METAL INDUSTRIES

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ENVE420

Industrial Pollution Control
Metal Industries

Metal wastes include wastes from

• Refining mills
• Plating mills
• Washing
Metal Industries

**Sources**

- Wastes not only from manufacturing of steel, but from many other materials (copper and aluminium)
- Wastes from renewing surfaces on used metallic parts (such as airplane engines prior to their return to service)
- Wastes from coating of one metal with another, for protective purposes (plating of silverware or business machines)

**Waste compositions**

Various concentrations of metallic substances, acids, alkalis, and grease

**Characterized by their**

Toxicity

Relatively low organic matter

Greases
Steel-mill wastes

Mainly from:
- by-product coke
- blast-furnace
- rolling-mill
- pickling

Wastes contain:
- Cyanogen compounds
- Phenols
- Ore
- Coke
- Limestone
- Acids
- Alkalis
- Soluble and insoluble oils
- Mill scale

Treated by:
- Recirculation
- Evaporation
- Benzol extraction
- Distillation
- Sedimentation
- Neutralization
- Skimming
- Flotation
- Aeration
By-Product Coke Process

Coal is heated in the absence of air to produce coke and other products.

Process involves a gas. Further processing of the gas leads to the major wastes.

Tar and ammonia are its main constituents.

Products from burning of 1 ton of coal

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>600-700 kg</td>
</tr>
<tr>
<td>((NH_4)_2SO_4)</td>
<td>8-12 kg</td>
</tr>
<tr>
<td>Tar</td>
<td>20-45 L</td>
</tr>
<tr>
<td>Gas</td>
<td>305-320 m$^3$</td>
</tr>
<tr>
<td>Phenol</td>
<td>45-900 g</td>
</tr>
<tr>
<td>Light oil</td>
<td>7.5-11 L</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>225-545 g</td>
</tr>
</tbody>
</table>

Quench tower $\rightarrow$ hot coke is deluged with water.

Coke dust present in quenching water is called ‘breeze’.
Coking process and three major coke plant wastes
By-Product Coke Process

Analyses of by-product coke-plant wastes [1].

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Source of wastes</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ammonia still</td>
<td>Final cooler*</td>
<td>Pure still</td>
<td>Combined</td>
</tr>
<tr>
<td>BOD, 5-day, 20°C</td>
<td>3974</td>
<td>218</td>
<td>647</td>
<td>53–125†</td>
</tr>
<tr>
<td>Total suspended solids, ppm</td>
<td>356</td>
<td>125</td>
<td>97</td>
<td>89‡</td>
</tr>
<tr>
<td>Volatile suspended solids, ppm</td>
<td>153</td>
<td>14</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Organic and NH₃-N, ppm</td>
<td>281</td>
<td>14</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>NH₃-N, ppm</td>
<td>187</td>
<td>20</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Phenol, ppm</td>
<td>2057</td>
<td>105</td>
<td>72</td>
<td>6.4§</td>
</tr>
<tr>
<td>Cyanide, ppm</td>
<td>110</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>8.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*No recirculation.
†Depending on compositing technique.
‡Average of 11 daily 24-hour composites, including coke breeze.
§Single-catch sample.
By-Product Coke Process

**Waste Treatment**

Recovery and removal units with high efficiencies

**Phenol**: main contaminant recovered

BOD can be reduced by about 1/3 by the practice of recirculation and reuse of contaminated waters

**By-product recovery**: for profit in the case of such materials as ammonium sulfate, crude tar, naphthalene, coke dust, coal gas, benzene, toluene, and xylene

**Quench water**: usually settled to remove coke dust, supernatant liquor from the settling tanks is reused for quenching
By-Product Coke Process

Gravity separators: to remove free oil from the wastes from benzol stills

Final cooler water is also recirculated, to reduce the amount of phenol being discharged to waste

Phenol is recovered primarily to prevent pollution of streams and to avoid the nuisance of taste in water supplies

Phenols may be removed by either conversion into nonodorous compounds or recovery as crude phenol or sodium phenolate, which have some commercial value

**Conversion**
- **Biological** (Activated sludge or trickling filtration)
- **Physical** (ammonia-still wastes used to quench incandescent coke, a process which evaporates the NH$_3$)
By-Product Coke Process

Steam-stripping operation, followed by mixing in a solution of caustic soda and renewing pure phenol with flue gas

The Koppers dephenolization process, using steam, caustic soda, and flue gas.

Lowers the phenol content by 80 to 90 % in ammonia-still wastes
## Treatment of Three Major Wastes

<table>
<thead>
<tr>
<th>NH$_3$ Still (1)</th>
<th>Final Cooler (2)</th>
<th>Pure Still (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>3974</td>
<td>647</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>110</td>
<td>125</td>
</tr>
<tr>
<td>CN</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>281</td>
<td></td>
</tr>
<tr>
<td>Organic +</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>NH$_4$N</td>
<td>2057</td>
<td></td>
</tr>
<tr>
<td>Phenol pH</td>
<td>8.9</td>
<td></td>
</tr>
</tbody>
</table>

### Operations

1. **Recover NA phenolate with NAOH during steam distillation.**
   Phenol is subsequently obtained by passing flue gas through.

