METAL INDUSTRIES

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ENVE420
Industrial Pollution Control

Metal Industries

Metal wastes include wastes from

- Refining mills
- Plating mills
- Washing

Metal Industries

SOURCES

Wastes not only from manufacturing of steel, but from many other materials (copper and aluminium)

Wastes from renewing surfaces on used metallic parts (such as airplane engines prior to their return to service)

Wastes from coating of one metal with another, for protective purposes (plating of silverware or business machines)

Waste compositions

Various concentrations of metallic substances, acids, alkalis, and grease

Characterized by their

Toxicity
Relatively low organic matter
Greases

Steel-mill wastes

Mainly from

- by-product coke
- blast-furnace
- rolling-mill
- pickling

Wastes contain

- Cyanogen compounds
- Phenols
- Ore
- Coke
- Limestone
- Acids
- Alkalis
- Soluble and insoluble oils
- Mill scale

Treated by

- Recirculation
- Evaporation
- Benzol extraction
- Distillation
- Sedimentation
- Neutralization
- Skimming
- Flotation
- Aeration

By-Product Coke Process

<u>Coal</u> is heated in the absence of air to produce <u>coke</u> and other products

Process involves a gas. Further processing of the gas leads to the major wastes.

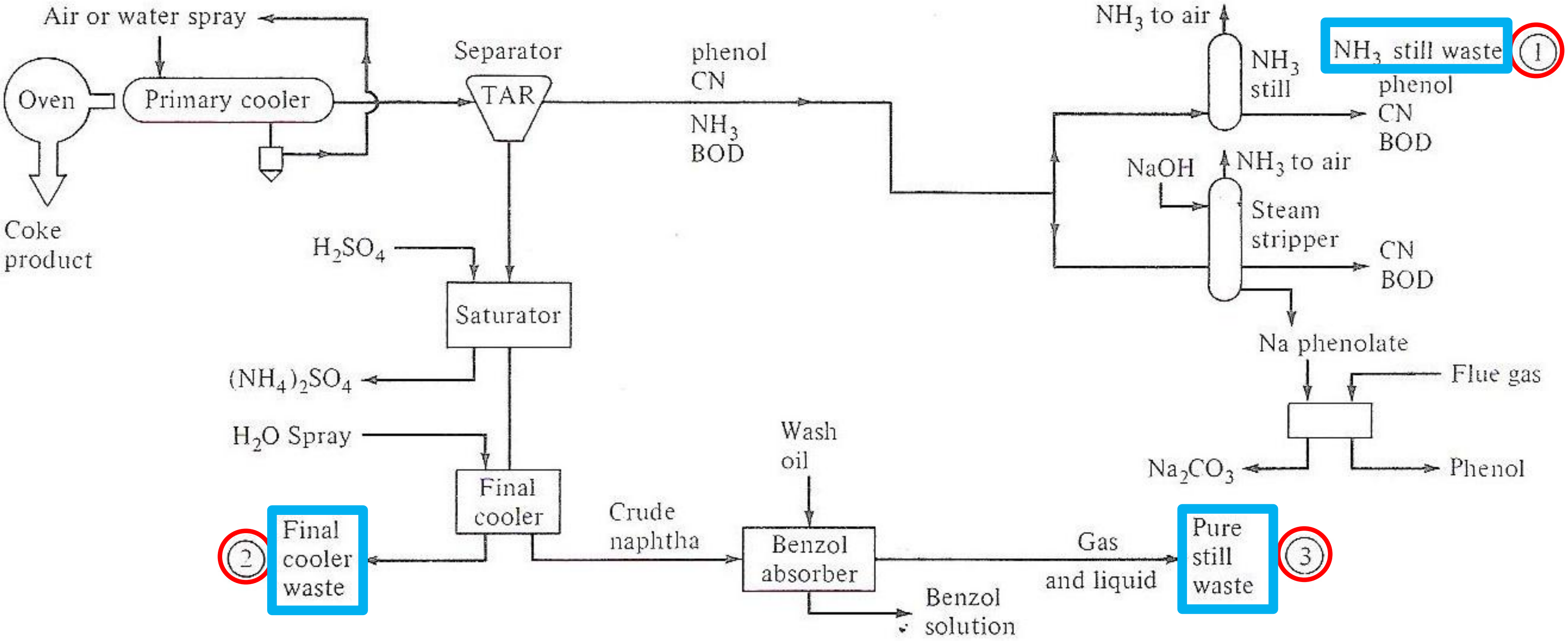
Tar and ammonia are its main constituents.

Products from burning of 1 ton of coal

Parameter	Value
Coke	600-700 kg
$(NH_4)_2SO_4$	8-12 kg
Tar	20-45 L
Gas	305-320 m^3
Phenol	45-900 g
Light oil	7.5-11 L
Naphthalene	225-545 g

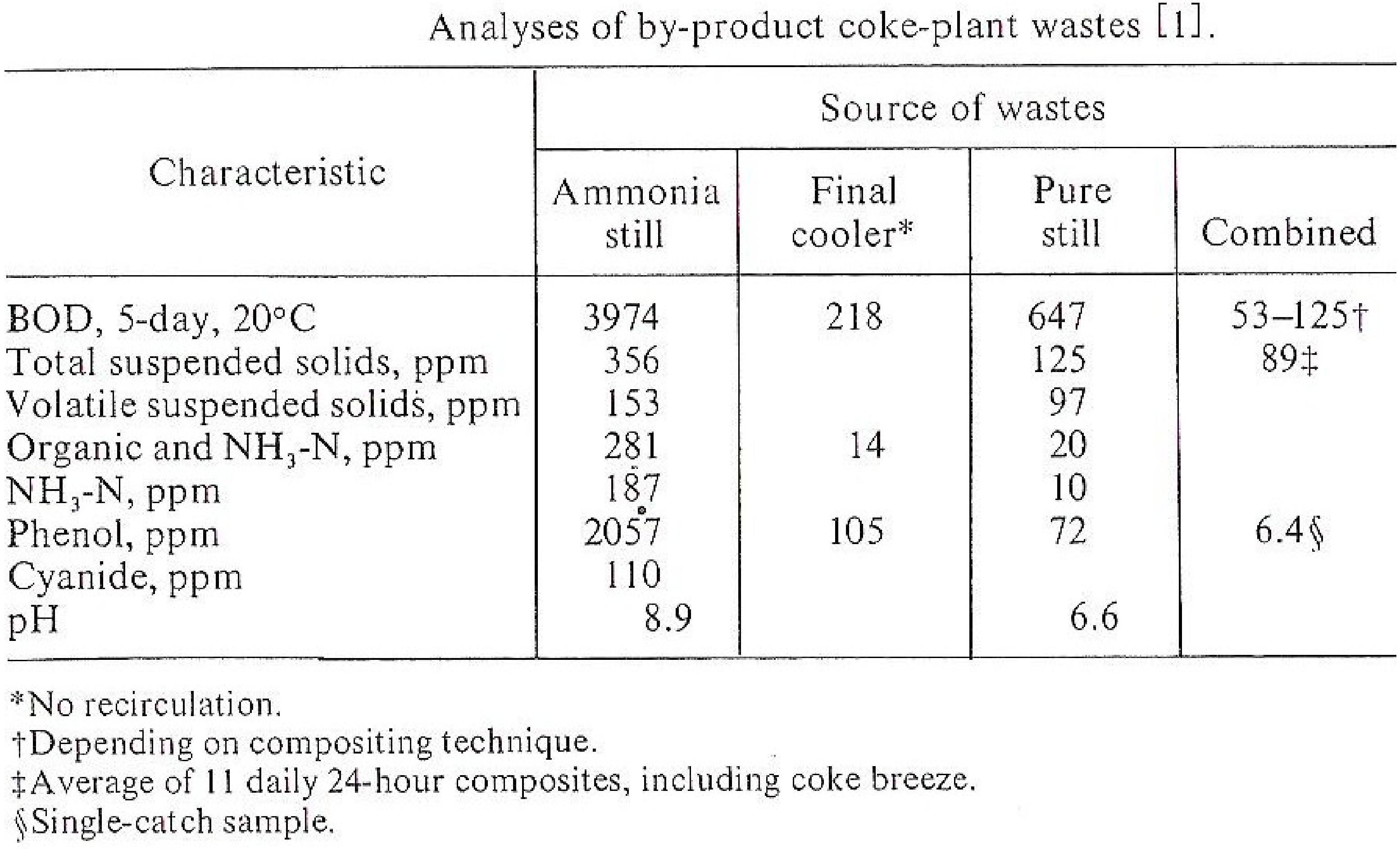
Quench tower → hot coke is deluged with water

Coke dust present in quenching water is called ‘breeze’



Coking process and three major coke plant wastes

By-Product Coke Process



Analyses of by-product coke-plant wastes [1].

Characteristic	Source of wastes			
	Ammonia still	Final cooler*	Pure still	Combined
BOD, 5-day, 20°C	3974	218	647	53–125†
Total suspended solids, ppm	356		125	89‡
Volatile suspended solids, ppm	153		97	
Organic and NH_3-N, ppm	281	14	20	
NH_3-N, ppm	187		10	
Phenol, ppm	2057	105	72	6.4§
Cyanide, ppm	110			
pH	8.9		6.6	

*No recirculation.

†Depending on compositing technique.

‡Average of 11 daily 24-hour composites, including coke breeze.

§Single-catch sample.

By-Product Coke Process

Waste Treatment

Recovery and removal units with high efficiencies
Phenol: main contaminant recovered

BOD can be reduced by about 1/3 by the practice of recirculation and reuse of contaminated waters

By-product recovery: for profit in the case of such materials as ammonium sulfate, crude tar, naphthalene, coke dust, coal gas, benzene, toluene, and xylene

Quench water: usually settled to remove coke dust, suparnatant liquor from the settling tanks is reused for quenching

By-Product Coke Process

Gravitiy separators: to remove free oil from the wastes from benzol stills

Final cooler water is also recirculated, to reduce the amount of phenol being discharged to waste

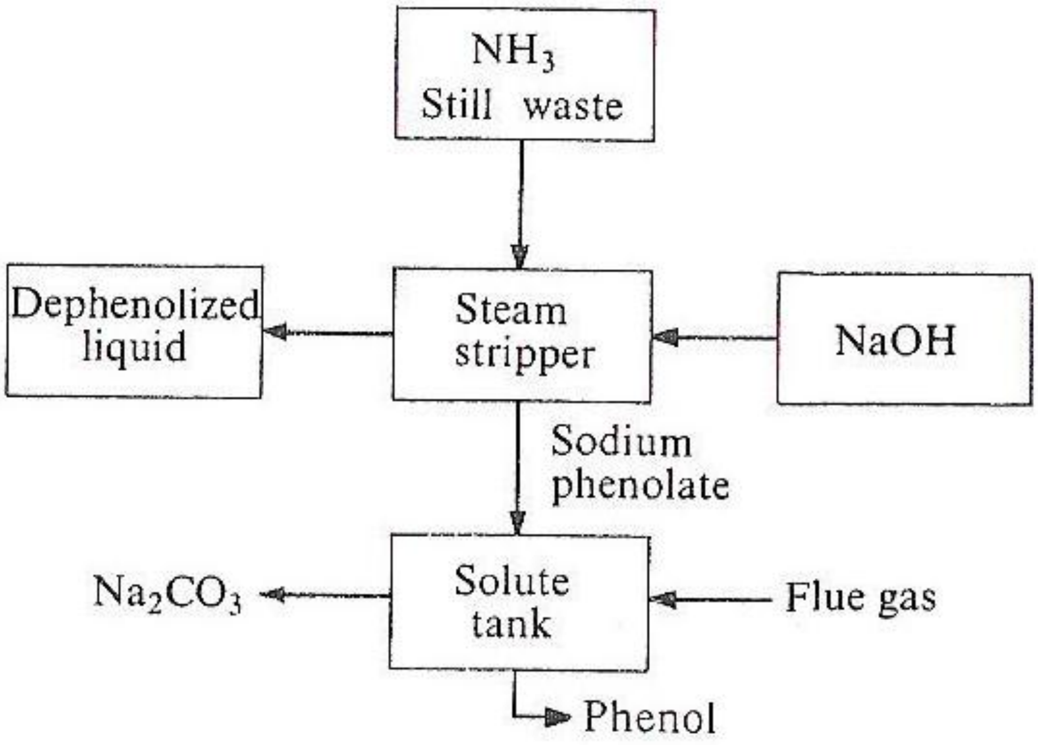
Phenol is recovered primarily to prevent pollution of streams and to avoid the nuisance of taste in water supplies

Phenols may be removed by either conversion into nonodorous compounds or recovery as crude phenol or sodium phenolate, which have some commercial value

Conversion

- Biological (Activated sludge or trickling filtration)
- Physical (ammonia-still wastes used to quench incandescent coke, a process which evaporates the NH_3)

By-Product Coke Process



The Koppers dephenolization process, using steam, caustic soda, and flue gas.

Steam-stripping operation, followed by mixing in a solution of caustic soda and renewing pure phenol with flue gas

Lowers the phenol content by 80 to 90 % in ammonia-still wastes

Treatment of three major wastes

NH_3 still (1)		Final cooler (2)	Pure still (3)
BOD	3974	218	647
suspended solids			125
CN	110		
NH_3	187		
ORGANIC	281	14	
+			
NH_4N	2057	105	72
PHENOL pH	8.9		
1. Recover NA phenolate with NAOH during steam distillation. Phenol is subsequently obtained by passing flue gas through. 2. Recirculate and reuse the contaminated NH_3 still wastewater for; (a) quenching (b) water sprays for primary and final coolers 3. Recover $(NH_2)SO_4$ by making acid with H_2SO_4 4. Biological treatment can be used to remove BOD and possibly to oxidize CN to $CO_2 + NO_2$.		1. Recirculate final cooler water. 2. Conbine the blowdown from this cooler with residual NH_3 still waste and subject both to biological treatment.	1. Settle to remove suspended solids and free oil. 2. Send supernatant (which contains some emulsified oils and BOD) to biological treatment if is a very serious consideration in ultinate disposal.

