WASTEWATER TREATMENT

How did I get this stuff?

- Treat, bury, incinerate the waste as last resort.
 - * Landfilling sludge cost \$200-\$500 ton.
 - * Incineration can be 4 times as expensive
- The Goal:
 - Eliminate the production of hazardous waste through process redesign or raw material substitution.
 - Recover and reuse waste whenever possible.
 - Segregate hazardous and non-hazardous waste.

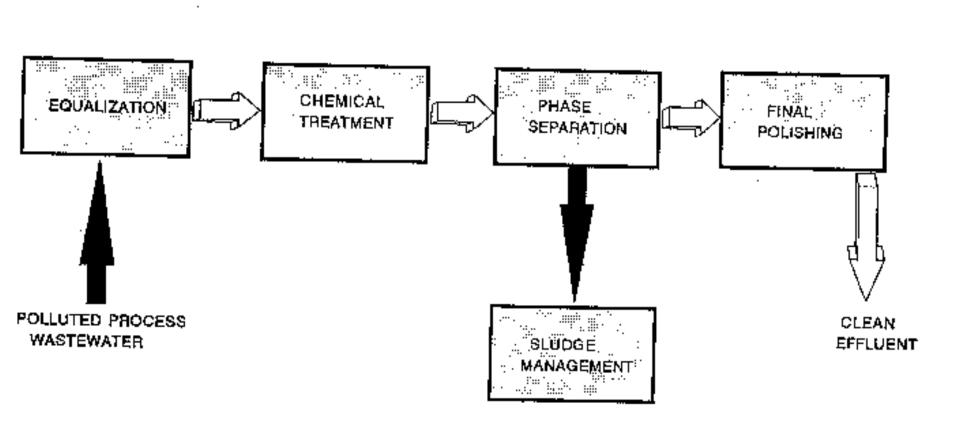


Why Treat? OPPORTUNITIES

- Comply with discharge limit
- Reduce water, chemical consumption
- Reuse water
- Avoid user charge
- Reduce monitoring costs
- Reduce Risk
- Improve knowledge of what's going on
- Improve product quality



WASTEWATER SYSTEM COMPONENTS

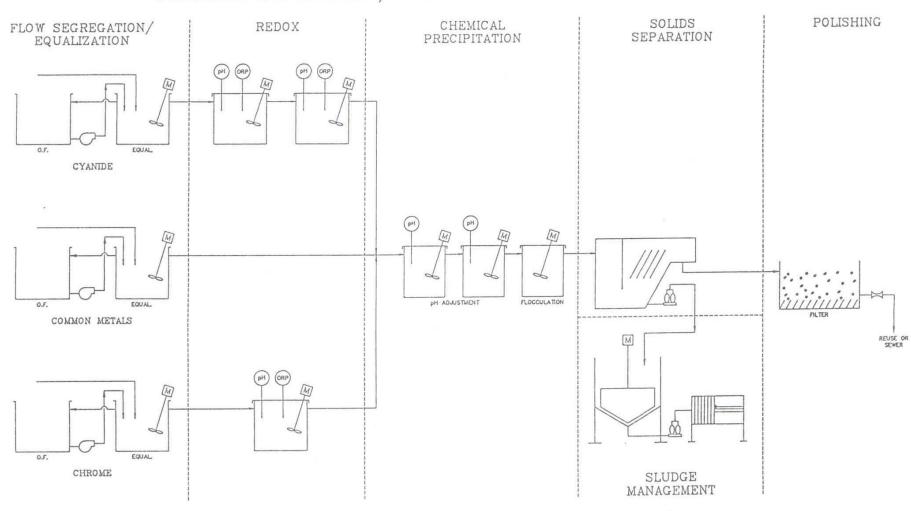


PROCESS SCHEME

- Collect separately
- Pretreat special waste (chrome, cyanide, oily waste)
- Equalize
- pH adjust (precipitation)
- Flash/flux (coagulation)
- Settling
- Polishing
- Residuals treatment
- Discharge



TYPICAL PHYSICAL / CHEMICAL TREATMENT SYSTEM



EQUALIZATION

Smoothing out the bumps, the system shock absorber

DEFINITION

Equalization dampens out the hydraulic and pollutant loads entering the wastewater treatment system. This allows the system to run efficiently at steady state.



EQUALIZATION

Smoothing out the bumps, the system shock absorber

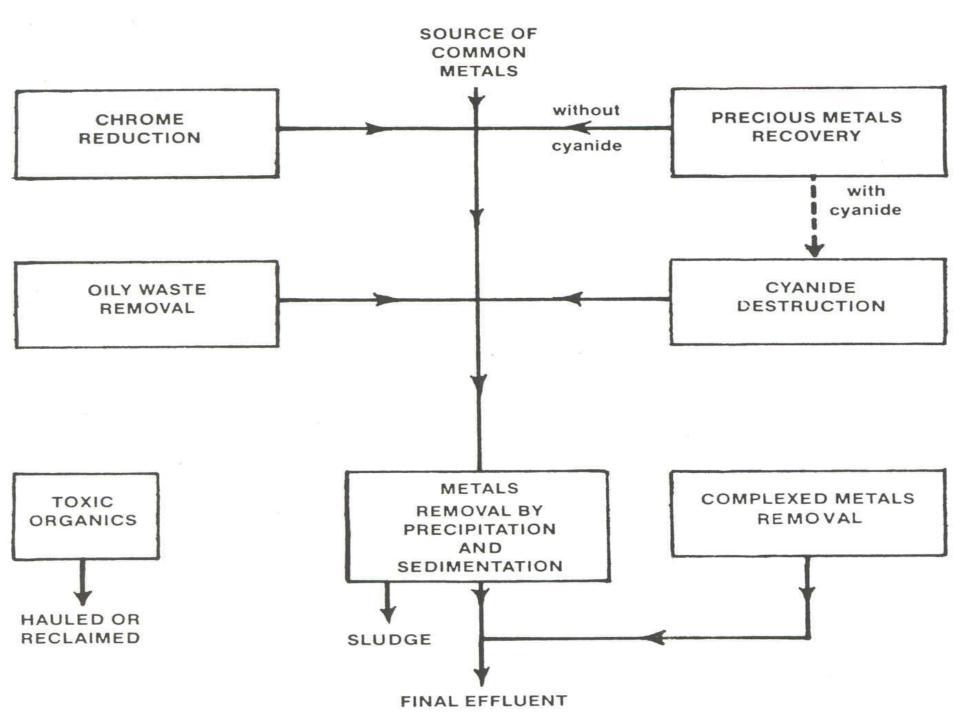
Flow Seperation

Separate incompatible waste streams to save equipment and operating costs

Separate:

- >Concentrated wastes from dilute wastes
- >Oily wastes from non-oily wastes
- >Hexavalent chromium, cyanide and common metal wastes from each other
- >Complexed wastes from non-complexed wastes
- >Toxic organics





EQUALIZATION

Smoothing out the bumps, the system shock absorber

Equalization

Equalization tanks must be large enough to dampen out peak hydraulic flows. It should also be fully mixed. In some industrial wastewaters aging also helps flocculation

Overflow Storage

Overflow storage tanks are used to store wastewater during system upsets. They may be combined with the equalization tank or installed as separate units.



PHYSICAL/CHEMICAL TREATMENT

Getting the stuff ready to get the stuff out

pH CONTROL

Most chemical treatment processes require pH control to optimize reactions. pH treatment and control by pH meter and reagent control system

REDOX (<u>RED</u>UCTION/<u>OX</u>IDATION) REACTIONS

Changing the oxidation state of pollutants to render them non-toxic or available for precipitation. Redox reactions are usually monitored and controlled by oxidation/reduction (ORP) probes which read out in millivolts. Oxidants cause ORP probes to read higher millivolts. Reductants cause ORP probes to read lower millivolts.



pH CONTROL

- Applications
 - Discharge limits pH 5 10
 - Metals Precipitation/Solubility
 - Oily waste phase separation
 - Redox
 - Chrome Reduction
 - Cyanide Oxidation



pH CONTROL

- pH is a scale of units developed to measure the quantity of free H+ (pOH is the measurement of OH) p means – log
- 0 is most acid7 is neutral14 is most basic; alkaline; caustic
- pH= -log 1/(H+)

