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

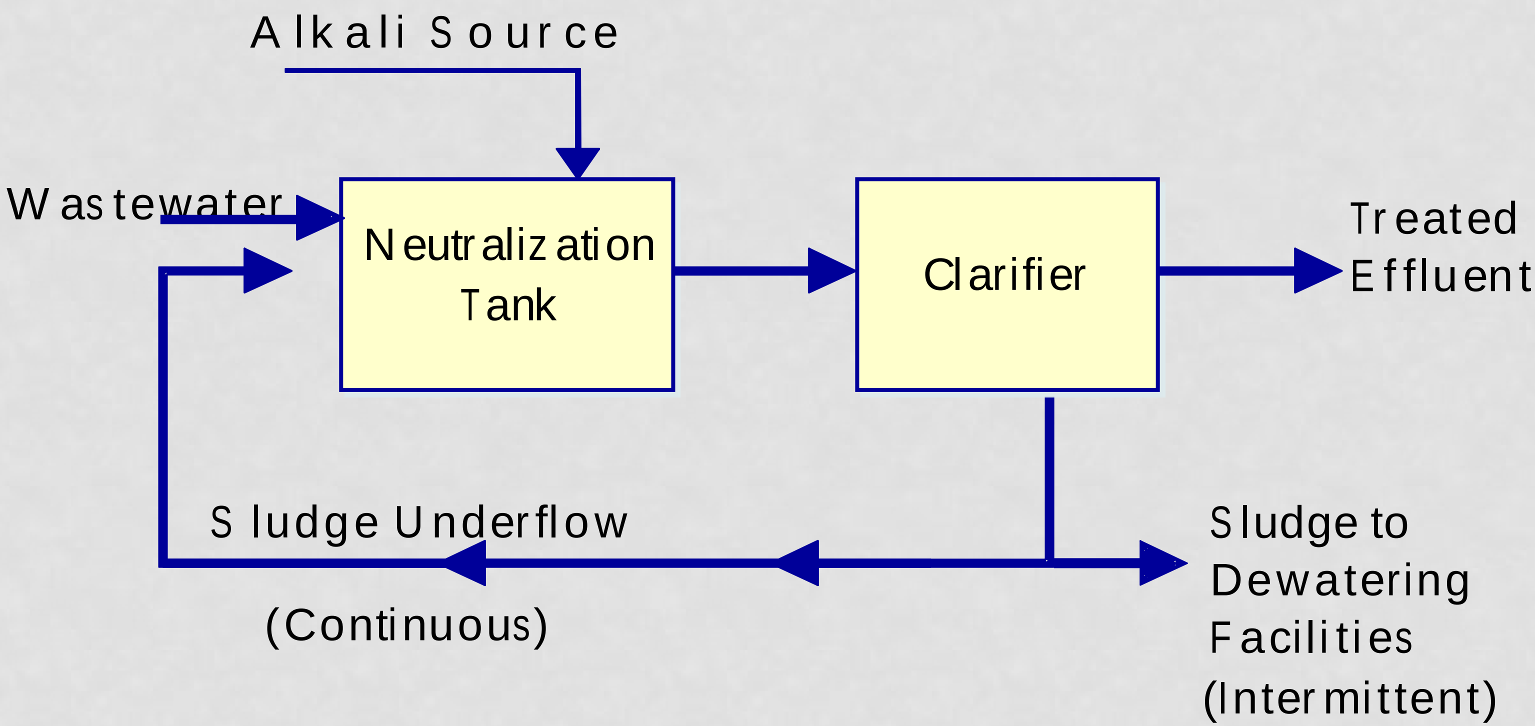
- Lime addition to precipitate sulfate in the form of gypsum CaSO4. $2H_2O$
  - Most common type of sulfate treatment
  - Amount of sulfate removal limited to gypsum solubility of particular site water ~ 1,600 mg/l - 2,000 mg/l SO_4
- Lime can be added as
  - Limestone, $CaCO_3$
  - Calcium oxide (quicklime), CaO
  - Calcium hydroxide (slaked lime), $Ca(OH)_2$
  - Hydrated lime (quicklime + water)
- Soda Ash (Na_2CO_3) 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



CHEMICAL TREATMENT

- Lime silos and solids contact clarifiers

Butte, Montana, USA

Superior, Arizona, USA

CHEMICAL TREATMENT

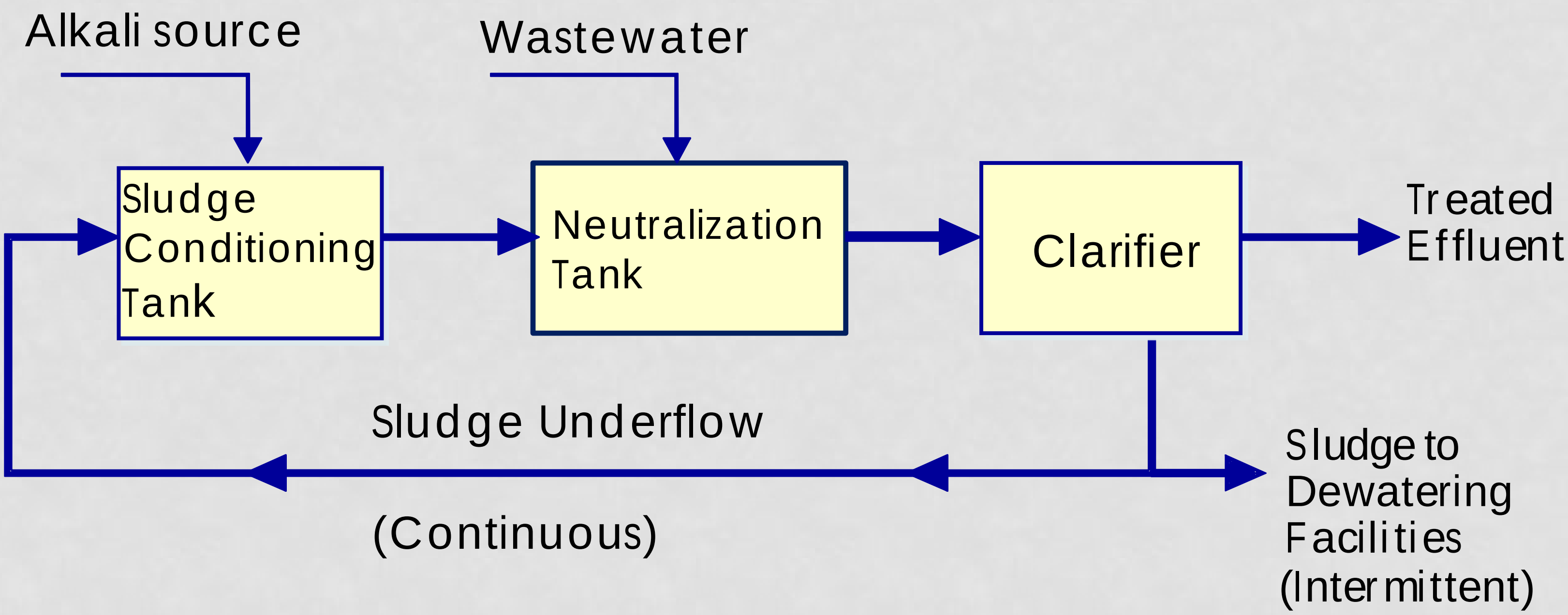
- Chemical mixing tanks

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 $CaCO_3$ and $CaSO_4$ precipitation

CHEMICAL TREATMENT

- Lime precipitation – high density sludge (HDS)

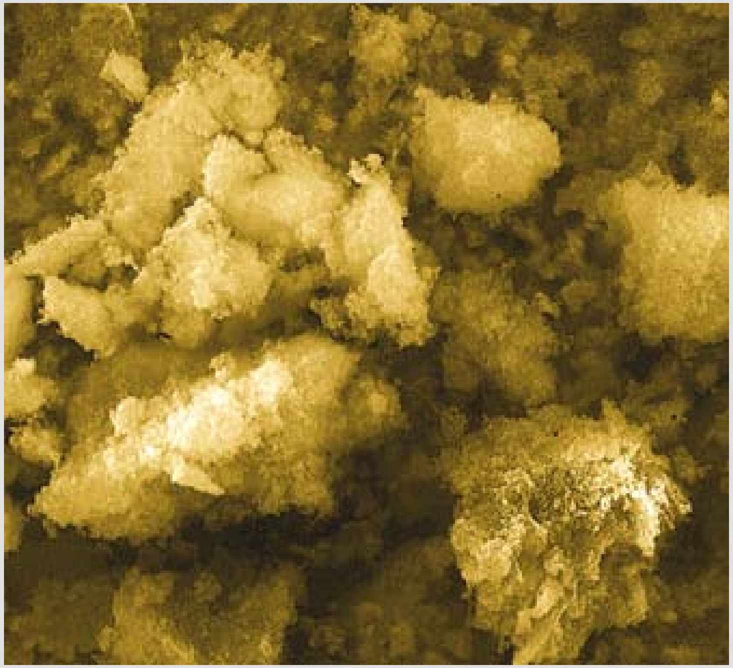


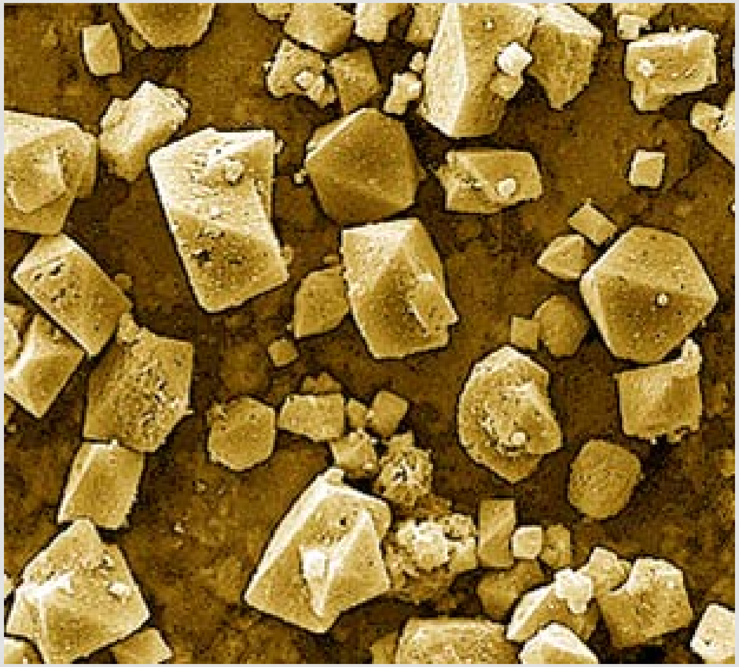
CHEMICAL TREATMENT

- 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

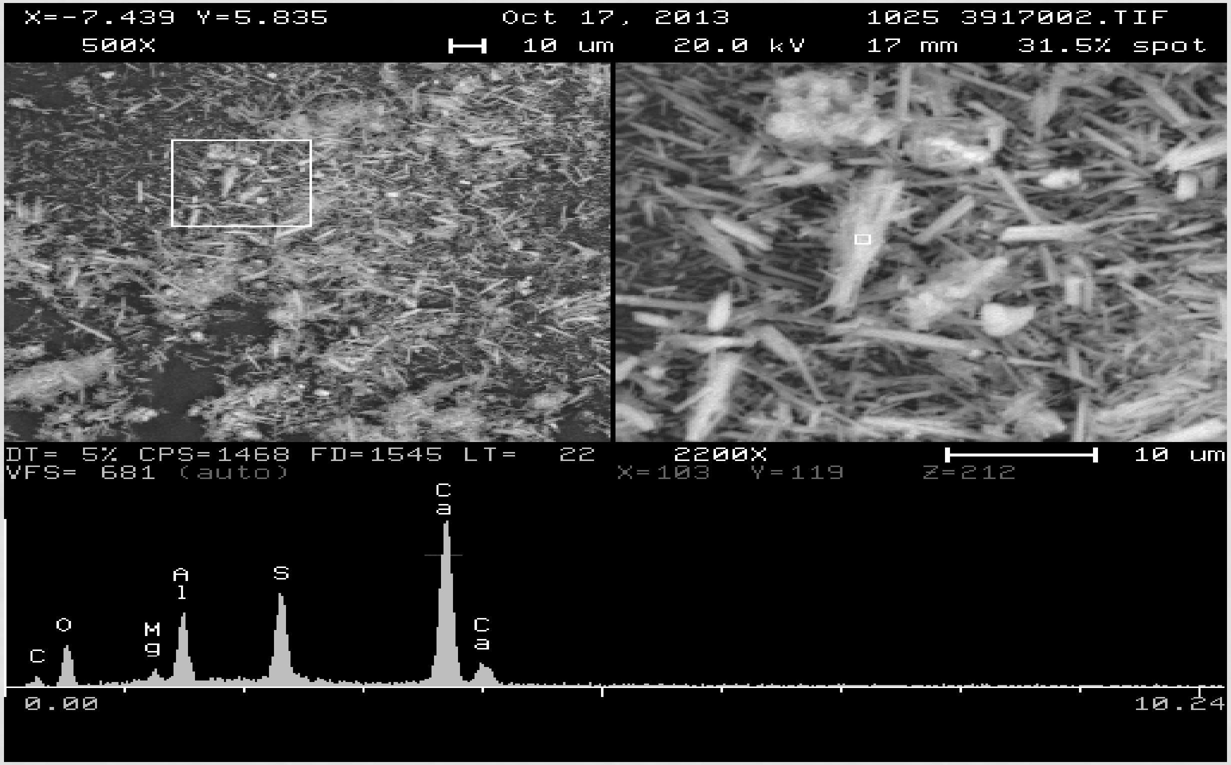
Process Variable	Conventional	Dense Sludge
Dewatered Sludge (% solids)	25 – 35	50 – 70
Clarifier Underflow (% solids)	2 – 4	20 – 30
Dewatering Time (hours)	2 – 3	0.5 – 1
Sludge Blanket Level (feet)	5 – 7	1 – 2

