}}{\text{cm}^3\text{soil}} \times \frac{1\text{cm}^3\text{Soil}}{0.15\text{cm}^3\text{H}_2\text{O}} \times \frac{1\text{gPb}}{1000\text{mgPb}} \times \frac{1\text{kgSoil}}{1000\text{gSoil}} \times \frac{1000\text{cm}^3\text{H}_2\text{O}}{\text{kgH}_2\text{O}}$$

$$\times \frac{1\text{molePb}}{207\text{gPb}} = \frac{4.2 \times 10^{-3} \text{ molesPb}}{\text{kgwater}}$$

Hence,  $p\text{Pb}_{\text{tot}} = 2.37$ . We can now estimate  $p\{\text{FeOHPb}\} = 2.37 - 0.89 = 1.48$  (about 3% of the surface sites). Hence,

$$p\text{Pb} = p\{\text{FeOHPb}\} - p\{\text{FeOH}\} - pK_s = 1.48 - 1.2 - (-11.0) = 11.28$$

Note how the FeOOH sorption greatly lowers the concentration of Pb. In the presence of FeOOH, all the  $\text{PbCO}_3$  would dissolve and Pb would be sorbed on the FeOOH.

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

**Solution:** The concentrations are

	mol/kg	pC
HCO <sub>3</sub> <sup>-</sup>	3.147 x 10 <sup>-3</sup>	2.50
Ba	1.75 x 10 <sup>-7</sup>	6.8
Ca	9.52 x 10 <sup>-3</sup>	2.0
Cl	8.09 x 10 <sup>-3</sup>	2.1
Fe <sup>+2</sup>	1.77 x 10 <sup>-5</sup>	4.75
K	4.45 x 10 <sup>-4</sup>	3.35
Mg	2.18 x 10 <sup>-3</sup>	2.66
Mn	1.24 x 10 <sup>-6</sup>	5.91
Na	7.96 x 10 <sup>-3</sup>	2.10
SO <sub>4</sub>	1.08 x 10 <sup>-2</sup>	1.97
Si	3.43 x 10 <sup>-4</sup>	3.46
Sr	6.73 x 10 <sup>-5</sup>	4.17

The resulting pQ values are as follows. Hence the groundwater is oversaturated in CaCO<sub>3</sub>, CaSO<sub>4</sub>·2H<sub>2</sub>O, BaSO<sub>4</sub>, Sepiolite and just at equilibrium with dolomite.

Equilibrium	pK	pQ
CaCO <sub>3</sub> = Ca <sup>2+</sup> + CO <sub>3</sub> <sup>-2</sup>	8.48	8.18
CO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> = HCO <sub>3</sub> <sup>-</sup>	-10.33	-----
MgSO <sub>4</sub> ·7H <sub>2</sub> O = Mg <sup>2+</sup> + SO <sub>4</sub> <sup>-2</sup> + 7H <sub>2</sub> O	1.96	4.63
BaSO <sub>4</sub> = Ba <sup>+2</sup> + SO <sub>4</sub> <sup>-2</sup>	9.98	8.77
CaSO <sub>4</sub> ·2H <sub>2</sub> O = Ca <sup>2+</sup> + SO <sub>4</sub> <sup>-2</sup> + 2H <sub>2</sub> O	4.85	3.97
SiO <sub>2</sub> (quartz) + 2H <sub>2</sub> O = H <sub>4</sub> SiO <sub>4</sub>	4.0	3.46
SiO <sub>2</sub> (amorphous) + 2H <sub>2</sub> O = H <sub>4</sub> SiO <sub>4</sub>	3.0	3.46
FeCO <sub>3</sub> = Fe <sup>2+</sup> + CO <sub>3</sub> <sup>-2</sup>	10.6	10.93
Mg <sub>2</sub> Si <sub>3</sub> O <sub>7.5</sub> OH:3H <sub>2</sub> O (sepiolite) + 0.5H <sub>2</sub> O + 4H <sup>+</sup> = 2Mg <sup>+2</sup> + 3H <sub>4</sub> SiO <sub>4</sub>	-15.91	-10.9
CaMg(CO <sub>3</sub> ) <sub>2</sub> (dolomite) = Ca <sup>+2</sup> + Mg <sup>+2</sup> + 2CO <sub>3</sub> <sup>-2</sup>	17.0	17.02

pCO<sub>3</sub> =  
6.18

**Second Part:**

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? You need the following equilibria:

$\text{Fe}(\text{OH})_3(\text{ferrihydrite}) + 3\text{H}^+ = \text{Fe}^{+3} + 3\text{H}_2\text{O}$	-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

Hint: work out the dominant Fe dissolved complex (e.g.  $\text{Fe}^{3+}$ ,  $\text{Fe}(\text{OH})_2^+$  or  $\text{Fe}(\text{OH})_3^0$ ) at pH 6.65 and the equilibrium expression for  $\text{Fe}(\text{OH})_3$  dissolving to give that complex.

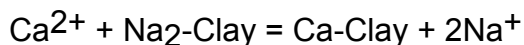
**Solution:** at pH 6.65 we have

$5.7 = 2(6.65) + \text{Fe}(\text{OH})_2^+ - \text{pFe}^{+3}$  so that  $\text{pFe}(\text{OH})_2^+ - \text{pFe}^{+3} = -7.6$ ; upon reflection, this means that  $[\text{Fe}(\text{OH})_2^+]/[\text{Fe}^{+3}] = 10^{7.6}$  and  $\text{Fe}(\text{OH})_2^+$  is the dominant species of iron. From the above equilibria, we get



At pH 6.65, with  $\text{pFe}_{\text{tot}} = 4.75$ , we get  $\text{pQ} = 4.75 - 6.65 = -1.9$ . Since  $\text{pQ} < \text{pK}$ , we will have ferrihydrite precipitate out when it reaches the surface (as it does, although in truth the reaction would be facilitated by chemolithoautotrophic bacteria..).

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.

Solution: Use the equilibrium expression

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

substitute the concentrations of Na and Ca to get

$$K_s = \frac{N_{Ca} [0.1]^2}{N_{Na}^2 [0.1]} = 2.35$$

or

$$N_{Ca} = 23.5 N_{Na}^2$$

we also have the fact that

$$N_{Ca} + N_{Na} = 1.0$$

hence we get a quadratic equation:

$$23.5 N_{Na}^2 + N_{Na} - 1.0 = 0$$

Using the quadratic formula, we get

$$N_{Na} = \frac{-1 \pm \sqrt{1 - 4(23.5)(-1)}}{2(23.5)} = 0.186 \text{ (or } -0.228)$$

Only the positive answer is physically meaningful.

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?

Again, use the equilibrium expression

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

substitute the new concentrations of Na and Ca to get

$$K_s = \frac{N_{Ca} [0.001]^2}{N_{Na}^2 [0.001]} = 2.35$$

or

$$N_{Ca} = 2350 N_{Na}^2$$

we also have

$$N_{Ca} + N_{Na} = 1.0$$

hence we get a quadratic equation:

$$2350 N_{Na}^2 + N_{Na} - 1.0 = 0$$

Using the quadratic formula, we get

$$N_{Na} = \frac{-1 \pm \sqrt{1 - 4(2350)(-1)}}{2(2350)} = 0.01$$

The much smaller Na content has important implications for the physical behavior of the clay (swelling).

4. Consider the uptake of Cs<sup>+</sup> by a Ca<sup>+2</sup> 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 at 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?

Solution:

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

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

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

$$K_D = \frac{(M_{Cs})}{[Cs^+]} = \left(\frac{K_s CEC^2}{[Ca^{2+}]} \left(\frac{CEC - M_{Cs}}{CEC}\right)\right)^{1/2}$$