Paper Authors: Craig Bartels, Ph.D., Rich Franks, Jeff Campbell

Paper Title: "Chemically Tolerant NF Membranes for Aggressive Industrial Applications"

Abstract

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 80C. 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

Ikeda, K., Nakano, T., Ito, H., Kubota, T., Yamamoto, S. *New Composite Charged Reverse Osmosis Membrane*, Desalination, 68, 1988, pp 109-119.

Spangenberg, C. W., Duranceau, S., Kutilek, J., *Membrane Manufacturer and Utility Implement Non-Traditional Membrane Acceptance Testing*, American Water Works Association – Water Quality Technology Conference, 2002.

Chemically Tolerant NF Membranes for Aggressive Industrial Applications

Craig R. Bartels, PhD
Rich Franks
Jeff Campbell

Hydranautics
Oceanside, CA

NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

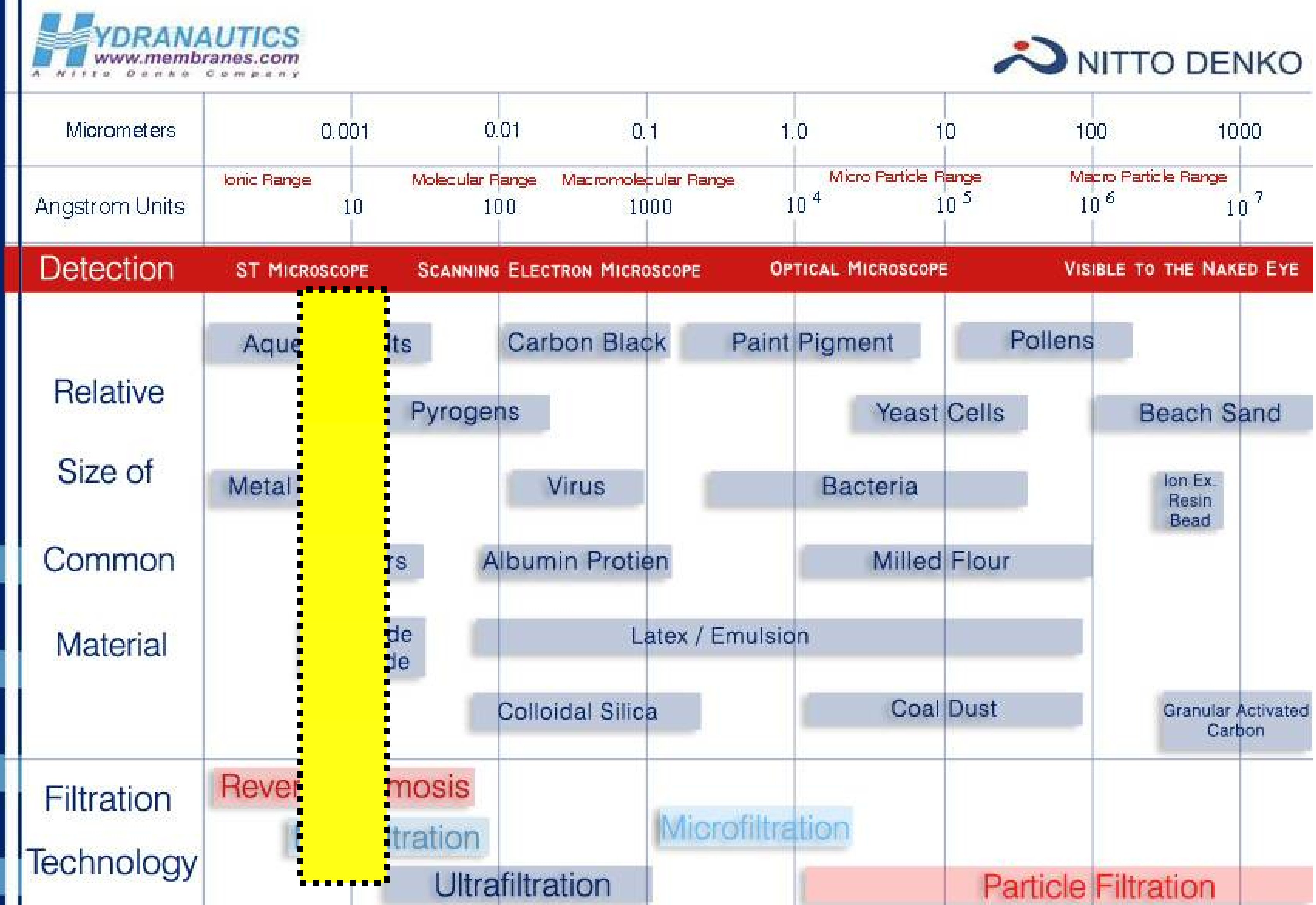
Membrane Process Applications:

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.



The Filtration Spectrum

1-800-CPA-Pure

401 Jones Rd, Oceanside, Ca 92054

Commercial Membranes for Treatment of Caustic Process Fluids

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

Manufacturer	Microdyn-Nadir	Koch	Nitto-Denko	Osmonics	DSS
Membrane	N30F	SelRO MPF-34	NTR-7470[a]	G-5 (GE) [a]	GR95PP
Material	Polyethersulfone hydrophilized	Composite	Polysulfone based	Proprietary	Polyethersulfone on polypropylene support
Nominal MWCO, g/mol	500[b,c]	200–300[d]	200–250	1000 [e]	2000
Water permeability, $l/(m^2 hbar)$	1–1.75[f]	2[g]		1.23[h]	
Max. temperature, °C	95	70	60	80	75
Max. pressure, bar	40	35	35	40	10
pH range	0–14	up to 20% NaOH	15% NaOH at 60°C	1–14	1–13
NaCl retention, %	25–35[i]	35[j]	70[k]	10	
Na_2SO_4 retention, %	85–95[l]				
Special features			Tolerates 100 ppm Cl_2		

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

Desalination 192 (2006) 303–314.
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*

NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

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

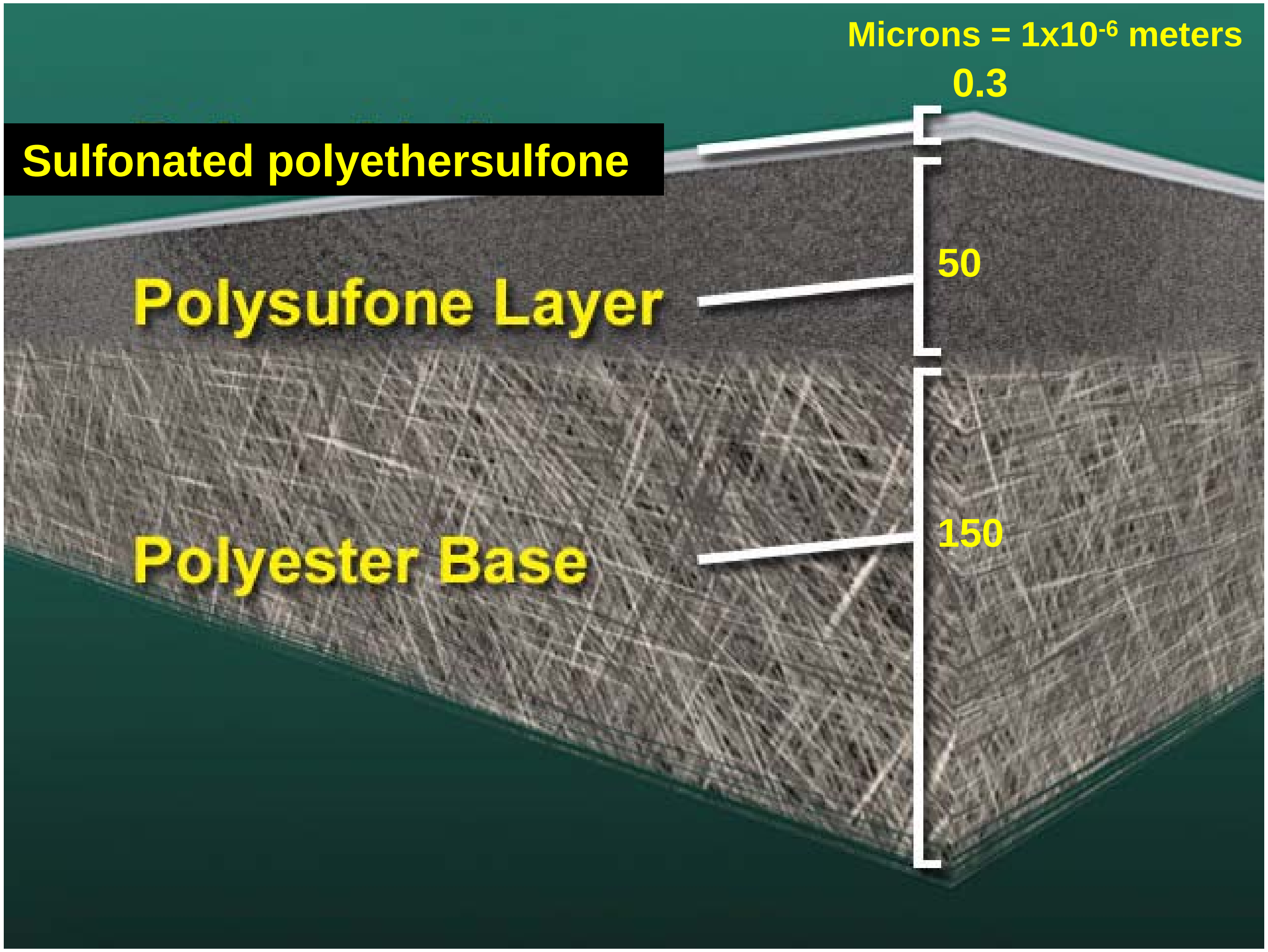
HYDRACoRe Development

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

NITTO DENKO

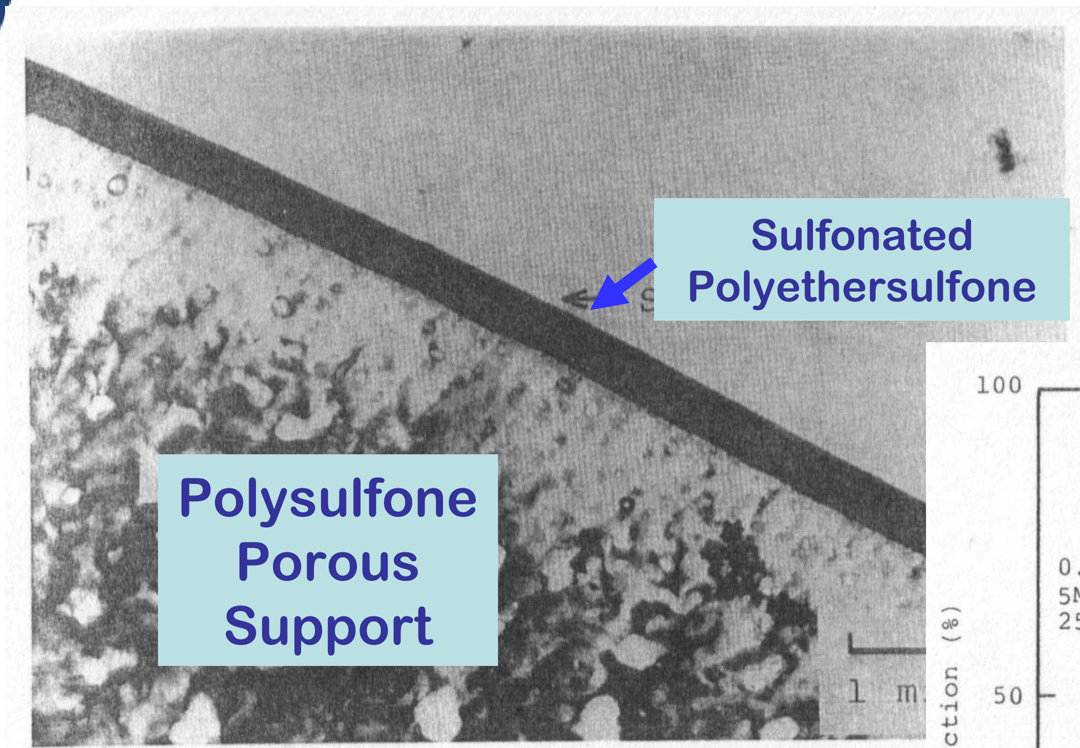
HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

Spiral Wound Element

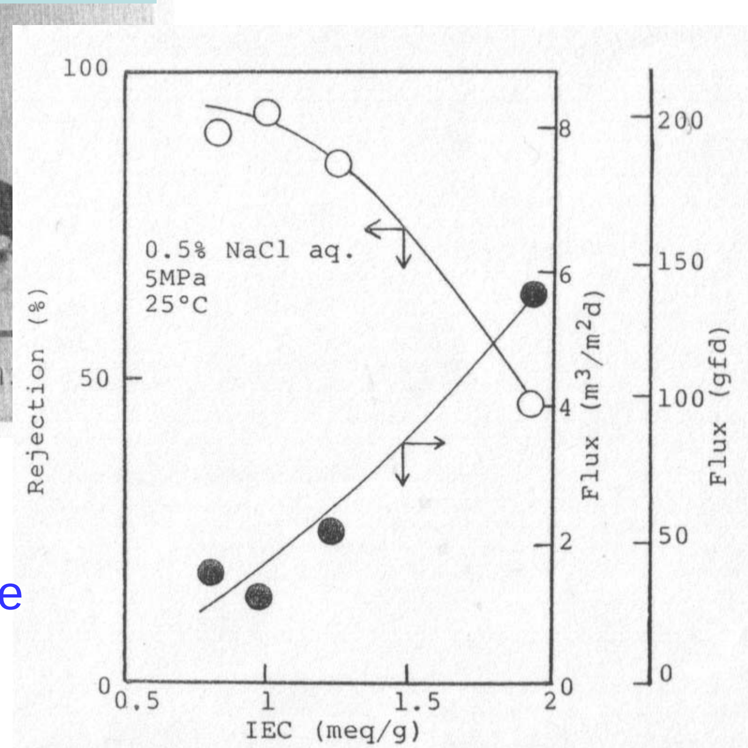


Membrane Characterization

Barrier Layer Cross-Section and Charge Density



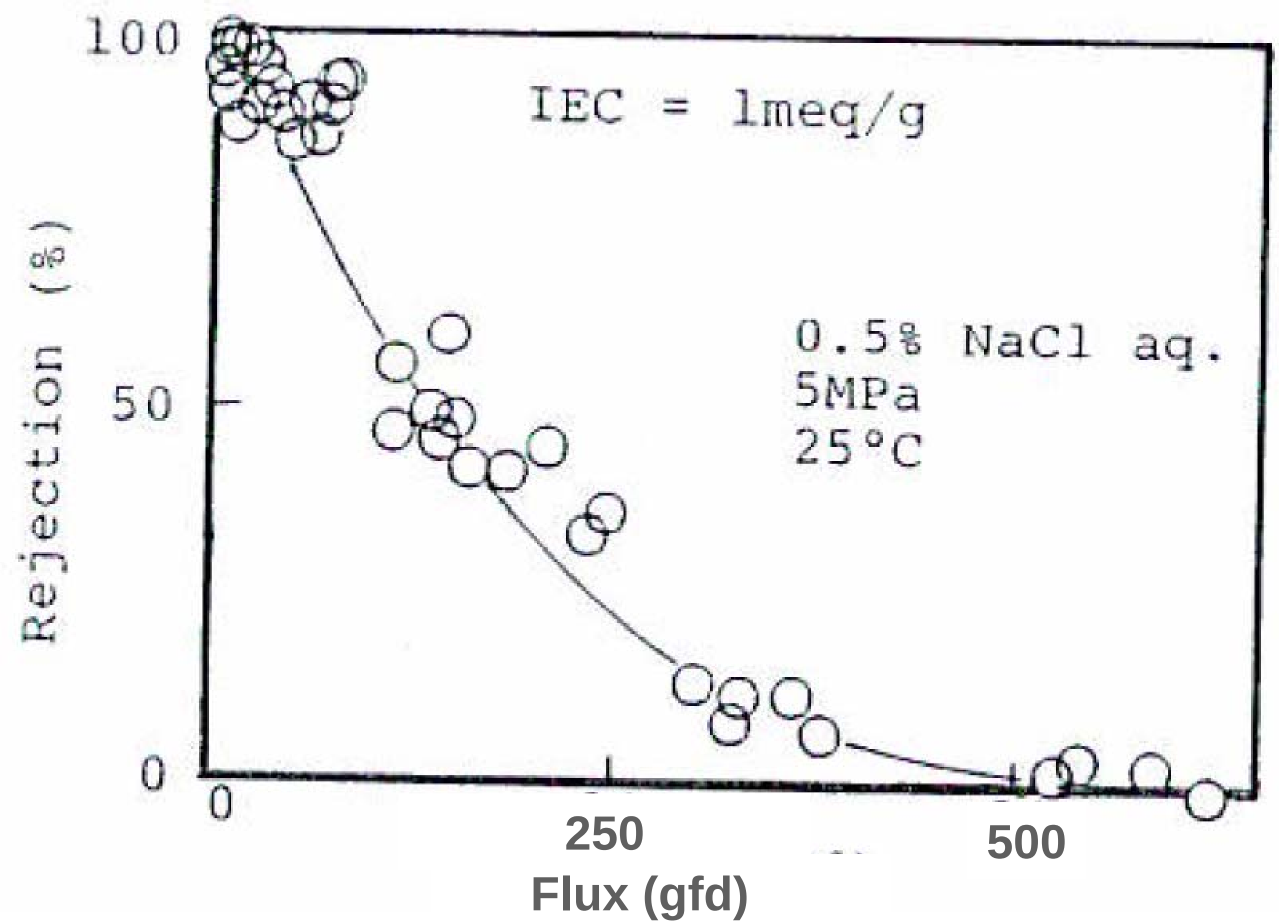
TEM of HYDRACoRe Surface.
1 micron:



Relationship between ion-exchange capacity and flux/rejection for various HYDRACoRe membranes