Blast Furnace

Wet scrubbers: used for wet scrubbing of blast furnace gas

downflow water sprays

It cleans the dust from the upflowing gases

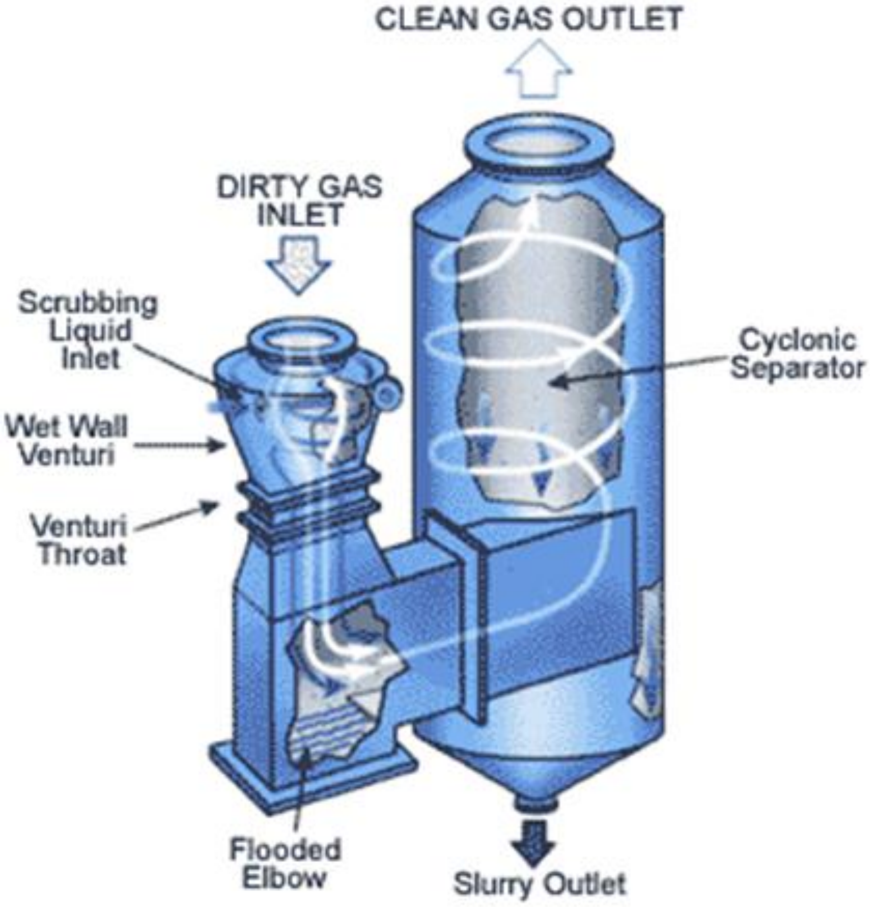
It is usually the an intermediate stage between the steps below:

dry (or cyclone) dust separation

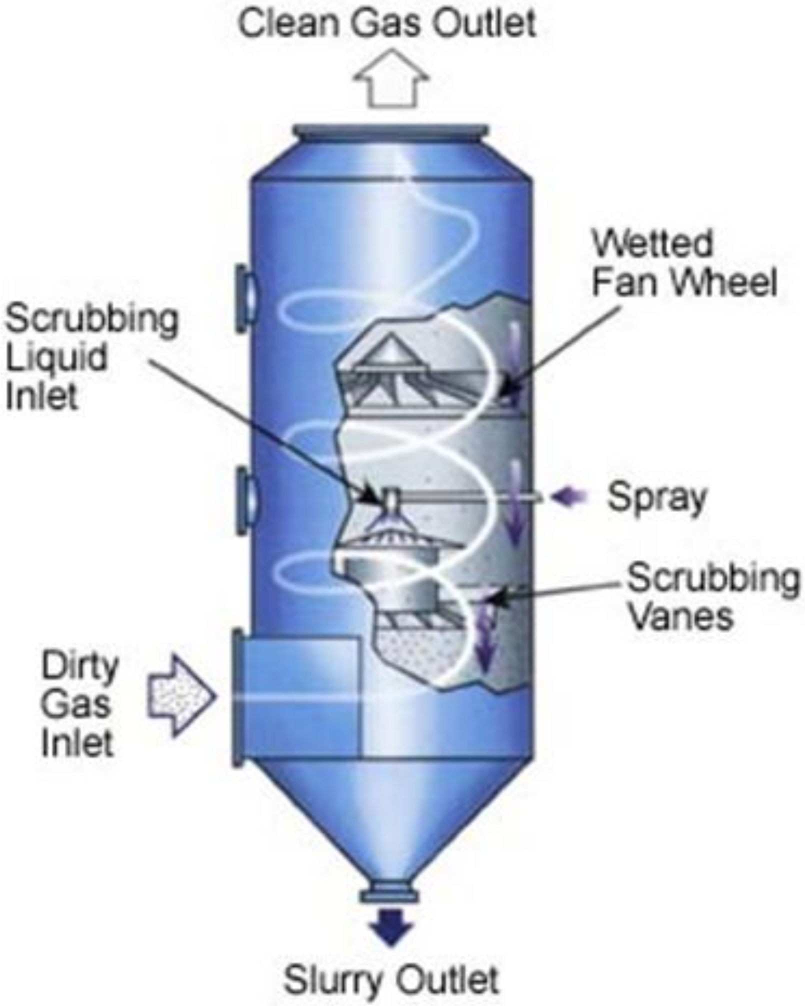
final electrostatic precipitation of the remaining fine particles

Gas washers or precipitators are periodically cleaned by flushing with water → adding to the flow of discolored water

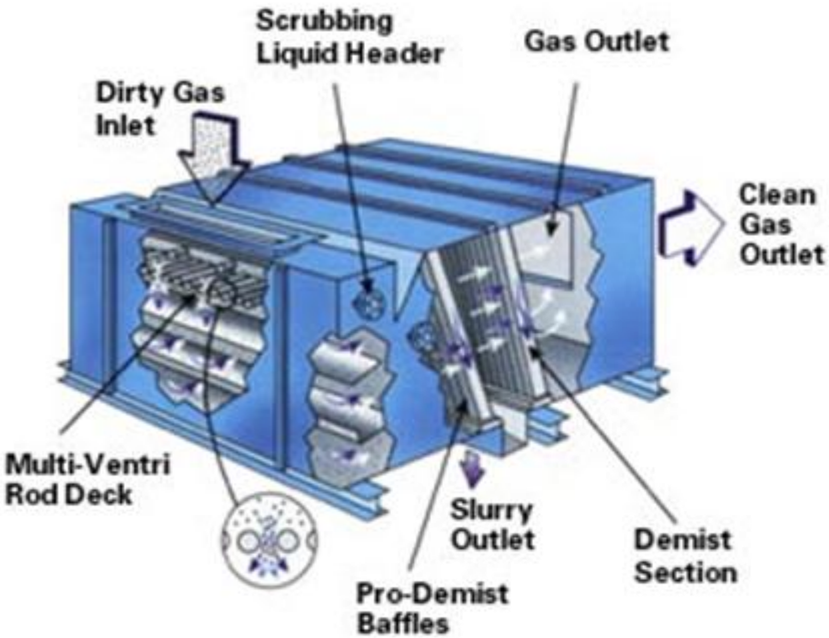
Wet Scrubbers



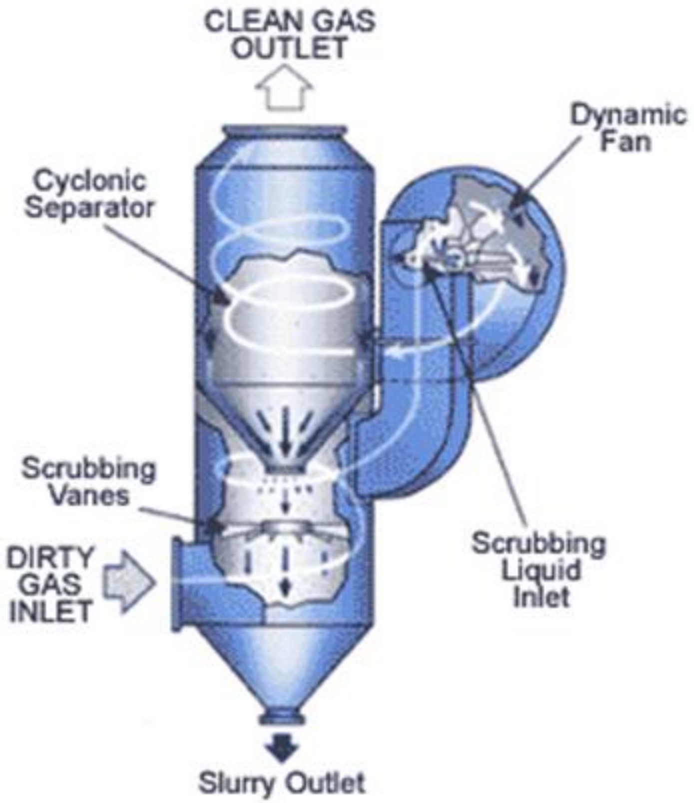
Venturi type



Microvane type



Multi-venturi type



Dynamic type

Wet Scrubbers

Wet Scrubbers

Packed tower type

Blast Furnace

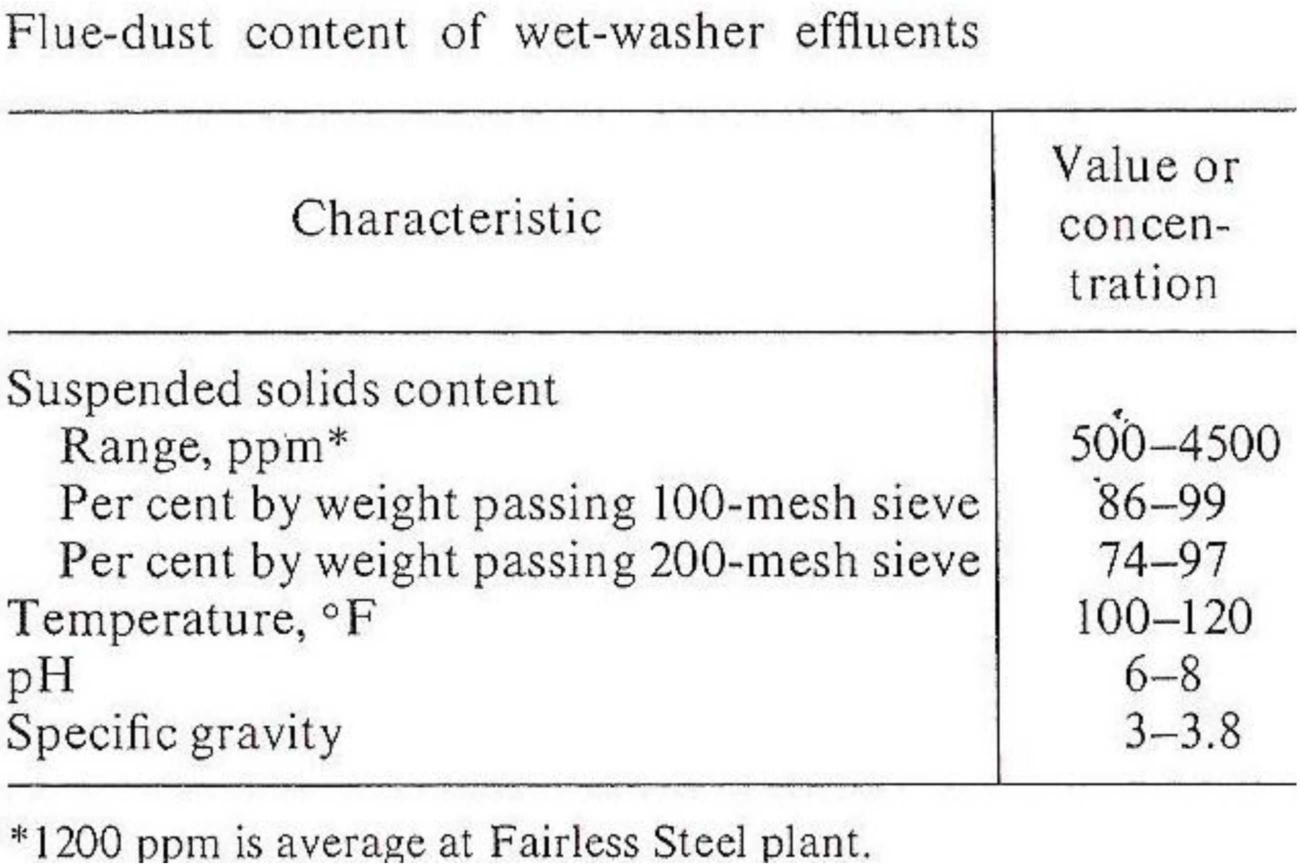
Blast furnace wet-scrubber effluent contains flue-dust solids, from washing the gas, composed of:

- iron oxide,
- alumina,
- silica,
- carbon,
- lime, and
- magnesium

The amount of each constituent, in comparison with the total quantity of dust, varies with

- type of ore used in the furnace,
- conditions of the furnace lining,
- quality of the coke used,
- number of furnaces in blast,
- amount of air being blown, and
- regularity and thoroughness of dumping and flushing of dry dust catchers

Blast Furnace



Flue-dust content of wet-washer effluents

Characteristic	Value or concentration
Suspended solids content	
Range, ppm*	500–4500
Per cent by weight passing 100-mesh sieve	86–99
Per cent by weight passing 200-mesh sieve	74–97
Temperature, °F	100–120
pH	6–8
Specific gravity	3–3.8

*1200 ppm is average at Fairless Steel plant.

70 % Fe_2O_3 (iron oxide)
12 % Silica of the flue dust content

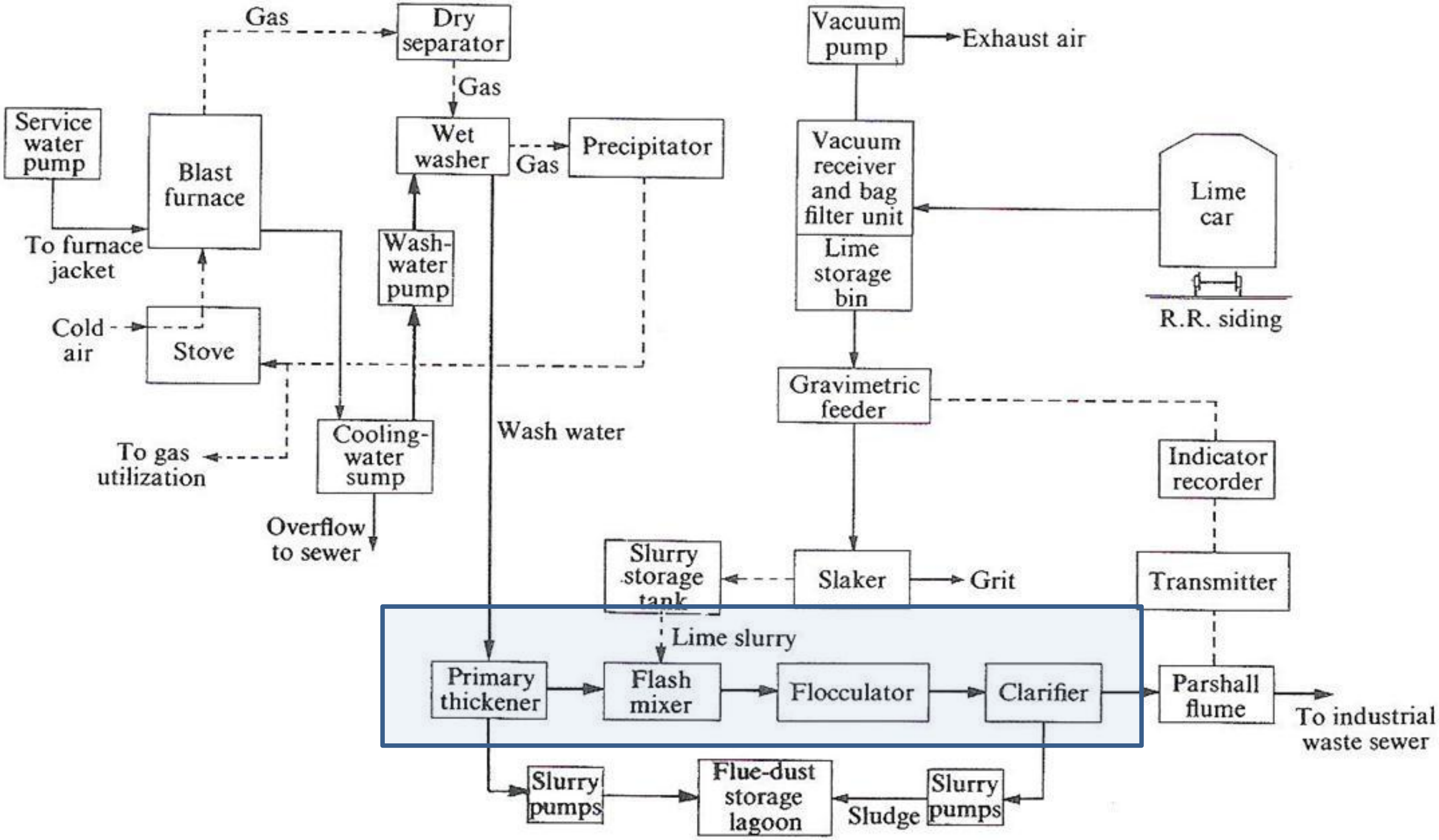
Blast Furnace

Waste Treatment

Treating the flue dust, sedimentation, followed by thickening the clarifier overflow with lime to encourage flocculation, has been found most effective for removing iron oxide and silica

90-95% of the suspended matter settles readily (one hour period) resulting effluent having less than 50 ppm Suspended Solids

Blast Furnace



Blast-furnace waste treatment process. (After Henderson and Baffa [33].)

