Nano-porous PEEK® Hollow Fiber-based Gas/Liquid Membrane Contactors for Sour Gas Treating

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Introduction

The workhorse of natural gas treating is the absorber/stripper plant based on amine solvent systems or in some cases on physical solvents. These solvent systems are used to remove carbon dioxide and/or hydrogen sulfide from natural gas. These systems work reliably most of the time, but they do have a number of limitations. One of the limitations is that the gas and liquid countercurrent flows are subject to hydraulic limitations, which, if exceeded, result in column flooding and/or entrainment which results in failures to meet product specifications. Gas/Liquid contacting in towers have limited turndown capability, again due, essentially, to hydraulic limitations. As more and more gas treating is or will be carried out offshore on platforms wherein floating LNG (FLNG) units are utilized, the weight and height limitations and sensitivity to motion may limit the applicability of conventional treating in packed or trayed towers. In remote areas, or in areas where security of workers may be an issue, the advantages of shop-fabricated, modular construction, coupled with the potential ability to essentially “drop-in” the system is of an obvious value.

The hollow fiber membrane contactor (HFMC) approach is not affected by the above constraints. The HFMC technology must nevertheless offer lower initial capital cost, factoring in installation cost and reduced platform cost (which results from reduced system weight). The technology must also be robust, reliable and safe. GTI and PoroGen Corp. have been developing a gas liquid membrane contactor based on porous PEEK hollow fiber systems. The development has been targeted to natural gas treating (for acid gas removal), power plant flue gas CO_2 capture, and syngas treatment. This technology can potentially be applied to any application where an absorption fluid is used to remove a constituent from gas, provided that all materials of the contactor module construction are compatible with the absorption fluid. The technology differs from the PoroGen PEEK-SEP™ membrane systems designed as gas-gas membrane treating systems[1]. The gas-gas separation technology developed by PoroGen Corporation has been commercialized for several membrane gas treating applications including natural gas dehydration, hydrocarbon dew point control and acid gas removal and a number of gas/liquid transfer applications such as removal of dissolved gases from liquids. However, the manufacturing and materials sciences knowledge from the PEEK-SEP™ is leveraged in this development.

GTI (at that time, GRI) has been involved in the development of gas/liquid membrane contactors since the mid-1990s. An earlier concept involving PTFE ribbon tube sheet membranes was tested in the laboratory and then in dehydration service in an 8-inch diameter module[2, 3]. GTI terminated development of this technology due to a number of technology limitations – most notably the ribbon tube's sensitivity to relatively small pressure differentials between gas and liquid streams, necessitating an expensive differential pressure control system, high cost of materials, and high manufacturing costs. Based on test results to date the current approach obviates these issues resulting in a robust and affordable alternative to present technology.

Although the technology is not offered commercially at this stage, we are making good progress towards advancing and qualifying the technology. Full-scale pilot tests are in the initial planning stage and will include commercial-scale HFMC modules in the pilot tests.

Technology Description

While the overall separation process for CO_2 or H_2S removal remains the same between a conventional column-based process and the membrane contactor process, the contacting vessel configuration undergoes significant changes with gas/liquid membrane contactor. The membrane contactor based on nano-porous, PEEK hollow-fiber membrane module offers several advantages over a conventional packed absorption tower. In the gas absorption membrane system, the gas flows inside the hollow fibers and the amine solvent flows exterior to hollow fibers. PEEK membranes are super-hydrophobic and nano-porous, that is, the solvent will not wet the membrane pores, and the nano-sized pores will remain gas filled. The result is extremely low resistance in the open pores to gas mass transfer.

One advantage of using a membrane contactor is the ability to keep the phases separated. It becomes possible to eliminate the usual limitations of packed towers caused by flooding and entrainment of the liquid by the up flowing gas. In the membrane absorber, the flow of gas and liquid can be varied independently and the contact area will then also be independent of the flow velocities as opposed to the behavior in a tower wherein the mass transfer area varies with the liquid load. Hollow fiber membrane configuration provides for a very high specific contacting area per unit volume (see Table 1) and several orders of magnitude higher mass transfer coefficient.

