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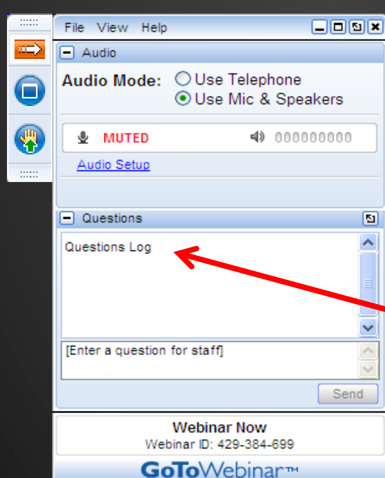

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Refinery Wastewater Treatment Case Studies

Design, Startup, and Troubleshooting

Thursday April 12, 2018
1:00 – 3:00 PM ET

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Today's Moderator

SIEMENS
Ingenuity for life

- Introduction of refinery wastewater treatment
  - Composition
  - Treatment requirements
  - Typical treatment process

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Today's Speakers

- Kar Munirathinam
  - *Design of a Membrane Bioreactor Plant for High TDS Refinery Wastewater*
- Jim Russell
  - *Biomass Settling Challenges for a newer Refinery ETP*
- John Faber
  - *Upgrading a Treatment Plant for Refinery Expansion*

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Refinery WWT

Introduction

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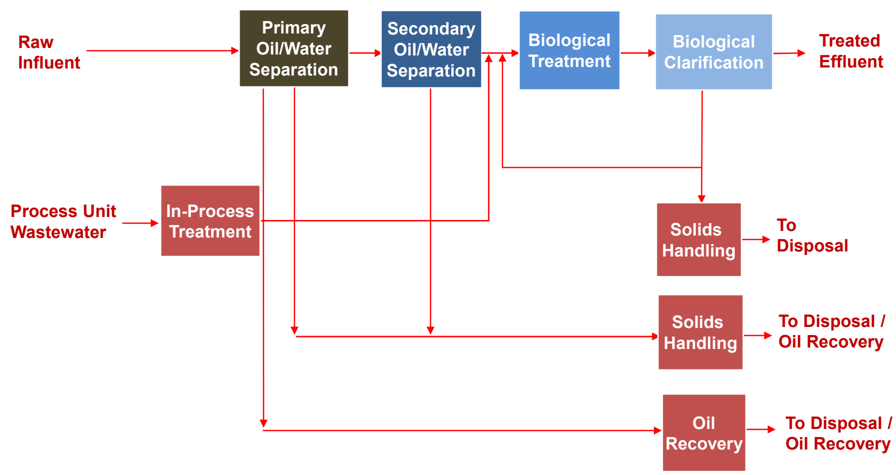
Constituents in refinery wastewater

- Oil & grease
- Organics
- Suspended solids
- Ammonia
- Total dissolved solids
- Metals

Treatment requirements

- Often receiving water discharge
  - COD / BOD
  - O&G
  - TSS
  - Ammonia / Total Nitrogen
  - Toxicity
  - Odor

Typical refinery water treatment



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Our Next Speaker

Kar Munirathinam, PhD

Chief Process Engineer
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TETRA TECH

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Design, Start Up, and Commissioning of a Membrane Bioreactor Plant Treating a High TDS Refinery Wastewater

Background

- BAPCO (Bahrain Petroleum Company) refinery, whose capacity is 267,000 BPSD (11.2 MGPD).
- Previous existing WW treatment:
  - API separator
  - Induced Air Flotation (IAF)
- To comply with the new Bahrain environmental regulation, BAPCO was required to add additional WW treatment processes (biological treatment for COD and nitrogen removal).

Background (Continued)

- Uncommon characteristics of the wastewater
  - high temperature (up to 48°C)
  - high TDS (up to 35,000 mgTDS/l)
  - low biodegradable COD
- Membrane Bioreactor (MBR) system was selected as a preferred treatment technology to overcome the poor flocculation of the activated sludge due to the high salinity.

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Plant Design

- System configuration:
  - 2 biological trains
  - Each trains composed of multiple cells: Anoxic and aerobic
  - 4 membrane tanks
- Design parameters:
  - SRT = 35 d
  - HRT = 8.3 h
  - MLSS = 5.4 g/l
  - RAS = 400%
  - F/M = 0.1 kgCOD/kgTSS/d
  - Nitrate recirculation = 200%

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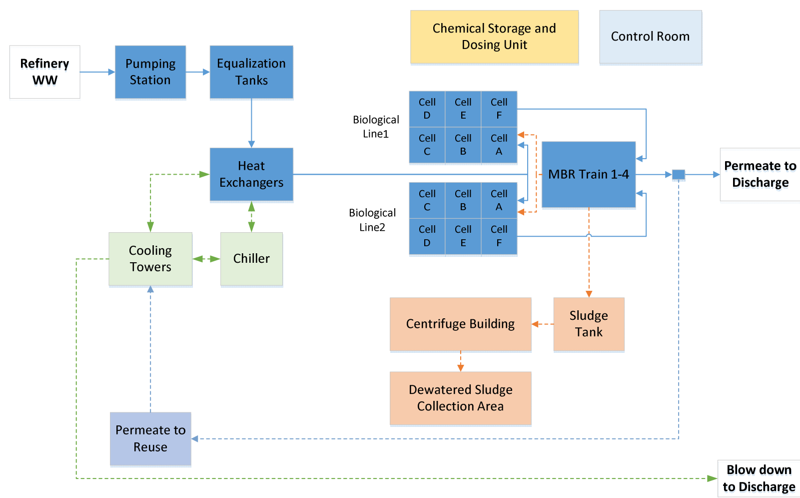
Plant Overview
Simplified Block Flow Diagram



