the Energy to Lead

Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture

DOE Contract No. DE-FE-0004787

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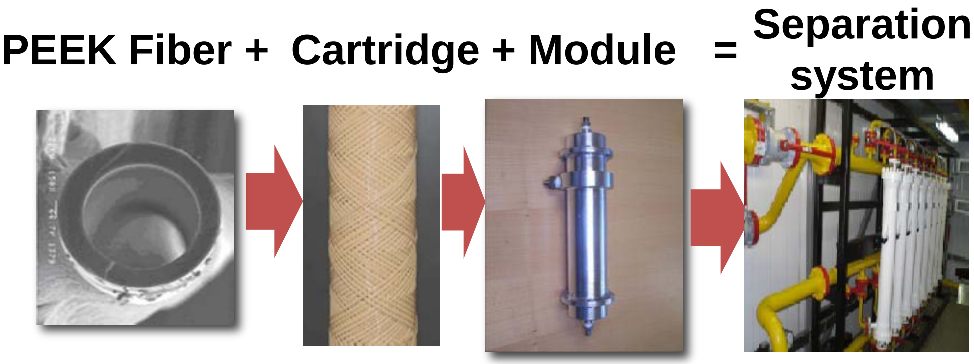
PoroGen INNOVATIVE MEMBRANE PRODUCTS

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



Project overview

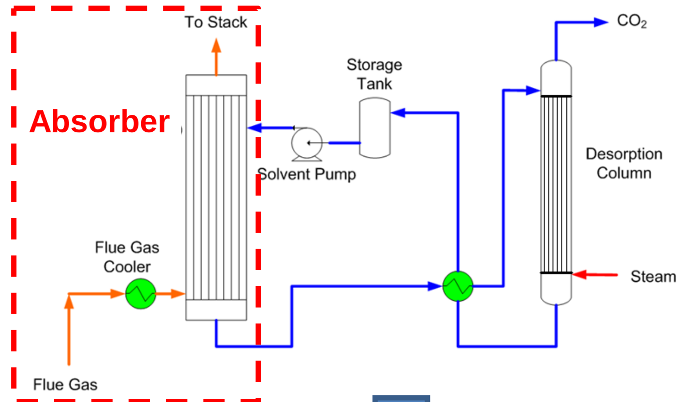
- **Funding**: \$3,736 K (DOE: \$2,986 K, Cost share: \$750 K)
  - BP1 budget: DOE: \$799 K, Cost share: \$200 K (20%)
  - BP2 budget: DOE: \$1,036 K, Cost share: \$262 K (20%)
  - BP3 budget: DOE: \$1,149 K, Cost share: \$287 K (20%)
- **Performance period**: Oct. 1, 2010 – Sept. 30, 2013
- **Project participants:**
  - GTI: process design and testing
  - PoroGen: membrane and membrane module development
  - Aker Process Systems: economic analysis
  - Midwest Generation: providing field test site

