Membrane TECHNOLOGY FORUM®

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Pushing Boundaries:

Vandstrom Inc.'s Innovations in Next Generation Membrane Development

John Charest

Membrane Scientist

VANDSTROM

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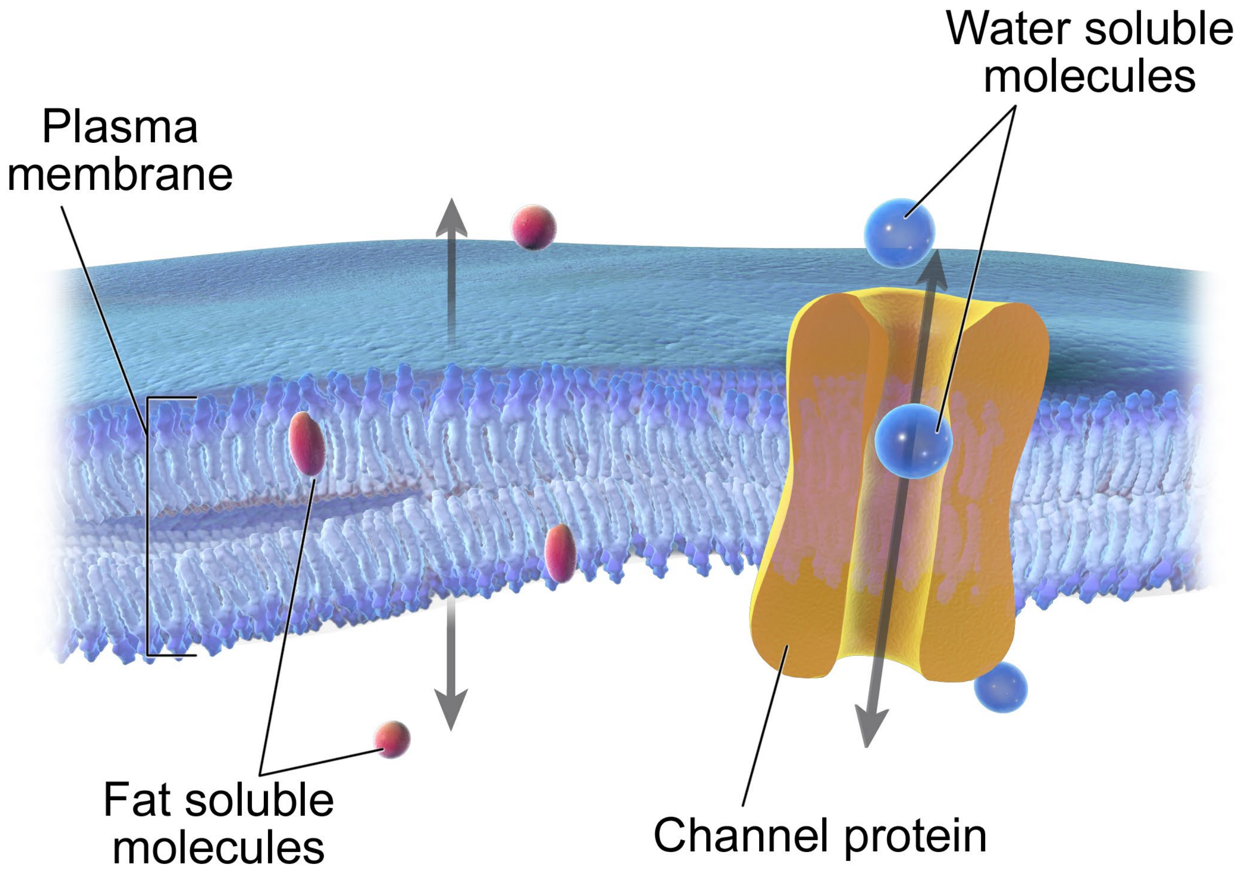
Vision of Vandstrom

Vandstrom strives to develop more efficient membrane technologies using the most efficient separation principle, which has evolved over billions of years.

“If everyone can do it, we shouldn’t do it – but if no one can do it, maybe we have a shot”.

- Mads Clausen

Grandfather of Vandstrom’s owner



[The Cell Membrane: Passive and Active Transport — The Biology Primer]

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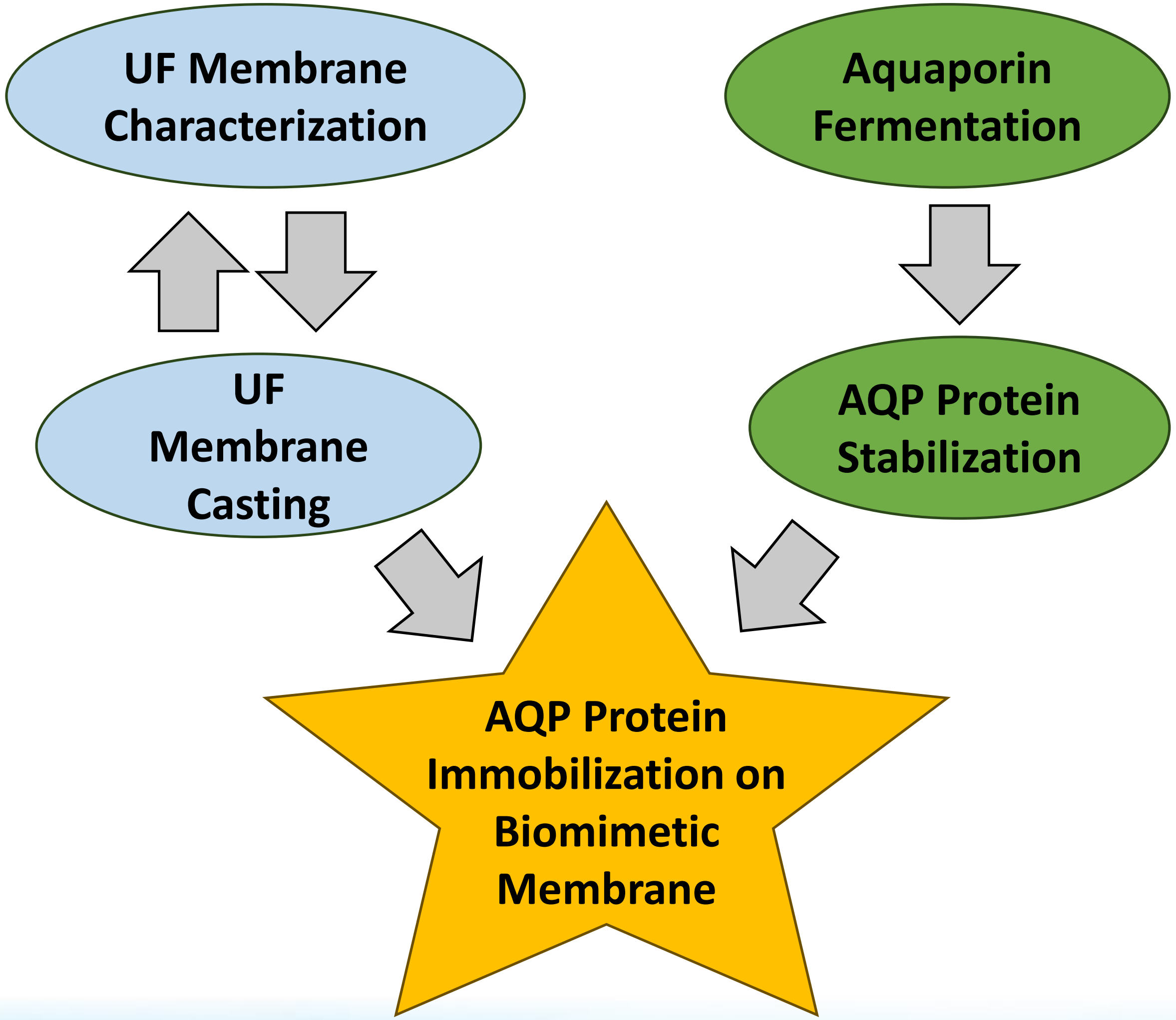
Introduction to Vandstrom, Inc.

- Vandstrom was founded to create biomimetic membranes
  - Vandstrom IP includes producing and isolating Aquaporin (AQP) proteins
  - AQP proteins facilitate water transport though cell membrane
- Vandstrom developed UF membrane as the support for the biomimetic, with potential to be used in Dairy Industry



Presentation Overview

Internal Vandstrom QC tests of UF membrane

- Developing a cost-efficient QC test to determine UF membrane's pore size

- Improving the UF casting process

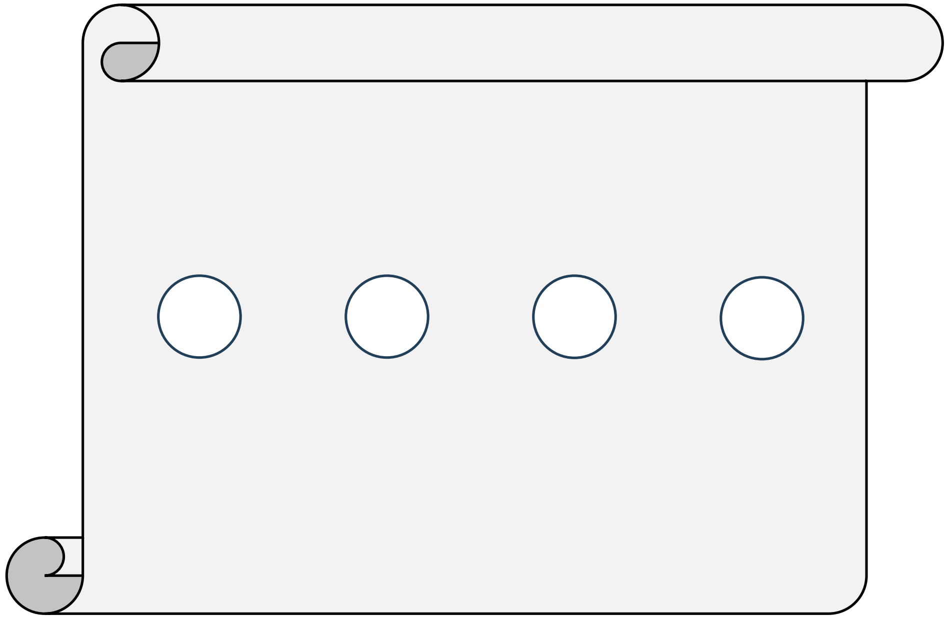
- Vandstrom's strategy for creating next generation of water filtration membranes

Membrane QC at Vandstrom

Vandstrom UF Membrane QC Process

For each UF membrane cast:

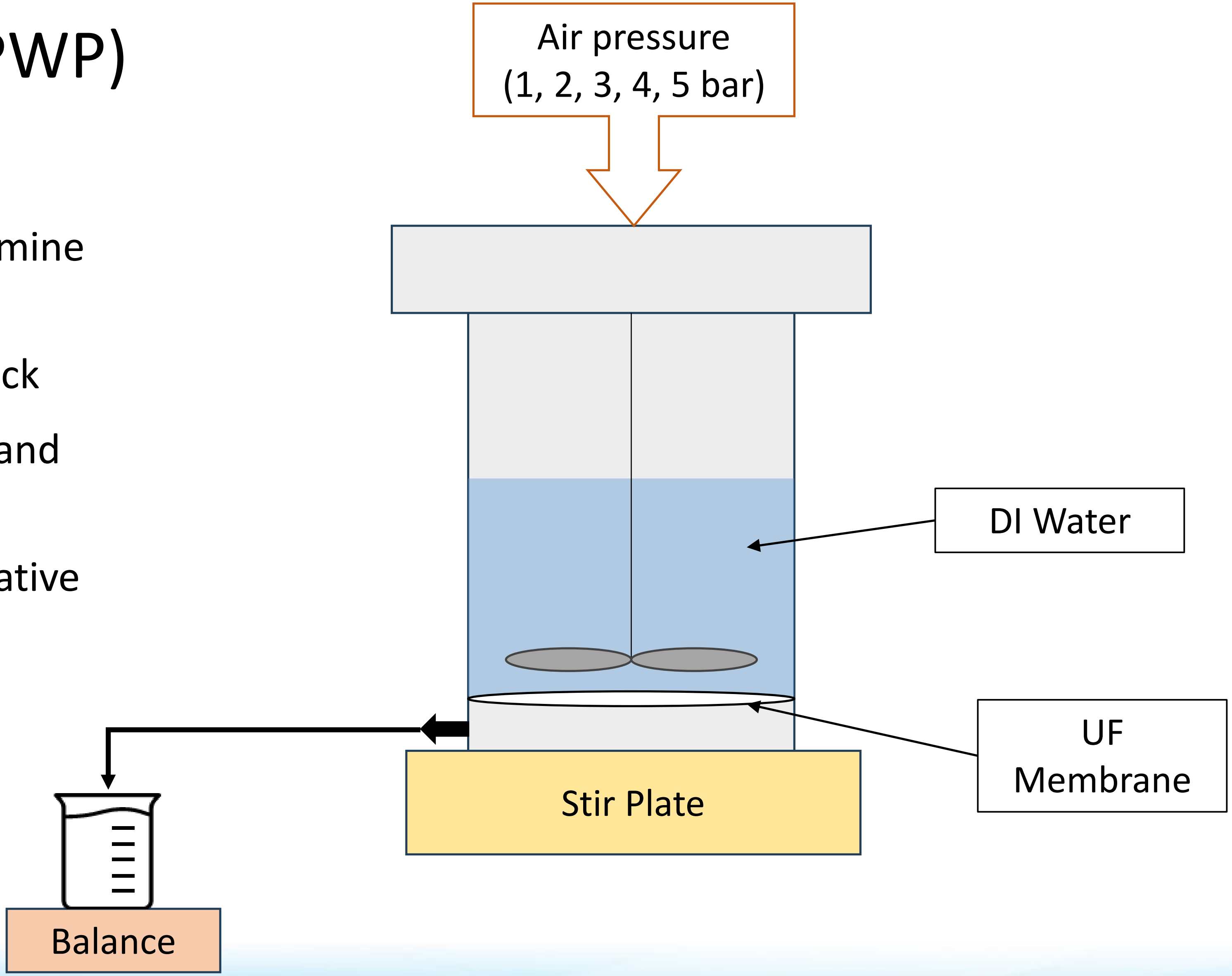
- Vandstrom creates >3,000 linear feet of membrane
- Membrane samples are tested in 4 different positions in the cross-machine direction, every 500 ft
- QC Tests:
  - Thickness: micrometer measurement
  - Pure Water Permeability (PWP): relative porosity determination
  - MWCO: pore size determination



Pure Water Permeability (PWP)

