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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

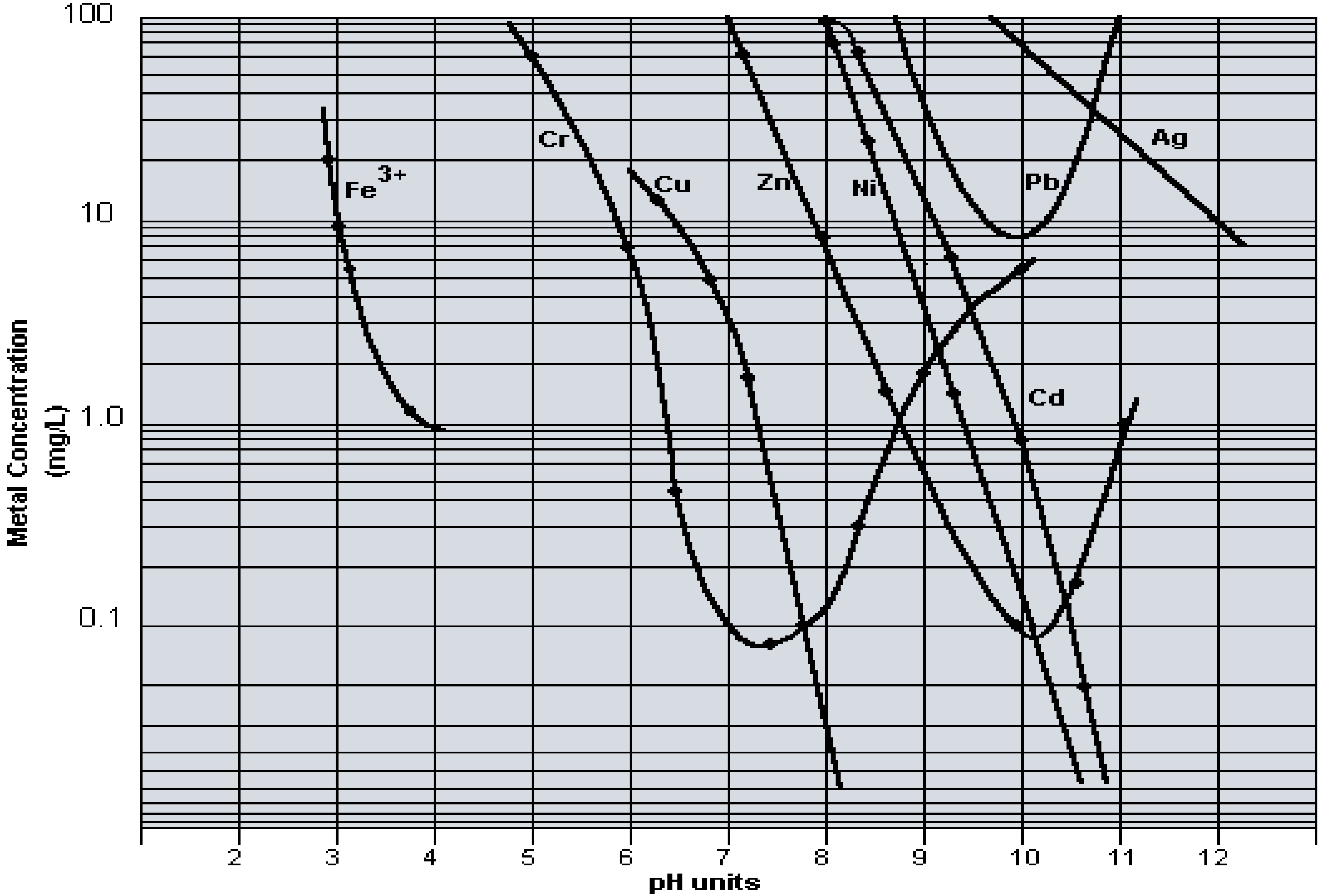
Basics

- **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^- used frequently; price increasing.
  - Sulfides: S^{2-} Stronger bond than hydroxide; H2S Potential
  - LIME, precipitates negative valence ions like Phosphate; adjusts pH, also a coagulant

