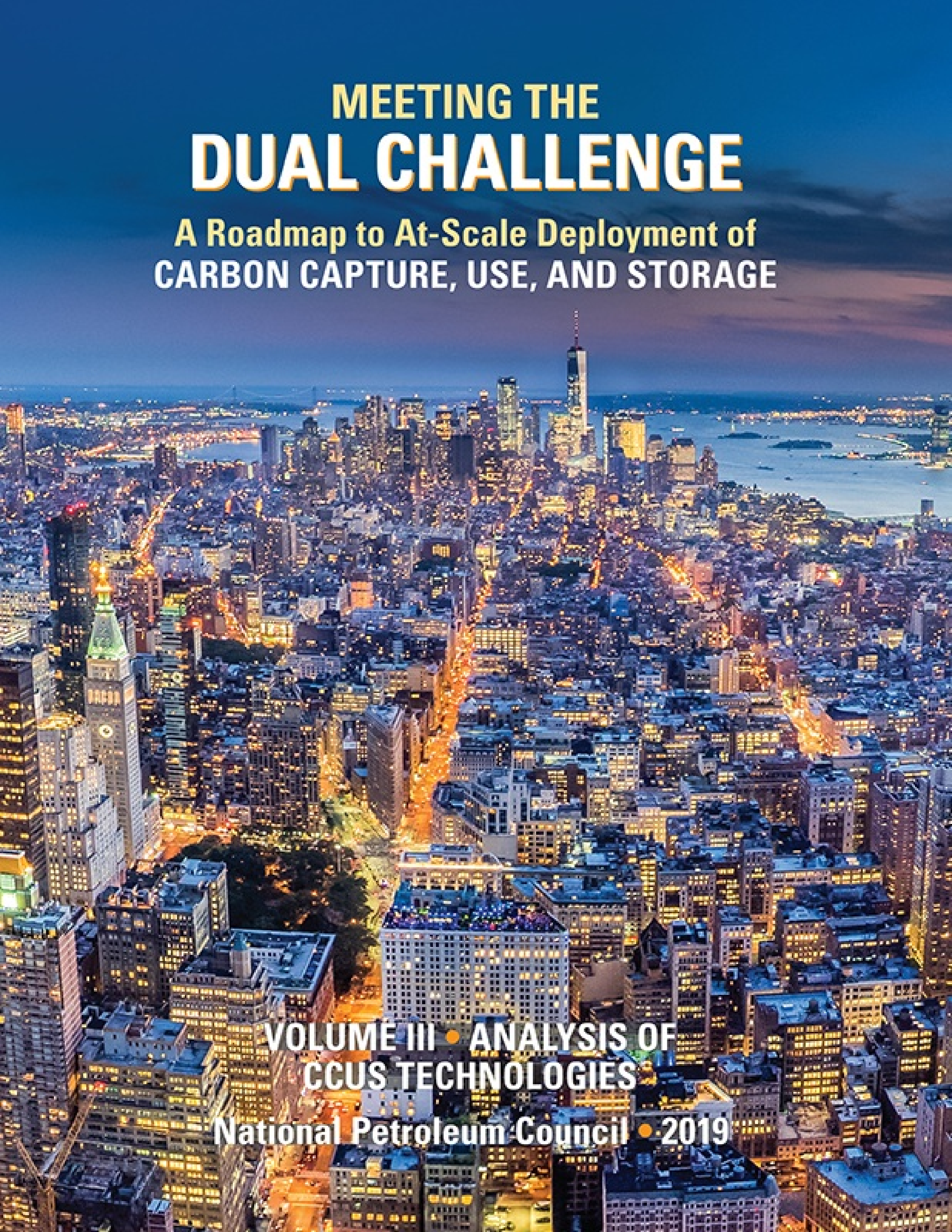

MEETING THE DUAL CHALLENGE

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

VOLUME III • ANALYSIS OF CCUS TECHNOLOGIES

National Petroleum Council • 2019

NATIONAL PETROLEUM COUNCIL
An Oil and Natural Gas Advisory Committee to the Secretary of Energy

1625 K Street, N.W.
Washington, D.C. 20006-1656

Phone: (202) 393-6100
Fax: (202) 331-8539

December 12, 2019

The Honorable Dan R. Brouillette

Secretary of Energy
Washington, D.C. 20585

Dear Mr. Secretary,

By letter dated September 21, 2017, Secretary of Energy Rick Perry requested the National Petroleum Council's (NPC) advice on actions needed to deploy commercial carbon capture, use, and storage (CCUS) technologies at scale into the U.S. energy and industrial marketplace. Achieving this objective will promote economic growth, create domestic jobs, protect the environment, and enhance energy security for the United States.

The response to the request required a study that considered technology options and readiness, market dynamics, cross-industry integration and infrastructure, legal and regulatory issues, policy mandates, economics and financing, environmental impact, and public acceptance. The effort involved over 300 participants from diverse backgrounds and organizations, 67% of whom are employed by organizations outside of the oil and natural gas industry.

Over the next two decades, global population and gross domestic product (GDP) are expected to grow significantly. Many outlooks anticipate a 25% to 30% increase in global energy demand by 2040 as well as a need to address rising greenhouse gas (GHG) emissions. The Council found in this "Roadmap to At-Scale Deployment of CCUS" that as global economies and populations continue to grow and prosper, the world faces the dual challenge of providing affordable, reliable energy while addressing the risks of climate change. Widespread CCUS deployment is essential to meeting this dual challenge at the lowest cost.

The United States is uniquely positioned as the world leader in CCUS and has substantial capability to drive widespread deployment. The United States currently deploys approximately 80% of the world's carbon dioxide (CO_2) capture capacity. However, the 25 million tonnes per annum (Mtpa) of CCUS capacity represents less than 1% of the U.S. CO_2 emissions from stationary sources. The study lays out a pathway through three phases of deployment – activation, expansion, and at-scale – that supports the growth of CCUS over the next 25 years, and details recommendations that enable each phase. In the first phase, clarifying existing tax policy and regulations could double existing U.S. capacity within the next 5 to 7 years. Extending and expanding current policies and developing a durable legal and regulatory framework could enable a second phase of CCUS projects (i.e., 75 to 85 Mtpa) within the next 15 years. Achieving CCUS deployment at scale (i.e., additional 350 to 400 Mtpa) within the next 25 years will require substantially increased support driven by national policies.

In addition, substantially increased government and private research, development, and demonstration (RD&D) is needed to improve CCUS performance, reduce costs, and advance alternatives beyond currently deployed technology. Increasing understanding and confidence in CCUS as a safe and reliable technology is essential for public and policy stakeholder support. The oil and natural gas industry is uniquely positioned to lead CCUS deployment due to its relevant expertise, capability, and resources.

The Council's policy, regulatory, and legal recommendations have been grouped into three phases:

Considering the activation phase, the NPC recommends the following:

- The IRS should clarify the Section 45Q requirements for credit transferability, options for demonstrating secure geologic storage, construction start definition, and credit recapture provisions.
- The Department of the Interior (DOI) and individual states should adopt regulations to authorize access to use pore space for geologic storage of CO_2 on federal and state lands.

Considering the expansion phase, the NPC recommends the following:

- Congress should amend Section 45Q to extend the construction start date, extend the duration of credits, lower the CO_2 volume threshold, and increase the value of the credit for storage and use applications.
- Congress should expand access to Section 48 tax credits and other existing financial incentives to all CCUS projects, effectively expanding current policies to a level of ~$90 per tonne to provide incentive for further economic investment.
- Congress should amend existing statutes to allow CO_2 storage in federal waters from all anthropogenic sources, and the Department of Energy (DOE) and DOI should establish processes to enable access to pore space and regulate CO_2 storage in federal waters.
- Concurrently with the activation phase, DOE should create a CO_2 pipeline working group to study the best way to harmonize the federal, state, and local permitting processes, establish tariffs, grant access,

administer eminent domain authority, and facilitate corridor planning. DOE should also convene an industry and stakeholder forum to develop a risk-based standard to address long-term liability.

Considering the at-scale phase, the NPC recommends the following:

- To achieve at-scale deployment of CCUS, concurrently with the expansion phase, congressional action should be taken to bring cumulative value of economic policies to about $110 per tonne.
- The oil and natural gas industry should continue to fund research and development at or above current levels in support of new and emerging CCUS technologies.

Concurrently with all three phases, and to achieve at-scale deployment of CCUS, Congress should increase the level of RD&D funding for CCUS technologies to $15 billion over the next 10 years, with a significant amount directed to less mature and emerging technologies that offer the greatest potential for a step change in performance and cost reduction.

Integral to success is adherence to the Council’s following recommendations for engaging stakeholders:

- Government, industry, and associated coalitions should design policy and public engagement opportunities to facilitate open discussion, simplify terminology, and build confidence that CCUS is a safe and secure means of managing emissions.
- The oil and natural gas industry should remain committed to improving its environmental performance

and the continued development of environmental safeguards.
- Commensurate with the level of policy enactment being recommended, the oil and natural gas industry should continue its investment in CCUS.

The attached report provides additional details and recommendations. The Council looks forward to sharing this study with you, your colleagues, and broader government and public audiences.

Respectfully submitted,

Greg L. Armstrong

Chair

Attachment

MEETING THE
DUAL CHALLENGE

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

VOLUME III • ANALYSIS OF CCUS TECHNOLOGIES

A Report of the National Petroleum Council
December 2019

Committee on Carbon Capture, Use, and Storage
John C. Mingé, Chair

NATIONAL PETROLEUM COUNCIL

The National Petroleum Council is a federal advisory committee to the Secretary of Energy.

The sole purpose of the National Petroleum Council is to advise, inform, and make recommendations to the Secretary of Energy on any matter requested by the Secretary relating to oil and natural gas or to the oil and gas industries.

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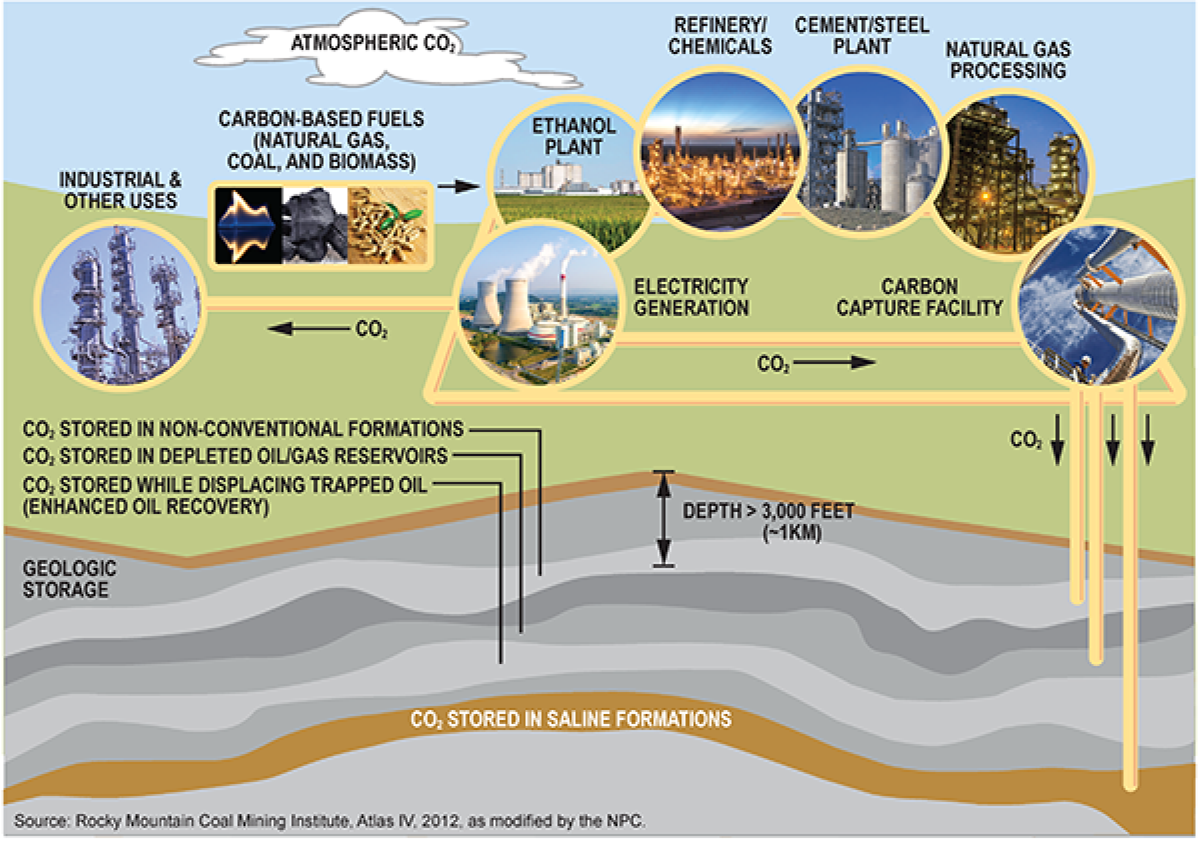
TECHNOLOGY INTRODUCTION

I. INTRODUCTION

Carbon capture, use, and storage (CCUS), including transport, combines processes and technologies to either reduce the level of carbon dioxide (CO_2) emitted to the atmosphere or remove CO_2 from the air. These technologies work together to capture (separate and purify) CO_2 from stationary sources so it can be compressed and transported to a suitable location where the CO_2 is converted into useable products or injected deep underground for safe, secure, and permanent storage.

CCUS can be delivered via a proven, safe, and well-understood suite of technologies, and Figure TI-1 illustrates a number of these technology combinations. CCUS has been deployed on large stationary source CO_2 emissions in several industries across the United States and globally, including applications in coal-fired power or electricity generation, natural gas processing, hydrogen and fertilizer production, bioethanol fermentation, liquid natural gas (LNG) in Australia, steel in Abu Dhabi, and others.



Source: Rocky Mountain Coal Mining Institute, Atlas IV, 2012, as modified by the NPC.

Figure TI-1. *Supply Chain for Carbon Capture, Use, and Storage*

Capturing CO_2 from the exhaust emissions from the source can also help to reduce the release to the atmosphere of other air pollutants, thus providing an environmental co-benefit (see Text Box at the end of this chapter).

This volume of the NPC CCUS study focuses on the technology components of the CCUS supply chain, which are presented in five chapters:

- CO_2 Capture

- CO_2 Transport
- CO_2 Geologic Storage
- CO_2 Enhanced Oil Recovery
- CO_2 Use.

Capture. CO_2 is produced in combination with other gases during industrial processes, including hydrocarbon-based power generation, steel and cement manufacture, hydrogen production, and refined fuels production. CO_2 results from the combustion of fossil fuels for energy and heat during these operations (combustion emissions), as well as from the processes themselves, such as during the creation of cement (process emissions). CO_2 capture is the separation of CO_2 from these other gases from the exhaust stream of a power plant, industrial flue (vent) gas emissions, or directly from the atmosphere. High-concentration CO_2 sources from ethanol fermentation can be dehydrated (removing entrained water) and compressed directly without requiring separation from an exhaust or flue gas mixture.

Transport. CO_2 transport refers to the transfer of CO_2 from one location to another, or between a CO_2 source and geologic sink or point of use, usually via pipelines. In the United States, over 70 million tonnes per annum (Mtpa) of CO_2 is transported from natural and anthropogenic sources via a pipeline network of more than 5,000 miles. This network represents approximately 85% of the current global CO_2 pipeline infrastructure. Most transported CO_2 is used for enhanced oil recovery (CO_2 EOR) in oil fields in the west, southwest, and Gulf Coast regions of the United States. CO_2 can also be transported safely by other means, including rail, truck, ship, and barge. Transport of CO_2 by ship offers an alternative solution for many regions of the world.

Storage. CO_2 storage, also called CO_2 geologic storage, refers to the injection and permanent trapping of CO_2 in deep underground reservoirs, typically in saline formations. Depleted oil and gas reservoirs, un-mineable coal seams, and basalts also have potential to store CO_2. Large-scale geologic storage in saline formations is understood and has been practiced for over 20 years, starting in Norway in 1996 at the Sleipner Field. The United States has been active in research in this area and has been storing CO_2 in saline formations at various scales of injection since the early 2000s, notably via the U.S. Department of Energy regional carbon sequestration projects. The United States also possesses one of the largest known geologic storage capacities in the world and most states in the continental United States possess some subsurface CO_2 storage potential.

Enhanced Oil Recovery. CO_2 EOR, a form of storage, is the process of injecting compressed CO_2 underground into an oil reservoir to recover more oil and natural gas than originally produced. The injected CO_2 liberates oil that was trapped in the pore spaces of the underground formations and the CO_2 remains trapped in the reservoir in its place. The incidental trapping of CO_2 that is injected for the purposes of EOR is an important co-benefit of the process, and 99% of the CO_2 injected is ultimately trapped in the subsurface formation.[1] The United States is a world leader in the application of CO_2 EOR and has more than 40 years of operational experience with this technology.

Use. CO_2 use represents a new generation of innovative technologies that convert CO_2 into products such as fuels, chemicals, and materials via chemical reactions or biological conversions. CO_2 use is the least mature component in the supply chain of CCUS technologies, but active research continues to pursue multiple technological pathways for converting CO_2 into products. Given the relative immaturity of these technologies, CO_2 use is likely to remain an outlet for only a small fraction of captured CO_2 over the next 10 to 20 years. However, these technologies hold promise for future emissions abatement.

Expanding the deployment of CCUS to the scale described in this study will require more efficient integration of the existing suite of technologies, the development of new and emerging technologies to deliver new CCUS pathways, and a reduction in the cost of delivering CCUS solutions. Continuing and expanded technology investment is warranted to deliver CO_2 mitigation methods at scale.

Investment in research, development, and demonstration (RD&D) in CCUS technologies, plus deployment of CCUS in early projects that integrate a suite of CCUS technologies at scale, offers numerous benefits. Continued CCUS RD&D offers the means to lower project integration costs through "learning by doing," scale-up of less mature technologies for potential application in commercial projects, and progress new and emerging technology solutions to create new and less costly CCUS pathways.

Less mature technology options exist for each component of the CCUS supply chain. Further development of these options offers opportunities for modularization, cost reductions, region-specific solutions, and cross-sector applications. The framing of CCUS component technologies in the form of technology readiness levels (TRLs) is presented below, providing a useful way of describing options and identifying opportunities that may become important in the future.

Reducing the cost of CCUS is essential to achieving at-scale deployment. CO_2 capture can represent up to 75% of the cost of CCUS when applied to large-scale stationary emissions sources. Development of transport infrastructure to connect CO_2 sources and sinks, and identification and characterization of large-scale geologic storage formations, offer other means of reducing the cost of at-scale CCUS deployment. With lower overall costs, the levels of incentives and financial support requested in Chapter 3, “Policy, Regulatory, and Legal Enablers,” should also decrease with time. (See Volume II of this report.)

Finally, the long-term growth of CCUS at scale will depend on the development of people and institutional capabilities across a broad spectrum of organizations, including academic, scientific, industry, trade organizations, professional societies, financial, government, think-tanks, and non-governmental organizations (NGOs). Investment in RD&D not only provides the funds to progress important research, but also supports development of the next generation of scientists, engineers, and entrepreneurs in advancing CCUS technologies, testing business models, and improving operational processes.

This introduction offers context on the following topics:

- Technology readiness and maturity

- Research, development, and demonstration opportunities
- Capability development.

These topics lead to a more detailed discussion of the CCUS component technologies presented in Chapters 5 through 9, and support the recommendations on RD&D noted in Chapter 3 in Volume II.

II. TECHNOLOGY READINESS AND MATURITY

The United States has made significant strides in the development of CCUS technologies during the last two decades, which has been aided by public-private partnerships that have driven cost reductions and performance improvements. Some technologies are in use and available for commercial deployment today while others require demonstration to prove their viability in a commercial setting. Other technologies remain in earlier stages of development.

Figure TI-2 describes the range of technology readiness levels (TRL) for many of the component technologies described in this study, using the U.S. Department of Energy’s TRL definitions.[2] Each technology is assigned a technology readiness level range that represents its stage of technical development and maturity (vertical axis). The TRL scale ranges from 1 (basic principle observed) through 9 (operational at scale). The higher the TRL level (i.e., ≥ 8), the closer a technology is to commercial readiness and deployment.

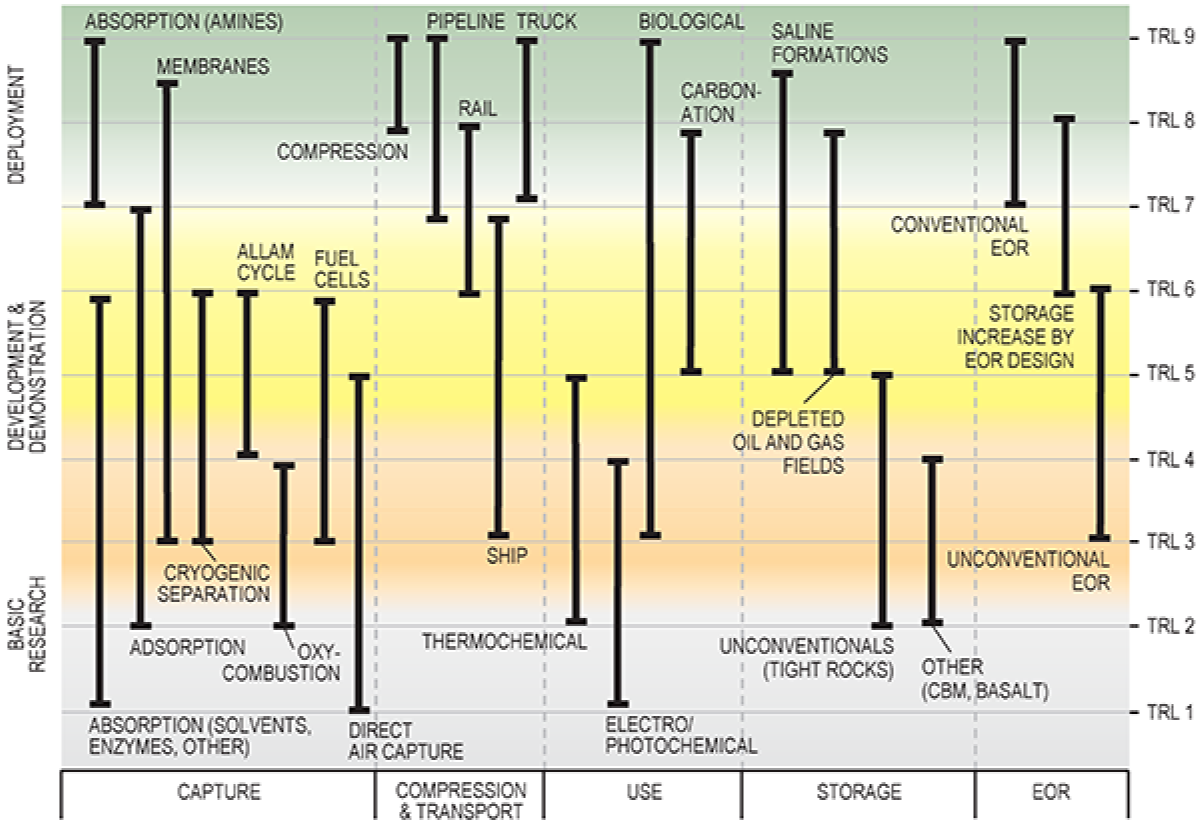


Figure TI-2. *Technology Readiness Level (TRL) Ranges for CCUS Technologies*

Figure TI-2 illustrates the TRL ranges of CCUS component technologies as assessed by members of the NPC CCUS Study Technology Task Group. Full CCUS supply chains can be executed today, but as Figure TI-2 shows, there is a limited suite of high TRL (greater than TRL 7) technology options available to deliver at-scale CCUS projects. Typical projects consist of CO_2 capture via amine absorption, transport from source to sink by pipeline, and the CO_2 injected deep underground for storage in saline formations or used for conventional CO_2 EOR.

In general, it is expected that there will be limited options for cost and efficiency improvements associated with high TRL technologies where transformational improvements are not anticipated. For these mature technologies, only incremental cost and performance gains are expected as a result of operational efficiency gains that come from “learning by doing” through the delivery of many examples of the same kinds of projects.

Alternatively, less mature and emerging technologies (TRL 6 and below) offer the greatest potential for step changes in performance and cost reductions. Figure TI-2 highlights a number of these less mature technologies that should benefit from continued progress in RD&D activity.

The technology chapters that follow include an assessment of the maturity of each technology component as well as a view on what is needed to achieve technical potential and scalability in the future. Please see Chapters 5 through 9 for additional details.

III. RESEARCH, DEVELOPMENT, AND DEMONSTRATION OPPORTUNITIES

To achieve more substantive cost reductions, improve performance, create competition, and accelerate innovation in support of at-scale CCUS deployment, continuing investment in the RD&D of emerging technologies is necessary and funding levels should increase.

A. The Case for RD&D

Commitment to RD&D and expansion of academic, government, and industry research across multiple technology pathways are required to reduce CCUS costs, create competition, and help accelerate innovation. Support for RD&D at all phases of technology development will drive improvements and offer more options to reduce CO_2. RD&D funding and activity should ramp up with time as the United States builds capability and the technology portfolio evolves and broadens.

Innovations in proven technologies are common once the technology is deployed many times. In addition to cost reductions and efficiencies gained through delivering multiple CCUS projects, technology enhancements that help increase efficiencies and drive down costs will occur because of:

- Delivery of many examples of the same kinds of projects and industry standardization leading to project execution and operational efficiencies, and
- Innovation and improvements in components, materials, and mechanisms improving the technologies themselves.

B. Potential for Step Change and Technology Maturity

One of the biggest challenges in technology development is the need to pilot and demonstrate emerging technologies, moving them from basic research to demonstrating proof of concept and actual deployment. The demonstration and deployment phases require significant increases in funding, project development skills, and planning and permitting capabilities. Planning and permitting is often a major hurdle to progressing a proven technology to commercialization.

Funding and government and industry collaborations are often required to move a proven technology forward.

The portfolio of basic research technologies for CCUS has the potential to deliver step changes in performance and cost by broadening the range of potential CCUS technology solutions and applications. Although there is great uncertainty in which technologies will fully mature, numerous concepts and technologies already exist, each of which requires research investment to mature. Many of these less-mature technologies hold promise for significant breakthroughs, but most remain unproven and success is uncertain.

With continued research and development, the portfolio of CCUS technologies will increase, potentially yielding a wider range of applications and low-carbon products (Figure TI-3). Some of these new technologies could offer a 10% to 30% improvement in the cost of large-scale CCUS applications over the next 20 to 30 years, as described in Chapter 2, “CCUS Supply Chains and Economics.” Investment in RD&D and infrastructure development could therefore yield a tenfold return in the longer term.

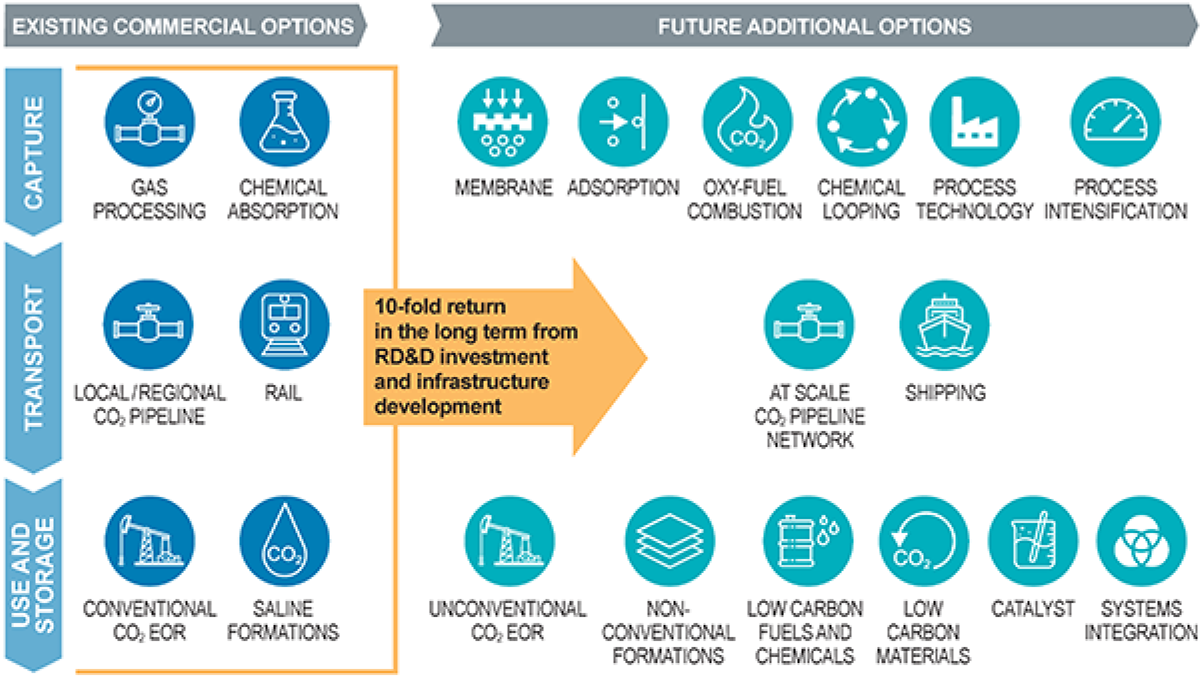


Figure TI-3. *Current and Future Portfolio of CCUS Technologies*

Chapter 3, "Policy, Regulatory, and Legal Enablers," describes this study's RD&D funding recommendations in detail, expanding from the current level of funding to accelerating the funding needed for deployment at scale.

IV. CAPABILITY DEVELOPMENT

The long-term growth of CCUS at scale also depends on the development of people and institutional capabilities across a broad spectrum of organizations, including academic, scientific, industry, trade organizations, professional societies, financial, government, think-tanks, and NGOs. Investment in RD&D not only provides the funds to progress important research, but also supports training and development of the next generations of scientists, engineers, and entrepreneurs in advancing CCUS technologies, testing business models, training people for capabilities in government permitting, and improving safe and environmentally sound operational processes.

Although the examples below do not represent an exhaustive list, they do provide insight into how capability development is necessary to support CCUS at scale.

A. Industries

Energy companies and other carbon-intensive industries will expand technical capabilities to plan, build, and deploy CCUS projects. The skills required to support this expansion will include operational safety, subsurface, environmental assessment, and project planning and execution. The oil and gas industry is uniquely positioned to lead CCUS deployment due to its relevant experience, capability, and technical and financial resources.

B. Academic and Scientific Incentivization

The creation of CCUS-specific academic disciplines, recognized by both industry and government, is necessary to support scale-up in deployment of CCUS. These disciplines could evolve in much the same way that computer science has evolved over the last few decades. Following this model, industry and government grants would provide the funding for the creation of “CCUS sciences” or “carbon engineering” departments at universities and laboratories. These departments might include the curricula for the science and engineering needed for CCUS technology development and also curricula for business schools and MBA programs, much like the “business of energy” programs developed at universities. Universities specializing in applicable basic research could receive industry and government grants to encourage advances in CCUS-related research.

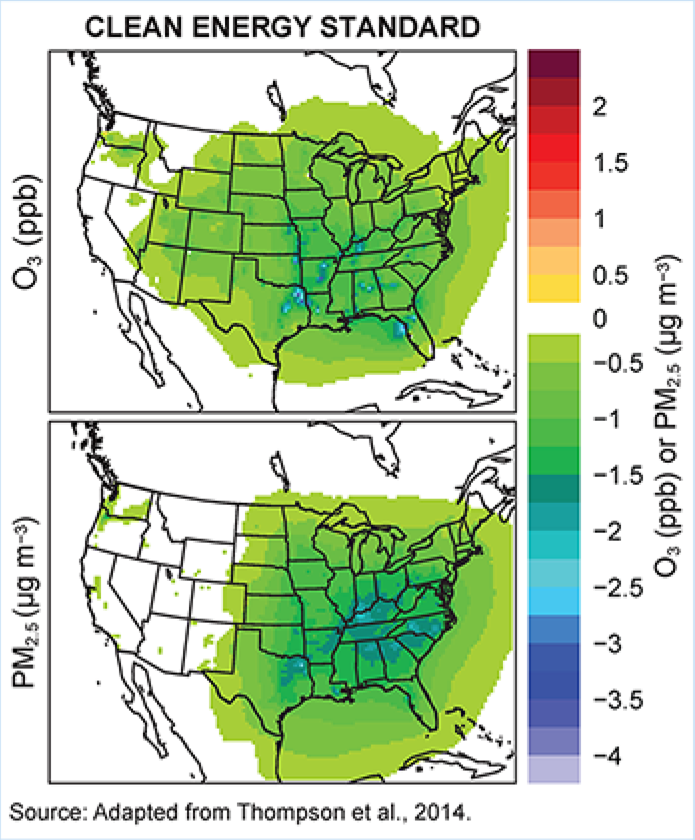
ADDITIONAL ENVIRONMENTAL BENEFITS OF CCUS

There are human health co-benefits from reducing greenhouse gases (GHGs) via CCUS, such as reductions in various conventional air pollutants. Actions designed to capture GHGs can benefit air quality. Capturing emissions from a variety of industrial sources (hydrocarbon-based power generation, steel and cement manufacture, hydrogen production, refined fuels production, etc.) will also separate out other air pollutants because the types of equipment used can also remove other impurities before or during the capture process.

One of these impurities—fine particulate matter of less than 2.5 microns in size ($PM_{2.5}$)—is entrained in gases from power plants and other industries and is recognized as an air pollutant.* Ozone (O_3), which is formed by chemical reactions between nitrogen oxides and volatile organic compounds, will also be captured. The concentrations of ground-level ozone and $PM_{2.5}$ can serve as air quality indicators.

One team of researchers modeled levels of ozone and $PM_{2.5}$ across the continental United States for certain future scenarios, including natural gas power generation coupled with CCUS.† The results are shown in the figure below in the form of spatial maps that show the difference in pollution concentration between a clean energy standard (CES) option, which includes natural gas with CCUS, and a reference case with no GHG emissions reductions. The figure presents two maps showing predicted changes by 2030 in ozone levels in the upper panel (O_3 season average daily maximum 8-h O_3, parts per billion [ppb]) and in $PM_{2.5}$ levels in the lower panel (annual average, microgram per cubic meter).

In summary, this research team's work predicts air quality improvements by 2030 associated with deployment of CCUS and other greenhouse gas reduction measures. Other researchers found similar results on a global scale. For example, one team showed that the global concentrations of $PM_{2.5}$ and ozone will both decline through the year 2100 as a result of assumed CCUS deployment.[‡]



Source: Adapted from Thompson et al., 2014.

Ozone and $PM_{2.5}$ Pollutant Levels in 2030

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* PM stands for particulate matter (also called particle pollution): the term for a mixture of solid particles and liquid droplets found in the air. $PM_{2.5}$ refers to fine inhalable particles, with diameters that are generally 2.5 micrometers and smaller; 2019 U.S. EPA.gov reference: https://www.epa.gov/pm-pollution/particulate-matter-pm-basics.

† Thompson, T. M., Rausch, S., Saari, R. K., and Selin, N. E., “A systems approach to evaluating the air quality co-benefits of US carbon policies,” *Nature Climate Change*, August 24, 2014, vol. 4, p. 917, Nature Publishing Group, https://www.nature.com/articles/nclimate2342#supplementary-information.

‡ West, J. J., Smith, S. J., Silva, R. A., Naik, V., Zhang, Y., Adelman, Z., Fry, M. M., Anenberg, S., Horowitz, L. W., and Lamarque, J.-F., “Co-benefits of mitigating global greenhouse gas emissions for future air quality and human health,” *Nature Climate Change*, September 22, 2013, Vol. 3, Nature Publishing Group, https://doi.org/10.1038/nclimate2009.

C. Industry Trade Organizations and Professional Societies

Industry trade organizations and professional societies could play a pivotal role in “socializing” CCUS to graduates from universities and technical training schools to help develop a CCUS workforce, encouraging them to pursue a career in industries dedicated to reducing and managing carbon emissions. These organizations could assist in facilitating general public understanding of how CCUS enables a broad range of industries, including low-carbon energy production, reduced carbon manufacturing, and reduced carbon building materials. Professional societies can also play a role in defining CCUS standards and accrediting third-party assessors.

D. Financial Institutions

Banks, institutional investors, government or sovereign investment funds, and private equity funds could all contribute to meeting the financial and investment needs of developing CCUS at scale. Sovereign and institutional investors could create investment vehicles that encourage the application and growth of CCUS technologies across many industries, which would help to foster a positive perception that investments in CCUS can profitably contribute to a lower carbon world. Financial vehicles could be created that encourage funding and loans for establishing entrepreneurial enterprises, such as small businesses, to provide products and services to every element of the CCUS value chain.

E. Think-Tanks and NGOs

The full impact of CCUS on industry, the global economy, environment, and society could be observed, measured, and reported on by think tanks, NGOs, and other independent coalitions. Organizations such as these could work closely with industry, policymakers, labor organizations, and each other to educate and inform the public about the benefits and challenges of CCUS and support policies that would enable at-scale deployment to meet societal and industrial demands, as described in Chapter 4, “Building Stakeholder Confidence,” in Volume II of this report.

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1 International Standards Organization, ISO 27916:2019, Carbon dioxide capture, transportation and geological storage – Carbon dioxide storage using enhanced oil recovery (CO2–EOR), https://www.iso.org/standard/65937.html.

2 U.S. Department of Energy, DOE G 413.3-4A Chg 1 (Admin Chg), Technology Readiness Assessment Guide, last update October 22, 2015, https://www.directives.doe.gov/directives-documents/400-series/0413.3-EGuide-04-admchg1.

Chapter Five

CO_2 CAPTURE

I. CHAPTER SUMMARY

Carbon dioxide (CO_2) is produced in combination with other gases during industrial processes, including hydrocarbon-based power generation, steel and cement manufacture, hydrogen production, and refined fuels production. CO_2 capture, also called carbon capture, refers to the separation of CO_2 from these other gases, including power plant exhaust streams, industrial flue (vent) gas, and process emissions, as well as from the atmosphere. A smaller subset of high-concentration CO_2 sources, such as those from bioethanol fermentation, can be dehydrated[1] and compressed directly without requiring separation from an exhaust or flue gas mixture.

CO_2 capture technologies are a key component of carbon capture, use, and storage (CCUS), including transport. The separation of CO_2 can be accomplished through the application of four main CO_2 capture technologies:

- Absorption, the uptake of CO_2 into the bulk phase of another material

- Adsorption, the uptake of CO_2 onto the surface of another material
- Membranes, which selectively separate CO_2 based on differences in solubility or diffusivity
- Cryogenic processes, which chill the gas stream to separate CO_2.

Each technology has advantages and challenges associated with its implementation in different industries. The appropriate capture technology for an industrial application depends on the size (i.e., volume) of the source gas stream to be handled, concentration of CO_2, contaminants in the gas mixture, pressure and temperature of the mixture, percent of CO_2 to be captured, and purity of the CO_2 that is desired downstream of the capture process. Each of these considerations will influence determination of the optimum technology and associated costs of CO_2 capture.

Absorption has been used as the primary means of separating CO_2 from gas mixtures for more than 40 years, establishing it as the most widely applied capture technology. As a result, absorption technology is substantially more mature than other capture technologies and is expected to be the primary choice for separation in the near- to mid-term. Adsorption and membrane technologies have been used in some industries, although application to date is generally less mature. And although cryogenic capture is at the earliest stage of application, it does have potential across several industries that will be discussed in this chapter.

In the United States, the primary industries with point-source emissions of CO_2 for which separation technologies have been or will need to be applied in the future include: electricity and power generation; petroleum and coal product manufacturing; pulp, paper, and paperboard mills; chemical manufacturing; cement and concrete production; iron and steel mills and ferro-alloy manufacturing; oil and gas processing; and pesticides, fertilizers and other agricultural chemical manufacturing, and bioethanol fermentation.

Over the past several decades, there have been a number of large-scale CO_2 capture projects operating in several of these industries. Most of these projects in the following list employ different amine solvents to capture CO_2 via absorption, and one employs vacuum swing adsorption.

- *Terrell Natural Gas Processing Plant, Texas, 1972*—This was the first CO_2 capture project of any type. An absorption-based physical solvent[2] was used to separate CO_2 from a high-pressure natural gas stream for onward transmission of the hydrocarbon gas to market.
- *Trona Plant, California, 1978*—This was the world's first project involving CO_2 capture at near-atmospheric conditions. A solvent technology was used in a conventional absorption process for post-combustion CO_2 capture. The plant, designed to capture 600 metric tons (tonnes) of CO_2 per day, operated successfully with its original equipment for 20 years.
- *Great Plains Synfuels Project, North Dakota, 2000*—A coal gasification facility that produces synthesis gas for

pipeline use with CO_2 captured via an absorption-based physical solvent.

- *Massachusetts Capture Project, 1991*—Fluor used absorption to capture CO_2 from a slipstream of flue gas from a natural gas-fired power plant to produce food-grade CO_2 for several years.
- *Sleipner Project, Norway, 1996*—Equinor (formerly Statoil) established the world's first offshore CO_2 storage project using amine absorption separation to remove CO_2 from the produced natural gas stream from the Sleipner West gas field. The project compresses and injects about 1 million tonnes per annum (Mtpa) of CO_2 into an offshore saline formation.
- *Steam Methane Reformer Project, Texas, 2013*—Air Products established the world's first steam methane reformer hydrogen production facility that uses a vacuum swing adsorption process to separate CO_2 that is subsequently used for enhanced oil recovery (CO_2 EOR) in the nearby Hastings Oil Field.
- *Boundary Dam Project, Canada, 2014*—This SaskPower facility uses amine absorption to capture CO_2 from the flue gas of a coal-fired power plant. The separated CO_2 is compressed, transported, and injected for CO_2 EOR at the Weyburn Field.
- *Quest CCS Project, Canada, 2015*—The project upgrades oil sands production by blending hydrogen into the crude oil. Hydrogen is generated onsite and a proprietary amine solvent separates the CO_2 that is subsequently injected for storage.

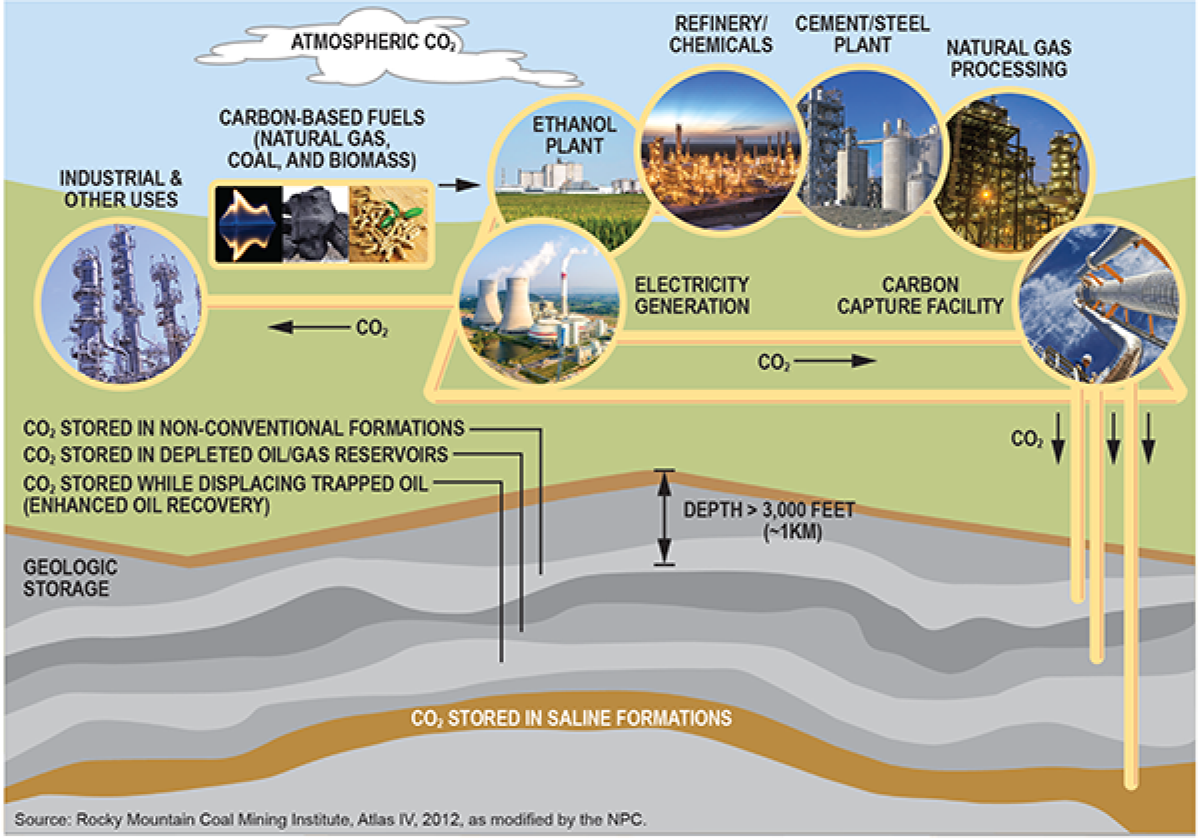
- *Petra Nova Project, Houston, Texas, 2016*—This facility, a joint venture between NRG Energy and JX Nippon Oil & Gas Exploration, uses amine absorption to capture CO_2 from the flue gas emissions of a coal-fired boiler. The separated CO_2 is compressed, transported, and injected for CO_2 EOR in the nearby West Ranch Oil Field.

The cost of implementing and maintaining CO_2 capture technologies varies widely and depends on the different requirements of specific applications, such as scale (volume), emissions source CO_2 concentration, and end-use purity of the CO_2. Higher concentration CO_2 sources or applications that require lower-outlet CO_2 purities are less costly to separate. Lower concentration sources or applications that require higher-outlet CO_2 purities are more costly. CO_2 capture often represents the largest cost component in the CCUS supply chain, accounting for as much as 75% of the project cost. Conversely, the cost of capture can be very low for projects associated with very high CO_2 concentration sources of 85% to 99%—natural gas processing or bioethanol fermentation—where only dehydration and compression of the CO_2 stream is required.

This chapter describes each of the main capture technologies and explains the research, development, and demonstration (RD&D) opportunities for each. It is important to note that there is no silver-bullet technology that would be able to capture all CO_2 emissions. What is needed to support at-scale deployment of CCUS in the United States is a diversified technology development program that includes collaboration from public and private sources in addition to durable funding mechanisms and stable legal and regulatory frameworks.

II. WHAT IS CO_2 CAPTURE?

CCUS, including transport, combines several technologies to reduce the level of CO_2 emitted to the atmosphere or remove CO_2 from the air. The CCUS process, as shown in Figure 5-1, involves the capture (separation and purification) of CO_2 from stationary sources so that it can be compressed and transported to a suitable location where it is converted into useable products or injected deep underground for safe, secure, and permanent storage.



Source: Rocky Mountain Coal Mining Institute, Atlas IV, 2012, as modified by the NPC.

Figure 5-1. *Supply Chain for Carbon Capture, Use, and Storage*

CO_2 is produced in combination with other gases during industrial processes, including hydrocarbon-based power generation, steel and cement manufacture, hydrogen production, and refined fuels production. CO_2 results from the combustion of fossil fuels for energy and heat during these operations (combustion emissions), as well as from the processes themselves, such as during cement production (process emissions). CO_2 capture refers to the separation of this CO_2 from these other gases, whether that is a power plant exhaust stream, industrial flue (vent) gas emissions, or the atmosphere. A smaller subset of CO_2 sources, typically of high CO_2 concentration, can be dehydrated and compressed without separation.

There are four main types of CO_2 capture technologies:

- Absorption, the uptake of CO_2 into the bulk phase of another material
- Adsorption, the uptake of CO_2 onto the surface of another material, including via pressure-swing and vacuum swing processes
- Membranes, which selectively separate CO_2 based on differences in solubility or diffusivity
- Cryogenic processes, which cool the gas stream to separate CO_2.

Each technology has advantages and challenges associated with its implementation in different industries. Figure 5-2 displays the technology readiness level (TRL) of the four main types of capture technologies as well the TRL of other technologies that are being developed. Each capture technology in the figure is assigned a TRL range (right vertical axis) that represents its stage of technical development (left vertical axis). The stages of technical development include “Basic Research,” “Development & Demonstration,” and “Deployment.” The higher the TRL level, the closer the technology is to commercial readiness and subsequent deployment. For example, in the far-left area of Figure 5-2, “Absorption (Amine)” has a TRL of 7 to 9 because it is a mature technology that has been commercially deployed for decades. Compare that to “Absorption (Solvents, Enzymes, Other)” with a TRL of 1 to 6 because it is a less mature technology that spans the “Basic Research” and “Development & Demonstration” stages.

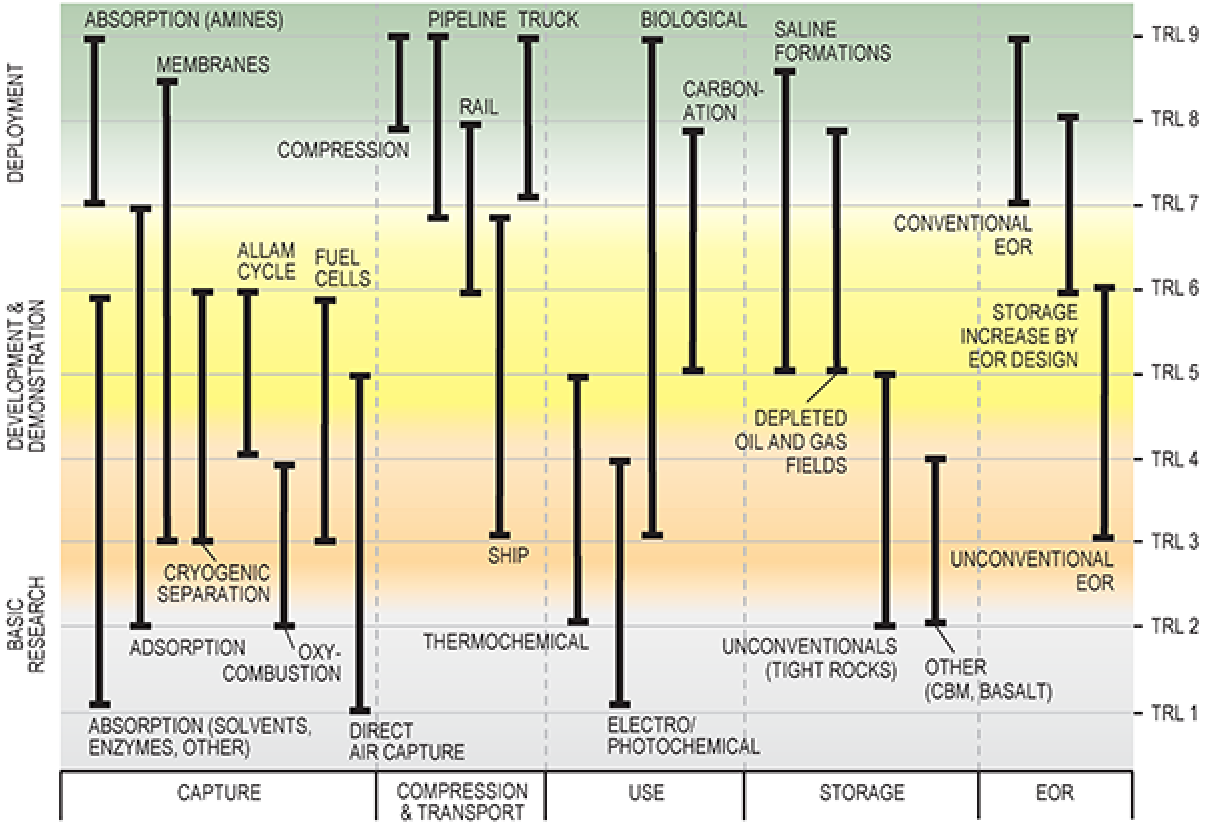


Figure 5-2. *Technology Readiness Level (TRL) Ranges for CCUS Technologies*

Amine absorption has been the primary method of separating CO_2 from gas mixtures for more than 40 years. Thus, it has the highest TRL range on Figure 5-2 and it is expected that it will continue to be the most widely used separation method in the near- to mid-term.

A. How CO_2 Concentration Affects Capture Costs

The concentration of CO_2 in the gas mixture is the means by which CO_2 capture facilities may be compared. CO_2 emission sources may be divided into three main categories: high concentration for CO_2 concentrations greater than 80% in the gas stream (i.e., bioethanol fermentation plants), intermediate concentration for CO_2 concentrations from 15% to 80% in the gas stream (i.e., iron and steel industries), and low concentration for CO_2 concentrations less than 15% in the gas stream (i.e., coal-fired and natural gas-fired power plants). In general, CO_2 capture for high-concentration streams requires only dehydration and compression. Physical solvents, sorbents (porous particles), or membranes can be used effectively for intermediate-concentration streams and chemical solvents or solid sorbents can be used for low-concentration streams.

The main factors that affect the cost of CO_2 capture are the concentration of CO_2 in the feed stream, purity of the captured CO_2 stream (level of contaminants), and scale or volume of CO_2 that needs to be captured. The scale or volume of CO_2 may be determined by the flow rate of the exhaust stream being treated and the fraction of CO_2 captured. Because these parameters influence the type and size of separation equipment required, they determine the capital cost of the system.

For example, an ethanol plant where the CO_2 purity in the exhaust gas mixture is as high as 99% only requires dehydration and compression equipment to effectively separate the CO_2. Alternatively, for a coal-fired power plant where the concentration of CO_2 in the flue gas is 12% to 15%, CO_2 separation and purification require large absorption columns filled with packing material and chemical solvents that are coupled to a regeneration column.

In general, CCUS facilities that separate CO_2 from dilute sources are larger in size, require more capital, and have higher operating expenses compared with facilities that separate CO_2 from highly concentrated gas mixtures. As the concentration of CO_2 in the feed stream increases, the capital cost of the project decreases because there is less equipment required for the separation process. More of the feed gas stream is CO_2 instead of other components, such as nitrogen. Similarly, as CO_2 concentration in the gas stream increases, the technology may rely more on a physical separation process rather than a chemical one, leading to reduced energy requirements for sorbent regeneration that reduce operating costs.

Figure 5-3 is a photograph of the NRG/JX Petra Nova Project near Houston, Texas. This facility uses amine absorption capture to separate low concentrations of CO_2 (~13%) from the flue (vent) gas stream at a coal-fired power plant.

Source: NRG Energy Case Studies, Petra Nova, Carbon capture and the future of coal power.

Figure 5-3. *NRG/JX Petra Nova CO_2 Capture Project near Houston, Texas*

Figure 5-4 shows the Air Products Steam Methane Reformer Project in Port Author, Texas. This hydrogen production facility uses an adsorption capture process on a relatively high-concentration CO_2 stream (>90%).

Source: Air Products and Chemicals, Inc.

Figure 5-4. *Air Products Steam Methane Reformer Project in Port Arthur, Texas*

Figure 5-5 is an image of the Archer Daniels Midland Company Illinois Industrial Carbon Capture and Storage Project in Decatur, Illinois. The project applies amine absorption capture to a high-concentration CO_2 (>95%) from corn ethanol production (bioethanol).

Source: Archer Daniels Midland Company.

Figure 5-5. *Illinois Industrial Carbon Capture and Storage Project in Decatur, Illinois*

Despite the relative differences between these projects, each one helps to illustrate the massive size requirements of these facilities, which translates to the high capital cost that is associated with the development of large-scale industrial CO_2 capture projects.

III. CO_2 CAPTURE TECHNOLOGIES AND APPLICATIONS

In thermodynamics, work performed by a system is the energy transferred by the system to its surroundings using a mechanism through which the system can exert macroscopic forces on its surroundings or change its state. Typically, the more work performed, the more energy that is required to deliver that work.

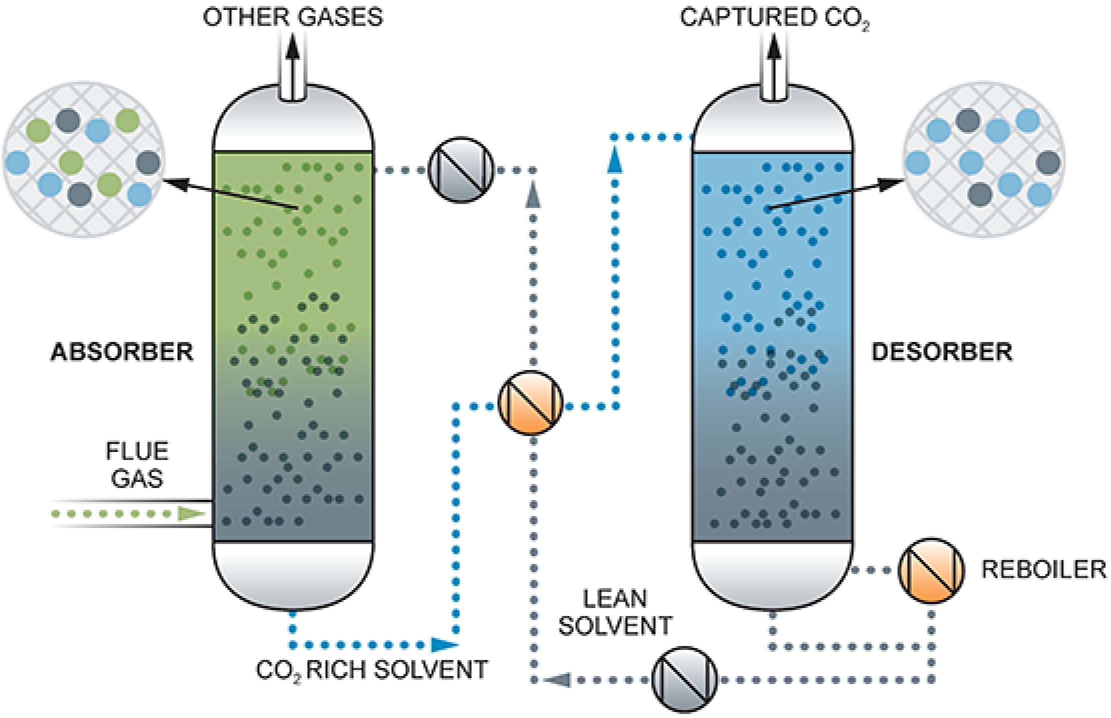
In terms of CO_2 capture, work is a useful measure of how much energy may be required to remove CO_2 from gas mixtures with different CO_2 concentrations, capture percentages desired, and outlet stream purities. The minimum work for CO_2 separation from a gas mixture decreases as the initial concentration of CO_2 in the stream increases. In addition, the minimum work increases as the required capture percentage and purity of the outlet stream of CO_2 increase. From a thermodynamic perspective, at constant temperature and pressure, the energy required to separate CO_2 is greatest when the CO_2 concentration (partial pressure) is lowest in the flue gas mixture and the required purity is highest in the separated stream. Typically, the higher the amount of energy required for separation, the higher the operating costs of the separation process will be.

The "second-law efficiency" is the ratio of this minimum work to the real work,[3] and it has been shown that this efficiency decreases with increasing dilution of CO_2 concentration. As a gas mixture becomes more dilute in CO_2 (lower CO_2 concentration), the second-law efficiency decreases, which means CO_2 capture becomes more difficult. This is expected because the percentage of unwanted or inert gas (mostly nitrogen) that needs to be processed is significantly higher.

A. How Capture Technology Works

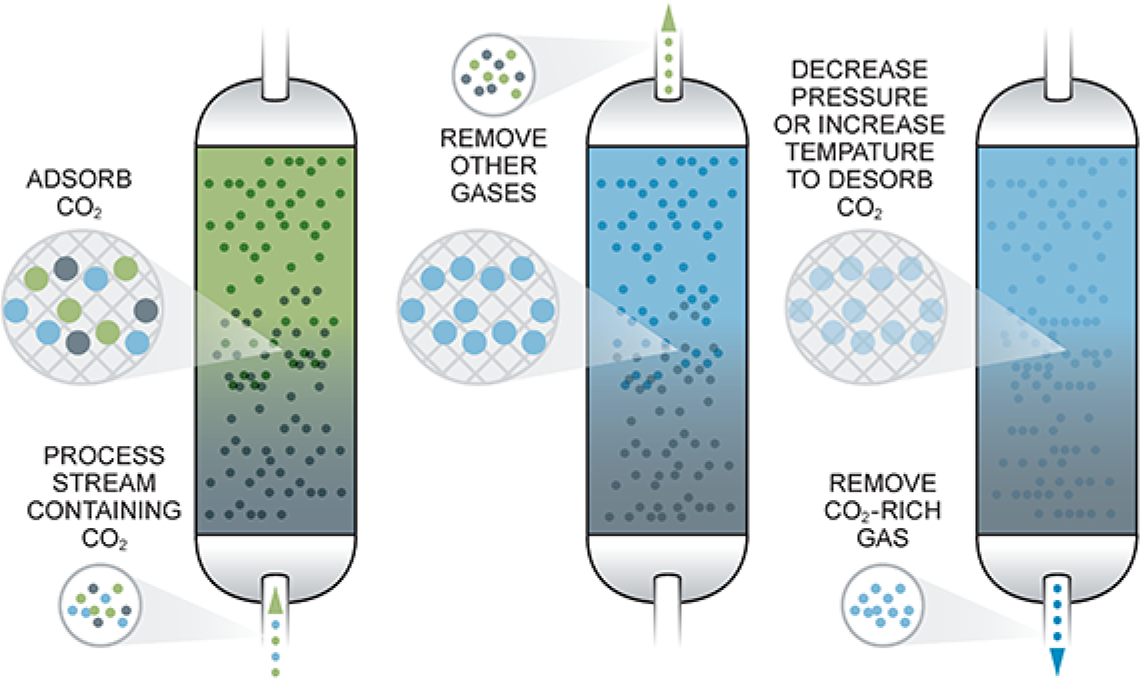
1. Introduction

The main CO_2 capture technologies—absorption, adsorption, membranes, and cryogenic distillation processes (Figures 5-6, 5-7, 5-8, and 5-9)—have the greatest near-term potential to reduce CO_2 emissions because they can be retro-fitted to existing fossil-fuel power plants and other industrial emitters.



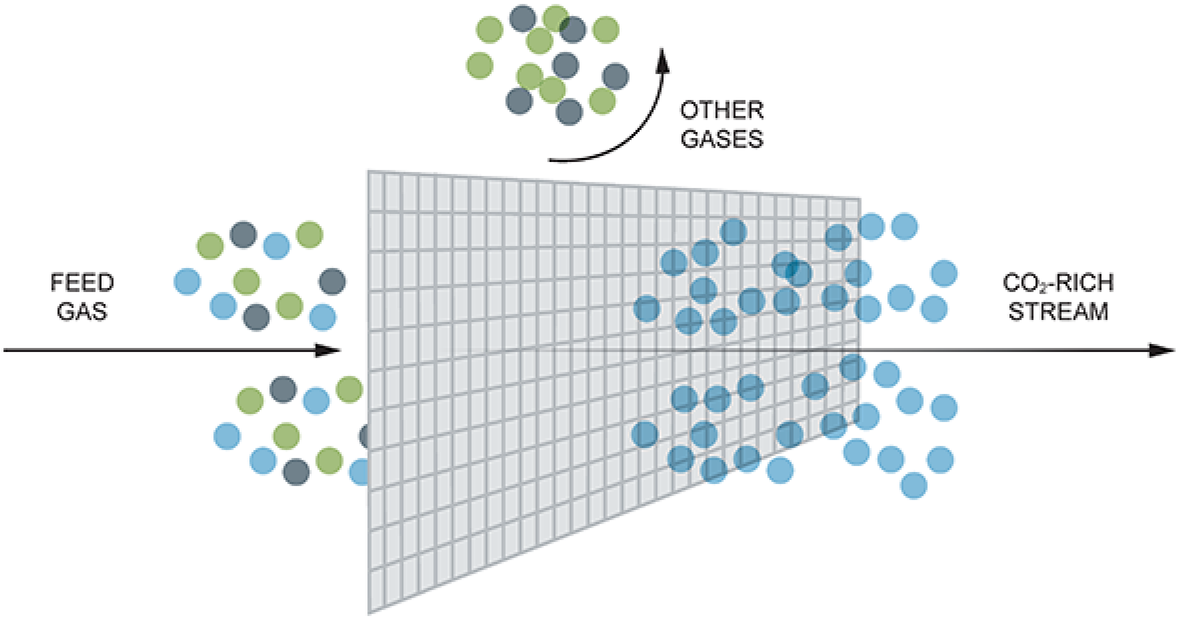
Source: CO2CRC.

Figure 5-6. *CO_2 Capture by Absorption*



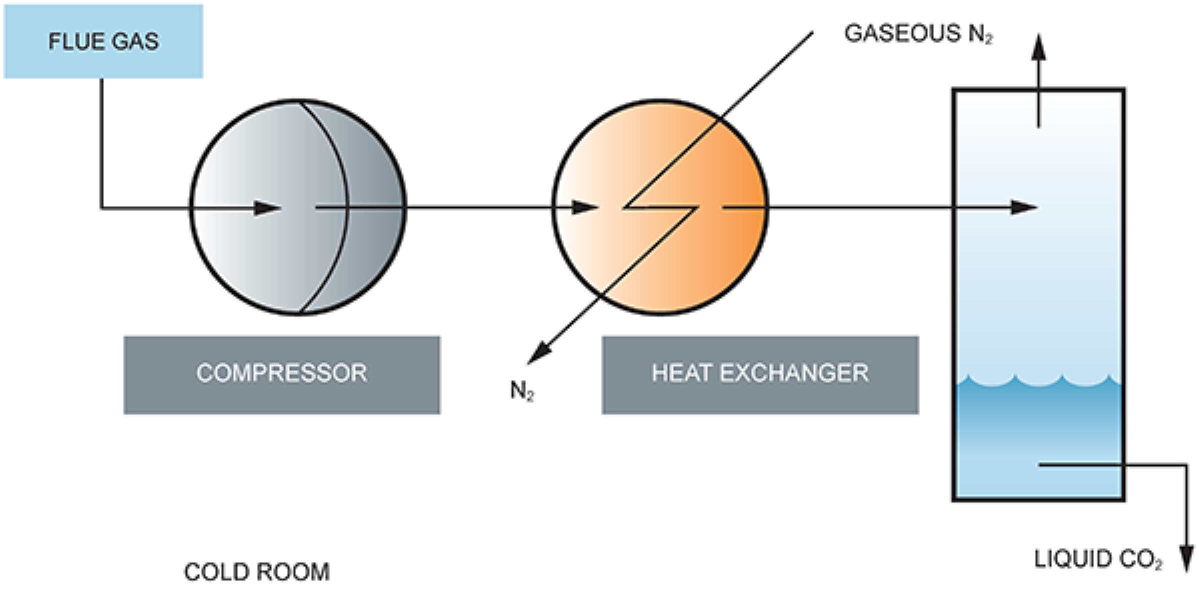
Source: CO2CRC.

Figure 5-7. *CO_2 Capture by Adsorption*



Source: CO2CRC.

Figure 5-8. *CO_2 Capture by Membranes*



Source: Aaron, D., and Tsouris, C., "Separation of CO2 from Flue Gas: A Review." *Separation Science Technology*, 2005.

Figure 5-9. *CO_2 Capture by Cryogenic Distillation*

A specific technology may have a marketplace advantage over other technologies given variable factors such as cost, operability, environmental footprint, CO_2 concentration in the feed gas stream, purity of CO_2 required in the outlet stream, and other practical aspects. However, even if a capture approach has an advantage in one market, it does not necessarily have the equivalent advantage across all markets. Hence, no single technology is necessarily superior across all industries in all markets.

2. Capture Technologies

a. Absorption

Absorption refers to the uptake of CO_2 into the bulk phase of another material, such as dissolving CO_2 molecules into a liquid solution. This is different than adsorption where CO_2 molecules adhere to the surfaces of another material (Figure 5-10).

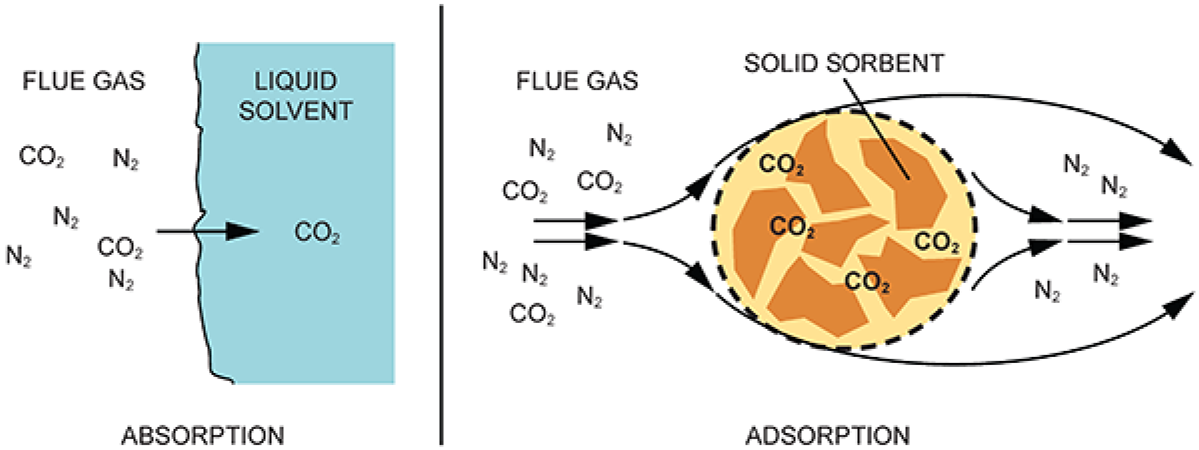


Figure 5-10. *Mechanisms of CO_2 Absorption and Adsorption*

Although absorption and adsorption rely on chemical and physical interactions between CO_2 and a separating material (solution or solid) to selectively separate CO_2 from the other constituents in a gas mixture, the interaction and process configurations differ. Both processes are used widely in the chemical, petrochemical, and other industries with absorption being far more common than adsorption for application in at-scale capture projects. As defined by this study, at-scale deployment is the capture of 600 Mtpa of CO_2, equivalent to CCUS being deployed on more than 20% of U.S. stationary emissions.

