Abrasion Resistant Ultrafiltration Membrane Enables Refinery Wastewater Reuse

Siemens Water Solutions
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Topics Addressed in this Presentation

- Requirements for reusing refinery wastewater
- Drivers for Activated Carbon in the Process
- Challenges for membranes
- Test data

Reuse – Irrigation Standards in Middle East

- TDS and chloride limits requires RO for many waters
- BOD limit will likely require biological WWT
- Applicable to both produced water & refinery WW reuse

	Saudi Arabia	Oman	Jordan
TDS (mg/L)	-	1500	1500
Cl	100	650	400
COD (mg/L)	-	150	-
BOD (mg/L)	10	15	-
TSS (mg/L)	10	15	-
O&G (mg/L)	Nil*	0.5	8*
Phenol (mg/L)	0.002	0.001	0.002
Turbidity (NTU)	5	-	-

* Free O&G

Reuse - How to Meet RO Feed Requirements?

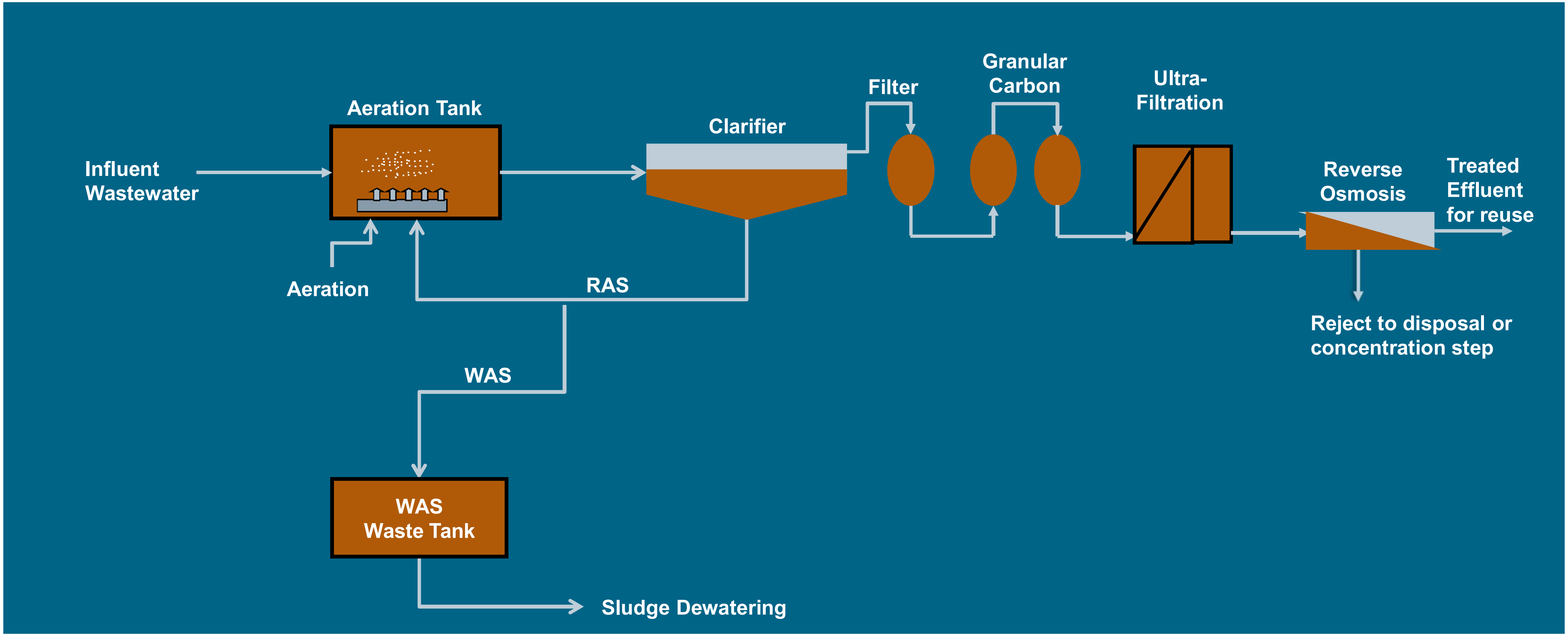
Refinery Wastewater Post Deoiling

- COD 300-1000 mg/L
- BOD 125-350 mg/L
- TSS 30-75 mg/L
- O&G 20-50 mg/L
- Phenols 5-30 mg/L

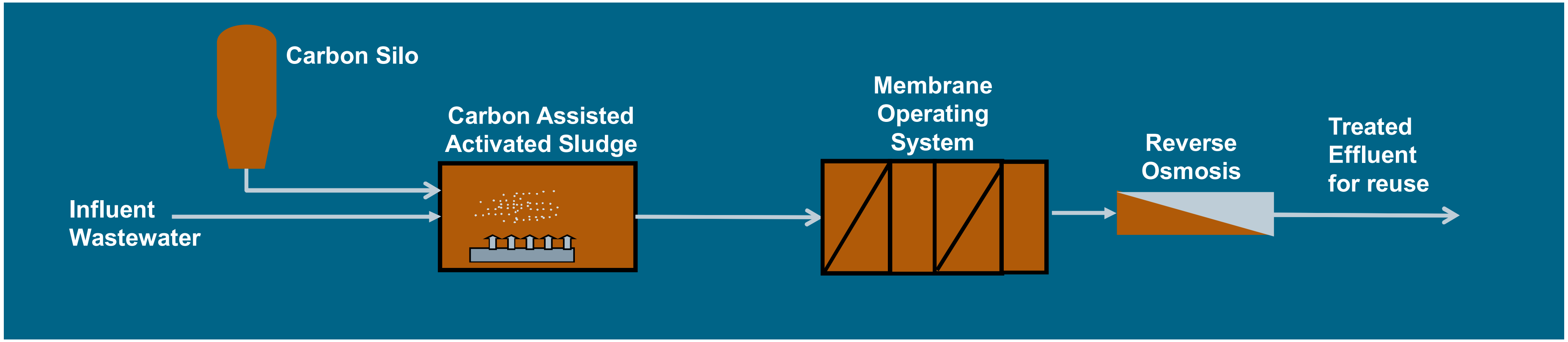
RO Feedwater

- COD – as low as possible
- TOC – membrane manufacturers recommend <3 mg/L
- O&G < 0.1 mg/L
- SDI < 5 – lower the better
- Turbidity < 1 NTU with < 0.5 NTU recommended for long-term, reliable operation

Conventional Approach to Pretreating Refinery Wastewater for Reverse Osmosis



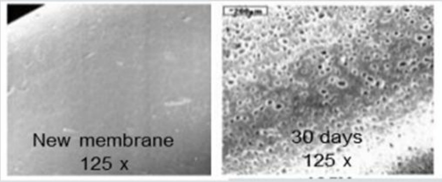
A Different Approach – Carbon Assisted MBR



Why is carbon beneficial in oily applications?

