

Metals Removal to Low Levels Using Chemical Precipitants

Angela Kowalski, ONDEO Nalco Company, Naperville, IL, USA

For many plating plants, the proposed Metal Products and Machinery (MP&M) reductions in effluent discharge limits for heavy metals would require improvements in existing wastewater treatment programs to ensure compliance. Effective metals removal by precipitation requires rendering soluble metals insoluble followed by good solids/liquid separation of the precipitated metals from the treated water. This presentation will review and compare chemical programs for heavy metals removal. These programs include sulfide precipitation, iron precipitation, small organic metal ion precipitants such as alkyl dithiocarbamates, clay blends and polymeric metal ion precipitants. The polymeric metal ion precipitant program may offer advantages over conventional programs. The polymeric program can effectively remove and flocculate metals and is expected to meet the new MP&M limits, even in the presence of chelants or complexing agents. A reduction in sludge generation may also be realized with the polymeric program and, in many cases, chemical feed can be automated.

For more information, contact:
Angela Kowalski
ONDEO Nalco Company
ONDEO Nalco Center
Naperville, IL 60563
akowalski@ondeo-nalco.com

INTRODUCTION

Increasing environmental concerns about heavy metals discharge have continued to fuel tightening metals discharge limits. The proposed Metal Products and Machinery (MP&M) effluent discharge limits for metals are, in many cases, significantly lower than existing limits.¹ Figure 1 compares the current and proposed regulations. Meeting these low discharge limits will necessitate making changes to existing wastewater treatment systems and plant operations.

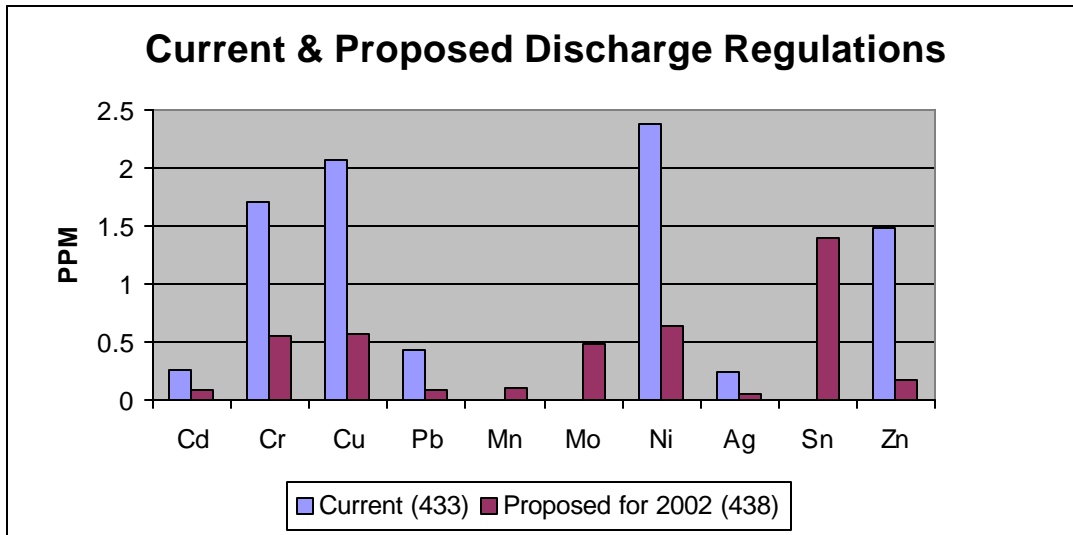


Figure 1. Current and proposed MP&M metal discharge limits.

The most widely used process for the removal of heavy metals from waste streams is chemical precipitation. This method is used by approximately 75 percent of the facilities that treat aqueous metal-bearing wastes. The choice of chemical program depends on the metals being removed, target levels of effluent metals, if metals are chelated or complexed and other components of the waste stream. Other considerations include whether a batch or continuous treatment process is used and sludge handling.

