

# **Precipitation of Heavy Metals from Wastewaters**

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## **Typical Heavy Metals Found in Industrial Wastewaters**

Heavy metals (as soluble ions) are common contaminants of industrial wastewaters. Because of their toxicity they are typically removed prior to wastewater discharge. The most common heavy metal contaminants are:

- Arsenic
- Barium
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Nickel
- Selenium
- Silver
- Zinc

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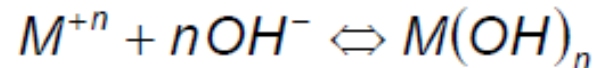
## **Precipitation of Heavy Metals**

- The heavy metal contents of wastewaters can be effectively removed to acceptable levels by precipitating the metal in an insoluble form.
- Heavy metals are typically precipitated from wastewater as:
  - ◇ hydroxides
  - ◇ sulfides or sometime sulfates
  - ◇ carbonates
- Metal co-precipitation during flocculation with iron or aluminum salts is also possible for some metals (e.g., arsenic).

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## Precipitation of Heavy Metals as Hydroxides

- Precipitation by hydroxide formation is the most common heavy metal precipitation method. The precipitation typically follows the reaction:



- Many heavy metals are amphoteric. Therefore their solubility reaches a minimum at a specific pH (different for each metal).

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## **Precipitation of Heavy Metals as Hydroxides (continued)**

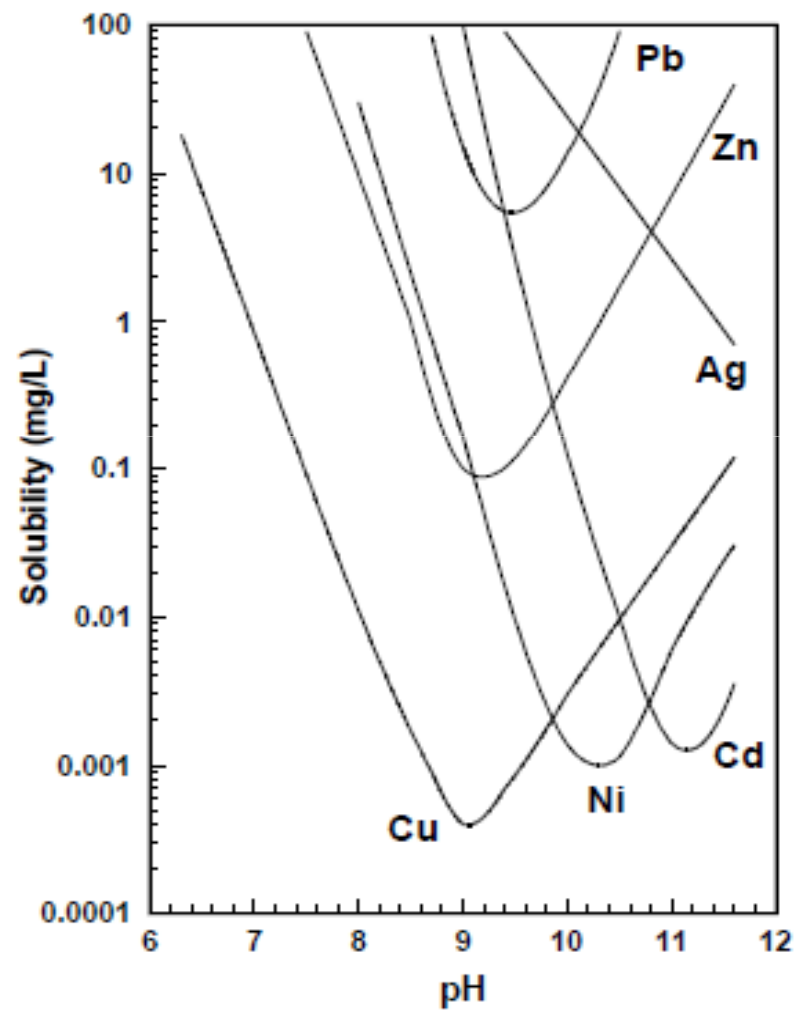
- The addition of caustic materials is used to raise the pH. The most common caustics are:
  - ◊ sodium hydroxide ( $\text{NaOH}$ )
  - ◊ calcium hydroxide ( $\text{Ca(OH)}_2$ ; lime)
- Sodium hydroxide is more expensive than lime.
- Lime has the advantage of also acting as a coagulant during the precipitation/settling process, whereas  $\text{NaOH}$  does not.

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## **Precipitation of Heavy Metals as Hydroxides (continued)**

- Lime must be produced on site (via slaking) from  $\text{CaO}$  (quicklime), and the resulting slurry continuously stirred to prevent cake formation.
- Lime may react with sulfates in the wastewater producing a hard precipitate and resulting in scaling formation.

