

Hybrid Solvent-Membrane Process for Pre-Combustion CO₂ Capture

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is assessing the potential of integrating small-scale modular pre-combustion carbon dioxide (CO₂) capture processes with small-scale modular coal gasification technologies. The research is focused on the development of a hybrid process combining hydrogen (H₂)-selective membranes followed by solvent capture for CO₂. NETL-RIC is developing an H₂-selective cross-linked polyamide nanofilm-based composite membrane for upstream CO₂ capture. NETL-RIC is also investigating the corrosion rates in carbon and stainless steels from solvent-based pre-combustion carbon capture processes.

technical goals

H₂-Selective Membranes

- Optimize a polymeric porous membrane support and polydimethylsiloxane (PDMS) gutter layer for the formation of an H₂-selective polyamide nanofilm for H₂/CO₂ separation at high temperatures.

CO₂-Selective Solvents

- Perform corrosion rate measurements for aqueous solutions and hydrophobic physical solvents under variable conditions of CO₂ partial pressure and temperature.
- Provide corrosion control strategies to process scale-up and materials.

technical content

Transitioning from traditional gasification technologies to more flexible and modular gasification processes will enable the use of alternative and cheaper local feedstocks (e.g., low-quality coal, biomass, and municipal solid waste), which will result in syngas of varying components and composition. Integrating small-scale, modular pre-combustion carbon capture systems with modular gasification offers the opportunity for cost reduction of novel capture processes through mass production of smaller capture units and learning curve effects. However, there is a need to identify carbon capture technologies that demonstrate advantages at a smaller, modular scale, as a traditional solvent-only absorption process (e.g., Selexol) may have a cost disadvantage at modular gasification scales. The results of a gap analysis and literature review (*"Modular CO₂ Capture Processes for Integration with Modular Scale Gasification Technologies: Literature Review and Gap Analysis for Future R&D"* – listed under available reports/technical papers/presentations) assessing the potential for modular carbon capture technologies to be applied to a variety of gasification products determined that H₂-selective membranes followed by solvent capture for CO₂ is promising for several modular-scale gasification processes and multiple product areas, such as electricity, H₂, and ammonia production. The use of hybrid capture processes can enhance the overall capture performance at modular scale, as the presence of one unit can mitigate the shortcomings of the other. Additionally, hybrid systems have lower capital and operating costs, are flexible in handling changes in feed

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Pre-Combustion Power Generation PSC

key technology:

Hybrid

project focus:

Solvent-Membrane Process Applied to Modular-Scale Pre-Combustion CO₂ Capture

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

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predecessor project:

2020 Carbon Capture FWP

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gas conditions, and can allow the recycle of streams back to the water-gas shift (WGS) system. Under flexible, small-scale conditions, there is also the potential for partial carbon capture at the module's capacity, which could be increased as needed with the addition of more modules that have demonstrated successful operation. Appropriately sized modular units for partial carbon capture could significantly reduce energy costs by using available waste heat.

H₂-Selective Membranes

Cross-linked polyamide membranes consist of a bottom porous support layer, an intermediate gutter layer, and a top polyamide selective layer (or polyamide nanofilm). The three components are being designed and developed dependently, as the physical and gas transport properties of each layer are greatly affected by the layer beneath it. The polyamide layer provides effective base H₂/CO₂ separation properties, while the porous support and gutter layer provide reinforcement without adding significant mass transfer resistance to the polyamide layer. The current reported cross-linked polyamide membrane exhibits H₂ permeance of 350 gas permeation units (GPU) and H₂/CO₂ selectivity of 50 at 140°C; however, the membrane was fabricated via traditional interfacial polymerization, through which the polyamide layer is 100–300 nm thick, with a wrinkled, ridge-and-valley structure. The aim of this project is to fabricate thinner sub-50 nm polyamide nanofilms via an improved interfacial polymerization approach to effectively boost H₂ permeance of the membranes.

