Solid-Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes

primary project goal

Luna Innovations is pursuing a systems-level approach to demonstrating a dual-phase membrane solid support technology for carbon dioxide (CO_2) separation. Luna is evaluating yttria-stabilized zirconia (YSZ) and its derivatives as standalone solid-phase supports and in the presence of a single molten carbonate electrolyte. Through modification of current YSZ supports, development of structure-property relationships, and prototype modeling of scaled-up technology form factors, Luna's solid-phase supports will have the unique potential to provide the performance and scalability to separate CO_2 from flue gas in the heat recovery steam generators (HRSGs). Successful demonstration of this dual-phase carbon capture and storage (CCS) technology will pave the way for retrofit in high-temperature exhausts found in power plant HRSGs.

technical goals

- Establish performance and design requirements for the dual-phase membrane technology, including the system, safety, and operating parameters for HRSG integration. Expand multitube module test capabilities.
- Design and fabricate a scalable CO_2 separation module prototype.
- Perform relevant testing on single and multitube membrane assemblies. Evaluate performance under relevant conditions in long-term (~months) tests to establish membrane durability and stability.
- Conduct a systems-level analysis and evaluate techno-economic viability.
- Evaluate membrane module performance results and create a module design for pilot-scale testing. Develop Phase III plan.

technical content

Luna Innovations, in partnership with Nooter/Eriksen, is leading the scale-up and demonstration of a new type of dual-phase membrane technology. The dual-phase membrane consists of a thin wall of nanoporous ceramic solid phase that retains a non-volatile molten phase within the pores with capillary action. The molten liquid phase selectively sorbs CO_2 with high concentrations and transport rates. The dual-phase membrane has been advanced with an active transport mechanism that powers CO_2 separation with H_2O's concentration gradient. This results in superior separation performance with an unrivaled combination of CO_2 permeability and selectivity of CO_2 over nitrogen (N_2). This Small Business Innovation Research (SBIR) program is focusing on developing YSZ nanoporous solid-phase materials to achieve the mechanical performance and form factors required for integration and operation inside an HRSG or boiler for operation at 150–500°C.

Currently, there is an unmet need for commercialized membrane systems that can efficiently separate CO_2 from power plant flue gas exhausts at thermally favorable conditions with reduced costs. The proposed solution is to develop an active transport membrane that uses the difference in water vapor concentration between low-pressure steam and the flue gas to drive CO_2 separation through the

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Membrane Support Materials & Module Design

participant:
Luna Innovations

project number:
SC0017124

predecessor projects:
N/A

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start date:
02.21.2017

percent complete:
85%

membrane. This approach has the potential to lower the total power plant parasitic power costs for carbon capture and compression by 30–40% in comparison with state-of-the-art solvent capture according to full-plant performance modeling in Thermoflex. These high-temperature membranes have greater potential for large-scale, energy-efficient separation by being directly integrated within power plant HRSGs, as shown in Figure 1. Luna's dual-phase membrane technology shows potential for meeting the power generation industry's needs by separating CO_2 from power plant flue gas under operational conditions (150–500°C) and with drastically reduced costs.

