

Removing Heavy Metals from Wastewater



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Introduction

This manual provides general guidelines on how to remove dissolved metals from wastewaters for discharge to sanitary sewer systems. Each of the various stages or operations of wastewater treatment will be discussed with their role in the metals removal process. The treatment train described is general for metals removal. Some variations will exist among different systems. This manual is intended to provide, in layman's terms, a better understanding of the precipitation process as applied to industrial wastewater treatment.

Definitions

The following words or phrases are commonly used when discussing metal removal.

Caustic - Refers to sodium hydroxide (NaOH). When caustic is added to water, the water becomes strongly alkaline (pH >> 7).

Concentration - The quantity of a material in a given volume of solution.

Dilute Solution - A weak solution; a relatively small quantity of a material in a large volume of solution (*i.e.*, water).

Heavy Metals - Metals, when in significant concentrations in water, that may pose detrimental health effects. Heavy metals include lead, silver, mercury, copper, nickel, chromium, zinc, cadmium and tin that must be removed to certain levels to meet discharge requirements.

Metal Hydroxides - When caustic is added to water containing heavy metals, a metal hydroxide solid or precipitate is formed.

mg/L - Milligrams per liter, a representation of the quantity of material present in a solution. Same value as ppm.

pH - A term used to describe the acid-base characteristics of water, typically measured by a pH meter. Specifically, the concentration of H⁺ ions in water. Formally, pH is the negative logarithm of the H⁺ concentration, *i.e.*, $\text{pH} = -\log [\text{H}^+]$. The following values indicate the classification of a water:

pH < 7 refers to acid solutions

pH > 7 refers to basic solutions

pH = 7 refers to neutral solutions

The following table details the H⁺ concentration in water, its relationship with the OH⁻ (hydroxide ion) concentration, and the resulting pH.

Table 1. Relation Between Ion Concentration and pH Value.

pH	Hydrogen Ion Concentration (moles/L)	Hydroxide Ion Concentration (moles/L)
	[H ⁺]	[OH ⁻]
0	1	1 X 10 ⁻¹⁴
1	0.1	1 X 10 ⁻¹³
2	0.01	1 X 10 ⁻¹²
3	0.001	1 X 10 ⁻¹¹
4	0.0001	1 X 10 ⁻¹⁰
5	0.00001	1 X 10 ⁻⁹
6	1 X 10 ⁻⁶	1 X 10 ⁻⁸
7	1 X 10 ⁻⁷	1 X 10 ⁻⁷
8	1 X 10 ⁻⁸	1 X 10 ⁻⁶
9	1 X 10 ⁻⁹	0.00001
10	1 X 10 ⁻¹⁰	0.0001
11	1 X 10 ⁻¹¹	0.001
12	1 X 10 ⁻¹²	0.01
13	1 X 10 ⁻¹³	0.1
14	1 X 10 ⁻¹⁴	1

Precipitation - 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 from the water.

Precipitation Region - The region on a solubility diagram that indicates the appropriate concentration and pH value for a metal to form a solid precipitate.

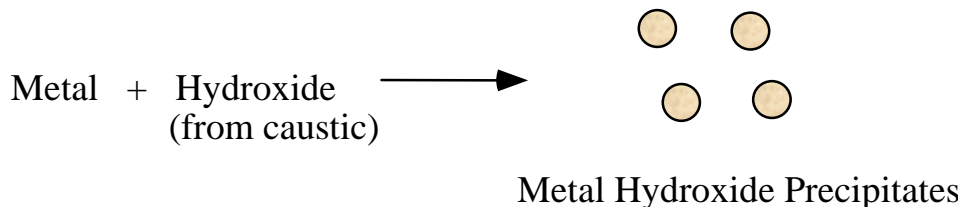
Solubility - Solubility defines a material's ability to go into solution (dissolve). Materials that are soluble readily dissolve in solution and do not precipitate. Substances that are insoluble do not easily dissolve in solution and stay in their solid form. The goal of metals removal in wastewater is to produce conditions so that metals are insoluble.

Solubility Diagram - A graph that reveals the solubility of metals (through the formation of metal hydroxides) at specific pH values.

Metal Treatment by Hydroxide Precipitation

As metals enter the treatment process, they are in a stable, dissolved aqueous form and are unable to form solids. The goal of metals treatment by hydroxide precipitation is then to adjust the pH (hydroxide ion concentration) of the water so that the metals will form insoluble precipitates. Once the metals precipitate and form solids, they can then easily be removed, and the water, now with low metal concentrations, can be discharged.

Metal precipitation is primarily dependent upon two factors: the concentration of the metal, and the pH of the water. Heavy 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. However, when one adds caustic to water which contains dissolved metals, the metals react with hydroxide ions to form metal hydroxide solids:



Note from Table 1 that high pH corresponds to high hydroxide concentrations. Visual representations of the pH values that promote metal precipitation are displayed in the next seven figures. Each figure represents the solubility of an individual metal at various pH values.

All of the figures illustrate how the solubility of a particular metal is directly controlled by pH. The y-axis displays the concentration of dissolved metal in the wastewater, in milligrams/liter (mg/L). Notice the wide variation in scale. The upper part of the scale shows a dissolved concentration of 100 mg/L. The lowest number on the scale is 0.001 mg/L. These solubility graphs display regions where the metals are soluble or insoluble. The region above the dark lines (the shaded areas) for each metal signifies that the metals should precipitate as metal hydroxides. This is referred to as the precipitation region. The region below or outside of the dark lines illustrates where the metals are dissolved in solution, no precipitation occurs, and no metal removal takes place.