Table 1. Gas-liquid contactor device surface area and volumetric mass transfer coefficient comparison

Gas-liquid contactor	**Specific surface area, (m^2/m^3)**	**Volumetric mass transfer coefficient, $(sec)^{-1}$**
Packed column (Countercurrent)	10 – 350	0.0004 – 0.07
Bubble column (Agitated)	100 – 2,000	0.003 – 0.04
Spray column	10 – 400	0.0007 – 0.075
Membrane contactor	**500 – 7,000**	**0.3 – 4.0**

Other advantages of a membrane contactor are elimination of foaming, avoidance of liquid mal-distribution (channeling), and the potential to reduce pick-up of certain gas contaminants that cause solvent degradation. Tidal- and wave-induced motion, as observed in floating platforms and ships, should not affect the performance of the HFMC, but can cause performance degradation by gas bypassing in conventional columns placed in such services.

At the core of new contactor technology are novel hollow-fiber membranes based on the chemically and thermally resistant commercial engineered polymer poly (ether ether ketone) or PEEK[1,2]. The PEEK membrane material utilized in the membrane contactor is a high-temperature engineered plastic that is extremely resistant to deterioration under the operating conditions encountered in typical gas absorption applications. It can withstand contact with most of the common treating solvents.

The membrane contactor constructed from porous, super-hydrophobic PEEK hollow-fiber membranes constitutes the novel, enabling feature of the technology. The hollow-fiber membrane has a water breakthrough pressure greater than several hundred psig. Hollow fiber membranes are ideally suited for gas/liquid transfer application since fibers can provide very high surface area to volume ratios and pressure of fluids on the bore side and the shell side (i.e., the liquid side and the gas side) can be maintained independently, which is not possible for conventional columns where fluids in contact are always at the same pressure.

The membrane absorber developed by PoroGen has been further tailored towards the specific needs of acid gas removal from natural gas for improved mass transfer of acid gases from the gas phase to the solvent phase. The robust hollow-fiber membrane exhibits a high intrinsic CO_2 permeance {>2000 GPU, 1 GPU=1×10^{-6} (cm^3[STP])/ ($cm^2 \cdot cm\ Hg \cdot sec$)} while still providing an absolute gas/liquid inter-phase barrier. The contactor module is constructed using computer-controlled helical winding of membrane hollow fibers and provides for a structured and compact mass transfer device of high separation efficiency.

Cartridge sizes used in laboratory tests were 2-inch diameter by 12-inch long containing about 10 ft^2 of membrane area or 2-inch diameter by 60-inch long and containing about 50 ft^2 of membrane area (as measured by the outside diameter of the fibers). The cartridge is installed into a pressure shell in a removable manner and sealed with O-rings.

Membrane module design and construction have significant impact on the overall gas mass transfer coefficient by minimizing liquid side resistance, maximizing the driving force and increasing the liquid side mass transport coefficient. The flow conditions on the shell-side of the membrane can be ill-defined for conventional membrane modules designed for filtration applications. 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 of the two phases, such as cocurrent, counter-current, or cross-flow. 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.

The following key design elements have been incorporated into the contactor to optimize performance:

a) 4-port counter-current flow to enable optimum driving force for the acid gas absorption;
b) structured hollow fiber packing by computer-controlled helical winding to minimize the absorption liquid malflow;

c) optimum fiber packing density to minimize the liquid pressure drop and minimize concentration polarization on the liquid side;
d) optimized winding pattern to promote the liquid-side gas mass transport; and
e) high CO_2 permeance hollow fiber that enhances gas phase mass transport.

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 concentration polarization. A wound cartridge with a controlled uniform structured packing is shown in Figure 1. The hollow fibers are arranged in a helical path, with the axis of the fibers running confluent to the principle direction of fluid flows.

Figure 1. Helically wound structured hollow fiber cartridge

Test System

GTI has multiple contactor test stands at its Des Plaines, Illinois facility. The HFMC test system configuration is shown schematically in Figure 2 and in the photograph of Figure 3.

