Metal Finishing
Wastewater Treatment

Presented by: David Calnan & CCI- A Chemical Corporation
Metal Finishing Wastewater Treatment Overview

- Why treat wastewater
- Sources of wastewater
- Waste disposal options
- Conventional on-site treatment methods
  - Physical treatment
  - Chemical treatment
- Trouble shooting
- Questions and answers
Metal Finishing WWT
Why Treat?


• Establish pre-treatment standards for industrial sources prior to treatment at publicly owned treatment works (POTW’s)
  – Prevent the introduction of pollutants into POTW’s which will interfere with the operation of the POTW or contaminate the sewage sludge;
  – Prevent the introduction of pollutants into POTW’s which will pass through the treatment works into the receiving waters or the atmosphere or otherwise be incompatible with the works; and
  – Improve the opportunities to recycle and reclaim wastewaters and the solids/sludge resulting from wastewater treatment.
Metal Finishing WWT
Why Treat?

- Publicly Owned Treatment Works (POTW) must meet strict limits for contaminants before discharging into natural water bodies.

- POTW’s are designed for residential and commercial organic waste, and minimal industrial inorganic waste.

- The EPA has given the POTW’s authority to develop by-laws regulating effluent discharges by industries.

- Not every region has the same limits and they are subject to change.

<table>
<thead>
<tr>
<th>Typical Sewer Discharge Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zinc</strong></td>
</tr>
<tr>
<td><strong>1.40 mg/L</strong></td>
</tr>
<tr>
<td><strong>Chromium (Total)</strong></td>
</tr>
<tr>
<td><strong>1.70 mg/L</strong></td>
</tr>
<tr>
<td><strong>Nickel</strong></td>
</tr>
<tr>
<td><strong>2.40 mg/L</strong></td>
</tr>
<tr>
<td><strong>Total Cyanide</strong></td>
</tr>
<tr>
<td><strong>0.50 mg/L</strong></td>
</tr>
<tr>
<td><strong>Total Phosphorus</strong></td>
</tr>
<tr>
<td><strong>10 mg/L</strong></td>
</tr>
<tr>
<td><strong>pH</strong></td>
</tr>
<tr>
<td><strong>5.5-9.5</strong></td>
</tr>
<tr>
<td><strong>Suspended Solids</strong></td>
</tr>
<tr>
<td><strong>50 mg/L</strong></td>
</tr>
</tbody>
</table>
Metal Finishing WWT Sources

• Metal finishing processes generate waste
  – Process baths age
    • Incoming oils/rust inhibitors.
    • Metal by-products sloughing off parts.
    • Secondary reactions creating contaminants.
  – Rinses contaminated with carryover
    • Solution is carried (drag out) from one tank to the next.
    • Increased demands on production increases drag out.
## Metal Finishing WWT Source Comparison Chart

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Batch Dumps</th>
<th>Rinses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical</strong></td>
<td>• Opaque</td>
<td>• Translucent</td>
</tr>
<tr>
<td></td>
<td>• 1-10% sludge</td>
<td>• Homogeneous</td>
</tr>
<tr>
<td></td>
<td>• Majority liquid</td>
<td>• 100% liquid</td>
</tr>
<tr>
<td></td>
<td>• Small Volume</td>
<td>• Large Volume</td>
</tr>
<tr>
<td><strong>Chemical</strong></td>
<td>• Aqueous</td>
<td>• Aqueous</td>
</tr>
<tr>
<td></td>
<td>• <strong>Concentrated</strong></td>
<td>• <strong>Dilute</strong></td>
</tr>
<tr>
<td></td>
<td>• Metals and/or Organics</td>
<td>• Metals and/or Organics</td>
</tr>
<tr>
<td></td>
<td>• pH 0.1-11</td>
<td>• pH 3-9</td>
</tr>
<tr>
<td><strong>Physiological</strong></td>
<td>• Corrosive</td>
<td>• Toxic</td>
</tr>
<tr>
<td></td>
<td>• Toxic</td>
<td>• Odorless</td>
</tr>
</tbody>
</table>
Metal Finishing WWT Disposal Options

• 100% removal, shipped off-site for treatment.
• Treat on-site by concentrating the contaminants and discharging wastewater in compliance with regulatory standards.

