Membranes for Water Treatment: Properties and Characterization

Ingo Pinna, Ph.D.
<table>
<thead>
<tr>
<th>Process</th>
<th>Separation Mechanism</th>
<th>Pore Size (Å)</th>
<th>Transport Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Filtration</td>
<td>Size Exclusion</td>
<td>&gt; 50,000</td>
<td>Macropores</td>
</tr>
<tr>
<td>Microfiltration (MF)</td>
<td>Size Exclusion</td>
<td>500 - 50,000</td>
<td>Macropores</td>
</tr>
<tr>
<td>Ultrafiltration (UF)</td>
<td>Size Exclusion</td>
<td>20 - 500</td>
<td>Mesopores</td>
</tr>
<tr>
<td>Reverse Osmosis (RO)</td>
<td>Solution/Diffusion</td>
<td>&lt; 10</td>
<td>Molecular (Nonporous)</td>
</tr>
</tbody>
</table>
Membrane Characteristics: Porous Membranes

**Microfiltration**

- Water
- Monovalent ions
- Multivalent ions
- Viruses
- Bacteria
- Suspended solids

**Ultrafiltration**

- Water
- Monovalent ions
- Multivalent ions
- Viruses
- Bacteria
- Suspended solids

MTR
Membrane Technology & Research

National Water Research Institute
Membrane Characteristics:
Non-Porous Membranes

Nanofiltration

Reverse Osmosis
Ideal Membranes for UF, NF and RO Applications

- High water flux (low capital cost)
- High solute rejection (high water purity)
- Long-term stability of water flux and rejection (Membrane fouling)
- Mechanical, chemical and thermal stability
- Minimum pre-treatment (backflushing and chemical treatment)
- Can be processed into large-scale membranes and modules
- Inexpensive!
Problems of Current Membranes Used in UF and RO Applications

- Poor long-term stability of water flux (Membrane Fouling)
- Backflushing and chemical treatment
- High membrane replacement cost
- Poor resistance to chlorine
- Membrane system size
Major Foulant Types in Natural and Industrial Wastewater

- Scaling
- Colloidal Fouling
- Organic Fouling
- Biofouling
Surface Structure of a Typical UF Membrane

PEI membrane surface, x 80000, ---- 0.1μm
Membrane Separation Processes and Characteristics

Unfouled Membrane

- Porous Surface

Fouled Membrane

- Surface Fouling
- Internal Fouling
Schematic Structures of Porous and Non-Porous UF Membranes

**Microporous Ultrafiltration Membrane**
- Selective skin layer
- Porous substrate

**Non-Porous Ultrafiltration Membrane**
- Non-porous hydrophilic
- Surface coating (0.1-0.5 µm)
- Porous substrate
Cross-Section of a Non-Porous UF Membrane

Nonporous Polymer Coating Layer (~ 0.3 µm)

Microporous Support Membrane
Long-Term Water Flux of Porous and Non-Porous Ultrafiltration Membranes

Water flux (L/m²•h) vs. Permeation Time (Days)

- Microporous PVDF module
- Non-porous Pebax 1074/PVDF module

Feed: 1% motor oil in water
Feed pressure: 150 psig
Feed temperature: 23°C

Water flush

Pure water
Fouling Index of Porous and Non-Porous Ultrafiltration Membranes for Separation of Oil/Water Emulsions

Fouling Index $\frac{H_2O(t)}{H_2O(0)}$

Permeation Time (Days)

Microporous PVDF module

Pebax 1074 module

pure water

water flush

0.01 0.1 1

Permeation Time (Days)
Long-Term Permeation Properties of Porous Ceramic and Ceramic/Polymer Composite Membranes

Feed: Bilge water; permeate flux: 40 gfd

Permeation Resistance (psi/gfd)

Time (hours)

Ceramic Module

Ceramic/Pebax 1074 Module

Backflush
Membrane Types Used in Ultrafiltration, Nanofiltration and Reverse Osmosis

Integral asymmetric membrane (Cellulose acetate)

- Selective layer (Material A)
- Microporous substrate (Material A)

Thin-film composite membrane (Polyamide)

- Selective layer (Material A)
- Microporous substrate (Material B)
## 2003 RO/NF Membrane Sales