Of the four main technologies, absorption is the only technology available for widespread commercial deployment, typically for separation of CO_2 from other gases in post-combustion applications.

Figure 5-11 shows a typical absorption-based process configuration. For CO_2 capture by absorption, molecules of CO_2 dissolve into the bulk of a liquid solvent. Flue (vent) gas, which can contain a range of CO_2 concentrations, and the liquid solvent contact each other in a column that provides interfacial area between the gas and liquid phases. The separation of CO_2 from flue gas occurs due to the high solubility of CO_2 in the solution relative to that of other flue gas constituents. Following this separation, the CO_2-rich solution is sent to a regenerator (also called a desorber or stripper) where it is typically heated to liberate CO_2 from the solution. The warm, CO_2-lean solution is then cooled in a heat exchanger and recycled back to the absorber for reuse, and the process continues.

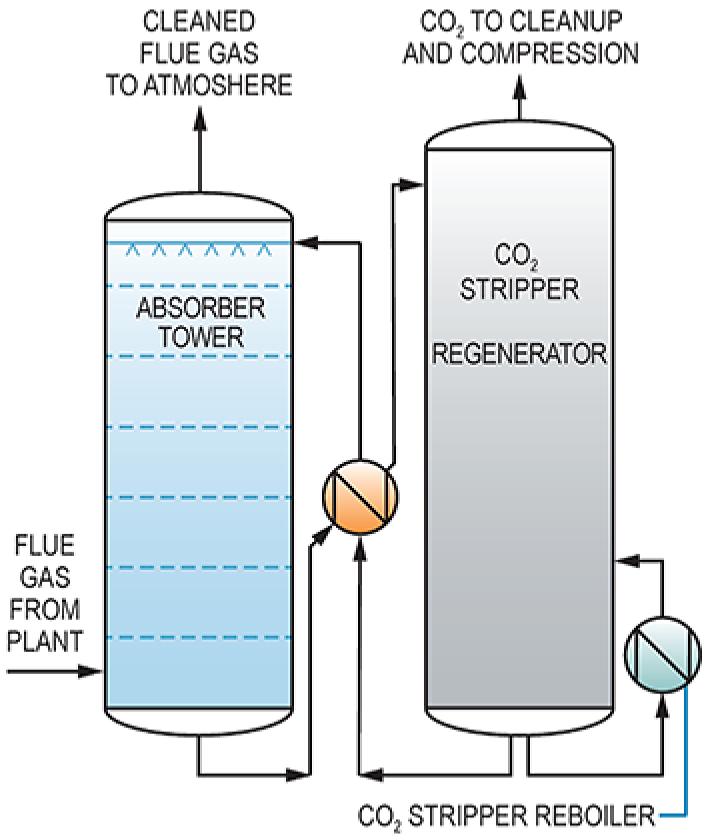


Figure 5-11. *Conventional Absorption-Regeneration Process*

Appendix E, "Mature Capture Technologies," provides substantially more technical detail on current generation CO_2 capture by absorption that is predominantly achieved via amine scrubbing technologies. The appendix details the long history of amine absorption research, development, and application. It includes information about the basic chemistry of the absorption process, advancements being developed, and energy criteria associated with absorption solvent selection. Appendix F, "Emerging Capture Technologies," provides some description of second-generation absorption technologies.

Conventional amine scrubbing will remain the dominant technology for CO_2 capture, particularly for post-combustion applications. It was the first capture technology developed and has been widely deployed across many industries. There are no technical challenges associated with conventional amine scrubbing, making it a viable process for the majority of industries that are anticipated to require CO_2 capture in the future.

b. Adsorption

Adsorption refers to the uptake of CO_2 molecules onto the surface of another material, where they adhere via weak Van der Waals forces (physisorption) or strong covalent bonding forces (chemisorption). Again, this contrasts with absorption where CO_2 molecules dissolve into the bulk of the material itself (Figure 5-10).

During adsorption, CO_2 molecules adhere to the surface of porous particles called sorbents (Figure 5-10). Solid sorbents selectively adsorb gas particles, which means they have a higher tendency to adsorb one type of molecule—in this case CO_2—relative to other molecules present in the gas mixture.

Throughout the history of manned space flight missions, solid sorbents have been used to remove CO_2 at low concentrations (<1%) from air. Regenerable sorbents have been used since the 1990s in space shuttles and for the International Space Station.

Adsorption processes can be implemented in several ways. The most common two are packed beds and fluidized beds, as shown in Figure 5-12. In a packed bed, adsorbent is loaded into a column and flue gas flows through the void spaces between the stationary adsorbent particles. In fluidized beds, flue gas flows at higher velocities such that the adsorbent particles are suspended in the gas flow. In both methods, the adsorbent selectively adsorbs more CO_2 relative to the other constituents passing through the column.

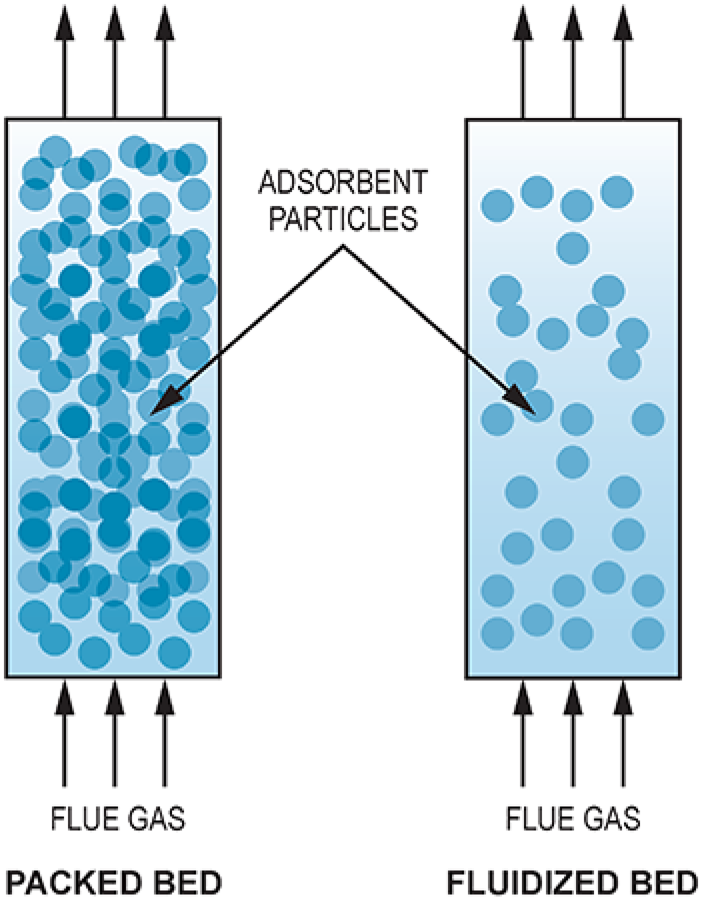


Figure 5-12. *The Packed Bed and Fluidized Bed Adsorption Processes*

During operation, the particles stacked in a packed bed gradually become saturated with CO_2 and are unable to adsorb more, after which point the CO_2 “breaks through” the bed to the outlet. In practice, feed gas flow is switched to a second packed bed before the first becomes fully saturated. While this second bed is being loaded, the first bed is regenerated by heating the adsorbent or lowering the pressure to release the adsorbed CO_2, which then exits the bed. The cycle is then repeated.

This cyclic process can be operated so that CO_2 is continuously removed from flue gas. Alternative paths to achieving this cycle are commonly referred to as pressure swing adsorption (PSA), vacuum swing adsorption (VSA), or temperature swing adsorption (TSA), depending on which approach is used to regenerate the bed. The adsorbent properties dictate the process design and how effectively CO_2 is separated from flue gas.

The PSA and VSA systems are typically associated with physiosorbents. For TSA systems, chemisorbents are designed so that CO_2 is absorbed on a large, solid surface area at low temperatures (40°C to 60°C). Regeneration is achieved by steam at temperatures of 80°C to 150°C. TSA systems usually employ rotary or circulating beds.

The CO_2-loaded adsorbent can also be regenerated in a fluidized bed. In general, a portion of or all the saturated solids in the bed are transported to a regenerator where they are regenerated by manipulating temperature or pressure and subsequently fed back into the reactor. Note that in either regeneration case—via pressure or temperature—the energy for separation in adsorption comes from changes in temperature or pressure imposed on the adsorbent when operating in a cyclic process.

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.[4] PSA with commercially available sorbents, such as a molecular sieve (zeolites), activated carbon, activated alumina, or silica gel are used to create relatively pure hydrogen (H_2) from the syngas to be used in the refinery process. At the Valero Energy refinery in Port Arthur, Texas, sorbents in a VSA process separate the CO_2 from the steam methane reformer syngas for injection in the West Hastings oil field for enhanced oil recovery. The CO_2 separation takes place upstream of the existing PSA process for capturing H_2.[5]

To advance sorbents as a viable at-scale CO_2 capture solution, research and development has been underway to demonstrate their low cost, thermal and chemical stability, resistance to attrition, low heat capacity, high CO_2 loading capacity, and high selectivity for CO_2. CO_2 capture adsorbents use either physical or chemical adsorption and may require less energy input compared to absorption capture with solvents, while offering greater flexibility in operating temperature ranges and fewer environmental impacts. Appendix F, “Emerging Capture Technologies,” provides more detail on this topic, explaining how this technology remains one of the more prospective emerging areas for CO_2 capture. The appendix also provides the history of adsorbent testing, ongoing and future work planned with adsorbents, and challenges and research needs in this area.

c. Membranes

Membranes enable the selective capture of CO_2 based on differences in solubility and diffusivity. For CO_2 capture via membranes, it is the relative selectivity of the membrane toward the gas species being passed through it that controls how the separated CO_2 stream is collected. Depending on this selectivity, a concentrated CO_2 stream may collect either on the upstream (retentate) side or the downstream (permeate) side of the membrane, as shown in Figure 5-13. However, most CO_2 separation membranes permeate CO_2 preferentially. Figure 5-8 illustrates the membrane capture process.

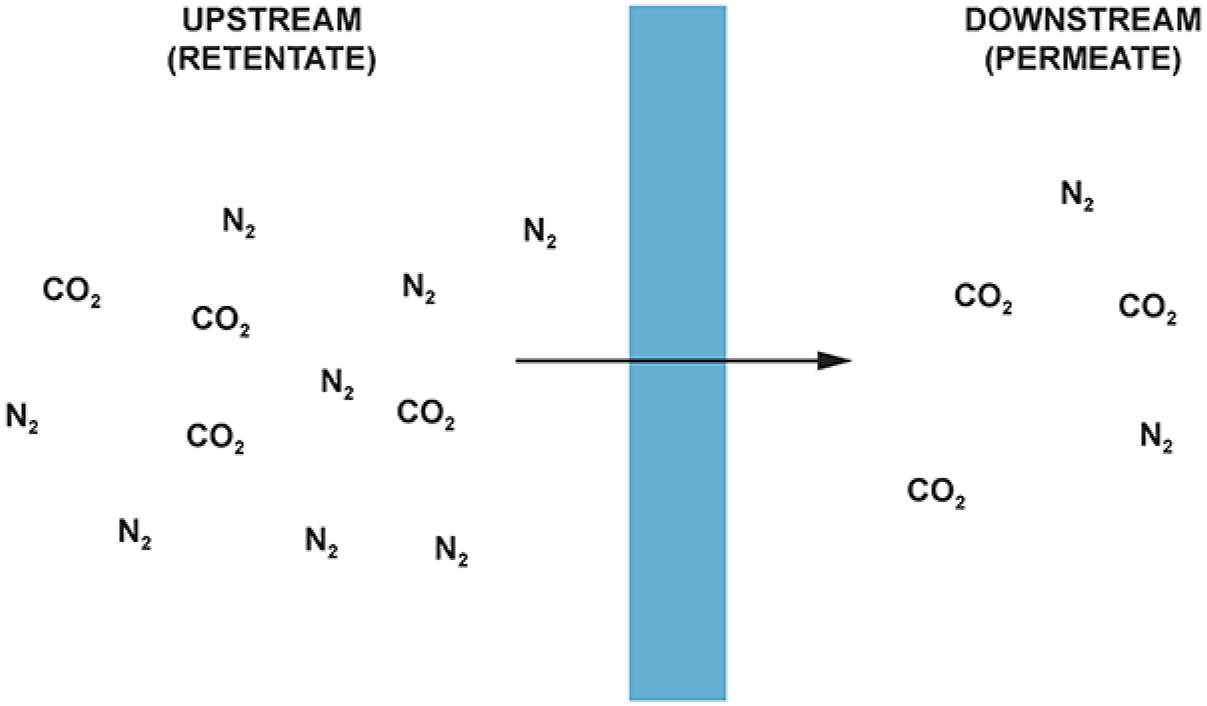


Figure 5-13. *Separation Mechanism in a CO_2-Selective Membrane*

The membrane materials used for CO_2 capture—in either pre- or post-combustion applications—can be divided into three major categories: polymeric membranes, dense metallic membranes, and porous inorganic membranes (PIMs). Each category has its own advantages and challenges. What distinguishes these membranes is their selectivity. While polymeric membranes and PIMs are usually selective toward CO_2 or H_2, dense metallic membranes such as palladium-based membranes usually exhibit very high selectivity toward H_2.

Application of polymeric membranes for CO_2 capture has been limited due to their low permeabilities and the thermal, mechanical, and chemical instabilities that arise during operating conditions. Dense palladium (Pd) or palladium-alloyed membranes mounted on ceramic or porous stainless-steel supports can be used for hydrogen separation in pre-combustion CO_2 capture. Unlike polymeric membranes, these Pd-based dense metallic membranes have higher permeabilities and exhibit higher stability against oxidation and carbonation. Pd-based membranes can be used at higher temperatures than polymeric membranes and show better resistance to high temperatures.

PIMs can be divided into three main categories: silicas, zeolites, and metal organic frameworks. These membranes can be selective toward either CO_2 or H_2, are characterized by their high permeabilities, and can be operated at higher temperatures. Due to these properties, PIMs have gained significant interest in the last decade and research continues.

One of the main advantages of membrane systems is that they are modular. Membrane units can be assembled in one manufacturing facility and then shipped to the location. In contrast, other capture technologies, such as amine absorption, may require building the system onsite.

One of the biggest challenges with membrane systems is that they are ineffective when handling the low pressures and low concentrations of CO_2 in conventional flue gas streams. Membrane systems perform best when inlet pressures and the CO_2 concentrations are high in the feed gas stream. Membranes can therefore be effective in industrial sectors where the CO_2 concentrations are high, such as at ammonia and ethanol plants. For power generation systems such as coal- or natural gas-fired power plants, however, their separation performance declines significantly. In order to keep their performance high in these systems, the surface area must be increased, which results in significant increases to capital costs.

Appendix F, “Emerging Capture Technologies,” provides more technical detail on membranes, the history of membrane testing, ongoing and future work planned, and the challenges and research needs in this area.

From a practical standpoint, the concentration of CO_2 in the gas stream impacts design decisions when the concentration dictates a substantive change in the facility design or implemented scale. For example, the lower cost of capture at ethanol fermentation facilities occur where high-concentration CO_2 off gases preclude the need for most separation equipment.

d. Cryogenic Processes

Cryogenic CO_2 capture is the separation of CO_2 from a gas stream by cooling that stream. Cryogenic separation processes depend on the different boiling points of various gases. The distillation to achieve these boiling points is performed in a cryogenic chamber. CO_2 can be separated as either a liquid or solid phase during cryogenic capture.

Before entering the cryogenic chamber, undesirable gaseous components such as sulfur oxides (SO_x), nitrogen oxides (NO_x), and water vapor must often be removed from the flue gas stream. This step can also be accomplished while the feed gas is being cooled if the process is designed for it. The remainder of the gas mixture, ideally a mixture of nitrogen and CO_2, is sent to the cryogenic chamber where the temperature and pressure are manipulated to liquefy the CO_2. Liquefied CO_2 is then collected at the bottom of cryogenic chamber while nitrogen, still in its gaseous state, exits through an outlet valve at the top of the chamber. Figure 5-9 illustrates the cryogenic distillation process.

CO_2 can also be separated as a solid phase during cryogenic capture. The flue gas stream is cooled to the point that solid CO_2 forms and can be collected. Because the CO_2 is captured as a solid, the need for significant compression (with associated equipment and energy requirements) is eliminated and can be accomplished by heating up the CO_2 to the gaseous state within a fixed volume. Cryogenic CO_2 capture avoids both chemical separation and the need for the separation material to interact with the CO_2. Thus, there is no separation medium to replace or be poisoned by contact with the flue gas, potentially making operation simpler. Instead, the key considerations are two-fold: (1) the efficient and effective heat transfer needed to chill the gas stream to the point that CO_2 forms a solid, and (2) the collection of that solid.

Cryogenic capture is a fairly new technology, and as such, many system integration activities and full demonstrations have not been tested at a meaningful scale. In addition, because CO_2 capture from a gas stream through solid deposition is a complex process, seemingly simple solutions may require additional process or integration steps for this process to become technically feasible. To prevent ice and moisture formation, the flue gas stream must be dehydrated before cryogenic capture. Also, because the entire energy requirement is supplied via electricity rather than a low-grade steam, the energy impact on the power plant may be higher than other processes. Cryogenic processes often rely on extensive heat integration, which makes startup and shutdown potentially difficult.

Appendix F, “Emerging Capture Technologies,” provides more technical detail on cryogenic capture, the history of cryogenic testing, ongoing and future work planned, and the challenges and research needs in this relatively nascent area.

e. Summary

Although all four capture methods separate CO_2 from the source gas mixture, the mechanisms of separation for each method differ on a molecular scale. The chemical solvents used during absorption and sorbents used during adsorption are often employed in industrial applications where the initial concentration of CO_2 in the source gas mixture is relatively dilute (<15%). Typical streams of this type include combustion exhaust streams and ambient air.

For other industrial processes where the concentration of CO_2 in the feed gas mixture may be significantly higher (>90%),[6] membranes, cryogenic technologies, physical solvents, and sorbents may be used. High-concentration CO_2 streams are typically sourced from ammonia processing units, ethanol production facilities, and hydrogen producing units.

The following section will briefly describe the range of industries where CO_2 separation using these capture technologies may have application.

3. Capture Opportunities by Sector

The appropriate carbon capture technology to apply in an industrial application depends on the size (volume) of the source gas stream, concentration of CO_2 in the gas mixture, and percent of CO_2 to be captured. Each of these considerations will influence determination of the optimum technology and associated costs of CO_2 capture.

In the United States, large stationary point-source emissions of CO_2 originate from a number of industries, including:

- Electricity and power generation
- Petroleum and coal product manufacturing
- Pulp, paper, and paperboard mills
- Chemical manufacturing

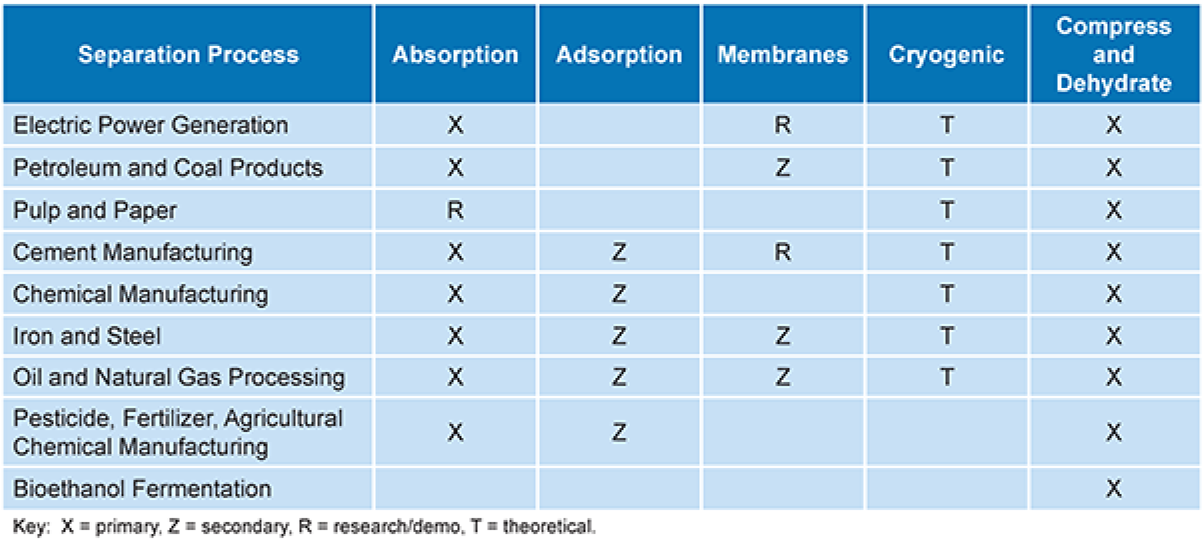
- Cement and concrete production
- Iron and steel mills and ferroalloy manufacturing
- Oil and gas processing
- Pesticides, fertilizers, and other agricultural chemical manufacturing
- Bioethanol fermentation.

The concentrations of CO_2 emitted from these sources vary from about l% to 5% for gas-fired power, 12% to 15% for coal-fired power, and >95% at a bioethanol production facility (due to the fermentation process).

Combustion from electricity and power generation represents more than half of the nationwide stationary point-source emissions. Two-thirds of that comes from coal-fired units. Capture of CO_2 emissions from coal-fired units have been the most thoroughly studied to date.

In addition, the electricity and power sector typically contains a single exhaust stream in which CO_2 capture may be applied. This is quite different from the stationary emissions associated with the broader industrial sector because the CO_2 emissions of these industries (chemical manufacturing, cement, iron, and steel, etc.) are a mix of CO_2 generated from heat, power, and the chemical process itself that goes into making the industry product (e.g., calcining[7] of carbonate for cement production evolves CO_2 by a decomposition reaction). These distributed emissions sources increase the challenge, and therefore the cost, of capturing CO_2 associated with these industries.

A summary of the industries in which the four separation/capture methods may be employed is provided in Table 5-1. As previously noted, absorption has the widest range of applicability given its decades of deployment experience, particularly with amines. Adsorption and membrane technologies offer potential solutions for some industries, although application to date is generally less mature. Finally, cryogenic CO_2 capture is at the earliest stage of application but has theoretical potential across several industries.



Separation Process	Absorption	Adsorption	Membranes	Cryogenic	Compress and Dehydrate
Electric Power Generation	X		R	T	X
Petroleum and Coal Products	X		Z	T	X
Pulp and Paper	R			T	X
Cement Manufacturing	X	Z	R	T	X
Chemical Manufacturing	X	Z		T	X
Iron and Steel	X	Z	Z	T	X
Oil and Natural Gas Processing	X	Z	Z	T	X
Pesticide, Fertilizer, Agricultural Chemical Manufacturing	X	Z			X
Bioethanol Fermentation					X

Key: X = primary, Z = secondary, R = research/demo, T = theoretical.

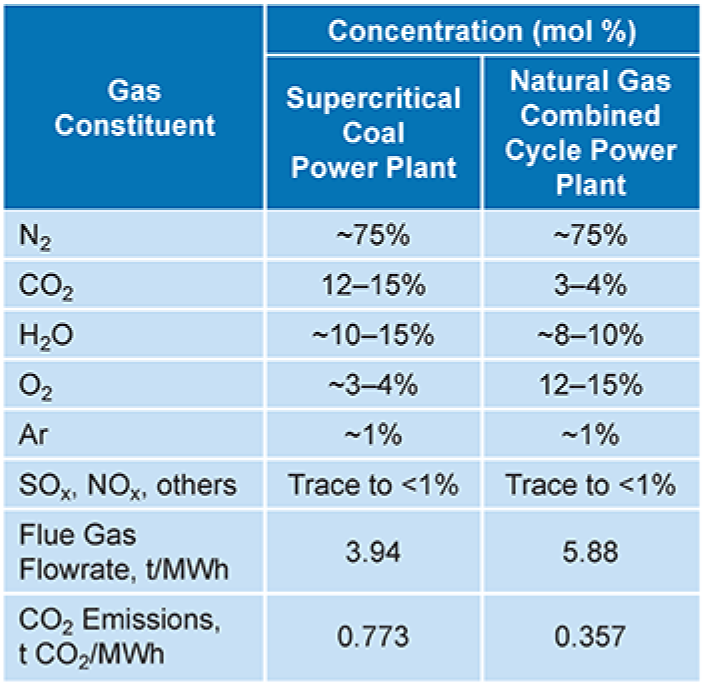
Table 5-1. *Application of Various Separation/Capture Processes in Selected Industries*

The following sections provide some detail on the industries summarized in Table 5-1, the nature and concentration of that industry’s CO_2 emissions source(s), and the challenges or opportunities for CO_2 capture that may exist.

a. Electric Power Generation

i. Post-combustion

Post-combustion capture refers to separating CO_2 from a flue gas derived from combusting fossil fuel in air, the dominant method of making power. Depending on the type of fossil fuel, CO_2 concentration is 3% to 15% in a mix of nitrogen, water, oxygen, argon, and various impurities formed either during combustion or that were in the fossil fuel. Table 5-2 shows typical flue gas composition for coal-fired supercritical and natural gas combined cycle power plants.



Gas Constituent	Concentration (mol %)	
	Supercritical Coal Power Plant	Natural Gas Combined Cycle Power Plant
N_2	~75%	~75%
CO_2	12–15%	3–4%
H_2O	~10–15%	~8–10%
O_2	~3–4%	12–15%
Ar	~1%	~1%
SO_x, NO_x, others	Trace to <1%	Trace to <1%
Flue Gas Flowrate, t/MWh	3.94	5.88
CO_2 Emissions, t CO_2/MWh	0.773	0.357

Table 5-2. *Gas Concentration in Flue Gas*

Because nitrogen is the predominant component compared with other components, the key separation is between CO_2 and N_2. Therefore, post-combustion capture technologies target CO_2-N_2 separation while ensuring the other flue gas constituents have minimal impact on the capture process or are removed before the capture process. As previously described, examples of post-combustion technologies include solvents, adsorption, membranes, and cryogenic separation.

ii. Oxy-Firing

Oxy-fuel combustion, also called oxy-firing, refers to combusting fossil fuels in oxygen (O_2) as opposed to air. Provided there is no ingress of atmospheric air into the combustor, the resulting flue gas is mostly CO_2 and water, and any impurities in the fuel. This stream can then be dehydrated and compressed. Combustion in pure O_2 results in very high combustor temperatures, so a portion of the CO_2-containing flue gas is recycled back and blended with the oxygen feed to limit the O_2 concentration in the combustor. This effectively reduces the temperature in the combustor while still producing a flue gas composed of predominantly CO_2 and water.

For most oxy-firing processes, oxygen usually comes from air and the key separation is O_2-N_2, which is commonly referred to as air separation. Large-scale air-separation units are typically cryogenic, but they are also energy intensive and thus reduce the net output of the power plant. To date, only small-scale oxy-firing pilots have been conducted, and while there have been a few large-scale oxy-firing projects announced in recent years, none have moved forward.

iii. Pre-combustion

Pre-combustion capture refers to partially oxidizing fossil fuels using steam and O_2 or air under high temperature and pressure to generate a mixture of CO, CO_2, and H_2, commonly known as synthesis gas or syngas. In a reaction called a water-gas shift, the carbon monoxide within the syngas is further reacted with water to make CO_2 and H_2 at high temperature and pressure. The CO_2 is separated from H_2, which is then combusted in air.

The key separation step is H_2-CO_2. However, because the gas stream is at high pressure, the separation is easier than for gas streams at lower pressures, such as post- or oxy-combustion. Physical solubility of CO_2 in a solvent is generally sufficient to provide a cost-effective means for the separation process itself; however, the capital cost of equipment is higher than for post-combustion capture systems.

iv. Chemical Looping

For application during power generation, chemical looping can be categorized as a flameless oxy-combustion technology. A relatively clean and concentrated stream of CO_2 is a by-product of this process. The novelty of this technology is its use of a metallic oxide as the oxygen carrier for a reaction that produces energy instead of requiring the combustion of a fossil fuel (or biomass) to produce that same energy. This produced energy can then be used to generate the steam required in a power generation application.

Since the fuel does not come in contact with air, the process inherently produces a CO_2 stream devoid of N_2. This negates the need for a back-end post-combustion CO_2 capture system.

Unlike conventional oxy-combustion systems, the chemical looping process does not need an air-separation unit to supply oxygen for combustion, resulting in relatively lower capital cost.

b. Pulp, Paper, and Paperboard Mills

There are two primary types of processes in the pulp and paper industry: mechanical mills and integrated kraft mills. The latter represents the majority. The kraft process generates a by-product from fiber extraction known as black liquor. This black liquor is often burned in a recovery boiler to provide steam to the combined heat and power (CHP) plant. The bulk of the CO_2 emissions is from these boilers—either recovery boilers or biomass boilers—and some emissions are from the lime kiln.

Two options for CO_2 capture have been investigated in pulp and paper mills: black liquor integrated gasification combined cycle (BLGCC) and biomass-based CHP systems in kraft pulp mills. Larger CO_2 emissions reductions have been achieved with post-combustion capture and chemical absorption from a recovery boiler and bark boiler[8] flue gases. However, higher electrical efficiency was achieved with BLGCC with partial pre-combustion CO_2 capture and no water-gas shift reaction before absorption.[9]

According to one study, “carbon negative” operations are possible by implementing a new biomass boiler and CCS system and replacing existing natural gas boilers and current hog fuel boilers, which burn bark and organic waste debris from forestry.[10] A key consideration for CO_2 capture from paper mills is that they are located near heavily forested, remote locations that tend to be far from industrial hubs and CO_2 transport pipelines.

c. Basic Chemical Manufacturing

The chemical industry is energy intensive, with feedstocks of oil, natural gas, and minerals. According to the Environmental Protection Agency, total emissions from the U.S. chemical sector in 2017 were 184.1 million tonnes of CO_2e, and this volume is projected to increase substantially over time. Important chemical products include ammonia, ethylene, propylene, and aromatics.

i. Ammonia

Ammonia production is achieved by combining nitrogen and hydrogen at high pressures over a catalyst during the Haber-Bosch process. During the process, superheated steam is mixed with natural gas in the steam methane reforming (SMR) process, producing hydrogen gas and carbon monoxide. The carbon monoxide from this reforming reaction interacts with water again during the water-gas shift reaction, as explained earlier, to produce more hydrogen and carbon dioxide.

Approximately 64% of the hydrogen consumed in the ammonia industry is used within a captive market, meaning that it is produced and consumed on the same site. Not all of the CO_2 generated in the production of synthetic ammonia is emitted directly to the atmosphere. At some plants, the produced CO_2 is captured and used to produce urea or methanol. Ammonia production is attractive because the CO_2 separation takes place in the plant itself and produces a high-purity stream of CO_2. Only dehydration and compression are required to effectively capture this CO_2.[11]

ii. Ethylene, Propylene, and Aromatics

Ethylene and propylene (olefins) are used in the petrochemical industry and produced by the cracking of saturated hydrocarbons, which produces hydrogen. Light off-gases are combusted with natural gas to provide heat for steam crackers[12] or process heaters. Flue gas from these operations is vented, releasing 7% to 12% of CO_2 into the atmosphere.

Olefins are heavily used in the petrochemical industry, particularly during polymer production to make plastics. Aromatics are important industrial products. The chemical reactions to produce olefins and aromatics do not produce CO_2, but the reaction requires superheated steam. The fuel burning to produce the steam creates a sizeable amount of CO_2.

d. Cement and Concrete Product Manufacturing

Concrete is formed by the mixture of sand, gravel, water, and cement. The cement is activated by water, which is the binder that holds the mixture together. The process for cement manufacture can use a multitude of fuel sources to provide the heat necessary for the drying, calcination,[13] and sintering processes. The main CO_2 emissions point source is the off-gas from the kiln where this process occurs (14% to 33% CO_2). A second major source is calcination of calcium carbonate to form calcium oxide/calcium silicate species.

The off-gas from the kiln may have a higher level of SOx and NOx, requiring scrubbing with flue gas desulfurization and the addition of selective catalytic reduction. A challenge to scaling up the post-combustion capture with amines in the cement industry is that the results from power plant demonstrations with amine solvents are not directly transferrable to the cement industry given that there can be multiple point-source emissions in the cement manufacturing process.[14,15]

e. Iron and Steel Mills and Ferroalloy Manufacturing

The production of steel can be divided into two main categories: primary and secondary. Primary steelmaking is the most common form of steel manufacture, accounting for approximately 65% of steel production worldwide. This uses two main process pathways: (1) blast furnace with a basic oxygen furnace (BF/BOF) and (2) direct-reduced iron with an electric arc furnace (DRI/EAF). Among these two options, the BF/BOF process dominates. Coke (a fossil-fuel residue) is used to reduce iron in a blast furnace (BF), producing crude iron[16] that is fed to the basic oxygen furnace (BOF) where pure oxygen reacts with pig iron to produce molten steel. As a result of iron ore reduction, CO_2 is produced as a by-product.

The iron and steel industry has many different CO_2 point sources distributed throughout the process. At an integrated iron and steel plant, 75% of emissions originate from the top gas of the BF and in small combustion units, 12% indirectly originates from electricity generation from the grid, and the balance originates from the coke oven gas (COG), BOF gas, and sintering. However, the BF gas and the COG streams are frequently used to produce electricity in the plant, creating several small CO_2 point sources distributed throughout the plant, thereby increasing the cost of CO_2 capture. Among the available sources, the highest CO_2 concentrations are the COG at roughly 27% by volume (vol%) and the blast furnace stove at roughly 21 vol%.

An option exists for capturing CO_2 directly from the BF post-combustion. This may require substantial changes to the facility depending on how the BF gas is used throughout the process. Technologies tested for CCUS in this industry today mostly involve BF post-combustion capture through absorption with solvents, pressure-swing adsorption, or membrane separation.

Secondary steelmaking, the second manufacturing category, involves using EAFs in the production of steel. This approach produces much less CO_2 per product than the BF/BOF route by melting recycled steel rather than reducing iron and generating process emissions. However, EAF implementation is limited to areas with sufficient amounts of recycled steel available.

The first CCUS facility in the iron and steel industry was the Abu Dhabi CCS Project established in 2016. The facility captures approximately 0.8 Mtpa of CO_2 at the Emirates Steel Industries, which is using it for EOR at an Abu Dhabi National Oil Company oil field. Other pilot scale initiatives, like POSCO in South Korea and the Stepwise Initiative in Sweden, illustrate the industry’s movement toward emission reductions.

f. Oil and Natural Gas Processing

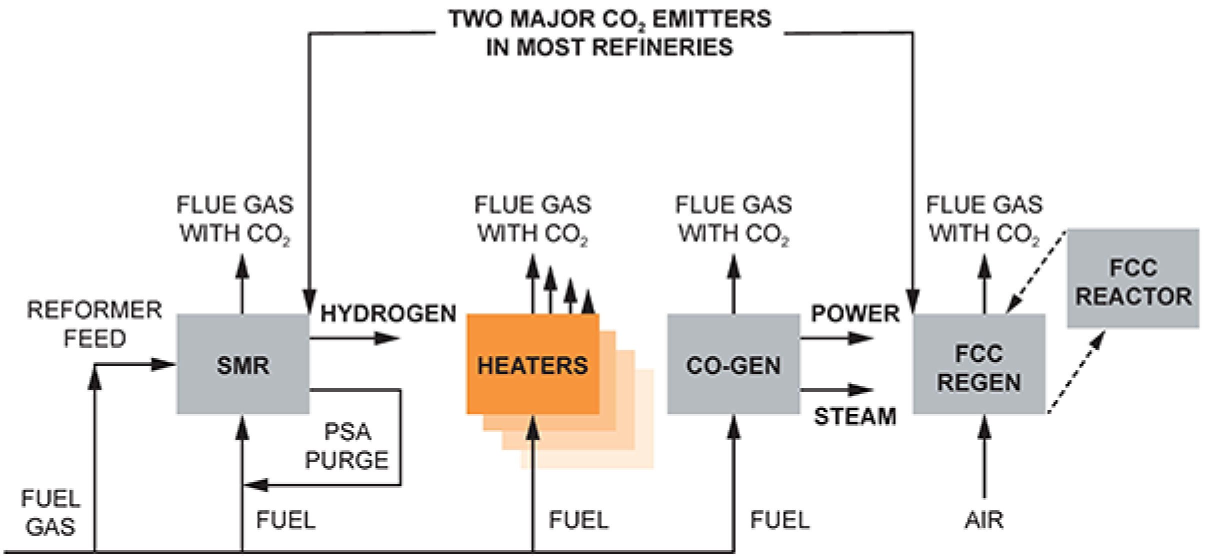
Operations in the oil and natural gas industry are usually divided into three categories: upstream, midstream, and downstream. Upstream refers to all the operations associated with the exploration and production of oil and natural gas. Midstream operations refer to the operations that transport and deliver the oil and natural gas from the wellhead to, for example, refineries. Midstream equipment includes pipelines, pumps and compressors, tank trucks, rail tank cars, etc. Downstream operations are those that deal with the refining of crude oil, the processing/treatment of natural gas, as well as distribution of the finished products.

The following focuses on petroleum refining of crude oil in downstream operations, as this could be an important source of CO_2 emissions for capture and CCUS.

i. Petroleum Refining

Petroleum refining accounts for 10% of U.S. industrial emissions. The majority of CO_2 emissions in petroleum refineries are from the furnaces and boilers, followed by the fluid catalytic cracker. The large numbers of disparate flue gas source streams in a refinery present a challenge for CO_2 capture at scale and would need to be combined. However, many process challenges would make this difficult in practice. Both oxy-combustion and post-combustion have been considered for CO_2 capture at refineries.[17]

The main CO_2 emissions sources from the refinery are fired heaters and boilers, NGCC co-generators, hydrogen plants, and fluid catalytic cracking (FCC) units (Figure 5-14). Each of the FCC units has its own separate flue gas stack, and the combustion sources are spread throughout the refinery, making the capture of CO_2 emissions from a refinery site challenging and expensive. The FCC is a large, single-point emitter in an oil refinery because it continuously regenerates the catalyst by burning off deposited carbon.

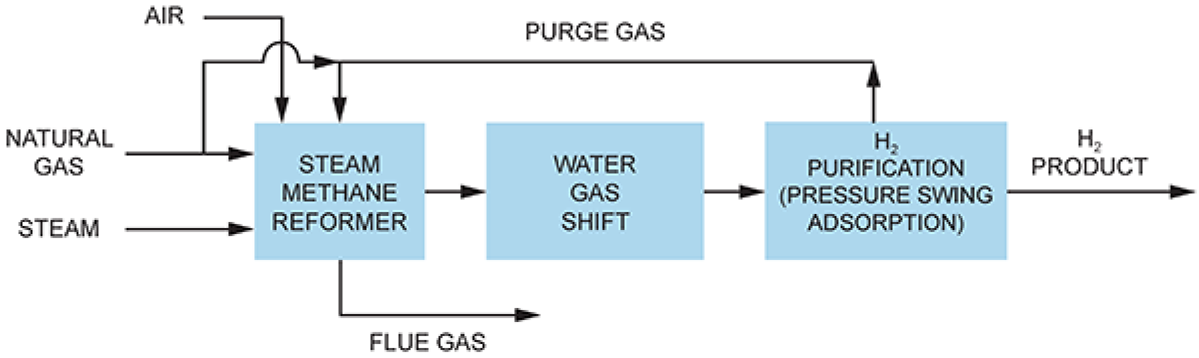


Note: SMR = steam methane reforming;
PSA = pressure swing adsorption;
FCC = fluid catalytic cracking.

Source: EPRI, *Program on Technology Innovation, Industrial Carbon Capture – Oil and Gas Sector*, product ID 3002010880.

Figure 5-14. *Refinery CO_2 Emission Sources*

The largest CO_2 point-source emitter will often be a hydrogen plant with its reformer furnace. Hydrogen production can be accomplished either by SMR or auto-thermal reforming. As was described for the ammonia production process, SMR uses a furnace to heat metal tubes where a reaction takes place with a catalyst, converting steam and light hydrocarbons (methane or refinery fuel gas) into H_2, CO_2, and carbon monoxide. The syngas is converted into more H_2 and CO_2 through a water-gas shift reaction. Then the H_2 is separated and purified by VSA or a PSA unit (Figure 5-15).



Source: EPRI, *Program on Technology Innovation, Industrial Carbon Capture – Oil and Gas Sector*, product ID 3002010880.

Figure 5-15. *Modern Hydrogen Plant*

Manufacture of hydrogen depends heavily on processing fossil fuels, and CO_2 is an unavoidable by-product of this process. There are few technological barriers to CO_2 capture in large-scale hydrogen production, and relatively rapid scale up of CCUS deployment could be expected.[18]

g. Pesticide, Fertilizer, and Other Agricultural Chemical Manufacturing

Nitrogen-based fertilizer is used throughout the world to replace nutrients in the soil for agriculture. Fertilizers are produced with natural gas in an energy-intensive process that extracts nitrogen from the air. A fairly pure CO_2 stream is produced that can be easily separated.

The most common nitrogen fertilizers are ammonia, ammonium nitrate, and urea. Much of the CO_2 produced in the production of ammonia from natural gas is used in the production of urea in the same facilities (see the description of ammonia production in the Basic Chemical Manufacturing section earlier in this chapter).

h. Bioethanol Production via Fermentation

High-purity CO_2 emissions are an output of fermentation processes, such as the production of bioethanol used as a transport fuel. These data are not available from the 2018 EPA Facility Level Information on Greenhouse Gases Tool database because it only provides emission data associated with industrial point sources.

The United States has 202 bioethanol plants, mostly co-located along the corn belt in the Midwest. The amount of CO_2 produced by fermentation is proportional to the quantity of ethanol produced and results in a high-concentration CO_2 stream (>95%). The collective CO_2 emissions from the fermentation process of ethanol production are 46.8 Mtpa.[19,20]

The capture of CO_2 from fermentation emissions from bioethanol results in negative emissions because biomass is net-zero according to the EPA. Furthermore, the separation of CO_2 during bioethanol fermentation is largely a process of dehydration and compression at relatively low cost. Given this, the fermentation emissions industry appears well-positioned for relatively rapid scale up of CCUS deployment.

i. Summary

Given the variability and complexity in the sources of emissions across the range of power and industrial sectors, no CO_2 capture approach has a technical advantage over the others for all cases across all industries. Factors such as cost, operability, environmental footprint, emissions, and other practical aspects give a specific technology a marketplace advantage. These advantages do not necessarily translate across even the same type of capture approaches, which means that a capture technology or approach that is viable in one industry may not have any potential in another industry. Even within a given industry, site-specific issues may give an advantage to one capture approach over another.

In general, absorption-based approaches are more mature and more widely applicable because they tend to be more economical at larger scales relative to other separation approaches (Table 5-1). As a result, there is far more commercial experience with absorption at large scales than other separation approaches, and the largest commercial deployments to date are absorption-based. Large-scale adsorption and membrane systems also exist, but they are not as common.

Additional R&D will enable every CO_2 capture method to advance—absorption, adsorption, membranes, cryogenic, or a hybrid of these—yet the commercial success of a specific method will depend on a multitude of factors and the industry in which it is being applied. Appendix F provides more information on these less mature technologies.

The main message is that there is no silver bullet, no single CO_2 capture technology that can address all stationary source CO_2 emissions. Hence, progressing a diversified capture technology research and development program continues to be warranted.

B. Reducing CO_2 Emissions versus Direct CO_2 Removal from the Atmosphere

The conventional CO_2 capture approaches explained in this chapter relate to the capture of CO_2 at the emissions source. Application of a capture technology can take place either as a retro-fit of an existing plant or as a new build. There are sectors that will continue to be difficult to decarbonize, such as fossil fuel-based transportation and industrial and home heating, among others. Although the cumulative emissions from the summation of these sources are significant, the volume of CO_2 emissions from each unit is not large enough to justify the outlay of capital that would be required for CO_2 capture.

Negative emissions technologies enable the direct removal of CO_2 from the atmosphere, thereby offering potential pathways to offset emissions that would otherwise be difficult to reduce, such as the projects noted earlier. Two identified negative emissions technologies are described next: biomass energy coupled with CO_2 capture and storage (BECCS) and direct air capture (DAC) with CCS.

1. BECCS

When biomass (plant life) uses solar energy to grow, it captures CO_2 from the atmosphere and converts it into sugars and fibers. The biomass is harvested and fed into a biomass-fired power plant to generate electricity. This biomass energy (bioenergy) can be coupled with conventional approaches to CO_2 capture, and the separated CO_2 is dehydrated, compressed, transported, and injected for geologic storage or used for CO_2 EOR.

Biomass has been co-fired with coal to generate power, though CCS has not yet been coupled to such power generation. Therefore, it is reasonable to assess that the TRL of BECCS would be TRL 4–5 (Figure 5-2).

The cost drivers for BECCS are similar to the ones for CCS. Factors that will be different include the transport and preparation of the biomass for power generation. Thus, the transport distance of the biomass feedstock will influence cost. Removing water and the preparation of the biomass into a form suitable for firing, such as pellets, also influence cost.

The scale of impact that BECCS could have depends on many factors, some of which are the quantity, quality, and seasonal variability of the biomass (modern or traditional biomass energy), the area of land used for energy crops and land use change, availability of the geologic storage capacity and CCS infrastructure, deployment rates, and social acceptability.

2. DAC with CCS

DAC is a technology in which the concentration of CO_2 in the Earth’s atmosphere (~410 parts per million) is captured directly, transported, injected, and stored in geologic formations.

Small proof-of-concept testing of DAC has been carried out by several companies—Climeworks, Global Thermostat, and Carbon Engineering. Thus, it is reasonable to assess the TRL of DAC to be in the early stages, TRL 1 through TRL 5 (Figure 5-2).

Given the dilute concentrations of CO_2 in the atmosphere (0.04%), the minimum thermodynamic work required for separating CO_2 with DAC can be two to three times higher than that of CO_2 capture from a natural gas-fired power plant. Thus, the reported costs associated with DAC are significantly higher than those reported from point-source capture, such as a natural gas-fired power plant. For instance, a 2019 report released by the National Academy of Sciences estimates the current cost of DAC at approximately \$600 per tonne of CO_2[21] (tCO_2) based upon established commercialized technology demonstrated by Climeworks. Although there have been reports of lower costs, these have yet to be realized because the projected technologies and DAC plants have yet to be demonstrated. When DAC is coupled to permanent storage or sequestration, more detailed cost estimates will have to be made.

IV. WHAT DRIVES THE COST OF CO_2 CAPTURE?

The cost of capture is typically the largest cost component in the CCUS process because of the large size of the equipment required to separate CO_2 from the flue gas mixture from a large-scale emission source. CO_2 capture can account for as much as 75% of the cost of the CCUS projects in industries where separation of CO_2 from the exhaust gas is required, such as power and electricity generation; cement, steel and chemical manufacturing; oil refining; and others.

There are, however, several industrial applications where the cost of CO_2 separation is relatively low because the CO_2 has already been separated as part of the process. The lowest cost for CCUS deployment is found in the natural gas processing, ammonia, and bioethanol production industries where the CO_2 exhaust stream from the associated processes is high (95% to 100%) and no CO_2 separation technology needs to be applied.

When CO_2 capture is required, the cost of capture depends on several factors. Important considerations include:

- Size (volume) of the source gas stream being processed
- Concentration of CO_2 in the gas mixture
- Contaminants in the gas mixture
- Pressure and temperature of the mixture
- Percent of CO_2 to be captured
- Purity of the CO_2 desired downstream of the capture process
- Site-specific factors, like geography, available space, retrofit or new build, and other environmental factors.

Higher concentration CO_2 sources or applications requiring lower outlet CO_2 purities are less costly to separate. Lower concentration sources, where CO_2 is in dilute form in the exhaust stream, or applications requiring higher outlet CO_2 purities are more costly. Ultimately, the CO_2 separation process requires energy to progress, and the energy requirements of the separation process have the largest impact on capture cost.

Absorption using amine solvents (amine absorption) is the most common capture technology used for the industrial application of CO_2 capture in CCUS projects. The technology is mature and has been deployed for decades (see Section III, "CO_2 Capture Technologies and Applications" earlier in this chapter, and Appendix E). Given this experience and the confidence in its application, amine absorption is likely to remain the predominant technology deployed for large-scale CCUS projects in the near term. The potential for cost reduction is expected to be relatively limited (10% to 20%) and associated with "learning by doing" as new integrated projects help to optimize efficiencies versus cost reduction from new innovations in amine absorption technology. The key to achieving these modest cost reductions will be minimizing the size of absorber tower and amine regenerator (stripper) units that are part of the amine absorption process (Figures 5-6 and 5-11), units that can represent more than 50% of the capital cost of the separation system.

The earlier stage capture technologies described in Section III of this chapter, "CO_2 Capture Technologies and Applications," and in Appendix F (solvents, adsorption, membranes, and cryogenic separation) are either substantially less mature than amine absorption or have not been deployed at the scale of amines in CCUS projects to date. Thus, it is with these technologies that the greatest opportunities for technological innovation may exist in the long term (10 to 20 years), and for potential reductions, or disruptions, in the cost of CO_2 capture (30% to 50%).

The next section describes a capture RD&D funding request that directs more investment toward these less mature capture technologies, among other objectives. Funding of these emerging technologies anticipates advancement of the more prospective ones toward pilot and demonstration testing in the future. This is described in more detail in Chapter 3, “Policy, Regulatory, and Legal Enablers,” in Volume II of this report.

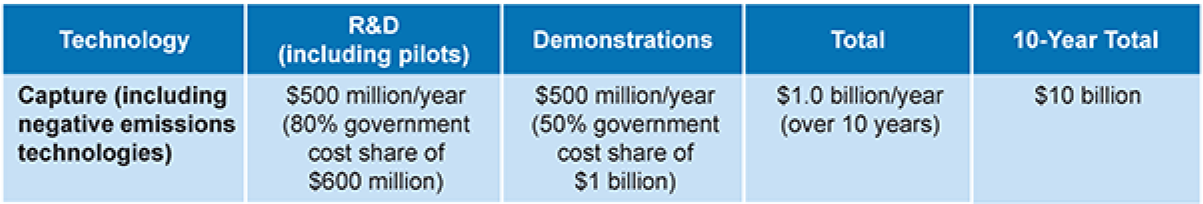
Chapter 2, “CCUS Supply Chains and Economics,” in Volume II, explains the CCUS cost curve used in this study.

V. RESEARCH, DEVELOPMENT, AND DEMONSTRATION NEEDS

Investment in RD&D of CO_2 capture technologies is the best way to progress new and emerging technology solutions, scale up less mature technologies, and lower the integration costs of more mature technologies. The business case for investing in CO_2 capture RD&D at-scale builds on the public-private model of federal government support that has already been established. Continued collaboration is a vital component to catalyzing widespread deployment of CO_2 capture technologies and CCUS.

Over the next decade, combined public and private investment in CO_2 capture technology RD&D estimated at

$1.6 billion per year is recommended, as shown in Table 5-3. The projected federal investment amount averages to about $1.0 billion per year. This assumes historical norms for the government cost-shares associated with research and development investment, including pilot testing (80%) and demonstration projects (50%).



Technology	R&D (including pilots)	Demonstrations	Total	10-Year Total
Capture (including negative emissions technologies)	$500 million/year (80% government cost share of $600 million)	$500 million/year (50% government cost share of $1 billion)	$1.0 billion/year (over 10 years)	$10 billion

Table 5-3. *Recommended Federal RD&D Funding Levels for CO_2 Capture*

Current funding levels from the FY19 enacted budget are $101 million for CO_2 capture and $60 million for advanced energy systems such as pressurized oxy-combustion, chemical looping combustion, supercritical CO_2 cycles, and hydrogen generator systems. The proposed RD&D plan would include the following emphases:

- Modify capture technologies to handle the differences between coal flue gas, natural gas flue gas, and industrial CO_2 gas sources.
- Advance development in solvents, sorbents, membranes, and cryogenic processes for gas separation as well as new energy cycles that would inherently capture CO_2 for storage or utilization.
- Develop a baseline against which improvements can be benchmarked and openly evaluated.

- Lower the overall cost of capture as well as capital, operating, and maintenance costs.
- Focus on operational flexibility of CO_2 capture systems to accommodate ramping up cycles.
- Evaluate partial capture to find the low-cost optimum for which the technologies and sectors would be most applicable.
- Investigate opportunities for the application of hybrid capture systems.

The recommended average annual investment into CO_2 capture technologies over the next 10 years are explained below:

- R&D, which includes basic science and applied research, bench-scale, and small pilots: $300 million per year for over a minimum of 10 years on CO_2 capture and advanced power cycles system development. Typically, the cost share is 80% federal.
- Large Pilots: $300 million per year over a minimum of 10 years at 80% federal cost share is needed for a large-scale pilot program.
- Demonstrations: $1.0 billion annually over 10 years to support the needed CCUS technology demonstrations at a total 50% federal cost share.

VI. CONCLUSIONS

CO_2 capture technologies are a key component in the deployment of CCUS. There are four main CO_2 capture technologies: absorption, adsorption, membranes, and cryogenic separation. Each technology offers advantages and challenges associated with implementation in different industries. Of these technologies, absorption has been the most heavily studied and deployed because it is the most mature technology, having been deployed for more than 40 years.

There are four main applications of CO_2 capture technologies, predominantly associated with the electric power generation sector: pre-combustion, post-combustion, oxy-firing, and chemical looping. Post-combustion capture is the most widely deployed application currently.

Simplified CO_2 capture (basic separation, dehydration, and compression) applications have also been applied successfully at scale in industries where the emissions stream has high concentrations of CO_2, like natural gas production and bioethanol fermentation, among others.

In the United States, the primary industries with point-source emissions of CO_2 for which separation technologies have been or will need to be applied in the future include: electricity and power generation; petroleum and coal product manufacturing; pulp, paper, and paperboard mills; chemical manufacturing; cement and concrete production; iron and steel mills and ferroalloy manufacturing; oil and natural gas processing; pesticides, fertilizers, and other agricultural chemical manufacturing; and bioethanol fermentation. A number of these industries have seen the deployment of large-scale integrated CCUS projects in the United States and around the globe, confirming the ability of the capture industry to integrate technologies and provide a basis for further expansion and commercialization of CO_2 capture technologies.

Conventional amine scrubbing is the oldest CO_2 capture technology. The biggest challenges with amine systems are their capital cost and the scarcity of full-scale demonstrations or facilities at industrial and gas-fired power plants. Due to the maturity of the solvent technology for CO_2 capture, the costs surrounding this approach have greater certainty compared with separation methods involving solid sorbents, membranes, or cryogenic techniques.

The development of new capture technologies has focused on the development of new solvents for absorption, new sorbent materials for adsorption, and assessing the challenges associated with membrane technologies. Due to the early-stage development of these technologies for CO_2 capture, the costs associated with these approaches are less certain. Capital cost reduction has not been a common focus but needs to be.

To date, much of the RD&D in the field of CO_2 capture has been related to the power generation sector, and specifically to coal-based power generation. RD&D activities should be expanded to include gas-fired power and other industrial sectors because achieving at-scale deployment of CCUS will require participation across all industrial sectors. Government investment in RD&D needs to expand and to continue to encourage public and private sector collaboration for the planning, piloting, and demonstration of emerging CO_2 capture technologies. Such collaboration should continue to provide support for test centers and facilities where technology hardening and demonstration can occur under real-world operating conditions to improve confidence in the necessary scale up of CCUS deployment.

Because no single CO_2 capture technology can meet the needs of every stationary source of CO_2 emissions, a diversified technology development program involving public and private collaboration and funding is necessary to support the scale up of CCUS deployment.

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[1] Dehydration removes entrained water, which is water that exists as free droplets suspended in the gas.

[2] Physical solvent systems may be used when the pressure of the gas stream being processed and the CO_2 concentration of the stream are sufficiently high. In most scenarios, however, the CO_2 concentration is <20%, which requires a chemical separation process by which CO_2 is selectively captured via a chemical reaction, i.e., chemical solvent.

[3] Minimum thermodynamic work is defined as the minimum energy required to separate CO_2 from a gas mixture with known input parameters, such as initial and final concentrations, percent capture, and temperature.

[4] Syngas, a short version of synthesis gas, is a mixture of CO, CO_2, and H_2.

[5] Department of Energy/National Energy Technology Laboratory Carbon Capture Program, *Carbon Dioxide Capture Handbook*, August 2015, Lyn Brickett, DOE contact.

[6] Bains, P., Psarras, P., and Wilcox, J. “CO_2 capture from the industry sector,” *Progress in Energy and Combustion Science* 63 (2017) 146-172.

[7] Calcining is the decomposition of calcium carbonate (limestone) to calcium oxide (lime) and carbon dioxide by heating the limestone to high temperatures in the presence of air or oxygen.

[8] Bark boilers are primarily used in pulp and paper mills to produce process steam for paper production. These boilers are especially efficient in the production of pulp and paper, as bark is a waste by-product of previous processes involved in paper making. Steam is generated when the bark waste is burned and converted to process steam that turns a turbine to produce electrical power.

[9] Mollersten, K., Gao, L., and Yan, J., “CO_2 Capture in Pulp and Paper Mills: CO_2 Balances and Preliminary Cost Assessment,” *Mitigation and Adaptation Strategies for Global Change* (2006) 11: 1129–1150.

10 McGrail, B. P. “Capture and Sequestration of CO2 at the Boise White Paper Mill,” Battelle Memorial Institute, PNWD-4203, 2010, under DE-FE0001992.

11 Department of Energy/National Energy Technology Laboratory, “Cost of Capturing CO2 from Industrial Sources,” January 2014.

12 Steam cracker units are facilities in which a feedstock such as naphtha, liquefied petroleum gas, ethane, propane, or butane is thermally cracked using steam in a bank of pyrolysis furnaces to produce lighter hydrocarbons.

13 Calcination is the process of heating carbonate at high temperatures (i.e., 900C) to form CO_2 and lime (CaO).

14 Department of Energy/National Energy Technology Laboratory, “Cost of Capturing CO2 from Industrial Sources,” January 2014.

15 Perez-Fortes, M. “CO2 Capture and Utilization in Cement and Iron and Steel Industries,” GHGT-12, *Energy Procedia* 63 (2014) 6534-6543.

16 Crude iron is an intermediate product of the iron industry and is obtained by smelting iron ore in a blast furnace.

17 Leeson, D., Mac Dowell N., Shah N., Petit, C., and Fennell, P. S. “A techno-economic analysis and systematic review of carbon capture and storage (CCS) applied to the iron and steel, cement, oil refining and pulp and paper industries, as well as other high purity sources,” *International Journal of Greenhouse Gas Control*, 61 (2017) 71–84.

18 Carbon Sequestration Leadership Forum, 2017.

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Chapter Six

CO_2 TRANSPORT

I. CHAPTER SUMMARY

CO_2 transport refers to the transfer of carbon dioxide (CO_2) from one location to another or between its source and point of use. CO_2 can be transported via pipeline, rail, truck, ship, and barge. The primary mode of large-scale CO_2 transport in the United States today is via pipeline, and in 2017, there were more than 5,000 miles of CO_2 pipelines in operation.

Pipeline transport of CO_2 dates back over 80 years and was initially associated with the dry ice and beverage business. More than 40 years ago, large-scale transport by pipeline began when CO_2 was used for enhanced oil recovery (EOR) operations, and this CO_2 was sourced primarily from natural deposits and gas processing plants. Approximately 90% of the CO_2 pipeline infrastructure in the United States today is used for CO_2 EOR operations. These pipelines were constructed to provide a direct link between a CO_2 source and an associated CO_2 sink (a reservoir), creating a pipeline industry that is independent of the ownership of the various assets involved in CO_2 EOR.

Wide-scale deployment of carbon capture, use, and storage (CCUS) across the United States will require expansion of the existing CO_2 pipeline infrastructure through looping, replacement, or other engineering modifications, as well as the construction of new pipelines. There is no expectation that alternative modes of CO_2 transport—rail, truck, ship, and barge—would be able to support the large volumes of CO_2 associated with wide-scale deployment of CCUS. CO_2 transport by rail and truck may be viable for shorter distances within the United States, and transport by ship using tankers can be scaled to meet international CO_2 transport needs.

There are several challenges to scaling-up CO_2 transport infrastructure that will need to be addressed to avoid construction delays and cost increases, such as permitting requirements, surface use issues, and environmental group activism (see Chapter 4, "Building Stakeholder Confidence," in Volume II of this report). Enabling some form of eminent domain in the states through which construction occurs could help but will not resolve all the issues associated with infrastructure expansion.

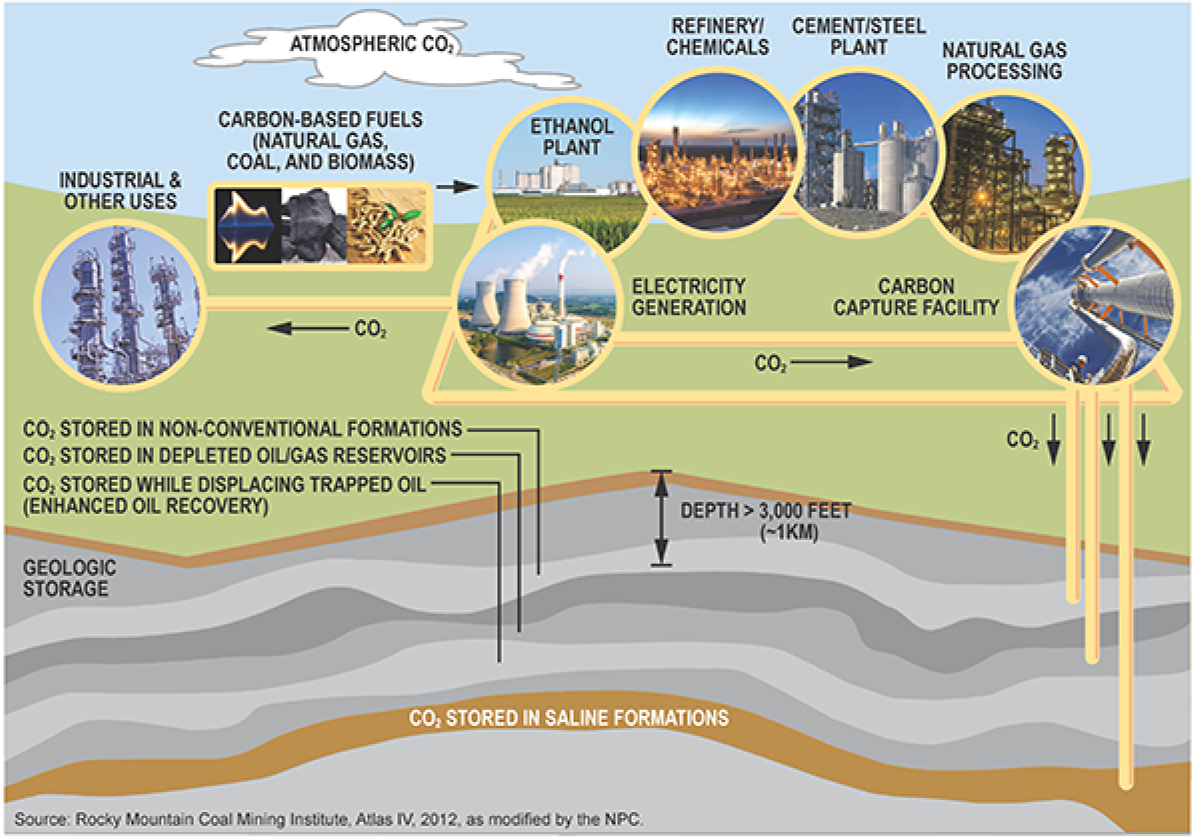
Eminent domain is the right of a government (or its agent) to take private property for public use. This right is subject to two conditions: the private property must be for public use, and just compensation must be paid to its owner. Two judicial tests are used to define public use. The first, a narrow interpretation, requires that the end use of the property taken must be open and available for actual use by the public. The second approach includes a broad scope of uses and property interests that yield some public benefit—

revenue generation, jobs, tax base, or development of industry.[1,2]

Many states have the authority to determine the siting of pipeline infrastructure under the public benefit approach. However, the added cost of construction and the lack of an integrated CO_2 pipeline network will likely be one of the major hurdles for wide-scale deployment of CCUS in the United States. Overcoming this hurdle would require a system-level analysis (current capacity versus future requirement) to optimize the ongoing development of CO_2 infrastructure to achieve widespread deployment.

II. WHAT IS CO_2 TRANSPORT?

CCUS, including transport, combines several technologies to reduce the level of CO_2 emitted to the atmosphere or remove CO_2 from the air. The CCUS process, as shown in Figure 6-1, involves the capture (separation and purification) of CO_2 from stationary sources so that it can be compressed and transported to a suitable location where it is converted into useable products or injected deep underground for safe, secure, and permanent storage.



Source: Rocky Mountain Coal Mining Institute, Atlas IV, 2012, as modified by the NPC.

Figure 6-1. *Supply Chain for Carbon Capture, Use, and Storage*

CO_2 transport refers to the transfer of CO_2 from one location to another or between its source and point of use. In most cases, the CO_2 described in this report is captured at a stationary emissions point source. Once captured, CO_2 must be compressed and transported to long-term geologic storage sites for dedicated underground storage, EOR production operations for incidental or associated trapping, or other sites for subsequent use in the production of products.

The transport of CO_2 is primarily accomplished using pipelines (Figure 6-2) operating at a pressure that enables the CO_2 to remain in a dense phase above a critical temperature. In its dense phase, the CO_2 is a highly compressed fluid that demonstrates properties of both a liquid and a gas. It is called a dense fluid, or supercritical fluid, to distinguish it from normal vapor and liquid. The word fluid refers to anything that will flow and applies to gas and liquid. Pure compounds in the dense phase normally have a better dissolving ability than they do in their liquid state. Compounds in dense phase have a viscosity like that of a gas, but a density closer to that of a liquid. The dense phase is the best condition for transporting CO_2 and injecting it into saline formations for geologic storage and into oil and natural gas reservoirs for EOR.

Figure 6-2. *Schematic Map of CO_2 Pipelines in the United States*

In addition to pipelines, CO_2 can also be transported via rail, truck, ship, and barge. In the United States, CO_2 is primarily transported for industrial purposes through more than 5,000 miles of CO_2 pipelines. The United States has more than 40 years of experience transporting CO_2 from natural deposits and gas processing plants for use in EOR operations.

III. STATUS OF TRANSPORT TECHNOLOGY

A. Current CO_2 Transport Options

CO_2 for industrial purposes is mainly transported in onshore pipelines. Although most of the CO_2 transported by pipeline is from natural sources, industrial or combustion sources do exist and are being captured, stored, and used in the United States. Aligning regulatory requirements and government incentives with environmental, operational, and financial risks would enable an increase in the captured industrial or combustion CO_2 volumes that could be captured, stored, and used.

The first offshore pipeline for transporting CO_2 was the Snøhvit pipeline in Norway. This pipeline has been transporting CO_2 from natural gas extraction through 95 miles of seabed pipeline from Hammerfest in northern Norway to the Snøhvit Field under the Barents Sea since May 2008.[3]

While natural gas is typically transported in gaseous form in high-pressure pipelines,[4] large volumes of CO_2 are easiest to transport in liquid or supercritical form.[5] Pipeline transportation of CO_2 over longer distances is most efficient and economical when the CO_2 is in the dense phase.[6] This means that the pressure in the pipeline must be kept at 1,080 psi and above. CO_2 must also be dehydrated to avoid corrosion of the pipeline.[7] Dehydrating the CO_2 entails removing the water from the gas mixture stream.

Ship transport of CO_2 occurs on a small scale in Europe, carrying approximately 1,000 metric tons (tonnes) of food-grade CO_2 from large point sources to coastal distribution terminals.[8] When Anthony Veder, a Dutch shipping company, built the Coral Carbonic vessel in 1999, it was the world's first purpose-built CO_2 tanker, capable of transporting 1,250 cubic meters, or about 1,250 tonnes of liquid CO_2. The existing fleet is transporting CO_2 with a pressure of around 217 to 290 psi and a temperature of about -22°F. For larger volumes, the parameters are likely to be around 101 psi and -58°F, near the triple point.[9]

Although transport of liquefied gases via barge is possible, dense phase CO_2 has not been transported by barge primarily due to a lack of demand for barge movement. Studies have outlined the use of barges in industrial hubs, such as the Port of Rotterdam, but these are not yet a reality.[10]

Transport of CO_2 by truck and rail is viable for small quantities, from 4 tonnes to a few hundred tonnes. Trucks can complement ship transport, moving small quantities of CO_2 from port CO_2 terminals to industrial sites for subsequent use. Trucks can also be used at some project sites, moving the CO_2 from where it is captured to a nearby storage location.