• Combination
  – Variables for consideration:
    • Frequency of disposal.
    • Cost of disposal.
    • Cost of operating treatment equipment.
    • Residual value of waste generated.
    • Floor space.
    • Capital expenditures.
Metal Finishing WWT Treatment On-Site

• The goal is to minimize/concentrate waste by rendering the majority of the wastewater suitable for sanitary disposal, and/or recycling.

• Methods of concentrating wastewater:
  – Physically, waste stays in its liquid form.
    • Single waste streams
    • Applied directly in process to extend bath life, i.e., Electro dialysis on chromate tank.
  – Chemically, wastewater changes from a liquid to a solid as a precipitate.
    • Waste streams may be combined.
    • Some streams require pre-treatment.
## Metal Finishing WWT
### On-site Treatment Comparison Chart

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1. Physical</th>
<th>2. Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Cost</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Footprint</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Operating Cost</td>
<td>Low?</td>
<td>High</td>
</tr>
<tr>
<td>Sensitivity to waste stream composition fluctuations</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Frequency of Use</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>
Metal Finishing WWT
Examples of Physical Treatment

• Ion Exchange
  – A charged media attracts contaminants and exchanges them for less toxic ions.

• Electro-dialysis
  – Ionic components are separated through a semi-permeable ion-selective membrane with the aid of electrical potential between two electrodes.

• Ultra-filtration
  – Pressure up to 100psi is applied to a solution across a porous membrane, used to remove dissolved or colloidal material.

• Reverse Osmosis
  – Water molecules are allowed to pass through a semi-permeable membrane at pressures up to 500psi, leaving dissolved salts behind.

• Evaporation
  – Drive off water using heat to reduce volume and concentrate contaminates.
Metal Finishing WWT
Chemical Treatment

• Objective
  – Chemically change the characteristics of liquid waste and allow for the simple physical removal of a sufficient amount of contaminants.

• Basics:
  – **Precipitate**: Formation of insoluble particles from dissolved materials in solution.
  – **Coagulate**: Destabilize particles in suspension to break colloidal bonds.
  – **Liquid-Solids Separation**: Micro-Filtration & Gravity settling.
Precipitation:
- Metals (+ve) Soluble metal ions are exposed to specific negative ions to form insoluble compounds:
  - Hydroxide, OH\(^-\), used frequently, price increasing.
  - Sulfides, S\(^{2-}\) Stronger bond than hydroxide
  - Carbamates, stronger bond than sulfide, toxic.
- Phosphates (-ve)
  - Soluble metal salts (Fe, Al, Ca, Mg) are added, in a specific pH range, to form insoluble precipitate with phosphate.
Metal Finishing WWT
Hydroxide Precipitation

Hydroxide Sources
- Sodium Hydroxide
- Lime
- Magnesium Hydroxide

Costs v. Sludge
- Increasing Low
- Low High
- Moderate Moderate

Hydroxide additions raise pH and increase precipitant dosage simultaneously.

\[ \text{Zn}^{2+} + 2\text{Na(OH)} \rightarrow \text{Zn(OH)}_2 + 2\text{Na}^+ \]
Limitations of Precipitation by Hydroxides:

- Hexavalent chromium and metal-cyanides require pretreatment.
- pH range, different metals precipitate at various pH levels and most are amphoteric.
- Chelation: new chelated alloy plating processes are problematic for hydroxide precipitation.
- Salts generation prevents water re-use.
- Hydrophilic sludge, sludge generated from hydroxide precipitation retains more water, even after pressing.
Metal Finishing WWT
Chemical Precipitation
Hydroxide Precipitation Chart
Metal Finishing WWT
Chemical Pre-Treatment

• Chemical Pre-Treatment:
  – Chelating agents prevent hydroxides from precipitating metals.
  – Pre-Treatment may be required.
    • Reduction, addition of electrons
    • Oxidation, removal of electrons.

• Hexavalent Chromium
  – Cr\(^{6+}\) (Hexavalent) will not precipitate as a hydroxide
  – Cr\(^{3+}\) (trivalent) will precipitate as a hydroxide.

