Getting the Most Out of Nafion™ Membranes

Clorosur Technical Seminar – Monterrey, Mexico
15 November, 2018

Agenda

- Overview
- Membrane Selection
- Membrane Protection
- Membrane Future Design
- Chemours Technical Service

Overview

- Membrane chloralkali production plays a crucial and increasing role in today's chloralkali industry.
- All aspects of the membrane operational life cycle from selection to handling through operation are critical.
- This presentation will discuss the basics of the membrane life cycle with the primary emphasis on membrane protection during installation and operation.
- The future direction, and implications, of membranes will also be discussed.

Membrane Selection

Membrane Selection

Membrane selection is a complex, non-trivial process.

- What to consider:
    - Electrolyzer technology and its condition
    - Control scheme and operational capability
    - Operational parameters, target values and ranges
    - Brine quality, power costs, risk tolerance, etc.
- There are many parameters that need to be optimized for each customer and their priorities.

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Membrane Protection

Membrane Protection

Protect the membrane over its life cycle, during:

- Storage
- Handling while unpackaging, pre-treating and installing
- Operation
  - Initial startup
  - Routine startups, shutdowns, and operations
  - Load shedding
  - Emergency shutdowns

Membrane Protection – Handling

Follow the membrane supplier's recommendations !

General guidelines:

- Ensure work areas are clean
- Ensure membrane contact surfaces are smooth, flat and free of debris, sharp edges and/or protrusions
- Membranes are fragile – avoid:
  - folding
  - kinking
  - dragging
  - pinching
  - impact damage
- Follow the recommended pre-treatment procedure for your membrane and situation

Membrane Protection – Operational

Follow the technology supplier's and the membrane supplier's recommendations - discuss any conflicts with both suppliers !

General guidelines for common items:

- Ensure that the electrolyte ionic (e.g. ~molar) strength is greater in the catholyte than the anolyte and that the catholyte level is maintained higher than the anolyte level at all times
- Avoid excessive differential pressures and/or differential pressure fluctuations, and avoid cold starts – the preferred startup temperature is ≥ 70 ºC (≤ 85 ºC)
- Minimize brine impurities, don't just target "in-spec"
  - Simply put, cleaner brine = longer life

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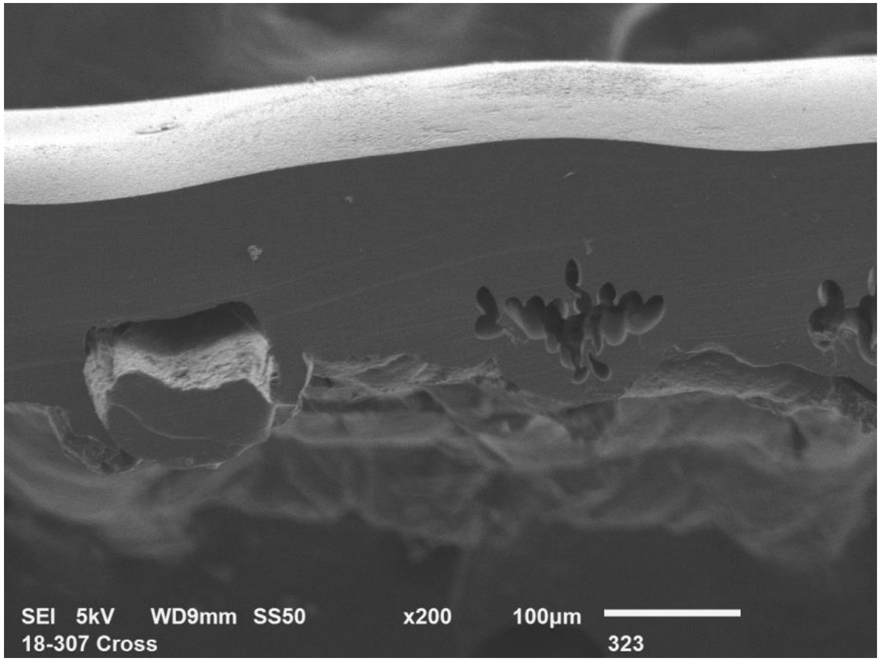
Membrane Protection – Example

Recent Analysis of N2030WX

- Continuously operated ~8.5 years at 5.5 kA/m^2
- 96.5% current efficiency in post-mortem, laboratory test
- +10mV versus new membrane expectation