2. **Recirculate and reuse the contaminated NH$_3$ still wastewater for:**
   - (a) quenching
   - (b) water sprays for primary and final coolers

3. **Recover (NH$_4$)$_2$SO$_4$ by making acid with H$_2$SO$_4$**

4. **Biological treatment can be used to remove BOD and possibly to oxidize CN to CO$_2$ + NO.$_{2}$.**

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1. **Recirculate final cooler water.**

2. **Combine the blowdown from this cooler with residual NH$_3$ still waste and subject both to biological treatment.**

3. **Settle to remove suspended solids and free oil.**

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2. **Send supernatant (which contains some emulsified oils and BOD) to biological treatment if is a very serious consideration in ultimate disposal.**
Blast Furnace

Wet scrubbers: used for wet scrubbing of blast furnace gas downflow water sprays
It cleans the dust from the upflowing gases

It is usually the an intermediate stage between the steps below:

- dry (or cyclone) dust separation
- final electrostatic precipitation of the remaining fine particles

Gas washers or precipitators are periodically cleaned by flushing with water → adding to the flow of discolored water
Wet Scrubbers

Venturi type

Microvane type
Multi-venturi type

Dynamic type

Wet Scrubbers
Wet Scrubbers

Packed tower type
Blast Furnace

Blast furnace wet-scrubber effluent contains flue-dust solids, from washing the gas, composed of:

- iron oxide,
- alumina,
- silica,
- carbon,
- lime, and
- magnesium

The amount of each constituent, in comparison with the total quantity of dust, varies with

- type of ore used in the furnace,
- conditions of the furnace lining,
- quality of the coke used,
- number of furnaces in blast,
- amount of air being blown, and
- regularity and thoroughness of dumping and flushing of dry dust catchers
# Blast Furnace

Flue-dust content of wet-washer effluents

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value or concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended solids content</td>
<td></td>
</tr>
<tr>
<td>Range, ppm*</td>
<td>500–4500</td>
</tr>
<tr>
<td>Per cent by weight passing 100-mesh sieve</td>
<td>86–99</td>
</tr>
<tr>
<td>Per cent by weight passing 200-mesh sieve</td>
<td>74–97</td>
</tr>
<tr>
<td>Temperature, °F</td>
<td>100–120</td>
</tr>
<tr>
<td>pH</td>
<td>6–8</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3–3.8</td>
</tr>
</tbody>
</table>

*1200 ppm is average at Fairless Steel plant.

70 % Fe₂O₃ (iron oxide)
12 % Silica of the flue dust content
Blast Furnace

Waste Treatment

Treating the flue dust, sedimentation, followed by thickening the clarifier overflow with lime to encourage flocculation, has been found most effective for removing iron oxide and silica.

90-95% of the suspended matter settles readily (one hour period) resulting effluent having less than 50 ppm Suspended Solids.
Blast Furnace

Blast-furnace waste treatment process. (After Henderson and Baffa [33].)
Pickling Process

Before applying the final finish to the steel products, the manufacturer must remove

• Dirt
• Grease
• Iron-oxide scale which accumulates on the metal during fabrication

**Pickling process:**
Immersing the steel in dilute sulfuric acid (15-25% wt)

**Waste produced:**
- Pickling liquor
- Unused acid
- Iron salts of the acid (Fe$^{2+}$ and Fe$^{3+}$)

• Fresh acid reacts with the iron salts in time
• As the acid is used it becomes weaker and must be renewed
Pickling Process

Amount of waste pickling liquor per ton of steel product depends on the size and type of plant.

One factor that increases the volume is that:
Since the steel products must be rinsed in water after they leave the pickling tank to remove all trace of acid, the rinse or wash water eventually becomes quite acidic and must also be discarded.

The volume of rinse water is 4-20 times that of the actual pickling liquor, although naturally it is far more dilute.

Pickling liquor:
- 0.5 to 2.0 % $\text{H}_2\text{SO}_4$ and
- 15 to 22 % $\text{FeSO}_4$

Wash water:
- 0.02 to 0.5 % $\text{H}_2\text{SO}_4$ and
- 0.03 to 0.45 % $\text{FeSO}_4$
Pickling Process

For most small steel plants, the recovery of by-products from waste pickling liquor is not economically feasible and they neutralize the liquor with lime.

Some companies obtain by-products:

- FeSO$_4$.H$_2$O
- H$_2$SO$_4$
- Fe$_2$(SO$_4$)$_3$
- Fe$^{3+}$
- Iron powder
- Fe$_3$O$_4$ for polishing or pigments
- Al$_2$(SO$_4$)$_3$

Neutralization of pickle-liquor waste with lime is costly, because
- there is no saleable end-product and there is a voluminous,
- slow settling sludge which is difficult to dispose of
Pickling Process

Blaw-Knox-Ruthner process for recovery of acid from spent pickle liquor:
(a) process flow diagram; (b) chemistry of process. (Courtesy Blaw-Knox Co.)
Pickling Process

HCl can be used instead of H$_2$SO$_4$

Benefits of HCl pickling are:
• Easier regeneration of acid
• No over pickling
• More flexibility on the line
• Elimination of the secondary scale breaker
• Higher pickling speeds
• 20% reduction in wastewater volume

Disadvantage:
Increased cost of HCl over H$_2$SO$_4$
Other Metal-Plant Wastes

Processors of several other metals besides steel are significant waste contributors.