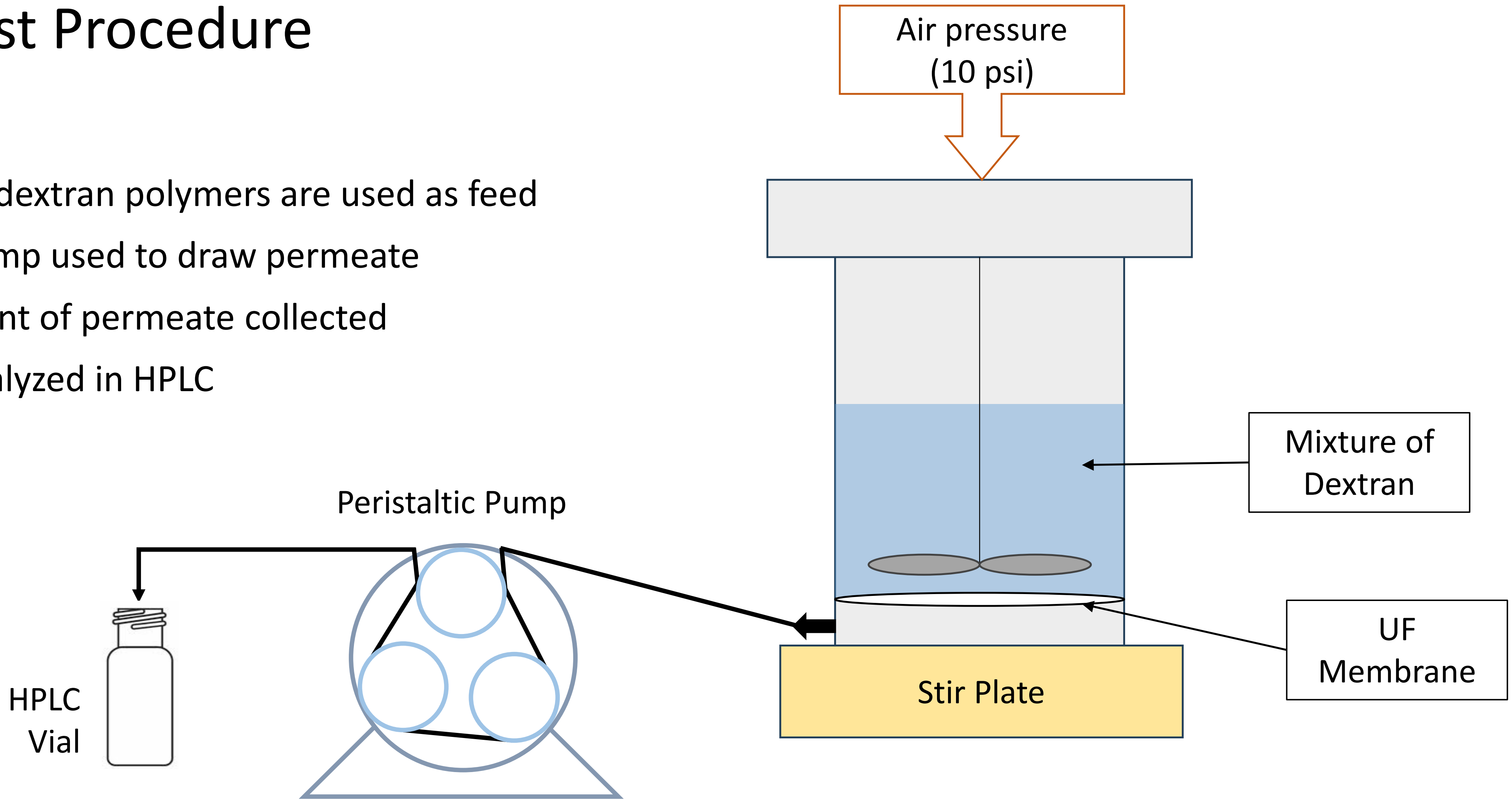
Measuring PWP is the easiest way to determine if the membrane produced is consistent

- PWP test is simple, economical, and quick
- PWP test could be done by one person and one dead end cell
- PWP more of quality control test for relative membrane porosity



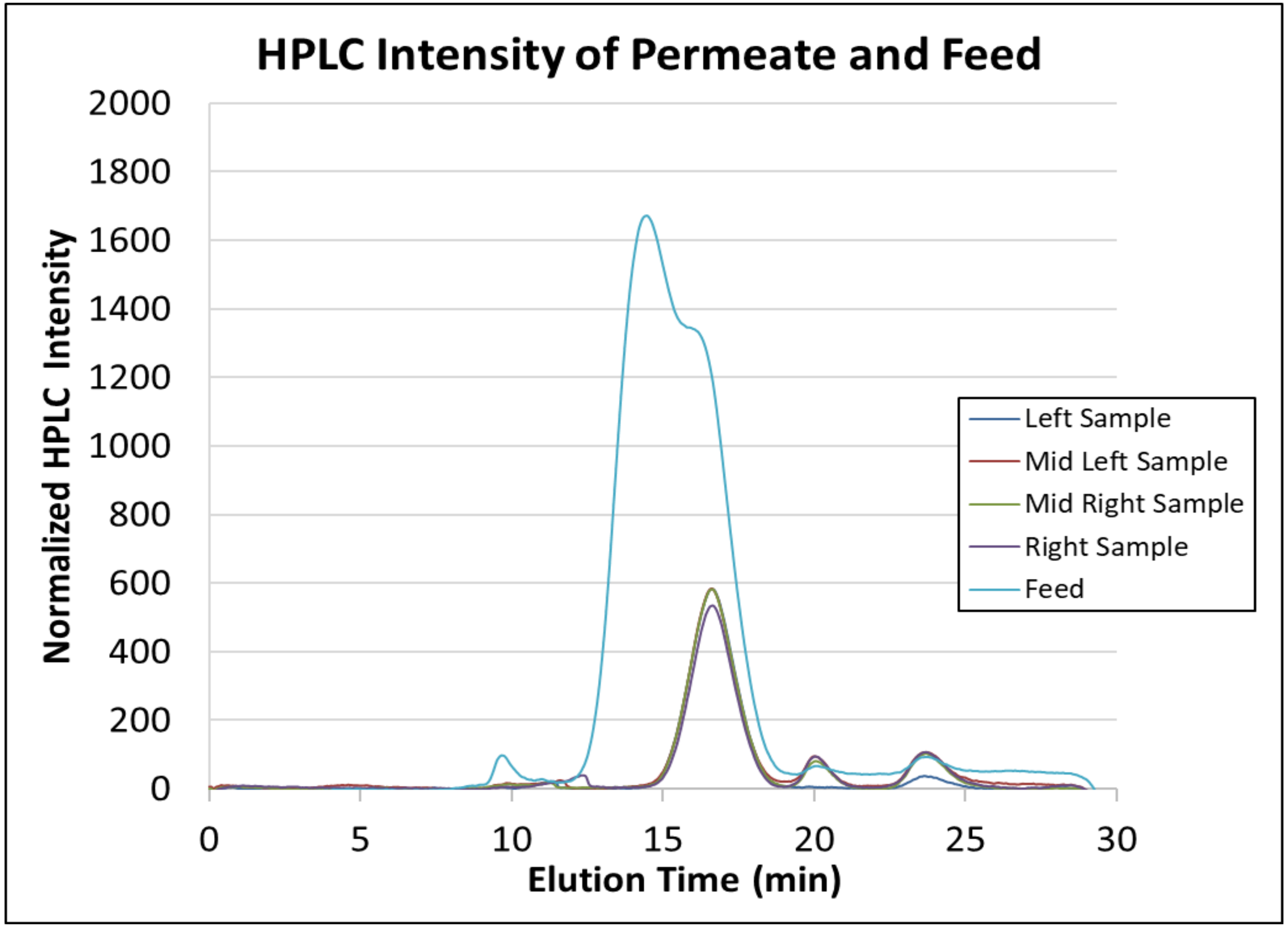
MWCO Test Procedure

- A solution of dextran polymers are used as feed
- Peristaltic pump used to draw permeate
- Precise amount of permeate collected
- Permeate analyzed in HPLC



MWCO Analysis

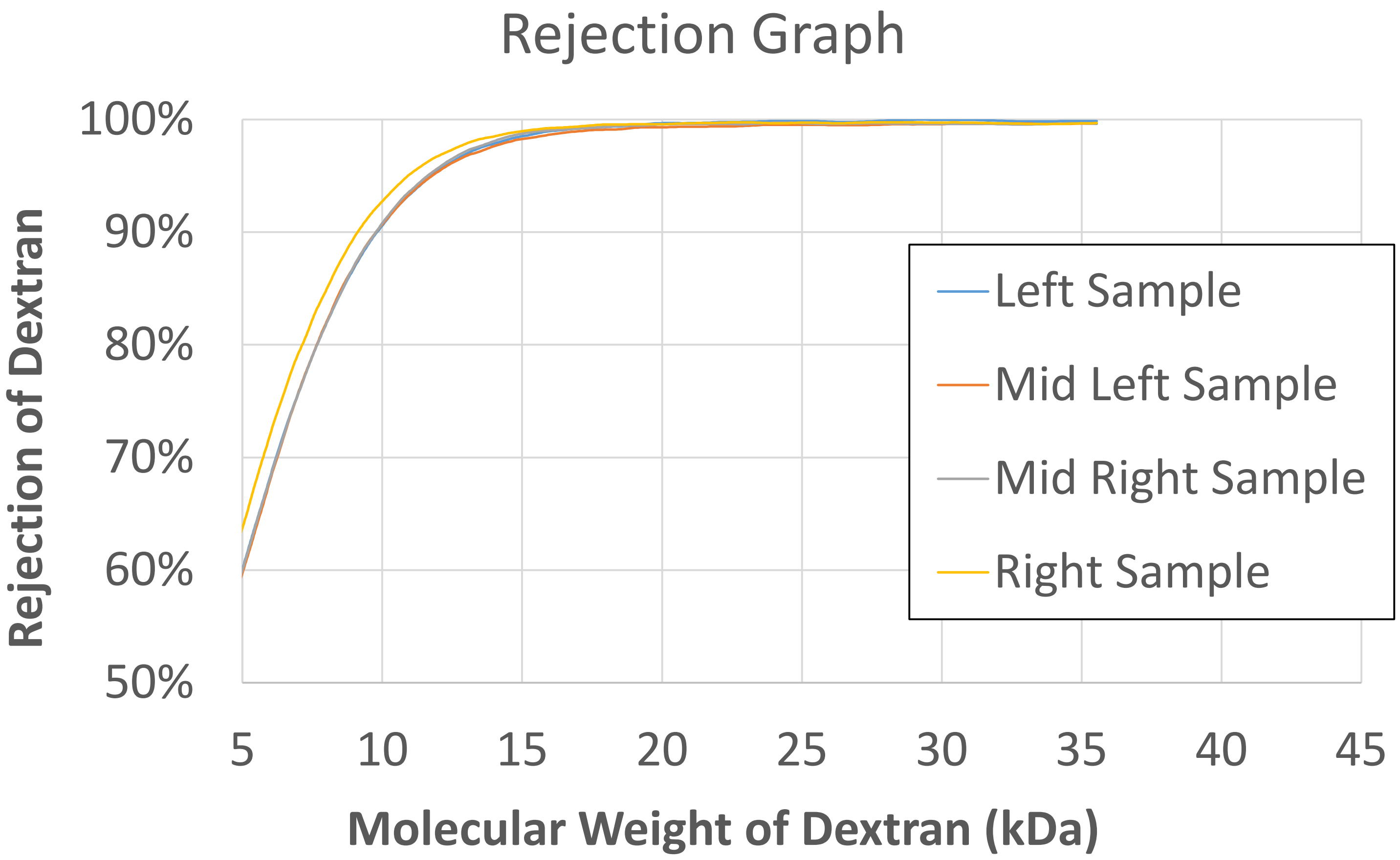
- HPLC separates polymers based on molecular weight
- Calibration curve converts elution time to MW (kDa)
- “90% MWCO” is when permeate signal intensity is 10% the feed’s signal intensity
- Analysis takes 30 minutes per sample



HPLC chromatograms of feed and permeates

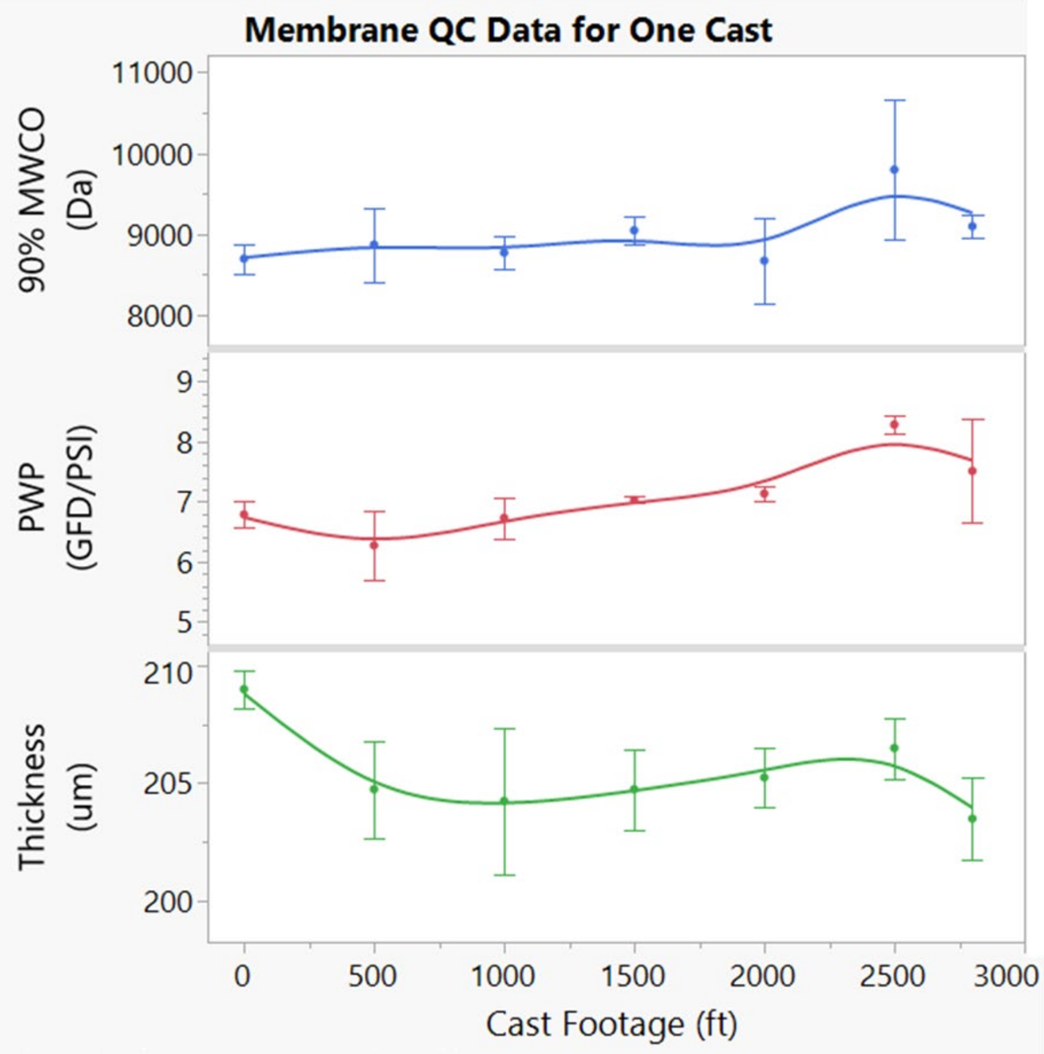
MWCO Analysis

- Previous graph is converted to rejection vs Dextran MW
  - Determined 90%, 95%, and 99% MWCO values in kDa
  - Able to determine relative distribution of pore sizes