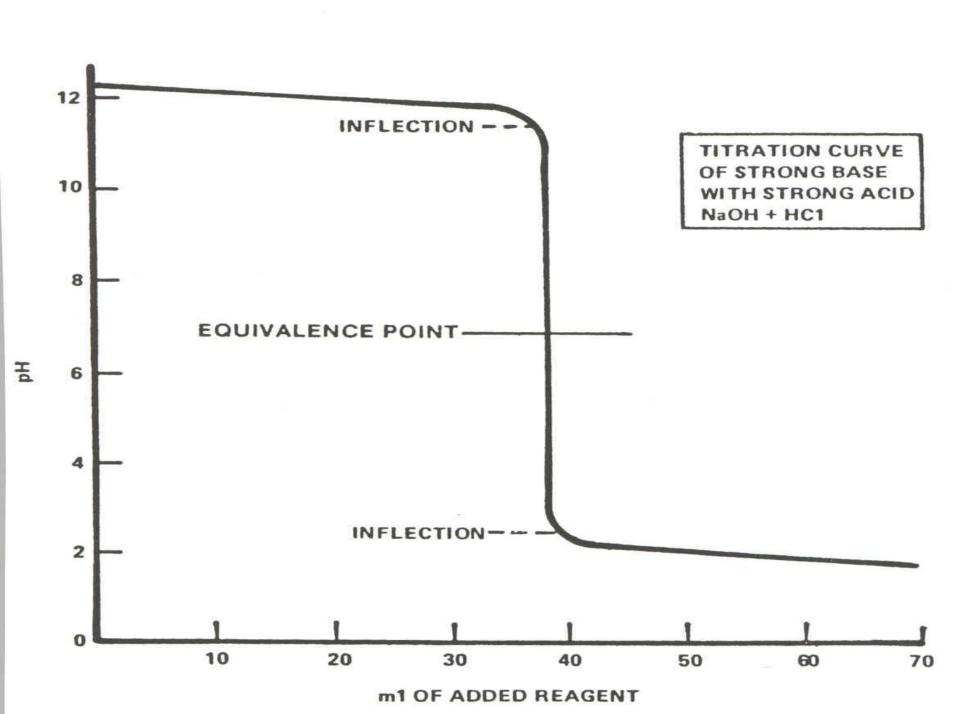
Main thing to understand from this is a pH unit change of 1 represents a H+ concentration of 10 fold



pH CONTROL

- Titration curve
 NaOH +HCl----→NaCl + H₂0
- pH probe placement in reaction tank is important
- Chemicals typically used for pH adjustment
 - Sodium hydroxide
 - Lime to raise pH
 - Sulfuric Acid to lower pH





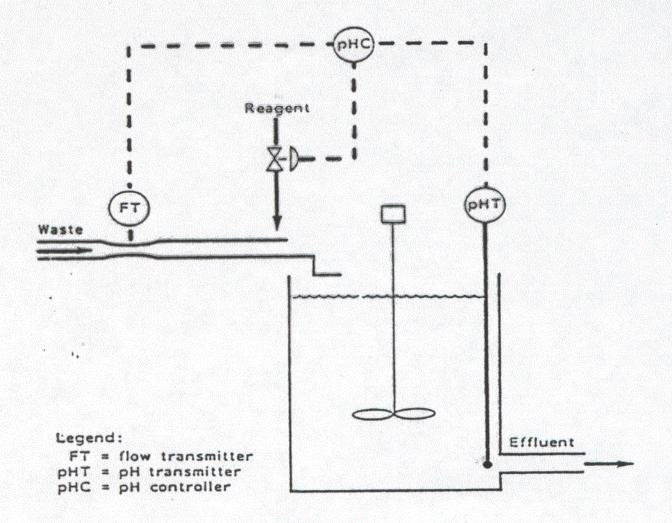


Figure 18. General purpose feedback controlled mixed reactor.

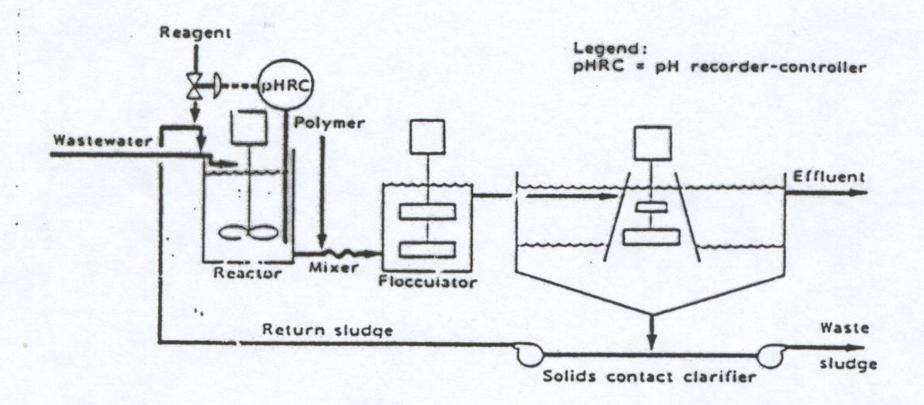
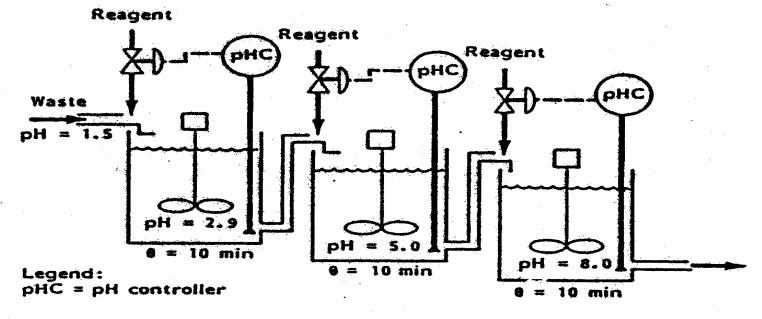
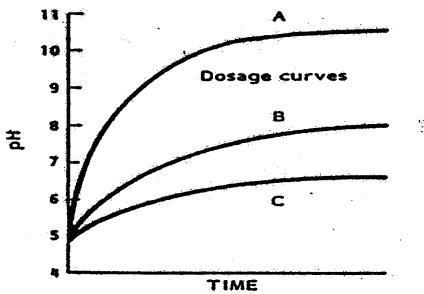
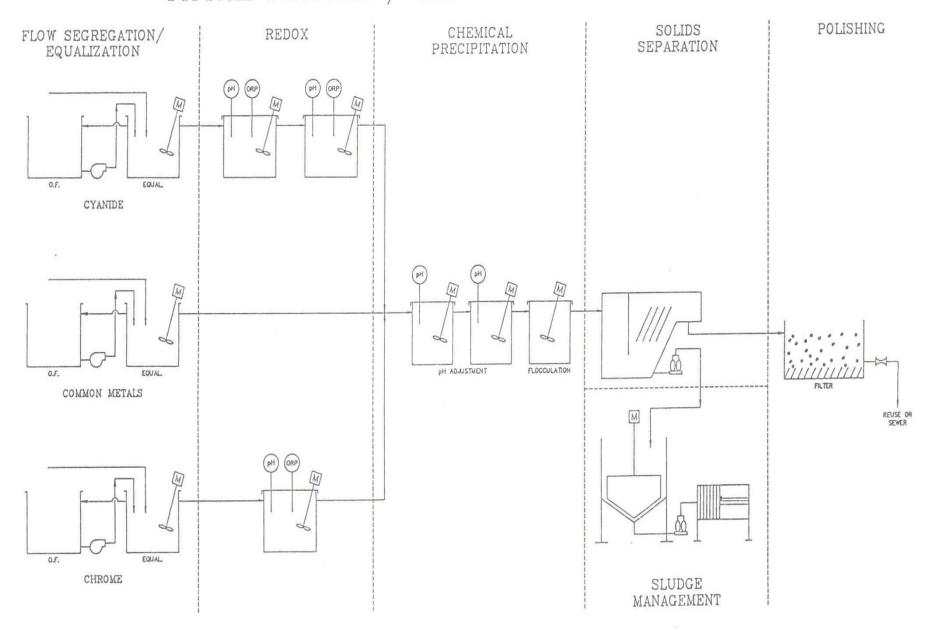


Figure 22. Process schematic for precipitation and separation of target substances.