Among these are:

- brass,
- copper,
- gold, and
- aluminium plants,

which are similar to steel mills in that impure metal is purified, worked and fabricated into final usable products.
*Raw material as mined

FeS₂-10-15% androsite (Al₂(SiO₃)₂) mainly CuS CuS₂ CuO CuFeO Calcoprite 4-5%

Old FeSO₄ oxidized waste 1 + Na₂CO₃ + SnCO₃

SO₂ + H₂O

H₂S₃O₆ + SO₂

H₂SO₄

Soluble CuSO₄ 15% of original copper in ore

+ Grinding + 15#/ton ore H₂SO₄ slaking

Cement Cu metal + FeSO₄ + Water wash + screening

Scrap iron

unused scrap

+ Acid FeSO₄ + Cu sludge

Copper 68% sold to refiners

Dried Settle

Insoluble Cu solids 85% of original copper in ore

Wash water + Classified

Slimes -325 mesh pH 2.8

Sand + 325 mesh -48 mesh + Lime

Pine Oil

Alkaline liquid gauge Ca(OH)₂ CaSiO₃ Fe₂SiO₃

+ CuS float + Floation

Grinding at pH 11

Cu precipitate 22% Cu 35% S 12% moisture

Oliver filter

Acid liq. and solid gauge Na₂CaSiO₃ Fe₂SiO₃

Waste 2

Waste 3

New Cyprus Mining Company copper mining and concentrating wastes.

*Previous ore was both richer in Cu and FeS so that pyrites could be recovered from gange and sold for acid (sulfuric) manufacturing.

Present market is poor for H₂SO₄ from pyrites because of abundance obtained from both natural gas and petroleum waste sour gas.
Metal-plating Wastes

After metals have been fabricated into the appropriate sizes and shapes to meet customers’ specifications, they are finished to final product requirements.

Finishing usually involves stripping, removal of undesirable oxides, cleaning and plating.

In plating, the metal to be plated acts as the cathode while the plating metal in solution serves as the anode.

Total liquid wastes from plating are not voluminous, but are extremely dangerous because of their toxic content.

The most important toxic contaminants are acids and metals, such as chromium, zinc, copper, nickel, tin, and cyanides.

Alkaline cleaners, grease, and oil are also found in the wastes.
Sulfuric acid anodizing
Phosphoric acid anodizing
Three typical processes

**Baths**
- STRIPPING: Solutions of acids $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, $\text{HCl}$, $\text{HF}$
- CLEANING: Organic Solvents & Wetting Agents
- PLATING: Solutions of the metal to be plated

**Wastes**
- Acids are used to remove dirt and oxide deposits from metal surfaces to ensure proper conditions for plating
- Organic solvents for removing oil and grease
- Metal salts e.g. chromic acid, cadmium oxide or copper cyanide

Wastes from these three processes are mainly composed of cyanides, chromates, acids, and alkalies.
Characteristics of metal-plating wastes

Most **stripping baths** are **acidic** in nature and consist of solutions of **sulfuric**, **nitric**, and **hydrochloric acid**, but **alkaline** baths containing **sodium sulfide**, **cyanide**, and **hydroxide** may also be used.

Usually the chemicals in the stripping solution are present in concentrations less than 10%.

**Cleaning** is carried out by **organic solvents**, **pickling**, or **alkaline cleaning compounds**.

Organic-emulsion cleaners are petroleum or coal-tar solvents coupled with an emulsifier.

Alkaline cleaners consist of sodium hydroxide, ortophosphate, complex phosphates, silicates, carbonates, some organic emulsifiers, and synthetic wetting agents.
Characteristics of metal-plating wastes

Cyanide salts are desirable, since they are good oxide solvents and in zinc plating they yield a brighter, less porous, galvanized plate

However, acid zinc sulfate is also being used in plating baths because it is said to conduct the current with less resistance than zinc cyanide

The total volume of wastes from metal-plating plants, usually expressed as gallons per finished number of metallic units, varies even more than the characteristics