QC Data for a 10k UF Cast

- Statical modelling software used to correlate casting conditions to QC results
- Narrow y-axis is used to show variability
  - High MWCO value at 2,500 ft likely random error during complicated test
  - Permeability variability between 6 and 8 has negligible effect on membrane performance in field
  - Thickness decrease over time likely due to increasing dope temperature



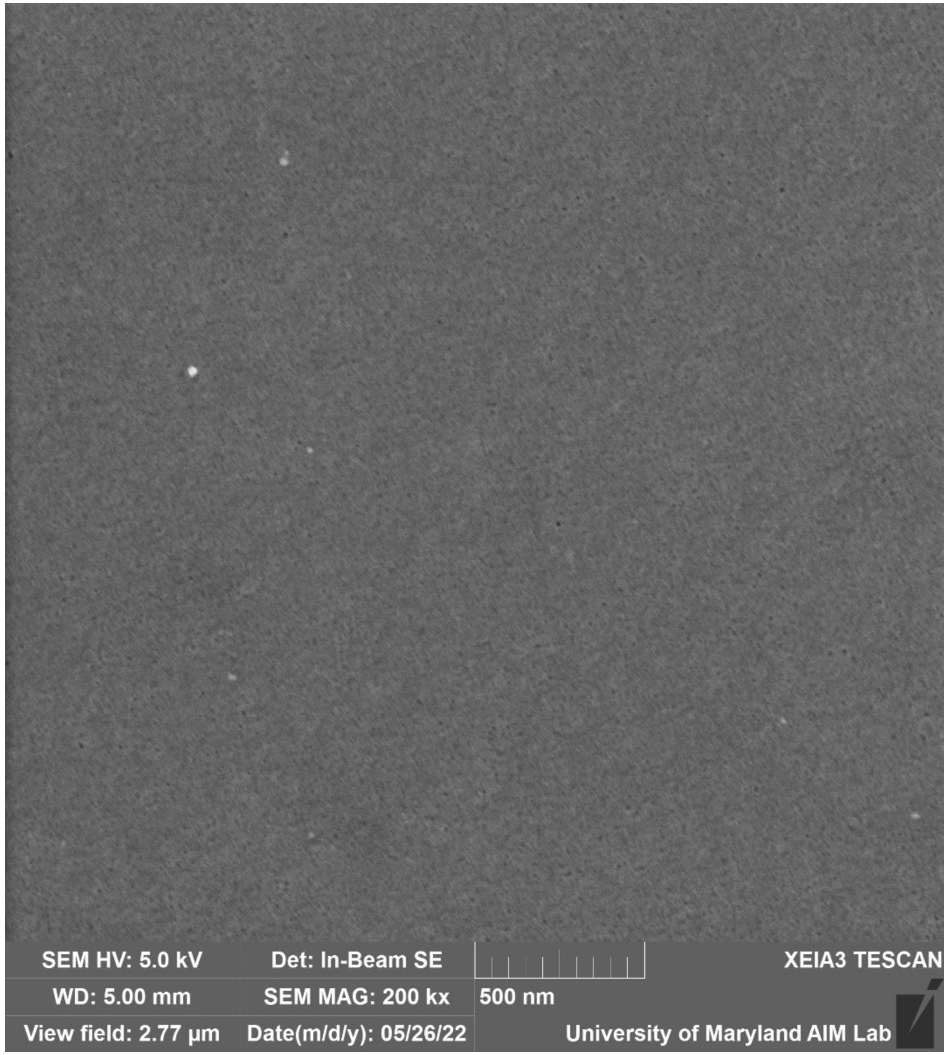
Each error bar is constructed using 1 standard deviation from the mean. n=4

Making Pore Size Determination More Cost Efficient

Developing a New Quality Control (QC) Test for Pore Size

<u>New QC test should:</u>

- Be usable by QC technicians in manufacturing
- Be a cross-flow test
- Accurately determine 90% MWCO value of membrane between 7 and 11 kDa



SEM Image of 10kDa Membrane at 200kX magnification

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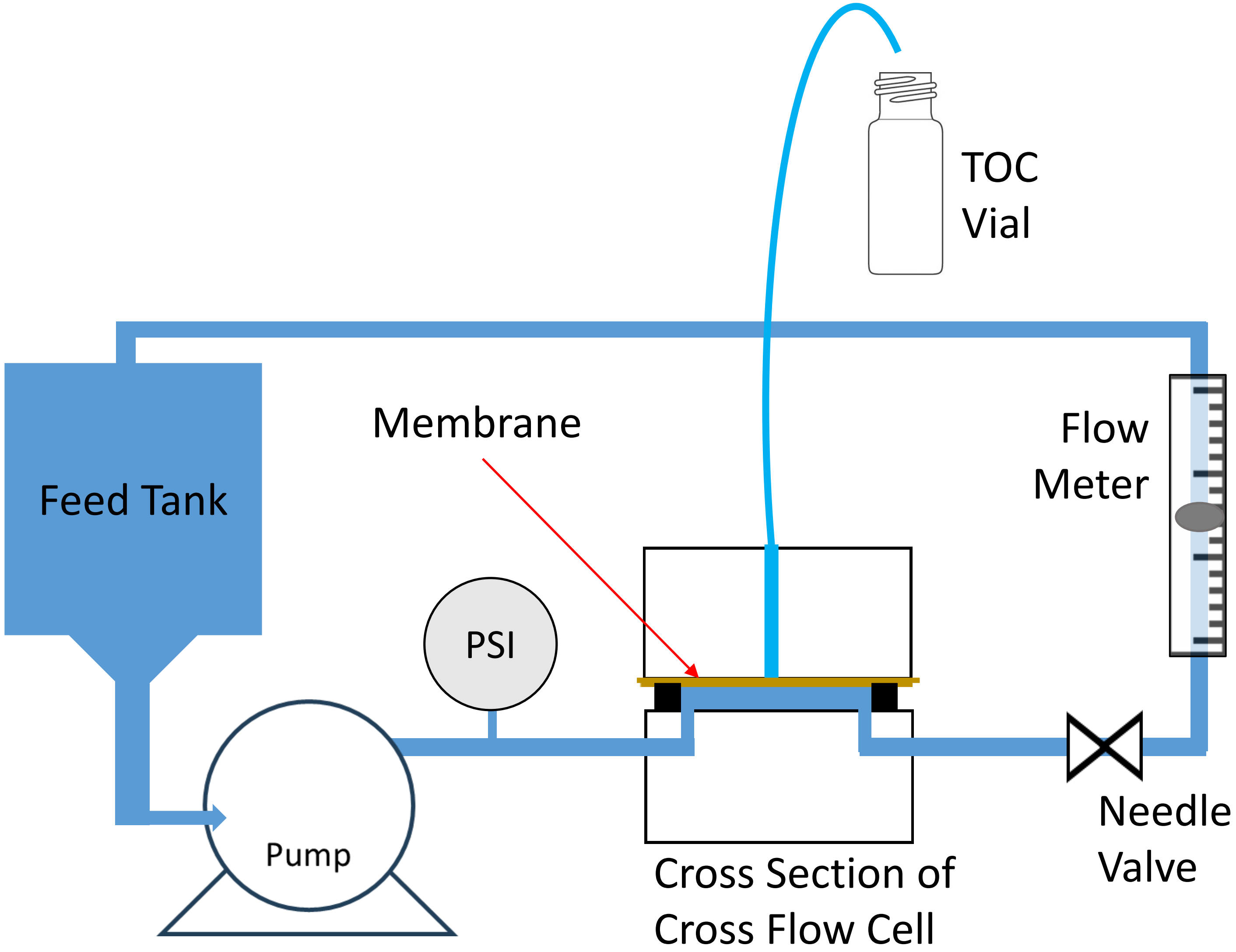
PEG Test Overview

- Polyethylene glycol (PEG) used as polymer marker
- PEG rejection was used to gauge pore size

$$Rejection\ \% = \left[1 - \left(\frac{Permeate\ Concentration}{Feed\ Concentration}\right)\right] \times 100\%$$



PEG Test System

- Cross flow system could test multiple membranes at once
- Hydraulic pistons open and close the membrane test cell
- Pressure and flow can be monitored and controlled for all cells

PEG Rejection Test Motivation

HPLC Determination of Pore Size:

- Results are in kilodaltons (kDa)
- Multiple sized Dextran markers used as feed
- Relatively high OPEX
  - Dextran markers are expensive
  - Columns for HPLC have a lifetime

PEG Rejection Test Motivation

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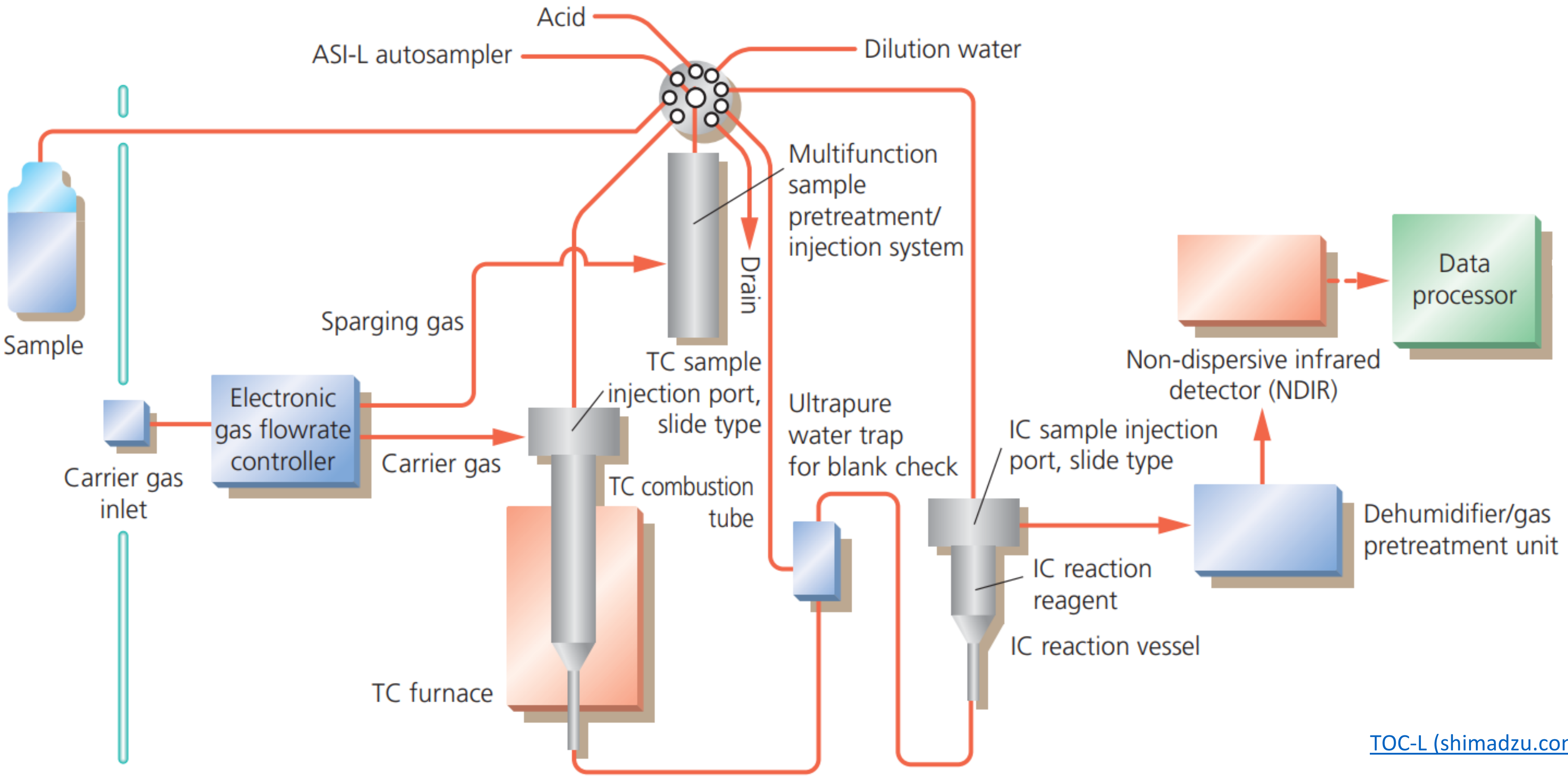
TOC Determination of Pore Size:

- Cross flow tests are more representative of element
- Faster, simpler test
- More economical
- Less likely to change over time, compared to HPLC columns
- Only single marker, so results are not directly translatable to kDa

Total Organic Carbon (TOC) Analyzer

- TOC could quickly and accurately determine carbon concentration
- TOC has auto-dilution and autosampler
- TOC turns organic carbon into CO_2 using heated catalyst beads



TOC-L (shimadzu.com)

Determined Variables Associated with PEG test

- PEG rejection could be affected by:
  - PEG concentration (ppm)
  - Feed flow rate (GPM)
  - Feed temperature (°C)
  - Feed pressure (psi)

Determined Variables Associated with PEG test

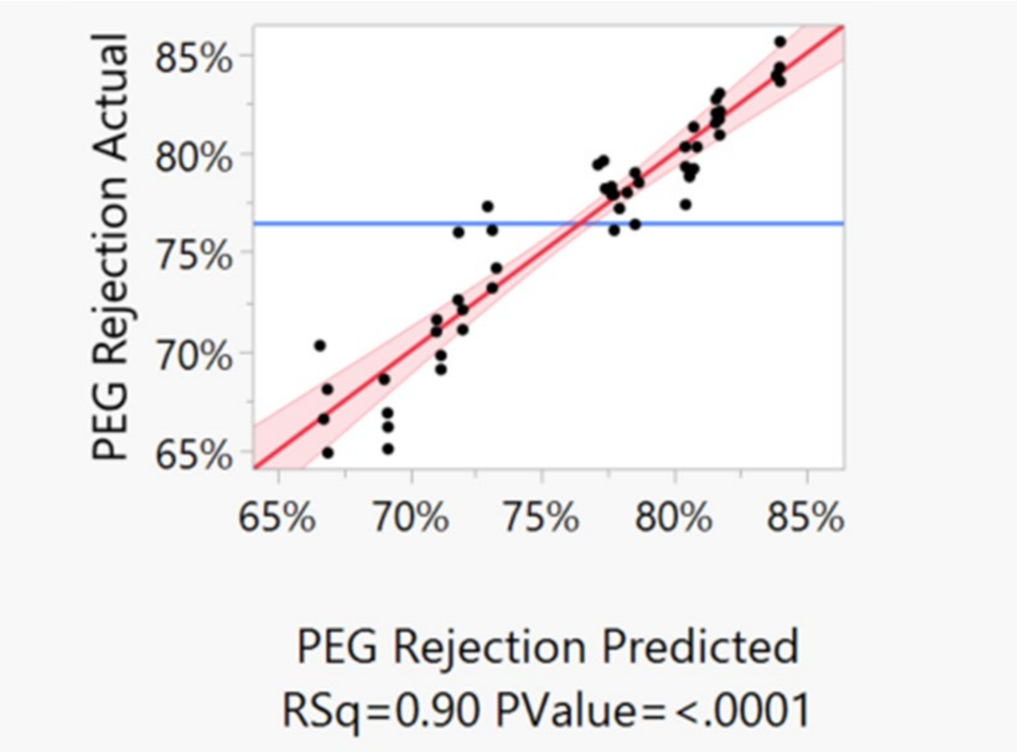
- PEG rejection could be affected by:
  - PEG concentration (ppm)
  - Feed flow rate (GPM)
  - Feed temperature (°C)
  - Feed pressure (psi)
- JMP used to design experiment to determine relative effect of different test variables.