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Membrane Protection – Brine

Sources of Impurities in Membrane Chloralkali Cells

1. Salt - multivalent cations, sulfate, silica, alumina, iodide, organics, etc.
2. Water - silica, multivalent cations, iodide, organics, etc.
3. Hardware - electrolyzer, piping, gaskets, instruments
4. Process - reaction generated & shutdown related

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Membrane Protection – Brine Impurity Effects

Non-Organic Impurities

- Most non-organic impurities:
  - Damage the membrane by precipitating within or near its surfaces
  - Disrupt the polymer integrity resulting in current efficiency reduction
  - Plug ionic transport pathways resulting in voltage increase
  - Precipitates are most often in the form of hydroxide, iodide, sulfate and alumina salts (often complex salts)

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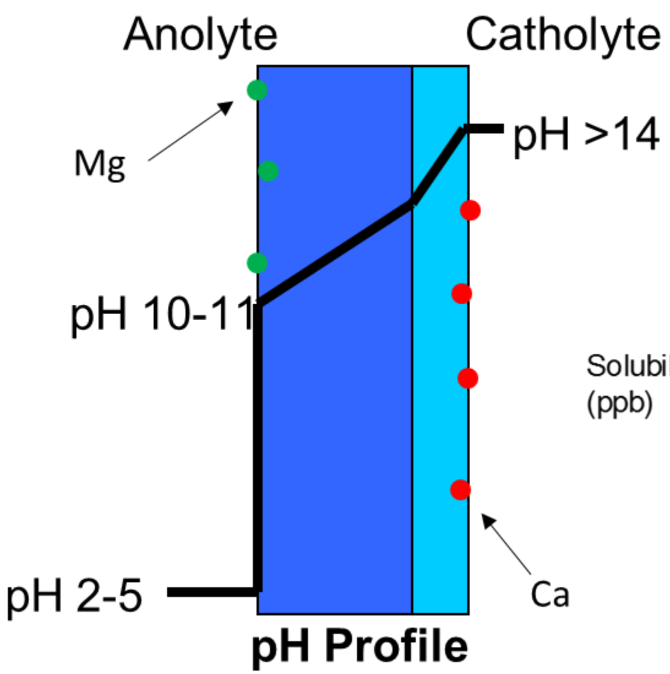
Membrane Protection – Brine Impurity Effects

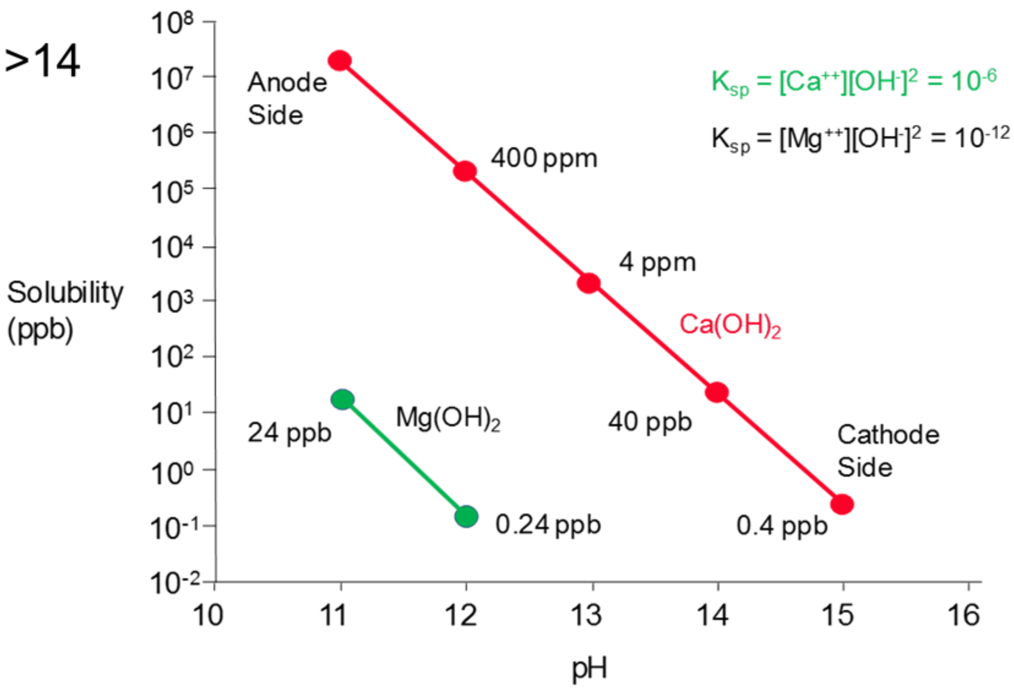
Organic Impurities

- Organic impurities can:
  - Cause current efficiency reduction through polymer swelling
    - Polymer swelling effects may be reversed upon return to good brine feed or result in some permanent damage
  - Cause foaming at the top of the electrolyzer resulting in blistering damage to the membrane