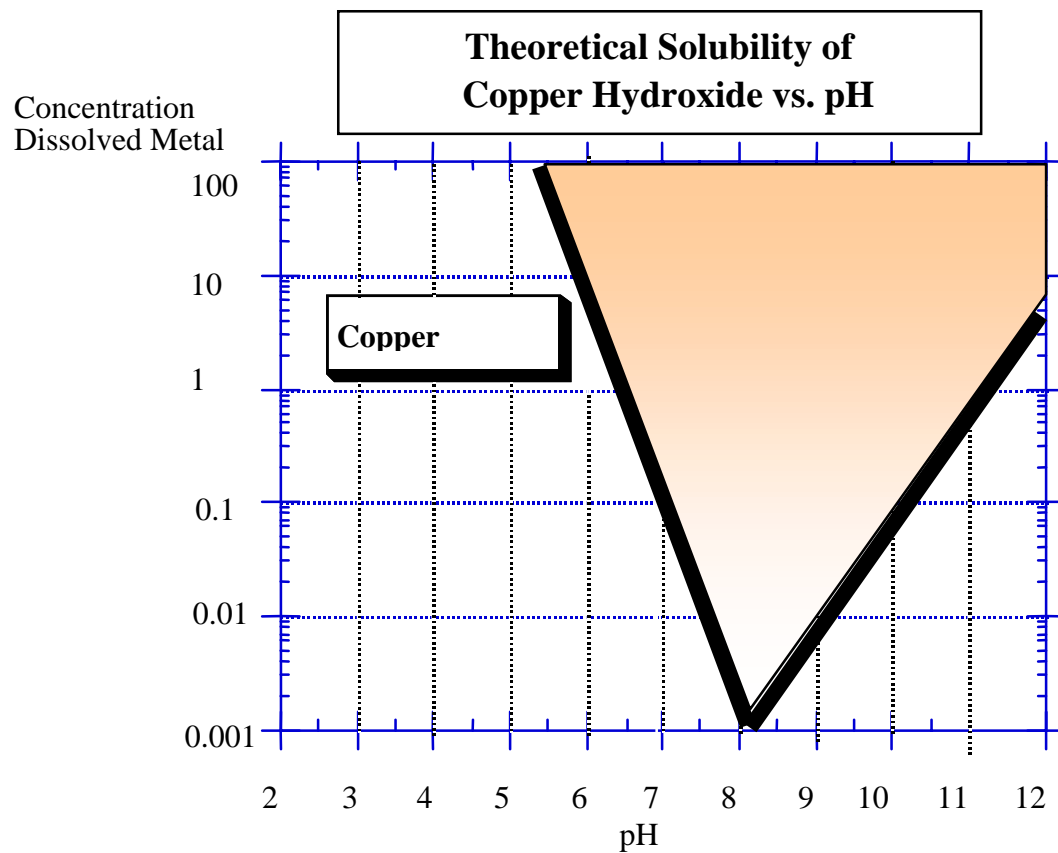


Figure 1 - Theoretical Solubility of Copper Hydroxide.¹

¹ Plating Waste Treatment, Cherry, K., Ann Arbor Science, 1982, p. 46.

With the exception of silver, notice that all of the metals display a minimum concentration at a particular pH. For example, in Figure 1, the lowest possible dissolved concentration of copper is approximately 0.001 mg/L, which occurs at a pH value of 8.1.

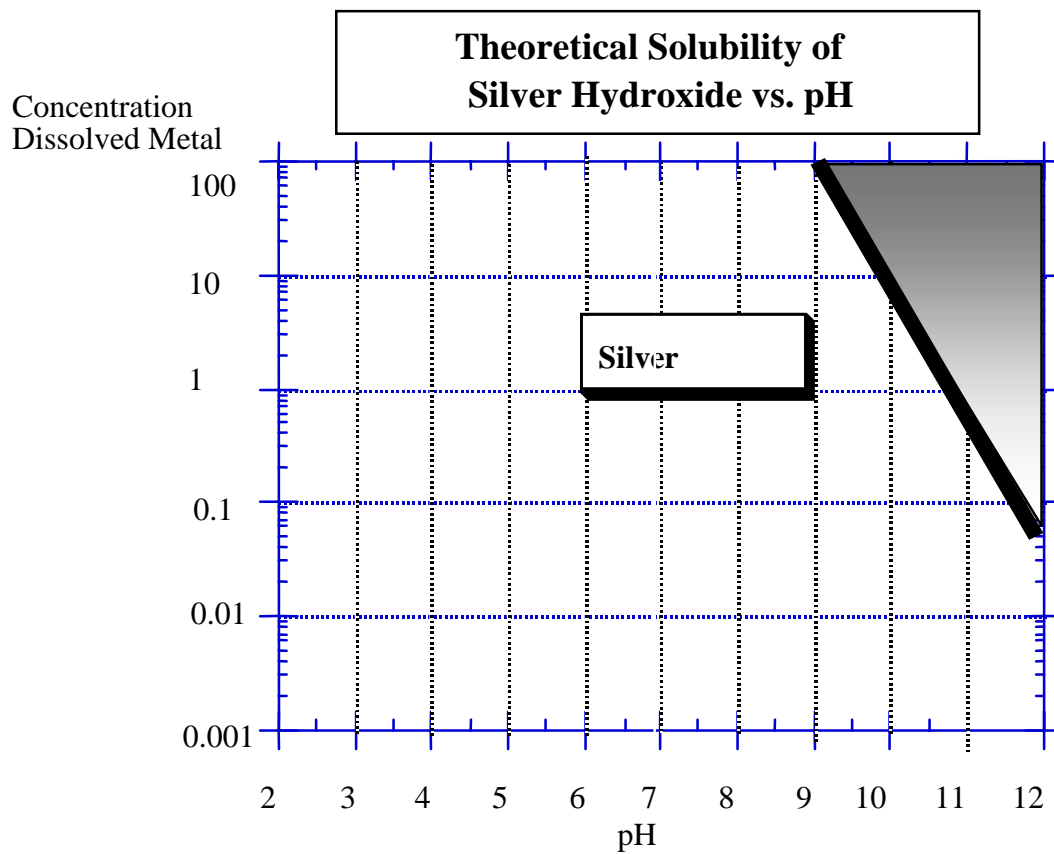


Figure 2 - Theoretical Solubility of Silver Hydroxide.

