the Energy to Lead

Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture

DOE Contract No. DE-FE-0004787

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July 10, 2013

PoroGen
INNOVATIVE MEMBRANE PRODUCTS

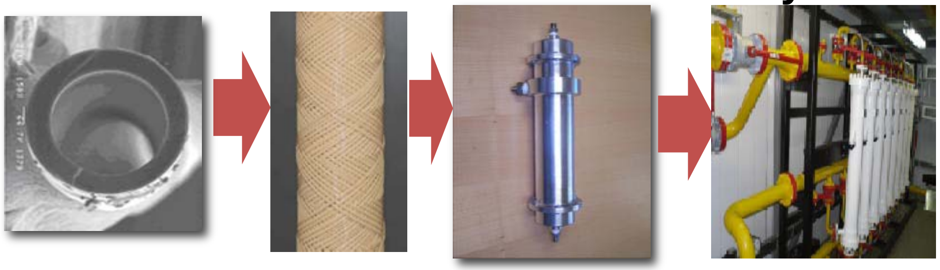
gti

Introduction to GTI and PoroGen

- Not-for-profit research company, providing energy and natural gas solutions to the industry since 1941
- Facilities
  - 18 acre campus near Chicago
  - 200,000 ft^2, 28 specialized labs

- 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

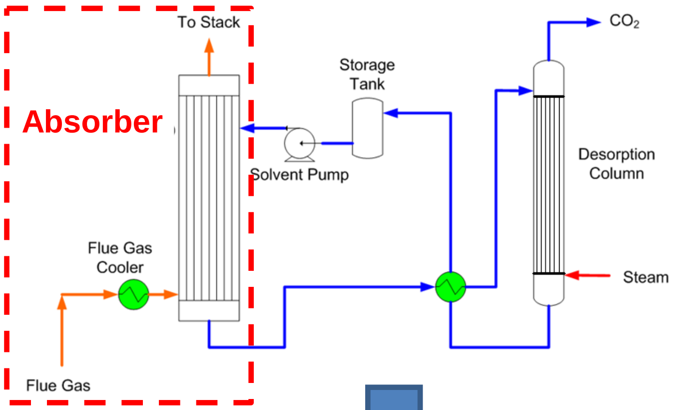
- **Funding**: $3,736 K (DOE: $2,986 K, Cost share: $750 K)
  - BP1 budget: DOE: $799 K, Cost share: $200 K (20%)
  - BP2 budget: DOE: $1,036 K, Cost share: $262 K (20%)
  - BP3 budget: DOE: $1,149 K, Cost share: $287 K (20%)
- **Performance period**: Oct. 1, 2010 – Dec. 31, 2013
- **Project participants:**
  - GTI: process design and testing
  - PoroGen: membrane and membrane module development
  - Midwest Generation: providing field test site

Objective and scope

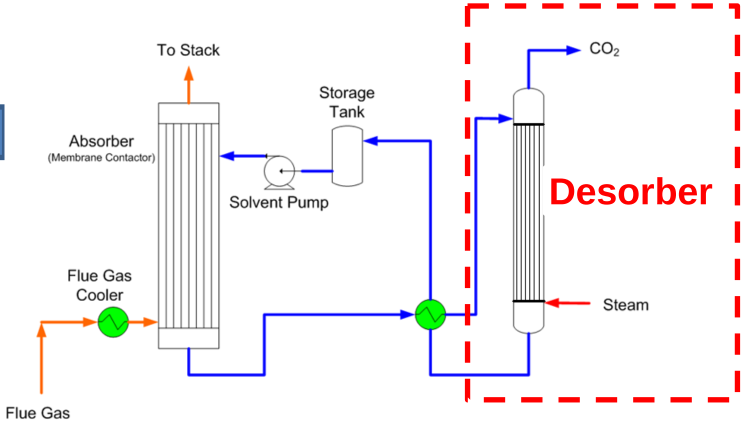
2010

Objective: develop PEEK membrane contactor technology to meet DOE's target of ≥ 90% CO_2 capture, < 35% increase in COE

