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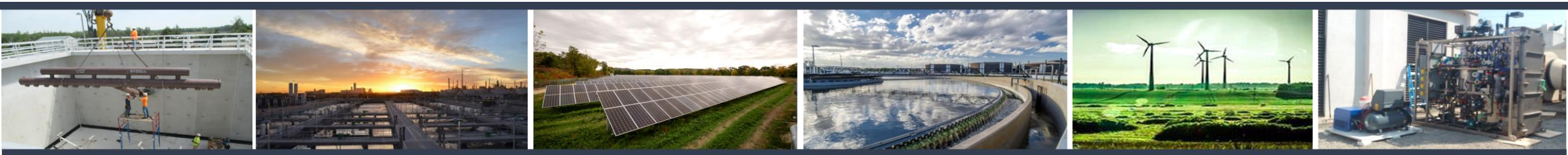
Los Angeles County Sanitation Districts
Converting Waste Into Resources

Stanley Consultants

LA DWP
Los Angeles Department of Water & Power

We will begin our presentation in a few minutes…



Water Management in Petroleum Industries

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Global Practice & Technology Leader in Wastewater & Sustainability | Black & Veatch

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Outline

- Background
- Water Management
  - Upstream & Midstream
  - Downstream & Marketing
- Water Treatment
- Wastewater Treatment
- Process Modeling
- Conclusions

Background

Major Natural Constituents of Crude Petroleum

Hydrocarbons

- Paraffins (C_nH_{2n+2}) - C1 to C4 as Dissolved Gases, Larger paraffins in liquid
- Naphthenes (C_nH_{2n}) - Saturated cyclic hydrocarbons
- Aromatics (C_nH2_{n-6}) - BTEX, PAHs, Phenols and other derivatives
- Olefins, Diolefin and Acetylenes – Introduced after processing of crudes

Organic Sulfur Compounds

- H_2S, mercaptans, organic sulfides, disulfides, etc.

Organic Nitrogenous Compounds

- Pyridine, Indole, Quinoline, Ethanol Amines

Oxygenates

- Primarily Naphthenic Acids quantified by Total Acid Number (TAN) expressed in mg of KOH to neutralize each gram of crude

Formation Water and Solids

- Basic Sediment and Water (BS&W)

Metals and Metalloids

- Primarily dissolved in water as chloride, sulfate and carbonate salts of Na, Ca, Mg, Ba, Sr, Fe, Hg, As, V, Se, and other trace elements including radionuclides

Additives in Crude Petroleum

Antifreeze Additives to oil and gas pipes

- Ethylene glycol (EG) for intermittent addition
- Methanol for continuous addition
- These alcohols are dissolved in water and carried over to processing step

Chlorinated Organics

- PCB and other chlorinated compounds not present in crude
- Sodium hypochlorite added to produced water as a biocide prior to reinjection

H_2S Suppressant in crude transport trucks and railcars

- Mono (M), Di (D) amines and their combinations

Petroleum Industry Business Sectors and their Water Footprints

Upstream

- Exploration and Production
  - Produced Water
  - Sanitary Water and Wastewater

Midstream

- Rainwater

Downstream

- Water for Cooling and Boiler Feed Make-up
- River Water
- Fire Water
- Process Wastewater
- Sanitary Water and Wastewater

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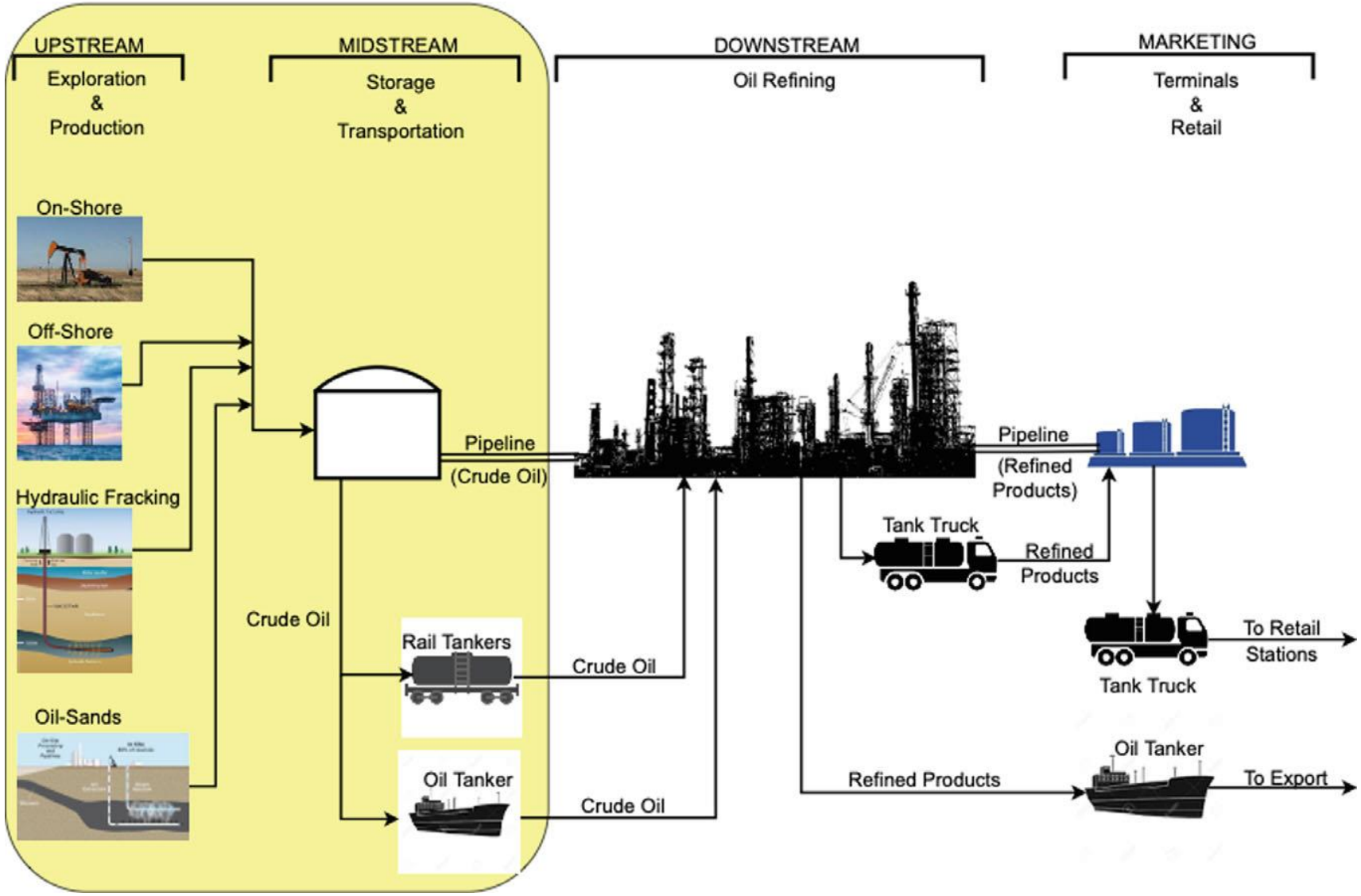
Water Management: Upstream & Midstream

Upstream & Midstream Operation



Petroleum Resources – Conventional and Unconventional (Source: US EIA)

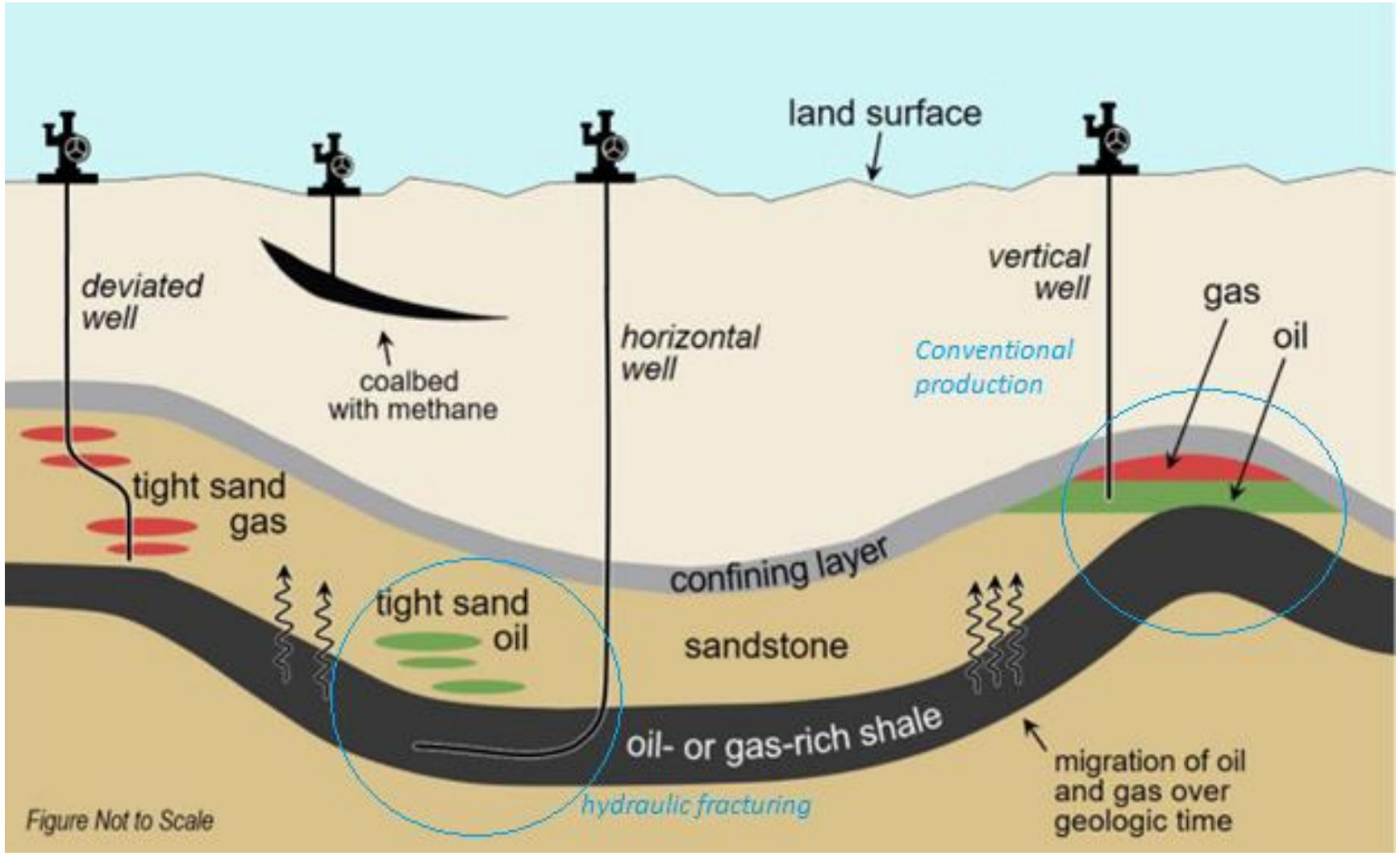
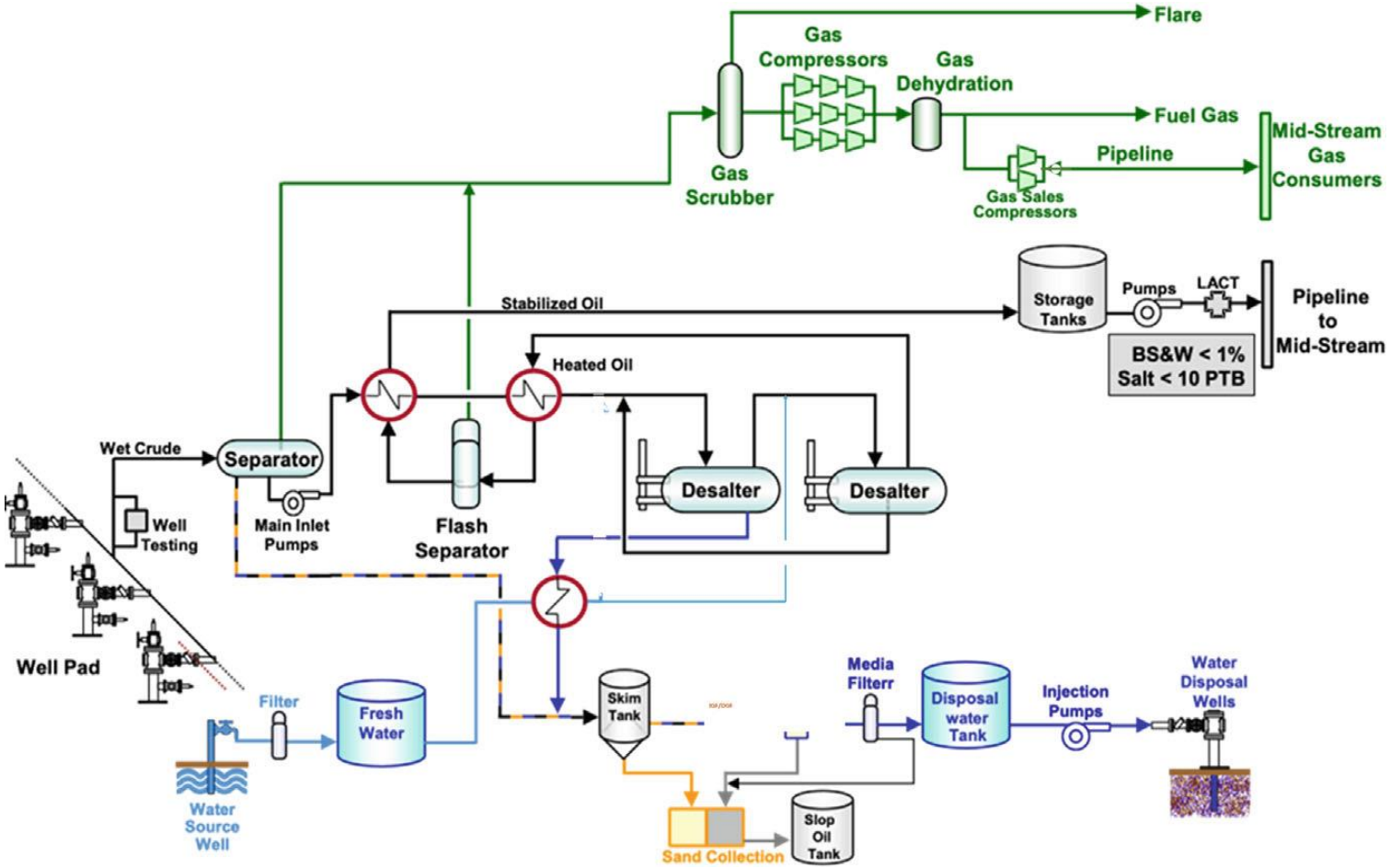
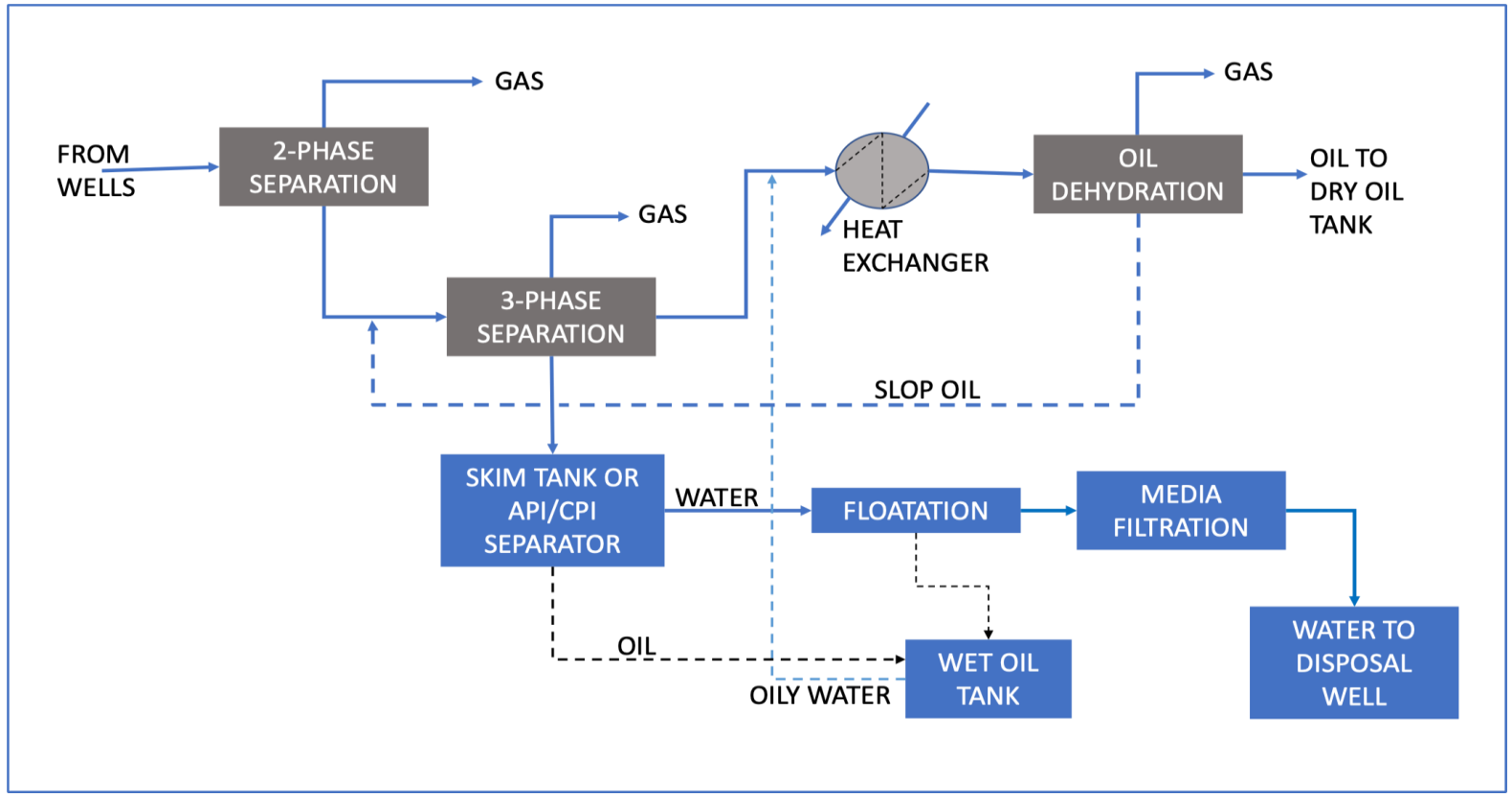