Pickling Process

Before applying the final finish to the steel products, the manufacturer must remove

- Dirt
- Grease
- Iron-oxide scale which accumulates on the metal during fabrication

Pickling process:
Immersing the steel in dilute sulfuric acid (15-25% wt)

Waste produced:

Pickling liquor

Unused acid

Iron salts of the acid (Fe^{2+} and Fe^{3+})

- Fresh acid reacts with the iron salts in time
- As the acid is used it becomes weaker and must be renewed

Pickling Process

Amount of waste pickling liquor per ton of steel product depends on the size and type of plant

One factor that increases the volume is that:
Since the steel products must be rinsed in water after they leave the pickling tank to remove all trace of acid, the rinse or wash water eventually becomes quite acidic and must also be discarded

The volume of rinse water is 4-20 times that of the actual pickling liquor, although naturally it is far more dilute

Pickling liquor:
0.5 to 2.0 % H_2SO_4 and
15 to 22 % $FeSO_4$

Wash water:
0.02 to 0.5 % H_2SO_4 and
0.03 to 0.45 % $FeSO_4$

Pickling Process

For most small steel plants, the recovery of by-products from waste pickling liquor is not economically feasible and they neutralize the liquor with lime

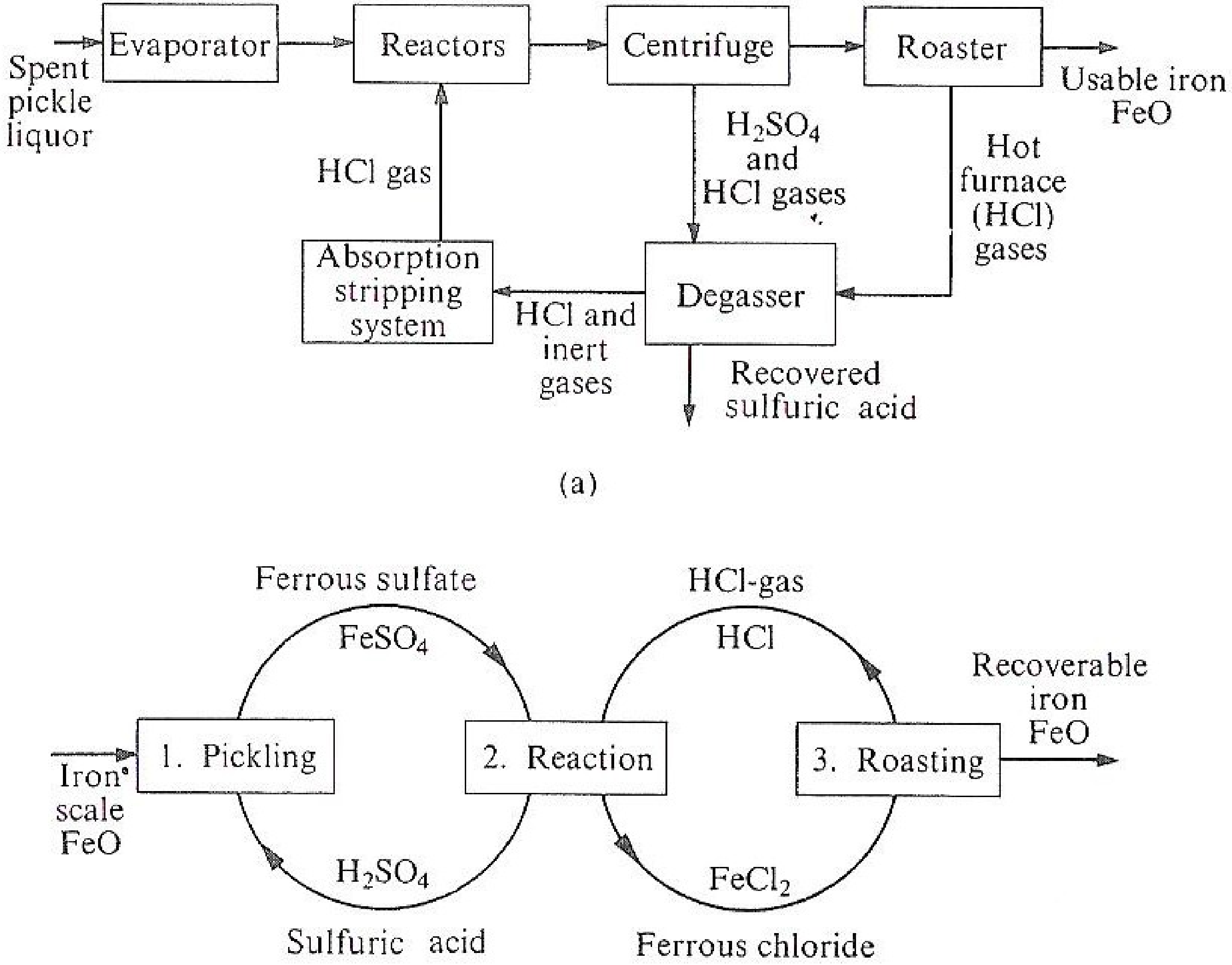
Some companies obtain by-products:

$FeSO_4.H_2O$
H_2SO_4
$Fe_2(SO_4)_3$
Fe^{3+}
Iron powder
Fe_3O_4 for polishing or pigments
$Al_2(SO_4)_3$

Neutralization of pickle-liquor waste with lime is costly, because

- there is no saleable end-product and there is a voluminous,
- slow settling sludge which is difficult to dispose of

Pickling Process



1. Pickling: $FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$
2. Reaction: $FeSO_4 + 2HCl \rightarrow FeCl_2 + H_2SO_4$
3. Roasting: $FeCl_2 + H_2O \rightarrow 2HCl + FeO$

Blaw-Knox-Ruthner process for recovery of acid from spent pickle liquor: (a) process flow diagram; (b) chemistry of process. (Courtesy Blaw-Knox Co.)

Pickling Process

HCl can be used instead of H_2SO_4

Benefits of HCl pickling are:

- Easier regeneration of acid
- No over pickling
- More flexibility on the line
- Elimination of the secondary scale breaker
- Higher pickling speeds
- 20% reduction in wastewater volume

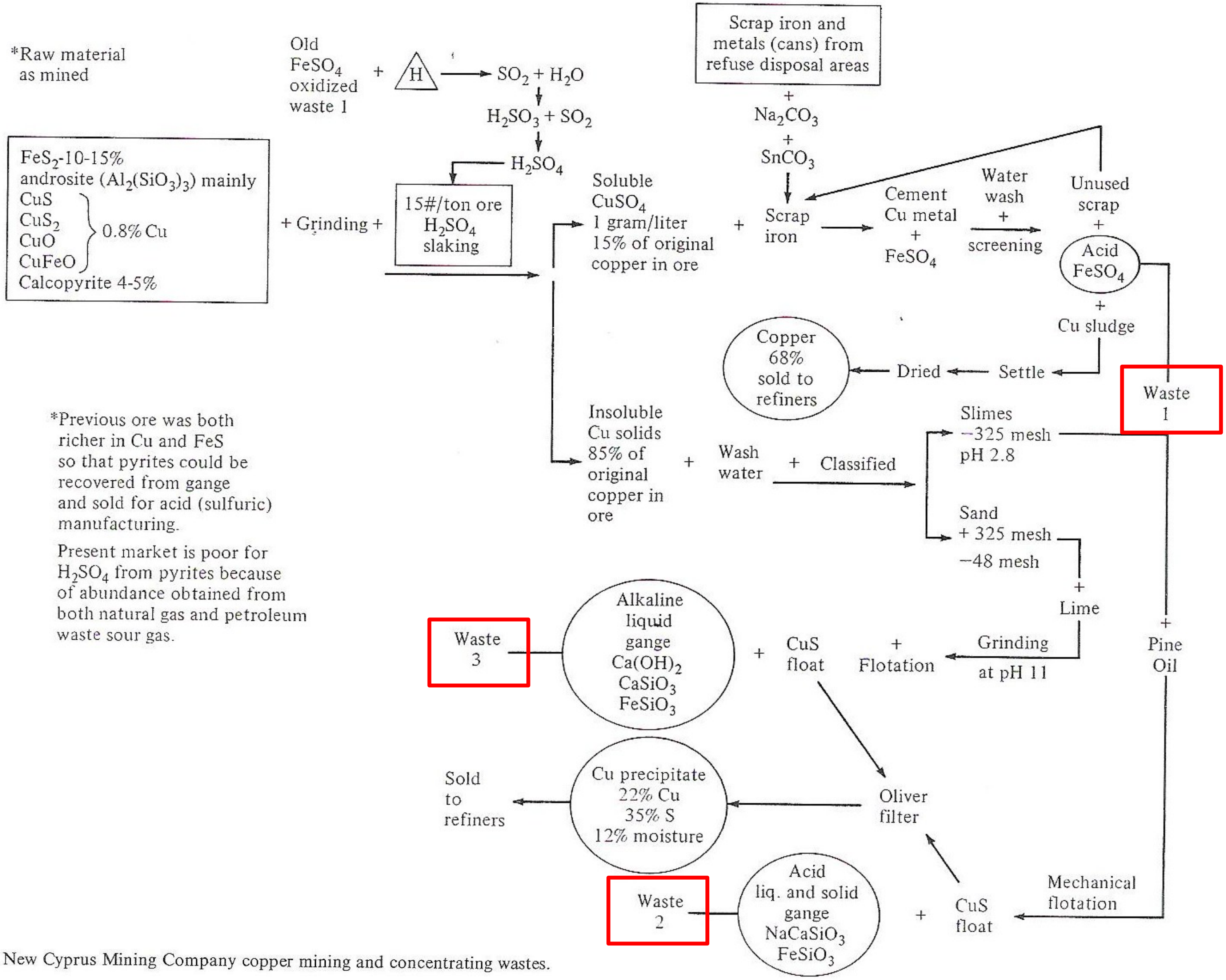
Disadvantage:
Increased cost of HCl over H_2SO_4

Other Metal-Plant Wastes

Processors of several other metals besides steel are significant waste contributors

Among these are:
- brass,
- copper,
- gold, and
- aluminium plants,

which are similar to steel mills in that impure metal is purified, worked and fabricated into final usable products

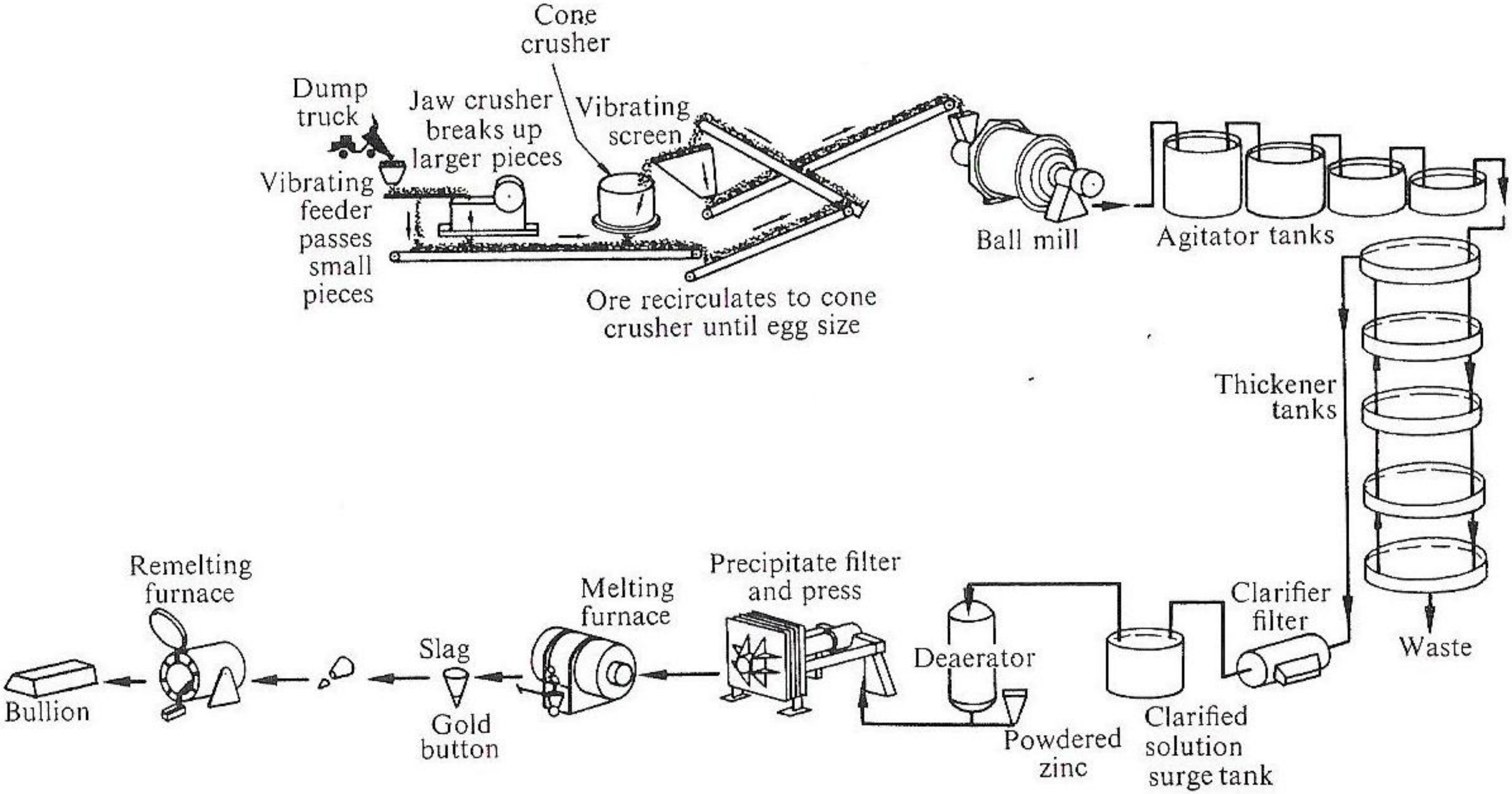


*Raw material as mined

*Previous ore was both richer in Cu and FeS so that pyrites could be recovered from gange and sold for acid (sulfuric) manufacturing.

