the Energy to Lead

# Hybrid Membrane/Absorption Process for Post-combustion $CO_2$ Capture

## DOE Contract No. DE-FE-0004787

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NETL $CO_2$ Capture Technology Meeting

August 22, 2011

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# Introduction to GTI and PoroGen

- Not-for-profit research company, providing energy and natural gas solutions to the industry since 1940s
- Facilities
  - 18 acre campus near Chicago
  - 200,000 ft$^2$, 28 specialized labs

PoroGen
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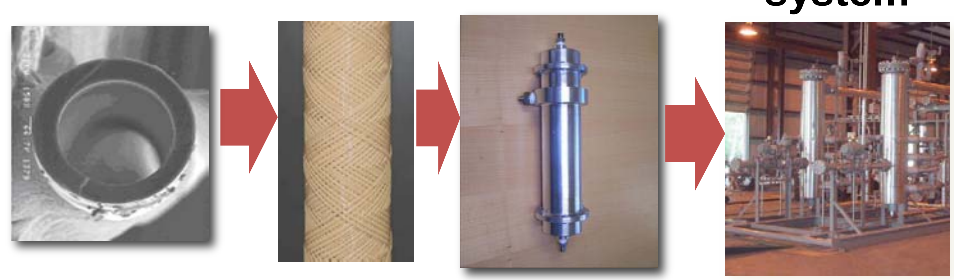
- Materials technology company commercially manufacturing products from high performance plastic PEEK (poly (ether ether ketone))
- Products ranging from membrane separation filters to heat transfer devices


**PEEK Fiber + Cartridge + Module = Separation system**



# Project overview

- **Funding**: \$3,736 K (DOE: \$2,986 K, Cost share: \$750 K)
  - Phase I budget: DOE: \$799 K, Cost share: \$200 K (20%)
  - Phase I spending by 7/31/2011: DOE: \$706 K (88.3%), Cost share: \$167 K (19.2%)
- **Performance period**: Oct. 1, 2010 – Sept. 30, 2013
- **Project objective**: to develop a cost effective separation technology for $CO_2$ capture from flue gases based on a PEEK hollow fiber membrane contactor technology
- **Project participants:**
  - GTI
  - PoroGen
  - Aker Process Systems
  - Midwest Generation

# Phase I (absorption) progress and status

Performance period: 10/1/10-9/30/11

- **Project performance**
  - Tasks 1-3: 100% complete; Task 4: 80%; Task 5: 80%, Task 6: 90%
  - Milestones 1-6 achieved; 7 is the Phase I report due by 10/30/11
- **Technical target achieved**

| Parameters | Target | Achieved value |
|---|---|---|
| Membrane intrinsic $CO_2$ permeance, GPU | ≥ 1,000 | >2,000 |
| $CO_2$ removal in one stage | ≥ 90% | ≥ 90% |
| Gas side pressure drop, psi | ≤ 2 | 1.6 |
| Mass transfer coefficient,$(sec)^{-1}$ | ≥ 1 | 1.7 |

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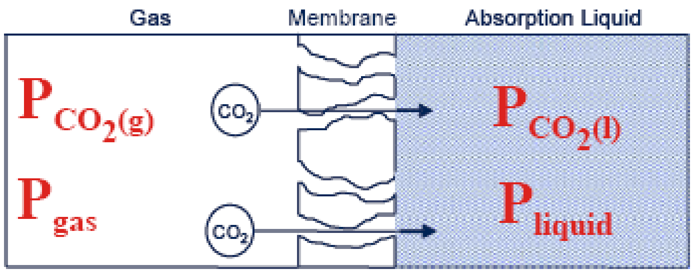
*1 GPU = 1 x $10^6$ $cm^3$ (STP)/$cm^2$ • s • cmHg

# What is a membrane contactor?

- High surface area membrane device that facilitates mass transfer
- Gas on one side, liquid on other side
- Membrane does not wet out in contact with liquid



