

NATIONAL PETROLEUM COUNCIL

Meeting the Dual Challenge

*A Roadmap to At-Scale Deployment of
Carbon Capture, Use, and Storage*

Appendix F

Emerging CO₂ Capture Technologies

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I. INTRODUCTION

This appendix describes less mature carbon dioxide (CO₂) capture technologies, what this study calls Emerging CO₂ Capture Technologies. The appendix divides these into four 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

This appendix concludes with a fifth 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 CO₂ resulting in a smaller absorber volume, a large CO₂ carrying capacity to reduce the amount of solvent needed to separate the CO₂ from the flue gas, a low enthalpy of reaction with CO₂ to reduce the energy needed to break the amine-CO₂ 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.

A. History of Testing Advanced Solvents

The DOE has developed a Program Portfolio of projects that addresses the key challenges of solvent based CO₂ capture. The projects, focused on addressing key barriers in technology deployment, are shown in Table F-1 from the DOE/National Energy Technology Laboratory (NETL) Carbon Capture Program—Carbon Dioxide Capture Handbook, August 2015.

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

PERFORMER	PROJECT FOCUS	BENEFITS	SCALEUP	CAPTIAL COSTS	PARASITIC LOAD	PROCESS INTEGRATION	WATER USE
Akermin	Enzyme catalyzed	Low regeneration energy			X		
Battelle PNNL	Non-aqueous CO ₂ -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	

A number of advanced solvents, in addition to process improvements and hybrid systems with potential to reduce CO₂ 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 CO₂ with at least 90% CO₂ capture, the technology was selected for funding by DOE for 10-MW demonstration at the University of Illinois.

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 Test Center 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.

Research Triangle Institute (RTI) 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 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 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 CO₂ 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 CO₂ capture. Parasitic load includes the work lost due to steam consumption for CCS and capture auxiliaries plus the energy required for compression of CO₂ 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 2015.¹

¹ Brickett, L., "DOE/NETL Carbon Capture Program-Carbon Dioxide Capture Handbook," (August 2015) U.S. Department of Energy, National Energy Technology Laboratory.

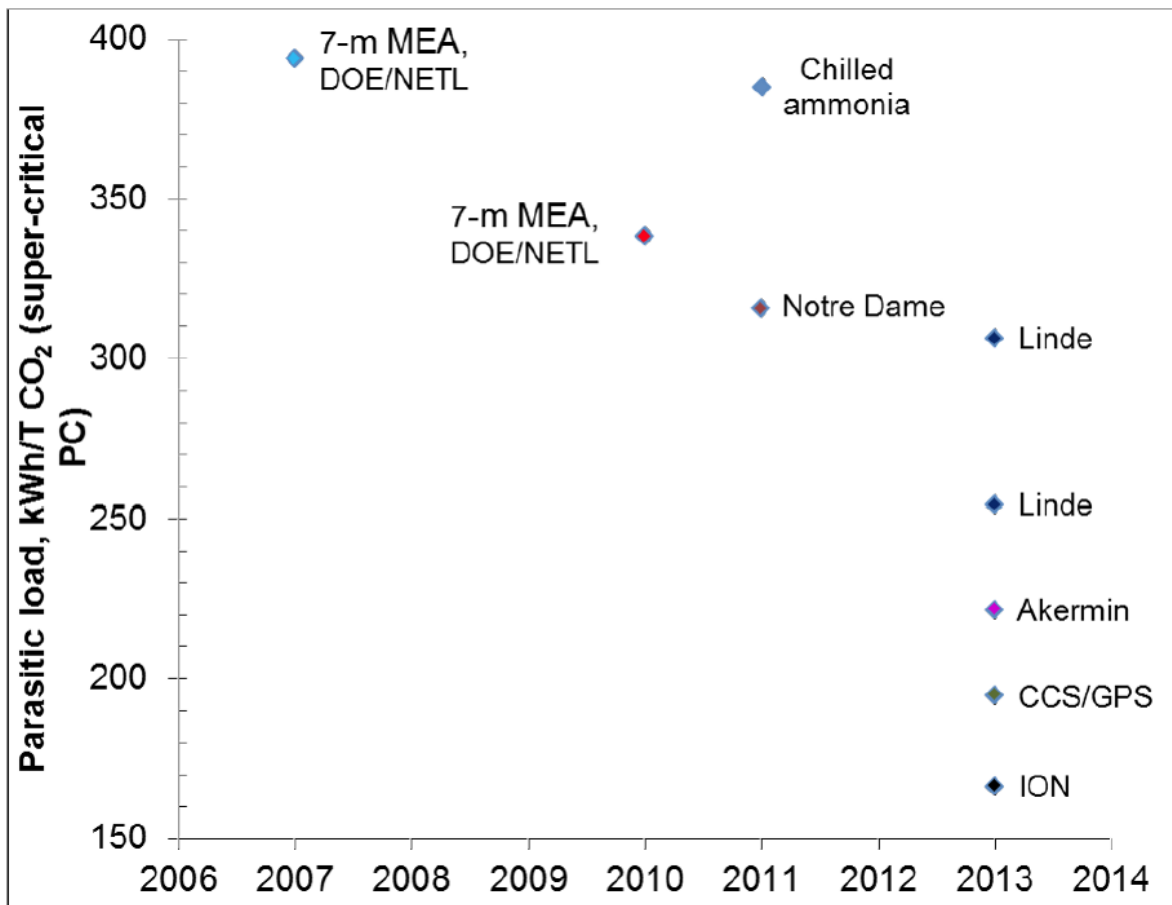


Figure F-1. Reduction in Parasitic Load for Solvent-Based Capture DOE/NETL Projects
 Source: DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015

