

# MEETING THE DUAL CHALLENGE

A Roadmap to At-Scale Deployment of  
CARBON CAPTURE, USE, AND STORAGE

APPENDIX F – EMERGING CO<sub>2</sub> CAPTURE  
TECHNOLOGIES



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# Appendix F

## EMERGING CO<sub>2</sub> CAPTURE TECHNOLOGIES

### I. INTRODUCTION

This appendix describes less mature carbon dioxide (CO<sub>2</sub>) capture technologies, what this study calls Emerging CO<sub>2</sub> Capture Technologies. The appendix divides these into five technology types, with a section devoted to each of the following:

- Absorption, including second-generation amines and other solvent types, but excluding the mature amine scrubbing technology described in Appendix E.
- Adsorbents and Adsorption
- Membranes
- Cryogenic distillation and the cryogenic process
- Allam-Fetvedt Cycle.

This appendix concludes with a section titled “U.S. DOE Funded Projects” that summarizes novel or transformational projects that have been sponsored by the Department of Energy (DOE), several of which involve hybrid capture approaches.

### II. ABSORPTION: SECOND GENERATION AMINES, NONAQUEOUS, WATER-LEAN, PHASE CHANGE SOLVENTS

Continued research and development is ongoing to address challenges to the deployment of advanced solvents. Some of the main characteristics of a desired solvent include a fast reaction with CO<sub>2</sub> resulting in a smaller absorber volume, a large CO<sub>2</sub> carrying capacity to reduce the amount of solvent needed to separate the CO<sub>2</sub> from the

flue gas, a low enthalpy of reaction with CO<sub>2</sub> to reduce the energy needed to break the amine-CO<sub>2</sub> bond in the regeneration process, and a low energy lost to vaporization of water and to heating to reduce the amount of steam used and the associated energy penalty. As shown in the Technology Readiness Level (TRL) chart in the Executive Summary of this report, absorption technologies range from TRL 1 to TRL 6 based on the U.S. DOE’s definitions.

#### A. History of Testing Advanced Solvents

DOE has developed a Program Portfolio of projects that addresses the key challenges of solvent-based CO<sub>2</sub> capture. The projects, focused on addressing key barriers in technology deployment, are shown in Table F-1 from the *DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook*, August 2015.

A number of advanced solvents, in addition to process improvements and hybrid systems with potential to reduce CO<sub>2</sub> capture costs, have been tested at the small pilot or bench scale at the National Carbon Capture Center (NCCC) and at other test facilities.

Linde/BASF tested OASE Blue solvent with innovative capture equipment such as a gravity-flow, interstage cooler and unique reboiler design at a 1.5 megawatt (MW) pilot-scale for more than 4,000 hours in 2015 and 2016 at NCCC. Demonstrating a regeneration energy as low as 2.7 gigajoule (GJ)/tonne CO<sub>2</sub> with at least 90% CO<sub>2</sub> capture, the technology was selected for funding by DOE for 10-MW demonstration at the University of Illinois.

Performer	Project Focus	Benefits	Scaleup	Capital Costs	Parasitic Load	Process Integration	Water Use
Akermin	Enzyme catalyzed	Low regeneration energy			X		
Battelle PNNL	Non-aqueous CO <sub>2</sub> -BOL	Low regeneration energy			X		
CCS, LLC	Process innovation	High-pressure regeneration			X		X
General Electric	Aminosilicone	Enhanced energetics	X		X		
ION Engineering	Organic/amine mixture	Enhanced energetics	X	X	X		
Linde	Advanced amine/process innovation	Single-process train	X	X	X	X	
Neumann Systems	Process innovation	Modular; solvent agnostic	X	X	X		
Novozymes	Enzyme catalyzed	Low regeneration energy			X		
RTI	Hydrophobic amine	Enhanced energetics			X		
Southern Company	Process innovation	Thermal management	X		X	X	
SRI International	Carbonate-based	Capital cost reduction			X	X	
University of Kentucky	Catalyzed	VOC eliminated/high pressure			X		
University of Kentucky	Advanced amine/process innovation	High-pressure regeneration	X	X	X	X	X
URS/University of Texas	Piperazine/process innovation	Enhanced energetics	X	X	X	X	

**Table F-1.** Barriers Addressed by the Solvent-Based Capture R&D Department of Energy/National Energy Technology Laboratory Program Portfolio

ION Engineering developed an advanced solvent that was demonstrated at NCCC in 2015 during an 1,100-hour campaign. With a 30+% reduction in regeneration energy requirements relative

to monoethanolamine (MEA), ION moved forward with larger-scale testing conducted at Technology Centre Mongstad (TCM) and has sought other opportunities to continue development.

University of Texas at Austin tested an advanced flash stripper with piperazine solvent (PZ) at NCCC in 2018, showing a 40% reduction in regeneration energy relative to MEA with further testing anticipated during 2019.

GE Global tested its continuous stirred-tank reactor and nonaqueous GAP-1 solvent at NCCC in 2016 and 2017. GE received DOE Phase I funding to evaluate a demonstration-scale 10-MW test at TCM but is not pursuing further development at this time.

RTI International (formerly Research Triangle Institute) operated a nonaqueous solvent at NCCC in 2018 and continues development with testing at TCM.

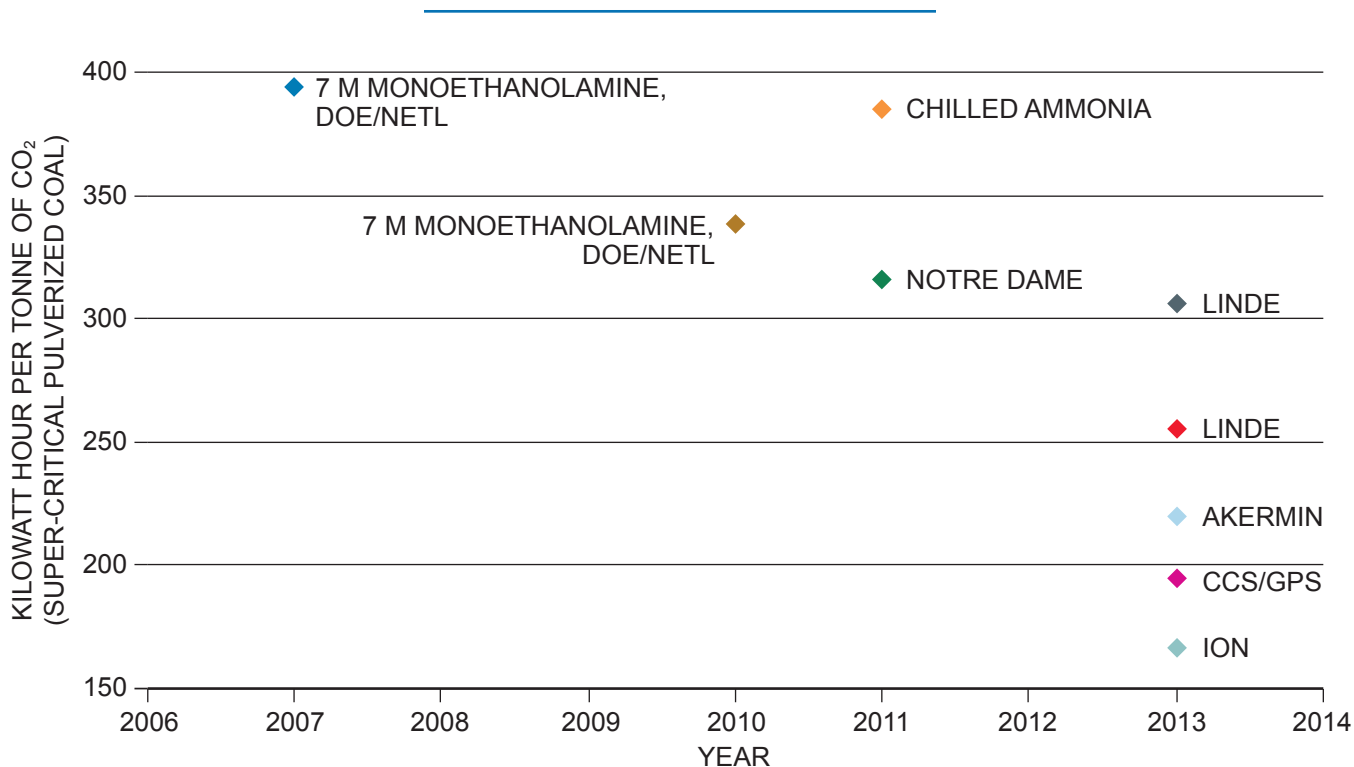
Codexis performed testing of a bench-scale system using carbonic anhydrase enzymes with methyl diethanolamine (MDEA) at NCCC in 2012. Although the testing confirmed the stability of the enzyme and robust system operation, plans to further develop the technology were delayed due to company changes in research priorities.

The University of Kentucky has performed field work for the two-stage stripping concept with a heat integration method using a Hitachi advanced solvent in a 0.7-MW small pilot system.

The University of Notre Dame has identified several promising ionic liquids (IL) for post-combustion CO<sub>2</sub> capture. Microencapsulation of these ILs in a polymer coating to alleviate high viscosity is being investigated at a lab-scale resulting in optimal heat of absorption.

Progress has been made to reduce the parasitic load and the energy penalty due to CO<sub>2</sub> capture. Parasitic load includes the work lost due to steam consumption for CCS and capture auxiliaries plus the energy required for compression of CO<sub>2</sub> from the stripper. Figure F-1 shows the progress in lowering parasitic load for solvent post-combustion capture in the DOE/NETL projects as of 2015.<sup>1</sup>

<sup>1</sup> U.S. Department of Energy, National Energy Technology Laboratory. (August 2015). *DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook*.



Source: DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015.

**Figure F-1.** Reduction in Parasitic Load for Solvent-Based Capture DOE/NETL Projects

## B. Future Work with Advanced Solvents

DOE's Transformational Large-Scale Pilots program began its Phase I kickoff in June 2018.<sup>2</sup> It is structured in three phases. This program supports the design, construction, and operation of two large-scale pilots (10-MW) for transformational coal technologies enabling a step change in coal powered system performance, efficiency, and cost of electricity. Phase I will include team commitments, site selection (and environmental analysis), pre-FEED (Front End Engineering Design) design basis, and cost share for Phase II. Two of the CO<sub>2</sub> capture projects chosen for Phase I are solvent projects.

The Board of Trustees of the University of Illinois will be investigating the Linde/BASF Advanced Post-Combustion CO<sub>2</sub> Capture Technology.

The University of Kentucky Research Foundation will be furthering their UKy-CAER Heat-Integrated Transformative CO<sub>2</sub> Capture Process.

DOE is supporting testing to scale up CO<sub>2</sub> capture technologies at engineering scale using existing host site infrastructure at TCM. Projects include the following:

- RTI International's Nonaqueous Solvent-Based Process
- SRI International's Mixed-Salt Process, using a physical solvent
- Fluor's Multi-Component Solvent Test, with a water-lean solvent.

Under DOE's Funding Opportunity Announcement (FOA) 1791 Area of Interest (AOI) 2, which includes initial engineering, testing, and design of a commercial-scale, post-combustion CO<sub>2</sub> capture system, a commercial-scale Techno-Economic Analysis (TEA) will be performed by ION Engineering with a nonaqueous solvent and by the University of North Dakota with an amine solvent.

<sup>2</sup> Litynski, J. (2018). Transformational Large Scale Pilots – Progress and Next Steps [PowerPoint slides].

At a bench scale, NETL will manage projects that concentrate on transformational technologies such as the following:

- The University of Illinois will advance a biphasic CO<sub>2</sub> absorption process.
- SRI International will develop further a water-lean, mixed salt based solvent technology.<sup>3</sup>
- ION Engineering will be conducting testing on a novel solvent to further understand the key performance indicators and validate performance.

A list of active and completed projects in the DOE/NETL Carbon Capture R&D Program for solvent-based post-combustion capture is shown in Table F-2.<sup>4</sup>

## C. Challenges and Research Needs for Solvents

The major research emphasis should include novel solvents such as nonaqueous, water-lean, and multiphase solvents, in addition to improving already existing solvents. The ideal solvent would have performance with high CO<sub>2</sub> capture, efficient regeneration of the solvent with low energy requirements, utilizing environmentally friendly processes. Since solvents are relatively mature and have been developed over several decades, research for transformational technologies needs to seek clear advantages over existing technologies (e.g., amines).

### 1. Water-Lean Solvents

Water-lean solvents maintain the chemical selectivity benefits of the water-based solvents while reducing the energy requirements for regeneration by exploiting the lower specific heat of organics compared to that of water. The novel solvents will also have the potential advantage of using the same infrastructure as the first- and second-generation aqueous amine processes.

All water-lean solvents employ variations of the following three formulations: carbamate,

<sup>3</sup> Litynski, J. (2018).

<sup>4</sup> U.S. Department of Energy, National Energy Technology Laboratory. (April 2018). *DOE/NETL Capture Program R&D: Compendium of Carbon Capture Technology*, 04.2018–1000.

