Membrane Filtration of Metal Plating Wastewater

A cost-effective and efficient processing solution

Overview:

A discussion of the suitability of New Logic’s patented VSEP Vibratory Membrane Filtration System in the treatment of wastewater from metal plating operations. Timely discussion covers the upcoming MP&M (Metal Plating and Manufacturing) regulations being formulated by the EPA as a result of the Clean Water Act.

Metal Plating Process:

The term electroplating means the coating of an object with a thin layer of metal by use of electricity. The metals most often used are gold, silver, chromium, copper, nickel, tin and zinc, but many others are used also. The object to be plated is usually a metal, but can be the same metal or a non-metal, such as a plastic grille for an automobile.

Electroplating usually takes place in a “tank” of solution containing the metal to be deposited on an object. This metal is in a dissolved form called ions. An ion is an atom that has lost or gained one or more electrons and is thus electrically charged. You cannot see ions, but the solution may show a certain color; a nickel solution, for example, is typically emerald green. The deposited metal, however, will be gray or silver in appearance.

When certain metallic chemicals dissolve in water, the metal atoms of these chemicals are freed to move about, but lose one or more electrons (negative charges) and, as a result, are positively charged. The object to be plated is negatively charged and attracts the positive metal ions, which then coat the object to be plated and regain the lost electrons to become metal again.

A familiar example of this process is the experiment often performed in which a key is plated with copper. The key (called the cathode) is connected to the negative terminal of a battery and is placed in a solution of vinegar, a weak acid. The positive terminal of the battery is connected to a piece of copper (called the anode—and often just a copper wire), which is placed in the solution. The acid slowly dissolves the wire, making copper ions that are then attracted to the key, regaining their lost electrons and becoming copper metal again, but now in the form of a thin coating on the key. The battery forces all this to happen and prevents the deposited copper from re-dissolving.

Rinsing Operations:

Rinsing follows many MP&M unit operations to remove dirt, oil, or chemicals (i.e., drag-out) remaining on parts or racks from a previous unit operation. Rinsing improves the quality of the surface finishing process and prevents the contamination of subsequent process baths. Rinse tank design and rinsing configuration are important factors influencing water usage. The key objectives of optimal rinse tank design are to quickly remove drag-out from the part and to disperse the drag-out throughout the rinse tank.

Rinsing operations can either be done in a single tank, a sequenced batch tank consisting of multiple rinses, or by spray rinsing. Reducing the amount of rinsewater or also reducing the amount of drag out are two ways to reduce wastewater treatment needs. Eventually the rinsewater becomes loaded with contaminants to be used and must be disposed of. Current regulations on the discharge of this rinsewater are in place and conventional treatment systems are capable of meeting these discharge limits.

New MP&M Regulations:

As mandated by the Clean Water Act recently implemented, the EPA is currently crafting new regulations on discharge from Metal Plating and Manufacturing operations. These new regulations are significantly tighter than current rules. While the EPA suggests several technologies that may be suitable, actual implementation of the treatment systems and compliance will become the responsibility of shop owners. The new regulations are currently in the comment and review stage and then will begin to be phased in starting next year.

Currently 10 metals are to be regulated. The final rules have not been made as the regulatory process is evolving. For example the EPA have decided to remove Aluminum and Iron from the regulated metals list. Current target limits for regulated metals are as follows.

Simple Plating Bath

Now look at the illustration. Positively charged copper ions are free in the solution, but are being attracted by the negatively charged key. As the ions contact the key, they regain their lost electrons and become copper metal and stick to the key wherever they touched it. This is the basic process of electroplating, and all forms of it work the same way.
Proposed EPA Regs on Discharge

<table>
<thead>
<tr>
<th>Metal</th>
<th>Symbol</th>
<th>Monthly Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>0.09 ppm</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>0.55 ppm</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>0.58 ppm</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>0.09 ppm</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>0.10 ppm</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Mo</td>
<td>0.49 ppm</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>0.64 ppm</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>0.06 ppm</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn</td>
<td>1.40 ppm</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>0.17 ppm</td>
</tr>
</tbody>
</table>

Designing to Meet MP&M Limits:

Metal finishing companies are in for a difficult time when they tackle the job of redesigning their treatment facilities to meet the proposed Metal Products and Machinery (MP&M) category limits. The published limits themselves are significantly lower than existing electroplating and metal finishing standards. However, if you are designing new or upgraded treatment processes, you must use even lower design values due to expected variability of treatment processes and other considerations. This article examines how EPA derived the proposed limits and how you can use this information to help establish your design criteria.

