Metal Speciation III

ENV-200

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Last lecture recap

We discussed the hard-soft classification scheme and how it allows us to predict the reactivity between metals and ligands.

We used the equilibrium approach to model metal speciation.

We performed an experiment to determine the hardness of water.

Today, we will discuss precipitation and dissolution reactions.

And we will figure our what caused the Flint water crisis!

Metal speciation

Precipitation and dissolution

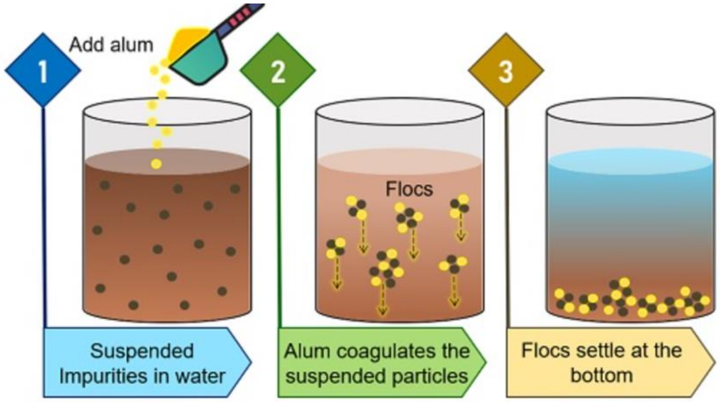
Learning objectives

You should be able to

1. formulate solubility equilibria and assess if a solution is undersaturated or oversaturated with respect to a solid phase.
2. determine which solid phases regulate the concentrations of elements in natural waters.
3. assess the solubility of solid phases using log-log diagrams.
4. optimize conditions in engineering applications based on your understanding of metal solubility.

Environmental engineering applications

- Water treatment: metal hydroxides are used for coagulation and flocculation processes (e.g., removal of natural organic matter, removal of phosphate, etc.)
- Removal of toxic metals from natural waters: precipitation and sorption to mineral surfaces (especially metal oxides) can remove metals from waters
- Passivation of pipes: formation of mineral passivation layer in water pipes can prevent corrosion



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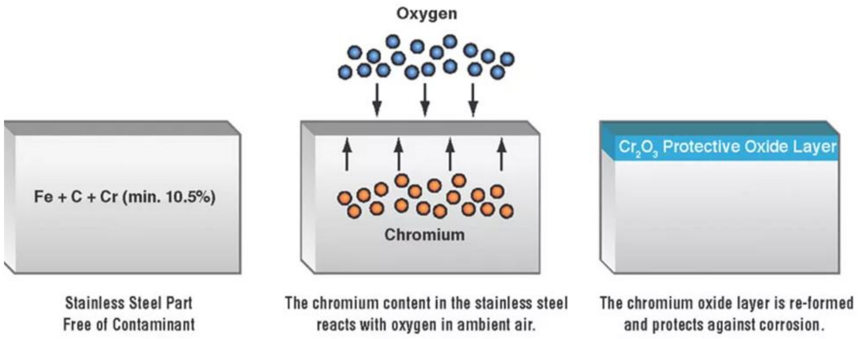
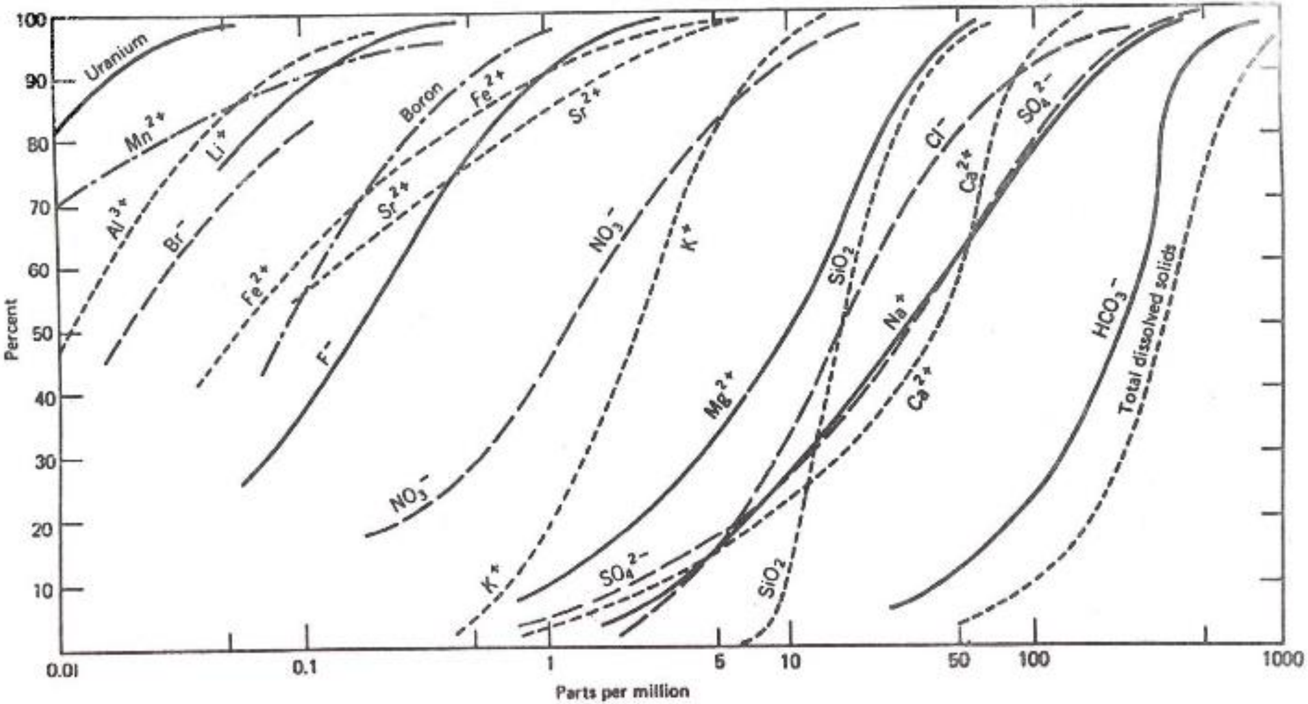