Given the large volumes of CO_2 that would need to be captured as CCUS is deployed at scale in the longer term, transport of CO_2 by truck and rail are not economical, scalable options. The cost of CO_2 transport by truck and rail ranges from three to ten times more per tonne than by pipeline transport due to economies of scale. Despite this, truck and rail transport could be important for smaller-scale point-to-point value chain solutions (for smaller capture volumes not accessible to pipeline options) during the early years of expanded CCUS deployment in the United States. These point-to-point solutions would require transport over shorter distances (200 miles or less for truck and 1,000 miles or less for rail), carrying CO_2 from a single specific source to a corresponding sink(s) where the CO_2 would be employed for purposes of either EOR or industrial use.

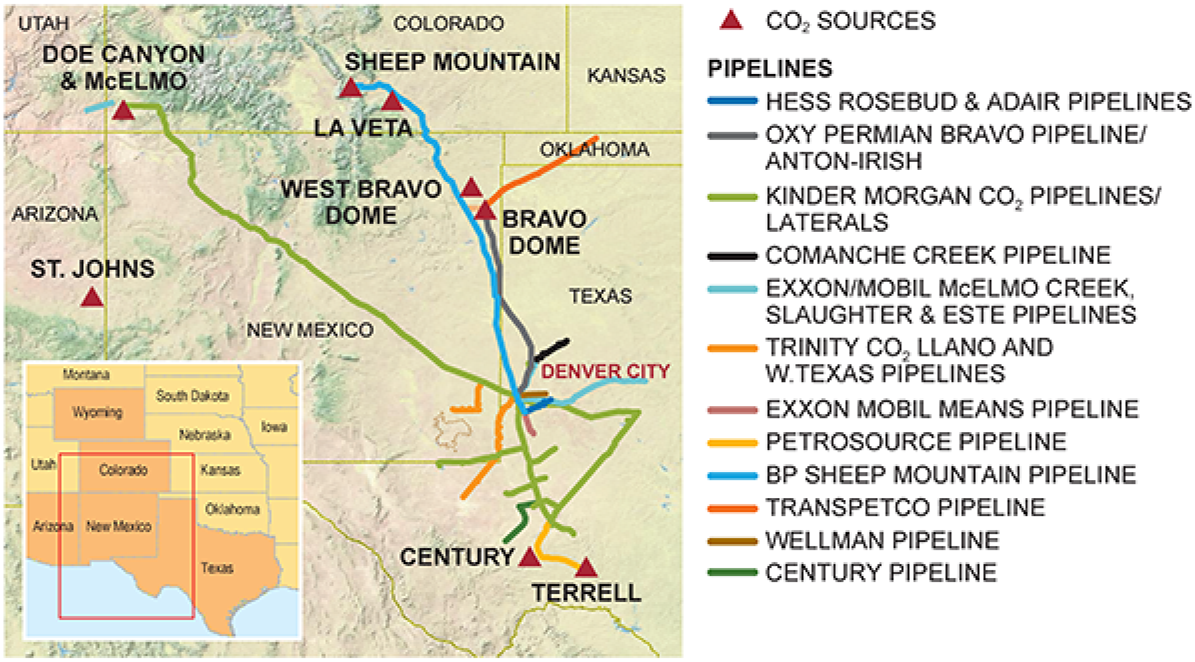
B. Large-Volume CO_2 Transport via Pipeline

Pipelines are the most common method of transporting the very large quantities of CO_2 involved in CCUS. Transporting various fluids via pipeline is a standard industrial practice, and extensive pipeline networks already exist around the world, on land and under the sea. In 2017, there were almost 535,000 miles of hazardous liquid and natural gas pipelines (gathering and transmission) in the United States, in addition to more than 2.2 million miles of natural gas distribution lines.

In 2017, there were more than 5,000 miles of CO_2 pipelines in the United States, the majority of which transport CO_2 from sources to EOR operations (Figure 6-2). These pipelines were primarily developed for CO_2 EOR purposes and it is the most extensive network in the world; elsewhere there is a small number of point-to-point pipelines. Most countries have little or no experience in CO_2 pipeline operation. In contrast, the U.S. pipeline network transports more than 66 million tonnes per annum (Mtpa), which is approximately 3.5 billion standard cubic feet per day (BSCF/D) of CO_2 every year.

The goal of expanding the CO_2 pipeline network to support wide-scale deployment of CCUS in the United States is one that hinges upon creating favorable economic conditions and permitting regulations. This expansion would need to increase by at least an order of magnitude in the next decade to transport the hundreds of thousands of tonnes of captured industrial or combustion source CO_2 needed to support wide-scale deployment.

Several regions in the United States have large CO_2 pipeline networks, including the Permian Basin, the Gulf Coast, and the Rocky Mountain area. The Permian Basin has the most extensive network, and Figure 6-3 shows this pipeline system, owned by Kinder Morgan and Occidental Petroleum. These companies transport nearly 2 BSCF/D (38 Mtpa) of CO_2 to eastern New Mexico, West Texas, and southeastern Utah. The pipelines carry CO_2 to internal and external customers who use it for EOR in mature oil fields.



Source: Kinder Morgan and Occidental Petroleum.

Figure 6-3. *Permian Basin CO_2 Pipeline Infrastructure for Kinder Morgan and Occidental Petroleum*

Kinder Morgan's longest CO_2 pipeline, the Cortez Pipeline, stretches 500 miles from southwestern Colorado to Denver City, Texas, and can transport 1.5 BSCF/D (28 Mtpa). Occidental Petroleum operates the Sheep Mountain and Bravo Dome Pipeline networks, which extend over 500 miles with capacity of nearly 0.7 BSCF/D (13 Mtpa).

Captured CO_2 from industrial sources could be used in the Permian Basin if pipeline infrastructure existed to connect the regions of these industrial sources with the Permian Basin CO_2 network that currently supplies customers. The existing CO_2 pipelines feeding EOR customers in the Permian Basin have transport capacity available and could be expanded. Furthermore, there are several EOR consumers of CO_2 in the Permian Basin that have varying demands for additional CO_2 and can facilitate matching industrial sources with other CO_2 consumers, such as existing customers that could use more and are short on CO_2 supply.

C. Alternatives to Pipeline Transport

It is generally understood that pipeline transport offers significant economies of scale for high volumes and flow rates of CO_2, but pipelines are capital intensive investments. In contrast, ship transport is less capital intensive and could be cost competitive for certain situations (i.e., transoceanic movements).

Although alternatives to pipeline transport of CO_2 exist—rail, truck, and barge—they are economically viable only over shorter distances and at a small scale. Different transport methods may prove useful in different regions or for smaller-scale point-to-point CO_2 transport solutions.

In the North Sea area, studies have shown that marine transport (by ship) could collect CO_2 from several point sources along a coastline. Large-scale ship transport of CO_2—from 9,800 to 41,000 tonnes—will likely have a lot in common with the shipment of liquefied petroleum gas (LPG). There is already a great deal of expertise in transporting LPG, which has developed into a global industry during the last 70 years.[11]

In Norway, there have been studies about creating a CO_2 transport system based on ship transport concepts. For example, one study assessed CO_2 transport options in

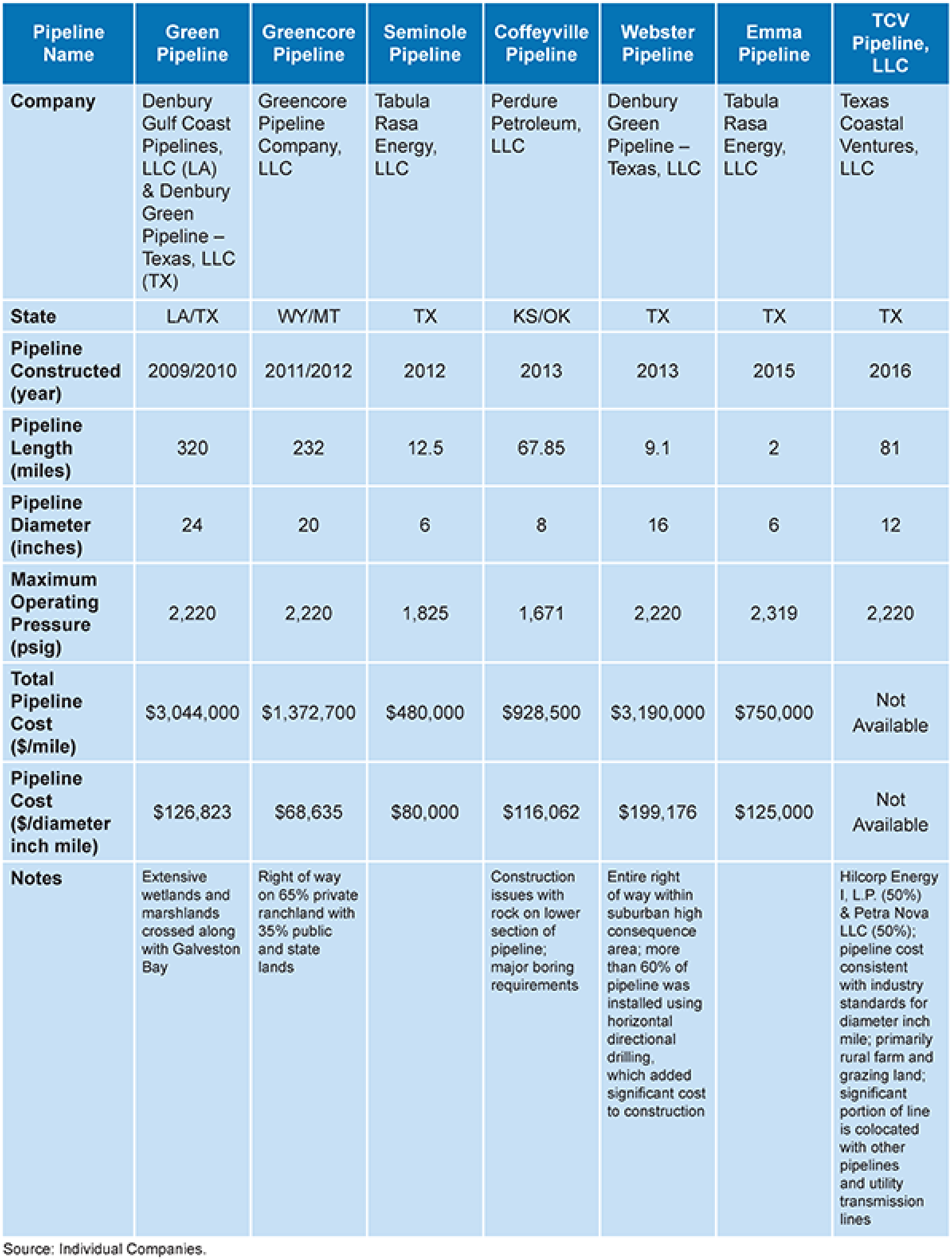
Nordic countries.[12] In the Nordic region, most of the stationary CO_2 emissions come from emission-intensive industries such as steel, cement, chemical, and petroleum refining. Because these are relatively small point sources in isolation and they are widely dispersed, ships would be the most cost-effective solution to transport CO_2 for storage in the North Sea.

CO_2 transport systems must consider national or regional conditions. The best approach is to tailor a transport system to a regional market. A tailored approach was used for the Dakota Gasification Company's Great Plains Synfuels Plant, which captures and transports CO_2 to the Cenovus Energy EOR project at Weyburn in Saskatchewan, Canada. When properly designed, a transport system could include a combination of pipeline, rail, truck, ship, and barge transport depending upon the needs of the regional market.

In the United States, other CO_2 transport options are unlikely to replace pipelines for large volumes. However, alternative transport options could complement the necessary pipeline network, supporting transport between CO_2 hubs and clusters depending on the volumes produced (captured) at the sites.

IV. RECENT PIPELINE CONSTRUCTION METRICS

In the past 10 years, the construction of CO_2 pipeline infrastructure in the United States has been limited to establishing point-to-point pipelines that connect an identified source of CO_2 to the corresponding sink(s) where the CO_2 is used for either EOR or industry. Table 6-1 summarizes the features of the known U.S. CO_2 pipelines constructed in the last 10 years and provides the cost per diameter inch mile for pipeline segments, illustrating how widely costs can vary. For example, the Greencore Pipeline is built across private ranchland as well as state and public lands in Wyoming and Montana and cost $68,635 per diameter inch mile. Contrast this with the Webster Pipeline built in a highly concentrated industrial and suburban area just south of Houston, Texas, that cost $199,176 per diameter inch mile. The reason for this broad range in pipeline cost relates to the construction challenges from different types of terrain or conditions (wetlands, flat or mountainous, urbanization) and right of way concerns that restrict access due to pipeline or utility corridors.



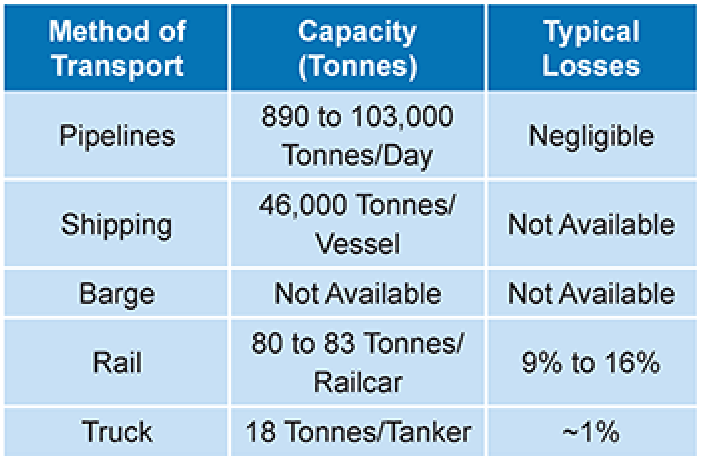
Pipeline Name	Green Pipeline	Greencore Pipeline	Seminole Pipeline	Coffeyville Pipeline	Webster Pipeline	Emma Pipeline	TCV Pipeline, LLC
Company	Denbury Gulf Coast Pipelines, LLC (LA) & Denbury Green Pipeline – Texas, LLC (TX)	Greencore Pipeline Company, LLC	Tabula Rasa Energy, LLC	Perdure Petroleum, LLC	Denbury Green Pipeline – Texas, LLC	Tabula Rasa Energy, LLC	Texas Coastal Ventures, LLC
State	LA/TX	WY/MT	TX	KS/OK	TX	TX	TX
Pipeline Constructed (year)	2009/2010	2011/2012	2012	2013	2013	2015	2016
Pipeline Length (miles)	320	232	12.5	67.85	9.1	2	81
Pipeline Diameter (inches)	24	20	6	8	16	6	12
Maximum Operating Pressure (psig)	2,220	2,220	1,825	1,671	2,220	2,319	2,220
Total Pipeline Cost ($/mile)	$3,044,000	$1,372,700	$480,000	$928,500	$3,190,000	$750,000	Not Available
Pipeline Cost ($/diameter inch mile)	$126,823	$68,635	$80,000	$116,062	$199,176	$125,000	Not Available
Notes	Extensive wetlands and marshlands crossed along with Galveston Bay	Right of way on 65% private ranchland with 35% public and state lands		Construction issues with rock on lower section of pipeline; major boring requirements	Entire right of way within suburban high consequence area; more than 60% of pipeline was installed using horizontal directional drilling, which added significant cost to construction		Hilcorp Energy I, L.P. (50%) & Petra Nova LLC (50%); pipeline cost consistent with industry standards for diameter inch mile; primarily rural farm and grazing land; significant portion of line is colocated with other pipelines and utility transmission lines

Source: Individual Companies.

Table 6-1. *Pipeline Characteristics and Costs*

V. TRANSPORT OPTIONS AND CO_2 QUALITY SPECIFICATIONS

Table 6-2 recaps CO_2 transport methods covered in this section with typical transport capacities and losses experienced.



Method of Transport	Capacity (Tonnes)	Typical Losses
Pipelines	890 to 103,000 Tonnes/Day	Negligible
Shipping	46,000 Tonnes/ Vessel	Not Available
Barge	Not Available	Not Available
Rail	80 to 83 Tonnes/ Railcar	9% to 16%
Truck	18 Tonnes/Tanker	~1%

Table 6-2. *Transport Options*

A. CO_2 Pipelines in the United States

CO_2 has been safely and reliably transported in the United States via large-scale commercial pipelines since 1972, when the Canyon Reef Carriers Pipeline was constructed in West Texas. During the last 50 years, there have been no fatalities associated with the transportation of CO_2 via pipeline. This outstanding safety record can be attributed to the standards that are used to construct, operate, and maintain CO_2 pipelines in the United States. Although CO_2 is not considered a hazardous material by the U.S. Department of Transportation, CO_2 pipelines are regulated because of the operating pressures of these pipelines.

These regulations are outlined under Title 49 of the Code of Federal Regulations (CFR), Part 195, Transportation of Hazardous Liquids by Pipeline, which applies to the transportation of hazardous liquids and carbon dioxide.

Under the U.S. Department of Transportation, the Pipeline and Hazardous Materials Administration (PHMSA) is responsible for regulating the movements of all hazardous materials, including pipelines in the United States. PHMSA sets the standards for safe construction and operation of CO_2 pipelines, including technical design specifications and the requirements for mechanical integrity management. States can act as the pipeline regulator if, at a minimum, their regulations comply with federal regulation. The majority of CO_2 pipeline routing, however, is dependent on state law.

To minimize costs, commercial CO_2 pipelines typically operate at pressures between 1,200 pounds per square inch gauge (psig) and 2,200 psig, with some pipelines having a maximum operating pressure of 2,500 psig to 2,800 psig. At these pressures, CO_2 is in a dense phase—either as a liquid or a supercritical fluid—depending on the temperature of the fluid in the pipeline. A dense phase fluid demonstrates properties of both a liquid and a gas. For dense phase CO_2, its density is like a liquid, which results in increased flow capacity for the pipeline. This flow capacity enables use of higher efficiency pumps, instead of compressors, to recover pressure losses in the pipeline due to friction and elevation changes.

Altering a CO_2 stream from a gaseous state in which it is generally obtained from a capture plant to a condition required for pipeline transportation, the gas must be compressed and undergo a phase change—from vapor to supercritical or dense phase. Although its physical and thermal properties are between those of the pure liquid and a gas in the supercritical or dense phase, CO_2 behaves very much like a liquid.

A CO_2 source facility that delivers a gas in a nondense vapor phase must increase the gas pressure from as low as 1 or 2 pounds per square inch (psi) to the supercritical phase of 1,080 psi or higher, which compresses the gas. Most, if not all, CO_2 pipeline systems operate in pressure ranges from 1,080 psi to 2,200 psi. There are three ways to compress CO_2:

1. Use of a nearly adiabatic[13] pathway, such as a single-shaft or multishaft, multistage centrifugal compressor with cooling between the stages (intercooling).
2. Use of a reciprocating compressor where crankshaft-driven pistons compress the gas phase with supercritical compression to the high-density region/area. Once the CO_2 is in the dense phase, it can be pumped through the pipeline.
3. Use of a reciprocating compressor where crankshaft-driven pistons compress the gas phase, equipment to condense/cool to the liquid phase, and pumping to achieve the pressure required.

Gas compression is used in the natural gas and process industries. CO_2 compression equipment is similar to the equipment used for natural gas, but the chemical and physical properties of CO_2 require modifications to compressor design, construction materials, and sizing.

Factors such as water content and corrosivity, discharge pressures, and inlet volumes may require different combinations of equipment and processes. The equipment can be powered by electricity, natural gas or diesel engines, steam, or a combination of these. Many factors must be considered when choosing which equipment may be the best fit.

The gas compression process can be expensive due to the facilities and operating expenses required. Before determining a unit cost for CO_2, it is important to consider how energy demand and waste heat from the compression process might be integrated with power and the CO_2 capture plant. The final design of a facility involves understanding the stream composition, volume (mass), electricity, heat integration, cooling water or refrigeration, compression, blowers, pumps, and reboiler loading for dehydration of the gas. Each facility has its unique challenges and solutions that will affect the cost per unit. Construction costs for smaller facilities, in the 2,750 tonnes per day range, could be $75 million while larger facilities could be as high as $750 million. In addition to these capital costs, annual operating expenses must also be considered. Life expectancy of a compression facility can be 20 years or more.

The cost of compression impacts the commodity value for the captured CO_2. The CO_2 must be in a dense phase when received by the transport pipeline. As a result, the cost of compression will either be an added expense for the entity that captures the CO_2, or it will create a reduction in the price received from the purchaser if the purchaser is absorbing the expense of the compression cost.

CO_2 pipelines are built using externally coated steel line pipe in accordance with PHMSA regulations. CO_2 composition quality specifications have been established to avoid pipeline corrosion. If liquid water is not present, the CO_2 is not corrosive and will not form corrosive products. Accordingly, CO_2 is dehydrated before introduction into pipelines. Oxygen and hydrogen sulfide concentrations are controlled to remain below the levels that can cause corrosion or stress cracking in the specific grade of steel used in the pipeline. In addition to external coatings, cathodic protection is also used to protect the pipelines from external corrosion.

Critical issues for CO_2 transport include:

- Safety and presence of hazardous substances in the CO_2 stream
- Avoidance of free (liquid) water formation
- Avoidance of hydrate formation
- Avoidance of corrosion or stress cracking
- Reduction of the CO_2 volume (increased density, which increases transport capacity).

The presence of certain impurities in CO_2, such as methane and nitrogen, can lead to reduced pipeline capacity. The presence of impurities shifts the boundary of the two-phase region toward higher operating pressures to keep the CO_2 in the supercritical or dense phase. Furthermore, the impurities can lower the density of CO_2, which also lowers the storage capacity for the CO_2. The type and level of impurities in the CO_2 stream depends on the emission source and the capture process.

Impurities in CO_2 have an impact on pipeline transportation and injection into EOR reservoirs (for incremental oil recovery and incidental trapping of the injected CO_2) and saline geologic formations (specifically for long-term storage of CO_2). The owner and/or operator of Class VI UIC injection wells must analyze the physical and chemical characteristics of the CO_2 stream to be injected for long-term underground storage (i.e., into saline geological formations). The purpose of this review is to confirm that the composition of the CO_2 remains consistent with the permit and the information on which predictions of no adverse interaction between the injectate and well materials or formation fluids were based. Any changes to the CO_2 stream could have implications for well integrity or subsurface geochemical reactions (e.g., reactions that could alter the corrosivity of the injectate or cause mineralization in the reservoir).

Regulated CO_2 used for dedicated, long-term geologic storage could face comingling issues if the pipeline was also transporting food and beverage grade CO_2 for industrial customers or for use in EOR. Therefore, owners of a CO_2 pipeline will have to determine if they can transport a comingled stream without adversely impacting what the CO_2 will be used for.

The impact impurities have on pipeline transportation, EOR, and injection into saline formations include the following:

- *Carbon dioxide (CO_2)* – Lower CO_2 purity causes increased piping diameter or pressure for a given volume of CO_2 to be transported and will require more stringent water specifications.
- *Water (H_2O)* – Can lead to corrosion and hydrate formation in the pipeline.
- *Hydrogen sulfide (H_2S)* – This is a corrosion concern; higher H_2S levels reduce the minimum miscibility pressure (MMP) in EOR and could lead to hydrogen-induced cracking in the pipeline.
- *Nitrogen (N_2)* – Higher N_2 levels require greater pumping/compression and raise the MMP for EOR.
- *Oxygen (O_2)* – The O_2 limits are set according to the technical requirements for storage and EOR; potential downhole problems from higher O_2 levels include microbial and algae growth and corrosion.
- *Temperature* – High temperatures can damage the external pipe coating and affect pipeline integrity; extremely low temperatures may affect the metal used to construct the pipeline.
- *Glycol* – Higher glycol levels can damage pump seals.
- *Delivery pressure* – Maintaining CO_2 in the dense phase for transportation and storage reduces transportation costs.
- *Carbon monoxide (CO)* – If water is present, CO can create acid, which would corrode the pipeline.
- *Incondensable gases* – The presence of incondensable gases increases the pressure, and thus energy

requirements for compression to keep CO_2 in dense phase.

- *Methane (CH_4)* – Higher levels require greater pumping/compression, as well as increasing the MMP for EOR.
- *Hydrogen (H_2)* – Higher levels require additional pumping/compression, mitigation for potential fracture issues, and raises MMP for EOR.
- *Argon (Ar)* – Higher energy consumption due to incondensable gas.
- *Sulfur oxides (SOx) and nitrogen oxides (NOx)* – Potentially could form corrosive acids.
- *Mercury (Hg)* – Hazardous waste stream, potential groundwater release issue.

Each pipeline system operating in the Gulf Coast, Permian Basin, and the Rocky Mountain area has defined quality specifications. While the group of impurities or contaminants are common between the systems, the limits for each are slightly different. The following ranges for quality specifications are currently in place across these various systems:

- *CO_2 Purity:* >95% volume
- *Water:* Range of <12 lbs to 45 lbs/MMcf (~250 to 950 parts per million by volume)
- *H_2S:* Range of <10 ppm to 45 ppm by weight
- *Nitrogen:* Range of <0.9% to 4% volume
- *Total Sulfur:* Range of <10 ppm to 35 ppm by weight

- *Oxygen:* <10 ppm by volume
- *Hydrocarbons:* Range of <4% to 5% volume
- *Temperature:* Range of <90°F to 120°F
- *Glycol:* <0.3 gallons/MMcf
- *Delivery Pressure:* Between 1,200 psig and 2,200 psig.

In 2019, more than 3.5 billion cubic feet of CO_2 was transported daily in the United States, equivalent to 66 Mtpa. The majority of CO_2 transported by pipeline is used in the EOR industry and travels in more than one pipeline during the journey from its source to a destination.

1. Is Repurposing Natural Gas Pipelines an Option?

The use of an existing natural gas pipeline is not a practical option for CO_2 transport for large flow rates of 1 BSCF/D (19 Mtpa) or more over long distances of hundreds of miles and more. Existing natural gas pipelines have a maximum pressure rating of 1,480 psig, which are defined by the American National Standards Institute (ANSI) as Class 600 pipelines. A pipeline built for CO_2 service is designed for 2,200 psig, which is an ANSI Class 900 pipeline. There are a few examples of an existing pipeline that was converted to CO_2 service for lower flow rates and/or shorter distances (<100 miles). For longer distances, however, the lower rating of an existing gas pipeline requires many more pump stations along the route compared with a pipeline built for CO_2 service.

Trimeric Corporation developed a simulation model to determine the pumping requirements for transport of CO_2 in a natural gas line that has been repurposed for this operation. Current CO_2 pipeline design guidelines establish the lowest CO_2 pipeline pressure at the pump station suction to be 1,400 psig at 105°F. The analysis showed that it is not possible to meet this guideline on a repurposed natural gas line because the pump stations would be only a few miles apart. The simulation used 1,200 psig (at 95°F) as the minimum suction pressure, because operating below this pressure would create the risk of pump cavitation (formation of bubbles or cavities in the liquid) and vapor lock. This condition could shut down the pipeline, which is a serious concern for the pipeline operator.

The simulation determined that more than 30 pump stations would be required along a 1,000-mile Class 600 pipeline route to move 1 BSCF/D (19 Mtpa) of CO_2 (95% purity) through a 30-inch pipeline with a pressure limit of 1,480 psig. However, this same 30-inch pipeline could potentially transport 200 to 300 MMSCF/D (4 to 6 Mtpa) if the pipeline route was shorter and ground temperatures were cooler. In addition, a favorable elevation profile can counteract friction losses, and the line could be a segment in a network of new lines and pump stations. Thus, there must be a detailed review of project specifics and conditions before determining if repurposing a natural gas pipeline is economically viable compared with constructing an entirely new pipeline.

The simulation also estimated a 20-year life cycle for the pipeline. The life-cycle analysis showed that a repurposed pipeline was, at best, equal in cost to a new pipeline and would more likely cost more than a new pipeline that is designed for CO_2 transport. The likelihood of identifying a viable existing pipeline for a long transport route is low. Even if one was located, the large number of pump stations required would not be operationally practical for a long-distance pipeline.

To answer the question about whether repurposing a natural gas pipeline for use with CO_2 is an option, the answer is that it depends on several factors. If the goal is to transport large volumes of CO_2 100 miles or more, then the lower pressure rating of existing natural gas pipelines makes it impractical to repurpose them for use with CO_2. However, natural gas pipelines could be repurposed if the diameters are large enough and throughput volumes are optimized for a tighter operating range. Each pipeline's potential should be studied based on the project-specific conditions being evaluated and verified that the conversion of the line from natural gas service to CO_2 services complies with PHMSA-Part 195 regulations.

For this reason, it is not anticipated that repurposing existing natural gas pipelines would significantly help develop an expanded CO_2 pipeline network in the United States. There may be some short sections of pipeline, or pipeline laterals, that could use a repurposed natural gas line, but project-specific engineering would be required to evaluate if this would be technically and economically viable.

B. Shipping

Ship transport of CO_2 is currently used only for liquefied food-grade CO_2 in Northern Europe. These ships are small and carry anthropogenic CO_2 captured from hydrogen production units used in industrial processes such as ammonia production. They carry the anthropogenic CO_2 to ports to be offloaded and delivered to the end user via truck transport.

Ships that carry CO_2 are similar in design to the ships currently used to transport LPG. LPG ships are designed to carry gases that are in a liquid or liquid-like dense phase state. The design is a low-temperature, medium-pressure vessel at 250 psig and -40°F. The average-sized LPG tanker could carry approximately 45,000 tonnes of CO_2. Each LPG ship costs about $200 million to build.

Ship transport is more economical if large bodies of water need to be crossed. Thus, ship transport from the East or West Coast of the United States to the U.S. Gulf Coast would likely be more economical than constructing new long-distance pipelines or repurposing gas pipelines where such ships are currently in service. Shipping CO_2 for EOR operations from industrialized countries, such as the United States or European countries, to less industrialized, oil-producing countries could provide climate and economic benefits.

Another economic benefit could come from transporting CO_2 to the United States from Europe or Asia on U.S. LPG tankers, for purposes of CO_2 EOR or paid geologic storage. Owners of the tankers would then be able to transport a commercial product in both directions, which should lower the shipping cost for both products.

The siting of a CO_2 shipping/receiving terminal must be carefully planned due to public safety concerns—exposure to CO_2 can cause asphyxiation. This requires modeling to determine the potential radius of exposure from the site to the surrounding public if the CO_2 were to escape containment.

C. Barge

Currently, there is no barge transport of CO_2 in the United States. However, the design of CO_2 barges would be like those used for LPG, requiring low temperature and medium pressure.

In locations where pipelines are uneconomic or impractical, and rivers or intracoastal waterways provide proximal access to EOR or geologic storage sites, transport of CO_2 via barge might be an economic option.

And, as already mentioned, the siting of a CO_2 shipping/receiving terminal must be carefully planned due to public safety concerns.

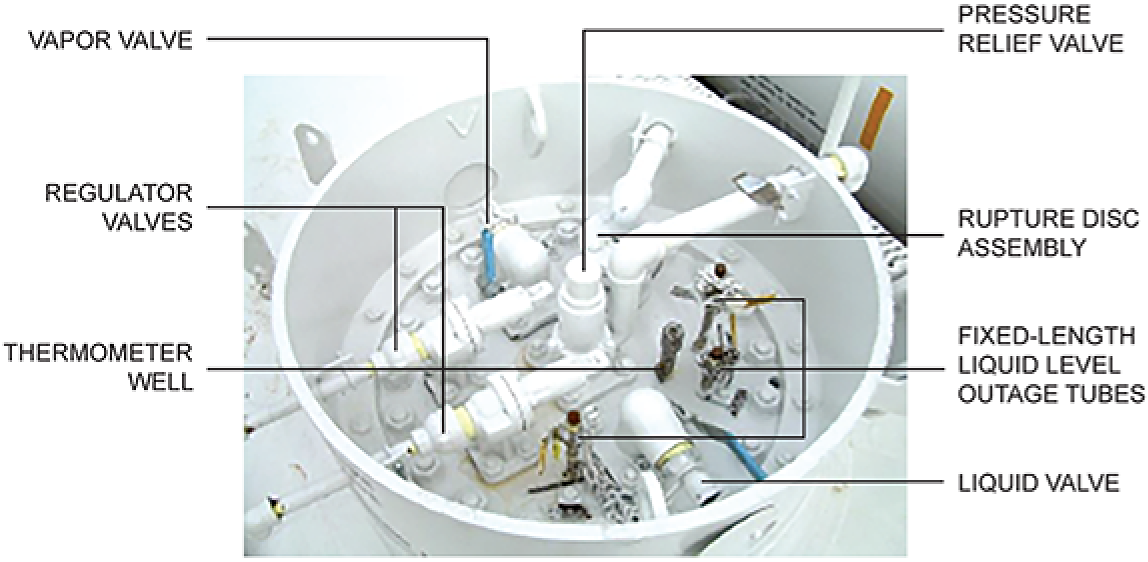
D. Rail

In 2017, U.S. and Canadian railroads safely transported more than 10,000 shipments of refrigerated CO_2 liquid, totaling more than 713,000 tonnes. Because the liquid-to-gas expansion ratio of CO_2 is 1:535,[14] it is more economical to transport CO_2 as a liquid—except in pipeline applications where high-density transport is achieved in the dense phase. Typical volumes lost during transit by rail car range from 9% to 16%, depending on the transit days and ambient temperature conditions.

The U.S. Department of Transportation (DOT) and Transport Canada authorize how refrigerated CO_2 liquid may be transported in Specification 105 tank cars. These cars have a capacity of 22,000 gallons (~83 tonnes) and a maximum gross weight of 286,000 pounds (130 tonnes). The current build price of a carbon dioxide tank car is approximately $170,000.

Tank cars transporting carbon dioxide are equipped with three types of pressure relief devices (shown in Figure 6-4):

1. A reclosing pressure relief valve set for no more than 75% of the tank test pressure
2. A nonreclosing safety vent designed to burst at a pressure less than the tank test pressure
3. Two regulating valves set to open at a pressure not to exceed 350 psig on a 500 psig test pressure tank or 400 psig on a 600 psig test pressure tank.



Source: Association of American Railroads, *Field Guide to Tank Cars*, 3rd edition, 2017.

Figure 6-4. *Pressure Relief Devices on Rail Tank Car*

Tank cars transporting CO_2 and NO_2 have the words “REGULATING VALVES VENTING NORMAL” stenciled on each side of the car. The venting of vapor from the regular valve is a normal function to reduce internal pressure through auto-refrigeration.

CO_2 tank cars are loaded at a pressure between 200 psig and 215 psig, and the CO_2 is a temperature of -16°F to -20°F. Tank cars have 5 inches of urethane foam insulation, which provides approximately 8 to 10 days of transport time before the CO_2 warms up. If pressure builds in a 500 psig test pressure tank, the first regulator valve vents at 340 psi. The second regulating valve will vent at 350 psi. If pressure continues to increase, the safety relief valve will open at 375 psi. If the CO_2 temperature continues to increase, the rupture disk will open at 486 psi. If a rupture disc fails and the pressure falls below 60 psig, the CO_2 liquid turns into dry ice.[15]

Recent study has investigated the potential for use of the “DOT113” tank car to transport CO_2. The DOT113, currently used for transport of Argon, would allow CO_2 to be transported without releasing product through regulating valves. Study is ongoing.

E. Truck

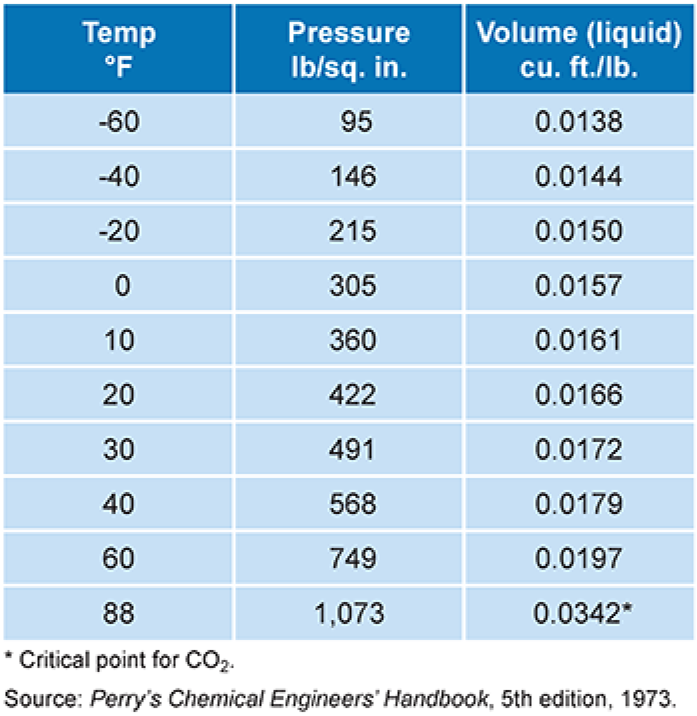
Truck transport of CO_2 in the United States is primarily for the beverage industry, traveling short distances to supply local markets. Each truck delivers approximately 18 tonnes of CO_2. Customers are less willing to pay for CO_2 liquid delivered by truck if the sourcing radius exceeds 150 miles, which increases the cost.

Truck transport loses a negligible amount of CO_2 (~1%), most of which occurs during the pressurization and depressurization of the trailer or storage tank while loading and unloading the CO_2. However, ambient temperature conditions can have an impact on total losses.

The design of this equipment is like the equipment used on LPG ships to maintain a low temperature and medium pressure. Truck transport of CO_2 is a good option for CCUS technology development during its project pilot stages because it requires little capital for sourcing the supply of the CO_2.

F. Intermodal Consideration

The conditions in which liquid CO_2 should be shipped via train, truck, or barge may be different from the current conditions in which liquid CO_2 is shipped. A range of temperatures and pressures for liquid CO_2 transport enables the initial compression and chilling to be optimized for injection into a pipeline that operates at the higher pressures and temperature required so the CO_2 remains in its dense phase. Table 6-3 presents the temperature and pressure ranges of interest. Liquid CO_2 transport might be cost effective given the cost of compressing and heating the CO_2 at pipeline intersections.



Temp °F	Pressure lb/sq. in.	Volume (liquid) cu. ft./lb.
-60	95	0.0138
-40	146	0.0144
-20	215	0.0150
0	305	0.0157
10	360	0.0161
20	422	0.0166
30	491	0.0172
40	568	0.0179
60	749	0.0197
88	1,073	0.0342*

* Critical point for CO_2.

Source: *Perry's Chemical Engineers' Handbook*, 5th edition, 1973.

Table 6-3. *Physical Characteristics ofSaturated Carbon*

VI. ENABLING WIDESPREAD DEPLOYMENT OF CCUS

A. The Need for Planned Expansion

Although the United States currently has the world's most extensive CO_2 pipeline network, more infrastructure is needed to support widespread deployment of CCUS in the United States. The magnitude of expansion required is defined by the future need to transport CO_2 from existing and new emission sources to EOR operations and geologic storage sites.

A few analyses have modeled extension of the U.S. CO_2 pipeline network to achieve CO_2 stabilization in the atmosphere, noted in parts per million (ppm), at different levels. One analysis modeled growth of the U.S. pipeline network under both 450 ppm and 550 ppm stabilization scenarios.[16] The less stringent 550 ppm stabilization scenario estimated that 11,000 miles of CO_2 pipeline must be added between 2010 and 2050 to the CO_2 pipeline system existing in 2009.[17] This scenario also estimated that in the near term, through 2030, the growth in CO_2 pipeline infrastructure that would be required across the United States equates to approximately doubling the CO_2 pipeline system that existed in 2009.[18]

In a more recent analysis by DOE in 2015, it was projected that the scale of U.S. CO_2 pipeline infrastructure would need to triple by 2030 to enable the delivery of carbon captured by the U.S. power sector to oil fields for CO_2 EOR and, to a lesser extent, for geologic storage in underground saline formations.[19] The report also notes that while this scenario would involve an unprecedented scale-up of CO_2 pipeline infrastructure, the pace would be comparable to what has been projected for pipeline construction in other sectors (in which many of the same companies operate).

These modeling approaches were based on climate-driven policy, but different drivers could be used to model the growth in scale of both CO_2 capture and injection, hence providing other means of quantifying the required infrastructure.

Regardless of the rationale for building and expanding existing networks, it appears that rather than constructing a multitude of new point-to-point pipelines, a more considered and strategic approach consisting of key trunk lines and connector pipelines would be economically advantageous for scaling CCUS deployment. Large-scale deployment of CCUS will require a marked increase in commitment by both government and industry to plan and build a CCUS system, of which a functioning transportation infrastructure is a critically important part. Although developing infrastructure will be done by industry in most cases, government commitment and leadership is particularly important in this regard.

There is currently some interest in Congress in providing financial support for construction of CO_2 transportation infrastructure, e.g. HR 4905, “Investing in Energy systems for the Transport of CO_2 Act of 2019.” As this bill was just recently introduced in Congress, neither the NPC nor the CCUS study team have analyzed the details of the proposed legislation; however, it is encouraging that there appears to be growing interest in supporting CO_2 infrastructure.

A strategic, planned approach will not only help the build-out of pipeline and other transport infrastructure, but will also facilitate the building of CO_2 capture projects in the future. In addition, project proponents—many of whom may not have knowledge nor interest in entering the pipeline business—may be able to tap into trunk lines with minor investment.

VII. CONCLUSIONS

The transport of CO_2 involves well understood technologies and has been done safely at scale for more than 40 years. CO_2 can be transported via pipeline, rail, truck, ship, and barge. In the United States, the primary mode of large-scale CO_2 transport is via pipeline, and there is a network of more than 5,000 miles of CO_2 pipelines operating today. Conclusions of this chapter include the following:

- Wide-scale deployment of CCUS in the United States will require a significant expansion of existing CO_2 pipeline infrastructure.
- Streamlined permitting would facilitate building strategic CO_2 trunk lines in key industrial and oil and gas regions of the country and could best be accomplished on a consultative basis between federal and state governments.
- Federal and state eminent domain authority for pipeline projects would facilitate faster development of infrastructure.

- U.S. industry already has extensive experience constructing and operating large-capacity CO_2 pipelines.
- PHMSA sets the standards for safe construction, operation, and technical design specifications and requirements for mechanical integrity management of CO_2 pipelines.
- Rail and truck transport of CO_2 can be solutions for shorter distances and more point-to-point options.
- The right government incentives (term/value of tax credits) will reduce risk for economic recovery of the development capital required for pipeline construction and operation.

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5 Regulated under PHMSA, Part 195, liquids pipeline regulations.

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9 Neele, F., Haugen, H. A., and Skagestad, R., "Ship transport of CO_2 – breaking the CO_2-EOR deadlock," *Energy Procedia*, 63 (2014): 2638-2644.

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13 Adiabatic means during the process, heat does not enter or leave the system.

14 An expansion ratio of 1:535 means 1 cubic foot of liquid CO_2 produces 535 cubic feet of CO_2 gas.

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Chapter Seven

CO_2 GEOLOGIC STORAGE

I. CHAPTER SUMMARY

Storing carbon dioxide (CO_2) in deep geologic formations, for the purpose of reducing greenhouse gas (GHG) emissions, began in 1996 with the Sleipner CO_2 storage project in Norway. When Equinor (formerly Statoil) began pumping 1 million tonnes per annum (Mtpa) of CO_2 into the offshore Utsira Formation in the Sleipner gas field, it paved the way for three additional large-scale projects in Norway, the United States, and Canada. These projects collectively have stored approximately 4 Mtpa. In 2019, the Gorgon Project in Western Australia initiated injection operations into a saline formation, and when at full operation in 2020, will store between 3 to 4 Mtpa. More than 20 years after the Sleipner project was established, there is now an extensive network of global knowledge about CO_2 storage, and the United States has emerged as a world leader on the topic. As of 2019, there are currently 19 large-scale carbon capture, use, and geologic storage (CCUS) projects operating around the world with a total storage volume of about 32 Mtpa. Ten of these projects are in the United States, accounting for a total storage volume of 25 Mtpa.

Safe, secure, and permanent geologic storage of CO_2 requires the presence of a sufficiently permeable rock formation, typically sandstone or carbonate, which is sealed by rocks on top that have a very low permeability. These formations need to be 1 kilometer (km) or deeper to ensure that the CO_2 is stored as a dense phase, also called a supercritical fluid. To protect underground drinking water aquifers, CO_2 storage is only permitted in saline formations that are saltier than 10,000 parts per million (ppm) total-dissolved-solids per the United States Environmental Protection Agency (EPA) Class VI Underground Injection Control (UIC) regulations. The geologic seal, typically a shale formation, must be continuous over the entire area where the CO_2 is stored and free of defects such as permeable faults, fractures, or leaky wellbore penetrations.

The CO_2 storage capacity estimates for the United States have been assessed by both the United States Department of Energy (DOE) and the United States Geological Survey (USGS). Both assessments indicate a very large potential for storage, with median estimates ranging from 3,000 to 8,600 billion metric tons (called gigatonnes or Gt) of CO_2. The economic potential, often referred to as a “storage reserve” is likely to be significantly lower, but how much lower is not known yet. Even conservative estimates are very large compared to the ~5 Gt CO_2/year emitted in the United States—of which about 50% or ~2.5 Gt CO_2/year is associated with large-scale stationary emissions sources—suggesting that storage capacity is unlikely to be a limiting factor in the United States. Other factors, such as access to CO_2 pipelines for transport, capture economics, public support, and local injectivity constraints, are likely to pose a greater challenge to at-scale deployment of CCUS in the United States.

Prospective geologic formations for CO_2 storage require adequate storage capacity, sufficient permeability, and a high-quality geologic seal. Additional considerations include an assessment of the risks of induced seismicity and the potential for CO_2 or brine leakage through preexisting boreholes. Brine is another term for saline water that naturally exists in a rock formation.

Cost estimates that include both capital expenditures and operating costs for storage in saline formations range from \$1 to \$18 per tonne of CO_2 (tCO_2) in 2013 dollars. For most sites in the United States, DOE estimates narrow the range from \$7 to \$13/tCO_2. The wide range reflects the site-specific nature of geologic storage projects. In 2019, preliminary cost estimates for storage sites in the Southeastern United States, which has excellent geologic conditions for storage, were as low as \$3/tCO_2.[1] Storage cost is primarily affected by the depth of the formation, volume of CO_2 to be stored, number of injection wells required, purity of the CO_2 stream, existing land uses, and ease of deploying surface and subsurface CO_2 monitoring programs.

In the United States, underground storage of CO_2 is regulated by the EPA’s UIC Program. Regulations for Class VI CO_2 storage wells were finalized in 2010. Six permits have been issued, but only two permits are active, both in Illinois, and only one of those permits is currently in active injection operations. Four permits were issued for the FutureGen 2.0 project in Illinois, but these were never used because the project was funded through the American Reinvestment and Recovery Act, which expired in 2015 before the project could be completed.

This chapter explains the following topics:

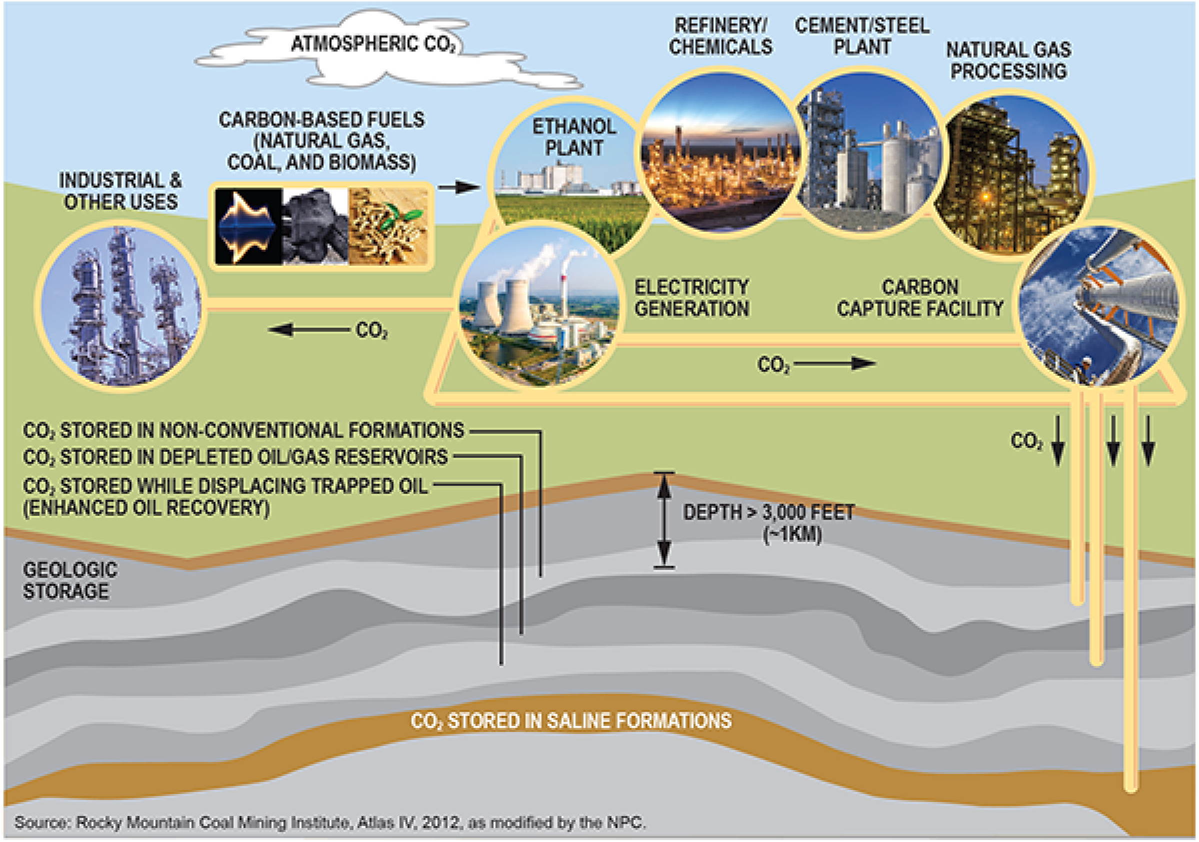
- Description of CO_2 geologic storage
- Current knowledge about geologic storage, including its costs and existing projects
- Geologic storage options and capacities in conventional and unconventional onshore conventional offshore formations, and depleted oil and natural gas fields
- Description of what is needed to enable at-scale deployment including incentives, access to onshore federal lands and offshore leases, and clarifying legal issues
- Issues that affect both CO_2 enhanced oil recovery (EOR) and CO_2 geologic storage
- Research and development needed to accelerate CO_2 storage.

In 2018, the National Academies of Science, Engineering, and Medicine completed a report on the key research needs associated with negative emissions technologies and secure sequestration (storage) of CO_2.[2] This chapter also acknowledges the findings from that report.

II. WHAT IS CO_2 GEOLOGIC STORAGE?

A. Describing CO_2 Storage

Carbon capture, use, and storage, including transport, combines processes and technologies to reduce the level of CO_2 emitted to the atmosphere or remove CO_2 from the air. These technologies work together to capture (separate and purify) CO_2 from stationary sources so that it can be compressed and transported to a suitable location where the CO_2 is converted into usable products or injected deep underground for safe, secure, and permanent storage. Figure 7-1 is a schematic showing the CCUS technologies.

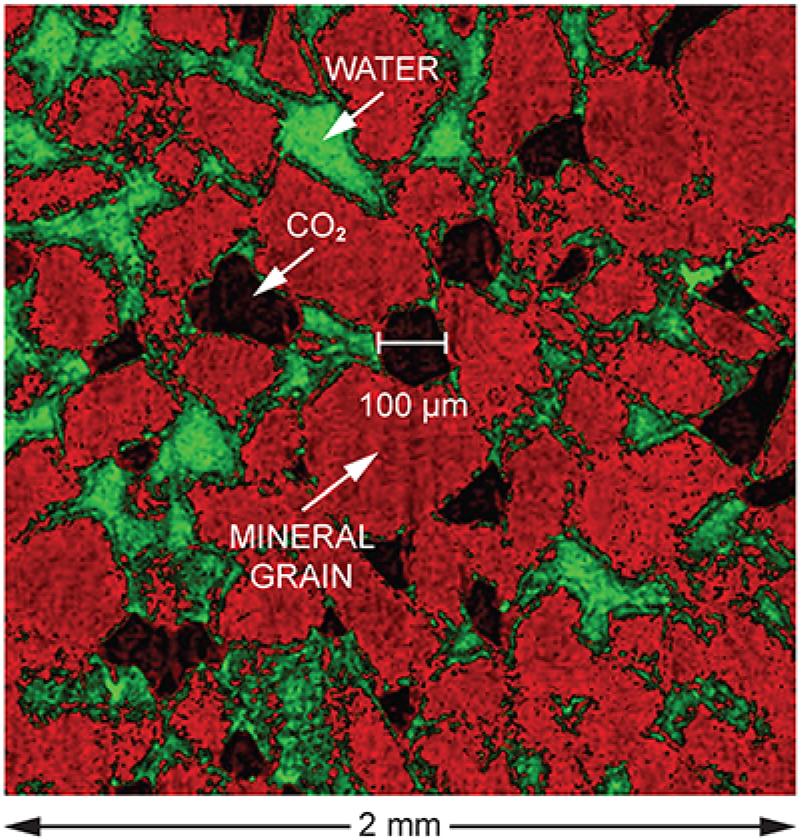


Source: Rocky Mountain Coal Mining Institute, Atlas IV, 2012, as modified by the NPC.

Figure 7-1. *Supply Chain for Carbon Capture, Use, and Storage*

Geologic storage refers to the process by which CO_2 is pumped underground into rocks such that it is permanently trapped so it cannot return to the atmosphere. The key to achieving this is identifying geologic formations that have two specific properties.

First, the formation rock must have sufficient pore space (porosity) in which CO_2 can be contained for storage and pathways connecting the pore space (permeability) so the CO_2 can be injected into and move within the formation. About 73% of the rocks on the Earth's surface meet these criteria. These are sedimentary rocks that were formed when small grains of sediment accumulated on seashores, deltas, ocean floors, riverbeds, and lakes over millions of years. Eventually the sediments were buried and became sandstone, which is largely composed of quartz grains, or carbonates, which results from the accumulation of small marine organisms and shells. Although sandstones and carbonates appear to be solid rock, they are filled with small void spaces called pores. When these types of rock are about a mile or more below the surface, under normal conditions the pores are filled with salty water, which is why they are called saline formations. Pushing the water out of the way, and filling the pore spaces with CO_2 instead, enables the storage of large volumes of CO_2. Figure 7-2 shows a microscopic image of the rocks in a saline formation storing CO_2. The rock grains are red, pore spaces filled with water are green, and pore spaces filled with CO_2 are black. Typically, 10% to 25% of the rock volume is made up of pores. A discussion of the potential capacity for storing CO_2 in sandstone and carbonate rocks is found in Section IIIA, Storage Options in Conventional Geologic Formations.



Source: Silin, D., Tomutsa, L., Benson, S. M., and Patzek, T. W. (2011). "Microtomography and pore-scale modeling of two-phase fluid distribution." Transport in Porous Media, 86 (2), 495-515.

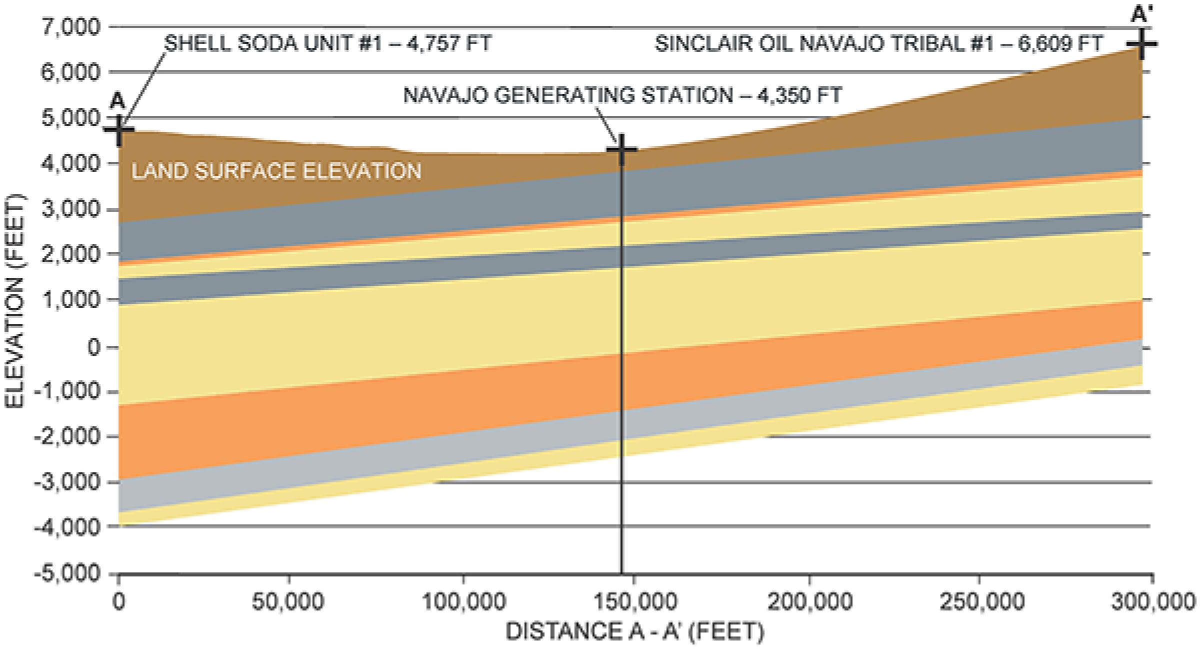
Figure 7-2. *Microscopic Image of Sandstone Showing Mineral Grains and Pore Spaces Filled with Water or* CO_2

The storage formations must be deep enough so that the natural pressure and temperature can maintain the CO_2 as a dense fluid, also called a supercritical fluid or state. Typically, the minimum depth required for this temperature and pressure are greater than or equal to about 3,000 feet (about 1 kilometer or 0.56 miles) depending on geothermal gradient. To protect underground drinking water aquifers, CO_2 storage is only permitted in saline formations that are saltier than 10,000 ppm Total Dissolved Solids (TDS) per EPA Class VI UIC regulations.

Second, a prospective storage reservoir must have a geologic seal above it. The sedimentary rock of a geologic seal must have a very low permeability that prevents CO_2 from leaving the storage formation. Seals are often made up of clay (shale), salt, or carbonate rocks with pores that are too small to enable the CO_2 to enter or pass through them.

When CO_2 is injected into the formation rock, it displaces some of the saline water—also called brine—in the formation, causing the reservoir's fluid pressure to increase. The pressure buildup increases the density of the brine and pore volume of the rock, making space in the reservoir to accommodate the incoming volume of CO_2. The magnitude of pressure buildup depends on the CO_2 injection rate, rock properties such as permeability, and the size of the storage reservoir. For large reservoirs with high permeability, the pressure buildup is small and does not present any storage safety concerns by damaging the reservoir and causing CO_2 leakage. In contrast, in a small, completely sealed reservoir, the pressure buildup may be rapid and large. A large pressure buildup would damage the geologic seal that sits on top of the storage formation, preventing fluids from escaping the reservoir. Avoiding damage to this seal requires limiting the rate of injection or extracting some of the displaced brine while the CO_2 injection is taking place. When CO_2 injection stops, reservoir pressure will gradually decrease until it returns to its pre-injection level.

Sandstone reservoirs with alternating layers of porous and permeable rock, sitting below a low-permeability geologic seal(s), are ideal for storing large volumes of CO_2 (Figure 7-3) because of their layered geology. These types of formations occur naturally and are rather prolific in the United States. When CO_2 storage operators select a reservoir, the goal is to identify one that has enough storage capacity (volume) to accommodate all the CO_2 that needs to be stored and has an extensive seal to ensure safe, secure, and permanent storage.



Source: Benson, S. M. and Cole, D. R. (2008). "CO2 Sequestration in Deep Sedimentary Formations." *Elements*, vol. 4, pp. 325-331.

Figure 7-3. *The Layered Geology of Sandstone (yellow) Below Shale Seals (grey) that Enables CO_2 Storage*

The Earth's naturally occurring geology provides the oldest proof that large quantities of CO_2 can be safely and securely trapped underground for millions of years. In 2005, the United Nations Intergovernmental Panel on Climate

Change concluded that, “The widespread presence of oil, gas, and CO_2 trapped in formations for many millions of years implies that within sedimentary basins, impermeable formations—called caprocks—of sufficient quality to confine CO_2 for geologic time periods are present.”[3] And in Mississippi, the CO_2 trapped in the Pisgah Anticline northeast of the Jackson Dome is thought to have been emplaced more than 65 million years ago.[4] This example is one among several deposits of natural CO_2 that exist in the United States and around the world, demonstrating that naturally occurring reservoir seals exist and are able to confine CO_2 for millions of years.

When compared to millions of years, the 100 years of intentional, underground storage of gases and liquids due to human activities is a relatively recent development. Humans have been storing natural gas securely in depleted oil and natural gas reservoirs and other formations for more than 40 years. Natural gas storage reservoirs are also good analogues for CO_2 storage and demonstrate that injected gas can be stored underground safely. Natural gas storage is used as a buffer between natural gas supply and demand. In 2019, there were more than 400 natural gas storage facilities operating in the United States and Canada with a total storage capacity exceeding 160 Mt.[5]

B. CO_2 Storage Projects Around the Globe

There have been several CCUS research programs conducted in Europe, the United States, Canada, Australia, and Japan since 1990. The global body of knowledge about CO_2 storage has been gleaned from these early commercial and demonstration carbon capture and storage (CCS) projects, including:

- Sleipner project, Norway: ~1 Mtpa stored, began in 1996
- Snøhvit project, Norway: ~0.8 Mtpa stored, began in 2008
- Frio pilot, United States: ~1.6 kilotonnes (Kt) stored 2004–2009
- Illinois-Decatur project, United States: ~1 Mtpa stored 2011–2014
- In Salah project, Algeria: ~1 Mtpa stored 2004–2011
- Ketzin project, Germany: ~70 Kt stored 2008–2014
- Plant Barry CCS project, United States: ~115 Kt stored 2012–2014
- Otway project, Australia: 15 Kt stored 2015–2016
- Aquistore project, Canada: ~110 Kt stored 2015–2017
- Lacq project, France: 51 Kt stored 2010–2013
- Tomakomai project, Japan: ~200 Kt stored 2016–2018
- Quest project, Canada: 1 Mtpa stored since 2015
- Illinois Industrial project, United States: 1 Mtpa stored since 2017
- Gorgon LNG project, Australia: injection operations started in 2019, increasing to 3 to 4 Mtpa in 2020.

International collaborations facilitated by organized networks such as the IEA Greenhouse Gas R&D Programme, Global CCS Institute, Carbon Sequestration Leadership Forum, and CO_2GeoNet were instrumental to creating a global scientific community dedicated to CO_2 storage.

C. Commercial CO_2 Injection Projects

Injection of CO_2 in the subsurface began in the 1960s with CO_2 EOR operations, many of which were in the United States. CO_2 injection is a common process applied in several industries, including oil and natural gas production, natural gas and hydrogen storage, municipal wastewater disposal, waste management, geothermal energy production, and aquifer recharge. The CO_2 injection process used across different industries is based on similar concepts and technologies and addresses similar technical and non-technical challenges.

Commercial storage projects in deep saline formations around the globe include Snøhvit in the North Sea and Aquistore in Canada, which operate at lower injection rates or intermittently. Chevron began CO_2 injection at the Gorgon Project on Barrow Island off the coast of Western Australia in 2019. When the project reaches full capacity of 3 to 4 Mtpa in 2020, it will be the largest commercial storage project in the world. Another commercial-scale operation that is no longer actively injecting CO_2 is the In Salah project in Algeria.

The projects highlighted in this section include offshore (Sleipner in Norway) and onshore (Illinois Industrial CCS and Quest in Canada) saline formation storage examples. The CO_2 for these projects is sourced from a variety of industrial activities, including natural gas processing, bioethanol fermentation, and heavy oil upgrading. Each project injects about 1 Mtpa of CO_2 into sandstone reservoirs.

1. Sleipner CCUS Project, Norway

Commercial CO_2 storage in deep saline formations was first implemented at the Sleipner CCUS project in Norway in 1996.[6] Sleipner is an offshore, platform-based CO_2 capture facility that is part of the Sleipner gas and condensate field development located approximately 155 miles (250 km) offshore southern Norway. The CO_2 stream at Sleipner is derived from natural gas processing and uses a solvent-based absorption, post-combustion capture process that is explained in Chapter 5, "CO_2 Capture." The Sleipner project has integrated commercial-scale CCUS with conventional oil and natural gas field development operations.

The CO_2 is injected and stored in the Utsira Formation about 0.6 mile (1 kilometer) below the seabed. By 2018, the Sleipner project had stored more than 17 Mt of CO_2 at an average annual injection rate of about 0.9 Mt/year. More recently, the Sleipner project began storing CO_2 captured from neighboring gas fields, giving it CCUS hub status.[7] Monitoring storage site performance and assuring safe containment through monitoring has been achieved through a series of time-lapse seismic data sets. These data sets provide important insights into the value and detection capabilities of remote geophysical monitoring methods.[8] The 23-year performance history at Sleipner is a testament to the value of careful well design and engineering.

2. Illinois Industrial Carbon Capture Project

The Illinois Industrial Carbon Capture and Storage project (IL-ICCS), led by the Archer Daniels Midland Company (ADM), is demonstrating an integrated system for collecting and geologically storing up to 3,000 tonnes/day of CO_2 from

ADM’s bioethanol plant in Decatur, Illinois. The CO_2 is captured at atmospheric pressure and high purity—greater than 99% purity on a moisture-free basis—from ADM’s corn-to-ethanol fermenters. The CO_2 stream is compressed, dehydrated, and delivered by an 8-inch diameter, 1-mile long pipeline to the injection wellhead.

The IL-ICCS project holds the first EPA UIC permit to operate a Class VI injection well. Injection of CO_2 at the IL-ICCS project uses a single injection well and began injection operations in April 2017. The site was designed to inject 3,000 tonne/day to meet an annual storage target of 1 Mt. The monitoring of injected CO_2 is performed within the Mount Simon Sandstone injection zone and above the storage reservoir by verification wells using geophysical surveys, pressure-temperature (P/T) sensors, and geochemical sampling. Shallow, environmental monitoring is ongoing and includes assessing groundwater via geochemical sampling and P/T monitoring, soil resistivity, and near-infrared aerial imagery.

3. Quest Project, Alberta Canada

The Quest Project owned by Shell Canada captures CO_2 produced at the Scotford Upgrader near Edmonton and then compresses, transports by pipeline, and injects the CO_2 for permanent onshore storage in a saline formation near Thorhild, Alberta. Shell completed drilling three wells about 1.2 miles (1.9 km) deep during 2012 and 2013 for the injection operations phase of the project. Injection began in two of the wells in 2015. Up to 1.2 Mtpa of CO_2 is being captured and there has been limited pressure buildup within the reservoir. Post-injection startup, monitoring, and verification activities have shifted to operational monitoring. Monitoring data indicates that no CO_2 has migrated outside of the injection reservoir to date.

III. STORAGE OPTIONS

Geologic storage of CO_2 requires injecting captured CO_2 into a subsurface formation that has enough porosity and permeability to store and transmit fluids. In addition, CO_2 needs to be injected into reservoirs where it can be permanently contained to prevent migration above and beyond the storage area.

In this study, CO_2 storage reservoirs are divided into conventional and unconventional reservoirs. Conventional formations have rock and fluid characteristics that enable gas and fluid to easily flow to or from wellbores drilled into the formation. The rock types that typically facilitate this include sandstone, limestone, dolomite, or a mixture of these rock types.[9]

Unconventional formations include a collection of rock types such as shale, and low-permeability (tight) sandstones, and some carbonates. Other possible subsurface CO_2 storage options include coal beds and basaltic and ultramafic rocks. Table 7-1 estimates the total technical storage capacity by type of formation in the United States, which was developed as part of DOE and USGS investigations. Median estimates for the technical storage potential in the United States range from about 3,000 to 8,600 Gt CO_2.[10]

Type of Geologic	Low	Median	High	Source(s)

Formation	(Gt CO_2)	(Gt CO_2)	(Gt CO_2)	
Conventional Onshore	2,379	8,328	21,633	National Energy Technology Laboratory (NETL) Carbon Storage Atlas (2015)[*]
	2,300	2,984	3,700	USGS (2013)[†]
Conventional Offshore	n/a	n/a	1,000	Southern States Energy Board (2013)[‡]
Shale	28[§]	134[¶]	171[#,**]	Nuttall et al. (2005),[§] Godec et al. (2013a),[¶] Godec et al. (2013b)[#]
Coal Beds	54	80	113	NETL Carbon Storage Atlas (2015)[*]
Basalt	n/a	n/a	n/a	
Depleted Oil and Natural Gas Reservoirs	190		230	NETL Carbon Storage Atlas (2015)[*]

[*] U.S. Department of Energy, National Energy Technology Laboratory. (2015). Carbon Storage Atlas (5th ed.; Atlas V) (DOE/NETL-2015/1709): 113 p., https://www.netl.doe.gov/research/coal/carbon-storage/natcarb-atlas.