BP1



BP2



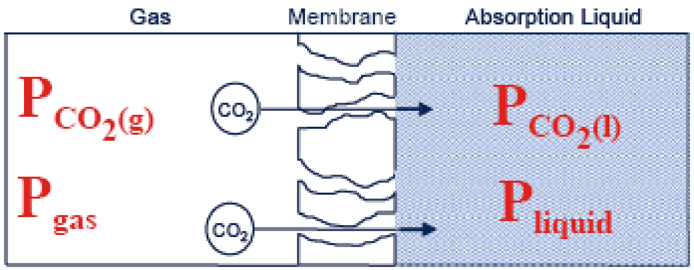
BP3

Integrate absorption/regeneration

Field testing

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

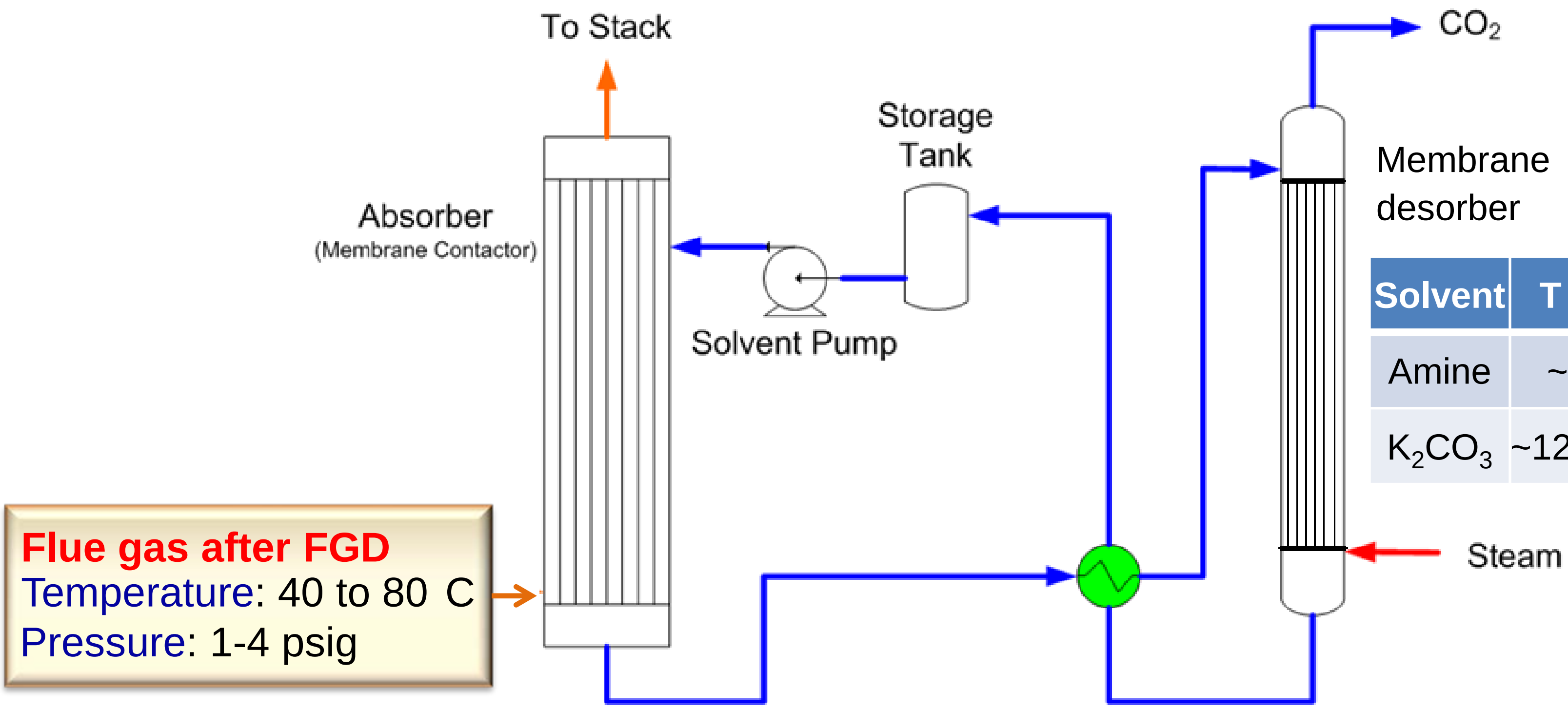


- **Separation mechanism**: CO_2 permeates through membrane and reacts with the solvent; N_2 does not react and has low solubility in solvent
- **Comparison to conventional membrane process**

Membrane technology	Need to create driving force?	CO_2/N_2 selectivity (α)	Can achieve >90% CO_2 removal and high CO_2 purity in one stage?
Conventional membrane process	Yes. Feed compression or permeate vacuum required	Determined by the dense "skin layer", typically $\alpha = 50$	No. Limited by pressure ratio, multi-step process required*
Membrane contactor	No. liquid side partial pressure of CO_2 close to zero	Determined by the solvent, $\alpha > 1000$	Yes

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

Process description

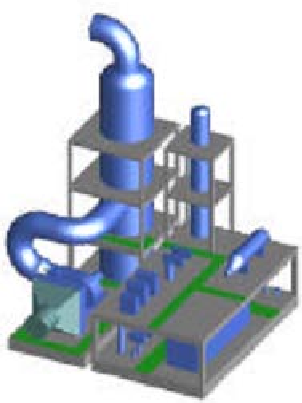


Solvent	T (ºC)	P (psig)
Amine	~120	1-10+
K_2CO_3	~120-150	1-20+

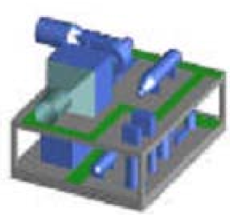
Process identical to DOE's benchmark technology amine plant except membrane absorber and desorber are used instead of absorption and regeneration towers

Membrane contactor has technical and economic advantages over conventional absorbers

Gas-liquid contactor	Specific surface area, (m^2/m^3)	Volumetric mass transfer coefficient, $(sec)^{-1}$
Packed column (Countercurrent)	100 – 350	0.0004 – 0.07
Bubble column (Agitated)	100 – 2,000	0.003 – 0.04
Spray column	10 – 400	0.0007 – 0.075
Membrane contactor	**1,000 – 7,000**	**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**

Olav Falk-Pedersen, Developments of gas/liquid contactors, Final report GRI contract 8325, December, 2002.

Technical and economic challenges and advantages of membrane contactor

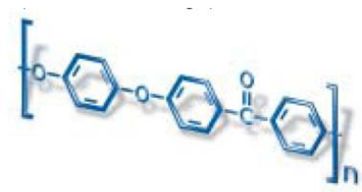
- Performance – Minimize overall mass transfer resistance
- Durability – Long-term membrane wetting in contact with solvent may affect performance
  - Improve membrane hydrophobicity
- Contactor scale-up and cost reduction
  - Make larger diameter module and reduce module cost

Advantages:

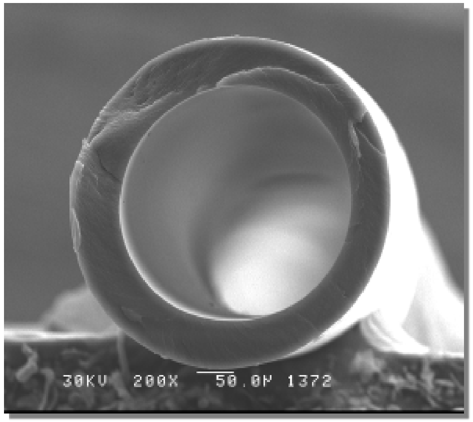
- Increased mass transfer reduces system size
- High specific surface area available for mass transfer
- Independent gas and liquid flow
- No flooding, solvent entrainment, and foaming

