BURGESS & NIPLE
Engineers ■ Environmental Scientists

Metals Treatment for Discharge Compliance and Potential Reuse

(OTCO-S12082-OM)

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Overview

- What is Metal Finishing
- Why do We Care?
- Treatment Methods
- The Next Frontier

WHAT IS METAL FINISHING?

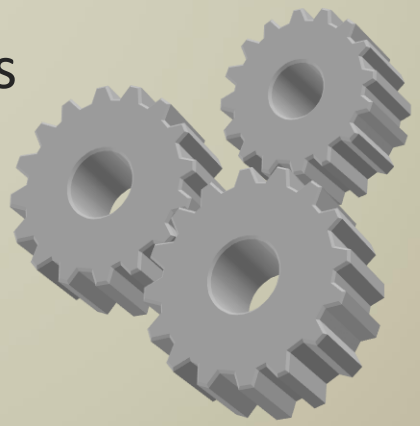
U.S. EPA Description

Metal finishing is the process of changing the surface of an object, for the purpose of improving its appearance and/or durability. Also, metal finishing is related to electroplating, which is the production of a thin surface coating of the metal upon another by electrodeposition

What is Metal Finishing?

Categorical Standard - 40 CFR 433

- Electroplating
- Electroless Plating
- Anodizing
- Coating (chromating, phosphating, and coloring)
- Chemical Etching and Milling
- Printed Circuit Board Manufacturers



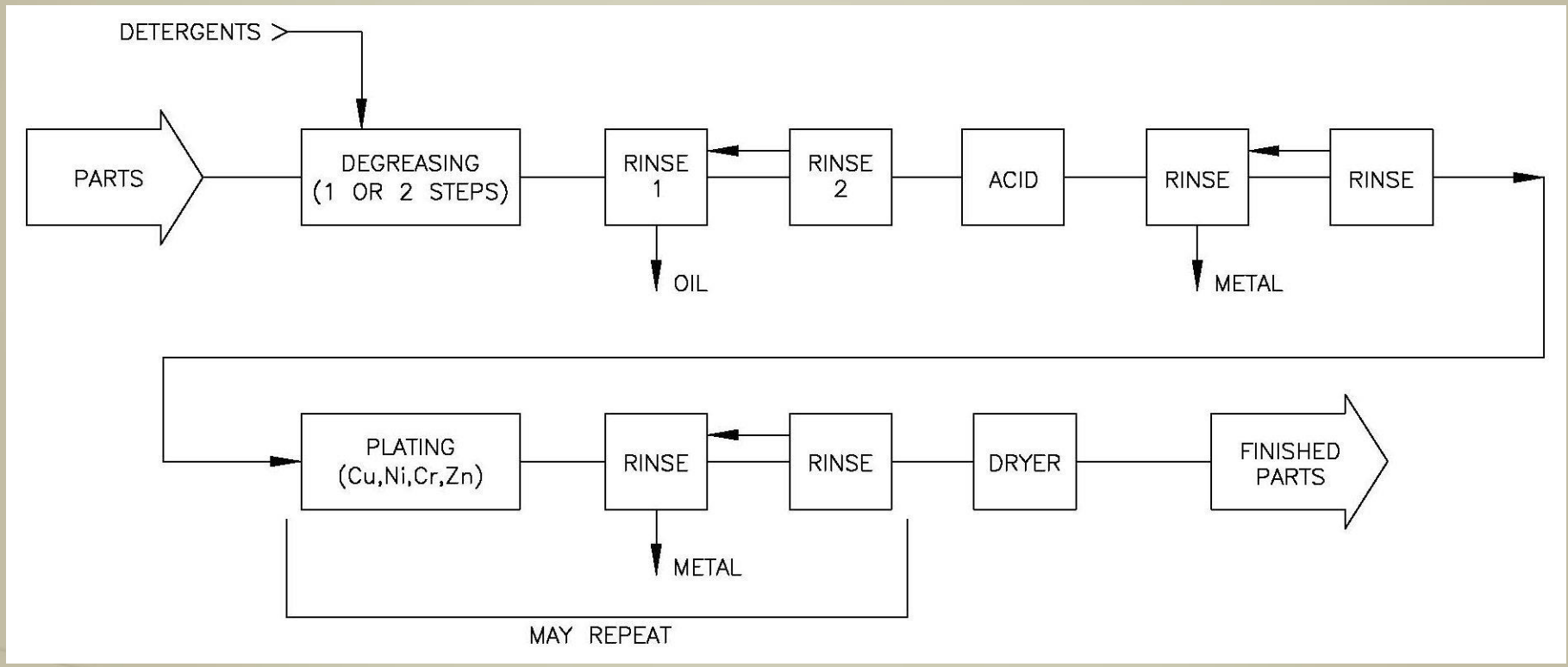
Metal Finishing Could Be…..

- Automobile Parts
- Home Appliances
- Grave Vaults
- Semi-Conductor
- Landscaping Furniture and Accessories
- Copier Rollers
- Job Shops

- Most classified as SIC 3471 and 3479 (Over 6000 in the US)

What is the Process?

- Typical plating process diagram



Wastewater Could Be From….

- ***Plating***
- Anodizing
- Brazing/soldering
- Galvanizing
- Coating
- Heat treating

- ***Cleaning***
- Machining
- Grinding
- Solvent Degreasing
- Paint Stripping
- Tumbling

Metal Finishing Wastewater

WHY DO WE CARE?

What is Wrong with Their Wastewater?

