1. The following two examples are from a chapter on adsorption in my as yet unpublished treatise on Physical/Chemical Treatment (co-authored with Desmond Lawler of UT Austin). Review the examples and try to reproduce them using Phreeqc. In the examples, \( q_i \) is used to represent adsorption density of species \( i \) in meq adsorbed per gram of ion exchange resin.

**Hints:**

1. Note that Phreeqc calculates Cu(2) speciation when it solves for the equilibrium solution composition (i.e., it computes concentrations of CuOH\(^+\), Cu(OH)\(_2\)^0, Cu(OH)\(^-\), etc.). If you input CuX\(_2\) as the only surface species, the program infers that none of the hydrolyzed species of Cu(2) are present on the exchanger. Hence, if a substantial amount of those species form in solution, they will not bind, and overall Cu sorption will be low (because Cu\(^{2+}\) conc'n will be much less than \( TOT\)Cu(2)). In the example problem shown below, this speciation issue is not considered. You can make your input more like the example by changing the pH to a value at which hydrolysis is negligible (e.g., pH 5).

2. The K given in the problem statement uses q values in meq/g and c values in meq/L. However, Phreeqc requires K values with q in mole fractions and c in mol/L. Therefore, to get Phreeqc to model the same problem as in the example, you must convert the given value of K into one that has the equivalent information, but is in units appropriate to Phreeqc. When you do that, the Phreeqc output should be close to that in the example, differing only because of the small amount of Cu hydrolysis that occurs and because Phreeqc adjusts for activity coefficients.

**Example 7-8.** The selectivity coefficient of a cation exchange resin for Cu\(^{2+}\) over Na\(^+\) is 4.5, when \( q \) and \( c \) are expressed in meq/g and meq/L, respectively. In a batch treatment process, an industrial waste containing 70 mg/L Cu\(^{2+}\) and no Na\(^+\) is contacted with 5.0 g/L of an ion exchange resin that has been pre-loaded with Na\(^+\). The exchange capacity of the resin is 1.5 meq/g.

What fraction of the copper in the original solution adsorbs, and what fraction of the sodium originally on the resin desorbs?

**Solution.** The selectivity coefficient for this system is:

\[
K_{\text{Cu/Na}} = 4.5 = \frac{q_{\text{Cu}}c_{\text{Na}}}{q_{\text{Na}}c_{\text{Cu}}}
\]

A mass balance on this batch system indicates that the total concentrations (dissolved plus adsorbed) of Na\(^+\) and Cu\(^{2+}\) are not affected by the treatment step. These concentrations, which we designate as \( c_{\text{tot}} \), can be computed based on the conditions in the waste and on the resin before they are mixed, as follows. (Note that the concentrations and adsorption densities are all based on equivalents, not moles.)

\[
c_{i,\text{tot}} = c_{i,\text{dissolved}} + q_{i}c_{\text{solid}}
\]
We can therefore write the following expressions describing the mass balances once the system reaches equilibrium:

\[ \frac{7.5 \text{ meq}}{L} = c_{Na, dissolved} + q_{Na} c_{solid} \]

\[ \frac{2.2 \text{ meq}}{L} = c_{Cu, dissolved} + q_{Cu} c_{solid} \]

Given that the sites in the ion exchange resin are assumed to be always fully occupied by Cu\(^{2+}\) or Na\(^+\), we can write the following equivalent-based site balance:

\[ q_{tot} = 1.5 \frac{\text{meq}}{g} = q_{Cu^{2+} (\text{equiv})} + q_{Na^{+} (\text{equiv})} \]

The balances on total Na\(^+\), total Cu\(^{2+}\), and total sites, plus the selectivity coefficient equation, provide four independent equations in four unknowns, and therefore can be solved simultaneously to yield a unique result. That result is:

\[ c_{Cu^{2+}} = 0.26 \frac{\text{meq}}{L} = 0.13 \frac{\text{mmol}}{L} = 8.26 \frac{\text{mg}}{L} \]

\[ c_{Na^{+}} = 1.94 \frac{\text{meq}}{L} = 1.94 \frac{\text{mmol}}{L} = 44.62 \frac{\text{mg}}{L} \]

\[ q_{Cu^{2+}} = 0.388 \frac{\text{meq}}{g} = 0.194 \frac{\text{mmol}}{g} = 12.32 \frac{\text{mg}}{g} \]

\[ q_{Na^{+}} = 1.112 \frac{\text{meq}}{g} = 1.112 \frac{\text{mmol}}{g} = 25.53 \frac{\text{mg}}{g} \]

Based on the above results, 8.26 mg/L Cu\(^{2+}\) remains in the treated solution, compared to 70 mg/L in the untreated solution, corresponding to 88.2% removal. The adsorption density of sodium on the original resin was 1.50 meq/g, of which 1.11 meq/g remains after the treatment step. Thus, 26% of the Na\(^+\) is released.

