CHAPTER (4)

Pretreatment & Primary Treatment

- Pretreatment of Industrial Wastes
- Equalization
- Neutralization
- Phase Separation (Oil Removal / Flotation

Pretreatment of Industrial Wastes

- Industrial wastewaters (IWW) can pose serious hazards to municipal collection and treatment systems because of their different properties. They may pass through the wastewater treatment plant (WWTP) untreated or they may concentrate in the sludge, rendering it a hazardous waste.

Specific objectives of the pretreatment are:

1) To prevent the introduction of pollutants into WWTPs that will interfere with their operation or disposal or reuse of reclaimed municipal wastewater and sludge.
2) To prevent the introduction of pollutants to WWTPs that will pass through the treatment works or otherwise be incompatible with such works.
3) To improve opportunities to recycle and reclaim industrial wastewaters and sludge.
4) Regulations ban the discharge of IWW to municipal systems, except for those with similar composition and properties.

Pretreatment of Industrial Wastes: Flow

Flow Separation:

Separate incompatible wastewater streams (effluents) to save equipment and operating costs.

Separate:

1. Concentrated wastes from dilute wastes
2. Oily wastes from non-oily wastes
3. Hexavalent chromium, cyanide and common metal wastes from each other
4. Complex wastes from non-complex wastes
5. Toxic organics from biodegradable organics

Pretreatment of Industrial Wastes: Composition

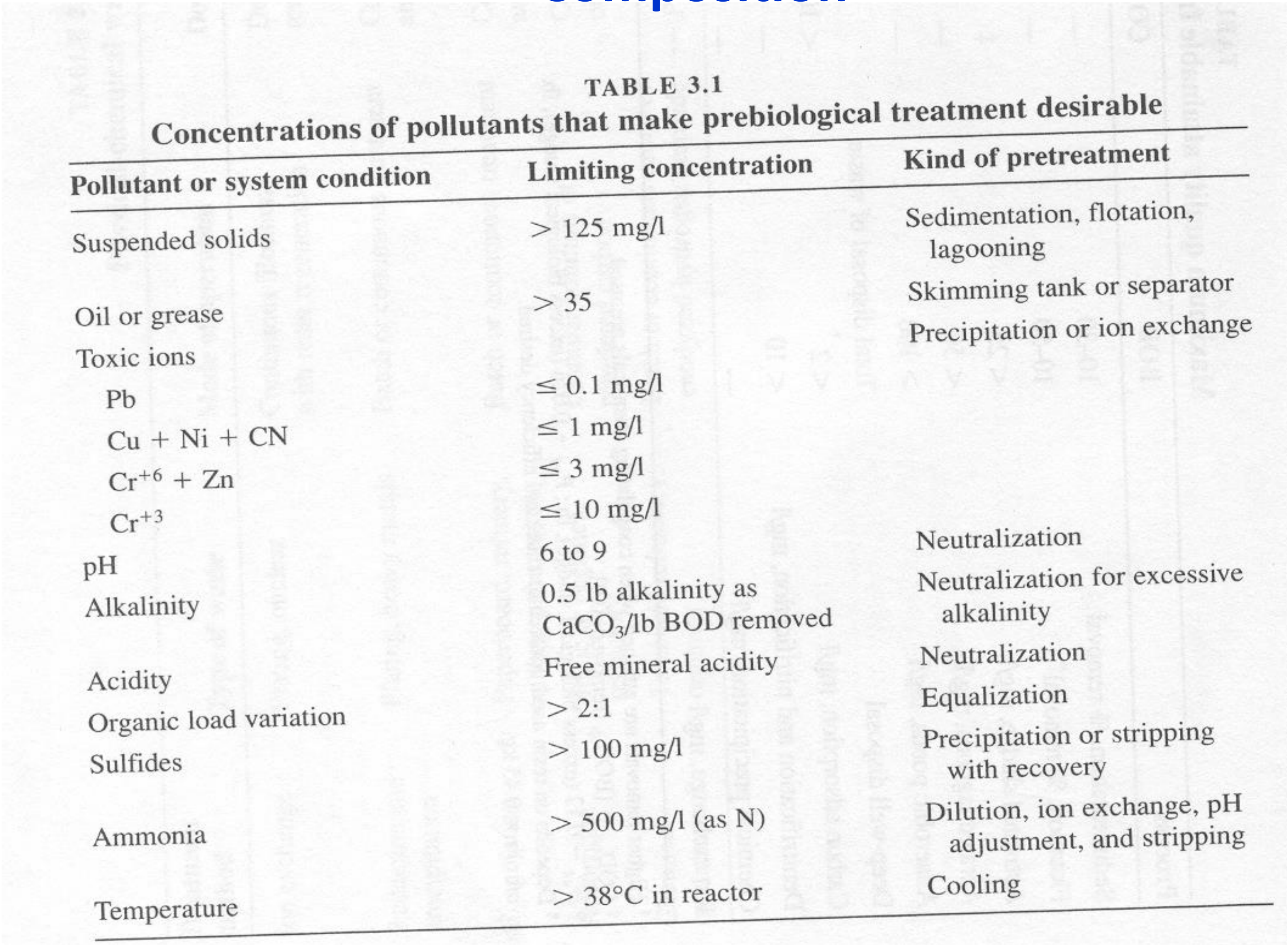


TABLE 3.1

Concentrations of pollutants that make prebiological treatment desirable

Pollutant or system condition	Limiting concentration	Kind of pretreatment
Suspended solids	> 125 mg/l	Sedimentation, flotation, lagooning
Oil or grease	> 35	Skimming tank or separator
Toxic ions		Precipitation or ion exchange
Pb	≤ 0.1 mg/l	
Cu + Ni + CN	≤ 1 mg/l	
Cr^{+6} + Zn	≤ 3 mg/l	
Cr^{+3}	≤ 10 mg/l	
pH	6 to 9	Neutralization
Alkalinity	0.5 lb alkalinity as $CaCO_3$/lb BOD removed	Neutralization for excessive alkalinity
Acidity	Free mineral acidity	Neutralization
Organic load variation	> 2:1	Equalization
Sulfides	> 100 mg/l	Precipitation or stripping with recovery
Ammonia	> 500 mg/l (as N)	Dilution, ion exchange, pH adjustment, and stripping
Temperature	> 38°C in reactor	Cooling

Equalization: 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.*

TYPES:

1. **Flow Equalization**: based on extra storage volume
2. **Composition Equalization**: based on mixing / homogenization
3. **Combined.**

- **Equalization tanks**: must be large enough to dampen out peak hydraulic flows. It should also be fully mixed.

- **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.

Equalization: Part of Pretreatment

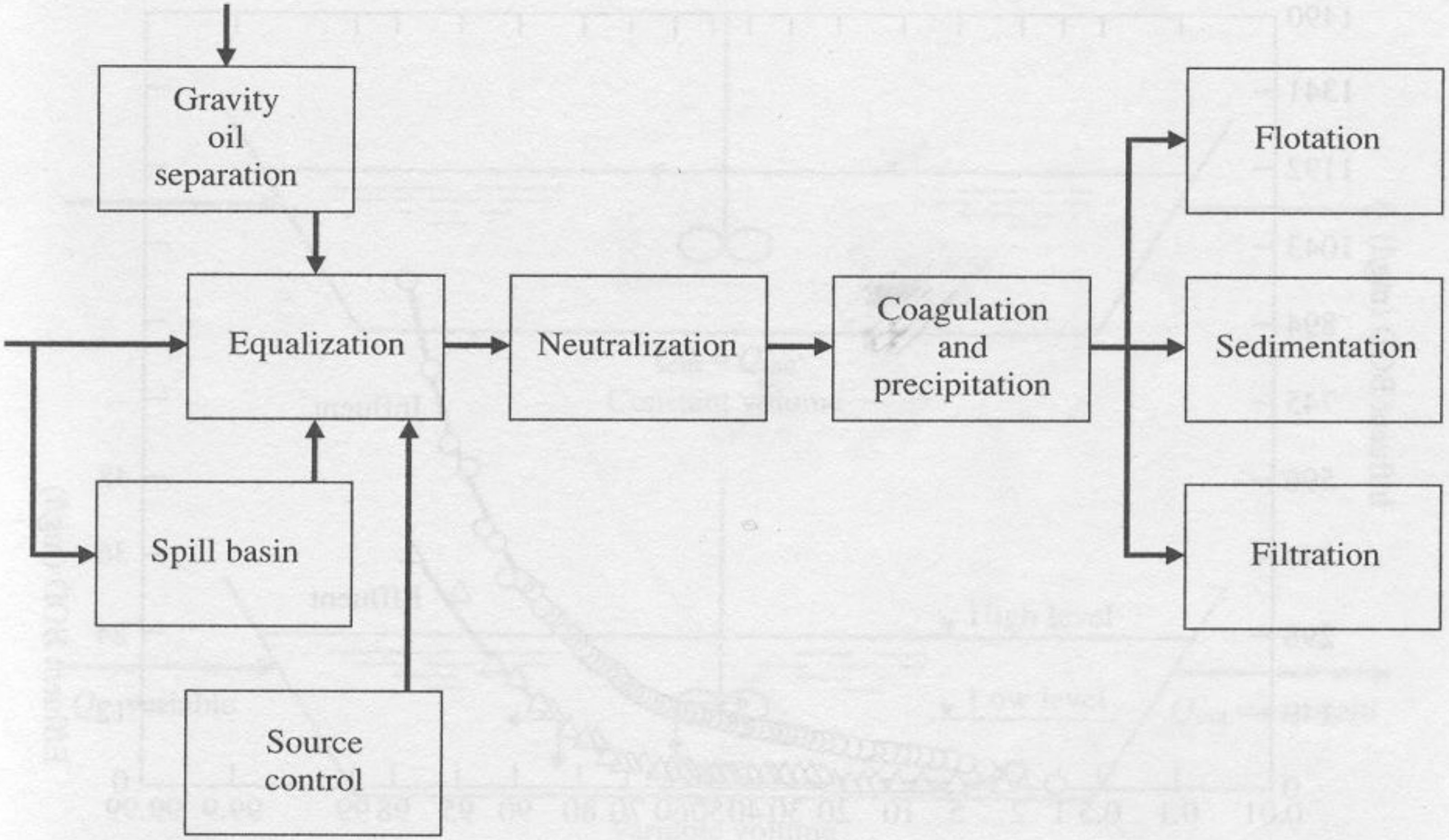
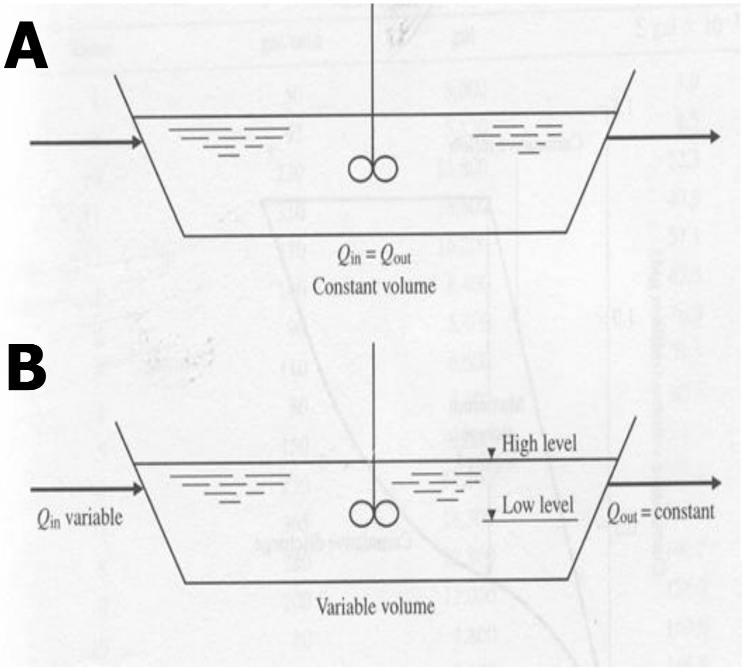
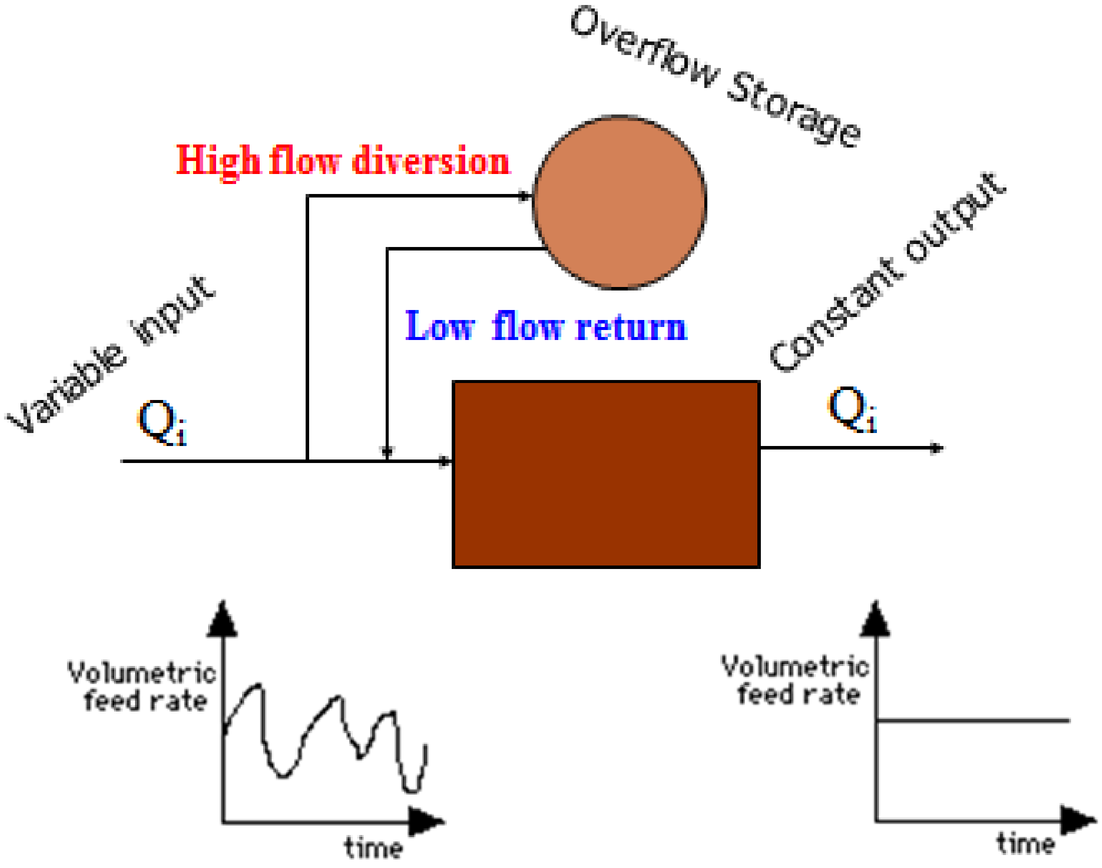