• Cyanide
  – Cyanide complex metals will not precipitate with hydroxides, for example: CuCN\(_2\)
Metal Finishing WWT
Chemical Pre-Treatment

• Metals reduction
  – Strong reducing agents, electron donors, are used to treat Hexavalent Chromium to trivalent chromium.
  – Reducing agents are used to precipitate chelated divalent metals.

• Metals oxidation
  – Strong oxidizers, electron receivers, are used to treat cyanide to cyanate.
  – Some chelating agents may be oxidized.
Metal Finishing WWT
Common Chelating Agents

- Ammonium Chloride
- Ammonium Hydroxide
- Ammonium Bifluoride
- Acetylacetone
- Citric Acid
- Chromotropic Acid
- Cyanide
- Diethylenetriinitrilopentaacetic Acid (DTPA)
- Dimeracaptopropanol
- Dimethylglyoxime
- Dipyridyl (2,2-Bipyridine)
- Diphenylthioformic Acid
- Ethylenediamine
- Ethylenediaminetetraacetic Acid (EDTA)
- Glyceric Acid
- Hydroxyethylethlenediamin
- Methyl Ethylalamine (MEA)

- Monosodium Phosphate
- Nitrilotriacetic Acid (NTA)
- Phenanthroline
- Phosphoric Acid
- Polyethyleneimine
- Potassium Xanthate
- Rochelle Salts (potassium sodium tartrate)
- Salicylaldoxime
- Sodium Citrate
- Sodium Fluoride
- Sodium Gluconate
- Sodium Pyrophosphate
- Tartaric Acid
- Thioglycolic Acid
- Thiourea
- Triethanolamine
- Trisodium Phosphate
- Quadrol
Metal Finishing WWT
Chemical Treatment Controls

• Chemical feeds: acids, caustics, reducing agents, & oxidizers, can be controlled by the Oxidation Reduction Potential (ORP) and pH.
  – ORP probe measures mV potential of solution against noble metal electrode.
  – pH probe measures conductivity of solution against reference electrolyte.

• There is an inverse movement of 60mV for every 1.0 point change in pH.
Sulfide precipitation is used in conjunction with hydroxide precipitation.

- Reduces consumption of hydroxides.
- Generates less solid waste that de-waters easier.
- Creates a more stable solid waste that passes TCLP testing.
- Acts as reducing agent improving overall removal of metals.
- Reduces Hexavalent chromium to a trivalent chromic sulfate in one step.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hydroxide</th>
<th>Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals Removal</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>pH Range</td>
<td>Narrow</td>
<td>Wider</td>
</tr>
<tr>
<td>Reducing Agent</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Chemistry Cost</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Sludge Volume</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Sludge Corrosiveness</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Safety</td>
<td>Corrosive</td>
<td>H$_2$S Potential</td>
</tr>
<tr>
<td>Frequency of Use</td>
<td>Common</td>
<td>Rare</td>
</tr>
</tbody>
</table>
Metal Finishing WWT
Sulfide Precipitation

Sulfide Precipitation Chart
<table>
<thead>
<tr>
<th>Treatment Chemical</th>
<th>Overall Cost</th>
<th>Sludge Load</th>
<th>Toxicity Potential</th>
<th>Reduce Scale</th>
<th>Salts in Effluent TDS</th>
<th>Precipitant and Reducing Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxide</td>
<td>moderate</td>
<td>moderate</td>
<td>low</td>
<td>no</td>
<td>low</td>
<td>precipitant</td>
</tr>
<tr>
<td>Iron</td>
<td>high</td>
<td>high</td>
<td>low</td>
<td>no</td>
<td>high</td>
<td>reducing agent</td>
</tr>
<tr>
<td>Carbamates</td>
<td>moderate</td>
<td>moderate</td>
<td>highest</td>
<td>no</td>
<td>moderate</td>
<td>both</td>
</tr>
<tr>
<td>Bisulfite</td>
<td>moderate</td>
<td>moderate</td>
<td>low</td>
<td>no</td>
<td>high</td>
<td>reducing agent</td>
</tr>
<tr>
<td>Sulfide</td>
<td>moderate</td>
<td>low</td>
<td>moderate</td>
<td>yes</td>
<td>moderate</td>
<td>both</td>
</tr>
<tr>
<td>Inorganic Coagulants</td>
<td>moderate</td>
<td>high</td>
<td>low</td>
<td>no</td>
<td>high</td>
<td>no</td>
</tr>
<tr>
<td>Buffered Multi- Sulfur Program</td>
<td>low</td>
<td>yes</td>
<td>low</td>
<td>yes</td>
<td>low</td>
<td>both</td>
</tr>
</tbody>
</table>
Coagulation of Colloids and Precipitates

