

SOLUBILITY OF METALS

- 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.

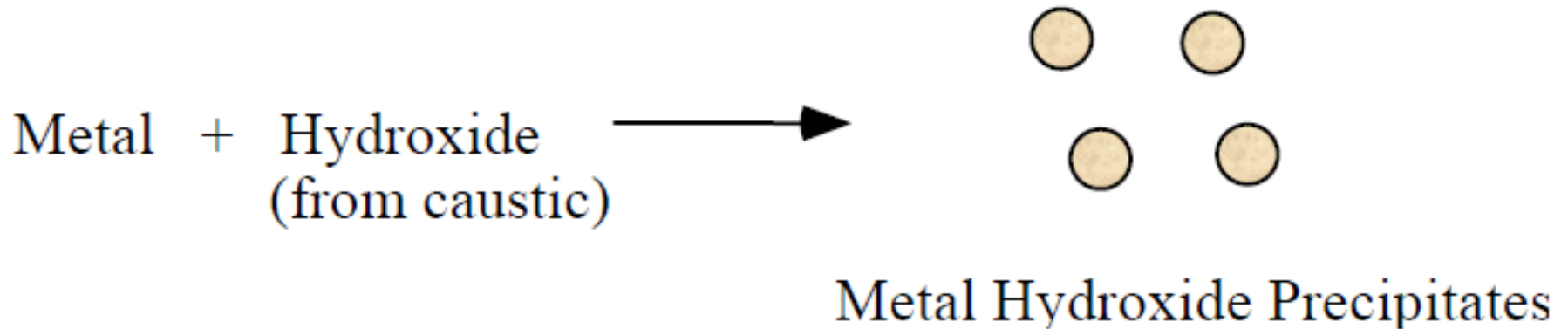
Solubility of Metals

- 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



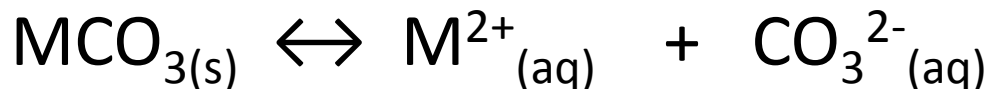
**Ref: Removing Heavy Metals from Wastewater
University of Maryland
Engineering Research Center Report, August 1994.**

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



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

- ✓ If $[\text{M}^{2+}] \cdot [\text{CO}_3^{2-}]$ is $> K_{sp}$ precipitation occurs
- ✓ If $[\text{M}^{2+}] \cdot [\text{CO}_3^{2-}]$ is $< K_{sp}$ no precipitation