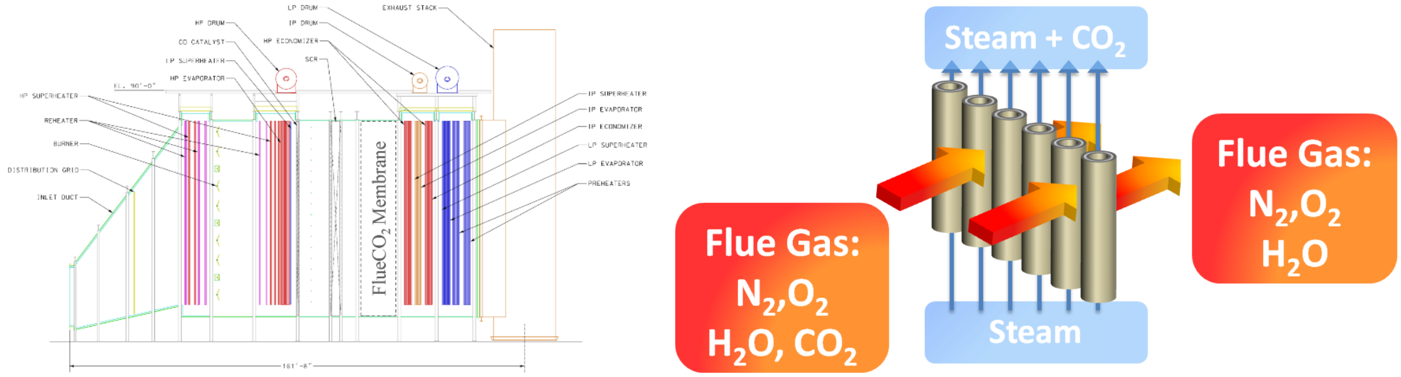

Figure 1: Luna's dual-phase membrane technology introduces a unique ability to implement carbon capture technologies into power plant HRSGs (150–500°C).

In the dual-phase membrane technology, a porous, solid material supports a non-volatile liquid electrolyte. Carbon dioxide actively absorbs into the molten electrolyte at the flue gas side, diffuses through the membrane as the carbonate ion (CO_3^{2-}) from high to low concentration, and desorbs from the membrane into a steam sweep gas (Figure 2). The steam sweep serves to both chemically desorb CO_2 and minimizes the concentration of permeated CO_2.

