Mining of Phosphate Rock and Treatment of the Waste

As will be discussed in class, phosphate rock is mined near the Gulf Coast of Florida by breaking up phosphate rock (primarily hydroxyapatite, \( \text{Ca}_5(\text{OH})(\text{PO}_4)_3 \)) with draglines and then converting it into a slurry with jets of water. (See the handout: Background Information on Phosphate Mining.) The water partially dissolves the rock but mostly it breaks it up into fine particles that can be easily transported by pipeline to a central processing plant. Today, most of the water is recycled to minimize discharging phosphate to the environment. But, it is still important to have some idea of the amount of \( \text{PO}_4 \) that will dissolve in the water so that the water management plans can be better designed. Your client in this case is the engineering/water quality group at a large phosphate mine in Polk County, FL.

Present you results as a memo, backed up with your calculation sheets.

1. As a base case, assume the water used is pure \( \text{H}_2\text{O} \). To be realistic, this water should be allowed to equilibrate with atmospheric \( \text{CO}_2 \). If the water achieves full equilibrium with hydroxyapatite, what is the total concentration of dissolved phosphate, \([\text{PO}_4]_T\), (i.e., sum of all dissolved species) in the resulting solution? Also please summarize the speciation of the equilibrated water. Those odd combinations you see among the aqueous species, such as \( \text{CaHCO}_3^+ \), are soluble combinations of ions known as ion pairs. We have tended to ignore them as minor up to now, but in this exercise they will start to become important. In your speciation tables, include only ion pairs that are more than about 5% of the total soluble component of interest. For hydroxyapatite use \( \log K_{\text{sp}} = -44.2 \)

2. The groundwater used in the jets is, of course, not pure water. The laboratory sent you the following analysis of the water that feeds the jets:

- Ca Hardness: 30 mg-CaCO\(_3\)/L
- Mg Hardness: 20 mg-CaCO\(_3\)/L
- SO\(_4\): 67.2 mg/L (as S)
- Alkalinity: \( 8.0 \times 10^{-4} \) eq/L

What is the total concentration of dissolved phosphate, \([\text{PO}_4]_T\) in the resulting solution? Also please summarize the speciation of the equilibrated water, as above. What is the percent reduction in the total soluble \( \text{PO}_4 \) and what is primarily responsible for the change?

3. An engineer at the mine has found that mildly acidifying the water causes the rock to crumble more readily into a slurry. Preliminary tests show that water acidified to pH 4 is much more effective than the raw water. Simply fix the pH, and then recognize that there is no longer any alkalinity in the system, so you can neglect \( \text{CO}_3 \). What is the total concentration of dissolved phosphate, \([\text{PO}_4]_T\) in the resulting solution? Summarize the speciation of the equilibrated water, as above. What is the percent change in the total soluble \( \text{PO}_4 \) from the prior question and what is primarily responsible for the change? Does the mining engineer perhaps need to consider some potential water pollution problems caused by his idea for using acidified water?

4. At the processing plant, the slurry of hydroxyapatite (HAp) is converted to phosphoric acid which is then shipped around the world to manufacture fertilizer and other products. The process is simple and effective. Sulfuric acid is mixed with the rock slurry. The reaction yields phosphoric acid and a gypsum precipitate by the following reaction:
\[ 5\text{H}_2\text{SO}_4 + \text{Ca}_5(\text{OH})(\text{PO}_4)_3 = 3\text{H}_3\text{PO}_4 + \text{H}_2\text{O} + 5\text{CaSO}_4 \text{(s)} \]

The liquid phosphoric acid is separated from the gypsum sludge which is disposed of in huge piles. (As noted in the supplementary info, the gypsum actually is pretty well dosed with residual phosphate and is called phosphogypsum. We will treat it here as pure gypsum).

Let’s do a simple re-creation of this reaction. Assume the reaction mixture is a slurry of 0.5 M H\text{}_2\text{SO}_4 and 31 g/L of hydroxyapatite (i.e., 0.1 mol/L of HAp as a finite solid). Eliminate the carbonate species entirely as they are irrelevant in such acid conditions). Remember that sulfuric acid has two protons per mole. Assume the slurry otherwise has the composition of the feed water.

How complete is the conversion of HAp to phosphoric acid? How effectively is Ca removed as a gypsum precipitate? If gypsum has two “waters of hydration” per mole (i.e., the correct formula is really CaSO\textsubscript{4}.2H\textsubscript{2}O), then how many metric tonnes of gypsum waste are produced for every tonne of HAp processed?

5. The phosphogypsum is disposed of in 200-ft high piles. The rainwater that leaches through the pile produces a mildly acidic, phosphate-rich effluent. A sample of the leachate yields the following analysis.

\begin{align*}
\text{pH} & = 5.2 \\
[\text{Ca}^2+] & = 7.2 \text{ mM} \\
[\text{SO}_4^{2-}] & = 7.0 \text{ mM} \\
[\text{PO}_4^{3-}] & = 0.3 \text{ mM}
\end{align*}

Because the pH is below the CO\textsubscript{2} equivalence point (~ 5.6 for Pco\textsubscript{2} = atmospheric)), you can expect a negative alkalinity, or a positive acidity. This means subtracting from the alkalinity eqn. all of the species that are protonated at this pH, such as HSO\textsubscript{4}-, H\textsubscript{3}PO\textsubscript{4}, H\textsubscript{2}PO\textsubscript{4}-, HPO\textsubscript{4}\textsuperscript{2-}, etc., using the appropriate multipliers for the number of H’s in the species (e.g., x3 for H\textsubscript{3}PO\textsubscript{4}). Since you fix the pH, this does not affect the set up of the problem, but it is reflected in the output, so try adding these “acidity species” up for yourself.

6. The plan is to capture the leachate and treat it with pickle liquor as a cheap source of Fe(III). There is some info about commercial pickle liquor in the attached materials. Assume the waste pickle liquor supplied to you is Ferric Sulfate (Fe as Fe(III)): Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}. An analysis from the supplier gives the following characteristics:

\begin{itemize}
  \item Form of Iron: Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}
  \item Iron Content: 1.3 lbs/gal (as Fe)
  \item Fraction of Iron that is Chemically Active: 36%
  \item Residual Acid: 1% w/w as H\textsubscript{2}SO\textsubscript{4}
\end{itemize}

a) Convert this engineering info into chemical concentrations by the usual mole conversions. Note that the acid content means there is 10 g of H\textsubscript{2}SO\textsubscript{4} per liter of solution. Use that to find the molarity of the acid, remembering that sulfuric is a diprotic acid. In all subsequent calculations, remember to include proportional amounts of protons for every mole of Fe\textsuperscript{3+} you use.

b) Because ferric phosphate (FePO\textsubscript{4} or strengite) is rather insoluble, try treating the waste by adding enough pickle liquor to the leachate to make the Fe equimolar to the total PO\textsubscript{4}. 