Plant Aerial View

Influent and Effluent Design Criteria

Parameter	Units	Minimum	Average	Max Month	Max Day	Final Effluent Specification Monthly Average	Final Effluent Specification Maximum
Flow	USgpm	2,750	3,492	4,013	4,400		
	mgd	3.96	5.03	5.78	6.34		
	m3/hr	625	793	912	999		
COD	kg/d	1,655	3,445	4,776	4,819		
	lb/d	3,648	7,595	10,529	10,624		
	mg/l	110	181	218	201	150	350
BOD	kg/d	857	1,295	1,735	1,799		
	lb/d	1,890	2,854	3,826	3,967		
	mg/l	57	68	79	75	25	50
TKN	kg/d	517	987	1,294	1,576		
	lb/d	1,140	2,176	2,852	3,475		
	mg/l	35	52	59	66	-	15
NH3	kg/d	324	493	648	749		
	lb/d	714	1,086	1,428	1,650		
	mg/l	22	26	30	31	1	3

Plant Start up

- The plant construction was completed in May 2013 and the startup activities started right after completion. The startup comprises of the following steps:
  - Biomass seeding from another plant
  - Biomass growth phase
  - TDS increase phase
  - Acclimation phase
  - Performance tests

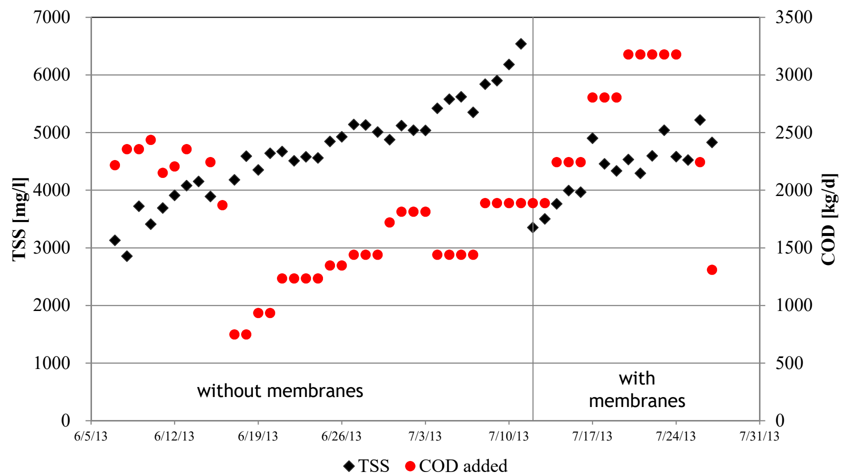
Biomass seeding

- To minimize use of of high quality water, treated effluent from a local municipal WWTP (TDS 2,500 mg/l) was used to fill the biological and membrane tanks
- Initial seeding was done with only 1 train
- The WWTP was started by seeding biomass from an already operating municipal plant (local municipal WWTP)
- Plant was filled with a treated effluent (to avoid shock to the biomass).
- Sludge taken from RAS (8,000 mg TSS/l, VSS/TSS ≈ 95%).
- 900 m^3 of sludge was transferred into the biological cells
- The final biomass concentration in the system was 3,100 mg TSS/l.

Biomass growth

- Promote biomass growth, adding acetic acid, urea and phosphoric acid.
- F/M = 0.1 kgCOD/kgTSS/d.
- System in recycle mode
  - Mixed liquor recycled from last cell to the first cell

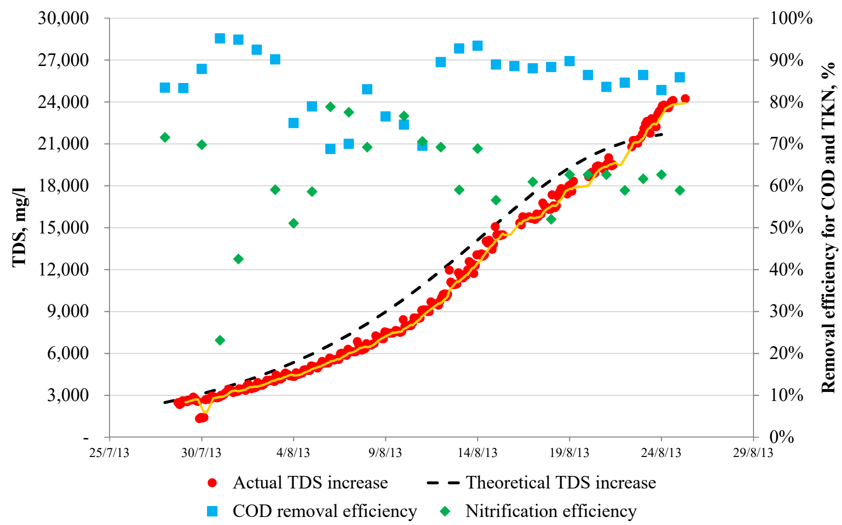
Biomass growth (Continued)



TDS increase

- TDS concentration of municipal plant effluent (2,500 mg/l) was much lower than TDS of refinery wastewater (24,000 – 38,000 mg/l).
- From literature review,
  - rapid stepwise increase in salt concentration causes inhibitory effect on nitrifying bacteria
  - It is not possible to achieve stable nitrification with Cl > 10,000 mg/l (while refinery WW has Cl ≈ 17,000 mg/l).
- A fast increase of the salinity can cause disruption of the biomass cell due to osmotic effect.
- Based on experience and literature review, TDS concentration was increased by 10% on a daily basis.

