3-10 Davis and Cornwell

The groundwater in Pherric, New Mexico contains 1.8 mg/liter of Fe^{+3}. What would the pH of the water have to be to precipitate out all but 0.3 mg/liter ?

<u>Preliminary discussion:</u> Iron in water can exist in 2 different ionic states, Fe^{+3} (ferric) and Fe^{+2} (ferrous). These cations can form precipitates with a variety of anions present in water if one or both exists in high enough concentrations. Ferrous iron exists in water devoid of oxygen. When water containing ferrous iron comes into contact with air it is oxidized to the ferric state. Once oxidized to the ferric state almost any iron in solution will precipitate out as ferric hydroxide. This is particularly true at pH values around 7.0.

The environmental significance of iron is that ferric iron in concentrations > 0.3 mg/liter will stain plumbing fixtures and clothes being washed. It may also impart an unpleasant taste or odor to potable water

Solubility products of some iron compounds:

$[Fe^{+2}]*[CO_3^{-2}]^2 = 3.13*10^{-11}$ ferrous carbonate

$[Fe^{+2}]*[OH^-]^2 = 4.79*10^{-17}$ ferrous hydroxide

$[Fe^{+3}]*[OH^-]^3 = 2.67*10^{-39}$ ferric hydroxide

<u>Solution</u> : Ferric iron reacts with hydroxide in water to form ferric hydroxide, $Fe(OH)_3$. This compound has a solubility product of $2.69*10^{-39}$. Since it is smaller than any other K_{sp} involving iron, this tells us that ferric hydroxide, $Fe(OH)_3$, will precipitate

$Fe_{ferric} := 1.8 \cdot \frac{mg}{liter}$ initial concentration of ferric iron in the groundwater

$K_{sp} = [Fe] \cdot ([OH])^3 = 2.69 \cdot 10^{-39} \cdot \frac{mole^4}{liter^4}$ note that the solubility product of ferric hydroxide is very small. I have included the units on K_{sp} because I am using Mathcad.

$K_{sp} := 2.69 \cdot 10^{-39} \cdot \frac{mole^4}{liter^4}$ Note that solubility products as well as equilibrium and kinetic constants can have strange units.

$[H] \cdot [OH] = 10^{-14}$ ion product of water $K_w := 10^{-14} \cdot \left(\frac{mole}{liter}\right)^2$

In this problem we have only Fe^{+3} and water, H_2O - both the solubility product equation and the ion product of water must be satisfied. The problem is essentially asking: what must the pH be for the soluble concentration of ferric iron in water to be 0.3 mg/liter ?

$$MW_{Fe} := 55.8 \cdot \frac{gm}{mole}$$

We can combine both equations into a single one relating the pH to the soluble iron concentration.

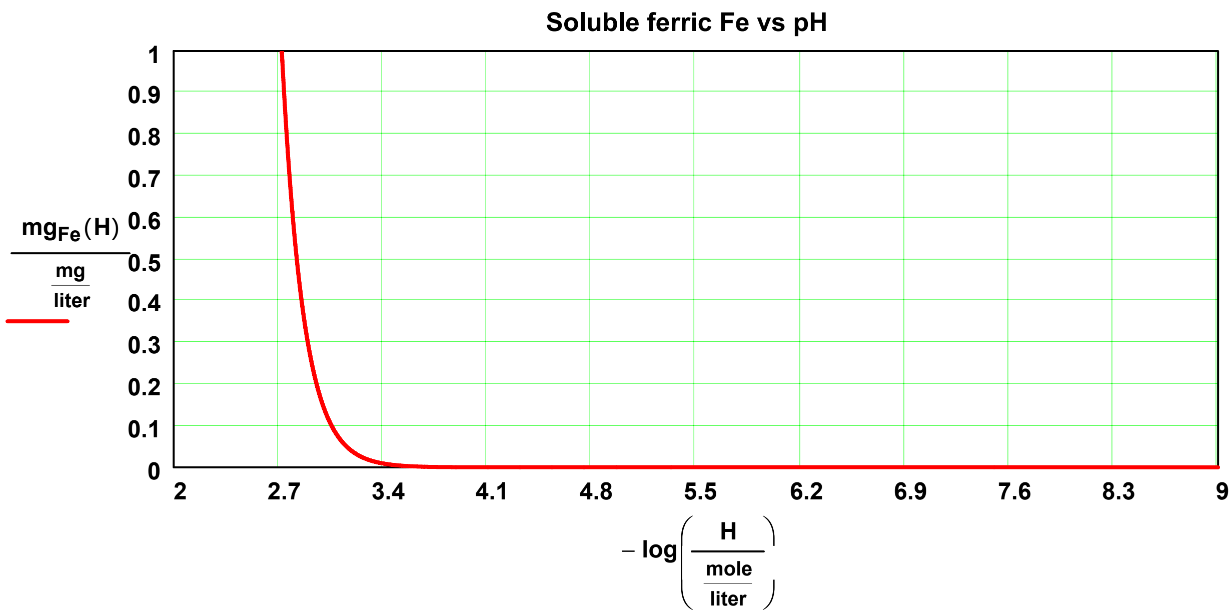
$$K_{sp} = mole_{Fe} \cdot \left(\frac{K_w}{H}\right)^3$$ **solve this for the moles of soluble ferric iron**

$$mole_{Fe}(H) = \frac{K_{sp}}{K_w^{\,3}} \cdot H^3$$

Now we can plot mg/liter of ferric iron vs the pH of the water.

