Petroleum Refinery Wastewater Treatment: Principles and Operational Challenges

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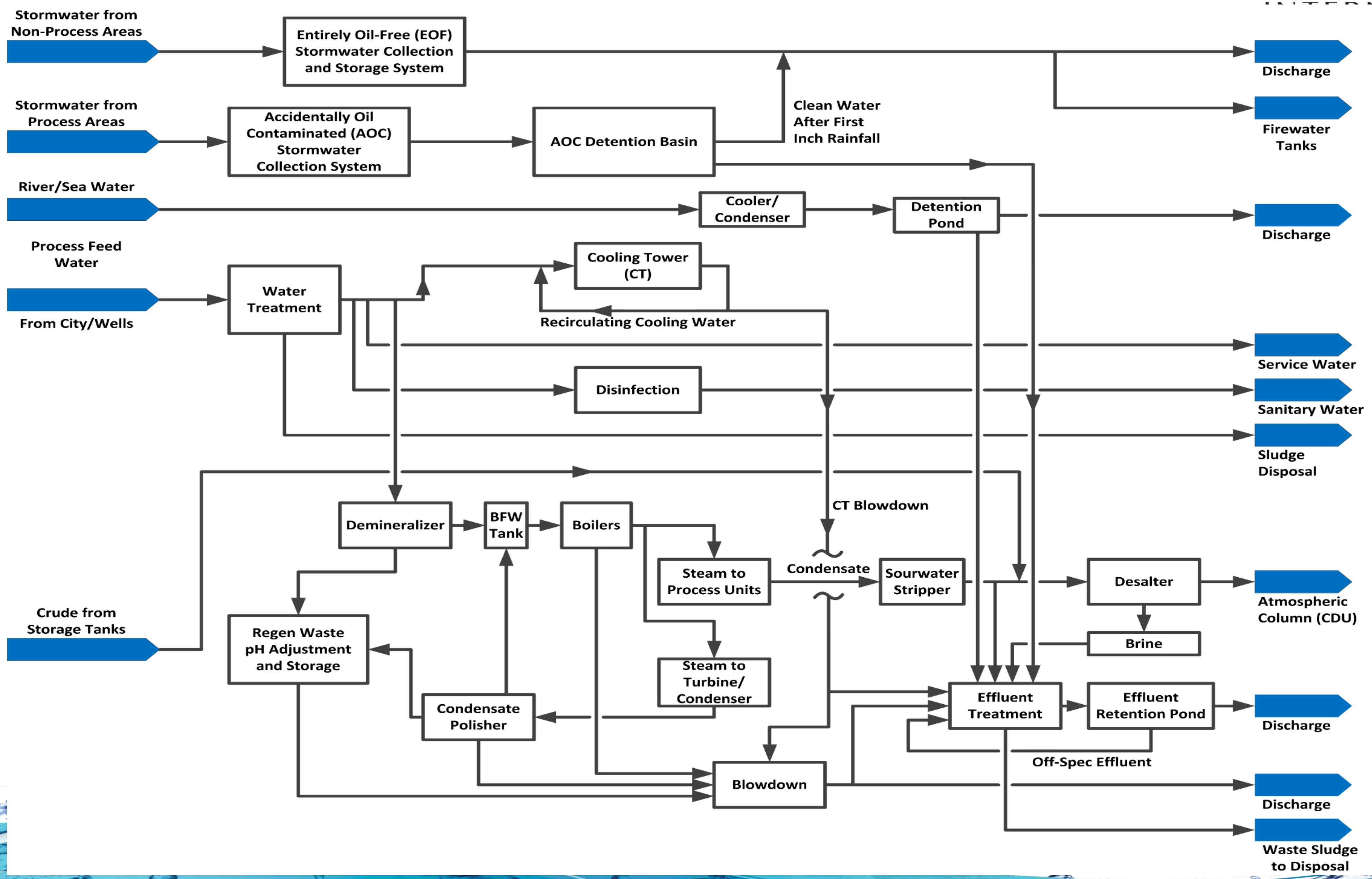
Outline