TDS increase (Continued)



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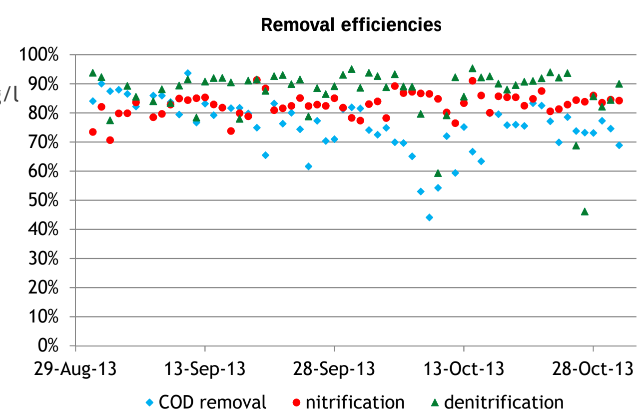
Acclimation phase

- SRT = 35 - 40 d
- RAS ratio = 3
- Added Urea = 27 mg/l
- Added COD for Denitrification



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Acclimation phase (Continued)

Summary of performance

	Effluent concentration	Removed Load	Efficiency
	mg/l	kg/d	%
COD	63	3000	76 ± 9
TKN	1.4	440	83 ± 4
NOx	4.8	419	87 ± 8

Performance Test

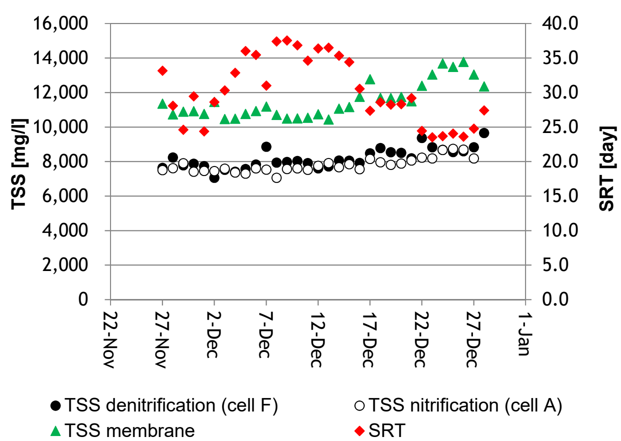
- Test condition:
  - Flow rate = 2,000 Usgpm (454 m3/h)
  - COD = 2,400 kg/d (acetic acid added to complete denitrification)
  - TKN = 650 kg/d (urea added)
  - Spent caustic flow rate = 1 Usgpm (0.23 m3/h)

Performance Test (Continued)

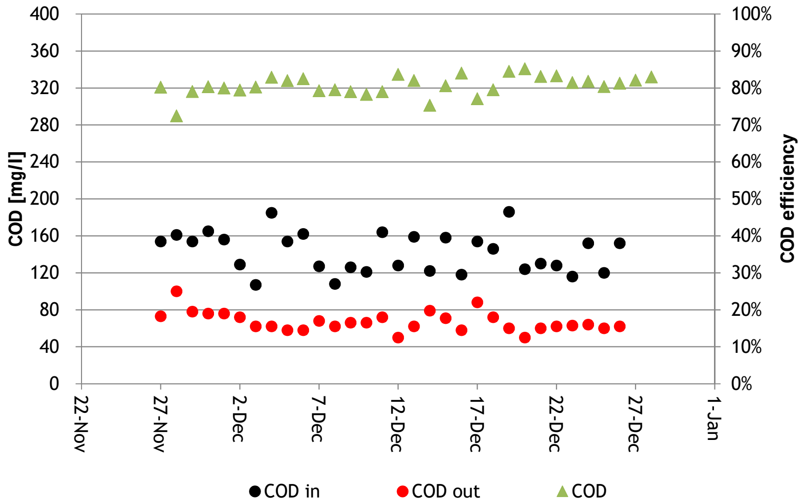
Parameter	Unit	Influent		Effluent		Limits (monthly average)
		Average	Max	Average	Max	
BOD	mg/L	81.7	115.0	4.1	6.0	25
COD	mg/L	142.2	186.0	67.0	100.0	150
TKN	mg/L	26.4	55.0	1.3	1.9	15
NH3	mg/L	18.1	46.0	0.2	0.4	1
NO3	mg/L	1.1	7.3	1.7	8.0	10 (max)
NO2	mg/L	0.0	0.0	0.2	0.6	1 (max)
Total P	mg/L	0.4	0.7	0.3	0.8	1
H2S	mg/L	6.6	16.8	< 1	< 1	0.5
TSS	mg/L	36.7	124.0	< 1	< 1	20
VSS	mg/L	21.0	44.0			
TDS	mg/L	26,015	28,190	26,320	28,650	

Performance Test (Continued)

- TSS = 7721 mg/l
- SRT = 30.5 (23.5 - 37.5), day
- F/M = 0.1 kgCOD/kgTSS/d



Performance Test (Continued)



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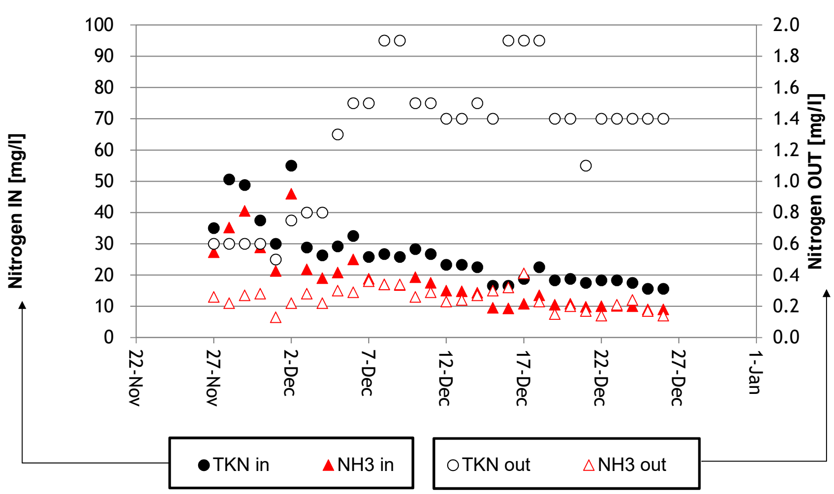
Performance Test (Continued)



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Conclusion

- The construction of the WWTP was completed in May 2013
- Startup, commissioning and performance testing executed in the second part of 2013.
- Main challenges:
  - Salinity difference between the seeded sludge and the BAPCO wastewater.
  - High temperature
- To avoid salinity shocks, a gradual increase of the salinity has been applied: 10% increase per day
- Excellent COD and Nitrogen removal during all phases.