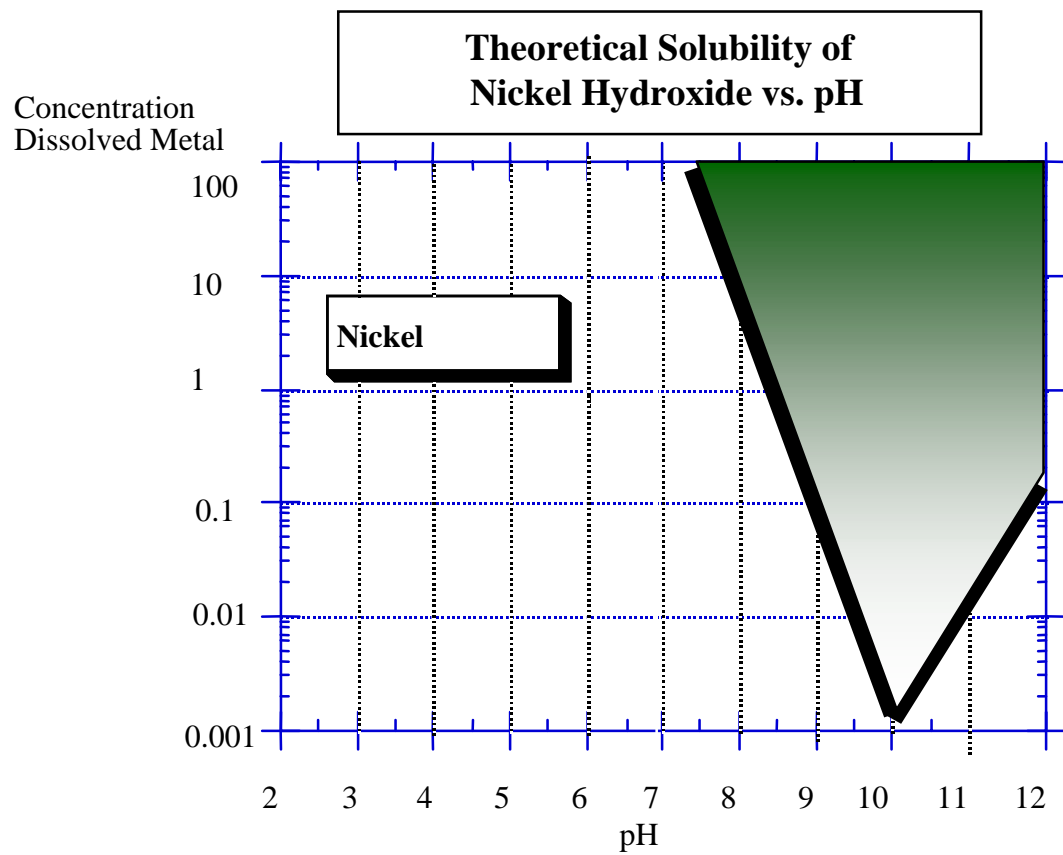


Figure 3 - Theoretical Solubility of Nickel Hydroxide.

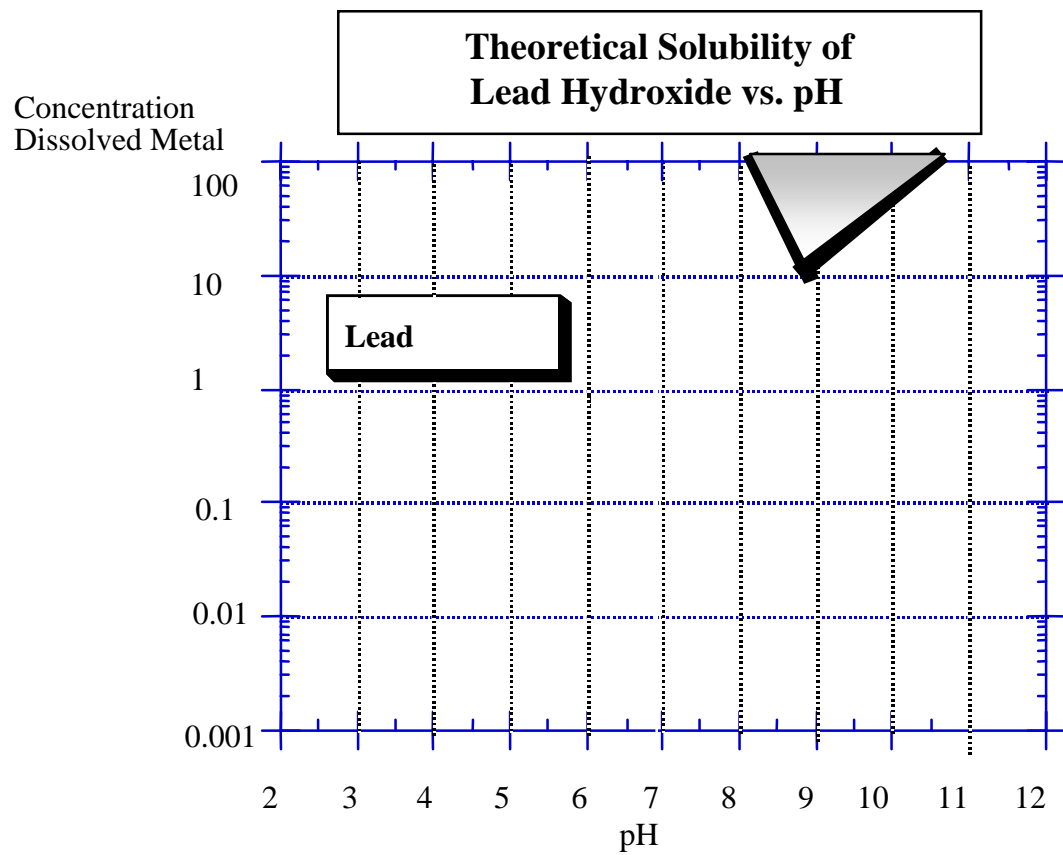


Figure 4 - Theoretical Solubility of Lead Hydroxide.