Objective and scope

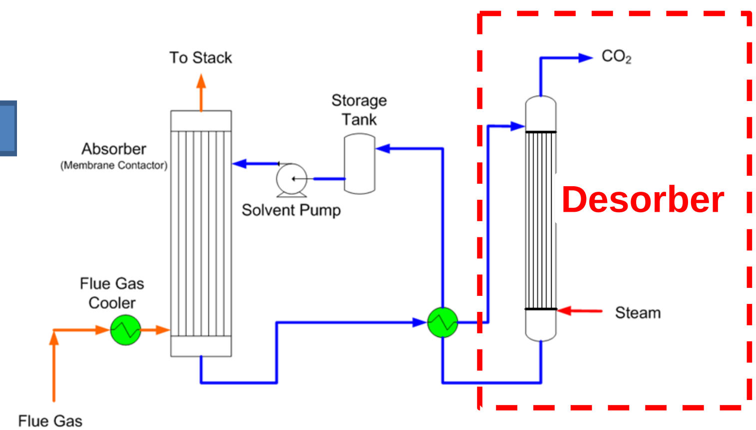
2010

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

BP1



BP2



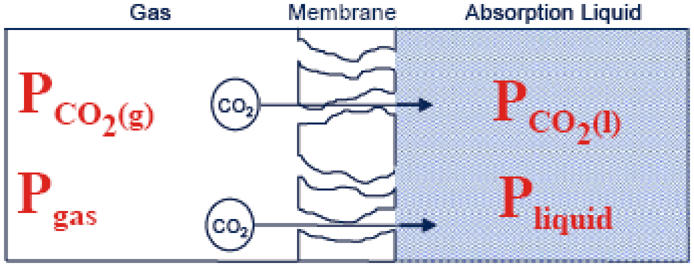
BP3

Integrate absorption/regeneration

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

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

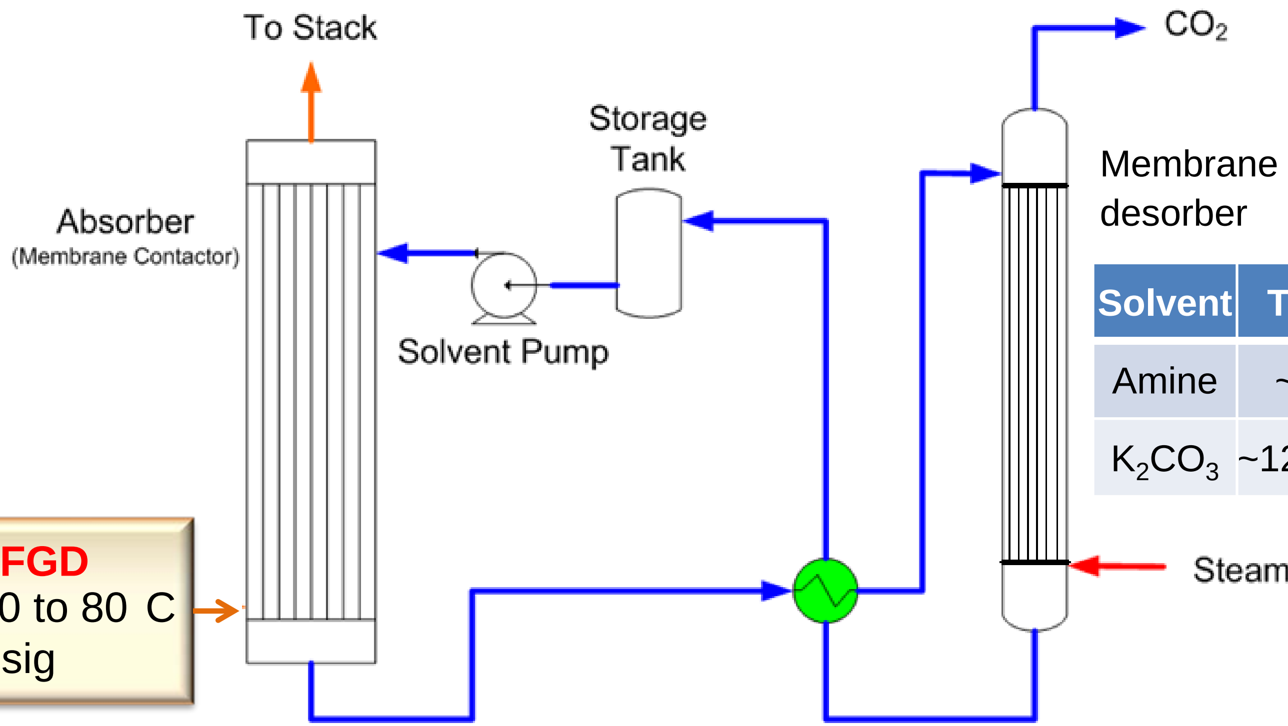


- **Separation mechanism**: CO_2 permeates through membrane and reacts with the solvent; N_2 does not react and has low solubility in solvent
- **Comparison to conventional membrane process**

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



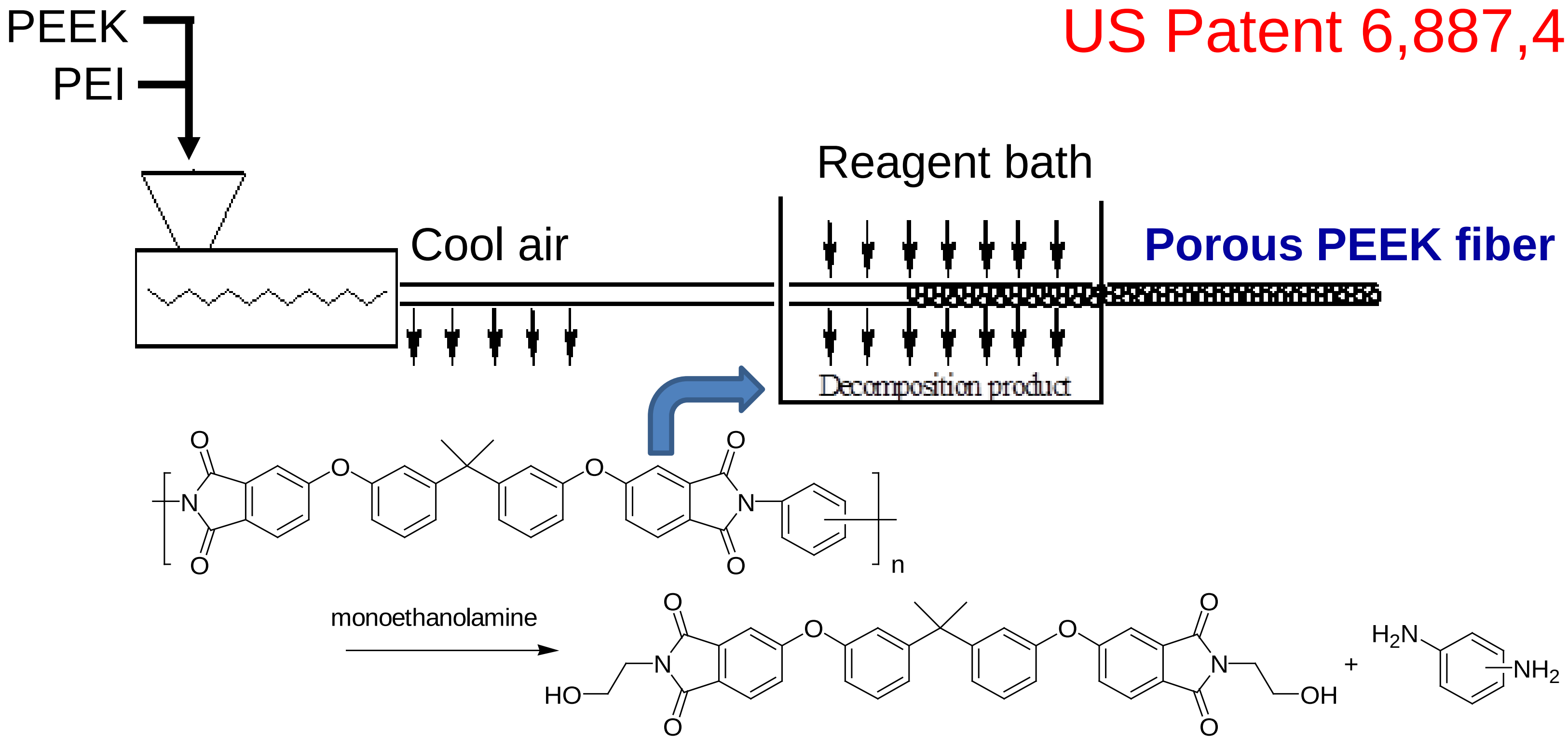
Solvent	T (ºC)	P (psig)
Amine	~120	1-10+
K_2CO_3	~120-150	1-20+