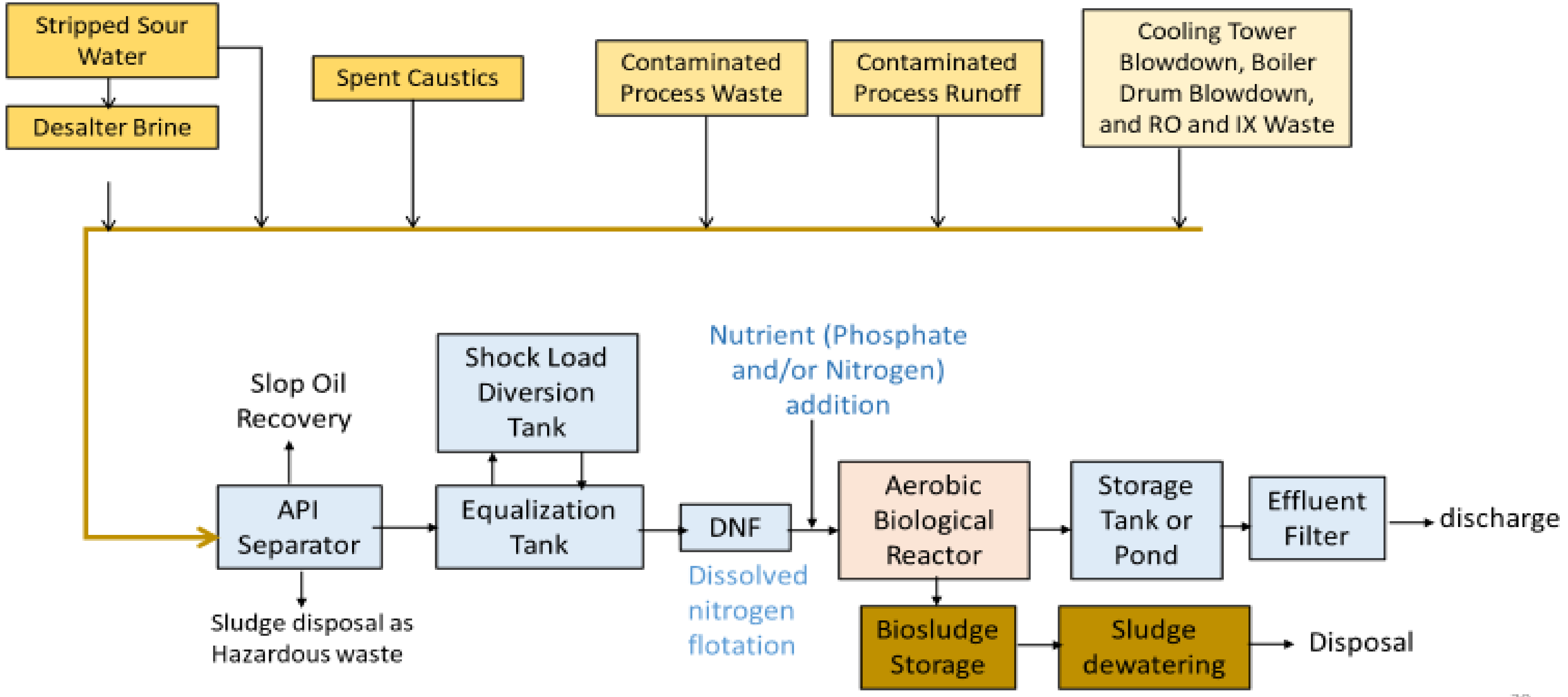
- Total Water Network in a Petroleum Refinery
- Process Water Management
- Wastewater Treatment
  - Primary Oil-Water Separation
  - Secondary Oil-Water Separation
  - Biological Wastewater Treatment
  - Treatment System Operating Challenges
- Fate of Treated Wastewater and Environmental Impacts of Discharge
- Summary and Conclusions

