Reading: Faure 13.5 (ion exchange)

Drever, The geochemistry of natural waters.
1) Section on “adsorption and coprecipitation controls”. It is in chapter 9 of the 3rd edition, chapter 15 in the 2nd edition. This is a short section.
2) Section on Colloid properties in the Clays Chapter (Chapter 5 in 2nd Ed.)

Additional resource: Langmuir, Aqueous Environmental Geochemistry. Chapter 10: Adsorption-Desorption reactions. This is very detailed, and I recommend it if you will need to consider sorption in your work.

Keystroke for = on the Mac is: Symbol Font, option-b

1) Are the surfaces of solids neutral, or are they charged?
   a. To be neutral, the atoms on the surface in contact with the solution would have to have all their charge satisfied by bonds within the solid.
   b. This is impossible- the structure of the solid is terminated at the surface- each atom would be "missing" half of the bonds that normally lead to charge balance within the solid
   c. So this means that
      i. the surface of a solid is a fuzzy transition zone between the structure of the solid and the structure of the solution
      ii. this transition zone will tend to attract ions from the solution because of the unsatisfied charge at the end of the solid
   d. Picture a crystal (could be a silicate, oxide, carbonate, or any other oxygen-dominated compound) in contact with pure water. The diagram below is a first guess at what this might look like. The oxygens that dominate the space inside the crystal are white. **The oxygens of the water are grey.**

   ![](diagram.png)

   **Things to consider:**
   1) The last row of oxygens in the crystal needs positive charges immediately to their left- oxygens are negatively charged; this must be balanced.
   2) But how much positive charge is needed?
   3) The water molecules can supply a small positive charge because they’re polar, but not enough.
   4) Would the amount of + charge needed differ between, for example, Kaolinite, Fe(OH)₃, MnO₂, and Al₂O₃?
   5) What happens when there is a defect in the crystal (e.g., substitution of Al³⁺ in a Si⁴⁺ site)?

2) If the crystal ends with oxygens, there is a need for + charges to balance the negative charge at the solid-solution interface.
   a. In pure water, only H⁺ is available to supply this + charge
   b. So H⁺ ions are attracted to the surface and neutralize the excess charge
   c. They become bonded to the surface
d. The strength with which $H^+$ ions are attracted depends on the bonding of the solid.

e. Surfaces can be protonated or deprotonated just like anions in solution.
   i. Similar chemical equations and mathematics are used.
   ii. Surfaces often acts as weak acids.

iii. For hydrous ferric oxides (approximate diagram above), $≡\text{FeOH}_2^+$, $≡\text{FeOH}$, and $≡\text{FeOH}^-$ are dominant at low, moderate and high pH, respectively.

f. At low pH (high $H^+$) surfaces tend to have an overall $+$ charge because there are many $H^+$ ions there.

g. Anions in solution are then attracted to the $+$ charged surfaces.

h. Note that there might still be some individual $-$ charged sites on the surfaces (caused by defects), even though the predominant charge is $+$.

i. At high pH, surfaces tend to have overall negative charge (cations attracted more).

j. At some pH, the surface has no net charge, this is called the point of zero charge (PZC)- it is the dividing line between $+$ and $-$ charge.

   i. In solutions with only protons as the important adsorbing species, the PZC is called the isoelectric point.
   ii. The highly important clay minerals tend to have lower PZC values (about 2 to about 4.5) and are generally negatively charged in natural waters.
   iii. Fe-oxyhydroxides have higher PZC values:
      1) Hematite: 4.2 to 6.9
      2) Geothite: 5.9 to 6.7
      3) Amorphous Fe(OH)$_3$: 8.5 to 8.8

iv. Gibbsite: 10.0

k. PZC changes when ions other than $H^+$ are adsorbed in large quantities.

3) Ions in solution other than $H^+$ are also attracted to surfaces, of course.
   a. Some ions are less strongly adsorbed on the sites than $H^+$ (e.g., Ca$^{2+}$, Mg$^{2+}$, Zn$^{2+}$).
   b. Some ions are more strongly adsorbed than $H^+$ (e.g., Cu$^{2+}$, Pb$^{2+}$, and UO$_2^{2+}$).

4) Surface Complexation models are used to calculate the population of the surface sites with the various complexes:
   a. Adsorption reactions are written for ions bonding with surface sites:
      e.g., $≡\text{FeOH} \leftrightarrow =\text{FeO}^- + H^+$
      e.g., $≡\text{FeOH}_2^+ \leftrightarrow =\text{FeOH} + H^+$
      e.g., $≡\text{FeOH}_2^+ + Na^+ \leftrightarrow =\text{FeO}Na + H^+$
      e.g., $=\text{FeO}^- + Ca^{2+} \leftrightarrow =\text{FeOCa}^+$
   b. For each reaction, a mass action equation is written.
i. The correct concentrations to put into the mass action equation is the concentration at the surface. This is NOT equal to the concentration in the solution far away from the surface, because the surface is charged.