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

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

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

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

$$y = b + mx$$

where $m=1$

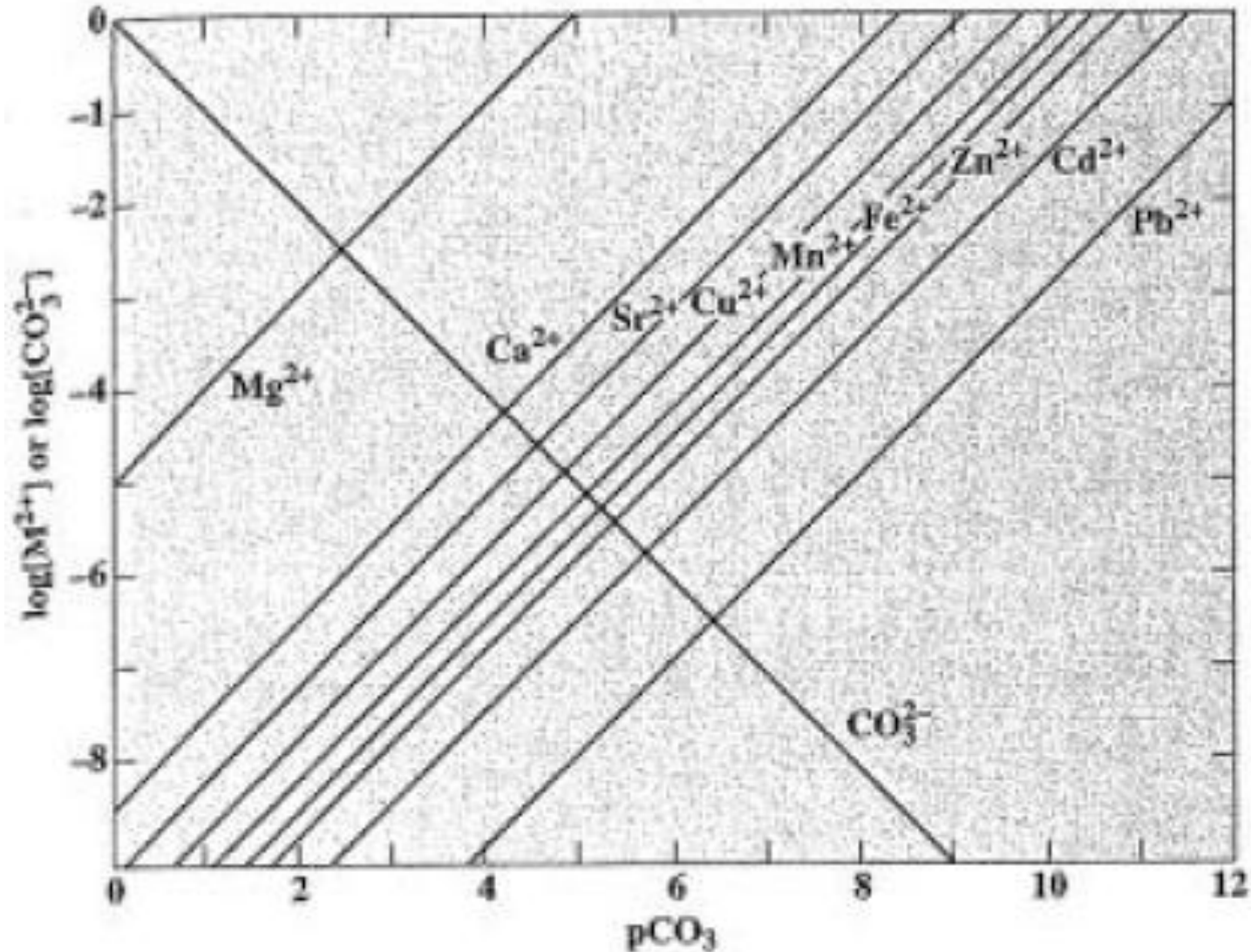
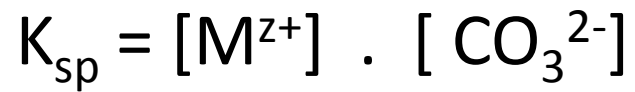


Figure 4.13 Log C diagram showing the solubility of various metallic carbonates at 25°C

For Figure 4.13



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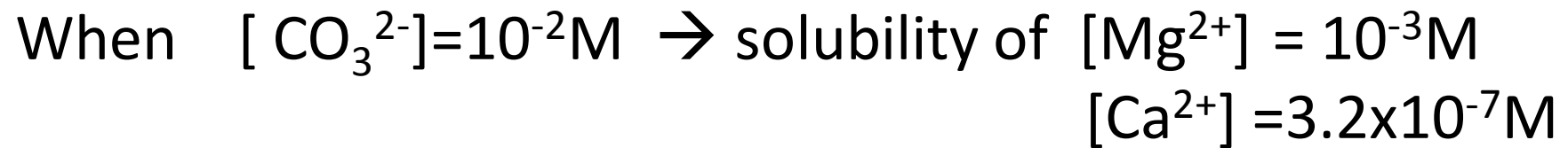
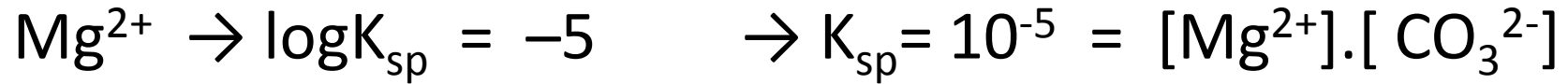
↓

Which Metal Carbonate is the least soluble one?

$\text{PbCO}_{3(s)}$ is the least soluble. Lowest K_{sp}

Which Metal Carbonate is the most soluble one?

$\text{MgCO}_{3(s)}$ is the most soluble one. Highest K_{sp}



- In hardness removal by chemical precipitation, Ca^{2+} is removed as CaCO_3 , but Mg^{2+} is removed as $\text{Mg}(\text{OH})_2$.
- 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 : $\text{pCO}_3^{2-} = 3$ Ca solubility? $K_{\text{sp}} = 10^{-8.5}$

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

This is the highest concentration of Ca^{2+} you can have in water when $[\text{CO}_3^{2-}] = 10^{-3}$ M.