- **Note the visible difference between the MBR effluent samples**
  - **Sample on left was treated with activated sludge conventional MBR**
  - **Sample on the right was treated with PACT MBR**

- **Note the visible difference in the ultrafiltration membranes used in bench scale MBRs treating the same wastewater.**
  - **The membrane on the top was in an MBR containing powdered carbon**
  - **The membrane on the bottom was in an MBR containing only activated sludge**
  - **Note that the activated carbon damaged the membrane on top causing failure**



Why is Carbon Beneficial for Oily Water Reuse Applications?

- Cartridge filters downstream of MBR fouled within 24 hours
  - Cartridge filter was replaced and fouled within 8 hours
  - RO membrane fouled within two days, testing was shut down
- The cartridge filter downstream of the PACT MBR did not foul during the entire 6 week test
  - Effluent sent to RO

PACT® MBR – RO Effluent

Silica (mg/L)	<0.20 (detection limit)
Turbidity (NTU)	0.10 – 0.18
TDS (mg/L)	26.75

MBR After 24 Hours

NEW

PACT MBR After 6 weeks

Development of Carbon Assisted MBR

1970-1975

Patents Awarded for the PACT® and WAR® processes

1977

First commercial PACT® installation

1983

First PACT® installation with a WAR® system

2006

Siemens receives order for Petro® MBR system for wastewater reuse for irrigation purposes. Non-refinery wastewater (bulk plants)

2007

Siemens performs a study with Saudi Aramco to treat oily refinery wastewater. Carbon was required to consistently meet discharge requirements. However abrasion was observed on the PVDF membranes.

2008-2014

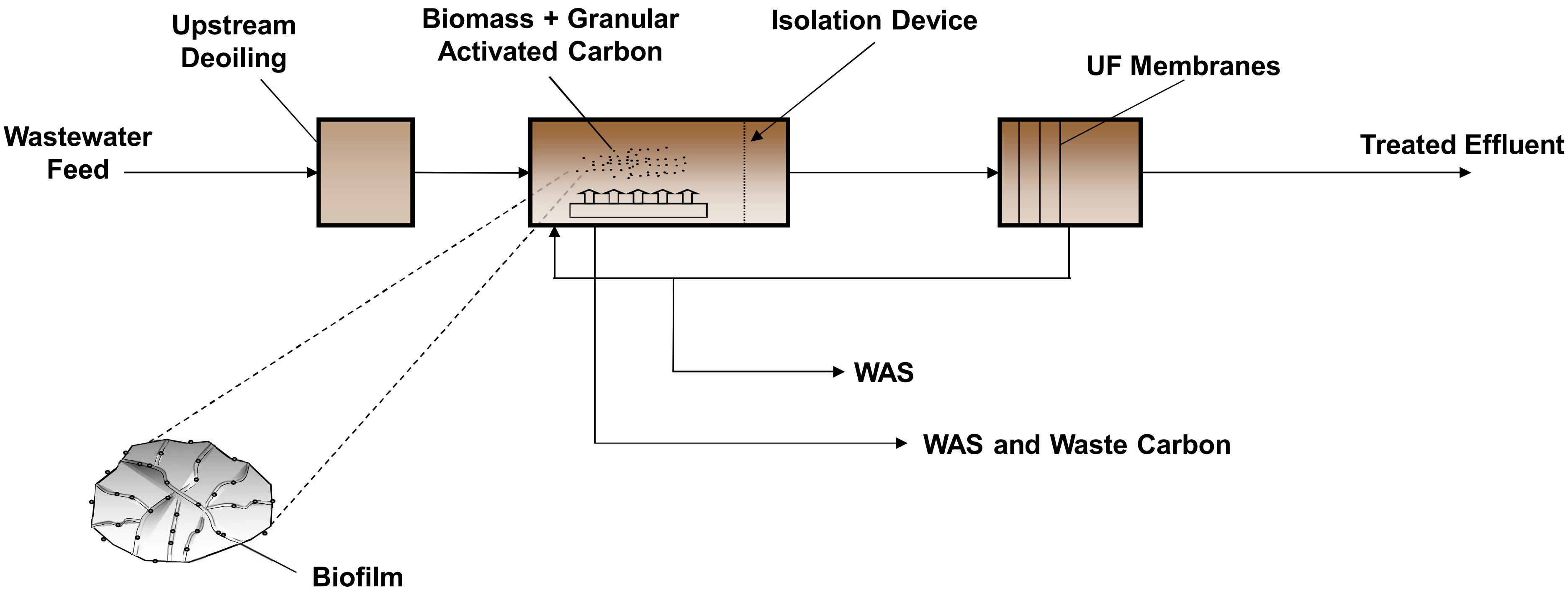
EcoRight® was developed using granular carbon and a separation device to allow for the use of PVDF membranes in carbon assisted MBR

2013-2017

Siemens Investigated, tested and identified a suitable membrane for abrasive environments and launches