## Solubility of Metal Hydroxides as a Function of pH



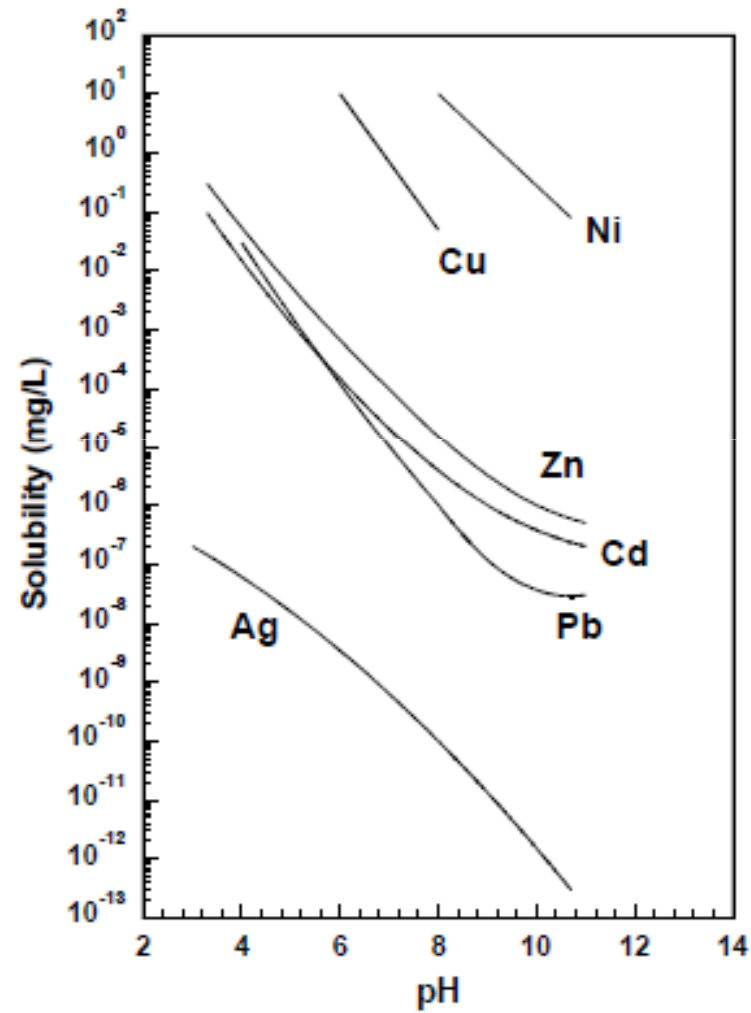
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## **Wastewater Pretreatment Prior to Metal Precipitation**

- If the wastewater contains complexing agents that can keep the metals in solution and prevent them from precipitating the complexing agent must be destroyed prior to metal precipitation as hydroxides.
- This is especially true for the case of cyanide salts because many heavy metals form strong complexes with cyanide.
- Cyanide is typically removed via oxidation with chlorine under alkaline conditions.



## Solubility of Metals Sulfides as a Function of pH



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## Precipitation of Heavy Metals as Sulfides

- Metal sulfides are typically very insoluble. Therefore metals can be precipitated by adding sulfide ions ( $S^{2-}$ ).
- Metal sulfides have much lower solubilities than the corresponding metal hydroxides, thus allowing lower residual metal concentrations in the treated wastewater.

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## Precipitation of Heavy Metals as Sulfides (continued)

- Hydrogen sulfide ( $\text{H}_2\text{S}$ ) is a weak acid and dissociates in two steps according to:



- Sulfide salts undergo hydrolysis, partially reforming the undissociated acid:



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## **Precipitation of Heavy Metals as Sulfides (continued)**

- $S^{2-}$  is not the dominating species until the pH is very high (~14). Hence, by adding a sulfide salt an equilibrium is generated resulting in only the partial formation of the  $S^{2-}$  ions actually used in precipitation.
- Sulfide precipitation is always conducted under alkaline conditions to promote sulfide ion formation.
- Sulfide precipitation is rather insensitive to the presence of chelating agents.

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## **Precipitation of Heavy Metals as Sulfides (continued)**

- Sulfide precipitates tend to form colloidal particles requiring the addition of coagulants to settle. However, sulfide sludges are easier to dewater than hydroxide sludges.
- Sulfide sludges are more prone to oxidation resulting in resolubilization of the metals as sulfates.
- Evolution of  $\text{H}_2\text{S}$  is a potential hazard if the pH is not carefully maintained in the alkaline region.