NETL is fabricating functioning polyamide thin-film composite (TFC) membranes for high-temperature H₂/CO₂ separation with the following approach (Figure 1): (1) fabricating a porous support thermally stable at 100–250°C, (2) coating a highly permeable PDMS gutter layer, (3) functionalizing the PDMS surface with amine groups, and (4) fabricating a highly cross-linked polyamide nanofilm on the amine-PDMS surface via precisely controlled interfacial polymerization. In this approach, the porous support's pore size, surface porosity, gutter layer thickness, and amine functionality can be tailored according to the resulting polyamide layer properties, with a goal of achieving defect-free polyamide as thin as possible. Screening tests performed in a mixed gas feed of 50% H₂/50% CO₂ are being used to identify the best-performing polyamide nanofilms (a target performance of H₂ permeance of ≥600 GPU and H₂/CO₂ selectivity ≥30 at 100–250°C) to be further evaluated with real shifted syngas. Note that the highest H₂/CO₂ permeance selectivity at room temperature was found to be 26 based on the literature survey of about 1,600 sets of different gas permeabilities in approximately 800 different polymers.

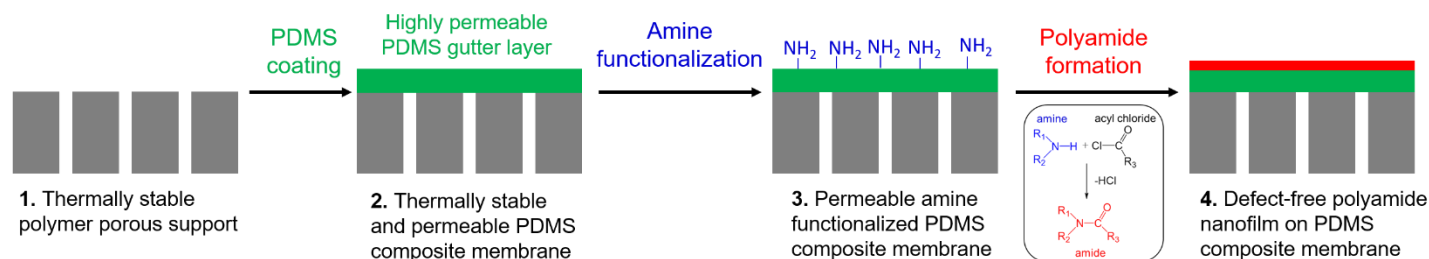


Figure 1: Preparation steps for a cross-linked polyamide nanofilm on a PDMS composite membrane.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Cross-linked polyamide	
Materials of Fabrication for Support Layer	—	Polymer/non-woven fabric	
Nominal Thickness of Selective Layer	μm	≤0.05	≤0.05
Membrane Geometry	—	Flat-sheet	Flat-sheet
Maximum Trans-Membrane Pressure	bar	—	—
Hours Tested without Significant Degradation	—	—	720
Manufacturing Cost for Membrane Material	\$/m ²	—	—
Membrane Performance			
Temperature	°C	150	100-250
H ₂ Pressure Normalized Flux	GPU or equivalent	350	600
H ₂ /H ₂ O Selectivity	—	—	—
H ₂ /CO ₂ Selectivity	—	38	30
H ₂ /H ₂ S Selectivity	—	—	—
Sulfur Tolerance	ppm	—	—
Type of Measurement	—	Pure-gas	Mixed-gas
Proposed Module Design			
Flow Arrangement	—	Spiral wound or plate-and-frame	
Packing Density	m ² /m ³	—	—
Shell-Side Fluid	—	—	—
Syngas Gas Flowrate	kg/hr	—	—
CO ₂ Recovery, Purity, and Pressure	%/%/bar	—	—
H ₂ Recovery, Purity, and Pressure	%/%/bar	—	—
Pressure Drops Shell/Tube Side	bar	—	—
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	—

Definitions:

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 cm³ (STP, 1 atm, 0°C ideal gas)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10⁻¹⁰ mol/m²-s-Pa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be used for mixture of gases found in desulfurized syngas.

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 co-current, 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 (H₂-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Selective layer materials employ the solution-diffusion mechanism to separate gas molecules and the driving forces are partial pressure differences across the membrane.

Contaminant Resistance – Not yet available.

Syngas Pretreatment Requirements – Not yet available.

Membrane Replacement Requirements – Not yet available.

Waste Streams Generated – Not yet available.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

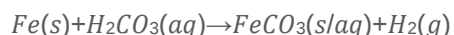
Proposed Module Design – Spiral wound or plate-and-frame. Note the module location, as well as the pressure, temperature, and composition of the gas entering the module.

