Industrial applications for RO and NF membranes have historically been limited to treatment of saline waters that may contain select organic species. These limitations have been due to the fact that traditional spiral wound RO and NF elements contain materials which can not tolerate aggressive solvents or harsh operating conditions. Also, these applications often have a propensity to foul membranes, and thus require membranes that can be aggressively cleaned.

The HYDRACoRe sulfonated polyethersulfone (SPES) membrane is a tight UF membrane which has a molecular weight cut-off around 1000 Daltons. It is a specialized composite membrane consisting of a 0.3 μm SPES separating layer, and a polysulfone support coated on a robust fabric material. Since it is made of polysulfone material, it has much greater chemical tolerance that the standard polyamide membrane. It can tolerate a continuous dose of 5 mg/l hypochlorite solution or shock cleaning with 200 mg/l of hypochlorite. Additionally, it can tolerate high and low pH solutions (pH 2-13), even at elevated temperatures. Another important characteristic of the HYDRACoRe membrane is its smooth surface relative to typical polyamide membranes. The HYDRACoRe membrane was initially used to treat chlorinated industrial wastewater, including highly colored streams from pulp and paper manufacturing (Ikeda, 1988). HYDRACoRe membranes have also been used to remove color from soy sauce and color from highly colored ground water (Spangenberg, 2002).

Recently, the HYDRACoRe has been prepared with a higher rejection SPES separating layer and with element materials which are stable at pH 13 and high temperature, up to 80°C. This configuration of the HYDRACoRe membrane is particularly suited to treating industrial wastewater effluents which come from caustic cleaning operations. The UF nature of this membrane can remove organic material from used caustic cleaning solutions so that the caustic solution can be reclaimed. Additional savings can be realized by treating the hot caustic solution so that caustic rinse water does not need to be cooled and reheated. This is an attractive alternative to adsorption technologies which have been traditionally used to decolorize these wastewaters.

A lab scale pilot test was run to prove the concept of reclaiming caustic wash water from a sugar fractionation process. When the decolorizing resin becomes loaded with the sugar impurities and color, it is regenerated with a high pH, high temperature (60°C) sodium chloride (10 to 14%) and sodium hydroxide (0.5 to 2%) solution. This waste stream was then treated with the HYDRACoRe70-pHT. Although initial testing showed fouling effects, these were managed with proper chemical treatment. Pilot data showed that 88% of the color was rejected by the HYDRACoRe-70pHT while 43% of the largest
sugar molecule, raffinose (594 Daltons) was rejected and 23% of the fructose (180 Daltons) was rejected.

After the HYDRACoRe-70pHT was successfully piloted, a number of plants of various sizes were installed. Based on plants currently in operation and the extensive piloting, a cost analysis has been done relating membrane performance to processing a metric ton of raw sugar to product. Our analysis shows that the nanofiltration membrane process saves approximately $0.50 per metric ton of raw sugar processed. Thus, plants of 1,000 to 4,000 metric tons /day refining capacity could realize a payback on the membrane system equipment within one year.

In summary, the HYDRACoRe-70pHT membrane effectively decolorizes and purifies brine regenerant under high pH and high temperature conditions while generating considerably less waste and less caustic to be neutralized.

References


Chemically Tolerant NF Membranes for Aggressive Industrial Applications

Craig R. Bartels, PhD
Rich Franks
Jeff Campbell

Hydranautics
Oceanside, CA
Membrane Process Applications: High pH Feed Streams

- Spent caustic recovery from clean-in-place of evaporators in the dairy industry (0.1 to 0.4% caustic)
- Recovery of wastewater from the mercerization of cotton fabrics (1.0 to 4.8% caustic)
- Removal of oxalate and other organic contaminants from sodium aluminate and sodium hydroxide in Bayer process streams (up to 17 wt-% caustic equivalent)
- Recovery of sodium hydroxide as an active chemical from bottle washing effluents of the beverage industry
- Separation of hemicellulose from process liquors in the production of viscose-type cellulosic textile fibers from wood (17 wt-% caustic soda)
- Color removal from alkaline effluents from ion exchange resin regeneration in the sugar industry.
<table>
<thead>
<tr>
<th>Micrometers</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
<th>1.0</th>
<th>10</th>
<th>100</th>
<th>1000</th>
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<tr>
<td>Angstrom Units</td>
<td>Ionic Range</td>
<td>Molecular Range</td>
<td>Macromolecular Range</td>
<td>Micro Particle Range</td>
<td>Macro Particle Range</td>
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<tr>
<td>10</td>
<td>100</td>
<td>1000</td>
<td>$10^4$</td>
<td>$10^5$</td>
<td>$10^6$</td>
<td>$10^7$</td>
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**Detection**