[†] U.S. Geological Survey Geologic Carbon Dioxide Storage Resources Assessment Team. (2013). “National assessment of geologic carbon dioxide storage resources—Results.” (ver. 1.1, September 2013): U.S. Geological Survey Circular 1386, 41 p., http://pubs.usgs.gov/circ/1386/.

[‡] Southern States Energy Board. (2013). “Preliminary Evaluation of Offshore Transport and Geologic Storage of Carbon Dioxide,” https://www.sseb.org/wp-content/uploads/2010/05/Offshore-Study-full2.pdf.

[§] Nuttall, B. C., Eble, C. F., Drahovzal, J. A., and Bustin, M. R. (2005). Analysis of Devonian black shales in Kentucky for potential carbon dioxide sequestration and enhanced natural gas production: Kentucky Geological Survey Final Report to U.S. Department of Energy, 120 p.

[¶] Godec, M. L., Jonsson, H., and Basava-Reddi, L. (2013a). “Potential global implications of gas production from shales and coal for geological CO2 storage.” *Energy Procedia*, vol. 37, 6656-6666.

Godec, M., Koperna, G., Petrusak, R., and Oudinot, A. (2013b). "Assessment of factors influencing CO2 storage capacity and injectivity in eastern U.S. gas shales," GHGT-11, *Energy Procedia*, vol. 37, 6644-6655.

**Benson, S., et al. (2005). "Underground geologic storage," in Metz, B., Davidson, O., de Coninck, H., Loos, M., and Meyer, L., eds., Intergovernmental Panel on Climate Change (IPCC) Special Report on Carbon Dioxide Capture and Storage, Cambridge, UK: Cambridge University Press. p. 195–276, https://www.ipcc.ch/report/carbon-dioxide-capture-and-storage/.

Table 7-1. *Storage Capacity Estimates for Different Geologic Formations in the United States*

The values in Table 7-1 are the technical potential for storing CO_2 and do not consider economic factors, risks of induced seismicity, or other constraints on the practicality of injecting CO_2 at commercial rates. Practical estimates of storage capacity were developed that considered whether sufficiently high rates of injection could be achieved, the proximity to faults, a lack of surface access, and if the presence of very thin sands makes injection more costly. Figure 7-4 illustrates the impact of each factor on reducing the practical storage capacity that could be available. The two most significant factors are reductions caused by limitations on the injection rate (40% reduction) and the presence of thin sands (20% reduction).

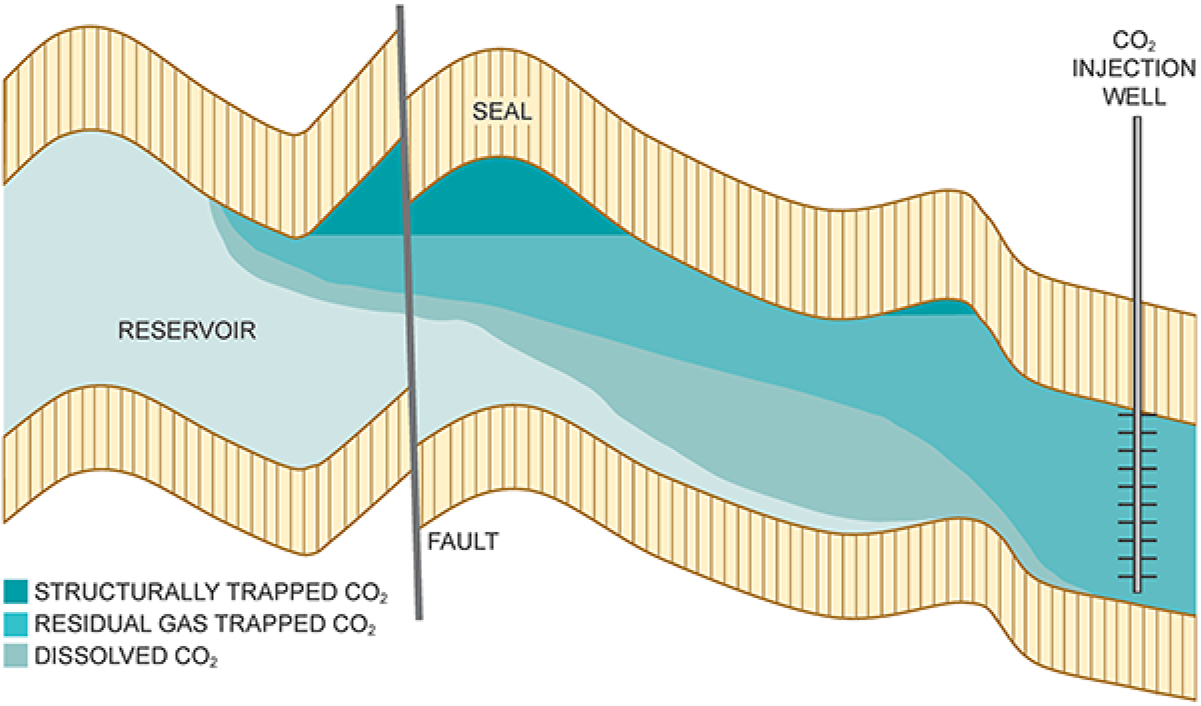


Figure 7-4. *How CO_2 Is Trapped in a Storage Formation*

Although practical storage capacity estimates are lower than previously published technical estimates, onshore subsurface storage capacity in the United States is enough to sustain a large-scale CO_2 storage industry. Different types of formations have different technical and practical storage capacity estimates due to differing reservoir properties. It is estimated that approximately 500 Gt of storage capacity in the United States is practically available today in reasonable proximity to CO_2 emissions sources or transport infrastructure[11] (see Chapter 2, "CCUS Supply Chains and Economics," in Volume II of this report).

A. Storage Options in Conventional Geologic Formations

1. Definition of Conventional Reservoirs

After CO_2 is captured, it needs to be compressed into a dense, liquid-like state called a supercritical fluid so it can be transported and injected into a formation. Compressing the captured CO_2 gas to a supercritical fluid enables more CO_2 to be stored because it has a higher density compared with gaseous CO_2.[12] In the United States, fresh subsurface sources of drinking water are protected by the Safe Drinking Water Act.

To be suitable for conventional storage of CO_2, the geologic formations must have an impermeable regional seal or series of seals (Figures 7-1 and 7-3). CO_2 in a supercritical fluid state is less dense than the fluids that initially fill the pore spaces in the rock. Hence after injection, the CO_2 slowly rises by buoyancy forces through the reservoir rocks until it encounters a low-permeability primary geologic seal. The sealing formations prevent CO_2 stored in the reservoirs from migrating into shallower groundwater aquifers, or to the surface where it could be released to the atmosphere. Once trapped below the primary seal, the CO_2 will remain permanently stored unless a mobile CO_2 plume encounters a permeable fault or fracture in the seal or a leaky wellbore.[13] However, this type of complication has not occurred at any of the CO_2 storage sites listed in the section on CO_2 Storage Projects around the globe, and careful site selection is the reason why it has not. Although primary geologic seals are important to retaining injected CO_2 underground, there are other mechanisms for immobilizing CO_2 to prevent leakage.

2. CO_2 Trapping in Conventional Reservoirs

Storage of CO_2 in conventional formations can use one of several trapping processes—buoyant, residual, solubility, and mineral.[14] In buoyant trapping, CO_2 generally flows upward slowly until it is immobilized in a stratigraphic or structural trap formed by the geologic seal (also called caprock), lateral seals, sealing faults, or other seals (Figure 7-4).[15] Residual trapping occurs as small droplets of CO_2 are left behind during the migration of a CO_2 plume through the porous reservoir rock. These droplets are trapped in the rock's pore spaces by interfacial (surface) tension. Solubility trapping dissolves 10% to 25% of the CO_2 almost instantly when it is injected into the formation. When injection stops, the CO_2 will continue to dissolve very slowly due to the convective mixing of dissolved CO_2 with the brine in the storage formation. For siliciclastic[16] (sandstone) reservoirs with a significant fraction of calcium, magnesium, and iron-rich minerals (e.g., feldspar and clay minerals), CO_2 mineral trapping may also occur over time (from years to decades) when the injected CO_2 dissolves into the reservoir fluids and reacts with the formation rock.

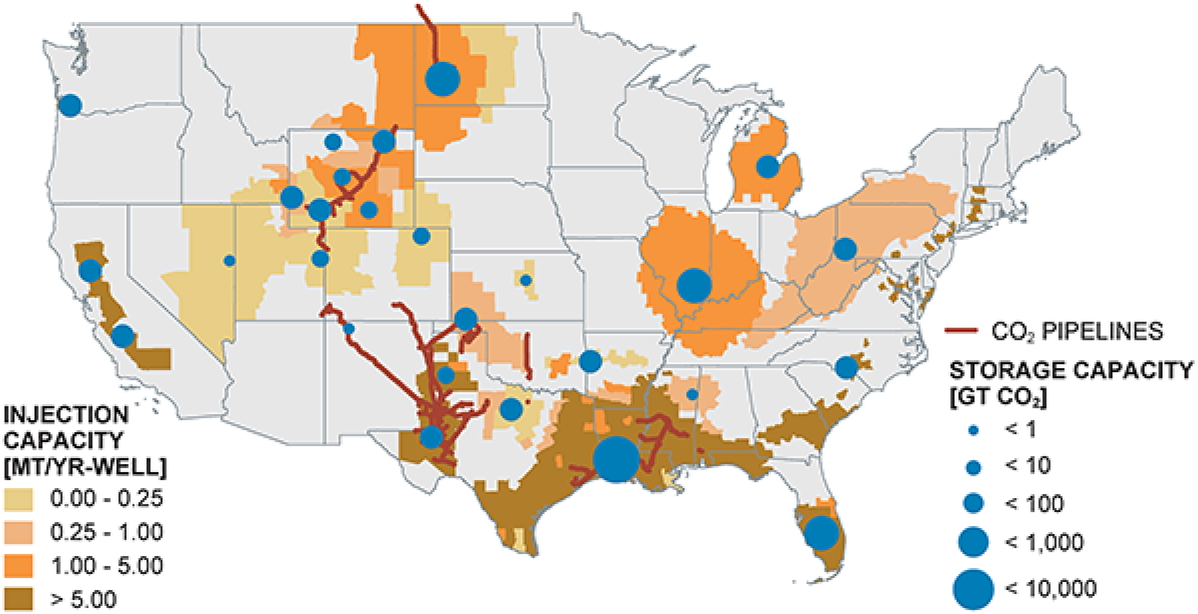
The minimum depth requirement of 3,000 feet (>900 meters) for a storage formation ensures that CO_2 is compressed in a supercritical state, which minimizes storage volume. CO_2 can be stored at depths greater than 13,000 feet (>4,000 meters) if favorable reservoir conditions exist. The lateral limit of the storage formation is defined by the location where the top of the storage formation reaches the defined depth limit.[17]

Mineral trapping is generally considered to be the slowest form of trapping in sandstone reservoirs. However, injection projects in the Columbia River and in Iceland have indicated that mineralization of CO_2 in basalts can take place much faster than previously believed—on the order of years. These findings have been documented in a 2013 USGS report[18] and by the projects themselves.

3. CO_2 Storage Resource Estimates for Conventional Reservoirs

National assessments of CO_2 storage resources have been conducted by several organizations. Most notable is the 2013 assessment by the USGS Geological Carbon Dioxide Storage Resources Assessment Team, and one in 2015 by the DOE’s National Energy Technology Laboratory (NETL). These assessments indicate that the United States may have mean or median total technical storage resources ranging from 3,000 to 8,600 Gt.

However, not all these resources are available for storing CO_2 due to reservoir pressure management considerations if large-scale CO_2 injection and storage is adopted nationwide (Figure 7-5).[19] Revised CO_2 storage resource estimates that include reservoir pressure management considerations is an area of ongoing research. Beyond overall regional storage capacity estimates, significant work has been performed with site-specific source-to-sink capacity estimates between Alabama Power’s Plant Barry and Citronelle Dome.[20]



Source: Baik, E., et al. (2018). "Geospatial analysis of near-term potential for carbon-negative bioenergy in the United States." Proceedings of the National Academy of Sciences, 115(13), 3290-3295.

Figure 7-5. *CO$_2$ Injectivity per Well and Storage Capacity in the United States*

The injectivity calculation in Figure 7-5 assumes that wells are far enough apart to avoid any pressure interference between the wells. If the wells are closer together, pressure interference between wells may limit injectivity.[21] As such, the injection capacity per well and storage capacity per basin cited should be considered maximum values. In addition, these represent average values for an entire formation; within a given formation, injectivity will be higher and lower than the values shown.

4. Challenges Associated with Storage Projects in Conventional Reservoirs

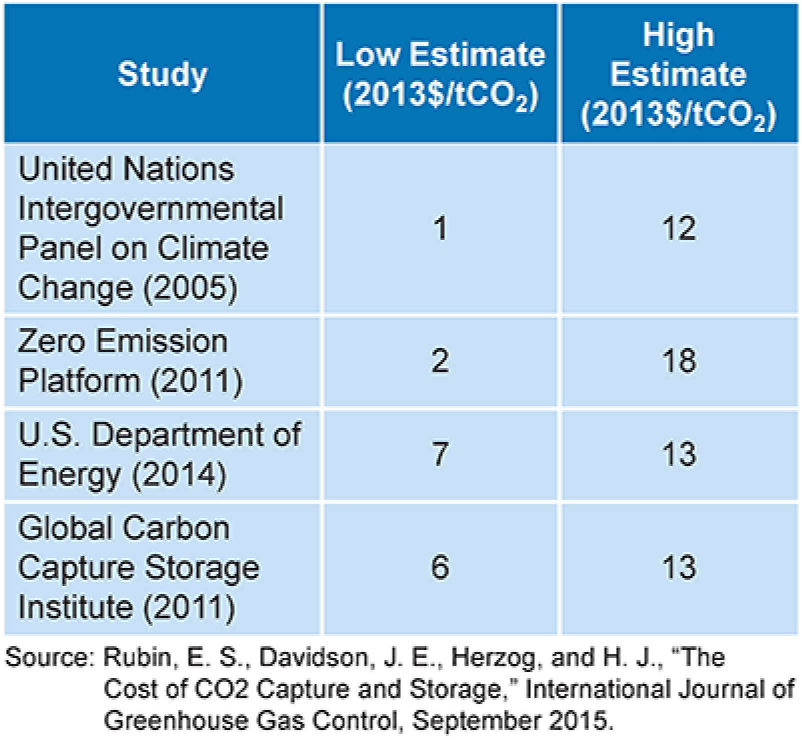
In 2018, the National Academies of Sciences, Engineering, and Medicine (NASEM) noted that in order to meet GHG reduction goals and limit the impact on global temperatures, the nations of the world need to capture and store at least 5 to 10 Gt of CO_2 per year in deep sedimentary formations. Besides the enormous infrastructure scale-up issues associated with such an undertaking, more research is needed to better manage how CO_2 storage projects in the same basin would interact with each other, both the CO_2 plumes and resulting pressure buildup (see Figure 7-9 in the Research and Development Needs section later in this chapter). Some of the research topics associated with geologic storage projects that NASEM identified in the 2018 report include:

- Quantifying and managing the risks of induced seismicity associated with subsurface injection of CO_2
- Increasing CO_2 injection site selection and characterization methods
- Improving the effectiveness of CO_2 injection site monitoring and lowering costs for monitoring and CO_2 storage verification
- Improving performance of trapping mechanisms and accelerating speed in trapping CO_2
- Developing reservoir engineering approaches for co-optimizing CO_2 EOR and associated CO_2 storage
- Assessing and managing risk in compromised or leaky CO_2 storage systems
- Improving simulation models for CO_2 storage performance prediction and confirmation

- Social sciences research for improving stakeholder engagement and informing the public about the need, opportunity, risks, and benefits of CO_2 storage in geologic formations.

5. Storage Costs in Conventional Formations

Costs for CO_2 storage have been estimated based on existing projects and cost models for various scenarios.[22] Estimates range from \$1 to \$18 per tCO_2 in 2013 dollars (Table 7-2). The most recent estimates from DOE in 2014 narrow the range from \$7 to \$13 per tCO_2, but several projects in the southeastern United States have documented total storage costs in the range of \$3 to \$6 per tCO_2.[23] The wide range reflects the highly site-specific nature of geologic storage projects. Primary variables include the depth of the formation, number of injection wells required, existing land uses, and ease of deploying monitoring programs. Costs include well drilling, injection, monitoring, maintenance, reporting, land acquisition and permits, and other incidental costs. They do not include costs associated with remediation activities that may be required in the case of well leakage, groundwater contamination, or managing the risks of induced seismicity with active pressure management.[24] Proper design and operations should avoid these complications, thus the costs associated with remediation are not included in these estimates.



Study	Low Estimate (2013\$/tCO_2)	High Estimate (2013\$/tCO_2)
United Nations Intergovernmental Panel on Climate Change (2005)	1	12
Zero Emission Platform (2011)	2	18
U.S. Department of Energy (2014)	7	13
Global Carbon Capture Storage Institute (2011)	6	13

Source: Rubin, E. S., Davidson, J. E., Herzog, and H. J., "The Cost of CO2 Capture and Storage," International Journal of Greenhouse Gas Control, September 2015.

Table 7-2. *Total Costs for CO_2 Storage in Geologic Formations from Different Studies*

In 2017, the NETL developed the FE/NETL CO_2 Saline Storage Cost Model, an open-source spreadsheet model for estimating the cost of storing CO_2 in saline formations.[25]

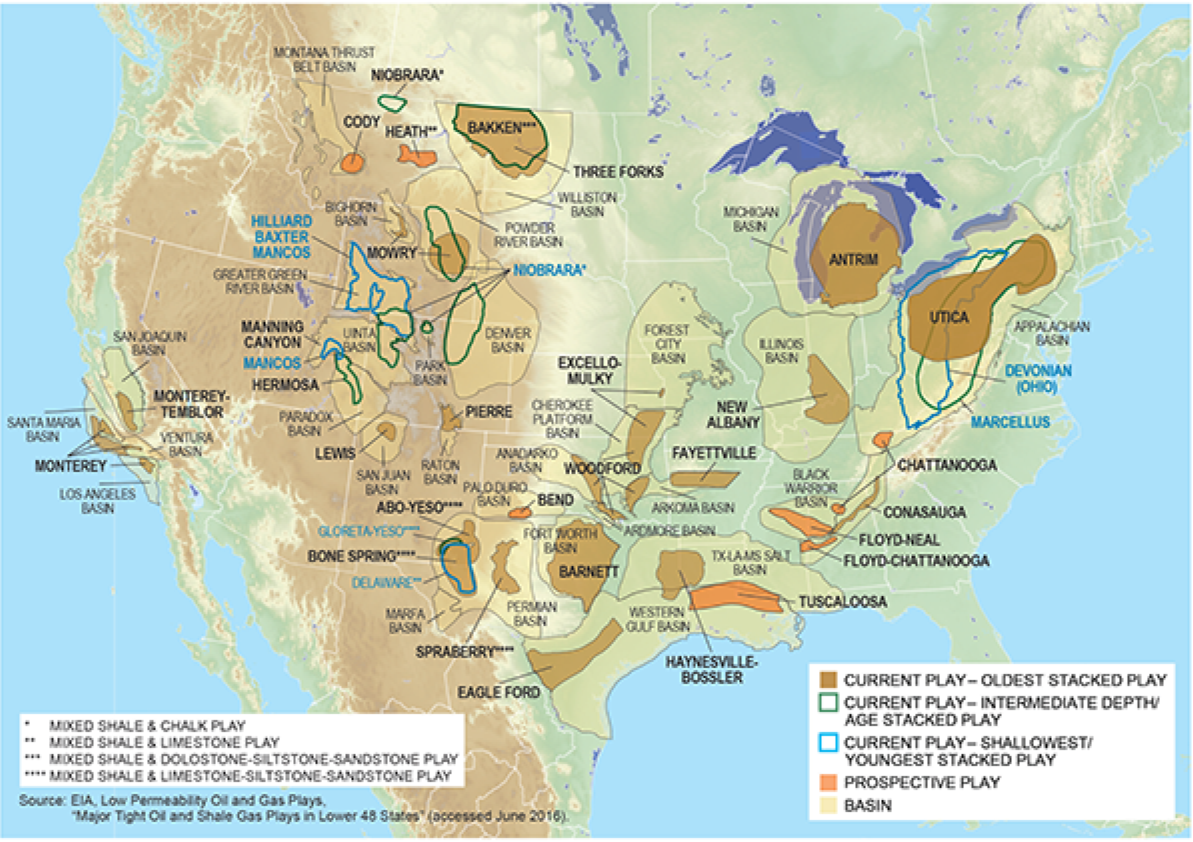
It is important to note that in the United States under the current EPA UIC Class VI regulatory regime for CO_2 storage, the storage operator must demonstrate financial assurance that certain specific activities can be conducted even if the operator were to become financially insolvent. These specific activities include being able to close injection wells properly at the end of CO_2 injection and to perform post-injection site monitoring and closure activities.

B. Storage in Unconventional Reservoirs

Unconventional reservoirs comprise low-permeability (tight) rocks containing hydrocarbons, rocks that may require horizontal drilling and hydraulic fracturing to enable commercial oil and natural gas production. These reservoirs have permeabilities in the microdarcy[26] range, or lower, and are typically associated with organic-rich shales with total organic carbon by weight percent from 0.5% to more than 10%. However, non-shale rocks—such as chalk, marlstones, tight limestone, dolomites, siltstones or sandstones—can also be classified as unconventional reservoirs. Tight non-shale rocks are often located near, or are interbedded with, organic-rich shales, which serve as source rocks for the hydrocarbons.

Dozens of rock formations that occur in parts of at least 20 states have been identified as having commercial unconventional oil or gas reserves. The Marcellus, Utica, Woodford, and Barnett Formations are examples of prolific gas-producing shales. The Bakken, Wolfcamp, Eagle Ford, and Bone Springs Formations are examples of prolific oil-producing shales. Many of these formations, such as the Eagle Ford and Bakken, produce both oil and natural gas in commercial volumes.

Figure 7-6 shows the locations and extent of Lower 48 U.S. unconventional oil and natural gas plays (does not present Alaska).[27] In 2017, most of the oil and natural gas produced in the United States came from unconventional reservoirs. The EIA estimates that in 2017, about 62% of total U.S. natural gas production was produced from shale formations, and a little more than 50% of total U.S. crude oil was produced from shale and unconventional tight non-shale formations.[28] The proliferation of drilling and production in unconventional reservoirs over the past decade has included them as potential targets for CO_2 storage.



Source: EIA, Low Permeability Oil and Gas Plays, "Major Tight Oil and Shale Gas Plays in Lower 48 States" (accessed June 2016).

Figure 7-6. *Unconventional Oil and Natural Gas Plays in the Lower 48 States*

There are several published estimates of CO_2 storage resources in unconventional oil and natural gas reservoirs. In 2005, Nuttall et al. estimated ~28 Gt of CO_2 can be technically stored in portions of the Ohio Shale and New Albany Shale.[29] In 2013, Godec et al. estimated a theoretical maximum CO_2 storage potential of 171 Gt for portions of the Marcellus Shale, although the technically accessible CO_2 storage is estimated at 55 Gt.[30] Tao and Clarens developed a production-based model to estimate theoretical CO_2 storage potentials and reported 10.4 Gt to 18.4 Gt of CO_2 could be stored in the Marcellus Shale by 2030.[31] Godec et al. used estimates of gas in place and economic ultimate recovery reported by the EIA in 2011[32] to estimate the technically accessible CO_2 storage potential of 134 Gt in 19 shale formations in the United States.[33] With respect to CO_2 storage in unconventional tight oil formations, the results of past research efforts suggest that the storage resource of the Bakken Formation ranges from a minimum of 160 Mt to as high as 3.2 Gt.[34] Though there is a lack of similar storage resource estimates for other tight oil formations, it is reasonable to assume that the Eagle Ford and Wolfcamp Formations in Texas, which are similar to the Bakken Formation, may have similar magnitudes of CO_2 storage capacities.

Although the literature suggests the CO_2 storage potential of unconventional reservoirs may be significant, those estimates are derived from studies based on laboratory experiments, modeling exercises, and unproven correlations of hydrocarbon resource-in-place estimates or production history compared with potential storage resource. There is a lack of knowledge about the fundamental physical and chemical mechanisms controlling many critical aspects of storage in unconventional reservoirs—injectivity, sweep/storage efficiency, and the roles of sorption, wettability, and thermal maturity—and this has precluded them for consideration as primary targets for CO_2 storage. The widespread exploitation of unconventional shale resources is a relatively recent development, within the last 10 to 15 years. Thus, the current level of knowledge about the mechanisms that affect storage of CO_2 in unconventional reservoirs is relatively low when compared with the knowledge of CO_2 injectivity and behavior in conventional reservoirs, which has more than 40 years of history.

To better evaluate the efficacy of CO_2 storage in unconventional reservoirs with tight oil, future research should focus on acquiring a better understanding of the factors that affect long-term injectivity, migration, and storage of CO_2 in different rock types. Both laboratory and modeling-based studies are needed to address questions of fluid and flow behavior in the context of relative permeability because these data are essential for accurately modeling CO_2 behavior in tight formations, especially those that are rich in organic carbon.

State and federal resources and permitting policies should emphasize ways to facilitate more CO_2-based pilot tests in oil and natural gas producing unconventional reservoirs. Because each formation is unique, it is important that tests are conducted in several different plays to capture the effects that variability in reservoir characteristics may have on CO_2 storage in unconventional reservoirs.

C. Regulations Governing CO_2 Storage in Offshore Formations

The United States offshore consists of submerged lands under the jurisdiction of the coastal states and submerged lands that are under federal jurisdiction, referred to as the

Outer Continental Shelf (OCS). The OCS consists of 2.3 billion acres of submerged lands, subsoil, and seabed lying between the seaward extent of the states' submerged lands and the seaward extent of federal jurisdiction. For most areas, federal jurisdiction begins three nautical miles from the shore baseline. However, for Texas and the Gulf Coast of Florida, federal jurisdiction begins nine nautical miles from the baseline, while for Louisiana, federal jurisdiction begins three nautical miles from the baseline. The seaward extent of U.S. federal jurisdiction typically extends to the Exclusive Economic Zone (EEZ), 200 nautical miles from the shore baseline. Beyond the EEZ are international waters.

The storage of CO_2 in the submerged lands within the states' jurisdiction is regulated by the United States EPA UIC program under the U.S. Safe Drinking Water Act of 1974. The Presidential Interagency Task Force on Carbon Capture and Storage examined the existing U.S. regulatory framework for CO_2 storage on the OCS. In 2010, the task force recommended the development of a comprehensive U.S. framework for leasing and regulating sub-seabed CO_2 storage operations on the OCS that addresses the broad range of relevant issues and applies appropriate environmental protections. However, this comprehensive framework has yet to be established. Therefore, the existing regulatory framework is shared across multiple federal agencies, including the Department of the Interior (DOI) and EPA, and may have jurisdictional gaps and redundancies.

1. Advantages of Offshore CO_2 Storage

As discussed in the following sections, there are many geologic formations in the offshore environment that are suitable for geologic storage of CO_2. Very little work has been performed in the breakdown of available storage capacity separating state from federal offshore formations. The extent, thickness, porosity, permeability, and security (suitable cap rock formations) make the injectivity and storage capacity of offshore formations ideal candidates for CO_2 storage. There may be advantages in conducting these operations offshore due to the following factors:

- The offshore environment is managed by state and federal entities instead of the private landowners for onshore environments that can potentially number in the hundreds.
- DOE has conducted, and continues to conduct, extensive research to assess the capacity potential of offshore geologic formations. There are also extensive data from existing oil and natural gas exploration and development —especially in the Gulf of Mexico (GOM) and, to a lesser extent, the Atlantic and Pacific Oceans—as well as other research that contributes to understanding the geologic environment offshore (site characterization, modeling, risk analyses, monitoring protocols).
- Extensive oil and natural gas experience in the GOM provide an extensive knowledge base for CO_2 storage operations in the same environment (e.g., drilling, well installation, decommissioning, analysis of environmental concerns, geologic and geophysical surveying, etc.).
- Some of the existing oil and natural gas infrastructure— platforms, wells, pipelines—could be repurposed for CO_2 storage. Repurposing existing infrastructure for CO_2 storage may be cheaper than decommissioning and removal.

- The offshore environment is distant from populated areas, so there would be no private residences near offshore storage sites.
- There are few or no underground sources of drinking water (USDWs) offshore; salinity in offshore geologic formations is generally more than the EPA limit, so the risk to USDWs is negligible to none.
- The ability to install plume and pressure management (relief wells) solutions. Produced water from these wells would require disposal in accordance with EPA regulations.
- Pressure from the overlying water column may help to keep the CO_2 in a dense phase, also called a supercritical fluid.
- Geologic and geophysical surveying for monitoring may have fewer impediments due to the lack of structures and landowners.

2. Potential Challenges of Offshore CO_2 Storage

There are several challenges to offshore CO_2 storage, such as:

- The lack of clarity regarding jurisdictions and regulatory regime could potentially delay the start of a new project.
- The existing statutory framework is complex and shared across multiple federal agencies and may have jurisdictional gaps and redundancies.
- Long-term liability remains with the operator.
- The potentially high cost of storing CO_2 offshore if there is no access to offshore infrastructure such as oil and

natural gas wells.

3. How to Enable Offshore CO_2 Storage Projects

There are several actions that would help to enable offshore CO_2 storage projects. The development of a comprehensive federal framework for leasing and regulating sub-seabed CO_2 storage operations on the OCS is vital to the success of these projects. The EPA has an existing legal and regulatory framework for projects in state waters, so clear federal direction on such matters is a necessity. In addition, this OCS legal framework should address long-term liability, which, for other programs such as oil and natural gas, currently remains with the operator. Reuse of infrastructure for CO_2 storage may also be addressed in the legal framework. Currently, oil and natural gas structures must be decommissioned soon after production has ceased. Targeting existing structures and enabling an extension for CO_2 storage use may facilitate project success. Finally, appropriate monitoring should be required throughout the life of the project and designed in a manner that facilitates clear regulatory direction during site closure.

4. Offshore CO_2 Injection Projects

According to the Global CCS Institute, in 2017 there were 10 offshore CO_2 injection projects operating, under construction, or undergoing advanced study.[35] Several injection facilities are operational in the Barents Sea and North Sea off the coasts of Norway and the Netherlands. Other operational CO_2 injection projects are offshore Brazil and Japan. Many countries are in the process of advanced study of selected offshore storage sites for development or are conducting detailed evaluation of their offshore storage resources.

The next two sections present some of the offshore storage sites listed in the Global CCS Institute online database that were operating or under construction at that time.

a. Operating Offshore Projects

Sleipner. In 1996, the Sleipner storage project in the Norwegian North Sea was the first large-scale offshore CO_2 storage facility in the world. CO_2 is separated from produced natural gas and reinjected into an offshore sandstone reservoir, the Sleipner gas field. Approximately 0.85 Mtpa of CO_2 has been injected and more than 17 Mt have been injected since the start of the project.

Snøhvit. The Snøhvit CO_2 storage site is associated with gas fields in the Barents Sea offshore Norway. CO_2 is captured and processed at a natural gas facility on an island in the north. The captured CO_2 is transported via pipeline to the Snøhvit Field offshore where it is injected into a storage reservoir. More than 4 Mt of CO_2 were stored between 2008 and 2018.

K12-B Field. CO_2 is captured at an offshore natural gas production facility and injected into a depleted gas reservoir, the K12-B gas field off the coast of the Netherlands. Injection of CO_2 began in 2004 and cumulative injection to date is estimated at more than 100,000 tonnes.

Santos Basin. The Petrobras Santos Basin Pre-Salt Oil Field CCUS Project located off the coast of Brazil has four CO_2

separation and injection systems aboard floating vessels anchored in the Santos Basin. The project started operations in 2013. CO_2 is separated on site as a part of natural gas processing and injected into the Lula and Sapinhoá oil fields for CO_2 EOR. In December 2016, the Santos Basin Pre-Salt development reached the milestone of 4 Mt of CO_2 injected into pre-salt fields.

Tomakomai. The Tomakomai CCUS Demonstration Project captures CO_2 from a hydrogen production unit at a refinery near Hokkaido, Japan. Approximately 100,000 tonnes of CO_2 per year over a 3-year period are being injected into two near-shore storage sites located 3 to 4 kilometers offshore. Post-injection monitoring will continue for 2 years after CO_2 injection stops.

b. Offshore CO_2 Storage Project Under Construction

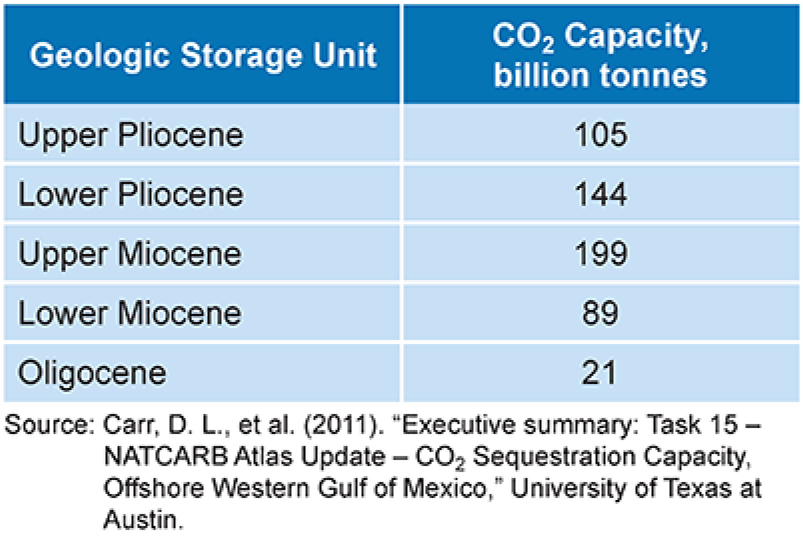
Haifeng Project. Two carbon capture test facilities will be installed at the Haifeng Power Plant Guangdong in China with offshore storage sites within the Pearl River Mouth Basin of the South China Sea. Total capture capacity for both facilities of the Haifeng Carbon Capture Demonstration Project is estimated at about 70 tonnes per day.

c. Offshore CO_2 Storage Options in the Gulf of Mexico

The states bordering the Gulf of Mexico (Texas, Louisiana, Mississippi, Alabama, Florida) have a high concentration of heavy industry and associated electrical power generation that creates an area of elevated CO_2 emissions. Significant reductions in national emissions could be achieved by focusing on extending onshore storage opportunities to access the large-volume offshore storage reservoirs in this region. The Gulf Coast region offers excellent source-sink matching, proven capture facilities (Air Products, Petra Nova), and developing transportation infrastructure (Denbury's Green CO_2 pipeline) for CO_2 EOR.

The Gulf of Mexico Basin is one of the largest-volume geologic sinks in the United States. It can accommodate CO_2 from local and regional sources and potentially serve as a storage resource for regions that lack local, suitable geology. As one of the most explored subsurface geologic basins in the world, the geologic and fluid systems of GOM hydrocarbons are well understood. The basin contains multiple geologic storage options, including previously unused porous and permeable sandstone formations that currently contain saline water (saline formations) and depleted oil and natural gas reservoirs from which hydrocarbons have been produced to near economic limits (depleted reservoirs).

Across the GOM region, many studies have been undertaken to characterize the subsurface in various formations. Results from numerous projects in the western GOM can be extrapolated to provide more information on the areas and formations within the greater GOM. Work completed in 2012 estimates that the total CO_2 capacity within the western GOM project area is 559 Gt. Table 7-3 provides estimates of the storage capacity distributed across the five major geologic storage units of the western GOM.[36]

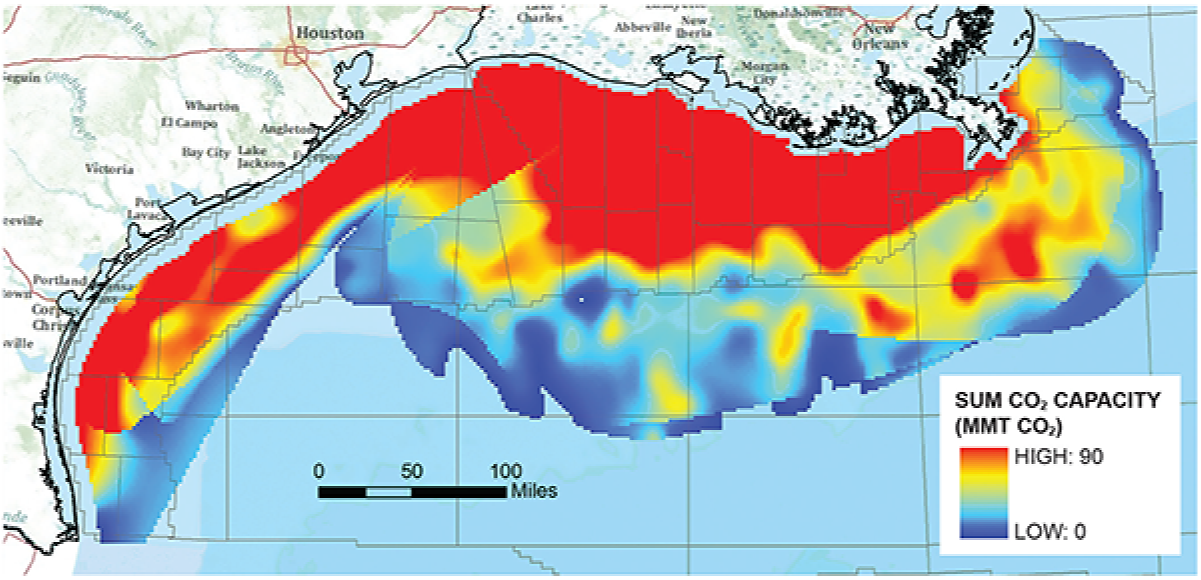


Geologic Storage Unit	CO_2 Capacity, billion tonnes
Upper Pliocene	105
Lower Pliocene	144
Upper Miocene	199
Lower Miocene	89
Oligocene	21

Source: Carr, D. L., et al. (2011). "Executive summary: Task 15 – NATCARB Atlas Update – CO_2 Sequestration Capacity, Offshore Western Gulf of Mexico," University of Texas at Austin.

Table 7-3. *Western Offshore Gulf of Mexico CO_2 Storage Capacity Estimates (P50 estimate)*

The greatest CO_2 storage capacity in the western GOM lies in Miocene and Pliocene deep saline sandstones. These reservoirs are particularly abundant offshore Louisiana. Substantial capacity, particularly in the Miocene, also occurs along the Texas coast (Figure 7-7).



Source: Carr, D. L., Trevino, R., Meckel, T., Brenton, C., Yang, C., and Miller, E. (2011). "Executive summary: Task 15 – NATCARB Atlas Update – CO_2 Sequestration Capacity, Offshore Western Gulf of Mexico," University of Texas at Austin, Gulf Coast Carbon Center.

Figure 7-7. *Potential CO_2 Storage in the Western Gulf of Mexico*

A 2010 project in the eastern Gulf of Mexico analyzed a 10,000-square mile area offshore Alabama and the western Florida Panhandle and suggested that about 170 Gt of CO_2 could be stored in Miocene sandstone, and at least 30 Gt could be stored in deeper Cretaceous formations.[37]

In 2018, the DOE awarded two projects for further study of storage and CO_2 EOR opportunities in the GOM. One project was awarded to the Southern States Energy Board (SSEB) and the other to the University of Texas, Bureau of Economic Geology (BEG). The SSEB project focuses on the eastern GOM while the BEG project focuses on the western GOM. The programs support the DOE's long-term objective to ensure a comprehensive assessment of the potential to implement offshore CO_2 subsea storage in the DOI's Bureau of Ocean Energy Management (BOEM), Outer Continental Shelf Oil, and Gas Leasing Program Planning Areas in the GOM. The goal of this effort is to expand the knowledge base required for commercially viable, secure, long-term, large-scale CO_2 subsea storage, with or without enhanced hydrocarbon recovery. The effort is also intended to support the DOE's long-term objective to ensure a comprehensive assessment of the potential to implement offshore CO_2 subsea storage in the GOM.

d. Offshore CO_2 Storage Options in the Atlantic Ocean

Offshore Atlantic CO_2 storage resources have been described by numerous authors, and in 2018 was the focus of two investigations by the Midwest Regional Carbon Sequestration Partnership and the Southeast Regional Carbon Sequestration Partnership, both of which are funded by DOE. Previous investigations[38] have identified CO_2 storage potential in Upper Jurassic and Cretaceous, which are aged saline reservoirs located below the seafloor in state-regulated Atlantic waters and the federal areas of the OCS. In addition to the Jurassic and Cretaceous saline reservoir storage potential in the offshore Atlantic, there is also potential for CO_2 mineralization storage in basaltic rock formations associated with Mesozoic-age rift basins found in offshore areas near New York, New Jersey, Georgia, and Florida.[39]

Offshore Atlantic CO_2 storage resources are largely uninvestigated because geologic information is limited. Fifty-one oil and natural gas exploration wells were drilled in the Atlantic OCS between 1976 and 1983.[40] All wells were abandoned as noncommercial at the time. In 2019, there are no active oil and natural gas leases in the Atlantic area.[41] The Delaware Geological Survey Outer Continental Shelf Core and Sample Repository[42] contains samples from all 51 oil and natural gas wells drilled in the Atlantic OCS offshore regions. Samples include cores, unwashed cuttings, vials containing samples processed for micropaleontology and palynology, and thin sections of core, cuttings, and micropaleontology and palynology splits. In addition, 10 wells were drilled in Florida State waters—Atlantic and Florida Bay—and the Straits of Florida OCS.[43] There is a large quantity of legacy seismic data that can be used to characterize the subsea geology.[44] However, approximately 80% of the mid- and south-Atlantic OCS areas have never been surveyed. Publicly available Atlantic offshore seismic data can be accessed at the National Archive of Marine Seismic Surveys.[45]

The northeast and Mid-Atlantic offshore areas under current evaluation for CO_2 storage resources by the Midwest Regional Carbon Sequestration Partnership include the Georges Bank Basin (New England), Long Island Platform, and Baltimore Canyon Trough (New Jersey, Delaware, Maryland).[46] Storage resources calculations were underway in 2018. The southeast Atlantic areas under investigation by the Southeast Regional Carbon Sequestration Partnership include the Carolina Trough (the Carolinas), Southeast Georgia Embayment (Georgia, Florida), and the Blake Plateau Basin (Georgia, Florida). Southeast Atlantic offshore regional CO_2 storage capacity in Upper Cretaceous strata is estimated to be approximately 32 Gt.[47]

One offshore Atlantic geologic storage project has been proposed off the coast of New Jersey by SCS Energy. The PurGen One project planned to capture CO_2 at a proposed power plant in Linden, New Jersey, and transport 70 miles offshore to an injection site through a 140-mile pipeline.[48] The CO_2 would have been injected into a Cretaceous age saline sandstone formation in the Baltimore Canyon Trough approximately 8,000 feet below the sea floor in a water depth of about 300 feet. The project was canceled in 2011 due to a lack of public support for a new coal-fired power plant.[49]

e. CO_2 Storage Options in the Pacific Ocean

Beneath Pacific waters of the United States offshore California, Oregon, Washington, Alaska, and Hawaii, current prospects for geologic CO_2 storage exist in known oil-producing basins in Southern California and Alaska. Additional opportunities, which were undergoing initial study, may lie in the basalt formations offshore of Washington, Oregon, and potentially Hawaii. These potential offshore storage areas have radically different geologic settings.

Potential targets for CO_2 geologic storage with or without associated CO_2 EOR include the producing oilfields and nonproducing structures (geologic traps) in offshore portions of the Los Angeles, Ventura, and Santa Maria Basins in southern California and the Cook Inlet Basin in Alaska. The onshore parts of the southern California basins were identified as strong prospects for CO_2 EOR in a 2005 study commissioned by DOE,[50] and the offshore part of each basin is geologically like the onshore part. Further, the offshore part of the Ventura Basin is continuous (geologically on-trend) with the onshore part. Although no offshore CO_2 injection projects exist to date, the economic pursuit of CO_2 EOR projects in these basins should yield local knowledge that will support eventual CO_2 injection projects not involving EOR (pure-storage projects). Possible CO_2 geologic storage offshore California would also be able to take advantage of many large CO_2 sources onshore that are nearby, and by the presence of existing drilling- and pipeline-related infrastructure.

Similarly, Alaska has producing offshore oilfields in the Cook Inlet Basin near Anchorage, demonstrating the presence of geologic structures appropriate for CO_2 storage. These structures may be injection targets for CO_2 currently emitted by onshore oil refineries and fossil-fuel power plants located nearby. While potential CCUS targets probably also exist in the Beaufort and Chukchi Seas (notably near Prudhoe Bay), the lack of a CO_2 source and the harsh operating environments render these locations infeasible in the near term.

There are no CO_2 geologic storage projects operating in the United States sector of the Pacific. The Pacific exclusive economic zone contains mainly clastic (versus carbonate) reservoir rock of Mesozoic and Cenozoic age. Compared with the Gulf of Mexico and midcontinent, the more active tectonic settings would limit storage prospectively in some areas. However, research on a new storage concept holds promise for secure CO_2 storage beneath the seafloor of large areas offshore Washington, Oregon, and Hawaii. The Cascadia CarbonSAFE Project seeks to inject CO_2 into basaltic rock, where it would eventually mineralize and become permanently stable. Vast areas of basaltic rock occur in ocean basins worldwide as well as in certain onshore areas, such as in Washington State, Russia, and India.

The Cascadia Project site has been extensively drilled and studied for geologic research purposes and has an instrumented observation network through which data are cabled onshore. The project conducted a prefeasibility study to evaluate the technical and nontechnical aspects of collecting and storing 50 Mt of CO_2 at the site. Its Phase I accomplishments include: (1) a compiled evaluation of industrial CO_2 sources and potential modes of transportation in the region, (2) an inventory of existing geophysical and geologic data in the area and evaluation of new data required to further assess storage potential and pre-/post-injection environmental monitoring needs, (3) an initial reservoir model of the potential storage complex, (4) a preliminary analysis of regulatory requirements, stakeholder, and financial needs for the offshore storage complex, and (5) a comprehensive project risk assessment analysis.

Preliminary simulations indicate that injectivity into the basalt rock is high, and that a 50 Mt CO_2 plume injected over a 20-year period will remain within the reservoir area for at least a 50-year period. Lab-based studies show that the injected CO_2 would be fully converted to carbonate minerals in 135 years or less.

D. CO_2 Storage in Depleted Hydrocarbon Reservoirs

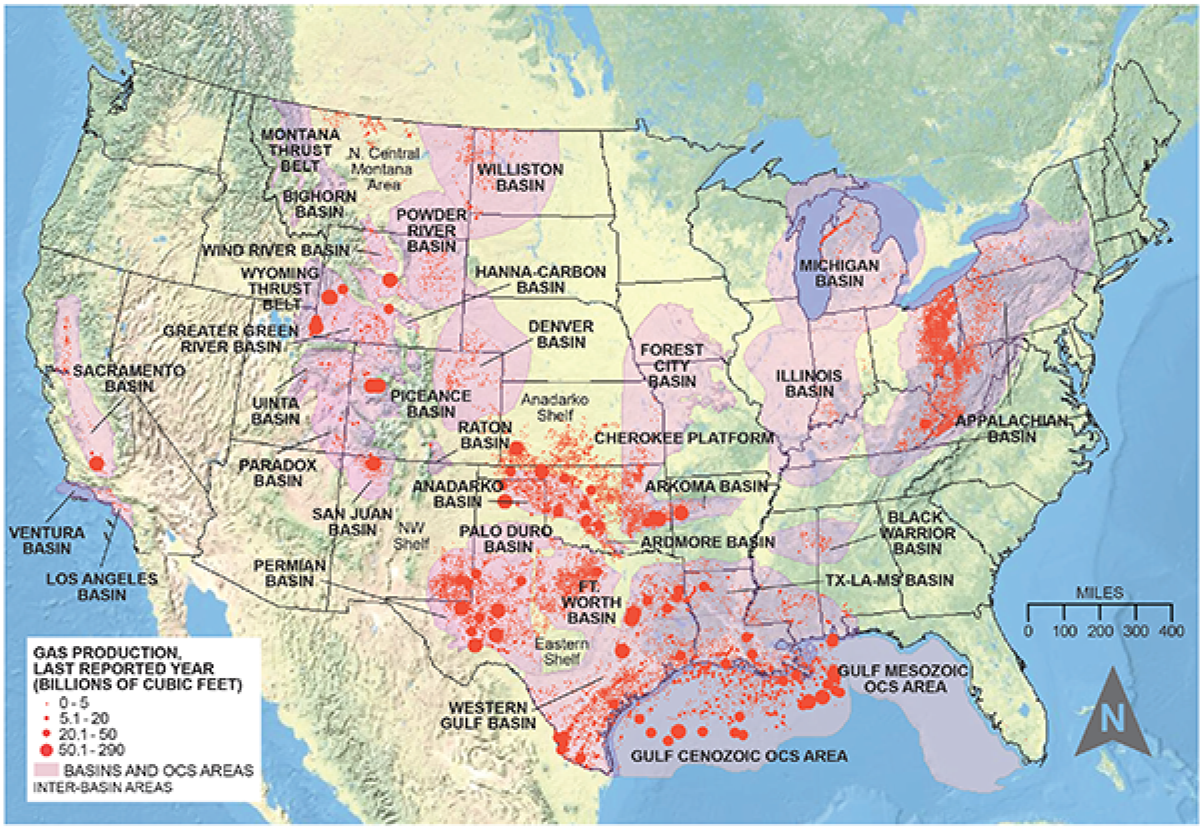
Conventional oil and natural gas reservoirs are porous rock formations, typically sandstones and carbonates, with structural geometries that contain trapped hydrocarbons. Using primary pressure-driven production methods, the production of oil from conventional reservoirs commonly yields 20% to 30% of the original hydrocarbon in place and 60% to 70% of the gas, and an additional 10% to 15% during secondary water flooding. Pore space vacancies generated during reservoir depletion create an ideal storage repository for CO_2 after the field has reached its economic production limit due, in large part, to the formation's well-established structural integrity that trapped buoyant fluids for millennia.

A potential advantage of these sites is that preexisting infrastructure may exist for storage due to prior field industrialization[51] and may have utility for CO_2 storage operations. There is also the potential for favorable source-sink matching with proximal stationary CO_2-emitting sources. Furthermore, oilfields with remaining oil after completion of primary and secondary recovery operations may be candidates for EOR methods, including CO_2 EOR. CO_2 storage can also take place adjacent to, above, or below depleted or active hydrocarbon reservoirs, realizing additional storage capacity while utilizing existing oilfield infrastructure.[52] Incidental CO_2 trapping associated with CO_2 EOR is described in Chapter 8, "CO_2 Enhanced Oil Recovery." CO_2 storage after the conclusion of CO_2 EOR operations may also present a good storage opportunity.

1. Advantages of CO_2 Storage in Depleted Hydrocarbon Reservoirs

The advantages to storing CO_2 in depleted hydrocarbon reservoirs include: (1) well-known and characterized reservoir properties, (2) established trapping and sealing mechanisms of buoyant fluids in structural and stratigraphic traps, (3) potential trapping of CO_2 in un-swept (remaining) oil and water rather than remaining as a separate phase, (4) reservoirs with weak water drive[53] may deplete pressure to further enhance storage capacity,[54] and (5) use of existing oilfield infrastructure, such as wells. These advantages enable more reliable and robust predictions of the long-term fate of the CO_2 in proven reservoirs, enhance storage capacity in amenable reservoirs, and reduce the overall costs of storage. Furthermore, CO_2 storage operations may face less opposition from stakeholders in regions with a history of hydrocarbon production.

An estimated 190 to 230 Gt of CO_2 storage capacity has been established in U.S. oil and natural gas reservoirs.[55] These fields are found in basins that cover an extensive portion of the onshore United States, from the Appalachian Basin in the east, the Permian and Gulf Basins in the south, and the Sacramento Basin in the west. Figure 7-8 shows the distribution of natural gas fields within those basins. Additional opportunities for storage may potentially exist after CO_2 EOR operations have ceased by offering a residual CO_2 saturation. This may act to enhance CO_2 injectivity and, in conjunction with further pressure depletion, enable improved storage capacity.



Source: EIA Maps, based on data from USGS, updated April 2009.

Figure 7-8. *Distribution of Natural Gas Production in the Lower 48 States*

2. Challenges of CO_2 Storage in Depleted Hydrocarbon Reservoirs

There are several technical challenges to using depleted oil fields for CO_2 storage. First, during the process of primary and secondary oil production, oil fields undergo large changes in stress that have irreversible effects on the rock properties. Not only does this permanently reduce the pore volume of the rock, but it can also make the rocks more susceptible to hydraulic fracturing.[56]

Second, hydrocarbons are produced from oil and natural gas reservoirs through wells that penetrate numerous stratigraphic intervals in the subsurface. These penetrations provide potential conduits for the leakage of CO_2 out of the reservoir, necessitating stringent well monitoring protocols. Any reactivation of hydrocarbon extraction activities in the field may result in additional leakage risks through newly drilled wells. And hydrocarbon well completion and stimulation practices may impact cap rock integrity. Although it is unlikely, there is also the potential that the cap rock may endure compaction damage when the reservoir's pore fluid pressure is decreased during production.[57]

Third, when injecting CO_2 into depleted reservoirs, proper modeling of multiphase flows in wells is needed to ensure that Joule-Thomson effects[58] in the wellbore do not lead to extreme cold temperatures that form ice and could damage the well or cement.

Legal issues also pose a challenge to storage in depleted oil and natural gas fields because hydrocarbon production leases do not address CO_2 injection or storage without the primary objective of hydrocarbon production. Injecting CO_2 into a depleted oil reservoir negates or complicates any future recovery of remaining oil resources if new technology or economic conditions might warrant such a scenario. Once hydrocarbon production ceases for a specified period, a lease agreement between the operator and oil or gas owner is typically terminated. CO_2 storage, therefore, necessitates developing a new contractual arrangement, and a primary challenge with CCUS is the ownership of subsurface pore space. Law reviews suggest it is likely that landowners will retain ownership of the pore space.[59] Therefore, any new framework may require a suite of new criteria to resolve the challenges facing CO_2 storage in depleted hydrocarbon reservoirs.

Storing additional CO_2 in an oil field after the completion of CO_2 EOR operations also poses some unique challenges. CO_2, and often water, are injected into the oil field during CO_2 EOR, and oil, natural gas, water, and CO_2 are produced. If the injection is optimized for CO_2 storage, any CO_2 produced will be recycled for reinjection into the reservoir. The average CO_2 saturations in the flooded portion of the oil field can be 20% or more. This contrasts with the average saturation of CO_2 of 5% to 8% in many CO_2 storage formations at the end of CO_2 injection. At the end of CO_2 EOR operations, if CO_2 continues to be injected into the same wells without removing brine or oil, the CO_2 may be pushed outside the boundaries of the oil field. This will require precise reservoir engineering to avoid this scenario by accessing any remaining storage space.

E. Other Storage Options

This section briefly describes other available geologic CO_2 storage options that have been investigated and tested at various scales. Two options are discussed here:

1. CO_2 injection and storage in deep subsurface coal beds; for example, during enhanced coalbed methane recovery
2. CO_2 mineralization to form solid carbonate phases in basaltic and ultramafic rocks and mine tailings.

Compared to the CO_2 storage resources that are available in deep saline formations and depleted oil and natural gas reservoirs in sedimentary basins, storage options in subsurface coal beds may be of local interest in areas where coal-bearing rocks occur. Conversely, vast CO_2 mineralization storage volumes may be available in onshore and offshore basalts. It should be noted that while some limited R&D is being performed in these alternative storage options, no demonstration- or commercial-scale projects have been conducted to determine the long-term feasibility of these storage options. Both technical and regulatory issues remain as barriers for commercial-scale development.

1. CO_2 Storage in Deep Subsurface Coal Beds

Coal is a rock composed primarily of preserved organic material. CO_2 injected into a coal bed rapidly absorbs into the organic material in coal and is trapped by a process called adsorption trapping. Deep coal beds, beds that may not be mined for economic or technical limitations, can be used to store CO_2. The target coal beds must have enough permeability to allow the injected CO_2 to reach far into the coal to be absorbed onto the organic material. However, laboratory research and field tests have shown that CO_2 injection into coal can decrease permeability and adversely impact CO_2 injectivity rates. The injected CO_2 does not need to be in the supercritical (dense phase) state for it to be adsorbed by coal, allowing CO_2 storage in coals to take place at shallower depths (at least 650 feet or 200 meters deep) than storage in oil and natural gas reservoirs or deep saline formations (at least 3,000 feet or 1 km deep). An added benefit to storing CO_2 in coal beds is that the injected CO_2 may displace methane that naturally occurs in most coal beds (CO_2-enhanced coalbed methane recovery). CO_2-enhanced coalbed methane recovery is analogous to CO_2 EOR in that the revenue from the sale of the produced hydrocarbons can help to offset the cost of CO_2 storage.

DOE's National Energy Technology Laboratory (2015)[60] estimated that the United States may have a median CO_2 storage capacity of 80 billion Mt in deep coal beds. There have been multiple CO_2-enhanced Coalbed Methane Recovery pilots and demonstration tests conducted worldwide.[61] However, according to the Global CCS Institute online database, there are no planned or active coal-bed CO_2 storage projects. This is due in part to the technical challenges encountered during pilot projects performed in the southeastern United States.

2. CO_2 Mineralization in Basaltic and Ultramafic Rocks

Geologic storage of CO_2 is possible by injecting it into subsurface basaltic and ultramafic rocks or by reacting CO_2-bearing fluid or gas with mine tailings rich in mafic minerals.[62,63] According to a 2018 report by NASEM, CO_2 mineralization may occur in one of three ways:

- Ex situ carbon mineralization—Solid mineral reactants are transported to a site of CO_2 capture then react with fluid or gas rich in CO_2
- Surficial carbon mineralization—CO_2-bearing fluid or gas reacts with mine tailings, alkaline industrial wastes, or

sedimentary formations rich in reactive rock fragments, all with a high proportion of reactive surface area

- In situ carbon mineralization—CO_2-bearing fluids are circulated through suitable reactive rock formations at depth.

With ex-situ or surficial mineralization, CO_2 is stored through reaction with crushed material at the surface to form a stable carbonate. Examples include captured CO_2 reacting with mafic and ultramafic mine tailings or industrial byproducts such as fly ash, cement kiln dust, and iron and steel slag.[64]

During in situ pilot studies of CO_2 injection into subsurface mafic rocks in Iceland and southeastern Washington, rapid subsurface carbonate mineralization has been shown to occur within 2 years after injection of CO_2.[65] In 2009, researchers began conducting a prefeasibility study for storing 50 Mt of CO_2 in oceanic basalts in the Cascadia Basin, offshore Washington, and British Columbia.[66]

A detailed assessment of CO_2 storage resources associated with mineralization has not been completed for the United States. However, there are significant mafic basalts and ultramafic rock volumes that could be used for the mineralization process. Suitable ex-situ and surficial carbon mineralization targets include asbestos or other ultramafic mine tailings, and in situ targets include ultramafic rocks on the East and West Coasts, the Columbia River Basalts in the Pacific Northwest, and the Midcontinent Rift Zone basalts in the midcontinent. Hawaii has volumes of potential in situ target reservoir rocks that could be used to mitigate local CO_2 emissions.[67] The 2018 NASEM report described the CO_2 mineralization potential in basaltic and ultramafic rocks as essentially unlimited and recommended increased funding for research to better quantify the CO_2 mineralization resources of the United States.

IV. ENABLING AT-SCALE DEPLOYMENT OF CO_2 STORAGE

A. Build on Other Efforts

The DOE's National Risk Assessment Partnership (NRAP) initiative is focused on developing the science base and associated toolsets to elucidate the behavior of CO_2 storage sites despite geologic uncertainty. Many decisions for a commercial CO_2 storage operation must be made before the detailed behavior of the site can be probed empirically during injection operations. These decisions relate to estimation of storage capacity, strategies to optimize storage, design of an effective and economic monitoring plan, and plan for site closure.

Utilizing resources and expertise across the DOE national lab complex, the NRAP initiative has been using a unique hybrid of physics-based simulations and empirical models to reveal how CO_2 storage systems are likely to perform over a range of variable conditions. The initiative is grounding these predictive tools in targeted experiments and field-based observations to quantify key processes associated with storage-system performance.

Several important findings relevant to commercial deployment of CO_2 storage have emerged from the NRAP initiative:

- If an adequate geologic model is available, the primary factors that affect how a storage site will respond to fluid injection and extraction can be predicted by using existing methods for predicting fluid flow, geochemical reactions, and geomechanical responses. Prediction accuracy is further improved after initial CO_2 plume monitoring data are available and used to calibrate the model. This is not meant to imply that the rate and direction of CO_2 plume movement in a reservoir can be predicted precisely using conventional approaches, or that all subsurface processes are completely understood or are fully embodied in conventional simulation methods. Rather, it acknowledges, for example, that a Darcy's law-based prediction of plume evolution has enough physics to inform a decision on CO_2 plume evolution, particularly in a statistical sense. Hence, NRAP has relied heavily on a battery of existing predictive simulators, extending them in new ways to address specific risk-related challenges.
- The major uncertainties in predictions of CO_2 plume evolution—which stem from variability in subsurface characteristics and the associated model parameters—can be bound at levels low enough to make better decisions than in the absence of this probabilistic information. A major challenge is to have grids[68] with fine enough resolution to capture the influence of thin, high-permeability layers.
- Post-injection monitoring plans that vary in time and location based on the evolving risk at the storage site are

as effective and significantly less costly than static monitoring plans based on a fixed time. Assessing case studies over a range of site characteristics and operational conditions, the NRAP initiative has found that the risk-related behavior of a storage site changes significantly during the 10-year time period after injection stops, meaning that effective monitoring plans can vary spatially and temporally.

- The most likely leakage-related scenarios result in small impacts. Further, with respect to aquifer impacts, many modeled leakages result in changes to groundwater that are below detection limits—in other words, below a no-impact threshold. Exceptions to this would be large leaks that could be readily detected during the injection phase of an operation.
- Leakage pathways in wellbores completed with Portland-based cements are likely to self-seal over time due to a combination of geochemical and geomechanical processes. However, other leakage pathways in wellbores could come from fatigue in the continuous cement and casing caused by the CO_2 injection mode, thermodynamic effects, etc.

B. Stakeholder Acceptance of Storage Security

Public support for CO_2 storage projects is of paramount importance at every level, from the local community to elected regional and state officials, and nongovernmental organizations interested in energy and climate solutions.[69] Community communications, outreach, and education can set the tone for the life of the project. Additional information about the importance of stakeholder engagement is discussed in Chapter 4, “Building Stakeholder Confidence,” in Volume II of this report.

C. Subsurface Pressure Management

The amount of CO_2 that needs to be sequestered for CCUS to have a meaningful impact on reducing emission could cause widespread pressure increases in the subsurface. Injecting large quantities of fluids (wastewater or CO_2) into the subsurface increases reservoir pressure, which could potentially compromise CO_2 containment, cause induced seismicity risk, and have a significant economic impact on a CCUS project. It is recognized that excessively large pressure increases in a reservoir might create new fractures or reactivate preexisting ones with the associated risk of induced seismicity or leakage. Furthermore, it can also limit the total capacity of the reservoir or the amount of CO_2 that can be injected per well.[70]

Extracting brine from a conventional storage formation is one potential option as a pressure management strategy that could reduce pressure buildup and might also help manage CO_2 plume migration and aerial extent—which impacts monitoring, verification, and accounting costs—and eventually provide desalinated or treated water for diverse uses.[71]

Pressure management has been implemented as part of the Gorgon project in Western Australia. Reservoir engineers identified that the number of potential CO_2 injection wells suggested for the project could be reduced by incorporating an active reservoir pressure management system. This involves extracting formation water from the Dupuy Formation at locations within pressure communication of the injection area but outside the range of the forecast CO_2 plume migration. The project includes four water production wells that will pump water from the Dupuy Formation using electrical submersible pumps. To reduce environmental impacts, that produced water will be reinjected into the overlying Barrow Group by two water disposal wells. It is expected that this system will produce approximately 60,000 to 80,000 barrels of water per day from the Dupuy Formation. That off-take rate was included in the reservoir simulations used to determine the CO_2 injection well count.[72]

However, in large-scale CCUS projects the magnitude of brine extraction necessary might lead to considerable water management and economic challenges. Aside from the Gorgon Project, for which CO_2 injection and storage started in August 2019, knowledge about the benefits and challenges of brine extraction comes from research studies and a few pilot projects, such as the DOE Brine Extraction Storage Test effort, which will extract brine for pressure management and test various treatment options to produce water suitable for surface use.[73]

Several strategies have been proposed regarding brine extraction as an approach for pressure management. These strategies include preproduction of brine before injecting CO_2 to increase reservoir capacity,[74] simultaneous brine extraction and CO_2 injection to maintain decreased pressure,[75] and brine extraction at specific critical locations (i.e., near faults) to minimize seismicity risk.[76]

Similarly, several uses for the produced brine have been proposed that include desalination and treatment, reinjection in overlying or underlying saline formations, or disposing of it in the sea. Identified options for the treated brine include offsetting water requirements for CO_2 capture, using for power plant cooling water, and using in agriculture or industrial settings, such as for lithium extraction.[77]

Challenges associated with the use of brine extraction techniques include the cost of additional wells for brine extraction, brine disposal, and the cost of desalination and treatment that will be essential for surface usage. However, this impact could be offset by additional revenue from brine reuse. Some studies suggest that for certain locations, almost the same brine volume as the injected CO_2 volume needs to be removed to prevent induced seismicity.[78] If this much brine were reinjected back into the subsurface in a seismically vulnerable area, this in and of itself would create concerns.

In summary, while brine extraction may be necessary or desirable for some locations, significant challenges remain, and more research is needed to assess the viability of brine extraction as a means of pressure management.

D. Matching a Source to a Sink

CO_2 source-sink matching involves pairing a stationary CO_2 emitter with a potential reservoir. This includes geologic formations such as depleted oil or gas reservoirs, potentially unmixable coal seams, saline formations, and unconventional resource reservoirs. In practice, potential storage sites will have limitations on both CO_2 storage capacity and injection rate that are subject to geological characteristics. Factors considered for appropriate pairing include distance from source to sink, availability of existing CO_2 pipelines to transport supercritical CO_2, depth and geologic attributes of the sink, population distribution near proposed projects, proximity to parks or public lands, and vulnerability of the overlying environment. It is also important to consider social factors—population distribution, community sentiment, private and municipal water supplies, regional environment, and protected areas. Utilizing regional storage hubs could provide value with multiple sources accessing one regionally significant sink.

The main issue associated with source-sink matching is the cost of transport to the storage site. Models for source-sink matching include integer linear programs, vector data-based multisource technics, raster data-based single-source, and sink-matching models. Based on such models, a decision support system is developed that considers the influence of several factors: reservoir capacity, geometry, injection pressure, sealing formation attributes, vertical proximity of USDWs, potential for enhanced oil or gas recovery, complex terrain factors (such as the slope of the terrain, bypassing urban areas and national parks, and crossing rivers, railways, or highways to find the lowest cost pathway between source and sink), population density, ownership, and social and political data.

Applying Big Data Analytics tools to decrease storage costs and de-risk a project requires highly detailed databases in a data structure that fits the computational models. NETL has developed the National Carbon Sequestration Database to facilitate the use of analytics to aid in source-sink matching. NETL has also funded programs to advance these analytical tools. The potential for reducing the overall costs of CCUS can be significant with respect to the identification of geologic sinks in proximity to the CO_2 emitting sources, which have been identified in several of the DOE’s CarbonSAFE and RCSP program projects. Continuing and expanding these efforts and providing potential operators access to these data will have help to accelerate the development of CCUS projects. Furthermore, the Internal Revenue Service Section 45Q tax credit has considerable influence on the cost effectiveness of CCUS projects where source-sink matching is concerned.

E. Pore Space Legal Rights

Before injecting CO_2 for geologic storage, the operator must own the pore space, have permission from the owner, or otherwise have the right to use the pore space. Therefore, the project developer will have to acquire the authorization to access and use pore space to avoid liability for subsurface trespass and nuisance before a geologic CO_2 storage field can be developed. A detailed discussion related to pore space and the challenges related to the development of a commercial-scale storage project is provided in Chapter 3, “Policy, Regulatory, and Legal Enablers,” in Volume II of this report.

F. State Primacy

The EPA regulates subsurface injection to protect USDWs via the Safe Drinking Water Act’s UIC program. In 2010, the EPA developed UIC Class VI rules for wells used to inject CO_2 specifically for the purpose of long-term geologic storage.

These Class VI rules cover items such as CO_2 injection and site characterization, well permitting, well construction and operational standards, testing, plugging, recordkeeping, corrective action, emergency and remedial response, closure and post-closure care, and associated financial assurance requirements.