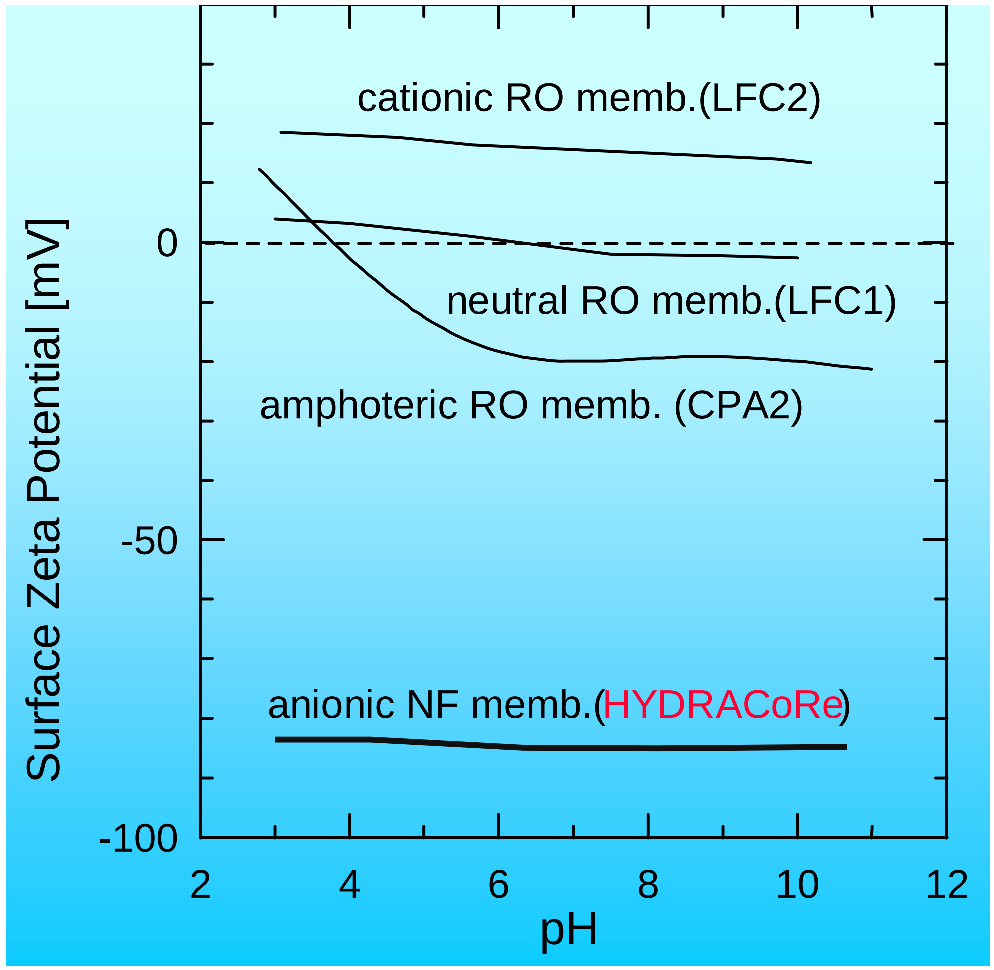
Membrane Characterization

Barrier Layer Cross-Section and Charge Density



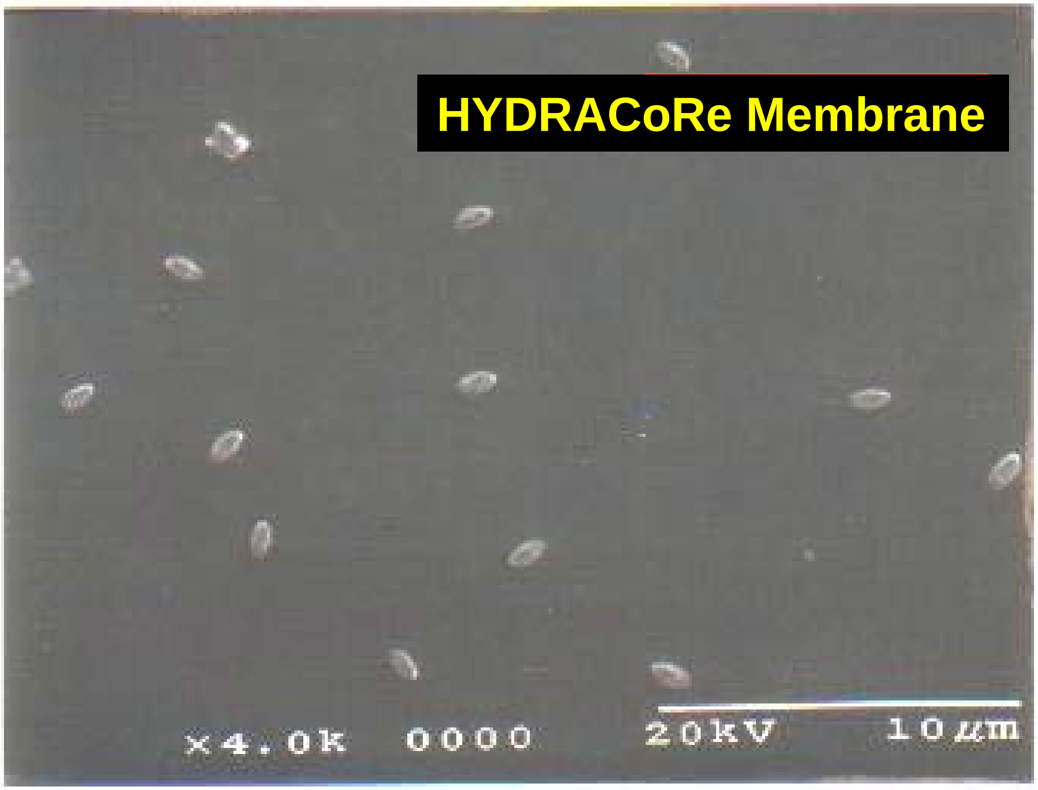
Membrane Characterization

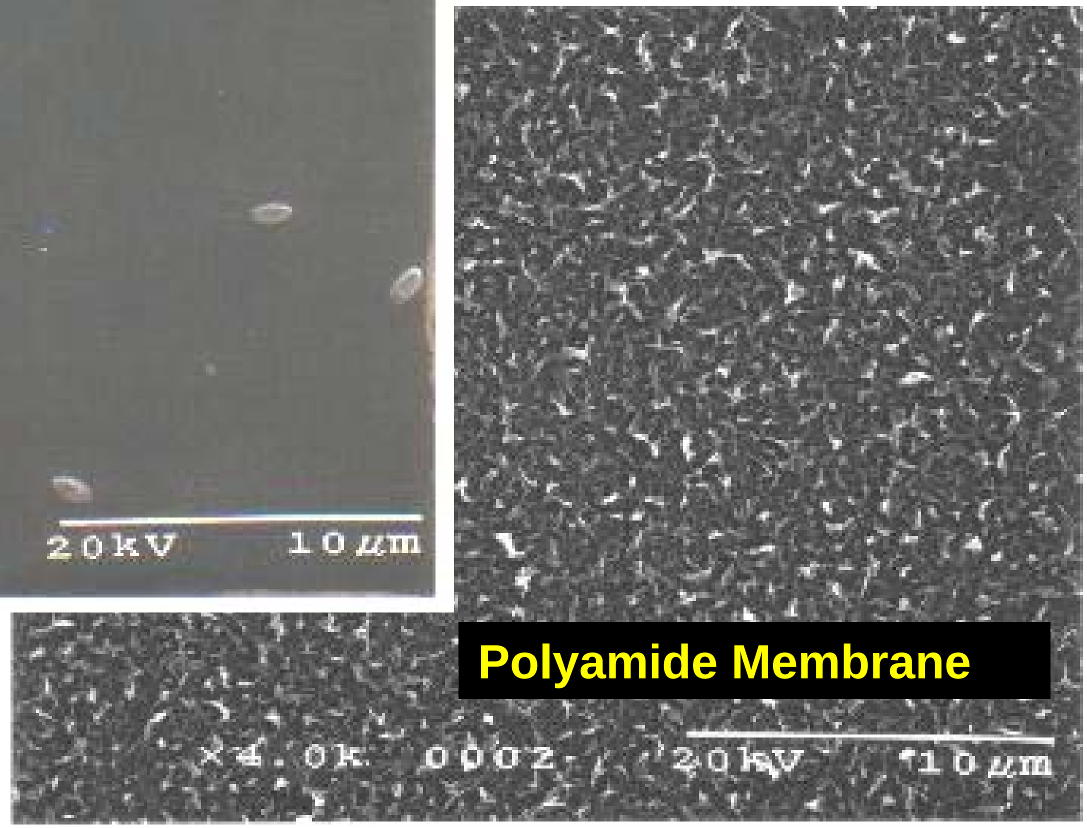
Surface Charge: Negative



Membrane Characterization

Smooth Surface



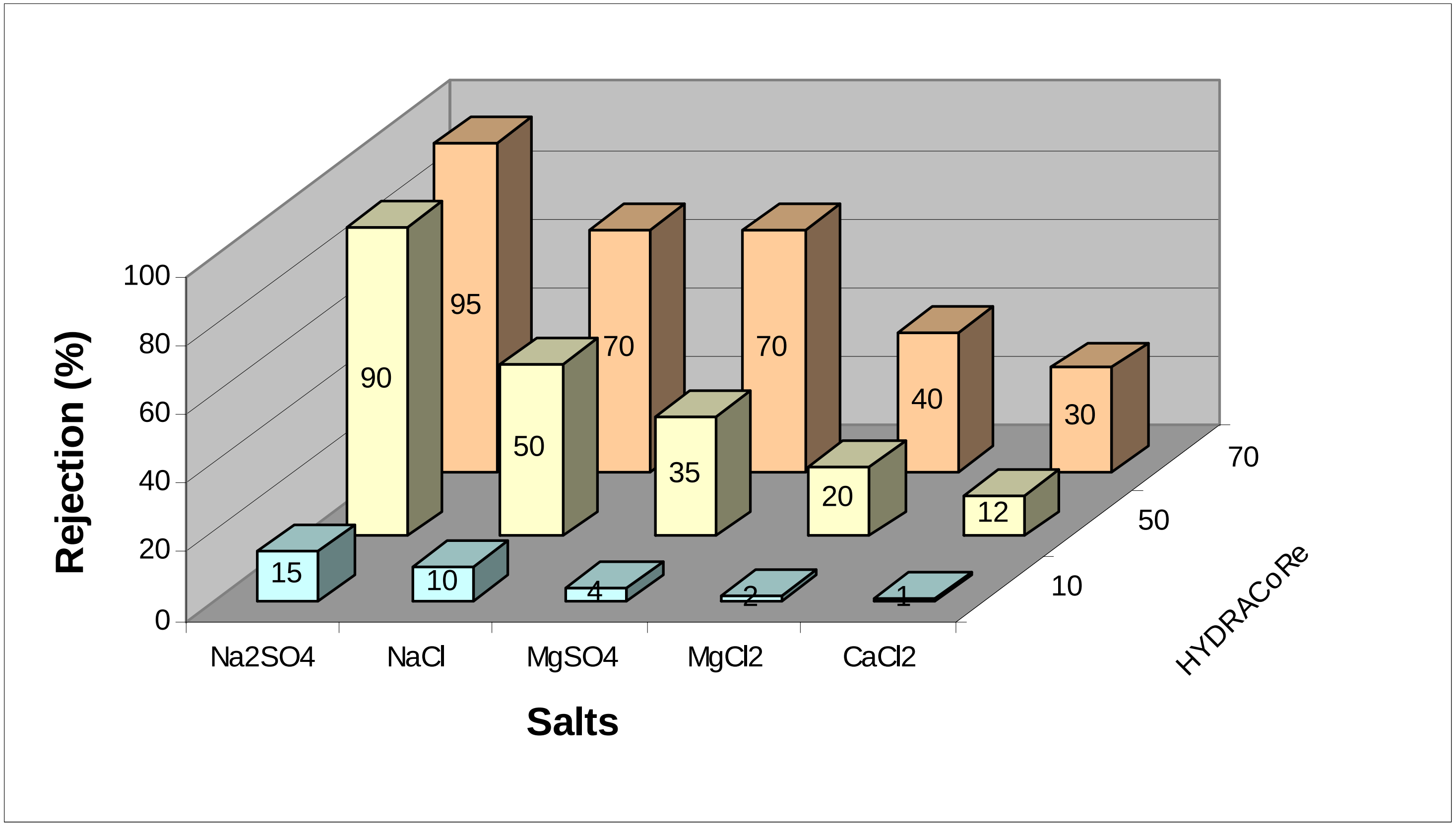


NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

Membrane Characterization

Ion Separation Properties

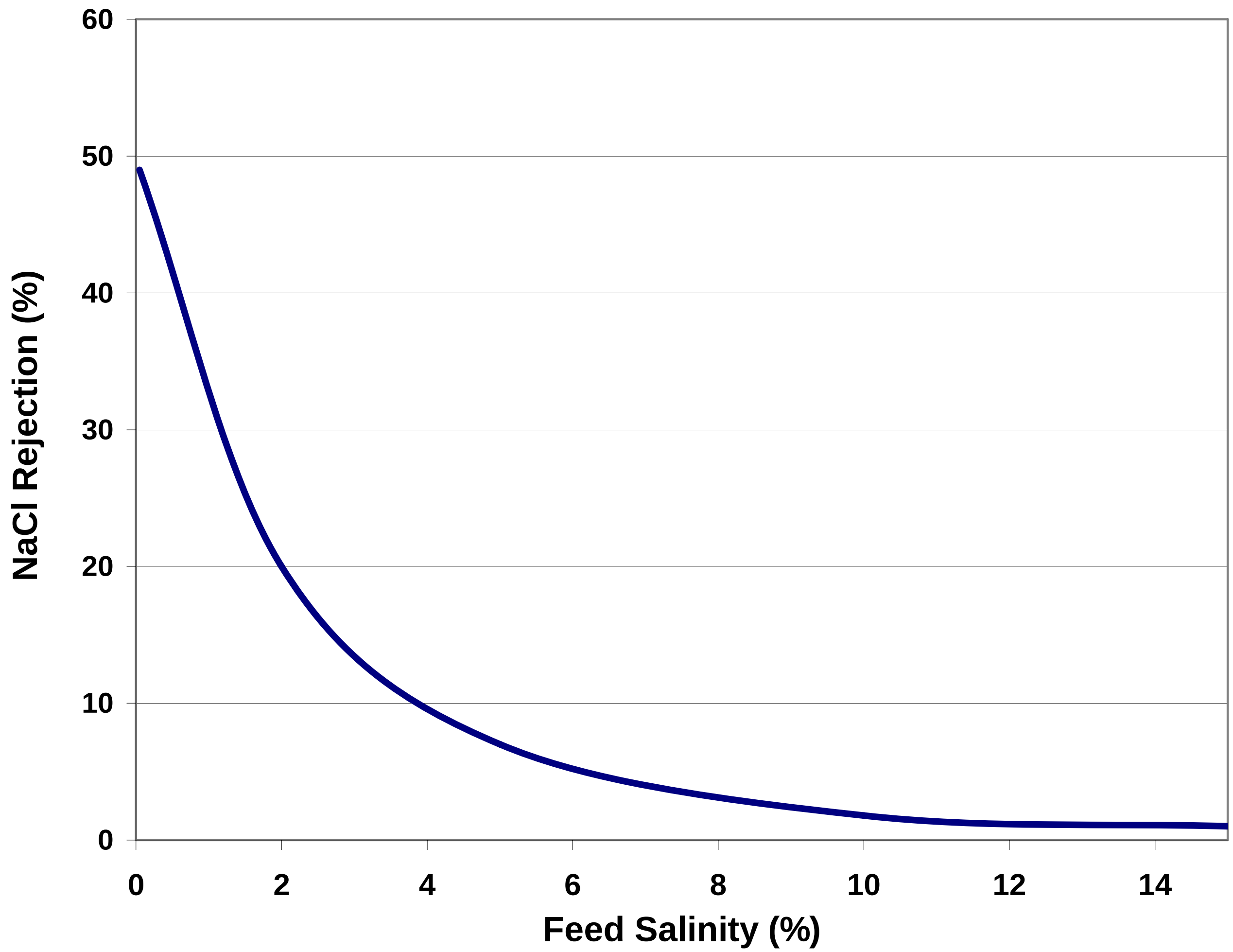


NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

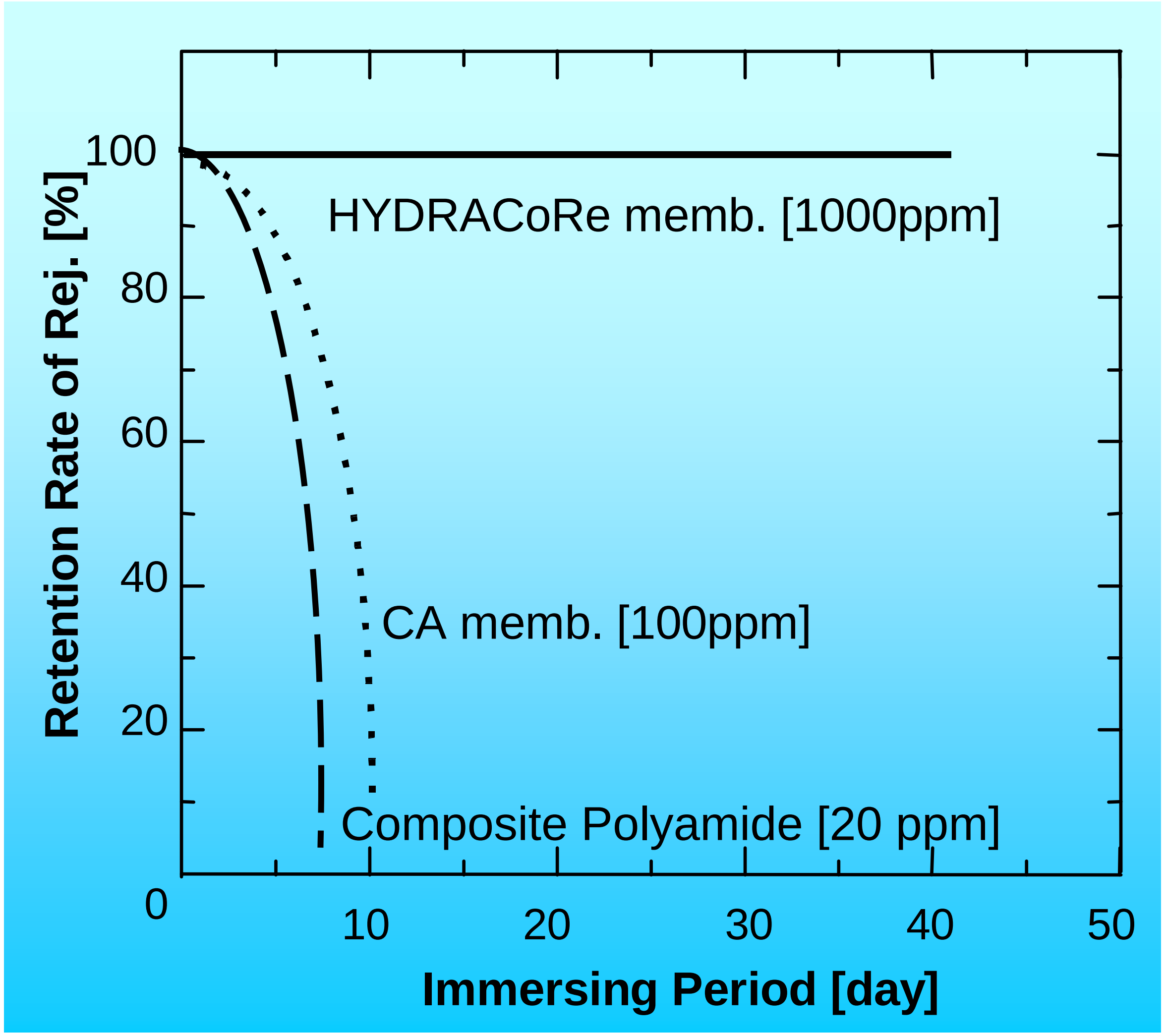
Membrane Characterization

Salinity Effect



Membrane Characterization

Chemical Stability



Membrane Characterization

Chemical Stability

Chemical Agent	Condition
Sulfuric Acid	pH 2
Hydrochloric Acid	pH 2
Nitric Acid	pH 2
Acetic Acid	1%
Oxalic Acid	2%
Citric Acid	2%
EDTA	2%
Sodium Hydrogensulfate	2%
NaOH	pH 13
Sodium hypochlorite	200 ppm
Formalin	0.5%

