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Chapter 4: **Internal Measures**

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4. Internal Measures (front-of-pipe)

4.1 Introduction

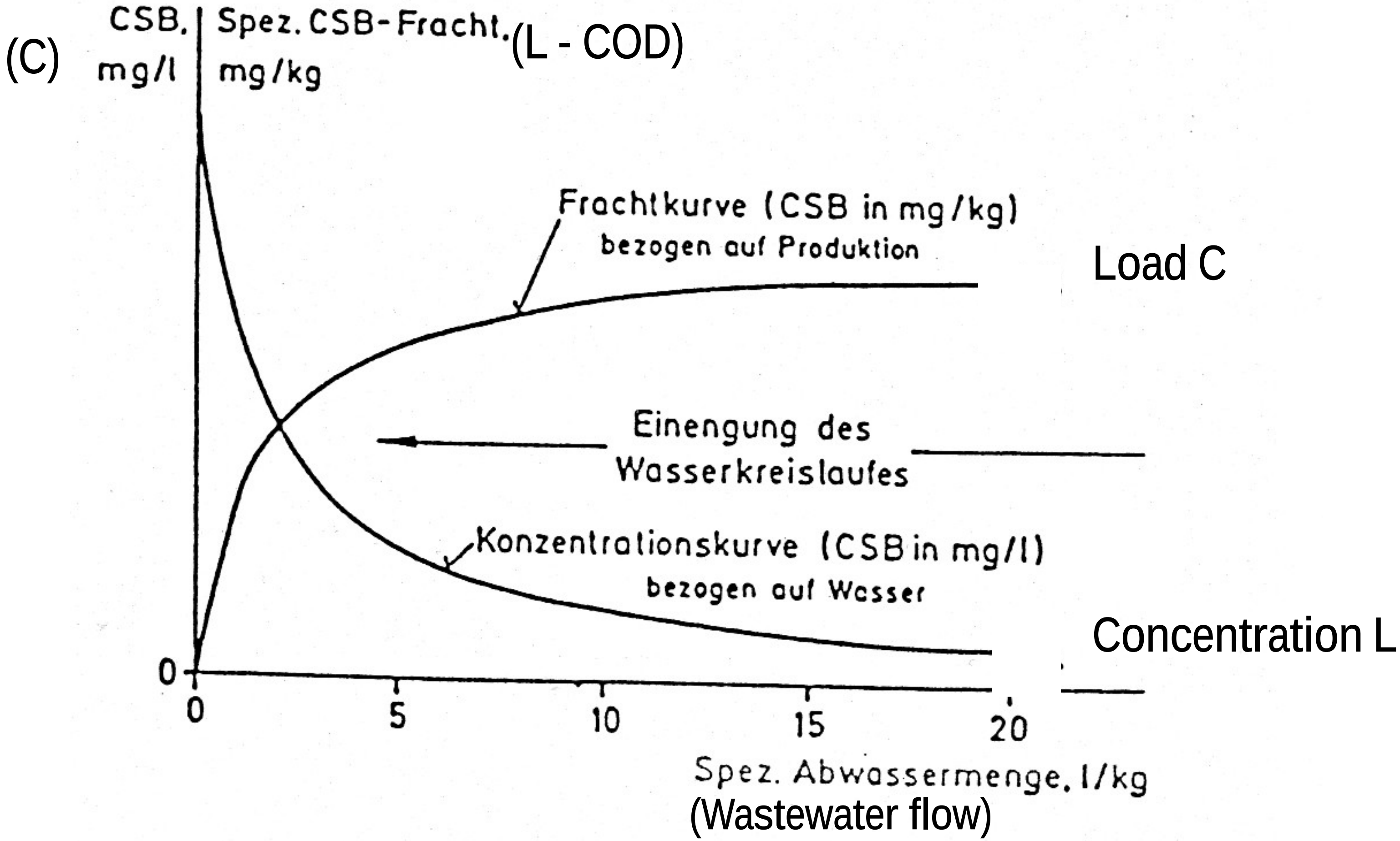
- processes with low water demand and wastewater discharge
- reuse of water
- recovery of valuable resources and waste material
- (wastewater treatment or pre-treatment)

Goals

- priority reduction of water flow

- priority reduction of contamination

- reduction of flow and contamination



Waste water concentration (C) and specific load (L) depending on the specific wastewaterflow (Q)

L = C x Q

4.2 MEASURES

General Measures

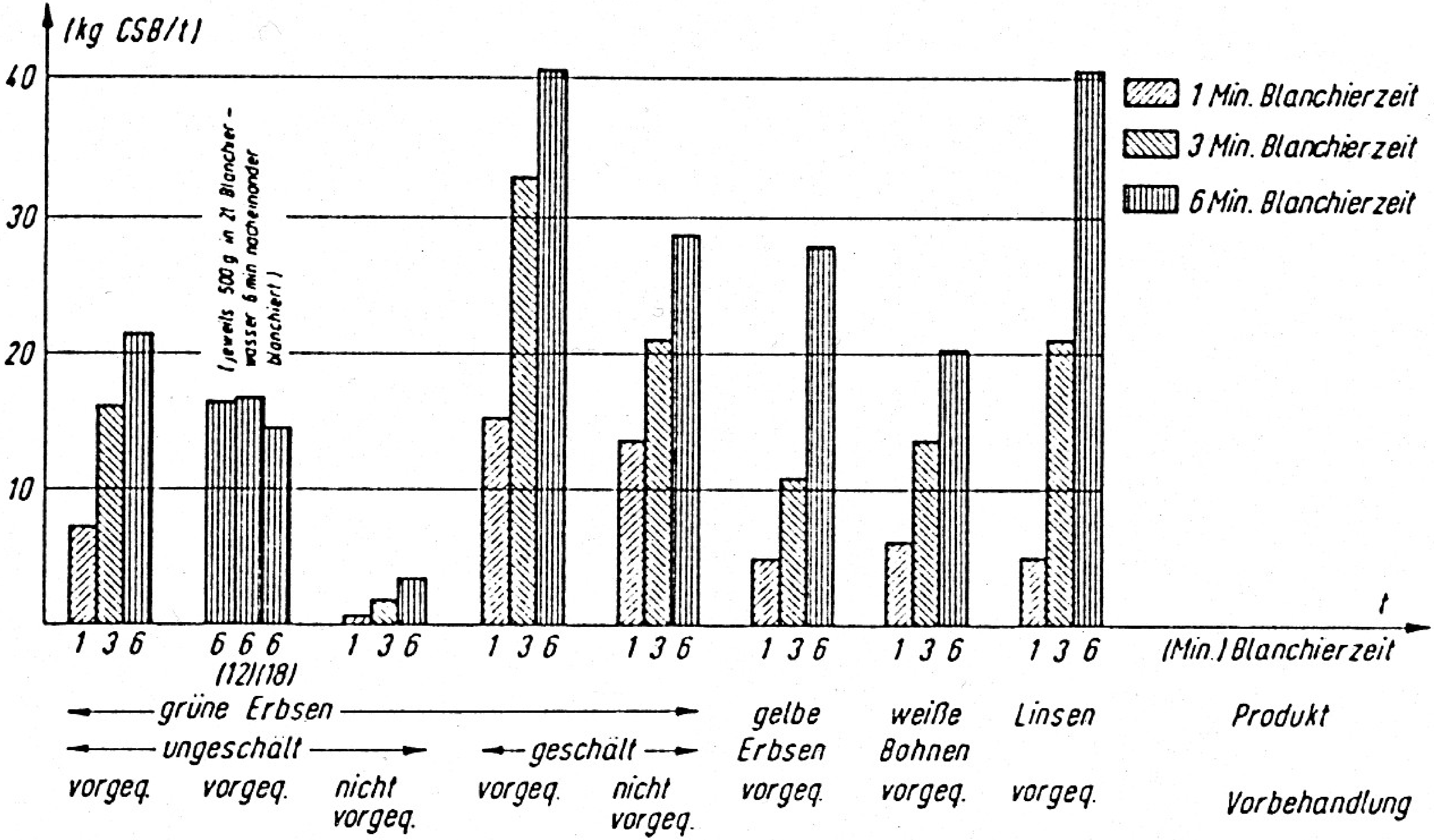
- training of employees (water saving)
- organisation
- water saving fittings
- reorganization of piping networks

Changes in production process

- reduction of water consumption/replacement of water (e.g. dry peeling)

