CO_2 CAPTURE BY SUB-AMBIENT MEMBRANE OPERATION

Pittsburgh, PA l July 8, 2012 l DOE NETLCO2 Capture Technology Meeting

AL DRTC Separations

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Air Liquide: Key Information

A world leader in industrial and medical gases

- Sales € 14.5 billion (~$20 billion) (2011)
- Over 1 million customers in 80 countries
- 46,500 employees worldwide
- 60% of R&D budget devoted to developing technologies designed to preserve the environment (energy savings, cleaner production, future energy development)

Proposed CO_2 Capture technology leverages AL strengths

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

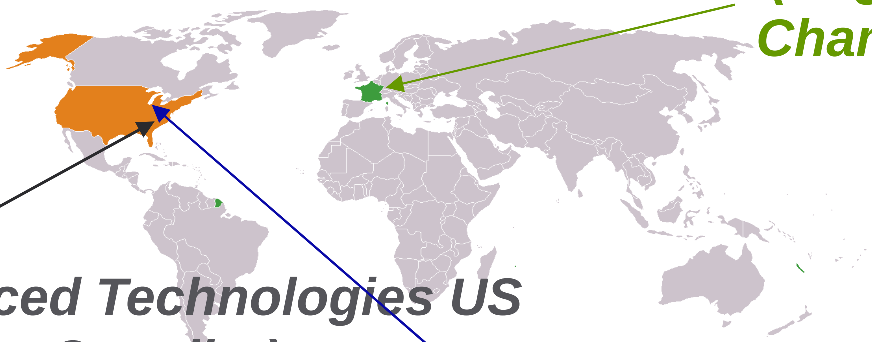
CO_2 Capture by Sub-Ambient Membrane Operation

DOE NETL Award No. DE-FE0004278

Funding : DOE - 1.266 M$; Cost share - 0.32 M$

Period of Performance: 10/01/2010 through 9/30/2012

Air Liquide Engineering
(Engineering process design)
Champigny, France



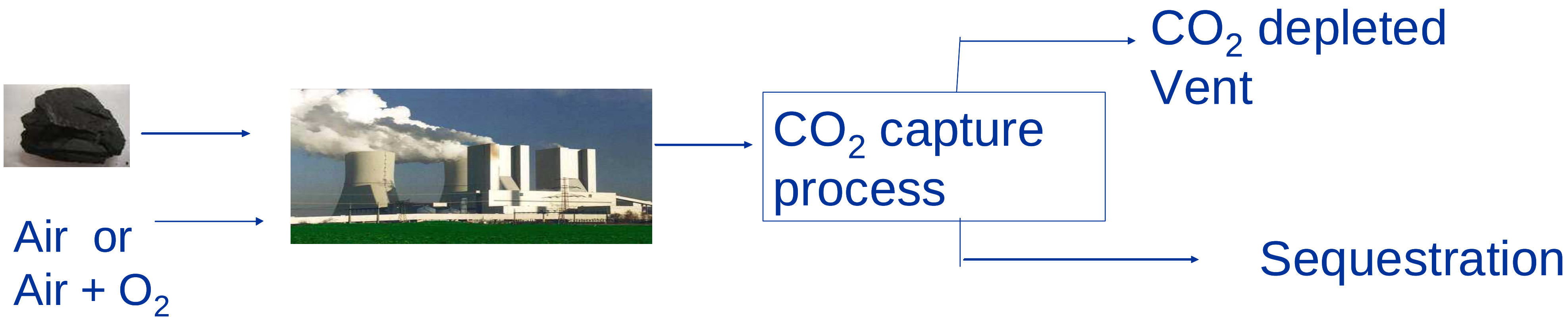
Air Liquide Advanced Technologies US
MEDAL (Membrane Supplier)
Newport, DE

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

2010 Post-combustion CO_2 Capture Projects

Project Manager: Andrew O'Palko

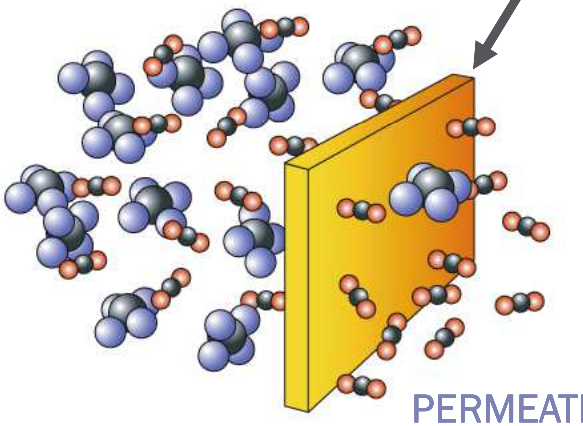
Post combustiion CO_2 capture from air fired coal flue gas



DOE criteria

- 90+% CO_2 recovery
- CO_2 product purity consistent with sequestration requirements
- < 35% increase in (20-year levelized) cost of electricity

Gas Transport through Polymeric Membranes



Permeability

$\mathcal{P} = D{*}S$

- Diffusivity- Related to size (Kinetic Diameter)
- Solubility - Related to condensability of penetrant (Critical Temperature)

Selectivity

$$\alpha = \left[\frac{\mathcal{P}_1}{\mathcal{P}_2}\right] = \left[\frac{D_1}{D_2}\right]\left[\frac{S_1}{S_2}\right]$$

	CO_2	N_2
$T_c(^oK)$	304	126
$D_{kinetic}(A)$	3.3	3.6

Both solubility and diffusivity favor CO_2 transport
CO_2 is selectively transported over N_2

Temperature dependence of gas transport in Membranes

Temperature dependence obeys the Arrhenius equation

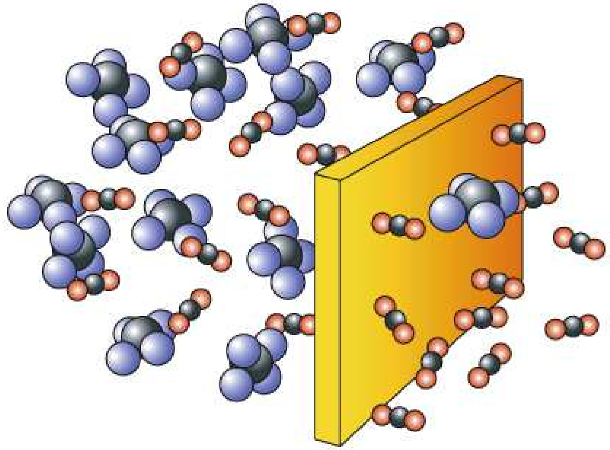
$P = P_o\ exp\ \{ -\Delta E_A^*/R\ (1/T-1/T_o)\}$

