Industrial Waste Water Characteristics

by

Dr. D.D. BASU
Former Additional Director, CPCB
&
Advisor, CSE

What is Waste Water?

- Waste Water is Used water that has been adversely affected in quality by anthropogenic influence.

- Waste Water in Industry is of two types :-
    1. Trade Effluent
    2. Sewage

Cont…

- Under Sec. 2(K) of Water Act it states

  " Trade Effluent" includes any liquid, gaseous or solid substance which is discharged from any premises used for carrying on any [industry, operation or process, or treatment or disposal system], other than domestic sewage.

Components of Waste Water Management

- Development of Water Balance
- Characterization of Waste Water
- Approach to Treatment Scheme
- Monitoring and Evaluation
- Treated Effluents Recycling or Disposal.

What are the Consumption Pattern of Water in Industry?

- Make up for the Cooling Water system
- Make for Fire Water
- Feed to Demineralization Plant
- Process Water
- Service Water
- Sanitary Water

TYPICAL EXAMPLE OF WATER USAGE PATTERN

	1	2	3	4	5
Cooling water make-up (m^3/day)	4800 (32.78)	690 (35.57)	2000 (55.04)	2223 (56.4)	21400 (35.91)
Feed to DM plant (m^3/day)	4800 (32.78)	280 (14.43)	840 (23.12)	1080 (27.4)	11200 (18.79)
Process water (m^3/day)	1200 (8.2)	290 (14.94)	271 (7.46)	271 (7)	15000 (25.17)
Service water (m^3/day)	2400 (16.39)	300 (15.46)	523 (14.39)	250 (6.3)	7000 (11.74)
Sanitary water (m^3/day)	1440 (9.84)	380 (19.58)	--	120 (2.9)	5000 (8.39)
Total (m^3/day)	14640 (100)	1940 (100)	3634 (100)	3944 (100)	59600 (100)

What are the Sources of Waste Water in Industry?

- Cooling Tower Blow down.
- D.M. Plant regeneration Waste Water and Boiler Blow Down.
- Process Waste Water
- Service Water and Strom Water.
- Sanitary Waste Water.

TYPICAL EXAMPLE OF WASTEWATER GENERATION

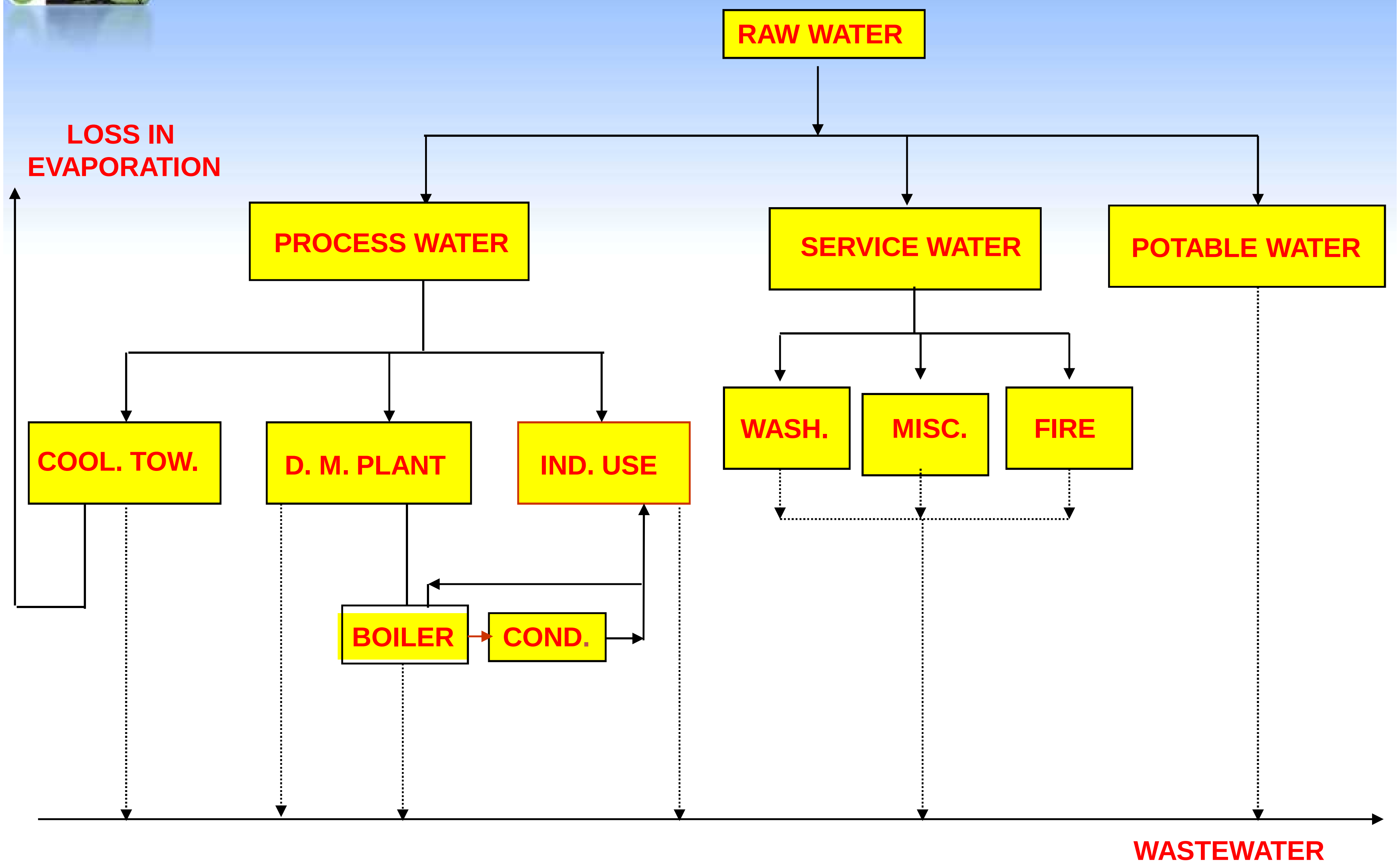
S. No.		Petrochemicals complex	Phenol cumene plant	Caprolactum plant	Large petrochemical complex
1	Cooling tower blow-down	50	*	17	11200
2	DM plant regeneration wastewater	50	3	-	1400
3	Process wastewater	110	12	11	14000
4	Service wastewater	90	13	22	(See note 1)
5	Sanitary wastewater	40	8	-	2500
Total		340	36	50	29100

NOTE:

* - Industry claims insignificant blow-down.

1. Service wastewater quantity is included in the process wastewater

WATER BALANCE



Cooling Water Management

- Functions of Cooling Tower:-

  Cooling Tower regulated temperature by dissipating heat from recirculating water used to cool chillers, air conditioning equipments or other process equipment. Heat is rejected primarily through evaporation. Therfore, by design cooling tower consumes significant amounts of water.

Factors for loss of water

- Evaporation – Major Source
- Drift – Water loss as a mist or small droplets
- Blow down or bleed off – control of concentration of total dissolved solids.
- Basin leaks or overflow – properly operated cooling tower should not have basin leaks or overflow. Good maintenance of system value and basin level control system is required.

The sum of water loss can be replaced by make up water

Make up water = Evaporation + Blow down + Drift

Concentration Ratio - The Key Parameter

A Key parameter used to evaluate cooling tower operations is concentration ratio.

$$\text{Concentration ratio} = \frac{\text{Concentration of TDS in Blowdown water}}{\text{Concentration of TDS in make up water}}$$

If Concentration ratio is high, water efficiency will be high but scaling, corrosion will be high.

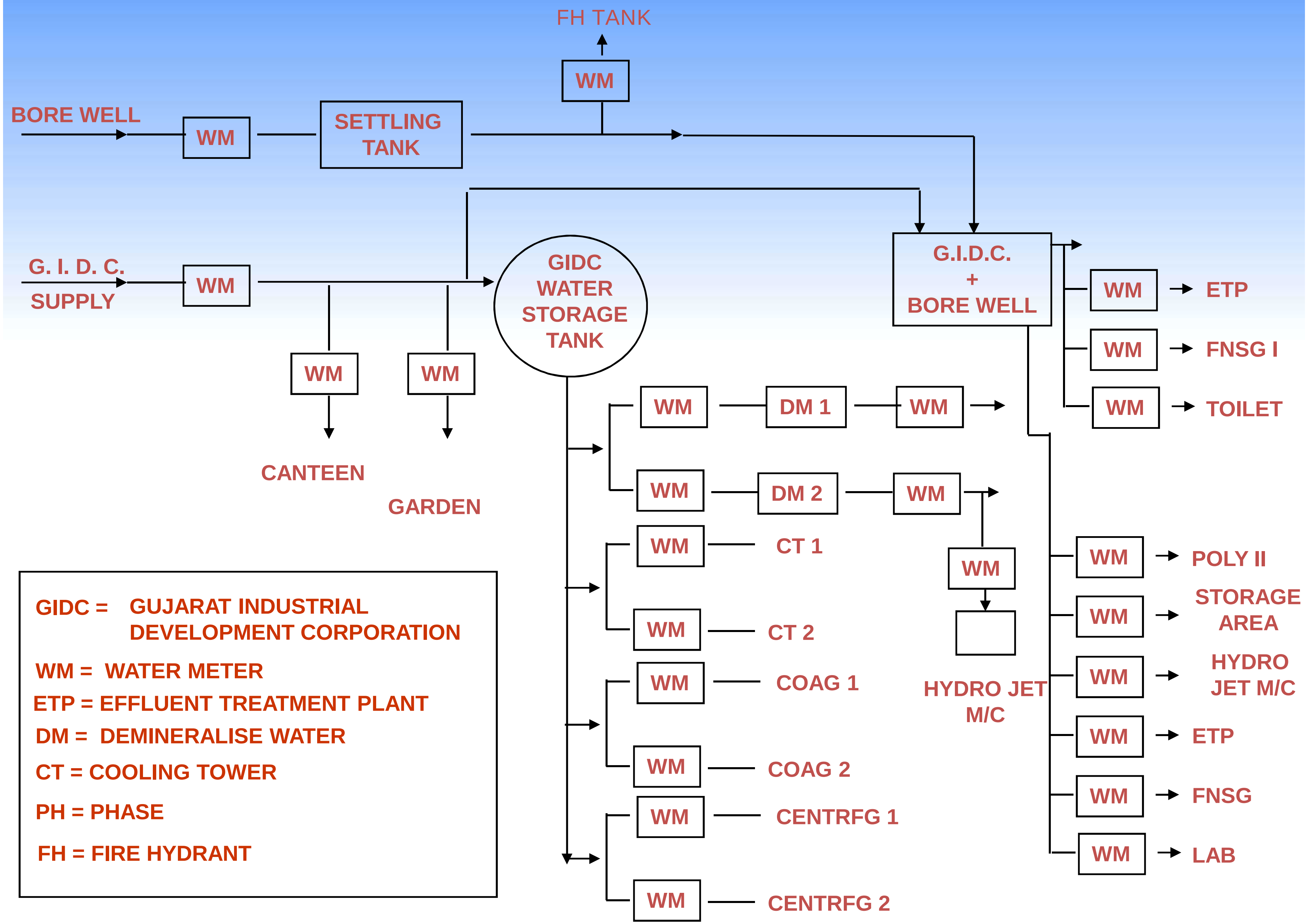
Water quality and Cycle of Concentration

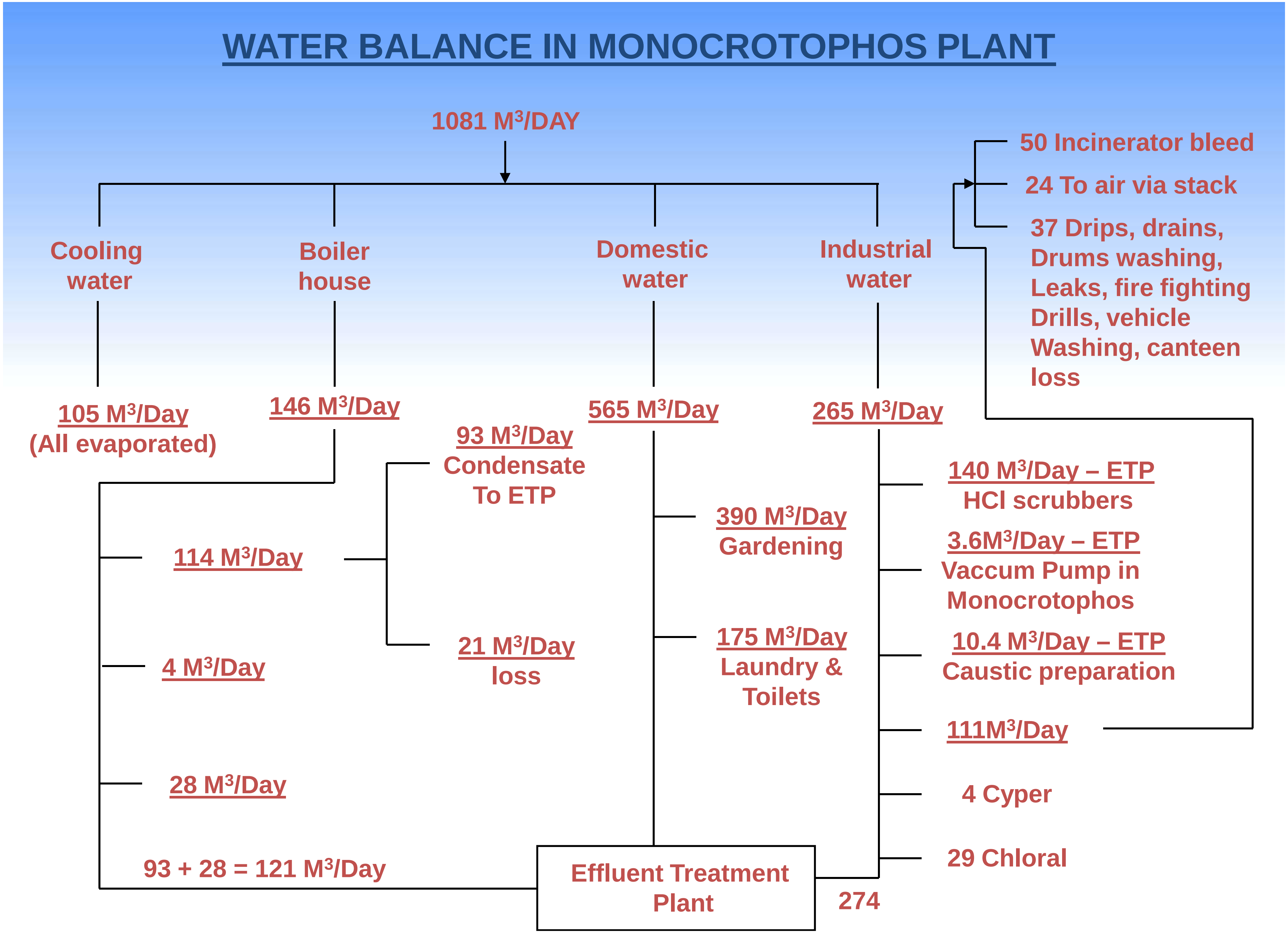
Water Status	Conductivity	Total Hardness mg/l as coc3	Calcium Hardness	Total Alkalinity	PH
Makeup water	600	300	150	200	7.5
2 coc	1200	600	300	400	8.0
4 coc	2400	1200	600	800	8.5
6 coc	3600	1800	900	1200	6.6
10 coc	6000	3000	1800	2000	9.0
This Indicates 4 to 6 cycle shall be the ideal coc for cooling tower recirculation source guidelines managing water cooling system for owners, operators, environmental managers SAN JOSE / SANTA CLARA Water pollution control Plants					

Best Management System

- Reuse of condensate water which has low minerals content and typically is generated in good amount when cooling tower load is high.
- Reuse and Recycle of treated effluent after appropriated treatment.
- Use softening plant to reduce total dissolved solids in makeup water.
- Use Treated Sewage as makeup water
- Install real time conductivity measurement to both raw water, makeup and blowdown water.
- Check and maintenance basin leaks or overflow
- Avoid ground water source as cooling tower makeup.

