PACT MBR Delivers New Design and Operating Criteria for Reuse of Refinery and Petrochemical Wastewater

AUTHORS

William J. Cunningham, P.E.

Andrea J. Larson, P.E.

KEYWORDS

Ceramic membrane, Chemical Oxygen Demand (COD), Membrane Bioreactor (MBR), Mixed Liquor Suspended Solids (MLSS), Membrane Operating System (MOS), Powdered Activated Carbon (PAC), Reverse Osmosis (RO), ultrafiltration (UF).

ABSTRACT

Water scarcity and environmental regulations are becoming strong drivers for reusing refinery wastewater. This end use requires multiple treatment steps not amendable to space constraints at many facilities. For this reason, Siemens undertook a 3-year study aimed at combining these steps into a single, robust and compact treatment process, for either a brownfield upgrade or greenfield installation, to deliver treated water quality suitable for reverse osmosis (RO) / reuse. The focus of this research effort was on current ultrafiltration (UF) materials and their abrasion resistance when operated as a biomass/powdered activated carbon membrane bioreactor (MBR).

This paper presents results of a 3-year study demonstrating the successful performance of biomass/powdered activated carbon MBR using submerged ceramic membranes. Effluent chemical oxygen demand (COD), turbidity, silt density index (SDI), transmembrane pressure (TMP), and fouling rate trends are presented, and footprint and total installed cost comparisons to traditional treatment approaches are made.

INTRODUCTION & BACKGROUND

Global water scarcity in several oil-producing regions of the world combined with a renewed emphasis on greater pollutant loading restrictions from refinery and petrochemical processes in places like China and the Middle East are driving the development of sustainable technologies focused on reusing wastewater for cooling water makeup and even boiler feed water (BFW). This end use requires multiple treatment steps following primary and secondary de-oiling, including 1) biological processes for degradable COD reduction; 2) carbon adsorption to remove recalcitrant, membrane fouling COD, or advanced oxidation followed by an additional biological wastewater treatment step; 3) sand filtration; and 4) UF membrane filtration as the final step prior to reverse osmosis. While these linked technologies have achieved a high-quality reusable water product at petrochemical facilities, space constraints for housing these individual process technologies at many facilities could limit the practicality of implementing high-quality water reuse programs. For this reason, Siemens undertook a 3-year study aimed at combining these discrete treatment steps into a single, economic, robust and compact treatment process, that could be implemented either as a brownfield upgrade or greenfield installation, to deliver treated water quality suitable for the final reverse osmosis treatment step. The focus of this research effort was on current UF materials and their abrasion resistance when operated as a biomass/powdered activated carbon MBR.

Several technology development trends have evolved that allow water reclamation to be a significant component of high-quality industrial water supply and environmental stewardship:

- Use of activated carbon treatment to achieve significant recalcitrant COD removal following biological treatment of petrochemical wastewaters protect against RO membrane fouling and allows greater water recovery rates.
- Advances in membrane technology and consequential cost reduction are resulting in greater acceptance of membrane technology for wastewater reuse.
- The range of materials now available for UF liquid/solids separation offers the design engineer far greater choices to better match membrane material compatibility with wastewater characteristics, including materials exhibiting far greater abrasion resistance than previously available.

The PACT MBR (powdered activated carbon treatment membrane bioreactor) approach offers several important enhancements over conventional activated sludge treatment systems. These advantages and enhancements include:

- Excellent stability - the PACT MBR system is much less prone to upsets and their consequent process disruptions versus conventional biological processes. The PACT system will buffer inlet organic contaminants by first adsorbing then giving the biology adequate time to grow and consume the excess.
- Removal of recalcitrant COD and difficult-to-degrade organic compounds - the COD that is not immediately metabolized by the bacteria is adsorbed by the carbon and recycled back to the aeration tank allowing the bacteria more time to acclimate to these organic compounds and degrade them. This is critically important to achieving the required high quality, low TOC content in the treated wastewater.
- Reduced effluent toxicity – PAC adsorbs toxins caused by residual, non-biodegradable organics and heavy metals, which also improves nitrification.
- Maximum activated carbon utilization - the carbon in the reactor is kept at retention times equal to the biomass sludge age.
- High system flexibility - the selection of the carbon dose, type of carbon, and mixed liquor concentration guarantee the optimization of the process and the possibility to develop custom treatment dedicated to the characteristics of the wastewater.
- Plot space - the PACT MBR is an improvement over standard biological processes with reduced footprint since the clarifiers and sand filter are replaced with compact ultrafiltration membranes.
- Onsite sludge destruction and carbon regeneration – PAC may be regenerated in a wet air regeneration (WAR) system thereby slashing sludge disposal costs with complete biomass solids destruction.

It is for these reasons that Siemens undertook a 3-year development effort to find cost effective, abrasion-resistant membranes for PACT MBR applications. As a result, this design will:

- Assure removal of reverse osmosis-fouling contaminants in a single process step
- Simplify process operations, and
- Minimize operating costs through the use of robust ceramic ultrafiltration membranes that:
    - are capable of operating in direct contact with PAC and wind-blown sand environments
    - able to withstand oil & grease (O&G) excursions that occur in petrochemical facilities
    - require less frequent cleaning cycles due to constant surface renewal from PAC contact despite mixed liquor suspended solids (MLSS) concentrations beyond conventional MBRs, and
    - deliver the required COD reduction with less costly PAC in lieu of more expensive granular activated carbon (GAC) in carbon column treatment.

In cases where reuse is desired but the water sources contain a higher than desired concentration of dissolved solids, treatment techniques like reverse osmosis membrane treatment are required. Due to the complexity of petrochemical and refinery wastewater, multiple treatment steps are necessary to prevent excess fouling of RO membranes. RO feedwater requirements are shown in Table 1.

Table 1. Refinery wastewater characteristics, post de-oiling versus recommended reverse osmosis feedwater quality.

Typical Oil and Gas Wastewater Characteristics	Refinery Wastewater Post De-Oiling	Recommended Reverse Osmosis Feedwater Quality
Biochemical Oxygen Demand (BOD)	125-350 mg/L	< 5 mg/L
Chemical Oxygen Demand (COD)	300-1000 mg/L	< 40.0 mg/L
Oil and Grease (O&G)	20-50 mg/L	< 0.1 mg/L
Phenols	5-30 mg/L	< 0.02 mg/L
Silt Density Index (SDI)	immeasurable	< 5
Total Organic Carbon (TOC)	80 – 300 mg/L	< 15.0 mg/L
Total Suspended Solids (TSS)	30-75 mg/L	< 2 mg/L
Turbidity	varies	< 1 NTU

The development of PACT MBR allows biological wastewater treatment, carbon adsorption of recalcitrant chemical oxygen demand, and solids separation into a single, economic, and compact step even for the most complex wastewaters.

