Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System, and Process Integration

primary project goals

Liquid Ion Solutions LLC, with Penn State University and Carbon Capture Scientific (CCS), LLC, will develop and validate a transformational hybrid membrane/solvent system for post-combustion carbon dioxide (CO_2) capture from flue gas. The hybrid technology is a two-stage CO_2 capture system combining a membrane separation process and an absorption/stripping process with heat integration between the absorption column and stripping column through a heat pump cycle. Process air is used to sweep the stripper, resulting in much lower regeneration temperatures and enabling heat integration to the point that no process steam is required. To reduce capital cost, a next-generation membrane technology with higher permeance will be developed. The interfacially controlled envelope (ICE) membrane will make use of a transport zone neglected in conventional mixed matrix membranes (MMMs). By carefully controlling the interface between the polymer and inorganic particles within the MMM, CO_2 transport will be encouraged and nitrogen transport diminished in the gap between the two phases. Since permeance is directly tied to membrane area and capital cost, the development of the ICE membranes will reduce the capital cost of the hybrid process below that of the baseline technologies. The research team will combine computer simulation with lab-scale experimentation using simulated flue gas to develop, optimize, and test ICE membranes; test the absorption column and air stripper; and provide data to complete a techno-economic analysis (TEA) of the hybrid technology.

technical goals

- Conduct computer simulations to better understand the various unit operations in the hybrid process and set experimental conditions for project testing. Integrate the simulations and optimize the hybrid system.
- Conduct initial testing of the Generation 0 ICE (neat polymer) membrane formulations. Develop and optimize polymers, select and modify necessary filler particles, examine and validate fabrication techniques, and construct an isochoric test unit.
- Modify and install an existing lab-scale, packed-bed absorption column, and then use it to investigate the absorption column performance at a reduced operating temperature.
- Prepare and characterize the Generation 1 ICE membranes using the isochoric membrane testing unit.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Solvent-Membrane Hybrid Capture System

participant:

Liquid Ion Solutions

project number:

FE0026464

predecessor projects:

N/A

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start date:

10.01.2015

percent complete:

100%

- Modify the absorption column based on computer simulation results, then install and test.
- Fabricate the two optimal Generation 1 ICE membrane compositions for simulated flue gas testing in the isobaric membrane test system.
- Conduct an initial technical and economic feasibility study.

technical content

The objective of the project was to achieve lab-scale demonstration of a transformational hybrid membrane/solvent system for the capture of CO_2 from flue gas. A novel process integration scheme was proposed to overcome the low partial pressure of CO_2 present in flue gas. This scheme took advantage of the potential synergies inherent in the membrane and solvent capture systems. The proposed hybrid technology replaced the second-stage membrane with a methyl diethanolamine (MDEA) solvent capture process. The combustion air was used as a sweeping gas in the solvent stripper. This overall configuration had the major advantages of requiring much less air and eliminating the problems associated with oxygen slip in the membrane-based systems. Even more importantly, because of the presence of the air sweep in the stripper, much lower temperatures were required for solvent regeneration, which enabled heat integration to the point that no process steam was required.

Twenty-two poly(phosphazenes) were synthesized and fully characterized to identify the most optimal candidate matrix poly(phosphazene) polymer for ICE membrane development. The team performed detailed chemical analysis, solvent solubility studies, film formability, adhesion studies, membrane casting procedures, and thermal characterization studies on the 22 candidate polymers.

The base polymer material, called MM16, was not a film former, and it lacked the needed mechanical properties. To overcome these challenges, a cross-linker chemistry was developed and introduced in MM16 (CO_2/nitrogen [N_2] selectivity of 90 and permeability of 900 was observed for the MM16 polymer). The crosslinked material was termed MM19, which achieved a CO_2/N_2 selectivity of 50 and a CO_2 permeability of 500 barrer. MM19 had good film forming, as well as mechanical properties needed to cast membranes, and was selected as the base polymer for developing the ICE-1 membranes incorporating surface modified nanoparticles.