Example 7-9. In Example 7-8, the equilibrium composition of an ion exchange system for removing Cu\(^{2+}\) from solution and replacing it with Na\(^+\) was determined. After the system has
equilibrated, the solution is drained, and a small volume of regenerant containing 2.5 mol/L Na\(^+\) is contacted with the resin. The resin concentration during this step is 500 g/L. Determine the equilibrium composition of the regenerant solution after it equilibrates with the resin.

**Solution.** The Cu\(^{2+}\)/Na\(^+\) selectivity coefficient is a pseudo-equilibrium constant for the exchange reaction and is the same (4.5) in the two systems. Ignoring (somewhat unrealistically) the changes in the activity coefficients of Cu\(^{2+}\) and Na\(^+\) that accompany the change in ionic strength, we can treat \( K_{\text{Cu}^{2+}/\text{Na}^+} \) as a true equilibrium constant, in which case it would be the same (4.5) in the treatment and regeneration steps. With that assumption, after the resin equilibrates with the regenerant solution, we can write:

\[
K_{\text{Cu}/\text{Na}} = 4.5 = \frac{q_{\text{Cu}} c_{\text{Na}}^2}{q_{\text{Na}}^2 c_{\text{Cu}}}
\]

where, as before, the units of \( q \) and \( c \) are meq/g and meq/L, respectively. We can also write mass balances on total Na\(^+\) and Cu\(^{2+}\) in the system, as before, although the numerical values differ in the two systems. For the regenerant system:

\[
c_{i,\text{tot}} = c_{i,\text{fresh regenerant}} + q_{i,\text{used resin}} c_{\text{solid}}
\]

\[
c_{\text{Na tot}} = \left(2.5 \frac{\text{mol}}{\text{L}} \right) \left(1.0 \frac{\text{equiv}}{\text{mol}}\right) + \left(1.112 \frac{\text{meq}}{\text{g}}\right) \left(500 \frac{\text{g}}{\text{L}}\right) \left(1 \frac{\text{equiv}}{1000 \text{ meq}}\right) = 3.056 \frac{\text{equiv}}{\text{L}}
\]

\[
c_{\text{Cu tot}} = 0.0 \frac{\text{equiv}}{\text{L}} + \left(0.388 \frac{\text{meq}}{\text{g}}\right) \left(500 \frac{\text{g}}{\text{L}}\right) \left(1 \frac{\text{equiv}}{1000 \text{ meq}}\right) = 0.194 \frac{\text{equiv}}{\text{L}}
\]

Also as in the previous example, the following site balance applies:

\[
q_{\text{tot}} = 1.5 \frac{\text{meq}}{\text{g}} = q_{\text{Cu}^{2+}} + q_{\text{Na}^+}
\]

Solving the four equations in four unknowns that apply to this system, we find:

\[
c_{\text{Cu}^{2+}} = \frac{97 \text{ mmol}}{\text{L}} = 97 \frac{\text{meq}}{\text{L}} = 6.15 \frac{\text{g}}{\text{L}}
\]

\[
c_{\text{Na}^+} = 2.31 \frac{\text{equiv}}{\text{L}} = 2.31 \frac{\text{mol}}{\text{L}} = 53.0 \frac{\text{g}}{\text{L}}
\]

\[
q_{\text{Cu}^{2+}} = 3.69 \times 10^{-4} \frac{\text{meq}}{\text{g}} = 1.84 \times 10^{-4} \frac{\text{mmol}}{\text{g}} = 0.012 \frac{\text{mg}}{\text{g}}
\]

\[
q_{\text{Na}^+} = 1.50 \frac{\text{meq}}{\text{g}} = 34.5 \frac{\text{mg}}{\text{g}}
\]
The regeneration is extremely effective, with virtually all of the Cu\(^{2+}\) being released. The Cu\(^{2+}\) concentration in the regenerant solution is 88 times that in the original waste and, after regeneration, the resin contains virtually no Cu\(^{2+}\), so it can be used as effectively in the next cycle as in the previous one.