but P= D*S

$D = D_o\ exp\ \{ -\Delta E_A/R\ (1/T-1/T_o)\}$

$S = S_o\ exp\ \{ -\Delta H_s/R\ (1/T-1/T_o)\}$

$\Delta E_A^* = \Delta E_A + \Delta H_s$

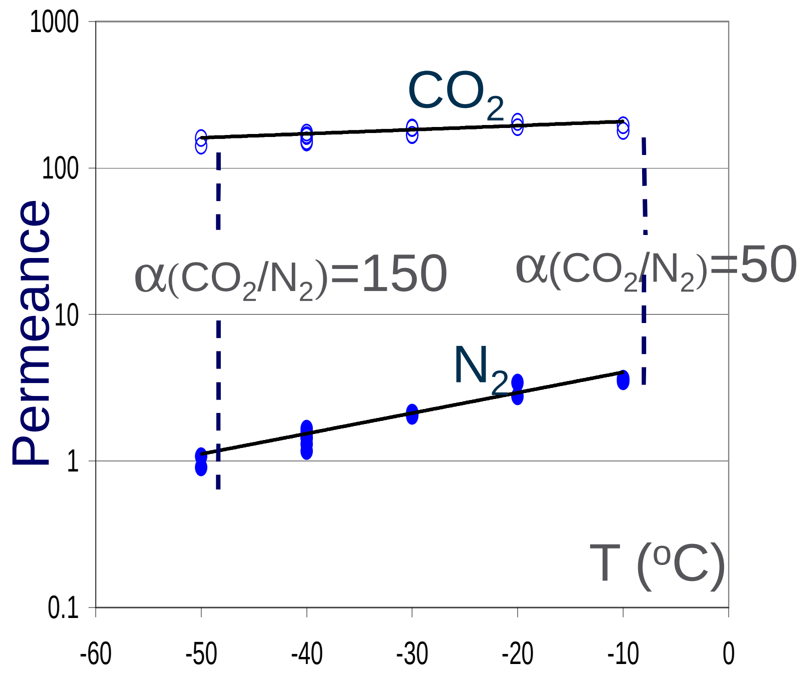


ΔE_A is always positive; energy required to execute a diffusional jump
ΔH_s is always negative; ¼ to ¾ heat of condensation at normal boiling point

	CO_2	N_2
T_c (°K)	304	126
D(A)	3.3	3.6

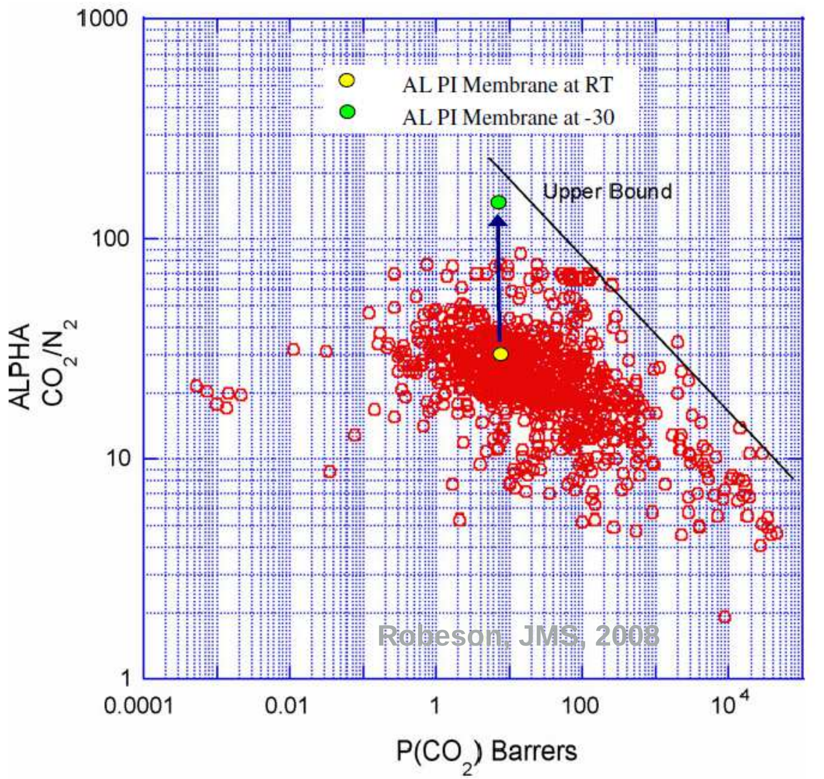
$\Delta E_A^*(CO_2)$ is always less than $\Delta E_A^*(N_2)$
$\alpha(CO_2/N_2)$ increases exponentially with decreasing temperature

Sub-Ambient Temperature Membrane Performance



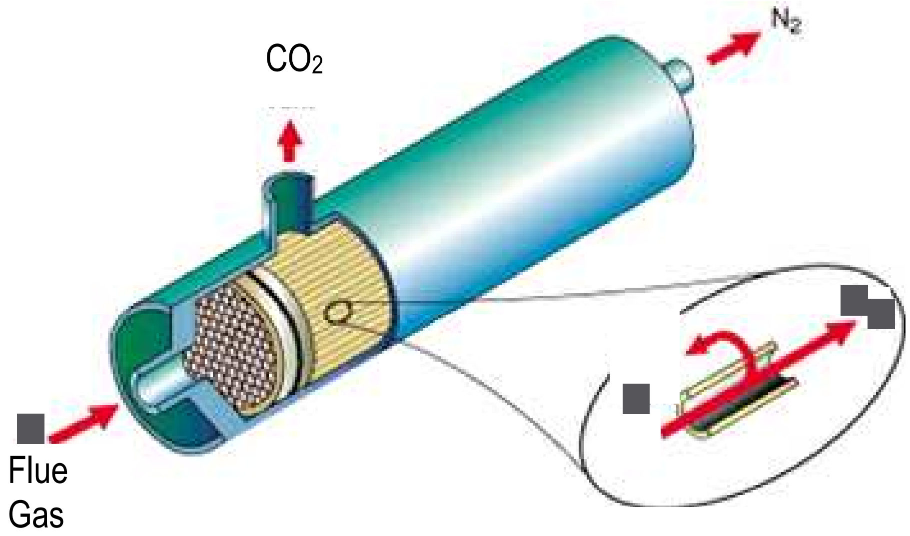
- For a *select few* polymer membranes temperature can be used to dramatically improve performance
- Selectivity can be increased with minimal change in CO_2 permeance
- The effect is due to a matching of the activation energy for diffusion and the heat of sorption.