- organizational improvements (e.g. reduction of contact time between product and process water)

- reduction of product losses



Specific COD-load of blanching water depending on blanching time and pretreatment of the product

Analytical data for different beverages

Getränk	pH-Wert	Ges.-Acidität m-Wert pH: 4,9 (ml/l)	Ges.-Acidität p-Wert pH: 9,5 (ml/l)	BSB_5 (mg/l)	$KMnO_4$-Verbr. (mg/l)	CSB (mg/l)	TOC (mg/l)
Milch							
Vollmilch	6,8	–	–	114000	198000	183000	70000
Buttermilch	5,3	–	–	61300	178000	101000	51500
Magermilch	6,7	–	–	91300	194000	147000	62000
Limonaden							
Zitronenlimonade	2,90	214	869	48000	213500	90000	30000
Fanta	2,69	401	1052	73450	264600	150000	42500
Coca-Cola	2,35	101	794	44600	251100	155000	43500
Schweppes Tonic	2,34	469	1474	38300	263700	147500	29000
Frucht- u. Gemüsesäfte							
Johannisbeer Nektar	2,67	694	1117	61000	328640	155000	52500
Kirsch Nektar	2,97	970	1433	54600	385520	183700	63700
Rote Bete Saft	4,00	261	826	37000	249640	120000	38750
Biere							
Export	4,45	52	1019	80500	47652	147500	40000
Karamalz	4,47	98	1295	103000	300000	150000	49000
Weine, Sekt							
Nahe-Trocken	3,87	462	951	84000	54000	212500	47500
Rheinh.-Spätlese	3,40	590	1103	85000	160100	237500	57500
Rheinh.-Kabinett	3,08	749	1226	73000	135000	195000	47500
Ungarn-Ausbruch	3,18	976	1177	137000	175800	285000	72500
Ahr-Rotwein	3,70	482	834	93000	66970	192500	47500
Sekt	2,95	770	1394	92200	110920	227500	58750
Spirituosen							
Doppelkorn	8,82	–	< 1	387500	34530	630000	145000
Weinbrand	3,78	15	35	346300	53370	635000	145000
Likör	3,72	94	222	384000	588600	660000	180000
Kräuterlikör	3,55	129	129	328000	580770	735000	200000

Change of transport system

- replacement of water for transport (e.g. by air)
- implementation of transport cycle (treatment in the cycle?)

Change of cleaning system

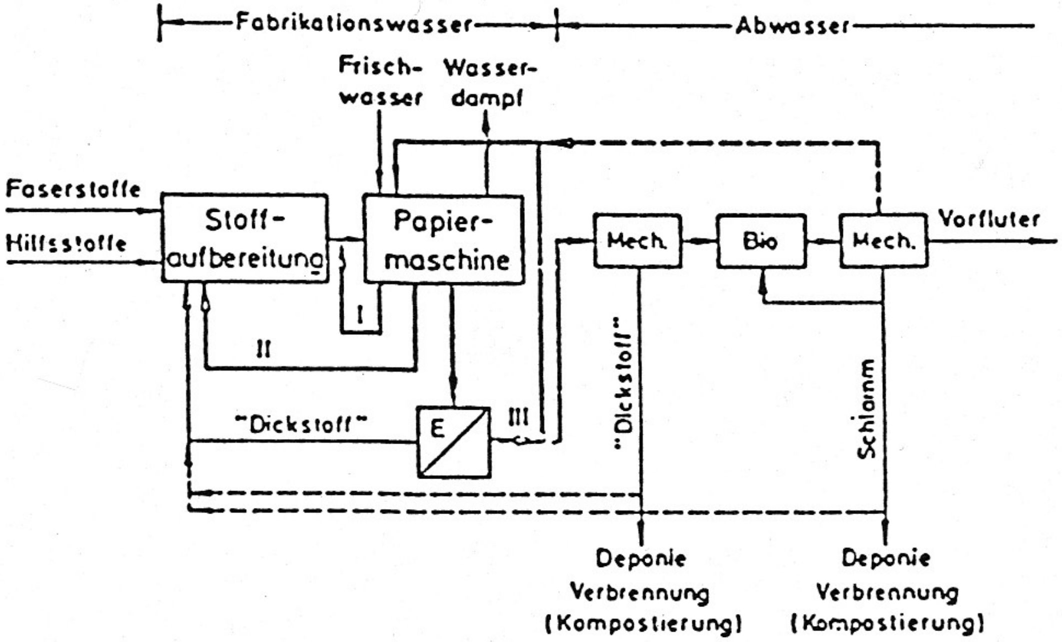
- product cleaning (e.g. recycling washing water)
- cleaning of tanks, pipes, machines (e.g. CIP)
- room cleaning (e.g. dry before wet, high-pressure systems)

Change of water pathways

- installation of cycles (open or closed = no losses by evaporation)
  cooling water, washing water,

- multiple-shift usage of low contaminated water
  - counter current flow system (production, washing, rinsing)

- separation of different wastewater streams (e.g. cooling water)



Simplified flow conditions in paper industry including
Primary and secondary wastewater treatment

E = "Entstoffung" (Sedimentation, Filtration oder Flotation)

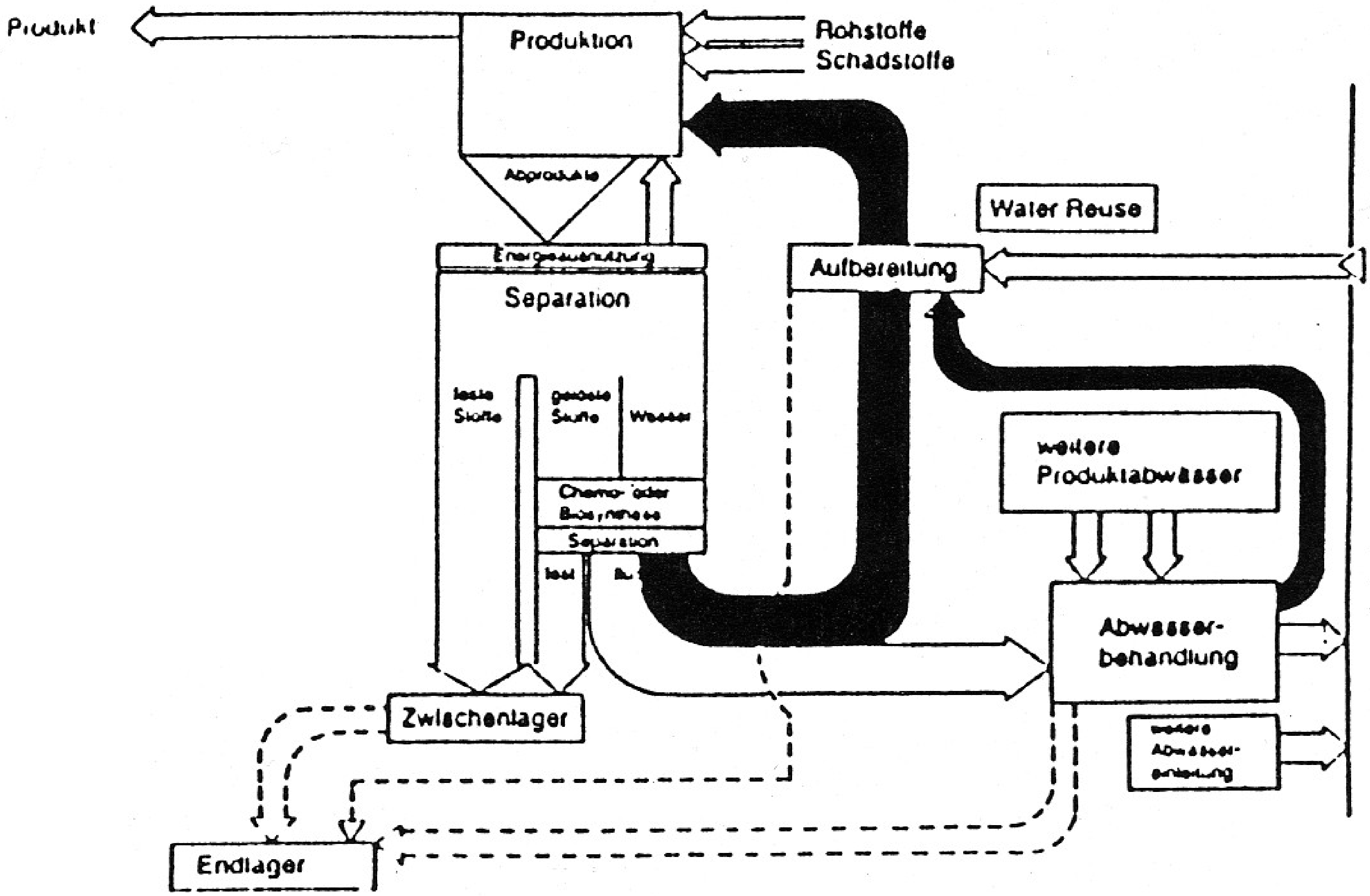
I = Primär-Kreislauf (Siebwasser I)