PEEK membrane can meet challenges

- Exceptional thermal, mechanical & chemical resistance



Polymer	Tensile modulus (GPA)	Tensile strength (MPa)	Max service temperature (ºC)
Teflon™	0.4-0.5	17-21	250
PVDF	0.8	48	150
Polysulfone	2.6	70	160
PEEK	**4**	**97**	**271**

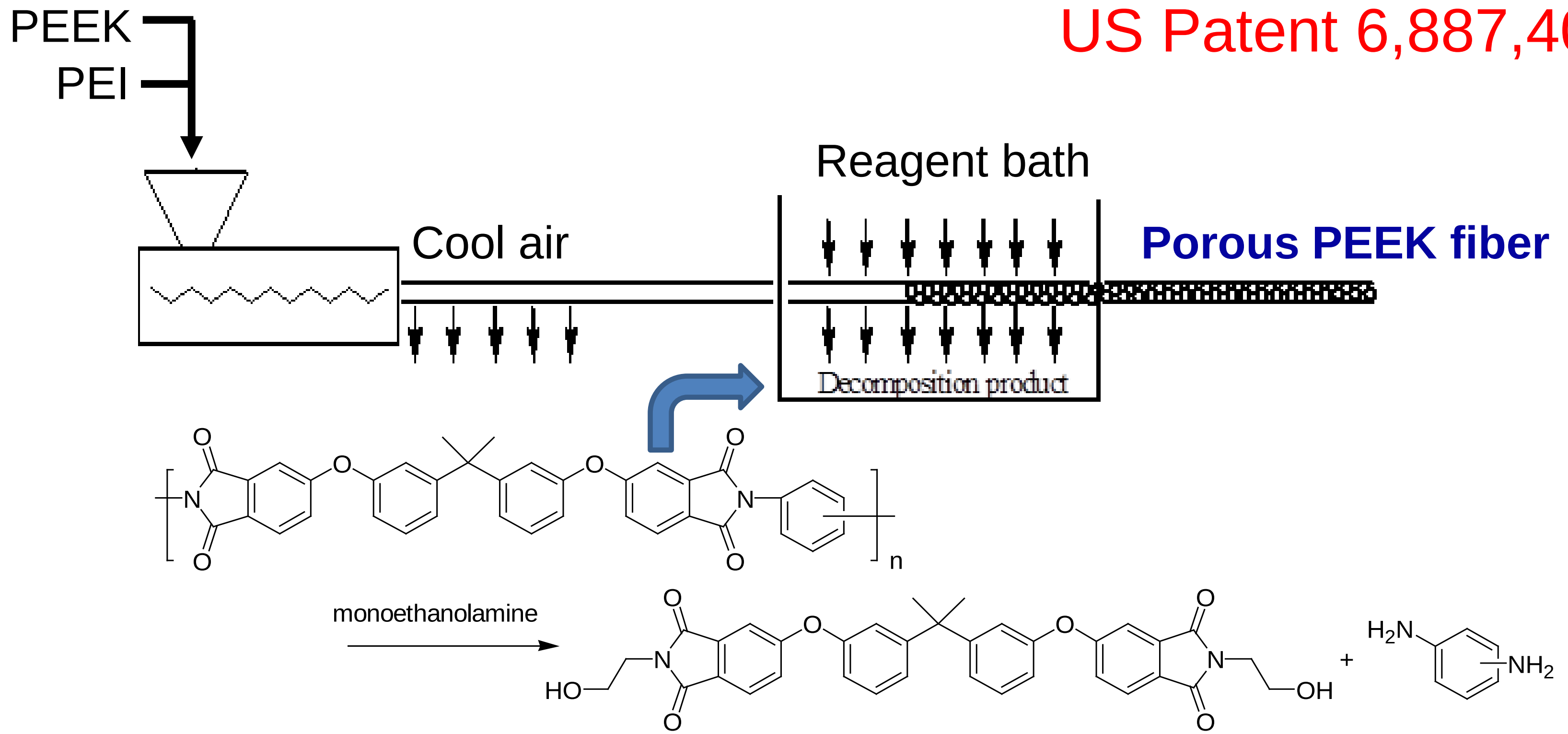


- Hollow fiber with high bulk porosity (50-80%), asymmetric pore size: 1 to 50 nm, and thus high gas flux
  - Helium permeance as high as 20,000 GPU*
- Super-hydrophobic, non wetting, ensures independent gas & liquid flow under flue gas conditions
- Structured hollow fiber membrane module design with high surface area for improved mass transfer

*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

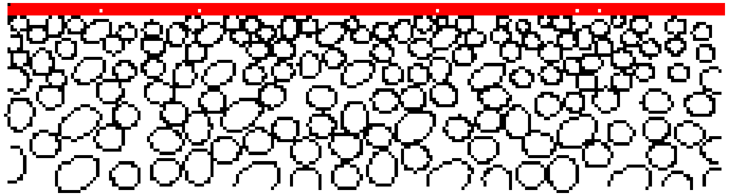


Hollow fiber morphology, and pore size are continuously improved to meet membrane contactor operating requirements