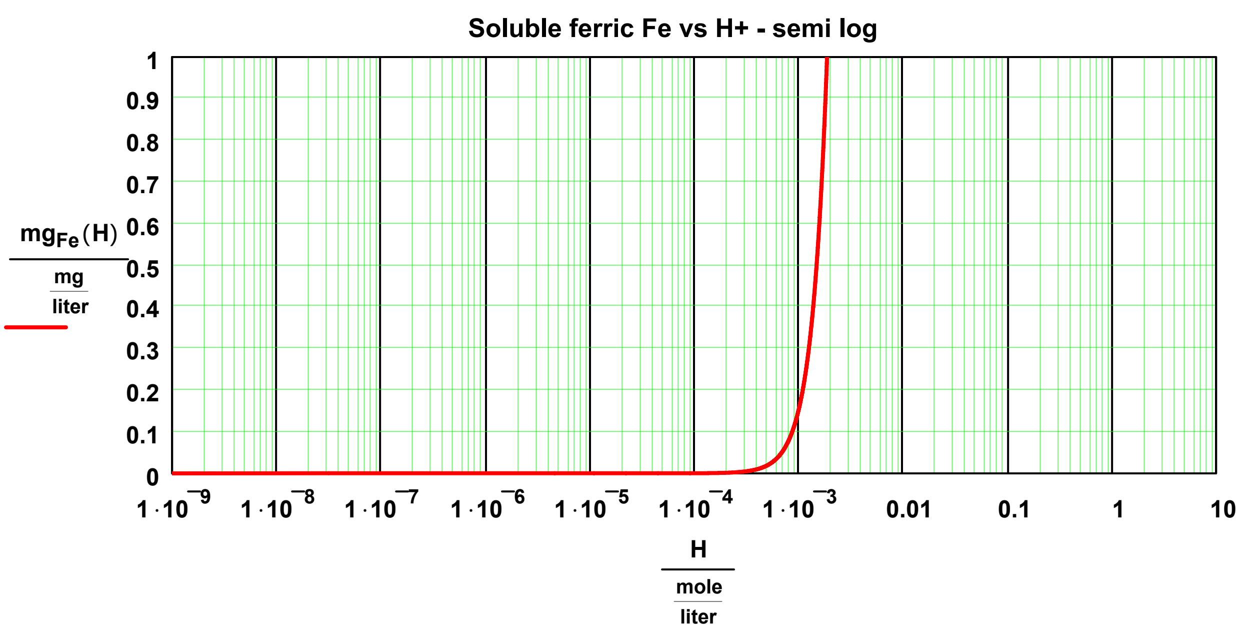
$$H := 1 \cdot 10^{-9} \cdot \frac{mol}{liter}, 1 \cdot 10^{-7.5} \cdot \frac{mol}{liter} .. 1 \cdot 10^{-2} \cdot \frac{mol}{liter}$$

$$mg_{Fe}(H) := \frac{K_{sp}}{K_w^{\,3}} \cdot H^3 \cdot MW_{Fe}$$ **Here we have multiplied by the molecular weight of iron to convert results to mg/liter**



Note that essentially no soluble ferric iron exists in water with a pH > 3.6

We can also plot the hydrogen ion concentration directly using a log scale



A water with a pH of about 2.9 can support a soluble ferric iron concentration of approximately 0.3 mg/liter.

Thus, we should not normally expect to measure ferric iron in water as it will have precipitated out as $Fe(OH)_3$.

Water generally contains both ferric (Fe^{+3}) and ferrous (Fe^{+2}) iron. As we have seen, any ferric iron will precipitate out immediately. The ferrous iron however, may be oxidized to the ferric form over time by oxygen in the water. If this happens it will precipitate out as ferric hydroxide also. This is the process that is generally responsible for iron stains on plumbing and clothes. For this reason the secondary iron standard for potable water is 0.3 mg/liter <u>total</u> iron.

The water which runs off slag heaps from coal mines often has a very low pH. It is referred to as "acid mine drainage". A characteristic of such waste streams is a very high dissolved iron content. If the acid mine drainage flows into a nearby stream which raises the pH this iron will precipitate out and form a brown covering on the stream bottom and give the water itself a brown color.