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

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

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

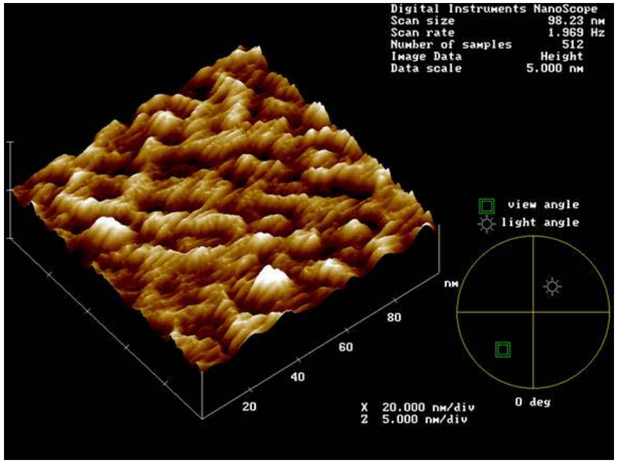
US Patent 6,887,408



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

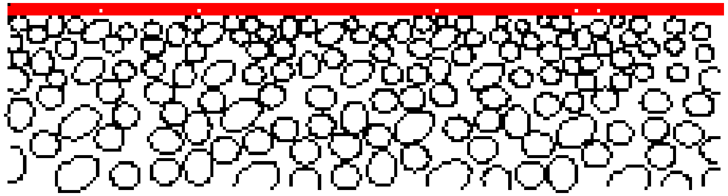
Two types of super-hydrophobic membranes under development

a) Nano-porous PEEK hollow fiber membrane



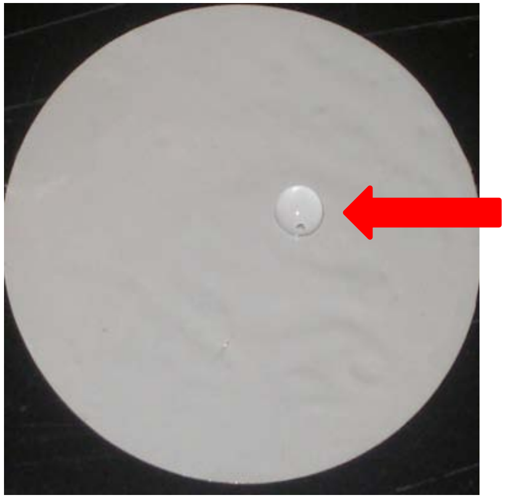
b) Composite PEEK hollow fiber membrane

Thin layer (0.1 μm) of smaller surface pores



Asymmetric porous structure

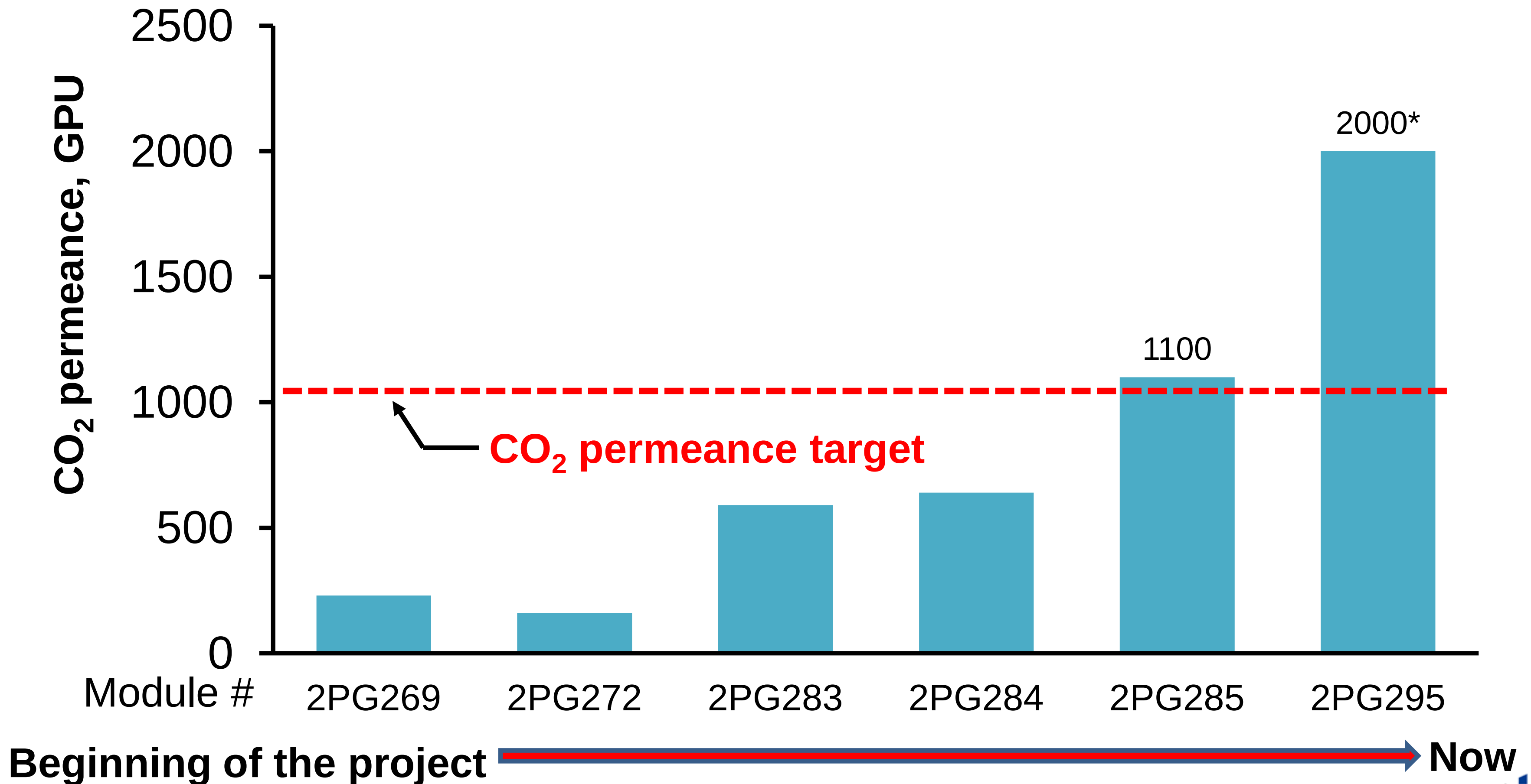
Super-hydrophobic surface not wetted by alcohol