CO₂-Selective Solvents

NETL-RIC is investigating the corrosion rates of steel alloys used in pre-combustion carbon capture process equipment in the presence of high-pressure CO₂, H₂, water, and capture solvents. While extensive studies have been performed to understand CO₂ corrosion mechanisms on carbon steel in different applications, such as amine-based CO₂ capture for post-combustion, natural gas transportation, and ultra-deep drilling, there is a lack of published data on corrosion rates of steel in pre-combustion CO₂ capture processes. With a better understanding of the corrosion mechanism in different physical solvents, corrosion control strategies can be proposed for process design and material development. The selection of optimal materials for piping, vessels, and all types of equipment is vital in ensuring the long-term performance and safety assertion of the capture plants through their lifetime. For instance, the levelized cost of capture (LCOC) for pre-combustion capture solvents could be reduced by up to 10% using carbon steel versus stainless steels, corresponding to a lifetime cost savings of up to \$80M at a 550-megawatt-electric (MWe)-scale power plant.

The project focus is on quantifying the corrosion rate and products to determine the corrosion mechanism experienced by carbon and stainless steel alloys in the presence of both commercial and NETL-RIC-developed solvents.

Carbon dioxide that is dissolved into water can react to form carbonic acid (H₂CO₃), which can corrode steel equipment through the reaction:



The generation of solid ferrous carbonate (FeCO₃) versus dissolved FeCO₃ is highly affected by environmental factors, including temperature, water concentration, CO₂ partial pressure, flowrate, and time. Corrosion by hydrogen sulfide (H₂S) can also occur in pre-combustion capture processes due to H₂ consuming the iron oxide passivation layer, which can increase the corrosion rate. Therefore, it is important to measure corrosion in the presence of CO₂ and H₂.

Current commercial pre-combustion solvents, such as Selexol, are hydrophilic and tend to absorb substantial amounts of water, which, in the presence of CO₂, can provide conditions that are conducive to corrosion of the metal. Solvents with high corrosion rates require thicker vessel walls, which can cause large upfront capital costs and could lead to undesirable down time for repairs to corroded elements in the capture system. Previous research at NETL has led to hydrophobic solvents (e.g., CASSH-1) that absorb minimal amounts of moisture, and which are expected to support far less corrosion under realistic carbon capture conditions.

A series of tests are being conducted to measure corrosion rates of two types of steel coupons (Carbon Steel C1020 and Stainless Steel SS304), with various commercial pre-combustion capture solvents and NETL-developed hydrophobic solvents, in the presence of pure CO₂ and under simulated syngas conditions (50% CO₂/50% H₂). The steel coupons are submerged for a period of one week to one month in a Parr reactor vessel under pressurized conditions of CO₂. Corrosion rates are then quantified by two methods: using the weight loss measurements of the coupons (gravimetric method) and by measuring the dissolved metals content in the post-test aqueous solutions. Table 2 shows that the corrosion rates for two NETL-patented solvents (dry disub-4PEG and CASSH-1) were below the detection limit after testing for more than 335 hours, indicating superior corrosion resistance compared with the other solvents tested, even for carbon steel. Tests are also being performed under varying temperatures, with the partial pressure of CO₂ adjusted to maintain constant CO₂ uptake, to determine the effect of temperature on the corrosion rate.

Computational simulations of the corrosion mechanisms are being performed using commercial software (OLI Studio) and the predicted rates of corrosion are being compared to the experimental data.