Total Water Network in a Petroleum Refinery



Refinery Wastewater Treatment Train

General Refinery Wastewater Treatment Scheme

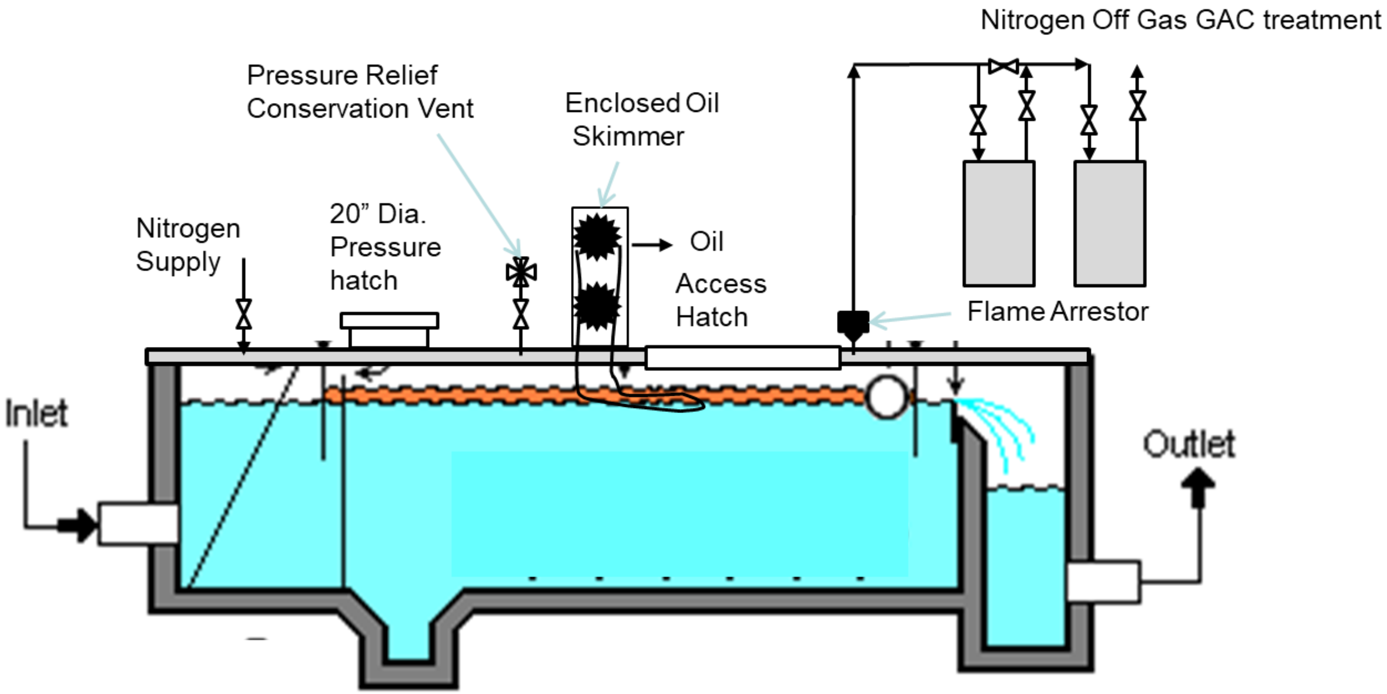


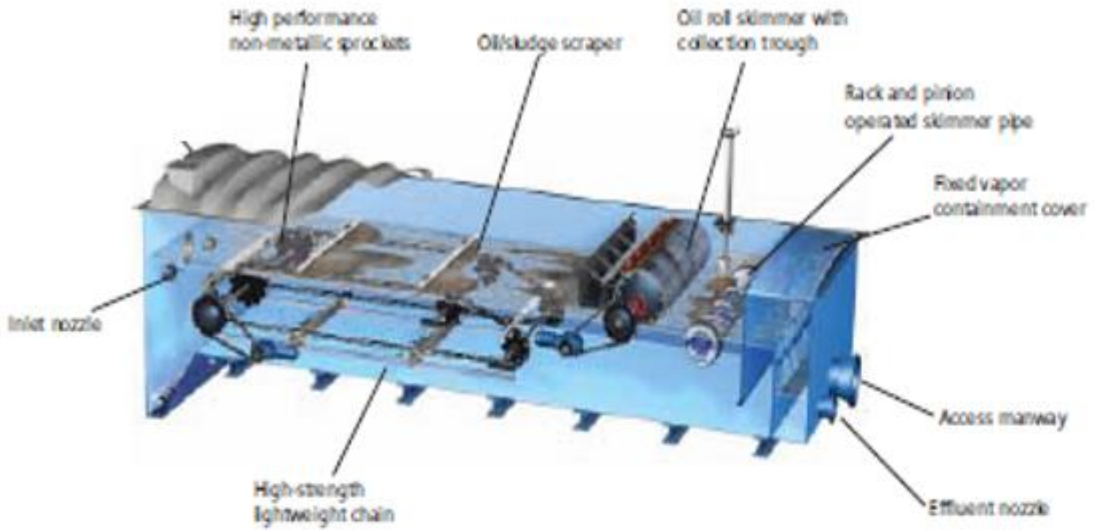
Primary Treatment

Primary Oil-Water Separation: API Separators

- Gravity separation of oil and solids from influent wastewater
- Typical effluent oil concentration range 50 – 150 mg/L
- Designed for free phase oil separation- based on crude type, temperature
- Process design governed by API Bulletin 421 1990
- Must be closed vented with controlled headspace to avoid lower explosive limit (LEL)
  - Nitrogen Filled
  - Pressure relief and conservation vent
  - Blow off hatch for roof integrity
  - Flame Arrestors