Since most plants use excessive chromates for plating, the concentration of chromium in chromium-plating bath waste will usually be several times the concentration of other metals in other baths
<table>
<thead>
<tr>
<th>Bath formulas</th>
<th>Metallic + cyanide concentrations, ppm</th>
<th>Rinse concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.5 gph drag-out*</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>40 oz/gal nickel sulfate</td>
<td>82,000 Ni</td>
<td>171 Ni</td>
</tr>
<tr>
<td>8 oz/gal nickel chloride</td>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>6 oz/gal boric acid</td>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>53 oz/gal chromic acid</td>
<td>207,000 Cr</td>
<td>431 Cr</td>
</tr>
<tr>
<td>0.53 oz/gal sulfuric acid</td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Copper (acid)</td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>27 oz/gal copper sulfate</td>
<td>51,500 Cu</td>
<td>107 Cu</td>
</tr>
<tr>
<td>6.5 oz/gal sulfuric acid</td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Copper (cyanide)</td>
<td></td>
<td>CN</td>
</tr>
<tr>
<td>3.0 oz/gal copper cyanide</td>
<td>12,400 Cu</td>
<td>2.8 Cu</td>
</tr>
<tr>
<td>4.5 oz/gal sodium cyanide</td>
<td>28,000 CN</td>
<td>58 CN</td>
</tr>
<tr>
<td>2.0 oz/gal sodium carbonate</td>
<td></td>
<td>CN</td>
</tr>
<tr>
<td>Copper (pyrophosphate)</td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>4 oz/gal copper (as proprietary mix)</td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>29 oz/gal sodium pyrophosphate</td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>0.4% ammonia (by volume)</td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Cadmium</td>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>3.5 oz/gal cadmium oxide</td>
<td>23,000 Cd</td>
<td>48 Cd</td>
</tr>
<tr>
<td>14.5 oz/gal sodium cyanide</td>
<td>57,700 CN</td>
<td>120 CN</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>8 oz/gal zinc cyanide</td>
<td>33,800 Zn</td>
<td>70 Zn</td>
</tr>
<tr>
<td>5.6 oz/gal sodium cyanide</td>
<td>48,900 CN</td>
<td>102 CN</td>
</tr>
<tr>
<td>10 oz/gal sodium hydroxide</td>
<td></td>
<td>CN</td>
</tr>
<tr>
<td>Brass</td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>4 oz/gal copper cyanide</td>
<td>21,000 Cu</td>
<td>44 Cu</td>
</tr>
<tr>
<td>1.25 oz/gal zinc cyanide</td>
<td>5,250 Zn</td>
<td>11 Zn</td>
</tr>
<tr>
<td>7.5 oz/gal sodium cyanide</td>
<td>47,500 CN</td>
<td>99 CN</td>
</tr>
<tr>
<td>4 oz/gal sodium carbonate</td>
<td></td>
<td>CN</td>
</tr>
<tr>
<td>Tin (alkaline)</td>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>16 oz/gal sodium stannate</td>
<td>53,000 Sn</td>
<td>110 Sn</td>
</tr>
<tr>
<td>1 oz/gal sodium hydroxide</td>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>2 oz/gal sodium acetate</td>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>Silver (cyanide)</td>
<td></td>
<td>Ag</td>
</tr>
<tr>
<td>4 oz/gal silver cyanide</td>
<td>24,600 Ag</td>
<td>51 Ag</td>
</tr>
<tr>
<td>4 oz/gal sodium cyanide</td>
<td>21,800 CN</td>
<td>45 CN</td>
</tr>
<tr>
<td>6 oz/gal sodium carbonate</td>
<td></td>
<td>CN</td>
</tr>
</tbody>
</table>

*Drag-out is the amount of solution carried out of the bath by the material being plated and the racks holding the material. Rinse rate is assumed to be 4 gpm.
## Flow chart for some common plating baths

<table>
<thead>
<tr>
<th>Copper plating</th>
<th>Nickel plating</th>
<th>Chrome plating</th>
<th>Zinc plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrocleaner (cathodic)</td>
<td>Electrocleaner (cathodic)</td>
<td>Electrocleaner (cathodic)</td>
<td>Electrocleaner (cathodic)</td>
</tr>
<tr>
<td>Running rinse →</td>
<td>Running rinse →</td>
<td>Running rinse →</td>
<td>Running rinse →</td>
</tr>
<tr>
<td>Hydrochloric acid dip (5%)</td>
<td>Running rinse →</td>
<td>Sulfuric acid dip</td>
<td>5% sulfuric acid dip</td>
</tr>
<tr>
<td>Running rinse →</td>
<td>5% sulfuric acid dip</td>
<td>Running rinse + spray →</td>
<td>Running rinse →</td>
</tr>
<tr>
<td>Copper cyanide “strike”</td>
<td>Running rinse →</td>
<td>Chrome solution</td>
<td>Zinc cyanide solution</td>
</tr>
<tr>
<td>Running rinse →</td>
<td>Bright nickel solution</td>
<td>Recovery rinse</td>
<td>Running rinse →</td>
</tr>
<tr>
<td>Running rinse →</td>
<td>Running rinse →</td>
<td>Mist spray rinse</td>
<td>Spray rinse →</td>
</tr>
<tr>
<td>Copper pyrophosphate solution</td>
<td>Soap dip</td>
<td>Running rinse →</td>
<td>Brightener still dip (HNO₃)</td>
</tr>
<tr>
<td>Running rinse →</td>
<td>Hot running rinse →</td>
<td>Hot still dip</td>
<td>Running rinse →</td>
</tr>
<tr>
<td>Hot rinse (slow overflow) →</td>
<td>Drying oven</td>
<td>Running rinse →</td>
<td>Running rinse →</td>
</tr>
<tr>
<td>Drying oven</td>
<td></td>
<td>Hot rinse (slow overflow) →</td>
<td>Drying oven</td>
</tr>
</tbody>
</table>

*Flow sheets for common types of conveyorized electroplating. (Wastes overflowing to final effluent are indicated by an arrow.)*
Plating-waste concentrations

