SHORT COURSE: MINE WATER TREATMENT TECHNOLOGIES, CASE STUDIES, AND COSTS

ESTABLISHED TREATMENT TECHNOLOGIES:
SULFATE, CYANIDE, SELENIUM
AND WASTE STREAM MANAGEMENT

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ACKNOWLEDGMENTS

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SULFATE TREATMENT
CHEMICAL TREATMENT

• Overview:
  • Chemical addition to precipitate sulfate compounds:
    • Lime – gypsum precipitation
    • Aluminum salt – ettringite precipitation
    • Barium salt – barium sulfate precipitation
  • Process equipment required
    • Chemical feed systems
    • Reaction tanks
    • Clarifier
  • Process flow schemes – LDS and HDS
  • Sludge management
    • Thickening and dewatering
CHEMICAL TREATMENT

- Lime addition to precipitate sulfate in the form of gypsum CaSO₄. 2H₂O
  - Most common type of sulfate treatment
  - Amount of sulfate removal limited to gypsum solubility of particular site water ~ 1,600 mg/l - 2,000 mg/l SO₄

- Lime can be added as
  - Limestone, CaCO₃
  - Calcium oxide (quicklime), CaO
  - Calcium hydroxide (slaked lime), Ca(OH)₂
  - Hydrated lime (quicklime + water)

- Soda Ash (Na₂CO₃) may also be required to balance precipitation reaction
CHEMICAL TREATMENT

• Lime precipitation accomplished using two standard approaches:
  • Low density sludge (LDS) – easily applied
  • High density sludge (HDS) – can only be used in certain water chemistries
CHEMICAL TREATMENT

- Lime precipitation-low density sludge

Diagram:

- Alkali Source
- Wastewater
- Neutralization Tank
- Clarifier
- Treated Effluent
- Sludge Underflow (Continuous)
- Sludge to Dewatering Facilities (Intermittent)
CHEMICAL TREATMENT

• Lime silos and solids contact clarifiers

Butte, Montana, USA
Superior, Arizona, USA
CHEMICAL TREATMENT

- Chemical mixing tanks
CHEMICAL TREATMENT

- Lime precipitation using HDS
  - Waste stream must have an acidic pH (less than 6 S.U.)
  - Waste stream must contain soluble metals
  - Primary metals: iron, chromium, zinc, copper, nickel or aluminum
  - Control pH to minimize conventional precipitation
  - Applicable for CaCO3 and CaSO4 precipitation
CHEMICAL TREATMENT

- Lime precipitation - high density sludge (HDS)

Alkali source → Sludge Conditioning Tank → Neutralization Tank → Clarifier → Treated Effluent

Wastewater

Sludge Underflow (Continuous)

Sludge to Dewatering Facilities (Intermittent)
CHEMICAL TREATMENT

- HDS process chemistry fundamentals
  - Acid neutralization and metal precipitation
  - Formation of soluble hydroxo complex ions under high alkaline pH condition, when lime/caustic is added to the precipitated sludge.
  - Adsorption of the charged species onto solid surface
  - Reaction between the adsorbed charged species and hydronium ions in water, forming stable metal oxide or oxyhydroxide
CHEMICAL TREATMENT

- Scanning electron micrographs (SEM) of conventional and densified sludge
CHEMICAL TREATMENT

• 17 Grams of DENSE Sludge

17 Grams of Conventional Sludge
## CHEMICAL TREATMENT

<table>
<thead>
<tr>
<th>Process Variable</th>
<th>Conventional</th>
<th>Dense Sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dewatered Sludge (% solids)</td>
<td>25 – 35</td>
<td>50 – 70</td>
</tr>
<tr>
<td>Clarifier Underflow (% solids)</td>
<td>2 – 4</td>
<td>20 – 30</td>
</tr>
<tr>
<td>Dewatering Time (hours)</td>
<td>2 – 3</td>
<td>0.5 – 1</td>
</tr>
<tr>
<td>Sludge Blanket Level (feet)</td>
<td>5 – 7</td>
<td>1 – 2</td>
</tr>
</tbody>
</table>
CHEMICAL TREATMENT

• Ettringite precipitation (SAVMIN™)
  • Aluminum added to water to form ettringite (calcium aluminum sulfate, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O)
  • Reaction at pH 11-13
  • Feasible for SO₄ < ~1,800 mg/l (gypsum solubility)
  • Sulfate removal to ~10’s mg/l - 000’s mg/l SO₄

• Aluminum form can be:
  • Aluminum hydroxide (Gibbsite), Al(OH)₃
  • Aluminum ion, Al⁰
  • Calcium aluminate
CHEMICAL TREATMENT

- Ettringite Crystals In Ettringite Reactor
CHEMICAL TREATMENT

- SAVMIN™ four-stage process (Lorax, 2003):

  ![Process flow diagram]

  - Ettringite slurry is destabilized with H₂SO₄ to produce gypsum and regenerate aluminum hydroxide.
CHEMICAL TREATMENT

- Ettringite precipitation with Gibbsite recovery
  - Aluminum recovered from Ettringite sludge and recycled to front end of process
- Recovered aluminum sludge sample
CHEMICAL TREATMENT

• Barium sulfate precipitation
  • Barium salt in form of:
    • Ba(OH)₂ – effective at wide pH range
    • BaCO₃ – less effective
    • BaS – effective at wide pH range
    • BaCl – reportedly used
  • Sulfate reduced to ~200 mg/l in effluent
  • BaSO₄ sludge produced – can be dewatered
  • Barium salts are expensive – therefore not widely used
    • Barium sludge can be recycled to reduce costs through production of elemental sulfur (in itself an expensive process)
CHEMICAL TREATMENT

