Treating Metal Finishing Wastewater

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Environmental Technology • March/April 1998

Wastewater from metal finishing industries contains high concentrations of contaminants which are hazardous to the environment and pose potential health risks to the public. With increasingly stringent regulations governing wastewater discharge and greater quantities of wastewater being produced, there is a growing need for more efficient and cost effective methods to remove heavy metals.

In accordance with the National Pollutant Discharge Elimination System (NPDES), as required by the Clean Water Act, metal finishers are required to pretreat their wastewater prior to releasing it to municipal sewers or surface waters. As the regulations governing the discharge of wastewater become more stringent, publicly owned treatment works have set lower discharge limits on heavy metals and other contaminants of concern. With the greater quantities of wastewater being produced and discharge limits being lowered, there is a need for more efficient processes to remove heavy metals.

Wastewater from metal finishing industries contains contaminants such as heavy metals, organic substances, cyanides, and suspended solids, at levels which are hazardous to the environment and pose potential health risks to the public. Heavy metals, in particular, are of great concern because of their toxicity to human and other biological life. Heavy metals typically present in metal finishing wastewater are cadmium, chromium, copper, lead, nickel, silver, tin, and zinc. Table 1 shows the EPA best practical control technology, BPT, limits for metal finishing effluent.

Table 1: BPT Limits for Metal Finishing Effluent

Parameter	Maximum allowable in 1 day (ppm)	Daily Average for 30 consecutive days (ppm)
Total Cadmium	0.69	0.26
Total Chromium	2.77	1.71
Total Copper	3.38	2.07
Total Lead	0.69	0.43
Total Nickel	3.98	2.38
Total Silver	0.43	0.24
Total Zinc	2.61	1.48
Total Cyanide	1.20	0.65
pH	6.0 - 9.5	6.0 - 9.5

Conventionally, metal finishing waste streams are treated by chemical means and the quality of treated effluents must meet discharge standards. The techniques used in the conventional treatment of metal finishing wastewater involve precipitation of heavy metals, flocculation, settling, and discharge. Such techniques take considerable time and require extensive setup. Each step takes place in a separate tank, and the entire treatment requires several adjustments of pH as well as the addition of acid, coagulant, lime or caustic, and polymeric flocculant. In addition, the process generates large volumes of sludge/waste which requires disposal and is normally hazardous due to the high concentrations of heavy metals.

The current accepted best available technology (BAT) for removal of heavy metals and other hazardous contaminants from wastewater is stabilization in a non leaching matrix (waste), so that they do not pose a hazard to the environment once the waste is placed in a landfill. This manipulation is normally carried out at waste treatment plants by reacting the generated waste with chemicals known as amendments and allowing the mixture to cure. This increases the cost of the treatment and places an extra burden on treatment facilities. Disposal of hazardous waste generated by the current practice of wastewater treatment increases the overall cost of the treatment by 50% to 200%, depending on the nature and level of metals in the waste. It is fair to assume that the cost of disposal of nonhazardous material is about 50% to 70% cheaper than for hazardous material of equal volume or weight. The overall cost of wastewater treatment includes both the cost of treating the water and the disposal of waste. For example, a facility in Michigan generates 2,000 gallons of chromium laden wastewater daily. The cost of treating the water alone is estimated at $ 25,000 to $ 30,000 per year, plus, the facility pays approximately $ 16,000 to $20,000 annually for waste disposal -- which results in a total of $ 41,000 to $ 50,000. Disposal cost sometimes exceeds that of water treatment, depending on the nature and level of contaminants.

Conventional Technology

In conventional treatment, precipitation is the technique of choice for the removal of dissolved heavy metals. Precipitation of heavy metals lowers the concentrations of all metals. The solubility of precipitated metal compounds is the key to this method's success; if a metal can form an insoluble compound, then the compound can be removed via clarification and filtration.

