Plating Wastewater Systems Management

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WASTEWATER SYSTEM DESCRIPTION

Wastewaters from all processes are collected by gravity flow into acid-alkali (rinses), chromate, cyanide, spent/stripping acids, and cleaner sumps. The acid concentrates and cleaner concentrates are gradually fed into chromate and acid-alkali (rinse) sumps, respectively.

Cyanide destruction is achieved by oxidation with sodium hypochlorite whereas hexavalent chrome is reduced to trivalent chrome with sodium metabisulfite. The oxidized cyanide and reduced chrome are sent to the neutralization tank; the pH is raised with sodium hydroxide for metal hydroxide precipitation. The treated wastewater is then mixed with an anionic polymer at the rate of 1 to 5 ppm to promote flocculation. Clarification is achieved through a slope plate clarifier, followed by final sand filter polishing prior to discharge into the sewer. The dewatering of sludge is achieved with a five cubic foot plate and frame filter press and is then removed and collected for landfill disposal.

TREATMENT OF CYANIDES

Successful wastewater treatment begins with the complete breakdown of cyanides, which is achieved by oxidation (achieved by alkaline chlorination) of simple cyanides present within the primary treatment stages.

Commercially available sodium hypochlorite is used at pH 11.0 to 12.0. In this pH range, the formation of by-product cyanogen chloride (CNCl, a highly toxic intermediate) is at a minimum. The presence of excess free chlorine (at least 1.0 ppm), detected by starch-iodide test paper, in the effluent indicates complete destruction of cyanides.

The effluent water normally contains small amounts of heavy metal cyanides, in addition to free cyanide, which give reactions analogous to sodium cyanide. Some metal cyanide complexes react very slowly with chlorine and require at least one hour retention time for complete destruction. The stable, less soluble cyanide complexes require specialized treatment for destruction and are only available at major treatment facilities, some of whom can handle only low complex cyanide concentrations. Furthermore, incomplete oxidation of cyanide wastewater when blended into further waste stream materials, such as hexavalent chromium/chromates along with the presence of iron and/or copper ions will result in the formation of ferricyanide complexes, which are resistant to alkaline chlorination processes.

TROUBLESHOOTING CYANIDE TREATMENT:

Influent Load Rate:

Check frequently and compare with treatment tank design criteria as excess flows will cause reduced reaction time. Minimize cyanide drag-out and water use from the production process.

Bleach Dosage Rate:

Fast dosage rates to highly concentrated wastes will result in the formation of ammonia and chloramines which will yield soluble metal ammonia complexes of Cu, Ni, and Cd that will increase the need for bleach by a factor of up to five times.

Treatment Tanks:

Ensure complete and turbulent mixing conditions and remove build up of solids, which will cause an apparent reduction time and incomplete oxidation reaction.

Reaction Chemicals:

Check the age of the sodium hypochlorite, the level in the feed tank, and the proper make up concentration of sodium hydroxide.

ORP Settings and pH:

Optimum pH is 11 and 9.0, respectively for the first and second stages of oxidation reactions. Ensure the first stage reaction is complete before proceeding to the second stage, by tests for absence of cyanide and the presence of a slight excess of chlorine with starch iodide test paper. Keep a record of pH, ORP and treatment tank performance for troubleshooting purposes.

Maintenance of pH/ORP Probes:

The bulb part of pH/ORP probes should be "religiously" but gently cleaned once a shift by wiping with alcohol to remove oil and grease. Any tenacious film of metal hydroxide on the probe can be removed by immersion in 10 to 20% hydrochloric acid, followed by thorough rinsing with distilled water. Keep a set of spare probes for damaged probe replacement and for determining when a probe is defective.

Stable Complexes Removal:

Stable cyanide complexes are effectively removed by increased retention time, increased chlorine dosage or by the addition of ferrous sulfate at the neutralization stage. It may be necessary to isolate and treat mixed streams separately using thermo-oxidation.

CHROMATE REDUCTION

Excessive chromium levels in the effluent water are primarily due to the presence of hexavalent chromium, which is reduced to trivalent chromium, followed by hydroxide precipitation. A variety of reducing agents have been suggested for chromium (VI) reduction including sodium bisulfite/metabisulfite, sulfur dioxide, and ferrous sulfate. Bowers et al[1] examined the use of scrap iron filings as a reducing agent; however, sodium metabisulfate is used for reduction at our waste treatment plant.

A small amount of sodium hydrosul-

fite dithionite is added at the neutralization stage to assure complete reduction of minute traces of hexavalent chromium, which might have escaped the reduction stage.

TROUBLESHOOTING CHROMATE REDUCTION:

Influent Load Rate:
Monitor and adjust the influent loading rate in the treatment tank to ensure complete reduction (by spot testing).

Reaction Chemicals:
Ensure that the "bisulfite" is fresh and a sufficient level is maintained in the feeder tank.