Alcohol droplet

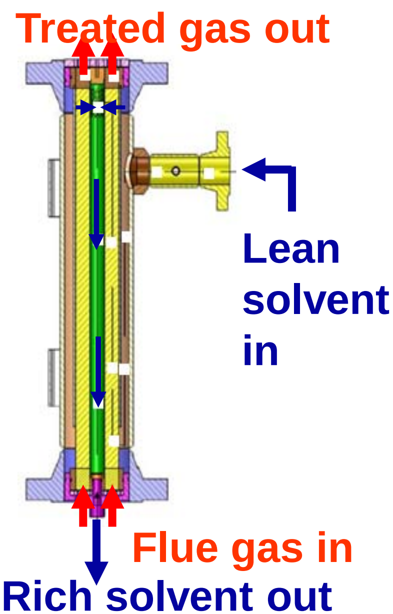
Membrane intrinsic CO_2 permeance exceeded initial target for commercial performance

More than 40 modules constructed by PoroGen



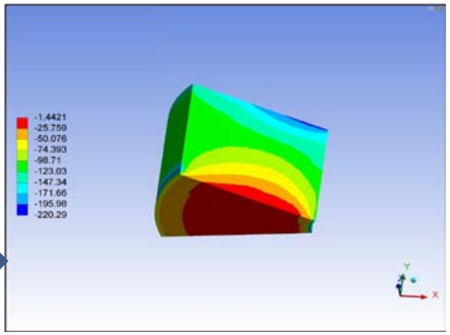
* Optimization on-going

Membrane module design and scale-up



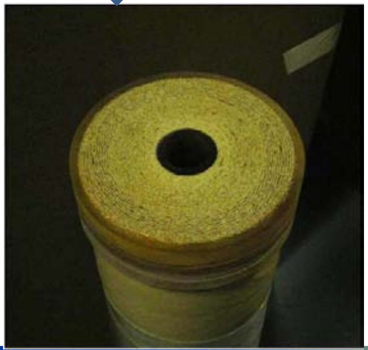
8 inch design model

- 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



8-inch structured packing module produced

BP1: Membrane Absorber Study

Bench-scale membrane absorber CO_2 capture performance demonstration

- **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 methyldiethanolamine = **aMDEA**

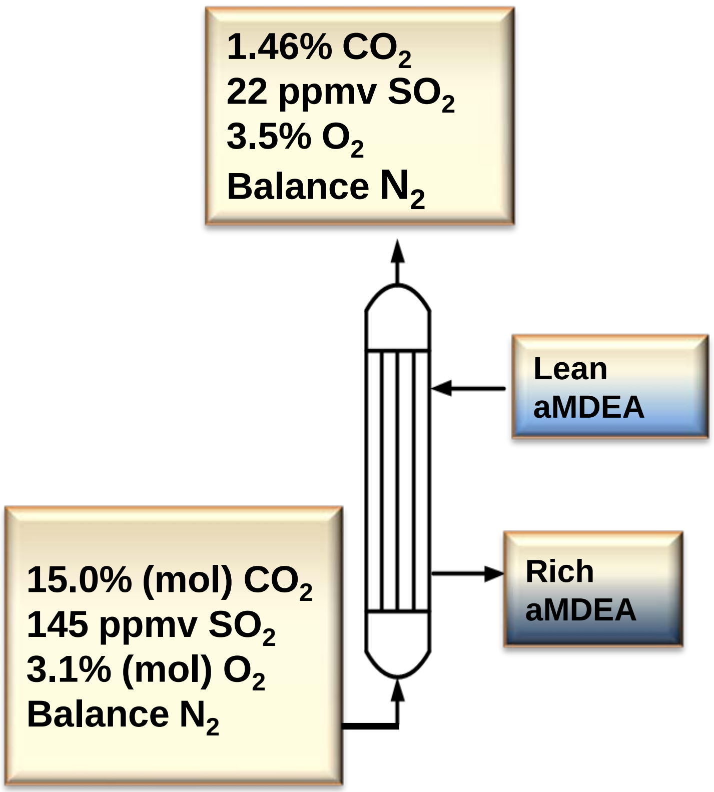
Technical goal achieved with commercial aMDEA and K_2CO_3/H_2O