Present market is poor for H_2SO_4 from pyrites because of abundance obtained from both natural gas and petroleum waste sour gas.

New Cyprus Mining Company copper mining and concentrating wastes.


Cone crusher
Dump truck
Jaw crusher breaks up larger pieces
Vibrating screen
Vibrating feeder passes small pieces
Ore recirculates to cone crusher until egg size
Ball mill
Agitator tanks
Thickener tanks
Waste
Clarifier filter
Clarified solution surge tank
Deaerator
Powdered zinc
Precipitate filter and press
Melting furnace
Slag
Gold button
Remelting furnace
Bullion

Metal-plating Wastes

After metals have been fabricated into the appropriate sizes and shapes to meet customers’ specifications, they are finished to final product requirements

Finishing usually involves <u>stripping</u>, <u>removal of undesirable oxides</u>, <u>cleaning</u> and <u>plating</u>

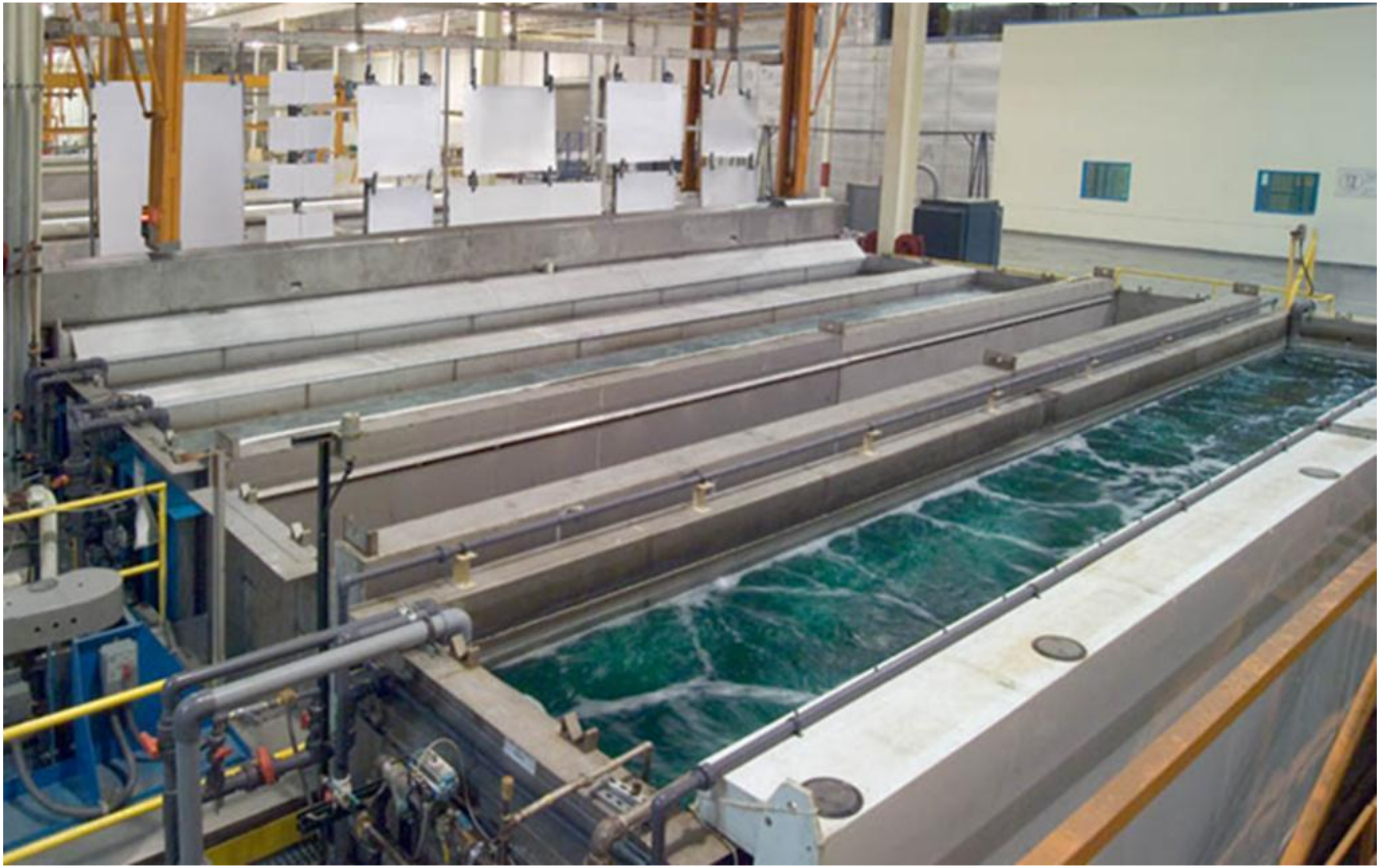
In plating, the <u>metal to be plated acts as the cathode</u> while the <u>plating metal in solution serves as the anode</u>

Total liquid wastes from plating are not voluminous, but are extremely dangerous because of their <u>toxic content</u>

The most important toxic contaminants are <u>acids</u> and metals, such as <u>chromium</u>, <u>zinc</u>, <u>copper</u>, <u>nickel</u>, <u>tin</u>, and <u>cyanides</u>

<u>Alkaline cleaners</u>, <u>grease</u>, and <u>oil</u> are also found in the wastes

Sulfuric acid anodizing



Phosphoric acid anodizing

Three typical processes	Baths	Wastes
STRIPPING	Solutions of acids H_2SO_4, HNO_3, HCl, HF	Acids are used to remove dirt and oxide deposits from metal surfaces to ensure proper conditions for plating
CLEANING	Organic Solvents & Wetting Agents	Organic solvents for removing oil and grease
PLATING	Solutions of the metal to be plated	Metal salts e.g. chromic acid, cadmium oxide or copper cyanide

Wastes from these three processes are mainly composed of cyanides, chromates, acids, and alkalies

Characteristics of metal-plating wastes

Most **stripping baths** are **acidic** in nature and consist of solutions of sulfuric, nitric, and hydrochloric acid, but **alkaline** baths containing sodium sulfide, cyanide, and hydroxide may also be used

Usually the chemicals in the stripping solution are present in concentrations less than 10%

Cleaning is carried out by organic solvents, pickling, or alkaline cleaning compounds

Organic-emulsion cleaners are petroleum or coal-tar solvents coupled with an emulsifier

Alkaline cleaners consist of sodium hydroxide, ortophosphate, complex phosphates, silicates, carbonates, some organic emulsifiers, and synthetic wetting agents

Characteristics of metal-plating wastes

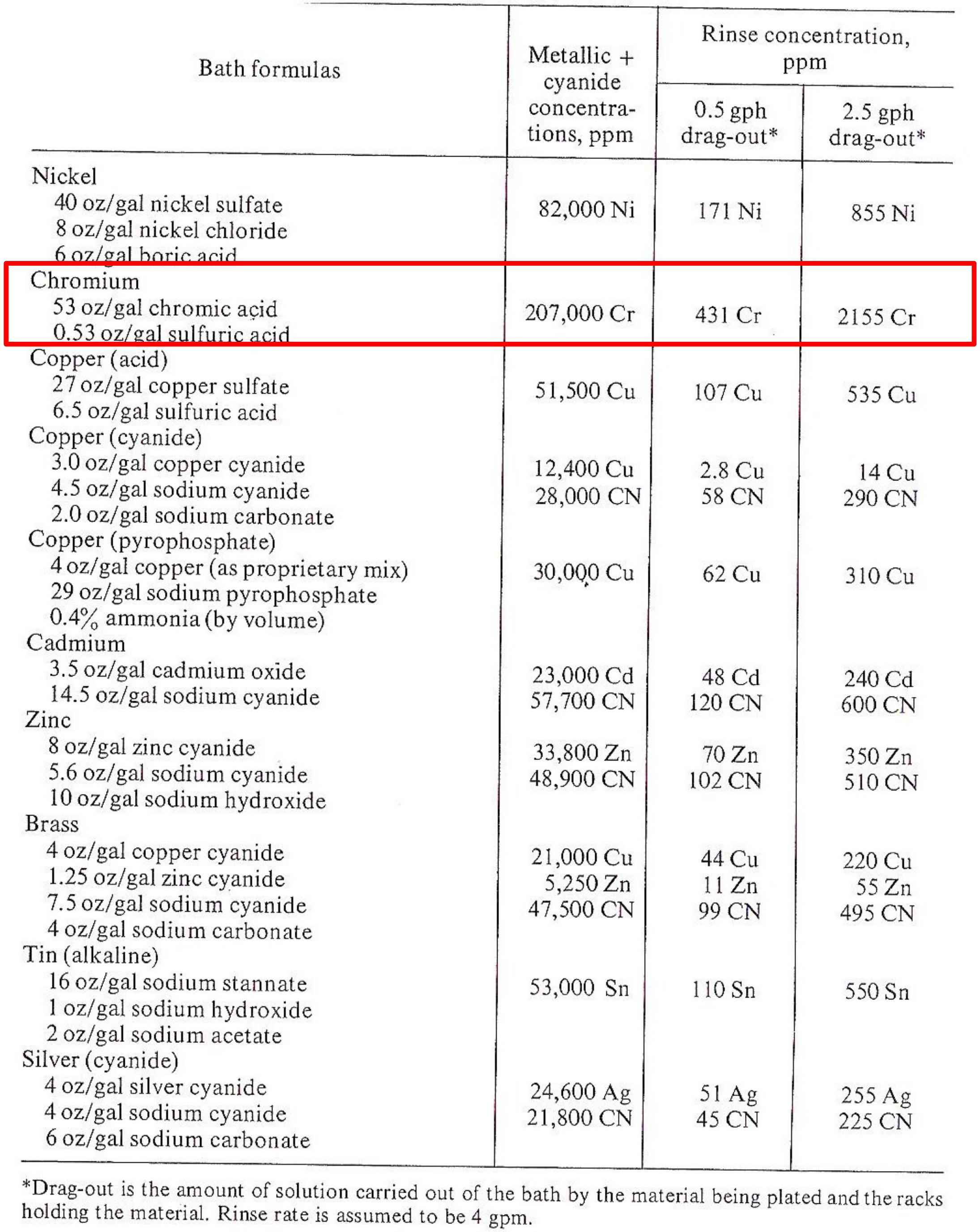
Cyanide salts are desirable, since they are good oxide solvents and in zinc plating they yield a brighter, less porous, galvanized plate

However, acid zinc sulfate is also being used in plating baths because it is said to conduct the current with less resistance than zinc cyanide

The total volume of wastes from metal-plating plants, usually expressed as gallons per finished number of metallic units, varies even more than the characteristics

Since most plants use excessive chromates for plating, the concentration of chromium in **chromium-plating bath waste** will usually be **several times the concentration of other metals in other baths**

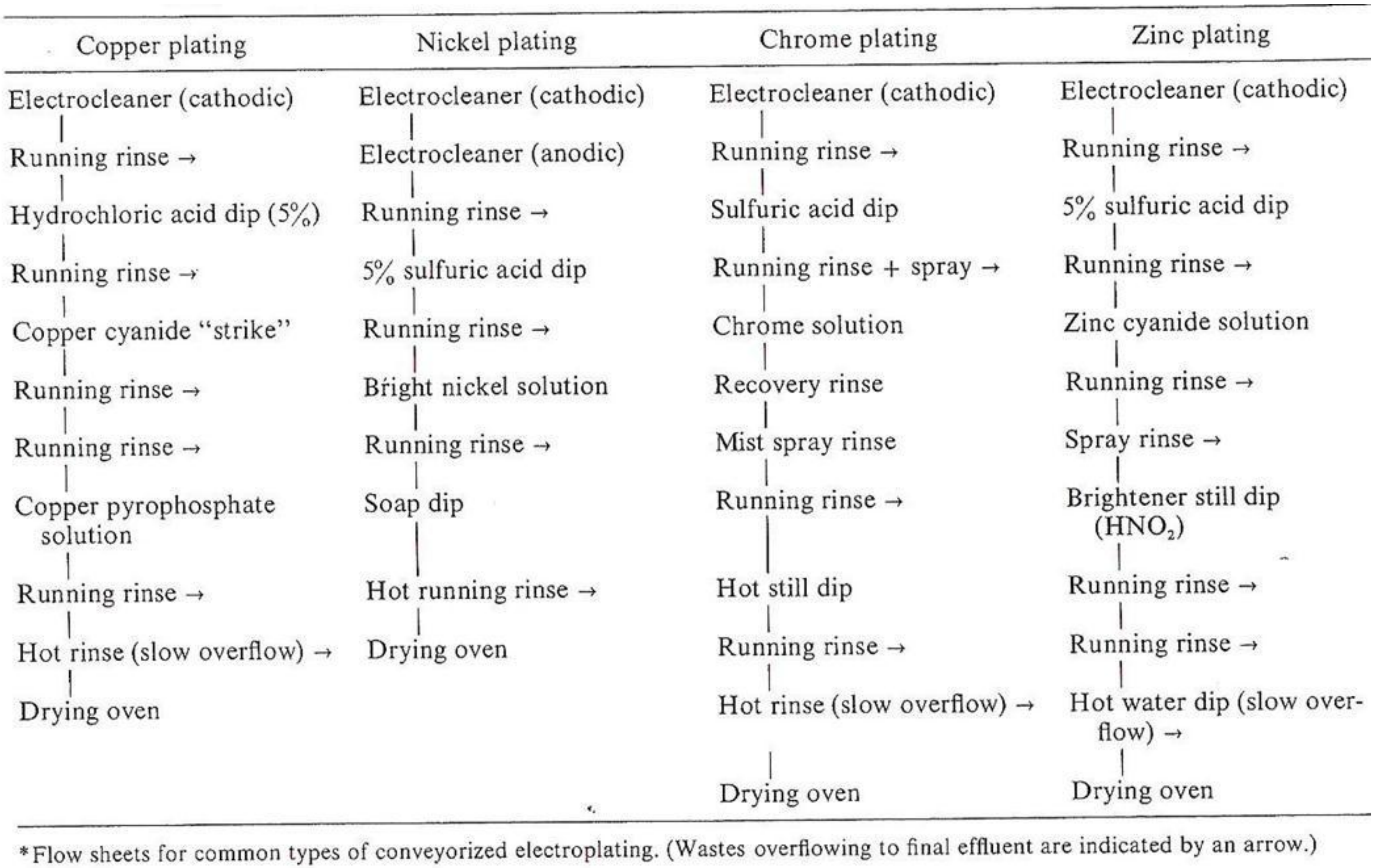
Common plating baths



Bath formulas	Metallic + cyanide concentrations, ppm	Rinse concentration, ppm	
		0.5 gph drag-out*	2.5 gph drag-out*
Nickel 40 oz/gal nickel sulfate 8 oz/gal nickel chloride 6 oz/gal boric acid	82,000 Ni	171 Ni	855 Ni
Chromium 53 oz/gal chromic acid 0.53 oz/gal sulfuric acid	207,000 Cr	431 Cr	2155 Cr
Copper (acid) 27 oz/gal copper sulfate 6.5 oz/gal sulfuric acid	51,500 Cu	107 Cu	535 Cu
Copper (cyanide) 3.0 oz/gal copper cyanide 4.5 oz/gal sodium cyanide 2.0 oz/gal sodium carbonate	12,400 Cu 28,000 CN	2.8 Cu 58 CN	14 Cu 290 CN
Copper (pyrophosphate) 4 oz/gal copper (as proprietary mix) 29 oz/gal sodium pyrophosphate 0.4% ammonia (by volume)	30,000 Cu	62 Cu	310 Cu
Cadmium 3.5 oz/gal cadmium oxide 14.5 oz/gal sodium cyanide	23,000 Cd 57,700 CN	48 Cd 120 CN	240 Cd 600 CN
Zinc 8 oz/gal zinc cyanide 5.6 oz/gal sodium cyanide 10 oz/gal sodium hydroxide	33,800 Zn 48,900 CN	70 Zn 102 CN	350 Zn 510 CN
Brass 4 oz/gal copper cyanide 1.25 oz/gal zinc cyanide 7.5 oz/gal sodium cyanide 4 oz/gal sodium carbonate	21,000 Cu 5,250 Zn 47,500 CN	44 Cu 11 Zn 99 CN	220 Cu 55 Zn 495 CN
Tin (alkaline) 16 oz/gal sodium stannate 1 oz/gal sodium hydroxide 2 oz/gal sodium acetate	53,000 Sn	110 Sn	550 Sn
Silver (cyanide) 4 oz/gal silver cyanide 4 oz/gal sodium cyanide 6 oz/gal sodium carbonate	24,600 Ag 21,800 CN	51 Ag 45 CN	255 Ag 225 CN

*Drag-out is the amount of solution carried out of the bath by the material being plated and the racks holding the material. Rinse rate is assumed to be 4 gpm.