- Barium sulfate precipitation (from Lorax, 2003)
  - Thermal reduction of \( \text{BaSO}_4 \rightarrow \text{BaS} \)
  - Recycling BaS
  - \( \text{H}_2\text{S} \) stripping
  - \( \text{H}_2\text{S} \) oxidation \( \rightarrow \) elemental S
CHEMICAL TREATMENT PROS/CONS

Advantages
• Broad industrial base, including in mining & minerals
• Can be adapted to remove other contaminants (silica, phosphates)
• Can achieve significant TDS removal, depending on the water chemistry
• Ettringite precipitation can be “tuned” to meet required sulfate limits
• Potential alternative to thermal treatment for brine management

Disadvantages
• Large chemical demand and corresponding waste solid disposal issues
• Most effective when [Ca] and [SO₄] are equivalent
FILTRATION

• Overview:
  • Not a stand-alone sulfate removal process
  • Particulate (total suspended solids, TSS) removal from clarifier overflow downstream of chemical precipitation
  • Required upstream of membrane-based sulfate removal
  • Filter backwash waste stream- solids need a home
  • Process equipment required
    • >1 µm: granular media filters (sand, anthracite, garnet)
    • 0.05 – 1 µm: micro filtration (MF),
    • 0.005 – 0.1 µm: ultra filtration (UF)
FILTRATION

• Granular media filter bank
Filtration

- Membrane filter skids
ION EXCHANGE

• Overview:
  • Ions displaced from insoluble ion exchange material by sulfate ions in water
  • Reversible process – regeneration
  • IX medium can be solid resins or liquid (LLX)
  • IX configurations:
    • Stand-alone IX
    • Downstream of chemical treatment for polishing
  • Brine regenerant to be managed
ION EXCHANGE

• How it works:
  • Resins are placed in reactor tanks or fluidized bed reactors to react with sulfate in feed water
  • Once resins reach the exchange capacity the resins are regenerated to their original condition with acids or bases
  • IX produces a brine containing sulfate ions removed from resin and unused regenerant solution
Loading Resins
- Cations removed from feed water by exchange with strong-acid cation resin (R-H)
- Alkalinity removed in degassing tower
- SO4 removed by weak-base anion resin (R-OH)

Regenerating Resins
- Sulphuric acid and Ca(OH)2 used to strip cation & anion resins
- Produces a gypsum slurry waste product
  Sulfate reduced < 50 mg/L

(Lorax, 2003)
ION EXCHANGE

- Ion exchange bank
ION EXCHANGE

Advantages

• Less pretreatment needed than with RO/NF
• More selective than RO
• Can achieve low sulfate limits
• High recovery (90-95%)
• Predictable performance
• Some proprietary technologies may yield a marketable product

Disadvantages

• Very limited in mining applications
• Large chemical demand
• IX yields a liquid waste brine requiring management
• Resin scaling, clumping, poisoning, attrition
PHYSICAL SEPARATION

- Overview:
  - Membrane separation
    - Microfiltration (MF)
    - Ultrafiltration (UF)
    - Nanofiltration (NF)
    - Reverse osmosis (RO)
PHYSICAL SEPARATION FILTRATION SPECTRUM

Micron = $1/1,000,000$ meter = $1/1,000$ millimeter = $0.001$ mm = $\mu$m
PHYSICAL SEPARATION
MEMBRANE BASICS

- Pressure-driven process
- Impurities/water
- Filtration Process
  - Microfiltration (MF)
  - Ultrafiltration (UF)
  - Nanofiltration (NF)
- Diffusion Process
  - Reverse Osmosis (RO)
PHYSICAL SEPARATION
MICROFILTRATION, ULTRAFILTRATION, & NANOFILTRATION

- MF
  - 0.05 – 1.0 μm

- UF
  - 0.005 – 0.1 μm
  - 1,000 – 500,000 MWCO

- NF
  - 0.001 – 0.01 μm
  - 200 – 10,000 MWCO
  - Divalent ions (Calcium)
  - “Softening membranes”

Cross section of UF membrane magnified 500 times.
PHYSICAL SEPARATION
CHOICE OF CONFIGURATION

• Spirals for low fouling process separation
  • Relatively low capital cost
• Hollow Fiber for raw water clarification and relatively low TSS
• Hollow Fiber less expensive than tubular
• Tubular for high TSS or emulsified oils
• Immersion / Vacuum used for biological processes (MBR) and growing
• Ceramics for high heat and where chemical resistance is important in process and cleaning
PHYSICAL SEPARATION
TUBULAR MF/UF
PHYSICAL SEPARATION
HOLLOW FIBER UF DESIGN

• ID of fibers typically 0.5 - 1.2 mm. (0.02 - 0.047 inch)
• Several thousand fibers bundled into a membrane element
• End of fibers cast in epoxy
• Spiral wound module

The permeate is drained spirally towards the centre.
• The RO elements are made in different sizes: 4”, 8”, 16”, 18” diameter and 40” or 60” long.
• RO’s typically use 8” x 40”.
• Membranes connected together in pressure vessels or housings typically made of fiberglass but can be stainless steel.
• Housings are supported by a structural frame along with instruments and electrical control panels.
PHYSICAL SEPARATION
EQUIPMENT DESIGN
2 X 34 M³/HR. RO
PHYSICAL SEPARATION
RO EQUIPMENT DESIGN