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
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 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

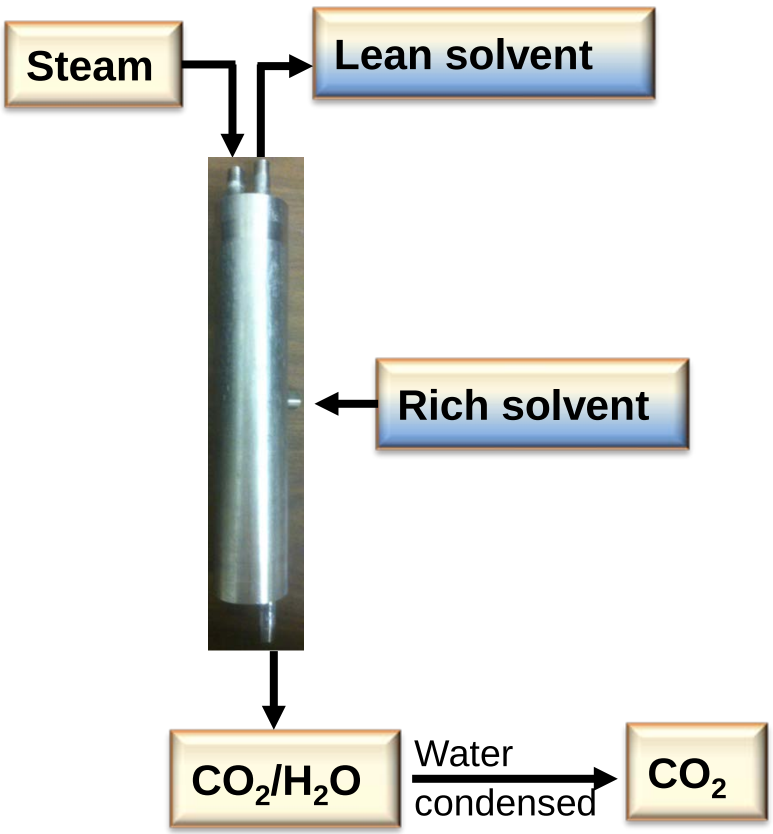
Bench-scale membrane desorber CO_2 stripping performance demonstration

- **Membrane module**: Performance can be essentially 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 60 tests**

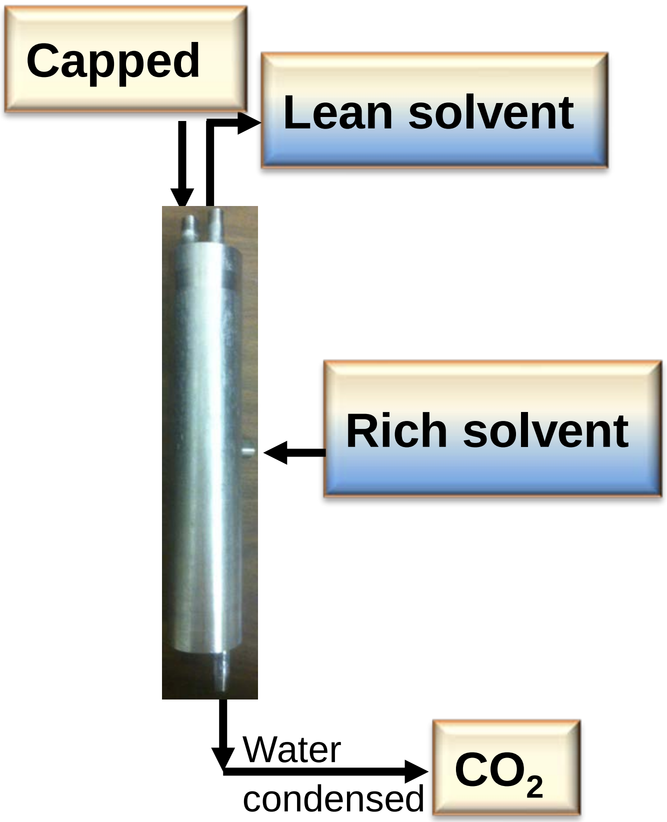
Module for lab testing (Ø2" x 15" long, $1m^2$)

Examples of Modes for solvent regeneration

Mode I (Steam Sweep)



Mode II (No Sweep)



High CO_2 stripping rate and high regeneration efficiency obtained

- CO_2 stripping rate: **4.1 $kg/m^2/h$**, **10 times higher** than the absorption rate. Thus, only **10%** membrane area is required for regeneration.
- CO_2 purity: **97%** (target is 95%), 3% is water vapor, can be further condensed.
- Regeneration efficiency: **66% in one stage**, and can be further increased by increasing operation temperature and optimizing process design.