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<tr>
<th>Relative</th>
<th>ST Microscope</th>
<th>Scanning Electron Microscope</th>
<th>Optical Microscope</th>
<th>Visible to the Naked Eye</th>
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<tr>
<td>Aquatics</td>
<td>Carbon Black</td>
<td>Paint Pigment</td>
<td>Pollens</td>
<td>Beach Sand</td>
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<td>Pyrogens</td>
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<tr>
<td>Metals</td>
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<td>Yeast Cells</td>
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<tr>
<td>Viruses</td>
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<td>Bacteria</td>
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<td>Common</td>
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<td>Antibiotics</td>
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<td>Milled Flour</td>
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<td>Proteins</td>
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<td>Material</td>
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<td>Colloidal Silica</td>
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<td>Coal Dust</td>
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<td>Latex / Emulsion</td>
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<tr>
<td>Filtration Technology</td>
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<td>Reverse Osmosis</td>
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<td>Microfiltration</td>
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<td>Particle Filtration</td>
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**The Filtration Spectrum**
# Commercial Membranes for Treatment of Caustic Process Fluids

Survey of alkali resistant nanofiltration and tight ultrafiltration membranes used in this study

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Microdyn-Nadir</th>
<th>Koch</th>
<th>Nitto-Denko</th>
<th>Osmonics</th>
<th>DSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane Material</td>
<td>N30F Polyethersulfone hydrophilized</td>
<td>SelRO MPF-34 Composite</td>
<td>NTR-7470 polyester based</td>
<td>G-5 (GE) Proprietary</td>
<td>GR95PP Polyethersulfone on polypropylene support</td>
</tr>
<tr>
<td>Nominal MWCO, g/mol</td>
<td>500&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>200–300&lt;sup&gt;d&lt;/sup&gt;</td>
<td>200–250</td>
<td>1000&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2000</td>
</tr>
<tr>
<td>Water permeability, L/(m&lt;sup&gt;2&lt;/sup&gt;hbar)</td>
<td>1–1.75&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2&lt;sup&gt;g&lt;/sup&gt;</td>
<td></td>
<td>1.23&lt;sup&gt;h&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Max. temperature, °C</td>
<td>95</td>
<td>70</td>
<td>60</td>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>Max. pressure, bar</td>
<td>40</td>
<td>35</td>
<td>up to 20% NaOH</td>
<td>35&lt;sup&gt;i&lt;/sup&gt;</td>
<td>40</td>
</tr>
<tr>
<td>pH range</td>
<td>0–14</td>
<td></td>
<td>15% NaOH at 60°C</td>
<td></td>
<td>1–14</td>
</tr>
<tr>
<td>NaCl retention, %</td>
<td>25–35&lt;sup&gt;j&lt;/sup&gt;</td>
<td></td>
<td>70&lt;sup&gt;k&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; retention, %</td>
<td>85–95&lt;sup&gt;l&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Special features</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tolerates 100 ppm Cl&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> special alkaline resistant type
<sup>b</sup> estimated from manufacturer’s retention data
<sup>c</sup> test conditions: 4% lactose, 40 bar, 20°C
<sup>d</sup> test conditions: 5% glucose, 30 bar, 30°C
<sup>e</sup> test conditions: Polyethylene glycols, 1000 mg/l, 25°C, 8.3 bar
<sup>f</sup> at 20°C
<sup>g</sup> at 30°C
<sup>h</sup> 25°C, 27.6 bar
<sup>i</sup> c = 0.5%, 40 bar, 20°C, 700 rpm
<sup>j</sup> c = 5%, 30 bar, 30°C
<sup>k</sup> c = 1500 ppm, 25°C
<sup>l</sup> c = 1.0%, 40 bar, 20°C, 700 rpm

Evaluation of alkali resistant nanofiltration membranes for the separation of emicellulose from concentrated alkaline process liquors
Robert Schlesingera, Gerhard Götzingerb, Herbert Sixtab, Anton Friedlc, Michael Harasekc*
Commercial Membranes for Treatment of Caustic Process Fluids