B. Future Work with Advanced Solvents

DOE’s Transformational Large-Scale Pilots program began its Phase I kickoff in June 2018.² 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 design basis, and cost share for Phase II. Two of the CO₂ 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 CO₂ Capture Technology.

The University of Kentucky Research Foundation will be furthering their UKy-CAER Heat-Integrated Transformative CO₂ Capture Process.

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

DOE is supporting testing to scale up CO₂ capture technologies at engineering scale using existing host site infrastructure at TCM. Projects include the following:

- Research Triangle Institute’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 CO₂ capture system, a commercial-scale TEA will be performed by ION Engineering with a nonaqueous solvent and by the University of North Dakota with an amine solvent.

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 CO₂ absorption process.
- SRI International will develop further a water-lean, mixed salt based solvent technology.³
- 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-2.⁴

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

Project Focus	Participant	Technology Maturity
ACTIVE		
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 ₂ 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 ₂ Capture Materials	University of Notre Dame	Lab
Direct Air Capture from Dilute CO ₂ Sources	Carbon Engineering LTD	Pilot-Scale
Nonaqueous Solvent	RTI International	Bench-Scale, Actual Flue

³ Litynski, J. (2018). Transformational Large Scale Pilots – Progress and Next Steps [PowerPoint slides].

⁴ U.S. Department of Energy. (April 2018). “Compendium of Carbon Capture Technology,” 04.2018–1000, National Energy Technology Laboratory.

		Gas
Linde/BASF CO ₂ 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 ₂ -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
COMPLETED		
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 ₂ 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 ₂ Capture Using AC-ABC Process	SRI International	0.15-MWe

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 CO₂ 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, alkylcarbonate, or azoline-carboxylate. These solvents are designed to be nonvolatile to minimize fugitive emissions. The enthalpies of CO₂ absorption for the water-lean solvents are comparable to those of aqueous solvents at -50 to -90 kilojoules per mol CO₂ (kJ/mol CO₂), 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 a lower reboiler energies of 1.7 to 2.6 gigajoules per tonne CO₂ (GJ/tonne CO₂) compared to the DOE NETL Case 10 with 3.5 GJ/tonne CO₂ and the second-generation amine scrubbing performance of 2.2-2.4 GJ/tonne CO₂. An increase of 2.1% to 7.1% in net plant efficiency is also expected compared to DOE NETL Case 10 with these solvents.⁵ 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 use significantly less energy than a second-generation aqueous amine and that the second-generation

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 CO₂ Capture: Fundamentals, Uncertainties, Opportunities, and Outlook." *Chemical Reviews* 117, p. 14.

amine scrubbing systems lose little efficiency and can be implemented with little additional capital cost.⁶

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 liquid/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 CO₂ 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 CO₂ at high pressure
- Precipitate bound CO₂ 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 CO₂ sources from a wide variety of industrial applications.⁷

4. Challenges to Power Retrofits

A challenge to the retrofitting of CO₂ capture in the power sector for mature amine technology is amine's susceptibility to parasitic, irreversible reactions with other species in the flue gas,

⁶ Rochelle, G. and Yuan Y. (April 2018) "Water-lean solvents for CO₂ Capture will Not Use Less Energy Than Aqueous Amines," Greenhouse Gas Control Technologies 14.

⁷ "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.

including SO_x, NO_x, mercury, and particulates. Therefore, a retrofit using amine technology is typically preceded by other scrubbers that remove these pollutants. Unfortunately, the cost of installing these scrubbers to enable a CO₂ 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_x to their elemental gases. The team is working to extend the technology to CO₂ capture.⁸

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.⁹

III. ADSORBENTS AND ADSORPTION

A. History of Testing Adsorbents

The removal of CO₂ from gas streams via adsorption is not a new concept. Throughout the manned space missions, solid sorbents have been used to remove CO₂ 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 CO₂ 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 CO₂.