- **Flux Rate**: Flow rate through the membrane per unit time
  - **GFD**: Gallons per square foot per day
  - **LMH**: Liters per square meter per hour

- Clean waters are designed for higher flux rates and dirty waters for lower flux rates
PHYSICAL SEPARATION
FLUX

- The higher the flux, the more rapid the membrane fouling
- Reduce fouling by:
  - Reducing the flux
  - Increasing cross-flow velocity
  - Reducing feedwater foulants
  - Altering chemical nature of foulants
  - Calcium Sulfate scaling potential and foulants
## Physical Separation Equipment Design

<table>
<thead>
<tr>
<th></th>
<th>Waste Water</th>
<th>Surface</th>
<th>Well</th>
<th>RO Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SDI</strong></td>
<td></td>
<td>&lt;5</td>
<td>&lt;3</td>
<td>&lt;1</td>
</tr>
<tr>
<td><strong>Flux (GFD)</strong></td>
<td>5-8</td>
<td>8-14</td>
<td>14-18</td>
<td>20-30</td>
</tr>
</tbody>
</table>
SDI is a method to determine the relative amount of silt or other foulants in a water.

Water is directed through a 0.45 micron filter paper at a constant pressure of 30 psig, and the time to fill 500 mls is measured at the start and then again after 15 minutes.

A formula is used and a number from 0 to 6.7 is calculated for a 15 minute SDI.

SDI is a measurement prediction but it is not an ABSOLUTE fouling indicator.
Two-Stage Membrane, 75% Recovery

1st Stage

2nd Stage

Permeate 75 gpm

Concentrate 25 gpm

4:2 Array

PHYSICAL SEPARATION
EQUIPMENT DESIGN

PHYSICAL SEPARATION EQUIPMENT DESIGN

Three-Stage Membrane, 88% Recovery

PHYSICAL SEPARATION
RO PROJECTION SOFTWARE

- ROSA by Dow Filmtec
  - www.dowwaterandprocess.com
  - More sophisticated
  - Crown typically uses ROSA and Dow RO membranes
- IMSDesign by Hydranautics
  - www.membranes.com
  - Easier to use
- RO PRO by Koch Membranes
  - www.kochmembrane.com
- TorayDS by Toray
  - www.toraywater.com
BIOLOGICAL TREATMENT

• Overview:
  • Two step process
  • Biological reduction
  • Residual forms
  • Reagent addition
  • Process schemes
  • Solids management
BIOLOGICAL TREATMENT

- Two step process to removal sulfur from system
- Typically applied to sulfate concentrations < 2000 mg/L
- Requires multiple ancillary processes
BIOLOGICAL TREATMENT

- Step 1- Biological reduction
  - Conversion of sulfate to sulfide by sulfate reducing bacteria (SRB)

Acceptors + Donors

- Conditions needed:
  - Sulfate reducing bacteria (SRB)
  - Acceptable pH
  - Donor
    - Direct- H₂, acetate, ethanol, lactate (only SRB required in reactor)
    - Indirect- glucose, cellulose, molasses, woodchips, hay, manure
      (fermentative bacteria required to convert organic matter to acceptable donor for SRB)
BIOLOGICAL TREATMENT

• Step 2 in the process defines solid residual forms:

  • Metal sulfides:
    • Sulfide can be combined with metals to form metal sulfides, thus both the metal and sulfide are removed from solution.
    • Depends on the availability of a source of metals
    • Management of metal sulfide sludge required

  • Elemental sulfur:
    • Sulfide can be oxidized to elemental sulfur via chemical or microbial catalyst.

• Both inorganic residuals forms may be produced at a single site

• Bacteria produced during process are another residual to manage
BIOLOGICAL TREATMENT

- Reagent addition
  - Donor:
    - $\text{H}_2$
    - Acetate
    - Ethanol
    - Molasses
    - Woodchips/hay/manure
  - pH adjustment (if needed):
    - Limestone
    - Lime
    - Sodium hydroxide
    - Sodium carbonate
BIOLOGICAL TREATMENT

- Active schemes
  - Bioreduction with metal precipitation using gas contactor (e.g., THIOTEQ™ Metal)

Feed water with sulfate and metals

Metal sulfides

Solids separation

Treated water

Sulfide gas + metals

Sulfide gas

Sulfate reducing bioreactor

Donor (H₂/organics)

Water with sulfate

Sulfide gas + metals

Feed water with sulfate and metals

Treated water
BIOLOGICAL TREATMENT

- Active schemes
  - Bioreduction with metal precipitation reaction in single reactor

Feed water with sulfate and metals → Sulfate reducing bioreactor → sulfide + metals → Solids separation → Metal sulfides → Treated water

Donor (H₂/organics)
BIOLOGICAL TREATMENT

- Active schemes
  - Bioreduction with metal sulfide in single reactor and elemental sulfur production
  
  e.g., SULFA TEQ™
BIOLOGICAL TREATMENT

- Passive schemes for biological sulfate removal
  - Uses reactions as active systems for removal

- Volumetric sulfate reduction rate limited
- Sulfate removal is typically a secondary effect of metal removal as sulfide, extent depends on metal amount present
- Control of elemental sulfur production difficult
- Sulfate removal not historical focus