Petro® PACT MBR

EcoRight™ Technology



Benefits and Limitations of the EcoRight^{TM} MBR Treating Oily WW

EcoRight^{TM} MBR Benefits

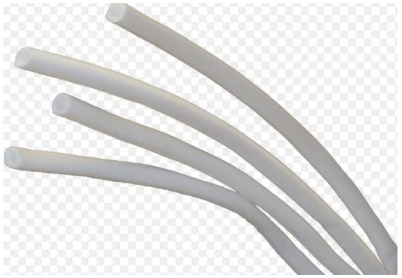
- Very stable system with the ability to handle upset conditions and recover
- Provides surface area for attached growth treatment
- **Green** technology – effluent reuse / same or lower energy requirements
- Minimizes concerns of abrasion on membranes allowing the use of lower cost materials
- Less carbon consumption vs. GAC polishing

EcoRight^{TM} MBR Limitations

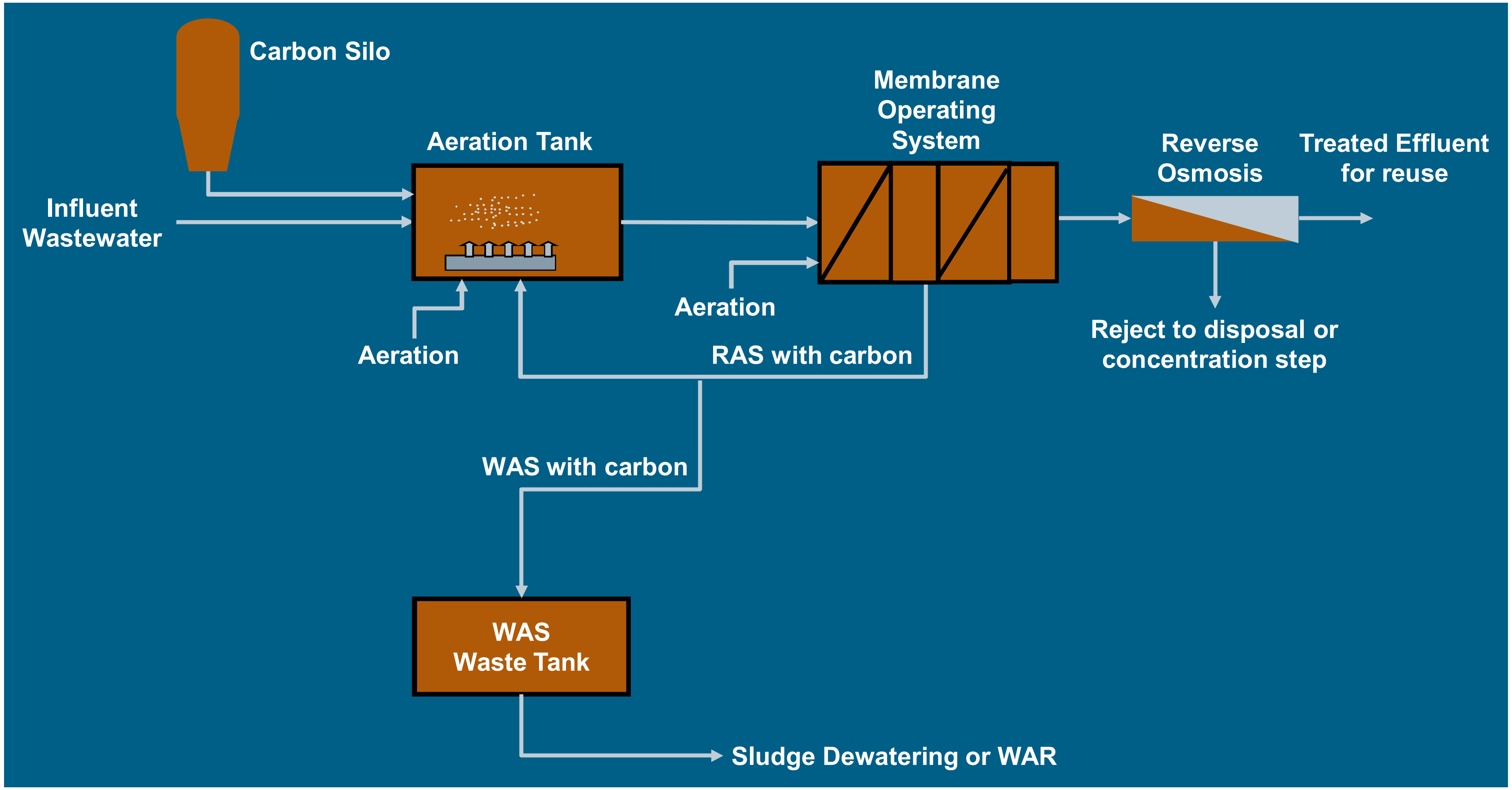
- **Activated carbon cannot be regenerated onsite causing an operational expense for fresh carbon**
- Biological regeneration of carbon is limited
- Additional equipment inside of the aeration tank is required for GAC suspension when compared to conventional activated sludge
- Best suited for applications that do not require a high carbon dose to meet treatment requirements

Advances in UF membranes

- 2013 – Siemens sells majority of water business that was not associated with the Oil & Gas market including Memcor
- 2014 – Siemens embarks on a study to identify membranes that could potentially be abrasion resistant to PAC
  - A paper study was conducted to identify potential membrane suppliers
  - 10 suppliers were chosen for bench scale abrasion testing using PAC – system has been operating for close to 3 years
  - 2 suppliers were identified from this testing and pilot tested

