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GTI Project 21081

Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture

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ABSTRACT

This report summarizes scientific/technical progress made for bench-scale membrane contactor technology for post-combustion CO_2 capture from DOE Contract No. DE-FE-0004787. Budget Period 1 (BP1) membrane absorber, Budget Period 2 (BP2) membrane desorber and Budget Period 3 (BP3) integrated system and field testing studies have been completed successfully and met or exceeded the technical targets ($\geq$ 90% CO_2 removal and CO_2 purity of 97% in one membrane stage). Significant breakthroughs are summarized below:

BP1 research: The feasibility of utilizing the poly (ether ether ketone), PEEK, based hollow fiber contractor (HFC) in combination with chemical solvents to separate and capture at least 90% of the CO_2 from simulated flue gases has been successfully established. Excellent progress has been made as we have achieved the BP1 goal: $\geq$ 1,000 membrane intrinsic CO_2 permeance, $\geq$ 90% CO_2 removal in one stage, $\leq$ 2 psi gas side pressure drop, and $\geq$ 1 $(sec)^{-1}$ mass transfer coefficient. Initial test results also show that the CO_2 capture performance, using activated Methyl Diethanol Amine (aMDEA) solvent, was not affected by flue gas contaminants O_2 (~3%), NO_2 (66 ppmv), and SO_2 (145 ppmv).

BP2 research: The feasibility of utilizing the PEEK HFC for CO_2-loaded solvent regeneration has been successfully established High CO_2 stripping flux, one order of magnitude higher than CO_2 absorption flux, have been achieved. Refined economic evaluation based on BP1 membrane absorber and BP2 membrane desorber laboratory test data indicate that the CO_2 capture costs are 36% lower than DOE's benchmark amine absorption technology.

BP3 research: A bench-scale system utilizing a membrane absorber and desorber was integrated into a continuous CO_2 capture process using contactors containing 10 to 20 ft^2 of membrane area. The integrated process operation was stable through a 100-hour laboratory test, utilizing a simulated flue gas stream. Greater than 90% CO_2 capture combined with 97% CO_2 product purity was achieved throughout the test. Membrane contactor modules have been scaled from bench scale 2-inch diameter by 12-inch long (20 ft^2 membrane surface area) modules to 4-inch diameter by 60-inch long pilot scale modules (165 ft^2 membrane surface area). Pilot scale modules were tested in an integrated absorption/regeneration system for CO_2 capture field tests at a coal-fired power plant (Midwest Generation's Will County Station located in Romeoville, IL). Absorption and regeneration contactors were constructed utilizing high performance super-hydrophobic, nano-porous PEEK membranes with CO_2 gas permeance of 2,000 GPU and a 1,000 GPU, respectively. Field tests using aMDEA solvent achieved greater than 90% CO_2 removal in a single stage. The absorption mass transfer coefficient was 1.2 $(sec)^{-1}$, exceeding the initial target of 1.0 $(sec)^{-1}$. This mass transfer coefficient is over one order of magnitude greater than that of conventional gas/liquid contacting equipment. The economic evaluation based on field tests data indicates that the CO_2 capture cost associated with membrane contactor technology is \$54.69 (Yr 2011\$)/tonne of CO_2 captured when using aMDEA as a solvent. It is projected that the DOE's 2025 cost goal of \$40 (Yr 2011\$)/tonne of CO_2 captured can be met by decreasing membrane module cost and by utilizing advanced CO_2 capture solvents. In the second stage of the field test, an advanced solvent, Hitachi's H3-1 was utilized. The use of H3-1 solvent increased mass transfer coefficient by 17% as compared to aMDEA solvent. The high mass transfer coefficient of H3-1 solvent combined with much more favorable solvent regeneration

requirements, indicate that the projected savings achievable with membrane contactor process can be further improved. H3-1 solvent will be used in the next pilot-scale development phase. The integrated absorption/regeneration process design and high performance membrane contactors developed in the current bench-scale program will be used as the base technology for future pilot-scale development.

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EXECUTIVE SUMMARY

The objective of this project was to develop cost effective separation technology based on a novel hollow fiber contactor (HFC) that will provide significant reduction in the cost of CO_2 capture from flue gases. The key component of the HFC process is the super-hydrophobic, nanoporous hollow fiber membrane, which is made from poly (ether ether ketone) (PEEK). PEEK is an engineering polymer with thermo-mechanical properties and chemical resistance superior to most commercial plastics including typical polymers used in membrane fabrication. The unique characteristics of PEEK allow the HFC device to be utilized successfully in challenging and aggressive chemical environments which are encountered in both absorption and regeneration steps of HFC process. These properties, combined with super-hydrophobicity, enable PEEK HFC to overcome pore wetting and chemical durability problems that have plagued prior HFC technologies.

A "real-world" assessment of the necessary and desirable features including the following elements has been undertaken during our bench-scale studies.

- **Membrane module**: The focus was to develop contactor membrane modules with target performance scalable to commercial contactor size.
- **Solvent**: All solvents used were commercially available; five different solvents were investigated throughout the study.
- **Feed Gas**: Both real and simulated flue gas compositions were used as feeds during tests. The effects of flue gas contaminants, such as O_2, NO_x, and SO_x on membrane contactor performance were investigated.
- **Stability**: Contactor performance stability in the integrated membrane absorber/desorber process has been conducted.
- **Techno-economic analysis**: CO_2 capture costs were determined for the combined integral absorption/regeneration process utilizing experimental results.

Significant progress has been made towards key milestones and technical goals through BP1 membrane absorber development stage, BP2 membrane desorber development stage and BP3 integrated system development and field tests.

BP1 Membrane Absorber Study

During BP1 of this program, GTI and PoroGen have established the feasibility of utilizing PEEK HFC in combination with chemical solvents to separate and capture at least 90% of the CO_2 from simulated flue gases. The membrane contactor is based on the super-hydrophobic nano-porous PEEK hollow fiber membrane. The membrane morphology and PEEK hollow fiber dimensions were optimized to meet operational requirements of CO_2 capture from the flue gas. Membrane intrinsic CO_2 permeance of 1,000 GPU was attained that exceeded initial BP1 goal. Membrane manufacturing procedures were established for production of 8-inch commercial size contactor modules and the design was validated through computational fluid dynamics modeling.

A post-combustion CO_2 capture gas/liquid membrane absorber skid has been constructed at GTI (skid footprint 12 ft x 5.5 ft x 12 ft). Bench scale 2-inch diameter by 12-inch to 60-inch long contactor modules were used to test CO_2 removal from simulated flue gas streams. The performance of the hybrid membrane/absorption process was investigated utilizing a number of solvent systems -DEA, MDEA, aMDEA, and aqueous activated potassium carbonate (K_2CO_3). A design of experiment test matrix was utilized throughout this study. The aMDEA and activated K_2CO_3/water solvents were selected for in depth testing and process optimization as both solvents have achieved our BP1 technical goals as shown in Table 1.

Table 1. Comparison of BP1 technical goal and achieved value.

Parameter	Goal	Achieved value	
		aMDEA	K_2CO_3
Membrane intrinsic CO_2 permeance, GPU	≥ 1,000	>1,000	
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

The effect of flue gas contaminants O_2, NO_2, and SO_2 on the contactor performance was evaluated. Tests with aMDEA solvent showed that the CO_2 capture performance using PEEK membrane contactors was not affected by these flue gas contaminants at levels consistent with Illinois basin coal feeds. Reduces levels of contaminant gas components sorption into the solvent were found.

Process economic evaluation was performed in BP1 of this project using DOE prescribed methods. This evaluation determined the cost of electricity at the DOE goal of 90% carbon capture. At a measured overall volumetric mass transfer coefficient of 1.7 $(sec)^{-1}$ and a membrane module costs of $\$80/m^2$, the total LCOE including CO_2 capture, sequestration and monitoring for a PC-based power plant can be reduced from 107.57 mills/kWh to 100.11 mills/kWh. This represents a 56% increase in LCOE over the no capture cost (DOE Case 9) compared to an 85% increase for DOE Case 10 when conventional amine process is used for CO_2 capture.

BP2 Membrane Desorber Study

During BP2 of this program, GTI and PoroGen have established the feasibility of utilizing PEEK hollow fiber membrane contactor for CO_2-loaded solvent regeneration. Regeneration contactor modules were constructed to enable four different operational modes of solvent regeneration. Regeneration contactor cartridges were sealed into pressure shells with special O-ring seals. E-8 epoxy formulation was developed for cartridge tubesheet construction to enable operation in aggressive environment prevailing during solvent regeneration. Laboratory test unit that enabled evaluation of the solvent regeneration step by membrane contactors has been designed and constructed at GTI. The system was utilized to conduct solvent regeneration experiments by membrane contactors.

Efficient CO_2 stripping of 8 wt% CO_2-loaded aMDEA solvent by membrane contactors has been established by 4 different modes of operation: I) using N_2 as a sweep gas, II) using steam as a sweep, III) regeneration without sweep, and IV) regeneration using porous hydrophilic membrane configuration. The first three modes listed above used the super-hydrophobic membrane. A porous hydrophilic membrane was used for mode IV. The Mode III and IV were selected for further testing and process optimization as they both have achieved our BP2 technical goals (Table 2).

Table 2. Comparison of BP2 technical goal and achieved value.

Parameters	**Goal**	**Mode III**	**Mode IV**
CO_2 purity	≥ 95%	97%	97%
Solvent lean enough for membrane absorber	Achieve	Achieved	Achieved

Membrane absorber stability at process design conditions was investigated by conducting continuous CO_2 capture test with aMDEA solvent for 120 hours. During this test, the membrane contactor absorber was integrated with a conventional solvent regeneration tower. The CO_2 loading of lean solvent remained low and constant throughout the experiment. The CO_2 removal rate was greater than 90% during the 120-hour test. The membrane contactor module showed good mechanical integrity and stable regeneration properties.

Membrane contactor regenerator/desorber performance stability was also evaluated. The contactor module was used for aMDEA solvent regeneration in 7 different regeneration tests with a total operational time in access of >35 hours. No significant changes in performance were observed and module structural integrity was not compromised.

The economic evaluation was refined based on the BP1 membrane absorber and BP2 membrane desorber laboratory test data. The results indicate a 54% increase in LCOE.

BP3 Integrated System and Field Testing

All BP3 technical goals have been met as shown in Table 3. A bench-scale system utilizing a membrane absorber contactor and membrane desorber contactor was constructed. The absorption and regeneration processes were integrated into a continuous CO_2 capture process. Bench scale 2-inch diameter (15-inch long) modules containing between 10 to 20 ft^2 of membrane area were utilized. The integrated process operation was stable through a 100-hour laboratory test, utilizing a simulated flue gas stream, with greater than 90% CO_2 capture and 97% CO_2 product purity achieved throughout the test.

Table 3. Comparison of BP3 technical goal and achieved value.

Parameters	**Goal**	**Testing results**
Continuous operation time in the lab	≥ 100 h	104 h with >90% CO_2 removal
Mass transfer coefficient of the 4" 2,000 GPU module in the field	>1.0 $(sec)^{-1}$	1.2 $(sec)^{-1}$

During BP3, membrane contactor module size has been scaled from 2-inch diameter bench-scale modules to 4-inch diameter 60-inch long pilot-scale modules with membrane surface area of 164 ft^2 per module. A pilot scale test system was constructed that incorporated these pilot size modules. The absorption contactor module was constructed utilizing hollow fiber membranes with CO_2 gas permeance of 2,000 GPU and the regeneration contactor module was constructed utilizing hollow fiber membranes with gas permeance of 1,000 GPU. The field tests were conducted at a coal-fired power plant (Midwest Generation's Will County Station located in Romeoville, IL). The aMDEA solvent was used in initial pilot field tests. The system showed greater than 90% CO_2 removal in one stage. The mass transfer coefficient for a 2,000 GPU contactor module absorber was 1.2 $(sec)^{-1}$, which exceeded the initial target of 1.0 $(sec)^{-1}$. This mass transfer coefficient is over one order of magnitude greater than that of conventional gas/liquid contacting equipment.

The concentration of SO_2 in the flue gas at test site was relatively low. To evaluate the effect of SO_2 on contactor system performance, a controlled amount of SO_2 was metered into the feed. During an 8-hour field test, the SO_2 concentration in the feed gas was increased to simulate burning Illinois coal. It was found that 470 ppmv SO_2 concentration in the flue gas did not affect CO_2 capture performance. The aMDEA solvent was used in this test.

Economic analysis based on field test results indicates that the cost of CO_2 captured using contactor membrane technology is \$54.69 (Yr 2011\$)/tonne of CO_2 captured when using aMDEA as the solvent. The DOE's 2025 cost goal of \$40 (Yr 2011\$)/tonne of CO_2 captured can be, however, potentially met by decreasing membrane module cost and by utilizing advanced solvents.

In the second stage of the field test, an advanced solvent, Hitachi's H3-1 (known to have lower regeneration energy consumption than aMDEA) was utilized. The use of H3-1 solvent increased mass transfer coefficient by 17% as compared to aMDEA solvent. The high mass transfer coefficient of H3-1 solvent combined with a much more favorable solvent regeneration requirements, indicate that the projected savings achievable with membrane contactor process can be further improved. H3-1 solvent will be used in the next pilot-scale development phase. The integrated absorption/regeneration process design developed in the current phase and high performance membrane contactors will be used as the base technology for future pilot-scale development.

Completion of Milestones

Bench-scale technology development has been successful as we have met all milestones as shown in Table 4.

Table 4. The completion of milestones through bench-scale studies.

M/ S#	Title or brief milestone description	Completion date	
		Planned	Actual
1	Tailor membrane for flue gas CO_2 separation with intrinsic CO_2 permeation rates from 1000 to 3000 GPU and gas side pressure drop less than or equal to 1 to 2 psi	01/31/11	08/31/11
2	Material specifications for manufacturing of 8-inch membrane contactor module determined. Membrane module blue print obtained.	09/30/11	08/31/11
3	Achieve 90% removal of CO_2 in one stage during laboratory testing using the membrane contactor process. Overall volumetric mass	09/30/11	08/31/11

	transfer coefficient greater or equal to 1.0 $(sec)^{-1}$.		
4	Selected solvent tests completed using design of experiment test matrix. Best solvent determined for further testing and process optimization.	09/30/11	09/30/11
5	Issue membrane contactor process design and economic evaluation report based on Phase I results.	09/30/11	09/30/11
6	Submit year one report.	12/31/11	12/31/11
7	Initial 2-inch module for regeneration designed and fabricated for testing.	01/31/12	01/31/12
8	Regeneration testing system designed, constructed and completed commissioning.	12/31/11	12/31/11
9	Achieve 95% CO_2 purity during regeneration laboratory testing. Obtain an overall volumetric mass transfer coefficient greater or equal to 1.5 and 1.0 $(sec)^{-1}$ for absorption and regeneration, respectively.	08/31/12	06/30/12
10	Issue field test unit design package for system construction.	09/30/12	09/30/12
11	Issue refined process design and economic evaluation reports using second period test results.	09/30/12	09/30/12
12	Submit year two report.	12/31/12	12/31/12
14	Demonstrate absorption membrane performance stability.	01/31/13	06/30/13
15	Demonstrate high temperature desorption membrane life.	01/31/13	02/28/13
16	Demonstrate 100 h of operating integrated absorption/desorption system.	03/31/13	02/28/13
17	Complete 4-inch (or 8-inch) field test module fabrication.	05/31/13	06/30/13
18	Complete initial field test unit shake down at GTI.	06/30/13	09/30/13
19	Complete site preparation and field test unit installation.	07/31/13	10/10/13
20	Operation of the field test unit at Midwest with slipstream of flue gas completed and test results collected according to pre-approved matrix.	11/30/13	11/30/13
21	Complete final economic evaluation based on field test results.	12/31/13	12/31/13
22	Submit final report.	01/31/14	01/31/14

INTRODUCTION AND OBJECTIVES

Introduction

The membrane contactor process (also known as hybrid membrane/absorption process) combines advantageous features of both absorption and membrane processes to provide a cost-effective solution for CO_2 capture from flue gases. In this process, CO_2-containing gas passes through one side of the membrane while a CO_2 selective solvent (typically an amine solution) flows on the other side. CO_2 permeates mainly through pores in the membrane and is absorbed in the solvent. The CO_2 rich solvent can be regenerated in a second membrane module operating in a reverse manner.

The membrane contactor process is different from a conventional membrane process, which separates gases by selective permeation through a dense membrane separation layer by a solution/diffusion mechanism, wherein the separation driving force is provided by the partial pressure difference of each gas component across the membrane. The conventional membrane process requires either flue gas compression, permeate side sweep, application of permeate-side vacuum, or a combination of these steps to provide the separation driving force. Elaborate process design and optimization becomes a prerequisite for a conventional membrane process in CO_2 capture from flue gases.[1] The main limitation of conventional membrane processes is the process pressure ratio (feed gas pressure/permeate gas pressure) limitation. In practical gas separation applications, the pressure ratio across the membrane is usually between 5 and 15.[2] When the membrane separation process is pressure ratio-limited, the product CO_2 concentration will be limited even when the membrane selectivity is much larger than the pressure ratio. Since the pressure ratio for a typical CO_2 flue gas capture process is low, multiple membrane stages are required to generate greater than 95% pure CO_2 product (DOE's target) from flue gases using the conventional membrane process.

In the hybrid membrane/absorption process, the permeate-side partial pressure of CO_2 can be considered close to zero due to the chemical reaction of CO_2 with the absorption solvent, and this overcomes the pressure ratio problem encountered by the conventional gas membrane process. Feed compression or permeate vacuum application are not required to create the separation driving force for gas molecules to be transported through the membrane, the process selectivity for the hybrid membrane/absorption process is determined by the chemical affinity of the absorption solvent to CO_2. Therefore, high purity CO_2 product can be realized in a single stage hybrid membrane/absorption process.

Hollow fiber membrane contactors for CO_2 capture, especially the absorption process, has been an object of intense research interest because they provide a very high surface area/volume ratio for the separation to take place.[3-7] This leads to a mass transfer coefficient that is 5 to 10 times greater than that which can be achieved in a conventional tower or column with trays or packing. Thus, the use of a membrane contactor instead of a conventional amine scrubber tower leads to a much smaller space requirement. This technology is well-suited for new and existing Pulverized Combustion (PC) power plants due to the reduced footprint requirement and a much lower visual impact as well as providing more options for placement in the confines of existing plants.

Objectives

The overall objective of this program was to develop cost effective separation technology for CO_2 capture from flue gases based on a hollow fiber membrane contactor that will provide a significant reduction in the cost of separating and capturing CO_2 from flue gases. Further objectives were to develop: (1) highly chemically inert and temperature stable PEEK hollow fiber membrane for contactors, (2) an integrated membrane absorber and desorber process design, and (3) an energy efficient process for CO_2 recovery from the flue gas. These objectives were planned to be accomplished in three budget periods.

BP1 OBJECTIVES AND TASKS

BP1 Objectives

BP1 objectives include establishing the feasibility of the absorption part of the process to capture CO_2 from the flue gas, developing and down selecting the most optimal membrane configuration for scale up, optimizing module design (hollow fiber dimension and packing configuration), evaluating absorbents and down selecting most optimal absorbent for scale-up, and performing process design and economic analysis based on the test data.

BP1 Scope of Work and Tasks

In BP1 research, comprehensive approaches have been applied to enhance and optimize the overall CO_2 mass transfer coefficient including:

- Optimizing the gas side mass transfer resistance
  - This is typically low and only optimization of the size of the hollow fiber bore diameter was required to minimize the gas flow pressure drop
- Optimizing the mass transfer coefficient in the membrane
  - Maximize the membrane pore size without inducing wetting
  - Optimize the wall thickness to balance membrane mechanical characteristics and the mass transfer resistance
- Optimizing the mass transfer coefficient in the liquid phase
  - Optimize the hollow fiber winding pattern and packing density to enhance the liquid turbulence, and thus minimize concentration polarization on the liquid side
  - Optimize the packing density to minimize the liquid flow resistance, i.e. liquid side pressure drop
  - Select ideal chemical absorbent with optimal kinetic and thermodynamic characteristics.

Tasks for the BP1 research are listed in Table 5. The technical comprehensive progress for each task is summarized in the next section.

Table 5. Tasks for the BP1 research.

Task #	Task Title	Estimated Completion (months from start) award)	Responsible Individual/Organization
Task 1	Tailor membrane performance towards flue gas separation	10	Research Scientist PoroGen Corporation (PGC)
Task 2	Contactor module design optimization	12	Research Scientists GTI and PGC
Task 3	CO_2capture performance demonstration by membrane	12	Research Scientists GTI and PGC

	contactor		
Task 4	Absorbent performance evaluation	12	Research Scientists GTI
Task 5	Membrane process design and economic evaluation	12	Research Scientists GTI, PGC and APS
Task 6	Project management	12	GTI PI and PGC co-PI

BP1 TECHNICAL PROGRESS

Task 1. Tailor Membrane Performance Towards Flue Gas Separation

Description of Work

In this task hollow fiber membranes for membrane contactor with properties tailored towards flue gas treatment will be developed. Several membrane variants will be prepared and evaluated. The membrane with the most optimal performance will be down selected for module scale up. Critical objective achieved upon completion of the task: PEEK hollow fiber membrane suitable for the preparation of membrane contactor is developed.

Subtask 1.1. Nano-porous PEEK hollow fiber substrate preparation

Experimental Methods

The hollow fiber membranes are manufactured from the best in class commercial engineering plastic, PEEK. Porous PEEK hollow fibers used in preparation of super-hydrophobic membranes are manufactured by a high temperature melt extrusion process. The process is used commercially by PoroGen to prepare fluid separation membranes. PoroGen manufactures porous PEEK hollow fibers from blends of PEEK polymer with PoroGen polyether imide (PEI) following procedures described in US Patent 6,887,408 assigned to PoroGen. The simplified process schematics is illustrated in Figure 1.

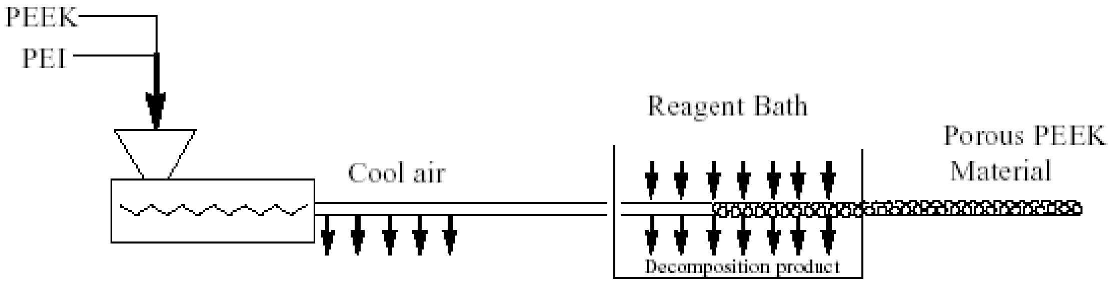


Figure 1. Process for the preparation of nano-porous PEEK materials (reagent bath monoethanolamine).

Results and Discussion

The following nano-porous PEEK hollow fiber substrate preparation parameters have been optimized for the target application:

(1) PEEK hollow fiber morphology. Optimization of porous hollow fiber preparation procedures was carried out by varying the processing conditions in the spinning line. It has been found that the processing conditions have a significant effect on the fiber stability in contact with solvents. Although hollow fibers are solvent stable in all solvents tested, some small degree of swelling can occur with the most aggressive solvents leading to the deformation in the hollow fiber cartridge that, in turn, can result in cartridge failure. Processing conditions at low temperatures resulted in hollow fiber membranes with higher levels of swelling in solvents. Optimum processing conditions have been identified with the resulting fiber exhibiting good dimensional stability in contact with solvents. The experimental variables included the precursor blend composition, spinning temperature profile, extruder screw design, spinning speed, and draw ratio. The 50/50 (weight ratios) (PEEK/PEI) blend composition was used with fiber take up speeds varied from 100 to 300ft/min.

PEEK is a semi-crystalline polymer and it is critical to maximize the degree of crystallization to obtain optimal mechanical, thermal, and chemical resistance characteristics. The processing conditions were optimized to attain degree of crystallinity of about 34% in porous PEEK hollow fibers, which is identical to the virgin PEEK material. PEEK/PEI blends can form spherulitic or lamellar morphologies that can affect final pore structure as shown in Figure 2.

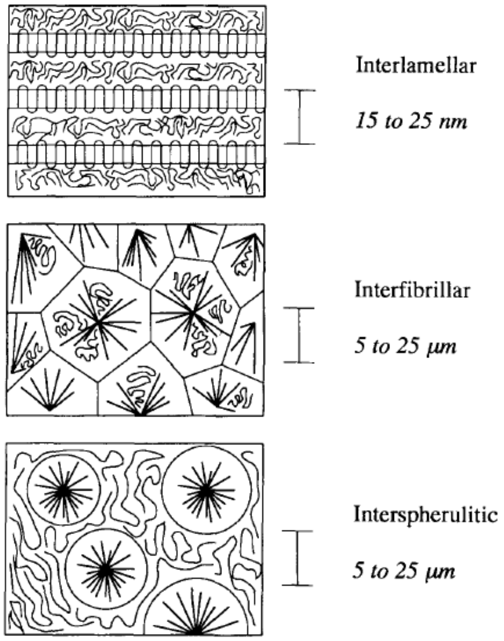


Figure 2. PEEK/PEI blend morphologies.

The processing conditions were systematically varied to obtain fiber morphology tailored towards contact with solvents (stability and non-wetting). The fiber compatibility with test solvents is discussed below.

(2) PEEK hollow fiber pore sizes. For successful operation of the contactor process, it is essential that: a) liquids are prevented from penetration into and passing through the membrane pores, and b) unimpeded transport of CO_2 from the feed to permeate side can occur. The first requirement can be satisfied if the membrane surface is sufficiently oleophobic (very low surface energy) such that no absorption solutions can wet out and wick by capillary forces into the pores (requiring a contact angle between the liquid and solid phases of greater than 90°), and the surface tensions of the liquid phases are sufficiently high that the capillary penetration pressure of liquid into a pore is well in excess of the maximum pressure difference across the membrane that might be encountered in the operation. Liquid penetration into the pores will lead to a dramatic decrease in mass transfer coefficient. The critical penetration pressure is defined by the classical Kelvin Equation:

$$\Delta p = 2\gamma \cos \theta / r \qquad (1)$$

where Δp is the pore-entry pressure, γ is the liquid surface tension, θ is the contact angle, and r is pore radius. The higher the surface tension of the liquid, the larger the contact angle (in excess of 90°), and the smaller the pore radius, the greater the intrusion pressure. There is a delicate balance between pore wettability and membrane mass transfer resistance. In order to have an unimpeded gas transport, the larger the pore size the better. On the other hand, in order to improve the non-wettability of the hollow fiber, the smaller the pore size the better. A delicate balance has to been found by extensive experimental work.

Three types of porous PEEK hollow fiber membranes with different average pore size were prepared. The pore size was affected by polyimide PoroGen selection and membrane preparation conditions. The average pore sizes based on the permporosimetry was 10 nm, 75 nm and 380 nm, respectively.

The nano-porous PEEK hollow fibers developed for the contactor application exhibit high gas permeation rates, which is a critical requirement for the preparation of high flux contactors.

Nano-porous PEEK hollow fibers with an asymmetric pore morphology, i.e. smaller diameter surface pores (1-5 nm) and larger size interior pores (15-50nm) were prepared. The surface layer with the smaller size pores was about 1 micron thick. The asymmetric structure enables preparation of super-hydrophobic membranes with improved non-wetting characteristics while maintaining high gas permeance. Hollow fibers with nanometer size surface pores are expected to exhibit Knudsen flow characteristics (gas flux is inversely proportional to the square root of the molecular weight) consistent with 1-5 nm size surface pores. Asymmetric PEEK hollow fibers in fact did exhibited gas separation factors consistent with the theoretic Knudsen flow.

The nano-porous PEEK hollow fiber substrates developed for the contactor application exhibit high gas permeation rates, which is a critical requirement for the preparation of high flux contactors. The gas permeance (O_2, N_2, and CO_2) of a typical asymmetric hollow fiber with 100 micron thick porous wall is in the range of 1000 to 3000 GPU (1 GPU = 1 x 10^6 cm^3 (STP)/(cm^2·s·cm Hg)).

(3) PEEK hollow fiber dimensions. Post-combustion CO_2 capture process conditions require development of hollow fibers with large diameter bore dimensions to minimize the feed side pressure drop. Even a small increase in the gas side pressure drop can introduce a significant energy penalty on CO_2 capture process. The standard fiber dimensions manufactured by PoroGen for gas separation applications were modified to meet flue gas treatment needs. The fiber ID must be increased to circa 25-20 mil ID to prevent excessive parasitic pressure drop when flowing flue gas through membrane contactor. Our target gas side flow pressure drop is less than or equal to 1 psi. To address this target objective, new hardware was procured, installed and debugged that included spinnerets and take up equipment. The initial spinning runs were highly successful. Precursor PEEK hollow fibers were spun with 30 X 25 mil outside diameter, OD, X inside diameter, ID, dimensions. The hollow fibers were treated to impart super-hydrophobic surface characteristic and underwent initial testing at PoroGen. The hollow fibers exhibited good mechanical characteristics and gas permeance. The large bore hollow fibers were successfully wound into 2-inch test modules. Laboratory scale modules were manufactured and provided to GTI for testing.

Subtask 1.2. Surface modification

Experimental Methods

In this subtask, the porous PEEK hollow fibers with graft perfluoropolymer surface were prepared. The super-hydrophobicity of the porous PEEK membrane was generated by surface modification with a functional perfluoro oligomer, such as PFC 504A/coE5 (containing reactive epoxy groups), commercially available from Cytonix Corporation. Prior to grafting with perfluoro oligomer the surface of the porous PEEK was first functionalized with ~ OH groups by reacting ketone groups in PEEK polymer backbone with monoethanolamine during the Reactive PoroGen Removal (RPR) process. The functionalized porous PEEK was prepared in a single step RPR process during porous PEEK fiber preparation following the teachings of US Patent 7,176,273. Following porous structure formation the functional ~ OH groups are reacted with perfluoro oligomers to form the oleophobic graft surface. Critical objective achieved upon completion of the task: PEEK hollow fiber membrane suitable for the preparation of membrane contactor is developed.

Results and Discussion

The hydroxyl groups as shown in Figure 3 are utilized as the anchor points for the subsequent grafting reaction with functional perfluoro hydrocarbon oligomer to render the pore surfaces oleophobic. The functional ~ OH groups are reacted with functional hydrophobic oligomers to form a hydrophobic graft surface. The grafting reaction with perfluorinated oligomer is illustrated schematically in Figure 4. Note that in Figure 4, Rf is a perfluoro hydrocarbon radical.

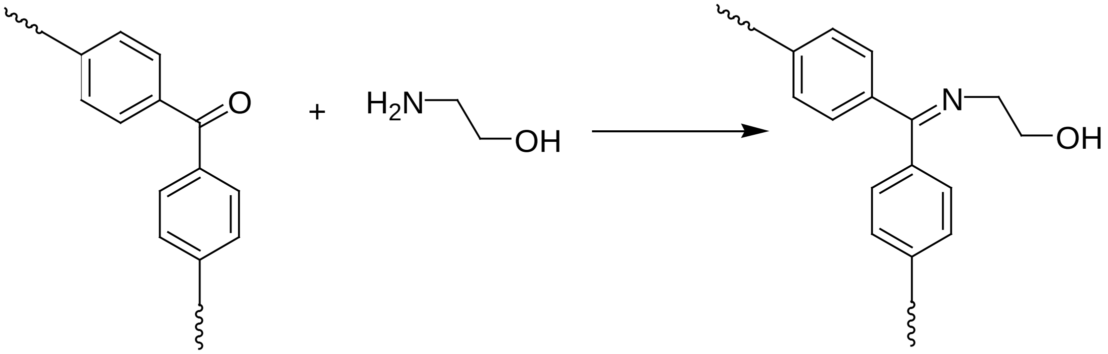


Figure 3. Surface functionalization of porous PEEK with ~ OH groups during preparation of porous PEEK hollow fiber.

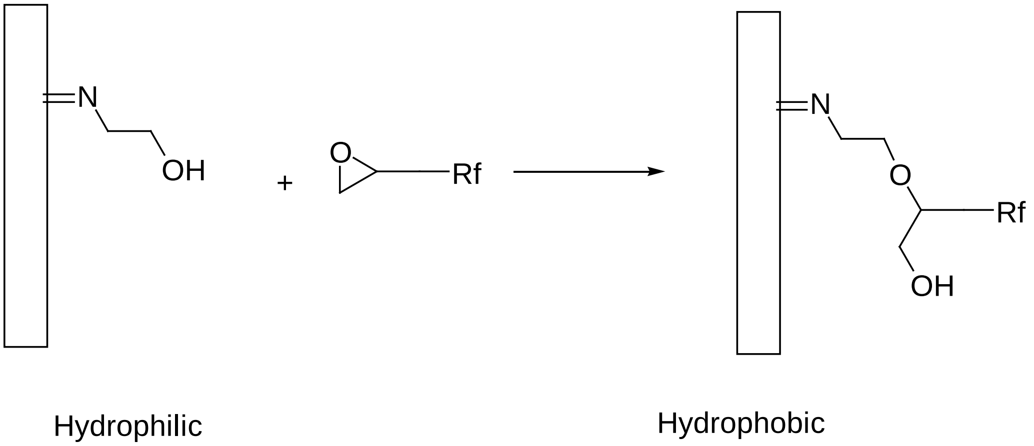


Figure 4. Preparation of hydrophobic PEEK membranes.

Porous PEEK membranes are super-hydrophobic and do not wet out in contact with solvent systems. Porous PEEK membranes wet out with water at pressure above several hundred psig and with isopropanol (IPA) at pressure above 20 psig. The super-hydrophobicity is due to a combination of nanometer size surface pores, exceptionally uniform pore size distribution, and the perfluoro-hydrocarbon surface chemistry. The surface pore diameter is in the range of 1 to 5 nm. The combination of nanometer size pores and perfluoro-hydrocarbon surface chemistry generate the super-hydrophobicity via so called “Lotus effect.” [8] The high contact angle of and the non-wetting of porous PEEK membrane surface by solvents (ethanol liquid drop) is shown in Figure 5.

Figure 5. High contact angle and the non-wetting properties of porous PEEK membrane surface.

Membrane non-wetting characteristics were evaluated extensively as a function of membrane preparation methodology and morphology. Several membrane variants showed good oleophobic (non-wetting) characteristics and did not wet out after exposure to MDEA solutions even at differential pressures as high as 60 psig (well in excess of expected field process conditions). The wettability tests were extended to include longer term exposure to MDEA solutions (≥100 hours), exposure to MDEA solutions at higher temperatures (50-60°C range) and exposure to MDEA solutions at a high liquid and gas pressure. Initial wettability tests were carried out by maintaining the liquid at elevated pressure and the gas at atmospheric pressure.

We have concluded that all PEEK based membranes tested did not wet out by water or MDEA/water solvent system. The leakage if any has developed only at high pressure differentials. The non-wetting behavior was exhibited by all types of membranes tested. However, duration of the test was relatively short – typically 24 hours and was carried out at room temperature. The test duration was increased and membranes were tested at higher temperatures as well. The test result showed that temperature had no effect on wetting characteristic (duration of test 24 hours). However, longer term duration showed membrane wet out for several membranes and not for others. The liquid collected from leaking membranes was analyzed for composition. The composition was identical to the liquid feed composition and this ruled out vapor condensation. The liquid breakthrough thus was assigned to wet out. The test conditions were "accelerated" and the "leaked" membranes were ruled out from use.