II = Sekundär-Kreislauf

III = Tertiär-Kreislauf (Abwasser)

Mech. = Mechanisches oder Chemisch-mechanisches Verfahren

Bio = Belebtschlammanlage



Wastewater reuse

Change of cooling system

- cooling water cycles
- substitution of cooling water (e.g. air, cooling liquids)

Recovery of resources and waste materials

- winning of products from residues (wine from wine lees)
- by products from liquid or solid product wastes (protein, lactose from whey)
  (feeding stuff from brewer grains, pomace)
- valuable resources from wastewater
  (filtration of fruit pieces for feeding stuff, fat from fat separators)

Recovery Processes

- Solvent Recovery.
  - Remove contaminants and restore the solvent to a usable/saleable quality.
  - Distillation.
    - Typically 75% recovery.
    - Production of still bottoms
  - Other recovery processes include
    - filtration, simple evaporation, centrifugation, stripping.

Recovery Processes

<u>Commonly Recycled Solvents</u>

Aliphatic Hydrocarbons

- Hexane
- *Aromatic Hydrocarbons*
- Benzene
- *Chlorinated Hydrocarbons*
- Trichloroethylene
- *Alcohols*
- Ethyl alcohol
- *Esters*
- Ethyl acetate

Recovery Processes

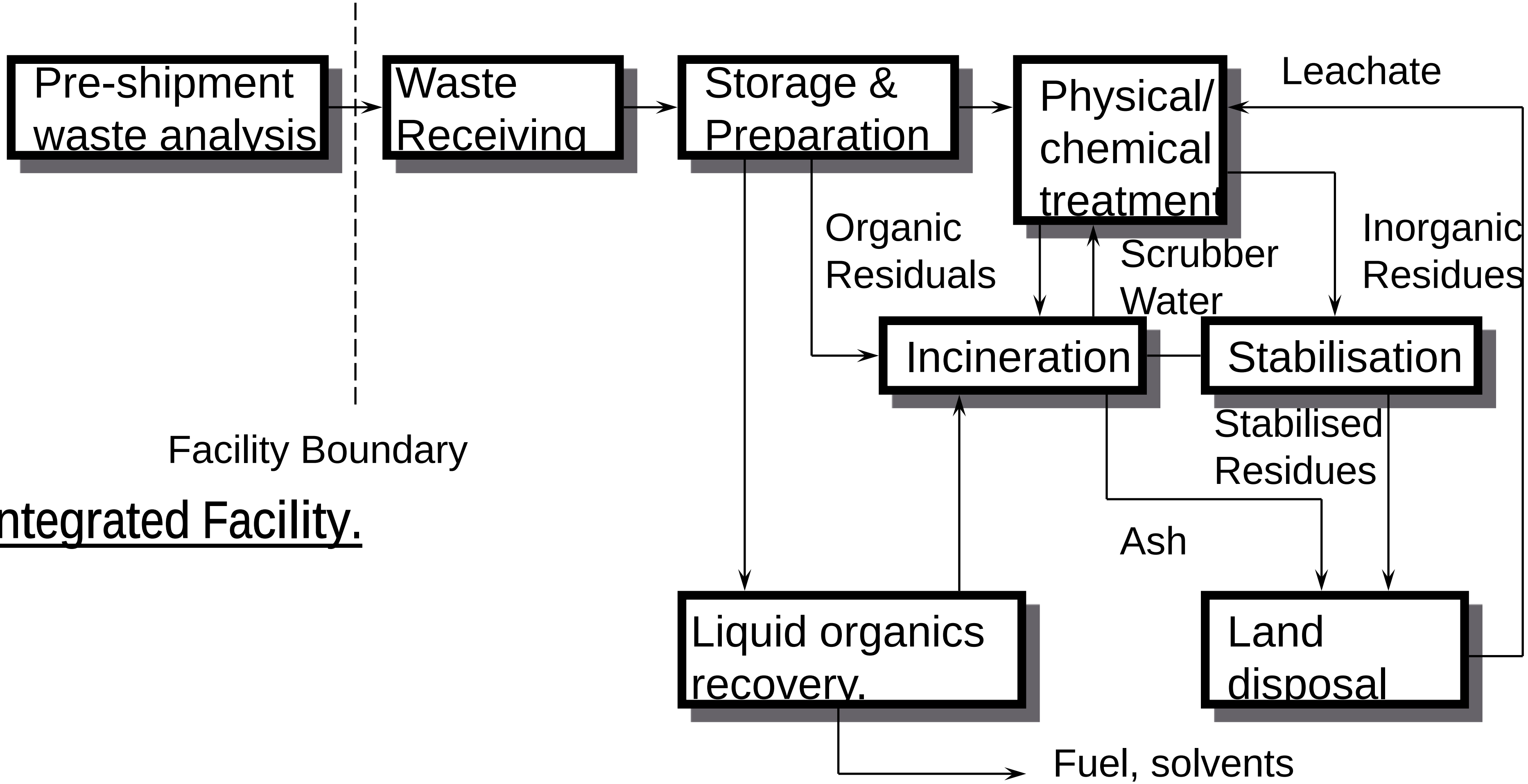
- Oil Recovery
  - *Re-refining of Spent Lubricating Oils.*
    - Produces virgin quality lubricating oil..
    - Distillation.
      - Most popular even though more capital intensive.
      - Produces lower volumes of waste (still bottoms)
  - *Other recovery techniques.*
    - Dissolved air flotation, ultrafiltration, burning in industrial boilers.

Recovery Processes

Metals Recovery

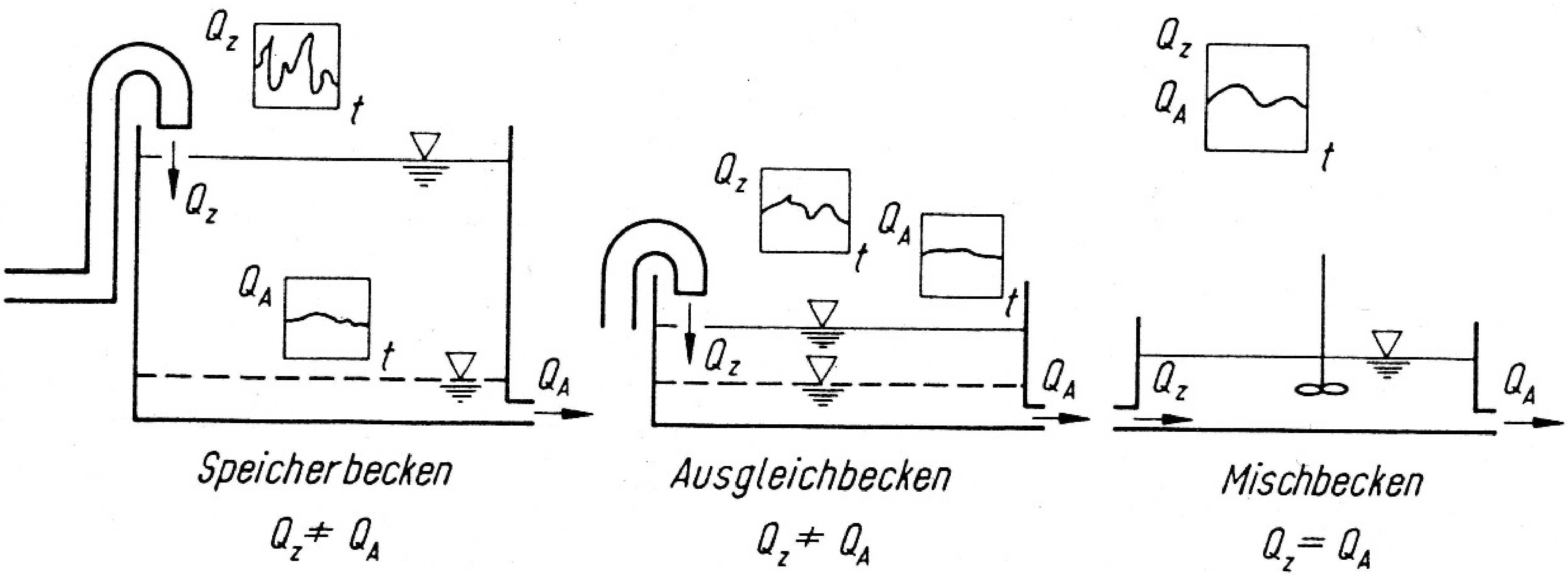
- Pyrometallurgical
  - differences in melting or boiling points.
- Hydrometallurgical
  - Separation of metals from liquid wastes by eg ion exchange, electrodialysis, membrane filtration, adsorption, precipitation.