TYPICAL PHYSICAL / CHEMICAL TREATMENT SYSTEM

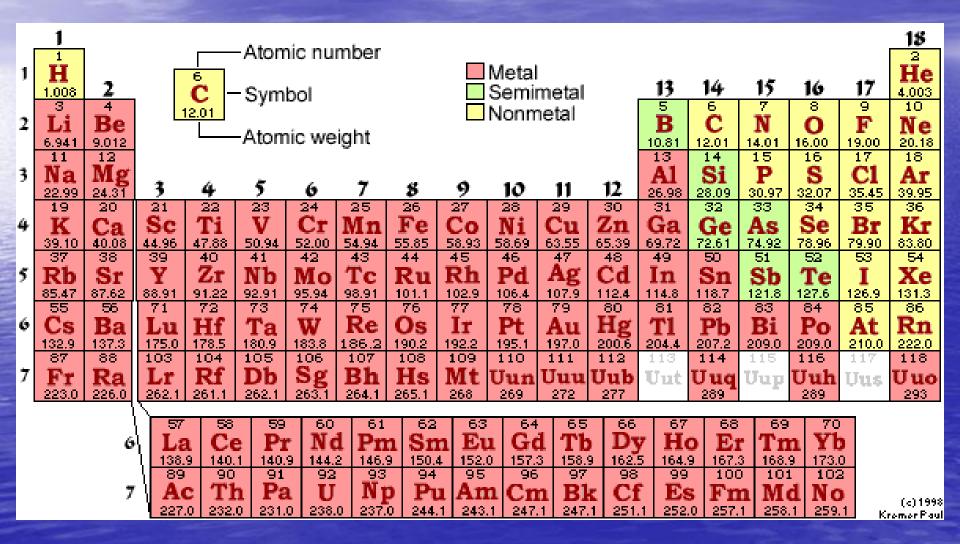


Oxidation-Reduction (ORP, REDOX)

- Oxidation numbers
 - Neutral vs. Ionic species
 - Periodic Chart
 - Oxidation number goes up with oxidation
 - Oxidation number goes down with reduction
 - Examples: NaCl, Cr(OH)₃, NiCl₂, H₂0, CO
- Oxidation-Reduction; the exchange of electrons
 - LEO loss of electrons is oxidation
 - GER gain of electrons is reduction
 - A reducing agent gives up electrons and is oxidized
 - An oxidizing agent accepts electrons and is reduced



Periodic table





Oxidation-Reduction (ORP, REDOX)

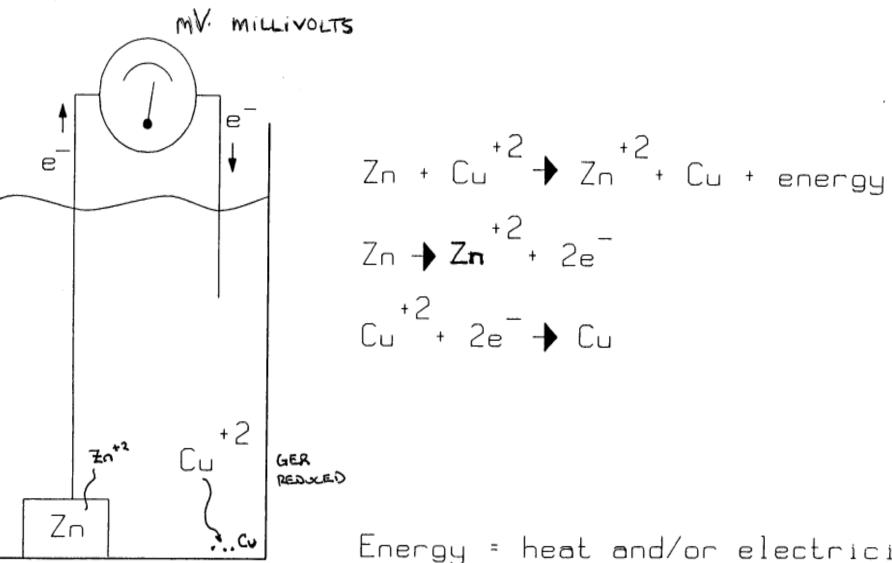
- Movement of electrons through a wire = electric current. When the copper solution and zinc metal are in contact with each other through a wire, heat & electric current are given off.
 - Example: zinc metal in a copper solution-Voltaic Reaction

$$Zn^{0} + Cu^{++} \leftarrow \rightarrow Zn^{++} + Cu^{0}$$

 $Zn^{0} \leftarrow \rightarrow Zn^{++} + 2e^{-}$
 $Cu^{++} + 2e^{-} \leftarrow \rightarrow Cu^{0}$



VOLTAIC CHEMICAL REACTION



LEO ひろいひってもひ Energy = heat and/or electricity

Oxidation-Reduction (ORP, REDOX)

- Electricity is measurable with a voltmeter-ORP METER MILLIVOLTS
 - Voltage is determined by:
 - The nature of the electrodes; gold vs. platinum (platinum is fouled by cyanide and sulfide; MUST BE KEPT CLEAN!)
 - The concentration of all the species in solution
 - The temperature
 - There is no ABSOLUTE voltage setting in any redox reaction



Oxidation-Reduction Examples

- OP Mg + 2H₃O⁺ → Mg⁺² + H₂ + 2H₂O
- \sim Zn + Cu⁺² \rightarrow Cu + Zn⁺²
- Ag + $2CN^{-} \rightarrow Ag(CN)_{2}^{-} + e^{-}$ (silver plating reaction at the anode)
- $^{\circ}$ Ag(CN)₂⁻ + e⁻ → Ag + 2CN⁻ (silver plating reaction at the cathode)
- $CrO_3 + 6H^+ + 6e^-$ → $Cr + 3H_2O$ (chromium plating reaction at the cathode)



Chromium Reduction

- Hexavalent chromium Cr⁺⁶ (orange or yellow)
 - Used for plating chrome, chrome conversion coating and etching with chromic acid
 - Extremely toxic
 - Increasing low discharge limits
 - Prefers to pick up O⁻² and form chromates which act like an anion and will not precipitate out as a metal hydroxide

$$CrO_3 + OH^- \rightarrow Cr(OH)_6$$



Trivalent Chromium Cr+3

- Blue or blue-green
- Reduced form of Cr+6
- Much less toxic
- Precipitates well as metal hydroxide



Chromium is reduced with the use of:

- Sulfur dioxide gas; SO₂ − pH 2 − 2.5
 - Poisonous gas, must be handled very carefully
 - Expensive manifolding and equipment needed
 - Least expensive chemical
 - Generally used in very large volume shops

$$SO_2 + H_2O \rightarrow H_2SO_3$$

(sulfur dioxide + water \rightarrow sulfurous acid)
 $3H_2SO_3 + 2H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 5H_2O$
(sulfurous acid + chromic acid \rightarrow chromic sulfate + water)



Chromium is reduced with the use of:

- Sodium bisulfite
 - $NaHSO_3 pH 2 2.5$
 - Generally used in smaller shops
- Sodium metabisulfite
 - Structurally different, Na₂S₂O₅
 - Works the same chemically

```
2H_2CrO_4 + 3NaHSO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 5H_2O
Chromic acid + Sodium bisulfite + sulfuric acid \rightarrow
chromic sulfate + sodium bisulfate + water
```



Chromium is reduced with the use of:

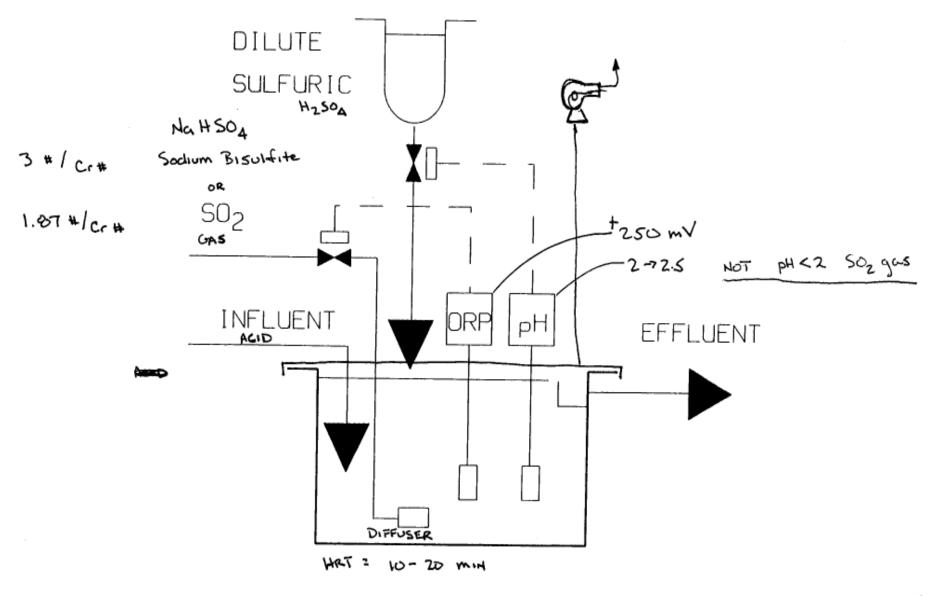
- Sodium hydrosulfite
 - Na₂S₂O₄ use at pH of 4
 - Used for batch treatments
 - Expensive
 - Will ignite in contact with water

 $Na_2S_2O_4 + 2H_2CrO_4 + 2H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4H_2O + Na_2SO_4$

- Sodium hydrosulfate + chromic acid + sulfuric acid → chromic sulfate + water + sodium sulfate
- Ferrous sulfate
 - FeSO₄