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 Adsorbent (PSA) systems, with commercially available sorbents such as molecular sieve (zeolites), activated carbon, activated alumina, or silica gel, are used to create relatively pure H₂ from the syngas to be used in the refinery process. At Valero Energy’s Port Arthur Texas refinery, sorbents in a vacuum swing adsorption process are separating out the CO₂ from the steam methane reformer syngas for injection in the West Hastings oil field for enhanced oil recovery. The CO₂ separation takes place upstream of the existing PSA process for capturing H₂.¹⁰

To advance sorbents as a viable CO₂ capture solution, research and development has been underway to demonstrate sorbents’ low cost, thermal and chemical stability, resistance to

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

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

¹⁰ Brickett, L., “DOE/NETL Carbon Capture Program-Carbon Dioxide Capture Handbook,” (August 2015) U.S. Department of Energy, National Energy Technology Laboratory.

attrition, low heat capacity, high CO₂ loading capacity, and high selectivity for CO₂. CO₂ 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.

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 CO₂. Figure F-2 shows the progress for sorbent-based capture to reduce the parasitic load.¹¹

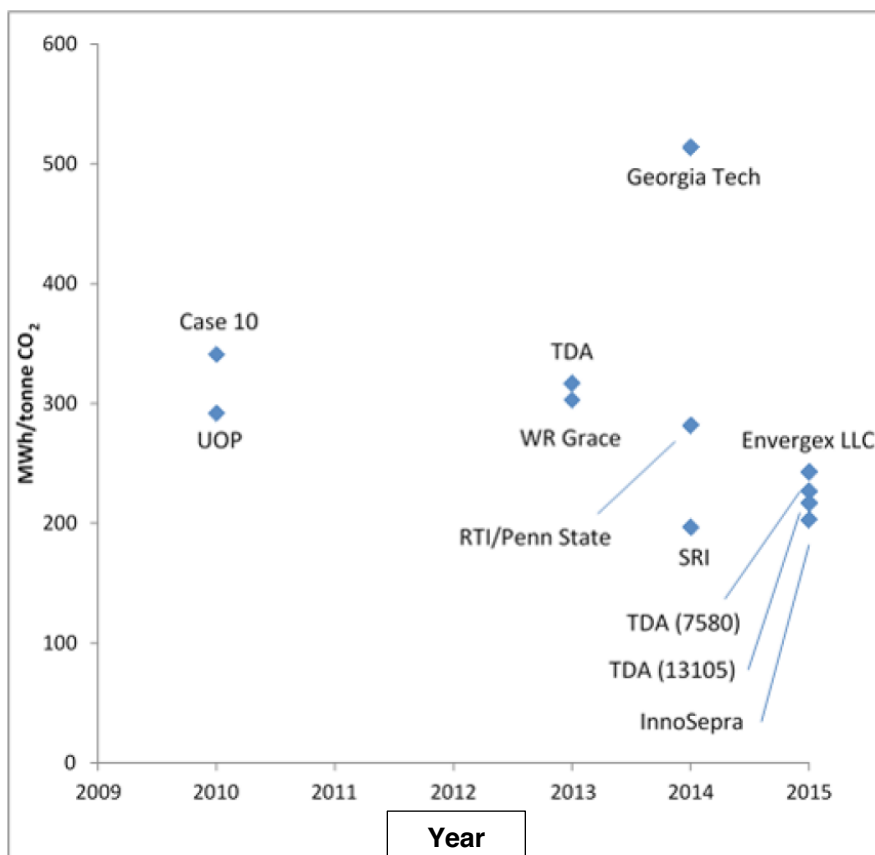


Figure F-2. Progress in Reducing the Energy Penalty of Sorbent-Based Capture

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 CO₂ capture capacity. Following testing at the center, NETL continued sorbent work to improve material

¹¹ Ibid.

characteristics, although the group's current CO₂ capture work is focused on membrane material development.

- Georgia Tech Research Corporation developed a rapid Temperature Swing Adsorbent (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 polyethyleneimine 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 CO₂ 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 CO₂ sorbent for pre-combustion syngas at the NCCC consistently demonstrated the capability to remove more than 90% CO₂. TDA also tested a combined WGS/CO₂ sorbent system with an innovative heat management component. When parameters were adjusted to achieve 90% CO conversion in the WGS stage, the overall CO₂ capture rate was greater than 95%. TDA scaled up testing from bench- to small-pilot-scale (0.1-MW) with a CO₂ sorbent (without water gas shift) process, again demonstrating high CO₂ 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 CO₂ 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 CO₂ 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.

Metallic oxide 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 CO₂ 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 types of favorable structures were identified. Study into the critical property of hydrothermal stability by UOP was also done in detail. Applying MOFs for CO₂ 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 regenerable 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.¹²

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 CO₂ 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.¹³

¹² U.S. Department of Energy. (January 2013). "Clean Coal Research Program: Carbon Capture Technology Program Plan," National Energy Technology Laboratory.

¹³ U.S. Department of Energy. (April 2018). "Compendium of Carbon Capture Technology," 04.2018-1000, National Energy Technology Laboratory.