2. The following example is from a chapter on kinetics in the same text as mentioned above. The rate constant for S oxidation is pH-dependent. Consider a solution is at a higher pH than in the example, causing the rate constant to be 10x its value at pH 7.5. The solution initially contains 2.0 x 10\(^{-4}\) mol/L \(\text{TOTS}(-2)\) and negligible dissolved oxygen. However, it is in contact with the atmosphere, and oxygen dissolves into the water at a rate that is proportional to the difference between the saturation concentration (in equilibrium with the atmosphere) and the concentration that is actually dissolved at that instant. The rate constant for the dissolution reaction is 0.144 h\(^{-1}\). Determine the concentrations of dissolved oxygen and total dissolved sulfide over a 3-day (72-hour) period. Use 20-minute time steps for the first four hours of the simulation, and 2-hour time steps thereafter.

**Example 3-6.** Oxidation of sulfide in natural waters is a complex process, due in part to the large number of intermediate products and side reactions. For instance, in addition to the dominant product (sulfate, SO\(_4^{2-}\)), the products of the reaction might include elemental sulfur (S\(^0\)), sulfite (SO\(_3^{2-}\)), thiosulfate (S\(_2\)O\(_3^{2-}\)), and several other sulfur species. Nevertheless, Chen and Morris (Environ. Sci. Technol. 6, 529 (1972)) reported good agreement of oxidation rates with the following empirical equation:

\[
  r_{\text{S(II)}} = -k c_S^{1.34} c_{\text{O}_2}^{0.56}
\]

where S(II) is the total sulfur in the \(-\text{II} oxidation state, } i.e., c_S = c_{\text{H}_2\text{S}} + c_{\text{HS}^-} + c_{\text{S}_2\text{O}_3^{2-}} \). For a solution at pH 7.5, \(k\) was reported to be 11.97 (mol/L\(^{-0.9}\)h\(^{-1}\).

A batch system contains 2.0 x 10\(^{-4}\) mol/L total dissolved sulfide and is buffered at pH 7.5. Assuming the overall reaction is \(\text{HS}^- + 2 \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+\), determine the percentage of the initial total sulfide that reacts over a 400-h reaction period for the following initial concentrations of dissolved oxygen \([c_{\text{O}_2}(0)]\):

(a) 4.0x10\(^{-3}\) mol/L (much more \(\text{O}_2\) than is required to oxidize all the sulfide)

(b) 4.0x10\(^{-4}\) mol/L (exactly the concentration of \(\text{O}_2\) that is required to oxidize all the sulfide)

(c) 3.0x10\(^{-4}\) mol/L (less \(\text{O}_2\) than is required to oxidize all the sulfide)
Solution. (a) For the given initial sulfide concentration \( c_S(0) = 2.0 \times 10^{-4} \text{ mol/L} \), the maximum amount of \( \text{O}_2 \) that could react (based on the stoichiometry) is \( 4.0 \times 10^{-4} \text{ mol/L} \), or 10% of \( c_{\text{O}_2}(0) \). Under these circumstances, it is reasonable to assume that \( c_{\text{O}_2} \) is approximately constant throughout the experiment at the value \( c_{\text{O}_2}(0) \). Because the reaction is taking place in a batch reactor, the mass balance on sulfide reduces to an equation indicating that the rate of reaction equals the rate of change of \( c_S \):

\[
\dot{V}r_{\text{S(II)}} = \dot{V} \frac{dc_S}{dt} = -\dot{V}k c_S^{1.34} c_{\text{O}_2}^{0.56} \tag{3-35}
\]

\[
\frac{dc_S}{dt} = -k^* c_S^{1.34} \tag{3-36}
\]

where, for the given conditions, \( k^* = k \left( c_{\text{O}_2}(0) \right)^{0.56} \). Inserting the known values, \( k^* = \)

\[
(11.97 \text{ (mol/L)}^{-0.9} \text{ h}^{-1}) \left( 4 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right)^{0.56} = 0.543 \frac{(\text{mol/L})^{-0.34}}{\text{h}}.
\]

Equation 3-36 can be integrated to yield:

\[
c_A(t) = \left[ \left( c_A(0) \right)^{1-1.34} + (1.34 - 1) k^* t \right]^{1-1.34}
\]

\[
c_S(400) = \left[ \left( c_S(0) \right)^{-0.34} + 0.34 \left( 0.543 \left( \text{mol/L} \right)^{-0.34} \right) (400 \text{ h}) \right]^{-0.34}
\]

\[
= 1.67 \times 10^{-6} \frac{\text{mol}}{\text{L}}
\]

\[
\% \text{ reacted } = \frac{2.0 \times 10^{-4} \frac{\text{mol}}{\text{L}} - 1.67 \times 10^{-5} \frac{\text{mol}}{\text{L}}}{2.0 \times 10^{-4} \frac{\text{mol}}{\text{L}}} \times 100\%
\]

\[
= 99.2\%
\]