A variety of nanoparticles were evaluated, including surface-modified Quantum dots (QD). However, it was clear during the project that surface-modified silica nanoparticles are optimal for making ICE membranes. A synthesis methodology was developed to place a variety of functional groups on the surface of nanoparticles. Overall, there were three different functional groups placed on 10- to 15-nm silica particles. The functional groups used were cyclohexyl, octadecyl, and ethylene glycol. It was found that MM19 and the cyclohexyl surface-modified silica particles were compatible with each other. These colloidal nanoparticles were obtained from Nissan chemicals and are available in large quantities. The surface modification reaction is scalable. Figure 1 illustrates the general synthesis scheme.

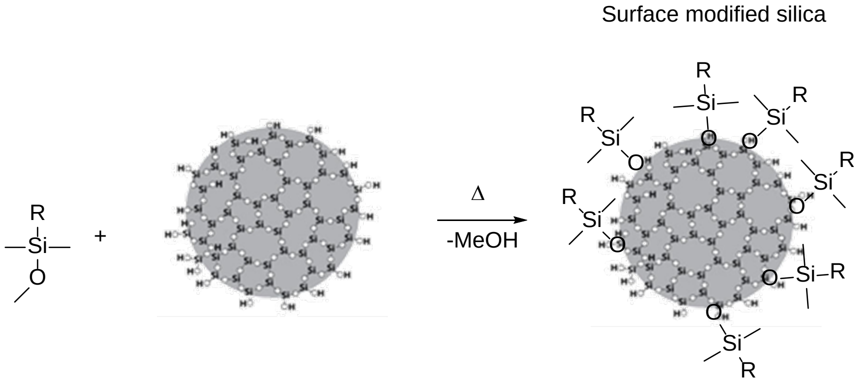


Figure 1: General synthesis scheme of surface modification for silica-nano material.

Additional membrane improvements were carried out by the team to optimize the mechanical and film casting properties. This included identifying the best support and lift-off procedures, as well as figuring out the additional types of crosslinker in the polymeric film. The team studied the impact of the support and determined which support would be ideal for this class of material. The team further improved the mechanical properties of the MM19 polymer by introducing a secondary crosslinking moiety. The addition of this crosslinking moiety resulted in interpenetrating networks (IPN) and improved membrane performance. The IPN approach is illustrated in Figure 2 with the chosen crosslinker. The team also developed an ultraviolet (UV)-initiator to cure the membranes extremely fast. Upon forming the IPN, the membranes obtained were mechanically robust. The implications of the vastly improved mechanical stability cannot be overstated, and lead to far more robust films. Synthesis of MM19 was routinely carried out at 20- to 40-gram scale.