Effective chemical precipitation of metals depends upon one or more of the following variables: 1) maintenance of an alkaline pH through the precipitation reaction and subsequent settling; 2) addition of a sufficient excess of treatment ions to drive the precipitation reaction to completion; 3) addition of an adequate supply of sacrificial ions (such as iron or aluminum) to ensure precipitation and removal of specific target ions; and 4) effective removal of precipitated solids.

OPTIONS FOR CHEMICAL PRECIPITATION OF METALS

Precipitation techniques currently being practiced on aqueous metal wastes include hydroxide (e.g., caustic or lime), ferrous sulfate, sulfide (soluble and insoluble), organic precipitants and polymeric precipitants. Each of these processes will be reviewed.

Hydroxide Precipitation

Precipitation as the metal hydroxide represents one of the least expensive treatments for heavy metals removal. The preferred reagent, from a cost standpoint, is quick lime, CaO or hydrated lime, Ca(OH)₂. Other precipitants such as caustic soda, NaOH, and to a lesser extent, magnesium hydroxide Mg(OH)₂, are also common. Caustic soda or sodium hydroxide (NaOH) has numerous advantages over lime: homogeneity of feed solution, production of soluble by-products under all pH conditions, rapid formation of hydroxyl ions, and excellent neutralization efficiency. However, caustic soda is always more expensive to use than lime. Magnesium oxide, MgO, or magnesium hydroxide, Mg(OH)₂, precipitation systems have shown to be effective in treating metal-

bearing waste streams that contain lower concentrations of dissolved metals (~50 mg/L). Since it is insoluble, MgO is a dense solid and the lower sludge volume results from compaction of the metal hydroxides. However, three- to four-fold stoichiometric excess of MgO must be added to reach pH values ranging between 8 and 9, which can cancel out its benefits.