FIGURE 3.1
Pretreatment technologies.

Note that
EQ tank is after suspended solids or oil separation

Types of Equalization Tanks





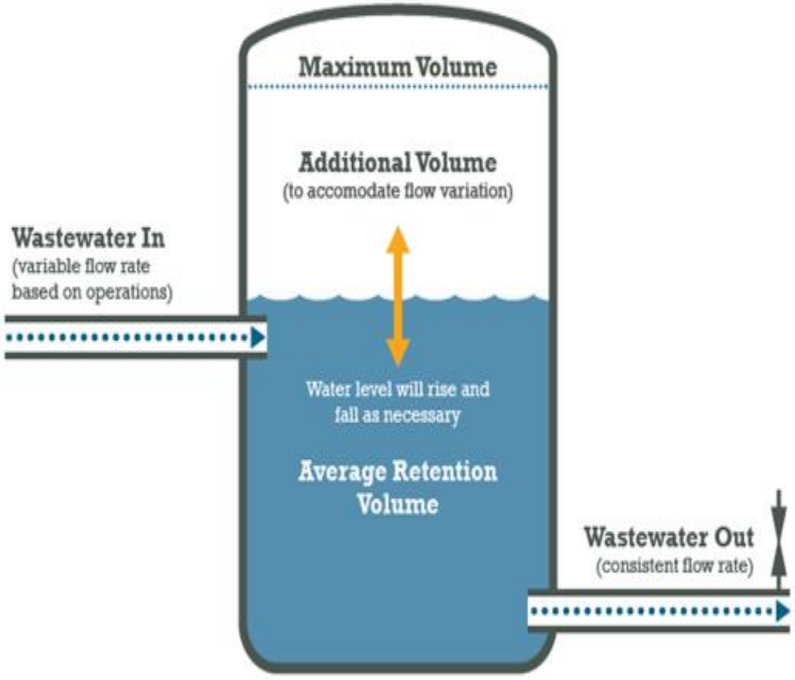
Ref. Eckenfelder's Industrial Water Pollution Control, 1999.

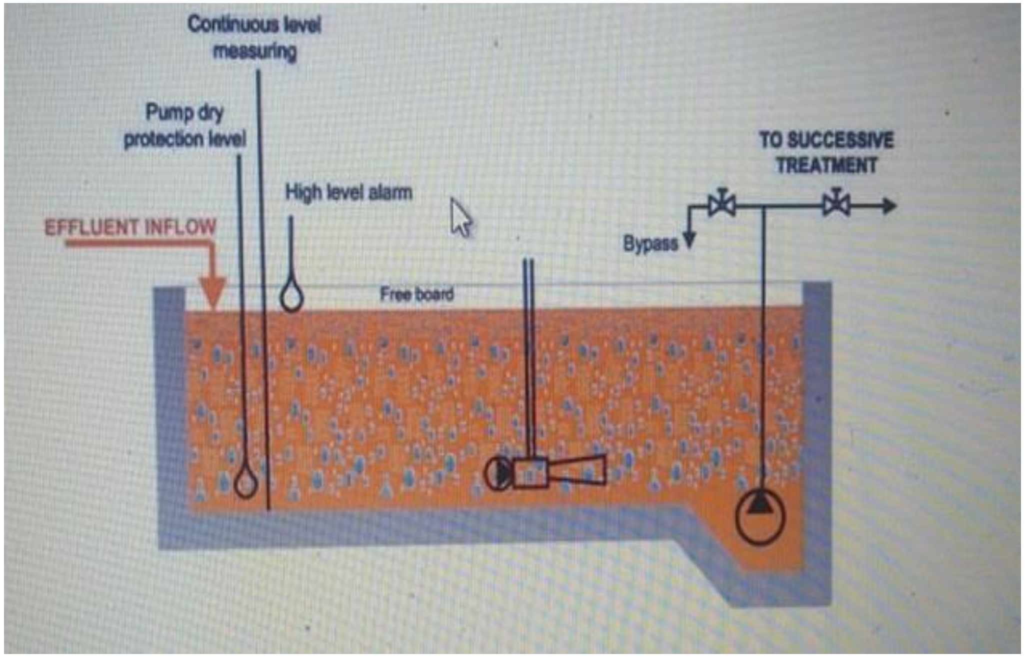
Purposes/Benefits of Equalization

1. To provide adequate dampening of organic fluctuations in order to prevent shock loading of biological systems.
2. To provide adequate pH control or to minimize the chemical requirements necessary for neutralization.
3. To minimize flow surges to physical chemical treatment systems (*e.g. coagulation, chlorination*) and permit chemical feed rates compatible with feeding equipment.
4. To provide continuous feed to biological systems over periods when the manufacture plant is not operating
5. To prevent high concentrations of toxic materials from entering the biological treatment plant.
6. Improvement of thickening performance due to consistency in solid loading.

Disadvantages of volume equalization

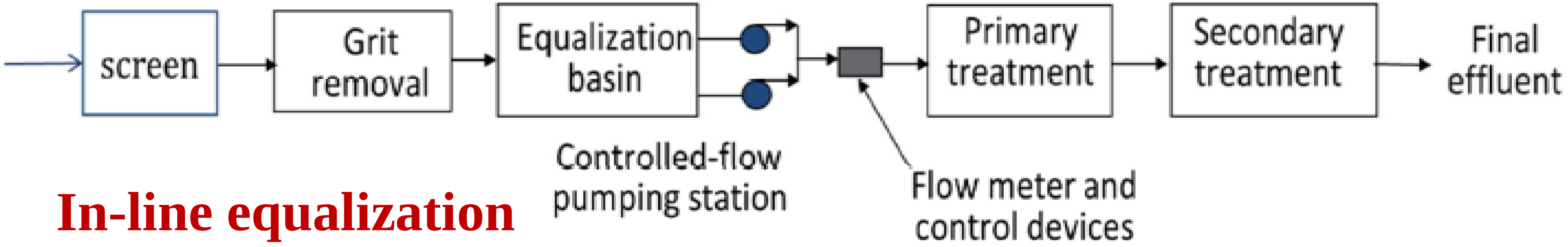
1. Relatively large land areas or sites are needed
2. Equalization facilities may have to be covered for odor control near residential areas.
3. Additional operation and maintenance is required.
4. Capital cost is increased.



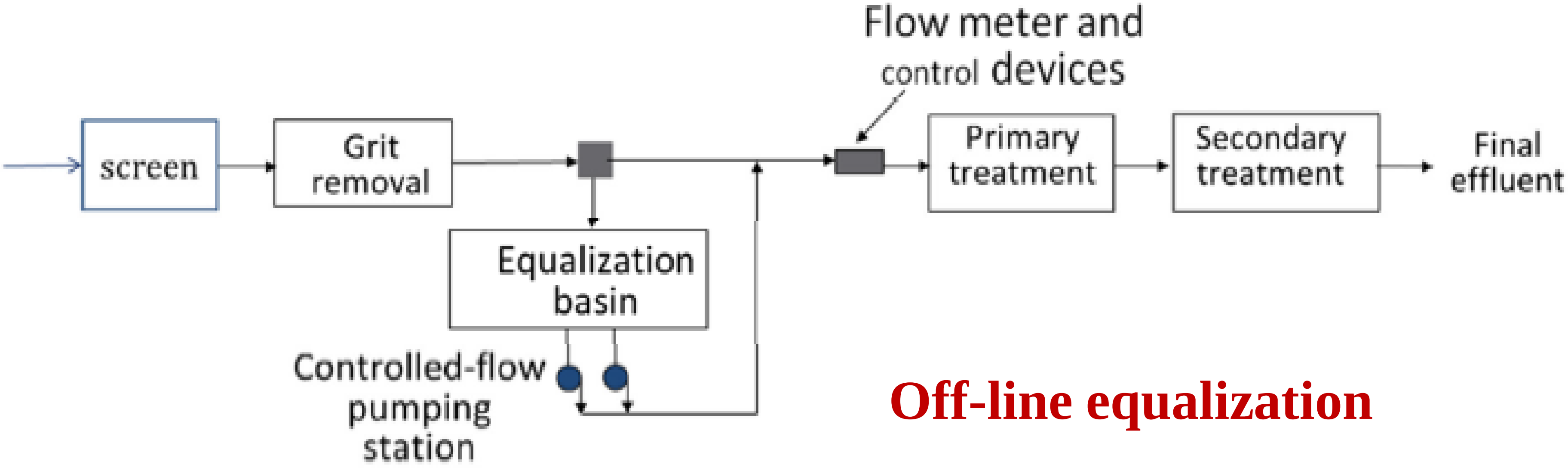


Equalization in Process Flow Sheet

- In-line equalization is more effective for leveling variations in concentration because the entire flow is blended with the entire contents of the holding tank.
  - Both in-line and off-line systems are effective ways to equalize flow volumes.
  - Off-line equalization used for high peak flow (e.g. rain) & diluting toxic components.

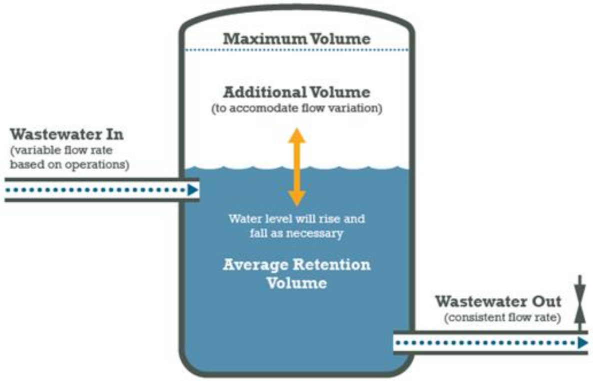


In-line equalization



Off-line equalization

Equalization Tank Design & Operation



- Needed equalization tank volume should calculated.
- Mixing requirements (power) for medium-strength municipal wastewater with suspended solids of 220 mg/L: $0.004 \sim 0.0088$ kW/m^3
- Air supply needed for the above, using mechanical aerators. $0.01 \sim 0.015$ $m^3/m^3 \cdot min$
- Pumping facilities are required.
- A flow-measuring device should be installed on the outlet.