PEG Concentration (ppm)	Feed Flow Rate (GPM)	Feed Temp. (°C)	Feed Pressure (Psi)
400	0.5	20	5
400	0.5	26	4
400	0.7	26	3
400	0.9	20	3
400	0.9	23	5
600	0.5	23	3
600	0.5	26	5
600	0.7	20	5
600	0.9	20	4
600	0.9	26	3
500	0.5	20	3
500	0.7	23	4
500	0.9	26	5

JMP Created Models to Determine Effect of Each Variable

High correlation (R^2 = 0.90) between the JMP model and the results, means:

- Variables were controlled and measured accurately
- Feeds and permeates were analyzed precisely by the TOC



JMP Created Models to Determine Effect of Each Variable

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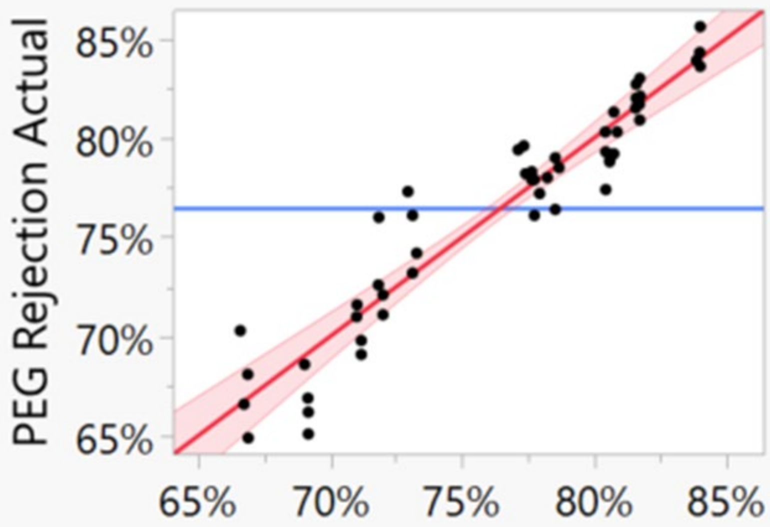
Effect summary shows all variables tested have significant impact on PEG rejection



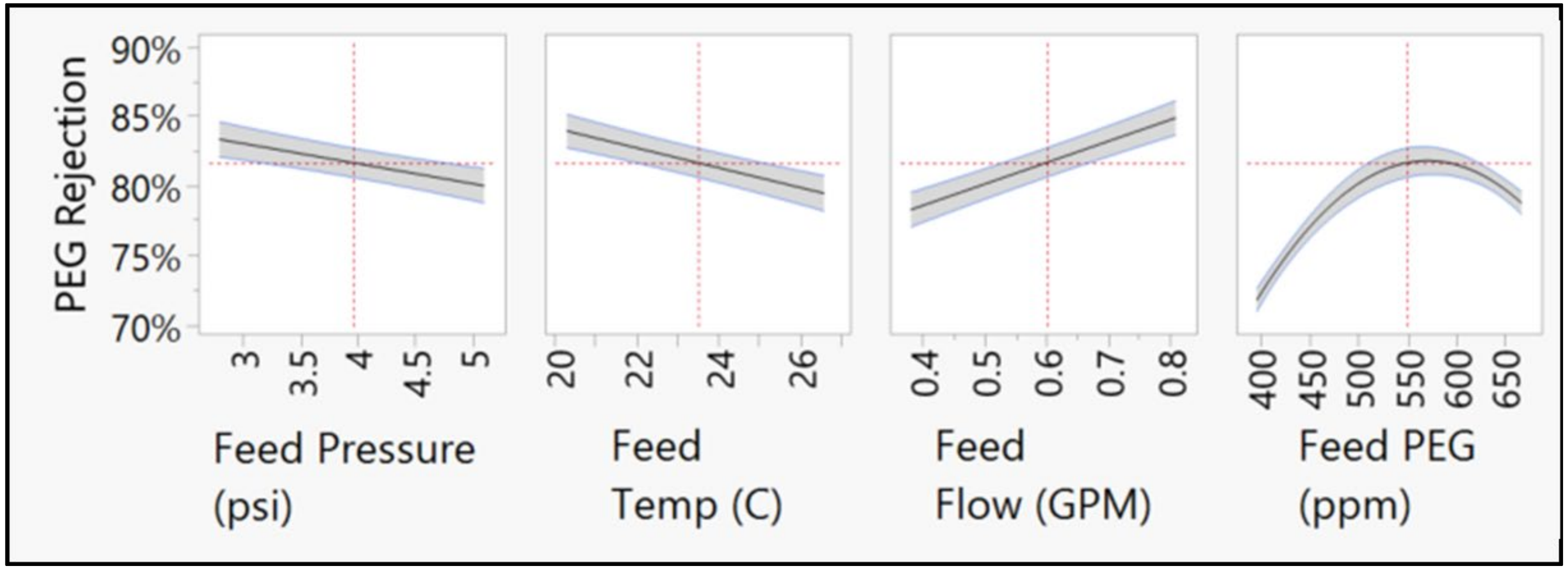
PEG Rejection Predicted
RSq=0.90 PValue=<.0001

Effect Summary

Source	PValue
Feed PEG Conce (ppm)	0.00000
Feed (GPM)	0.00000
Feed PEG Conce (ppm)*Feed PEG Conce (ppm)	0.00000
Feed Temp (C)	0.00000
Feed Pressure (PSI)	0.00001

Variables’ Effects on PEG Rejection

- Higher feed pressure leads to lower rejection
- Higher feed flow rate leads to higher rejection
- PEG rejection lowers when in feed temperature increases
- PEG concentration has minimal impact between 500-600 ppm.



If we control these 4 test variables, we will have repeatable test results

Choosing PEG Rejection Test Conditions

PEG Rejection Test Conditions:

- Feed Pressure: 4.0 psi
- Feed Flow: 0.8 GPM
- Feed Temp: 22.5 to 23.0°C
- Feed Conc.: 500 to 550 ppm

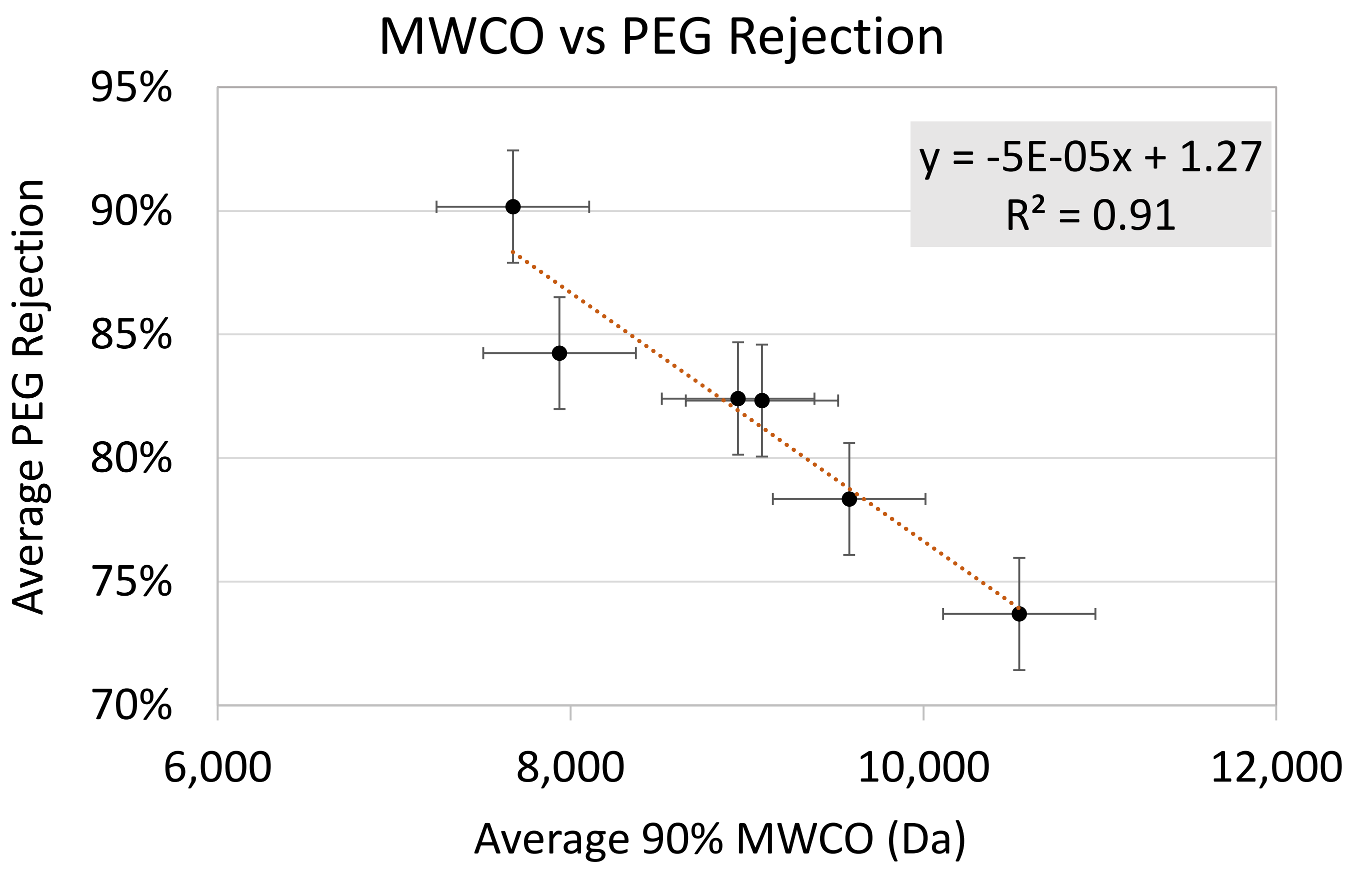
- Low pressure, similar to MWCO test

Converting PEG Rejection Results to MWCO Results

- Multiple grades of UF membranes were cast on the pilot caster
- These casts were extensively tested using MWCO and PEG rejection test

Converting PEG Rejection Results to MWCO Results

- Multiple grades of UF membranes were cast on the pilot caster
- These casts were extensively tested using MWCO and PEG rejection test
- High R^2 value correlating PEG rejection to 90% MWCO values
- Lower coefficient of variability for PEG rejection



Error bars represent 1 standard deviation from the mean

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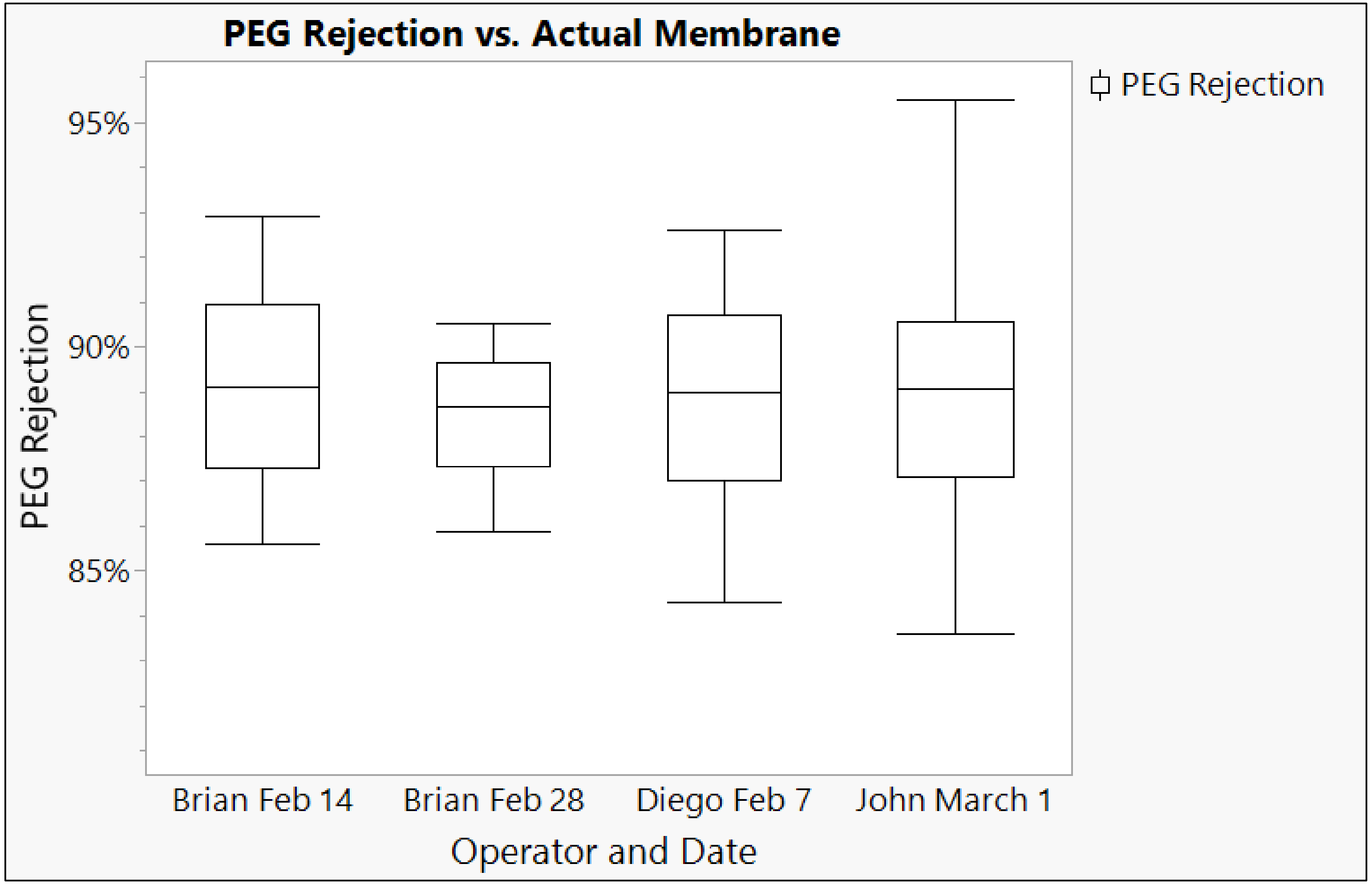
PEG Test Repeatability and Reliability

After SOP was written, trials were conducted to confirm reproducibility of the test.