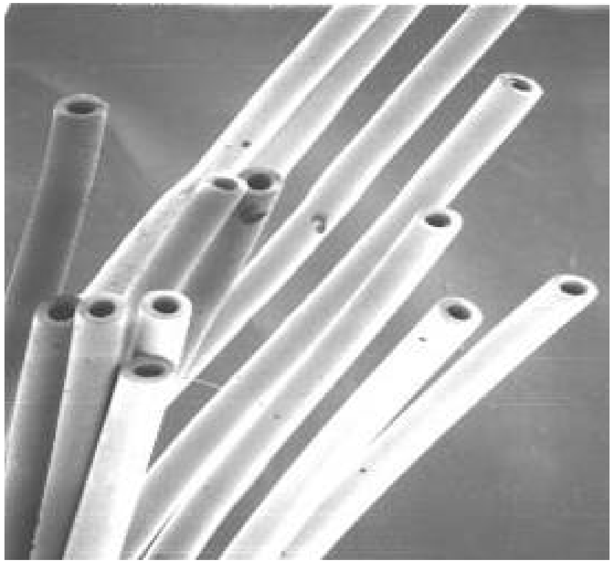
A commercial AL Membrane operated at less than -10°C has unique combination of high CO_2 permeance and CO_2/N_2 selectivity



Intrinsic permeability at -30°C inferred from known film data at RT + fiber data at RT and -30°C

Cold Membrane Process Based on Existing AL Membrane

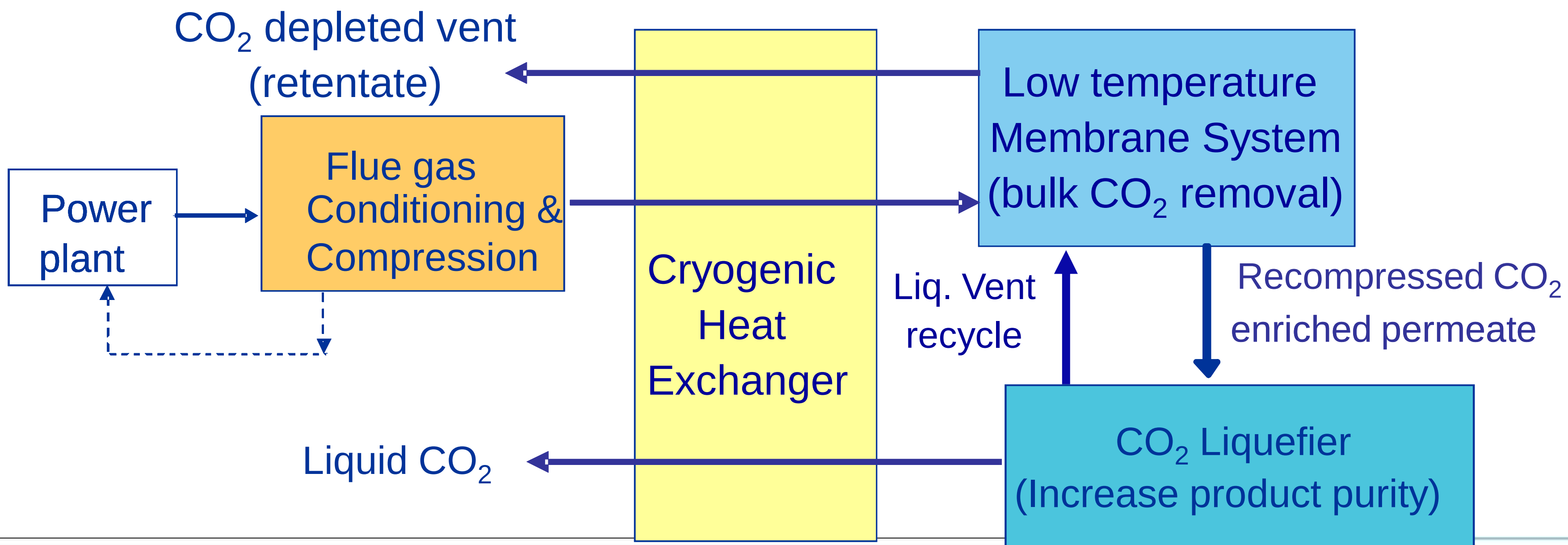




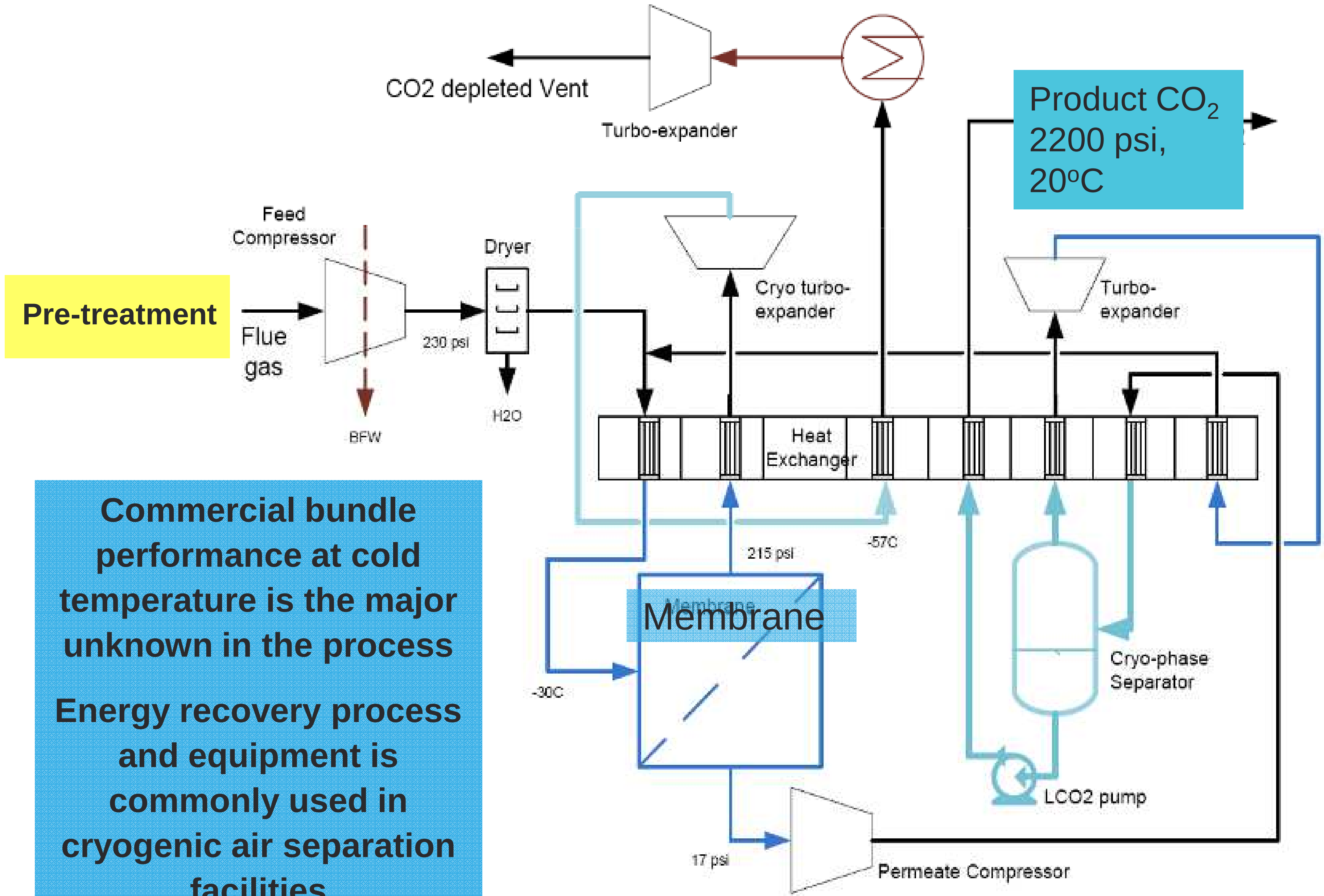
Hollow fiber membranes are providing cost effective solutions (~ $20/m²) in very large (up to Bscfd) CO_2/natural gas separation applications