METHODOLOGY

Testing for PACT MBR began in 2007 which led to the development of EcoRight. At the time, only the Memcor membrane was considered since it was owned by Siemens. Testing of the Memcor membrane after only a few months led to significant membrane damage from abrasion. Consequently, separation of carbon prior to the Memcor membrane was required which required use of larger particle size GAC. However, PAC has several advantages over GAC including:

- Lower aeration requirement for suspension
- Higher carbon utilization – more surface area/weight
- Typically half the cost of GAC on a weight basis
- Possible onsite carbon regeneration with WAR, which greatly reduces sludge disposal

Consequently, an abrasion resistant membrane was desired for use with PAC.

Siemens commenced this three-year study with a literature search to screen the membrane industry for potential membranes that would survive in a carbon environment. No membranes were known or claimed to be abrasion resistant to activated carbon. Siemens selected seven membranes from six membrane suppliers to include a variety of membrane configurations and materials. UF membrane materials investigated included PVDF (polyvinylidene fluoride), PTFE (polytetrafluoroethylene), alumina oxide ceramic, silica carbide ceramic, PSU/PVP, (polysulfone/polyvidone), and PES (polyether-sulfone) as shown in Table 2.

Table 2. Ultrafiltration membrane configurations tested.

Configuration	Material	Pore size (microns)
Hollow fiber	PTFE	0.08
Hollow fiber	PVDF	0.04
Flat sheet	Ceramic (Alumina oxide)	0.1
Flat sheet	Ceramic (Alumina oxide)	0.5
Flat sheet	PSU/PVP with PET backing	0.1
Flat sheet	PES with PET backing	0.04
Flat sheet	Ceramic (SiC)	0.2

Each membrane was first screened through two separate three-year bench tests. The first test was a carbon only abrasion test. In this test, coupons or single fibers were suspended in three types of carbon at 10,000 mg/L. Air diffusers kept the carbon suspended.

Siemens did the following to ensure representative results for this test:

- Maintained a 30 day SRT by wasting carbon and adding virgin carbon.
- Set up a control for each membrane, with membranes suspended in a tank with aeration but no carbon.

- Performed a routine clean-in-place (CIP) procedure to expose the membranes to the same chemicals as those in flow-through tests.

The second test was a flow-through bench test with mini-modules. Each mini-module was operated in parallel with a target concentration of 14 g/L MLSS with over 70% PAC. TMPs, flux, and temperature were continuously recorded through a programmable logic controller (PLC). A picture of the setup is shown in Figure 1.

Figure 1. Flow-through bench PACT MBR setup.

At the conclusion of the flow-through bench test, membrane samples were compared to virgin and membranes in the carbon only abrasion test. Scanning Electron Microscope (SEM) analysis was used to examine the membrane surface and membrane cross sections.

After 1.5 years of bench test results, Siemens selected Meiden ceramic membranes for seven months of piloting to validate scale-up with commercial sized membranes. The target MLSS in the system was about 18,000 mg/L with a SRT of 20 days. PAC was dosed for a target concentration of 15,500 mg/L. TMPs, flux, and temperature were continuously recorded through a PLC and compared to bench results. Samples were also collected to monitor effluent quality including SDI, turbidity, TOC, and COD. Most of the test was conducted at 17 LMH; however, additional test conditions were performed up to 30 LMH.

Table 3 describes the membrane specifications for each Meiden flat sheet. Piloting was conducted with one module containing 25 full sized sheets, providing 12.5 m^2 of membrane area. The pilot system is pictured in Figure 2. Commercial modules may contain single stacks of up to 200 sheets and may be double stacked, totaling 400 sheets with 200 m^2 membrane area as shown in Figure 3.

Table 3. Meiden flat sheet membrane specifications.

	Description
Configuration	Flat sheet outside to inside filtration
MOC	Alumina ceramic
Pore size (microns)	0.10 (nominal)
Surface area (m^2)	0.5
Dimensions WxHxT (mm)	281 x 1,046 x 12
Dry weight (kg)	1.8

Figure 2. Pilot system PACT MBR setup.

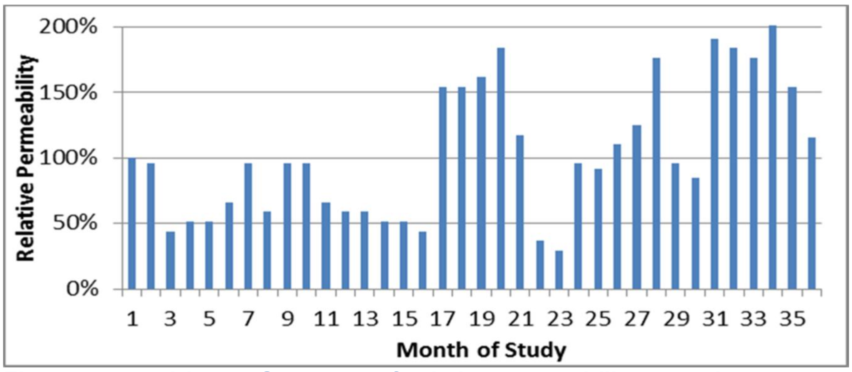
Figure 3. Assembled double stack module.

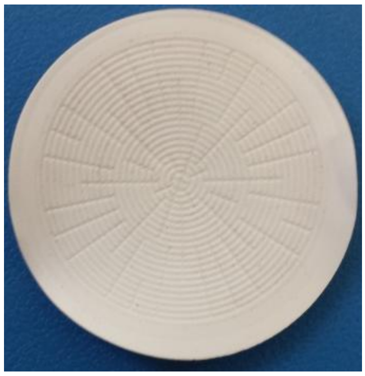
Feed for the bench and pilot flow-through tests used a portion of petrochemical wastewater. Due to limited feedwater, Siemens formulated a feed recipe to comprise the remainder of the COD.

RESULTS

Bench test – flow-through tests

After operating for three years at a target flux of 17 LMH, the membrane maintained low TMP and good permeability as shown in Figures 4a. Regular cleanings recommended by the membrane suppliers were performed to ensure no irreversible fouling over the 36 month test period. Permeability at the end of 36 months of operation was even higher than at the beginning of the test. During the entire three years of continuous testing, Siemens did not observe any carbon in the filtrate. The SDI value at the end of the study was 3.6 with no solids in the filtrate as shown in Figures 4b.