Acid-Base Neutralization

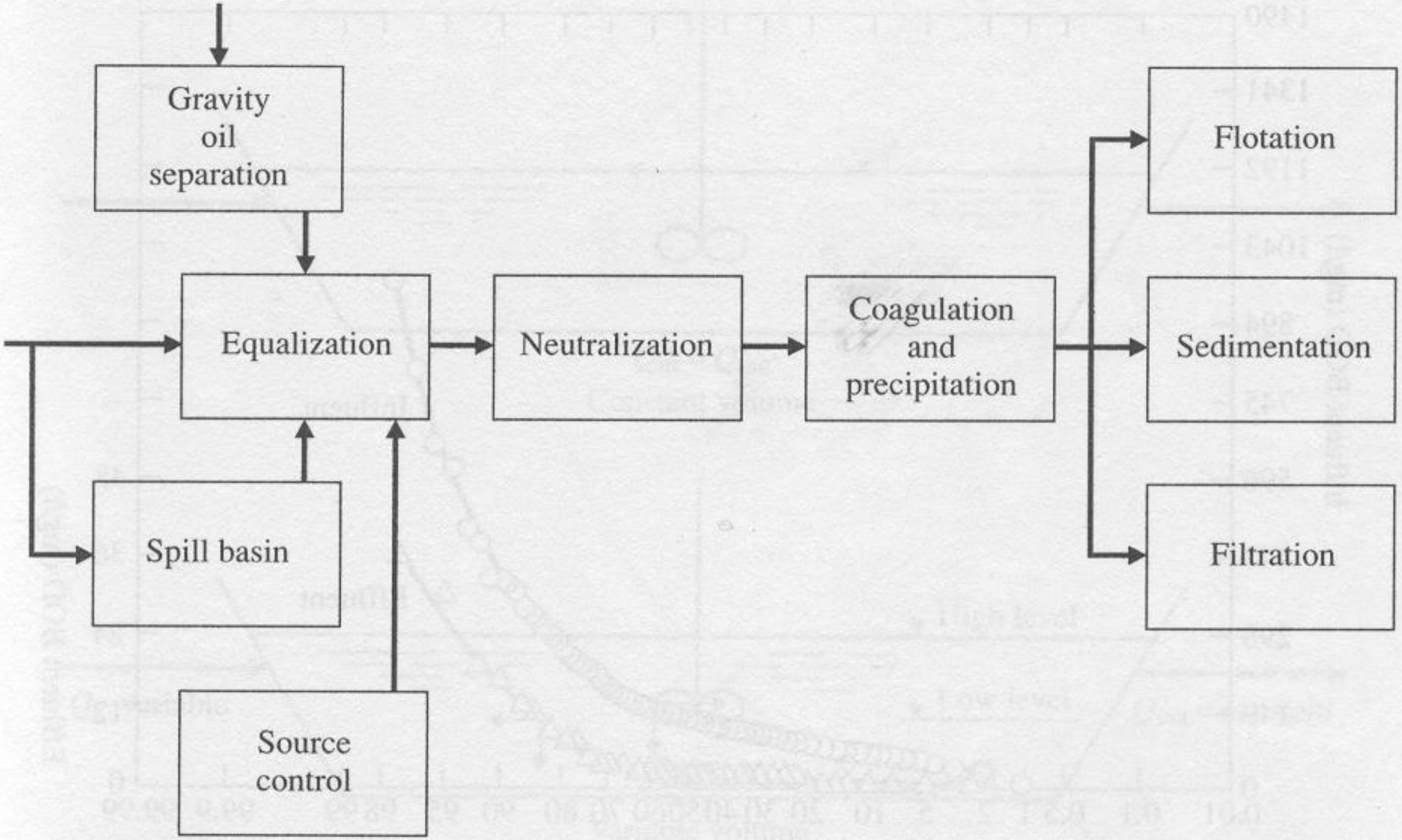
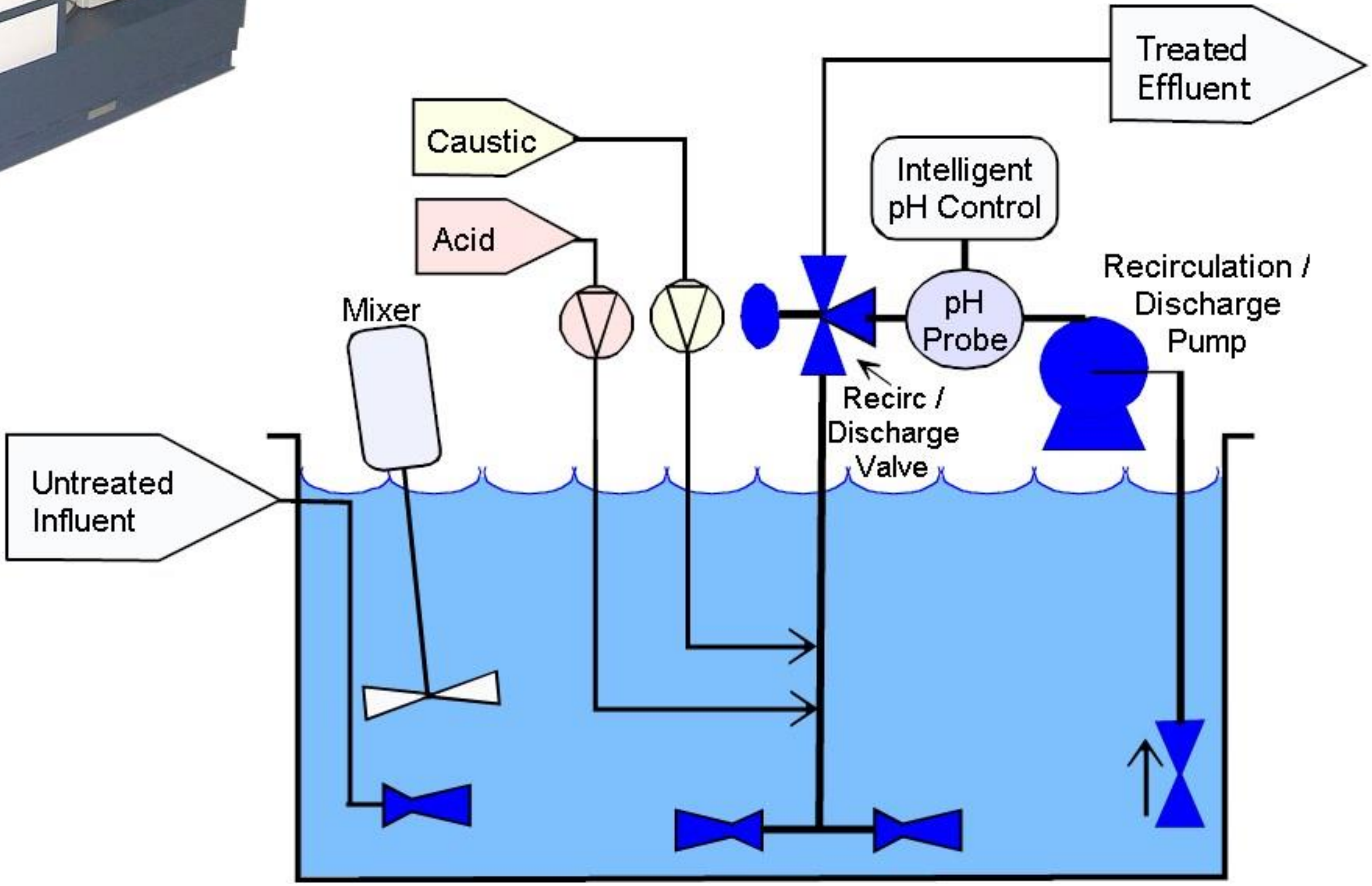


FIGURE 3.1
Pretreatment technologies.

Neutralization

- **CONTROL of pH**
  1. Most chemical treatment processes require pH control to optimize reactions.
  2. pH control requires by pH meter and reagent addition system
- **Applications**
  1. Reduction / Oxidation (RedOx)
     - *Chrome Reduction*
     - *Cyanide Oxidation*
  2. Metals Precipitation/Decreasing Solubility
  3. Chemical stabilization for corrosion control (protect equipment)
  4. Discharge limits
- **Desired pH depends upon**
  1) the subsequent treatment units (coagulation, chemical precipitation, biological)
  2) discharge receiving system (e.g. for municipal sewer, pH range is 6-9; depends on local standards.

Waste Neutralization: pH Control



Neutralization Methods

1) Mixing acid & alkaline wastes so that the net effect is a neutral pH,
2) Passing acid wastes through beds of limestone,
3) Mixing acid wastes with lime slurries,
4) Adding proper proportions of concentrated solution of caustic soda or soda ash to acid wastes,
5) Blowing waste boiler flue gas through alkaline waste,
6) Adding compressed CO_2 to alkaline wastes, and
7) Adding sulfuric acid to alkaline wastes.

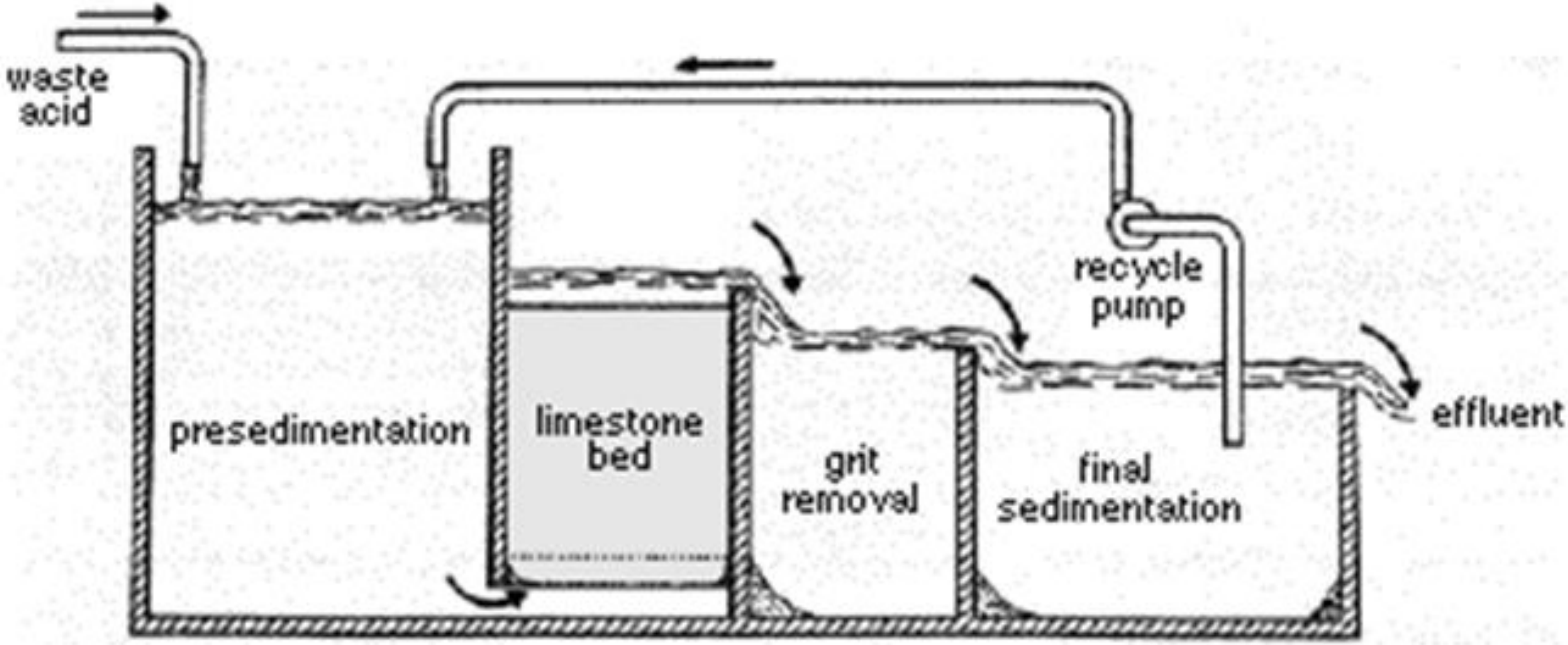
Limestone treatment for acid wastes

Passing acid wastes through beds of limestone.

$$\mathbf{CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3}$$

Operating conditions :