The Class VI regulations can be implemented by the EPA or adopted by states, territories, or tribes as the primary enforcement authority. Designation of this authority outside of the EPA is called primacy. Primacy authorizes a state, territory, or tribe to implement regulatory responsibilities associated with the UIC program. States must apply for primacy and be granted authority through EPA review and rulemaking.

In 2013, North Dakota became the first state to seek primacy from the EPA for the Class VI UIC program and was granted authority in July 2017. The North Dakota Industrial Commission amended its own carbon sequestration rules to align with the federal regulations. In 2019, the only other state perusing primacy for the Class VI program was Wyoming. The state of Wyoming filed its application for Class VI primacy with the EPA in Region 8 on January 2018 through the Wyoming Department of Environmental Quality. As of April 2019, that application is still pending, and no additional information is available.

The benefits of state primacy for the Class VI UIC program are numerous. However, because there is little funding available from the EPA for state UIC programs, there is limited incentive for states to take primacy for the Class VI program. It would be helpful if states had access to information about the benefits of receiving Class VI primacy, the process and experience of states that have primacy for other well classes, and financial support for developing a Class VI primacy application and implementing the program for commercial projects.

A more detailed discussion of state primacy and its implications is discussed in Chapter 3.

V. CROSSCUTTING ISSUES FOR CO_2 EOR AND CO_2 STORAGE

Storage projects can be broadly divided into two types. Dedicated CO_2 storage involves the underground injection of anthropogenic CO_2 (from industrial sources) for the sole purpose of GHG mitigation. Incidental or associated storage occurs when CO_2 is injected for other purposes, such as CO_2 EOR.

It is important to note that in the United States, less than 30% of the CO_2 used for CO_2 EOR is from anthropogenic sources; the remainder comes from natural sources. There have been more than 100 commercial CO_2 EOR projects in the United States since the 1970s, and experience has shown that CO_2 EOR produces incremental oil and permanently traps CO_2.

In contrast, dedicated CO_2 storage is a relatively nascent industry with a few commercial-scale projects operating around the world—those storing more than approximately 0.5 Mtpa of CO_2. Although incidental or associated storage is a physical consequence of EOR, operators of such sites might not seek recognition of GHG mitigation benefits because of various economic, regulatory, or legal factors. CO_2 EOR projects are driven by the economic benefit of producing oil that may not be recoverable by primary production methods. Historically, the trapping of CO_2 has been a result of the CO_2 EOR process, rather than an explicit objective of the CO_2 EOR process. During CO_2 EOR operations, CO_2 is produced with the recovered oil, separated and purified, and reinjected for additional oil recovery. The result of this closed-loop CO_2 system is that associated storage infrastructure requirements tend to be more complex than those for dedicated storage, which does not include oil production.

Although the primary goals of dedicated and associated storage may be different, the two do share several key crosscutting aspects. Both dedicated and associated storage result in the secure storage of anthropogenic CO_2, providing mitigation for GHG emissions. Both require similar geologic conditions, engineering approaches, monitoring technologies, and social license to operate. With respect to geologic conditions, both types of storage require reservoir rocks with enough injectivity and storage capacity to support commercial-scale CO_2 injection. Thick, sealing rocks are also necessary for both types of storage to ensure that the injected CO_2 does not migrate outside of the permitted zone. Subsurface engineering approaches and requirements for drilling, operating, and maintaining wells are similar and the technologies and protocols used are essentially interchangeable. Many surface infrastructure elements—pipelines, compressors, wellheads, and Supervisory Control and Data Systems—are also largely the same, regardless of whether they are for associated or dedicated storage.

Monitoring the injection of CO_2 and its subsequent movement in the subsurface is an essential component of both CO_2 EOR and dedicated storage projects.

While general principles and technologies are common to dedicated and associated storage, site-specific factors will always impart unique qualities to each project. Dedicated storage sites have significantly fewer well penetrations compared with associated storage via CO_2 EOR. It is also important to note that there are differences between CO_2 storage and EOR categories, particularly with respect to monitoring and tax incentives. CO_2 EOR operators tend to refer to monitoring as reservoir surveillance, while dedicated storage operators call it monitoring, verification, and accounting. Regardless of the terminology, the technologies used to determine the disposition of the injected CO_2 are largely the same.

There are, however, striking differences between associated and dedicated storage in terms of the regulatory requirements for monitoring and how the data generated by those activities are used. For EOR operators, the primary purpose of gathering monitoring data is to better understand the efficiency of their operation, typically in terms of CO_2 utilization rates measured in units of CO_2 (either purchased or injected) per unit of oil. Monitoring for dedicated storage places more emphasis on determining the areal extent and geometry of the CO_2 plume and detecting any movement of CO_2 out of the designated storage zone. Both CO_2 EOR and dedicated storage projects use monitoring technologies, such as wellhead pressure gauges, to ensure safe operations and reduce operational risk.

In addition to sharing monitoring approaches and technologies, there are also important crosscutting aspects between saline storage and EOR that result from operations in stacked reservoirs. Operations in stacked reservoirs occur when CO_2 is injected into saline reservoirs that are above or below oil reservoirs. The surface infrastructure constructed for development of the oil field, especially that which is used for CO_2 EOR, can be used for saline storage projects in reservoirs that are above or below the oil reservoir. The geological characterization that has been used to develop the oil resources (data from well logs and seismic surveys) will give a saline storage project a detailed understanding of critical properties such as reservoir depth, thickness, and architecture at the earliest stages of the project. This will always be the case for saline resources above an oil reservoir, and sometimes the case for saline resources below an oil reservoir, although there are typically fewer wells that penetrate below any given oil reservoir. Dedicated storage projects in saline reservoirs below oil fields must contend with challenges from drilling through the oil reservoir, including zones of abnormal pressure conditions (higher or lower pressures than expected) and ensuring that well drilling and completion operations do not inadvertently damage the oil reservoir. There are also challenges when distinguishing multiple overlapping CO_2 plumes in zones above or below an active CO_2 EOR project. Advancements in monitoring technologies, including improvements in geophysical and acoustic data acquisition and processing, are needed to address those challenges.

In some instances, a dedicated storage project may be conducted in the same rock formation as the oil reservoir, but in a water-saturated zone that is geologically downdip from the main area of oil saturation, that is in the reservoir's "water leg." Like saline storage resources above and below an oil reservoir, dedicated storage in the water leg of an oil reservoir can benefit from, and dovetail with, the infrastructure, characterization, and monitoring elements of a nearby CO_2 EOR project. However, migrating the injected CO_2 from the water leg into the oil reservoir will complicate CO_2 monitoring and accounting for both the dedicated storage project and the CO_2 EOR project, which can lead to complications in the certification of storage by government agencies and qualification of Section 45Q tax credits. CO_2 storage in stacked reservoirs and water leg reservoirs may also face challenges from pore space ownership and mineral lease issues. Clarifying existing state and federal policies and regulations and, in some cases, new legislative directives that address the crosscutting aspects of dedicated storage and CO_2 EOR, may be necessary.

VI. RESEARCH AND DEVELOPMENT NEEDS

Ramping up global CO_2 storage in geologic formations to a scale of gigatonnes per year is an enormous task. For example, increasing global storage of CO_2 to 1 Gt/year—a scale equivalent to approximately 40% of United States stationary source CO_2 emissions—would require a fifteenfold increase beyond the CO_2 EOR and storage operations that exist around the world in 2019. There is already a broad level of technical expertise from more than 20 years of CO_2 storage experience and 100 years of oil and natural gas operations to increase the number of geologic storage projects in oil and natural gas reservoirs and saline formations.

However, for global CO_2 storage to expand to a 1 Gt CO_2/year level and beyond, much more intensive use of storage resources will be necessary, requiring better information to assess risks, to inform site characterization and source-sink matching, and providing assurances that permanent storage will be safe and secure. The 2018 NASEM report on CO_2 Removal and Secure Sequestration and the International Initiative Mission Innovation Workshop on CO_2 Capture and Sequestration, provide comprehensive assessments of research needs. In this chapter, the focus is on those R&D needs that will support the rapid scale-up of CO_2 storage in geologic formations in the United States.

Globally, there is a significant amount of experience from the previously cited CO_2 storage projects injecting at the scale of 1 Mt/year, and there are several other projects at a smaller scale. There are distinct challenges to rapidly increasing the number of large-scale CCUS projects in the United States, such as how the presence of multiple CO_2 storage projects in a single basin might interact with each other through overlapping pressure buildups and CO_2 plume comingling and the continued research about the commercial viability of using unconventional formations (shale, basalt) for large-scale CO_2 injections.

Figure 7-9 presents a sketch providing a spatial comparison to illustrate the extent to which injecting CO_2

into a saline formation causes pressure buildup in the formation and the area surrounding it. The individual footprint of a CO_2 plume in a saline formation may extend 30 km^2 to 300 km^2, but the area in which pressure buildup occurs is even larger. If there are multiple CO_2 injection projects within the same saline formation, the pressure buildup from the projects will be additive, extending the buildup over a larger area.

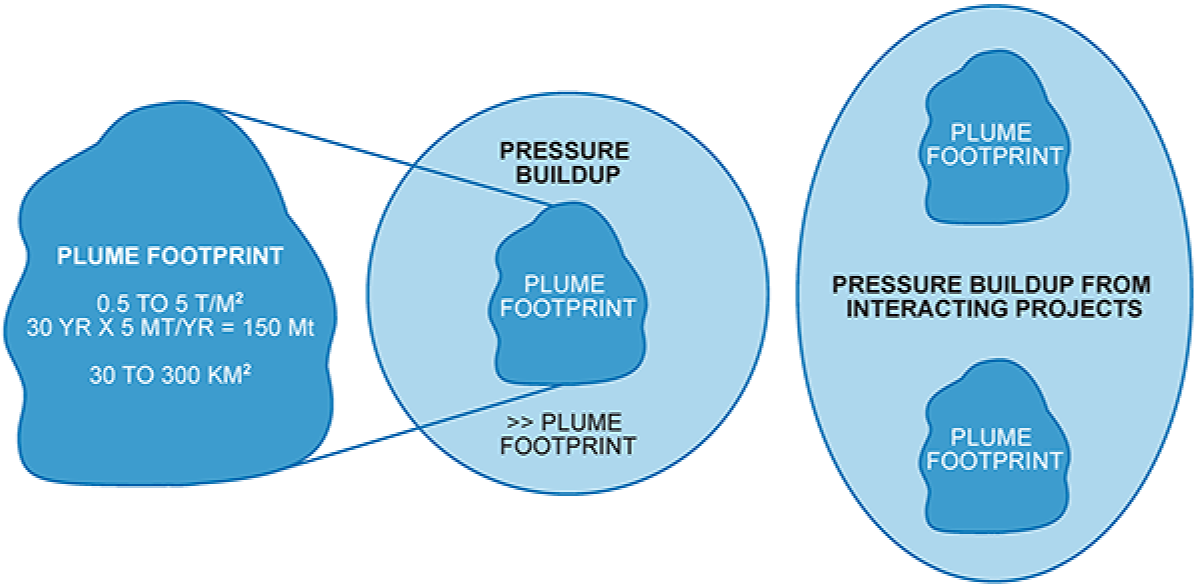


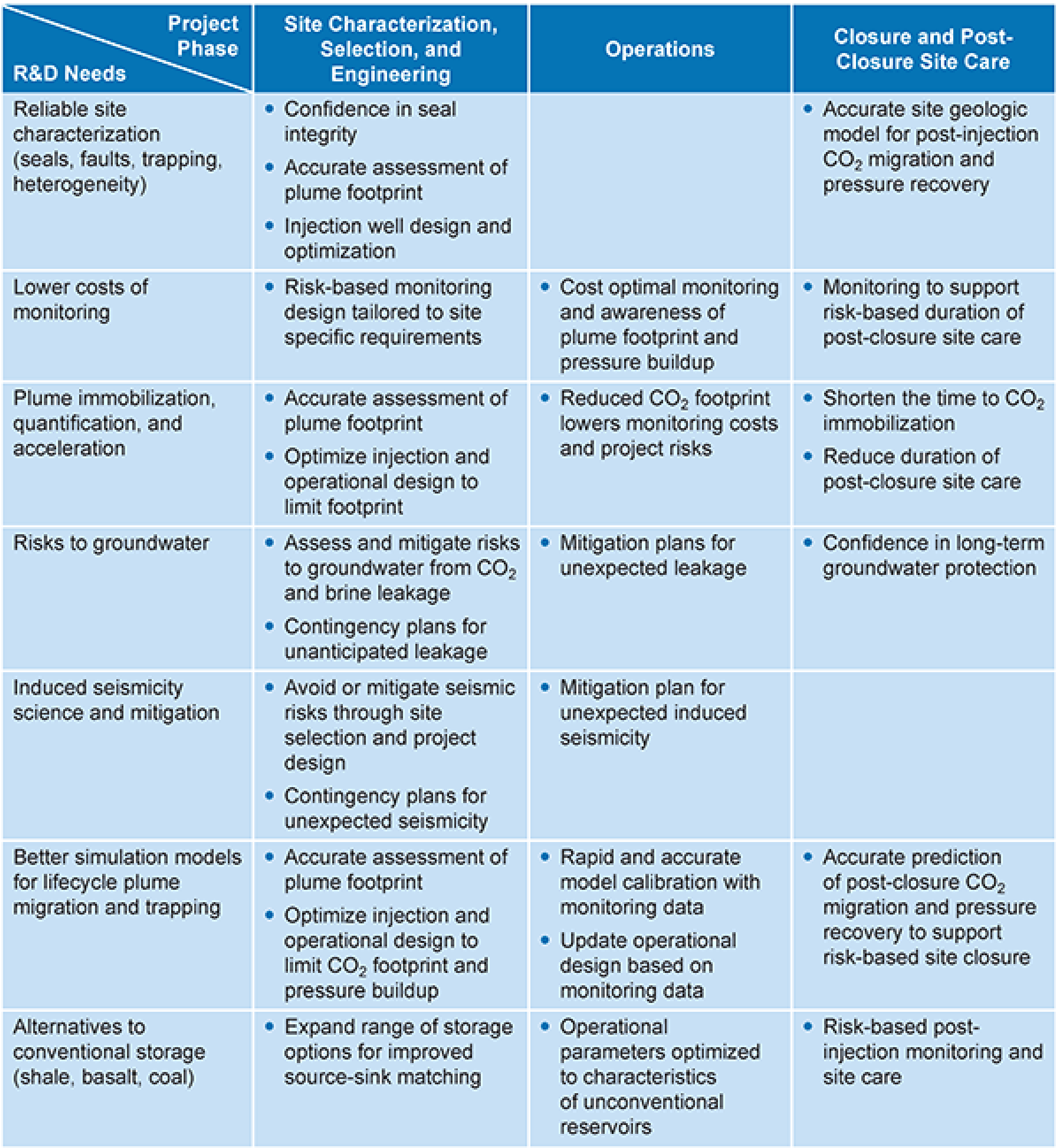
Figure 7-9. *Spatial Comparison of a CO_2 Plume and Area of Pressure Buildup it Affects*

Given the need to address the challenges, research priorities include:

- Increasing the efficiency of site characterization and selection methods

- Increasing pore space utilization by improving confidence in CO_2 plume immobilization mechanisms and accelerating their speed in immobilizing CO_2
- Improving coupled models for optimizing and predicting CO_2 flow and transport, geomechanics, and geochemical reactions, including leveraging capabilities in the oil and natural gas industry
- Lowering the cost of monitoring and developing new monitoring technologies
- Quantifying and managing the risks of induced seismicity
- Investigating the feasibility of Mt/year storage in alternatives to sandstone and carbonate reservoirs, including ultramafic rocks (basalt) and low-permeability rocks (shale)
- Conducting social sciences research for improving stakeholder engagement and informing the public about the need, opportunity, risks, and benefits of CO_2 storage in geologic formations.

These research activities will address many of the practical and financial challenges facing operators who are contemplating new large-scale storage projects. Table 7-4 details how the proposed research activities address these needs. Current R&D programs address the needs of fundamental storage science, storage site characterization and drilling, and pilot- and demonstration-scale CO_2 injection projects. Combining additional pilot and demonstration projects with CO_2 storage R&D will help the nascent CO_2 storage industry achieve at-scale deployment in the United States. These projects would also establish valuable infrastructure during the R&D phase that could then be used for commercial-scale deployment.



Project Phase R&D Needs	Site Characterization, Selection, and Engineering	Operations	Closure and Post-Closure Site Care
Reliable site characterization (seals, faults, trapping, heterogeneity)	• Confidence in seal integrity • Accurate assessment of plume footprint • Injection well design and optimization		• Accurate site geologic model for post-injection CO_2 migration and pressure recovery
Lower costs of monitoring	• Risk-based monitoring design tailored to site specific requirements	• Cost optimal monitoring and awareness of plume footprint and pressure buildup	• Monitoring to support risk-based duration of post-closure site care
Plume immobilization, quantification, and acceleration	• Accurate assessment of plume footprint • Optimize injection and operational design to limit footprint	• Reduced CO_2 footprint lowers monitoring costs and project risks	• Shorten the time to CO_2 immobilization • Reduce duration of post-closure site care
Risks to groundwater	• Assess and mitigate risks to groundwater from CO_2 and brine leakage • Contingency plans for unanticipated leakage	• Mitigation plans for unexpected leakage	• Confidence in long-term groundwater protection
Induced seismicity science and mitigation	• Avoid or mitigate seismic risks through site selection and project design • Contingency plans for unexpected seismicity	• Mitigation plan for unexpected induced seismicity	
Better simulation models for lifecycle plume migration and trapping	• Accurate assessment of plume footprint • Optimize injection and operational design to limit CO_2 footprint and pressure buildup	• Rapid and accurate model calibration with monitoring data • Update operational design based on monitoring data	• Accurate prediction of post-closure CO_2 migration and pressure recovery to support risk-based site closure
Alternatives to conventional storage (shale, basalt, coal)	• Expand range of storage options for improved source-sink matching	• Operational parameters optimized to characteristics of unconventional reservoirs	• Risk-based post-injection monitoring and site care

Table 7-4. *Research Needs for Different Phases of a Geologic CO_2 Storage Project*

It is recommended that an increase of the current DOE R&D budget for geologic storage by $400 million per year for the next 10 years could be allocated as follows:

- $80 million to the Regional Initiative to Accelerate CCUS Deployment (for a total appropriation of $100 million per year)
- $100 million for characterization of geologic storage formations, including offshore, that have scale potential through the CarbonSAFE program or similar initiatives (for a total appropriation of $150 million per year)
- $220 million per year to enable field-scale projects that collect data and geologic samples used to advance the science of long-term CO_2 storage security.

These R&D activities also play a critical role in increasing the industrial workforce needed to carry out these activities.[79] These projects should also provide a testing opportunity for monitoring and predictive modeling of CO_2 in the subsurface at-scale.

VII. PRIORITIES FOR ACHIEVING AT-SCALE DEPLOYMENT OF CCUS

This study has identified three phases projected to occur over a 25-year period to achieve at-scale deployment of CCUS in the United States—activation phase, expansion phase, and at-scale phase. Each phase is defined by the primary actions that need to occur within a relative timeframe, including near-term, mid-term, and long-term priorities. The phases and their priorities are based on the abatement cost curve analysis presented in Chapter 2, “CCUS Supply Chains and Economics,” in Volume II of this report.

A. Near-Term Priorities for the Activation Phase

1. Increased Funding for R&D

As of October 2019, there were 19 large-scale CCUS projects operating around the world with a total storage capacity of about 32 Mtpa of CO_2. Ten of these projects are in the United States with a total storage capacity of 25 Mtpa. Enabling an additional 25 Mtpa to 40 Mtpa of CO_2 storage during the next 5 to 7 years of the CCUS activation phase would require doubling the current R&D budget for geologic sequestration to about $250 million/year short-term research priorities include:

- Increasing the efficiency of site characterization and selection methods
- Increasing pore space utilization by improving confidence in CO_2 plume immobilization mechanisms and accelerating their speed in immobilizing CO_2
- Improving coupled models for optimizing and predicting CO_2 flow and transport, geomechanics, and geochemical reactions, including leveraging capabilities in the oil and natural gas industry
- Lowering the cost of monitoring and developing new monitoring technologies
- Quantifying and managing the risks of induced seismicity
- Investigating the feasibility of Mt/year storage in alternatives to sandstone and carbonate reservoirs,

including ultramafic rocks (basalt) and low-permeability rocks (shale)

- Conducting social sciences research for improving stakeholder engagement and informing the public about the need, opportunity, risks, and benefits of CO_2 storage in geologic formations.

Table 7-4 details how the proposed research activities address the needs of each phase of a geologic storage project to illustrate how it will benefit industry operators. For example, new methods for using the available pore space more efficiently will reduce the cost of characterizing a site by limiting the area that must be characterized. During the operational phase of a project, high-reliability and low-cost monitoring programs that are targeted to the largest project-specific risks will increase stakeholder confidence that groundwater resources are protected, and site-workers and the public are safe. For the closure and post-closure phase, proven models for predicting the long-term behavior of stored CO_2 will help to shorten the post-closure site care period by providing tools for the operator to demonstrate that USDWs would not be endangered after the injection period stops. In addition to providing valuable knowledge, university-based research programs will ensure a pipeline of qualified talent to increase the workforce capacity that will be needed to support the scale-up of CO_2 capture and storage operations.

2. Class VI Permit Reform

Some aspects of the Class VI regulations for CO_2 storage are problematic for increased adoption of CCUS. Improvements and reform of Class VI regulations include optimizing permit process efficiency to shorten the time it takes to obtain a permit by improving the level of coordination between the permit applicant and the regulatory authority that grants the permit. Other potential improvements to the regulatory process include adopting risk-based monitoring approaches, clarifying that site closure is allowed when drinking water aquifers are no longer endangered, providing flexibility for CO_2 plume tracking requirements, adopting a risk-based approach for the post-closure monitoring period, subdividing the area of review into two regions (one for the CO_2 plume and one for the pressure buildup), and developing an approach for defining the area of review for naturally over-pressured storage reservoirs. These issues are discussed in more detail in Chapter 3.

3. Section 45Q Tax Reform and Clarification

The FUTURE Act passed as part of the 2018 budget appropriation provides a tax credit of \$50/tonne (by 2026) of CO_2 stored in a saline formation. The Section 45Q tax credit has the potential to dramatically increase deployment of CO_2 storage in the United States. However, several issues must be addressed, including: clarifying what is required to demonstrate “secure geologic storage;” establishing regulations for recapturing the credit if the CO_2 ceases to be properly captured, disposed of, or reused as a tertiary injectant; and providing developers with clarity, either through regulation or guidance, on what constitutes “beginning of construction.” Section 45Q is discussed in more detail in Chapter 3.

4. Access to Onshore Federal Lands

One of the hurdles for owners of stationary sources of CO_2 who want to implement commercial-scale geologic storage is securing a sufficiently large tract of land and associated subsurface pore space to develop a geologic storage site. Federal lands present a unique opportunity to achieve this due to single ownership of large, continuous acreage, a large portion of which contains formations with ample CO_2 storage capacity. The estimated CO_2 storage capacity beneath federal lands ranges between 126 and 375 Gt. New regulations and processes are needed to enable use of federal lands for CO_2 storage. These issues are also discussed further in Chapter 3.

B. Medium-Term Priorities for the Expansion Phase

1. R&D and Workforce Capacity

The expansion phase could enable an additional 75 to 85 Mtpa of CO_2 storage within the next 15 years. Research that addresses medium-term priorities will be needed to address the gaps in knowledge that emerge as the CCUS industry begins to grow. Continued advances in data science, machine learning, advanced sensing, and other innovations are likely to benefit CO_2 geologic storage. Research programs at universities will increase the workforce of engineers, geoscientists, and other disciplines with the level of technical expertise needed to support the increasing number of CO_2 storage projects and supporting infrastructure that will be developed during the 15 years of the Expansion Phase.

2. State Primacy

The EPA and, in some cases the states, have the permitting authority and oversight of the Class VI program. Approval of primary enforcement responsibility to the states is termed primacy. States either incorporate the federal standards by reference or develop their own state regulations for approval by rule through the EPA. There are many benefits to establishing state primacy, which includes aligning state objectives, improved coordination of the Class VI program, leveraging state experience, and establishing a business advantage. However, because there is minimal funding available from the EPA (as appropriated by Congress) for all state UIC programs, there is little funding incentive for states to take primacy for the Class VI program. It would be beneficial if funding was increased and used to develop a Class VI primacy application and program for commercial-scale projects. It would also be helpful if states had access to information about the benefits of receiving Class VI primacy, the process, and experience of states that have primacy for other well classes.

3. Pore Space Legal Rights

Before injecting CO_2 into the subsurface for geologic storage, the operator must own the pore space, have permission from the owner, or have the right to use the pore space. The laws concerning property rights are a basic concern of state law rather than federal law. Pore space ownership is rooted in the ad coelom doctrine where “the ownership of land may be divided horizontally, vertically or otherwise either above or below the ground.” The issue of pore space legal rights is complicated by the fact that for a large CO_2 storage project, the CO_2 plume may extend over hundreds of square miles, and the pressure buildup extends over an even larger area. For large projects, including those identified as CO_2 storage hubs where multiple property and pore space owners are likely to be involved in the process of acquiring pore spaces rights, resolving issues related to property rights and competing uses of the subsurface could have a large impact on the commercial viability of CO_2 storage. It is recommended that federal and state governments coordinate to establish a process for permitting the access and use of pore space for geologic storage projects on privately owned lands.

C. Long-Term Priorities for the At-Scale Phase

1. Access to Conventional Offshore Formations

The at-scale phase increases total U.S. storage capacity from CCUS to approximately 500 Mtpa within the next 25 years. This level of storage would require access to conventional offshore formation. The OCS includes submerged lands under the jurisdiction of the federal government and coastal states. Some of the benefits of offshore CO_2 storage include the fact that it is managed by state and federal entities rather than private landowners. There is also extensive oil and natural gas experience in the Gulf of Mexico that is transferable to CO_2 storage, and existing oil and natural gas infrastructure could be repurposed for CO_2 storage. Offshore storage also puts few or no USDWs at risk, and pressure management of the formation by extracting brine is likely easier. Finally, geologic and geophysical surveying for monitoring offshore storage may be subject to fewer impediments due to the lack of numerous structures and landowners. Offshore storage could be enabled by requirements for monitoring for the life of the project but designed in a manner that facilitates the ease of site closure after storage operations terminate.

2. Continued R&D and Workforce Capacity Development

Like the expansion phase, research that addresses the long-term priorities of the at-scale phase will be needed to address the gaps in knowledge that emerge as the CCUS industry continues to grow. Continued advances in data science, machine learning, advanced sensing, and other innovations are likely to benefit CO_2 geologic storage. Research programs at universities will increase the workforce of engineers, geoscientists, and other disciplines with the level of technical expertise needed to support the increasing number of CO_2 storage projects and supporting infrastructure that will be developed during the 25 years of the at-scale phase.

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Chapter Eight

CO_2 ENHANCED OIL RECOVERY

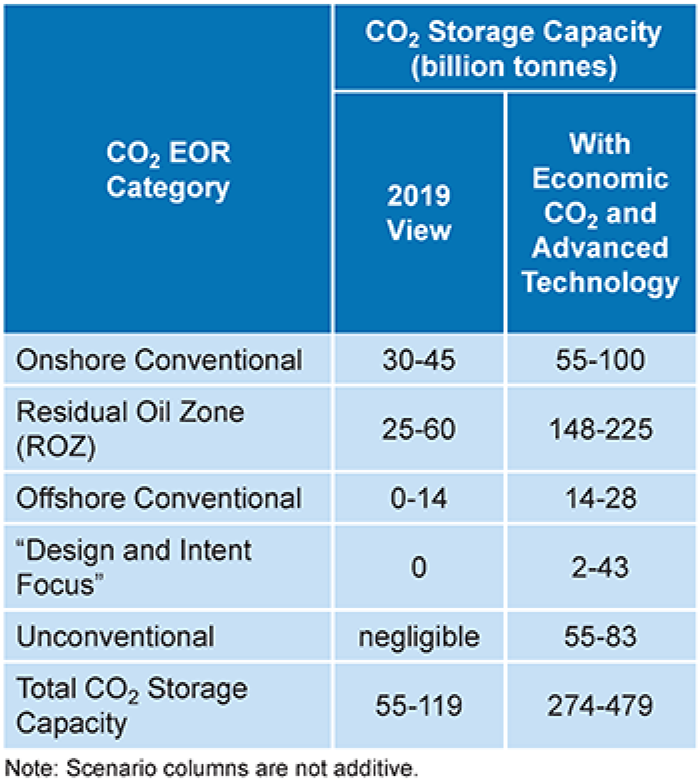
I. CHAPTER SUMMARY

Carbon dioxide enhanced oil recovery (CO_2 EOR) involves the injection of CO_2 into the reservoir rock of an existing oil field to recover more oil and natural gas than would otherwise have been produced. The injected CO_2 trades places with oil that is released from minute pore spaces within the reservoir rock. This exchange results in the CO_2 becoming trapped by capillary pressure within this same pore space, dissolving in the residual fluids present in the pore space, or eventually becoming mineralized. The trapping of CO_2 during the EOR process is incidental to the primary purpose of producing oil.

CO_2 EOR is a mature and regulated technology that has been applied for more than 40 years. The process benefits the environment when CO_2 from industrial sources—called anthropogenic CO_2—is captured, injected, and trapped underground, thereby reducing greenhouse gas emissions by providing large-scale CO_2 storage.

Enhanced oil recovery from existing fields requires fewer resources than its alternative, which is to install infrastructure and equipment to develop new oil field locations. Studies estimate that oil produced from existing fields using CO_2 EOR with anthropogenic CO_2 has 63% fewer emissions than oil produced without CO_2 EOR.[1] The CO_2 EOR process yields liquid fuels with a lower carbon emissions intensity, maximizes the efficient use of existing infrastructure, and reduces land and habitat disturbance.

The U.S. CO_2 storage capacity generated by EOR processes is estimated at 55 billion tonnes (Bt) to 119 Bt under “2019 View” in Table 8-1. Accessing this storage capacity could help produce 84 billion to 181 billion barrels of stranded oil. In 2018, CO_2 EOR used more than 30 million tonnes of natural CO_2 from underground deposits, which could be replaced with anthropogenic CO_2 if a pipeline infrastructure to transport it were available. A pipeline system is also needed to enable widespread deployment of CO_2 EOR for carbon capture, use, and storage (CCUS) projects that are included in the activation, expansion and at-scale phases described by the cost curve in Chapter 2, “CCUS Supply Chains and Economics,” in Volume II of this report. This pipeline infrastructure system will involve many stakeholders and requires government incentives for support and construction.



CO_2 EOR Category	CO_2 Storage Capacity (billion tonnes)	
	2019 View	With Economic CO_2 and Advanced Technology
Onshore Conventional	30-45	55-100
Residual Oil Zone (ROZ)	25-60	148-225
Offshore Conventional	0-14	14-28
"Design and Intent Focus"	0	2-43
Unconventional	negligible	55-83
Total CO_2 Storage Capacity	55-119	274-479

Note: Scenario columns are not additive.

Table 8-1. *Estimated CO_2 Storage Capacity in the United States Associated with CO_2 EOR*

Table 8-1 estimates the CO_2 storage capacity in the United States both for prevailing conditions (2019 View) and when economic CO_2 and advanced technology are available. With these factors considered, it is estimated that total CO_2 storage capacity in the United States could expand to between 274 Bt and 479 Bt. In the short-to-medium term, it is expected that CO_2 EOR could store between about 150 and 200 million tonnes per year. The storage capacity is widely distributed across the United States.

Historically, the retention of CO_2 during the EOR process has been incidental to the primary purpose of producing oil and is commonly referred to as associated CO_2 storage.[2]

The amount of CO_2 that is stored in underground reservoirs during CO_2 EOR is specific to each oil field. This volume can be quantified and verified using either the Monitoring, Reporting, and Verification Plan from the U.S. Environmental Protection Agency (EPA), or other accepted standards combined with independently accredited verification.

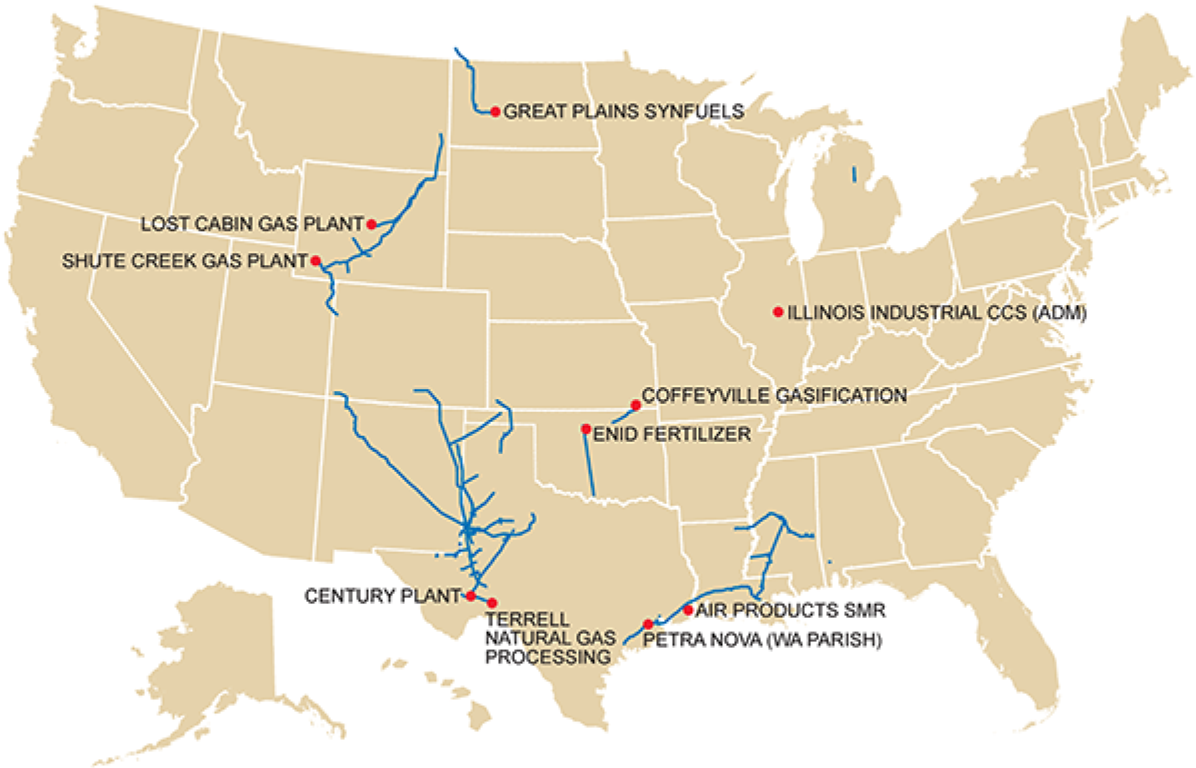
There are more than 150 individual CO_2 EOR projects around the world that use either anthropogenic CO_2 or natural CO_2 from underground deposits. The primary factor that limits growth in the number of CO_2 EOR projects is the locally available and affordable CO_2 that can be delivered at a price below which CO_2 EOR projects can be economically financed. In 2018, Congress expanded and reformed the 45Q tax credit which has encouraged some U.S. companies to actively pursue the development of projects that will capture CO_2 from industrial sources for use in EOR.

During the CO_2 EOR process, 40% to 60% by volume of the injected CO_2 is produced with the oil, then recycled and reinjected back into the reservoir. This closed-loop process means that, at the end of the injection period, nearly all of the injected CO_2 is retained in the reservoir and less than 1% of the originally injected volume is lost to fugitive emissions and operational losses.[3]

During the injection process, brine water is commonly alternated with CO_2 in a process called water alternating gas (WAG), which minimizes the amount of CO_2 needed and enables the injected CO_2 to contact more of the reservoir area. Methods using foam or gel to thicken the injected CO_2 are also beneficial to oil recovery and increase the amount of CO_2 that is sequestered during the CO_2 EOR process. However, because these additives are expensive, they are rarely used.

Even when existing oil field infrastructure is in place, the incremental cost of developing a large CO_2 EOR project can be substantial. Such projects can be economically challenged because the increase in oil production may occur a year or more after initial CO_2 injection. This causes a delay in positive cash flow. In addition, large anthropogenic CO_2 sources are often hundreds of miles away from the oil and natural gas reservoirs that would benefit from CO_2 EOR. Reservoirs that can store CO_2 are called sinks, and the cost of transporting CO_2 from a source to a sink is a primary factor in deciding whether CO_2 EOR would be economical.

CO_2 can be transported over land by pipeline, rail, or truck. Pipeline transport is the preferred method of moving large volumes of CO_2 without interruptions. In certain areas of the United States, the CO_2 EOR industry has already installed local pipeline networks to move CO_2 from source fields to EOR projects (Figure 8-1). However, a larger superhighway-like CO_2 pipeline system is necessary to transport large volumes of anthropogenic CO_2 from sources to sinks. Incentives for pipeline infrastructure construction and tax credits, such as the Section 45Q tax incentive, would help ensure that investments in CCUS provide a sustained return on investment.



Source: Melzer Consulting.

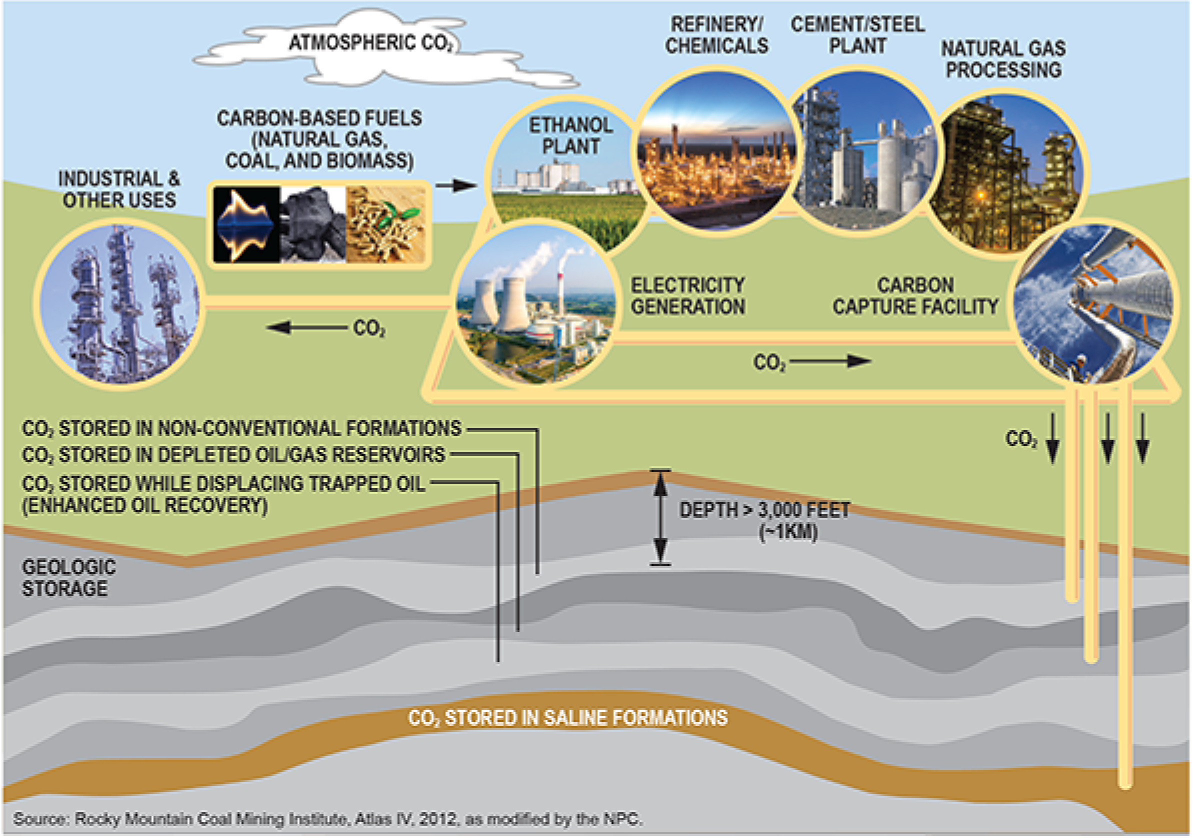
Figure 8-1. *Active U.S. CO_2 EOR Infrastructure and Projects*

The petroleum industry has considerable expertise in siting and operating CO_2 EOR projects in an environmentally responsible manner. CO_2 EOR has an excellent safety and environmental record. Leveraging CO_2 EOR industry experts for the development of more CO_2 storage sites is a logical choice for managing CO_2 emission reductions in a proven, safe, and environmentally sound way.

II. WHAT IS CO_2 EOR?

A. Understanding the EOR Process

CCUS, including transport, combines processes and technologies to reduce the level of CO_2 emitted to the atmosphere or remove CO_2 from the air. These technologies work together to capture (separate and purify) CO_2 from stationary sources so that it can be compressed and transported to a suitable location where the CO_2 is converted into useable products or injected deep underground for safe, secure, and permanent storage. Figure 8-2 is a schematic showing the CCUS technologies.



Source: Rocky Mountain Coal Mining Institute, Atlas IV, 2012, as modified by the NPC.

Figure 8-2. *Supply Chain for Carbon Capture, Use, and Storage*

The CO_2 EOR process involves pumping CO_2 into reservoir rock where it trades places with the oil that is trapped in the minute pore spaces of the underground rock formation. This exchange releases oil but traps the injected CO_2 within the same pore space.

The trapping of CO_2 during the EOR process is incidental to the primary purpose of producing oil. For this reason, the result is often referred to as “incidental, or associated CO_2 storage,” when long-term retention of the trapped CO_2 is verified. The text box titled “Certifying Secure Geologic Storage of CO_2 through EOR” provides an explanation of how CO_2 that is geologically trapped during CO_2 EOR is certified as being securely stored over the long-term.

CERTIFYING SECURE GEOLOGIC STORAGE OF CO_2 THROUGH EOR

CO_2 Geologically Trapped during CO_2 EOR Operations

Several natural forces cause CO_2 to be trapped in the reservoir during CO_2 EOR operations, including:

- A competent geologic seal to trap free CO_2
- Trapping in the pore space due to capillary pressure effects
- Dissolution in formation water that will not move to a shallower formation and come out of solution
- Mineralization (not a major factor except in the very long term).

Within this report, it is referred to as "trapped" or "retained" CO_2. Other reports may refer to this as "associated trapping," "associated storage," "geologic storage," or "incidental storage."

Certified Secure Geologic Storage

Geologically trapped CO_2 can be certified as being securely stored after an approved process is followed to determine that retention is demonstrated to be long term. Examples include the U.S. Environmental Protection Agency's Monitoring, Reporting and Verification Plan (MRV Plan) or any other approved and accepted standard. In this report, such storage is referred to as “secure geologic storage,” “associated storage, when long term retention is verified,” or “permanent storage.” Other reports may also refer to this as “sequestration” or “permanent sequestration.”

During the last 40 years, CO_2 EOR operations in the United States have injected more than 1 Bt of CO_2, and experience has shown that more than 99% of the CO_2 remains safely trapped underground after CO_2 injection is completed.[4]

All oil and gas wells produce a mixture of oil, natural gas, and brine fluids. During CO_2 EOR operations, some wells are dedicated to CO_2 injection and others to fluid production. In the producer wells, a portion of the CO_2 injected underground is produced back with the oil, natural gas, and brine mixture. The produced CO_2 is separated from the rest of the mixture in a closed-loop system and recycled back underground via reinjection (Figure 8-3). The brine produced is also separated from the oil and returned to an underground reservoir.

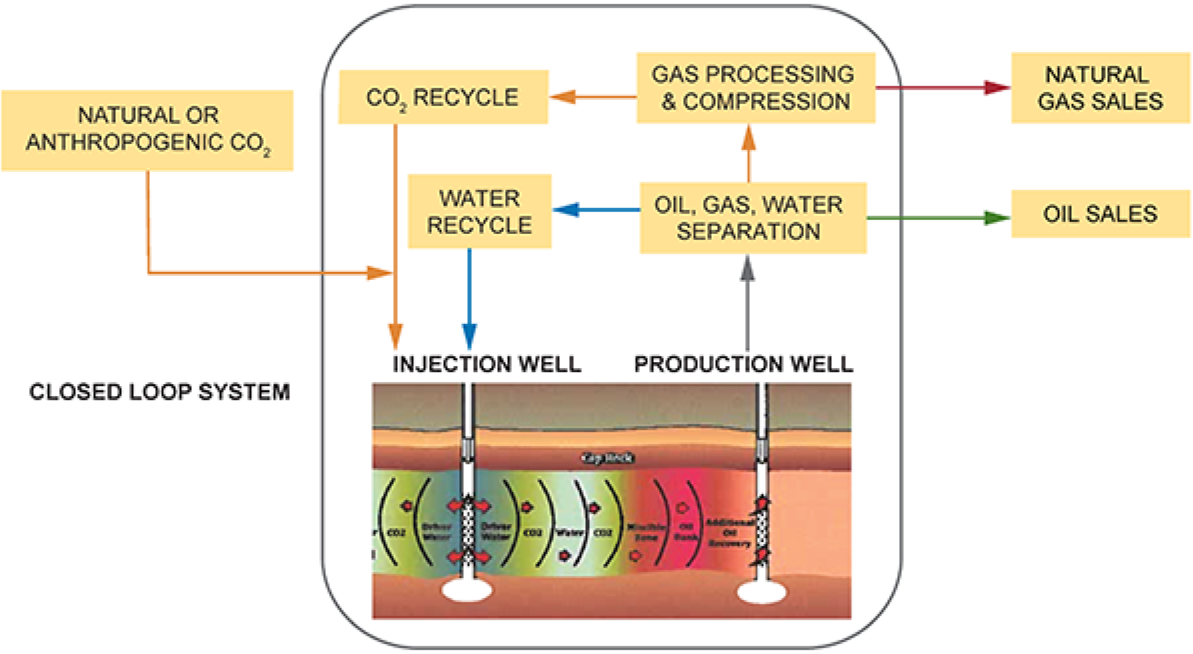


Figure 8-3. *Typical Flow Diagram for CO_2 EOR*

When describing the CO_2 EOR process, the amount of CO_2 trapped to produce a barrel of oil is called the CO_2 utilization factor (UF). The CO_2 UF number varies according to the specific geology, fluid characteristics, and design of each EOR project. The term is also used to determine the total amount of CO_2 that each field can store during EOR.

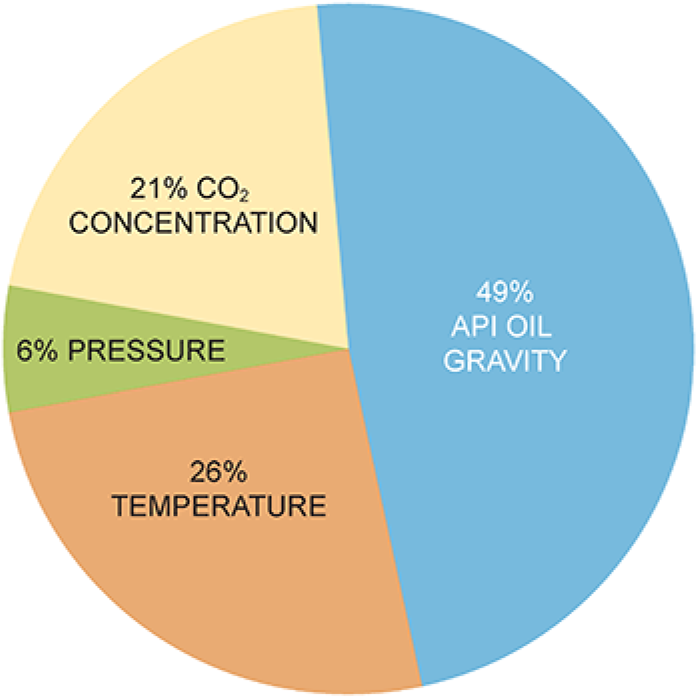
Most people understand that oil and water do not mix, but that honey and water will mix. Miscibility is a measure of how well two liquids will mix or dissolve together; if they will not mix, they are termed immiscible. CO_2 and oil can be miscible or immiscible depending on the pressure, temperature, and chemical makeup of the oil.

During the extraction of oil and natural gas, a reservoir's permeability describes how easily a fluid will flow through the rock. Permeability is measured in units called darcies or millidarcies. A higher permeability value means that fluid will flow through the rock more easily. In a reservoir, hydrocarbon pore volume (HCPV) is the fraction of the pore space, or void space, in the rock that contains oil or natural gas. To access the oil and natural gas in a reservoir, pipe is cemented into the well after it is drilled; this pipe is called “casing.”

B. How CO_2 EOR Works

CO_2 EOR is a process where CO_2 is injected into oil fields to enhance the recovery of oil from underground petroleum deposits. The injected CO_2 acts as a solvent to swell the volume of oil that sits in the reservoir’s pore spaces. The swelling of the oil lowers its viscosity, which in turn enables the oil to flow more easily toward the producing wells.

CO_2 is usually injected into the reservoir under pressure as a dense phase. Fluids in the dense phase have a viscosity like that of a gas, but a density closer to that of a liquid. Four primary factors impact how much oil will swell when it comes into contact with CO_2 (Figure 8-4).[5]



Source: Ahmadi et al., "Hybrid Connectionist Model Determines CO2-Oil Swelling Factor," *Petroleum Science*, April 2018.

Figure 8-4. *Relative Importance of theIndependent Variables Affecting Oil Swellingin the Presence of* CO_2

CO_2 can also extract the intermediate components of oil (i.e., organic compounds, hydrocarbons with different molecular weights) through repeated contact, which results in vaporization of the oil into lean gas. This is the basis for the vaporizing gas drive mechanism that achieves multiple-contact miscibility between CO_2 and oil. If the CO_2 is sufficiently enriched with these intermediate components during vaporization such that miscibility results with the oil, then the CO_2 and oil are said to have achieved multiple-contact miscibility. CO_2 EOR projects can be conducted under miscible or immiscible conditions, but miscible projects are more commercially viable, hence more common.

1. Miscible CO_2 EOR Process

Miscibility between CO_2 and oil is required if the CO_2 is to act as a solvent to efficiently enhance the recovery of oil from underground reservoirs. The minimum miscibility pressure (MMP) is the reservoir pressure above which CO_2 and oil combine into a single-phase fluid. Miscibility can occur at first contact between the two fluids. If conditions are not ideal for first-contact miscibility, the fluids may still achieve miscibility through multiple contacts, during which the CO_2 and oil mix into a CO_2-rich phase.

When the composition of gas and liquid phases become sufficiently alike, the interface between the two starts to disappear and lower interfacial tensions and miscibility occurs. The advantage of a miscible CO_2 process is that the oil's volume is increased through swelling and its viscosity is lowered, causing more oil to become mobile and travel to the producing wells.

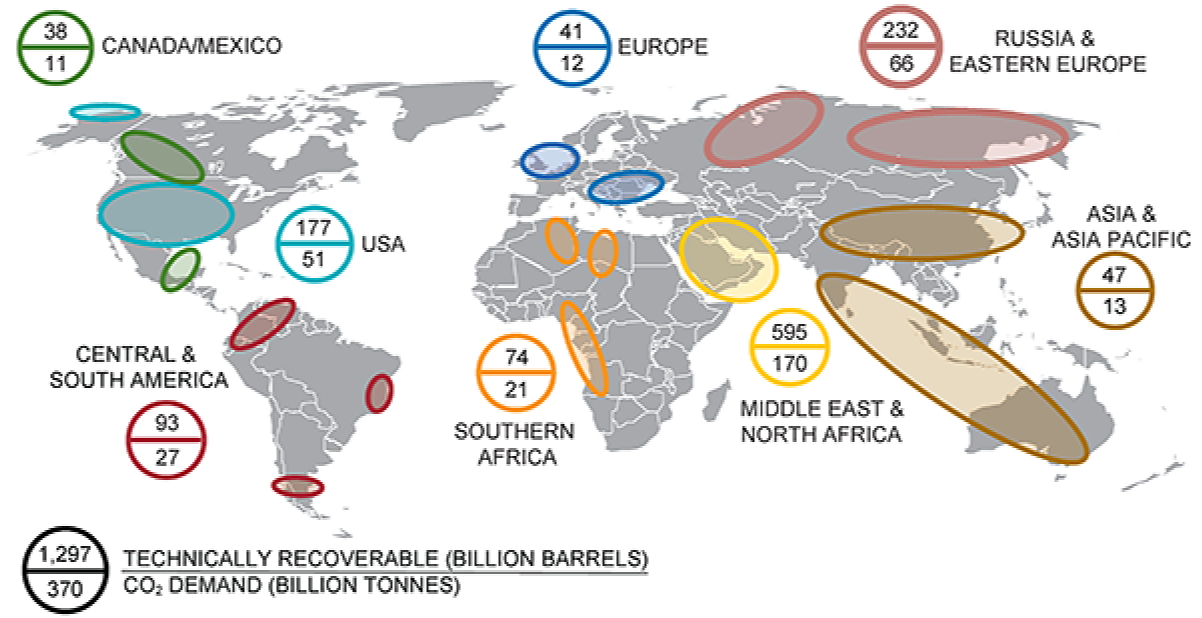
2. Immiscible CO_2 EOR Process

In some fields, the MMP is greater than the pressure at which the reservoir seal, or caprock, could be compromised, possibly causing a leakage path for CO_2 and the reservoir fluids. In these fields, an immiscible CO_2 EOR process occurs at operating pressures below the MMP, which prevents reservoir pressure from falling by replacing the produced oil, water, and natural gas with CO_2. The CO_2 vaporizes and swells the oil by lowering the surface tension, and although it does so to a lesser extent than in the miscible process, it still enhances oil flow.

Because the immiscible process is less effective in producing oil and leaves more residual oil in the reservoir than does a miscible CO_2 EOR process, there are very few immiscible CO_2 injection projects operating today. The immiscible process can be quite effective in recovering oil from what are called “tilted reservoirs.” These reservoirs result when the geologic formations have been tilted over time to high angles relative to the horizontal positions at which they were deposited millions of years ago. Tilted reservoirs often benefit from the application of gravity drainage recovery mechanisms, where oil flows downward toward production wells when a buoyant fluid, such as CO_2, is injected at the top of the oil column.

III. CO_2 EOR STORAGE CAPACITY AND DEPLOYMENT ENABLERS

Onshore and offshore in the United States, there is an estimated 414 billion barrels of remaining oil in place that would be left in-situ without application of tertiary recovery operations such as CO_2 EOR.[6] Of this volume, 177 billion barrels of oil is technically amenable to recovery through CO_2 EOR. This would require injecting 51 Bt of CO_2, though only a portion of this is economical to pursue presently (Figure 8-5).[7] The CO_2 volume requirement increases to 370 Bt to recover nearly 1.3 trillion barrels of oil worldwide, with the United States, Middle East, North Africa, Eastern Europe, and Russia containing most of the potential for CO_2 EOR and its associated storage volume.



Source: IEA Greenhouse Gas R&D Programme, "CO_2 Storage in Depleted Oilfields: Global Application Criteria for Carbon Dioxide Enhanced Oil Recovery," December 2009.

Figure 8-5. *Worldwide CO_2 EOR Potential in Conventional Fields*

For example, the San Andres carbonate reservoir of the Permian Basin (West Texas and eastern New Mexico) supports conventional CO_2 EOR and is one of the largest residual oil zone (ROZ) complexes in the United States. A ROZ is an interval of oil that remains in a hydrocarbon reservoir after natural water flooding has occurred over geologic time. (More detail about how a ROZ is created is provided in the Residual Oil Zone section later in this chapter). A combination of detailed geophysical log and numerical modeling work and several ROZ EOR development projects have estimated that 43 Bt of associated CO_2 storage could be achieved through the recovery of 69 billion barrels of oil in the San Andres reservoir alone.[8] If other geographical areas with potential storage are included, total ROZ storage capacity in the United States would be 148 Bt to 225 Bt of CO_2.

The potential production associated with CO_2 EOR in unconventional oil reservoirs, also called shale or tight reservoirs, could be substantial because average recovery in these types of reservoirs is less than 10% of the original oil in place when using primary methods. However, the industry is only just beginning to understand how the CO_2 EOR process can be used in these complicated reservoirs. Although continuous injection, pattern-based CO_2 EOR (i.e., where dedicated injector wells push fluids to dedicated producing wells) has been challenging in unconventional reservoirs, there has been some success with cyclic CO_2 injection operations (i.e., where injection and production take place in the same well(s) at different times). The application of EOR in unconventional reservoirs could recover nearly the same volume of oil as is achieved with primary recovery techniques.

In 2019, the U.S. Energy Information Administration estimated that there were 113 billion barrels (bbl) of technically recoverable oil in shale oil reservoirs within the United States.[9] This equates to approximately 110 billion barrels of EOR production potential. Assuming net CO_2 UFs of 0.5 to 0.75 tonnes of CO_2 per barrel of oil recovered (10 Mcf/bbl to 15 Mcf/bbl) are achieved, the resulting CO_2

demand could add an associated storage volume of 55 Bt to 83 Bt in the United States.

Table 8-1, found earlier in this chapter, provides estimates of CO_2 storage capacities for several reservoir categories in the United States associated with CO_2 EOR. The table presents estimates for two different scenarios: a “2019 View” and when “Economic CO_2 and Advanced Technology” are available.

The 2019 View lists the CO_2 volumes that can be stored using currently available technologies. In this scenario, the total CO_2 storage capacity is 55 Bt to 119 Bt. The 2019 View suggests a negligible storage contribution from CO_2 EOR projects in unconventional (or shale) reservoirs because most unconventional efforts presently are at the research and development or small pilot stage. Furthermore, the 2019 View assumes no additional CO_2 capacity will result from CO_2 EOR projects designed with an intent to maximize storage of CO_2.

In Table 8-1, the midpoint of CO_2 storage capacity for onshore conventional (37 Bt) and the high point for offshore conventional (14 Bt) total 51 Bt. This sum corresponds with the 51 Bt shown in the bottom half of the circle associated with the United States in Figure 8-5, denoting CO_2 demand in billion tonnes.

In the Economic CO_2 and Advanced Technology scenario, the assumption is that there will be technological advances and affordable anthropogenic CO_2 will become available. Under this scenario, the total associated storage capacities could potentially increase to four to five times the volumes described by the 2019 View. Although offshore storage from CO_2 EOR is not expected to increase substantially in the near term, offshore CO_2 storage could occur where oil reservoirs are connected to large saline formations (see Chapter 7, "CO_2 Geologic Storage").

Given access to more affordable CO_2 and technological advances, and assuming a CO_2 utilization factor of 20 Mcf/bbl, onshore conventional storage opportunities could increase by as much as 50%. This would significantly increase the storage capacity of ROZ reservoirs, doubling the use of this commercial resource. Incremental additions to capacity due to new storage designs could also improve storage estimates from 1% to 20%. Finally, the development of new technologies could have a positive impact on unconventional reservoirs, adding significant CO_2 demand and associated storage capacity, which could enable total CO_2 EOR-associated storage to grow in range to between 274 Bt and 479 Bt.

Transporting large volumes of anthropogenic CO_2 in the United States from sources to sinks requires substantial expansion of the CO_2 pipeline infrastructure that currently exists. Chapters 2 and 3 in Volume II present pathways and recommendations to progress development of interstate CO_2 pipeline infrastructure.

Expanding the application of CO_2 EOR in the United States can provide long-term storage of anthropogenic CO_2 that is less costly than many of the alternative CO_2 storage approaches, given the revenue that can be generated from incremental oil recovery, and leveraging of infrastructure that already exists in many locations.

The U.S. Internal Revenue Service (IRS) Section 45Q tax credit offers an incentive by which the economics of the CO_2 EOR process can be improved. The attributes of the Section 45Q tax credit are discussed in Chapter 3, “Policy, Regulatory, and Legal Enablers,” in Volume II of this report.

The IRS also offers an EOR tax credit under Section 43 of the Internal Revenue Code to help offset the high upfront capital cost associated with a CO_2 EOR project. The credit was put in place in 1991 to incentivize the deployment of new and significantly expanded EOR projects during periods of low oil prices. Unfortunately, the Section 43 tax credit has been ineffective given the low floor price required for companies to use the incentive. Chapter 3 also discusses the Section 43 tax credit.

IV. FACTORS THAT AFFECT THE CO_2 EOR PROCESS

CO_2 EOR includes many factors that interact to increase the amount of oil that can be recovered while incidentally trapping the CO_2 used in the process. All these factors are considered and managed during the design and operation of CO_2 EOR projects to achieve technological and economical success. Some of these factors are summarized in this section.

A. Subsurface Considerations

From a reservoir standpoint, most medium-to-light (>22 degrees API gravity)[10] oil-bearing geological formations with sufficient matrix porosity and permeability can be used for CO_2 EOR. However, many conditions must be met to achieve a commercially successful CO_2 EOR project.

Achieving MMP is almost always needed for CO_2 to be an effective EOR agent.[11] When existing fields are converted to CO_2 EOR, it is sometimes necessary to repressurize the reservoir to increase reservoir pressure to a point above the MMP.

Injectivity is a measure of how easily CO_2 and water can move from an injection well into the reservoir over a given period. It is a function of the reservoir's total thickness, permeability, and the reservoir pressure differential relative to injection pressure at the wellbore. It also depends on the viscosity of the fluid used for injection. Better injectivity means that oil can be recovered more quickly, thereby improving project economics.

Understanding the reservoir's geology can make the difference between economic success and failure. The formation rock properties are never completely uniform throughout the reservoir. Yet the closer a reservoir is to having uniformity in static properties and dynamic flow characteristics, the better the CO_2 EOR process will perform in the reservoir.

B. Typical CO_2 EOR Field Performance Parameters

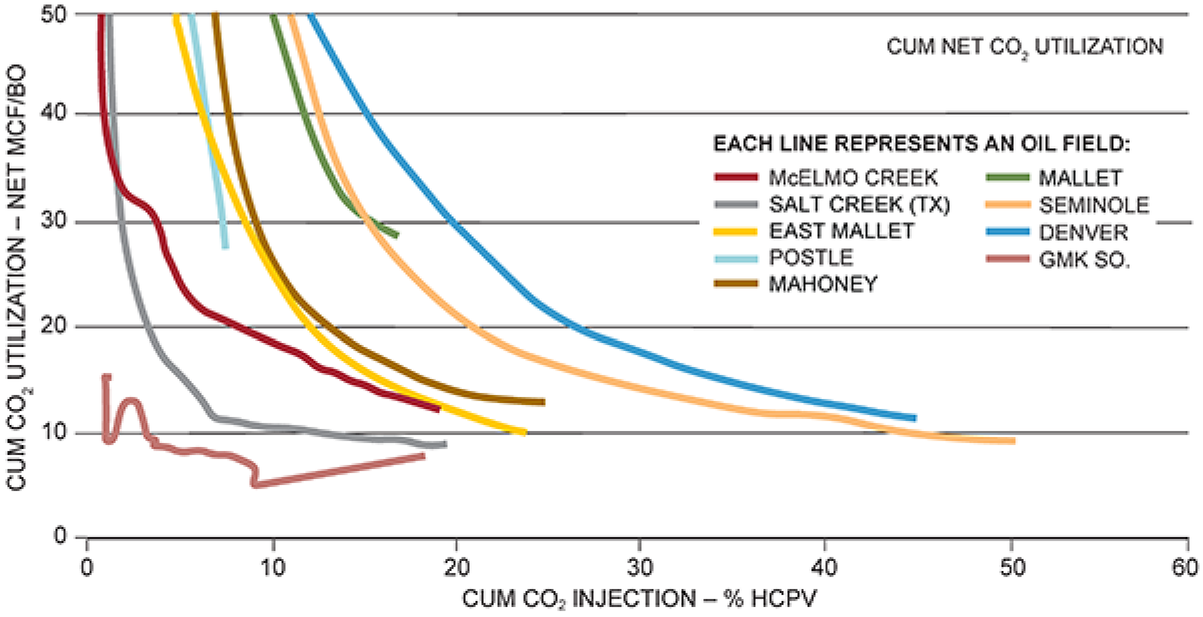
Several key factors control the success of CO_2 EOR projects. These include:

- Access to an affordable supply of CO_2
- The lateral sweep efficiency (within each pattern) of the project
- Whether the CO_2 is miscible at reservoir pressure
- The size of the target oil reservoir.

Lateral sweep efficiency describes the amount of the total reservoir area that is contacted (or swept) by CO_2. Using WAG in the process is one way to increase lateral sweep efficiency. Efforts to maximize the lateral sweep efficiency are undertaken for each pattern of a CO_2 EOR project. Patterns refer to the manner in which injection and production wells are situated in relation to each other. Two common pattern types are line drive, where there are alternating lines of injection wells and production wells drilled in the field, and five-spot, where an injection well is drilled at or near the middle of a box with producing wells drilled at each of the four corners.

Once the CO_2 EOR project is operating, several metrics are used to manage and measure its technical and commercial performance. Oil production and CO_2 injection volumes are commonly monitored using a normalization technique where both the oil and CO_2 volumes are divided by the development area’s original HCPV. Each of these volumes needs to be calculated using the densities of oil, water, and CO_2 at reservoir temperature and pressure. This enables comparison of one project’s performance with another project, as well as the performance of individual well patterns within a project to other patterns in the same project.

As previously stated, the amount of newly sourced CO_2 required to produce a barrel of oil is called the utilization factor and is usually measured in thousands of standard cubic feet of CO_2 per produced barrel of oil (Mscf/bbl). A typical UF for a mature project might be 15 Mscf/bbl. When the project starts, the UF is infinite because no oil production can yet be attributed to the CO_2 contacting the oil in the reservoir. The UF decreases as cumulative CO_2 injection as a percent of HCPV increases (Figure 8-6). The UF can be stated using the newly sourced volumes (net utilization) or total volumes (gross utilization) of CO_2. Total volumes include the amount of CO_2 that is recycled.



Note: Field Scale: Cum = cumulative, BO = barrels of oil under standard conditions.
Source: Melzer Consulting, personal communications.

Figure 8-6. *CO_2 EOR Project Performance Using Hydrocarbon Pore Volume (HCPV)*

C. Managing a CO_2 EOR Project

To optimize oil production while protecting reservoir integrity, injection pressure at the injection wellbore must be maintained below reservoir fracture pressure. During CO_2 EOR, injection and production volumes are managed to maintain the desired reservoir pressure and to prevent CO_2 migration outside the intended patterns and zone. To achieve this, the pressures at injection and production wells are monitored, and the CO_2 injection volumes and produced fluids are carefully metered.

Injection and production well profile logs are used as monitoring tools to confirm how the CO_2 is vertically distributed across the formation. Production data serve as an additional monitoring tool to identify when CO_2 arrives at producing wells.

Near the end of a CO_2 EOR project, when CO_2 injection is no longer economically viable, reservoir simulation models and field experience have shown that more oil can be recovered by injecting water after the final CO_2 injection cycle. This is called the chase water phase of CO_2 EOR. The volume of oil that can be recovered in this manner ranges from 1% to 6% of the original oil in place. During this chase water phase, the small volume of CO_2 dissolved in the oil that is recovered may be used in another CO_2 EOR project, or it can be sequestered using other means.

D. Associated CO_2 Storage Incidental to CO_2 EOR

Several natural forces inevitably cause CO_2 to be retained in the reservoir during the CO_2 EOR process. Some CO_2 remains in the pore space previously occupied by oil or water that has been produced, some is trapped by capillary forces as an immobile residual phase, some is dissolved in the formation water, and some is dissolved with the remaining residual hydrocarbons. A portion of the injected CO_2 is also produced along with the reservoir fluids.

This produced CO_2 is separated from other products in surface production facilities and recycled for reinjection into the reservoir. This closed-loop process results in all of the supplied CO_2 being retained in the reservoir by the end of the CO_2 injection period, with the exception of minimal fugitive emissions and operational losses that are typically less than 1% of the original injected volume.[12] The amount of CO_2 that a reservoir can permanently trap is about 40% to 50% of the original hydrocarbon pore volume.[13]

E. Safety Performance

CO_2 EOR has been safely practiced in the United States for more than 40 years in thousands of wells in fields across a broad range of geological settings. Safe CO_2 EOR operations begin with careful site selection to ensure that the geology is secure and will trap CO_2. Potential pathways for leakage of CO_2 during EOR operations are evaluated and addressed, and mitigated if necessary, during the site selection phase of CO_2 EOR.

1. Risks

Risks associated with CO_2 EOR include the possibility of CO_2 finding a leakage pathway either into the atmosphere or underground sources of drinking water. Wellbores are a potential leakage pathway in CO_2 EOR projects. The next section, Well Construction, provides an explanation of how wells are constructed, maintained, and monitored under the supervision of governing agencies (see the CO_2 EOR Oversight section) to ensure safe and secure operations. Any problems that develop or occur with wells can generally be quickly resolved or remediated.