Flow chart for some common plating baths



Copper plating	Nickel plating	Chrome plating	Zinc plating
Electrocleaner (cathodic)	Electrocleaner (cathodic)	Electrocleaner (cathodic)	Electrocleaner (cathodic)
Running rinse →	Electrocleaner (anodic)	Running rinse →	Running rinse →
Hydrochloric acid dip (5%)	Running rinse →	Sulfuric acid dip	5% sulfuric acid dip
Running rinse →	5% sulfuric acid dip	Running rinse + spray →	Running rinse →
Copper cyanide "strike"	Running rinse →	Chrome solution	Zinc cyanide solution
Running rinse →	Bright nickel solution	Recovery rinse	Running rinse →
Running rinse →	Running rinse →	Mist spray rinse	Spray rinse →
Copper pyrophosphate solution	Soap dip	Running rinse →	Brightener still dip (HNO_2)
Running rinse →	Hot running rinse →	Hot still dip	Running rinse →
Hot rinse (slow overflow) →	Drying oven	Running rinse →	Running rinse →
Drying oven		Hot rinse (slow overflow) →	Hot water dip (slow overflow) →
		Drying oven	Drying oven

*Flow sheets for common types of conveyorized electroplating. (Wastes overflowing to final effluent are indicated by an arrow.)

Plating-waste concentrations

Plant	pH	Cu, ppm	Fe, ppm	Ni, ppm	Zn, ppm	Chromium, ppm		Cn, ppm
						+6	Total	
A	3.2	16	11	0	0	0	1.0	6
A	10.4	19	3	0	0	0	0.5	14
B	4.1	58	1.2	0	0	204	246	0.2
C	2.8	11		0.2		3	7	1.2
D	2.0	300	10	0	82	0	0	0.7
E	2.4	35	8			555	612	1.2
E	10.7	14	4	19		32	39	2.0
F	10.5	6	2	25	39			10
G	11.3	18	18	26		36		15

Treatment of metal-plating wastes

The methods used for disposal of waste from plating operations can be divided into two clases:

(1) Modifications in design and/or operation within the manufacturing process to minimize or eliminate the waste problem

(2) Installation of a chemical (sometimes physical) treatment plant to destroy or remove toxic and objectionable materials in plating-room effluents

Treatment of metal-plating wastes

Modifications include

(1) Installing a gravity-fed, nonoverflowing emergency holding tank for toxic metals and their salts
(2) Eliminating breakable containers for concentrated material
(3) Designing special drip pans, spray rinses, and shaking mechanisms
(4) Reducing spillage, drag-out leak to the floor, or other losses, by curbing the area and discharging these losses to a holding tank
(5) Using high-pressure fog rinses rather than high volume water washes
(6) Reclaiming valuable metals from concentrated plating-bath wastes
(7) Evaporating reclaimed wastes to desired volume and returning to plating bath at rate equal to loss from bath
(8) Recirculating wet-washer wastes from fume scrubbers

Treatment of metal-plating wastes

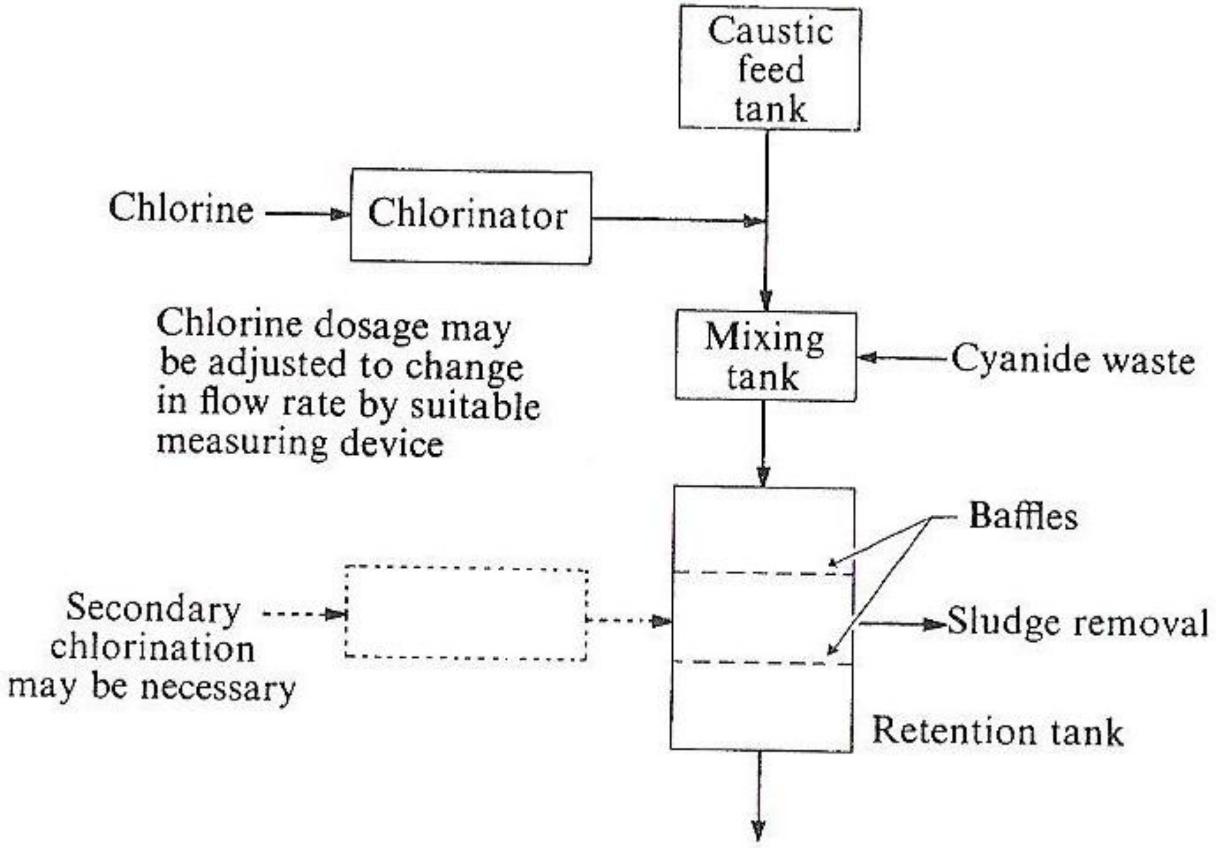
Treatment of plating wastes by chemical and physical means are designed primarily to accomplish three objectives: Removal of

Cyanides
Chromium
All other metals, oil and greases

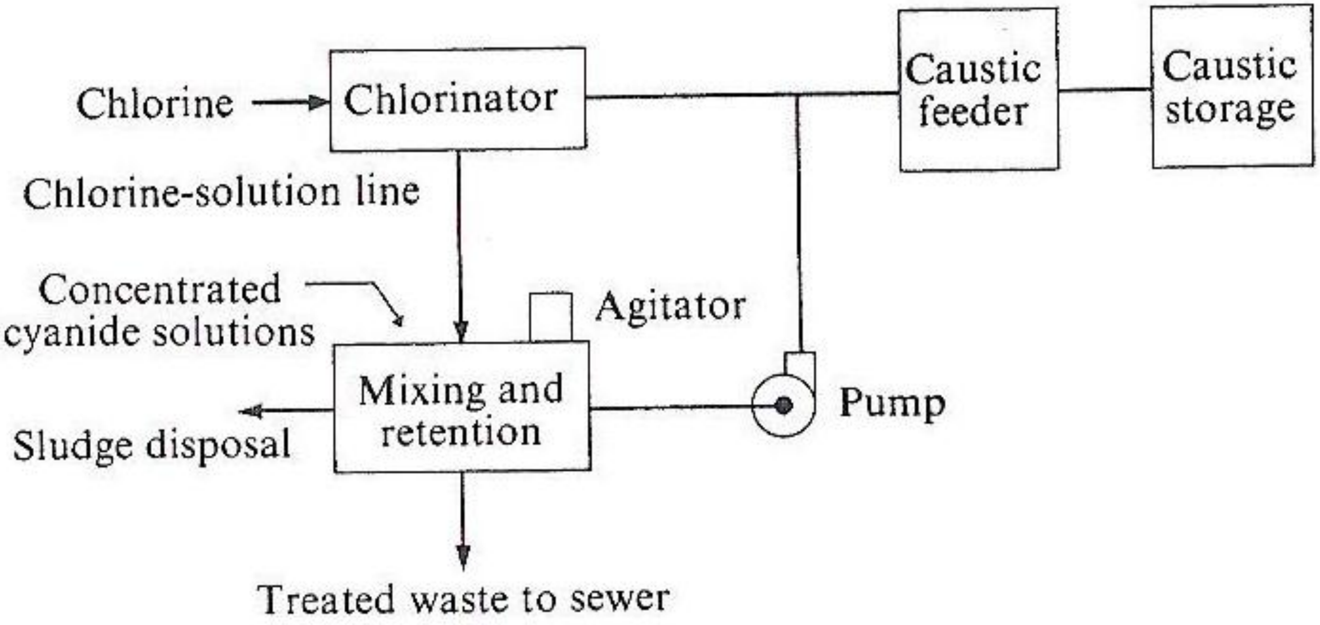
Treatment of cyanides

(1) Chlorination (gas)
(2) Hypochlorites
(3) ClO_2
(4) O_3 (ozonation)
(5) Conversion to less toxic cyanide complexes
(6) Electrolytic oxidation
(7) Acidification
(8) Lime-sulfur method
(9) Ion exchange
(10) Heating to dryness

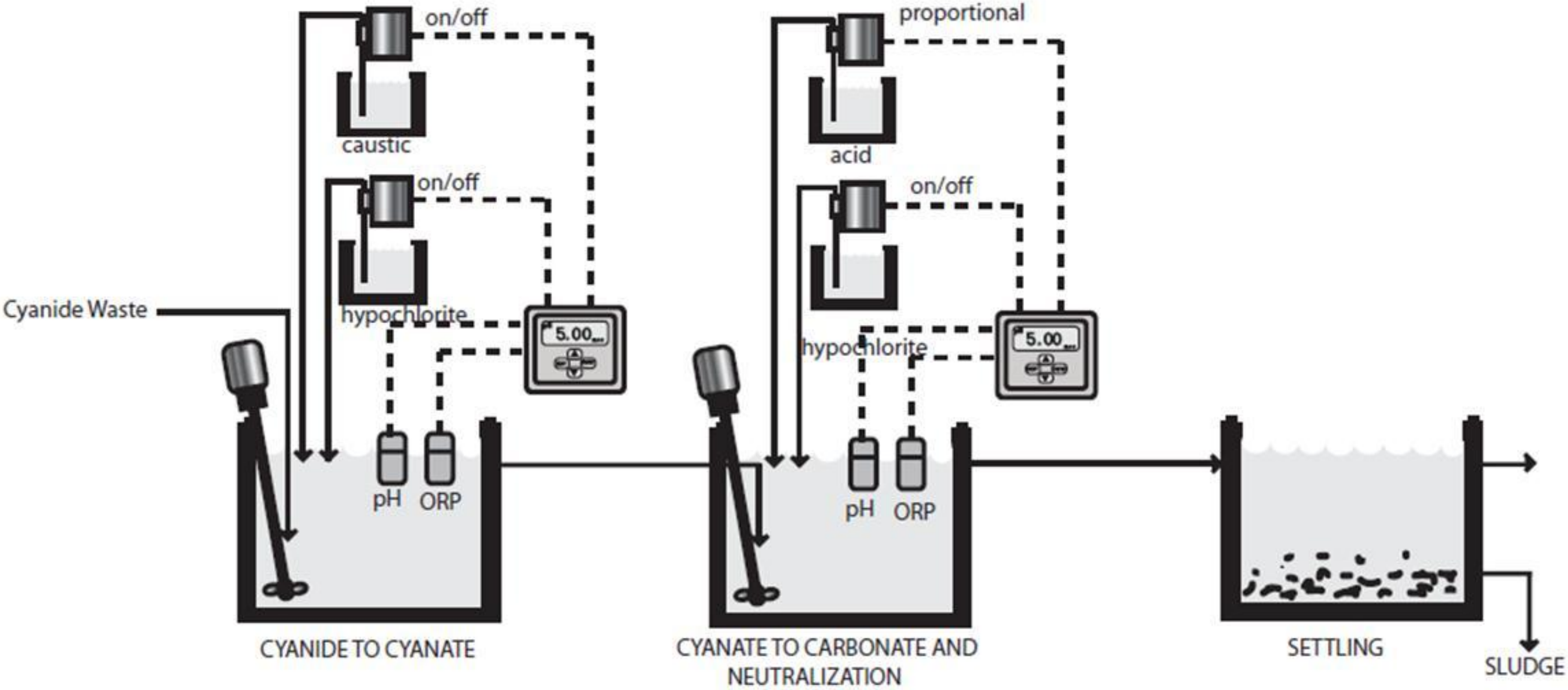
Treatment of cyanides is mostly accomplished by alkaline chlorination



Continuous chlorination of cyanide wastes.