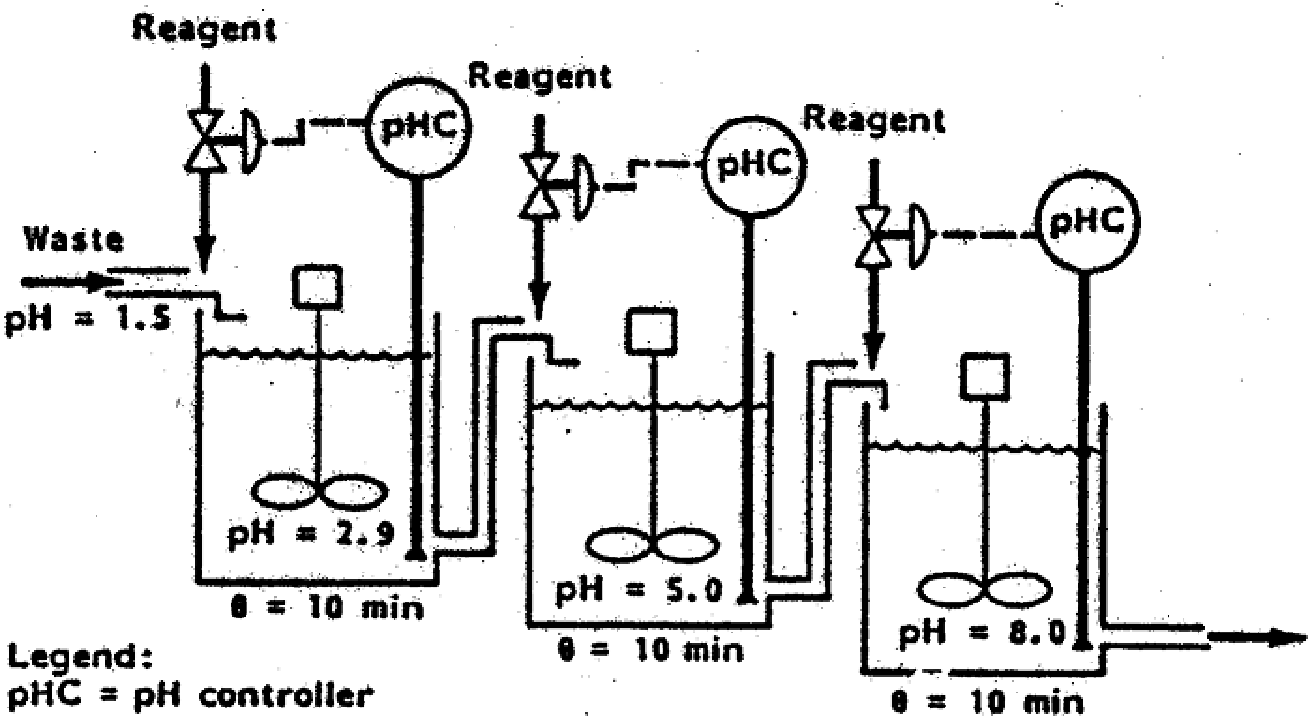
- H_2SO_4 solution should be diluted to 5% or less,
- H_2SO_4 be applied at 5 gpm/ft^2 or less to avoid fouling the bed.
- Disposing the used limestone is a serious drawback.



Lime slurry treatment for acid wastes

Mixing acid wastes with lime slurries.

- More reactive than limestone
- No fouling is expected.
- Use of hydrated lime for large scale treatment may be problematic since it possesses poor flow properties.



Caustic- Soda Treatment for acid wastes

- Using NaOH (caustic soda) and /or Na_2CO_3 (soda ash) to neutralize acid wastes.

- It has the following advantages over lime treatment:
  1) process is faster
  2) smaller volume of Na_2CO_3 is needed
  3) reaction products are soluble and do not increase water hardness.
  4) suitable for small volumes

- Disadvantage : more costly, NaOH risk of spills.

Caustic- Soda Treatment for acid wastes

- To neutralize carbonic and sulfuric wastes using caustic-soda , the following reactions take place:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3,$$

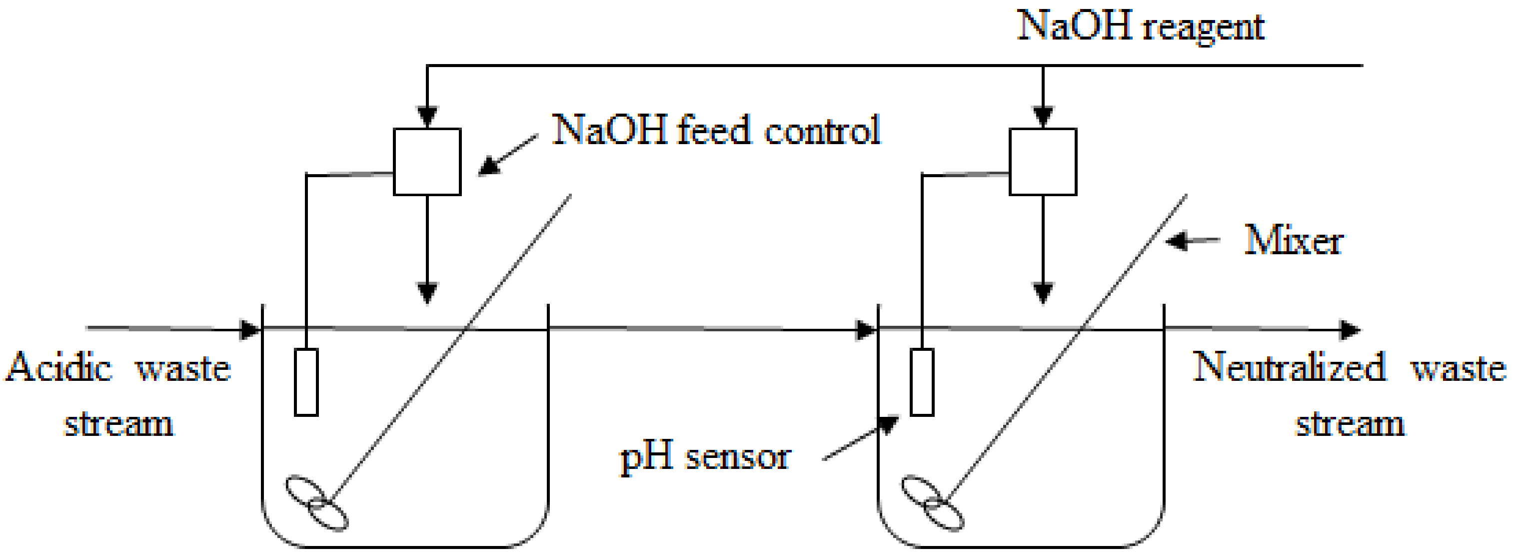
$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O,$$

$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O,$$

$$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + HOH$$

- The end products depend on the pH desired.

For instance, @pH=6 , $NaHSO_4$ is the greater part of the products.



Using waste boiler flue gas

- Well-burned stack gases contain about 14 % CO_2 which can be utilized to neutralize alkaline waste:

$$CO_2 + H_2O \rightarrow H_2CO_3,$$

$$2NaOH + H2CO_3 \rightarrow Na_2CO_3 + 2H_2O,$$

$$Na_2CO_3 + H_2CO_3 \rightarrow NaHCO_3 + HOH,$$

Relative Cost of Alkalinity Chemicals

Chemical	Equiv. weight	1995 Cost ($/tonne)	kg alkalinity/ kg chemical	1995 Cost/tonne alkalinity
CaO	28	$120	1.8	$68
NaOH	40	$800	1.25	$640
Na_2CO_3	53	$400	1.9	$210
$NaHCO_3$	84	$400	0.6	$670
NH_4OH	14	$800	3.6	$220
MgO	20	$360	2.5	$140

PHASE SEPARATIONS

- The process by which chemicals of low solubility or insoluble materials are removed from water.

- **SETTLING** *(see other courses)*

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

PHASE SEPARATIONS

FLOTATION

- ❑ Flotation is the process by which pollutants *lighter* than water are removed from water.
- ❑ The pollutants may be
  1. naturally lighter than water such as oil and grease, or
  2. they may be made lighter than water by attaching micro-bubbles to them such as dissolved air flotation (DAF).

AIR STRIPPING *(see tertiary / advanced treatment)*

- ❑ 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
  1. sparging air through the wastewater, or
  2. by pumping the wastewater over a media tower.

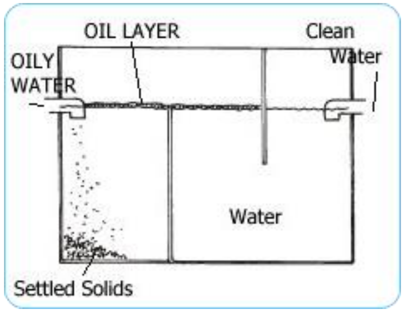
Oil/Water Separators

1. The basic principle of difference in gravity between the phases (L/L or S/L) is employed in separation of the two phases.
2. Therefore, phase with high density will settle and with lower density float to the surface of fluid.
3. The **effectiveness of this technique** is influenced by difference in density, viscosity, the medium, temperature, turbulence, nature of impurity, etc.
4. According to Stoke's Law,
    - ☐ a 100-micron diameter oil droplet will rise approximately 6 inches in water every ten minutes.
    - ☐ a 20-micron diameter oil droplet will take over two hours to rise the same distance.
5. Because an oil droplet must rise approximately 48 inches to reach the water surface in a typical gravity- type oil/water separator, smaller droplets may pass through uncollected.

Oil / Water Separators

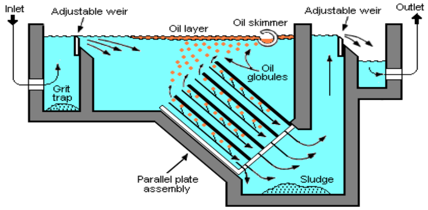
SEPARATORS

- Gravity oil/water separators (API):
  1. Free oil is floated to the surface of a tank and then skimmed.
  2. Removal of oil particles > 0.015 cm
  3. Not effective with emulsified oils.
  4. Effluent oil concentration 50 mg/L

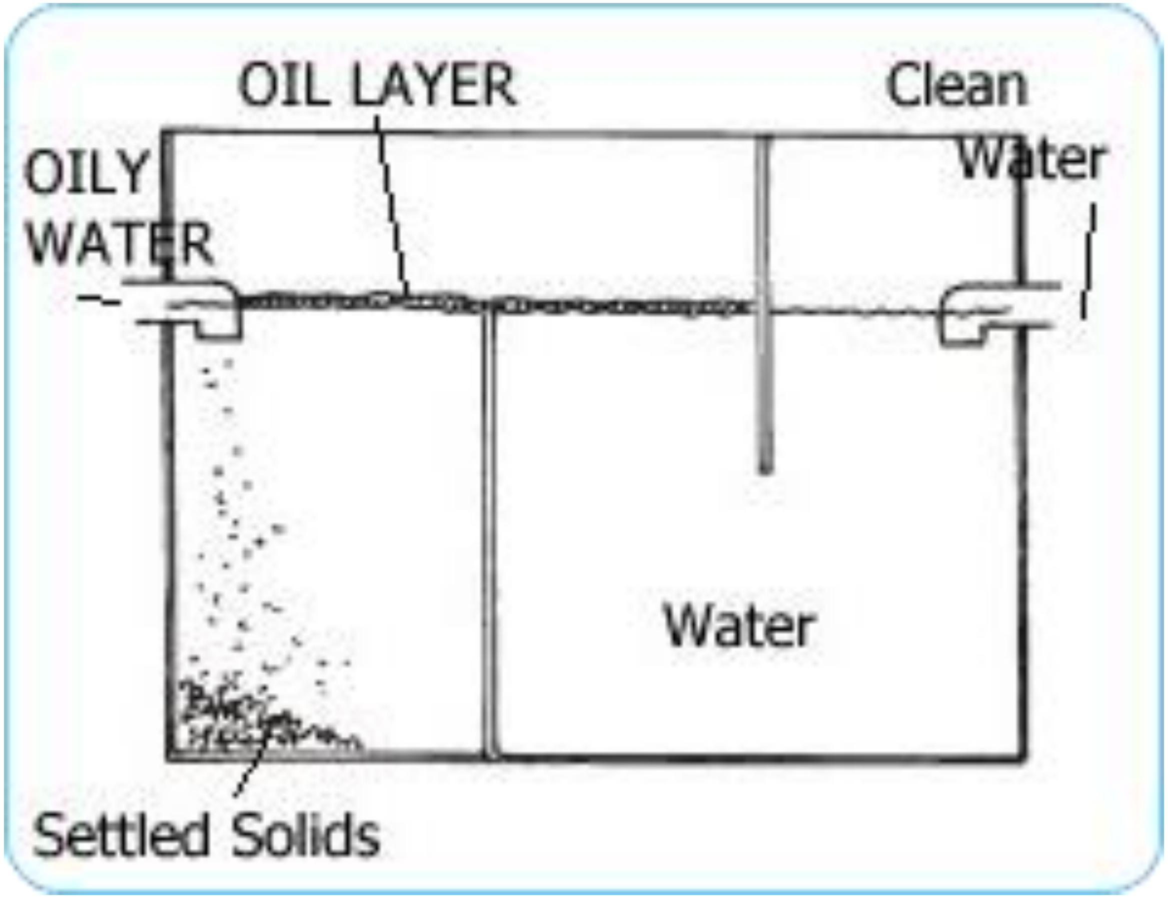


- Coalescing oil/water separators (Corrugated parallel plate):
  1. Oil particles form beads and float to surface.
  2. Plastic or other oil-attracting media used
  3. Separate oil droplets > 0.006 cm
  4. More efficient that gravity separation