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

Post-Combustion Project Focus	Participant	Technology Maturity
ACTIVE		
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
COMPLETED		
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 ₂ Capture	RTI International	Bench-Scale, Simulated Flue Gas
Cross-Heat Exchanger for Sorbent-Based CO ₂ 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 ₂ Removal from Flue Gas Using Microporous MOFs	UOP	Lab
A Dry Sorbent-Based Post-Combustion CO ₂ Capture	Research Triangle Institute	Bench-Scale, 1-tonner per day, Actual Flue Gas
Pre-Combustion Project Focus	Participant	Technology Maturity
ACTIVE		
High Capacity Regenerable Sorbent	TDA Research, Inc.	0.1-MWe

COMPLETED		
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

TSA systems being tested are provided in the following list. TSA is where CO₂ 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-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 CO₂ at the pilot unit in Hinwil, Switzerland
- Inventys VeloxoTherm – rotary wheel with diamine-functionalized commercial silica gel, pilot underway at NRG Energy
- TDA Research alumina sorbents (fixed bed, steam regeneration)
- Seibu Giku ceramic wheel.

Pressure and Vacuum Swing Adsorbent (VSA) systems have numerous vendors that are undergoing research. These typically use physisorbents in fixed beds.

Opportunities for adsorbent CO₂ capture include enriching natural gas from wells with high CO₂ content, coal or biomass gasification, CO₂ recovery from food and dry ice industries, and CO₂ recovery from petrochemical, oil, steel, cement, landfill gas. At the Otway Basin CO₂CRC facility, testing of capture materials to develop cost-effective processes to capture CO₂ from high CO₂ content natural gas wells.¹⁴

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 metric tons 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

¹⁴ Webley, P. Singh, R., and Xiao, P. (April 2017). “Adsorption Processes for CO₂ Capture: An Overview,” presentation at CO₂ Summit III: Pathways to Carbon Capture, Utilization, and Storage Deployment, ECI Digital Archives.

that will capture 30 to 600 tpd of CO₂ 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 CO₂ 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.¹⁵

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 CO₂ capacity than the field tests at NCCC of approximately 60x scale.¹⁶

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 CO₂ separation with the sorbent extracting the remainder to achieve 90% capture.¹⁷

C. Challenges and Research Needs for Adsorbents

CO₂ capture based on sorption/desorption of gases by a solid have 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 CO₂ capture applications and be able to integrate the two predictively with modeling and computational tools.

Four principal challenges were cited in using sorbents in CO₂ capture as absorbents 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

¹⁵ Inventys Inc. (2018). Manufacturing & Testing Centre. Retrieved from <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 CO₂ Capture Project Technology Review Meeting.

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

- Advance the long-term reactivity, recyclability, and robust physical properties of materials within the process
- Produce optimal integration between materials and process engineering.

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 CO₂ capture since sorbents should selectively bind only CO₂. MOFs can also be tuned for other industrially important gas-gas separations, so their path to market may be driven by applications other than CO₂ 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.¹⁸ 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 CO₂ capture capacity than other sorbents. The MOF can be used in CO₂ capture from exhaust gas, but it is also applicable to CO₂ capture from other process streams such as CO₂-methane separations following anaerobic digestion.¹⁹

The leading materials for CO₂ 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,

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

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

or VSA to the real time demand for the capture plant. One key strategy has been to reduce the cycle time in operations.²⁰

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 CO₂.²¹

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-absorbent 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 CO₂ adsorption step. Also, the CO₂ adsorption bed is regenerated with low level heat.
- Rensselaer Polytechnic Institute is developing a transformational, molecular layer deposition, 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 CO₂ 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 CO₂ capture capacity degradation over time.

IV. 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 CO₂ capture processes, the

²⁰ “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.

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

use of membranes for large CO₂ 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 MMt 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 CO₂ separation has many advantages compared to other capture approaches. They have simple operation with no chemical reactions, no moving parts, and no temperature or pressure swings. Since the membrane 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.

Several significant challenges for membrane CO₂ capture technologies result in a less favorable cost compared to other technologies. CO₂ permeability and permselectivity 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. Membrane 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 ($\text{mol s}^{-1}\text{m}^{-2}\text{Pa}^{-1}$). 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.²²

²² 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>.

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.