Task 2. Contactor Module Design Optimization

Description of Work

In this task the contactor module design will be optimized towards flue gas CO_2 separation application. A four port module design will be utilized (two ports for gas introduction and removal and two ports for liquid introduction and removal). The module will be constructed employing computer controlled helical winding process. Winding equipment currently in place at PGC will be utilized. The structured hollow fiber packing will be optimized. The optimization parameters will include wind angle, wind phase and packing density. The pressure drop will be minimized while optimizing mass transfer coefficient. Critical objective achieved upon completion of the task: Contactor module tailored towards flue gas application is designed.

Experimental Methods

Membrane modules for laboratory scale tests have been prepared. The hollow fiber membrane modules were of the four port counter-current flow design. The contactor module design is directed to the counter-current flow configuration which is thermodynamically the most efficient. The design further takes into account gas side and liquid side pressure drops. The flow configuration and the general layout are shown in Figure 6.

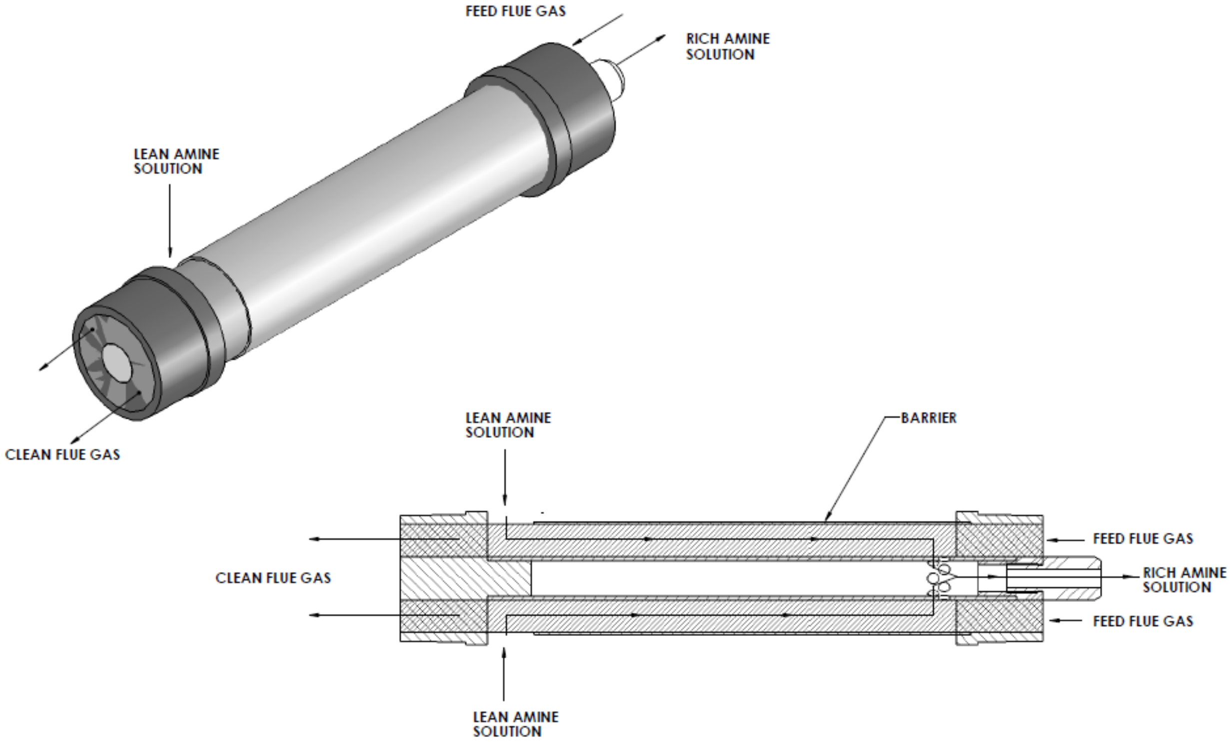


Figure 6. Laboratory scale contactor module design.

The hollow fiber cartridges were formed by a computer-controlled helical winding. The cartridge size was 2-inch diameter by 12-inch or 60-inch long and contained about 20 ft^2 of membrane area (as measured on the outside diameter of the fibers). The cartridge was housed in a pressure vessel and sealed with O-rings.

Results and Discussion

Membrane module design and construction have significant impact on the overall gas mass transport coefficient by minimizing liquid side resistance, maximizing the driving force and increasing the liquid side mass transport coefficient. For the conventional membrane modules designed for filtration applications, the flow conditions on the shell-side of the membrane can be generally ill-defined. However, for the membrane gas absorber the flow conditions must be well defined on both sides of the membrane to achieve good mass transfer. Important design features of a module include the regularity of fibers (poly-dispersity and spatial arrangements of fibers), packing density and the relative flow directions such as parallel, i.e., concurrently, counter-currently, and cross-flows of the two phases. The liquid flow can either be on the bore or shell sides. PoroGen's hollow fiber membrane module has been designed to operate with liquid on the shell side and gas flow on the bore side. A general empirical correlation for parallel-flow hollow fiber membrane contactors can be expressed as :

$$Sh \propto f(\varphi)(\frac{d}{L})^{\alpha} \mathrm{Re}^{\beta} Sc^{\gamma} \qquad (2)$$

where Sh is the Sherwood number, φ is the packing density; α, β, and γ are constants; Sc is the Schmidt number; and Re is the Reynolds number.

The following key design elements and development work have been employed or carried out in this task: (a) a 4-port counter current flow design, enabling optimum driving force for the CO_2 absorption; (b) computerized structural packing minimizing the absorption liquid malflow; (c) optimum fiber packing density to minimize the liquid pressure drop and optimize the liquid flow turbulence; (d) optimized winding patterns to promote the liquid side gas mass transport; and (e) curved hollow fiber with enhanced gas phase mass transport.

Happel's free surface model can be used to characterize the outer fiber velocity profile, which is related to the liquid phase mass transfer. The laminar parabolic velocity profile in the outside of fibers is:

$$\mathbf{V}_{z\text{-shell}} = 2\,u \left[1 - \left(\frac{r_o}{r_e}\right)^2\right] \frac{(r/r_e)^2 - (r_o/r_e)^2 + 2\ln(r_o/r)}{3 + (r_o/r_e)^4 - 4(r_o/r_e)^2 + 4\ln(r_o/r_e)} \qquad (3)$$

Where u, r, r_3, r_2 represent the average velocity, radial coordinate, radius of free surface and fiber outer radius, respectively.r_3 is defined as:

$$r_3 = \left(\frac{1}{1-\varnothing}\right)^{1/2} \cdot r_2 \qquad (4)$$

in which $\varnothing$ is the volume fraction of the void.

The hollow fiber placement within the module was controlled through computer controlled helical fiber winding. The process generates a structured packing configuration minimizing channeling, bypassing, and minimizing concentration polarization. A wound cartridge with a controlled uniform structured packing is shown in Figure 7. The hollow fibers are arranged in a helical path, with the axis of the fibers running confluent to the principle direction of fluid flow. To enable the thermodynamically most efficient counter-current flow, the packing density in the cartridge must be uniform. Also, flow bypassing, and entrance and exit effects must be minimized. The fiber packing density and packing uniformity was controlled to ensure an optimal flow distribution with minimal pressure drop on both the feed and the permeate sides.

Figure 7. Helically wound structured hollow fiber cartridge.

Several methodologies have been utilized to modify the membrane cartridge packing density and winding patterns: different winding angles, different advancing gaps, and different number of filaments in the tow (such as 2, 4, 8, etc.).

The initial test results carried out at GTI indicated the presence of a significant resistance on the liquid side of the membrane contactor as well as a membrane resistance that reduced the overall mass transfer coefficient. The resistance is exacerbated by the low partial pressure of CO_2 in the flue gas (low driving force) that increases the concentration polarization. To address the problem, modifications to winding procedures were introduced that reduced liquid side resistance. Fiber spacing was increased and winding process was transitioned to placing fewer fibers in the tow per run. Initial modules were produced with placing a larger number of fibers per run. We also modified winding computer programs and the winding processes to decrease liquid side resistance further.

Tube sheets are a critical structural component of membrane contactor module. PoroGen manufactures PEEK membrane modules for aggressive solvent applications and high temperature gas separation (up to 150 °C). Epoxy materials for tube sheet preparations used in these applications have been tested extensively. PoroGen has selected several candidate epoxy materials from existing library for initial evaluation of compatibility with amine solvent system. Several tube sheet epoxy systems were tested against 50/50 MDEA/H_2O solution for 2700 hours at 70 °C. The epoxies were E8, NV75, R3 and C-com. The initial evaluation consisted of measuring weight change (loss or gain) gravimetrically. The best epoxy was E8 that had less than 1% change after exposure (increase in weight) as shown in the Table 6. Thus, E8 was selected for membrane absorber.

Table 6. Epoxy exposure test results.

Epoxy	E8	NV75	R3	C-Com
Weight change, %	0.62	1.25	4.8	2.3

Exposed to 50/50 by weight MDEA/H_2O solution for 2,700 hours at 70 °C

Task 3. CO_2 Capture Performance Demonstration by Membrane Contactor

Subtask 3.1 Membrane test unit construction

Description of Work

In this subtask, a laboratory test unit will be constructed. The contactor laboratory test system available at GTI will be modified to conduct flue gas treatment tests while the new unit is under construction. The test unit will allow for the evaluation of CO_2 separation performance by membrane contactors equipped with PEEK hollow fiber membranes. Water vapor saturated carbon dioxide/nitrogen gas mixtures will be utilized as a simulated flue gas feed composition. The test unit will be used to support membrane development, expedite absorbent selection and for absorption process optimization. Critical objective achieved upon completion of the task: Capability of the membrane contactor equipped with novel membranes to separate CO_2 from simulated flue gas is demonstrated.

Experimental Method

Work was completed to modify the existing test unit (Figure 8) and a new additional test unit was built and put into operation under the appropriate test conditions for flue gas carbon capture. A P&ID (piping and instrumentation diagram) of the new test unit is presented in Figure 9.

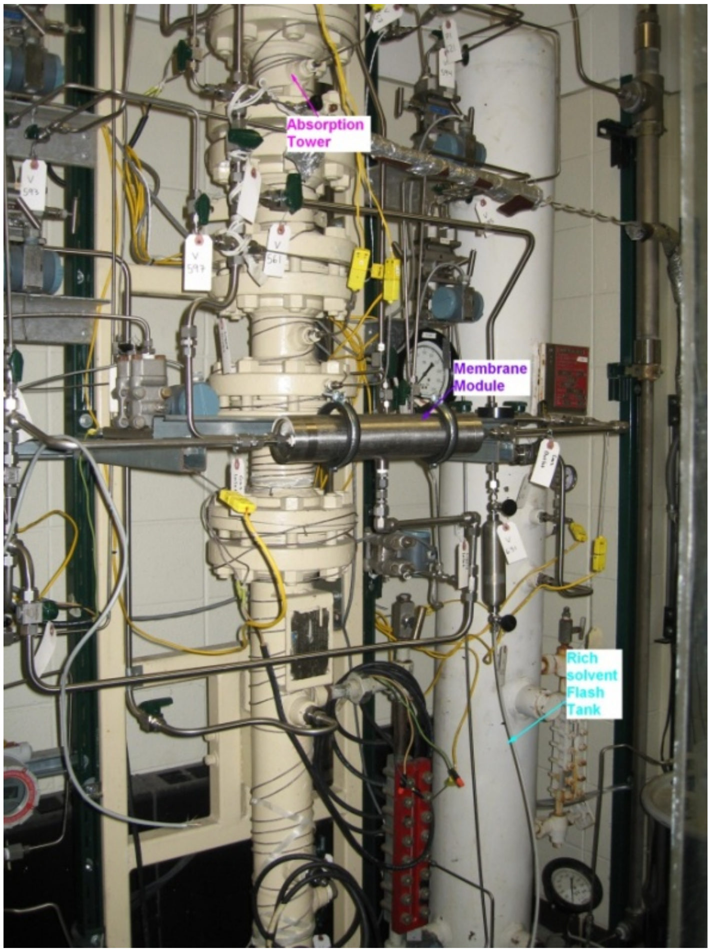


Figure 8. Picture of the modified existing membrane test unit.

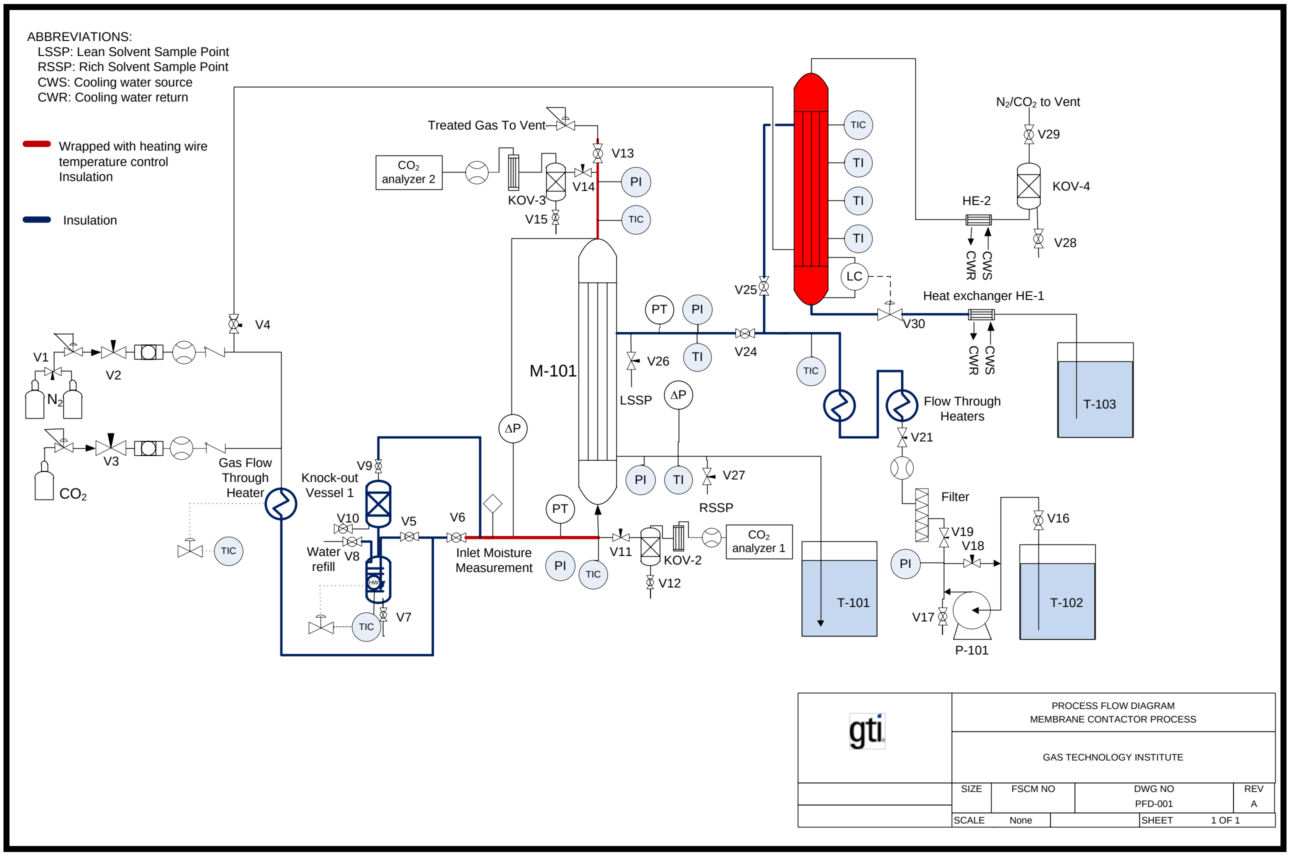


Figure 9. P&ID of the new post-combustion membrane contactor test apparatus.

Results and Discussion

Photo of the new test unit is shown in Figure 10. The photo of the process control and data acquisition system is shown in Figure 11. This unit has the following characteristics:

- Designed to a scale representing 25 kW equivalents of CO_2 capture (0.5 tons/day)
- Skid footprint: 12' x 5.5' x 12'
- Use of National Instrument process control and data acquisition with safety guards on temperature, pressure, and liquid levels
- The unit is used for BP1 for absorption testing. A desorption tower with packed column is used for solvent regeneration.
- In BP2, a membrane contactor desorber system is expected to be added to the back side of the skid.

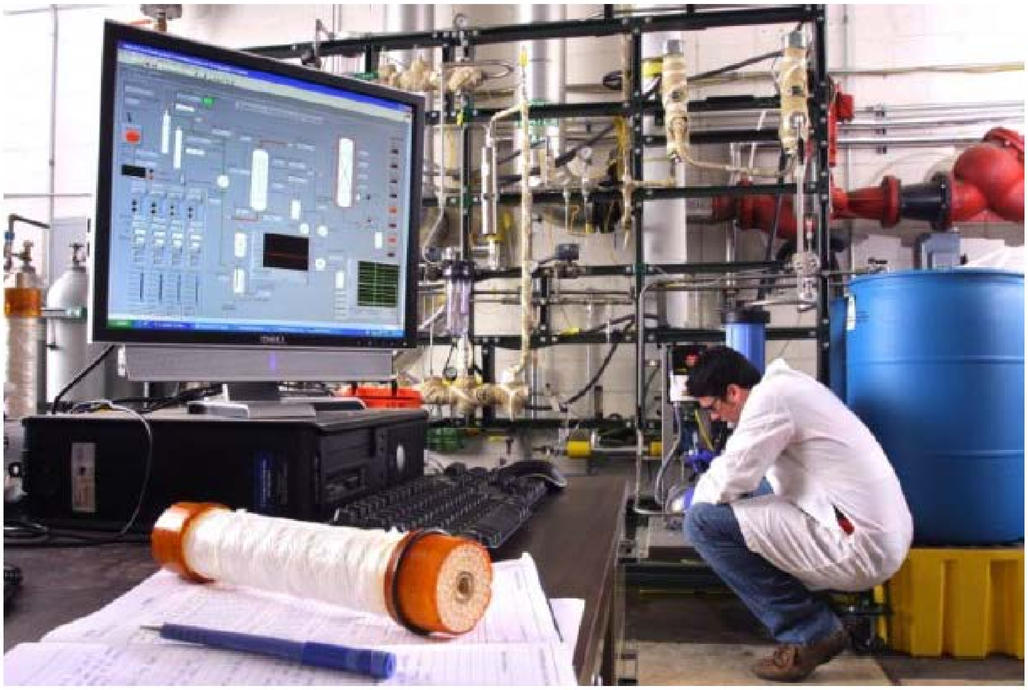
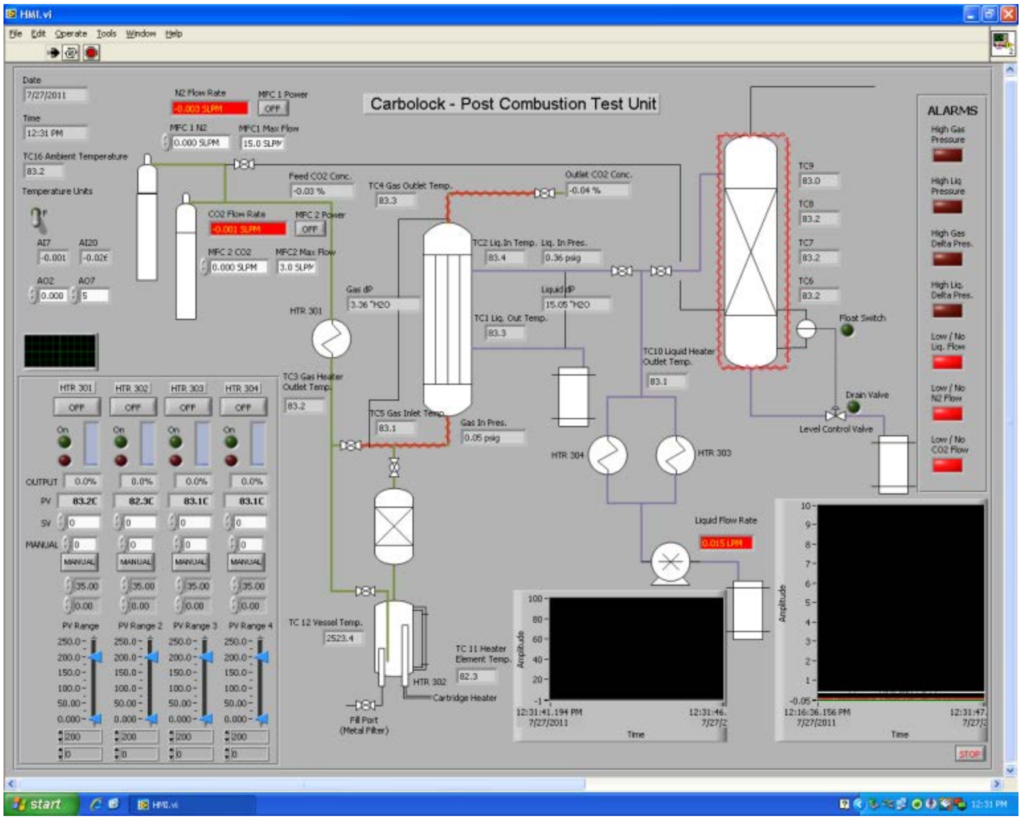


Figure 10. Photograph of the new post-combustion membrane contactor test apparatus.



Date: 7/27/2011

Time: 12:31 PM

TC16 Ambient Temperature: 83.2

AI7: -0.001

AI20: -0.02€

AO2: 0.000

AO7: 5

N2 Flow Rate: -0.003 SLPM

MFC 1 N2: 0.000 SLPM

MFC1 Max Flow: 15.0 SLPM

CO2 Flow Rate: -0.001 SLPM

MFC 2 CO2: 0.000 SLPM

MFC2 Max Flow: 3.0 SLPM

Feed CO2 Conc.: -0.03 %

TC4 Gas Outlet Temp.: 83.3

Outlet CO2 Conc.: -0.04 %

TC2 Liq.In Temp.: 83.4

Liq. In Pres.: 0.36 psig

Gas dP: 3.36 "H2O

Liquid dP: 15.05 "H2O

TC1 Liq. Out Temp.: 83.3

TC3 Gas Heater Outlet Temp.: 83.2

TC5 Gas Inlet Temp.: 83.1

Gas In Pres.: 0.05 psig

TC10 Liquid Heater Outlet Temp.: 83.1

TC9: 83.0

TC8: 83.2

TC7: 83.2

TC6: 83.2

Liquid Flow Rate: 0.015 LPM

TC 12 Vessel Temp.: 2523.4

TC 11 Heater Element Temp.: 82.3

	HTR 301	HTR 302	HTR 303	HTR 304
	OFF	OFF	OFF	OFF
OUTPUT	0.0%	0.0%	0.0%	0.0%
PV	83.2C	82.3C	83.1C	83.1C
SV	0	0	0	0
MANUAL	0	0	0	0
	35.00	35.00	35.00	35.00
	0.00	0.00	0.00	0.00
	PV Range	PV Range 2	PV Range 3	PV Range 4
	200	200	200	200
	0	0	0	0

Figure 11. Photograph of the process control and data acquisition for the membrane skid.

Subtask 3.2 CO_2 capture performance demonstration

Description of Work

CO_2 capture from a synthetic flue gas by the membrane contactor (module size circa 20 ft^2) will be measured. The feed gas will be comprised of a CO_2/N_2 mixture saturated with water vapor. In advanced stages of experiments, the feed gas will include contaminant components such as oxygen, SO_x, and NO_x. The tests will assess the membrane's ability to block contaminants from reaching the solvent media. Two solvent systems, promoted hot carbonate and MDEA, will be evaluated initially as absorbents while the contactor membrane is tested in the absorption mode. The performance will be measured at isothermal conditions at solvent temperatures of 20 °C, 45 °C and 60 °C. The gas flow will be measured utilizing mass flow-meters. The separation performance will be assessed by measuring gas component concentrations (CO_2, N_2, and water vapor) in the feed and the retentate gases utilizing gas chromatography (GC) or Infrared CO_2 analyzers. The absorption process parameters will be optimized in terms of solvent flow, pressure drop, temperature and CO_2 loading. A factorial design of experiments will be used to screen the variables.

Experimental Methods

Several 2-inch diameter by 12-inch long PEEK membrane modules were received by GTI. Test plan for Subtask 3.2 with MDEA and carbonate solvents were developed and communicated with DOE program manager and summarized in Table 7.

Table 7. General test parameters for laboratory tests.

Parameter	Condition
Lean solvent CO_2 loading	0.02 mol/mol
Gas feed	Simulated flue gas CO_2 inlet concentration: 13 to 16 mol% (balance N_2)
Gas inlet temperature	100 to 135°F
Pressure drop	To be measured (both gas and solvent sides)
Membrane contactor surface area	~10 ft^2
Inlet gas pressure	< 6 psig
Moisture	Saturation

Results and Discussion

Tests with 50 wt% MDEA solvent were conducted using simulated flue gas. The test results are show in Table 8. The low volumetric mass transfer coefficients and CO_2 permeances suggested that the mass transfer coefficient was low. Our analysis indicates that the unexpected low mass transfer coefficient was mainly due to: 1) low membrane intrinsic CO_2 permeance (for example, the membrane intrinsic CO_2 permeance was only ~ 160 GPU for module 2PG271), and 2) the high liquid side resistance stemming from concentration polarization. We have since started to improve membrane intrinsic CO_2 permeance and reduce liquid side resistance.

Table 8. CO_2 capture test results for laboratory tests.

Module	Gas flow rate, SCFH	CO_2 removal,%	K_Ga_v, 1/s	CO_2 permeance, GPU	Solvent
2PG249	14.5	43.8	0.20	100	50 wt% MDEA
2PG249	6.8	67.2	0.18	93	50 wt% MDEA
2PG249	6.5	55.4	0.13	64	50 wt% MDEA
2PG271	51.3	31.3	0.38	175	20 wt% K_2CO_3
2PG271	15.0	53.7	0.27	131	20 wt% K_2CO_3
2PG271	7.6	69.3	0.22	110	20 wt% K_2CO_3
2PG271	7.6	65.1	0.19	94	15% K_2CO_3/ 8%DEA
2PG271	7.6	68.9	0.21	106	15% K_2CO_3/ 8%DEA

By modification and optimization of membrane synthesis, we have achieved membrane intrinsic CO_2 permeance of 1,100 GPU for module 2PG285. This permeance exceeded the initial target for commercial performance of 1,000 GPU.

Membrane module 2PG285 was tested for CO_2 capture with 20% K_2CO_3/8%DEA. To overcome liquid side mass transfer resistance, winding patterns for module 2PG285 had been modified. We also used a slightly higher solvent temperature to improve mass transfer. As shown in Table 9, we have achieved close to 90% CO_2 removal in one stage with CO_2 permeance as high as 762 GPU. The volumetric mass transfer coefficient was as high as 1.35 $(sec)^{-1}$, exceeding the milestone target of 1.0 $(sec)^{-1}$.

Table 9. Membrane contactor testing results using module 2PG285 and K_2CO_3 solvent.

Solvent temperature, °F	Total gas flow SCFH	CO_2 removal, %	K_Ga_v, $(sec)^{-1}$	CO_2 permeance, GPU
152.4	7.4	87.4	1.35	764
155.4	7.4	87.3	1.35	762

Task 4. Absorbent Performance Evaluation

Description of Work

Two solvent systems will be evaluated. The initial solvent systems were chosen to minimize energy of regeneration and solvent degradation while optimizing CO_2 loading. The two solvent systems are promoted hot carbonate and tertiary amine (MDEA). The mass transfer coefficients for both solvent systems will be measured and optimal system will be down selected. Critical objective achieved upon completion of the task: Optimal solvent system selected for bench-scale tests.

Experimental Methods

In conjunction with Subtask 3.2, tests were conducted to determine mass transfer coefficient with chemical solvents. We have initially investigated four solvents: diethanolamine (DEA), methyldiethanolamine (MDEA), activated MDEA (aMDEA), and aqueous activated potassium carbonate (K_2CO_3). A center point design of experiment test matrix has been used for the measurements.

The membrane modules used in this task were usually with an OD of 17-18 mil and ID of 8-12 mil. In a separate experiment, we tested a module (2PG287) made of larger diameter fibers. The gas side pressure drop as a function of gas flow rate was investigated for this module.

In addition to N_2, H_2O, CO_2, flue gases have contaminants, such as O_2, NO_x, SO_x, and fine particulates; the effects of O_2, NO_x and SO_x were investigated in this task. We tested the following two simulated flue gas feed mixtures:

a) 145 ppmv SO_2, 3.06% O_2, 14.96% CO_2, and balance N_2,
b) 66 ppmv SO_2, 3.27% O_2, 12.98% CO_2, and balance N_2.

Results and Discussion

1. Absorbent performance evaluation

Table 10 shows the module 2PG285 test results with MDEA, DEA, and aqueous K_2CO_3 solvents. Among these solvents, both DEA and promoted potassium carbonate solvents are very promising. The CO_2 permeances measured from contactor testing range from 600 to 770 GPU, close to the membrane intrinsic CO_2 permeances, indicating a low liquid-side transport resistance. We have also obtained 90% CO_2 removal from simulated flue gas in a single stage during these tests. These results indicate that for solvents with higher reaction rates, liquid-side resistance diminishes and membrane resistance dominates. Further improvement in mass transfer for these solvent systems has to come from intrinsic membrane resistance reduction.

Table 10. Module 2PG285 test results with various solvents.

Solvent	Total gas flow SCFH	CO_2 removal, %	K_Ga_v, 1/s	CO_2 permeance, GPU
40 wt% MDEA	2.1	74.8	0.395	207
40 wt% MDEA	2.1	65.4	0.304	159
40 wt% MDEA	5.7	30.1	0.264	139
40 wt% MDEA	5.7	52.2	0.538	282
30 wt% DEA	5.5	79.6	1.194	629

30 wt% DEA	5.5	80.5	1.230	646
30 wt% DEA	2.1	96.6	1.273	667
30 wt% DEA	2.1	97.2	1.421	746
30 wt% DEA	2.9	92.6	1.139	599
30 wt% DEA	2.9	93.1	1.178	619
20% K_2CO_3/ 8% DEA	7.4	87.4	1.35	764
20% K_2CO_3/ 8% DEA	7.4	87.3	1.35	762

The CO_2 permeance measured from contactor testing with MDEA solvent was equivalent to about only 200 GPU. The intrinsic permeation rate of the 2PG285 membrane for CO_2 is about 1,100 GPU for pure gas. This indicates that the unexpected low mass transfer coefficient for MDEA is mainly due to the liquid-side resistance stemming from concentration polarization. To overcome the high liquid-side mass transfer resistance, we have introduced addition of promoters to the solvent to improve kinetics (i.e. aMDEA solvent was formulated). By using aMDEA, the measured equivalent CO_2 permeances in contactor testing was close to the membrane intrinsic CO_2 permeance. For example, for module 2PG286 with intrinsic CO_2 permeance of 800-1000 GPU, the calculated CO_2 permeance in membrane contactor with aMDEA solvent was 970 GPU at 90% CO_2 removal, as shown in Table 11. This is a good indication that there is little concentration polarization. In addition, winding patterns have been modified to reduce concentration polarization. However, with further improvement in membrane CO_2 permeance, concentration polarization may come back into play. Further modification of winding procedures may become necessary. The design of experiment test matrix results also indicate that for some of the runs, we have achieved our BP1 technical targets for 90% CO_2 removal in single stage, ≤ 2 psi gas side pressure drop, and ≥ 1 $(\text{sec})^{-1}$ mass transfer coefficient by using aMDEA solvent.

Table 11. Module 2PG286 test results with aMDEA solvent.

Order of data point	Gas flow rate, SLPM	CO_2 removal, %	CO_2 permeance GPU	Gas side ΔP, psi	K_Ga_v, 1/s
1	3.3	92	971	1.8	1.7
2	3.4	90	969	1.6	1.7
3	3.3	90	948	1.7	1.7
4	3.3	92	983	1.7	1.7
5	9.9	53	1063	3.6	1.9
6	9.9	49	943	3.6	1.7
7	6.6	68	1102	3.4	1.9
8	6.6	68	1092	3.5	1.9
9	10.0	53	1060	3.6	1.9
10	5.1	78	1066	2.7	1.9
11	3.3	90	950	1.8	1.7
12	5.1	78	1073	2.7	1.9
13	5.1	76	1027	2.8	1.8

14	5.1	78	1067	2.7	1.9
15	5.1	79	1084	2.8	1.9
16	6.6	57	863	3.2	1.5
17	6.6	67	1082	3.3	1.9
18	5.1	74	990	2.6	1.8
19	5.1	69	869	3.0	1.5
20	5.1	62	743	3.3	1.3
21	3.3	64	531	2.3	0.9
22	6.6	38	495	3.6	0.9
23	6.6	56	790	3.6	1.4
24	3.3	83	796	2.3	1.4
25	3.4	87	905	1.8	1.6
26	5.0	66	813	3.0	1.4

2. Test results for module made of larger diameter fibers

Another approach to overcome concentration polarization and reduce gas side pressure drop is to use larger diameter hollow fibers in membrane module. Larger diameter hollow fibers were manufactured and modifications to winding patterns were made to accommodate the increased dimensions. The fibers in module 2PG287 had larger OD and ID. Modules with increase fiber size were tested for CO_2 capture. The 90% CO_2 capture was obtained. Figure 12 shows the gas side pressure drop as a function of gas flow rate. Further analysis indicates that gas side pressure drop would be less than 2 psi when using this type of fiber for the construction of 8-inch-diameter, 60-inch-long commercial size modules for field testing.

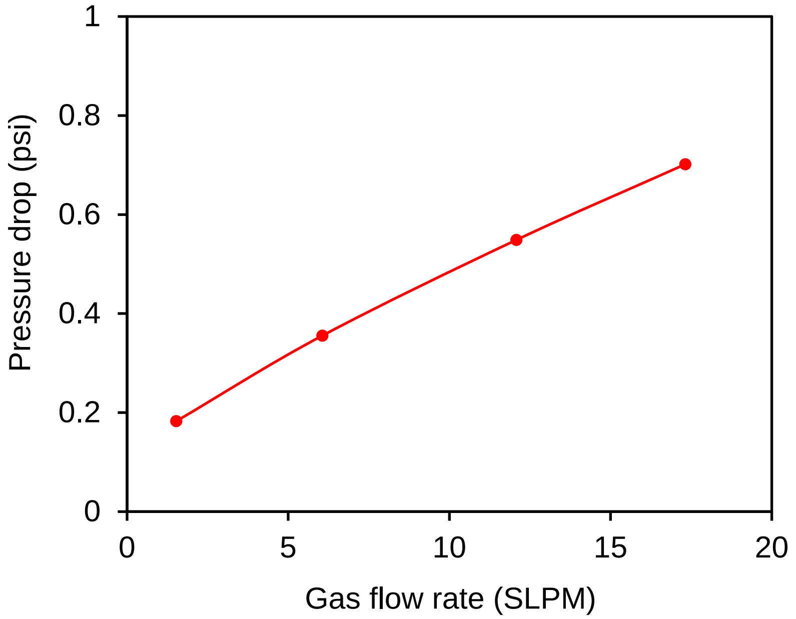


Figure 12. Gas side pressure drop as a function of gas flow rate for module 2PG287.

3. Effects of flue gas contaminants

To determine effect of potential contaminants typically present in the flue gas the feed gas composition was modified to include SO_2 and O_2. Contactors were tested with feed gas that contained 145 ppmv SO_2, 3.06% O_2, 14.96% CO_2, and balance N_2. Membrane contactor module with intrinsic CO_2 permeance of 800 GPU was utilized and aMDEA was utilized as a solvent. At steady state, the outlet gas composition was 1.46% CO_2, 22 ppmv SO_2, 3.5% O_2, and balance N_2. The measured membrane contactor performance is shown in Table 12.

