FINAL TECHNICAL REPORT
January 1, 2014, through December 31, 2014

Project Title: **PILOT TEST OF A NANOPOROUS, SUPER-HYDROPHOBIC MEMBRANE CONTACTOR PROCESS FOR POST-COMBUSTION CO_2 CAPTURE - PHASE 1**

ICCI Project Number: DEV14-1
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ABSTRACT

The hollow fiber membrane contactor (HFMC) 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 flue gas passes through one side of the polyether ether ketone (PEEK) HFMC, while a CO_2 selective solvent flows on the other side. CO_2 permeates through the hollow fiber membrane pores and is chemically absorbed into the solvent. The CO_2 rich solvent is regenerated in a second PEEK HFMC module operated in a reverse manner. The current pilot scale test project is a continuation of the bench-scale technology development. Through Phase 1 study, substantial progress has been made toward key milestones of the current 1 MW_e pilot-scale (20 ton CO_2/day) development of super-hydrophobic PEEK HFMC process for post-combustion CO_2 capture. Hitachi's advanced solvent H3-1 was initially proposed as prime test solvent in the current program. However, due to the lack of necessary fundamental data for H3-1 to complete the preliminary Techno-Economic Analysis (TEA), the prime test solvent has been switched from H3-1 to activated methyldiethanolamine (aMDEA). The preliminary Environmental, Health & Safety study (EH&S) and TEA based on the aMDEA solvent has been completed. The estimated cost of CO_2 capture for our HFMC technology is 49.35 $/tonne of CO_2 captured when using a mass transfer coefficient of 1.2 $(sec)^{-1}$, obtained from our bench-scale field testing.

Bench-scale testing has been performed in support of the pilot-scale design effort. Single-gas permeation measurements for 2-inch diameter modules indicated that one of the critical milestones for membrane development, target intrinsic CO_2 permeance of 1,700-2,000 GPU, has been achieved. A number of factors that may have had an effect on the membrane contactor stability, specifically during start-up and shutdown cycles, have been investigated. With a new start-up/shutdown procedure, the CO_2 capture performance for a new module remained stable for at least 2 weeks.

Another major accomplishment of the Phase 1 study is the design of an energy efficient two-stage flash solvent regeneration process for CO_2 capture. Process simulation by Aspen HYSYS® suggested the new design could save as much as 20% of the overall compression power. The new design has been validated experimentally. A patent application based on this design has been filed. Fabrication of 8-inch modules and design of the 1 MW_e pilot plant are ongoing and will be completed by June 30, 2015.

EXECUTIVE SUMMARY

The Phase 1 program has the following 5 tasks:

- Task 1: Project management
- Task 2: Preliminary TEA and EH&S study
- Task 3: Determination of scaling parameters for 2,000 GPU hollow fiber membrane modules
- Task 4: Bench-scale testing in support of the pilot-scale design effort
- Task 5: Design and costing of the 1MW$_e$ equivalent CO_2 capture system

Task 1: Joint development agreements between GTI and team members have been signed. In addition to day-to-day management of the project, we are holding weekly teleconferencing meetings with project team members to discuss project activities and technical issues. A slight change in project direction was made by switching the prime test solvent from H3-1 to aMDEA due to the lack of fundamental data for H3-1 solvent.

Task 2: The preliminary TEA was based on bench-scale field testing data with aMDEA solvent completed in 2013 at the Midwest Generation's Will County Station site where a mass transfer coefficient of 1.2 $(sec)^{-1}$ was obtained at 93% CO_2 removal. In the current pilot-scale program, the target mass transfer coefficient was 2.0 $(sec)^{-1}$ at 90% CO_2 removal. The TEA compared the HFMC technology with DOE's Cases 11 (without CO_2 capture) and 12 (use of amine plant for CO_2 capture). The estimated cost of the HFMC technology in conjunction with aMDEA solvent is 49.35 \$/tonne of CO_2 captured when using the mass transfer coefficient of 1.2 $(sec)^{-1}$. A preliminary EH&S study has been completed, which includes the preliminary EH&S risk assessment involving design, engineering, construction, operation and testing of a 1 MW$_e$ hollow fiber gas liquid membrane contactor-based post-combustion capture pilot plant incorporating PEEK-based super hydrophobic nanoporous hollow fiber membrane contactor technology and aMDEA solvent.

Task 3: Under this task, PoroGen optimized their PEEK membranes and membrane modules for long-term CO_2 capture operation. Membrane module factors that might affect long-term CO_2 capture performance, such as O-rings, epoxy/fiber interface in tubesheets, "wet out" of the hydrophobic surface in long-term operation, and module start-up/shutdown procedures, have been investigated. The target intrinsic CO_2 permeance of 1,700 to 2,000 GPU has been achieved in 2-inch diameter modules. In addition to the development of long-term operation, PoroGen continues its production of larger inner-diameter hollow fibers for operation at a lower pressure drop. A lower pressure drop for flow through the hollow fiber membrane directly translates into savings on operating costs. The PEEK fibers used in the field testing had an inner diameter of 13 mi, pressure drop observed in these were 5 psi. The new fibers will have an inner diameter of 20 mil and is expected to lower the gas side pressure drop to 18% of that obtained for the old fibers. PoroGen is also scaling up the modules from 2-inch to 8-inch in diameter.

Task 4: Membrane module factors that might affect contactor stability during start-up and shutdown cycles have been identified. With a new start-up/shutdown procedure, the CO_2 capture performance remained stable for at least 2 weeks for a new module. In addition to technical progress on membrane absorption stability, significant progress was made on solvent regeneration. A new process that uses one-stage of high-pressure flash followed by one-stage of low-pressure flash was designed for CO_2 loaded rich solvent regeneration. Process simulation by Aspen HYSYS® suggested the new design should save as much as 20% of the overall compression power. The new design has been experimentally validated. A patent application based on this design has been filed.

Task 5: Design and costing of the $1MW_e$ equivalent CO_2 capture system have commenced. To date, process flow diagram and material balance based on the preliminary TEA have been essentially completed. Adjustments have been made for two months of continuous operations at NCCC. Other progress includes:

- Equipment for integrated membrane absorption and desorption processes has been identified,
- Major process control loops have been formulated,
- Piping and instrumentation diagrams (P&ID) have been initiated, and
- Preliminary review for P&ID has been completed.

Discussions with the host site National Carbon Capture Center (NCCC) at Wilsonville, Al about operating philosophy and duties for each party are ongoing.

