Refinery Wastewater Treatment Using Two-Stage Attached Growth Bioreactors for Organics Removal and Nitrification

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ABSTRACT

Treatment of petroleum refinery wastewater using the activated sludge process is widespread across the industry. However, attached growth biological treatment is also getting more attention and has been utilized in a few refinery wastewater treatment plants (WWTPs). The Valero Energy Corporation (Valero) Jean-Gaulin Refinery is upgrading its WWTP to meet discharge requirements for effluent toxicity, chemical oxygen demand (COD), total suspended solids (TSS) and ammonia nitrogen (NH_3-N). The existing WWTP includes an aerated lagoon system after pretreatment for oil and solids removal. Based on a desktop study completed in 2015, attached growth biological treatment was selected to replace the existing aerated lagoon system for improved removal of NH_3-N, which had been identified as a major cause of past effluent toxicity incidents. To confirm expected treatment performance, a pilot study was performed with two different attached growth technologies: moving bed biofilm reactor (MBBR) and fixed bed biofilm reactor (FBBR). Near steady-state pilot data were used to calibrate the BioWin® process simulator for subsequent design of the full-scale plant. Modeling was also used to evaluate various equalization (EQ) scenarios to dampen peak influent COD and total Kjeldahl nitrogen (TKN) wasteloads. Pilot study results and findings of the EQ analysis are presented in this paper. Implications of these evaluations for design of the full-scale WWTP are discussed.

KEYWORDS: refinery wastewater, equalization, nitrification, process modeling, attached growth, MBBR, FBBR, effluent toxicity

INTRODUCTION

The Valero Jean-Gaulin Refinery is located on the south shore of the St. Lawrence River in Levis, Quebec, Canada. The Refinery was brought on line in 1971 and has undergone several major upgrades in the intervening years, with a current rated crude oil throughput capacity of 265,000 barrels per day. Wastewater generated at the Refinery is currently treated in a WWTP consisting of primary oil/water separation in circular, above ground tanks, followed by dissolved gas flotation (DGF) and biological treatment in a single-train aerated lagoon system (Aeration Basin followed by a Settling Basin). An aerial view of the WWTP is shown in Figure 1. Wastewater collection is provided by two separate sewer systems: oily water and accidently contaminated water (including rain water). The accidently contaminated sewer bypasses the primary oil/water separation tanks and enters the WWTP directly upstream of the DGF.

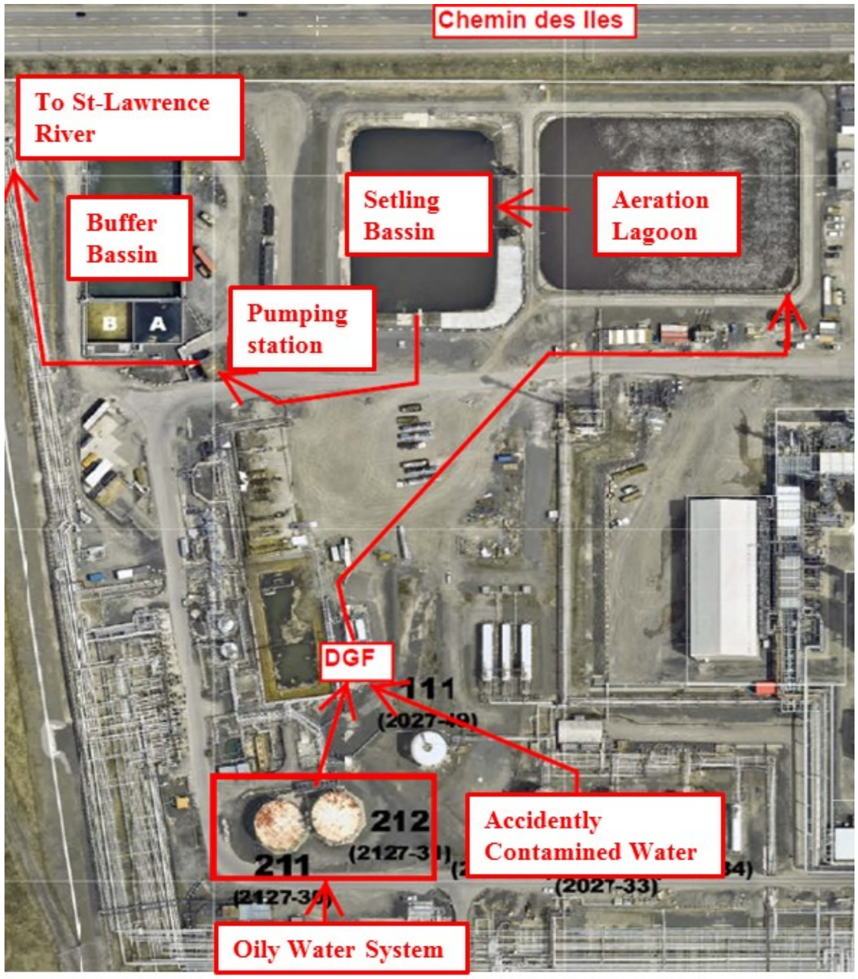


Figure 1: Existing WWTP Configuration at Valero Jean-Gaulin Refinery

Valero's existing single-train biological treatment facilities cannot be taken off line for maintenance. Furthermore, the Refinery has faced wastewater treatment challenges mainly attributed to processing new types of crude oil with higher and more variable contaminant loads. The main contributors to higher wasteloads are the crude unit desalters (a continuous source) and drainage water from crude oil storage tanks (processed by the WWTP on a batch basis). The Refinery has also experienced occasional effluent toxicity incidents in recent years. After analysis of various possible causes of toxicity, NH_3-N was identified as the most probable. Treatment of NH_3-N to very low concentrations is required to ensure that the final effluent consistently meets all provincial and federal regulations.

From its initial evaluation, Valero selected MBBR and FBBR as the most cost-effective options for the WWTP upgrade. Valero decided to pilot these technologies to better understand how effluent quality would be affected by reactor hydraulic retention time (HRT), influent COD and TKN (loading and variability), and biofilm loading rates. Both MBBR and FBBR use a high surface area media contained within a reactor tank for biofilm attachment. Consequently, the biofilm is retained within the reactor. Biomass sheared from the media due to excess growth exits the reactor as TSS in treated wastewater that must be separated before discharge.

A key aspect of this project involved definition of a target effluent NH_3-N value to ensure consistent compliance with the toxicity limit. It was recognized that temperature and pH would also affect the toxicity potential of the treated wastewater. The interaction between pH, temperature, total NH_3-N and effluent toxicity will be further discussed in this paper.

PILOT STUDY OBJECTIVES

The pilot study was carried out in a phased approach to address the following objectives:

Acclimation Phase

- Establish biomass growth on the media
- Demonstrate both COD and NH_3-N removal in single-stage and two-stage configurations

Average Conditions Phase

- Determine the MBBR/FBBR surface area loading rates (SALR), g TKN/m^2/day and g COD/m^2/day, required to meet effluent quality targets for NH_3-N
- Determine required HRT for MBBR/FBBR to meet target effluent quality
- Confirm that MBBR/FBBR processes will pass the Environment Canada 96-hr rainbow trout toxicity test
- Determine solids yield for MBBR/FBBR (kg TSS produced/kg COD removed)
- Determine settling characteristics of the biosolids generated by the MBBR/FBBR process

As the pilot study progressed, more was learned about daily COD and TKN wasteload variations at the Refinery. Based on this additional information, the Peak Conditions phase was separated into extended duration spike tests using ammonium chloride (NH_4Cl) as a supplemental TKN source and short duration crude oil storage tank drainage tests.

Peak Conditions Phase – Extended Duration

- Determine response of MBBR/FBBR to simulated TKN spikes in the untreated wastewater during full-scale operation
- Develop targeted approach for testing events such as tank drainages on the stability of biological treatment

Peak Conditions Phase – Short Duration

- Determine if a two-stage or three stage MBBR configuration would be more effective for meeting effluent NH_3-N targets under short duration peak loading events
- Analyze tank drainage tests to determine the HRT required for an EQ tank to achieve acceptable variability in the biological treatment system influent

PILOT PLANT DESCRIPTION

Pilot Equipment

The pilot facility was housed inside two containers: one 8 ft x 40 ft and the other 8 ft x 53 ft, with the following equipment installed:

- One feed tank equipped with a mechanical mixer to receive DGF effluent. The feed tank volume was 1,000 L. DGF effluent entered the feed tank by gravity from the Skimmer Tank at WWTP
- Two 10 mm screens (one in service, one standby), at the inlet of the feed tank
- One feed pump with a recirculation line to the feed tank and a pressure controller
- Initially, flow rotameters were installed for each MBBR system and FBBR system, with manual flow control valves for the influent to each reactor. These were upgraded with magnetic flow meters on the influent lines to each reactor, with flow totalization and a manual flow control valve
- One discrete settling column, for solids separation testing. The height of the column allowed for maximum gravity fill from the reactors, with 8 sampling ports equally spaced from the bottom. The column was equipped with air for initial mixing

Figure 2 is a simplified process flow diagram (PFD) of the pilot plant.