Ex : $\text{pCO}_3^{2-} = 3$ $[\text{Ca}^{2+}] = 10^{-4} \text{ M}$ is this water stable?

No!!!

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

So precipitation occurs.

Ex : $p\text{CO}_3^{2-} = 1$ $[\text{Ca}^{2+}] = 10^{-7} \text{ M}$, will precipitation occur?

Yes!!!

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

Slightly greater than K_{sp} . So precipitation occurs.

Ex : $\text{CO}_3^{2-} = 10^{-3} \text{ M}$, $[\text{Ca}^{2+}] ? \text{ in mg/L}$

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

$$10^{-5.5} \text{ M} = 3.2 \times 10^{-6} \frac{\text{mol}}{\text{L}} \times \frac{40 \text{ g}}{\text{mol}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 0.128 \text{ mg/L}$$

Solubility of Hydroxide Salts



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

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

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

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

$$K_w = 10^{-14} = [H^+].[OH^-]$$

$$p K_w = pH + pOH$$

$$pOH = p K_w - pH$$

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

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

↓

↓

↓

Y

=

b

- m.X



When pH \uparrow , [OH] \uparrow , [M⁺] \downarrow

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

\downarrow

\uparrow

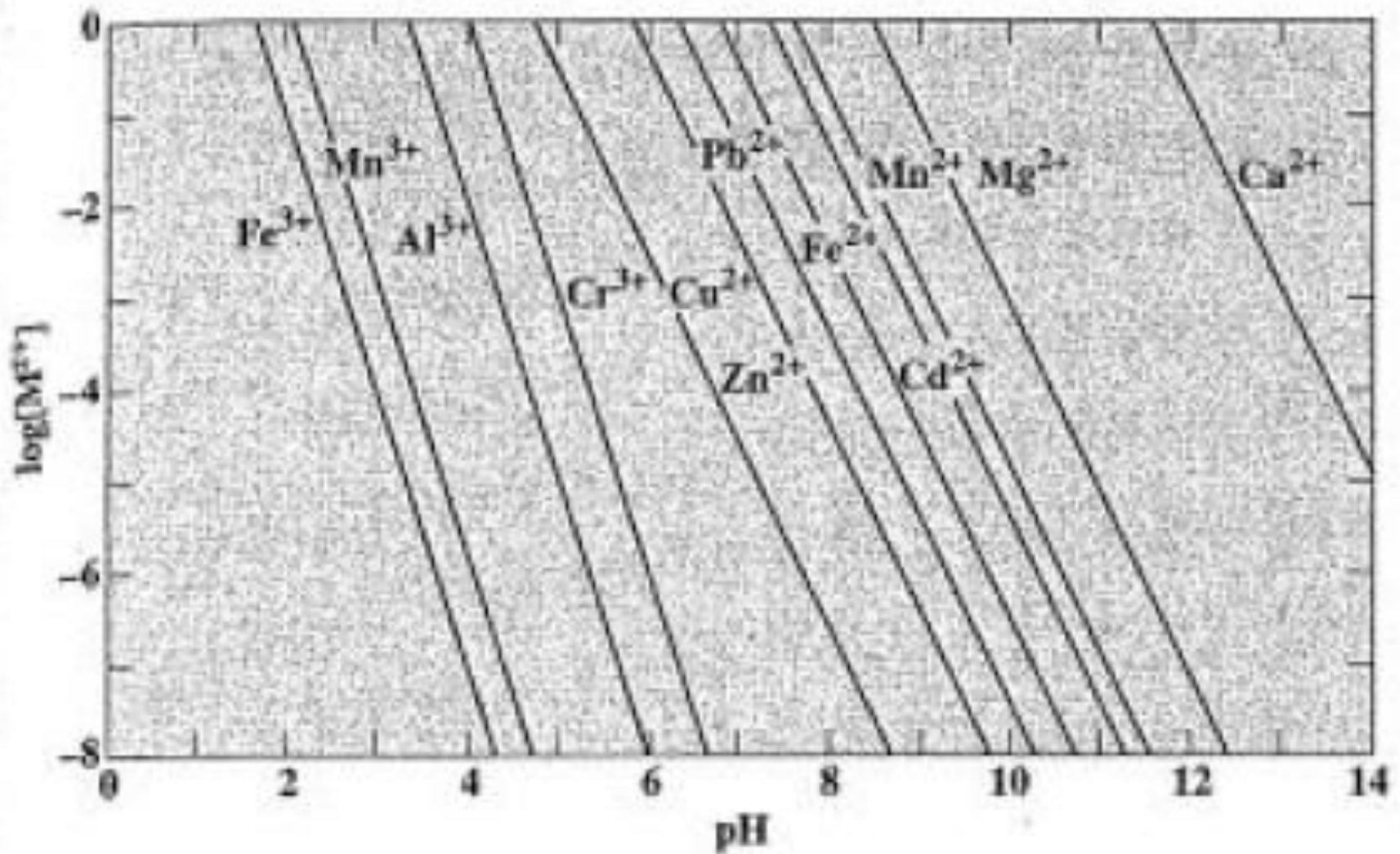


Figure 4.14 Log C diagram showing the solubility of various metallic hydroxides.