- Heavy Metals – Cadmium, Chromium, Copper, Lead, Nickel, Zinc
- Oil & Grease – Petroleum Based
- MBAS
- pH

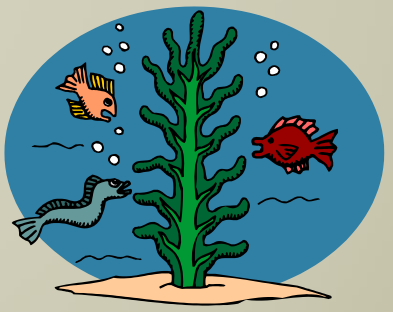
Impacts to POTW

- Biological system not efficient for metals
- Low pH can destroy microbes
- Toxicity to microbes (Cu as low as 1mg/L)
- Poor solids removal
- Failure to Meet NPDES limits

- Sludge Disposal Restrictions

Aquatic Life Impacts

- High Concentrations may be toxic
- Lower concentrations increase occurrence of:
  - Growth and Development Reductions
  - Organ Damage
  - Cancer
  - Neurological Impacts
- Low pH discharges



How is the Wastewater Regulated?

Off-site disposal – may be hazardous?

- Listed (F007 – F012, Cyanide)

- Characteristic
  - Ignitable
  - **Corrosive**
  - Reactive
  - **Toxic**

How is Metal Finishing Regulated?

- Local sewer use ordinances
- 40 CFR 433 – Metal Finishing Categorical Standards

Pretreatment Standards, mg/L (New Sources)

Parameter	Daily Max.	Monthly Avg.
Cadmium	0.11	0.07
Chromium	2.77	1.71
Copper	3.38	2.07
Lead	0.69	0.43
Nickel	3.98	2.38
Silver	0.43	0.24
Zinc	2.61	1.48
Cyanide	1.20	0.65
TTO	2.13	---

How to meet the discharge limits

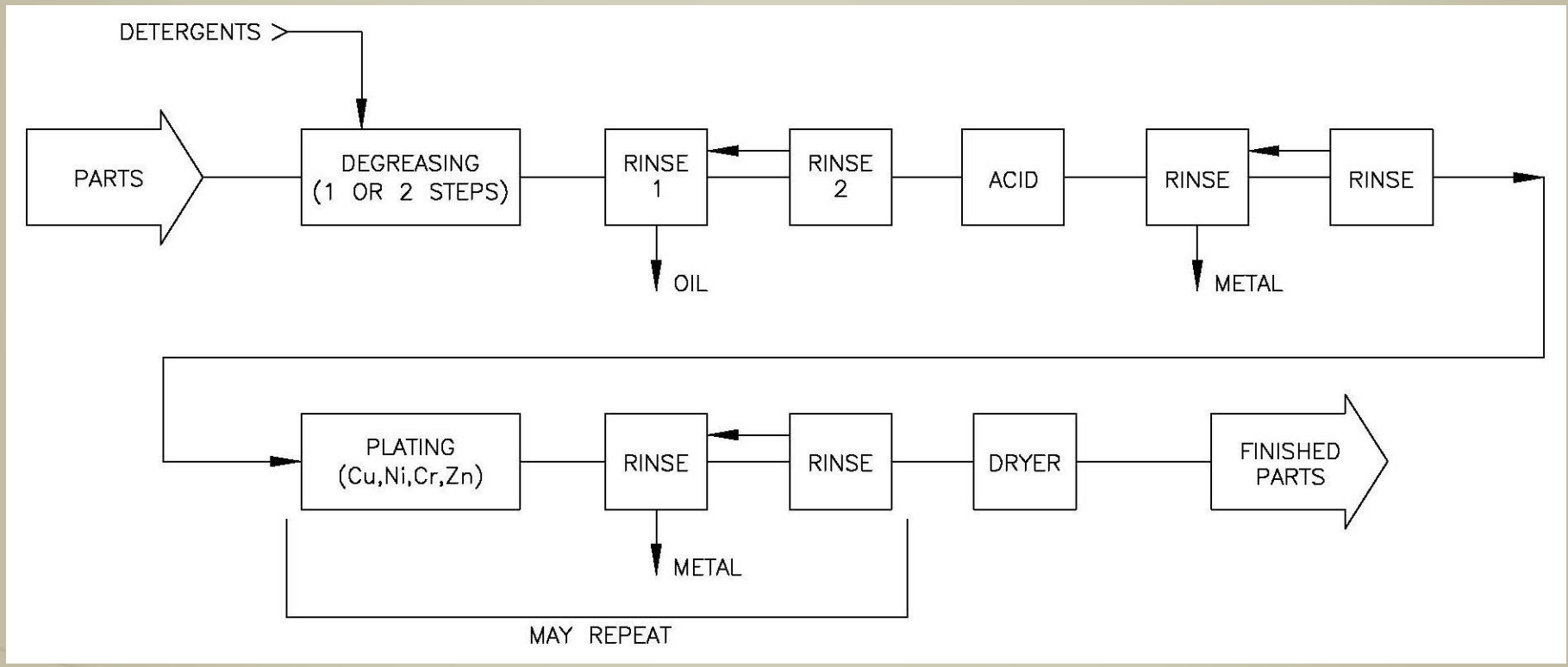
TREATMENT METHODS

Treatment is not for Metal Finishing Alone

- Die Casting Operations (40 CFR 464)
- Glass Manufacturing (lead)
- Plastics (copper within color additives)
- Power Plants (Coal Pile Runoff)

Wastewater Concerns?

- Typical plating process diagram



Divide and Conquer

- Oil and Grease

- Heavy Metals

Oil and Grease Removal

TREATMENT METHODS

Oil and Grease

- Sources
  - Parts Cleaners
  - Air Compressor Condensate
  - Leaks/Spills

Emulsified or Free Oil

- Free Oil – Will rise rapidly to a water tank surface. Oil droplet size of 150 microns or more.