Batch chlorination of cyanide wastes


on/off
caustic
on/off
hypochlorite
5.00
Cyanide Waste
pH
ORP
CYANIDE TO CYANATE
proportional
acid
on/off
hypochlorite
5.00
pH
ORP
CYANATE TO CARBONATE AND NEUTRALIZATION
SETTLING
SLUDGE

Treatment of metal-plating wastes

Chromium-bearing plating wastes are normally segregated from cyanide wastes, since they must be reduced and acidified (to convert the hexavalent chromium to the trivalent stage) before precipitation can occur

Although it is possible to precipitate the chromium directly in the hexavalent form with barium chloride, this method is not widely used

Removal of other metals such as Cu, Zn, Ni, Fe, and greases is usually accomplished by neutralization followed by chemical precipitation

Treatment of metal-plating wastes

Sufficient alkalinity, usually $Ca(OH)_2$ or NaOH, is added prior to chlorination to bring the waste to a pH of about 11, thus ensuring the complete oxidation of cyanide

$$\begin{aligned}&2NaCN + 5Cl_2 + 12NaOH \\ &\rightarrow N_2 + 2Na_2CO_3 + 10NaCl + 6H_2O.\end{aligned}$$

Violent agitation must accompany the chlorination, to prevent the cyanide salt of sodium or calcium from precipitating out prior to oxidation

Presence of other metals may also interfere with cyanide oxidation, because of the formation of metal cyanide complexes

Extended chlorination may be necessary under these conditions. Sometimes a full 24-hour chlorination period may be required for complete oxidation

Treatment of metal-plating wastes

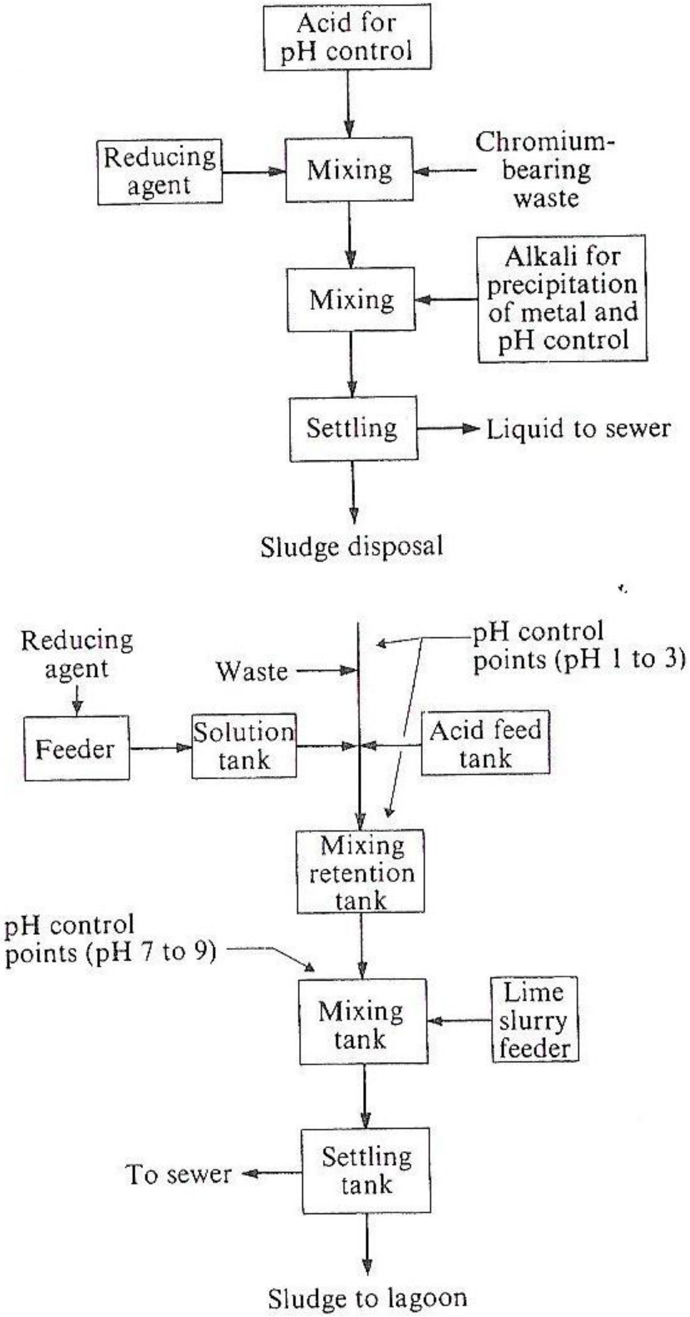
Chromium reduction and precipitation:

Chromium-plating-waste treatment by reduction and precipitation involves reducing the hexavalent chromium (Cr^{6+} as chromic acid or chromates) in the waste to the trivalent stage (Cr^{3+}) with reducing agents such as $\underline{FeSO_4}$, $\underline{SO_2}$, or $\underline{NaHSO_3}$

Sufficient free mineral acid should also be present to combine with the reduced chromium and to maintain a residual pH of 3.0 or lower, which will ensure complete reaction

When the reduction is complete, an alkali (usually lime slurry) is added, to neutralize the acid and precipitate the trivalent chromium

$$\begin{aligned}
&H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \\
&\qquad \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O, \\
&Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4, \\
&Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4.
\end{aligned}$$



Reduction and precipitation of chromium.

Treatment of metal-plating wastes

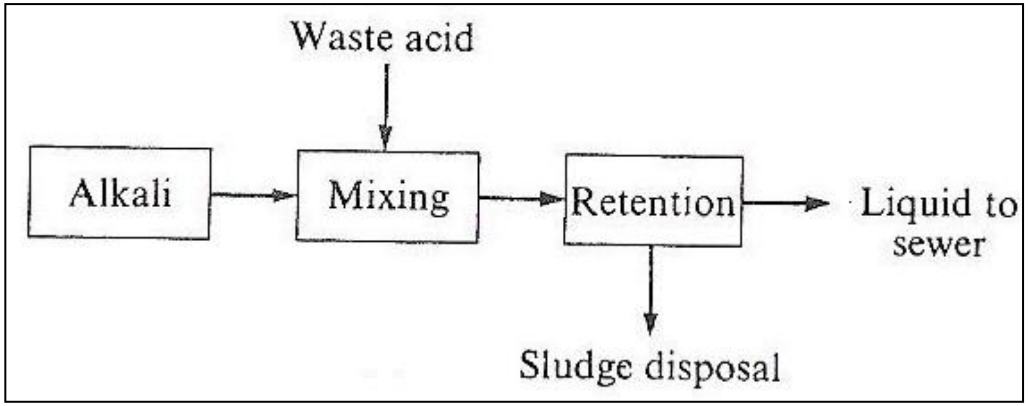
Neutralization

Treatment of other metal, oil, and grease-bearing wastes by neutralization and precipitation usually involves recombining the wastes with previously oxidized cyanide and reduced chromium wastes for subsequent and final treatment

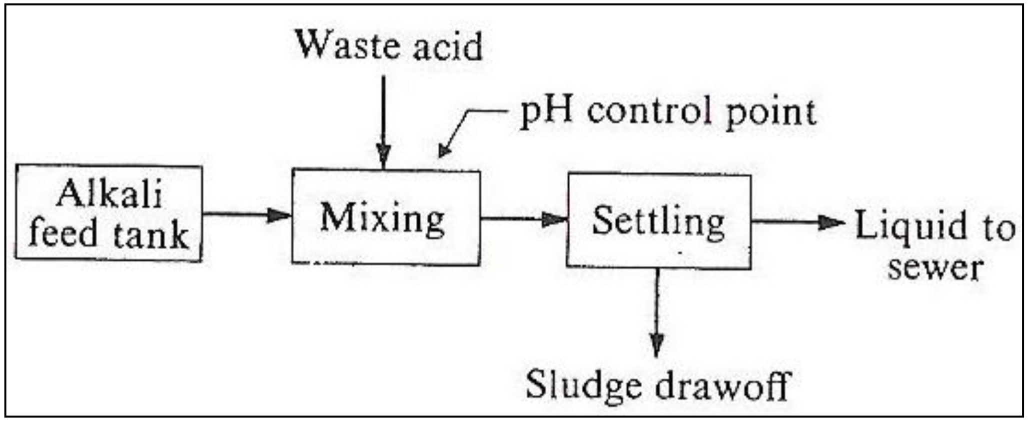
If the combined waste is acid, an alkali (usually 5 to 10% lime slurry) is added to neutralize and precipitate the metals

The floc produced is large and quite heavy, and hence the velocity of flow is decreased after adequate flocculation has occured

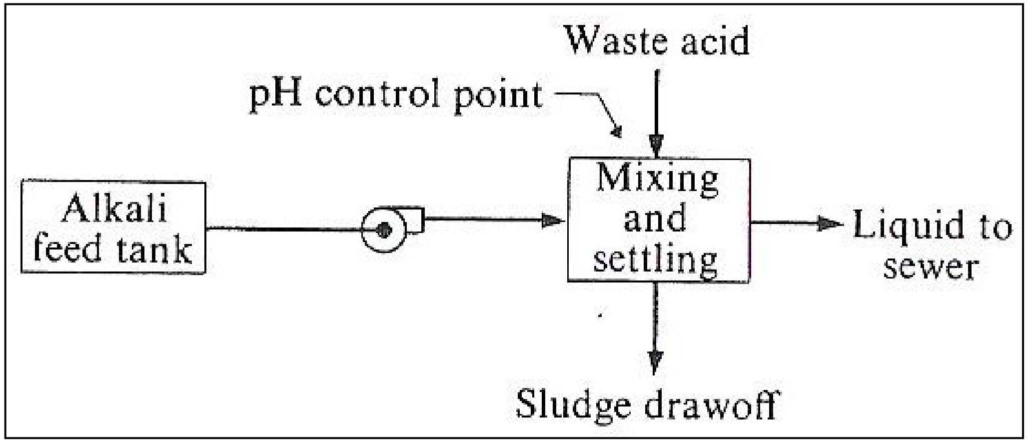
Waste is then allowed to settle. Sludge is removed and usually lagooned, since this is the most economical treatment for the slow-drying metal sludges



(a) Acid neutralization



(b) Continuous acid neutralization



(b) Batch acid neutralization

Treatment of metal-plating wastes

Recovery

Recovery practices are mainly those involving ion exchange and evaporation

Use of ion exchanger is only an application of water-softening methods, and its best application is in the treatment of rinse water following plating operations, so that little or no foreign contamination other than the recoverable metal is present

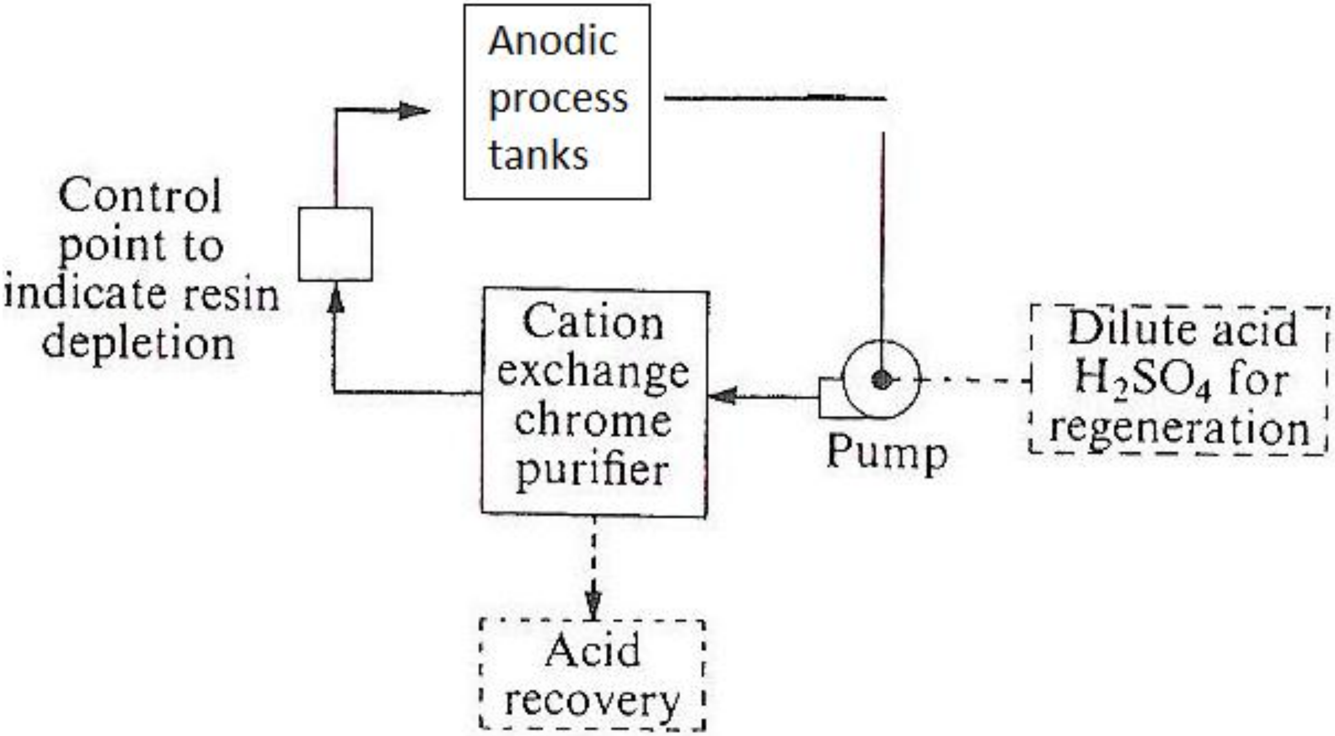
Rinse water is passed through beds of cationic and anionic resins selected for the particular application, and the deionized water is recycled through the rinse tank