https://www.thefabricator.com/thefabricator/article/testingmeasuring/passivation-basics-will-this-stainless-steel-rust-

Composition of natural waters

- Waters acquire their chemical characteristics by
  - Dissolution of minerals
  - Chemical reactions with solids, liquids, and gases
- Variation in water composition can be explained by
  - Environmental history of the water
  - Chemical reactions of the rock-water-air system
- First approximation
  - Fresh water: CO_2 of the atmosphere vs. mineral rock
  - Seawater: acid-base titration of acids of volcanoes vs. bases of rocks

Composition of natural waters



- Cumulative curves showing the frequency distribution of constituents in natural waters
- Many constituents show little variation, e.g., dissolved silica: $10^{-3.8}$ to $10^{-3.2}$ M; H^+: $10^{-6.5}$ to $10^{-8.5}$ M

Weathering

- Weathering encompasses a variety of processes that decompose rocks
  - Mechanical weathering: fragmentation or loss of materials without chemical change
  - Chemical weathering: chemical reaction of minerals in rocks and soils with acidic and oxidizing substances
- Important for
  - Water composition
  - Soil fertility
  - Biological diversity
  - Agricultural productivity

Anthropogenic impacts

- Humans have played a big role in increasing weathering
  - Mining & extracting buried fossil fuels increases chemical & mechanical weathering (e.g. acid mine drainage)
  - Agriculture increases chemical weathering due to more plant growth
  - Construction & clearing land for agriculture increases mechanical weathering
- Result: significant quantities of dissolved materials are added to surface water
- Humans have increased the global mechanical weathering rate by a factor of 2
- This results in the accumulation of more sediments in rivers & deltas

Chemical weathering: sequence of mineral stability

Mineral	Reaction equation	Solubility
Rock salt (Halite)	$NaCl\ (KCl) \rightleftharpoons Na^+(K^+) + Cl^-$	very good
Gipsum (Anhydrit)	$CaSO_4 \cdot 2\,H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2\,H_2O$	good
Calcite	$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2\,HCO_3^-$	intermediate
Dolomite	$CaMg(CO_3)_2 + 2\,H_2CO_3 \rightleftharpoons Ca^{2+} + Mg^{2+} + 4\,HCO_3^-$	intermediate
Aluminum silicates		
	primary minerals + $H_2CO_3 \rightarrow$ Base cations + $H_4SiO_4 + HCO_3^-$ $Al(OH)_3$ + secondary minerals	small
Quarz	$SiO_2 + 2\,H_2O \rightleftharpoons H_4SiO_4$	small
Gibbsite	$Al(OH)_3 + 3\,H^+ \rightleftharpoons Al^{3+} + 3\,H_2O$	very small
Goethite	$FeOOH + 3\,H^+ \rightleftharpoons Fe^{3+} + 2\,H_2O$	very small