Treatment Tank:
Ensure complete mixing and periodic removal of solids from the treatment tank.

Optimum pH:
Maintain reduction pH between 1.5 and 2.0, as higher pH values will slow the reaction time.

ORP Settings:
ORP settings are determined by jar tests. Plot hexavalent chrome concentration versus ORP, at a constant pH.

Segregate Streams:
The chrome reduction stream should be kept separate from the cyanide stream, otherwise any excess oxidizing agent will reoxidize trivalent chrome back to hexavalent chrome.

Control Reduction:
Reduction conditions must be controlled so as not to reduce other metal species which are then more difficult to precipitate in the neutralization stage.

Lime Addition:
The addition of lime in conjunction with caustic soda facilitates the metal hydroxide settling and subsequent removal.

Colloidal Formation:
Insufficient precipitation of chromium as $Cr(OH)_3$ and the formation of colloidal chromium hydroxide will result in inadequate settling in the clarifier and pass through of the "sand filter" media. Addition of lime at the neutralization stage will prevent such colloidal formation, on the assumption that the reduction reaction was complete.

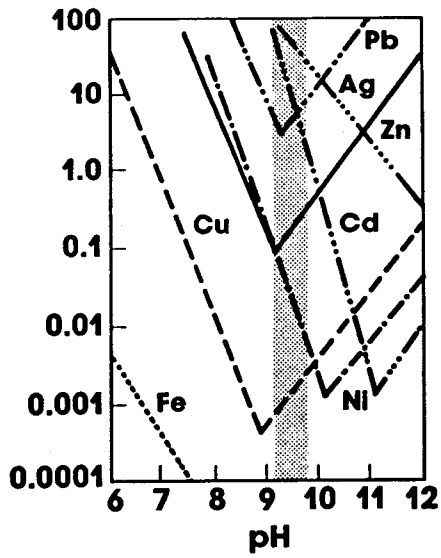

Fig. 1. Theoretical solubilities in mg/L of metal hydroxides as a function of pH.

The chromium reduction, precipitation reactions are crucial not only from the removal of hexavalent chrome, but to what extent other metals such as zinc, cadmium, etc, are removed.

NEUTRALIZATION AND METAL PRECIPITATION

The purpose of the neutralization is to precipitate the dissolved toxic metals by adjusting the pH to a point at which those metals present are least soluble.

The acid alkali rinses, oxidized cyanide and reduced chrome wastewaters in either mixed or separate streams are pH adjusted, usually raised, with an alkali, lime or caustic soda, thereby increasing the hydroxide ion concentration and causing precipitation.

Each metal has an optimum pH for maximum metal removal (See Fig. 1) and when several different metals are present, the optimum pH is a compromise situation, say 8.5 to 9.5, which reflects the overall minimum concentrations of the mixture. A pH level which is too high can actually resolubilize precipitated metal hydroxides.

The presence of chelating agents or gelatinous, low density solids can exert great influence at the high pH required for alkaline precipitation. This phenomenon is aggravated if the treatment system had high chelate concentrations at the primary treatment stages and the alkaline chlorination was performed with overheating (detected by ammonia odor). The formation of ammonium salts, e.g. $(NH_4)_2CO_3$, at a high pH and temperature will evolve ammonia gas. Ammonia in excess of 500 ppm at the clarification stage is a definite danger, as a strong chelator and the affinity of most heavy metals to ammonia is well established. Effluent problems associated with copper, zinc, nickel, and cadmium are common in high ammonia media.

RECENT PRECIPITATION TRENDS

In the presence of some organics or a high concentration of heavy metals (e.g. zinc), hydroxide precipitation alone is not sufficient due to the solubility constant effect. This necessitates the use of other precipitation methods.

SULFIDE PRECIPITATION:

This method is recommended where heavy metals are the major problem in the effluent. The process removes only those metal ions which can form insoluble metal sulfides (except chromium) from its complexes and will not affect cyanides or other anions. In fact, it might increase cyanide due to the breakdown of stable metal iron cyanide complexes. The degree of sulfide precipitation is dependent on the specific chelating agent and the metal ion present.

Hydrated sodium sulfide flakes are recommended over ammonium sulfide, even though the latter is a cheaper raw material, to prevent the formation of metal ammonium complexes.

Sulfide precipitation should only be employed to assist hydroxide precipitation and not as the sole method. Having excess sulfide ion in the treatment tanks will cause sulfide effluent problems and/or will cause the breakdown of certain insolubles, such as zinc, nickel, copper, iron cyanides, and thus release free cyanide in the post waste treatment system.

In addition, the excess sulfide in wastewaters containing mercury, will form HgS_2 complex, which is soluble in the treatment with pH of 8 to 10.