TABLE 2: EXPERIMENTAL AND SIMULATED CORROSION RATES IN BASELINE AQUEOUS AND PRE-COMBUSTION CO₂ CAPTURE PHYSICAL SOLVENTS

Solvent	DI H ₂ O	1M NaCl	1M NaHCO ₃	3M MEA	wet MDEA	90%PEGDME / 10%H ₂ O	98%PEGDME / 2%H ₂ O	dry disub-4PEG	dry CASSH1
Temperature (°C)	21	21	21	21	21	21	21	21	21
CO ₂ pressure (atm)	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Total test time (hr)	164	167	167	167	219	335	335	335	529
CR on SS304 (μm/yr)	1.1 ± 0.6	2.0 ± 0.5	1 ± 1	2 ± 1	1.2 ± 0.5	1.5 ± 0.5	1.0 ± 0.5	0.0 ± 0.4	0.0 ± 0.3
CR on C1020 (μm/yr)	300 ± 150	500 ± 100	25 ± 20	60 ± 20	2 ± 1	20 ± 10	7 ± 3	0.0 ± 0.4	0.0 ± 0.3
OLI Simulations									
pH	3.5	3.3	6.6	7.3	NA	NA	NA	NA	NA
CR on SS304 (μm/yr)	3	7	3	3	NA	NA	NA	NA	NA
CR on CS_G10100 (μm/yr)	5600	5100	500	200	NA	NA	NA	NA	NA

Note: Corrosion rates shown were calculated by gravimetric method for two different types of steel.

technology advantages

- The combination of H₂-selective membranes with CO₂-selective solvents creates an efficient and size-reduced process that is ideal for modular gasification scales.
- Integrating small-scale, modular pre-combustion carbon capture systems with modular gasification offers the opportunity for cost reduction of novel capture processes through mass production of smaller capture systems.
- The modular-scale pre-combustion capture process developed in this project will also be relevant to H₂ generation from steam methane reforming applications.
- NETL has existing subcontracts or collaborations with two major modular gasification research centers—the University of North Dakota's Environmental Research Center (UNDEERC) and the University of Kentucky's Center for Applied Energy Research (UK-CAER).

R&D challenges

- Developing a polyamide nanofilm composite membrane that is thermally stable at elevated temperatures of 100–250°C and achieves H₂ permeance of greater than or equal to 600 GPU and H₂/CO₂ selectivity greater than or equal to 30.
- Obtaining corrosion rate measurements under pre-combustion CO₂ capture conditions is challenging due to the capture of CO₂ occurring at relatively high pressure.
- Long exposure time is required to obtain repeatable and reliable corrosion rates, as they tend to be high initially before reaching a steady state.
- Obtaining corrosion rates in the presence of H₂S requires significant safety processes to manage any possible leak of H₂S.
- Temperature and CO₂ partial pressure can affect the CO₂ corrosion rate by affecting the uptake of CO₂ into the solvent.
- Water concentration in solvents can affect the rate and extent of corrosion, especially under acidic conditions.

status

A polymer porous support was successfully fabricated via a phase inversion technique and a series of laboratory-scale PDMS gutter layer membrane coupons were fabricated on top of the porous supports. The thermal stability of the polymer porous supports was evaluated by comparing the gas permeances before and after thermal treatments at 100–200°C for two to 24 hours. The treatments had no significant effect on gas permeances, and the optimized porous supports showed a pure-gas H₂ permeance greater than 60,000 GPU. The H₂ and CO₂ permeances and physical aging behaviors of the PDMS gutter layer membrane coupons were investigated at 25–150°C, resulting in no significant physical aging (<10% permeance reduction) over the course of 1,152 hours (48 days). Based on the developed PDMS gutter layer membranes, 11 polyamide nanofilm coupons were fabricated and tested for H₂/CO₂ separation at 25–150°C. The best sample showed

H₂ permeance of 350 GPU and H₂/CO₂ selectivity of 38 at 150°C. The polyamide nanofilm is undergoing testing at temperatures greater than 150°C with the goal of increasing H₂ permeance. Machine learning techniques are being used for computational screening of polymers for H₂/CO₂ separation. The screening protocol allows for the down-selection of materials, so that the top 10 polymer precursor materials with the desired free volume characteristics, high permeability and selectivity, and tolerance to contaminants (e.g., sulfur) for selective hydrogen separations are selected for generating carbon molecular sieve (CMS) membranes.

Corrosion rates were measured in carbon steel and stainless steel for eight different solvents and aqueous solutions in the presence of pure CO₂ and mixed gas composition of 50% CO₂/50% H₂ at two different pressure conditions (100 and 400 pounds per square inch gauge [psig]) and temperature conditions (21 and 40°C). Corrosion rates and solution speciation were simulated by OLI Studio software and compared well with experimental data for stainless steels.

[available reports/technical papers/presentations](#)

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