Table 12. Contactor module performance with feed containing O_2 and SO_2.

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

In a separate test the contactor module performance was evaluated with feed gas containing 66 ppmv NO_2, 3.27% O_2, 12.98% CO_2, and balance N_2. Membrane contactor module with a lower intrinsic CO_2 permeance of 580 GPU was utilized and aMDEA was utilized as a solvent. At steady state, the outlet gas composition was 1.35% CO_2, 6.4 ppmv NO_2, 2.95% O_2, and balance N_2. The measured membrane contactor performance is shown in Table 13.

Table 13. Contactor module performance with feed containing O_2 and NO_2.

CO_2 removal	91%
Mass transfer coefficient, $(sec)^{-1}$	0.83
Gas side ΔP, psi	1.2

Task 5. Membrane Process Design and Economic Evaluation

Description of Work

Preliminary flue gas separation process design based on the novel membrane contactor will be carried out and the process economics evaluated. The analyses will provide for initial design of process conditions that in turn will provide feedback for the hollow fiber module flow dynamics requirements. The flow dynamic's modeling output will provide input for module design, i.e. selection of hollow fiber dimensions and fiber packing density. The thermodynamically most efficient counter-current flow configuration will be utilized. The initial flue gas treatment economics will be performed by GTI and Aker Process Systems (APS). Critical objective achieved upon completion of the task: A preliminary process for CO_2 capture from flue gas by novel membrane contactor has been developed and initial process economics evaluated.

Economic Evaluation-Method

Initial process economics modeling was carried out assuming the substitution of a membrane contactor for CO_2 absorption step only, while still using a packed column for solvent regeneration.

Design Basis

- We have used the cost estimates for the DOE Case 9 (Cost estimation with no CO_2 capture) and Case 10 (Cost estimation with CO_2 capture using MEA plant) [9] as the Base Case that represents current benchmark technology (monoethanolamine (MEA) plant) status for electric power generation with CO_2 removal (including transport, storage and monitoring) from flue gas generated in a nominal 550 MW_e pulverized coal boiler. These scoping economic numbers for the membrane contactor technology, based on two different solvents (namely, an activated K_2CO_3 solvent, and an aMDEA solvent), were developed to estimate economic advantages of a hybrid membrane absorption/conventional regeneration process over the DOE Case 10. The experimental CO_2 flux data at 90% CO_2 removal obtained for these solvents were used in our cost estimates.
- The total CO_2 removal rate for these designs cases is about 626.2 metric tons/hour, corresponding to 90% CO_2 capture from a nominal 550 MWe, subcritical pulverized coal power plant.

Economic Evaluation-Results and Discussion

Estimates on CAPEX

Design changes for the membrane contactor cases due to differences in reboiler heat duties differences in the reboiler heat-duty requirements for the regeneration of CO_2-rich solvent would lead to changes in (i) net electric power generation and (ii) capital costs for the reboiler as well as for the LP steam turbine units. The estimated reboiler heat duties per g-mol of CO_2 for the three design cases are:

Solvent type	MEA used in DOE Case 10	Activated K_2CO_3	aMDEA
Heat duty, Btu/lb CO_2	1,521[a]	523[b]	1,187[c]

a. Estimated from the total LP steam need in the Regenerator Unit
b. For the K_2CO_3-based Enhanced LoHeat Benfield process, [10] this value has been reported as 18,000-25,000 Btu/lbmol CO_2; we have assumed a value of 23,000 Btu/lbmol CO_2
c. Estimated as the sum of the (i) heat of desorption (14.0 kcal/gmol), (ii) heat of vaporization of water (10.3 kcal/gmol) and (iii) sensible heat required to bring the rich solution to the temperature of the stripper (4.7 kcal/gmol)

The major changes for the two membrane contactor design cases are:

- For the membrane contactor application using activated K_2CO_3, there would be significant reduction in the usage of low pressure (LP) steam for the solvent regeneration unit. For the DOE Case 10, total LP steam flow (at 168 psia and 743°F) to the amine unit is about 1.995

million lb/hr. For the membrane contactor case, the total LP steam required would be about 685,900 lb/hr, which would result in an excess LP steam of about 1,309,058 lb/hr. This extra steam can be used in the existing LP steam turbine to generate about 117,400 kW of additional electric power. In this context, we would need to correspondingly increase the CAPEX (estimated for the DOE Case 10) of the turbine system. This reduction in steam usage would also reduce the CAPEX of the reboiler unit of the stripper system.

- For the membrane contactor design case using the aMDEA solvent, the total LP steam required for solvent regeneration would be about 1.557 million lb/hr.

- Based on a study by Nexant/Bechtel,[11] a typical capital investment (Table 14) for the absorber unit is approximately 27% of the total cost of the Amine-based CO_2 removal process (estimated at $436 MM, 2006$, for the DOE Case 10). This absorber will be replaced by a membrane contactor unit. According to this Nexant study, the typical investment for the reboiler unit is approximately 15% of the total cost of the amine process. The reboilers for the membrane plants are prorated on steam requirements.

Table 14. Key capital cost distribution factors for a typical amine plant for CO_2 removal.

Absorber	27%
Rich/lean exchanger	19%
Reboiler & other heat exchangers	15%
Stripper	10%
Feed cooler	9%
Flue gas blower	9%
Pumps	8%
Others	3%

- For the extra electric power generation in the membrane contactor case using the activated K_2CO_3 solvent, we have increased the CAPEX (includes LP steam turbine and extra condenser area requirements, etc.) by about $30 MM. Based on the DOE Case 10, for a 680-MW steam turbine unit, the total CAPEX is $125.3MM (Yr 2006$). For an extra 117.4 MW of electric power generation, we would need an additional capital of about $37 MM (using a 0.7 scale factor). We have reduced this number by 20% to account for the usage of LP steam only (vs. high pressure/intermediate pressure/low pressure (HP/IP/LP) steam usage in the DOE estimate).

- The CAPEX of the membrane contactor unit is based on the experimentally obtained CO_2 removal flux. The total flue gas flow to the membrane unit would be about 265,166 lbmol/hr, or about 791 std. m^3/sec. For the K_2CO_3 case, this would correspond to a total membrane area of about 1.6278 million square meters. For the base case design using this membrane contactor:
  - The cost of the membrane system (woven PEEK hollow fiber membranes assembled in as a module and installed in a canister) has been assumed at $80/$m^2$ (Yr 2006$).

- Total installed cost of the membrane unit (membrane system mounted to the skid) is assumed to be 1.2 x cost of membrane system.

The changes in total CAPEX for the two design cases relative to the DOE Case 10 are summarized in Table 15.

Table 15. Key changes in CAPEX (Yr 2006$).

Item	DOE Case 10 (amine plant)	Membrane contactor	
		K_2CO_3 solvent	aMDEA solvent
Absorber unit of the amine plant, $MM (@27% of total amine plant)	+ 118	-	-
Reboiler unit of the amine plant (@ 15%), $MM	+65	22	39
Extra CAPEX for LP steam turbine plus accessories, $MM		10	12
Membrane unit, $MM		104	117
Other equipment, $MM	253	209	209
Total CAPEX for the CO_2 capture unit, $MM	436	345	377

Estimates on Plant Performance (Electric Load Requirements)

The electric power load data for the membrane cases are summarized in Table 16. The overall thermal efficiency (HHV basis) for the membrane case using the aMDEA solvent would be about 26.6% compared to about (i) 24.9% for the DOE Case 10 and (ii) 30.0% for the membrane case using activated K_2CO_3 solvent.

Table 16. Electric power requirements for various units.

Design Case	DOE Case 9	DOE Case 10	Membrane contactor	
			K_2CO_3 solvent	aMDEA solvent
Transformer loss, kWe	1,830	2,380	2,790	2,517
Steam turbine Auxiliary, kW_e	400	400	470	423
Other units, kW_e	30,640	127,530	127,530	127,530
Total auxiliaries, kW_e	32,870	130,310	133,570	130,470
Gross steam turbine Power, kW_e	583,315	679,923	797,323	719,231
Net power, kW_e	550,445	549,613	663,753	588,761
As received coal feed, lb/hr	437,699	646,589	646,589	646,589
Total thermal input,	1,496,479	2,210,668	2,210,668	2,210,668

kWe				
Net plant efficiency, HHV%	36.8	24.9	30.0	26.6

Cost of Power Generation, mills/kWhr

The key data on various levelized cost of electricity (LCOE) costs for the design cases are summarized in Table 17. As shown, with the base case assumptions for the membrane contactor using the activated K_2CO_3 solvent, the increase in the LCOE is about 56% over the DOE Case 9. For the membrane contactor case using the aMDEA solvent, the increase in the LCOE is about 68%.

Table 17. Comparative data on LCOE.

Parameter	DOE Case 9	DOE Case 10	Membrane contactor	
			K_2CO_3 solvent	aMDEA solvent
As-received coal feed rate, metric tons/day	4,765	7,039	5,937	6,584
Capital cost, mills/kWh	34.14	68.05	58.5	61.10
Fixed operating costs, mills/kWh	3.99	5.81	4.82	5.43
Variable operating costs, mills/kWh	5.80	10.82	8.65	9.73
Coal, mills/kWh	20.14	29.78	24.68	27.83
CO_2 transport, storage & monitoring, mills/kWh		3.91	3.48	3.48
Total LCOE, mills/kWhr	64.00	118.36	100.11	107.57
Increase over no capture LCOE, %	--	85	56	68

Task 6. Project management and final report

Description of Work

GTI will coordinate all project activities with PoroGen and will report technical progress and financial status to DOE throughout the duration of the project. Periodic teleconferencing meetings will be held to review program technical performance, schedule, and budget, and to resolve issues between all active participants. Scheduling software will be used to help keep the project on time and within budget. Technology transfer to the industry will be through presentations at conferences under this task, as well as briefing to DOE. GTI will revise the Project Management Plan by including details from the negotiation process and will be updated as the project progresses. This plan will be used to report schedule and budget variances. The final report will be submitted 36 months after the start of the program.

Project Activities/Products/Deliverables

Project activities, products and deliverables are summarized below:

- We attended the required kickoff meeting (to complete Milestone 1) and presented a project overview including project objectives, project schedule and budget at the National Energy Technology Laboratory in Pittsburgh, PA on November 15, 2010.
- Project Management Plan was submitted and approved by DOE. The approved management plan mirrored the proposal with minor modification.
- We have submitted quarterly reports describing the experimental design, actual status of and progress of the project, milestone status, any proposed changes in the project schedule, and recent results and findings from each of the tasks.
- Revised Project Management Plan was submitted and approved by DOE. This revised PMP addressed the work breakdown structure, preliminary risk assessment and risk management approach, and project schedule and planned expenditures, labor mix and hours, planned travel, all by task, and budget period for the total project.
- We attended and presented project status at the DOE annual program review meetings (NETL CO_2 Capture Technology Meeting) in Pittsburgh on August 22, 2011.
- We submitted the BP1 technical report at the end of year 1.

BP1 SUMMARY

The feasibility of utilizing hollow fiber membrane contactor in combination with chemical solvents to separate and capture at least 90% of the CO_2 from simulated flue gases has been successfully established. Excellent progress was made towards all objectives of this project. The BP1 goals were achieved: $\geq$ 1,000 GPU intrinsic membrane CO_2 permeance, $\geq$ 90% CO_2 removal in one stage, $\leq$ 2 psi gas side pressure drop, and $\geq 1\ (\text{sec})^{-1}$ mass transfer coefficient. Economic evaluation based on BP1 membrane absorber lab test data indicates a 55% increase in COE.

BP2 OBJECTIVES AND TASKS

BP2 Objectives

The BP2 II objective is to develop an energy efficient regeneration process that enables collection of sequestration ready CO_2 at elevated pressures. The tasks include construction of a high temperature contactor regeneration test system, fabrication of membrane contactor modules tailored for high temperature operation, testing of the contactor regeneration process stability and sensitivity to process variables, and membrane contactor stability and life cycle assessment. Additional tasks of BP2 work are the design of a bench scale test unit, initiation of the planning process for the proposed membrane contactor technology field test at a PC power plant site, and refinement of the process economics based on the lab test data.

BP2 Scope of Work and Tasks

In BP2 of this program, a membrane contactor for the regeneration step will be designed and constructed, a high temperature solvent regeneration test system designed and built and extensive solvent regeneration tests carried out. Also, the combined sorption/desorption process for CO_2 capture from flue gas will be developed and the bench scale system design completed. Desorption of CO_2 from rich alkanolamine solvents utilizing a hollow fiber membrane contactor under high temperature regeneration conditions to enable collection of high pressure CO_2 will be demonstrated and the operating conditions will be optimized.

Tasks for the BP2 research are listed in Table 18.

Table 18. BP2 work plan.

Task #	Task Title	Estimated Completion (months from award)	Responsible Individual/Organization
7	Design and construction of membrane contactor for regeneration step	16	Research Scientist: PGC
8	Regeneration system design and construction	15	Research Scientists: GTI
9	Membrane contactor stability and life testing	20	Research Scientists: GTI and PGC
10	Lab scale regeneration tests	23	Research Scientists: GTI
11	Design of bench scale system	24	Research Engineers: GTI and PGC
12	Refine process design and economic evaluation	24	GTI, PGC and APS Engineers
13	BP2 project management	24	GTI PI and PGC Tech Lead

BP2 TECHNICAL PROGRESS

Task 7. Design and construction of membrane contactor for regeneration step

Description of Work

In this task, the contactor design will be optimized towards high temperature CO_2 regeneration process. Module components including epoxy tubesheets, O-rings and housing compatible with high temperature and elevated pressure operation will be developed. Critical objective achieved upon completion of the task: membrane contactor for regeneration step of operation has been developed.

Experimental Methods, Results and Discussion

Two types of contactor modules equipped with different type of hollow fiber membranes have been designed for membrane solvent regenerator/desorber: 1) Type I utilized super-hydrophobic PEEK hollow fiber membranes, and 2) Type II utilized nano-porous hydrophilic PEEK membranes.

The two regeneration types contactors differed in process conditions and required contactors to be constructed from high temperature chemically resistant materials to insure reliable long-term operation in contact with target process fluids. A unified contactor module material construction scope was developed for solvent regeneration that can be adopted for both module types. The contactor design with super-hydrophobic hollow fibers is shown in Figure 13.

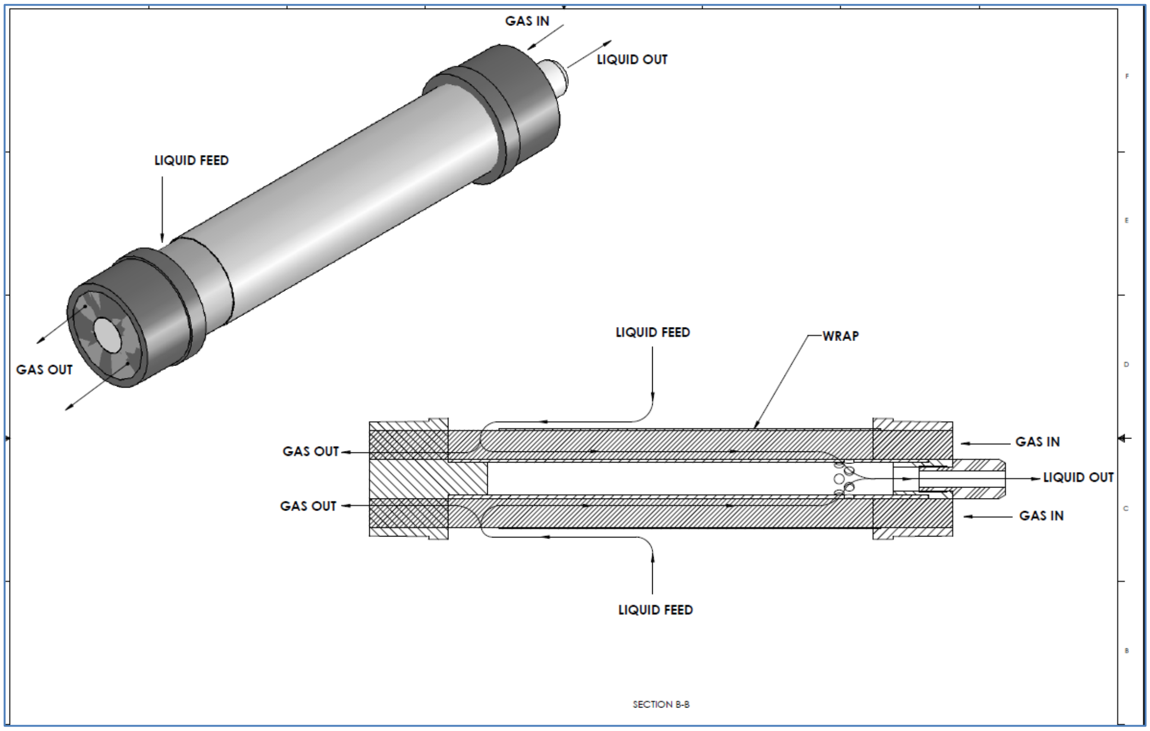


Figure 13. Hollow fiber contactor module design adopted for solvent regeneration process.

In this design, rich solvent is introduced to the shell side of hollow fibers at one terminal end and the lean solvent is removed from the opposite terminal end. Nitrogen can be injected into hollow fiber bores and this mode of regeneration was used in initial evaluation tests. Alternatively CO_2 can be removed from the solvent by application of vacuum to the bore side. Steam can be injected into hollow fiber bores to promote carbon dioxide removal as well. However, in most tests the pre-heated rich solvent was introduced on the shell side of the contactor modules and the carbon dioxide released from the solvent removed through hollow fiber bores.

The contactor modules equipped with nano-porous hydrophilic PEEK hollow fiber membranes operated in a different mode. With hydrophilic membranes installed in the contactor module, the rich liquid was introduced through the bores of the hollow fibers and the lean liquid and carbon dioxide streams were removed on the shell side of hollow fibers. The separation between liquid and carbon dioxide took place during transport through the porous wall.

Following preliminary tests, the membrane desorber module design has been further optimized. The optimization includes hollow fiber dimensions, morphology and module packing density to minimize pressure drops and maximize thermodynamic efficiency. After extensive evaluation materials of cartridge construction such as epoxy tubesheet material, O-rings, etc. were down selected for regeneration contactor construction. The module housing in all cases was stainless steel.

High temperature and corrosive environment encountered during the regeneration process impose severe demands on materials of construction. Initial tests have shown that all conventional O-ring materials have failed after several hundred hours of operation at target application process conditions. Only O-rings manufactured from specialty materials have shown good stability in initial tests and were adopted for regeneration module construction. The specialty O-rings with custom target dimensions were tested at high temperature conditions (125 ˚C) and showed good integrity. The seal integrity was confirmed by long term tests.

E-8 epoxy formulation was selected for tubesheet construction and initial regeneration contactors were constructed using this epoxy formulation. The mechanical properties were adequate in initial tests. The main concern for long term operation is the material’s creep. An accelerated test was initiated where deformation of the tubesheet under 30 psig differential pressure was measured at 125 ˚C (mechanical displacement measured). No creep was detected in tubesheets after several hundred hours of testing.t Pressure shells were constructed from stainless steel and did not add to materials compatibility concern. A number of contactor modules equipped with hydrophobic hollow fibers were constructed and used in solvent regeneration tests.

Several additional 2-inch modules equipped with hydrophilic PEEK hollow fibers were also constructed for regeneration experiments. The design of these regeneration modules and process configuration are conceptually different. This experimental design has been evaluated by GTI, and PoroGen has optimizing contactor design based on the feedback from GTI’s regeneration tests.

Task 8. Regeneration system design and construction

Description of Work

In this task, a laboratory test unit that will allow for the evaluation of the solvent regeneration step in a membrane contactor configuration and CO_2 collection at elevated pressures will be designed and constructed. The solvent will be regenerated at temperatures up to 140 °C and the CO_2 will be collected at incrementally higher pressure; 1, 2, 5 and 10 atm. The system design will also enable solvent regeneration with direct steam sweep. A low pressure steam generator will be utilized. The test unit will be used to support development of an optimal regeneration membrane contactor and for solvent regeneration process optimization. Critical objective achieved upon completion of the task: membrane contactor regeneration system is designed and constructed.

Experimental Methods, Results and Discussion

Work was completed to construct solvent regeneration/desorber test unit. P&ID of the regeneration part of the test skid is presented in Figure 14. A photo of the test unit is shown in Figure 15.

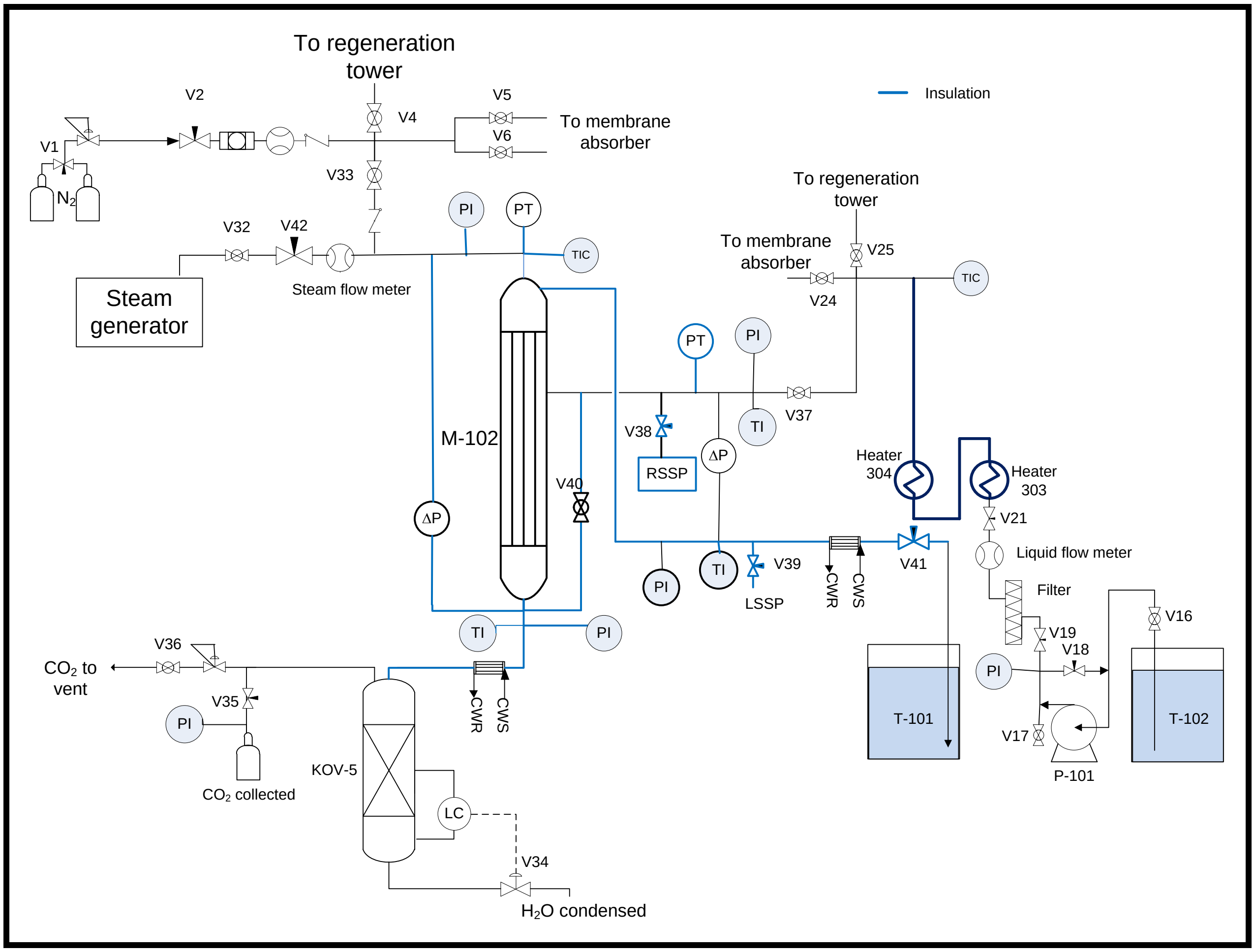


Figure 14. P&ID of the membrane desorber test apparatus.

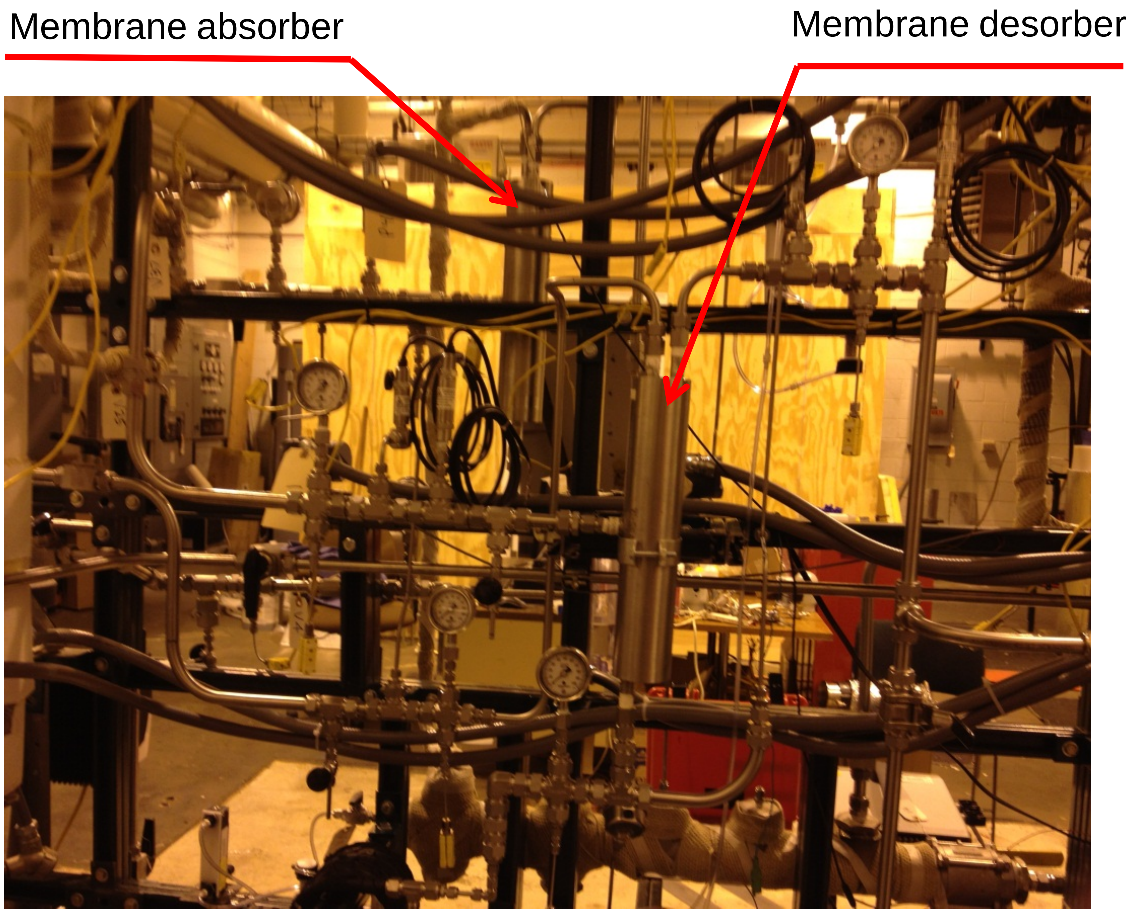


Figure 15. Photo of the membrane desorber unit. The membrane absorber unit is in the back section of the skid.

This unit has the following characteristics:

- The dimensions of membrane desorption unit of the skid -12’ x 5.5’ x 12’. The back side of the photo is the membrane absorber unit.
- The system incorporates National Instrument process control and data acquisition system with safety guards for temperature, pressure, and liquid levels.

Task 9. Membrane contactor stability and life testing

Description of Work

The Team will test the membrane contactor module to determine contactor stability at process design conditions and contactor life. Each module component will be tested for compatibility with the different solvents in addition to determining the long term contactor stability at proposed operating conditions. Accelerated life tests will be carried out separately on membrane coupons and epoxy tube sheet samples at elevated temperature conditions. Mechanical properties and permeation properties will be tested periodically to determine the rate of degradation. Critical objective achieved upon completion of the task: Membrane contactor durability will be determined and adequate life expectancy demonstrated.

Experimental Methods, Results and Discussion

We have identified critical components that must to undergo stability and life testing based on the module design developed in Task 7. The test program entails exposure of major critical contactor components such as PEEK membrane, epoxy tubesheet, and O-rings to solvent system at target elevated temperature. The membrane stability was evaluated by comparing initial gas transport characteristics to gas transport characteristics after predetermined exposure. The epoxy materials characteristics (tensile strength and modulus) prior to and after exposure were compared as well. The effect of solvent on O-rings was examined visually; the extent of swelling if any was measured as well as the ability to provide fluid tight seal after exposure.

The super-hydrophobic hollow fiber membrane showed some shrinkage under target operating conditions after several hundred hours of exposure to solvents at the target temperatures. However, this dimensional change did not result in membrane rupture or damage and significant change in gas permeance. The dimensional change did not affect hollow fiber/epoxy interphase. The change did not require significant changes to module design to prevent flow by-passing and channeling that are known to reduce mass transfer coefficient. The hydrophilic membrane did not show as significant dimensional change.

Contactor stability at absorption process design conditions was investigated by performing CO_2 capture for 124 hours continuously, aMDEA solvent was utilized. In this test the absorption contactor operation was not integrated with contactor regeneration operation. During this test the solvent was recirculated to the feed drum without regenerating, causing the CO_2 loading of the solvent to increase with time. The CO_2 removal rate has decreased from 90% to 75% because of the increased CO_2 loading of the solvent. In a separate follow up test, we have investigated membrane contactor stability by integrating the membrane absorber and regeneration tower so that the CO_2 loading of lean solvent remained low and constant during the test. The operating conditions are listed in Table 19.

Table 19. Long-term stability operating conditions.

Parameter	Condition
Absorption	
Gas inlet temperature	105 to 108 °F
Simulated flue gas CO_2 inlet concentration	17.2 mol% (balance N_2)
Membrane contactor surface area	1.5 ft^2
Gas flow rate	1 SLPM
Inlet gas pressure	3.6-3.8 psig
Liquid inlet temperature	70-85°F
Liquid flow rate	0.40 L/min
Inlet liquid pressure	4.4-6.6 psig
Desorption	
Liquid temperature after heaters	195-202 °F
Liquid temperature at the top of tower	185-202 °F
Liquid flow rate	0.40 L/min
N_2 stripping flow rate	1 SLPM

Figure 16 shows that the CO_2 removal rate during the test was greater than 90% throughout the test (120 hours). The mass transfer coefficient (Figure 17) showed a maximum after running for 24 hours, and then stabilized in the next 96 hours. The gas side pressure drop, as shown in Figure 18, was stable and remained less than 0.7 psi throughout the experiment. Figure 19 shows that the liquid side pressure drop was also stable during the test period.

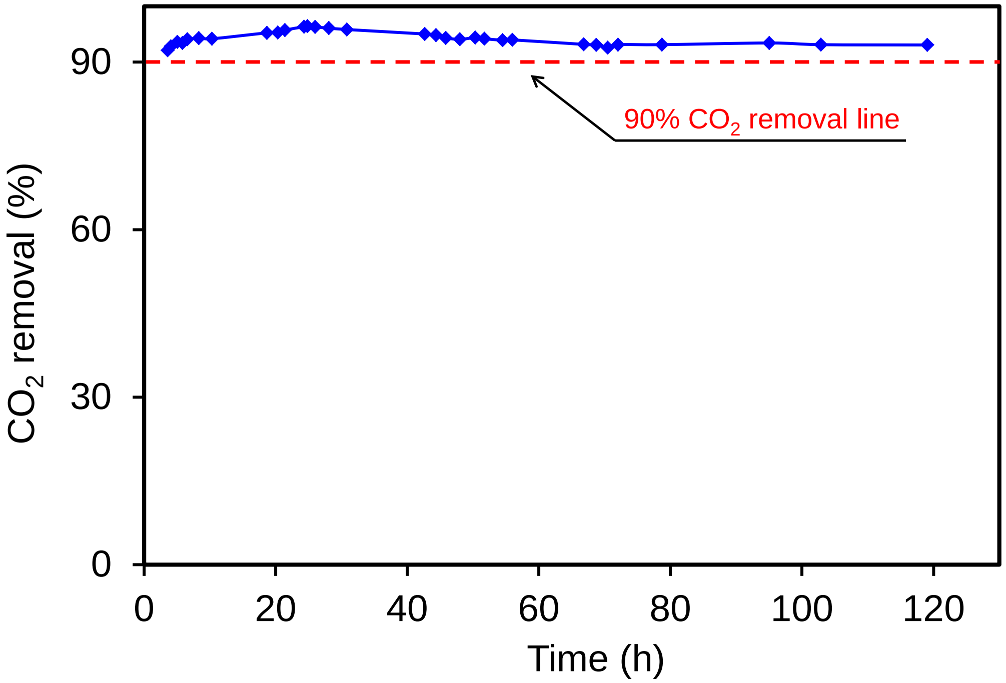


Figure 16. CO_2 removal rate as a function of operating time (module 2PG283).

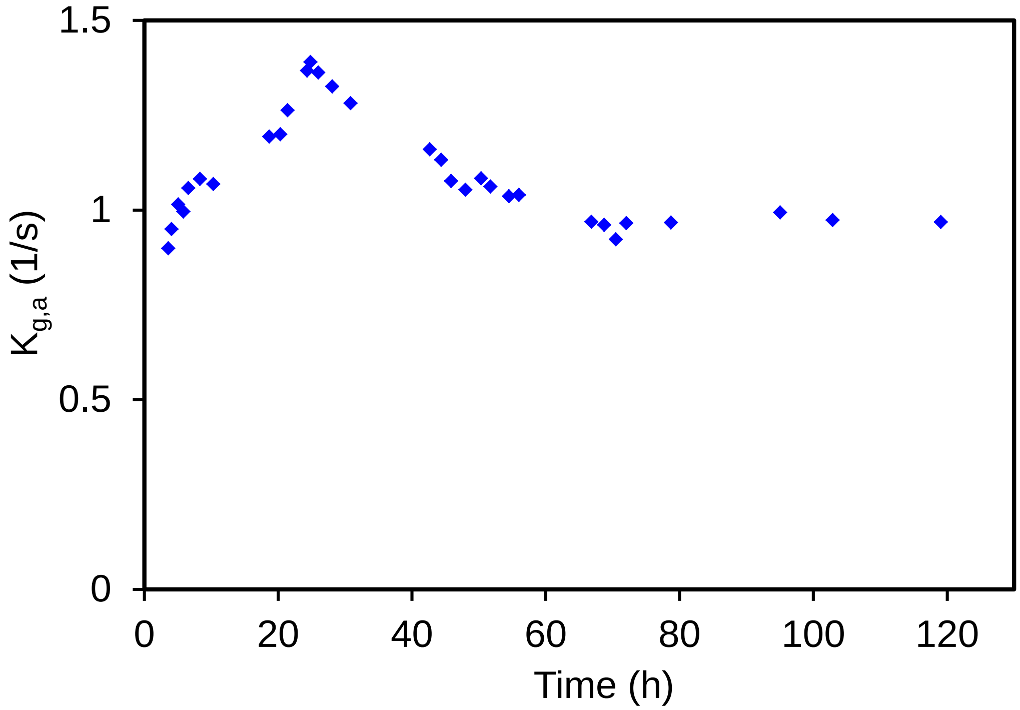


Figure 17. Mass transfer coefficient as a function of operating time (module 2PG283).