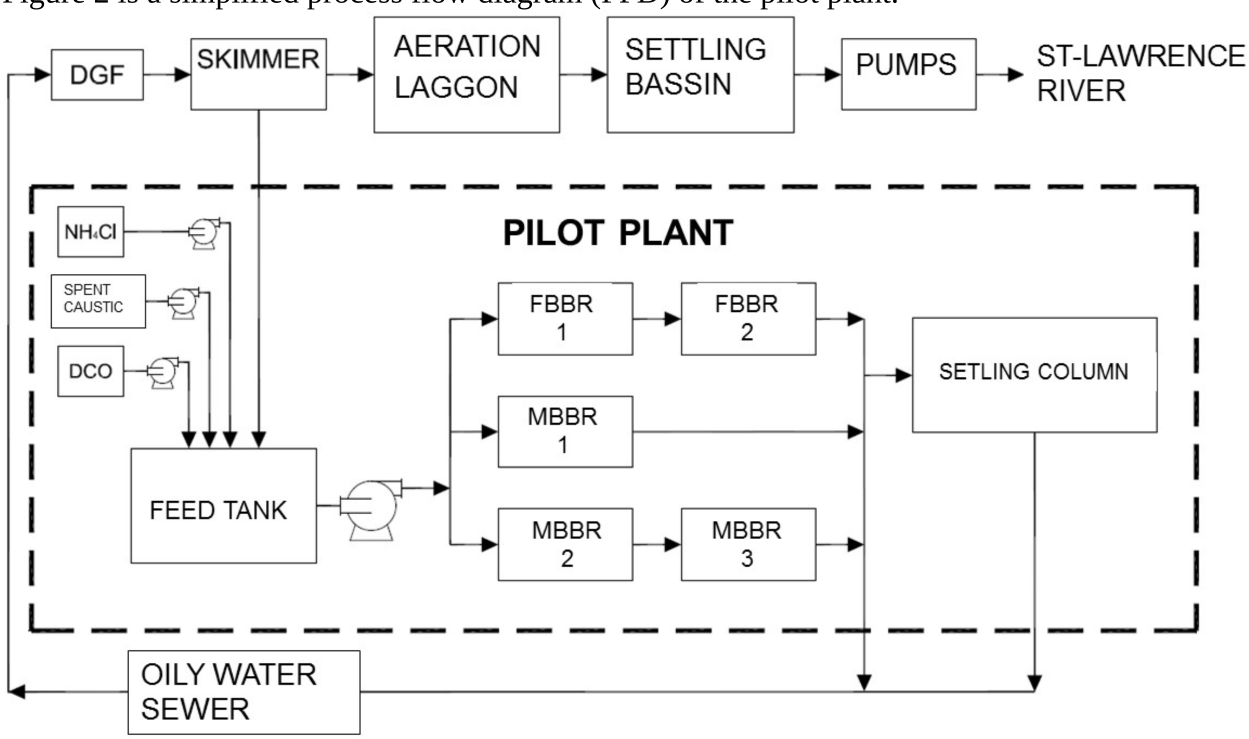


Figure 2: Pilot Plant Simplified PFD

Three skid-mounted MBBR reactor systems were provided by World Water Works, Inc., Oklahoma City, Oklahoma. These units were delivered complete with media carrier elements, sieve assemblies, aeration grid, blower with bypass to control air to the reactor, and electrical panel. The MBBR reactor volumes and media characteristics are presented in Table 1.

Table 1: MBBR Reactor and Media Characteristics

Parameter	Unit	MBBR1 – Single Stage MBBR	MBBR2 – 1st Stage MBBR	MBBR 3 – 2nd Stage MBBR
Water Volume	**m^3**	2.22	2.22	2.22
Media Fill Fraction	**%**	55%	45%	45%
Media Volume	**m^3**	1.22	1.0	1.0
Media Specific Surface Area (Average)	**m^2/m^3**	533	650	650
Media Total Surface Area	**m^2**	650	650	650

Photographs of the MBBR pilot reactors and media are below.

Figure 3: MBBR Reactors

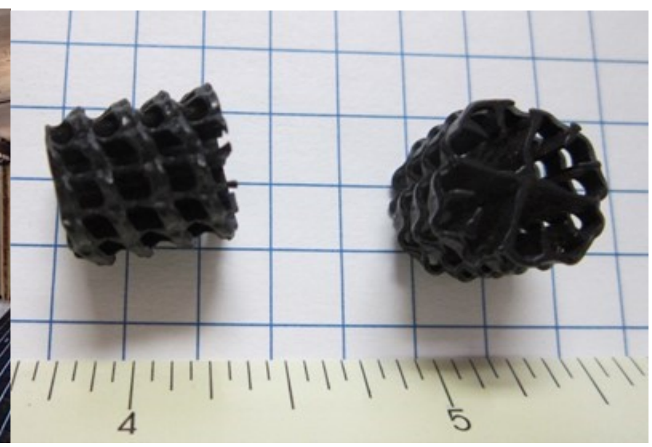


Figure 4: MBBR Media

Two-skid mounted FBBR systems were provided by Brentwood Industries, Inc., Reading, Pennsylvania. Each skid contained the FBBR media, support system, aeration diffusers, air piping, aeration blower (one common to both skids) with bypass to control air to the reactors and start switch panel. The FBBR reactor volume and media characteristics are presented in Table 2.

Table 2: FBBR Reactor and Media Characteristics

Parameter	Unit	FBBR1 – 1st Stage FBBR	FBBR 2 – 2nd Stage FBBR
Water Volume	**m^3**	1.05	1.05
Media Fill Fraction	**%**	40%	40%
Media Volume	**m^3**	0.42	0.42
Media Specific Surface Area	**m^2/m^3**	180	180
Media Total Surface Area	**m^2**	76	76

A photograph of the FBBR pilot reactors is below.

Figure 5: FBBR Reactors

Chemical Feed Systems

Three supplemental chemical feed systems were used in the pilot plant, as shown on the PFD (Figure 2): spent caustic (at a flow proportional to the Refinery's spent caustic production rate), 20% NH_4Cl (supplemental TKN source to reach the influent design point and provide wasteload spikes) and crude tank water draw (supplemental COD spikes).

In the recent years, the Refinery has cut back on spent caustic treatment through the existing WWTP due to the known impact of high pH on effluent toxicity related to NH_3-N. Off-site spent caustic disposal has been a substantial operating expense. The WWTP upgrade will include capability to treat all spent caustic on site and eliminate off-site disposal. Therefore, the pilot study included consistent addition of spent caustic during the Average and Peak Conditions phases. A residual alkalinity concentration of approximately 100 mg/L (as calcium carbonate, $CaCO_3$) was targeted in the MBBR and FBBR reactor effluents. The spent caustic was stored in a 1,000 L tote and metered to the feed tank at a rate of 1.7-2.3 L/hr.

During the pilot study, COD in DGF effluent was lower than the project design basis. Design COD SALR values were achieved by adding water drawn from crude oil storage tanks to provide supplemental COD and more closely represent expected influent characteristics of the full-scale unit. Tank draw water was collected and stored in 1,000 L totes. A metering pump fed the tank draws to the pilot unit feed tank, with the flow rate varying with the COD concentration in the tote. Depending on crude oil type, COD concentrations in storage tank water draws varied from 7,500 mg/L to 18,000 mg/L. The influent (DGF effluent) COD concentration averaged approximately 150 mg/L, and the target COD to the pilot units was approximately 275 mg/L.