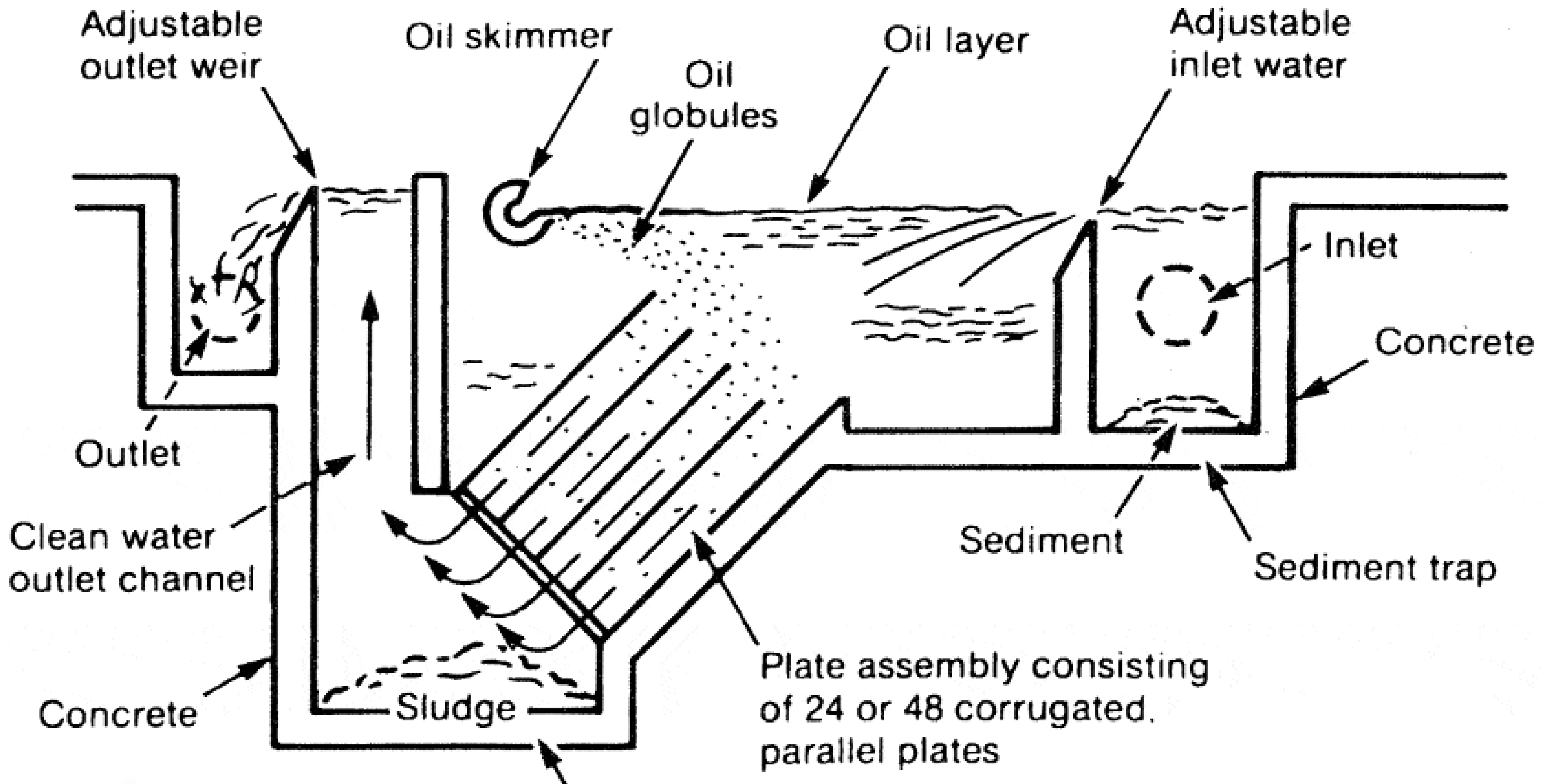
     (effluent conc. < 50 mg/L)



Simple Gravity oil/water separators
(natural flotation)



Parallel Corrugated Plate O/W Interceptor



See animation @
http://www.plateseparator.com/

Other Oil/Water Separators

- **Ultrafiltration units**

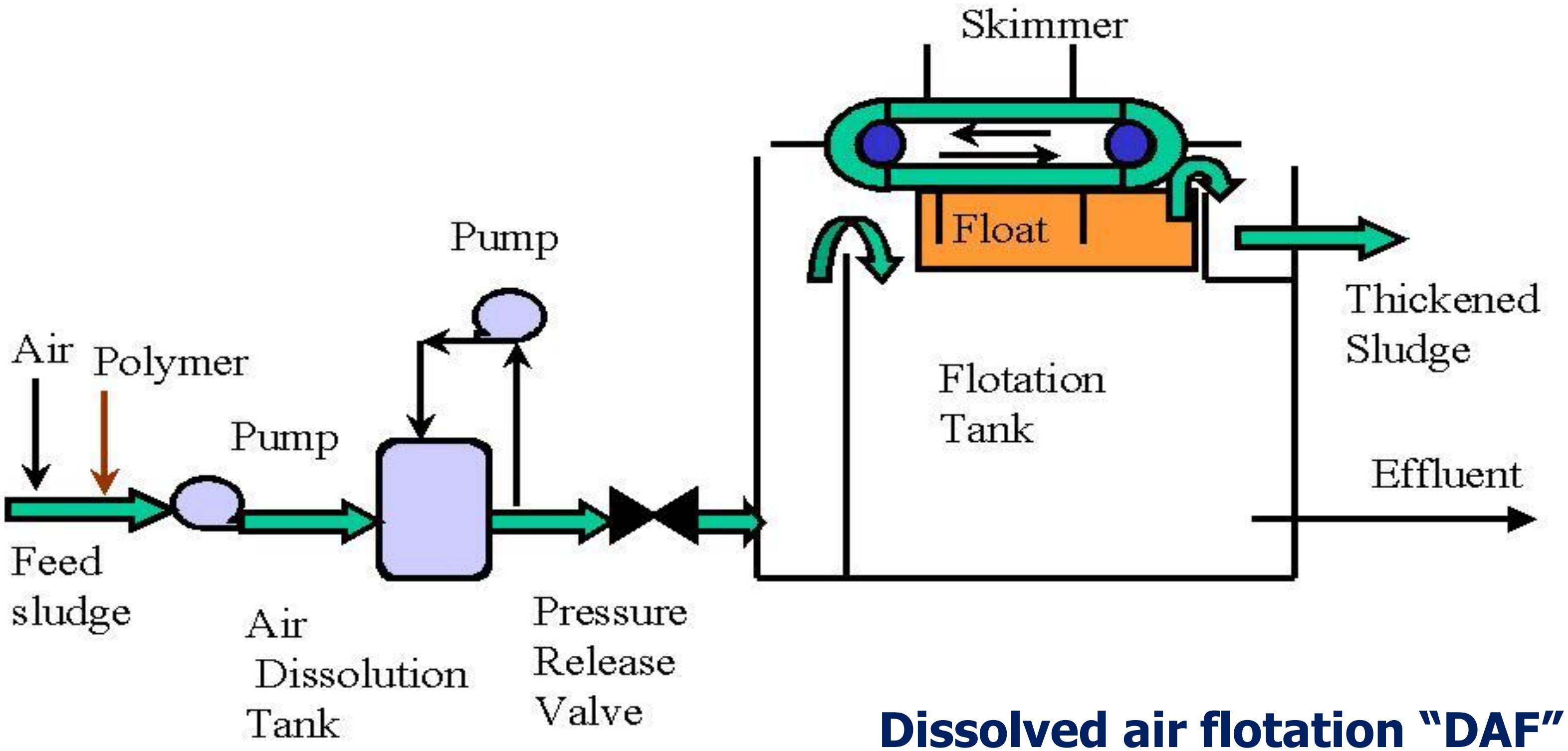
(See Membrane Separation)

1. Filters allow water to pass but *not oils*
2. Remove a greater amount of *oil and grease*
3. Require more maintenance.
4. High cost.

- **Dissolved air flotation (DAF)**
- DAF involves separation of oil and grease or solid particles from the water phase by attaching the solids to fine air bubbles to decrease the density of the particles so that they float instead of sinking.

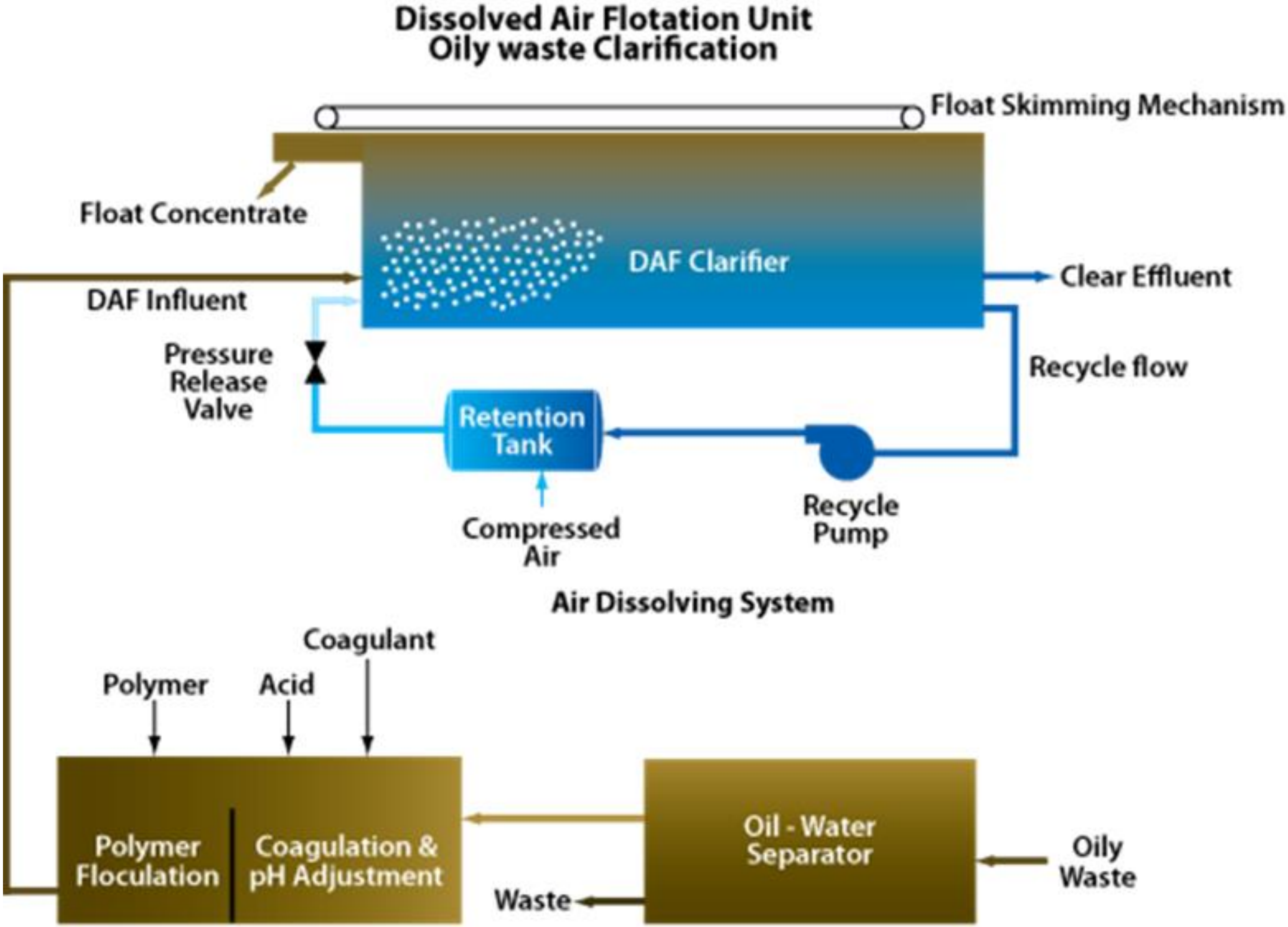
FLOTATION

- Flotation is a process for removing suspended particles or oil from water by bringing particles to the surface of the liquid.
- **Flotation Types used in WWT**
  1. Simple (gravity) flotation: Opposite to settling
  2. Dissolved air flotation "DAF" , with or without Coagulation.
  3. Electroflotation.