Multiple operators on different days used the system and had the same results.

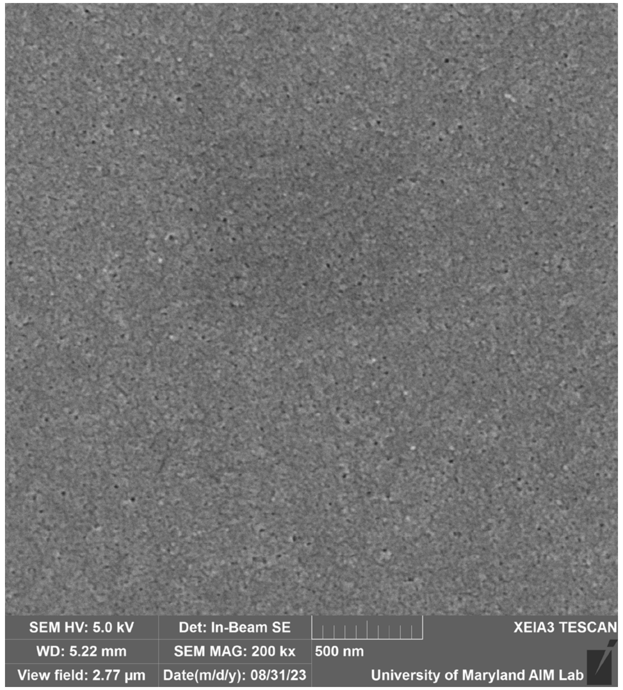


Developing New QC Tests

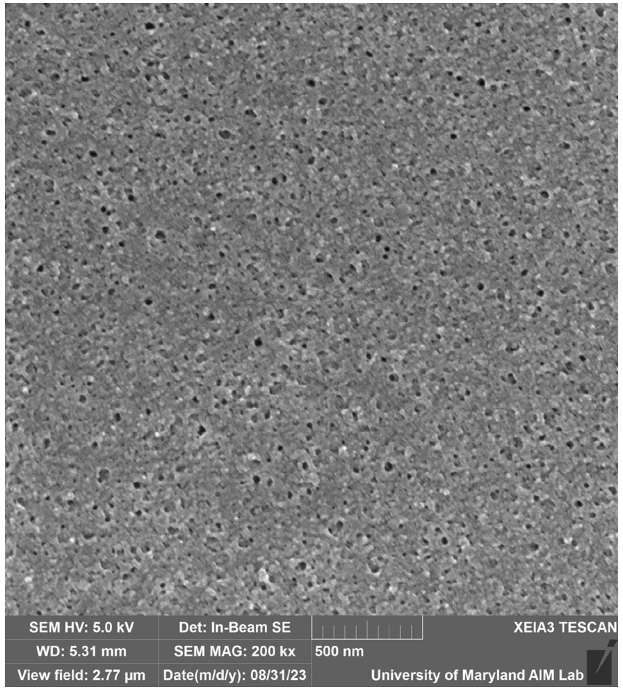
Test development for other flat sheet membranes:

- Increase marker size for more open membranes
- Increase feed pressure for membranes with smaller pores

MWCO 25 kDa



MWCO 75 kDa



SEM images of membrane surfaces at 200kx magnification

Developing New QC Tests

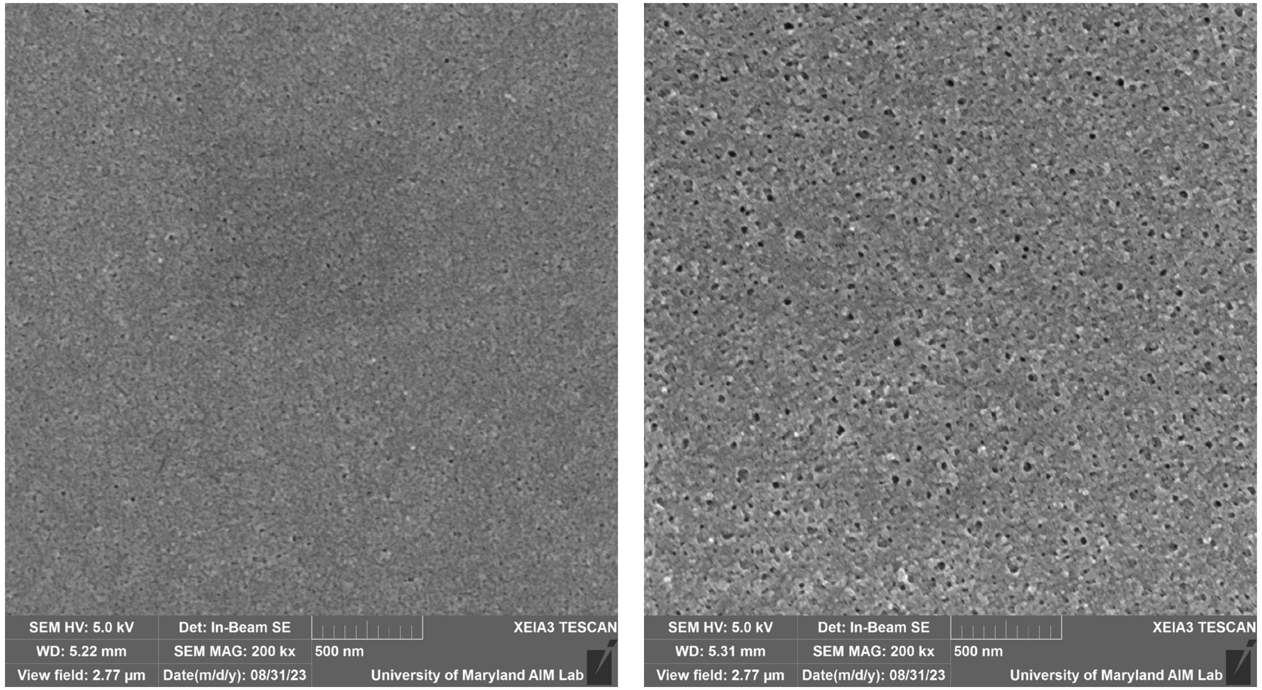
Test development for other flat sheet membranes:

- Increase marker size for more open membranes
- Increase feed pressure for membranes with smaller pores

<u>Non-Destructive Element Defect Detection:</u>

Using a large single marker in conjunction with the TOC to determine defect size in elements

MWCO 25 kDa   MWCO 75 kDa



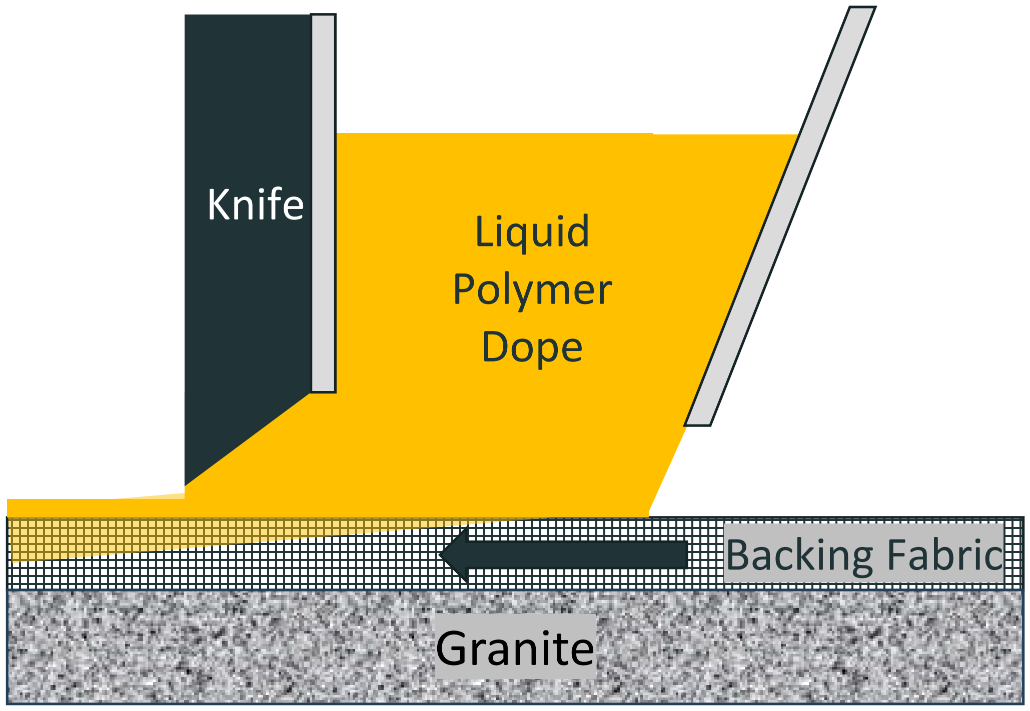
SEM images of membrane surfaces at 200kx magnification

Improving Knife-Over-Granite UF Casting

Knife Over Granite Casting

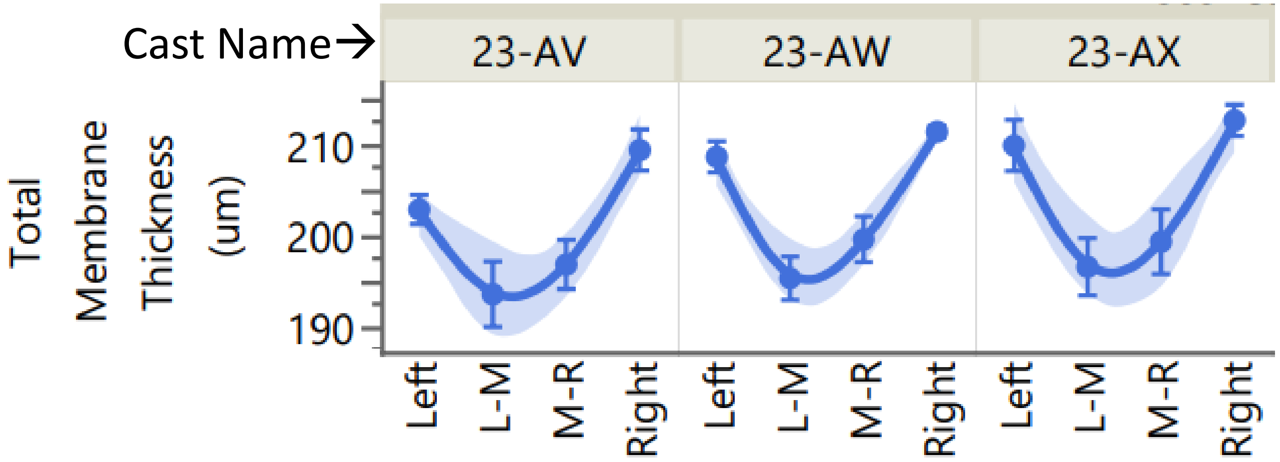
- Many manufacturers use slot die for UF casting
- Knife over granite is a simpler method for casting UF membranes
- With improvements in backing fabric uniformity, the risk of tear outs is minimized.
- Vandstrom was able to produce consistent membrane using knife over granite

Cross Section of Knife Over Granite Process



Nonuniform Thickness Distribution

- Initially, there were issues with thickness uniformity of the UF membrane
- Edges thicker than the middle

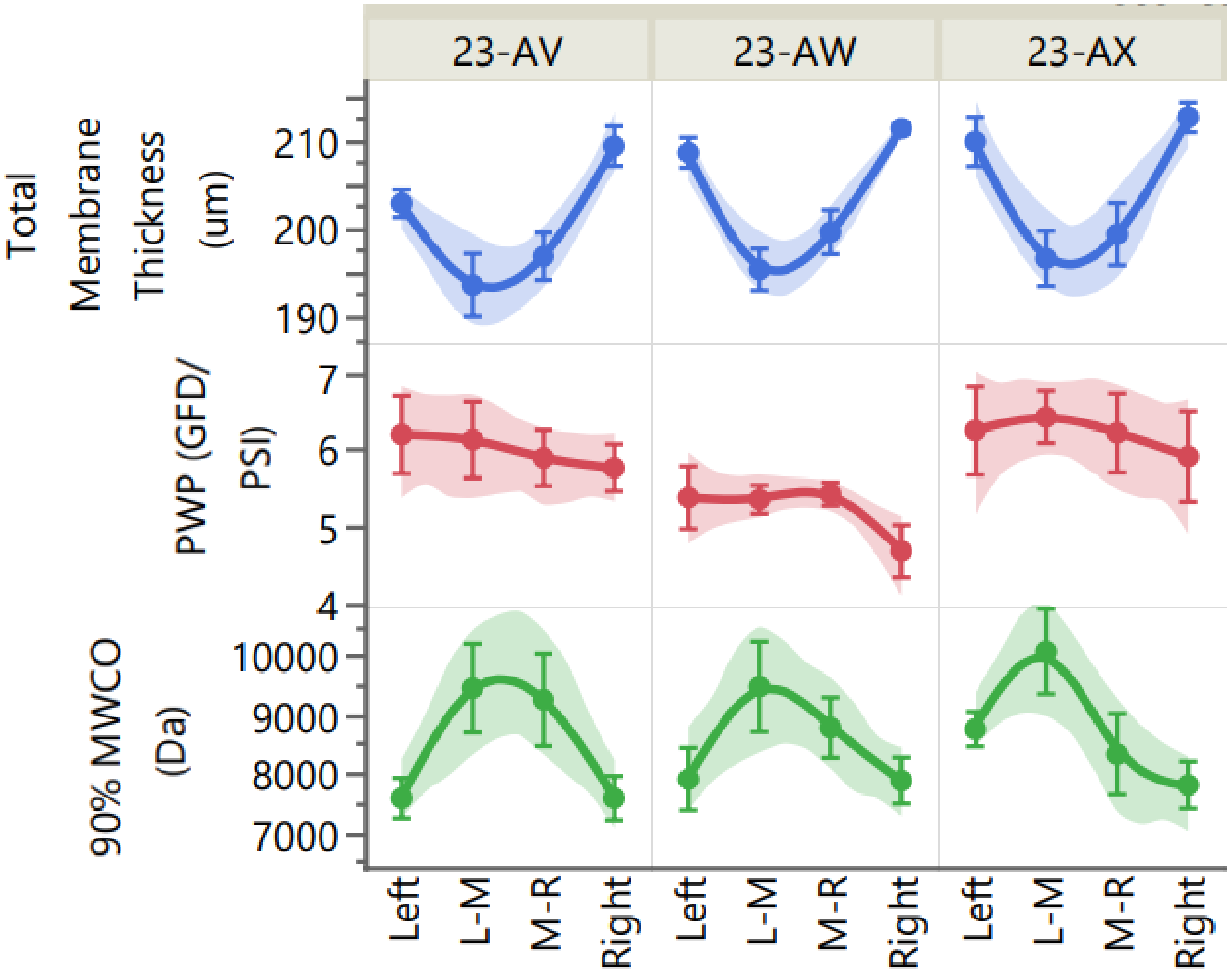


Nonuniform Thickness Distribution = Inconsistent Membrane Performance

- Initially, there were issues with thickness uniformity of the UF membrane
- Edges thicker than the middle