Conclusion (Continued)

- Performance test conducted on one single train, applying the maximum specific COD and TKN load considered during the design.
- Excellent performance, meeting the limits for all the parameters.
- COD removal efficiency: 80.6%
- Nitrification always complete:
  - TKN removal efficiency: 98%
  - Residual TKN concentration: 1.3 mg/l
- Denitrification complete, provided that required amount of acetic acid was dosed.
- Successfull use of spent caustic as COD and alkalinity source without any inhibitory effect for the biomass.

Our Next Speaker

Jim Russell

Environmental Engineer

Chevron

Biomass Settling Challenges of a newer Refinery ETP

Presented at WEFTEC 2015, updated with subsequent efforts including CFD modeling

New Refinery ETP Start-Up and Settling Challenges, Driver and Design

- Pascagoula's new ammonia limits are based on the state's water quality criteria for ammonia, issued 11/2006, became effective 11/2009
  - 3.2 mg/l monthly average, 21 mg/l daily max
  - Typical feed averages 45 ppm NH_3, range 30 – 100 ppm.
  - Past effluent ammonia performance was 10-20 ppm.
- How to Meet?
  - New 20-mile long discharge pipe/diffuser? Expensive, Risky Permitting.
  - Discharge to city of Pascagoula? Local facility too small.
  - Short timeline, eliminating time for pilot studies and various technology options
  - Decided to fast-track conventional activated sludge

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New Refinery ETP Start-Up and Settling Challenges

Old facility was surface-aerated, short hydraulic residence time, relied on extensive ponds for settling, no settling issues, not an activated sludge system.

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New Refinery ETP Start-Up and Settling Challenges - The New Plant

New Eqpt.

Main Sump

EQ tanks

DNFs

Aeration basins

Clarifiers

Chemicals

Biomass Dewatering

(Cooling)

Initial Indications of Biomass Problems

- Severe Problems with biomass Dewatering

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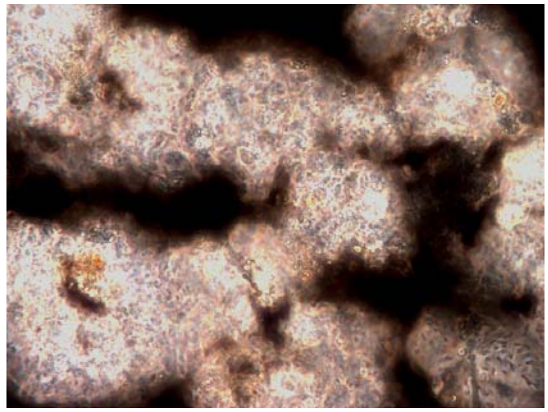
Biomass Settling Troubleshooting – exocellular slime or zoogloeas?

- India Ink Staining indicated exocellular slime
- Others indicated

problem was zoogloea. What's the difference? Symptoms largely similar, but causes are different



Biomass De-Watering Problems, initial Troubleshooting

- Initial analysis indicated excessive exocellular slime.
  - Nutrient deficiencies are common causes of exocellular slime.
  - By contrast, zoogloeas caused by high F/M, readily degradable compounds
- Wastewater has excess nitrogen – so must be other nutrients
  - New ETP was built with phosphoric acid addition system.
  - ETP feed often has relatively high sulfides, 50 - 100 ppm or so. Could sulfides be making trace metals unavailable?
  - Testing biomass for micronutrient deficiency turned out to be quite problematic, hard to analyze to sufficiently low detection.

Biomass Settling Trials

Various Methods Tried to Improve Settling

- Adding Calcium Chloride – analysis indicated a monovalent-to-divalent ratio of 26 to 1. Improved to 7 to 1
- Adding a micronutrient supplement
- Adding a mineral settling aid
- Adding flocculant to the clarifiers (caused an upset) and subsequently adding coagulant
- Improving reliability of phosphoric acid addition system
  - poor reliability eventually linked to using the wrong grade of phosphoric acid – need food grade instead of farm grade
- Minor Improvements seemed to result, though still high SVIs (often 200 – 300)

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Fire-Foam impact on Poorly Settling Biomass - Hurricane Isaac 8/2012

3 million gal of foam-containing wastewater created via sunk product tank roofs

- Highlighted importance of having good settling biomass – compromised settling impaired ability to handle upset.
- High cost of long-term inventory of foam-containing water.
- Run-off was significantly improved by pre-addition of anti-foam and bypassing primary separation.

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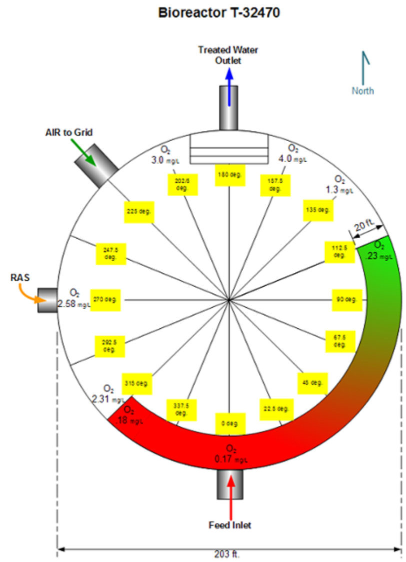
Indications of Maldistribution

A Perimeter DO survey in 2010 had indicated maldistribution in the aeration basin

- Attributed to edge effects, incorrectly



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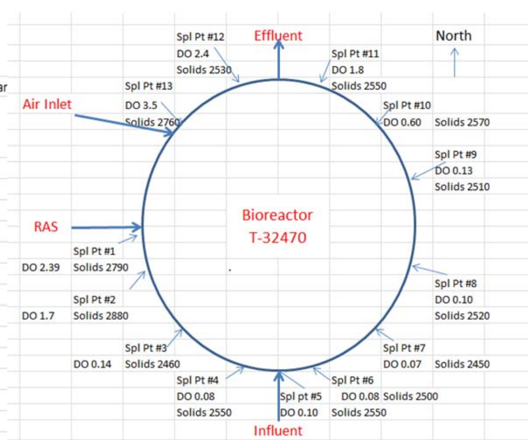
Indications of Maldistribution

A more detailed DO survey on 8/2013 revealed maldistribution was not an edge effect

ORP & O2 results referenced below are samples 10 ft from side wall ar

Spl Position Number	ORP	O2	Solids	DOUR	Soluble COD
1	75	2.39	2790	16.2	539
2	37	1.7	2880	42.7	424
3	-270	0.14	2460	218	451
4	-300	0.08	2550	62.4	455
5	-157	0.1	2550	138	386
6	-197	0.08	2500	220	407
7	-180	0.07	2450	140	676
8	-166	0.1	2520	192	524
9	-117	0.13	2510	146	480
10	-36	0.6	2570	52	399
11	29	1.8	2550	24	380
12	43	2.4	2530	33	550
13	59	3.5	2760	12.7	373



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Indications of Maldistribution

Survey indicated severe maldistribution at air rate of 11k scfm, despite achieving outlet target of 2.0 ppm DO.