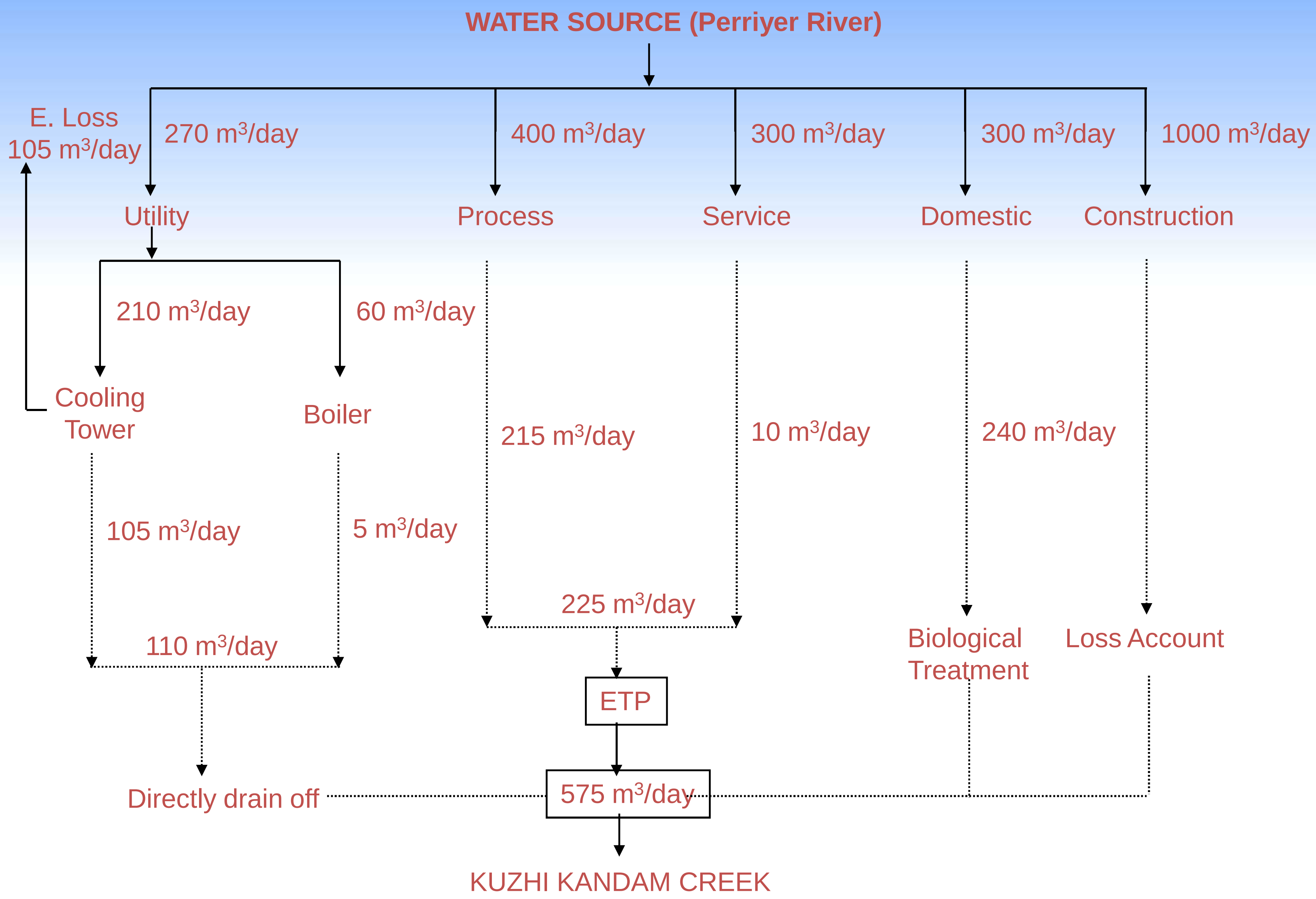
WATER DISTRIBUTION NETWORK





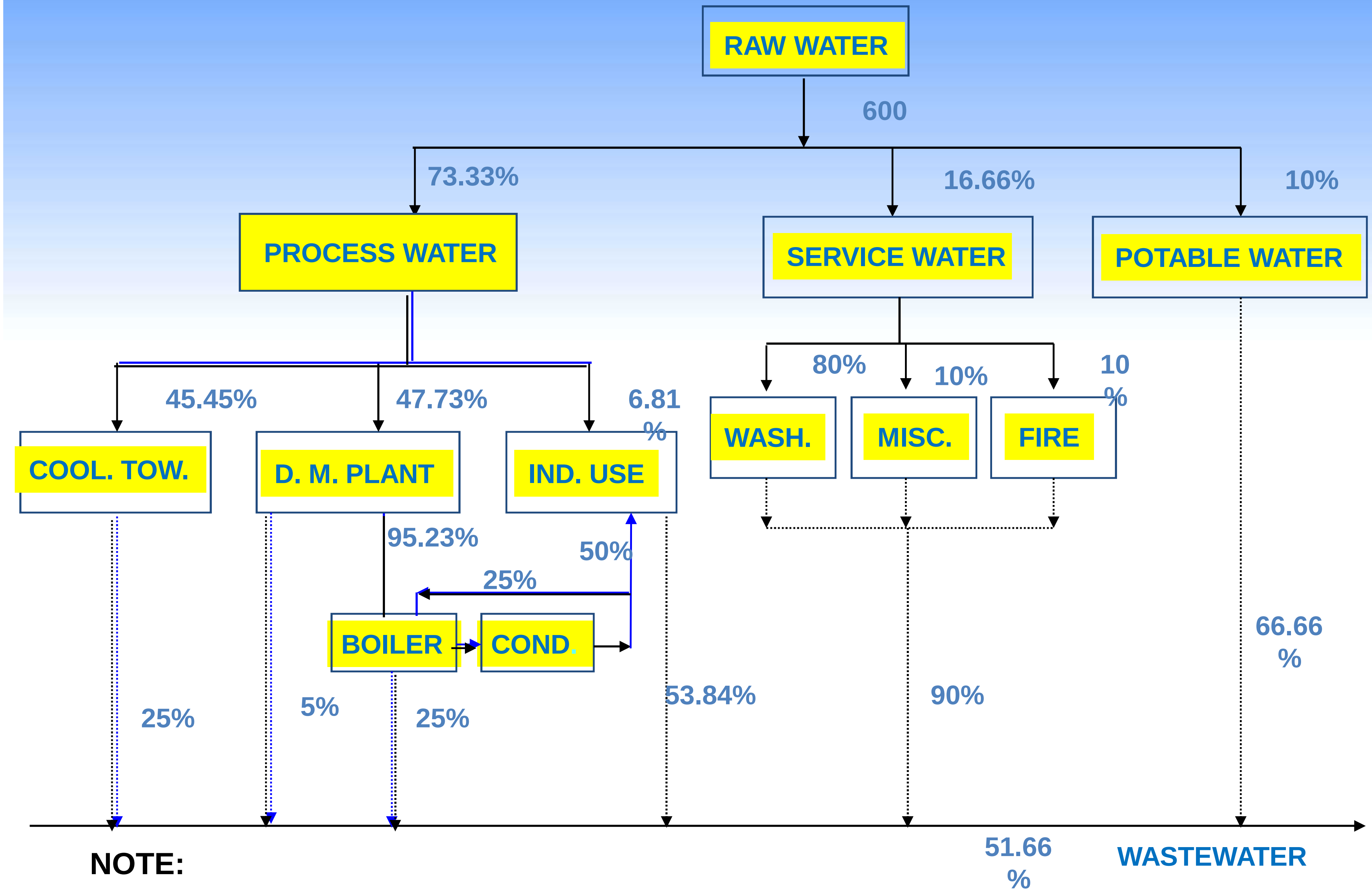
WATER BALANCE IN MONOCROTOPHOS PLANT
1081 M3/DAY
Cooling water
Boiler house
Domestic water
Industrial water
50 Incinerator bleed
24 To air via stack
37 Drips, drains, Drums washing, Leaks, fire fighting Drills, vehicle Washing, canteen loss
105 M3/Day (All evaporated)
146 M3/Day
565 M3/Day
265 M3/Day
93 M3/Day Condensate To ETP
140 M3/Day – ETP HCl scrubbers
390 M3/Day Gardening
114 M3/Day
3.6M3/Day – ETP Vaccum Pump in Monocrotophos
21 M3/Day loss
175 M3/Day Laundry & Toilets
4 M3/Day
10.4 M3/Day – ETP Caustic preparation
111M3/Day
28 M3/Day
4 Cyper
29 Chloral
93 + 28 = 121 M3/Day
Effluent Treatment Plant
274

WATER BALANCE IN HIL PLANT



Thumb Rule for Water Balance

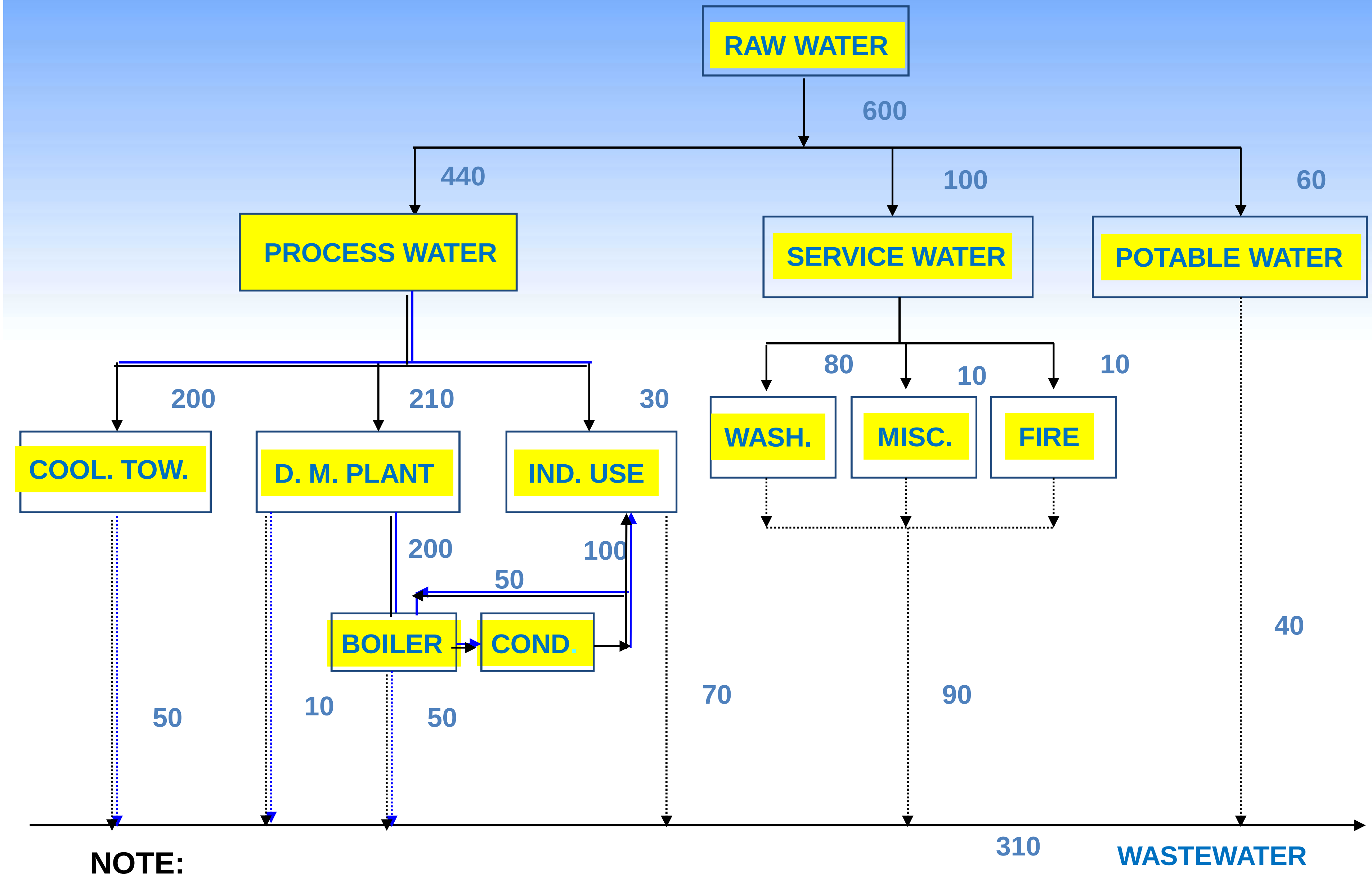
MASS BALANCE OF WATER CONSUMPTION AND EFFLUENT GENERATION



NOTE:

All the values in cubic meter / hour.

MASS BALANCE OF WATER CONSUMPTION AND EFFLUENT GENERATION



NOTE:

All the values in cubic meter / hour.