- SelRO MPF Composite
  - Koch Membranes
  - 200-300 MWCO
  - Up to 20% NaOH
  - 70 C

- Polyethersulfone Variants
  - Osmonics, DSS, Microdyne-Nadir
  - 1000-2500 MWCO
  - pH 1-14
  - 70-80 C
HYDRACoRe Development

- Nanofilter: MWC = 1000 Daltons
- First Developed: 1980s
- Developed by: Nitto Electric Industrial Co
- Designation: NTR-7450
- Application: Color Separation - Soy Sauce
Spiral Wound Element

Microns = $1 \times 10^{-6}$ meters

Sulfonated polyethersulfone

Polysulfone Layer

Polyester Base
Membrane Characterization
Barrier Layer Cross-Section and Charge Density

TEM of HYDRACoRe Surface.
1 micron:

Sulfonated Polyethersulfone

Polysulfone Porous Support

Relationship between ion-exchange capacity and flux/rejection for various HYDRACoRe membranes
Membrane Characterization
Barrier Layer Cross-Section and Charge Density

Rejection (%) vs. Flux (gfd)

IEC = 1 meq/g

0.5% NaCl aq.
5MPa
25°C
Membrane Characterization

Surface Charge: Negative

![Graph showing surface zeta potential vs pH for different types of membranes]

- Cationic RO memb. (LFC2)
- Neutral RO memb. (LFC1)
- Amphoteric RO memb. (CPA2)
- Anionic NF memb. (HYDRACoRe)
Membrane Characterization
Smooth Surface

HYDRACoRe Membrane

Polyamide Membrane
Membrane Characterization
Ion Separation Properties

![Bar graph showing rejection (%) for different salts]

- **Salts**
  - Na2SO4
  - NaCl
  - MgSO4
  - MgCl2
  - CaCl2

- **Rejection (%)**

  - Na2SO4: 15
  - NaCl: 90
  - MgSO4: 50
  - MgCl2: 70
  - CaCl2: 40
  - HYDRACoRe: 30

- **Values**
  - 0
  - 20
  - 40
  - 60
  - 80
  - 100
Membrane Characterization

Salinity Effect

![Graph showing NaCl rejection vs. feed salinity]
Membrane Characterization

Chemical Stability

Retention Rate of Rej. [%]

Immersing Period [day]

HYDRACoRe memb. [1000ppm]

CA memb. [100ppm]

Composite Polyamide [20 ppm]
## Membrane Characterization
### Chemical Stability

<table>
<thead>
<tr>
<th>Chemical Agent</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid</td>
<td>pH 2</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>pH 2</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>pH 2</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1%</td>
</tr>
<tr>
<td>Oxalic Acid</td>
<td>2%</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>2%</td>
</tr>
<tr>
<td>EDTA</td>
<td>2%</td>
</tr>
<tr>
<td>Sodium Hydrogensulfate</td>
<td>2%</td>
</tr>
<tr>
<td>NaOH</td>
<td>pH 13</td>
</tr>
<tr>
<td>Sodium hypochlorite</td>
<td>200 ppm</td>
</tr>
<tr>
<td>Formalin</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
Applications
Groundwater Color Removal

Irvine Ranch Water District
3 Trains
434 Elements per Train
Feed = 340 cu. Perm = 3 cu
Feed Press 6.2 bar
92% Recovery
26 lmh (15.3 gfd)
Applications
Dye Bath Waste Treatment
Applications
Dye Bath Waste Treatment
Typical HYDRACoRe System

Feed

RO Feed Pump

6 RO Elements/Vessel

Concentrate

Product
HYDRACoRe System
HYDRACoRe Improvements
Required for Extreme Applications

- Low and High pH Tolerant Materials
- Up to 20% NaOH required
- Temperature Compatibility up to 80°C
- Rejection of low molecular weight organics
Spiral Wound Element Issues for High pH Feed Streams

1. Membrane (Fabric, Barrier Layer)
2. Leaf Glue
3. Permeate Carrier
Materials of Construction
Feed/Permeate Spacers
Selection of Leaf Adhesive must be Compatible with Manufacturing Process
HYDRACoRe 70pHT
Modiﬁed for pH 14, 80°C
- Same Membrane (MWCO ~ 500 Daltons)
- Modiﬁed Plastic Parts
- Modiﬁed Outer-wrap
- Modiﬁed Adhesives
- Modiﬁed Feed and Permeate Spacers
Hemicellulose Retention by HYDRACoRe 7470 Treating Process Fluid Containing 17% Caustic