Hydroxide Precipitation Chart



Limitations of Hydroxide Precipitation

Hydroxides raise pH and increase precipitant dosage

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

- 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

CHELANTS

Chelate (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

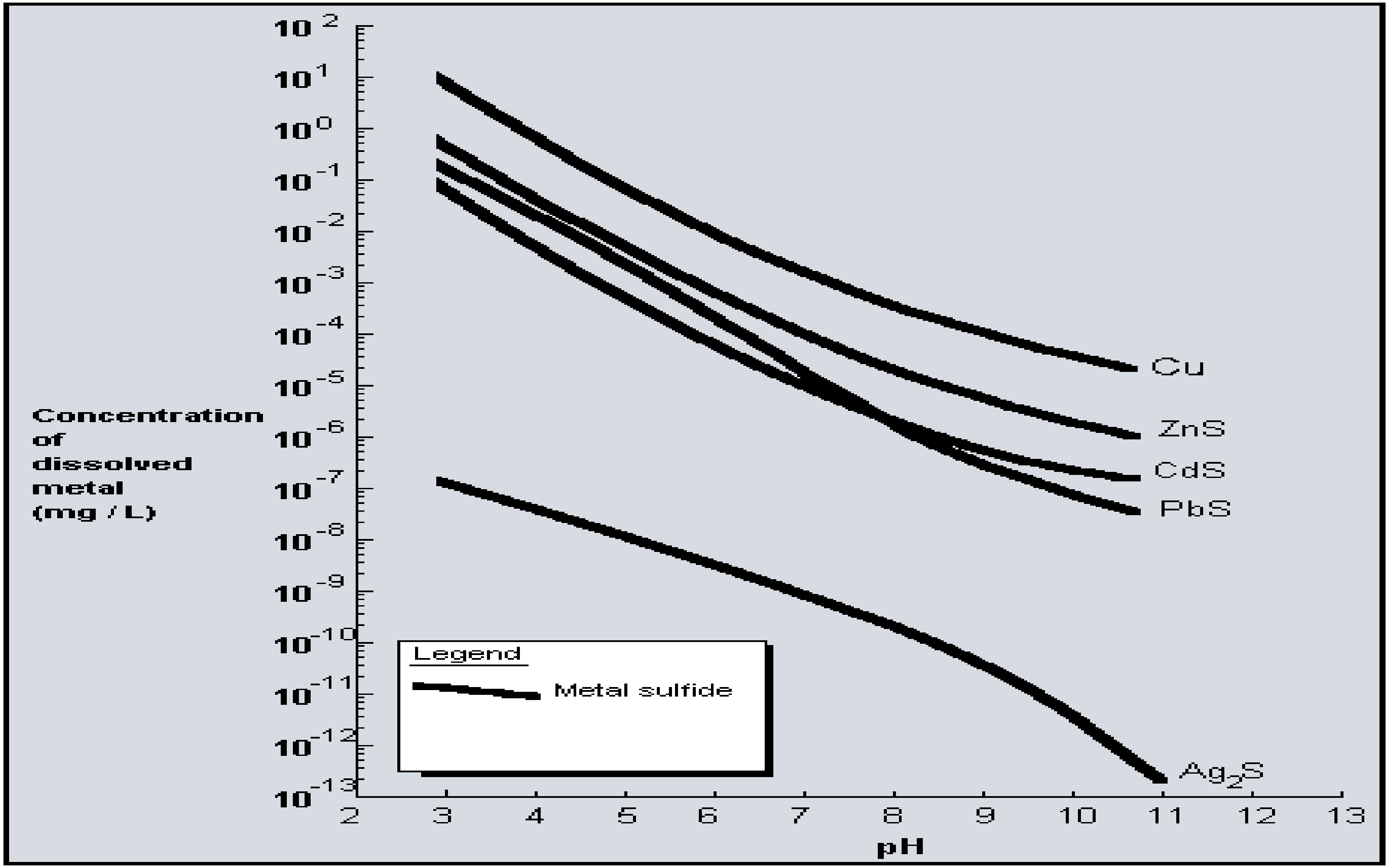
Common Chelants

- Ammonium Chloride
- Ammonium Hydroxide
- Ammonium Bifluoride
- Acetylacetone
- Citric Acid
- Chromotropic Acid
- Cyanide
- Diethylenetrinitrilopentaacetic Acid
- Dimeracaptopropanol
- Dimethylglyoxime
- Dipyridyl (2,2-Bipyridine)
- Diphenylthioformic Acid
- Ethylenediamine
- Ethylenediaminetetraacetic Acid (EDTA)
- **GLUCANATE**
- Hydroxyethylethylenediamin
- 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



