Treatment of Heavy Metals in Wastewaters

What wastewater-treatment method is most cost-effective for electroplating and finishing operations? Here are the alternatives.

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The Federal Government has allowed the General Pretreatment Regulations to take effect as of January 31, 1982 (46 Federal Register 4518). In addition, regulations for the electroplating industry have been reissued in the January 13, 1982 Federal Register with a compliance date of January 28, 1984. These regulations include maximum discharge criteria for heavy metals. These limitations closely parallel the present criteria promulgated for the plating/surface-finishing industry. The heavy-metals limitations can be broken down into two basic classifications — discharges less than 10,000 gallons per day, and those discharges greater than 10,000 gallons per day to Publicly Owned Treatment Works (POTW). There are complicated formulas for removal credits, but most platers will probably opt to comply with one of the two discharge schedules below (Table 1 and Table 2).

This paper will present a discussion of alternative methods used to treat the typical heavy-metal wastewaters most often generated by electro-plating and surface-finishing operations. Before considering any form of wastewater treatment, it is essential that the manufacturer review and reduce his water usage wherever feasible. This can be done with rinse-tank controllers (conductivity), counterflow rinsing, flow restrictors, and foot pedals. Water-usage reductions will permit the manufacturer to reduce the volume of wastewater generated and thus reduce the capital cost of the wastewater-treatment system.

### Table 1
LIMITATIONS FOR DISCHARGES MORE THAN 10,000 GALLONS PER DAY TO POTW

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Maximum Per Day (mg/l)</th>
<th>Maximum for 4 Consecutive Days (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Chromium*</td>
<td>7.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Copper</td>
<td>4.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Cyanide*</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Gold</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Lead</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Nickel</td>
<td>4.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Zinc</td>
<td>4.2</td>
<td>2.6</td>
</tr>
<tr>
<td>Total Metals</td>
<td>10.5</td>
<td>6.8</td>
</tr>
</tbody>
</table>

### Table 2
LIMITATIONS FOR DISCHARGES LESS THAN 10,000 GALLONS PER DAY TO POTW

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Average of Daily Values For Four Consecutive Monitoring Days Not to Exceed (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN, Amenable</td>
<td>5.0</td>
</tr>
<tr>
<td>Cd</td>
<td>1.2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.6</td>
</tr>
</tbody>
</table>

After water-saving steps have been taken, flow studies and analyses of the waste streams must be conducted. With this basic information, wastewater treatment equipment can be selected and sized. Batch treatment can be used, where flows are small, irregular, or where the strength of the waste may be quite high or extremely variable [1]. A typical batch-treatment system is shown in Figure 1. Batch systems are available in various modes, ranging from completely manual to fully automatic with a programmable controller. With a batch-treatment system, all treatment operations can be performed in one vessel, depending upon the presence of cyanide/chrome-bearing wastes. Continuous systems require the use of separate integral reaction units for each treatment reaction.

Any wastewaters which contain high amounts of oils must first pass through some type of oil-separation equipment. Floating oils can be skimmed mechanically, while emulsified oils can be forced to separate either with chemical aids, a coalescer, or with ultrafiltration. If BOD/COD is present in excess of the discharge criteria, either aeration or carbon adsorption must be used to reduce the BOD/COD to dischargeable levels [2].

**ORIGIN OF WASTES**

Cyanide-bearing wastes generally originate from cyanide-bearing cleaners, cyanide dips, and plating solutions for the following metals: copper, zinc, cadmium, brass, bronze, silver, and gold. Both concentrated and dilute wastes are possible. Concentrated wastes are the result of discarding spent solutions. Dilute wastewaters are the result of dragout or carry-over from a process solution which is rinsed off the part. The two should be treated together with the concentrated cyanide wastes bled into the dilute stream. Cyanide waste streams should be segregated from other wastes for treatment.
Chromate-bearing wastes originate from plating, bright dip, conversion coating, and anodizing. Again, wastes may be dilute or concentrated. Dilute wastes result from drag-out or carry-over from the process solution, which is removed from the work-piece, while concentrated streams result from the periodic dumping of spent baths or solutions. The two streams should be treated together with the concentrated chromate stream being bled into the dilute stream. Chromate streams must be segregated from other wastes for treatment.