Weathering rates depend on relative concentrations in rock but in general the order is: Ca > Na > Mg > K > Si > Fe > Al

Chemical weathering

- Dominant form of chemical weathering: carbonation reaction
  - Plant roots and microbes release CO_2 through respiration
  - $H_2O + CO_2 \rightleftharpoons H_2CO_3$
  - Local H_2CO_3 concentrations in soils can be much higher than concentrations for water in equilibrium with the atmosphere
- Plants and microbes further increase weathering by releasing acids that lower pH and can chelate metals (increased dissolution rate, increased solubility, and increased mobility of metals)
- Other factors that influence chemical weathering rate include
  - Rock type (see previous slide)
  - Climate (faster at higher temperature and precipitation)
    - Tropical forests > temperate forests
    - Forests > grasslands > deserts

Chemical weathering

Incongruent dissolution: only some of the constituents of the primary mineral are dissolved

- Example: carbonic acid and silicate rocks

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow 2Na^+ + 2HCO_3^- + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4$$

- Primary mineral albite ($NaAlSi_3O_8$) is converted to a secondary mineral kaolinite ($Al_2Si_2O_5(OH)_4$)

Congruent dissolution: no initial solids remain after dissolution

- Example: carbonic acid and limestone

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

Examples of dissolution reactions

Consider the dissolution of apatite:

$$Ca_5(PO_4)_3OH + 4H_2CO_3 \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4HCO_3^{-} + H_2O$$

a. Is the dissolution reaction congruent or incongruent?

b. Where did we encounter apatite before?

Apatite is the only primary mineral with significant phosphorus content. Phosphorus is often a limiting nutrient for plant growth.

Examples of dissolution reactions

Consider the dissolution of pyrite:

$$4FeS_2 + 8H_2O + 15O_2 \rightarrow 2Fe_2O_3 + 16H^+ + 8SO_4^{2-}$$

a. Is the dissolution reaction congruent or incongruent?

b. Why is the water orange-red?

This oxidative dissolution reaction accounts for the acidity of runoff in many mining operations (acid mine drainage)

Ion activity

Until now, we have been using ion concentrations instead of activity. However, concentration is, strictly speaking, only applicable to ideal solutions under standard conditions (no interactions between species). In electrolyte solutions (solutions with $I \neq 0$) this is not the case! Various interactions between species can occur, most importantly electrostatic effects (attraction between ions with opposite charge). These interactions influence the behavior of the ions and don't allow to treat every ion in the solution independently. To accurately do equilibrium calculations in electrolyte solutions, we use ion activity instead of ion concentration to account for this non-ideal behavior under non-standard conditions.

Standard conditions: $T = 25\ °C$, $P = 1$ atm, $I = 0$

$I = 0$ → most common source for non-ideal behavior

activity of compound i is indicated by { i }
concentration of compound i is indicated by [i]

Ion activity

Ionic strength I expresses the concentration of electrolytes (cations and anions) in solution:

$$I = 0.5 \sum C_i z_i^2$$

where C_i = concentration of the ion i and z_i = charge of the ion i

Example 1: 1 mM NaCl:

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

Example 2: 1 mM $CaCl_2$:

$$I = 0.5 *(C_{Ca2+} * z^2_{Ca2+} + C_{Cl-} * z^2_{Cl-}) = 0.5*(10^{-3} * 2^2 + 2 * 10^{-3} * (-1)^2) = 3 * 10^{-3}\ M$$

Typical ionic strength of freshwater: 0.004 – 0.02 M

Typical ionic strength of seawater: 0.7 M

Ion activity

Activity coefficient is the relation between activity and concentration:

$$\{ i \} = \gamma_i * [i]$$

γ_i = activity coefficient

γ_i is a function of the charge of the ion and the total ionic strength

Several methods exist to calculate γ_i . The most common one is the Davies equation (valid up to I = 0.5 M):