CHEMICAL TREATMENT

- Ettringite precipitation (SAVMIN™)
  - Aluminum added to water to form ettringite (calcium aluminum sulfate, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$
  - Reaction at pH 11-13
  - Feasible for SO_4 < ~ 1,800 mg/l (gypsum solubility)
  - Sulfate removal to ~10's mg/l - 000's mg/l SO_4
- Aluminum form can be:
  - Aluminum hydroxide (Gibbsite), $Al(OH)_3$
  - Aluminum ion, Al^0
  - calcium aluminate

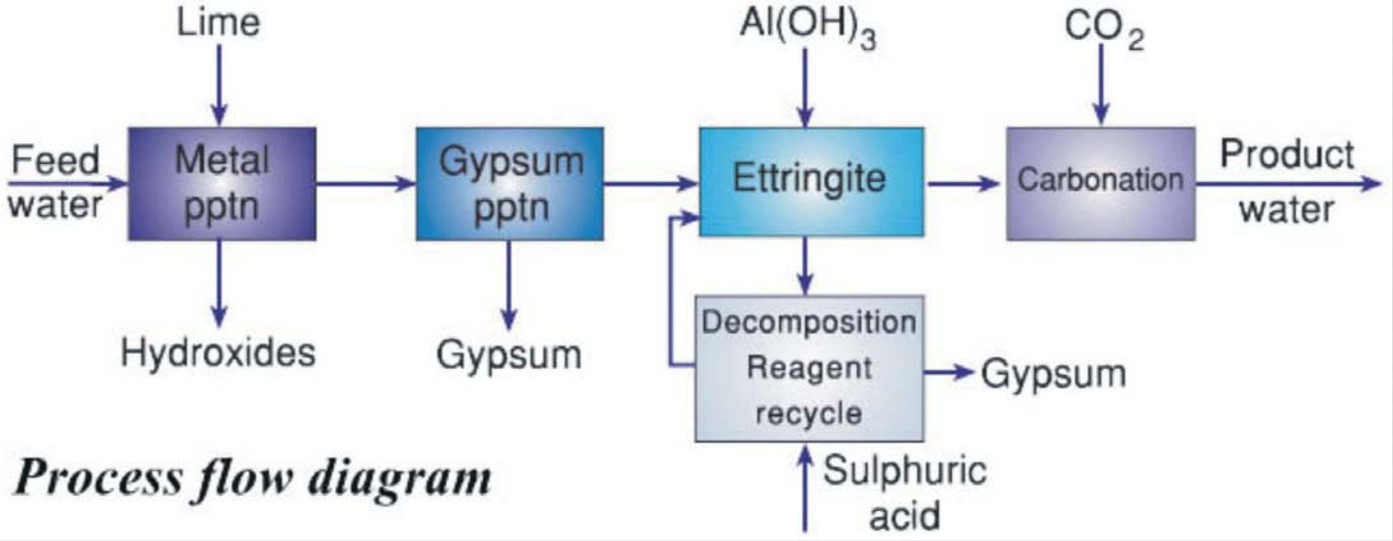
CHEMICAL TREATMENT

- Ettringite Crystals In Ettringite Reactor



CHEMICAL TREATMENT

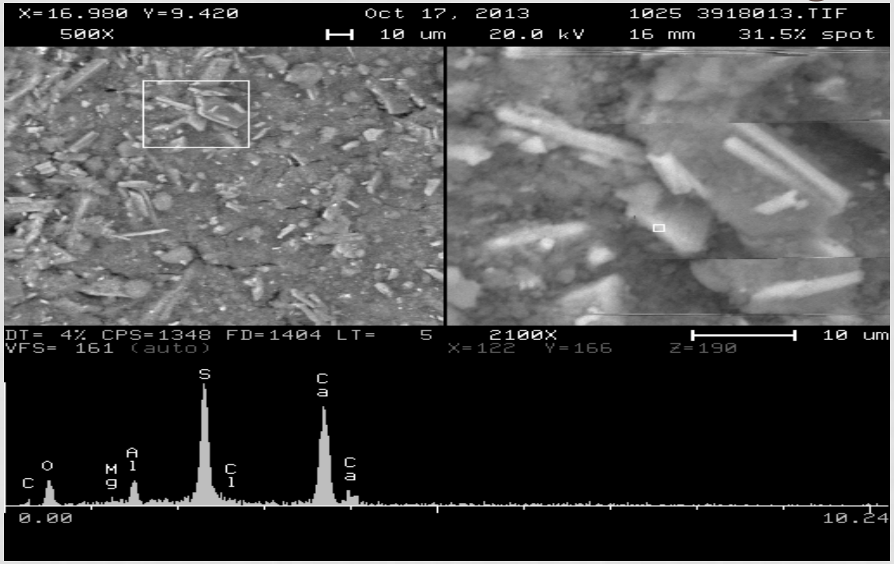
- SAVMIN™ four-stage process (Lorax, 2003):



- Ettringite slurry is destabilized with H_2SO_4 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

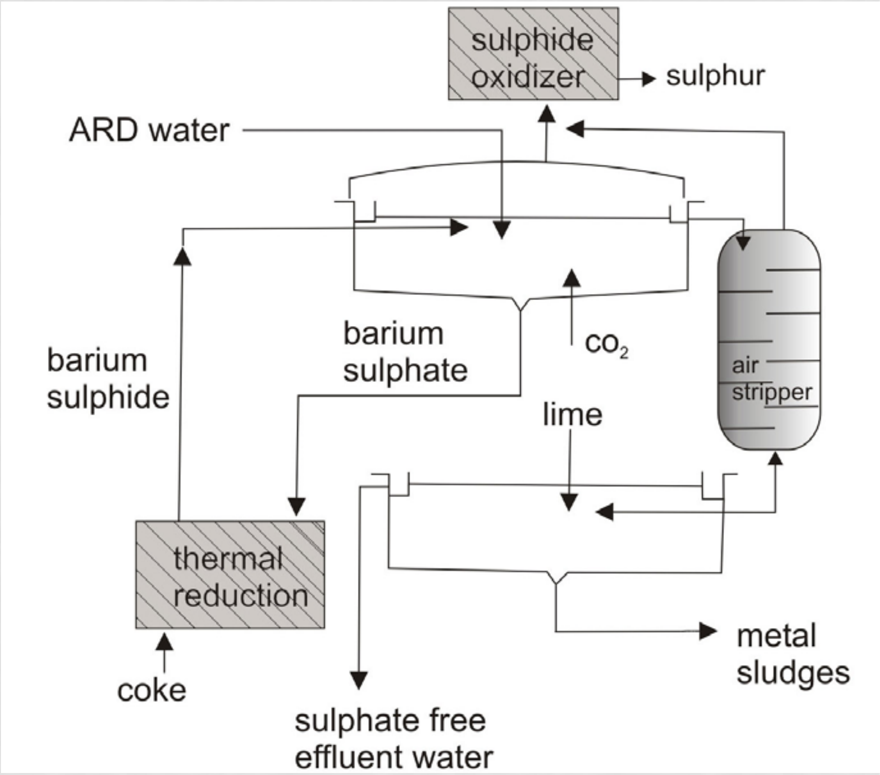


CHEMICAL TREATMENT

- Barium sulfate precipitation
  - Barium salt in form of:
    - $Ba(OH)_2$ – effective at wide pH range
    - $BaCO_3$ – less effective
    - BaS – effective at wide pH range
    - BaCl – reportedly used
- Sulfate reduced to ~ 200 mg/l in effluent
- $BaSO_4$ 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
    $BaSO_4$ >> BaS
  - Recycling BaS
  - H_2S stripping
  - H2S oxidation >> 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 [SO_4] 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

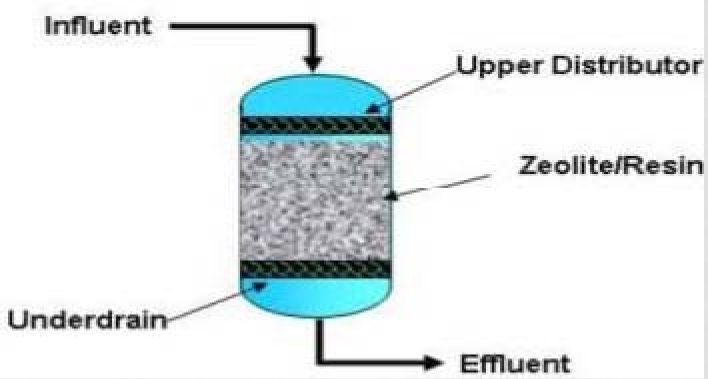
- Membrane filter skids

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



ION EXCHANGE GYP-CIX®

Loading Resins

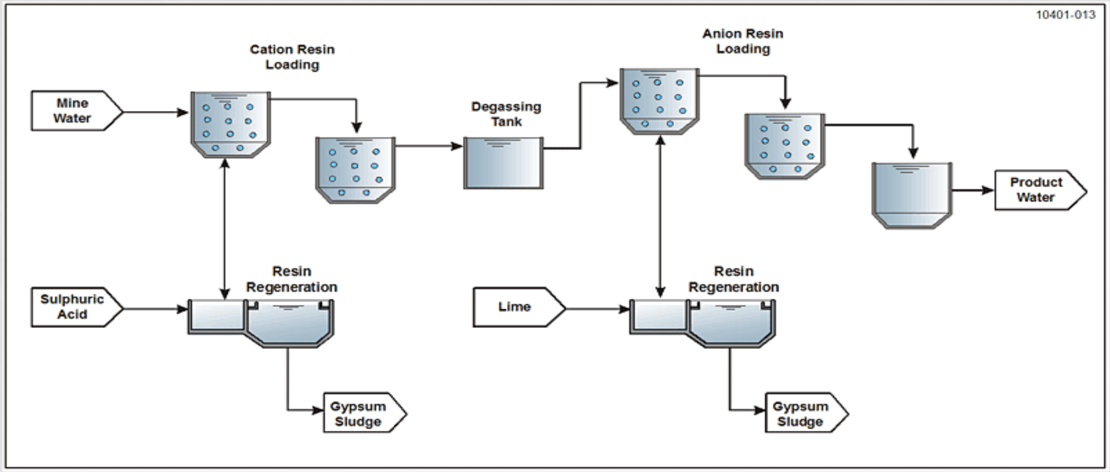
- Cations removed from feed water by exchange with strong-acid cation resin (R-H)
- Alkalinity removed in degassing tower
- SO4 removed by weak-base anion resin (R-OH)

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)



(INAP, 2014)

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

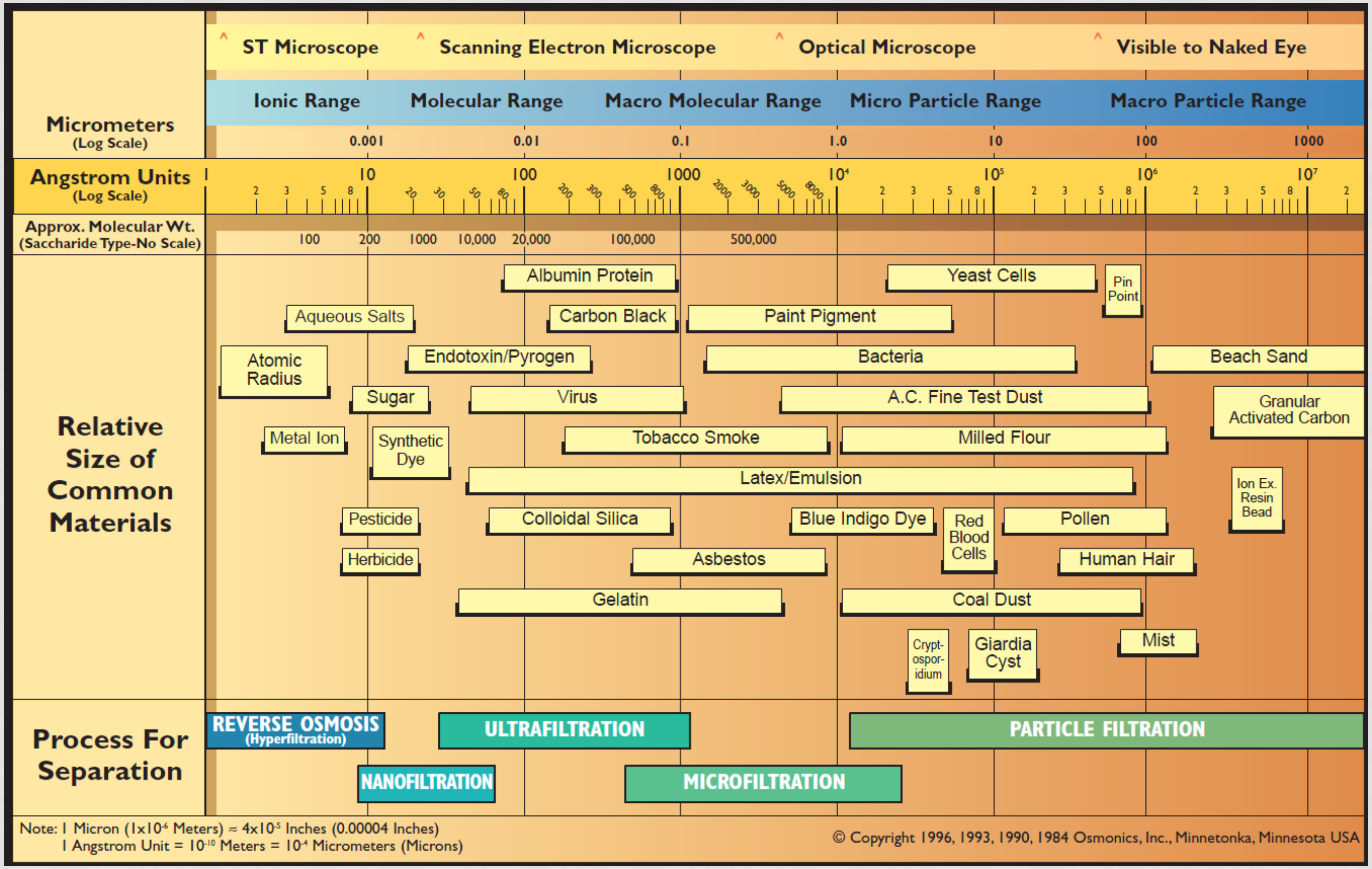
Disadvantages

- 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)