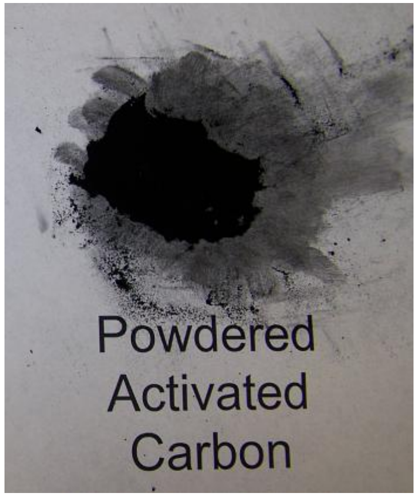


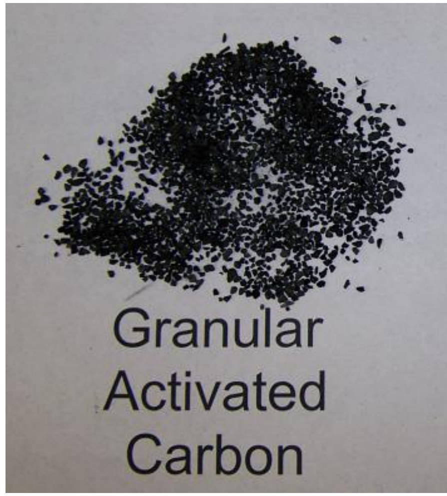
PACT® MBR Process



Advantages of PACT Over GAC

- Greater carbon efficiency
- PAC helps to reduce fouling on UF membranes
- PAC typically half the cost of GAC on a weight basis
- Possible onsite regeneration with wet air regeneration, which greatly reduces sludge disposal
- Lower VOC emissions from aeration basins
- Can tailor carbon dose easily to meet effluent leading to increased operational flexibility
- Increased sludge settleability





Wet Air Regeneration (WAR)

- Efficiently and effectively recover the powdered activated carbon with less than 10% attrition during each cycle
- Simultaneously destroy the biomass and adsorbed organics
- Can operate auto-thermally due to heat release of the oxidation process
- Reduce or eliminate sludge disposal, only having a non-hazardous ash residual
- Eliminate any sludge disposal environmental liability

Challenges of PACT MBR development

- **Identifying membranes that are abrasion resistant to a high concentration of activated carbon while also being cost effective for the purpose.**
- Identifying process conditions to utilize with this membrane to minimize fouling potential and maximize uptime.
- Identifying maintenance cleaning protocols to ensure long term life of the membranes.

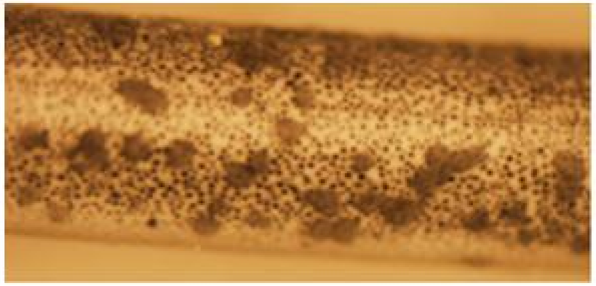
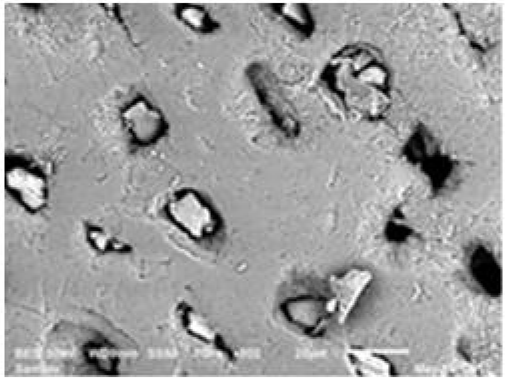
Abrasion Testing Protocol

- There was concerns with every idea for accelerated membrane abrasion testing.
- Decided that to test for a 3+ year duration in a flow through configuration in an operating PACT plant.
- In parallel performed cassette mixing tests where samples could be pulled on a periodic basis and analyzed.
- Used Scanning Electron Microscope analysis and water chemistry to monitor

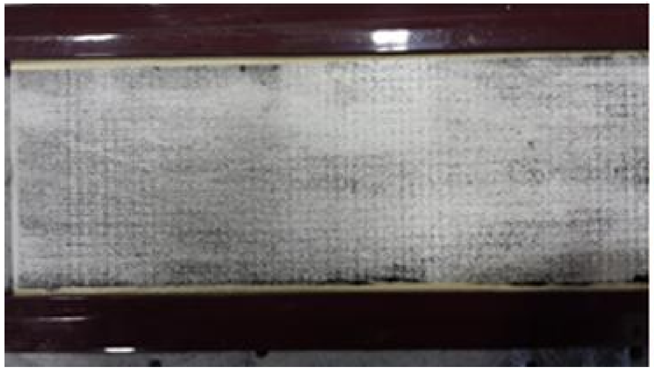
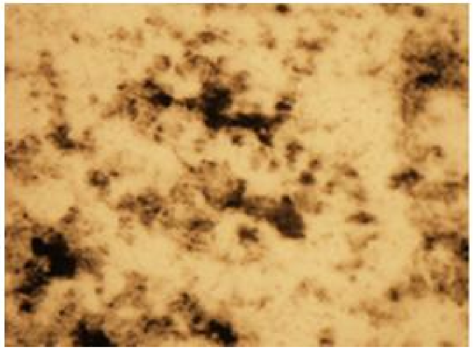
The Refined Sample Set of Membranes After the Paper Search

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

Results from SEM Analysis

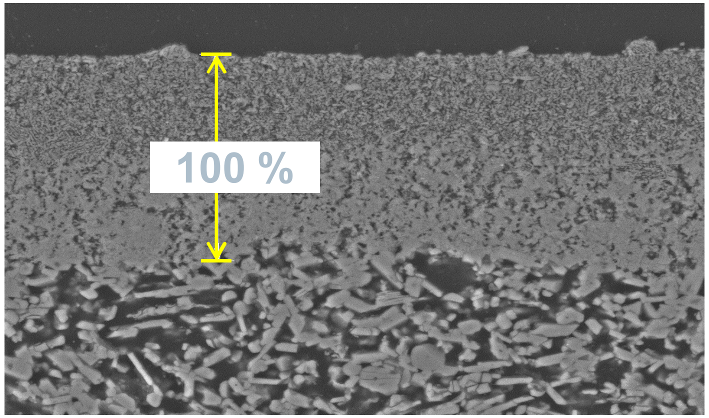
- PVDF Membrane that experienced abrasion