- Emulsified - Mixture of 2 or more liquids not normally miscible, but held in suspension by mechanical or chemical means such that they are partially dissolved in each – Dissolved Oil

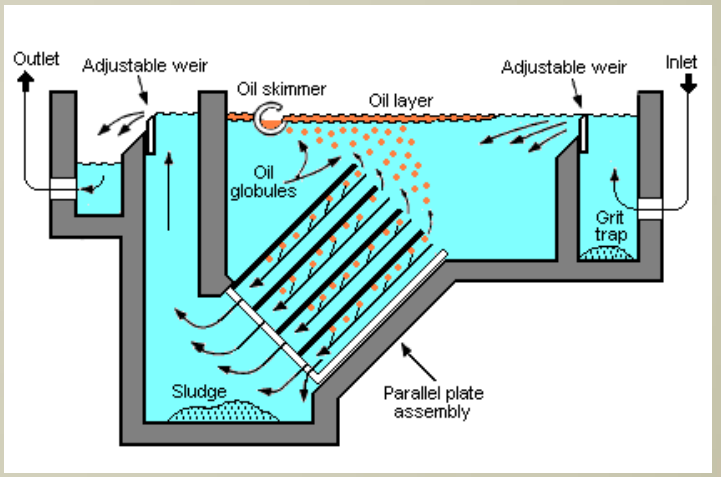
How to Break Emulsions?

- High heat (150 – 220 F)
- Acid (hydrochloric or sulfuric to pH 3.5 S.U. or lower)
- Chemical (aluminum sulfate and polymer)

Oil & Grease (free oil)

- Gravity Separation (Oil/Water Separator)

- Skimming Methods
  - Rope
  - Mop
  - Beach Plates
  - Pipe Skimmers

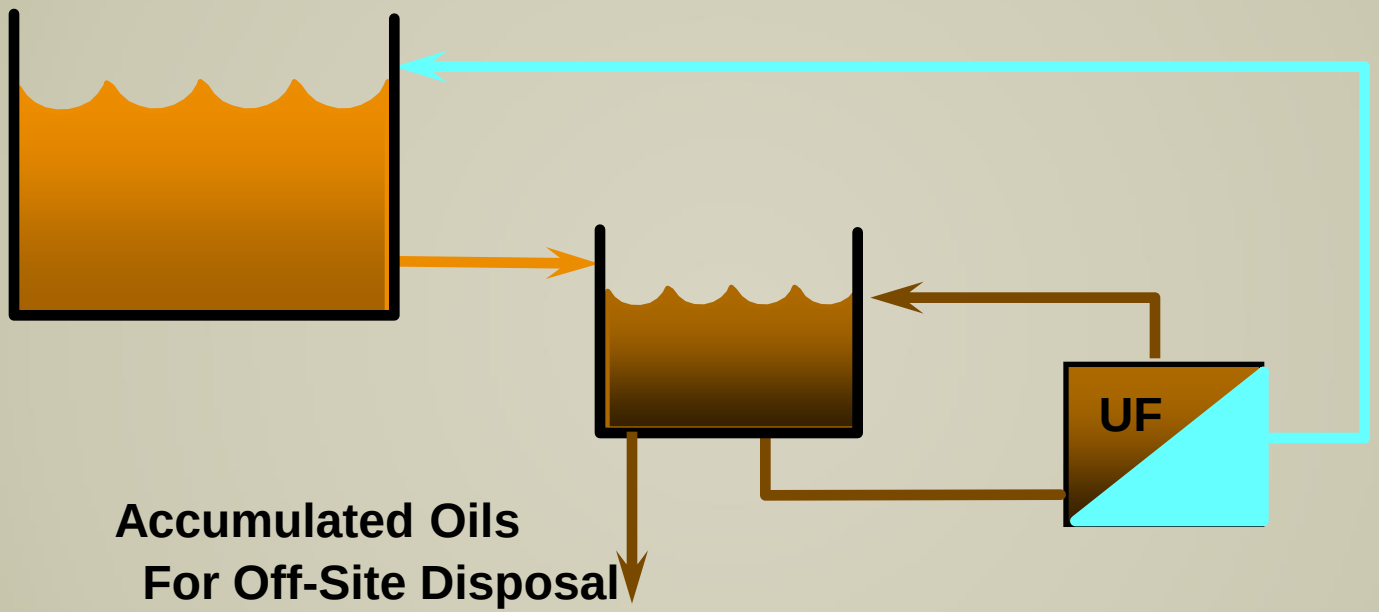


Oil & Grease

- Dissolved Air Flotation (DAF) Clarifier

  Air assistance to gravity

Ultra-Filter Operation



Oil & Grease

- Ultra-Filtration

Heavy Metals Removal

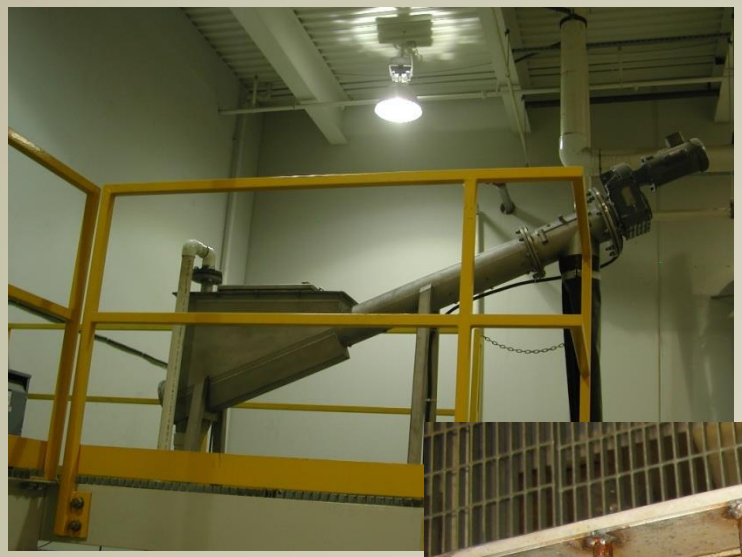
TREATMENT METHODS

What Form is It?