- Air rate was close to design expected rate
- Met goal of 15 scfm/1000 ft^3, for good mixing
  - Internal target is 20-30 scfm/1000 ft3.
  - Air flow was roughly 3xs another consultant's recommendation for mixing of 0.12 scfm/ft^2.
- Clearly these design targets alone did not achieve good mixing in this aeration basin

Air Rate Test-runs

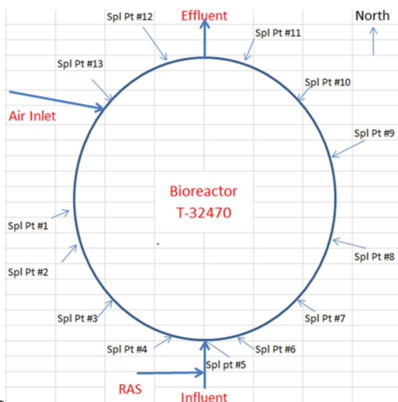
Test-run was conducted on air rate, ramped from 11k scfm to 22k scfm

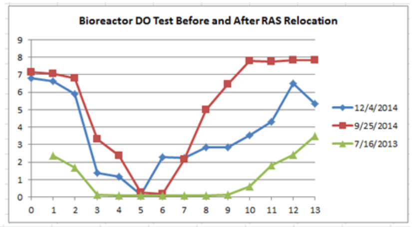
- Even at 22k scfm, with outlet DO at 6.5 ppm, many sample points had low DOs and negative ORPs.
- High air rate was not sustainable, as entrained air was impacting clarifier settling plus excessive power.
- DO and ORP worst on side opposite the RAS recycle
- Project eventually funded to reroute RAS in with the feed

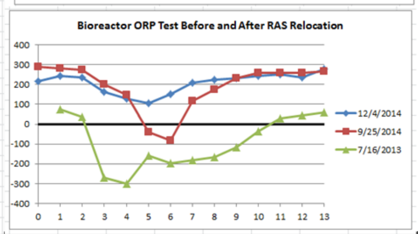
RAS Reroute

Rerouted RAS from side-entry to combined with feed, in attempt to correct bioreactor maldistribution

New Perimeter DO survey after RAS reroute at 16k scfm







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RAS Reroute Conclusions

RAS Reroute helped reduce maldistribution but did not fully resolve. Still usually have poor settling.

- Currently running at an outlet DO around 6 ppm with air rate around 16k scfm
- Waste biomass filter-pressing improved some, considered generally acceptable now.
- SVIs still often above 200, zoogloea still abundant. Sometimes SVIs are in the 100s.
- Reducing dosings of micronutrients and $CaCl_2$, later stopped altogether without noticeable impact

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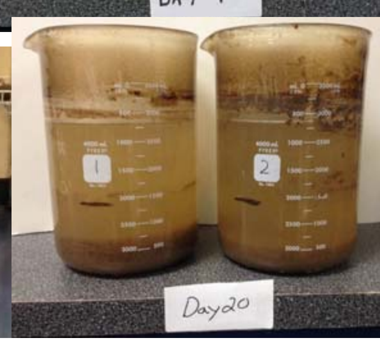
Refinery ETP Settling Challenges – Path Forward

After RAS effort, needed to assess next steps

- Pilot testing
- CFD modeling/adding mixers
- Possibly add feed distributor in currently O/S aeration basin.
- Investigate source(s) of readily degradable organics acids – feed testing shows some acetic acid.

Pilot-Testing

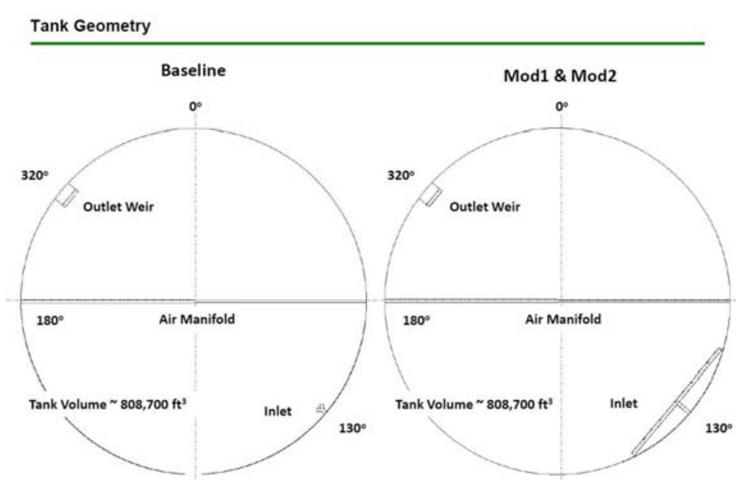
- At an offsite lab, ran SBR pilot with refinery feed and biomass
- Due to small scale of pilot, easy to operate with complete mixing
- After about a sludge age, biomass settling properties improved significantly