Membrane Protection – Brine

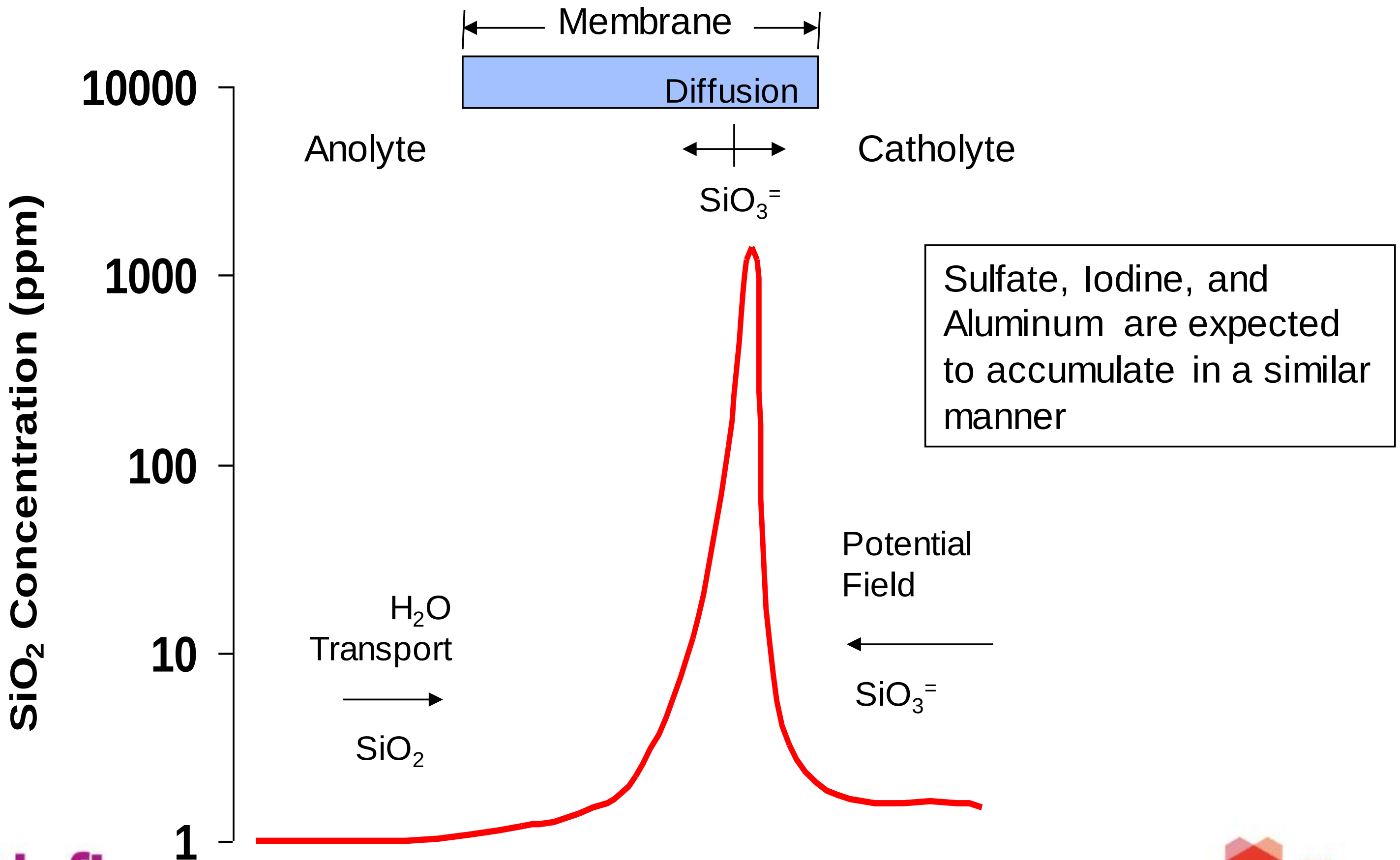
Magnesium and Calcium Precipitation in Membrane