OBJECTIVES

The objectives for the Phase 1 of this pilot-scale development were to 1) develop preliminary Techno-Economic Analysis (TEA) and Environmental, Health & Safety study (EH&S) based on bench-scale test data, 2) determine scaling parameters for commercial hollow fiber membrane modules with 2,000 GPU measuring 8-inch diameter by 60-inch long, and 3) design a HFMC pilot system for flue gas CO_2 capture at 1 MW_e equivalent scale (20 ton CO_2/day).

INTRODUCTION AND BACKGROUND

The membrane contactor technology is a hybrid membrane/absorption process that takes advantages of both the compact nature of the membrane process and the high selectivity of the absorption process. Conventional membrane process operates by a solution/diffusion mechanism and the separation driving force is provided by the partial pressure difference of each component across the membrane. This process requires either flue gas compression, permeate sweep, application of permeate side vacuum, or combination of these steps to provide the separation driving force required. Elaborate process design and optimization becomes a prerequisite for conventional membrane processes 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). The available CO_2 pressure ratio in a coal powered flue gas is only about 3 and is limited by economies of compression or vacuum level. The concentration of the product CO_2 is consequently limited to about 32%. Thus, when the membrane separation process is pressure ratio limited and is unaffected by the membrane selectivity since it is already much larger than the pressure ratio, the product CO_2 concentration will be limited. This thermodynamic limitation cannot be overcome by further increases in membrane selectivity. Hence not possible to generate greater than 32% pure CO_2 product from flue gases in one stage using the conventional membrane process.

The hybrid membrane/absorption process is not limited by the pressure ratio and 99% pure CO_2 product can be generated in a single stage. The process selectivity approaches thousands and is determined by the chemical affinity of the absorption solvent to CO_2. While the porous super-hydrophobic membrane can offer only limited selectivity for the gaseous species present in the flue gas stream, membrane selectivity is not required.

The hollow fiber membrane utilized in the hybrid membrane absorption process also provides a very high surface area/volume ratio for the separation to take place, which results in a mass transfer coefficient that is 5 to 10 times greater than achievable in a conventional tower or column with trays or packing. Therefore, the membrane contactor may be 50-70% smaller in volume than conventional equipment. This will enable installation at existing power plant sites where availability of space for carbon capture equipment can be limited.

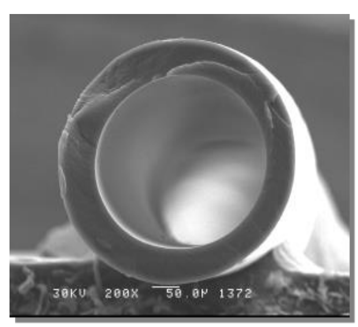
In a prior funded 3-year bench-scale development program, high CO_2 capture level (> 90% removal) and high CO_2 product purity (> 95%) had been demonstrated in compact hollow fiber membrane modules in a single-stage process configuration. Laboratory tests included absorption and desorption steps integrated 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 integrated absorption/desorption HFMC technology was demonstrated at a coal-fired power plant (Midwest Generation, Will County Station in Romeoville, IL) using 4-inch diameter modules with a membrane surface area of 164 ft^2 per module. Results showed greater than 90% CO_2 removal and 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. The CO_2 capture performance in the field test was not affected by flue gas contaminants SO_2 and NO_x.

Under the current 4-year pilot-scale program consisting of four phases, this being the first Phase, the PEEK HFMC technology is being scaled from the bench scale to a pilot scale. Overall objectives are: to build a 1 MW_e equivalent pilot-scale CO_2 capture (20 ton CO_2/day) hollow fiber contactor system with commercially available aMDEA solvent, conduct field tests on actual flue gas at the National Carbon Capture Center (NCCC), perform a continuous, steady-state operation for a minimum of two months, and gather data necessary for process scale-up. The goal of this technology development project is to validate the potential to achieve DOE's Carbon Capture performance goal of 90%, CO_2 capture rate with 95%, and CO_2 purity at a cost of \$40/tonne of CO_2 captured.

EXPERIMENTAL PROCEDURES

Membrane and Membrane Module Fabrication

The porous PEEK hollow fibers as seen in Figure 1a, were manufactured by a high temperature melt extrusion process [2]. Figure 1b shows a typical cross-section scanning electron microscope (SEM) view of the fibers, which nominally have outside diameters of 0.4-0.7 mm and wall thicknesses of 0.07-0.12 mm.

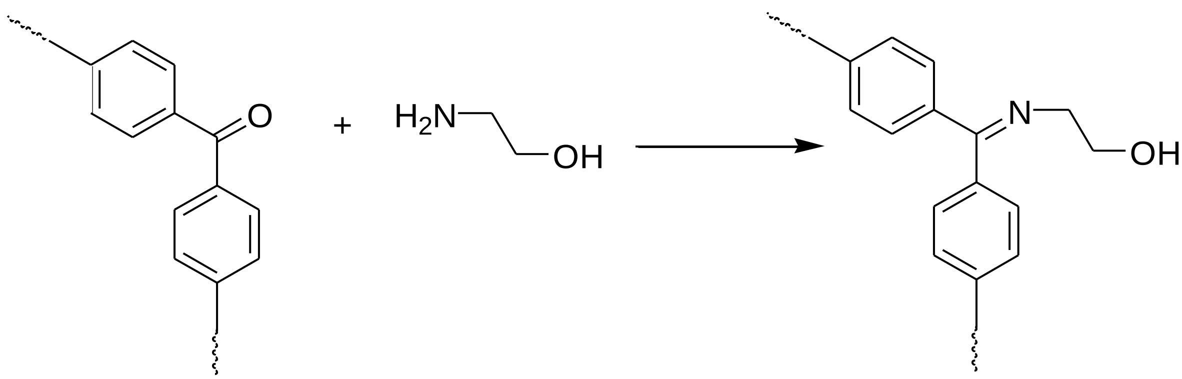


(a) (b)