Applications

Groundwater Color Removal

Irvine Ranch Water District

3 Trains

434 Elements per Train

Feed = 340 cu Perm = 3 cu

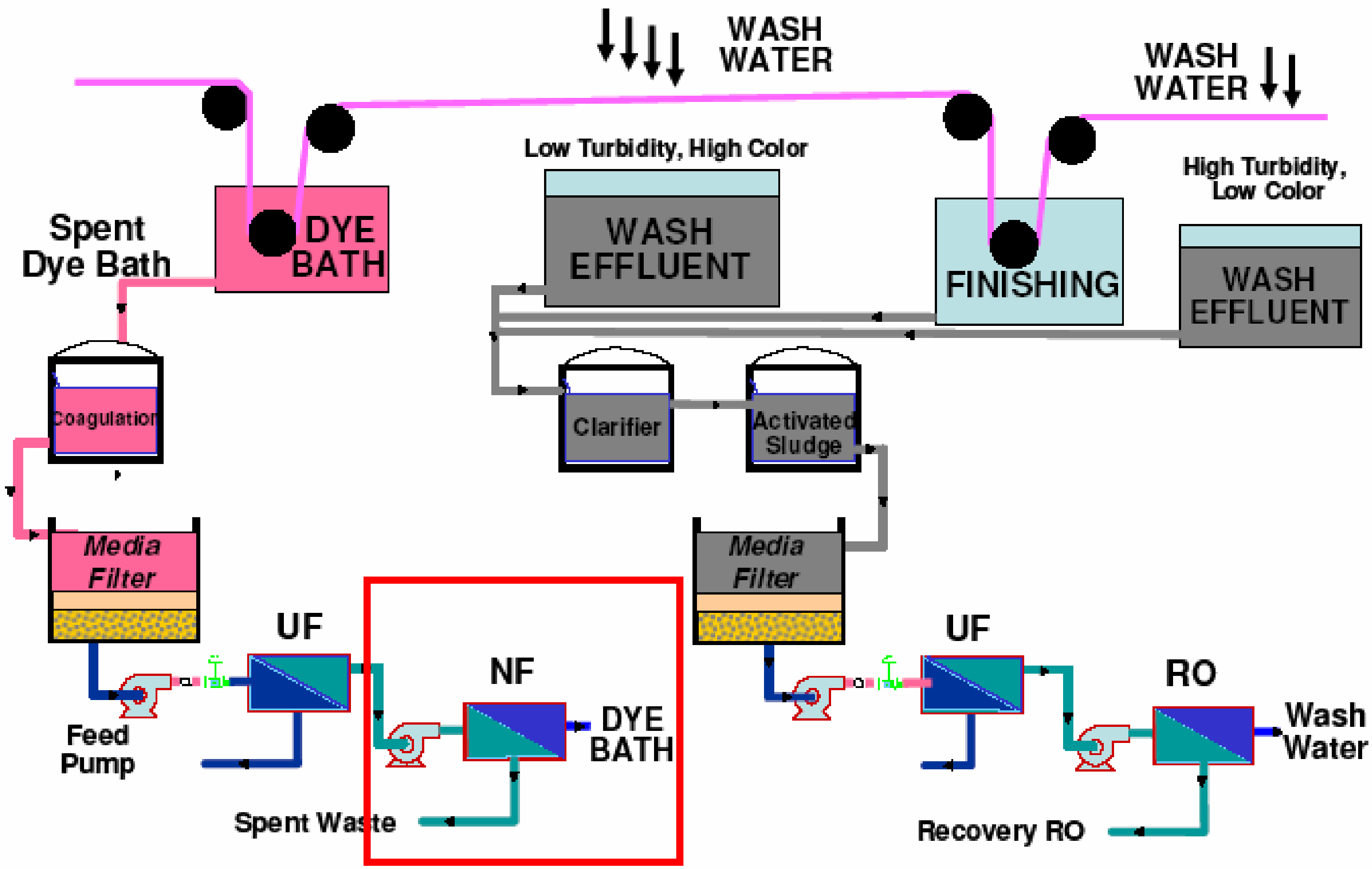
Feed Press 6.2 bar

92% Recovery

26 lmh (15.3 gfd)