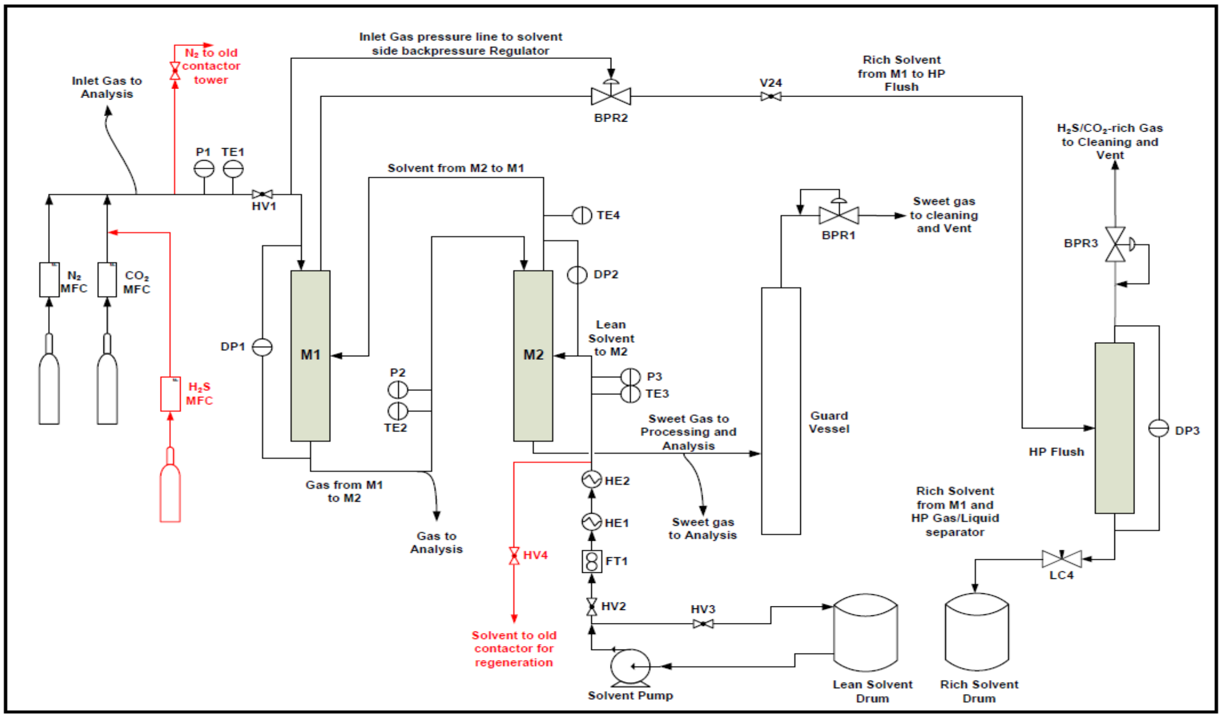

Figure 2 Laboratory HFMC test system schematic

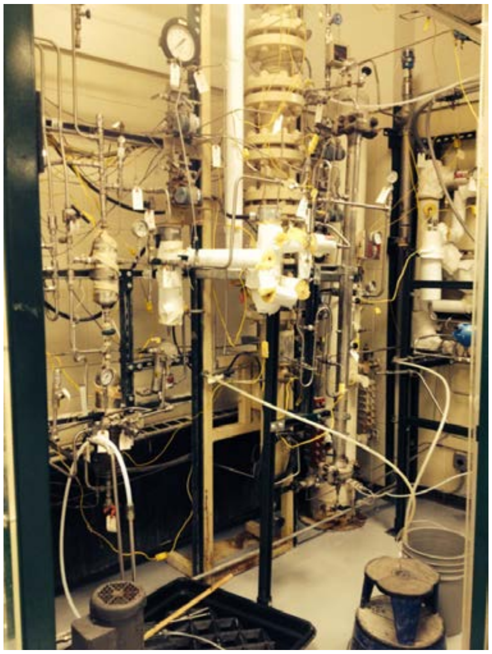

Figure 3 Photograph of HFMC laboratory facility

Gas from cylinders is fed through mass flow controllers at the desired pressure (up to ~70 bar) to generate gas mixtures of target composition and pressure. The gas mixture is fed into bore side of HFMC at the same time a lean solvent is pumped counter-currently to the gas flow into shell side of membrane contactor (M1, Figure 2). The treated gas exiting M1 is then routed to vent, through a scrubber. The scrubber is required since in some tests the feed gas contains H_2S along with CO_2. Due to the risks of using highly combustible, high-pressure methane as the main component of the gas, nitrogen was used instead. This change in gas composition is not expected to have any significant effect on the performance of the system since both nitrogen and CH_4 do not react with amine and are not very soluble in aqueous alkanolamine mixtures. The rich solvent is flashed and the flash gas joins the treated gas upstream of the scrubber. The flashed rich solvent is sent to the rich solvent drum and is not directly re-used in the experiments (except in a few experiments where an integrated absorber/desorber system was tested with continuous solvent flow). Gas composition measurements were carried out using a gas chromatograph and solution loadings were determined by titration.