<table>
<thead>
<tr>
<th>Plant</th>
<th>pH</th>
<th>Cu, ppm</th>
<th>Fe, ppm</th>
<th>Ni, ppm</th>
<th>Zn, ppm</th>
<th>Chromium, ppm</th>
<th>Cu, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.2</td>
<td>16</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>A</td>
<td>10.4</td>
<td>19</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>4.1</td>
<td>58</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td>204</td>
<td>246</td>
</tr>
<tr>
<td>C</td>
<td>2.8</td>
<td>11</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>D</td>
<td>2.0</td>
<td>300</td>
<td>10</td>
<td>0</td>
<td>82</td>
<td>555</td>
<td>612</td>
</tr>
<tr>
<td>E</td>
<td>2.4</td>
<td>35</td>
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<td>F</td>
<td>10.7</td>
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<tr>
<td>G</td>
<td>11.3</td>
<td>18</td>
<td>18</td>
<td>26</td>
<td>39</td>
<td>36</td>
<td>39</td>
</tr>
</tbody>
</table>
Treatment of metal-plating wastes

The methods used for disposal of waste from plating operations can be divided into two classes:

(1) Modifications in design and/or operation within the manufacturing process to minimize or eliminate the waste problem

(2) Installation of a chemical (sometimes physical) treatment plant to destroy or remove toxic and objectionable materials in plating-room effluents
Treatment of metal-plating wastes

Modifications include

(1) Installing a gravity-fed, nonoverflowing emergency holding tank for toxic metals and their salts
(2) Eliminating breakable containers for concentrated material
(3) Designing special drip pans, spray rinses, and shaking mechanisms
(4) Reducing spillage, drag-out leak to the floor, or other losses, by curbing the area and discharging these losses to a holding tank
(5) Using high-pressure fog rinses rather than high volume water washes
(6) Reclaiming valuable metals from concentrated plating-bath wastes
(7) Evaporating reclaimed wastes to desired volume and returning to plating bath at rate equal to loss from bath
(8) Recirculating wet-washer wastes from fume scrubbers
Treatment of metal-plating wastes

Treatment of plating wastes by chemical and physical means are designed primarily to accomplish three objectives: Removal of

- Cyanides
- Chromium
- All other metals, oil and greases

Treatment of cyanides

1. Chlorination (gas)
2. Hypochlorites
3. ClO₂
4. O₃ (ozonation)
5. Conversion to less toxic cyanide complexes
6. Electrolytic oxidation
7. Acidification
8. Lime-sulfur method
9. Ion exchange
10. Heating to dryness

Treatment of cyanides is mostly accomplished by alkaline chlorination
Continuous chlorination of cyanide wastes.
Batch chlorination of cyanide wastes

Chlorine → Chlorinator → Caustic feeder → Caustic storage

Chlorine-solution line

Concentrated cyanide solutions → Agitator → Mixing and retention

Sludge disposal

Pump

Treated waste to sewer
Treatment of metal-plating wastes

Chromium-bearing plating wastes are normally segregated from cyanide wastes, since they must be reduced and acidified (to convert the hexavalent chromium to the trivalent stage) before precipitation can occur.

Although it is possible to precipitate the chromium directly in the hexavalent form with barium chloride, this method is not widely used.

Removal of other metals such as Cu, Zn, Ni, Fe, and greases is usually accomplished by neutralization followed by chemical precipitation.
Treatment of metal-plating wastes

Sufficient alkalinity, usually Ca(OH)$_2$ or NaOH, is added prior to chlorination to bring the waste to a pH of about 11, thus ensuring the complete oxidation of cyanide.

\[
2\text{NaCN} + 5\text{Cl}_2 + 12\text{NaOH} \rightarrow \text{N}_2 + 2\text{Na}_2\text{CO}_3 + 10\text{NaCl} + 6\text{H}_2\text{O}.
\]

Violent agitation must accompany the chlorination, to prevent the cyanide salt of sodium or calcium from precipitating out prior to oxidation.

Presence of other metals may also interfere with cyanide oxidation, because of the formation of metal cyanide complexes.

Extended chlorination may be necessary under these conditions. Sometimes a full 24-hour chlorination period may be required for complete oxidation.
Treatment of metal-plating wastes

Chromium reduction and precipitation:

Chromium-plating-waste treatment by reduction and precipitation involves reducing the hexavalent chromium (Cr$^{6+}$ as chromic acid or chromates) in the waste to the trivalent stage (Cr$^{3+}$) with reducing agents such as FeSO$_4$, SO$_2$, or NaHSO$_3$.

Sufficient free mineral acid should also be present to combine with the reduced chromium and to maintain a residual pH of 3.0 or lower, which will ensure complete reaction.

When the reduction is complete, an alkali (usually lime slurry) is added, to neutralize the acid and precipitate the trivalent chromium.

\[
\begin{align*}
\text{H}_2\text{Cr}_2\text{O}_7 + 6\text{FeSO}_4 + 6\text{H}_2\text{SO}_4 &\rightarrow \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O}, \\
\text{Cr}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 &\rightarrow 2\text{Cr(OH)}_3 + 3\text{CaSO}_4, \\
\text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 &\rightarrow 2\text{Fe(OH)}_3 + 3\text{CaSO}_4.
\end{align*}
\]
Reduction and precipitation of chromium.
Treatment of metal-plating wastes

**Neutralization**

Treatment of other metal, oil, and grease-bearing wastes by neutralization and precipitation usually involves recombining the wastes with previously oxidized cyanide and reduced chromium wastes for subsequent and final treatment.