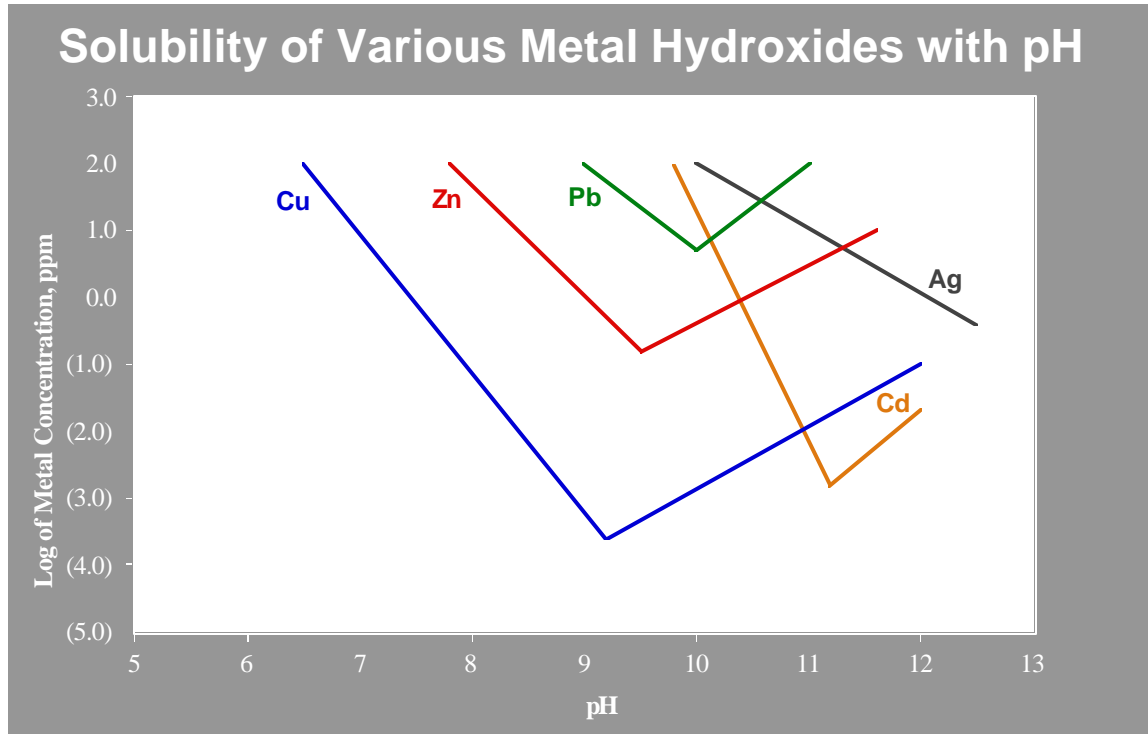


Figure 2. Solubilities for Metal Hydroxides as a function of pH

Hydroxide precipitation can be automatically controlled by pH and has been used effectively in industry. Figure 2 shows optimum pH for some metal hydroxides. When followed by flocculation and filtration, it can remove metals to below 1 ppm, if optimized. However, there are many limitations to this technology, as follows:

1. The hydroxide sludge tends to resolubilize as pH is increased or decreased.
2. The precipitation is ineffective in the presence of chelants or complexing agents.
3. In mixed metals wastes, the optimum pH for each metal varies, and multiple precipitation steps have to be practiced to remove all metals to low levels. This is often impractical.
4. Some metals (such as Pb) are difficult to remove to < 1 ppm by hydroxide precipitation.
5. Metal hydroxides take a relatively long mixing time to form discrete particles; thus, in systems with large flows and short retention times, this method is impractical.
6. Hydroxide sludge is amorphous, voluminous and difficult to dewater, resulting in high sludge haul-off costs.

Free Versus Chelated or Complexed Metals

When metal compounds are dissolved in water, the metallic components exist as positively charged, freely moving ions in the solution. These “free” metal ions react to surround themselves with negative ions or polar molecules present in the solution. The number of such molecules or negative ions that coordinate with the metal ion varies, but for most heavy metals (copper, nickel and iron - the common metals of industry) it is usually 4 or 6. These centers of activity for the metal may be termed reactive sites. In an aqueous solution containing only a simple metal salt, water molecules occupy the reactive sites.

When materials are added that interact more strongly or compete more effectively than water for the reaction site, the water is displaced, and the metal ion acquires a new set of properties. This happens when chelants or complexing agents are present. Many industrial wastewaters contain these materials, such as ammonia. As an example, when hydrated copper ions come into contact with ammonia, the four reactive sites with water are displaced by ammonia. Because the ammonia forms a stronger attachment than does the water, the resultant ammonia-copper complex is stable in solution. The ammonia can only be replaced by adding to the system a material that forms an even more stable complex with copper.

The presence of chelants and complexing agents in wastewater keeps metals dissolved over a broad pH range. In order to treat and remove these dissolved metals, an insoluble metal complex has to be formed, i.e., use of a metal ion precipitant. The following chemical precipitants can be used to remove both non-chelated and chelated metals.

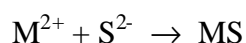
Iron Displacement

Metals removal using iron co-precipitation is very common. The metals-bearing wastewater is mixed with a ferrous salt (FeSO_4). At low pH (pH 4), the iron displaces the chelant from the metal of interest, and then the pH is raised (pH 7-9) with alkali to precipitate the metal hydroxide. A polymer flocculant is sometimes added to aid settling. Although ferrous sulfate is relatively inexpensive and can be used to treat chelated or complexed metals, the program has some disadvantages including:

1. Very high sludge volumes because the program requires high doses of ferrous sulfate that generate iron hydroxide.
2. Use of ferrous sulfate contributes sulfates to treated water.
3. Use of a lot of acids/bases.
4. Difficult to achieve the metals discharge limits consistently because there is no automation.

Sulfide Precipitation

Similar to hydroxide precipitation, sulfide precipitation is a process that converts soluble metal ions into insoluble sulfide compounds (MS) through contact between a metal ion (M^{2+}) and a sulfide ion (S^{2-}):



Sulfide precipitation offers several advantages:

1. Attainment of a high degree of metal removal due to low solubility of metal sulfides.
2. Effective removal in the presence of chelants and complexing agents. (Cyanide must be oxidized prior to treatment.)
3. Sludge is less subject to leaching than the corresponding hydroxide sludge.
4. Sludge is easier to filter and dewater than hydroxide sludge.