The Gulf Coast Carbon Center at the Bureau of Economic Geology studied the SACROC CO_2 EOR project for evidence of groundwater contamination. That study concluded that the shallow drinking water over SACROC has not been impacted by CO_2 injection, providing a strong case study to the ability to safely sequester CO_2 in deep subsurface reservoirs via this process.[14]

Operational safety risks are naturally present in the compression and injection of the CO_2. These risks were examined in a 2009 study by researchers at the Bureau of Economic Geology; the study concluded "the CO_2 EOR industry has an excellent safety record."[15]

2. Induced Seismicity

Seismicity induced through human activity is a public concern. Seismic events induced by injection into oil fields are rare but have occurred when large volumes of fluid are injected into underground zones near or within fault zones and when there is little or no fluid withdrawal. These conditions can create a localized pressure increase and reduce friction at fault surface interfaces, which can induce seismicity. Induced seismicity is usually associated with fields that produce large volumes of salt water concurrent with hydrocarbon production and that dispose of that water by injecting it into saline formations near basement rock. Basement rock is the rock layer below which hydrocarbon reservoirs are not expected to be found and are usually older, deformed igneous or metamorphic rocks.

CO_2 EOR projects mitigate the risks of induced seismicity by balancing fluid injection and withdrawal volumes to maintain the target reservoir pressure so it stays below the reservoir fracture pressure. Simulation models help to quantify this target reservoir pressure.

Some seismicity has been associated with CO_2 EOR activity, but this is rare. At the Cogdell CO_2 EOR project in the Permian Basin of West Texas, seismic events with a Richter Scale (RS) magnitude of 4.4 or less were reported during a period of gas injection from 2006 to 2011.[16] Seismic events were also recorded at that location when the field was undergoing brine water injection from 1975 to 1982, before CO_2 EOR operations commenced. Adjacent fields undergoing CO_2 EOR along the same structural geologic trend, such as Kelley-Snyder and Salt Creek, did not incur any seismic events during CO_2 EOR operations.[17] It has been suggested that the seismic events noted during CO_2 injection at Cogdell were reactivations of induced fractures formed during the period of brine water injection in 1975-82, and that the sudden large increases in CO_2 injection rates may have been the cause of the subsequent seismic events during 2006-11. To resolve this problem, injection rates were reduced, and the induced seismic events stopped.

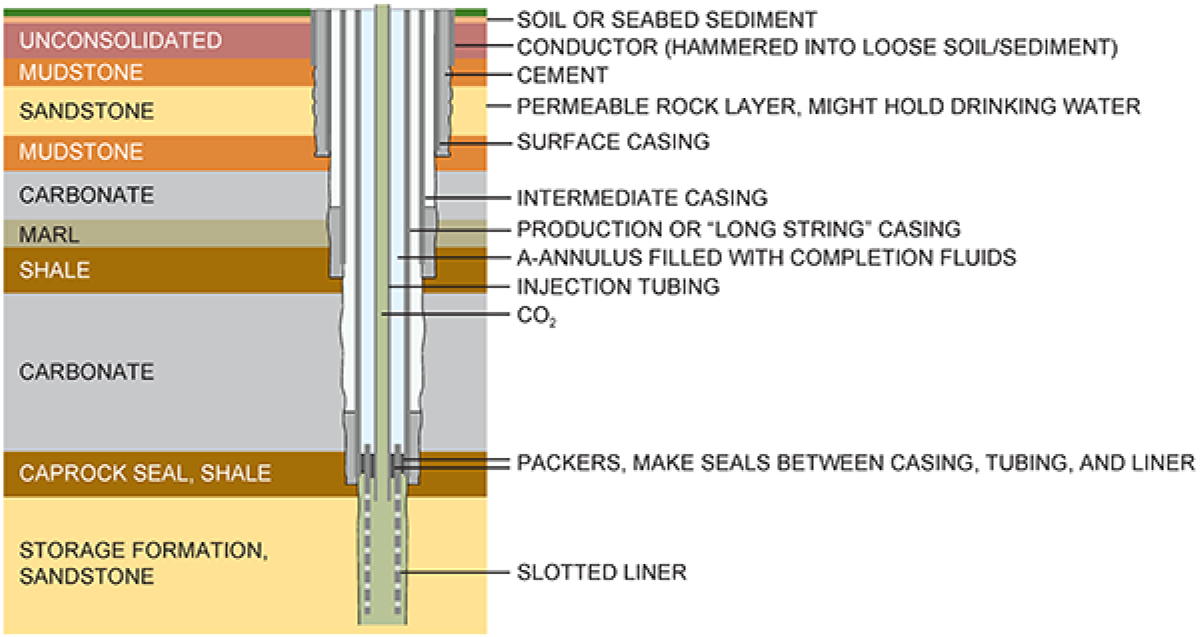
Seismic events typically must be above a RS magnitude 3 for humans to feel them. Significant events are normally associated with seismic magnitudes above 5 or 6. Microseismic events, on the other hand, are typically associated with RS magnitudes near 0. Microseismic monitoring of the CO_2 EOR project in the Aneth Field, Paradox Basin, Utah, for example, shows that induced seismicity is not observed when there is no buildup of pressure in the reservoir. It has been concluded that microseismicity is largely absent in this CO_2 EOR project possibly due to the minimal change in net volume, defined as total injected fluid volume minus total produced-fluid volume, and the common practice of CO_2 EOR implementation after brine water injection, which allowed for the strain energy along preexisting fractures to be released through pressure recovery and maintenance of the brine water injection project.[18]

In summary, seismicity induced by CO_2 EOR has a very low statistical probability of occurrence. When induced seismicity does occur, it has been proven that methods exist to effectively mitigate (halt) the circumstances that lead to the seismicity.

F. Well Construction

CO_2 EOR projects require U.S. EPA Underground Injection Control (UIC) Class II permitted injection wells. UIC Class II wells must meet certain construction requirements. Thirty-four states and four territories have been granted primary enforcement authority (primacy) by the EPA to issue these Class II permits under state equivalency requirements. Some of these states and territories have adopted additional rules. For example, federal UIC rules require an owner or operator to case and cement wells to prevent movement of fluid into or between underground sources of drinking water.[19] Texas Railroad Commission rules require that CO_2 projects isolate and seal off all productive zones, potential flow zones, and zones with corrosive formation fluids in all wells, including Class II wells, to prevent the vertical migration of fluids, including gases.[20] The California Division of Oil, Gas, and Geothermal Resources has a similar requirement when a well is stimulated.[21]

Sealing is accomplished by deploying concentric pieces of steel pipe (casing strings) that are cemented into place underground (Figure 8-7). These casing strings and other well construction requirements protect underground sources of drinking water and facilitate vertical containment to the target zone of injected CO_2. To produce a well, the casing is perforated at the depth interval where the oil reservoir is located. A smaller diameter steel pipe string (tubing) is then lowered into the well through the production casing string. Injection and production take place by pumping or allowing fluids to flow through the tubing strings in injection and production wells, respectively.



Source: Owain Tucker. (2018). *Carbon Capture and Storage*, IOP Publishing.

Figure 8-7. *Typical Wellbore Construction Using Concentric Pipe Strings Cemented in Placeto Provide Isolation Between Geologic Formations*

CO_2 EOR well construction cementing requirements have proven sufficient to maintain long-term well integrity. Where temperatures and pressures are relatively low, specialized casing and tubing may be employed in newly drilled wells to resist corrosion. In addition, active corrosion inhibitor programs are a standard practice to prevent corrosion damage to the injection tubing. For example, in 2006 a team of researchers at the Los Alamos National Laboratory recovered a core sample from the 30-year-old SACROC CO_2 EOR project to study long-term cement integrity in injector wells.[22] The sample included casing, cement, and the shale caprock. The study found that the cement had a permeability to air in the range of 0.1 millidarcy and thus had retained its capacity to provide isolation to fluid flow, including CO_2.

In the last decade, the use of horizontal wells has increased because of their ability to improve reservoir contact. These wells can be designed to access pockets of previously bypassed oil and to improve the sweep of oil toward existing production wells.

CO_2 EOR projects are usually conducted in oil fields that have already produced oil and contain large numbers of preexisting wells. Poorly plugged or damaged wells penetrating targeted formations could become pathways for injected CO_2 to leak into other formations or into the soil or the atmosphere. Care is taken before and during injection operations to prevent leakage. Before beginning a CO_2 EOR project, each well is reviewed to characterize its construction and remediate any identified issues. Well monitoring is also performed during operations to ensure that all well components continue to maintain integrity.[23]

G. CO_2 EOR Oversight

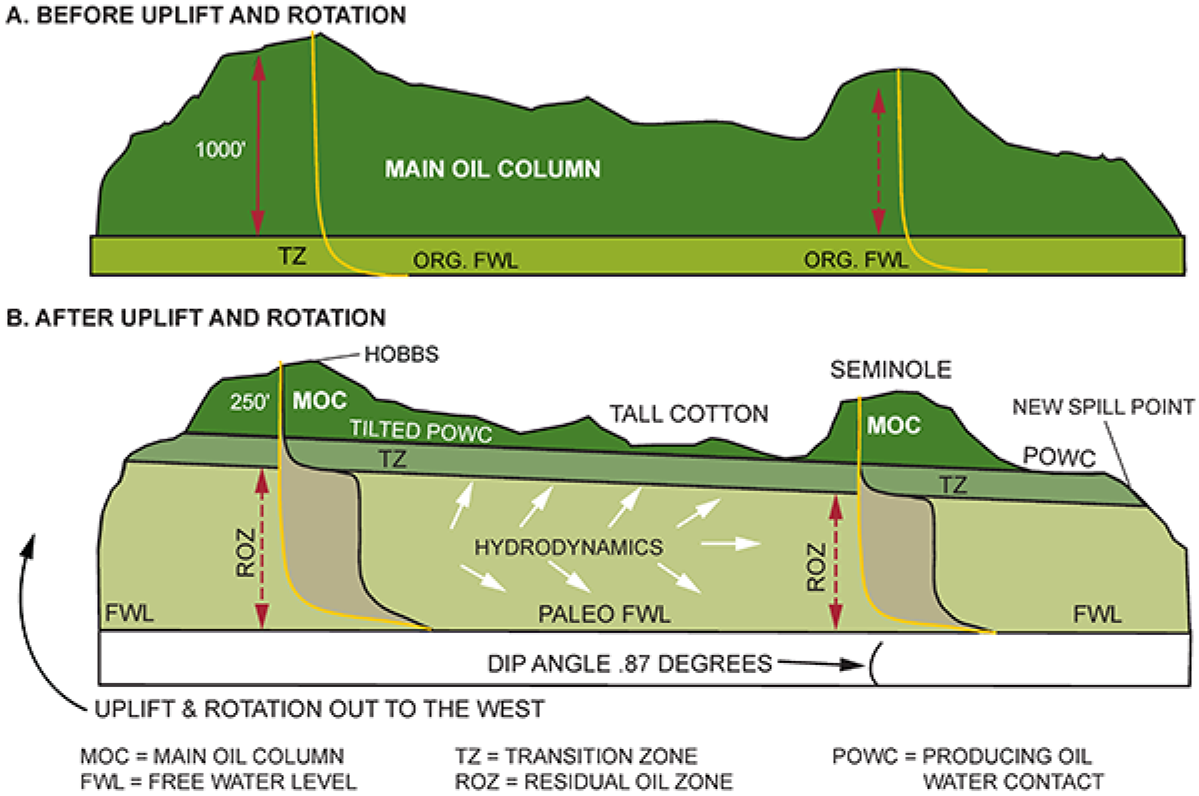
Carbon dioxide injection activities associated with enhanced oil recovery are regulated under Class II of the EPA's UIC program, and most of the oil and natural gas states have delegated primary enforcement authority, or primacy, over the activities which are also subject to federal oversight. Under this delegated authority, state regulations pertaining to CO_2 handling and injection are extensive. The UIC program and primacy are discussed further in Chapter 3.

Because groundwater is an important source of drinking water in the United States, the UIC program is designed to prevent potential contamination of underground sources of drinking water as a result of the operation of injection wells. States that have primacy must either meet the EPA's strict construction and conversion standards and regular testing and inspection requirements, or demonstrate that their program is effective in preventing endangerment of underground sources of drinking water while including requirements for permitting, inspections, monitoring, record-keeping, and reporting. Although the UIC program's focus is drinking water, compliance with UIC Class II requirements also ensures that properly designed and installed injection wells will prevent vertical movement of CO_2 through well casings, thus confining injected CO_2 to the intended target zones.

H. Residual Oil Zone

A residual oil zone is a remnant interval of oil that remains in a hydrocarbon reservoir after natural water flooding that occurs over geologic time. A ROZ is created when an oil reservoir is modified due to uplift, faulting, hydrodynamics, insufficient seal capacity, tilting, or a combination of these, resulting in previously mobile oil being displaced by encroaching water.

For example, Figure 8-8 shows how a ROZ formed from uplift due to compressional tectonics to the west of the Permian Basin during the Laramide Orogeny, between 80 million and 35 million years ago, exposing large reservoir outcrops at the surface. Part A shows the formation after oil seeped into it from a source rock and became trapped in a large main oil column. In Part B, note the tilted producing oil-water contact and original main oil column (MOC) in the structural highs after uplift and rotation have occurred. Also, note in Part B, the ROZ resides between a transition zone below the MOC and the free water level.[24] Uplift between A and B led to the migration of water down along the dip from west to east through the subsurface strata, displacing or flushing large volumes of trapped oil in the adjacent Grayburg, San Andres, and Clearfork oil reservoirs. This flushed zone in Part B is the ROZ. The result of this flushing process over geologic time yields a result that is very similar to a modern-day brine water injection project.



Source: Occidental internal communication (Jim Cooper, Technical Lead Petrophysics, Permian EOR); and "Enabling Large-scale CCS using Offshore CO_2 Utilization and Storage Infrastructure Developments," Carbon Sequestration Leadership Forum, November 2017.

Figure 8-8. *The Creation of a Residual Oil Zone After Tilting and Hydrodynamic Sweep*

CO_2 EOR functions the same when applied in a ROZ as it does in the main oil column and transition zones of a given oil field or area. The CO_2 becomes miscible with any residual oil, causing the oil volume to swell and lowering its viscosity. This enables oil still trapped in a ROZ to become mobile and move to producing wells while the CO_2 trades places with the oil and is subsequently trapped in the reservoir.

CO_2 EOR is successfully being used to develop ROZs, in particular in the Permian Basin. However, using CO_2 EOR in a ROZ is not widely practiced due to the lack of large volumes of affordable CO_2 and because CO_2 EOR in higher oil saturation main oil columns is usually more economically attractive to recover. This suggests that more ROZs could become viable investment opportunities for CO_2 EOR when affordable CO_2 is made available.

I. Offshore

There are no offshore CO_2 EOR projects in the United States, although five CO_2 EOR pilot projects were conducted in the Gulf of Mexico during the 1980s. The first at-scale offshore CO_2 EOR project started at the Lula Field offshore Brazil in 2011 and is still active.[25] Downhole processes are similar for onshore and offshore CO_2 EOR settings. If offshore CO_2 EOR can be implemented economically in the United States, it will provide an untapped resource for producing additional oil and storing significant volumes of anthropogenic CO_2. The incremental challenges for offshore implementation compared with onshore projects may include the following:

- Offshore operations are conducted either from a surface-piercing structure or platform, or from subsea facilities tied back to a platform, all of which typically have higher development and operating costs than onshore facilities.
- Well patterns for producing reservoirs differ significantly between onshore and offshore projects. This is due to the higher well densities typically associated with onshore developments relative to offshore, and the common requirement for special drilling or well spacing considerations offshore. Offshore wells tend to be drilled

horizontally or at high angles from the vertical because they need to reach distant areas of the reservoir from a central platform. More widely spaced wells offshore leads to longer lag times between injection and production responses, and to less efficient reservoir sweep by the injected CO_2.

- The financial investment required to modify existing platforms, wells, and other installations for CO_2 EOR will be higher offshore than onshore, and lost revenue during the facility modification process can be a significant factor. Most existing platforms will not have been designed in anticipation of CO_2 EOR operations and there is limited space to accommodate the equipment required to maintain the closed-loop system used in CO_2 EOR.
- Operational maintenance is costlier offshore than onshore.
- In an offshore CO_2 EOR operation, CO_2 will be delivered by ship or offshore pipeline, which creates additional costs when compared with onshore operation. The CO_2 may be injected directly into the wells or temporarily stored in floating storage vessels, enabling a choice of injection strategies.

Despite these challenges, the advantageous aspects of offshore CO_2 EOR include the following:

- Offshore leases are owned by single (federal or state) licensing authorities, whereas onshore projects often require the cooperation of multiple leaseholders.
- Frequently larger field sizes offshore may offer significant potential for higher additional production from CO_2 EOR.

Data from international offshore CO_2 saline formation injection projects will be helpful in designing the transport and injection components of the facilities for offshore CO_2 EOR. There are at least 10 offshore CO_2 injection projects operating, under construction, or undergoing advanced study according to the Global CCS Institute.[26] Several injection facilities are operational in the Barents Sea, North Sea off the coasts of Norway and the Netherlands, and offshore Japan.

J. Unconventional Reservoirs

In 2017, oil production from unconventional shale reservoirs was nearly 5 million barrels per day, or about 50% of total U.S. production supply.[27] These reservoirs are under primary production, but their ultra-low permeabilities will result in primary recovery factors ranging from 3% to 10% of the original oil in place. This leaves a significant volume of hydrocarbons underground. Research efforts for improving oil recovery in unconventional reservoirs are being undertaken by universities, industry, and the Department of Energy. New research suggest that use of CO_2 could improve recovery factors by as much as 3% to 5% through the application of various primary and secondary EOR processes, such as CO_2 stimulation and CO_2 repressurization, respectively.

Unconventional reservoirs are very different from the conventional reservoirs typically used for CO_2 EOR. The primary difference is in reservoir permeability. Unconventional oil reservoirs often have permeability values in the nanodarcy range but conventional reservoirs have permeabilities in the millidarcy range. Because of these ultra-low permeabilities, unconventional oil reservoirs are often drilled in blocks of 80 acres and completed with horizontal wellbores of 1 to 3 miles in length, and requiring several hydraulic fracture treatments along the wellbore to unlock the oil. The combination of closely spaced horizontal wellbores and hydraulic fracturing creates injection conformance and lateral sweep efficiency challenges for continuous pattern-based CO_2 injection.

EOR models for conventional reservoirs do not describe well what happens in unconventional reservoirs. Instead of pushing fluids through the rock, as is the recovery mechanism for CO_2 EOR in conventional reservoirs, in unconventional reservoirs the injected CO_2 engages with the oil in rock local to the injection well, liberating it so that it can be produced back with the CO_2 via the injection will itself, now functioning as a producing well. In the lab, attempting to push oil through a tight formation core does not work, but when a shale sample is left to soak in gas or surfactant, oil can be produced. This has resulted in the industry’s testing of cyclic, or “huff-n-puff,” EOR methods for unconventional reservoirs where injection and production occur using the same well.

One major review assessed the status of unconventional (tight oil) activity for five major producing basins.[28] The review identified the major challenges and gaps to be addressed by research and development that could lead to more efficient recovery of tight oil using EOR, which included:

- Rigorously characterizing and defining the natural and induced fracture systems in unconventional oil formations

- Establishing CO_2 injectivity and its entry into the unconventional oil reservoir’s matrix
- Establishing the relative importance of unconventional oil EOR mechanisms
- Achieving increased reservoir conformance by the injected EOR fluid
- Defining reservoir conditions and well completion methods favorable for EOR in unconventional reservoirs
- Achieving pattern-based CO_2 EOR in unconventional reservoirs
- Addressing the unique challenges of conducting EOR in low-permeability unconventional oil sands
- Improving EOR monitoring and diagnostic technologies and practices for unconventional oil
- Conducting fully integrated laboratory research, reservoir modeling, and pilot EOR projects in each tight oil basin or formation.

Research from entities such as the National Energy Technology Laboratory (NETL) is needed to develop methods that may result in commercial CO_2 EOR opportunities in unconventional reservoirs. This research should start soon so that the results can be put into use within 5 to 10 years. A specific R&D investment recommendation is quantified in the Research and Development Needs section of this chapter as well as in Chapter 3.

V. COMMERCIAL EXPERIENCE AND PERFORMANCE

CO_2 EOR has proven to be technically and economically viable in a variety of fields in the United States and abroad. The tools and knowledge to select reservoirs for CO_2 EOR and to design successful projects are well established. Examples of these are shown in Appendix G of this report, "CO_2 EOR Case Studies," where case studies of the Denver Unit in the Permian Basin of West Texas, the Bell Creek Field in the Powder River Basin of Montana, and the Northern Niagaran Pinnacle Reef Trend in the Michigan Basin of Michigan are highlighted.

These examples show that CO_2 EOR has been applied in diverse reservoir types in the United States with successful and predictable results. The case studies also show that although every CO_2 EOR project is different, the basic principles of geologic characterization, well and facility construction, and monitoring and management have been successfully applied for each project. The result is that more oil is produced out of existing fields while the CO_2 used in the process is subsequently trapped underground. The oil produced from CO_2 EOR has 63% lower carbon emissions intensity than oil produced by other methods.

A. Infrastructure Needs for CO_2 EOR

CO_2 EOR projects require infrastructure to handle the injection, production, separation, and recycling of CO_2 in a closed-loop system. This infrastructure includes equipment within the oil field and outside the field. Infrastructure outside the field is commonly shared among several CO_2 EOR projects, creating economies of scale.

1. Within the Field

The addition of new facilities and equipment within the field is needed when developing CO_2 EOR projects. Figure 8-9 presents a simplified schematic that shows the key components and stages of a CO_2 EOR operation. This infrastructure is used to receive CO_2 that is delivered to the field and to distribute it to the injection wells located throughout the field. On the production side, well testing and fluids separation equipment, often located at centralized processing facilities called central tank batteries, must be modified to accept the gaseous CO_2 that is produced, then to recompress the CO_2 so that it may be reinjected in the closed-loop process.

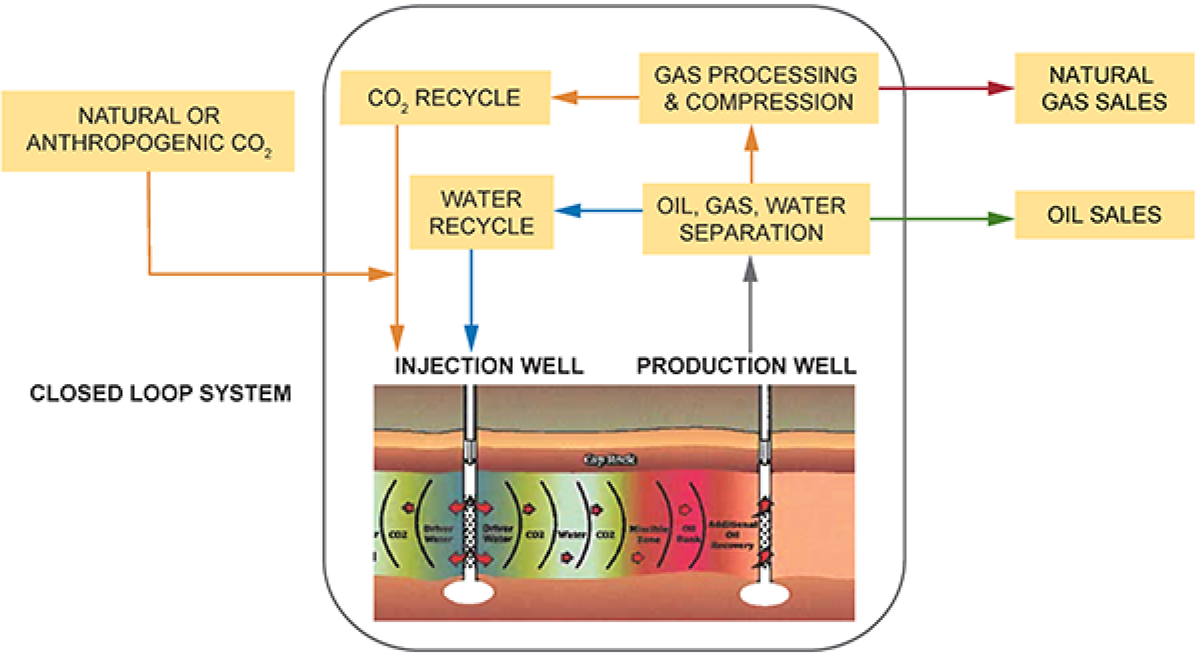


Figure 8-9. *Typical Flow Diagram for CO_2 EOR*

The key specific equipment needed for CO_2 EOR are:

- Injection manifolds capable of accommodating a WAG process.
- Injection well instrumentation and metering capable of measuring the two separate fluids associated with WAG injection—water and dense phase CO_2—each with different volumetric properties.
- Producing well instrumentation and metering to measure the amount of gas, oil, and water of each producer well.
- Produced-fluid handling systems, including a remote well testing facility (satellite) and a central tank battery designed to separate oil, water, and gas streams and that can accommodate high concentrations of CO_2. Before entering the high-pressure, three-phase separator, the EOR fluid production mixture is typically treated with demulsifiers, scale inhibitors, and corrosion inhibitors to aid the fluids separation process and protect the process equipment.
- Reinjection Compression Plant (RCP) for produced gas from the high-pressure three-phase separator (that contains CO_2 and hydrocarbon gas) to compress the mixture for transmission to a gas recovery plant where CO_2 will be separated from hydrocarbon gases for recycling. The CO_2 content in the gas stream impacts compressor operation and requires careful monitoring and adjustments. Sensors may be located upstream of this compressor to quantify the amount of CO_2 being produced.
- CO_2 recovery plant capable of separating out a pure CO_2 stream from the produced gas for recompression and

reinjection, and the collection of natural gas liquids for sale. There are several CO_2 separation options available (chemical solvents, physical solvents, membranes, cryogenic processes, etc.) depending on the nature of the produced gas, the throughput rate, and other factors. Each has advantages and disadvantages, and sometimes a combination of these is required.[29] An alternative to building a CO_2 recovery plant is to reinject the produced gas stream using the RCP, which is only viable if the gas composition would not adversely affect the MMP.

- High-volume artificial lift systems capable of handling high volumes of liquid before gas breakthrough in the reservoir and CO_2 in the produced gas after breakthrough. One option is to use compressed, recycled CO_2 as a gas lift fluid.[30]

An overview of facilities supporting the supply, distribution, and injection of the CO_2 for EOR follows.

a. Supply

CO_2 is generally supplied to CO_2 EOR projects via transmission pipelines. Volumes are measured through a custody transfer meter that enables CO_2 ownership to transfer from the CO_2 supplier to the CO_2 user (the field). The CO_2 is in dense phase and typically at a density above 35 lbs/cu ft. This higher density minimizes pressure drops in the supply pipeline and enables the use of centrifugal pumps (versus more costly compressors) to add pressure to the fluid en route to the user.

Often the supply pressure is in the 2,000 psig range and is sufficient to enable direct distribution to the wellheads through the distribution system discussed below. Typical supply specifications include 95% CO_2 purity with most of the non-CO_2 components being hydrocarbons and nitrogen. The water content specification is usually 30 lbs H_2O/MMscf to eliminate corrosion concerns from using internally bare carbon steel piping materials at the temperatures and pressures the supply system operates.[31] Oxygen concentration should generally be below 10 parts per million by volume to avoid conflicts with the reservoir.

b. Distribution

The CO_2 distribution system is generally the point where CO_2 supply pipeline regulatory requirements end and the field operations begin. The distribution system connects the CO_2 supply to the CO_2 injection wells. After the field begins to produce CO_2, the distribution system is where the produced, separated, and compressed CO_2 (recycled CO_2) is combined with the CO_2 supply stream. Generally, the CO_2 supply and recycle streams are combined before reaching the first injection well so that CO_2 injection composition and temperature are consistent across all wells at a given point in time.

c. Injection

The distribution system terminates at an injection well. Injection may be controlled by pressure or rate. Injection pressure is regulated to not exceed the maximum allowable surface injection pressure to ensure reservoir integrity is maintained regardless of control methodology. The injection well may also inject water if the system is designed for WAG.

d. Closed Loop

Some injected CO_2 is incidentally trapped on the first pass through the reservoir. Some is produced via the production wells where it is then recycled to be trapped on subsequent passes through the reservoir. The production wells produce hydrocarbon liquids and water, along with any returned CO_2 and hydrocarbon gas. On the surface, liquid components are separated from the gases, and the returned CO_2 is subsequently separated from hydrocarbon gases, thereby enabling the produced CO_2 to be reinjected (recycled). This represents a closed-loop system where all CO_2 is ultimately stored in the reservoir once long-term retention is verified.

2. Outside the Field

The proximity of neighboring fields with CO_2 EOR operations or potential will sometimes drive the siting of the RCP and CO_2 plant so that the facilities may be shared between several fields to take advantage of economies of scale. For isolated developments, the well test satellites, RCF, and CO_2 plant may be developed as a single complex. In certain areas of West Texas, for example, the population density of fields undergoing CO_2 EOR justifies the pipeline costs associated with gathering production from multiple fields and using shared RCP and a single CO_2 plant.

Facilities for new CO_2 EOR projects typically require several years to design and construct, be they sited inside or outside the field. There is also a relatively large investment made in the construction of these facilities. Once built and commissioned, these facilities can have a useful life of more than 20 years.

B. Economic Factors and Considerations

CO_2 EOR development costs are an important driver in the economics of CO_2 EOR projects. These costs are difficult to generalize since they are highly dependent upon the type, size, and location of the project being developed, and the depth of the play.[32] Costs can also vary considerably due to well configurations and whether or not existing wells and equipment can be repurposed for CO_2 EOR operations. Most CO_2 EOR plays have their own set of idiosyncrasies that can impact overall project economics in positive and negative ways.

There is, however, a broad set of costs that are common to most CO_2 EOR applications. These include:

- Cost of the supply of CO_2 for injection purposes
- Cost to drill a series of CO_2 injection wells, and/or converting selected producing wells to injection wells
- Cost to install surface facilities needed to separate, measure, recycle, and transport the CO_2 into the subsurface
- Cost of added compression
- Cost to provide additional surface equipment that is needed.

In addition, there are other economic factors that impact overall CO_2 EOR profitability, particularly those associated with financing these types of projects. Appendix H explores each of these factors and examines how the component costs vary and change CO_2 EOR project economics.

VI. OPTIMIZING CO_2 STORAGE IN CO_2 EOR

In general, contacting the maximum amount of oil-saturated reservoir rock with CO_2 will also result in maximization of the CO_2 trapped in the subsurface. However, in a business context where CO_2 supply can represent a substantial cost, CO_2 EOR operators often prefer to minimize CO_2 supply purchases, hence, to minimize net CO_2 utilization. Net CO_2 utilization is derived by dividing the amount of newly provided or acquired CO_2 in thousands of cubic feet by the barrels of oil production, both measured at standard conditions.

A consequence of this practice has been to leave a portion of the oil reservoir uncontacted by CO_2 due to the cost of contacting hard-to-reach areas. If cost were not an object, technologies such as CO_2 thickeners or CO_2 foams would be used more frequently to contact more of the oil-saturated reservoir area. These products make the fluid properties of CO_2 closer to those of the oil so that it will spread away from the injection wells and contact more of the in-situ rock volume, thereby resulting in the recovery of additional oil and the associated storage of additional CO_2.

When CO_2 EOR projects reach the post-CO_2 injection phase, it is common to continue injecting water during what is called the chase water phase. The primary purpose of chase water is to produce additional oil and recover any still-mobile CO_2 for use in another CO_2 project.

However, if the value of leaving the mobile CO_2 volume in the reservoir were higher than the value of recovering the injectant for use in subsequent projects, there would be an incentive to eliminate the chase water phase and to continue to inject CO_2. Additionally, produced CO_2 could be reinjected in lieu of the chase water. If the economics of the continuing production process were positive, the removal of additional oil and water from the reservoir would enable additional CO_2 to be injected and trapped.

Following are several alternatives to increasing the amount of CO_2 trapped during CO_2 EOR operations:

- Use geomodeling and reservoir engineering configured in a way to improve subsurface characterization. The WAG schedule can also be optimized to maximize CO_2 sequestration.
- Relax the gas oil ratio (GOR) constraints and/or EOR efficiency target. Most CO_2 EOR WAG projects have been designed with a tapering policy when reaching a high GOR or a low EOR efficiency because of the marginal added net present value, and thus a better CO_2 cost allocation. Increasing the CO_2 injection per pattern requires parallel optimization of infill well locations. Infill wells are new wells drilled to form the selected injection

pattern when installing a CO_2 EOR project in an existing field where the wells are in a different pattern.

- Revive and enhance methods for improving the mobility ratio between CO_2, water, and residual oil by using CO_2 foam, stabilizing foam agent (polymer, nanoparticles), CO_2 direct thickener, or polymer in water.
- Lower the oil miscibility pressure with CO_2 by incorporating additives (i.e., liquefied petroleum gas) to target heavier oils or de-gassed oil from primary recovery.

Any enhancements that would intentionally target increasing CO_2 trapping and that would not result in more efficient recovery of hydrocarbons at the same time, would have to be properly vetted to ensure that mineral estate and surface estate interests are taken into consideration.

VII. RESEARCH AND DEVELOPMENT NEEDS

The first CO_2 EOR projects implemented in the United States in the early 1970s operated with a combination of high CO_2 costs and low oil prices.[33] Because of the limited capability to monitor and control the subsurface movement of the injected CO_2, operators were encouraged to inject relatively small volumes of CO_2. Advances in monitoring and control techniques, and more readily available volumes of affordable CO_2, led to the injection of larger volumes of CO_2. These injected volumes are monitored and controlled to ensure that they contact, displace, and recover oil rather than simply circulating CO_2 through the reservoir’s higher permeability zones.

In addition to larger volumes of injected CO_2, the implementation of tapered WAG injection schemes has become common practice to better control CO_2 mobility, to improve conformance and sweep efficiency, and to avoid bypassing areas of the reservoir that contain residual oil. Tapered WAG is when the size of the water and/or CO_2 volumes in each successive cycle is changed in a tapered manner. These control measures, along with the application of more advanced well drilling and completions strategies to improve the contact of bypassed oil, have led to steady improvements in residual oil recovery efficiencies.[34]

Expanded application of CO_2 EOR in conventional reservoirs will most likely not result from the development of entirely new tools or technologies. Instead, it will be through the advancement of existing methods and their application to a larger number of reservoirs in basins with existing CO_2 EOR projects and in basins where CO_2 EOR has not yet been implemented.

Research is needed to develop methods that may result in commercial CO_2 EOR opportunities in unconventional reservoirs. More generally, R&D investment of $100 million per year is recommended, to be directed to better understanding CO_2 trapping mechanisms and magnitudes in unconventional and conventional CO_2 EOR reservoirs, as well as in nonconventional storage opportunities (basalts and coal seams).

Two particular CO_2 EOR technologies that would benefit from further research include vertical and horizontal conformance controls to maximize sweep efficiency, and advanced compositional modeling techniques to better predict and enhance performance.

A. Vertical and Horizontal Conformance Controls to Maximize Sweep Efficiency

Methods for improving sweep efficiency include the WAG process, the surfactant alternating gas (SAG) process, and the use of stabilized CO_2 foams created with surfactants.

Adding a surfactant to the injected water used in the WAG process helps to reduce the trapping of oil in small pores through wettability alteration (wettability is the ability of a liquid to maintain contact with a solid surface—in this case the formation rock). Application of SAG can improve recovery over WAG alone.[35] Gel-based polymer solutions that crosslink in-situ and preformed particle-gel dispersions are also used in the water injection stage of the WAG process to counter high-permeability flow paths.

The use of CO_2-water foam stabilized with soluble surfactants can increase CO_2 viscosity and improve the mobility ratio in a CO_2 EOR project, leading to improved sweep efficiency. There have been many successful laboratory-scale tests involving water-soluble surfactants capable of stabilizing CO_2-in-brine foams.[36] Thirteen reports of pilot tests conducted between 1984 and 1994 have been published, most of which were aimed at attaining conformance control, and five of which were considered successful technically. However, it appears that polymer and surfactant additives coupled with WAG have largely replaced the use of foams as a conformance-control technique, especially in extremely high-permeability flow paths where foams are generally ineffective. Recently, however, laboratory-scale testing of foam stabilization with water-dispersible nanoparticles has been carried out in an attempt to address surfactant-to-rock adsorption losses and chemical instability of the surfactant.[37] Additional research into the development of robust and cost-effective nanoparticle-stabilized CO_2 foams coupled with field testing is needed to help determine whether or not this option has potential for both conventional and unconventional reservoirs.

Another method that has been investigated involves the thickening of injected CO_2 using a variety of chemicals. Developing cost-effective, reliable thickening agents for CO_2 using polymers has been a challenge.[38] High molecular weight polymers only dissolve in CO_2 at pressures much higher than the MMP. Smaller molecule thickeners designed to form macro-molecular structures did not produce a significant viscosity increase. Research into this area would help to expand the already large storage capacity of CO_2 EOR.

B. Compositional Modeling Techniques for Unconventional Reservoirs

There are about 29 reservoir simulators available to better predict and enhance the performance of CO_2 EOR in unconventional reservoirs. Only a subset of these simulators is suitable for predicting performance of miscible EOR processes. Accurate modeling of miscible EOR processes using natural gas or CO_2 as an injectant requires a simulator that can represent the various physical processes underway. Compositional simulators predict the phase behavior of the fluids in the reservoir as well as the sweep behavior. This enables the prediction of incremental oil recovery and solvent utilization efficiency to optimize variables such as solvent composition, operating pressure, slug size, WAG ratio, injection-well placement, and injection rate.

A 3D compositional reservoir simulator calculates the flow of solvent, oil, and water phases in three dimensions as well as the flow of multiple components in the solvent and oil phases. It also computes the phase equilibrium of the oil and solvent phases (i.e., the equilibrium compositions and relative volumes of the solvent and oil phases) in each gridblock of the simulator. In addition, it computes solvent- and oil-phase densities.[39] The equilibrium compositions and densities are calculated with an equation of state. Using the calculated phase compositions and densities, the solvent and oil viscosity and other properties such as interfacial tension are estimated from correlations.[40]

The primary disadvantages of a compositional simulator are the degree of grid refinement often required to compute oil recovery accurately and the computing time required for fine-grid simulations. These factors generally preclude using a compositional simulator directly for full-field simulations unless a scaling-up technique is used to transfer the information developed from fine-grid reference-model simulations on a limited reservoir scale to coarse-grid simulations on the full-field model scale.

DOE has funded the development of a CO_2 EOR model that was designed to aid in accelerating CO_2 EOR technical studies for small-to mid-sized oil field operators within the United States. The objective was to develop a tool that includes a capability for addressing all the significant physical and chemical factors that impact the flow and recovery of reservoir fluids, yet make the simulation model building and evaluation process fast enough that an integrated feasibility study could be completed in a fairly short time period. The software integrates a user interface (COZView) for pre-and post-processing of simulation results with a 3D, 3-phase, 4-component reservoir simulator (COZSim) capable of modeling CO_2 EOR in oil reservoirs. The product enjoyed some use following its release in 2012 and has been used to perform screening studies and then incorporated into subsequent models.

There are opportunities for improving the use of compositional modeling for CO_2 EOR in unconventional reservoirs. These improvements include adding the ability to model adsorption and vaporization mechanisms to track oil movement in the reservoir, determining specific drive mechanisms by which oil makes its way to the producing wellbores, and the coupling of wellbore and subsurface modeling to predict conditions where condensate deposition in the wellbore would occur.

VIII. CONCLUSIONS

CO_2 EOR is a process that can trap significant volumes of CO_2 and help produce more crude oil from existing oil fields. This results in oil that may be produced with a lower carbon footprint than conventional oil. CO_2 EOR has increased oil recovery from existing fields for more than 40 years and traps the CO_2 that is used during a closed-loop CO_2 injection and recycle process. Once injected into a reservoir, CO_2 acts as a solvent to swell the volume of oil, lower its viscosity, and enhance its ability to move through a reservoir from injection wells toward production wells. It is a proven technique to maximize hydrocarbon recovery from new oil fields and extend the life of mature oil fields.

Industry and academia have developed a thorough understanding of how CO_2 interacts with hydrocarbons, gas, water, and reservoir rock to predict the extent of the CO_2 plume, ensuring safe and secure associated storage of CO_2 in EOR projects. The fraction of injected CO_2 that is produced can be compressed and recycled back into the reservoir using a closed-loop system such that nearly all of the CO_2 brought to the project is ultimately trapped in the reservoir.

The availability of affordable CO_2 from anthropogenic sources, combined with advances in the technologies used in CO_2 EOR, would significantly increase the associated CO_2 storage potential in the United States to a range between 274 Bt and 479 Bt. Much of this potential storage capacity is accessible now, and more can be made available with proper planning and with government assistance through tax credits and support for building a pipeline infrastructure system. The following list of actions would enable a wider scale deployment of CO_2 EOR in the United States.

A. Near Term (0 to 5 Years)

The share of oil production from CO_2 EOR projects in the global oil production mix is not high and is predominantly located in the midwestern United States. The economic model of CO_2 EOR is reservoir-and site-specific, and the pace of development is constrained by the amount of CO_2 that can be sourced affordably in close proximity to oil fields that are amenable to CO_2 EOR.

1. CO_2 EOR is an effective and safe CCUS process, but many of the anthropogenic sources of CO_2 are located far away from the regions where CO_2 EOR projects are currently operating and other areas where it is suitable for deployment. Work remains to develop pipeline infrastructure in the United States to move CO_2 from point sources, where capture technologies can be applied, to the geographic locations of oil-bearing formations where CO_2 EOR can be used to increase oil production and safely store the CO_2. More information about constructing CO_2 pipeline infrastructure can be found in Chapter 6, "CO_2 Transport."
2. The Internal Revenue Code Section 45Q tax credit was put in place to incentivize the capture and storage of anthropogenic CO_2. The Section 43 credit was intended to incentivize investment in EOR projects during periods of low oil price. The ways that both of these tax credits can be enhanced to enable more CO_2 EOR in the future are described in Chapter 3.
3. Unconventional reservoirs account for 50% of U.S. crude oil production. These reservoirs have ultra-low permeability, which limits a conventional CO_2 EOR process where CO_2 and water are injected into dedicated

injection wells to push oil to producer wells. Congress should encourage research managed by NETL in the next five years to develop methods that can be used to apply CO_2 EOR commercially to unconventional reservoirs and to understand the associated CO_2 retention potential. This is needed so that widespread CO_2 EOR operations in unconventional reservoirs can begin within 5 to 10 years.

B. Mid Term (5 to 10 Years)

1. Offshore CO_2 EOR would benefit from further research and testing to bring down the cost of implementation. The high cost of offshore development has resulted in fewer wells being drilled offshore relative to a comparable onshore development. Fewer wells negatively affects oil recovery efficiency, leaving a large amount of oil in offshore reservoirs that could be targeted by CO_2 EOR. In addition to lower well costs, the development of smaller, lower-cost compression equipment used for recycling the produced gas in a CO_2 EOR project would help overcome the economic hurdles that are necessary to make offshore projects viable from an investment standpoint.
2. Existing and future CO_2 EOR projects could increase the efficiency of oil recovery, and trap larger volumes of CO_2, if the viscosity of the injected CO_2 could be increased. Research into identifying low-cost thickeners and/or foaming agents for CO_2 could result in an increase in the amount of CO_2 stored in CO_2 EOR projects.

C. Long Term (10+ Years)

Reducing global CO_2 emissions while delivering increased energy supplies will require efforts from many stakeholders. CO_2 EOR offers the means of delivering this energy while also offering substantial incidental CO_2 storage capacity in service of both objectives. Expanding the application of CO_2 EOR processes globally will support the uptake of CCUS, while leveraging the skills, experience, and knowledge developed in the United States over the past 40 years.

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Chapter Nine

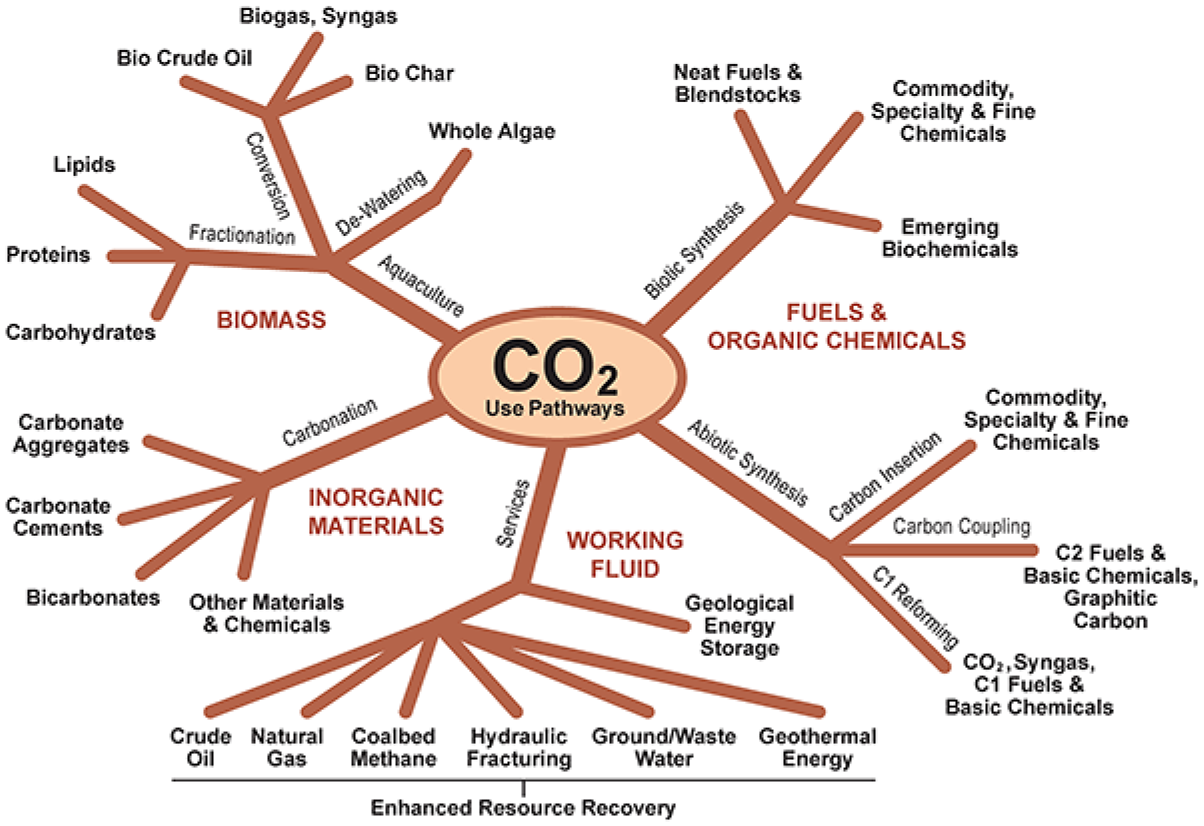
CO_2 USE

I. CHAPTER SUMMARY

Carbon dioxide use converts CO_2 into valuable products through chemical reactions or biological conversions. The CO_2 used can be sourced from natural or anthropogenic sources. Carbon is used to produce fuels, polymers, industrial chemicals, carbon nanotubes, and building products such as carbonates and cement. It is also used in the production of steel, electronics, and consumable goods. Some CO_2-derived products, such as construction materials, could significantly expand their use of CO_2. Although CO_2 use is already an important part of creating many of the products society depends on, expanding its use is a viable route to establishing sustainable carbon use for generations to come.

There are four main types of CO_2 use technologies: (1) thermochemical, (2) electrochemical and photochemical, (3) carbonation, and (4) biological conversion.

These processes lead to four potential use pathways in which CO_2 is converted into products: (1) fuels and organic chemicals, (2) biomass, (3) inorganic materials, and (4) working fluids (Figure 9-1). Some of these product pathways reduce the carbon intensity of products made with fossil fuels and have a large CO_2 storage potential in the products, chemicals, or fuels that are produced.



Source: JM Energy Consulting, Inc, 2019.

Figure 9-1. *CO_2 Use Pathways*

While the potential of CO_2 use is compelling, there are significant challenges to overcome before CO_2 use technologies can be deployed at scale. These include:

- *Technology Maturation* — Advancements have been made to understand the fundamental science of converting CO_2 into products. Efforts to bridge the gap from concept or laboratory scale to commercial-scale viability are required. Most CO_2 use technologies are at a low level of technical maturity and will need significant research, development, and demonstration (RD&D) to progress.

- *Costs and Energy Efficiency* — One of the fundamental challenges of CO_2 use is that the activation and conversion of CO_2 to chemicals, fuels, and materials requires significant amounts of energy. Thus, at-scale deployment of CO_2 use technologies will depend on technology advancement and the availability of affordable, renewable energy—or alternative forms of low-carbon energy—and inexpensive, clean hydrogen. This is becoming a more realistic proposition because renewable electricity is now at a competitive level with fossil power in many markets, but it may still be years or decades before commercial-scale deployment is possible.
- *Permanence and Indirect Impacts* — The permanence of carbon used in products is an important factor in determining the net environmental impact of CO_2 use. For example, beverage companies purchase CO_2 for carbonating soda but, as soon as the can is opened, the CO_2 is released. If the CO_2 used for carbonation were captured from an industrial source and displaced geologically extracted CO_2, there would still be an indirect benefit for displacing geologic carbon. It is for this reason that quality life-cycle analyses will be critical in determining the net carbon reduction potential of any CO_2 use technologies. The need to account for permanence and indirect impacts necessitates development of accurate and rigorous life-cycle analysis methodologies or standards.

Although there are several use pathways, CO_2 use alone is insufficient to dramatically reduce CO_2 emissions in the next couple of decades because the amount of CO_2 emitted from all sources greatly exceeds the quantity of carbon-sequestering products currently produced, even concrete. In addition, most use technologies are at a relatively low technology readiness level, and it takes about two decades to develop and commercialize capital-intensive energy and environmental processes.

Increased investment in fundamental research and commercialization support is essential to expedite the pace at which CO_2 use technologies would be ready for commercial-scale deployment. However, the potential of CO_2 use to decrease CO_2 emissions is impossible to quantify at this stage of development. Furthermore, the timeline to market and scale of CO_2 use opportunities is likely to differ across the United States, Europe, and Asia due to competing factors such as technological development, proximity to markets, and access to low-cost renewable energy or hydrogen.

Progressing CO_2 use options offers synergies if it is done in parallel with other carbon capture and storage (CCS) and energy storage development activities. CCS is necessary to provide the large-scale reductions in emissions that are needed in the next two decades. The early stage development of CO_2 use in various products could accelerate the deployment of CO_2 geological storage by offsetting the cost of CCS and CO_2 transport with end-product revenues. Also, converting CO_2 to high-energy density or high-value chemicals, fuels, and materials using excess renewable energy to provide a wide range of marketable products would provide an alternative to today's limited energy storage capacity. This could offer a type of seasonal storage of renewable energy.

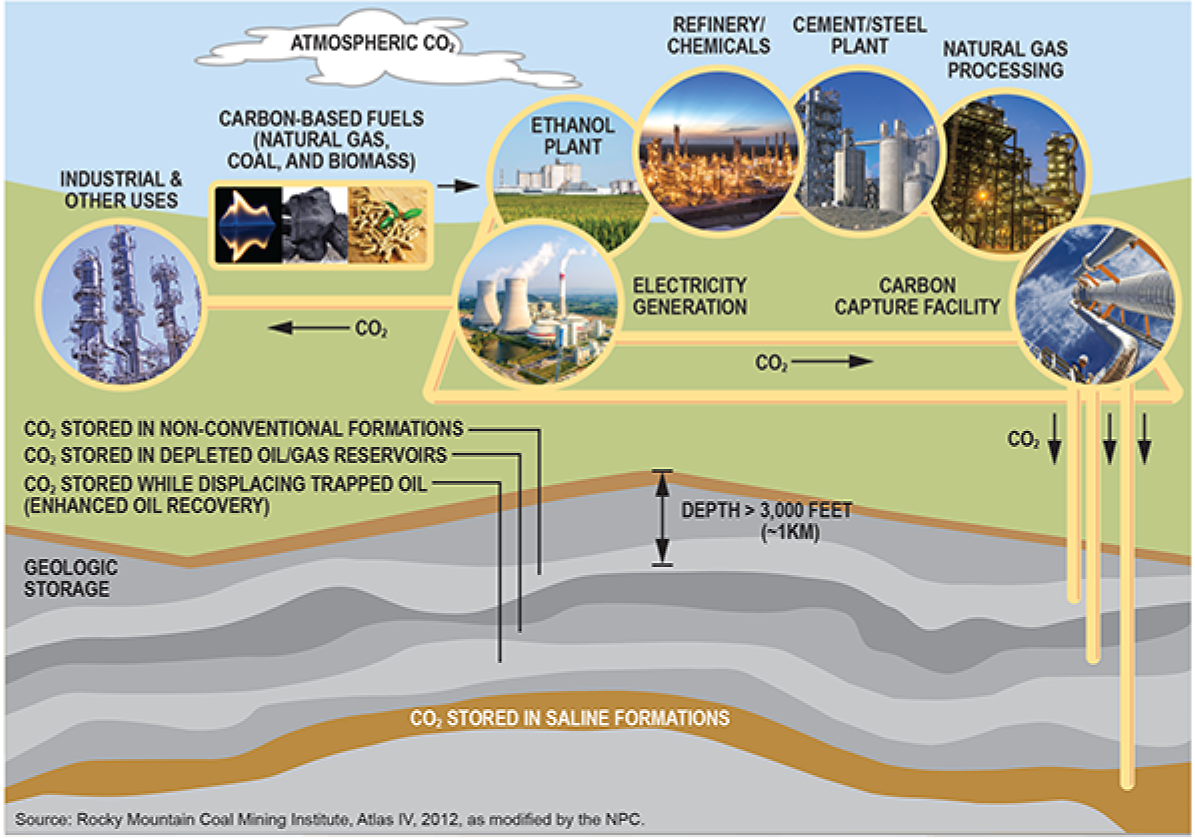
CO_2 use may appeal to society more readily than other aspects of carbon capture, use, and storage (CCUS), smoothing the pathway to public acceptance. For example, a mattress made with CO_2 captured from a cement plant could be more sustainable, or green, than alternative means of manufacturing that mattress. CO_2 use technologies might present a unique means of entering the global marketplace in the same way as have organic foods and green products, such as shoes and clothing made of recycled plastics. Early introduction of CO_2 use opportunities could improve public awareness and acceptance of CCUS as a method to reduce CO_2 emissions in the next couple of decades.

CO_2 use can play a unique and important role in carbon management and progressing national CO_2 emissions reduction objectives. CO_2 use technologies offer a range of opportunities to create products from CO_2 emissions over the long term, but multiple challenges must be addressed before these technologies can be employed at scale. CO_2 use has the potential to drive technology disruption and has a role to play in delivering negative emissions.

This chapter discusses the main CO_2 use pathways, the potential areas of application of CO_2 use, and priority topics for RD&D.

II. WHAT IS CO_2 USE?

CCUS, including transport, combines several processes and technologies to reduce the level of CO_2 emitted to the atmosphere or remove CO_2 from the air. The CCUS process, as shown in Figure 9-2, involves the capture (separation and purification) of CO_2 from stationary sources so that it can be transported to a suitable location where it is converted into useable products or injected deep underground for safe, secure, and permanent storage.



Source: Rocky Mountain Coal Mining Institute, Atlas IV, 2012, as modified by the NPC.

Figure 9-2. *Supply Chain for Carbon Capture, Use, and Storage*

Carbon is one of the most abundant elements on Earth. Its use in various forms has been essential to modern society and the world’s economy. Examples of the application of carbon in the economy include fuels, fertilizers, polymers, industrial chemicals, building materials, carbon nanotubes, and many others. It would be difficult to find any materials and products that do not contain carbon or have not resulted in CO_2 emissions during production or utilization.

Unfortunately, CO_2 cannot be burned to generate heat or energy, so it is described as having a low accessible chemical energy—it is chemically inactive. Thus, CO_2 requires a relatively large amount of energy to convert it into products that contain a higher energy. It is these higher-energy products, such as fuels, that can be burned to emit heat. Furthermore, most of these higher-energy products require hydrogen as a co-reactant, and this hydrogen should be produced via a more sustainable process if the carbon intensity of the final product is to be reduced.

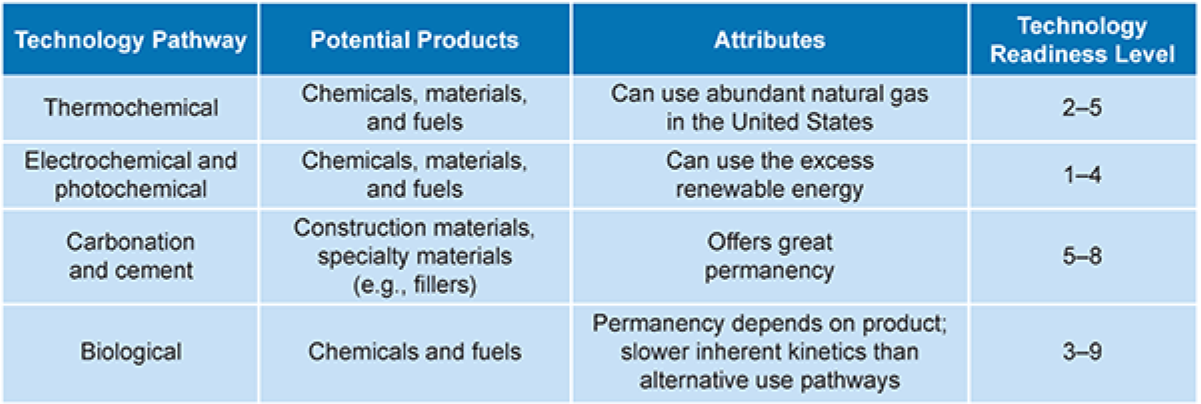
CO_2 use technologies convert CO_2 into products via chemical reactions or biological conversions. There are four main types of CO_2 use technologies: (1) thermochemical, (2) electrochemical and photochemical, (3) carbonation, and (4) biological conversion. There is a wide range of potential CO_2 use technology pathways and products that have been identified, each of which is being actively researched. Some of these product pathways reduce the carbon intensity of products made with fossil fuels and have a large CO_2 storage potential in the products, chemicals, or fuels that are produced. For example, the current production of construction materials, such as cement, results in large CO_2

emissions, but innovative cement production using CO_2, or carbonates produced using CO_2, could significantly reduce the net CO_2 emissions in the construction industry while storing CO_2 in the form of buildings.

Most CO_2 use technologies are at a low technology readiness level (TRL) and will need substantial research, development, and demonstration (RD&D) funding to progress. It takes about two decades to develop and commercialize capital-intensive energy and environmental processes. Thus, investment in CO_2 use RD&D funding and commercialization support is essential to expedite the use of CO_2 as a substitute feedstock[1] for traditional extractive single-use sources.

III. CO_2 USE TECHNOLOGY PATHWAYS AND POTENTIAL PRODUCT OPTIONS

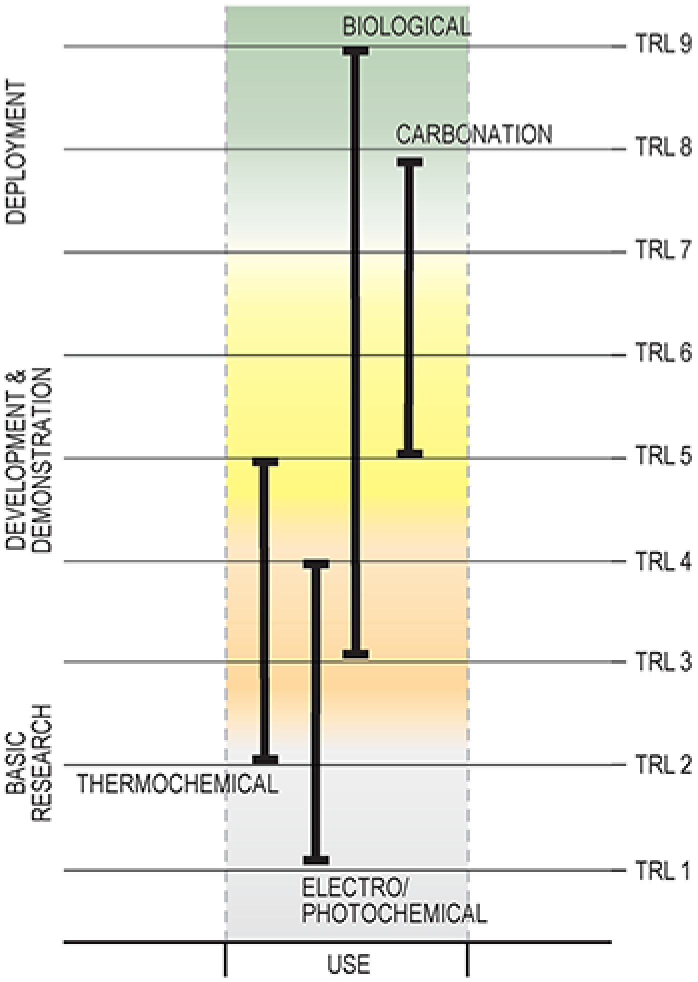
The CO_2 use technologies described in this chapter are divided into four pathways, or categories, based on the reactions involved and their TRL. As shown in Table 9-1, each technology is at a different stage of development and has its own attributes and commercialization potential.



Technology Pathway	Potential Products	Attributes	Technology Readiness Level
Thermochemical	Chemicals, materials, and fuels	Can use abundant natural gas in the United States	2–5
Electrochemical and photochemical	Chemicals, materials, and fuels	Can use the excess renewable energy	1–4
Carbonation and cement	Construction materials, specialty materials (e.g., fillers)	Offers great permanency	5–8
Biological	Chemicals and fuels	Permanency depends on product; slower inherent kinetics than alternative use pathways	3–9

Table 9-1. *Current Status of CO_2 Use Technologies*

Figure 9-3 displays the technology readiness level of the four main types of use technologies listed in Table 9-1. Each technology pathway on the figure is assigned a TRL range (right vertical axis) that represents its stage of technical development (left vertical axis). The stages of technical development include basic research, development and demonstration, and deployment. The higher the TRL level, the closer the technology is to commercial readiness and subsequent deployment. Most CO_2 use technologies are relatively immature, yet each use category displays a range of TRLs. This is indicative of the challenges and range of opportunities for advancement that may exist across these technology pathways.



Source: Figure ES-18.

Figure 9-3. *Technology Readiness Level (TRL) Ranges for CCUS Use Technologies*

A. Thermochemical CO_2 Conversion

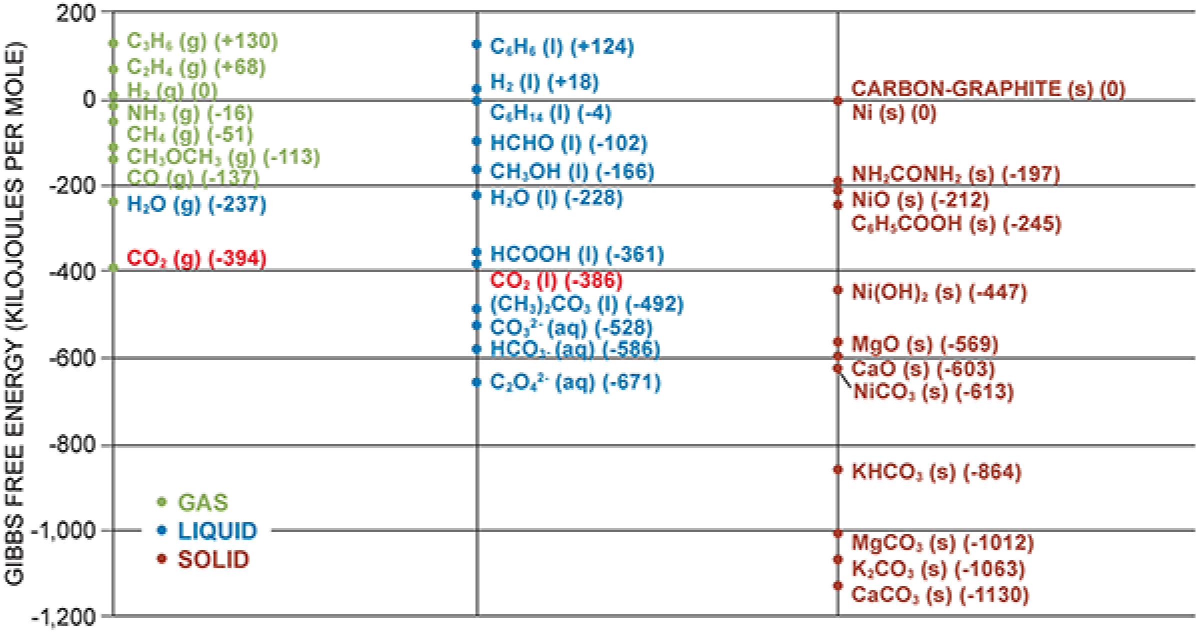
Thermochemical CO_2 conversion refers to a myriad of high-temperature reactions—such as catalytic hydrogenation, reforming, and oxidation—that produce a range of useful hydrocarbon products. The types of products include olefins (C_2–C_4), paraffins (C_5+), aromatics, alcohols, organic carbonates, carboxylic acids, and a wide range of polymers. Almost every thermochemical reaction requires the use of catalysts for the reaction to proceed at a reasonable rate, and CO_2 plays varying roles in the different reaction pathways. The CO_2 can be used as a feedstock, a co-reactant, or a mild oxidant.[2]

There have been remarkable advances using new catalysts to increase the selectivity[3] of CO_2 hydrogenation into desired products—either hydrocarbons or alcohol. These include:

- New bimetallic catalysts for CO_2 conversion to olefins and C_5+ hydrocarbons (i.e., iron-cobalt [Fe-Co] and iron-copper [Fe-Cu] on various supports) or to methanol (i.e., palladium-copper [Pd-Cu])
- New metal-oxide hybrid catalysts (i.e., Fe_3O_4-FeC_n/ZSM-5)
- New binary oxide-based multicomponents or hybrid catalysts (i.e., In_2O_3-ZrO_2/ZSM-5 and ZnO-ZrO_2/ZSM-5 hybrids) for CO_2 hydrogenation to energy-rich hydrocarbon and alcohol products in the past decade.

Computational research has contributed significantly to developing a fundamental understanding of surface interactions and reaction pathways.

One of the major challenges associated with CO_2 conversion is the thermodynamic stability of the CO_2 molecule itself (Figure 9-4).[4] This refers to the fact that CO_2 typically needs to be reacted with high-energy reagents such as hydrogen (H_2) or epoxides for processes to be thermodynamically favorable. Figure 9-4 uses Gibbs free energy in kilojoules per mole (kJ/mole) to illustrate that the lower the Gibbs free energy, the lower the energetic value of the gases, liquids, and solids shown. Thus, to make products that have a higher Gibbs free energy than CO_2, additional low-carbon intensity energy inputs will be required.



Source: Song, C.S., "Global Challenges and Strategies for Control, Conversion and Use of CO_2 for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing," *Catalysis Today,* 2006, 115, 2–32.

Figure 9-4. *Thermodynamic Considerations for Converting CO_2 to Chemicals and Fuels*

Generation of these reagents, especially of H_2, requires large amounts of fossil fuel resources, so they lack the net CO_2 benefit that would be desired from a life-cycle emissions perspective. For net CO_2 emissions reductions to occur from thermochemical processes involving CO_2 and H_2, the source H_2 must have a low-carbon footprint. For H_2 to have a low-carbon footprint, it must be generated from a renewable source, such as electrolysis of water, using electricity generated from renewable or fossil fuel energy from carbon neutral sources.

Current examples of large-scale products that are made commercially from CO_2 are limited, though there are many product pathways at a smaller scale. For example, CO_2 is combined with ammonia to make urea in a process that uses some of the CO_2 generated during the production of H_2 from natural gas for ammonia synthesis. Although urea is one of the largest CO_2 applications—annual global CO_2 demand in 2017 was 157 million tonnes—using CO_2 to produce urea does not permanently sequester the CO_2. Methanol is industrially produced from synthesis gas (syngas), composed of carbon monoxide (CO) and H_2, but up to 30% of the CO_2 can be incorporated into the starting gas stream and is also converted to product. Systems for the direct hydrogenation of CO_2 to methanol are also operating industrially but produce only a small fraction of the total methanol produced globally and are not cost competitive unless there are strong financial incentives for CO_2 use. Over the last decade several polymers have begun to be produced from CO_2, offering another pathway of potentially scalable relevance.

The range of chemicals that are produced from CO_2 could be increased if more efficient technologies were developed, low-carbon energy sources were available, and financial incentives were in place. Improvements in technology and financial incentives could increase the market share of chemicals that are produced from CO_2 capture because they must compete with less expensive non-CO_2 based routes. For practical application, integration of the conversion processes with a more efficient and geographically compact CO_2 capture process may be preferred for chemical processing.[5]

1. Technology to Market Experience

There are a few examples of thermochemical conversion of CO_2 into products (fuels, methanol, and polyurethane foam) that are currently available in the market or are approaching market availability.

In Dresden, Germany, Sunfire built a pilot plant from 2013 to 2014 that can produce 160 liters (~1 barrel) of hydrocarbons a day from CO_2 using a three-stage process: (1) H_2 production by electrolysis with renewable electricity, (2) CO_2 hydrogenation to CO, and (3) Fischer-Tropsch conversion of the CO to generate hydrocarbons.[6] Sunfire reported an electricity-to-fuel carbon efficiency of 70%.