If the combined waste is acid, an alkali (usually 5 to 10% lime slurry) is added to neutralize and precipitate the metals.

The floc produced is large and quite heavy, and hence the velocity of flow is decreased after adequate flocculation has occurred.

Waste is then allowed to settle. Sludge is removed and usually lagooned, since this is the most economical treatment for the slow-drying metal sludges.
(a) Acid neutralization

(b) Continuous acid neutralization

(b) Batch acid neutralization
Treatment of metal-plating wastes

Recovery

Recovery practices are mainly those involving ion exchange and evaporation.

Use of ion exchanger is only an application of water-softening methods, and its best application is in the treatment of rinse water following plating operations, so that little or no foreign contamination other than the recoverable metal is present.

Rinse water is passed through beds of cationic and anionic resins selected for the particular application, and the deionized water is recycled through the rinse tank.
Treatment of metal-plating wastes

Recovery

Ion beds must be regenerated periodically. The regenerating solution containing the concentrated metal salts may require further treatment prior to its reuse in plating operations.

Chrome, nickel, and copper acid-type plating solutions may be reclaimed from the rinse tank by evaporation, the concentrated solution is then returned to the plating systems.
Chrome purifier and recovery system.
Overall Process of a Metal Finishing Plant

- Chrome Bath
- Rinse Tank
- Filtration
- Amberlyst 16Wet
- Amberlyst A21
- Amberlyst 16Wet
- HCl Regen.
- NaOH Regen.
- HCl Regen.

To Chemical Treatment
1 g/L Ca\(^{2+}\), 1 g/L Na\(^+\), 5 ppm Zn\(^{2+}\), 5 ppm Ni\(^{2+}\), 2 ppm Cu\(^{2+}\), pH: 7, 20 BV
Chromic acid recovery by vacuum evaporation

Chromic acid recovery by vacuum evaporation:

- **Still dip rinse**
- **Still (steam jacket)**
- **Separator**
- **Condenser**
- **Ejector (vacuum supply)**
  - Steam
  - Cooling water
- **Distilled water receiver**
- **Concentrated chromic acid returns to plating tank**
- **Reused for rinse or solution makeup**
114 m$^3$/d of a waste containing 49 mg/L Cr$^{6+}$, 11 mg/L Cu, and 12 mg/L Zn is to be treated daily by using SO$_2$.

Compute the chemical requirements and the daily sludge production

(assume the waste contains 5 mg/L O$_2$)
EXAMPLE 4.2. 30,000 gal/d (114 m³/d) of a waste containing 49 mg/l Cr⁶⁺, 11 mg/l Cu, and 12 mg/l Zn is to be treated daily by using SO₂. Compute the chemical requirements and the daily sludge production. (Assume the waste contains 5 mg/l O₂.)

Solution.

(a) SO₂ requirements are as follows. For Cr⁶⁺

\[
1.85 \left( \frac{\text{mg SO}_2}{\text{mg Cr}^6+} \right) \times 49(\text{mg Cr}^6+/1) \times 8.34 \left( \frac{\text{lb/million gal}}{\text{mg/l}} \right) \\
\times 0.03 \text{ million gal/d} = 22.7 \text{ lb/d} \quad (10.3 \text{ kg/d})
\]

and for O₂, where 1 part of O₂ requires 4 parts of SO₂:

\[
4 \left( \frac{\text{mg SO}_2}{\text{mg O}_2} \right) \times 5(\text{mg O}_2/1) \times 8.34 \times 0.03 = 5.0 \text{ lb/d} \quad (2.3 \text{ kg/d})
\]

Total = 27.7 lb/d \quad (12.6 \text{ kg/d})

(b) Lime requirements are as follows. For Cr³⁺:

\[
2.38 \left( \frac{\text{mg lime}}{\text{mg Cr}^3+} \right) \times 49 \times 8.34 \times 0.03 = 29.2 \text{ lb/d} \quad (13.3 \text{ kg/d})
\]

and for Cu and Zn (each part of Cu and Zn requiring 1.3 parts of 90 percent lime for precipitation):

\[
1.3 \left( \frac{\text{mg lime}}{\text{mg Cu or Zn}} \right) \times 23(\text{mg Cu and Zn/1}) \times 8.34 \times 0.03 = 7.5 \text{ lb/d} \quad (3.4 \text{ kg/d})
\]

Total = 36.7 lb/d \quad (16.7 \text{ kg/d})
(c) Sludge production is:

\[
1.98 \left( \frac{\text{mg Cr(OH)\textsubscript{3}}}{\text{mg Cr}^{6+}} \right) \times 49 \times 8.34 \times 0.03 = 24.3 \text{ lb/d Cr(OH)\textsubscript{3}} \quad (11 \text{ kg/d})
\]

\[
1.53 \left( \frac{\text{mg sludge}}{\text{mg Cu or Zn}} \right) \times 23 \times 8.34 \times 0.03
\]

\[
= 8.8 \text{ lb/d Cu(OH\textsubscript{2}) and Zn(OH\textsubscript{2})} \quad (4 \text{ kg/d})
\]