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

$A = 1.82*10^{-6} (\varepsilon T)^{-3/2}$

ε = dielectric constant

use A = 0.5 for water at 25 °C

If $I = 0 \rightarrow \log \gamma_i = 0 \rightarrow \gamma_i = 1 \rightarrow [i] = \{ i \}$

Exercise 1: Ion activity

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

Solubility

- Solubility: maximum concentration of a solute that can dissolve in a solvent at a given temperature.
- Link to hydrolysis: Formation of a precipitate can be considered the final stage in the formation of polynuclear complexes

Solubility

- Equilibrium equation
- Solubility product K_{s0}
  - index 0: only simple ions are involved
  - solid phases have activity = 1
- Ion activity product IAP
  - product of actual ion activities

$$M_nX_m\,(s) \rightleftharpoons n\,M(aq) + m\,X(aq)$$

$$K_{s0} = \frac{\{M(aq)\}^n\,\{X(aq)\}^m}{\{MnXm(s)\}} = \{M(aq)\}^n\,\{X(aq)\}^m$$

$$IAP = \{M(aq)\}^n_{actual}\;\{X(aq)\}^m_{actual}$$

IAP < K_{s0} :	undersaturation (solid phase cannot precipitate, solid phase that is present will dissolve)
IAP = K_{s0} :	in equilibrium
IAP > K_{s0} :	oversaturation, solid phase will precipitate

Exercise 2: Freshwater vs. seawater

Freshwater and seawater have very different ion concentrations and thus, chemical species will have different activities. This exercise illustrates the effect of these differences on the dissolution of calcite ($CaCO_3$).

1. A lake is at 25°C with measured pH = 8.30 and is equilibrated with the atmosphere ($[CO_3^{2-}] = 1.153 * 10^{-5}$ M). The dissolved calcium concentration is 0.25 mM. Assume negligible ionic strength. Compute the IAP for calcite. The K_{s0} for calcite is $3.31 * 10^{-9}$.

Exercise 2: Freshwater vs. seawater

2. Now consider surface seawater at 25°C, a salinity of 35, and a pH of 8.1. Use the following concentrations: $[Ca^{2+}]$ = 10.3 mM, $[CO_3^{2-}]$ = 200 µM. What is the IAP for calcite? Consider activity coefficients of γ_{Ca2+}= 0.23 and γ_{CO32-} = 0.2 in your calculations. The K_{s0} for calcite is 3.31 * 10^{-9}.

Solubility of metals in natural waters

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

Exercise 3: Gypsum in natural waters

1. Is each water sample (water of Lake Zürich vs. groundwater in Glattfelden) undersaturated, at equilibrium, or supersaturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$)? Assume $\gamma_i = 1$.