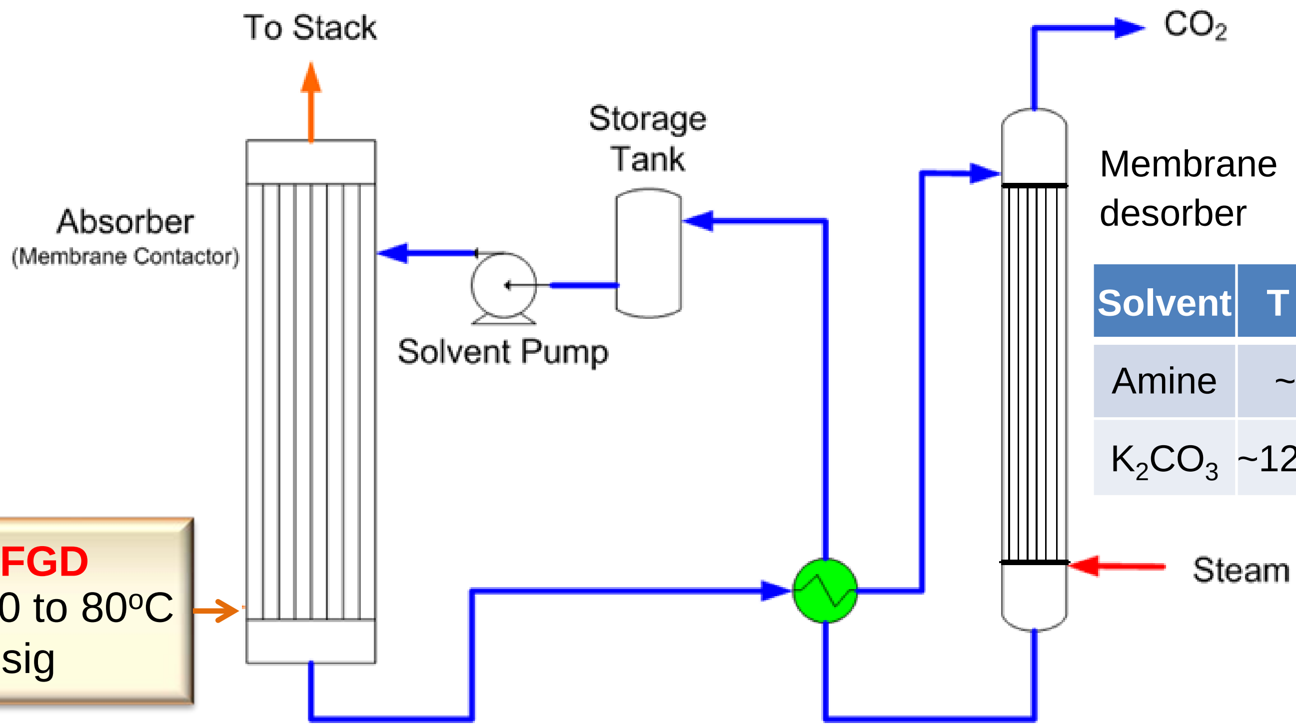

- **<u>Separation mechanism</u>**: $CO_2$ permeates through membrane and reacts with the solvent; $N_2$ does not react and has low solubility in solvent
- **<u>Comparison to conventional membrane process</u>**

| Membrane technology | Need to create driving force? | Can achieve >90% $CO_2$ removal and high $CO_2$ purity in one stage? |
|---|---|---|
| Conventional membrane process | Yes. Feed compression or permeate vacuum required | No. Limited by pressure ratio, multi-step process required* |
| Membrane contactor | No. liquid side partial pressure of $CO_2$ close to zero | Yes. |



* DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update, May 2011

# Process description

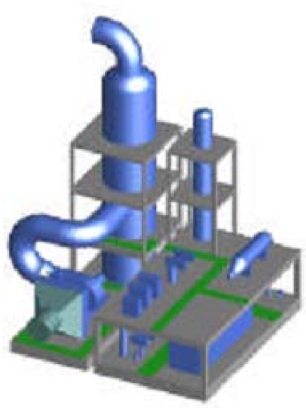



| Solvent | T (ºC) | P (psig) |
|---|---|---|
| Amine | ~120 | 1-10+ |
| $K_2CO_3$ | ~120-150 | 1-20+ |

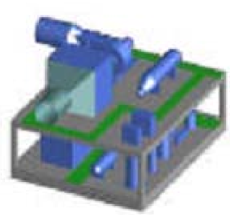
**Flue gas after FGD**
Temperature: 40 to 80ºC
Pressure: 1-4 psig

# Membrane contactor has technical and economic advantages over conventional absorbers

| Gas-liquid contactor | Specific surface area, ($cm^2/cm^3$) | Volumetric mass transfer coefficient, $(sec)^{-1}$ |
|---|---|---|
| **Packed column (Countercurrent)** | 0.1 – 3.5 | 0.0004 – 0.07 |
| **Bubble column (Agitated)** | 1 – 20 | 0.003 – 0.04 |
| **Spray column** | 0.1 – 4 | 0.0007 – 0.075 |
| **Membrane contactor** | **1 – 70** | **0.3 – 4.0** |



Conventional Amine Scrubber Column



Membrane Contactor

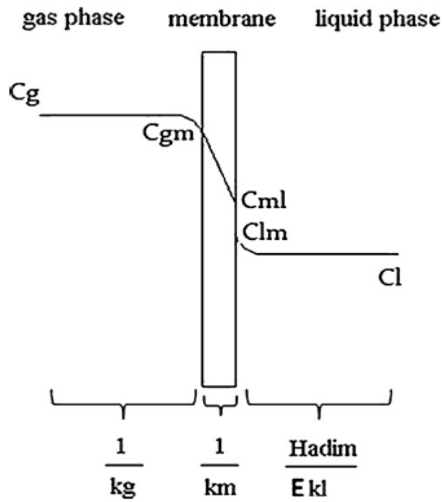
**Membrane contactor savings:**

- Capital cost: 35%
- Operating cost: 40%
- Total operating weight: 47%
- Footprint requirement: 40%
- Height requirement: 60%