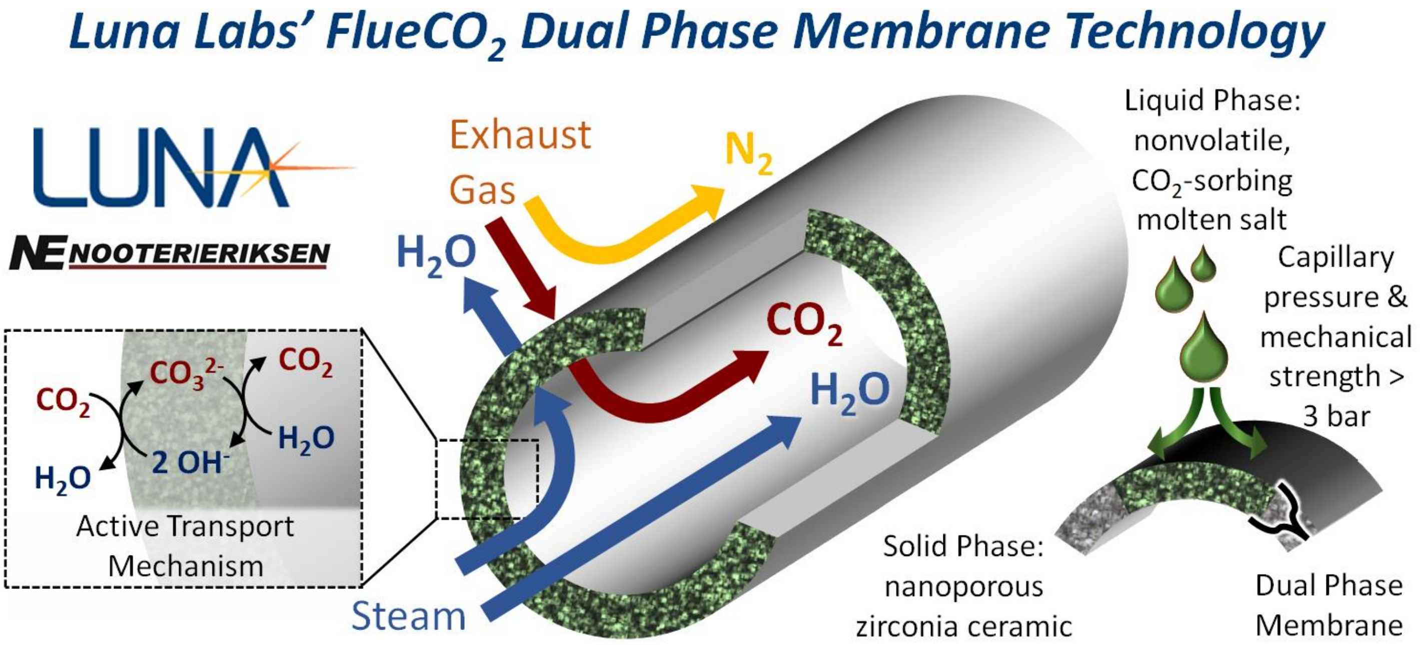

Figure 2: Luna Innovations dual-phase membrane technology for highly efficient and scalable CCS.

The unique operational conditions and performance capabilities of Luna's membrane enables a new opportunity to achieve more energy-efficient and less-expensive carbon capture. This membrane is not limited by the same physics governing Robeson's upper bound as conventional, polymer-based membranes and enables unrivaled combinations of permeability and selectivity (Figure 3). Such a novel system has never before been scaled-up to demonstrate the technical feasibility at the membrane module scale. The operating parameters of the membrane system are shown in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Molten hydroxide dual phase	
Materials of Fabrication for Support Layer	—	Metal oxide	
Nominal Thickness of Selective Layer	µm	950	<50
Membrane Geometry	—	tubes	cartridge
Max Trans-Membrane Pressure	bar	1.3	1.3
Hours Tested without Significant Degradation	—	400	5,000
Manufacturing Cost for Membrane Material	$/m^2	750	1,200
Membrane Performance			
Temperature	°C	150 - 550	150 - 550
CO_2 Pressure Normalized Flux	GPU or equivalent	800	>6,000
CO_2/H_2O Selectivity	—	undetermined	1
CO_2/N_2 Selectivity	—	999	>99
CO_2/SO_2 Selectivity	—	undetermined	0.5
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	75	
Shell-Side Fluid	—	steam	
Flue Gas Flowrate	kg/hr	2,200	
CO_2 Recovery, Purity, and Pressure	%/%/bar	98%, >99%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.01/sweep: <0.03	

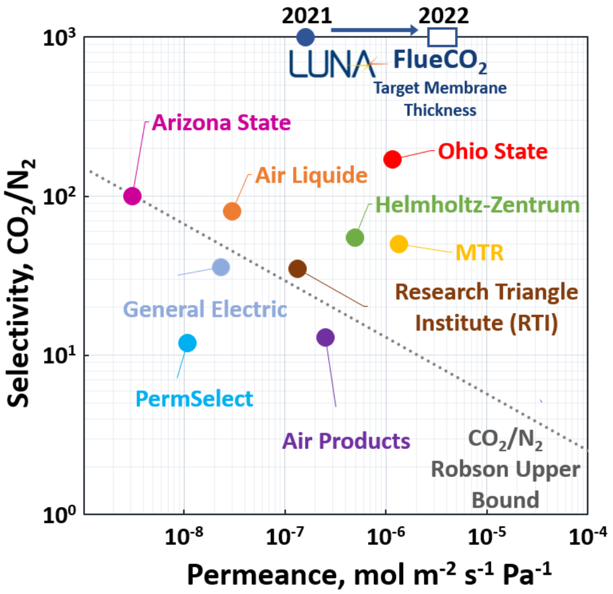

Figure 3: In a Robeson plot comparison, the Luna team's membrane (star) outperforms other CO_2 separation membrane technologies funded by the National Energy Technology Laboratory (NETL).

