Exercise 1: Solubility of anhydrite and gypsum

Meret Aeppli

Determine the state of saturation of seawater of normal salinity with respect to anhydrite ($CaSO_4(s)$).

$\{Ca^{2+}\} = 2.4 * 10^{-3}$ M

$\{SO_4^{2-}\} = 1.9 * 10^{-3}$ M

$K_{s0} = 4.2 * 10^{-5}$

Exercise 1: Solution

$IAP = \{M(aq)\}^{n}_{actual}\ \{X(aq)\}^{m}_{actual} = 4.7 * 10^{-6}$

$K_{s0} = 4.2 * 10^{-5}$

Hence, K_{s0} > IAP and the solution is undersaturated with respect to anhydrite.

Exercise 2: Ion activity

What are the activity and concentration of Na^+ in a solution of 1 mM NaCl?

Exercise 2: Solution

First, determine I. Before (example 1 from 2 slides ago), we found that in a 1 mM NaCl solution:

$I = 0.5 * (C_{Na+} * z^2_{Na+} + C_{Cl-} * z^2_{Cl-}) = 0.5 * (10^{-3} * 1^2 + 10^{-3} * (-1)^2) = 10^{-3}$ M

Then determine γ_i :

$$\log\gamma_i = -A \cdot z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 \cdot I \right) = -0.5 \cdot 1 \cdot \left(\frac{\sqrt{0.001}}{1+\sqrt{0.001}} - 0.2 \cdot 0.001 \right) = -0.01523$$

$\gamma_i = 10^{-0.01523} = 0.966$

Therefore, $\{Na^+\}$ = 0.966 mM, whereas $[Na^+]$ = 1 mM

Exercise 3: Solubility in natural waters

- Which factors influence metal solubility?
- Does an increase/decrease of these factors have a positive or negative effect on solubility?

Solubility of metals in natural waters

- Temperature
  - Solubility of salts increases with increasing temperature
  - Entropy effect
- Salinity
  - Solubility increases with increasing salinity
  - Due to inter-ionic interactions
- pH
  - Important for minerals that have anions that can be protonated/deprotonated
  - Protonation of basic anion (lower pH) increases solubility
- Complexation
  - Solubility increases with increasing complexation
  - Due to masking of metal ion

Exercise 4: Multiple solid phases

Consider an anoxic water at pH 6.8 and $\{HCO_3^-\} = 10^{-4}$ eq L^{-1} (assume $\gamma_i = 1$).

Is the solubility of Fe(II) dominated by siderite ($FeCO_3(s)$) or $Fe(OH)_2(s)$? Note that the solid that gives the lowest concentration of soluble Fe(II) controls the solubility for a given set of conditions.

$FeCO_3(s) = Fe^{2+} + CO_3^{2-}$	$\log K_{s0} = -10.4$
$H^+ + CO_3^{2-} = HCO_3^-$	$-\log K_2 = +10.1$
$Fe(OH)_2(s) = Fe^{2+} + 2OH^-$	$\log K_{s0} = -14.5$
$2H^+ + 2OH^- = 2H_2O$	$-2\log K_w = +27.8$

Exercise 4: Solution

- $FeCO_3(s)$

$FeCO_3(s) = Fe^{2+} + CO_3^{2-}$	$\log K_{s0} = -10.4$	eq. 1
$H^+ + CO_3^{2-} = HCO_3^-$	$-\log K_2 = +10.1$	eq. 2
$FeCO_3(s) + H^+ = Fe^{2+} + HCO_3^-$	$\log {}^*K_s = -0.3$	1+2 combined