BIOLOGICAL TREATMENT

- Passive schemes for biological sulfate removal
  - Constructed/Compost wetlands
  - Sulfate reducing bioreactors (solid organic)
  - Sulfate reducing bioreactor (liquid organic)
  - Permeable reactive barriers
BIOLOGICAL TREATMENT

- Solid waste management
  - Metal sulfide sludge
    - Sludge must be dewatered for disposal
    - Cost of disposal depends on metal content
  - Elemental sulfur
    - Elemental sulfur must be dewatered and dried for beneficial use
  - Bacterial solids
    - Bacterial solids must be dewatered for disposal
    - Cost of disposal depends on metal content
  - Spent cellulose based materials
    - Cellulose based materials must be managed for disposal
    - Cost of disposal depends on metal content
CYANIDE TREATMENT
CYANIDE TREATMENT

• Overview
  • Cyanide complexity
  • Sources
  • Chemistry
  • Analytical
  • Treatment
CYANIDE TREATMENT

• Cyanide complexity
  • Cyanide forms complex with 28 elements
  • About 72 metal-cyanide complexes exist
  • Cyanide dissolves gold and silver by forming complexes
  • Also forms complexes with other metals [Hg, Zn, Cu, Fe, Ni, etc.]
    • This increases cyanide consumption
CYANIDE TREATMENT

• Cyanide sources
  • Waste barren solution
  • Leached tailings slurry
  • Slurry from flotation process waste streams contain:
    • Free cyanide, metal-cyanide complexes of copper, iron, nickel, zinc, etc.
    • Reaction product of sulfur and cyanide (S$_2^-$, S$_2$O$_{3}^{2-}$, SCN-, CNO-, NH$_3$, etc)
    • Arsenic, antimony, molybdenum, silica
## Cyanide Treatment

### Analyses of Barren Solutions and Tailings Pond Effluents

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Barren Solution</th>
<th>Tailings Pond</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>70 - 90</td>
<td>0.3 - 30</td>
</tr>
<tr>
<td>Fe</td>
<td>10 - 40</td>
<td>0.3 - 8.5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.5 - 10</td>
<td>0.1 - 2.0</td>
</tr>
<tr>
<td>Zn</td>
<td>12 - 85</td>
<td>0.2 - 1.0</td>
</tr>
<tr>
<td>Cu</td>
<td>6 - 300</td>
<td>0.3 - 16</td>
</tr>
<tr>
<td>As</td>
<td>-</td>
<td>0.01 - 30</td>
</tr>
<tr>
<td>SCN</td>
<td>40 - 400</td>
<td>-</td>
</tr>
</tbody>
</table>

All values in mg/l; data from six mine sites
• Cyanide chemistry (in a brief summary)
  • Free CN: ionic cyanide (CN-) released from simple and complex cyanides by dissociation
  • Exists in two forms: CN ion (CN-) and HCN (HCN → H+ + CN-)
    • HCN is a weak acid; pKa = 9.31 (200°C)
  • Relative portion of HCN & CN- depends on pH and temperature
    • pH < 7.5 – Cyanide exists as HCN (>99%)
    • pH > 10.5 – Cyanide exists as CN- (>99%): Found in process slurry waste or Barren Solution
CYANIDE TREATMENT

• Cyanide chemistry (continued)
  • General Formula: AaM(CN)b
    • A: Alkali metal ion (Na/K), a: # of cations
    • M: Transition metal (Fe, Cu, Co, Ni, Au, Ag, etc)
    • b: # of cyanide group
  • Alkali metal-cyanide dissociates in water and generates complex radical ion [Fe(CN)63-]
    • Complex radical ions are very stable and highly soluble
    • Zinc and cadmium form the weakest complex
    • Silver and copper are moderately strong
    • Iron, cobalt, and gold are the strongest complex

• Suggested reading: Mudder, et. al., 2001
CYANIDE TREATMENT

• Analytical Methods
  • Total Cyanide: Measured by Reflux Mineral Acid distillation method. Includes complex iron-cyanide, WAD, free cyanide, and other inorganic complexes
  • Amenable Cyanide: Difference between total CN before and after chlorination
  • Weak-Acid-Dissociable Cyanide (WAD): Distillation method as Total Cyanide but weak acid is used. Includes CN ion, HCN, and some complexes (cadmium, copper, nickel, silver, and zinc)
  • Free Cyanide: Titration with AgNO₃, ion specific electrode, Solvent extraction or sparging HCN and collecting it for subsequent cyanide analysis. Includes CN⁻ and HCN
CYANIDE TREATMENT

- Analytical methods (continued)
  - Interferences:
    - Oxidizing agents, sulfides, SCN, nitrite and nitrate, carbonates, sulfates, and other sulfur compounds, and metals
CYANIDE TREATMENT

- Treatability testing – word of caution
  - CN concentrations in water samples can rapidly change due to volatile and complexing nature of CN
  - Perform treatability testing at or near source location if at all possible; otherwise testing may not be representative of actual conditions
• Treatment Methods
  • Natural degradation: volatilization/biodegradation/oxidation/dilution
  • Oxidation processes: chlorination/ozonation/hydrogen peroxide/INCO Process [SO₂ + air]
  • Acidification and stripping with reneutralization (cyanide removal and recovery)
  • Adsorption process: activated carbon/IX
  • Precipitation by metal-cyanide complexation reaction
  • Evaporation
  • Biological
**CYANIDE TREATMENT**