There are a few methods for the precipitation of heavy metals, namely as hydroxides, sulfides, and carbonates. However, the two main methods currently in use are hydroxides and sulfides. Table 2 shows solubility of metal hydroxides and sulfides. Both methods involve a reaction of the metal cation with either OH^- or S^{2-} to form the corresponding insoluble metal hydroxide or sulfide, as shown below.

$$M^{2+} + 2\,OH^- \rightarrow M(OH)_2$$
$$M^{2+} + S^{2-} \rightarrow MS$$

Table 2. Solubility of Hydroxides and Sulfides of Heavy Metals

Metal (Ion)	**Concentration of metal Ion, mg/L**	
	Hydroxide	**Sulfide**
Cadmium (Cd^{2+})	**2.3×10^{-5}**	**6.7×10^{-10}**
Chromium (Cr^{3+})	**8.4×10^{-4}**	**No ppt.**
Cobalt (Co^{2+})	**2.2×10^{-1}**	**1.0×10^{-8}**
Copper (Cu^{2+})	**2.2×10^{-2}**	**5.8×10^{-18}**
Iron (Fe^{2+})	**8.9×10^{-1}**	**3.4×10^{-5}**
Iron (Fe^{3+})	**1.0×10^{-4}**	**No ppt.**
Lead ($Pb^{2=}$)	**2.1**	**3.8×10^{-9}**
Manganese (Mn^{2+})	**1.2**	**2.1×10^{-3}**
Mercury (Hg^{2+})	**3.9×10^{-4}**	**9.0×10^{-20}**
Nickel (Ni^{2+})	**6.9×10^{-3}**	**6.9×10^{-8}**
Silver (Ag^{+})	**13.3**	**7.4×10^{-12}**
Tin (Sn^{2+})	**1.1×10^{-4}**	**3.8×10^{-8}**
Zinc Zn^{2+})	**1.1**	**2.3×10^{-7}**

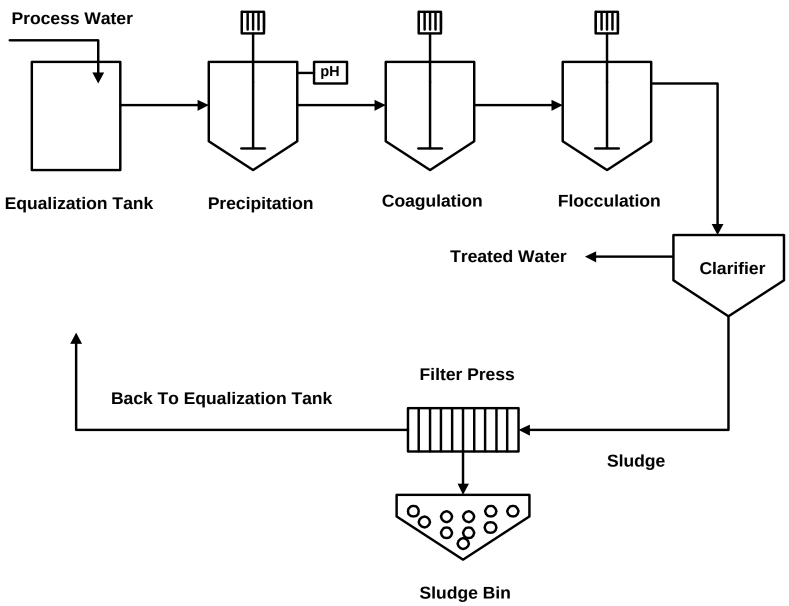
The most widely used method is precipitation of heavy metals as hydroxides, a process which is pH sensitive. In metal finishing wastewater, multiple metals are present at high levels. Therefore, the most effective pH must be determined prior to treatment. Most, but not all, heavy metal hydroxides precipitate at a pH in the range of 8.5 – 9.5. Beyond this narrow range, metal hydroxide may resolubilize or not form completely. Table 3 shows pH ranges for the formation of metal hydroxides.