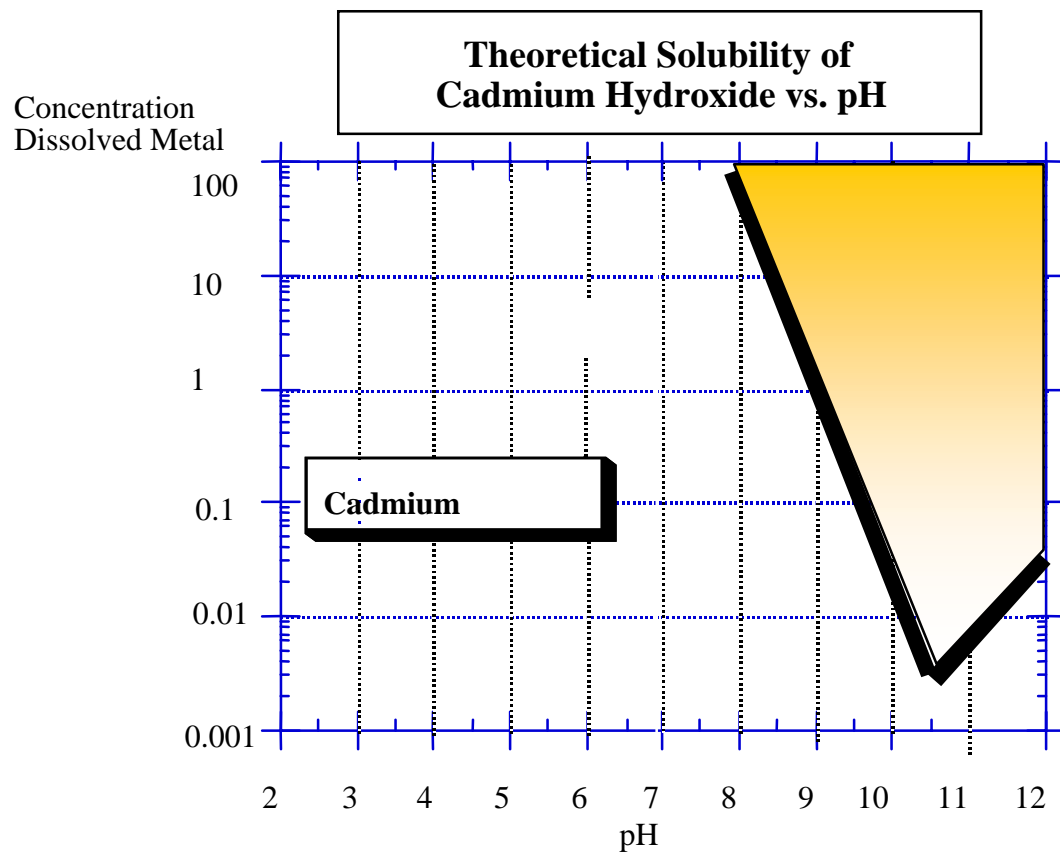


Figure 5 - Theoretical Solubility of Cadmium Hydroxide.

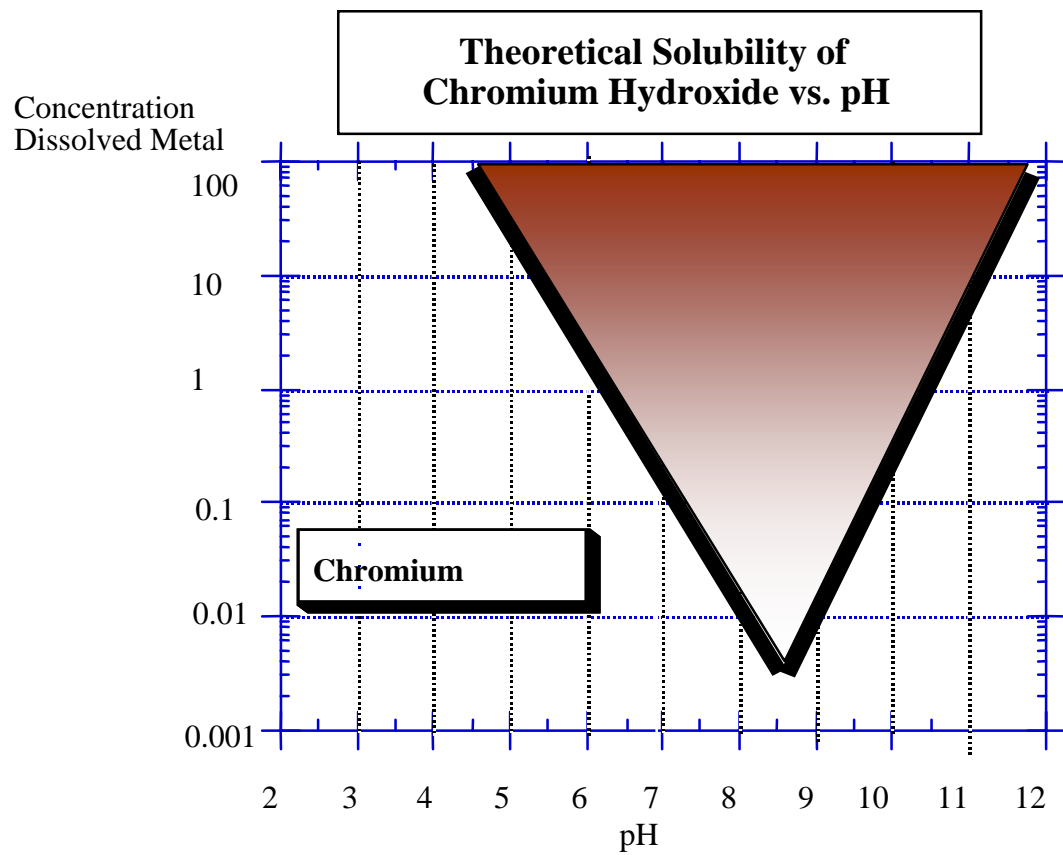


Figure 6 - Theoretical Solubility of Chromium Hydroxide.