Photo by Documerica on Unsplash

Conventional Onshore Production

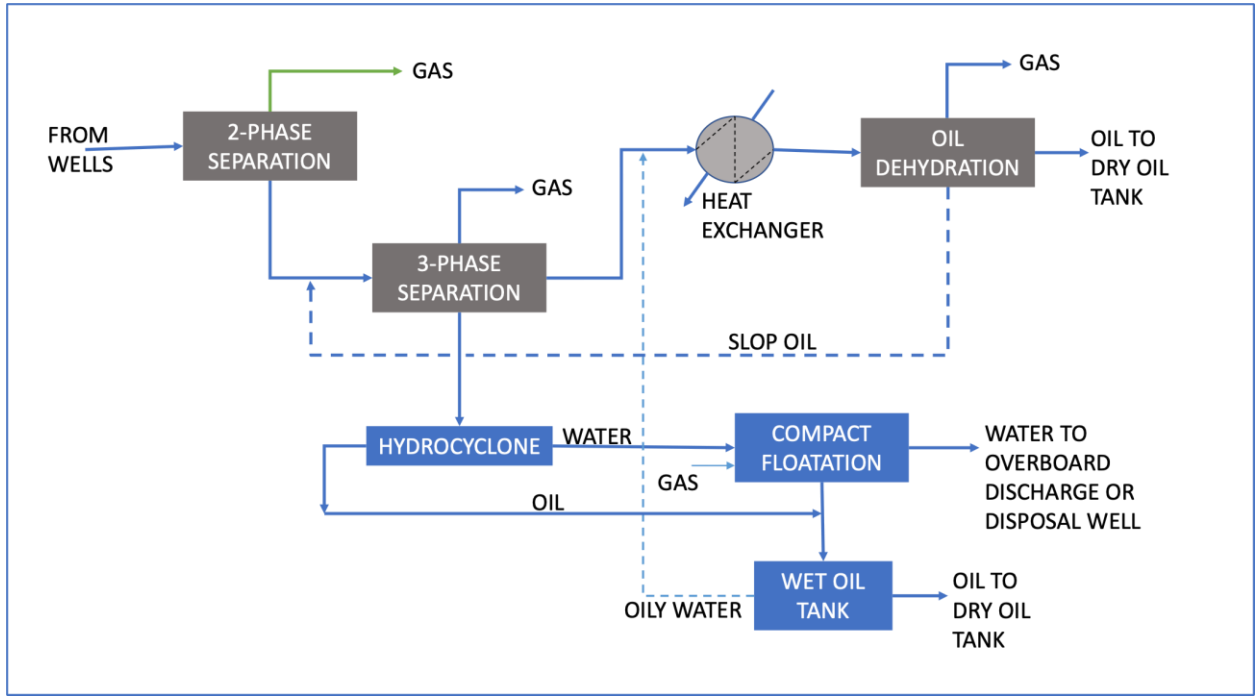


Produced Water Treatment for Conventional Onshore Production



Produced Water Treatment for Conventional Offshore Production

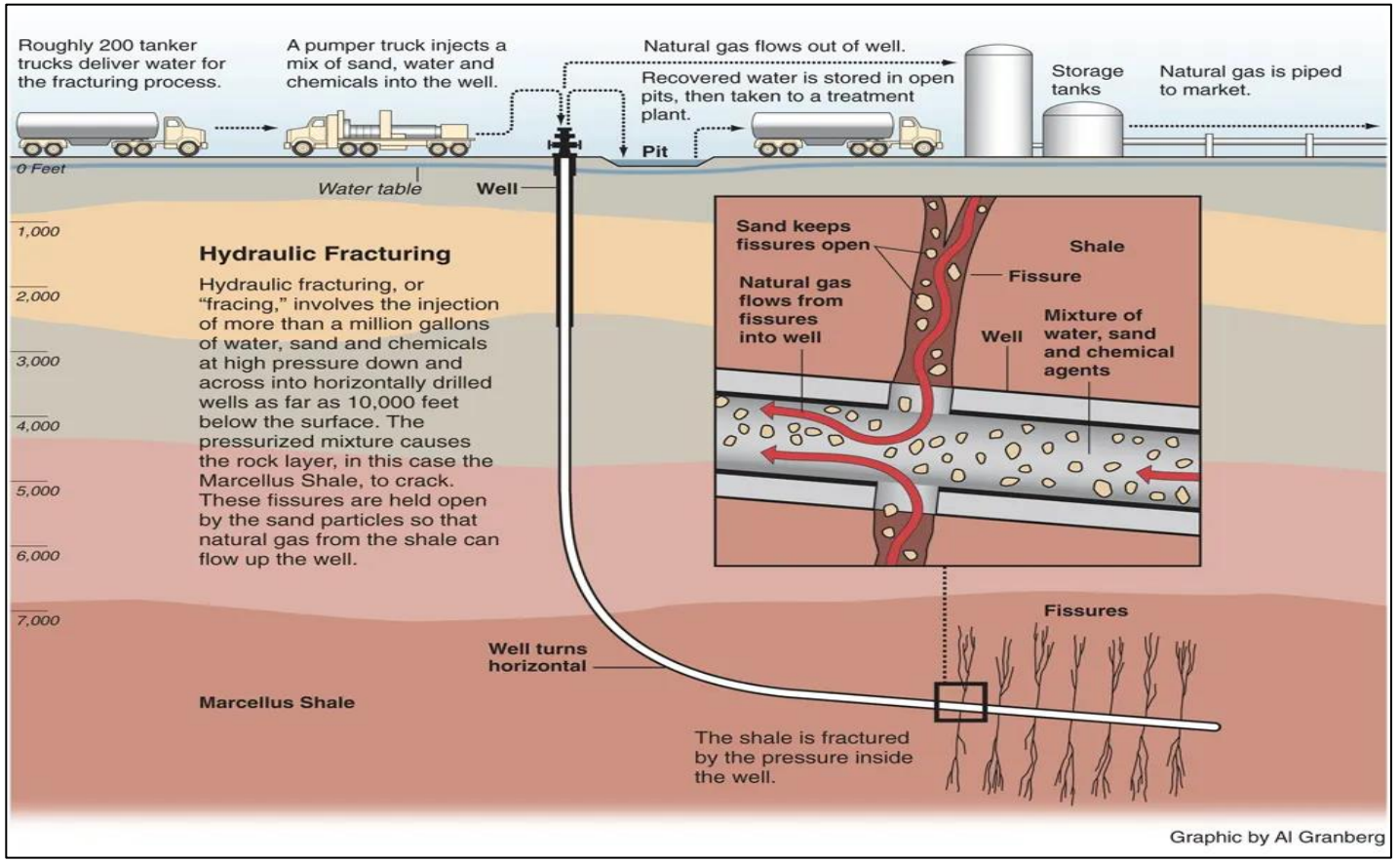
Offshore production platform and Floating Production Storage and Offloading (FPSO) Platform in Gulf of Thailand (Rawlins 2017)



Biological treatment in compact packages is used when necessary to treat high COD from antifreeze methanol and EG dosing

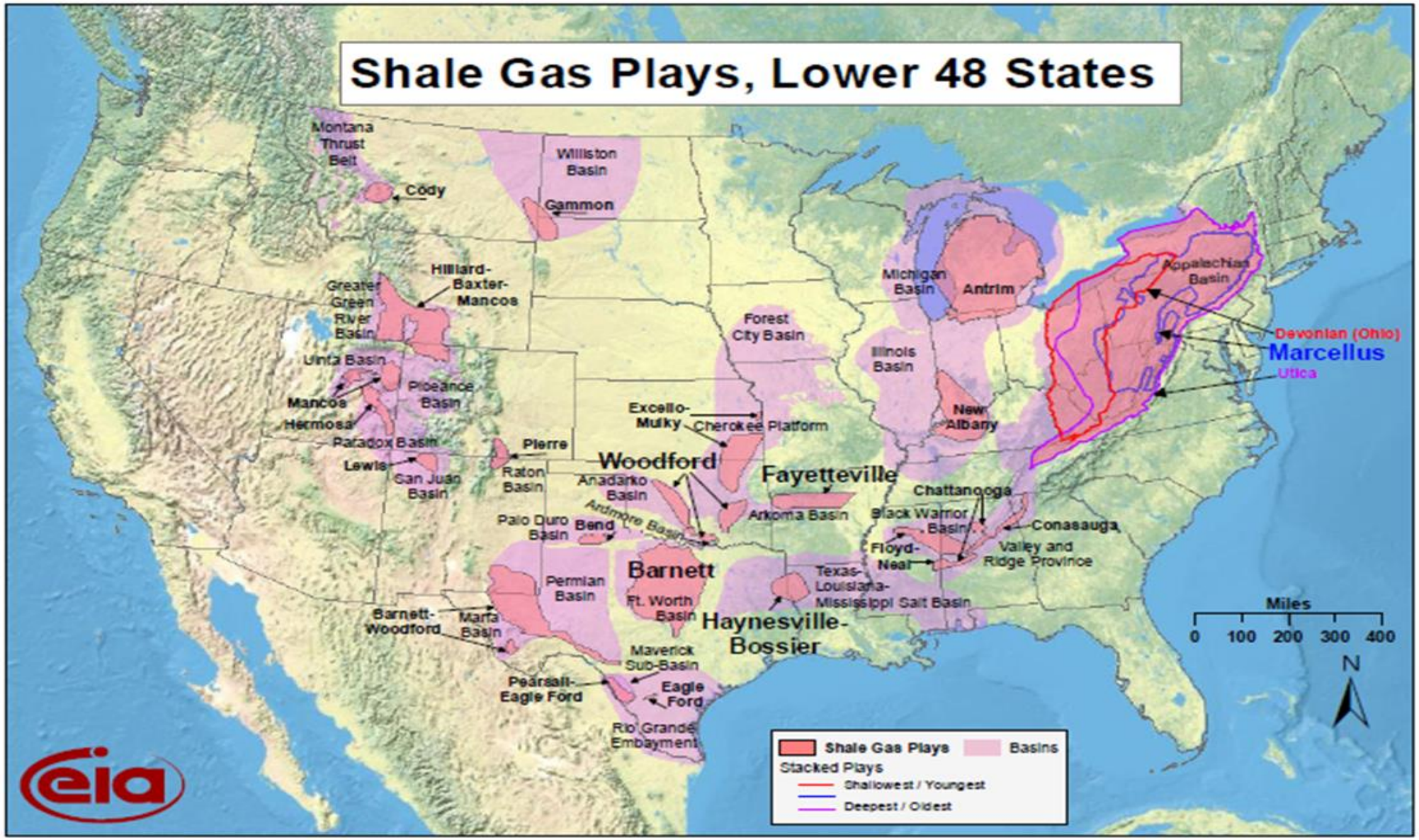
Unconventional Production by Hydraulic Fracturing

Photo by Colton Sturgeon on Unsplash



Detail of hydraulic fracturing mechanism (Granberg and Schmidt 2010)

Shale Gas Situation in the US



Source: Energy Information Administration based on data from various published studies.
Updated: March 10, 2010

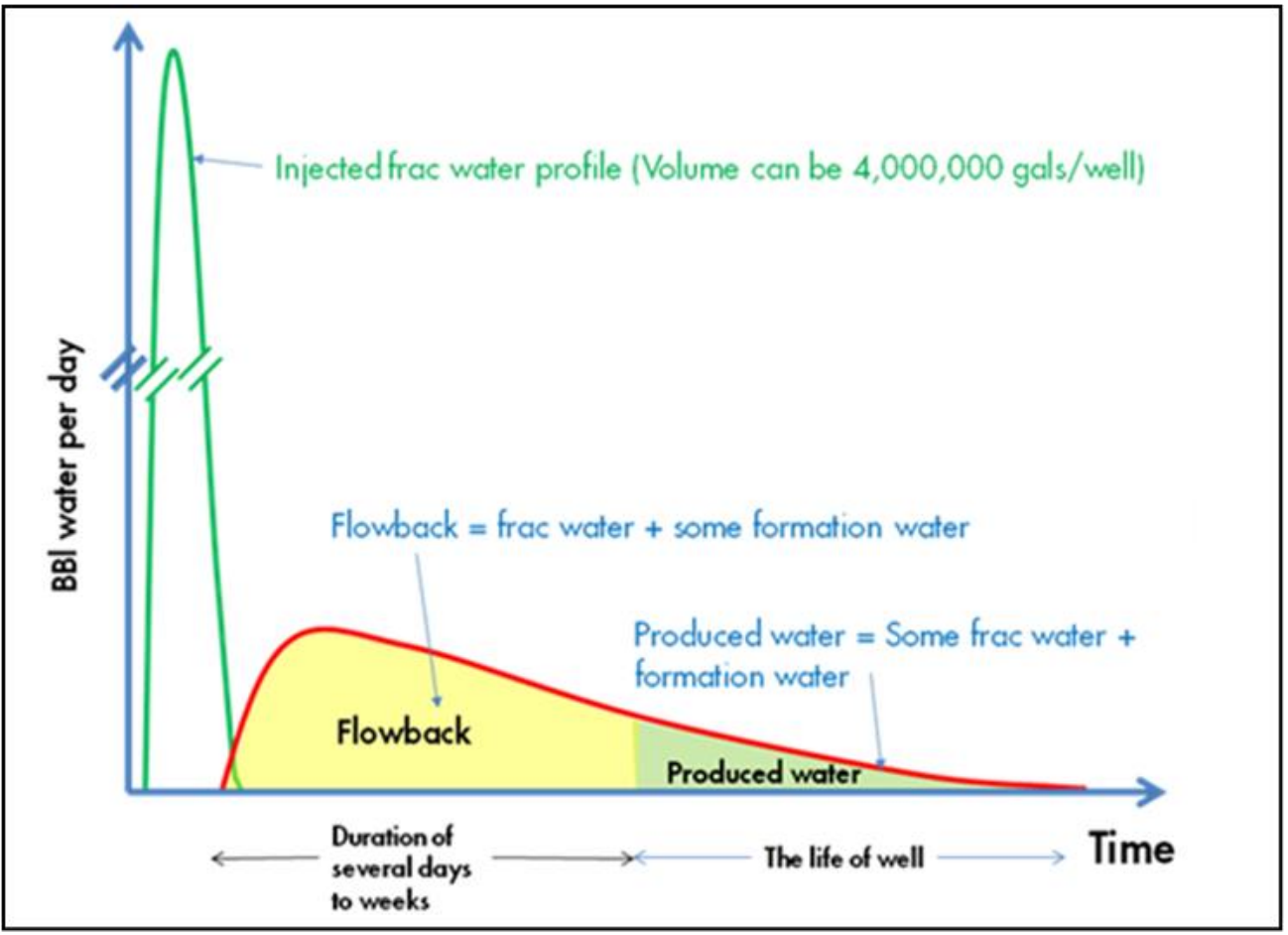
Frac Water Composition

(Source: Modern Shale Gas -A Primer, US DOE '09)

