

Petroleum Refinery, Ethylene and Gas Plant Wastewater Treatment Presentation

Wastewater Treatment
Treatment Options & Key Design Issues

Agenda

Downstream Experience

Oily Wastewater Treatment

- Primary Oil/Water Separators – API Separators (Roughing Step)
- Secondary Oil/Water Separators – DGF Separators (Polishing Step)
- VOC Containment/Treatment

Wastewater Equalization

Secondary Treatment - Biological Treatment Options

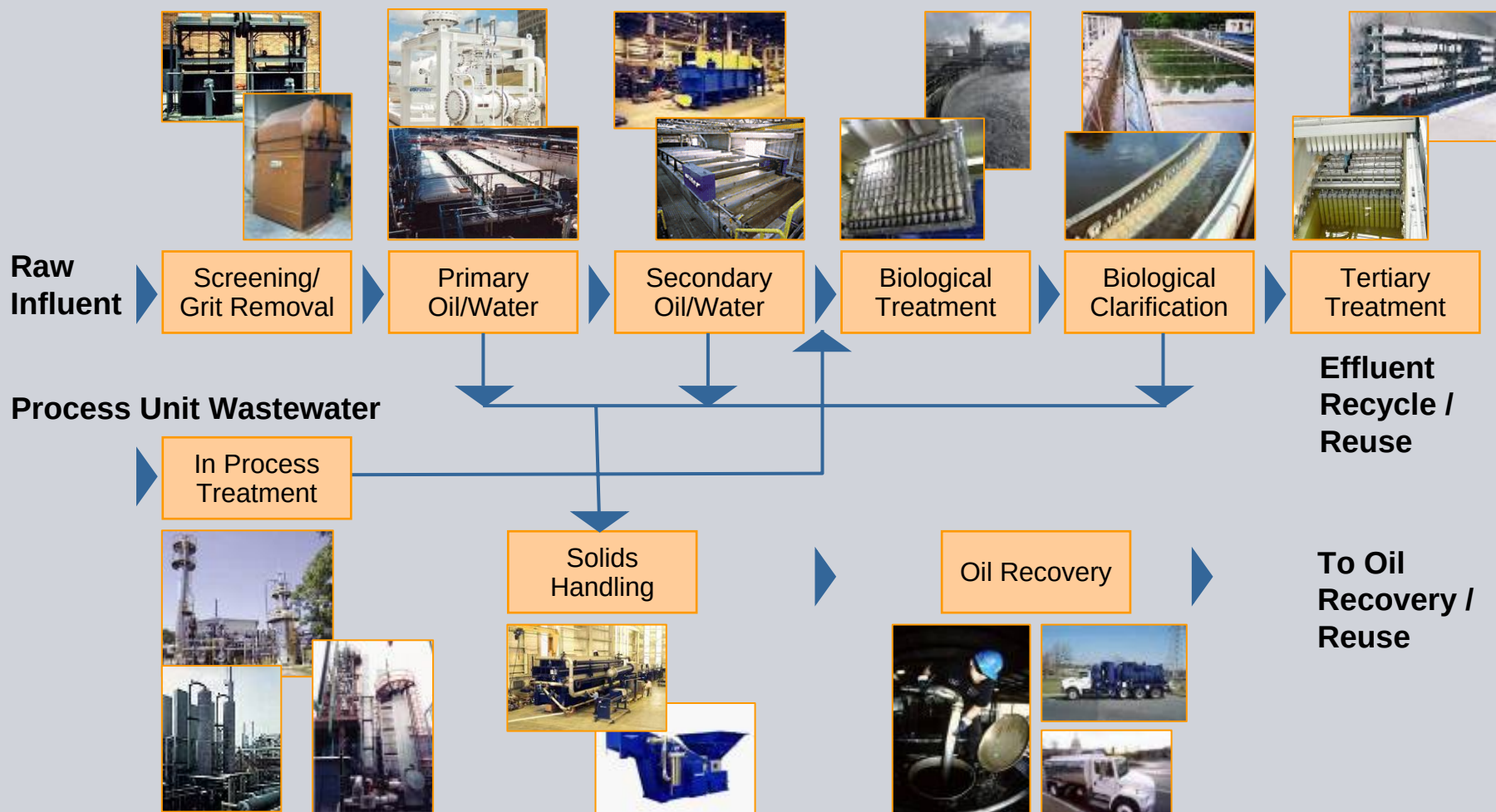
Secondary Clarification

Tertiary Treatment - Recycle/Reuse

- Filtration – Membrane and Media
- Activated Carbon
- Reverse Osmosis

Typical Petroleum / Petrochemical Wastewater Treatment System

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The Petroleum / Petrochemical Industry Leader in Technology and Application Experience

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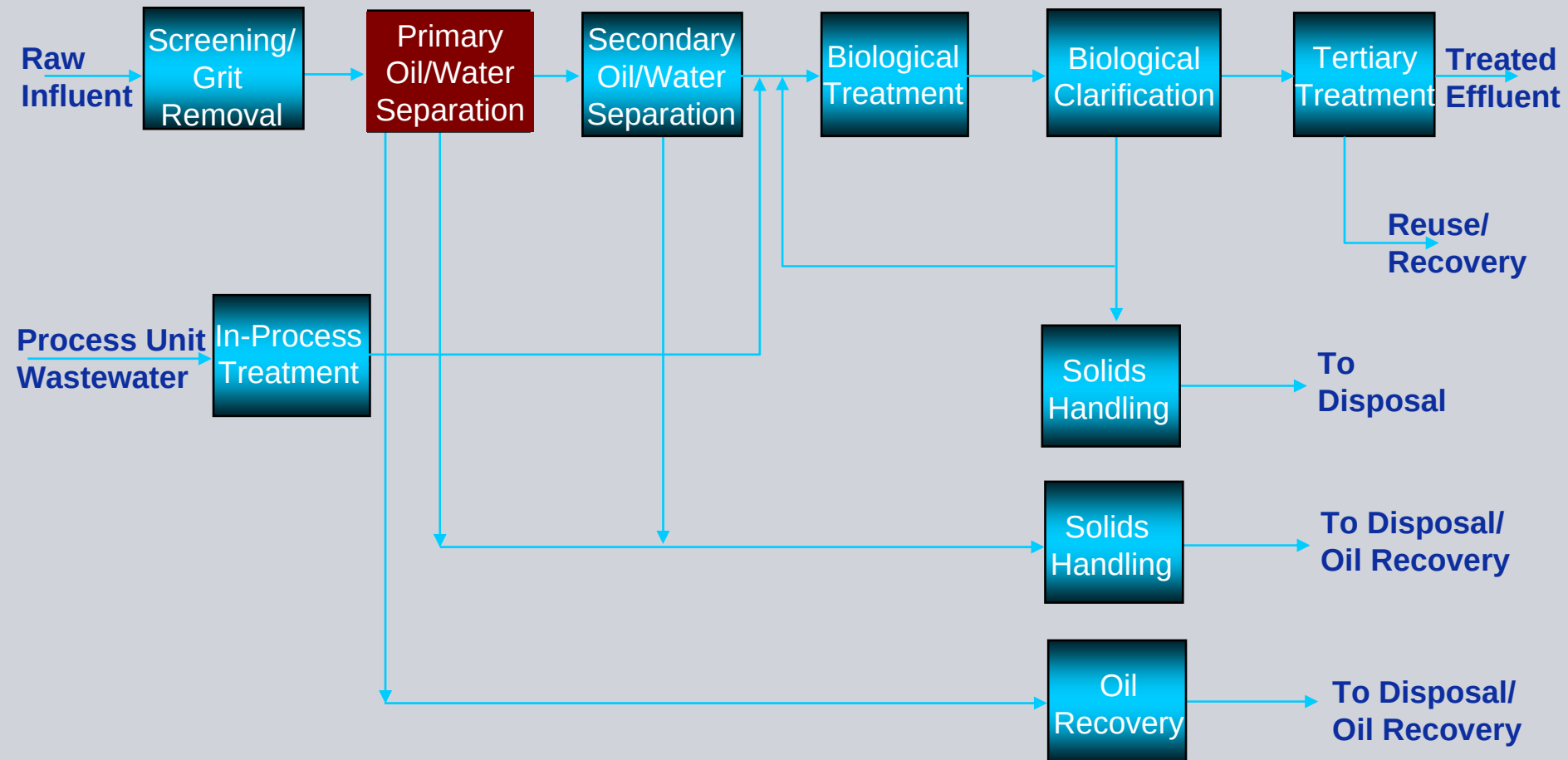
Technologies Developments for the Refining and Petrochemical Industry

- Introduced Tow-Bro Clarifier - 1928
- Introduced API Separator - 1937
- Introduced Wet Air Oxidation - 1950
- Introduced DAF Separator - 1953
- Introduced RBC/SBC - 1969
- Introduced PACT® System - 1972
- Introduced Jet Aeration - 1981
- Introduced GAC Fluid Bed - 1987
- Over 1500 Installations Worldwide



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Typical Oily Water Treatment System



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Primary Oil/Water Separation Treatment Objectives



- Removal of large amount of oil and suspended solids from wastewater. Influent conditions are typically 300 to 10,000 ppm oil and TSS.
- Effluent requirements are typically 100 - 300 ppm oil and TSS.

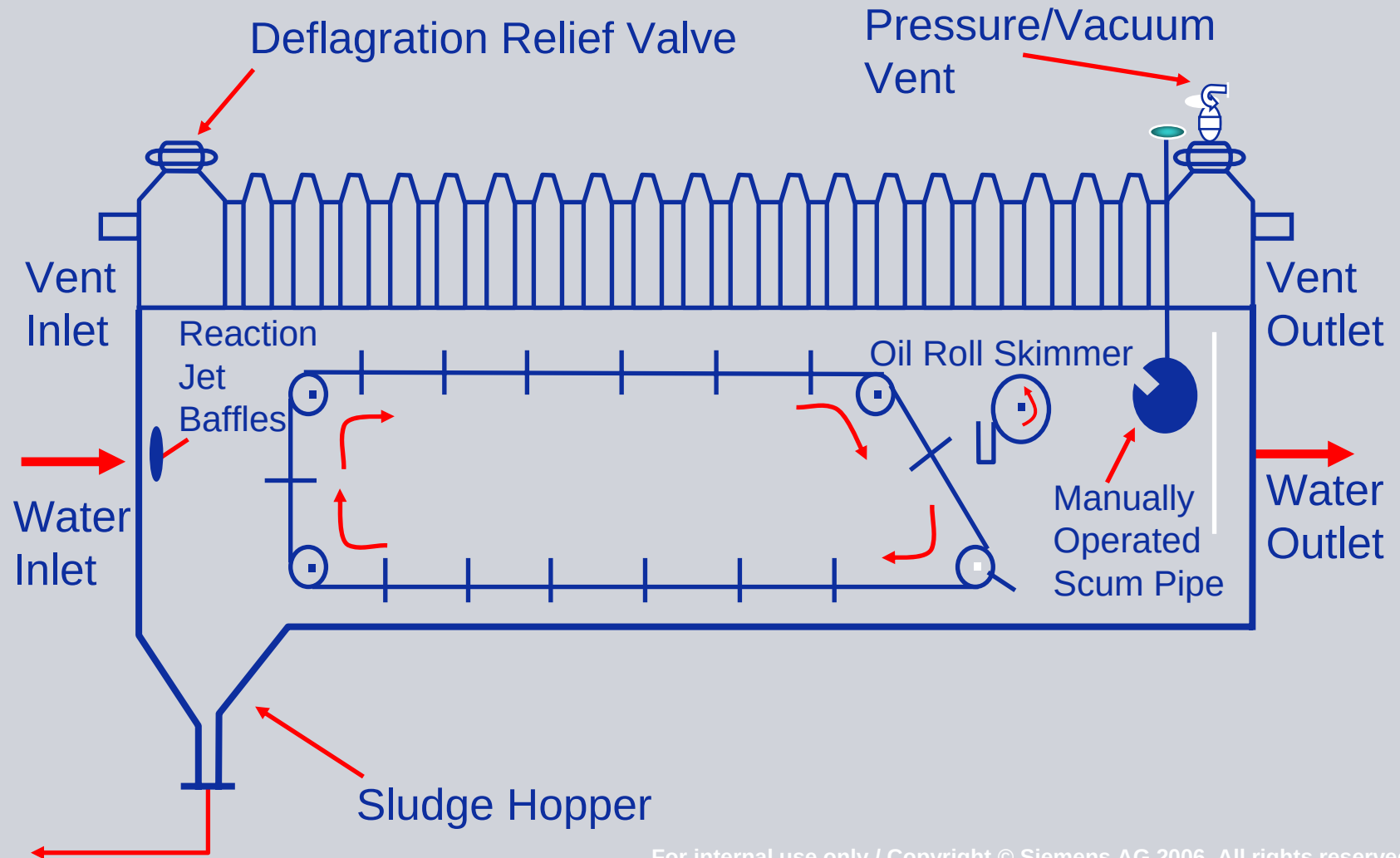
Primary Oil/Water Separator Options

API Separator – Most Common
CPI Separator

Both technologies provide oil and solids separation from water based on Stokes Law. In other words, they rely on the difference in specific gravity between oil, water and solids, to provide separation of these components in oily wastewater.

API Separator

Principles of Operation



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API Separator

Typical Applications and Operating Conditions

- Typically used in Petroleum Refineries and some Petrochemical Facilities.
- Influent Oil: 300 ppm to 10,000 ppm.
- Influent TSS: 300 ppm to 10,000 ppm.
- Effluent: 50 to 200 ppm oil and TSS.



API Separator

Advantages

- Ability to process wastewater with high TSS concentrations, up to 20,000 PPM.
- Non-metallic collector component resist corrosion and are easy to install.
- Concentrated oil removal.
- Responsive to variations in flow and load.

■ Disadvantages

- Large area required.
- Higher costs.



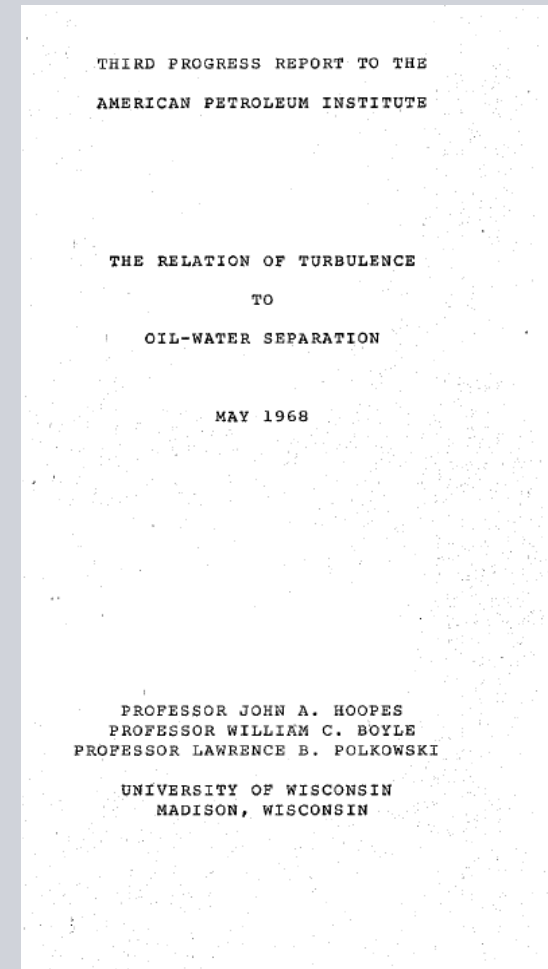
API Separator

Design Requirements

- Designed to the requirements of API Publication 421
- Developed in the early 1950's

Design Parameters

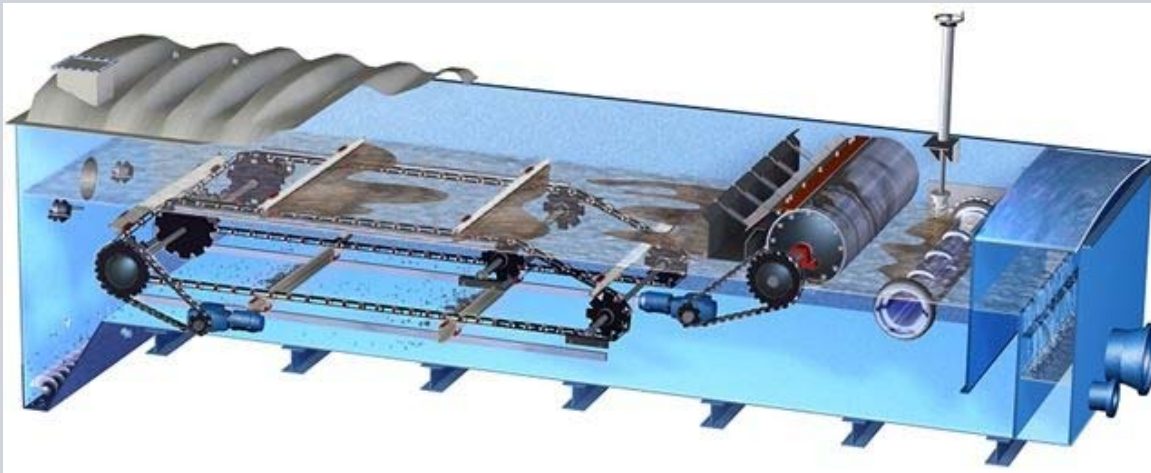
- Flowrate
- Oil Specific Gravity (typically between 0.91 to 0.95).
- Wastewater Temperature (typically between 70 F to 110 F)
- Wastewater Specific Gravity
- Oil Droplet Removal Size (150 micron is recommended). Designing for larger droplet size removal will decrease the size of the API separator.



API Separator

Design Requirements

- Length to Width Ratio Must be at least 5:1
- Depth to Width Ratio must be at least 0.3 to 0.5
- Depth must be between 3 ft and 8 ft
- Tank width must be between 3 ft and 20 ft
- Horizontal velocity must not exceed 3.0 feet per minute.



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API Separator

Transporting Oily Wastewater
to Oil/Water Separators

- Gravity (Preferred)



- Pumping
(Not Preferred)



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API Separator

Pumping Oily Wastewater Can:

- Emulsify oil due to high pH (>10) and due to pump shear (turbulence).
- Coat inert solids with oil creating neutral density particles that do not separate or can create a floating layer of solids on the separator surface that is difficult to remove.
- When you must pump, use low shear pumps such as Archimedes screw pumps.