*Data by Aker Process Systems*

# Technical and economic challenges of applying membrane contactor to existing PC plants

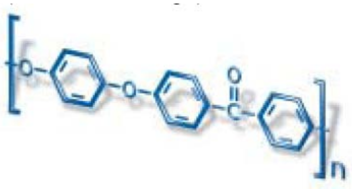
- Performance – overall mass transfer resistance consists of three parts
  - Minimize each resistance
- Durability – Long-term membrane wetting in contact with solvent can affect performance
  - Improve membrane hydrophobicity
- Contactor scale-up and cost reduction
  - Make larger diameter membrane module and reduce membrane module cost
- Particulate matter
  - Determine its impact on membrane lifetime in Phase III



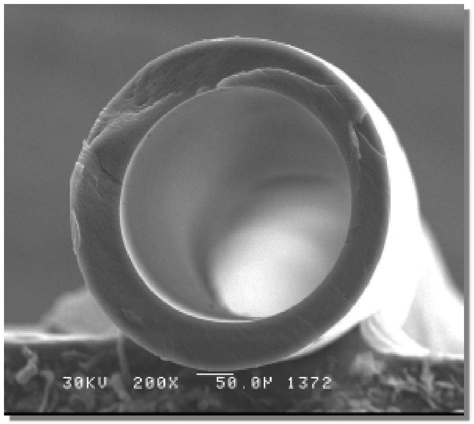

$$\frac{1}{K} = \frac{1}{k_g} + \frac{1}{k_m} + \frac{H_{adim}}{E \cdot k_l}$$

- Overall mass transfer coefficient K (cm/s)
  - In the gas phase, $k_g$
  - In the membrane, $k_m$
  - In the liquid phase, $k_l$
- $H_{adim}$: non-dimensional Henry's constant
- *E:* enhancement factor due to reaction

# PEEK membrane can meet challenges



- Exceptional thermal, mechanical & chemical resistance
- Hollow fiber with high bulk porosity (50-80%), asymmetric pore size: 1 to 50 nm, and thus high gas flux
  - Helium permeance as high as 19,000 GPU
- Super-hydrophobic, non wetting, ensures independent gas & liquid flow under flue gas conditions
- Structured hollow fiber membrane module design with high surface area for improved mass transfer



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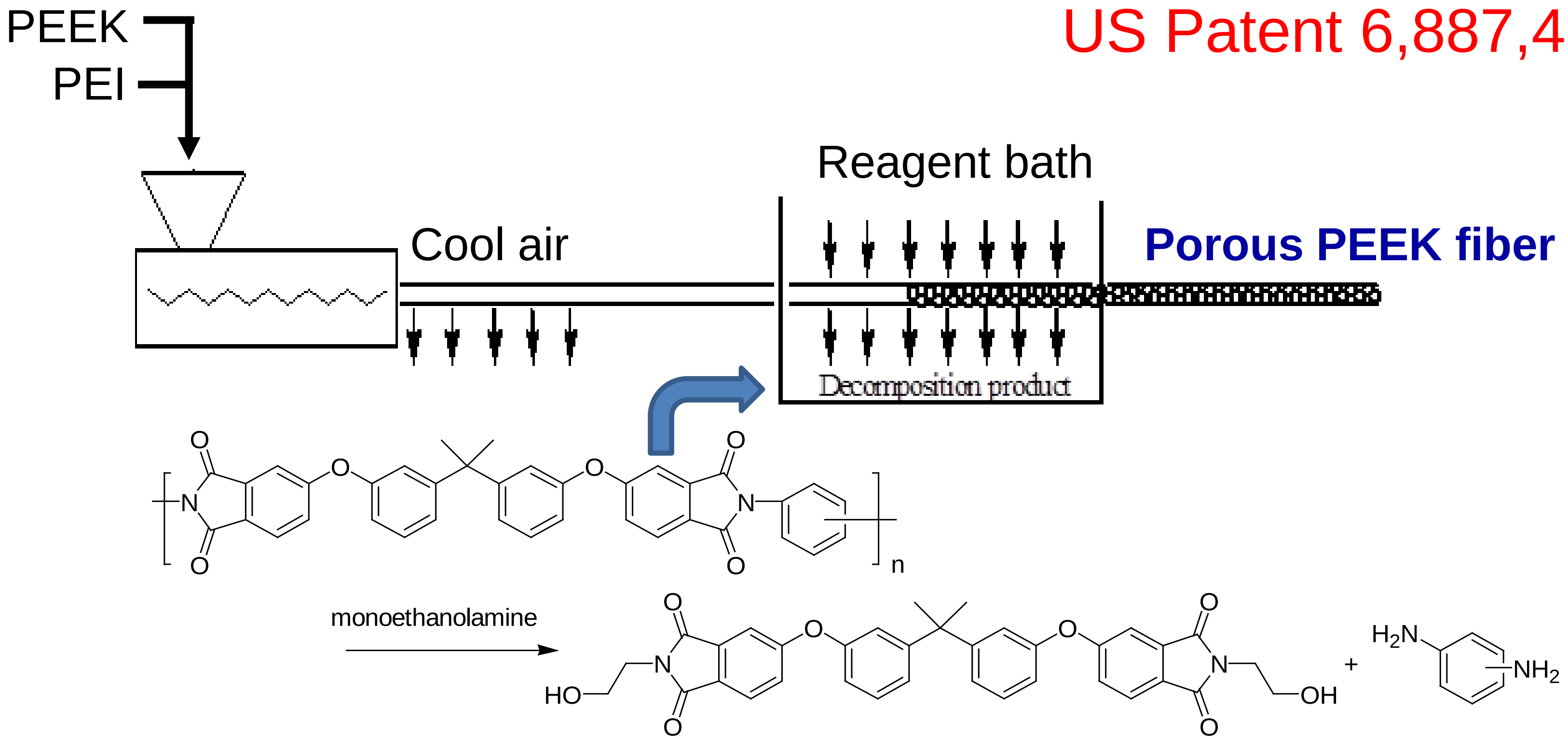
*1 GPU = 1 x $10^6$ $cm^3$ (STP)/$cm^2$ • s • cmHg