Project Focus	Participant	Technology Maturity
<b>ACTIVE</b>		
Novel Electrochemical Regeneration of Amine Solvents	Massachusetts Institute of Technology	1-MWe
Slipstream Demonstration Using Advanced Solvents, Heat Integration, and Membrane Separation	University of Kentucky	0.7-MWe
Biphasic CO <sub>2</sub> Absorption with Liquid-Liquid Phase Separation	University of Illinois at Urbana-Champaign	Lab
Piperazine Solvent with Flash Regeneration	URS Group	0.5-MWe
Microencapsulated CO <sub>2</sub> Capture Materials	University of Notre Dame	Lab
Direct Air Capture from Dilute CO <sub>2</sub> Sources	Carbon Engineering LTD	Pilot-Scale
Nonaqueous Solvent	RTI International	Bench-Scale, Actual Flue Gas
Linde/BASF CO <sub>2</sub> Capture Process	University of Illinois at Urbana-Champaign	15-MWe
Low-Aqueous Solvent	ION Engineering, LLC	0.6-MWe and 12-MWe
Phase-Changing Absorbent	GE Global Research	Bench-Scale, Simulated Flue Gas
CO <sub>2</sub> -Binding Organic Liquid Solvents	Pacific Northwest National Laboratory	Lab
Aminosilicone Solvent	GE Global Research	10-MWe
Ammonia- and Potassium Carbonate-Based Mixed-Salt Solvent	SRI International	Bench-Scale, Simulated Flue Gas
Amine-Based Solvent and Process Improvements	Southern Company Services, Inc.	25-MWe
Waste Heat Integration	Southern Company Services, Inc.	Pilot-Scale, Actual Flue Gas
<b>COMPLETED</b>		
Slipstream Novel Amine-Based Post-Combustion Process	Linde LLC	1.5-MWe
Chilled Ammonia Process Improvements	GE Power	Bench-Scale, Simulated Flue Gas
Carbonic Anhydrase Catalyzed Advanced Carbonate and Non-Volatile Salt Solution ("Solvents")	Akermin, Inc.	Bench-Scale, Actual Flue Gas
Carbon Absorber Retrofit Equipment	Neumann Systems Group	0.5-MWe
Novel Absorption/Stripper Process	William Marsh Rice University	Bench-Scale, Simulated Flue Gas
Gas-Pressurized Stripping	Carbon Capture Scientific	Bench-Scale, Real Flue Gas
Solvent + Enzyme and Vacuum Regeneration Technology	Novozymes North America, Inc.	Bench-Scale, Simulated Flue Gas
Optimized Solvent Formulation	Babcock & Wilcox	Bench-Scale Simulated and Actual Flue Gas
Hot Carbonate Absorption with Crystallization-Enabled High-Pressure Stripping	University of Illinois at Urbana-Champaign	Lab
Chemical Additives for CO <sub>2</sub> Capture	Lawrence Berkeley National Laboratory	Bench-Scale, Simulated Flue Gas
Self-concentrating Amine Absorbent	3H Company, LLC	Lab
Ionic Liquids	University of Notre Dame	Lab
Novel Integrated Vacuum Carbonate Process	Illinois State Geological Survey	Lab
POSTCAP Capture and Sequestration	Siemens Energy Inc.	2.5-MW
Reversible Ionic Liquids	Georgia Tech Research Corporation	Lab
Phase Transitional Absorption	Hampton University	Lab
(Pre-Combustion) CO <sub>2</sub> Capture Using AC-ABC Process	SRI International	0.15-MWe

**Table F-2.** Post-Combustion Solvent Projects in DOE/NETL Carbon Capture Program

alkylcarbonate, or azoline-carboxylate. These solvents are designed to be nonvolatile to minimize fugitive emissions. The enthalpies of CO<sub>2</sub> absorption for the water-lean solvents are comparable to those of aqueous solvents at -50 to -90 kilojoules per mole CO<sub>2</sub> (kJ/mol CO<sub>2</sub>), demonstrating similar viability and selectivity for post-combustion capture.

Water-lean solvents have been shown to deliver efficiency gains. Distinguishing properties relative to aqueous solvents include physical state, contact angle, wettability, viscosity, volatility, thermal conductance, and solvation free energy.

Water-lean solvents have reported lower reboiler energies of 1.7 to 2.6 gigajoules per tonne CO<sub>2</sub> (GJ/tonne CO<sub>2</sub>) compared to the DOE NETL Case 10 with 3.5 GJ/tonne CO<sub>2</sub> and the second-generation amine scrubbing performance of 2.2-2.4 GJ/tonne CO<sub>2</sub>. An increase of 2.1% to 7.1% in net plant efficiency is also expected compared to DOE NETL Case 10 with these solvents.<sup>5</sup> However, there is debate as to whether the capital cost will be that much lower due to the higher viscosity of the organic solvents, with arguments that water-lean amine will not significantly reduce energy use compared to a second-generation aqueous amine and that the second-generation amine scrubbing systems lose little efficiency and can be implemented with little additional capital cost.<sup>6</sup>

Most water-lean solvents tolerate acceptable levels of water. All have shown stable water loading (up to 10 weight %) without need for extensive water management equipment. There are no reported instances of aerosols or foaming, and these solvents also may be less corrosive than the aqueous solvents.

## 2. Multiphase Solvents

Multiphase solvents can develop more than one liquid phase (de-mixing) or they can form a liq-

5 Heldebrant, D. J., Koech, P. K., Glezakou, V. A., Rousseau, R., Malhotra, D., and Cantu, D. C. (2017). "Water-Lean Solvents for Post-Combustion CO<sub>2</sub> Capture: Fundamentals, Uncertainties, Opportunities, and Outlook," *Chemical Reviews* 117, p. 14.

6 Rochelle, G. and Yuan Y. "Water-Lean Solvents for CO<sub>2</sub> Capture Will Not Use Less Energy Than Aqueous Amines," 14th Greenhouse Gas Control Technologies Conference, Melbourne, 21-26 October 2018 (GHTG 14).

uid/solid assembly (precipitating). Phase change during the absorption/desorption process of capture has the potential to greatly enhance performance. The opportunities that phase change could present are as follows:

- Ability to form a high-density CO<sub>2</sub> rich phase so that only part of the solvent will need regeneration
- Intensification of desorption at lower temperatures of less than 100°C by using waste low-value, heat streams
- Release of CO<sub>2</sub> at high pressure
- Precipitate bound CO<sub>2</sub> or the reactant.

Systems that incorporate combinations of amines, inorganic salts, organic solvents, and water have only been studied recently and have shown the potential for reduced energy requirements and improved performance.

## 3. System Studies and Modeling

Molecular modeling and simulation tools have advanced tremendously. The challenge is to accurately predict the properties of a potential solvent using the molecular understanding obtained by using these tools. Using the lessons learned in bench- and pilot-scale solvent system testing with improvements in modeling will more accurately enable the design of new, effective solvent systems. Advances in fundamental theory and computational and experimental capabilities will enable design of solvent systems for a range of CO<sub>2</sub> sources from a wide variety of industrial applications.<sup>7</sup>

## 4. Challenges to Power Retrofits

A challenge to the retrofitting of CO<sub>2</sub> capture in the power sector for mature amine technology is amine's susceptibility to parasitic, irreversible reactions with other species in the flue gas, including SO<sub>x</sub>, NO<sub>x</sub>, mercury, and particulates. Therefore, a retrofit using amine technology is typically preceded by installation of other

7 U.S. Department of Energy, Office of Fossil Energy, "Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage," Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts' Workshop, September 2017. Mission Innovation.



scrubbers that remove these pollutants. Unfortunately, the cost of installing these scrubbers to enable a CO<sub>2</sub> capture retrofit with amines is prohibitive. Early-stage technologies may overcome this multi-pollutant challenge by removing all the pollutants.

Zerronox offers a pulsed electron beam technology originating from the Naval Research Laboratory. The beam reduces acid gases like NO<sub>x</sub> to their elemental gases. The team is working to extend the technology to CO<sub>2</sub> capture.<sup>8</sup>

The CEFCO Process uses aerodynamic physics (shockwaves) to achieve what they call “free jet collision scrubbing” to separate pollutants in flue gas. Unlike sorbent-based processes, this process is truly continuous.<sup>9</sup>

### III. ADSORBENTS AND ADSORPTION

#### A. History of Testing Adsorbents

The removal of CO<sub>2</sub> from gas streams via adsorption is not a new concept. Throughout the manned space missions, solid sorbents have been used to remove CO<sub>2</sub> at low concentrations (<1%) from air. Regenerable sorbents have been employed since the 1990s in the space shuttle and for the International Space Station.

Cryogenic air separation uses sorbent material to remove water vapor and CO<sub>2</sub> from feed air typically in molecular sieve units. Zeolite 13X is commonly used since zeolites in general have a high affinity for water and great selectivity for CO<sub>2</sub>.

Hydrogen recovery at refineries is the most common application of sorbents in large gas separation operations. The hydrogen is separated out of the gas mixture from the steam methane reformer syngas. The pressure swing adsorption (PSA) systems, with commercially available sorbents such as molecular sieve (zeolites), activated carbon, activated alumina, or silica gel, are used to create relatively pure H<sub>2</sub> from the syngas to be used in the refinery process. At Valero Energy’s Port Arthur Texas refinery, sorbents in a vacuum

swing adsorption (VSA) process are separating out the CO<sub>2</sub> from the steam methane reformer syngas for injection in the West Hastings oil field for enhanced oil recovery. The CO<sub>2</sub> separation takes place upstream of the existing PSA process for capturing H<sub>2</sub>.<sup>10</sup>

To advance sorbents as a viable CO<sub>2</sub> capture solution, research and development has been underway to demonstrate sorbents’ low cost, thermal and chemical stability, resistance to attrition, low heat capacity, high CO<sub>2</sub> loading capacity, and high selectivity for CO<sub>2</sub>. CO<sub>2</sub> capture adsorbents employ either physical or chemical adsorption, and compared to solvents may offer lower energy penalty, greater flexibility in operating temperature ranges, and smaller environmental impacts. As shown in the TRL chart in the Executive Summary of this report, adsorption technologies range from TRL 2 to TRL 7 based on the U.S. DOE’s definitions.

To gauge the progress in technological advancements in the area of adsorbents, a good metric for comparison is the reduction of energy penalty in terms of MWh/tonne CO<sub>2</sub>. Figure F-2 shows the progress for sorbent-based capture to reduce the parasitic load.<sup>11</sup>

Numerous completed DOE-supported projects based on amine-based adsorbents include the following:

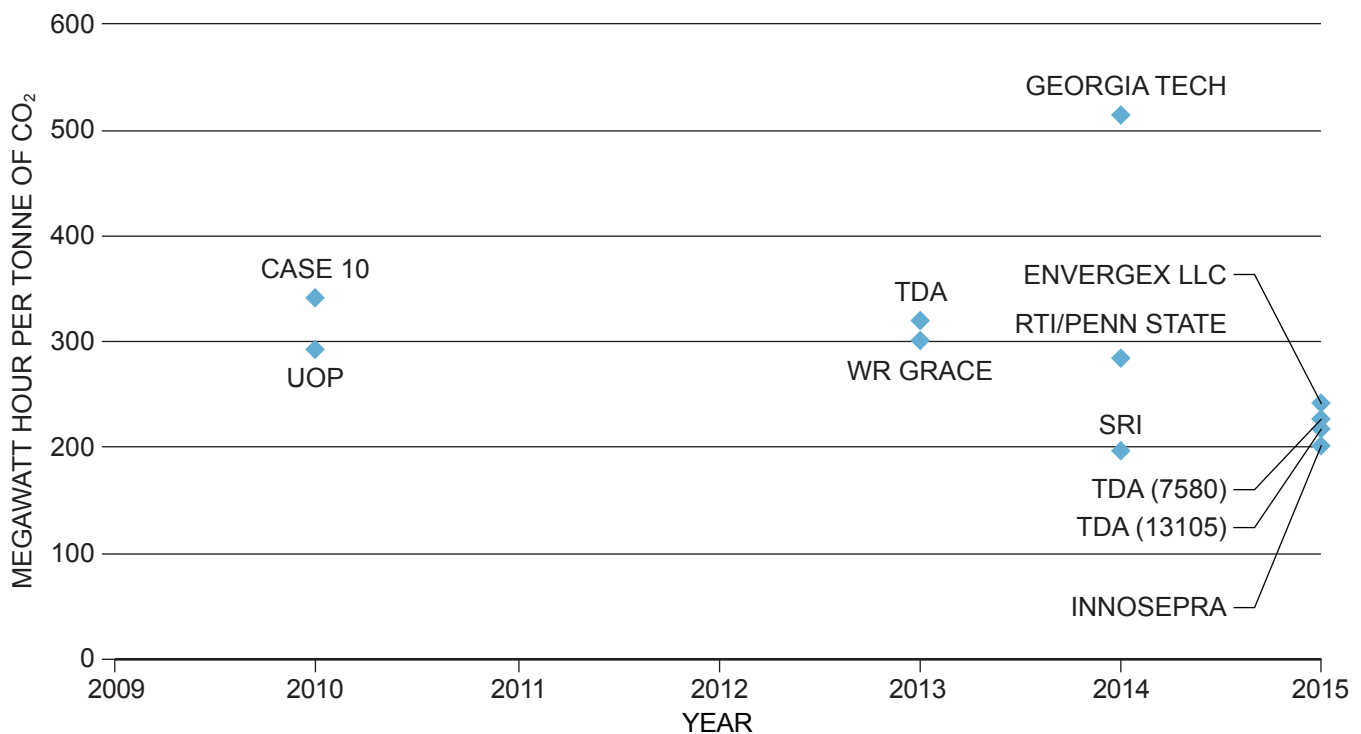
- NETL’s Research and Innovation Center staff operated a bench-scale sorbent unit at NCCC in 2014 to evaluate accumulation of trace elements and sorbent degradation with silica-supported amine sorbents. The unit operated in circulating and batch modes, with post-test thermo-gravimetric analysis of sorbent samples showing no permanent loss of CO<sub>2</sub> capture capacity. Following testing at the center, NETL continued sorbent work to improve material characteristics, although the group’s current CO<sub>2</sub> capture work is focused on membrane material development.

