Wilson Environmental
ENGINEERED WATER & WASTEWATER SYSTEMS

Removing Heavy Metals From Wastewater by Hydroxide Precipitation

Introduction:

The intent of this paper is to provide general information to assist in understanding chemical treatment systems commonly used to remove heavy metals from wastewater by hydroxide precipitation.

Heavy metals include; cadmium, chromium, copper, lead, mercury, nickel, silver and Zinc.

Definitions

Caustic: Caustic is another name for sodium hydroxide (NaOH). When added to water caustic will raise the pH making the water alkaline (pH >7). Increasing the amount of Hydroxide in the wastewater.

Chelating Agents: Chelating agents are compounds that are commonly used in cleaners, especially Alkaline cleaners. Common chelates are Ethylenediaminetetraacetic Acid (EDTA), Nitriliacetic Acid (NTA), Hydroxyethlenediaminetriacetic (HEDTA), Diethylenetri Aminentaacetic (DTPA) citric and oxoic acids. Chelating agents form metal complexes with heavy metals, making removal by hydroxide precipitation difficult.

Equalization Tanks: Equalization tanks are required for most wastewater treatment systems to provide a consistent flow rate and consistent characteristics. Equalization tanks are used to collect wastewater over a period of time that is sufficient to “equalize” the flow so that the wastewater system receives a wastewater stream that is as consistent as possible.

As a rule of thumb. If the total flow occurs in less than 10 hours a day or if the characteristics of the wastewater varies from day to day an equalization tank is required. The actual size will of course be based on a case by case basis.

Heavy Metals: The Heavy metals are elements with high atomic weights, eg: cadmium, chromium, copper, lead, mercury, nickel, silver and Zinc. Heavy

metals can damage living organisms at low concentrations and tend to accumulate in the food chain.

Industrial wastewater: Industrial wastewater may be composed of various chemicals, toxins, heavy metals, pharmaceuticals, petroleum based oils and greases. By weight industrial wastewater varies considerably and may have as much as 5 % solids.

Industrial Wastewater Permits: All industrial discharges to a public sewer system are subject to general and specific prohibitions identified in the Code of Federal Regulations identified in 40 (CFR) 403.6 which prohibits the discharge of any pollutant that may impair worker or public health and safety, or that might upset or pass through the wastewater treatment plant untreated. Always check with your local sewage treatment authority for permit requirements.

Ions: An atom or group of atoms with an electric charge. The charge is generated by the atom gaining or losing an electron, usually through bonding. Forming either a **Cation** or an **Anion**.

> **Cation:** An atom loses electrons and has a positive charge, example: Ca2+.
>
> **Anion:** An atom gains electrons and has a negative charge. example: Cl-.

Metal Ions: Metals usually form cations, having a + charge, while non-metals usually form anions, - charge..

Metal Hydroxide: Metal hydroxides are formed when a hydroxide ion (OH-) bonds to the metal ion forming an insoluble metal precipitate. This occurs when caustic or lime is added to water containing heavy metals to form the metal hydroxide solid or precipitate.

pH: pH is a measure of how acidic or basic a solution is. In technical terms pH is a measure of the concentration of Hydrogen Ions or of Hydroxide Ions. The pH scale runs from 0 to 14. From 0 pH to 7 pH is acidic, having more Hydrogen Ions, and from 7 pH to 14 pH is basic, having more Hydroxide Ions, also called alkaline. A pH of 7 is neutral, having an equal number of Hydrogen Ions and Hydroxide Ions.

Polymers: Very long chain molecules that act like nets in the wastewater to entangle and trap particulate matter to create flocs. As the particulate matter is trapped, the trapped material begins to increase in size and form flocs. The flocs will tend to settle and can be easily separated.

Precipitate: An insoluble solid.

Solubility: Is a materials ability to dissolve into solution. Materials are generally classified as either soluble or insoluble.

> **Soluble:** Material readily dissolves and is not in a solid form.
>
> **Insoluble:** Materials that do not easily dissolve and tend to stay in solid form.

Solubility Curves: A graph that shows the solubility of a metal at varying pH values. Also known as speciation curves, because the graph shows where the metal ion is converted to a metal hydroxide.

Basic Chemistry

The chemistry of metals removal is to covert the dissolved metal ions to an insoluble metal hydroxide that will precipitate and be removed form the wastewater allowing the treated wastewater to be discharged to the local sanitary sewer.

Precipitation of heavy metals in wastewater is dependent on two factors. The concentration of the metal ion and on the pH of the wastewater. Heavy metals in wastewater are usually in trace amounts (1 mg/l to 100 mg/l) and are usually present in neutral to acidic pH values. The lower the concentration of the metal ion the more difficult it is to remove.

When caustic or lime is added to wastewater that contains dissolved metals the metal ion reacts with the Hydroxide Ion to form an insoluble Metal Hydroxide.