$\log [Fe^{2+}] = \log {}^*K_s - pH - \log [HCO_3^-]$

At pH 6.8, $[Fe^{2+}] = [Fe(II)]$ and thus <u>$\log [Fe(II)] = -3.1$</u>

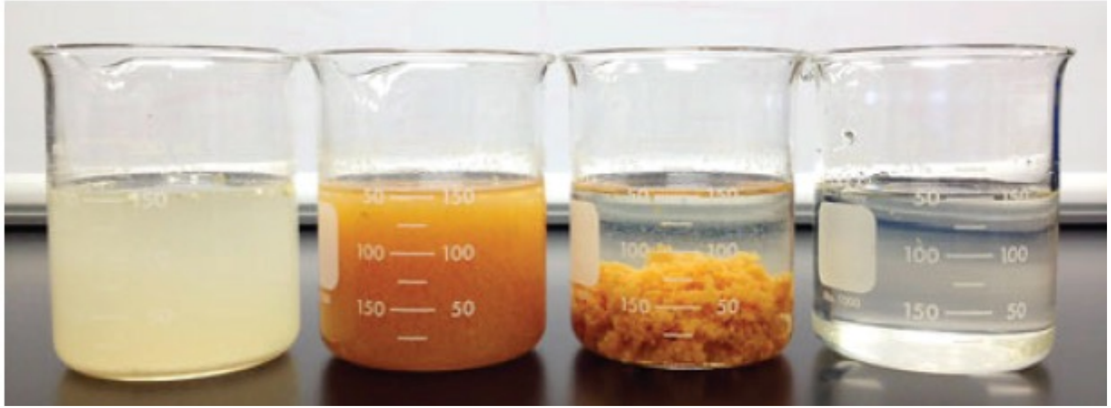
- $Fe(OH)_2(s)$

$Fe(OH)_2(s) = Fe^{2+} + 2OH^-$	$\log K_{s0} = -14.5$
$2H^+ + 2OH^- = 2H_2O$	$-2\log K_w = +27.8$
$Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	$\log {}^*K_s = +13.3$

Thus, $\log [Fe^{2+}] = \log {}^*K_s - 2pH$ and <u>$\log [Fe(II)] = -0.3$</u>

- Because [Fe(II)] is smaller for hypothetical equilibrium with $FeCO_3(s)$ than with $Fe(OH)_2$, $FeCO_3(s)$ is more stable than $Fe(OH)_2(s)$.

Exercise 5: Flocculation



Flocculation is a process by which a chemical coagulant added to the water acts to facilitate bonding between particles, creating larger aggregates which are easier to separate. The method is widely used in water treatment plants.

Example by Urs Von Gunten

Exercise 5: Flocculation

Aluminium is often used as a flocculant in water treatment. To achieve the best results, the pH of minimum solubility should be used. To identify the pH of minimum solubility, sketch the aluminum speciation as a function of pH in a log-log plot.

$Al(OH)_3(s) = Al^{3+} + 3\ OH^-$	$\log K_{s0} = -33.9$	eq. 1
$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$	$\log {}^*K_1 = -5$	eq. 2
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	$\log {}^*\beta_2 = -10.13$	eq. 3
$Al^{3+} + 3H_2O = Al(OH)_3(aq) + 3H^+$	$\log {}^*\beta_3 = -16.63$	eq. 4
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	$\log {}^*\beta_4 = -22.2$	eq. 5
$H_2O = H^+ + OH^-$	$\log K_w = -14.0$	eq. 6

Exercise 5: Flocculation

From eq. 6 it follows that $K_w = [OH^-][H^+]$, thus $[OH\text{-}] = K_w / [H^+]$

Fill this expression into eq. 1 to get $[Al^{3+}] = K_{s0}\,[H^+]^3 / K_w^{\;3}$

Taking logs: $\log [Al^{3+}] = \log(K_{s0}\,K_w^{-3}) - 3\,pH = \underline{8.1 - 3\,pH}$

From eq. 2 it follows that $[Al(OH)^{2+}] = [Al^{3+}]\;{}^*K_1 / [H^+] = K_{s0}\;{}^*K_1\,[H^+]^2 / K_w^{\;3}$

And thus $\log [Al(OH)^{2+}] = \log(K_{s0}\,K_w^{-3}\;{}^*K_1) - 2\,pH = \underline{3.1 - 2\,pH}$

$Al(OH)_2^{\;+} = [Al^{3+}]\;{}^*\beta_2 / [H^+]^2 = K_{s0}\;{}^*\beta_2\,[H^+] / K_w^{\;3}$

$\log [Al(OH)_2^{\;+}] = \log(K_{s0}\,K_w^{-3}\;{}^*\beta_2) - pH = \underline{-2.0 - pH}$