Dissolved air flotation "DAF"

Dissolved Air Flotation DAF with Coagulation



Mechanism of DAF

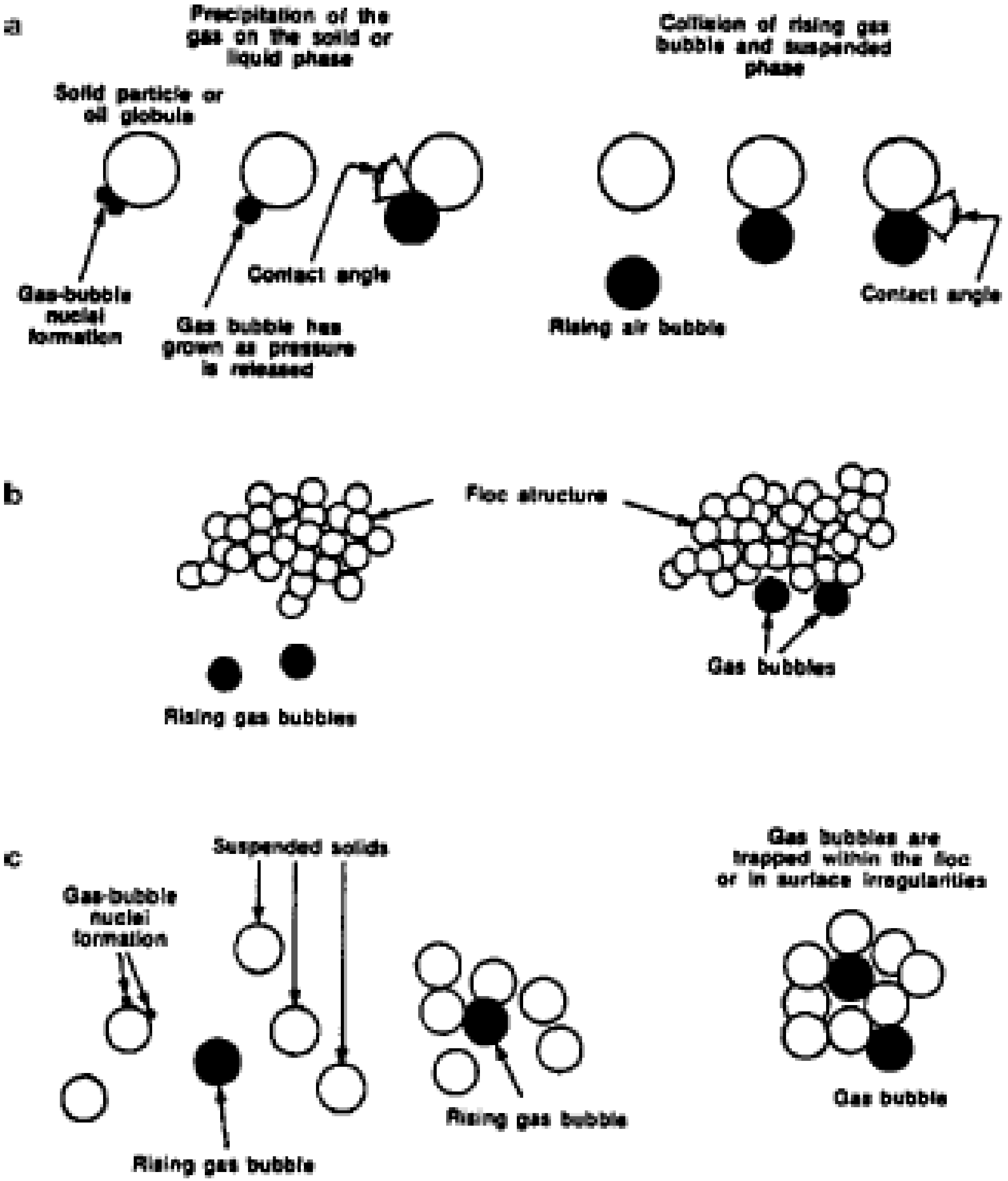


Fig. 1.1. Mechanisms of bubble/droplet formation and adhesion in dissolved air flotation.

Ref. Handbook of Environ Eng, Vol. 12
Flotation Technology

Dissolved Air Flotation DAF

- Principal components of DAF system
  1) Pressurized pump → elevated pressure to increase solubility (3-5 atm will reach saturation)
  2) Air-injection facilities (blowers)
  3) Retention tank (saturation tank) → 1-3 min
  4) Back pressure regulation device → constant head on pressurizing pump
  5) Flotation unit → circular or rectangular, with a skimming device
- Key variables in flotation system design
  - Pressure, Recycle ratio, Feed solids concentration, Retention period
  - For clarification, retention time: 20 – 30 min & loading rate: 0.06 – 0.16 $m^3/min\text{-}m^2$
  - For thickening: longer retention time (t_R)

DAF Operating Factors

- Performance of DAF systems has been reported to be dependent on several factors:
  1. the solids concentration
  2. the ratio of air to solids (A/S)

- Key factors in the successful operation of DAF units are
  1. the maintenance of proper pH
  2. proper flow rates
  3. the continuous presence of trained operators

AIR SOLUBILITY AND RELEASE

- The saturation of air in water is directly proportional to pressure and inversely proportional to temperature.

$$s = s_a \frac{P}{P_a} - s_a$$

where s = air released at atmospheric pressure per unit volume at 100 percent saturation, cm^3/l
s_a = air saturation at atmospheric pressure, cm^3/l
P = absolute pressure
P_a = atmospheric pressure

$$s = s_a \left(\frac{P}{P_a} - 1 \right)$$

P should be > Pa (1 atm)
When P=Pa, s = 0

Recommended Range: 2.7< P <3.4 atm (or 40-60 psi)

- Since the solubility in *industrial wastes* may be *less than* that in water, a correction have to be applied :

$$s = s_a \left(\frac{fP}{P_a} - 1 \right)$$

where f is the fraction of saturation in the retention tank.

Air-to-Solid Ratio

- The performance of a flotation system depends upon having *sufficient air bubbles present to float substantially all of the suspended solids .*
- An insufficient quantity of air will result in only partial flotation of the solids, and excessive air will yield no improvement.

$$\frac{A}{S} = \frac{s_a R}{S_a Q}\left(\frac{fP}{P_a} - 1\right)$$

where Q = wastewater flow
R = pressurized recycle
S_a = influent oil and/or suspended solids **concentration**

- When pressurized recycle is used:

$$\frac{A}{S} = \frac{1.3 s_a R(P - 1)}{Q S_a}$$

where s_a = air saturation, cm^3/l
R = pressurized volume, l
P = absolute pressure, atm
Q = waste flow, l
S_a = influent suspended solids, mg/l

Design & Operation Parameters

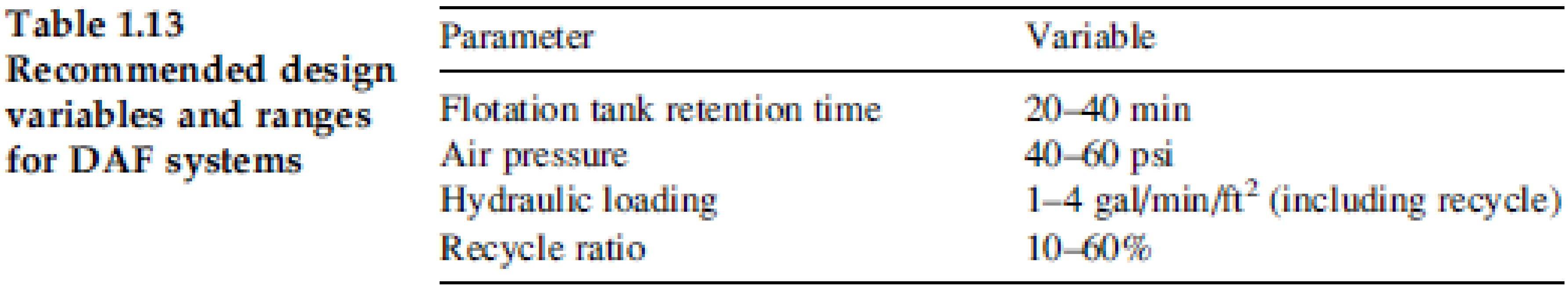


Table 1.13
Recommended design variables and ranges for DAF systems

Parameter	Variable
Flotation tank retention time	20–40 min
Air pressure	40–60 psi
Hydraulic loading	1–4 gal/min/ft^2 (including recycle)
Recycle ratio	10–60%

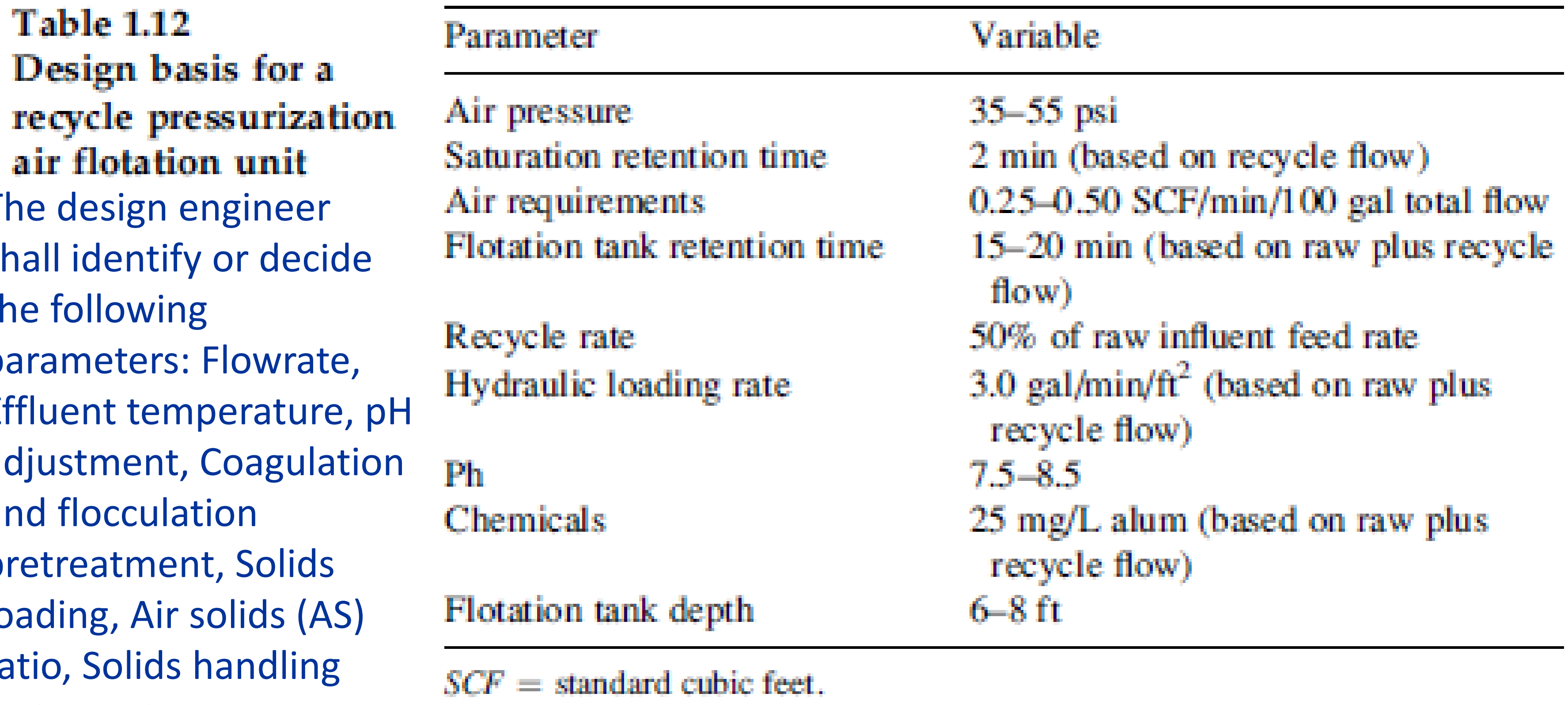


Table 1.12
Design basis for a recycle pressurization air flotation unit

Parameter	Variable
Air pressure	35–55 psi
Saturation retention time	2 min (based on recycle flow)
Air requirements	0.25–0.50 SCF/min/100 gal total flow
Flotation tank retention time	15–20 min (based on raw plus recycle flow)
Recycle rate	50% of raw influent feed rate
Hydraulic loading rate	3.0 gal/min/ft^2 (based on raw plus recycle flow)
Ph	7.5–8.5
Chemicals	25 mg/L alum (based on raw plus recycle flow)
Flotation tank depth	6–8 ft

SCF = standard cubic feet.

The design engineer shall identify or decide the following parameters: Flowrate, Effluent temperature, pH adjustment, Coagulation and flocculation pretreatment, Solids loading, Air solids (AS) ratio, Solids handling system, etc.