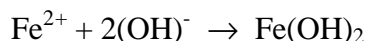
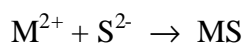
Disadvantages include:

1. Coagulation/flocculation is necessary for good metal removal, but optimization of this process can be difficult.
2. Hydrogen sulfide (H_2S) generation and toxicity to humans is a concern.
3. Excess sulfide is a regulated contaminant in many effluents.

The two main processes for sulfide precipitation are soluble sulfide precipitation (SSP) and insoluble sulfide precipitation (ISP).

In soluble sulfide precipitation (SSP), water-soluble sulfides such as sodium sulfide, Na₂S, or sodium hydrosulfide, NaHS, are used. The major problem with sulfide reagents is potential production of hydrogen sulfide, H₂S, especially when acidic wastewater is being treated. Also, the sulfide ion itself is toxic to aquatic organisms and must be rigidly controlled to minimize excess sulfide in treated water. If the dosage of dissolved sulfide is too high, the precipitation will yield particulate fines that are slow to settle and difficult to filter. The addition of coagulants, such as calcium or aluminum salts and cationic polymer, helps remedy this problem, but coagulant demand changes rapidly, making optimizing of solids-liquids separation difficult to achieve.

The insoluble sulfide process (ISP) mixes a wastewater with a slurry of slightly soluble FeS that dissociates to sulfide and iron ions. The sulfide is released in the presence of other heavy metals having more affinity for the sulfide ion than iron. By maintaining the pH between 8.5 and 9, free iron forms the hydroxide complex and precipitates out of solution. Excess FeS is filtered or settled along with the metal sulfide precipitate, generating a sulfide-free effluent. Like the SSP method, coagulants or flocculants will enhance the removal of metal sulfides. The following reactions occur when FeS is added to a solution containing dissolved metals and metal hydroxides:



Several proprietary systems are currently available that incorporate various aspects of the ISP to achieve metals reduction and removal. One process uses a FeS slurry prepared fresh from FeSO₄ and NaHS. The concurrently released Fe will precipitate as its hydroxide. Despite increased metals removal, this method produces more sludge than either the hydroxide or SSP systems. Handling of these chemicals is also a concern.

Small Organic Precipitants

Small molecule organic precipitants such as alkyl dithiocarbamates (DTC) and trithiocarbonates (TTC) are used extensively in metal finishing and electronics industries in the U.S. These precipitants react stoichiometrically with metal ions and show similar characteristics in use. In this discussion, we will use DTC as an example, but keep in mind that TTC shows similar characteristics. Like sodium sulfide, the small molecule organic precipitants can remove metals in the presence of chelants and complexing agents, but safety and handling concerns about using these precipitants are reduced relative to sodium sulfide.

In treating dilute rinse waters containing low concentrations of metals, say below 50 ppm (mg/L), the resulting metal-DTC complexes form colloidal particles in suspension, i.e., particles that will not settle in a reasonable period of time. In some wastewaters, these particles are so small that they appear only as color, carrying metal ions into the effluent. Thus, efficient removal of metal ions from plant effluent necessitates using appropriate coagulation/flocculation techniques for colloidal suspensions.

To destabilize colloidal suspensions, two basic mechanisms have been described as helping to form sufficiently large aggregates to cause settling. The first, referred to as “coagulation,” reduces the net electrostatic repulsion at the particle surface; the product that performs this function is a “coagulant.” The second, known as “flocculation,” is aggregation by chemical bridging between particles; the product for this function is a “flocculant.” Typically, both coagulants and flocculants are used with DTC and TTC.

Small organic molecule precipitation can be difficult to optimize. This is because most wastewaters contain dispersants such as dissolved oils, organics and surfactants. These dispersants inhibit the aggregation of particles, increasing the dosage requirements for coagulants and, sometimes, flocculants. In many of these applications, small organic precipitants are overfed to guarantee compliance. Since these precipitants are negatively charged molecules, product overfeed tends to disperse the precipitated particles. In applications where the initial metals levels are less than 5 ppm, it is more difficult to achieve discharge limits using small organic molecule precipitants, because the low solids make it difficult to form good floc.