Cold Membrane Process Design Concept

- Pre-concentration of CO_2 by **highly selective cold membrane** before liquefier
- **Efficient recovery** of compression energy
  - BFW generation
  - 2 retentate expansions
- **Energy integration** between membrane / liquefier through heat exchange
  - Retentate expansion provides cooling for liquefier
  - Liquid CO_2 pumped to sequestration pressure



Hybrid Membrane + CPU Configuration



Commercial bundle performance at cold temperature is the major unknown in the process

Energy recovery process and equipment is commonly used in cryogenic air separation facilities

Detailed Project Objectives

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
4. Evaluate effect of expected contaminant levels (SO_x, NO_x) on membrane performance (lab tests)
5. Refine process simulation for integrated process; recalculate LCOE
6. Based on LCOE results, prepare PFD for potential field test

Project Main Tasks and Timeline

Task / Subtask	Task description	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
		Project Start: 10-1-2010 End 9-30-2012							
		Project Year 1				Project Year 2			
1	Kickoff meeting								
	PHASE 1: Experimental work								
2	**Demonstrate commercial scale bundle operation at sub-ambient temperature**								
2.1	Fabricate closed loop sub-ambient CO2/N2 test system			M 1					
2.2	Test mechanical integrity of bundle/housing					M 3			
2.3	Map bundle performance								
2.4	Long term test at cold temperature								
3	**Laboratory Scale Flue Gas Contaminant Testing**								
3.1	Modify lab cryo-test bench for low temperature SOx and NOx testing								
3.2	Measure SOx and NOx membrane performance on mini-permeator				M 2				
	PHASE 2: Design work								
4	**Sub-ambient Membrane/Cryogenic System Design**								
4.1	Use Phase I data to estimate LCOE increase for CO2 capture.								
4.2	With DOE input, develop PFD for slip-stream demonstration								M 4
	In progress								
	Finished								
	Projected								

Task 2 : Demonstrate commercial scale bundle operation at sub-ambient temperature

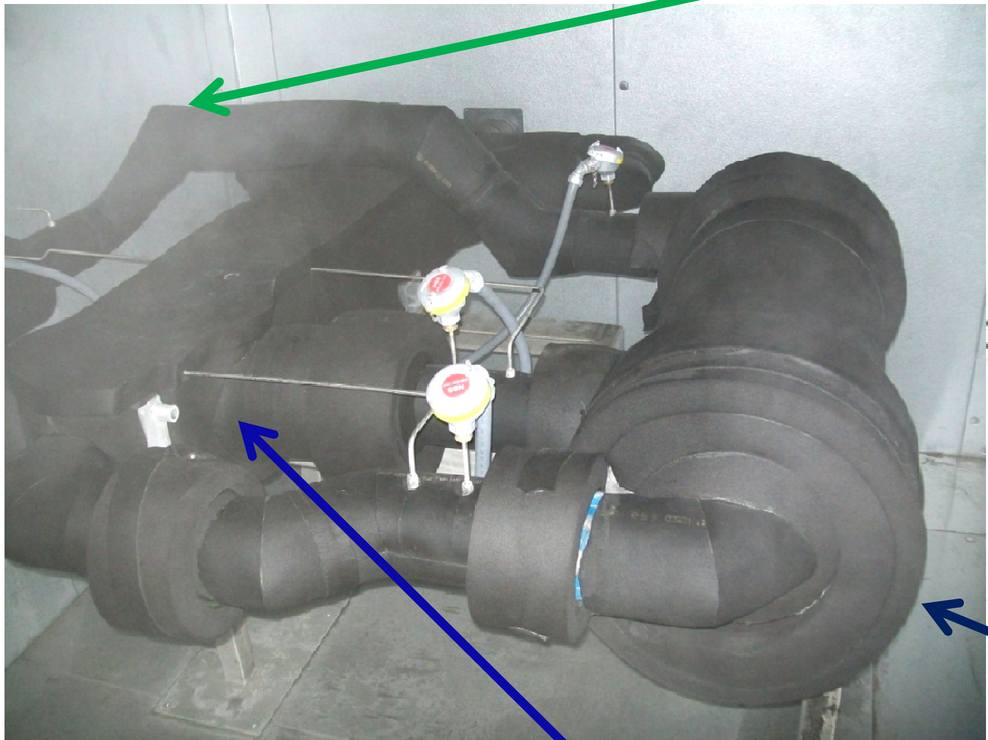
Task 3 : Laboratory Scale Flue Gas Contaminant Testing