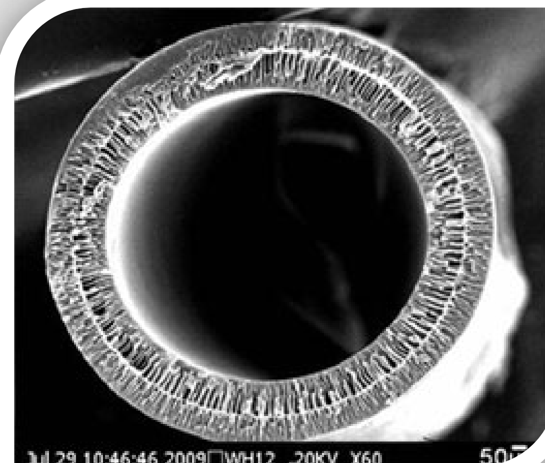
PHYSICAL SEPARATION FILTRATION SPECTRUM

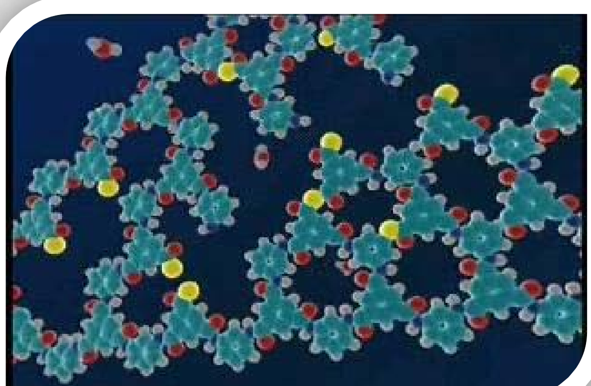


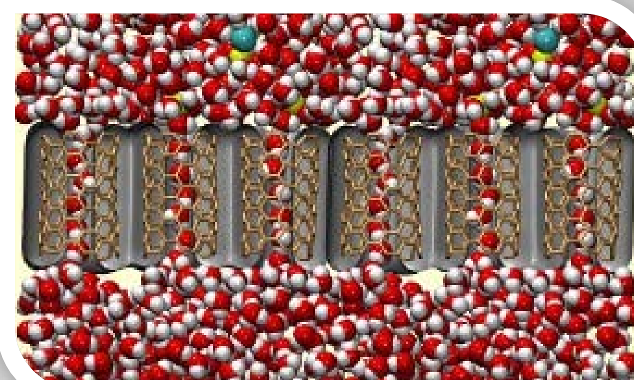
Micron = 1/1,000,000 meter = 1/1,000 millimeter = 0.001 mm = μm

PHYSICAL SEPARATION MEMBRANE BASICS

- Pressure-driven process
- Impurities/water
- Filtration Process
  - Microfiltration (MF)
  - Ultrafiltration (UF)
  - Nanofiltration (NF)
- Diffusion Process
  - Reverse Osmosis (RO)

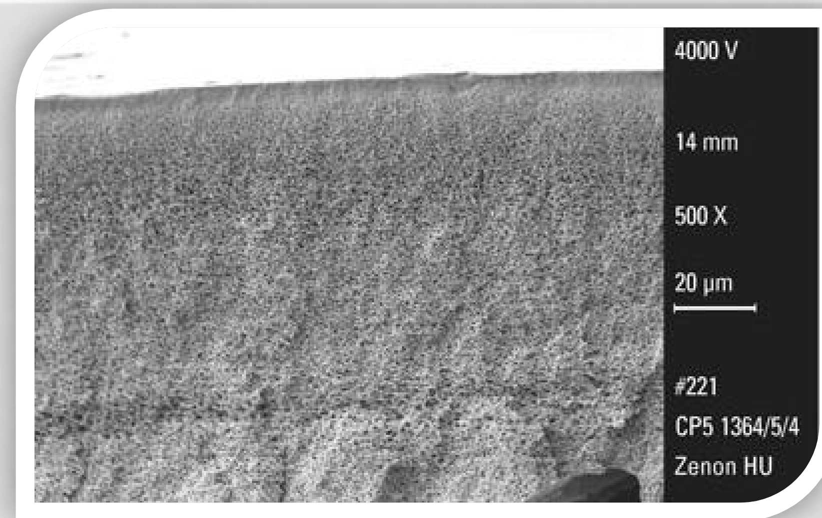




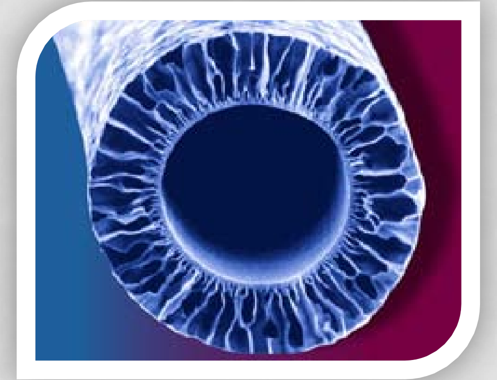


PHYSICAL SEPARATION
MICROFILTRATION, ULTRAFILTRATION, & NANOFILTRATION

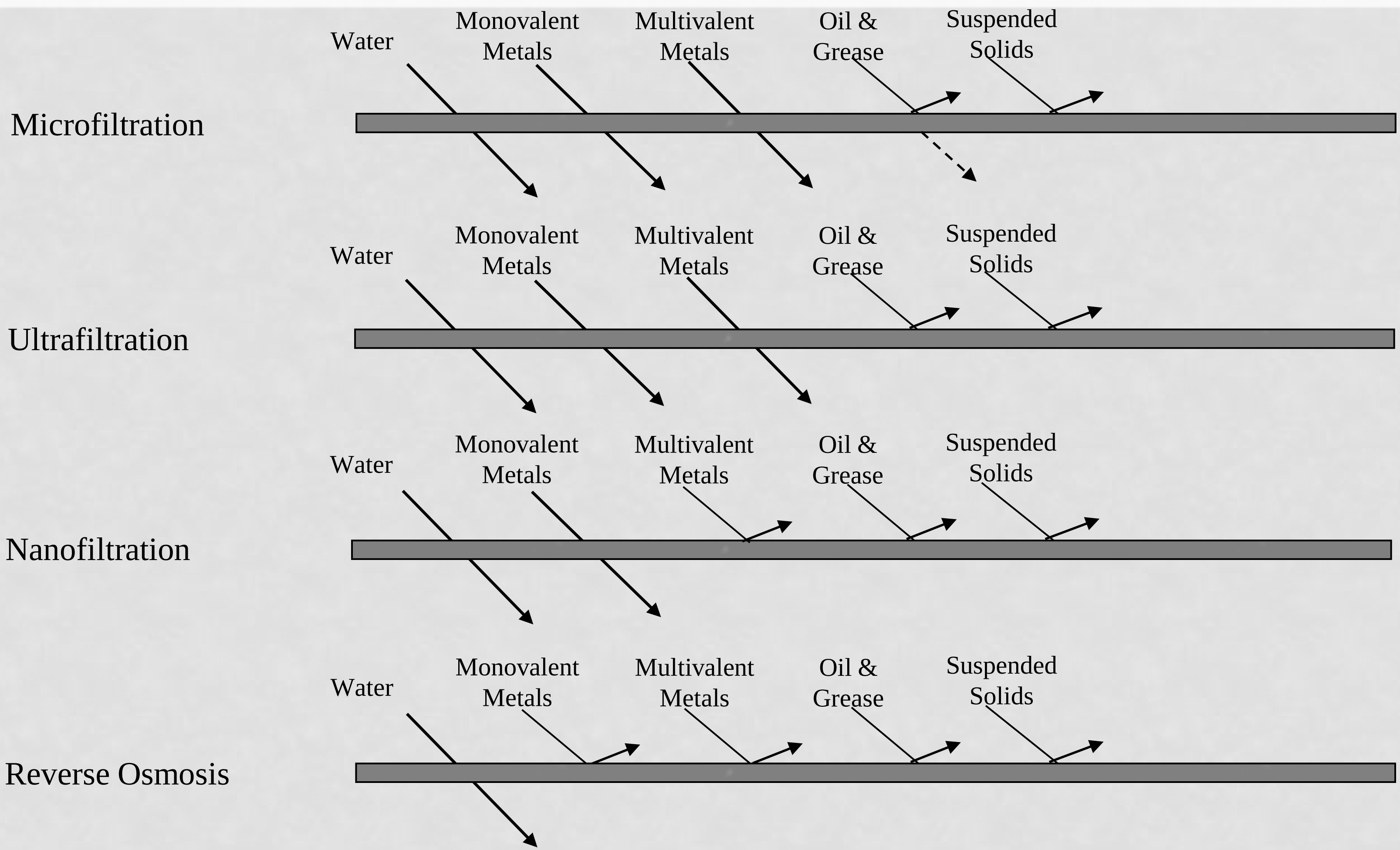
- MF
  - 0.05 – 1.0 μm
- UF
  - 0.005 – 0.1 μm
  - 1,000 – 500,000 MWCO
- NF
  - 0.001 – 0.01 μm
  - 200 – 10,000 MWCO
  - Divalent ions (Calcium)
  - “Softening membranes”



Cross section of UF membrane magnified 500 times.



PHYSICAL SEPARATION MF, UF, NF, & RO



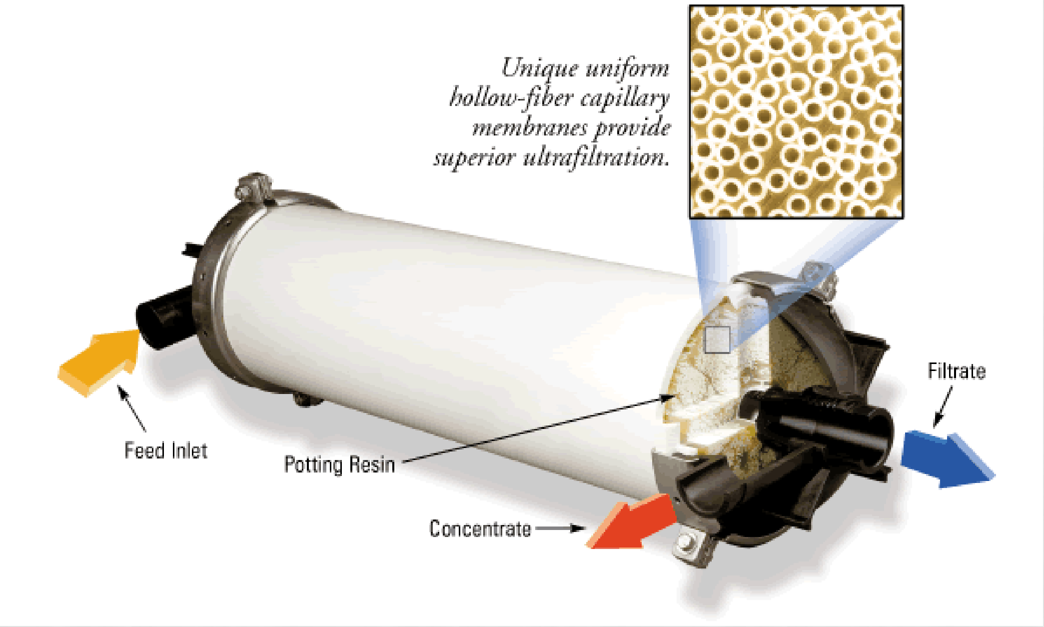
PHYSICAL SEPARATION CHOICE OF CONFIGURATION

- 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

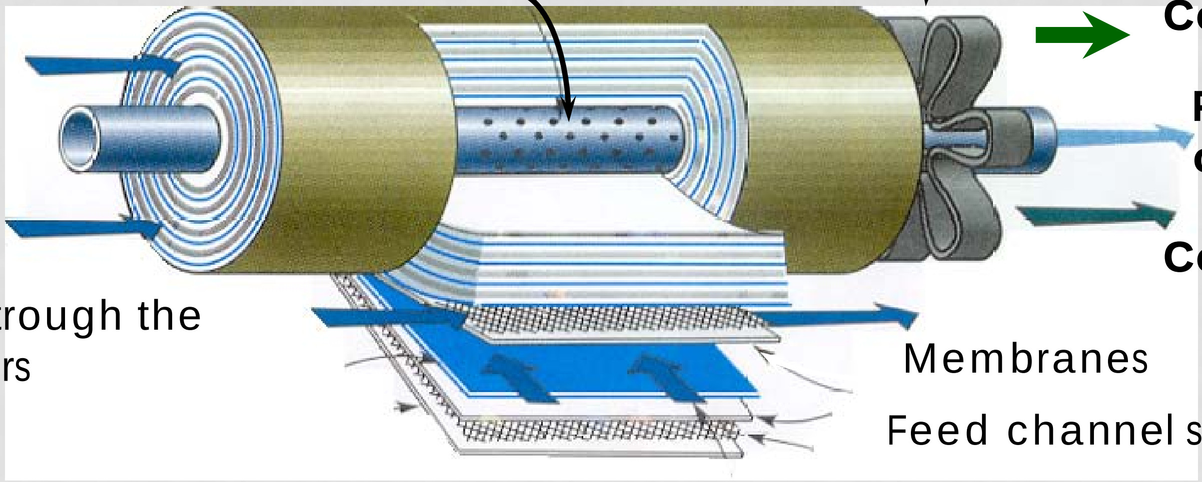
PHYSICAL SEPARATION HOLLOW FIBER UF DESIGN