Figures 4a and b. 4a. Summary of relative permeability over three years of operation. 4b. SDI paper after three years of operation.

After three years of operation, the flux was increased from 17 LMH to 23 LMH for two weeks. Permeability was maintained, with a fouling rate of only 0.09 kPa/day (0.01 psi/day) over these two weeks despite no routine cleanings performed.

The appearance of the membrane after 36 months of operation is shown in Figure 12. The film of solids on the membrane was easily rubbed off. SEM images at three different magnifications are shown in Figure 6. Comparison of the virgin membrane and membranes after three years of operating in the PACT environment show virtually no differences.

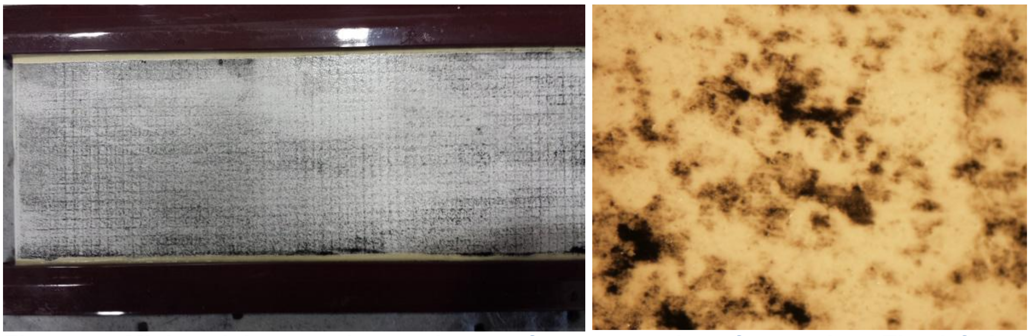


Figure 5. Mini-module ceramic membrane after 36 months of operation. The left image is the entire membrane module. The right image is a close-up of the surface (~100 x).

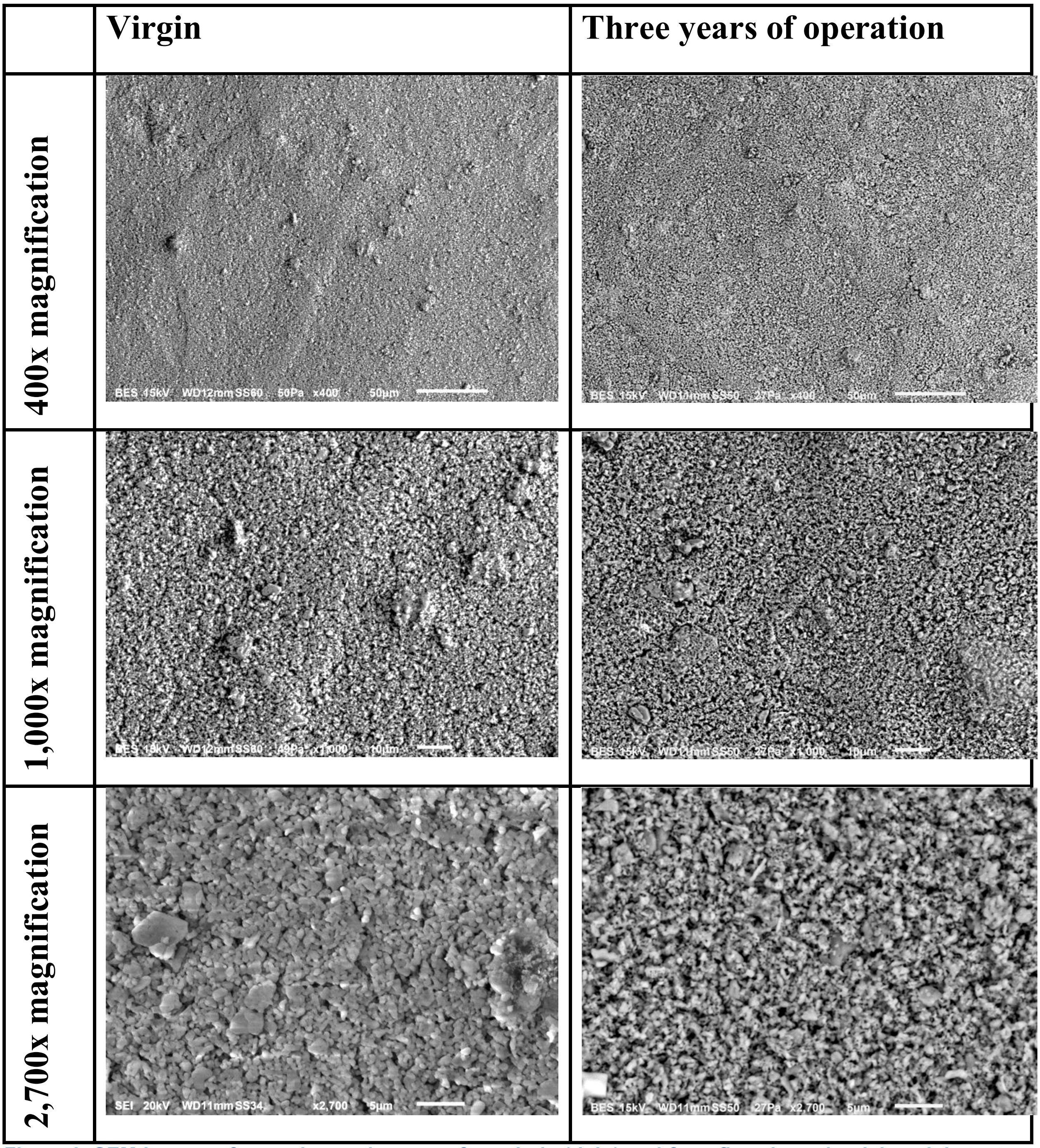


Figure 6. SEM images of ceramic membrane surface virgin (right) and from flow-through mini-module tests after three years of operation at 400x (top), 1,000x (middle) and 2,700x (bottom) magnification.

Bench test – carbon-only abrasion tests

SEM analysis was performed at 0, 3, 6, 9, 12, 18, 24, 30, and 36 months of operation in each of three carbons. Despite polymeric membranes showing significant surface morphology changes, no surface morphology changes were observed on the ceramic membranes as illustrated by Figure 7. The polymeric membrane already showed significant pore enlargement and surface morphology changes after only 9 months whereas the ceramic membrane was unchanged after 36 months, which matches results of the flow-through bench tests.