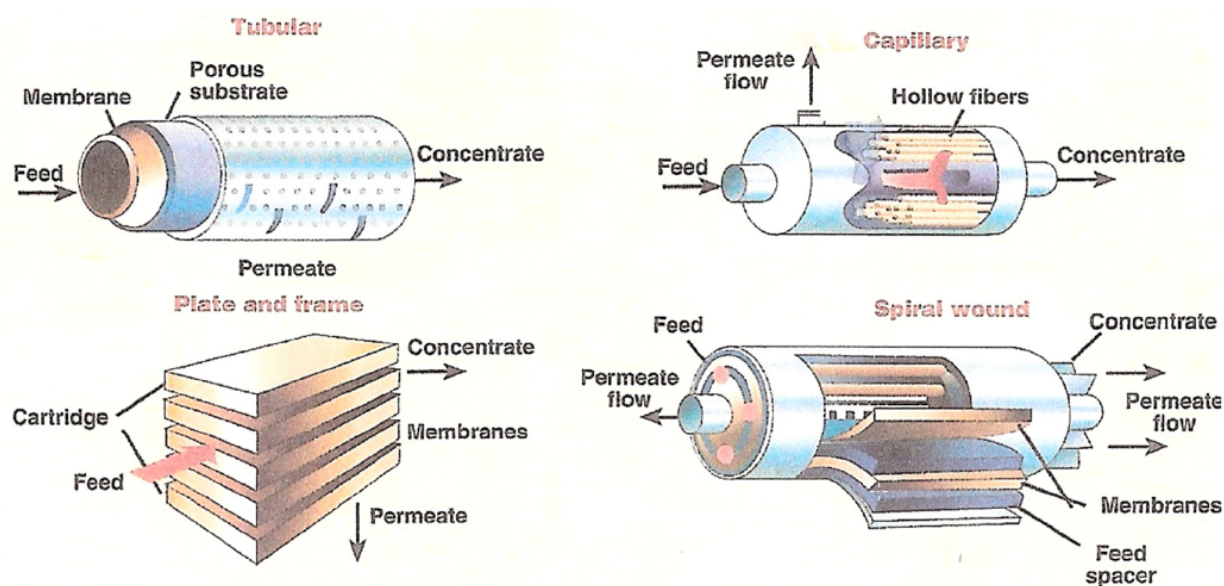


Figure F-3. Common Membrane Designs

Sources: Torzewski, K., ed. (March 2009). "Facts at your Fingertips—Membrane Configuration," *Chemical Engineering*, <https://www.chemengonline.com/facts-at-your-fingertips-membranes/?printmode=1>. and DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook, August 2015

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.

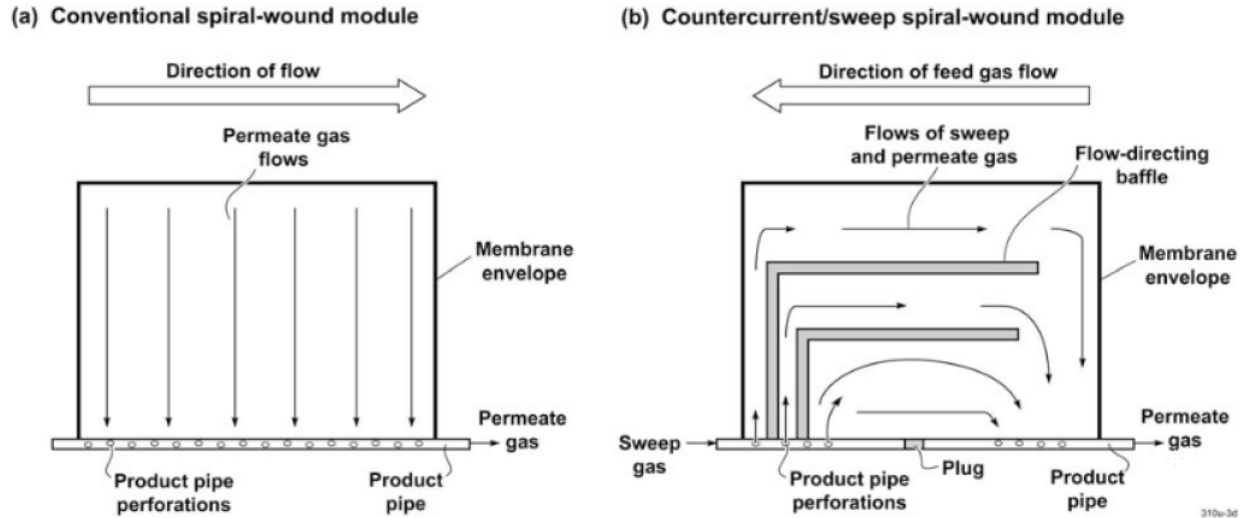


Figure F-4. Spiral-Wound Membrane Module Flow Patterns

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

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.