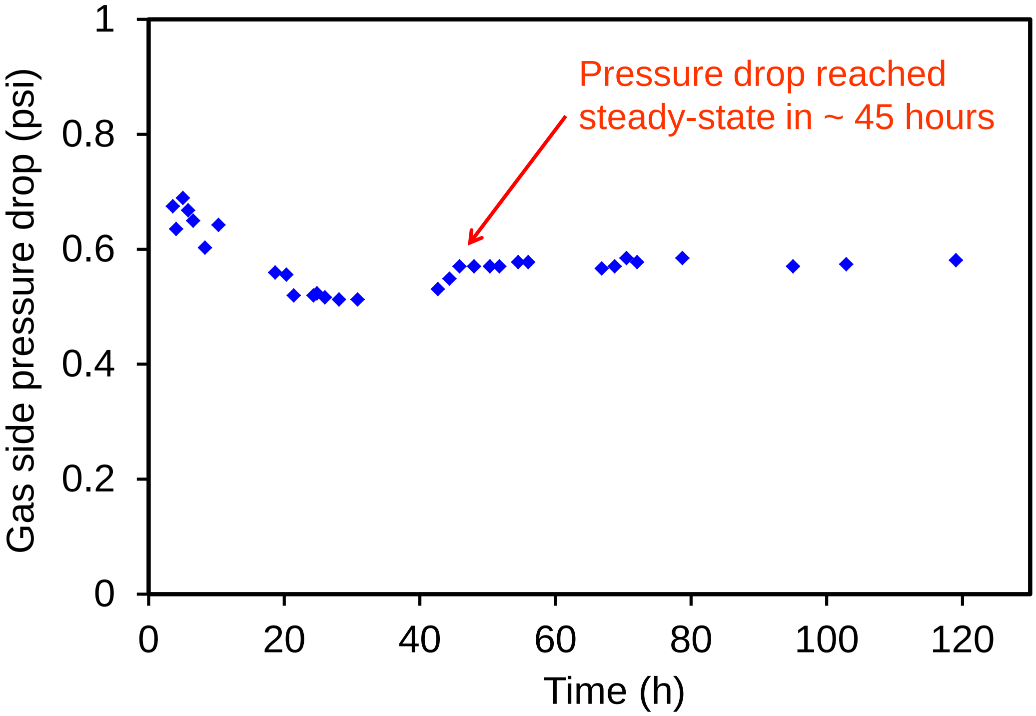


Figure 18. Gas side pressure drop as a function of operating time (module 2PG283).

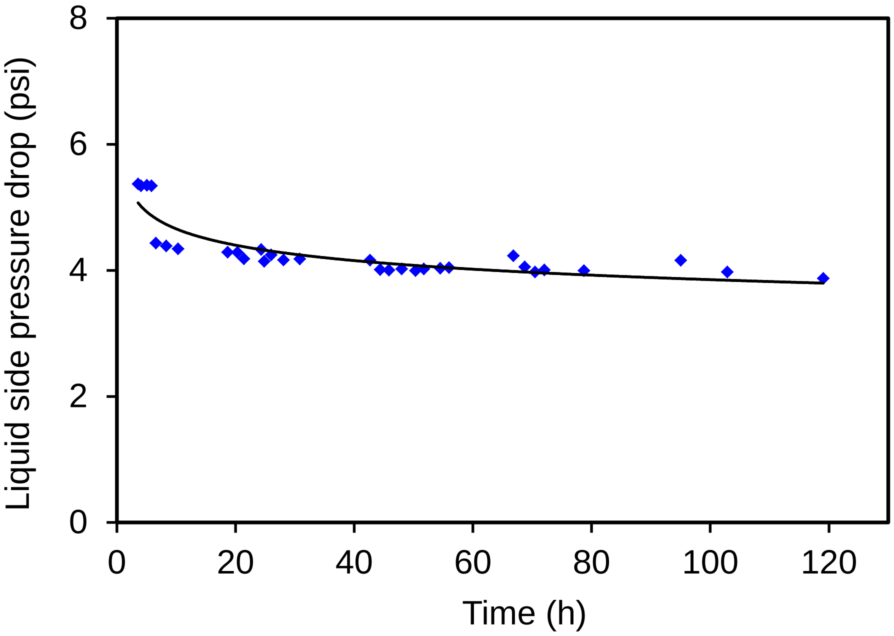


Figure 19. Liquid side pressure drop as a function of operating time (module 2PG283).

Table 20 summarizes the history of module 2PG283 and its intrinsic permeances for CO_2 and N_2 after each sequential test. Note that this module has been used for a number of membrane contactor tests since it was produced. After all listed tests, the membrane intrinsic permeance for CO_2 and N_2 remained essentially identical to the initial measured values, indicating good mechanical properties and stable permeation properties.

Table 20. Contactor module membrane intrinsic permeances for CO_2 and N_2 (module 2PG283).

Condition	Tested date	Intrinsic permeances, GPU	
		CO_2	N_2
Initial membrane module	6/22/2011*	586 ± 13	130 ± 1.5
Module after being used for CO_2 capture for a feed that contains 66 ppmv NO_2, 3.27% O_2, 12.98% CO_2, balance N_2. Then, it was washed with D.I. water and dried.	11/11/2011 **	595	137
Module after being used for CO_2 capture for 124 hours, wetted with aMDEA solvent for 55 days. Then, it was washed with D.I. water and dried.	1/17/2012*	586 ± 14	133 ± 6.8
Module after being used for CO_2 capture for 120 hours in an integrated membrane absorber/regeneration system. Then, it was washed with D.I. water and dried.	4/20/2012*	548 ± 43	121 ± 15

*: Intrinsic permeances for CO_2 and N_2 were measured at three different trans-membrane pressures. The average permeances are listed in the table. All the ± values are standard deviations.

**: Intrinsic permeances for CO_2 and N_2 were measured at one trans-membrane pressure.

Initial membrane desorber performance stability was also evaluated. Module 2PG381 has been periodically used in the aMDEA solvent regeneration 7 different sequential tests, duration of each test has been about 5 hours. In these tests, the CO_2-loaded solvent was sent to the bore side of the module equipped with hydrophobic membrane fibers. The liquid side pressure drop (pressure differential between liquid inlet and outlet) was observed to remain constant at 6 psi. The rich solvent temperature was about 110 $^{\circ}$C. There were no significant dimensional and structural changes for the contactor.

Task 10. Lab scale solvent regeneration tests

Description of Work

In this task, membrane contactor modules will be tested and the regeneration process optimized in terms of solvent flow, pressure drop, temperature and CO_2 collection at elevated pressures. Hindered amine regeneration at high temperature conditions to generate high pressure CO_2 will be compared with sweep steam carbonate regeneration. The most economical regeneration process will be down selected for bench test. Critical objective achieved upon completion of the task: Membrane contactor regeneration process optimized.

Experimental Methods, Results and Discussion

Membrane contactor based CO_2 stripping experiments from rich solvents has been investigated in several configurations/modes of operation as follows:

<u>Mode I</u>: Regeneration was conducted for a 1.87 wt% CO_2-loaded aMDEA aqueous solution using N_2 as a sweep gas to facilitate CO_2 transport. Note that the use of N_2 sweep gas is not a commercial solution for regeneration, but it provides a quick indication of qualification of membrane desorber materials of construction and the regeneration equipment. Initial test was carried with contactor equipped with hydrophobic hollow fiber membrane with intrinsic permeance for CO_2 of 210 GPU. Flow configuration used in this test is shown in Figure 20.

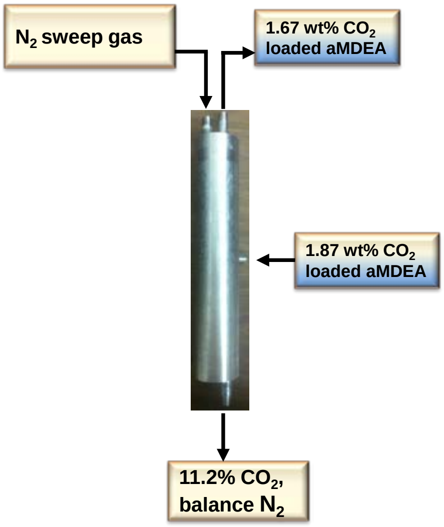


Figure 20. Flow configuration for membrane desorber using N_2 as a sweep gas.

The highest regeneration temperature investigated in this test was 93 °C. The contactor generated lower CO_2 loading solvent indicating efficient regeneration.

Mode II: In this test steam was used as a sweep fluid (it simultaneously also provided some heat). Regeneration was carried out for 8 wt% CO_2-loaded aMDEA solution. The flow configuration is shown in Figure 21. In the test, liquid and steam flow rates were kept at 0.49 L/min and 0.10 kg/min, respectively. Other operating conditions and the CO_2 stripping rates are shown in Table 21. The highest CO_2 stripping rate observed in the temperature range tested was 9.9 L/min/m^2. This flow configuration has also been used for the regeneration of a CO_2-loaded activated K_2CO_3 solvent. A CO_2 stripping rate of 1.0 L/min/m^2 was observed at temperature of 113 °C.

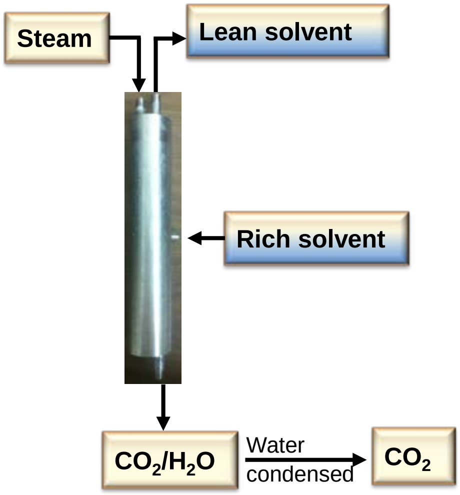


Figure 21. Flow configuration for membrane desorber using steam stripping.

Table 21. Membrane contactor regeneration performance using steam sweep.

Average temperature (°C)		Pressure drop (psi)		CO_2 stripping rate (L/min/m^2)
Liquid side	Steam side	Liquid side	Steam side	
61.7	94.7	2.5	20.4	9.9
92.2	99.2	4.7	20.4	7.5
114.2	101.7	3.0	20.4	4.3

Mode III: This mode carried out solvent regeneration without a sweep gas on the hollow fiber bore side. Regeneration was carried out using 8 wt% CO_2-loaded aMDEA. The flow configuration is shown in Figure 22. The contactor was equipped with hydrophobic hollow fiber membrane with measured intrinsic permeance for CO_2 of 290 GPU. In the regeneration test, the liquid flow rate was kept at 0.51 L/min. Table 22 shows the CO_2 stripping rates through this module at two different temperatures.

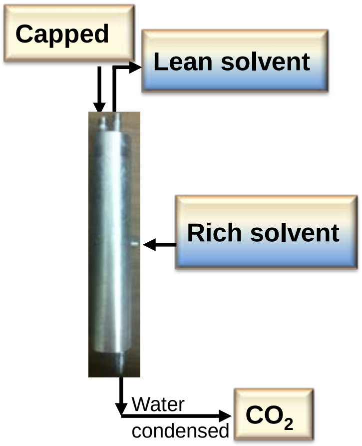


Figure 22. Flow configuration for membrane desorber without sweep gas.

Table 22. Contactor regeneration performance without sweep gas.

Liquid side average temp. (°C)	CO_2 stripping rate	
	L/min/m^2	kg/m^2/h
75.4	5.2	0.61
85.4	8.2	0.97

To evaluate the effect of liquid to gas ratio on the regeneration performance a 2 inch diameter contactor module 22 inch long was utilized. The contactor was tested in the identical mode. CO_2 stripping rate was as high as 2.8 kg/m^2/h at regeneration temperature of 104 °C.

Mode IV: Membrane desorber equipped with nano-porous hydrophilic membranes was also tested for solvent regeneration. In this mode, the rich solvent is fed to the tube side the fibers. Most of the solvent stays in the fiber, whereas some of the solvent permeates from the inside of the fiber to the outside and is collected at the distal bottom end of the contactor module. During transport of rich liquid, the CO_2 is separated and collected at the top of the membrane contactor. The typical flow configuration and performance are shown in Figure 23.

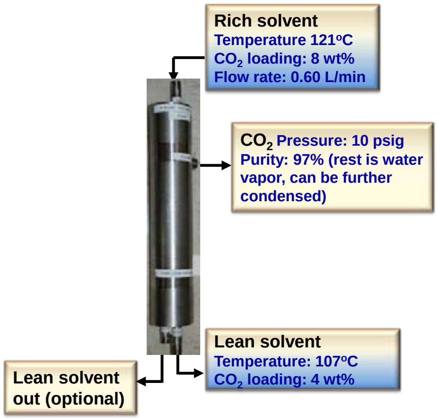


Figure 23. Typical flow configuration and performance for a membrane desorber using nano-porous hydrophilic membrane.

The CO_2 stripping rate at operating conditions shown in Figure 23 was as high as 4.1 kg/m^2/h. The one-stage regeneration efficiency was 53% limited by the small membrane area of this contactor module (4.1 ft^2).

Note that regeneration Mode IV (Figure 24) is different from ordinary membrane contactor processes which employ either dense membranes (Figure 25a) or hydrophobic microporous membranes under non-wetting conditions (the membrane pores are filled by the gaseous phase as shown in Figure 25b).

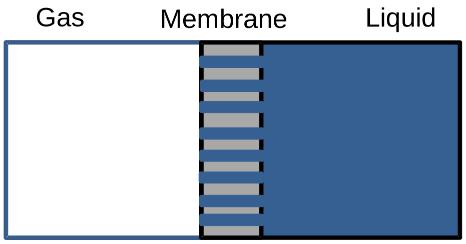
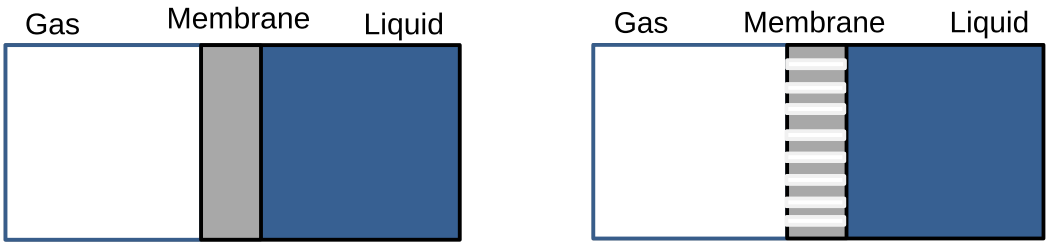


Figure 24. Diagram of membrane based solvent regeneration process using porous hydrophilic membrane (the membrane pores are filled with liquid).



(a) (b)

Figure 25. Diagram of membrane contactor based solvent regeneration processes using: (a) dense membranes, and (b) hydrophobic, microporous membranes under non-wetting conditions (the membrane pores are filled by the gaseous phase).

It has been reported extensively that pore wet-out is detrimental to successful operation of membrane contactors as it significantly reduces mass transfer rates by creating a stagnant liquid film in the pores of the membrane.[12-14] For example, in the Reference 12, Hoff emphasized the importance of preventing liquid from penetrating into membrane pores as the mass transfer would then be limited by molecular diffusion through the liquid layer with diffusivities 10,000 times lower than in the gas phase. Compared to those reported in the literature, mass transfer rates for solvent regeneration using the porous hydrophilic membrane were surprisingly high. Additional tests were carried to confirm this high mass transfer rates. CO_2-loaded aMDEA solvent regeneration was carried out using two modules in series. Note that the rich solvent was pre-heated and fed to the tube side of the fibers. During the testing, small amount of lean solvent was collected at the bottom of the shell side, indicating that some liquid as well as gas had permeated from the tube side to the shell side, and the membrane was wetted during operation.

In summary, two types of membrane contactor modules have been tested in a number of operating modes. Four regeneration modes have been investigated and optimized in terms of solvent flow, pressure drop, and operating temperature. Mode III (hydrophobic membrane without sweep) and Mode IV (hydrophilic membrane without sweep) are of outmost interest.

Task 11. Design of bench scale system

Description of Work

In this task, the design of a bench scale unit will be carried out. The unit design will be coordinated with requirements of timing, material, labor at Midwest Generation’s Joliet Power Station with SO_x, and NO_x control equipment necessary to bring the flue gas composition equivalent to that of burning IL coal. Critical objective achieved upon completion of the task: Bench scale system for field test is designed.

Experimental Methods, Results and Discussion:

The feasibility of manufacturing high productivity contactor membranes was established during BP1. However, further development and scale-up of the manufacturing process were required to address construction of full size contactor modules for the BP3 field tests. Large diameter fiber (large bore diameter) is required for the commercial contactor to minimize feed side pressure drop. The initial feasibility of manufacturing a porous PEEK hollow fiber of target dimensions was established during BP1. The manufacturing scale up of the high permeability membrane and the large dimension bore fiber were combined and this activity was addressed. Hardware required for the manufacture of the large bore fiber on commercial production equipment was procured, installed and tested in several 100,000 ft fiber length runs. The prerequisite manufacturing equipment included extruder mixing screw and spinneret of a size required for the production of the target dimension fiber (about 20 mil bore) while maintaining high spinning speed. Three runs were conducted at slightly different draw down conditions. The fiber OD and ID sizes varied during each run to determine dimensional stability and porous fiber permeability.

The construction of the integrated absorption/regeneration bench-scale system was completed.

The system consists of an absorption membrane module, a stripper module, and an additional conventional steam stripping section to enable independent evaluation of absorption section. The P&ID of the system is shown in Figure 26. Note that the conventional stripping section allows shake down and testing of the absorber independent of the regenerator.

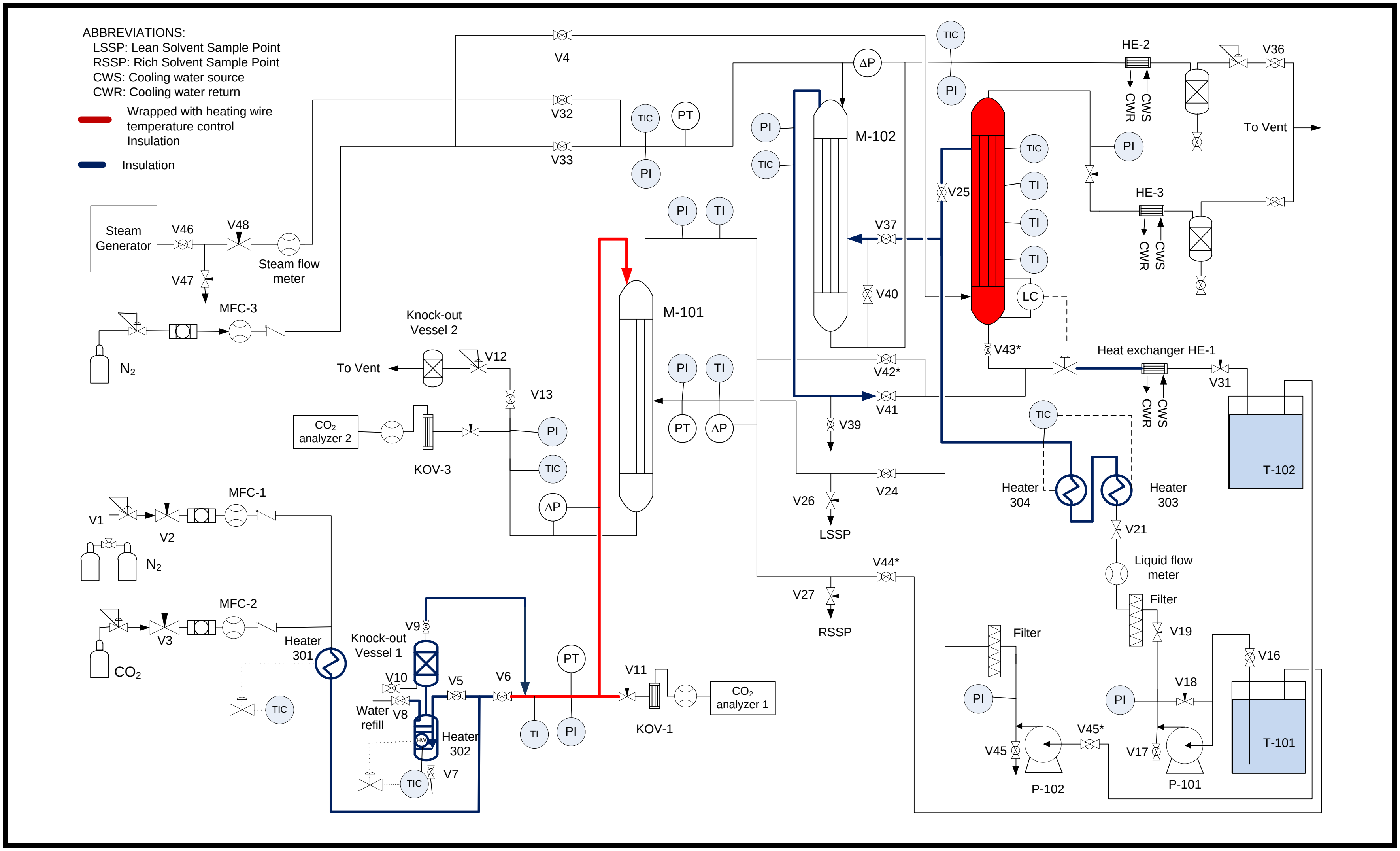


Figure 26. P&ID of the bench-scale system.

The system included all prerequisite components - piping, valves, fittings, filters, temperature transducers, pressure transducers, pressure gauges, pressure drop transducers, sample ports. The system is sized for 25 kW_e equivalent CO_2 capture (50.6 lb/hr of CO_2). Table 23 shows required upgrades for the system when switching from lab-scale tests to pilot field tests.

Table 23. Required system upgrades when switching from lab-scale tests to pilot tests.

Equipment /Instrument	Lab-scale	Bench-scale
Membrane absorber	Ø2" x 15" long	Ø4" x 60" long
Membrane stripper	Ø2" x 15" long	Ø4" x 60" long
Pumps	0-2 L/min	0-10 L/min
Gas flow meters	CO_2: 0-22 SLPM, N_2: 0-150 SLPM	0-2000 L/min
Heater for desorber	10 kW_e	72 kW_e
Knockout vessels		3 vessels with level controls
CO_2 analyzers	CO_2 analyzers 1 (S158-15, 0-15% range) and 2 (S158, 0-10% range)	To be determined
Blower	-	To be determined
Heat exchangers and coolers	-	We have heat exchangers, need to determine coolers
LabVIEW control		To be determined

Task 12. Refine economic evaluation

Description of Work

In this task, the process economics will be updated based on the optimized sorption and desorption test results.

Results and Discussion

We have used the cost estimates for the DOE Case 9 (Cost estimation with no CO_2 capture) and Case 10 (Cost estimation with CO_2 capture using MEA plant)[9] as the Base Case that represents current benchmark technology (monoethanolamine (MEA) plant) status for electric power generation with CO_2 removal (including transport, storage and monitoring) from flue gas generated in a nominal 550 MW_e pulverized coal boiler. These scoping economic numbers for the membrane contactor technology, based on two different solvents (namely, an activated K_2CO_3 solvent, and an aMDEA solvent), were developed to estimate economic advantages of a hybrid membrane absorption/conventional regeneration process over the DOE Case 10. The experimental CO_2 flux data at 90% CO_2 removal obtained for these solvents were used in our cost estimates.

The experimental CO_2 stripping flux obtained in solvent regeneration was used in the cost estimate. The total CO_2 removal rate for these designs cases is about 626.2 metric tons/hour, corresponding to 90% CO_2 capture from a nominal 550 MW_e, subcritical pulverized coal power plant.

Estimates on CAPEX

Differences in the reboiler heat-duty requirements for the regeneration of CO_2-rich solvent would lead to changes in (i) net electric power generation and (ii) capital costs for the reboiler as well as for the LP steam turbine units. The estimated reboiler heat duties per g-mol of CO_2 for the three design cases are shown in Table 24.

Table 24. The estimated reboiler heat duties per g-mol of CO_2 for the three design cases.

Solvent type	MEA used in DOE Case 10	Activated K_2CO_3	aMDEA
Heat duty, Btu/lb CO_2	1,521[a]	523[b]	1,187[c]

d. Estimated from the total LP steam need in the Regenerator Unit
e. For the K_2CO_3-based Enhanced LoHeat Benfield process,[10] this value has been reported as 18,000-25,000 Btu/lbmol CO_2; we have assumed a value of 23,000 Btu/lbmol CO_2
f. Estimated as the sum of the (i) heat of desorption (14.0 kcal/gmol), (ii) heat of vaporization of water (10.3 kcal/gmol) and (iii) sensible heat required to bring the rich solution to the temperature of the stripper (4.7 kcal/gmol)

The major changes for the two membrane contactor design cases are:

- For the membrane contactor application using activated K_2CO_3, there would be significant reduction in the usage of low pressure (LP) steam for the solvent regeneration unit. For the DOE Case 10, total LP steam flow (at 168 psia and 743°F) to the amine unit is about 1.995 million lb/hr. For the membrane contactor case, the total LP steam required would be about 685,900 lb/hr, which would result in an excess LP steam of about 1,309,058 lb/hr. This extra steam can be used in the existing LP steam turbine to generate about 117,400 kW_e of additional electric power. In this context, we would need to correspondingly increase the CAPEX (estimated for the DOE Case 10) of the turbine system. This reduction in steam usage would also reduce the CAPEX of the reboiler unit of the stripper system.
- For the membrane contactor design case using the aMDEA solvent, the total LP steam required for solvent regeneration would be about 1.557 million lb/hr.
- Based on a study by Nexant/Bechtel,[11] a typical capital investment (Table 25) for the absorber unit is approximately 27% of the total cost of the Amine-based CO_2 removal process (estimated at \$436 MM, 2006\$, for the DOE Case 10). This absorber will be

replaced by a membrane contactor unit. According to this Nexant study, the typical investment for the reboiler unit is approximately 15% of the total cost of the amine process. The reboilers for the membrane plants are prorated on steam requirements.

Table 25. Key capital cost distribution factors for a typical amine plant for CO_2 removal.

Absorber	27%
Rich/lean exchanger	19%
Reboiler & other heat exchangers	15%
Stripper	10%
Feed cooler	9%
Flue gas blower	9%
Pumps	8%
Others	3%

The changes in total CAPEX for the two design cases relative to the DOE Case 10 are summarized in Table 26.

Table 26. Key changes in CAPEX (Yr 2006$).

Item	DOE Case 10 (amine plant)	Membrane contactor	
		K_2CO_3 solvent	aMDEA solvent
Absorber unit of the amine plant, $MM (@27% of total amine plant)	118	-	-
Reboiler unit of the amine plant (@ 15%), $MM	65	22	39
Stripper	44	10	12
Membrane unit, $MM		104	117
Other equipment, $MM	209	209	209
Total CAPEX for the CO_2 capture unit, $MM	436	345	377

Cost of Power Generation, mills/kWh

The key data on various levelized cost of electricity (LCOE) costs for the design cases are summarized in Table 27.

Table 27. Comparative data on LCOE.

Parameter	DOE Case 9	DOE Case 10	Membrane contactor	
			K_2CO_3	aMDEA
As-received coal feed rate, metric tons/day	4,765	7,039	5,837	6,584
Capital cost, mills/kWh	34.14	68.05	57.04	59.73
Fixed operating costs,	3.99	5.81	4.82	5.43

mills/kWh				
Variable operating costs, mills/kWh	5.80	10.82	8.65	9.73
Coal, mills/kWh	20.14	29.78	24.68	27.83
CO_2 transport, storage & monitoring, mills/kWh		3.91	3.48	3.48
Total LCOE, mills/kWh	64.00	118.36	98.67	106.21
Increase over no capture LCOE, %	--	85	54%	66%

Progress Towards Goal

The overall goal of DOE/NETL's carbon capture R&D is to develop advanced technologies that achieve 90% CO_2 capture at less than a 35% increase in COE for post-combustion capture for new and existing coal-fired power plants. Table 28 shows that the DOE target of a 35% increase in COE can be met by decreasing membrane module cost and by utilizing new, advanced solvents.

Table 28. LCOE for various cases.

Cases	LCOE, $/MWh ($K_2CO_3$ solvent)	Increase over no capture LCOE, %
DOE Case - 9 with no CO_2 capture	64	--
DOE Case-10 state-of-the-art technology with CO_2 capture	118.36	85
BP1 status membrane contactor	100.11	56
With membrane stripper $80/$m^2$	98.67	54
Reduce module costs from $80 to $30/$m^2$	97.33	52
With membrane stripper $30 /$m^2$	94.52	48
Use of new, advanced solvents	On trajectory to meet DOE target	
DOE capture target	86.4	35

Task 13. BP2 project management

Description of Work

GTI will coordinate all project activities with PGC and APS and will report technical progress and financial status to DOE throughout the duration of the project. GTI will update the Project Management Plan as the project progresses. This plan will be used to report schedule and budget variances.

Project Activities/Products/Deliverables

BP2 Q1, Q2, Q3, and Q4 Technical Progress Reports, and the Annual Report have been submitted in addition to day-to-day project management. We are preparing an US Patent application based on the regeneration results. We submitted the continuous application for Budget Period 3 study. DOE Project Manager has approved BP3 research. The objectives and tasks for BP3 are given in the APPENDICES.

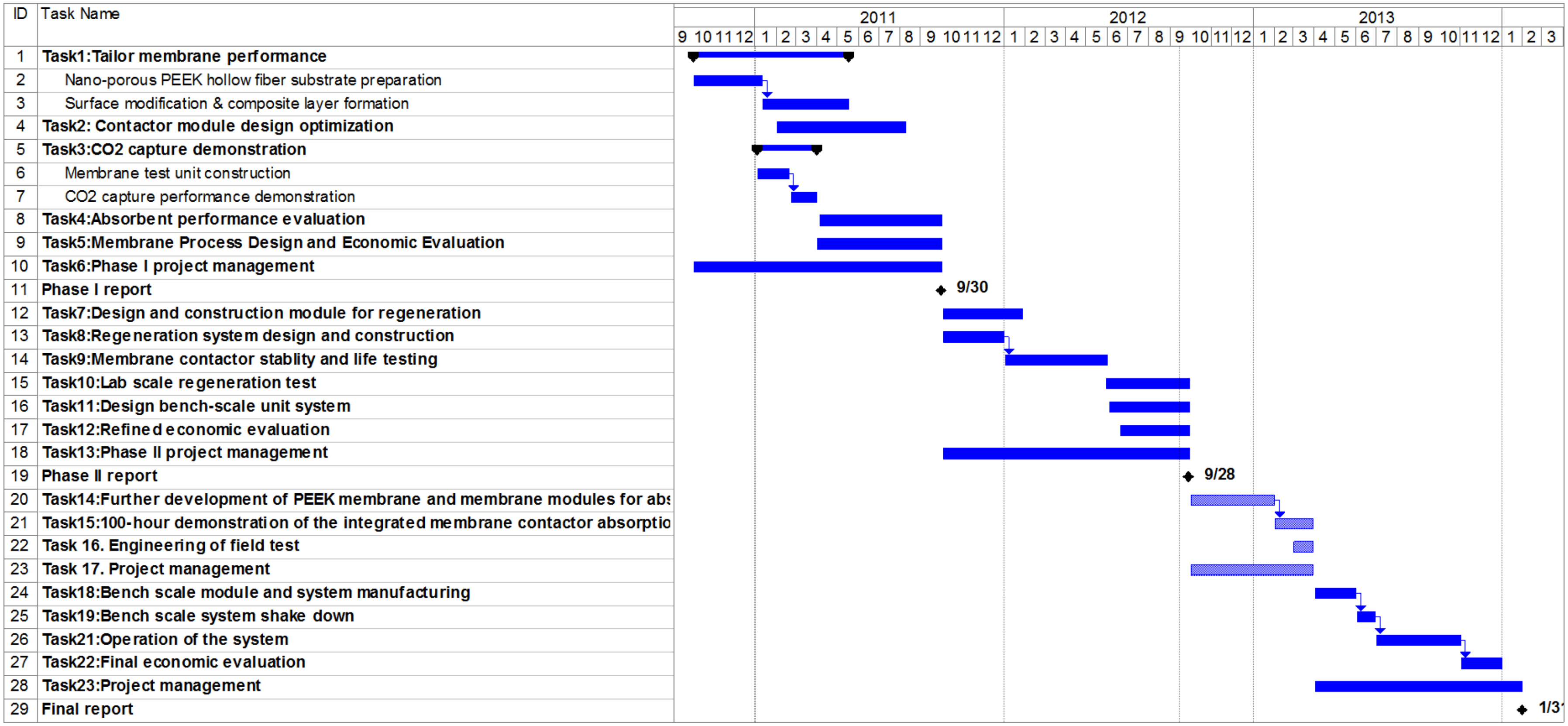
The following article has been submitted for publication during BP2:

- Shiguang Li, Dennis J. Rocha, S. James Zhou, Howard S. Meyer, Benjamin Bikson, Yong Ding, "Post-combustion CO_2 capture using super-hydrophobic, polyether ether ketone, hollow fiber membrane contactors", *Journal of Membrane Science*, Submitted for publication.

The following **presentations** have been made during BP2:

- The Eleventh Annual Carbon Capture, Utilization & Sequestration Conference, April 30 – May 3, 2012, David L. Lawrence Convention Center, Pittsburgh, PA, USA.
- 37th International Technical Conference on Clean Coal and Fuel Systems, June 3-7, 2012, Clearwater, FL, USA.
- NAMS 2012, June 9-13, 2012, New Orleans, LA, USA.
- Alberta Innovates CO_2 Capture Workshop, June 19, 2012, Calgary, Canada
- ICCI Project Review Meeting, June 25, 2012, Carterville, IL, USA
- DOE NETL CO_2 Capture Technology Meeting, July 9-13, 2012, Pittsburgh, PA, USA.

Revised Project Management Plan was submitted and approved by DOE on September 14. The schedule is shown in Figure 27.



ID	Task Name
1	**Task1:Tailor membrane performance**
2	Nano-porous PEEK hollow fiber substrate preparation
3	Surface modification & composite layer formation
4	**Task2: Contactor module design optimization**
5	**Task3:CO2 capture demonstration**
6	Membrane test unit construction
7	CO2 capture performance demonstration
8	**Task4:Absorbent performance evaluation**
9	**Task5:Membrane Process Design and Economic Evaluation**
10	**Task6:Phase I project management**
11	**Phase I report**
12	**Task7:Design and construction module for regeneration**
13	**Task8:Regeneration system design and construction**
14	**Task9:Membrane contactor stablity and life testing**
15	**Task10:Lab scale regeneration test**
16	**Task11:Design bench-scale unit system**
17	**Task12:Refined economic evaluation**
18	**Task13:Phase II project management**
19	**Phase II report**
20	**Task14:Further development of PEEK membrane and membrane modules for abs**
21	**Task15:100-hour demonstration of the integrated membrane contactor absorptio**
22	**Task 16. Engineering of field test**
23	**Task 17. Project management**
24	**Task18:Bench scale module and system manufacturing**
25	**Task19:Bench scale system shake down**
26	**Task21:Operation of the system**
27	**Task22:Final economic evaluation**
28	**Task23:Project management**
29	**Final report**

Figure 27. Final project schedule.

During BP2, in addition to Tasks 7-13 other activities were carried to advance technology commercialization.

Activities/Results in addition to Tasks 7-13

It was noted in Task 12 description that the DOE target of a 35% increase in COE can be met by decreasing membrane module cost and by utilizing new, advanced solvents. We have tested the advanced solvent: H3-1 from Hitachi in addition to solvents proposed originally. Lab tests with H3-1 solvent showed a 15% higher mass transfer coefficient than the aMDEA solvent in CO_2 capture tests (Figure 28). Detailed information regarding H3-1 solvent is proprietary to Hitachi, Ltd.; economic evaluation for the H3-1 solvent at this point cannot be provided. Nether less, the H3-1 solvent is known to have a lower regeneration energy consumption than aMDEA, and is expected to exhibit a better economics than aMDEA solvent. These results indicate that the projected savings achievable with H3-1 can be increased by the use of the PEEK membrane contactor.

