Advanced Water Reuse in Petrochemical and Refining Facilities: Global Perspective and Case Studies

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Brown and Caldwell
Membrane Processes

• Pressure Driven Membrane Processes

• *Low Pressure Membranes*
  • Microfiltration (MF)
  • Ultrafiltration (UF)

• *High Pressure Membranes*
  • Nanofiltration (NF)
  • Hyperfiltration or Reverse Osmosis (RO)

• Electric Voltage-Driven Membranes
  • Electrodialysis (ED)
  • Electrodialysis Reversal (EDR)
## Relative Removal Capabilities of Pressure-Driven Membrane Processes

<table>
<thead>
<tr>
<th>Molecular Weight (approx..)</th>
<th>Ionic Range</th>
<th>Molecular Range</th>
<th>Separation Process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.001 (nanometer)</td>
<td>0.01</td>
<td>Reverse Osmosis</td>
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<tr>
<td></td>
<td>0.1</td>
<td>Macro Molecular Range</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>Micro Molecular Range</td>
<td>Microfiltration</td>
</tr>
<tr>
<td></td>
<td>100 Macro Particle Range</td>
<td>1000</td>
<td>Conventional Filtration (granular media)</td>
</tr>
<tr>
<td>Dissolved Salts (ions)</td>
<td>100</td>
<td>1,000</td>
<td>Nano filtration</td>
</tr>
<tr>
<td>Organics (e.g., Color)</td>
<td>100,000</td>
<td>500,000</td>
<td>MBR</td>
</tr>
<tr>
<td>Viruses</td>
<td>10,000</td>
<td>50,000</td>
<td>Membrane Bioreactor (MBR)</td>
</tr>
<tr>
<td>Bacteria</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
</tr>
<tr>
<td>Algae</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
</tr>
<tr>
<td>Cysts</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
</tr>
<tr>
<td>Clays</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
</tr>
<tr>
<td>Asbestos Fibers</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
</tr>
</tbody>
</table>
Drastic Increase of MF/UF Uses Since 1996

Global Low Pressure Installed Capacity
(Through December 2006)

Installed Capacity, MGD

- Annual Capacity
- Cumulative Capacity
Advanced Treatment forReuse Since Late 1990’s
• MF/UF Mostly Hollow Fiber Type
• Both Submerged and Pressure Configurations Used
• California Has >10 Advanced Treatment Plants
• Largest Pressure UF/RO is 100 mgd (Kuwait)
• Largest Submerged MF/RO is 70 mgd (OCWD GWRS)
• Singapore Has 5-6 UF/RO Plants Totaling >100 mgd (NEWater)
• Australia Has Several MF/RO or UF/RO Plants Totaling >65 mgd

MF/UF with RO for Municipal WW Reuse
History of Membrane Use in Petro Industries

• RO w/ DI for Boiler Feed and Process Uses
• UF/RO for Boiler Feed Pretreatment Since 1999
• VSEP RO for Selenium Removal from Stripped Sour Water
• MF/RO Treated Municipal Effluent for Boiler Feed in Refineries (e.g. Chevron w/ West Basin MWD and EBMUD)
• UF/RO for In-plant Reuse (Since 2000)
• MBR or MBR/RO for Compliance & In-plant Reuse
• ~30 UF or UF/RO Systems Since 2000 Worldwide
### Global Installations at Refinery (R)/Petrochemical (P) Sites as of 2014 (1/3)