The use of contactors for absorption and regeneration steps was first carried out independently and later integrated into a continuous process. Solvent pre-loaded with CO_2, at a predetermined lean loading, was fed to the absorption membrane(s) in standalone absorption tests. It has been demonstrated in these absorption tests that the acid gas concentration in the product can be reduced to below 50 ppmv CO_2 provided sufficiently lean solvent is used in the absorption process. This low CO_2 concentration is required to meet LNG specification. A maximum CO_2 specification of 2 vol%, typical for pipeline operations, can be attained with less lean solvent feed. The regeneration flow scheme is shown in Figure 4.

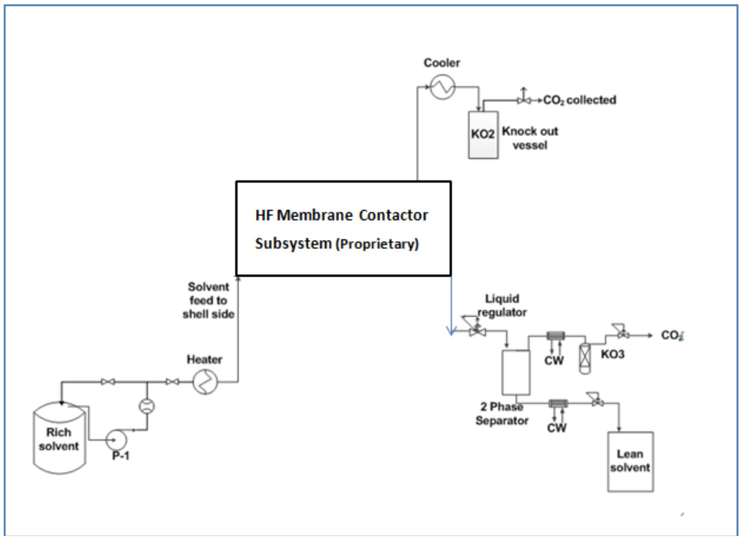

Figure 4. Diagram of a two-stage regeneration process with HFMC

A number of different regeneration configurations were evaluated, some using steam injection and others without, but the above shown scheme has been tested most extensively and adopted for the pilot field test. Details within the regeneration subsystem are proprietary, but all streams entering and leaving the subsystem are shown. The pre-heated rich solvent is introduced into the shell side of a membrane contactor module. The CO_2-depleted solvent leaving this membrane unit is then sent to a two-phase separator. The solvent leaving the two-phase separator is the lean product that is fed to the membrane absorber in integrated testing or else is pre-loaded to another desired loading.

Test Results

Laboratory tests have been carried out with 2-inch diameter contactor modules of different lengths (different contact area) and gas to liquid ratios. In the laboratory test system sets up certified gas composition of a desired CO_2 concentration (CO_2 in nitrogen) were utilized. The tests were carried out in the apparatus depicted above in Figures 2 - 4. Experiments were carried out at constant pressure and controlled by backpressure regulators in the system. Temperatures of incoming gases were at ambient conditions. The test result of a representative run is shown in Figure 5, wherein a gas with 7.75 vol% CO_2 (bal. N_2) has been fed at a number of different flow rates into the membrane contactor while the outlet CO_2 product concentration was measured. The liquid flow was 1.65 L/min. The solvent system utilized was activated MDEA (total amine 40 wt% of which 8 wt% is piperazine). The test was carried out at 950 psia feed pressure with inlet solvent temperature