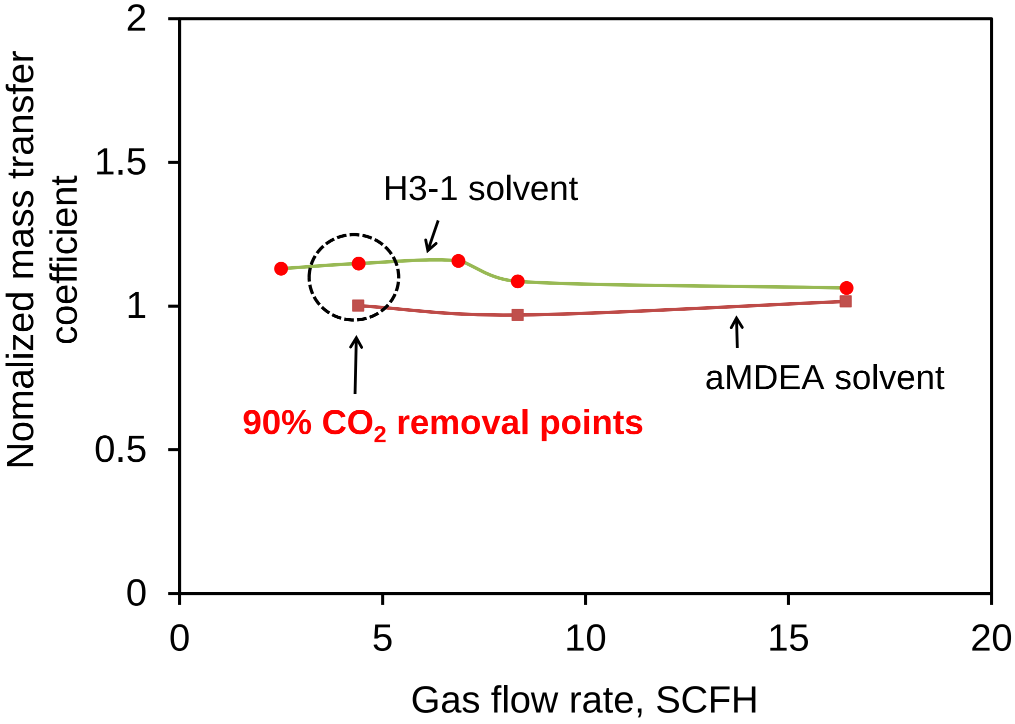


Figure 28. Normalized mass transfer coefficients for H3-1 and aMDEA solvents as a function of gas flow rate (module 2PG368).

BP2 SUMMARY

The feasibility of utilizing hollow fiber PEEK membrane contactor for CO_2-loaded solvent regeneration has been successfully established. Excellent progress is being made in all aspects of this project as we have achieved CO_2 stripping flux one order of magnitude higher than CO_2 absorption flux. Refined economic evaluation based on BP1 membrane absorber and BP2 membrane desorber lab testing data indicates a 54% increase in COE. We have designed and constructed the bench-scaled unit in which only minor changes for equipment/instrument are required for the system to be used in the pilot field test.

BP3 OBJECTIVES AND TASKS

BP3 Objectives

The first objective of the BP3 (Tasks 14 to 17) is to complete development of PEEK membranes and membrane modules for the absorber and desorber to verify performance of an integrated system in the laboratory for at least 100 hours. The second objective (Tasks 18 to 23) is to demonstrate the proposed membrane contactor technology on a bench-scale system. The bench-scale system will consist of two membrane modules (one for absorption and the other for stripping) each with an active membrane area of 100 ft^2 to 800 ft^2.

BP3 Scope of Work and Tasks

BP3 has two budget periods, BP3A and BP3B. In BP3A, PEEK membrane contactors for CO_2 absorption and solvent regeneration will be further developed to increase the mass transfer coefficient and improve high temperature solvent resistance, and the modules will be tested for performance as a function of time. The integrated absorption/desorption membrane contactor process for CO_2 capture from flue gas will be developed and verified in the laboratory. Engineering of the bench-scale field test system will also take place to determine the flue gas take-off point, power and steam requirements, and analytical needs. In BP3B, the hollow-fiber membrane contactor technology will undergo bench-scale field testing at Midwest Generation's power plant site. The process design to be tested will be fully integrated and representative of scalable size membrane contactors. Table 29 shows the BP3 work plan. Please note that the estimated completions for Tasks 18-20 have been updated based on the latest version of the PMP.

Table 29. BP3 work plan.

Task #	Task Title	Estimated Completion	Responsible Individual/Organization
BP3A			
14	Further development of PEEK membrane and membrane modules for absorption and solvent regeneration	01/31/2013	Research Scientist at PGC and GTI
15	100-hour lab testing of the integrated membrane contactor absorption and solvent regeneration process in the laboratory	03/31/2013	Research Scientists at GTI
16	Engineering of the field test system	03/31/2013	Research Scientists at GTI
17	BP3A project management	03/31/2013	GTI PI and PGC Technical Lead
BP3B			
18	Bench scale module and system manufacture	07/31/2013	Research Scientist at PGC and GTI
19	Initial bench scale system shake down	08/31/2013	GTI PI and PGC Technical Lead
20	Site preparation and system installation at the	08/31/2013	Research Scientists at

	plant		GTI
21	Operation of the field test system	11/30/2013	Research Scientists at GTI
22	Final economic evaluation	12/31/2013	Research Scientists at GTI
23	BP3B project management	01/31/2014	GTI PI and PGC Technical Lead

BP3 TECHNICAL PROGRESS

Task 14. Further development of PEEK membrane and membrane modules for absorption and solvent regeneration

Description of Work

In this task, the hollow-fiber membrane with properties tailored towards flue gas CO_2 absorption will be further developed for enhanced mass transfer from the current level of 0.4 kg CO_2/hr/m^2. We will also demonstrate the ability to achieve a consistent mass transfer coefficient to at least the current level. Membrane module design and construction will also be further studied to increase the overall gas mass transfer coefficient by minimizing liquid side resistance, maximizing the driving force and increasing the liquid side mass transfer coefficient. Important design features of a module include the regularity of fibers (poly-dispersity and spatial arrangements of fibers) and packing density. The desorption membrane contactor design will be further developed towards membrane contactor operational stability under high-temperature CO_2 regeneration process conditions.

Experimental Methods, Results and Discussion

The objective of this task was to produce larger surface area membrane contactor modules that could achieve consistent mass transfer coefficient of at least 0.4 kg CO_2/hr/m^2 at 90% removal with aMDEA solvent. This value was obtained from smaller-area modules circa 1-2 ft^2 during BP1 study. To bring membrane contactor technology for post-combustion CO_2 capture from laboratory- and bench-scale to commercialization, it was important to reproduce the 0.4 kg CO_2/hr/m^2 at 90% removal with larger surface area membrane modules.

In the first quarter of BP3 study, we tested a number of modules with surface areas between 2.1 and 8.2 ft^2 (Table 30). Their CO_2 capture rate at 90% CO_2 removal varied between 0.09 and 0.20 kg/m^2/h, lower than our target of 0.4 kg/m^2/h. Scientists and engineers at PoroGen and GTI evaluated key issues that caused contactor modules to exhibit low mass transfer coefficients, identified key issues and took corrective actions. A new series of modules (2PG471 and 2PG472) were designed and constructed by PoroGen and shipped to GTI for absorption testing. As shown in Table 30, the changes in contactor design have been successful in reproducing the 0.4 kg/hr/m^2 membrane adsorption performance exhibited by early stage, small area size modules (aMDEA used as a solvent). As contactor membrane surface area was increased from 1.2 ft^2 (module 2PG471) to 4.4 ft^2 (module 2PG472), the CO_2 removal rate remained the same (0.44 kg/m^2/hr).

Table 30. Membrane absorption performance.

Module	Membrane area, ft^2	CO_2 capture rate at 90% removal with aMDEA solvent, $kg/m^2/h$
Best modules tested in BP1 membrane absorption study		
2PG285	1.3	0.4
2PG286	1.2	0.4
Modules tested in the 1st quarter of BP3		
2PG368	2.1	0.15
2PG390	8.2	0.10
2PG407	4.6	0.09
2PG432	2.8	0.16
2PG433	2.8	0.09
2PG434	6.8	0.20
2PG435	6.8	0.20
2PG438	6.8	0.20
Modules tested in the 2nd quarter of BP3		
2PG471	1.2	0.44
2PG472	4.4	0.44

Task 15. 100-hour lab testing of the integrated membrane contactor absorption and solvent regeneration process in the laboratory

Description of Work

In this task, we will integrate the membrane contactor CO_2 absorption process with the membrane contactor solvent regeneration process to complete the solvent utilization cycle using 2-inch modules. We will operate the integrated system under complete solvent recycle and CO_2 capture mode for at least 100 hours to validate the process while separating 90% of the carbon dioxide in the feed stream.

Experimental Methods, Results and Discussion

The system performance was shaken down and issues such as flow rate control, temperature control, level control, and issues with number of analytical measurements in the integrated system were identified. We then addressed these issues and the 100-hour integrated membrane contactor absorption and solvent regeneration lab test s has been conducted.

The process flow diagram (PFD) of the integrated membrane contactor absorption and solvent regeneration system is shown in Figure 29.

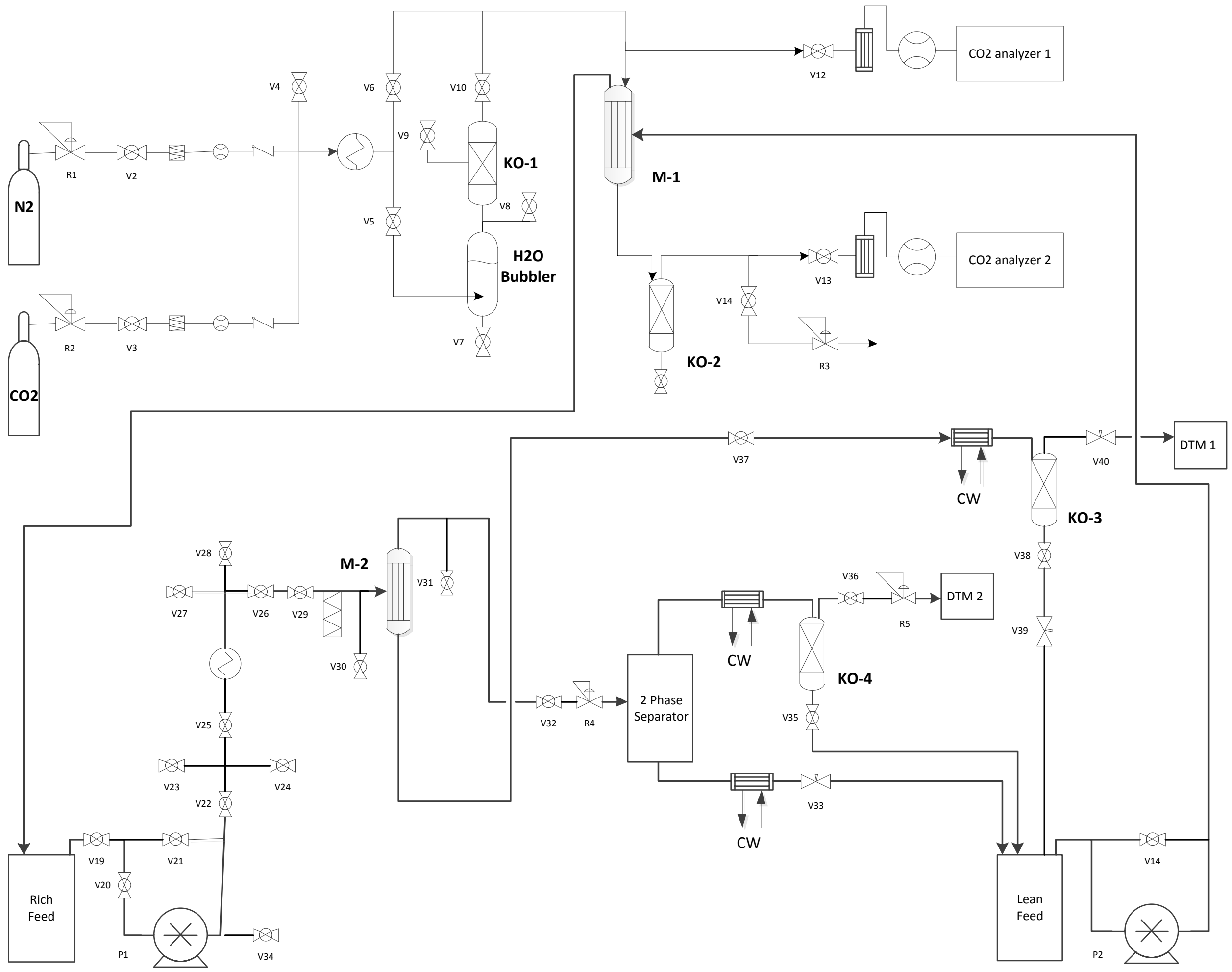


Figure 29. PFD of the integrated membrane contactor absorber/desorber system.

Two-inch diameter membrane modules (15-inch long) were used in this test. The Membrane absorber and desorber operating conditions are shown in Table 31. Testing was performed with simulated flue gas (13 % CO_2 feed) with a target gas flow rate of 2.3 L/min. The two most important parameters measured were the CO_2 concentrations in gas streams (inlet and outlet of membrane absorber) and CO_2 content in the solvent streams (inlet and outlet of membrane desorber). The former is measured by a CO_2 analyzer (S158-15, CO_2 concentration in 0-15 % (mole) range) and the latter is measured by titration. GTI has developed an analytical procedure using titration that can measure CO_2 content in amine-based solvent as low as 0.3 wt.% with high accuracy.

Table 31. Integrated membrane absorber and desorber operating conditions.

Parameter	Condition
Membrane Absorption	
Gas inlet temperature	98.7-126.2 °F
Simulated flue gas CO_2 inlet concentration	13 mol.% (balance N_2)
Membrane module	2PG448
Membrane contactor surface area	3.0 ft^2
Initial gas flow rate	2.3 SLPM
Inlet gas pressure	1.32-3.77 psig
Liquid inlet temperature	70.8-101.5 °F
Liquid flow rate	0.5 L/min
Inlet liquid pressure	0.9-4.64 psig
CO_2 capture rate at 90% removal with aMDEA solvent	0.10 $kg/m^2/h$
Membrane Desorption	
Solvent inlet temperature	230-260 °F
Solvent outlet temperature	220-250 °F
Liquid flow rate	0.5 L/min
Solvent inlet pressure	43-55 psig
Solvent pressure drop across the membrane	40 psig
Membrane module	2PG306
CO_2 stripping rate from rich aMDEA	0.24-0.3 L/min

As shown in Figure 30, the integrated test with simulated flue gas (13 % CO_2 feed) was initiated at point A, with the total gas flow rate of 2.3 L/min. CO_2 removal higher than 90% has been achieved for the first 42 hours. At point B, a solvent level control failure caused the liquid side temperature to rise above the gas side temperature. As a result, water vapor condensed in the contactor, leading to a drop in CO_2 removal performance in the next 9 hours. At point C, the N_2 flow rate through hollow fiber bores of the absorber was increased by a factor of 7.5 (CO_2 flow rate kept unchanged) to dry out the contactor and maintained for the next 6 hours. At point D, the N_2 flow rate was reset to the original value, and the measured CO_2 removal rate was 86.6 %, indicating the contactor had not been completely dried out. We then decreased the total gas flow rate to 1.84 L/min while still maintaining a 13 % CO_2 feed. The CO_2 removal rate remained higher than 90 % in the next 46 hours.

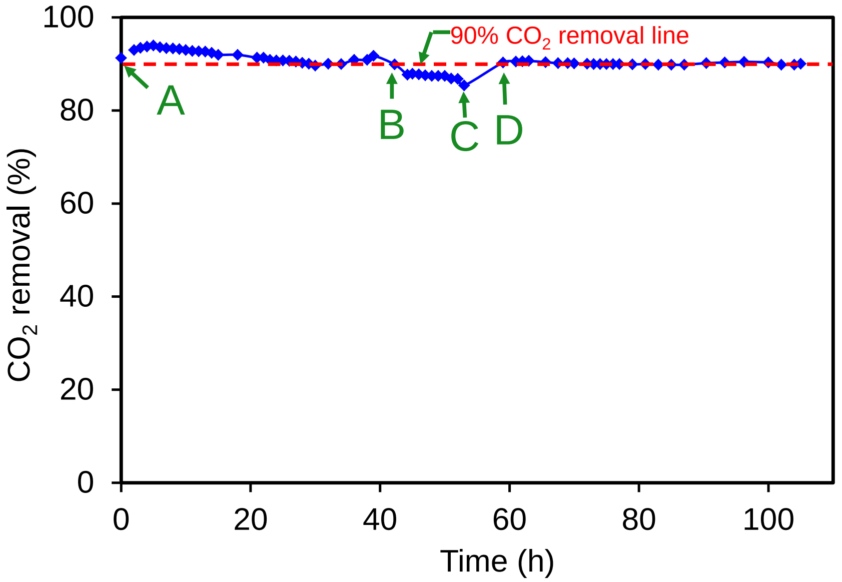


Figure 30. CO_2 removal rate as a function of operating time (module 2PG448).

During the operation of the integrated absorption/desorption the regeneration module operation was monitored. The CO_2 contents of the aMDEA solvent fed to the membrane absorber was measured every 24 hours by the titration method. Measured concentrations are shown in Table 32. The measured concentration varies within experimental error of the titration method (±20%) for such low CO_2 contents, indicating the CO_2 content of the aMDEA solvent remained essentially constant during the test.

Table 32. Lean solvent CO_2 concentration fed to the membrane absorber.

Date	CO_2 content obtained by titration analyses
Day 1	0.35 wt.%
Day 2	0.35 wt.%
Day 3	0.37 wt.%
Day 4	0.41 wt.%
Day 5	0.40 wt.%

Task 16. Engineering of the field test system

Description of Work

In this task, engineering of the field test system will take place to determine the flue gas take-off point, power and steam requirements, location of the unit, and analytical needs. Preliminary safety reviews will be conducted with the plant personnel.

Experimental Methods, Results and Discussion

A detailed field testing plan was sent to Midwest Generation. The summary information is given below:

- Test unit details
    - Footprint: 6 ft. (W) x 14 ft. (L) x 12 ft. (H)

  - Weight: 1000 lbs.
  - Flue gas flow rate: 70 ACFM (61 SCFM)
  - Pipe size for flue gas take off/return: > 2 inch Sch. 40
  - Chemical inventory: 1 drum aMDEA-40 % in water
- Utility needs
  - Electric: three 120 V and 20 A for pumps, computers and sensors, 480 V and 40 A for solvent heaters
  - Cooling water (city water): 5 gallon/min
- Operating philosophy
  - GTI to operate the unit
  - Midwest has the ability to shut unit down
  - Test duration 30 to 50 days
  - There is an 8-hour test with increased SO_2 concentration (~150ppmv) to simulate burning IL6 coal
  - Test unit removed from site after test by GTI

On May 30, 2013 Midwest Generation informed us that the test site will be changed from the Joliet Station to the Will County Station in Romeoville, IL. The major process difference in relocating the test to the Will County was that the temperature of the flue gas was higher, about 300 °F. This would affect the sizing of the primary heat exchanger of the system. Will County station site visit was conducted the potential system placement location (Figure 31) and the required flue gas source and utilities identified.

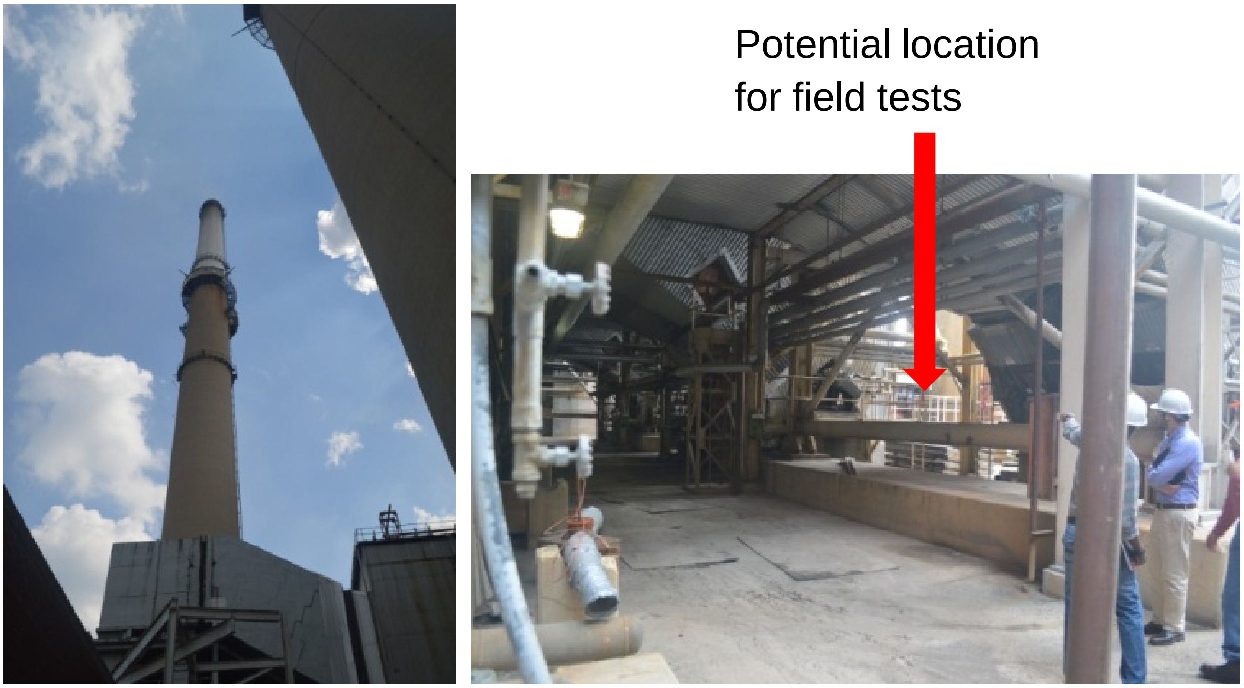


Figure 31. Potential test system location at Midwest Power Generation plant.

Task 17. BP3A Project management

Description of Work

GTI will coordinate all project activities with PGC and will report technical progress and financial status to DOE throughout the duration of the project. Periodic teleconference meetings will be held to review program technical performance, schedule, and budget, and to resolve issues between all active participants. Scheduling software will be used to help keep the project on time and within budget. Technology transfer to the industry will be through presentations at conferences under this task, as well as briefing to DOE. GTI will update the Project Management Plan as the project progresses.

Project Activities/Products/Deliverables

In addition to day-to-day project management, we had several teleconferences with DOE/NETL Project Manager. Based upon the progress on BP3A studies, we sent a milestone update letter to DOE. We then got an approval to process our continuation to the second phase of Budget Period 3 covering Tasks 18-23.

Task 18. Bench scale module and system manufacture

Description of Work

In this task, several membrane contactor modules will be fabricated using the designs and processes developed in BP1 and BP2 of the project and the bench scale test system will be constructed based on the design completed in BP3.

Subtask 18.1. Membrane module construction

In this subtask, at least two membrane modules for bench scale tests will be prepared (for both sorption and regeneration stages). The hollow fiber cartridge will be formed by computer-controlled helical winding. The module size will be circa 4- or 8-inch diameter by 60-inch long and contain about 100 to 800 ft^2 of membrane area. The absorption contactor cartridges will be housed in a SS304 housing and the de-sorption contactor cartridge will be housed in a SS316 (or SS304) stainless steel housing.

Experimental Methods, Results and Discussion

The overall transport resistance for CO_2 in membrane contactors comes from three parts: the gas phase, the membrane, and the liquid phase. The resistance in the gas phase is typically very small. The resistance in the liquid phase is a function of contactor module design, i.e. flow dynamics, and solvent characteristics. Once the solvent is selected and operating conditions are determined, the resistance in the membrane phase becomes the restricting parameter to the overall membrane contactor performance. The resistance in the membrane phase is a function of membrane structure. Membrane intrinsic CO_2 permeance is a good indication of transport resistance in the membrane; high intrinsic CO_2 permeance is important in attaining high CO_2 capture rates in membrane contactor mode.

By modifying and optimizing membrane preparation procedures, PoroGen has produced PEEK hollow fiber membranes with intrinsic CO_2 permeances as high as 2,000 GPU. The high CO_2 permeance obtained exceeds the initial program target for commercial contactor performance that was set at 1,000 GPU.

The design and construction of larger surface area module for pilot test was completed by PoroGen. Figure 32 shows module cartridge scale-up from bench to commercial size. We will be eventually using full-scale 8-inch diameter modules for the final pilot test. For bench-scale field test at Midwest Generation, contactor cartridges of the following size were constructed - 4-inch diameter by 5-ft. long for both absorption and regeneration stages. Scaling factors were addressed during scale up cartridge construction.

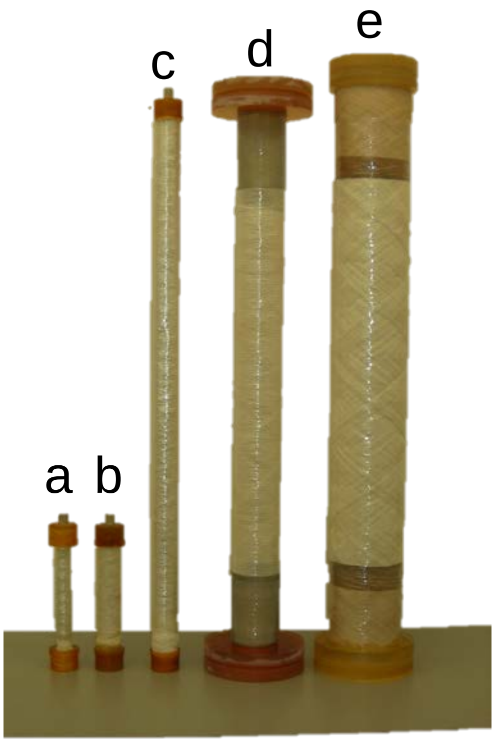


Figure 32. Contactor module cartridge scale-up from laboratory to commercial size: a) 2-inch bench – 1.2 ft^2, b) 2-inch bench – 5 ft^2, c) 2-inch bench – 30 ft^2, d) 4-inch transition – 164 ft^2, e) 8-inch commercial – 640 ft^2

The contactor cartridge is housed in an 8-inch pressure shell designed for flue gas operation. A photo of the 4-inch module contains about 117.5 ft^2 of hollow fiber membrane area is shown in Figure 33. Please note that a 2-inch diameter module used in lab tests is also shown in Figure 33 for comparison.

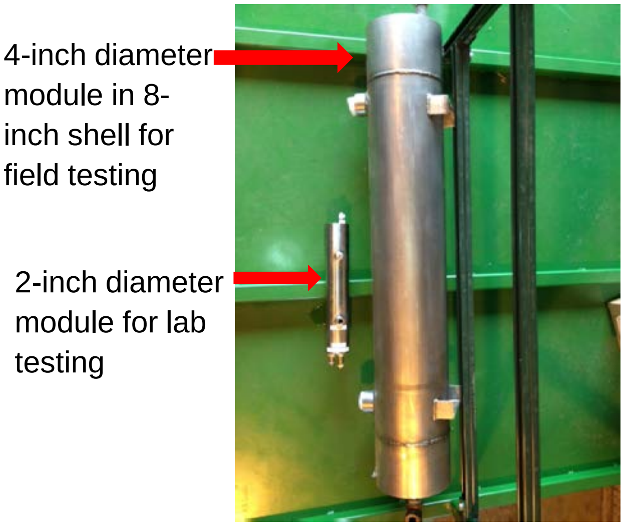


Figure 33. A 4-inch diameter module in 8-inch shell for field testing.

The intrinsic CO_2 permeance had remained constant as membrane area increased from 1-4 ft^2 2-inch to ~164 ft^2 4-inch diameter modules. The contactor performance of 164 ft^2 modules can be evaluated only in the field due to high feed gas flow requirements.

Subtask 18.2. Bench scale system construction

In this subtask, the test system will be fabricated based on the PI&D and components specified. Critical objective achieved upon completion of the task: Bench scale system for field test is constructed.

Experimental Methods, Results and Discussion

Because the Will County power station flue gas temperature was high ~300°F (our field testing site), installation of direct contactor cooler (DCC) along with other equipment was required upstream of the membrane absorber. To make the whole bench scale system compact, we made a decision to construct a completely new unit. Figure 34 shows a photo of the system constructed. Figure 34 shows the P&ID of the bench-scale system. This system was equipped with two 4-inch diameter modules: one for absorption, the other for desorption.

Figure 34. Photo of the field test system.

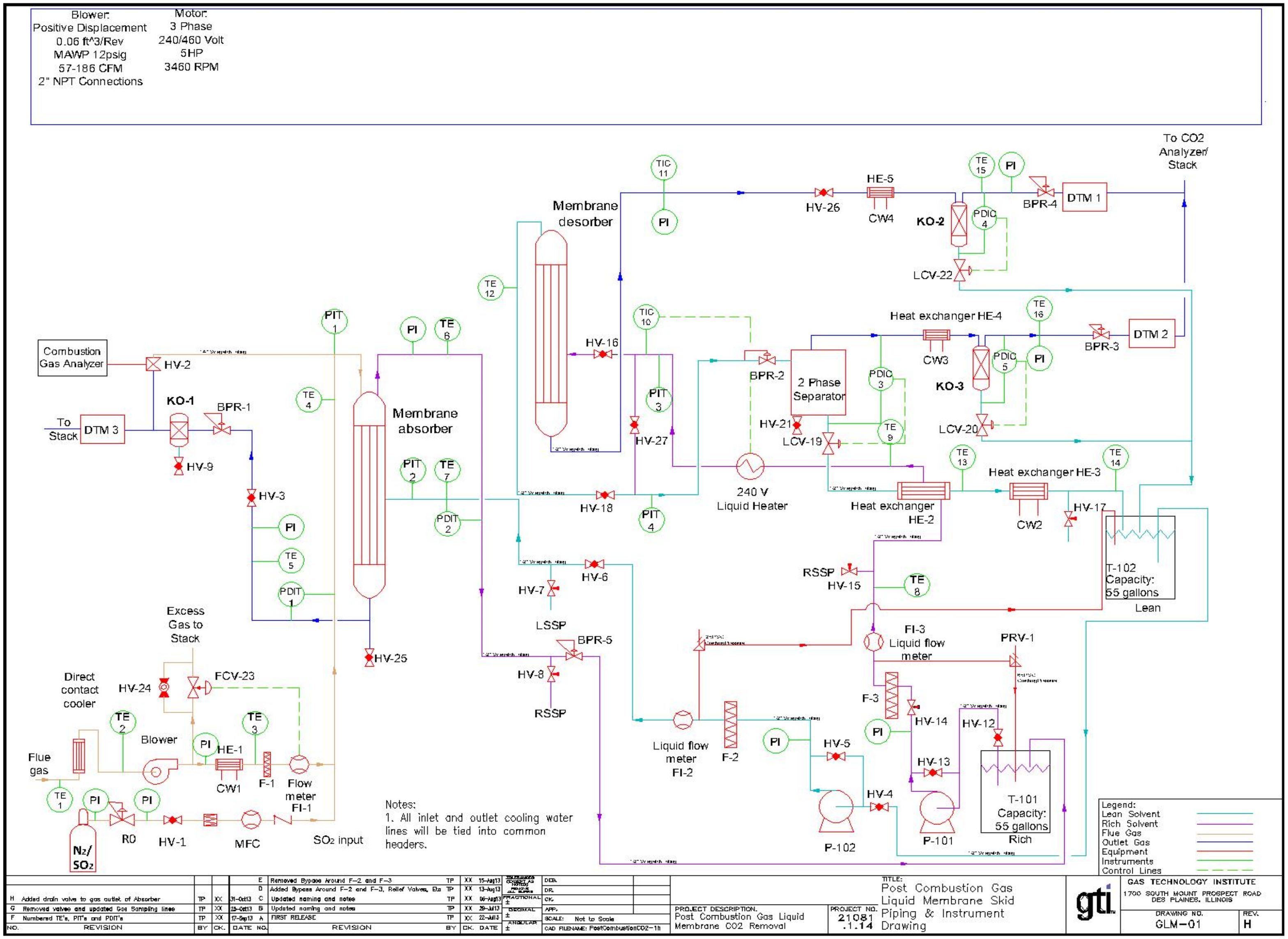


Figure 35. P&ID of the field testing system.

High temperature and corrosive environment encountered during the regeneration process impose severe demands on materials of construction. O-rings manufactured from specialty material have been used in the 4-inch membrane desorber construction. E-8 epoxy formulation was selected for tubesheet construction. The regeneration module was equipped with hydrophobic PEEK hollow fibers with intrinsic CO_2 permeances of 1,000 GPU, which was sufficient for the bench-scale field desorption testing based on our analysis.

Two 4-inch cartridges were prepared for the membrane contactor absorption field test: the first contactor was equipped with membranes with intrinsic CO_2 permeance of 1,000 GPU, the second module was equipped with membranes with intrinsic CO_2 permeance of 2,000 GPU. 2,000 GPU permeance hollow fibers had a larger inner bore diameter (13.2 mil) than the 1,000 GPU hollow fibers (8.8 mil). Please note that our membrane contactor process can operate at close to atmospheric pressure. The only requirement related to pressure of membrane contactor process is that the inlet flue gas pressure must be slightly higher than the ambient pressure in order to ensure uniform flue gas flow through the hollow fibers; the lower the pressure drop for flow through the hollow fiber membrane, the more saving on operating costs. In our post-combustion CO_2 capture process, a majority of feed gas (~ 88%) remains in the tube side. Thus, the pressure drop for flow through the hollow fiber membrane can be simply estimated by the Hagen–Poiseuille equation:

$$\Delta P = \frac{8Q\eta L}{\pi \cdot r^4} \tag{5}$$

Where Q is the volumetric flow rate, η the absolute viscosity of the fluid, L the length of the hollow fiber, and r the hydraulic radius of the hollow fiber. Equation 1 suggests gas-side pressure drop increases linearly with fiber length L and $1/r^4$ for a fixed gas flow rate. Therefore, after switching from old fibers (ID: 8.8 mil) to new fibers (ID: 13.2), the gas side pressure drop through the new 2,000 GPU fibers is expected to be only 20% of that obtained for the old 1,000 GPU fibers.

Task 19. Initial bench scale system shake down

Description of Work

In this task, the assembled test system will undergo initial component and operational shake down at GTI site prior to the field installation. Any system and/or operational deficiencies will be corrected at this time. Operation of the integrated membrane absorber/desorber field test unit will operate with reduced gas flow and full liquid flow with no leaks or other operational issues.

Experimental Methods, Results and Discussion

We did a complete shakedown of the unit using air in the gas side and water in the liquid side. A large part of the work focused on leak checking the unit, verifying the overall operability of the unit and completing the programming of the Data Acquisition System. Issues have been identified and resolved. The safety items were also completed which included alarm set points, alarm indication, emergency shut offs and interlocks.

Task 20. Site preparation and system installation at the plant

Description of Work

In this task, the Midwest Generation's Will County Station site will be prepared to receive the system for installation and the system will be installed at the site with all necessary connections for feed, product, cooling, and waste disposal. All safety reviews and operational plans will be agreed on with the plant personnel.