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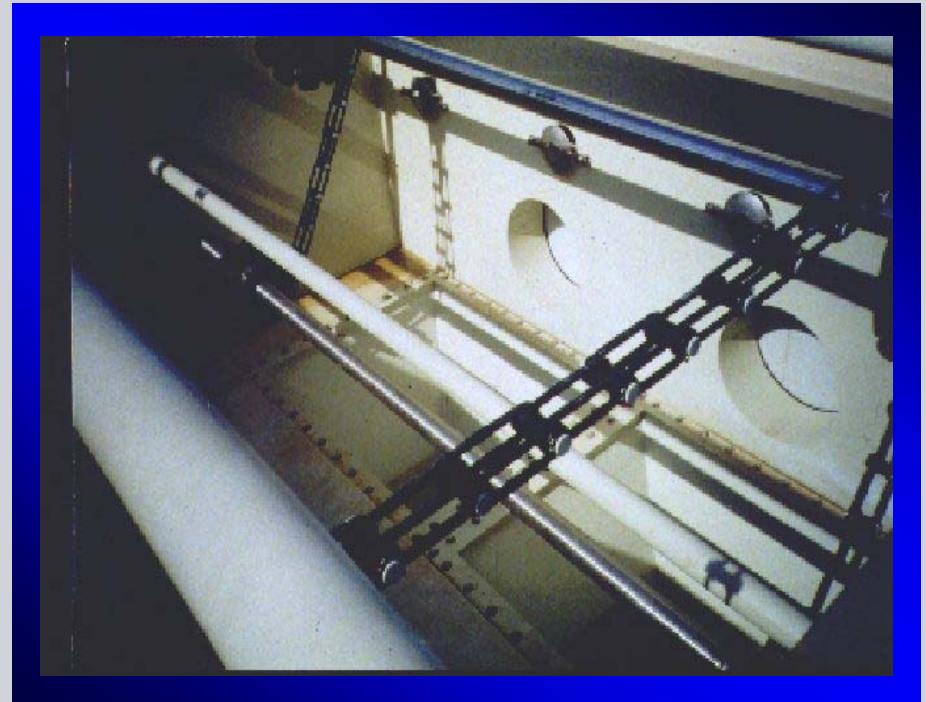
API Separator

Sludge Removal

The most important part of ANY API separator design. If you cannot remove the sludge from an API separator, the unit will fail

API bottoms are:

- Very heavy (8% solids)
- Oily and sticky (like asphalt)
- Very viscous



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API Separator

Sludge Removal

- API bottoms cannot be pumped with centrifugal pumps
- Must use a positive displacement pump
- Do not use progressive cavity pumps (rotating parts)
- Do use diaphragm pumps or peristaltic pumps
- Locate sludge pumps with flooded suction
- Locate sludge pumps close to separator sludge withdrawal point
- Use valved cleanouts on suction and discharge pipe

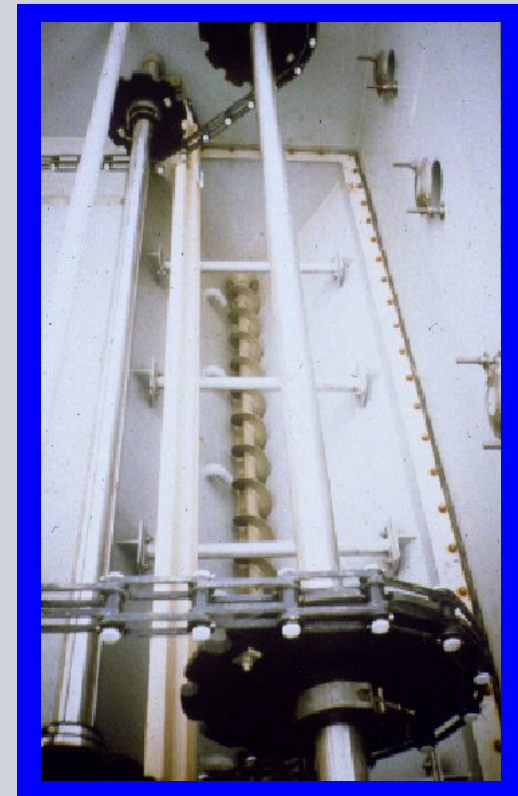
API Separator

Sludge Removal

Use multiple sludge
hoppers with
minimum 60° slope



Use a screw
conveyor



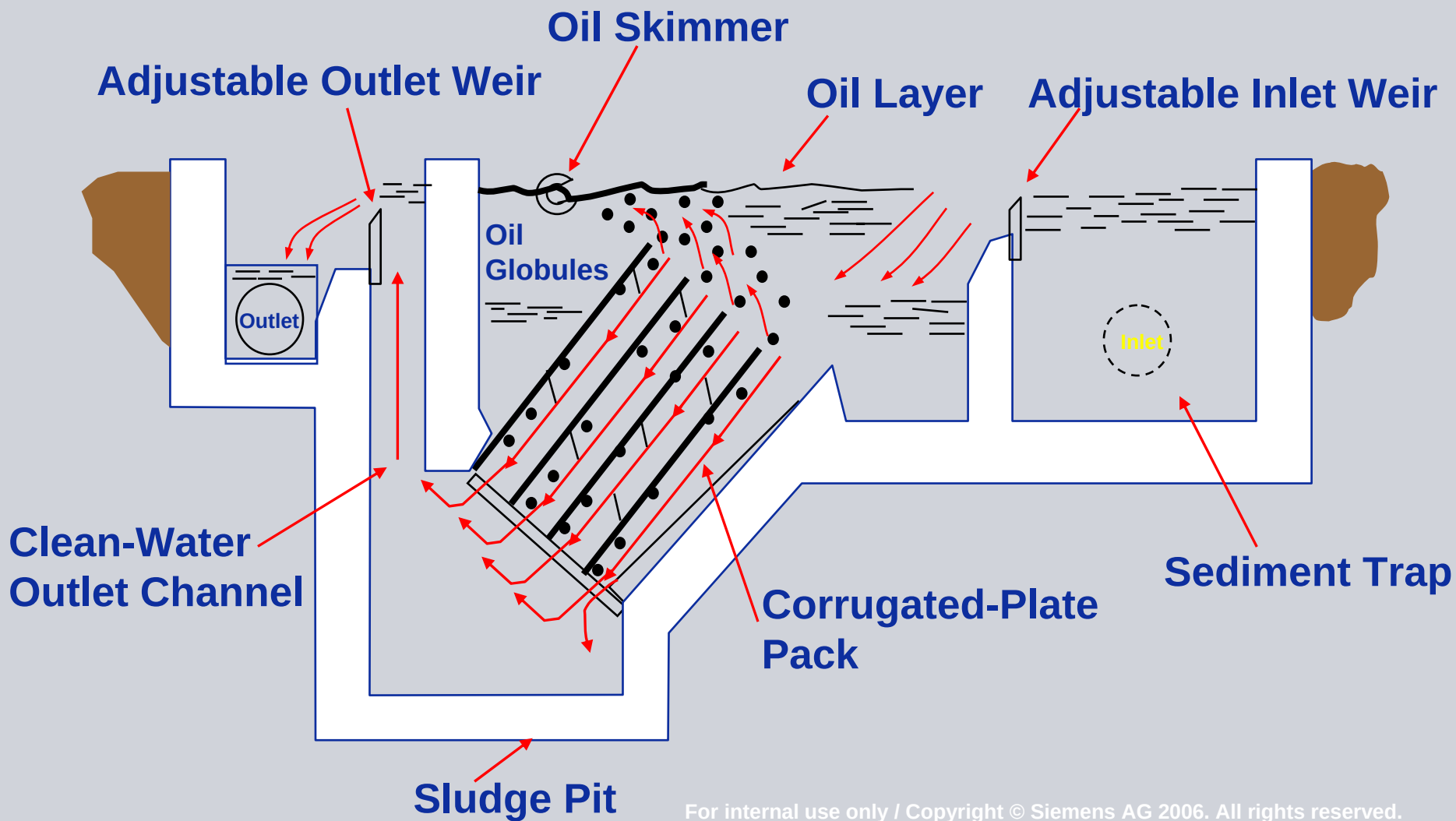
- OR -

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CPI Separator

Principles of Operation

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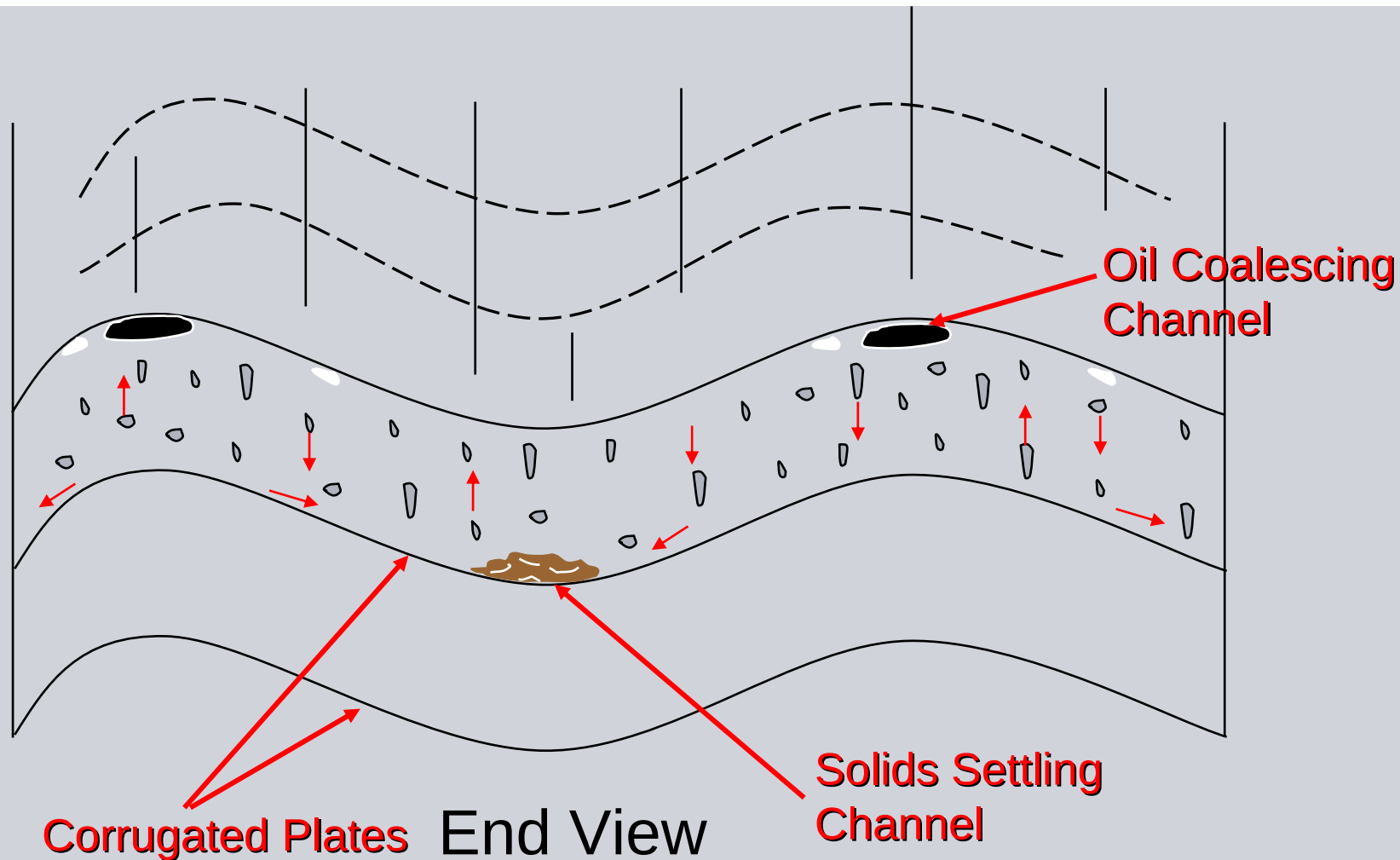


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CPI Separator

Principles of Operation

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CPI Separator

Typical Applications and Operating Conditions

- Normally used in petrochemical plants with low TSS wastewater or in treatment of produced water in oil fields after production separators.
- Influent oil: 200 to 10,000 ppm.
- Influent TSS: Less than 100 to 200 ppm, dependent upon type of oil present.



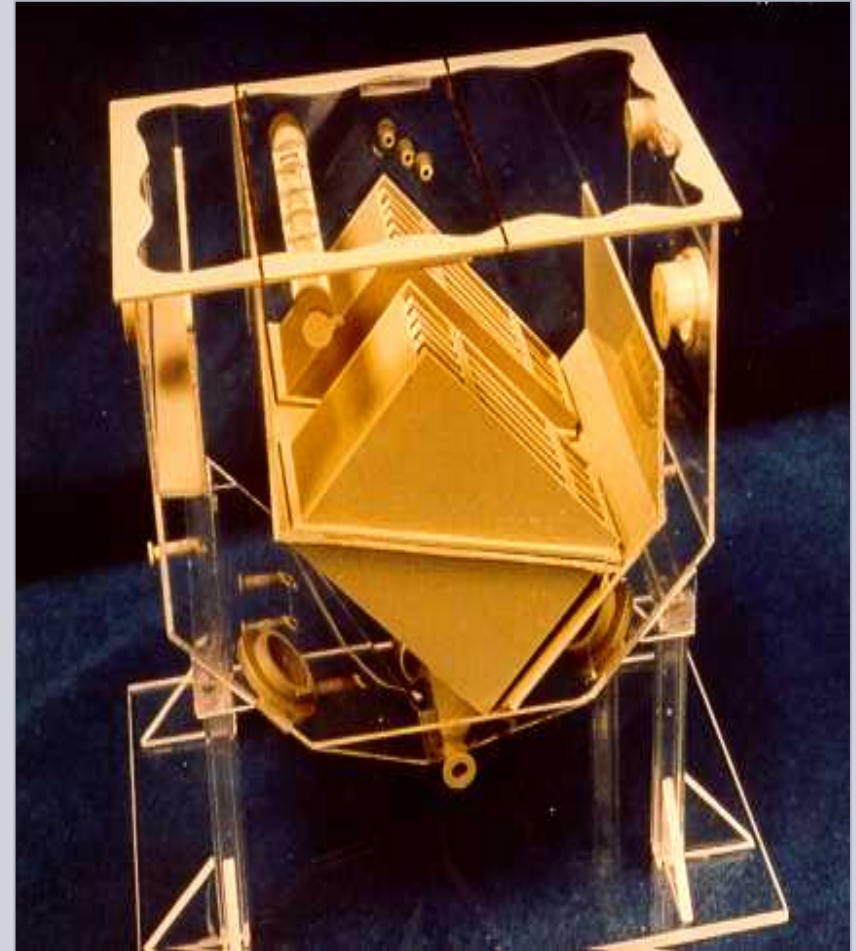
CPI Separator

Advantages

- Very small space requirements.
- Low capital costs.
- Easy to cover for VOC and odor control.

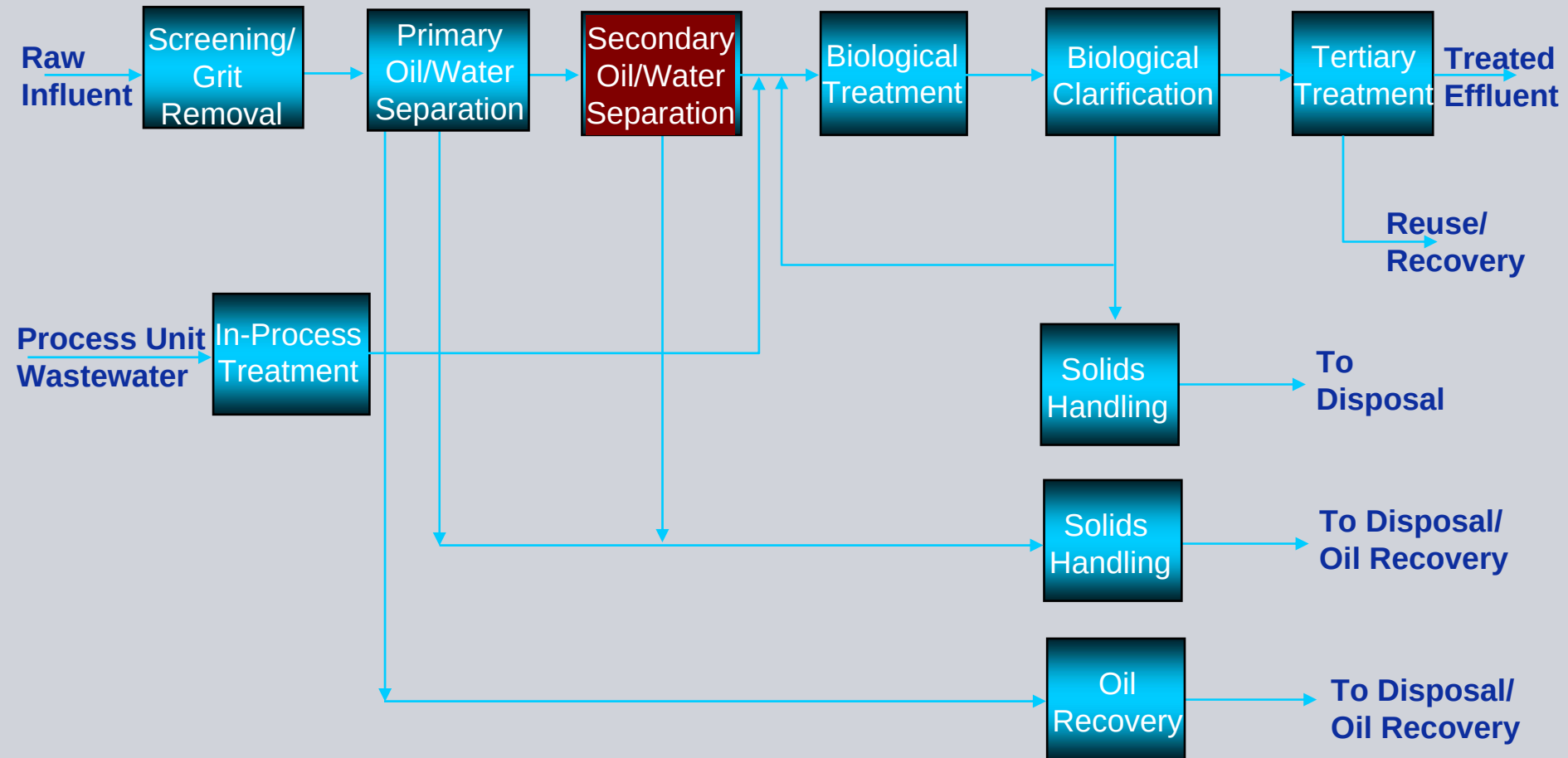
■ Disadvantages

- Not recommended for TSS concentrations above 100 to 200 ppm.
- Not tolerant to variations in flow and load.