- 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



PHYSICAL SEPARATION
REVERSE OSMOSIS: MEMBRANE & TECHNOLOGIES

- Spiral wound module



The permeate is drained spirally towards the centre

PHYSICAL SEPARATION
BASIC RO EQUIPMENT DESIGN

- 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 M^3/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

	Waste Water	Surface	Well	RO Permeate
SDI		<5	<3	<1
Flux (GFD)	5-8	8-14	14-18	20-30

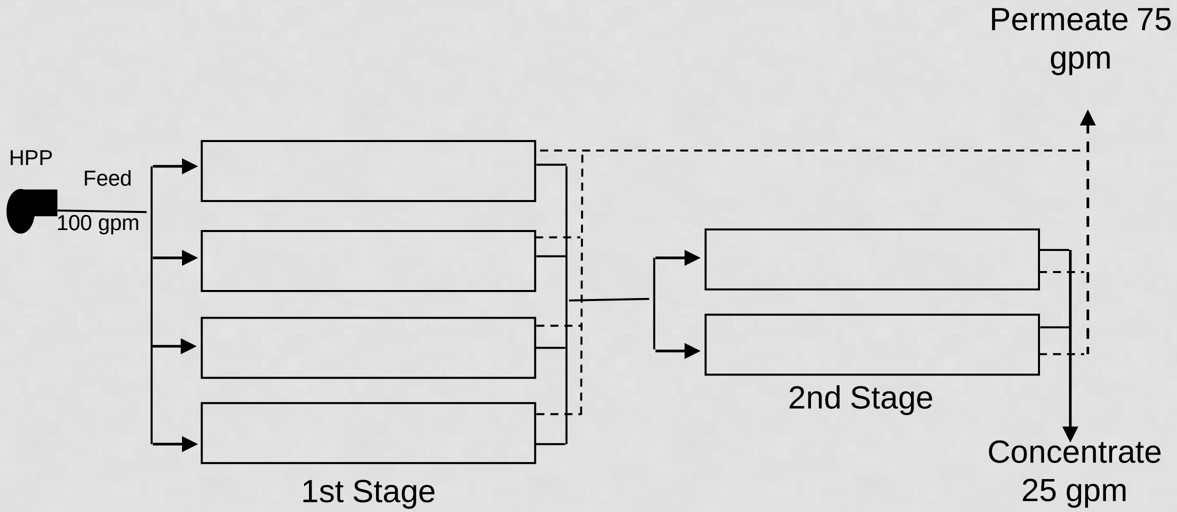
PHYSICAL SEPARATION
SILT DENSITY INDEX (SDI)

- 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

PHYSICAL SEPARATION EQUIPMENT DESIGN

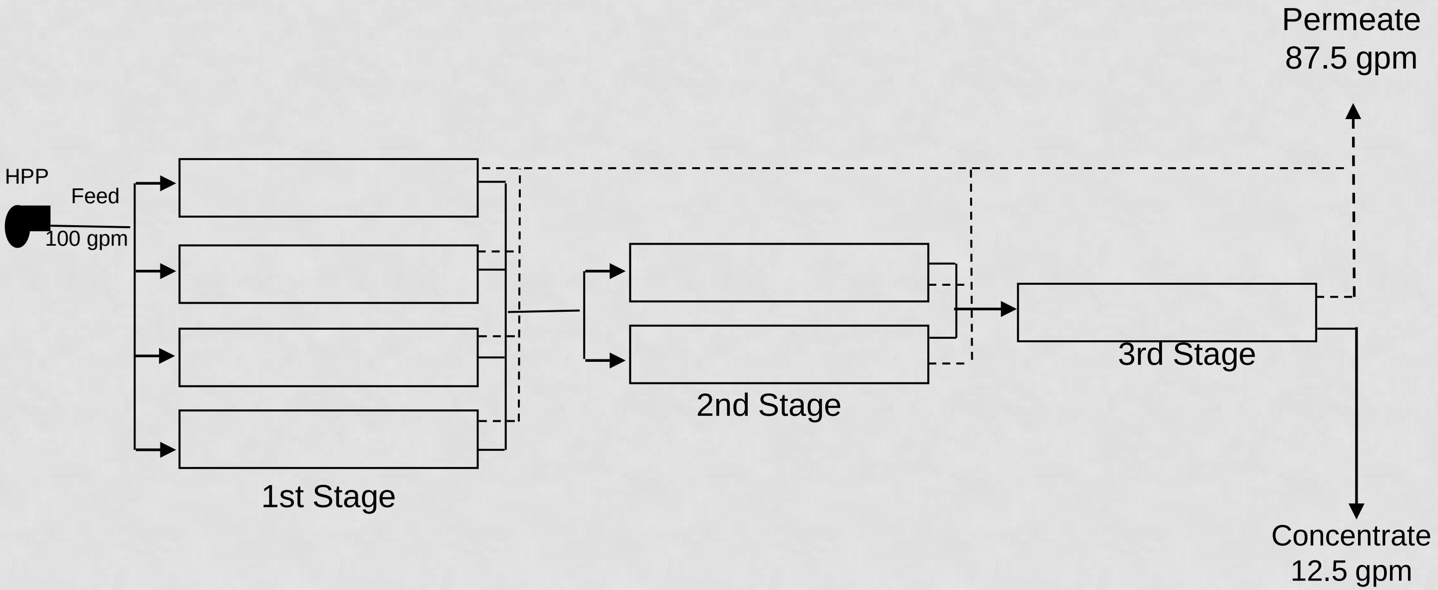
Two-Stage Membrane, 75% Recovery



4:2 Array

PHYSICAL SEPARATION EQUIPMENT DESIGN

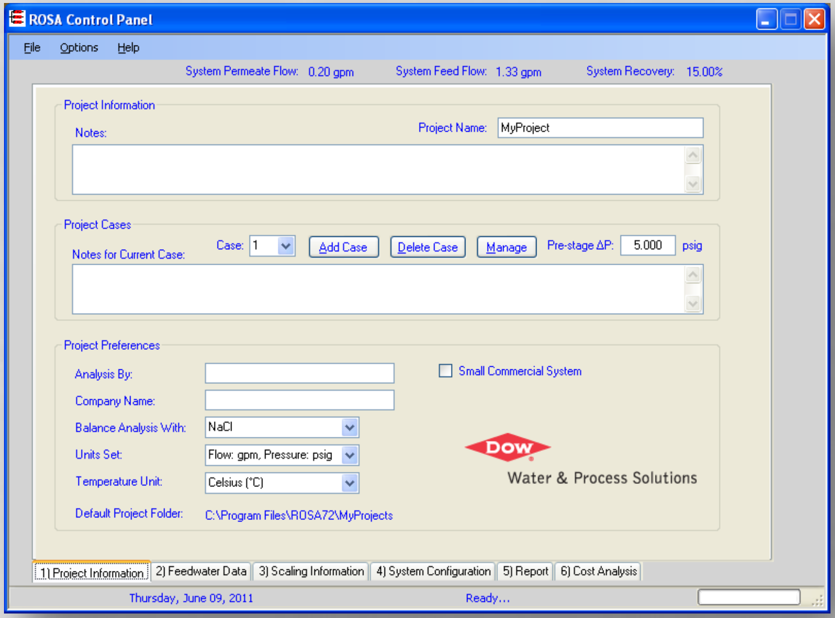
Three-Stage Membrane, 88% Recovery



4:2:1 Array

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
- ROPRO by Koch Membranes
  - www.kochmembrane.com
- TorayDS by Toray
  - www.toraywater.com

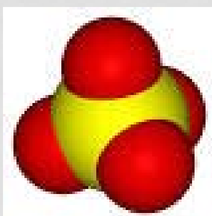


BIOLOGICAL TREATMENT

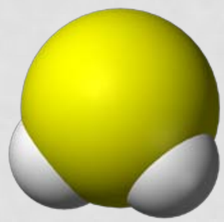
- Overview:
  - Two step process
  - Biological reduction
  - Residual forms
  - Reagent addition
  - Process schemes
  - Solids management

BIOLOGICAL TREATMENT

- Two step process to removal sulfur from system



sulfate



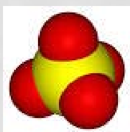
sulfide

precipitates

- 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)



SO_4^-

+ H_2/organic $\xrightarrow[\text{catalyst}]{\text{SRB}}$

H_2S

+ HCO_3^- + more bacteria

Acceptor + Donor

- Conditions needed:

Sulfate reducing bacteria (SRB)

Acceptable pH

Donor

- Direct-H_2, 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

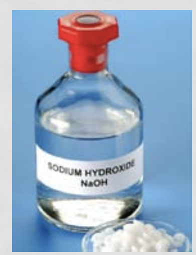
- Step 2 in the process defines solid residual forms:
  - Metal sulfides:
    - Sulfide can be combined with metals to form metal sulfides, thus both the metal and sulfide are removed from solution.
    - Depends on the availability of a source of metals
    - Management of metal sulfide sludge required

  - 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

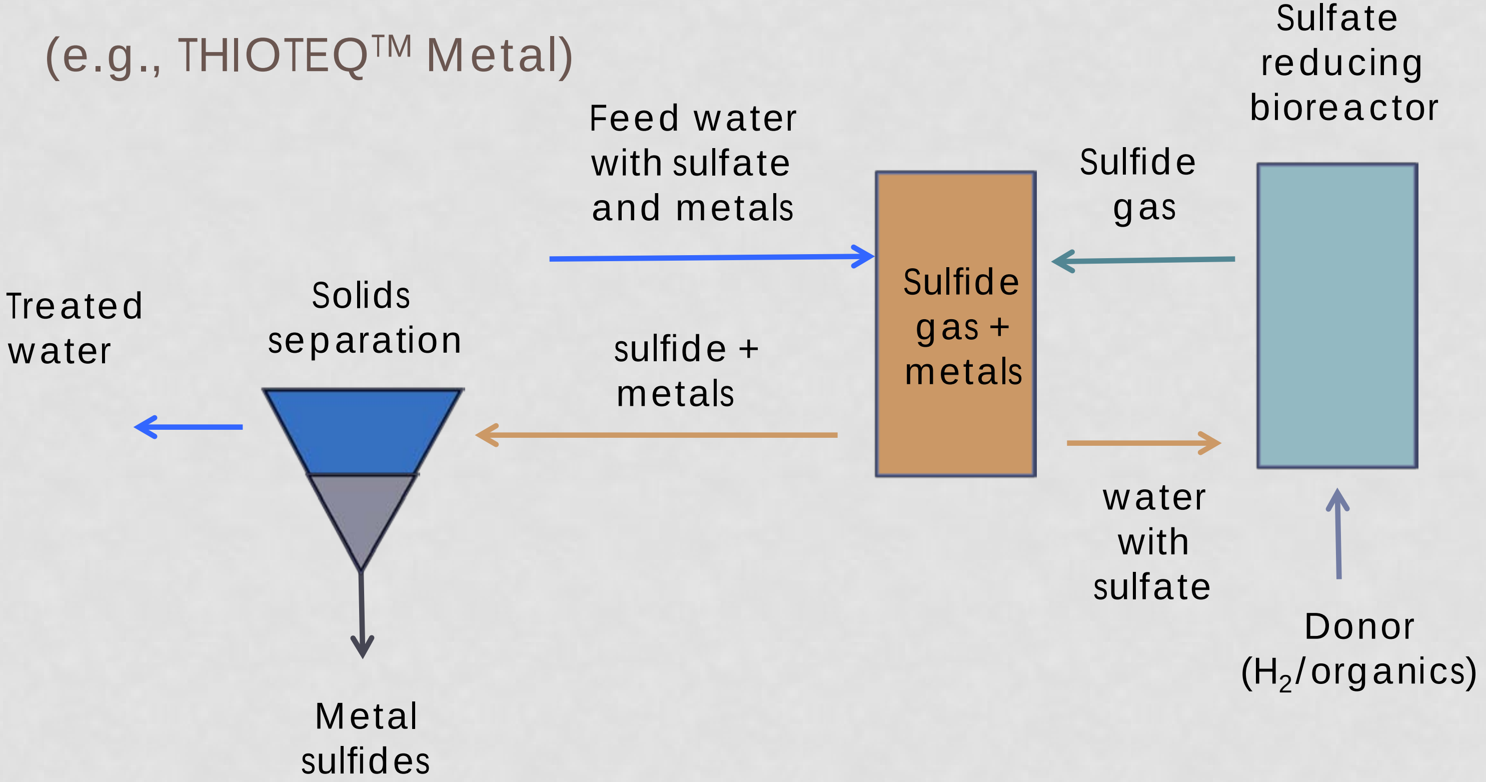
- Reagent addition
  - Donor:
    - H_2
    - Acetate
    - Ethanol
    - Molasses
    - Woodchips/hay/manure
  - pH adjustment (if needed):
    - Limestone
    - Lime
    - Sodium hydroxide
    - Sodium carbonate



