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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Saudi Arabia</th>
<th>Oman</th>
<th>Jordan</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS (mg/L)</td>
<td>-</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Cl</td>
<td>100</td>
<td>650</td>
<td>400</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>-</td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>10</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>10</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>O&amp;G (mg/L)</td>
<td>Nil*</td>
<td>0.5</td>
<td>8*</td>
</tr>
<tr>
<td>Phenol (mg/L)</td>
<td>0.002</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Free O&G
### Reuse - How to Meet RO Feed Requirements?

<table>
<thead>
<tr>
<th>Reﬁnery Wastewater Post Deoiling</th>
<th>RO Feedwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>• COD 300-1000 mg/L</td>
<td>• COD – as low as possible</td>
</tr>
<tr>
<td>• BOD 125-350 mg/L</td>
<td>• TOC – membrane manufacturers recommend &lt;3 mg/L</td>
</tr>
<tr>
<td>• TSS 30-75 mg/L</td>
<td>• O&amp;G &lt; 0.1 mg/L</td>
</tr>
<tr>
<td>• O&amp;G 20-50 mg/L</td>
<td>• SDI &lt; 5 – lower the better</td>
</tr>
<tr>
<td>• Phenols 5-30 mg/L</td>
<td>• Turbidity &lt; 1 NTU with &lt; 0.5 NTU recommended for long-term, reliable operation</td>
</tr>
</tbody>
</table>
Conventional Approach to Pretreating Refinery Wastewater for Reverse Osmosis

**Influent Wastewater**

- **Aeration Tank**
  - Aeration
  - RAS

- **Clarifier**
  - Filter
  - Granular Carbon

- **Ultra-Filtration**

**Treated Effluent for reuse**

- **Reverse Osmosis**
- **Reject to disposal or concentration step**

**WAS Waste Tank**

- **Sludge Dewatering**
A Different Approach – Carbon Assisted MBR

Influent Wastewater → Carbon Assisted Activated Sludge → Membrane Operating System → Reverse Osmosis → Treated Effluent for reuse
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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (mg/L)</td>
<td>&lt;0.20 (detection limit)</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.10 – 0.18</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>26.75</td>
</tr>
</tbody>
</table>
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 launched Petro® PACT MBR
EcoRight™ Technology

- Upstream Deoiling
- Biomass + Granular Activated Carbon
- Isolation Device
- UF Membranes
- Treated Effluent
- Wastewater Feed
- WAS
- WAS and Waste Carbon
- Biofilm
Benefits and Limitations of the EcoRight™ MBR Treating Oily WW

**EcoRight™ 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™ 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

Influent Wastewater -> Carbon Silo

Aeration Tank

Aeration Tank -> Aeration Operating System

Aeration Tank -> RAS with carbon

WAS with carbon -> WAS Waste Tank

WAS Waste Tank -> Sludge Dewatering or WAR

Aerator with carbon

Reverse Osmosis

Treated Effluent for reuse

Reject to disposal or concentration step
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

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Material</th>
<th>Pore size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow fiber</td>
<td>PTFE</td>
<td>0.08</td>
</tr>
<tr>
<td>Hollow fiber</td>
<td>PVDF</td>
<td>0.04</td>
</tr>
<tr>
<td>Flat sheet</td>
<td>Ceramic (Alumina oxide)</td>
<td>0.1</td>
</tr>
<tr>
<td>Flat sheet</td>
<td>Ceramic (Alumina oxide)</td>
<td>0.5</td>
</tr>
<tr>
<td>Flat sheet</td>
<td>PSU/PVP with PET backing</td>
<td>0.1</td>
</tr>
<tr>
<td>Flat sheet</td>
<td>PES with PET backing</td>
<td>0.04</td>
</tr>
<tr>
<td>Flat sheet</td>
<td>Ceramic (SiC)</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Results from SEM Analysis

- PVDF Membrane that experienced abrasion
- Ceramic Membrane that showed no sign of damage
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)

SDI sample taken immediately following a maintenance clean

RO quality feedwater
PACT MBR Full Scale Results - Performance Data – Turbidity

![Graph showing turbidity over months. The graph compares Ceramic Membrane performance to the Recommended Limit. RO quality feedwater is indicated.]
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

Refrinery 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

<table>
<thead>
<tr>
<th>Process</th>
<th>Benefits</th>
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</thead>
<tbody>
<tr>
<td><strong>Deoiling</strong></td>
<td>• Removes free oil</td>
</tr>
<tr>
<td><strong>Biological treatment</strong></td>
<td>• Treats biodegradable organics</td>
</tr>
<tr>
<td></td>
<td>• Converts organic and ammonia nitrogen to nitrogen gas</td>
</tr>
<tr>
<td><strong>Carbon treatment</strong></td>
<td>• Adsorbs recalcitrant organics</td>
</tr>
<tr>
<td></td>
<td>• Adsorbs metals</td>
</tr>
<tr>
<td></td>
<td>• Adorbs VOCs and odor</td>
</tr>
<tr>
<td><strong>Solids removal</strong></td>
<td>• Removal of biomass</td>
</tr>
<tr>
<td></td>
<td>• Removal of activated carbon</td>
</tr>
</tbody>
</table>