AIR SOLUBILITY

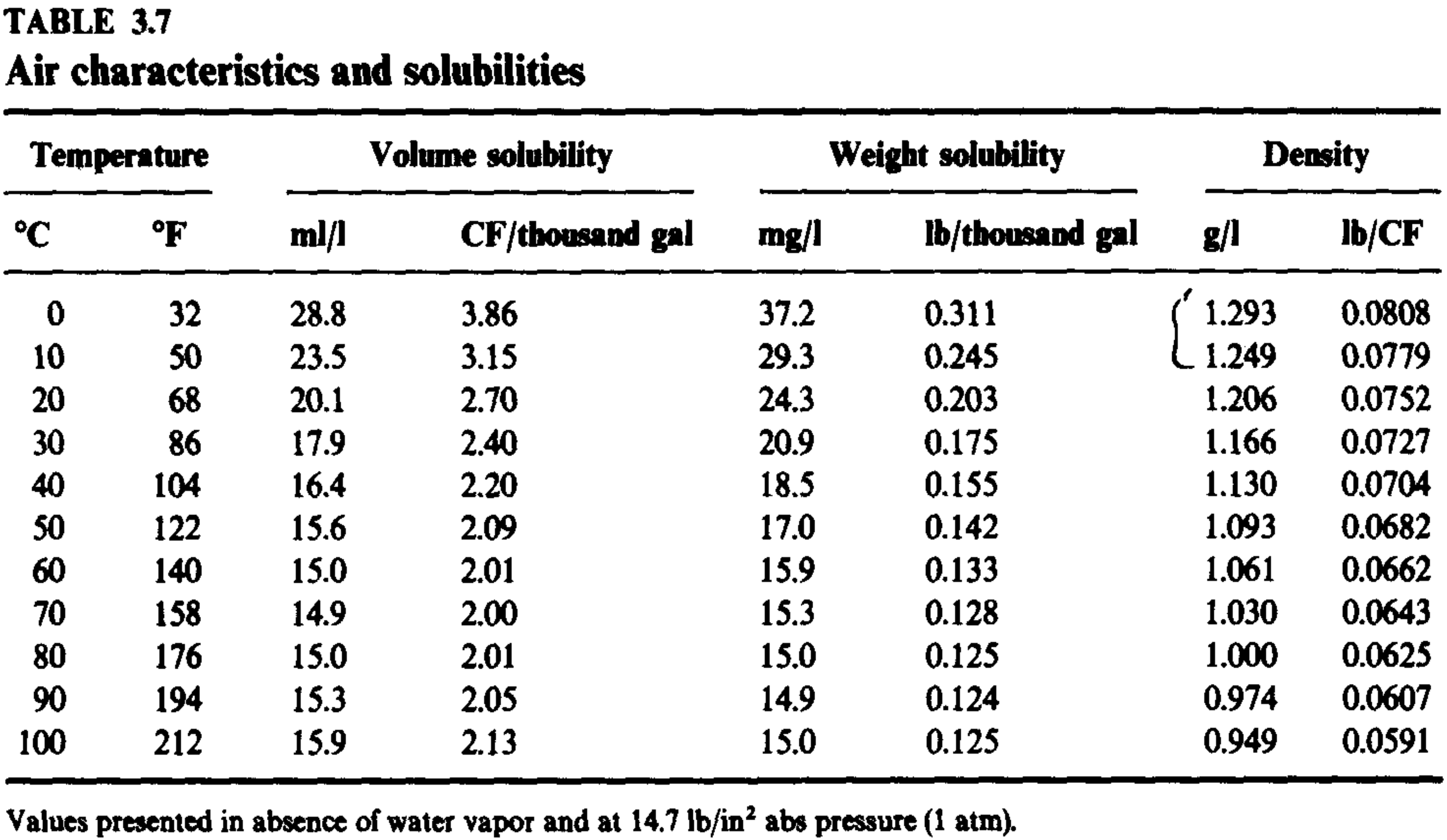


TABLE 3.7

Air characteristics and solubilities

Temperature		Volume solubility		Weight solubility		Density	
°C	°F	ml/l	CF/thousand gal	mg/l	lb/thousand gal	g/l	lb/CF
0	32	28.8	3.86	37.2	0.311	1.293	0.0808
10	50	23.5	3.15	29.3	0.245	1.249	0.0779
20	68	20.1	2.70	24.3	0.203	1.206	0.0752
30	86	17.9	2.40	20.9	0.175	1.166	0.0727
40	104	16.4	2.20	18.5	0.155	1.130	0.0704
50	122	15.6	2.09	17.0	0.142	1.093	0.0682
60	140	15.0	2.01	15.9	0.133	1.061	0.0662
70	158	14.9	2.00	15.3	0.128	1.030	0.0643
80	176	15.0	2.01	15.0	0.125	1.000	0.0625
90	194	15.3	2.05	14.9	0.124	0.974	0.0607
100	212	15.9	2.13	15.0	0.125	0.949	0.0591

Values presented in absence of water vapor and at 14.7 lb/in^2 abs pressure (1 atm).

Air-to-Solid Ratio

- The performance of a flotation unit terms of effluent quality and solids concentration in the float can be related to an **air/solids ratio:**

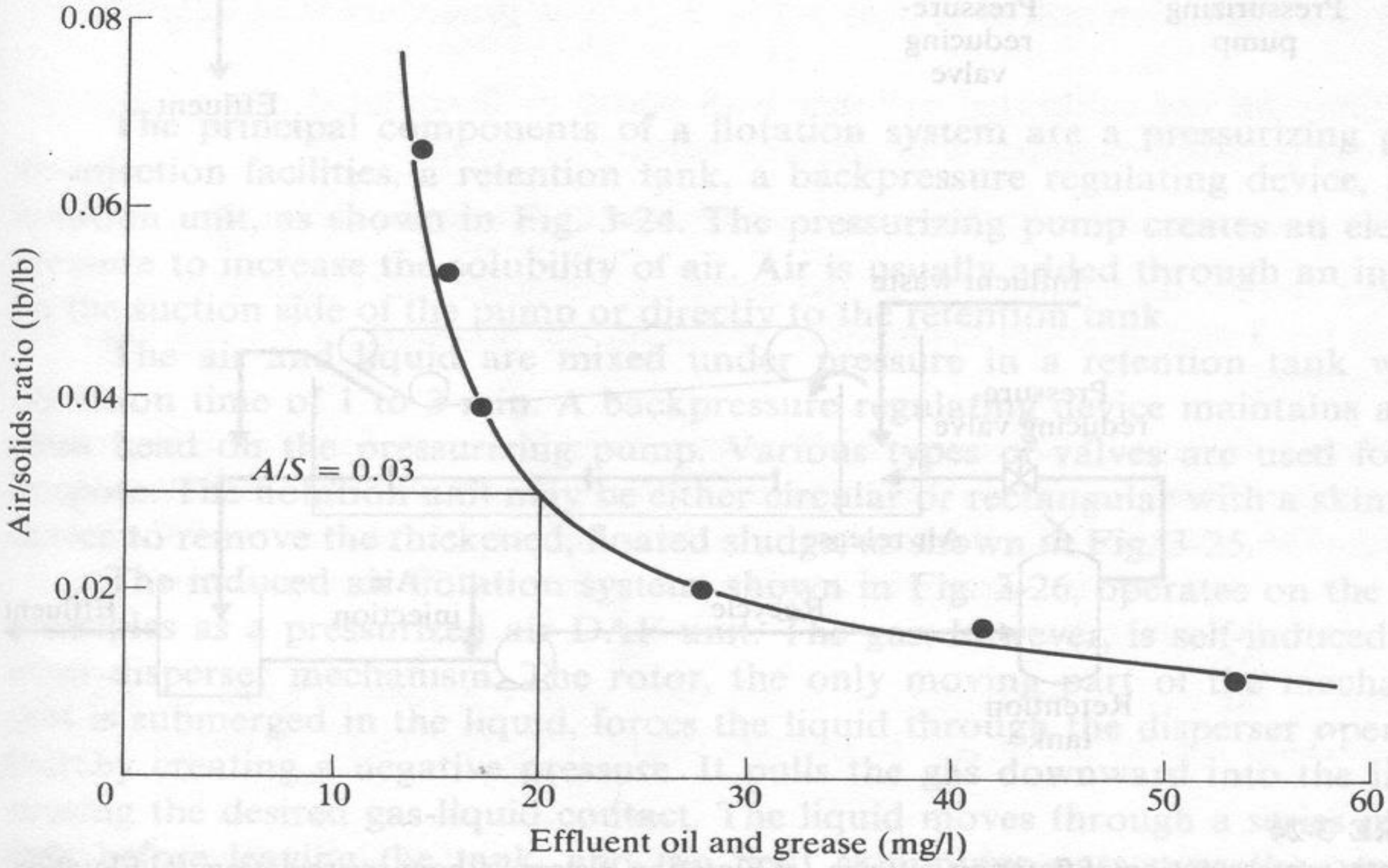


FIGURE 3-23
Effects of *A*/*S* on effluent quality.