ii. Example. For equilibrium between H\(^+\) adsorbed onto the surface of a ferric oxide and H\(^+\) in the solution at the surface:

\[
K = \frac{[FeOH][H_\text{s}^+]}{[FeOH_\text{ads}^+]} \quad \text{where } [H_\text{s}^+] \text{ is the concentration at the surface}
\]

c. Calculating \([H_\text{s}^+]\) is complicated, because the charged surface tends to attract positive ions (leading to higher concentrations there) and repel negative ones

i. Depends on the surface charge of the solid

ii. Depends on pH and T

iii. Depends on ionic strength, because the surface potential gets negated increasingly as more ions are present (I think)

iv. For example, for hydrous ferric oxide (HFO) at pH=6, T=298K and Ionic strength=0.01M, \([H_\text{s}^+]\)= 0.014\((H^+)\). \([H_\text{s}^+]\) is relatively small because the surface has a positive charge at this pH (see above) and repels H\(^+\).

v. Computer models are used to approximate/model all this

d. Also, ions may:

i. bond directly to a surface (= “inner sphere complex”)

ii. be separated from the surface by a solvation sphere (= “outer sphere complex”)

iii. So...Some models have “strong” and “weak” sites in them and ions bond to both

   – Other models allow the user to specify which type of complex forms for each ion in solution

5) Geochemical modeling software usually employs surface complexation models.

a. The calculations are iterative, and very similar to the iterative calculations used for aqueous speciation calculations

b. The surface potentials of available surfaces are calculated according to the pH, T, and solution composition

c. Chemical equations are evaluated for all surface complexation reactions

d. \(\Delta G\) is calculated for each reaction

e. Just as with the aqueous speciation calculations, the routine finds the most stable surface complexes (those with the most negative \(\Delta G\)), and increases those, and decreases others until it finds the lowest G state for the system.

6) Exchange reactions: Another way to consider adsorption equilibrium. See Faure text.

   e.g., CaX + 2Na\(^+\) = 2NaX + Ca\(^{2+}\)

   a. This does not take into account the changes in sites with pH and Ionic Strength

   b. But to some extent those issues “cancel out” because this only considers competition between Ca and Na.

   c. The mass action expression is:

   \[
   K_{Na-Ca} = \frac{[NaX][Ca^{2+}]}{[CaX][Na^+]^2}
   \]

d. Defining activities for adsorbed ions is difficult. We can use the molar concentrations per gram of exchanger as an approximation.
\[
K_{Na-Ca} = \frac{(NaX)^2[Ca^{2+}]}{(CaX)[Na^+]^2}\]

(parentheses mean “moles per gram exchanger” or similar concentration unit.

e. Note that if we start with a clay in equilibrium with a certain solution, then increase both Na\(^+\) and Ca\(^{2+}\) concentration by a factor of 2, the ratio Na\(_2\)X:CaX increases by a factor of 2!

7) Less complex, **empirical models** that work for some conditions:

a. **Distribution coefficient (\(K_d\)) model.** Assumes linear relationship between aqueous activity and adsorbed mass:
\[c_s = K_d \cdot c_{aq}\]
(c\(_s\) and c\(_{aq}\) are the adsorbed and aqueous concentrations, \(K_d\) is a constant derived by fitting laboratory or field data)
Reasonable for certain conditions:
   i. Small concentration of the adsorbing ion
   ii. A measured \(K_d\) is applicable ONLY for a specific solid, solution and T
   iii. Must measure a new \(K_d\) for every field site

b. \(K_d\) approach modified for organic molecules that adsorb strongly to organic matter and not to silicates and oxides:
   i. Define \(K_{OC} = (\text{micrograms adsorbed per gram organic C}) / \text{mg/L}\)
   ii. \(K_d = K_{OC} \times f_{OC}\) where \(f_{OC}\) is the weight fraction of organic C in the solid
   iii. \(f_{OC}\) is typically of order 0.01 (i.e., sediments have a few percent organic matter in them)

c. **Freundlich “Isotherms”**. A function that roughly fits the non-linearity at higher concentrations:
\[c_s = K \cdot (c_{aq})^n\]
(\(n\) is an additional constant, usually between 0.9 and 1.4)

![Graph showing Freundlich Isotherms](image)

d. **Langmuir Isotherms.** One problem with the Freundlich isotherms is that real solids have a limited number of sorption sites and when the concentration of the adsorbing species gets very high, all of the sites are taken and further increases in concentration do not result in increased sorption. The Langmuir isotherm does a better job of modeling this:
\[c_s = \frac{ac_{aq}}{1 + bc_{aq}}\]
(\(a\) and \(b\) are empirical constants)

…this it can be derived from the mass action expression for the reaction
\[\equiv\text{SOH} + M^{+}_{(aq)} = \equiv\text{SOHM}^{+}\]
(with the condition that the total number of sites be constant, i.e., \((\equiv\text{SOH}) + (\equiv\text{SOHM}^{+}) = \text{constant}\)
ii. An equivalent form - easier to use:

\[ c_x = \frac{b c_{aq} N_{\text{max}}}{1 + b c_{aq}} \]

where \( N_{\text{max}} \) is the maximum number of sorption sites that can be occupied by the ion. The slope of the line at low concentration = \( b N_{\text{max}} \).

![Graph](image)

This is a plot for \( N_{\text{max}} = 100 \) and \( b = 0.1 \).

iii. Problem: This does not account for competing ions in solution.

iv. Competitive Langmuir Model tries to model this competition.

1) Same idea, similar equations, BUT...

2) Adsorbing ions compete with each other, in that the total number of sites, for all adsorbing species, is a constant:

\[ (=\text{SOH}) + \Sigma (=\text{SOHM}_i) = N_{\text{max}} \]