In Phase I of this project, the Luna Innovations team targeted solid-phase support materials with high strength, increased CO_2 separation capabilities, and stability in the presence of the new molten electrolyte formulations. It was critical that these materials were evaluated in context of the HRSG operational conditions to demonstrate their mechanical, thermal, and chemical stability, as well as their scale-up to larger membrane systems. Luna developed the capability to manufacture membranes using nanoporous YSZ tubes procured from CoorsTek Ceramics. The nanoporous (~100 nm) ceramic materials from CoorsTek are 4 mol% YSZ tubes with 1/4-inch outside diameter (OD) and 3/16-inch inside diameter (ID). These tubes are initially extruded to 120 centimeters (cm) and then cut into smaller segments for this stage of testing by Luna. The mechanical properties of this high-strength ceramic material were characterized and determined to be scalable for the operational conditions expected for the membrane. The solid-phase materials, fabrication methods, and design features were successfully developed in Phase I to manufacture and test multitube membrane modules in Phase II. Media and Process Technology began supplying the ceramic materials in the Phase II project. The methods for manufacturing complete membrane systems from the ceramic materials has been scaled-up to simultaneously manufacture multiple tube membranes using process automation. Quality control procedures have been developed for key stages of the manufacturing process.

Luna has reviewed the options for designing the CO_2 separation membrane module. Tube-based form factor designs remain the most reliable option for further developing and scaling-up the membrane technology primarily based upon the maturity of possible ceramic material manufacturing methods, as well as the supporting technical capabilities required to develop a complete, functional membrane module. The current tube module design is based upon a Swagelok flange and custom interface to multiple short tube samples (Figure 4). This design minimizes module development costs by using commercially available off-the-shelf (COTS) parts whenever possible, while also supporting flexibility and adaptability. The goal is to develop and demonstrate the construction and operation of a small module of six 40-cm long single tubes. Once the basic design and construction approach is established, it is expected to be relatively easy to scale-up by using larger numbers of longer tubes. Larger Swagelok flange sizes will enable scale-up to 19 single-channel tubes or eight of the multichannel tubes. CoorsTek tube lengths can be extended to 120 cm. The initial multitube module has been manufactured and demonstrated to enable scaled-up test and evaluation. A more advanced cartridge membrane design has been developed through multi-physics modeling that includes computational fluid dynamics. Proprietary cartridge membrane features have been developed to simplify manufacturing, increase surface area packing density, and minimize pressure drop while enhancing exhaust gas mixing. Intentional exhaust gas mixing was required because the laminar flow patterns developing at 2.0–2.5 m/s exhaust gas flow rates result in depleted CO_2 concentrations at the membrane surface.

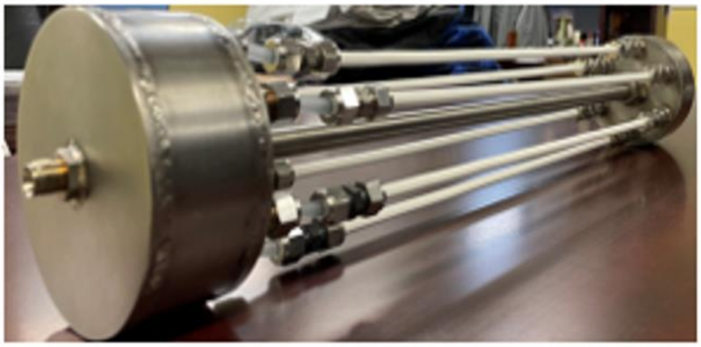

Figure 4: The non-proprietary multitube membrane module with six tubes has been revised to reduce the manufacturing time and costs, while also enabling easier and more flexible modifications for evolution and scale-up.

Luna has continued to achieve both faster CO_2 permeation rates and lower operational temperatures (Figure 5). The transition to lower operational temperatures is important to enable installation of the membrane system into the HRSG near the low-pressure steam evaporator, where the flue gas has reached temperatures 150–200°C. Capturing the CO_2 at lower temperatures lowers separation energy costs. The present low-temperature electrolyte was selected for high CO_2 permeation rates, as well as a relatively wide operational temperature range of 150–300°C. The low-temperature limit of the membrane is generally governed by the freezing of the molten electrolyte phase.