Additive	Composition (% v/v)	Function
HCl (15% Solution)	0.123	Dissolve Minerals for Fracture
Glutaraldehyde	0.001	Biocide
Ammonium Persulfate	0.010	Emulsion Breaker
N, N Dimethyl Formamide	0.002	Corrosion Inhibitor
Borate Salts	0.007	Crosslinker to Maintain Viscosity
Polyacrilamide/Mineral Oil	0.088	Friction Reducer to Flow
Guar Gum (Hydroxymethyl Cellulose)	0.056	Gel to Suspend Proppant (Sand)
Citric Acid	0.004	Prevents Iron Precipitation
Potassium Chloride	0.060	Stabilizes Clay in shale formation
Ammonium Bislufite	0.002	Oxygen Scavenger to Prevent Corossion
Sodium/Potassium Carbonate	0.011	pH Adjusting Agent
Ethylene Glycol	0.043	Scale Inhibitor
Various Surfactants and Co-surfactant (Isopropanol)	0.085	Helps Improve Viscosity
Proppant (Sand)	0.500	Fracturing Agent
Water	99.5	Carrier Fluid

Water Usage, Production and Characteristics in Hydraulic Fracturing

Water Quantities

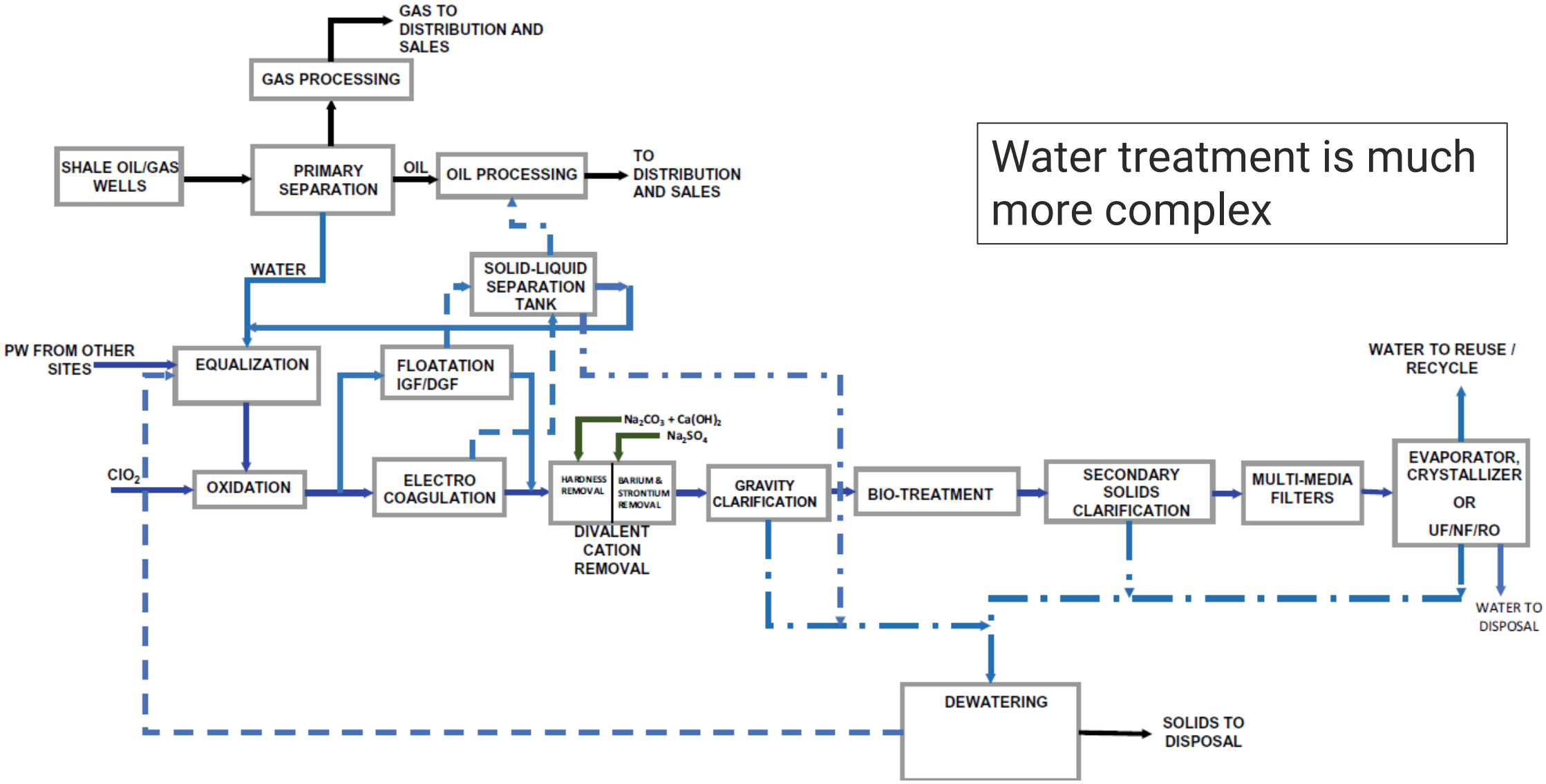


Flow profiles and duration of flowback and produced water from hydrofracturing operations (Sun, WEFTEC 2012)

Produced Water Characteristics

Parameter	Unit	Bakken Shale	Permian Basin
Total Dissolved Solids (TDS)	mg/L	235,000	154,000
Dissolved Organic Carbon (DOC)	mg/L	200	2,000
pH	su	5 - 7	6.3 – 6.5
Alkalinity	mg/L as $CaCO_3$	550	250
Total Hardness	mg/L as $CaCO_3$	35,000	15,500
Turbidity	NTU	140	100
Ammonia	mg/L	N/R	530
Barium	mg/L	20	50
Boron	mg/L	750	60
Calcium	mg/L	33,450	5,000
Iron	mg/L	250	25
Magnesium	mg/L	2,000	850
Potassium	mg/L	13,500	850
Sodium	mg/L	120,000	45,000
Strontium	mg/L	3,000	1,100
Chloride	mg/L	17,000–200,000	120,000
Sulfate	mg/L	10 – 2,050	250

Unconventional Production by Hydraulic Fracturing



Water treatment is much more complex

Major Challenges in Upstream Produced Water Treatment

Unconventional Production

Thermal EOR

- Limited number of sites, primarily Canadian Rockies
- Require produced water advanced treatment and steam generation facility on site

Hydrofracturing at Oil and Gas Bearing Shale Formations

- Very large quantity with very high salinity which renders it unsuitable for beneficial use
- Treatment necessary to remove divalent cations Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}
- Produced Water at Marcellus contain radionuclides Ra 226/228, U 233/234/235/236
- Underground injection becoming increasingly difficult due to seismicity and stricter regulations

Conventional Production

Conventional On shore

- Easy operation and produced water treatment limited to only TSS and O&G removal
- Dwindling resources, only ~10% of US domestic production

Conventional Offshore

- Certain reserves, primarily gas resources production temperature is low leading to solid gas hydrate formation and require dosing of antifreeze chemicals ethylene glycol and methanol. These increase produced water COD and require biotreatment

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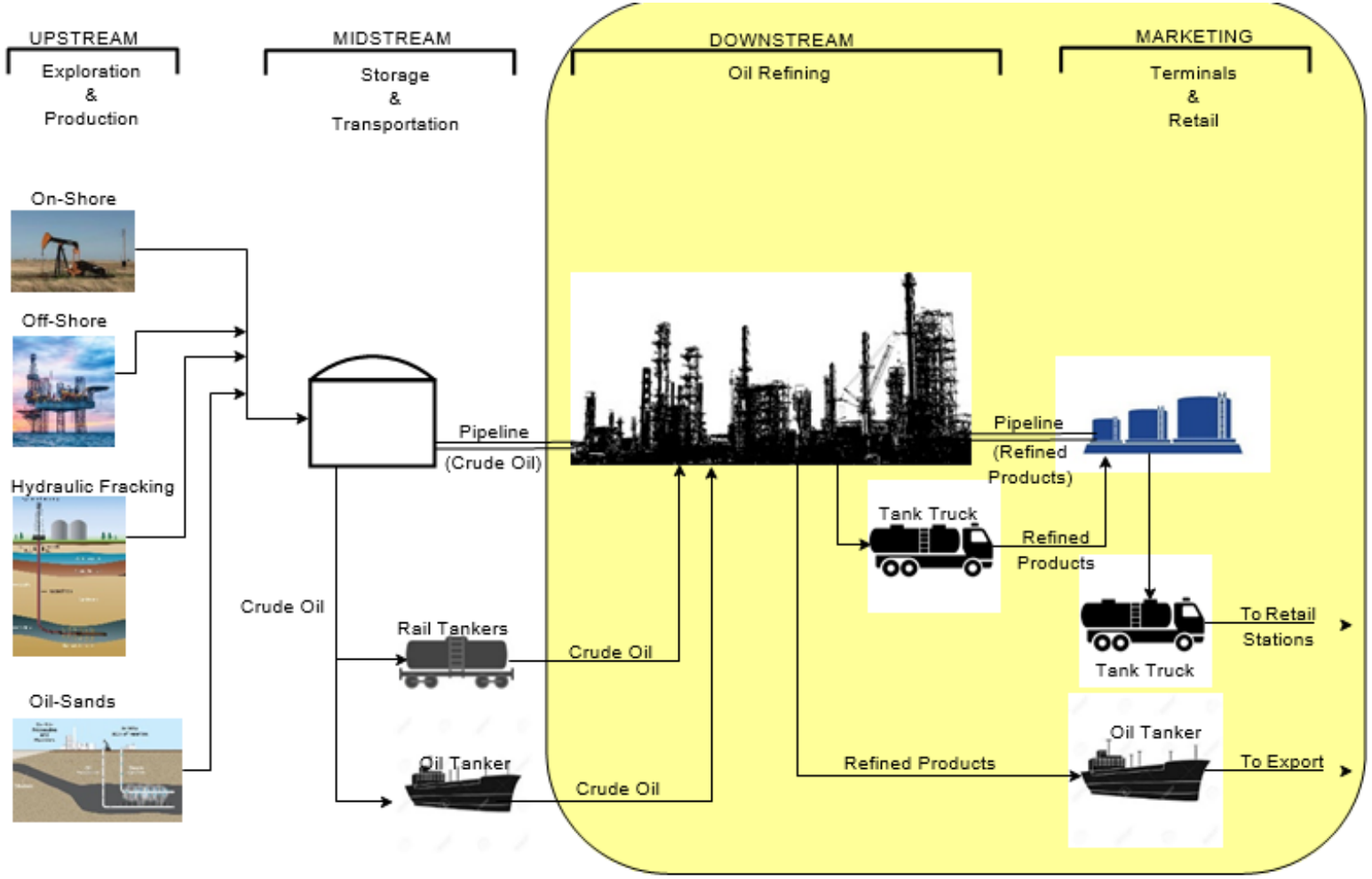
Water Management: Downstream & Marketing

Downstream Operation = Refineries

Photo by Patrick Hendry on Unsplash

Downstream Operation



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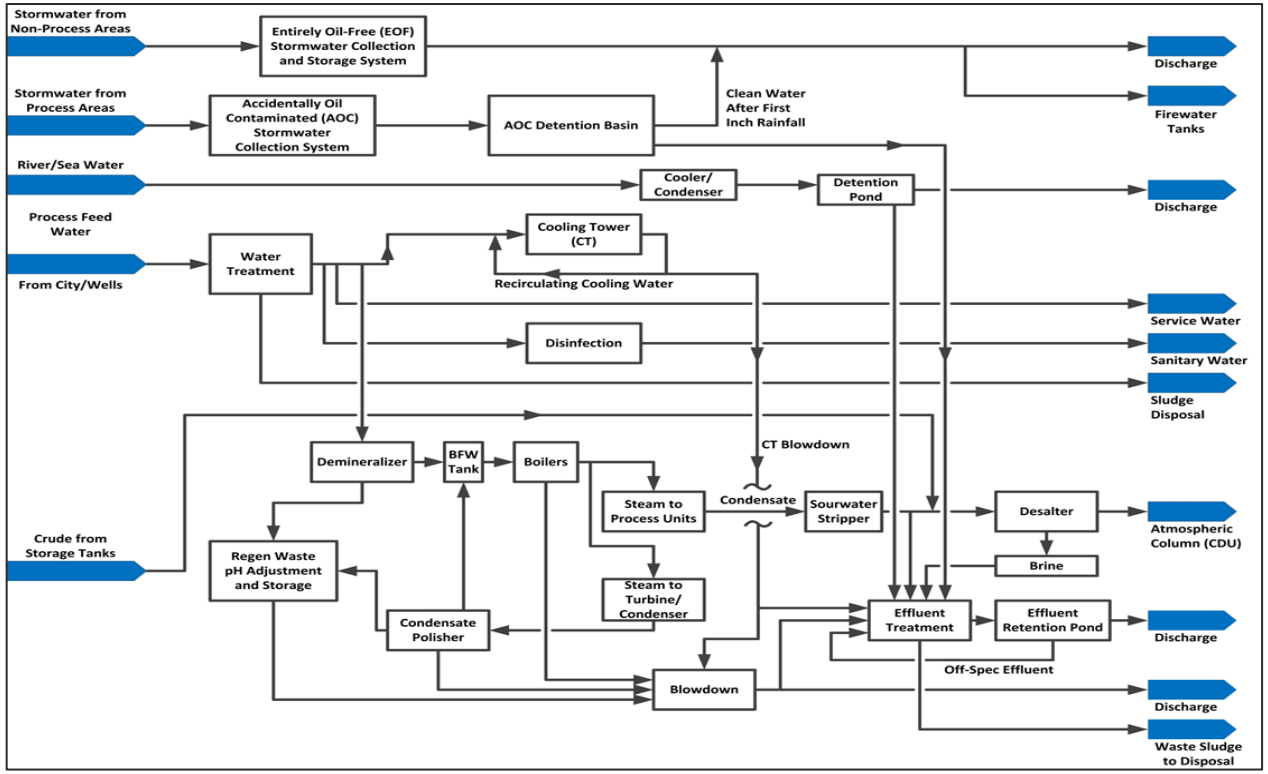
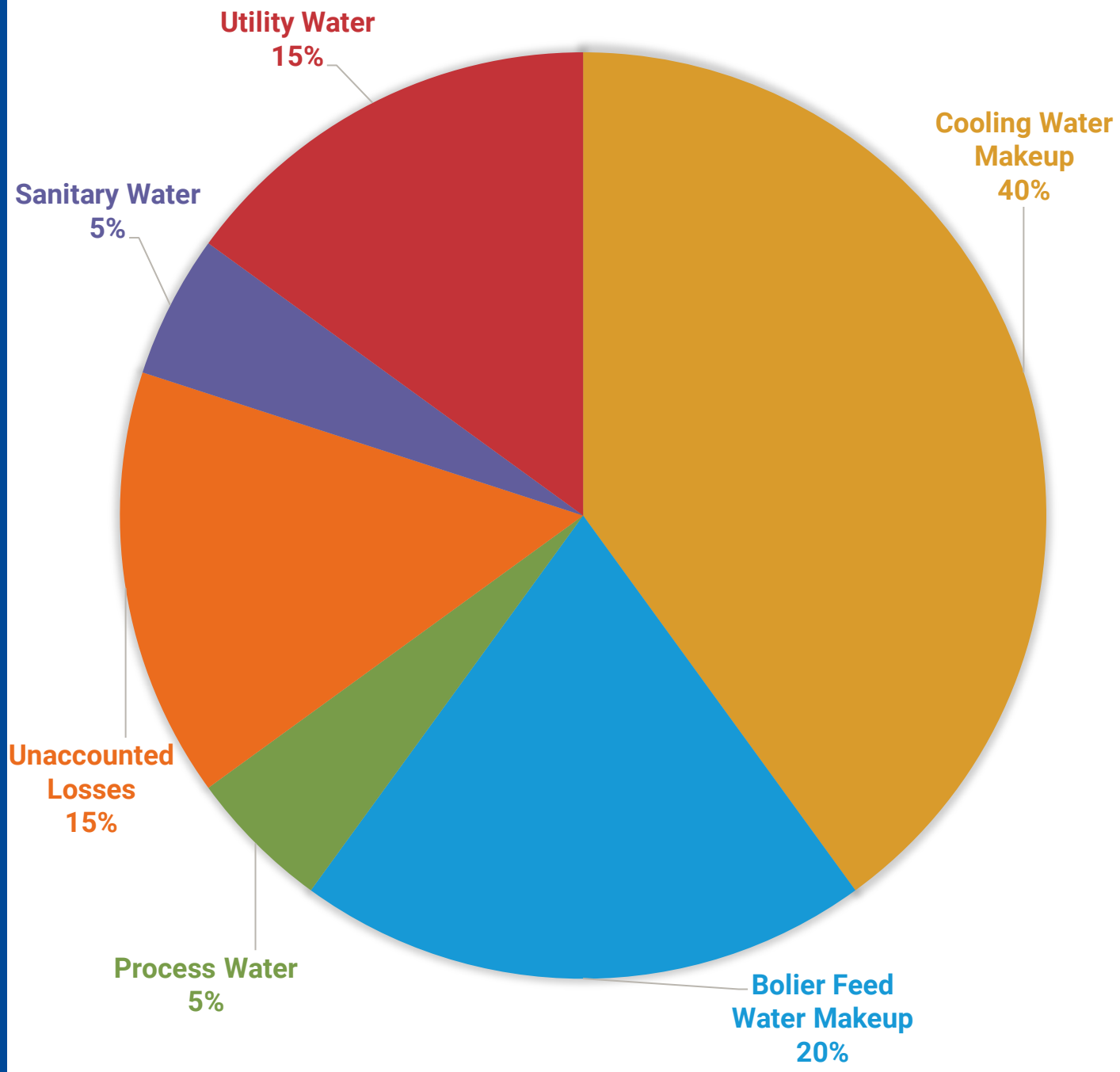
Water Treatment