Standard process engineering practice dictates overdesign and redundancy. Therefore extremely low levels of these metals must be planned for in the treatment system design.

How were the limits derived?

EPA’s methodology for deriving MP&M limits is published in their MP&M Development Document.[1] The Job Shops standards cover ten metals (Cd, Cu, Cr, Pb, Mn, Mo, Ni, Ag, Sn, Zn), plus other parameters, and are based on the performance of actual treatment systems that employ a hydroxide precipitation, sedimentation treatment process, and some pollution prevention.

For each facility, EPA calculated the average daily effluent concentration of each metal during a sampling period (2-5 days). However, data from some of the ten facilities were not used in the calculation of limits. Metals data were excluded for many reasons, such as, if a particular metal was never detected in the raw wastewater for a given facility.

By using median calculations for each of the metals from 10 shops as a baseline, the result is that none of the 10 shops tested would be able to meet 100% compliance with the new regulations.

How to be sure of meeting the limits:

Companies that endeavor to be in 100% compliance cannot use the MP&M effluent limits as design or target effluent concentrations due to the documented variability treatment systems. However, if performed in reverse order, EPA’s derivation of limits provides a glimpse of what it takes to avoid any violations.

If you divide the limits by a variability factor, you arrive at a safe design level. This value is 1.2 to 5.0 times lower than the limit (it varies from metal to metal). It is important to note that EPA calculated limits independently for each metal parameter, such as cadmium, chromium, and nickel. EPA’s calculations do not take into account any influence that may exist from the presence of multiple metals in the same effluent. Since most job shops apply more than one type of metal coating and process various base metals, this will likely be problematic and as shown below, most companies will need to target effluent concentrations lower than the published new regulations. Also, most facilities will likely have to utilize more technology than identified by the EPA guidelines to achieve these limits.

The problem of multiple metals:

The facilities selected by EPA for establishing the MP&M limits would be expected to violate the MP&M limits for at least one parameter and some facilities would be expected to violate the limits up to four parameters under the new regulations.

It appears that certain combinations of metals may cause more difficulty than others. For example, all facilities had both nickel and zinc in their effluent. Of these facilities, only one was able to meet the Regs for both nickel and zinc during the brief sampling period. The nickel-zinc dilemma may be due to the fact that the pH for minimum solubility of nickel hydroxide and zinc hydroxide (formed during precipitation) are significantly different, making it technically difficult to simultaneously reduce the concentration of both metals. Other combinations of metals that appear to present problems are copper-chromium and lead-nickel.

Difficulty in Process Design

To avoid violations of the proposed MP&M limits, most job shops will need to select target concentrations below the published Regs. Due to the complexity caused by combinations of metals and to a lack of available data, it is recommended that suitable design or target concentrations be identified through pilot testing. Further, it appears that some common combinations of metals (e.g., Ni-Zn) may present a technical hurdle that cannot be solved by using the prescribed precipitation-sedimentation process. In such cases, it may be necessary to use more advanced technology.

First Things First: TSS

Since EPA may not even consider data from treatment systems that exceed 50 mg/L of total suspended solids (TSS), sample the exit of your clarification system, and have it analyzed for TSS. If your results are well under 50 mg/L, proceed to conduct the full data gathering effort...
on your wastewater to verify compliance. If the TSS is above 50mg/L, or your metals show higher levels than that shown in the new regulations, your treatment system will need to be redone.

What are your options?

Flocculation followed by Clarification -

The drawbacks with this option will be the uncertainty of the final discharge amounts of the various metals over the long term. Variations in the effectiveness of the chemical precipitation and throughput to the clarifier leave open the possibility of process upsets and fines.

