2017 NETL CO_2 Capture Technology Project Review Meeting:

Air Liquide

CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas (FE0013163)

Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules (FE0026422)

August 22, 2017

A. Augustine, T. Chaubey, R. Gagliano, S. Kulkarni, S. Fu, D. Hasse, T. Li, D. Kratzer, M. Bennett, M. | R&D
J.-M. Gauthier, R. Hutchinson, W. Wheeler, R. Warwick | MEDAL

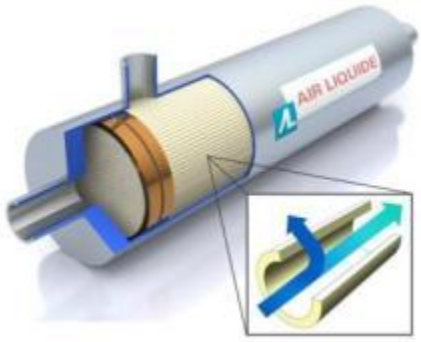
Air Liquide & MEDAL

Air Liquide: world leader in industrial and medical gases

68,000 employees

$19 billion sales (2016)

Air Liquide Advanced Separations, MEDAL



N_2 applications / markets

- OBIGGS
- Maritime
- Food & Bev
- UB Oil Drilling
- CB Inerting

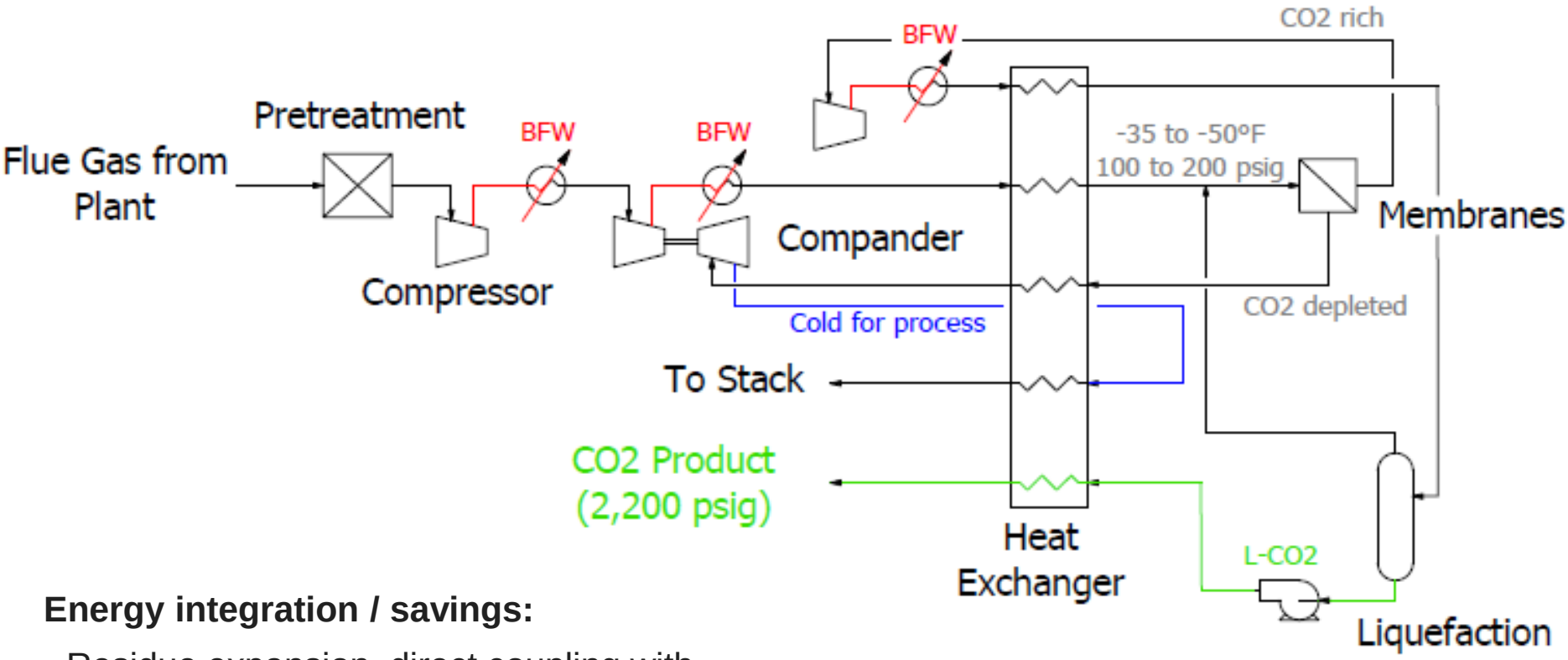
H_2 applications / markets

- Refinery Off-gas Streams
- Chemical Synthesis

CO_2 applications / markets

- NG Sweetening
- EOR
- NG Trimming
- CO_2 Capture / CO_2 Sourcing
- Fuel Gas
- Biogas

Background: Cold Membrane Process



Energy integration / savings:

- Residue expansion, direct coupling with compression
- Pumping of liquid CO_2
- Boiler feed water (BFW) sufficient for entire power plant steam cycle

Drawbacks:

- High membrane capital cost
- Energy intensive

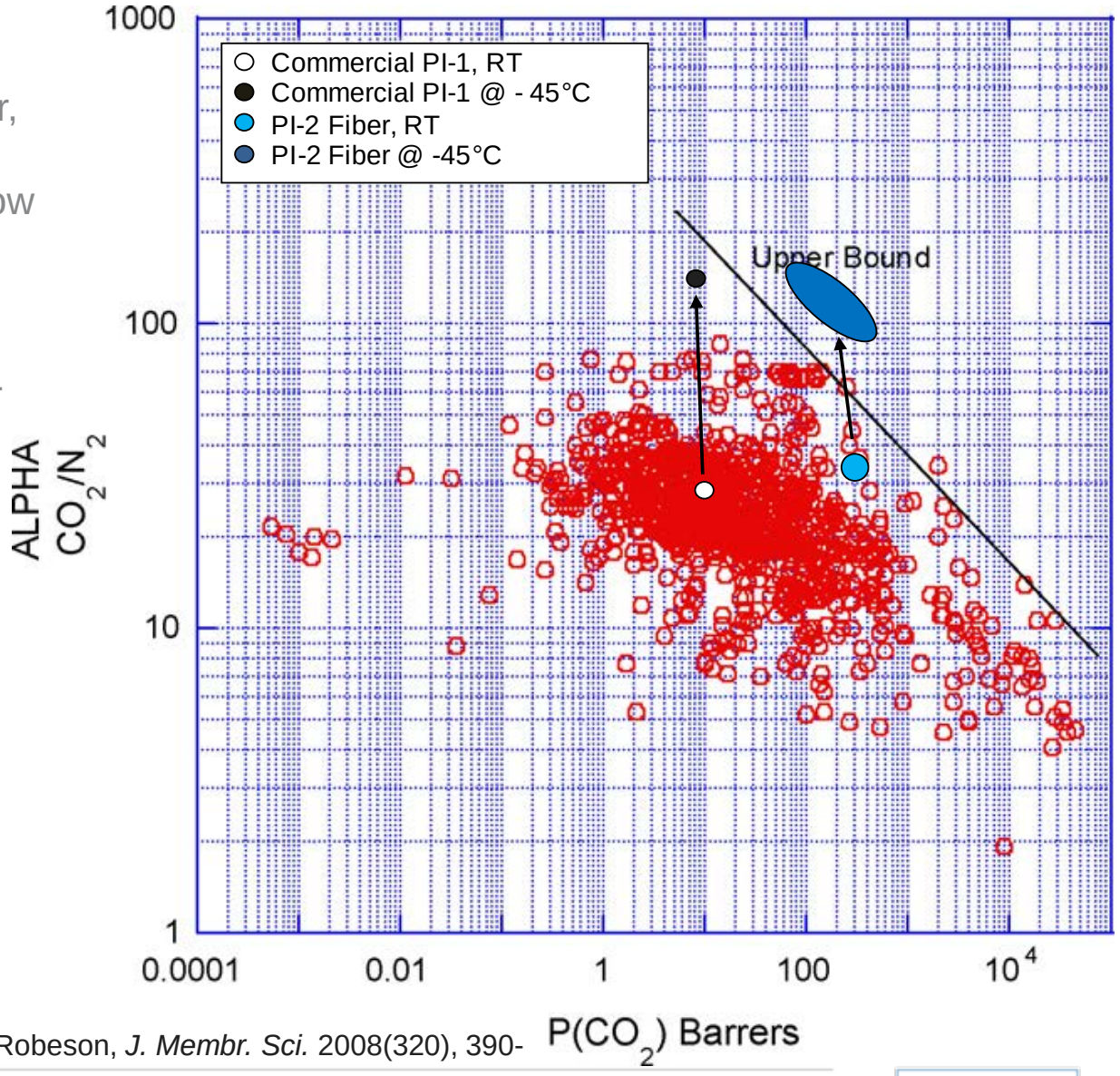
Background: Novel PI-2 Membrane Material

PI-1 standard product

- 1,000's of modules per year, dozens of applications
- Performance improves at low temperature

PI-2 novel material

- Permeation properties near Robeson* upper bound
- Spinnable
- Performance at NCCC over 500+ hours



*Robeson, *J. Membr. Sci.* 2008(320), 390-

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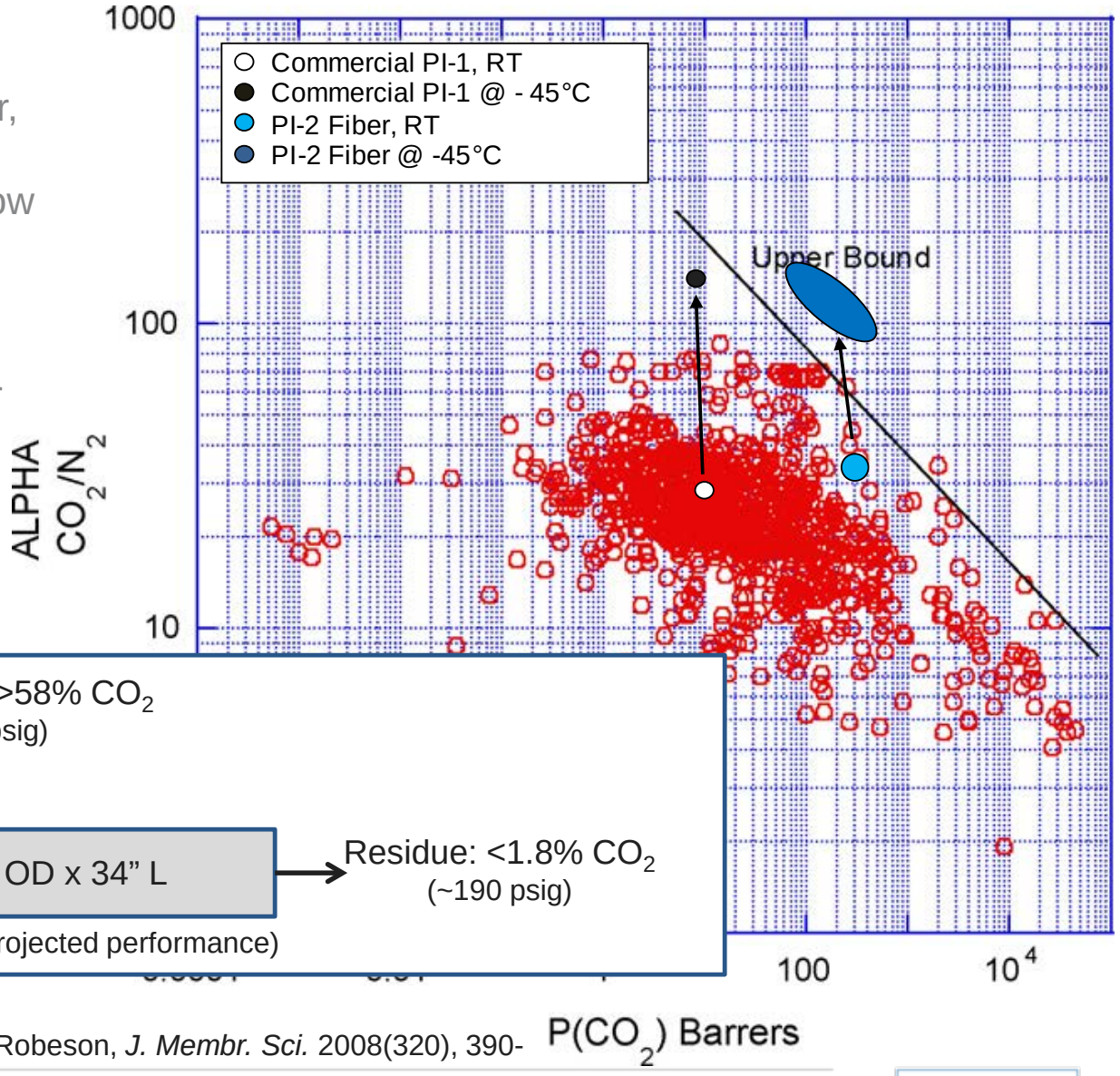