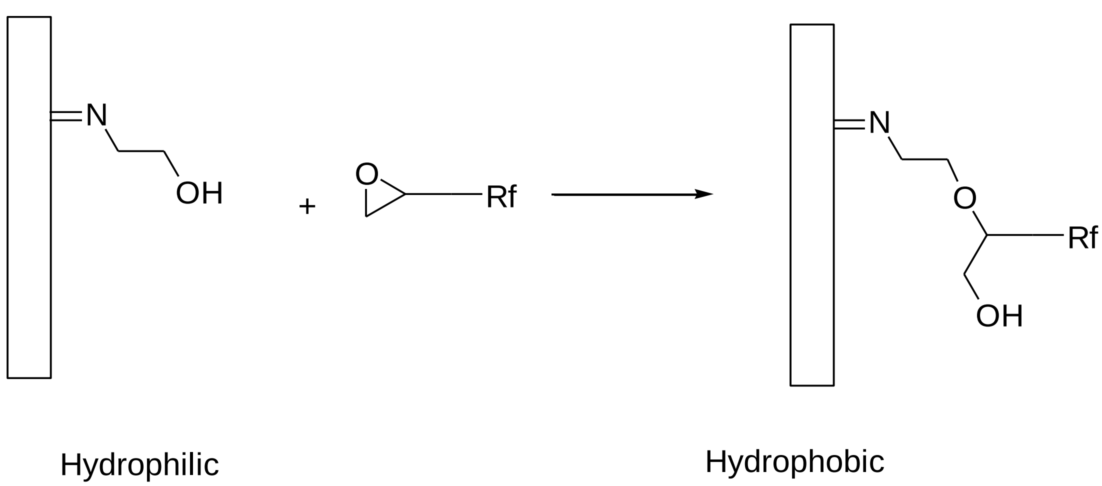
Figure 1. PEEK views: a) hollow fibers, and b) SEM cross-section view.

The membrane in the membrane contactor operates in a non-wetting mode with the liquid side pressure below the breakthrough, to maintain independent gas and liquid flows. The PEEK material itself is hydrophilic. Surface modification to make it hydrophobic is critical for the HFMC technology.

The super-hydrophobicity surface was generated by surface modification with a functional perfluoro oligomer shown in Figure 2. Prior to grafting with the perfluoro oligomer, the surface of the porous PEEK was functionalized with -OH groups by reacting ketone groups in the PEEK polymer backbone with monoethanolamine. The functionalized porous PEEK was prepared in a single step Reactive Porogen Removal process during porous PEEK fiber preparation according to US Patent 7,176,273 [3].



(a)



(b)

Figure 2. Membrane surface modification: (a) functionalization of porous PEEK with -OH groups, and (b) reaction to form hydrophobic surface.

The super-hydrophobic hollow fibers were packaged into cartridges utilizing computer controlled helical winding for a uniform structured packing. Overall flow configuration in the cartridge was counter-current to maximize the thermodynamic efficiency. The cartridge was installed into a pressure housing and sealed with O-rings to form the membrane module. Figure 3 illustrates progression of manufacturing steps from powers to membrane module.

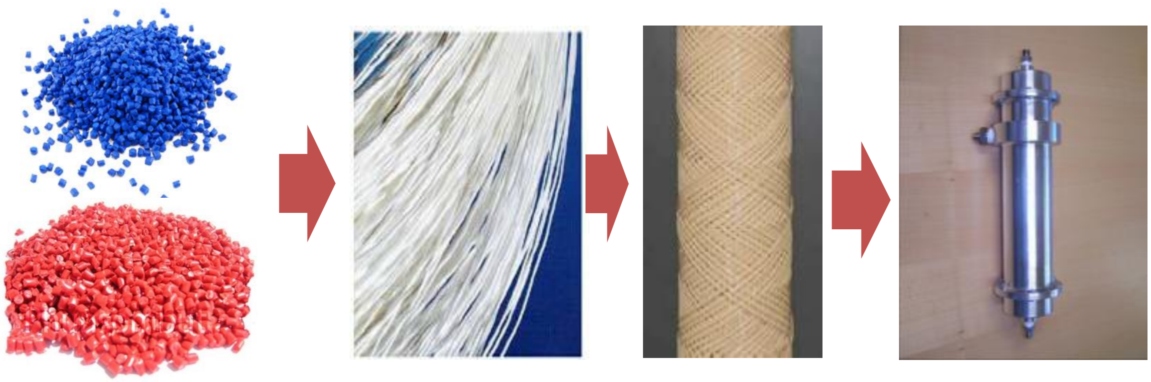


Figure 3. Progression of manufacturing steps from powders to membrane module.

Membrane Module Characterization

The non-wetting characteristics of membrane modules were determined by pressurizing a feed liquid in the shell side of the module and observing collection of liquid in the tube side, if any. Any liquid collected on the tube side would indicate a wet out of the membrane. The liquid used in these quality control tests was MDEA/water (50/50 volume) solution. The wettability tests were extended to include longer term exposure to the aqueous MDEA solution ($\geqslant$100 hours) at higher temperatures (50-60^{o}C). This was comparable to flue gas conditions.

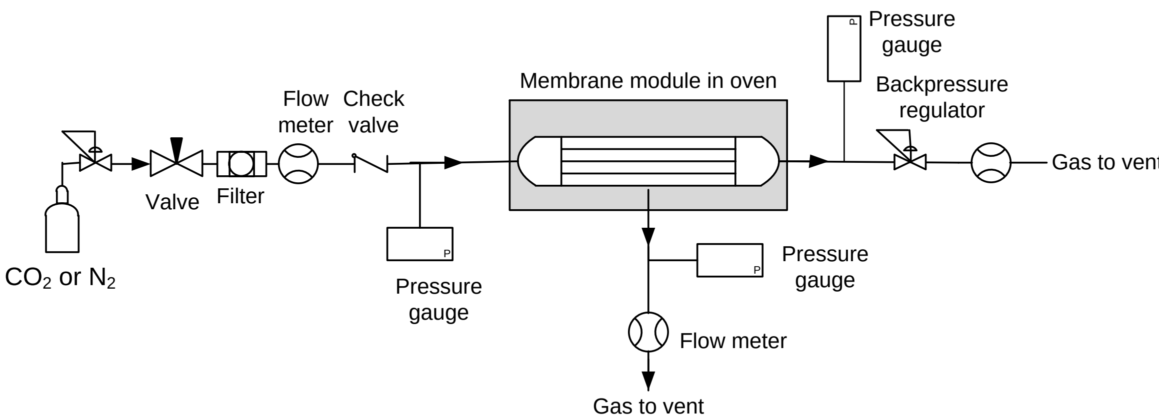


Figure 4. Process diagram for membrane intrinsic permeance testing.

The membrane intrinsic gas permeation property for CO_2 was measured in a flow system shown in Figure 4. CO_2 was fed to the tube side of the module and flux measured using gas flow meter. The pressure normalized flux, permeance, is denoted as follows:

$$P = \frac{J}{\Delta p} \quad (1)$$

$$\Delta p = P_{tube} - P_{shell} \quad (2)$$

where J is the steady state flux through the membrane; Δp is pressure differential between the tube and shell sides. The pressure drop was observed between inlet and outlet of the tube side, and thus an average tube-side pressure was used for calculation in Equation 2.