- Ceramic Membrane that showed no sign of damage

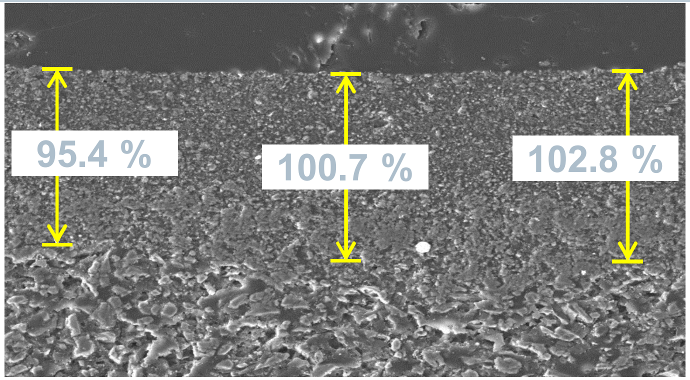
PACT MBR Abrasion Resistance

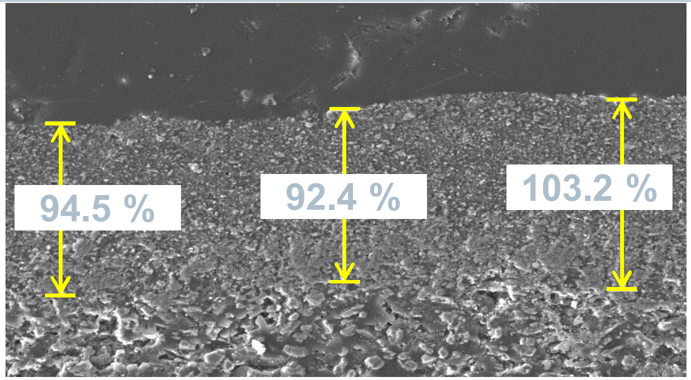
[Blank (Non-exposed Coupon)]



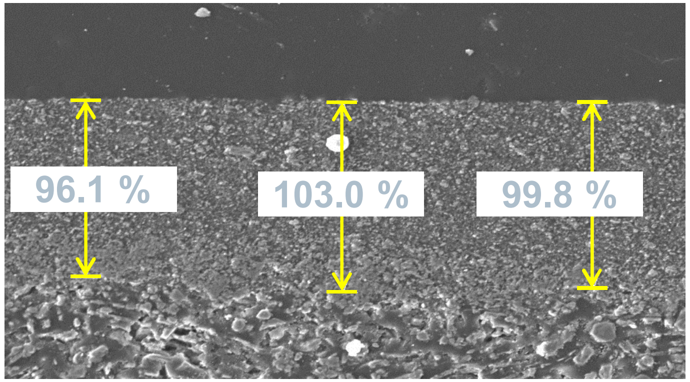
[Filtration Layer Thickness of Exposed Coupon]