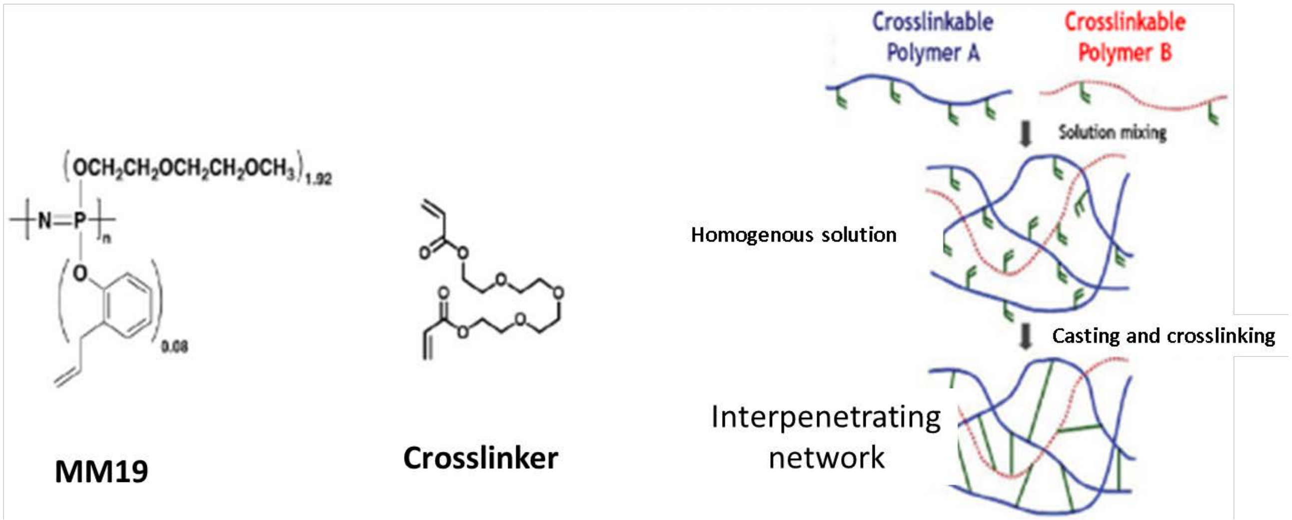


Figure 2: Accessing robust films using interpenetrating approach.

The membrane testing had many interdependent variables, and understanding them was important to developing an optimal membrane material. The team performed detailed design of experiment studies and built a test matrix to yield statistically relevant data. This matrix evaluated 30 different membrane compositions and was used to determine the most optimal composition for these membranes. These results are summarized in Figure 3. The membrane compositions number 1, 4, 9, 20, and 25 showed promise for the application. These materials show permeability of over 1,200 barrer and CO_2/N_2 selectivity over 35. The team was able to achieve 5X higher permeability that the current state-of-the-art materials.

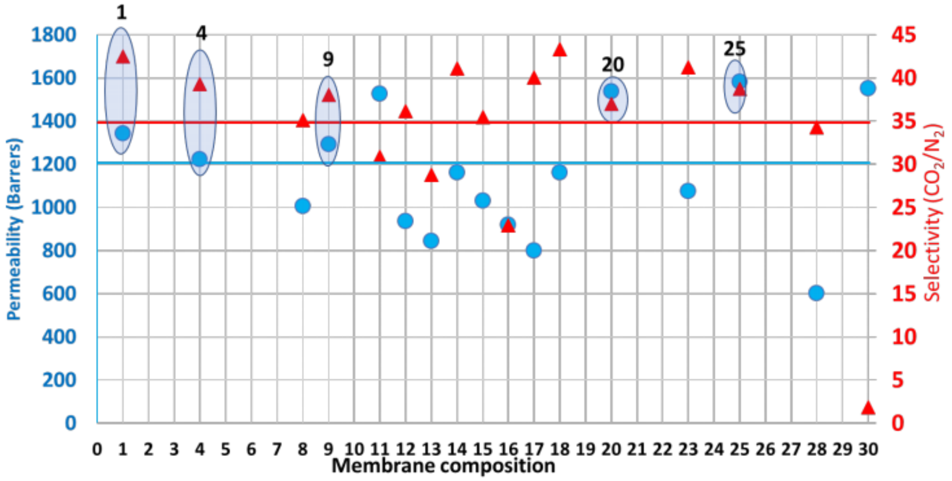


Figure 3: Testing results obtained from the isobaric unit. The blue line is the cutoff for the permeability (1,200 barrers), and the red line is the cutoff for selectivity (35 CO_2/N_2). Five compositions have permeability over 1,200 and selectivity over 35.

The initial simulation work for the membrane system, absorption/air stripping system, heat pump cycle, and optimization of the hybrid process was conducted by CCS LLC. On the membrane side, the team determined that it was economical to choose a one-stage compression unit over two-stage compression and refrigeration steps due to lack of additional performance and increased cost. On the solvent side, it was determined that an operating temperature of 25°C was the most economical temperature for the absorption process. The initial simulation provided the guidelines to perform the CO_2 absorption experiments.