  - Off Gas Purge to Combustion or GAC

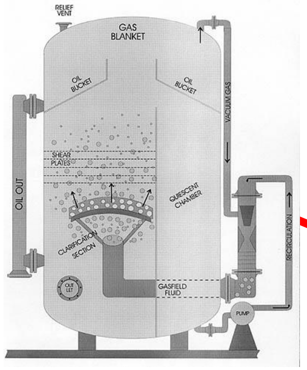
Primary Oil-Water Separation: API Separators





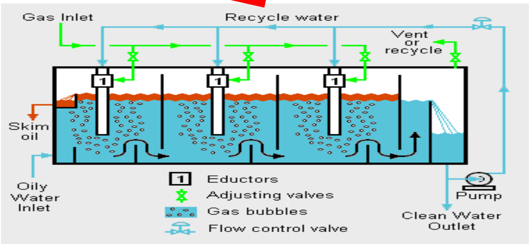
Secondary Oil-Water Separation: Floatation Separators

Bubble Classification	Micro	Medium	Macro

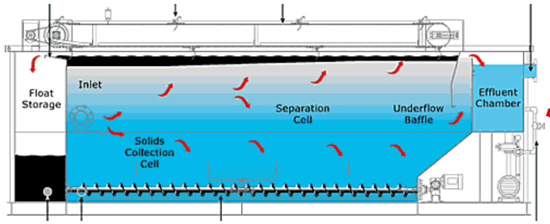


Mechanical IGF

Educator IGF



New generation of vertical Flotation units and others



Conventional DAF, DNF

1 µ | 10 µ | 100 µ | 1000 µ | 10 mm

Bubble Size

Biological Treatment

Fundament Principle of Aerobic Biological Treatment
Heterotrophic Bacteria

Organic material + O_2 + NH_3 + PO_4 + micronutrients (S, Na, K, Ca, Mg, Cl, Fe, …..)

$\xrightarrow{\text{growth}}$ New cells + CO_2 + H_2O + Microbial byproducts + (-ΔE)