In July 2017, Sunfire announced a plan to build the first commercial plant to produce an environmentally friendly crude oil substitute called Blue Crude. The plant will be built in Heroya, Norway, in 2020 and have an electric capacity of 20 MW, producing 8,000 tonnes of Blue Crude per year. This should be enough to provide fuel for 13,000 cars per year. The Blue Crude target price is less than €2 per liter. When the Heroya plant is running at full capacity, production of Blue Crude will prevent 21,000 tonnes of CO_2 emissions that producing the fuels from fossil fuel would have generated. Currently, the rate at which the fuel can be produced is slow and many more plants that are the same size as the Heroya plant would be required for this CO_2 use technology to be suitable for widespread adoption. The cost of the fuel is also higher than conventional fuel sources.

In Iceland, Carbon Recycling International (CRI) built a CO_2-to-methanol plant in Svartsengi that was completed in 2012. The CO_2 is captured from flue gas released by a geothermal power plant located next to the CRI facility. The plant uses electricity to make H_2, which is used for the catalytic hydrogenation of CO_2 to methanol. In 2015, CRI expanded the plant from a capacity of 1.3 million liters per year to more than 5 million liters per year. The plant now recycles 5.5 thousand tonnes of CO_2 per year that would otherwise be released into the atmosphere.

Unfortunately, the process is economically feasible only in Iceland for three reasons: (1) the availability of low-cost electricity required to generate the H_2, (2) the high concentration of CO_2 in the flue gas (85% to 90%), which substantially lowers the cost of CO_2 compared with more traditional flue gas streams that contain lower amounts of CO_2, and (3) the European Union requirement that a certain fraction of liquid fuels, such as methanol, must be produced in a sustainable fashion. At this stage, it would not be economically feasible to implement this CO_2 use technology in other locations, and the scale of the plant is also significantly smaller than most traditional methanol production plants.

Covestro has developed and commercialized a new flexible polyurethane foam that incorporates a CO_2-based polyol made by copolymerization of CO_2 and propylene. The foam is used in mattresses and was first released on the market in 2016. The polyol contains a CO_2-content of approximately 20%, which is obtained from a nearby ammonia plant. The production of the polyol still results in net emissions of CO_2, but emissions are reduced due to the use of CO_2 as a feedstock compared with the traditional non-CO_2 based route to these polyols. From a life-cycle perspective, additional benefits from replacing part of the propylene oxide with polyol are reflected in lower toxicity, eutrophication, and acidification.[7,8] The scale at which the CO_2-derived polyols are produced is approximately 60 times smaller than conventional polyol plants, but plans are in place to build a larger plant that is only three times smaller than a conventional plant. As of 2018, the new process appears to be a commercial success, but longer-term evaluation is required.

2. Product Options

There are a range of products that can be formed from CO_2. For example, the hydrogenation of CO_2 can produce olefins, liquid hydrocarbons, including aromatics, syngas, methanol, dimethyl ether, formic acid, and other chemicals. In general, these products are currently produced using petroleum, natural gas, or syngas ($CO+H_2$) using processes that have been optimized to operate with low profit margins. Nevertheless, the catalytic hydrogenation of CO_2 using H_2 produced from a renewable energy source could significantly contribute to the sustainable production of chemicals, materials, and fuels if efficient and selective processes are developed. The major challenges that need to be resolved for the development of new technology for CO_2

conversion are associated with the thermodynamic and kinetic stability of CO_2.

One of the simplest products that can be made from CO_2 is carbon monoxide (CO). This can be achieved using the reverse water-gas shift process. Specifically, H_2 and CO_2 is converted into CO and water (H_2O), though the process requires heat to proceed.

Another potentially important C1 product that can be synthesized from CO_2 is formic acid. Formic acid is currently produced through the reaction of CO with methanol to generate methyl formate. Although formic acid has a relatively small market size—about 700 kilotonnes per year globally—new markets are being explored, such as its use as an intermediate and a hydrogen carrier.

Methanol is a highly desirable target from CO_2 hydrogenation because it has potential as a chemical building block and a fuel. It has been recognized that the presence of CO_2 in or addition of CO_2 to the feed gas of CO and H_2 is beneficial for methanol synthesis over commercial Cu-ZnO-Al_2O_3 catalyst. Many studies have reported on the improvement of the Cu-ZnO-based catalysts with various promoters and modifiers. However, in the past 5 years, there has been substantial progress in developing fundamentally new catalyst formulations for CO_2 hydrogenation to methanol.

Aromatics are important for the production of chemicals and polymers and constitute about one-third of the market for commodity petrochemicals. However, the production of aromatics relies heavily on petroleum, so CO_2

hydrogenation to aromatics is a promising alternative route that has emerged for carbon mitigation purposes.

The direct incorporation of CO_2 into polymers is an area where some technology is at a commercial stage and other efforts are still in the research phase. The possibility of using CO_2 as feedstock for polymers, followed by circular management practices (e.g., increased recycling), provide the potential to keep the CO_2 out of the atmosphere for longer periods of time compared to chemicals or fuels. Polycarbonates, which have applications as a component in polyurethanes as well as in the electronics, transport, and construction industries, are the major type of polymer produced from CO_2.

Two types of polycarbonates can be produced through the copolymerization of CO_2 with epoxides by sequentially alternating one molecule of CO_2 and one molecule of epoxide that only contains carbonate groups, or using a statistical arrangement containing ether linkages that are generated when two ring-opened epoxides are adjacent to each other. Statistical polycarbonates, which are often referred to as polyether carbonates, have more desirable properties for industrial applications because alternating polycarbonates have low glass transition temperatures. Commercial processes, however, have already been developed to form both alternating polycarbonates and polyether carbonates. These are not yet conducted at a significant industrial scale because the products tend to be for niche applications and there are many opportunities to develop new polymers with unique properties from CO_2. This may be achieved by increasing the range of epoxides that can be efficiently copolymerized with CO_2 or developing systems that are derived from renewable epoxide feedstocks. Homogeneous catalysis likely provides the best initial opportunity for making progress in this area due to the control it can exert over selectivity.

Carboxylic acids, several of which are produced on a very large scale, have numerous industrial applications and could, in principle, be prepared by inserting CO_2 into a carbon-hydrogen (C–H) bond of a hydrocarbon. In most cases, however, inserting CO_2 into a C–H bond is thermodynamically unfavorable. Thus, most catalytic processes for generating carboxylic acids from CO_2 and bases are performed in the presence of a base. Currently, catalytic systems to produce acrylic acid, methacrylic acid, benzoic acid, and furan-2,5-dicarboxylic acid have been established. These systems are still in the research phase though, and some of the problems that need to be resolved include low catalyst turnover numbers, the need for expensive stoichiometric additives for thermodynamic reasons, and low reactions rates.

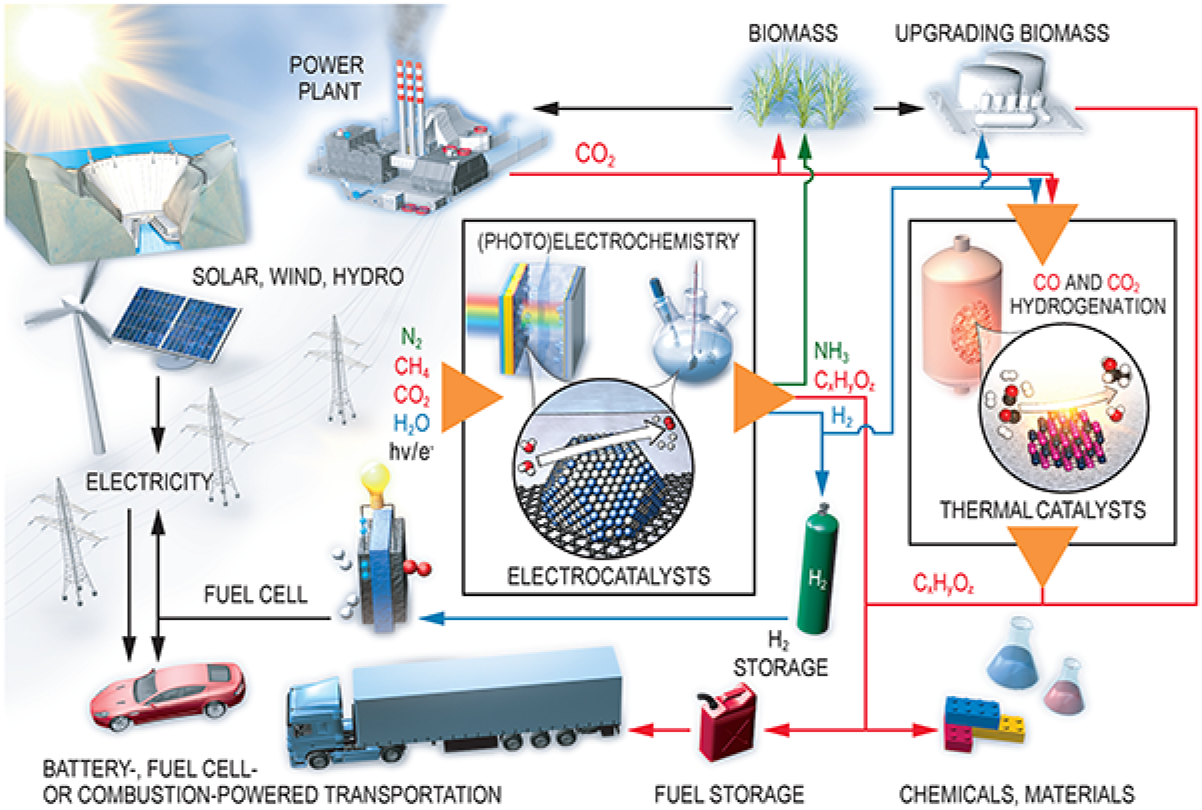
Conversion of CO_2 to carbon products—carbon black, carbon nanotubes, and carbon nanofibers, all via the patented Noyes Process—is being developed by Solid Carbon Products in Provo, Utah. Their process uses either hydrogen or natural gas as the energy source to catalytically convert CO_2 to elemental carbon materials and nanomaterials. Carbon black is a commodity material that is used in tires and composites.

B. Electrochemical and Photochemical CO_2 Conversion

Electrochemical and photochemical CO_2 conversion uses electrons and protons to activate CO_2 to produce a wide array of products. For electrochemical conversion, electricity is used to provide energy for the CO_2 conversion reaction. The electrochemical pathway can employ electricity from various sources, including renewable energy from solar and wind, which provides flexibility in energy sourcing. The photochemical conversion pathway uses sunlight to convert CO_2 and water into solar fuels using photochemistry.

One of the main challenges of both electrochemical and photochemical conversion of CO_2 is its competition with the hydrogen evolution reaction that has a similar reduction-oxidization (redox)[9] potential as the CO_2 reduction reaction. As a result, substantial effort is being dedicated to developing reaction systems that favor the conversion of CO_2 to chemicals and fuels.

Electrochemical conversion of CO_2 (CO_2 electrolysis) is capable of producing a wide array of products. Utilizing electrochemical reduction reactions, CO_2 has been successfully converted into both single carbon (C_1) and multicarbon products (C_2+). The simplest reduction product generated from CO_2 is CO, which has been well researched and is the closest to being commercially available. In addition, different designs of flow reactors have been developed to produce CO with an electric efficiency of more than 90%. Figure 9-5 shows various catalytic pathways (both thermochemical and electrochemical) to produce sustainable fuels and chemicals using carbon-free energy sources.



Sources: Seh et al., "Combining theory and experiment in electrocatalysis: Insights into materials design," *Science*, January 13, 2017, 355(6321); and 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, 2017.

Figure 9-5. *A Vision for the Future: Sustainable Production of Fuels and Chemicals, Using Carbon-Free Energy and Sustainable Feedstocks*

The reactor design that produces the highest performance is the solid-oxide reactor (SOE), which can produce nearly pure CO at rates of 2 cubic meters per hour. Even though SOEs demonstrate very good performance operating at powers in the kilowatt scale, they need to operate at very high temperatures of greater than 1,000 K (727C) to overcome the resistance from the ceramic electrode. Ambient temperature electrolyzers (ATEs) provide another option for producing CO without the need for heating to such extreme levels. State-of-the-art ATEs using a silver cathode, and either dissolved CO_2 or humidified CO_2, produce CO at high efficiencies but suffer from suboptimal performance, partially due to energy losses in the anode. A strategy to overcome these losses is to pair the electrolyzer with water electrolysis to produce syngas (CO and H_2). In certain markets, syngas has a higher value than pure CO because it can be fed into a secondary reactor to be upgraded to higher-value products.

While CO_2 to CO conversion has shown promising results and is nearing commercial availability, CO_2 conversion to C_2+ products as well as other C_1 products has proved significantly more difficult to accomplish. Because the reduction potentials of many C_2+ products are very similar, selectivity and performance are typically very low. As a result, significant research has been done to optimize these systems to produce C_2+ products more efficiently, both electrochemically and photochemically. Recent findings in electrochemical reduction have been successful in producing C_2 and C_3 products using homogeneous and heterogeneous catalysts. However, these catalysts require significant optimization due to their low specificity toward desired products.

In general, there are strong trade-offs between the selectivity of the process, the rate of conversion, and the overall energy use toward the desired product. Current studies utilizing computational tools have been successful in identifying key intermediates as well as transport phenomena to better understand the CO_2 reduction reactions. From these studies there is hope that a direct CO_2

electrolyzer can be developed to produce the desired C_2+ products directly, mitigating the need for a full chemical plant. Other reactor designs that use a CO_2 electrolyzer to produce CO followed by a CO electrolyzer have also been tested. Although these reactors have shown promising results, they are still in the early stages of development and far from commercial application.

Photochemical conversion is the reduction of CO_2 via photocatalysis, where sunlight is used to convert CO_2 and water into solar fuels using photochemistry. Photochemistry relies on photon-induced transitions between the electronic states of the catalyst and consequent interaction with the molecular orbitals of adsorbed reactant species. Both processes occur in the same material that serves as the photocatalyst.

While indirect approaches such as electrochemistry rely on an alternative energy input (electricity) produced by an external device (photovoltaic cell or other low-carbon electrical power source) and the resulting electrical potential to split the strong double carbon-oxygen bond (C=O), photocatalysis uses light to catalyze the reaction. Photochemical conversion methods provide an advantage over the use of electrochemical methods because there is no need to input energy into the system. A wide array of catalysts has been tested, typically using a solution of CO_2 and water, with the primary products being CO, CH_4, and CH_3OH. Some studies have shown production of C2+ products, but at much lower rates than the electrochemical methods. Even with the higher selectivity shown with the photochemical approach, reaction rates are still far too low for commercial use. As a result, significant research is necessary to optimize photochemical systems before they will be ready for commercial use.

The complete photochemistry mechanism involves light absorption to induce charge carrier separation, followed by the transport of carriers to the active surface sites for catalytic CO_2 reduction. Photocatalysts are often hybrid materials involving a semiconductor embedded with a metal or metal-oxide co-catalyst (platinum [Pt], palladium [Pd], copper [Cu], ruthenium [Ru], nickel-oxide [NiO_2], ruthenium-oxide [RuO_2]) and can include a sensitizing agent to increase light absorption. Nanostructuring strategies have largely dominated the research and development of photocatalysts, and nanoparticle catalysts are favored for their readily tunable surface properties. It has been reported that the use of high surface area support materials can also offer increased dispersion, stability, and photoresponse of the nanoparticle catalysts, resulting in their improved efficiency and durability. Despite nanostructuring breakthroughs, the principal challenge of photochemistry remains the limited adsorption and use of the solar spectrum by existing photocatalysts.

CO_2 can also be reduced directly via homogeneous photocatalysis. Homogeneous catalysts are typically metal complexes that serve the dual function of light absorber and active site. Because molecular catalysts often rely on expensive and rare metals (like ruthenium [Ru] and rhodium [Rh]), they have limited potential for industrial scaling. Currently, a lack of standardization for reported measurements has impeded proper benchmarking of photocatalytic CO_2 reduction. Formation rates of products remain on the order of micromoles per gram of catalysts per hour (μmol $gcat^{-1}$ h^{-1}).

Emergence of novel carbon-based materials (e.g., graphitic carbon nitride) as photocatalysts is encouraging because these systems can be process-intensified to conduct capture and conversion in one step. Advancement in nanoscience has enabled synthesis of morphology-controlled nanomaterials with tunable properties to enhance light harvesting and energy efficiencies in the system.

There remain several challenges associated with CO_2 use through electrochemical and photochemical approaches. Selectivity and the pace of reaction rates into desired products require improvements before they will become industry or market ready. Also, electrochemical and photochemical systems must address challenges related to the concentration and purity of realistic CO_2 sources (diluted and contaminated), as well as the intermittency of renewable electricity and sunlight. With further research and development, CO_2 electrochemical and photochemical reductions are potentially economical approaches for carbon use.

1. Technology to Market Experience

A few examples of electrochemical conversion of CO_2 exist, all of which involve conversion to carbon monoxide. Currently, there are no equivalent photochemical conversion activities at this scale:

- Opus 12 has developed a PEM-based[10] polymer electrolyte cell that has achieved high selectivity and current density for CO_2 conversion to CO. The team is also pursuing the means to produce other products such as methane, ethylene, and ethanol. The core innovation of the Opus 12 team is their polymer electrolyte membrane electrode assembly that can be substituted for the conventional platinum-coated monoethanolamine (MEA) in a PEM water electrolyzer.

- Haldor Topsoe used a solid-oxide technology to convert CO_2 to CO. However, the operating temperature of this process is high (700°C to 850°C), which limits its range of applicability when integrated with intermittent renewable energy sources. The technology has, however, proven to have high energy efficiency and offer opportunity for waste-heat recovery and heat integration. Haldor Topsoe is marketing a high-temperature electrochemical cell capable of generating CO from CO_2 at a commercial scale.
- Dioxide Materials has developed a low-temperature electrochemical technology and is already marketing this technology for laboratory use.

2. Product Options

The electrochemical reduction of CO_2 can proceed through a two-, four-, six-, eight-, twelve-, or eighteen-electron reduction pathway to produce various gaseous products (carbon monoxide, methane, ethylene) and liquid products (formic acid, methanol, ethanol, n-propanol, acetate).[11] Other minor products have also reported including gloyoxal, ethylene glycol, acetaldehyde, propionaldehyde, etc.[12] Similar products can be made via photochemical pathways.

C. Carbonation and Cement Uses of CO_2

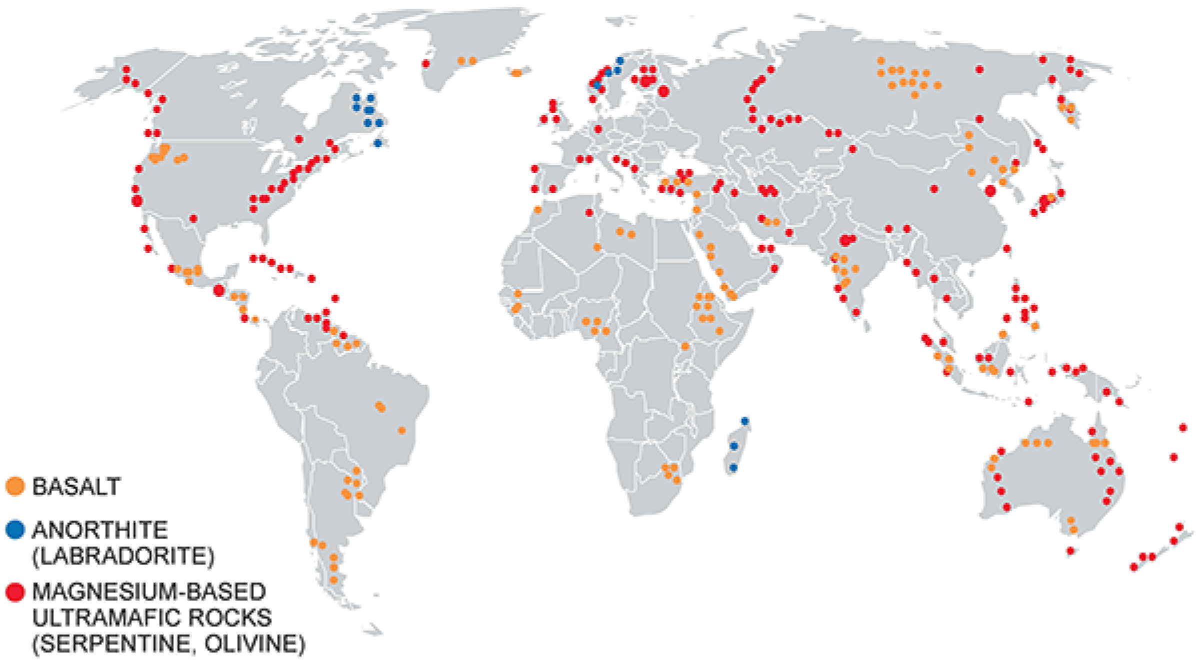
Carbonation, or carbon mineralization, refers to the inorganic reaction pathway that transforms gaseous CO_2 into solid carbonates, typically in a permanent way, in the form of thermodynamically stable and environmentally benign mineral carbonates. The carbonation of alkaline minerals mimics the natural alteration of calcium- and magnesium-rich rocks as they react with atmospheric CO_2 over geological timescales.[13] Examples of carbon mineralization in nature include the weathering of rocks on the Earth's surface and the underground formation of carbonate rocks such as limestone.

The carbon mineralization reaction occurs very slowly in nature. CO_2 use technologies accelerate the natural weathering process of calcium- and magnesium-bearing minerals and rocks. Alkaline industrial wastes containing high concentrations of calcium and magnesium can also be used for carbon mineralization.

The carbonation pathway can be used to produce more sustainable products, like green construction materials. Cement curing can also use CO_2 instead of steam, which significantly reduces the energy requirement. As a result, a carbon credit can be earned for the CO_2 that is not released during the production of concrete blocks.

It is estimated that the natural reserves of calcium and magnesium silicates near the Earth's surface are enough to store all the CO_2 that could be produced from all the identified fossil fuel reserves that are recoverable.[14] Still, substantial scale up and acceleration of the mineral carbonation reaction through process intensification routes is required if the rate of CO_2 emissions from industrial sources is to be matched, and if carbonation in an economical and net-positive manner is to be achieved.[15,16,17,18]

In this context, evaluating the potential of carbon mineralization for CO_2 use and storage is important. Several gigatonnes of carbon can be converted in natural geologic materials while 200 Mt to 300 Mt of CO_2 can be converted to calcium and magnesium carbonates in alkaline industrial residues annually.[19,20] Figure 9-6 shows the availability globally of calcium- and magnesium-bearing, naturally occurring rocks and minerals for carbon mineralization.



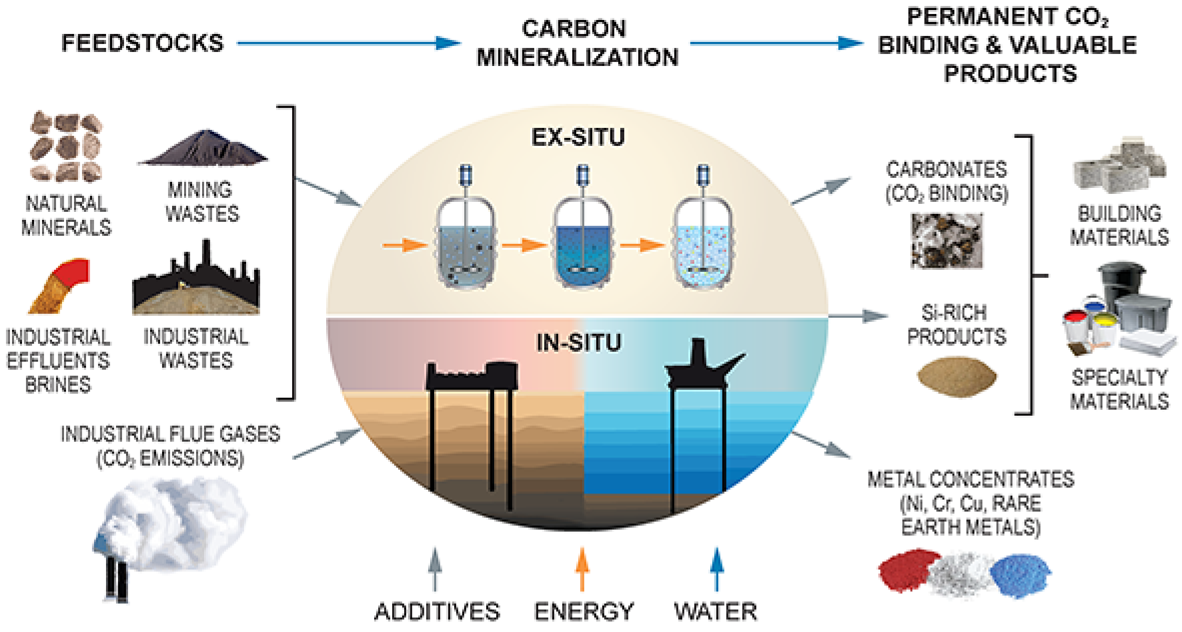
Sources: Gadikota, G., and Park, A-H. A., "Accelerated Carbonation of Ca- and Mg-Bearing Minerals and Industrial Wastes Using CO_2," in *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st ed., 2014; and Gadikota, G., "Geo-Chemo-Physical Studies of Carbon Mineralization for Natural and Engineered Carbon Storage" (PhD diss., Columbia University, 2014).

Figure 9-6. *Global Distribution of Continental Rocks and Minerals with CO_2 Storage Capabilities*

Carbon mineralization can also be applied to a variety of industrial waste materials. These materials are typically by-products of high-temperature processes, such as slags and fly ashes, but can also include tailings (waste) from mineral processing operations and other suitable waste materials.[21,22,23,24,25] These wastes are generally inorganic, alkaline, and possess a high amount of calcium or possibly magnesium. The advantage of calcium waste is that it has greater reactivity due to the lower Gibbs free energy of the carbonation reaction.

Industrial waste materials also have several advantages compared to natural minerals. They tend to be generated in industrial areas near large CO_2 point sources, often have low to negative market prices, and possess higher reactivities because of their inherent chemical instability. Wastes are also generally available in particulate form, which is favorable in terms of specific surface area.

Other benefits in addition to CO_2 conversion to carbonates include stabilization of leaching, basicity, and structural integrity that further enable the valorization of waste materials, either via reduced waste treatment or landfilling costs, or the production of marketable products. The reduction of industrial waste stockpiling reduces our reliance on land resources. However, the availability of these alkaline industrial residues, which is significantly lower than that of natural minerals, and the relative amounts of calcium and magnesium in these residues dictates the extent to which CO_2 can be converted to calcium and magnesium carbonates. Figure 9-7 shows various carbon mineralization pathways utilizing different feedstocks to fix CO_2 into value-added solid carbonate products. Efforts to colocate processes for CO_2 conversion to calcium and magnesium carbonates with the sources of alkaline industrial residues need to consider the relative abundance of CO_2 emissions and the quantity of alkaline industrial residues.

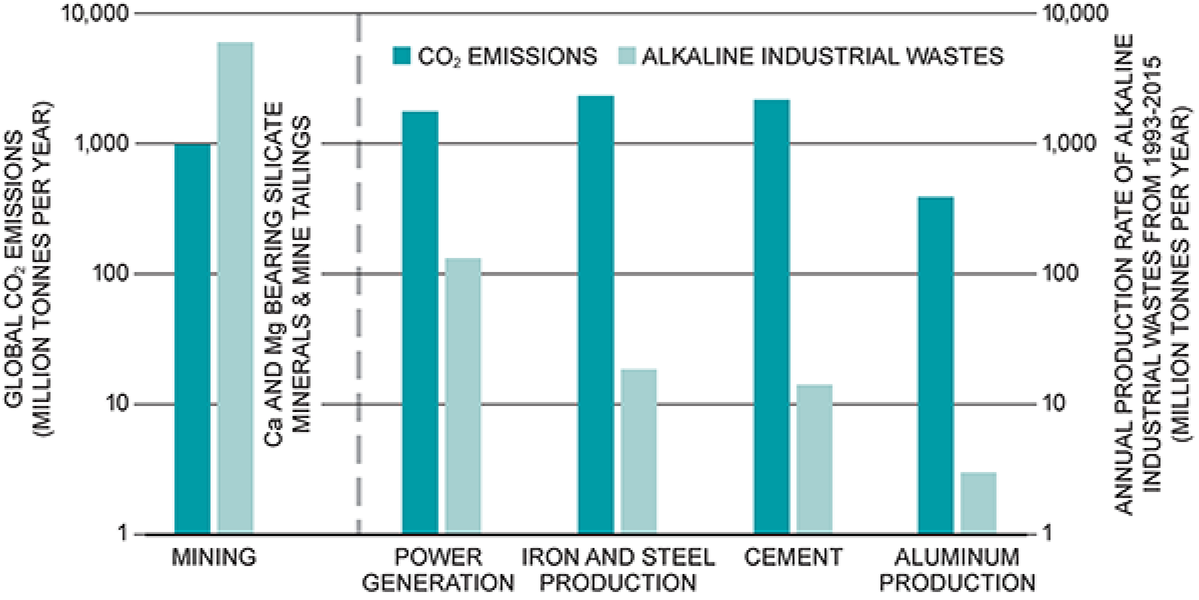


Source: U.S. Department of Energy, Office of Fossil Energy, *Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage*, Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts' Workshop, 2017.

Image courtesy of Florent Bourgeois, Laboratoire de Génie Chimique; Au-Hung Park and Xiaozhou Sean Zhou, Columbia University.

Figure 9-7. *Scheme of Carbon Mineralization and Range of its Products*

Figure 9-8 shows the annual U.S. CO_2 emission rates produced from each industrial sector and the corresponding co-generated alkaline industrial residues. These data suggest that the potential for carbon mineralization using alkaline industrial residues produced in the mining sector to exceed the sector's CO_2 emissions, unlike in the case of power generation, iron and steel production, and cement and aluminum production. However, additional factors such as conversion efficiency, reactor design (e.g., heat input and grinding requirements), and material handling must be investigated on a case-by-case basis to determine the relative carbon footprint and life cycle of each proposed project.



Sources: Sources: Gadikota, G., Fricker, K., Jang, S-H., and Park, A-H.A., "Carbonation of Silicate Minerals and Industrial Wastes and Their Potential Use as Sustainable Construction Materials," in *Advances in CO_2 Capture, Sequestration, and Conversion*, 1194:12–295, ACS Symposium Series, American Chemical Society, 2015; and Bodénan, F., Bourgeois, F., Petiot, C., Augé, T., Bonfils, B., Julcour-Lebigue, C., Guyot, F., et al., "Ex Situ Mineral Carbonation for CO_2 mitigation: Evaluation of Mining Waste Resources, Aqueous Carbonation Processability and Life Cycle Assessment (Carmex Project)," *Minerals Engineering*, May 2014.

Figure 9-8. *U.S. Annual Emission Rate of CO_2 Produced by Industrial Sector and Corresponding Co-Generated Alkaline Industrial Wastes*

One issue is that mineralization of natural minerals or alkaline wastes does not produce only carbonates. The dissolution process yields a mixture of phases as the dissolution of calcium (Ca) and magnesium (Mg) is generally congruent with the other elements present inside the mineralization feedstock. Mineralization of silica-bearing feedstocks can produce amorphous silica, which can be valuable. Invariably, mineralized products will bear some initial feedstock particles that have not undergone mineralization. Moreover, the dissolution of mineralization feedstocks will liberate metals in the leached solution that could also be concentrated via purification techniques and valorized. The Mission Innovation report published in 2018 introduces the concept of enhanced metal recovery, which uses mineralization specifically for extraction of valuable metals from mineralization feedstocks.[26] A critical mass of research on these topics has formed in recent years, which has been primarily reported at international conferences on Accelerated Carbonation for Environmental and Materials Engineering, held in London (2006), Rome (2008), Turku (2010), Leuven (2013), New York City (2015), and Newcastle (2018). With this context, the following sections focus on the different pathways available for the accelerated conversion of CO_2 to calcium and magnesium carbonates.

1. Technology to Market Experience

The efforts in commercializing the conversion of CO_2 to carbonates can be broadly classified into four categories. The first category involves converting CO_2 to carbonate-bearing chemicals such as sodium bicarbonate. This approach is being commercialized by Carbon Free Chemicals. The second is geared toward using CO_2 for curing building materials as proposed by Solidia Technologies and CarbonCure. A third category involves converting CO_2 to carbonates using waste residues (fly ash, steel slag) for integration into building materials, which is being scaled up by Carbon8, GreenOre, Mineral Carbonation

International, and Carbstone Innovation. Fourth, Carbon Upcycling Technologies is reacting waste CO_2 with solid feedstock (fly ash, petcoke, graphite) to create stable, high-strength solid nanoparticles.

One of the key advantages of commercializing technologies associated with CO_2 conversion to carbonates is the additional environmental benefits that accrue beyond the CO_2 used and converted to carbonates. The CO_2 curing approach utilized by Solidia Technologies eliminates at least 1.5 gigatonnes of CO_2, reduces the use of fresh water reserves by 3 trillion tons, reduces energy consumption by 260 million barrels of oil, and eliminates 100 million tonnes of concrete landfill waste.[27] Using a patented process known as hydrothermal liquid phase sintering, cementitious materials are prepared at temperatures much lower than conventional sintering temperatures.[28] Further, CO_2 loaded with MEA can be directly reacted with calcium silicate to produce calcium carbonate.[29]

Another company, CarbonCure, is injecting CO_2 directly into concrete to not only sequester it but to increase concrete performance and reduce the amount of cement—a high CO_2 footprint component—needed in the concrete mixture. Start-ups such as GreenOre and Mineral Carbonation International are converting steel slag produced by Baotao Steel in China to carbonated materials. Both direct and indirect approaches of converting CO_2 to carbonates starting with steel slag as the precursor material were evaluated. Further, the carbonate-bearing materials are being evaluated for their potential use as construction materials. These commercial activities illustrate the success in translating innovations in converting CO_2 to carbonates into the marketplace.

Most industrial developments involve production of calcium carbonates even though Mg is far more abundant. The potential for developing mineralization technologies that produce Mg-based construction materials is significant. This potential remains to be harvested. There are currently numerous public domain patents about magnesia-based hydraulic binders, dating as far as 1889.[30] It remains to be seen whether Mg-based mineralization products can be utilized to produce commercially and normatively acceptable binders for the construction sector, whether structural or nonstructural. Using Mg-based mineralization products to produce road infrastructure is also worth pursuing.

2. Product Options

For mineral carbonation to become economically feasible, the valorization of the resulting material could help reduce the overall cost of the process. This section outlines some recent developments with this objective, mainly to produce construction materials that either contain carbonated products or are formed by means of carbonation.

Calcium carbonate is a mineral with several applications, and it is indispensable in the industries of paper, paint, and plastic where it is used as a filler or pigment. Calcium carbonate is also used as filler or coating pigment in rubbers and adhesives; as extender and pH buffer in paints; as filler and color stabilizer in concrete; for environmental pollution control and remediation in flue gas and water treatment; in fertilizers and animal feed as calcium supply; and in the production of glass, ceramics, cosmetics, and hygienic products. Due to the strict quality requirements for other industrial uses, however, it is preferable to synthesize calcium carbonate under controlled conditions as precipitated calcium carbonate (PCC). This product has the same chemical composition as any other naturally occurring calcium carbonate (chalk, limestone, marble), except it is produced artificially under conditions that result in a high-quality product with specific characteristics.

High-purity limestone (97% to 98%) in $CaCO_3$ is typically used as the calcium source for the production of PCC. One recent research trend, however, is the use of alternative sources of calcium for PCC synthesis. One team of researchers has reported on using dolomite $[CaMg(CO_3)_2]$ as the starting material,[31] while another team has developed an indirect aqueous carbonation process for producing high-grade PCC (>99 weight% $CaCO_3$) starting from waste gypsum ($CaSO_4 \cdot 2H_2O$).[32]

Calcium carbonate that is industrially used as a filler or pigment is most commonly calcite due to its stability and easy production routes. Aragonite, however, presents some improved physical and mechanical properties. Polyvinyl alcohol or polypropylene composites with aragonite filler show improved tensile strength, impact strength, glass temperature, and decomposition temperature,[33] while aragonite-containing paper coating benefits from improved brightness, opacity, strength, and printability.[34]

Several researchers have shown that finely milled basic oxygen furnace (BOF) slag, a waste product from the steel industry, can be used as a cement replacement in mortars and concretes.[35,36,37,38] Others have combined BOF slag with blast furnace slag[39] where it acts as a basic activator due to its free lime content. However, because the use of BOF slag as a binder requires intense grinding and given its high metallic iron content, this processing step requires a high-energy demand that incurs high cost. Carbon mitigation would come in the form of using the slag as a binder rather than a more carbon-intensive product such as Portland cement.

However, aggregates can also be an attractive product outlet for carbonated minerals. One research team calculated the CO_2 sequestration capacity through mineral carbonation of alkaline industrial wastes that can be subsequently used as aggregates in the construction domain at 7.6 Mt CO_2/year for the United States.[40] Out of that quantity, 0.6 Mt CO_2/year represents the amount of emissions avoided by reducing the exploitation of natural sand, gravel, granite, and limestone. Besides capture of CO_2, which is desirable for emissions reduction, mineral carbonation has also been reported to yield positive effects in terms of basicity and the leaching behavior of alkaline earth metals, heavy metals, and metalloids from steelmaking slags.[41]

Beyond construction materials, which is the largest volume outlet for carbonated minerals, one research team has identified a second product outlet for carbonation within oil-shale power plants by utilizing the C–a$_2$+-saturated alkaline water (pH 12–13) that is recycled between the plant and sedimentation ponds for transport of the ash to wet, open-air deposits.[42] The goal is to intensify the water neutralization process and use the wastewater as a calcium source for the production of PCC. The PCC formed is characterized by a regular rhombohedral structure and a homogeneous particle size (~5 μm) distribution. It has also been discovered that to avoid agglomeration of the particles and redissolution of $CaCO_3$, the neutralization process must be divided into two stages: PCC precipitation and separation at high pH values in the first stage, followed by decreasing the residual alkalinity of the wastewater to acceptable disposal levels (pH ~8–8.5) in the second stage.

D. Biological CO_2 Use

Biological CO_2 use refers to the conversion of CO_2 to biomass, chemicals, and fuels via biological pathways. Photosynthetic CO_2 conversion mimics natural plant growth that occurs in sunlight. Photosynthesis can use natural and artificial light to grow algae and cyanobacteria to produce bioenergy.

There are several unique nonphotosynthetic pathways being considered as well. For nonphotosynthetic conversion, the required energy comes from reduced inorganic compounds or the waste gases from industrial sources (spent syngas from steel plants) instead of the sun. Microorganisms can produce biofuels (ethanol) in dark conditions by using the energy in waste gases (CO, CH_4, H_2). In recent years, hybrid schemes combining chemical conversion of CO_2 to C_1 compounds (formate, CO), and the biological conversion of C_1 compounds into C_2+ compounds, are being developed to synergistically enhance the overall conversion process and improve selectivity toward a target product.

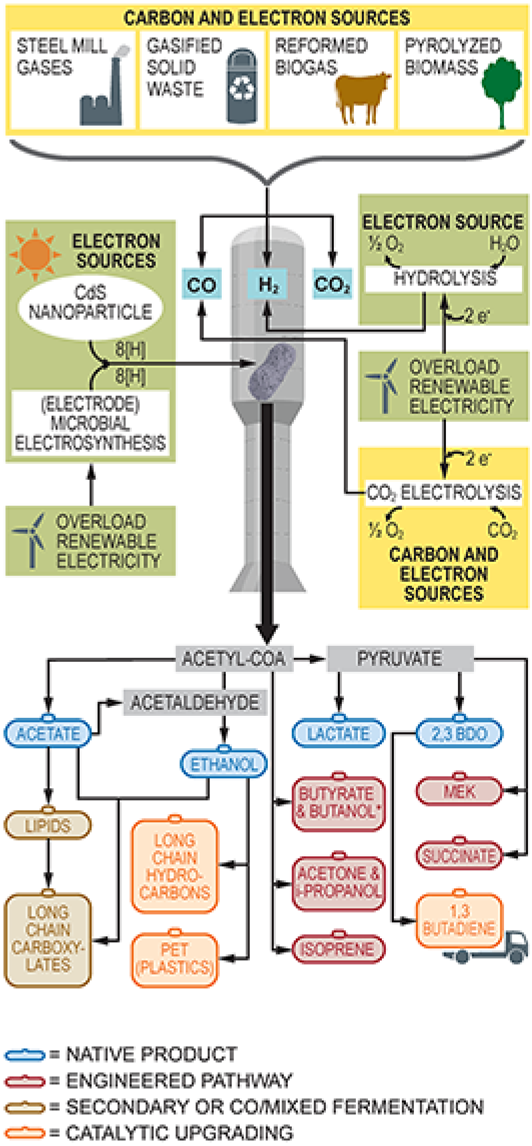
Microorganisms can capture and convert CO_2 into chemicals, chemical intermediate, or fuels through either photosynthetic or nonphotosynthetic processes. Pathways include the direct conversion of CO_2 using sunlight and photosynthetic microorganisms, artificial light and microorganisms, and hybrid approaches that use electricity to help generate components for CO_2 that can be converted utilizing biological pathways. Photosynthetic microorganisms such as green algae or cyanobacteria have been used as found in nature or modified using genetic manipulation tools to convert CO_2 into precursors for the generation of fuels and chemicals, dietary proteins and as directed generation of compounds such as ethanol, butanol, 2,3-butanediol, 1,3-propanediol, ethylene, isoprene, squalene, and farnesene.

Photosynthetic Processes. Initially there was a strong economic case for developing algal-based biofuels to either augment or replace petroleum-based fuels. More recently, the case has been less clear because algae cultivation has presented significant challenges, including inefficient capture of total solar radiation energy (3% to 6%), limitations of algae to effectively convert CO_2, and the cost and development of infrastructure for physically processing the algae (dewatering and extraction). To compensate for the low efficiencies, cultivation ponds or bioreactors are often designed to maximize light exposure through large volume and surface area, which makes algal cultivation land and water intensive. Multiple reports describe the state of the science and research challenges for algal biofuels.[43]

Nonphotosynthetic Processes. Light-independent CO_2 fixation may occur within nonphotosynthetic biological processes that use chemolithotrophic microorganisms. Chemolithotrophs derive their energy from the oxidation of reduced inorganic compounds (molecular hydrogen, carbon monoxide, sulfides) and their carbon from CO_2. Several companies (Lanzatech, Coskata, INEOS) have attempted to use a class of chemolithotrophs (acetogens) to convert CO_2 to fuels and chemicals via gas fermentation.

Gas fermentation using chemolithotrophic microorganisms known as acetogens has been demonstrated using CO, H_2, and CO_2 gas mixtures as a feedstock. Certain acetogens can produce reduced products such as ethanol and 2,3-butanediol. Acetogens possess a biological water-gas shift capability that enables them to reversibly undertake the conversion of CO and H_2O to H_2 and CO_2. This bioreaction enables these organisms to operate across a broad array of gas compositions to produce reduced products such as ethanol. It also enables processes that use these organisms to tolerate rapid fluctuations in the composition of feed gas streams, removing the need for stable or fixed gas ratios while still producing valuable products with high selectivity.

Figure 9-9 is an overview of proposed feedstocks and the products generated using gas fermentation. In the figure, feedstocks to the gas fermentation platform are highlighted in yellow (carbon and electron sources) and green (electron sources). The feedstocks shown are at various stages of commercial deployment. Synthesis of all the products shown in the figure has been demonstrated, including (1) native products (blue text), (2) synthetic products produced through genetic modification (red text), (3) products generated through secondary fermentation of co-mixed cultures (brown text), and (4) products achieved through additional catalytic upgrading (orange text).



ACRONYMS:

2,3-BDO = 2,3-BUTANEDIOL

CdS = CADMIUM SULFIDE

MEK = METHYL ETHYL KETONE

*Butyrate and butanol are both native and engineered products, depending on organism.

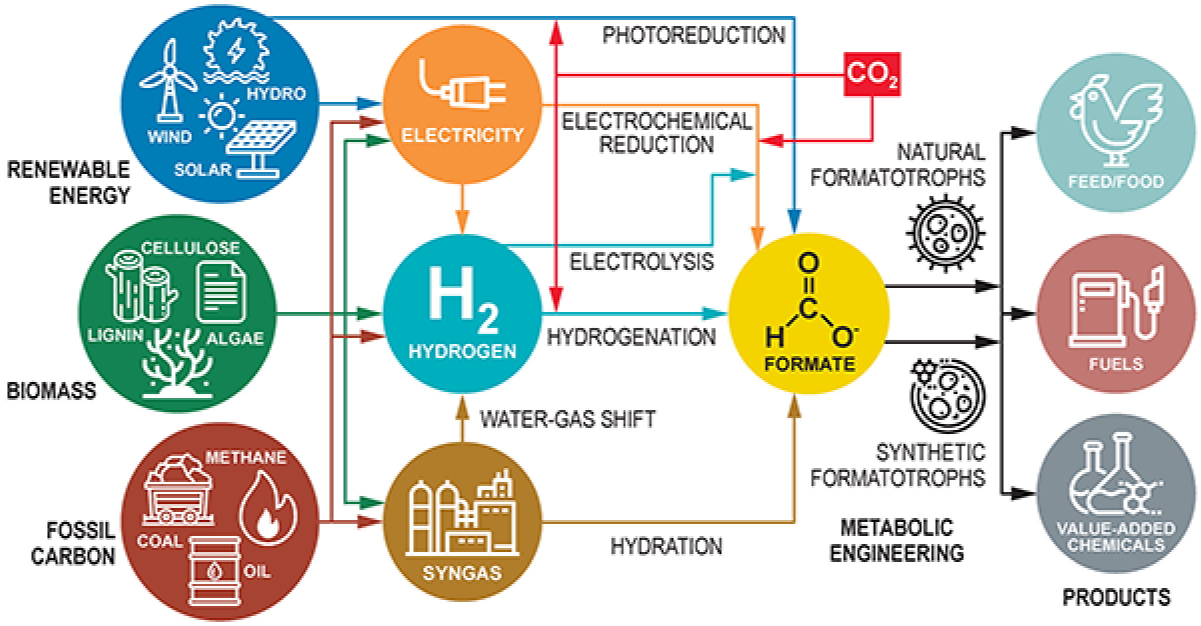
Source: Liew, F., Martin, M.E., Tappel, R.C., Heijstra, B.D., Mihalcea, C., Kopke, M., "Gas Fermentation – A Flexible Platform for Commercial Scale Production of Low-Carbon-Fuels and Chemicals from Was and Renewable Feedstocks," *Frontiers in Microbiology*, 7, (2016), p.1.

Figure 9-9. *Overview of Feedstocks and Product Options for Gas Fermentation*

Microbial Electrosynthesis. An alternative nonphotosynthetic route for biological use of CO_2 is providing reducing equivalents directly to a microorganism from electricity. This microbial electrosynthesis (MES) process has shown promise for using electrical current to reduce CO_2 to multicarbon products. MES can be an efficient process with 85% electron recovery, but challenges remain due to cultivation and maintenance of a dense biofilm on the cathode, electron transfer to this biofilm, and scale up of the overall system.

Hybrid Approaches. Gas fermentation of CO_2 to products is being scaled and commercialized, and it would be an ideal technology to combine with an electrochemical or chemical process that converts CO_2 to CO. Hybrid approaches combining electrochemical and biological processes are also being proposed where electrochemistry is used to reduce water and CO_2 into reactive intermediates such as H_2, CO, and formate that can be used as feedstocks to biological processes. To date, electrochemistry has been effective for a two-electron transfer reaction such as the generation of H_2 via water splitting, reduction of CO_2 to CO, and the reduction of CO_2 to formate. However, electrochemistry has not yet been effective at converting CO_2 and water to more complex molecules required for today’s fuels or chemicals. Biological routes are not as efficient at the conversion of water and CO_2, but can convert compounds such as H_2, CO, and formate into fuels, chemicals, and nutrients.

With low-cost renewable electricity becoming a reality, such a hybrid approach could provide a cost-competitive route to generate a broad variety of fuels, chemicals, and nutrients using CO_2 as a carbon feedstock. Figure 9-10 shows a hybrid approach proposed by the Bar-Even group that combines the generation of a formate intermediate followed by biological upgrading of the formate to fuels or chemicals.[44] As Bar-Even explains the formate bio-economy concept, multiple approaches could support the synthesis of formic acid and formate from available sources. Formate could be then consumed by natural formatotrophic microbes or microbes engineered to efficiently assimilate formate to produce fuels, value-added chemicals, and protein meal for animal or human consumption.



Source: Yishai, O., Lindner, S.N., Gonzalez de la Cruz, J., Tenneboim, H., and Bar-Even, A., "The formate bio-economy," *Current Opinion in Chemical Biology*, 35, (2016) p1.

Figure 9-10. *Schematic Representation of the Formate Bio-Economy Concept*

1. Technology to Market Experience

Several examples exist where companies are progressing precommercial and early commercial applications of biological conversion of CO_2.

Qualitas Health is using green algae within open pond systems to generate nutrients such as omega-3, a high-value nutraceutical product. Algenol is using green algae within a photobioreactor system based on bags to generate similar products. In addition to using natural sunlight as an energy source, artificial light photobioreactor systems that generate a specific wavelength of light using highly efficient LED light systems are also being investigated. These artificial light systems would become cost-effective as more low-cost electricity becomes available with the deployment of more renewable electricity generation resources—wind, solar, and emissions-free fossil power plants with CO_2 capture and geological storage. Pond Technologies is demonstrating that these artificial light photobioreactor systems can convert CO_2 from a cement plant to generate fish food.

LanzaTech has commercialized a gas fermentation approach. Their first commercial facility produces 46,000 tonnes of ethanol from a waste gas produced from a steel mill in China. This approach offers a path to convert waste streams from industry, society (municipal solid waste), and agriculture into fuel and chemical products.

There have been large investments in algal biofuels technologies by start-ups such as Algenol, Cellana, and Sapphire as well as established companies such as ExxonMobil and Shell. While these companies initially focused on the generation of biofuels when crude oil prices were $100/barrel, numerous start-up companies either did not survive or pivoted to the generation of higher valued products such as protein and food supplement (omega-3) when the price of oil decreased to less than $40/barrel.

What follows is a list of companies and the type of biological conversion process they are pursuing along with brief assessments of the successes and challenges of each.

a. Photosynthetic Processes

ExxonMobil has partnered with Synthetic Genomics to develop algae capable of generating high yields of oil from CO_2, water, and sunlight. This partnership also announced that they are moving from the research and development (R&D) phase to the engineering phase and will begin conducting open pond studies in the next few years.

Qualitas Health is currently operating two algae farms using open pond technologies. At the Imperial Farm in Texas there are 45 acres of cultivation area and another 98 acres at the Columbus, New Mexico, site. Qualitas Health is also marketing two products: omega-3 and AlmegaPL (a high-quality EPA-rich omega-3).

Algenol has photobioreactor technologies that use bags, sunlight, and stack gases. Algenol is using this technology to generate blue-green algae that is capable of generating a range of all-natural products.

Pond Technologies uses an artificial light photobioreactor to grow algae from CO_2 that is used to produce fish food and algae-based superfoods, like spirulina and chlorella, that provide nutritious, vegan supplements for human consumption. Pond has a 20,000-liter demonstration unit that uses off-gas from a cement plant.

Global Microalgae and Cellana employ flue gas as their source of CO_2 and the U.S. Department of Energy is funding two projects using coal-derived flue gas. For one project, the University of Kentucky is Partnering with Duke Energy, and at the other, MicroBio Engineering is partnering with Orlando PUC.

Sapphire Energy developed open pond algae technology for the generation of oils for fuel production. The company built and operated the world’s first commercial demonstration algae-to-energy facility near Columbus, New Mexico. Several demonstrations were conducted using oil generated from Sapphire technology, including test flights conducted by Continental Airlines and Japan Airlines. Between 2008 and 2012, the company raised more than $244 million in funding from investors and received $104.5 million via government grants and loan guarantees. However, by 2017, with crude oil prices at around $50/barrel—half the price of the late 2010s—Sapphire Energy ceased to exist. In 2017, it was bought by a farmer for pennies on the dollar.

Joule Unlimited developed genetically engineered cyanobacteria to produce diesel fuel or gasoline with only sunlight, water, and carbon dioxide. After raising more than $200 million in funding in 2007, plans for a commercial plant near Hobbs, New Mexico, were scrapped and the company was shut down in 2017 due to the decline in oil prices.

b. Nonphotosynthetic Processes (Gas Fermentation)

LanzaTech has commercialized a gas fermentation technology for the generation of ethanol and butanediol from CO-rich streams (steel mill off-gases) using a proprietary microbe in the family of acetogens (a gas-fermenting organism). LanzaTech has taken advantage of stack gases rich in CO, such as those from steel production, to develop and commercialize their gas fermentation technology beginning with ethanol as their first production plants to convert emissions from these processes to fuels and chemicals. Other facilities that use solid waste streams from agriculture and municipal waste employ gasification to produce a syngas that can be converted by gas fermentation to fuels and chemicals are also in development. LanzaTech has developed a specialized flow-through reactor system that effectively contacts the CO rich off-gas with their microbes.

LanzaTech has successfully started its first plant in China with a stated capacity of 46,000 tonnes of ethanol and has commercial units under construction in Europe, India, South Africa, and the United States. The company has developed a comprehensive genetic engineering capability for its gas fermenting microbial chassis. This has enabled the modification of its proprietary organism to facilitate the production of chemical products from the gas streams that it can access. LanzaTech has also demonstrated and certified a technology to further upgrade ethanol to jet fuel using a catalytic process technology.

Use of combined gases streams (H_2 and CO_2) has been demonstrated in the lab for gas fermentation by

NovoNutrients, which produces a high-protein aquafeed product.

INEOS Bio built and operated an 8-million-gallon-per-year semi-commercial facility as a joint venture with New Planet Energy Holdings, LLC. This facility used a gas fermentation technology to convert municipal solid waste and cellulosic feedstocks into ethanol. The facility was also capable of producing up to 6 MW of electricity. The facility was commissioned in 2012 and INEOS claimed production of ethanol in 2013. In 2014, the company announced a major turnaround as it was discovered that little to no ethanol was produced due to the production of low levels of hydrogen cyanide. The installation of wet scrubbers to remove the hydrogen cyanide was expected to solve this problem. In 2016, INEOS announced it was selling its ethanol business because the market for ethanol had changed and the economic drivers for its technology were no longer aligned with its strategic objectives. The Vero Beach facility was sold in early 2018 to a consortium led by Texas-based Frankens Energy.[45]

Coskata was incorporated in 2006 to develop a gas fermentation technology to generate ethanol from gas generated via the gasification of wood chips. The company operated a semi-commercial pilot plant in Madison, Pennsylvania, but in 2015, the company went out of business. Coskata's technology formed the basis of a new company, Synata Bio, but the technology has not been scaled further.

c. Microbial Electrosynthesis

Currently, microbial electrosynthesis research and development is found primarily in either academic or government laboratories.

d. Hybrid Approaches

Hybrid approaches that combine the concept of using electrochemical techniques to generate reactive intermediates from CO_2 followed by the biological conversion of the generated reactive intermediates to valued-added projects has been the subject of research conducted by academia and government labs. The nearest term commercial approach would be the electrochemical conversion of CO_2 to CO followed by conversion using gas fermentation technology such as the technology being commercialized by LanzaTech.

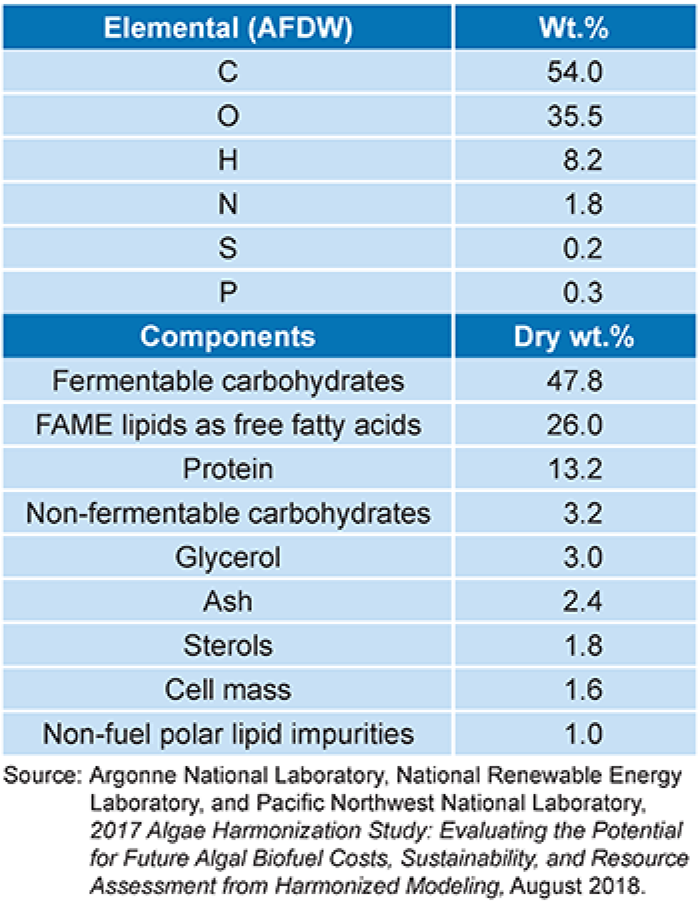
e. Energy Extraction Technologies

Several efforts using CO_2 as a solvent in various extraction or synthesis processes have been launched. Examples include using supercritical CO_2 for botanical and plant oil extraction by Apeks Supercritical and Natac, respectively. Further, using supercritical CO_2 as a solvent in the synthesis of metal-organic frameworks has been proposed by ACSYNAM. The production of graphitic carbon for use in lithium-ion batteries via the electrochemical separation of CO_2 was proposed by Saratoga Energy Research Partners, LLC. SuperCritical Technologies is working toward using supercritical CO_2 power cycles to simplify power generation. In addition to resource extraction, using CO_2 in energy extraction is being evaluated. TerraCOH has been exploring the potential for using CO_2 as a working fluid—an alternative to water—in enhanced geothermal systems. These are just a few examples of current commercialization efforts related to using CO_2 for energy and resource recovery.

2. Product Options

An advantage of microalgae is their ability to produce a range of products with differing values, providing a stepwise path to market entry. Some of those products, such as astaxanthin, a nutraceutical, command prices near $1 million per ton because their polyunsaturated fats and protein content have intermediate value as feed supplements.

Table 9-2 shows the composition of a genus of high-carbohydrate algae called Scenedesmus.[46] This analysis shows a fatty-acid-methyl-ester lipid content of 26% and fermentable carbohydrates of 47.8%. The extracted lipids from green algae may be processed to biodiesel through transesterification and esterification, which involves reacting the oils with short-chain alcohols. Alternatively, the algae oil may be hydrogenated with hydrogen in a catalytic reactor to generate renewable diesel. Renewable diesel may be further processed in a catalytic isomerization process to generate a renewable jet fuel. The fermentable carbohydrates can be extracted and used for fermentation of fuels such as ethanol, isobutanol, or the higher valued products such as succinic acid.



Elemental (AFDW)	Wt.%
C	54.0
O	35.5
H	8.2
N	1.8
S	0.2
P	0.3
Components	**Dry wt.%**
Fermentable carbohydrates	47.8
FAME lipids as free fatty acids	26.0
Protein	13.2
Non-fermentable carbohydrates	3.2
Glycerol	3.0
Ash	2.4
Sterols	1.8
Cell mass	1.6
Non-fuel polar lipid impurities	1.0

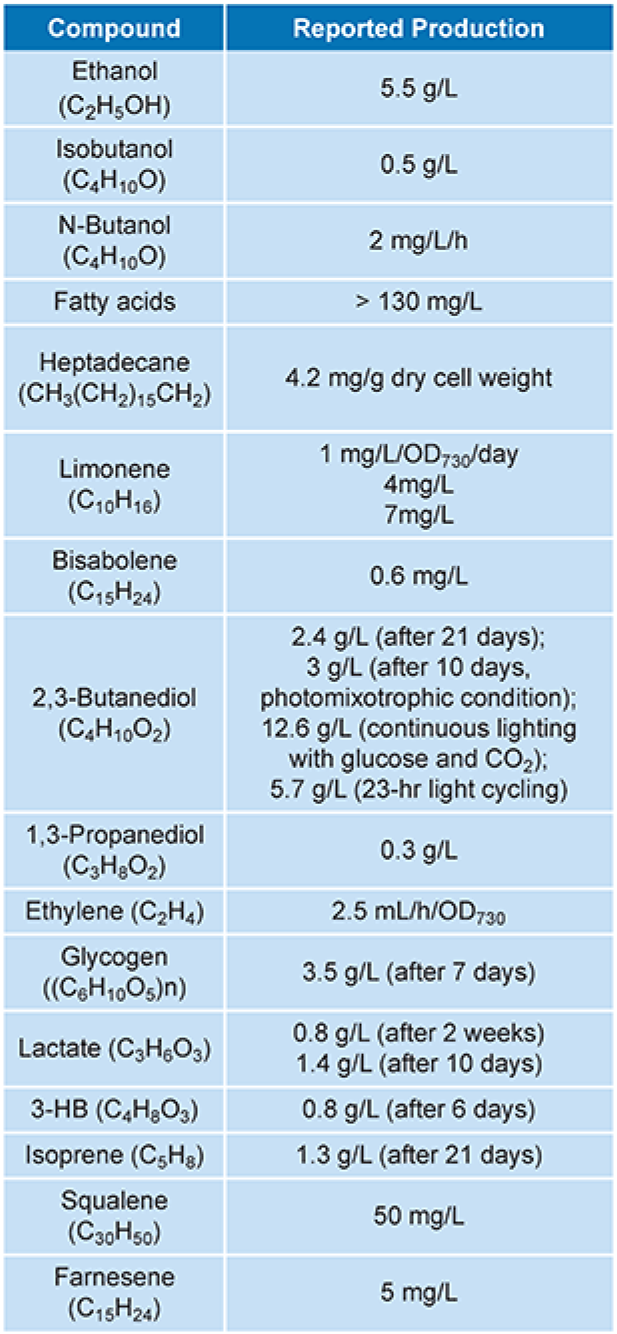
Source: Argonne National Laboratory, National Renewable Energy Laboratory, and Pacific Northwest National Laboratory, *2017 Algae Harmonization Study: Evaluating the Potential for Future Algal Biofuel Costs, Sustainability, and Resource Assessment from Harmonized Modeling*, August 2018.

Table 9-2. *Elemental and Component Compositions Based on High-Carbohydrate Scenedesmus Biomass*

Green algae has an amino acid profile that compares favorably with common food protein and could be an attractive source of dietary protein as animal feed and for human consumption. Green algae is also an attractive source of polyunsaturated fatty acids (omega-3)—eicosapentaenoic acid and docosahexaenoic acid). Omega-3 fatty acids have a place in the consumer market, currently dominated by fish oils, as nutraceutical products.

Table 9-3 shows a summary of commodity chemicals and fuels that can be generated from CO_2 using cyanobacteria.

The fuels and fuel precursors that can be produced include ethanol, butanol, fatty acids, heptadecane, limonene, and bisabolene. Chemicals that can be produced include 2,3-butanediol, 1,3-propanediol, ethylene, glycogen, lactate, 3-hydroxypropionic acid, isoprene, squalene, and farnesene.



Compound	Reported Production
Ethanol (C_2H_5OH)	5.5 g/L
Isobutanol ($C_4H_{10}O$)	0.5 g/L
N-Butanol ($C_4H_{10}O$)	2 mg/L/h
Fatty acids	> 130 mg/L
Heptadecane ($CH_3(CH_2)_{15}CH_2$)	4.2 mg/g dry cell weight
Limonene ($C_{10}H_{16}$)	1 mg/L/OD_{730}/day 4mg/L 7mg/L
Bisabolene ($C_{15}H_{24}$)	0.6 mg/L
2,3-Butanediol ($C_4H_{10}O_2$)	2.4 g/L (after 21 days); 3 g/L (after 10 days, photomixotrophic condition); 12.6 g/L (continuous lighting with glucose and CO_2); 5.7 g/L (23-hr light cycling)
1,3-Propanediol ($C_3H_8O_2$)	0.3 g/L
Ethylene (C_2H_4)	2.5 mL/h/OD_{730}
Glycogen ($(C_6H_{10}O_5)n$)	3.5 g/L (after 7 days)
Lactate ($C_3H_6O_3$)	0.8 g/L (after 2 weeks) 1.4 g/L (after 10 days)
3-HB ($C_4H_8O_3$)	0.8 g/L (after 6 days)
Isoprene (C_5H_8)	1.3 g/L (after 21 days)
Squalene ($C_{30}H_{50}$)	50 mg/L
Farnesene ($C_{15}H_{24}$)	5 mg/L

Source: National Academies of Sciences, Engineering, and Medicine. (2019). *Gaseous Carbon Waste Streams Utilization: Status and Research Needs.* Washington, DC: The National Academies Press.

Table 9-3. *Commodity Chemicals and Fuels That Are Currently Synthesized from CO_2 from Cyanobacteria and Their Reported Production*

Phytonix Solar Chemicals in Black Mountain, North Carolina, uses genetically engineered cyanobacteria to produce longer chain alcohols, including 1-octanol, which are considered to be a biodiesel.

Bench-top scale experiments have shown that MES technologies can generate ethanol, acetic acid, and butyric acid at low levels while products generated from a hybrid approach with gas fermentation as the biological step would generate ethanol, 2,3-butanediol, isopropanol, as well as potentially generating higher valued chemicals.

IV. LIFE-CYCLE ANALYSIS

The importance of accurate and rigorous life-cycle analyses on CO_2 use cannot be overstated. There is considerable thermodynamic difficulty in capturing CO_2 and then converting this CO_2 into a saleable product via processes that require significant energy input. Given that the primary driver of CO_2 use is to reduce or eliminate net carbon emissions to the atmosphere, it is necessary to approach all carbon capture and use (CCU) applications with life-cycle analyses in mind to determine and quantify a realistic reduction in CO_2 emissions for a product or process.

Life-cycle analysis needs to address the direct and indirect impacts from CO_2 emissions. Direct impacts are those associated with the long-term sequestration of CO_2, which is based on the assumption that the CO_2 will not be re-released to the atmosphere. CCU takes credit for the CO_2 that is permanently embedded in the product or process minus the CO_2 that is emitted upstream (mining, transport, processing). Indirect impacts are those claimed due to the potential replacement of an existing product or value chain.

For products such as CO_2-fuels or some chemicals (urea), the CO_2 storage time is very short, ranging from a few days to a few months. Short storage times have no impact on the atmospheric concentration of CO_2, so life-cycle analyses of these types of products can realistically only claim credit for indirect impacts on emissions.[47]

For products like construction aggregates or oil from CO_2 enhanced oil recovery (EOR), life-cycle analyses account for direct and indirect impacts because the CO_2 is sequestered for longer period of times (from centuries to thousands of years) and the CO_2-based product could also replace conventional fossil fuel value chains.[48,49,50,51]

For other products, like chemical intermediates or CO_2-based polyurethanes or polyols, there is debate on what their CO_2 storage time is and its impact on net CO_2 emissions. Current life-cycle analyses of polyols in the literature consider the storage time to be too short to claim direct impacts, and thus only account for indirect impacts.[52,53] However, the lifetime of a plastic item varies from days to decades depending upon the item’s application and end-of-life management practices—recycling, landfilling, incinerating. It is expected that the CO_2 storage time for some applications could be extended well beyond 50 years through recycling.

Thus, differences in the types of CCU products, expected market sizes, and how direct and indirect impacts are accounted for have resulted in a broad range of values for the potential of CCU as a net carbon emissions reduction option.[54,55,56,57] For these reasons, a life-cycle analysis effort similar to the National Energy Technology Laboratory's Bituminous Baseline Reports is suggested, which provides transparent metrics and a standard analysis for determining the cost associated with carbon capture technologies deployed on a variety of fossil fuel power plants. While the reports do not cover every conceivable outcome and are a representation of a typical technology deployment, they are a useful and valuable tool in determining the various sensitivities of technologies and for making relative comparisons.

Finally, it is notable that CCU may have the opportunity to address safety and toxicity concerns associated with the current reagents used in conventional polymer production. Two teams of researchers indicated a decrease in scores for eutrophication, acidification, and toxicity, which are due to the replacement of propylene oxide by CO_2.[58,59] Another team, however, indicates that CO_2-based polymers have higher material intensity (raw material input and total material requirement) than fossil-based polymers and that balances between process safety and overall resource consumption may also be of interest for life-cycle analyses.

V. RESEARCH AND DEVELOPMENT NEEDS

It will take many technologies to address the wide range of CO_2 use pathways, and they will require support to meet the stringent requirements of transitioning from basic research to commercialization. As mentioned earlier in the chapter, the deployment of these technologies will depend on the availability of affordable renewable energy and green (water splitting) and blue (fossil-based) hydrogen sources. Thus, it is difficult to estimate the timing of commercialization for each CO_2 use technology. The high-level R&D needs are listed in the following sections and are quite specific for each conversion pathway. Finally, a consolidated R&D funding support recommendation for CO_2 use is quantified at the end of this section.