Metal + Hydroxide (caustic or Lime) = Metal Hydroxide Precipitate

The solubility curve below shows the relationship between various metal ions and pH. The Y axis shows the concentration of the metal in the wastewater and the X axis shows the pH.

For Example: To remove copper (Cu) from wastewater the line on the graph shows a drop in Cu concentration as the pH is raised. A pH of about 8.2 (low point of the Cu line) as shown on the graph is optimal for removing Cu. Higher pH values higher than 8.2 are not advantageous.

For Zinc (Zn) note that a pH of 9.8 to 10.2 is the low point and is therefor the desired pH value to remove zinc.

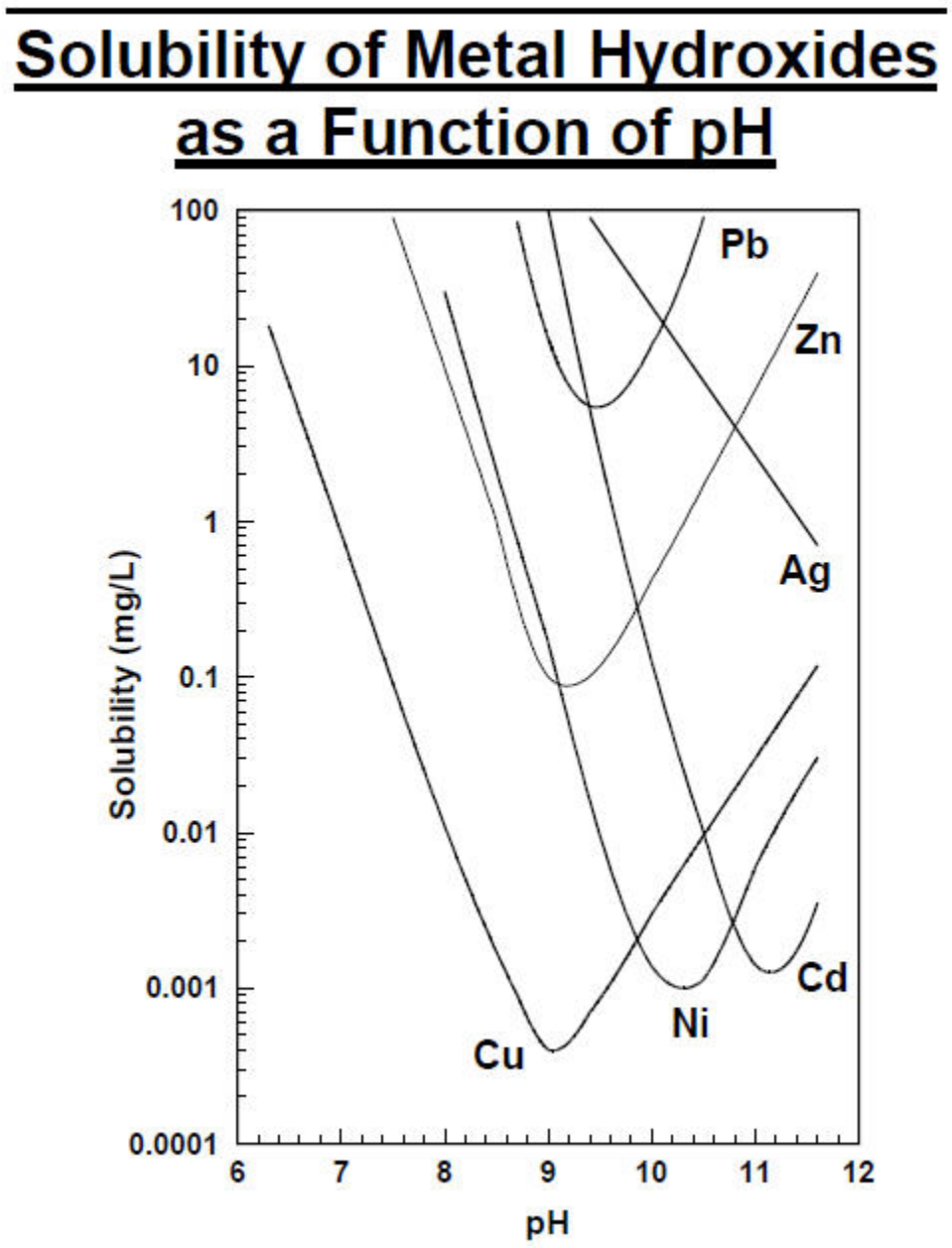

Figure 1 Solubility Curves

Multiple Metals in Wastewater:

When more that one metal is present the pH value is generally adjusted to the average pH value. If three or more metals are present a step approach may be needed. We recommend a pH value of 9.5 for multiply metals. This should be confirmed by jar testing.