Treatment of metal-plating wastes

Recovery

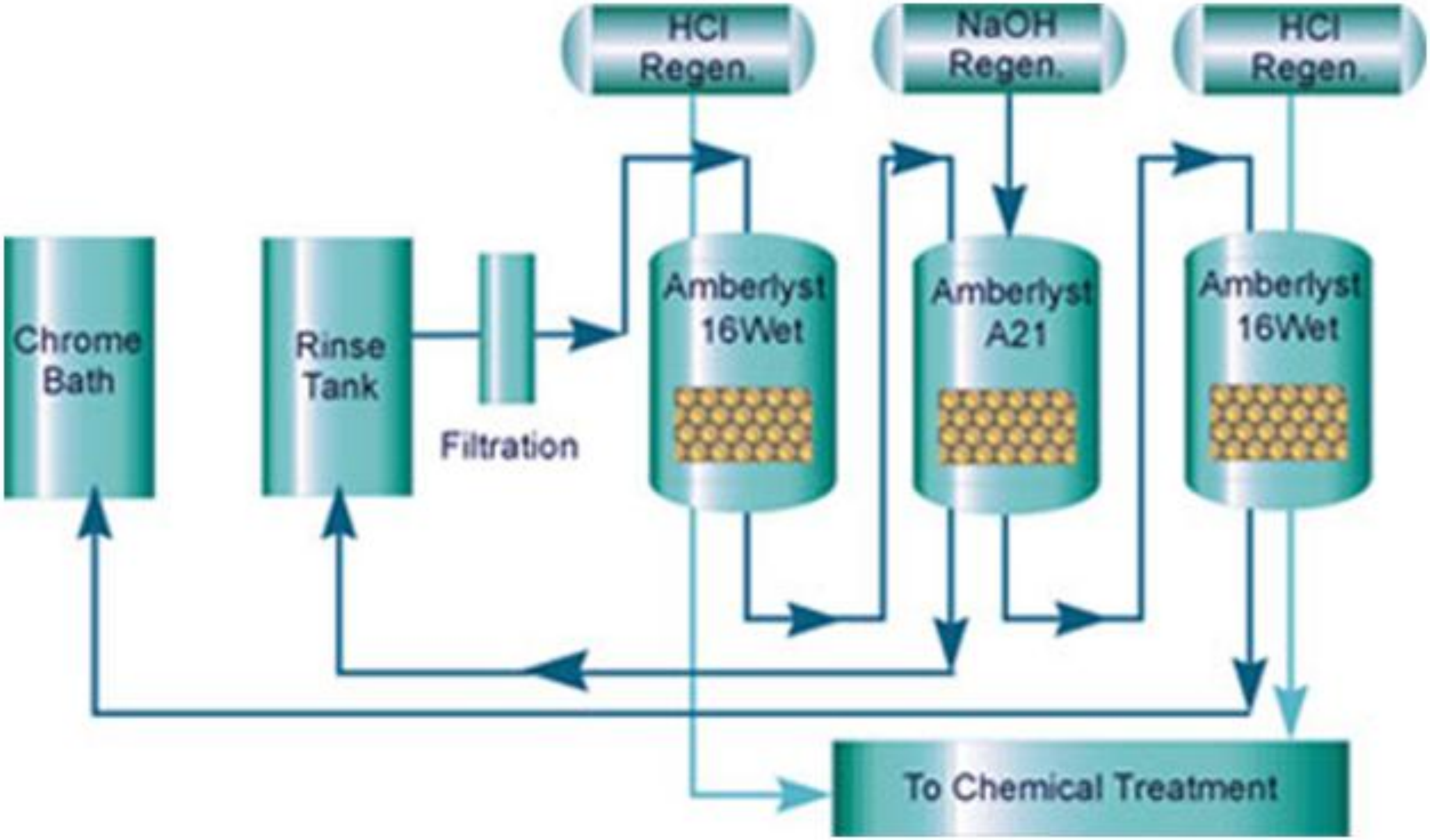
Ion beds must be regenerated periodically. The regenerating solution containing the concentrated metal salts may require further treatment prior to its reuse in plating operations

Chrome, nickel, and copper acid-type plating solutions may be reclaimed from the rinse tank by evaporation, the concentrated solution is then returned to the plating systems

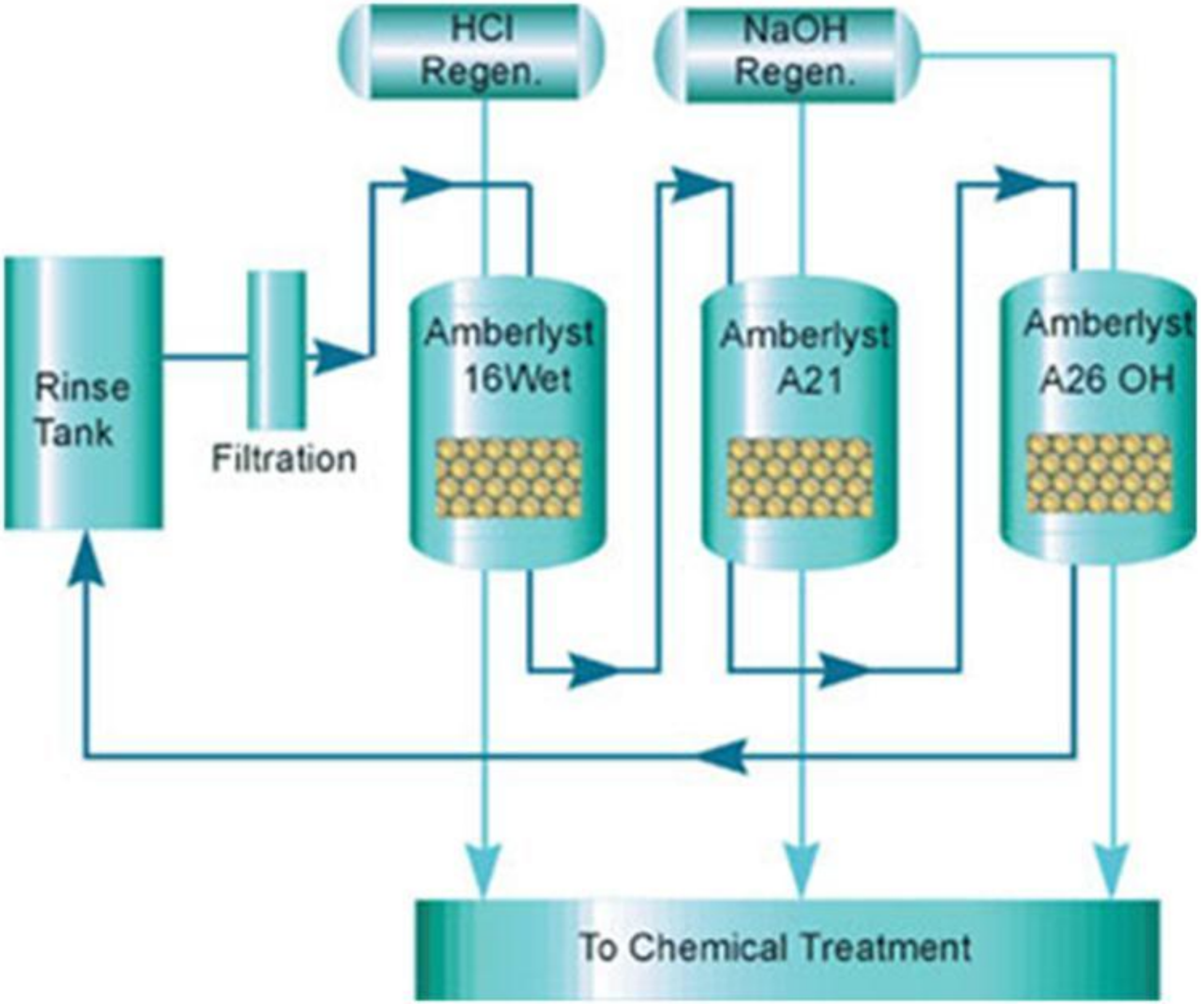


Chrome purifier and recovery system

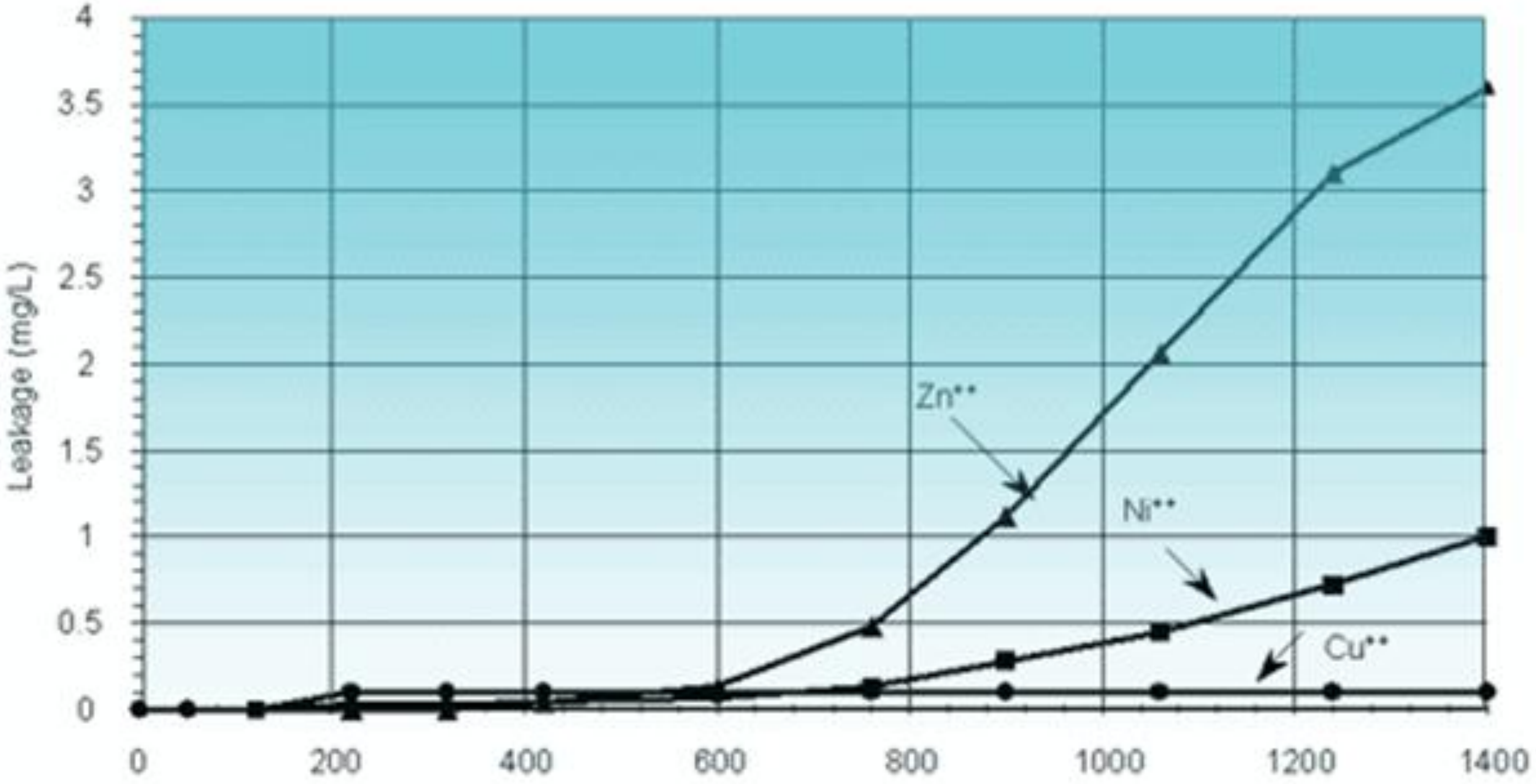
Overall Process of a Metal Finishing Plant



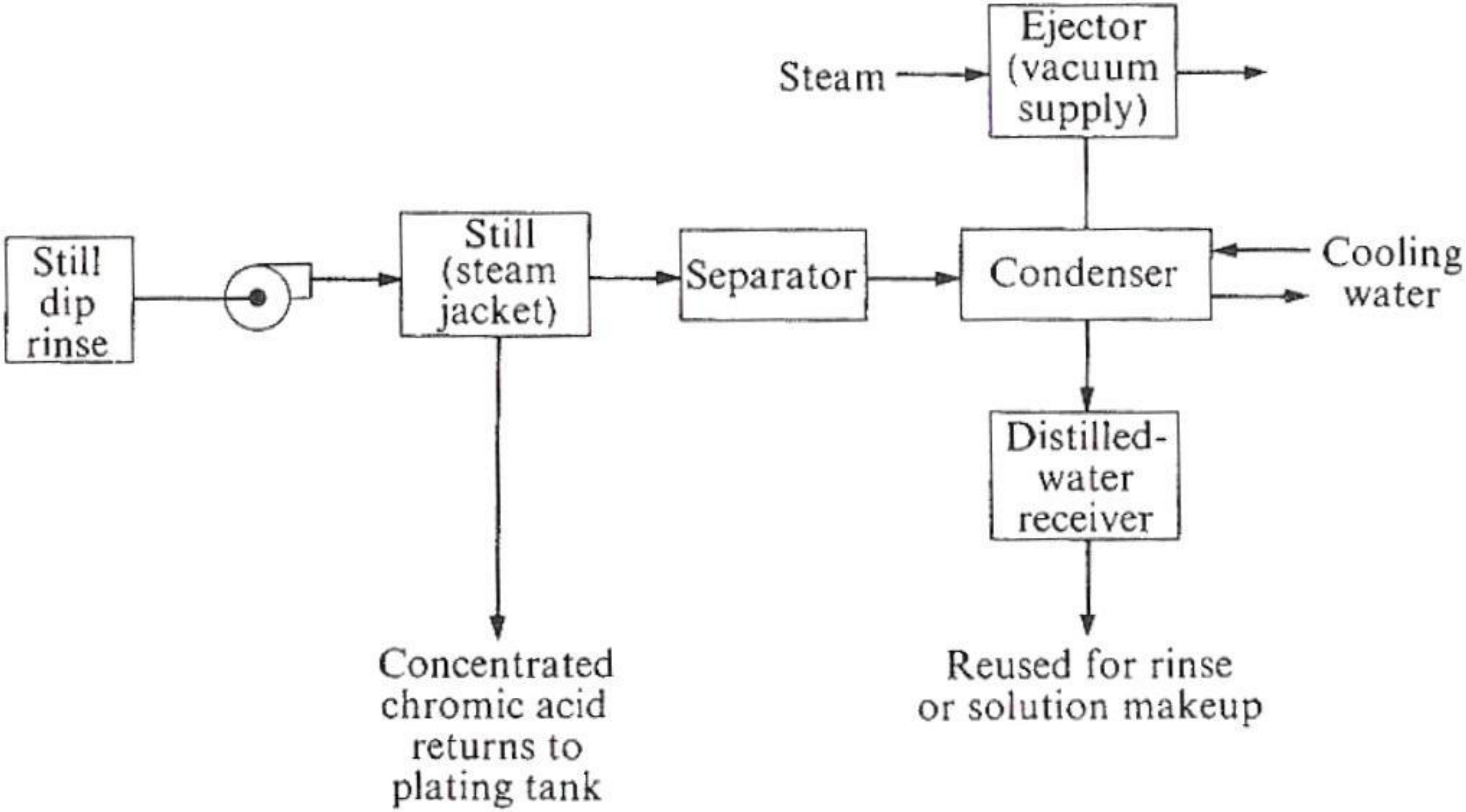
Rinse Water Recycling



1 g/L Ca^{2+}, 1 g/L Na^{+}, 5 ppm Zn^{2+}, 5 ppm Ni^{2+}, 2 ppm Cu^{2+}, pH: 7, 20 BV



Chromic acid recovery by vacuum evaporation



114 m^3/d of a waste containing 49 mg/L Cr^{6+}, 11 mg/L Cu, and 12 mg/L Zn is to be treated daily by using SO_2.

Compute the chemical requirements and the daily sludge production

(assume the waste contains 5 mg/L O_2)

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EXAMPLE 4.2. 30,000 gal/d (114 m^3/d) of a waste containing 49 mg/l Cr^{6+}, 11 mg/l Cu, and 12 mg/l Zn is to be treated daily by using SO_2. Compute the chemical requirements and the daily sludge production. (Assume the waste contains 5 mg/l O_2.)

Solution.