Absorption and air stripping simulations were conducted using the ProTreat software package. Industrial operating conditions were used in the simulations to study the effect of several parameters on packing height, including operating temperature, gas-to-liquid (G/L) ratio, and air flow rates for CO_2 stripping in the desorption step. A simulation program that integrated an absorber and a stripper into the heat pump cycle was created, and further optimization work was carried out to reduce the energy consumption of the heat pump cycle. Preliminary optimization work revealed that the moisture contained in the stripping air would impact the performance of the heat pump cycle.

An existing lab-scale, packed-bed absorption column was modified and installed to investigate the absorption column performance at a reduced operating temperature. The installed absorption column can be seen in Figure 4. Parametric tests were performed to investigate the influence of G/L ratio and operating temperature on the CO_2 removal rate. Tests were run at three operating temperatures (15, 25, and 35°C). For each operating temperature, three G/L ratios were studied. For the hybrid process to work successfully, the absorption process needed to achieve at least 85% CO_2 removal. The parametric test results were in reasonable agreement with the computer simulations, showing that 85% CO_2 removal was achievable.

Figure 4: Installed absorption column.

On the membrane side of the simulation, an internally developed program was used to simulate the membrane separation step. Simulation work confirmed that major improvements in membrane performance were needed to produce CO_2 with 95% purity via one-stage membrane separation. Adding a simple compression and refrigeration step after the membrane separation allowed CO_2 with 95% purity to be produced in a more practical way.

The absorption column previously used was modified by CCS LLC based on computer simulation results to form the air stripper column. The modified air stripping column was installed and tested. This stripper column was then used to perform parametric testing. Preliminary parametric tests were carried out by the CCS LLC team. The variables to be investigated include stripping operating temperature, stripping air flow rate, and G/L ratio. For each test condition, data was collected once the operation reached steady-state. The parametric tests were mainly performed to investigate the influence of G/L ratio and operating temperature on CO_2 desorption. The tests were conducted at different operating temperatures (45 to 65°C) with different G/L ratios (80 to 160 L air/L solvent).

Several successful absorption/desorption cycles were identified: they were cycles with absorption temperature/desorption temperature of 15/55°C, 25/55°C, and 35/65°C. By combining the experiments and computer simulation results in the hybrid process, the following optimal processing conditions were obtained:

- Absorption temperature: 30°C.
- Desorption temperature: 60°C.
- Lean loading: 6.0 wt%.
- G/L ratio: 92 L air/L solvent.
- Number of inter-stage heating: 2.

The systematic parametric tests and computer simulations revealed that an absorption/stripping cycle between 30/60°C was optimal for the hybrid process. A heat pump cycle with a temperature lift of 40°C was enough for the absorption/stripping cycle when 80% of the combustion air was used in the stripping column, fulfilling the success criteria. In addition, the column heights of both the absorber and stripper were reasonable, at 25 meters or less for the Case B12B-scale power plant.

A considerable effort was spent on figuring out how the MM19 could be scaled-up. The synthesis of MM19 included multiple purification steps that were never a problem at smaller scales. However, the team's attempts at synthesizing polymers over 40 grams ran into difficulty. The general synthesis scheme is provided in Figure 5. It is also important to note that the chloropolymer is extremely reactive to air. The formation of the sodium salts are separate synthesis steps.