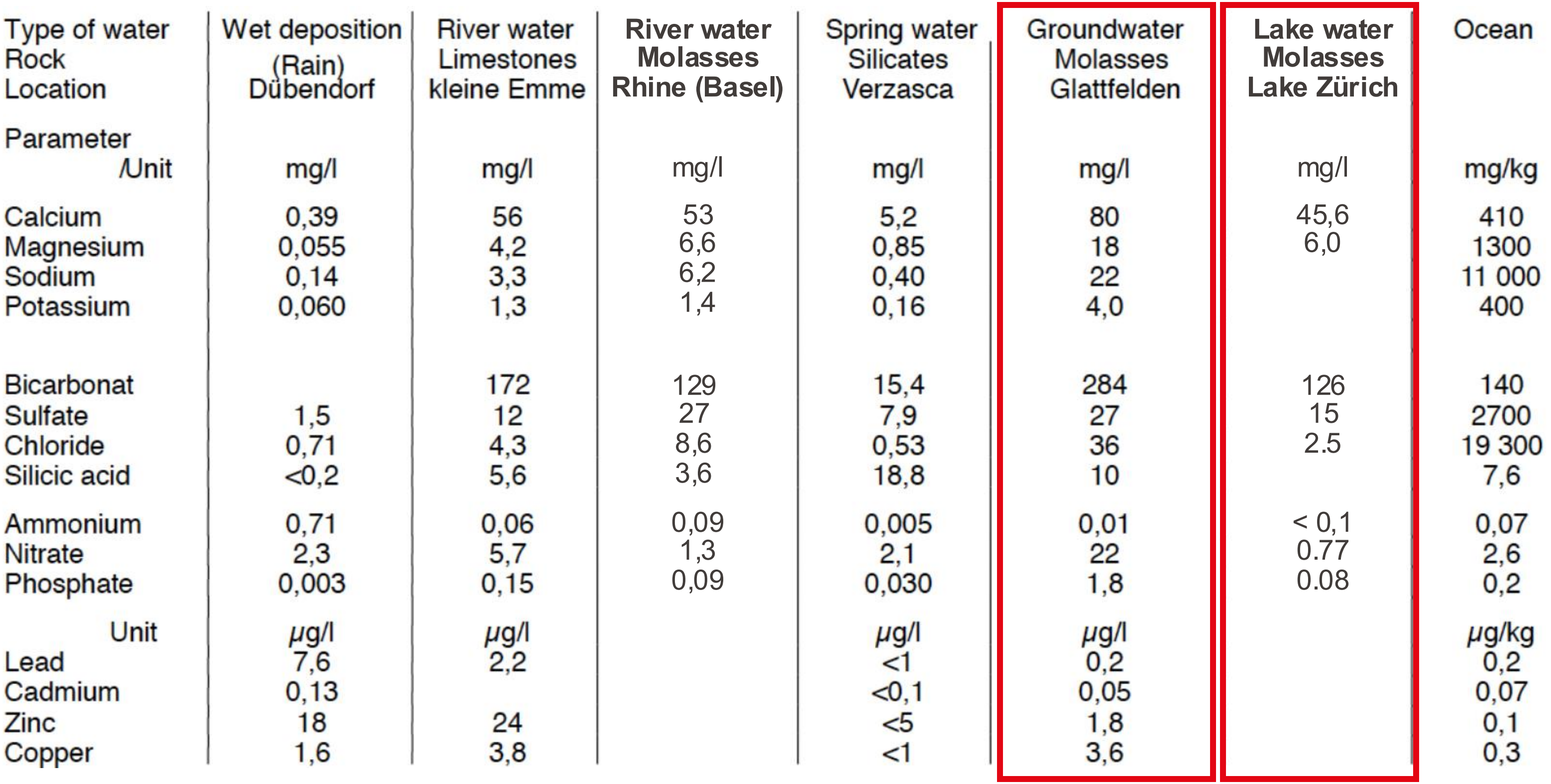
   $CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-}$ $K_{s0} = 10^{-4.58}$

   M_w Ca^{2+} = 40.08 g/mol

   M_w SO_4^{2-} = 96.06 g/mol

2. Why do lake water and groundwater differ in their chemical composition and degree of mineral saturation?

Exercise 3: Gypsum in natural waters



Type of water Rock Location	Wet deposition (Rain) Dübendorf	River water Limestones kleine Emme	**River water Molasses Rhine (Basel)**	Spring water Silicates Verzasca	Groundwater Molasses Glattfelden	**Lake water Molasses Lake Zürich**	Ocean
Parameter /Unit	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/kg
Calcium	0,39	56	53	5,2	80	45,6	410
Magnesium	0,055	4,2	6,6	0,85	18	6,0	1300
Sodium	0,14	3,3	6,2	0,40	22		11 000
Potassium	0,060	1,3	1,4	0,16	4,0		400
Bicarbonat		172	129	15,4	284	126	140
Sulfate	1,5	12	27	7,9	27	15	2700
Chloride	0,71	4,3	8,6	0,53	36	2.5	19 300
Silicic acid	<0,2	5,6	3,6	18,8	10		7,6
Ammonium	0,71	0,06	0,09	0,005	0,01	< 0,1	0,07
Nitrate	2,3	5,7	1,3	2,1	22	0.77	2,6
Phosphate	0,003	0,15	0,09	0,030	1,8	0.08	0,2
Unit	µg/l	µg/l		µg/l	µg/l		µg/kg
Lead	7,6	2,2		<1	0,2		0,2
Cadmium	0,13			<0,1	0,05		0,07
Zinc	18	24		<5	1,8		0,1
Copper	1,6	3,8		<1	3,6		0,3