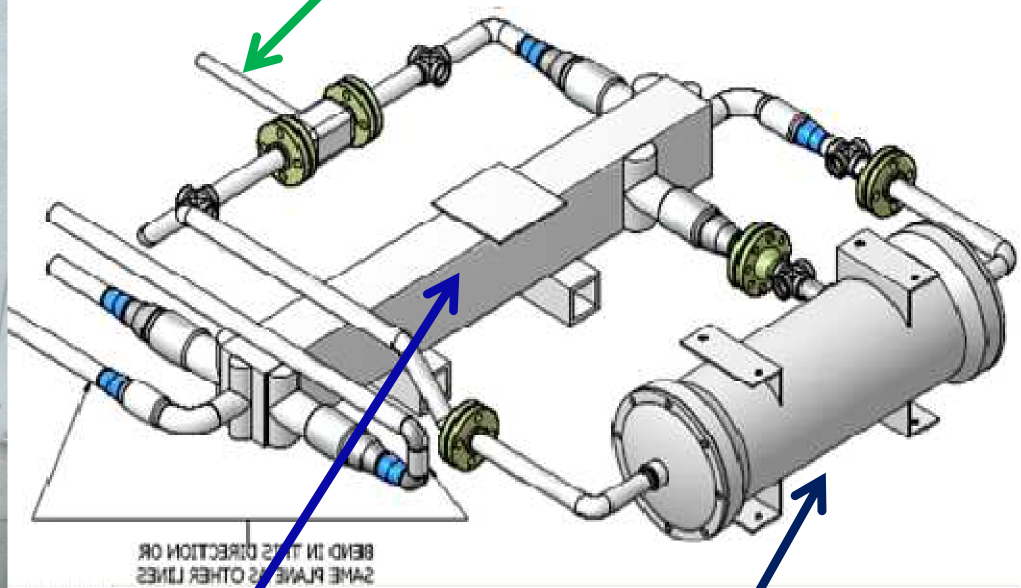
Task 4 : Sub-ambient Membrane/Cryogenic System Design

Task 2-M2.1: Skid in Operation for over a year

Cold Membrane Module and Heat Exchanger

Expansion Valve



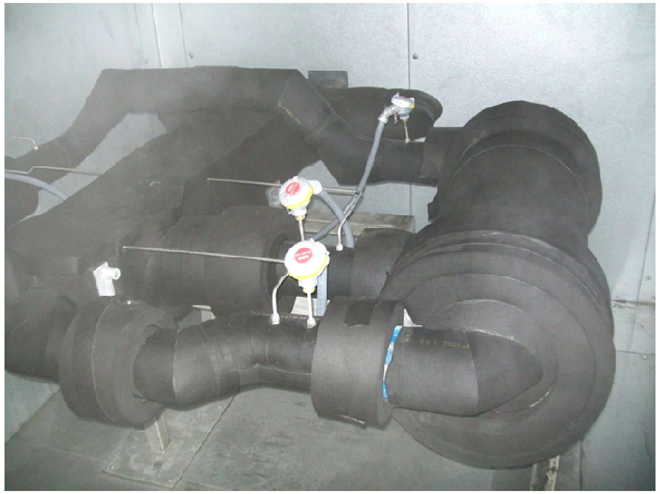


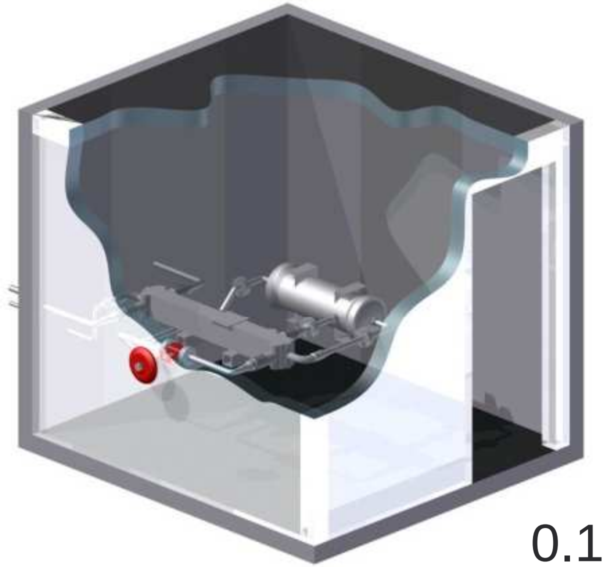
Heat Exchanger

Membrane Module

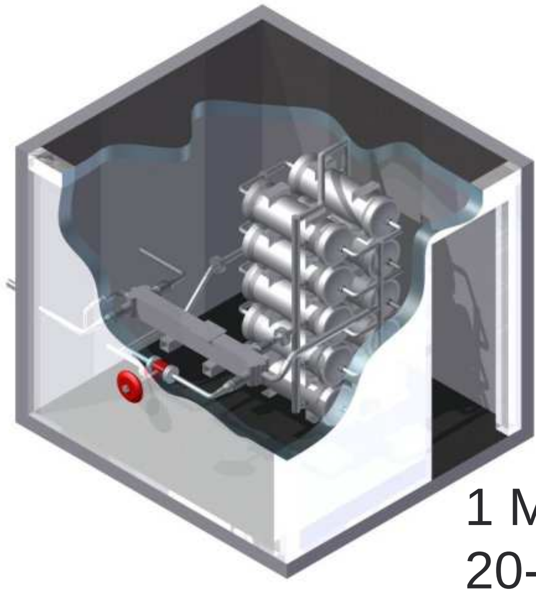
- Main cooling is provided by expansion of pressurized residue stream
- Housed in cold box to compensate for heat leaks