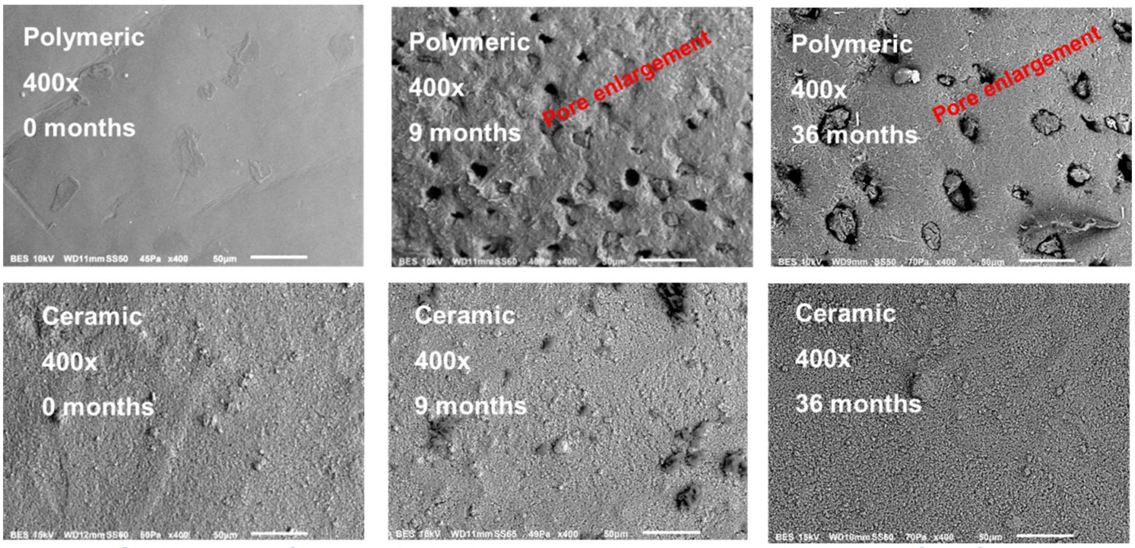


Figure 7. SEM images of polymeric (top) and ceramic membrane (bottom) surface from the carbon-only abrasion test, all at 400x magnification.

3D analysis was also performed on coupons after 36 months of testing in the offline coupon abrasion test. This analysis showed that the difference in height across the membrane was less than the thickness of the membrane layer and an acceptable thickness of filtration layer was maintained. Filtration thickness of exposed coupon measured 92.4 – 103.2% of the virgin membrane, showing that the filtration layer is maintained.

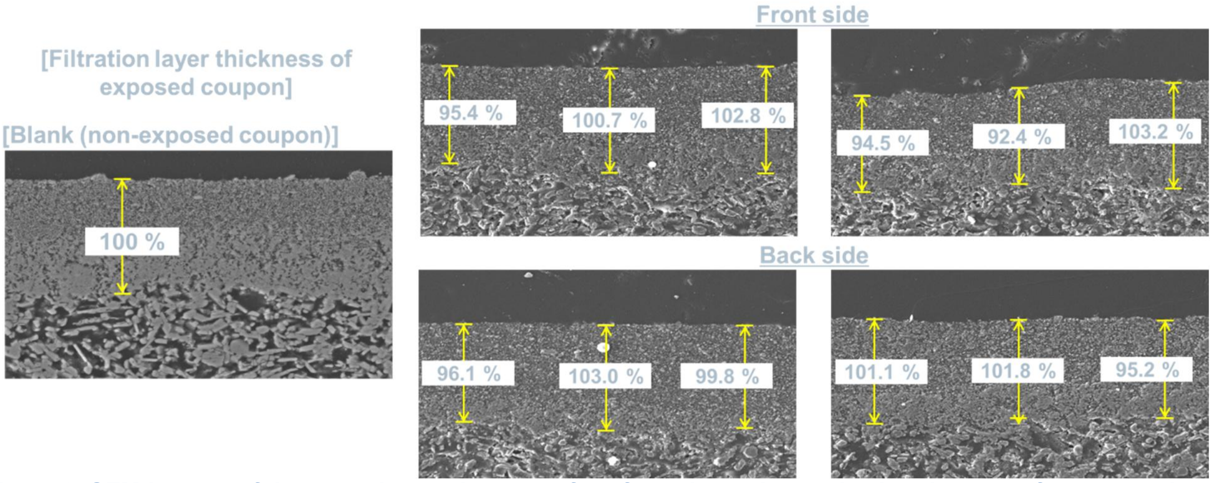


Figure 8. SEM images of the ceramic membrane surface from the carbon-only abrasion test after 36 months of operation. The left SEM image shows a cross section of a virgin membrane. The right images show the cross sections of the membranes after 36 months of operation. Images courtesy of Akitoshi Nakagawa, Meidensha Corporation.

Pilot test – flow-through tests

A summary of operational parameters and filtrate quality during pilot testing are shown in Table 4. For the duration of pilot testing, filtrate quality was excellent, with 44 of 45 samples under 0.2 NTU turbidity, 16 of 17 SDI values under 4, all six samples under 10 mg/L COD, and all seven samples under 2 mg/L TOC. These results all exceed reverse osmosis feedwater requirements presented in Table 1. Samples of feed, feed to the MBR, and filtrate are pictured in Figure 9.

Table 4. Summary of operational parameters and filtrate quality of ceramic membranes during pilot testing.

Total MLSS (mg/L)	Average = 19,246 Standard Deviation = 1,929
Carbon (mg/L)	Average = 11,500 Standard Deviation = 1,147
Biomass (mg/L)	Average = 4,504 Standard Deviation = 1,132
Feed COD (mg/L)	Average = 594 Standard Deviation = 219
Filtrate COD (mg/L)	Maximum = 9
Filtrate TOC (mg/L)	Maximum < 2
Filtrate Turbidity (NTU)	Maximum = 0.14* Average = 0.04* Standard Deviation = 0.05*
Filtrate SDI	Average = 2.2* Standard Deviation = 0.8*