Total = 33.1 lb/d \quad (15 \text{ kg/d})

If the sludge concentrates to 1.5 percent by weight, the volume that will require disposal each day can be calculated as follows:

\[
\frac{33.1 \text{ lb/d}}{0.015 \text{ lb solids/lb sludge} \times 8.34 \text{ lb/gal}} = 265 \text{ gal/d} \quad (1.0 \text{ m}^3/\text{d})
\]

It should be noted that some of the copper and zinc will be soluble unless the final pH after lime addition exceeds pH 9.0.
A general plating plant operates 16 h/d, 5 d/week. The total discharge of rinsewaters has the following characteristics:

- Copper: 22 mg/L as Cu
- Zinc: 10 mg/L as Zn
- Nickel: 15 mg/L as Ni
- Chromium: 130 mg/L as CrO₃

Rate of flow is 0.19 m³/min, and in-plant separation is not feasible. Design an exchanger system to include water and chromium recovery.

### Operating characteristics of the ion exchanger:

<table>
<thead>
<tr>
<th></th>
<th>Exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>Anion</td>
</tr>
<tr>
<td>Regenerant</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
</tr>
<tr>
<td>Dosage, kg/m³</td>
<td>192</td>
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<tr>
<td>Concentration, %</td>
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</tr>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Flow rate, m³/min.m³</td>
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<tr>
<td>Operating capacity</td>
<td>1.5 eg/L</td>
</tr>
<tr>
<td></td>
<td>60.8 kg CrO₃/m³</td>
</tr>
</tbody>
</table>
Example 9.1. A general plating plant operates 16 h/d, 5 d/week. The total discharge of rinsewaters has the following characteristics:

- Copper: 22 mg/l as Cu
- Zinc: 10 mg/l as Zn
- Nickel: 15 mg/l as Ni
- Chromium: 130 mg/l as CrO₃

The rate of flow is 50 gal/min (0.19 m³/min), and in-plant separation is not feasible. Design an exchanger system to include water and chromium recovery. The operating characteristics of the cation exchanger are given in Table 9.3.

Solution.

Anion exchanger
In the anion exchanger, CrO₃ is exchanged for OH.

\[
130 \text{ mg/l} \times 50 \text{ gal/min} \times 60 \text{ min/h} \times 16 \text{ h/d} \times 8.34 \times 10^{-6} \text{ lb/gal/mg/l} = 52 \text{ lb/d}
\]

For a resin capacity of 3.8 lb CrO₃/ft³ at a regeneration level of 4.8 lb NaOH/ft³ and a daily regeneration,

\[
\text{Volume of resin} = \frac{52}{3.8} = 13.7 \text{ ft}^3 \quad (0.39 \text{ m}^3)
\]

Treatment flow rate is 3.6 gal/(min · ft³) [0.48 m³/(min · m³)], for a resin depth of 30 in (0.76 m), 2 units, 2 ft (0.61 in) diameter by 30 in (0.76 in) deep, plus 50 percent for bed expansion.
Regeneration

NaOH required = 4.8 × 13.7 = 66 lb/reg (30 kg/reg)

<table>
<thead>
<tr>
<th></th>
<th>Exchanger</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cation</td>
<td>Anion</td>
</tr>
<tr>
<td>Regenerant</td>
<td>H₂SO₄</td>
<td>NaOH</td>
</tr>
<tr>
<td>Dosage, lb/ft³</td>
<td>12</td>
<td>4.8</td>
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<tr>
<td>Concentration, %</td>
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<td>10</td>
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<tr>
<td>Flow rate</td>
<td>0.5 gal/(min · ft³)</td>
<td>3.8 lb CrO₃/ft³</td>
</tr>
<tr>
<td>Operating capacity</td>
<td>1.5 equiv wt/l</td>
<td></td>
</tr>
</tbody>
</table>

*Note:*
lb/ft³ = 16.0 kg/m³
gal/(min · ft³) = 0.134 m³/(min · m³)
Regenerant tank volume = 66 lb NaOH $\times \frac{1}{0.10} \times \frac{1}{9.6}$ lb reg/gal

= 68 gal (0.26 m$^3$)

Rinse requirement at 100 gal/ft$^3$ = 1370 gal (5.2 m$^3$)

**Cation exchanger**

The cations to be removed are:

\[
\begin{align*}
\text{Zn} & \quad \frac{10 \text{ mg/l}}{32.7 \text{ mg/meq}} = 0.306 \text{ meq/l} \\
\text{Cu} & \quad \frac{22 \text{ mg/l}}{31.8 \text{ mg/meq}} = 0.693 \text{ meq/l} \\
\text{Ni} & \quad \frac{15 \text{ mg/l}}{29.4 \text{ mg/meq}} = 0.511 \text{ meq/l}
\end{align*}
\]

In the cation unit, Cu, Zn, and Ni are exchanged for H$^+$. 
The total daily equivalents are
\[(0.306 + 0.693 + 0.511) \times 10^{-3} \times 50 \times 60 \times 16 \times 3.78 \text{ l/gal} = 273 \text{ equiv wt/d} \]

For an operating capacity of 1.5 equiv wt/l at a regeneration level of 12 lb H₂SO₄/ft³ (5 percent), the resin required for a 2-d regeneration is
\[
\frac{273 \times 2}{1.5 \times 28.3 \text{ l/ft³}} = 13.0 \text{ ft³ resin} \quad (0.36 \text{ m³})
\]

The treatment flow rate is 3.8 gal/(min · ft²) [0.51 m³/(min · m²)]. Use 2 units, 2 ft (0.61 m) diameter by 30 in (0.76 m) deep plus 50 percent for bed expansion.