(*a*) SO_2 requirements are as follows. For Cr^{6+}

$$1.85\left(\frac{\text{mg } SO_2}{\text{mg } Cr^{6+}}\right) \times 49(\text{mg } Cr^{6+}/1) \times 8.34\left(\frac{\text{lb/million gal}}{\text{mg/1}}\right)$$

$$\times\ 0.03 \text{ million gal/d} = 22.7 \text{ lb/d} \qquad (10.3 \text{ kg/d})$$

and for O_2, where 1 part of O_2 requires 4 parts of SO_2:

$$4\left(\frac{\text{mg } SO_2}{\text{mg } O_2}\right) \times 5(\text{mg } O_2/1) \times 8.34 \times 0.03 = 5.0 \text{ lb/d} \qquad (2.3 \text{ kg/d})$$

$$\text{Total} = 27.7 \text{ lb/d} \qquad (12.6 \text{ kg/d})$$

(*b*) Lime requirements are as follows. For Cr^{3+}:

$$2.38\left(\frac{\text{mg lime}}{\text{mg } Cr^{3+}}\right) \times 49 \times 8.34 \times 0.03 = 29.2 \text{ lb/d} \qquad (13.3 \text{ kg/d})$$

and for Cu and Zn (each part of Cu and Zn requiring 1.3 parts of 90 percent lime for precipitation):

$$1.3\left(\frac{\text{mg lime}}{\text{mg Cu or Zn}}\right) \times 23(\text{mg Cu and Zn/1}) \times 8.34 \times 0.03 = 7.5 \text{ lb/d} \qquad (3.4 \text{ kg/d})$$

$$\text{Total} = 36.7 \text{ lb/d} \qquad (16.7 \text{ kg/d})$$

(*c*) Sludge production is:

$$1.98\left(\frac{\text{mg Cr(OH)}_3}{\text{mg Cr}^{6+}}\right) \times 49 \times 8.34 \times 0.03 = 24.3 \text{ lb/d Cr(OH)}_3 \qquad (11 \text{ kg/d})$$

$$1.53\left(\frac{\text{mg sludge}}{\text{mg Cu or Zn}}\right) \times 23 \times 8.34 \times 0.03$$

$$= 8.8 \text{ lb/d Cu(OH}_2\text{) and Zn(OH}_2\text{)} \qquad (4 \text{ kg/d})$$

$$\text{Total} = 33.1 \text{ lb/d} \qquad (15 \text{ kg/d})$$

If the sludge concentrates to 1.5 percent by weight, the volume that will require disposal each day can be calculated as follows:

$$\frac{33.1 \text{ lb/d}}{0.015 \text{ lb solids/lb sludge} \times 8.34 \text{ lb/gal}} = 265 \text{ gal/d} \qquad (1.0 \text{ m}^3\text{/d})$$

It should be noted that some of the copper and zinc will be soluble unless the final pH after lime addition exceeds pH 9.0.

A general plating plant operates 16 h/d, 5 d/week. The total discharge of rinsewaters has the following characteristics:

Copper	22 mg/L as Cu
Zinc	10 mg/L as Zn
Nickel	15 mg/L as Ni
Chromium	130 mg/L as CrO_3

Rate of flow is 0.19 m^3/min, and in-plant separation is not feasible. Design an exchanger system to include water and chromium recovery.

Operating characteristics of the ion exchanger:

	Exchanger	
	Cation	Anion
Regenerant	H_2SO_4	NaOH
Dosage, kg/m^3	192	76.8
Concentration, %	5	10
Flow rate, m^3/min.m^3	0.067	
Operating capacity	1.5 eg/L	60.8 kg CrO_3/m^3

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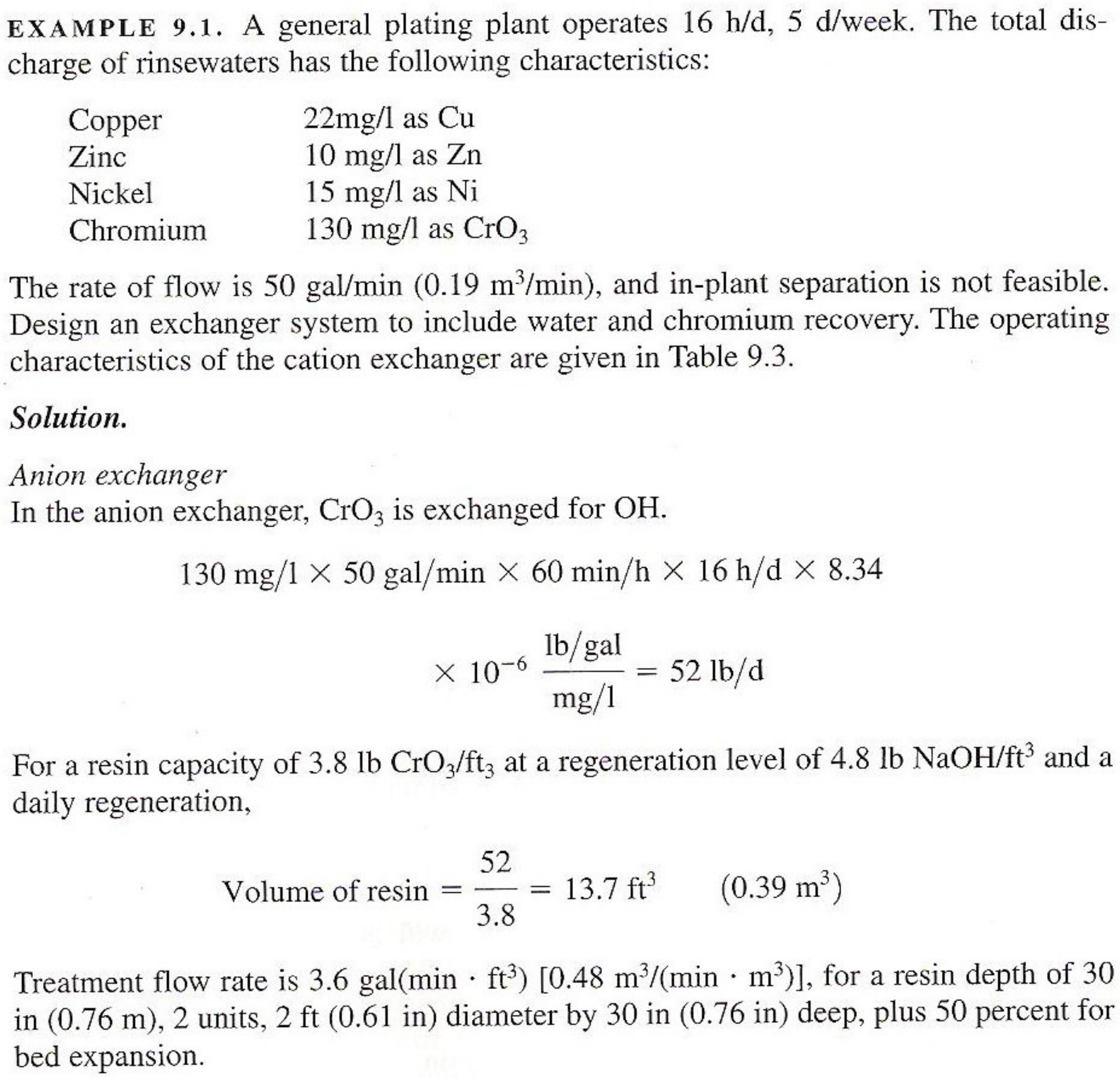

EXAMPLE 9.1. A general plating plant operates 16 h/d, 5 d/week. The total discharge of rinsewaters has the following characteristics:

Copper	22mg/l as Cu
Zinc	10 mg/l as Zn
Nickel	15 mg/l as Ni
Chromium	130 mg/l as CrO_3

The rate of flow is 50 gal/min (0.19 m^3/min), and in-plant separation is not feasible. Design an exchanger system to include water and chromium recovery. The operating characteristics of the cation exchanger are given in Table 9.3.

Solution.

Anion exchanger
In the anion exchanger, CrO_3 is exchanged for OH.

$$130 \text{ mg/l} \times 50 \text{ gal/min} \times 60 \text{ min/h} \times 16 \text{ h/d} \times 8.34$$

$$\times 10^{-6} \frac{\text{lb/gal}}{\text{mg/l}} = 52 \text{ lb/d}$$

For a resin capacity of 3.8 lb CrO_3/ft_3 at a regeneration level of 4.8 lb NaOH/ft^3 and a daily regeneration,

$$\text{Volume of resin} = \frac{52}{3.8} = 13.7 \text{ ft}^3 \qquad (0.39 \text{ m}^3)$$

Treatment flow rate is 3.6 gal(min · ft^3) [0.48 m^3/(min · m^3)], for a resin depth of 30 in (0.76 m), 2 units, 2 ft (0.61 in) diameter by 30 in (0.76 in) deep, plus 50 percent for bed expansion.

Regeneration

$$\text{NaOH required} = 4.8 \times 13.7 = 66 \text{ lb/reg} \qquad (30 \text{ kg/reg})$$

TABLE 9.3

	Exchanger	
	Cation	**Anion**
Regenerant	H_2SO_4	NaOH
Dosage, lb/ft^3	12	4.8
Concentration, %	5	10
Flow rate	0.5 gal/(min · ft^3)	
Operating capacity	1.5 equiv wt/l	3.8 lb CrO_3/ft^3

Note:
lb/ft^3 = 16.0 kg/m^3
gal/(min · ft^3) = 0.134 m^3/(min · m^3)

$$\text{Regenerant tank volume} = 66\ \text{lb NaOH} \times \frac{1}{0.10} \times \frac{1}{9.6} \qquad \text{lb reg/gal}$$

$$= 68\ \text{gal} \qquad (0.26\ \text{m}^3)$$

$$\text{Rinse requirement at } 100\ \text{gal/ft}^3 = 1370\ \text{gal} \qquad (5.2\ \text{m}^3)$$

Cation exchanger

The cations to be removed are:

$$\text{Zn} \quad \frac{10\ \text{mg/l}}{32.7\ \text{mg/meq}} = 0.306\ \text{meq/l}$$

$$\text{Cu} \quad \frac{22\ \text{mg/l}}{31.8\ \text{mg/meq}} = 0.693\ \text{meq/l}$$

$$\text{Ni} \quad \frac{15\ \text{mg/l}}{29.4\ \text{mg/meq}} = 0.511\ \text{meq/l}$$

In the cation unit, Cu, Zn, and Ni are exchanged for H^+.

The total daily equivalents are

$$(0.306 + 0.693 + 0.511) \times 10^{-3} \times 50 \times 60 \times 16 \times 3.78 \text{ l/gal} = 273 \text{ equiv wt/d}$$

For an operating capacity of 1.5 equiv wt/l at a regeneration level of 12 lb H_2SO_4/ft^3 (5 percent), the resin required for a 2-d regeneration is

$$\frac{273 \times 2}{1.5 \times 28.3 \text{ l/ft}^3} = 13.0 \text{ ft}^3 \text{ resin} \qquad (0.36 \text{ m}^3)$$

The treatment flow rate is 3.8 gal/(min · ft^3) [0.51 m^3/(min · m^3)]. Use 2 units, 2 ft (0.61 m) diameter by 30 in (0.76 m) deep plus 50 percent for bed expansion.

Regeneration

Using 5 percent H_2SO_4 at 12 lb/ft^3, H_2SO_4 required is

$$12 \times 13 = 156 \text{ lb} \qquad (71 \text{ kg})$$

$$\text{Regenerant tank} = 156 \times \frac{1}{0.05} \times \frac{1}{1.0383 \times 8.34 \text{ lb/gal}}$$

$$= 360 \text{ gal} \qquad (1.36 \text{ m}^3)$$

where 1.0383 is the specific gravity of 5% H_2SO_4.

$$\text{Rinse requirement} = 120\ \text{gal/ft}^3 \times 13\ \text{ft}^3 = 1560\ \text{gal} \quad (5.9\ \text{m}^3)$$

Anion regenerant capacity for chromium recovery:

$$\text{Sodium} = \frac{66\ \text{lb NaOH} \times 453\ \text{g/lb}}{40\ \text{g/equiv wt}} = 750\ \text{equiv wt}$$

If it is assumed that 70 percent of anion exchanger regenerant will pass through the cation unit, 525 equiv wt must be exchanged, which is compatible with the capacity of the cation units.

A wastewater has a flow of 10 000 L/d containing 130 mg/L CN^-

Compute the Cl_2 requirement for the alkaline chlorination of this wastewater for CN^- removal

(a) Consider oxidation to CNO^-
(b) Consider complete oxidation to HCO_3^- and N_2

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EXAMPLE 10.2. How much Cl_2 must be supplied to oxidize 130 mg/l cyanide (as CN) given a flow of 10,000 l/d?

(*a*) Consider oxidation to CNO^-.
(*b*) Consider complete oxidation to HCO_3^- and N_2.

First, consider that Cl_2 reacts with water to produce HOCl and HCl:

$$Cl_2 + H_2O \longleftrightarrow HOCl + HCl$$

Therefore, only half of our chlorine is effective. Next, all calculations must be done on a molar basis, or molecular weight of CN = 12 + 14 = 26 g/mole. Then

$$\frac{130 \text{ mg/l cyanide}}{(26 \text{ g/mole})(1000 \text{ mg/g})} = 5.0 \times 10^{-3} \text{ M}$$

Solution.

(*a*) Combine Reactions 1 and 2 [Eqs. (10.10*a*) and (10.10*b*)] to give an overall reaction of CN^- to CNO^-:

$$\text{Reaction 1} + \text{Reaction 2} = CN^- + OCL^- \rightarrow CNO^- + Cl^-$$

Therefore, 1 mole of OCL^- is required for each CN^-:

$$5 \times 10^{-3} \text{ MCN}^- \left(\frac{1 \text{ mole OCl}^-}{1 \text{ mole CN}^-}\right) = 5 \times 10^{-3} \text{ M OCl}^- \text{ required}$$

$$= \frac{\text{stoichiometric dosage}}{5 \times 10^{-3} \text{ M Cl}_2 \text{ required}}$$

Finally, for a 10,000 l/d flow:

$$(5 \times 10^{-3} \text{ mole } Cl_2/1)(10{,}000 \text{ l/d}) = 50 \text{ moles } Cl_2/\text{d}$$

then $Cl_2 = 71$ g/mole, or

$$\frac{(50 \text{ moles } Cl_2/\text{d})(71 \text{ g/mole})}{1000 \text{ g/kg}} = 3.55 \text{ kg } Cl_2/\text{d}$$

and, since dosage is 1 to 2 times stoichiometric, depending on the metal complexed with CN^- (see Table 10.5), the actual required dose = 3.55 to 7.10 kg Cl_2/d.
(*b*) Consider Reaction 3 [Eq. (10.10*c*)]:

$$ZCNO^- + 3HOCl \rightarrow 2HCO_3{}^- + N_2 + 3Cl^- + H^+$$

Note that 3 moles HOCl produced per 2 moles CNO^- and 1 mole CNO^- produced per mole CN^- are initially present (100 percent conversion). Therefore,

$$5 \times 10^{-3} \text{ M}CNO^- = \left(\frac{3 \text{ moles HOCl}}{2 \text{ moles } CNO^-}\right)(10{,}000 \text{ l/d})\left(\frac{71 \text{ g/mole}}{1000 \text{ g/kg}}\right) = 5.33 \text{ kg } Cl_2/\text{d}$$

and the total requirement is step 1 + step 2, or

$$Cl_2 = (3.55 \text{ to } 7.10 \text{ kg/d}) + 5.33 \text{ kg/d} = 8.88 \text{ to } 12.43 \text{ kg } Cl_2/\text{d}$$