WASTEWATER CHARACTERISATION

WASTE WATER CHARACTERIZATION

Total solid (TS)

Residue after evaporation and dried at 103°- 105° C

Total volatile solids (TVS)

Those solids which are burnt off or volatilized when the TS are ignited

Total fixed solids (TFS)

Residue that remains after TS is ignited [500 + 50°C]

TVS = TS - TFS

Total suspended solids **(TSS)**

(Portion of TS retained at filter paper and dried at 105°C)

Volatile Suspended Solids (VSS)

TSS when burnt off at 500° ± 50°C

Fixed Suspended Solids (FSS)

Residue remains when TSS are ignited [500° ± 50°C]

VSS = TSS - FSS

Total dissolved solids **(TDS)**

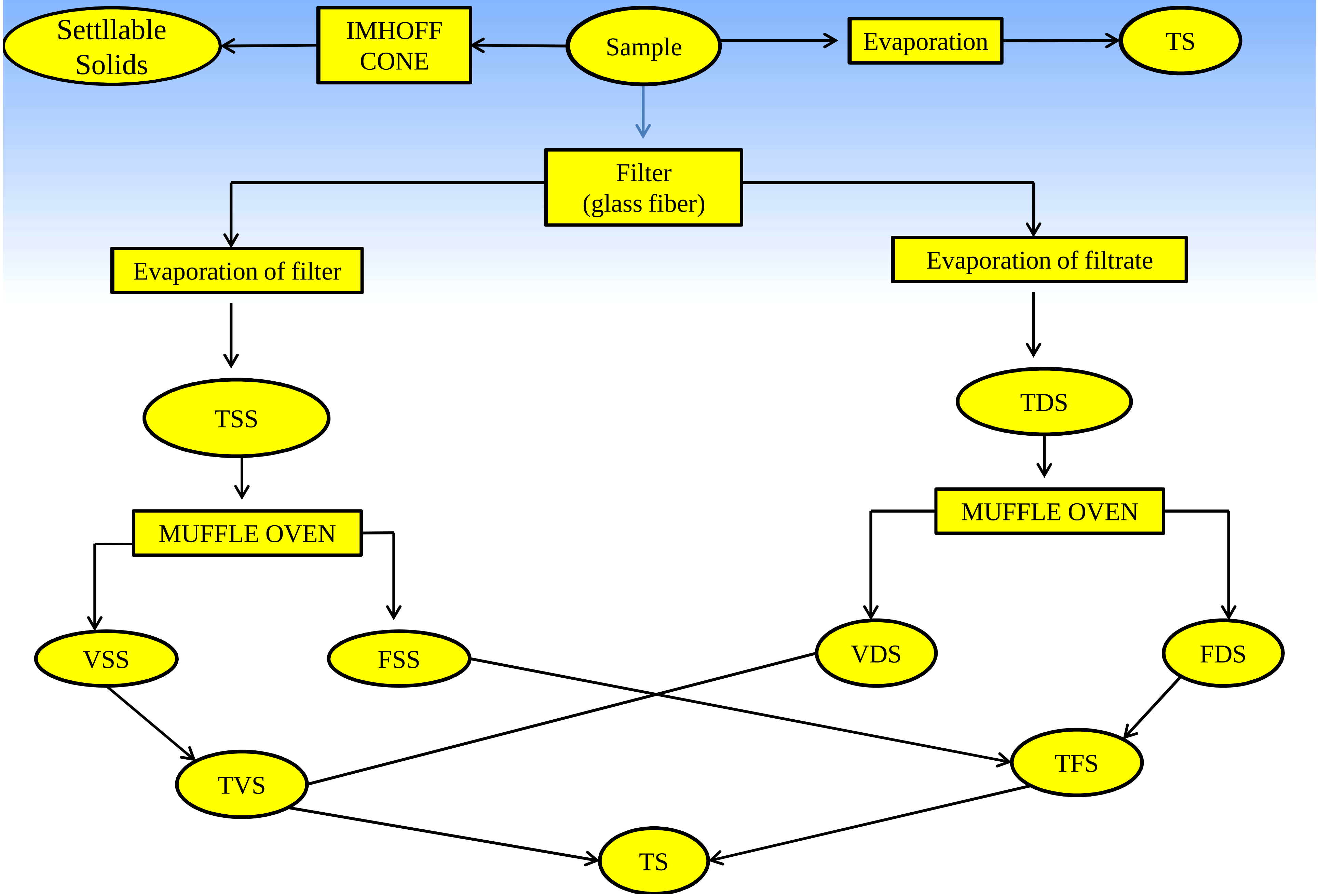
Total Volatile dissolved solids VDS (burnt off at 500° ± 50°C)

Fixed Dissolved Solids (FDS)

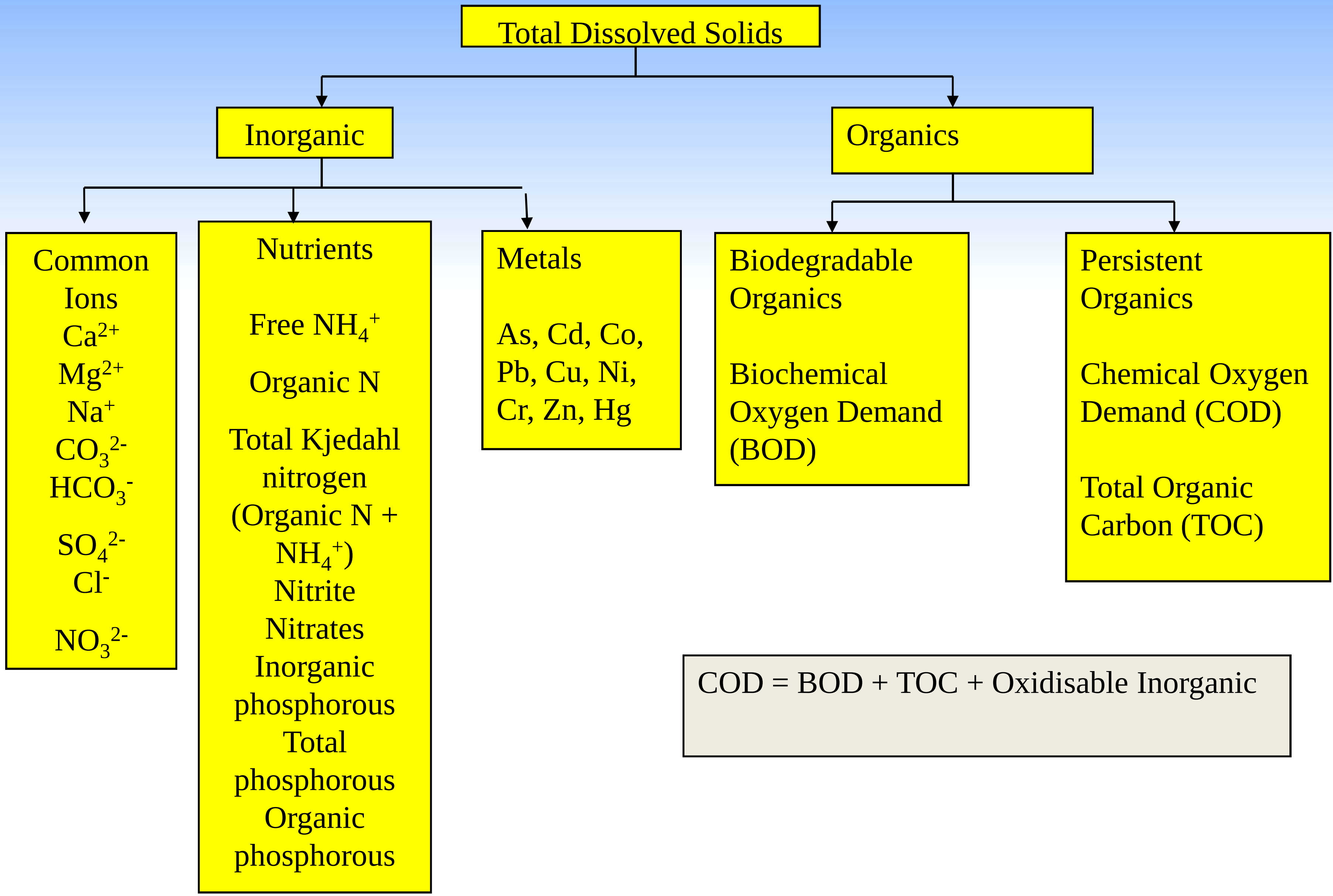
Residue remains when TDS is ignited at [500° ± 50°C]

TDS = TS - TSS

INTER RELATIONSHIP OF SOLIDS



CHEMICAL CHARACTERIZATION OF TOTAL DISSOLVED SOLIDS



COD = BOD + TOC + Oxidisable Inorganic

EXAMPLE 2-4 Analysis of Solids Data The following test results were obtained for a wastewater sample taken at the headworks to a wastewater-treatment plant. All of the tests were performed using a sample size of 50 mL. Determine the concentration of the total solids, total volatile solids, suspended solids, volatile suspended solids, total dissolved solids and total volatile dissolved solids. The samples used in the solids analysis were all either evaporated, dried or ignited to constant weight.

Tare mass of evaporating dish = 53.5433 g
Mass of evaporating dish + residue after evaporation at 105°C = 54.5794 g
Mass of evaporating dish + residue after ignition at 550°C = 53.5625 g
Tare mass of Whatman GF/C filter after drying at 105°C = 1.5433 g
Mass of Whatman GF/C filter and residue after drying at 105°C = 1.5554 g
Mass of Whatman GF/C filter and residue after ignition at 550°C = 1.5476 g

Solution

1. **Determine of total solids**

$$\text{TS} = \frac{(\text{mass of evaporatin g dish plus residue, g}) - (\text{mass of evaporatin g dish, g})}{\text{sample size, L}}$$

$$TS = \frac{[(53.5794 - 53.5433)g](10^3 mg/g)}{0.050L} = 722 mg/L$$

2. Determine total volatile solids

$$TVS = \frac{(mass\ of\ evaporating\ \text{dish} + \text{residue}, \text{g}) - (mass\ \text{of evaporating dish} + \text{residue after ignition, g})}{sample\ \text{size, L}}$$

$$TVS = \frac{[(53.5794 - 53.5625)g](10^3\ mg/g)}{0.050\,L} = 338\,mg/L$$

3. Determine the total suspended solids

$$TSS = \frac{(residue\ \text{on filter after drying, g}) - (\text{tare mass of filter after drying, g})}{sample\ \text{size, L}}$$

$$TSS = \frac{[(1.5554 - 1.5433)g](10^3\ mg/g)}{0.050\ L} = 242\ mg/L$$

4. Determine the volatile suspended solids

$$VSS = \frac{(\textit{residue} \text{ on filter after drying}, \text{g}) - (\textit{residue} \text{ on filter after ignition}, \text{g})}{\textit{sample} \text{ size, L}}$$

$$VSS = \frac{[(1.5554 - 1.5476)g][(10^3 mg/g)]}{0.050L} = 156 mg/L$$

5. Determine the total dissolved solids

TDS = TS – TSS = 722 – 242 = 480 mg/L

6. Determine the volatile dissolved solids

VDS = TVS – VSS = 338 – 156 = 182 mg/L

Example 2-2 Checking the accuracy of analytical measurements The following analysis has been completed on a filtered effluent, from an extended aeration wastewater-treatment plant, that is to be used for landscape watering. Check the accuracy of the given analysis to check if the analysis is sufficiently accurate, based on the criteria given above:

Cation	Conc., mg/L	Anion	Conc., mg/L
Ca^{++}	82.2	HCO_3^-	220.0
Mg^{++}	17.9	SO_4^{--}	98.3
Na^+	46.4	Cl^-	78.0
K^+	15.5	NO_3^-	25.6

Solution 1. Prepare a cation-anion balance

Cation	Conc., mg/L	mg/ meq	meq/L	Anion	Conc., mg/L	mg/ meq	meq/L
Ca^{++}	82.2	20.04	4.10	HCO_3^-	220.0	61.02	3.61
Mg^{++}	17.9	12.15	1.47	SO_4^{--}	98.3	48.03	2.05
Na^+	46.4	23.00	2.02	Cl^-	78.0	35.45	2.20
K^+	15.5	39.10	0.40	NO_3^-	25.6	62.01	0.41

$$\sum cations = 7.99 \qquad \sum anions = 8.7$$

2. Check the accuracy of the cation anion balance using eqs (2-5)

$$\text{Percent difference} = 100 \text{ X } \frac{\left(\sum \text{cations} - \sum \text{anions}\right)}{\left(\sum \text{cations} + \sum \text{anions}\right)}$$

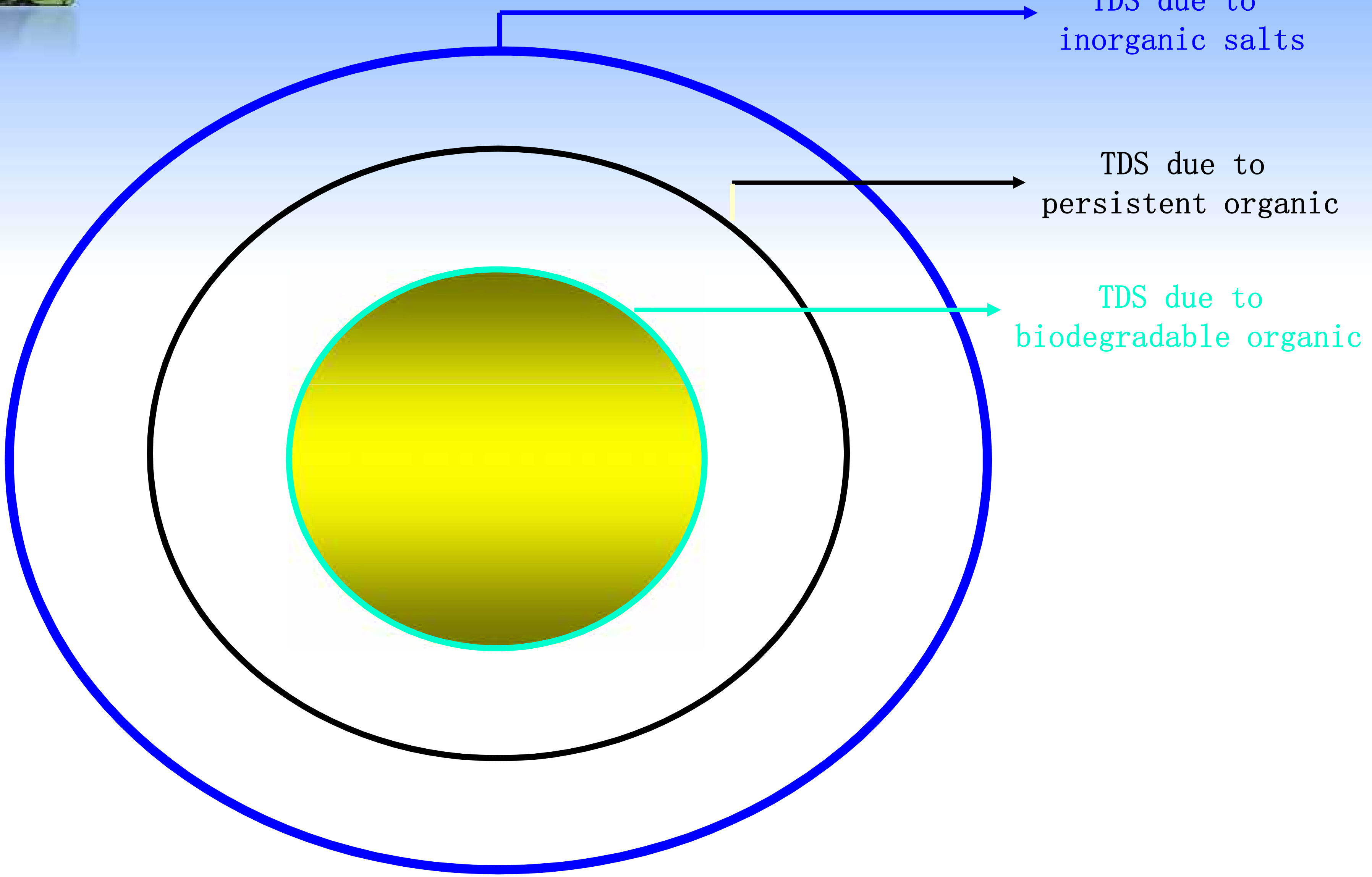
$$\text{Percent difference} = 100 \text{ X } \frac{(7.99 - 8.27)}{(7.99 + 8.27)} = -1.27\%$$

For a total anion concentration between 3 and 10 meq/L, the acceptable difference must be equal to or less than 2% (see table above); thus, the analysis is of sufficient accuracy.