Table 3. Ranges of pH for Precipitation Of Metal Hydroxides

Metal	pH Range
Cadmium	9.0 - 11.0
Chromium (III)	6.5 - 7.0
Copper	7.0 - 7.5
Iron (III)	5.0 - 5.5
Lead	8.5 - 9.0
Nickel	9.0 - 11.0
Silver	9.0 - 12.0
Zinc	8.0 - 8.5

Heavy metal hydroxides precipitate as colloidal, charged particles that require the addition of coagulants such as alum or iron compounds to reduce the charge and allow the particles to grow in size. To facilitate sedimentation, the coagulated particles are flocculated using flocculants. Sedimentation of metal laden floc/sludge takes place in a clarifier or settling tank. The clear supernatant can then be discharged, if it meets regulatory limits and the sludge is pressed through a filter press to produce a semi-solid waste. Figure 1 shows a diagram of a conventional treatment system set up.

Figure 1. Conventional Treatment System



Although sulfide and carbonate precipitation are less pH dependent and afford effluents of high quality, they are not generally the methods of choice due to: toxicity of sulfide; reactivity of sulfide-containing sludge with acids to generate toxic hydrogen sulfide gas; and that sulfide-containing sludge may not disposable in some states. In addition, the chemical cost is high; carbonate precipitate costs about four to eight times that of hydroxide, and sulfide precipitation is about 10 t0 20 times that of hydroxide.

Sludge Disposal

Disposal of sludge generated in the current practice is a challenging problem for environmental authorities. There is always the potential that precipitated heavy metals will resolubilize if the pH drops below the optimum range. Decomposition of municipal garbage and humic material generates organic acids (lowers the pH) which in turn increases the solubility of heavy metals (leaching out). Sulfide and cyanide containing wastes, in particular, pose a great hazard as they can react with such organic acids and generate toxic hydrogen sulfide and hydrogen cyanide gases.

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Waste is generally placed in disposal pits or landfills that have minimal impact on ground water. Where these conditions do not exist, it may be necessary to install collection systems to collect leachates for subsequent removal of heavy metals by precipitation or other means (pump and treat technique).

Chemical treatment to minimize the leachibility of heavy metal sludge have been developed. Metals containing sludge are treated with amendments that render them stable or less soluble. Such treatment of hazardous waste is an integral part of most landfill programs. However, these manipulations add to the already high cost of wastewater treatment; they typically account for 60% to 80% of the waste disposal cost.

A New Alternative to Conventional Treatment

The chemical precipitation technique, currently used by most metal finishing businesses, is time consuming and requires extensive equipment and handling, especially if it were a batch process. The process uses several dangerous and sometimes toxic liquid chemicals, some of which are known to freeze in cold climates. Some of the problems associated with such conditions include clogging of feed lines and accumulation of solid on the bottom of feed tanks, which could result in a significant change in the concentration of the liquid chemical solution. This upsets the treatment, as they may require interrupting the process altogether, or having to add more liquid to achieve the desired result. It could also require heating the area where feed tanks are located in order to maintain the fluid nature of the chemicals, which, in turn, adds to the treatment cost. In addition, in the event of a spill, liquid chemical are not easy to contain or clean up.

The precipitation method does not ensure total compliance for all metals present in the waste stream since all hydroxides are not completely precipitated at a single pH. Polishing with scavengers is often required in order to meet regulatory discharge standards. If the treated water does not meet discharge standards, the water is returned and goes through the treatment again until its quality is acceptable.

A recently developed alternative treatment uses a mineral-based agent to remove contaminants such as heavy metals, oil & grease, and suspended solids from wastewater. The agent has a high affinity for heavy metals, and the treatment itself is less dependent on pH than metal hydroxide precipitation. The agent reacts with metals such as zinc, copper, lead, and chromium at levels as high as 10,000 mg/L or higher. The high capacity for metals is independent of pH or the presence of oil, surfactants, chelants, complexing agents, suspended solids, and hardness.