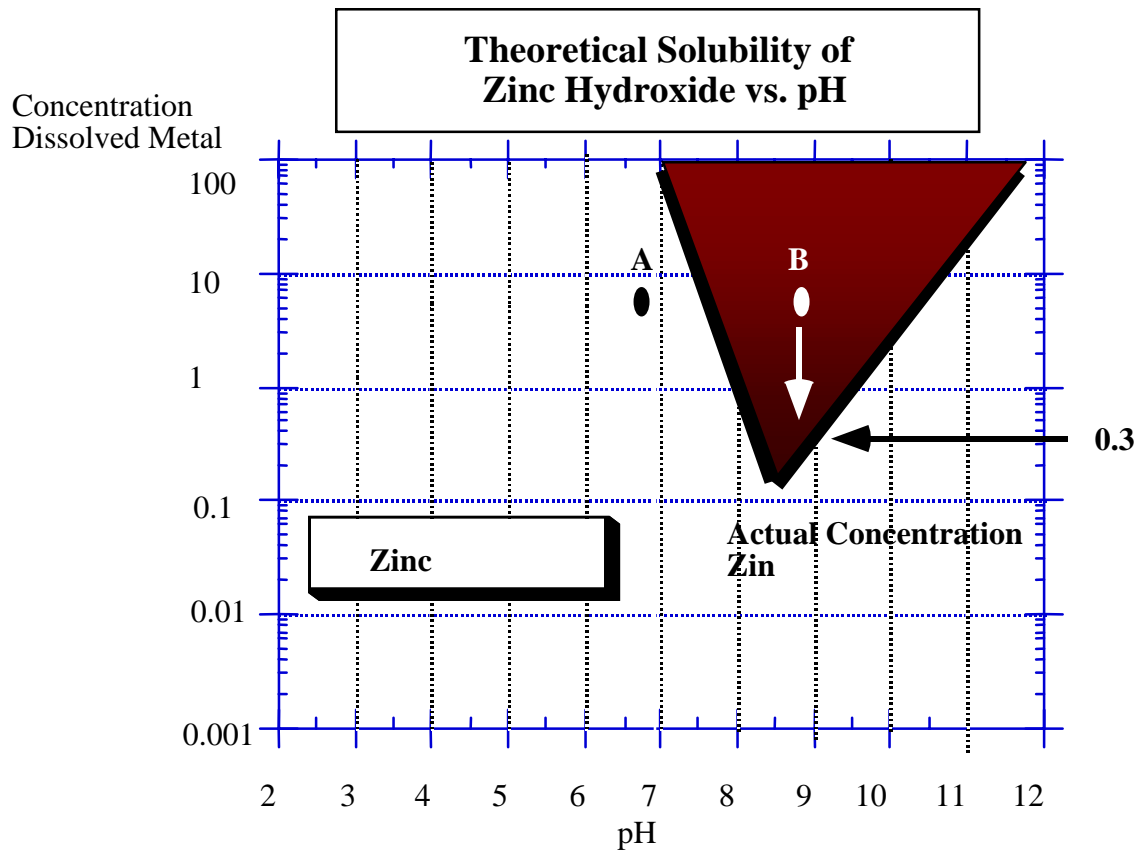


Figure 7 - Theoretical Solubility of Zinc Hydroxide.

Figure 7 can be used to determine how the concentration of zinc in water is affected by pH. Suppose a wastewater contains dissolved zinc at 4 mg/L and is at pH = 6.8. This is shown at point **A** in the diagram. Since this point is below the bold lines in the solubility graph, this indicates that zinc is only present as a dissolved metal. It is not in a solid form and under these conditions it will not precipitate.

Since this is contrary to what we hope to achieve in zinc removal, we need to adjust the pH of the water by adding caustic. Point **B** reveals this pH adjustment from pH 6.8 to 8.6 (*i.e.*, a horizontal line). Above the dark solubility lines, zinc forms zinc hydroxide solids, as is shown by the shaded area. At this new pH value, for example, most of the zinc forms zinc hydroxide and precipitates out of solution. The dissolved zinc concentration is obtained from the solubility line at this pH (*i.e.*, 0.3 mg/L). This is the theoretical amount of zinc that would be in the discharged wastewater after this treatment. The difference of 3.7 mg/L has formed a solid - the metal hydroxide, which is the sludge.

Thus, simply adjusting the pH from 6.8 to 8.6 has effectively precipitated most of the dissolved metal from the water. Since all metals display similar effects, it is clear that the adjustment of pH is critical when the metal is to be removed from the wastewater.

However, the metals now exist in another phase or state (*i.e.*, as small solid particles). Metal removal is not complete until these metal solids are physically removed from the wastewater, typically by subsequent sedimentation and filtration processes, as explained in the next section.

The metal solubilities presented in the previous figures are based on an ideal wastewater. Some variations in the exact values of the metal concentrations will occur due to the presence of other substances in the wastewater. Compounds such as cyanide or ammonia can inhibit precipitation of metals, and limit their removal to the point where discharge limits can be exceeded. Also, note that not all metals have the same minimum solubility. Therefore in a wastewater where multiple metals are present, as a general rule, pH should be adjusted to an average value, approximately 9.

Unit Operations of Wastewater Treatment

Metal removal occurs through the use of several unit operations, as displayed in Figure 8. Figure 8 also shows the points in the treatment process where the pH must be adjusted to insure adequate metals and metals solids removal.