- **Oxidation Treatment – Chlorination**
  - Removes Free and WAD Cyanide under alkaline conditions
  - Cyanide can be partially or fully oxidized
  - \( \text{CNCl} \) is volatile at \( \text{pH} < 8 \), and extremely toxic.
  - Slow kinetics at \( \text{pH} < 8 \). Fast kinetics at \( \text{pH} 10 \) to 10.5 (completed within 15 minutes)
  - **Chlorination must be done in COVERED TANK with VENT**
  - Reaction rate increases with increase in temperature
  - Does not remove stable iron and cobalt cyanide complex
**CYANIDE TREATMENT**

**Chlorination Advantages**

- Well established process; process control is reliable
- Free and WAD forms of CN, as well as SCN are oxidized
- Easy availability of chlorine/hypochlorite
- Adaptable to continuous or batch operation
- Ammonia generated can be removed

**Chlorination Disadvantages**

- High concentration of CN and SCN, chlorine consumption high
- Process pH, ORP, and chlorine dosage must be controlled
- Doesn’t remove iron complex cyanide
- End products contain free chlorine and chloramines
CYANIDE TREATMENT

- Oxidation with Peroxide
  - $\text{H}_2\text{O}_2$ destroys $\text{CN}^-$, $\text{HCN}$, weak complex of (Cu, Ni, Zn, and Cd) cyanide
  - Effective in presence of catalyst (Cu$^{2+}$)
    - Soluble Cu$^{2+}$ can be present from extraction or be added

- Two Step Reaction
  - (1) $\text{CN}^- + \text{H}_2\text{O}_2 \rightarrow \text{CNO}^- + \text{H}_2\text{O}$ [alkaline pH: 9.0 – 9.5]
  - (2) $\text{CNO}^- + 2\text{H}_2\text{O}$ (Hydrolysis) + $\text{H}^+$ $\rightarrow$ $\text{NH}_4^+$ + $\text{HCO}_3^-$ [pH < 7]

- Doesn’t oxidize iron-cyanide complex, but precipitates as copper-iron-cyanide complex
• Oxidation with ozone
  • Ozone destroys: CN-, HCN, WAD (complex of Zn, Cd, and Cu), and SCN
  • Two step reaction
    • (1) CN- + O3 → CNO- + O2 [Fast: 10 – 15 Minutes]
    • (2) 2CNO- + O3 → N2 + 2HCO3 [slow reaction]
    • Reaction pH: 8 - 11
  • Does not oxidize iron cyanide complex
  • Combination of O3/UV completely oxidizes iron cyanide (Expensive)
CYANIDE TREATMENT

**INCO SO$_2$ Oxidation**
- Oxidizes free and complex cyanides (except Fe(CN)$_6^{4-}$)
- Iron complex cyanide is removed as insoluble zinc/copper ferrocyanide [Cu$_2$Fe(CN)$_6$ or Zn$_2$Fe(CN)$_6$]
- CN$^- + O_2 + SO_2 + H_2O = CNO^- + H_2SO_4$ (Cu$_2+$ catalyst)
- Reaction pH: 9 – 9.5
- SO$_2$: 2.5%
- Copper: 50 mg/l
- Kinetics: Rapid (10 minutes)
CYANIDE TREATMENT

- Iron-cyanide precipitation
  - Source: tailings pond water
  - $\text{Fe}^{3+} + 6\text{CN}^- \rightarrow \text{Fe}([\text{CN}]_{6}^{3-} \rightarrow \text{Fe}([\text{CN}]_{6}^{4-})$
    - Very stable and highly soluble
    - Usually exists as both forms
  - Precipitates as a highly insoluble iron-ferro/ferri cyanide complex
    - $4\text{Fe}^{2+} + 3\text{Fe}([\text{CN}]_{6}^{4-} \rightarrow \text{Fe}_4[\text{Fe}([\text{CN}]_{6}]_{3(s)} \text{ [Prussian Blue]}
    - $\text{Fe}^{3+} + \text{Fe} ([\text{CN}]_{6}^{3-} \rightarrow \text{Fe}_2([\text{CN}]_{6})_{6(s)} \text{ [Berlin Green]}
  - Optimum reaction pH: 6.5 – 7.0
  - Fe : CN =9:1 to 30:1
  - Reaction Time: 10 min (without free CN) and 40 min (with free CN)
  - Need to remove excess Fe$^{2+}$ by aeration and precipitation at pH >7.0
  - Need a very reliable clarifier for solid/liquid separation
  - All tanks must be covered with vent for SAFETY
CYANIDE TREATMENT

- Cyanide treatment using membranes
  - Water recovery, Cl, SO4, and TDS removal
  - RO membrane rejects: CN- and ferro/ferri cyanide complex [Fe(CN)64-]
  - Does not reject HCN; need to convert HCN to CN-
  - Feed water pH must be alkaline for CN-
  - % rejection of CN- : 90 to 95%
  - % rejection of ferro/ferri cyanide Fe(CN)64- : >99%
  - Cyanide is concentrated in brine; need to manage the brine
## COMPARISON OF DIFFERENT PROCESSES FOR CYANIDE REMOVAL FROM GOLD MILL EFFLUENT

