

3-9 Davis and Cornwell, pg 247

PART 1. How many mg/l of magnesium ion ( $Mg^{+2}$ ) can remain in solution in a water which contains .001000 M hydroxyl ion (i.e  $pOH = 3$ ) ? Magnesium is a divalent cation and as such causes hardness. One way of removing magnesium hardness is to raise the pH and precipitate it out as magnesium hydroxide.

PART 2. Compute and plot the soluble  $Mg^{+2}$  remaining in solution (in mg/liter) for pH values ranging from 9 to 12. Plot the data on arithmetic axes as well semi-logarithmic axes.

**Concept:** When magnesium is present in water in sufficient concentrations it will form insoluble precipitates with hydroxide ions,  $Mg(OH)_2$ . The quantities of these ions which must be present before precipitation occurs is determined by the solubility product for the precipitate.



use solubility product expression for magnesium hydroxide,  $Mg(OH)_2$ . The general expression for a solubility product for a precipitate  $A_nB_m$  is:

$$[A]^n[B]^m = K_{sp}$$

$$(Mg) \cdot (OH^2) = K_{sp}$$

$$K_{sp} := 1.81 \cdot 10^{-11} \cdot \left( \frac{\text{mole}}{\text{liter}} \right)^3$$

Obtained from reference material - See Table A-9, pg 876 Davis and Cornwell 3<sup>rd</sup> edition. Small values of  $K_{sp}$  imply low solubility.

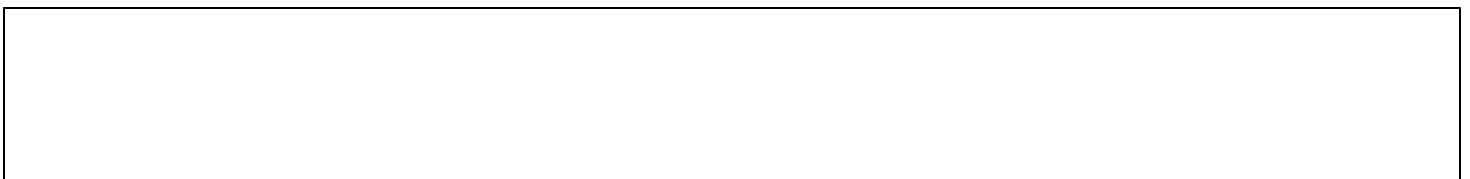
$$pK_{sp} := -\log \left[ \frac{K_{sp}}{\left( \frac{\text{mole}}{\text{liter}} \right)^3} \right]$$

$$pK_{sp} = 10.742$$

$$\text{ion product of water} - K_w := 1 \cdot 10^{-14} \cdot \left( \frac{\text{mole}}{\text{liter}} \right)^2$$

$$MW_{Mg} := 24.3 \cdot \frac{\text{gm}}{\text{mole}} \quad \text{molecular weight Mg}$$

$$MW_{OH} := 17 \cdot \frac{\text{gm}}{\text{mole}} \quad \text{molecular weight OH}^-$$



$$(\text{Mg}) \cdot [(\text{OH}^-)^2] = K_{\text{sp}} \implies$$

$$\text{Mg} := \frac{K_{\text{sp}}}{\left[ (\text{OH}^-)^2 \cdot \left( \frac{\text{mole}}{\text{liter}} \right)^2 \right]}$$

$$\text{Mg} = 1.81 \times 10^{-5} \frac{\text{mole}}{\text{liter}} \quad \text{maximum solubility in mole/liter when } [\text{OH}^-] = .00100 \text{ mole/liter}$$

$$\text{Mg}_{\text{mg\_per\_l}} := \text{Mg} \cdot \text{MW}_{\text{Mg}} \implies \text{Mg}_{\text{mg\_per\_l}} = 0.4398 \frac{\text{mg}}{\text{liter}} \quad \text{Mg}^{+2} \text{ solubility in mg/liter}$$

As I have mentioned before a single number doesn't tell us much about what is going on. Lets plot the pH as a function of the possible  $\text{Mg}^{+2}$  concentration

$$[\text{Mg}] \cdot ([\text{OH}^-])^2 = K_{\text{sp}}$$

$$\text{The A.W. of magnesium } \text{MW}_{\text{Mg}} = 24.3 \frac{\text{gm}}{\text{mole}}$$