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## Precipitation of Heavy Metals as Carbonates

- Some metals (lead, cadmium, nickel) form insoluble carbonates that can be used in carbonate precipitation.
- Some wastewaters already contain enough carbonates to allow precipitation to occur. Alternatively, inorganic carbonates (e.g.,  $\text{Na}_2\text{CO}_3$ ) can be added.

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## Precipitation of Heavy Metals as Carbonates (continued)

- Carbonate precipitation takes place only if carbonate ions ( $\text{CO}_3^{-2}$ ) are present. Free carbonate ions are present only if the pH is high. A caustic is often added to raise the pH.
- High pH's also promote the precipitation of the metals as hydroxides. Hence, carbonate precipitation is often a co-precipitation.

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## **Precipitation of Heavy Metals as Carbonates (continued)**

- pH values above 10 promote the formation of metal hydroxy complexes that can increase the metal solubility and reduce the precipitation effectiveness.
- Carbonate precipitates settle and can be dewatered more easily than the corresponding hydroxide precipitates.



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## **Arsenic in Industrial Wastewaters**

Arsenic is present in the wastewaters of a number of industries producing:

- metallurgical products
- glassware and ceramic
- tannery products
- dye stuff
- pesticides
- synthetic chemicals
- petroleum refinery products

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## Precipitation of Arsenic from Industrial Wastewaters

- Arsenic can be removed by precipitation as sulfide, through the addition of sodium sulfide or hydrogen sulfide to the wastewater. The effluent concentration is 0.05 ppm
- Arsenic can also be removed by co-precipitation with  $\text{FeCl}_3$  when a  $\text{Fe}(\text{OH})_3$  floc is formed. The effluent concentration is 0.005 ppm

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## **Barium in Industrial Wastewaters**

**Barium is present in the wastewaters of a number of industries producing:**

- **metallurgical products**
- **glassware and ceramic**
- **dye stuff**
- **explosives**
- **rubber products**

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## **Precipitation of Barium from Industrial Wastewaters**

- Barium can be removed by precipitation as sulfate, by adding any sulfate ion source
- The solubility of barium sulfate is 1.4 ppm
- Even lower residual barium concentrations (0.5 ppm) can be obtained using an excess of sulfate ions

Note: 1 ppm = 1 mg/L

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## **Cadmium in Industrial Wastewaters**

Cadmium is present in the wastewaters of a number of industries producing:

- metallurgical products
- ceramics
- electroplated products
- photographic products
- pigments
- textiles
- synthetic chemicals

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## **Precipitation of Cadmium from Industrial Wastewaters**

- Cadmium can be removed by precipitation as hydroxide at pH ranging from 8 (solubility: 1 ppm) to 11 (solubility: 0.05 ppm)
- Cadmium can be removed by precipitation as sulfide. The effluent concentration is 0.05 ppm
- Cadmium can also be removed by co-precipitation at pH 6.5 with  $\text{FeCl}_3$  when a  $\text{Fe}(\text{OH})_3$  floc is formed. The effluent concentration is 0.008 ppm

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## **Precipitation of Cadmium from Industrial Wastewaters**

- Cadmium can also be removed by precipitation as carbonate. The pH required in this case is between 7.5 and 8.5. The effluent concentration is comparable to that obtained through hydroxide precipitation at high pH
- Cyanides interfere with any of these processes and must be removed prior to cadmium precipitation

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## **Chromium in Industrial Wastewaters**

Chromium is present in the wastewaters of a number of industries producing:

- steel manufacturing
- chrome plated products
- tannery products
- dye stuff
- paints



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## **Precipitation of Chromium from Industrial Wastewaters**

Chromium is typically precipitated in two steps:

- hexavalent chromium ( $\text{Cr}^{+6}$ ) is reduced to trivalent chromium ( $\text{Cr}^{+3}$ ). Compounds such as  $\text{FeSO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_5$  (sodium bisulfite) or  $\text{SO}_2$  (sulfur dioxide) are used as reducing agents. The reaction is conducted at low pH ( $< 3$ )
- trivalent chromium is precipitated as  $\text{Cr}(\text{OH})_3$ . Lime is typically used for the precipitation reaction. The effluent concentration is 0.2 ppm at pH 7.5

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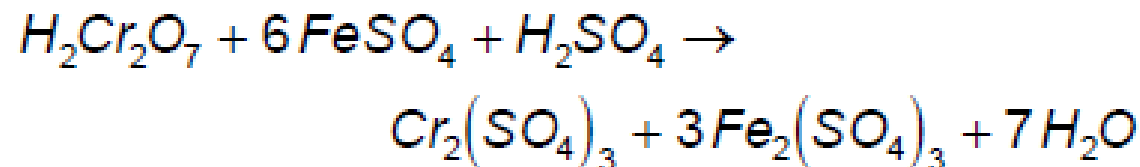
## **Precipitation of Chromium from Industrial Wastewaters**