Two moles of \( \text{O}_2 \) are consumed for each mole of \( \text{S} \) oxidized, so the amount of \( \text{O}_2 \) reacted is

\[
(0.992) (2.0 \times 10^{-4} \text{ mol/L}) (2), \text{ or } 3.97 \times 10^{-4} \text{ mol/L}. \text{ This is approximately 10\% of the initial } \text{O}_2 \text{ concentration, so the assumption of constant } \text{O}_2 \text{ concentration is reasonable. If we wanted to be more accurate, we could re-solve the problem using an average, but still constant } \text{O}_2.
\]
concentration equal to 95% of \( c_{O_2}(0) \), or to be as accurate as possible, we could consider the \( O_2 \) concentration to vary over time, as described in part \( e \) below.

(b) The key to solving the problem for the case where \( c_{O_2}(0) = 2c_S(0) \) is to note that, by stoichiometry, the amount of \( O_2 \) consumed \((-\Delta c_{O_2})\), is twice the amount of \( S \) consumed \((-\Delta c_S)\). Thus,

\[
\Delta c_{O_2} = 2\Delta c_S
\]

\[
c_{O_2}(t) - c_{O_2}(0) = 2\left(c_S(t) - c_S(0)\right)
\]

Substituting the initial values, we obtain:

\[
c_{O_2}(t) - 4 \times 10^{-4} \text{ mol L}^{-1} = 2\left(c_S(t) - 2 \times 10^{-4} \text{ mol L}^{-1}\right)
\]

\[
c_{O_2}(t) = 2c_S(t)
\]

That is, since the initial \( O_2 \) and \( S \) concentrations are in the stoichiometric ratio, their concentrations remain in that ratio throughout the course of the reaction. Substituting this relationship into Equation 3-35, we obtain:

\[-\frac{dc_S}{dt} = kc_S^{1.34}c_{O_2}^{0.56}\]

\[= kc_S^{1.34}(2c_S)^{0.56}\]

\[= 2^{0.56}kc_S^{1.90} = k^n c_S^{1.90}\]

where \( k^n = 2^{0.56} \times 11.97 \left(\text{mol/L}\right)^{-0.9} \text{ h}^{-1} = 17.6 \left(\text{mol/L}\right)^{-0.9} \text{ h}^{-1}\)

Once again, we have a rate expression of the form \(-\frac{dc_S}{dt} = -kc_S^n\), in this case with \( n = 1.90 \).

Analogous to the case in part \( a \), integration yields:

\[
c_S(400) = \left[\left(c_S(0)\right)^{-0.90} + 0.90 \left(17.6 \left(\text{mol/L}\right)^{-0.90} \text{ h}^{-1}\right)(400 \text{ h})\right]^{\frac{1}{-0.90}}
\]

\[= 4.31 \times 10^{-5} \text{ mol L}^{-1}\]
% reacted = \( \left( \frac{2.0 \times 10^{-4} - 4.31 \times 10^{-5}}{2.0 \times 10^{-4}} \right) \times 100\% = 78\% \)

Note that the extent of oxidation is considerably less than in part a because the concentration of O\(_2\) throughout the reaction period is less.

(c) For the conditions specified in this system, the reactants are not present in their stoichiometric ratio, and neither reactant can be approximated to be constant during the course of the reaction. Once again, the approach is to write and solve the mass balance on sulfide. However, in this case, the differential equation cannot be solved analytically. Nevertheless, a numerical solution is possible. Taking small time steps, the amount of S consumed during each step can be approximated from the rate expression, as follows:

\[
\frac{-dc_s}{dt} = k c_s^{1.34} c_{O_2}^{0.56}
\]

\[
\Delta c_s \approx -k c_s^{1.34} c_{O_2}^{0.56} \Delta t
\]

Also, by stoichiometry:

\[
\Delta c_{O_2} = 2\Delta c_s
\]

Based on a spreadsheet analysis using 1-h time steps and the recursive equation
\( c_s(t + \Delta t) = c_s(t) + \Delta c_s \), the course of the reaction is followed. The concentrations of S and O\(_2\) as a function of time are shown in Figure 3-10. After 400 h, \( c_s \) and \( c_{O_2} \) are \( 6.21 \times 10^{-5} \) mol/L and \( 2.42 \times 10^{-5} \) mol/L, respectively, and 69% of the sulfide has reacted.
Figure 3-10. Concentrations of total sulfide species and dissolved oxygen as a function of time for Example 3-6c.