$\xrightarrow{\text{Decay w/ } O_2}$ Soluble and insoluble decaying end products

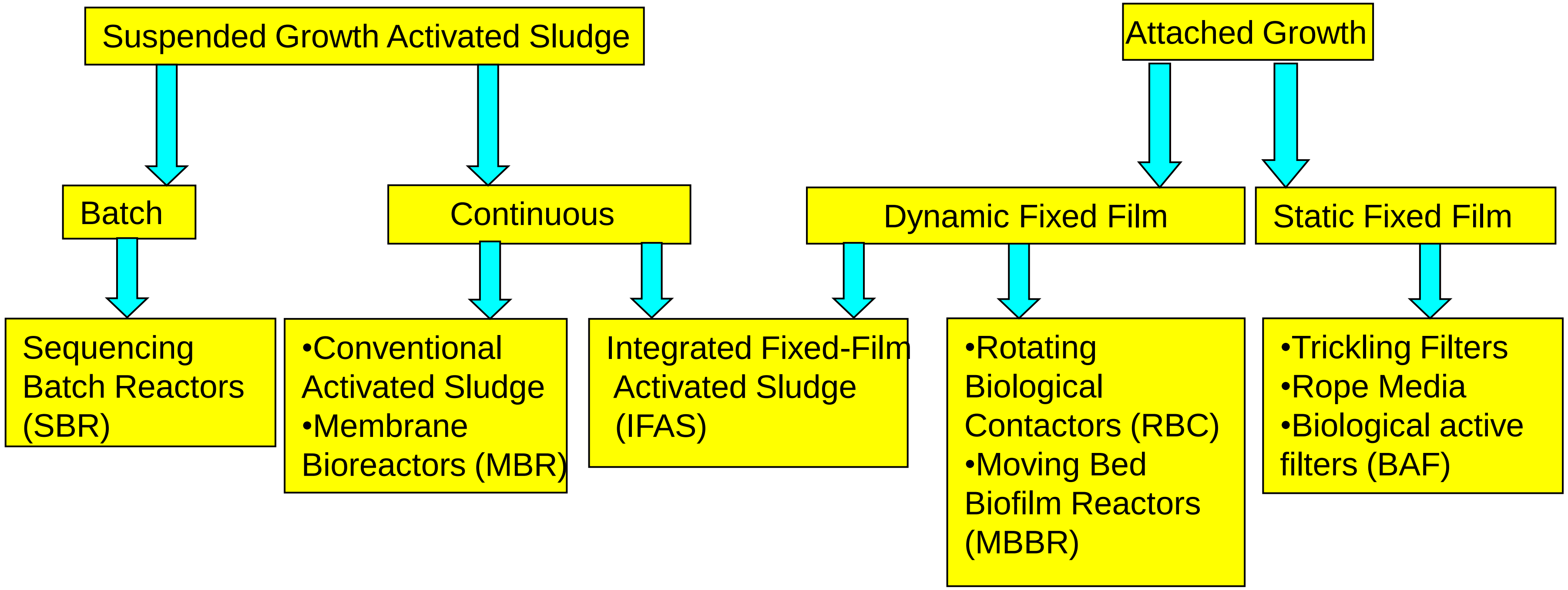
According to Dr. M.C.M. van Loosdrecht of Technical University of Delft:

"In wastewater treatment the fate of BOD or COD (heterotrophic growth) is determined by the stoichiometry only and the fate of inorganic nutrients (NH_3, NO_2, NO_3, and PO_4) in addition, is also determined by the microbial kinetics"