Permeate: >58% CO_2
(~1 psig)

Feed: 3,300 Nm^3/h
(0.6 MWe eq.)
18% CO_2, 200 psig, -45°C

12" OD x 34" L

(1 module, projected performance)

Residue: <1.8% CO_2
(~190 psig)

*Robeson, *J. Membr. Sci.* 2008(320), 390-

Project Organization: DOE/NETL Awards

DE-FE0013163	DOE	AL
Cost Share	$5.12MM	$1.28MM
Total Budget	$6.4MM	

DE-FE0026422	DOE	AL
Cost Share	$3.00MM	$0.97MM
Total Budget	$3.97MM	

Oct-2013

- **Improve commercial bundle performance**
- **Early development PI-2**
- **Field-test at NCCC**

Oct-2015

Apr-2017

- **Develop PI-2 to 4” OD, bench scale and test**
- **Develop to commercial scale**
- **Field-test at NCCC**

Dec-2018

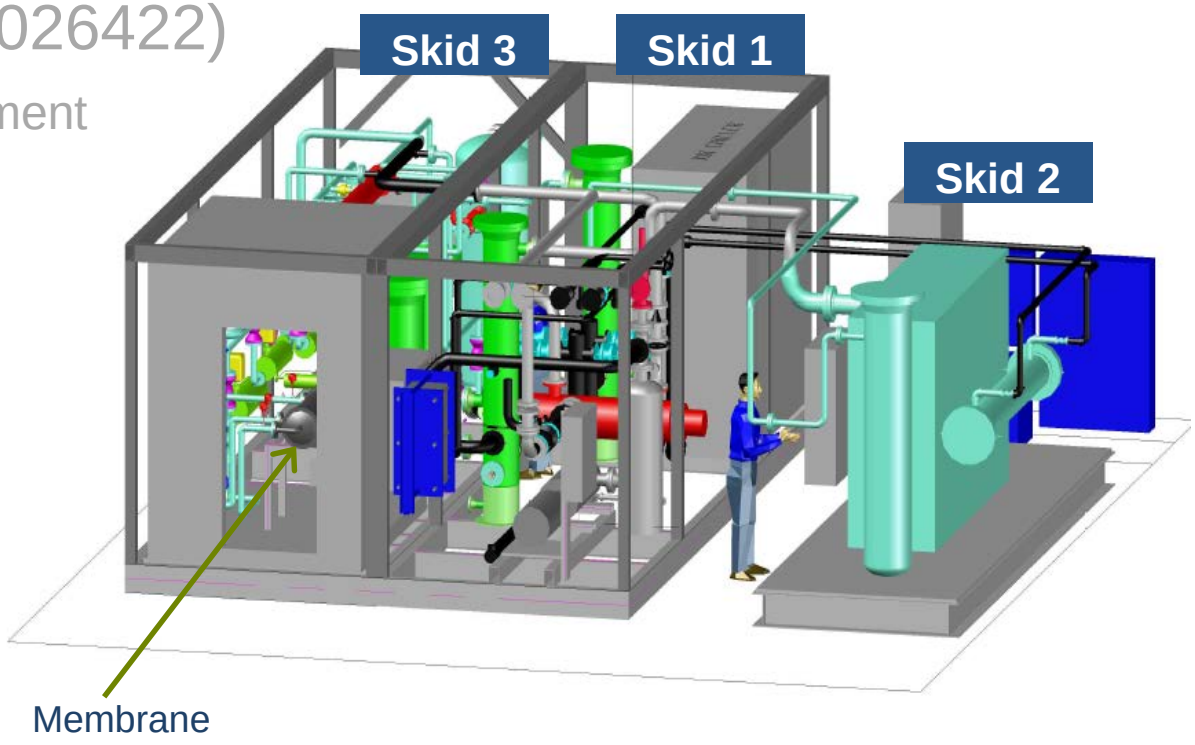
NETL Project Manager: José Figueroa

Project Team:

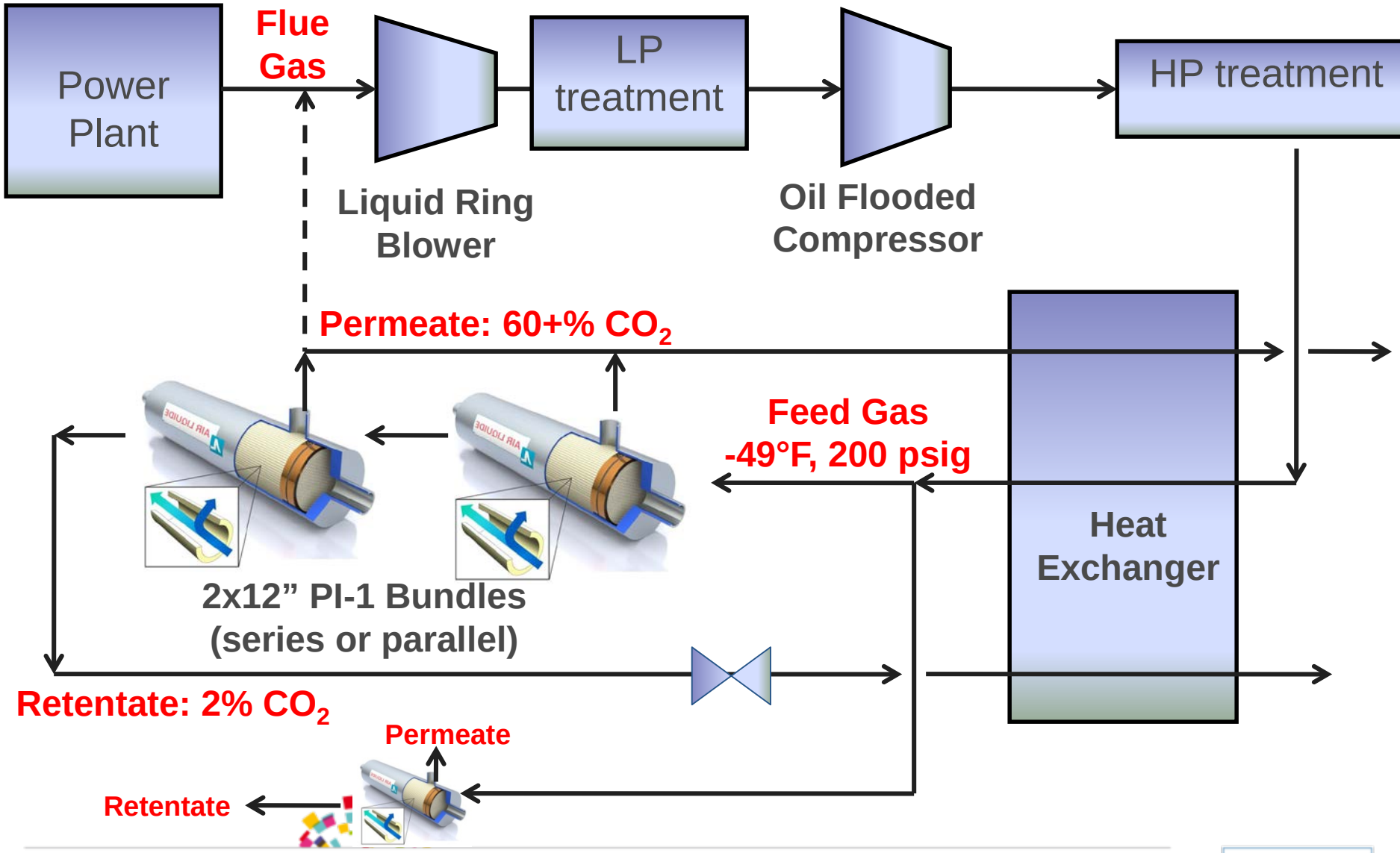
- Air Liquide R&D – Sudhir Kulkarni, Trapti Chaubey, David Hasse, Ted Li, Madhava Kosuri, Shilu Fu, Jiefu Ma, Monaca McNall, Jacob Brumback, Dean Kratzer, Michael Bennett, Judy Huss, Dennis Calvetti, Robert Sokola, Gerard Gagliano, Jean-Pierre Tranier, Robert Gagliano, David Edwards, Deborah Hutchinson, Yang Jiang, Ian Moskowitz
- MEDAL/ALAS - Karl Beers, Jean-Marie Gauthier, Alfredo Velasco, Dana Husnay, Ed Sanders
- E&C – Mike Turney, Paul Terrien
- Parsons - Brad Knutson, Surajit Amrit, Jay Hellinger, Tom Moe, Louis Wheat
- Test partner – National Carbon Capture Center

Agenda

- Technology & Project Overview
- **NCCC Testing (FE0013163)**
  - Membrane testing
  - Analytical campaign
- PI-2 Scale-up (FE0026422)
  - Manufacturing development and testing
  - Acid gas contaminants
- Next Steps
  - PI-2 scale-up to 6” size
  - Back to NCCC