Solid (Easy)

Dissolved (Complicated)

Solids Removal - Screening



Solids Removal – Gravity Separation

Solids Removal - Filtration

Dissolved Metals

- Membrane Filtration (Reverse Osmosis)
- Ion Exchange (Water Softening)
- Chemical Precipitation

Dissolved Metal – Reverse Osmosis

Advantages

- Effective
- Removes more than just the metals

Disadvantages

- Requires feed stream with low solids content
- Creates more concentrated waste stream of dissolved metals
- Requires high energy

Ion Exchange

Advantages

- Efficient
- Can regenerate the media on or off-site
- Off-site regeneration eliminates waste stream at the plant

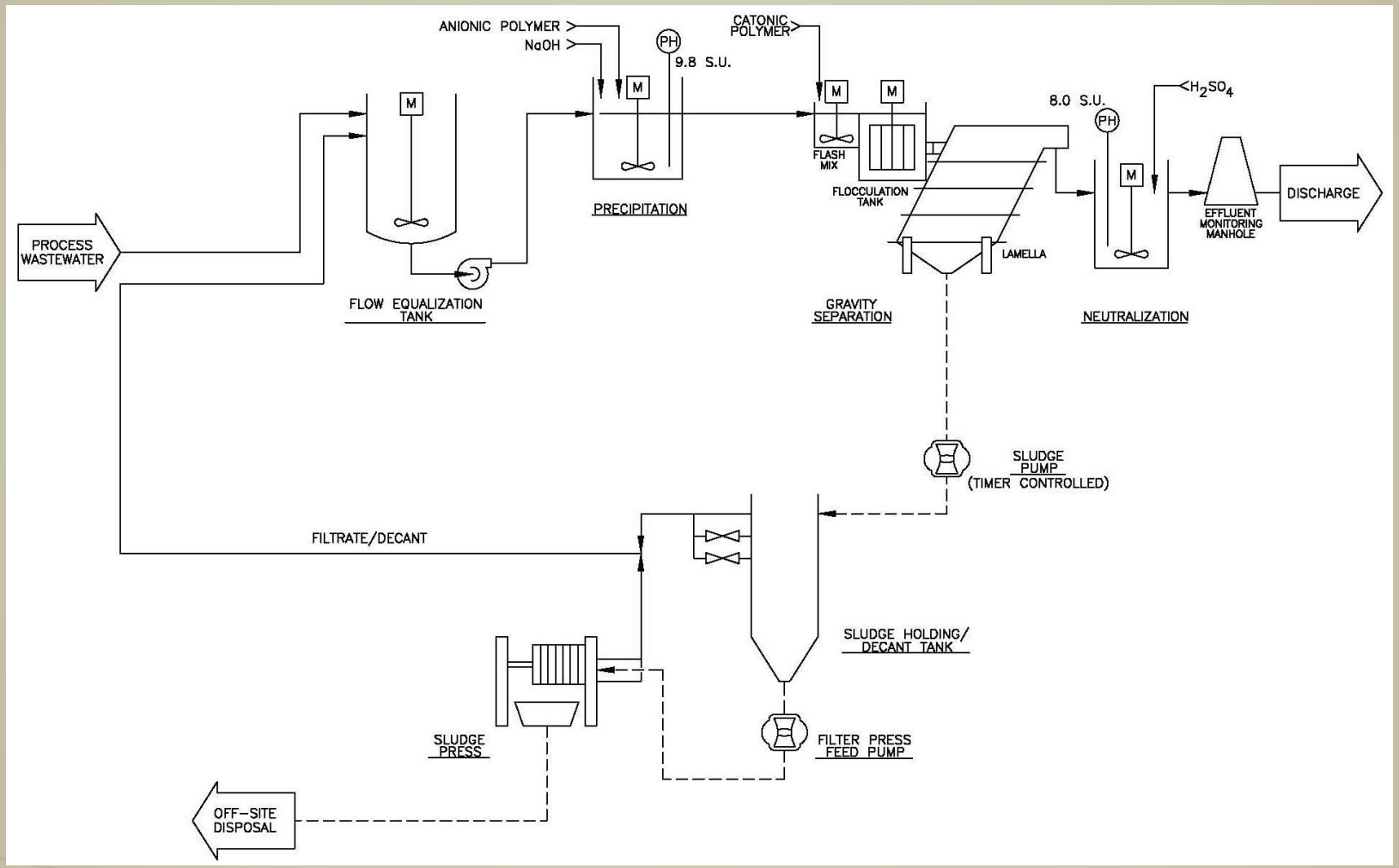
Disadvantages

- Requires low solids feed
- On-site regeneration creates concentrated waste stream of dissolved metals
- Media can be cost prohibitive

Dissolved Metals

- Membrane Filtration (Reverse Osmosis)
- Ion Exchange (Water Softening)
- **Chemical Precipitation**