Total Water Network In a Petroleum Refinery

- **Stormwater handling and disposal**
  - Entirely Oil Free (EOF) water
  - Accidentally Oil Contaminated (AOC) water
- **Firewater storage and handling**
- **River/sea water**
- **Feed water treatment**
  - Water treatment
  - Cooling water and blowdown disposal
  - Demineralization
  - Condensate polishing
  - Boiler blowdown and demineralizer regeneration waste disposal
- **Process water management**
  - Sour water stripping
  - Crude desalting and brine disposal
- **Wastewater treatment**
  - Primary Treatment – Physicochemical
  - Secondary Treatment – Biological
  - Tertiary Treatment – Final Polishing

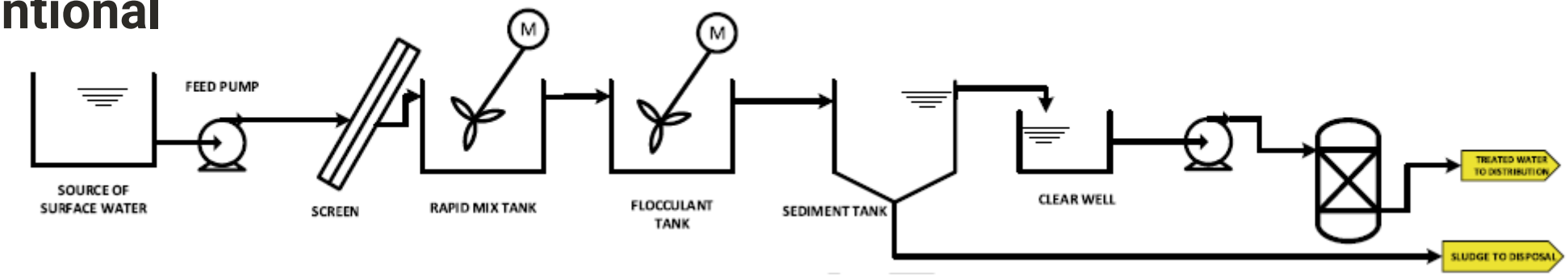


Water use in refineries

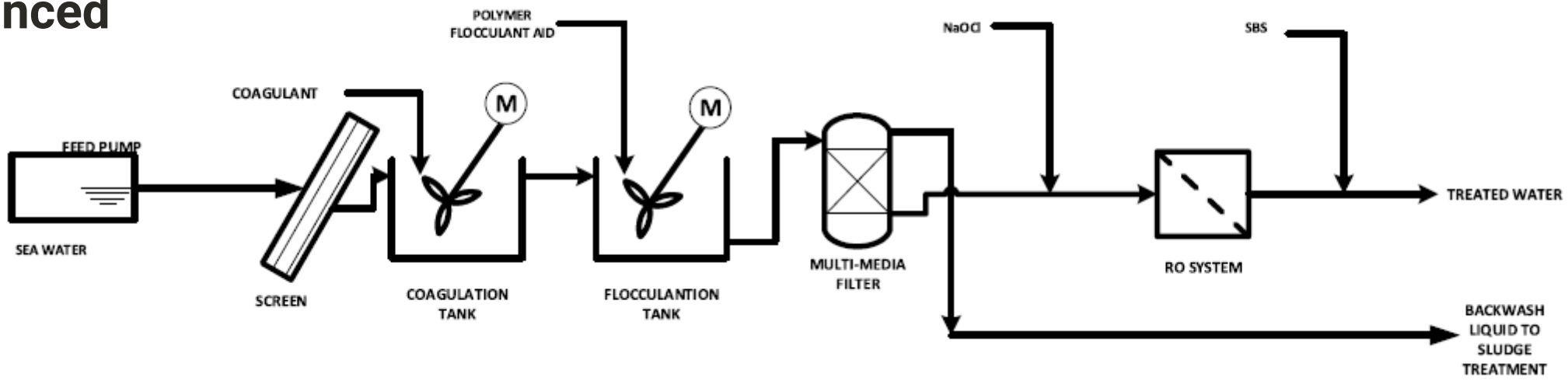


Water Treatment Process Train

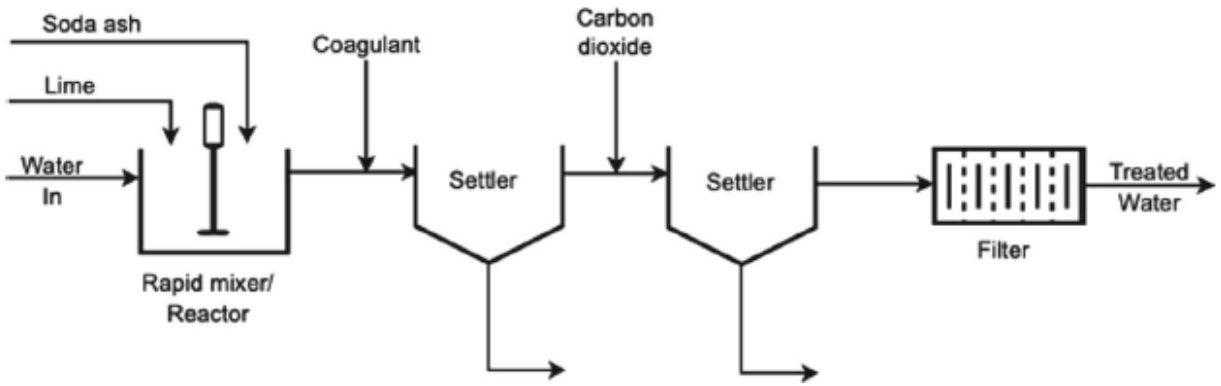
Conventional



Advanced

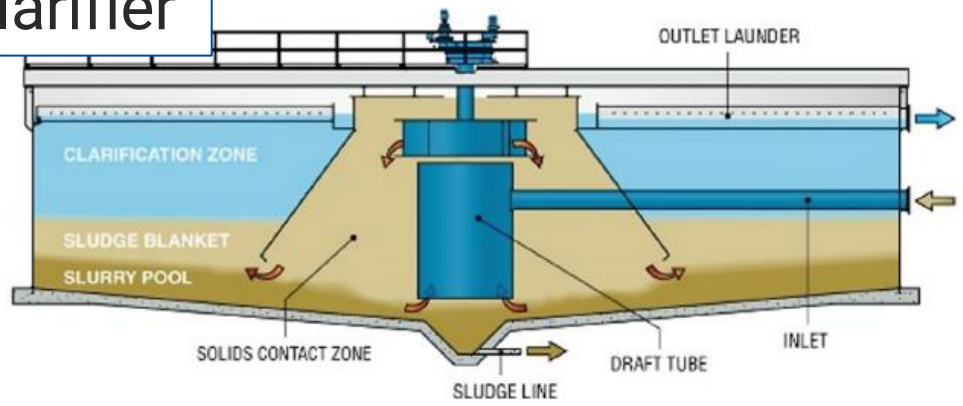


Water Treatment Unit Operations – Primary Treatment



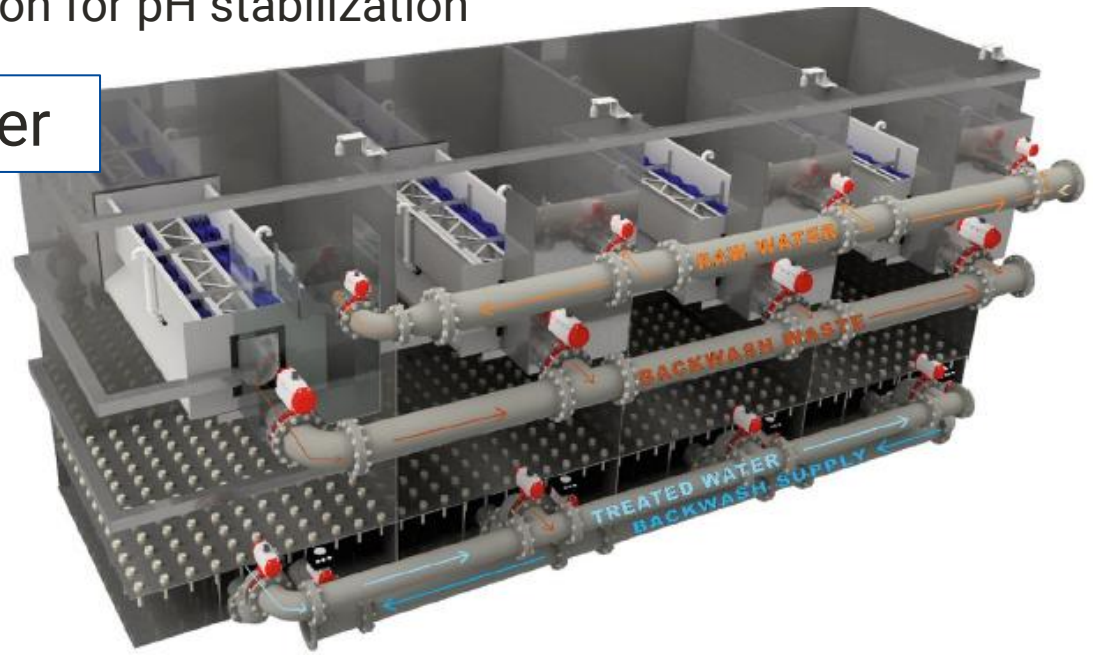
Flow diagram for lime-soda softening with recarbonation for pH stabilization

Clarifier



Schematic view of solid contact clarifier (*Source* WesTech Engineering Co.,)

Filter



View of rectangular gravity filter with internal details (*Source* WesTech Engineering Co.,)

Water Demineralization

Purpose of demineralization:

- Remove inorganic (and ionic) TDS and prepare water for feeding boilers to raise high pressure steam
- Steam used to drive power turbines, vacuum ejectors, and in strippers and distillation columns
- Treated water fed to demineralizer

Demineralization process by IX, or RO, or their combination:

- IX process consists of:
  - Cation removal
  - Decarbonation
  - Anion removal
  - Fine polishing for silica removal
- RO process consists of:
  - UF to remove suspended solids
  - RO to remove dissolved solids

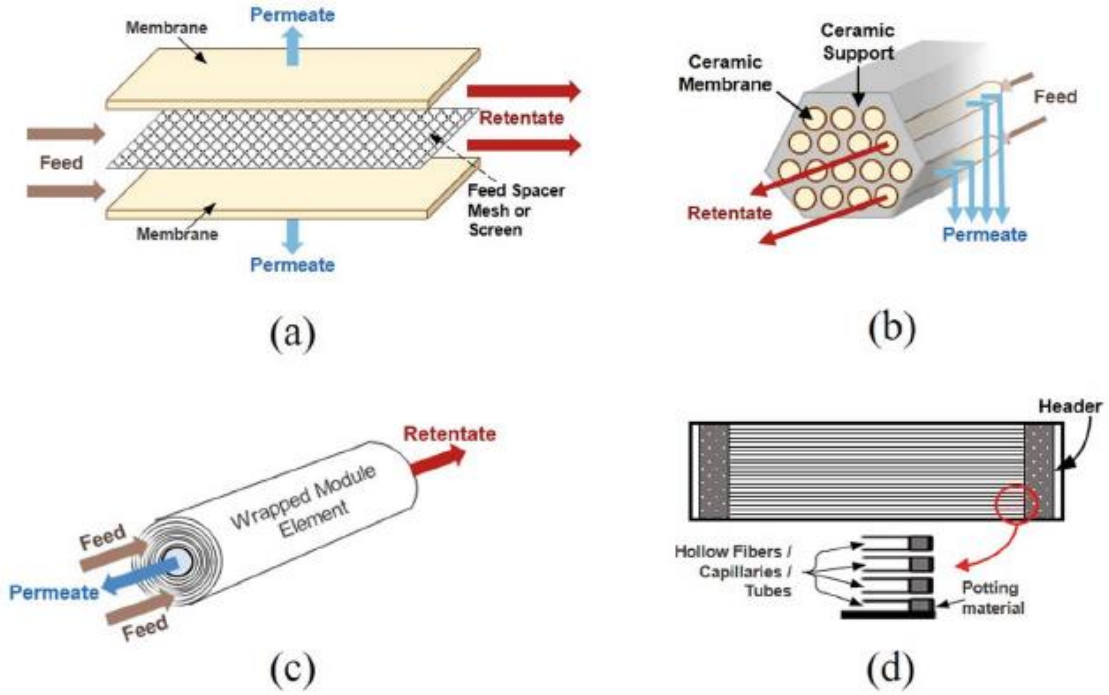
IX resins:

- Regenerated periodically by caustic and acid solutions that produce waste streams requiring pH neutralization before disposal

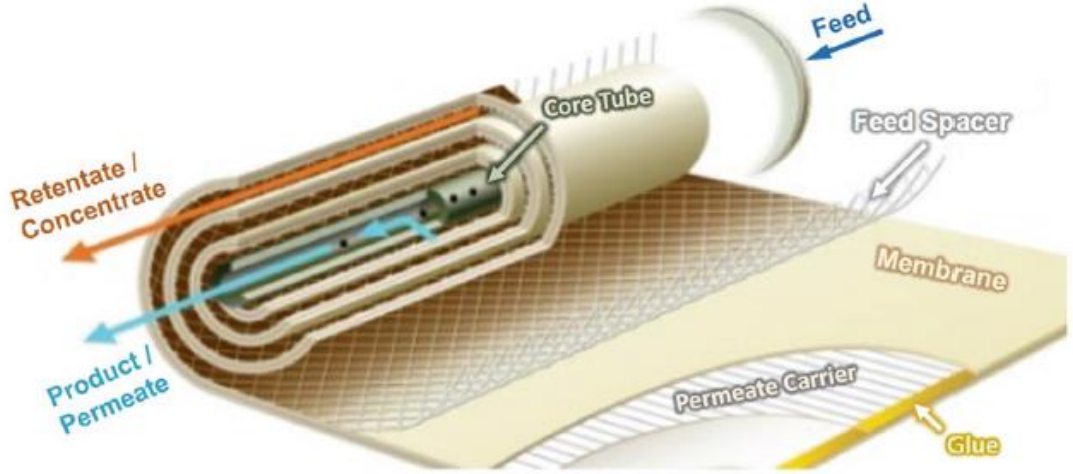
RO membranes:

- Produce a fraction of the feed as concentrate that needs proper disposal

Water Treatment Unit Operations – Advanced Treatment



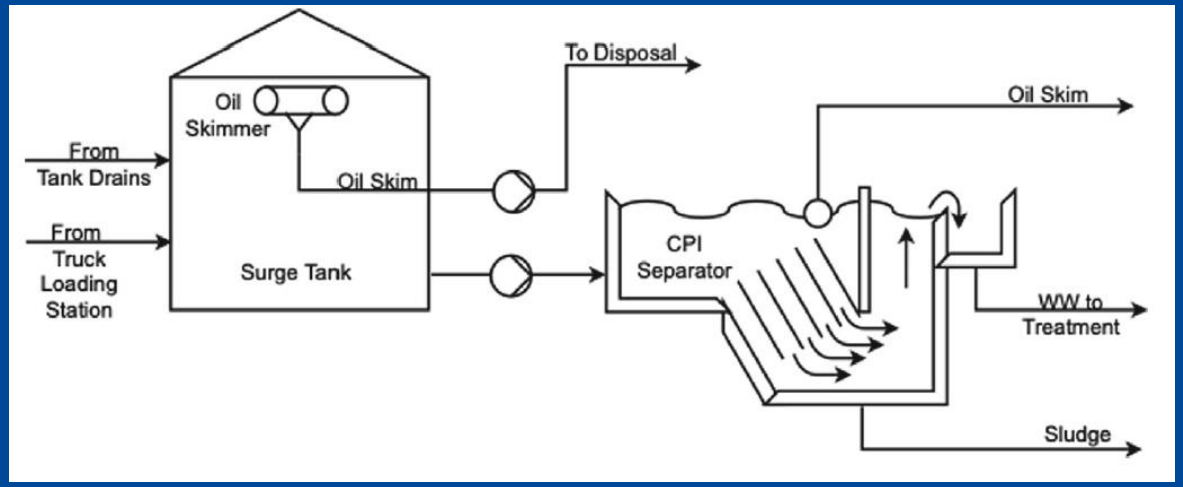
Configurations for **a** Flat Plate, **b** Tubular, **c** Spirally Wound and **d** Hollow Fiber (HF) Membrane Modules (Photo Courtesy of Nitto Global Membranes Division- Reprinted with Permission)



Functioning of RO module (Photo Courtesy of Nitto Global Membranes Division- Reprinted with Permission)

Also… GAC and Ion Exchange

Marketing
= Distribution Terminals



Managing run-off

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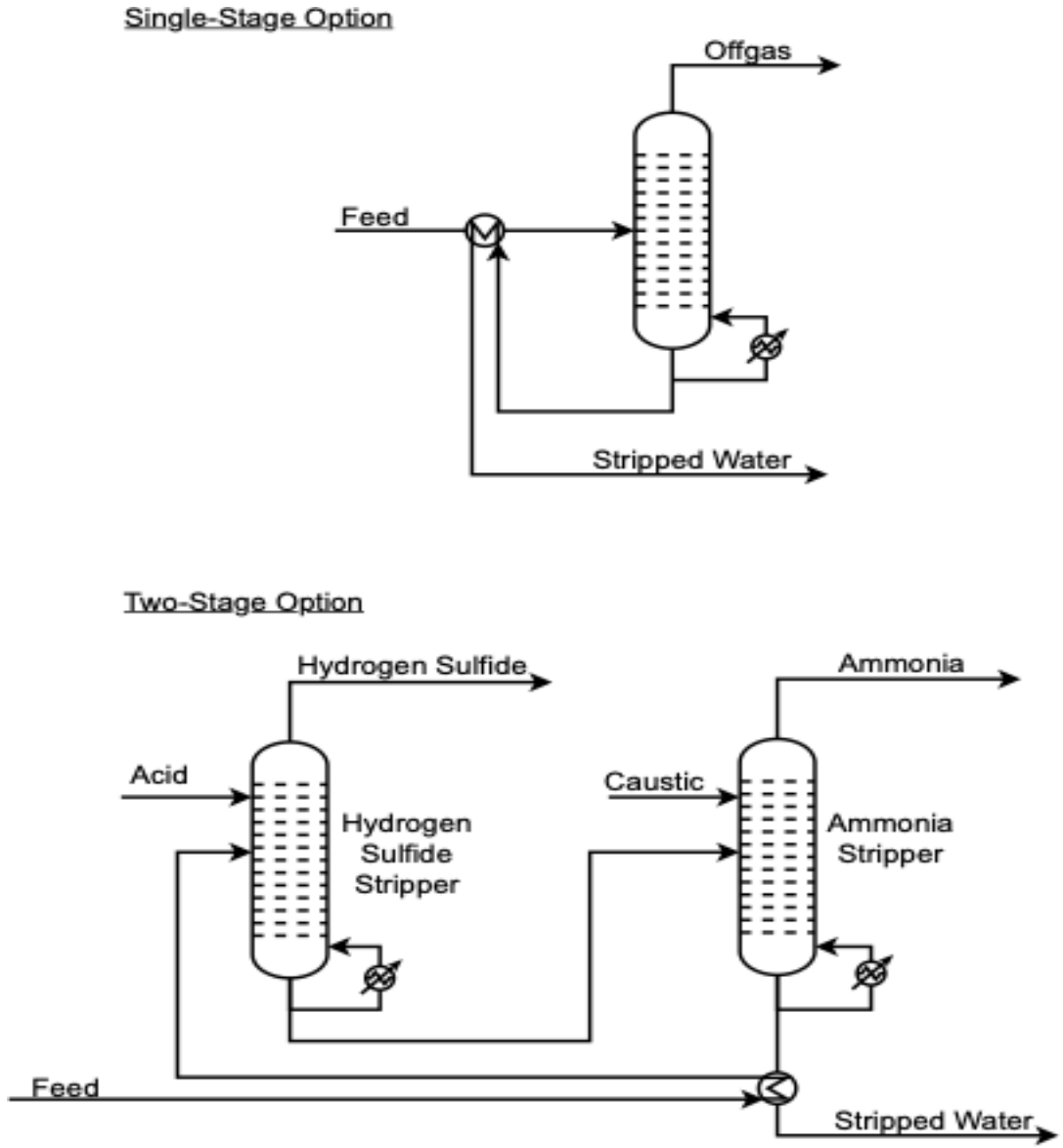
Wastewater Treatment

Secondary Treatment: Typical Refinery Wastewater Characteristics Influent and Effluent Biological Reactors

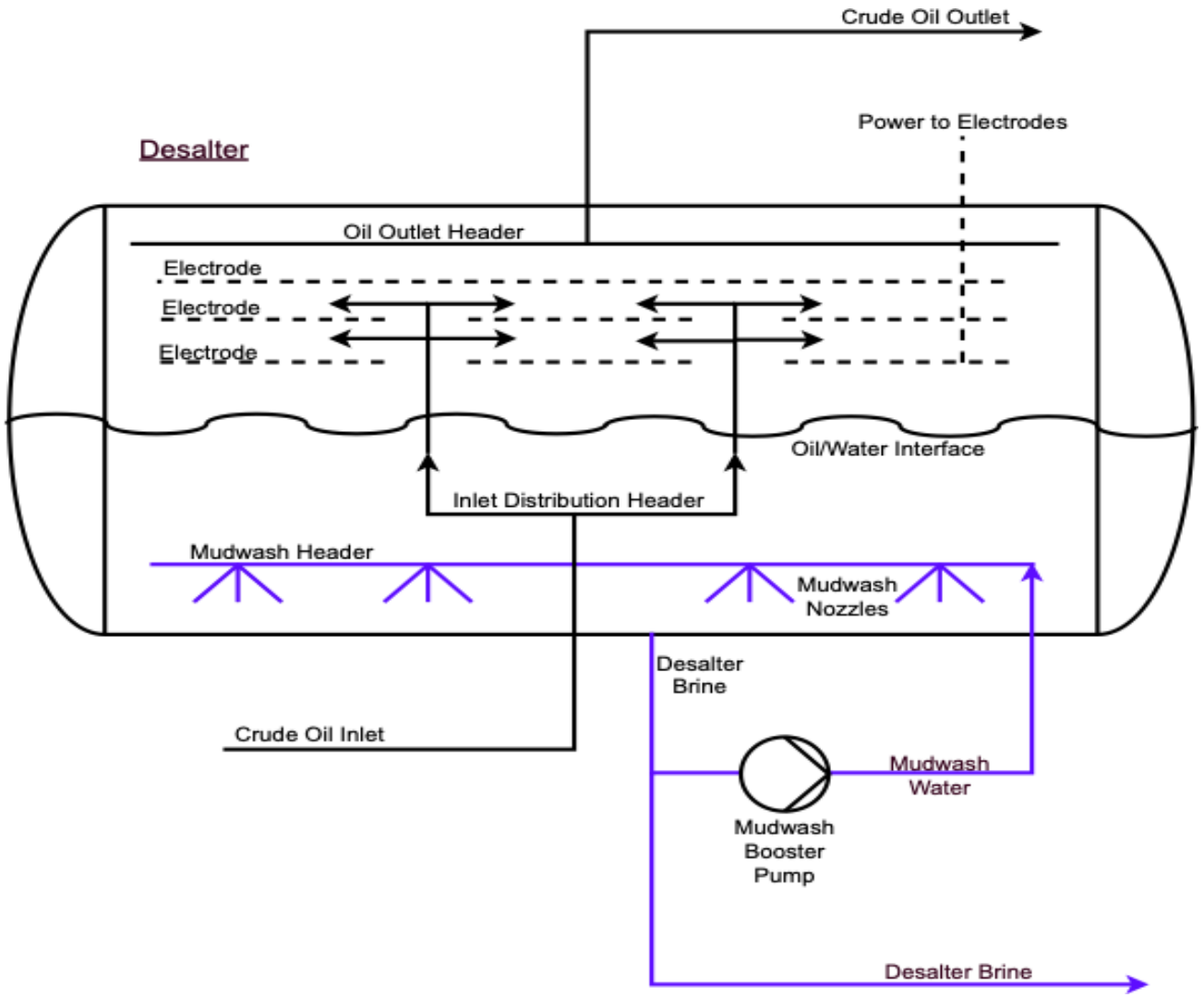
Parameter	Biotreatment Influent	Biotreatment Efluent with BOD Removal + Nitrification	Biotreatment Effluent with BOD and Nitrogen Removal
Temperature, deg C	20-35	20-30	20-30
pH, su	6.5-9	6.5-8.5	6.5-8.5
BOD, mg/L	120-150	15 (soluble)	10 (soluble)
COD, mg/L	200-400	50-60	50-60
TSS, mg/L	50-80	50-80	10-15
Ammonia-N	25-40	5-10	1-5
TN, mg/L	25-40	5-10	1-3
TP, mg/L	8-15	5-8	5-8
Oil & Grease, mg/L	30-50	0-5	0-5
Aromatics, mg/L	25-35	2-5	2-5

Process Water Collection and Treatment: Sour Water Stripper



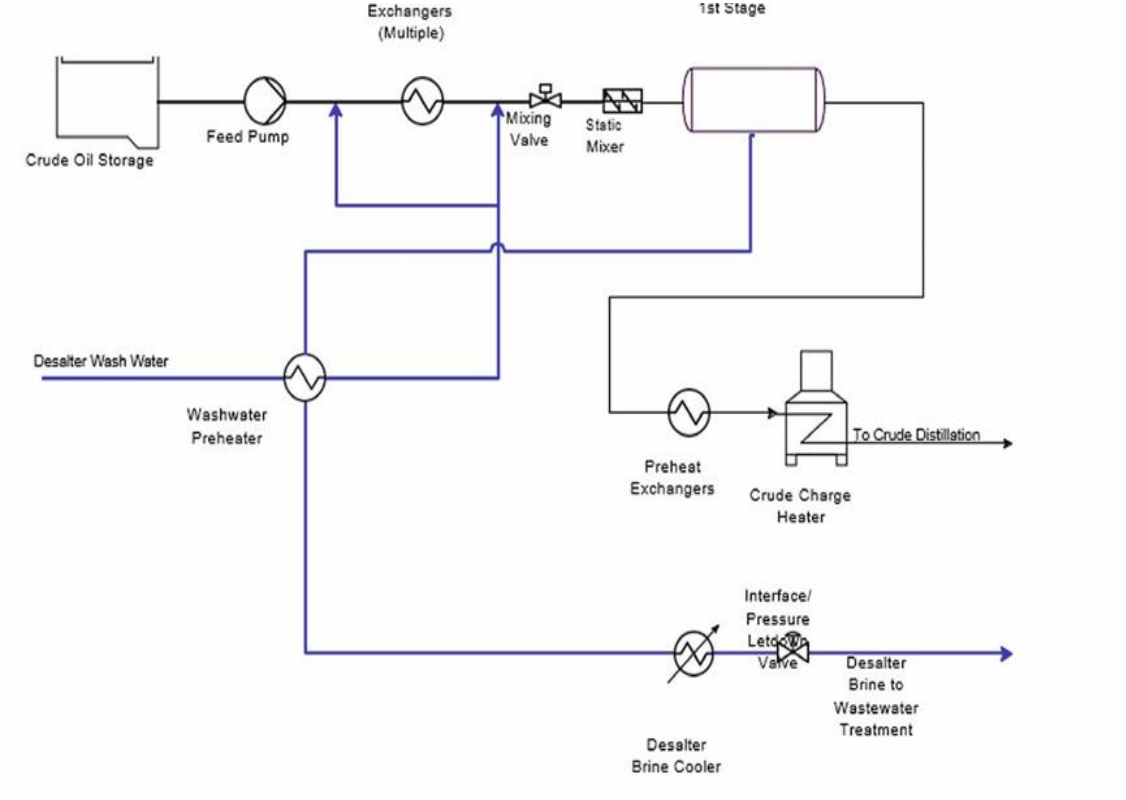
Sour Water Stripper Options

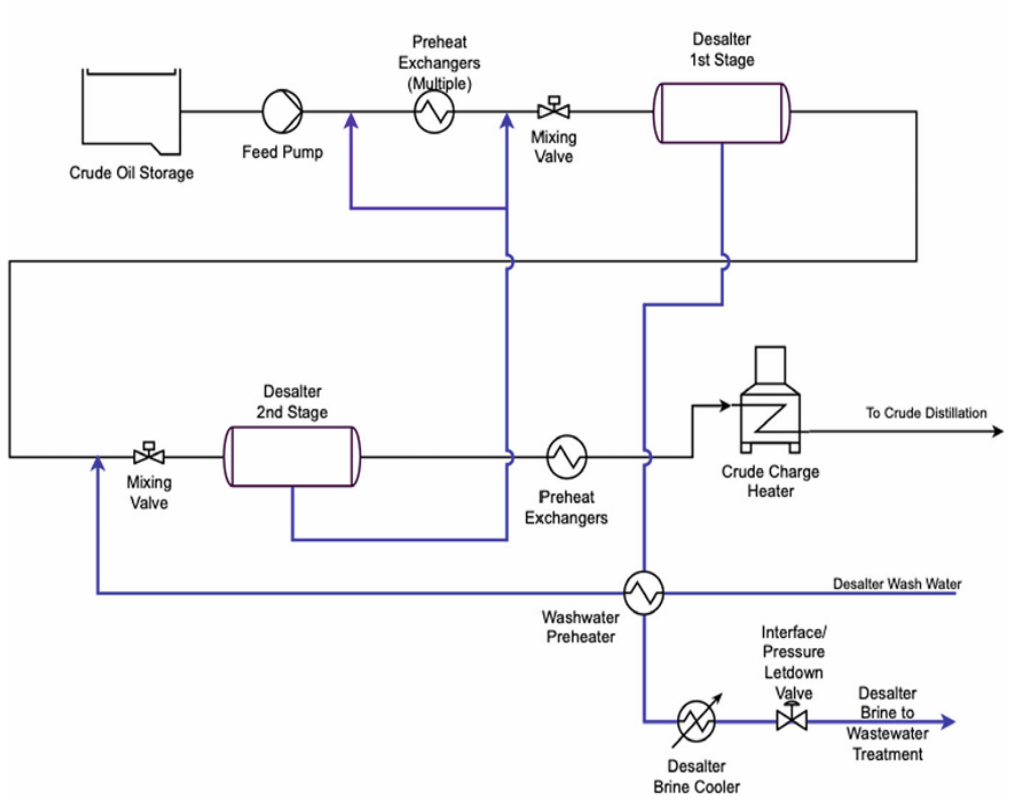
Process Water Collection and Treatment: Desalter



Desalter internal details

Process Water Flow through Desalter Arrangement: Single Stage vs. Two Stage





Internal View of EDGE Desalter (Forum Energy Technologies, Houston, TX)