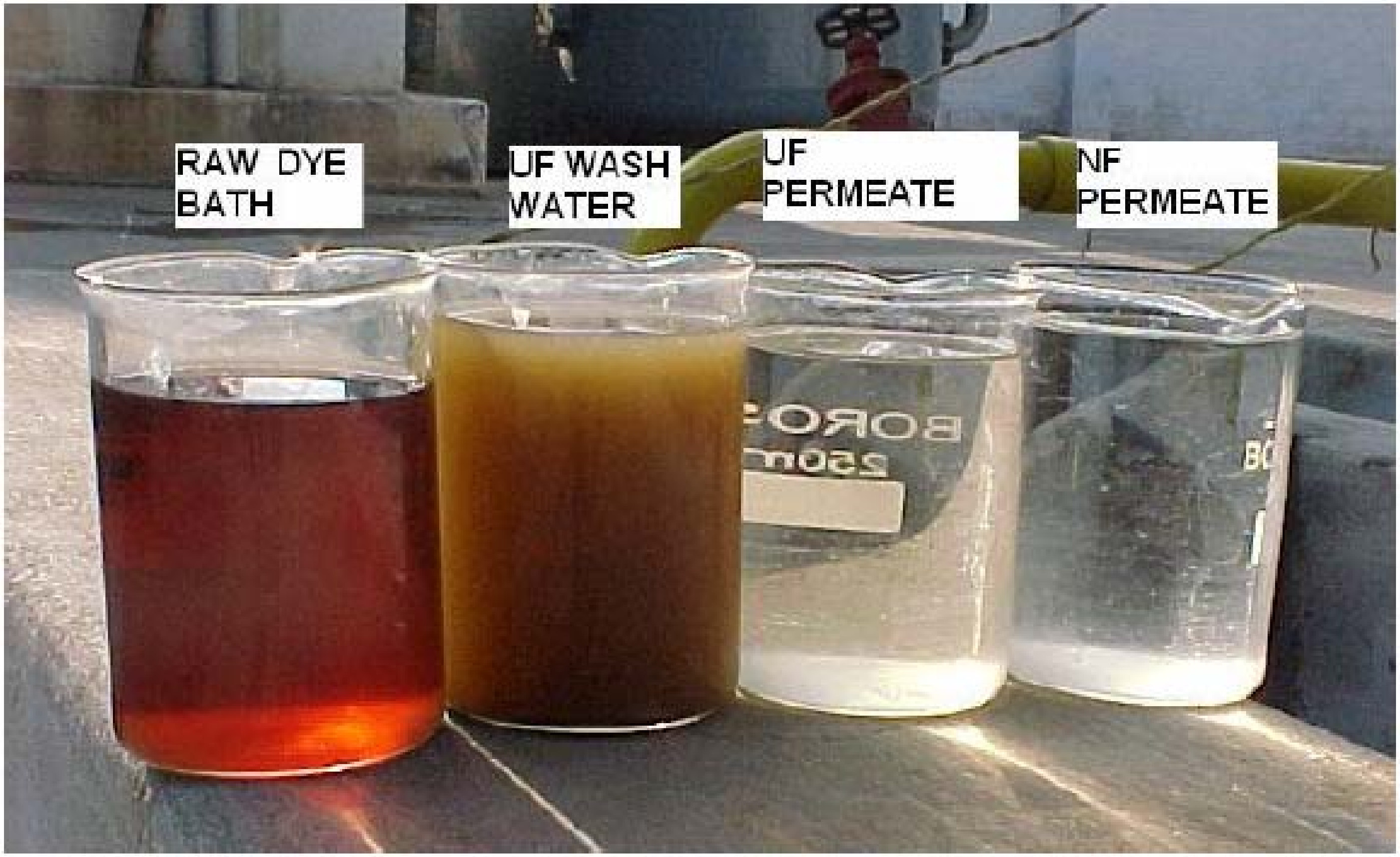
Applications

Dye Bath Waste Treatment

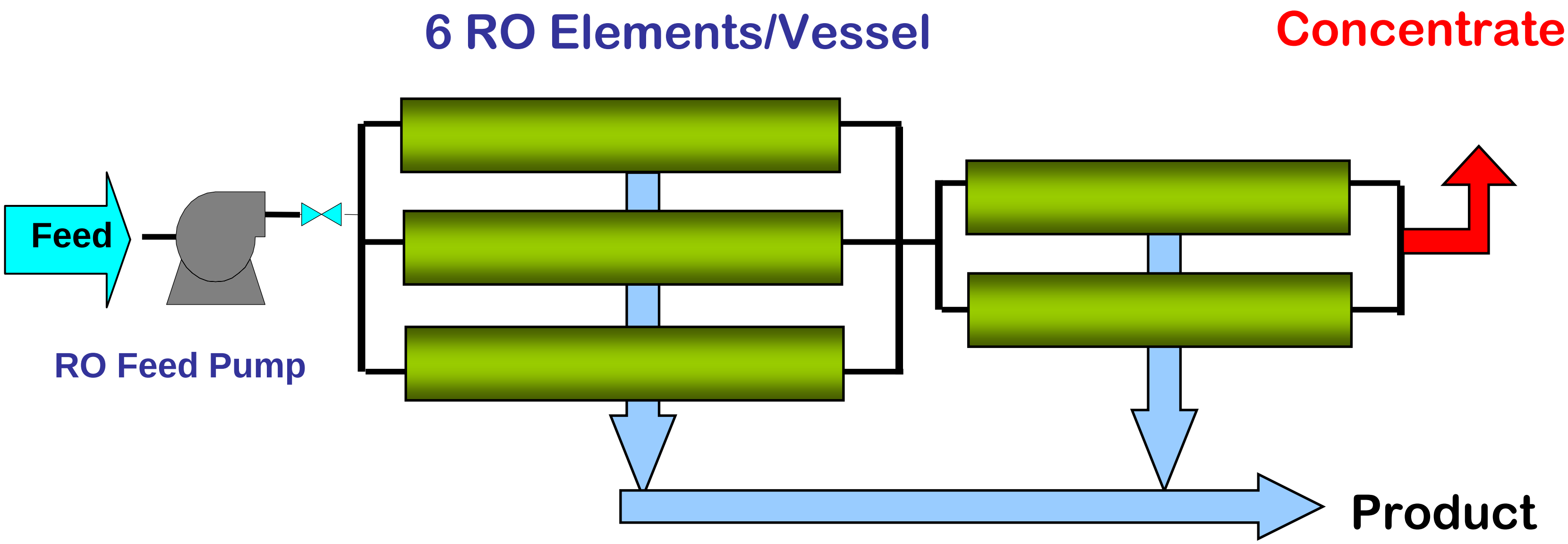


Applications

Dye Bath Waste Treatment



Typical HYDRACoRe System



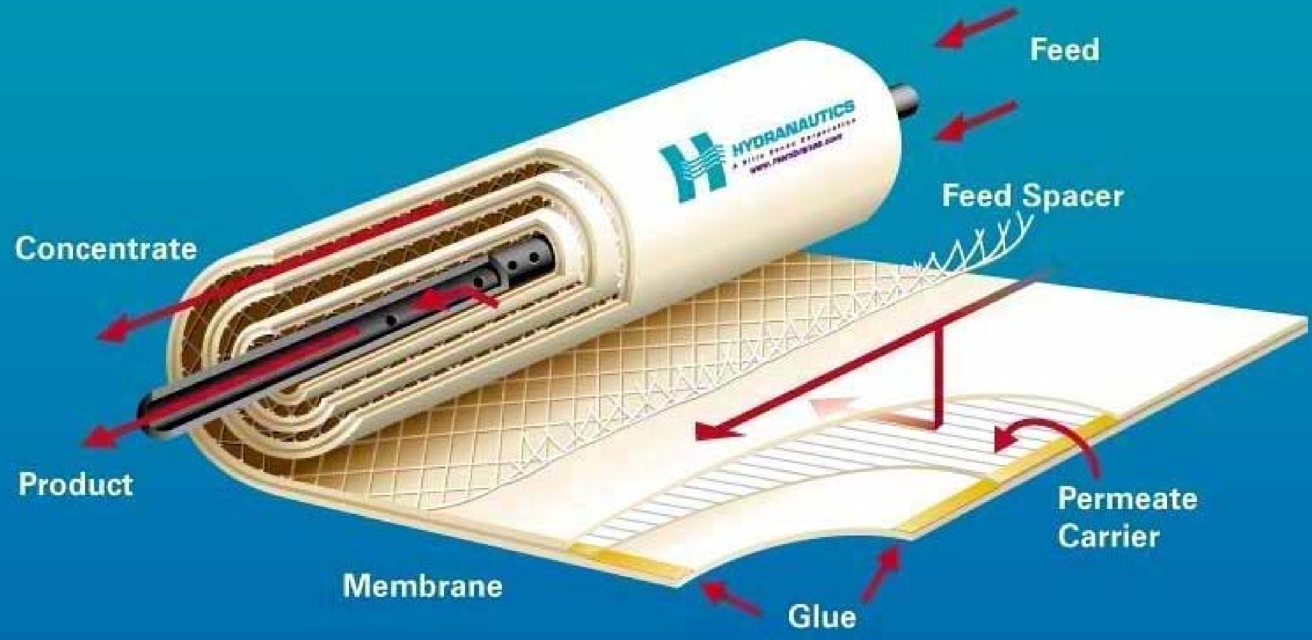
HYDRACoRe System

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

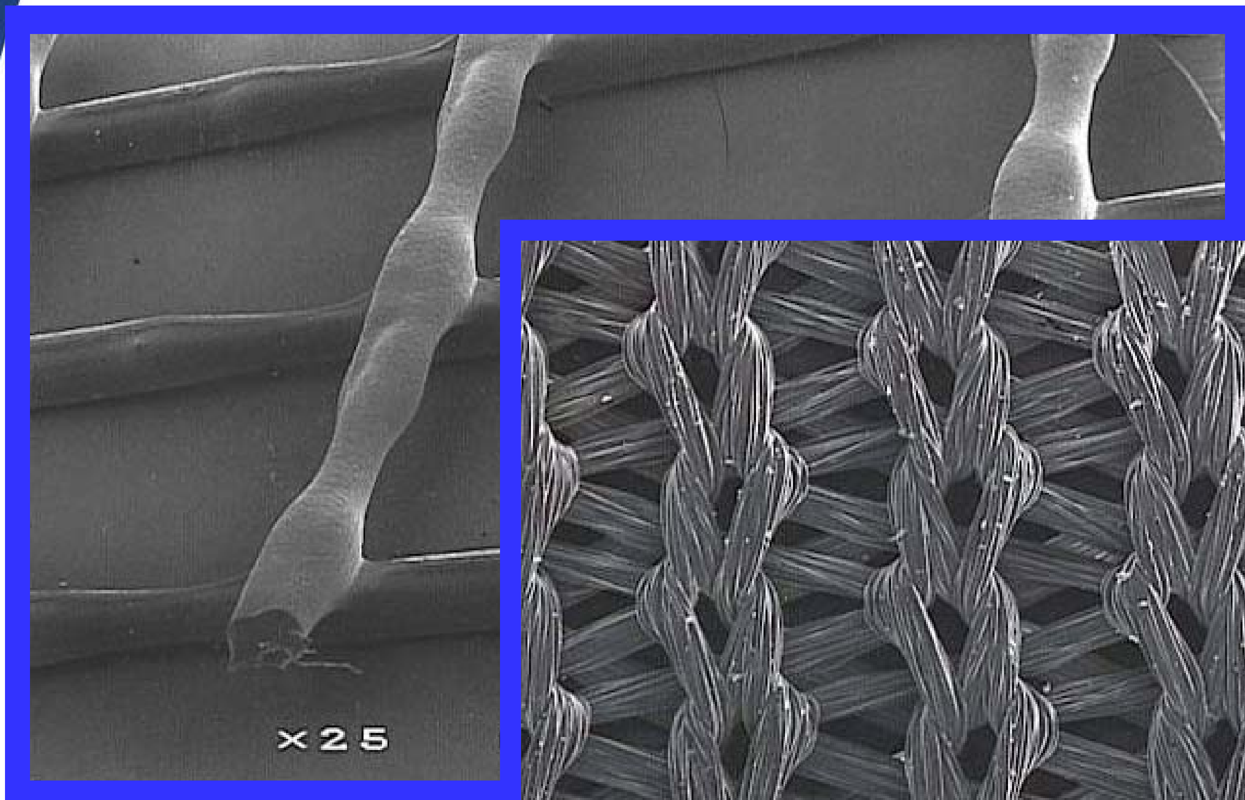
Spiral Wound Element Issues for High pH Feed Streams

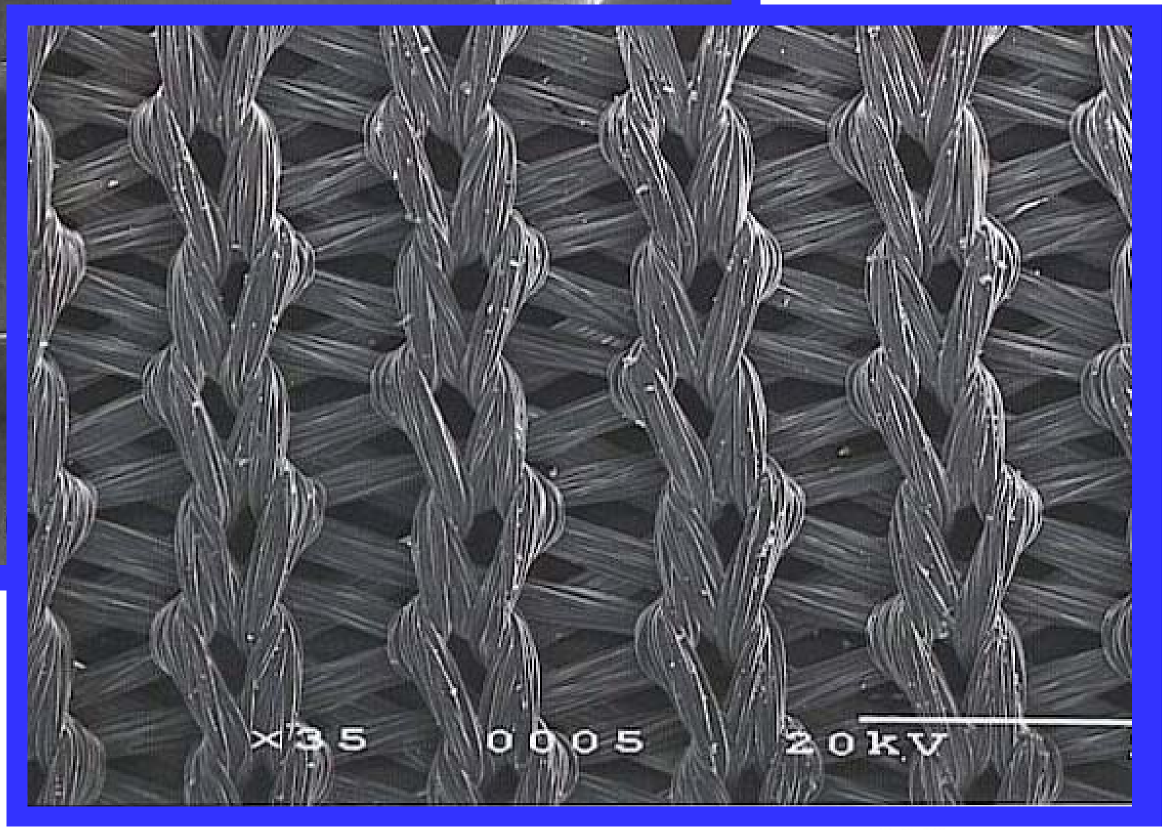
1. Membrane (Fabric, Barrier Layer)
2. Leaf Glue
3. Permeate Carrier