- Coagulation is the de-stabilization of colloidal particles.

- Colloid or Colloidal Dispersion:
  - A form of matter suspended between a true solution and a mixture.
  - Microscopic particles of one substance said to be distributed through the solvent phase of another.

- Characteristics of Colloids:
  - Sizes range from 0.001 to 1 micrometers.
  - Slow to very slow settling rate (.5m/hr – 0.5m/yr.)
  - Colloids may be colored or translucent.
Metal Finishing WWT
Chemical Treatment/Coagulation

• Types of Colloids
  – Hydrophilic colloids.
    • Responsible for coloring water.
    • Typically organic creating hydrogen bonds with water molecules.
  – Hydrophobic colloids
    • Mineral in nature
    • Negatively charged surfaces generate a mutual repulsion, making agglomeration impossible

• Elimination of Colloids: achieved by an addition of an agglomerating agent (coagulant) that neutralizes the electro-static charge.
Metal Finishing WWT
Coagulation

Coagulant Basics:

– Characteristics
  • Mineral or organic
  • Always cationic with a strong density of charge
  • Low to very low molecular weight

– Main Groups
  • Polyamines
  • PolyDADMAC
  • Metal Salts (FeCl₂, CaCl₂, PAC)
  • Organo-Metalic blends
Coagulant Basics:

- **Practical usage:**
  - **Organic coagulants** generate clear water but add little weight to the solids generated.
  - **Inorganic coagulants** generate clear water and weight, but contribute to caustic usage and sludge generation.
  - Certain waste streams will benefit from a specific blend of inorganic and organic based coagulants particular to the majority of contaminants found in the influent.

- **Overfeed:**
  - Overfeed of a coagulant will generate a very small particle size that will not flocculate. If you let a sample of the solution settle, over a long period of time a layer of clear water will appear on the top.

- **Underfeed:**
  - Underfeed of a coagulant will leave cloudy water with little defined liquid-solids separation. If you let a sample of the solution settle, no clear water will form at the top.
## Metal Finishing WWT
### Liquid Solids Separation

<table>
<thead>
<tr>
<th>Method</th>
<th>Operator</th>
<th>Sludge</th>
<th>Compliance</th>
<th>Interface</th>
<th>Generation</th>
<th>Assurance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarification</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro-Filtration</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum Filter</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td></td>
<td></td>
<td>High</td>
</tr>
</tbody>
</table>
Clarification or Gravity Settling:

- A solids loading must be maintained at proper levels:
  - Lamella recommends that 10% of the overall flow-rate be constantly drawn off the bottom of the clarifier.
  - 20% solids should be maintained in the clarifier to promote “up-flow filtration.”
    - Take a sample from the middle port/spigot on the bottom of the clarifier and let the solids settle for 2-hours. There should be approximately 20% solids by volume in the sample for proper “up-flow filtration.”

- Clarifiers can accumulate scale causing the channeling of solids that elevate TSS.
  - Sulfamic acid is recommended as a safe and economical method for removing scale from Clarifiers.
Metal Finishing WWT
Liquid-Solids Separation

Clarification or Gravity Settling requires flocculation with a high molecular weight anionic or cationic polymer.

– Polymer make-up:
  • Run the Polymer Feed Tank as low as feasibly possible.
  • Add the undiluted polymer to the mixing tank when the mixer is just covered by water, let mix for 5-10-minutes, then fill.
  • Diluted polymer should stretch between 1” and 2” before breaking.