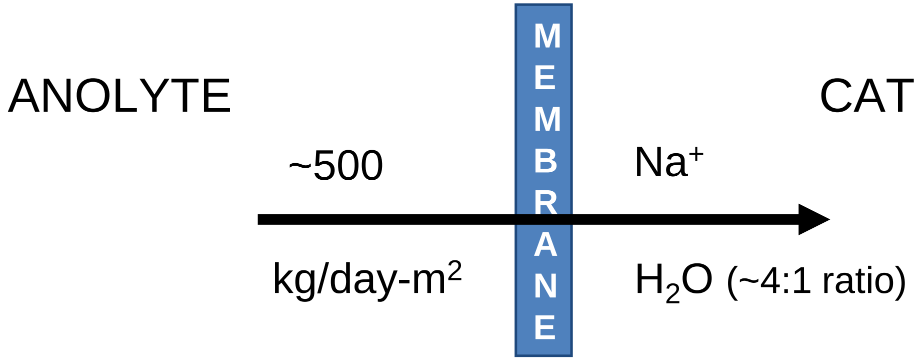
Membrane Protection – Brine

Predicted Silica Concentration Profile Across an Operating Membrane



Membrane Protection – Brine

Effect of 1 ppm Contaminant Membrane Mass Transport



Membrane weight ~ 350 g/m^2 (dry)

6 kA/m^2, 60 month life, 90% uptime

840,000 kg transported

<u>x 10^{-6}</u> (1 ppm wt/wt basis)

840 g/m^2 Weight of Contaminant (100% deposited)

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Membrane Protection – Brine

Recommended Brine Impurity Limits for Chloralkali Plants Using Nafion™ Membranes

Impurity	Limit at 4 kA/m²	Limit at 4–6 kA/m²	Limit at 6–7 kA/m²	Primary Effect(s) on Performance if Limit Is Exceeded	Method(s) of Control (common)
Calcium and Magnesium (Ca + Mg)	<30 ppb (total)	<20 ppb (total)	<20 ppb (total)	Ca: Current efficiency (CE) decline. Mg: Voltage increase.	Ion exchange
Strontium (Sr)	<500 ppb	<400 ppb	<200 ppb	CE decline, small voltage increase.	Ion exchange
Barium (Ba)	<1.0 ppm	<500 ppb	<200 ppb	CE decline and voltage increase.	Ion exchange
Iodine (I)	<1.0 ppm	<200 ppb	<100 ppb	CE decline, possible voltage increase.	Purge of brine loop
Sodium Sulfate[1] (Na2SO4)	4–10 g/L	4–8 g/L	4–8 g/L	CE decline.	• Primary treatment • Purge of brine loop • Filtration • Ion exchange
Aluminum (Al)	<100 ppb	<100 ppb	<50 ppb	CE decline.	• Primary treatment • Ion exchange
Silica (SiO2)	<10 ppm	<6 ppm	<5 ppm	CE decline.	Primary treatment
Iron (Fe)	<1 ppm	<1 ppm	<100 ppb	None in moderate quantity. In large quantity, voltage can be elevated and permanent void damage can occur.	Monitor anti-caking agent content in raw salt
Total Organic Carbon (TOC)	<7 ppm	<7 ppm	<7 ppm	CE decline, increase in voltage, possible permanent membrane damage.	Elimination of source; filtration with activated carbon

[1]Minimum recommendation is to reduce effects of barium and iodide.