To summarize, advantages are:

1. Attainment of a high degree of metal removal due to low solubility of metal-small molecule complex.
2. Effective removal in the presence of chelants and complexing agents. (Cyanide must be oxidized prior to treatment.)
3. Decreased safety and handling concerns relative to sodium sulfide.
4. Sludge is less subject to leaching than the corresponding hydroxide sludge.
5. Sludge is easier to filter and dewater than hydroxide sludge.

Disadvantages are:

1. May be difficult to optimize coagulation/flocculation, solids/liquid separation.
2. May not be effective for low level metal removal due to carryover solids.
3. Automation for small molecule precipitant feed (ORP), but not for coagulant feed.
4. DTC is now regulated in some effluents.

Polymeric Metal Ion Precipitant

A polymeric metal ion precipitant* reacts with soluble metals to form insoluble complexes just like the small molecule organic precipitants. However, because the metal binding groups are bound to a polymer backbone, simultaneous metal precipitation and clarification occur. As such, good solids/liquid separation is easier to achieve and usually does not require optimization of a second chemical (coagulant). Another advantage of the metal precipitating groups being attached to the polymer is that the aquatic toxicity is reduced relative to alkyl DTC.

The polymeric precipitant works over a wide pH range, but in most applications works best at near neutral pH (7-9). The pH of treatment is chosen to optimize solids/liquid separation of the polymer-precipitated metals. In cases where a mixture of chelated and free metals are present, there is a trade-off between hydroxide co-precipitation and polymer precipitation. Testing over a pH range is necessary to determine the best treatment pH for the application.

The sludge generated from polymeric precipitant treatment can be hazardous or non-hazardous, depending on the application and the customer's permit. In most applications, there is a 25-90% decrease in sludge volume over conventional technology. This can reduce sludge disposal costs. A lower sludge volume results in a higher metals content of the sludge. If the opportunity for metals recovery from the sludge exists, the higher metals content can make the sludge more valuable. Sludge volume can be further minimized when feed of the polymeric precipitant is automated. The proprietary automation** can minimize chemical use and cost and ensure enough chemical is fed as demand fluctuates.

* NALMET®, ONDEO Nalco Company, Naperville, IL

** NALMET® Monitor & Controller, ONDEO Nalco Company, Naperville, IL

In some applications, there is a high charge demand from other contaminants, such as detergents or dispersed oils. In these cases, it may be necessary to pre-treat the water to remove charge demand for cost-effective polymeric precipitant treatment.

To summarize, advantages of using a polymeric precipitant are:

1. Use one product instead of two.
2. Consistently effective metals removal due to low solubility of metal polymer complex and good solids/liquid separation.
3. Effective removal in the presence of chelants and complexing agents. (Cyanide must be oxidized prior to treatment.)
4. Decreased toxicity relative to alkyl-DTC.
5. Ease of use - it's automated!
6. Sludge is less subject to leaching than the corresponding hydroxide sludge.
7. Sludge is easier to filter and dewater than hydroxide sludge.

COMPARISON OF HEAVY METAL TREATMENT TECHNOLOGIES

Table 1 gives a quick comparison on available precipitation technologies commonly employed today for soluble metal removal.

	Polymeric Precipitant	OH	Na ₂ S	FeSO ₄	DTC	TTC
Chemical Cost	mod	low	low	low	mod	mod
Sludge Disposal Cost	mod	high	high	high	mod	mod
Treat Chelated Metals?	yes	no	yes	yes	yes	yes
Low Levels?	yes	maybe	maybe	maybe	maybe	maybe
Mixed Metals?	yes	maybe	maybe	maybe	yes	yes
Solid/Liquid Separation	easy	tough	tough	tough	tough	tough
Toxicity of product	mod	non-toxic	human toxic	mod	high	mod
Automation Available?	Proprietary Controller	pH	no	no	ORP	ORP
Ease of use	easy	easy	hard	hard	hard	hard