Feed Solution for Cell Test:
Chemical oxygen demand (COD), mg/l 44,200
Total organic carbon (TOC), mg/l 17,000
Sodium hydroxide, g/l 202.96
Total alkali, g/l 207.18

Molecular Weight Cut-Off ~ 380

<table>
<thead>
<tr>
<th>Element</th>
<th>HYDRACoRe 70</th>
<th>HYDRACoRe 70pHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Sulfonated polyethersulfone (365 sq. ft.)</td>
<td>Sulfonated polyethersulfone (275 sq. ft.)</td>
</tr>
<tr>
<td>Element</td>
<td>FRP</td>
<td>Cage Wrapped</td>
</tr>
<tr>
<td>Membrane</td>
<td>Polyester</td>
<td>proprietary</td>
</tr>
<tr>
<td>pH (Max)</td>
<td>11.5</td>
<td>14</td>
</tr>
<tr>
<td>Temperature (Max)</td>
<td>50 C</td>
<td>80 C</td>
</tr>
</tbody>
</table>
Cane Sugar Process
Conventional Commercial Process

Sugar Cane

NaCl + NaOH

Water

Decoloring

Evaporation

Crystallization

Conditioning and Storage

Juicing

Ion Exchange
Brine Stream

Water
Cane Sugar Process
Brine Regenerate Decolorization

Sugar Cane → Brine Stream

NaCl + NaOH → Decoloring

Water → Evaporation

90% recovered → Ion Exchange

10% to waste → Brine Stream

Evaporation → Crystallization

Juicing → Conditioning and Storage
HYDRACoRe 70pHT
Brine Regeneration System

2 Vessels
4 Elements/Vessel

IX Brine
11.5 gpm (2.6 m³/hr)

Feed

Press ~145 psi (10 bar)
Color 115,000 ICU
NaCl 10%

Foulants
Particles
Bio-growth
Mg(OH)2
CaCO3

Concentrate
2.3 gpm (0.52 m³/hr)
Color 515,000 ICU
NaCl 10%
NaOH 2%

Permeate

Color 15,000 ICU
NaCl 10%
NaOH 2%
HYDRACoRe Performance
Brine Regenerate Decolorization

Plant Data Trend
System Start-up April 2005

Decolorisation (%) vs. Pressure in (bar)
HYDRACoRe70 pHT
Brine System Cleaning

1. Cleaning every 2 weeks

2. Drain system and rinse with water

3. Nitric / Phosphoric Acid Blend, pH 2, 50 C, 30 minutes

4. Rinse

5. NaOH / KOH alkaline detergent to pH 11.5-12, 200 ppm NaOCl, 30 minutes, 50 deg C

6. Rinse with water
HYDRACoRe70 pH7T
Economic Analysis

CONVENTIONAL SYSTEM

- $0.77 / metric ton - Cost of chemicals to decolorize sugar
  - NaOH $0.47 / mton
  - NaCl $0.30 / mton

NEW MEMBRANE-BASED SYSTEM

- $0.27 / metric ton - Cost of decolorized sugar with HYDRACoRe 70pH7T
  - Membrane replacement $0.10 / mton
  - NaOH $0.09 / mton
  - NaCl $0.06 / mton
  - Cleaning + energy $0.02 / mton

Cost Savings $0.50 / metric ton of raw sugar processed!
Summary of HYDRACoRe 70 pHT System

- NF membrane can decolorize/purify brine regenerant under high pH/high temperature conditions.
- Process generates considerably less waste and less caustic to be neutralized.
- Saves a minimum of $0.50 / metric ton of raw sugar processed, based solely on non-regulatory, non-feed discharge assumptions.
- Greater savings if brine neutralization is required and plant was charged for discharge.
- Plants of 1,000 to 4,000 metric tons /day refining capacity could realize a payback within one year.
- Additional brine can be used for regeneration and recycled at the lower cost.
Conclusions

- Membrane technology does exist for treating caustic solutions with a 1-10% caustic and temperatures as high as 60-80°C.
- Current membrane technology allows for the separation of organic material with at least 500 MW from caustic solutions.
- Selection of the optimum membrane depends on the characteristic of the organic material.
- System design should be conservative due to inherent variations of the feed stream, membrane and operating conditions. Piloting is recommended for most cases.