Dissolved Metals – Chemical Precipitation



Dissolved Metals – Chemical Precipitation

- Sodium Hydroxide
- Sodium Sulfide
- Lime

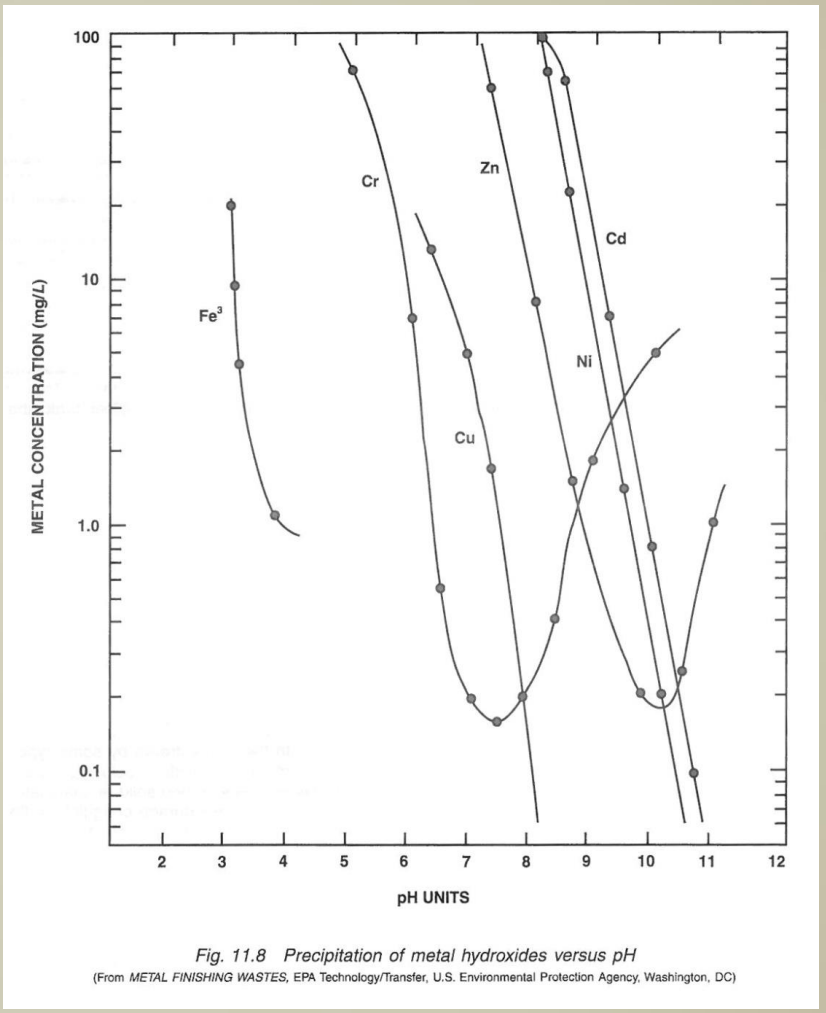
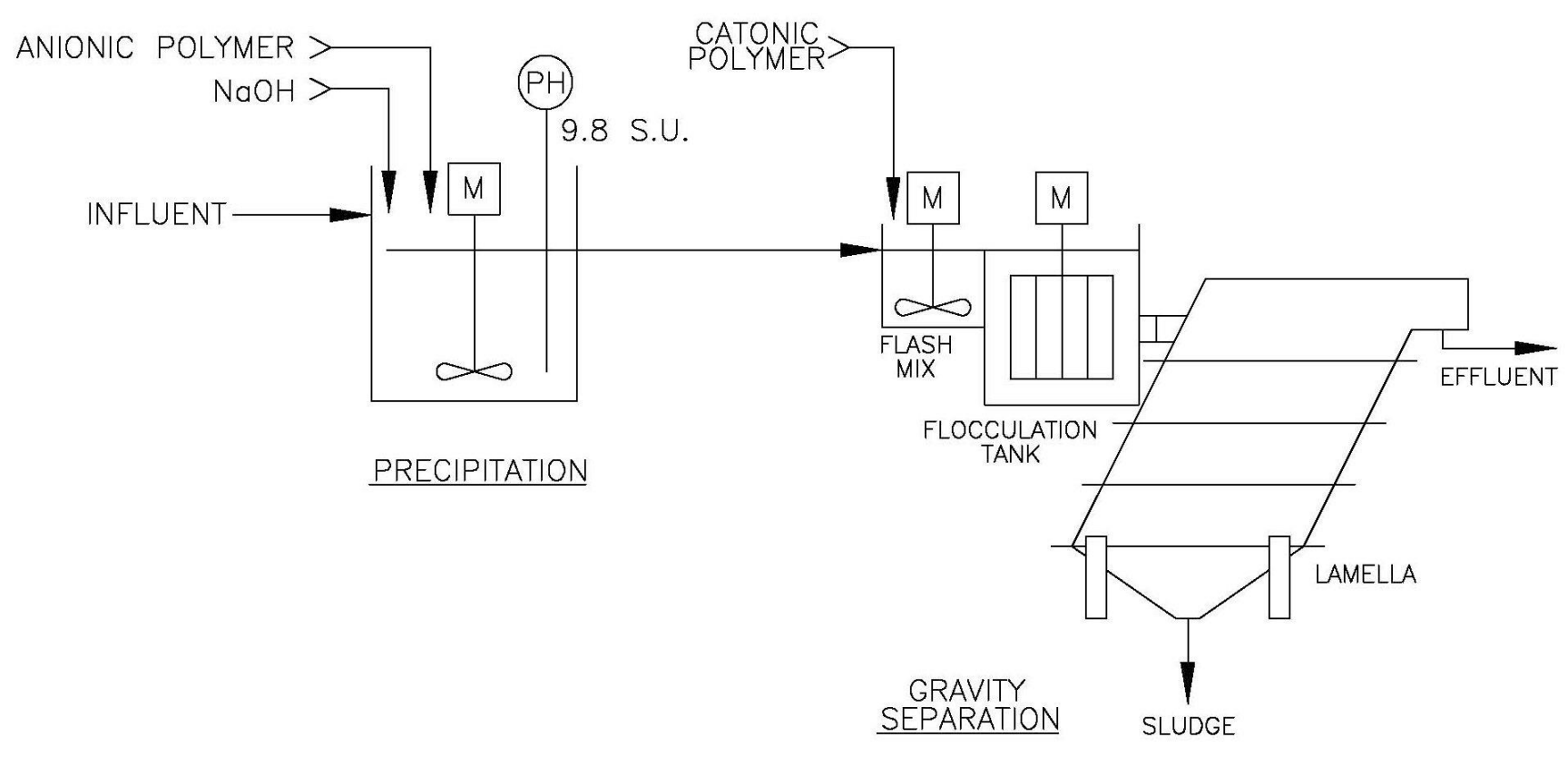