Large Cold Box…Commercial Freezer





0.1 MWe
2-2.5 TPD CO_2



1 MWe
20-25 TPD CO_2

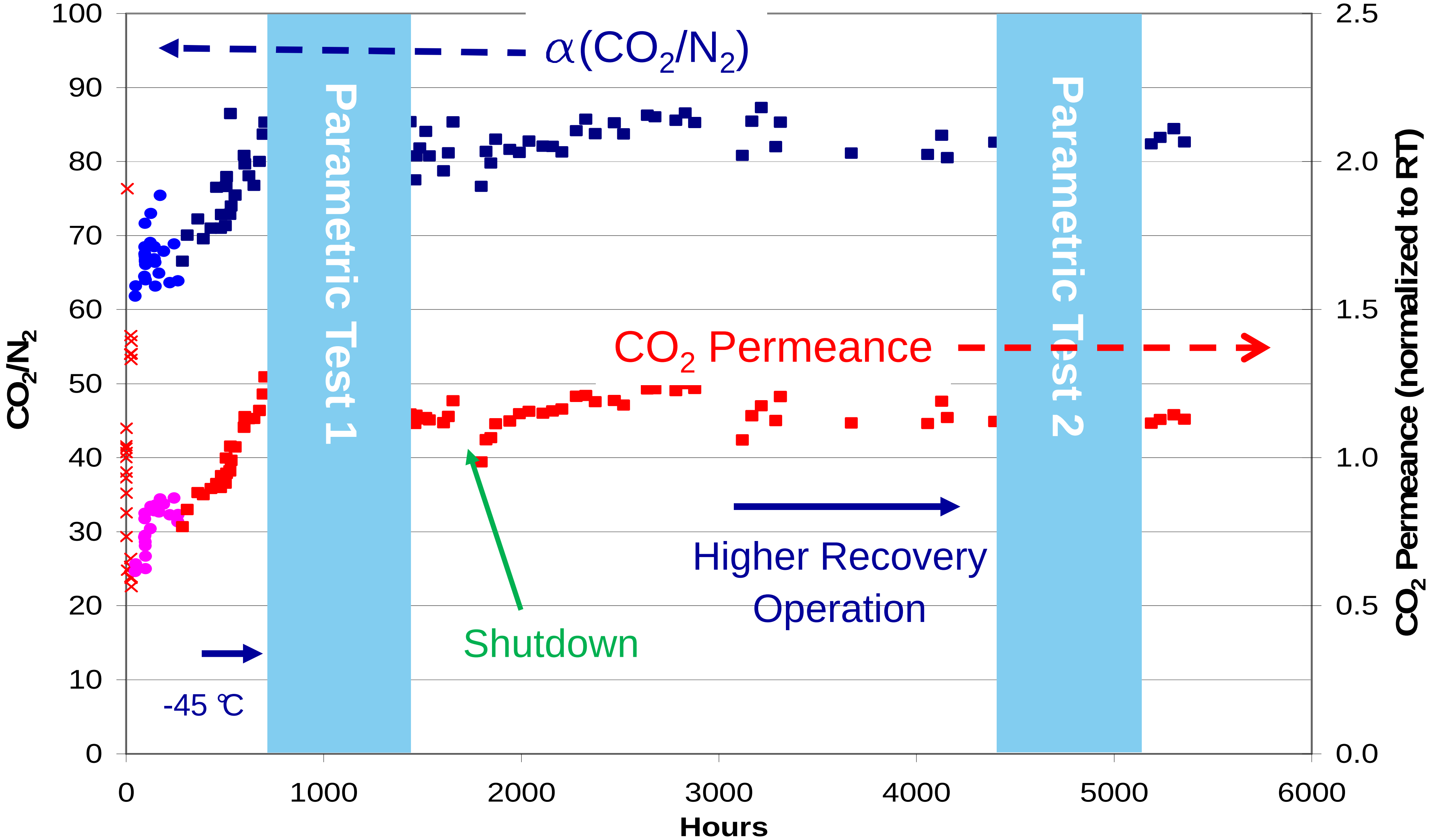
Cold box is oversized

- Lower cost than insulated cold box
- Provides easy access for modifications
- Provides additional space required for larger scale field test
- JT cooling provides sufficient cooling

Task 2-M2.2: Mechanical Integrity Test of 12" Bundle

- 12" bundle operated for 2 months
- Exposed to pressures up to 200 psig, temperatures as low as -60℃ and CO_2 concentrations from 15% to 30%
- Successfully completed multiple start-ups and shut-downs (Cool downs and warm-up) and a few ESD's
- No signs of mechanical degradation
  - Stable performance demonstrated -(1st week separation data similar to 6th week separation data)
  - Specified O-ring seals were intact
  - Designed compressed gas flow was insufficient to allow accurate back-calculation of membrane performance. 6" bundle used for all performance measurements.

Task 1-M2.3 &2.4: Endurance Testing with 6" Bundle



No evidence of productivity loss over 225 days

TASK 2: Summary of DOE Skid Test Findings

- **MEDAL membrane modules are compatible with sub-ambient service**
  - 12” bundle passed mechanical integrity test
  - 6” bundle performance stable over 6 months of operation

- **Commercial module (6” bundle) permeance higher and CO_2/N_2 selectivity was lower than obtained on laboratory permeators**
  - Performance change insufficient to change interest in the process
  - Favorable trade-off between capital and operating cost

    7% increase in specific energy of capture

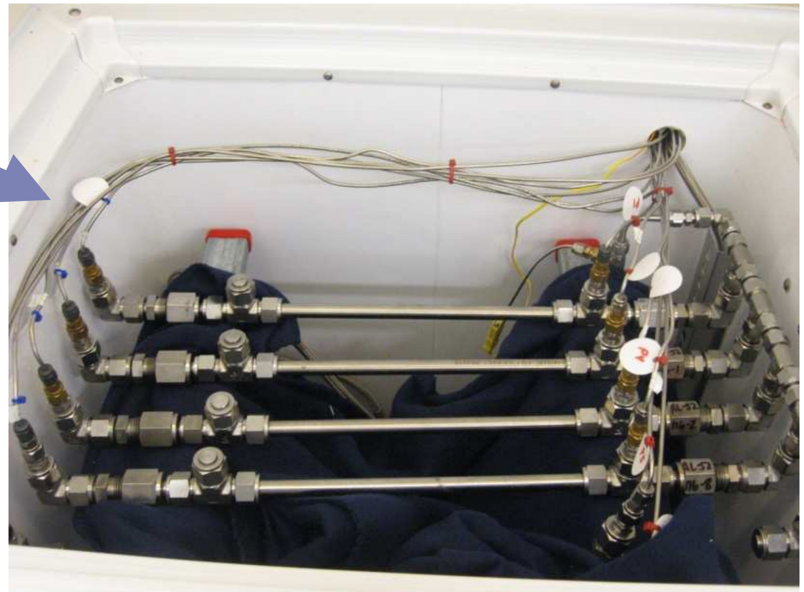
    40% decrease in membrane surface area

  - **Testing must be extended to determine module lifetime**

Task 3 M3.1: Laboratory Testing for Acid Gas Separation

How do acid gases split in cold membrane process?