Sulfide and Chromium

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

$$Cr^{+6} + 1.5CaS_2O_3 + 1.5H_2O \rightarrow Cr^{+3} + CaSO_4 + 1.5S + 3H^+$$

- Cr^{+6} = Hexavalent Chromium
- CaS_2O_3 = Calcium Polysulfide
- Cr^{+3} = Trivalent Chromium
- $CaSO_4$ = Calcium Sulfate
- S = Sulfur
- H^+ = Hydrogen Ion

Fenton Reaction

- Oxidize non-cyanide (Organic) chelants at a low pH ***<u>using iron, peroxide, and acid</u>***

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

$$\mathbf{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-}$$

- Hydroxyl generated is a powerful, non-selective oxidant

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

HO• + PO3 = PO43

Lime Precipitation

One Calcium Ion with Two Hydroxyl Ions

- Reduces Sodium Hydroxide Consumption
- Reduces Sulfates in the Effluent - $CaSO_4$
- Treats Gluconates
- Precipitates Fluorides
- Removes Phosphates - $Ca_3(PO_4)_2$

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 $CaSO_4$ 9.1×10^{-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

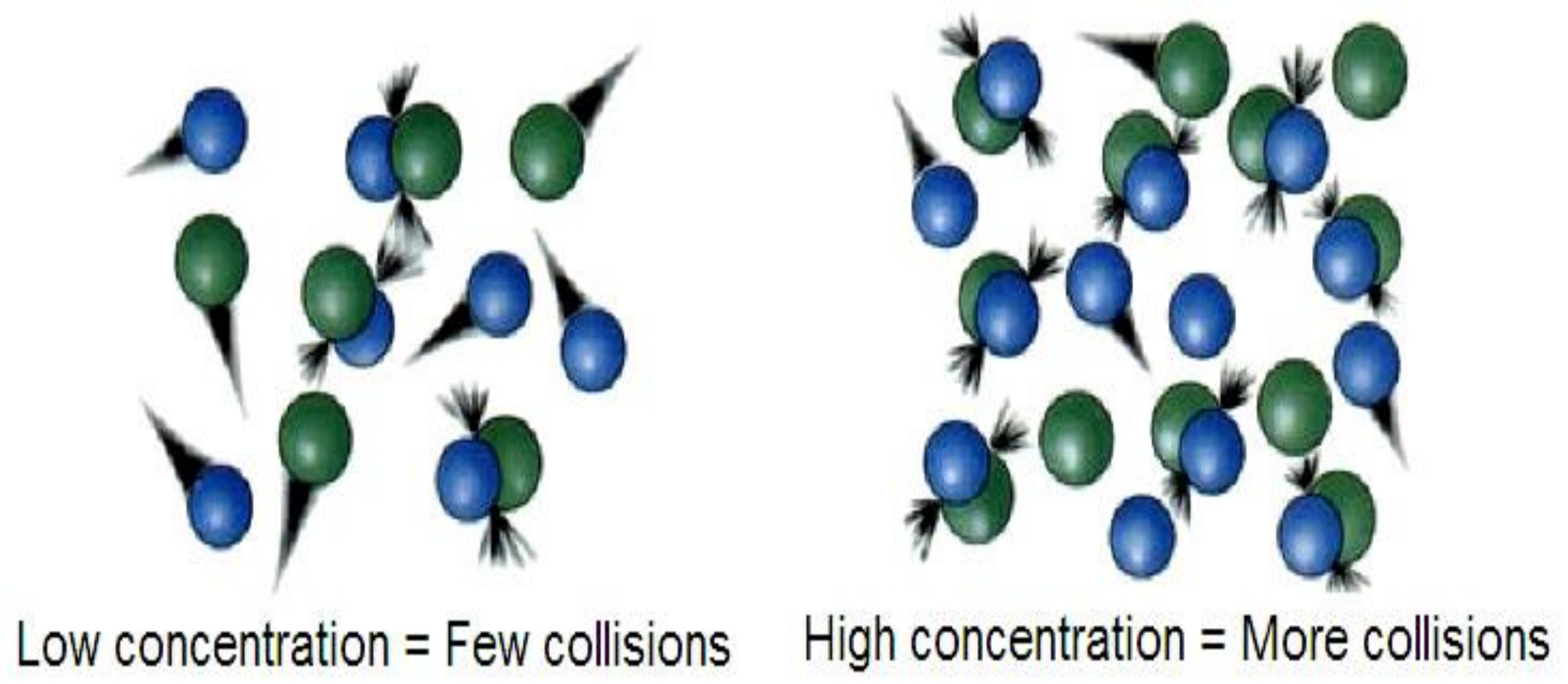
- Allows for lower saturation ratio of OH ions