In the treatment process, the agent is added to the agitated wastewater in a treatment tank where a dense floc forms, settles very fast, and is easily dewatered. On average, it takes between 3 to 10 minutes after turbulence has ceased for the floc to settle completely. The treatment can be used in both continuous and batch processes and is implemented using existing equipment. In addition, the treatment agent can be tailored to fit the chemistry of the waste stream. Figure 2 shows a typical setup for this treatment.

Waste generated in the new treatment does not require post treatment to render it safe for disposal. The composition of the treatment chemical stabilizes contaminants in the waste, especially heavy metals, and renders them less available. In other word, it lowers the solubility of metals and, consequently, the waste passes the Toxicity Characteristic Leaching Procedure (TCLP) test and meets the regulatory requirements for nonhazardous materials.

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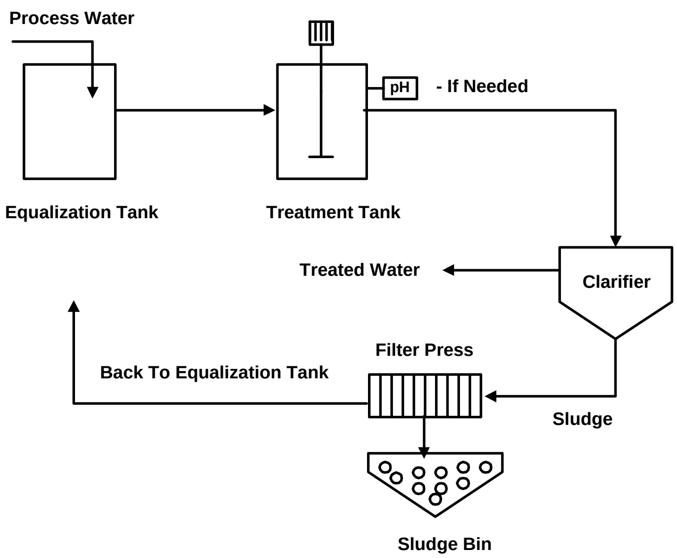
Figure 2. Typical Setup for Treatment System Using Mineral-Based Agent



Case Studies

Case 1: Metal Plating

A plating facility in Michigan has a highly acidic waste stream (pH < 1) that contains high levels of chromium, zinc, and iron as well as a number of chelating and complexing chemicals. The facility has a treatment system that operates in a continuous process at a flow rate of 56 gpm. The system utilizes Fe^{2+} from the acid pickling bath to reduce chromium (VI) in the waste stream. Lime slurry is added to the acidic water in a mixing tank to precipitate metal hydroxides. A flocculant is added to the water to enhance sedimentation in the clarifier. The treated effluent overflows to a holding tank, passes through a sand filter and then released to the sewer. Sodium dithiocarbamate is used to precipitate metals in chelated or complexed forms and to maintain metal concentrations in the effluent at the compliance level. Accumulated sludge in the clarifier is withdrawn periodically and forced through a filter press and the waste is dried on a bed drier and hauled away as hazardous material.

Case 1 Parameters	Daily Maximum ppm	Before Treatment ppm	After Treatment ppm
Cadmium	1.20	1.30	< 0.002
Chromium	7.00	127.00	< 0.05
Zinc	4.20	145.20	0.22
Iron	1,000.00	> 10,000	< 1.0
PH	6.0 - 9.5	< 1	8.70

With the new treatment, mixing the product with the waste stream took about three to four minutes to bring about the formation of large floc that settled completely within three to five minutes. Treated effluent showed concentrations for metals about 10 times lower than municipal discharge limits. This treatment eliminated the need to use lime, flocculant and the noxious dithiocarbamate. Analysis of leachate (TCLP) showed zinc and 339 ppm and chromium at < 0.5 ppm; regulatory limits are 500 ppm for zinc and 5 ppm for chromium. The waste is nonhazardous which results in a significant saving on transport cost.