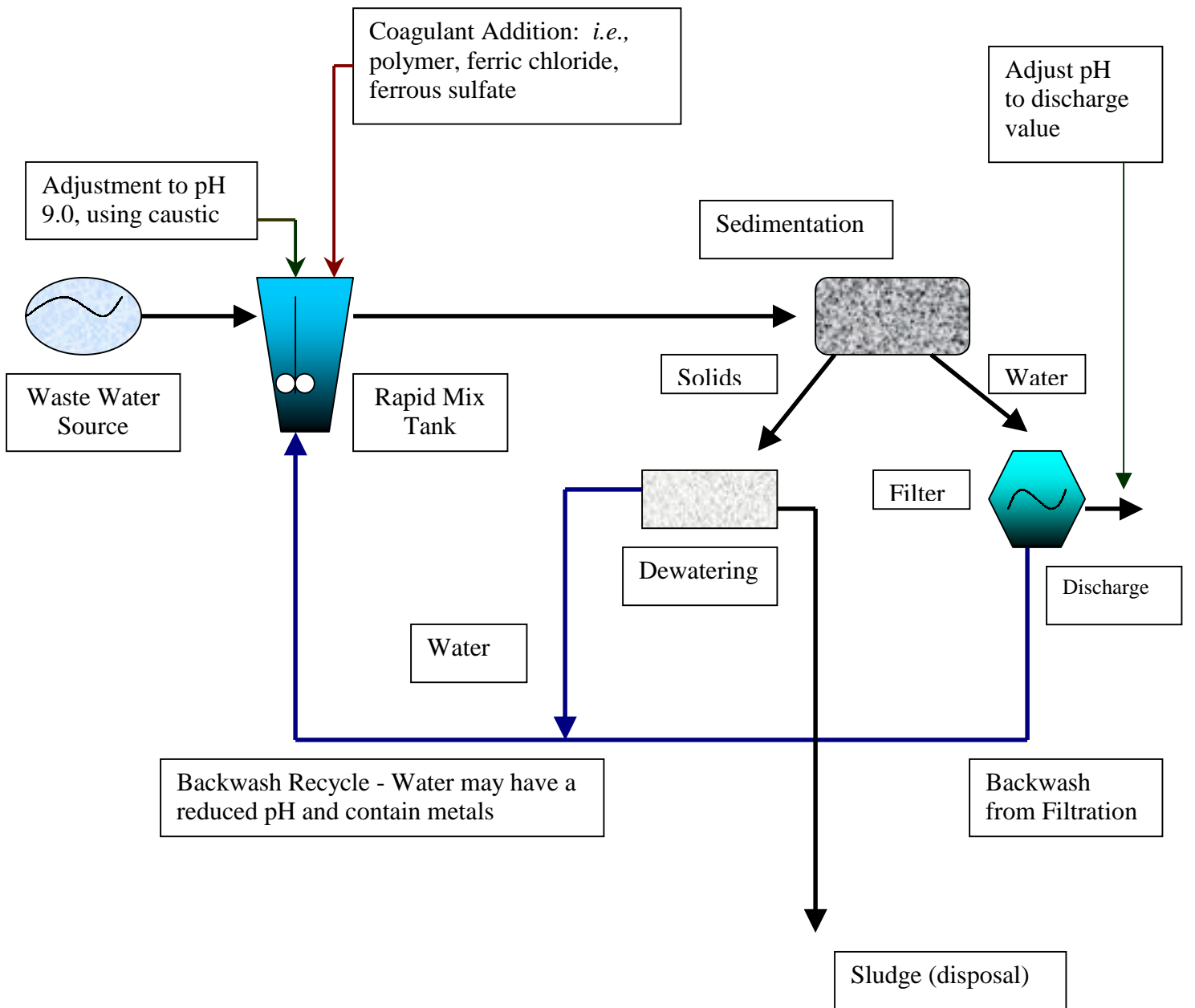


Figure 8 - The Processes of a Conventional Metals Precipitation Treatment Plant

1. Rapid Mix

The goal of the rapid mix operation is to first raise the wastewater pH to form metal hydroxide particles, as discussed above. After the addition of caustic, the next step is to add aluminum or iron salts, or organic polymers (coagulants) directly to the wastewater. These polymers attach to the metal solids particles. The small metal hydroxide particles become entangled in these polymers, causing the particle size to increase (form flocs), which promotes settling. This effect is illustrated in Figure 9.

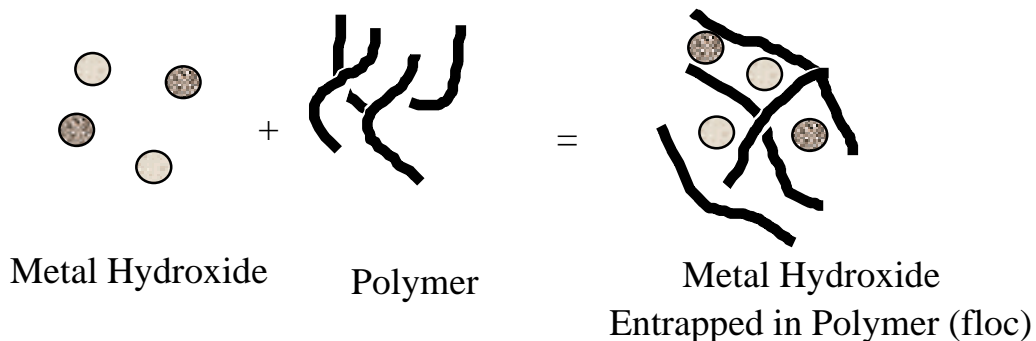


Figure 9 - Aggregation of Metal Hydroxides.