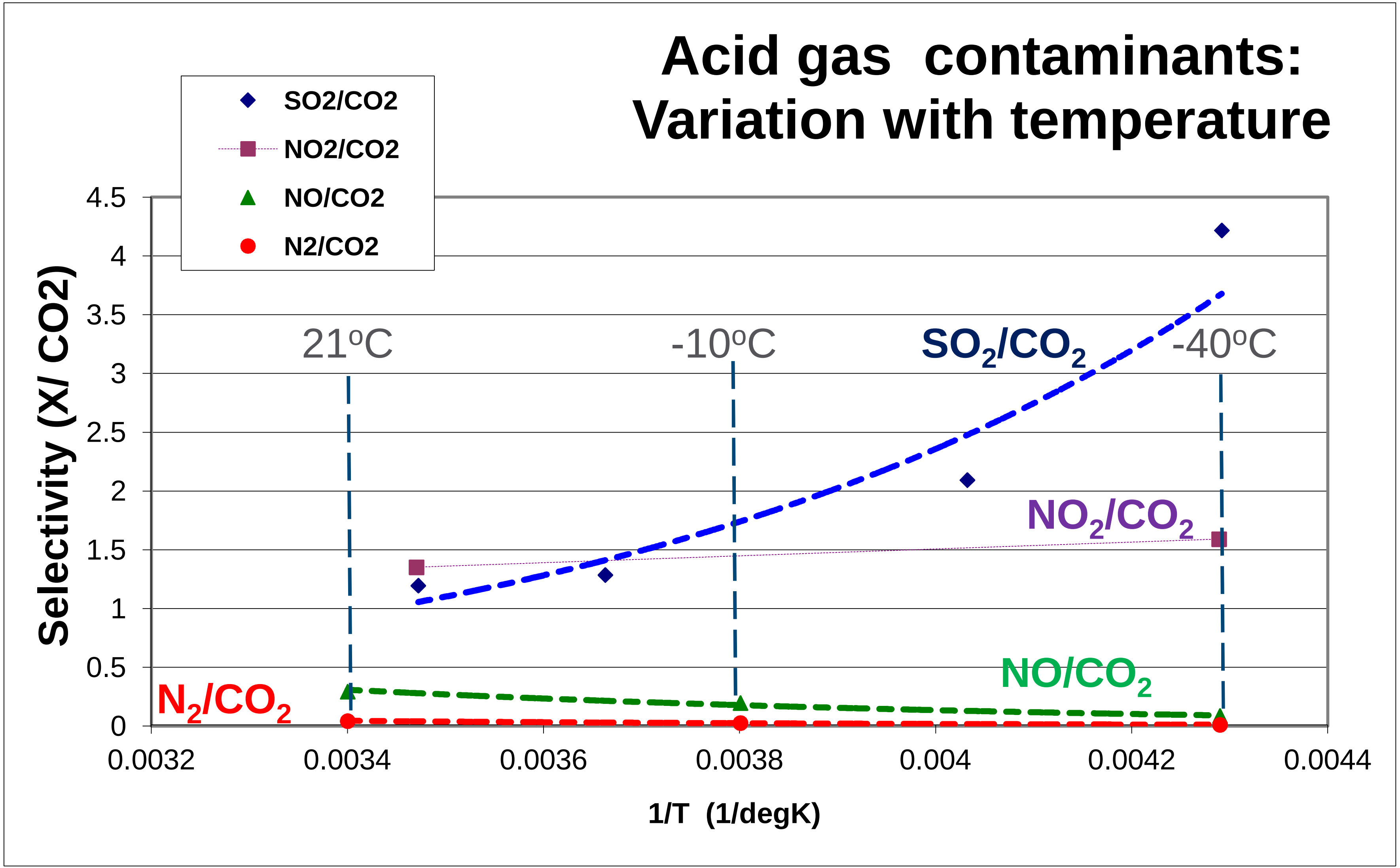
- Existing low temperature laboratory test system modified for acid gas testing
- Concentration analysis performed by GC / IR



20% CO_2 in N_2

100 ppm SO_2 or NO_2 or NO

TASK 3 M3.2 Summary: Permeance of Acid Gases



20% CO_2/N_2 mixtures with ~ 100 ppm each acid gas, 150 psi

Risk Factors Addressed by Project Testing

Risk Factor	Mitigation	Status
Uneven contraction of module components may cause performance degradation	MEDAL Technology support to change components if this problem is diagnosed	Mechanical integrity test passed (12" bundle)
Non-ideality in commercial module may degrade separation performance	Some slack in economics (selectivity > 90).	Fiber in bundle is more productive / less selective. Operate at -45C
Acid gas component effect	Lab measurements to demonstrate effect if any	SO_2, NO_2 and NO permeance verified at lab scale
Residual dust effect	If field experience indicates a problem, shell-side operation will be considered	TBD

Path Forward (Task 4)

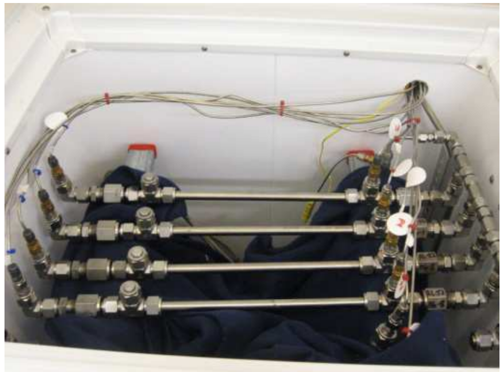
- **Experimentally validated commercial membrane performance is slightly lower selectivity and higher flux than assumed for original process cost calculation**
  - Favorable trade-off between capital and operating cost
    - ~ 7% increase in specific energy of capture
    - ~ 40% decrease in membrane surface area

- **Air Liquide Engineering finalizing budgetary capital cost estimation for conceptual 550MW facility based on vendor quotes and internal cost estimation tools as basis for LCOE recalculation**

Path Forward (Task 4)

- Project Objectives achieved on time and on budget
- Cost estimation details to be discussed with DOE / NETL for consensus on potential to meet DOE targets
- Positive consensus, PFD for potential field test will be developed (Task 4.2)