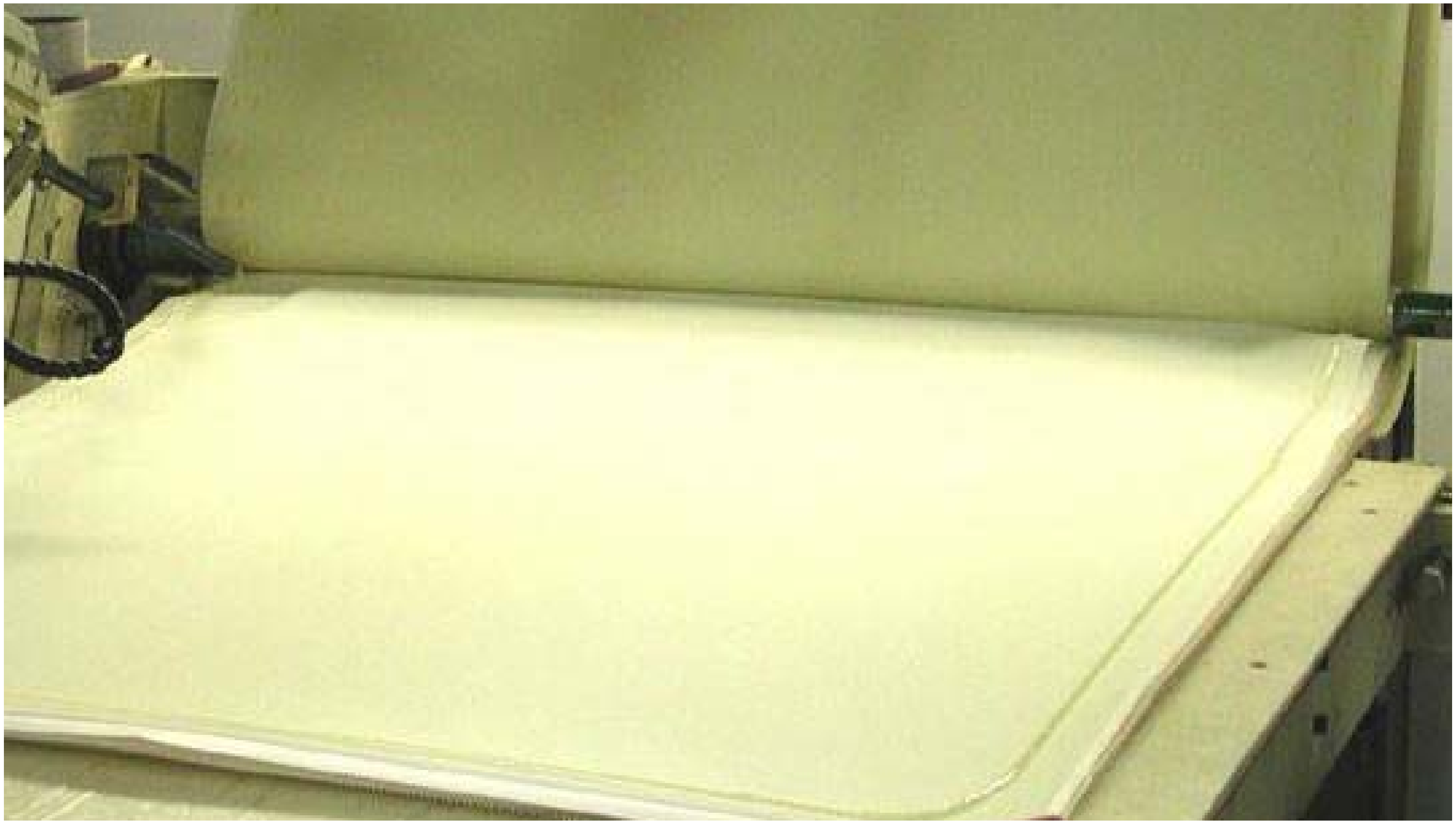
Materials of Construction

Feed/Permeate Spacers





Selection of Leaf Adhesive must be Compatible with Manufacturing Process



NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

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

→

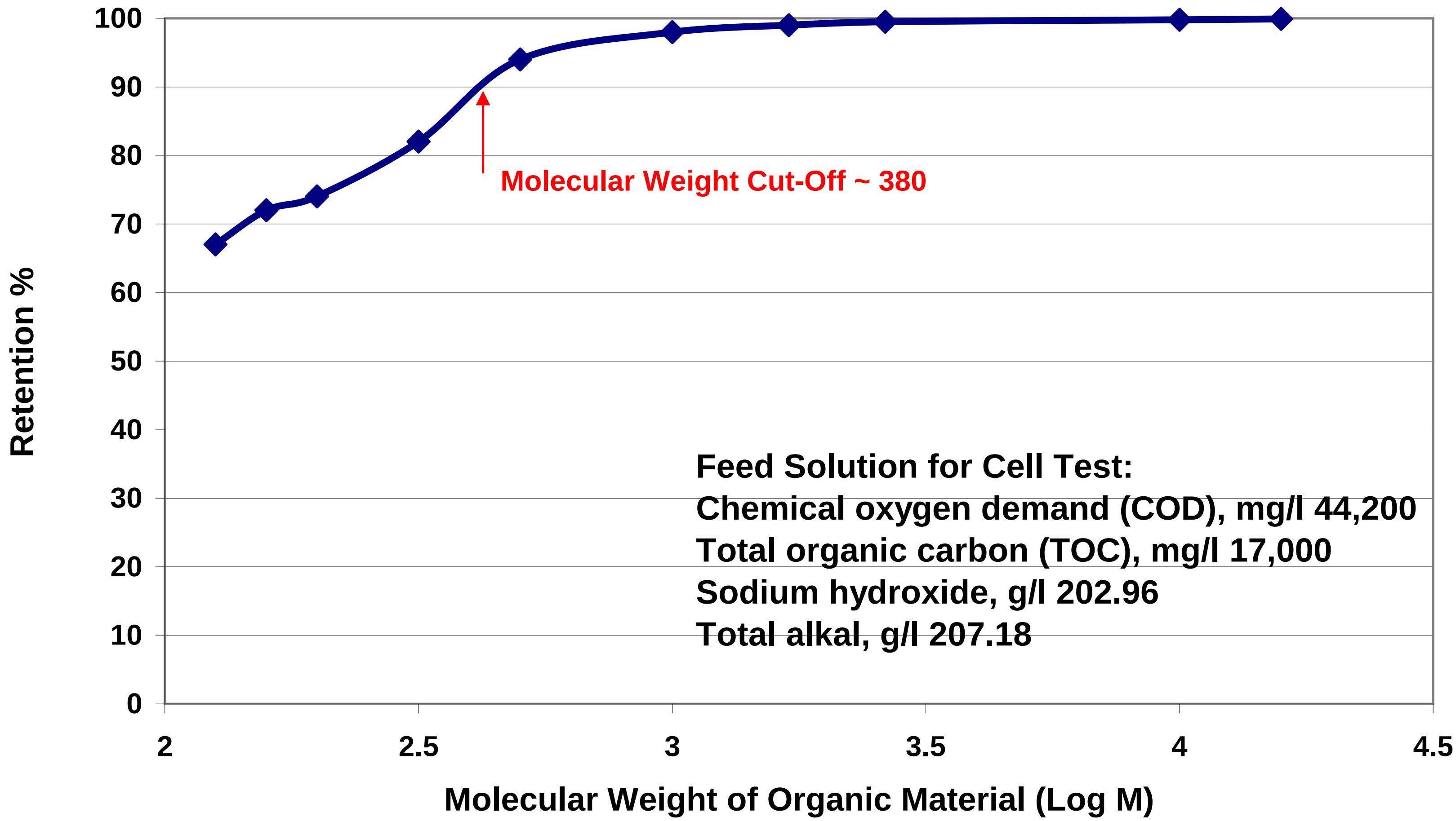
HYDRACoRe 70pHT

NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

Hemicellulose Retention by HYDRACoRe 7470 Treating Process Fluid Containing 17% Caustic

500 psi (35 bar), 49 C



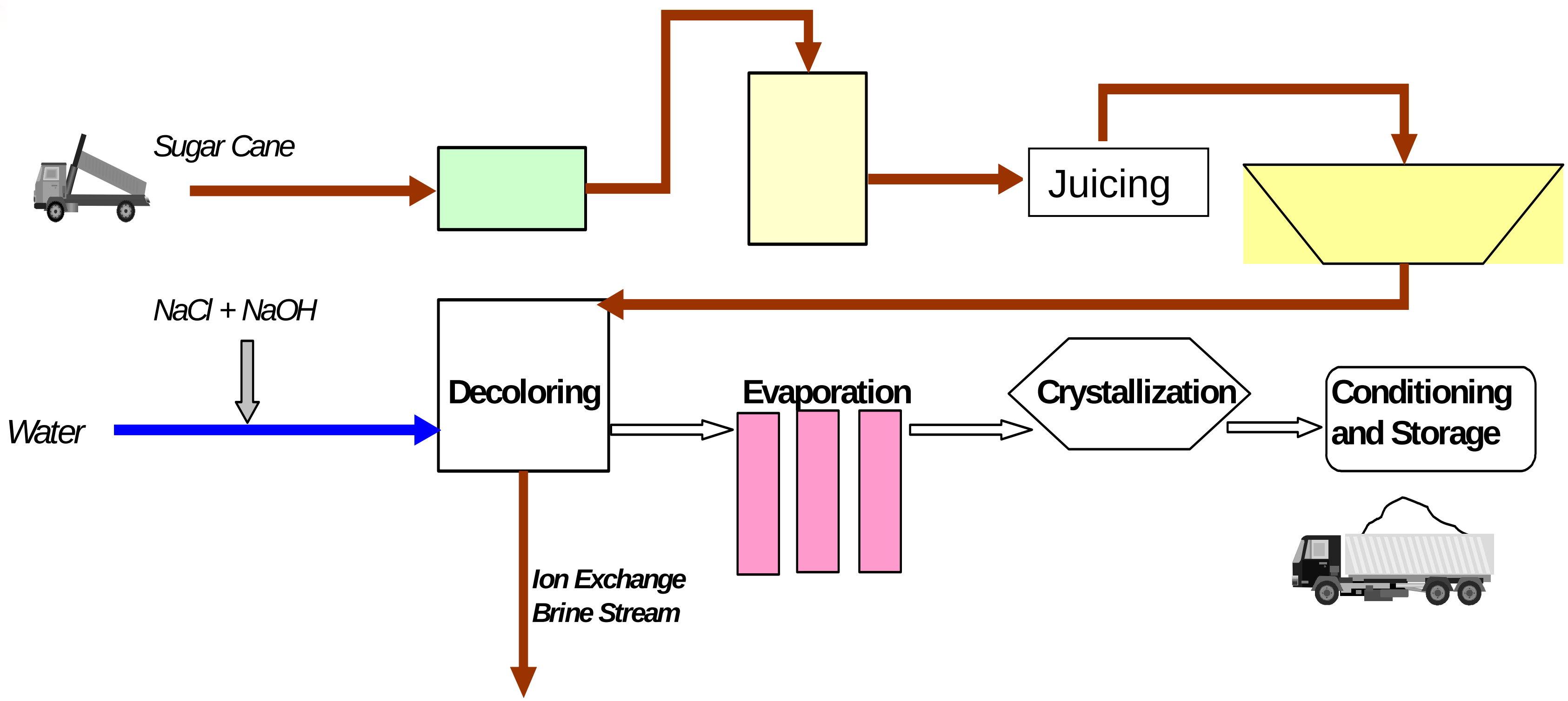
Ref: R. Schlesinger et al. / Desalination 192 (2006) 303–314

HYDRACoRe 70pHT

Element	HYDRACoRe 70	HYDRACoRe 70pHT
Membrane	Sulfonated polyethersulfone (365 sq. ft.)	Sulfonated polyethersulfone (275 sq. ft.)
Element	FRP	Cage Wrapped
Membrane Materials	Polyester	proprietary
pH (Max)	11.5	14
Temperature (Max)	50 C	80 C