Phase II 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

* Calculated based on a mass transfer coefficient of 1.0 (sec)$^{-1}$ for regeneration

Updated COE and increase in COE when use of membrane regeneration is considered

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%
BP1 status: membrane absorber	**100.11**	**56%**
BP2 status: membrane desorber	**98.67**	**54%**

R&D strategy to meet DOE's target

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%
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BP2 status: membrane desorber	**98.67**	**54%**
R&D strategy to meet DOE's target		
1) Module cost ↓ from \$80 to \$30/m^2	95.64	48%
2) Advanced solvent	On trajectory to meet DOE target	

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Plan for the rest of BP2

#	Plans for future testing in BP2
1	Further membrane development based on regeneration testing results so far.
2	Modes III and IV are currently down selected for further study. Operation conditions will be further optimized to down select one mode for Phase III.
3	After regeneration mode is down selected, use of reflux in membrane desorber to improve regeneration efficiency (target: “lean” solvent lean enough for membrane absorber).
4	Refinement of the process economics based on the lab test data .
5	Finalize testing plan for Phase III.

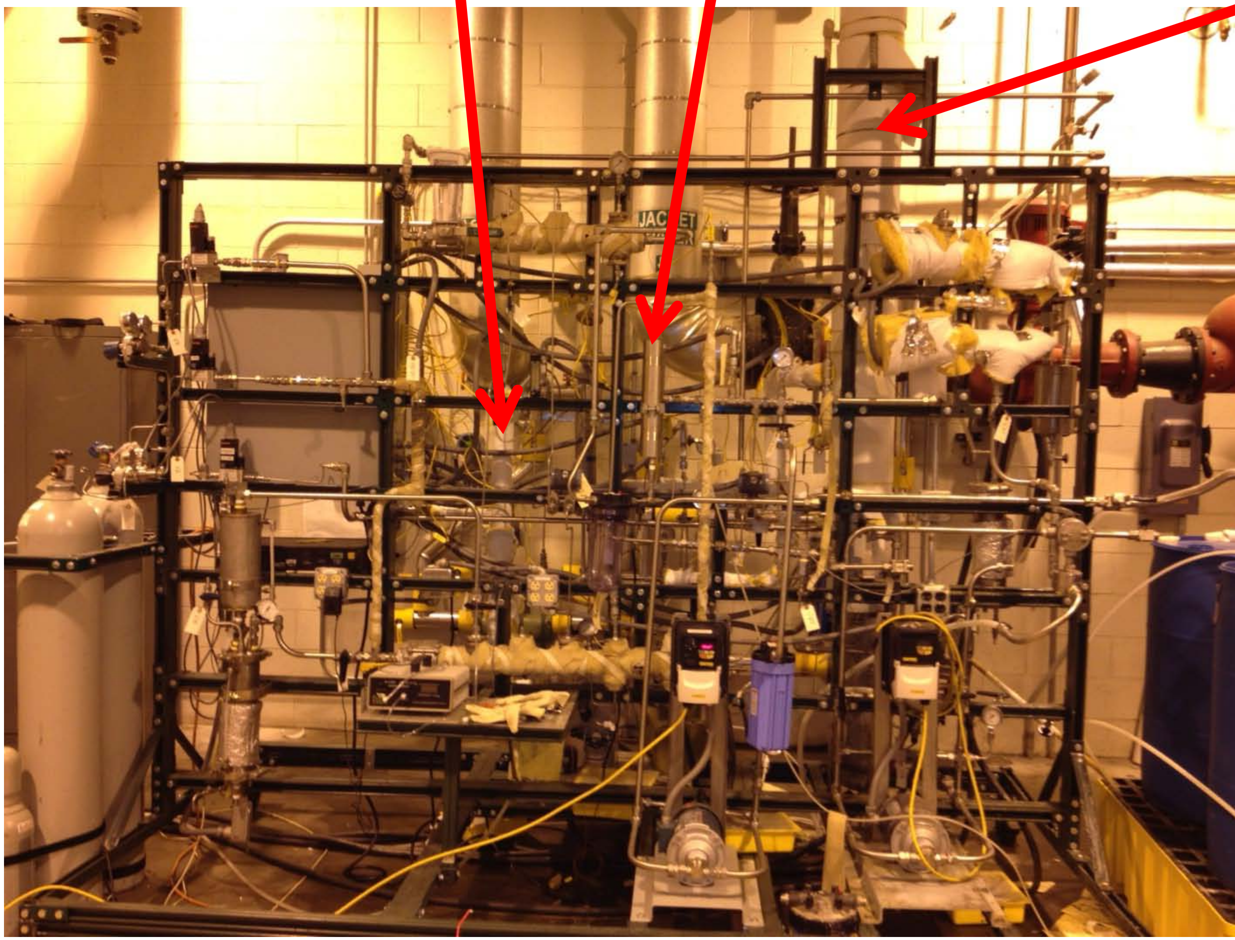
Readiness and Plan for BP3: Integrated Absorber/Regeneration