<table>
<thead>
<tr>
<th>Process</th>
<th>CN-/HCN</th>
<th>Zn/Cd Complex</th>
<th>Cu/Ni complex</th>
<th>Fe(CN)₆ complex</th>
<th>SCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Deg.</td>
<td>Yes</td>
<td>partial</td>
<td>No</td>
<td>No</td>
<td>partial</td>
</tr>
<tr>
<td>Acid/Strip/abs.</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>partial</td>
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<tr>
<td>Chlorination</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>No</td>
<td>yes</td>
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<tr>
<td>Ozone</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>with UV</td>
<td>yes</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>yes</td>
<td>yes</td>
<td>partial</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>GAC</td>
<td>No</td>
<td>partial</td>
<td>yes</td>
<td>yes</td>
<td>No</td>
</tr>
<tr>
<td>Cu treated GAC</td>
<td>partial</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>No</td>
</tr>
<tr>
<td>IX</td>
<td>No</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>possible</td>
</tr>
<tr>
<td>IX (water treated with Cu)</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>possible</td>
</tr>
</tbody>
</table>
**CYANIDE TREATMENT**

- Biological CN treatment
  - Thiocyanate and cyanide are **TOXIC** to biological treatment but are also **BIO DEGRADABLE**
  - Cyanide, cyanate and thiocyanate contain nitrogen and release nitrogen as $\text{NH}_4\text{-N}$ during biodegradation
  - Need to include in the nitrogen balance to ensure sufficient treatment capacity
  - Metals removal required prior to biological treatment if high metal content - metal toxicity
CYANIDE TREATMENT

- Common types of biological processes
  - Fixed film systems - provide a support for biomass growth
    - Trickling filter
    - Moving Bed Biofilm Reactor (MBBR)
  - Suspended growth systems maintain biomass concentration by internal recirculation
    - Activated Sludge
## CYANIDE TREATMENT

- Fixed film compared to suspended growth systems

<table>
<thead>
<tr>
<th>Fixed Film Processes</th>
<th>Suspended Growth Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Can maintain nitrifying biomass at low temperature as they are fixed to the carriers</td>
<td>Nitrification at low temperature requires extremely long sludge ages - large basin</td>
</tr>
<tr>
<td>More resistant to shock loads as only outer layer of biofilm gets to see bulk toxin concentration</td>
<td>Entire floc is exposed to toxic shocks</td>
</tr>
<tr>
<td>Small footprint - limited construction on site</td>
<td>Larger footprint</td>
</tr>
</tbody>
</table>
SELENIUM TREATMENT
SELENIUM TREATMENT

• Overview
  • Selenium treatment fundamentals
  • Selenium iron co-precipitation
  • Biological treatment
VALANCE STATE OF SELENIUM

- Selenium treatment depends on valance state
- Valance/Oxidation state:
  - Primarily as: Selenite (IV); Selenate (VI)
  - Se (- II); Se (0)
- Exists as water soluble selenium complex [i.e., Selenocyanate]
**SELENIUM CHEMISTRY**

- Principal aqueous forms of inorganic selenium:
  - Selenate (VI)
  - Selenite (IV)
    - Se (VI) predominates under oxidizing environment as $\text{SeO}_4^{2-}$ above pH 1.6
    - Se (IV) presents under moderately reducing condition pH $< 8.15$ ($\text{HSeO}_3^-$) and pH $> 8.15$ ($\text{SeO}_3^{2-}$)
KEY TERMINOLOGY REVIEW

- Biological oxidation and reduction
  - Oxidation - removal of electrons
  - Reduction - addition of electrons
- Electron donor and acceptors
  - Electron donor - material being oxidized
  - Electron acceptor - material being reduced
KEY WASTEWATER CONSTITUENTS

- **Electron donors (food for biomass)**
  - Organic Matter or Carbon Source Measured and expressed as degradable COD
  - CO2 and biomass are the products

- **Electron acceptors**
  - Oxygen (aerobic environment)
  - Preferred acceptor
  - Reduced product: H2O

- **ORP Driven**
BIOLOGICAL TREATMENT

- Reduction of Selenium by Microbes
  - \( \text{Se (VI)} \rightarrow \text{Se (VI)} \rightarrow \text{Se (II)} \rightarrow \text{Se}^0 \)

  \[
  \text{SeO}_4^{2-} + \text{organic carbon} \rightarrow \text{SeO}_3^{2-} + \text{organic carbon} \rightarrow \text{Se}_0 + \text{CO}_2 + \text{H}_2\text{O}
  \]

- Anoxic Conditions
  - Heterotrophic bacteria
  - Organics + Selenite/Selenate + N + P
  - New Cells + \( \text{CO}_2 + \text{H}_2\text{O} + \text{Se}^0 \)

- Attached Growth Biological Process

- Water temperature influences reaction rate >> hydraulic residence time (HRT)
BIOLOGICAL TREATMENT

Selenate → Selenite → Selenium

Carbon Dioxide → Organic Carbon

ATP
EXTERNAL CHEMICALS NEEDED

- Readily degradable organic carbon
- Phosphorus (if needed)
- Micronutrients (if needed)
- Ammonia nitrogen (nutrient) for aerobic polishing
- Note: if excess Nitrate is present it will need to be degraded in the biological process.
ATTACHED GROWTH SYSTEMS

- Fluidized Bed Reactor (FBR)
- Fixed Bed or Packed Bed Reactor (PBR)
- Electro-Biochemical Reactor (EBR)
- Moving Bed Biological Reactor (MBBR)
ATTACHED GROWTH SYSTEMS (CONT.)