**Regeneration**
Using 5 percent H₂SO₄ at 12 lb/ft³, H₂SO₄ required is
\[12 \times 13 = 156 \text{ lb} \quad (71 \text{ kg})\]

Regenerant tank = \[156 \times \frac{1}{0.05} \times \frac{1}{1.0383 \times 8.34 \text{ lb/gal}}\]
\[= 360 \text{ gal} \quad (1.36 \text{ m³})\]

where 1.0383 is the specific gravity of 5% H₂SO₄.
Rinse requirement = 120 gal/ft\(^3\) \times 13 \text{ ft}^3 = 1560 \text{ gal} \quad (5.9 \text{ m}^3)

Anion regenerant capacity for chromium recovery:

\[
\text{Sodium} = \frac{66 \text{ lb NaOH} \times 453 \text{ g/lb}}{40 \text{ g/equiv wt}} = 750 \text{ equiv wt}
\]

If it is assumed that 70 percent of anion exchanger regenerant will pass through the cation unit, 525 equiv wt must be exchanged, which is compatible with the capacity of the cation units.
A wastewater has a flow of 10 000 L/d containing 130 mg/L CN⁻

Compute the Cl₂ requirement for the alkaline chlorination of this wastewater for CN⁻ removal

(a) Consider oxidation to CNO⁻
(b) Consider complete oxidation to HCO₃⁻ and N₂
EXAMPLE 10.2. How much Cl$_2$ must be supplied to oxidize 130 mg/l cyanide (as CN) given a flow of 10,000 l/d?

(a) Consider oxidation to CNO$^-$.
(b) Consider complete oxidation to HCO$_3^-$ and N$_2$.

First, consider that Cl$_2$ reacts with water to produce HOCl and HCl:

$$\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{HCl}$$

Therefore, only half of our chlorine is effective. Next, all calculations must be done on a molar basis, or molecular weight of CN = 12 + 14 = 26 g/mole. Then

$$\frac{130 \text{ mg/l cyanide}}{(26 \text{ g/mole})(1000 \text{ mg/g})} = 5.0 \times 10^{-3} \text{ M}$$

Solution.

(a) Combine Reactions 1 and 2 [Eqs. (10.10a) and (10.10b)] to give an overall reaction of CN$^-$ to CNO$^-$:

Reaction 1 + Reaction 2 = CN$^-$ + OCl$^- \rightarrow$ CNO$^-$ + Cl$^-$

Therefore, 1 mole of OCl$^-$ is required for each CN$^-$:

$$5 \times 10^{-3} \text{ MCN}^- \left( \frac{1 \text{ mole OCl}^-}{1 \text{ mole CN}^-} \right) = 5 \times 10^{-3} \text{ M OCl}^- \text{ required}$$

$$= \text{ stoichiometric dosage}$$

$$5 \times 10^{-3} \text{ M Cl}_2 \text{ required}$$
Finally, for a 10,000 l/d flow:

\[
(5 \times 10^{-3} \text{ mole Cl}_2/\text{l})(10,000 \text{ l/d}) = 50 \text{ moles Cl}_2/\text{d}
\]

then \( \text{Cl}_2 = 71 \text{ g/mole} \), or

\[
\frac{(50 \text{ moles Cl}_2/\text{d})(71 \text{ g/mole})}{1000 \text{ g/kg}} = 3.55 \text{ kg Cl}_2/\text{d}
\]

and, since dosage is 1 to 2 times stoichiometric, depending on the metal complexed with \( \text{CN}^- \) (see Table 10.5), the actual required dose = 3.55 to 7.10 kg Cl\(_2\)/d.

(b) Consider Reaction 3 [Eq. (10.10c)]:

\[
\text{ZCNO}^- + 3\text{HOCl} \rightarrow 2\text{HCO}_3^- + \text{N}_2 + 3\text{Cl}^- + \text{H}^+
\]

Note that 3 moles HOCl produced per 2 moles CNO\(^-\) and 1 mole CNO\(^-\) produced per mole CN\(^-\) are initially present (100 percent conversion). Therefore,

\[
5 \times 10^{-3} \text{ McNO}^- = \left( \frac{3 \text{ moles HOCl}}{2 \text{ moles CNO}^-} \right)(10,000 \text{ l/d}) \left( \frac{71 \text{ g/mole}}{1000 \text{ g/kg}} \right) = 5.33 \text{ kg Cl}_2/\text{d}
\]

and the total requirement is step 1 + step 2, or

\[
\text{Cl}_2 = (3.55 \text{ to } 7.10 \text{ kg/d}) + 5.33 \text{ kg/d} = 8.88 \text{ to } 12.43 \text{ kg Cl}_2/\text{d}
\]