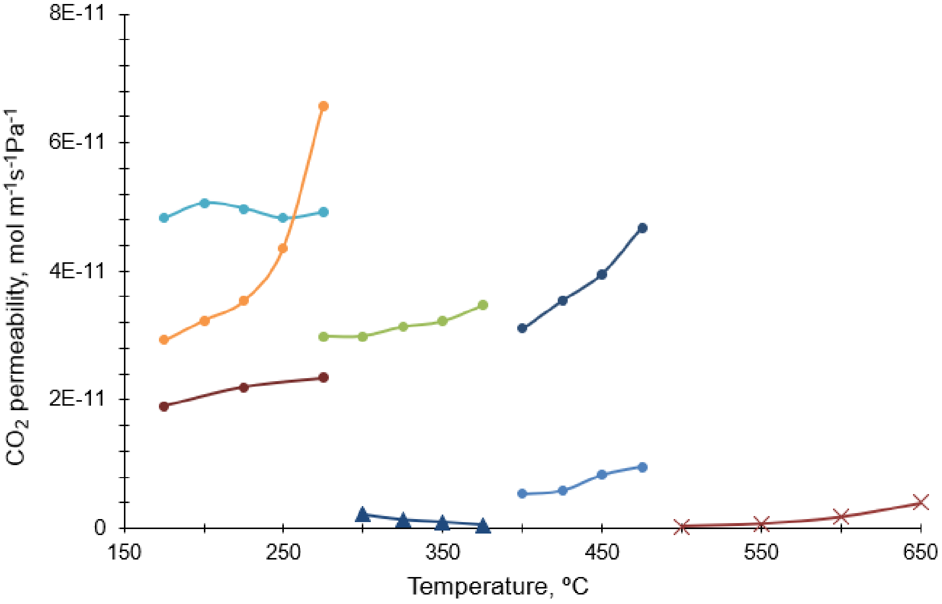

Figure 5: Progress in both improving the CO_2 permeability and decreasing the membrane operational temperatures for more efficient integration into new and retrofitted HRSGs of NGCC power plants.

Nooter/Eriksen has modeled the integration of the CO_2 capture membranes into a natural gas combined cycle (NGCC) power plant (Figure 6). The FlueCO$_2$ NGCC was derived directly from the National Energy Technology Laboratory (NETL) B31A base case and features a proprietary approach to recovering electrical power. The energy penalty of carbon capture by the FlueCO$_2$ NGCC are 7% in comparison against the simulated B31A case. The full plant model performances of FlueCO$_2$ and B31A plants were simulated in Thermoflex as a function of gas turbine load, environmental conditions, and carbon capture rate. Half of the penalty (3.5%) is from the CO_2 compressors and the other half of the energy penalty (3.5%) is due to altered flow of low-pressure steam. The main risk to not achieving this performance target upon scaling-up is in losing the stoichiometric coupling of CO_2 to H_2O by the active transport mechanism (Figure 2). A dynamic cost modeling tool developed to evaluate the membrane unit size as a function of cost predicts a 98% CO_2 capture rate for optimized economics. Nooter/Eriksen has asserted that no features of the FlueCO$_2$ NGCC plant design will apparently affect the dynamic responsiveness of power output as the plant ramps up/down in load or cycling on/off. Retaining the dynamic flexibility of NGCC power plants is critical for retaining economic competitiveness when the supply and demand of power to the electrical grid cycle on a daily basis.