- Magnesium hardness can be reduced by raising the pH to 11 or greater and precipitating $\text{Mg}(\text{OH})_2$.
- 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 $\text{Cu}(\text{OH})_2$ precipitate is formed in 1L of wastewater ?

pH =7.8 minimum pH, from Figure 4.14

Cu^{2+} removed

$$10^{-2} \text{ M} - 10^{-6} \text{ M} \approx 10^{-2} \text{ M}$$

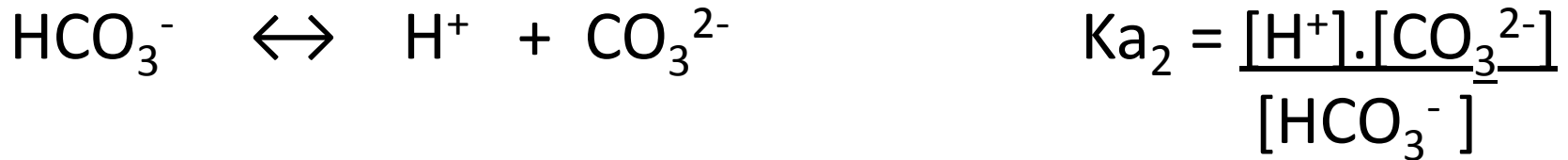
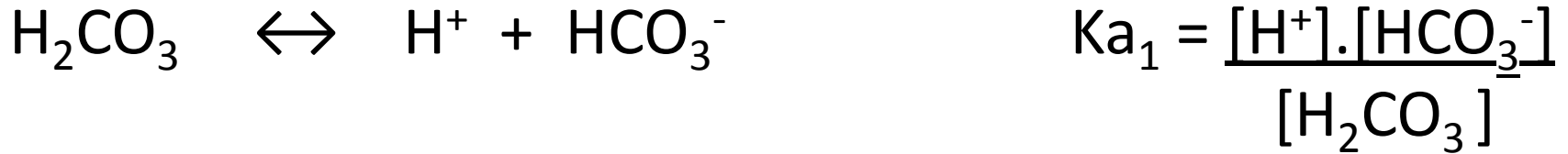
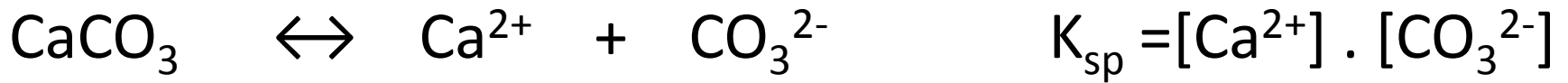
$10^{-2} \text{ mol Cu}^{2+}$ is removed in 1 L of wastewater.

Therefore, $10^{-2} \text{ mol Cu}(\text{OH})_2$ is formed.

$$= 10^{-2} \text{ mol Cu}(\text{OH})_2 \times 97,500 \text{ mg/mol} = \mathbf{97.5 \text{ mg Cu}(\text{OH})_2 \text{ precipitate}}$$

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.



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

$$\text{TOTCO}_3 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\text{CB} = 2.[\text{Ca}^{2+}] + [\text{H}^+] = 2.[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$$

$$\alpha_2 = \frac{[\text{CO}_3^-]}{\text{TOTCO}_3} = \frac{1}{1 + \frac{[\text{H}^+]^2}{K_{a,1} \times K_{a,2}} + \frac{[\text{H}^+]}{K_{a,2}}}$$

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

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

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

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

When CaCO_3 precipitates TOTCO_3 changes.