Acid/alkali wastes make up the balance of the wastewater stream from most platers/finishers. The acids are generated from acid cleaners or pickling solutions, bright dips, acid dips, and their subsequent rinses. Alkalies result from alkaline degreasing and cleaning solutions and their subsequent rinses. The acid/alkali wastes, the cyanide-bearing wastes, the chromate-bearing wastes, nickel, copper, and zinc acid plating baths/rinse all contain heavy metals.

**Conventional Treatment**

The most common method of treatment of cyanide wastes is alkaline chlorination. The chlorine may be added directly as chlorine gas, or in the form of sodium hypochlorite solution. The complete destruction of cyanide, i.e., conversion to carbon dioxide and nitrogen is a two-step oxidation process. The chemical reactions for the process with sodium hypochlorite are shown in Figure 2.

When chlorine gas is used, sodium hydroxide must be added in the initial reaction to form sodium hypochlorite. Oxidation of the cyanides then proceeds by the same mechanism. Both stages of the reaction are pH-dependent. With the first stage, the reaction rate decreases as the pH decreases. In the second stage, the reaction rate increases as the pH increases. It is, however, very important to note that, in the second stage, pH below 7 must be avoided since at these low pH's cyanate will convert to ammonia.

The use of ozone as an oxidizing agent for cyanides is growing in popularity. The oxidation process occurs at ambient temperatures and can easily be automated. The major disadvantage is that ozone must be generated on-site and is relatively expensive. In addition, oxidation beyond the cyanate level is limited.

![Diagram 1](image1)

**Figure 1. Typical batch-treatment system.**

![Diagram 2](image2)

**Figure 2. Cyanide oxidation.**

The chromate-bearing wastes must first undergo reduction from the hexavalent state to the trivalent state. This can be accomplished with various reducing agents, the most common being sodium metabisulfite, ferrous sulfate, and sulfur dioxide. The reaction of sodium metabisulfite with chromate is shown in Figure 3.

The oxidation-reduction potential can be used to plot the course of the reduction reaction for chromate and the oxidation reaction for cyanide. Thus, an ORP meter/controller is an essential component, along with a pH meter/controller to assure proper treatment of cyanide and hexavalent chrome. Once they have been treated they can be combined with the general acid/alkali wastes for subsequent pH adjustment and the precipitation of heavy metals.

Single-stage continuous neutralizers are usually suitable for electro-plating wastes, using acids, sodium hydroxide, or lime. If the wastewater is subject to rapid pH variations or flow variations, a two-stage system should be used [1]. The retention time in each vessel is typically ten minutes. The term “neutralizer” is a misnomer today, because of the treatment to a specific pH for optimum heavy-metals removal. Metals precipitate at various levels of pH, depending on various factors such as: the metal itself, the insoluble salt that has been formed (e.g., hydroxide, sulfate, etc.), the presence of complexing agents such as EDTA (ethylene diamine tetraacetic acid), ammonia, acetic acids, etc. [3]. Theoretical curves for the precipitation of various metals as hydroxides are shown in Figure 4.

When two or more heavy metals are present in the same waste stream, the optimum pH for precipitation may be different than the optimum pH for one particular ion. In order to determine the optimum treatment process, a bench-scale laboratory testing program should be conducted and should include the use of various chemicals and various pH ranges to determine their effect in producing the best effluent. Various polymers should also be tested for their use in improving the settleability of the metal precipitates. Polymer is typically added immediately after pH adjustment in a flocculation vessel. The flocculated wastewater is then permitted to settle.

Various types of settling vessels are available. They include conventional center feed-peripheral discharge circuits.
The clarifier overflow may contain residual suspended solids requiring removal with a polishing filter. This ensures maximum removal of metals. A dual-media gravity filter or pressure filter is the most prevalent choice for filtration. When the filter reaches terminal head loss, it must be backwashed, which takes 15-20 minutes. During this time, it is out of service, with the main sump (feeding the pH-adjustment unit) holding the incoming flow. One alternate to this is to use a duplex filtration system assuring continuous operation. Effluent polishing can also be provided continuously with the larger DynaSand Filter which is a continuous-backwashing, upflow, deep-bed granular media filter. The feed is introduced into the bottom of the unit and flows upward through a series of riser tubes and is then evenly distributed through the distribution hood. The influent flows upward counter to the downward-moving sand bed; the filtered effluent then exists via an overflow weir. The sand bed and the accumulated solids are drawn downward into the suction of an airlift pipe at the center of the filter which transfers the slurry upward through the center of the unit. The scouring action frees the solids and they are then separated in the washer/separator which returns the sand to the filter and the solids to the reject stream. This device permits continuous backwashing utilizing 2-3% of the flow. The filtered, treated wastewater is then discharged to the POTW.