Case 2: Circuitboard Manufacturing

An Illinois-based circuitboard manufacturing has a wastewater treatment system that operates at 130 gpm daily. The waste stream contains mainly copper and lead, with other heavy metals -- found in solder and flux -- as minor constituents.

The system operates by drawing wastewater from the various sumps (etching, plating, etc.) to an equalization tank. The stream is then fed to three mixing tanks in series. In the first tank, acid/ inorganic coagulant mixture is added. Caustic soda is added in the second tank to raise the pH and precipitate metal hydroxides. In the third tank a polymeric flocculant is added to effect the formation of large floc and enhance sedimentation in the clarifier. Overflow from clarifier flows to a neutralization tank, where pH is adjusted with acid and then flows to a holding tank. The neutralized effluent is pumped through a sand filter, then to a holding tank, and finally released to the sewer. Sludge from the clarifier is drained into a tank where it is mixed with thickeners and is periodically forced through a filter press. The semi-dry waste is hauled away as a hazardous material.

Case 2 Parameters	Daily Maximum ppm	Before Treatment ppm	After Treatment ppm
Copper	3.00	25.20	1.30
Lead	1.00	7.30	< 0.05
Nickel	3.00	< 0.05	< 0.05
PH	6.0 - 9.5	7.80	8.50

Laboratory tests showed that a dose of 500 ppm of the product was sufficient to reduce the level of copper to 0.30 ppm and that of lead to < 0.05 ppm. The product also reduced the concentrations of phosphorus, COD and total dissolved solids, TDS. The treated water is clear and can be recycled. Treatment with the new product eliminated the need for all liquid chemicals, neutralization tank, and sludge thickening, produced a very clear effluent that meets municipal standards and generated nonhazardous waste.

Case 3: Plating Operation

A plating service in eastern Michigan generates about 6000 gallons of wastewater daily. The main metallic contaminants in the water are zinc, chromium, copper, and cadmium. Local discharge standards are very stringent and require that a limit of 1 ppm be met for zinc, chromium and copper and 0.004 ppm for cadmium. The facility has a treatment system that consists of an equalization tank, a treatment tank where caustic is added to precipitate metal hydroxides, and a settling tank, where a flocculant is introduced to effect sedimentation. Precipitation of zinc and cadmium requires that pH is set at 12. As a result, water from the settling tank has to be neutralized with acid to bring pH to 9.5. The water then flows to a holding tank and finally passes through a sand filter before it is released to the sewer. Liquid sludge from settling tank is withdrawn periodically and hauled away. It was always difficult to meet discharge requirement on a routine basis.

Case 3 Parameters	Daily Maximum ppm	Before Treatment ppm	After Treatment ppm
Cadmium	0.004	0.790	< 0.005
Chromium	1.00	5.10	<0.10
Copper	1.00	4.12	0.35
Zinc	1.00	37.40	0.50
PH	6.5 - 9.5	7.40	8.0 - 8.5

Treatment with the mineral-based agent at a dose of about 1000 ppm brought about compliance and maintained the levels of metal in treated effluent at 0.5 ppm for zinc, 0.1 ppm for chromium, 0.35 ppm for copper, < 0.004 for cadmium, and effluent's pH is in the range of 8.0 to 8.5. In addition, the agent reduced the levels of phosphorus and COD in the discharge. The treatment eliminated the need for a neutralization tank, holding tank, and sand filter.

Conclusion

While chemical precipitation is widely used in the treatment of metal finishing effluent, the process is tedious and requires the use of several liquid chemicals to complete the metal removal step. The heavy metals may also be present in complexed forms and not amenable to precipitation -- which means failure to maintain compliance. The process generates mostly hazardous waste that requires further treatment that, in turn, adds to the cost of the treatment.

A new process that uses a mineral-based agent provides an effective alternative for the removal of heavy metals and other contaminants from metal finishing waste streams. The treatment produces high quality effluents that meet or exceed discharge standards and generates nonhazardous waste that does not endanger the environment or public health.

MORE INFORMATION

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