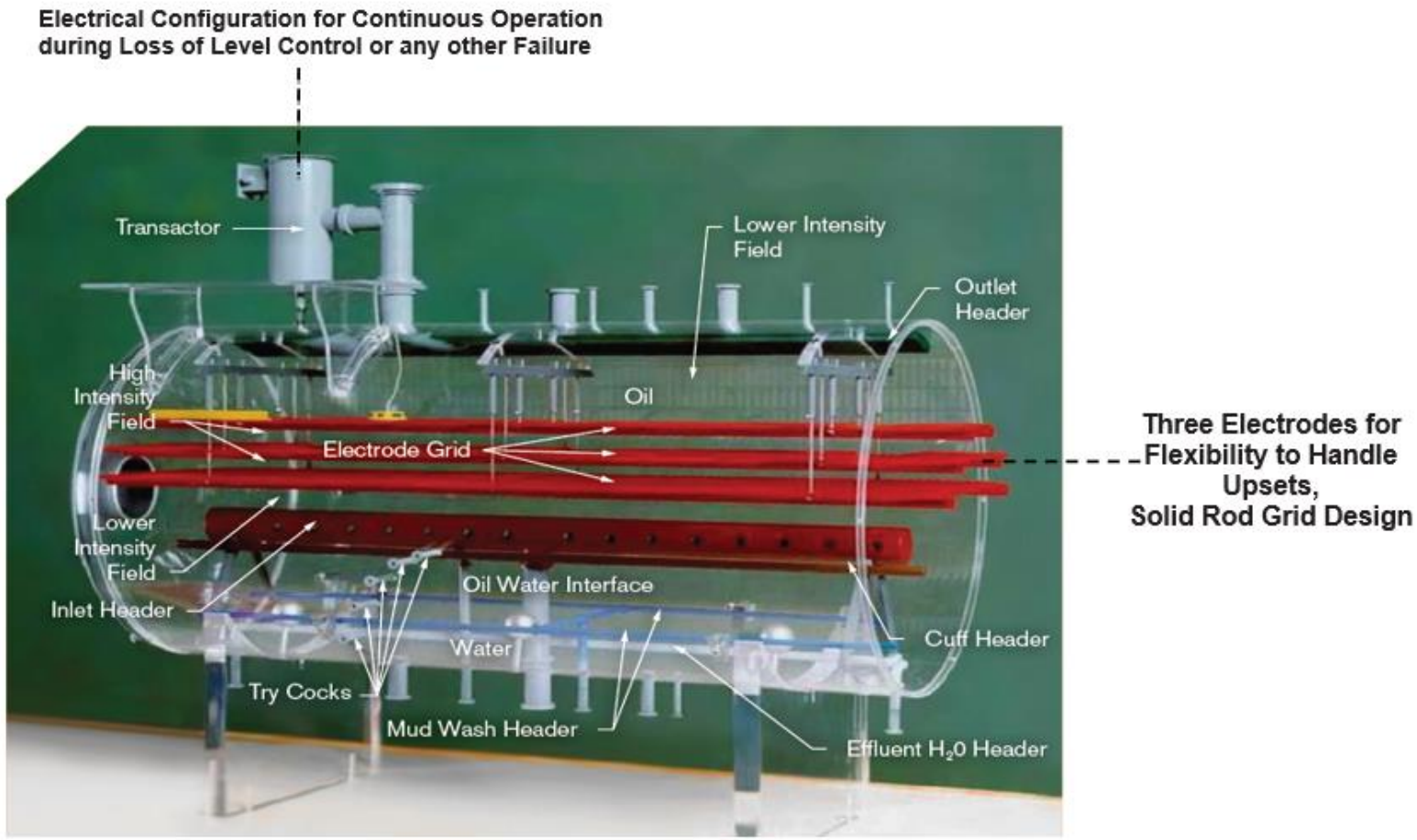
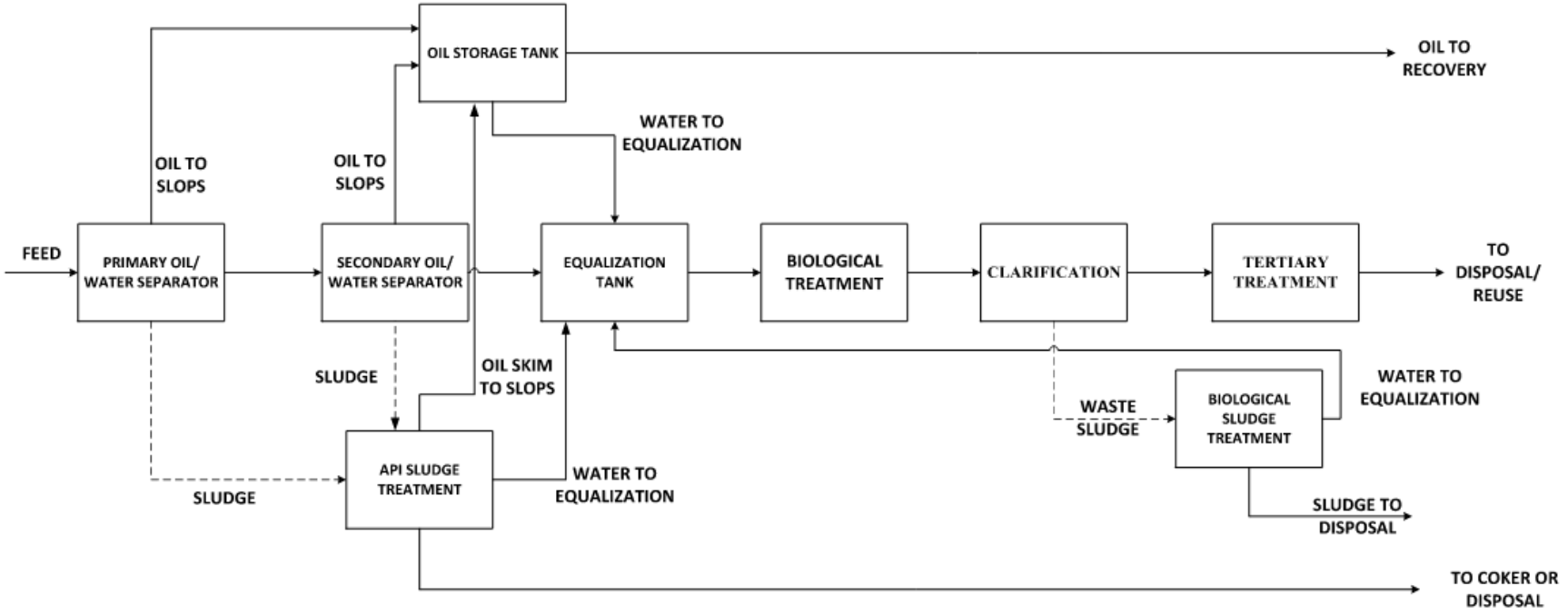


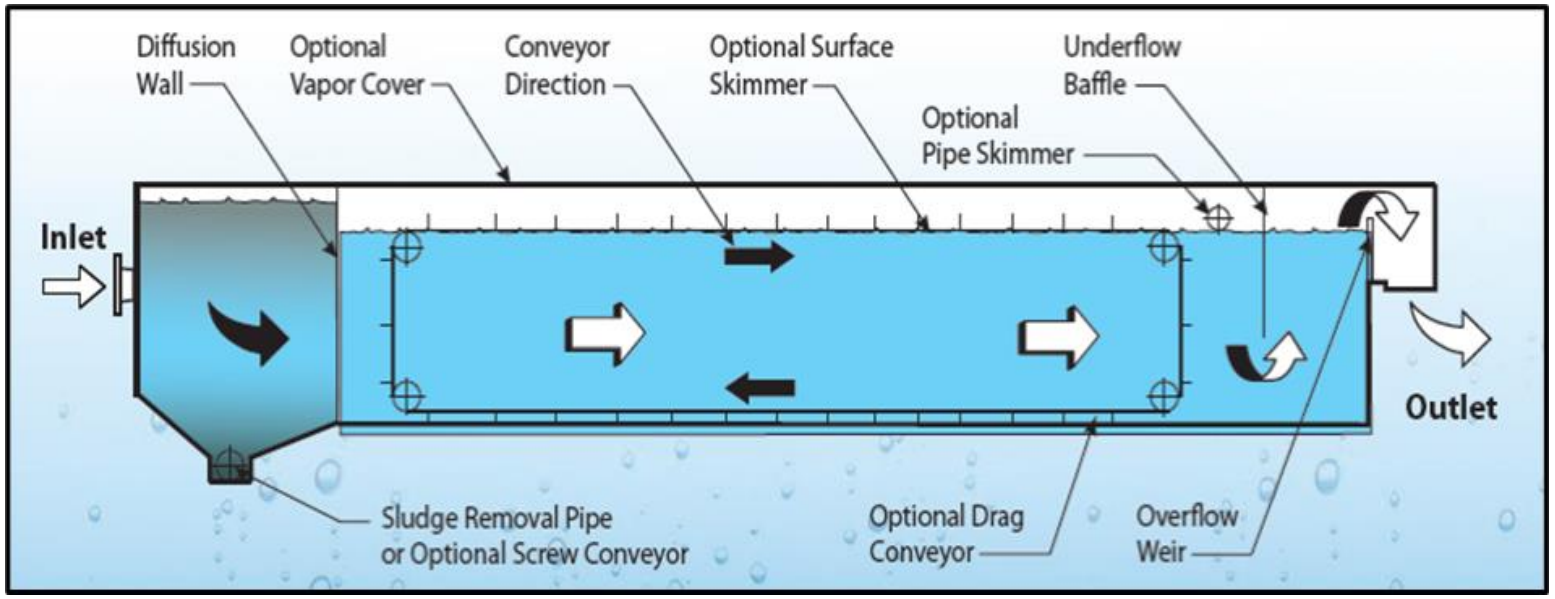

Photo by Paul Teysen on Unsplash

Wastewater Treatment Process Flow Diagram



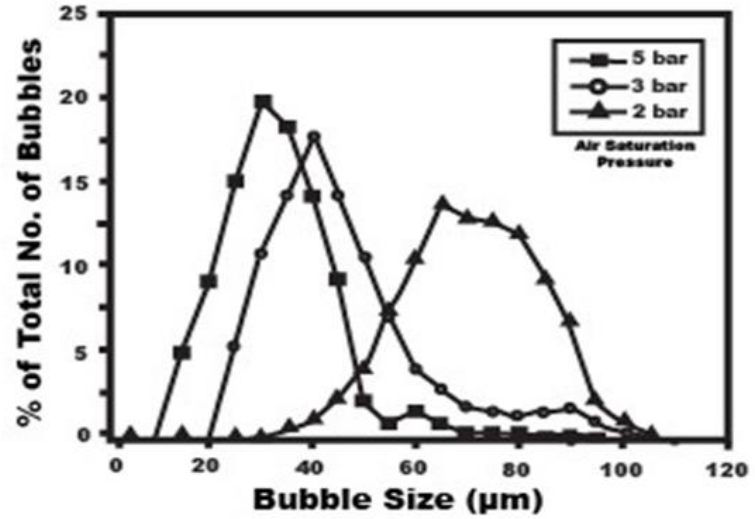
Wastewater Treatment – Primary Treatment: Primary Oil-Water Separation by API/CPI

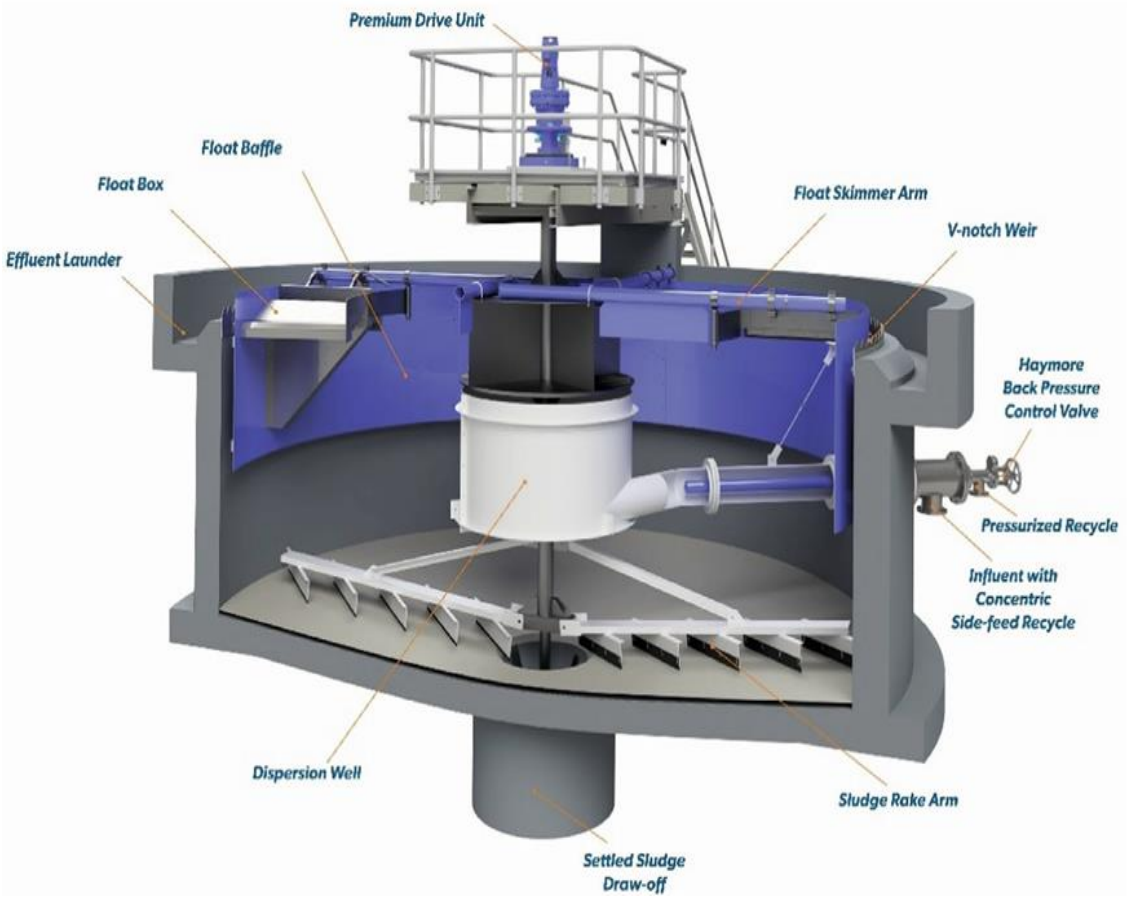
Removes bulk of Free Phase Oil Droplets ≥ 150 µm size
Influent O&G Concentration from 200 to 80,000 mg/L
Effluent O&G Concentration 40 to 200 mg/L



Wastewater Treatment – Primary Treatment: Secondary Oil-Water Separation by DAF/DGF and IAF/IGF

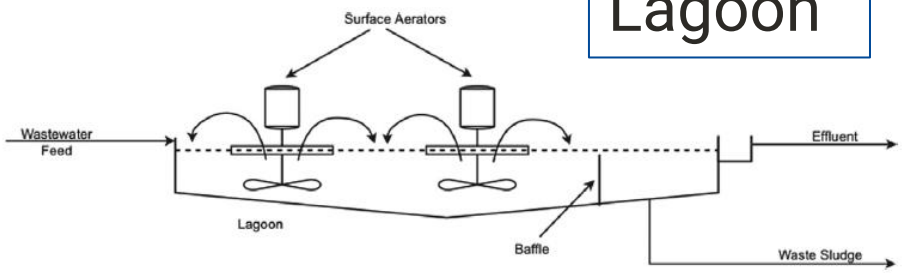
- Removes emulsified oil 5 – 20 µm
- Feed O&G 80 to 200 mg/L
- Effluent O&G ~ 25 mg/L
- DAF/DGF Air bubble ~10 – 100 µm
- IAF/IGF Air bubble ~ 500 – 1000 µm