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Typical Oily Water Treatment System



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Secondary Oil/Water Separation Treatment Objectives

- Treatment objective is typically 5 to 30 ppm oil, dependent upon discharge requirements, or downstream treatment processes.
- The amount of influent oil a secondary oil/water separator can process is 100 to 500 ppm, depending upon the technology selected.
- Oil can be present as:
 - Emulsified Oil
 - Fine Oil Droplets
 - Neutral Density Oil Wetted Solids
- Typically would like to see oil < 30 ppm to a biological treatment process. Other discharge requirements may be more stringent.
- It is important to remove oil emulsions before biological treatment. Biological treatment normally breaks oil emulsions to form free oil in biological treatment systems.

Secondary Oil/Water Separator

Methods used for Secondary Oil/Water Separation

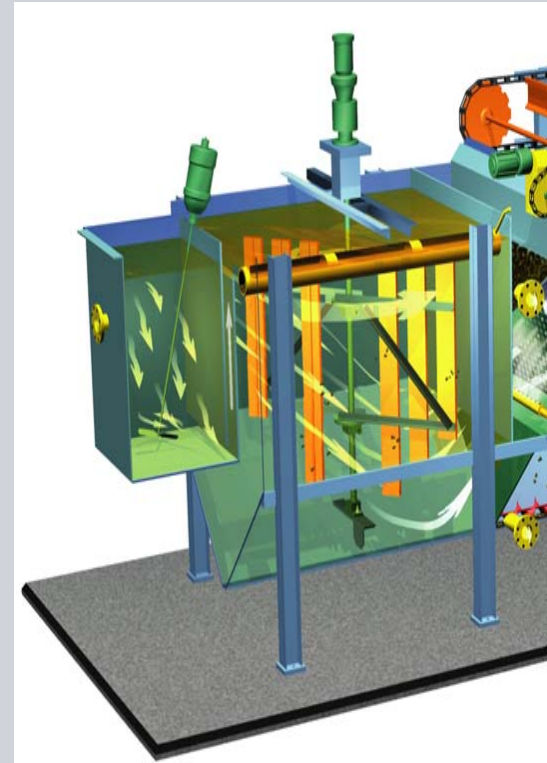
- Dissolved Air/Gas Flotation Separator (DAF or DGF Separators) – Most Common
- Induced Air/Gas Flotation Separator (IAF or IGF Separators)
- Walnut Shell Filter – Least Common

Secondary oil/water separation relies on a some other mechanism, other than gravity, to assist with removal of oil and suspended solids from wastewater.

Secondary Oil/Water Separation

Secondary oil/water separation is normally a two step process consisting of chemical conditioning and physical separation of oil and TSS from wastewater.

- Coagulation typically breaks oil emulsions which are present. Oil emulsions are becoming more common, and more difficult to treat, in petroleum industry wastewater.
- Coagulation is typically 30 seconds to 2 minutes in duration.
- Flocculation builds fine discrete oil and TSS particles into larger particles which are easier to remove.
- Flocculation is typically 5 to 15 minutes in duration

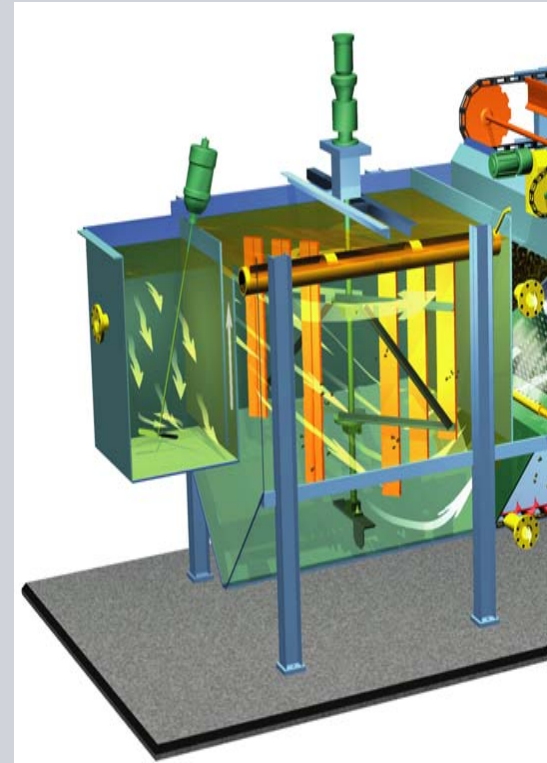


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Secondary Oil/Water Separation

Even after oil emulsions are broken and small discrete oil and solids particles are built into larger particles, the floc can still be very fragile..

- Turbulence can shear and break floc particles into smaller particles, which are more difficult to remove.
- Turbulence can also re-emulsify oil
- Eliminating or substantially reducing turbulence in the physical separation step can be very important to good oil and TSS removal.



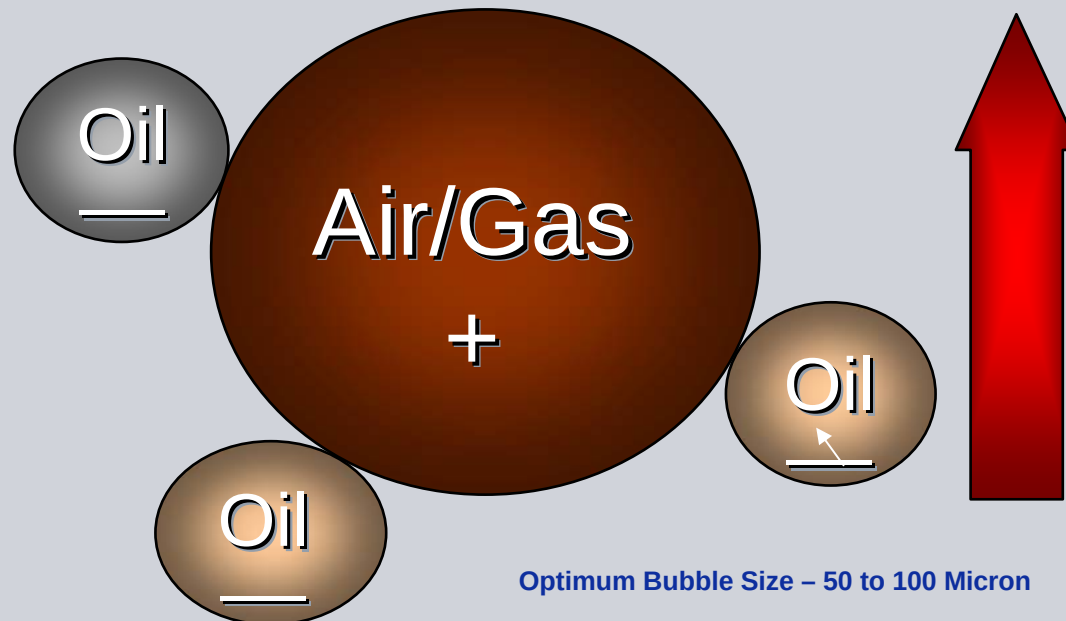
DAF/DGF Separators

Principle of Operation

The “Soda Water” Effect

Pre-dissolves Gas in Wastewater

Uses bubble attachment to oil/solids particles to “float” particles from wastewater

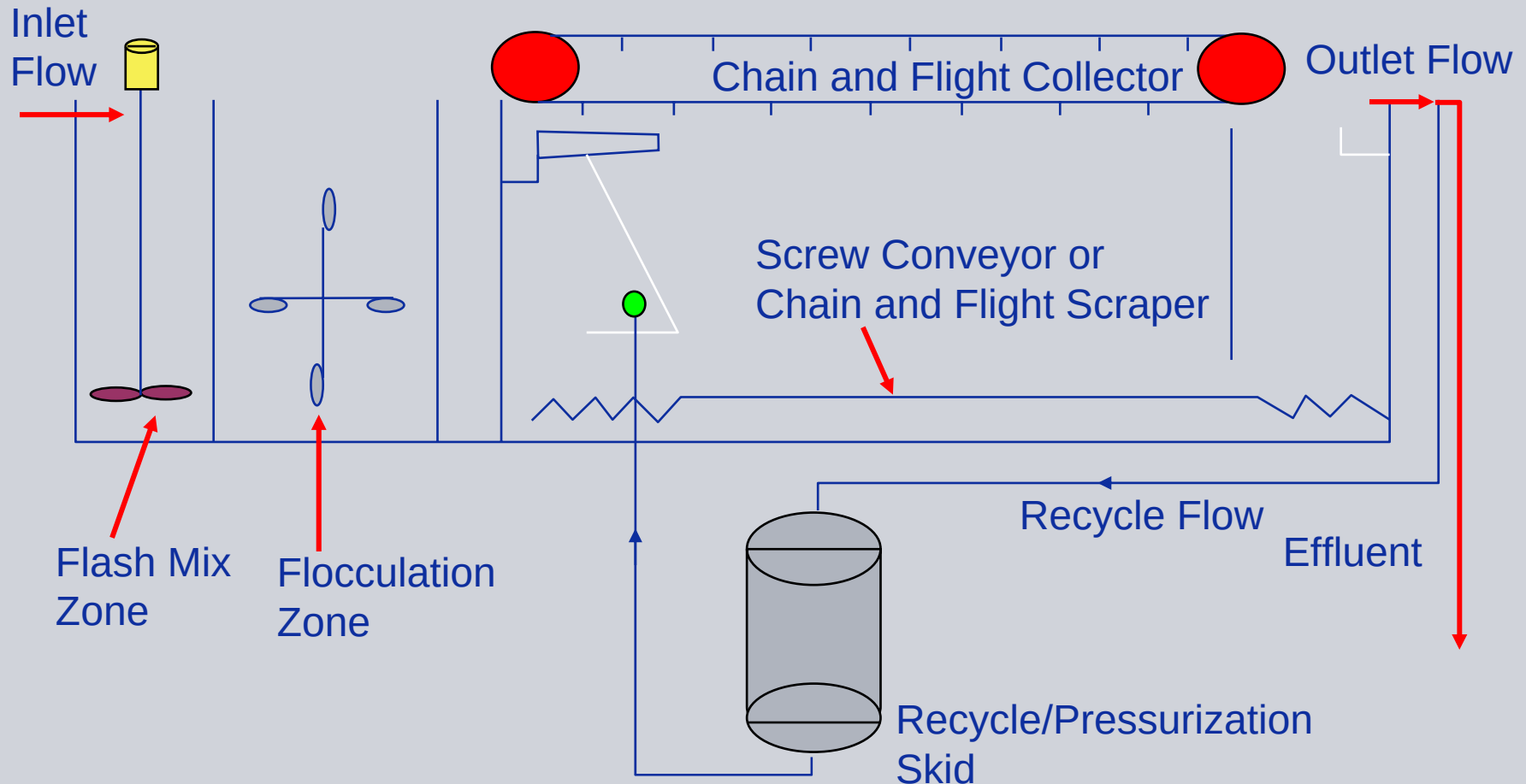


Optimum Bubble Size – 50 to 100 Micron

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DAF/DGF Separators

Principle of Operation



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DAF/DGF Separators

Typical Applications and Operating Conditions

- Most common method of oil and TSS removal in refineries and petrochemical plants.
- Influent oil and TSS concentrations up to 500 ppm.
- Up to 95% removal of oil and TSS
- Hydraulic loading rates are typically 1.5 to 3.0 gpm/ft² for rectangular units and 1.0 to 2.0 gom/ft² for circular units. This includes the recycle flow.



DAF/DGF Separators

Typical Applications and Operating Conditions

- Recycle flow is typically 20% to 33% of the forward flow.
- Operating pressure in the gas saturation tank is typically 50 to 55 psi for most petroleum refining applications.
- Air to solids ratios do not come into play until oil and TSS concentrations exceed 1000 ppm each, which is typically a thickening application.

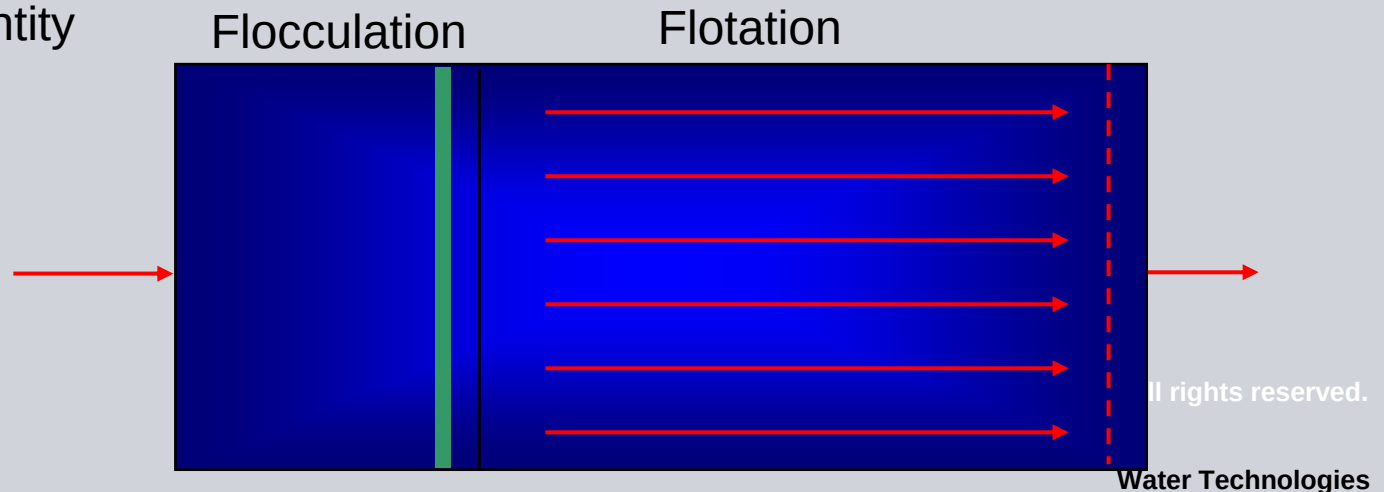
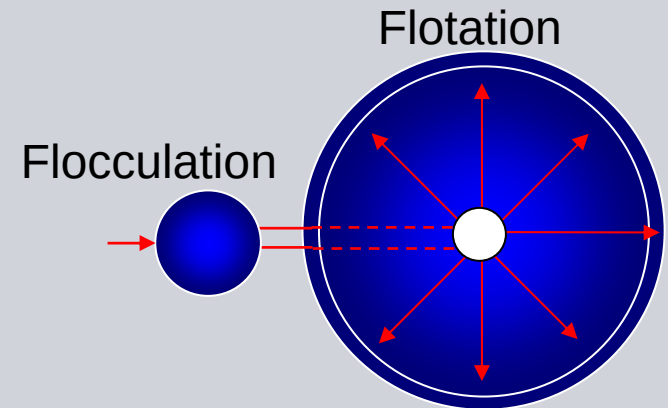


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Rectangular vs. Circular

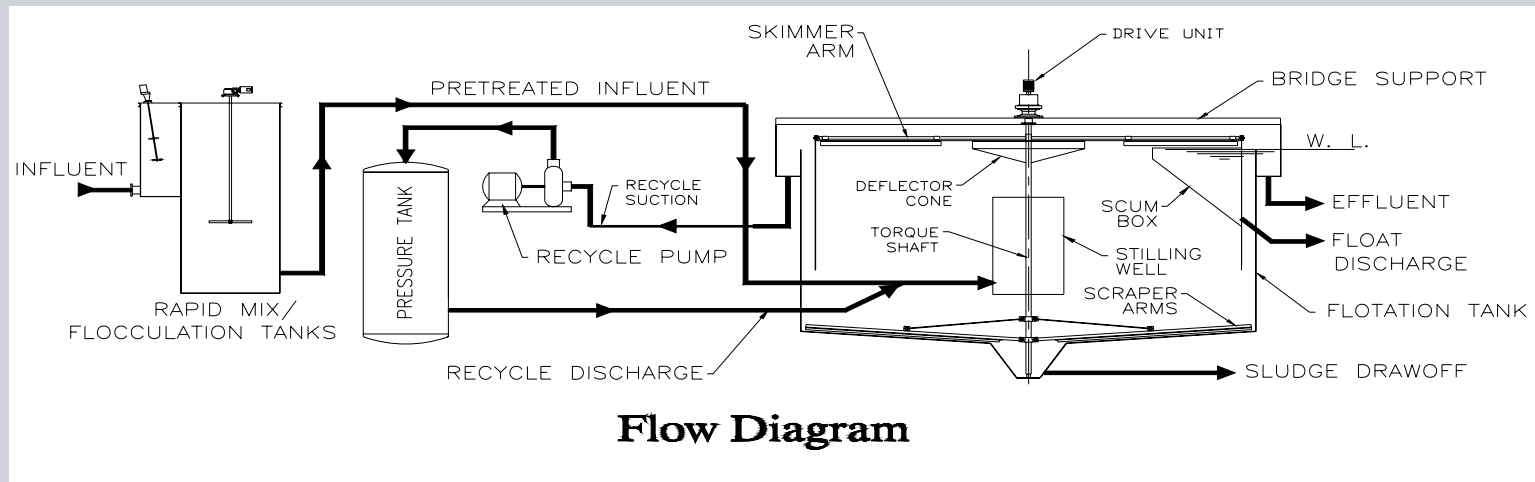
Rectangular Advantages over Circular Design

- Flow pattern – Plug Flow
- Skimming effectiveness – Perpendicular to flow insure positive removal.
- Effluent weir adjustment – Easier with rectangular.
- Flash mixing and flocculation – Less stress on flocculated oil and TSS
- Footprint, quantity



Circular DAF

- Package systems up to 10' diameter
- Modular from 10' to 20' diameter
- Field-erected
- Steel or concrete tanks



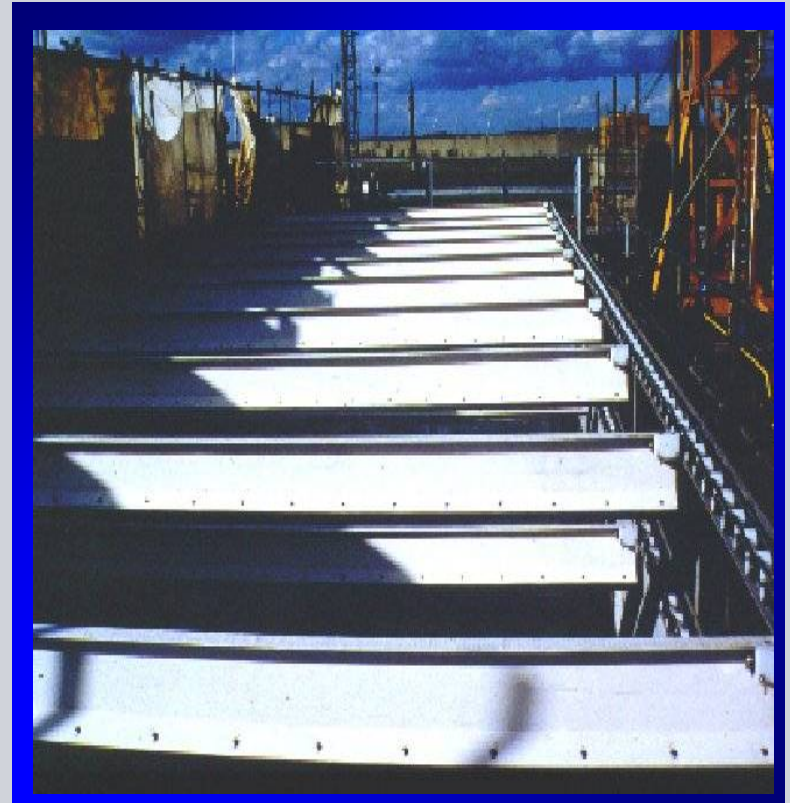
DAF/DGF Separators

Advantages

- Tolerant of changes in wastewater strength and flow.
- Integral chemical conditioning provides good removal of oil emulsions.
- Low sludge production, 0.1 to 0.5% of forward flow.
- Consider non-metallic collector components for corrosion resistance.