CONTINUOUS TREATMENT PROCESS FOR CHROMIUM BEARING RINSE WATER



CHROME REDUCTION

Chromium Reduction

- Millivolt reading approximately +250
 - Spot testing is necessary kits available using diphenylcarbazide in acetone
 - Get to know your system
 - Spot test on regular basis
 - Overdosing causes:
 - SO₂ gas formation
 - Flocculation inhibition
 - Underdosing causes:
 - Incomplete chrome reduction
 - Effluent violations for chrome
- Proper pH control is necessary because:
 - Too high will slow reaction to be ineffective
 - Too low will produce sulfur dioxide gas (<2 pH)



Chromium Reduction

- Safety considerations
 - Release of sulfur dioxide gas due to:
 - pH too low <2 (pH control to be in proper range)</p>
 - Sulfuric acid
 - Corrosive, will burn skin and clothing
 - Chromic acid
 - Oxidizer, corrosive
 - Protective safety equipment
 - Tank venting
 - Rubber gloves
 - Safety glasses
 - Rubber apron



Chrome Reduction Problem

 1500 gallons of a cleaner is contaminated with 20 mg/L of hexavalent chromium. How many pounds of sodium hydrosulfite will be needed to reduce the chrome to trivalent? Consider that 6.1 pounds of sodium hydrosulfite are needed for reduction of each pound of hex chrome. $1500gal\ 3.79L\ 20mg$ 1g $1oz\ 1lbCr^{+6}\ 6.1lbNaS_2O_4$ x

$$\frac{1500gal}{1} \frac{3.79L}{1gal} \frac{20mg}{1L} \frac{1g}{1000mg} \frac{1oz}{28g} \frac{1lbCr^{+6}}{16oz} \frac{6.1lbNaS_2O_4}{1lbCr^{+6}} = \frac{x}{0.254}$$

x = 1.55lbs



Cyanide Oxidation (destruction) Alkaline Chlorination

- Cyanide is used in electroplating because it dissolves metals easily due to COMPLEXING
 - Complexed cyanide not amenable to chlorination
 - Iron cyanide Fe(CN)₆-4
 - cobalt cyanide
 - WILL PASS THROUGH SYSTEM TO SLUDGE
 - EFFLUENT
 - Requires extra efforts (heat, stronger, oxidizers, etc)
 - Complexed cyanide amenable to chlorination
 - Very slowly nickel cyanide Ni(CN)₄-2
 - Slowly copper cyanide Cu(CN)₃-2
 - gold cyanide
 - silver cyanide Ag(CN)₂-1
 - Readily sodium cyanide NaCN
 - potassium cyanide KCN
 - cadmium cyanide Cd(CN)₄-2
 - zinc cyanide Zn(CN)₄-2
 - Measurability of total vs. amenable cyanide (AMINE is R-NH₂)



Oxidation-Reduction Reactions

First stage

Raise pH (if needed) with sodium hydroxide and add chlorine

NaCN + NaOCl + H₂O → CNCl + 2NaOH → NaCNO + NaCl + H₂O

Very rapid; pH must be above 10 ORP 500-600 mV

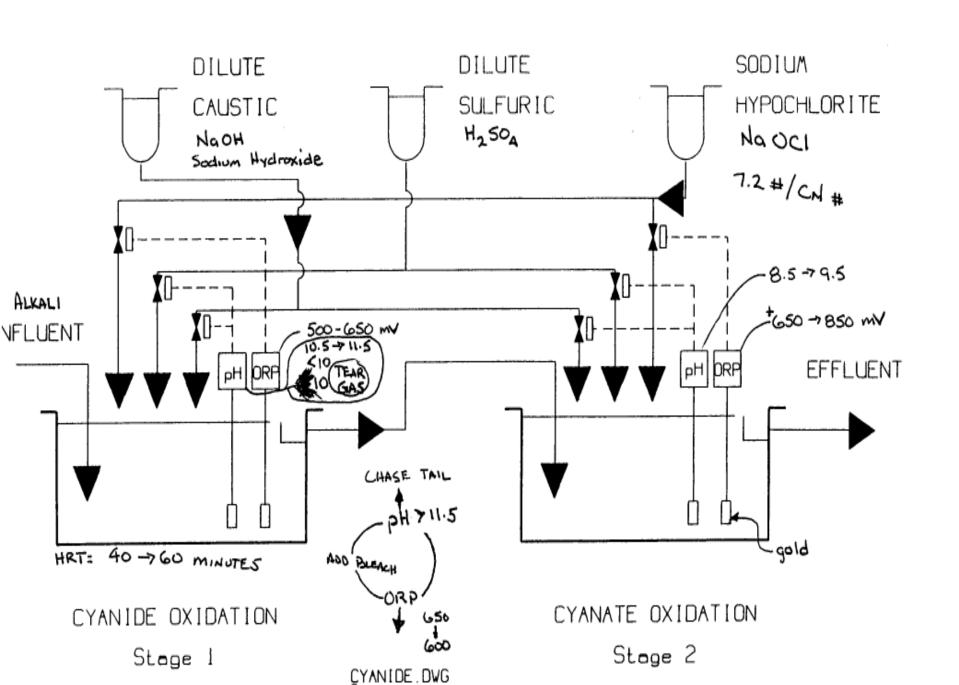
Second stage

Lower pH with sulfuric acid and add more chlorine

 $2NaCNO + NaOCl + H₂O \rightarrow 2CO₂ + N₂ + 3NaCl + 2NaOH$

Slower; pH must be between 8.5-9.5 ORP 650-850 mV





Oxidation-Reduction Reactions

- The full reaction requires 7.2 pounds of NaOCI/pound of CN⁻ and sufficient retention time to react properly (dependent on concentration & flow of system)
 - Usually supplied as 15% solution
 - Can also use Cl₂ gas, but utilized less due to manifolding and handling demands
- Other chlorine demanding chemicals may consume chlorine
 - Anything that will react with an oxidizer (a reducing agent)
- A well run system will virtually destroy ALL amendable cyanide



Cyanide Oxidation (destruction) Alkaline Chlorination

- Trouble Shooting
 - Too much bleach
 - Bleaches potassium iodide paper so you think you don't have enough
 - Floating floc due to gassing
 - OXIDIZES chrome back to hex Add bleach
 - Cause pH vs. ORP problem
 - Not enough bleach
 - Incomplete oxidation of cyanide effluent violations







Cyanide Oxidation (destruction) Alkaline Chlorination

- Batch Treatments if an accident will occur, it will be during batch treatments
 - Operator inter-communication
 - Cyanogen chloride evolution
 - Minimum 1 hour with ortho-tolidine test
- Cyanide Safety
 - Quickly fatal
 - Cyanide analytical capability
 - Air testing capability
 - Self-contained breathing apparatus
 - Cyanide antidote
 - Labels for pipes, tanks, etc



Cyanide Safety

PHYSIOLOGY: Cyanide enters the blood stream via inhalation, ingestion, and skin absorption. It is picked up by the hemoglobin molecule in the red blood cells instead of oxygen. It, thereby, blocks the blood cells from picking up and distributing oxygen to the body cells, causing cell death.



Cyanide Oxidation Problem

$$\frac{x}{0.846lbCN} = \frac{7.2lbNaOCl}{1lbCN}$$

$$x = 6.1lbNaOCl$$

$$\frac{6.1lbNaOCl}{1.53lb/gal} = 4gallonNaOCl$$

REDUCTION/OXIDATION REACTIONS

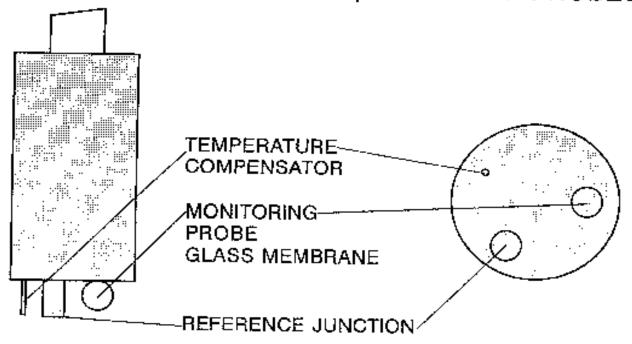
Purpose: Use pH and ORP controls to add chemicals which oxidize or reduce pollutants,

Design Conditions: Mixed, vented tanks, pH and ORP controls, redundant systems.