<table>
<thead>
<tr>
<th>Location</th>
<th>Startup</th>
<th>Size (mgd)</th>
<th>Process/Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPCO, Kaohsiung, Taiwan</td>
<td>4/2000</td>
<td>2.4</td>
<td>UF (Koch) + RO (P)</td>
</tr>
<tr>
<td>PEMEX, Minatitlan, Mexico</td>
<td>11/2001</td>
<td>6.9</td>
<td>ZW Tertiary + RO (R)</td>
</tr>
<tr>
<td>Marathon Oil, KY, USA</td>
<td>7/2003</td>
<td>0.05</td>
<td>ZW MBR (Oil Barge)</td>
</tr>
<tr>
<td>MOL Rt., Hungary</td>
<td>11/2003</td>
<td>0.13</td>
<td>ZW MBR (R)</td>
</tr>
<tr>
<td>Borsodchem, Hungary</td>
<td>5/2004</td>
<td>0.16</td>
<td>ZW MBR + RO (R)</td>
</tr>
<tr>
<td>Beijing Yanshan, China</td>
<td>7/2004</td>
<td>6.8</td>
<td>ZW Tertiary + RO (P)</td>
</tr>
<tr>
<td>Sinopec Yanshan, China</td>
<td>2005</td>
<td>3.6</td>
<td>UF (DOW) + RO (R)</td>
</tr>
<tr>
<td>Syndial, Porto Marghera, Italy</td>
<td>11/2005</td>
<td>12.5</td>
<td>ZW MBR (P)</td>
</tr>
<tr>
<td>FHR Pine Bend Refinery, Minnesota, USA</td>
<td>2006</td>
<td>1.4</td>
<td>UF (GE MW Series) + RO (R)</td>
</tr>
<tr>
<td>Formosa Plastics, Taiwan</td>
<td>3/2006</td>
<td>6.6</td>
<td>ZW MBR (P)</td>
</tr>
<tr>
<td>Syndial, Manfredonia, Italy</td>
<td>9/2006</td>
<td>0.76</td>
<td>ZW Tertiary (P)</td>
</tr>
</tbody>
</table>
## Global Installations at Refinery/Petrochemical Sites as of 2014 (2/3)

<table>
<thead>
<tr>
<th>Location</th>
<th>Startup</th>
<th>Size (m³/d)</th>
<th>Process/Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENI R&amp;M, Taranto, Italy</td>
<td>9/2006</td>
<td>3.5</td>
<td>ZW MBR + RO (R)</td>
</tr>
<tr>
<td>Sasol Secunda, South Africa</td>
<td>2006</td>
<td>3.3</td>
<td>ZW + RO (R)</td>
</tr>
<tr>
<td>Indian Oil Corp., Panipat, Haryana, India</td>
<td>12/2006; 7/2009</td>
<td>5.7; 5.7</td>
<td>UF (Norit) + RO + ZLD (R/P)</td>
</tr>
<tr>
<td>Chennai Petro Corp., Tamil Nadu, India</td>
<td>2007</td>
<td>2.5</td>
<td>UF (Norit) + RO (R)</td>
</tr>
<tr>
<td>Conoco Philips, Hull, UK</td>
<td>7/2007</td>
<td>3.8</td>
<td>ZW Tertiary + RO (R)</td>
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<tr>
<td>Pars Refinery, Iran</td>
<td>2007</td>
<td>0.51</td>
<td>ZW MBR (R)</td>
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<tr>
<td>Bina Refinery, India</td>
<td>12/2008</td>
<td>2.4</td>
<td>ZW MBR (P)</td>
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<tr>
<td>Jamnagar Refin., India</td>
<td>1/2009</td>
<td>0.70</td>
<td>HERO™ (R)</td>
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<tr>
<td>HPCL Refinery, India</td>
<td>4/2009</td>
<td>1.9</td>
<td>ZW MBR (R)</td>
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<tr>
<td>REVAP Refinery, (Petrobras) Brazil</td>
<td>6/2010</td>
<td>1.9</td>
<td>ZW MBR (R)</td>
</tr>
<tr>
<td>HPCL Mittal Refinery, India</td>
<td>10/2010</td>
<td>3.2</td>
<td>ZW MBR + RO (R)</td>
</tr>
</tbody>
</table>
## Global Installations at Refinery/Petrochemical Sites as of 2014 (3/3)