# PoroGen has a patented process for preparation of nano-porous PEEK hollow fiber membrane

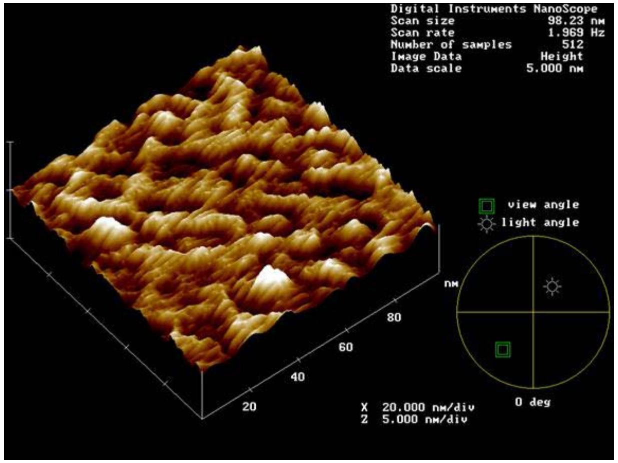
US Patent 6,887,408



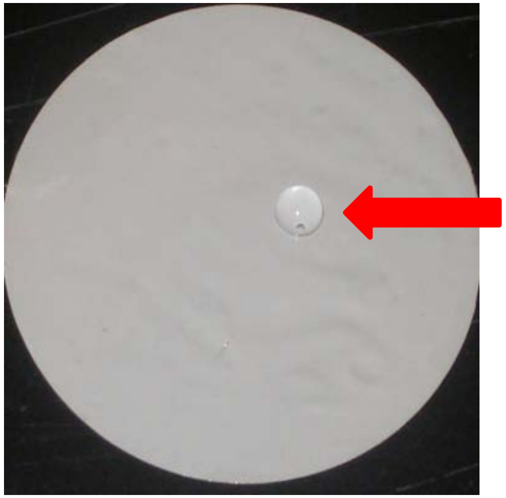

Hollow fiber morphology, and pore size have been optimized to meet membrane contactor operating requirements