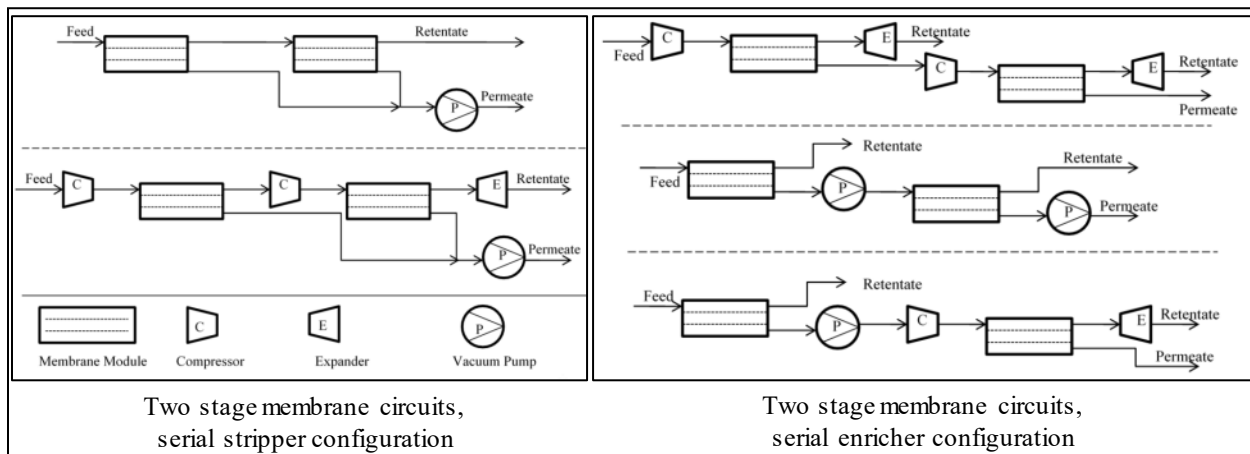


Figure F-5. Two Stage Membrane Circuits

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

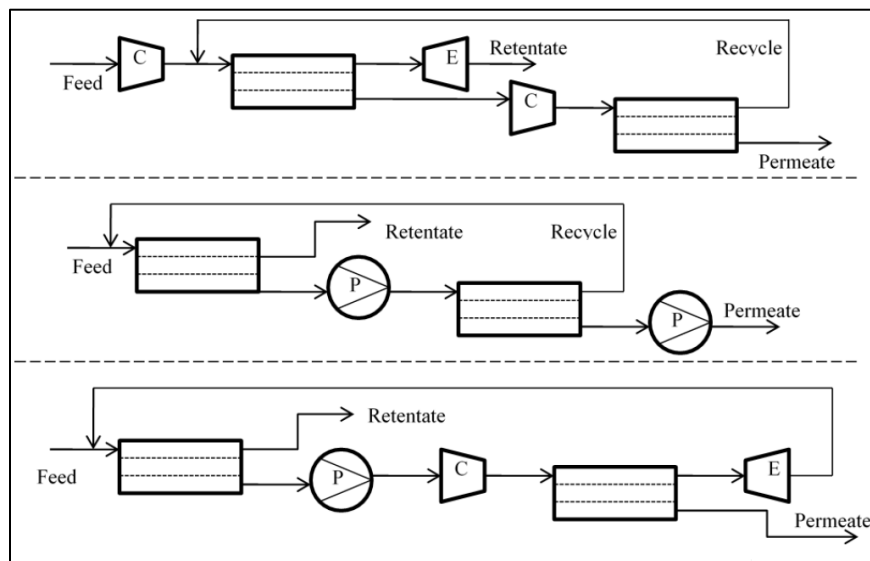


Figure F-6. Two Stage Membrane Circuits – Enricher with Recycle Configuration

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

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 as 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 CO₂ permeate away from the membrane surface, the permeate side has near zero CO₂ 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 CO₂ 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.

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 CO₂ 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 CO₂ 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 CO₂ selectivity at subzero temperatures to efficiently separate CO₂ from flue gas. Testing at NCCC focused on development and scale-up of the novel PI-2 membrane material featuring significantly higher CO₂ flux than commercially available material. The PI-2 module achieved 10 times the normalized CO₂ 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 CO₂ 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 m² of membrane area. Capture was from a high CO₂ content flue gas of 17 mol% wet basis. The test results showed that 70 mol % CO₂ purity can be easily achieved in a single stage.²³

The dense metal H₂-selective membrane technology that allows production of CO₂-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 (H₂ production capacity of 40 Nm³/h, 150 kWth), using membranes with thicknesses of about 15 to 20 micrometers (μm),²⁴ efforts have been focused on the development a of thinner palladium layers within the membranes (i.e., <5 microns). A 98-tube membrane separator (1.8 m²) has been tested in coal-derived syngas at the University of North Dakota Energy and Environmental Research Center.²⁵ Other activities include tests at the NCCC²⁶ under adverse industrial conditions. In 2017, Reinertsen AS and SINTEF demonstrated a 3 m² membrane module on a syngas-side stream of the Statoil Methanol Plant at Tjeldbergodden, Norway.²⁷

²³ "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. E. (2017). "Performance of a pilot-scale multitube membrane module under coal-derived syngas for hydrogen production and separation," *Journal of Membrane Science* 523, 515-523.

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 CO₂ capture and hydrogen production," *Energy Procedia* 114, 37-45.

Refer to Table F-4 for active and completed DOE/NETL membrane projects.²⁸

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

Post-Combustion Project Focus	Participant	Technology Maturity
ACTIVE		
Selective Membranes for <1% CO ₂ 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
COMPLETED (in Appendix)		
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	Research Triangle Institute	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
ACTIVE		
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
COMPLETED		
High-Temperature Polymer-Based Membrane	Los Alamos National Laboratory	Bench-Scale, Simulated Syngas
Dual-Phase Ceramic-	Arizona State University	Lab

²⁸ U.S. Department of Energy. (April 2018). "Compendium of Carbon Capture Technology," 04.2018–1000, National Energy Technology Laboratory.