Problems

S.No.	Cation	Sample	Anion	Sample
1.	Ca^{2+}	121.3	HCO_3^-	280
2.	Mg^{2+}	36.2	SO_4^{2-}	116
3.	Na^+	8.1	Cl^-	61
4.	K^+	12	NO_3^-	15.6

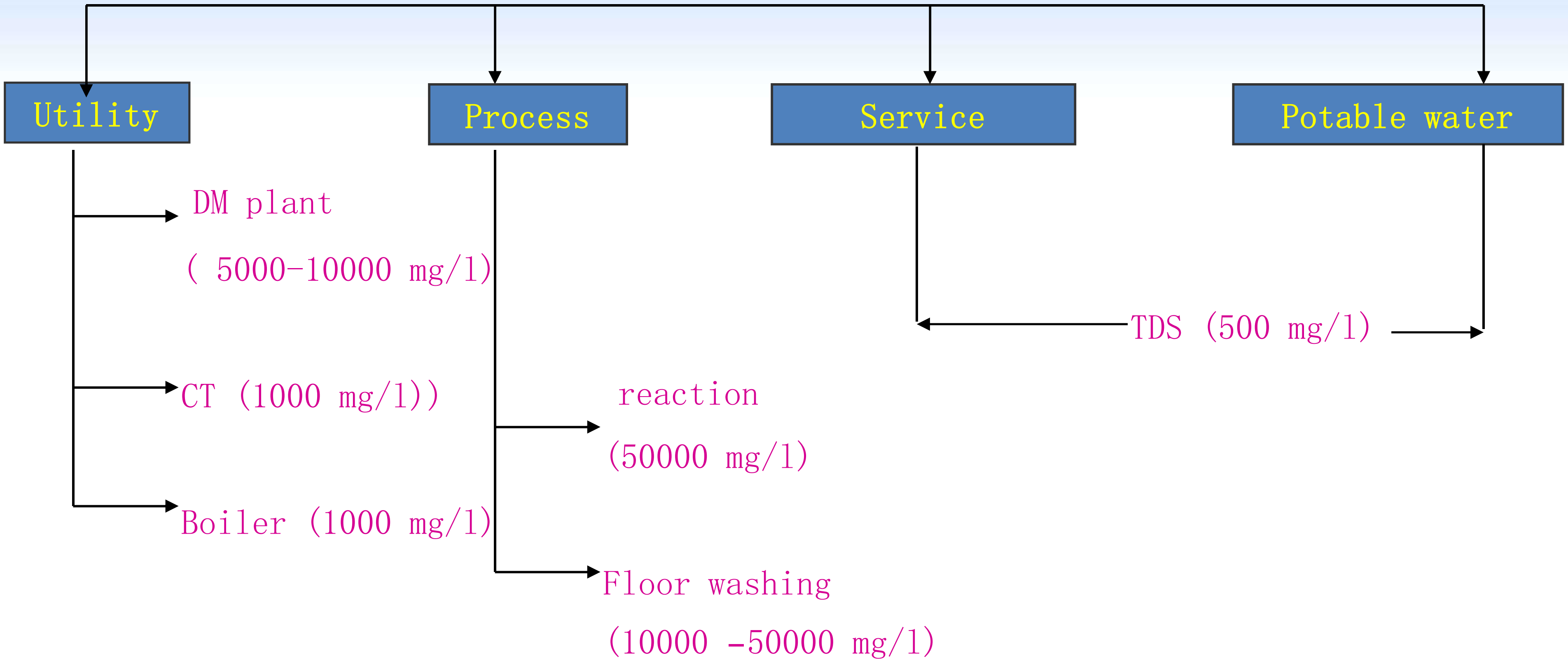
TDS / BOD / COD RELATIONSHIP



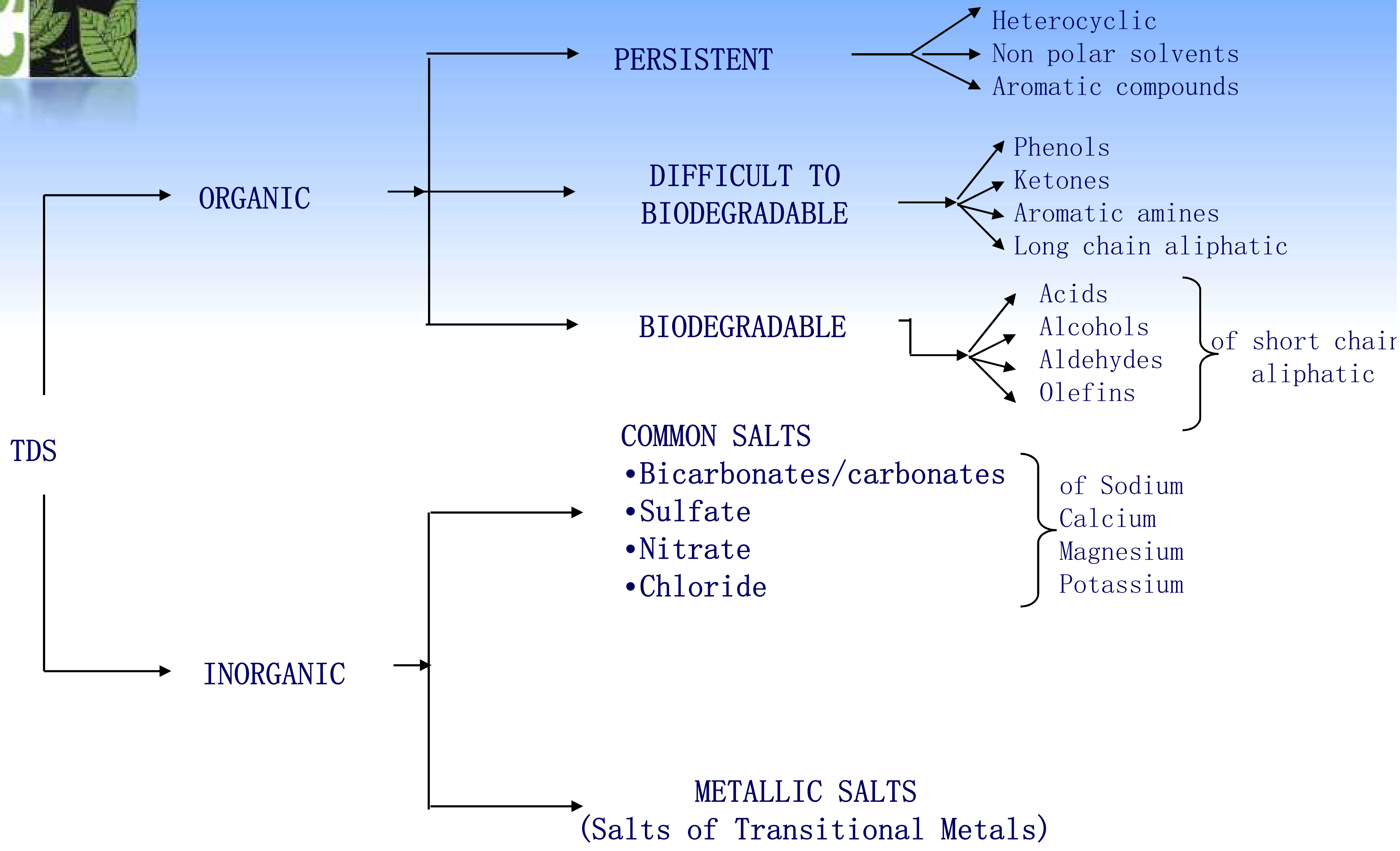
GENESIS OF TDS

- Chemical reaction in the process
- Use of salts as preserving agent
- The utilities provided in the industry
  such as DM plant, boiler (blow down)
  and cooling tower (blow down)

TDS in effluent streams arising from Synthetic organic processing Industry



NATURE OF TOTAL DISSOLVED SOLIDS



Strategies for management of TDS in effluents

1. In plant Control measures

   - process modifications
   - Promotion of 4-R concept

2. Plant practices

   - Segregation of streams
   - Characterization of streams

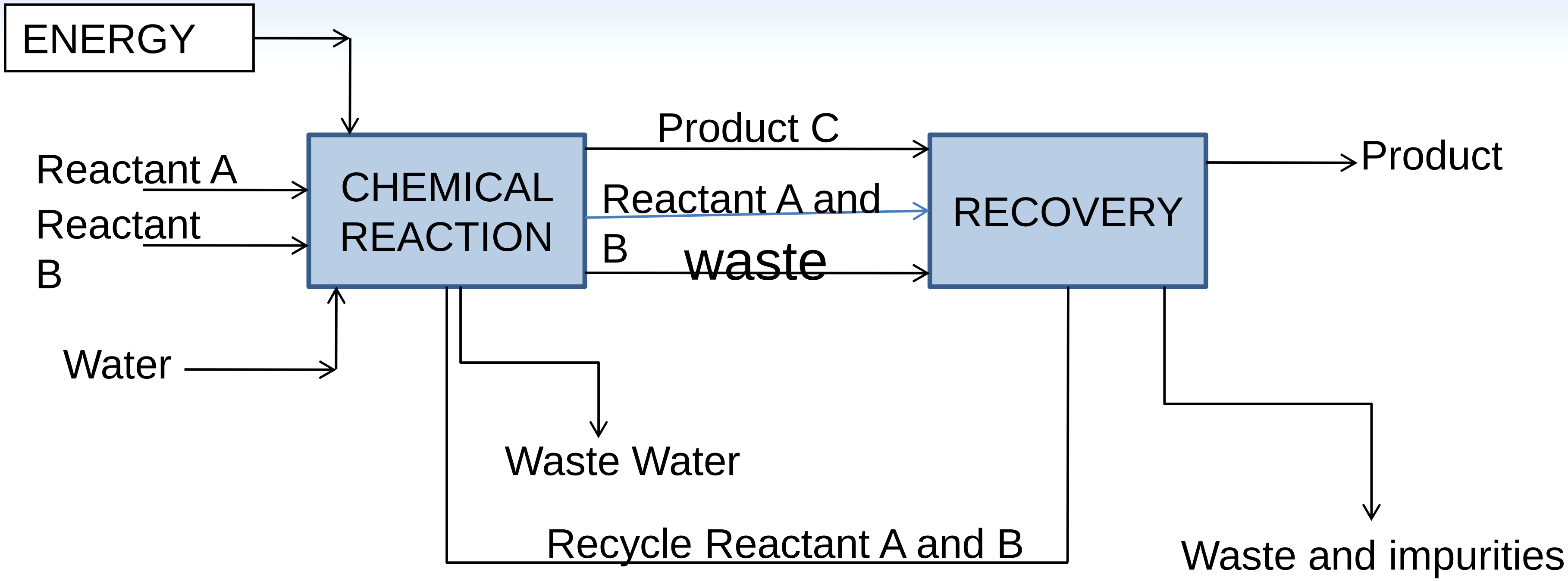
UNDER STANDING WASTE GENERATION FROM INDUSTRIAL OPERATION

TYPES OF INDUSTRIES

Processing	Synthesis	Inorganic chemicals
• **Oil refinery**	• **Bulk drug**	• **Soda ash**
• **Petrochemical**	• **Pesticides**	• **Chloro-alkali**
• **Milk Dairies**	• **Basic organic chemicals**	• **Fertilizers**
• **Sugar & Distillaries**	• **Paints**	
• **Agro Based Industries**	• **Dye and dye intermediates**	

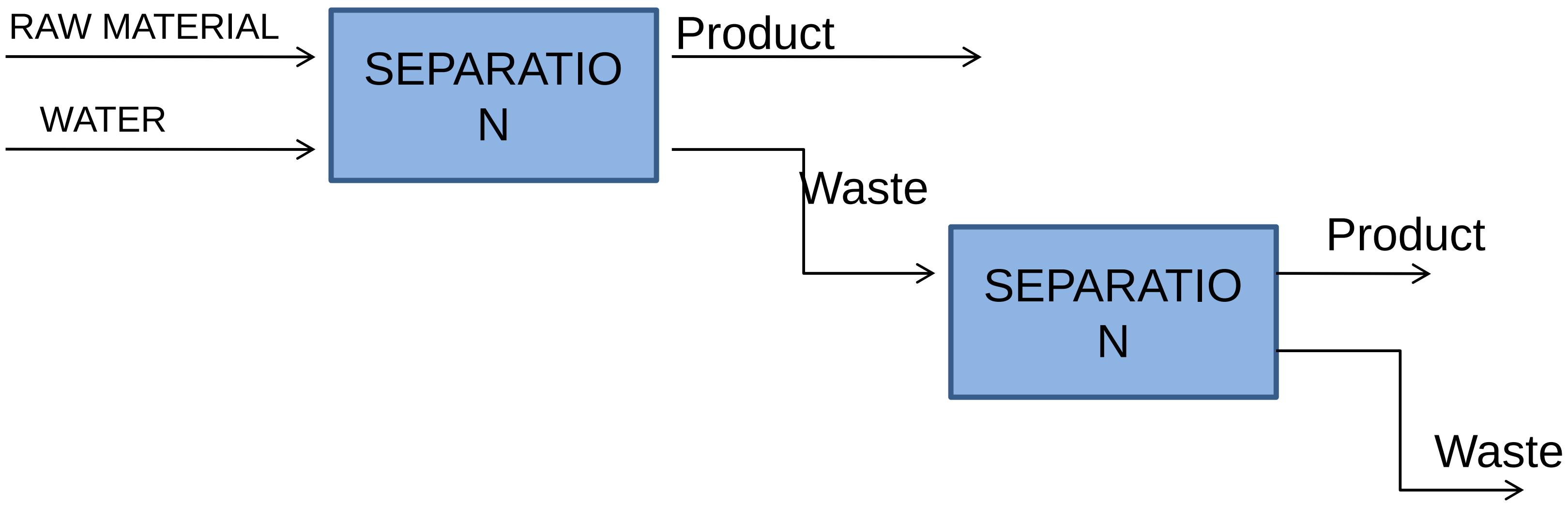
Waste generation from system

- System 1: Production of New Product (SYNTHESIS)