Membrane contactor skid constructed

Membrane desorber

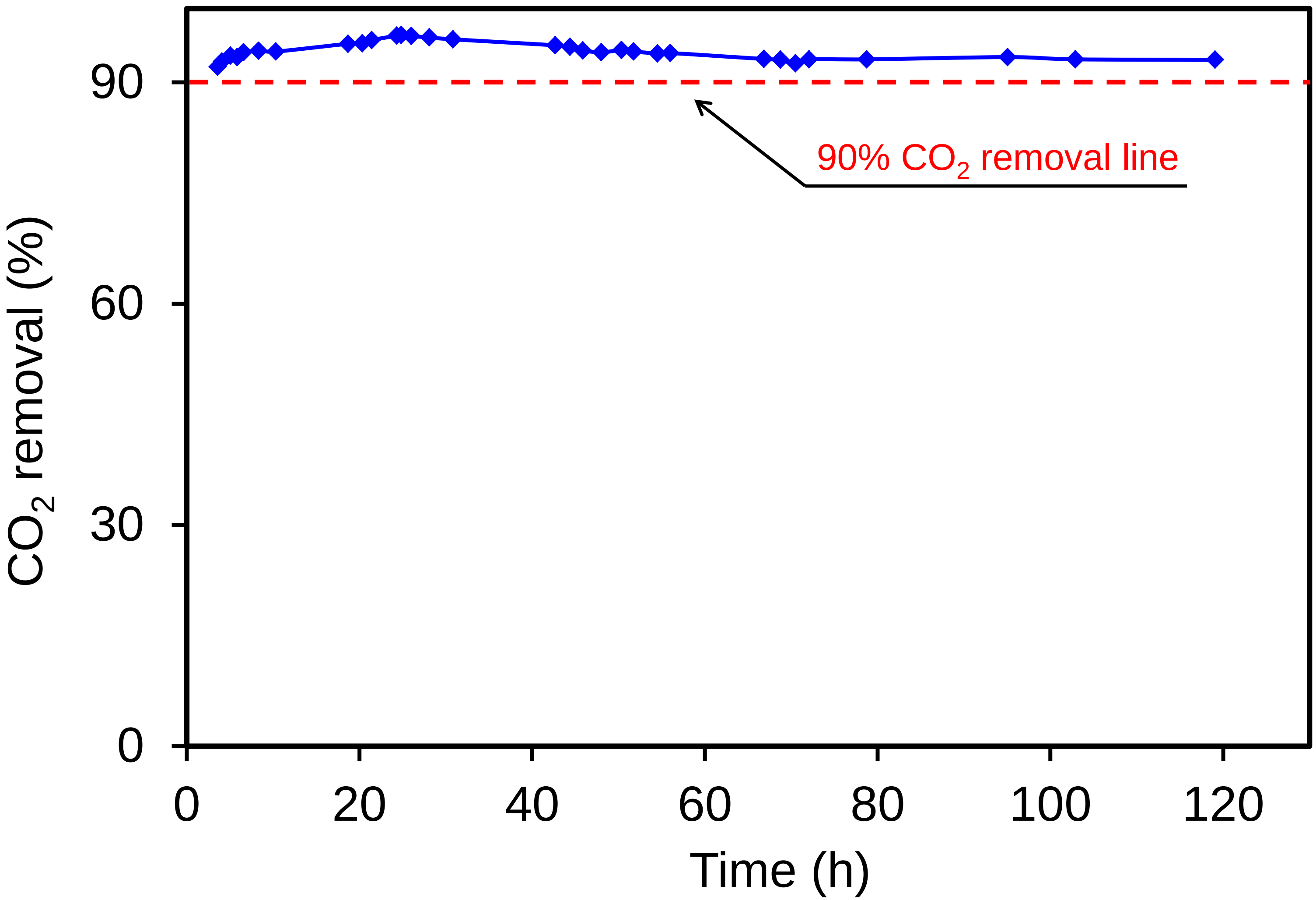
Membrane absorber

Desorption tower (backup plan)