8 Zerronox, “Cleaner Emissions with Electrons,” (2015). <http://www.zerronox.com/index.html>.

9 CEFCO, <http://www.cefcoglobal.com/>.

10 U.S. Department of Energy, National Energy Technology Laboratory, *DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook*, August 2015.

11 *DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook*, August 2015.



Source: DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015.

**Figure F-2.** Progress in Reducing the Energy Penalty of Sorbent-Based Capture

- Georgia Tech Research Corporation developed a rapid temperature swing adsorption (TSA) system using polymer/supported amine composite hollow fibers at the bench scale. The fast cycling would significantly reduce capital costs and heat integration of the adsorption step would decrease the operating costs.
- ADA-Environmental Solutions performed 1-kW scale field tests with four supported amine sorbents.
- Aspen Aerogels, Inc. designed an amine functionalized aerogel sorbent, developed a production process, and tested at a bench scale to complete a techno-economic analysis of the system.
- RTI International developed a polyethylenimine supported over silica in a molecular basket sorbent to make a more cost-effective alternative.
- The University of Akron developed low-cost sorbents by integrating metal monoliths with amine-grafted silica, which they tested at a 15-kW scale.

DOE’s research portfolio in carbon-based adsorbents includes many projects performed by TDA Research:

- TDA Research has developed a CO<sub>2</sub> capture process using dry, alkalized alumina sorbent, featuring low cost, low heat of adsorption, and capability of near-isothermal, low-pressure operation to achieve lower regeneration energy than solvent-based processes. TDA has installed a small post-combustion pilot-scale test unit at NCCC and will complete testing in 2019.
- TDA Research’s testing of a solid CO<sub>2</sub> sorbent for pre-combustion syngas at the NCCC consistently demonstrated the capability to remove more than 90% CO<sub>2</sub>. TDA also tested a combined WGS/CO<sub>2</sub> sorbent system with an innovative heat management component. When parameters were adjusted to achieve 90% CO conversion in the WGS stage, the overall CO<sub>2</sub> capture rate was greater than 95%. TDA scaled up testing from bench- to small-pilot-scale (0.1-MW) with a CO<sub>2</sub> sorbent (without water

gas shift) process, again demonstrating high CO<sub>2</sub> capture and stable operation. After tests at the NCCC, the TDA 0.1-MW test skid was shipped to China's Sinopec facility for further testing.

- SRI International tested a bench-scale sorbent process at NCCC in 2013 and 2014 using carbon microbead sorbents, which offer low heat requirements, high CO<sub>2</sub> adsorption capacity, and excellent selectivity. Performance indicators were lower than expected based on previous testing of SRI's smaller unit at the University of Toledo, with CO<sub>2</sub> capture efficiency at 70%. Although measures were identified to improve performance, SRI currently has no plans for further testing.

The zeolite-based projects supported by DOE in the past emphasized the overall capture cycle and the improvement of zeolite structure in the beds.

- For example, W. R. Grace investigated a rapid PSA process with simplified heat management using a commercially available zeolite adsorbent crushed and coated onto a metal foil structure.
- Also, Innosepra LLC developed a microporous material with low heat of adsorption and novel process cycles.

Metal-organic frameworks (MOFs) are highly designable and tailorable with limitless combinations of metals and organic compounds and can be used for many different applications such as CO<sub>2</sub> capture. MOFs are strong 3D structures with exceptional surface area. MOFs have the potential to be superior to zeolites and other sorbents; however, cost of materials and stability in the presence of water vapor are challenges. In 2007 to 2010, UOP investigated a large selection of MOFs, narrowing to seven that exceeded targets, and identified types of favorable structures. Study into the critical property of hydrothermal stability by UOP was also done in detail. Applying MOFs for CO<sub>2</sub> capture is currently a very active research area.

Other past projects sponsored by DOE/NETL include the University of North Dakota where researchers developed a process using regen-

erable metal carbonate-based sorbent resulting in low regeneration energy penalty. And NRG Energy along with Inventys developed the VeloxoTherm™ technology platform, an intensified and rapid-cycle temperature swing adsorption process designed to test a wide-range of sorbent types. Inventys has made plans to utilize the platform at NCCC and TCM.<sup>12</sup>

For further discussion, please refer to the completed projects described in the 2018 *DOE/NETL Capture Program R&D: Compendium of Carbon Capture Technology* report.

## B. Planned Work with Adsorbents

DOE/NETL's focus for sorbents includes development of low-cost, durable sorbents that have high selectivity, high CO<sub>2</sub> adsorption capacity, and little to no attrition during multiple regeneration cycles. Table F-3 lists the ongoing sorbent projects as well as the completed projects in the carbon capture program.<sup>13</sup>

TSA systems being tested are provided in the following list. TSA is where CO<sub>2</sub> is adsorbed on a high surface area solid at low temperature (40°C to 60°C) and are regenerated by steam (80°C to 150°C). Typically, these are chemisorbents in rotary beds or circulating beds.

- RTI International's Dry Carbonate Process – sodium carbonate to sodium bicarbonate reaction for post-combustion
- KIER (Korean Institute of Energy Research) process with dual fluidized beds at a pilot-scale (10 MWe)
- Climeworks – Distributed Air Capture with amine impregnated cellulose fibers; 900 t/yr CO<sub>2</sub> at the pilot unit in Hinwil, Switzerland
- Inventys VeloxoTherm – rotary wheel with diamine-functionalized commercial silica gel, pilot underway at NRG Energy

<sup>12</sup> U.S. Department of Energy, National Energy Technology Laboratory. (January 2013). *Clean Coal Research Program: Carbon Capture Technology Program Plan*.

<sup>13</sup> U.S. Department of Energy, National Energy Technology Laboratory. (April 2018). *DOE/NETL Capture Program R&D: Compendium of Carbon Capture Technology*, 04.2018–1000.

Post-Combustion Project Focus	Participant	Technology Maturity
<b>ACTIVE</b>		
Pressure Swing Adsorption Process with Novel Sorbent	Georgia Tech Research Corporation	Lab
Porous Polymer Networks	Texas A&M University	Lab
Novel Solid Sorbent	SRI International	Bench-Scale, Actual Flue Gas
Alkalized Alumina Solid Sorbent	TDA Research, Inc.	0.5-MWe
Fluidizable Solid Sorbents	Research Triangle Institute	Lab
<b>COMPLETED</b>		
Advanced Aerogel Sorbents	Aspen Aerogels, Inc.	Bench-Scale, Simulated Flue Gas
Temperature Swing Adsorption with Structured Sorbent	NRG Energy, Inc.	
Rapid Pressure Swing Adsorption	W. R. Grace and Co.	Bench-Scale, Simulated Flue Gas
Advanced Solid Sorbents and Processes for CO <sub>2</sub> Capture	RTI International	Bench-Scale, Simulated Flue Gas
Cross-Heat Exchanger for Sorbent-Based CO <sub>2</sub> Capture	ADA-ES, Inc.	Bench-Scale, Simulated Flue Gas
Low-Cost, High-Capacity Regenerable Sorbent	TDA Research, Inc.	Bench-Scale, Actual Flue Gas
Rapid Temperature Swing Adsorption	Georgia Tech Research Corporation	Bench-Scale, Simulated Flue Gas
Novel Adsorption Process	InnoSeptra, LLC	Bench-Scale, Actual Flue Gas
Hybrid Sorption Using Solid Sorbents	University of North Dakota	Bench-Scale, Actual Flue Gas
Metal Monolithic Amine-Grafted Zeolites	University of Akron	15-kW, Simulated Flue Gas
CO <sub>2</sub> Removal from Flue Gas Using Microporous MOFs	UOP	Lab
A Dry Sorbent-Based Post-Combustion CO <sub>2</sub> Capture	RTI International	Bench-Scale, 1 tonne per day, Actual Flue Gas
Pre-Combustion Project Focus	Participant	Technology Maturity
<b>ACTIVE</b>		
High Capacity Regenerable Sorbent	TDA Research, Inc.	0.1-MWe
<b>COMPLETED</b>		
Sorbent Development for WGS	URS Group	Bench-Scale Simulated Syngas
Novel Concepts Project Focus	Participant	Technology Maturity
Novel Concepts/Integrated Temperature and Pressure Swing Carbon Capture System	Altex Technologies Corporation	Lab

**Table F-3.** Sorbent Projects in U.S. Department of Energy/  
National Energy Technology Laboratory Carbon Capture Program

- TDA Research alumina sorbents (fixed bed, steam regeneration)
- Seibu Giku ceramic wheel.

PSA and VSA systems have numerous vendors that are undergoing research. These typically use physisorbents in fixed beds.

Opportunities for adsorbent CO<sub>2</sub> capture include enriching natural gas from wells with high CO<sub>2</sub> content, coal or biomass gasification, CO<sub>2</sub> recovery from food and dry ice industries, and CO<sub>2</sub> recovery from petrochemical, oil, steel, cement, landfill gas. At the Otway Basin Cooperative Research Center for Greenhouse Gas

Technologies (CO2CRC) facility, testing of capture materials to develop cost-effective processes to capture CO<sub>2</sub> from high CO<sub>2</sub> content natural gas wells.<sup>14</sup>

More work continues in Saskatchewan, Canada, where Inventys and Husky Energy will begin pilot testing in Q1 2019 with the VeloxoTherm Process capture system. This system uses structured solid sorbent in a rotary mechanical contactor to enable rapid sorption/desorption and temperature cycling. The testing at Husky Energy is a 30 tonnes per day (TPD) pilot demonstration. A 0.5 TPD field demonstration plant is already at this location for rapid development of new adsorbent structures. Inventys is offering commercial modular skid plants that will capture 30 to 600 TPD of CO<sub>2</sub> at \$30 to \$100/tonne. Inventys' first fully commercial manufacturing line is expected to be at full capacity by the end of 2020.

To accelerate the development and commercialization of second-generation CO<sub>2</sub> capture with new sorbent materials, Inventys in partnership established the International Carbon Capture Center for Solid Sorbent Survey. The objective of the center is to move novel sorbent material from the laboratory to the real-world conditions and to establish new standards in the characterization of new sorbent material and perform benchmarking of capture processes with rapid cycling. The testing with the VeloxoTherm technology platform at 100 to 500 kg/day has been deployed at the facilities of Inventys in Vancouver, British Columbia, and the National Carbon Capture Center in the United States, and the Technology Centre Mongstad in Norway.<sup>15</sup>

TDA Research started commissioning their pre-combustion PSA sorbent system at Sinopec's Nanhua Plant in October 2018. This system was previously tested at the NCCC in 2017. The test skid was modified to maintain a slightly higher

CO<sub>2</sub> capacity than the field tests at NCCC of approximately 60x scale.<sup>16</sup>

Under the Scaling of Carbon Capture Technologies to Engineering Scales using Existing Host Site Infrastructure (FOA 1791 AOI 1), TDA Research will be designing, constructing, and operating a 1-MW post-combustion hybrid membrane-sorbent system. The polymeric membrane will be developed by Membrane Technology and Research, Inc. (MTR) and will provide the bulk of the CO<sub>2</sub> separation with the sorbent extracting the remainder to achieve 90% capture.<sup>17</sup>

### C. Challenges and Research Needs for Adsorbents

CO<sub>2</sub> capture based on sorption/desorption of gases by a solid has the potential to greatly reduce the energy requirements and the capital costs compared to the current capture technologies. The key challenge for sorbents is to pair the newly developed, tailored materials with the specific CO<sub>2</sub> capture applications and be able to integrate the two predictively with modeling and computational tools.

Four principal challenges were cited in using sorbents in CO<sub>2</sub> capture as adsorbents as well as in looping technologies:

- Design and create tailor-made materials with the desired attributes
- Understand the relationship at the molecular, microscopic, and macroscopic levels between the structure and the properties of the material
- Advance the long-term reactivity, recyclability, and robust physical properties of materials within the process
- Produce optimal integration between materials and process engineering.

14 Webley, P., Singh, R., and Xiao, P. (April 2017). "Adsorption Processes for CO<sub>2</sub> Capture: An Overview," presentation at CO<sub>2</sub> Summit III: Pathways to Carbon Capture, Utilization, and Storage Deployment, ECI Digital Archives.

15 Inventys Inc. (2018). Manufacturing & Testing Centre <http://inventysinc.com/technology/>.

16 Alptekin, G. (2018). "Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System," (Contract No. DE-FE-0013105), presented at the 2018 DOE/NETL CO<sub>2</sub> Capture Project Technology Review Meeting.

17 U.S. Department of Energy. (February 2018). "Energy Department Invests \$44M in Advanced Carbon Capture Technologies Projects." <https://www.energy.gov/articles/energy-department-invests-44m-advanced-carbon-capture-technologies-projects>.

Over the last 15 years, new porous adsorbent materials with molecular designed attributes have proliferated in the form of MOFs, covalent organic frameworks, and several other types of porous polymer materials. These advanced solids will require less infrastructure and lower capture costs. These porous materials have not been limited to a bed configuration but are also applicable to membranes.