CHEMICAL POLLUTANT	pH CONTROL	ORP CONTROL	CHEMICALS USED	HRT (1) (minutes)
Cyanide			<u>-</u> -	··
1st Stage	>10.5	350 mv	Sodium Hypochiorite	40-60
2nd Stage	8.5-9.0	600 mv	Sodium Hypochlorite	40-60
			Alternative Oxidants	
			Ozone/UV	
			Hydrogen Peroxide	
			Chlorine Dioxide	
Phenois	6.0-9.0	400-600 mv	Ozone/UV	10-20
			Hydrogen Peroxide/	
			Ferrous Sulfate	
			Potassium Permanganate	
			Chlorine Dioxide	
Chromium VI	<2.5	250-300 mv	Sodium Sulfite	10-20
			Ferrous Sulfate	

¹⁾ rtHT = hydraulic retention time, obtained by dividing the tank volume by the flow rate.

CARE AND FEEDING OF pH AND ORP PROBES



 Turn off chemical feed systems before cleaning or calibrating probes.

3.Do not clean and calibrate probes at the same time.

Clean probes frequently.
 HCl for high pH control.
 Mild detergent for oil and grease.

Replace probes as necessary.
 The avorage probe life is six months to one year.

PHYSICAL/CHEMICAL TREATMENT

Getting the stuff ready to get the stuff out

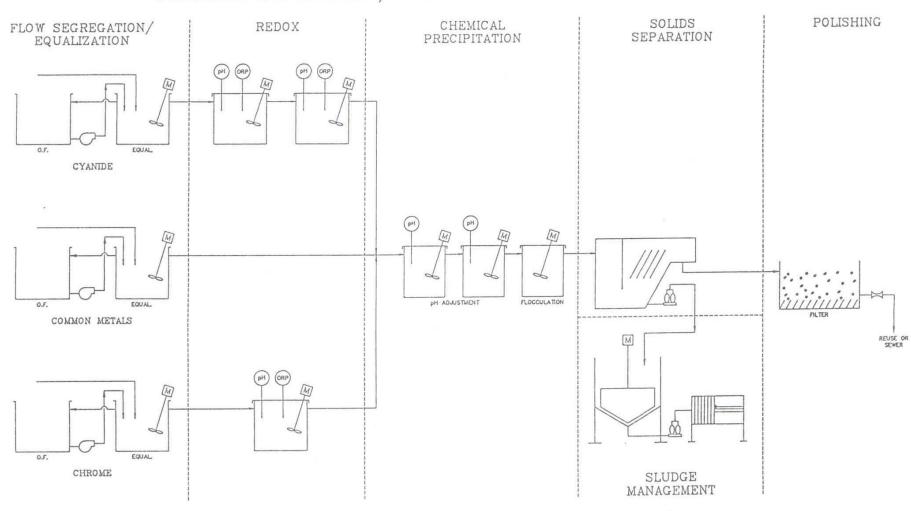
SOLUBILITY REACTIONS

Pollutants such as metals, oils, and proteins can be made insoluble in water by changing pH. This characteristic is known as the solubility product (Ksp) of a chemical.

Solubility reactions are usually monitored and controlled by pH probes which read out in standard pH units (o-14). Bases cause pH probes to read lower.



TYPICAL PHYSICAL / CHEMICAL TREATMENT SYSTEM



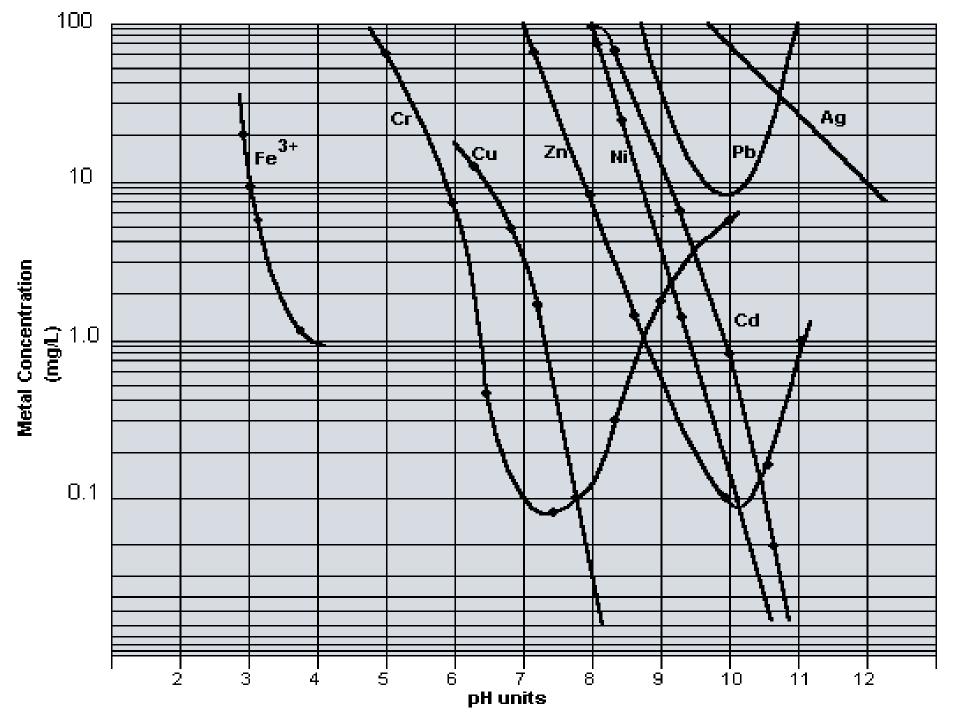
CHEMICAL SEPARATION

Purpose: Create two phases (water/pollutant) for separation.

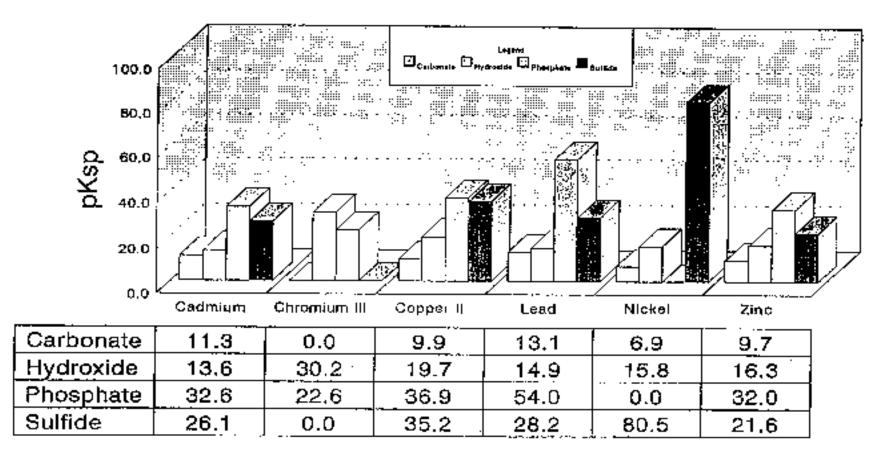
Design Conditions: Mixed tanks, pH controls, redundant systems.

CHEMICAL POLLUTANT	pH CONTROL	CHEMICALS USED	HRT (1) (minutes)
Metal Hydroxides	See Ksp Solubility Chart	Sodium Hydroxide Soda Ash Lime Magnesium Hydroxide	15-20 Per Stage 15-20 45-60 Per Stage 45-60 Per Stage
Oil, Grease, Wax (see footnote 2)	1-2	Sulfuric Acid Hydrochloric Acid	240+
Proteins	Isoelectric Point	Sulfuric Acid	20-40

⁽¹⁾ HRT = hydraulic retention time, obtained by dividing the tank volume by the flow rate. (2) This reaction is often enhanced by heating this wastewater to between 140°F and 180°F.



THE SOLUBILITY OF STUFF pKsp VALUES OF COMMON METAL SALTS



Common Metals

A zero denotes no available data

 $Ksp = \{M^+\} \{Salt\}, pKsp = -log Ksp \}$

A larcilipKsp value means low metal solubility, it will be removed in the clarifier

COPRECIPITATION OF SOLUBLE METALS

$$FeSO_4 + O_2 + OH ----> Fe(OH)_3 + SO_2$$

$$Fe(OH)_3 + O_2 + H_2O - FeOOH + H$$

MECHANISM OF REACTION:

Adsorption on Fe(OH)₃
Coprecipitation Fe(5-x)Pb(x)O₄
Entrapment Fe₃O₄(Pb)OH

After Rao and Werwie, Johnson Cormols, Personnal Communication, 9/10/87

CHEMICAL TREATMENT

Getting the stuff ready to get the stuff out

COAGULATION/FLOCCULATION

Coagulation is the process of adding inorganic or organic chemicals to wastewater in order to begin the separation process. Most coagulants are cationic.

Flocculation is the process of adding inorganic or organic chemicals to wastewater in order to increase the size of coagulated particles. Most flocculants are anionic.



COAGULATION/FLOCCULATION

Making little stuff big

COAGULATION

Coagulation is the process of increasing the mean diameter of colloidal particles in water by neutralizing their surface charge (called a zeta potential). Coagulants are also used to tie up or overcome interfering compounds such as emulsifiers, chelants, or complexing agents. Coagulants start the separation process.