Membrane Contactor CO_2 Capture Testing

The membrane modules were mounted on a membrane contactor skid for CO_2 capture testing, as shown in the process flow diagram in Figure 5. Mass flow controllers were used to control feed gas composition from pure CO_2 and N_2 gases, which were in the molar ratio of 13:87 if not indicated otherwise. The mixed gas stream was heated by a flow-through heater and then sent to a bubbler filled with water to humidify the gas. Humidity measurements indicated that the stream after the knock-out vessel was saturated with water at any given temperature. This stream was then directed to the tube side of the module and the lean solvent was directed to the shell side of the module, as shown in Figure 5.

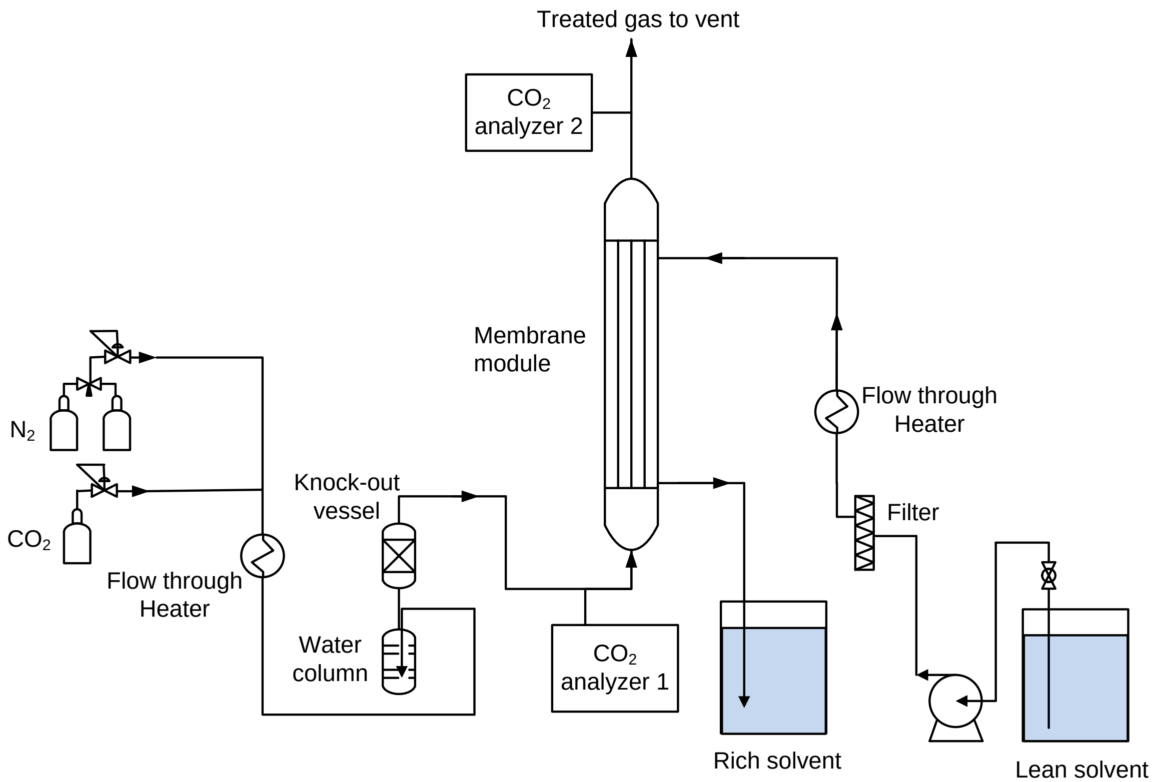


Figure 5. Process diagram for bench-scale membrane contactor CO_2 absorption testing.

During tests, gas-side CO_2 permeated through the membrane and was absorbed in the solvent. The CO_2 concentrations of the simulated flue gas feed at the gas inlet and CO_2-depleted gas residue at the outlet were measured by a CO_2 analyzer and CO_2 content in the solvent was measured by titration. A 40 wt.% aMDEA/H_2O was used as the solvent. An analytical procedure created in-house that involves using to measure CO_2 content in amine-based solvent as low as 0.3 wt.% with high accuracy was used. For comparison with conventional contactors, volumetric mass transfer coefficient ($K_G A_v$, *(sec)*$^{-1}$) was used in the current study and calculated as follows,

$$K_G A_v = K_G \times A_v \tag{3}$$

where K_G the mass is transfer coefficient (m/s), and A_v is the specific surface area per volume of the membrane module.

RESULTS AND DISCUSSION

Task 1. Project management

Agreements between GTI and team members, PoroGen and Trimetric, have been signed.

During the course of process simulation, it was observed that proper simulation of the H3-1 solvent with process simulation software required additional validation of existing fundamental data with field data, potential need to collect fundamental data and validation of simulation predictions. This data was not readily provided by Mitsubishi Hitachi Power Systems Company, or other H3-1 users. Therefore, after consultation with different funding agencies, it was decided that aMDEA would be used as a prime test solvent and process simulation solvent for completing the preliminary TEA.

Task 2. Preliminary techno-economic analysis and EH&S study

Preliminary techno-economic analysis (TEA)

Preliminary TEA was based on prior bench-scale field testing completed at the Midwest Generation's Will County Station site (located in Romeoville, IL) in 2013 conducted using aMDEA solvent. The flue gas composition measured on the upstream of the membrane absorber is listed in Table 2. The measured relative humidity of the flue gas before the blower was 39% at 130°F.

Table 2. Flue gas composition**.**

Element	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	

Mass transfer coefficient obtained during the field testing was 1.2 (sec)$^{-1}$ at 93% CO_2 removal. This mass transfer coefficient is over one order of magnitude greater than those of conventional contactors with packed columns (0.0007 – 0.075 $(sec)^{-1}$). The TEA establishes a quantitative basis by which the HFMC carbon capture process may be evaluated and identifies key design parameters and process characteristics that impact techno-economic performance and feasibility.

The preliminary TEA used DOE's Cases 11 (without capture) and 12 (benchmark amine plants) as comparison bases [4]. Table 3 shows the estimated cost of CO_2 capture for the HFMC technology is 49.35 \$/tonne of CO_2 captured when using a mass transfer coefficient of 1.2 $(sec)^{-1}$.