Recall general equations for soluble hydroxo species

Soluble hydroxo species:

$Me(OH)_{n-1}^{(m-n+1)+} + OH^- \rightleftharpoons Me(OH)_n^{(m-n)+}$

$$K_n = \frac{\{Me(OH)_n{}^{(m-n)+}\}}{\{Me(OH)_{n-1(}{}^{m-n+1)+}\}\{OH^-\}}$$

Or:

$Me(OH)_{n-1}^{(m-n+1)+} + H_2O \rightleftharpoons Me(OH)_n^{(m-n)+} + H^+$

$${}^*K_n = K_n \cdot K_w = \frac{\{Me(OH)_n{}^{(m-n)+}\}\{H^+\}}{\{Me(OH)_{n-1}{}^{(m-n+1)+}\}}$$

We can express reactions both in terms of OH^- (K has no prefix) or H_2O (K has prefix *)

m = valence of the metal; n = number of hydroxides

General equations for metal hydroxides

Equilibrium of metal hydroxide with metal ion:

$Me(OH)_m\,(s) \rightleftharpoons Me^{m+} + m\,OH^-$

$$K_{s0} = \{M^{m+}\}\,\{OH^-\}^m \text{ or } {}^*K_{s0} = \frac{\{M^{m+}\}}{\{H^+\}^m}$$

Equilibrium with soluble hydroxo species:

$Me(OH)_m\,(s) \rightleftharpoons Me(OH)_n^{(m-n)+} + (m-n)OH^-$

$$K_s = \{Me(OH)_n{}^{(m-n)+}\}\,\{OH^-\}^{(m-n)}$$

Or:

$Me(OH)_m\,(s) + (m-n)H^+ \rightleftharpoons Me(OH)_n^{(m-n)+} + (m-n)H_2O$

$$^*K_s = \frac{\{Me(OH)_n{}^{(m-n)+}\}}{\{H^+\}^{(m-n)}}$$

Dissolved species: $\{Me\}_T = \{Me^{m+}\} + \sum\{Me(OH)_n{}^{(m-n)+}\}$

$$K_n = \frac{\{Me(OH)_n{}^{(m-n)+}\}}{\{Me(OH)_{n-1(}{}^{m-n+1)+}\}\{OH^-\}}$$

$$^*K_n = K_n \cdot K_w = \frac{\{Me(OH)_n{}^{(m-n)+}\}\{H^+\}}{\{Me(OH)_{n-1}{}^{(m-n+1)+}\}}$$

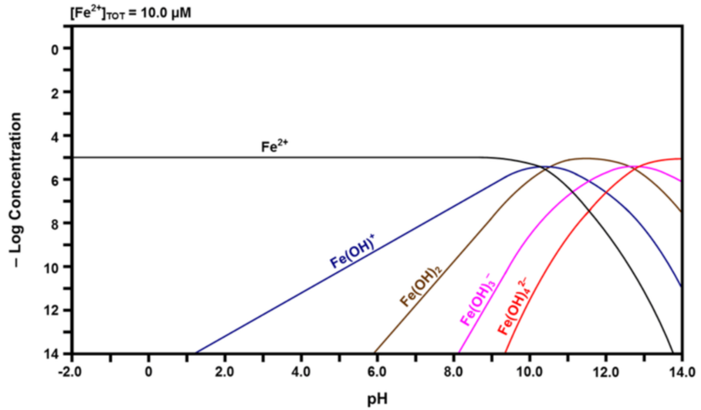
Exercise 4: Multiple solid phases

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

(Fe(II) encompasses all soluble iron species with an oxidation state of (+II); at pH 6.8, the dominant species is free aqueous Fe^{2+}, so we neglect any hydroxo- or carbonato complexes)

$FeCO_3(s) = Fe^{2+} + CO_3^{2-}$	$\log K_{s0} = -10.4$
$H^+ + CO_3^{2-} = HCO_3^-$	$-\log K_{a2} = +10.33$
$Fe(OH)_2(s) = Fe^{2+} + 2OH^-$	$\log K_{s0} = -14.5$
$2H^+ + 2OH^- = 2H_2O$	$-2\log K_w = +27.8$



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.