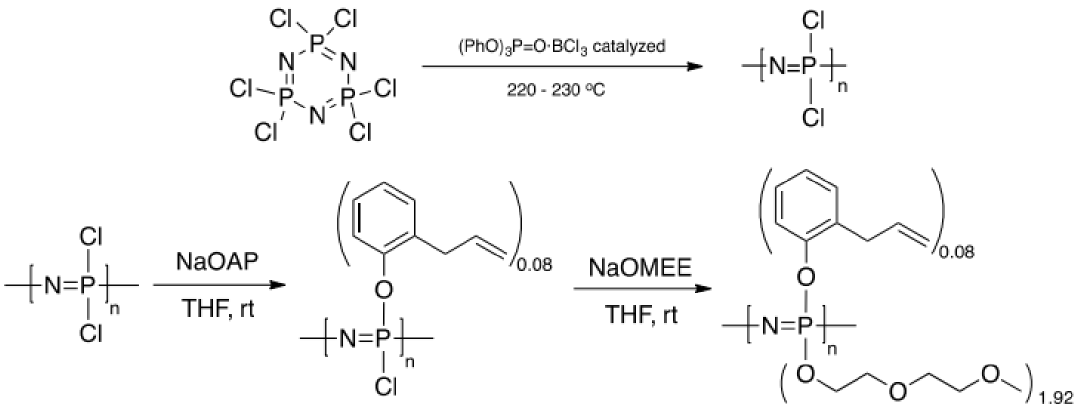
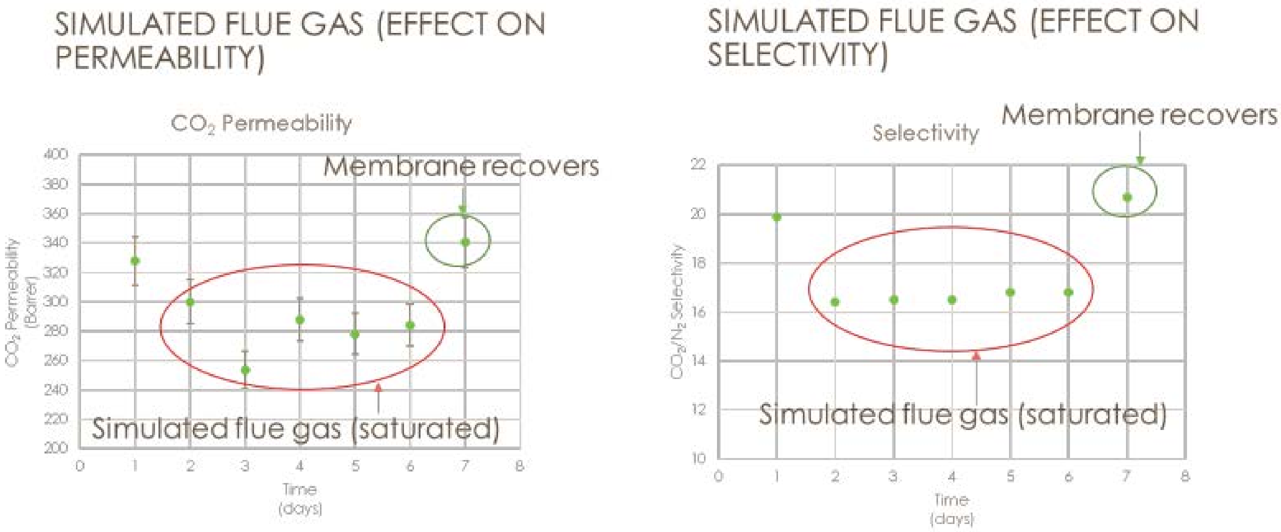


Figure 5: General scheme for the synthesis of MM19 polymer.

There were other problems that also started to show up, such as batch-to-batch variation from the chemical suppliers. The chloro-precursor for poly(phosphazene) quality became an issue as well. A significant effort was spent on the scale-up of these polymers and benchmarking them against the originally obtained polymers. However, the team was unable to benchmark the large-scale material with small-scale synthesized results.

The team evaluated the impact of contaminants on the membrane performance. It was found that upon introduction of contaminants, the permeability and selectivity is lowered. However, the membranes recovered upon removal of the contaminants.


SIMULATED FLUE GAS (EFFECT ON PERMEABILITY)

SIMULATED FLUE GAS (EFFECT ON SELECTIVITY)

Figure 6: Simulated flue gas studies on ICE-1 membranes.

Figure 6 illustrated that despite the problems with synthesis, the overall ICE membrane concept holds true. The ICE membranes were not affected by the addition of contaminants to the simulated flue gas (50 parts per million [ppm] sulfur dioxide [SO_2] and 70 ppm nitrogen dioxide [NO_2] with 7.8 g of water [H_2O]/kg of air [16% relative humidity]), and upon removal, they recover.