DAF as Part of IWWT

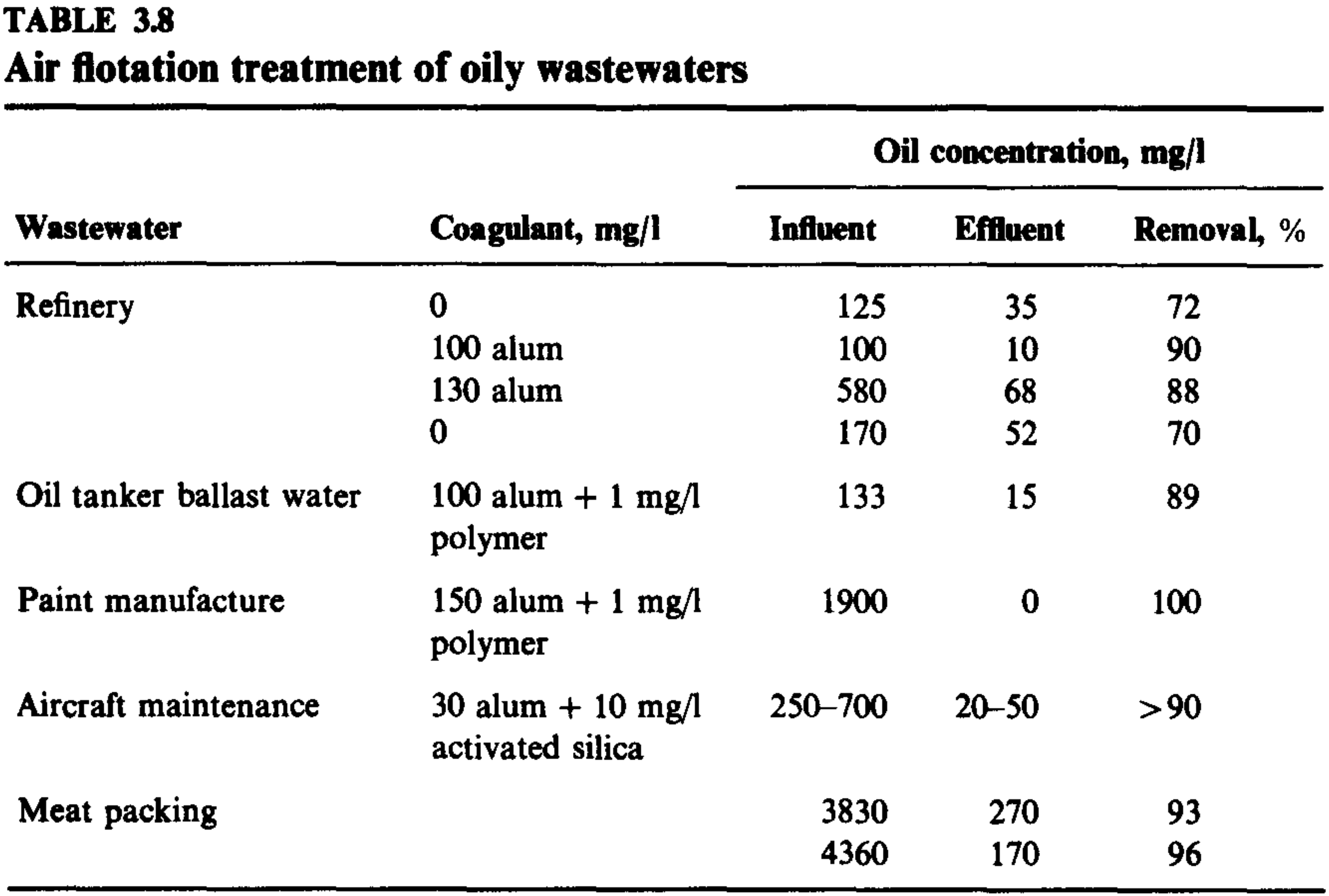


TABLE 3.8

Air flotation treatment of oily wastewaters

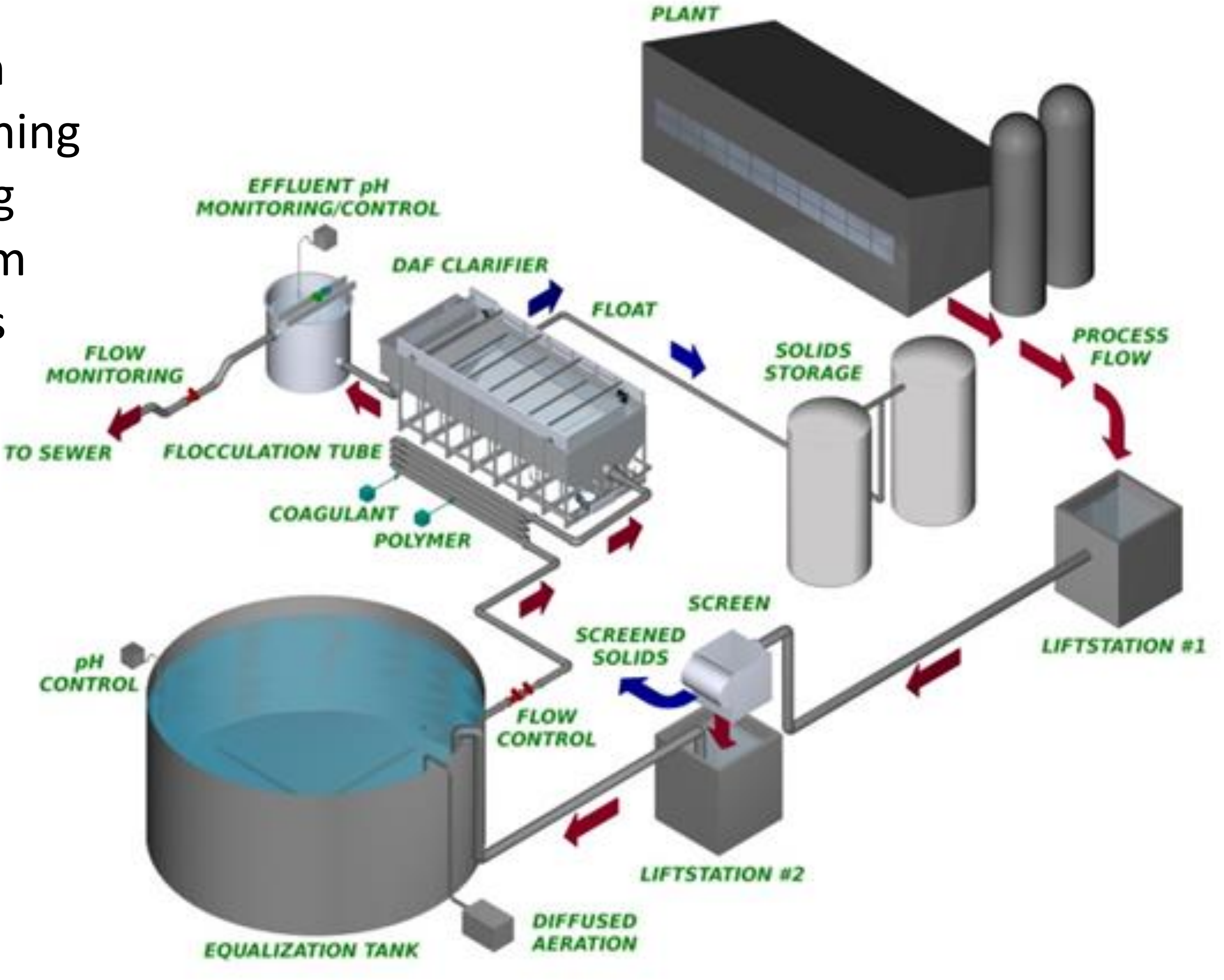
		Oil concentration, mg/l		
Wastewater	**Coagulant, mg/l**	**Influent**	**Effluent**	**Removal, %**
Refinery	0	125	35	72
	100 alum	100	10	90
	130 alum	580	68	88
	0	170	52	70
Oil tanker ballast water	100 alum + 1 mg/l polymer	133	15	89
Paint manufacture	150 alum + 1 mg/l polymer	1900	0	100
Aircraft maintenance	30 alum + 10 mg/l activated silica	250–700	20–50	>90
Meat packing		3830	270	93
		4360	170	96

DAF as Part of IWWT

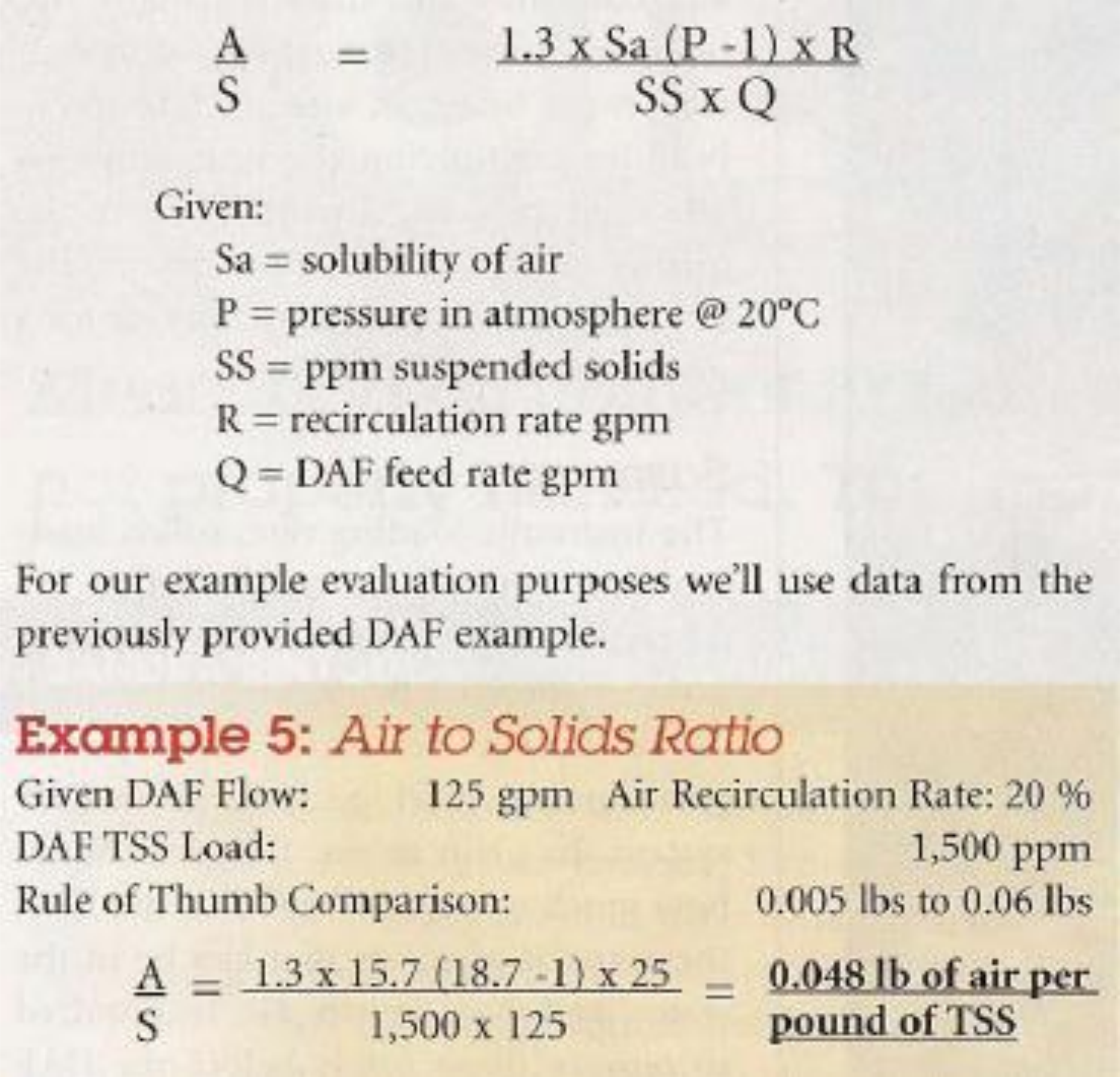
Examples:

wastes from

- food canning & packing
- Petroleum refineries



Dissolved Air Flotation



$$\frac{A}{S} = \frac{1.3 \times Sa\,(P - 1) \times R}{SS \times Q}$$

Given:

Sa = solubility of air
P = pressure in atmosphere @ 20°C
SS = ppm suspended solids
R = recirculation rate gpm
Q = DAF feed rate gpm

For our example evaluation purposes we'll use data from the previously provided DAF example.

Example 5: *Air to Solids Ratio*

Given DAF Flow: 125 gpm Air Recirculation Rate: 20 %
DAF TSS Load: 1,500 ppm
Rule of Thumb Comparison: 0.005 lbs to 0.06 lbs

$$\frac{A}{S} = \frac{1.3 \times 15.7\,(18.7 - 1) \times 25}{1{,}500 \times 125} =$$ **0.048 lb of air per pound of TSS**

Electroflotation

- Electroflotation unit is the equipment for industrial wastewater treatment from heavy metals, oil, surfactants and suspended solids.
- Electroflotation is a process of floating of pollutants to water surface by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively.
- Electroflotation module consists of electroflotation cell with insoluble electrodes, tanks for alkali and flocculant solutions, pumps, rectifier of 100-150 A with voltage of 24 V, sludge collecting system (Skimmer).
- Electroflotation unit made of polypropylene, high-reliability equipment.
- Capacity of unit may range from 1 to 50 m3/h.

Electroflotation

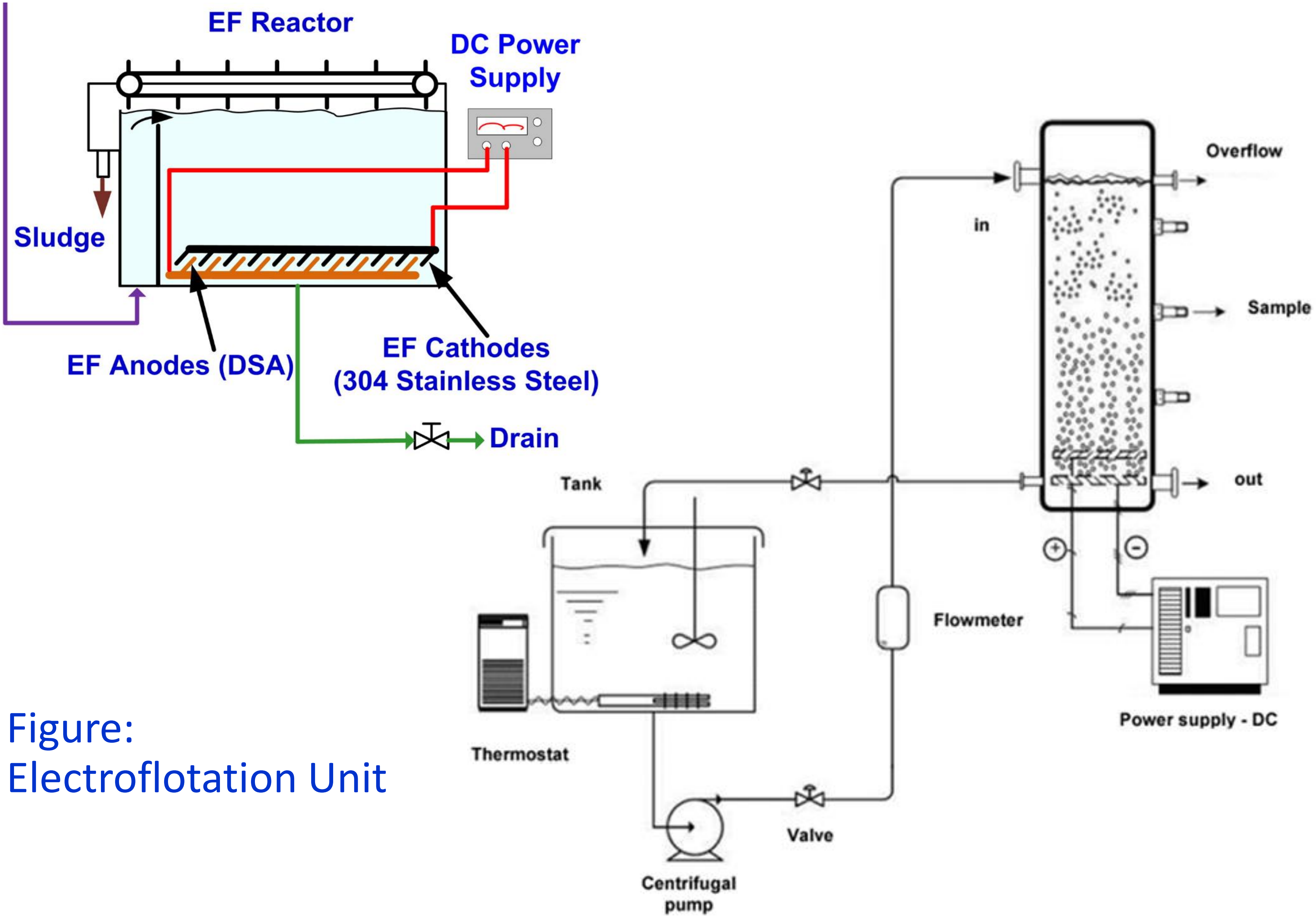


Figure:
Electroflotation Unit