2. Sedimentation

Once particles become enmeshed in the polymer, they are allowed to settle so that they are removed from the wastewater. The particles settle since they are heavier than water. This settling occurs in the sedimentation tanks. Sedimentation tanks, in contrast to rapid mixing units, are designed to have no mixing, to produce a calm flow for settling. Figure 10 depicts a sedimentation basin with metal hydroxide particles settling.

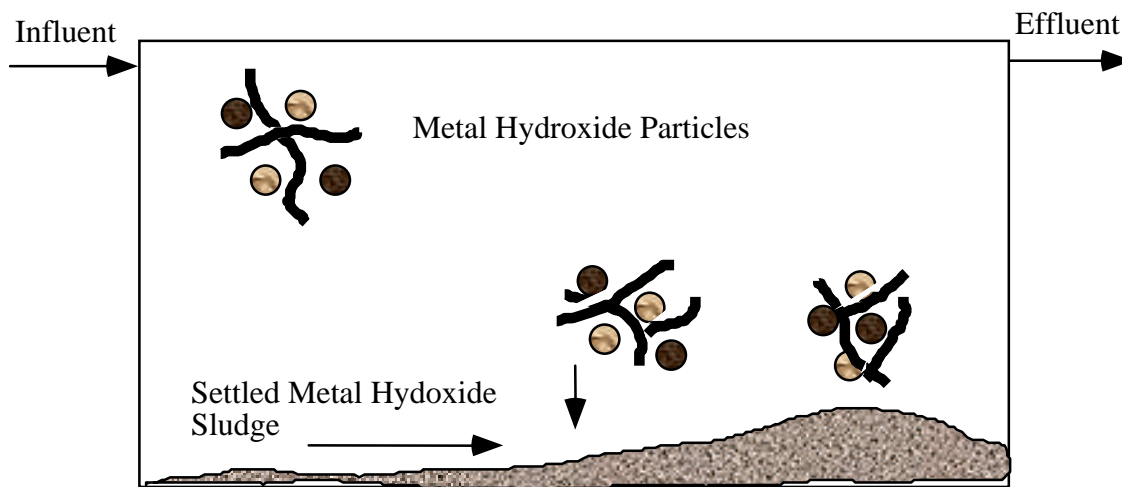


Figure 10 - A Sedimentation Basin with Metal Hydroxide Sludge Formation. Optimized sedimentation basins have minimal baffling. As a result, there is no turbulence as the water flows through the unit.

The pH during sedimentation must be maintained at approximately 9.0 to ensure that none of the metal hydroxides redissolve and become soluble in the water. A detention time of 1.5 to 3 hours is usually adequate to accomplish efficient settling.

3. Filtration

Water emerging from the sedimentation basin is routed to the filtration unit.

The filtration unit is designed to trap those particles that did not settle in the sedimentation basin (because they were too small) or did not have sufficient time to settle and were carried out of the basin.

Water entering the filtration unit is passed through silica sand, diatomaceous earth, carbon, or cloth to capture the remaining metal hydroxide particles. Metal particles stick to the filtering material and are removed from the water. Filtration completes the metal treatment process. Only now should the pH be reduced for discharge, if necessary, or pH can now be adjusted for water reuse. Figure 11 depicts a typical filtration unit.

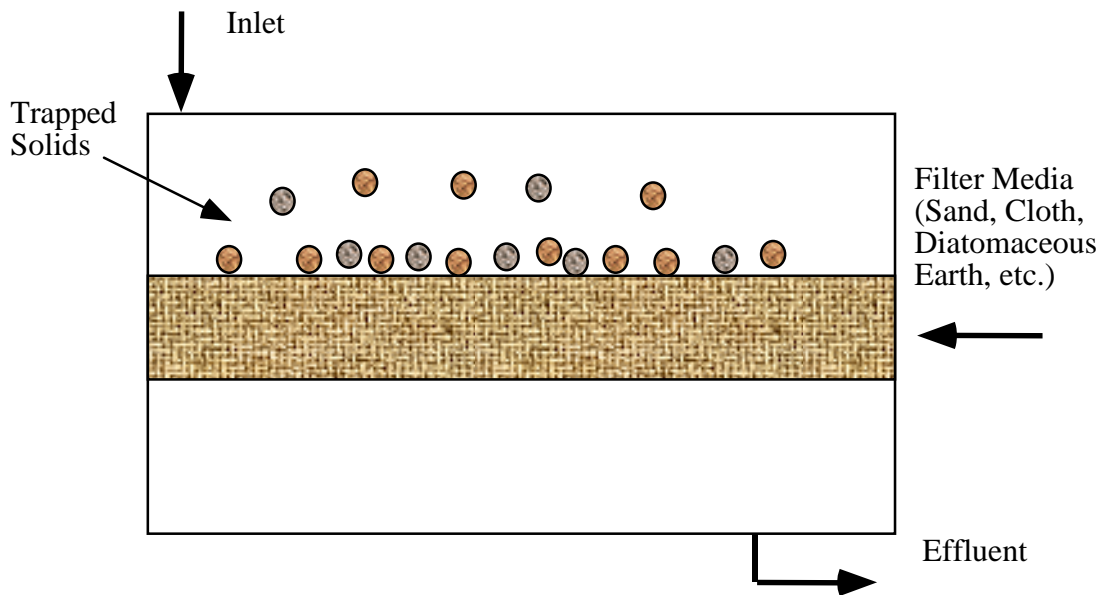


Figure 11 - Filtration Unit for Metals Removal.

As filtration progresses and more metal hydroxides and other solids clog the filter material, pressure drop through the filter rises and some solids may pass through the filter. When either of these two situations occurs, the filter must be backwashed by reversing the flow of water through the filter. This backwash water is sent back to the rapid mix tank for mixing with the incoming water since it contains a significant concentration of solids from the dislodging that has occurred. Furthermore, the pH of this water (since it will be diluted with incoming water) may drop significantly and pose the problem of redissolving all of the metal hydroxides solids.