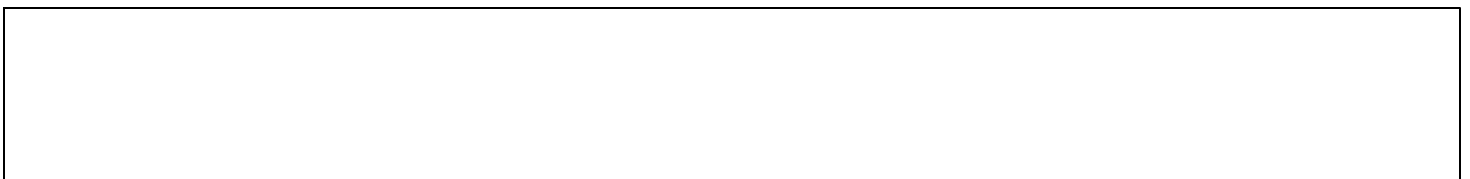
$$\text{Now, convert the soluble } \text{Mg}^{+2} \text{ concentration to milligrams per liter: } \text{Mg} = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} \cdot \text{MW}_{\text{Mg}}$$

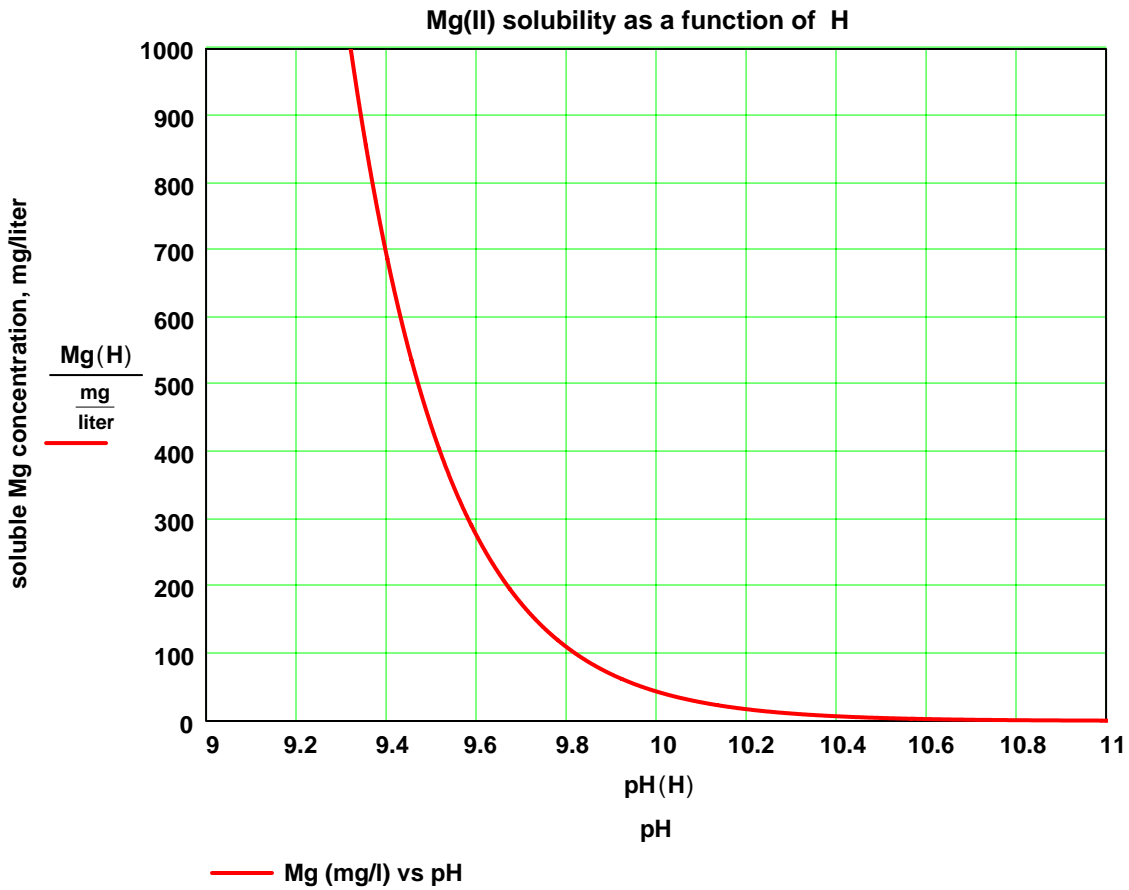
$$\text{substituting for OH we get : } \text{Mg}(\text{H}) := \frac{K_{\text{sp}}}{\left( \frac{K_{\text{w}}}{\text{H}} \right)^2} \cdot \text{MW}_{\text{Mg}}$$