Fig. 11.8 Precipitation of metal hydroxides versus pH
(From *METAL FINISHING WASTES*, EPA Technology/Transfer, U.S. Environmental Protection Agency, Washington, DC)

Chemical Precipitation Steps

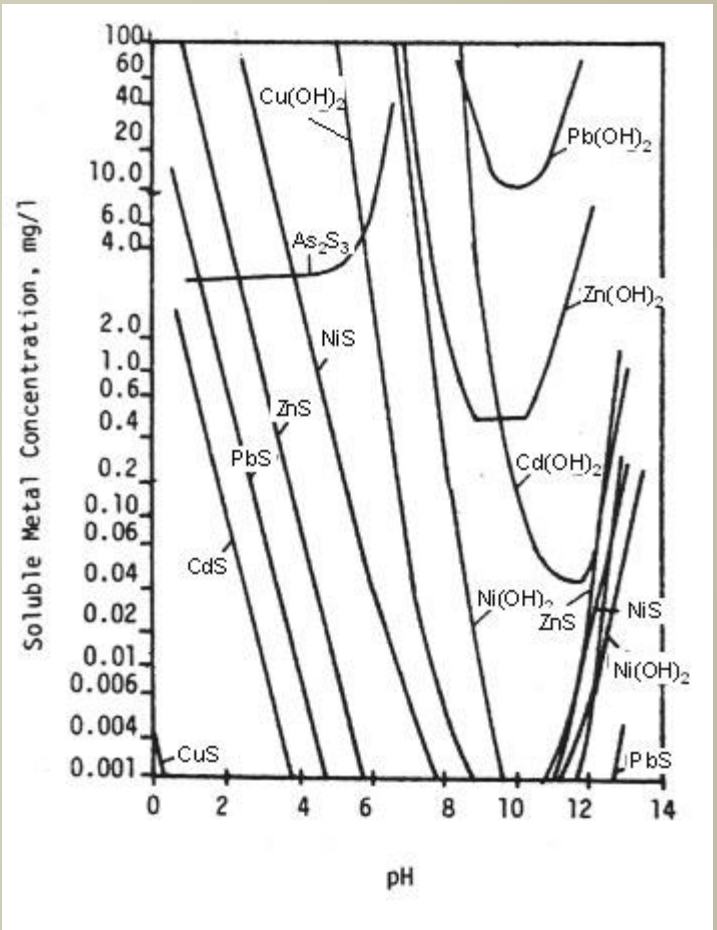


Hydroxides (Sodium and Magnesium)

- Most commonly used by industry
  - Less Expensive
  - Relatively low solids generation
  - Low toxicity
- 50% Sodium Hydroxide freezes at 60 F (use 20% solution)
- Magnesium Hydroxide – safer to use

Sulfide Precipitation

- Lower solubility over larger pH Range
- Less sensitive to surfactants
- Hex-chrome without reduction step
- Sludge more dense
- Can be corrosive or toxic

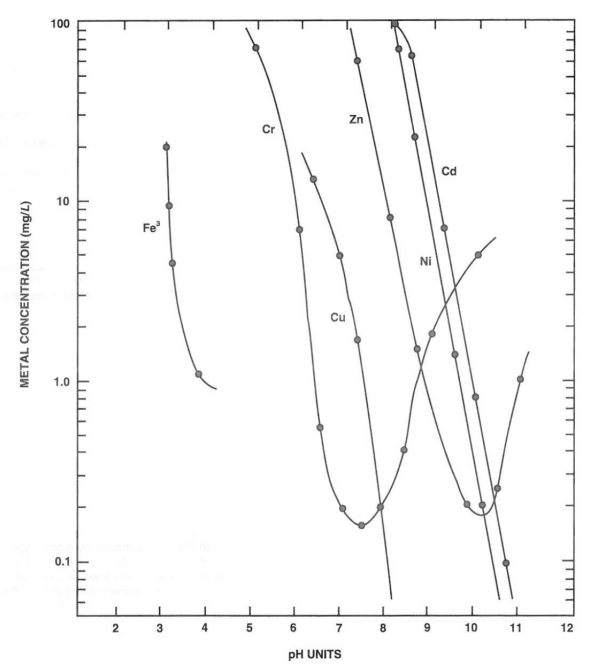


Lime?