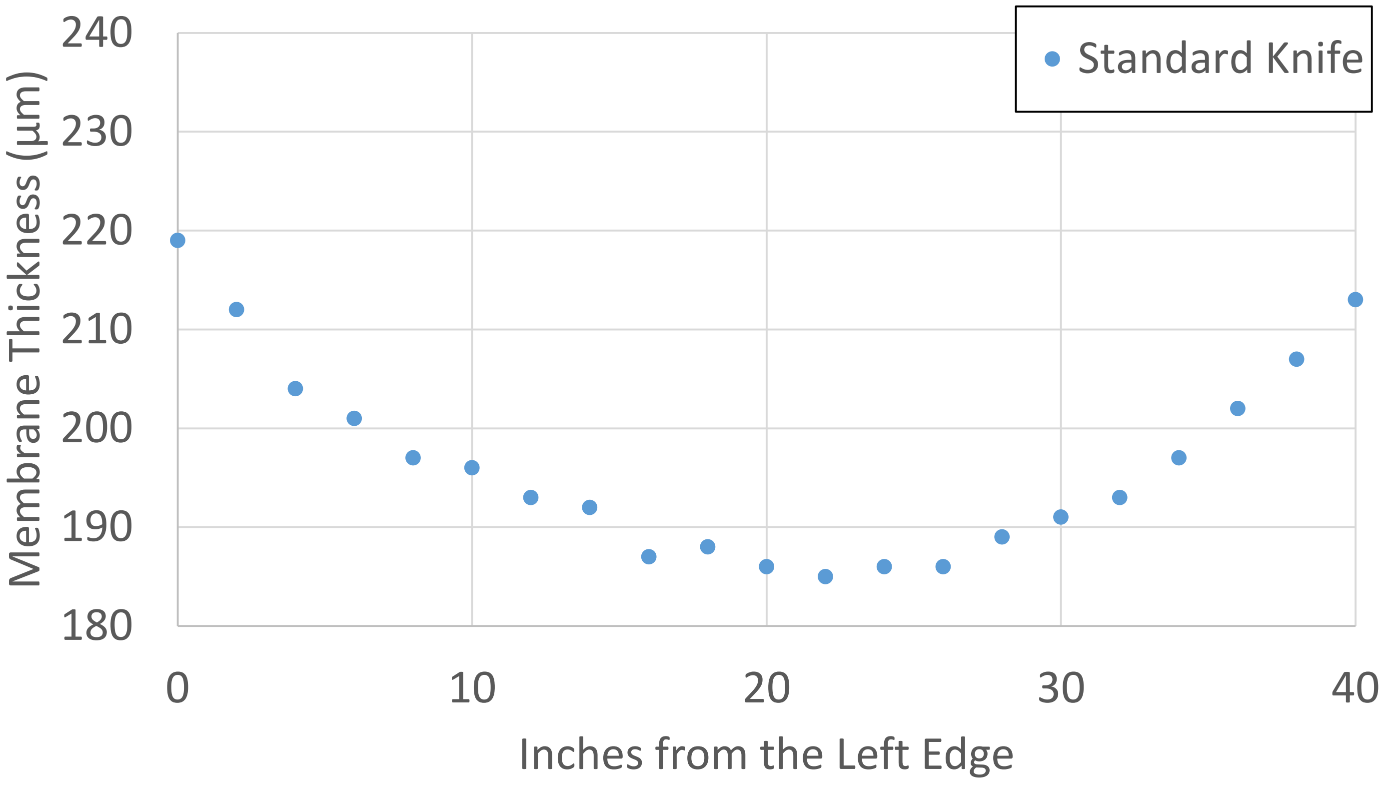
Thickness resulted in nonuniform performances:

- MWCO was higher in the thinner middle
- Pure water permeability lower for thicker membranes



Troubleshooting Thickness

- On right is the thickness of a standard membrane cast
  - Thickness measured every 2 inches
- The source of the thickness profile was not obvious:
  - The knife was machined straight
  - The distance between knife and granite was measured to be consistent



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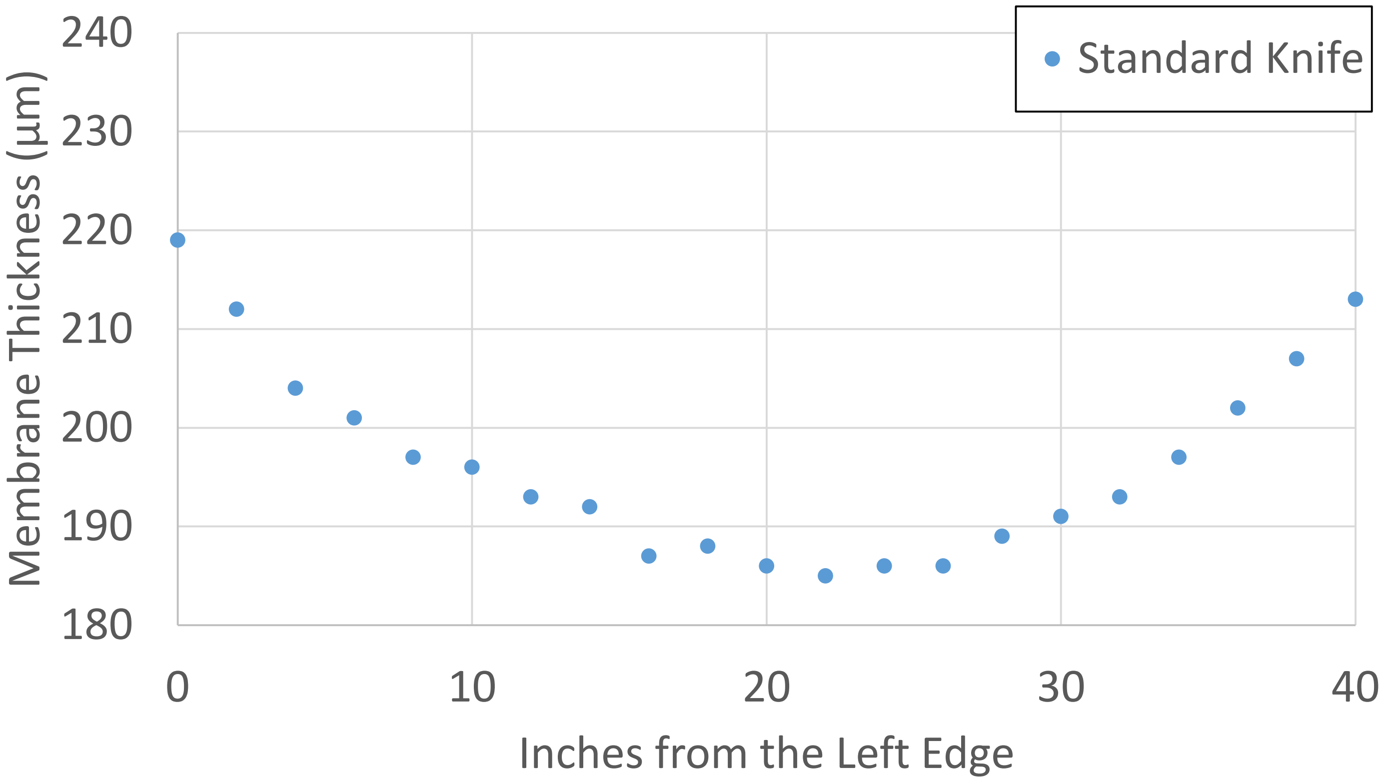
Thickness Measurements in Cross Machine Direction

In a normal cast:

- The knife was bolted to steel frame
  - The frame connected to a tank of cold-water
  - Knife was cold during the run



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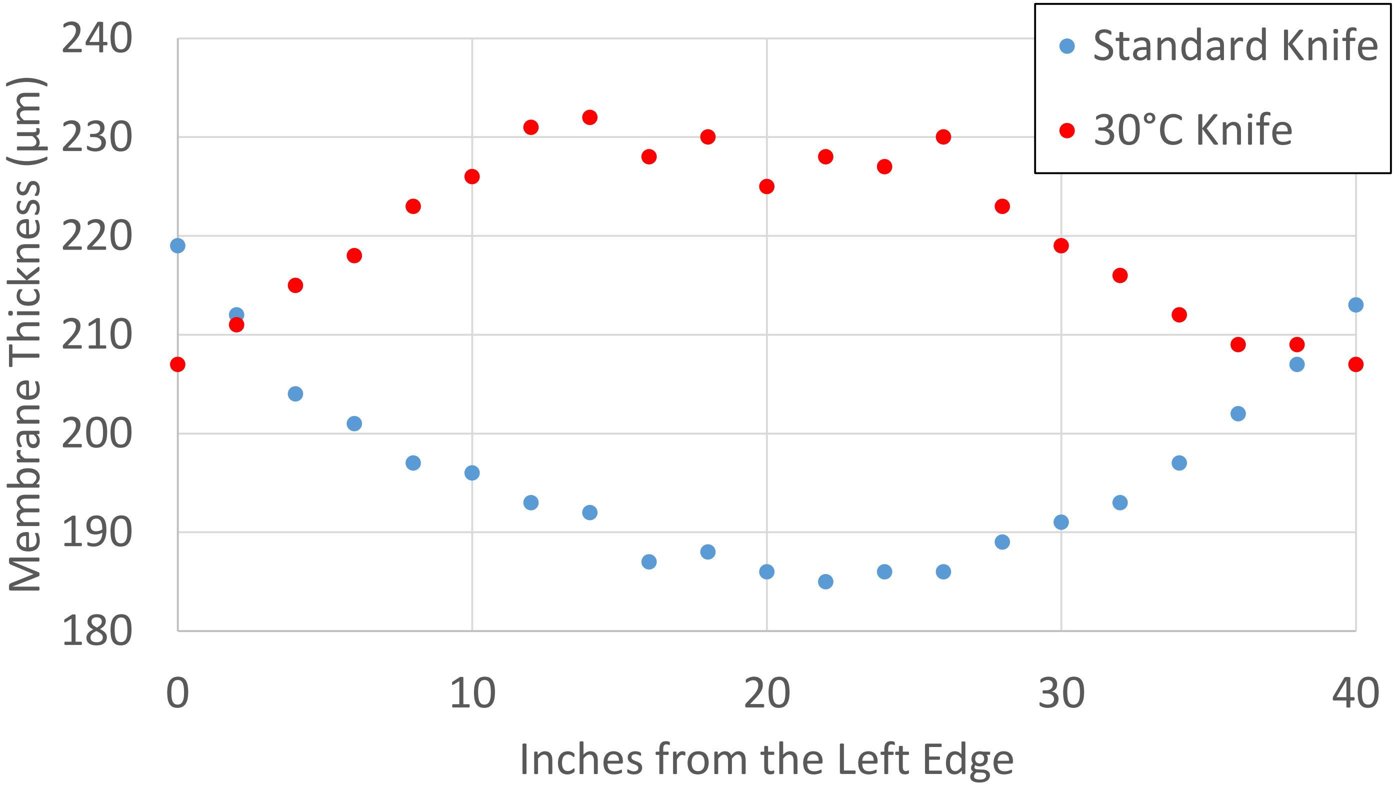
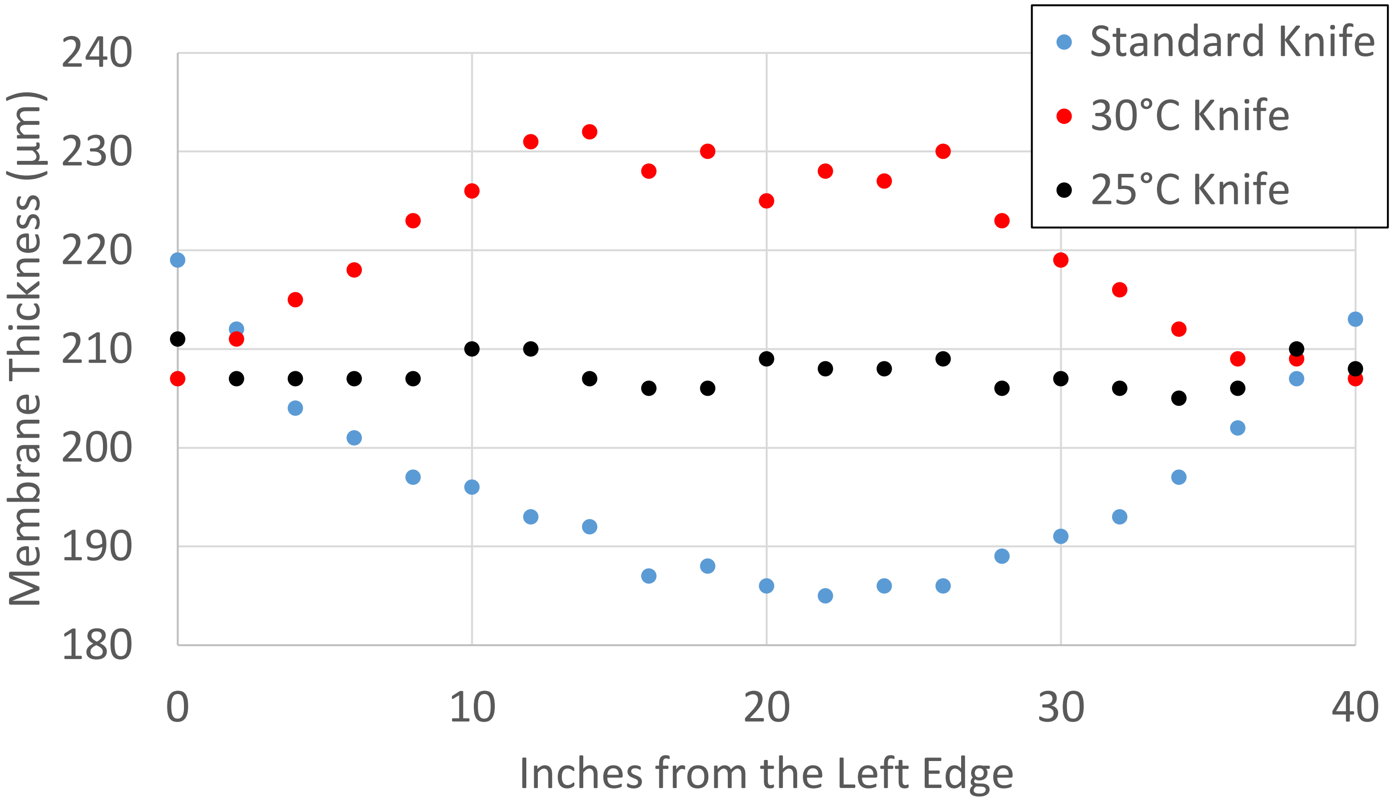
Thickness Measurements in Cross Machine Direction