Jar Testing:

Because of the potential presence of multiple metal in the wastewater and the potential for chelating compounds in the wastewater and other chemicals that may interfere with forming the metal hydroxide, it is strongly recommended that the hydroxide precipitation reaction always be characterized through laboratory treatability tests before proceeding to plant scale.

In addition to free radical scavengers, the process is inhibited by (iron) chelates, phosphates, EDTA, and citric/oxalic acids.

Bench testing equipment is readily available from suppliers of scientific equipment.

Chelated Metals:

Chelated metals are generally not treated by Hydroxide Precipitation alone. Wastewaters with chelated metals may need to use ion exchange, reverse osmosis or nano-filtration. Chelated metals can also be chemically treated with a dithiocarbamate (DTC) to break the metal-chelate into free metal and free chelate. (DTC is toxic to marine life and harmful to the environment). These techniques to remove metal-chelates are more costly than hydroxide precipitation and are beyond the scope of this paper.

Pilot Testing:

Pilot testing is sometimes recommended if favorable results are obtained from the bench scale testing.

Pilot testing can be described as on site testing at the actual location under actual conditions. This is accomplished by taking a real time side stream of the wastewater and testing the actual process that is being considered before going to full-scale construction. Pilot testing is optional.

Effect of Reaction Time On Metal Hydroxide Formation:

The time needed to complete the metal hydroxide formation will depend on the several variables, most notably pH and wastewater strength. Typical reaction times are 30 - 60 minutes. Actual reaction time will vary with the organic loading and type of organic chemicals that are present in the wastewater that are also undergoing chemical reactions as the pH is raised. For more complex or more concentrated wastes, the reaction may take several hours.

General Steps to Remove Metals From Wastewater:

The procedure requires the following steps:

1. **pH adjustment:** Wastewater is first drawn from an Equalization tank to the rapid mix tank also called a reactor tank where the pH is adjusted to 9.0 to 9.5. This is done by the addition of Caustic (NaOH) or lime. The higher pH will generate the Hydroxide Ion. The Hydroxide ion will react with the metal ion forming the Metal Hydroxide predicate.

   Caustic dosage is typically less than 5 gallons for 1,000 gallons of wastewater. Note: Caustic, Sodium Hydroxide can be purchased in liquid or in dry flakes. Liquid caustic is generally purchased in 55 gallon drums or in 290 gallon totes.

2. **Polymer Addition:** A small amount of polymer is added to create a floc (flakes of precipitate material visible to the eye). Typical dosage of Polymer is 2 oz. per 1,000 gallons. Purchased in 5 gallon containers. The polymer will produce

flocs in the wastewater that will settle.

3. **Settling**: Settling of the flocs can be accomplished in a settling tank or in a clarifier. If using an open settling tank, allow to settle for one hour or more, no mixing or turbulent flow. Clarifier's can be used and have the advantage of taking less time to settle of a settling tank. Inclined plate clarifiers are recommended.

4. **Decant:** The clear water is now removed by decanting from the settling vessel (clarifier).

5. **Solids Removal:** The settled solids are removed and sent to a filter press to remove excess water. The filter press will produce what is called filter cake. The solid residues, like a cake, can usually be sent to a landfill for disposal.

Note: Jar testing should be conducted to determine dosage rates.

Process Equipment

Rapid Mix Tank: Rapid mix tank is a mixed tank where the pH is adjusted to the desired level, usually 9.0 to 9.5 for most metals, by adding caustic. Polymer is also added for rapid mixing.

Clarifier: Clarifier is typically an inclined plate clarifier where clear treated water rises to the top and the solids settle on the clarifier plates and slide to the bottom for removal. The pH in the clarifier is kept at 9.0 to 9.5 to prevent the metal hydroxides from dissolving back into the wastewater.

Dewatering: The solids that are removed from the clarifier are sent to sludge thickening tank. This is generally a cone bottom tank where the solids collect on the bottom and the water is roved from a point near the top. The bottom sludge is pumped to a dewatering device such as a filter press or de-watering box.

Final Filter: The final filter is to remove any particulate matter that may still be present in the wastewater. Commonly used filters are sand filters, paper indexing filters or multi media filters.

Discharge Tank: Filtered water can be held in an optional treated wastewater tank for testing before discharging to the sewer. Some cities require a discharge tank as permit condition.

Equipment Automation

Both batch systems and continuous systems can be fully automated to control the entire process.

Summary

- Wastewater containing dissolved metal compounds can be treated using Hydroxide Precipitation chemistry.
- Hydroxide Precipitation chemistry has been used in industrial applications for decades.
- Jar Testing is recommended prior to purchasing any wastewater system.
- Chelating compounds can block the hydroxide precipitation reaction.
- Industrial sewer permits are required for sewer discharge.
- Check discharge limits in your sewer use permit for compliance.
- Batch and continuous systems can be fully automated.

References

University of Houston: Civil Engineering Dept.