Carbonate Membrane Reactor		
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
ACTIVE		
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 ₂ Capture	Liquid Ion Solutions LLC	Lab
Novel Concepts/Encapsulation of Solvents in Permeable Membrane for CO ₂ Capture	LLNL – Lawrence Livermore National Laboratory	Lab

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.²⁹ 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,

²⁹ U.S. Department of Energy. (April 2018). “Compendium of Carbon Capture Technology,” 04.2018–1000, National Energy Technology Laboratory.

MTR will also be testing in the Engineering-Scale program at TCM with their Advanced Polaris CO₂ Membrane.

For FOA 1791 AOI 2, EPRI will perform an initial engineering design and cost estimate of a Post-Combustion CO₂ 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, 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.³⁰

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 CO₂ 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 CO₂/N₂ 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 CO₂ from flue gas streams (aka CO₂ 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 CO₂ 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. CO₂ capture through phase change has been proposed and developed as a means of removing CO₂ from power plant flue-gas streams. There are several major advantages of cryogenic CO₂ 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 CO₂ is pumped to pressure as a liquid minimizing compression energy, and the energy consumption per ton of CO₂ captured overall is low. Drawbacks include difficulties associated

³⁰ “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.

with solids formation and handling and large heat transfer areas with tight temperature approaches.³¹

A. History of Testing the Cryogenic Process

Cryogenic CO₂ capture processes come in many forms such as a thermal swing process, an inertial carbon extraction system, cryogenic CO₂ capture external cooling loop, and cryogenic CO₂ capture compressed flue gas.

A thermal swing process freezes CO₂ 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 CO₂ capture has energy efficiency advantages that stem from ease of liquid-solid separation and this process pressurizes the CO₂ when it is a liquid as opposed when it is a gas. Another advantage is that other gas impurities are separated from the gas.³²

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 CO₂ 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 CO₂ 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_x, NO_x, and mercury.³³

CCC is a retrofit, post-combustion method that uses phase change to separate CO₂ and other pollutants from gases. CO₂ is cooled to a low temperature (about -140°C) that it de-sublimates, or changes from a gas to a solid. The solid CO₂ 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 until 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

³¹ Berger, A. et al. "Evaluation of Cryogenic Systems for Post Combustion CO₂ Capture," GHGT-14, Oct. 2018.

³² Jensen, Mark, "Energy Process Enabled by Cryogenic Carbon Capture" (2015). All Theses and Dissertations. 5711,

https://scholarsarchive.byu.edu/etd/5711?utm_source=scholarsarchive.byu.edu%2Fetd%2F5711&utm_medium=PDF&utm_campaign=PDFCoverPages.

³³ Herzog, H. (2018). *Carbon Capture*. Boston, MA: Massachusetts Institute of Technology Press.

and natural gas), and an experimental reactor (coal, natural gas, and biomass).³⁴ Cryopur, EReiE and others have performed pilot tests and GE has done simulation work to evaluate the technology.³⁵ SES's cryogenic process was part of the demonstration of the first project to collect cement kiln CO₂ for utilization in concrete production. Emissions from the Cementos Argos' Roberta cement plant near Calera, Alabama, were captured by SES. The captured CO₂ was transported and used in concrete operations equipped with CarbonCure's CO₂ utilization technology. This project was an extension of the Team CarbonCure's participation in the NRG COSIA Carbon XPRIZE Challenge.³⁶

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 CO₂ avoided (~\$30/tonne captured) with no plant integration. Using existing plant infrastructure should reduce the cost further.³⁷

B. Planned Work with the Cryogenic Process

SES is preparing for a 500+ hour test at another PacifiCorp Power Plant and is designing a 100-TPD system (commercial-scale for industrial sector, pilot-scale for power generation) for further testing.³⁸ 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).³⁹

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

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

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

³⁴ Sayre, A. et al. (July 2017). Field Testing of Cryogenic Carbon Capture. CMTC-486652-MS.

³⁵ IEAGHG, "Assessment of emerging CO₂ capture technologies and their potential to reduce costs," 2014/TR4, December 2014.

³⁶ 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/carboncure-consortium-closes-carbon-loop-cement-and-concrete-industries/>.

³⁷ Sayre, A. et al. (July 2017). Field Testing of Cryogenic Carbon Capture. CMTC-486652-MS.

³⁸ Ibid.

³⁹ U.S. Department of Energy. (April 2018). "Compendium of Carbon Capture Technology," 04.2018–1000, National Energy Technology Laboratory.