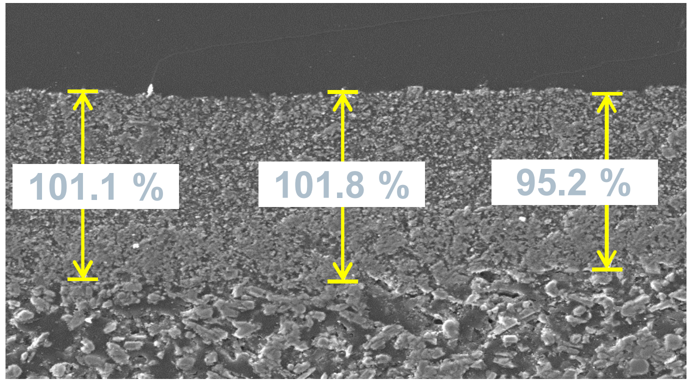
Front side





Back side

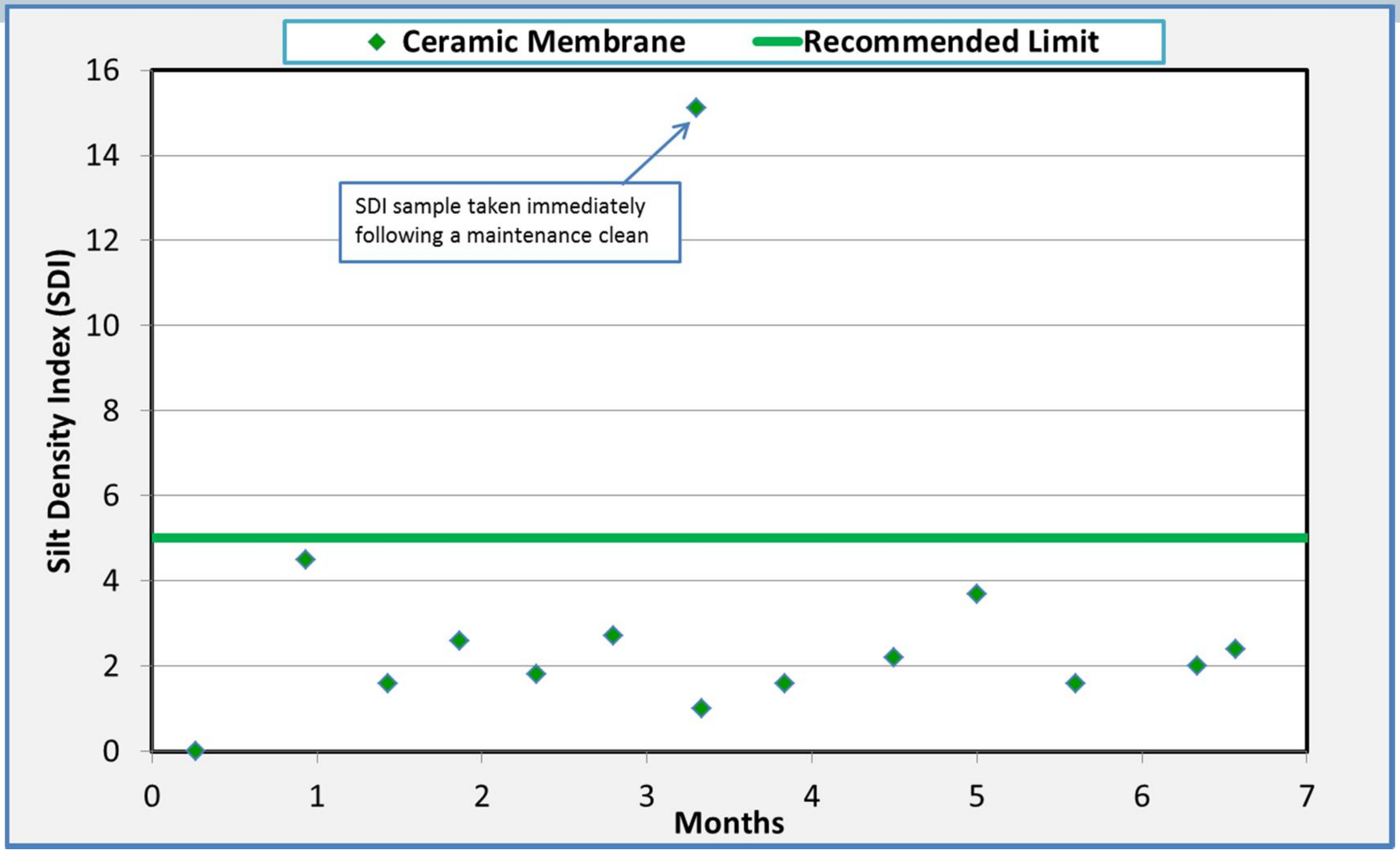




Filtration Thickness of Exposed Coupon measured 92.4 – 103.2% of Non-exposed Coupon.

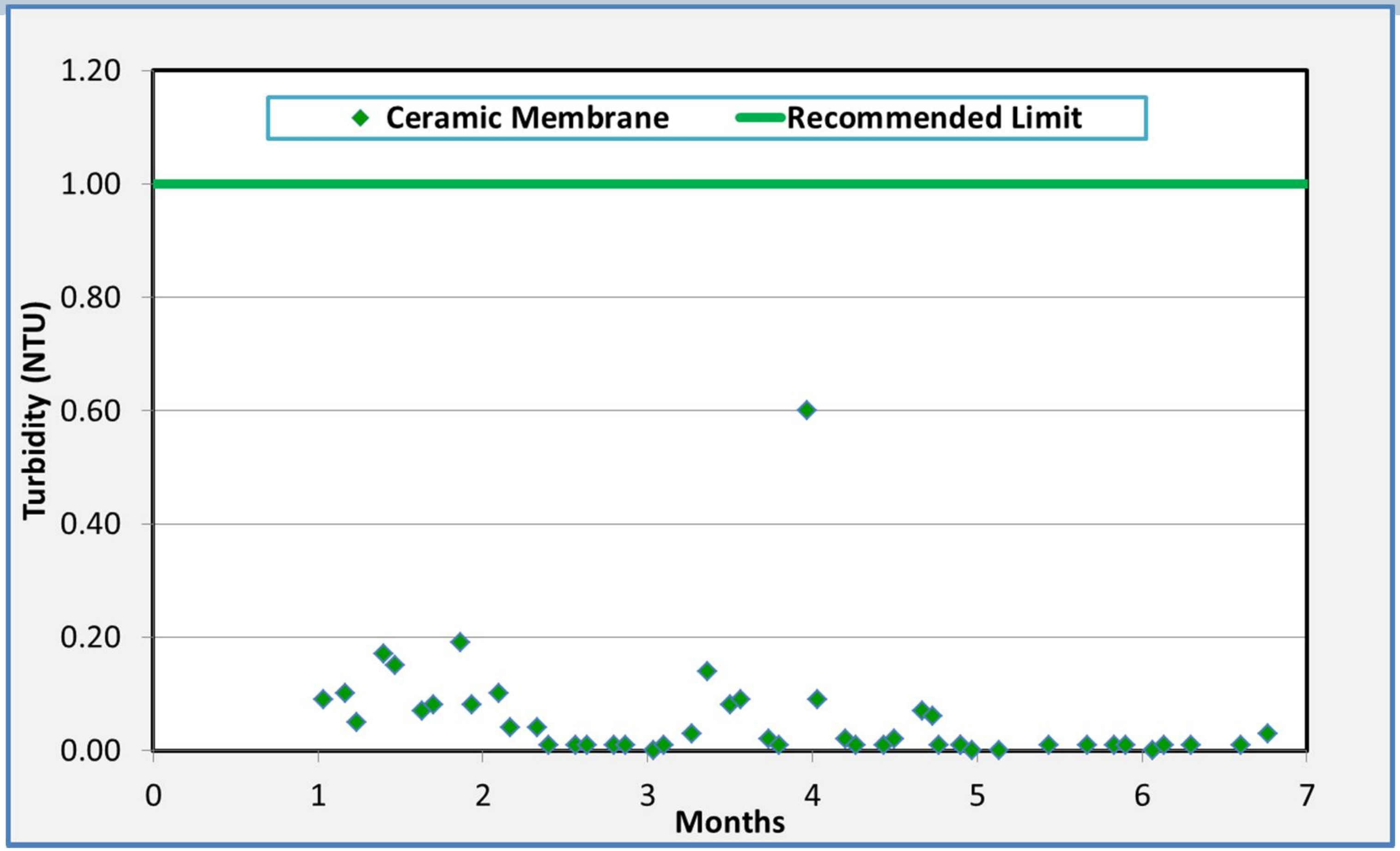
No membrane abrasion observed

PACT MBR Full Scale Results - Performance Data – Silt Density Index (SDI)



RO quality feedwater

PACT MBR Full Scale Results - Performance Data – Turbidity



RO quality feedwater

Membrane Autopsy After Pilot Test

- After 7 months of operation no fouling was observed on the membrane surface
- No cake was observed on the membrane surface due to the scouring action of the activated carbon
- No CIP (clean in place) cleaning required during the duration of the pilot study
- No visual abrasion observed to the eye or when analyzed via scanning electron microscope