*excluding one outlier data point

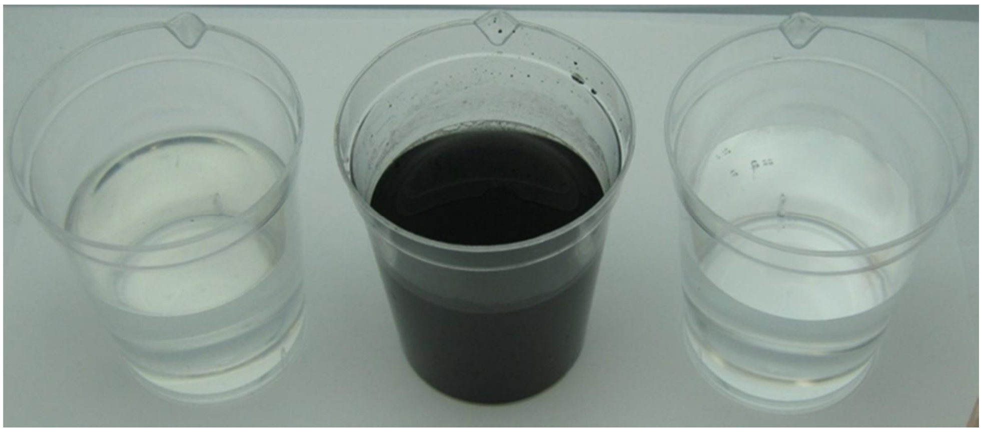


Figure 9. Feed (left), feed to MBR (middle), and PACT MBR filtrate (right) during pilot testing.

No solids were measured in the filtrate since the membrane is a physical barrier to separate the solids. As shown in Figure 10, the filtrate was significantly below the reverse osmosis vendor's recommendation for turbidity. Average turbidity was under 0.1 NTU.

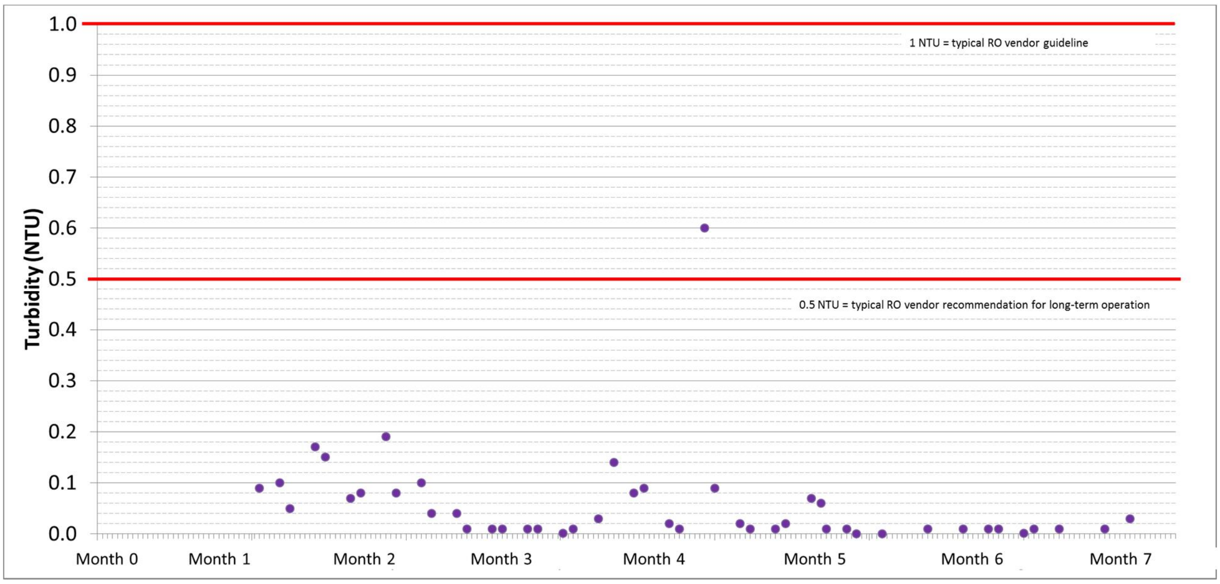


Figure 10. Filtrate turbidity of the PACT MBR filtrate. Horizontal lines with RO targets for comparison.

Filtrate SDI values were also excellent as indicated by Figure 11. The only filtrate SDI value above 5 was recorded immediately following a weekly maintenance clean and the SDI value the following day was only 1.0. Since the SDI filter paper was discolored but not black, it is believed that residual chemicals from the cleaning resulted in the high SDI value. The remainder of SDI values, averaging 2.2, was below the SDI value recommended for RO feedwater.

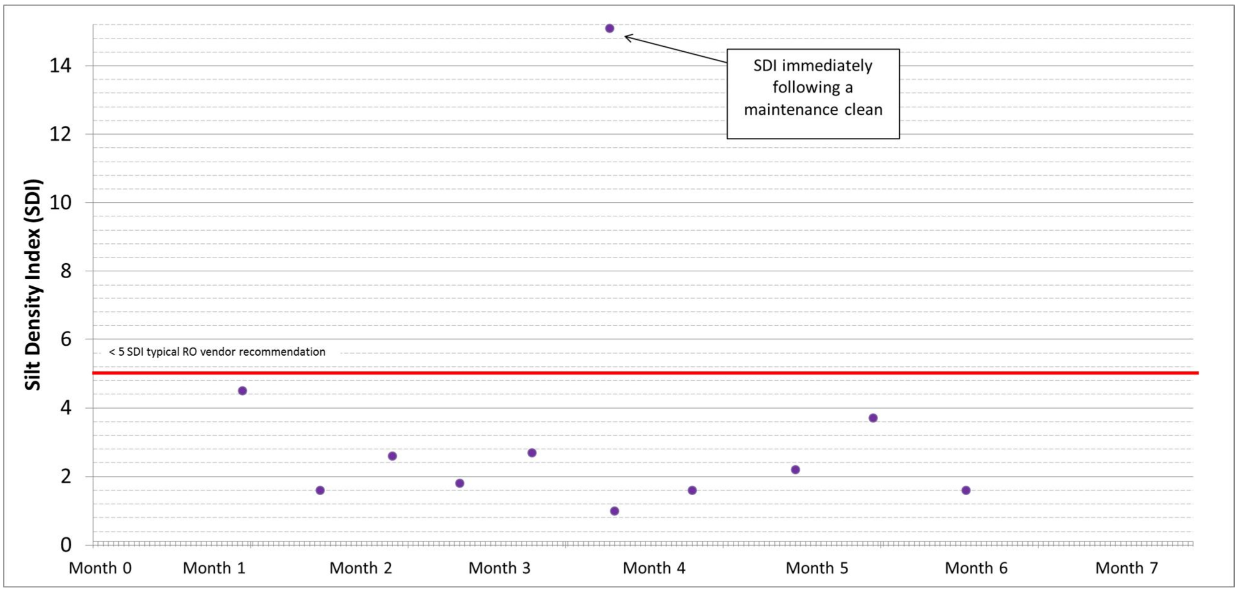


Figure 11. Filtrate SDI value of the PACT MBR filtrate. Horizontal line with RO target for comparison.