• For low Se concentration wastewater, attached growth system is best suited to grow sufficient biomass
• Biomass grows as a biofilm on a solid support
• Pollutants present in the wastewater are removed by the biofilm
• Some attached growth processes contain fixed media over which the wastewater flows
• Other attached growth processes contain mobile media kept in suspension by fluid flow
Fluidized Bed Reactor (FBR)

- An up-flow attached growth system
- Wastewater is passed through a granular solid media at high enough velocity to suspend the media to behave as a fluid
- Fluidization keeps the media with attached biomass in suspension and expanded in depth to provide good contact of water with biomass for effective treatment
- Uses sand or granular activated carbon as a media for biomass attachment
- Post treatment of suspended solids and particulate selenium removal
- Pilot and full scale systems at mine sites
- Envirogen Technologies
ATTACHED GROWTH SYSTEMS (CONT.)

- Fluidized Bed Reactor
ATTACHED GROWTH SYSTEMS (CONT.)

- Fluidized Bed Reactor
Packed bed reactor (PBR)

- Packed bed of solid-phase media such as sand or granular activated carbon
- Operates in downflow mode
- Pre-treatment of suspended solids required to prevent clogging of media
- Post treatment of suspended solids and particulate selenium removal
- Periodic back flushing is needed to remove the dead biomass.
- Pilot and full scale systems at mine sites
- GEABM®
ATTACHED GROWTH SYSTEMS (CONT.)

Packed bed reactor (PBR)
ATTACHED GROWTH SYSTEMS (CONT.)

Electro-Biochemical Reactor (EBR)

• Packed bed upflow reactor
• Low DC voltage supplies excess electrons instead of nutrients and chemicals
• Pilot and full scale utilized at mine sites
• Inotec (see Inotec presentation at Tuesday afternoon session)
Moving Bed Bioreactor (MBBR)

- Fluidized bed anoxic/aerobic treatment system.
- Uses a proprietary high surface area media
- Pilot and full scale systems at mine sites
- Post treatment of suspended solids and particulate selenium removal
- Veolia AnoxKaldnes™
LIQUID-SOLIDS SEPARATION

- Effluent will contain suspended solids including elemental (particulate) selenium and sloughed off biomass from the media.
- A portion of the reduced elemental selenium may potentially reoxidize to soluble selenite/selenate.
- It is critical that these solids be removed prior to aerobic biological polishing treatment.
- Aerobic polishing treatment may be necessary to remove residual degradable organics (BOD/COD) and to increase the dissolved oxygen prior to final discharge.
AEROBIC POLISHING TREATMENT

• Anoxic/anaerobic reactor effluent will have low ORP (-200 to -400 mV) and residual organics.
• After liquid-solids separation, the effluent may need to be treated aerobically to increase the dissolved oxygen (to positive ORP) and to remove any residual degradable organics (BOD).
• Aerobic biological treatment can be an aeration tank or a moving bed bioreactor (MBBR) depending on the type of upstream anoxic/anaerobic bioreactor.
ION EXCHANGE

- Selenium ions exchanged for like-charged ions by electrostatic attraction.
- Specialty resins used specifically for Se.
- Exchange capacity can be reduced by competing anions (sulfate, nitrate).
- Pre-treatment for TSS removal likely required.
- Resin regeneration required.
- Concentrated regenerant needs a home, or further treatment such as electrochemical reduction (BioteQ Selen-IX™).
- Pilot scale at mine sites (full scale applications unknown to author).
CO-PRECIPITATION

• Iron co-precipitation removes vast majority of selenite; removes very little selenate or elemental selenium
• Two-step process utilizing ferric salt
• Ferric hydroxide and ferrihydrite precipitate with concurrent adsorption of selenium on the particulate surface
• Clarification and filtration required downstream of reaction vessel
• Widely implemented full scale at mine sites
Adsorption technologies

- Adsorption treatment utilizes sorptive media in a reactor vessel to reduce selenite and selenate to elemental Se.
- Four types of sorptive media identified:
  - MAR Systems (known as SORBSTAR),
  - SAMMS (Self-assembled Monolayers on Mesoporous Support),
  - Zero Valent Iron (ZVI) and
  - SMI (Sulphur Modified Iron nanoparticles).
- Laboratory testing showed that SMI was effective at reducing selenate. SORBSTAR, SAMMS and ZVI were not effective (confidential client).
• Water temperature does not appear to substantially influence reaction kinetics
• Reaction vessel operated in upflow mode
• Pre-treatment of suspended solids required to prevent clogging of media
• The media releases small amounts of dissolved iron. This must be oxidized and post filtration may be needed
• Media cannot be regenerated but passes TCLP when exhausted
• Pilot testing stage
• SMI Media Conceptual Flow Sheet

ADSORPTION TECHNOLOGIES (CONT.)
WASTE STREAM MANAGEMENT
CHEMICAL TREATMENT SLUDGE

• Chemical sludge - primarily gypsum and metal hydroxides
• Formed in “sludge blanket” in clarifier bottom
• Sludge is periodically “bled” from clarifier for disposal
• Typically 2% - 4% solids by weight in LDS, 20% - 30% solids by weight in HDS
• Low density sludge can be thickened in cone-bottom tank up to 10% solids by weight
• Thickened solids can be de-watered with filter press
WASTE STREAM MANAGEMENT
CHEMICAL TREATMENT SLUDGE

- Cone bottom tank for sludge thickening
- Filter press for de-watering
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