Let's examine a range of values

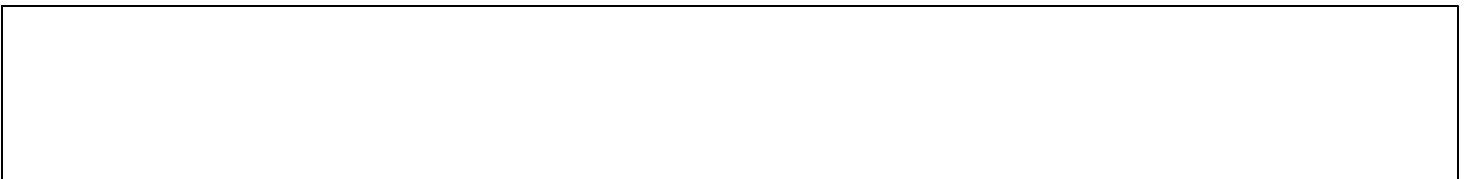
$$\text{H} := 1 \cdot 10^{-9} \frac{\text{mole}}{\text{liter}}, 10^{-9.0001} \frac{\text{mole}}{\text{liter}} \dots 1 \cdot 10^{-12} \frac{\text{mole}}{\text{liter}}$$

$$\text{pH}(\text{H}) := -\log \left( \frac{\text{H}}{\frac{\text{mole}}{\text{liter}}} \right)$$

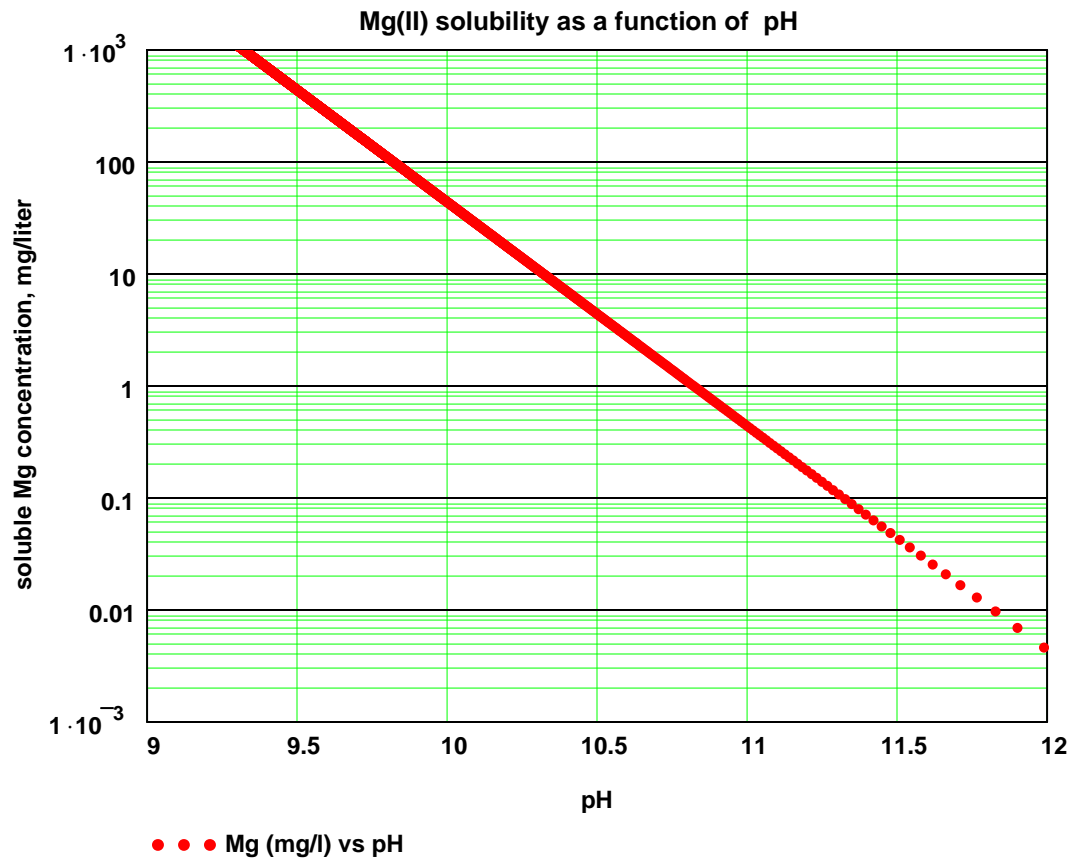




The plot above shows that in order to remove  $Mg^{+2}$  from solution we need to raise the pH to around 10.5 or higher. Keep in mind that these calculations say NOTHING about how well the  $Mg(OH)_2$  precipitate particles will actually settle out in a clarifier.



Below is the same plot as above using a log scale for magnesium concentration



**Conclusion:** You can remove  $Mg^{+2}$  as  $Mg(OH)_2$  by raising the pH of water. Substantial quantities of soluble  $Mg^{+2}$  can exist at pH values below 10.5. Notice the wide range in values of  $Mg^{+2}$  obtained in the calculations.

How would you adjust the pH of a water if you wanted to remove  $Mg^{+2}$  by precipitation as the oxide,  $Mg(OH)_2$ ? Specifically, what TYPE of chemical would you use.