PACT® MBR Performance

- Total MLSS concentration ~ 10,000 - 20,000 mg/L average
- Ultrafiltration for Liquid/Solids Separation
- Effluent TSS <1 mg/L
- Effluent COD 30 - 70 mg/L
- Effluent TOC <10 mg/L

Contact

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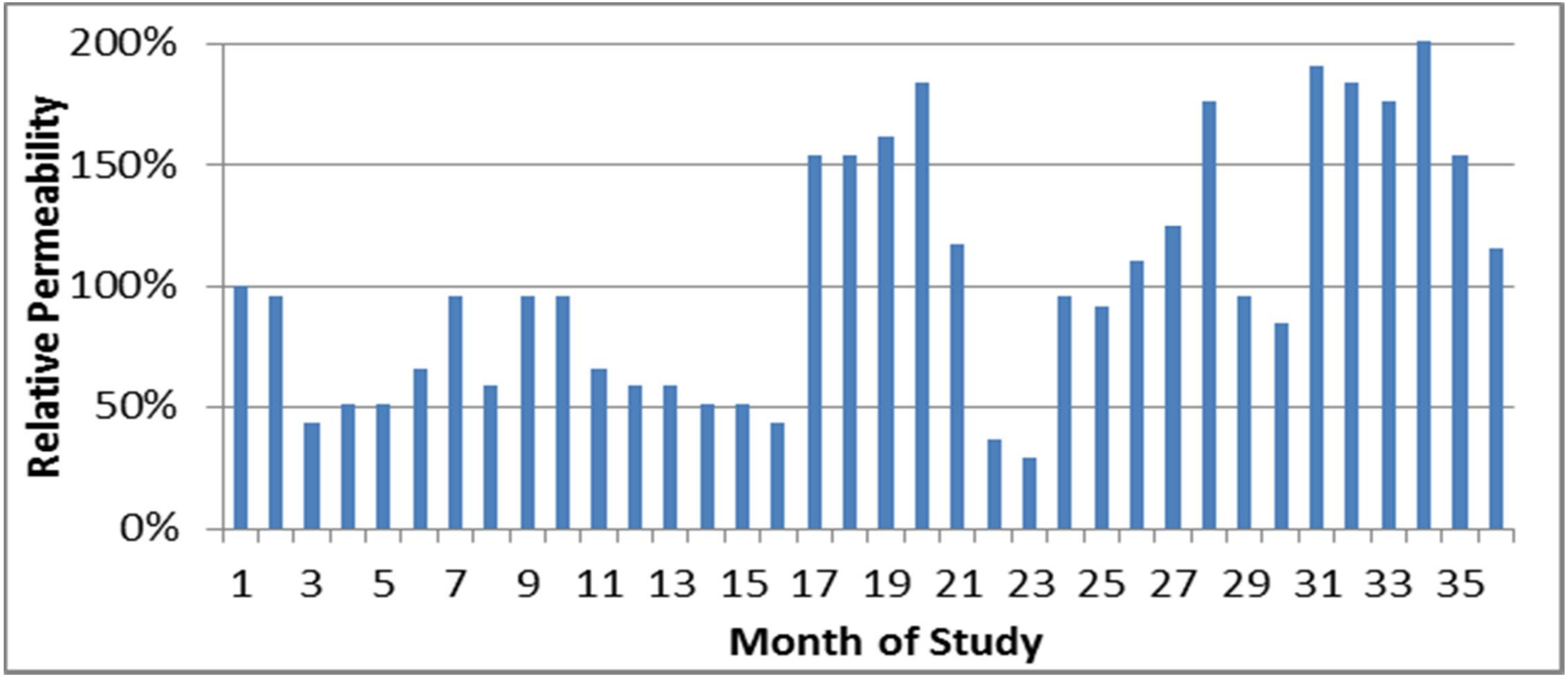
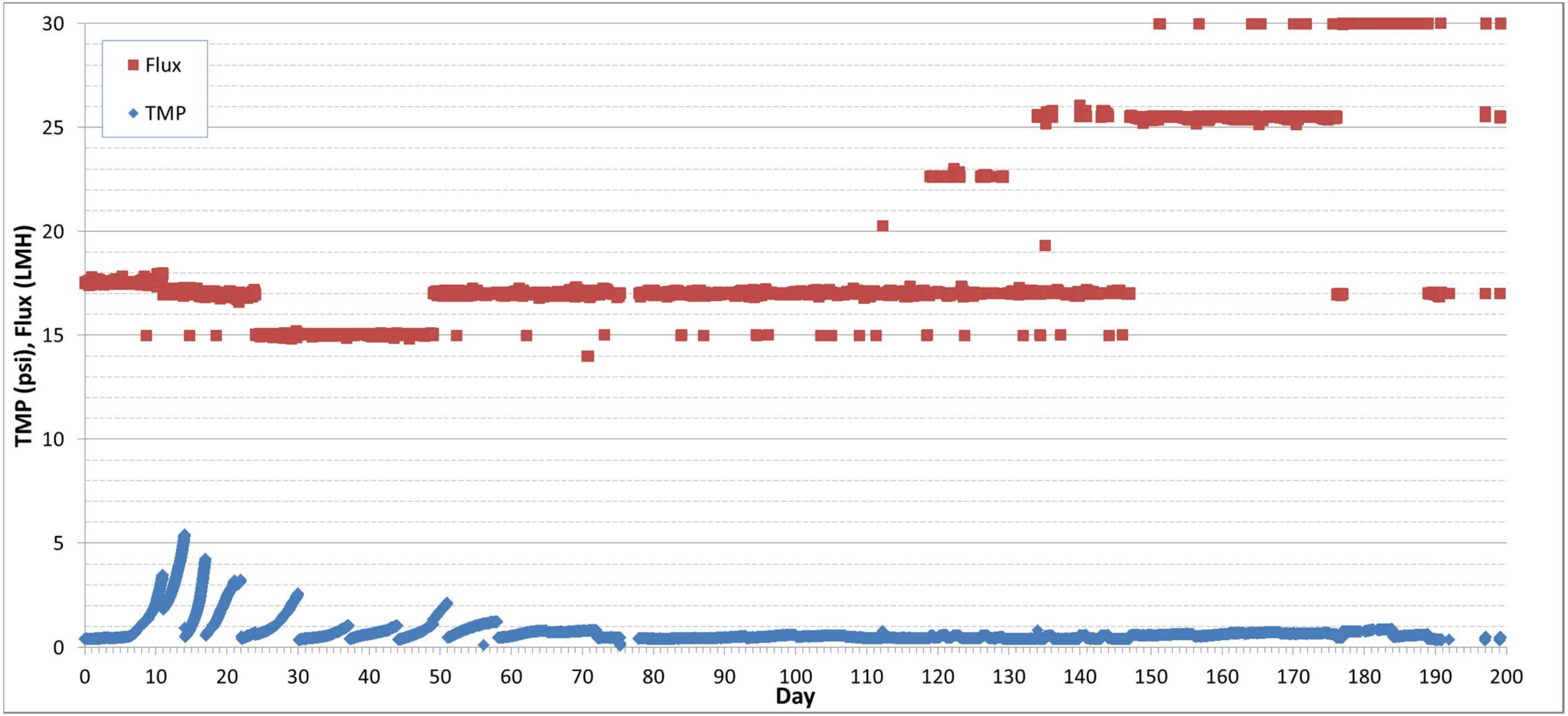
Back Up Slides