The performances of the power plant equipped with the hybrid process and Baseline Case B12B were compared. Results showed that the power plant equipped with the hybrid CO_2 capture process had a thermal efficiency of 33.4%. This was better than the Baseline Case B12B, which was 32.5%. However, the cost of electricity (COE) for the hybrid process was \$146.3/megawatt-hour (MWh), which was higher than the \$142.8/MWh for Case B12B. It is important to note that these analyses were performed based on building a new power plant. For a retrofitting case, since the hybrid CO_2 capture technology would not require steam from an existing power plant, no modifications of the existing power plant would be needed. In the case of a retrofit, the capital cost of the hybrid CO_2 capture process could be lower and potentially a better fit for a CO_2 capture case.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	109.255	N/A
Normal Boiling Point	°C	N/A	N/A
Normal Freezing Point	°C	-	N/A
Vapor Pressure @ 15°C	bar	《1Pa	N/A
Manufacturing Cost for Solvent	\$/kg	《3	N/A
Working Solution			
Concentration	kg/kg	1/1	N/A
Specific Gravity (15°C/15°C)	-	1.09	N/A
Specific Heat Capacity @ STP	kJ/kg-K	2.978	N/A
Viscosity @ 15°C	cP	10.2	N/A
Absorption			
Pressure	bar	1	1
Temperature	°C	30	30
Equilibrium CO_2 Loading	mol/mol	0.494	0.348
Heat of Absorption	kJ/mol CO_2	55.99	55.99
Solution Viscosity	cP	10.2	10.2

Desorption			
Pressure	bar	1	1
Temperature	°C	60	60
Equilibrium CO_2 Loading	mol/mol	0.347	0.347
Heat of Desorption	kJ/mol CO_2	55.99	55.99
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	-	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 / 95 / ~20	
Absorber Pressure Drop	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	plate-and-frame	plate-and-frame
Max Trans-Membrane Pressure	bar	1.1	1.1
Hours Tested without Significant Degradation	—	- (simulated coal)	- (simulated coal)
Manufacturing Cost for Membrane Material	$/m^2	-	-
Membrane Performance			
Temperature	°C	40	40
CO_2 Pressure Normalized Flux	GPU or equivalent	5,000	5,000
CO_2/H_2O Selectivity	—	2	2
CO_2/N_2 Selectivity	—	44	44
CO_2/SO_2 Selectivity	—	-	-
Type of Measurement	—	simulated coal	simulated coal
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	-	
Shell-Side Fluid	—	-	
Flue Gas Flowrate	kg/hr	-	
CO_2 Recovery, Purity, and Pressure	%/%/bar	50, 95,140	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Foaming Tendency – For a flue gas environment, no foaming should be expected.

Flue Gas Pretreatment Requirements –SO_2 removal is required.

Solvent Makeup Requirements – Without water wash at the tops of both absorber and stripper, the makeup rate is about 10kg/hr MDEA and 20kg/hr piperazine (PZ).

Waste Streams Generated – A waste stream will be created only if a solvent reclamation process is installed.