Disadvantages

- Higher cost and larger footprint compared to other technologies.



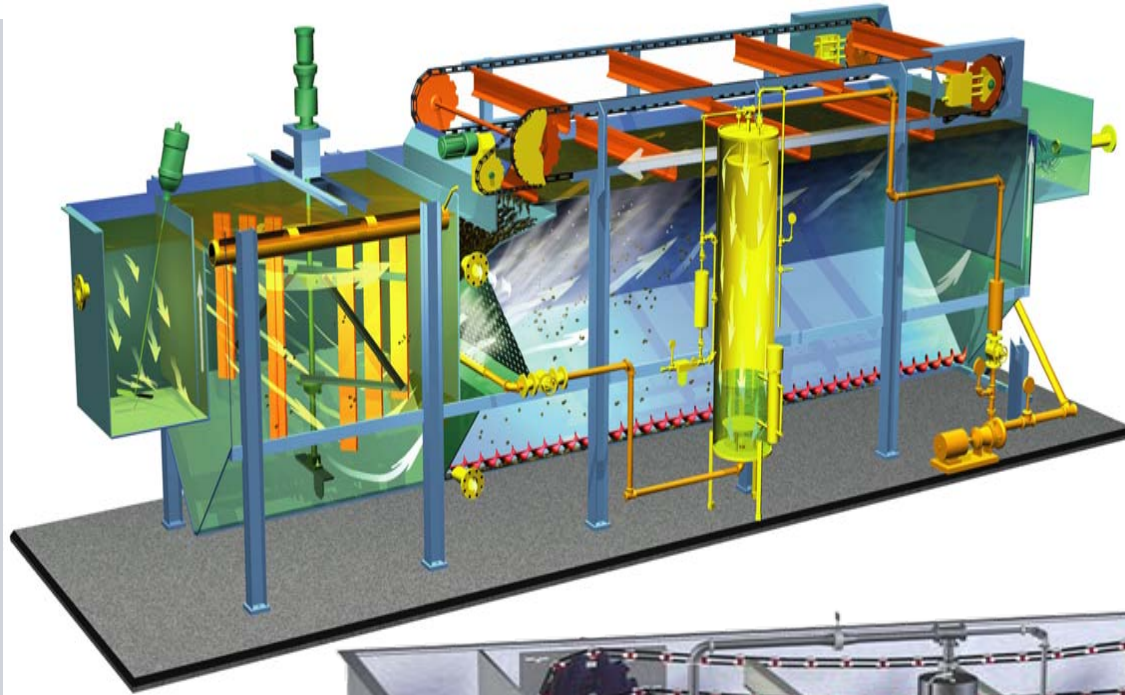
Folded Flow® DAF/DGF Separator

- Hydraulic loading rates up to 12 gpm/ft² (29.3 m/hr)

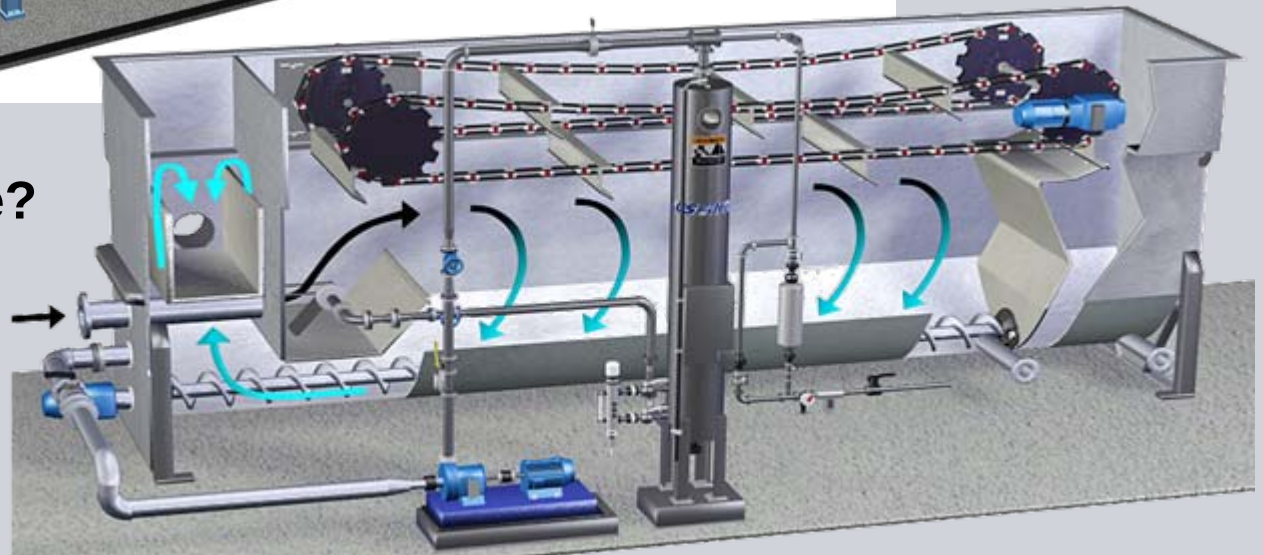


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Folded Flow® DAF/DGF Separator

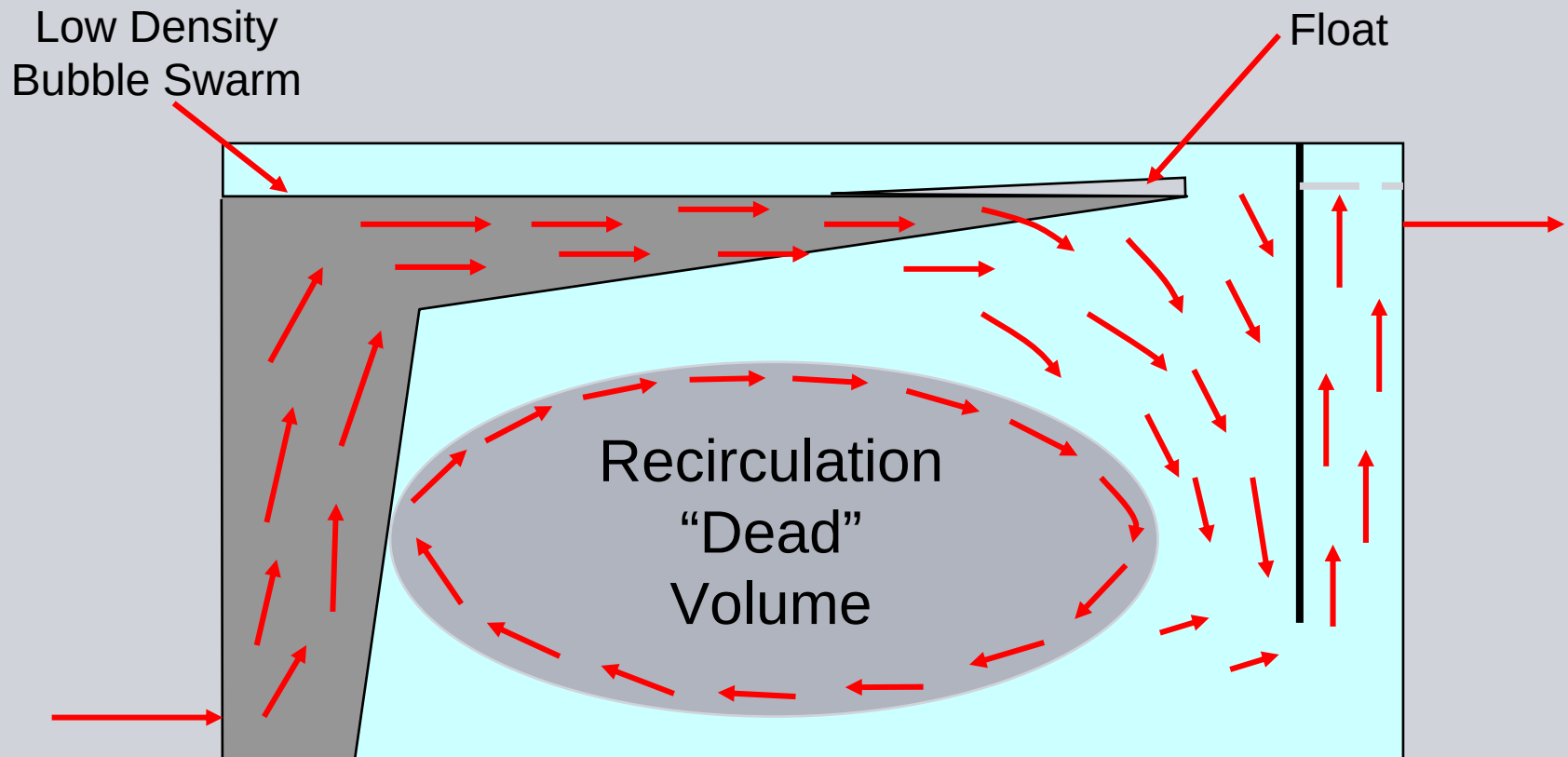


Why The Difference?



Folded Flow® DAF/DGF Separator

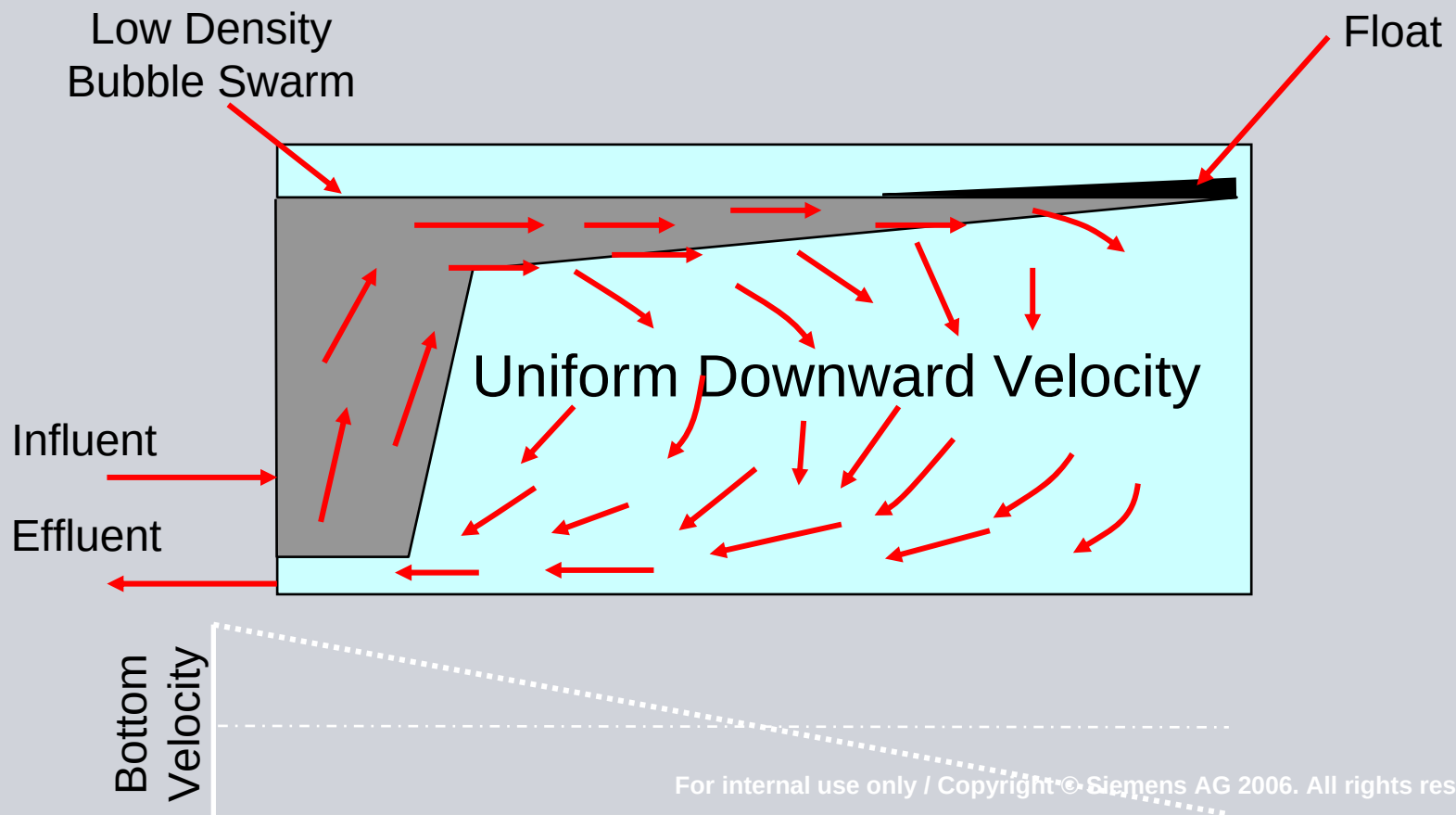
Conventional “Straight Through” DGF



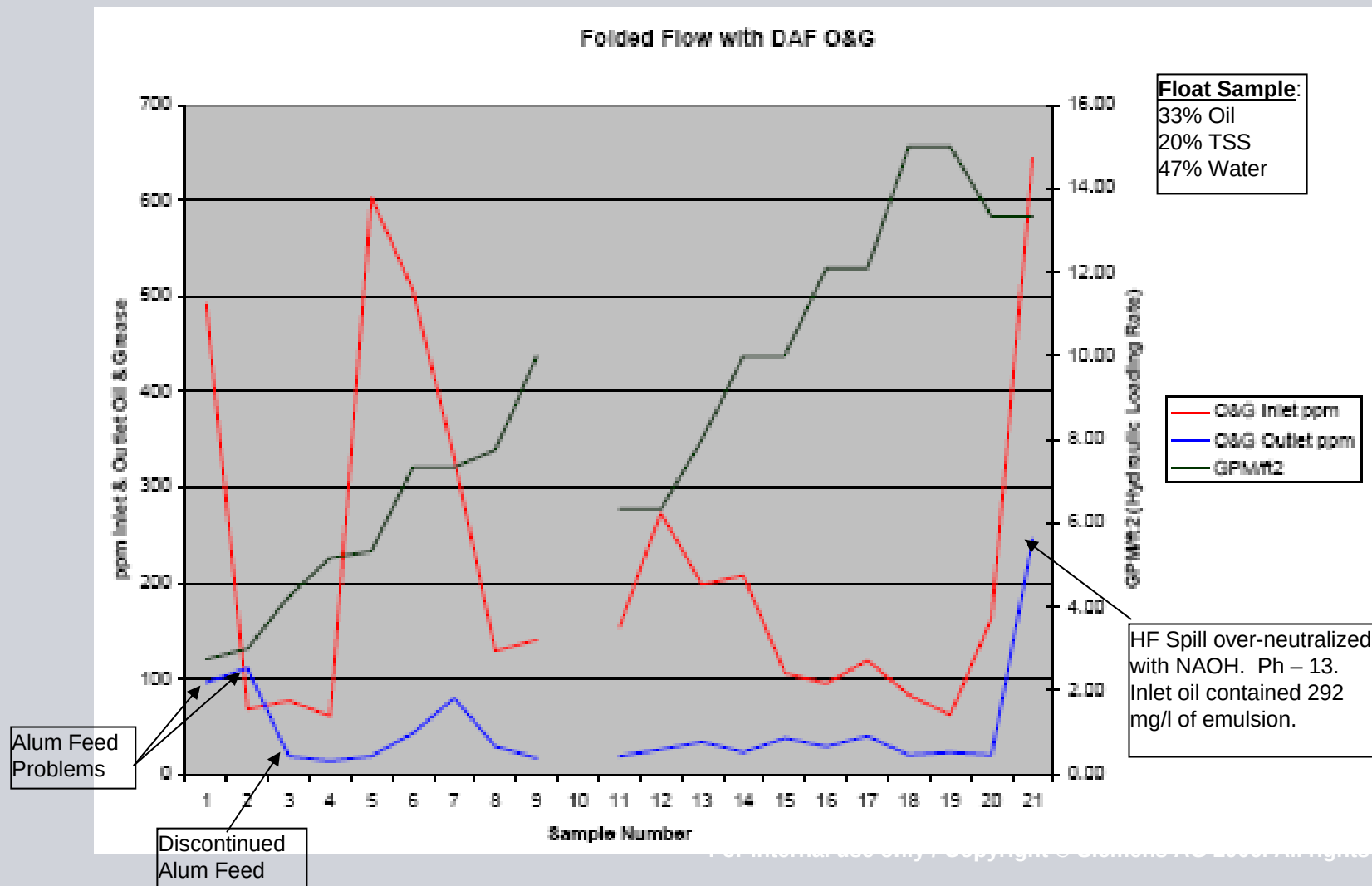
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Folded Flow® DAF/DGF Separator