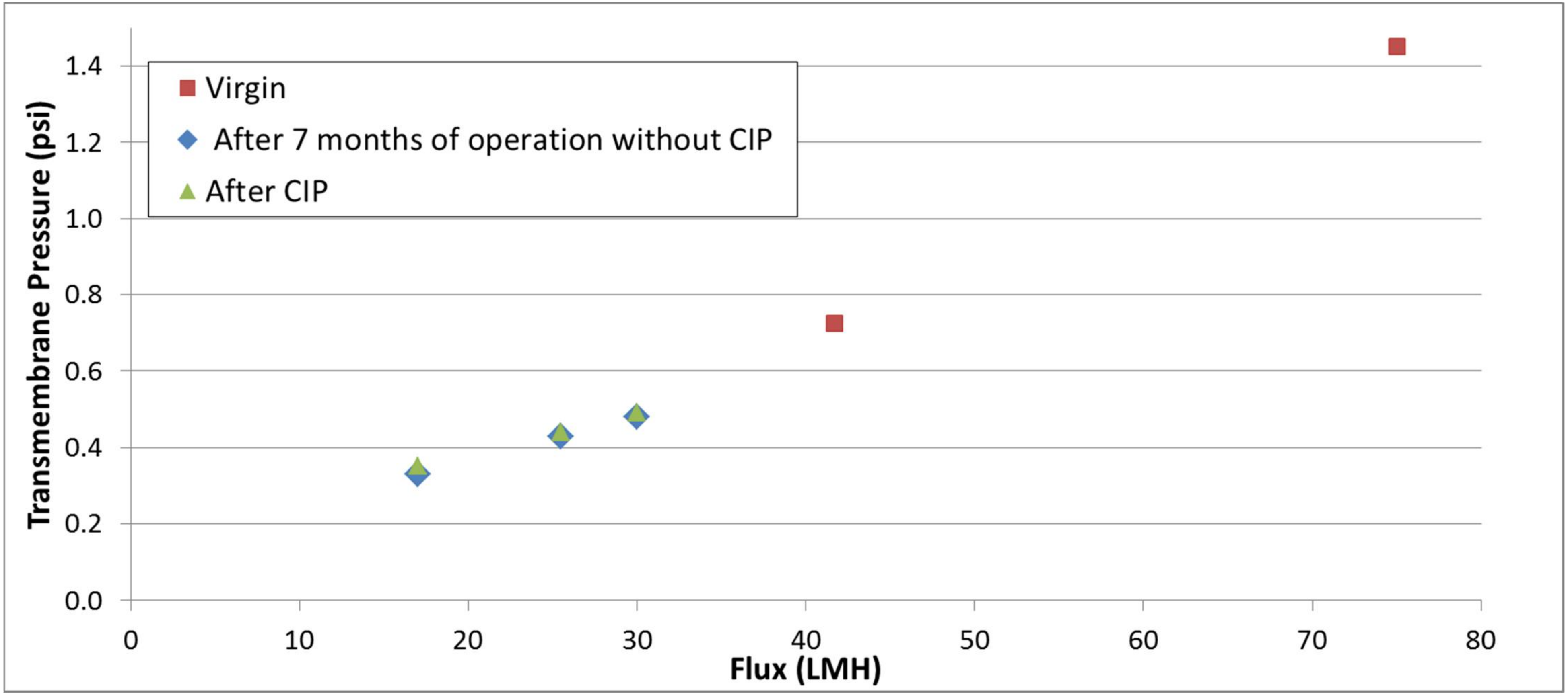
PACT MBR - Three Years of Maintained Permeability



PACT MBR Full Scale Results - High Solids Fouling, Or Not?



PACT MBR Full Scale Results - Maintaining High Permeability



Proof that carbon

Case Study:

Refinery Reuse with PACT / WAR

Treatment for direct reuse as cooling tower make-up

Case Study

Refinery required upgrades

- expansion – doubled capacity
- regulations

2016 start-up

PACT / WAR

- Solved organic treatment, nitrification, spare requirement problems

Koi fish pond demonstrating effluent following treatment

Drivers for industrial reuse

Water availability

Tight discharge limits or restrictions on discharge volume

High cost of water purchase/discharge vs. cost of wastewater treatment

Discharge permitting issues

Public image

Challenges for refinery wastewater reuse

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

Pretreating for reuse

Deoiling	• Removes free oil
Biological treatment	• Treats biodegradable organics • Converts organic and ammonia nitrogen to nitrogen gas
Carbon treatment	• Adsorbs recalcitrant organics • Adsorbs metals • Adorbs VOCs and odor
Solids removal	• Removal of biomass • Removal of activated carbon