Lime (Calcium Hydroxide)

- Lime is highly insoluble (co-precipitation)
- Dense Sludge
- Used in solid form

Chrome Removal
(Reduction may be required)



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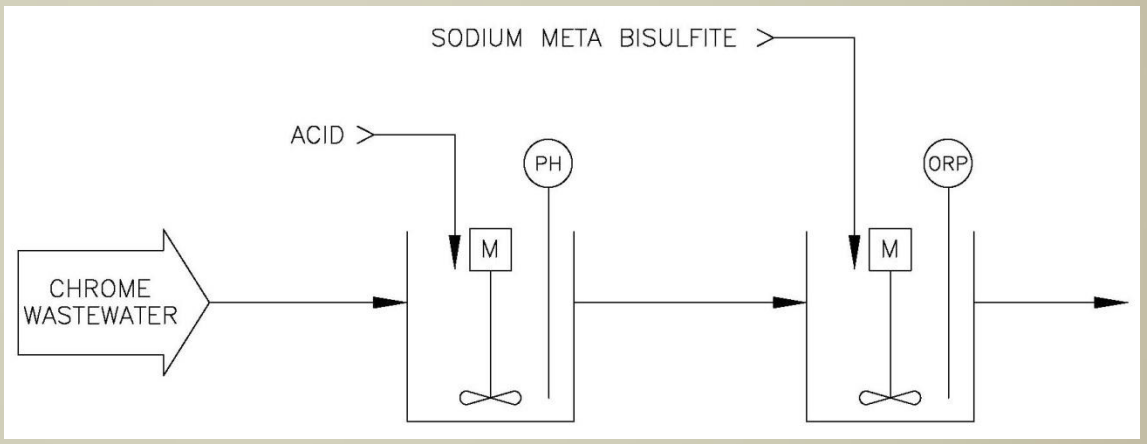


Potential Interferences

- Oil and Grease
- Ammonia – raises metal solubility (chlorine or ozone destruction)
- Chelating Agents (EDTA)
- Surfactants

Chemical Feed

Critical to treatment success

- metal precipitation
- floc formation
- effluent neutralization

Solids Conditioning

- Co-Precipitation and/or Polymers

Dissolved Metals – Chemical Precipitation

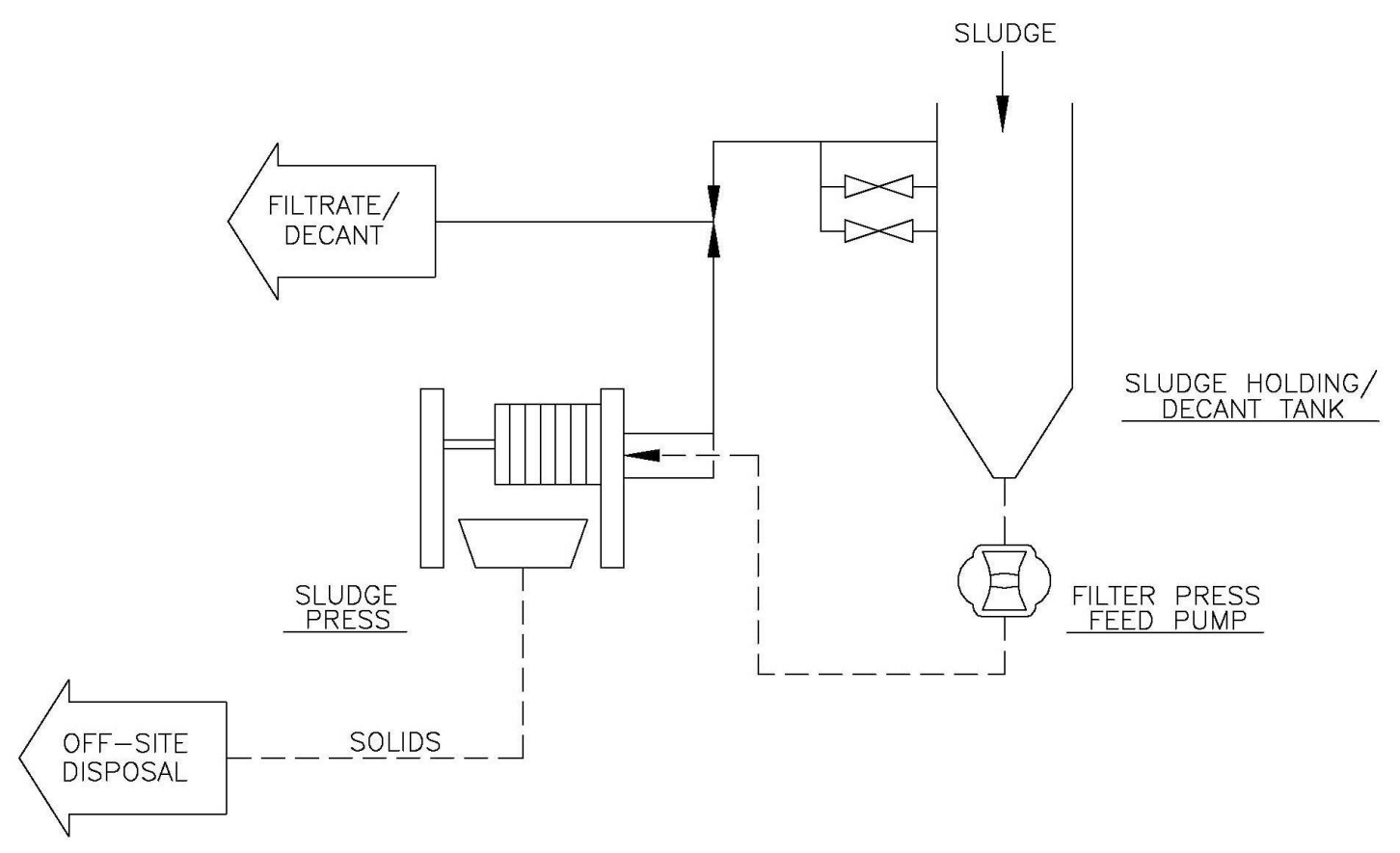
- Now it is a Solid – Gravity Separation and/or Filtration

Dissolved Metals – Chemical Precipitation

- Now it is a solid – Membrane Filtration

- Micro; Ultra; Nano; Reverse Osmosis

Solids Handling



Solids Handling – Sludge Disposal

- Sludge Press (Belt, Plate & Frame)
- Dryers
- Off-Site Hauling

Hazardous Waste…..?