Process Design Concept –

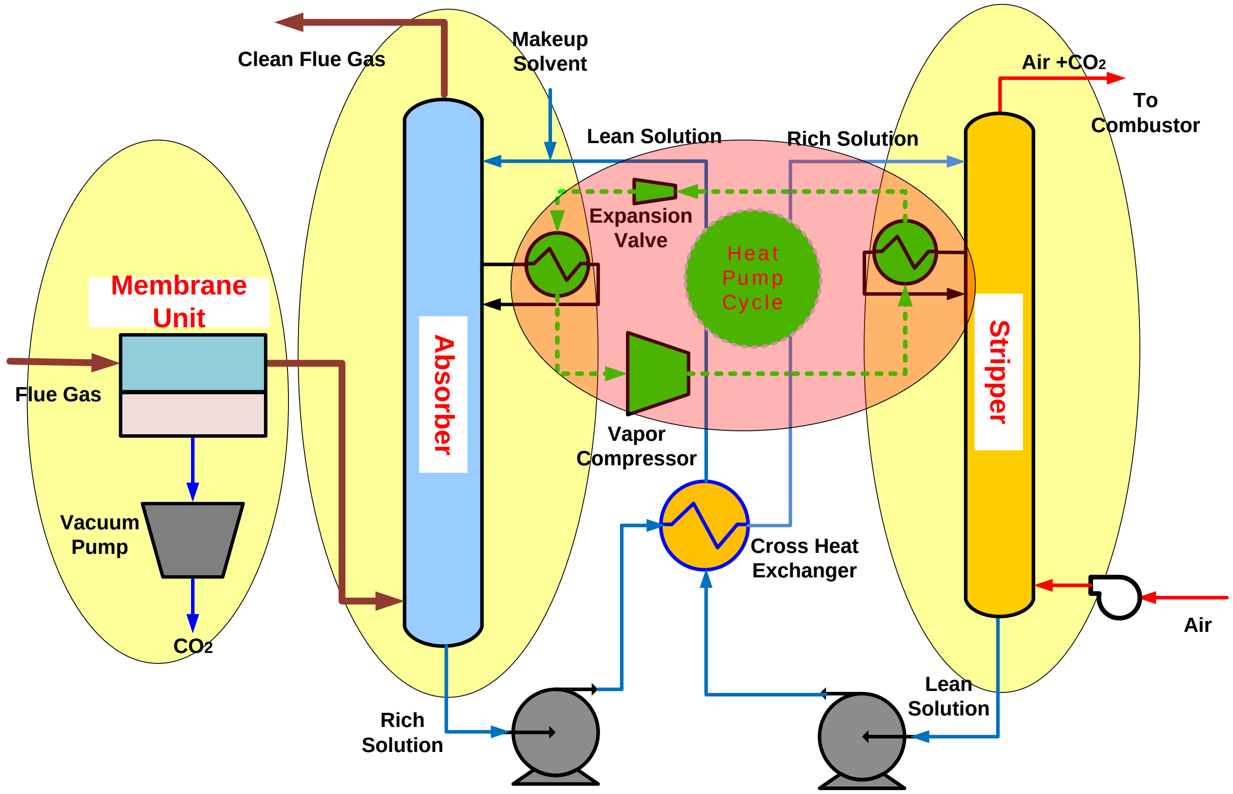


Figure 7: Overall membrane/solvent integrated process.

Membrane Permeation Mechanism – The membranes developed under this project are polar, rubbery/elastic with very low glass transition temperatures allowing higher permeabilities. The overall separation occurs mainly due to the solubility of CO_2 in the polymer, which is further facilitated by interfaces of the surface modified nano particles resulting in improved permeabilities.

Contaminant Resistance – The surface-modified nanoparticles are not affected by the addition of simulated flue gas and the addition of contaminants (50 ppm SO_2 and 70 ppm NO_2 with 7.8g of H_2O/kg of air [16% relative humidity]).

Membrane Replacement Requirements – Outside project scope.

technology advantages

- Polyphosphazenes have excellent chemical and thermal stability.
- Steam extraction is not required.
- Stripper operating pressure is flexible (depending on low-quality heat).
- The high-permeance membrane reduces capital costs.
- The heat pump cycle and use of air sweep for stripping eliminate the need for steam extraction, reducing parasitic power and operating expenditures.

R&D challenges

- Polyphosphazene performance is uncertain.
- Scale-up is a problem.
- The heat pump has high energy consumption.
- The long-term durability of the membrane in actual flue gas and variable conditions has not been determined.

status

This project has concluded.

available reports/technical papers/presentations

Nulwala, H. "Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System and Process Integration," Final Report, December 2018. *https://www.osti.gov/servlets/purl/1484714/*.

Nulwala, H. "Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System and Process Integration," Budget Period 2 Review, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0026464-BP2-Review-Presentation-08-03-17.pdf*.

Nulwala, H. "Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System and Process Integration," Project Kickoff Meeting, Pittsburgh, PA, October 2015. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0026464-Kickoff-Presentation.pdf*.