Treatment Processes

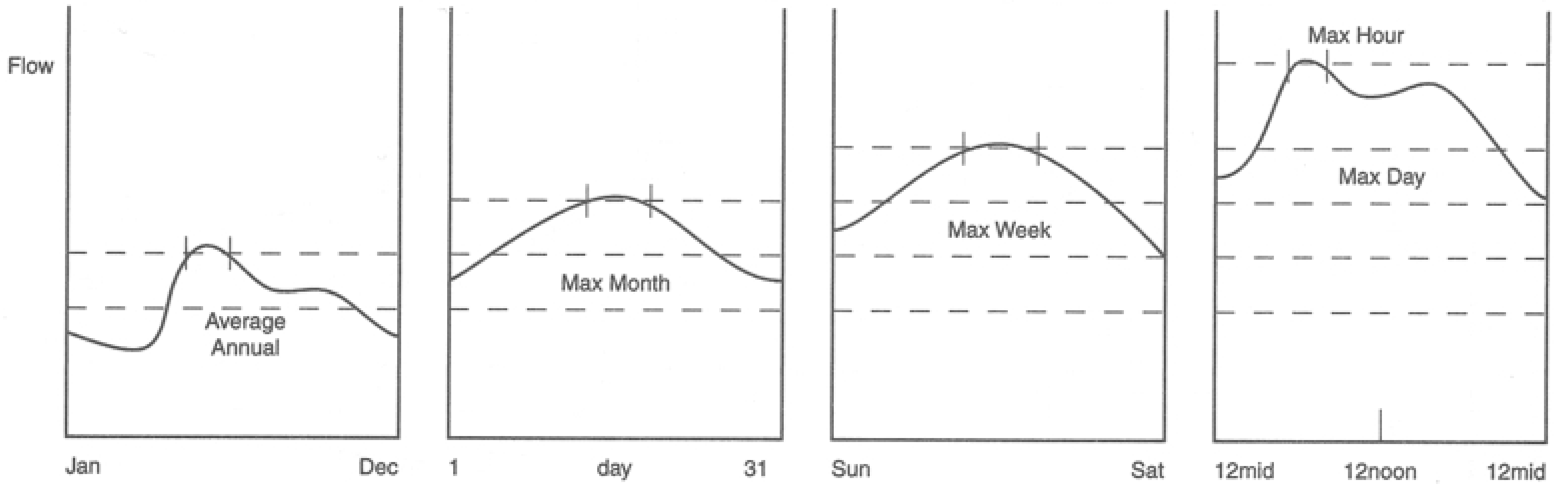


<u>Integrated Facility.</u>

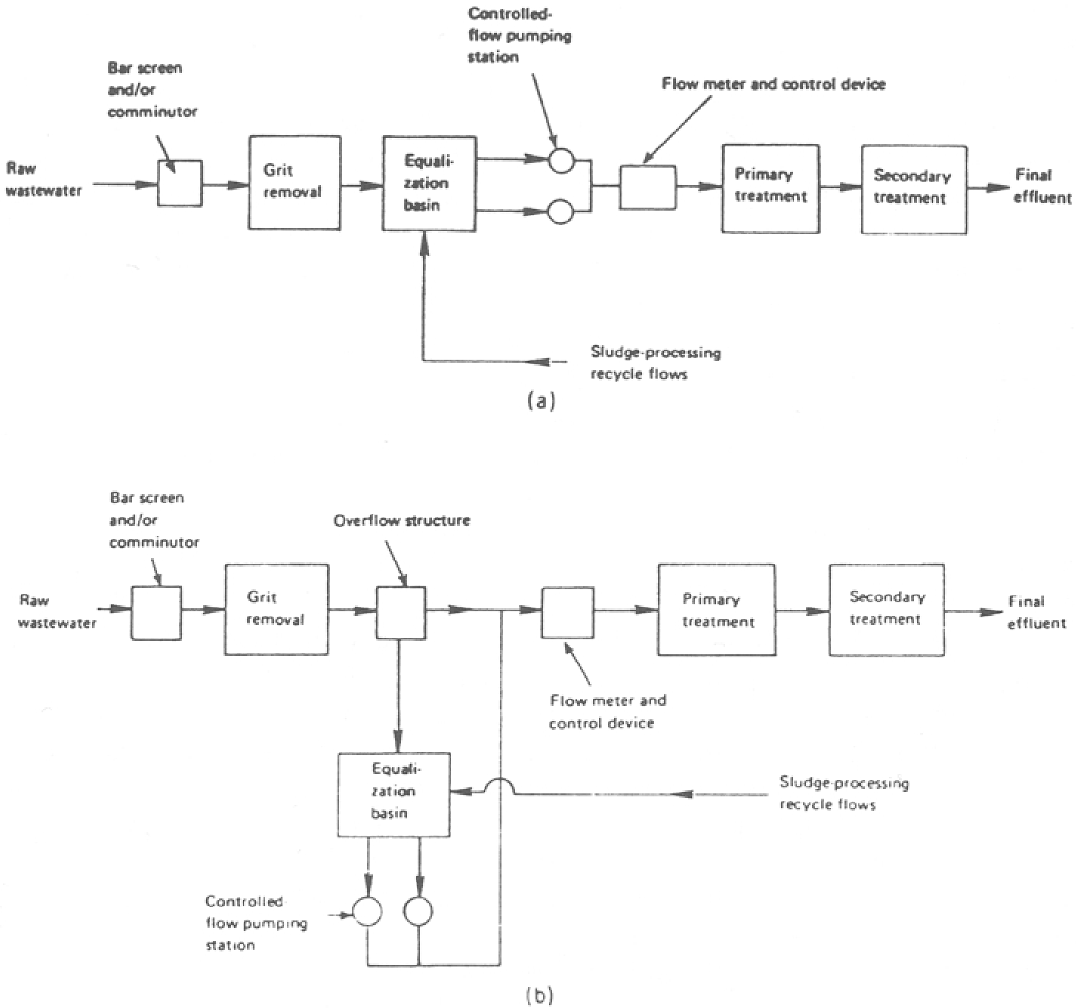
4.3 Storage, Mixing, balancing



Properties of storage-, balancing- and mixingtanks



Flow variation at a wastewater treatment plant.



Two equalization schemes: (a) in-line equalization and (b) side-line equalization.

mixing tank:

$$c_e = c_o - (c_o - c_R) * e^{-t * \frac{Q}{V}}$$

c_e … effluent concentration

c_o … influent concentration

c_R … initial concentration in tank (t=0)

Q … inflow

V … tank volume

t … time

mixing energy:

V (m^3)	N (W/m^3)
500	20-40
1000	10-15
2000	5-10

4.4 CHEMICAL TREATMENT

- Mainly liquid wastes and slurries.
- Inorganic and organic contaminants.
- Chemical Processes
  - *transform* the hazardous substances in order to facilitate separation, or conversion to a non-hazardous substance:
    - Neutralisation of high/low pH liquids/slurries.
    - Precipitation.
    - Coagulation and flocculation.
    - Oxidation/reduction.
- Physical Processes
  - *separate* the hazardous component
    - Sedimentation
    - Flotation
    - Centrifugation
    - Membrane separation.

Neutralisation

Target pH

For transportation and disposal:

- pH > 2.5 and < 11.5

To meet conditions for further treatment:

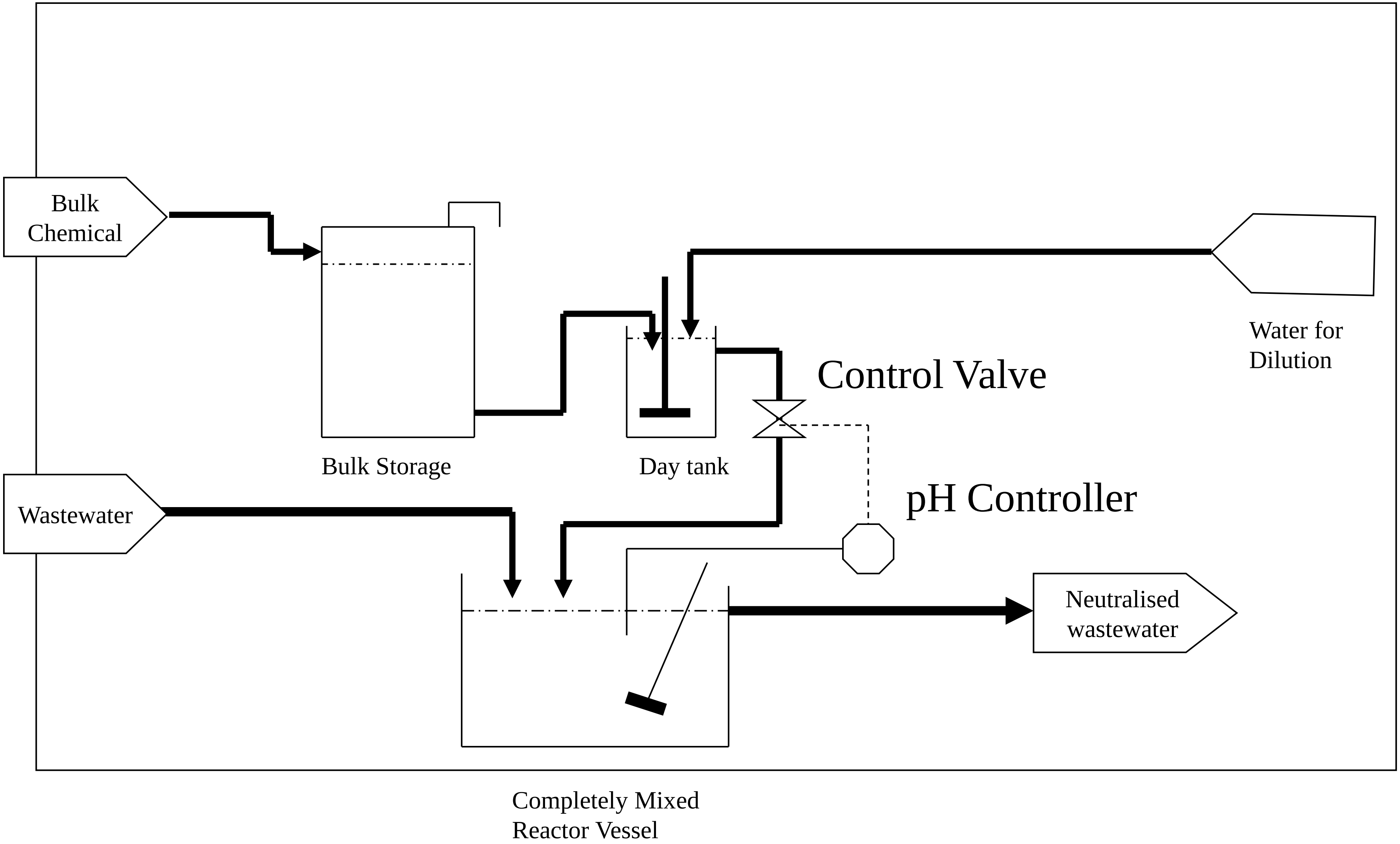
- chemical (process specific)
- biological pH >6.5 and < 8.5
- Cyanide oxidation pH 8.5

for acidic or alkaline waters

$$\mathbf{HCl + NaOH} \rightarrow \mathbf{NaCl + H_2}O$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow \mathbf{CaSO}_4 + 2(H_2O)$$

Neutralisation



Precipitation

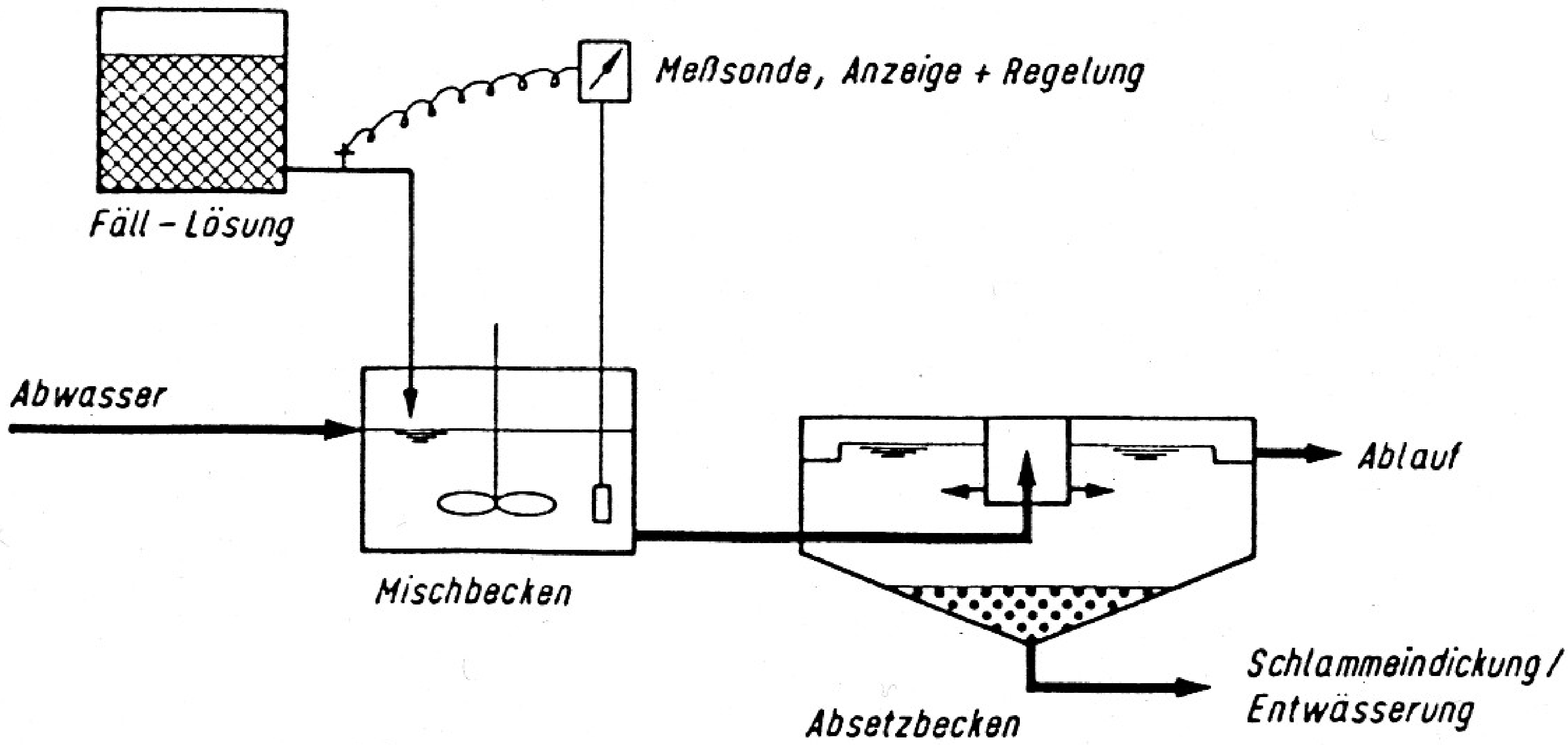
conversion of dissolved substances in suspended and settleable ones,

such as P, heavy metals

- Removal of *metals* as insoluble hydroxides:
  - cadmium, copper, lead, manganese, zinc, chromium (after reduction to trivalent form)
  - $ZnSO_4 + 2NaOH = Zn(OH)_2\downarrow + Na_2SO_4$

    Fe2 (SO4)3 + 3 Ca(OH)2 → 2 Fe (OH)3 + 3 CaSO4

- Precipitation of ***detergents and fats.***
- Optimum pH determined in ***"jar tests"***
- Precipitation often forms small particles which do not readily settle.
- Removal enhanced by ***coagulation***



Flow scheme of a precipitation device

- Reactor design.
  - Batch
    - Small volumes, variable waste characteristics, narrow output range.
    - Batch time
      - filling, reaction, emptying.
    - Sensor and control system
      - set point or set point and mark
  - Completely mixed or plug flow.
    - Any significant flowrate
    - Single or multi-stage
    - Sensor and control system.
      - Reduce variability of input e.g. constant flow.
      - pH sensor and proportional controller controlling a pump discharge or an automatic valve.
      - Sensitivity of control affected by valve or pump system hydraulics
    - Residence time
      - typically 12 to 20 minutes HRT (0.5 to 2 mins required for mixing)

Flocculation

- Enhances the settleability of coagulated particles by forming large agglomerates.
- Polyelectrolytes most common form.
- Large organic molecules, non-ionic, anionic, cationic.
- Maturation, and flocculation in a gently mixed zone (gate stirrer, 10 to 15 min residence time)
- Stock solution made up to approx 0.5% w/v
- Typical dosage 0.5 to 10 mg/l.

Flocculation

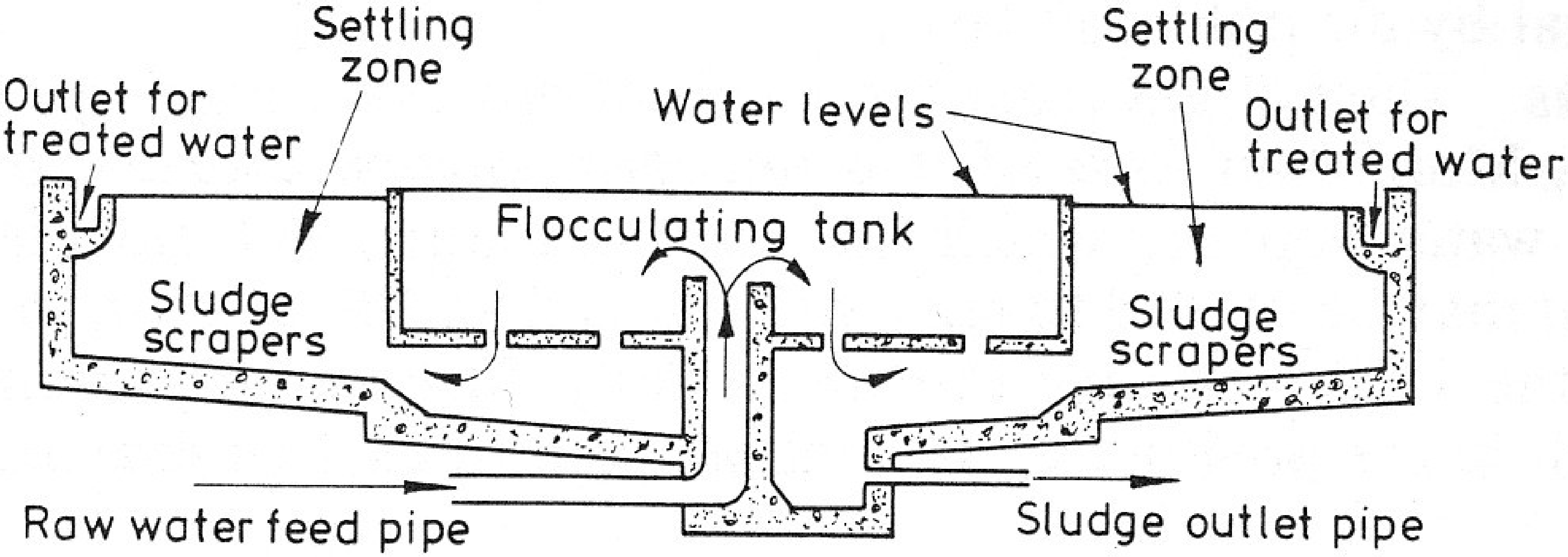
- Mechanism of flocculation
  - Adsorption of the polymer on the solid
  - Cross-linkage of the segments of the polymers, bridging colloids.
  - Formation of a loose 3-D structure.
  - Close range chemical reaction (hydrogen bonding) more important than electrostatic interaction.

- Flocculator Design
  - Rate directly proportional to the velocity gradient, G (s^{-1})
  - Number of particle collisions function of the velocity gradient multiplied by the residence time, t (s)

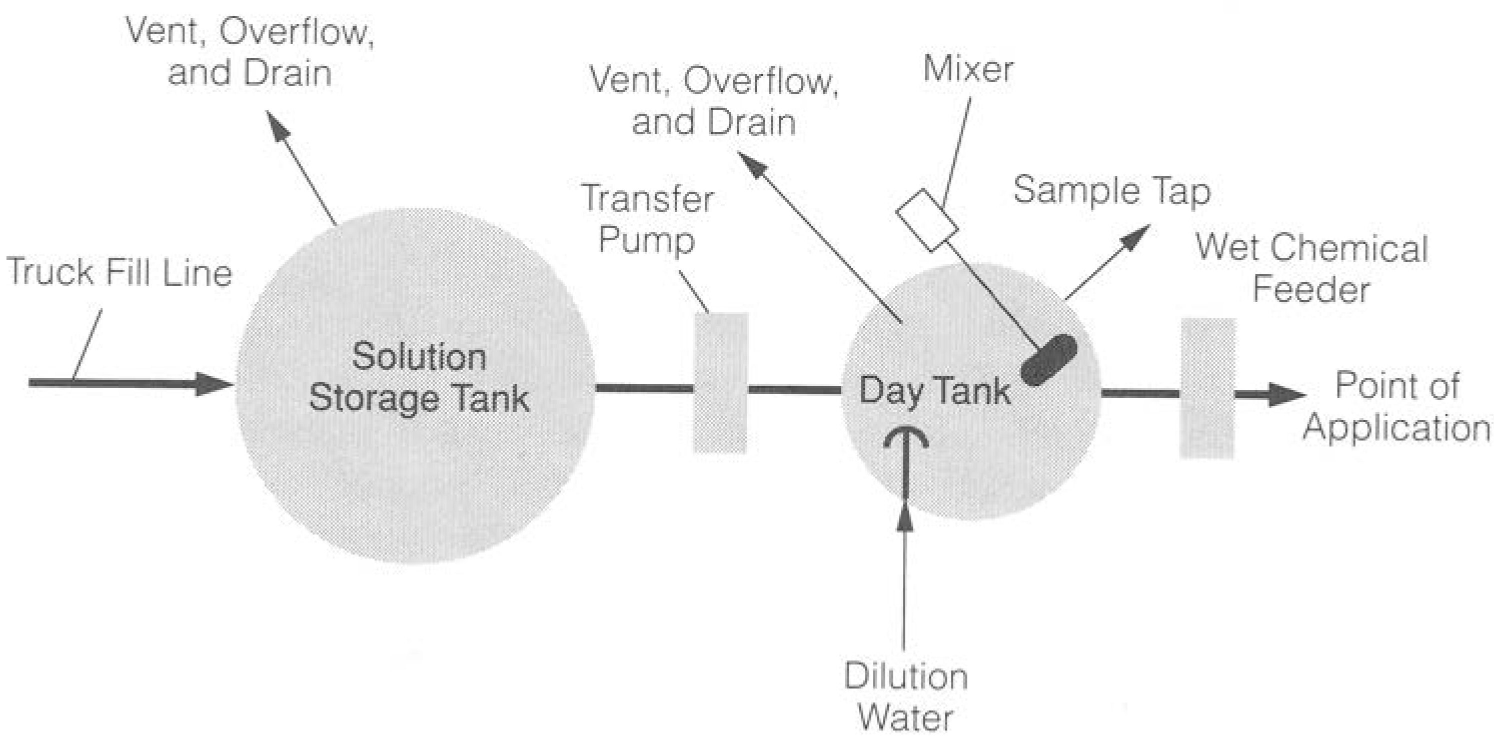
$$Gt = \frac{1}{Q}\{PV/\mu\}^{0.5}$$

where Q is the flow	(m^3/s)
P is the useful power input	(watts)
V is the volume	(m^3)
μ is the absolute viscosity	(Ns/m^2)

- Flocculator Design
  - G for Al and Fe salts 20 to 75 s^{-1}
  - Maturation, and flocculation in a gently mixed zone (10 to 15 min residence time)
  - Baffled basin, with horizontally or vertically mounted paddle flocculators
    - 2 to 15 rpm
    - 0.2 to 0.8 m/s peripheral velocity.