<table>
<thead>
<tr>
<th>Company</th>
<th>Sales ($ MM)</th>
<th>Share (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow/Filmtech</td>
<td>115</td>
<td>34</td>
</tr>
<tr>
<td>Nitto Denko/Hydranautics</td>
<td>99</td>
<td>30</td>
</tr>
<tr>
<td>Toray</td>
<td>36</td>
<td>11</td>
</tr>
<tr>
<td>GE Osmonics</td>
<td>27</td>
<td>8</td>
</tr>
<tr>
<td>Koch/Fluid Systems</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>Toyobo</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>TriSep</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Others</td>
<td>15</td>
<td>4</td>
</tr>
</tbody>
</table>

(Supplement of *Ultrapure Water* 21, 2004)
### 2003 RO/NF Module Sales Distribution

<table>
<thead>
<tr>
<th>Module Type</th>
<th>Market Share (%)</th>
</tr>
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<tbody>
<tr>
<td>Polyamide spiral-wound (8’x40’)</td>
<td>91</td>
</tr>
<tr>
<td>Cellulose acetate hollow fiber module</td>
<td>5</td>
</tr>
<tr>
<td>Plate-and-frame</td>
<td>4</td>
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</tbody>
</table>

- Expected RO/NF membrane lifetime ~ 3-5 years.
- Actual RO/NF membrane lifetime ~ 7-12 years.
- Membrane replacement makes up for ~ 60% of annual sales.

(Supplement of *Ultrapure Water 21, 2004*)
Incremental Changes in Spiral-Wound RO Module Performance

Figure of Merit = \((\text{Productivity}) \times (\frac{1}{\text{Salt Passage}})\)

Cost

<table>
<thead>
<tr>
<th>Year</th>
<th>Cost (Normalized to 1980 U.S.$)</th>
<th>Productivity (Normalized to 1980)</th>
<th>Reciprocal Salt Passage (Normalized to 1980)</th>
<th>Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>1985</td>
<td>0.65</td>
<td>1.10</td>
<td>1.56</td>
<td>2.6</td>
</tr>
<tr>
<td>1990</td>
<td>0.34</td>
<td>1.32</td>
<td>2.01</td>
<td>7.9</td>
</tr>
<tr>
<td>1995</td>
<td>0.19</td>
<td>1.66</td>
<td>3.52</td>
<td>30.8</td>
</tr>
<tr>
<td>1999</td>
<td>0.14</td>
<td>1.94</td>
<td>7.04</td>
<td>99.3</td>
</tr>
</tbody>
</table>

Dave Furukawa (1999)
Interfacial Polymerization for Preparation of Thin-Film Composite RO Membranes

- Aqueous amine solution
- Porous support
- Hydrocarbon/acid chloride solution
- Heat cure
- Polyamide layer ~ 0.1-0.2 µm
Formation of FT 30 Thin-Film Composite Membrane

\[
\text{NH}_2 + \text{CIOCl} \rightarrow \text{NHCO} \quad \text{CO} \quad \text{COOH}
\]
Formation of PEC 1000 Thin-Film Composite Membrane

Chemical reactions involved in the formation of PEC 1000 thin-film composite membrane.

Reaction formula:

\[
\text{HOH}_2\text{CH}_2\text{C} + \text{C}(\text{HOH})_2\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4 \rightarrow \text{Product}
\]
Rejection and Water Flux of RO Seawater Desalination Membranes

NaCl rejection (%)

99.99
99.98
99.95
99.9
99.9
99.5
99.3
99
98
97
96
95
90
0.01
0.1
1.0
10

Riley (1991)
Cellulose triacetate
Crosslinked polyether (Toray PEC-1000)
Crosslinked fully aromatic polyamide (SWC, SW-30)
Linear fully aromatic polyamide (PermaSep)
Other thin-film interfacial composite membranes (NS100, PA 300 type)
Asymmetric cellulose diacetate membranes

Minimum rejection for single-stage seawater operation

Flux (m³/m²-day)
Organic Solute Rejection of Commercial RO Membranes
Surface Structures of Interfacial Aromatic Polyamide Composite Membranes

Cross-Section of Interfacial Polyamide Composite Membranes (BW 30)

Ridge and valley structure
~ 0.2 - 0.5 μm

Selective layer
~ 500 - 1,000 Å
Surface Structure of Uncoated and Coated RO Membranes

Uncoated

Coated
Surface Structure of Uncoated and Coated RO Membranes (AFM)

ESPA-3

ESPA-3 - coated

AFM pictures courtesy of Jennifer Louie, Stanford University
Performance of Commercial and Modified RO Membranes for Wastewater Treatment

Feed: 900 ppm mineral oil; 100 surfactant DC 193
Pressure: 500 psig
Temperature: 25°C
Financial support was provided by Office of Naval Research and SERDP

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