Table 3. Cost of electricity and cost of CO_2 capture comparison.

Item	**Unit**	**Case 11**	**Case 12**	**GTI HFMC with aMDEA solvent**	
Mass transfer coefficient	$(sec)^{-1}$			1.2 (bench-scale tested)	2.0 (target of the pilot-scale program)
COE - no TS&M	mills/kWh		137.3	127.1	122.1
COE - total	mills/kWh	80.95	147.3	137.1	132.1
Incremental cost of CO_2 capture - No TS&M	mills/kWh		56.3	46.2	41.2
Increase in COE - No TS&M	%		69.6%	57.0%	50.9%
Increase in COE - total	%		81.9%	69.4%	63.2%
/Cost of CO_2 capture - no TS&M	**\$/tonne**		**56.47**	**49.35**	**44.00**

Figure 6 shows cost of electricity for items including capital, fixed O&M, variable O&M, CO_2 TS&M and fuel for various cases including DOE's Cases 11 and 12, and the HFMC technology with the aMDEA solvent. Note that a methodology correction factor of 2.07 was applied to capture system equipment except hollow fibers for costs shown in Table 3. However, in the sensitivity cases in Figure 6, the impact of the cost methodology correction factor was evaluated for the benchmark aMDEA case with the existing 1.2 $(sec)^{-1}$, obtained during bench-scale field testing and target absorber mass transfer coefficient (1.2 $(sec)^{-1}$). Figure 6 indicates that the savings for the HFMC technology are mainly from the capital.

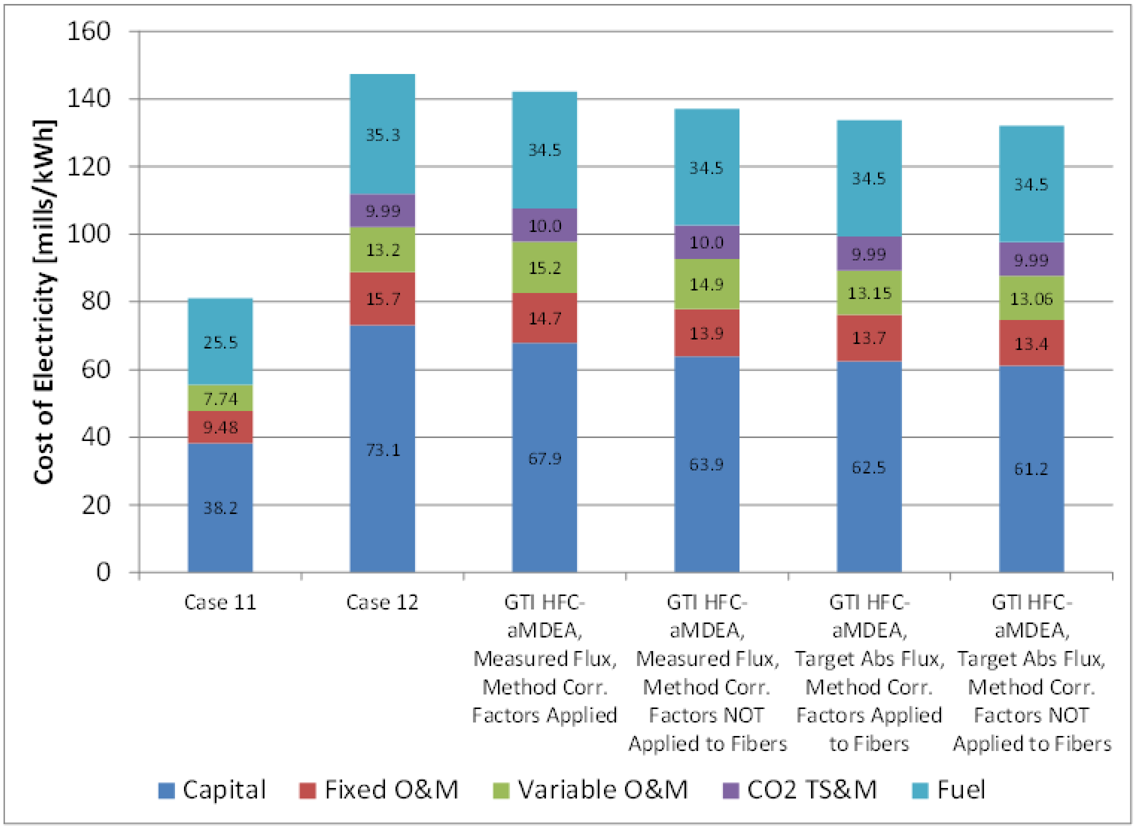


Figure 6. Cost of electricity for each item for various cases.

EH&S study

GTI has completed the preliminary EH&S study, which includes the preliminary EH&S risk assessment involving the design, engineering, construction, operation and testing of a 1 MW_e hollow fiber gas liquid membrane contactor-based post-combustion capture pilot plant incorporating PEEK-based super hydrophobic nanoporous hollow fiber membrane contactor technology and aMDEA solvent.

Currently, the project is at the beginning of the pilot plant design and detailed engineering phase. A preliminary EH&S risk assessment was performed to assess the risks associated with the 1 MW_e slipstream pilot-scale test to be conducted at the National Carbon Capture Center (NCCC) operated by Southern Company Services. The preliminary risk assessment incorporates a number of systematic processes and requirements, as noted below:

- Pilot and commercial-scale processes built by or commissioned to a third party constructor by GTI, and operated by GTI, require detailed material and energy balances, completion of detailed drawings (piping and P&ID), HAZOP study, operating procedures, start-up and shut-down procedures and checklists, accumulation of all MSDSs for all chemicals, specification of PPE, completion of relevant safety training, and development of JSA. GTI will also address the code and regulatory compliance requirements as well as the requirements and input from the technology owner/partner (PoroGen) and the site owner (NCCC).

- As per DOE-NETL requirements, an environmental questionnaire (National Environmental Policy Act implementing procedures) has been completed for this project in conjunction with the host site organization (NCCC).
- A preliminary HAZOP study will be conducted based on the PFD and the actions from this will be either incorporated into updating the pilot plant design and procedures, or slated for implementation during the construction, commissioning and operations/testing periods.

The preliminary EH&S study summarized the key plant EH&S concepts and approach. Key EH&S risk factors assessed and addressed as part of the overall approach were provided in tabular form including the risk mitigation factors.

The study also described the technology as applied to carbon capture from flue gas as well as the PEEK membrane contactor manufacturing process. Additional safety-related information beyond the required information has also been given.