Super-hydrophobic membranes developed

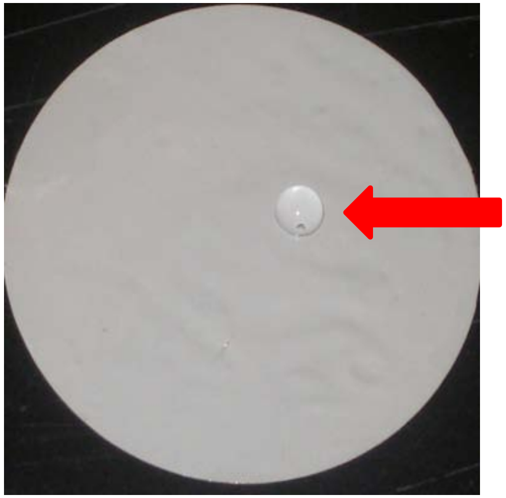
- Composite membrane

Thin layer (0.1 μm) of smaller surface pores



Asymmetric porous structure

- Super-hydrophobic surface not wetted by alcohol

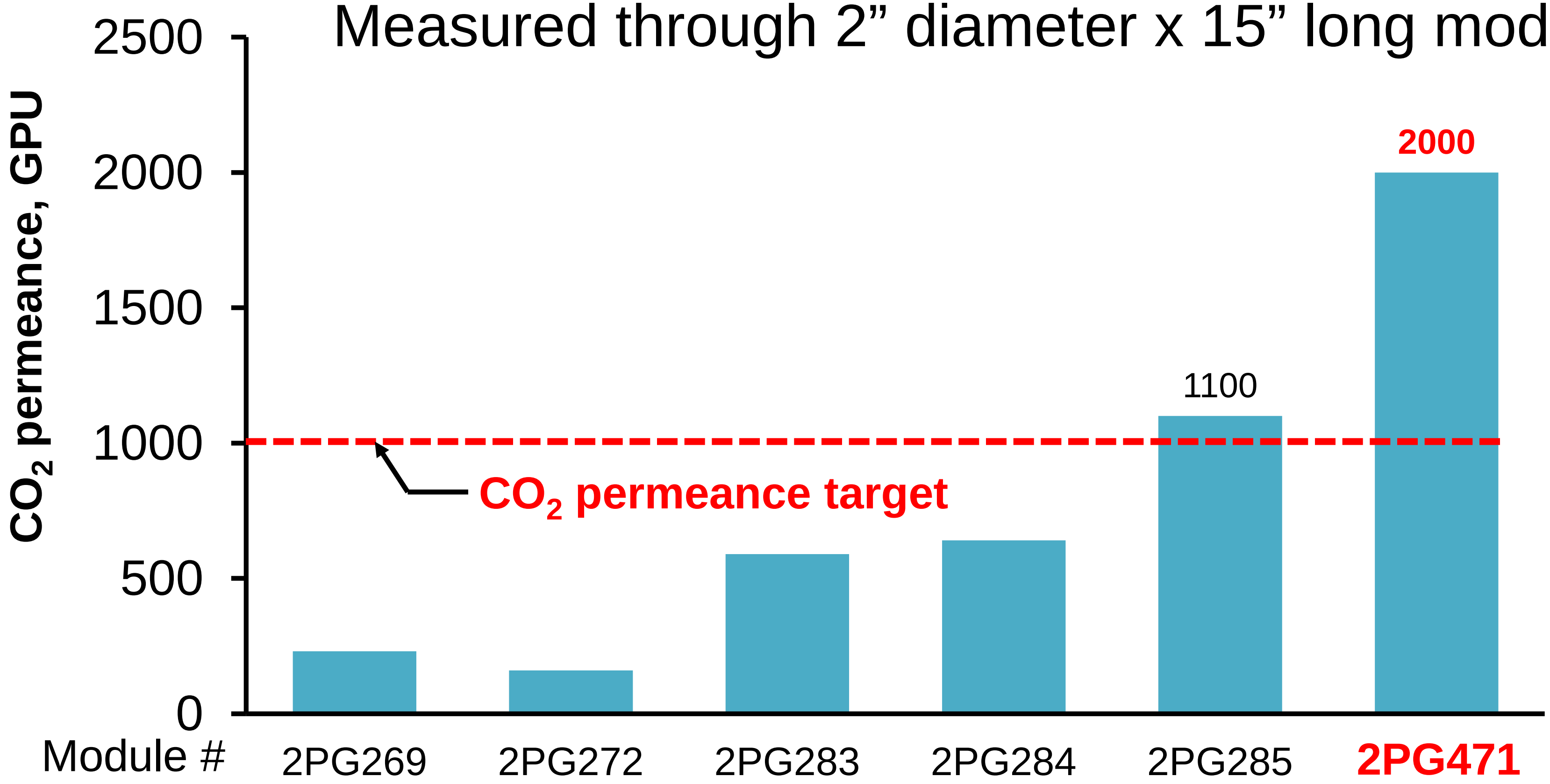


Alcohol droplet

Recent modules achieved 2,000 GPU membrane intrinsic CO_2 permeance

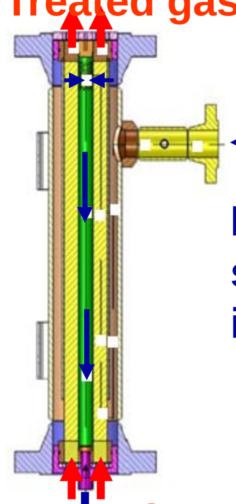
More than 200 modules constructed by PoroGen

Measured through 2” diameter x 15” long modules



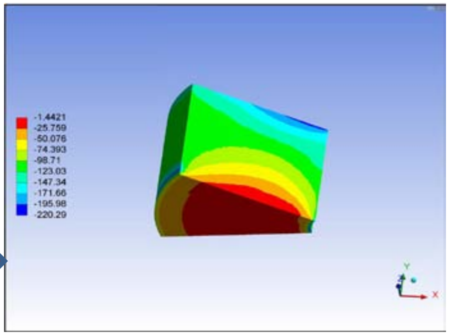
Beginning of the project → **Now**

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 (lab-scale) to 100 m^2 (8-inch commercial module)
- Production capability of 8” diameter module on commercial scale equipment established