After an initial stabilization period, the PACT MBR system exhibited stable operation, maintaining less than 7 kPa (1 psi) TMP, even up to a flux of 30 LMH as shown in Figure 12. At a flux of 17 LMH, TMPs ranged from 2 to 5 kPa (0.3 to 0.7 psi), resulting in a permeability of 300 to 580 LMH/bar. As shown in Figure 9, the fouling rate was at or under 0.2 kPa/day (0.02 psi/day) after acclimation. In fact, the highest permeability of the test occurred at the end of the seven month study indicating no fouling despite only weekly maintenance cleans and no CIPs. When the flux was increased, there was minimal TMP and fouling rate increases, as illustrated in Figure 13, even at a flux of 30 LMH.

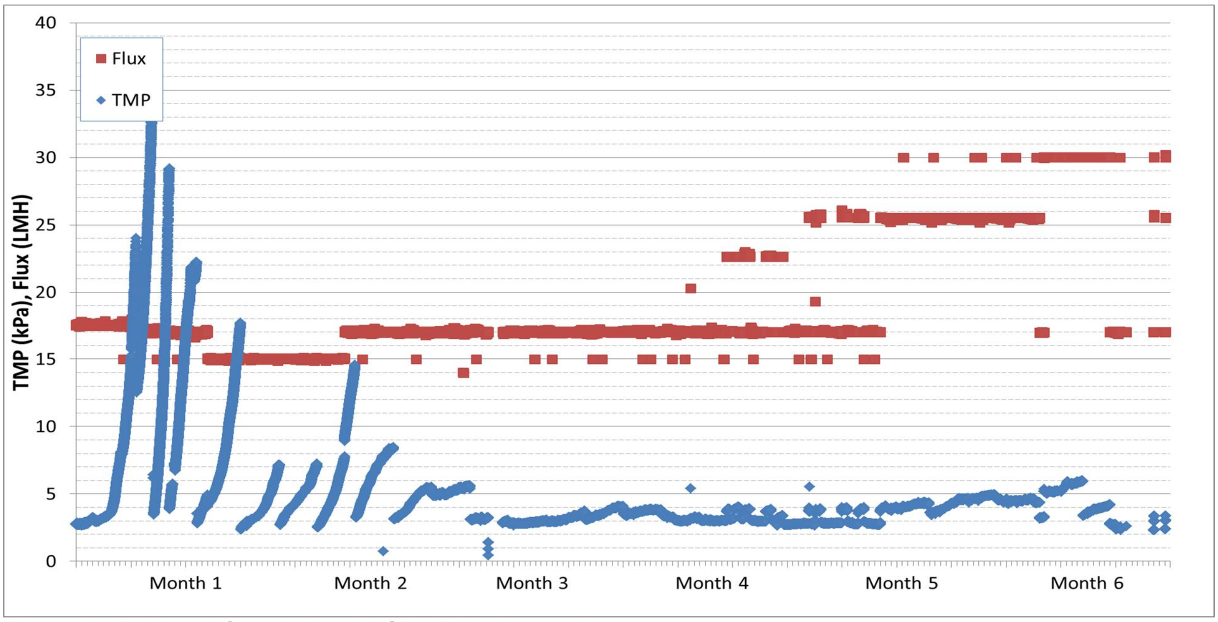


Figure 12. TMP and flux during PACT MBR pilot testing.

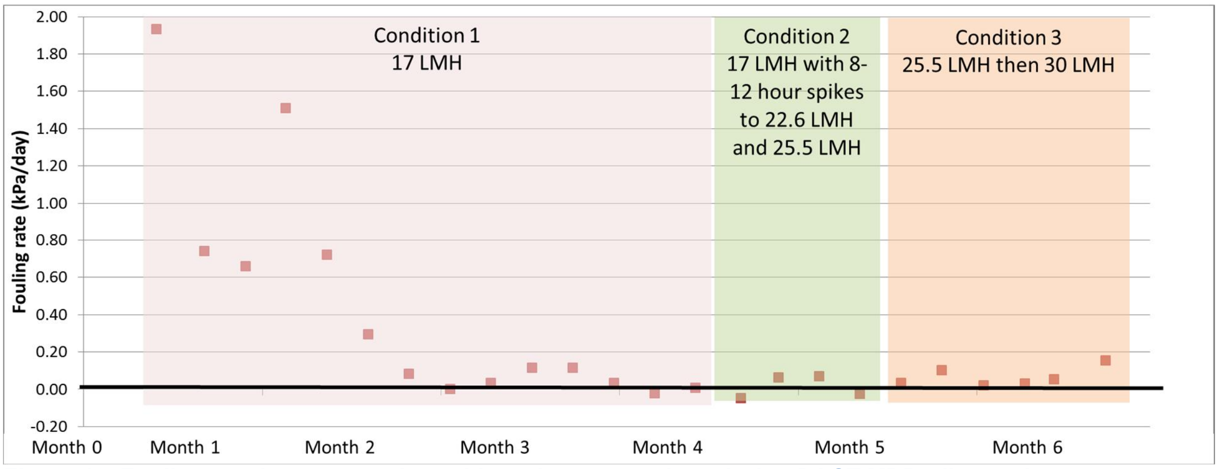


Figure 13. Fouling rate between each weekly maintenance clean during PACT MBR pilot testing.

Clean water permeability verified no irreversible fouling over the test period. At the conclusion of the seven month test, clean water permeability was compared before and after CIP as shown in Figure 11. Despite no CIPs, the clean water permeability was excellent, matching that of a new membrane. Consequently, a CIP did not change the clean water permeability.