Task 3. Determination of scaling parameters for 2,000 GPU hollow fiber membrane modules

Under this task, PoroGen has been optimizing their PEEK membranes and membrane modules for long-term CO_2 capture operation. Membrane module factors that might affect long-term CO_2 capture performance, such as O-rings, epoxy/fiber interface in tubesheets, "wet out" of the hydrophobic surface in long-term operation, and module start-up/shutdown procedures, have been investigated. PoroGen has fabricated the new fibers, installed them into 2-inch modules, and shipped the modules to GTI for testing in gas/liquid contactor mode. Based on testing results, GTI provided feedback to PoroGen for the membrane and module improvements. Table 4 lists the modules tested in contactor mode and their intrinsic CO_2 permeances. One of the critical milestones for the membrane development, target intrinsic CO_2 permeance of 1,700-2,000 GPU, has been achieved for the following modules: 2PG-518, 2PG-518re, 2PG-636, 2PG-637, and 2PG634. Conditions for making these modules will be used in the future membrane module fabrication.

Table 4. Modules tested in contactor mode and their intrinsic CO_2 permeances.

Cartridge No.	Number of fibers	Active fiber area (inside, cm^2)	Pure CO_2 permeance (GPU)
2PG-518	1216	4026	1773
2PG-609	1360	5776	1449
2PG-518re	1216	4026	2178
2PG-636	864	5327	1785
2PG-637	720	5862	1858
2PG634	1216	5287	1825
2PG635	1216	5287	1459
2PG630	1216	5287	1062
2PG631	1216	5287	1204
2PG-651	1216	5287	1361
2PG-652	1360	5913	1372
2PG-632	1360	4548	815
2PG-522	1360	4412	902
2PG-523	1360	4412	1054

The membrane contactor process can operate at close to atmospheric pressure with the only pressure requirement being 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. In the 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:

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

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 4 suggests gas-side pressure drop increases linearly with fiber length L and $1/r^4$ for a fixed gas flow rate. The PEEK fibers used in a previous field demonstration had an inner diameter of 13 mil, and the observed pressure drop was 5 psi. New fibers fabricated by PoroGen have an inner diameter of 20 mil. Due to this change in inner diameter, it is expected the gas side pressure drop through the 20-mil fibers will be reduces to only 18% of that obtained for the old fibers.

Once the testing of the larger fibers is complete PoroGen will scale up the modules from 2-inch to 8-inch in module diameter. The expected delivery date for 8-inch diameter modules is February 2015.

Task 4. Bench-scale testing in support of the pilot-scale design effort

<u>Testing module factors that might affect CO_2 capture performance</u>

The CO_2 capture and operation stability for the membrane modules fabricated by

PoroGen have been tested in gas/liquid contactor mode at GTI. Based on the testing results, we have the following conclusions:

- No problems with O-ring seals were noted through tests of multiple 2-inch diameter modules, some after prolonged operation;
- Development of tubesheet fabrication procedure has been completed; and
- No “wet out” of the hydrophobic membrane surface after long-term operation has been observed based on single-gas CO_2 permeation measurements before and after contactor testing

<u>Module performance stability under start-up/shutdown cycles</u>

PEEK membrane modules exhibit good mechanical properties and stable permeation properties during CO_2 capture with aMDEA solvent for 120 hours. Modules have been tested with varying surface treatment, pore size, and winding angles under start-up and shutdown cycles. In such tests, a membrane absorption operation was typically started with lean aMDEA solvents (CO_2 loading: 0-2 wt.%). After steady state was reached, the CO_2 absorption continued to run for 1-2 hours and CO_2 permeation flux was monitored. During shutdown procedure, after CO_2 removal performance tests, the liquid side and gas side pressures were released, a small amount of N_2 was flown on the gas side, whereas the liquid side solvent was drained. This was carried out for a couple of days after which the module was tested again for CO_2 removal performance. Figure 7 shows that the normalized mass transfer coefficient decreased with increasing start-up and shutdown cycles for membrane module 609 by using this shutdown procedure. This indicated that the membrane module had been degraded, and new start-up/shutdown procedure would be required.

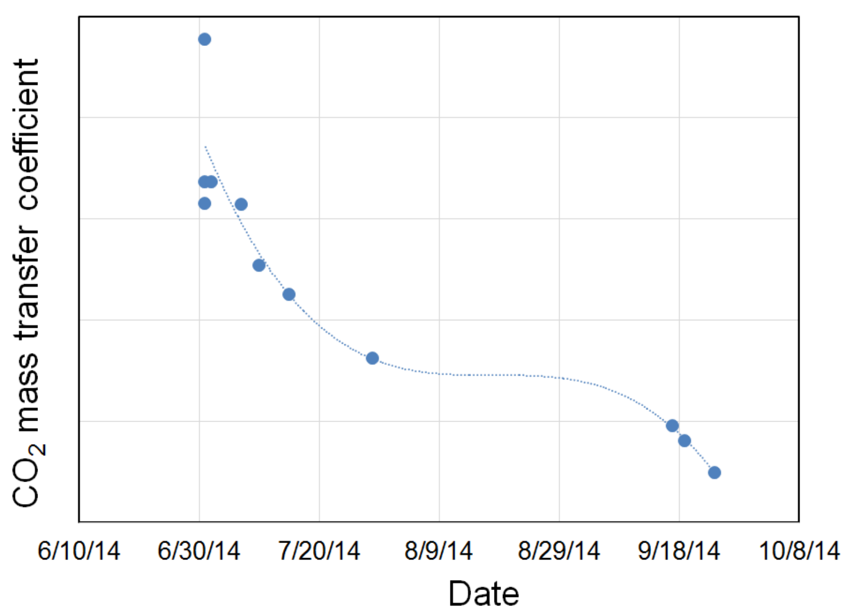


Figure 7. Run chronology for module 609.

A new shutdown procedure consisting of draining the liquid without a N_2 purge has been incorporated into the procedure for membrane module testing. Figure 8 shows that a stable CO_2 capture performance during 2 weeks of testing using a new module with the shutdown procedure.