Waste generation from system

- System 2: Processing Industry

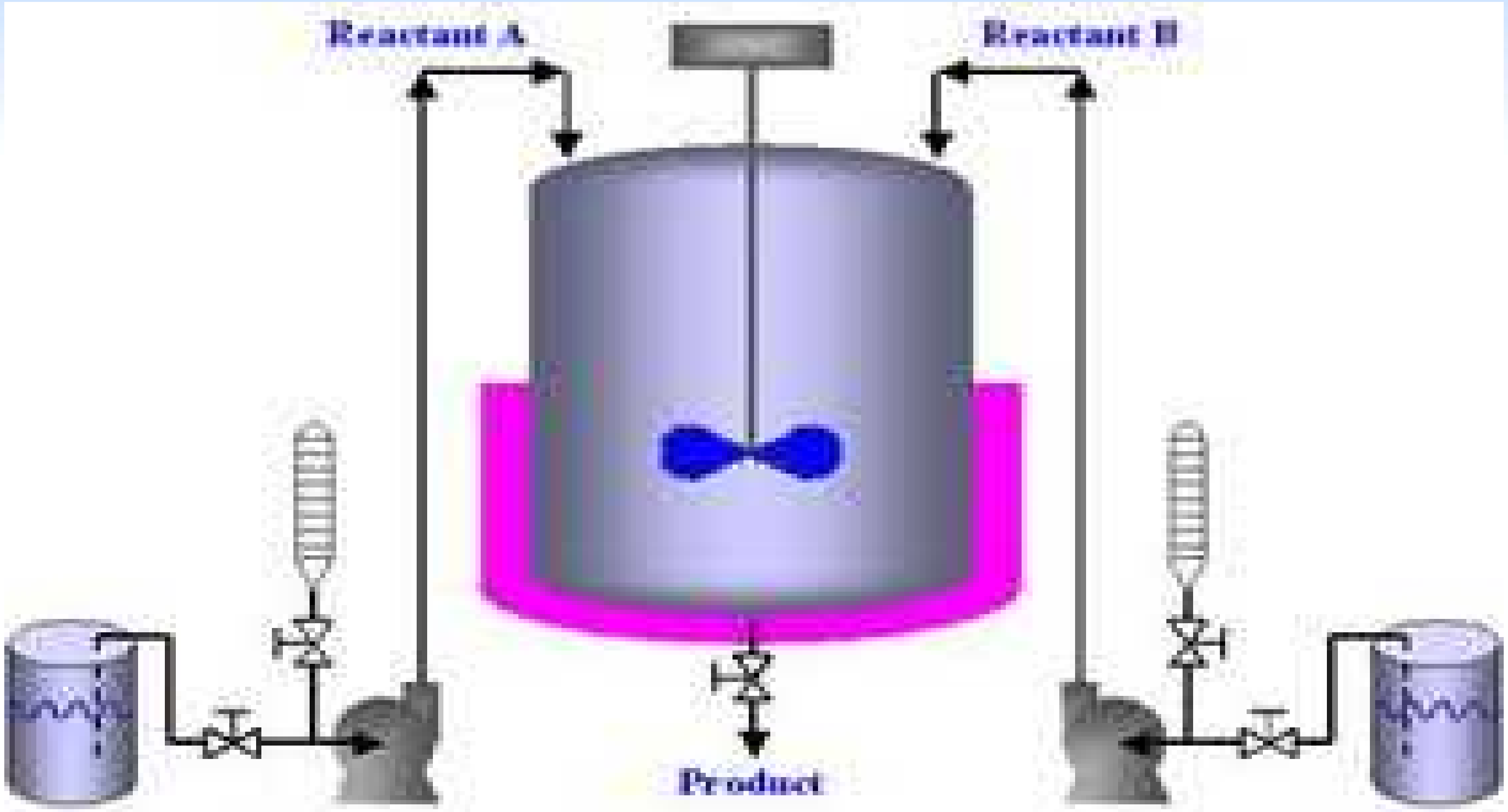


Types of Reactors

Batch Process

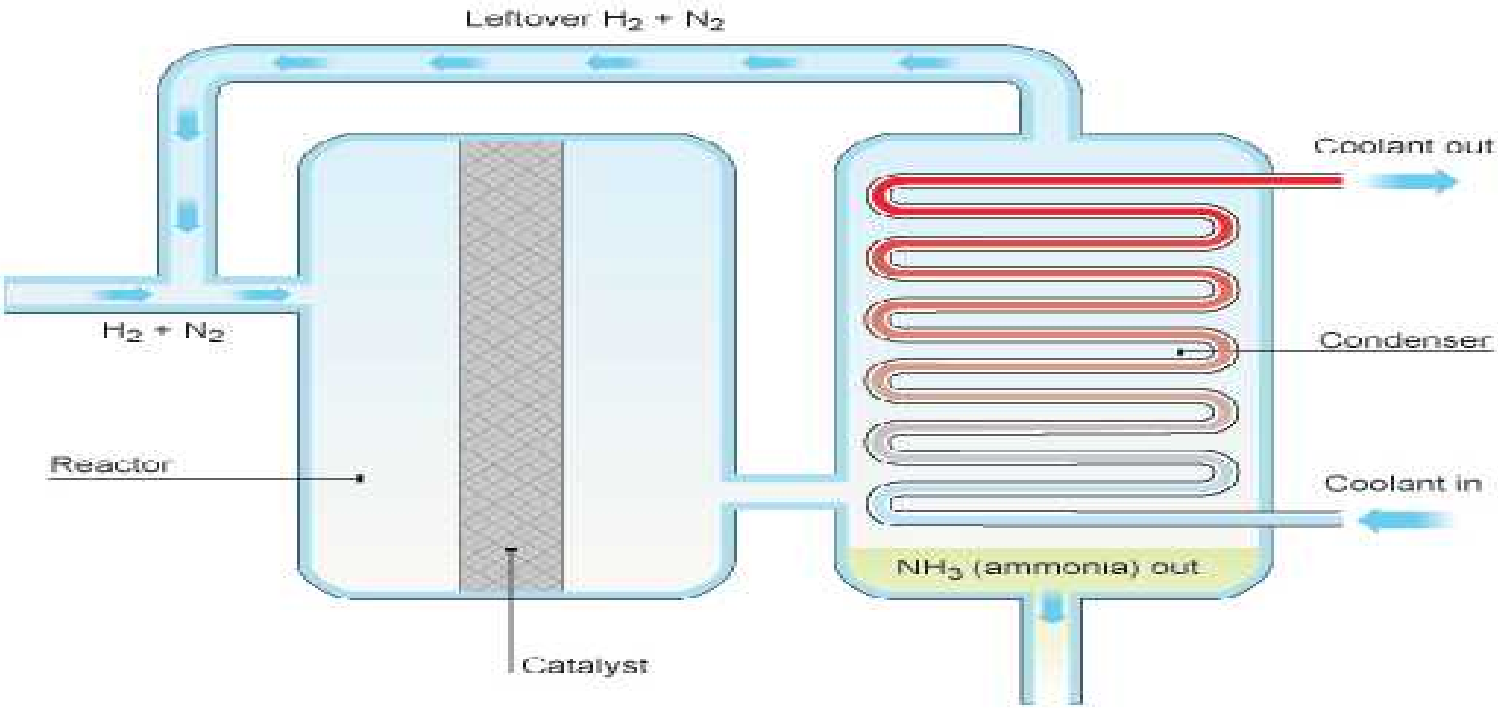
Manufacturing products or treating materials in batches, by

passing the output of one process to subsequent processes.



Continuous Process

Continuous process is used to manufacture, produce, or process materials without interruption. The materials, either dry bulk or fluids that are being processed are continuously in motion, undergoing chemical reactions or subject to mechanical or heat treatment.



UNIT OPERATION

- Unit Operation

In chemical engineering and related fields, a **unit operation** is a basic step in a process. Unit operations involve bringing a physical change such as separation, crystallization, evaporation, filtration etc. For example, in milk processing, homogenization, pasteurization, chilling, and packaging are each unit operations which are connected to create the overall process. A process may have many unit operations to obtain the desired product.

UNIT OPERATION

Chemical engineering unit operations consist of five classes:

- ✖ Fluid flow processes, including fluids transportation, filtration, solids fluidization
- ✖ Heat transfer processes, including evaporation, condensation
- ✖ Mass transfer processes, including gas absorption, distillation, extraction, adsorption, drying
- ✖ Thermodynamic processes, including gas liquefaction, refrigeration
- ✖ Mechanical processes, including solids transportation, crushing and pulverization, screening and sieving

UNIT PROCESS

- Unit Process
- A **Unit Process** is a step in manufacturing in which chemical reaction takes place, *e.g*, the oxidation of paraxylene to terephthalic acid is a unit process, the hydrogenation of vegetable oil to ghee is a unit process.

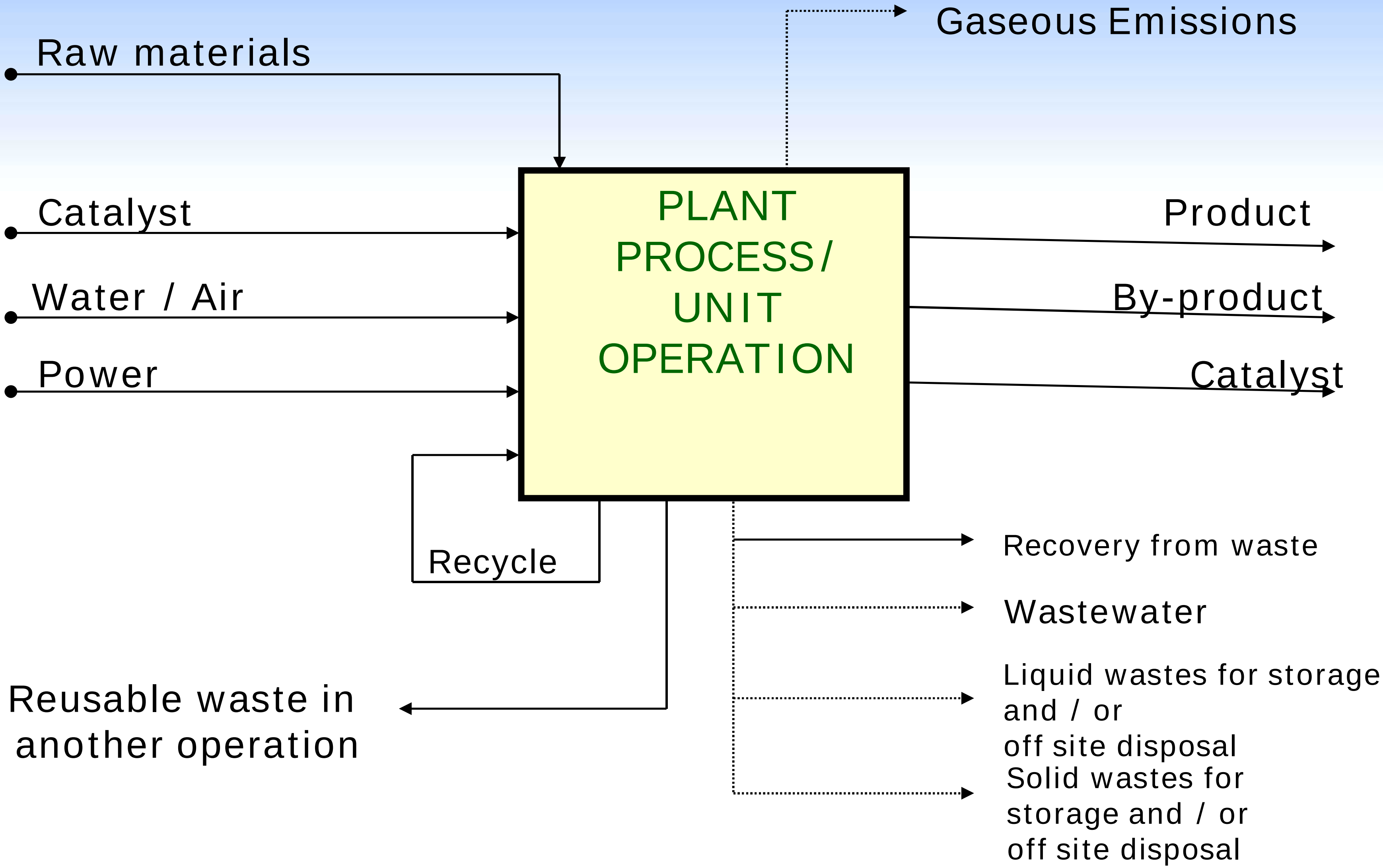
For example

- Alkylation
- Carboxylation
- Acetylation

UNIT PROCESS

- ✖Molecular Condensation
- ✖Cyclisation
- ✖Dehydration
- ✖Halogenation
- ✖Oxidation
- ✖Sulphonation
- ✖Nitration
- ✖Amination