Experimental Methods, Results and Discussion

After completing initial shakedown of the field testing system at GTI, the system was moved to the Midwest Generation's Will County Station site (located in Romeoville, IL) on October 1, 2013. GTI engineers together with Midwest Generation engineers reviewed bench-scale CO_2 capture program, operational details, and completed HAZOP analysis while providing Midwest Generation with all related safety documentation (including MSDS of each solvent to be used). GTI engineers were also trained to work on site at the facility for the field tests stage of the program. After permit from the Illinois Environmental Protection Agency was received, Midwest Generation engineers and technicians installed GTI's membrane contactor skid at the site with all necessary connections for feed and product gases, and cooling water supply and return. A process flow diagram, Figure 36, shows how the membrane contactor skid is integrated with the flue gas system at the Midwest Generation Will County Station. The flue gas was taken downstream of the induced draught (ID) fan, cooled by DCC and sent to skid blower, which boosted the flue gas pressure to approximately 2-6 psig. The flue gas was then cooled by an indirect cooler, filtered and sent to the membrane absorber. The CO_2 permeated through the membrane and was absorbed into the solvent. The CO_2-rich solvent was regenerated in the membrane desorber. Both the treated flue gas and stripped CO_2 stream from membrane desorber were sent back to the upstream of the ID fan. A photo of the installed system is shown in Figure 37.

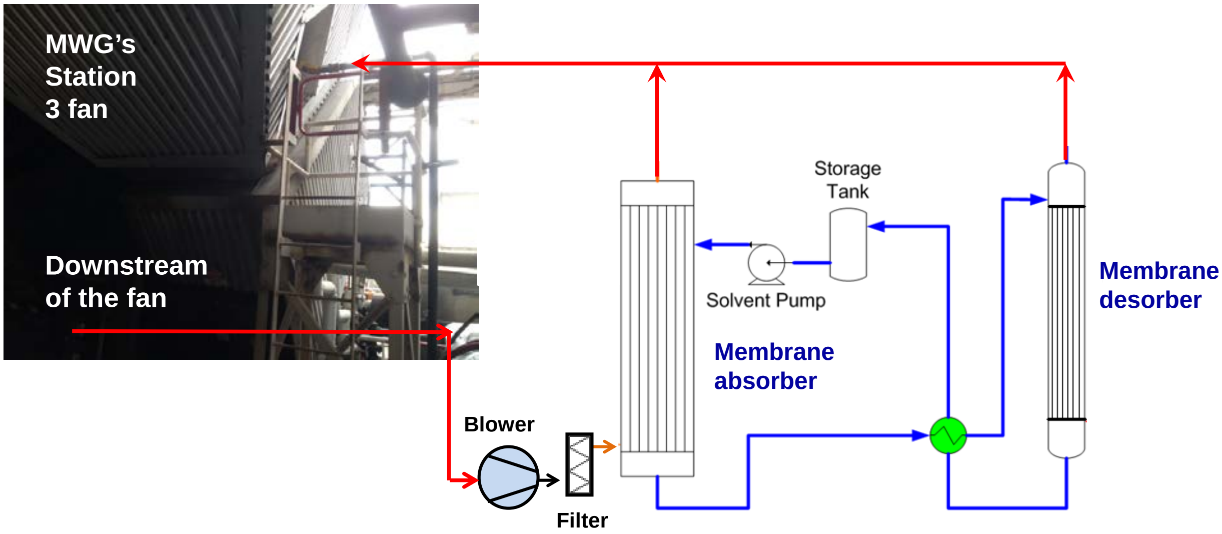


Figure 36. Process flow diagram.

Figure 37. Photo of the installed field test system.

Task 21. Operation of the field test system

Description of Work

In this task, the field test system will be operated with a flue gas slipstream from the Midwest Generation's Will County Station conditioned to mimic the flue gas compositions of burning IL coal. Performance parameters, process cost data and life time estimate of the membrane module under realistic feed conditions will be performed.

Experimental Methods, Results and Discussion

Once the system was installed at the plant, some electrical rewiring had to be completed due to the plant main feed being 208 V instead of 240 V. During initial operation, some minor issues emerged. Some debris was found in the outlet of the two-phase separator causing the vessel to drain slowly. This issue has been addressed by cleaning ducts downstream of the two-phase separator. The magnetic controller for the liquid heater was damaged and needed to be replaced. Once these issues were identified and corrected, the field test system was operated with flue gas slipstream from the Midwest Generation Will County Station.

The flue gas composition measured on the upstream of the membrane absorber is listed in Table 33. The composition was measured by a Horiba portable PG-250 gas analyzer. The measured relative humidity of the flue gas before the blower was 39% at 130 °F. The CO_2 concentration was lower than expected, indicating a potential air leak into their system.

Table 33. Flue gas composition**.**

Component	Concentration
CO_2	9.58 vol.%
NO_x	49.4 ppmv
SO_2	0.6 ppmv
CO	103.8 ppmv
O_2	10.88 vol.%
Balance: N_2 , water vapor and trace elements	

Due to the high inlet temperature of the flue gas, the field test unit was equipped with a direct contact cooler (DCC) for cooling the flue gas to the cooling water temperature before the blower. Since the DCC was placed on the suction side of the blower, issues arose due to the vacuum created by the blower, preventing proper drainage of the DCC. All the water injected into the DCC was sucked into the blower causing it to shut down automatically. This issue was resolved by eliminating water injection into the DCC and using the DCC as an air cooling device only. Due to the larger surface area and packing in the DCC, it worked well to cool the flue gas temperature to levels that the blower could handle.

During initial shake down the integrated absorption/desorption system was run with 1,000 GPU contactor module. After all of the initial issues were resolved, the 2000 GPU membrane absorber contactor module was installed. The membrane absorber and desorber operating conditions are shown in Table 34.

Table 34. Integrated membrane absorber and desorber operating conditions.

Parameter	Condition
Membrane Absorption	
Solvents	40 wt.% aMDEA/H_2O, and H3-1
Membrane module	PG326, PG347
Membrane contactor surface area	117.5 ft^2 for PG326 (a 1,000 GPU module) and 164 ft^2 for PG347 (a 2,000 GPU module)
Gas inlet temperature	46-60 °F
Flue gas composition	Listed in Table 33
Gas flow rate	17-250 L/min
Inlet gas pressure	1.20-1.70 psig
Solvent inlet temperature	55-61°F
Solvent flow rate	1-6 L/min
Inlet solvent pressure	4-12 psig
Membrane Desorption	
Solvents	40 wt.% aMDEA/H_2O and H3-1
Membrane module	PG325
Membrane contactor surface area	117.5 ft^2
Solvent inlet temperature	220-250 °F
Solvent outlet temperature	160-220 °F
Liquid flow rate	1-2 L/min
Solvent inlet pressure	40-55 psig
Solvent pressure drop across the membrane	40 psig

The SO_2 concentration in the feed flue gas was relatively low. Additional SO_2 was metered into the skid feed gas. Tests were conducted with ~ 450-470 ppmv SO_2 in the skid feed to mimic the flue gas compositions of burning Illinois coal. Membrane absorber contactor module with 1,000 GPU CO_2 permeance (PG326) was used in these tests. During the test, 90 % CO_2 removal was achieved (Figure 38). The membrane regeneration system worked well and provided sufficiently lean solvent for the membrane absorber to remove 90% or more of the CO_2.

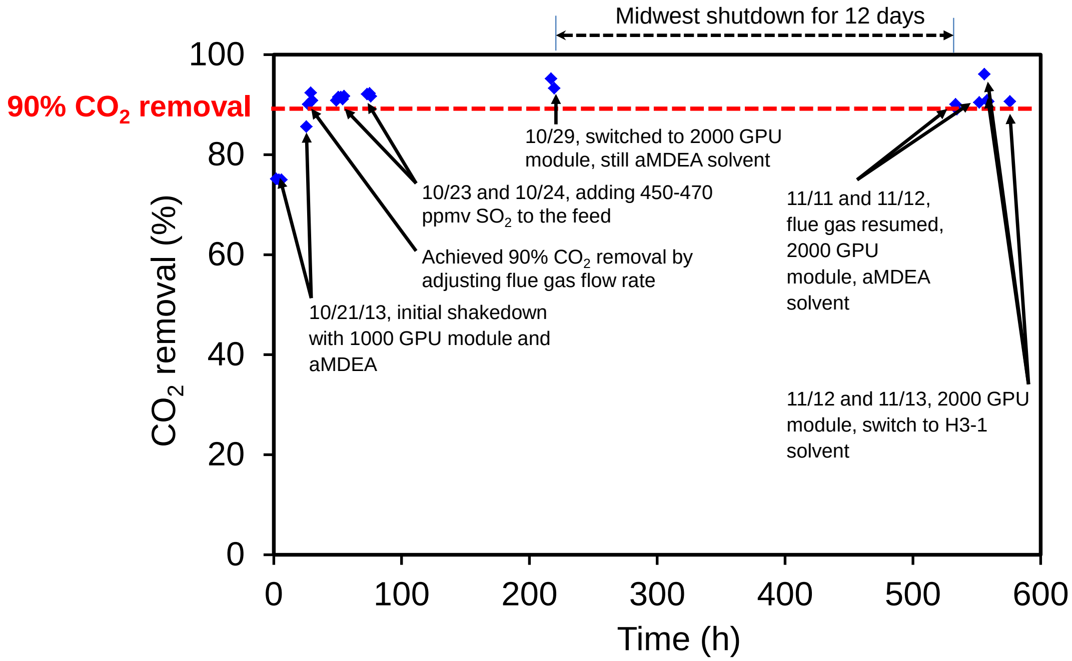


Figure 38. Run chronology.

Effect of flue gas contaminants

In an 8-hour test with increased SO_2 concentration to simulate burning Illinois coal (indicated 10/23 and 10/24 on Figure 38), we found that the field CO_2 capture performance was not affected by flue gas contaminant SO_2. The solvent throughout this test was aMDEA.

CO_2 capture performance of the 2,000 GPU module

With assistance from a PoroGen technician, the 1,000 GPU contactor absorber used in initial test was replaced with 2,000 GPU contactor module absorber. Greater than 90% CO_2 removal in one stage was achieved. The mass transfer coefficient was 1.2 $(sec)^{-1}$ at 93% CO_2 removal, exceeding the initial target of 1.0 $(sec)^{-1}$. This mass transfer coefficient is over one order of magnitude greater than those of conventional contactors with packed columns (0.0007 – 0.075 $[sec]^{-1}$).

Gas velocity and residence time in the 4-inch diameter contactor module tested in the field were greater than those of the 2-inch diameter bench scale modules tested in the lab (Table 35), which could affect mass transfer coefficient.

Table 35. Gas velocities and residence times in 2-inch and 4-inch diameter modules.

Module	Gas velocity in fiber, m/s	Gas residence time in fiber, s
2-inch module (15-inch long) 2PG472	3.3	0.12
4-inch module (60-inch long) PG347	4.8	0.32

Table 36 shows that the liquid velocity in the 4-inch module was much lower than that of the 2-inch module. Lower liquid velocity means less turbulence, which may cause a higher resistance in the liquid phase.

Table 36. Liquid flow rates and velocities in 2-inch and 4-inch diameter modules.

Module	Membrane area, ft^2	Liquid flow rate, L/min	Liquid velocity in module, m/s
2-inch module 2PG472	4.4	0.5	0.0097
4-inch module 347	164	1.0	0.0039

The lower mass transfer coefficient for the 4-inch module was most likely due to the higher resistance in the liquid phase. In our future test, higher liquid velocities will be used to achieve higher mass transfer coefficients.

CO_2 loading of the rich-solvent

Rich solvent CO_2 loading is an important parameter that must be considered in the process design. The higher CO_2 loading of the rich solvent, the lower is the amount of liquid to be heated and circulated, and thus the energy saving during regeneration is higher. We have calculated the rich solvent CO_2 loadings for runs with both 2-inch and 4-inch modules. The rich solvent CO_2 loading was much higher for 4-inch module (relative to the 2-inch module) as shown in Table 37. The rich solvent CO_2 loading of 0.6 wt.% in the lab test of 2-inch module would be too low for a practical operation. By contrast, the rich solvent CO_2 loading of 5.2 wt.% was comparable to that used in conventional packed column operation. Please note that CO_2 loading of 5.2 wt.% is ~65% of saturation of the aMDEA solvent.

Table 37. Rich solvent CO_2 loadings in 2-inch and 4-inch diameter modules.

Module	Flue gas flow rate, L/min	Liquid flow rate, L/min	L/G ratio, L/L	Rich solvent CO_2 loading, wt.%	Mass transfer coefficient, $(sec)^{-1}$
2-inch module 2PG472	12	0.5	0.042	0.6%	1.7
4-inch module 347	245	1.0	0.0041	5.2%	1.2

CO_2 capture performance with H3-1 solvent

CO_2 capture using advanced solvent H3-1 was also carried out. The H3-1 solvent is known to have a lower regeneration energy consumption than aMDEA solvent. Our field tests with H3-1 solvent showed it resulted in a 17% higher mass transfer coefficient than the aMDEA solvent (Table 38). The CO_2 removal level in one stage was also higher with the H3-1 solvent (92.7%) as compared to the aMDEA solvent (90.4%) even though the L/G ratio was lower for the H3-1 solvent. These factors, plus the improved regeneration shown elsewhere, indicate the projected savings achievable with our membrane contactor process can be further improved with the use of H3-1 solvent. H3-1 is the solvent that we proposed to use in our pilot-scale development where we will be able to obtain a sufficient heat and material balance for the regenerator as well as the absorber. The operation conditions and the mass transfer coefficient obtained in the field for the

4-inch module will be used as basis for future design and development of full-scale 8-inch modules.

Table 38. Comparison of CO_2 capture performances for aMDEA and H3-1 solvents.

Solvent	Flue gas flow rate, L/min	Liquid flow rate, L/min	L/G ratio, L/L	CO_2 removal in one stage	Normalized mass transfer coefficient
aMDEA	230	1.85	0.0080	90.4%	1
H3-1	241	1.07	0.0044	92.7%	1.17

Task 22. Final economic evaluation

Description of Work

In this task, we will perform final economic evaluation based on the bench scale field test data.

Results and Discussion

Please see the detailed Techno-Economic Analysis (TEA) Report starting from page 85.

Task 23. BP3B Project management

Description of Work

GTI will coordinate all project activities with PGC and will report technical progress and financial status to DOE throughout the duration of the project. Periodic teleconferencing meetings will be held to review program technical performance, schedule, and budget, and to resolve issues between all active participants. Scheduling software will be used to help keep the project on time and within budget. Technology transfer to the industry will be through presentations at conferences under this task, as well as briefing to DOE. The final report will be submitted 41 months after the start of the program. GTI will update the Project Management Plan as the project progresses.

Project Activities/Products/Deliverables

BP3 Q1, Q2, Q3, and Q4 Technical Progress Reports, and the Annual Report have been submitted in addition to day-to-day project management.

The following **paper** has been published in BP3:

- Shiguang Li, Dennis J. Rocha, S. James Zhou, Howard S. Meyer, Benjamin Bikson, Yong Ding, “Post-combustion CO_2 capture using super-hydrophobic, polyether ether ketone, hollow fiber membrane contactors”, *Journal of Membrane Sci.*, 430, 79-86, 2013.

The following **presentations** have been made during BP3:

1. S. James Zhou, Shiguang Li, Howard Meyer, Yong Ding and Ben Bikson, “Nano-porous PEEK Hollow-Fiber Contactor for Solvent Regeneration in CO_2 Capture Applications”, the 12th Annual Conference on Carbon Capture Utilization & Sequestration, May 13 - 16, 2013, Pittsburgh, PA.
2. S. James Zhou, Shiguang Li, Howard Meyer, Yong Ding and Ben Bikson, "Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture," DOE NETL CO2 Capture Technology Meeting, July 8-11, 2013, Pittsburgh, PA, USA.
3. Ajay Makkuni, Shiguang Li, Tim Tamale, S. James Zhou, Howard Meyer, Yong Ding and Ben Bikson, " Mathematical Modeling of Hollow Fiber Gas-Liquid Membrane Contactors for Acid Gas Removal," AIChE Annual Meeting, November 6th, 2013, San Francisco, USA.
4. S. James Zhou, Shiguang Li, Travis Pyrzynski, Howard Meyer, Yong Ding, Ben Bikson, Song Wu, and Katherine Searcy, "Pilot Test of a Nanoporous, Super-hydrophobic Membrane Contactor Process for Post-combustion CO_2 Capture," DOE NETL Kickoff Meeting, November 13, 2013, Pittsburgh, PA, USA.
5. S. James Zhou, Shiguang Li, and Howard Meyer, "Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture-Phase III," ICCI Project Review Meeting, December 18, 2013, Fairview Heights, IL USA.

BP3 SUMMARY

A bench-scale system utilizing a membrane absorber and desorber was integrated into a continuous CO_2 capture process using 2-inch diameter modules containing circa 20 ft^2 of membrane area. The integrated process operation was stable through a 100-hour laboratory test, utilizing a simulated flue gas stream, with greater than 90% CO_2 capture and 97% CO_2 product purity achieved throughout the test. Membrane modules have been scaled from 2-inch diameter to 4-inch diameter (membrane surface area of 164 ft^2 per module) for field testing in a coal-fired power plant (Midwest Generation’s Will County Station located in Romeoville, IL). The field test unit with a 4-inch 2,000 GPU module in conjunction with aMDEA solvent showed greater than 90% CO_2 removal in one stage. The mass transfer coefficient for absorption was 1.2 $(sec)^{-1}$, exceeding the target of 1.0 $(sec)^{-1}$. The field CO_2 capture performance was not affected by flue gas contaminants SO_2 and NO_x. Field tests with an advanced H3-1 solvent at lower L/G ratio showed it has a 17% higher mass transfer coefficient than the aMDEA solvent. The projected savings achievable with our membrane contactor process can be further improved with the use of H3-1 solvent due to lower regeneration energy and lower solvent recirculation rate. The operation conditions and the mass transfer coefficient obtained in the field for the 4” module will be used as basis for future design and development of full-scale 8” modules in our pilot-scale development program.

FINAL TECHNO-ECONOMIC ANALYSIS REPORT

Figure 39 shows our Techno-Economic Analysis (TEA) procedure. The TEA includes 1) field test output, 2) membrane performance modeling, 3) membrane process modeling, 4) cost modeling in comparison to DOE cases 9 and 10, and 5) sensitivity analysis and strategy to achieve DOE's 2025 cost goal. The experimental conditions and mass transfer coefficient obtained in the field with the aMDEA solvent were used as basis for the membrane performance modeling, whereas the membrane performance modeling output and the process of the field testing were used as basis for the membrane process modeling for commercial applications.

The major economic evaluation bases are listed below:

- The field testing results obtained for an integrated membrane absorption/desorption process in conjunction with aMDEA solvent tested in a coal-fired power plant (Midwest Generation's Will County Station located in Romeoville, IL)
- Flue gas CO_2 concentration of 14 (mol%), and 90% CO_2 capture from a nominal 550 MW_e, subcritical pulverized coal power plant.
- The costs of the membrane module assumed at \$80 (Yr 2006\$) /m^2.

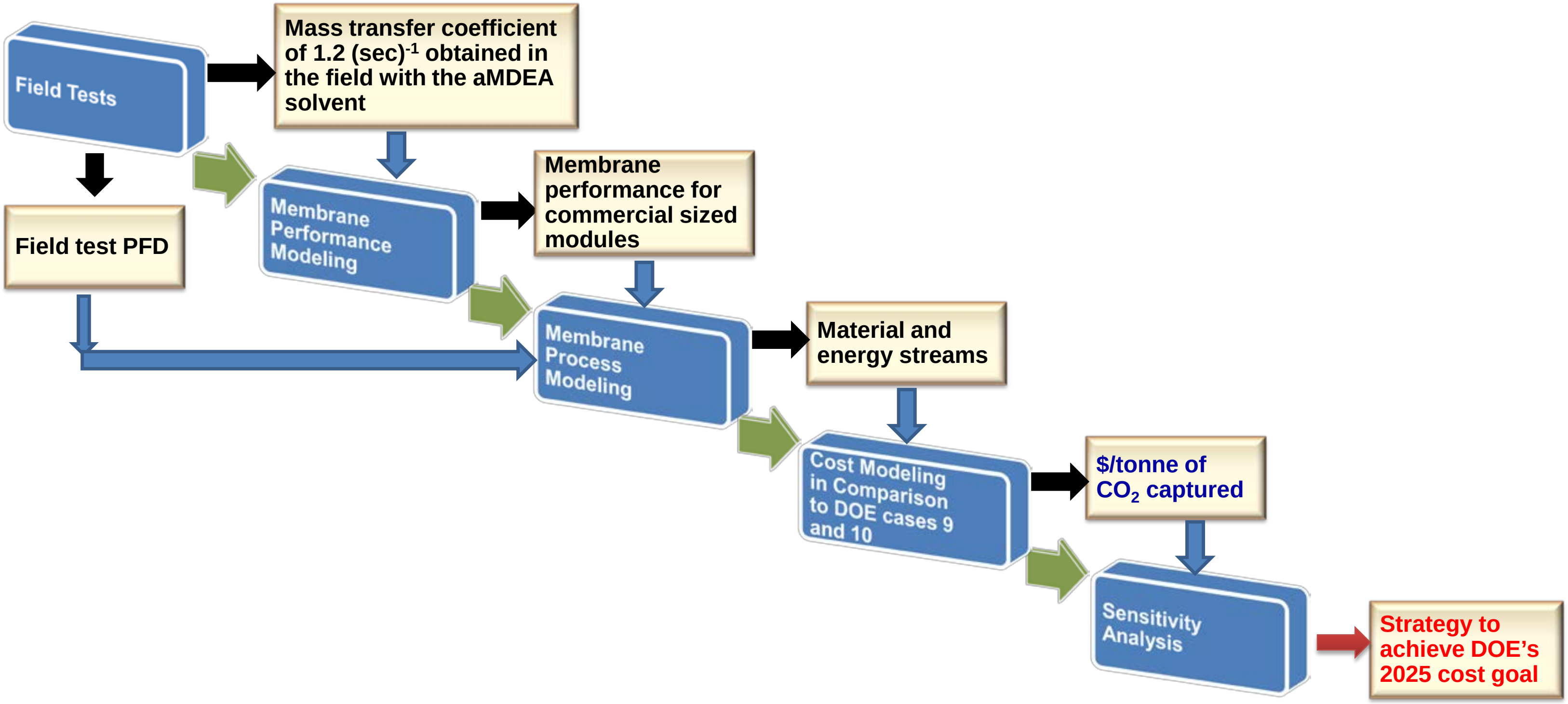


Figure 39. TEA procedure.

Fields Tests Output

The State-Point Data based on membrane is shown in Table 39. A selective layer is not required in the membrane contactor process. The membrane layer (thickness less than 0.1 μm) mainly provides a barrier between the phases. The critical property of this layer is super-hydrophobicity, ensuring the membrane operates in a non-wetting mode. The HFC process selectivity is actually determined by the chemical affinity of the absorption solvent to CO_2 over N_2. CO_2/N_2 process selectivity greater than 1,000 was obtained in the bench-scale study.

Table 39. State-Point Data (membrane based) for HFC systems

	Units	**Measured/ Estimated Performance**
Materials Properties		
Materials of Fabrication for Selective Layer		Not applicable for membrane contactor
Materials of Fabrication for Support Layer		PEEK
Nominal Thickness of Selective Layer (μm)		Not applicable for membrane contactor
Membrane Geometry		Hollow fiber
Max Trans-Membrane Pressure	Bar	4
Hours tested without significant degradation		200 hours
Membrane Performance		
Temperature	°C	Absorber: 8-24 °C Desorber: 100-140 °C
Pressure Normalized Flux for Permeate (CO_2)	GPU or equivalent	2,000
CO_2/H_2O Selectivity	-	Not applicable
CO_2/N_2 Selectivity	-	>1000
CO_2/SO_2 Selectivity	-	0.64
Type of Measurement	-	Coal-fired power plant flue gas
Flow Arrangement	-	Counter-current hollow fiber
Packing Density	m^2/m^3	2,000
Shell-Side Fluid	-	Liquid amine solvent

In our test, the flue gas composition on the upstream of the membrane absorber was 9.58 vol.% CO_2, 49.4 ppmv NO_x, 0.6 ppmv SO_2, 103.8 ppmv CO, 10.88 vol.% O_2 , and balance N_2, water vapor and trace elements. The composition was measured by a Horiba portable PG-250 gas analyzer. The measured relative humidity of the flue gas before the blower was 39% at 130°F.

Because PEEK membrane contactor technology also has “solvent” feature, State-Point Data based on solvent (aMDEA) are listed in Table 40.

Table 40. State-Point Data (solvent-based) for HFC systems.

	Units	**Measured/Estimated Performance**
Pure Solvent		
Molecular Weight	mol^{-1}	119.16
Normal Boiling Point	°C	247.3
Normal Freezing Point	°C	-21
Vapor Pressure @ 15^oC	bara	3.10E-06
Working Solution		
Concentration	kg/kg	0.40
Specific Gravity ($15^oC/15^oC$)	-	1.04
Specific Heat Capacity @ STP	kJ/kg-K	3.467
Viscosity @ STP	cP	7.361
Surface Tension @ STP	dyn/cm	56.135
Absorption		
Pressure	bara	1.1
Temperature	°C	40
Equilibrium CO_2 Loading	mol/mol	0.66
Heat of Absorption	kJ/mol CO_2	-53.9
Solution Viscosity	cP	2.253
Desorption		
Pressure	bara	2
Temperature	°C	120
Equilibrium CO_2 Loading	mol/mol	0.08
Heat of Desorption	kJ/mol CO_2	-67.7

Figure 40 shows a P&ID of the field testing system. The major testing results for a 2,000 GPU membrane absorber are shown in Table 41. These results along with the experimental conditions were used as basses for the membrane performance modeling.

Table 41. Major testing results obtained in the field.

Module	CO_2 feed concen.	Gas velocity in fiber, m/s	Liquid velocity in module, m/s	Rich solvent CO_2 loading, wt.%	Mass transfer coefficient, $(sec)^{-1}$
4-inch module 347	9.2%	4.8	0.0039	5.2%	1.2

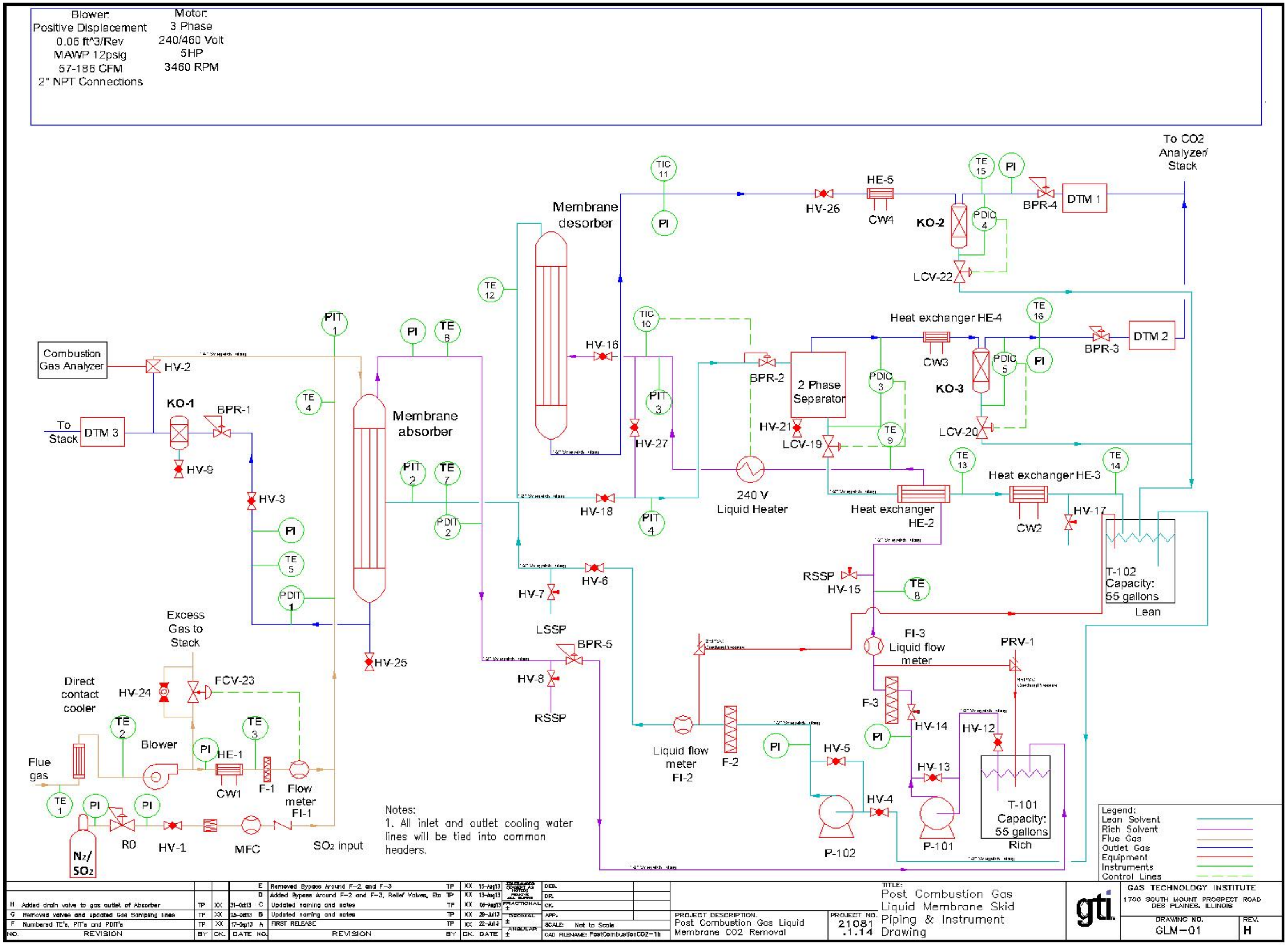


Figure 40. P&ID of the field testing system.

Membrane Performance Modeling

The CO_2 concentration profile in the membrane contactor is shown in Figure 41. The C_g, C_{gm}, C_{ml}, C_{lm} and C_l are the CO_2 concentration in the gas phase, at the gas-membrane interface, at the membrane-liquid interface, at the liquid-membrane interface and in the liquid, respectively.

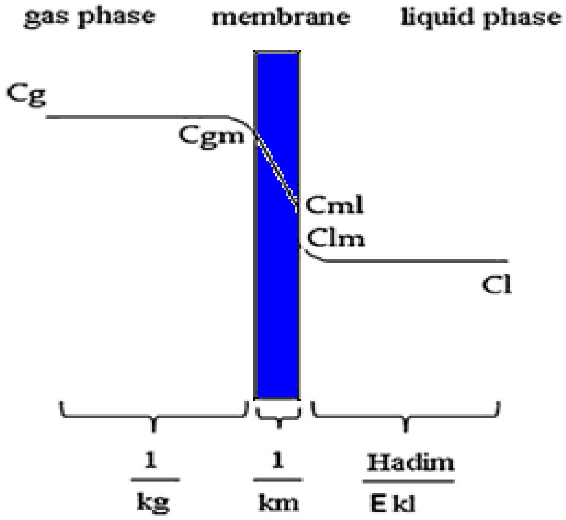


Figure 41. CO_2 concentration profile in a membrane contactor.

The CO_2 mass transfer coefficient for a gas-liquid absorption process can be expressed as follows:

$$\frac{1}{K}=\frac{1}{k_g}+\frac{1}{k_m}+\frac{H_{a\dim}}{E\cdot k_l} \tag{6}$$

Where K is the overall mass transfer coefficient [cm/s], k_g is the mass transfer coefficient in the gas phase [cm/s], k_m the mass transfer coefficient in the membrane [cm/s], k_l the mass transfer coefficient in the liquid phase [cm/s], H_{adim} the non-dimensional Henry's constant, and E the enhancement factor due to chemical reaction. The overall resistance to CO_2 transport and the overall mass transfer coefficient have an inverse relationship. Equation 1 shows the overall resistance comes from three parts: in the gas phase, in the membrane, and in the liquid phase. The resistance in the gas phase is typically very small. The resistance in the membrane phase is a function of membrane structure. The resistance in the liquid phase is a function of contactor module design, i.e. flow dynamics, and solvent characteristics.

The three resistances have been considered in our membrane performance modeling study, which is based on the previous modeling work by APS and by the work of Hoff.[12] In general, model development includes: 1) description of the gas and liquid flows, 2) mass transport, 3) energy transport, 4) equilibrium model, 5) kinetic model, and 6) subset of routines and functions for calculating physical properties. The various components of the model are schematized in Figure 42.

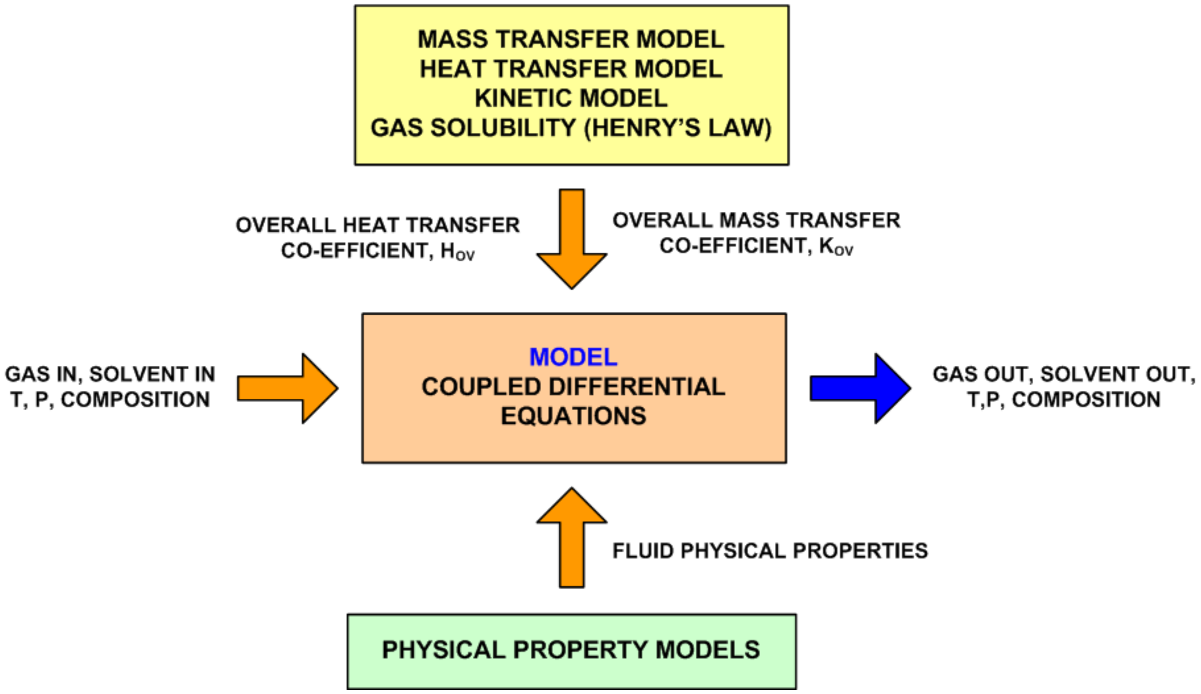


Figure 42. Components of the membrane gas absorber model**.**

Mass and Energy Transport

In the model, one has essentially a gas phase and a liquid phase with the membrane acting as the interface, and the transport equations coupling at the interface. The heat and mass transfer in the gas phase is formulated in terms of bulk transfer coefficients (*k*-mass transfer and h-heat transfer). In the liquid phase, the transport models are in terms of diffusivity (*D*, mass transfer) and thermal conductivity (λ, heat transfer). The gas flow is considered being perfectly mixed laterally and in axial plug flow. It is further assumed that the gas flows co-current or counter current to the liquid flow. In this system, the liquid flow characteristics will be in the laminar region as the Reynolds number is well below 100. The flow is fully developed with a Hagen-Poiseuille radial velocity profile that can be written as:

$$v_z = 2v_{z,av}\left(1-\left(\frac{r}{R_i}\right)^2\right) \qquad (7)$$

where $v_{z,av}$ is the average velocity, r is the variable radius of the bore and Ri is the inner bore diameter.