“Optimized” Folded Flow™ DGF



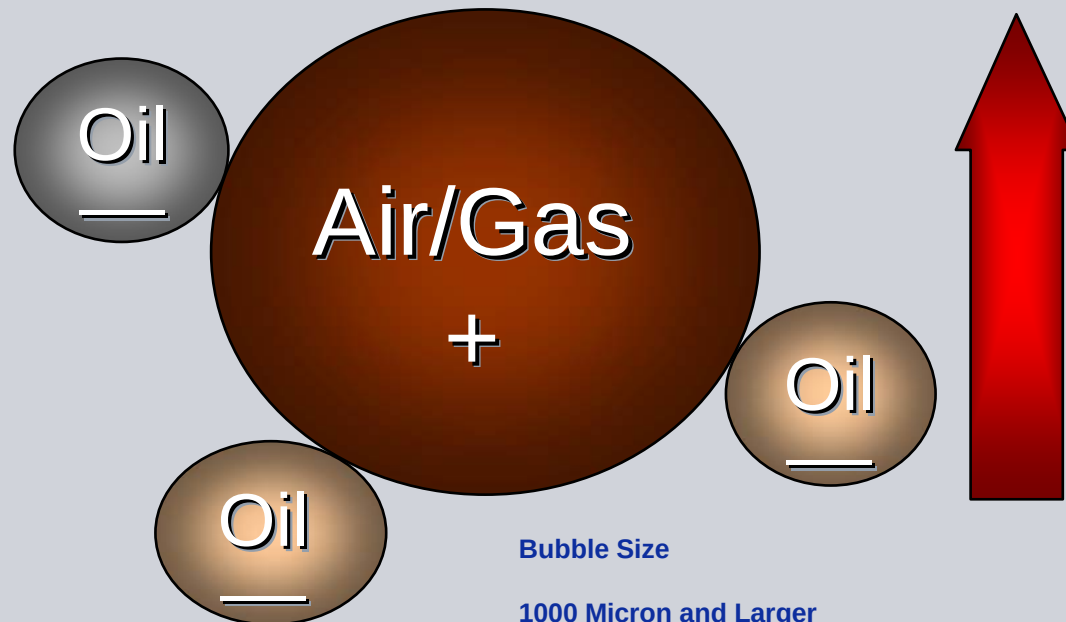
Folded Flow® DAF/DGF Separator Refinery Pilot Study



IAF/IGF Separators

Principle of Operation

Gas is Dispersed into Small Bubbles
Uses bubble attachment to oil/solids particles to “float”
particles from wastewater

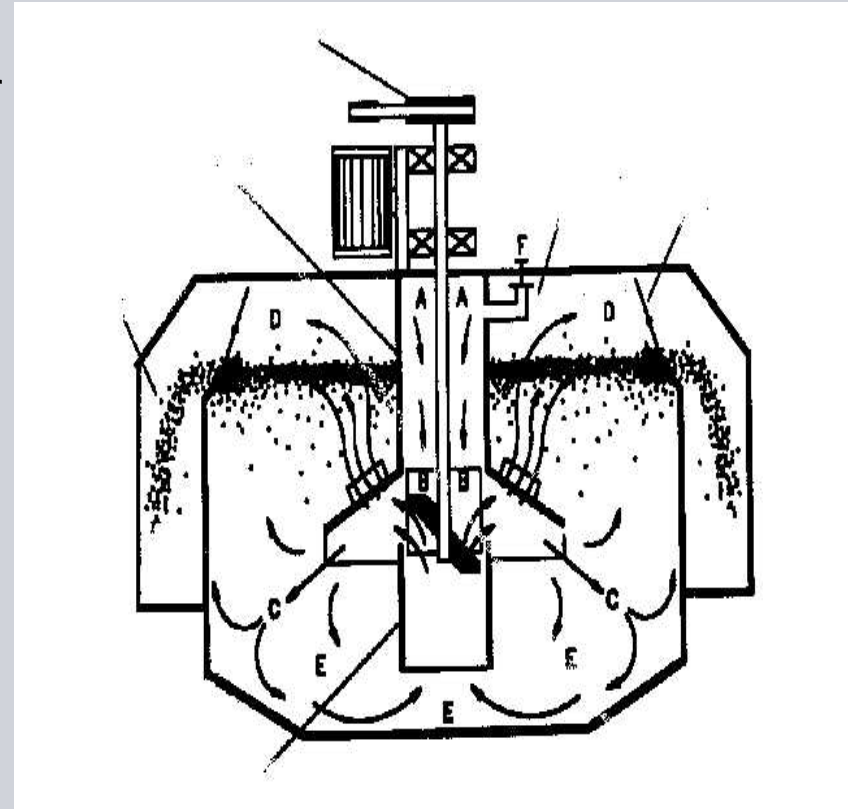


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IAF/IGF Separators

Principle of Operation

- The gas is educted into the wastewater using either a mechanical mixer (shown) or a recirculation pump.
- The gas is then dispersed into small bubbles using the mechanical mixer (shown) or an impingement plate.
- Creates a frothing effect, whereby oil is removed from the wastewater.



IAF/IGF Separators

Typical Applications and Operating Conditions

- Typically used in oil production with some minor applications in refineries and petrochemical plants.
- Works best on applications with consistent wastewater characteristics and no oil emulsions.
- Influent oil concentrations less than 300 ppm.
- 90 to 95% removal of oil.
- Not designed to remove TSS (TSS less than 100 ppm).



IAF/IGF Separators

Advantages

- Small footprint.
- Lower costs.



Disadvantages

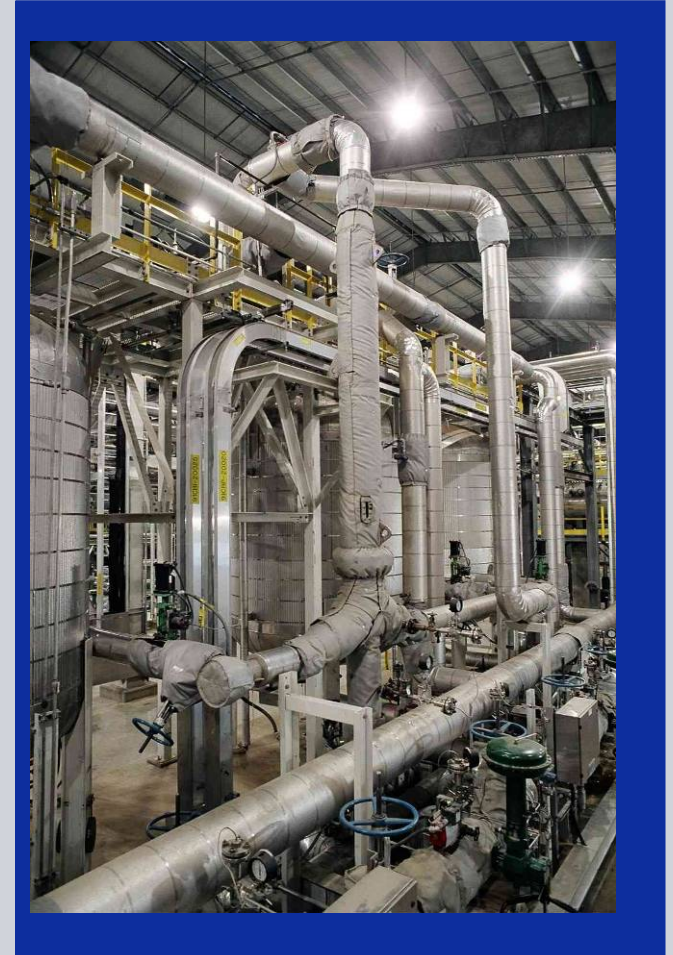
- Higher sludge production, 2 to 10% of the forward flow.
- Less tolerant of flow and load variations.
- Poor removal of oil emulsions.
- Limited TSS removal efficiency.

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Walnut Shell Filters

Principle of Operation

- Operates very similar to a media filter, except the media is crushed walnut shells.
- Walnut shells have very high affinity to attract oil.
- Once the oil adsorption capacity of the walnut shells is reached, based on differential pressure, the walnut shells are hydraulically removed from the filter where the oil is centrifugally removed from the media. The walnut shells are then sluiced back into the filter vessel.

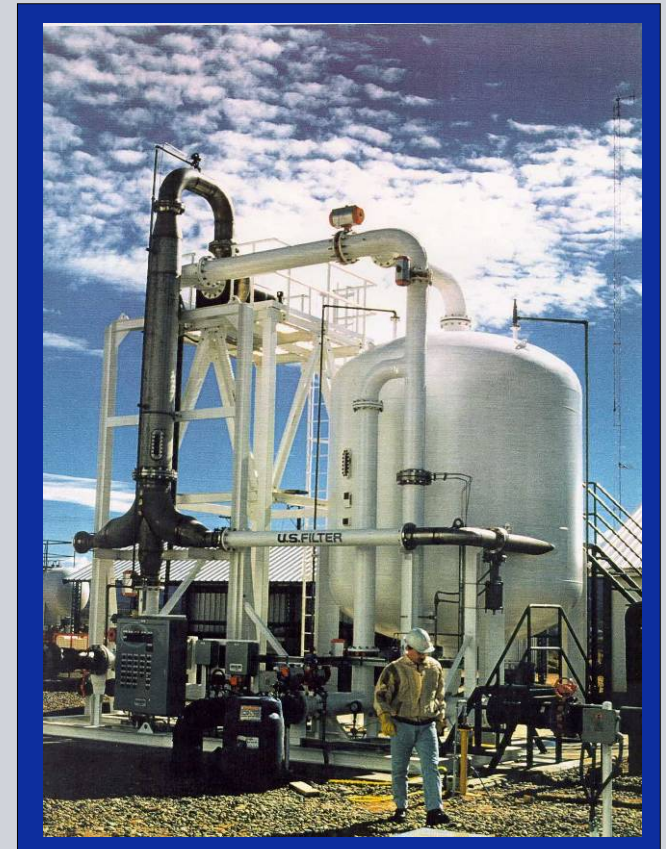


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Walnut Shell Filters

Typical Applications and Operating Conditions

- Typically used in facilities with strict oil discharge requirements, that do not have downstream treatment processes, such as biological treatment.
- Sometimes used with systems that have downstream membrane processes such as MBR.
- Influent oil concentrations less than 100 ppm.
- Effluent oil less than 5 ppm.



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Walnut Shell Filters

Advantages

- Can achieve very low effluent oil concentrations, 1 to 5 ppm.

Disadvantages

- Not a good TSS removal device.
- High capital cost.



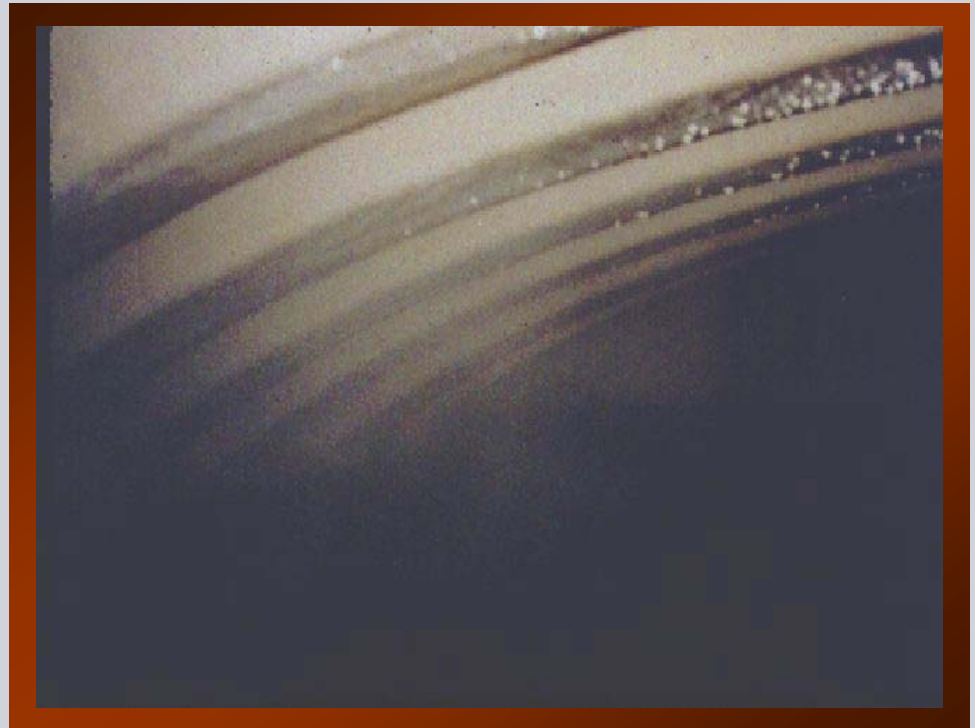
Oil/Water Separators

VOC Containment/Treatment

Safety is a valid concern!!!!

Fires/Explosions have occurred in refinery oil/water separators.

- Methods to mitigate explosion risks.
- VOC Containment Methods
- VOC Control Methods



Oil/Water Separators

Risk Assessment - Safety

Potential Hazard	Solution
Explosion from accumulated gases	Eliminate oxygen from the vapor space. Purge with inert gases.
Spark from static electricity	Properly ground equipment. Special coatings to reduce static build-up.
Spark from electrical devices	Locate all electrical devices on equipment exteriors. Use explosion-proof devices.
Spontaneous combustion	Do not use carbon steel wearing parts. Hydrogen sulfide forms iron sulfide. Spontaneous combustion occurs when exposed to air.

Vapor Containment Covers - Floating

Advantages:

- Eliminates vapor space above MOST of the separator. Fixed cover still required over oil skimmers.
- Well suited for covering existing concrete basins.

Disadvantages

- Drain holes can allow oil to flow onto cover surface.
- Does not allow skimming to the top of the water surface.
- May not eliminate VOC/odor emissions.



Vapor Containment Covers - Fixed

Advantages

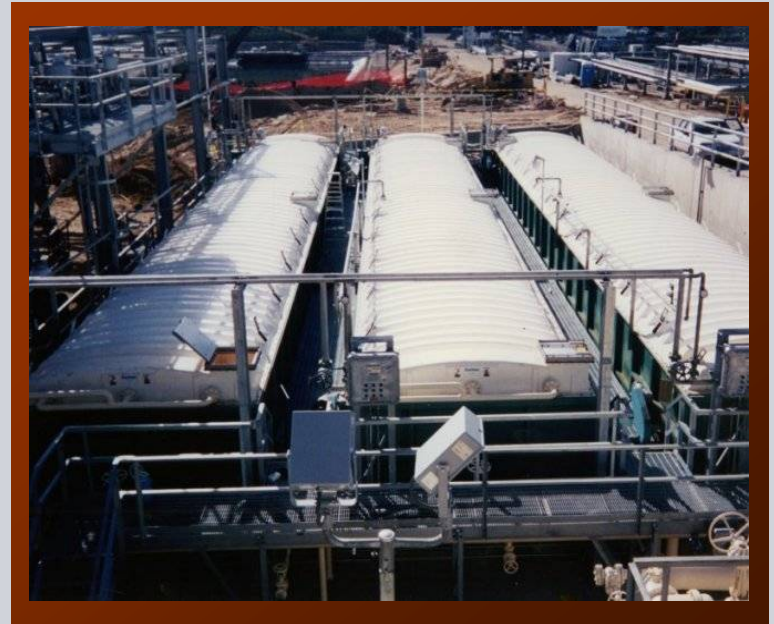
- Allows skimming to the water surface.
- Easy to remove for maintenance.

Disadvantages

- Numerous seams can be difficult to seal. Covers should minimize liner meters of seam length.
- Vapor space exists that can potentially be explosive.
- Difficult to retrofit onto existing separators.

Materials

- Steel – Recommended due to minimal seams
- Aluminum
- Fiberglass



Fixed Vapor Containment Covers Safety Equipment



Combination access/deflagration vents
Combination Vacuum/pressure relief valves



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Purge/Blanketing Gases

Primary Oil/Water Separators:

- Nitrogen is the most common purge or blanketing gas. Fuel gas or methane gas have also been used. The type of purge or blanketing gas selected with, in part, be determined by the type of VOC control device used.
- Blanketing, maintaining a positive internal pressure on the covers, is normally recommended to control operating costs.
- A slight internal pressure, 4" wc, is applied to the covers to maintain an oxygen deficient atmosphere.
- Venting is controlled through blanket gas pressure regulators and pressure relief valves which are provided with the separators.

Secondary Oil/Water Separators

- Same as Primary Oil/Water Separators, except the blanking gas is normally added continuously as the floatation gas.

Off-Gas/VOC Control Devices

Primary Oil/Water Separators:

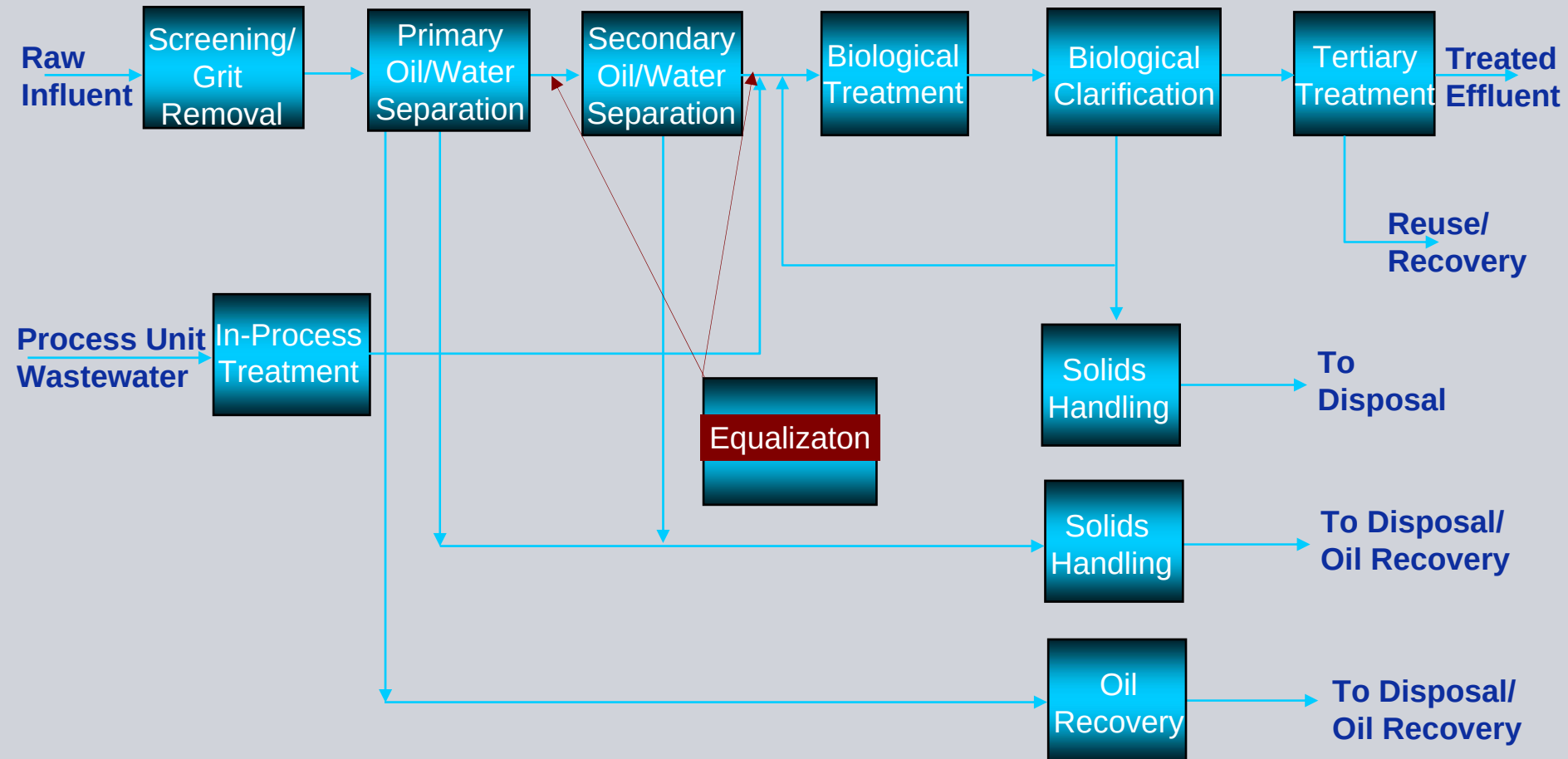
- Activated carbon is normally the most cost effective as the separators are only blanketed with gas, not continually purges. Carbon usage is minimal.