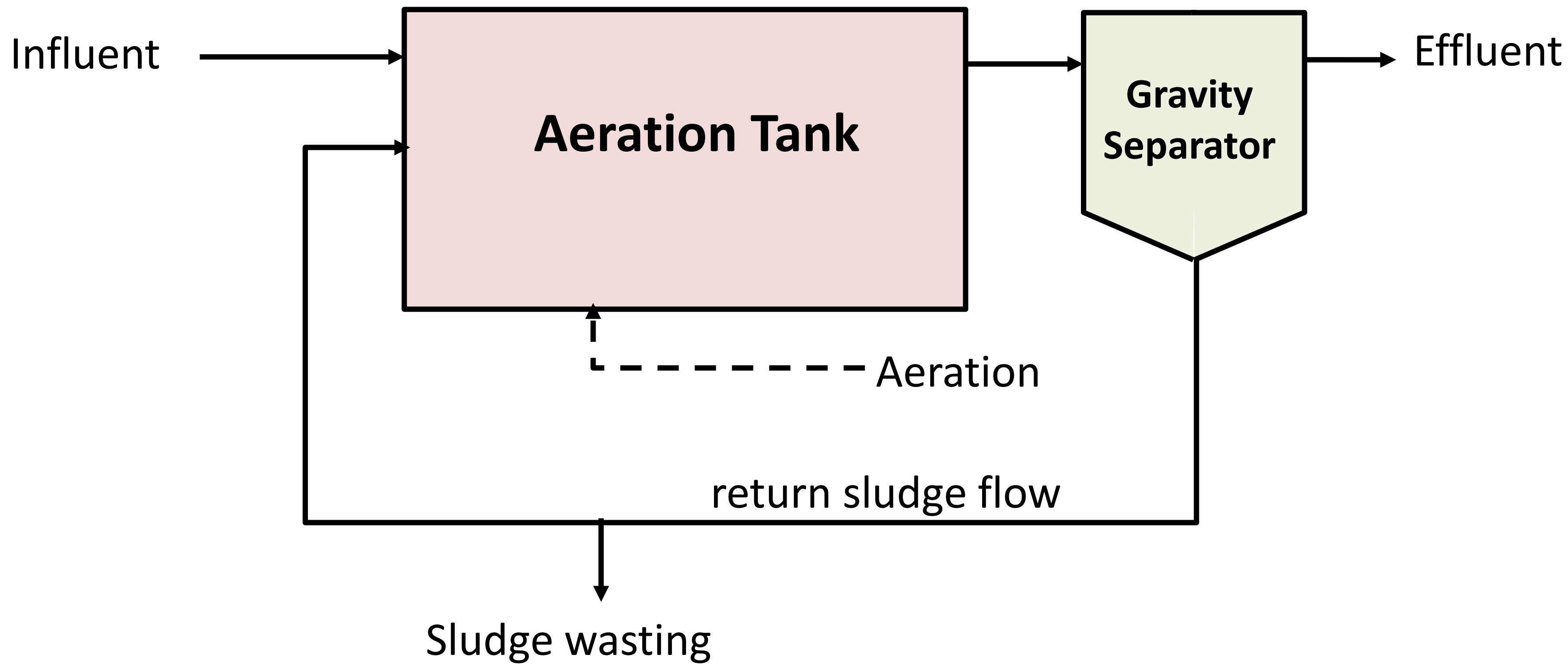
To simplify:
For BOD Removal systems - stoichiometry controls (DO, Nutrients)
For nitrification systems - kinetics controls (DO, Nutrients, Reactor size, Operating SRT)

Biological Wastewater Treatment Technologies

- In suspended growth biological treatment is carried out by discrete cells dispersed in the reactor.
- In attached growth microbial cells are attached on to solid surfaces and kept together by self-produced matrix of extracellular polymeric substances (EPS) as layers of biofilm.



Suspended Growth Process: Conventional Activated Sludge (CAS)

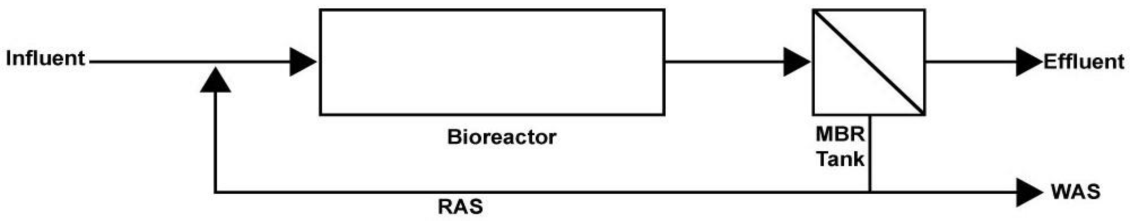


Development of New Treatment Processes

- Over last two decades several new treatment processes developed to address new demands of the society
- Drivers
  - Increasing need to recycle and reuse treated wastewater globally;
  - Need to treat increasing volumes of wastewater resulting from increased throughput in refineries; and
  - Increasingly tighter regulations calling for low level nutrients in treated effluent.
- Processes
  - Membrane Bioreactors (MBR)
  - Moving Bed Bioreactors (MBBR)
  - Integrated Fixed Film Activated Sludge (IFAS)