Heat and Mass Transfer across Membrane

Flux across membrane

The flux through the membrane includes both gas film and membrane mass transfer resistances in series, and can be written as

$$N_i = \frac{1}{RT_g\left(\frac{1}{k'_{i,g}}+\frac{1}{k'_{i,m}}\right)}\left(p_i - H_i c_{i,s}\right) + x_i \sum\nolimits_i N_i \qquad (8)$$

Where N_i is the molar flux of component i from the gas phase to the liquid phase passing through the membrane with the flux based on the inner surface area of the membrane tubes, p_i is partial pressure, H_i is the Henry's law constant, $c_{i,s}$ is the concentration of the component at the interface, all of component i. The gas and membrane mass transfer coefficients are respectively $k_{i,g}$ and $k_{i,m}$ with $k'_{i,g}$ high compared to $k'_{i,m}$.

Conductive sensible heat flux across membrane

The conductive heat flux equation across the membrane also uses a resistance in series approach. T_g is the gas phase temperature and $T_{l,s}$ is the temperature at the gas-liquid interface. Similar to the mass transfer model, the gas side coefficient h_g is high compared to the membrane side heat transfer coefficient, h_m. The mathematical expression is:

$$Q = \frac{1}{\left(\frac{1}{h_g}+\frac{1}{h_m}\right)}\left(T_g - T_{l,s}\right) \tag{9}$$

Equations for the Gas Phase

Mass balance for gas phase

The mass balance equation for the gas phase with plug flow assumption can be written as

$$-\frac{dn_{tot}}{dz} = \sum_i N_i \frac{a}{\varepsilon_g} \tag{10}$$

where, n_{tot} is the molar flux of the gas phase referred to the free gas cross-sectional area. Here, a (m^2/m^3) is the specific inner surface area of the membrane module, and ε_g is the fraction of the total area available for gas flow.

Using the ideal gas law in the gas phase mathematical treatment, the ensuing differential equations are solved for the gas velocity derivative and partial pressure of a component. The relevant equations can be given as:

$$n_{tot} = \frac{Pv_g}{RT_g} \tag{11}$$

$$\frac{\partial v_g}{\partial z} = -\frac{v_g}{P}\frac{\partial P}{\partial z} + \frac{v_g}{T_g}\frac{\partial T_g}{\partial z} - \frac{RT_g}{P}\sum_i N_i \frac{a}{\varepsilon_g} \tag{12}$$

$$n_i = \frac{p_i v_g}{RT_g} \tag{13}$$

$$\frac{\partial p_i}{\partial z} = -\frac{p_i}{v_g}\frac{\partial v_g}{\partial z} + \frac{p_i}{T_g}\frac{\partial T_g}{\partial z} - \frac{RT_g}{v_g}N_i \frac{a}{\varepsilon_g} \tag{14}$$

Where v_g is the gas velocity, T_g is the gas temperature, P is the total pressure and p_i is the partial pressure of component i.

Heat balance for the gas phase

Assuming no frictional heat and heat loss to the surroundings, the thermal balance for the gas phase can be written as

$$Q = \sum_i c_{p,i}\, n_i \frac{\partial T_g}{\partial z} \tag{15}$$

where, $c_{p,i}$ is the specific heat of component i.

Equations for the Liquid Phase

Mass transfer

In the liquid phase, the transport mechanism is by convection in the axial direction and diffusion (Fick's law) in the radial direction. The balance equation for a reactive component i with the parabolic velocity profile can be written as

$$2v_{z,av}\left(1-\left(\frac{r}{R_i}\right)^2\right)\frac{\partial c_i}{\partial z}=D_i\left(\frac{1}{r}\frac{\partial c_i}{\partial r}+\frac{\partial^2 c_i}{\partial r^2}\right)+\frac{\partial D_i}{\partial r}\frac{\partial c_i}{\partial r}+R_i(c_i,T) \qquad (16)$$

where $R_i(c_i,T)$ is the rate of formation/disappearance of component i.

Heat Transfer

In a similar manner, the heat balance equation in the liquid phase can be written as

$$2v_{z,av}\left(1-\left(\frac{r}{R_i}\right)^2\right)c_{p,l}\rho\frac{\partial T}{\partial z}=\lambda_l\left(\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial r^2}\right)+R_i(c_i,T)(-\Delta H_r) \qquad (17)$$

where, λ_l is the thermal conductivity of the amine mixture and the ΔH_r is heat of reaction.
The solution procedure of the membrane gas absorber model is given in Appendix I.

Equilibrium Model

The equilibrium model concerns itself with the calculation of non-idealities, in other words, the calculation of activity coefficients for the liquid phase components and fugacity coefficients for the gas phase components. Equilibrium concentrations enter the calculations as reaction rates are formulated in terms of "departure of equilibrium" or $C - C_{eq}$, where C_{eq} is the equilibrium concentration.

The relevant physical and chemical equilibria are considered for the calculation of non-idealities. The various reactions for CO_2 absorption by solvents MDEA and MEA are as follows:

Reactions of absorbing gas components with water, **e.g., CO_2**

$$2H_2O = H_3O^+ + OH^- \qquad (18)$$

$$2H_2O + CO_2 = H_3O^+ + HCO_3^- \qquad (19)$$

$$H_2O + HCO_3^- = H_3O^+ + CO_3^{2-} \qquad (20)$$

Deprotonation reaction for amine, **e.g., MDEA**

$$H_2O + MDEAH^+ = H_3O^+ + MDEA \qquad (21)$$

The equilibrium model is standalone because different non-ideal models can be used to calculate the activity and fugacity coefficients. In the equilibrium model development the treatment by Hoff (2003) is followed for verification.

Reaction Rates

The intrinsic rate of reactions with the appropriate temperature dependent rate constants are taken from the literature. As an example, the rate expression for CO_2 consumption in MEA or MDEA solvent[8] is given by

$$rCO_2 = k_{2,OH-}\, C_{CO2}\, C_{OH-} + k_{2,amine}\, C_{amine}\left(C_{CO2} - C_{CO2,\ eq}\right) \qquad (22)$$

Note that the stoichiometry of the reactions can be used to determine the rate of consumption/formation of other components.

Modeling Package

We have built up an Excel file entitled “MembCalc.xls” for communicating with Aspen Plus and Aspen Properties. It can also be used as a standalone Excel file. The various sheets in the Excel file are named

1. Aspen_IntParams
2. Aspen_RealParams
3. Aspen_Input
4. Aspen_Output
5. Aspen_Output_Membrane
6. Components Properties
7. Membrane Properties
8. Mass Transfer Coefficients
9. Model
10. Plot

The first five sheets are linked to Aspen Plus. These sheets contain information on the input and output streams, and parameters that are input through the user defined arrays in Aspen Plus. The sheet “Component Properties” calculates physical properties (e.g., density, viscosity) using Aspen Plus Properties functions. The user can also input physical properties independently into the respective Excel cells. The Excel sheet “Membrane Properties” contains the physical dimensions of the membrane module. The individual and overall mass transfer coefficients are calculated in the sheet “Mass Transfer Coefficients”. The model equations and results are in the “Model” sheet. Finally, the results are plotted in the “Plot” sheet.

The Excel file in conjunction with Aspen Simulator can be used in three different modes:

- Stand alone Excel File
- Excel with Aspen Properties
- Excel with Aspen Plus

Stand Alone Excel File

The components and physical properties are input in the “Component Properties” sheet. It is important to use Aspen Component ID for the various components; this is not necessary for the standalone application. The reason is Aspen Properties use Aspen Component IDs for calculating pure and mixture properties (e.g., molecular weight, density). The user input field cells are bolded orange. The various symbols for the entries (e.g., Tin_G, Pin_G) correspond to Excel variables and can be seen by pressing “CTRL + F3”. The advantage of declaring variables as opposed to simple cell referencing is that the variables can be conveniently used in any sheet of the Excel workbook. The functions of the various sheets are summarized in the table below:

Table 42. Excel sheets: use in standalone Excel Mode

Excel sheet	Comments
Component properties	Components, inlet gas and solvent conditions, physical properties are inputted here
Membrane properties	Membrane module dimensions are inputted here. Related properties such as specific surface area are calculated in this sheet
Mass transfer coefficients	The individual and overall mass transfer coefficients are calculated here
Model	The model equations and results are contained in this sheet
Plot	Plots the results in the "Model" sheet

Excel with Aspen Properties

In this mode, an Aspen Property file containing the various components must be created. The property file in turn is linked to the Excel file and the link must be created prior to use. The path of the Aspen property file can be seen at the top of the "Component Properties" sheet., the only difference compared to the standalone Excel mode is that the physical properties are calculated using Aspen Properties functions rather than specified in the Component properties Excel sheet.

Table 43. Excel sheets: use in Aspen Properties Mode

Excel sheet	Comments
Component properties	User input for inlet gas and solvent conditions. The physical properties such as density, viscosity are calculated by Aspen Properties
Membrane properties	Membrane module dimensions are input here. Related properties such as specific surface area are calculated in this sheet
Mass transfer coefficients	The individual and overall mass transfer coefficients are calculated here
Model	The model equations and results are contained in this sheet
Plot	Plots the results in the "Model" sheet

Excel with Aspen Plus

The Excel file is linked to the Aspen Plus simulation through the Membrane block properties. In Aspen Plus the numerical work is mostly done by FORTRAN functions that are invisible to the user. Here the numerical work is done by Excel which is visible to the user.

Table 44. Excel sheets: use in Aspen Plus Mode

Excel sheet	Comments
Aspen_IntParams	Sheet is linked to the user defined array for the custom Membrane block. Any integer parameters of the model that is input from Aspen Plus will be written to this sheet
Aspen_RealParams	Sheet is linked to the user defined array for the custom Membrane

	block. Any integer parameters of the model that is input from Aspen Plus will be written to this sheet
Aspen_Input	The input streams and conditions for the custom Membrane block are written to this sheet
Aspen_Output	The output streams and conditions as calculated by the Excel model will be available in this sheet. The output streams in turn can be the input of a subsequent Aspen Plus block
Aspen_Output_Membrane	Simply a copy of the Aspen Output for further processing
Component Properties	User input for inlet gas and solvent conditions. The physical properties such as density, viscosity are input by user or calculated by Aspen Properties
Membrane Properties	Membrane module dimensions are input here. Related properties such as specific surface area are calculated in this sheet
Mass Transfer Coefficients	The individual and overall mass transfer coefficients are calculated here
Model	The model equations and results are contained in this sheet
Plot	Plots the results in the "Model" sheet

An illustration of the use of custom membrane block connected to a Gibbs Reactor is shown in Figure 43. As alluded to earlier, the downstream block can be any Aspen Plus block. The outlet streams as calculated by the Excel model will serve as the input to the downstream block. Figure 50 shows the program flow the modeling study.

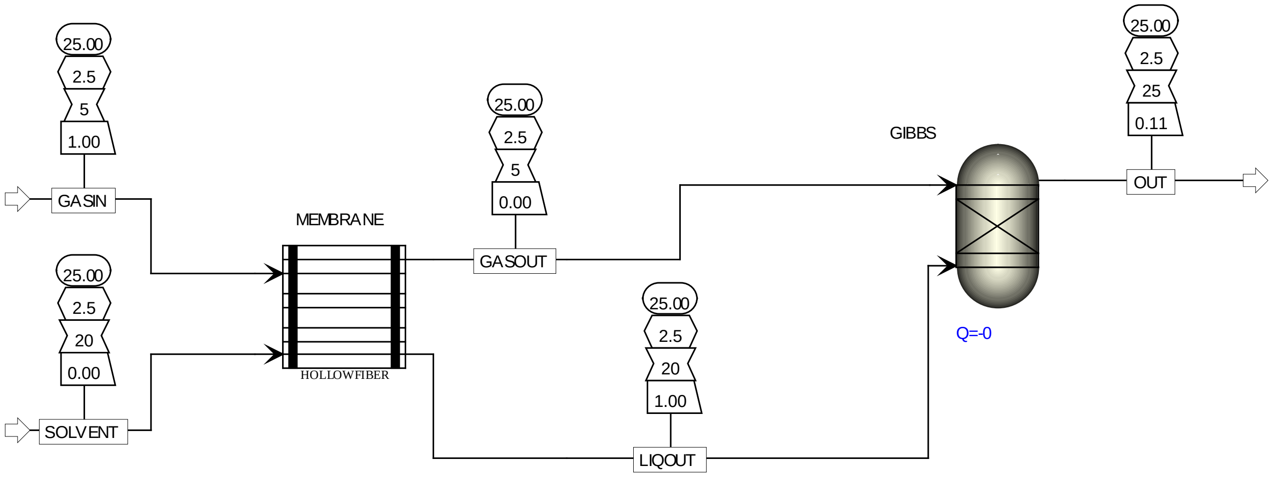


Figure 43. Custom membrane block with a Gibbs reactor downstream.

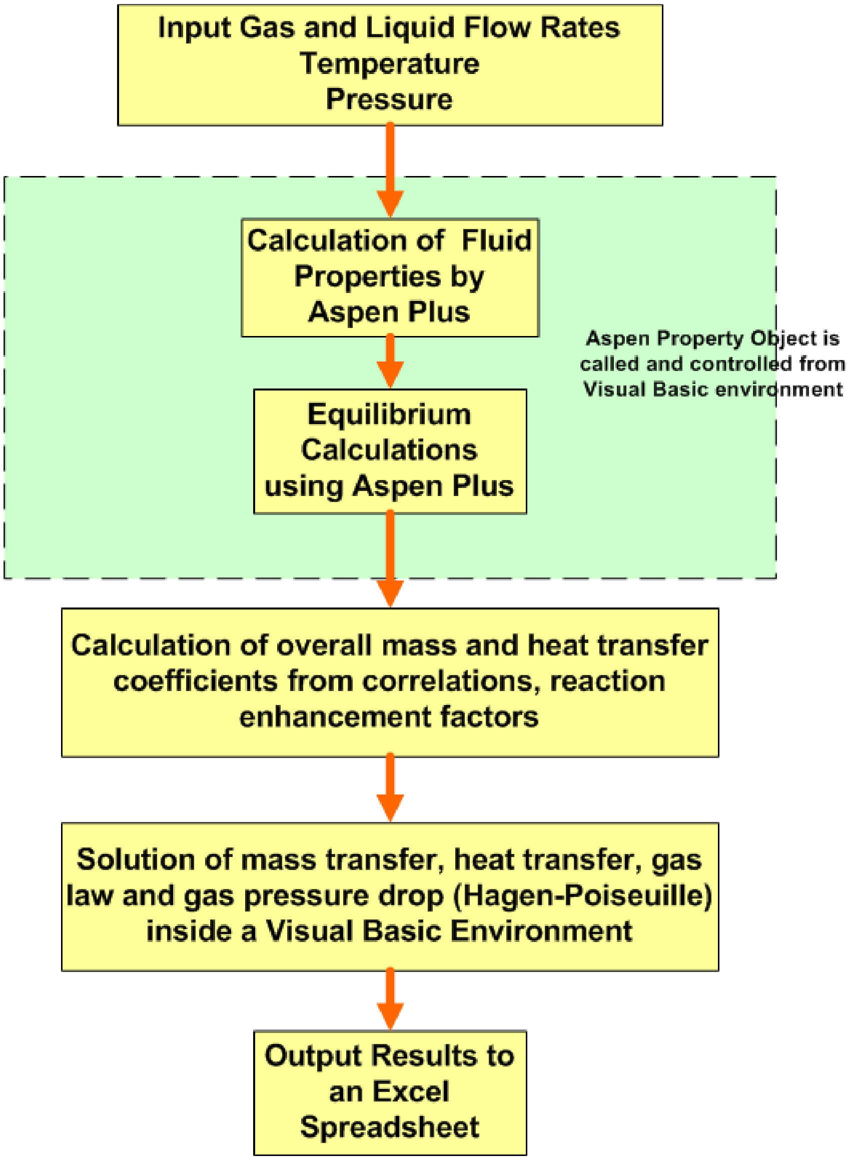


Figure 44. Program flow the modeling study.

Example of Model Output for Lab Testing

Figure 45 compares modeling results with experimental data. Model results fit experimental data well (Figure 46).

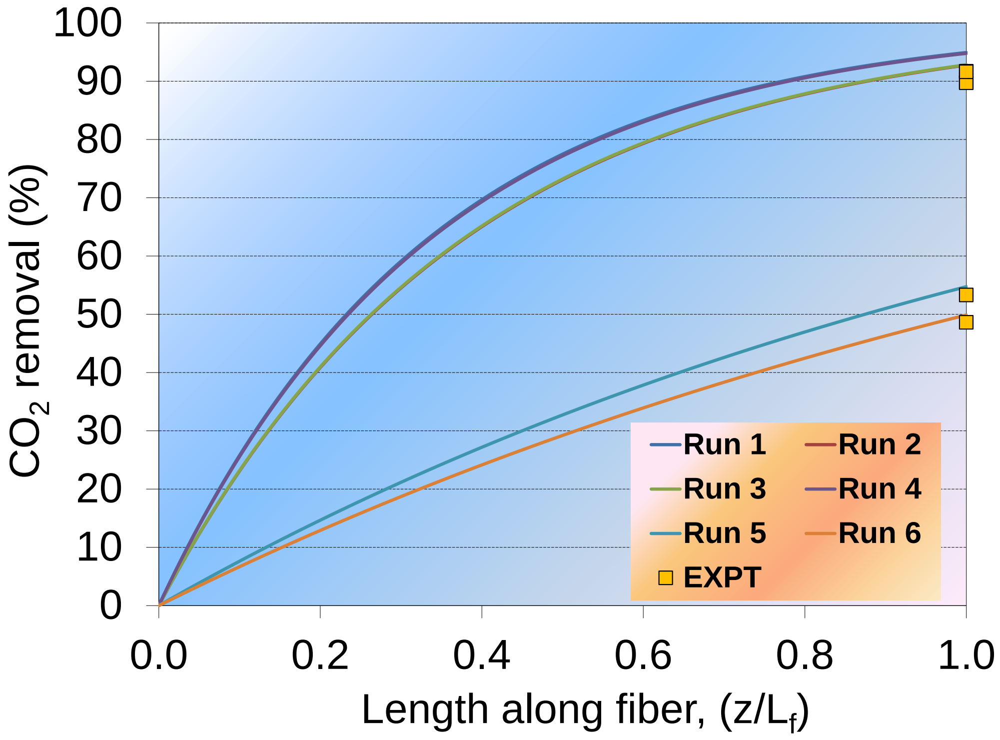


Figure 45. Comparison of modeling and experimental results.

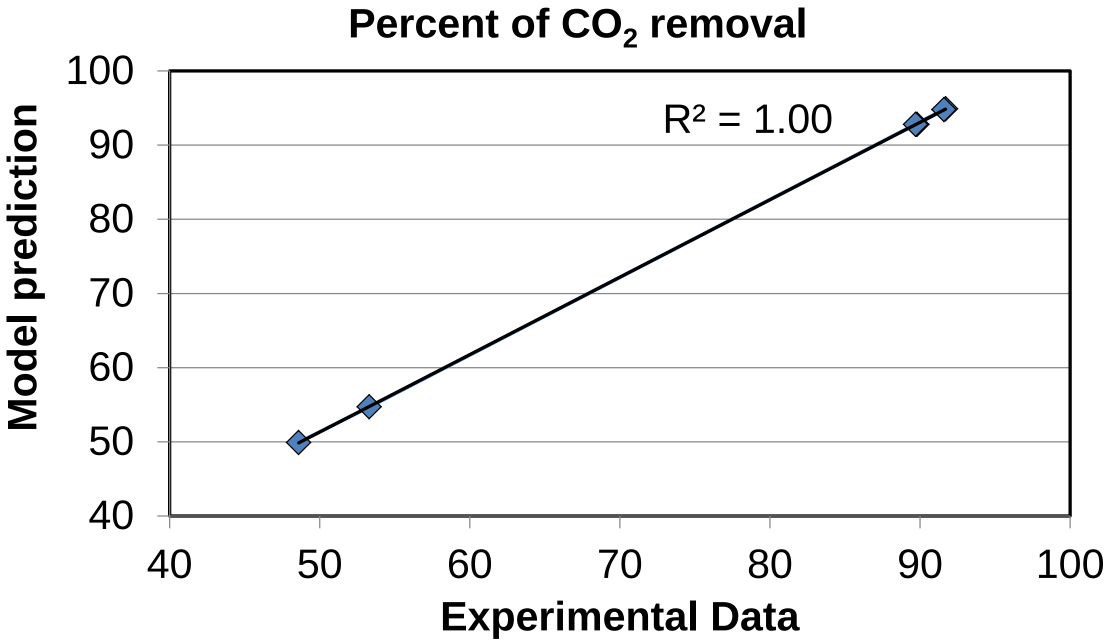
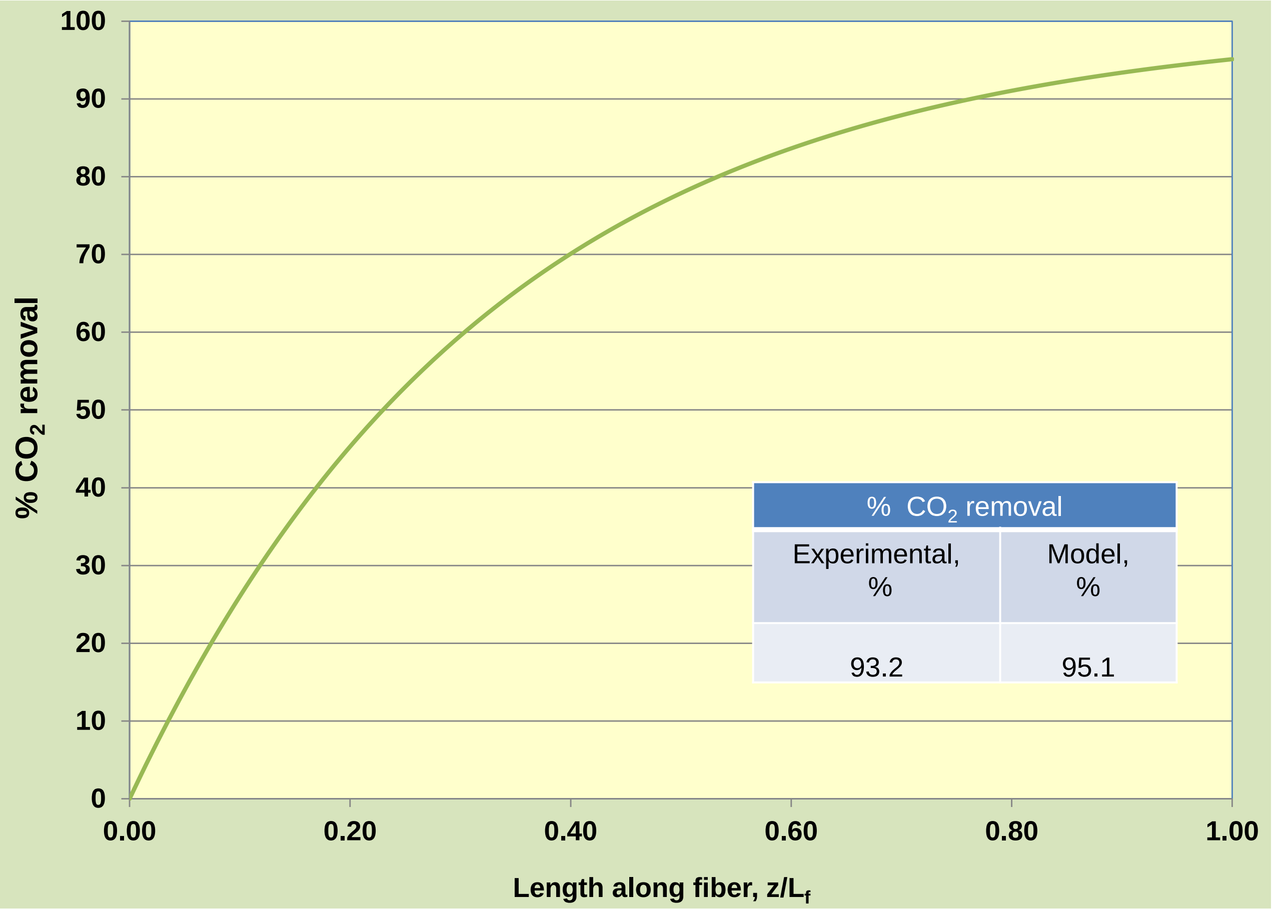


Figure 46. Model results fit experimental data.

Example of Model Output of Membrane Performance for Fielding Testing

Figure 47 shows that CO_2 removal level obtained in the field (93.2%) was close to that predicted by the model (95.1%) for a field test unit with a 4-inch 2,000 GPU module in conjunction with aMDEA solvent.



% CO_2 removal	
Experimental, %	Model, %
93.2	95.1

Figure 47. Modeling results for a field run.

Model Output of Membrane Performance for Commercial Scale Modules

The model was then used for predicting membrane performance for commercial scale modules (8-inch diameter and 60-inch long with a surface of 640 ft^2) that will be used in our pilot-scale development and commercial applications.

The predicted operation conditions and mass transfer coefficient at 90% CO_2 removal level for an 8-inch module that will be used in the pilot-scale development and commercial applications are shown in Table 45. The CO_2 concentration of the flue gas for this modeling study was 14 (vol.)%, which is also the flue gas CO_2 concentration at the National Carbon Capture Center (NCCC). The operation conditions and mass transfer coefficient obtained for the 4-inch module (PG347) tested in Midwest Generation are also shown in Table 45 for comparison.

Table 45. Scaling factors and predicted performance of commercial module

Module	CO_2 feed concentration	Gas velocity in fiber, m/s	Liquid velocity in module, m/s	CO_2 removal level	Mass transfer coefficient, $(sec)^{-1}$
4-inch module tested at Midwest Generation	9.2%	4.8	0.0039	93%	1.2
8-inch module to be used in the pilot-scale development and commercial application	14%	5.9	0.01	90%	1.4

Membrane Processing Modeling

Membrane performance modeling results (Table 52) and the process of the field testing were used as basis for the membrane process modeling for commercial applications. Aspen HYSYS software was used to model the CO_2 capture process at a scale corresponding to 550 MW net electric capacity.

Figure 48 shows the preliminary PFD of the PEEK membrane contactor process for the pilot-scale testing and commercial applications. Basically, in the absorption step of the process flue gas is sent through the hollow fiber membrane tubes while a CO_2-selective solvent flows around the outer surface of the hollow fiber membrane tubes, allowing CO_2 to permeate through the membrane and absorb into the solvent. In the desorption step of the process, the CO_2-rich solvent is regenerated in a second hollow fiber contactor (HFC) device operated in a reverse transport mode.

The HYSYS simulation flowsheet is shown in Figure 49. In the HYSYS simulation, material and energy balance blocks were used in place of the membrane absorber and membrane desorber. The inlet and outlet stream compositions for these blocks were determined from the bench-scale test data. The flue gas inlet stream conditions were those after the flue gas conditioning block (not shown in the HYSYS flowsheet).

The material and energy balance from the HYSYS simulation are shown in Tables 46. It should be noted that the HYSYS simulation is for a nominal inlet flue gas flow of 100 kgmol/hr. It can be easily scaled to a 550 MWe net power plant by using the total flue gas flow generated by this power plant.

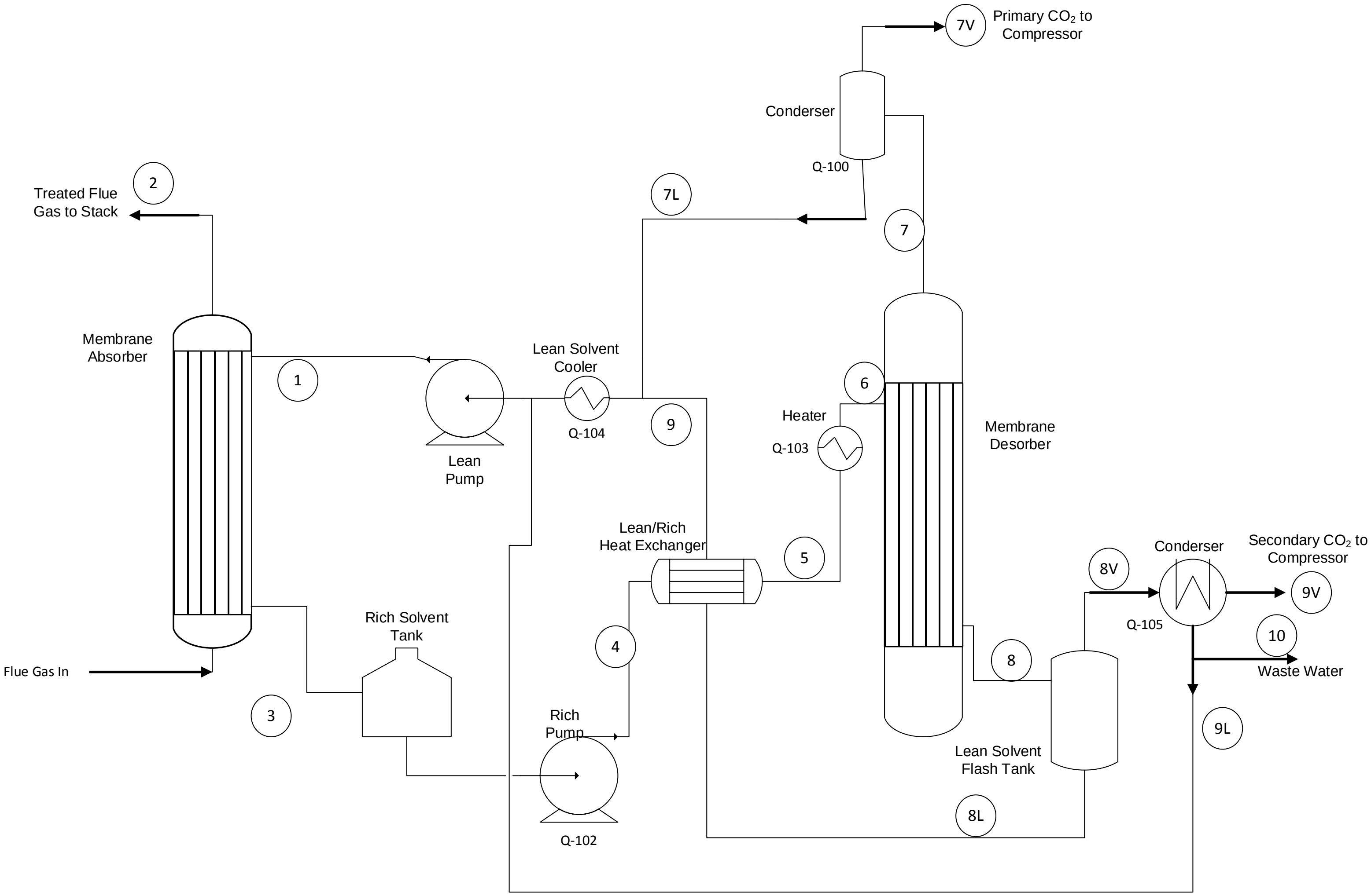


Figure 48. PFD of the PEEK membrane contactor process.

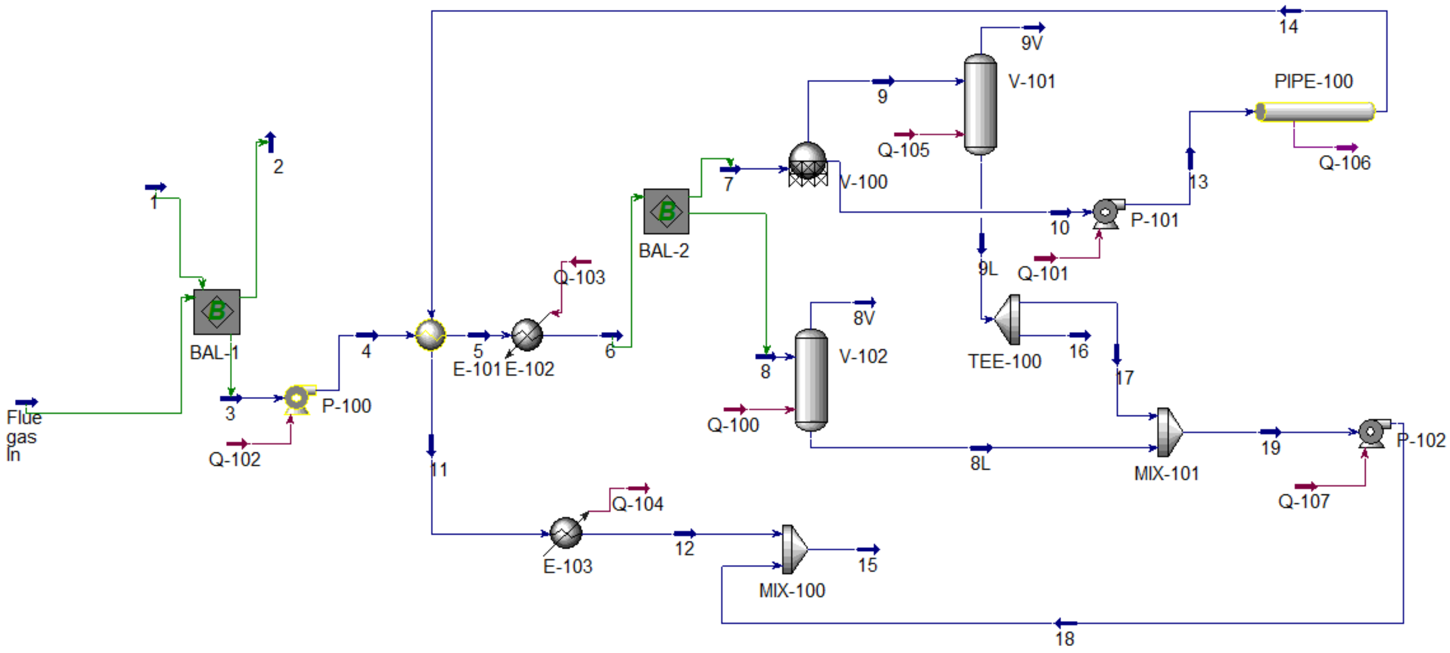


Figure 49. HYSYS flow diagram for PEEK membrane contactor CO_2 capture process modeling.

Table 46. Stream table from HYSYS simulation.