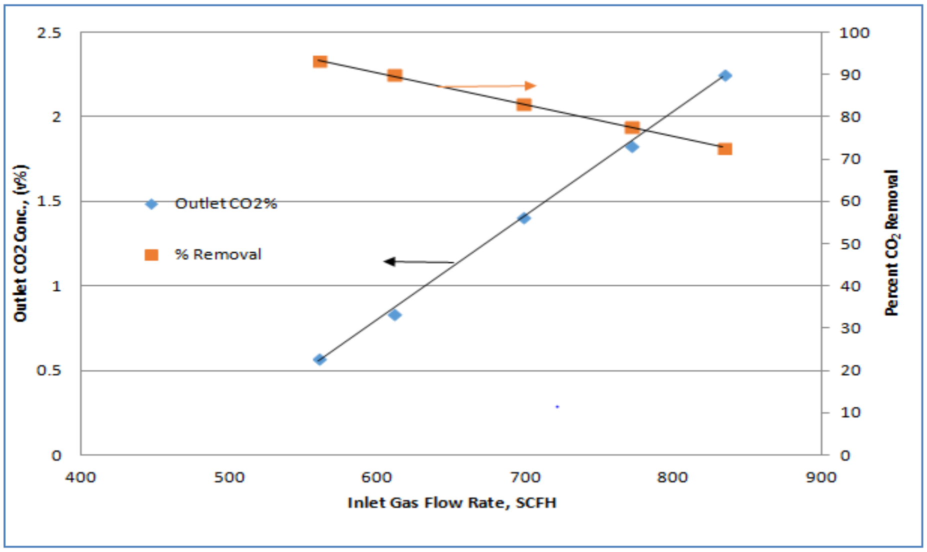

Figure 5 Outlet CO_2 vs. Flow rate

at 76 °F. At the feed gas flow rates of up to about 800 SCFH utilizing lean aMDEA, the HFMC met the typical product pipeline specification of 2 vol% CO_2. The measured data were used to determine the overall mass transfer coefficient, K_Ga, which averaged ~0.62 s^{-1} with a standard deviation of 0.04 s^{-1}. Higher gas throughputs led to higher overall mass transfer coefficients within the measured range.

We have also carried out experiments to determine the ability of HFMC to meet the LNG product specification of 50 ppmv CO_2. In these tests the feed solvent CO_2 loading was reduced to an appropriate level, and the inlet CO_2 feed gas concentration was set at 1 vol%. The feed gas pressure was 940 psig and the liquid inlet temperature was 71 °F. The product purity of 26 ppmv CO_2 was attained at the outlet gas flow of 297 SCFH and 45 ppmv CO_2 spec was attained at 520 SCFH flow, corresponding to mass transfer coefficients of 0.5 and 0.7 s^{-1}, respectively. The liquid flow was set at 0.35 L/min throughout the test. At the end of the run, the feed gas was spiked with H_2S with concentrations of 250 and subsequently 400 ppmv. The test was repeated for the 520 SCFH total feed flow case. When the feed gas with the lower H_2S concentration was used there was no detectable H_2S in the treated gas. When the feed gas with 400 ppmv H_2S concentration was used, the H_2S concentration in the treated gas was 4 ppmv. The CO_2 level remained in the 45 – 51 ppmv range throughout these tests. These tests demonstrated the ability of HFMC to efficiently remove all acid gases that may be present in the feed gas. Throughout these tests a solvent feed source with a fixed lean CO_2 content was used, i.e., in-line regeneration was not performed continuously; rather the solvent was pre-loaded to the desired lean loading.

Initial solvent regeneration tests using HFMC were conducted separately from the absorption tests. In follow up tests the regeneration step was integrated with the absorption step in continuous runs. In an example of one (separate) regeneration test using HFMC, a CO_2 saturated aMDEA solvent (the solvent was saturated to 8 wt% CO_2 loading) was used as a liquid feed. Testing results indicated that the HFMC regeneration unit removed 90% of the CO_2 from the rich solvent. The gas collected during regeneration had a CO_2 content of 97% (balance was water vapor which can be condensed). The CO_2 content of the outlet lean solvent was approximately 10% of that of the feed solvent CO_2 concentration or 0.8 to 1.0 wt%. In another example of solvent regeneration using HFMC, the feed aMDEA solvent had a CO_2 content of 1 wt%. The product solvent had a CO_2 content of 0.1 wt% or 0.0064 mol CO_2/mol amine.

Results of integrated absorption/regeneration operation using HFMC in both absorption and regeneration steps are presented in Figure 6, in this test the feed gas containing 1 vol% CO_2 was treated to meet ~50 ppmv product purity target. The solvent system utilized in this test was aMDEA with 40 wt% total amine content of which 8 wt% was piperazine.