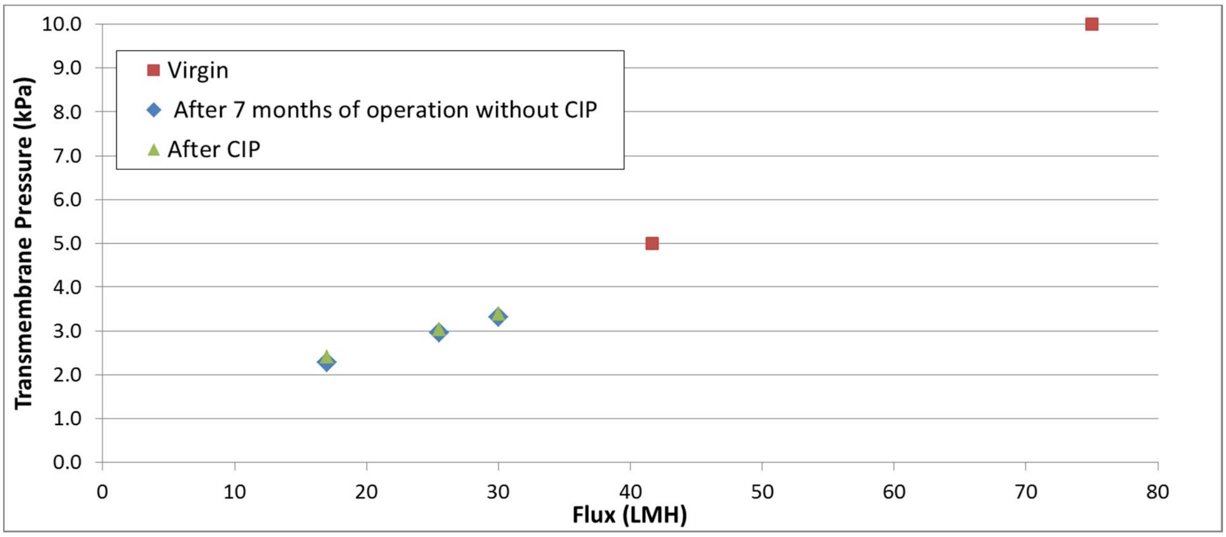


Figure 14. Clean water permeability comparison of before and after seven months PACT MBR pilot testing.

Following testing, Siemens disassembled the module and examined each flat sheet membrane. Siemens observed very few solids observed on the sheets. Note that the sheets with the most solids buildup were at the end of the air scour header which would be different in larger modules. Pictures of the module and elements at the end of the study are shown in Figure 15.

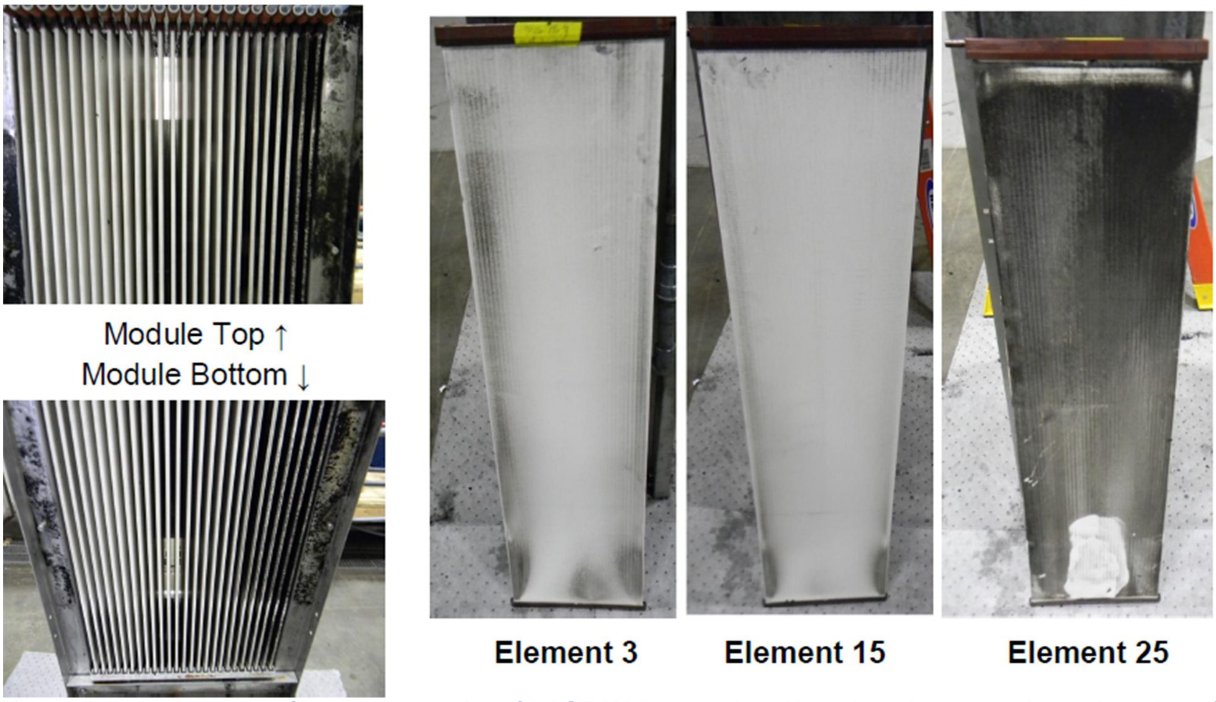


Figure 15. Pilot module after seven months of PACT MBR operation. Note that element 25 is on the edge of the module.

SEM and microscopic abrasion evaluation compared the virgin and used membrane surface morphology to determine if the surface changed. Samples from three locations on three panels were analyzed. There are very little differences between the virgin and used membrane which also match 36 month bench results. One SEM image is presented below.

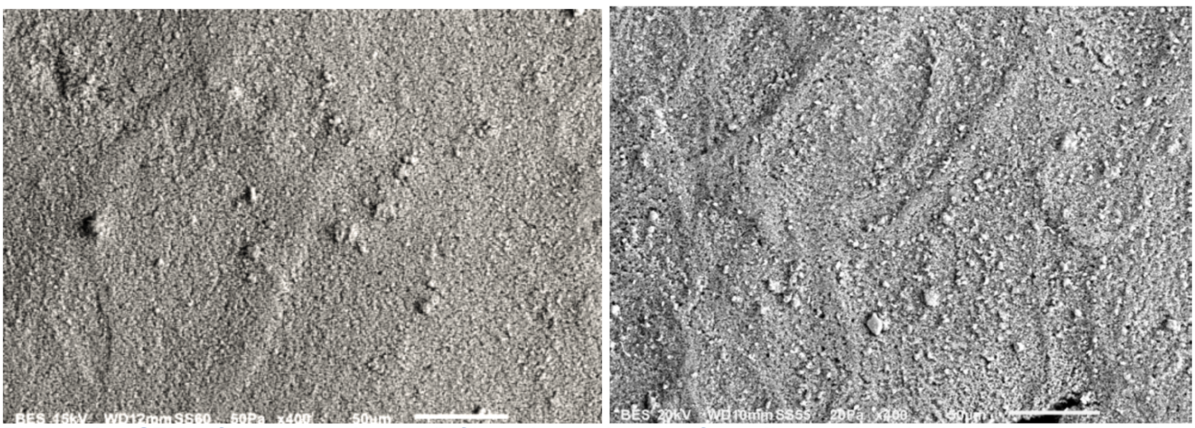


Figure 16. SEM of new membrane (left) and membrane after pilot testing (right), both at 400 times magnification.