# Two types of super-hydrophobic membranes under development

**a)** Nano-porous PEEK hollow fiber membrane



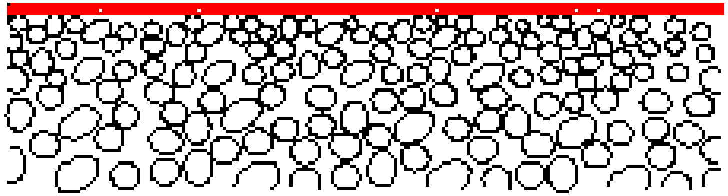

Super-hydrophobic surface not wetted by alcohol



Alcohol droplet

**b)** Composite PEEK hollow fiber membrane

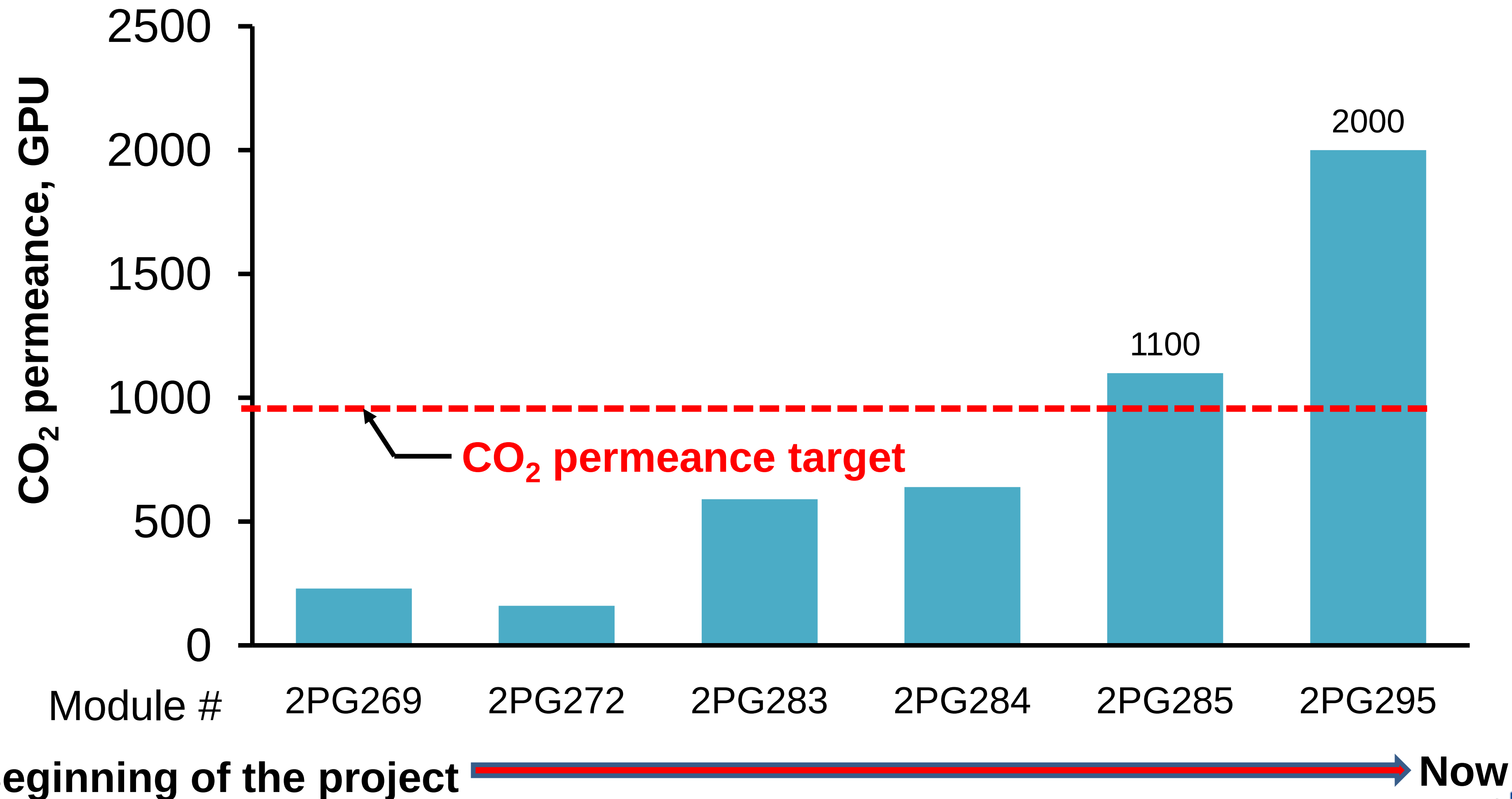
**Thin layer (0.1 μm) of smaller surface pores**