Over the 4+ hour duration of the test, the product CO_2 exit concentration was maintained between 57 and 62 ppmv, with the exception of one point at 70 ppmv (@~220 min). Concentrations of CO_2 below 50 ppmv can be obtained at gas flow rates lower than rates used in this particular experiment, but our objective in this test was to demonstrate stable operation over a longer timeframe than obtained previously in the separate, non-integrated tests. The solvent inventory in this test was estimated to turn over 7 times during the testing (it was regenerated 7 times). The overall material balance for this test was within 2% on CO_2 (the CO_2 released during the flash was calculated).

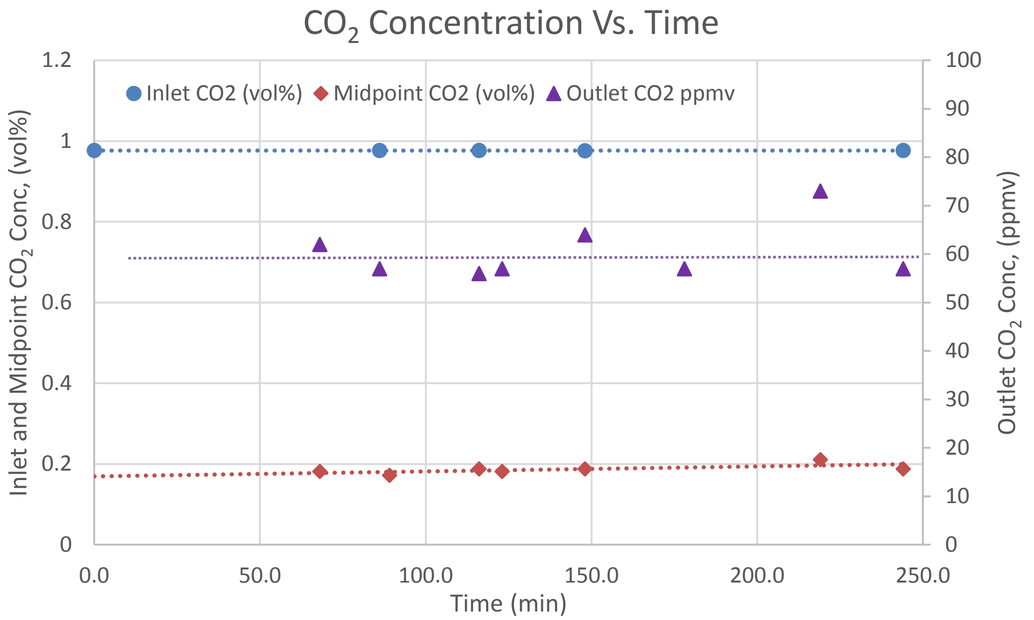

Figure 6 CO_2 Concentration in feed and product streams vs. time (for the treatment of nominal 1 vol% inlet concentration feed to 50 ppmv concentration product)

Additional fully-integrated absorption/regeneration test using HFMCs was carried out to demonstrate ability of the system to meet standard CO_2 pipeline gas specification. The results are shown in Figure 7.This test was carried out at 500 psig for the same reasons as was the previous test (limited feed gas availability) and utilizing the same solvent system (40 wt% aMDEA). A single HFMC absorber module was used.