New sorbents, specifically MOFs offer to combine the high surface area of zeolites and activated carbons with tailored, tunable pore geometry and chemistry to enhance their selectivity. This is important for CO<sub>2</sub> capture since sorbents should selectively bind only CO<sub>2</sub>. MOFs can also be tuned for other industrially important gas-gas separations, so their path to market may be driven by applications other than CO<sub>2</sub> capture. Two examples of MOFs used in other gas separation process are from NuMat Technologies, Inc. and Mosaic Materials, Inc. NuMat is a spinoff from Northwestern University that combines high-throughput computational modeling and experimentation to develop new MOFs. NuMat was recently awarded a \$9M contract from the U.S. Army to produce MOFs to protect soldiers from toxic agents.<sup>18</sup> Mosaic Materials, a spinoff from the University of California Berkeley, is developing a MOF that uses a unique “cooperative binding” mechanism that gives the material higher CO<sub>2</sub> capture capacity than other sorbents. The MOF can be used in CO<sub>2</sub> capture from exhaust gas, but it is also applicable to CO<sub>2</sub> capture from other process streams such as CO<sub>2</sub>-methane separations following anaerobic digestion.<sup>19</sup>

The leading materials for CO<sub>2</sub> capture that offer targeted molecular design (e.g., MOFs) have all been discovered in the last 5 years. There are a few bench-scale testing sites available now that will allow the validation of the technologies including looping.

There are challenges to contacting gas with a solid adsorbent in a compact, efficient manner so

that the driving force can be applied with minimal energy and materials. Further research is needed into how to optimally expose the gas to the materials to get sorption/desorption. Much emphasis is given to matching the material with the process. The first step is to determine the driving force to use (temperature, pressure, or vacuum cycling). And then, what combination is needed to absorb and desorb so that the required feed conditions and other specifications are met. There is a strong dependence of the driving force with the feed conditions.

Other challenges center around impurity removal, heat management, and fluid flow. Important design considerations include the need for flexible operation to adapt the cycling of PSA, TSA, or VSA to the real time demand for the capture plant. One key strategy has been to reduce the cycle time in operations.<sup>20</sup>

MOFs exhibit sharp temperature and pressure stepwise pathways to absorption and desorption which lead to lower parasitic energy loads and faster kinetic rates. Key challenges for these materials include sensitivity to oxidation, water, and degradation caused by CO<sub>2</sub>.<sup>21</sup>

In the newly awarded FOA 1792, organizations that are pursuing bench-scale testing in the sorbents area include the following:

- Electricore, Inc. is developing a process that includes a dual-adsorbent bi-layer structured adsorbent design with a thermal conductive matrix that will allow faster thermal swings than a conventional process.
- InnoSeptra, LLC is developing a novel sorbent-based process consisting of a flue gas purification step, a moisture removal step, and a CO<sub>2</sub> adsorption step. Also, the CO<sub>2</sub> adsorption bed is regenerated with low level heat.
- Rensselaer Polytechnic Institute is developing a transformational, molecular layer deposition,

<sup>18</sup> Bomgardner, M. (December 16, 2018). “NuMat Gets Contract to Build a Metal-Organic Framework Facility.” *Chemical & Engineering News*, vol. 96, no. 49. <https://cen.acs.org/business/specialty-chemicals/NuMat-contract-build-metal-organic/96/i49>.

<sup>19</sup> Mosaic. (2018). <https://mosaicmaterials.com/>.

<sup>20</sup> U.S. Department of Energy, Office of Fossil Energy, “Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage,” Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts’ Workshop, September 2017. Mission Innovation.

<sup>21</sup> Inventys Inc. (2018). Manufacturing & Testing Centre. <http://inventysinc.com/technology/>.

tailor-made, size-sieving sorbent process. The technology will integrate these novel sorbents with an innovative PSA process for post-combustion capture.

- TDA Research, Inc. will work on addressing the early stage development of a transformational high-capacity adsorbent with a vacuum concentration swing adsorption process and will evaluate at bench scale in actual coal-fired flue gas.

Not awarded in FOA 1792, Auburn University is investigating solid sorbent-based long-term CO<sub>2</sub> removal without capture capacity degradation by introducing a regenerative three-stage cycling in a reduction-carbonation-calcination process. This regeneration of composite solid sorbent at high temperature would possibly resolve the persistent problem of CO<sub>2</sub> capture capacity degradation over time.

## V. MEMBRANES

### A. History of Testing Membranes

Large surface area membranes with high flux were first developed for reverse osmosis purposes in late 1960s to early 1970s. In 1980, Monsanto developed the first commercial gas separation membrane, called PRISM, mainly used for hydrogen separation from refinery waste gases. Since membranes are competing against the more established, less costly CO<sub>2</sub> capture processes, the use of membranes for large CO<sub>2</sub> gas separation has been limited to small scale natural gas purification. One commercial project that uses membrane separation is the Petrobras Lula Oil Field CCS Project capturing 0.7 million tonnes per year. Improvements in flux and selectivity as well as polymer materials and fabrication have continuously decreased the cost of membranes for gas separation. Some examples of commercially available membranes are the PRISM by Air Products, MEDAL by Air Liquide, and PolySep by UOP.

Membrane-based CO<sub>2</sub> separation has many advantages compared to other capture approaches. Membrane module systems have simple operation with no chemical reactions, no moving parts, and no temperature or pres-

sure swings. Since these modules can be valved so that individual modules can be swapped in and out, changes in the module system will not affect the entire process. This configuration also allows for large turn down ratios of as low as 30% to greater than 100%. Also, extremely high on-stream factors can be achieved. Since the membrane module systems are highly modular, they typically have a small footprint and are easily scalable. Membranes can tolerate high concentrations of acid gases and are inert to oxygen. They also have the potential for inherent energy efficiency and no additional water use. The TRL chart in the Executive Summary of this report shows membrane technologies ranging from TRL 3 to TRL 8+.

Several significant challenges for membrane CO<sub>2</sub> capture technologies result in a less favorable cost compared to other technologies. CO<sub>2</sub> permeability and permeance of gas separation membranes is lower than desired resulting in large membrane areas and higher capital costs due to a larger footprint of membrane modules. Steam is not required in membrane systems; however, auxiliary power is often needed for compression or vacuum pumps to provide driving force for separation. And, membrane life and effectiveness can be reduced by contaminants in the gas feed. Life of the modules is a critical factor for the cost of these systems.

The membrane acts as a filter. Some molecules are allowed to permeate through, while others are blocked from passing. Membranes can separate gases from a mixture due to differences in permeability through the membrane for the different gases. The gas flux across a unit membrane area under a unit pressure gradient through a unit membrane thickness is called permeability, in moles per second per meter squared per Pascal (mol s<sup>-1</sup>m<sup>-2</sup>Pa<sup>-1</sup>). The selectivity is a ratio of the permeability of gas A to the permeability of gas B, or the ratio of permeabilities of different gases through the same membrane. To achieve separation by the membrane, a large difference in permeabilities of the gases is preferred. The differences in physical and/or chemical properties of the gases as well as how they interact with the membrane determine permeability. Some separation mechanisms are size sieving, surface

diffusion, solution diffusion, facilitated transport, and ion transport. Since the feed gas is pressurized to achieve a high flux and the membrane is very thin, at several hundred nanometers to several microns, the membrane is coated onto a thick, porous substrate to have mechanical strength to resist this force.<sup>22</sup>

There are four main configuration options for module designs, two mechanical designs and two material-type configurations. For the mechanical design there are tubular and plate and frame options. For the tubular design, numerous tubes can be placed into a single cylindrical vessel and this is called a shell and tube design.

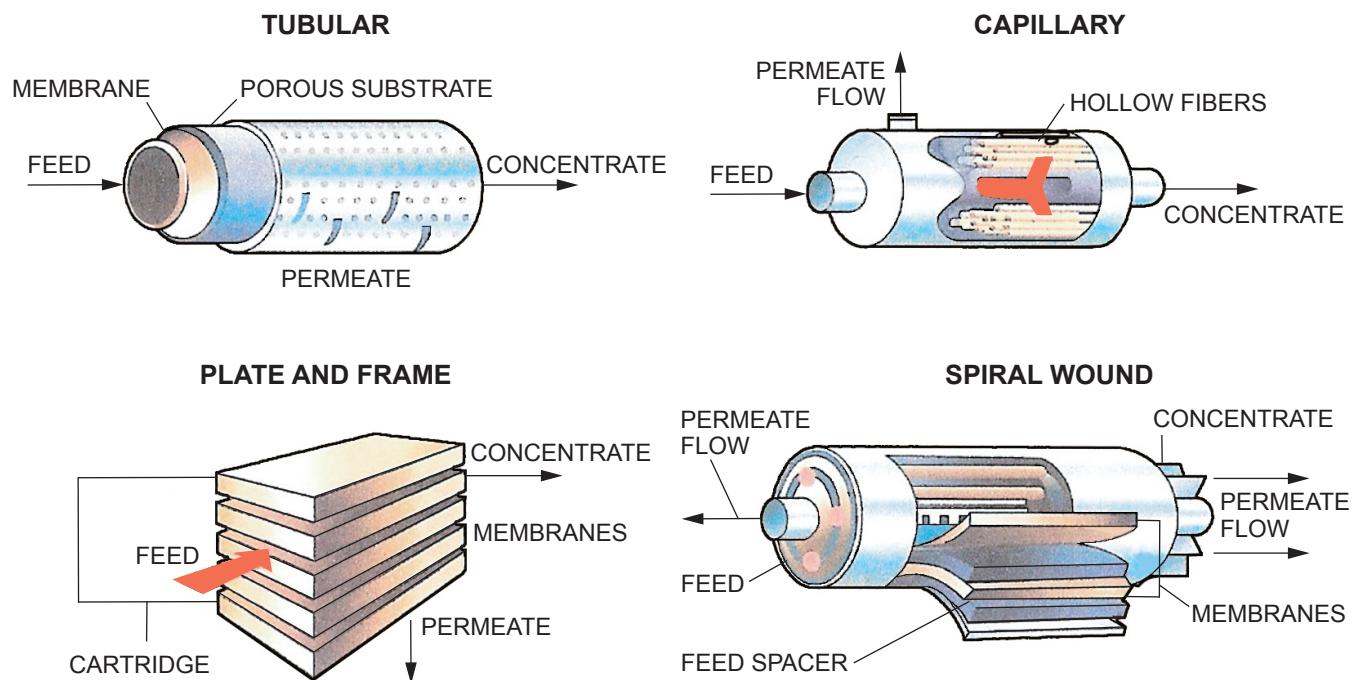
For the material-type configurations, there are the hollow fiber and sheet fabrications. Hollow fibers have an outside, thin layer of dense polymer supported by a porous structured sublayer. In a module, thousands of these hollow fibers are

bundled together cylindrically over a central core which is a perforated tube called a bore.

Or, membrane modules can be made with thin sheets of polymer arranged in spiral wound fashion. The feed gas enters the module and flows between the membrane leaves. The retentate flows over the leaves and exits the other end whereas the permeate spirals inward to a central core collection tube. Refer to Figure F-3.

MTR has developed a unique spiral wound-type module (see Figure F-4). This module introduces sweep gas on the permeate side thus creating driving force with no additional pressurization. The permeate central collection tube has a plug in the middle to form a counter-current permeate flow to the feed gas flow. Another less widely used membrane module tested by MTR is the plate and frame configuration with flat membrane sheets and use of sweep combustion air. This configuration provides a compact large membrane area with low pressure drop. Using the sweep gas for separation driving force instead of compressors or vacuum pumps will reduce the cost of capital and energy use of the system.

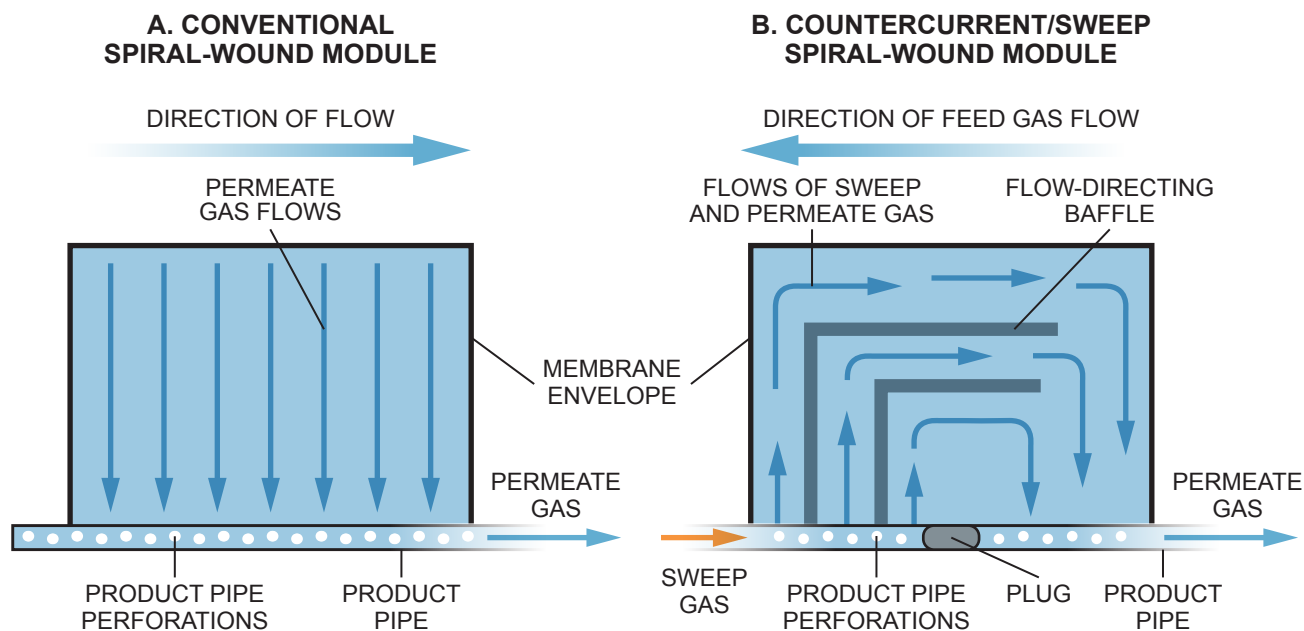
<sup>22</sup> Ji, G., and M. Zhao. (2017). "Membrane Separation Technology in Carbon Capture," in *Recent Advances in Carbon Capture and Storage* p. 59-90, InTechOpen, <https://www.intechopen.com/books/recent-advances-in-carbon-capture-and-storage/membrane-separation-technology-in-carbon-capture>.