Based on the characteristics and relatively constant full-scale production rate of spent caustic at the Refinery, the biological system required 23 mg/L NH_3-N in the influent for nitrification to destroy the incoming alkalinity. The DGF effluent NH_3-N was approximately 7.0 mg/L during the pilot study. Hence, the NH_3-N supplement was approximately 16 mg/L. This NH_3-N value

(23 mg/L) is referred to as the baseline concentration. Supplemental TKN and was added to the pilot influent in the form of NH_4Cl solution (54,000 mg/L NH_3-N). The NH_4Cl solution was pumped from a 1,000 L tote at a rate of 0.5-0.62 L/hr.

Monitoring and Sampling

Field personnel followed a prescribed sampling and analytical program to monitor the performance of the pilot plant. Grab samples of the blended feed tank (MBBR/FBBR influent) and reactor effluent were collected seven days per week for analysis of critical parameters. Daily analytical measurements included total COD, COD after filtration at 0.45 micron (µm), NH_3-N, pH, temperature, dissolved oxygen (DO), TSS, and TKN (feed only). Intermittent analytical parameters included nitrate-nitrogen (NO_3-N), nitrite-nitrogen (NO_2-N), volatile suspended solids (VSS), total and filtered 5-day biochemical oxygen demand (BOD_5), alkalinity, oil and grease, and total and filtered phosphorus.

Daily samples from the existing DGF effluent composite sampler were analyzed to establish influent characteristics and requirements for addition of spent caustic, tank draws, and supplemental TKN.

A photograph of the MBBR media with adhered biomass is below:

Figure 6: MBBR Media with Attached Biomass

PILOT STUDY RESULTS

The pilot unit was operated in three phases, as noted previously. The Acclimation Phase grew sufficient biomass for subsequent testing and supported preliminary decisions on MBBR reactor configurations and HRT. Results from the Average Conditions Phase and Peak Conditions Phase are the focus of this paper.

During the Average Conditions Phase, FBBR and MBBR technologies were tested at SALR values based on vendor recommendations to compare COD and NH_3-N removal. The three systems piloted included:

- Single-Stage MBBR
- Two-Stage MBBR
- Two-Stage FBBR

As discussed below, a two-stage biological system was selected for the Peak Conditions phase based on overall reliability and on the well-established engineering practice of concentrating COD removal in Stage 1 and NH_3-N removal in Stage 2.

The Peak Conditions Phase first focused on how each system would respond to an extended duration TKN spike. Two different peak scenarios were tested: 48 hr and 24 hr. Additionally, the two-stage MBBR and FBBR systems were tested at increased COD SALR values and similar HRTs.

During the extended duration spikes, it was observed that actual peak conditions at the Refinery occurred over shorter durations than 24-48 hr and were often due to crude oil storage tank drainage events. These incidents typically lasted approximately 4 hr. Due to the frequency of tank water drainages and the potential for high influent COD and TKN concentrations, the pilot unit was reconfigured to test the concept of a third MBBR stage for handling short duration peak events.

Detailed analysis of tank drainage events during the pilot study improved our understanding of potential influent variability and the ability of the biological system to react under dynamic loading conditions. This understanding was key to the eventual development of a full-scale design that would meet the effluent NH_3-N target on a continuous basis.

Average Conditions Phase – Results

The Average Conditions Phase ran from November 11, 2016 to February 7, 2017. Operational and performance data was averaged from December 15, 2016 to February 7, 2017, coinciding with installation of magnetic flowmeters on the reactor feed lines.

The reactor influent COD concentration was increased to test a staged approach that would optimize growth conditions for the two major types of microorganisms responsible for biological wastewater treatment: heterotrophs to remove organics (measured as COD or BOD_5) and autotrophs to nitrify (oxidize NH_3-N to NO_3-N). Heterotrophs grow significantly faster than autotrophs and will outcompete the nitrifiers for media attachment sites as long as biodegradable COD is present in the wastewater. A staged approach creates an environment that allows both heterotrophs and autotrophs to grow, targeting heterotrophic bacterial growth in the first stage and autotrophic bacterial growth in the second and any subsequent stages. This translates to targeted removal of COD/BOD_5 followed by removal of NH_3-N.

The NH_3-N target or baseline influent concentration was 23 mg/L for this phase. The organic nitrogen content of the wastewater can fluctuate based on crude oil type and averaged approximately 1-2 mg/L. Average operating conditions for the MBBR and FBBR are presented in Table 3.

Table 3: Average MBBR and FBBR Operational Parameters
(15 December 2016 – 7 February 2017)

Parameter	Unit	Feed Tank	Single Stage MBBR	1st Stage MBBR[1]	Overall 2 Stage MBBR	Overall 2 Stage FBBR
Flow	**m^3/hr**	1.8	0.8	0.8	0.8	0.2
HRT	**hr**	--	2.8	2.9	5.8	9.0
Temperature	**°C**	25.5	26.1	26.1	25.0	24.2
pH	**s.u.**	9.1	7.6	7.6	7.7	8.0
DO	**mg/L**	--	5.8	5.9	6.8	8.4
COD SALR[2]	**g/m^2/day**	--	7.26	6.95	3.47	9.10
TKN SALR[3]	**g/m^2/day**	--	0.87	0.83	0.41	1.09

Notes: 1. 1st stage MBBR data are added for comparison with the single-stage MBBR
2. COD SALR targets were 4.31 g/m^2/day for two-stage MBBR and 13.05 g/m^2/day for two-stage FBBR
3. TKN SALR targets were 0.36 g/m^2/day for two-stage MBBR and 1.09 g/m^2/day for two-stage FBBR

The COD SALR targets were difficult to achieve consistently due to DGF effluent variability and the changing COD concentration of crude oil storage tank water draws. The TKN SALR targets were easier to achieve.

Table 4 presents average treatment performance of the single-stage MBBR and each two-stage system for December 15, 2016 to February 7, 2017:

Table 4: Average Pilot Unit Performance (15 December 2016 – 7 February 2017)

Parameter	Unit	Feed Tank	Single Stage MBBR	1st Stage MBBR	Overall 2 Stage MBBR	Overall 2 Stage FBBR
NH_3-N Removal	**%**	--	87%	65%	95%	95%
TKN	**mg/L**	29.4	4.2	10.1	2.4	2.7
NH_3-N	**mg/L**	23.0	2.7	7.7	1.1	1.2
NO_3-N	**mg/L**	0.4	21.0	14.8	21.4	21.4
NO_2-N	**mg/L**	0.1	0.1	0.2	0.1	0.1
COD Removal	**%**	--	70%	69%	68%	70%
COD	**mg/L**	247	72	71	72	64
BOD_5	**mg/L**	64	7	9	6	3
TSS Yield	**kg TSS/kg COD Removed**	--	0.56	0.59	0.44	0.31
TSS	**mg/L**	42	100	106	76	59
VSS	**mg/L**	19	65	62	60	50

Notes: Feed tank values are unfiltered and reactor effluent values are filtered (0.45 µm).

The single-stage MBBR did not perform as well as the two-stage MBBR in terms of NH_3-N removal. The effluent NH_3-N target was 1.5 mg/L during this phase, while the single-stage MBBR effluent averaged 2.7 mg/L NH_3-N. For this reason, the single-stage MBBR was decommissioned.

The two-stage fixed film systems performed very well and nitrification was consistent and excellent, as summarized below.

- TKN SALRs for both MBBR and FBBR were close to target values
- NH_3-N removal was 95% for both MBBR and FBBR, which corresponds to an effluent NH_3-N concentration of approximately 1 mg/L
- A stable effluent NO_3-N value of around 20 mg/L was achieved for both technologies
- Effluent NO_2-N concentrations were negligible for both technologies
- An excellent nitrogen balance was demonstrated for all pilot units. On average, the sum of effluent nitrogen species (TKN, NO_3-N, NO_2-N and biomass N) accounted for approximately 94-102% of the influent nitrogen, assuming a typical effluent biomass containing 0.08 mg N per mg VSS

COD/BOD_5 removal was very similar for both technologies during this phase:

- The MBBR effluent filtered COD averaged 72 mg/L and the filtered BOD_5 averaged 5.7 mg/L
- The FBBR effluent filtered COD averaged 64 mg/L and the filtered BOD_5 averaged 3 mg/L
- The MBBR exhibited higher solids yields (higher effluent TSS and VSS) than the FBBR

Very low soluble effluent BOD_5 values indicate nearly complete oxidation of influent biodegradable organics in each pilot reactor. The residual filtered effluent COD values suggest that slowly biodegradable and non-degradable organics represent 25-30% of the influent COD. The relatively better performance of the FBBR could be a result of its higher HRT compared to the MBBR, allowing more time to degrade the residual COD.