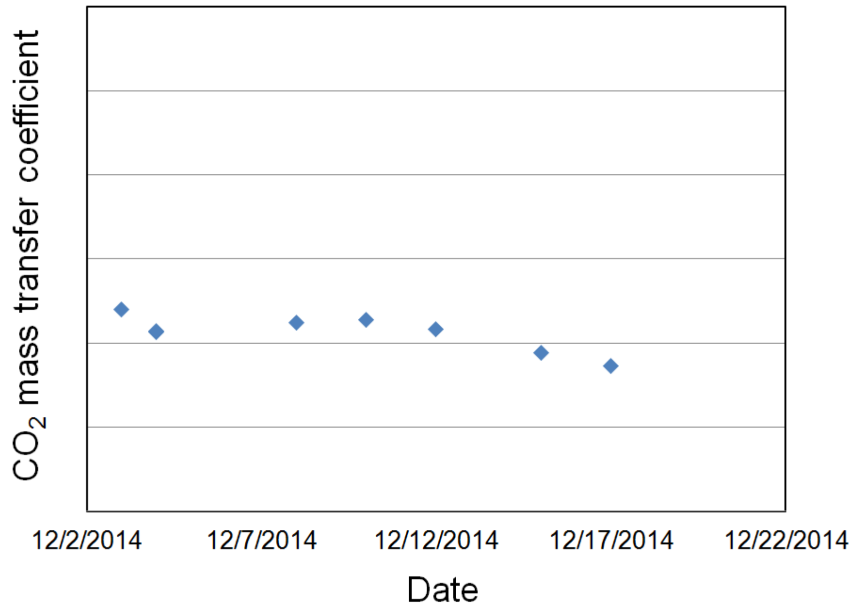


Figure 8. Run chronology for module 523.

PoroGen scientists and engineers are still improving membrane and modules toward long-term steady-state operation. The goal is to achieve membrane modules that possess high CO_2 permeation rate and operation stability. It should be noted that CO_2 permeation rate does not decline during continuous operation and multiple shutdowns.

<u>New design for rich solvent regeneration</u>

In addition to technical progress on membrane absorption stability, significant progress was also achieved on rich solvent regeneration. An energy efficient solvent regeneration process was designed for CO_2 capture. This process is a new and novel way of regenerating CO_2 laden rich amine solvent for amine based CO_2 absorption process. It is particularly suited for regenerating CO_2 laden rich amine solvent in the post-combustion CO_2 capture process. The process lowers the overall power requirement for CO_2 compression and regenerates the solvent for recirculating to the absorber side of the CO_2 capture process.

The solvent regeneration process has been simulated using Aspen HYSYS® and can be seen in Figure 9. CO_2 is removed by the rich solvent at different pressures depending on the regeneration temperature.

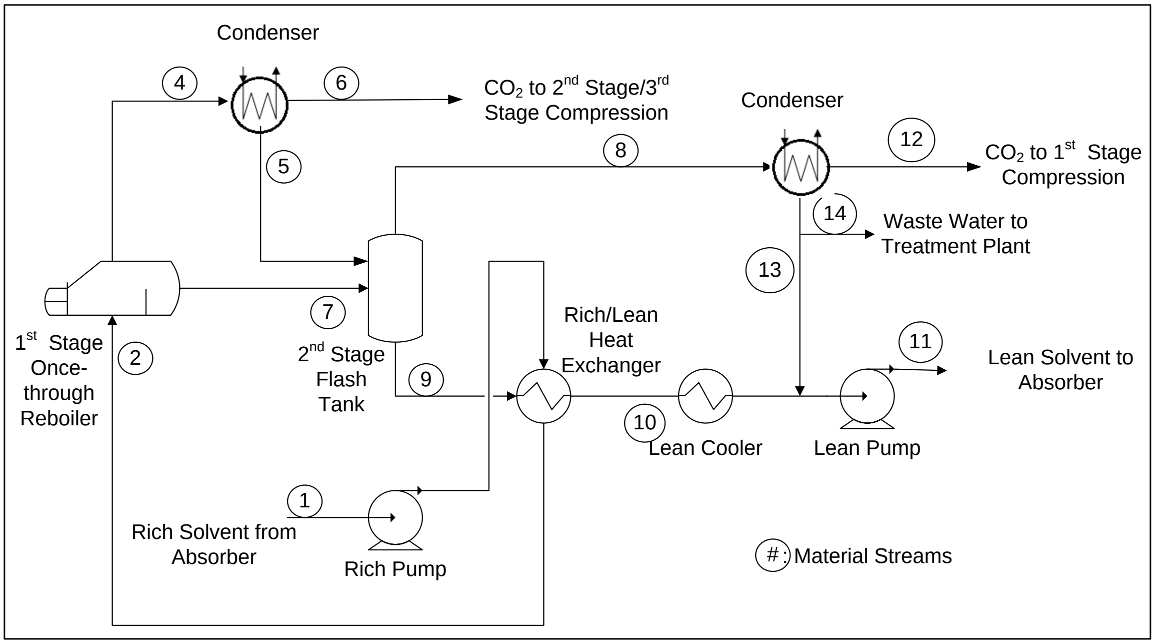


Figure 9. Two-stage flash regeneration process flow diagram.

The first stage uses a once-through "reboiler" at elevated pressures to heat the rich solvent to the desired regeneration temperature and separates the vapor and liquid streams. The vapor stream, after cooling to a condensed water vapor phase, contains greater than 95 mol% CO_2 and is at a pressure suitable for feeding to the suction side of the second or the third stage of the CO_2 compression train. Partially regenerated solvent is then flashed at the inlet pressure of the first stage of the CO_2 compression train. After the two stages of flash, lean solvent is ready to be cooled and sent back to the absorption process for removing CO_2 from the flue gas. The process seeks to provide a two-stage solvent regeneration and CO_2 recovery and compression process wherein the overall energy required for the complete process is reduced and/or wherein at least part of the CO_2 is recovered at a pressure higher than the suction side pressure of the second or third stage of the CO_2 compression train so as to reduce the power required for compression of the carbon dioxide.

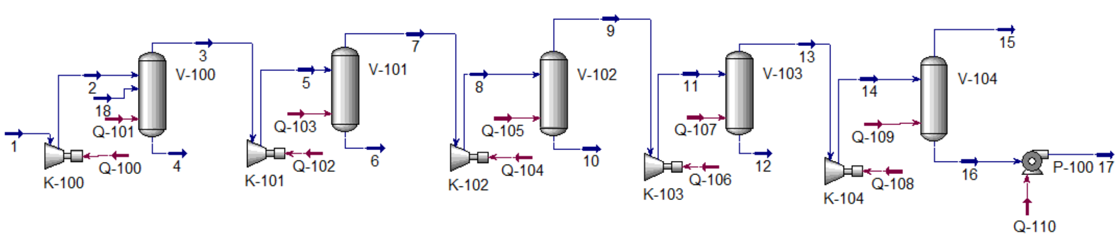


Figure 10. Six-stage compression train.