COAGULATION/FLOCCULATION

Making little stuff big

TYPES OF COAGULANTS

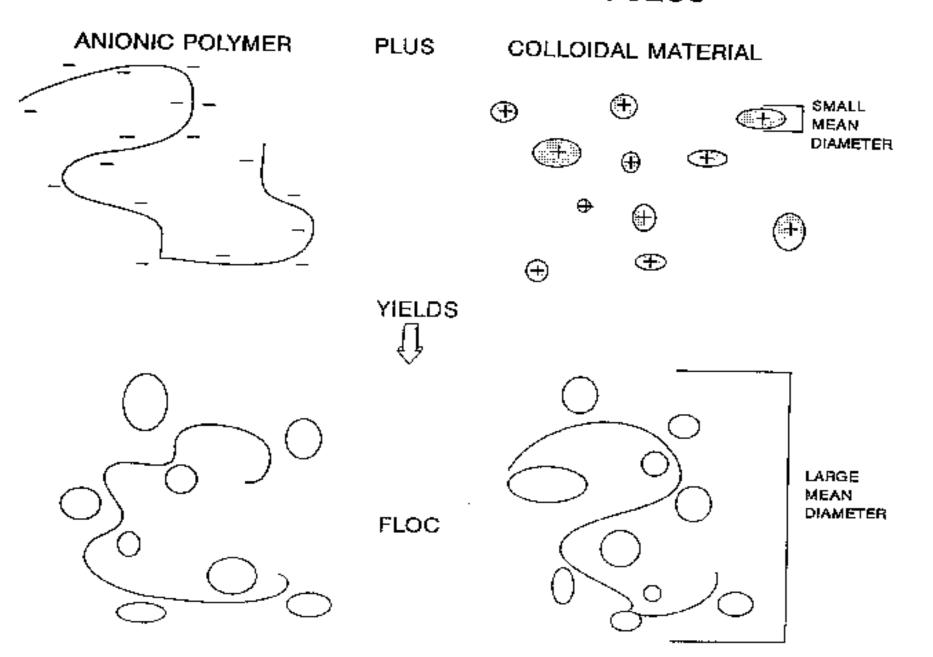
Coagulants can be organic or inorganic chemicals. Examples of organic coagulants include cationic polymers, co-polymers or cationic polymers and metal salts, and natural polymers such as gums or lechithans. Examples of inorganic coagulants include base metal salts such as calcium and magnesium hydroxides, as well as the metal salts aluminum sulfate, ferrous sulfate, ferric chloride, calcium chloride, and magnesium sulfate.

FLOCCULATION

Flocculation is a continuation of the particle growth process in which coagulated particles increase in mean diameter with the aid of long-chained, anionic polymers. This increase is accomplished by gentle agitation which promotes the collision and adhesion of coagulated particles.



THE FLOCCULATION PROCESS



PHASE SEPARATIONS

Taking stuff out of water

PHASE SEPARATIONS

The process by which chemicals of low solubility are removed from water.

SETTLING

Settling or sedimentation is the process by which pollutants heavier than water are removed from water. The larger the particle and the heavier the particle with respect to water, the faster it settles. Clarifiers are the most common process unit used to remove solids from water. Grit, sand, and metal hydroxides are the most common pollutants removed by clarifiers.



STOKES, HAZEN, AND SEDIMENTATION

It's a rock group

WHAT'S IT MEAN?

The larger the floc diameter (rx2), the better stuff settles. The heavier stuff is, the better it settles.

The true capacity of a clarifier is obtained by dividing its flow rate by its surface area (gpm/ft²).

If you put plates in a clarifier at a 60 degree angle, you can increase its effective surface area.

Buy more beer.



STOKES, HAZEN, AND SEDIMENTATION

It's a rock group

- HAZEN'S THEORY OF SEDIMENTATION
 - Hazen's theory covers a lot of territory. His most important theory states that the beer will run out before the Cheetos. His next most important theory states:
- A. The depth of a clarifier is unimportant. Only the clarifier surface area impacts settling.
- B. Horizontal plates (false bottoms) will provide a surface to receive sediment. The more plates, the more efficient the clarifier.
- C. Particles undergo differential sedimentation based on their size and specific gravity (we're back to Stokes).



STOKES, HAZEN, AND SEDIMENTATION

It's a rock group

STOKES' LAW

```
y = 0.22 \times g \times r^2 \times [(s - s') / e]
```

Where: v = settling velocity

g = acceleration due to gravity

s = density of stuff settling

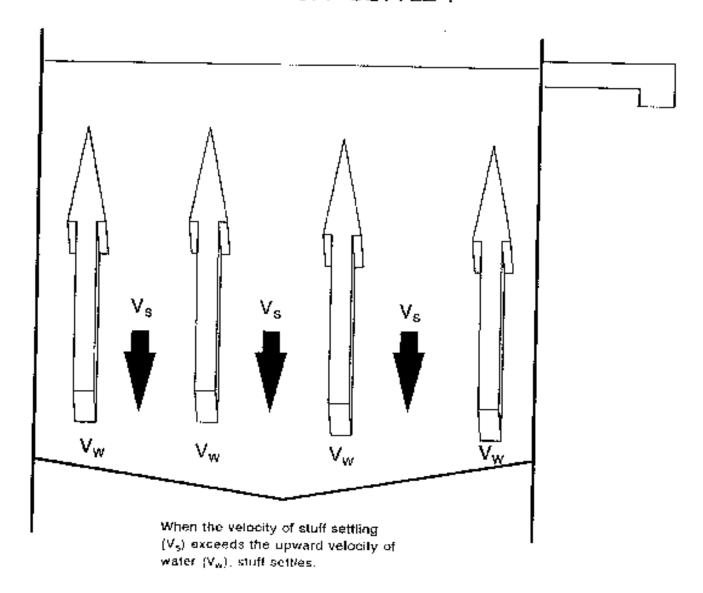
s' = density of water

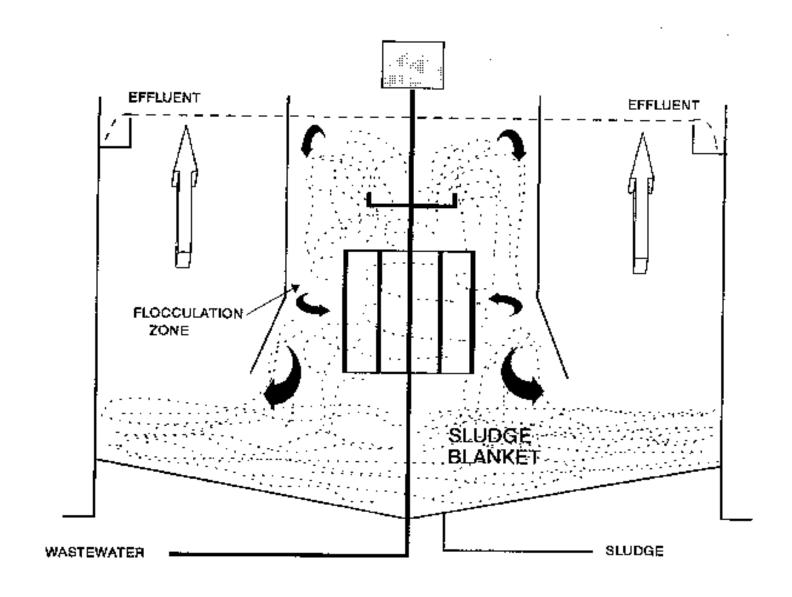
e = viscosity of water

r = radius of the stuff settling

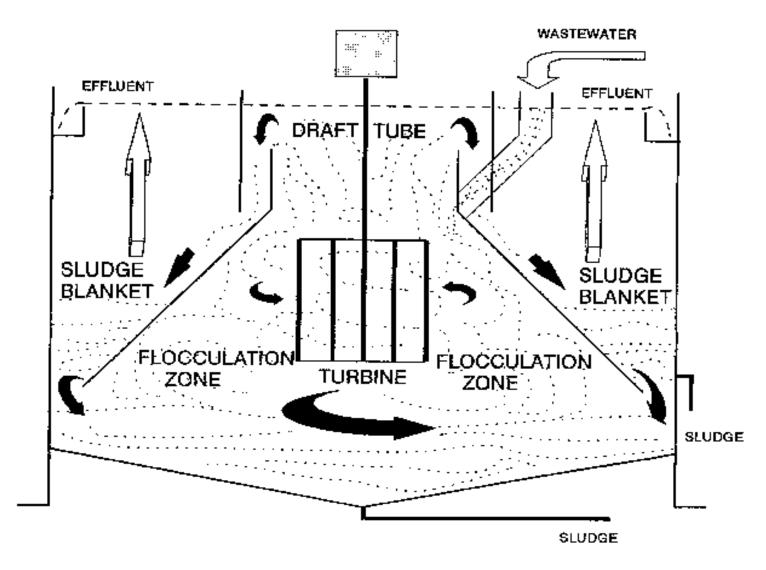


HOW DOES STUFF SETTLE?