The efficacy of a staged reactor design was confirmed in this phase. Nitrification was incomplete in the first stage reactors. Soluble COD removal in the second stage MBBRs was negligible. These results confirmed the process design philosophy of targeted COD removal in the first stage and nitrification in the second stage. With little degradable COD available after the first stage, the second stage provided an ideal environment for growth of nitrifying biomass.

After conducting simulation modeling and consulting with vendors, it was determined that the FBBR would require much larger and thus more costly full-scale reactors than the MBBR. From that, it was concluded that the FBBR would need to operate at higher SALRs to compete from a capital cost standpoint. To compare these technologies equally during the next phase, nearly equal HRTs were established, resulting in higher TKN and COD SALR target values in the FBBRs. The SALR values were increased by 100% for the FBBR and 50% for the MBBR, while the HRTs were kept similar.

The influent temperature varied (17-30°C) during the Average Conditions Phase. For BioWin® modeling of a two-stage MBBR, only those days with a consistent temperature of approximately 26°C were averaged for model calibration. These results are presented in Table 5 below:

Table 5: Consistent Temperature Two-Stage MBBR Results (2 January - 7 February 2017)

Parameter	Unit	Feed Tank	1st Stage MBBR	Overall 2 Stage MBBR
TKN	**mg/L**	28.8	8.6	2.5
NH_3-N	**mg/L**	21.7	7.5	1.4
NO_3-N	**mg/L**	--	14.3	20.4
COD	**mg/L**	227	76	70
TSS Yield	**kg TSS/kg COD Removed**	--	--	0.48
TSS	**mg/L**	--	96	75
VSS	**mg/L**	--	64	63

Note: Feed tank values are totals and effluents are filtered (0.45 µm).

Peak Conditions Phase – Results

The main objective of this phase was to test the response of the MBBR and FBBR to peak loading conditions. The duration and maximum concentration of peak COD and TKN loadings were estimated based on 99th percentile values taken from historical data for the existing WWTP. However, as the pilot study progressed, it was observed that the Refinery's oily wastewater could vary significantly over short time periods depending on the type of crude oil processed and on periodic drainages of crude storage tank water. Therefore, this phase was further separated into peak loading conditions of extended duration and short duration.

The extended duration tests used external NH_4Cl spikes to increase the TKN SALR to the 99th percentile value, followed by observation of the recovery time of the two technologies in regard to effluent NH_3-N. The extended duration tests included two 48-hr spike tests and one 24-hr test. After conclusion of the 24-hr test, daily and highly variable tank drainages were observed to be occurring at the Refinery. These tank drainages were having a noticeable effect on the performance of the pilot reactors and warranted further investigation. This led to the short duration tests, which focused on testing 4-hr tank drainages. All short-duration tank drainages were evaluated with increased sampling frequency.

As noted above, the flow rate to the MBBR stayed the same during this phase, but flow to the FBBR increased from 0.2 m^3/hr to 0.4 m^3/hr to test the two technologies at similar HRTs. Supplemental COD was increased to test higher COD SALR values, up to the 75th percentile value of the historical data set (target influent COD concentration increased from 275 mg/L to 314 mg/L). The NH_3-N concentration was increased from 23 mg/L to a target of 35 mg/L, corresponding to the 99th percentile value in the historical data set (maximum design condition). When the pilot unit was not experiencing an NH_4Cl spike event, the TKN supplement was reduced to keep NH_3-N closer to the baseline concentration.

Extended Duration Peak Loading Conditions

The duration for extended peak conditions was initially estimated to be approximately 24-48 hr (Table 6). The pilot units were also monitored on the day following each spiking event to determine reactor recovery time.

Table 6: Operating Parameters for Peak Conditions and Extended Duration NH_4Cl Spike Tests (10 February 2017 – 1 March 2017)

Time Period	Parameter	Unit	Feed Tank		Overall 2 Stage MBBR		Overall 2 Stage FBBR	
			Avg	99th	Avg	99th	Avg	99th
	Flow	**m^3/hr**	1.5	--	1.1	--	0.4	--
	HRT	**hr**	--	--	4.1	--	5.5	--
	Temperature	**°C**	27.1	--	26.8	--	26.3	--
	pH	**S.U.**	9.0	--	7.6	--	7.8	--
	DO	**mg/L**	--	--	5.8	--	7.2	--
Feb 14 (48 hr)								
	COD SALR	**g/m^2/day**	--	--	6.87	12.00	20.91	36.03
	TKN SALR	**g/m^2/day**	--	--	0.76	0.93	2.30	2.78
Feb 21 (48 hr)								
	COD SALR	**g/m^2/day**	--	--	6.24	6.62	19.77	21.43
	TKN SALR	**g/m^2/day**	--	--	0.85	1.00	2.69	3.18
Feb 28 (24 hr)								
	COD SALR	**g/m^2/day**	--	--	4.63	4.75	15.72	17.03
	TKN SALR	**g/m^2/day**	--	--	0.65	0.75	2.34	2.51

Note: Flow, temperature, pH and DO remained consistent and are averaged from February 10, 2017 – March 1, 2017. SALR values were not consistent over these dates and are only averaged during the NH_4Cl spike tests: Feb 14-16, Feb 21-23, and Feb 28-Mar 1, respectively.

The SALRs achieved during the 48-hr tests were closer to the target values. It was difficult to achieve SALR targets during the third NH_4Cl spike test due to DGF effluent variability. Additionally, immediately following this test, it was realized that tank drainage events were occurring overnight and affecting the pilot reactors. Table 7 summarizes the reactor performance during extended peak loading conditions.

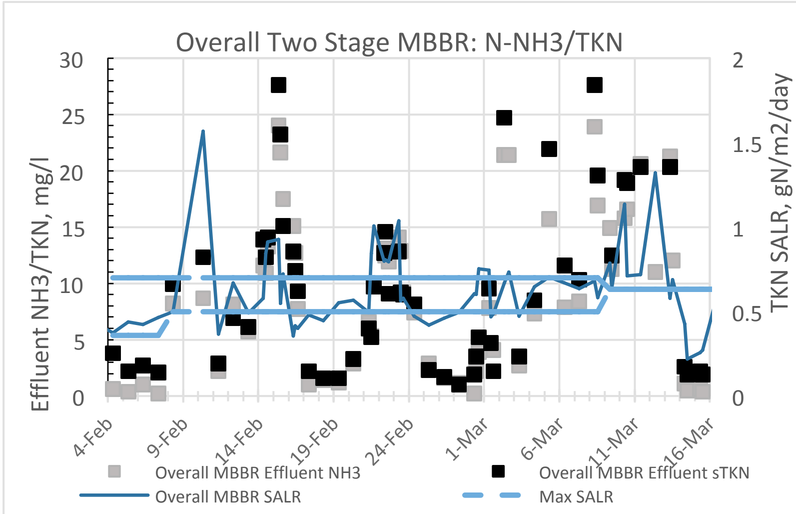
Table 7: Reactor Performance for Extended Duration NH_4Cl Spike Tests

Spike Test	**Parameter**	**Unit**	**Feed Tank**		**Overall 2 Stage MBBR**		**Overall 2 Stage FBBR**	
			Avg	99th	Avg	99th	Avg	99th
February 14 (48 hr)								
	TKN	**mg/L**	37.2	45.7	17.7	27.4	20.1	28.4
	NH_3-N	**mg/L**	30.4	34.2	16.5	23.9	19.1	24.0
	NO_3-N	**mg/L**	--	--	12.8	14.4	8.0	12.6
	NO_2-N	**mg/L**	--	--	0.1	0.1	0.4	0.4
	COD	**mg/L**	339	592	201	398	217	419
	TSS	**mg/L**	--	--	120	134	94	101
February 21 (48 hr)								
	TKN	**mg/L**	40.7	48.0	10.3	14.5	19.0	22.9
	NH_3-N	**mg/L**	33.7	36.0	10.5	13.1	19.9	22.7
	NO_3-N	**mg/L**	--	--	18.6	18.8	9.1	9.5
	NO_2-N	**mg/L**	--	--	0.1	0.1	0.3	0.3
	COD	**mg/L**	299	323	83	91	99	111
	TSS	**mg/L**	--	--	75	75	60	60
February 28 (24 hour)								
	TKN	**mg/L**	33.0	39.9	3.5	5.2	11.4	13.9
	NH_3-N	**mg/L**	25.2	31.5	2.1	3.9	10.0	12.2
	NO_3-N	**mg/L**	--	--	20.1	21.1	10.9	11.6
	NO_2-N	**mg/L**	--	--	0.1	0.1	0.2	0.2
	COD	**mg/L**	234	247	66	72	84	104
	TSS	**mg/L**	--	--	88	88	57	57

Note: Feed tank samples were analyzed for total COD and TKN. Reactor effluent samples were filtered (0.45 µm) .