Secondary Oil/Water Separators:

- Activated carbon is again the most common, but since gas is normally exhausted continuously, carbon usage can be high on larger systems. In these instances, thermal oxidizers have also been used. Occasionally, flares are also used. Bio-filters have shown little success.



Typical Oily Water Treatment System

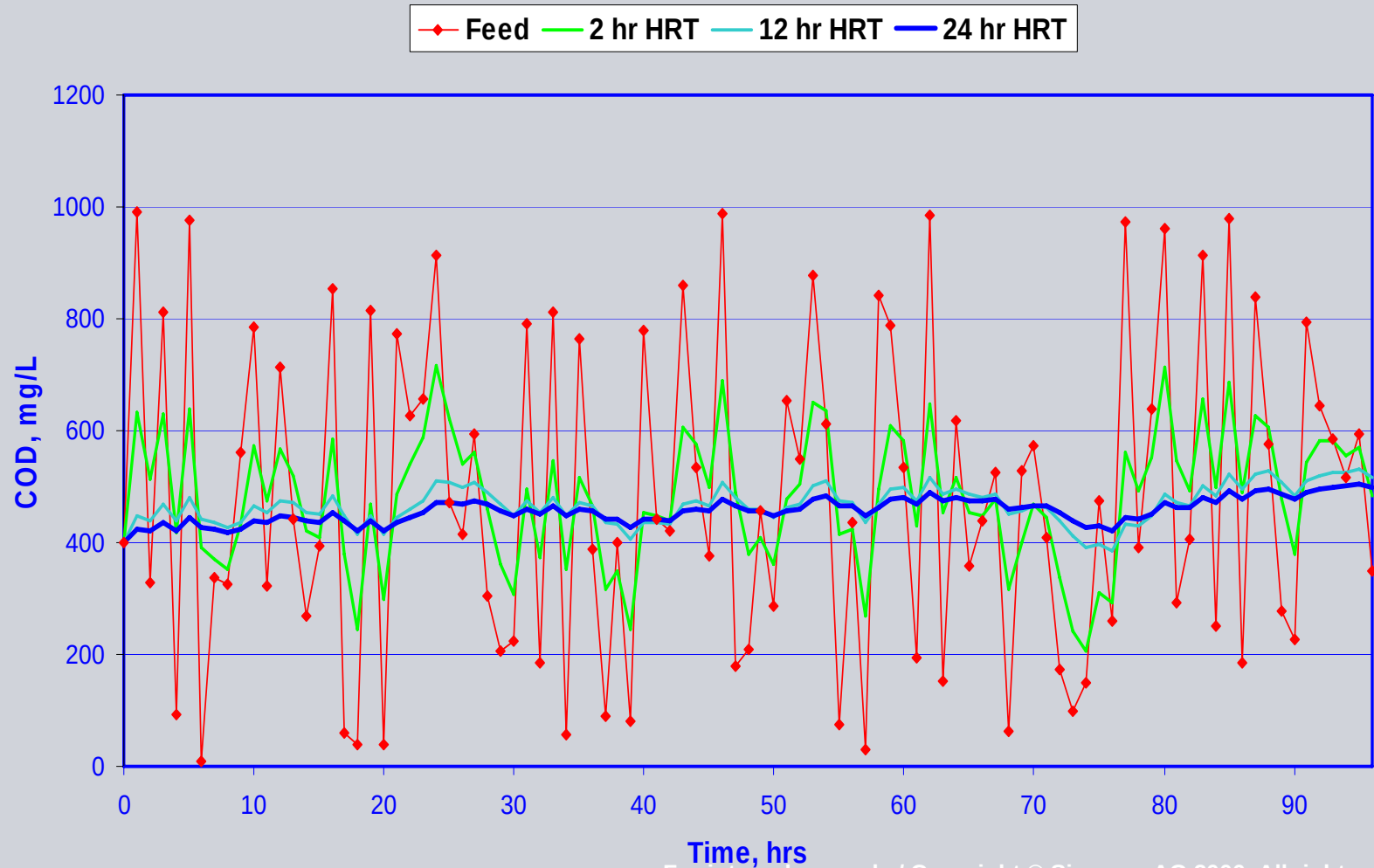


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Wastewater Equalization

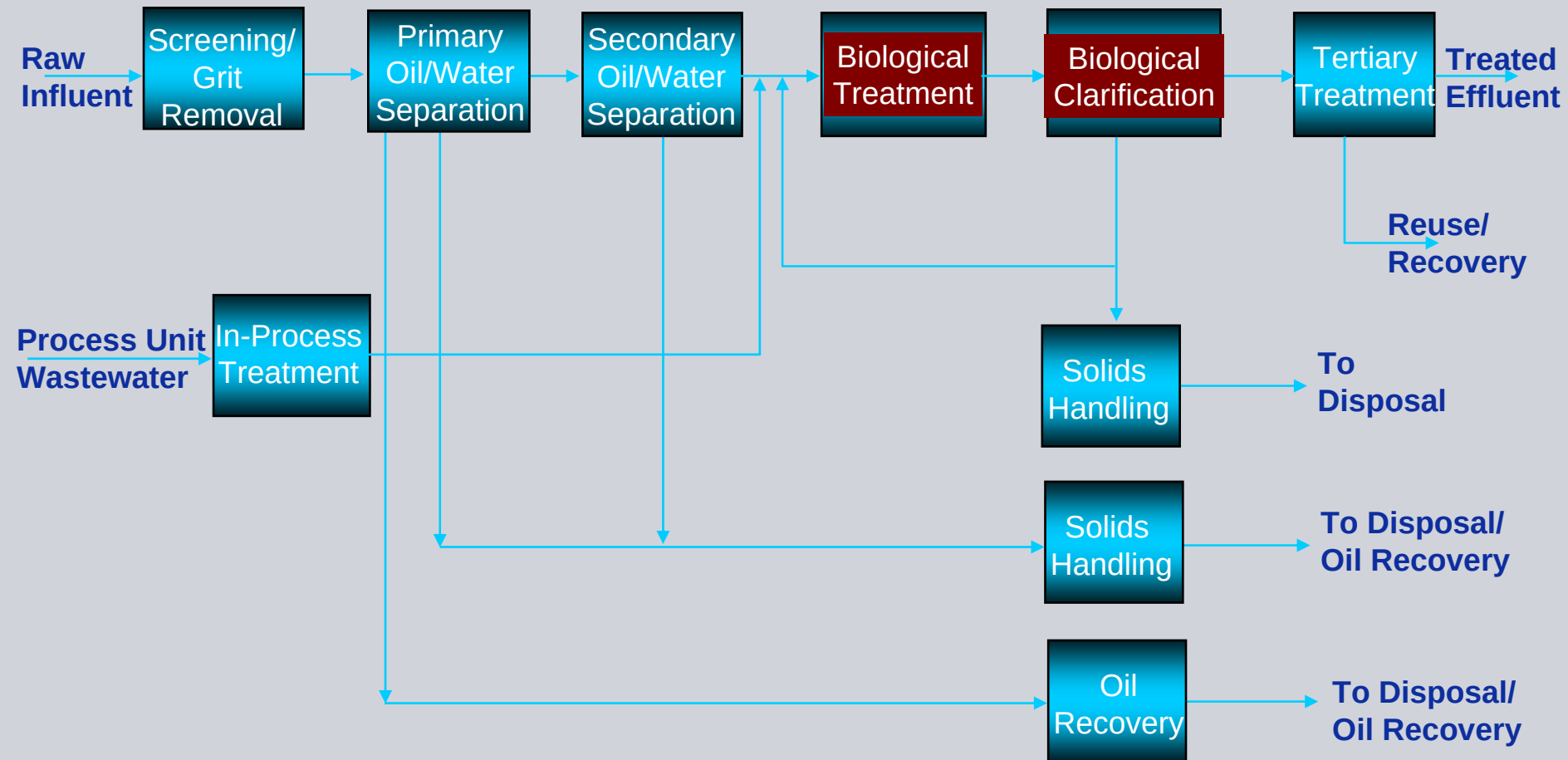
- Purpose
 - Smooth out variations in flow and contaminants
 - Minimize hydraulic shock loading to WWTP process equipment
 - Minimize contaminant shock loading to biological treatment
- Methodology
 - Typically located after the oil/water separators
 - Flow diversion/control of stormwater
 - Completely mixed fixed volume tank
- Effective volume (retention time)
 - Magnitude of contaminant variation
 - Duration of contaminant variation
 - For petroleum facilities, 12 to 24 hours is desired.

Wastewater Equalization



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Typical Oily Water Treatment System



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Biological Treatment

Aeration Devices
Membrane Bio-Reactors (MBR)



This information is applicable to both oily wastewater and municipal wastewater treatment.



Biological Treatment

Typical Applications and Operating Conditions

- Designed primarily for removal of biodegradable organic matter, nitrogen and phosphorus compounds, and N_2S
- Normally applied after primary treatment where inert solids and oils are removed from the wastewater.
- Used to achieve effluent BOD and TSS concentrations of 30 ppm or less.
- Effluent COD concentrations are dependent upon the application.



Biological Treatment

Principals of Operation

Organic
Chemicals

Carbon
Dioxide

Oxygen

Nutrients

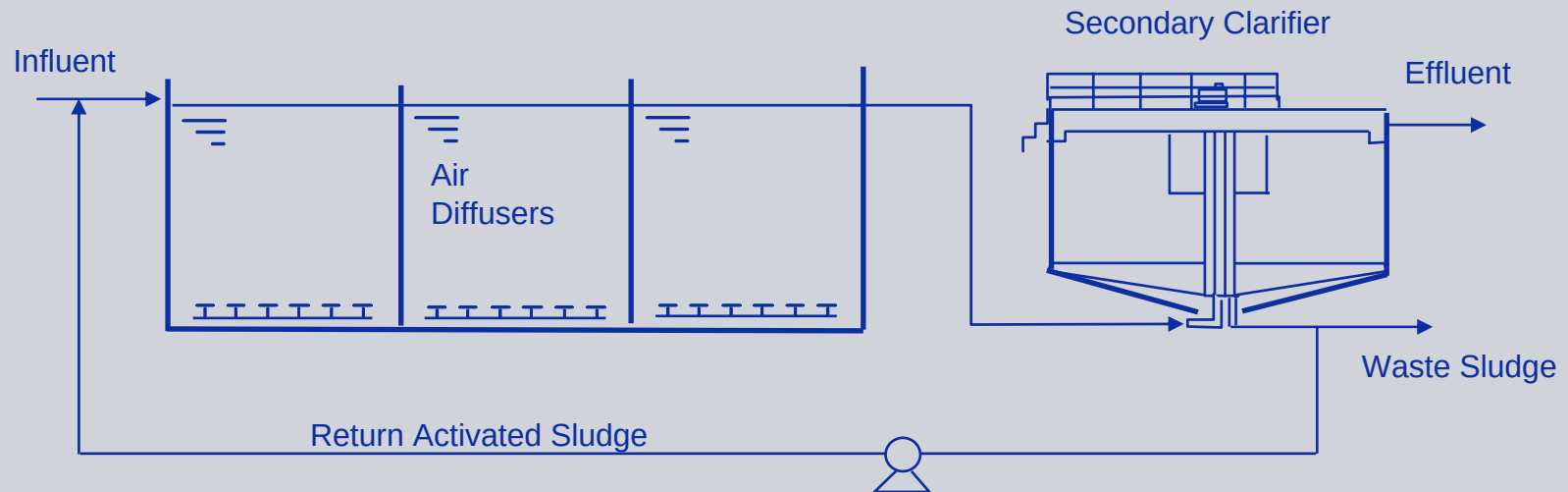
Bacteria

Cell
Mass

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Biological Treatment

Principles of Operation



Biological Treatment Options

Fine Bubble Aeration

Advantages

- Very high oxygen transfer efficiency (low energy consumption).
- Low VOC and odor emissions.

Disadvantages

- Diffusers require periodic cleaning.
- The aeration device is submerged and must be removed from the tankage for cleaning.
- Can add heat to wastewater.



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Biological Treatment Options

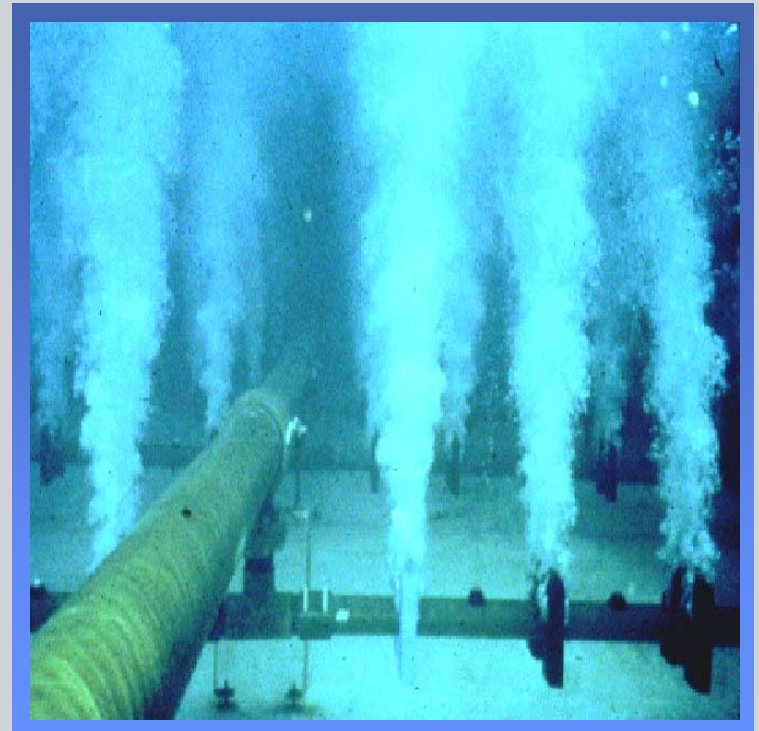
Coarse Bubble Aeration

Advantages

- Non-plug design requires very little maintenance, if any.
- Low O&M costs.

Disadvantages

- Not very energy efficient.
- The aeration device is submerged and must be removed from the tankage for cleaning.
- Can add heat to the wastewater.
- Higher potential for VOC and odor emissions.



Biological Treatment Options

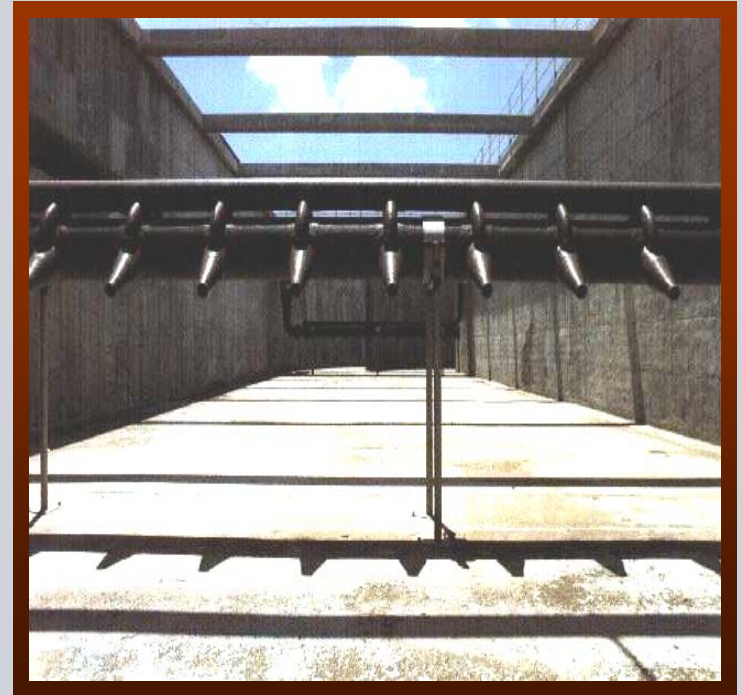
Jet Aeration

Advantages

- Non-plug design requires very little maintenance
- Low O&M costs.
- Energy efficient.
- Very good process flexibility.

Disadvantages

- The aeration device is submerged and must be removed from the tankage for maintenance.
- Can add heat to wastewater.
- Requires an external recirculation pump for jet mixing feature.



Biological Treatment Options

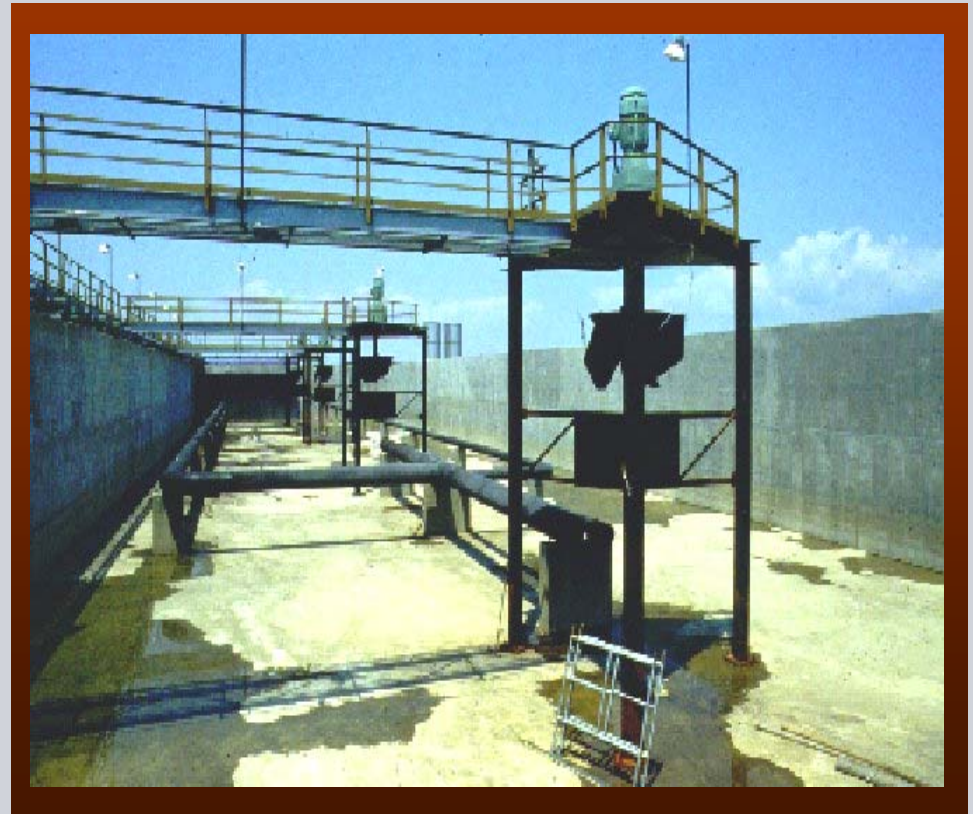
Surface Aerators

Advantages

- Located above the water surface.
- Can be maintained without draining the treatment basin.
- Can provide cooling of hot wastewater.
- Low costs

Disadvantages

- Very energy inefficient.
- Very high potential for odors and VOC emissions.
- Very large space requirements.