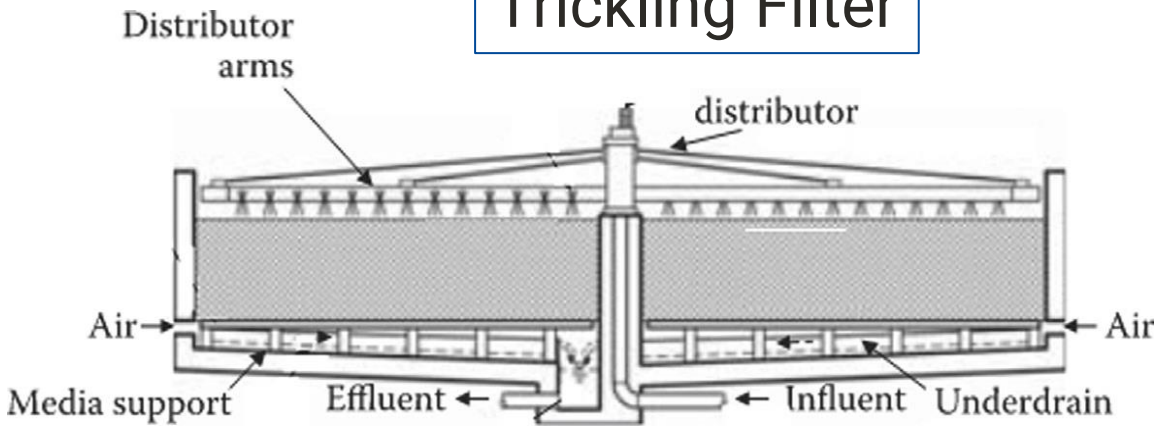


Traditional Biological Treatment – Attached Growth and Suspended Growth

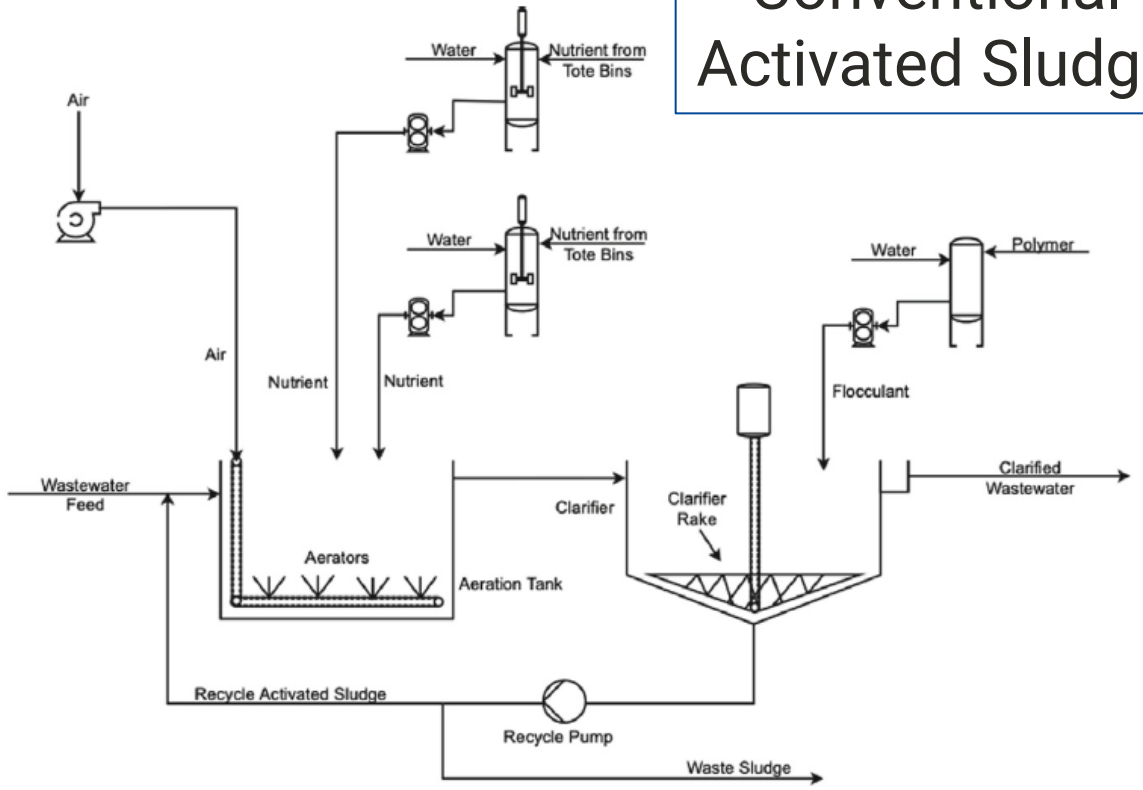
Lagoon



Trickling Filter

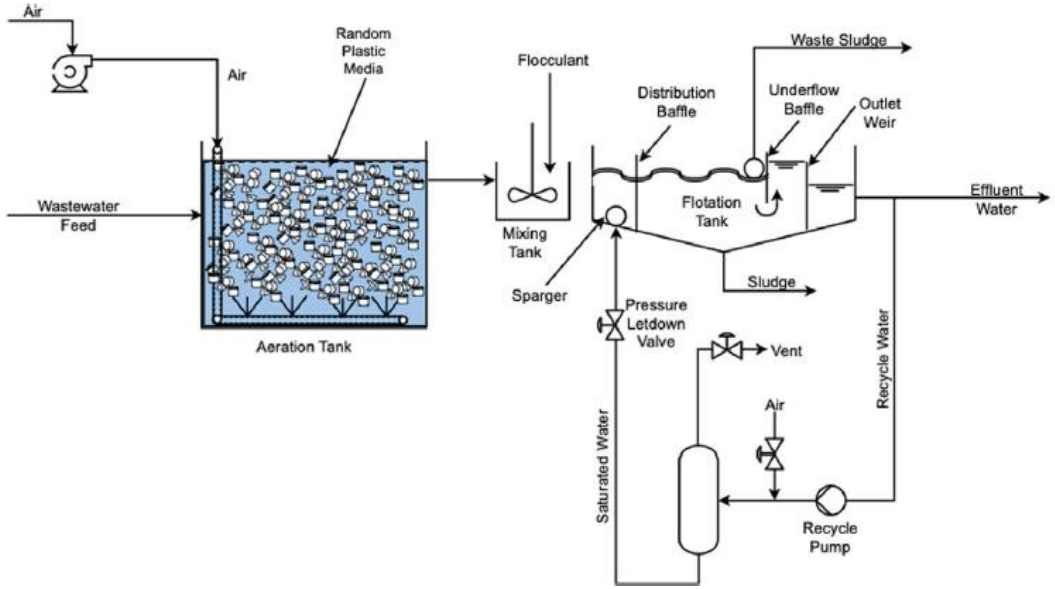


Conventional Activated Sludge

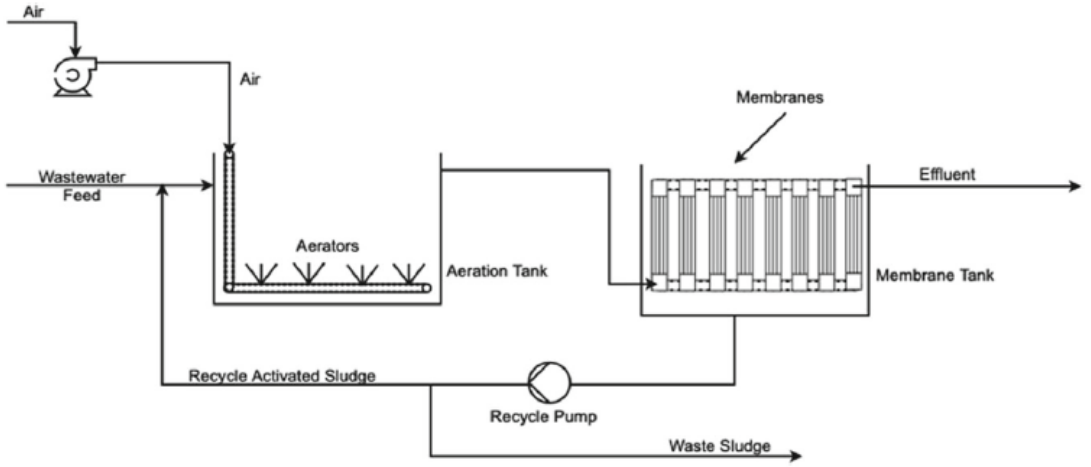


Wastewater Treatment – Secondary Treatment

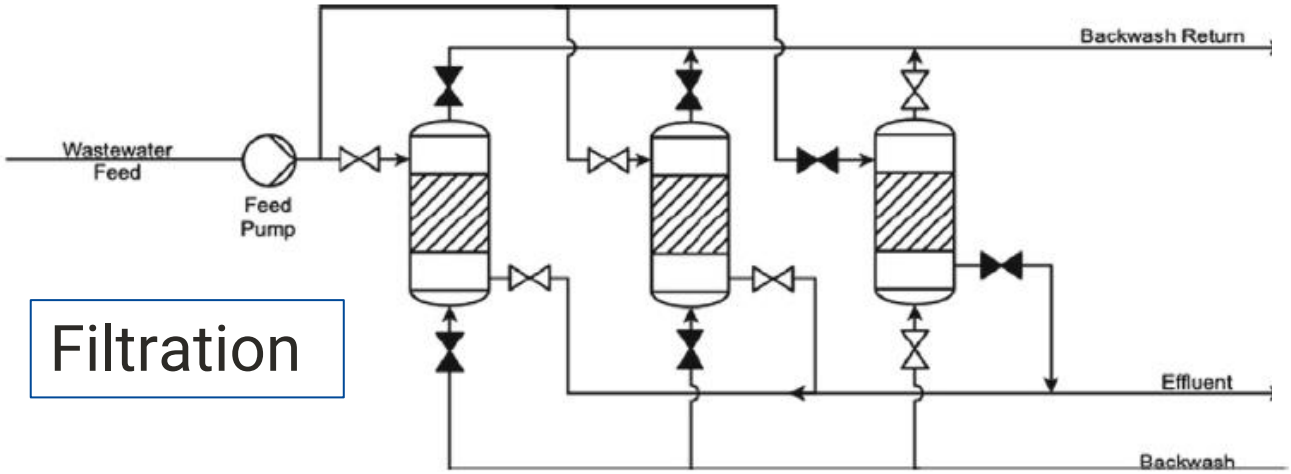
Moving Bed Bio-Reactor (MBBR)



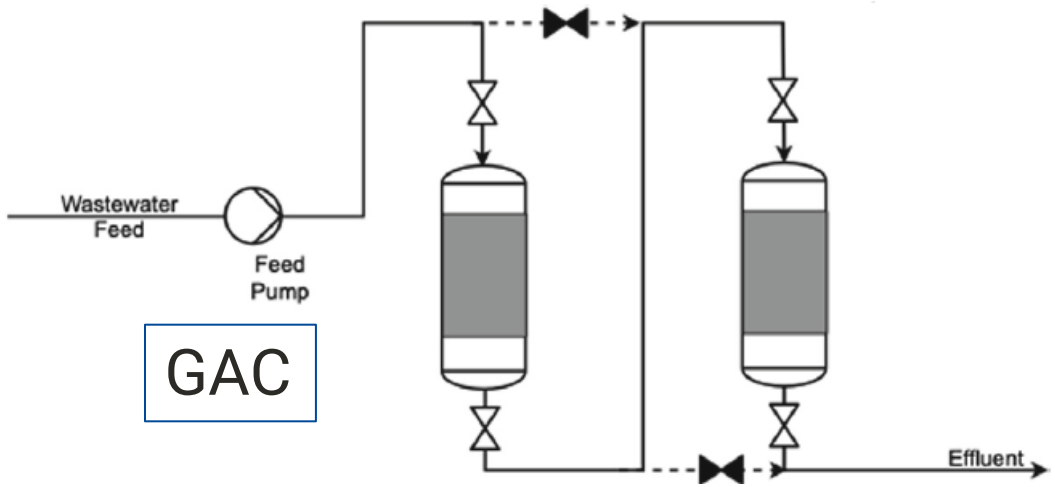
Membrane Bio-Reactor (MBR)



Wastewater Treatment – Tertiary Treatment for stricter effluent limits or reuse

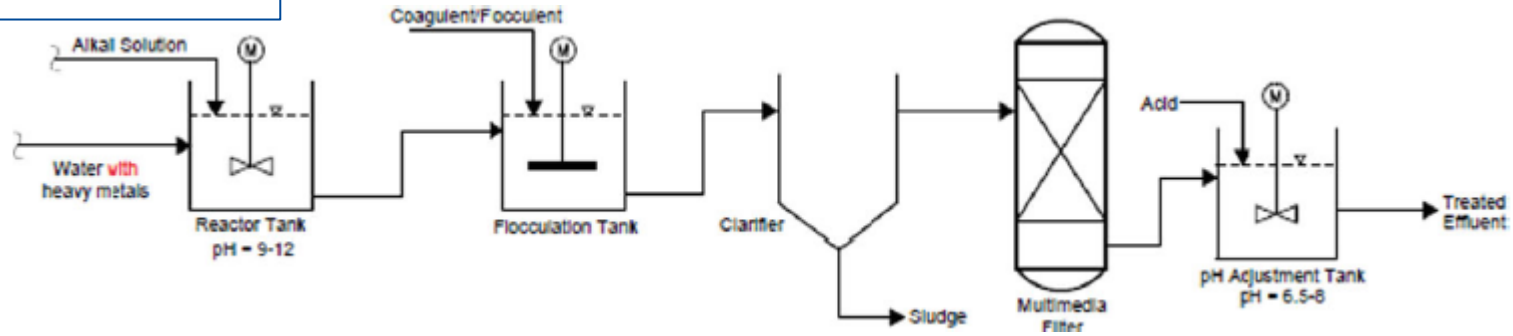


Filtration



GAC

Advanced Treatment



Schematic view of metal removal process from wastewater by hydroxide precipitation

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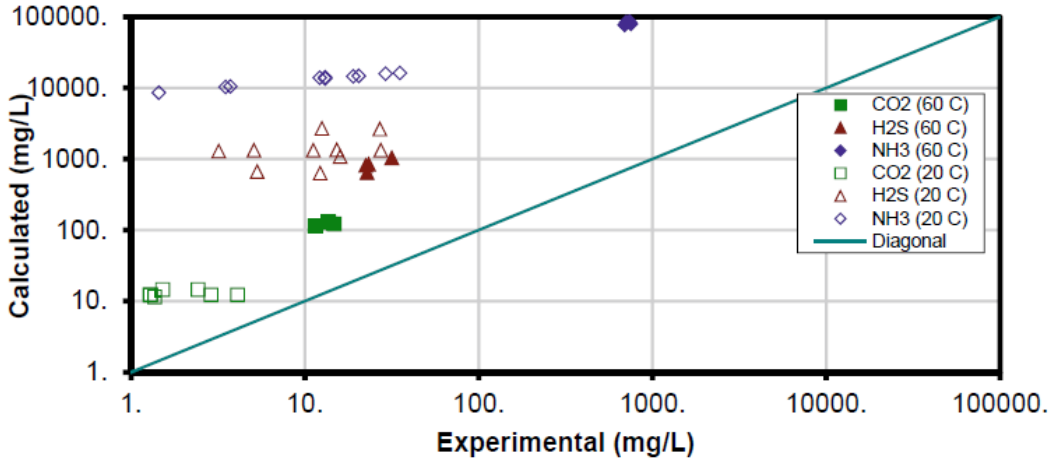
Process Modeling

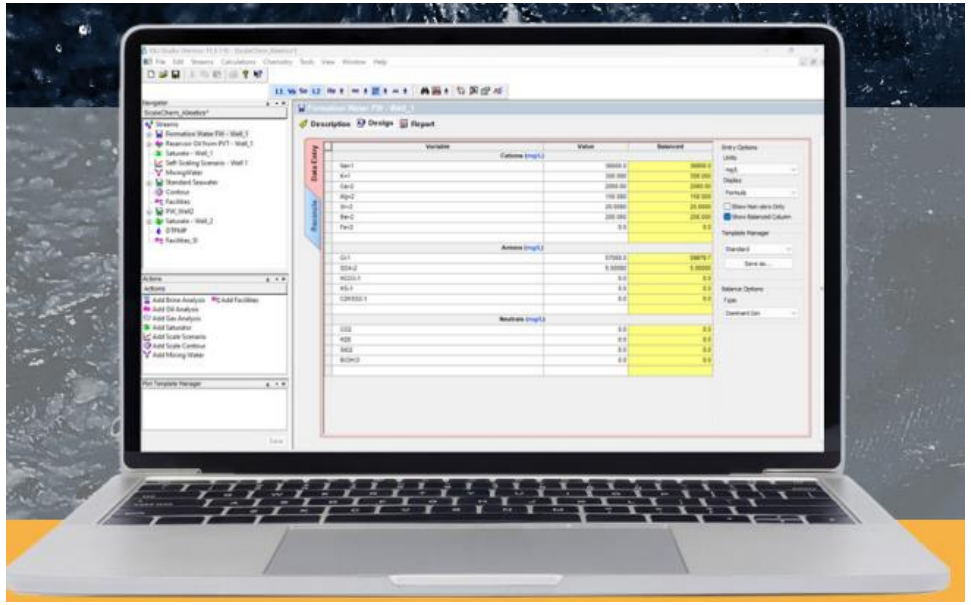
Process Modeling – Scaling

Basic Hand Calculations…

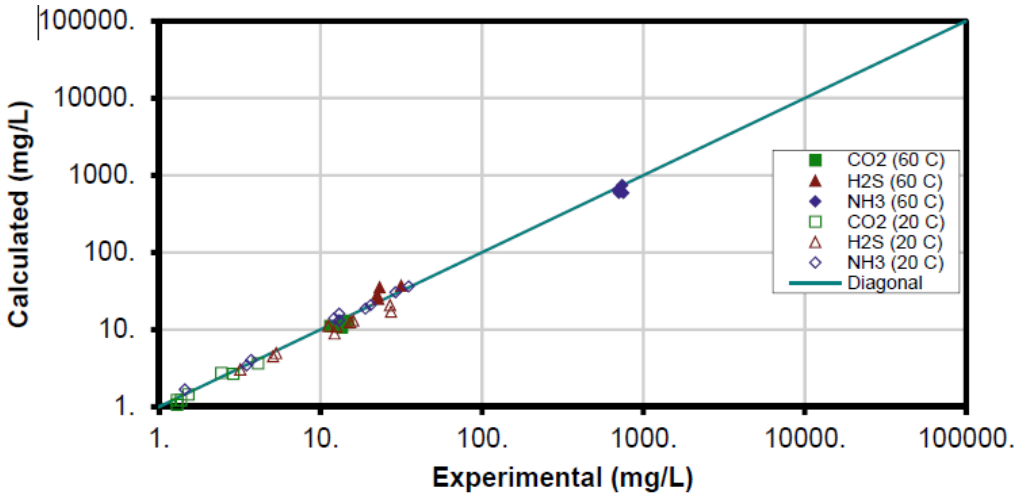


Parity plot for CO_2, H_2S and NH_3 vapor pressures when only the Henry's constant is used to predict solubility (with no aqueous speciation)