The extended duration influent spikes closely matched the NH_3-N target concentration of 35 mg/L. During these tests, effluent NH_3-N concentrations for both technologies were similar for the first test, but the MBBR outperformed the FBBR on the next 48-hr test and the subsequent 24-hr test. These results suggest that FBBR could not perform as well as the MBBR at a similar HRT.

The extended duration tests were important to determine how the reactors would perform during peak loading events. These tests showed that it could take longer than one day for the reactors to recover after long durations at peak loading, resulting in high residual NH_3-N in the effluent. Figure 7 shows that effluent NH_3-N levels did not return to baseline after the spiking test, especially for the FBBR after the second and third tests. Recovery of the MBBR was faster than the FBBR. Though these tests represent extreme cases of peak loading not expected to occur at full scale, they did provide insight into MBBR and FBBR response to influent variability.



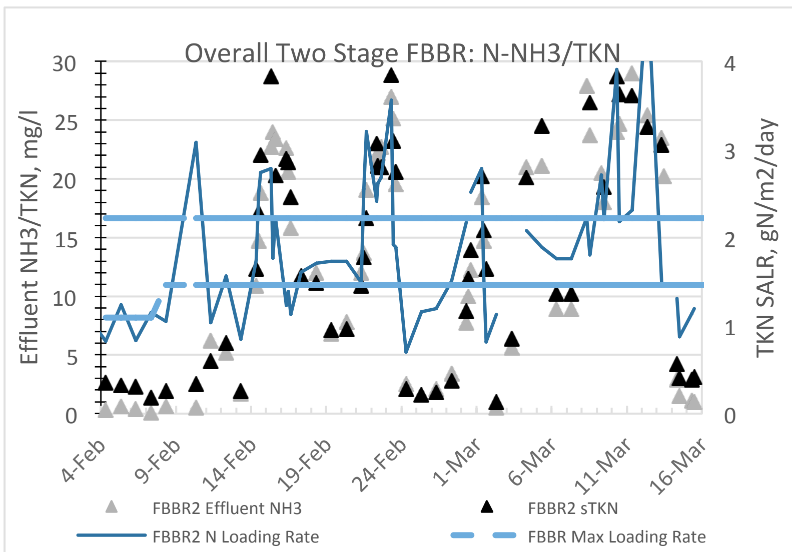


Figure 7: MBBR and FBBR Performance During Extended Duration NH_4Cl Spikes (February 14-28) and Unplanned Refinery Events (March 1-16)

Technology Decision

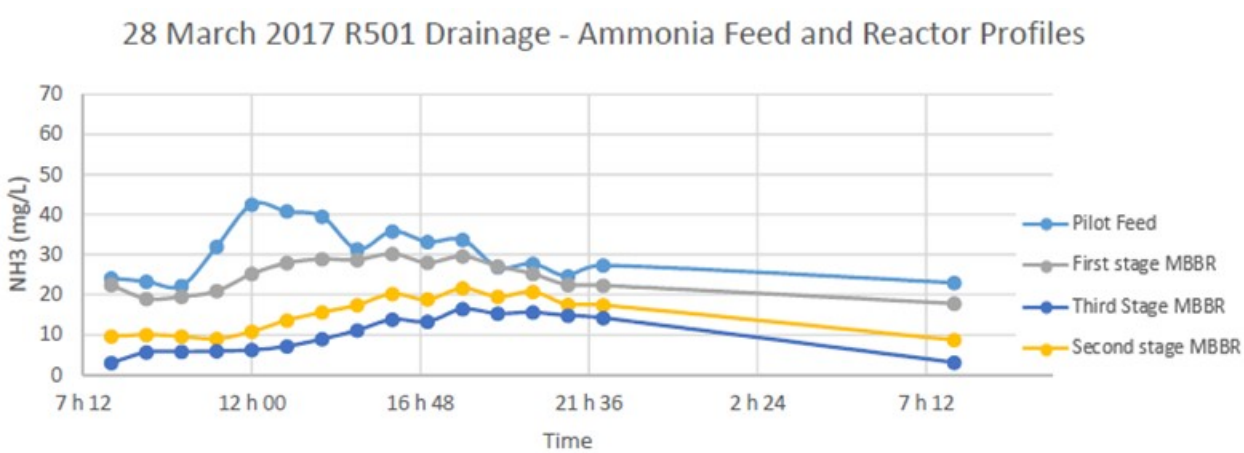
The FBBR exhibited longer recovery times during two of the three extended duration NH_4Cl spikes and then took much longer to recover after crude oil storage tank drainage events. Reactor effluent NO_3-N levels were adversely affected after the tank drainages and did not recover to the same extent as the MBBR.

Without as much media surface area, the FBBR biofilm would have to be much thicker to have the same total biomass as MBBR tanks of equal volume. This may not have been achieved in the FBBR given the nature of the technology and diffusion kinetics for DO, substrates, and nutrients, which may not be favorable for thicker films. On the other hand, FBBR tanks would have to be much larger than MBBR tanks to provide the same media surface area, SALR, and biofilm thickness. Overall, the FBBR could not maintain stable nitrification at a lower HRT or when challenged by highly variable influent loadings. Therefore, FBBR technology was not considered for further pilot testing.

Short Duration Peak Conditions

Once a decision was made to focus on MBBR technology exclusively, the pilot study continued to test short duration peak loading conditions more closely resembling those seen at the Refinery. Crude oil storage tank drainage represents a high concentration TKN source that in theory could be fed to the WWTP on specific days and monitored. However, even if the occurrence of these short duration spikes was known, their magnitude, duration and impacts on biological treatment were not well understood because of the limited number of analyses performed during normal operation of the existing WWTP. Additionally, the Refinery has very little control on when and for how long these operations happen given the rapid pace at which crude oil storage tanks are filled and then drained to allow oil to be processed without interruption. Several short duration peak condition tests were performed to evaluate the impact of tank drainage events on MBBR performance.

There is a substantial difference between normal and peak TKN concentrations in the WWTP influent. Given this, we anticipated the need for supplemental TKN to grow sufficient nitrifying biomass to manage peak loadings. The original intent was to continuously add TKN to the biological system influent and then cut back on the supplement during spikes. Short duration peak tests were performed with and without the supplemental TKN cut back to evaluate performance of the system during unplanned and planned spiking events. The unplanned event was characterized by constant addition of supplement throughout the spike while supplement injection was stopped during the planned event. The figures below show two of these tests.