SYSTEM ADVANTAGES

PACT MBR allows biological wastewater treatment, carbon adsorption of recalcitrant chemical oxygen demand (COD), and solids separation into a single, compact step. In a conventional treatment approach, multiple steps would be required for equivalent treatment as shown in Figure 17. The membrane is a physical barrier to separate the solids while having a smaller footprint than a clarifier. As a result, the PACT MBR reduces the overall footprint by nearly half (see Figure 18). Footprint is particularly appealing in areas where footprint is limited, such as the case for many retrofits.

Figure 17. Conventional treatment approach to achieve water reuse quality.

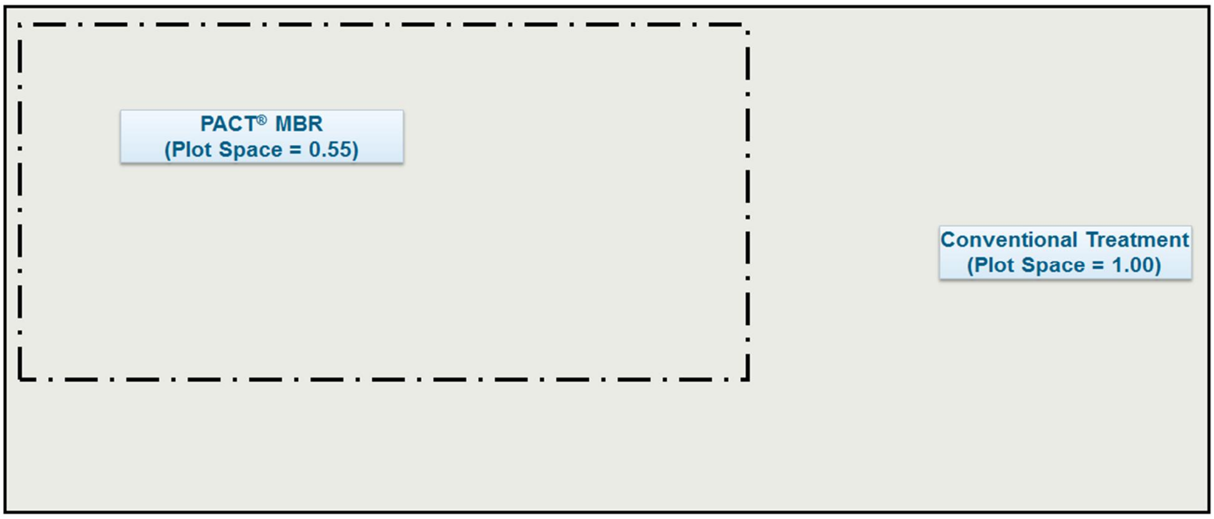


Figure 18. System footprint reduction with PACT® MBR over conventional treatment.

Along with the footprint reduction, onsite site construction costs are reduced. A third party analysis at three different flow rates (300, 600, 1000 m3/hr) by Pöyry determined that the PACT MBR system has a total installation cost savings of 14 to 17% over the conventional treatment approach as shown in Figure 19.

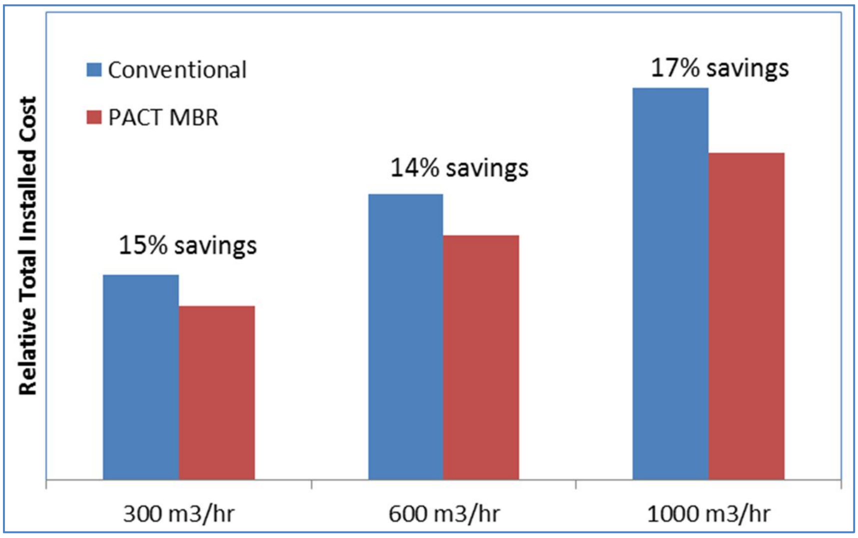


Figure 19. Relative total installed cost savings of PACT MBR over conventional activated sludge system.

SUMMARY

After a three year study, including a 7-month pilot study using full-scale membranes and petrochemical wastewater, the following results are reported:

- Submerged ceramic membranes offered superior abrasion resistance to contact with PAC, even after three years of exposure.
- MLSS concentrations in the membrane tank achieved 19,000 mg/L with an estimated PAC concentration of over 70%. Operating sludge age averaged 20 days, typical for refinery and petrochemical wastewaters with nitrification requirements.
- 17 LMH flux was maintained at transmembrane pressures less than 7 kPa (1 psi).
- No clean-in-place (CIP) procedures were needed during the seven months of testing on the full-scale membranes. The presence of PAC within the MLSS matrix appeared to keep the flat sheet ceramic panel surface free of organic foulants and prevented solids caking onto the membrane surface.
- RO feedwater quality was achieved, with filtrate COD, TOC, turbidity, and SDI of <10 mg/L, <2 mg/L, <0.5 NTU, and <2 respectively.
- System footprint and total installed costs are lower than conventional technologies for equivalent effluent quality.

As a result, PACT MBR with ceramic membranes allows both existing and new facilities to produce a high quality effluent suitable for reverse osmosis (RO) / reuse in a single, economic, robust, and compact treatment process for even the most difficult-to-treat wastewaters.