- Provides seed crystals for secondary nucleation

- Sludge return increases the reaction rate

- Improves yield of ALL chemicals employed

Reaction Rate



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

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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”

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REVERSE OSMOSIS

EFFLUENT EVALUATION

	PRE	CCI				POST	CCI	
Ion	Raw Water mg/L	Concentrate mg/L	Permeate mg/L	PERMIT LIMIT	Ion	Raw Water mg/L	Concentrate mg/L	Permeate mg/L
Cd	0.02	**0.08**	ND	**0.07**	Cd	0.01	**0.04**	ND
Cr	0.67	**2.68**	0.01	**2.30**	Cr	0.44	**1.76**	0.01
Cu	0.88	**3.52**	0.01	**2.00**	Cu	0.36	**1.44**	ND
Ni	1.10	**4.40**	0.02	**1.80**	Ni	0.27	**1.08**	0.01
Zn	1.48	**5.92**	0.01	**1.70**	Zn	0.32	**1.28**	0.01
Ca	2.00	13.32	0.01		Ca	58.93	235.72	0.12
Na	859.69	3438.76	214.92		Na	365.00	1445.70	5.95
SO4	1219.83	4879.32	304.96		SO4	344.71	1188.01	0.69
F	14.24	56.96	3.56		F	4.02	16.08	1.01
NO3	14.20	56.80	3.55		NO3	20.40	79.23	0.93
MISC	233.87	935.48	58.47		MISC	149.56	598.24	37.39
TDS	**2347.98**	**9397.24**	**585.52**		**TDS**	**944.02**	**2970.34**	**8.73**
pH	7.00	6.31	4.25		pH	7.70	6.70	4.47

CHEMICAL COST COMPARISON

Chemical		Current		Proposed	
	Cost Per	Units Per Year	Annual Cost	Units Per Year	Annual Cost
	L/Kg				
Caustic Soda	$0.49	98,700.00	$48,363	49,350	$24,182
Sulfuric Acid	$0.54	27,500.00	$14,850	13,750	$7,425
Sodium Bisulfite	$0.81	17,500.00	$14,175		
Calcium Chloride	$0.42	14,000.00	$5,880		
Emulsion Polymer	$8.25	264.00	$2,178		
TDS PROGRAM					
Hydrogen Peroxide	$2.65			1,600	$4,240
Lime	$0.59			8,225	$4,853
Reducing Agent	$2.85			8,750	$24,938
Chelate Break	$2.54			2,917	$7,408
Latex Based Polymer	$8.25			232	$1,917
CHEMICAL COSTS			***$85,446***		***$74,962***
	Cost Per Tonnes	Tonnes Per Year	Annual Cost	Tonnes Per Year	Annual Cost
Disposal Cost	$60.00	240	$14,400	160	$9,600
15%	***Total Cost of Current Program***		***$99,846***		
Annual Savings	***Total Cost of Proposed Program***				***$84,562***
	Estimated Annual Savings				***$15,284***

THANK YOU

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