Ion Exchange Resins -

An effective treatment system, but cannot handle more than 500 ppm TDS and therefore must be used in tandem with other pretreatment systems.

Conventional Membrane Systems -

Also suffer from limits on TDS, TSS, and organic constituents. Depending on the process conventional membrane systems would be a part of a multi stage treatment process. Also, crossflow systems will require high fluid velocity to avoid diffusion polarization of the membrane and consequently reduced flux. The result of this is poor % recovery of filtrate which can be sewered. The reject from conventional membrane systems could be further treated by yet another treatment process or hauled as waste. Since operating costs such as hauling are part of any equipment purchasing decisions, the % recovery with crossflow filters is not very attractive.

Vibrational Membrane System

New Logic Research manufactures a patented vibrating membrane system called VSEP (Vibratory Shear Enhanced process). The membrane filtration system can be built using one of over 200 membranes ranging from reverse osmosis to microfiltration. By using reverse osmosis membranes, VSEP is capable of molecular separation and can produce 99% rejection of multivalent ions such as Chromium and 90-95% rejection of monovalent ions. The patented vibratory process reduces the rate of fouling and overcomes the diffusion polarization problem that plagues conventional crossflow systems. In other words, VSEP allows the option for reverse osmosis membrane filtration as an effective treatment system for metal plating wastewater.

The resulting filtrate would be well below the new EPA regulations with regard to ppm amounts of metals. Using other treatment systems would involve a substantial risk that the final effluent would be off spec. That could be catastrophic if the system is installed and paid for and the new regulations have taken effect.

VSEP offers these major advantages:

- 95-98% recovery of sewerable filtrate and greatly reduced hauling costs
- VSEP can be used as the sole treatment process providing excellent simplicity
- Footprint for 30-60 gpm system is about 100 SF
- Energy consumption is about 20-25 Hp
- No chemical pretreatment or flocculation is required
- Modular units comprise the system and range in throughput from 1 gpm to 2 Million GPD
- VSEP is already proven in metals removal and industrial wastewater treatment

- There are virtually not restrictions on TSS TDS or organics for VSEP influent
Results using V_SEP

V_SEP’s Reverse Osmosis membrane module is capable of treating Metal Plating Wastewater and providing a filtrate, which is well below the new proposed MP&M regulations. The V_SEP process does not involve any chemical addition and meets the criteria of a process engineer’s needs for inline automated production. V_SEP modules containing about 1300 SF (120m2) of filtration media are modular and can be run in parallel as needed to meet any process flow requirements.

Process Description

The dirtiest “Drag-out Rinse” liquid is pumped into the V_SEP system for filtration. The viscosity of the material plays a big part in the rate of filtration. Heat will help to decrease the viscosity of the slurry and therefore improves the throughput of the V_SEP system. The Drag-out Rinse is pumped into the V_SEP Filter Pack at about 450 psi. As filtrate is removed by filtration, the contents of the filter pack are concentrated and volume reduced until the desired % recovery is reached. Each V_SEP unit can process about 39,000 gallons per day. The permeate can be sent back around as the initial rinse water or used for other purposes in the plant. The concentrate contains 5-15% of valuable metals that can be recovered using other techniques and then recycled.

When the permeate rate drops off, the Filter Pack is cleaned automatically using New Logic’s formulated membrane cleaners out of a Clean in Place tank of about 200 gallons. This is done by recirculating the cleaner with pressure and vibration to dissolve foulants that have found their way to the membrane. Months of pilot testing and also actual site conditions have shown that the membrane is able to clean up very well and the results from week to week are predictable and stable.

