Precipitation is the process of producing solids within a solution.

In metals removal, it is desirable to precipitate as much metal solid as possible so that it can be removed or separated from water.

Once the metals precipitate and form solids, they can then easily be removed, and the water, now with low metal concentrations, can be discharged safely.
Solubility of Metals

- Solubility is the ability of a substance to go into solution (dissolve).
- Substances that are soluble readily dissolve in solution and do not precipitate.
- Substances that are insoluble do not easily dissolve in solution and stay in their solid form.
In wastewater, metals are present in a stable, dissolved aqueous form and are unable to form solids.

The goal of metals removal in wastewater is to produce conditions so that metals are insoluble. **For example**, for metal removal by metal hydroxide precipitation, adjust the pH (hydroxide ion concentration) of water so that the metals will form insoluble precipitates.
Metal removal by Metal Hydroxide precipitation

Ref: Removing Heavy Metals from Wastewater
University of Maryland
Metal precipitation is primarily dependent upon two factors:

i. the concentration of the metal,

ii. the pH of the water.

Metals are usually present in wastewaters in dilute quantities (1 - 100 mg/L) and at neutral or acidic pH values (< 7.0). Both of these factors are disadvantageous with regard to metals removal.
Solubility of Metals

$$\text{MCO}_3(s) \leftrightarrow \text{M}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)}$$

$$K_{sp} = [\text{M}^{2+}].[\text{CO}_3^{2-}]$$

✓ If $[\text{M}^{2+}].[\text{CO}_3^{2-}]$ is $> K_{sp}$ precipitation occurs

✓ If $[\text{M}^{2+}].[\text{CO}_3^{2-}]$ is $< K_{sp}$ no precipitation
\[ [M^{2+}][CO_3^{2-}] = K_{sp} \]

\[ \log[M^{2+}] + \log[CO_3^{2-}] = \log K_{sp} \]

\[ \log[M^{2+}] = \log K_{sp} - \log[CO_3^{2-}] \]

\[ \log[M^{2+}] = \log K_{sp} + pCO_3 \]

\[ y = b + mx \]

where \( m = 1 \)
Figure 4.13 Log C diagram showing the solubility of various metallic carbonates at 25°C
For Figure 4.13

$pCO_3^{2-} \uparrow \quad [CO_3^{2-}] \downarrow$

$K_{sp} = [M^{z+}] \cdot [CO_3^{2-}]$

$\uparrow \quad \downarrow$
Which Metal Carbonate is the least soluble one?

PbCO$_3$(s) is the least soluble. Lowest K$_{sp}$

Which Metal Carbonate is the most soluble one?

MgCO$_3$(s) is the most soluble one. Highest K$_{sp}$
\[
\text{Mg}^{2+} \rightarrow \log K_{sp} = -5 \quad \rightarrow K_{sp} = 10^{-5} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]
\]

\[
\text{Ca}^{2+} \rightarrow \log K_{sp} = -8.5 \quad \rightarrow K_{sp} = 3.2 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]
\]

When \([\text{CO}_3^{2-}] = 10^{-2} \text{M} \rightarrow \text{solubility of} \quad [\text{Mg}^{2+}] = 10^{-3} \text{M} \quad [\text{Ca}^{2+}] = 3.2 \times 10^{-7} \text{M} \]
• In hardness removal by chemical precipitation, Ca\(^{2+}\) is removed as CaCO\(_3\), but Mg\(^{2+}\) is removed as Mg(OH)\(_2\).
• Because Mg solubility is higher than Ca and requires very large amounts of CO\(_3^{2-}\).
• So we do not choose to add CO\(_3^{2-}\) to remove Mg.
Ex: \( p\text{CO}_3^{2-} = 3 \) Ca solubility? \( K_{sp} = 10^{-8.5} \)

\[
[\text{CO}_3^{2-}] = 10^{-3} \quad [\text{Ca}^{2+}] = 10^{-5.8} \text{ M from Figure 4.13}
\]

This is the highest concentration of \( \text{Ca}^{2+} \) you can have in water when \( [\text{CO}_3^{2-}] = 10^{-3} \text{ M} \).
Ex: \[ p\text{CO}_3^{2-} = 3 \quad [\text{Ca}^{2+}] = 10^{-4} \text{ M} \text{ is this water stable?} \]

No!!!

\[ [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] = 10^{-4} \cdot 10^{-3} = 10^{-7} > K_{sp} = 10^{-8.5} \]

So precipitation occurs.
Ex: \( \text{pCO}_3^{2-} = 1 \quad [\text{Ca}^{2+}] = 10^{-7} \text{ M}, \) will precipitation occur?

Yes!!!

\[ [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] = 10^{-7}. \quad 10^{-1} = 10^{-8} > K_{sp} \]

Slightly greater than \( K_{sp} \). So precipitation occurs.
Ex: \( \text{CO}_3^{2-} = 10^{-3} \text{ M}, \quad [\text{Ca}^{2+}] \ ? \text{ in mg/L} \)

From Figure 4.13 \( [\text{Ca}^{2+}] = 10^{-5.5} \text{ M} \)

\[
10^{-5.5} \text{ M} = 3.2 \times 10^{-6} \frac{\text{mol}}{\text{L}} \times 40 \text{ g} \times 1000 \text{ mg} = 0.128 \text{ mg/L}
\]
Solubility of Hydroxide Salts

$$\text{M(OH)}_z(s) \leftrightarrow \text{M}^{z+} + z\text{OH}^-$$

$$K_{sp} = [\text{M}^{z+}][\text{OH}^-]^z$$

$log[\text{M}^{z+}]$ is a function of pH

$$\log K_{sp} = \log[\text{M}^{z+}] + \log[\text{OH}^-]^z$$

$$\log[\text{M}^{z+}] = \log K_{sp} - z \log[\text{OH}^-]$$
\[ K_w = 10^{-14} = [H^+].[OH^-] \]

\[ p\ K_w = pH + pOH \]

\[ pOH = p\ K_w - pH \]

\[ \log[M^{z+}] = \log K_{sp} - z(pH - pK_w) \]

\[ \log[M^{z+}] = \log K_{sp} + zpK_w - zpH \]

\[ Y = b - m.X \]
\[
\text{M(OH)}_{z(s)} \leftrightarrow \text{M}^{z+} + z\text{OH}^-
\]

When \( \text{pH} \uparrow \), \( [\text{OH}] \uparrow \), \( [\text{M}^+] \downarrow \)

\[
K_{sp} = [\text{M}^{z+}] \cdot [\text{OH}^-]
\]

\[\downarrow \quad \uparrow\]
Figure 4.14 Log C diagram showing the solubility of various metallic hydroxides.
• Magnesium hardness can be reduced by raising the pH to 11 or greater and precipitating Mg(OH)$_2$.

• Copper, zinc, and chromium are often removed from metal containing wastewaters by precipitating at a pH of 7 or above.
Ex: \([\text{Cu}^{2+}] = 10^{-2} \text{ M}\) in wastewater. We want to reduce it down to \([\text{Cu}^{2+}] = 10^{-6} \text{ M}\). What should be the pH? How much \(\text{Cu(OH)}_2\) precipitate is formed in 1 L of wastewater?

\[\text{pH} = 7.8 \text{ minimum pH, from Figure 4.14}\]

\(\text{Cu}^{2+}\) removed

\[10^{-2} \text{ M} - 10^{-6} \text{ M} \approx 10^{-2} \text{ M}\]

10\(^{-2}\) mol \(\text{Cu}^{2+}\) is removed in 1 L of wastewater. Therefore, 10\(^{-2}\) mol \(\text{Cu(OH)}_2\) is formed.

\[= 10^{-2} \text{ mol } \text{Cu(OH)}_2 \times 97,500 \text{ mg/mol} = \textbf{97.5 mg Cu(OH)}_2 \text{ precipitate}\]
Ex: Initial conditions of wastewater is $10^{-2}$ M Pb$^{2+}$, pH = 7. We want to reduce the Pb$^{2+}$ to $10^{-4}$ M. What would be the pH?