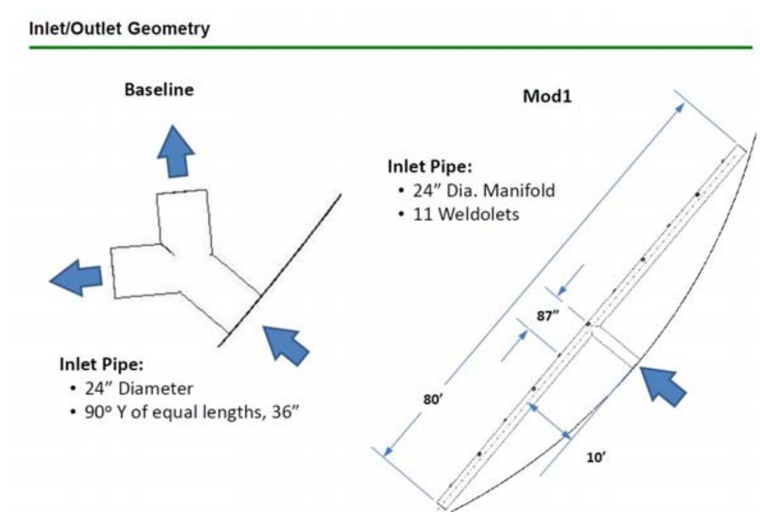
Computer Fluid-Dynamics Modeling

- As we approached the time to swap aeration basins for tank inspection, it is a good opportunity for adding a feed distributor
- Needed project justification for new feed distributor, so elected to pursue CFD modeling

Tank Geometries
current and proposed distributors

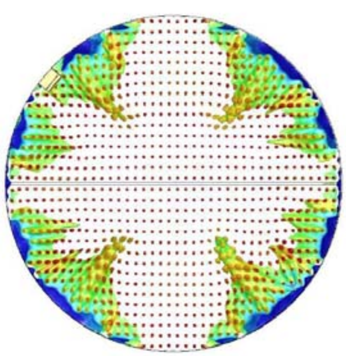


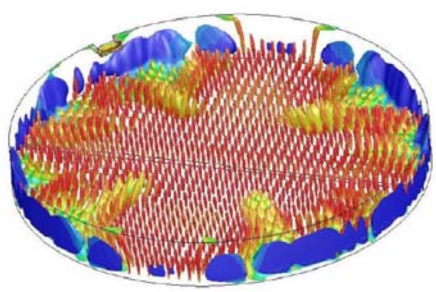
Distributor Details



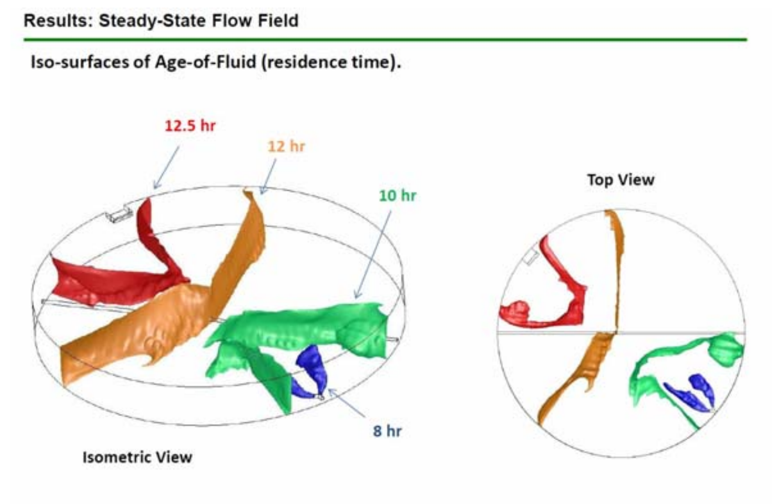
CFD Modeling Results

Iso-surface of 50 ft/min velocity magnitude colored by ‘z’ velocity component (ft/min).

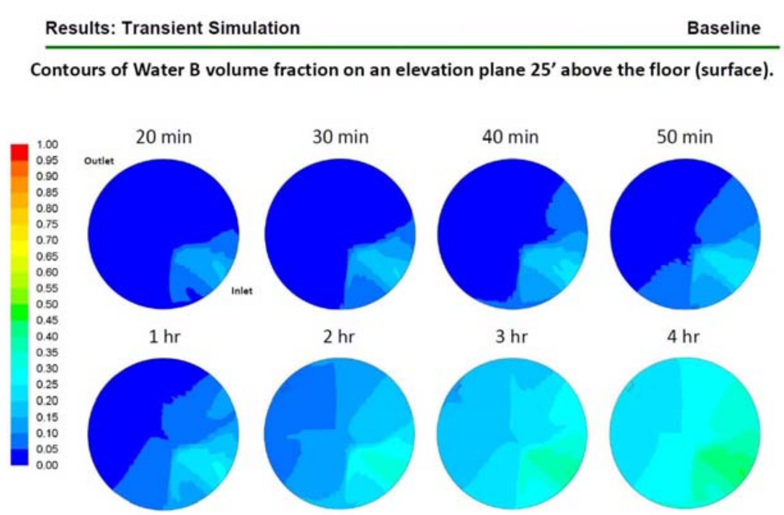




Age of Fluid – Base Case



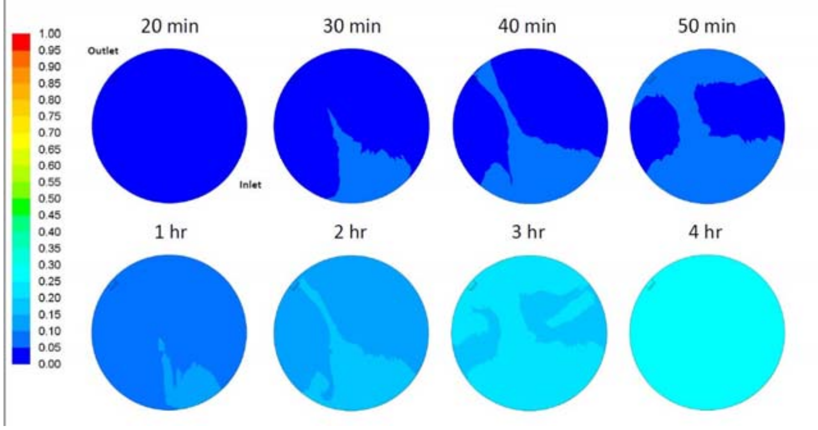
Baseline Water B Fractions



New Distributor Water B Fractions

Results: Transient Simulation **Mod2**

Contours of Water B volume fraction on an elevation plane 25' above the floor (surface).