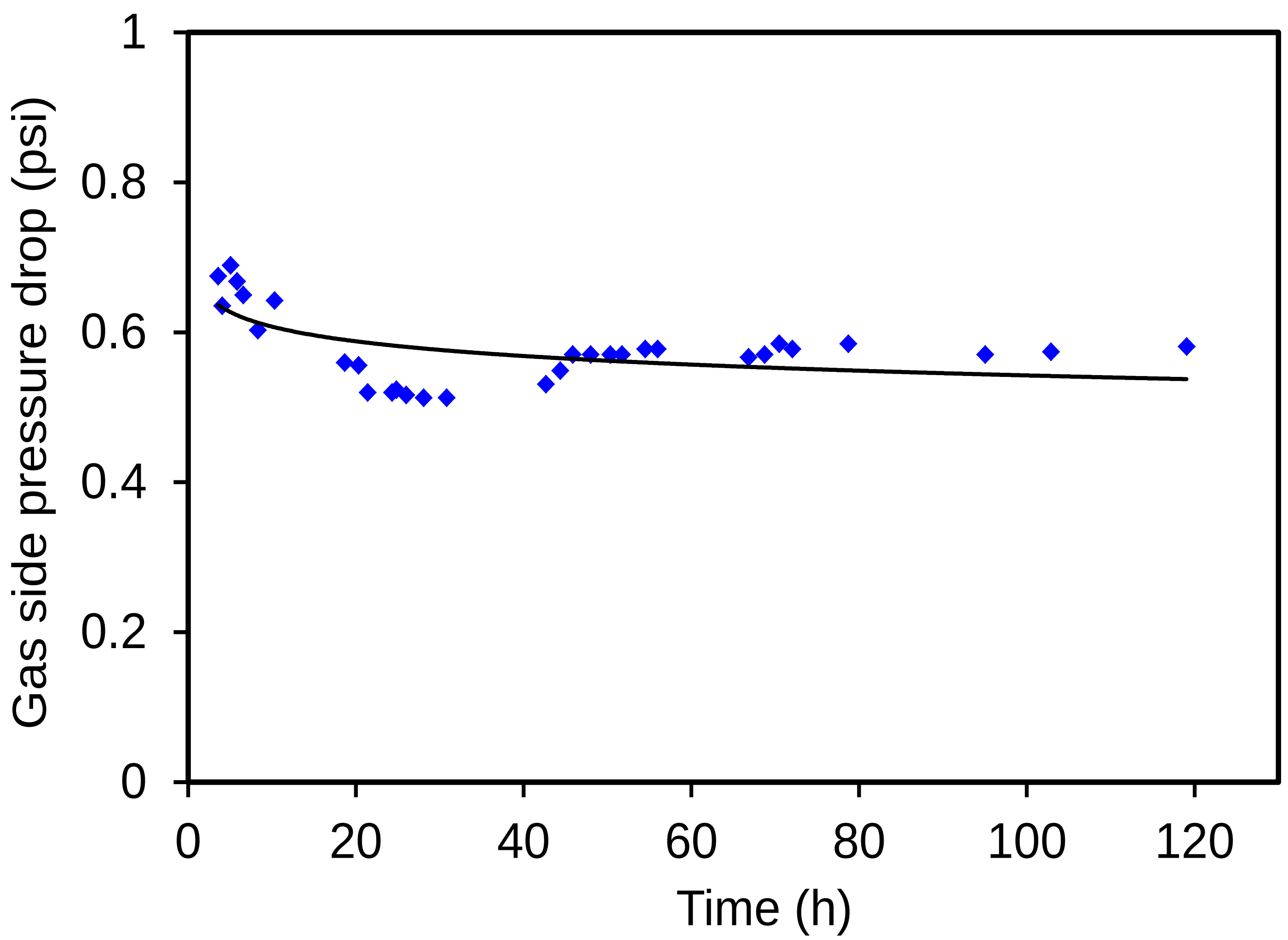


- Designed for **25 KW** equivalents of CO_2 capture (0.5 ton/day)
- Phase I: absorption
  Phase II: regeneration
  Phase III: Integrate absorption/regeneration for field testing

CO_2 removal rate > 90% during the time investigated (120 hours)



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

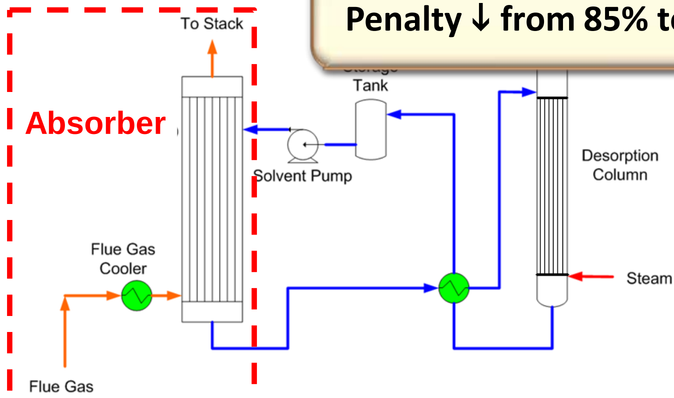


Plans for Future Testing and Development

Plans for future testing and development in this project

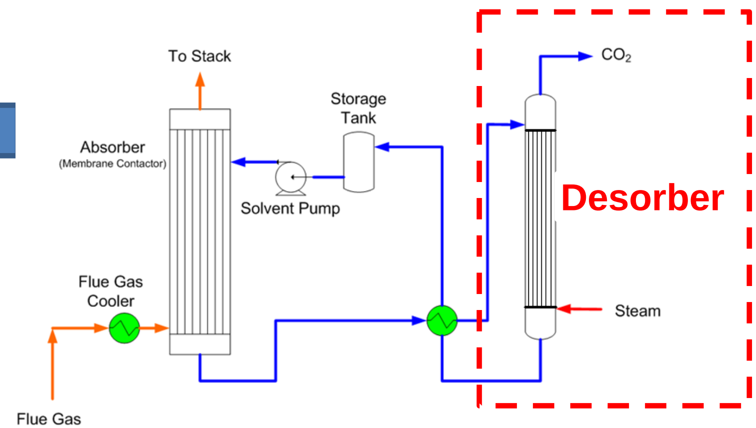
2010

2011



Economic Evaluation: COE Penalty ↓ from 85% to 56%

2012



1) Optimize membrane and system design to improve regeneration efficiency

2) Refine economic evaluation based on optimized sorption and desorption test results

2013

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

3) Integrate absorption and regeneration

4) Field testing for **25 kW** equivalents of CO_2 capture (**0.5 ton/day**)

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	4 or 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 25 MWe demonstration plants

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
  - Feasibility of contactor module scale-up demonstrated
  - Economic evaluation based on membrane absorber only indicates a 56% increase in COE.
- **BP2** membrane desorbers
  - Technical goal for CO_2 purity (97%) and CO_2 stripping rate (4.1 $kg/m^2/h$) achieved. Operation optimization is on-going to ensure "lean" solvent is lean enough for membrane absorber
  - Evaluation per membrane absorber + desorber testing so far indicates a 54% increase in COE.
- In preparation for **BP3**
  - Completed constructing bench-scale membrane skid, integration of membrane absorber/regeneration tower, membrane module and performance stable with aMDEA solvent.

Acknowledgements

- Financial support
  - DOE-NETL
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- DOE NETL José Figueroa