BIOLOGICAL TREATMENT

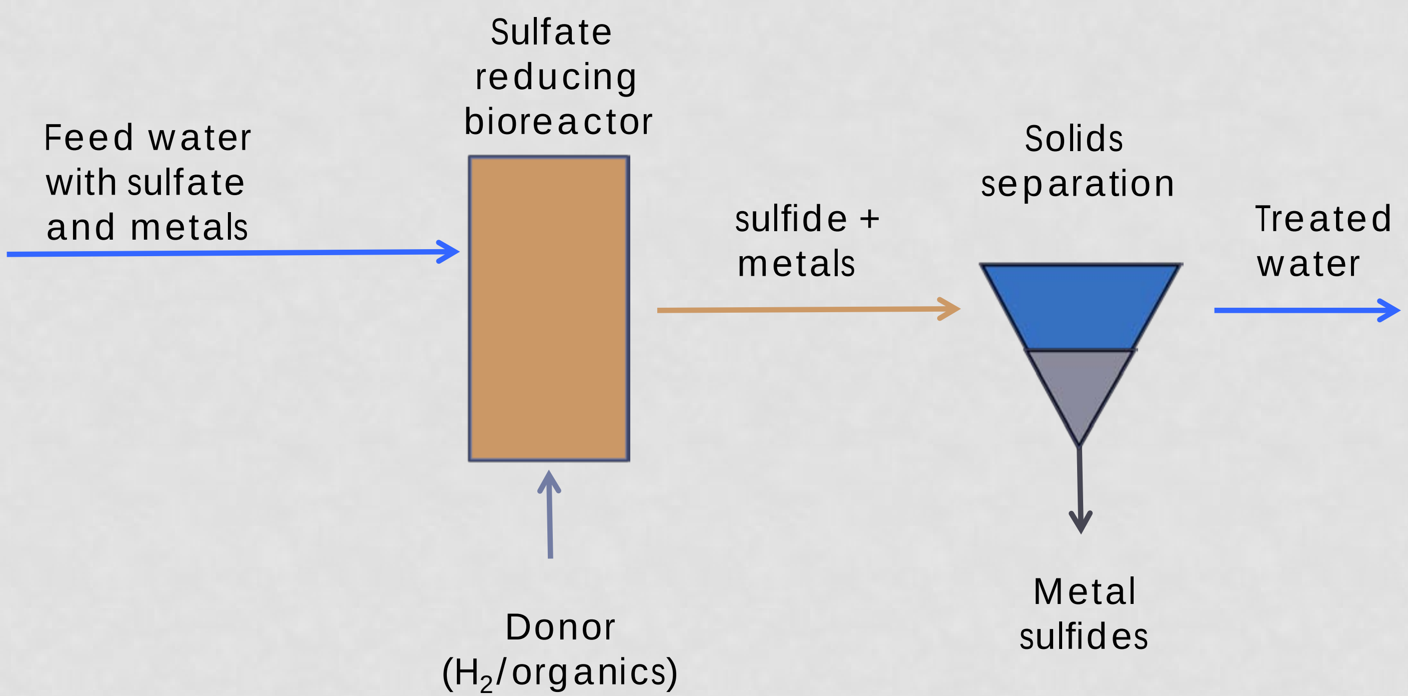
- Active schemes
  - Bioreduction with metal precipitation using gas contactor

(e.g., THIOTEQ™ Metal)



BIOLOGICAL TREATMENT

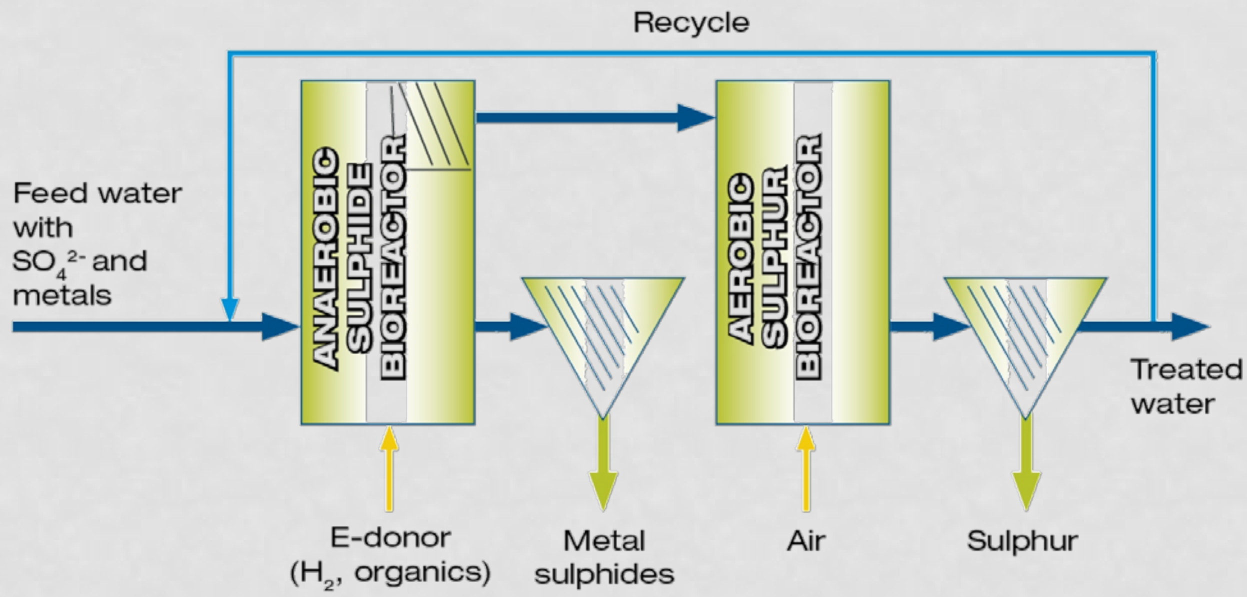
- Active schemes
  - Bioreduction with metal precipitation reaction in single reactor



BIOLOGICAL TREATMENT

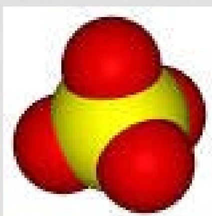
- Active schemes
  - Bioreduction with metal sulfide in single reactor and elemental sulfur production

e.g., SULFATEQ™

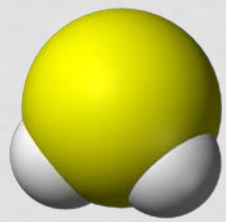


BIOLOGICAL TREATMENT

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



sulfate



sulfide

precipitates

  - 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 of metal content
  - Elemental sulfur
    - Elemental sulfur must be dewatered and dried for beneficial use
  - Bacterial solids
    - Bacteria 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-}, $S_2O_3^{2-}$, SCN^-, CNO^-, NH_3, etc)
    - Arsenic, antimony, molybdenum, silica

CYANIDE TREATMENT

Analyses of Barren Solutions and Tailings Pond Effluents

Parameters	Barren Solution	Tailings Pond
CN	70 - 90	0.3 - 30
Fe	10 - 40	0.3 - 8.5
Ni	0.5 – 10	0.1 – 2.0
Zn	12 – 85	0.2 – 1.0
Cu	6 – 300	0.3 – 16
As	-	0.01 – 30
SCN	40 – 400 -	-
All values in mg/l; data from six mine sites		

CYANIDE TREATMENT

- 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 ($HCN \rightarrow H^+ + CN^-$)
    - HCN is a weak acid; pKa = 9.31 (200c)
  - 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

CYANIDE TREATMENT

- 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
  - CNCl is volatile at pH <8, and extremely toxic.
  - Slow kinetics at pH <8. Fast kinetics at 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
  - H_2O_2 destroys CN^-, 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) $CN^- + H_2O_2 \rightarrow CNO^- + H_2O$ [alkaline pH: 9.0 – 9.5]
    - (2) $CNO^- + 2H_2O$ (Hydrolysis) $+ H^+ \rightarrow NH_4^+ + HCO_3^-$ [pH < 7]
  - Doesn't oxidize iron-cyanide complex, but precipitates as copper-iron-cyanide complex

CYANIDE TREATMENT

- Oxidation with ozone
  - Ozone destroys: CN^-, HCN, WAD (complex of Zn, Cd, and Cu), and SCN
  - Two step reaction
    - (1) $CN^- + O_3 \rightarrow CNO^- + O_2$ [Fast: 10 – 15 Minutes]
    - (2) $2CNO^- + O_3 \rightarrow N_2 + 2HCO_3$ [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)64-)
  - Iron complex cyanide is removed as insoluble zinc/copper ferrocyanide [Cu2Fe(CN)6 or Zn2Fe(CN)6]
  - CN- + O2 + SO2 + H2O = CNO- + H2SO4 (Cu2+ catalyst)
  - Reaction pH: 9 – 9.5
  - SO2: 2.5%
  - Copper: 50 mg/l
  - Kinetics: Rapid (10 minutes)

CYANIDE TREATMENT

- Iron-cyanide precipitation
  - Source: tailings pond water
  - $Fe^{3+} + 6CN^{-} \rightarrow Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-}$
    - Very stable and highly soluble
    - Usually exists as both forms
  - Precipitates as a highly insoluble iron- ferro/ferri cyanide complex
    - $4Fe^{2+} + 3Fe(CN)_6^{4-} \rightarrow Fe_4[Fe(CN)_6]_{3(s)}$ [Prussian Blue]
    - $Fe^{3+} + Fe(CN)_6^{3-} \rightarrow Fe_2(CN)_{6(s)}$ [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

CYANIDE TREATMENT

COMPARISON OF DIFFERENT PROCESSES FOR CYANIDE REMOVAL FROM GOLD MILL EFFLUENT

	Suitability for Removal of				
Process	**CN-/HCN**	**Zn/Cd Complex**	**Cu/Ni complex**	**$Fe(CN)_6$ complex**	**SCN**
Natural Deg.	Yes	partial	No	No	partial
Acid/Strip/abs.	yes	yes	yes	yes	partial
Chlorination	yes	yes	yes	No	yes
Ozone	yes	yes	yes	with UV	yes
H2O2	yes	yes	partial	No	No
GAC	No	partial	yes	yes	No
Cu treated GAC	partial	yes	yes	yes	No
IX	No	yes	yes	yes	possible
IX (water Treated with Cu)	yes	yes	yes	yes	possible

CYANIDE TREATMENT

- Biological CN treatment
  - Thiocyanate and cyanide are TOXIC to biological treatment but are also BIODEGRADABLE
  - Cyanide, cyanate and thiocyanate contain nitrogen and release nitrogen as NH_4-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

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

SELENIUM TREATMENT

SELENIUM TREATMENT

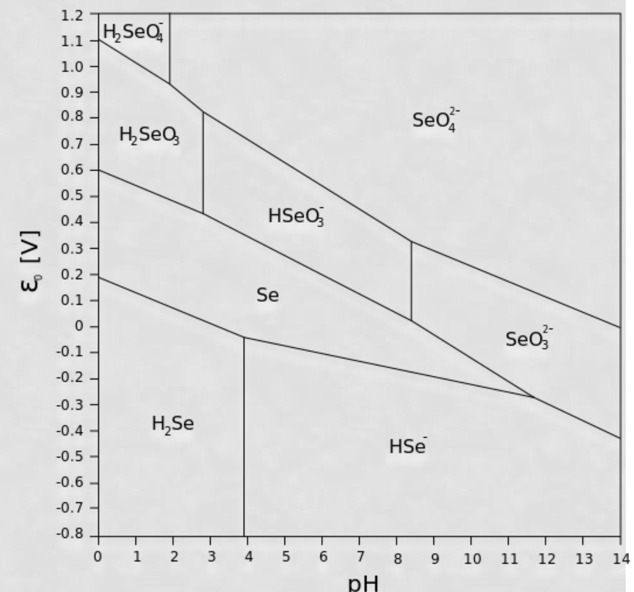
- Overview
  - Selenium treatment fundamentals
  - Selenium iron co-precipitation
  - Biological treatment

VALANCE STATE OF SELENIUM

- Selenium treatment depends on valance state
- Valance/Oxidation state:

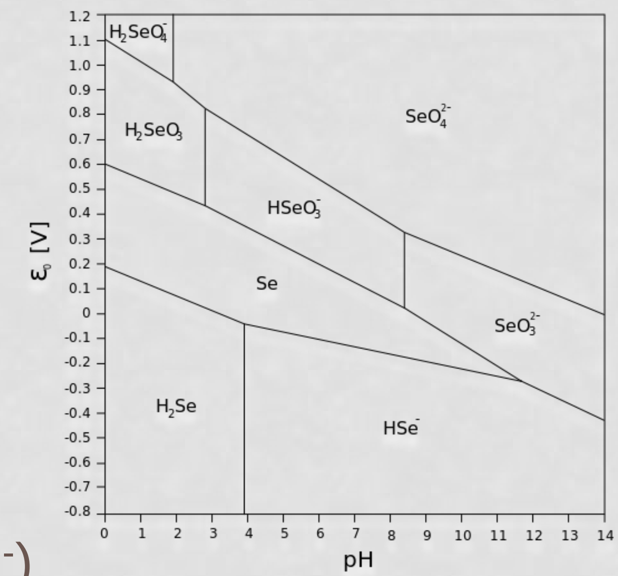
  Primarily as: Selenite (IV); Selenate (VI)

  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 SeO_4^{2-} above pH 1.6
    - Se (IV) presents under moderately reducing condition pH < 8.15 ($HSeO_3^-$) and pH > 8.15 (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
  - CO_2 and biomass are the products

- Electron acceptors
  - Oxygen (aerobic environment)
  - Preferred acceptor
  - Reduced product: H_2O

