Wastewater Treatment: Reducing Salts Generated During Treatment to Promote Water Re-Use

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Objective

• Cost-effective effluent recovery utilizing chemical pre-treatment to minimize Salts & Total Dissolved Solids (TDS) generation

Basics

• Precipitate: Form insoluble particles in wastewater
• Coagulate: Eliminate colloidal particle dispersion
• Separate: Remove solids from effluent
Precipitation

• Exposing soluble metal ions to specific negative ions forming insoluble compounds
  • Hydroxide: OH\textsuperscript{−} used frequently; price increasing.
  • Sulfides: S\textsuperscript{2−} Stronger bond than hydroxide; H\textsubscript{2}S Potential
  • LIME, precipitates negative valence ions like Phosphate; adjusts pH, also a coagulant
Hydroxide Precipitation Chart

The chart displays the relationship between pH units and metal concentration (mg/L) for various metals: Fe³⁺, Cr, Cu, Zn, Ni, Pb, Ag, and Cd. The x-axis represents pH units ranging from 2 to 12, and the y-axis represents metal concentration ranging from 0.01 to 100 mg/L. The lines indicate the pH at which each metal begins to precipitate as a hydroxide.
Limitations of Hydroxide Precipitation

Hydroxides raise pH and increase precipitant dosage

- \( \text{Zn}^{2+} + 2\text{Na(OH)} \rightarrow \text{Zn(OH)}_2 + 2\text{Na}^+ \)

- Excessive salts generated – high TDS
- Metals precipitate at different pH levels; “amphoteric”
- Chelation: E-Nickel, E-Copper, chelated-alloys (ZnNi)
- Generates hydrophilic sludge
- Hexavalent chromium/metal-cyanides require pre-treatment
Chebrate (Greek for “CLAW”)

• Polydentate organic-ligands prevent hydroxides from precipitating metals

Alternative Treatments may be required:

Metals reduction:

• Strong reducing agents, electron donors, are used to precipitate divalent metals

Chelant oxidation:

• Strong oxidizers, electron receivers, are used to destabilize chelating agents
Common Chelants

- Ammonium Chloride
- Ammonium Hydroxide
- Ammonium Bifluoride
- Acetylacetone
- Citric Acid
- Chromotropic Acid
- Cyanide
- Diethylenetriaminepentaacetic Acid
- Dimeracaptopropanol
- Dimethylglyoxime
- Dipyridyl (2,2-Bipyridine)
- Diphenylthioformic Acid
- Ethylenediamine
- Ethylenediaminetetraacetic Acid (EDTA)
- GLUCANATE
- Hydroxyethyl ethylenediamin
- 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 Pyrophosphate
- Tartaric Acid
- Thioglycolic Acid
- Thiourea
- Triethanolamine
- Trisodium Phosphate
- Quadrol
Sulfide Precipitation

• Stronger reductant than hydroxide
• Treats the metal, not the chelant
• Precipitates Hexavalent Chromium
• Generates fewer salts
• Less hydrophilic sludge; better de-watering
• Generated sludge passes TCLP (Total Contaminants Leaching Potential) testing
Sulfide Precipitation Chart

- Cu
- ZnS
- CdS
- PbS
- Ag₂S

Legend:
- Metal sulfide

Concentration of dissolved metal (mg/L)

pH

10⁻²
10⁻¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
Sulfide and Chromium

Chromium reduction - Hexavalent to Trivalent (below)
Trivalent chromium precipitates as chromium hydroxide
[Cr(OH)3]

\[
\text{Cr}^{+6} + 1.5\text{CaS}_2\text{O}_3 + 1.5\text{H}_2\text{O} \rightarrow \text{Cr}^{+3} + \text{CaSO}_4 + 1.5\text{S} + 3\text{H}^+ 
\]

- \text{Cr}^{+6} = \text{Hexavalent Chromium}
- \text{CaS}_2\text{O}_3 = \text{Calcium Polysulfide}
- \text{Cr}^{+3} = \text{Trivalent Chromium}
- \text{CaSO}_4 = \text{Calcium Sulfate}
- \text{S} = \text{Sulfur}
- \text{H}^+ = \text{Hydrogen Ion}
Fenton Reaction

• Oxidize non-cyanide (Organic) chelants at a low pH using iron, peroxide, and acid

• H.J.H Fenton discovery (1894); used to oxidize/treat organic water pollutants - phenols, formaldehyde, BTEX, pesticides, etc.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}\cdot + \text{OH}^- 
\]

• Hydroxyl generated is a powerful, non-selective oxidant

• Oxidizes the highly water soluble salt sodium-Orthophosphite to form Orthophosphate.

\[
\text{HO}\cdot + \text{PO}_3 = \text{PO}_4^{3-}
\]
Lime Precipitation

One Calcium Ion with Two Hydroxyl Ions

- Reduces Sodium Hydroxide Consumption
- Reduces Sulfates in the Effluent - $\text{CaSO}_4$
- Treats Gluconates
- Precipitates Fluorides
- Removes Phosphates - $\text{Ca}_3(\text{PO}_4)_2$
Solubility Rules