Figure 10 shows the compression train for the CO_2 generated by conventional column regeneration. This train has 5 stages of compression and one stage of pumping. This is because after stage 5, the CO_2 stream is in the liquid state and a pump is much more efficient in boosting the pressure of liquid than a compressor. Stream 18 is shown to be fed to the first stage discharge side cooler to be mixed with stream 2 after first stage compression. Stream 18 can also be fed to the second stage discharge side cooler to be mixed with stream 5 after second stage compression.

The new regeneration process is capable of varying the temperature of the first stage “reboiler” and the pressure of the CO_2 stream. The temperature is chosen to match the second or third stage suction-side pressure of the compressor wherein the amount and pressure of CO_2 removed from the rich solvent in the first stage is a function of this temperature. The simulation results shown in Table 5 illustrate the impact of varying the temperature of the first-stage reboiler on the distribution of CO_2 different pressures in streams 6 and 12 in Figure 9, and the reduction in overall compression power. Note that with a temperature of 140°C and pressure of 120 psig for the first-stage reboiler, the saving is as much as 20% of the overall compression power.

Table 5. Effect of varying the temperature of the first-stage reboiler on reduction in compression power

Temperature of the 1st stage reboiler (°C)	Pressure of the 1st stage reboiler (psia)	% of CO_2 to 3rd stage compression	% of CO_2 to 2nd stage compression	% of CO_2 to 1st stage compression	% reduction in compression power
140	120	50.3%	0%	49.7%	20.1%
130	100	0%	66.7%	33.3%	12.6%
120	80	0%	50.7%	49.3%	9.6%
120*	20	0%	0%	100%	0%

*Conventional column regeneration

Figure 11 shows an example of testing parameters and result for this new design. Both higher pressure (50 psig) and lower pressure (5 psig) CO_2 were collected. The CO_2 loadings for the rich and lean solvents were 8.14 wt.% and 0.98 wt.%, respectively. Note that the lean solvent (0.98 wt.% CO_2 loading) is “lean” enough that can be directly sent to the membrane absorber for 90% CO_2 removal for flue gases.

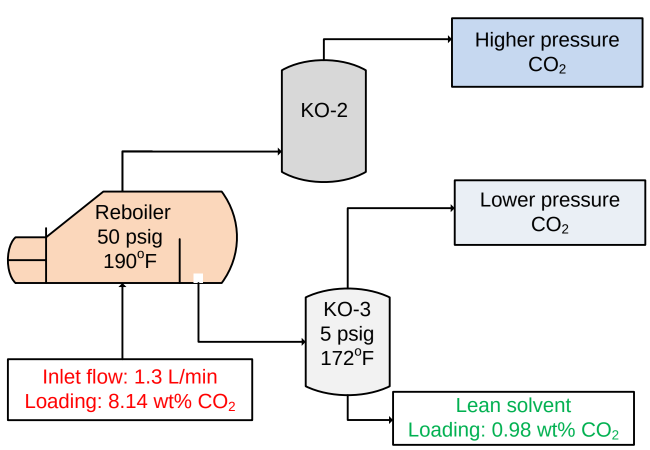


Figure 11. Testing parameters and result for the new regeneration design.

Task 5. Design and costing of the 1MW_e equivalent CO_2 capture system

The preparation of a design package for the 1MW_e HFMC pilot-scale unit was initiated. GTI Institute Engineer Dr. James Aderhold, who has 40 years of technical and management accomplishments, ranging from product/process conceptualization through commercialization in the refining, chemicals, automotive, and natural gas industries, is the design lead. The pilot unit is on schedule to be installed at the NCCC by November 2016. A bid package will be developed by GTI, and detailed engineering and fabrication of the HFMC and membrane skids will be completed by an engineering vendor. The pilot-plant design package is expected to include:

- Cost to build with a +/- 10% accuracy
- Final process flow diagram, general arrangement drawings, and elevation drawings (PDF files legible at 8.5 inches by 11 inches) with written process description
- Pilot plant electricity, heat, and water consumption; waste generation and management/tie-ins to the existing host facility
- Slipstream feed conditions: pressure, temperature, flow rate, gas composition, and contaminant levels that represent the actual flue gas
- Liquid side conditions: pressure, temperature, flow rate, and lean loading.
- Estimated CO_2 delivery conditions: pressure, temperature, flow rate, and gas composition
- Start-up, steady-state operation, and shut-down procedures for the proposed pilot process
- Protocols, methods, measurements, and quality assurance for baseline and performance testing.

To date, process flow diagram and material balance based on preliminary TEA have been essentially completed. Adjustments have been made for two months of continuous operations at NCCC. Other progress includes:

- Equipment for integrated membrane absorption and desorption processes has been identified,
- Major process control loops have been formulated,
- Piping and instrumentation diagrams (P&ID) have been initiated, and
- Preliminary review for P&ID has been completed.

Discussions with the host site National Carbon Capture Center (NCCC) at Wilsonville, Al about operating philosophy and duties for each party are ongoing.

CONCLUSIONS AND RECOMMENDATIONS

Through Phase 1 of this study, substantial progress has been made toward key milestones of the current 1 MW_e pilot-scale development. Significant breakthroughs include:

- Preliminary EH&S study and TEA have been completed.
- Cost of HFMC with aMDEA solvent has been calculated to be 22% lower than the benchmark DOE Case 12 (with CO_2 capture using amine plant).
- Intrinsic CO_2 permeance of 1,700-2,000 GPU has been achieved for 2-inch diameter modules. Larger inner diameter modules are under fabrication to meet the pressure drop goal ($\leq$ 2 psi). 8-inch diameter modules will be delivered for membrane contactor CO_2 capture testing early 2015.
- Membrane module factors that might affect CO_2 capture performance, such as O-rings, epoxy/fiber interface in tubesheets, wet out of hydrophobic surface in long-term operation, and module start-up/shutdown procedures, have been investigated toward long-term steady-state operation.
- A new process for regeneration has been designed. Process simulation by Aspen HYSYS® suggested the new design should save as much as 20% of the overall compression power. The new design has been validated experimentally. A patent application based on this design has been filed.
- Fabrication of 8-inch module and design of 1 MW_e pilot plant are ongoing, and will be completed by June 30, 2015 during our Phase 2 study.

In Phase 2 of the program, research will be focused on testing and improving CO_2 capture performance and stability of the 8-inch diameter modules.

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