- ORP Driven

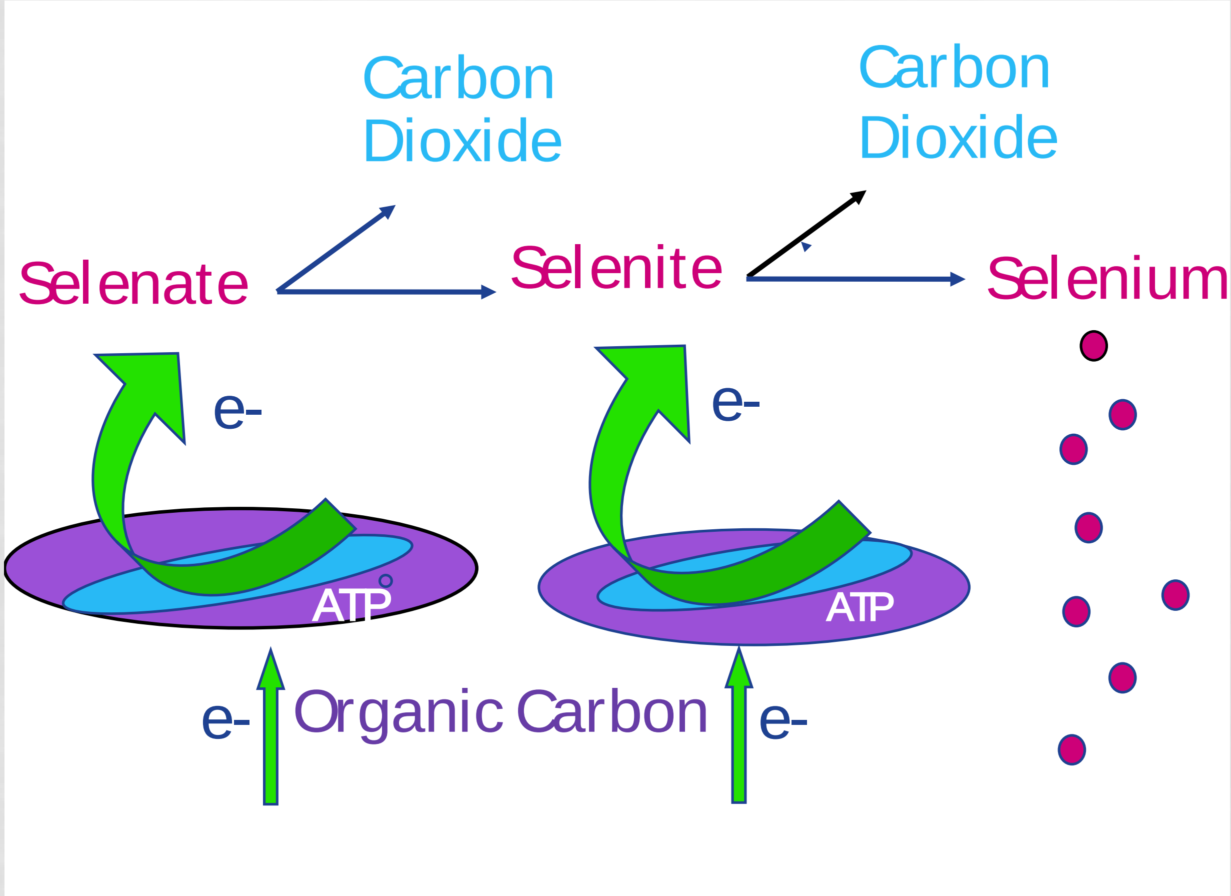
BIOLOGICAL TREATMENT

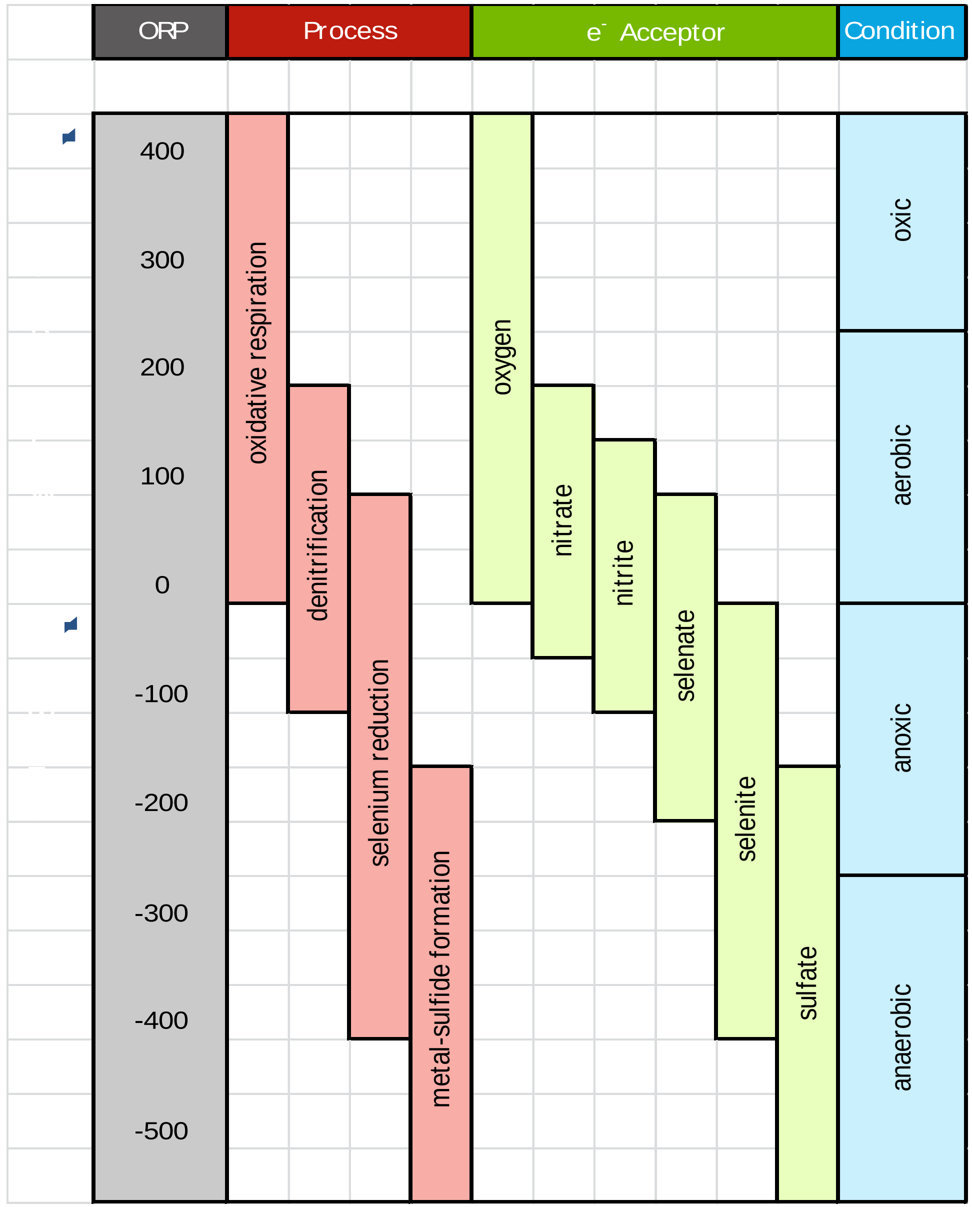
- Reduction of Selenium by Microbes
  - Se (VI) --- Se(VI) ----- Se(II) -----Se^0

$$SeO_4^{2-} + \text{organic carbon} \rightarrow SeO_3^{2-} + \text{organic carbon} \rightarrow Se_0 + CO_2 + H_2O$$

- Anoxic Conditions
  - Heterotrophic bacteria
  - Organics + Selenite/Selenate + N + P
  - New Cells + CO_2 + H_2O + Se^0
- Attached Growth Biological Process
- Water temperature influences reaction rate>>hydraulic residence time (HRT)

BIOLOGICAL TREATMENT




ORP
Process
e- Acceptor
Condition
400
300
200
100
0
-100
-200
-300
-400
-500
oxidative respiration
denitrification
selenium reduction
metal-sulfide formation
oxygen
nitrate
nitrite
selenate
selenite
sulfate
oxic
aerobic
anoxic
anaerobic

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

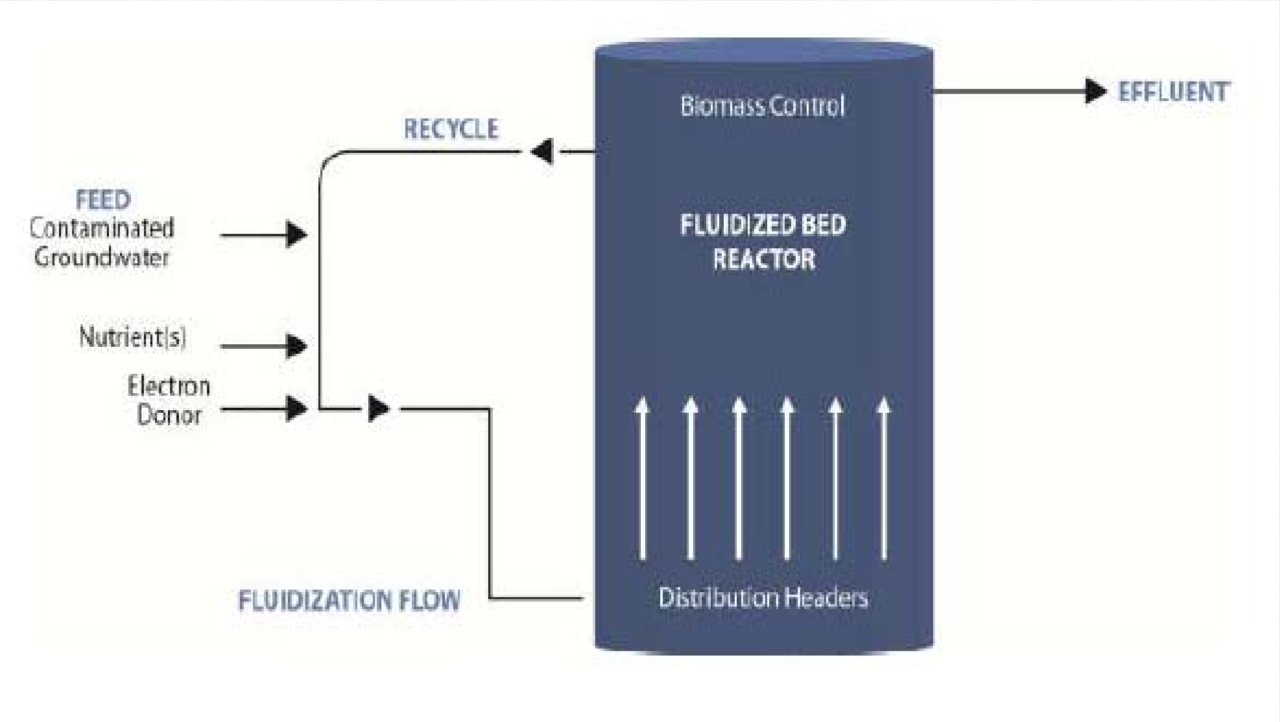
ATTACHED GROWTH SYSTEMS (CONT.)

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

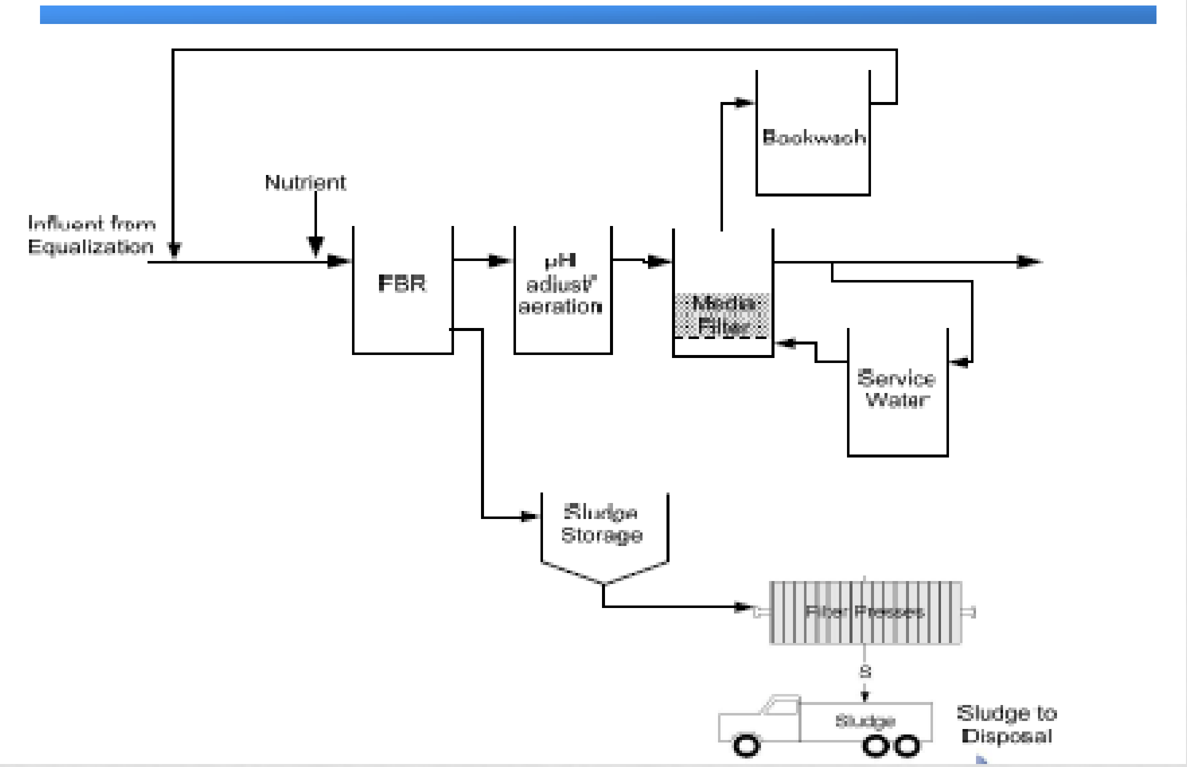
ATTACHED GROWTH SYSTEMS (CONT.)