Answer: Increase pH to 8.5 or 9. pH = 8.3 is the equilibrium pH.
CaCO$_3$ $\leftrightarrow$ Ca$^{2+}$ + CO$_3^{2-}$ \hspace{1cm} K_{sp} = [Ca^{2+}] \cdot [CO_3^{2-}] \\
H_2CO_3$ $\leftrightarrow$ H$^+$ + HCO$_3^-$ \hspace{1cm} K_a_1 = \frac{[H^+].[HCO_3^-]}{[H_2CO_3]} \\
HCO$_3^-$ $\leftrightarrow$ H$^+$ + CO$_3^{2-}$ \hspace{1cm} K_a_2 = \frac{[H^+].[CO_3^{2-}]}{[HCO_3^-]} \\
H_2O$ $\leftrightarrow$ H$^+$ + OH$^-$ \hspace{1cm} K_w = [H^+].[OH^-] \\

[CO$_3^{2-}$] is a function of pH

TOTCO$_3$ = [H$_2$CO$_3$] + [HCO$_3^-$] + [CO$_3^{2-}$] \\
CB = 2.[Ca^{2+}] + [H^+] = 2.[CO$_3^{2-}$] + [HCO$_3^-$] + [OH^-]
$$\alpha_2 = \frac{[\text{CO}_3^\equiv]}{\text{TOTCO}_3} = \frac{1}{1 + \frac{[H^+]^2}{K_{a,1} \times K_{a,2}}} + \frac{[H^+]}{K_{a,2}}$$

$$[\text{CO}_3^\equiv] = \frac{\text{TOTCO}_3}{1 + \frac{[H^+]^2}{K_{a,1} \times K_{a,2}}} + \frac{[H^+]}{K_{a,2}}$$

$$K_{sp} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]$$

$$[\text{Ca}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^\equiv]}$$
When $\text{CaCO}_3$ precipitates $\text{TOTCO}_3$ changes.
Figure 4.15 Log C diagram showing the solubility of Ca$^{2+}$ ions with respect to TOTCO$_3$ and pH.
Ex: A water sample contains $10^{-2} \text{M Ca}^{2+} \text{M}$, $C_T = 10^{-4} \text{M}$ and pH = 7.5. Will CaCO$_3$ precipitate in this water? If the answer is no, at what pH will precipitation occur?

Answer

No, CaCO$_3$ precipitation at pH 7.5

pH of saturation is 8.0.

If the water pH is raised above this value CaCO$_3$ precipitation will occur.
**Ex**: What is the maximum solubility of Ca$^{2+}$ in water with a pH of 10 and $C_T = 10^{-2} \text{M}$

**Answer**

$[\text{Ca}^{2+}] = 10^{-6} \text{ M}$ (from Figure 4.15)
Ex: A water has an initial \([\text{Ca}^{2+}]_{\text{ini}} = 4 \times 10^{-3} \text{ M}\) and \(C_T = 10^{-2}\text{ M}\). It is desired to reduce \([\text{Ca}^{2+}]\) to \(10^{-4}\text{ M}\) by precipitation of \(\text{CaCO}_3\). What will be the final \(C_T\)? What should be the solution pH?

**Answer**

After precipitation there will be less \(C_T\).

Change in \([\text{Ca}^{2+}] = 4 \times 10^{-3} \text{ M} – 10^{-4} \text{ M} = 3.9 \times 10^{-4} \text{ M}\)

\(3.9 \times 10^{-4} \text{ M} = \text{Change in } [\text{CO}_3^{2-}]\) because there is 1:1 molar ratio in the ppt rxn.

\(10^{-2} \text{ M} – 3.9 \times 10^{-3} \text{ M} = 6.1 \times 10^{-3} \text{ M}\) is the new \(C_T\).

From Figure 4.15 saturation pH is about 9.0

Therefore, pH should be raised to above 9.0