	Unit	**Flue gas In**	**2**	**1**	**3**	**5**	**8**	**11**	**6**	**7**	**12**	**10**	**9**
Vapour Fraction		1	1	0	0	0	1	0	0	0	0	0	1
Temperature	*C*	40.0	43.5	40.0	61.0	99.4	120.0	68.0	120.0	112.6	40.1	109.5	109.5
Pressure	*kPa*	118.6	102.7	173.7	118.6	627.4	158.6	242.7	558.5	503.3	173.7	158.6	158.6
Molar Flow	*kgmole/h*	100.0	86.0	350.0	364.0	364.0	20.0	341.3	364.0	344.0	341.3	341.3	2.66
Mass Flow	*kg/h*	2999.3	2396.9	9557.4	10159.7	10159.7	698.2	9401.3	10159.7	9461.5	9401.3	9401.3	60.3
Std Ideal Liq Vol Flow	*m3/h*	5.134	4.403	9.448	10.179	10.179	0.823	9.291	10.179	9.356	9.291	9.291	0.065
Heat Flow	*kJ/h*	-7352550.6	-1927399.4	-105614134.3	-111039285.5	-109578021.5	-6737190.0	-102252887.6	-108279572.7	-101542385.0	-103144407.9	-100839459.0	-702925.9
Molar Enthalpy	*kJ/kgmole*	-73525.5	-22411.6	-301754.7	-305053.0	-301038.5	-336859.5	-299559.8	-297471.4	-295181.4	-302171.6	-295419.0	-264642.5
Comp Mole Frac (CO2)		0.14956	0.01739	0.00357	0.04042	0.04042	0.64987	0.00365	0.04042	0.00498	0.00365	0.00365	0.17590
Comp Mole Frac (H2S)		0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mole Frac (Nitrogen)		0.75259	0.87504	0.00000	0.00002	0.00002	0.00010	0.00000	0.00002	0.00001	0.00000	0.00000	0.00142
Comp Mole Frac (MDEAmine)		0.00000	0.00000	0.09094	0.08744	0.08744	0.00000	0.09325	0.08744	0.09253	0.09325	0.09325	0.00033
Comp Mole Frac (Argon)		0.00897	0.01037	0.00001	0.00002	0.00002	0.00000	0.00001	0.00002	0.00002	0.00001	0.00001	0.00177
Comp Mole Frac (H2O)		0.06251	0.06660	0.90548	0.87209	0.87209	0.34993	0.90310	0.87209	0.90245	0.90310	0.90310	0.81942
Comp Mole Frac (Oxygen)		0.02637	0.03060	0.00000	0.00001	0.00001	0.00010	0.00000	0.00001	0.00001	0.00000	0.00000	0.00116
	Unit	**4**	**15**	**9V**	**9L**	**16**	**17**	**8V**	**8L**	**13**	**14**	**18**	**19**
Vapour Fraction		0	0	1	0	0	0	1	0	0	0	0	0
Temperature	*C*	63.5	40.0	32.2	32.2	32.2	32.2	32.2	32.2	109.6	109.9	32.2	32.2
Pressure	*kPa*	834.3	173.7	137.9	137.9	137.9	137.9	137.9	137.9	449.5	380.6	173.7	137.9
Molar Flow	*kgmole/h*	364.0	350.0	0.494	2.16	0.0314	2.13	13.5	6.53	341.3	341.3	8.66	8.66
Mass Flow	*kg/h*	10159.7	9557.5	21.2	39.1	0.6	38.5	580.6	117.7	9401.3	9401.3	156.2	156.2
Std Ideal Liq Vol Flow	*m3/h*	10.1791	9.4479	0.0258	0.0392	0.0006	0.0386	0.7047	0.1179	9.2914	9.2914	0.1566	0.1566
Heat Flow	*kJ/h*	-111006925.3	-105613900.0	-187108.5	-617051.4	-8960.9	-608090.4	-5225580.7	-1861409.2	-100835752.1	-100823983.8	-2469492.2	-2469499.7
Molar Enthalpy	*kJ/kgmole*	-304964.1	-301754.0	-378822.8	-285379.6	-285379.6	-285379.6	-387807.6	-285259.2	-295408.1	-295373.7	-285288.0	-285288.8
Comp Mole Frac (CO2)		0.04042	0.00358	0.94145	0.00102	0.00102	0.00102	0.96427	0.00064	0.00365	0.00365	0.00073	0.00073
Comp Mole Frac (H2S)		0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mole Frac (Nitrogen)		0.00002	0.00000	0.00763	0.00000	0.00000	0.00000	0.00015	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mole Frac (MDEAmine)		0.08744	0.09094	0.00000	0.00041	0.00041	0.00041	0.00000	0.00000	0.09325	0.09325	0.00010	0.00010
Comp Mole Frac (Argon)		0.00002	0.00001	0.00928	0.00006	0.00006	0.00006	0.00000	0.00000	0.00001	0.00001	0.00002	0.00002
Comp Mole Frac (H2O)		0.87209	0.90547	0.03542	0.99851	0.99851	0.99851	0.03543	0.99937	0.90310	0.90310	0.99915	0.99915
Comp Mole Frac (Oxygen)		0.00001	0.00000	0.00622	0.00000	0.00000	0.00000	0.00015	0.00000	0.00000	0.00000	0.00000	0.00000

Cost Modeling in Comparison to DOE Cases 9 and 12

The output of the membrane processing modeling was used in our cost modeling study.

We have used the cost estimates for the DOE Case 9 (Cost estimation with no CO_2 capture) and Case 10 (Cost estimation with CO_2 capture using MEA plant) as the base cases that represent the current benchmark technology (monoethanolamine (MEA) plant) status for electric power generation with CO_2 removal (including transport, storage and monitoring) from flue gas generated in a nominal 550 MW_e pulverized coal plant.

Table 47 shows the US DOE/NETL Case 9 (subcritical PC without CO_2) total plant cost summary, whereas Table 48 shows Case 9's initial and annual operating and maintenance costs. The plant size is 550 MW_e (net).

Table 49 shows the US DOE/NETL Case 10 (subcritical PC with CO_2) total plant cost summary, whereas Table 50 shows Case 10's initial and annual operating and maintenance costs. The plant size is 550 MW_e (net).

Table 47. US DOE/NETL Case 9 (subcritical PC without CO$_2$) total plant cost Summary; plant size: 550MW$_e$ (net), estimate type: conceptual, cost base (December) 2006 ($x1000).

Acct No. Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Toal Plant Cost	
			Direct	Indirect				Process	Project	K$	$/KW
1COAL&SORBENTHANDLING	$16,102	$4,348	$9,748	$0	$0	$30,198	$2,706	$0	$4,936	$37,840	$69
2COAL&SORBENTPREP&FEED	$10,847	$629	$2,750	$0	$0	$14,227	$1,247	$0	$2,321	$17,795	$32
3FEEDWATER&MISC.BOPSYSTEMS	$37,503	$0	$18,011	$0	$0	$55,514	$5,071	$0	$9,963	$70,548	$128
4.1PCBoiler&Accessories	$127,763	$0	$82,570	$0	$0	$210,334	$20,391	$0	$23,072	$253,797	$461
4.2SCR(w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4-4.9BoilerBoP(w/IDFans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
SUBTOTAL4	$127,763	$0	$82,570	$0	$0	$210,334	$20,391	$0	$23,072	$253,797	$461
5FLUEGASCLEANUP	$83,756	$0	$28,598	$0	$0	$112,354	$10,675	$0	$12,303	$135,332	$246
6.1CombustionTurbineGenerator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
6.2-6.9CombustionTurbineOther	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
SUBTOTAL6	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
7.1HeatRecoverySteamGenerator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
7.2-7.9HRSGAccessories,DuctworkandStack	$17,476	$1,006	$11,965	$0	$0	$30,447	$2,787	$0	$4,336	$37,570	$68
SUBTOTAL7	$17,476	$1,006	$11,965	$0	$0	$30,447	$2,787	$0	$4,336	$37,570	$68
8.1SteamTG&Accessories	$47,000	$0	$6,220	$0	$0	$53,220	$5,095	$0	$5,832	$64,147	$117
8.2-8.9TurbinePlantAuxiliariesandSteamPiping	$22,612	$1,045	$12,107	$0	$0	$35,764	$3,134	$0	$5,418	$44,316	$81
SUBTOTAL8	$69,612	$1,045	$18,328	$0	$0	$88,984	$8,230	$0	$11,249	$108,463	$197
9COOLINGWATERSYSTEM	$11,659	$6,571	$11,683	$0	$0	$29,913	$2,792	$0	$4,499	$37,204	$68
10ASH/SPENTSORBENTHANDLINGSYS	$4,383	$138	$5,829	$0	$0	$10,350	$985	$0	$1,166	$12,502	$23
11ACCESSORYELECTRICPLANT	$15,802	$6,032	$17,773	$0	$0	$39,607	$3,506	$0	$5,366	$48,479	$88
12INSTRUMENTATION&CONTROL	$8,006	$0	$8,413	$0	$0	$16,419	$1,503	$0	$2,204	$20,126	$37
13IMPROVEMENTSTOSITE	$2,833	$1,629	$5,752	$0	$0	$10,214	$1,003	$0	$2,243	$13,460	$24
14BUILDINGS&STRUCTURES	$0	$22,304	$21,358	$0	$0	$43,662	$3,934	$0	$11,899	$59,495	$108
TOTALCOST	$405,742	$43,703	$242,779	$0	$0	$692,224	$64,830	$0	$95,558	$852,612	$1,549

Table 48. US DOE/NETL Case 9 (subcritical PC without CO_2) initial and annual operating and maintenance costs; plant size: 550MW_e (net), estimate type: conceptual, cost base (December) 2006 ($x1000).

Consumables	Consumption		Unit Cost	Initial Cost	Annual Cost	Annual Unit Cost
	Initial	/Day			$	$/kW-net
Water (/1000 gallons)	0	4,472.64	1.03	$0	$1,429,266	0.000350
Chemicals						
MU & WT Chem.(lb)	151,553	21,650	0.16	$24,976	$1,106,970	0.000270
Limestone (ton)	3,661	523	20.6	$75,419	$3,342,699	0.000820
Carbon (Mercury Removal)(lb)	0	0	0	$0	$0	0.000000
MEA Solvent (ton)	0	0	2,142.40	$0	$0	0.000000
NaOH (tons)	0	0	412.96	$0	$0	0.000000
H2SO4 (tons)	0	0	132.15	$0	$0	0.000000
Corrosion Inhibitor	0	0	0	$0	$0	0.000000
Activated Carbon (lb)	0	0	1	$0	$0	0.000000
Ammonia (28% NH3) ton	550	79	123.6	$67,984	$3,013,146	0.000740
Subtotal Chemicals				$168,379	$7,462,815	0.001820
Other						
Supplemental Fuel (MBtu)	0	0	0	$0	$0	0.000000
SCR Catalyst (m3) w/equip.	0.47	5,500.00	$0	$794,147	$0.00	
Emission Penalties	0	0	0	$0	$0	0.000000
Subtotal Other				$0	$794,147	0.00019
Waste Disposal						
Fly ash (ton)	0	102	15.45	$0	$488,290	0.00012
Bottom Ash (ton)	0	407	15.45	$0	$1,953,046	0.00048
Subtotal-Waste Disposal				$0	$2,441,336	0.00060
By-products & Emissions						
Gypsum(tons)	0	823	0	$0	$0	0.00000
Subtotal By-Products				$0	$0	0.00000
TOTAL VARIABLE OPERATING COSTS				$168,379	$20,531,979	0.00501
Fuel (ton)	157,562	5,252	42.11	$6,634,942	$68,616,356	0.016740

Table 49. US DOE/NETL Case 10 (subcritical PC with CO_2) total plant cost Summary; plant size: 550 MW_e (net), estimate type: conceptual, cost base (December) 2006 ($x1000).

Acct No. Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Toal Plant Cost	
			Direct	Indirect				Process	Project	K$	$/KW
1 COAL & SORBENT HANDLING	$20,525	$5,540	$12,420	$0	$0	$38,485	$3,449	$0	$6,290	$37,373	$68
2 COAL & SORBENT PREP&FEED	$13,990	$807	$3,544	$0	$0	$18,342	$1,608	$0	$2,992	$17,780	$32
3 FEED WATER &MISC. BOP SYSTEMS	$53,307	$0	$25,510	$0	$0	$78,817	$7,217	$0	$14,343	$77,792	$141
4.1 PC Boiler & Accessories	$167,758	$0	$108,417	$0	$0	$276,176	$26,774	$0	$30,295	$258,265	$470
4.2 SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3 Open$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4-4.9 Boiler BoP (w/IDFans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
SUBTOTAL 4	$167,758	$0	$108,417	$0	$0	$276,176	$26,774	$0	$30,295	$258,265	$470
5 FLUE GAS CLEANUP	$109,618	$0	$37,721	$0	$0	$147,340	$14,000	$0	$16,134	$137,542	$250
5B CO2 REMOVAL & COMPRESSION	$299,500	$0	$89,850	$0	$0	$389,350	$38,935	$0	$30,000	$458,285	$833
6.1 Combustion Turbine Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
6.2-6.9 Combustion Turbine Other	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
SUBTOTAL 6	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
7.1 Heat Recovery Steam Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
7.2-7.9 HRSG Accessories, Ductwork and Stack	$19,363	$1,062	$13,228	$0	$0	$33,653	$3,074	$0	$4,824	$32,202	$59
SUBTOTAL 7	$19,363	$1,062	$13,228	$0	$0	$33,653	$3,074	$0	$4,824	$32,202	$59
8.1 Steam TG & Accessories	$52,758	$0	$6,989	$0	$0	$59,747	$5,720	$0	$6,547	$55,811	$101
8.2-8.9 Turbine Plant Auxiliaries and Steam Piping	$26,773	$1,170	$15,006	$0	$0	$42,949	$3,737	$0	$6,617	$41,310	$75
SUBTOTAL 8	$79,532	$1,170	$21,995	$0	$0	$102,697	$9,457	$0	$13,163	$97,121	$177
9 COOLING WATER SYSTEM	$21,405	$11,272	$20,092	$0	$0	$52,768	$4,916	$0	$7,834	$50,776	$92
10 ASH/SPENT SORBENT HANDLING SYS	$5,440	$171	$7,234	$0	$0	$12,844	$1,223	$0	$1,448	$15,515	$28
11 ACCESSORY ELECTRIC PLANT	$20,789	$10,729	$30,669	$0	$0	$62,187	$5,554	$0	$8,642	$59,198	$108
12 INSTRUMENTATION & CONTROL	$9,150	$0	$9,615	$0	$0	$18,765	$1,718	$938	$2,635	$24,056	$44
13 IMPROVEMENT STO SITE	$3,201	$1,840	$6,500	$0	$0	$11,541	$1,133	$0	$2,535	$15,210	$28
14 BUILDINGS & STRUCTURES	$0	$24,892	$23,781	$0	$0	$48,672	$4,385	$0	$7,959	$61,016	$111
TOTAL COST	$767,510	$57,483	$394,827	$0	$0	$1,219,819	$114,645	$56,977	$199,835	$1,591,277	$2,895

Table 50. US DOE/NETL Case 10 (subcritical PC with CO_2) initial and annual operating and maintenance costs; plant size: 550 MW_e (net), estimate type: conceptual, cost base (December) 2006 ($x1000).

Consumables	Consumption		Unit Cost	Initial Cost	Annual Cost	Annual Unit Cost
	Initial	/Day			$	$/kW-net
MU & WT Chem. (lb)	343,946	49,135	0.16	$56,682	$2,512,244	0.000610
Limestone (ton)	5,372	767	20.6	$110,669	$4,905,029	0.001200
Carbon (Mercury Removal) (lb)	0	0	0	$0	$0	0.000000
MEA Solvent (ton)	1,174	1.67	2,142.40	$2,515,178	$1,108,686	0.000270
NaOH (tons)	82	8.18	412.96	$33,863	$1,048,541	0.000260
H2SO4 (tons)	79	7.91	132.15	$10,440	$324,224	0.000080
Corrosion Inhibitor	0	0	0	$162,300	$7,730	0.000000
Activated Carbon (lb)	0	1,992	1	$0	$618,018	0.000150
Ammonia (28% NH3) ton	813	116	123.6	$100,439	$4,451,615	0.001090
Subtotal	Chemicals			$2,989,571	$14,976,086	0.003660
Other						
Supplemental Fuel (MBtu)	0	0	0	$0	$0	0.000000
SCR Catalyst (m3)	w/equip.	0.68	5,500.00	$0	$1,168,014	0.000290
Emission Penalties	0	0	0	$0	$0	0.000000
Subtotal	Other			$0	$1,168,014	0.000290
Waste	Disposal					
Flyash (ton)	0	144	15.45	$0	$690,819	0.000170
Bottom Ash (ton)	0	577	15.45	$0	$2,763,393	0.000680
Subtotal-Waste	Disposal			$0	$3,454,212	0.000840
By-products	&	Emissions				
Gypsum (tons)	0	1,196	0	$0	$0	0.000000
Subtotal	By-Products			$0	$0	0.000000
TOTAL	VARIABLE	OPERATING	COSTS	$2,989,571	$30,627,855	0.009360
Fuel (ton)	209,488	6,435	42.11	$8,821,536	$84,070,878	0.017449
CO2 transport, storage, and monitoring			3.4		$14,492,246.02	$0.003008

Estimates on CAPEX of membrane contactor process

Differences in the reboiler heat-duty requirements for the regeneration of CO_2-rich solvent would lead to changes in (i) net electric power generation and (ii) capital costs for the reboiler as well as for the LP steam turbine units. The estimated reboiler heat duties per g-mol of CO_2 for the two design cases are shown in Table 51.

Table 51. The estimated reboiler heat duties per g-mol of CO_2 for the three design cases.

Solvent type	MEA used in DOE Case 10	aMDEA
Heat duty, Btu/lb CO_2	1,521[a]	1,187[b]

a: Estimated from the total LP steam need in the Regenerator Unit.
b: Estimated as the sum of the (i) heat of desorption (14.0 kcal/gmol), (ii) heat of vaporization of water (10.3 kcal/gmol) and (iii) sensible heat required to bring the rich solution to the temperature of the stripper (4.7 kcal/gmol)

Based on a study by Nexant/Bechtel,[10] a typical capital investment (Table 52) for the absorber unit is approximately 27% of the total cost of the amine-based CO_2 removal process (estimated at $436 MM, Yr 2006$, for the DOE Case 10). This absorber will be replaced by a membrane contactor unit. According to this Nexant study, the typical investment for the reboiler unit is approximately 15% of the total cost of the amine process. The reboilers for the membrane plants are prorated on steam requirements.

Table 52. Key capital cost distribution factors for a typical amine plant for CO_2 removal.

Absorber	27%
Rich/lean exchanger	19%
Reboiler & other heat exchangers	15%
Stripper	10%
Feed cooler	9%
Flue gas blower	9%
Pumps	8%
Others	3%

The changes in total CAPEX for the two design cases relative to the DOE Case 10 are summarized in Table 53.

Table 53. Key changes in CAPEX (Yr 2006$).

Item	DOE Case 10 (amine plant)	Membrane contactor with aMDEA solvent
Absorber unit of the amine plant, $MM (@27% of total amine plant)	118	-
Reboiler unit of the amine plant (@ 15%), $MM	65	39
Stripper	44	5
Membrane unit, $MM		15
Other equipment, $MM	209	209
Total CAPEX for the CO_2 capture unit, $MM	436	268

Itemized costs of installed equipment and materials used in the CO_2 capture

Itemized costs of installed equipment and materials used in the CO_2 capture are listed in Table 54.

Table 54. Summary of auxiliary load and cost of installed equipment and materials used in the CO$_2$ capture.

POWER SUMMARY (Gross Power at Generator Terminals, kWe)	Case 10	Case 9	Membrane contactor with aMDEA
TOTAL (STEAM TURBINE) POWER, kWe	679,923	583,315	664,848
AUXILIARY LOAD SUMMARY, kWe (Note 1)			
Coal Handling and Conveying	520	420	486
Limestone Handling & Reagent Preparation	1,400	950	1,309
Pulverizers	4,400	2,980	4,115
Ash Handling	840	570	786
Primary Air Fans	2,060	1,390	1,927
Forced Draft Fans	2,620	1,770	2,451
Induced Draft Fans	11,180	7,590	10,377
SCR	80		75
Baghouse	100		94
FGD Pumps and Agitators	4,680	3,170	4,377
Amine System Auxiliaries	23,500		16,000
CO2 Compression	51,610		48,272
Condensate Pumps	1,210	1,390	1,132
Miscellaneous Balance of Plant (Note 2)	2,000	2,000	1,871
Steam Turbine Auxiliaries	400	400	400
Circulating Water Pumps	14,060	5,440	12,151
Cooling Tower Fans	7,270	2,810	6,800
Transformer Loss	2,380	1,830	2,227
TOTAL AUXILIARIES, kWe	130,310	32,870	114,848
NET POWER, kWe	549,613	550,445	550,000
Net Plant Efficiency (HHV)	24.90%	36.80%	26.60%
Net Plant Heat Rate (Btu/kWh)	13,724	9,276	12,836
CONDENSER COOLING DUTY 106 kJ/h (106 Btu/h)	2,318 (2,199)	2,656 (2,520)	2,656 (2,520)
CONSUMABLES			
As-Received Coal Feed, (lb/h)	646,589	437,699	604,764
As-Received Coal Feed, (ton/day)	7,759	5,252	7,257
Limestone Sorbent Feed, (lb/h)	63,956	43,585	59,872
Thermal Input, kWt	2,210,668	1,496,479	2,067,669
Makeup water, (gpm)	14,098	6,212	10,884
Coal Heating Value (MMBTU/hr)	7,543	5,106	7,055
CO2 Removed, (lb/h)	1,380,530	-	1,290,704
Membrane area, m2	1,565,495	-	2,090,905
Absorber Cost of membrane ($80/m2)			$ 167,272,424.67
Membrane stripper area, m2	223,642	-	209,091
Stripper cost of membrane ($80/m2)			$ 16,727,242.47
As-Received Coal Feed, (mT/day)	7,039	4,765	6,584
CO2 Removed, (t/yr)	6,046,721	-	5,653,284
As-Received Coal Feed, (ton/day)	7,759	5,252	7,257
CO2 removal plant cost	$ 436,000		$ 195,742.60
CO2 compression plant	$48,450		$ 45,315.98
Base Plant Case 10 without CO2 capture CAPEX	$1,106,827		$ 1,035,231.23
Base Plant Case 10 with CO2 capture CAPEX at $80/m2	$1,591,277	$852,612	$ 1,460,289.47
TOTAL FIXED OPERATING COSTS	$20,541,525	$13,580,249	$19,212,784.05
TOTAL VARIABLE OPERATING COSTS	$38,284,819	$20,531,979	$35,808,342.36
Fuel Costs ($42.11/ton) at 85% capacity	$101,369,333	$68,620,493	$94,812,197
CO2 TS&M ($3.4/ton)	$17,475,025		$16,337,989

Cost of Power Generation, mills/kWh

The key data on various levelized cost of electricity (LCOE) costs for the design cases are calculated from the data in Table 54 and are summarized in Table 55.

Table 55. Comparative data on LCOE.

Parameter	DOE Case 9	DOE Case 10	Membrane contactor with aMDEA solvent
As-received coal feed rate, metric tons/day	5,252	7,759	7, 257
Capital cost, mills/kWh	34.14	$68.00	$55.33
Fixed operating costs, mills/kWh	3.99	$6.03	$5.00
Variable operating costs, mills/kWh	5.80	$10.81	$8.97
Coal, mills/kWh	20.14	$29.76	$24.68
CO_2 transport, storage & monitoring, mills/kWh		$4.20	$3.48
Total LCOE, mills/kWh	64.07	$118.80	$97.46
Additional LCOE due to CO_2 capture (mills/kWh)	-	$54.73	$45.84
Cost saving to DOE's benchmark (Case 10)	-	0	16.24%
$ (Yr 2011 base)/tonne of CO_2 captured		65.30	54.69

Table 55 indicates cost saving compared to benchmark technology (Case 10) is 16.24% for membrane contactor with aMDEA solvent. Note that our cost evaluation is based on Yr 2006$. The cost at different years can be adjusted by Chemical Engineering Plant Cost Index. Here we assume the saving percentage, which is a relative number, keeps almost constant with year. On Year 2011 base, the benchmark technology costs approximately $65.30/tonne of CO_2 captured.[15] Thus, the cost of our membrane contactor technology is $54.69 (Yr 2011$)/tonne of CO_2 captured when using aMDEA solvent based on the same percentage savings.

Estimates on Plant Performance (Electric Load Requirements)

The electric power load data for the membrane cases are summarized in Table 56. The overall thermal efficiency (HHV basis) for the membrane case using the aMDEA solvent would be about 26.6% compared to about 24.9% for the DOE Case 10.

Table 56. Electric power requirements for various units.

Design Case	DOE Case 9	DOE Case 10	Membrane contactor with aMDEA solvent
Transformer loss, kWe	1,830	2,380	2,227
Steam turbine Auxiliary, kW_e	400	400	400
Other units, kW_e	30,640	127,530	112,221
Total auxiliaries, kW_e	32,870	130,310	114,847
Gross steam turbine Power, kW_e	583,315	679,923	664,848
Net power, kW_e	550,445	549,613	550,000

As received coal feed, lb/hr	437,699	646,589	604,764
Total thermal input, kWe	1,496,479	2,210,668	2,067,669
Net plant efficiency, HHV%	36.8	24.9	26.6%

Sensitivity analysis and strategy to achieve DOE's 2025 cost goal

The overall goal of DOE/NETL's carbon capture R&D is to develop advanced technologies that achieve 90% CO_2 capture with 95% CO_2 purity at a cost of \$40 (Yr 2011\$)/tonne of CO_2 captured by 2025 for new and existing coal-fired power plants.

Figure 50 shows that by reducing membrane module costs from current \$80 (Yr 2006\$) to \$30 (Yr 2006\$)/m^2, the CO_2 capture costs will be dropped to \$48.83 (Yr 2011\$)/tonne of CO_2 captured. Please note that cost of the membrane module is the largest contributor to the overall cost of the membrane contactor system. Current estimated cost of a packaged PEEK membrane module for small-scale application is about \$80 (Yr 2006\$)/m^2. This cost will drop to about \$30(Yr 2006\$)/m^2 for large-scale applications which is comparable to membrane costs for water treatment application; membrane costs for reverse osmosis desalination have decreased by more than order of magnitude in the recent decade due to advantages of large-scale manufacturing. The membrane module costs per m^2 will also decrease with the application of larger diameter modules that will decrease the number of modules and associated interconnecting piping and flanges. Development of 30-inch diameter contactor module is currently planned by our partner PoroGen for natural gas treatment segment.

Figure 50 also shows that at a membrane cost of \$30(Yr 2006\$)/m^2, the CO_2 capture costs will be dropped from \$48.83 to \$47.42 (Yr 2011\$)/tonne of CO_2 captured as mass transfer coefficient increases from 1.4 to 2 $(sec.)^{-1}$.

Sensitivity analysis for membrane contractor process with aMDEA solvent suggests that the CO_2 capture costs are about \$46.37 at a membrane cost of \$15(Yr 2006\$)/m^2 and a mass transfer coefficient of 2 $(sec.)^{-1}$. To meet DOE's Year 2025 cost goal of \$40 (Yr 2011\$)/tonne of CO_2 captured, advanced solvents should be used in conjunction with our membrane contactor technology. In our pilot-scale development supported by DOE-NETL, Hitachi's advanced H3-1 will be used.

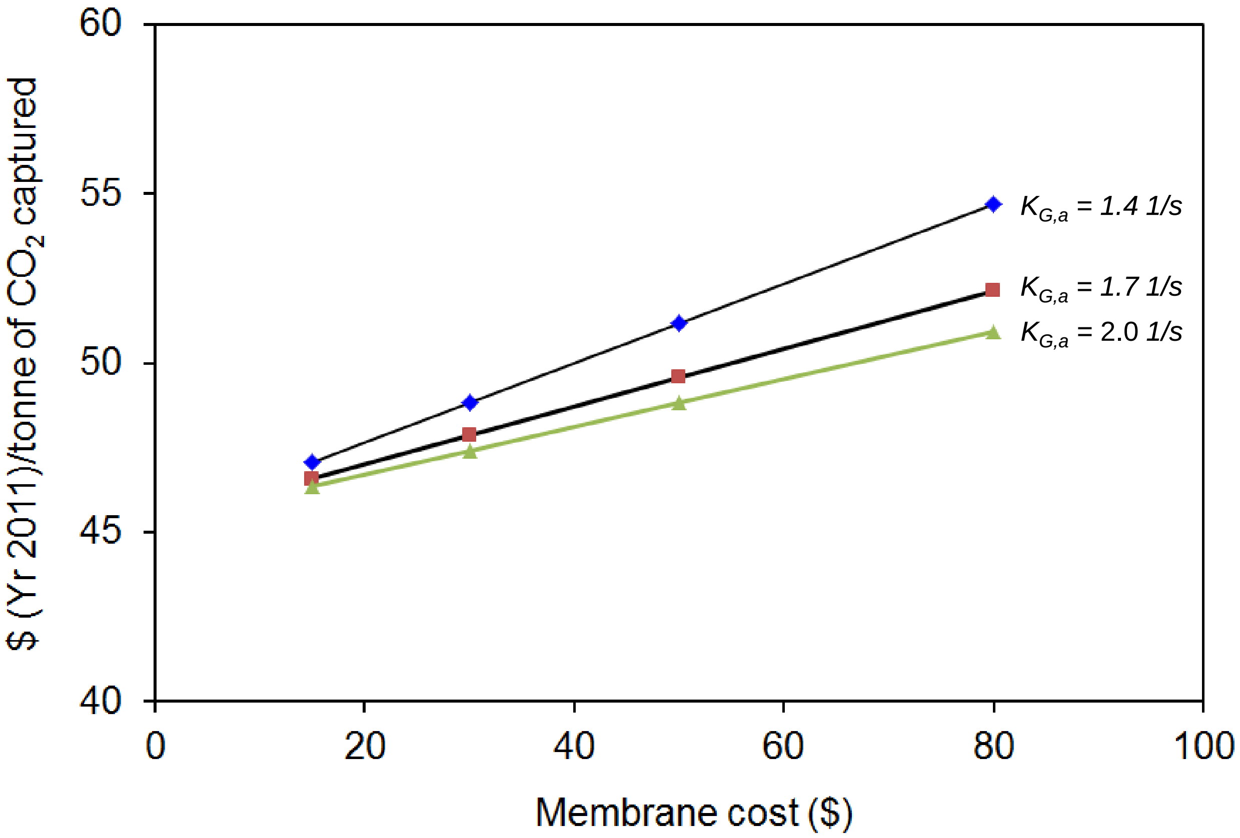


Figure 50. Sensitivity analysis for membrane contractor process with aMDEA solvent: $ (Yr 2011)/tonne of CO_2 captured as a function of membrane cost at difference mass transfer coefficients.

Preliminary field testing results and TEA

We tested the H3-1 solvent that is known to have a lower regeneration energy consumption than aMDEA. Our field testing with H3-1 solvent showed it has a 17% higher mass transfer coefficient than the aMDEA solvent (see Table 57). The CO_2 removal in one stage was also higher with the H3-1 solvent (92.7%) as compared to the aMDEA solvent (90.4%) even though the L/G ratio was lower for the H3-1 solvent. These, plus the improved regeneration, indicate the projected savings achievable with our membrane contactor process can be further improved with the use of H3-1 solvent.

Table 57. Comparison of CO_2 capture performances for aMDEA and H3-1 solvents.

Solvent	Flue gas flow rate, L/min	Liquid flow rate, L/min	L/G ratio, L/L	CO_2 removal in one stage	Normalized mass transfer coefficient
aMDEA	230	1.85	0.0080	90.4%	1
H3-1	241	1.07	0.0044	92.7%	1.17

Under GTI's pilot-scale development program supported by DOE (DE-FE0012829), Trimeric Corporation, in collaboration with GTI, PoroGen, and Hitachi is working on a detailed TEA which will be submitted as a topical report (~50 pages in length) that includes major equipment sizing and energy and mass balances. The basic design will provide the streams associated or affected with the proposed technology being researched in this project with the Hitachi H3-1 solvent, inclusive of the interconnections with the base plant. The basis for the analysis will be a net 550 MWe power plant in accordance with NETL guidelines. The objective of this task is to conduct process modeling studies that will provide detailed mass and energy balances to conduct an economic assessment of the proposed process. Process modeling will also be conducted in order to optimize the proposed process, determine power plant integration strategies, and conduct sensitivity analyses.

The preliminary TEA for our membrane contactor in conjunction with H3-1 solvent will be submitted to the DOE/NETL as a topic report.

CONCLUSION

We have made substantial progress towards key project milestones and advanced the hybrid membrane/absorption technology significantly. We have met all technical goals in all budget periods. Significant breakthroughs include:

- PEEK membrane contactor has shown exceptionally high CO_2 capture rates due to the high membrane intrinsic CO_2 permeance as well as the structured PEEK hollow fiber module configuration. CO_2 gas permeance of 2,000 GPU was attained by optimizing the membrane preparation procedures.
- Membrane absorber laboratory tests showed mass transfer coefficients as high as 1.7 $(sec)^{-1}$ was obtained. This value is 1-2 orders of magnitude higher than those of conventional absorbers.
- Membrane desorber laboratory tests showed CO_2 stripping flux was one order of magnitude higher than CO_2 absorption flux.
- In laboratory tests, the absorption and desorption steps were integrated into a continuous CO_2 capture process utilizing 2-inch diameter bench-scale modules containing 10 to 20 ft^2 of membrane area. The integrated process operation was stable through a 100-hour test, utilizing a simulated flue gas stream, with greater than 90% CO_2 capture and 97% CO_2 product purity achieved throughout the test.
- The PEEK membrane module has been scaled from 2-inch diameter by 15 inch to 4-inch diameter by 60 inch. The membrane surface area has been scaled from about 5 ft^2 to 160 ft^2 per module. The 4-inch diameter modules were utilized in both absorption and regeneration in field tests. The membrane contactor system showed greater than 90% CO_2 removal with 97% CO_2 product purity with aMDEA solvent in the field. The mass transfer coefficient in the absorption step was 1.2 $(sec)^{-1}$, which is over an order of magnitude greater than that of conventional column contactors.
- Field testing showed that flue gas contaminants SO_2 and NO_x did not affect CO_2 capture performance.
- The updated economic evaluation based on field testing data indicates the costs of our membrane contactor technology are \$54.69 (Yr 2011 base) per tonne of CO_2 captured when using aMDEA solvent and at a membrane cost of \$80/m^2. This cost decreases to \$48/tonne of CO_2 captured at a membrane cost of \$30/m^2. The DOE's 2025 cost goal of \$40 (Yr 2011\$)/tonne of CO_2 captured can be met by decreasing membrane module cost and by utilizing advanced solvents.
- Field testing with an advanced H3-1 solvent showed it has a 17% higher mass transfer coefficient than the aMDEA solvent and 50% lower solvent circulation rate. H3-1 is the solvent that will be used in our pilot-scale development. The projected savings achievable with our membrane contactor process can be further improved with the use of H3-1 solvent.

GRAPHICAL MATERIALS LIST(S)

Tables

Figures

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LIST OF ACRONYMS AND ABBREVIATIONS

AIChE: American Institute of Chemical Engineers
aMDEA: activated methyldiethanolamine
APS: Aker Process Systems
BP: Budget Period
CAPEX: Capital Expenditures
COE: cost of electricity
DCC: direct contactor cooler
DEA: diethanolamine
D.I.: Deionized Water
DOE: U.S. Department of Energy
CAPEX: Capital Expenditures
GC: Gas Chromatography
GPU: Gas Permeation Units
GTI: Gas Technology Institute
H3-1: Proprietary solvent of Hitachi
ICCI: Illinois Clean Coal Institute
ID: Inner diameter
K_2CO_3: Potassium Carbonate
kWh: kilowatt hour
LCOE: levelized cost of electricity
L/G: Liquid to Gas ratio, units of gallons per 1,000 actual cubic feet, liters/cubic meter, or L/L
LP: low pressure
MDEA: methyldiethanolamine
MEA: monoethanolamine
MM: million
MW_e: megawatt electrical
MW_t: megawatt thermal
MWh: megawatt hour
M/S: Milestone
NETL: National Energy Technology Laboratory

OD: Outer diameter
OPEX: Operating Costs
P&ID: piping and instrumentation diagram
PC: Pulverized Coal
PEEK: poly (ether ether ketone)
PEI: polyether imide
PGC: PoroGen Corporation
PI: Principal Investigator
PMP: Project Management Plan
ppmv: parts per million by volume
RPR: Reactive PoroGen Removal
SLPM: liters per minute at standard temperature and pressure conditions
wt.%: weight percent
Yr 2011$: cost expressed in 2011 dollars