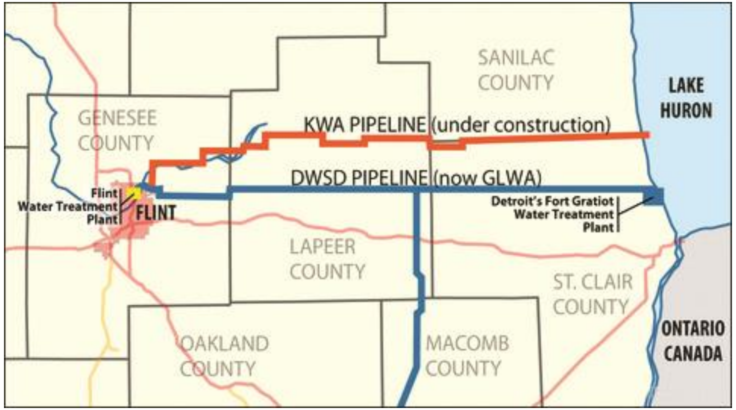
Example by Urs Von Gunten

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

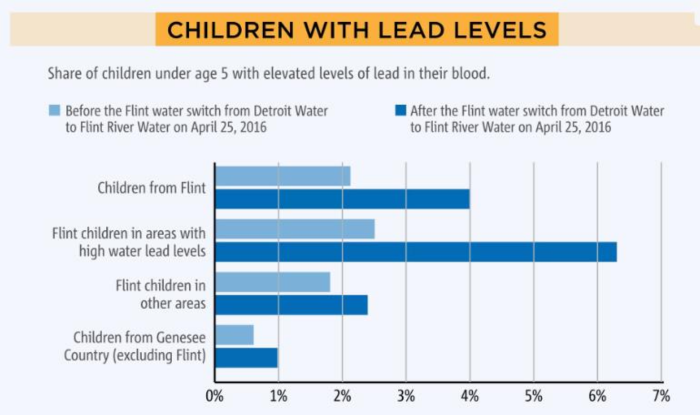
Environmental engineering challenge: Flint water crisis

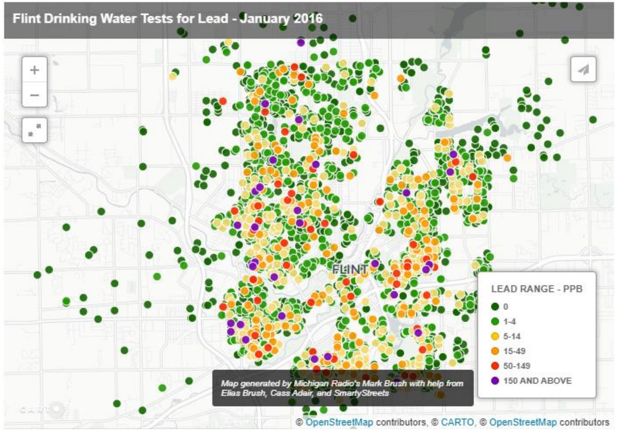


Why did the switch to Flint's river water cause this catastrophe?

Images: The Flint Water Project; Map: Regina H. Boone/Detrois Free Press/Zuma Press

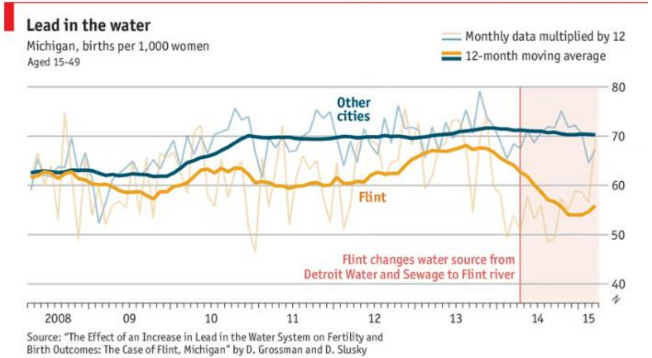
Environmental engineering challenge: Flint water crisis