The reactions involved in chromium precipitation are:

*Reduction reaction (at pH < 3):*



(i.e., 1.85 ppm SO<sub>2</sub>/ppm Cr) or, alternatively:



*Precipitation reaction (at pH of 8 to 9):*



(i.e., 2.13 ppm Ca(OH)<sub>2</sub>/ppm Cr)

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## **Copper in Industrial Wastewaters**

Copper is present in the wastewaters of a number of industries producing:

- Chemicals using copper salts
- Chemicals using copper catalyst
- Metal processing products
- Metal plated products

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## Precipitation of Copper from Industrial Wastewaters

- Copper can be removed by precipitation as hydroxide at pH ranging from 9 to 10.3 (solubility: 0.01 ppm as cupric oxide)
- Copper can be removed by precipitation as sulfide at pH 8.5. The resulting effluent concentration is 0.01 - 0.02 ppm
- The presence of cyanide or ammonia may interfere with copper precipitation. In such a case activated carbon can be used to remove copper cyanide

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## **Lead in Industrial Wastewaters**

Lead is present in the wastewaters of a number of industries producing:

- batteries
- pigments
- printing products

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## **Precipitation of Lead from Industrial Wastewaters**

- Lead can be removed by precipitation as hydroxide (lime) at pH 11.5. The effluent concentration is 0.02 to 0.2 ppm
- Lead can be removed by precipitation as sulfide at pH 7.5 to 8.5
- Lead can also be removed by precipitation as carbonate. The pH required in this case is between 7.5 and 8.5. The effluent concentration is comparable to that obtained through hydroxide precipitation at high pH

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## **Mercury in Industrial Wastewaters**

Mercury is present in the wastewaters of a number of industries producing:

- chlor-alkali
- explosive
- electronic products
- pesticides
- petrochemical products

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## Precipitation of Mercury from Industrial Wastewaters

- Mercury can be removed by precipitation as sulfide, through the addition of sodium sulfide or hydrogen sulfide to the wastewater. The effluent concentration is 0.01 ppm
- Mercury can be removed by co-precipitation with alum. The effluent concentration is 0.001 to 0.01 ppm
- Mercury can be removed by co-precipitation with  $\text{FeCl}_3$  when a  $\text{Fe}(\text{OH})_3$  floc is formed. The effluent concentration is 0.0005 to 0.005 ppm



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## **Nickel in Industrial Wastewaters**

Nickel is present in the wastewaters of a number of industries producing:

- Metal products (e.g., aircrafts)
- Steel
- Chemicals

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## **Precipitation of Nickel from Industrial Wastewaters**

- Nickel can be removed by precipitation as hydroxide at pH ranging from 10 to 11 (solubility: 0.12 ppm)
- Nickel can be also be removed by precipitation as sulfate or carbonate
- The presence of cyanide may interfere with nickel precipitation

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## Metal Complexation

- Many transition metals (e.g., Cd, Co, Cu, Fe, Hg, Ni, Zn) can form complexes with a number of different ligands such as hydroxides, sulfides, chlorides, cyanides, EDTA (ethylenediaminetetraacetic acid).
- Metal complexes (e.g.,  $\text{Na}_2\text{Cd}(\text{CN})_4$ , sodium cadmiocyanide) can increase the solubility of a metal far beyond what the solubility of the metal is (e.g., as hydroxide).

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## **Precipitation of Complexed Metals**

- Precipitation of complexed metals is typically impossible until the metal complex is destroyed or the equilibrium is shifted by adding massive amounts of the precipitant.
- Oxidation is typically the most common method to destroy metal complexes.
- Oxidants such as chlorine, hypochlorite, and ozone are often used for this purpose.
- After the complexing agent is destroyed the metals are precipitated as usual.

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## **Cyanide Removal Via Alkaline Chlorination**

- Cyanides are compounds that need to be removed prior to wastewater discharge.
- Furthermore, cyanides often form metal complexes that must be destroyed before the metals are precipitated.
- Wastewaters containing cyanides (up to 1000 mg/L) are often treated with sodium hypochlorite ( $\text{NaClO}$ ) or chlorine gas mixed with sodium hydroxide (to form sodium hypochlorite) in a two-step process.

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## Cyanide Removal Via Alkaline Chlorination (continued)

- The first step is the conversion of cyanide ( $\text{CN}^-$ ) to cyanate ion ( $\text{OCN}^-$ ) in a two-reaction sequence at a pH above 10 (reaction time: 30 min. to 2 h):



- The second step is the oxidation of cyanate with hypochlorite at pH 8.5 to increase the kinetics (reaction time: 10 min. to 1 h):