- We heated the knife and observed the opposite profile



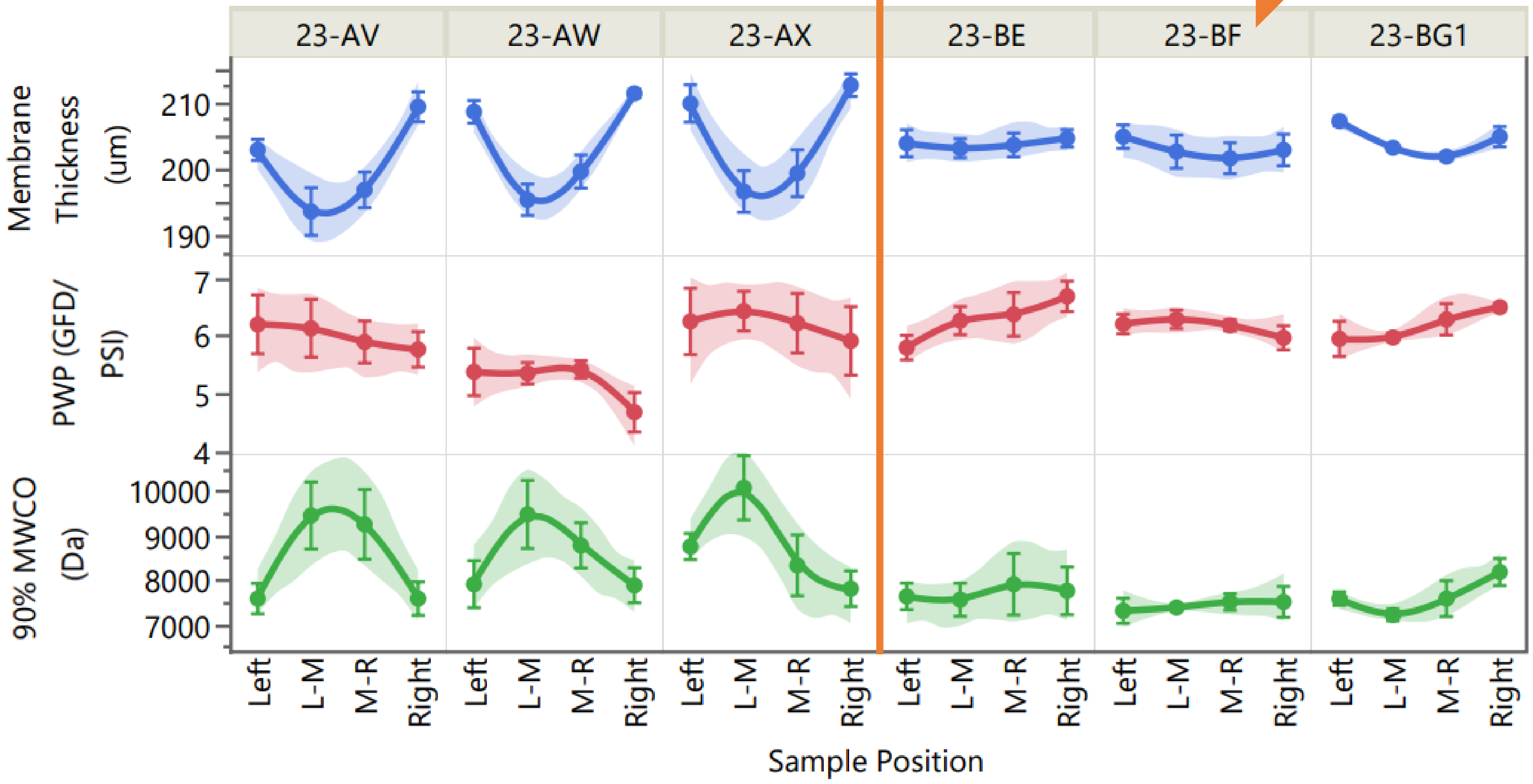
Thickness Measurements in Cross Machine Direction

- We built a temperature control system for the knife
- Observed incredibly flat membrane profile



Improved Thickness Distribution = Improved Membrane Properties

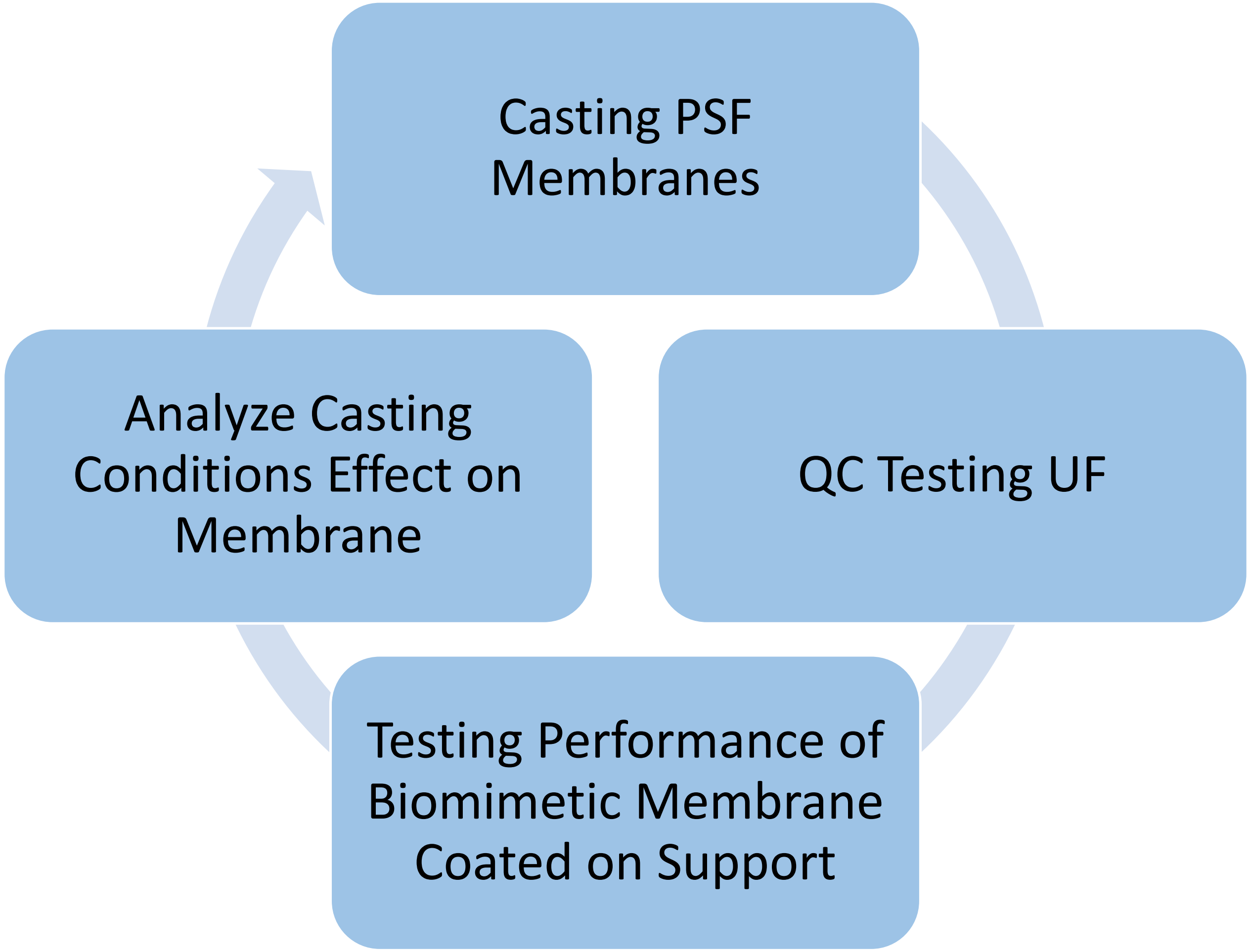
After Temperature Control Established on Knife



Casting PSF Membrane Supports for Biomimetic Membranes

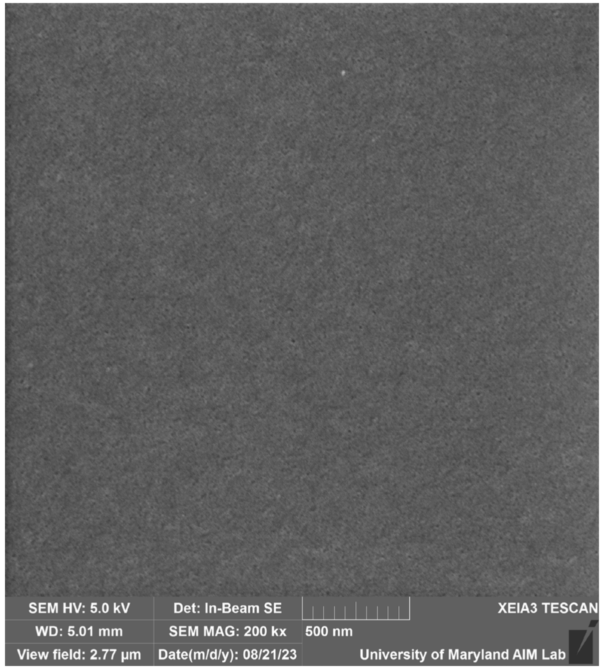
Lessons learned from 10kDa UF development are being applied to support casting:

- Cast membranes with uniform thickness
- High level of testing to ensure uniform UF membranes are cast
- New QC test development for new membranes