Map created by Michigan Radio

Fertility rates fell by 12%, while fetal deaths increased

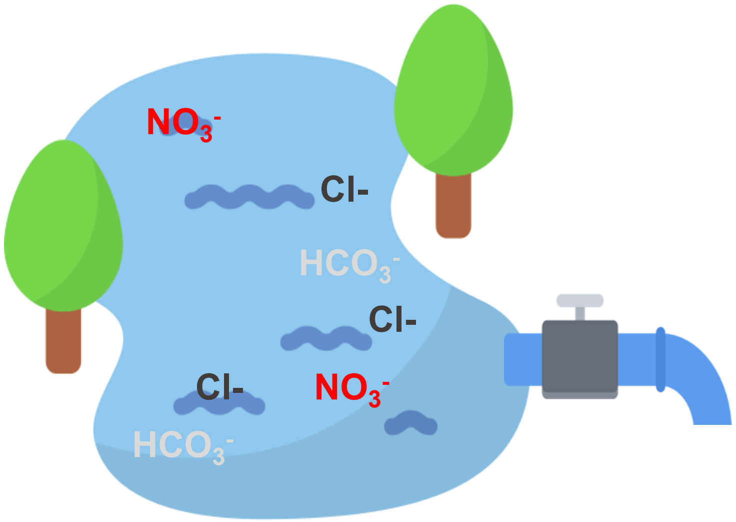


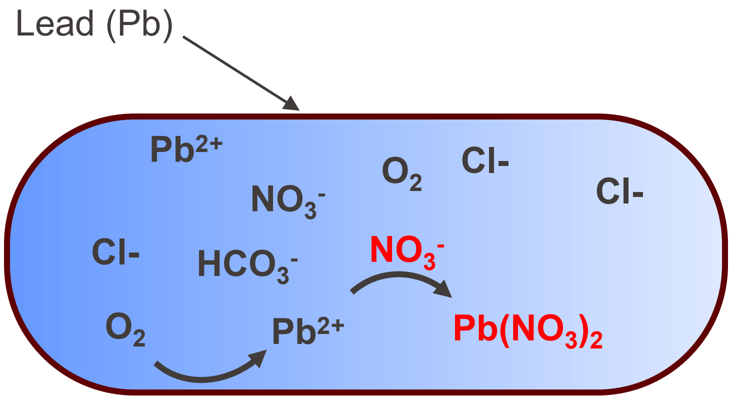
Source: "The Effect of an Increase in Lead in the Water System on Fertility and Birth Outcomes: The Case of Flint, Michigan" by D. Grossman and D. Slusky

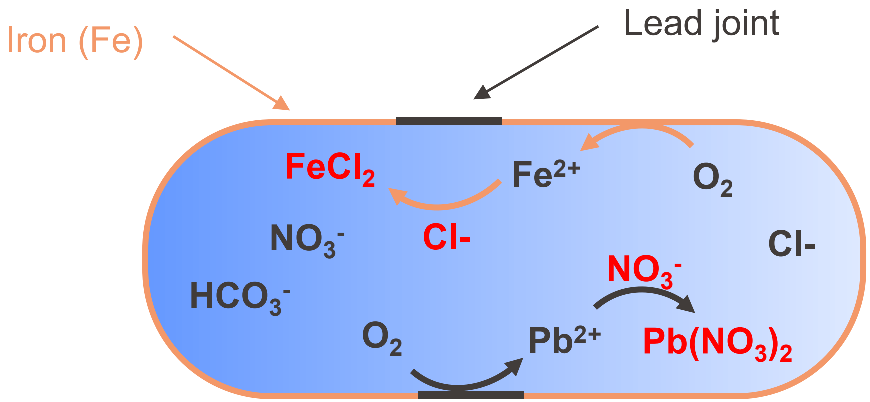
Economist.com

In addition to lead, Flint also experienced problems with pathogens and subsequently with harmful disinfection byproducts.

Reactions of lead and iron pipes with lake water







Flint water crisis- before 2014

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- 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?

Summary

- The composition of natural waters is in part dependent on the history of mineral dissolution reactions.
- Chemical weathering describes the chemical reaction of minerals with acid and oxidizing substances.
- A comparison between the ion activity product and the solubility product of a solid phase allows us to estimate whether or not the solid phase will form under given conditions.
- The solubility of metals in natural waters is affected, amongst other factors, by temperature, salinity, pH, and complexation.
- The Flint water crisis was caused by a shift in water chemistry that led to the dissolution of the mineral passivation layer on the pipes, thereby exposing the underlying Pb and Fe.