$Al(OH)_3 = [Al^{3+}]\;{}^*\beta_3 / [H^+]^3 = K_{s0}\;{}^*\beta_3 / K_w^{\;3}$

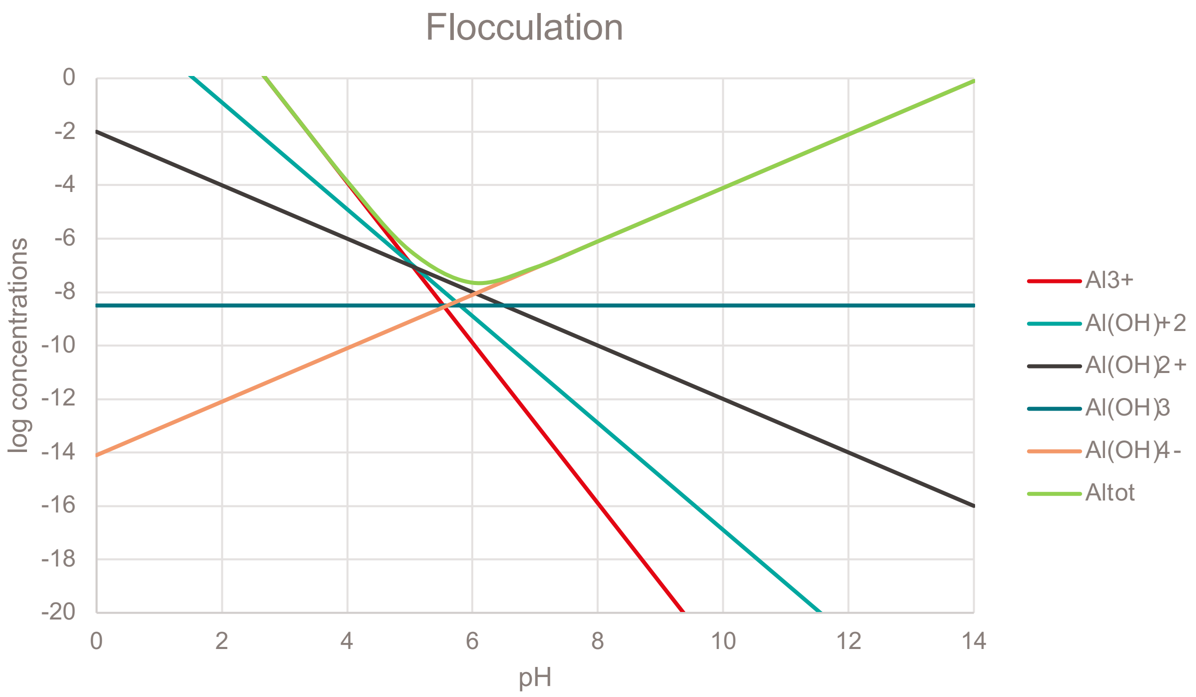
$\log [Al(OH)_3] = \log(K_{s0}\,K_w^{-3}\;{}^*\beta_3) = \underline{-8.5}$

$Al(OH)_4^{\;-} = [Al^{3+}]\;{}^*\beta_4 / [H^+]^4 = K_{s0}\;{}^*\beta_4\,[H^+]^{-1} / K_w^{\;3}$

$\log [Al(OH)_4^{\;-}] = \log(K_{s0}\,K_w^{-3}\;{}^*\beta_4) + pH = \underline{-14.1 + pH}$

Meret Aeppli

Exercise 5: Solution



The best results will be obtained at pH 6 when Al_{tot} is lowest.

Flint water crisis- before 2014

Meret Aeppli

Phosphate (PO_4^{3-}) was added to precipitate all metal cations and inhibit corrosion in the Detroit plant.

a. What reactions can phosphate (use Na_3PO_4) undergo with $FeCl_2(aq)$ and $Pb(NO_3)_2(aq)$ in solution?

b. What effect does the addition of PO_4^{3-} have on pH?