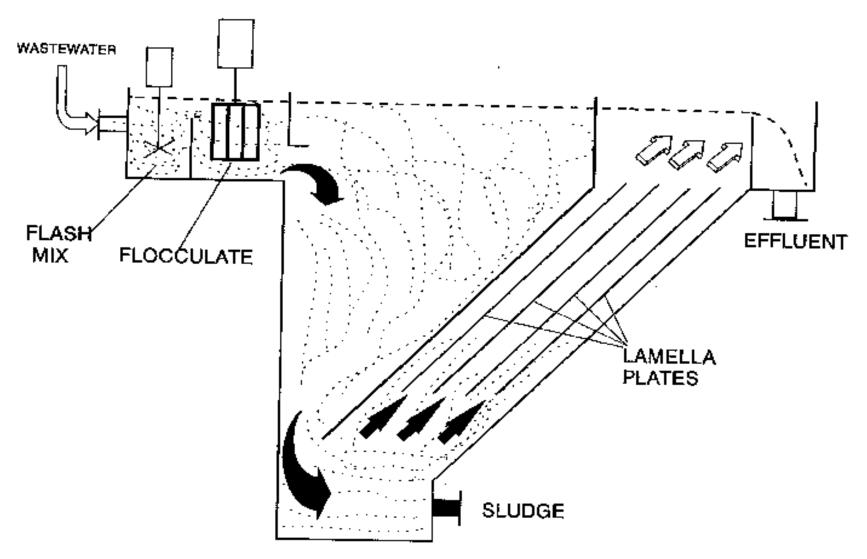




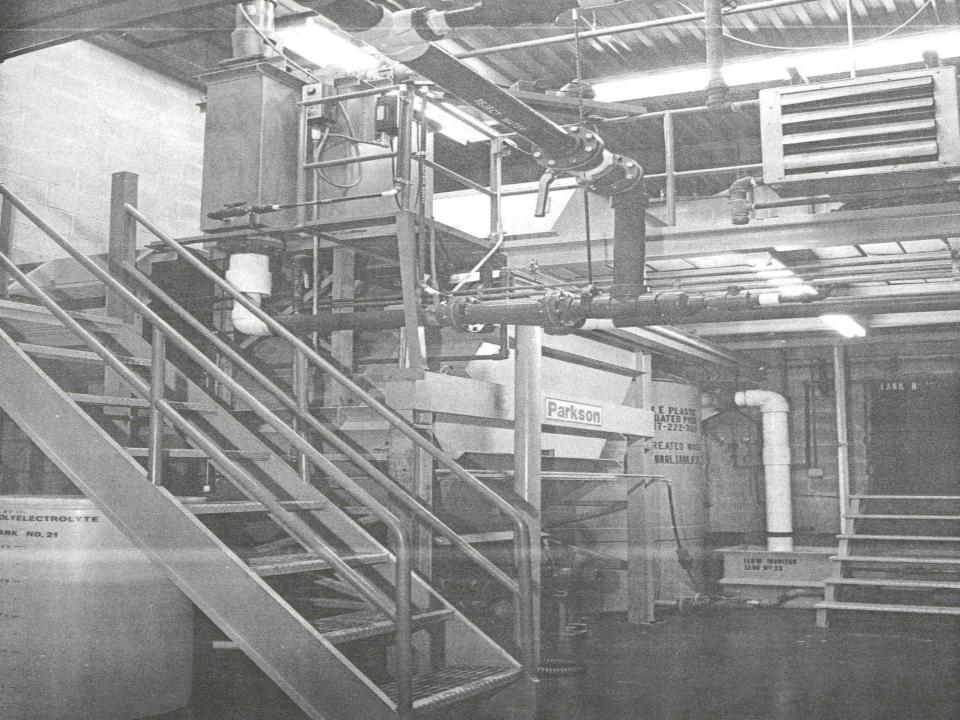
CIRCULAR CLARIFIER



REACTOR CLARIFIER



HIGH RATE CLARIFIER



PHASE SEPARATIONS

Taking stuff out of water

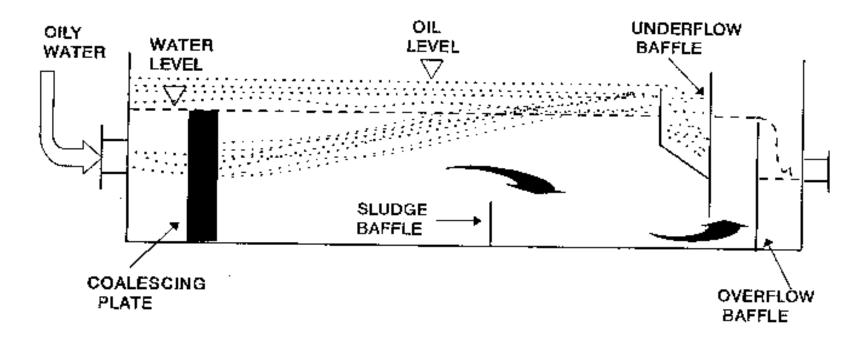
FLOATING

Floating or flotation is the process by which pollutants lighter than water are removed from water. The pollutants may be naturally lighter than water such as oil and grease, or they may be made lighter than water by attaching microbubbles to them such as dissolved air flotation (DAF).

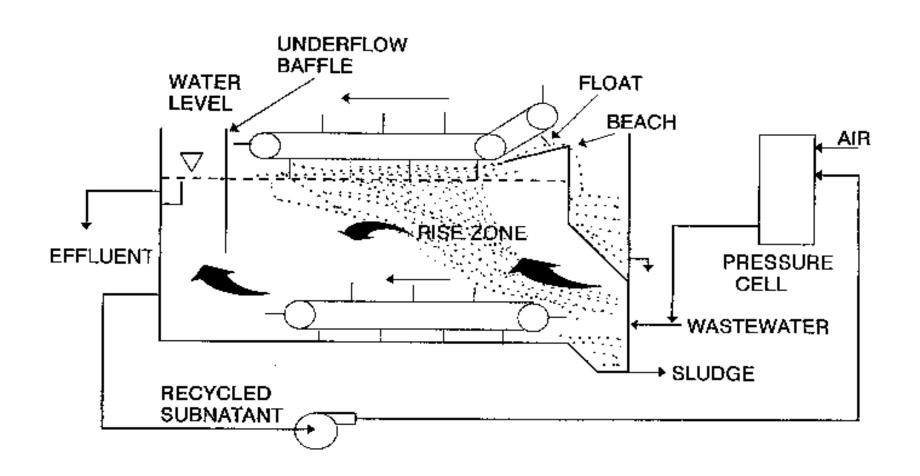
AIR STRIPPING

Air stripping is the process by which volatile chemicals which are insoluble in water are removed from water by increasing the chemical's contact with air. This may be done by sparging air through the wastewater or by pumping the wastewater over a media tower.





API OIL/WATER SEPARATOR



DISSOLVED AIR FLOTATION

FINAL POLISHING

Taking iddy biddy stuff out of wastewater

DEFINITION

Final polishing is the process of removing small residual pollutant concentrations from wastewater.

PHYSICAL POLISHING

Physical polishing is the process of filtering small quantities of particulates from wastewater. Physical polishing processes include sand filters, cartridge filters, leaf filters, various media filters, and ultrafiltration.