Process Flow Diagram - NCCC



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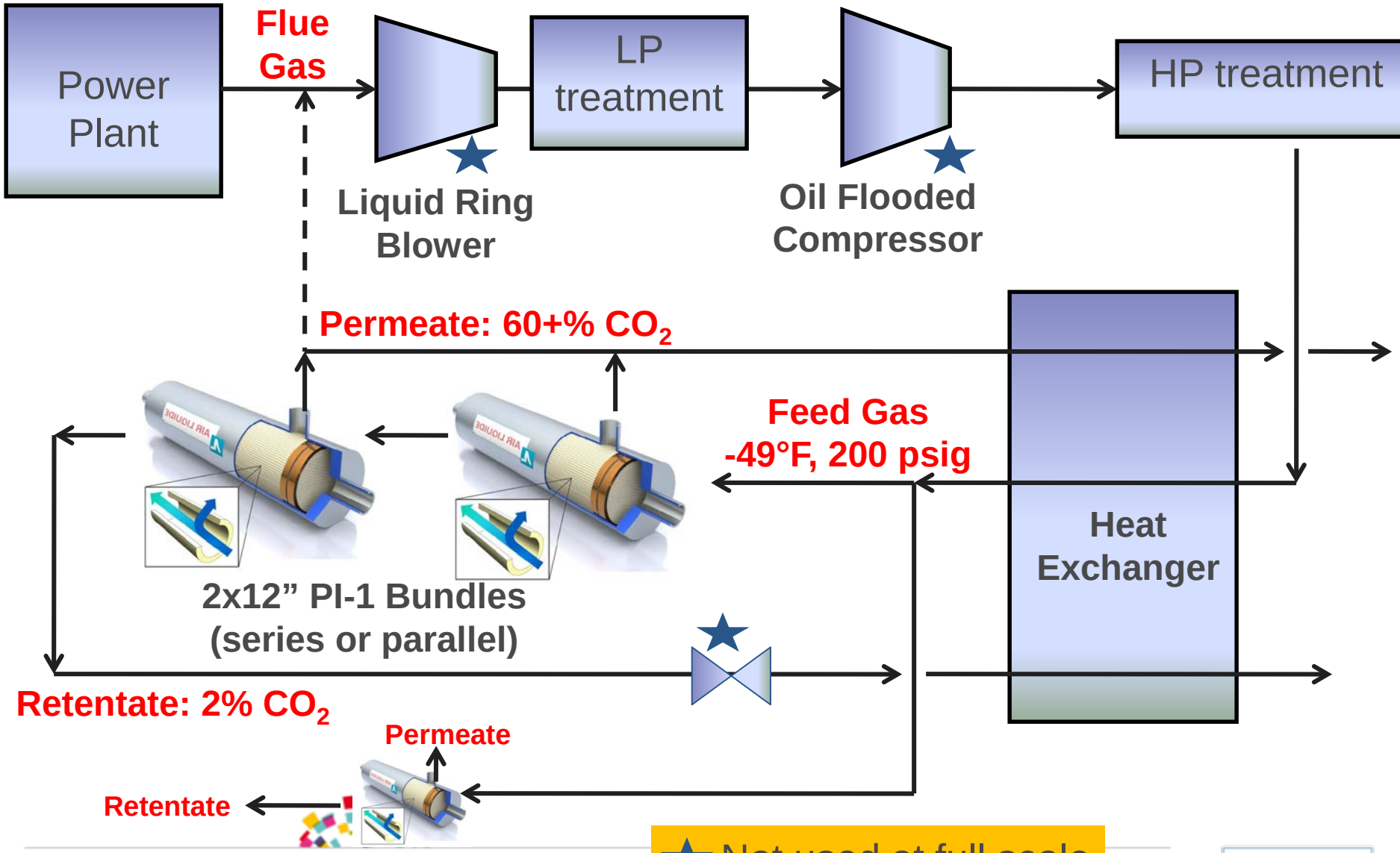
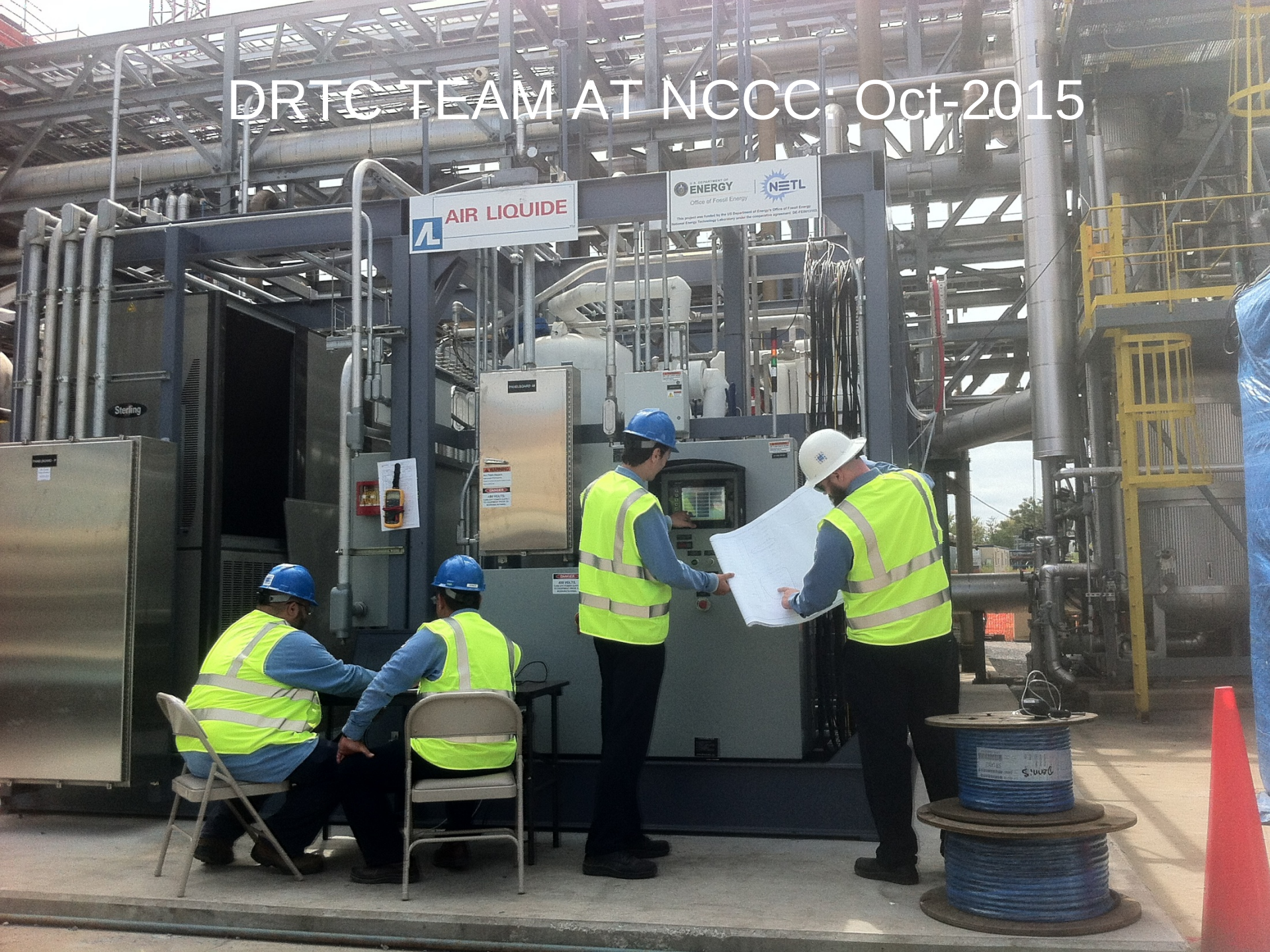
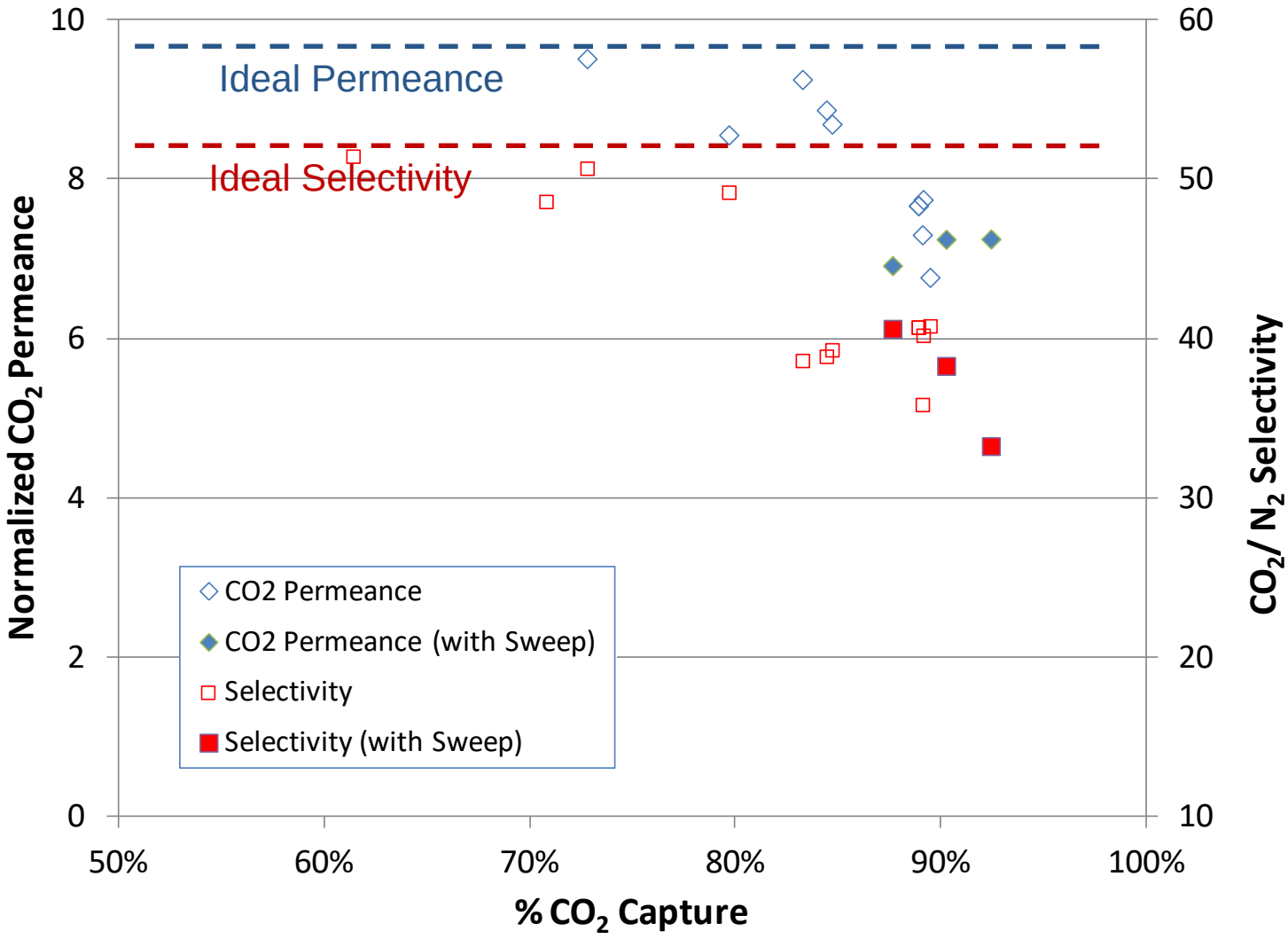


DRTC TEAM AT NCCC: Oct-2015

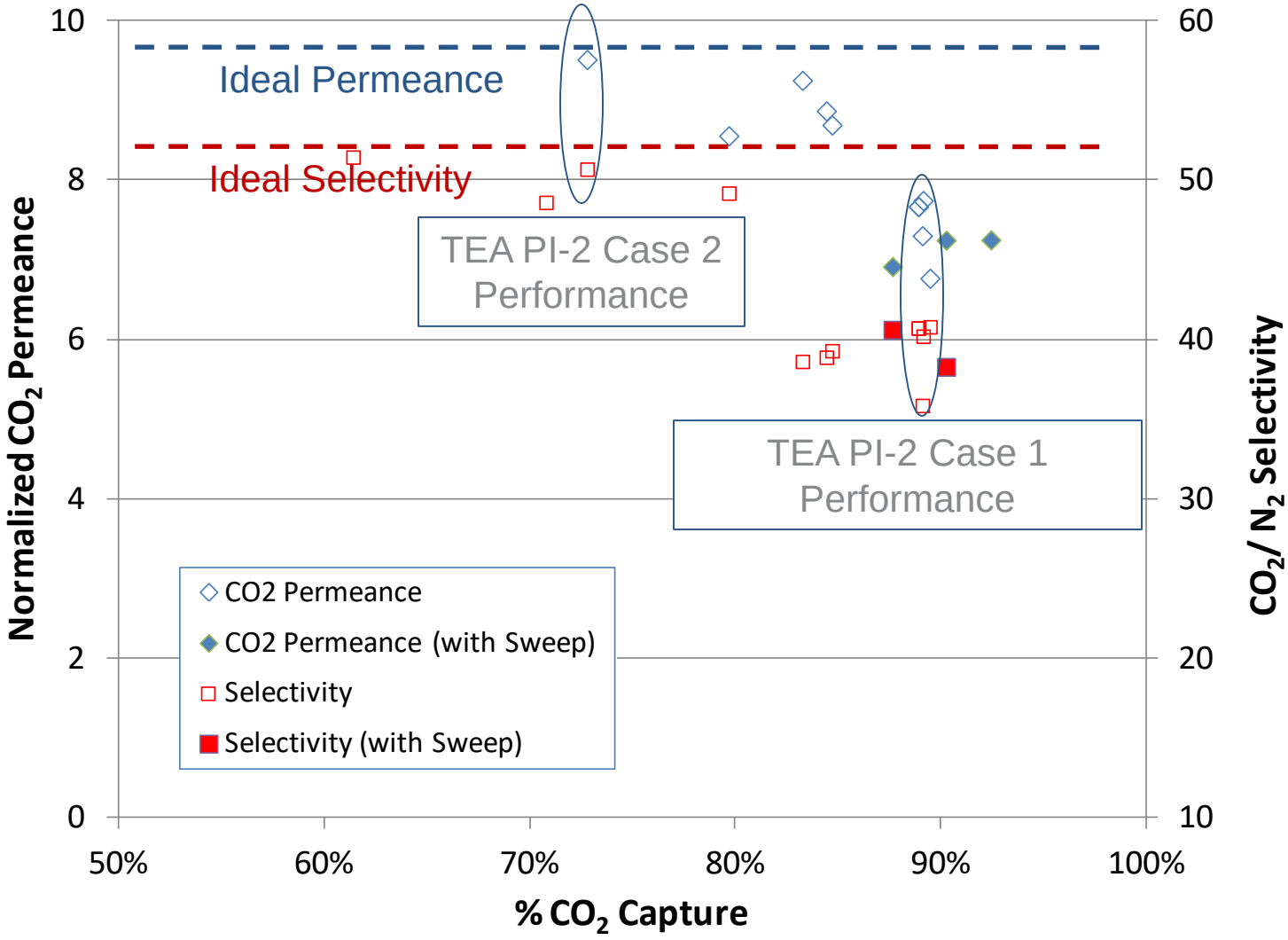


1” PI-2 Bundle Parametric Testing at NCCC



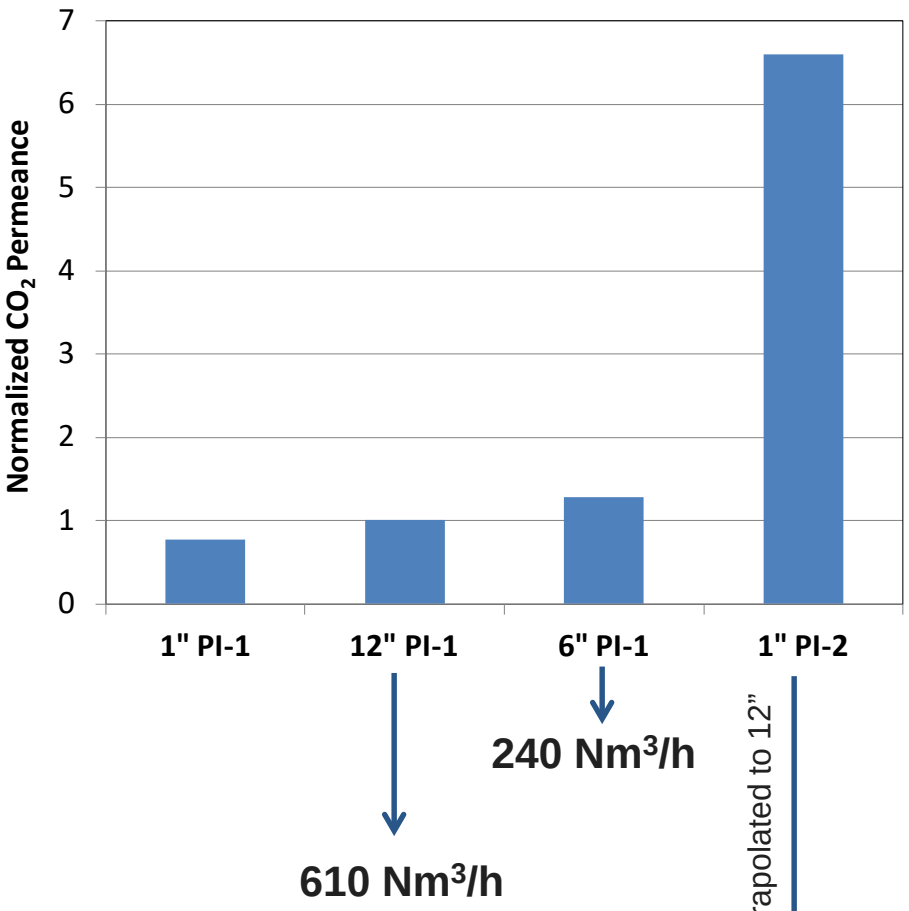
1” PI-2 bundle has non-ideal flow, no impact of sweep

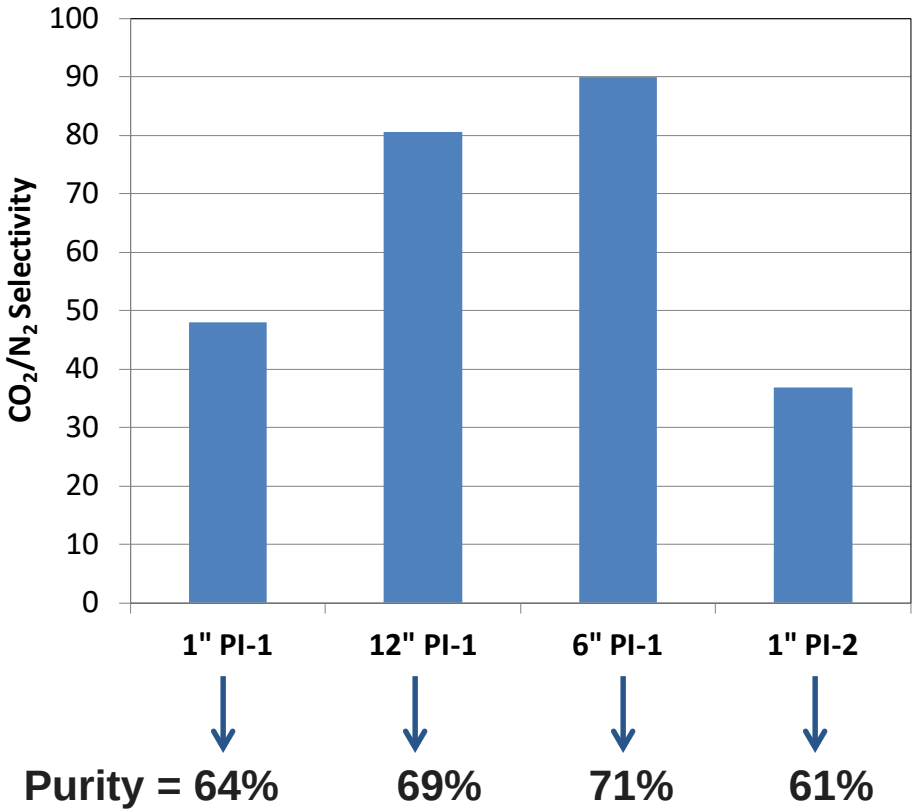
1” PI-2 Bundle Parametric Testing at NCCC



1” PI-2 bundle has non-ideal flow, no impact of sweep

12” PI-1 vs PI-2 Bundle Performance



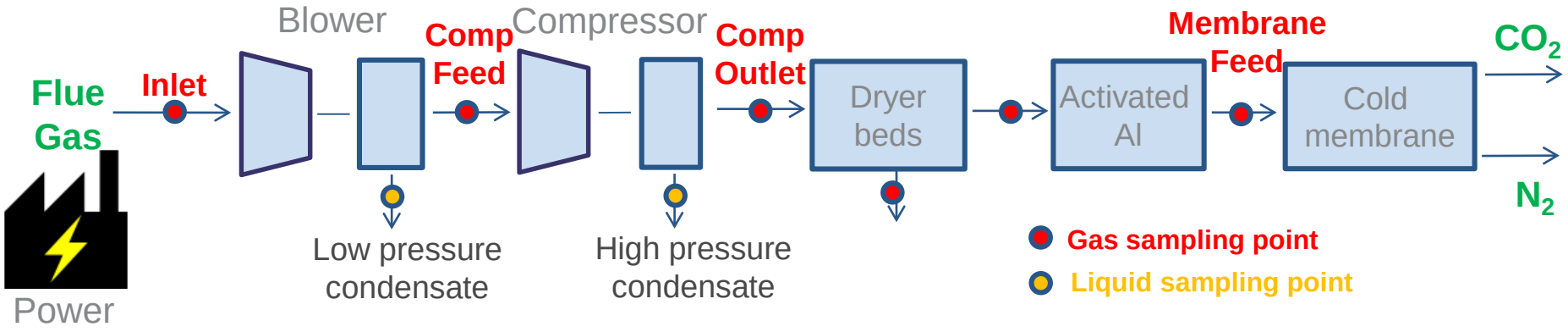


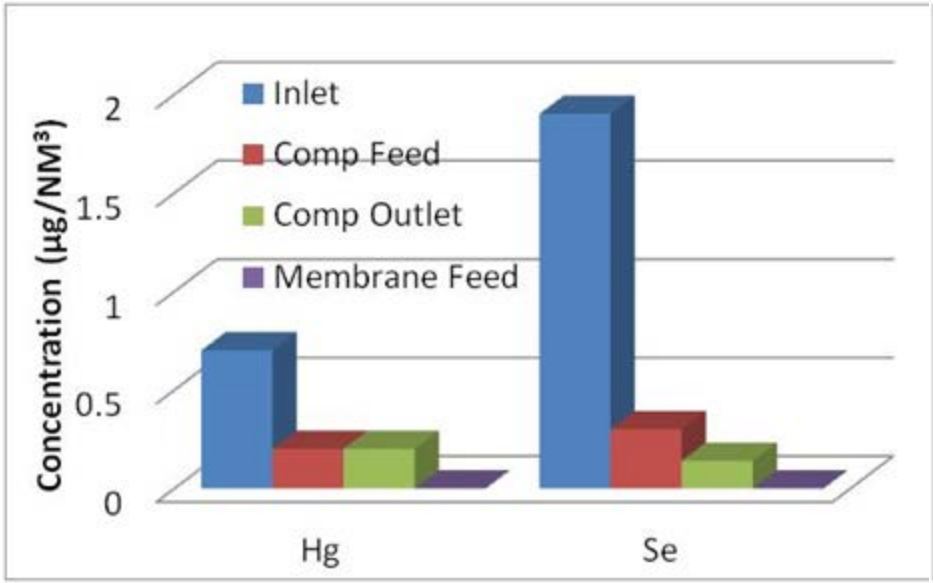
Higher productivity → Lower CAPEX

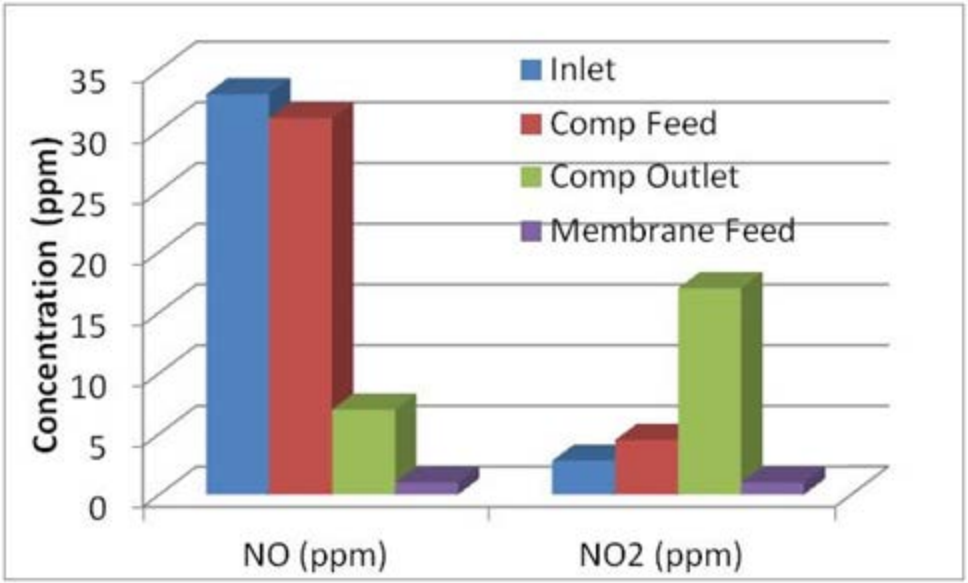
2,500 Nm³/h to 3,300 Nm³/h

Higher purity → Lower OPEX

Analytical Campaign to Track Impurities

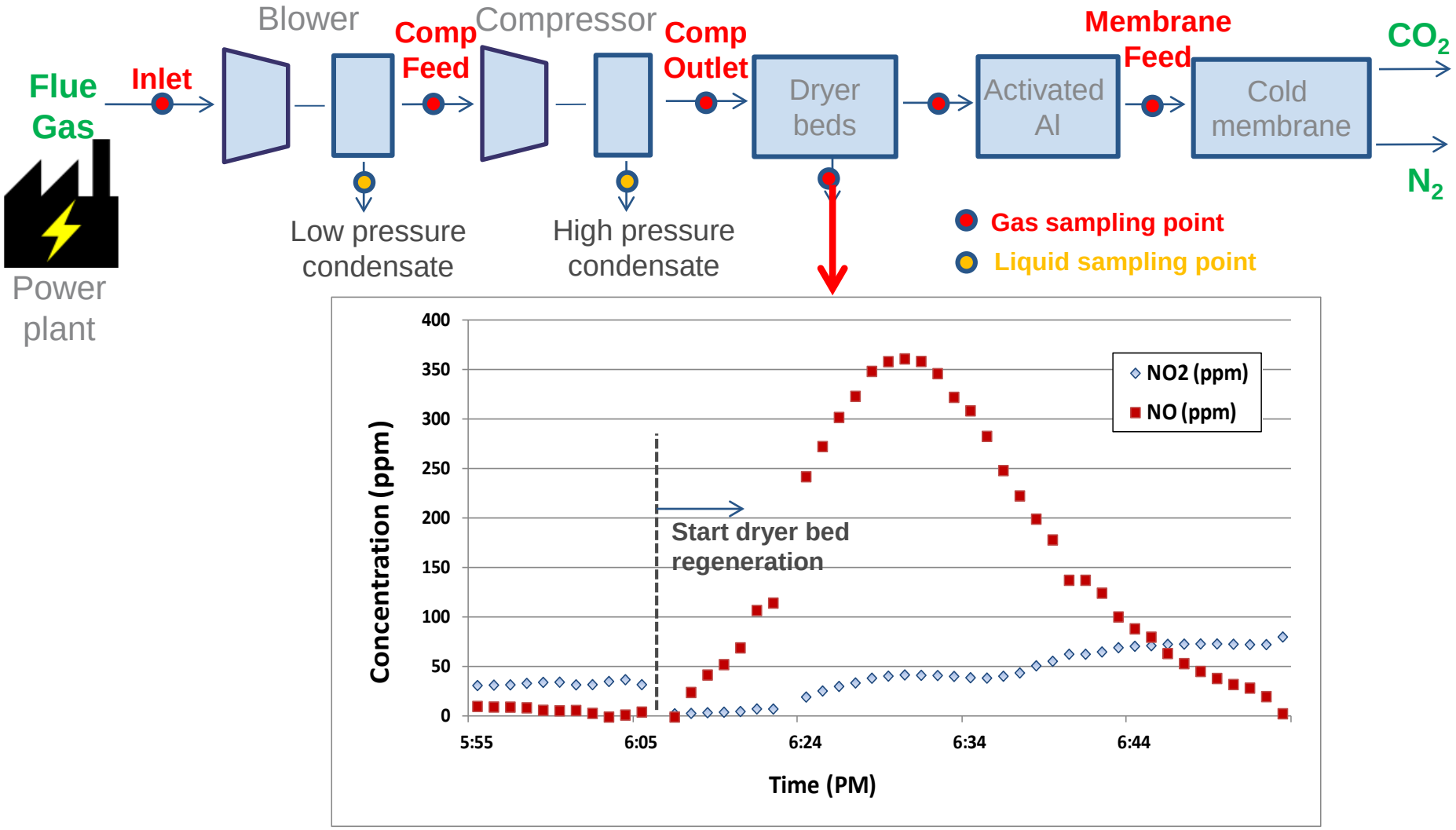






*Results of Arsenic are all below detection limit

Analytical Campaign to Track Impurities

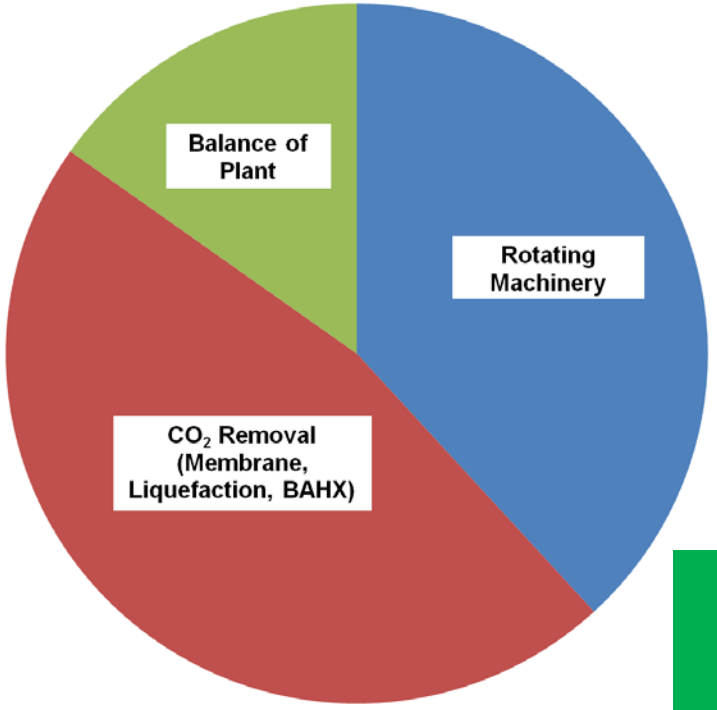


Impurities are mitigated in pre-treatment, undetectable after the activated alumina bed.

Techno-Economic Analysis

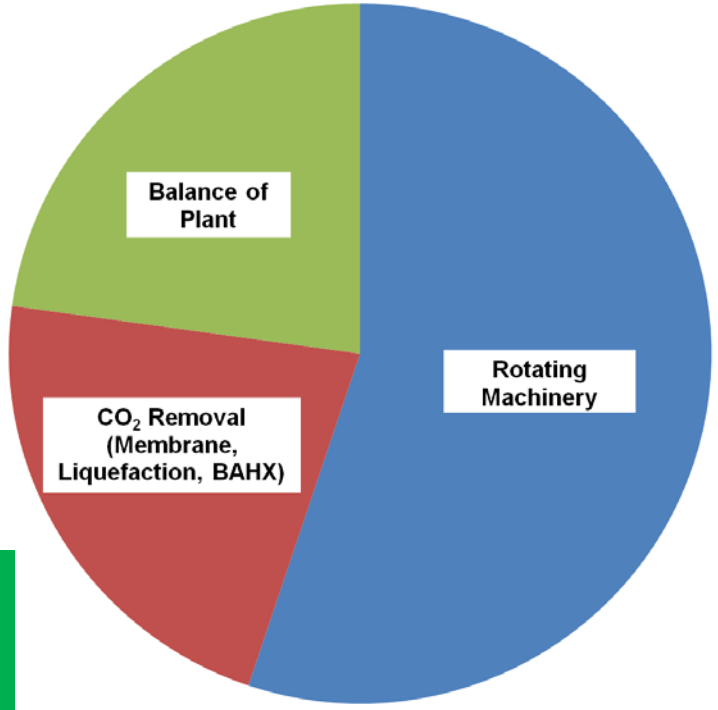
	Case 12 (Amine)	Cold Membrane (PI-1)	PI-2
Power Plant Cost (MM$)	1,366	1,305	1,326
CO_2 Capture System (MM$)	593	357	254
Total Plant Cost (MM$)	1,959	1,662	1,580
CO_2 Capture Cost ($/tonne)	**55**	**40 – 45***	**38 – 42***

* Cost range is based on sensitivity analysis



Cold Membrane (PI-1)

PI-2: big cost reduction on membranes



Projected PI-2

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- NCCC Testing (FE0013163)
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- **PI-2 Scale-up (FE0026422)**
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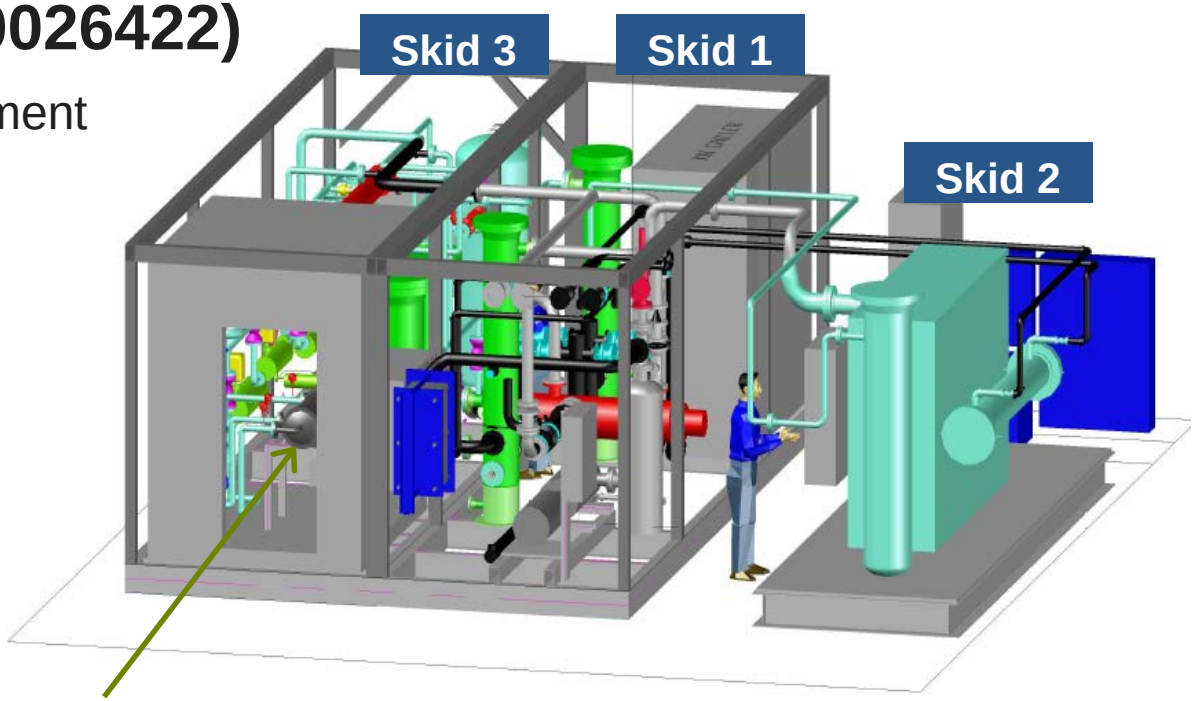
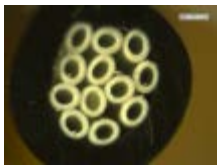
  - Acid gas contaminants
- Next Steps
  - PI-2 scale-up to 6” size
  - Back to NCCC



Manufacturing Development

	OD (in)	Length (ft)	Fiber Count	Spinning Device	Fabrication Technique
Mini permeator	0.25 - 0.5”	1.6’	<1000	1-hole lab unit	Hand
Permeator	1”		1 – 5x		Skein
Skein module	2.5”	2.8’	15 – 20x	12-hole “DSU”	
R&D prototype bundle	2.5 - 4”		15 – 20x		Forming
6” bundle (commercial)	6”		50 – 90x	24/36-hole production unit	
12” bundle (commercial)	12”		>200x		

Spinning Equipment (DSU): Spinning | Post-spin handling → **Fiber Processing / Handling**: Washing | Drying | Bobbin winding → **Forming Equipment**: Tube-sheet forming | Machining





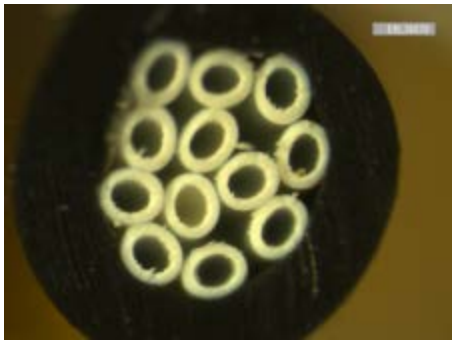
Fiber Synthesis & Bundle Forming

PI-2 fiber synthesized on the DSU

Periodic samples for quality control:

Sample #	Normalized CO_2 Perm*	CO_2/N_2 Select*	Fiber ID
1	24.6	27.8	
2	22.0	31	
3	26.9	28	
4	20.6	26	
5	24.9	35	
6	17.6	27	
Average	22.8	**29.1**	
Std Dev	**11.6%**	**14.7%**	**3.6%**

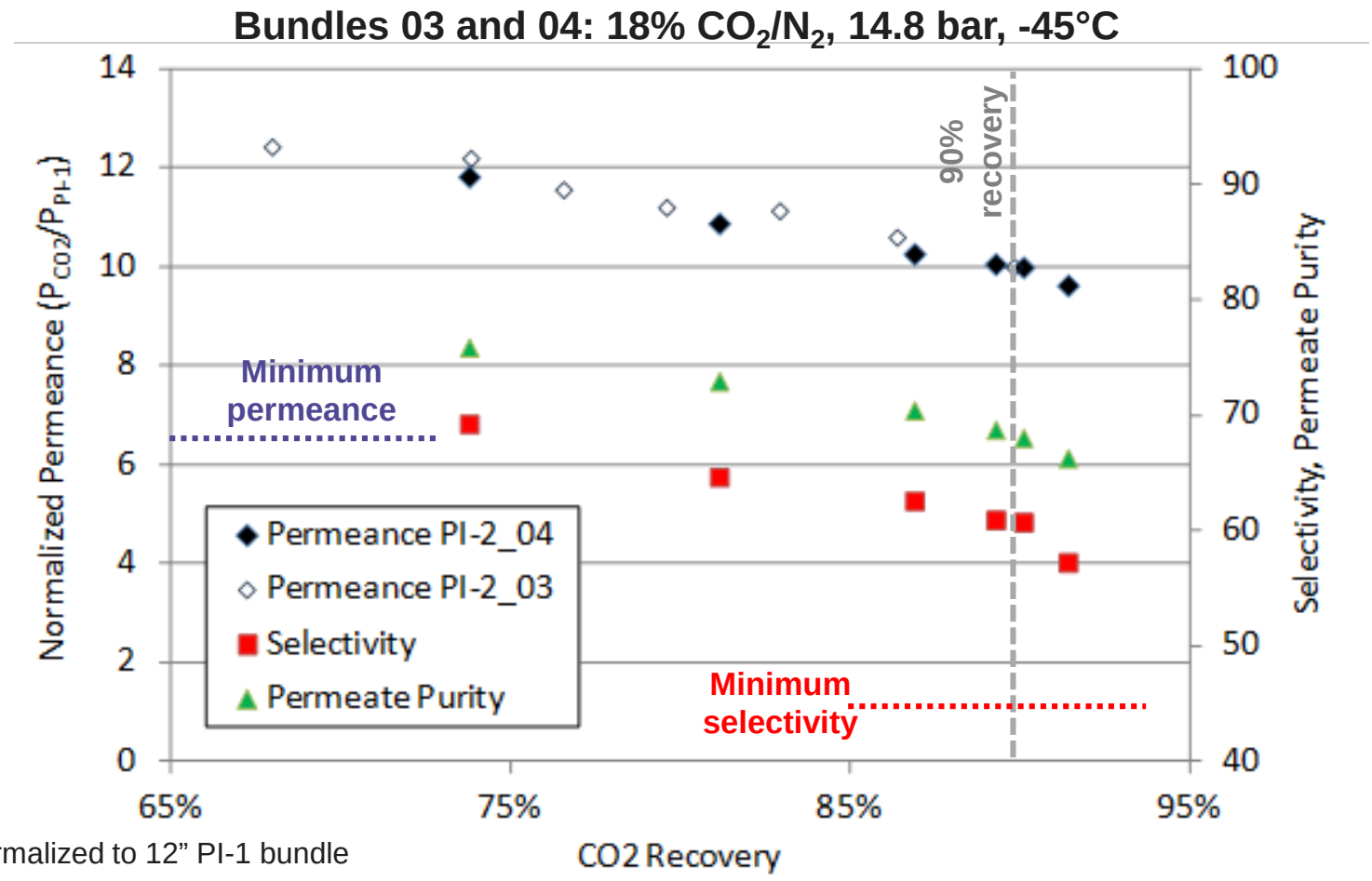
*Normalized to 12” PI-1 bundle performance, ambient temperature



- Fiber performance was consistent and agreed with previous lab-scale results

- Fiber “formed” into two prototype bundles

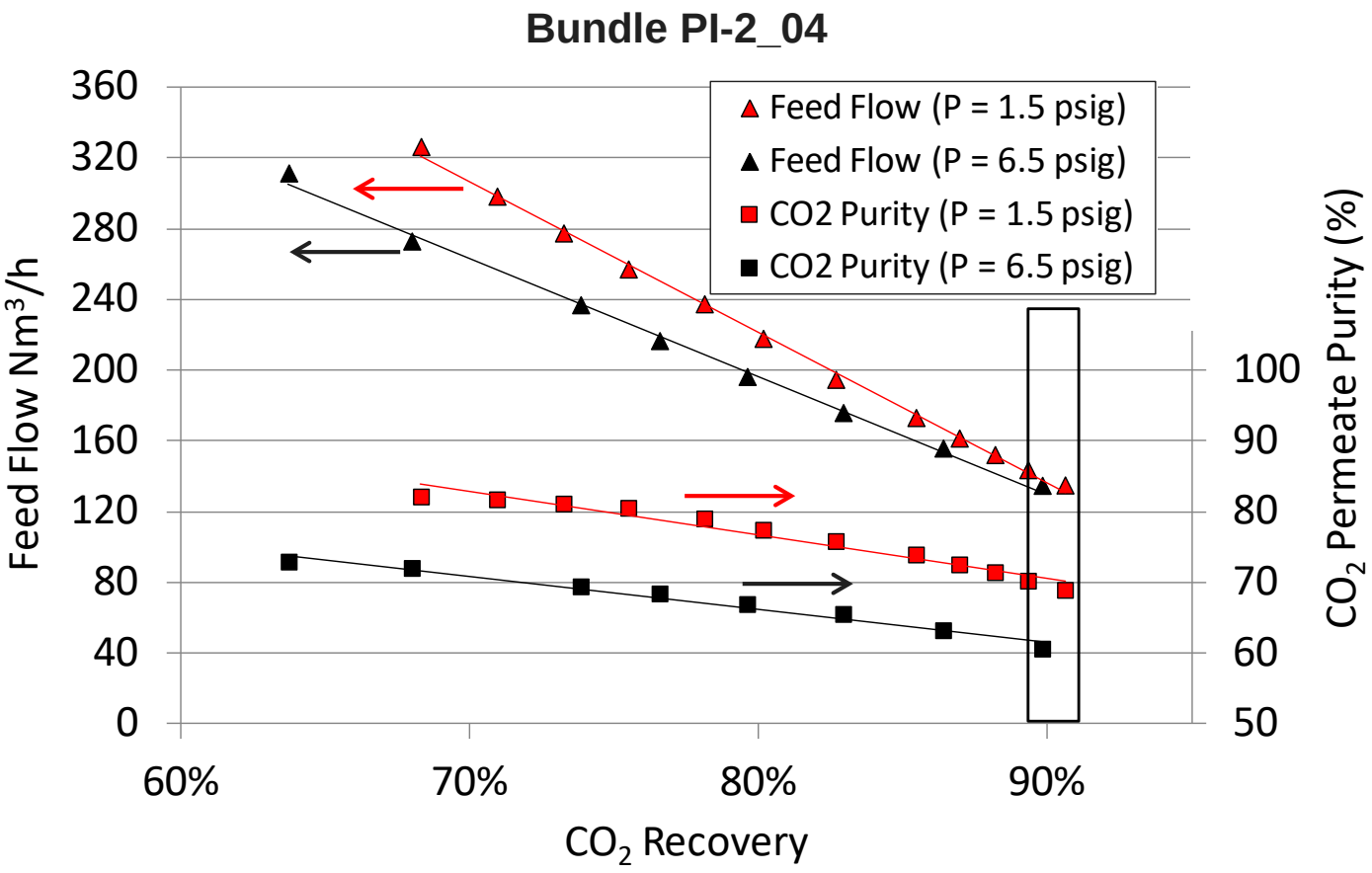
4” Prototype Bundle Performance



*Normalized to 12” PI-1 bundle performance

- Permeance and selectivity exceeding targets for 90% recovery
- Similar performance confirms manufacturing reproducibility

4” Prototype Bundle Performance

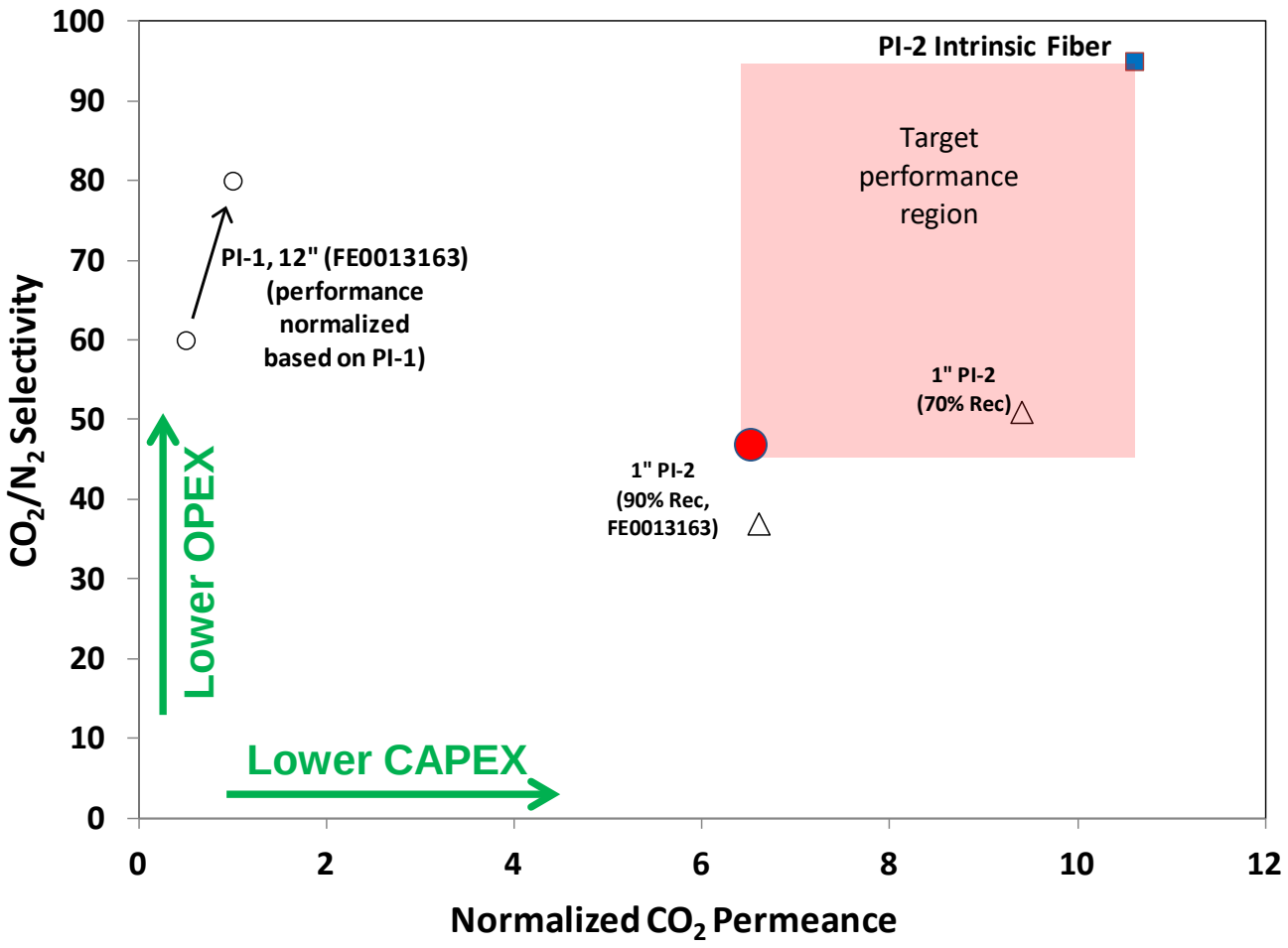


Full scale conditions:
18% CO_2/N_2 feed,
200 psig, -45°C, 1.5 psig permeate

Success criteria:
90 Nm^3/h feed flow,
90% CO_2 recovery,
58% permeate purity

- Performance improvement by process design (low permeate pressure, matches large scale conditions)
- CO_2 purity improvement leads to lower recycle flow, lower specific energy

4” Prototype Bundle Performance

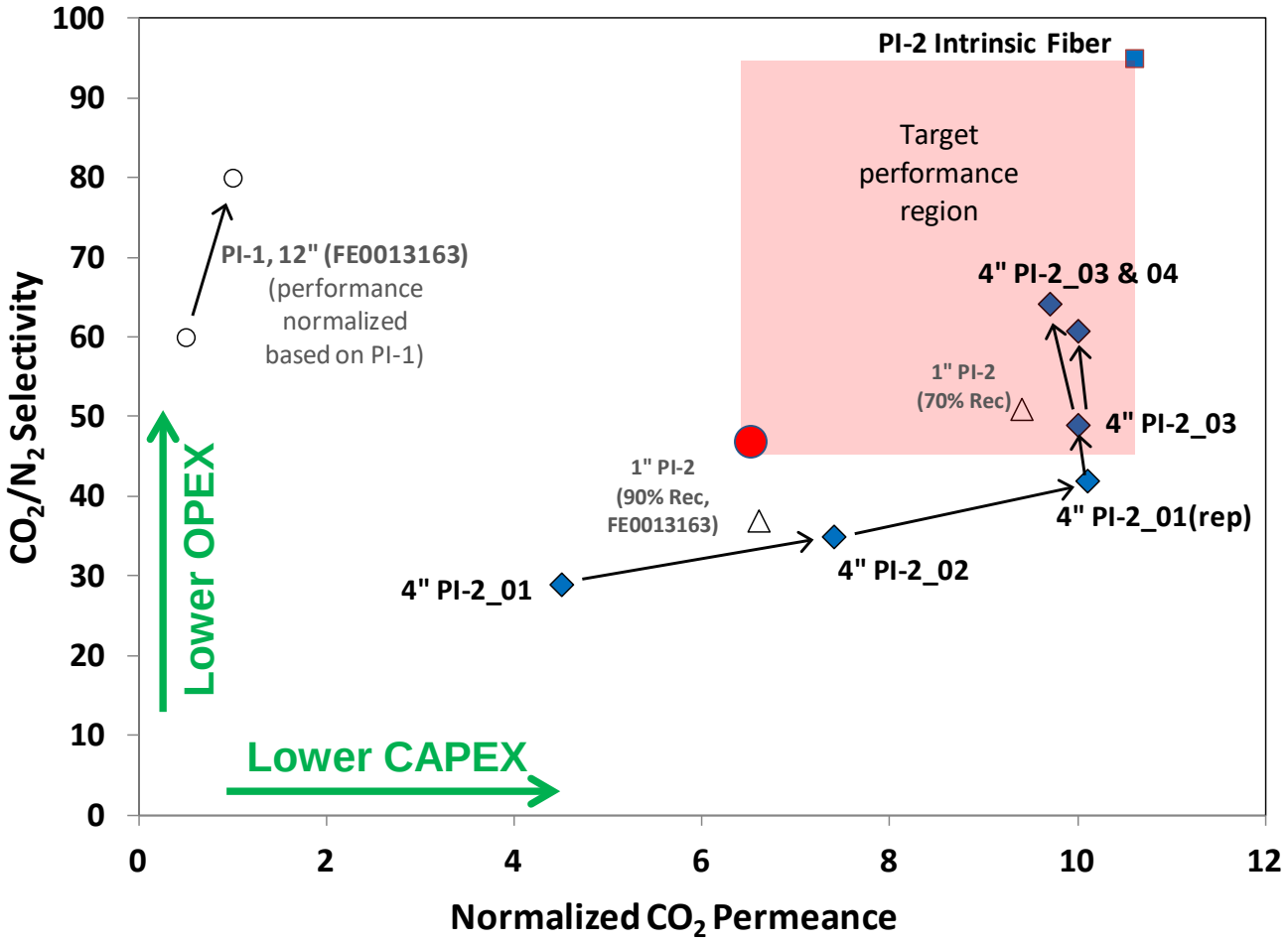


- Significant improvement by using ‘forming’ method in scale-up
- Lessons learned resulting in further performance gains

1) Epoxy application for tubesheet
2) Post-treatment solution concentration
3) Outer wrap layer positioning
4) Optimize fiber OD

Success criteria:
90 Nm^3/h feed flow,
90% CO_2 recovery,
58% permeate purity

4” Prototype Bundle Performance



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4) Optimize fiber OD

Success criteria:
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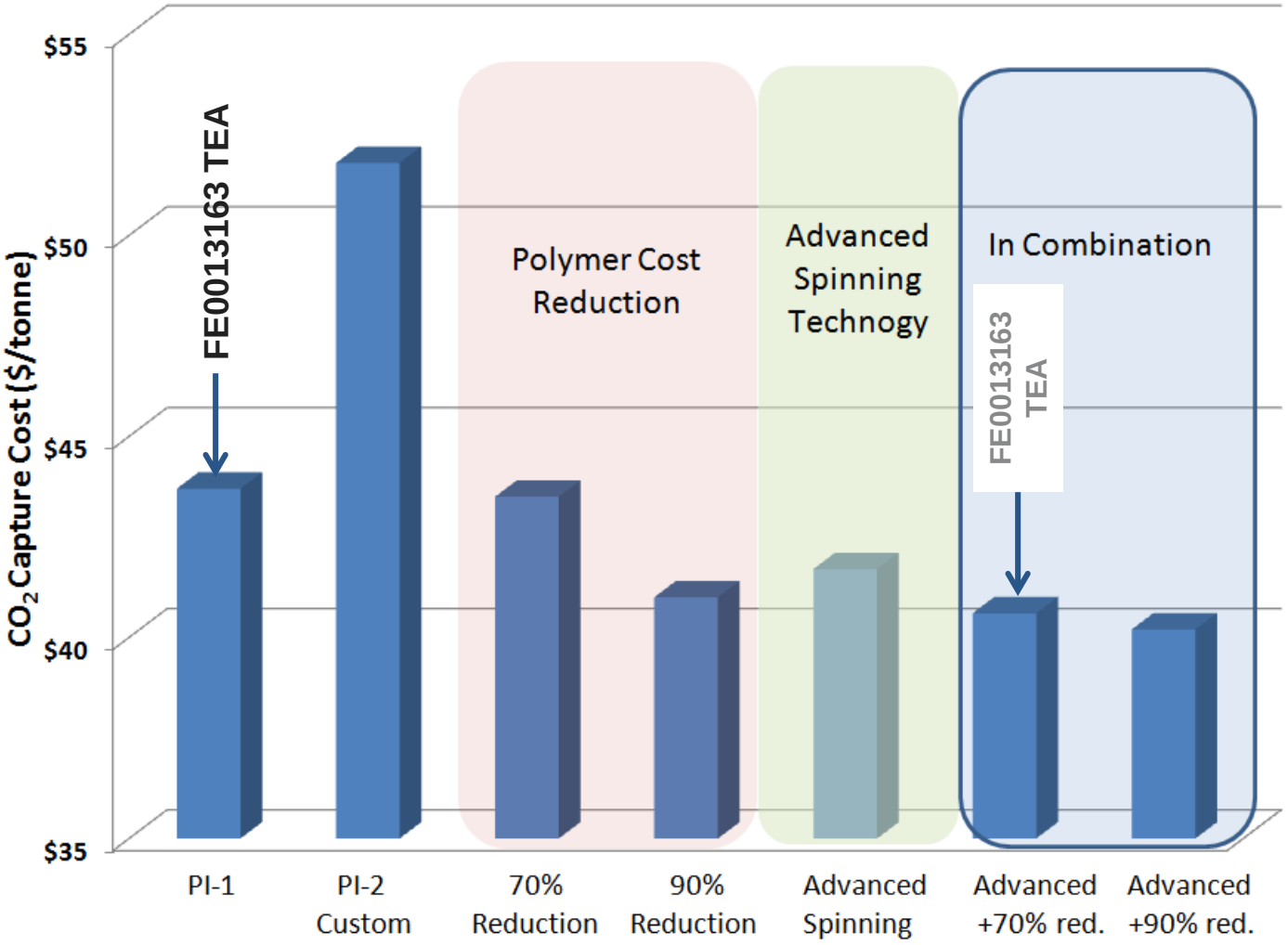
90% CO_2 recovery,
58% permeate purity

Fiber Manufacturing Cost Analysis

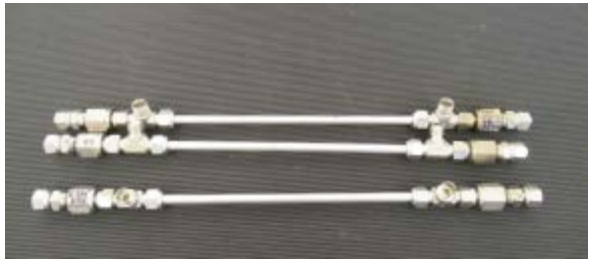
What are relative merits of cost-saving approaches?