Greater than 0.1 mole/Liter = Soluble
Between 0.1 and 0.01 mole/Liter = Slightly Soluble
Less than 0.01 mole/Liter = Insoluble

• Sodium, potassium, and ammonium salts are soluble
• Nitrates, acetates and perchlorates are soluble
• Most chlorides, bromides and iodides are soluble
• Sulfides, oxides and hydroxides are insoluble
• All sulfates are soluble except barium and CALCIUM

Calcium Sulfate $\text{CaSO}_4 \ 9.1 \times 10^{-6}$
Coagulation

Adding agglomerating agents (coagulants) de-stabilizes colloidal particles

Colloidal Dispersion:
Intermediate form of matter (suspended microscopic particles) between a true solution and a mixture

Types of Colloids:
• Hydrophilic organic - responsible for coloring water
• Hydrophobic mineral - negatively charged surfaces;

Mutual repulsion prevents agglomeration
Coagulants

Mineral or organic; always cationic; strong charge density; very low molecular weight

Organic “polymers”:
• Expensive; lower dosage rates
• Minimize caustic consumption = lower TDS
• Does not generate sludge nor promote settling

Inorganic “metal salts”:
• Inexpensive; higher dosage rates
• Contribute to caustic usage = higher TDS
• Generates sludge and promotes settling

Most waste streams benefit from a blend
SLUDGE DENSIFICATION

• Generates dense, less gelatinous precipitate with superior handling and disposal properties

• Requires slurry recycling to incrementally adjust pH

• Allows for lower saturation ratio of OH ions

• Provides seed crystals for secondary nucleation

• Sludge return increases the reaction rate

• Improves yield of ALL chemicals employed
Reaction Rate

Low concentration = Few collisions

High concentration = More collisions
STEPS FOR WATER RE-USE

• Oxidation of Non-Cyanide Chelants

• Reduction of Metals

• Neutralización

• Liquid-Solids Separation

• Reverse Osmosis.
OXIDATION

• First Treatment Tank/EQ
  - Combine non-cyanide waste streams
  - Mix with air or return line on transfer pump

• Peroxide:
  - Feed using ORP or by volume
  - Spent chrome as an oxidizer

• Acid:
  - pH below 4.5
  - Spent Acid

• Iron:
  - If required
  - Blended chelant treatments are available
METALS REDUCTION

• Second Treatment Tank/pH 1

• pH between 3 and 7

• Solids Return at 10% of the overall flow rate

• Lime for pH adjustment (50ppm by weight)

• Sulfide for metals precipitation and chrome reduction
NEUTRALIZATION

• Sodium Hydroxide is fed to maintain a pH between 8.8 and 10.0

• A filtered sample from Neutralization determines effectiveness of overall metals removal

• Pre-Floc is formed; or, low molecular weight cationic coagulant is required

• Clarity of settling determines coagulant dosage
SOLIDS SEPARATION

Gravity Settling

• **Increased use** of inorganic TDS-generating coagulants
• High molecular weight polymers **add TDS**
• Post-clarification filtration may be required
• **Latex-based polymers yield lower residual TDS**

Micro-Filtration

• **Reduced use** of inorganic TDS-generating coagulants
• **Lower TSS** = Better overall metals removal
• Higher water recovery possible.
REVERSE OSMOSIS

• Reverse Osmosis (RO) may be used to remove the remaining salts in the effluent

• Reduced TDS chemical pre-treatment will allow for 50% to 90% recovery of wastewater

• Reject from RO (Concentrated Brine) may be suitable for discharge; or evaporated for Zero Liquid Discharge” ZLD”
REVERSE OSMOSIS
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<th>Ion</th>
<th>PRE</th>
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<th>CCI</th>
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<th>POST</th>
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<td>Permeate</td>
<td>PERMIT</td>
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<td>Cd</td>
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## Chemical Cost Comparison

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<th>Chemical</th>
<th>Current</th>
<th>Proposed</th>
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<tbody>
<tr>
<td></td>
<td>Cost Per L/Kg</td>
<td>Units Per Year</td>
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<td>Caustic Soda</td>
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<td>Emulsion Polymer</td>
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### TDS Program

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<tr>
<th>Chemical</th>
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<tr>
<td></td>
<td>Cost Per L/Kg</td>
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<td>Hydrogen Peroxide</td>
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### Chemical Costs

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<td><strong>Cost Per Tonnes</strong></td>
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<tr>
<td><strong>Annual Cost</strong></td>
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| Disposal Cost          | $60.00  | 240      | $14,400 |
|                        |         | 160      | $9,600  |

**Total Cost of Current Program** $99,846

**Total Cost of Proposed Program** $84,562

**Estimated Annual Savings** $15,284
THANK YOU

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