Sources: Torzewski, K., "Facts at your Fingertips—Membrane Configuration," *Chemical Engineering*, March 15, 2008; and DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015.

**Figure F-3.** Common Membrane Designs





Source: DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015.

**Figure F-4.** Spiral-Wound Membrane Module Flow Patterns

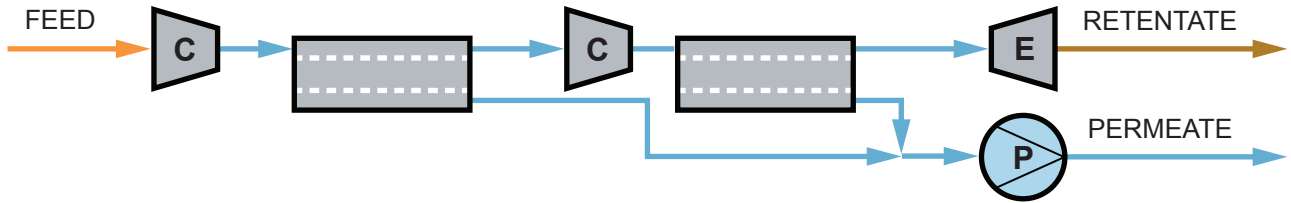
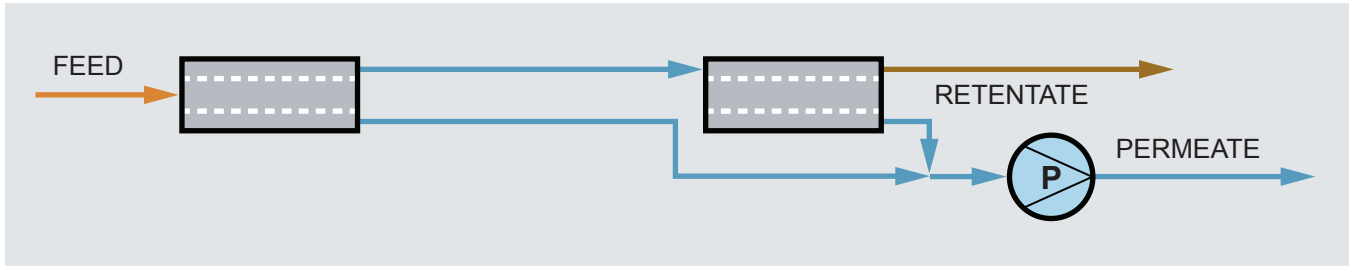
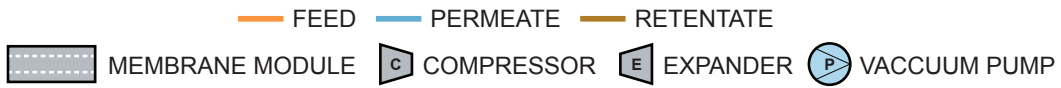
The separation of gases with a membrane is dependent on the permeability and the selectivity for the target component in the gas to be removed. The current membranes are limited in these characteristics such that a single stage separator cannot attain the high removal and purity objectives like achieving 90% capture and 95% purity.

The process configurations for membrane separation systems are typically a two-stage process, as shown in Figure F-5, with either the retentate from the first stage as feed for the second stage (stripper circuit) or the permeate as the feed to the second stage (enricher circuit). Serial enricher circuits have been found to be the most energy efficient, with improved efficiency achieved when the second-stage retentate is recycled to the beginning of the cycle in Figure F-6. Most arrangements include compression or vacuum pumping, which tends to add cost. MTR's process solution incorporates the combustion air as a sweep gas to provide the driving force, reducing the need for the energy intensive process units.

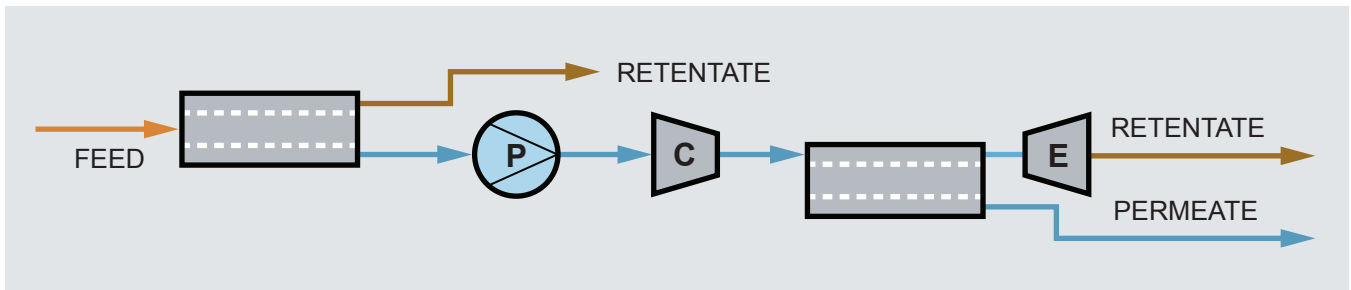
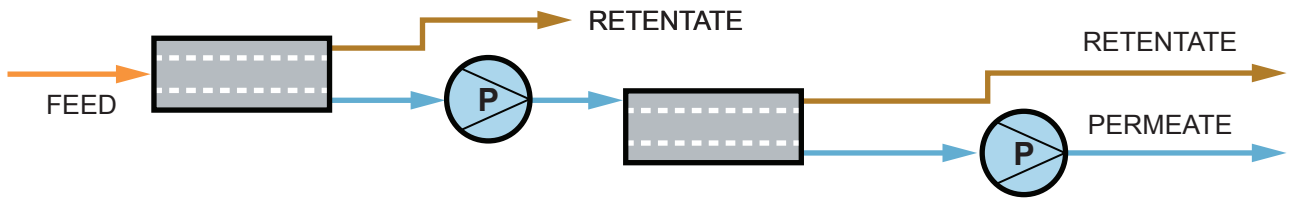
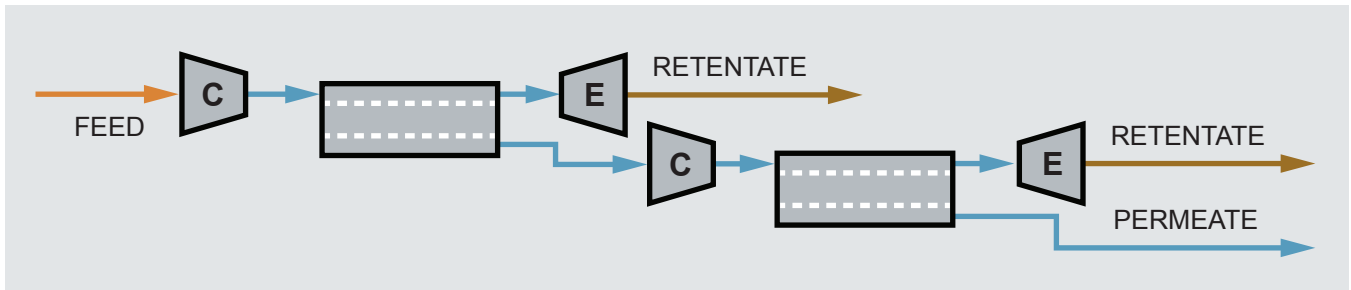
Hybrid combinations of solvent or sorbent with the membrane process have been emphasized

in the latest capture R&D in order to enhance performance or improve energy efficiency. For example, MTR's membrane process will be combined with an absorption column with 5 meters piperazine as the solvent at the initial separation. And the Gas Technology Institute is testing their membrane contactor, which incorporates a polyether ether ketone (PEEK) hollow fiber membrane having flue gas on one side of the membrane and amine MDEA solvent on the other side. Since the solvent takes the CO<sub>2</sub> permeate away from the membrane surface, the permeate side has near zero CO<sub>2</sub> partial pressure creating the separation driving force without compression or vacuum.

Gas separation membranes are currently used in industry for hydrogen separation in ammonia production and petrochemical plants, for separating nitrogen from air, removing CO<sub>2</sub> from natural gas, and recovering volatile organic compounds from air or nitrogen. The most commonly used membranes for gas separation are made of polymers. The types of membranes include polymers, ceramics, supported liquid membranes (facilitated transport membranes), metallic, and others such as zeolites.



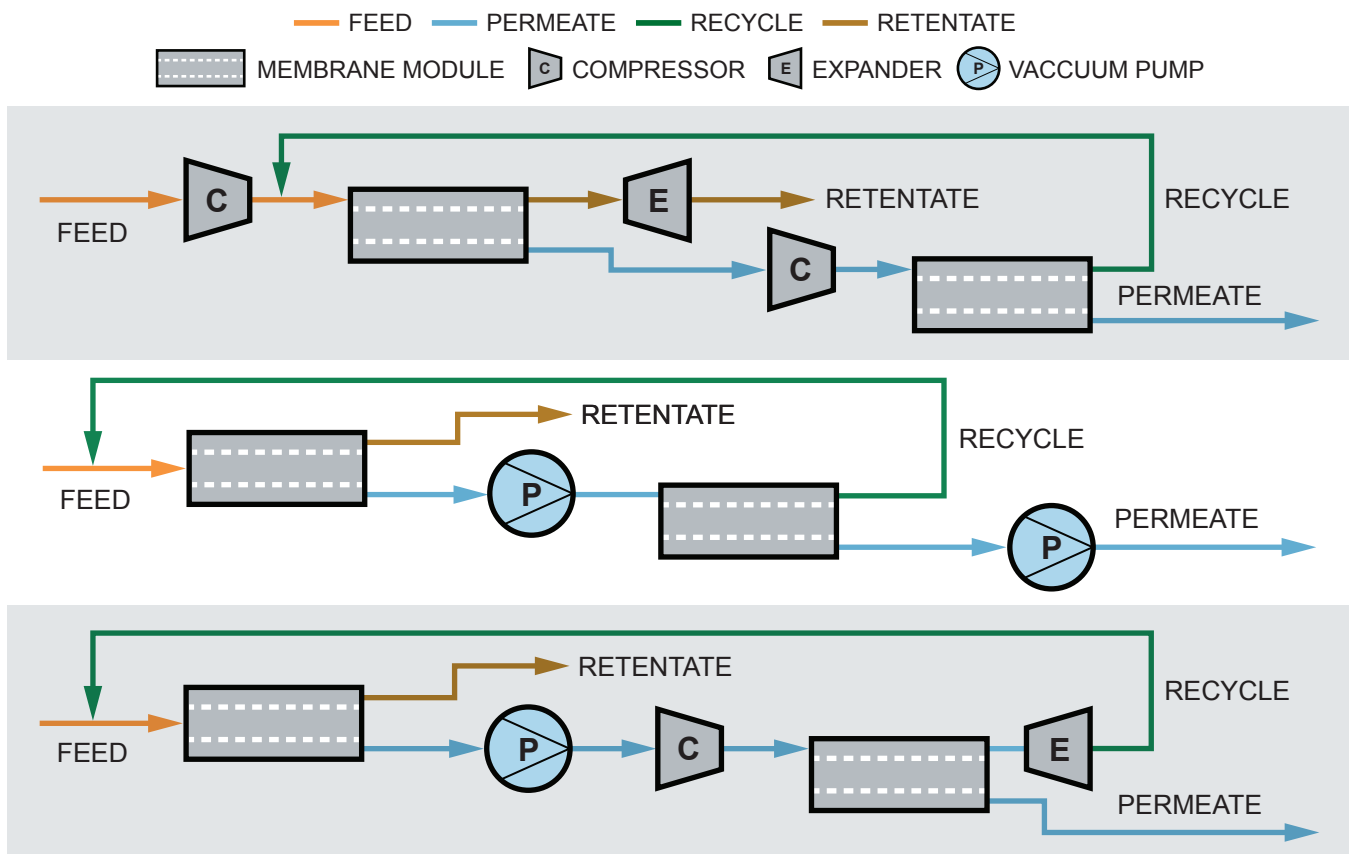
**SERIAL STRIPPER CONFIGURATION**



**SERIAL ENRICHER CONFIGURATION**

Source: DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015.

**Figure F-5.** Two-Stage Membrane Circuits – Serial Stripper Configuration and Serial Enricher Configuration



Source: DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015.

**Figure F-6.** Two-Stage Membrane Circuits – Serial Enricher with Recycle Configuration

Some of the membrane projects that have been tested or are ongoing are described here:

- Membrane Technology and Research developed a two-step membrane, with the first step operating at vacuum and at a low stage cut, and the second step incorporating sweep gas to provide a final CO<sub>2</sub> capture rate of 90%. After successfully operating a bench-scale unit at the NCCC beginning in 2011, MTR employed the lessons learned to construct and test a pilot-scale version. Continued development included operation of the larger-scale unit at a Babcock & Wilcox pilot coal-fired boiler for the first operation with CO<sub>2</sub> recycle to a boiler by a membrane process, larger-scale operation at TCM, and participation in a DOE Phase I project for demonstration at a commercial NRG Energy coal-fired power plant.
- Air Liquide evaluated a cold membrane process that combines high-permeance membrane materials with high CO<sub>2</sub> selectivity at subzero

temperatures to efficiently separate CO<sub>2</sub> from flue gas. Testing at NCCC focused on development and scale-up of the novel PI-2 membrane material featuring significantly higher CO<sub>2</sub> flux than commercially available material. The PI-2 module achieved 10 times the normalized CO<sub>2</sub> permeance of the commercial module. Air Liquide continues further testing at NCCC.