Biological Treatment Options

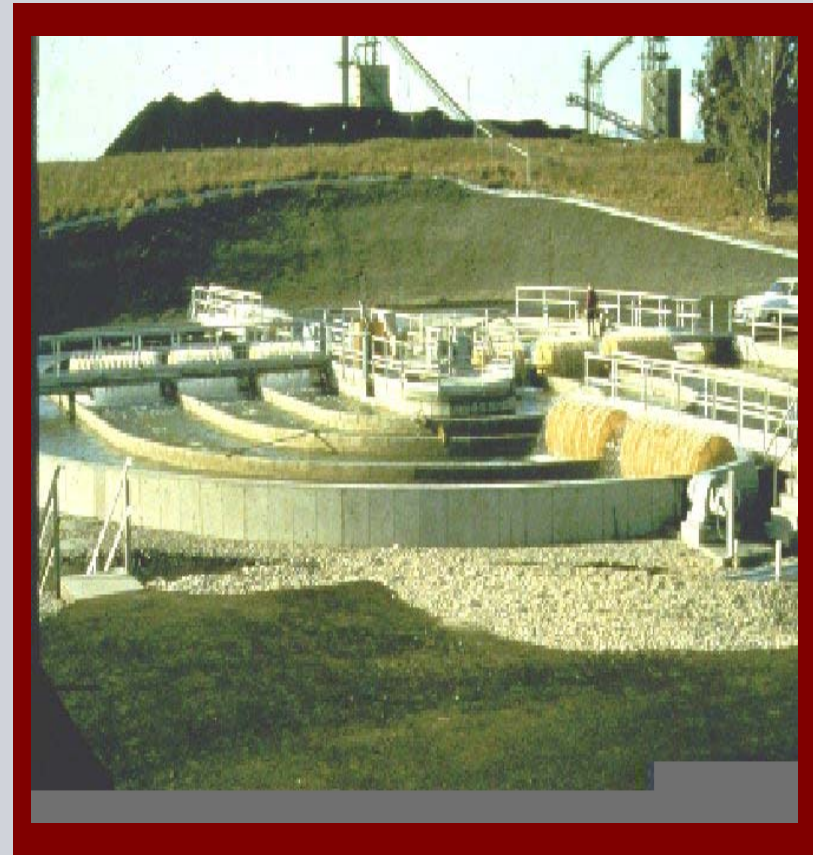
Oxidation Ditch

Advantages

- Aeration devices are above the water level and can be maintained without draining the tank.
- Good process flexibility due to multi-channel design.
- Can provide good cooling of warm wastewater.
- Very energy efficient.

Disadvantages

- Large area requirement.
- High potential for odor and VOC emissions.



Biological Treatment Options

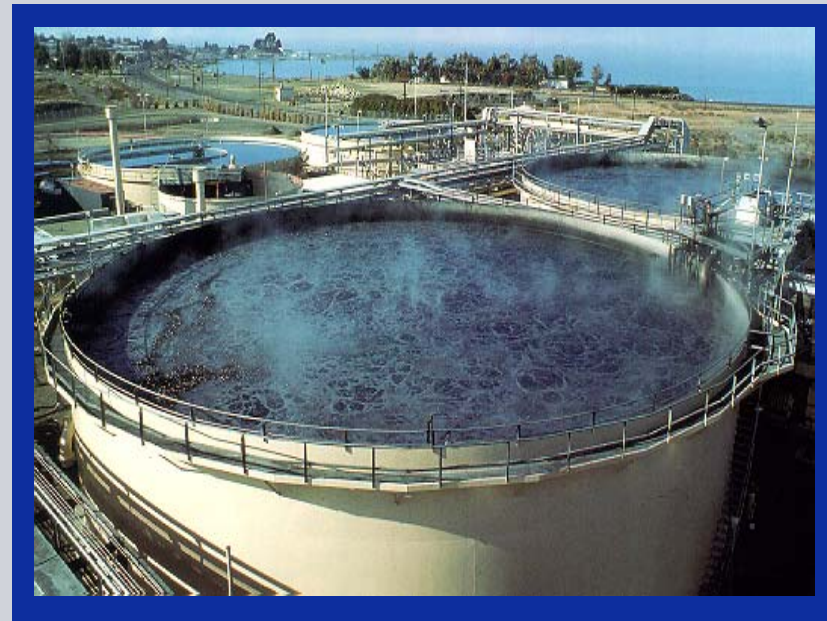
Powdered Activated Carbon Treatment

Advantages

- Activated carbon is added to biological treatment systems to remove difficult to degrade organic compounds (COD).
- Used in conjunction with all previously mentioned biological treatment devices.
- Very good recovery to upset conditions.

Disadvantages

- Additional cost for activated carbon.
- Greater sludge generation.



Biological Treatment Options

Membrane Bio-Reactor

Principle of Operations

- Replaces the conventional gravity clarifier.
- Provides an impermeable barrier for solids.



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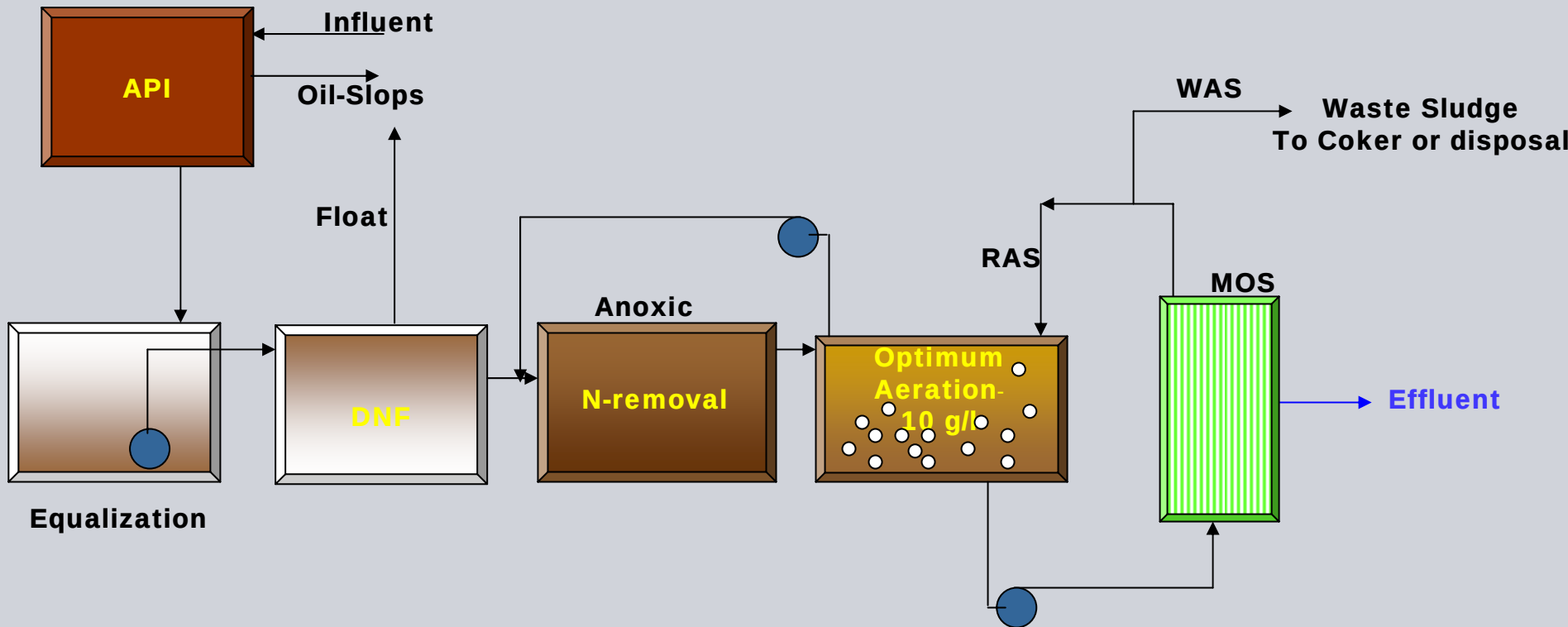
What is Petro™ MBR?

- Membrane Bio-Reactor *Process* and equipment designed for the marketplace (system solution)
- A Biological Treatment Process for Waste Water Treatment
- Can utilize almost any biological process
- Distinguishing aspect is separating bio solids from the cleaned water with membranes in lieu of a gravity clarifier
- Membranes used are typically in the low Microfiltration to high ultrafiltration range

General Process Description

Petro™ MBR

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Petro™ MBR Membrane Operating System

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Biological Treatment

Evaluation Parameter	Disc Aeration	Surface Aerator	Fine Bubble Aeration	Coarse Bubble Aeration	Jet Aeration	Sequencing Batch Reactor *	Membrane Bioreactor*	PACT*
Effective Bioassay/Toxicity Control	ü	ü	ü	ü	ü	ü	ü	ü
Effective BOD Removal Efficiency	ü	ü	ü	ü	ü	ü	ü	ü
Effective COD Removal Efficiency	ü	ü	ü	ü	ü	ü	ü	ü
Low O&M Costs				ü	ü			
Low Sludge Production							ü	
Low Sludge Disposal Costs							ü	ü
Good Operability: Winter					ü	ü	ü	
Good Operability: Summer	ü	ü	ü	ü	ü	ü	ü	ü
Good Performance: High Water Temperature	ü	ü					ü	ü
Good Performance: Low Water Temperature					ü	ü	ü	ü
Minimal Operator Attention								
Quick Upset Recovery						ü		ü
Easy Expandability								
Efficient Nitrification	ü		ü	ü	ü	ü	ü	ü
Easy to Cover for VOC Containment			ü	ü	ü			
Low VOC Stripping Potential			ü			ü	ü	ü
Easy Installation		ü						
Minimal Space Requirements			ü	ü	ü	ü	ü	ü

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Biological Clarification Gravity Clarifiers

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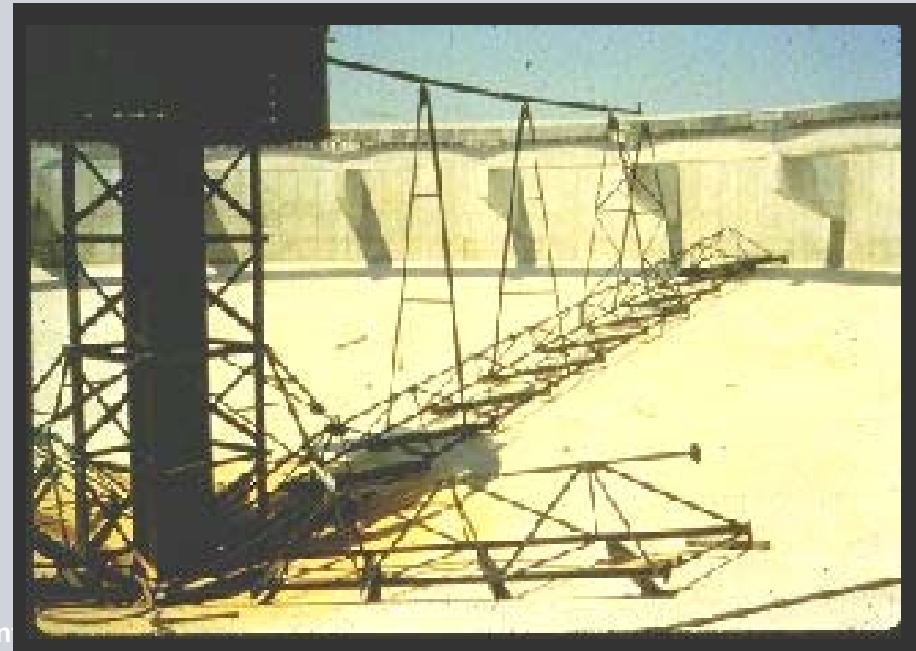
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Biological Clarification

Gravity Clarifiers

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Scraper Clarifier



For in

Biological Clarification Gravity Clarifiers

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Tow-Bro® Clarifier



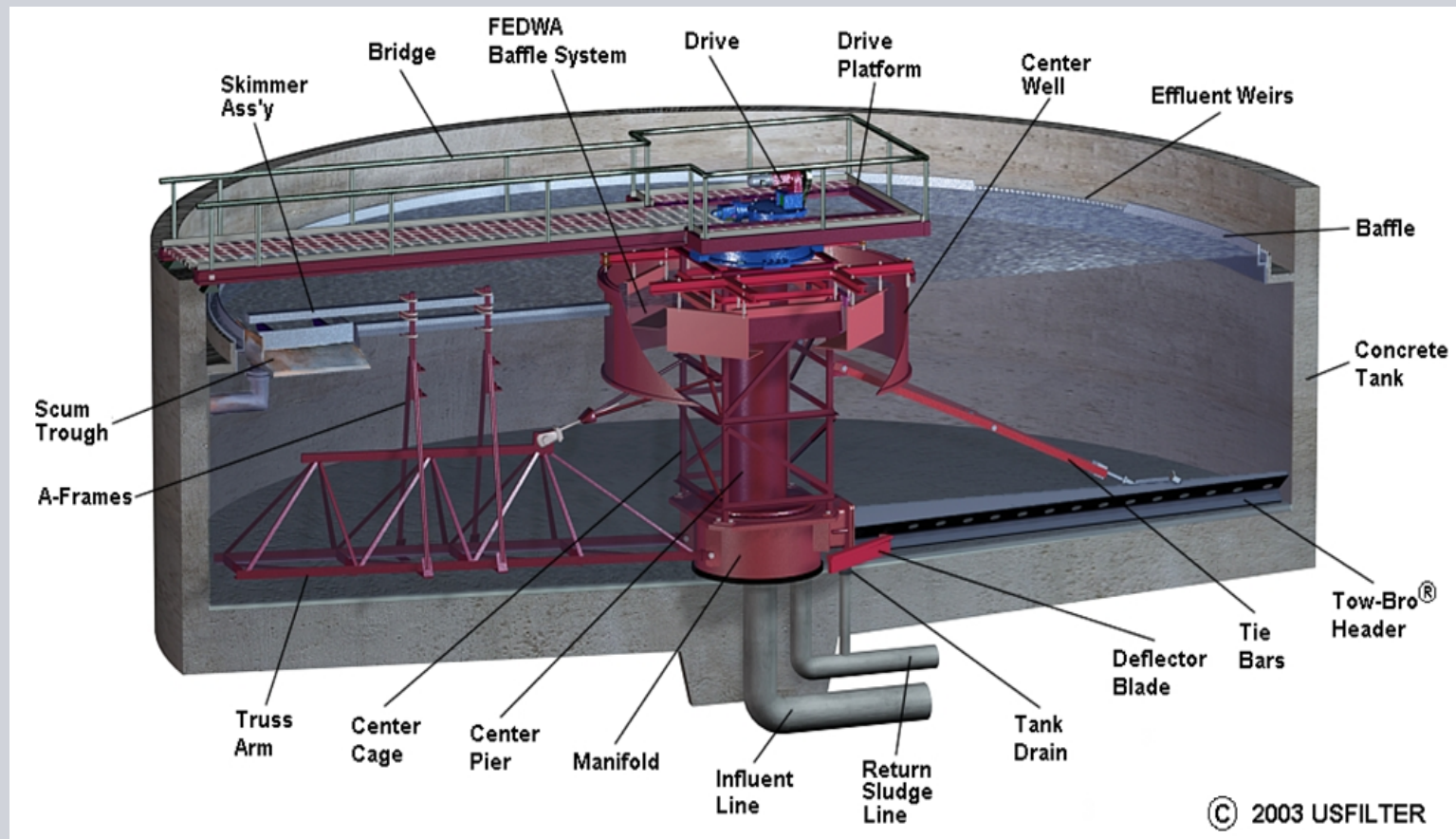
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Biological Clarification

Gravity Clarifiers

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Tow-Bro Secondary Clarifier



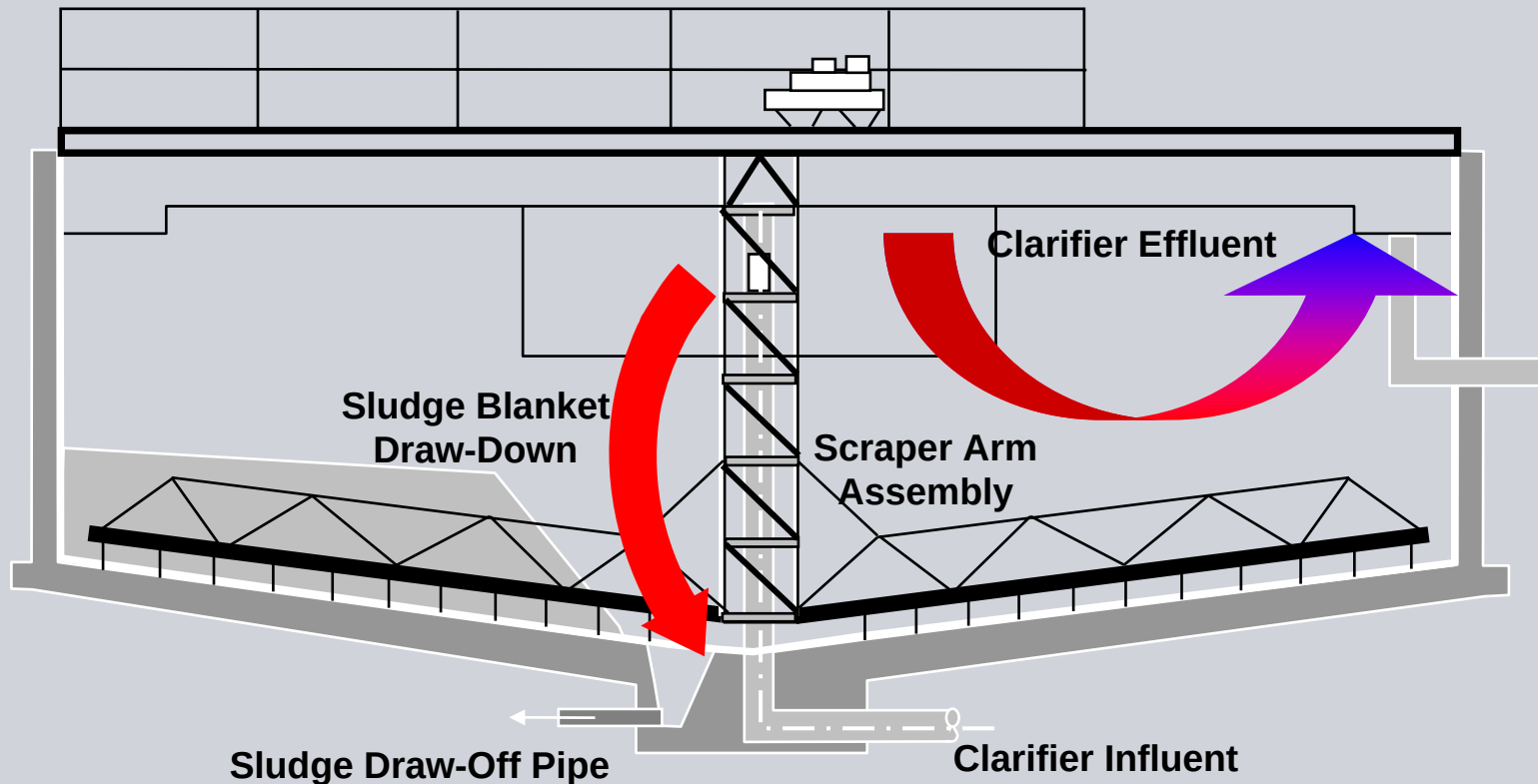
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Biological Clarification