After the sludge has been collected from the clarifier, it is pumped to a sludge-thickening device. Usually, a conical-bottom tank is used with decant connections located on the side of the tank. This enables the initial collected sludge to be concentrated from 1-2% solids by weight to a final concentration of 4-8% solids by weight. Thickening improves the performance and efficiency of the final dewatering process and results in substantial volume reductions to reduce both the disposal and handling costs. From the sludge-thickening tank the sludge can be further dewatered with the use of a centrifuge, vacuum filter, or a plate-and-frame filter press.

A vacuum filter can work either continuously or as a batch operation. The common type of vacuum filter is the rotary-drum vacuum filter. This unit has three basic zones of operation: 1) slurry pick-up, 2) cake-drying area, 3) scraper/discharge. The system is constructed as a cylinder with various types of filter media. The cylinder is usually submerged about 40% with the speed of rotation set to obtain optimum pick-up, dewatering, and cake removal with the filtrate returned to the main process sump for re-treatment. The dewatered cake contains from 20-30% solids.

The filter press is one of the most common devices utilized for the dewatering of metal-hydroxide sludges. The system consists of a frame to support the plates. Plates can be either of the gasketed or non-gasketed type. Typically, the press is opened or closed with either a hydraulic system or a hand crank. The hydraulic system reduces the manual cranking labor. Once the press has been closed, the sludge is pumped to the press, where it disperses to each chamber simultaneously. Under pressure, the solids deposit uniformly on the surface of the cloth with the initial build-up acting as a filter. In most applications, the cake will build up to completely fill the chamber in about a two-hour period with the pump “stalling-out” when the chambers are full. The pump is then turned off and air is blown into one of the discharge ports of the press to remove any excess water and to separate the cake from the filter media. The press is then opened and the dewatered cake removed from the unit. The press typically produces sludge containing 20-40% solids by weight, while requiring only minimal manual labor.

In applications where the volume of sludge to be dewatered is large, the use of a centrifuge is very economical. The slurry is fed to the center of the unit, where it is accelerated with the rotational speed of the unit and packs on the outside bowl of the unit with the clear liquid collected through a filter screen. The heavier solids are forced towards the sludge discharge where they are typically removed by a screw conveyor. The concentrate is returned to the main process sump for reprocessing. Centrifuges can produce dewatered cakes of 15-25% solids by weight.

Bag filters are also used on occasion to dewater sludge. Some units utilize a series of open filter bags, while others utilize pumps to feed bags in a central housing. The bags can produce cakes ranging from 6-12% solids by weight. Once the sludge has been dewatered, it must be disposed of and this requirement is often the major factor in selecting a more effective dewatering process.

SULFIDE PRECIPITATION

Sulfide precipitation can be more practical than hydroxide precipitation in removing chromium because it directly reduces the hexavalent chrome to its trivalent state, eliminating the need for intermediate pH control. Sulfide precipitation is accomplished with either the soluble-sulfide or insoluble-sulfide process. With the insoluble process, an excess of ferrous sulfide is added, enabling the iron to give up its sulfide and to precipitate any metal with a lower solubility than the ferrous sulfide. With alkaline pH, the iron precipitates in the hydroxide form. In the soluble-sulfide process, a sulfide-ion probe is utilized to measure/control the addition of soluble sulfides such as sodium sulfide or sodium hydrosulfide. The soluble-sulfide system typically requires a higher chemical demand and produces a larger volume of sludge than hydroxide precipitation. Sulfide precipitation is relatively insensitive to the presence of most chelating agents and performs well on many complexed heavy metals. But sludge disposal can present a problem with no adequate data available to confirm the existence of sulfide sludges with long-term stability and it therefore may be difficult to obtain regulatory agency approval to dispose of the sludge in some areas.

ELECTROCHEMICAL REDUCTION

Chromium reduction is the most common application for electrochemical reduction/precipitation. This process utilizes consumable iron electrodes and electricity to generate ferrous ions, which react with the hexavalent chrome to produce trivalent chrome. Because of the introduction of ferrous ions into the waste stream, some additional solids will be generated. Maintenance includes biweekly replacement of electrodes and washing of electrodes (10-15 minutes/day). The conventional chromium reduction system has a combined treatment and sludge-disposal cost advantage over the electrochemical method when the influent Cr+6 exceeds 5 ppm.