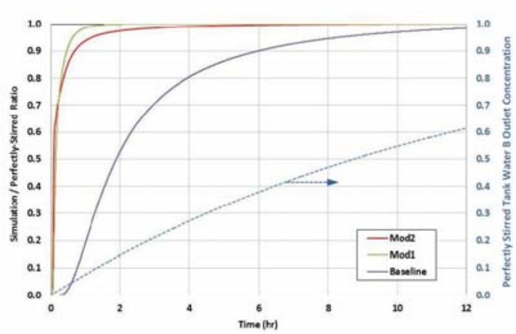


Approach to CSTR

Results: Transient Simulation

A transient simulation was run to visualize the distribution and mixing of fluid entering the bioreactor.

- The transient simulation considers two identical liquid species labeled Water A and Water B.
- The simulation is initialized with a previously obtained steady-state solution; which considered only Water A.
- Water B is specified at the inlet boundary for the transient simulation.
- Shown in the graph to the right are the ratios of the simulation prediction of Water B outlet concentration to that of a simple, perfectly stirred bioreactor.
- Also shown (blue dashed line) is the outlet concentration of Water B calculated on the basis of a perfectly stirred bioreactor (not accounting for air injection).



New Distributor

Almost ready to go, just need a new tank bottom….

Biomass Settling/Mixing Lessons Learned

- Do not assume that air rates above industry guidelines alone are adequate for good mixing
- Conduct DO surveys early and cover as much of the basin as possible
- Consider additional DO measurement locations
- Possibly avoid designs with high width/depth ratios?
- Understand the differences between exocellular slime and zoogloea.
- Utilize CFD Modeling

Our Next Speaker

John Faber

Wastewater Discipline Technology Leader

ExxonMobil

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WWTP Revamp Design

Upgrading a Wastewater Treatment Plant for a Refinery Expansion

Energy lives here

John Faber, P.E.
ExxonMobil Research & Engineering

Water Environment Federation
Webinar: Refinery Wastewater Treatment Case Studies
April 2018

Agenda:

Site project overview

WWTP impact

Option selection process

Progress from design to startup

Site Project Overview

Antwerp Refinery – Coker Project

- Refinery in operation since 1953
- Production capacity of approximately 320,000 bbls/day
- The Antwerp Refinery is currently building an new coker unit for converting heavy, high-sulfur residual oils into transportation fuels such as diesel and marine gas oil

- The project, valued at US $1 billion, follows other investments in Antwerp, including construction of a 130 megawatt cogeneration unit in 2008 and a diesel hydrotreater in 2010

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What is a Coker?

- Process Unit that receives the heaviest hydrocarbon fraction (i.e., residual fuel oil) and thermally cracks the molecules into smaller fractions which are further refined and treated to become naphtha range (e.g., gasoline) and distillate range (e.g., diesel) products
- Three types of coking processes:
  - Delayed Coking
  - FLUID COKING®
  - FLEXICOKING®

- Delayed and FLUID COKING® produce a solid-phase coke which is removed from the process and sold as a product
- Delayed Coking is a semi-batch process using multiple vessel pairs
  - On-line vessel receives hot feed and sends cracked vapor to fractionator
  - Off-line vessel is cleared for coke removal

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New Wastewater Streams

- Antwerp's Delayed Coker Project is creating new wastewater streams and impacting others
- Wastewater streams include:
  - Purge water from coker vessel quenching and coke cutting
  - Sour water from coker fractionator overhead
  - Sour water from new flare water seal
  - Additional sour water from hydrotreating and sulfur treating units
  - Additional utility/service water, sanitary wastewater, storm water
- Contaminant load from new wastewater streams predicted by sampling streams at other refineries with similar processes
  - Total Organic Carbon (TOC)
  - Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)
  - Total Kjeldahl Nitrogen (TKN)
  - Other specific contaminants of concern

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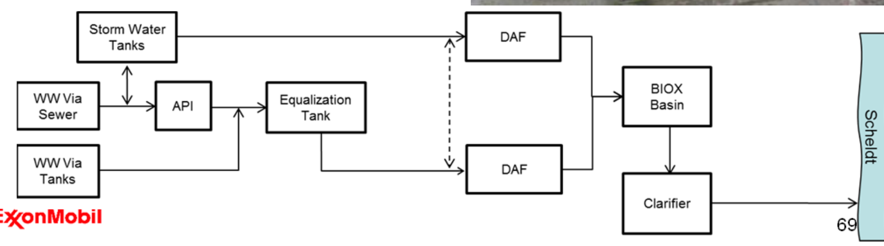
WWTP Impact

Impact to Wastewater Treatment Plant

- Site's WWTP consists of oil/water separators, equalization tanks, two parallel dissolved air flotation units, and a single train activated sludge biological oxidation (BIOX) unit.
- Hydraulically, all units have capacity to handle the project's additional flow
  - Storm water storage system also has sufficient capacity to manage new storm water runoff



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Impact to BIOX

- Hydraulic Residence Time
  - Current average HRT of ~6.5 hrs would be reduced to < 6 hrs
- Aeration Demand
  - The future Actual Oxygen Requirement (AOR) from the new load would exceed the current aeration capacity
- Food-to-Microorganism Ratio and MLSS
  - The current F/M is within the expected range for refinery wastewater treatment, but the MLSS is ~7,000 mg/L
    - This high MLSS concentration affects clarifier performance due to high solids flux, especially as the flow approaches design capacity
    - To keep the future F/M within similar range, the additional load would drive MLSS concentration higher, further impacting clarifier solids flux
- Therefore, a BIOX expansion was required to maintain effluent quality