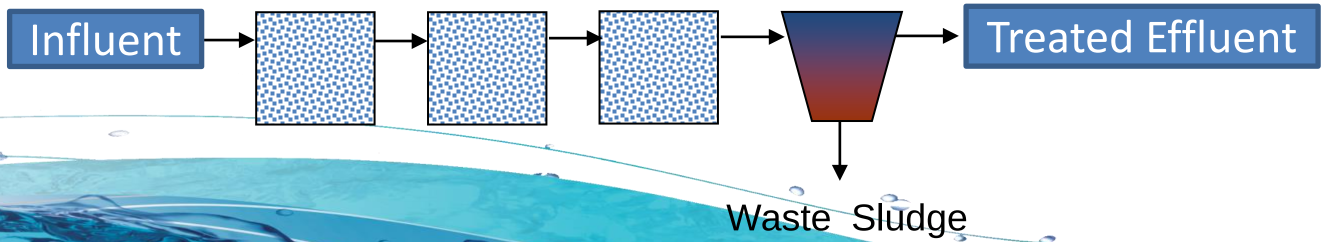
Membrane Bioreactor (MBR)

- Activated sludge followed by ultrafiltration (UF) for solid-liquid separation
- Very high-quality effluent – TSS < 2 mg/L
- Rejects pathogens and significantly reduces downstream disinfection needs
- Very effective as a biological nutrient removal (BNR) process
- Solid-liquid separation and effluent quality unaffected by filaments
- Allows very high MLSS in 8,000 – 10,000 mg/L range
- Helps achieve high SRT in small reactor volume and footprint area
- Major disadvantages:
  - Influent to be significantly free from large objects, grit and other components that can foul or damage membrane
  - Influent screen 1 mm opening size necessary
  - Influent has to be significantly free from O&G
  - High capital and O&M cost



Moving Bed Biological Reactor (MBBR)

- Attached growth process
- Once through process, no RAS
- Biomass attached on media surface as fixed film and media suspended in the reactor
- Reactor contains plastic (HDPE, polypropylene, etc.) media occupying 35% to 60% of empty tank volume
- Aeration keeps media suspended and provides DO for respiration
- Aeration system similar to activated sludge process, primarily by air blowers and coarse bubble diffusers
- Excess growth sloughs off and leaves with effluent
- Limit influent solids size to <6 mm by influent screen
- Screen (6 to 10 mm) on the effluent line prevent media loss by carryover