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 CO₂, 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 CO₂ removal pretreatment steps are to remove the two species that would form a solid as they are chilled at atmospheric pressure. For cryogenic CO₂ 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 CO₂ capture process could be envisioned in which there is no lost work from heat transfer or heat loss. We would then be able to compare existing processes to this idealized process to benchmark performance and understand potential for improvements.⁴⁰

A challenge for using cryogenics for flue gases is that CO₂ does not form a liquid at atmospheric pressures. Pure CO₂ gas forms a solid (dry ice) when it is cooled to -78.5 C (its sublimation point). So, cryogenic separation of CO₂ from flue gas is possible, but the formation of solids makes it difficult.⁴¹ 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 test at larger scale is the key path to commercialization.⁴²

⁴⁰ Berger, A. et al. “Evaluation of Cryogenic Systems for Post Combustion CO₂ Capture,” GHGT-14, Oct. 2018.

⁴¹ Herzog, H. (2018). *Carbon Capture*. Boston, MA: Massachusetts Institute of Technology Press.

⁴² IEA Greenhouse Gas R&D Programme. (December 2014). *Assessment of emerging CO₂ capture technologies and their potential to reduce costs*, 2014/TR4.

VI. 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.⁴³

Table F-6. Emerging CO₂ Capture Technologies

Technology/Project	Description	Organization	Award
Phase-Changing Ionic Liquids	Using special ionic liquids (ILs) to remove CO ₂ 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 ₂ . Upon heating, the CO ₂ is released for storage, and the ILs re-solidify and donate some of the heat generated in the process to facilitate further CO ₂ release.	University of Notre Dame	\$2,559,562
Hybrid Solvent-Membrane CO ₂ Capture	Hybrid approach to capture CO ₂ CO ₂ is removed as flue gas is passed through an aqueous ammonium-based solvent. Carbon-rich solution from the CO ₂ 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 ₂ 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 ₂ out of coal-	Colorado University Boulder	\$3,650,557

⁴³ Carbon Sequestration Leadership Forum. SUPPORTING DEVELOPMENT OF 2ND AND 3RD GENERATION CARBON CAPTURE TECHNOLOGIES: Mapping technologies and relevant test facilities, Rev: 08 and final 16 December 2015.

	<p>derived flue gas exhaust while restricting the flow of other materials through it.</p> <p>Design involves few chemicals or moving parts</p> <p>More mechanically stable than current technologies.</p> <p>The team is now working to further optimize the gelled materials for CO₂ separation and create a membrane layer that is less than 1 micrometer thick.</p>		
Metal Organic Framework Research	<p>Identification of the best MOFs for use in capturing CO₂ from the flue gas of coal-fired power plants.</p> <p>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 CO₂ from coal exhaust.</p> <p>The model predicts a significant decrease in parasitic energy penalty from 30% for traditional processes to 15% for an optimized MOF.</p> <p>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.</p>	University of California Berkeley	\$4,961,298
Synthetic Catalysts for CO ₂ Storage	<p>A synthetic catalyst is designed with the same function as carbonic anhydrase, an enzyme in the human lungs that helps to separate CO₂ from the blood. The catalyst can be used to quickly capture CO₂ from coal exhaust, just as the natural enzyme does in our lungs.</p> <p>Development of encapsulating chemical solvents in permeable microspheres that will greatly increase the speed of binding of CO₂.</p>	Lawrence Livermore National Laboratory	\$3,632,000
Composite Membranes for CO ₂ Capture	<p>Development of an enhanced membrane by fitting MOFs, into hollow fiber membranes.</p>	Georgia Tech Research Corporation	\$998,928

	<p>Analyzing MOFs based on their permeability and selectivity toward CO₂.</p> <p>The composite membrane would be highly stable, withstanding the harsh gas environment found in coal exhaust.</p>		
CO ₂ Capture with Liquid-to-Solid Absorbents	<p>Development of a unique CO₂ capture process in which a liquid absorbent changes into a solid upon contact with CO₂.</p> <p>Once in solid form, the material can be separated and the CO₂ can be released for storage by heating. Upon heating, the absorbent returns to its liquid form, where it can be reused to capture more CO₂.</p> <p>The approach is more efficient than other solvent-based processes because it avoids the heating of extraneous solvents such as water.</p>	GE	\$3,692,967
Better Enzymes for Carbon Capture	<p>Development of new and efficient forms of enzymes known as carbonic anhydrases.</p> <p>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.</p> <p>The enzymes' properties will be modified to withstand high temperatures and large swings in chemical composition.</p>	Codexis	\$4,657,045
Electrochemical Carbon Capture	<p>Development of an electrochemical technology to capture CO₂.</p> <p>This technology cuts both the energy requirements and cost of CO₂ capture technology in half compared to today's best methods.</p> <p>This technology will increase the cost of electricity generation by 85%.</p>	Arizona State University	\$3,471,515
Syngas into Fuel	<p>An iron-based material along with a unique process are developed to convert syngas into electricity, H₂,</p>	Ohio State University	\$7,099,904

	<p>and/or liquid fuel with zero CO₂ emissions.</p> <p>An iron-based oxygen carrier is used to generate CO₂ and H₂ from syngas in separate, pure product streams by means of a circulating bed reactor configuration.</p> <p>The end products of the system are H₂, electricity, and/or liquid fuel, all of which are useful sources of power that can come from coal or syngas derived from biomass.</p>		
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