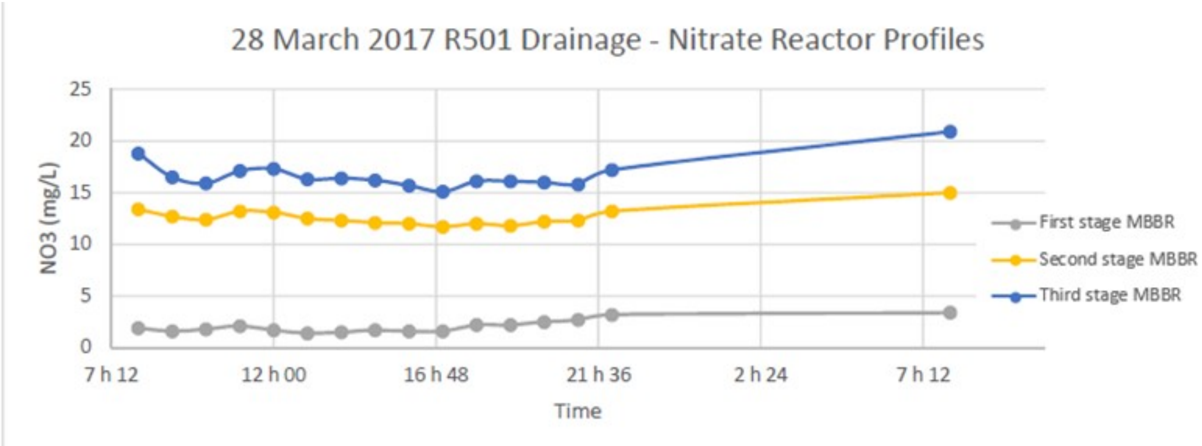
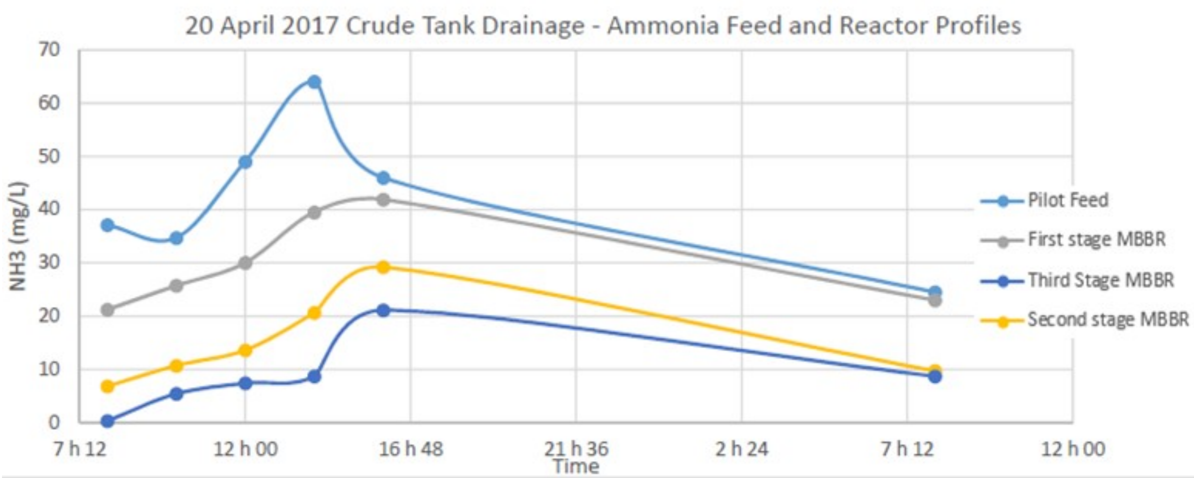


Figure 8: "Unplanned" Spike Test - 28 March 2017
NH_3-N and NO_3-N Profiles from R501 Tank Drainage Test

This first test demonstrated that tank drainages could increase influent NH_3-N above the original design maximum of 35 mg/L. It also demonstrated that NH_3-N in the reactor effluents would increase due to the tank drainage and stay at an increased level for up to 10 hours after the spiking event ended.



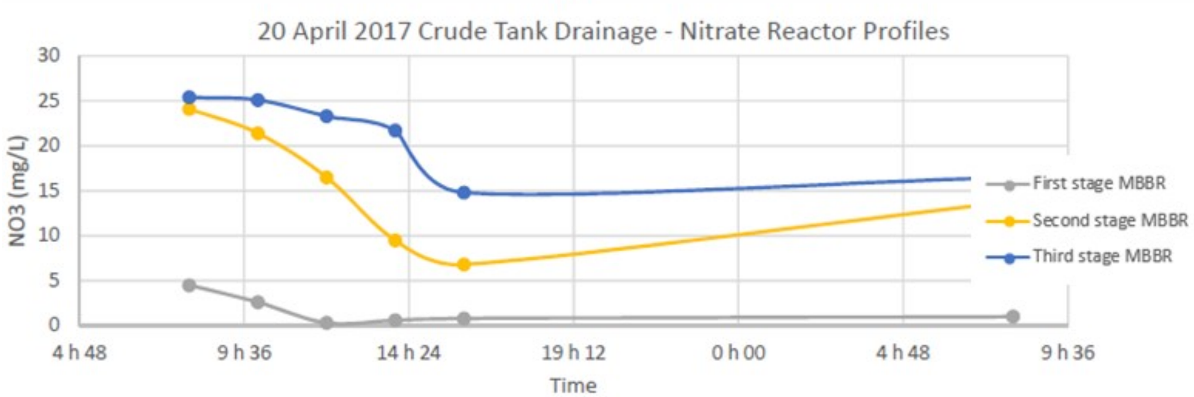


Figure 9: "Planned" Spike Test - 20 April 2017
NH_3-N and NO_3-N Profiles from R501 Tank Drainage Test

Flow coming from the rain water sewer system was lower during the test shown on Figure 9, which reduced dilution of the spike. The NH_3-N concentration of the crude tank water was also higher than the previous test. This resulted in a high NH_3-N concentration in the pilot unit feed tank, 64 mg/L, despite a reduction of the supplemental NH_4Cl to 17 mg/L. Furthermore, all the reactors also showed some degree of nitrification inhibition, evidenced by less than expected production of NO_3-N. This test demonstrated that high concentration and undiluted crude oil storage tank drainage could have a significant impact on the biological treatment system.

The lack of predictability and the speed at which the tank drainage events happen proved that the concept of supplementing influent TKN would be hard to implement and control effectively in a full-scale system. These test results also indicated that the treated effluent NH_3-N concentration could be higher than the target value as a result of short duration spikes that can occur at the Refinery. Hence, influent EQ was evaluated as an alternative to manage peak influent TKN wasteloads.

The short duration spike tests also helped to confirm that the upstream oil/water separation tanks (R211/R212), which are unmixed, were very inefficient at dampening influent TKN spikes coming from crude oil storage tank drainage. Figure 10 compares the observed pilot unit feed tank NH_3-N concentration from the April 20, 2017 drainage event to what it would have been if R211/R212 were perfectly mixed.

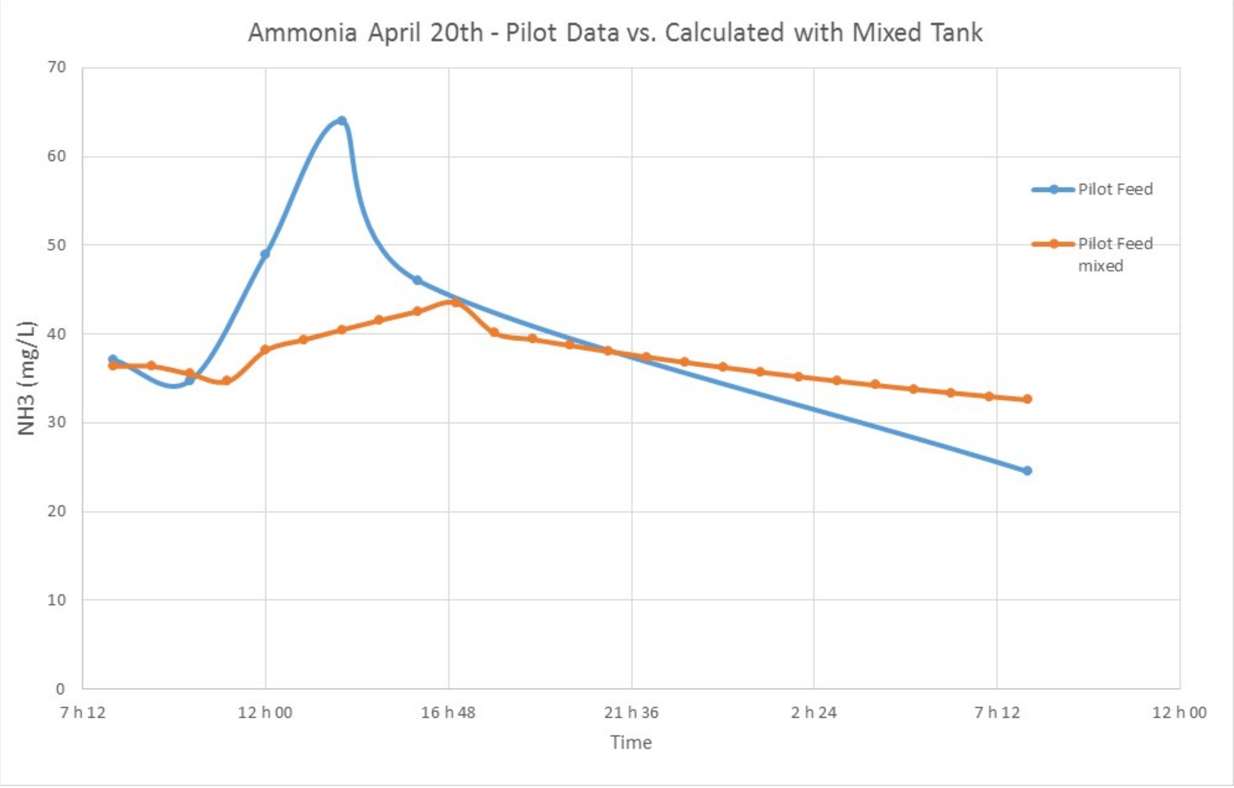


Figure 10: 20 April 2017 Pilot Reactor Influent NH_3-N Profiles from R501 Tank Drainage Test Actual vs. Mixed Upstream Tanks

Figure 10 demonstrates that the current configuration of R211/R212 provides very little EQ of crude oil storage tank drainage containing high TKN concentrations, resulting in a major short-term increase in biological treatment system loading compared to what would be experienced with adequate upstream EQ. It was concluded that an EQ step should be added to the project scope to protect the bioreactors from short-term influent TKN spikes associated with certain types of crude oil processed at the Refinery.