- Gas Technology Institute developed a hollow fiber gas-liquid membrane contactor to replace conventional packed-bed columns in solvent systems to improve CO<sub>2</sub> absorption efficiency. GTI conducted testing at NCCC in 2017 and 2018 and made plans for additional testing in 2019.

The performance of facilitated transport membranes have been assessed at the Norcem cement factory in Norway employing hollow fiber membrane modules with up to 18 m<sup>2</sup> of membrane area. Capture was from a high CO<sub>2</sub> content flue gas of 17 mol% wet basis. The test results showed

that 70 mol % CO<sub>2</sub> purity can be easily achieved in a single stage.<sup>23</sup>

The dense metal H<sub>2</sub>-selective membrane technology that allows production of CO<sub>2</sub>-free hydrogen from syngas has greatly progressed during the past 10 years. Since Tokyo Gas' demonstration of its membrane reformer with natural gas as the feed (H<sub>2</sub> production capacity of 40 Nm<sup>3</sup>/h, 150 kWth), using membranes with thicknesses of about 15 to 20 micrometers (μm),<sup>24</sup> efforts have been focused on the development of thinner palladium layers within the membranes (i.e., <5 microns). A 98-tube membrane separator (1.8 m<sup>2</sup>) has been tested in coal-derived syngas at the University of North Dakota Energy and Environmental Research Center.<sup>25</sup> Other activities include tests at the NCCC<sup>26</sup> under adverse industrial conditions. In 2017, Reinertsen AS and SINTEF demonstrated a 3 m<sup>2</sup> membrane module on a syngas-side stream of the Statoil Methanol Plant at Tjeldbergodden, Norway.<sup>27</sup>

Refer to Table F-4 for active and completed DOE/NETL membrane projects.

## B. Planned Work with Membranes

DOE/NETL's current focus for membrane capture includes development of low-cost, robust membranes that have characteristics of improved

permeability and selectivity, stability—both thermal and physical, and tolerance for flue gas contaminants or syngas, and integration capability into low pressure drop modules. Membranes for pre-combustion must also be capable of operating in system temperatures of up to 500°F.<sup>28</sup> The current and past technology projects for post- and pre-combustion as well as novel emerging membrane capture projects are listed in Table F-4.

For Phase I of the Transformational Large-Scale Pilots program (FOA 1788), MTR will be assembling a team and host site and a pre-FEED design basis for consideration in Phase II. Also, MTR will also be testing in the Engineering-Scale program at TCM with their Advanced Polaris CO<sub>2</sub> Membrane.

For FOA 1791 AOI 2, EPRI will perform an initial engineering design and cost estimate of a Post-Combustion CO<sub>2</sub> Capture system for Duke Energy's East Bend Station using membrane-based technology.

In developing transformational materials and processes, some of the membrane projects follow:

- Gas Technology Institute will perform tests on bench scale graphene oxide-based membranes and processes (GO-1 and GO-2 membranes integrated into the proposed process).
- MTR will also develop a composite membrane consisting of two parallel technology developments. First, is to double membrane permeance through overcoming flow restrictions by replacing conventional porous supports used to fabricate composite membranes by using self-assembly isoporous supports. Second is to double the mixed-gas selectivity of the MTR Polaris membrane by building on work for new materials by State University of New York at Buffalo.
- University of Kentucky Research Foundation will investigate a process with decoupling absorber kinetics and solvent regeneration through membrane dewatering and in-column heat transfer. The process consists of a temperature-controlled absorber,

23 U.S. Department of Energy, Office of Fossil Energy, "Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage," Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts' Workshop, September 2017. Mission Innovation.

24 Yasuda, I., Shirasaki, Y., Tsuneki, T., Asakura, T., Kataoka, A., and Shinkai, H. (2003). "Development of membrane reformer for highly-efficient hydrogen production from natural gas," *Proceedings of Hydrogen Power Theoretical & Engineering Solutions International Symposium V* (Hypothesis V), p. 97.

25 Schwartz, J., Makuch, D., Way, D. J., Porter, J. J., Patki, N., Kelley, M., Stanislawski, J. and Tolbert, S. (2015). "Advanced Hydrogen Transport Membrane for Coal Gasification," final report DE-FE0004908, U.S. Department of Energy.

26 Castro-Dominguez, B., Mardilovich, I. P., Ma, R., Kazantzis, N. K., Dixon, A. G., and Ma, Y. H. (2017). "Performance of a pilot-scale multitube membrane module under coal-derived syngas for hydrogen production and separation," *Journal of Membrane Science* 523, 515-525.

27 Peters, T. A., Rørvik, P. M., Sunde, T. O., Stange, M., Roness, F., Reinertsen, T. R., Ræder, J. H., Larring, Y., and Bredesen R. (2017). "Palladium (Pd) membranes as key enabling technology for pre-combustion CO<sub>2</sub> capture and hydrogen production," *Energy Procedia* 114, 37-45.

28 U.S. Department of Energy, National Energy Technology Laboratory. (April 2018). *DOE/NETL Capture Program R&D: Compendium of Carbon Capture Technology*, 04.2018-1000.

Post-Combustion Project Focus	Participant	Technology Maturity
<b>ACTIVE</b>		
Selective Membranes for <1% CO <sub>2</sub> Sources	Ohio State University	Lab
Subambient Temperature Membrane	American Air Liquide, Inc.	0.3-MWe
Polaris Membrane/Boiler Integration	Membrane Technology and Research, Inc.	1-MWe
<b>COMPLETED (in Appendix)</b>		
Inorganic/Polymer Composite Membrane	Ohio State University	Pilot-Scale, Actual Flue Gas
Composite Hollow Fiber Membranes	GE Global Research	Bench-Scale, Simulated Flue Gas
Low-Pressure Membrane Contactors (Mega-Module)	Membrane Technology and Research, Inc.	Bench-Scale, Simulated and Actual Flue Gas
Hollow-Fiber, Polymeric Membrane	RTI International	Bench-Scale, Simulated Flue Gas
Biomimetic Membrane	Carbozyme	Lab
Dual Functional, Silica-Based Membrane	University of New Mexico	Lab
Pre-Combustion Project Focus	Participant	Technology Maturity
<b>ACTIVE</b>		
Zeolite Membrane Reactor	Arizona State University	Bench-Scale, Actual Syngas
Mixed Matrix Membranes	State University of New York, Buffalo	Bench-Scale, Actual Syngas
PBI Polymer Membrane	SRI International	Bench-Scale, Actual Syngas
Two-Stage Membrane Separation: Carbon Molecular Sieve Membrane Reactor followed by Pd-Based Membrane	Media and Process Technology, Inc.	Bench-Scale, Actual Syngas
<b>COMPLETED</b>		
High-Temperature Polymer-Based Membrane	Los Alamos National Laboratory	Bench-Scale, Simulated Syngas
Dual-Phase Ceramic-Carbonate Membrane Reactor	Arizona State University	Lab
Pd-Alloys for Sulfur/Carbon Resistance	Pall Corporation	Lab
Hydrogen-Selective Zeolite Membranes	University of Minnesota	Bench-Scale, Simulated Syngas
Pressure Swing Membrane Absorption Device and Process	New Jersey Institute of Technology	Lab
Nanoporous, Superhydrophobic Membrane Contactor Process	Gas Technology Institute	Bench-Scale, Simulated Syngas
Polymer Membrane Process Development	Membrane Technology and Research, Inc.	Bench-Scale, Actual Syngas
Novel Concepts Project Focus	Participant	Technology Maturity
<b>ACTIVE</b>		
Electrochemical Membranes	FuelCell Energy Inc.	3-MWe
Hybrid GO-PEEK Membrane Process	Gas Technology Institute – GTI	Lab
Novel Concepts/ICE Membrane for Post-Combustion CO <sub>2</sub> Capture	Liquid Ion Solutions LLC	Lab
Novel Concepts/Encapsulation of Solvents in Permeable Membrane for CO <sub>2</sub> Capture	LLNL – Lawrence Livermore National Laboratory	Lab

Source: U.S. Department of Energy, National Energy Technology Laboratory. (April 2018). *DOE/NETL Capture Program R&D: Compendium of Carbon Capture Technology*, 04.2018–1000.

**Table F-4.** Membrane Projects in DOE/NETL Carbon Capture Program

a membrane-based dewatering unit, and a multiple-feed pressurized stripper. This process can be used with most advanced solvents.

### C. Challenges and Research Needs for Membranes

Over a brief period of about 12 years, membranes have entered the market and become the preferred capture approach for several applications. In reference to CCUS, membranes are efficient, compact and modular, simple to use, and environmentally friendly.

Polymeric membranes have been used extensively at large scale in hydrogen recovery, nitrogen production, natural gas treatment, and vapor recovery sectors.

Research for membranes focuses on polymeric, hybrid, carbon metallic, and ceramic membranes, as well as composite and dual-phase membranes. The two main areas of research are (1) developing an understanding of the transport phenomena at the membrane interface in new materials, and (2) fabrication of new design and methods to produce membrane structures or modules at large scale.

Recent investigations have shown the importance of understanding the membrane interfaces and how the properties here affect reactivity and transport processes. To make significant strides in membranes, the knowledge of how to control the properties at the interfaces is imperative.

Manufacture of novel membrane materials into effective membrane structures has many challenges, in the forming of a dense, thin layer of novel material on a support structure and in building the membrane structure into a mechanical module unit. An area of opportunity is the reduction of concentration polarization related to these high-flux membranes and where they are applied. Membrane separation properties such as surface absorption and diffusion will change with operating conditions.

Another area of research will be material specific. The concern is around trace components

in the feed gas and their effect on stability of the new membrane material.<sup>29</sup>

The organizations awarded DOE funding through FOA 1792 for membrane testing are the following:

- The Ohio State University is developing novel transformational polymer membranes and a two-stage process for CO<sub>2</sub> capture from flue gas. The proposed membrane material is a novel synthesized membrane material with simple membrane module fabrication.
- The State University of New York at Buffalo is developing advanced membranes that will be solubility-selective, mixed matrix membranes comprised of soluble metal-organic polyhedra in rubbery functional polymers for CO<sub>2</sub>/N<sub>2</sub> separation.

Other work is ongoing at the University of Colorado Boulder in fabricating and evaluating curable polymer membranes containing amine functionalities for use in highly selective removal of CO<sub>2</sub> from flue gas streams (aka CO<sub>2</sub> CCRIMP). Also, C-Crete Technologies LLC (C-Crete) is developing protocol to control and design nanoporous calcium-silicate materials with advanced properties for post-combustion CO<sub>2</sub> capture. The goal is to develop low-cost, energy efficient, and chemically/thermally stable calcium-silicate membranes with highly ordered and controllable pores.

### V. CRYOGENIC DISTILLATION AND THE CRYOGENIC PROCESS

Phase change can be used to separate components from a gas stream. This is typically accomplished by cooling the gas stream until one or more of the components change phase to either a dense liquid or solid phase that can be physically separated from the noncondensing species. CO<sub>2</sub> capture through phase change has been proposed and developed as a means of removing CO<sub>2</sub> from power plant flue-gas streams.

<sup>29</sup> U.S. Department of Energy, Office of Fossil Energy, "Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage," Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts' Workshop, September 2017. Mission Innovation.

There are several major advantages of cryogenic CO<sub>2</sub> capture over amine capture systems, including that there is a physical rather than a chemical separation performed, there is no impact on the steam cycle of the associated power plant, the CO<sub>2</sub> is pumped to pressure as a liquid minimizing compression energy, and the energy consumption per ton of CO<sub>2</sub> captured overall is low. Drawbacks include difficulties associated with solids formation and handling and large heat transfer areas with tight temperature approaches.<sup>30</sup> As shown in the TRL chart in the Executive Summary of this report, cryogenic process technologies range from TRL 3 to TRL 6.

## A. History of Testing the Cryogenic Process

Cryogenic CO<sub>2</sub> capture processes come in many forms such as a thermal swing process, an inertial carbon extraction system, cryogenic CO<sub>2</sub> capture external cooling loop, and cryogenic CO<sub>2</sub> capture compressed flue gas.

A thermal swing process freezes CO<sub>2</sub> as a solid onto a surface of a heat exchanger. Alstom and Shell have investigated this process, but it has slowed investigation. In an inertial carbon extraction system, the process expands flue gas through a nozzle and a cyclone separates the solids from the gas. The process of cryogenic CO<sub>2</sub> capture has energy efficiency advantages that stem from ease of liquid-solid separation and this process pressurizes the CO<sub>2</sub> when it is a liquid as opposed when it is a gas. Another advantage is that other gas impurities are separated from the gas.<sup>31</sup>

In 1986, ExxonMobil demonstrated their Controlled Freeze Zone (CFZ) technology at the Clear Lake Pilot Plant near Houston by processing natural gas with levels of CO<sub>2</sub> as high as 65%. This technology removes impurities from natural gas

using cryogenic distillation methods. In 2008, a commercial demonstration plant was constructed at its Shute Creek Treatment Facility in LaBarge, Wyoming, with formal testing from March 2012 to November 2013. ExxonMobil is offering CFZ technology commercially.