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Option Selection Process

Initial Options Screened

- Add second train using Integrated BIOX System (reactor + clarifier)
  - Not required, since existing clarifier could handle the additional flow
- Add Moving Bed Biofilm Reactor (MBBR) ahead of BIOX
  - Addresses COD load increase and supports nitrification
  - However, the future influent TKN load was increasing, making it more difficult to meet the Total Nitrogen (TN) limit without some TN reduction
- Add second BIOX reactor in parallel to existing train
  - A configuration with denitrification provides TN reduction
  - However, nitrates from existing train were still a concern for meeting a potential lower TN limit forecasted to be received in the future
  - This option would also complicate operation of two very different BIOX trains using the same clarifier
- Add second BIOX reactor in series with existing train

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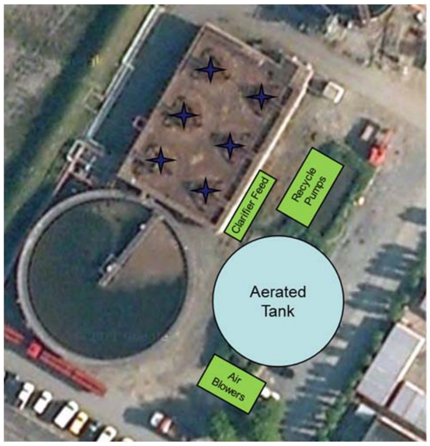
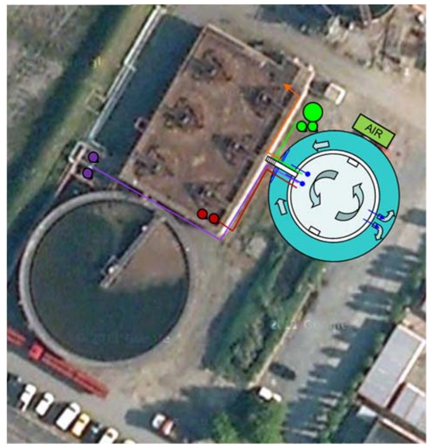
Expand Existing BIOX

- Option #1: Add new aeration tank, and convert existing basin into anoxic zone



- Option #2: Add new tank, with both anoxic and aerobic zones, ahead of basin



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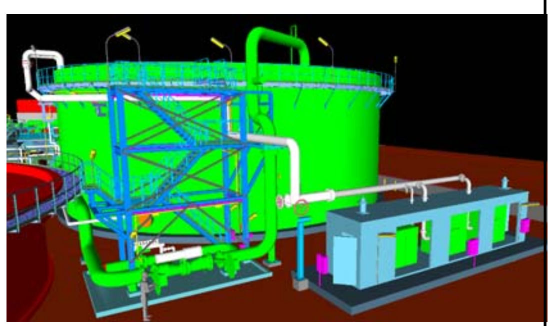
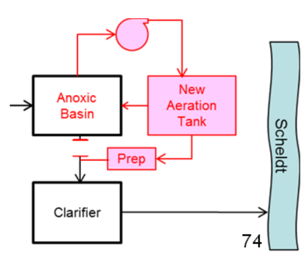
Lead Option Selection: Option #1

SCOPE INCLUDES:



- Add new aeration tank
  - Water depth in tank needs to be greater than basin due to plot restriction
  - Equip with coarse-bubble diffusers and air blowers
- Convert existing basin into an anoxic zone
  - Replace surface aerators with mechanical mixers
  - Due to floor baffles, need to place mixers in former aerator positions
- Add pumps to transfer liquor from basin to tank
- Add controlled recycle from tank to basin inlet
- Tie-in tank outlet to clarifier feed with flocculation channel



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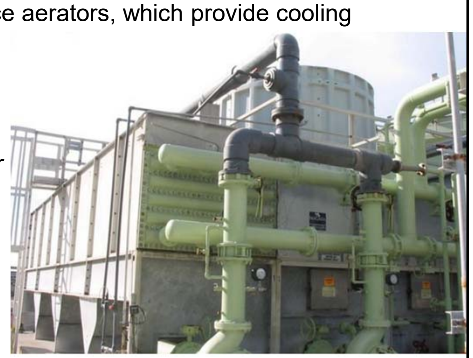
Progress From Design to Startup

New Challenge with Temperature

- Site has an effluent temperature limit: 35°C (95°F) when ambient temperature > 25°C (77°F); but otherwise limit is 30°C (86°F)
- Site has been able to maintain effluent temperature below these limits, but two project changes would create new difficulty:
  - Project will be increasing heat load to influent wastewater
  - WWTP upgrade will take away surface aerators, which provide cooling (not ideal during winter, but essential otherwise)
- Solution: add wet-surface air cooler
  - WSAC acts as a tube heat exchanger and cooling tower in one
  - Process wastewater passes through cooling tubes, so that volatile organics are not stripped out



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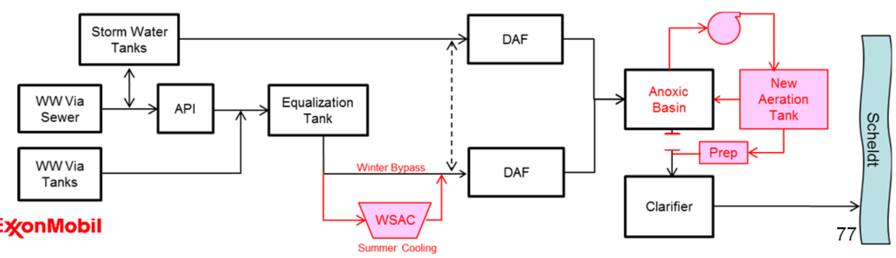
Facility Startup Plans

Progress to date:

- ☑ Commission new blowers
- ☑ Aeration grid levelness test
- ☑ Commission new aeration tank, circulate with aeration basin
- ☑ Commission flocculation channel, route tank outlet to clarifier
- ☑ Replace basin aerators with mixers one at a time
- ❑ Coker startup
- ❑ Commission WSAC in summer



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New Plant Footprint

Before | *After*

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Questions?

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Questions?

Water Environment Federation
the water quality people