AMMONIA-RELATED EFFLUENT TOXICITY

As noted previously, elimination of effluent toxicity due to NH_3-N is a major objective of the Valero Jean-Gaulin Refinery WWTP upgrade project. It was therefore important to identify the effluent maximum NH_3-N concentration that would ensure constant compliance with the 96-hour rainbow trout acute toxicity test specified by Environment Canada. An effluent is considered toxic by this test if more than 50% of the fish do not survive the 96-hour exposure period.

Ammonia occurs in two forms in water, ionized (NH_4^+) and unionized or "free" (NH_3). It is the latter form which is highly toxic to aquatic life, especially fish. The equilibrium between the two forms of ammonia is driven by pH and temperature (United States Environmental Protection Agency, 2013). The unionized ammonia concentration can be calculated as follows:

$$\mathbf{NH_3 = Total\ Ammonia \div (1 + 10^{pKa-pH})}$$

Where:

Total Ammonia = NH_3 plus NH_4^+, expressed in mg/L
pKa = 0.09018 + 2729.92/T, where T is the ambient water temperature in °K
pH = effluent pH

The standard toxicity test method in Canada is conducted at a constant temperature of 15°C (Environment Canada, 2016). Therefore, the only two test variables that can affect the "free" ammonia concentration, and thus ammonia-related toxicity, are the total ammonia concentration and pH.

Numerous studies have been performed since the 1950s to define the toxic limit of ammonia in fresh water (United States Environmental Protection Agency, 2013). Both Environment Canada and Quebec provincial regulators have established guidelines on total NH_3-N concentrations that have a high potential of causing lethality in the rainbow trout toxicity test (Environment Canada, 2016; MDDELCC, 2013). These guidelines are shown in Figure 11 below and compared to the calculated "free" ammonia concentration.

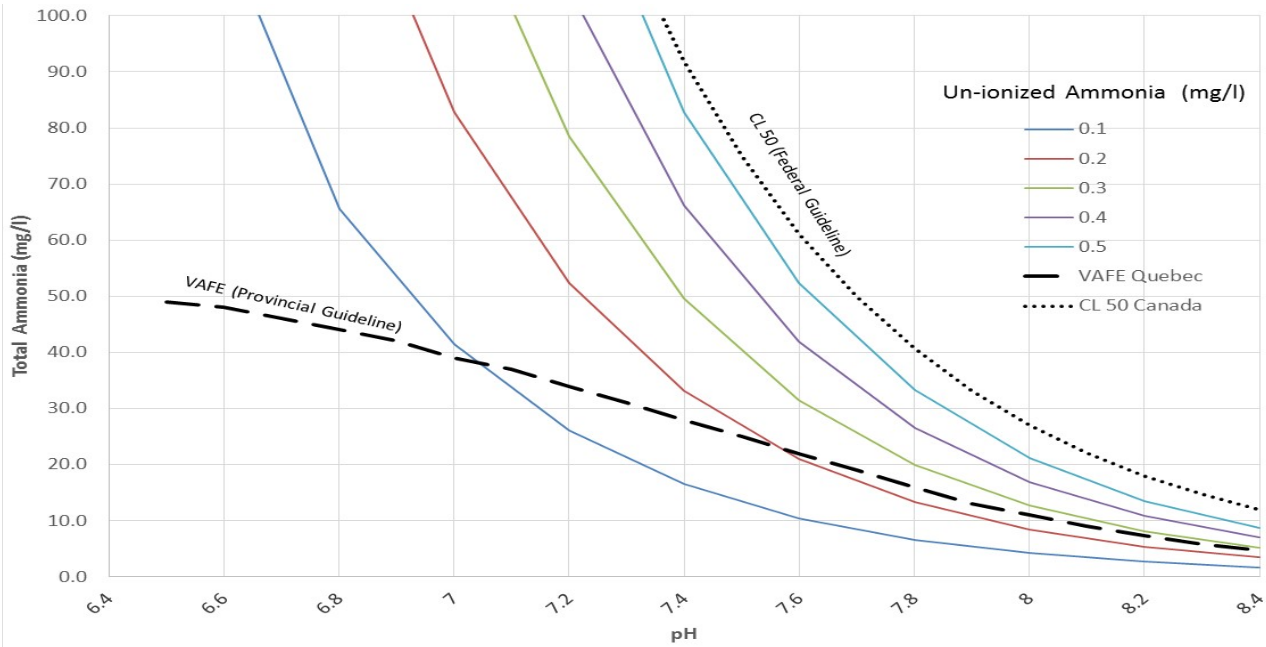


Figure 11: "Free" and Total Ammonia Concentration Limits for Fish Toxicity vs. pH

As can be seen, the Canadian federal guidelines correspond to a "free" ammonia concentration slightly greater than 0.5 mg/L. This criterion was developed for the 96-hour rainbow trout toxicity test. The Quebec provincial guideline is based on work done by the British Columbia Ministry of Environment (Norden and Pommen, 1986) and is presented as a general guideline for fish toxicity final acute values. The "free" ammonia concentration corresponding to the Quebec provincial guideline is 0.1-0.3 mg/L at pH 7-8, which is typical for the Refinery's WWTP final effluent.

Based on these guidelines, the Refinery's historical toxicity test results, and also understanding that other unknown contaminants could contribute to effluent toxicity, a design maximum effluent target of 0.1 mg/L "free" ammonia was established for the WWTP upgrade project.

It is also important to note that aeration during the acute toxicity test may cause the pH of an effluent sample to rise due to equilibration of carbon dioxide (CO_2) between the wastewater and the atmosphere (Environment Canada, 2013). This pH rise would increase the fraction of total ammonia in the "free" form, therefore increasing the sample's potential to exhibit acute toxicity to fish. Historically, the Refinery has seen pH increase by up to 0.5 standard units during a typical 96-hour acute toxicity test. Table 8 below shows how the allowable total ammonia concentration varies with pH given the 0.1 mg/L target for "free" ammonia. These calculations emphasize the importance of good pH control in conjunction with reliable nitrification to minimize the risk of effluent toxicity due to "free" ammonia in the WWTP discharge.

Table 8: Allowable Total Ammonia Corresponding to 0.1 mg/L "Free" Ammonia

Effluent pH	Toxicity Test Final pH	Toxicity Test Temperature	Percentage of "Free" Ammonia at Test Final pH	Allowable Total Ammonia
s.u.	s.u.	°C	%	mg/L
7	7.5	15	0.76	13.2
7.1	7.6	15	0.95	10.5
7.2	7.7	15	1.2	8.3
7.3	7.8	15	1.5	6.7
7.4	7.9	15	1.89	5.3
7.5	8	15	2.36	4.2

EQ MODELING

BioWin® modeling of various EQ scenarios was performed to predict the resulting effluent NH_3-N concentration after two-stage MBBR treatment, with dissolved air flotation (DAF) as the final solid/liquid separation step. The BioWin® model calibrated with MBBR pilot data was used for this evaluation. In the model, a crude oil storage tank water drainage of 25 m^3/hr for 4 hr at 1,250 mg/L TKN was combined with the average wastewater flow of 440 m^3/hr. Different configurations were evaluated with and without upstream and downstream EQ. These scenarios are presented in Table 9 below.