OH = hydroxide precipitation; DTC = alkyl dithiocarbamate; TTC = trithiocarbonate

CLAY BLENDS FOR METALS REMOVAL

Clays have historically been used for wastewater. They are used as weighting agents and can add bulk to the voluminous metal-hydroxide sludge, making them easier to flocculate and settle. Blended, clay-based products are currently being used for metals removal. These products are different from the metal ion precipitants in that they are intended to pH adjust, coagulate and flocculate wastewater in one step. The products are fed dry or, in some cases, can be slurried. It is thought that metals adsorb onto clay surface. The blended product may contain a metal ion precipitant to remove chelated or complexed metals. These products may be effective for wastewaters with oil or dispersancy because these contaminants can also adsorb onto the clay surface. High doses of these products are used, so the resulting high sludge volumes can create high sludge disposal costs. Also, clay retains water, so sludge may be difficult to dewater.

WHAT CAN BE DONE TO OPTIMIZE THE CURRENT WASTEWATER TREATMENT SYSTEM?

A survey of production and the waste treatment system may reveal practices that can be changed to improve operations in the waste treatment system. It is always optimal to equalize waste streams in metals removal applications. Equalization of wastewaters from all of the processes in the plant going to the waste treatment system ensures a homogeneous wastewater is entering the waste treatment system. This minimizes adjustment

of chemical doses and ensures effective removal of metals. Good mixing and long retention times in tanks where the metal ion precipitant is fed also improve metals removal.

Concentrated baths of metals are sometimes “dumped” into the waste treatment system. When these baths contain an excess of the chelant or complexing agent, this practice can have a significant negative impact on the waste treatment system and should be avoided. Excess chelants present in the wastewater sharply increase metals removal chemical required to effectively remove chelated metals because the precipitant must compete with chelant to form the metal-precipitant complex and precipitate the metal. The greater the concentration of chelant, the larger the precipitant dose required. Also, surfactants and dispersants in the baths can have a negative impact on solids/liquid separation, resulting in carryover floc. Efforts should be made to minimize large dumps of chelants to prevent upsets to the waste treatment system and to minimize the dose of precipitant dose required for effective metals removal. If baths containing chelants or complexing agents are dumped periodically, consider segregating the spent baths and slowly “bleeding” them into the waste treatment system.

In the waste treatment system, solids/liquid separation must be optimized to prevent floc carryover. Metals discharge limits are based on total metals (soluble and insoluble) in the effluent wastewater, so any metals-containing floc will increase the total metals in the wastewater. Because upsets to the waste treatment system can occur, barrier filtration, including membrane filtration, should be considered prior to water discharge. Barrier filtration eliminates the possibility of solids carryover.

Even after optimizing solids/liquid separation, some applications may find that target metals levels cannot be met. In these cases, effluent “polishing” should be considered. Effluent “polishing” should also be considered when the wastewater contains a mixture of chelated and non-chelated metals. Non-chelated metals can be removed by hydroxide precipitation and the resulting wastewater can be treated with a metal ion precipitant; precipitated solids are removed by filtration. The polymeric metal ion precipitant is a good choice for polishing applications because metals precipitation and coagulation result from using a single chemistry. This two-stage approach can be more cost effective than using a metal ion precipitant to treat all of the wastewater.

SUMMARY

Metals removal is a two-stage process, rendering soluble metals insoluble, followed by good solids/liquid separation. If chelants or complexing agents are present in the wastewater, hydroxide precipitation cannot be used for metals removal, and a metal ion precipitant must be used. If target metals levels are not being met, a plant survey can identify improvements/practical operational changes to minimize challenges in the waste treatment system and improve metals removal. If these efforts do not produce target effluent metals levels, then one can explore using other metal precipitating chemistries and augment the system with polishing filtration equipment, if necessary.

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REFERENCES

1. U.S. Federal Register, Vol. 66, No. 2, Jan. 3, 2001.