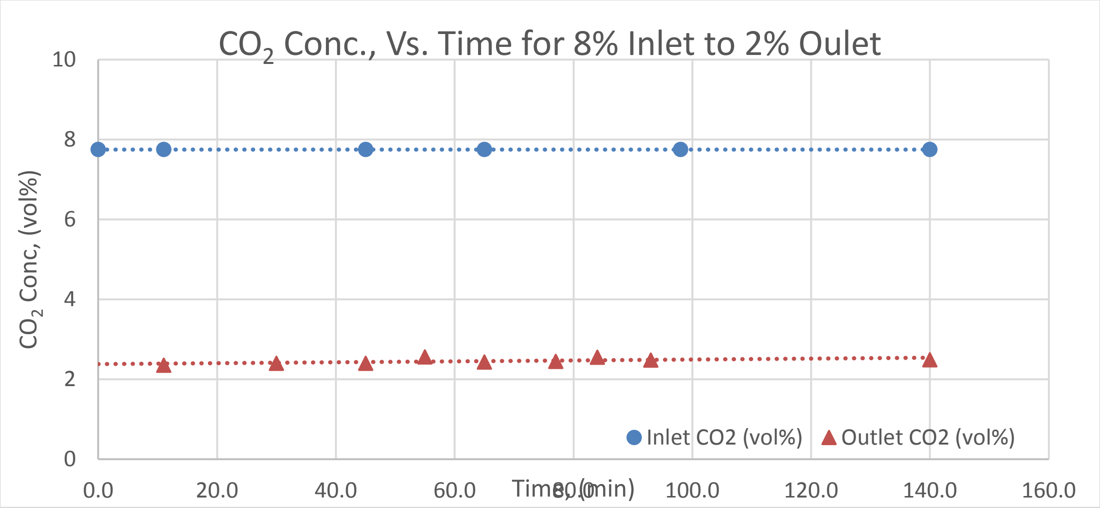

Figure 7 CO_2 Concentration in feed and product streams vs. time (for treatment of nominal 8 vol% CO_2 content feed gas to 2.5 vol% CO_2 content product gas)

The final integrated test was carried out for 24 hours continuously. The CO_2 removal performance data from this test are presented in Figure 8. This test was carried out using a boost compressor recirculating nitrogen gas and with CO_2 mixed in upstream of the HFMC module to enable the desired run length, but otherwise at the same nominal conditions as the test whose results are reported in Figure 8. However, the performance stabilizes for the rest of the test. During this test the solvent was circulated through the system approximately 23 times (number of turnovers).

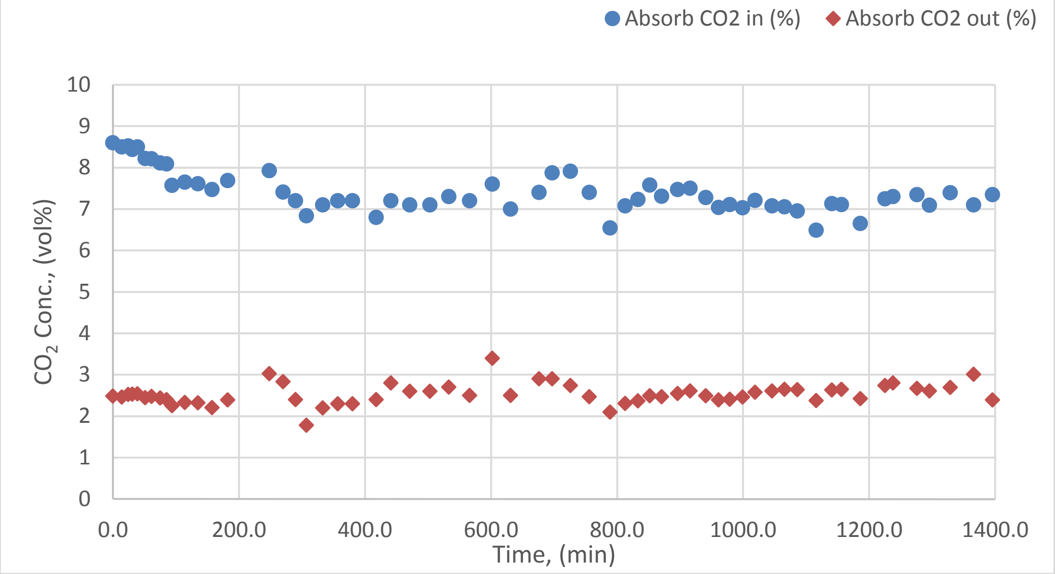

Figure 8 CO_2 Concentration of feed and product gas streams vs. time for HFMC Absorber

Conclusions

GTI and PoroGen have developed a novel hollow fiber membrane contactor technology with applicability to a broad range of gas separation processes including acid gas removal from natural gas, and pre- and post-combustion CO_2 capture from syngas and flue gases. The membrane contactor replaces conventional contactor towers with smaller, lighter weight modular units that provide volume savings on the order of 75%. The HFMC was utilized in both absorption and solvent regeneration steps with both steps integrated into a continuous gas treating process. PEEK membrane contactors exhibit high mass transfer rates and withstand aggressive conditions prevalent in the acid gas absorption step and the subsequent regeneration step. The ability of the HFMC to achieve LNG specifications will enable the use of this technology for FLNG market, where the weight and size advantages are particularly valuable. The technology is expected to not be adversely affected by motion, flooding and related hydraulic issues.

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