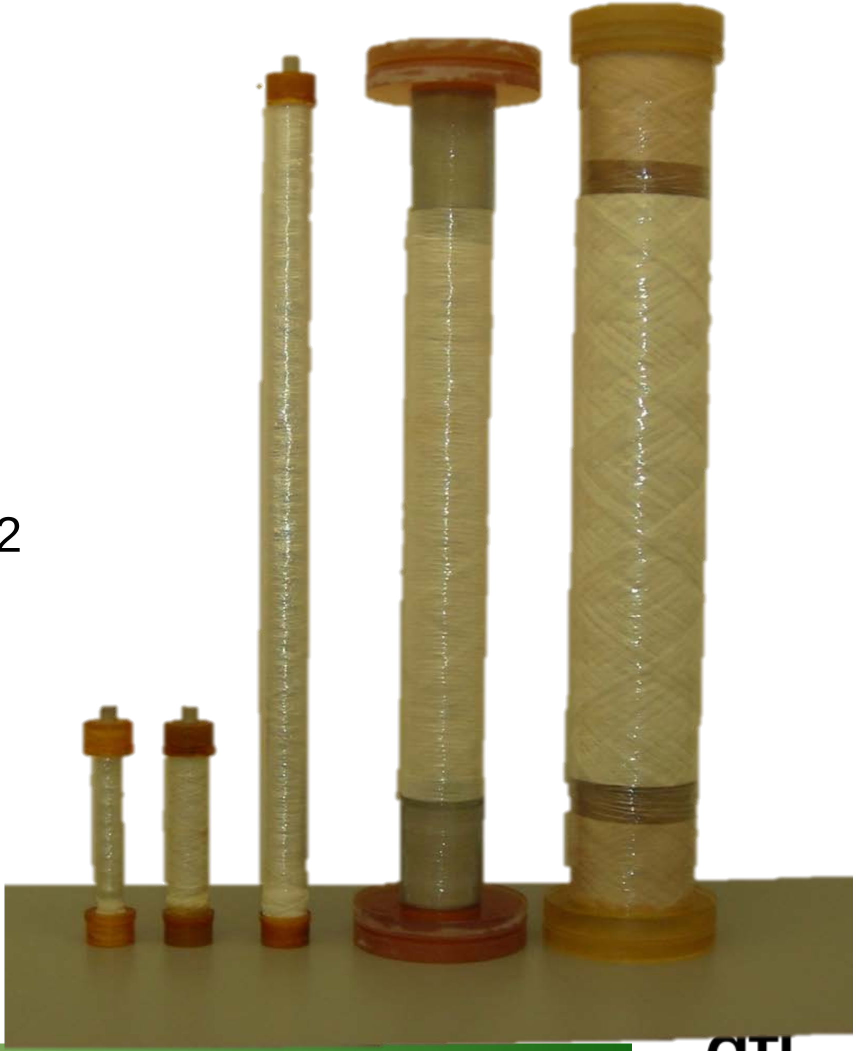

Tubesheet CFD stress analysis

Cartridge tubesheet for Ø8” x 60” long module

Manufacturing 8-inch modules on-going

Module cartridge scale-up from bench to commercial

- 2" bench – 1.2 ft^2
- 2" bench – 5 ft^2
- 2" bench – 50 ft^2
- 4" field – 250 ft^2
- 8" commercial – 1,000 ft^2



BP1: Membrane Absorber Study

Bench-scale membrane absorber CO_2 capture performance testing

- **Feed**: Simulated flue gas compositions (N_2 + CO_2 saturated H_2O, SOx, NOx, O_2) at temperature and pressure conditions after FGD.
- **Membrane module**: Performance can be essentially linearly scaled to commercial size modules
  - Uncertainty exists because gas/liquid contactor interface issues
  - Additional factors affect mass transfer coefficient
- **Solvents**: Commercial aMDEA (40 wt%) and activated K_2CO_3 (20 wt%), testing of advanced solvents planned
- **Use of design of experiment test matrix**: totally **over 140 tests**

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

Activated **m**ethyl**d**i**e**thanol**a**mine = **aMDEA**

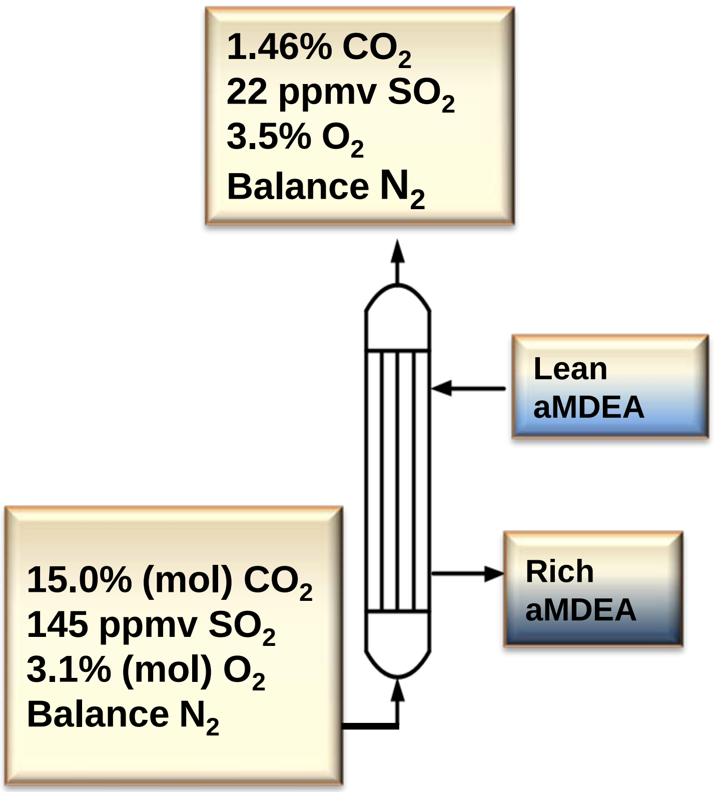
BP1 technical goal achieved with commercial aMDEA and K_2CO_3/H_2O