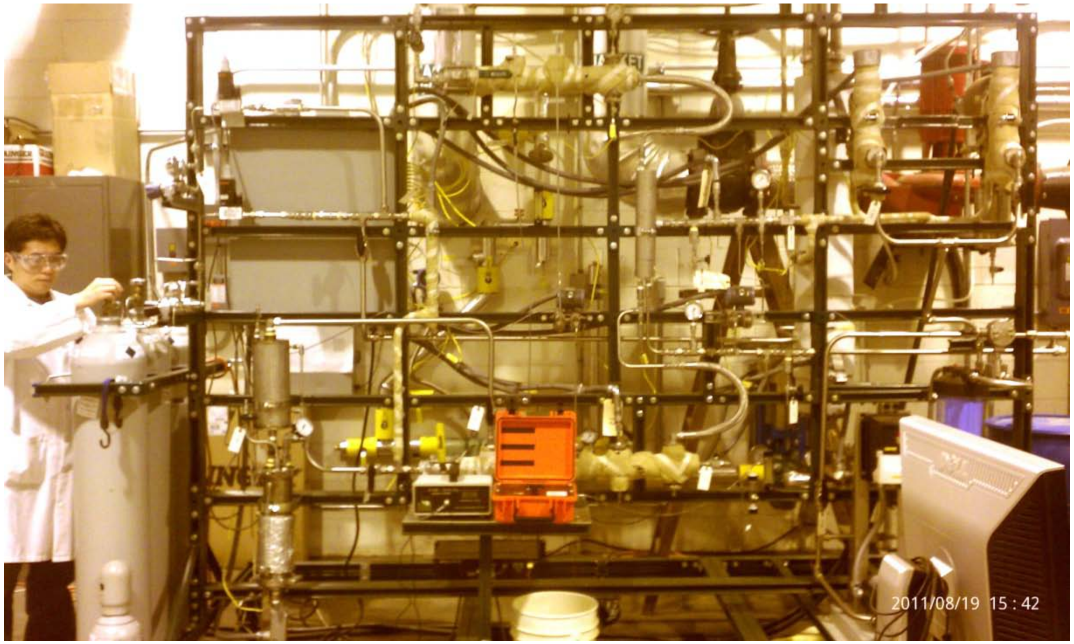
**Asymmetric porous structure**

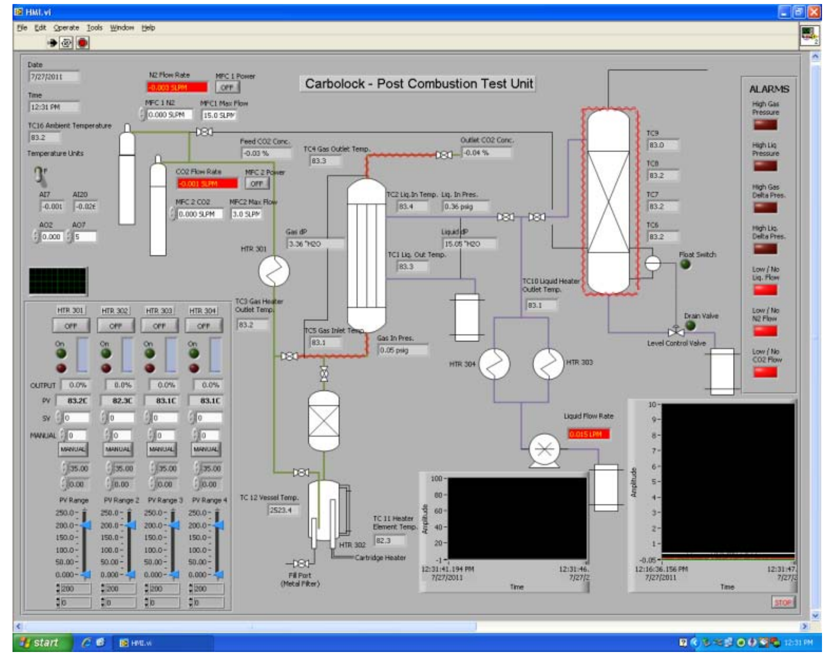
# Membrane intrinsic $CO_2$ permeance exceeded initial target commercial performance

More than 30 modules constructed by PoroGen



# Post-combustion $CO_2$ capture gas/liquid membrane contactor skid constructed




- Designed for 25 KW equivalents of $CO_2$ capture (0.5 ton/day)
- Phase I: absorption testing, Phase II: regeneration testing, Phase III: Integrate absorption and regeneration, ship to Midwest Generation for field testing

# Bench-scale membrane contactor $CO_2$ capture performance demonstration

- **<u>Feed</u>**: use of temperature and pressure conditions after FGD, and simulated flue gas compositions (saturated $H_2O$, SOx, NOx, $O_2$)
- **<u>Membrane module</u>**: tested performance can be linearly scaled to commercial size modules
- **<u>Solvents</u>**: commercial aMDEA (40 wt%) and activated $K_2CO_3$ (20% wt%), test of advanced solvents planned
- **<u>Use of design of experiment test matrix</u>**: totally **over 140 tests**,  gas flow rate: 1-10 L/min,  liquid flow rate: 0.1-1 L/min

Module for lab testing (Ø2” x 15” long, $1m^2$)

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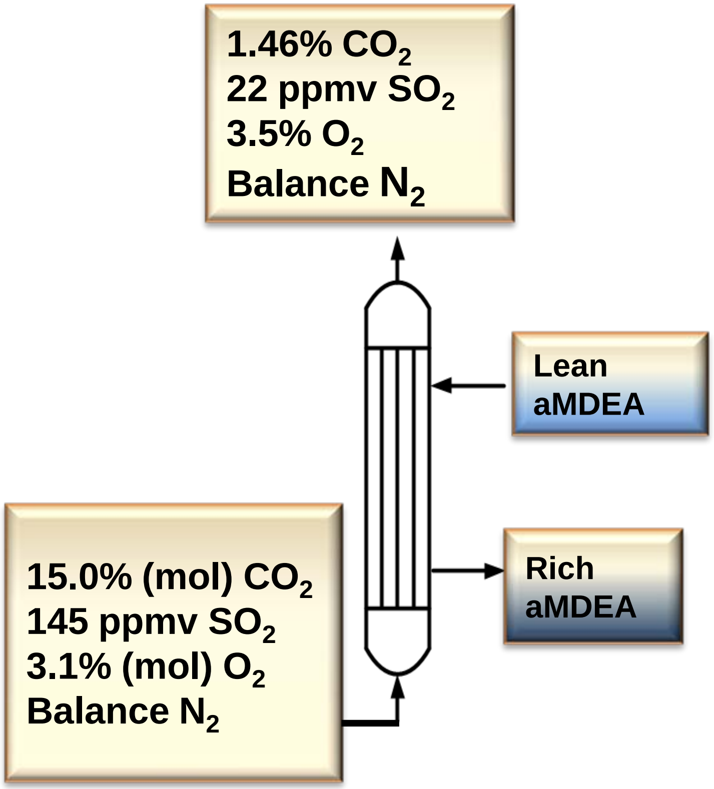
# Phase I technical goal achieved with commercial aMDEA and $K_2CO_3/H_2O$