<table>
<thead>
<tr>
<th>Location</th>
<th>Startup</th>
<th>Size (mgd)</th>
<th>Process/Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bina Refinery, India</td>
<td>2011</td>
<td>2.4</td>
<td>ZW MBR (R)</td>
</tr>
<tr>
<td>Taneco Refinery, Phase I, Russia</td>
<td>2011</td>
<td>4.4</td>
<td>ZW MBR + EDR + RO (R)</td>
</tr>
<tr>
<td>Antipinsky, Russia</td>
<td>2013</td>
<td>2.4</td>
<td>ZW MBR (R/P)</td>
</tr>
<tr>
<td>Novokuibyshevsk, Russia</td>
<td>2013</td>
<td>15.9</td>
<td>ZW MBR</td>
</tr>
<tr>
<td>CCRL, SK, Canada</td>
<td>2014</td>
<td>2.3</td>
<td>MBR + HERO (R)</td>
</tr>
<tr>
<td>Petrobras Comperj, Brazil</td>
<td>2014</td>
<td>4.8</td>
<td>ZW MBR (R)</td>
</tr>
<tr>
<td>CPC Lin Yuan, Taiwan</td>
<td>2014</td>
<td>1.0</td>
<td>MBR + RO (P)</td>
</tr>
<tr>
<td>Bashneft Refinery</td>
<td>(2015)</td>
<td>22</td>
<td>ZW MBR + EDR + RO + AO</td>
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<tr>
<td>Eagle Ford Refinery, TX. USA</td>
<td>(2015)</td>
<td>0.19</td>
<td>ZW MBR (R)</td>
</tr>
<tr>
<td>Marathon Oil, MI. USA</td>
<td>(2015)</td>
<td>4.6</td>
<td>ZW MBR (R)</td>
</tr>
</tbody>
</table>
3 Representative Case Studies

- CAPCO Petrochemical UF/RO WW Reclamation System in Kaohsiung, Taiwan
- PEMEX Minatitlan Refinery UF/RO Water Reuse System in Mexico
- Sasol Synfuels Refinery, South Africa
Case Study No. 1 – CAPCO UF/RO Plant

- CAPCO is One of the Largest PTA Plants in the World
- Large Water Consumption for Cooling Water and High Purity Water for Boilers and Process
- Identified In-plant Water Reuse Project in a 1994 Water Management Study
- Completed Pilot Testing in 1995-96
- Completed Advanced Reuse Treatment Plant Construction in 1999
- Commissioned in 2000
- Successfully Operated for >14 Years
Relation of Wastewater Reclamation System with Plant Water Systems at CAPCO, Taiwan

Water Company

- Cooling Towers
  - C.T. Blowdown
  - Reclaimed Water

- Deionization System
  - DI Water
  - DI Regeneration Waste

- Process and Boilers
  - Process Wastewater

- Organic WWTS
  - Inorganic WWTS
  - Treated Effluent

- Wastewater Reclamation System
  - UF/RO Rejects

- Other Plant Uses
  - Misc. Wastewater
  - Discharge to Joint WWTP
Wastewater Recovery Treatment System Block Flow Diagram
Full Scale Implementation

- **First Phase**: 2.4/1.8 mgd
- **Design/Build**: 2 Years
- **Space Limitation**: Four-Story Building
- **Capital Cost**: US $15 Million
- **Commissioned**: April 2000
Full Scale Plant

Four-Story Building
Vertical GAC Filters

Horizontal Dual Media Filters
UF Cartridges (Koch PM100)
14 Years of Performance at CAPCO - UF

- Flux: 85.9 L/m²/h (50.6 gfd)
- Recovery: 92%
- Effluent Turbidity: <0.1 NTU
- 5 Koch UF Skids – Each w/ 109 6-inch PM100 Cartridges
- CIP Frequency: 4 Weeks
- Average Membrane Life: 6 Years
- Converted to 10-in Cartridge System
Converted 10-inch UF System
14 Years of Performance at CAPCO - RO

• 8 Trains of 2-Stage RO w/ 5:3 Array
• Membrane: Filmtech BW30-400
• Flux: 22 L/m²/h (13 gfd)
• Recovery: 80%
• Initial Chlorine Oxidation Caused Replacement of Membranes in 5 Trains
• Subsequent CIP Frequency: 1-2 years
• Average Membrane Life: >4 Years
Case Study No. 2 – PEMEX Refinery, Mexico