- Brine generated from membrane treatment
- Overview:
  - Brine recycle without further treatment
  - Brine recycle including further treatment
    - Brine recovery RO
    - Sulfate desaturation
    - Sulfate desaturation plus Ettringite precipitation
    - Sulfate desaturation, ettringite precipitation, aluminum recovery
  - Further concentration using evaporation + crystallization
• Brine recycle without further treatment
  • Highly dependant on TDS of brine
  • Brine TDS < 10,000 mg/l added back to front end of treatment quickly affects membrane recovery and increases scaling potential
  • Might be applicable in short-term batch treatment circumstances, e.g., reducing water volume in pond
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

- Brine recovery RO
  - 1st stage RO/NF brine to 2nd RO
  - Can increase overall system recovery by ~50%

Diagram:
- Raw Water → 1st stage brine → Permeate → Brine disposal
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

- Sulfate brine desaturation
  - Brine from membrane treated with lime precipitation to desaturate SO_4 to gypsum solubility
    - Example: brine SO_4 10,000 mg/l >> 1,500 mg/l with accompanying gypsum sludge
  - Desaturated brine to be managed
    - Potential to route back to primary RO/NF
    - Route to ettringite process with or without aluminum recovery
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

- Evaporation & crystallization
  - Reduce/eliminate volume of liquid waste
  - Generate high-quality water for reuse in upstream processes
  - Achieve zero liquid discharge generally for sulfate/chloride removal to low levels
  - Pond remediation or closure
  - Product recovery
WASTE STREAM MANAGEMENT MEMBRANE BRINE

- Volume reduction:
  - Membrane concentration (previously discussed)
  - Falling film evaporation
- Zero Liquid Discharge (ZLD) or Zero Liquid Waste (ZLW)
  - Evaporation pond
  - Spray dryer
  - Forced circulation crystallization
Volume Reduction: Falling Film Evaporation

- Achieves higher concentrations than RO: 20 – 25 wt% TDS
- Higher capital and operating cost
- Usually no appreciable chemical addition or sludge generation
- Unable to go to “dry” solids
- Good quality water is recovered (~5 – 20 ppm TDS)
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

Falling Film Vapor Compression Evaporator

WASTE STREAM MANAGEMENT
MEMBRANE BRINE

• ZLD, ZLW: Evaporation Pond
  • Low operating cost - requires maintenance and monitoring
  • Capital cost can be fairly high
  • Geographically specific
  • Water is not recovered
  • Remediation Liability
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

- ZLD, ZLW: Spray Dryer
  - Fairly low capital cost
  - Energy inefficient – only applicable for very small flows
  - Emission point source
  - Natural gas combustion
  - Baghouse vent
  - Water is not recovered
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

ZLD, ZLW: Forced Circulation Crystallizer

- Higher capital and operating cost than falling film evaporator
- Solids separation by centrifuge or pressure filter
- Able to crystallize out pure salts for sale (requires further processing)
- Able to get land-fillable solid product
- Water is recovered (~25 – 50 ppm non-volatile TDS)
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

Forced circulation crystallizer

- Crystallizer
- Vapor Body
- NCG Vent
- Crystallizer Heater
- Recirculation Pump
- Compression Device
- Dewatering Device
- Recovered Water
- Feed
- Slurry Tank
- Solids to Disposal
- Disposal
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

Water Removal Comparison

Recovered Water, %

Total Solids in Concentrate, wt%

RO  EVAP  Crystallizer

30,000 ppm Feed

5,000 ppm Feed
Drivers affecting evaluated cost: membranes

- Inexpensive materials (plastic and stainless steel)
- Low power consumption (relatively low pressure)
- Pretreatment requirements can affect cost
- Cost of chemicals
- Cost of disposal
Drivers affecting evaluated cost: Falling Film Evaporation

- Higher cost materials
  - Stainless steels (austenitic, duplex, super duplex superaustenitic)
  - Titanium often used for tubes
- Higher power consumption
  - Vaporization
  - Boiling point rise
- Minimal chemical use
Drivers affecting evaluated cost: Forced Circulation Crystallization

• Expensive materials
  • Ni-Cr-Mo alloys (Inconel 625, Hastelloy C276)
  • Pd-alloyed Titanium (Gr 12 or 16) used for tubes
• Moderate footprint – moderate equipment weight
• High power consumption
  • High TDS results in high BPR
• Solids separation adds cost
  • Centrifuge
  • Automatic belt pressure filter
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

Relative costs of brine concentration

Evaluated Cost Comparison

Relative Evaluated Cost, %

Total Solids, wt%

Forced Circulation Crystallization

Falling Film

Membrane

CLOSING COMMENTS
COMPLETE WATER ANALYSIS

- Calcium
- Magnesium
- Sodium
- Potassium
- Strontium
- Barium
- Iron
  - Total, dissolved and ferrous
- Aluminum
  - Total and dissolved
- pH
- Hydrogen Sulfide
- Bicarbonate
- Sulfate
- Chloride
- Nitrate
- Fluoride
- Phosphate (total)
- Silica (dissolved)
- Total Dissolved Solids (TDS)
- Conductivity
TECHNOLOGY SELECTION CONSIDERATIONS

• Effluent requirements differentiate appropriate technologies.
• Projects typically require removal of several constituents requiring multiple process steps; this typically adds OpEx and/or CapEx.
• Most projects are unique when pertinent design factors are considered; be cautious if comparing your project to others.
REFERENCES


SUGGESTED FURTHER READING


• The International Network for Acid Prevention. Treatment of Sulphate in Mine Effluents. Lorax Environmental. October, 2003