Models include complex speciation for more accurate estimation of scaling potential



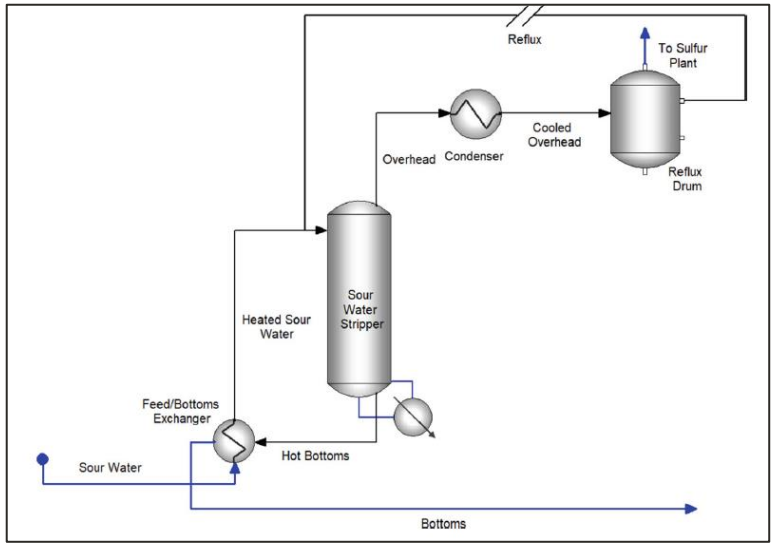
Model-based Calculation



Parity plot for CO_2, H_2S and NH_3 solubility in water when a full speciation model is used to predict solubility

Process Modeling – Sour Water Stripping

Parameters	
Temperature (°C)	50.0
Pressure (atm)	1.1
Total Flow (kg/hr)	25000.0
Inflows (ppm (mass))	
H2O	9.81e5
H2S	8000.0
NH3	6000.0
CO2	3000.0
SO2	1500.0
NaCl	100.0
NaHCO3	100.0
CaCl2	100.0
MgCl2	100.0
KCl	100.0
NaOH	0.0
Total	**1.0e6**

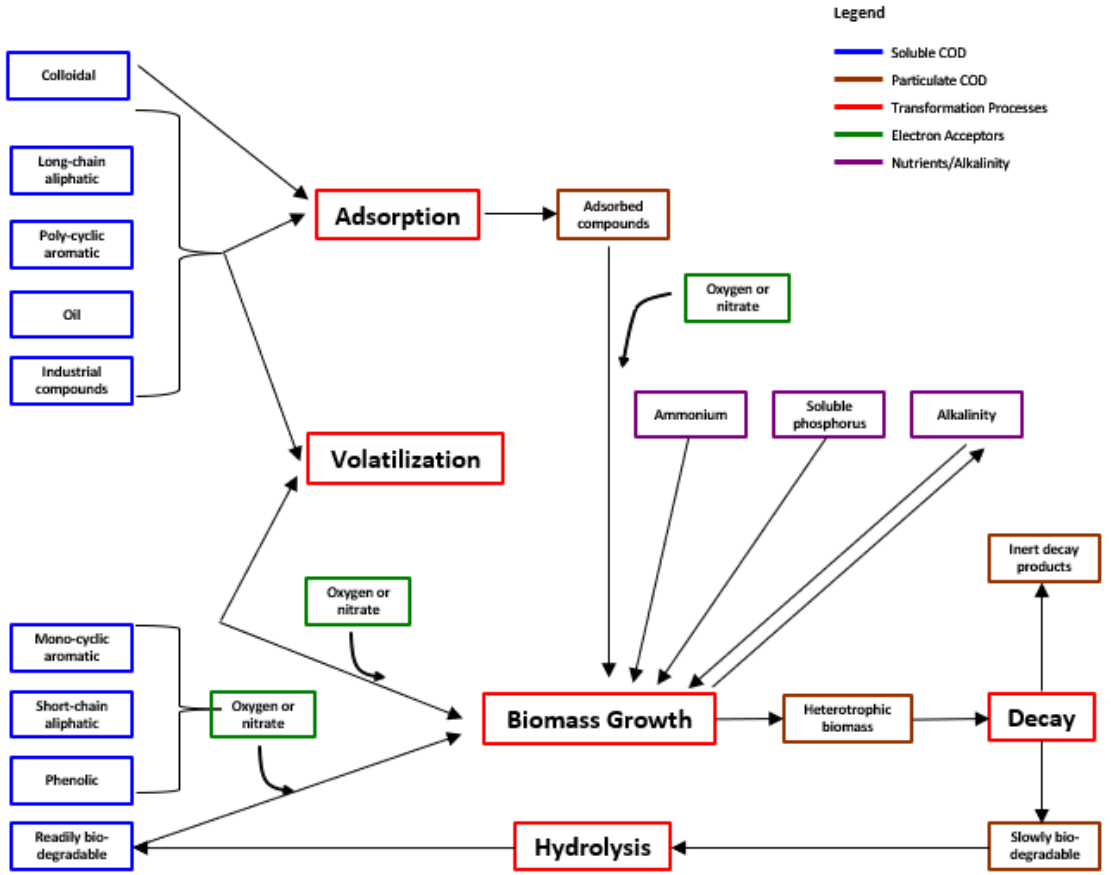


OLI systems flowsheet esp used to model the electrolyte chemistry in a sour water stripper

Bottoms	
T (◦C)	119.566
pH	7.35577
CO_2, Liq1, apparent (mg/L)	0.0154348
H_2S, Liq1, apparent (mg/L)	4.72467
NH_3, Liq1, apparent (mg/L)	1291.28

Reflux	
T (◦C)	85.0
pH	8.18022
CO_2, Liq1, apparent (mg/L)	18361.7
H_2S, Liq1, apparent (mg/L)	29272.3
NH_3, Liq1, apparent (mg/L)	57759.9

Process Modeling – Biological Treatment



COD transformation processes in MantisIW (adsorption, volatilization, and heterotrophic growth/decay)

Process Modeling – Biological Treatment

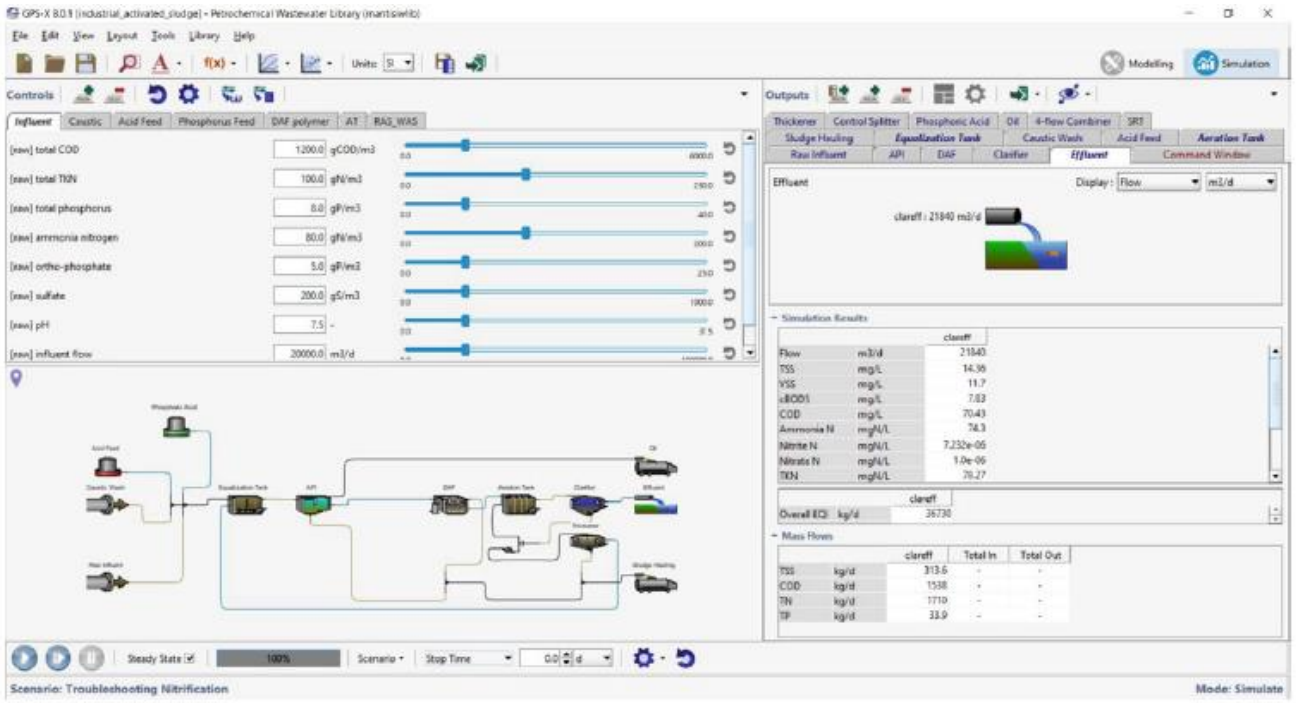


Fig. 6.35 Output from MantisIW model showing high effluent ammonia

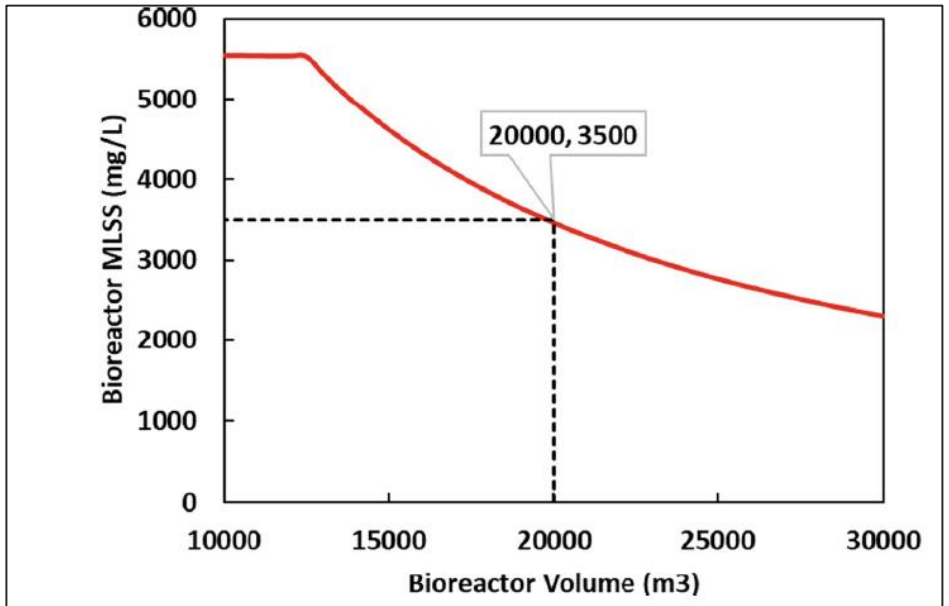


Fig. 6.30 Sensitivity analysis on the bioreactor volume

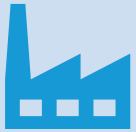
Table 6.16 Simulation results with "optimized" bioreactor volume

Model output	Value	Units
Effluent BOD_5	5.8	mgBOD/L
Effluent TSS	12.6	mg/L
Effluent ammonia	1.05	mgN/L
Bioreactor MLSS	3,457	mg/L
Bioreactor DO	1.99	mg/L
Total volatile emissions	84.8	kg/d

Conclusions

Conclusions

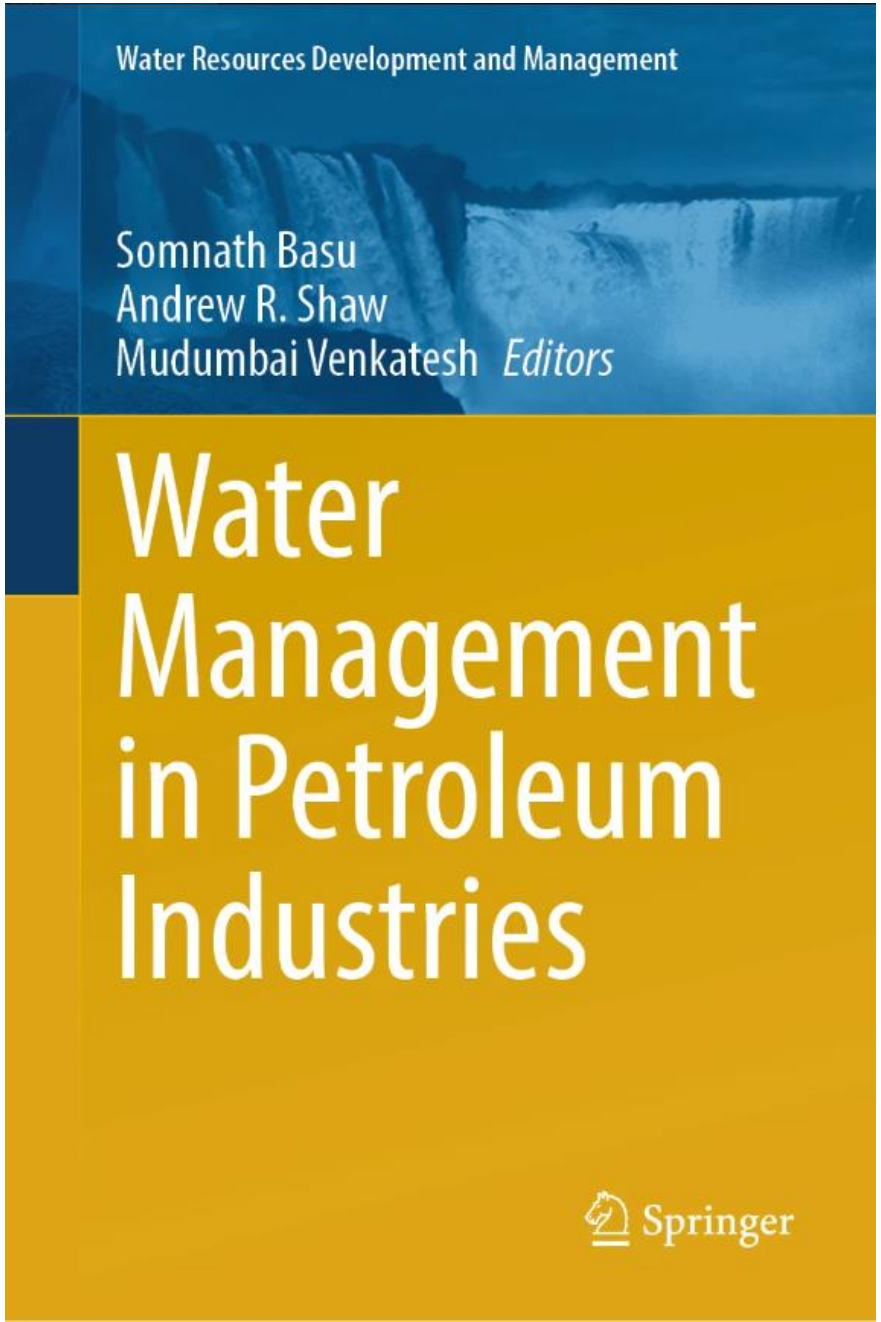
Water is vital for life



Water plays a vital role in the petroleum industry

We must manage it well

Much of today's material drawn from…



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