| Parameters | Goal | aMDEA | $K_2CO_3$ |
|---|---|---|---|
| $CO_2$ removal in one stage | ≥ 90% | 90% | 94% |
| Gas side ΔP, psi | ≤ 2 | 1.6 | 1.3 |
| Mass transfer coefficient,(sec)$^{-1}$ | ≥ 1 | 1.7 | 1.8 |

# $CO_2$ removal rate is not affected by $O_2$ and $SO_x$ contaminants in feed

Module 2PG286

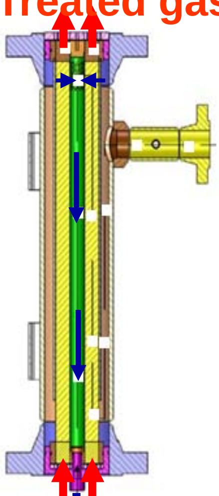



- **Measured results**:

| | |
|---|---|
| $CO_2$ removal | 91% |
| Mass transfer coefficient,(sec)$^{-1}$ | 1.6 |
| Gas side ΔP, psi | 1.6 |
| $CO_2$ capture rate, kg/h/m$^2$ | 0.5 |

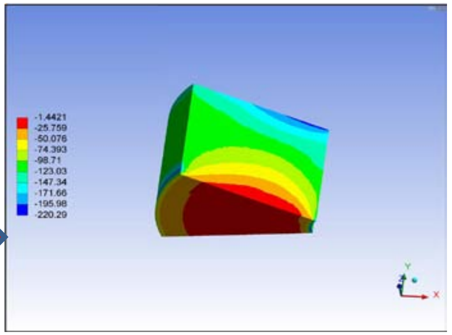
- **Compared to conventional amine scrubber**
  - 15% less of the inlet $SO_2$ was absorbed by the solvent. The formation of heat-stable salts will be reduced

# Membrane module design and scale-up



8 inch design model

- Design of commercial size, flue gas $CO_2$ capture module completed
- Design validated through CFD modeling
- Scaling up from 1 $m^2$ to 100 $m^2$ (8-inch commercial module)
- Production of 8" diameter module on commercial equipment established



Tubesheet CFD stress analysis

Cartridge tubesheet for Ø8" x 60" long module

Equipment to produce 8-inch modules

# Economic evaluation bases

- Membrane cost for commercial size 8-inch modules ($80/m²)
- 90% $CO_2$ removal, $CO_2$ removal at a flux of 0.4 $kg/m^2/h$ (equivalent mass transfer coefficient of 1.7 $s^{-1}$)
- $K_2CO_3$/water solvent
- Contactor used for absorption only, use of packed column for regeneration
- DOE/NETL-2007/1281“Cost and Performance Baseline for Fossil Energy Plants”

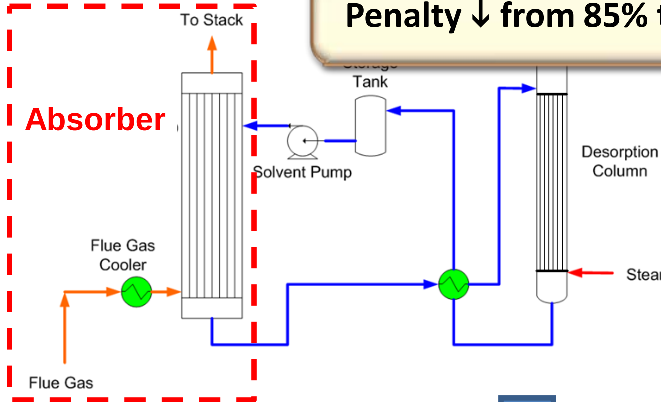
# Cost of electricity (COE) and increase in COE

| Case | COE, mills/kWhr | Increase in COE |
|---|---|---|
| DOE Case 9 no capture | 64.00 | -- |
| DOE Case 10 state of the art (amine plant) | 118.36 | 85% |
| Phase I status: membrane absorber | **98.93** | **55%** |
| **Sensitivity study** | | |
| Module cost ↓ from \$80 to \$30/$m^2$ | 95.64 | 49% |
| $CO_2$ removal rate ↑ from 0.4 to 1.2 kg/$m^2$/h | 92.24 | 44% |
| \$30/$m^2$ module cost + 1.2 kg/$m^2$/h $CO_2$ removal rate | 88.95 | 39% |
| Phase II regeneration improvements | On trajectory to meet DOE target | |
| DOE capture target | **86.40** | **35%** |