Flocculator-clarifier, one-pass system, in cross-section, showing the concrete tank. The undermentioned are not shown: the rotating half-bridge and its sludge scrapers in the settling zones; the stirrers in the flocculating tank: the sludge scrapers below the flocculating tank



Typical liquid chemical-feed system.

Oxidation

- In general, used to ***detoxify*** waste by transforming the waste components.
- Organic molecules
  - converted to carbon dioxide and water, or
  - less toxic intermediates - may be more biodegradable.
- *Common oxidising agents* are:
  - chlorine
  - ozone (high free energy but decomposes)
  - hydrogen peroxide (often with UV light 500 watts/l)
  - oxygen

- Oxidising agents are *non specific.*
  - components other than the target need to be at low concentrations - cost.
  - some components can become more toxic eg hydrocarbons in a chlorine oxidation.
- Some oxidising agents are *enhanced by UV light* e.g. ozone and hydrogen peroxide.
- *Typical uses* of oxidation:
  - Cyanide
  - chlorinated VOCs
  - phenols

Oxidation by Hydrogen Peroxide.

- Characteristics
  - Very soluble in water (provided as 50% solution)
  - Strong oxidant, similar to ozone, produces the hydroxyl radical in the presence of the catalyst Fenton's reagent (iron based)
- Application
  - High solubility leads to simple dosing and mixing systems.
  - Effectiveness can be enhanced by UV light.
  - Typical catalyst requirements 0.05 mg $Fe^{2=}$/mg H_2O_2
  - Similar to ozone in applications.

Oxidation by Ozone

- Characteristics
  - Gas at normal temperatures and pressures
  - Powerful oxidant through the formation of the hydroxyl radical in water (• OH)
  - Rapidly dissociates to oxygen.
- Application
  - Reaction rates can be slow
    - enhance with UV light.
  - Can fully oxidise organics or partially oxidise toxic organics to biodegradable forms
    - can also generate more toxic forms e.g. aromatics to phenolics at pH above 9.
  - Must be generated on-site and added in gaseous form
  - Expensive.

Oxidation by Chlorine

- Cyanide Waste Treatment by Alkaline Oxidation

Reaction 1 $NaCN + Cl_2 \rightleftharpoons CNCl + NaCl$

Reaction 2 $CNCl + 2NaOH = NaCNO + 2H_2O + NaCl$

Reaction 3 $2NaCNO + 4NaOH + 3Cl_2 \rightleftharpoons 2CO_2 + 6NaCl + N_2 + 2H_2O$

- Note:
- Must have alkaline conditions pH > 8.0
- Reaction 1 is instantaneous at all pH's
- > pH 8.5 reaction 2 complete in 30 mins
- Reaction 3 most rapid at pH 6.5 to 6.8, but pH 8.5 selected to accommodate earlier reactions.
- At pH 8.5 reaction 3 complete in 10 mins, at pH 9.6, complete in 40 mins.

Reduction

Reduction of Chromium Wastes (Cr VI to Cr III)

- Ferrous sulphate Reducing Agent
  - *Acidic reaction pH < 3.0*
    - **Hexavalent** chromium + ferrous sulphate + sulphuric acid $\rightleftarrows$ **Trivalent** chromium sulphate + ferric sulphate + sodium sulphate.
  - *Alkaline precipitation pH 8.5 - 9.5*
    - **Trivalent** chromium sulphate and ferric sulphate precipitated as **trivalent** chromium hydroxide and ferric hydroxide
  - Notes.
    - Sludge production
    - excess iron required (2.5 times the theoretical amount)

Reduction of Hexavalent Chromium with Sulphur Dioxide

- Sulphur Dioxide Reducing Agent
  - *Two-stage reaction to produce precipitate of chromium hydroxide.*
  - Dissolution of Gaseous SO_2

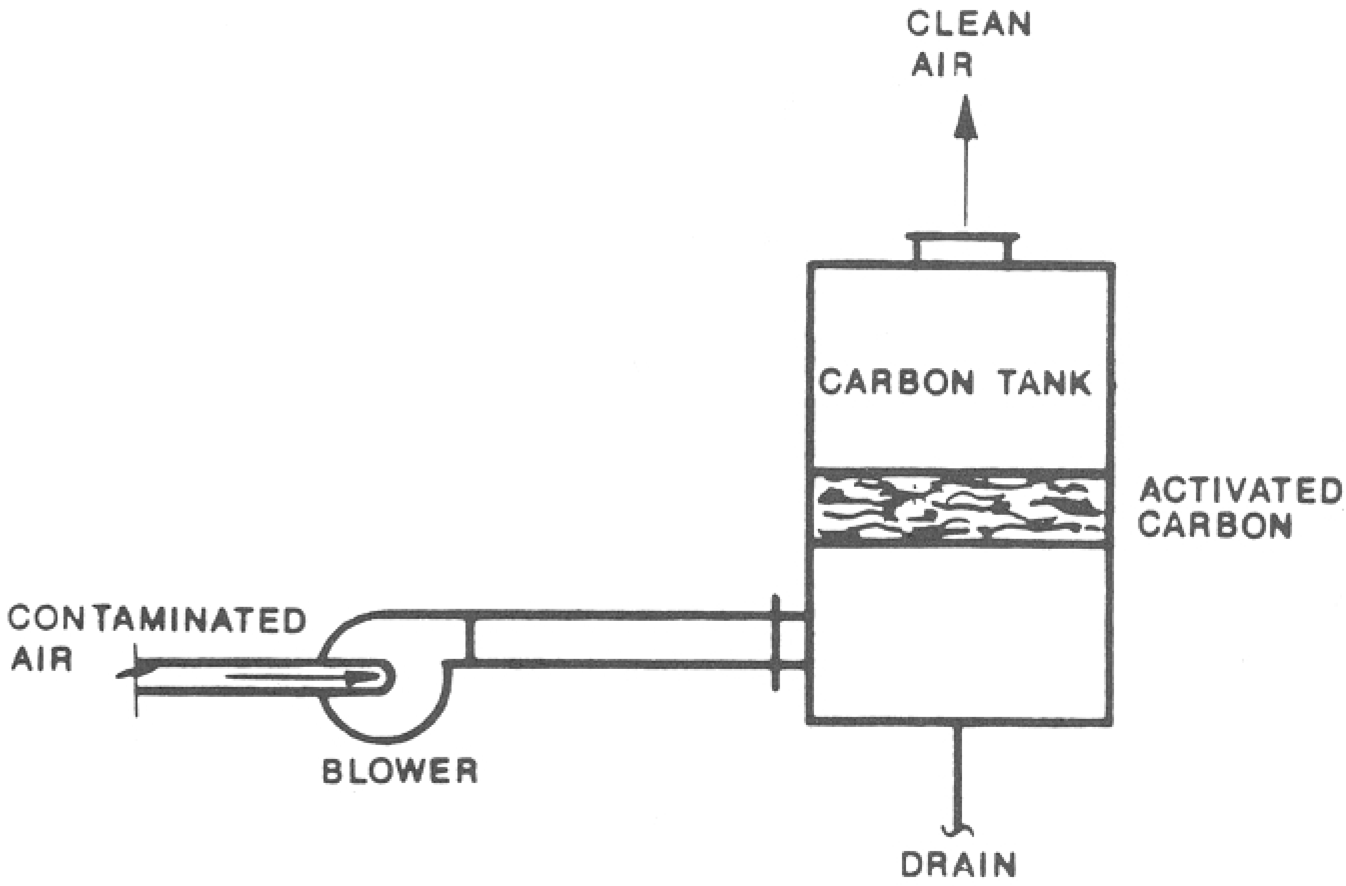
    $3SO_2 + 3H_2O \rightarrow 3H_2SO_3$
  - Stage 1:

    $2CrO_3 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 3H_2O$
  - Stage 2:

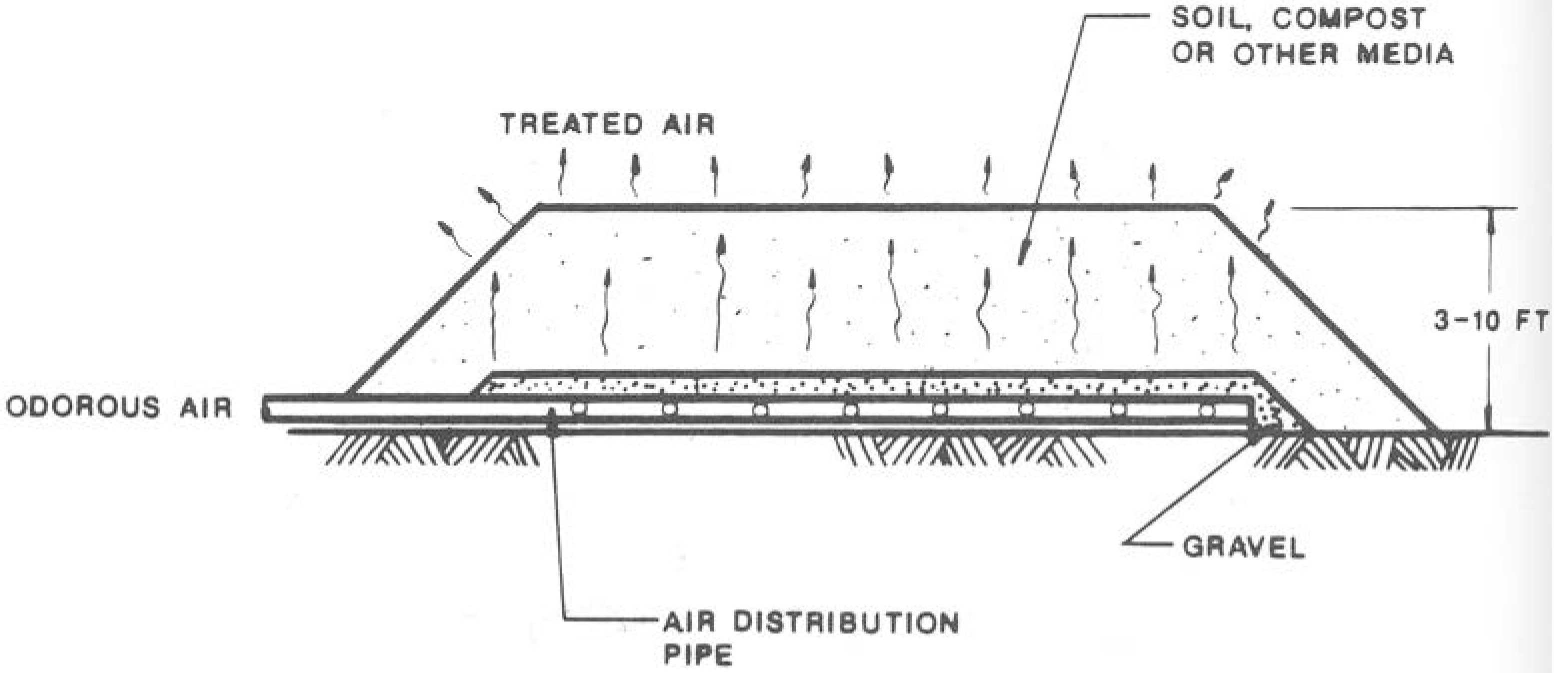
    Lime added to precipitate $Cr(OH)_3$

    $3Ca(OH)_2 + Cr_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Cr(OH)_3$
  - Benefits:
    - Less sludge (stoichiometric requirements in stage 1)
    - Rapid stage 1 reaction (10 to 20 minutes)

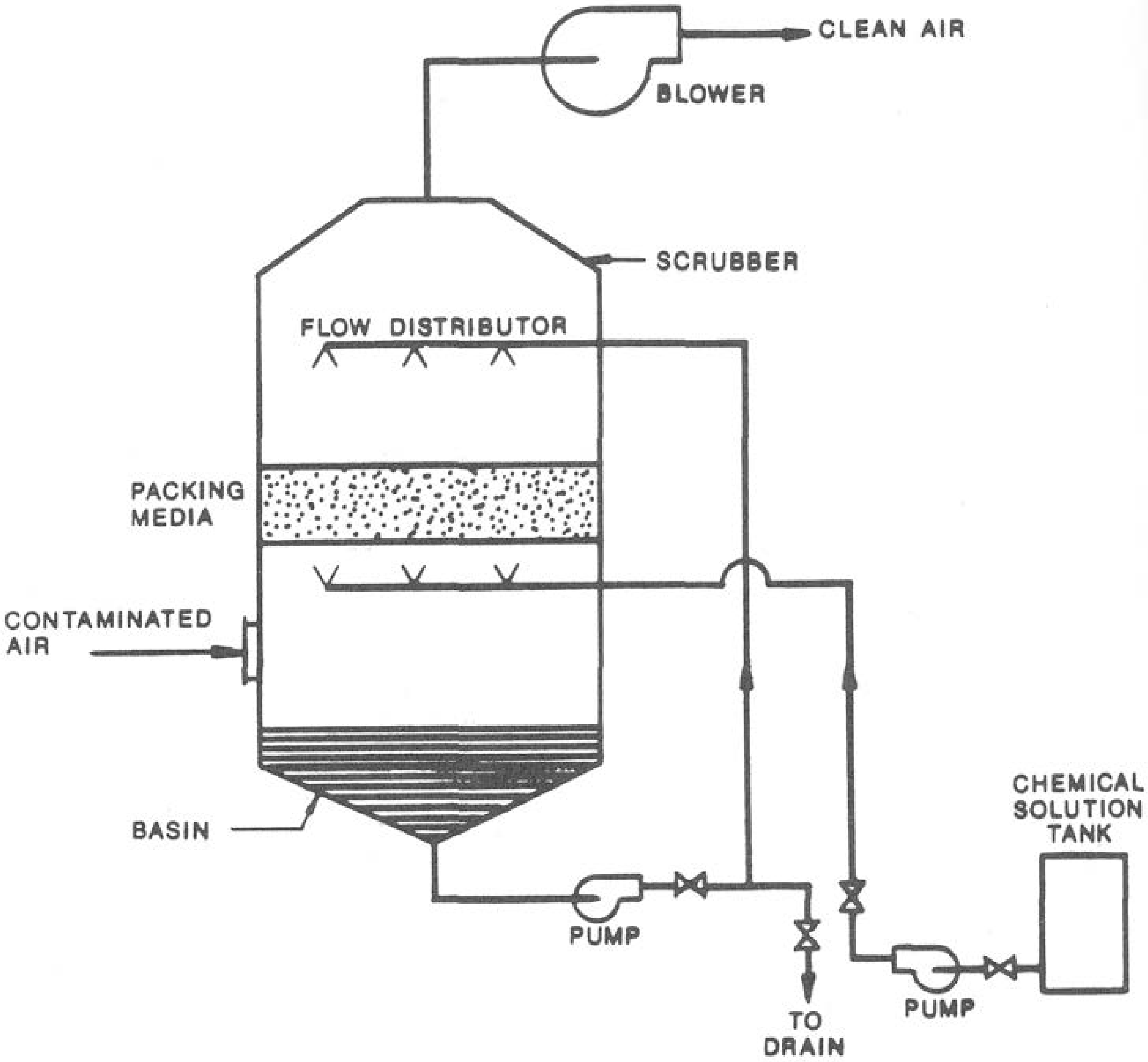
4.5 ODOR CONTROL



Activated carbon adsorption system.



Biological filter odor control system.



Wet packed bed scrubber odor control system.

Methods of odorous air treatment: advantages and disadvantages.

Treatment method	Advantages	Disadvantages
Adsorption systems	Simple operation Reliable and consistent Additives can enhance treatment Can accommodate varying gas flows	Costly media regeneration Adsorbent capacity used rapidly Additives can cause corrosive environment Particulate material can plug media
Biological systems	Simple operation No regenerant chemicals Treat variety of compounds Economical to treat high volume of gas	Require substantial space Reliability sometimes questionable Gas transfer limitations Process control limited Particulate material can plug media Require balanced environmental condition
Combustion systems	Reliable at high temperatures Oxidize compound not treated chemically nor biologically	Costly if dedicated system Can cause problems with incinerator Backup system required when incinerator not in use
Ozonation	High-potency oxidant Simple operation	Costly Experienced significant operating problems Difficult to control dosage High maintenance costs Toxic off-gas if not properly destructed
Wet scrubbers		
Packed beds	Wide-scale use Can economically treat high gas flows High mass-transfer efficiency Effectively handles changes in odorous compound concentrations	Recycle odorous compounds High chemical regenerant usage Can be high maintenance Chemical carry-over in treated gas Applicable to only certain compounds
Mist systems	Low-pressure drop Accommodate high flow rate High mass-transfer efficiency No chemical regenerant recycle	High energy requirements High maintenance Mist carry-over in treated gas Slow response to changing concentrations