Development Roadmap



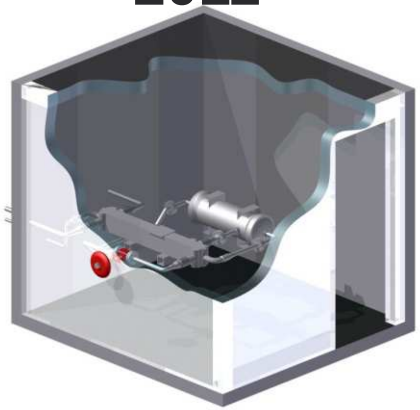
Lab scale

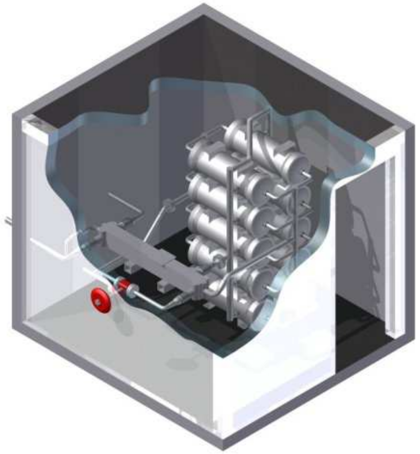
2008

Bench scale

0.1 MWe

2011





Field Test

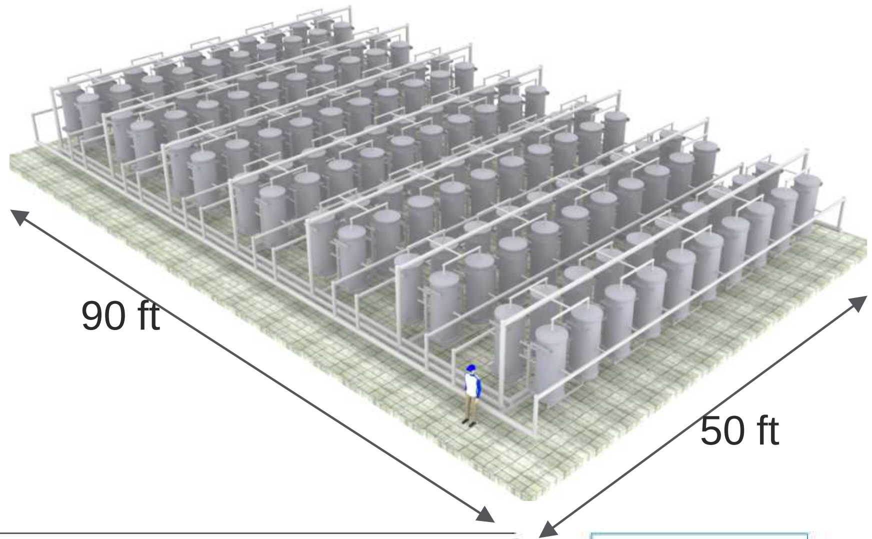
1.0 Mwe

2013-2014

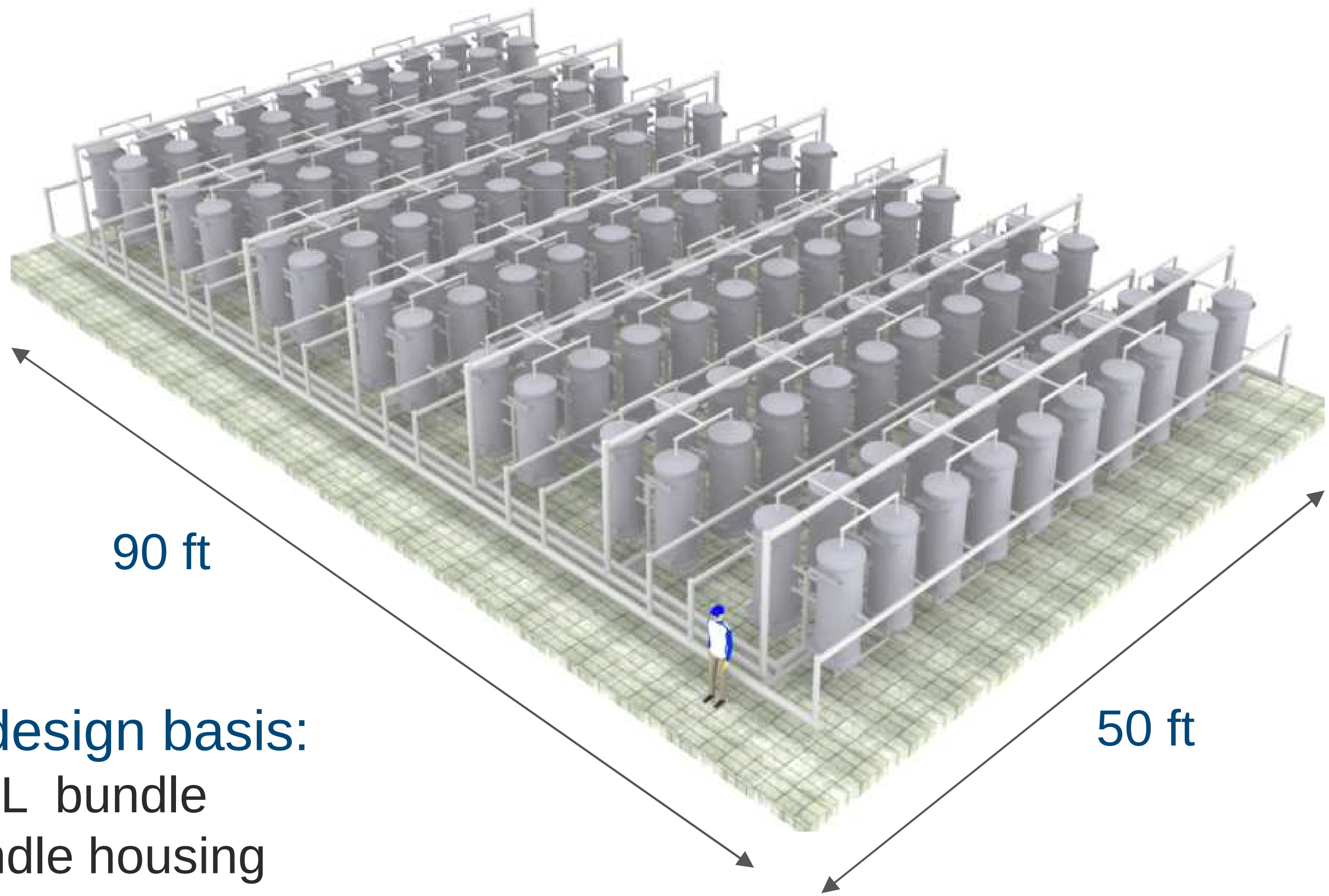
Full scale

550 MWe

2020-2030



Conceptual 550 MWe Membrane footprint



Conceptual design basis:

36" D x 40" L bundle

Duplex bundle housing

140 housings

Acknowledgements

DOE/NETL

- Andrew O'Palko – NETL Project Manager

Air Liquide

- Ryan Adelman, Engineering Support Group
- Facilities Team
- Dean Kratzer, Mike Bennett, and other members of the Separations Group
- Karl Beers, Bob Boyle and colleagues at MEDAL
- Vianney Meunier, Nicola Chambron, M Leclerc at Air Liquide Engineering

End of presentation
Thank you for your attention