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Membrane
Future Design

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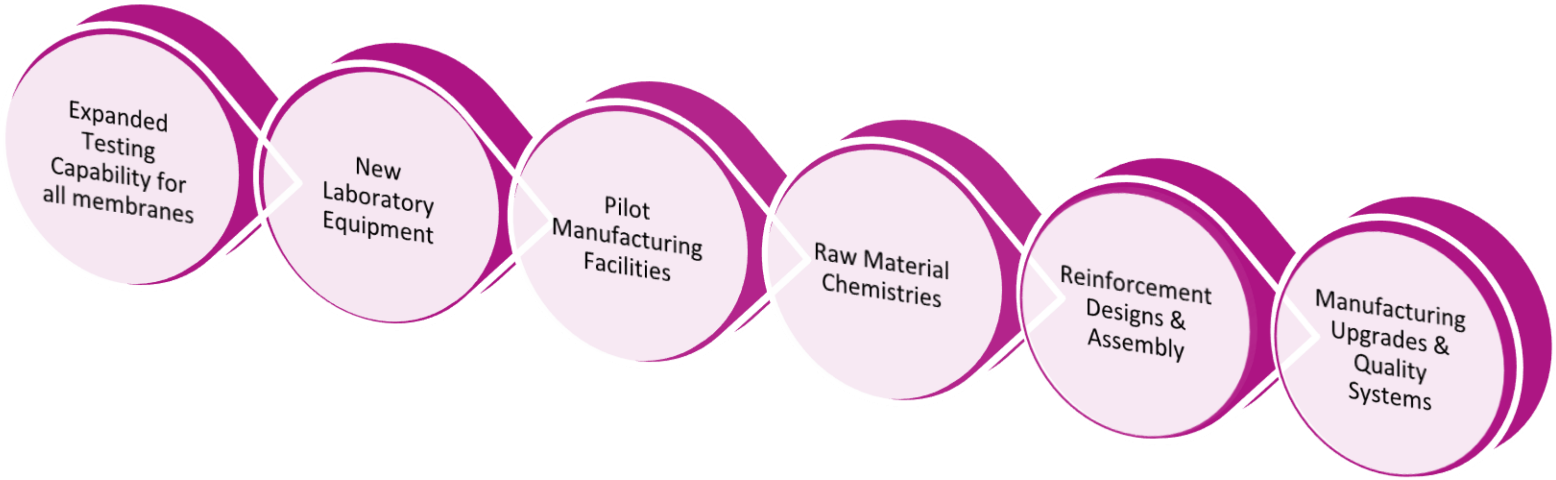
Research & Technology: A Comprehensive Approach to Membrane Innovation



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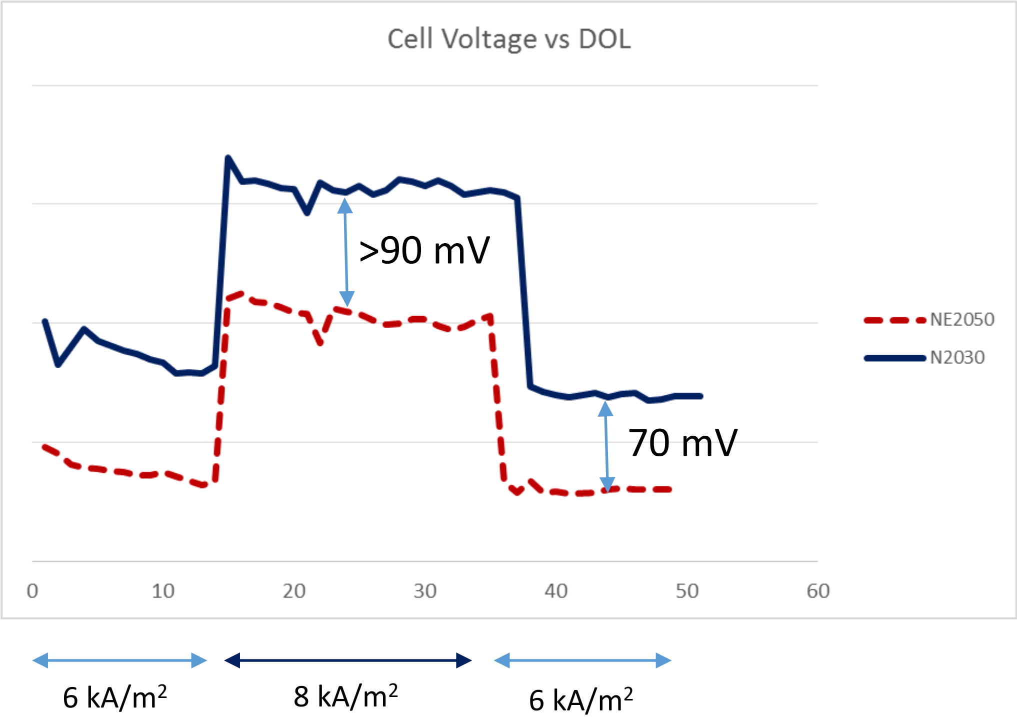
Membrane Future – Chemours™ Test

High Current Density Test



N2050 membrane performs equivalent to N2030, with lower voltage and stable CE

SEM analysis after test shows no difference in membrane types. Membrane structure and CE stable

Test Conditions
Zero-gap cells, 100 cm^2 , 90°C

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Chemours Technical Service Team

Chemours Technical Service Team

Our mission: Ensure Nafion™ membrane users get maximum value from our products

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Thank you