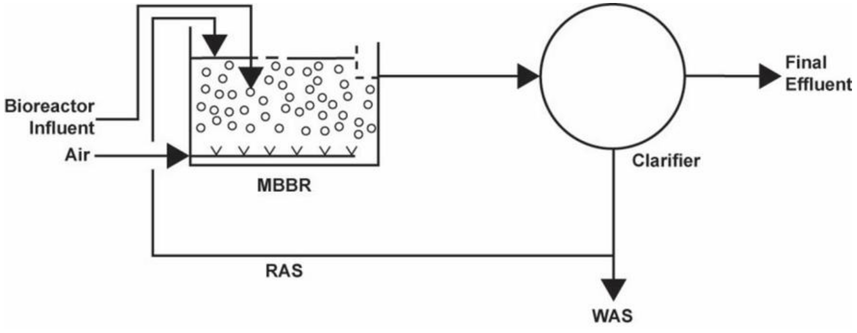


Moving Bed Biological Reactor (MBBR): Advantages and Disadvantages

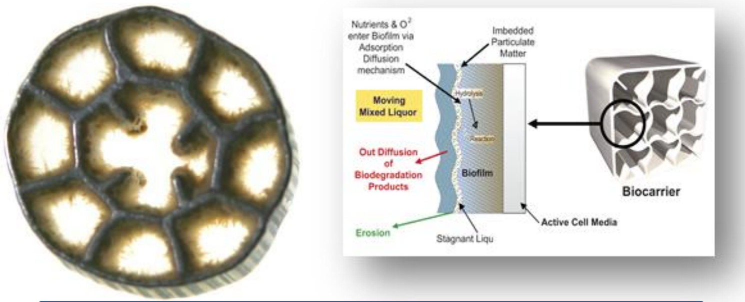
- Advantages
  - Suitable for treating high flows and loads with limited available footprint
  - Biomass population is equivalent to 1,000 to 5,000 mg/L as suspended solids
  - Post nitrification and denitrification can be added to upgrade existing plants to nutrient removal facilities
  - Resilient to peak flows and shock loads
  - Resistant to toxic shocks
  - Free from sludge bulking due to filaments
  - Simple, hands free operation
- Disadvantages
  - Higher aeration (DO ~ 3 mg/L) requirement than CAS
  - High mixed liquor SVI (>150 mL/L) requiring DAF as opposed to secondary clarifier

Integrated Fixed Film Activated Sludge (IFAS) Reactor

- Hybrid between suspended growth and fixed film processes
- Requires RAS, WAS and F:M control
- Can effectively increase the MLSS of the reactor by 150 to 200%
- Most applicable where space limitations require both suspended and fixed film inventory
- Upgrade of existing activated sludge for N&P removal without adding new reactor volume
- MLSS ~ 2000-2500 mg/L and SVI ~ 100-150 mL/L, so existing secondary clarifier is adequate
- Meets stringent NH3-N and TN limits
- Can integrate with Bio-P control



IFAS Process Schematic



Attached Growth on MBBR and IFAS Media Surface

Wastewater Treatment System Operating Challenges

Challenges with Front End Oil/Solids Removal Systems

1. Covering primary separation tanks due to Air Toxic regulation makes the operation and maintenance of these units very difficult. Skimming the oil layer and removal of settled solids become difficult.
2. These difficulties lead to the following issues:
   - Bottom sludge scrapper tends to jamming, leading to sludge accumulation and mechanical breakage
   - Produced sludge streams sometimes are classified as hazardous waste, making their handling and disposal expensive, leading to accumulation of solids due to logistics also.
   - Difficult to remove skimmed oil layer leads to oil carry over to the treated effluent.
   - Decrease the overall treatment efficiency.
   - Periodically send shock loadings of "free" oil to the downstream secondary oil removal process, normally DNF (dissolved nitrogen flotation) unit
3. Sludge accumulation in equalization tanks and spill diversion tanks can significantly reduce capacity, leading to the loss of the function of damping the impact of spills and shock loadings,
4. Improper functioning of front-end pretreatment affects performance of the biological treatment system that can potentially cause frequent non-compliances.

Challenges with Biological Treatment System

- Foaming in activated sludge tanks leading to spillage due to excessive oil carryover
- Poor solid-liquid separation in clarifier due to sludge bulking
- Excessive amines in wastewater leading to excessive DO demand, process failure and permit violation
- Ammonia shock loads to biotreatment due to amine spillage and/or sour water stripper malfunction, leading to nitrite lock
- Poor biotreatment performance due to inadequate nutrients, especially phosphorus, which is typically absent in refinery waste
- Poor DO distribution in sludge flocs, or films
- Effluent pond malfunction due to algal growth leading to diurnal pH and DO inversion, and excessive TSS carryover in treated effluent discharge

Summary and Conclusions

- Effective wastewater treatment is critical to the success of uninterrupted refinery operation
- Process water management plays a very important role in petroleum refineries - central to both hydrocarbon processing and effluent treatment
- The operation of a refinery wastewater treatment system is an integrated process impacted by source control for spill reduction from the upstream units
- Growing trend of use of opportunity crudes makes the downstream hydrocarbon and wastewater treatment processes vulnerable to upset, leading to unscheduled shutdowns
- Operating engineer and operating staff's training is important
- The capital improvement may be required for some facilities however one has to utilize the existing system the best one can under the current economical conditions
- Each problem is unique and there is no generic solution
- Understanding the basics is the key.

Thank you

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Questions????