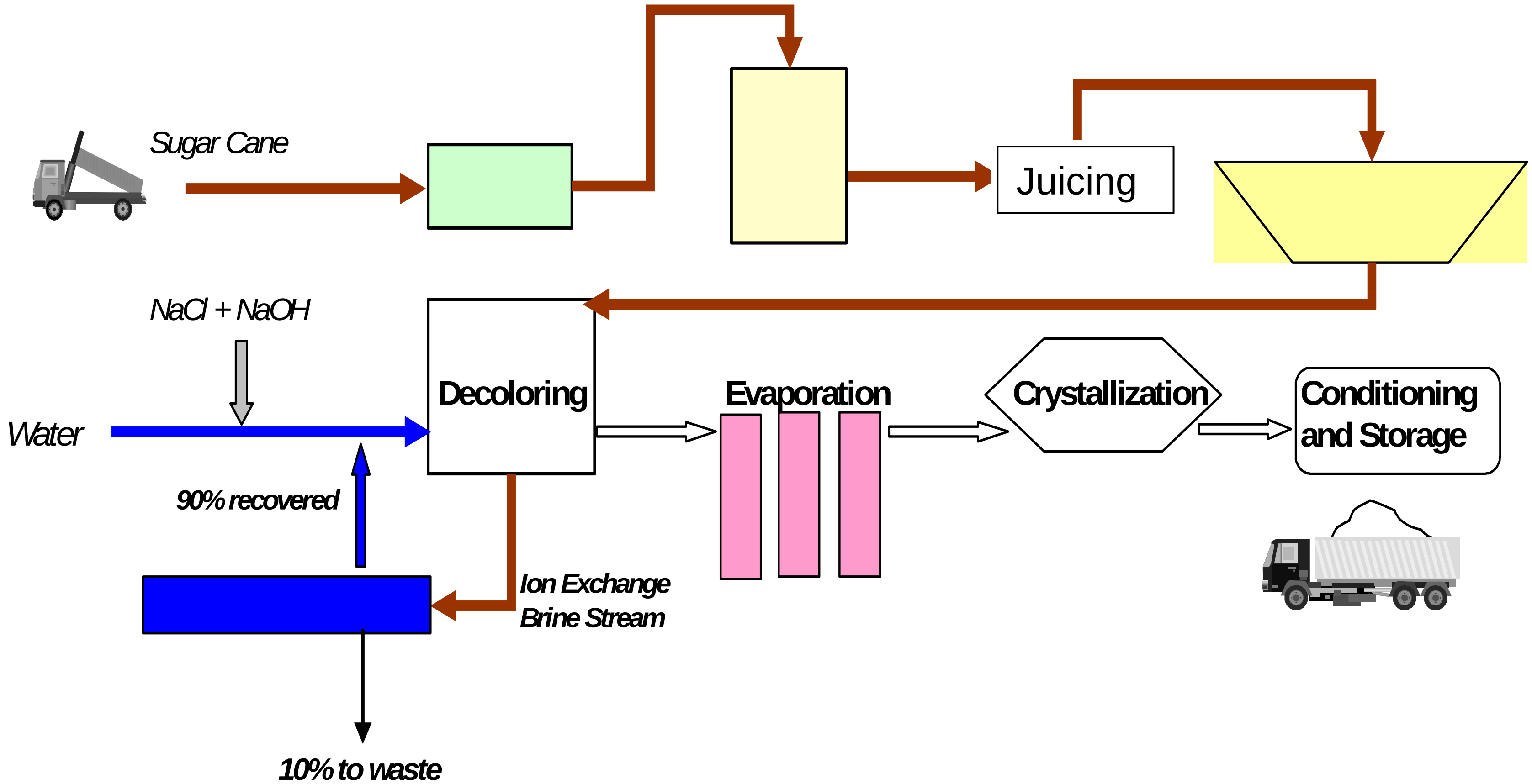
Cane Sugar Process

Conventional Commercial Process



Cane Sugar Process

Brine Regenerate Decolorizaton

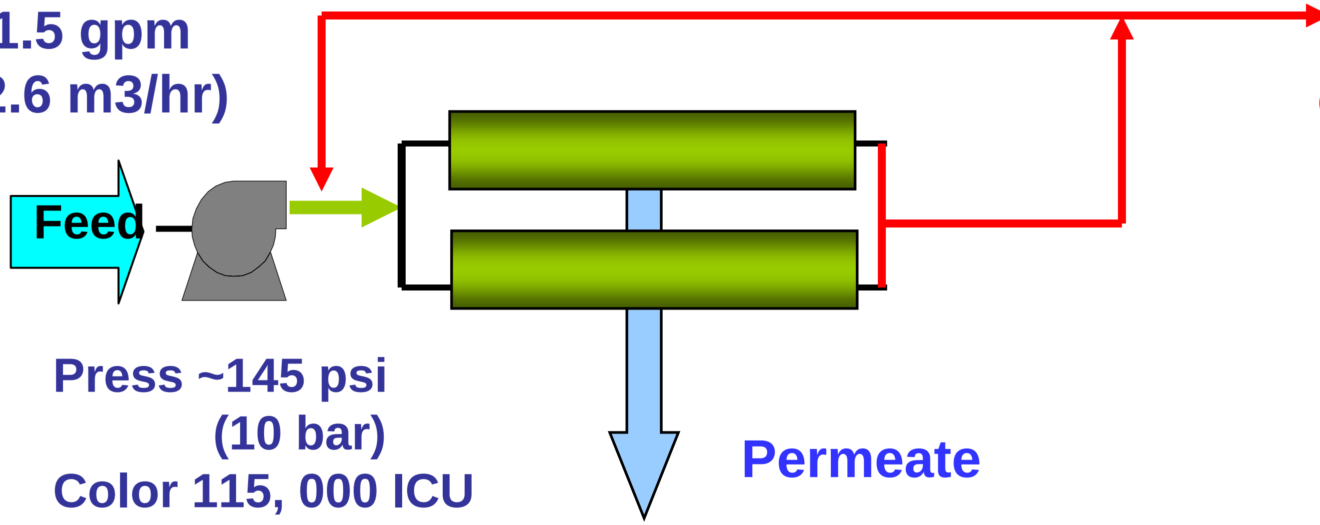


HYDRACoRe 70pHT

Brine Regeneration System

2 Vessels
4 Elements/Vessel

IX Brine
11.5 gpm
(2.6 m3/hr)



Concentrate
2.3 gpm
(0.52 m3/hr)

Color 515, 000 ICU
NaCl 10%
NaOH 2%

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

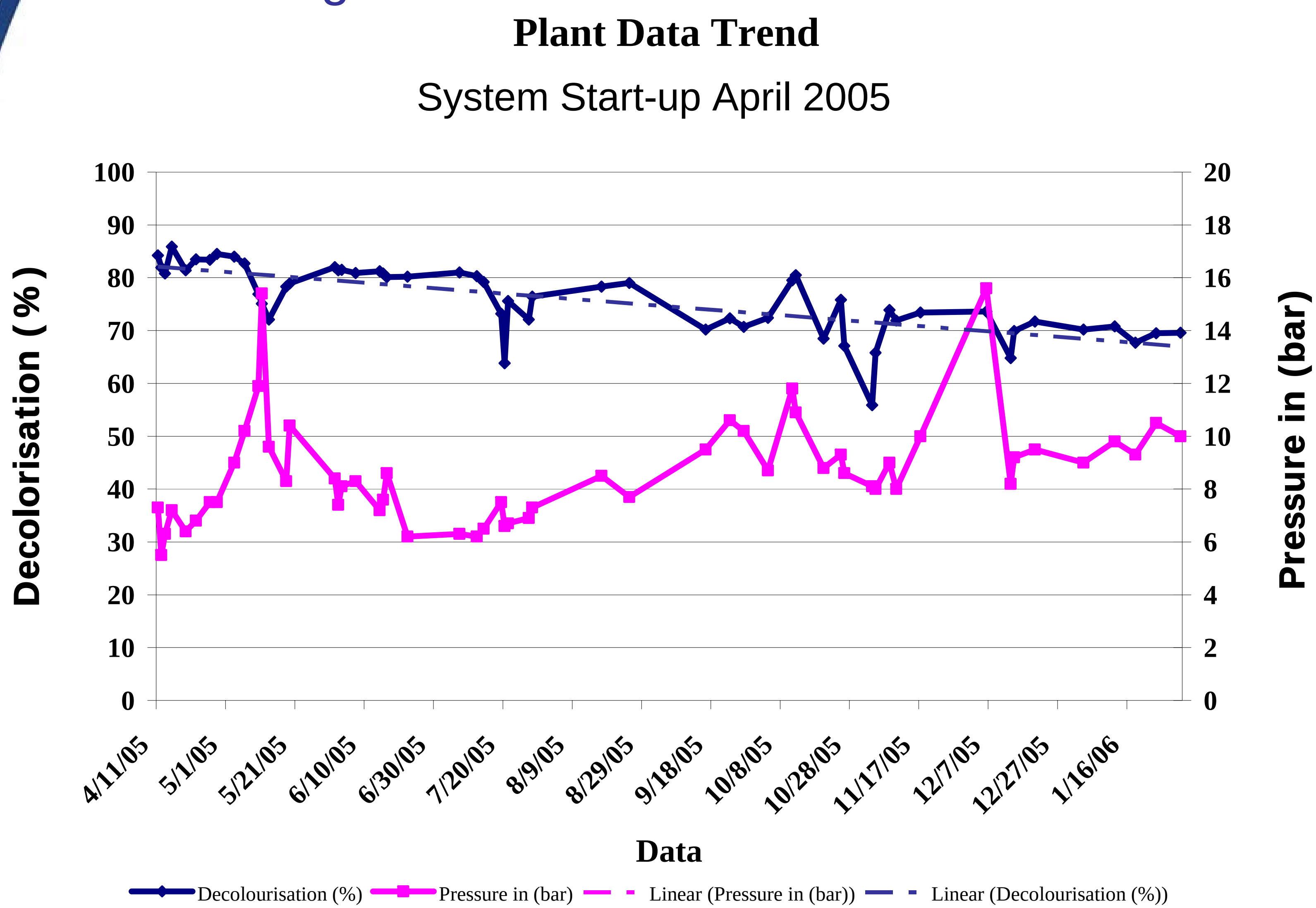
Foulants
Particles
Bio-growth
Mg(OH)2
CaCO3

Permeate

Color 15,000 ICU
NaCl 10%
NaOH 2%

HYDRACoRe Performance

Brine Regenerate Decolorization



NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

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 pHT

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 70pHT
  - **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/purifie 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.