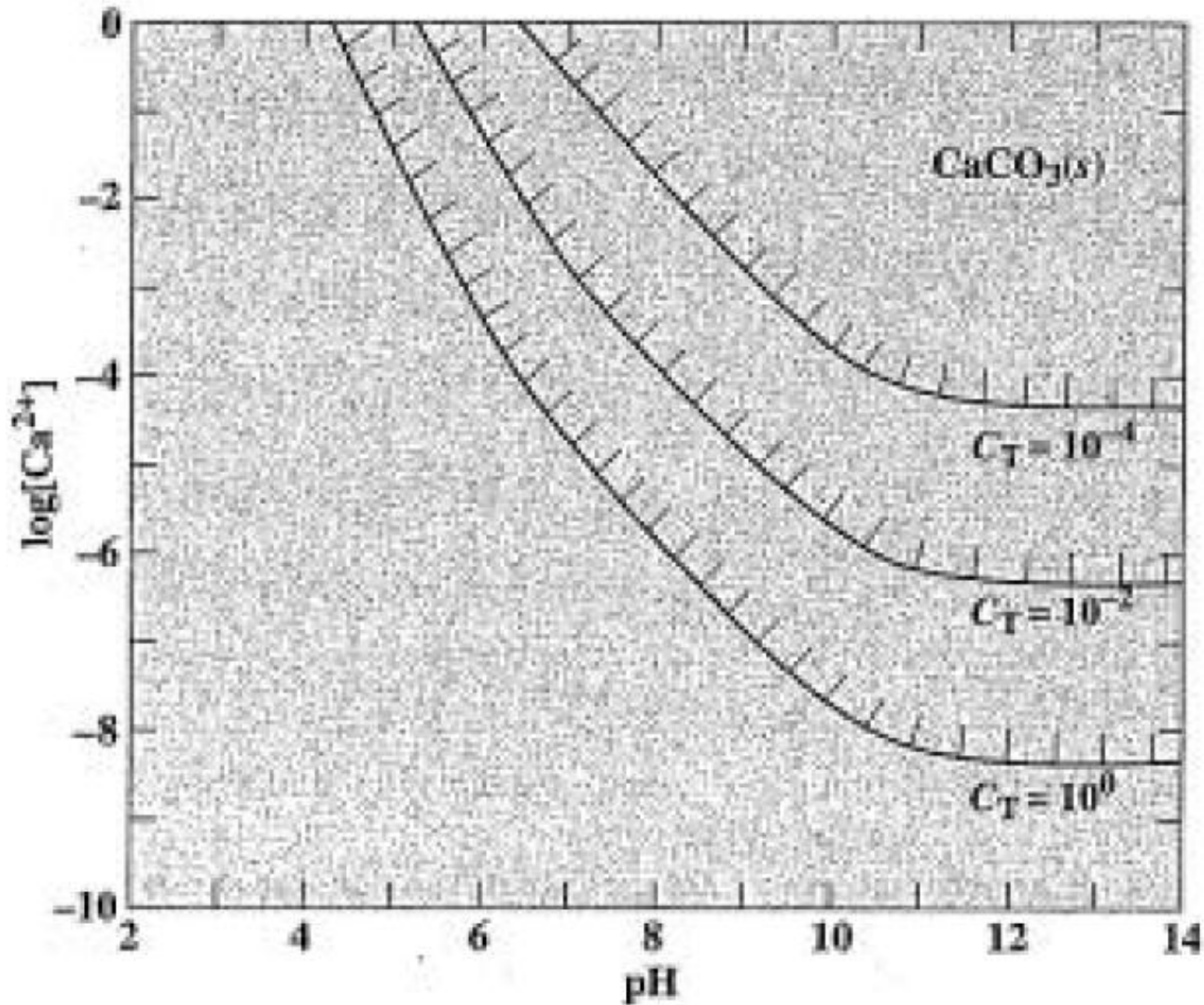


Figure 4.15 Log C diagram showing the solubility of Ca^{2+} ions with respect to TOTCO_3 and pH.

Ex : A water sample contains 10^{-2}M Ca^{2+} M, $C_T = 10^{-4}\text{M}$ and $\text{pH} = 7.5$. 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} M by precipitation of 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.

$10^{-2} \text{ M} - 3.9 \times 10^{-4} \text{ M} = 6.1 \times 10^{-3} \text{ M}$ is the new C_T .

From Figure 4.15 saturation pH is about 9.0

Therefore, pH should be raised to above 9.0