Gravity Clarifiers

Center-Feed Clarifier

Short Circuits

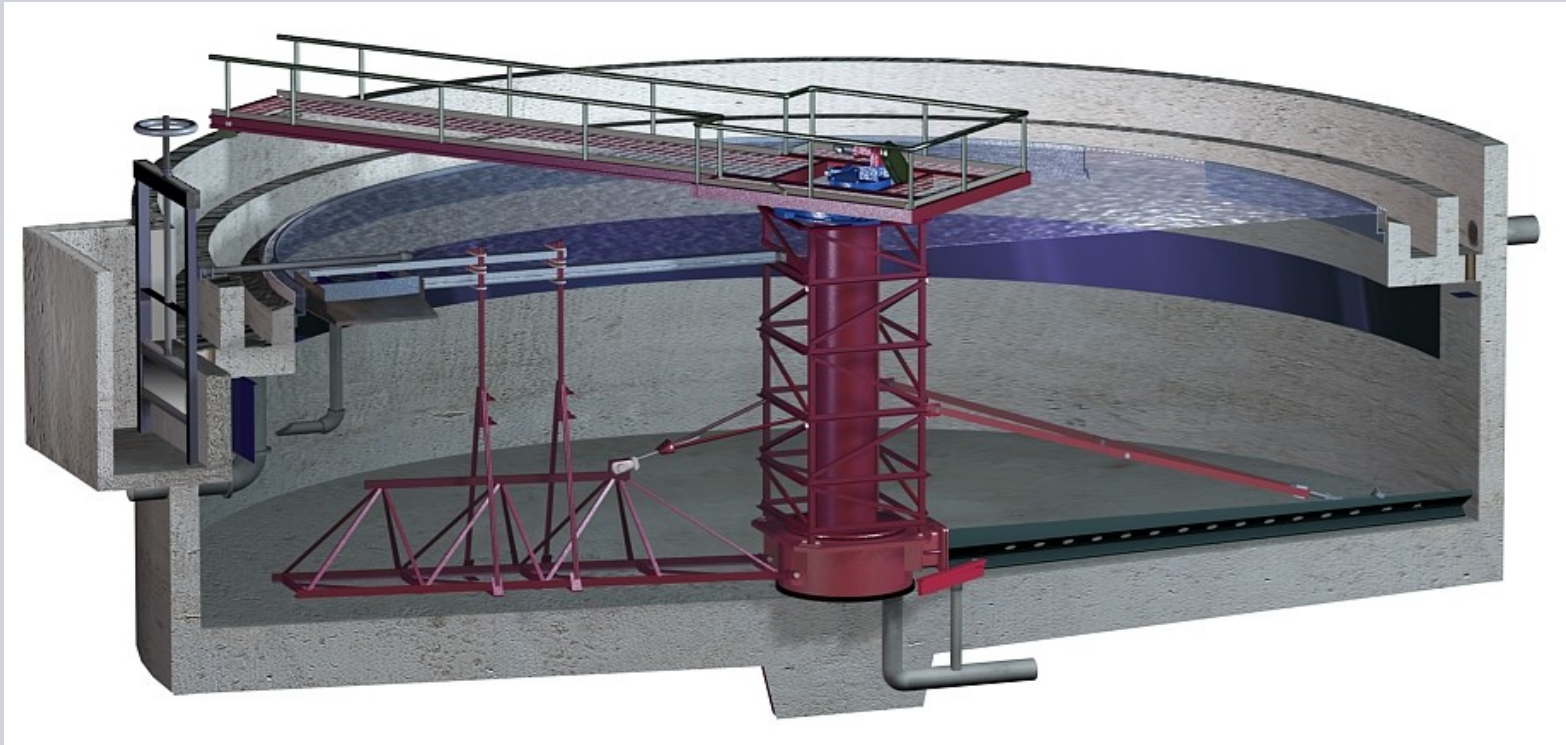


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Biological Clarification Gravity Clarifiers

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Rim-Flo® Clarifier – High Performance

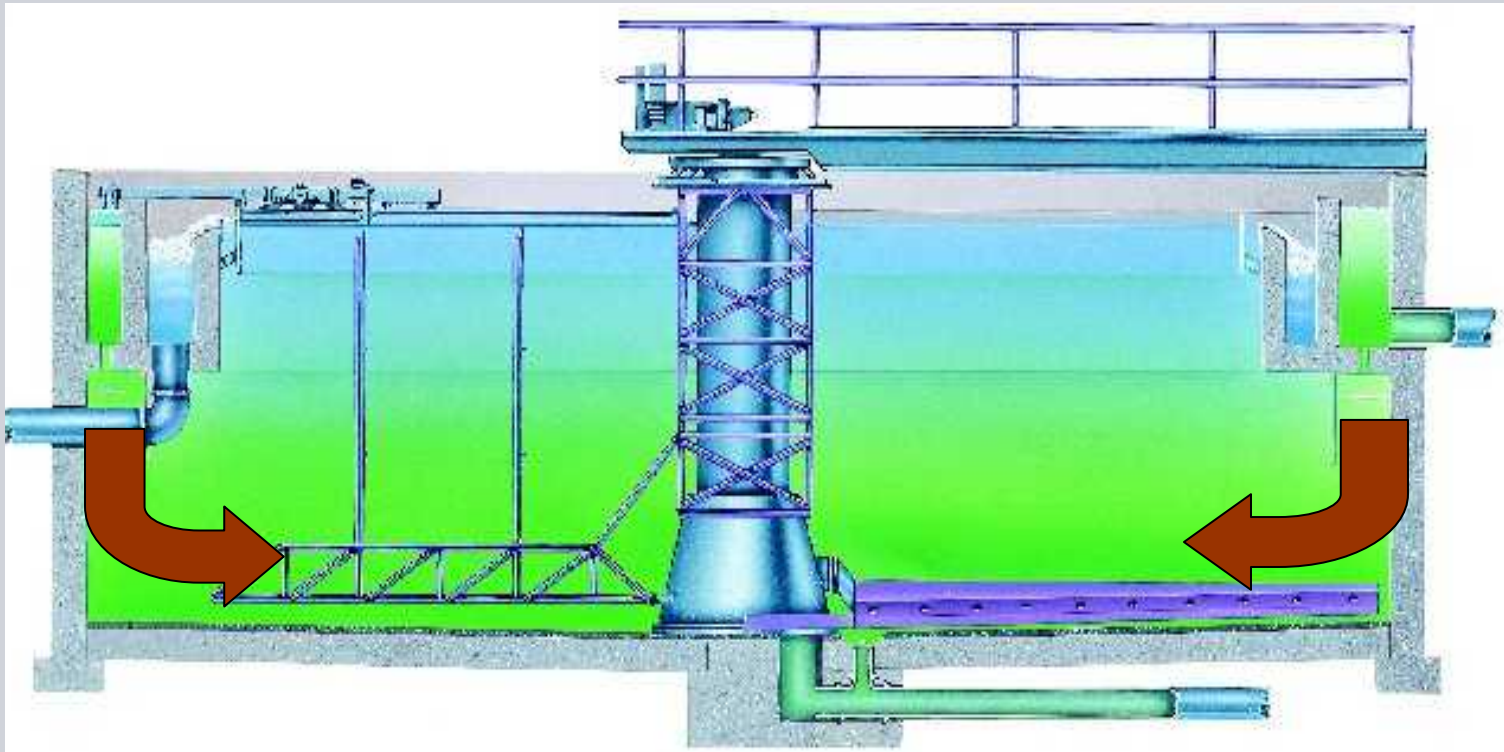


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Biological Clarification Gravity Clarifiers

SIEMENS

Rim-Flo® Clarifier



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Clarifier Surface Loading Rates*

Center Feed:	400-500 gpd/ft ² 0.68 – 0.85 m ³ /m ² /h
Rim-Flo® (Peripheral Feed):	600-800 gpd/ft ² 1.02 – 1.36 m ³ /m ² /h

*** For 20 mg/l TSS, typically**

Hydraulically Stable Design

Minimize water surface elevation differential between aeration basins and final clarifiers

Avoid turbulence in aeration effluent drop boxed which can entrain air

Keep transfer pipe velocity between 0.61 to 1.8 m/sec (2 to 6 ft/sec) to avoid floc shear

Biological Clarification

Gravity Clarifiers

Hydraulically Stable Design

Excessive turbulence can shear delicate biological floc, turning a final clarifier into a floating scum nightmare



Biological Clarification Gravity Clarifiers

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Hydraulically Stable Design



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Biological Clarification

Gravity Clarifiers

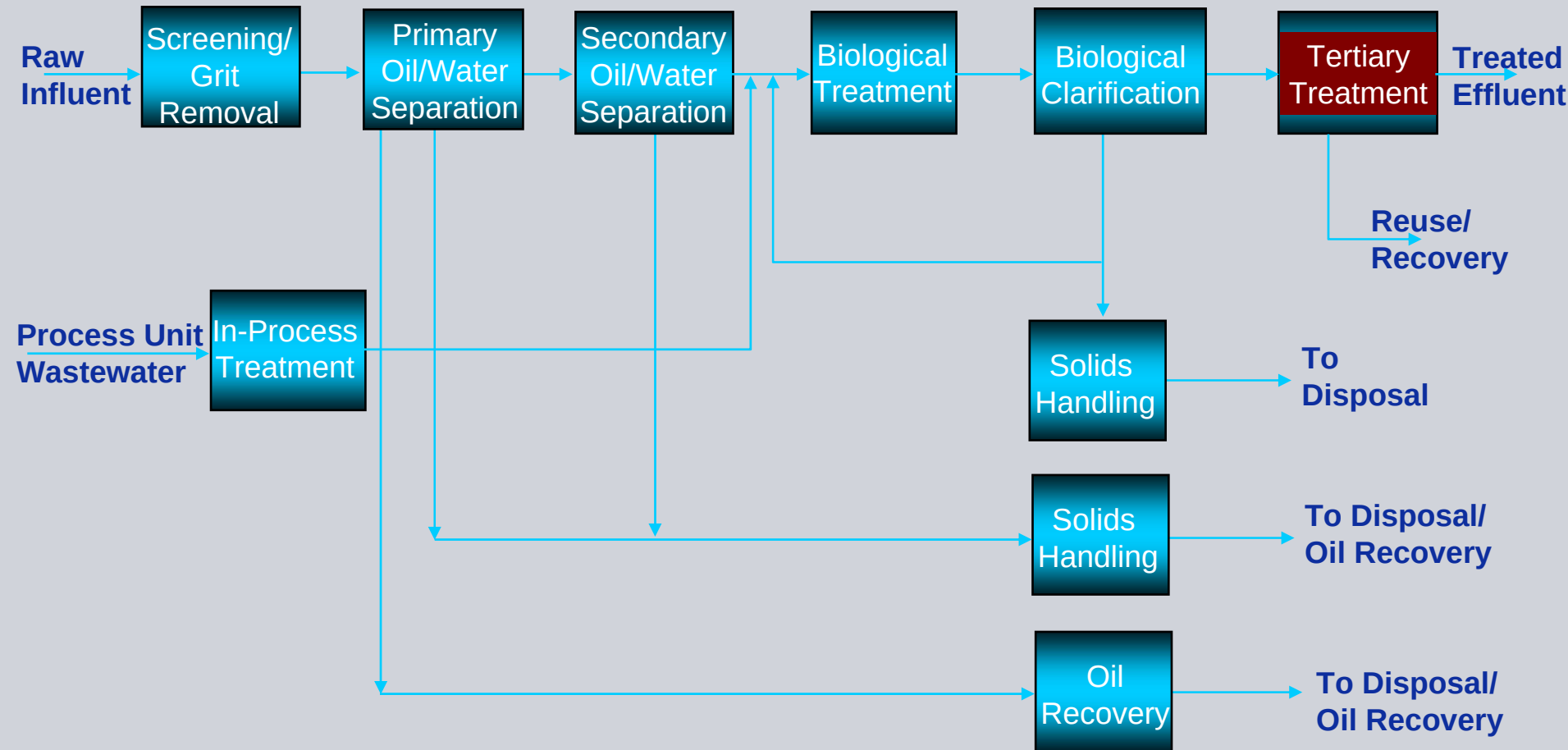
Skimming

Always consider dual skimmers and scum troughs for removal of floating biological solids, scum oil, and grease



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Typical Oily Water Treatment System



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Tertiary Treatment

Typical Applications

- Provide additional treatment to meet strict wastewater discharge requirements.
- Provide additional treatment to allow wastewater to be reused.

Typical Treatment Methods

- Media Filtration
- Activated Carbon
- Microfilter Membranes



Media Filters

Principle of Operation

- Gravity or pressure design with granular media bed
- One to three layers (coarse to fine) of filtration media
- Flows from top, through media, out the bottom
- Large capacity and low pressure drop
- Suspended solids captured in media bed
- Suspended solids removed by backwashing
- Air scour may also be used to increase backwashing effectiveness



Media Filters

Typical Applications and Operating Conditions

- Filtration of:
 - Biological effluent
- Inlet parameters
 - Solids < 30 mg/L
 - Turbidity < 30 NTU
 - Particles > 10 micron
- Outlet parameters
 - Solids < 5-10 mg/L
 - Turbidity < 1 NTU
 - Particles 2 - 5 micron
 - 98% removal
 - Requires coagulant or flocculent feed



Media Filters

Advantages

- Can operate at very high rates approaching 10 gpm/ft².
- Very good turbidity control.

Disadvantages

- Not recommended for oil removal. High oil concentrations can plug and foul media to the point it needs to be replaced



Carbon Adsorption

Principle of Operation

- Very high surface area per unit volume
 - One pound (one liter) has enough surface area to cover more than 80 soccer fields.
- Hydrophobic surface
 - Poor affinity for water
 - Strong affinity for organic compounds.
- Used for adsorption of organic compounds, particularly dissolved organics.



Carbon Adsorption

Typical Applications and Operating Conditions

- Wastewater treatment to remove difficult to degrade organic compounds after biological treatment.
- Carbon can be added to the biological treatment as PACT (Previously discussed) or can be used to polish biological effluent.
- Typically used in low strength and low flow conditions to avoid high carbon consumption.
- Carbon can be reactivated through incineration or steam contact.



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Carbon Adsorption

Advantages

- Extremely high removal of non-biodegradable organic compounds.
- Lower capital costs.

Disadvantages

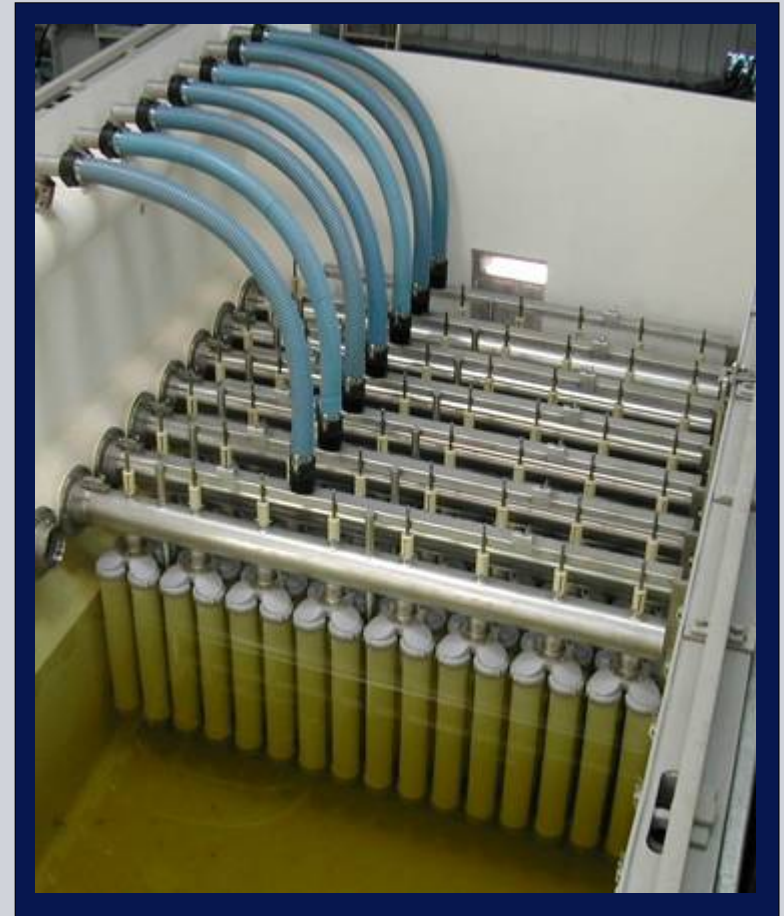
- To keep operations costs low, a incineration reactivation facility should be close by.
- High operating costs.
- Carbon handling facilities required.
- Requires media filters as pretreatment to remove TSS.



Microfiltration

Typical Applications and Operating Conditions

- Operates very similar to an MBR, but since the solids loading is lower, the flux rate is higher.
- Completely remove unwanted solids greater than 0.1 micron.
- $\text{BOD} < 5 \text{ mg/l}$, $\text{TSS} < 1 \text{ mg/l}$
- Turbidity $< 0.2 \text{ NTU}$
- Higher capital costs than media filters or carbon filters.
- Great for expansion of existing biological treatment systems



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