Module 2PG285, 1100 GPU

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 SOx, and NOx contaminants in feed

Module 2PG286, 1000 GPU



- **Measured results**:

CO_2 removal	91%
Mass transfer coefficient,$(sec)^{-1}$	1.6
Gas side ΔP, psi	1.6

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

Another test showed CO_2 removal rate is not affected by NO_x

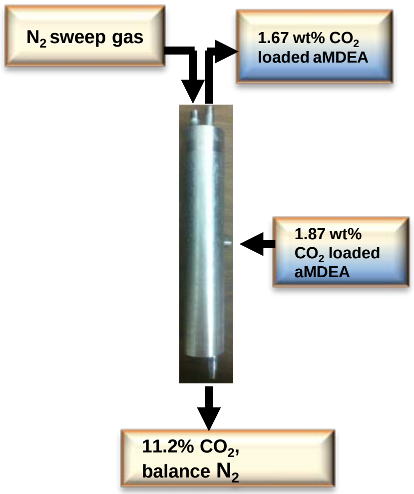
BP2: Membrane Desorber Study

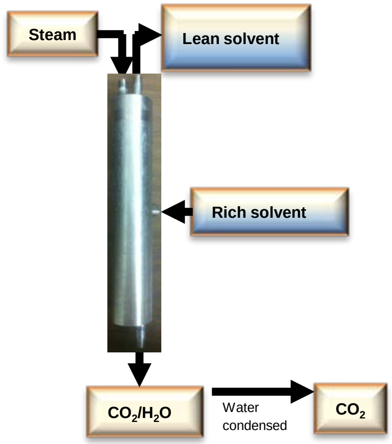
Bench-scale membrane desorber CO_2 stripping performance testing

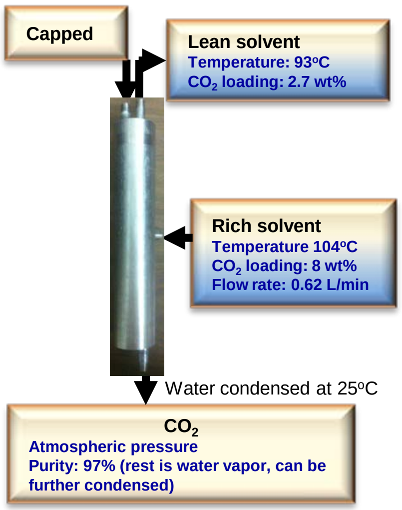
- **Membrane module**: Performance can essentially be linearly scaled to commercial size modules
- **Liquid feed**: CO_2 loaded aMDEA and activated K_2CO_3 rich solvents, flow rate: 0.2-0.7 L/min
- **Four flow configurations (Modes) investigated:** **over 80 tests**

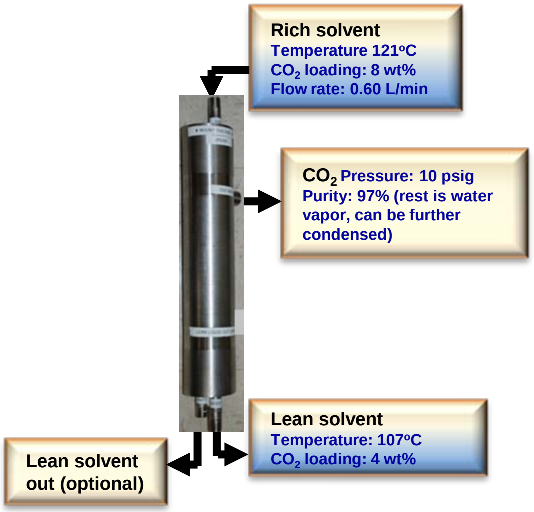
Module for lab testing (Ø2" x 15" long, $1 m^2$)

Four regeneration modes of operation with aMDEA and K_2CO_3 solvents









Mode I

Hydrophobic

N_2 sweep

Shell liquid feed

Shakedown

Mode II

Hydrophobic

Steam sweep

Shell liquid feed

CO_2 stripping rate: **0.51 kg/m²/h**

Mode III

Hydrophobic

No sweep

Shell liquid feed

CO_2 stripping rate: **2.8 kg/m²/h**

Mode IV

Hydrophilic

No sweep

Bore liquid feed

CO_2 stripping rate: **4.1 kg/m²/h**

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BP2 technical goal achieved

Parameters	Goal	Mode III	Mode IV
CO_2 purity	≥ 95%	97%	97%
CO_2 stripping rate ($kg/m^2/h$)	≥ 0.25	2.8	4.1

Economic evaluation bases

- Membrane module cost for commercial size (8-inch): $80/m^2
- CO_2 removal at 90% CO_2 using 1000 GPU membranes
- DOE/NETL-2007/1281"Cost and Performance Baseline for Fossil Energy Plants"

R&D strategy to meet DOE's target

Case	COE, $/MWhr	Increase in COE	$/Tonne CO_2 Captured*
DOE Case 9 no capture	64.00	--	
DOE Case 10 state of the art (amine plant)	118.36	85%	$65.30
BP 1 membrane absorber	**100.11**	**56%**	**$43.02**
BP 2 membrane desorber	**98.67**	**54%**	**$41.50**
R&D strategy to meet DOE's target			
1) Module cost from $80 to $30/m^2	95.64	48%	$36.87
2) Advanced solvent	More energy saving		