CALCIUM AND MAGNESIUM HYDROXIDE PRECIPITATION:

The addition of calcium chloride or lime often aids metal precipitation by entrapping water molecules and finely suspended particles. Also, some weaker complexes prefer association with the calcium ion rather than the heavy metal ions; however, lime addition increases the volume of sludge and

eventually increases sludge disposal costs.

The sodium hydroxide precipitation process often produces inadequately suspended solids thereby producing soft, difficult to dewater sludge. The use of magnesium hydroxide/sodium hydroxide (90:10) at pH 7.5 to 9.5, to a zinc plating stream has provided improved, high solids sludge and overall better water quality.

COPRECIPITATION WITH IRON:

This method involves the removal of soluble ferrous iron innate to the wastewater (additional iron can be added if required) at a pH of 7.5 to 8.0 in a specially designed reactor. As the ferric iron forms, it coprecipitates with the soluble metals removing them from the solution after becoming locked within a stable iron matrix, which forms a dense, highly flocculated solid.

METAL REMOVAL WITH SODIUM DIETHYLDITHIOCARBONATE:

Wing and Rayford[2] reported on the treatment of copper and nickel rinse with the use of sodium diethyldithiocarbonate (SDTC), and claimed complete removal of metals over a wide pH range when other complexing or chelating agents were present in the wastewater.

FLOCCULATION AND CLARIFICATION

After neutralization, precipitated solids are usually treated with coagulants and anionic polyelectrolytes, to increase particle size and settling rates. The correct type and concentration (from 1 to 5 ppm) of floc are based on preliminary jar testing, to achieve "cottage cheese" resembling flakes. The optimum flocculation pH is 7.5 to 8.5 and outside this range floc stability is greatly affected.

FLOCCULATION CHECK LIST:

1. Ensure anionic polymer floc stock is not too old.
2. The stock and floc tanks should have gentle mixing without a vortex. Insufficient mixing can lead to disproportionate amounts of polymer in the same tank or may cause the floc particles to shear and restabilize.[3]
3. Periodic cleaning of the flocculation tank is essential for the removal of built up solids, which would otherwise cause reduction in floc retention time.

Wastewater gravity feeds from the flocculation module to an inclined, shallow depth sedimentation known as lamella gravity settler and/or slope plate clarifier. The sludge is continually drawn out of the sludge chamber, preferably to another sludge thickening or holding tank, to increase consistency prior to filter press plate dewatering. The clarified "clear water" decants by gravity over the weir for final polishing in a sand filter prior to discharge into the city sewerage system.

CLARIFIER TROUBLESHOOTING:

The presence of visible particulate material in the effluent usually is attributed to a problem in or around the clarifier.

Solids Loading Rate:

- Evaluate and minimize plating and rinse drag-out by recovery techniques and reduction of overall water usage.
- Increase the sludge withdrawal rate to minimize "rat holing" in the clarifier. Sludge handling capabilities of the thickener and/or filter press may have to be increased.
- Continuous problems in the settling of solids can be overcome by the introduction of activated carbon slurry (10% W/V) which thereby improves the surface charges of the system.
- Use of lime, magnesium, aluminum, and ferrous salts need to be continuously reviewed as they add to the increased solids and should be balanced and/or eliminated if not essential.

Clogged Plates:

- Regular cleaning of plates and openings is essential as they get coated with oil, grease, and excess polymer. Otherwise, the upflow velocity in the clarifier is increased.
- Evaluate and minimize the source of clogging contaminants.
- Separate collection and batch treatment of oils at low pH by breaking the oil emulsion in addition to skimming the floating oil.

Sludge Layer:

- Regulate and minimize the on/off of treatment transfer pumps, otherwise the slow downward motion of particulate is either upset or reversed.

Clarifier Turbidity:

- The flocculation of precipitated metal hydroxide is vitally important and lack of proper flocculation will result in increased turbidity in the clarifier overflow.

CONCLUSION

The various factors affecting the individual selection of a waste treatment system are governed by the type of waste(s), water usage, and the discharge requirements. The final choice should be based on overall considerations of the type of wastes versus the financial limitations of the company. The chosen system should then be designed, built, and serviced by a reputable company with field service technicians available.

Comprehensive understanding and maintenance of the system, basic chemical background, identification of problems, accurate water testing, complete documentation, and a positive attitude on the operator's part are crucial to effective operation.

A waste minimization strategy based on a well considered waste management plan, incorporating regulations, production needs, technology, and economics is an essential part of any plating business. **MF**

References

1. A.R. Bowers et al, Metal Finishing, 84, 37 (Nov. 1984).
2. Wing and Rayford, Plating and Surface Finishing, 62 (Jan. 1982).
3. G. Norgaard et al, Plating and Surface Finishing, 26 (Feb. 1986).

METAL FINISHING

OCTOBER 1988
VOLUME 86, NUMBER 10

FEATURES

Pollution Control

COVER

Final pour of molten metal into molds. Photo courtesy Behr Precious Metals Co., Rockford, IL

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