FINAL POLISHING

Taking iddy biddy stuff out of wastewater

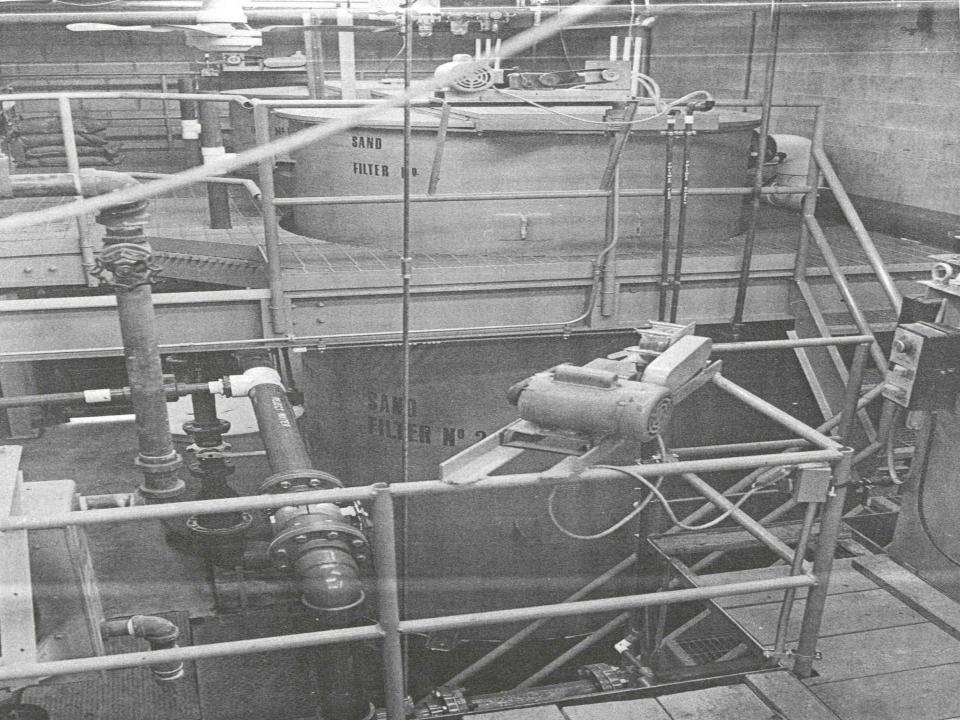
CHEMICAL POLISHING

Chemical polishing is the process of removing small quantities of soluble pollutants from wastewater. Chemical polishing processes include activated carbon, ion exchange and electrodialysis.

MEMBRANE POLISHING

Membrane processes use a semi-permeable membrane to separate pollutants from wastewater. Examples of membrane processes include reverse osmosis, ultrafiltration, and electrodialysis.





SLUDGE MANAGEMENT

What can I do with all this #%\$@&* stuff?

DEFINITION

Sludge management is the process of concentrating the residuals removed from the wastewater.

SLUDGE THICKENING

This process involves increasing the sludge solids from the system's primary solids separation system. Gravity thickeners take advantage of the particulate's settling characteristics. DAF systems use microbubble flotation. Rotary screens use different size screens. All thickening processes increase sludge solids concentrations from 0.5%-1.0% to 3.0%-5.0%. The sludge is still pumpable at these concentrations.



SLUDGE MANAGEMENT

What can I do with all this #%\$@&* stuff?

SLUDGE DEWATERING

Sludge dewatering processes take the sludge from 3.0%-5.0% solids to greater than 20% solids. At this stage the sludge is cakelike in texture. Dewatering processes include filter presses, belt presses, vacuum drums, and centrifuges.

SLUDGE DRYING

Sludge dryers increase the sludge solids to the 60%-70% range. They can be direct fired, indirect fired, gas, electric, or steam heated. Their purpose is to reduce the volume of sludge by removing the entrained water.

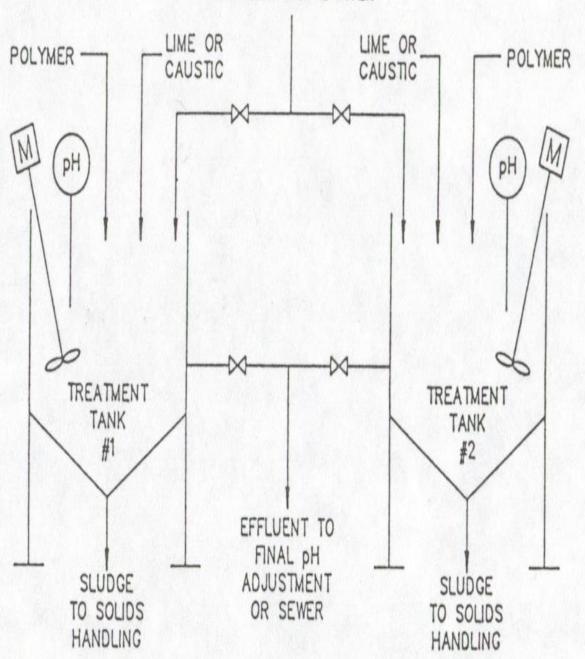


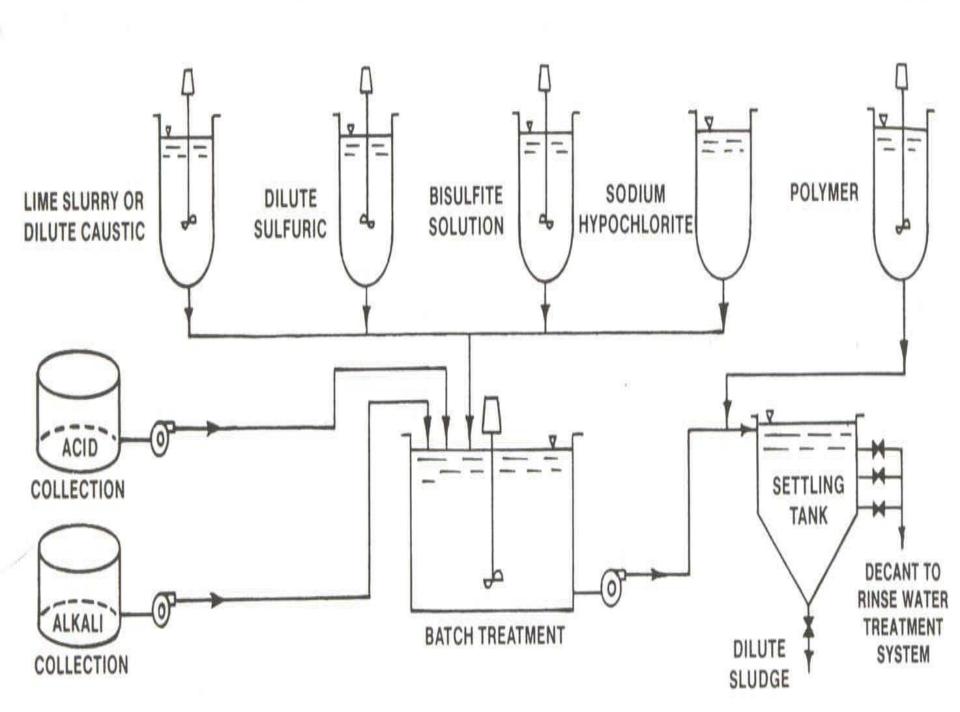
BATCH TREATMENT

- Simplest and most dependable
- Easier control
- Discharge to sewer is satisfactory
- Typical for low flow
- Variability in waste streams
- Special pretreatment steps
 - Cyanide destruction
 - Chrome reduction
 - Chelate breaking
 - High concentration batches
- Multiple tanks



PROCESS WASTEWATER

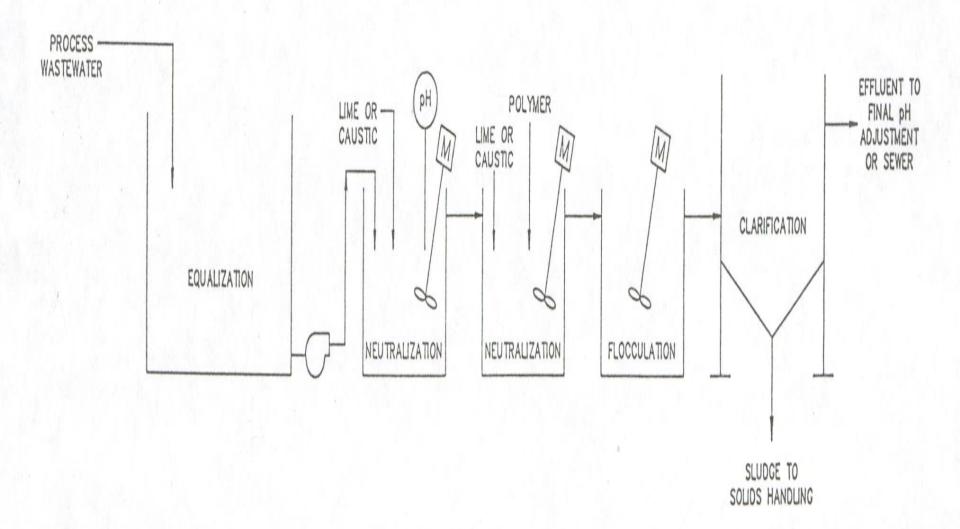




CONTINUOUS TREATMENT

- Relatively higher flows
- Fluctuated flow and concentrations
 - Equalized first
- Gravity flow through vs. pump
 - Hydraulic profile
- More dependent on automation
 - Chemical conditioning
 - Flow rate
- Retention time
 - pH adjust
 - Flash
 - Floc
 - Settling
 - Other reactions





TYPICAL CONTINUOUS TREATMENT SYSTEM FOR METAL PRECIPITATION