Flint water crisis- before 2014

a. Phosphate formed solid phases with Fe(II) and Pb(II) which resulted in the formation of a passivation layer in the pipes:

$$2Na_3PO_4 + 3FeCl_2 \rightleftharpoons Fe_3(PO_4)_2(s) + 6NaCl$$

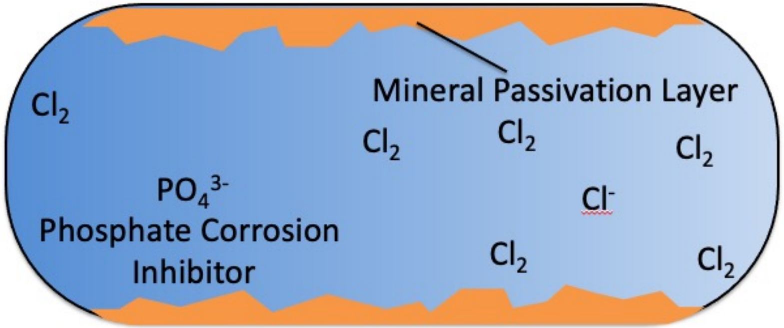
$$2Na_3PO_4 + 3Pb(NO_3)_2 \rightleftharpoons Pb_3(PO_4)_2(s) + 6NaNO_3$$

b. Furthermore, phosphate buffered pH

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$$

$$PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}$$

$$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2(s)$$



Flint water crisis- after 2014

Flint's water supply was switched to the city's own water treatment plant on the Flint River. Phosphate was NOT added to the Flint River water in the new plant.

a. What effects does this have on the passivation layer in the pipes and why?
b. In the absence of a passivation layer, what other chemical reactions can occur between the water and metals in the pipes?

Flint water crisis- after 2014

a. Effect of phosphate removal:
   - Removal of dissolved $Fe^{2+/3+}$ and $Pb^{2+/4+}$ no longer possible
   - Acidic river water directly dissolves passivation layer by neutralizing OH^-
   - Result: The passivation layer dissolved, exposing the metal pipes.

b. This lead to corrosion of the pipes as metals came in contact with oxidants O_2 and Cl^-
   - Pb is oxidized by O_2 to Pb^{2+} which is mobile
   - Iron corrosion (reaction with O_2) leads to rust-colored water
   - Exposed iron reduced free chlorine which is used as disinfectant in this system

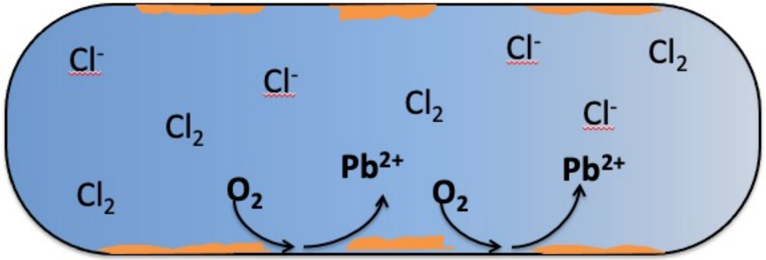
Flint water crisis- after 2014

Redox reactions will be the topic of the next class!

Lead pipes: lead is oxidized by dissolved oxygen

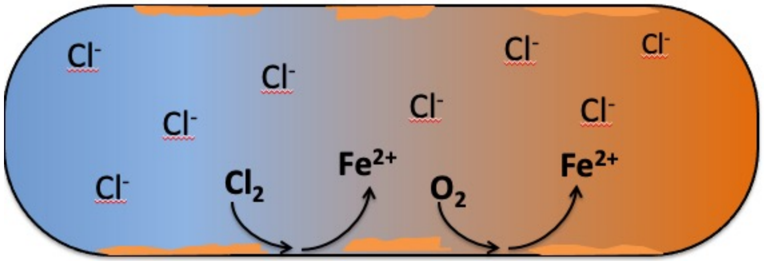
$$2Pb(s) + O_2 + 4H^+ \rightleftharpoons 2Pb^{2+}(aq) + 2H_2O$$

$$2Fe(s) + O_2 + 4H^+ \rightleftharpoons 2Fe^{2+}(aq) + 2H_2O$$



Iron pipes: iron is oxidized by dissolved oxygen and chlorine. Precipitation of iron oxides turns water rust colored.

$$Fe(s) + Cl_2 \rightleftharpoons FeCl_2$$



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