– Polymer feed rate:
  • A sample taken from the flocculation tank should have the solids settling in a slight mound.
  • If the solids settle with a peak, or in a ball, the polymer is overfed.
    – Excess polymer generates cloudy water and wet filter press dumps.
  • If the solids settle flat, or concave, the polymer is underfed.
    – Underfed polymer increases Total Suspended Solids (TSS.)
Micro-Filtration:

- Requires superior coagulation.
  - Too large a particle will blind the membranes.
  - Too small a particle will impinge the membranes.
  - The correct particle size will slough off the membrane back to the concentration tank.

- Benefits:
  - Generates less sludge that de-waters better.
  - Reduces TSS and insures compliance.
  - Can be used before an RO to promote water re-use.
  - Overall reduced chemical costs.
Metal Finishing WWT
Liquid Solids Separation

Vacuum Filtration: requires added solids loading with an absorbent material added to filter solids/precipitate.

– No filter press is required.
– Improved organics removal.
– Frequent down-time due to loading of absorbent onto the vacuum filtration unit.
– “Ensured compliance.”
Metal Finishing WWT
De-Watering Solids

• De-Watering via Filter Press:
  – Press plates creates cavities for solids to collect and water passes through clothes on plates.
  – 20% to 40% solids are achieved.
  – Solids are shipped off-site and the water from the press is discharged back to the system or directly to drain.

• Operation of a Filter:
  – Start filtration at a low psi (20-40lbs) to create an initial layer of solids on the filter clothes.
  – When there is over 15-seconds between pump cycles, increase the pressure by another 20lbs.
  – Slowly increase the psi until the pressure is at the required level to fill the press.
  – Filling the press in this manner prevents the solids from impinging the filter clothes and retaining water in the solids.
  – Each “psi” layer acts as its own filter for the next higher psi layer.
Metal Finishing WWT
Trouble Shooting

- Excessive solids in the system
- High metals levels in the effluent
- Suspended solids in the effluent
- Cleaner & Concentrate treatments
- Ground loop faults
- Poor equalization
- Operator training/documentation
- Housekeeping
Metal Finishing WWT
Trouble Shooting

- **Excessive solids in the system:**
  - Meter in concentrates at a controlled rate.
  - Review chemical treatment program.
  - Air-sparge the system with an air lance from front to back.

- **High metals levels:**
  - Filter effluent to determine if the metals are in solution or suspended solids.
  - Check for cyanide, some plating processes generate cyanide.
  - Check pH level, there is a drop in pH when solids are removed from the system.
  - Review chemical treatment program.

- **Suspended solids:**
  - Scale in a clarifier can channel solids with hydraulic pressure.
  - Look for a vortex in the treatment tanks that will entrain air.
  - Check for leaks in pumps that will entrain air.
  - Check for oxidizers in the system.
  - Overfeeding reducing agents can mitigate this problem.
Metal Finishing WWT Trouble Shooting

• Treatment of cleaners or concentrates:
  – Some pre-treatment may allow for easier process through the WWT system.
  – Concentrates can settle in storage leaving a non-homogenous solution for feeding to the system.
  – Mixing allows for easier treatment.
    • The feed-pump can be used by installing a return line to the concentrate storage tank.
    • Mixing and pre-treatment make it easier to feed concentrates through the system.

• Ground loop faults:
  – Stray currents may interfere with the operation of meters and probes.
  – Mixers wear-out over time, and can give off a current.
  – Some tanks or mixers need to be grounded.
Metal Finishing WWT
Trouble Shooting

• Poor equalization:
  – Proper equalization reduces chemical costs and prevents “slugs” from disrupting the system.
  – EQ Tanks should be run with at 40% to 60% capacity.
  – Keeping the EQ Tank low “in case” is a “self-fulfilling prophecy.”

• Operator training/documentation:
  – If there is more than one operator, variances in treatment methods occur.
  – A standardized worksheet will generate some conformity.
  – Creating a graph that shows who is doing what and when will help manage the situation.
  – “if you can’t measure it, you can’t manage it.”

• Housekeeping:
  – Problems with plating solutions or rinses can be dumped to WWT without prior knowledge.
  – A pH chart recorder in the EQ tank can record erratic changes in the pH.
  – If there is a constant problem with unscheduled dumps, shut-off the water.