PICTORIAL REPRESENTATION OF UNIT OPERATION/PROCESS



Best Practicable Approach to Waste Water Characterization and Treatment Scheme

IDENTIFICATION OF WASTERWATER STREAMS
CAPTAN – A Case Study

- Step 1 – **Chlorination** of Carbon Disulphide

$CS_2 + 6HCl + 4H_2O + 5\ Cl_2 \rightarrow 6HCl + H_2SO_4 + 6HCl + CSCl_4$

- Step 2 – **Washing & Dilution** of **$CSCl_4$**

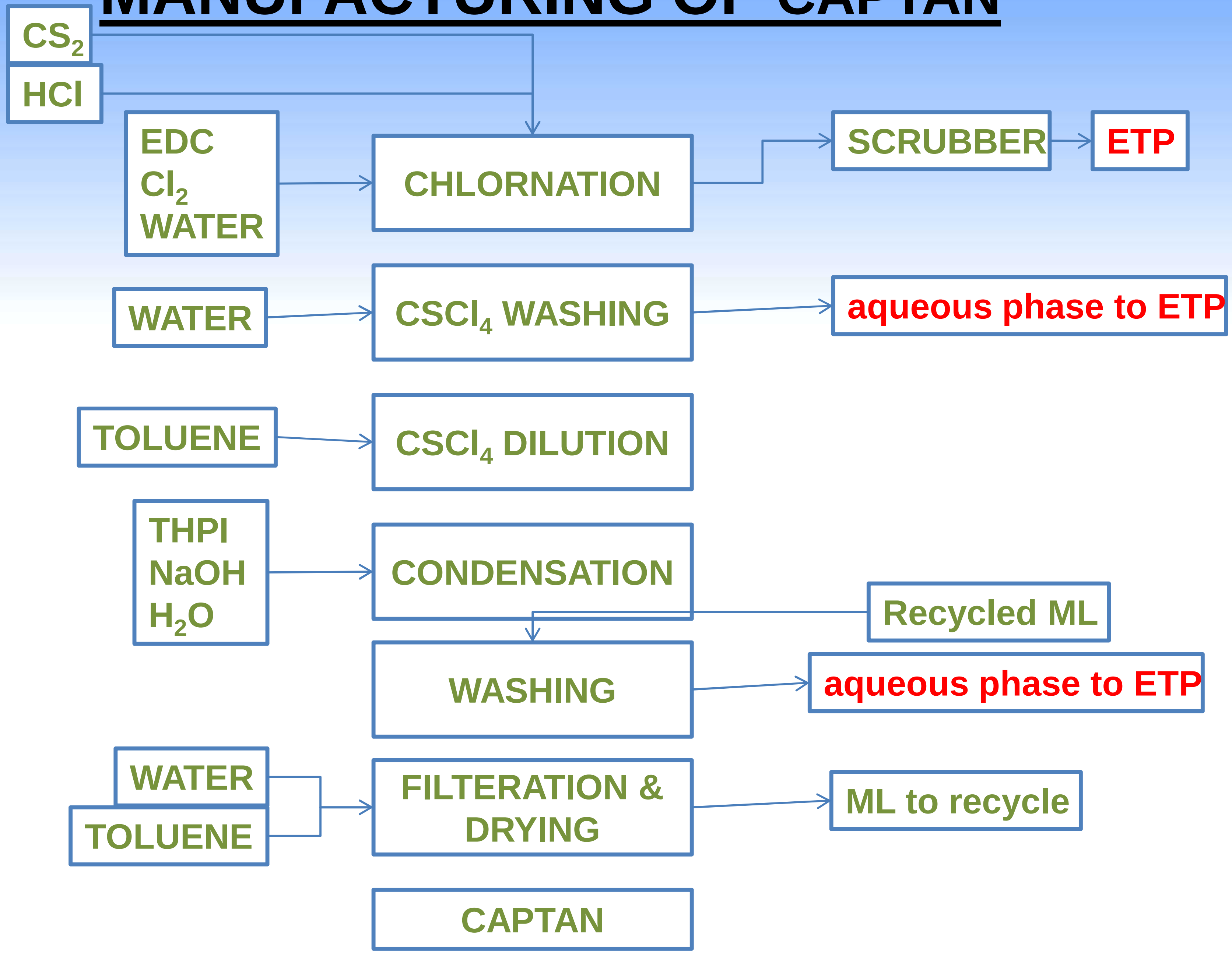
- Step 3 – **Condensation**

$CSCl_4$ + NaOH + Tetra Hydro Pthelic Amide → Captan + NaCl

- Step 4 – **Washing**

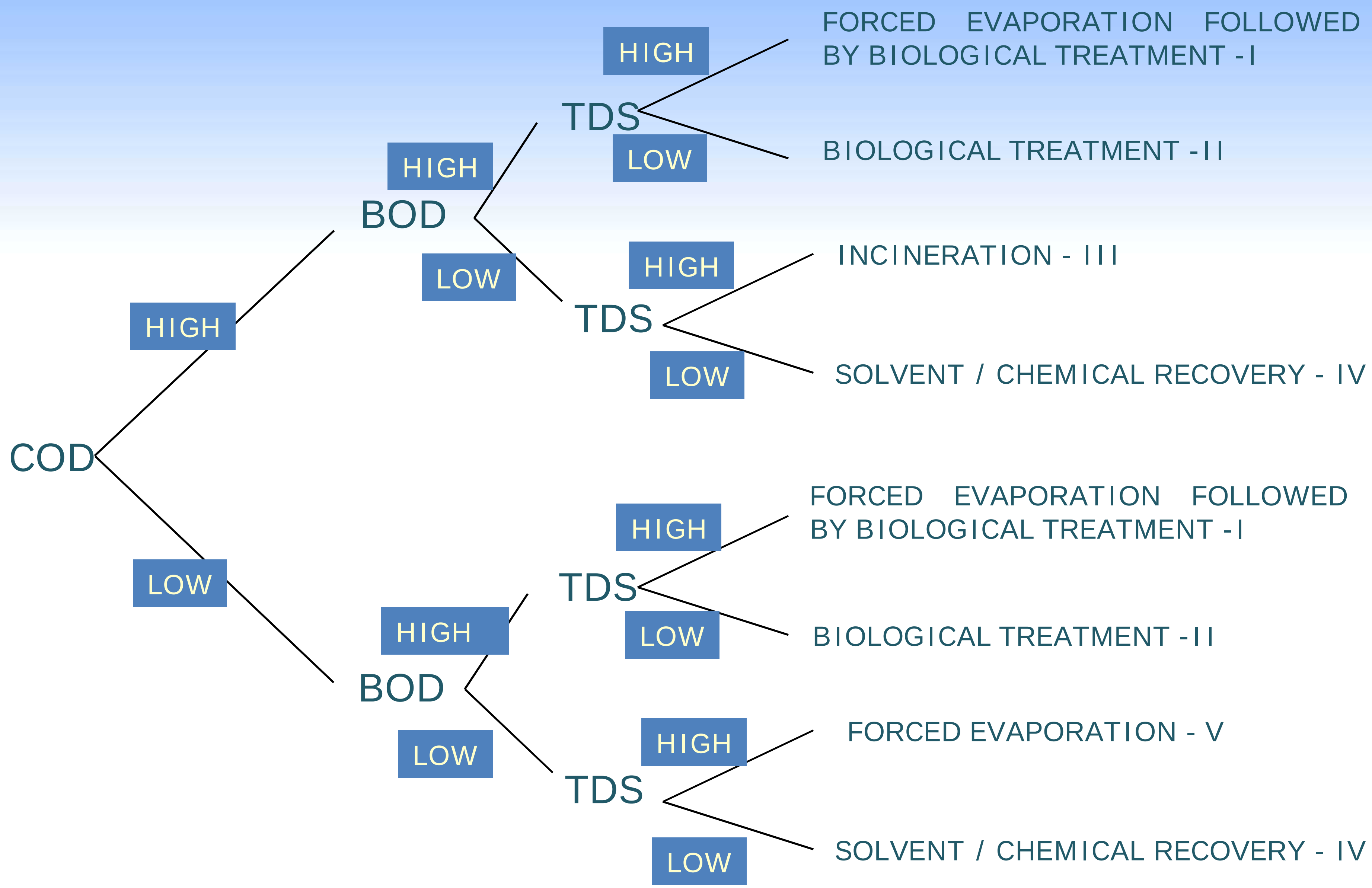
- Step 5 - **Filtration & Drying**

PROCESS FLOW DIAGRAM FOR MANUFACTURING OF CAPTAN

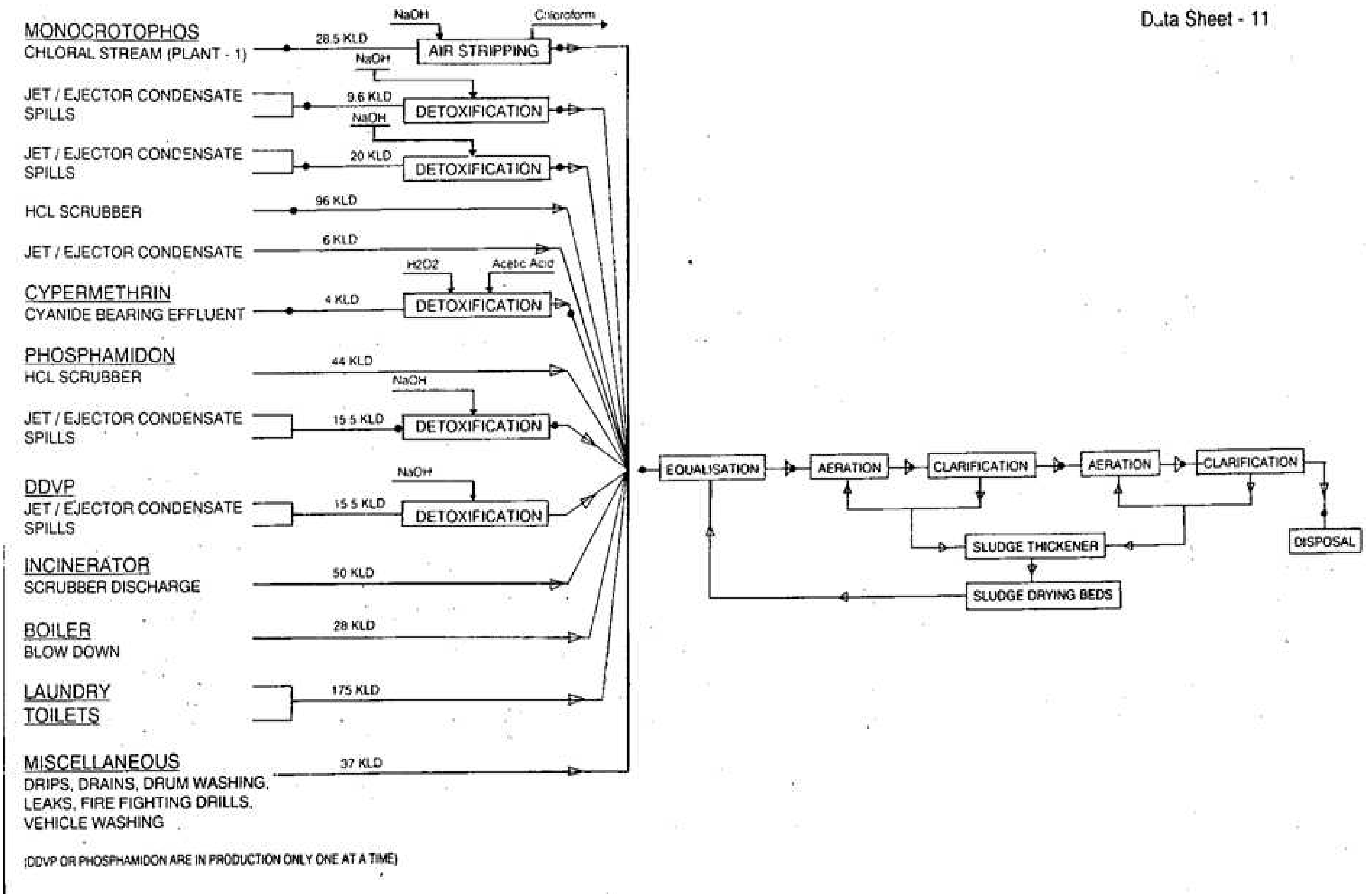


SEGREGATION OF STREAMS

STREAMWISE BEST PRACTICABLE TECHNOLOGY IN CHEMICAL INDUSTRIES

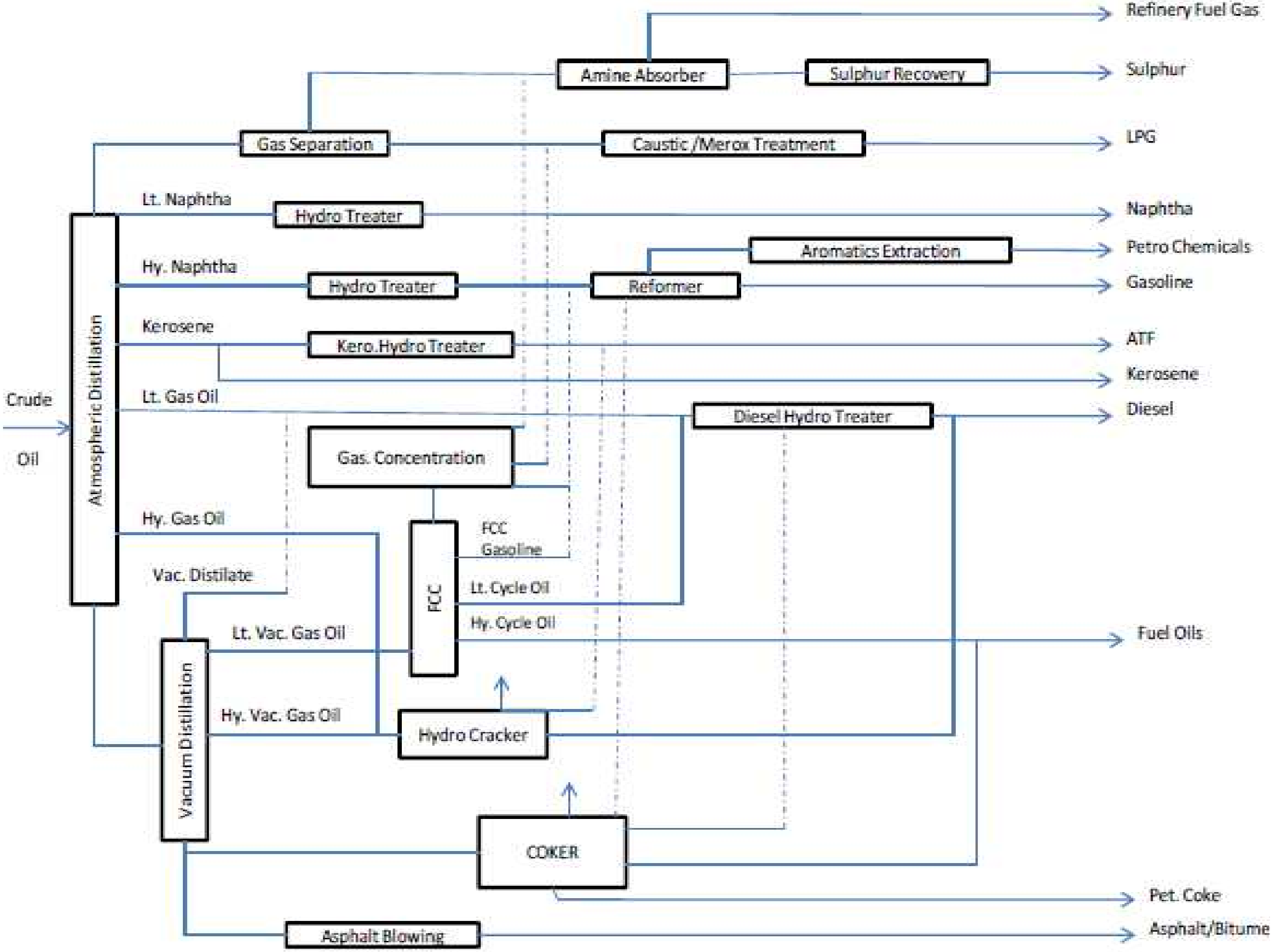


INTEGRETED WASTEWATER SYSTEM (ISBL & OSBL)