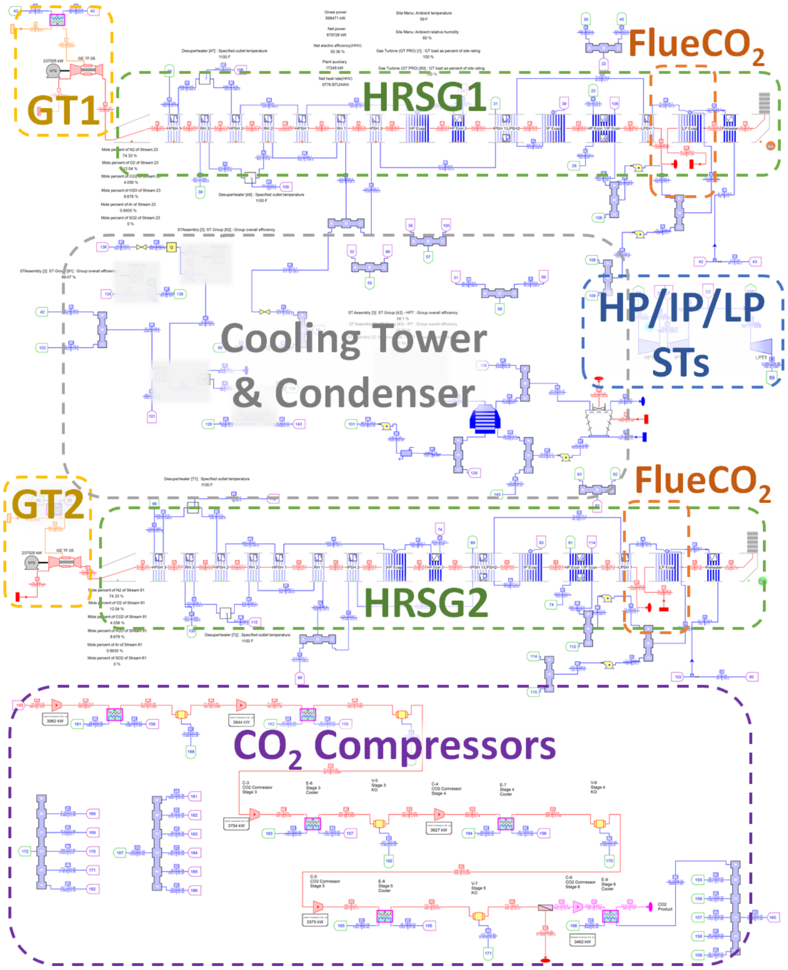

Figure 6: Thermoflex model of $FlueCO_2$ NGCC.

The costing methodology NETL prescribed for the B31A NGCC (base; no carbon capture) and B31B NGCC (control, solvent caron capture) cases were strictly adhered to for economic performance evaluations. Every line of the $FlueCO_2$, B31A, and B31B costing tables were converted into an interactive Microsoft spreadsheet tool that is available upon request for review. The formatting, color coding, and other features of the NETL costing tables have been replicated to facilitate ease of navigation of the spreadsheet costing tool. The spreadsheet costing tool enables direct comparisons between the three NGCC plants for relevant inputs (fuel price, electricity price, capacity factor, 45Q credits, carbon tax, CO_2 capture rate) and outputs (breakeven prices, levelized cost of electricity, 30-year net present value, capital and operating expenses). The $FlueCO_2$ NGCC outperforms the B31B NGCC in plausible scenarios due higher energy efficiency and lower capital costs (Figure 7). The $FlueCO_2$ capital costs of capture are dominated by the membranes and CO_2 compressors. The main risk is failing to achieve the target membrane costs within a five-year lifetime (all other additional equipment is commercially available with established costs). The high capital costs of the B31B plant are compounded by taxes, insurance, and interest. A techno-economic analysis (TEA) was performed as a part of this study. The economic data obtained from the systems-level analysis is shown in Table 2.