- Fluidized Bed Reactor



ATTACHED GROWTH SYSTEMS (CONT.)

- Fluidized Bed Reactor



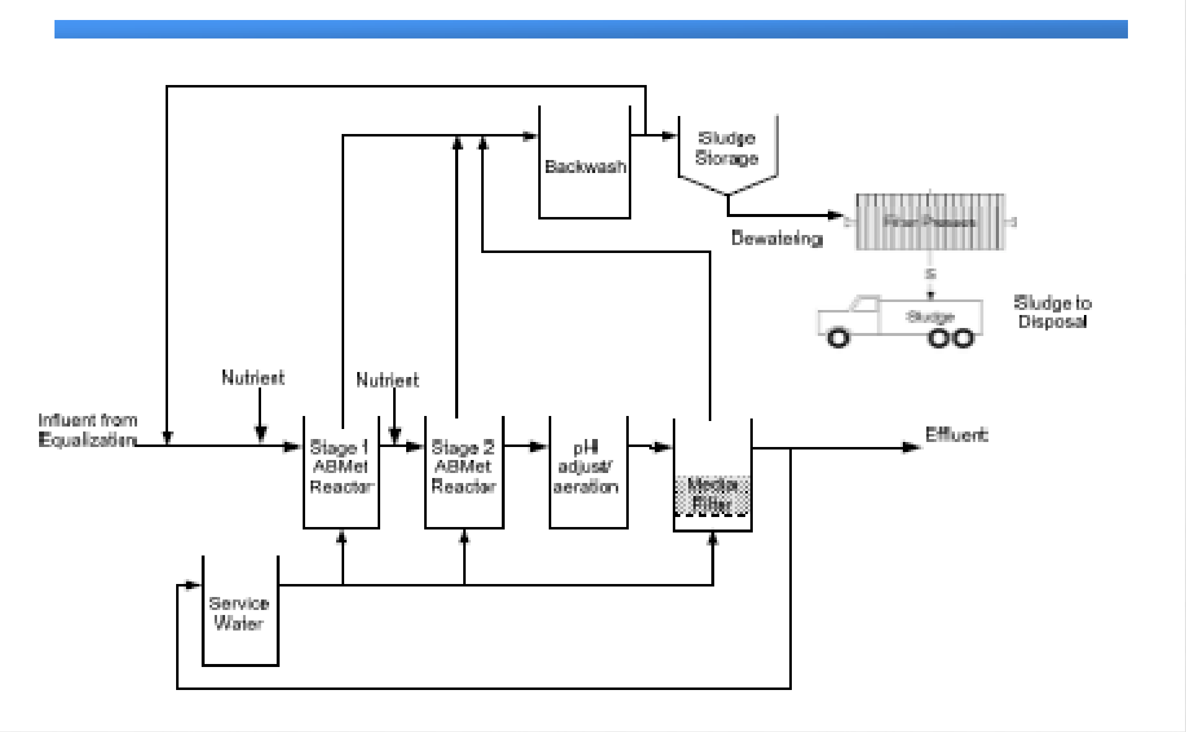
ATTACHED GROWTH SYSTEMS (CONT.)

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
- GE ABMet®

ATTACHED GROWTH SYSTEMS (CONT.)

Packed bed reactor (PBR)



ATTACHED GROWTH SYSTEMS (CONT.)

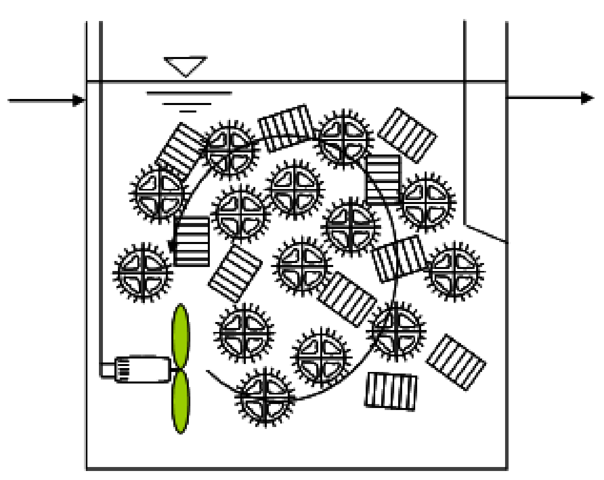
Electro-Biochemical Reactor (EBR)

- 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)

ATTACHED GROWTH SYSTEMS (CONT.)

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

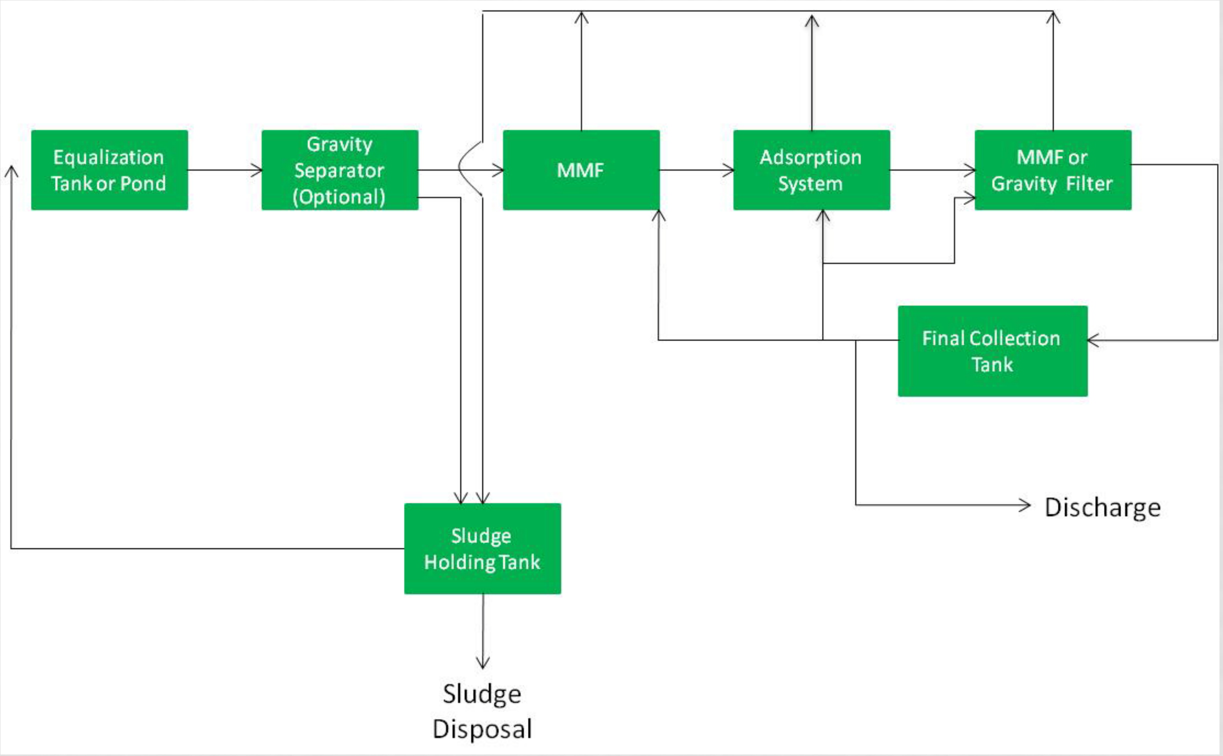
- Adsorption treatment utilizes sorptive media in a reactor vessel to reduce selenite and selenate to elemental Se
- Four types of sorptive media identified:
  - MAR Systems (known as SORBSTAR),
  - SAMMS (Self-assembled Monolayers on Mesoporus Support),
  - Zero Valent Iron (ZVI) and
  - SMI (Sulphur Modified Iron nanoparticles).
- Laboratory testing showed that SMI was effective at reducing selenate. SORBSTAR, SAMMS and ZVI were not effective (confidential client).

ADSORPTION TECHNOLOGIES (CONT.)

- 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

ADSORPTION TECHNOLOGIES (CONT.)