Table 9: BioWin® EQ Modeling Scenarios

Options	1 (Base Case)	3A	3B	4A	4B
Upstream EQ	None	2 APIs + 2 EQ Tanks	2 APIs + 2 EQ Tanks	2 APIs + 2 EQ Tanks	2 APIs + 2 EQ Tanks
Flow to Upstream EQ[3,4]	N/A	465 m^3/hr	225 m^3/hr	465 m^3/hr	225 m^3/hr
MBBRs	2-stage	2-stage	2-stage	2-stage	2-stage
MBBR Operating Temp[2]	26°C	18°C (no steam)	18°C (no steam)	18°C (no steam)	18°C (no steam)
TKN Supplement	Yes – to obtain 25 mg/L MBBR influent	None	None	None	None
Biosolids Removal	Settling Basin	Settling Basin	Settling Basin	DAF	DAF
Downstream EQ[1]	4,250 m^3 (25%)	4,250 m^3 (25%)	4,250 m^3 (25%)	None	None

Notes
1. Downstream EQ volume reduced to 25% of the actual Settling Basin volume (17,000 m^3) to account for lack of mechanical mixing
2. Temperature = 18°C corresponds to the 25th percentile of the pilot plant influent temperature data
3. Flow = 465 m^3/hr corresponds to an EQ tank location downstream of the DGF
4. Flow = 225 m^3/hr corresponds to an EQ tank location upstream of the DGF (oily water sewer only)

EQ modeling results for all scenarios are presented in Table 10.

Table 10: BioWin® EQ Modeling Results

EQ Scenario	1 (Base Case)	3A	3B	4A	4B
MBBR Influent Daily Maximum TKN, mg/L	91.2	31.0	21.8	31.0	21.8
Final Effluent Peak NH_3-N, mg/L	9.4	6.0	3.1	8.2	4.0
Final Effluent Daily Average NH_3-N, mg/L	2.7	2.1	1.3	2.1	1.3

Based on the modeling results, it can be seen that the Scenario 1, the base case without upstream EQ, results in a high peak influent TKN concentration that was identified as causing nitrification inhibition during the pilot tests. Scenario 4B was selected for the full-scale WWTP upgrade. This configuration meets the target effluent NH_3-N concentration of approximately 1.0 mg/L daily average and never exceeds the peak NH_3-N concentration (4.2 mg/L) that could cause effluent toxicity at pH 7.5 (compare Table 8 and Table 10).

Scenario 4B will also eliminate the existing Settling Basin (see Figure 1). In order to provide some safety margin for the future full scale operation, the effluent target has been established at pH 7.2 maximum. With the expected 0.5 pH maximum shift during the toxicity test, this would allow the effluent NH_3-N to be as high as 8.3 mg/L (see Table 8), roughly twice the expected instantaneous maximum concentration predicted for Scenario 4B.

The BioWin® modeling configuration and results for Scenario 4B are shown in the following figures.

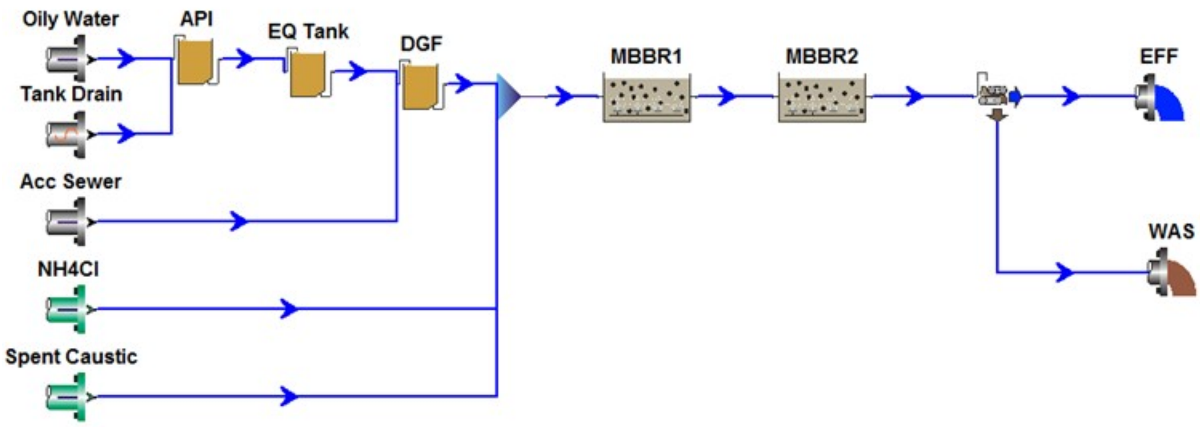


Figure 12: BioWin Model Layout for Scenario 4B

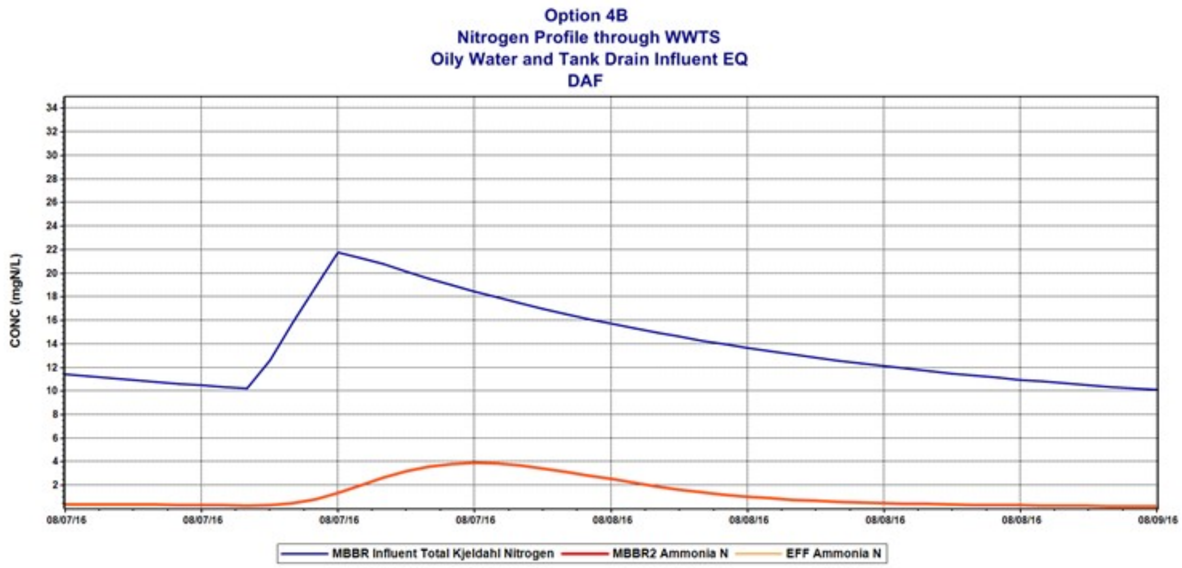


Figure 13: BioWin® Model Results Scenario 4B

SUMMARY AND CONCLUSION

FBBR and MBBR technologies were evaluated in pilot plants operated at various COD and TKN SALRs and temperatures. Key learnings are summarized below:

- At similar HRTs, the MBBR performed better than the FBBR during extended peak loading conditions. Also, the MBBR recovered from spike loadings faster than the FBBR. Hence, MBBR was selected as the preferred technology for the WWTP upgrade. In order to provide similar COD degradation and nitrification performance, the FBBR reactors would have to be at least 50% larger than the MBBR reactors.
- Over an extended period of testing, performance of a two-stage MBBR was similar to a three-stage MBBR. Hence, two-stage MBBR was selected for the full-scale design.
- The total HRT of the two-stage MBBR was determined to be approximately 6 hr.
- Average COD removal for the two-stage MBBR system was 68% at a COD SALR of approximately 3.5 g COD/m^2/day. The effluent filtered COD was 72 mg/L.
- Various TKN peak loading scenarios were tested to determine an operating range for a two-stage MBBR system. A shorter (4 hr) peak loading scenario with a TKN SALR value no more than 0.47 g TKN/m^2/day resulted in a daily average effluent NH_3-N less than 4.5 mg/L. The corresponding baseline TKN SALR value for the overall system at the 23 mg/L (95th percentile) maximum design condition was 0.31 g TKN/m^2/day.
- The observed solids yield for the two-stage MBBR operating at 26°C was approximately 0.48 kg TSS/kg COD removed.
- EQ is required to dampen peak influent TKN concentrations resulting from crude oil storage tank water drainage. The existing two oil/water separation tanks (R211/R212) will be converted to mixed EQ tanks upstream of the existing DGF system.

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