INTEGRATED WASTEWATER TREATMENT

The integrated-system approach incorporates the waste-treatment step as part of the actual plating operation. In this type of system, the drag-out on the work-piece is treated in a rinse tank that contains the treatment chemical. For example, immediately following the chromic-acid bath there would be a chromic-acid waste-treatment rinse. This rinse would be in a closed loop with a chromium waste-treatment reservoir which is continually dosed with the required make-up sodium bisulfite, or other reducing agent. Following the treatment rinse, there would be a water rinse tank which would discharge to the conventional waste-treatment system for pH adjustment and removal of...
Electrolytic techniques have recently been utilized to plate out dissolved metals, reduce chromium, and to oxidize cyanide from wastewater. The major operating cost is evaporation to take advantage of processes, inhibiting any thermal operation additives and reducing energy consumption. This sludge is very stable with no leachate problems evident. ISX is very effective in the treatment of complexed copper but can also be used with most heavy metals.

**ELECTROLYTIC TECHNIQUES**

Electrolytic techniques have recently been utilized to plate out dissolved metals, reduce chromium, and to oxidize cyanide from wastewater. The major operating cost is evaporation to take advantage of processes, inhibiting any thermal operation additives and reducing energy consumption. This approach is particularly effective in treating complexed copper but can also be applied to most heavy metals.

**ION EXCHANGE**

Ion exchange is a reversible chemical reaction, where an ion from the solution is exchanged for a similarly charged ion attached to a solid particle. Typically, synthetic organic resins are utilized because of their superior capabilities of being manufactured for specific applications. The organic resin is composed of polyelectrolytes with a high molecular weight, which can exchange their mobile ions with those of a similar charge in the surrounding medium. Ion exchange is ideally suited for dilute solutions, with the treated water being of very high purity. Although every known metal has been recovered, separated, and purified by some ion-exchange process in the laboratory, on a commercial scale only a few are treated with ion exchange. Economics plays the major role in determining whether it is feasible to treat with ion exchange.

There are various types of resins, but the two basic classifications are cationic and anionic. The cationic resins have positively charged mobile ions available for exchange, while the anionic have negatively charged mobile ions available for exchange. Both of these groups can be further classified as strong- or weak-base anion exchangers, or strong- or weak-acid cation exchangers, and are so named because of their chemical behavior. Most industrial applications utilize columns with fixed beds of ion-exchange resin. Once the resin has become exhausted, the system must be regenerated. A cationic resin is regenerated with acid, which elutes the collected positively charged ions and replaces them with $\text{H}^+$ ions followed by a slow water rinse to remove any residual acid. An anionic resin is regenerated with caustic which elutes the collected negatively charged ions and replaces them with $\text{OH}^-$ ions.

Ion exchange is used in the metals and plating industries to remove trace pollutants from wastewater after a conventional system or to recover bath-solution drag-out from rinse water and to return the purified water for re-use. One example is the use of ion exchange to recover and return chromic acid to the bath. The rinses are first collected in a holding tank, where they are pumped at a constant rate through a sand filter and an activated-carbon filter. Four columns are utilized, two anion columns and two cation columns. The flow is first pumped to the cation column and then through two anion columns. The cation column is utilized to remove any heavy-metal contaminants while the anion columns remove the hexavalent chromium from the rinse water. When the first anion column has been ex-
hausted, it is removed from operation and regenerated with caustic and returned on-line as the second column. The caustic regenerant stream is now sodium chromate and is passed to the second cationic column. The sodium ions are exchanged for hydrogen ions, producing chromic acid and water, and can be returned to the bath. When the cationic columns are exhausted, they must be regenerated with caustic, with the regenerant treated for removal of heavy metals and pH adjustment.

The major disadvantage of the ion-exchange system is the need to be regenerated after exhaustion. This produces a concentrated waste stream which has to either be treated or hauled away for disposal.

**ELECTRODIALYSIS**

Electrodialysis is used to concentrate or separate ionic species in a water solution. A water solution is passed through alternately placed anionic and cationic permeable membranes with an electric potential applied across the membranes. The electric potential provides the force to enable ion migration. Therefore, there are two hydraulic circuits, one which is ion-depleted while the other is ion-concentrated. The electrical potential across the membrane determines the degree of purification/concentration needed to return the plating chemicals to the bath [2].

**LITERATURE CITED**