4. Sludge Treatment

The solids produced in the sedimentation stage (and possibly solids from filtration) are denoted as a sludge and periodically removed. In diatomaceous earth and fiber filters, the entire filter media (diatomaceous earth, filter cartridge) is dumped with the captured metal hydroxide solids. This sludge may be sent to a dewatering stage to remove excess water and leave only solids. The water from the dewatering stage may not be completely free of metals and should be piped to the rapid mix tank.

The sludge now contains the precipitated metal hydroxide solids, made up of identifiable quantities of heavy metals, which are regulated according to state and federal guidelines. The solids produced from heavy metal wastewater treatment must then be disposed of as a hazardous waste.

Additional Considerations for Plating Type Wastes:

1. Plating Waste Treatment - Cyanide Oxidation

Cyanides are widely used in the electroplating industry. The cyanide wastewater flow is treated by an alkaline chlorination process for oxidation of cyanides to carbon dioxide and nitrogen. This treatment is prior to metals removal. Industries not using cyanide will not have this treatment stage.

Cyanide treatment consists of two reaction tanks. In the first tank, conditions are adjusted to oxidize cyanides to cyanates by the introduction of chlorine and caustic to maintain a pH range of 9.5 to 10.0. Chlorine is typically added as chlorine gas or sodium hypochlorite. In the second reaction tank, conditions are maintained to oxidize cyanate to carbon dioxide and nitrogen. Additional chlorine is added and adequate caustic is mixed in to maintain a pH of 8.0. An additional tank may be added for holding and treatment to meet discharge limitations. Detention times of 45 minutes for each reaction tank is sufficient. A diagram of the cyanide oxidation process is shown in Figure 12.

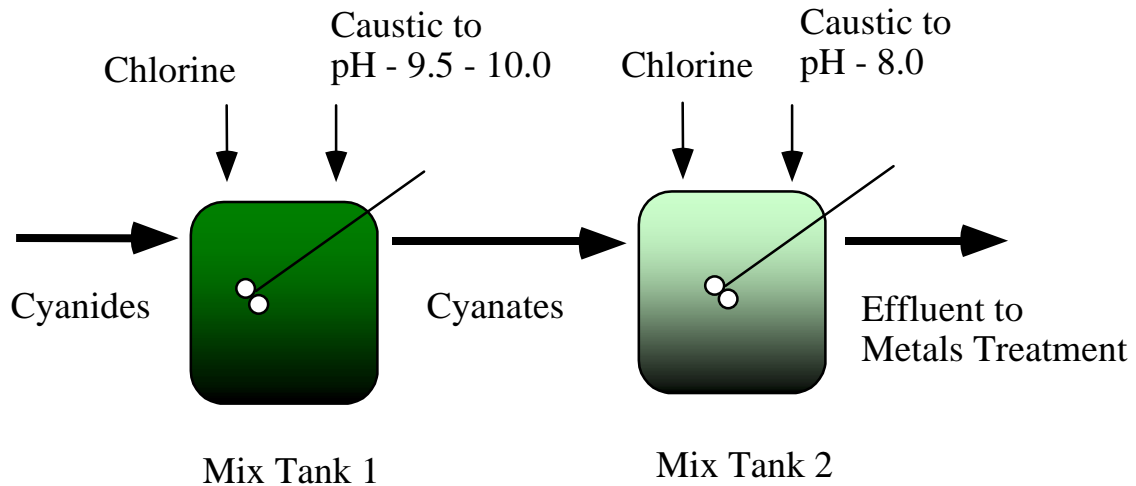


Figure 12 - Cyanide Oxidation.

2. Plating Waste Treatment - Chromium Reduction

Chromium is a common surface coating and its discharge into water poses a serious environmental hazard. Water containing hexavalent chromium is treated with a chemical reduction process. Sulfur dioxide, sodium bisulfite or ferrous sulfate is added to the wastewater and the pH is lowered to 3.0 or less using acid (typically sulfuric acid). A retention time of 45 minutes is usually maintained to ensure adequate mixing and reaction with the sulfur dioxide or other chemicals.

This process converts chromium from the hexavalent form to the trivalent form. The trivalent form can be treated similar to other metals (Figure 6) and the effluent from this process is treated with the other metals wastewater. Figure 13 illustrates the chromium reduction process.

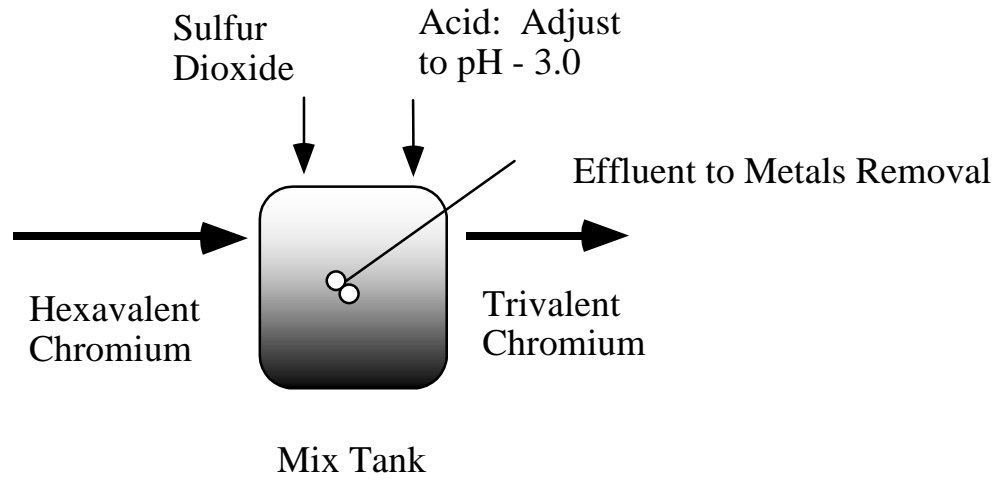


Figure 13 - Chromium Reduction.