# Plans for future testing and development in this project

**2010**

**2011**

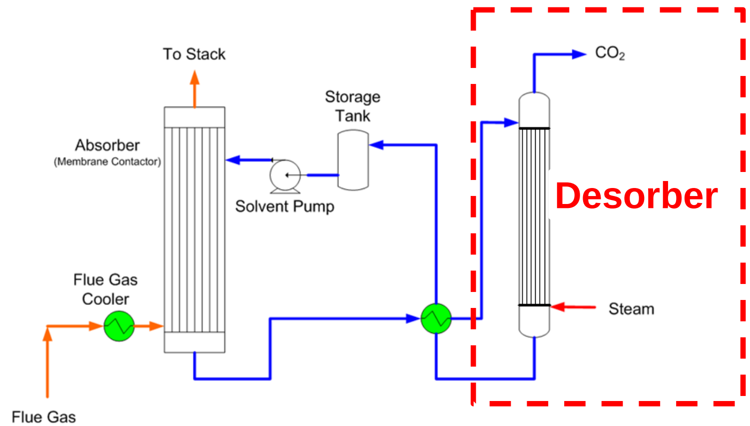



**Economic Evaluation: COE Penalty ↓ from 85% to 55%**

1) Test the membrane with intrinsic $CO_2$ permeance of 2000 GPU

2) Test a feed containing NOx

**2012**




3) Increase membrane thermal stability so that it can be used in regeneration

4) Membrane desorber testing

**2013**

**Approach DOE's target: ≥ 90% $CO_2$ capture, < 35% increase in COE**

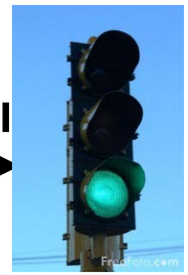

5) Integrate absorption and regeneration

6) Field testing for **25 KW** equivalents of $CO_2$ capture (**0.5 ton/day**)

# Scale-up and risk mitigation for commercialization

**Equipment needs to be scaled up**

**Membrane Absorber** → **Phase I**

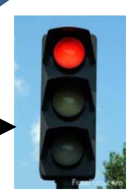


- Achieved phase I technical goal
- Membrane module has been scaled-up to **commercial size** (8-inch) at PoroGen. Larger scale modules will reduce cost further.
- **Commercial solvents** being used (advanced solvents possible)

Commercial 8-inch module

**Membrane desorber** → **Phase II** → **Work?**

- Cost will be further reduced to approach DOE target



- Risk management: **commercial regeneration tower** can be used. Need to further increase $CO_2$ flux to achieve cost savings target

# Technology implementation timeline after this project

| Time | Development | $CO_2$ capture, Ton/day | Module diameter | Projected # of modules* |
|---|---|---|---|---|
| **By 2013** | 25 KWe bench-scale (Current project, Phase III) | 0.5 | 8-inch | 1 (more than sufficient) |
| **By 2015** | 2.5 MWe pilot scale | 50 | 8-inch | 17 |
| | | | 16-inch | 5 |
| **By 2018** | 25 MWe demonstration | 500 | 8-inch | 170 |
| | | | 30-inch | 14 |

* Calculated based on:

- $CO_2$ flux of 1.2 kg/m$^2$/h
- Module area:
  - Current Ø8-inch module: 100 m$^2$
  - Projected Ø16-inch module: 400 m$^2$
  - Projected Ø30-inch module: 1400 m$^2$

PoroGen has equipment capacity to produce 8-inch modules for several 25MWe demonstration plants

# Summary

- Membrane absorbers technical goal achieved

| Parameters | Goal | Achieved value |
|---|---|---|
| Membrane intrinsic $CO_2$ permeance, GPU | ≥ 1,000 | >2,000 |
| $CO_2$ removal in one stage | ≥ 90% | ≥ 90% |
| Gas side pressure drop, psi | ≤ 2 | 1.6 |
| Mass transfer coefficient,$(sec)^{-1}$ | ≥ 1 | 1.7 |

- Feasibility of contactor module scale-up demonstrated
- Phase II is to apply membrane contactor in regeneration step
- Economic evaluation based on Phase I membrane absorber lab testing data indicates a 55% increase in COE

# Acknowledgements


- Financial support
  - DOE-NETL
  - ICCI (Illinois Clean Coal Institute)
  - Midwest Generation
- DOE NETL José Figueroa