Typical V_SEP Performance:

<table>
<thead>
<tr>
<th>Feed</th>
<th>Permeate</th>
</tr>
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<tbody>
<tr>
<td>Nickel</td>
<td>800 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>50 mg/L</td>
</tr>
<tr>
<td>Zinc</td>
<td>100 mg/L</td>
</tr>
<tr>
<td>Copper</td>
<td>70 mg/L</td>
</tr>
<tr>
<td>Chrome</td>
<td>1500 mg/L</td>
</tr>
<tr>
<td>TSS</td>
<td>15,000 mg/L</td>
</tr>
</tbody>
</table>

System Operation:

This process is run almost completely automatically. Miscellaneous recirc lines and instrumentation are not shown for clarity. The control valves from the rinse tanks open on timed intervals or when conductivity rises. Control Valves opening initiates the feed pump at minimum frequency and gradually spins up to set point. The concentrate valve then throttles to maintain flow. Once pressure reaches 30 psi, vibration initiates. Once all other functions are operating, the throttling concentrate valve initializes to open and close at preset time intervals. Shut down reverses all these steps.

V_SEP ... A New Standard in Rapid Separation
System Components

The V♦SEP system is configurable for manual mode where the operator would initiate operating sequences, or for full automation including seamless cleaning operations with round robin cleaning or multiple units. The V♦SEP has a PLC (Programmable Logic Controller) which monitors pressure, flow rate, and frequency. It also provides the safety in operation by monitoring conditions and initiating an alarm shut down should some configurable parameters be reached. The controls include the PLC, Operator display, and process instrumentation.

Other V♦SEP Applications

Mining and chemical processing applications predominate the possible uses for V♦SEP:

- Acid Mine Drainage
- Radioactive Nuclei Removal
- Metals Removal from wastewater
- Arsenic Removal
- Titanium Dioxide Concentration
- Railcar Wash
- Calcium Carbonate Dewatering
- Product Recovery from Wastewater
- Kaolin and Bentonite Clay Concentration

Company Profile

New Logic has developed a cutting edge technology for effective membrane filtration and has provided a solution for age-old waste problems as well as new ways for chemical processing. New Logic is a privately held corporation located in Emeryville, CA approximately 10 miles from San Francisco. New Logic markets, engineers, and manufactures a membrane dewatering and filtration systems used for chemical processing, waste streams, pulp & paper processing, mining operations, and drinking water applications. The V♦SEP technology was invented by Dr. Brad Culkin in 1985. Dr. Culkin holds a Ph. D. in Chemical Engineering and was formerly a senior scientist with Dorr-Oliver Corporation. V♦SEP was originally developed as an economic system that would efficiently separate plasma from whole blood. The company received a contract to produce a membrane filtration prototype, which would later be incorporated into a blood analyzer system.

Current maximum filter size is about 2000 Square Feet per Filter Pack. These units are modular and can be used in parallel or in series. Successful V♦SEP systems are in place now world wide including Europe, Central Asia, Southeast Asia, Australia, South America, Canada, Mexico, and of course here in the United States. New Logic offers a strong engineering staff to assist customers in the design, development, and testing of their filtration systems. After outgrowing two previous locations in the last ten years, New Logic is now located in a 40,000 square foot manufacturing building in Emeryville.

The plant has extensive equipment and machinery for manufacturing nearly all the V♦SEP parts. Manufacturing, assembly, and testing of all equipment takes place at this site. Systems and procedures are in place and geared towards high standards of quality control and have met the acceptance criteria of stringent applications such as nuclear waste processing.

V♦SEP Drive System

The Filter Pack is mounted on the V♦SEP base unit and contains about 1300 SF, (120m2), of membrane area and is constructed out of high temperature materials.

The V♦SEP drive system, which supports and vibrates the Filter Pack is engineered using space age alloys and materials to withstand the applied stress from a resonating frequency of about 50 hz. Each base unit is fully stress tested and the factory prior to shipment. The V♦SEP drive system is made up of the Seismic Mass, Torsion Spring, Eccentric Bearing, and Lower Pressure Plate.

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Pilot Testing

The first step in the system design would be pilot testing for each application. During this process the appropriate membrane can be selected for filtrate that will meet the new regulations. Also, flow rates can be measured for scale up calculations and estimates of equipment sizes can be made for budgetary estimates.

For more information, you can contact New Logic’s staff of experienced Sales Engineers and Applications Specialists. While we are based in Emeryville California, we have sales offices and representatives around the world to assist you.

References:

