CO2 CAPTURE BY SUB-AMBIENT MEMBRANE OPERATION

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Air Liquide: Key Information

A world leader in industrial and medical gases

> 42,000 employees

€ 13.5 billion sales (2010)

Proposed new technology leverages AL strengths

- Air Liquide core expertise in gas separation, cryogenics and gas handling
- MEDAL – Established membrane manufacturer for N_2, H_2 and CO_2 applications
- Strong program related to coal oxy-combustion

CO_2 Capture by Sub-Ambient Membrane Operation

- **Bench scale test of CO_2 separation using a hollow fiber membrane module at sub-ambient temperatures**
- **Funding Request:**
  - **DOE: 1.266 M$; Cost share: 0.32 M$**
- **Duration – 24 months**

Air Liquide Advanced Technologies US – MEDAL (membrane manufacturing)

American Air Liquide Delaware Research & Technology Center (Separations, Combustion, Analysis..)

Air Liquide America Process and Construction (Engineering process design)

Project Main Tasks and Timeline

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	PHASE 1: Experimental work	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1	Demonstrate commercial scale bundle operation at sub-ambient temperature								
1.1	Design and fabrication of a closed loop sub-ambient test system for CO2/N2			M1					
1.2	Test mechanical integrity of bundle/housing assembly at sub-ambient temperature								
1.3	Map bundle performance as a function of temperature, pressure and composition								
1.4	Demonstrate enhanced membrane performance over long term at cold temperature							M3	
2	Laboratory Scale Flue Gas Contaminant Testing								
2.1	Modify lab cryo-test bench for low temperature SOx and NOx testing								
2.2	Measure SOx and NOx membrane performance on mini-permeator				M2				
	PHASE 2: Design work								
3	Sub-ambient Membrane/Cryogenic System Design								
3.1	Use Phase I data to design commercial facility and estimate LCOE increase for CO2 capture.								
3.2	Use Phase I data to design and develop budget estimate of a slip-stream demonstration unit.								M4
	In progress								
	Finished								
	Projected								

Task 1 : Demonstrate commercial scale bundle operation at sub-ambient temperature

Task 2 : Laboratory Scale Flue Gas Contaminant Testing

Task 3 : Sub-ambient Membrane/Cryogenic System Design

Detailed Project Objectives

1. Verify mechanical integrity of commercial scale membrane module structural components at sub-ambient temperatures.

2. Demonstrate high permeance - selectivity performance with a commercial scale membrane module in a bench-scale test skid

3. Demonstrate long term operability of the sub-ambient temperature membrane skid

4. Evaluate effect of expected contaminant levels (SOx, NOx) on membrane performance (lab tests)

5. Refine process simulation for integrated process with flue gas conditioning and liquefier

6. Design slip-stream-scale unit for possible field test

Cold Membrane Test Skid

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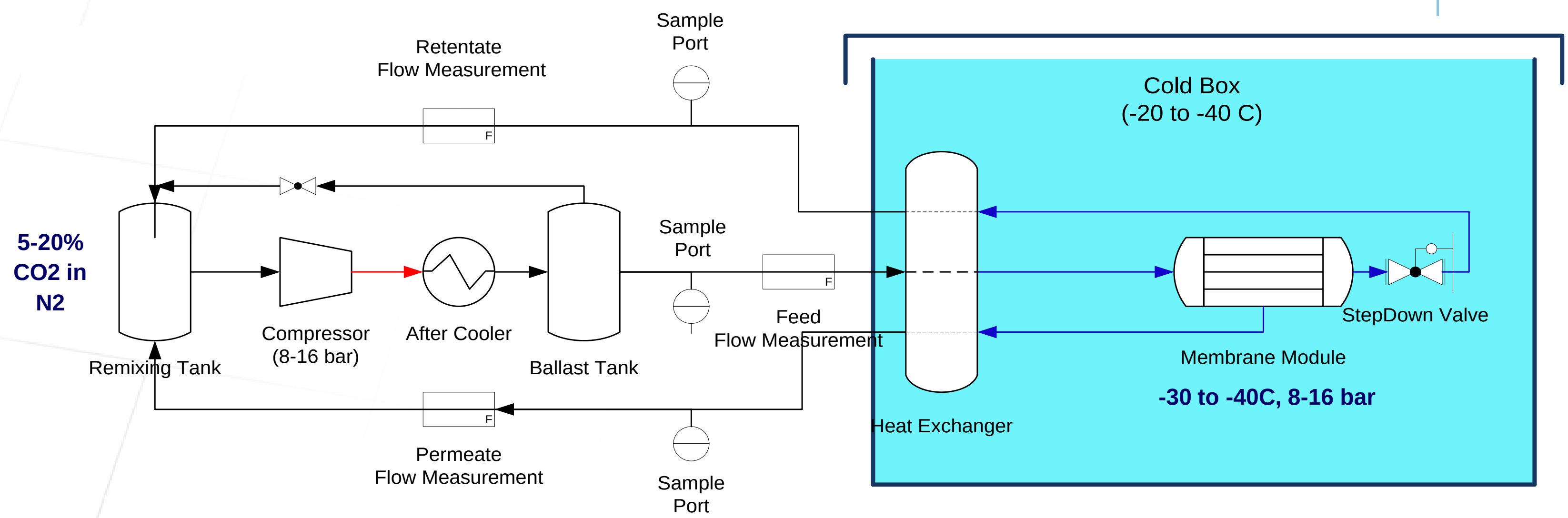
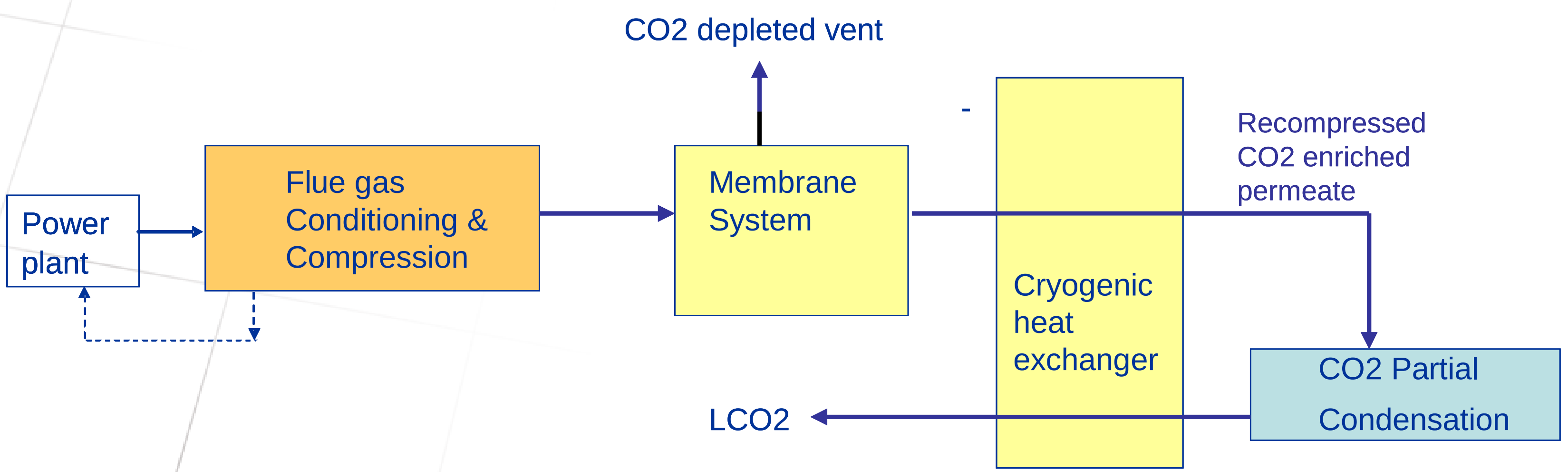


1. **Verify mechanical integrity of commercial membrane module structural components at sub-ambient temperatures.**
2. **Demonstrate high permeance - selectivity performance with a commercial membrane module in a bench-scale test skid.**
3. **Demonstrate long term operability of the sub-ambient temperature membrane skid without external source of refrigeration.**

Conventional Membrane Pre-concentration

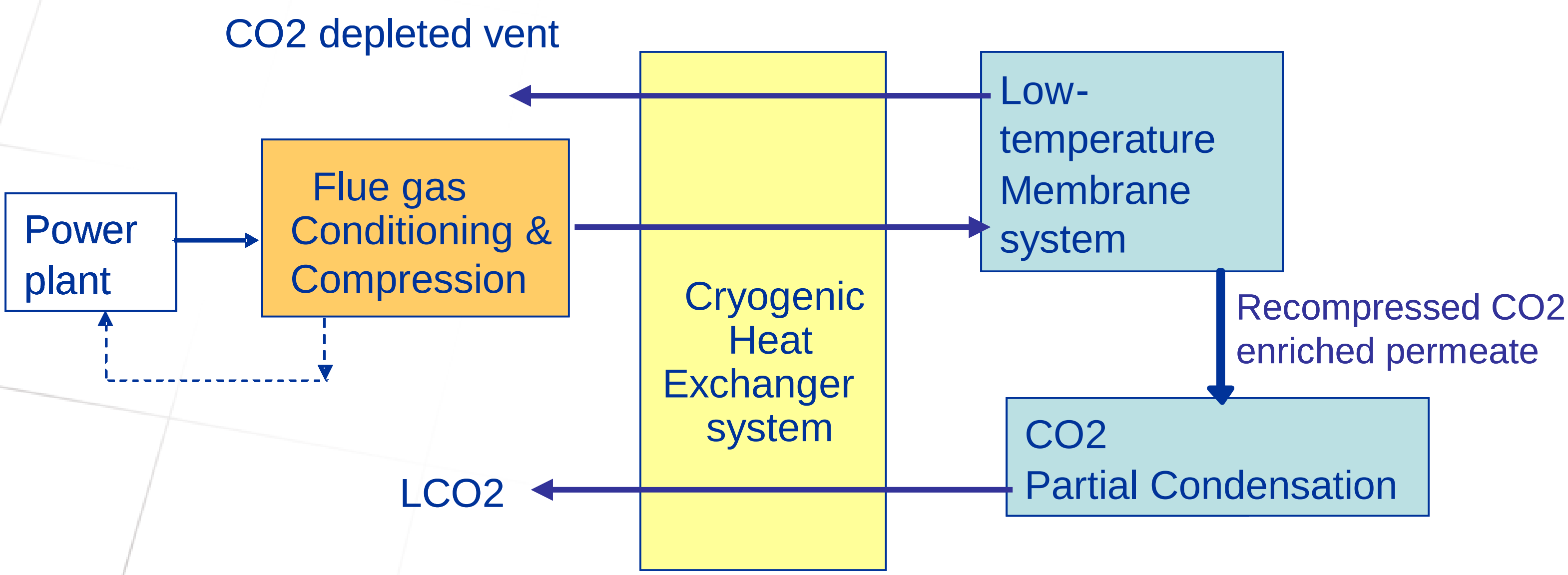
- Hybrid system required to economically meet 90% CO_2 recovery + sequestration purity (95 - 99 %) requirements for air fired coal flue gas

- Membrane pre-concentration of CO_2 followed by CO_2 Liquefier
  - With Membrane alone, difficult to produce high purity (>95% CO_2)
  - Membrane needed to operate CO_2 Liquefier at moderate pressures

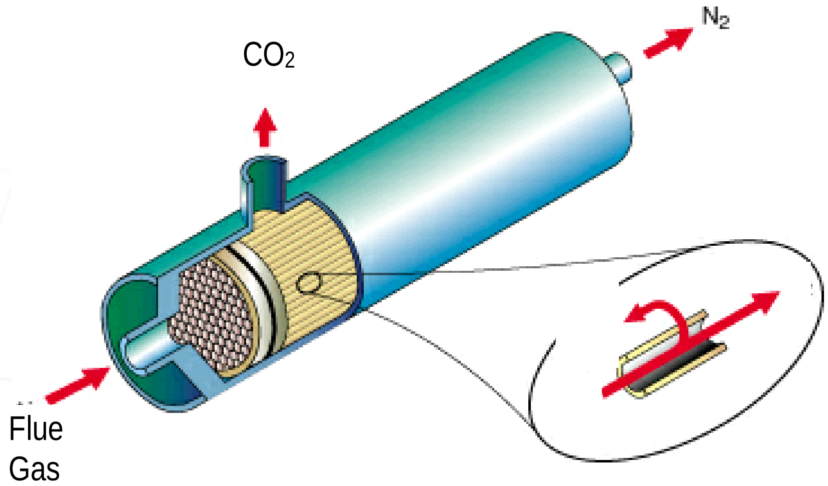


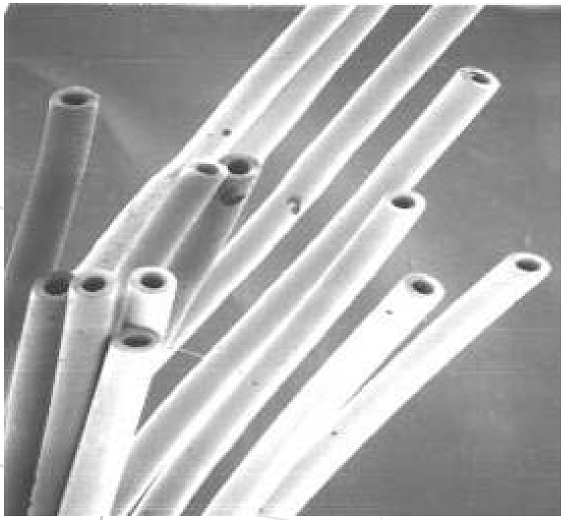
Cold Membrane Concept

- Pre-concentration of CO_2 by **highly selective cold membrane** before CPU Liquefier
- **Energy integration** between membrane / liquefier through heat exchange
- **Partial recovery** of compression energy



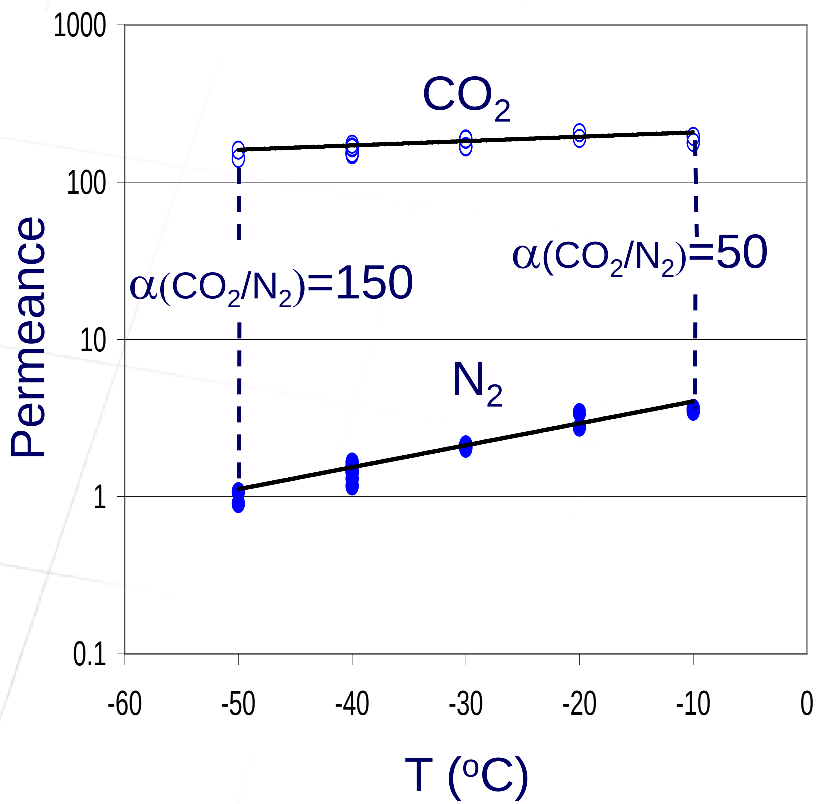
Cold Membrane Process Based on Existing AL Membrane

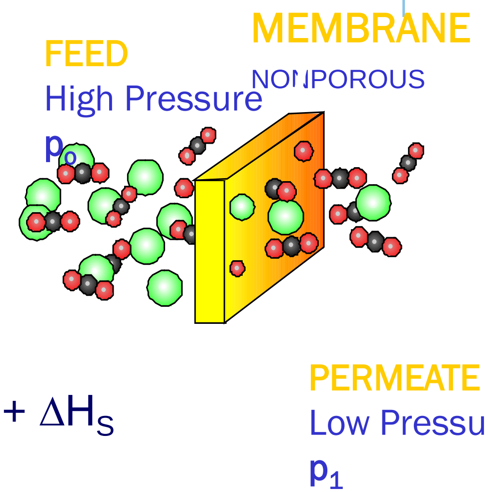




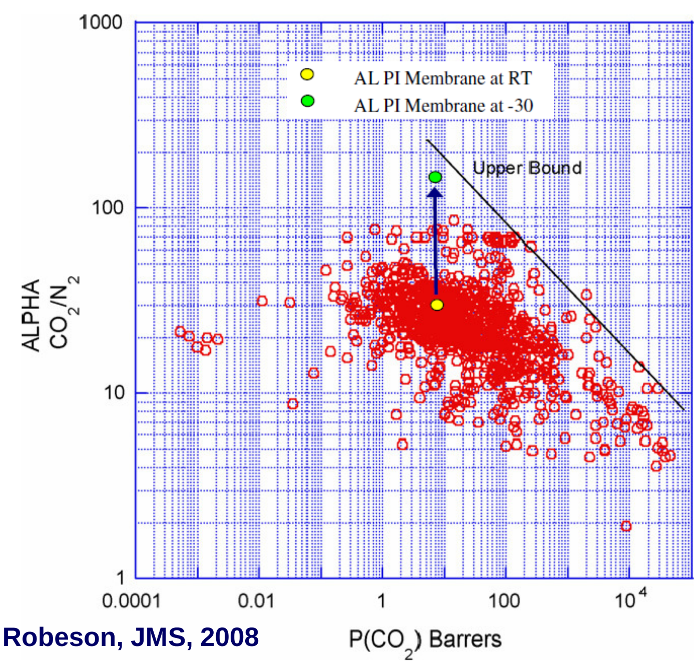
Hollow fiber membrane provides most cost effective solution for large gas separation applications

Sub-ambient Temperature Membrane Performance





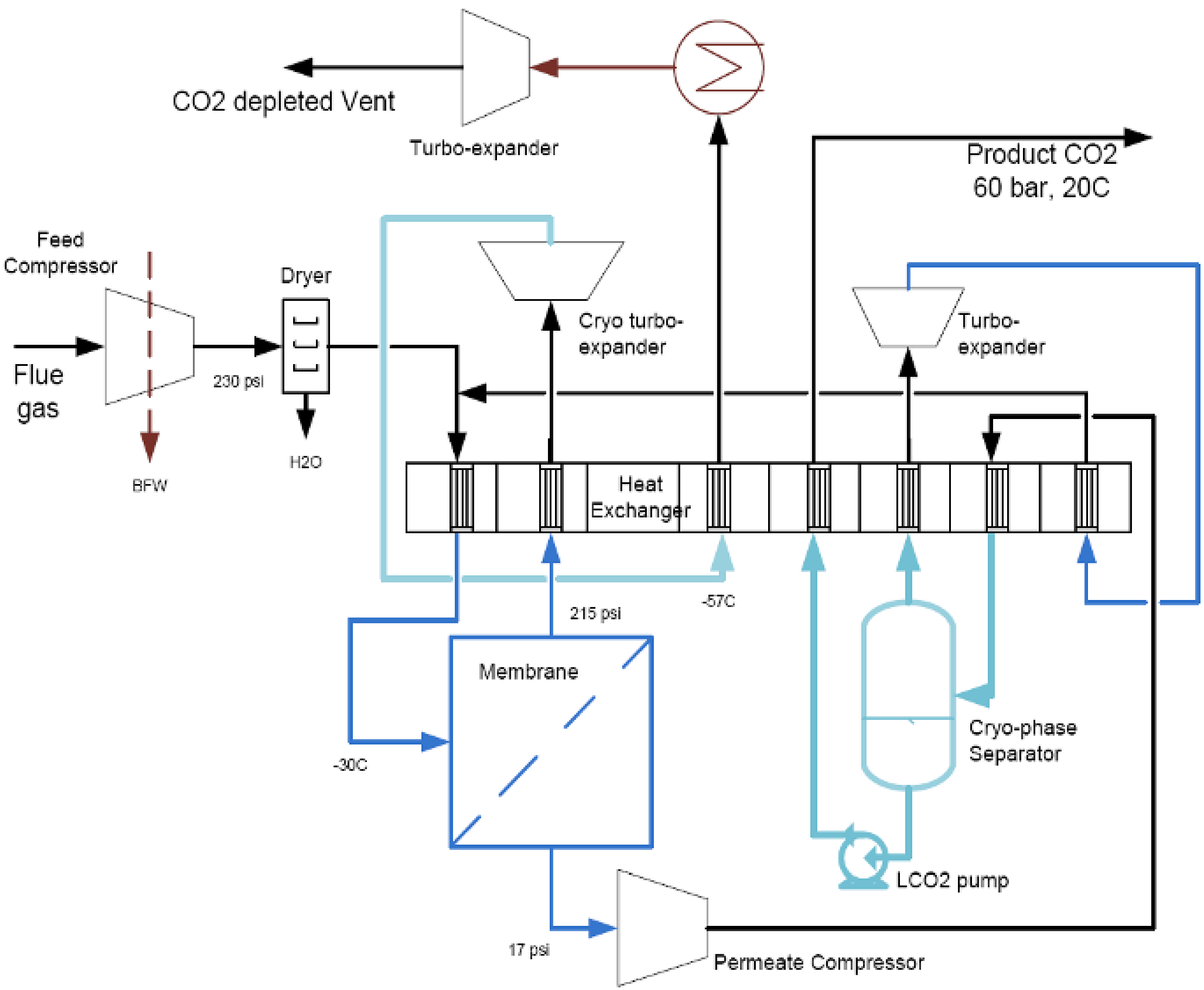
$$E_P = E_D + \Delta H_S$$



Robeson, JMS, 2008

Existing AL Membrane operated at < -10 C has unique combination of high CO_2 permeance and CO_2 / N_2 selectivity

Hybrid Membrane + CPU Configuration



Why High Membrane Selectivity Pays Off

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Permeate stream is smaller and higher CO_2 purity

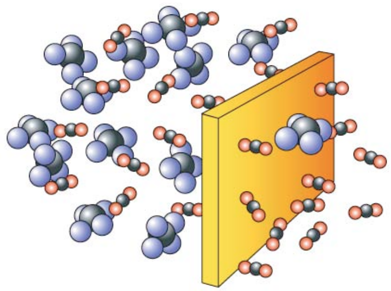
- **Increases efficiency of CO_2 liquefaction**
- **Decreases internal recycle.**

Membrane Operating Temperature	**Ambient (20-30°C)**	**-30°C**
	Energy Use [kW]	
Feed Compression	94.6	94.6
Permeate Compression	40	21.1
	Energy Credit [kW]	
Cryogenic Turbo-expansion	0	22.3
Ambient Turbo-expansion	36.2	31.2
Boiler Feed Water Credit	16.4	15.8
	Overall energy for CO_2 capture	
Specific energy kW-hr/Ton[CO2]	326	204

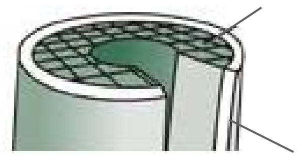
Expected Development Challenges

- Challenges specific to sub-ambient membrane operation
  - Module materials
  - Permeance-selectivity of commercial module
  - Long term module performance stability
- Integration of membrane process
  - Energy integration with CPU
  - Energy integration with power plant
    - Compression and Turbo-expansion schemes
    - Heat economizers and Exergy conservation
  - Large but feasible membrane area production
- Contaminant specific challenges
  - Acid gas (NO_x, SO_2) separation
  - Compressor materials
  - Particulate removal
  - Hg
  - Water handling

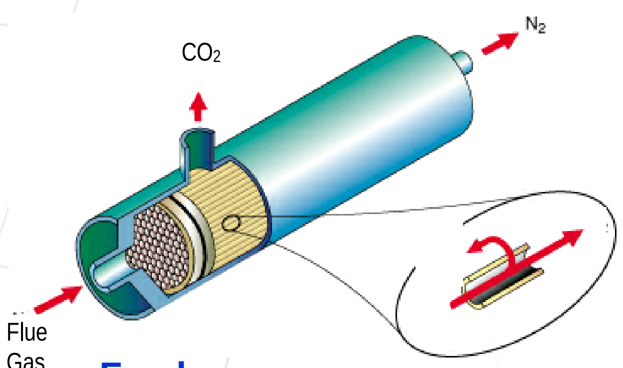
Components of a Membrane System



POLYMER SCIENCE:
Membrane Separation
Technology



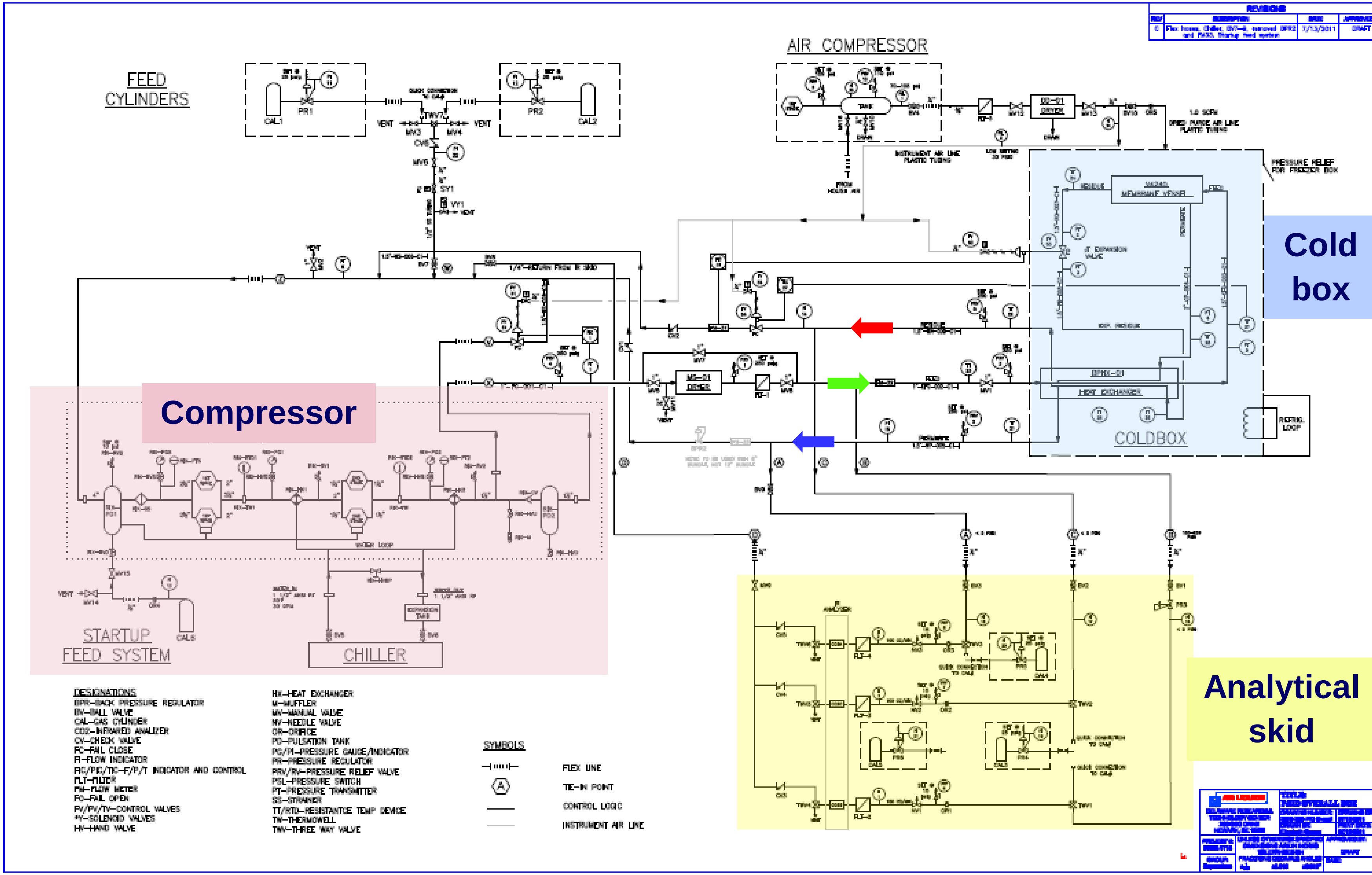
MEMBRANE
TECHNOLOGY



**BUNDLE DESIGN
AND HOUSING**

PROCESS DESIGN:
Integration of Membrane
Into Commercial System

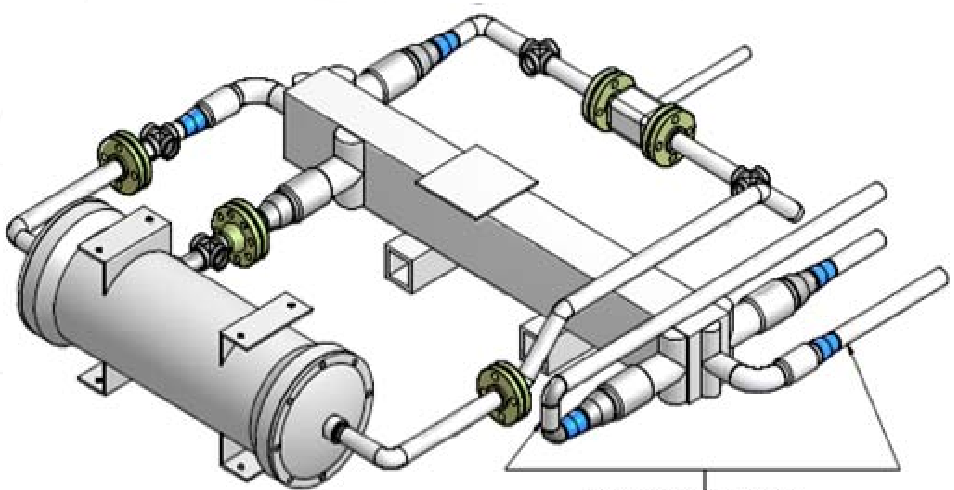
P&ID of Test Skid



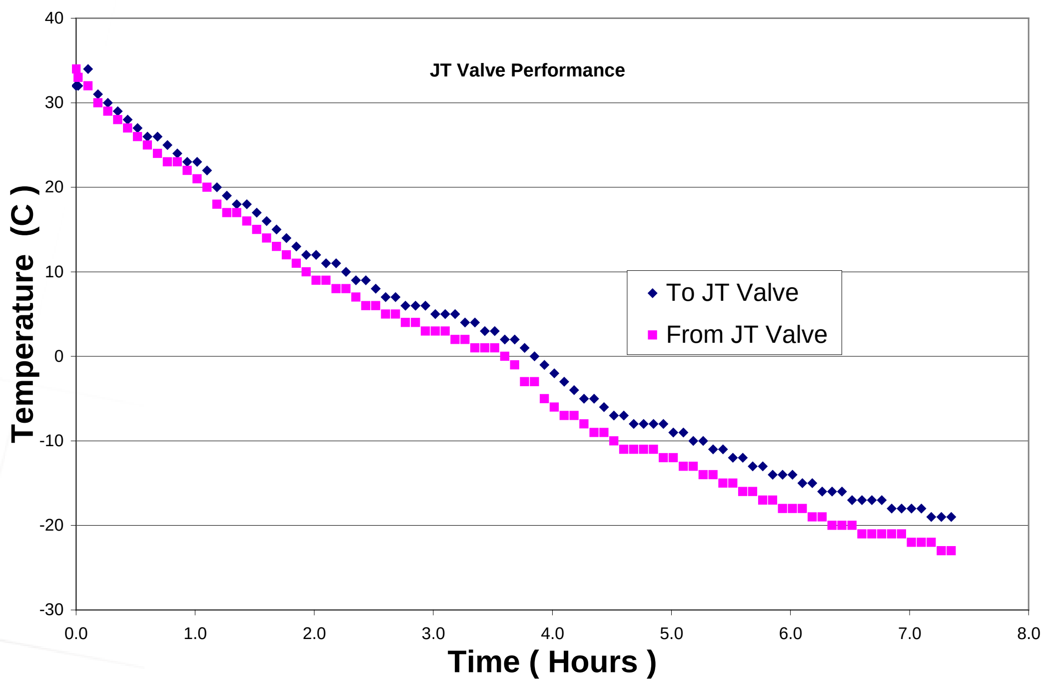
Skid in Operation

E. Corson **D. Kratzer**

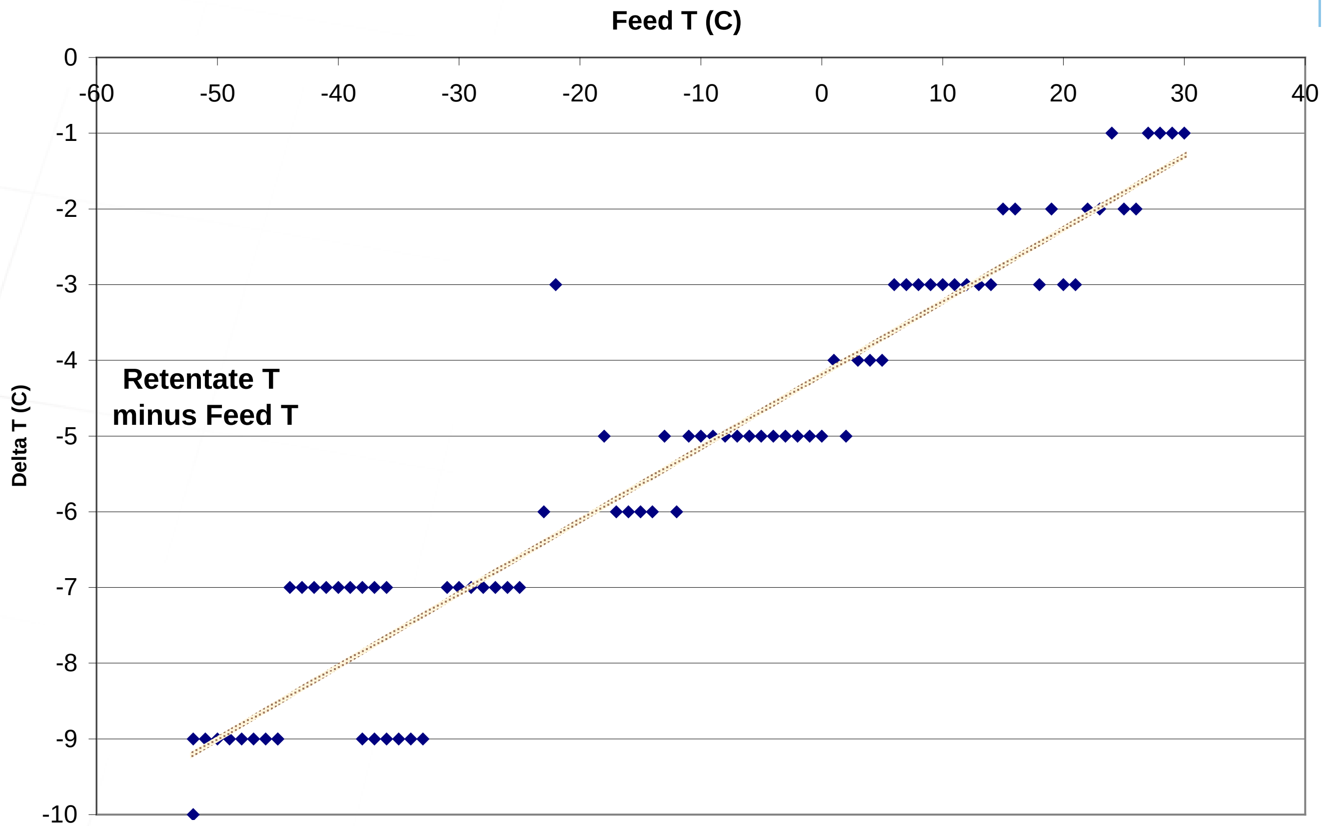
Gas Cooling Scheme



Incremental cooling of feed gas by heat-exchange with expanded residue stream & permeate



Gas Cooling Scheme : Approach temperature



- **Accumulation of cooling effect allows feed to be cooled to < -50 C. Operating target is -30 to -40°C**
- **Temperature maintained by adjusting pressure expansion ratio across J-T valve**

Mechanical Integrity Test

- **Largest commercial MEDAL bundle (12")**
  - Most rigorous test of mechanical integrity
  - Leak-free operation particularly important for high selectivity

- CTE analysis to choose bundle assembly components
  - Several O-rings (materials / hardness / type) have been shortlisted on recommendation of vendor experts

- Laboratory verification of tube-sheet epoxy to fiber adhesion

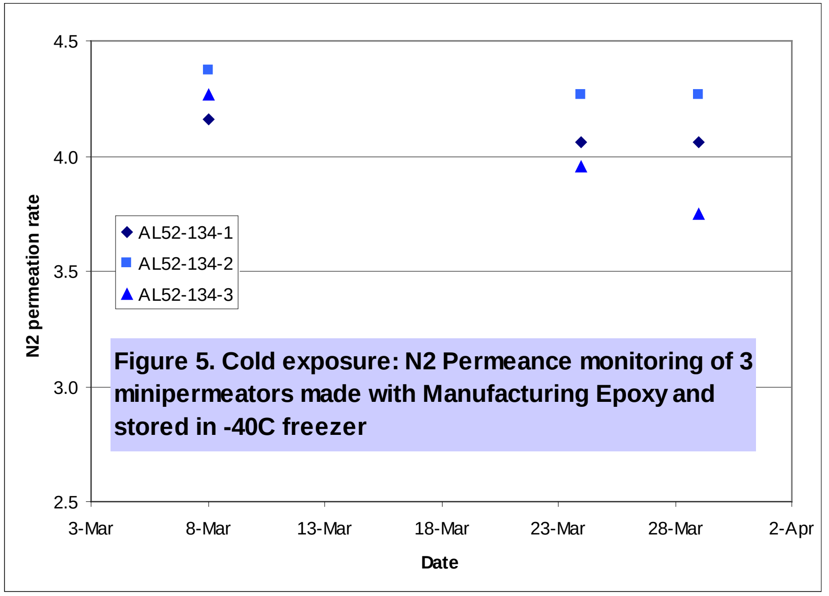
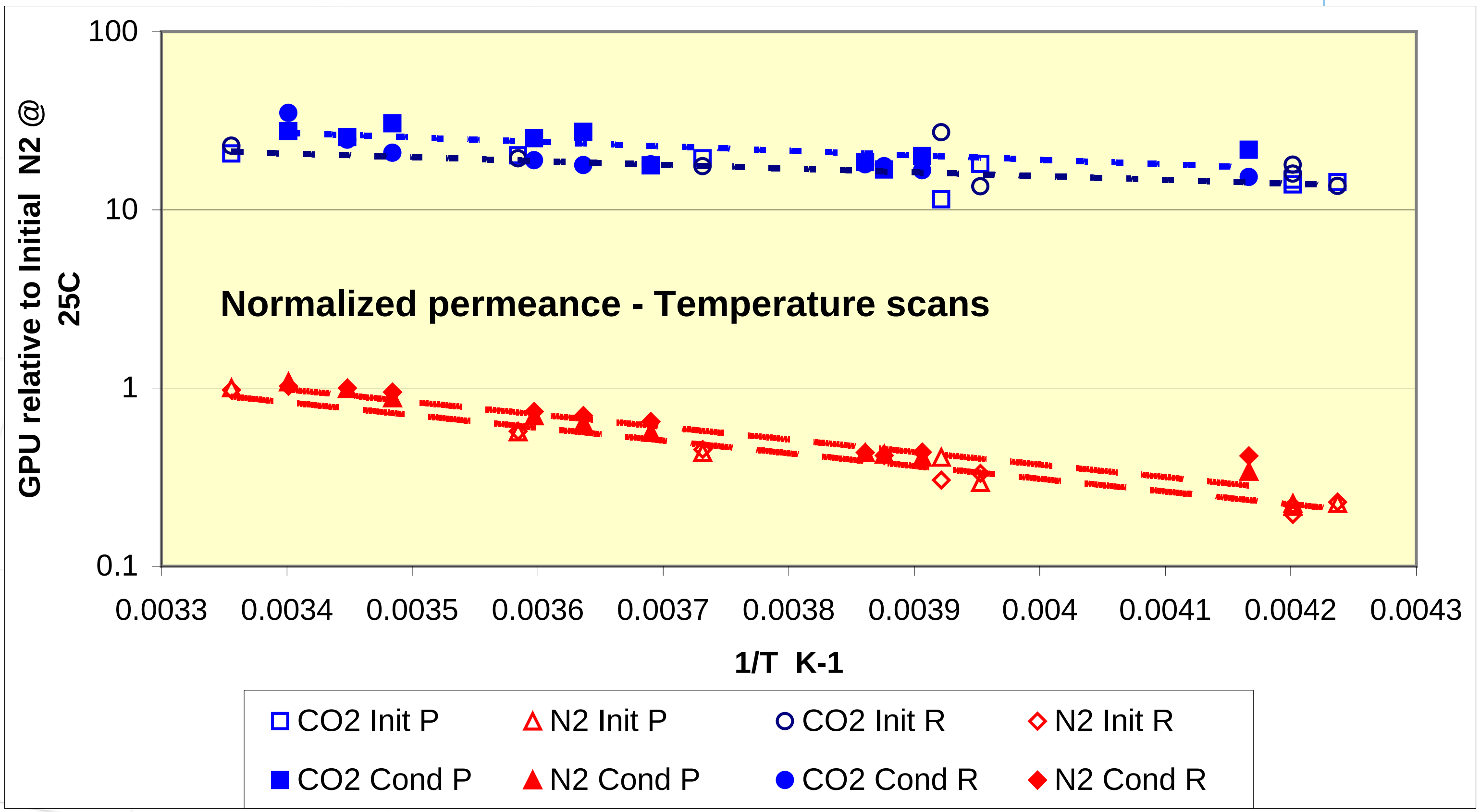


Figure 5. Cold exposure: N2 Permeance monitoring of 3 minipermeators made with Manufacturing Epoxy and stored in -40C freezer

Mechanical Integrity Test Under Way

- 12" bundle has been operating since 7/5/11
- Exposed to pressures up to 15 bar , temperatures down to -60 C and CO_2 concentrations of 15 – 30%.
- Withstood several shut-downs and re-starts
- Performance has been stable (1st week separation data similar to 6th week separation data)
- Various techniques (pure gas vs. mixed gas, varied stage cut and pressure, tracer molecules) used to diagnose performance
- Target date is 12/2011 for completion of mechanical integrity test(s)

Temperature Response for Bundle Matches Lab Data

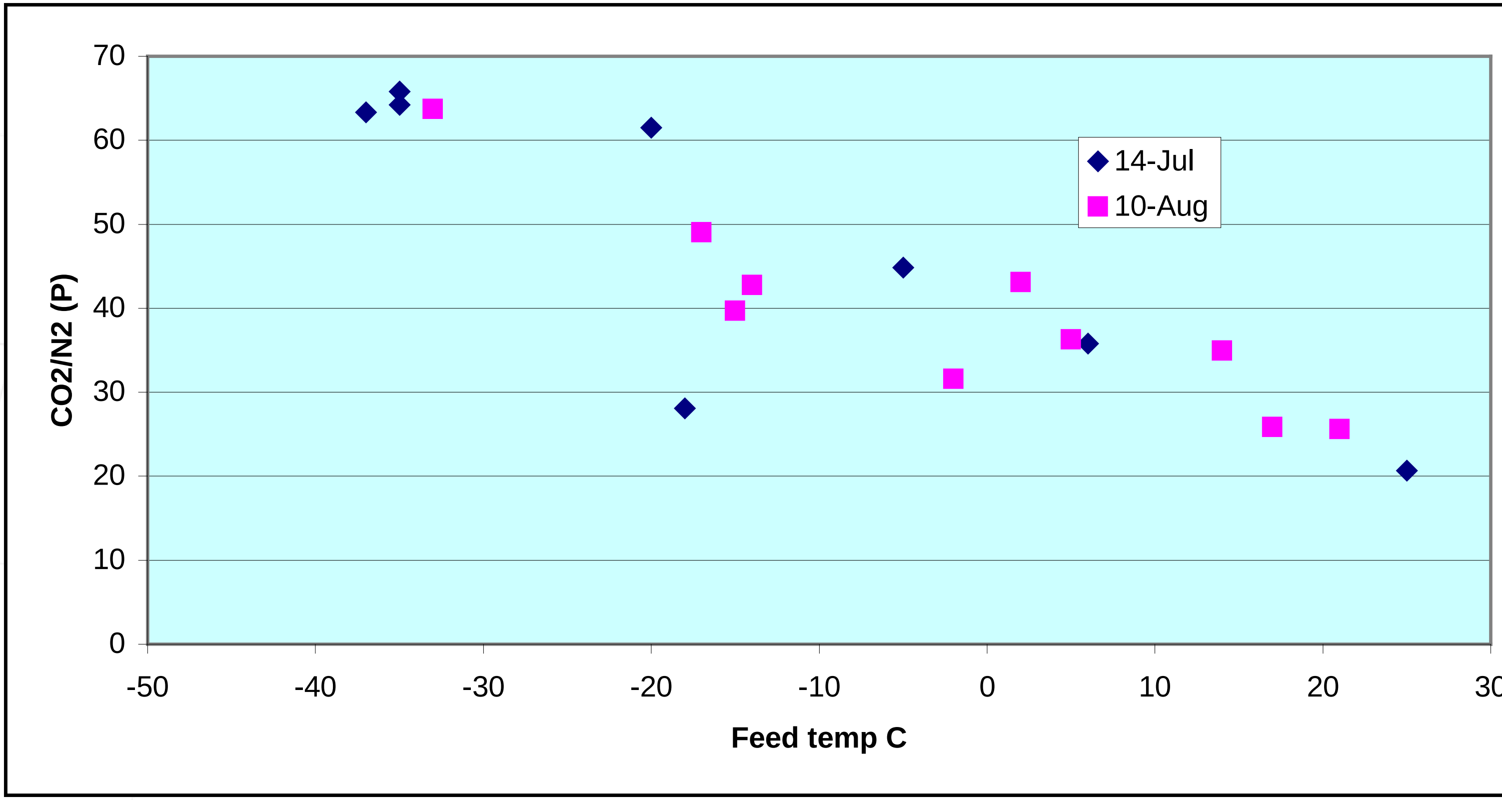


As temperature is decreased:

CO_2 permeance is relatively constant

N_2 permeance declines ~ 3x

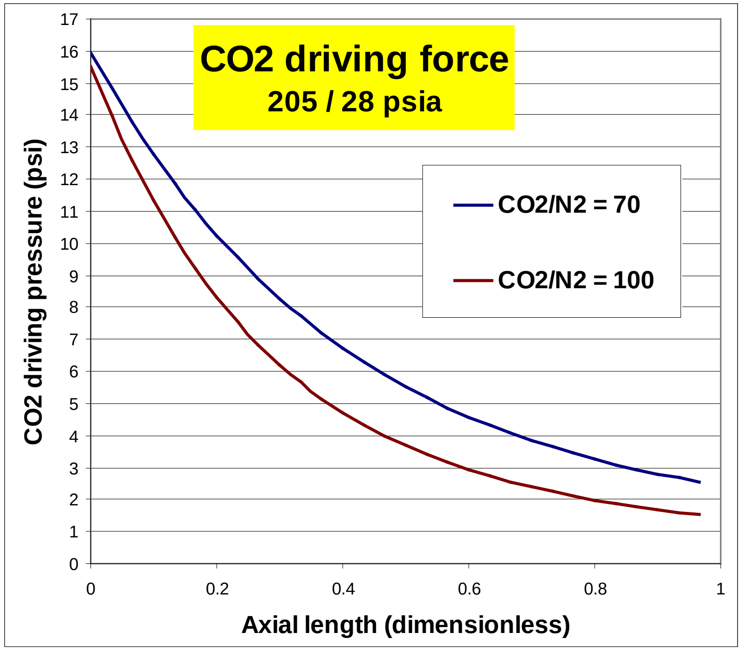
Separation Performance Over First Month Testing



- **Tracer molecule and stage cut performance being used to differentiate possible small leak vs flow non-ideality**

Parametric Study of Separation Performance

- Membrane performance back-calculation with larger bundle is less reliable
  - Pinch effects from low driving pressure



- After completion of mechanical integrity test, expect to change to 6" bundle for parametric studies of membrane performance

Path Forward

- Proceed with planned skid testing
  - Complete 12” bundle mechanical integrity test (Q5)
  - Performance mapping with 6” bundle (end Q5 and Q8)
  - Long term test (Q5 – Q8)

- Revise process simulations using actual bundle performance data to reassess potential to meet DOE targets

- Field test will be proposed if revised simulation results are still positive