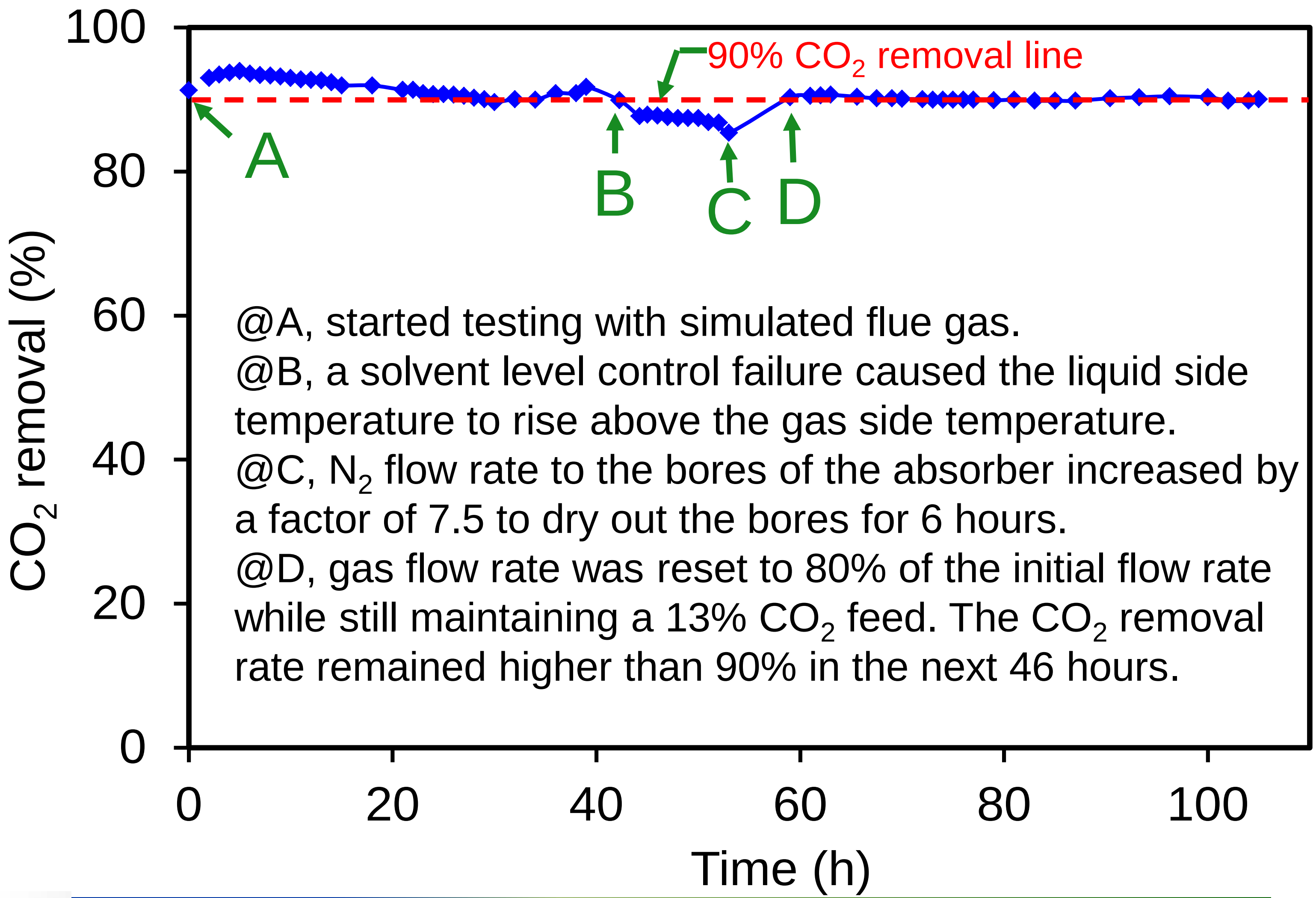
* In 2011 dollars

BP3: Integrated Absorber/Regeneration and Field Testing

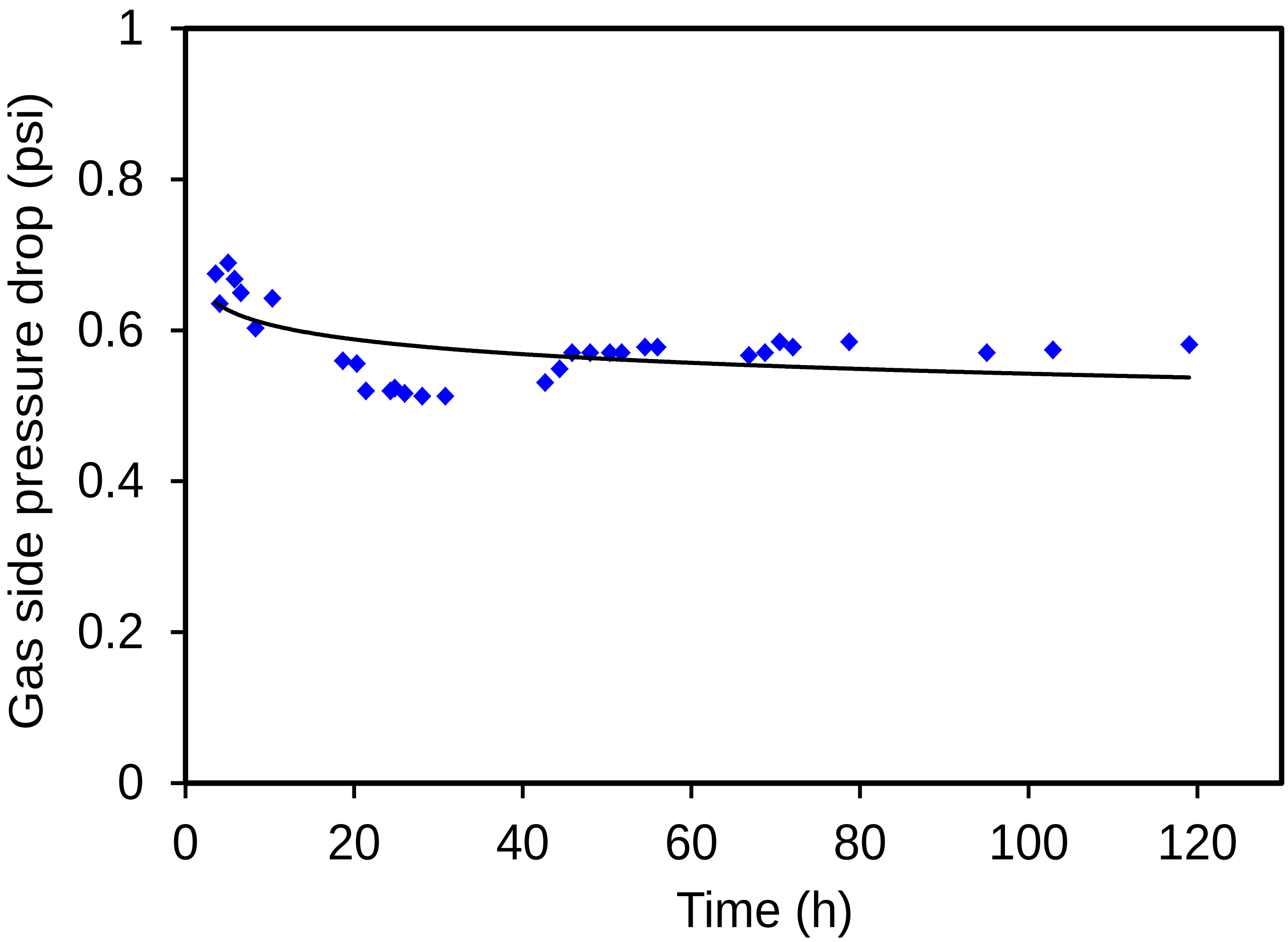
Integrated bench-scale system

System currently being modified for field tests

100-hour integrated membrane contactor absorption/regeneration testing completed



Gas side pressure drop stable and remained less than 0.7 psi (target is less than 2 psi)



Performance can be linearly scaled for field testing

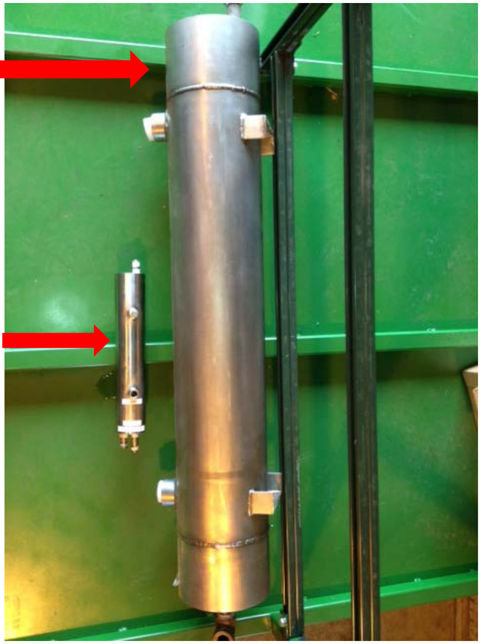
- CO_2 removal rate remained constant as membrane area increased from 1.2 ft^2 to 4.4 ft^2
- Intrinsic CO_2 permeance remained constant as membrane area increased from 1-4 ft^2 2-inch to ~250 ft^2 4-inch diameter modules
- Contactor performance will be validated in the field

Module*	Membrane area, ft^2	Overall mass transfer coefficient for CO_2 capture at 90% using aMDEA solvent, (1/s)
2PG285	1.2	1.7
2PG471	1.2	1.8
2PG472	4.4	1.8

* 2PG285 was developed in BP1
2PG470 and 471 are recent modules

4-inch diameter module in 8-inch shell for field testing

2-inch diameter module for lab testing



Field testing site determined, tests scheduled to start in August, 2013

- Site: Midwest's Will County Station in Romeoville, IL
- Source for the required flue gas and utilities discussed during June 10's site visit

Potential location for field tests

Technology implementation timeline

Time	Development	Module diameter	Projected # of modules*
By 2013	Bench-scale (Current project, Phase III)	4-inch	1
By 2017	1 MWe pilot scale (Proposal submitted to DOE)	8-inch	7
By 2020	25 MWe demonstration	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's new facility currently has equipment capacity to produce 1,000 eight-inch membrane modules annually.

Summary

- **BP1** membrane absorbers
  - Technical goal achieved: ≥90% CO_2 removal in one stage; gas side pressure drop: 1.6 psi; mass transfer coefficient: 1.7 1/s
- **BP2** membrane desorbers
  - Technical goal for CO_2 purity (97%) and CO_2 stripping rate (4.1 $kg/m^2/h$) achieved
  - Economic evaluation indicates a 54% increase in COE
- **BP3** integrated absorber/regeneration and field testing
  - A 100-hour, integrated absorber/desorber test completed, and CO_2 removal rate higher than 90% has been achieved
  - Performance improvements continue
  - Testing indicated contactor performance can be linearly scaled. This will be further validated in the field by using 4-inch modules
  - Unit for field tests is under modification, field testing site determined, tests scheduled to start in August, 2013

Acknowledgements

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