- One of Mexico’s largest refineries (173,200 bpd)
- Located in Minatitlan, Mexico
- WW treatment allows for recycle
- Design WW flow rate of 300 L/s (7 MGD)

- Treatment includes:
  - Dissolved air flotation
  - Conventional Biological Treatment
  - ZeeWeed UF Tertiary Filtration
  - Reverse Osmosis
- Overall water recycle efficiency is approximately 70% based on RO permeate
PEMEX Refinery, Mexico

- ZeeWeed system design:
  - Peak Flow – 300 L/s (~ 6 MGD)
  - Recovery- 90 to 95%
  - 7 parallel ZW500b trains (6 operating + 1 standby)
  - 11 cassettes per train (expandable to 15)

- Effluent Quality Requirements:
  - TSS < 1 mg/l
  - Turbidity < 0.1 NTU
  - SDI < 3

- Commissioned in November 2001
PEMEX – Flow Diagram

- Refinery Wastewater 333 Lps
- Bioreactor
- Oil/Water Separator
- Secondary Clarifier
- ZeeWeed® UF Operating at 90% Recovery
  8 Trains of 11 cassettes of ZW500b Elements

- UF Permeate 300 Lps < 0.2 NTU < 3 SDI
- UF Rejection 33 Lps
- RO Permeate 240 Lps for Recycle to Refinery

- Reverse Osmosis System Operating at 80% Recovery
- RO Reject 60 Lps
PEMEX Refinery, Mexico

GE Process Trains

GE Building
Case Study No. 3 - Sasol Synfuels Refinery, South Africa

- Sasol Synfuels operates the world’s only coal-based synfuels manufacturing facility located at Secunda Refinery
- Produces synthesis gas from coal
- Intermediate products: most of South Africa’s chemical building blocks including ethylene, propylene, ammonia, phenolics & solvents
- Final products: petrol, diesel, liquefied petroleum gas, chemical feedstocks and industrial pipeline gas
Sasol, South Africa

- Sasol Synfuels current production capacity: equivalent to a 170,000 bpd conventional oil refinery
- Supplies >20% of the country’s fuel needs
- South Africa began importing fuel in 2006 because its refineries have hit capacity constraints
- Pressure to boost Synfuel output from its Secunda plant by up to 20% over the next nine years
- Impending cleaner fuels legislation also required refinery changes
Sasol, South Africa

- Refinery and Polymer Manufacturing Expansion
  Increased Water Demand by 3.6 mgd
- Local Water Supply Limited
- Treat & Recycle Cooling Tower BD to Meet Additional Water Demand
- 5.3 mgd $\rightarrow$ 3.6 mgd RO Demineralized Water + 1.0 mgd Mixed Bed Polished Water
- Total Recovery = 67%
Sasol, South Africa

CT Blowdown Treatment Processes:

- Fine Screening
- Cold-Lime Softening w/ Silica Removal (Multiflo)
- ZeeWeed 500 UF
- Ion Exchange Softening
- RO
- Partial Mixed Bed Demineralization

Sasol Secunda Refinery
Sasol, South Africa

5.3 mgd ZeeWeed UF System:

• 3 trains x 4 cassettes (+ 1 spare)
  ZeeWeed 500 UF membranes
  (48 modules/cassette)

• Sequential aeration
  (low energy)
Discussions and Conclusions

• The History of Using Membranes for In-plant Reuse at Petro Facilities Started in 2000 (CAPCO)
• Approx 30 Significant UF/RO, MBR and MBR/RO Systems Installed as of 2014
• Several New Projects are Expected to be Online in 2015

• Pilot Testing Projects Conducted (USA, Middle East, Others)
• Some Unsuccessful Projects Not Reported
• Membranes are Capable of Treating Petro Wastewaters
• Pilot Testing is Recommended Prior to Implementation
Questions?

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