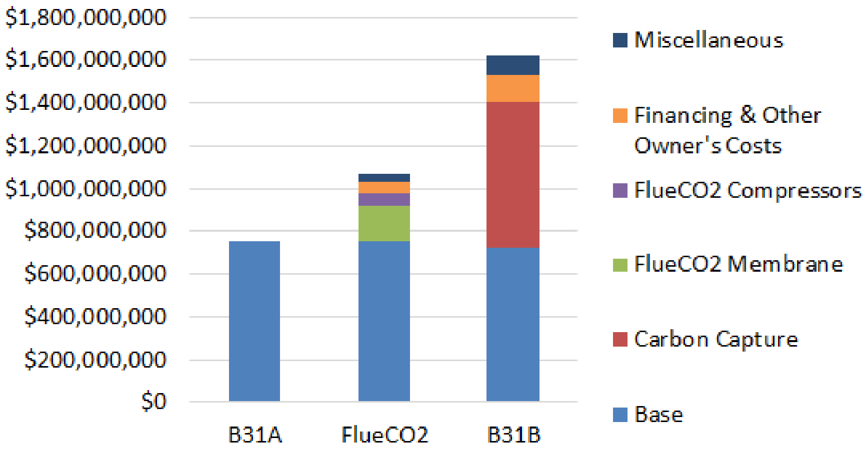

Figure 7: Total as-spent cost (TASC) contributions to the 30-year net present value (NPV) analyses, where B31A = 760 MWe.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Reference (B31B)	Reference (B31A)	Current R&D Value	Target R&D Value
Total As-Spent Cost	$/MW	2,635	1,040	1,713	1,800
Heat Rate	BTU/kWhr	7,159	6,363	7,078	7,100
Cost of Carbon Captured	$/tonne CO_2	69.16	N/A	29.69	35
Cost of Carbon Avoided	$/tonne CO_2	90.48	N/A	42.59	45
Breakeven CO_2 Price	$/tonne CO_2	79.60	N/A	38.18	40
Capital Expenditures	$/MWhr	25.03	9.88	16.12	18
Operating Expenditures	$/MWhr	14.22	5.31	9.82	10
Cost of Electricity	$/MWhr	39.25	15.19	25.93	28
Levelized Cost of Electricity	$/MWhr	70.89	43.31	57.13	60

The approach to retrofitting existing NGCCs is presently under consideration. If the target membrane performance metrics are achieved, there is enough space already available in the HRSG to incorporate the membrane system. The membranes could therefore be incorporated to retrofit existing HRSGs for carbon capture. Retrofits of HRSGs of existing NGCC power plants are expected to comprise the largest and most valuable market to target for commercialization.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

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:

Membrane Permeation Mechanism – Permeation through the membrane occurs by the high concentration of H_2O in the steam sweep, selective gas sorption reactions (bicarbonate and carbonate mechanisms).

Contaminant Resistance – Significant quantities of ash in coal power plants represents a contaminant hazard for the membranes. NGCC power plants have therefore been identified as the target application.

Flue Gas Pretreatment Requirements – The temperature must be less than 450°C.

Membrane Replacement Requirements – The membrane lifetime is currently unknown.

Waste Streams Generated – The membrane process will generate a zirconia-based composite that may be recyclable.

technology advantages

- High performance separation with active transport mechanism.
- Highly efficient NGCC/HRSG integration approach.
- Low capital and operational costs.
- Modular design allows for easy integration with new and existing power plants.

R&D challenges

- Long-term stability of ceramic materials.
- Retaining membrane cost projections throughout the scale-up process.
- Avoiding steam leakage by active transport mechanism.

status

Phase I of the project was completed in 2017. Phase II objectives (pilot-scale testing, integration with HRSG, system-level analysis) are underway, and a final report is expected by the end of 2022.

available reports/technical papers/presentations

Ceron, M., Lai, L., Amiri, A., Monte, M., Katta, S., Kelly, J., Worsley, M., Merrill, M., Kim, S., Campbell, P. "Surpassing the conventional limitations of CO_2 separation membranes with hydroxide/ceramic dual-phase membranes," Journal of Membrane Science, 2018, Vol. 567, pages 191-198. *https://www.sciencedirect.com/science/article/pii/S0376738818318209*.

Merrill, M. "Passive CO_2 Separation Membranes for Hot Flue Gases," presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-Separation-Membranes_Aug%202018.pdf*.

Merrill, M. "Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes," Phase I Final Review Meeting, Pittsburgh, PA, November 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/DE-SC0017142%20Solid%20Membrane%20Materials%20Final%20Review%20NETL%2020171129.pdf*.

Merrill, M. “Passive CO_2 Separation Membranes for Hot Flue Gases,” presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-CO2Separation_Aug%202017.pdf*.