- SMI Media Conceptual Flow Sheet



WASTE STREAM MANAGEMENT

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

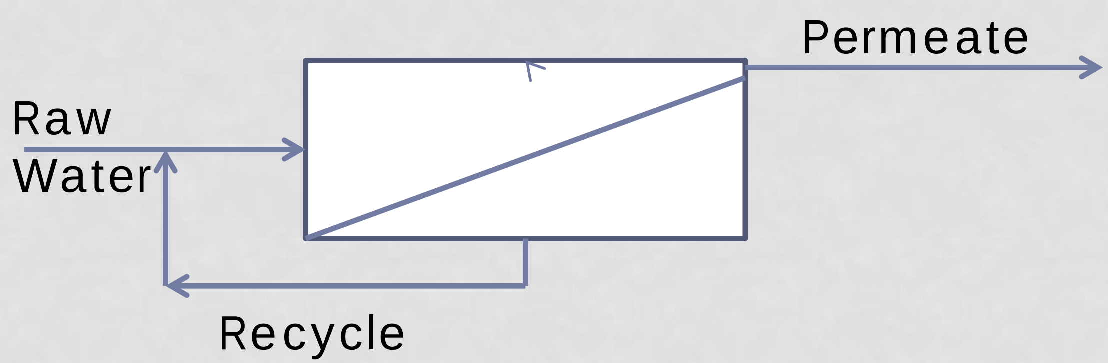
- Filter press for de-watering

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

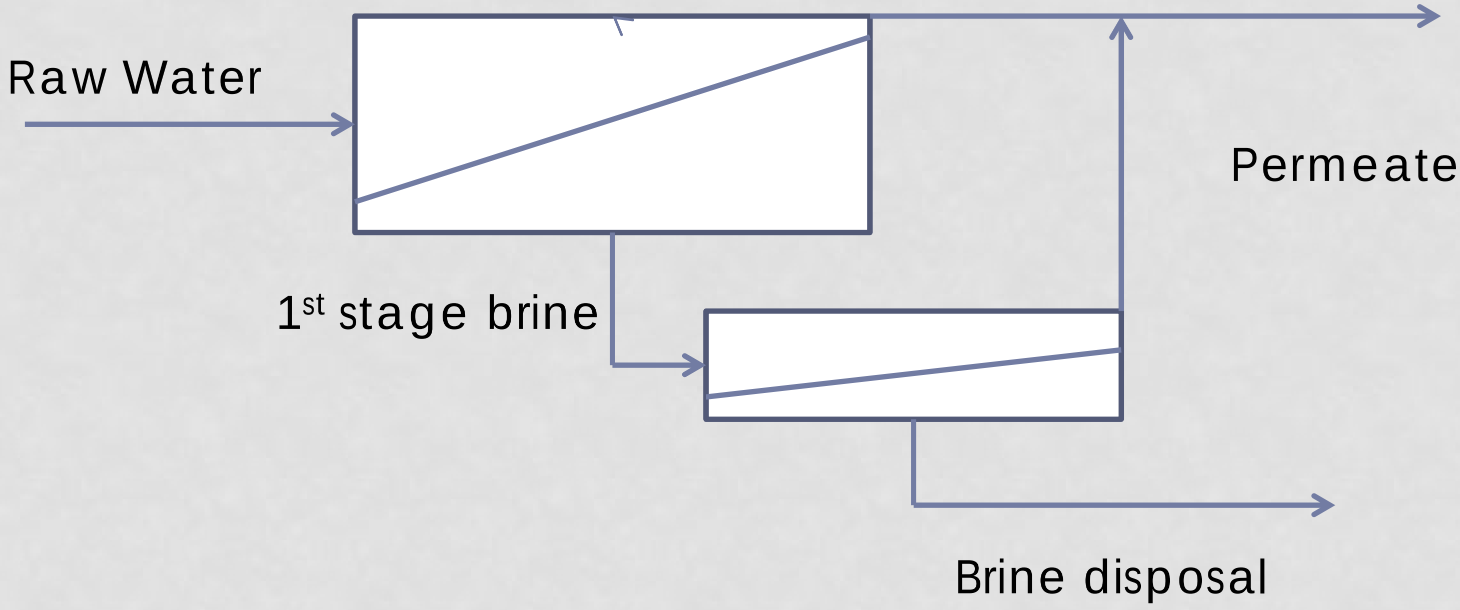
WASTE STREAM MANAGEMENT MEMBRANE BRINE

- 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%



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

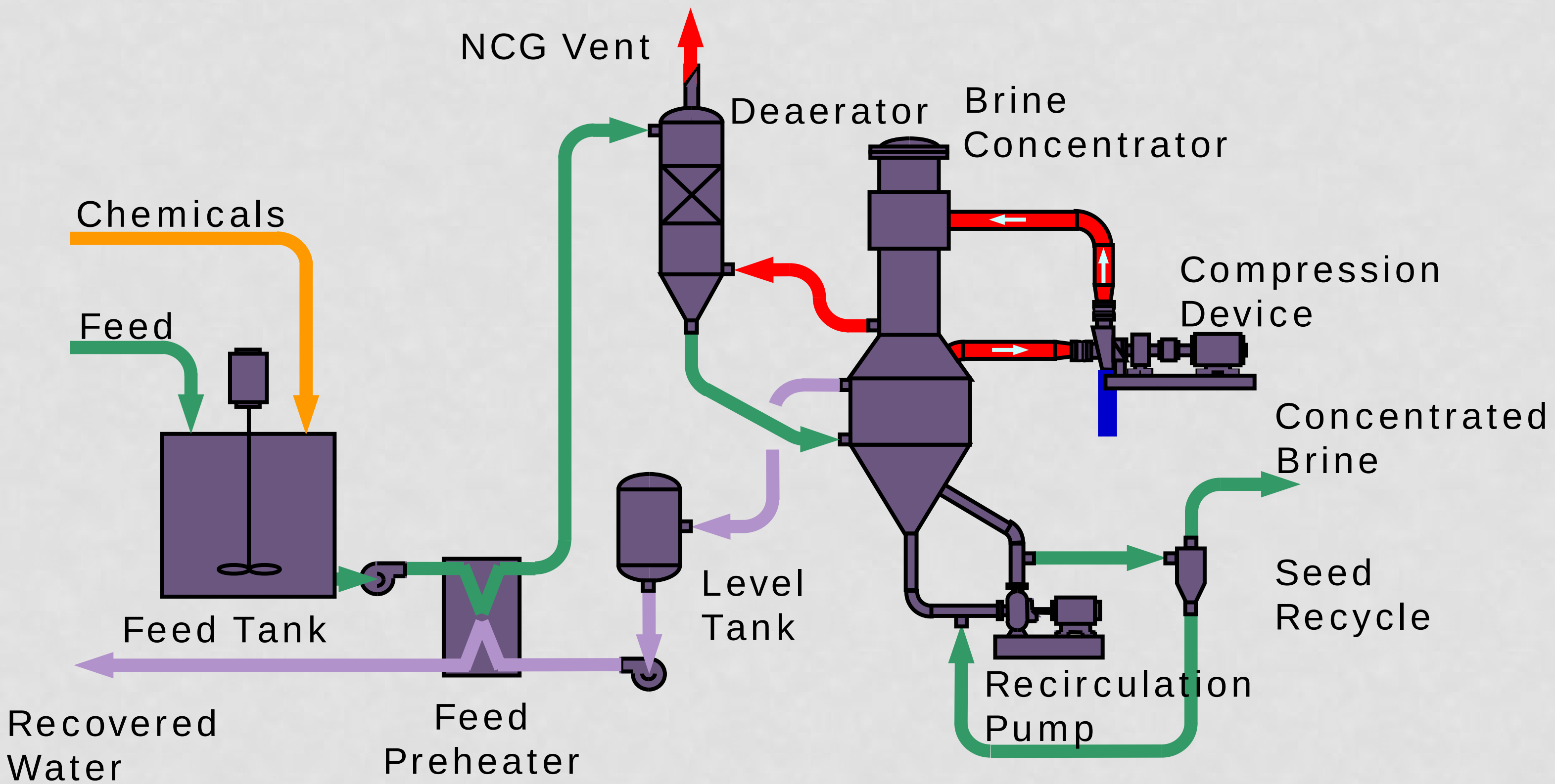
WASTE STREAM MANAGEMENT MEMBRANE BRINE

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

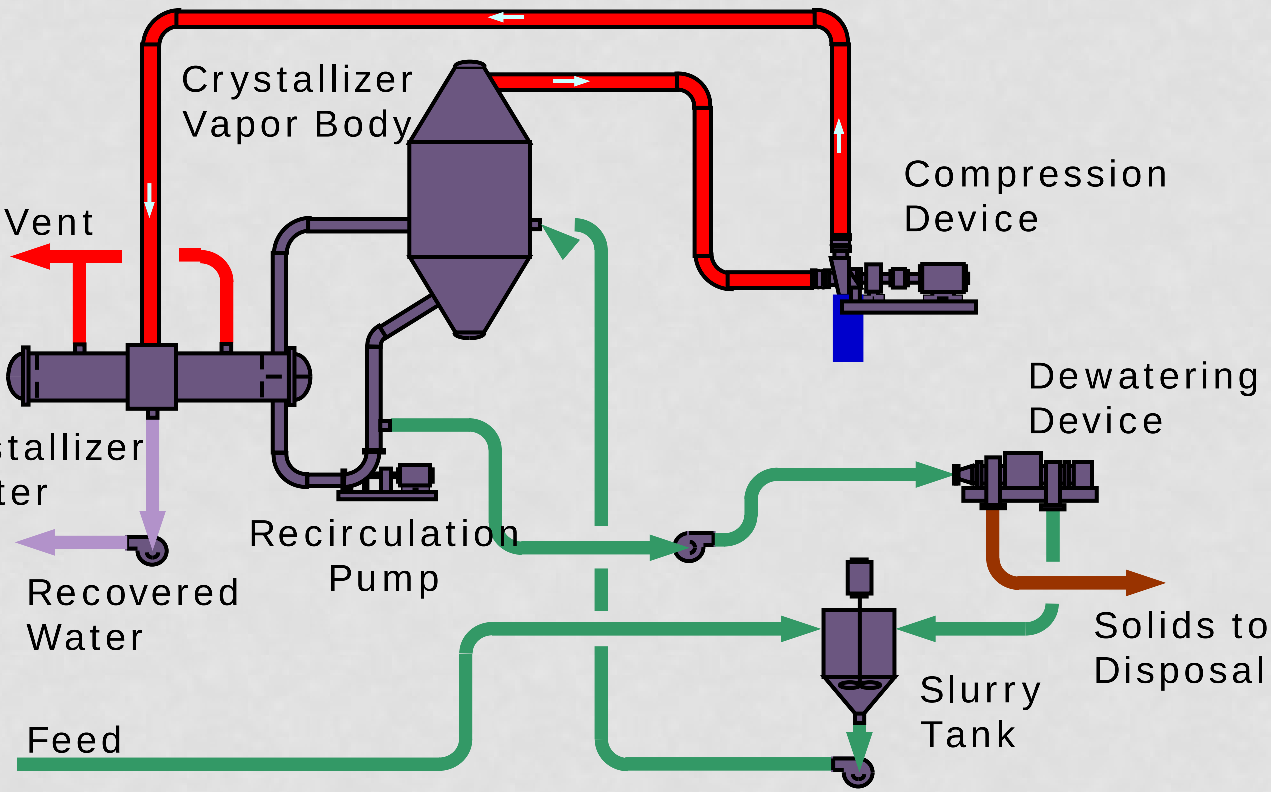
WASTE STREAM MANAGEMENT MEMBRANE BRINE

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)

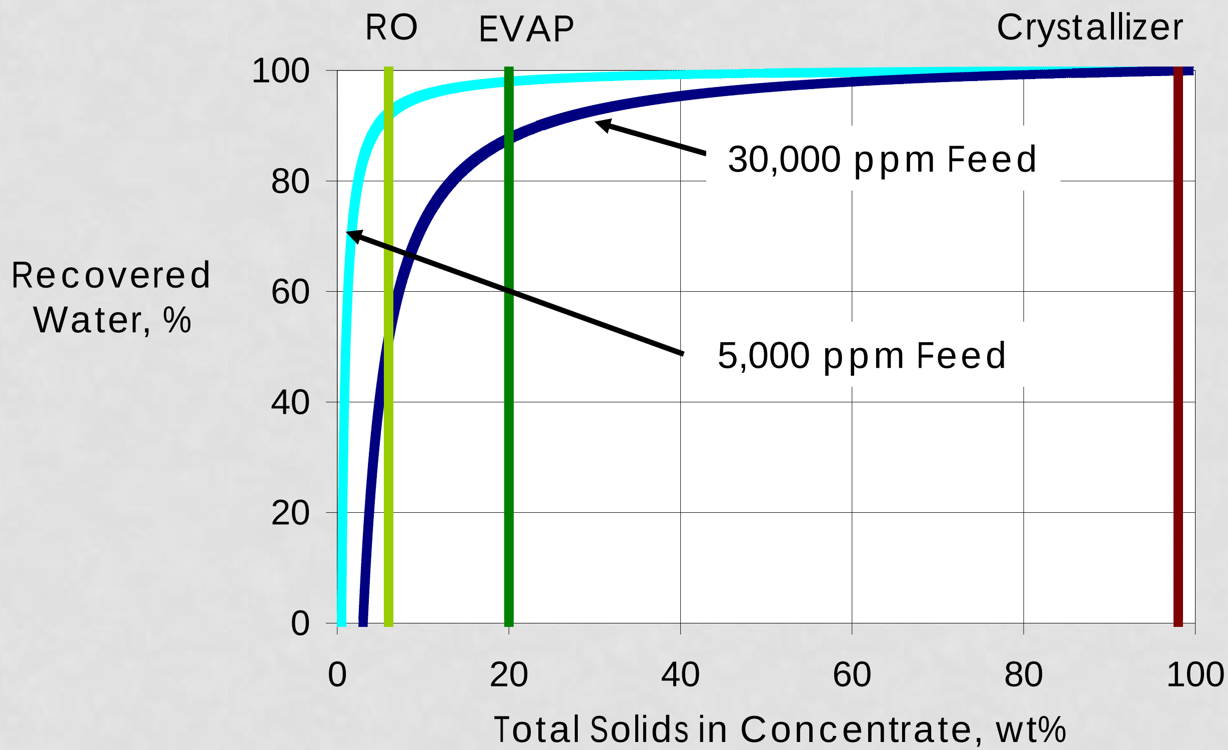
WASTE STREAM MANAGEMENT
MEMBRANE BRINE

Forced circulation crystallizer



WASTE STREAM MANAGEMENT MEMBRANE BRINE

Water Removal Comparison



WASTE STREAM MANAGEMENT MEMBRANE BRINE

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

WASTE STREAM MANAGEMENT MEMBRANE BRINE

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

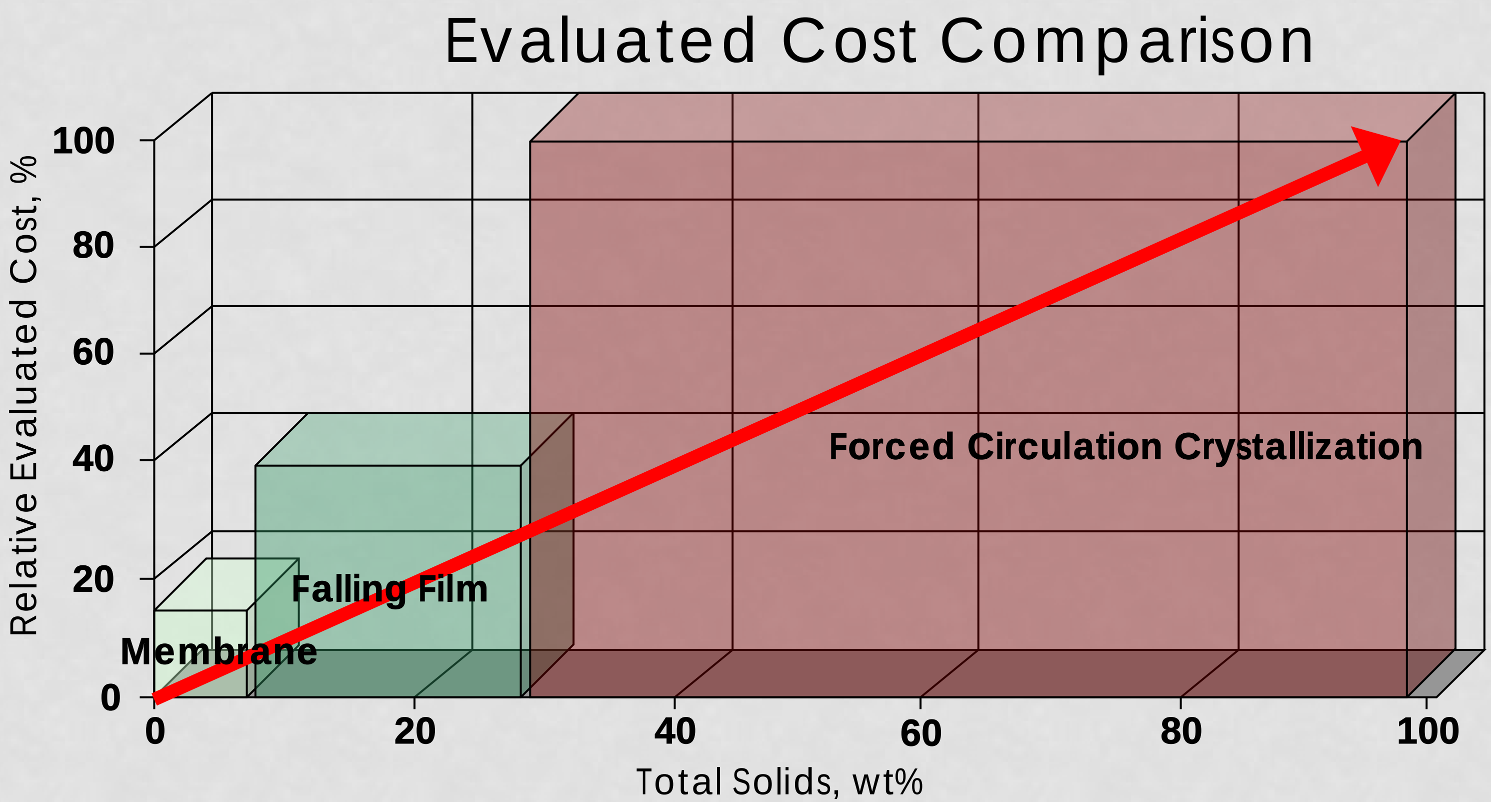
WASTE STREAM MANAGEMENT MEMBRANE BRINE

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



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 AND SUGGESTED READING

REFERENCES

- INAP, 2014. The International Network for Acid Prevention Global Acid Rock Drainage Guide, Rev 1. October 21, 2014. http://www.gardguide.com/images/5/5f/TheGlobalAcidRockDrainageGuide.pdf
- Lorax, 2003. Treatment of Sulfate in Mine Effluents. Lorax Environmental, October, 2003

SUGGESTED FURTHER READING

- The International Network for Acid Prevention Global Acid Rock Drainage Guide, Rev 1. October 21, 2014. Available at gardguide.com
- The International Network for Acid Prevention. Treatment of Sulphate in Mine Effluents. Lorax Environmental. October, 2003
- Chemistry and Treatment of Cyanidation Wastes. T. Mudder, M. Botz, A. Smith. Mining Journal Books Ltd. 2001.