- Listed Wastes

  F006 – Electroplating Treatment Sludge

  F019 – Aluminum Conversion Coating Sludge

- Characteristics (TCLP)

Dissolved Metals – Chemical Precipitation

Advantages

- Dependable Process
- Easily adjusted for Large or Small Volumes
- High or Low Concentrations
- Will remove more than just metals
- Creates solid waste

Disadvantages

- Chemical Costs can be high
- Does require on-going operation/maintenance
- Solid waste may be classified as hazardous
- Subject to chemical upsets

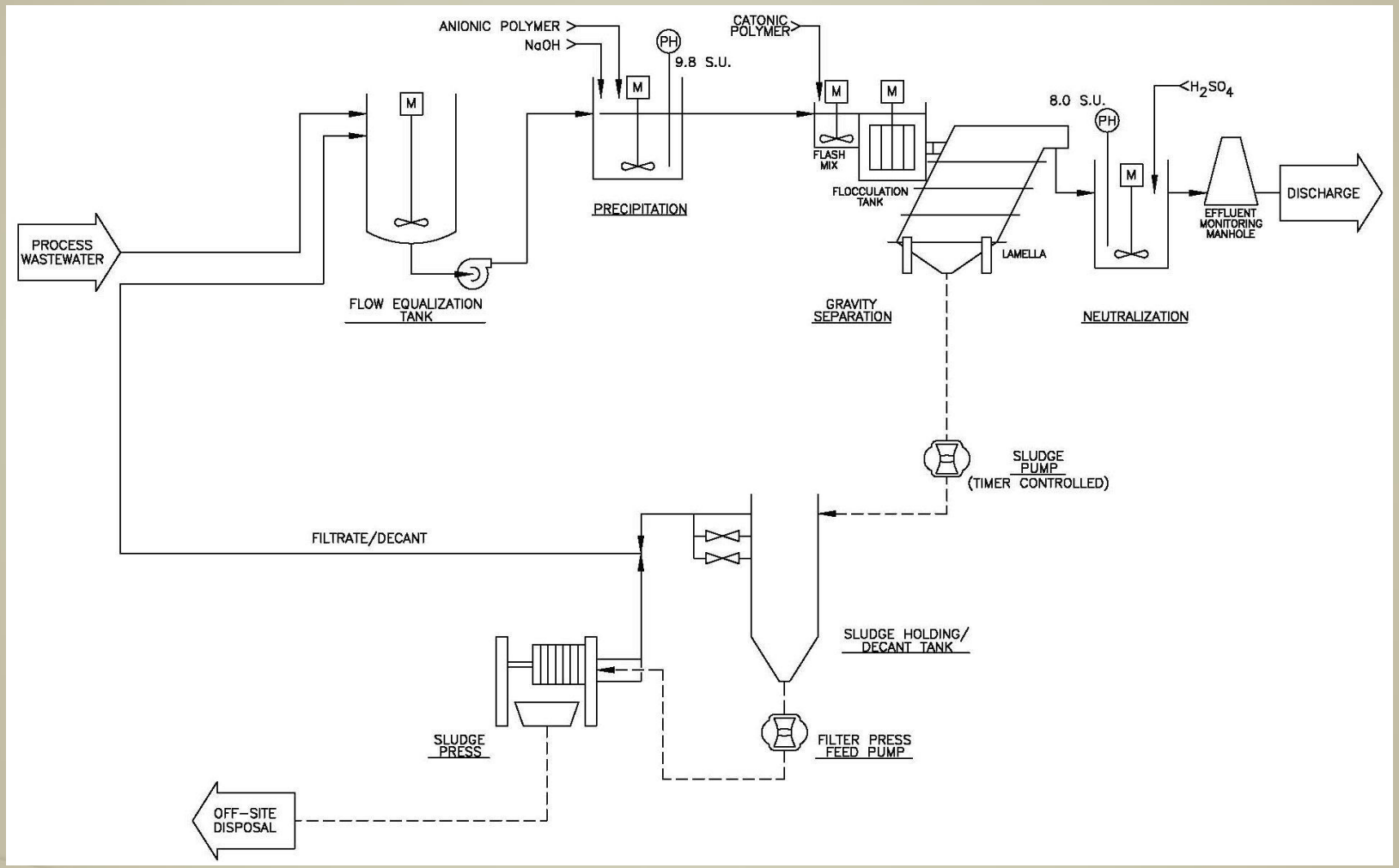
Upset Conditions

- Oil & Grease cannot be divided
- Surfactants
- Concentrated Baths
- Variability of Wastewater
- Spill Control
- Cooling Water (non-contact)

An Operator's Best Friend…..

"We never know what is coming at us on any given day, so I can never have too many spare tanks"

Dissolved Metals – Chemical Precipitation



Cyanide

- Oxidation Step 1 – Cyanide to Cyanate

  Chlorine or Peroxide (ORP Controlled)

  High pH (>10.0 S.U.)

- Oxidation Step 2 – Cyanate to CO2 and N2

  Chlorine or Peroxide (ORP Controlled)

  Lower pH (8.5 – 9.0 S.U.)

What is Next for Metal Finishing?

THE NEXT FRONTIER

The Next Frontier

- Pollution Prevention/Wastewater Reuse
- Total Dissolved Solids
- Nutrients (Ammonia/Phosphorus)

Pollution Prevention

- Counter Flow Rinsing
- Chrome Removal
- Automated Process Operations
- Extended Bath Life

Wastewater Reuse

- Non-contact Cooling Water (cooling towers)
- Cleaning Operations
- Additional Filtration or Ion Exchange

The Next Frontier

- Pollution Prevention/Wastewater Reuse
- Total Dissolved Solids
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Questions?

Thank You!