Sustainable Energy Solutions (SES) LLC has developed a process, cryogenic CO<sub>2</sub> capture (CCC), that has process flexibility, does not need to integrate with the power plant (it is plug and play with only electricity needed), can load follow, and has the ability to capture other flue gas trace components, SO<sub>x</sub>, NO<sub>x</sub>, and mercury.<sup>32</sup>

CCC is a retrofit, post-combustion method that uses phase change to separate CO<sub>2</sub> and other pollutants from gases. CO<sub>2</sub> is cooled to a low temperature (about -140°C) that it de-sublimates, or changes from a gas to a solid. The solid CO<sub>2</sub> is separated from the remaining light gases, melted, pressurized, and delivered at pipeline pressure. The technology originated at Brigham Young University and was developed with support from DOE ARPA-e's IMPACCT program.

SES has operated several small pilot units (1 TPD and 0.25 TPD) from 2014 through the present with 95-99% capture at a Pacificorp power station near Glenrock, Wyoming (coal), Holcim's Devil's Slide plant in Utah (cement processing), and at Brigham Young University's heating plant (coal and natural gas), and an experimental reactor (coal, natural gas, and biomass).<sup>33</sup> Cryopur, EReiE and others have performed pilot tests and GE has done simulation work to evaluate the technology.<sup>34</sup> SES's cryogenic process was part of the demonstration of the first project to collect cement kiln CO<sub>2</sub> for utilization in concrete production. Emissions from the Cementos Argos' Roberta cement plant near Calera, Alabama, were captured by SES. The captured CO<sub>2</sub> was transported and used in concrete operations equipped with CarbonCure's CO<sub>2</sub> utilization technology. This project was an extension of

30 Berger, A. et al. "Evaluation of Cryogenic Systems for Post Combustion CO<sub>2</sub> Capture," 14th Greenhouse Gas Control Technologies Conference, Melbourne, 21-26 October 2018 (GHGT-14).

31 Jensen, M., (2015). "Energy Process Enabled by Cryogenic Carbon Capture." Theses and Dissertations. 5711. [https://scholarsarchive.byu.edu/etd/5711?utm\\_source=scholarsarchive.byu.edu%2Fetd%2F5711&utm\\_medium=PDF&utm\\_campaign=PDFCoverPages](https://scholarsarchive.byu.edu/etd/5711?utm_source=scholarsarchive.byu.edu%2Fetd%2F5711&utm_medium=PDF&utm_campaign=PDFCoverPages).

32 Herzog, H. (2018). *Carbon Capture*. Boston, MA: Massachusetts Institute of Technology Press.

33 Sayre, A. et al. (July 2017). "Field Testing of Cryogenic Carbon Capture." CMTC-486652-MS.

34 IEAGHG, "Assessment of emerging CO<sub>2</sub> capture technologies and their potential to reduce costs," 2014/TR4, December 2014.

the Team CarbonCure’s participation in the NRG COSIA Carbon XPRIZE Challenge.<sup>35</sup>

Using the same cost assumptions in the *NETL Cost and Performance Baseline* report Volume 1 Revision 2a, September 2013, the CCC cost is reported at \$35/tonne CO<sub>2</sub> avoided (~\$30/tonne captured) with no plant integration. Using existing plant infrastructure should reduce the cost further.<sup>36</sup>

## B. Planned Work with the Cryogenic Process

SES is preparing for a 500+ hour test at another Pacificorp Power Plant and is designing a 100TPD system (commercial-scale for industrial sector, pilot-scale for power generation) for further testing.<sup>37</sup> In the Post-Combustion Novel Concepts area, DOE/NETL has two active projects for cryogenic separation for capture with SES and Orbital ATK (Table F-5).<sup>38</sup>

## C. Challenges and Research Needs for Cryogenic Process

Carbon dioxide undergoes deposition to form a solid when condensed below its triple point pressure of 517 kPa. When a component undergoes deposition in a stream that is being cooled, it does so on the lowest temperature surface, forming a barrier to heat transfer and plugging

the flow of traditional heat exchangers. The difficulty of removing a solid through deposition in a continuous process is best illustrated by looking at moisture removal. Dehydrating gas streams above 0°C is almost exclusively accomplished through moisture condensation and liquid collection. However, water forms solid ice below 0°C, making a continuous dehydration process that uses phase change extremely difficult. Instead, a range of dehydration options exist for low dew-point applications that include liquid desiccants, such as glycols, and solid desiccants, such as silicas and zeolites.

Cryogenic gas separations are used at large scale—primarily for air separation operations. For cryogenic air separation the inlet air is dehydrated, scrubbed of CO<sub>2</sub>, then chilled, liquefied and distilled to separate air into its individual components of oxygen, nitrogen, and other components at very low temperatures. The dehydration and CO<sub>2</sub> removal pretreatment steps are to remove the two species that would form a solid as they are chilled at atmospheric pressure. For cryogenic CO<sub>2</sub> capture, moisture removal presents a similar challenge. Below 0°C the gas stream either has to be dehydrated to a dew point of approximately -100°C (<0.1 PPM) or cooled in a way that does not involve heat transfer through fixed surfaces.

For all cryogenic systems, thermal integration and temperature management is required to minimize the energy consumption of the process. Thermal recuperation that uses the available cooling potential in cold internal streams or products to cool incoming gas or internal streams has to be carefully designed to minimize the exergy loss due to internal heat transfer or rejection to the environment. An idealized cryogenic CO<sub>2</sub> capture process could be envisioned in which there is no lost work from

35 Smith, M. (February 2018). “CarbonCure consortium closes the carbon loop for the cement and concrete industries,” *JWN Energy*, <https://www.jwnenergy.com/article/2018/2/carbon-cure-consortium-closes-carbon-loop-cement-and-concrete-industries/>.

36 Sayre, A. et al. (July 2017).

37 Sayre, A. et al. (July 2017).

38 U.S. Department of Energy, National Energy Technology Laboratory. (April 2018). *DOE/NETL Capture Program R&D: Compendium of Carbon Capture Technology*, 04.2018–1000.

Project Focus	Participant	Technology Maturity
Novel Concepts/Cryogenic Carbon Capture Process	Sustainable Energy Solutions, LLC	Bench-Scale, Actual Flue Gas
Supersonic Inertial CO <sub>2</sub> Extraction System	Orbital ATK Inc.	Bench-Scale, Simulated Flue Gas

**Table F-5.** Cryogenic Process Projects in DOE/NETL Carbon Capture Program



heat transfer or heat loss. One would then be able to compare existing processes to this idealized process to benchmark performance and understand potential for improvements.<sup>39</sup>

A challenge for using cryogenics for flue gases is that CO<sub>2</sub> does not form a liquid at atmospheric pressures. Pure CO<sub>2</sub> gas forms a solid (dry ice) when it is cooled to -78.5 C (its sublimation point). So, cryogenic separation of CO<sub>2</sub> from flue gas is possible, but the formation of solids makes it difficult.<sup>40</sup> Equipment for the technology typically consists of designs and construction of refrigeration systems and heat exchangers that are well-developed. However, the engineering of cyclic operation for frosting and defrosting at a reliable, commercial scale may be difficult. A

39 Berger, A. et al. "Evaluation of Cryogenic Systems for Post Combustion CO<sub>2</sub> Capture," 14th Greenhouse Gas Control Technologies Conference Melbourne, 21-26 October 2018 (GHGT-14).

40 Herzog, H. (2018). *Carbon Capture*. Boston, MA: Massachusetts Institute of Technology Press.

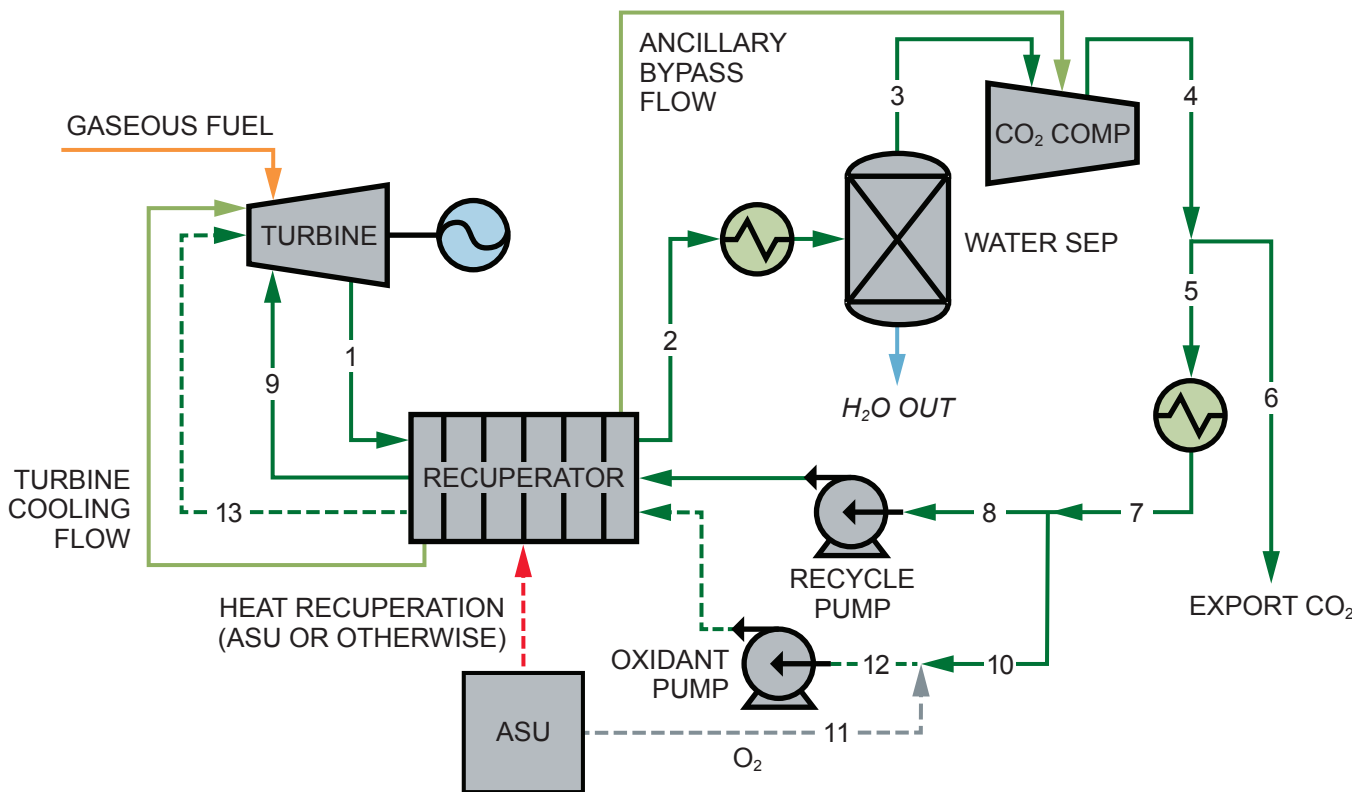
test at larger scale is the key path to commercialization.<sup>41</sup>

## IV. ALLAM-FETVEDT CYCLE

### A. Allam-Fetvedt Cycle Process

The Allam-Fetvedt (AF) cycle is a process that generates power from hydrocarbons while capturing the generated CO<sub>2</sub> and water. As depicted in Figure F-7, the AF cycle takes a novel approach to reducing emissions from fossil fuel power generation through the use of an oxy-combustion cycle that employs high-pressure supercritical CO<sub>2</sub> as a working fluid in a highly recuperated manner. At the core of the cycle is a supercritical CO<sub>2</sub> loop, where high-pressure CO<sub>2</sub> passes through a turbine, is cooled to remove water and impurities, and then is re-pressurized and reheated in a heat

41 IEA Greenhouse Gas R&D Programme. (December 2014). *Assessment of emerging CO<sub>2</sub> capture technologies and their potential to reduce costs*, 2014/TR4.



\* ASU = air separation unit

Source: Allam, R. et al. (2017). "Demonstration of the Allam Cycle: An update on the development status of a high efficiency supercritical carbon dioxide power process employing full carbon capture," *Energy Procedia*, Vol. 114, pages 5948-5966.

**Figure F-7.** Process Schematic of a Simplified Commercial-Scale Natural Gas Allam-Fetvedt Cycle

exchanger against the hot turbine exhaust stream and returned to the combustor. The inherent operational characteristics of the AF cycle allow it to avoid the necessity of additional capture, clean-up, and compression systems for CCUS. The AF cycle is able to utilize a variety of hydrocarbon fuels. The TRL chart in the Executive Summary of this report shows AF cycle technology ranging from TRL 4 to TRL 6, based on the U.S. DOE's definitions.

The Allam-Fetvedt cycle is most simply explained when plotted on a pressure-enthalpy (P-H) diagram for carbon dioxide. The P-H diagram shown in Figure F-8 has pressure (P) logarithmically spaced on the x-axis and enthalpy (H), a measure of energy, is linearly spaced on the y-axis.<sup>42</sup> Points on this diagram represent the conditions of the CO<sub>2</sub> working fluid at various points within the AF cycle. Entropy, a measure of a system's thermal energy unavailable for conversion into mechanical work, is represented by the beige lines. These entropy lines should avoid being crossed when moving up and down in pressure. For example, in the turbine this is represented by the line going from the upper right of the diagram down to the lower left (labelled "2" in Figure F-8). Moving from right to left along the x-axis represents the energy that is generated, and the right-left distance of line "2" is the amount of power the turbine produces. Moving from left to right along the x-axis requires thermal energy to be injected into the system (such as via combustion of fuel). Temperature is represented by the vertical/semivertical blue lines.

To the right, temperature and enthalpy move together, but the temperature lines move very differently. Note that at the left part of line "3," the temperature lines are clumped together. Observe the small amount of enthalpy that leaves the system from a drop in temperature of five of the blue lines. Next, focus on line "6." For a temperature rise of five blue lines, notice how much more enthalpy is created in the system. One of the

most important advantages of the AF cycle comes the exploitation of this difference between the left part of line "3" and line "6."