Industrial Water Accounting

A case study on Refineries



Refinery Fuel Gas
Amine Absorber
Sulphur Recovery
Sulphur
Gas Separation
Caustic /Merox Treatment
LPG
Lt. Naphtha
Hydro Treater
Naphtha
Aromatics Extraction
Petro Chemicals
Hy. Naphtha
Hydro Treater
Reformer
Gasoline
Kerosene
Kero.Hydro Treater
ATF
Kerosene
Crude
Oil
Atmospheric Distillation
Lt. Gas Oil
Diesel Hydro Treater
Diesel
Gas. Concentration
Hy. Gas Oil
FCC
FCC
Gasoline
Vac. Distilate
Lt. Cycle Oil
Hy. Cycle Oil
Lt. Vac. Gas Oil
Fuel Oils
Vacuum Distillation
Hy. Vac. Gas Oil
Hydro Cracker
COKER
Pet. Coke
Asphalt Blowing
Asphalt/Bitume

The Process of Refinery

- **Desalter unit washes out salt from the crude oil before it enters the atmospheric distillation unit. Atmospheric distillation unit distills crude oil into fractions.**

- **Vacuum distillation unit further distills residual bottoms after atmospheric distillation.**

- **Naphtha hydrotreater unit uses hydrogen to desulfurize naphtha from atmospheric distillation. Must hydrotreat the naphtha before sending to a Catalytic Reformer unit.**

- **Catalytic reformer unit is used to convert the naphtha-boiling range molecules into higher octane reformate (reformer product). The reformate has higher content of aromatics and cyclic hydrocarbons). An important byproduct of a reformer is hydrogen released during the catalyst reaction. The hydrogen is used either in the hydrotreaters or the hydrocracker.**
- **Distillate hydrotreater unit desulfurizes distillates (such as diesel) after atmospheric distillation.**

- **Fluid catalytic cracker (FCC) unit upgrades heavier fractions into lighter, more valuable products.**

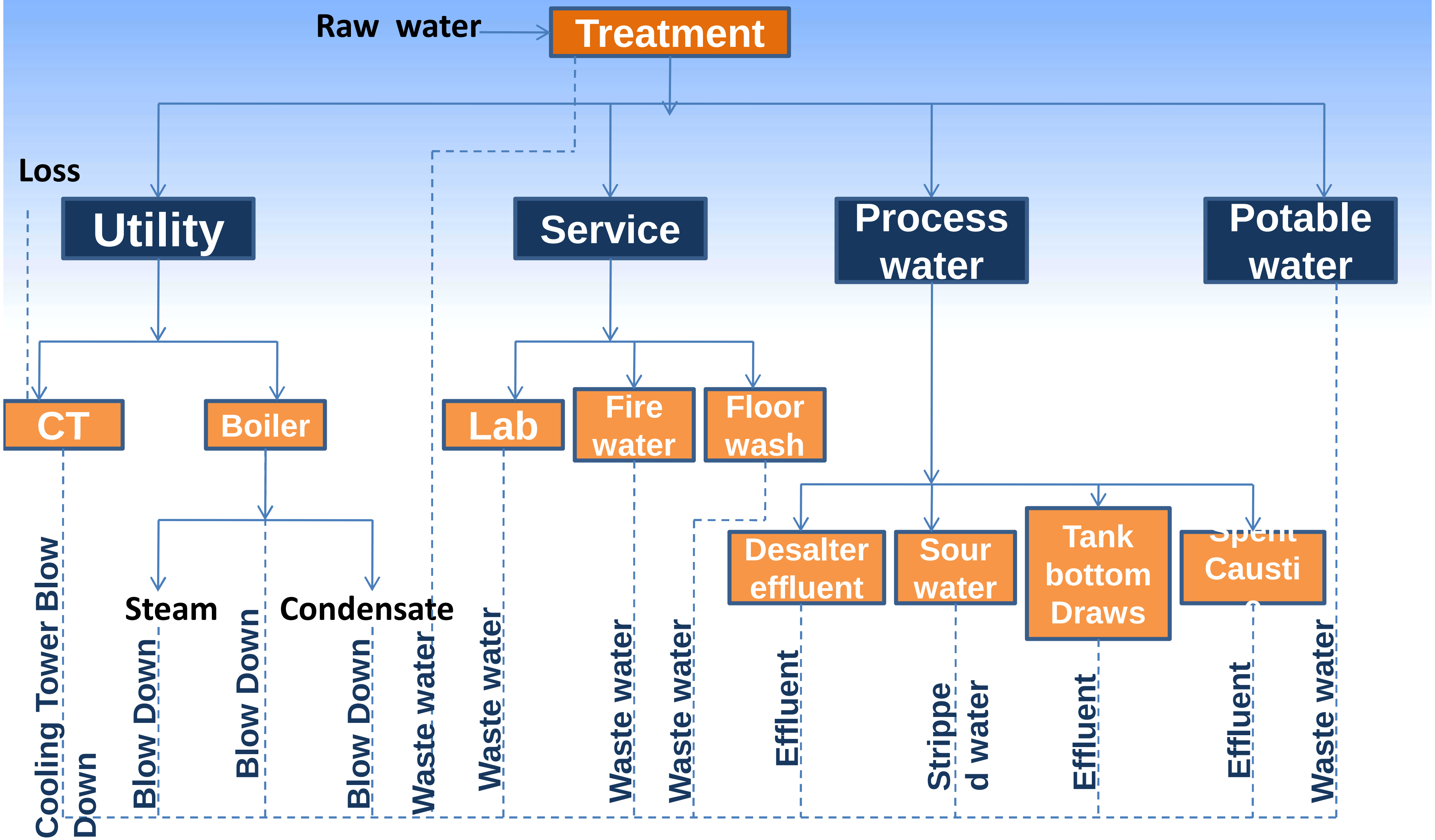
- **Steam reforming unit** produces hydrogen for the hydrotreaters or hydrocracker. Liquified gas storage vessels store propane and similar gaseous fuels at pressure sufficient to maintain them in liquid form. These are usually spherical vessels or "bullets" (i.e., horizontal vessels with rounded ends). Storage tanks store crude oil and finished products, usually cylindrical, with some sort of vapor emission control and surrounded by an earthen berm to contain spills.

- **Amine gas treater**, **Claus unit**, and **tail gas treatment** convert hydrogen sulfide from hydrodesulfurization into elemental sulfur. Utility units such as cooling towers circulate cooling water, boiler plants generates steam, and instrument air systems include pneumatically operated control valves and an electrical substation.

- **Solvent refining units** use solvent such as cresol or furfural to remove unwanted, mainly aromatics from lubricating oil stock or diesel stock.

- **Solvent dewaxing units** remove the heavy waxy constituents petrolatum from vacuum distillation products

Water Balance (Refineries)



Wastewater consumption, Wastewater generation & recycling

SL. NO.	Capacity (category)	Fresh water consumption (m^3/ton of crude)	Effluent Generated (m^3/ton of crude)	Effluent discharged (m^3/ton of crude)	% of recycled water
1.	1 – 5 (MMTPA)	2189 + 750*	981.5	231.5	25.5
2.	5 – 10 (MMTPA)	706.16 + 306.3*	503.5	197.16	30
3.	10 – 15 (MMTPA)	1688.8 + 479*	532	76.66	23
4.	25 – 35 (MMTPA)	690 + 277.5*	285	-	28

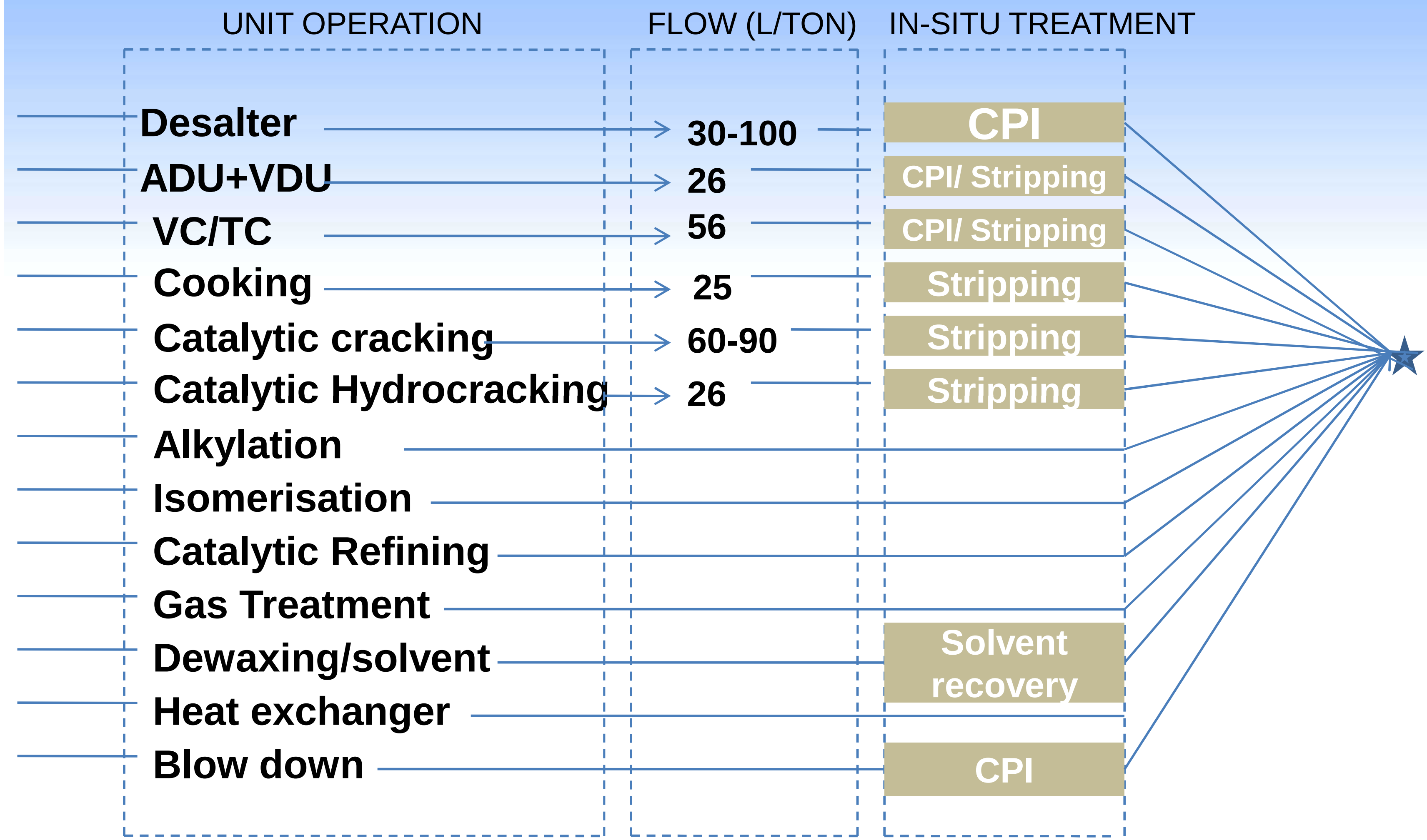
* Reuse/recycle of treated effluent (m^3/ton of crude)

➢ Representative Concentrations of Pollutants in Typical Refinery Effluents

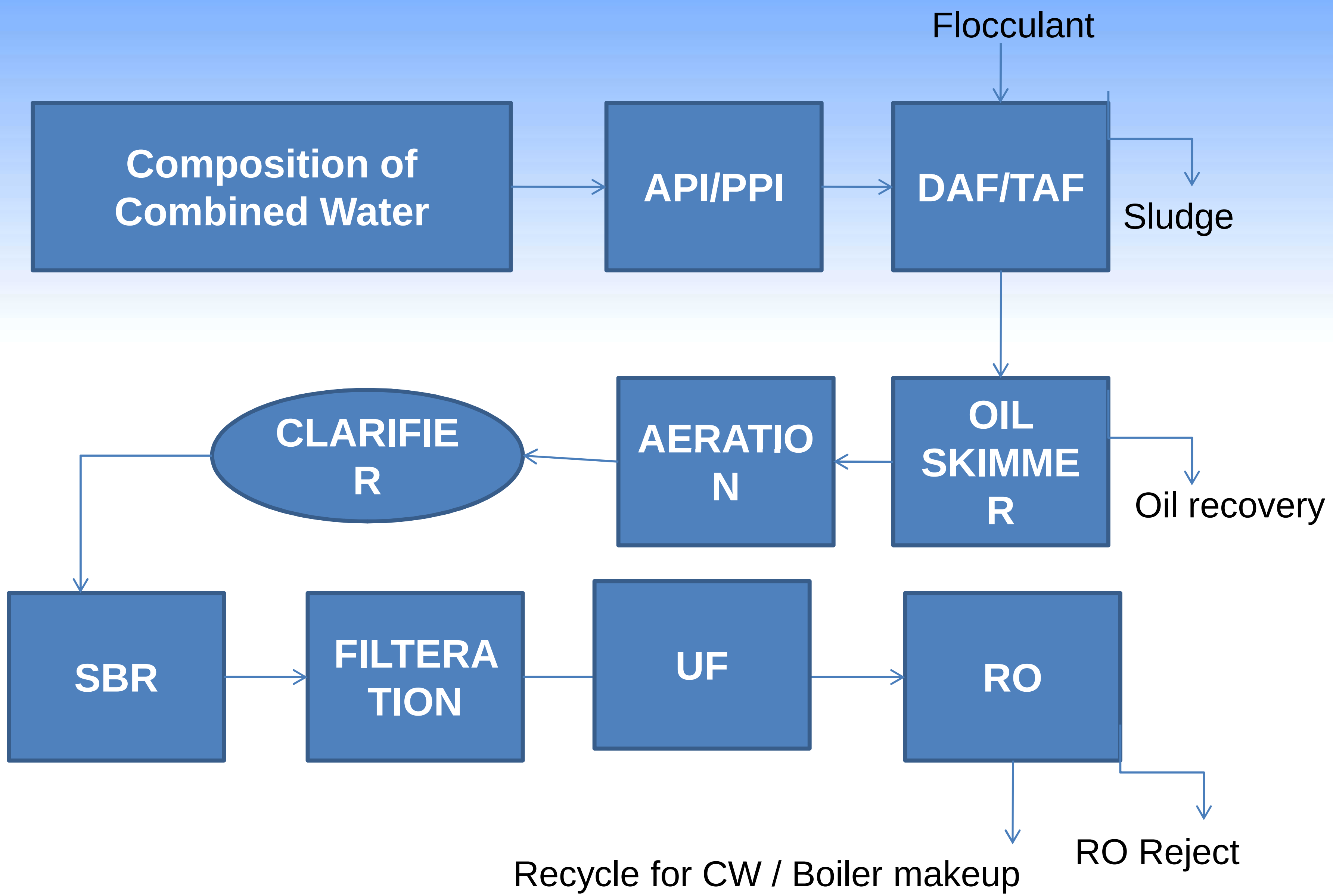
	Oil	H_2S (RSH)	NH_3 (NH_4+)	Phenols	BOD COD TOC	CN- (CNS-)	TSS
Distillation Units	XX	XX	XX	X	XX	-	XX
Hydrotreatment	XX	XX(X)	XX(X)	--	XX	--	--
Visbreaking	XX	XX	XX	XX	XX	X	X
Catalytic Cracking	XX	XXX	XXX	XX	XX	X	X
Hydrocracking	XX	XXX	XXX	--	X	-	-
Lube Oil	XX	X	X	-	XX	-	-
Spent Caustic	XX	XX	-	XXX	XXX	X	X
Ballast Water	X	-	-	X	X	X	X
Utilities (Rain)	-(X)	-	-	-	X	-	-
Sanitary/Domestic	-	-	X	-	X	-	XX