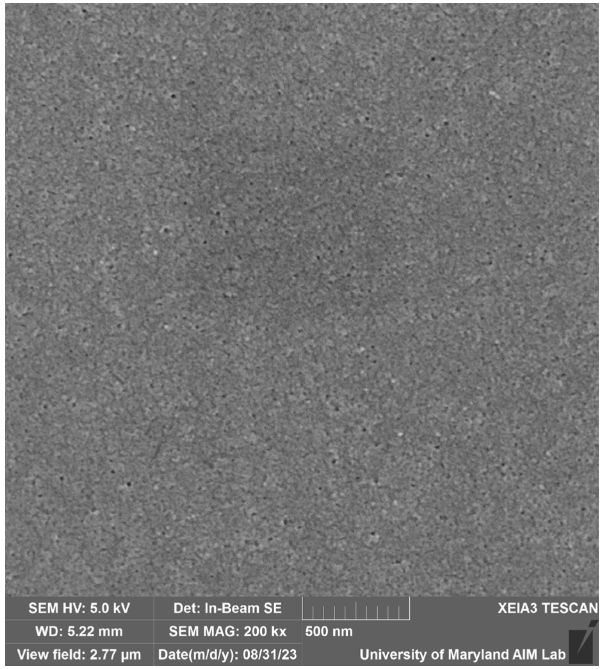


SEM Images Membranes with Higher MWCO Values

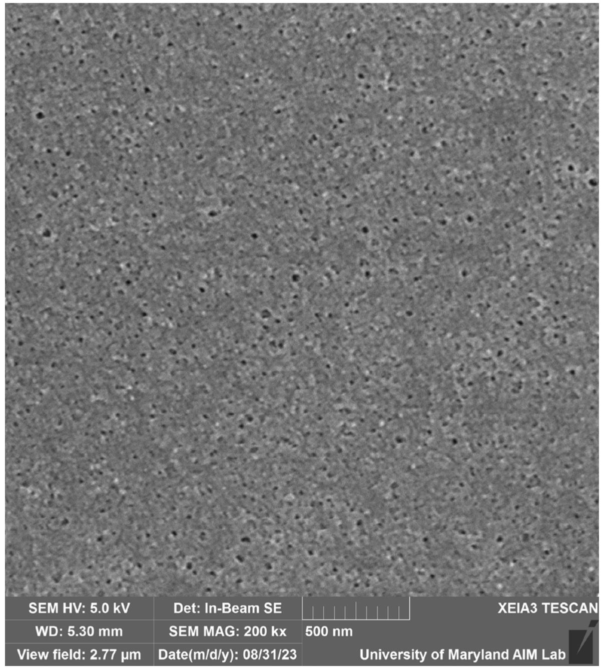
MWCO 10 kDa



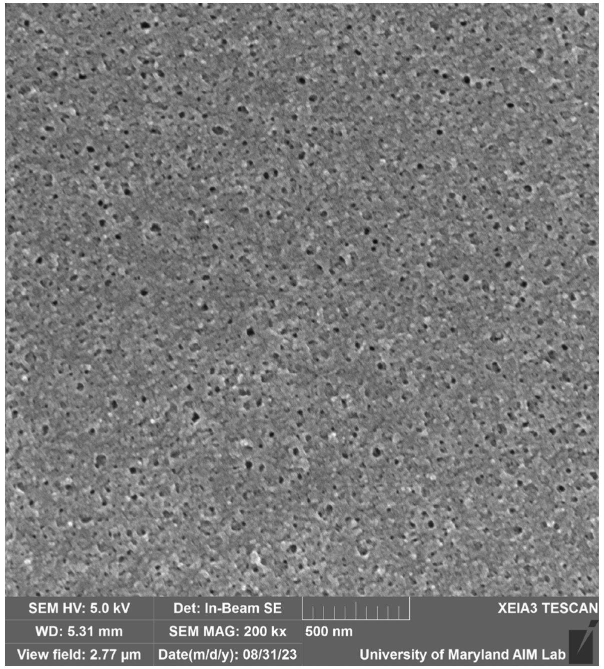
MWCO 25 kDa



MWCO 55 kDa



MWCO 75 kDa

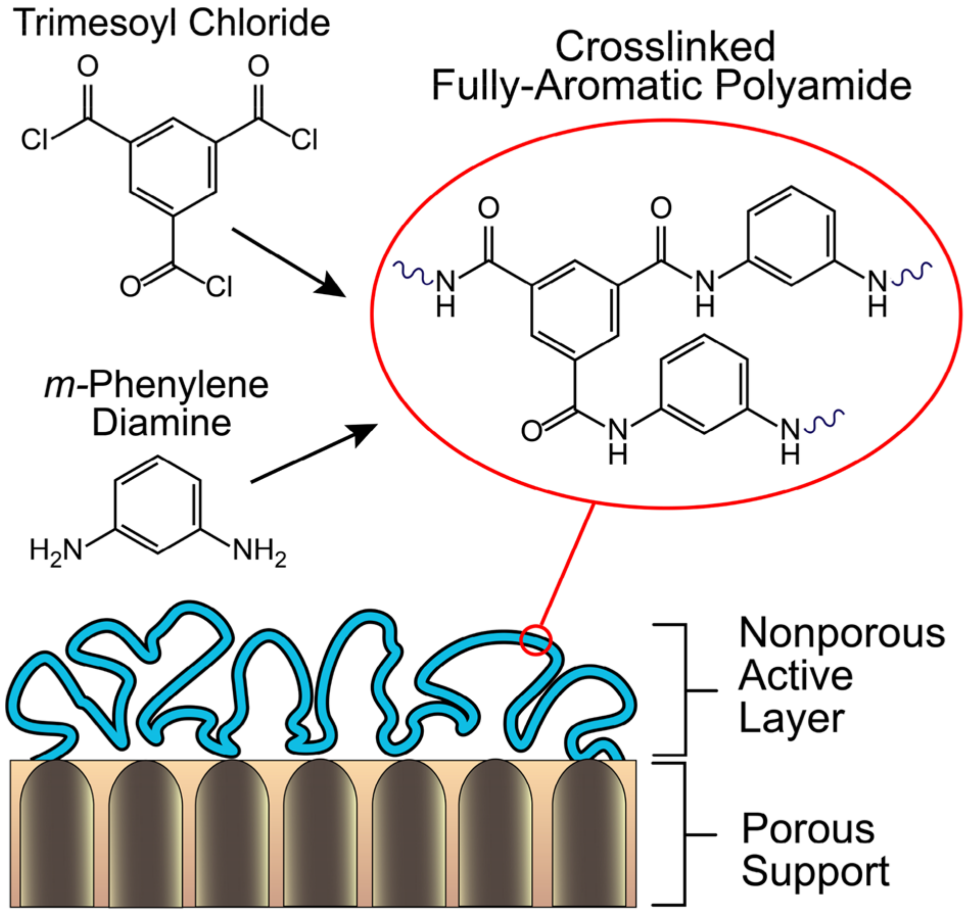


SEM images of membrane surfaces at 200kx magnification

Biomimetic Membrane Development

RO Membrane Limitations

- Polyamide membranes have been around since the late 1970s
- Despite 50+ years of work, there are still challenges facing RO membranes
  - Trade off between permeability and salt rejection.
  - Polyamides have poor separation of ammonia, nitrates, urea and boron.
  - High energy consumption.



ACS Nano *2020, 14, 10894−10916*

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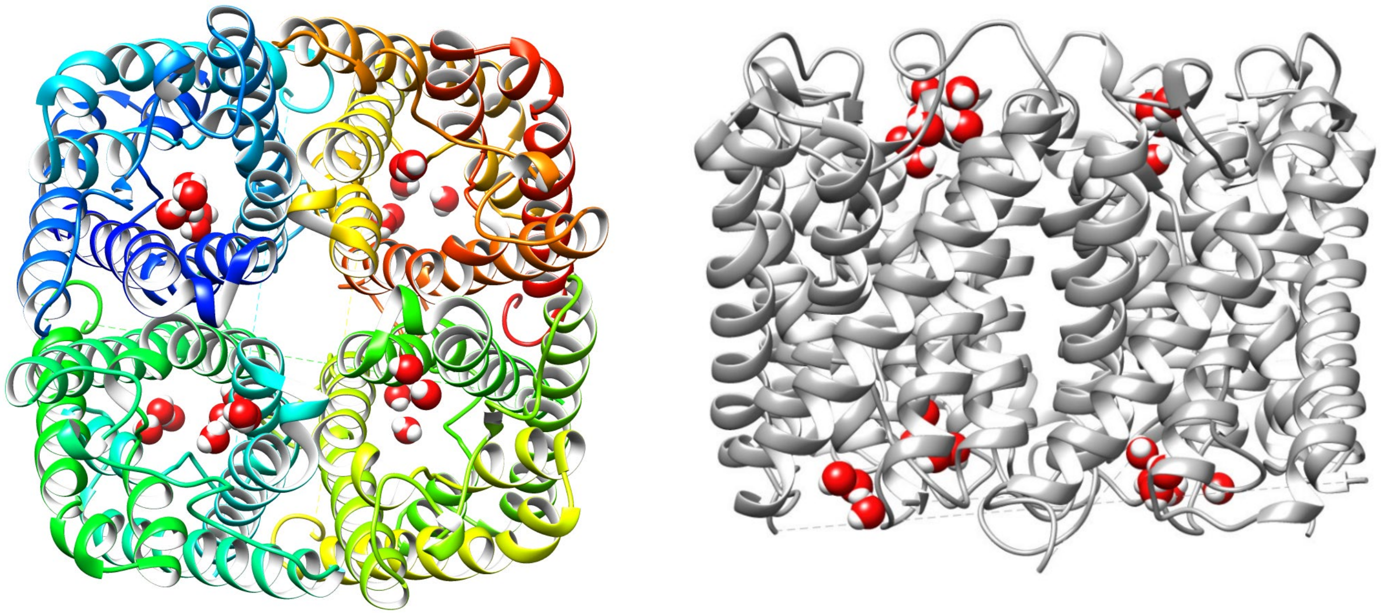
Focusing on Biomimetic Membranes

- Using lessons learned from dairy UF development to create Biomimetic Support Membrane
- Vandstrom was founded to explore biomimetic membranes and we are focusing on a promising path
- AQP proteins have selectivity filter that only allows water to pass

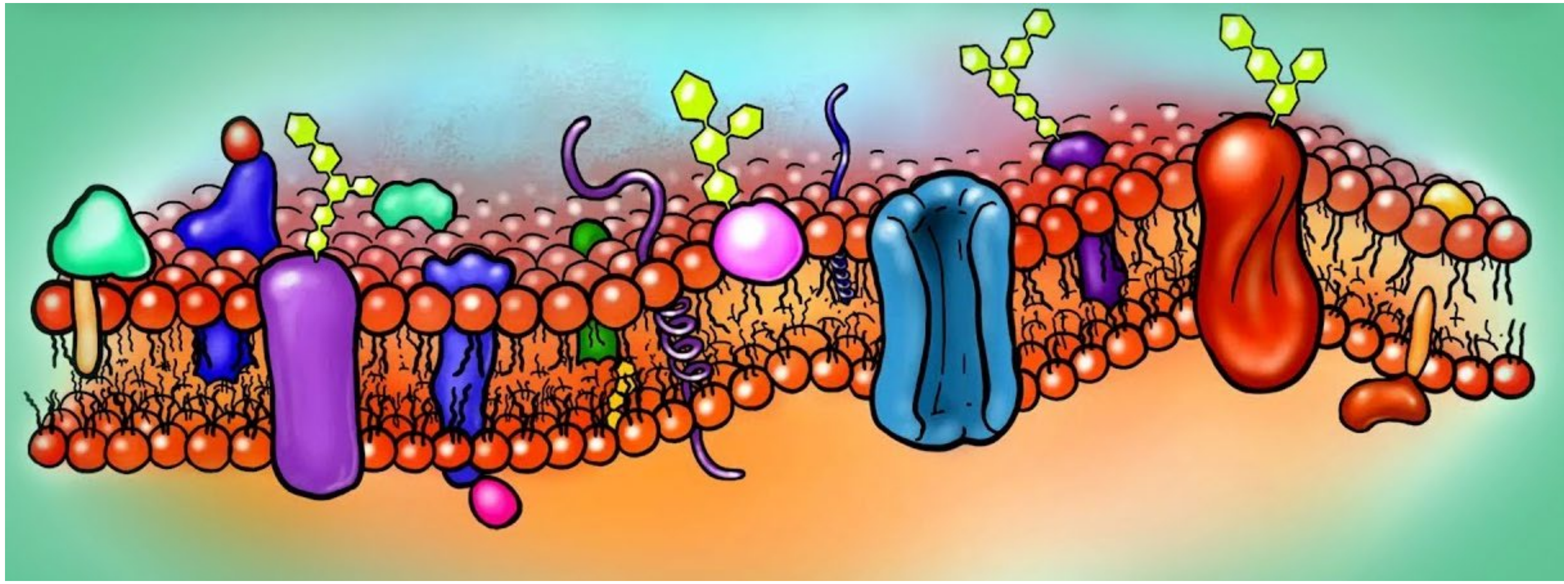
Aquaporin Protein

Top View | Side View



Many Possible Biomimetic Membranes

- There are many types of membrane proteins facilitating transport
- Developing best way to adhere protein-channel-based membranes
- Designing membranes tailored for specific ion separation



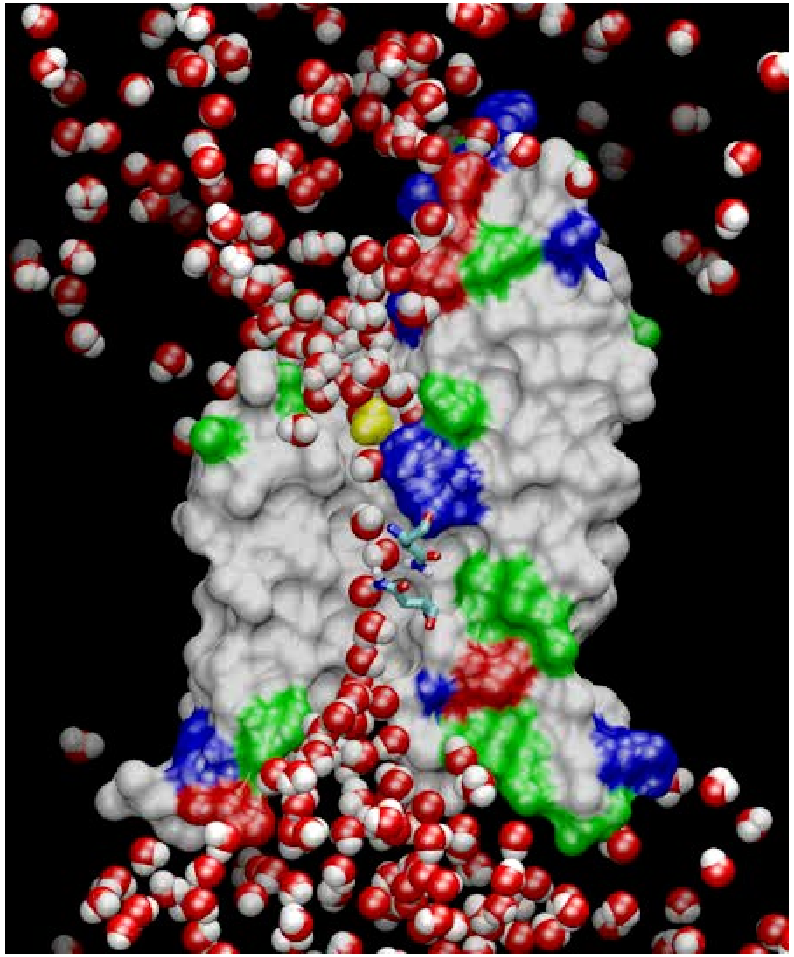
MEMBRANE PROTEINS - Types and Functions (youtube.com)

Thank You for Listening

The Art of Water Transport in Aquaporins

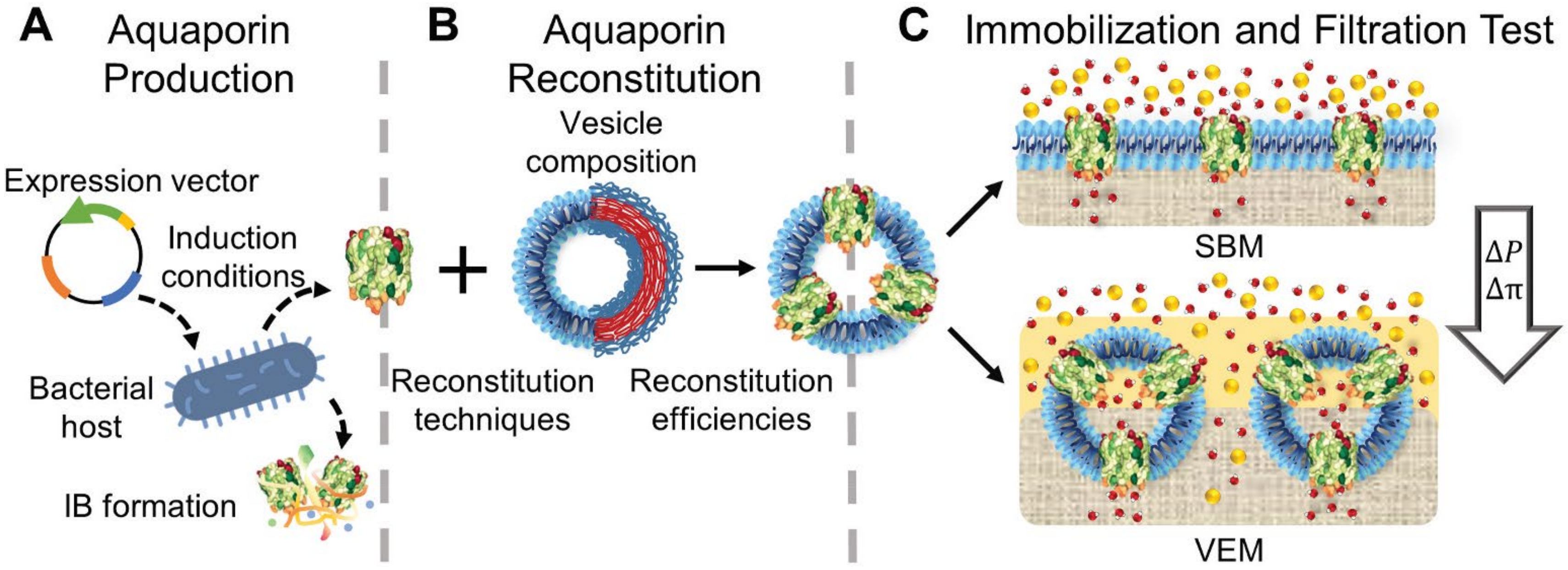
- Selectivity comes from the small channel inside the AQP
- Video from Univ. of Illinois simulates Aquaporin functioning in FO-mode over span of 100 nanoseconds
- In FO-mode, osmotic pressure drives water molecules towards the more concentrated solution

https://www.ks.uiuc.edu/Research/aquaporins/



Biomimetic Membrane Fabrication Strategy

A) Fermentation of AQP
B) Putting AQP into vesicle nanoparticles
C) Immobilizing AQP nanoparticles at the interface of the RO membrane



Separation & Purification Reviews, 2022, 51.3, 340-357