- Best value is composite formulation
- With low polymer price monolith fiber yields CO_2 capture cost savings
- Pursuing both approaches



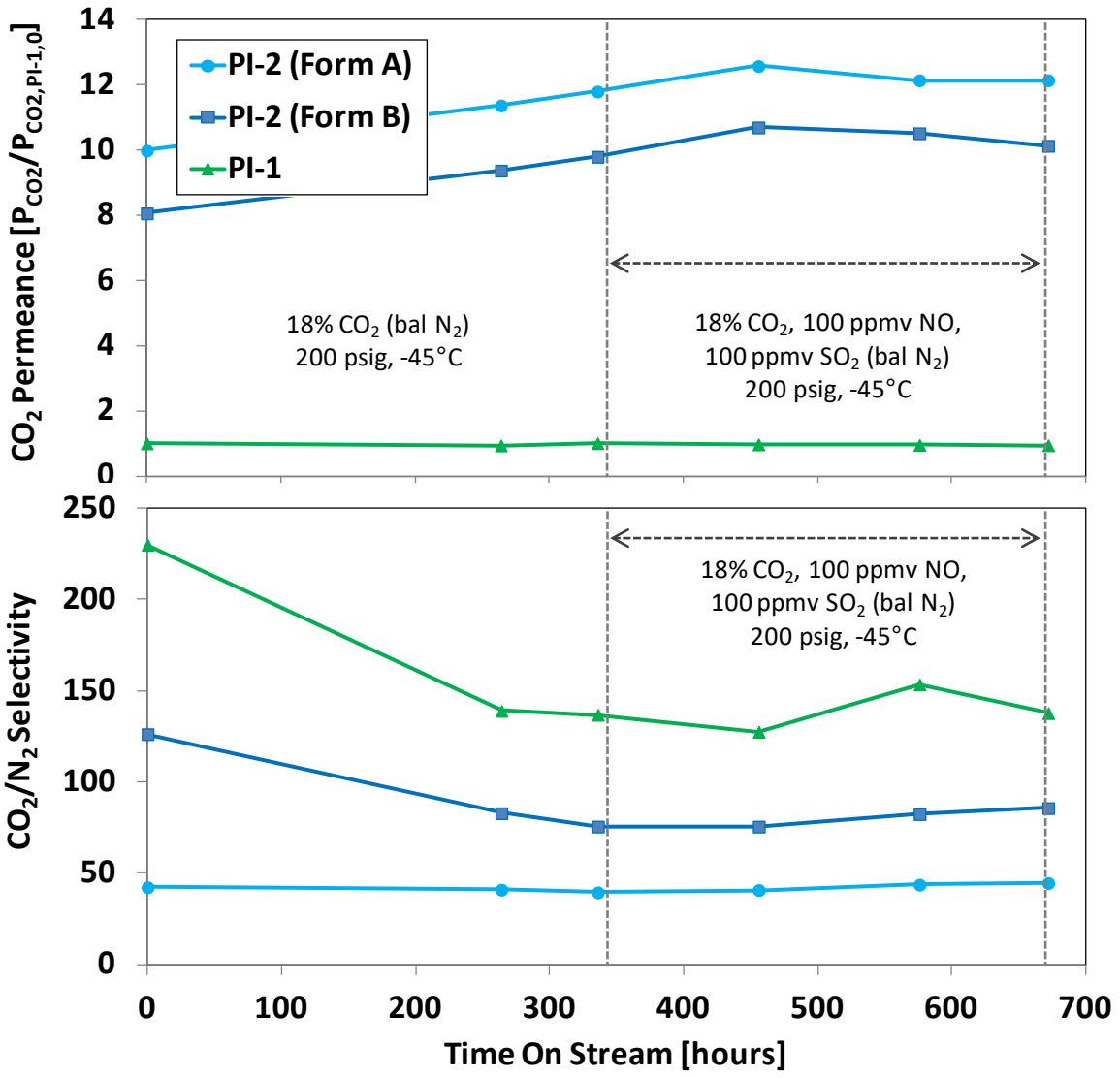
Acid Gas Contaminant Testing

Effect of acid gas contaminants on PI-2 fiber: ¼" mini modules, tested with synthetic gas mixtures, temperature controlled by lab refrigerator



100 ppm NO & 100 ppm SO_2

- PI-2 fiber permeance and selectivity tolerant towards NO and SO_2
- Typical levels in flue gas after FGD: 1 – 5 ppm SO_2, 50 ppm NO



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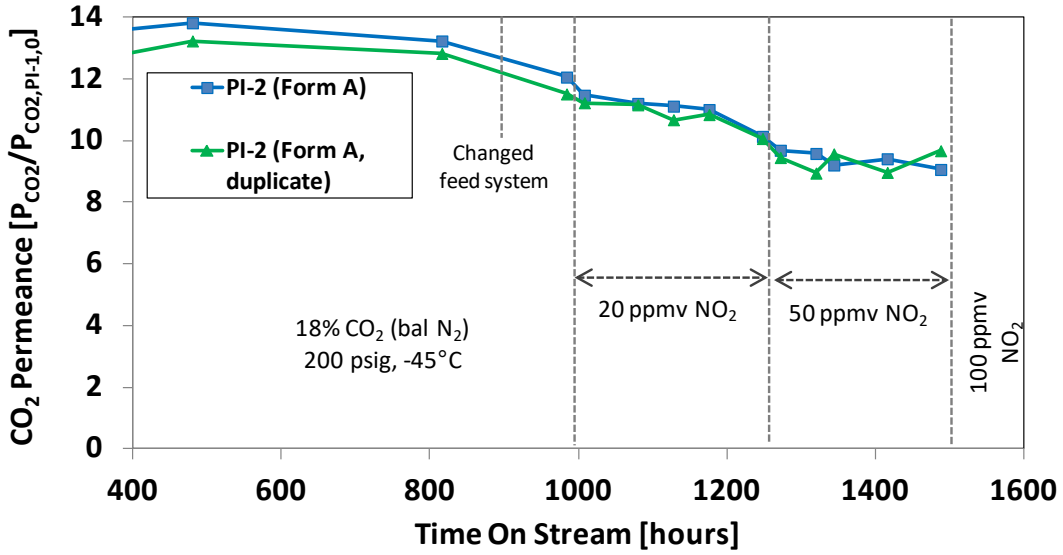

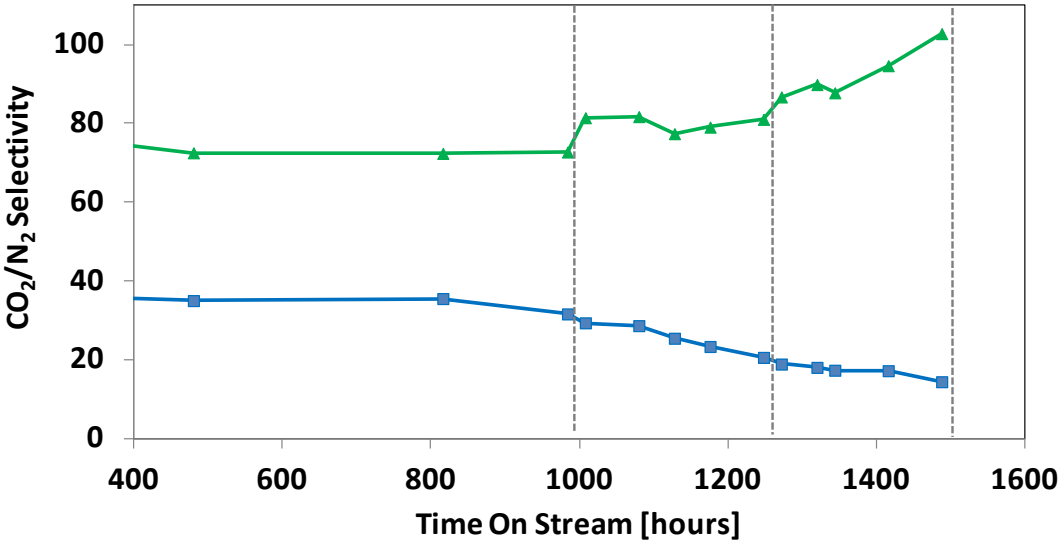

100 ppm NO_2 (not shown)

- Nearly complete loss of permeance due to 100 ppm NO_2!
- Cause was identified as solvent effect of gas on fiber micro-structure

20 – 50 ppm NO_2

- Minor decline in permeance due to 20-50 ppm NO_2
- Represents SCR failure case, 1 – 3 ppm NO_2 typical from 0.3 MWe field-test unit
- Long-term exposure to 5 ppm: **No problem**
- Short-term exposure to 50 ppm: **No problem**

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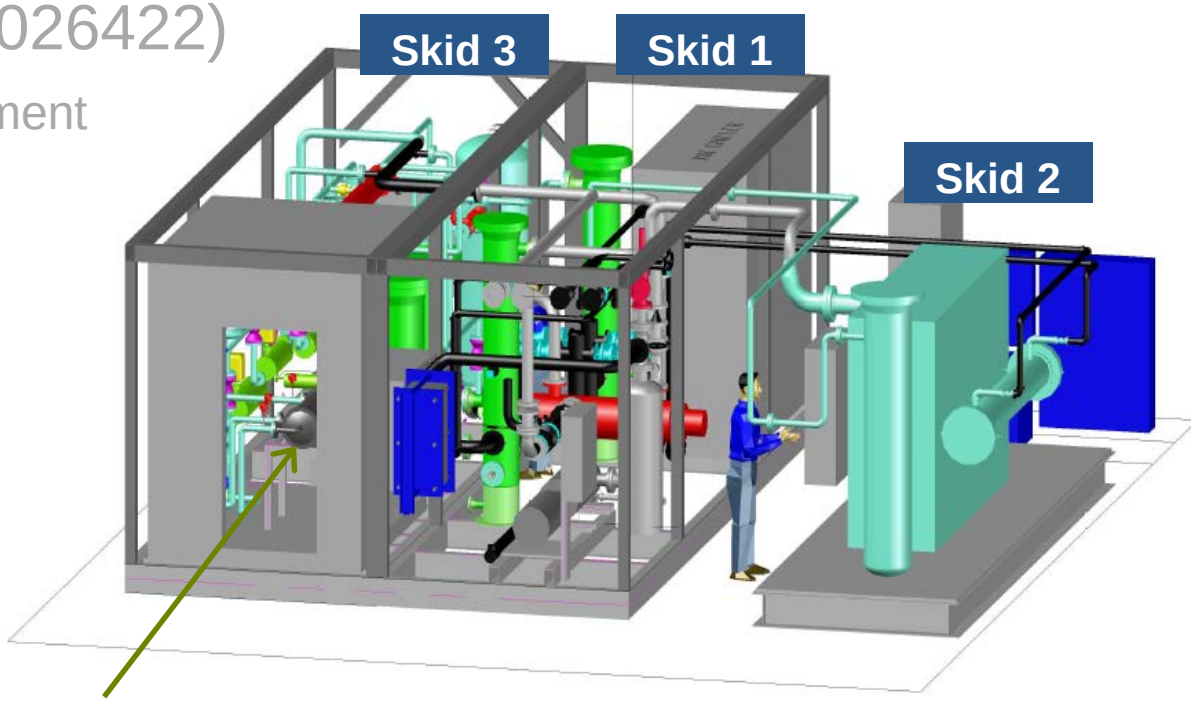

First 6” Commercial Bundle

- **Commercial PI-2 bundle preparation**
  - Polymer procurement scaled up to 5 lb (2.5 kg) scale)
  - Fiber spun on DSU for full 6” bundle fabrication (>90% yield)
  - QC testing: 24 - 30 times PI-1 permeance, 30 CO_2/N_2 selectivity (room temperature, post-treated) - excellent performance, best batch yet!
  - Bundle formed, QC by air test: performance was in line with previous 4” bundles

Next Steps

Budget Period 2: July 2017 to December 2018

- Manufacturing several 6” bundles (6 – 8), test on 0.1 MWe skid in Newark, DE
- Field-test at NCCC, 0.3 MWe scale
  - First test window: November 2017!
- Techno-economic analysis for PI-2
  - Updated manufacturing cost
  - Performance from field testing
  - Novel process designs considered

0.3 MWe Field-Test Unit at NCCC, Pilot Bay 3 (DE-FE0013163)

Acknowledgments / Disclaimer

- US DOE: José Figueroa, Sheldon Funk
- NCCC: Frank Morton, Tony Wu
- Air Liquide: Rob Gagliano, Shilu Fu, Sudhir Kulkarni, Dave Hasse, Mike Bennett, Dean Kratzer, Jean-Marie Gauthier

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Research & Development

Opening new ways

THANK YOU FOR YOUR ATTENTION