Key: X=<50 mg/l; XX=50-500 mg/l; XXX=>500 mg/l

ISBL

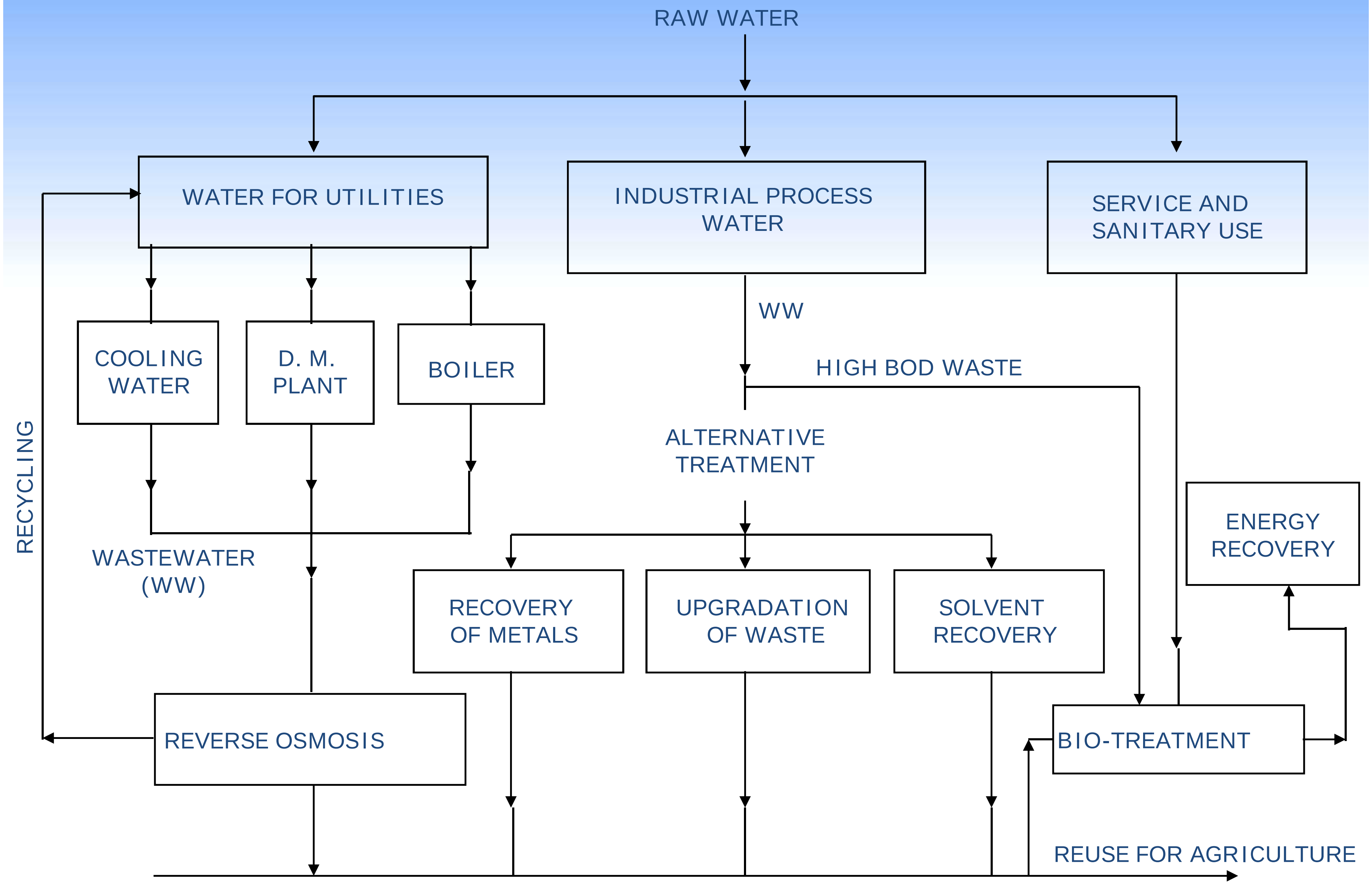

UNIT OPERATION
FLOW (L/TON)
IN-SITU TREATMENT
Desalter
30-100
CPI
ADU+VDU
26
CPI/ Stripping
VC/TC
56
CPI/ Stripping
Cooking
25
Stripping
Catalytic cracking
60-90
Stripping
Catalytic Hydrocracking
26
Stripping
Alkylation
Isomerisation
Catalytic Refining
Gas Treatment
Dewaxing/solvent
Solvent recovery
Heat exchanger
Blow down
CPI

OSBL

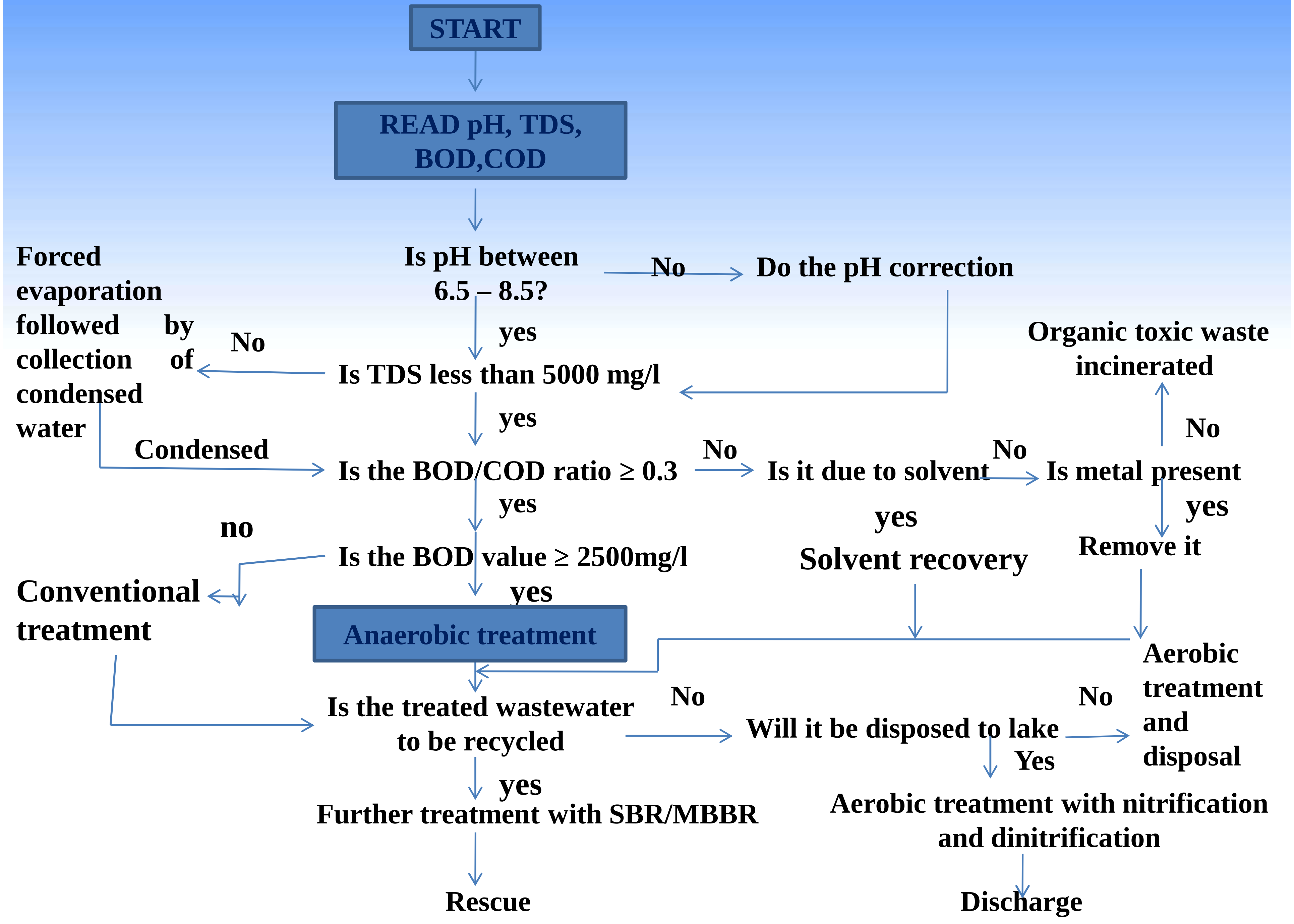

Flocculant
Composition of Combined Water
API/PPI
DAF/TAF
Sludge
OIL SKIMME R
Oil recovery
AERATIO N
CLARIFIE R
SBR
FILTERA TION
UF
RO
Recycle for CW / Boiler makeup
RO Reject

Treated Effluent Option of Renovation, Recycling and Reuse.

POSSIBLE OPTIONS OF RENOVATION, RECYCLING AND REUSE OF WASTEWATER



HOW TO CHOOSE INDUSTRIAL WASTEWATER TREATMENT SCHEME



What will be the appropriate treatment?

Problem no 1

If pH -5.5, BOD – 3000mg/l, COD – 5000 mg/l, BOD-COD ratio – 0.6, SS – 100 mg/l

Problem no 2

If pH -6.5, BOD – 600mg/l, COD – 1000 mg/l, BOD-COD ratio – 0.6, SS – 200 mg/l

Problem no 3

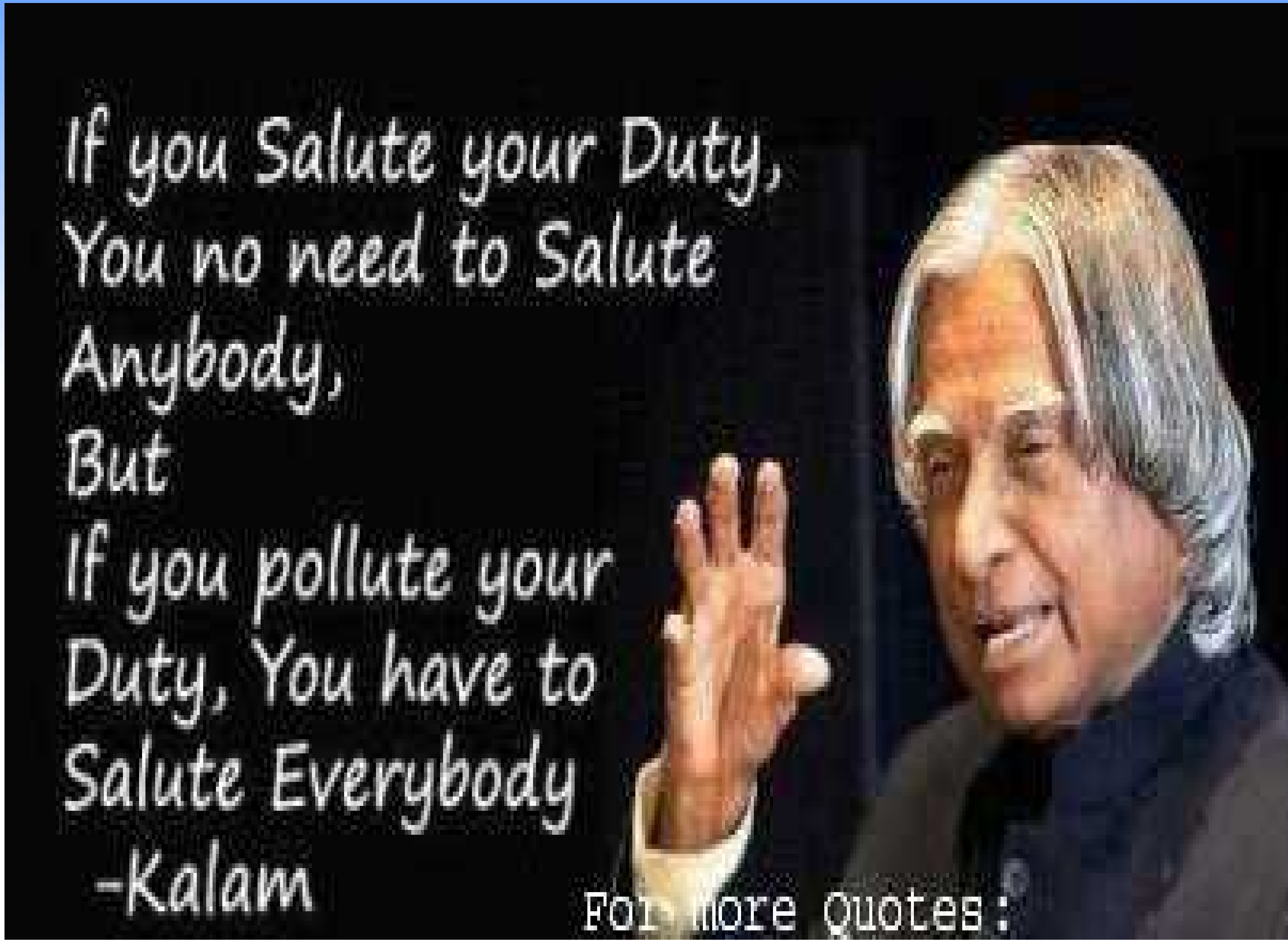
If pH -7.5, BOD – 1000mg/l, oil and grease – 100mg/l, COD – 3000 mg/l, SS – 200 mg/l

Problem no 4

If pH -8.00, BOD – 200mg/l, COD – 3000 mg/l

Problem no 5

If pH -6.5 -8.5, BOD – 250mg/l, COD – 500 mg/l, SS – 150 mg/l.


If you Salute your Duty,
You no need to Salute
Anybody,
But
If you pollute your
Duty, You have to
Salute Everybody
-Kalam
For more Quotes:

THANK YOU!