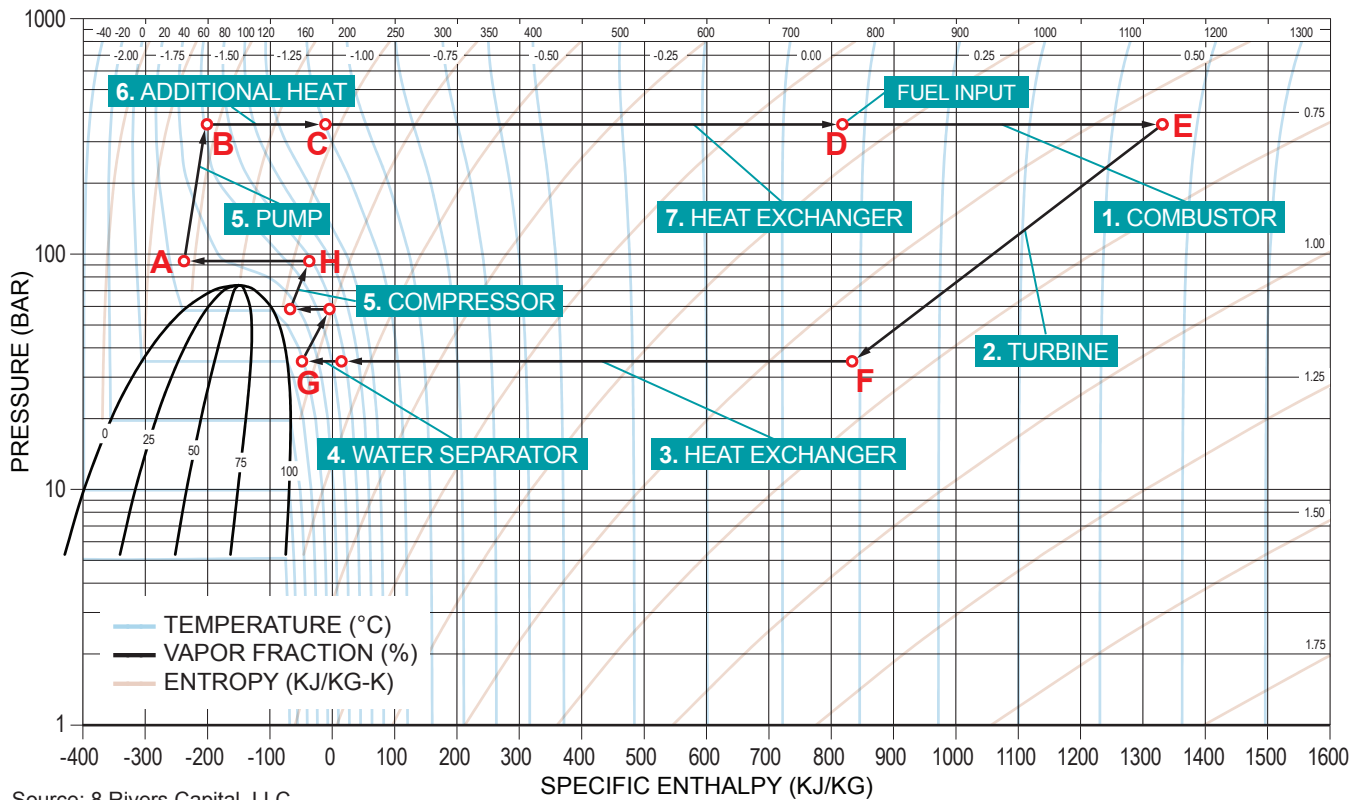
The black parabola on the far left represents the bi-phasic "dome" for CO<sub>2</sub>. Within this dome CO<sub>2</sub> is a mixture of both gas and liquid. At conditions to the left of the dome, CO<sub>2</sub> is liquid. At conditions to the right, CO<sub>2</sub> is a gas. Above the top of the dome, CO<sub>2</sub> becomes supercritical. In the supercritical realm, CO<sub>2</sub> does not undergo a "phase transition" (changing from liquid to gas, and vice versa); instead, CO<sub>2</sub> flows like a liquid while at the same time filling the space it occupies.

Another important aspect of the AF cycle can be seen by following the beige entropy lines. Think of these as "railroad tracks." Thus, on the right, when the gases are going through the turbine, the drop-in pressure follows the railroad tracks down, and the turbine produces the amount of energy equal to the difference between the enthalpy value at the upper right of the diagonal line and the enthalpy at the lower left of the same line. By contrast, on the left, these railroad tracks are steeper, and those for the pump are steeper (nearly vertical) than those for the compressor. That means the system uses less energy to increase in pressure than the energy it produced in the turbine from the drop-in pressure. Further, on the left, note that less energy is required by the pump than to compressor (the entropy lines are steeper for the former than the latter). The AF cycle exploits this fact to increase its efficiency.

The system design point is where the turbine exhaust stream goes into the heat exchanger (where lines two and three meet at point F). The limitation here is dictated based on commercially available alloys capable of operating under the conditions demanded by the AF cycle. A detailed stepwise explanation of the thermodynamic AF cycle (Figure F-8) is as follows:

- A-B: Shaft-driven wheel pump of recycled CO<sub>2</sub> to circa 110 bar pressure
- B-C: Heating of recycled CO<sub>2</sub> (45% proportion) and oxidant stream in recuperative heat exchanger (stage 1 and 2) recovering low grade heat from turbine exhaust flow

<sup>42</sup> Enthalpy and temperature are similar concepts, but enthalpy is a true measure of the usable energy that goes into and out of a system. For example, a certain amount of heat (enthalpy) is needed to take water from room temperature up to just below the boiling point. Yet, seven times that amount of heat (enthalpy) is required to take water from just below the boiling point to just over the boiling point. Despite that massive amount of heat, the temperature of water barely changed. Yes, a watched pot really does not boil!



Source: 8 Rivers Capital, LLC.

**Figure F-8.** Pressure-Enthalpy Diagram of the Allam-Fetvedt Cycle

- C-D: Heating of recycled CO<sub>2</sub> and oxidant stream in recuperative heat exchanger (stage 3) recovering
- D-E: Primary combustor heat input from oxy-combustion and sCO<sub>2</sub> recycle flow up to turbine inlet
- E-F: Turbine expansion work output from circa 300 bara to 30 bara
- F-G: Cooling of turbine exhaust (predominantly CO<sub>2</sub>/H<sub>2</sub>O vapor) in recuperative heat exchanger (stages 3, 2, and 1)
- G-H: Multi-stage compression of recycle CO<sub>2</sub> to required pump inlet pressure
- H-A: Aftercooler.

## B. Planned Work with Allam-Fetvedt Cycle – NET Power

In 2009, 8 Rivers Capital, a technology development firm set out to develop an idea for a new type of clean coal power plant. In 2011, 8 Rivers and NET Power entered into an agreement with

Toshiba for the turbine and combustor engineering program, then with The Shaw Group (now McDermott) invested \$50M in 2012, followed by Exelon’s \$100M in 2014, and in October of 2018 Oxy Low Carbon Ventures, Occidental Petroleum’s venture arm dedicated to reducing/eliminating emissions, invested an undisclosed sum. The partnership has provided the funding necessary to build and operate a 50MWth NET Power test facility in La Porte, Texas, and to begin commercial deployments happening now. Construction of this first-of-a-kind project began in March 2016 and was completed in December 2017. The facility completed commissioning in April 2018, with first fire occurring in May, and combustor testing successfully concluded in August. The completion of combustor testing proved basic feasibility, operability, and safety of the combustor and the fundamental Allam-Fetvedt cycle itself. Full system tests are currently ongoing.

The first stage of testing at the demonstration facility utilized the full cycle in addition to a specially designed commercial-scale combustor

Technology/ Project	Description	Organization	Award
Phase- Changing Ionic Liquids	Using special ionic liquids (ILs) to remove CO <sub>2</sub> from the gas exhaust of coal-fired power plants. New class of ILs that are solid at room temperature and change to liquid when they bind to CO <sub>2</sub> . Upon heating, the CO <sub>2</sub> is released for storage, and the ILs re-solidify and donate some of the heat generated in the process to facilitate further CO <sub>2</sub> release.	University of Notre Dame	\$2,559,562
Hybrid Solvent- Membrane CO <sub>2</sub> Capture	Hybrid approach to capture CO <sub>2</sub> . CO <sub>2</sub> is removed as flue gas is passed through an aqueous ammonium-based solvent. Carbon-rich solution from the CO <sub>2</sub> absorber is passed through a membrane that is designed to selectively transport the bound carbon, enhancing its concentration on the permeate side. Combining the best of both membrane- and solvent-based carbon capture technologies.	University of Kentucky	\$1,516,908
Gelled Ionic Liquid-Based Membranes	Using a membrane made of a gelled IL to capture CO <sub>2</sub> from the exhaust of coal-fired power plants. The membranes are created by spraying the gelled ILs in thin layers onto porous support structures using a specialized coating technique. The new membrane is highly efficient at pulling CO <sub>2</sub> out of coal-derived flue gas exhaust while restricting the flow of other materials through it. Design involves few chemicals or moving parts. More mechanically stable than current technologies. The team is now working to further optimize the gelled materials for CO <sub>2</sub> separation and create a membrane layer that is less than 1 micrometer thick.	Colorado University Boulder	\$3,650,557
Metal Organic Framework Research	Identification of the best MOFs for use in capturing CO <sub>2</sub> from the flue gas of coal-fired power plants. Use of high-throughput instrumentation to analyze nearly 100 materials at a time, screening them for the characteristics that optimize their ability to selectively adsorb CO <sub>2</sub> from coal exhaust. The model predicts a significant decrease in parasitic energy penalty from 30% for traditional processes to 15% for an optimized MOF. UC Berkeley also demonstrated scalability of the optimized adsorbent to over 300g and prepared a pelletized form that is suitable for testing in fixed bed reactors.	University of California Berkeley	\$4,961,298
Synthetic Catalysts for CO <sub>2</sub> Storage	A synthetic catalyst is designed with the same function as carbonic anhydrase, an enzyme in the human lungs that helps to separate CO <sub>2</sub> from the blood. The catalyst can be used to quickly capture CO <sub>2</sub> from coal exhaust, just as the natural enzyme does in our lungs. Development of encapsulating chemical solvents in permeable microspheres that will greatly increase the speed of binding of CO <sub>2</sub> .	Lawrence Livermore National Laboratory	\$3,632,000
Composite Membranes for CO <sub>2</sub> Capture	Development of an enhanced membrane by fitting MOFs, into hollow fiber membranes. Analyzing MOFs based on their permeability and selectivity toward CO <sub>2</sub> . The composite membrane would be highly stable, withstanding the harsh gas environment found in coal exhaust.	Georgia Tech Research Corporation	\$998,928
CO <sub>2</sub> Capture with Liquid- to-Solid Absorbents	Development of a unique CO <sub>2</sub> capture process in which a liquid absorbent changes into a solid upon contact with CO <sub>2</sub> . Once in solid form, the material can be separated and the CO <sub>2</sub> can be released for storage by heating. Upon heating, the absorbent returns to its liquid form, where it can be reused to capture more CO <sub>2</sub> . The approach is more efficient than other solvent-based processes because it avoids the heating of extraneous solvents such as water.	GE	\$3,692,967
Better Enzymes for Carbon Capture	Development of new and efficient forms of enzymes known as carbonic anhydrases. Carbonic anhydrases are common and are among the fastest enzymes, but they are not robust enough to withstand the harsh environment found in the power plant exhaust steams. The enzymes' properties will be modified to withstand high temperatures and large swings in chemical composition.	Codexis	\$4,657,045
Electro- chemical Carbon Capture	Development of an electrochemical technology to capture CO <sub>2</sub> . This technology cuts both the energy requirements and cost of CO <sub>2</sub> capture technology in half compared to today's best methods. This technology will increase the cost of electricity generation by 85%.	Arizona State University	\$3,471,515
Syngas into Fuel	An iron-based material along with a unique process are developed to convert syngas into electricity, H <sub>2</sub> , and/or liquid fuel with zero CO <sub>2</sub> emissions. An iron-based oxygen carrier is used to generate CO <sub>2</sub> and H <sub>2</sub> from syngas in separate, pure product streams by means of a circulating bed reactor configuration. The end products of the system are H <sub>2</sub> , electricity, and/or liquid fuel, all of which are useful sources of power that can come from coal or syngas derived from biomass.	Ohio State University	\$7,099,904

**Table F-6. Emerging CO<sub>2</sub> Capture Technologies**

test stand to accommodate the testing of the commercial-scale combustor in a recirculating fashion akin to the final design and operation of the overall cycle. The second stage, underway at the time of this report, utilizes the full cycle design to accommodate integrated hot operation of both the combustor and turbine for full process demonstration. The facility will likely be used into the future as a test facility for various types of equipment and sub-systems that have the potential to increase the cycles performance. In addition to the demonstration plant, NET Power is developing a full commercial-scale offering and has completed a comprehensive pre-FEED (Front End Engineering Design) to confirm preliminary

information on the expected economics of its 300 MWe natural gas plant. At the time of this study engineering work on several commercial units globally were underway.

## VII. U.S. DOE FUNDED PROJECTS

Table F-6 gives descriptions of novel, transformational projects that have been funded by DOE, several of which are hybrid capture approaches.<sup>43</sup>

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<sup>43</sup> Carbon Sequestration Leadership Forum. "Supporting Development of 2nd and 3rd Generation Carbon Capture Technologies: Mapping technologies and relevant test facilities," Rev: 08 and final December 16, 2015.