A. Thermochemical

Future study should continue to improve the selectivity, activity, and stability of the catalytic materials and include both theoretical and experimental characterization for fundamental understanding, which would help to identify mechanistic pathways. For catalysts that have proved to be active, selective, water-resistant, and cost-effective in the range of lower temperatures—such as from 373 K to 573 K where hydrogenation is more thermodynamically favored—long-term stability in catalytic performance should be examined as well as the solutions to prevent deactivation.

Other key challenges that need to be resolved for many CO_2 conversion reactions are improving selectivity to the desired products and catalyst stability with regard to by-products, such as water, and impurities in feedstocks. The latter is particularly important but is often not studied in detail when new catalysts are developed, especially in academic laboratories. Thus, joint efforts between academia and industry would be beneficial.

More laboratory research and computational study, as well as pilot-scale research and development, are required for establishing efficient and practical processes for CO_2 use to promote sustainable development and to reduce rising CO_2 emissions. Meanwhile, investigations on developing more efficient and cost-effective ways to produce H_2 from water using renewable energy is also indispensable for CO_2 hydrogenation with environmental and economic viability in the near term.

B. Electrochemical and Photochemical

The main research in this area includes the development of novel catalysts for better selectivity, activity, and stability; polymer membranes with high robustness and ionic conductivities; and novel cell or multicell stack design and manufacturing. The development of an effective cathode for CO_2 reduction is a major obstacle that has garnered much research attention. Although both homogeneous and heterogeneous catalysts for CO_2 electroreduction have been extensively studied, heterogeneous catalysts are more likely to be implemented in practical systems considering their robustness.

In the case of C_1 products, Faradaic efficiencies for CO and formic acid have been consistently high (>80%) with the majority of these catalysts being silver-based for CO production and tin-based for formic acid production. This is important because reduced Faradaic efficiencies require additional energy input to drive the reaction. If a low Faradaic reaction is coupled with a high carbon intensity energy source, then life-cycle CO_2 emissions will increase and intended carbon mitigation will not be achieved. Therefore, highly efficient pathways with low-carbon energy sources should be pursued. Alternative anodic reaction with better energetic efficiency should also be investigated.

The electrochemical and photochemical conversion pathways share similar challenges but also differ in terms of light harvesting, device design, etc. The scale up of catalysts, membrane systems, and cells would be another important R&D area.

The development of novel electrolytes that can provide high CO_2 solubility is also an important R&D area, and it has great potential to combine CO_2 capture and conversion into a single process that improves overall efficiency. The development of hybrid systems combining electrochemical and photochemical systems with thermochemical and biochemical conversion pathways will be very important for transformative technological advancements.

C. Carbonation and Cement

Carbonation has the largest potential for immediate CO_2 use and long-term sequestration. However, the barriers to entry are typically associated with colocating the CO_2 sources with the necessary mineral feedstocks. In addition, there could be resistance to adopting alternative building materials which would need to be addressed through product certification.

While the chemistry of carbon mineralization and concrete curing are relatively understood, these chemistries can be quickly complicated as the feedstock changes. Thus, deeper understanding of integrated reaction pathways, the use of chemical (ligands) and biological catalysts (carbonic anhydrase), and innovative separation of valuable products (carbonates) and by-products (metals and rare earth elements) are required for the future deployment of these technologies. The optimization of the overall reaction will also involve the advanced understanding of chemo-morphological-mechanical coupling and, thus, both modeling and experimental studies should be carried out for various carbonation feedstocks. The characterization and performance testing of produced materials for various applications ranging from paper fillers to construction materials will also be important. At larger scales of R&D, the energy and materials integration for process intensification should be investigated to ensure the net CO_2 sequestration benefit.

D. Biological

Biological conversion is slower than alternative CO_2 use pathways given the inherent kinetics of this technology. There are many pathways and corresponding TRL levels associated with biological CO_2 conversion, and progressing multiple approaches for moving biological conversion forward, in particularly for accelerating the kinetics, is worthwhile. For technologies at a lower TRL, additional research must be complemented by additional mechanisms, such as renewable fuel standards or other fiscal incentives, to create a market for biological CO_2 conversion products. Algae technologies using natural sunlight should be developed to generate high valued but low-volume nutraceuticals. Artificial light biophotoreactors technologies that are currently being commercialized should be applied to the systems with renewable electricity combined with highly efficient LED light sources for generation of algae-derived nutraceuticals, proteins, and chemicals. In both cases, light efficiency, selectivity, and associated reactor systems for the production of higher volume and the lower cost of chemicals and fuels should be investigated. Gas fermentation also has several challenges, including effective mass transfer in the gas-to-liquid phase and product separation. These challenges should be studied in both lab- and pilot-scale projects.

As discussed earlier, hybrid systems have great potential to overcome R&D challenges in each pathway. It has been suggested that CO_2 to C_1 conversion is easier via a chemical pathway while C_1 to C_2+ conversion would be easier via a biological pathway. Therefore, understanding how to combine different reactions into a single system or combined systems should be investigated in both fundamental and large-scale research projects. The integration of intermittent energy sources into a biological system would also be challenging because the time scale for biological conversion and the availability of renewable energy in a given time period may not match.

E. Multilevel R&D Funding Structure

Considering these R&D challenges and needs, this study recommends $500 million over 10 years for support of basic science. This is particularly important for CO_2 use technologies because many of them are still at a low TRL.

Fundamental research funding is very important to advance science and engineering related to these technological areas by providing enough government support. Funding for multiple principal investigator activities and center grants focused on scientific discoveries should be created. Interdisciplinary research is very important for

CO_2 technologies because they require expertise in a wide range of fundamental areas, including materials, catalysis, reaction engineering, and systems engineering. Collaborations between academia and industry should be encouraged via center grants. Previous versions of ARPA-E type funding for the acceleration of tech-to-market transitions can support academic researchers in working with industrial partners, and the New ARPA-E type funding can be awarded to start-up companies.

In addition, the study recommends a second tranche of $500 million in funding over 10 years—for years 5 to 15—to support pilots, demonstration projects, and progression toward deployment by building on successes that emerge from the earlier, basic science funding phase. To progress this, it is recommended that projects are field deployed to at least the level of the National Carbon Capture Center, Wyoming Integrated Test Center, or a similar practical demonstration environment that uses real flue gas sources in an industrial environment.

VI. CONCLUSIONS

CO_2 use offers an important set of tools for reducing carbon emissions while creating economic opportunities through the production of products that are necessary for industrialized society. Even though the near-term scale of potential reductions delivered by CO_2 use will be much smaller than can be achieved by CO_2 geologic storage (described in Chapter 7, “CO_2 Geologic Storage”) and CO_2 EOR (described in Chapter 8, “CO_2 Enhanced Oil Recovery”), there will be niche opportunities for CO_2 use to create value in markets by providing the necessary carbon-based or carbon-consuming products for advanced economies.

These opportunities should be pursued in parallel with geologic storage and EOR as a potential means to offset carbon mitigation costs while advancing the field so that CO_2 use may scale up in the coming decades. EOR and geologic storage are necessary and scalable in the near term, but for carbon emissions to continue to decrease, carbon-based products will eventually need to be sourced from CO_2 rather than fossil fuel feedstocks—unless those feedstocks are low carbon from the application of CCUS. This will require a significant investment in RD&D, time, and increasing knowledge resources.

The four main types of CO_2 use technologies—thermochemical, electrochemical and photochemical, carbonation, and biological conversion—are all worthy of progression because not every pathway will be feasible in all regions. Many considerations, such as local environmental factors, markets, and access to affordable low-carbon energy sources will be present domestically and abroad in various ratios. For this reason, it is necessary to consider all approaches without prematurely defining winners because certain technologies may prove to be beneficial domestically while others may prove themselves in export markets.

Through continued investment, a nearly limitless array of products can potentially be brought to market via a number of CO_2 use pathways. The engineered use of CO_2 as a feedstock can impact a wide range of carbon-based products such as fuels, fertilizers, polymers, industrial chemicals, building materials such as carbonates and cements, carbon nanotubes, and other products that are critical to the global economy.

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APPENDICES

Appendix E:
Mature CO_2 Capture Technologies

Appendix F:
Emerging CO_2 Capture Technologies

Appendix G:
CO_2 Enhanced Oil Recovery Case Studies

Appendix H:

CO_2 Enhanced Oil Recovery Economic Factors and Considerations

Appendix E

MATURE CO_2 CAPTURE TECHNOLOGIES

I. INTRODUCTION

This appendix describes the absorption carbon dioxide (CO_2) capture technology known as amine scrubbing. Amine scrubbing is a mature absorption technology, one that has been practiced and refined at-scale for more than 40 years.

II. ABSORPTION: AMINE SCRUBBING

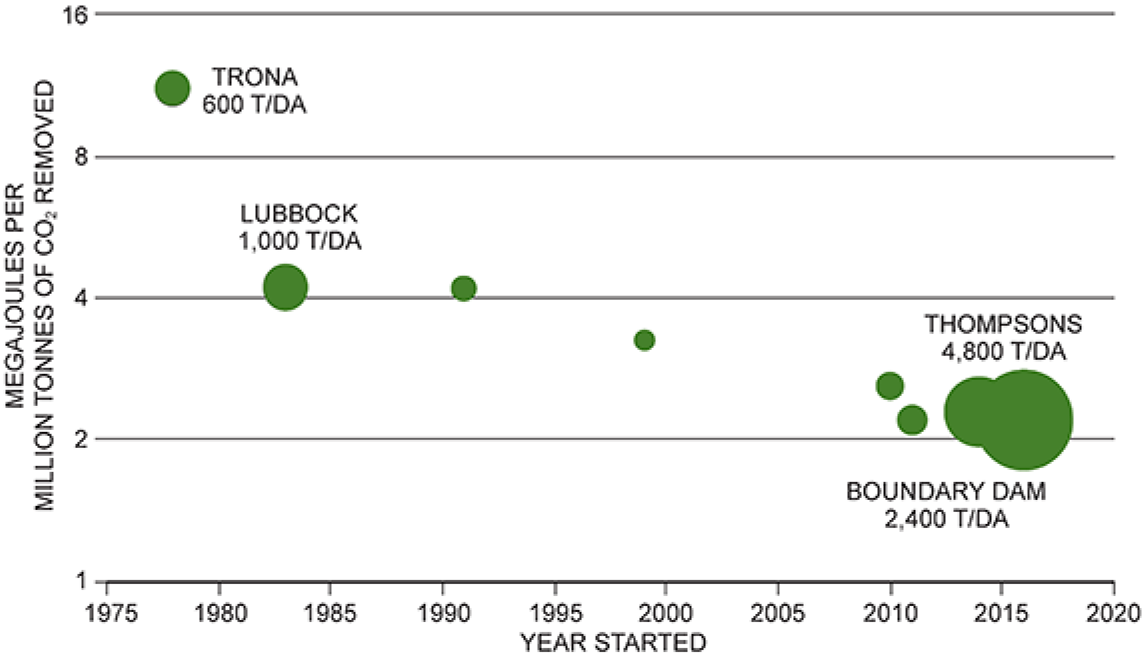
A. Introduction

This appendix reviews the technical results and opportunities for improving conventional aqueous amine scrubbing for CO_2 capture, based in large part on Rochelle.[1] The history of conventional amine scrubbing includes more than 30 applications on flue gas from gas combustion and six on flue gas from coal. Improvements in the process design and solvent selection have resulted in continuous reduction of energy use and capital cost. By analogy to the development of limestone slurry scrubbing for flue gas desulfurization, amine scrubbing has been and will continue to be the technology of choice for CO_2 capture.

Important process improvements have been developed for absorber intercooling and stripper configurations. New solvents have been selected and developed based on four energy properties: absorption rate, capacity, heat of absorption, and maximum temperature from thermal degradation. Other important solvent properties include resistance to oxidation, nitrosamine formation, amine aerosol formation, and amine volatility.

B. History

Improvements in energy consumption have been made over time. Figure E-1 shows the heat duty of select commercial units using capture on combustion gases from 1976 to the present. At Lubbock in 1983 the reboiler duty decreased with the substitution of 30% monoethanolamine (MEA) for 20% MEA. At the Mitsubishi Heavy Industries (MHI) plant in 1999, 30% MEA was replaced with KS-1 (an MHI amine). At a newer MHI plant in 2009, additional energy savings resulted from stripper process modifications.[2] The Cansolv plant at Boundary Dam (start-up in 2014) achieved energy savings with a new solvent and the use of lean vapor compression at the stripper.

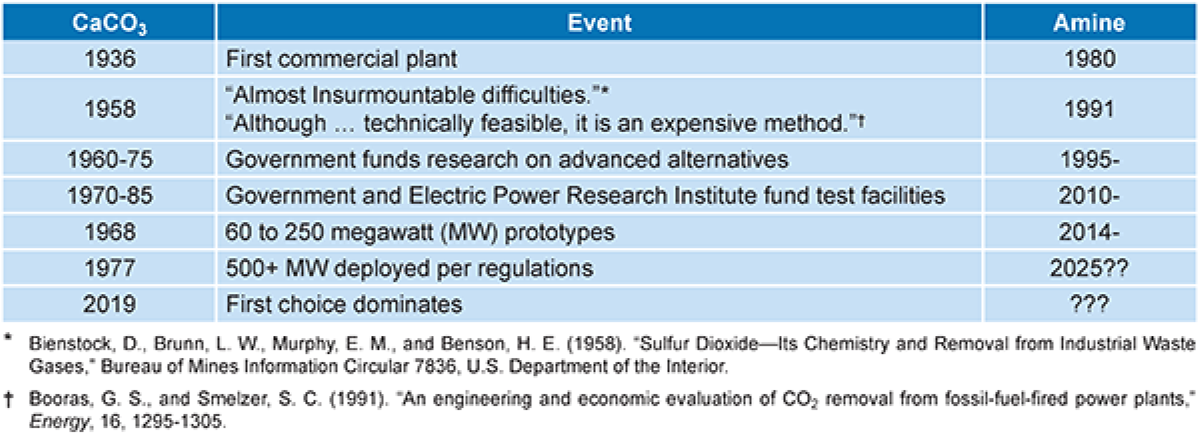


Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at 12th Greenhouse Gas Control Technologies Conference, Austin, Texas.

Figure E-1. *Heat Duty of Notable Commercial Units for CO_2 Capture by Amine Scrubbing*

C. Analogy to Limestone Slurry Scrubbing

Table E-1 compares the development timeline of limestone slurry scrubbing for flue gas desulfurization to that of amine scrubbing for CO_2 capture. They were both identified as the initial technology of choice. However, because of technical difficulties and high cost projections, research and development (R&D) activities focused on advancing promising alternatives. Limestone slurry scrubbing is now the dominant technology for flue gas desulfurization. It is probable that amine scrubbing will be the primary technology for CO_2 capture from coal-fired power plants and possibly for other applications as it already has a higher technology readiness levels. However, it is possibly not the blanket solution for application in other sectors since chemical approaches are only necessary for low CO_2 concentrations (i.e., <15%) as mentioned in Chapter 5.



$CaCO_3$	Event	Amine
1936	First commercial plant	1980
1958	"Almost Insurmountable difficulties."* "Although ... technically feasible, it is an expensive method."†	1991
1960-75	Government funds research on advanced alternatives	1995-
1970-85	Government and Electric Power Research Institute fund test facilities	2010-
1968	60 to 250 megawatt (MW) prototypes	2014-
1977	500+ MW deployed per regulations	2025??
2019	First choice dominates	???

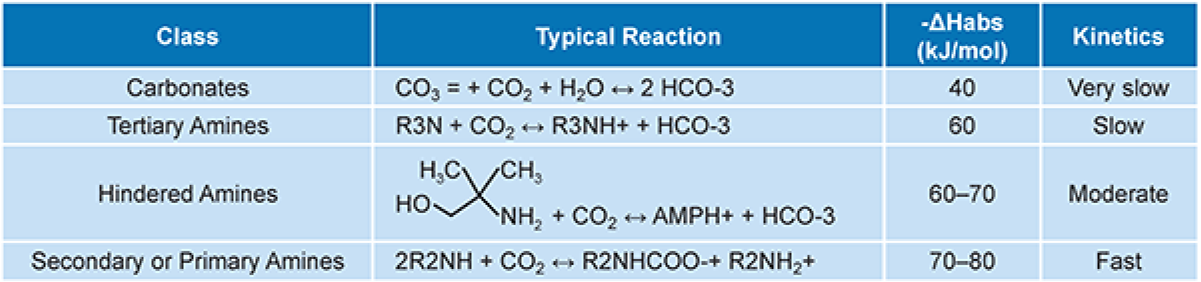
* Bienstock, D., Brunn, L. W., Murphy, E. M., and Benson, H. E. (1958). "Sulfur Dioxide—Its Chemistry and Removal from Industrial Waste Gases," Bureau of Mines Information Circular 7836, U.S. Department of the Interior.

† Booras, G. S., and Smelzer, S. C. (1991). "An engineering and economic evaluation of CO_2 removal from fossil-fuel-fired power plants," *Energy*, 16, 1295-1305.

Table E-1. *History Repeats in the Development of Limestone Slurry Scrubbing and Amine Scrubbing*

D. Basic Chemistry and Rates

Four classes of aqueous solvents can be considered for CO_2 absorption/stripping (Table E-2): carbonates, tertiary amines, hindered amines, and secondary or primary amines.



Class	Typical Reaction	-ΔHabs (kJ/mol)	Kinetics
Carbonates	CO_3 = + CO_2 + H_2O ↔ 2 HCO-3	40	Very slow
Tertiary Amines	R3N + CO_2 ↔ R3NH+ + HCO-3	60	Slow
Hindered Amines	H_3C CH_3 HO NH_2 + CO_2 ↔ AMPH+ + HCO-3	60–70	Moderate
Secondary or Primary Amines	2R2NH + CO_2 ↔ R2NHCOO-+ R2NH_2+	70–80	Fast

Table E-2. *Alternative Aqueous Amine Chemistry*

These four differ in heat of CO_2 absorption, kinetics of CO_2 absorption, and intrinsic CO_2 stoichiometry. Hot potassium carbonate is offered in a process by Honeywell UOP. It operates isothermally near 100ºC with pressure swing regeneration; its low heat of absorption is unfavorable for thermal swing regeneration. Tertiary amines such as methyldiethanolamine (MDEA) are used in blends with rate promoters such as piperazine (PZ). Hindered amines such as aminomethylpropanol (AMP) can be used alone or in combination with rate promoters. Secondary or primary amines such as MEA and PZ can be used alone or as rate promoters with tertiary amines, hindered amines, or potassium carbonate.

Water is an essential component of these amine solvents. In the absence of other constraints such as solid precipitation, the water concentration is optimized to trade off viscosity and the intrinsic CO_2 capacity. Lower viscosity enhances the heat and mass transfer performance. Water also provides stripping steam in the regeneration, which permits operation at greater pressure. In the simple stripper, water in the stripper overhead reduces energy performance. However, regeneration configurations, such as the advanced flash stripper, eliminate this disadvantage. Furthermore, polar solvents will always contain water from the flue gas. Therefore, it is not reasonable to suggest that solvents with little or no water will necessarily be better than conventional aqueous solvents.[3]

E. Simple Flowsheet

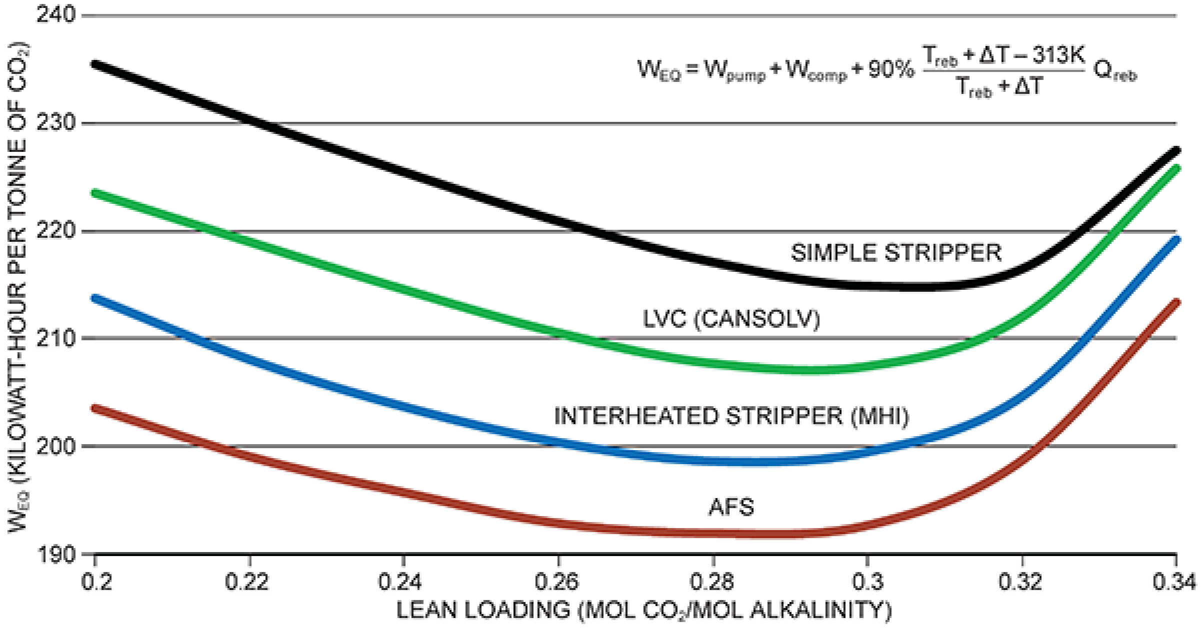
The amine scrubbing process relies upon thermal swing regeneration, which works best with lower absorber temperature and greater stripper temperature. In the conventional process the inlet flue gas and lean solvent would be cooled to 30ºC to 40ºC with cooling water or ambient air. The stripper temperature (and pressure) would be limited by the thermal degradation of the solvent or by the conveniently available temperatures of the condensing steam or other heat source.

The energy use of the amine scrubbing process can be as much as 50% of the annualized process cost. In a power plant, as much as 40% of the steam may be extracted from the power cycle at 3 to 6 bar for use in the reboiler. Electricity will be used to compress the CO_2 to a final pressure of 100 to 150 bar. The total loss of electricity production may be approximated as equivalent work (W_{EQ}) by the relationship:

$$W_{EQ} = W_{pump} + W_{comp} + 90\% \frac{T_{reb} + \Delta T - 313K}{T_{reb} + \Delta T} Q_{reb}$$

The effect of reboiler duty on the electricity burden is represented by a Carnot efficiency that increases with the condensing temperature of the steam, including a ΔT for the reboiler (5ºC to 10ºC) and 90% efficiency for the turbine.

Figure E-2 shows that the selected lean loading can be used to minimize equivalent work. At higher lean loading, the working capacity is reduced and the sensible heat requirement increases. At lower lean loading, more steam is required to strip the solvent. Lower lean loading also enhances the rate behavior of the absorber.

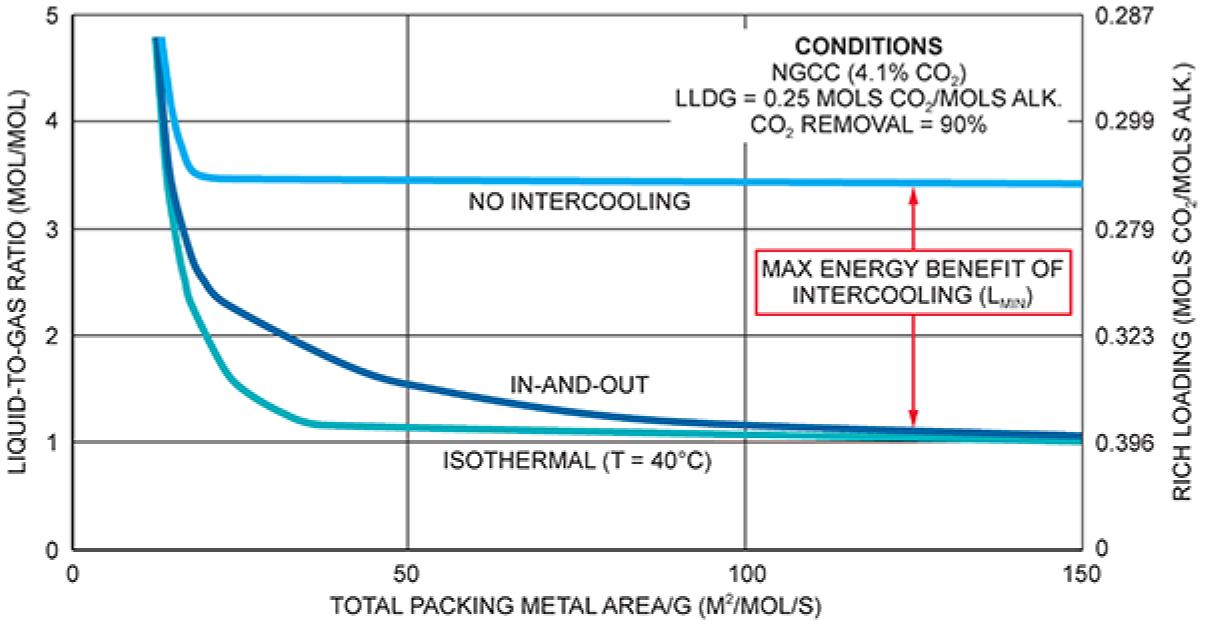


Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at 12th Greenhouse Gas Control Technologies Conference, Austin, Texas.

Figure E-2. *Electricity Burden with Alternative Stripper Configurations. 8 m PZ, 150°C, 150 bar CO_2, Wmin = 113 kilowatt-hour per tonne CO_2*

F. Advanced Absorption

Figure E-3 shows the tradeoff between the total packing area (capital cost) and the solvent rate (rich loading, energy performance). At a given lean loading and infinite packing area, there is a minimum solvent rate or liquid-to-gas ratio (L/G ratio).[4] As in the common distillation process, the economic optimum packing area probably occurs at the solvent rate between 1.1 and 1.3 times the minimum rate.



Source: Sachde, D. J. and Rochelle, G. T. (2014). "Absorber Intercooling Configurations using Aqueous Piperazine for Capture from Sources with 4 to 27% CO_2," *Energy Procedia*, 63, 1637-1656.

Figure E-3. *Effect of Intercooling on Packing Area, 8 m PZ*

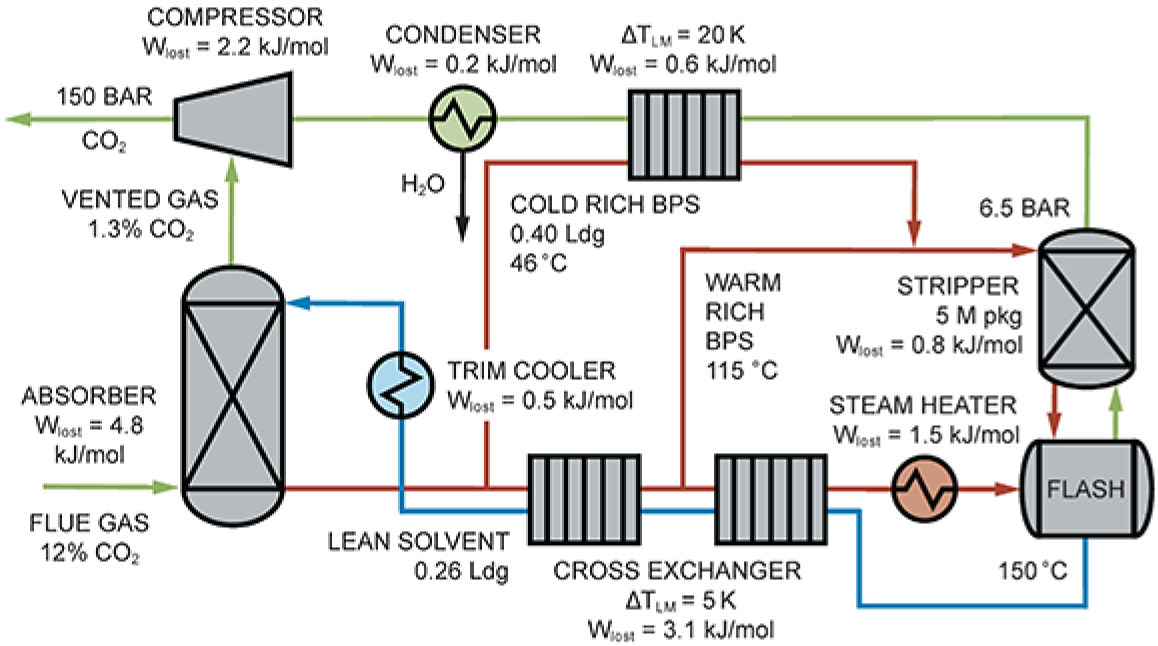
CO_2 absorption is an exothermic reaction which results in a temperature bulge (temperature increase) in the absorber. In many cases, intercooling may be used to reduce the absorber packing cost and increase the rich loading. Figure E-3 shows that the effect of intercooling on required packing area is significant even at lower lean loading. More complex intercooling configurations such as pump around the bottom section of packing may be useful at lean loading greater than a critical value.[5]

The contractor design for the absorber for CO_2 capture has improved from that used for acid gas treating. The larger demonstrations of CO_2 capture use modern structured packing with larger a corrugation angle to minimize pressure drop while maintaining equivalent wetted area for mass transfer.[6] The earliest absorbers in capture systems were round, carbon steel vessels. Boundary Dam uses a rectangular concrete absorber. The MHI design at Thompsons uses a rectangular metal absorber to treat 240 MW of coal-fired flue gas. Full-scale commercial designs will probably use a single rectangular absorber to treat all of the flue gas from one boiler.

G. Advanced Regeneration Systems

The simple stripper loses efficiency because of water vapor that passes overhead and is condensed with no heat recovery. Numerous process configurations have been proposed and tested to address this weakness. Figure E-2 compares the energy performance of the three most significant stripper enhancements to that of simple stripping. Large scale commercial applications of amine scrubbing will probably utilize these or similar configurations to enhance energy performance. The interheated stripper is an important part of the Energy Saving Process (ESP) used by MHI in several smaller commercial units and was likely adopted for the 240 MW plant at Thompsons. Lean vapor compression (LVC) is included with the Boundary Dam project. It has been tested in several pilot plants including the Fluor process at Wilhelmshaven.

Figure E-4 gives an energy analysis with the advanced flash stripper using piperazine. This configuration has been successfully tested in pilot plants at the University of Texas and the National Carbon Capture Center.[7,8] Rich solvent with a loading of 0.4 mol/equivalent PZ is fed to two cross exchangers in series with a convective steam heater to the sump of the stripper. The hot lean solution is returned through the exchangers. Cold rich solvent is bypassed through an exchanger to recover latent and sensible heat from the CO_2 product. Warm rich solvent is extracted between the exchangers near its bubble point temperature at the pressure of the stripper, then combined with the heated cold rich bypass and fed to the top of the stripper to recover the latent heat of water from the primary flash.

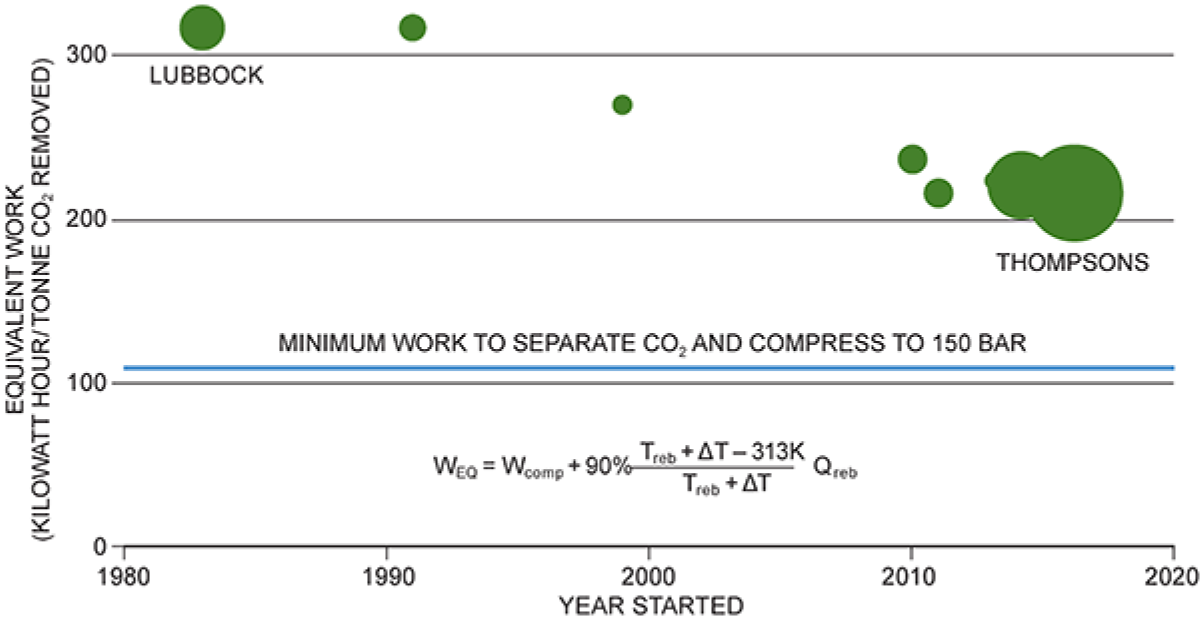


Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at 12th Greenhouse Gas Control Technologies Conference, Austin, Texas.

Figure E-4. *Lost Work with the Advanced Flash Stripper (8 m PZ),* $W_{EQ} = 31.1$ *kJ/mol,* $W_{min} = 18$ *kJ/mol,* $W_{lost} = 13.7$ *kJ/mol*

Because the advanced flash stripper is optimized by adjusting the rates of cold and warm bypass, it is able to recover practically all of the heat in the stripper overhead. Therefore, most of the exergy is lost in tradeoffs of capital cost with work loss. Exergy is lost in the absorber (4.8 kJ/mol) with the driving force for absorption; this is ultimately a tradeoff of packing capital cost and energy lost. Approximately 3.1 kJ/mol is lost in the cross-exchanger with the heat transfer ΔT, a tradeoff of exchanger area capital cost and energy. Roughly 2.2 kJ/mol is lost in the intercooled, adiabatic compressor, perhaps to be minimized by operating the stripper at greater T/P. Around 1.5 kJ/mol is lost with the ΔT in the steam heater, mostly a tradeoff of heater capital with work loss.

Figure E-5 shows that the electricity burden with advanced amine scrubbing is approaching the minimum work (113 kWh/tonne CO_2 removed) required to separate and compress the CO_2 to a pressure of 150 bar. The advanced flash stripper is expected to reduce this burden by another 4%, but these process innovations are producing diminishing returns. It is possible to expect ultimate requirement of 200 kWh/tonne, with a thermodynamic efficiency of 56%, but there is little room left for reduction of the electricity burden.



Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at Greenhouse Gas Control Technologies 12, Austin, Texas.

Figure E-5. *Electricity Burden of Commercial Units*

H. Energy Criteria for Solvent Selection

Four solvent properties dominate the selection of solvents based on energy performance—working capacity of the solvent, its CO_2 absorption rate, heat of CO_2 absorption, and thermal degradation. With an advanced process configuration, each of these solvent properties is tied to an important capital cost/energy use tradeoff.

Solvent capacity for CO_2 determines the capital cost and energy loss of the cross exchanger. The rate of CO_2 absorption determines the absorber packing requirement and loss of work as driving force. The heat of CO_2 absorption and maximum operating temperature determine the compressor, reboiler, and stripper capital cost and lost work.

1. Capacity

The capital and energy cost of the cross exchanger depend on the working capacity of the solvent through a trade-off of the exchanger size and approach temperature. The effect of solvent capacity would be eliminated with an infinitely large exchanger, but that would result in a prohibitive capital cost.

At the optimum conditions of a plate-and-frame exchanger, the energy cost and the capital cost depend on the working capacity of the solvent and its important heat transfer properties as given by the normalized working capacity of the solvent, ΔC_{norm} (mol CO_2/kg solvent):[9]

$$\Delta C_{norm} = \Delta C_{solv}\left(\frac{k}{k_{5\,m\,PZ}}\right)^{0.325}\left(\frac{C_p}{C_{p,5\,m\,PZ}}\right)^{-0.825}\left(\frac{\mu}{\mu_{5\,m\,PZ}}\right)^{-0.175}$$

The working capacity of the solvent (ΔC_{solv}, mol CO_2/kg solvent) must be estimated with adjustment for the performance of the absorber. A consistent rich loading for all solvents can be estimated as the loading that gives an equilibrium partial pressure of 5 kPa at 40ºC. This gives a reasonable driving force at the bottom of an absorber with an inlet at 40ºC and 12% CO_2 (coal flue gas). The lean loading can be estimated as that which gives an equilibrium partial pressure of 0.5 kPa at 40ºC. With 90% CO_2 this condition gives the same relative driving force, is achievable using intercooling with most solvents, and frequently minimizes the energy requirement of the stripper.

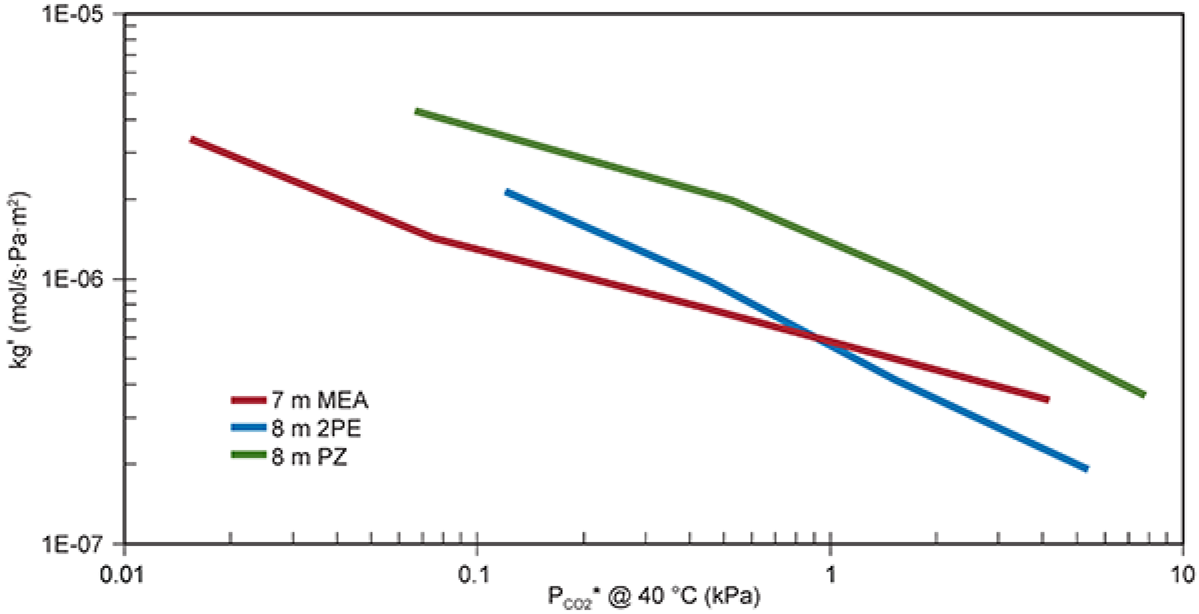
2. CO_2 Absorption Rate

CO_2 is usually absorbed into aqueous amine by the mechanism of mass transfer with fast reaction in the liquid boundary layer. The liquid film resistance for mass transfer in MEA can be expressed in terms of the CO_2 partial pressure driving force by:[10]

$$\frac{1}{k_g'} = \frac{\gamma_{CO2}^{0.5} H_{CO2,\,H2O}}{\sqrt{k\gamma^2{}_{MEA}[MEA]_i^2\, D_{CO2}}} + \frac{1}{k_{l,prod}^o}\left(\frac{\Delta P_{CO2}^*}{\Delta[CO_2]_T}\right)$$

At normal absorption conditions the absorption rate does not depend on $k^o_{l,prod}$ (a function of packing properties and fluid mechanics) but it does depend on the square root of the kinetics (a property of the solvent). The important property of the packing is the wetted area.

As shown in Figure E-6, kg’ decreases with increasing equilibrium CO_2 partial pressure over the solution, which is a surrogate for the CO_2 loading.



Source: Chen, X. "Carbon Dioxide Thermodynamics, Kinetics, and Mass Transfer in Aqueous Piperazine Derivatives and Other Amines," (Ph.D. dissertation, University of Texas at Austin, 2011).

Figure E-6. *Normalized CO_2 Absorption Rate at 40°C Measured by Wetted Wall Column*

The kinetics of CO_2 reaction with primary and secondary amines can be given by the base-catalyzed mechanism:[11]

$$r_{CO2} = -\sum k_B[B]Amine[CO_2]$$

The base, B, can be water, the parent amine, or another amine species.

The CO_2 reaction rate with tertiary amines is much slower. This reversible fast reaction must occur in the boundary layer or bulk solution to provide a route to the equilibrium concentration of bicarbonate. Usually tertiary amines for CO_2 capture are used with a rate promoter such as a primary or secondary amine.

3. Heat of CO_2 Absorption

Greater heat of CO_2 absorption (ΔH) will improve the energy performance of amine scrubbing with thermal swing regeneration because the vapor pressure of CO_2 (P^*_{CO2}) increases with temperature (T) and the heat of absorption, as explained by the Clausius-Clapeyron relationship:

$$\frac{d\ln(P^*_{CO2})}{d\frac{1}{T}} = -\frac{\Delta H}{R}$$

Greater stripper temperature (and pressure) will also be beneficial in many cases.

Two components of the reboiler heat duty go in opposite directions with the heat of absorption. The heat duty in mol steam/mol CO_2 removed (S_{rxn}) will be directly proportional to the heat of CO_2 absorption (ΔH_{CO2}):

$$S_{rxn} = {}^{\Delta H_{CO_2}}\!\big/_{\Delta H_{H_2O}}$$

The heat duty associated with the stripping steam (S_{H_2O}) will decrease with increasing heat of CO_2 absorption:

$$S_{H_2O} = \left[\frac{H_2O}{CO_2}\right]_A EXP\left[\frac{-(\Delta H_{CO2} - \Delta H_{H2O})}{R}\left(\frac{1}{T_A} - \frac{1}{T_S}\right)\right]$$

The pressure of the stripper (P_{CO2}) will also increase with the heat of CO_2 absorption:

$$P_{CO2} = P_{CO2,lean\ abs} \exp\left(\frac{\Delta H_{CO2}}{R}\left[\frac{1}{313} - \frac{1}{T_{max}}\right]\right)$$

$$P_{total} = P_{CO2} + P_{H2O}\ (T_{max})$$

The maximum temperature of the stripper (T_{max}) will usually be determined by the thermal degradation of the solvent. Compression work will be reduced at greater P_{total}/greater T_{max}. Greater stripper temperature will require greater steam temperature and increase the work equivalent of the steam heat per the relationship for W_{EQ}.

4. Thermal Degradation

Thermal degradation of the solvent sets the maximum stripper T/P. If the stripper is operated at the maximum temperature compatible with the conveniently available steam pressure, the stripper and compressor capital cost will be minimized and the overall performance will be improved. Therefore, it can be expected that an optimized design will operate the stripper 5ºC to 10ºC colder than the available condensing steam temperature or at T_{max}, whichever is lower. In a new plant it will usually be ideal to select a condensing steam temperature that is 5ºC to 10ºC hotter than T_{max}.

The thermal degradation property of a solvent can be specified as its T_{max}—the temperature at which the thermal degradation rate constant of the loaded solvent is 2%/week or $2.9e^{-8}$ s^{-1}. The T_{max} of MEA is about 120ºC. Namjoshi tabulated available T_{max} for a number of solvents. Rochelle describes four important degradation mechanisms:[12,13]

- “Diamine structures where two secondary or primary Ns are separated by two or three carbons readily degrade at T_{max} of 104 to 118°C in the presence of CO_2 to produce cyclic ureas (imidazolidinone).”[14]
- “Primary and secondary alkanolamines with two or three carbons between the N and oxygen degrade by reversibly forming a cyclic oxazolidinone from the carbamate, which then reacts with another amine to form a dimer of the starting amine.”[15] T_{max} varies from 102 to 127°C.
- In blends of tertiary amines with secondary or primary amines the reactive amine will react with alpha carbons on the protonated tertiary amine, especially with methyl groups. Tertiary blends with piperazine have T_{max} from 120 to 140°C.
- Piperazines, morpholine, piperidines, and long chain diamines degrade by ring closing or opening with T_{max} from 140 to 170°C.

I. Solvent Management Criteria

Other important solvent properties determine the loss of solvent and the resulting secondary environmental impact. Oxidative degradation of the solvent is a problem unique to flue gas treating. The formation and decomposition of nitrosamine represents an important side reaction with flue gas impurities that can result in toxic products. Amine volatility and its loss as an amine aerosol may be the most significant secondary environmental impact.

1. Oxidative Degradation

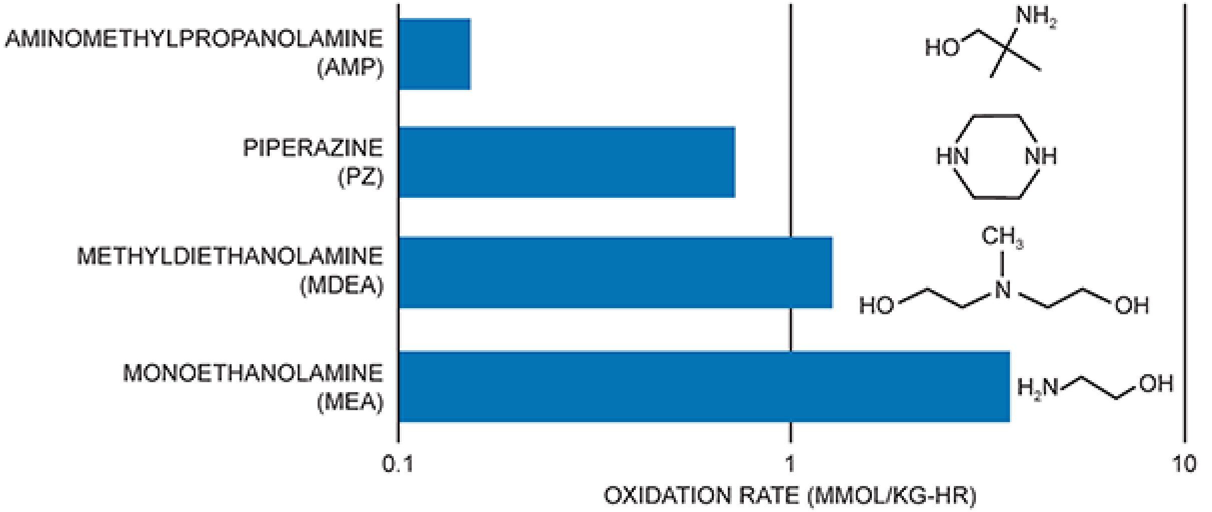
Amine oxidation is a unique problem in the application of amine scrubbing to CO_2 capture from oxygen-containing flue gas. Even with numerous detailed investigations over the last 15 years, there is not yet a clear understanding of the mechanisms by which it takes place.

Chi,[16] Goff,[17] and Voice[18] showed that Fe++, Mn++ (from corrosion or leaching of fly ash), and Cu++ (added as a corrosion inhibitor) are potent catalysts of MEA oxidation.

Sexton,[19] Freeman,[20] and Voice[21] identified a number of amines including PZ and MDEA that are resistant to oxidation at absorber conditions. Goff and Voice identified a number of oxidation inhibitors including Inhibitor A that are effective at absorber T, but these seem to fail at stripper T in a cyclic system.[22,23] In a simple world, the resistant amines or other amines with oxidation inhibitors would react at elevated exchanger and stripper temperature with the saturated level of dissolved oxygen left in the rich solution from the absorber. This lower level of oxidation could be further minimized by stripping out the dissolved oxygen before the rich solution is heated.

In bench-scale experiments with cycling to stripper temperature, Closmann[24] and Voice[25] showed that the elevated temperature of the stripper results in levels of oxidation that can only be explained by a shuttle mechanism. Higher concentrations of dissolved metal (such as Fe++) may oxidize in the absorber (to Fe+++) and then serve as oxidizing agents at the stripper temperature. Dissolved metals appear to be critical to this mechanism, so oxidation would be minimized by reducing corrosion, utilizing thermal reclaiming, and otherwise minimizing the accumulation of dissolved metals. The amount of oxidation would also be minimized by reducing the time and temperature at stripper conditions.

Amine selection also impacts the oxidation rate with the shuttle mechanism. With the cycling apparatus, Voice showed that the oxidation of selected amines can vary by a factor of 20 (Figure E-7).[26] PZ and tertiary amines such as MDEA are resistant to oxidation. Hindered amines such as AMP are especially resistant.



Source: Voice, A. K., "Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing," (Ph.D. dissertation, University of Texas at Austin, 2013).

Figure E-7. *Oxidation Rate of Common Amines with Cycling from 55°C to 120°C*

Sexton quantified a number of the oxidation products of MEA.[27] Formate and ammonia appear as oxidation products that are common to practically all amines. At stripper conditions, the formate equilibrates with the respective amide of a parent primary or secondary amine. Aldehydes and their respective imines and hemiaminals are also common in many systems. Many of the aldehyde species are in reversible equilibria, but there can be stable species such as hydroxyethylimidizole (HEI) formed in MEA systems from ammonia, MEA, glyoxal, and formaldehyde. PZ oxidizes to 2-hydroxy-piperazine, a stable hemiaminal.

Unfortunately, primary and tertiary amines oxidize to form some secondary amines, so these systems are not immune to nitrosamine formation. MEA oxidizes to make some hydroxyethylglycine. MDEA oxidizes to make large quantities of diethanolamine.

2. Nitrosamine

All amines are oxidized by NO_2 from the flue gas. Secondary amines react with nitrite at stripper conditions to make carcinogenic nitrosamines that may create significant secondary environmental impacts. Fine has completed a comprehensive model of the nitrosamine cycle.[28]

NO_2 contained in the flue gas as 2% to 5% of the total NOx is partially removed in a typical SO_2 polishing scrubber. With the addition of thiosulfate to inhibit sulfite oxidation, 70% to 95% of the NO_2 can be removed in the polishing scrubber.[29]

Residual NO_2 will be removed in the amine absorber by reaction with the amine in the liquid to produce oxidized amine and nitrite. Secondary and tertiary amines will remove 90% to 99% of the NO_2. Primary amines react more slowly and may remove as little as 50%.

NO_2 may also catalyze amine oxidation in the absorber by acting as a free radical initiator. In pilot plant testing, the oxidation of piperazine is always significantly greater in the presence of >1 ppm NO_2.[30]

At the temperature and residence time of the stripper, practically all of the nitrite reacts with the amine. Reaction with secondary amine produces stoichiometric nitrosamine. Reaction with primary and tertiary amine is slower and produces oxidation products and N_2. Since solvents comprising tertiary and/or primary amines will have secondary amines that are products of degradation, nitrosamines will still be produced at the stripper condition.

At the temperature of the stripper, the nitrosamine thermally degrades to oxidation products and probably N_2O. The nitrosamine will accumulate to a steady-state concentration where the rate of production from NO_2 incursion into the absorber is equal to the rate of thermal decomposition. Estimated values of steady-state nitrosamine with 120°C stripping that vary from 0.9 millimolar (mM) in MEA to 20.5 mM in MDEA/PZ.[31]

Nitrosamine accumulation can be managed by solvent selection, high temperature stripping, NO_2 removal in the polishing scrubber, and upstream NOx controls.

3. Amine Volatility

Although moderate levels of amine volatility (10 to 100 ppm) are managed by the water wash at the absorber gas outlet, excessive amine volatility will require a more costly water wash system. Amines with low or no volatility cannot be reclaimed easily by evaporation. Therefore, we are looking for amine solvent with a moderate or possibly low volatility.

Nguyen[32] and Du[33] measured amine volatility in water for 44 solvents. Du correlated the Henry's constant, H_{amine} (Pa), of amine in water with 14 structure parameters:[34]

$$ln\ H_{amine,\mathrm{313.15K}}\ (Pa) = 17.5 + \sum k_j\ n_j$$

where k_j is the parameter value for functional group j, and n_j is the number of occurrences of group j in an amine structure.

Amines with acceptable volatility all have at least two hydrophilic groups (N, O, OH, etc.). Amines with more than three hydrophilic groups are essentially nonvolatile. Alkyl groups on tertiary amines substantially increase volatility. Adding molecular weight as alkyl groups always increases the amine volatility.

The effect of CO_2 loading on amine volatility varies with the solvent. In MDEA or AMP, the volatility of the amine slightly increases with CO_2 loading because the bicarbonate salts out the somewhat hydrophobic amine. In PZ and other polyamines, CO_2 loading significantly reduces the volatility of the amine by speciating it out as a carbamate or protonated amine ion.

4. Amine Aerosol Emissions

Flue gas that contains significant aerosol nuclei (>106 particles/cm^3) as H_2SO_4 (1 to 10 parts per million by volume (ppmv)), fine fly ash, etc., may result in economically and environmentally unacceptable amine emissions as liquid aerosol (<2.5 µm drops). A number of pilot plants with coal-fired flue gas and other dirty gas sources have observed total carryover exceeding 10 ppm amine with a water wash that should have reduced the emissions of vapor amine to <2 ppm.

One explanation is that the aqueous nuclei have an amine solvent concentration that is rich in CO_2. The bulk amine solvent has a lower CO_2 loading. With most amines, the amine vapor pressure over the bulk solvent is greater than that of the aerosol, so amine transfers to the aerosol, taking with it CO_2 and water. If the nuclei only grow a little (to <2.5 μm), they are not captured in the water wash. If there is growth to greater than 2.5 μm, these drops may be captured in the water wash. With this complicated mechanism, results should be expected to vary with the solvent, process, and flue gas source.

Nevertheless, MHI, Aker, and BASF have all reported successful testing of countermeasures to minimize amine aerosol emissions. Aker has patented and demonstrated use of greater temperature in the top of the absorber.[35,36] BASF discusses use of a dry bed of packing between the absorber and water wash.[37] MHI reports work identifying the problem as SO_3 in the flue gas and resolving the problem with countermeasures. Mertens et al. showed that the appropriate use of a gas/gas heat exchanger before the flue gas desulfurization system would minimize H_2SO_4 nuclei before the amine scrubber and therefore reduce amine aerosol emissions. TNO demonstrated the use of a Brownian Diffusion Filter to remove the aerosol after the water wash.[38] Despite these measures this is an open problem area, the mechanisms and countermeasures of which are not completely understood.

Aerosol emissions have not been observed in pilot plants or commercial units with coal-fired flue gas that has passed through a bag filter, usually with injection of activated carbon or hydrated lime that removes any SO_3.

5. Amine Cost and Availability

Amine molecules are expensive and are likely to remain so. Even if oxidation and thermal degradation can be minimized there will be steady-state and episodal impurities in the flue gas, especially from coal, that will result in amine losses and prohibitive makeup costs. MEA losses equivalent to $1 to $2/tonne CO_2 are acceptable with an amine price of $2/kg. With five times less loss, an amine cost of $10/kg might be acceptable.

The amine price will be related to the number of reaction steps to get from common raw material to the amine. MEA requires three steps:

Ethane > Ethylene > ethylene oxide > MEA

Piperazine can be synthesized from MEA with one more step or produced as a co-product of ethylenediamine with three steps:

Ethane > Ethylene > Ethane dichloride > PZ

HMPD (4-hydroxy-1-methyl-piperidine) requires 7 steps and will probably be too expensive unless another route can be found with fewer steps:

Propane > propylene > ethyl-methacrylate > Michael
addition > Dieckmann condensation > Decarboxylation >
hydrogenation > HMPD

6. Molecular Weight

Large molecules are not attractive. The equivalent weight (molecular weight/number of active amine groups) is an indicator of the cost of amine inventory and makeup in the event of degradation; more kilograms of amine are required to get the same performance.

Even if the equivalent weight is acceptable, large molecules result in greater solvent viscosity. Greater viscosity reduces the heat transfer coefficient and the diffusion coefficient of CO_2 and amine. Large molecules also have intrinsically reduced diffusion coefficients of their own.

7. Corrosion

Most amine solvents are not compatible with carbon steel at all conditions. Structured packing and the plates for plate-and-frame exchangers are thin and require stainless steel regardless.

Corrosion measurements with MEA solvents suggest that stainless steel should be used at practically all conditions. However, several solvents including MDEA and PZ are not corrosive to carbon steel at lower temperature or form a protective film of $FeCO_3$ that may protect carbon steel at stripper temperature.

Corrosion measurements with PZ bench-scale and pilot-scale experiments; have shown that carbon steel is resistant to corrosion at absorber temperature but fails at stripper temperature when there is a larger concentration of degradation products.[39,40] SS 316L can also fail at 150ºC in the stripper.

Materials selection will play a critical role in commercial plant reliability and capital cost. Corrosion measurements and understanding represent an important need to minimize risk and cost.

J. Summary of Important Representative Solvents

The experimental properties of amine solvents tested at the University of Texas at Austin are summarized by Li.[41] Coal-fired flue gas was used as the basis for estimating the parameters. The capacity was evaluated at loading that gives an equilibrium CO_2 partial pressure at 40ºC of 5 kPa at rich conditions and 0.5 kPa at lean conditions.

1. Monoethanolamine

MEA is an important candidate for CO_2 capture by amine scrubbing because it is the least expensive of the important solvents. It is produced in large quantities from the reaction of ammonia and ethylene oxide, a primary raw material for antifreeze polyester. It is a primary amine near the optimum pKa so it has an average rate of CO_2 absorption and above average normalized capacity with excellent viscosity. Its heat of CO_2 absorption is high, so it performs well with thermal swing regeneration.

Unfortunately, MEA is prone to oxidative degradation and its T_{max} for thermal degradation is 120ºC. Oxidation inhibitors, nitrogen sparging to remove dissolved oxygen, or other methods will be required to manage oxidation.

2. Piperazine

PZ is an excellent solvent alternative. More work has been published on this second generation solvent than on others. With the highest rate of CO_2 absorption, 5 m (30 wt %) PZ is 2.6 times faster than MEA. Its normalized capacity is 22% greater than 7 m MEA. Its heat of absorption is low (64 kJ/mol), but with excellent thermal stability, P_{max} is 14 bar, so that can make up for the lower ΔH_{abs}. Piperazine interacts with NO_2/nitrite to produce nitrosamine. However, the nitrosamine is easily degraded at 150°C, which is achievable with the thermally stable PZ.

3. PZ Blends

Most tertiary and hindered amines react too slowly with CO_2 to provide an acceptable rate of CO_2 absorption. However, they usually provide excellent capacity; the greatest normalized capacity (1.14) is achieved with 4.8 m AMP or 8 m 2-PE, both hindered amines. Therefore, a blend of PZ or another fast amine with a tertiary or hindered amine usually provides good rate and good capacity. Unfortunately, PZ usually accelerates the thermal degradation of the other amine, so few of these blends have high T_{max} or P_{max}. Furthermore, mononitrosopiperazine will accumulate in most of these solvents that regenerate at 120^{o}C, so the nitrosamine must be managed by NO_2 prescrubbing or other means.

Although 7 m MDEA/2 m PZ duplicates many of the good properties of PZ, it does not have its issues of solid solubility. MDEA/PZ has been used for many years as a gas treating solvent. It is not as resistant as PZ to oxidation but is more stable than MEA. Thermal degradation limits regeneration to 120^{o}C.

Although 2 m PZ with 4 m 2-amino-2-methyl-1-propanol (AMP) also has properties comparable to 5 m PZ, it has no issues of solid solubility. It should be just as stable or more stable to oxidation but is limited by thermal degradation to 128°C. AMP has a greater volatility than MEA in lean solution, so water wash will be more critical.

Although practically equivalent to 5 m PZ in rate, capacity, and thermal stability, 2 m PZ with 3 m 4-hydroxy-1-methyl-piperidine (HMPD) does not have any issue with solid solubility. The HMPD component is comparable in volatility to MEA. However, the production of HMPD requires four reaction steps from ethylmethacrylate, so the cost of the amine will be high.

K. Conclusions

Conventional amine scrubbing was first used decades ago and has continued to be a dominant technology for post-combustion capture. There are no insurmountable technical problems in its deployment.

Second generation amine scrubbing will provide an energy performance better than 50% thermodynamic efficiency, with an electricity burden approaching 200 kWh/tonne CO_2 in the coal-fired application.

Amine aerosol emissions and amine oxidation are not yet completely understood and managed. These loss mechanisms will need to be addressed in any significant commercial application of amine scrubbing.

Corrosion/materials selection is not well understood and must be addressed for each new solvent development.

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Appendix F

EMERGING CO_2 CAPTURE TECHNOLOGIES

I. INTRODUCTION

This appendix describes less mature carbon dioxide (CO_2) capture technologies, what this study calls Emerging CO_2 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.

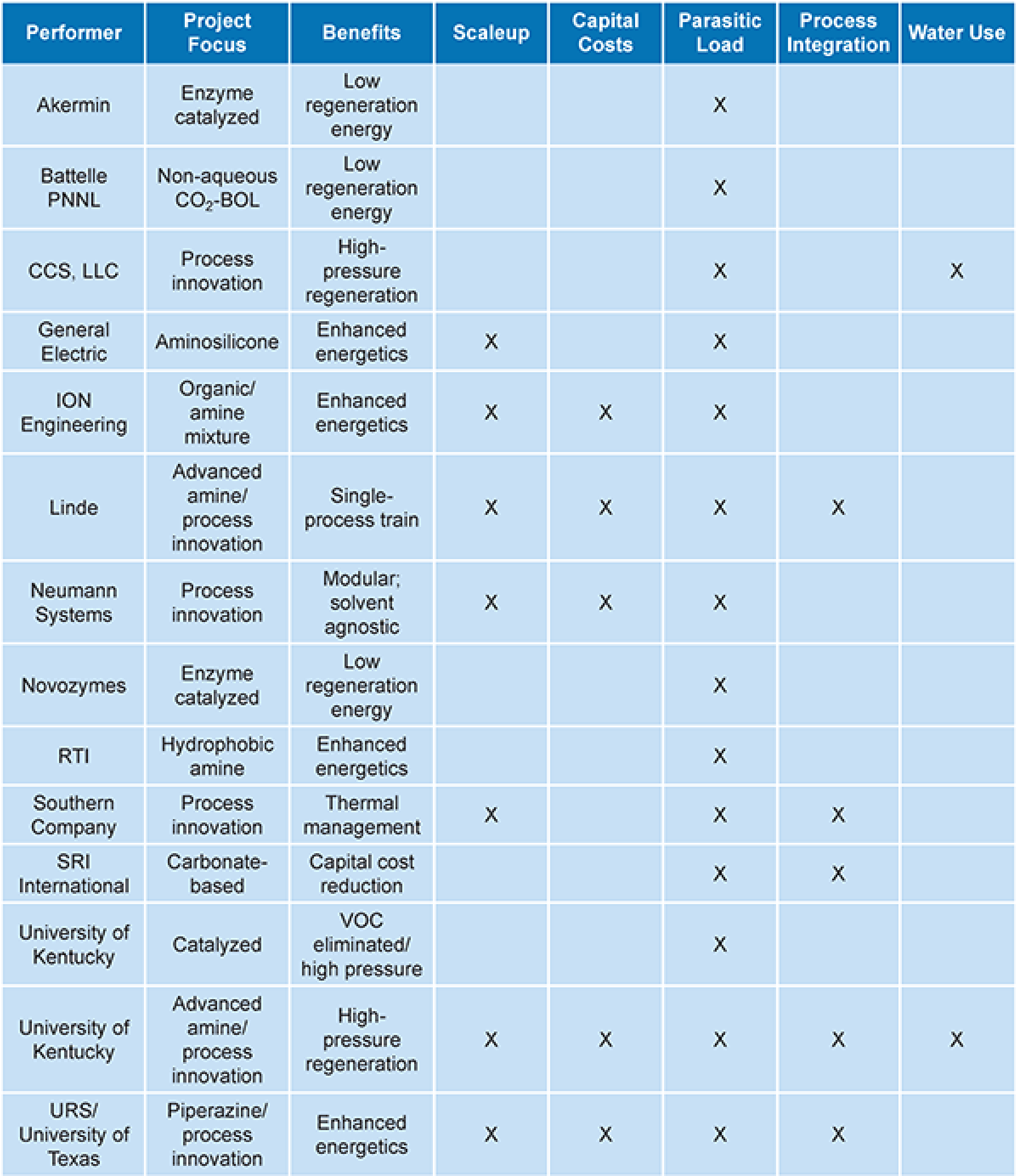
This appendix concludes with a section titled "U.S. DOE Funded Projects" that summarizes novel or transformational projects that have been sponsored by the Department of Energy (DOE), several of which involve hybrid capture approaches.

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_2 resulting in a smaller absorber volume, a large CO_2 carrying capacity to reduce the amount of solvent needed to separate the CO_2 from the flue gas, a low enthalpy of reaction with CO_2 to reduce the energy needed to break the amine-CO_2 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_2 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.



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_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	

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

A number of advanced solvents, in addition to process improvements and hybrid systems with potential to reduce CO_2 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_2 with at least 90% CO_2 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 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.

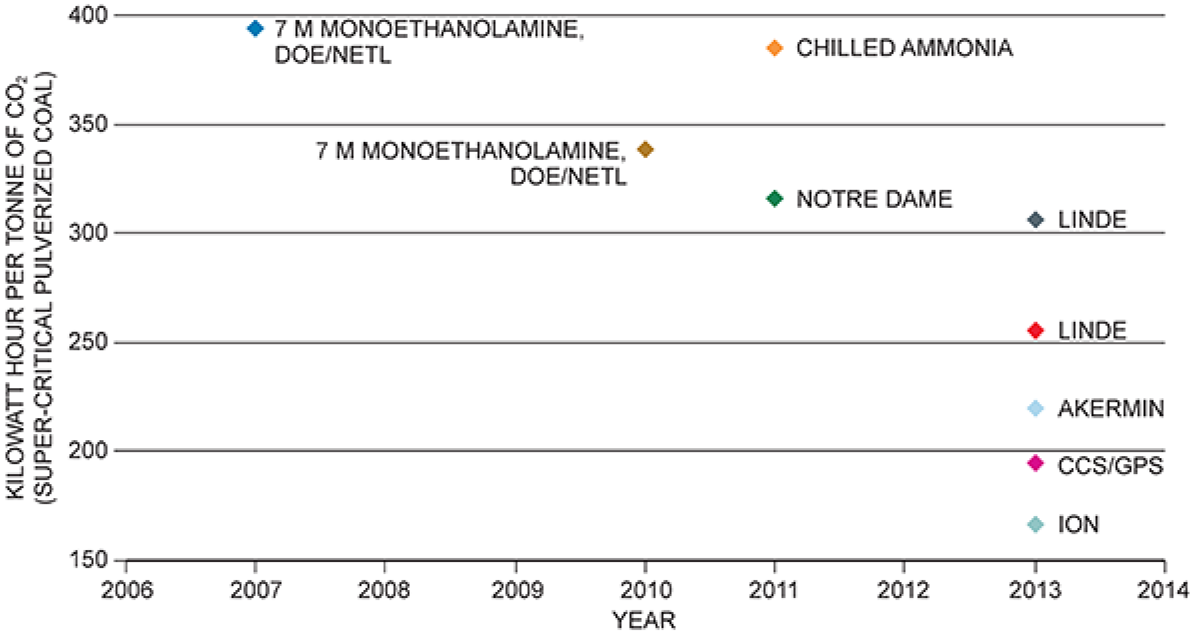
RTI International (formerly Research Triangle Institute) operated a nonaqueous solvent at NCCC in 2018 and continues development with testing at TCM.

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_2 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_2 capture. Parasitic load includes the work lost due to steam consumption for CCS and capture auxiliaries plus the energy required for compression of CO_2 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]



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

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

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 (Front End Engineering Design) design basis, and cost share for Phase II. Two of the CO_2 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_2 Capture Technology.

The University of Kentucky Research Foundation will be furthering their UKy-CAER Heat-Integrated Transformative CO_2 Capture Process.

DOE is supporting testing to scale up CO_2 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_2 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.

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_2 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]

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 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

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

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_2 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 CO_2 absorption for the water-lean solvents are comparable to those of aqueous solvents at -50 to -90 kilojoules per mole CO_2 (kJ/mol CO_2), 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_2 (GJ/tonne CO_2) compared to the DOE NETL Case 10 with 3.5 GJ/tonne CO_2 and the second-generation amine scrubbing performance of 2.2-2.4 GJ/tonne CO_2. 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 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.[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 CO_2 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_2 at high pressure
- Precipitate bound CO_2 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_2 sources from a wide variety of industrial applications.[7]

4. Challenges to Power Retrofits

A challenge to the retrofitting of CO_2 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 SOx, NOx, mercury, and particulates. Therefore, a retrofit using amine technology is typically preceded by installation of other scrubbers that remove these pollutants. Unfortunately, the cost of installing these scrubbers to enable a CO_2 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 NOx to their elemental gases. The team is working to extend the technology to CO_2 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

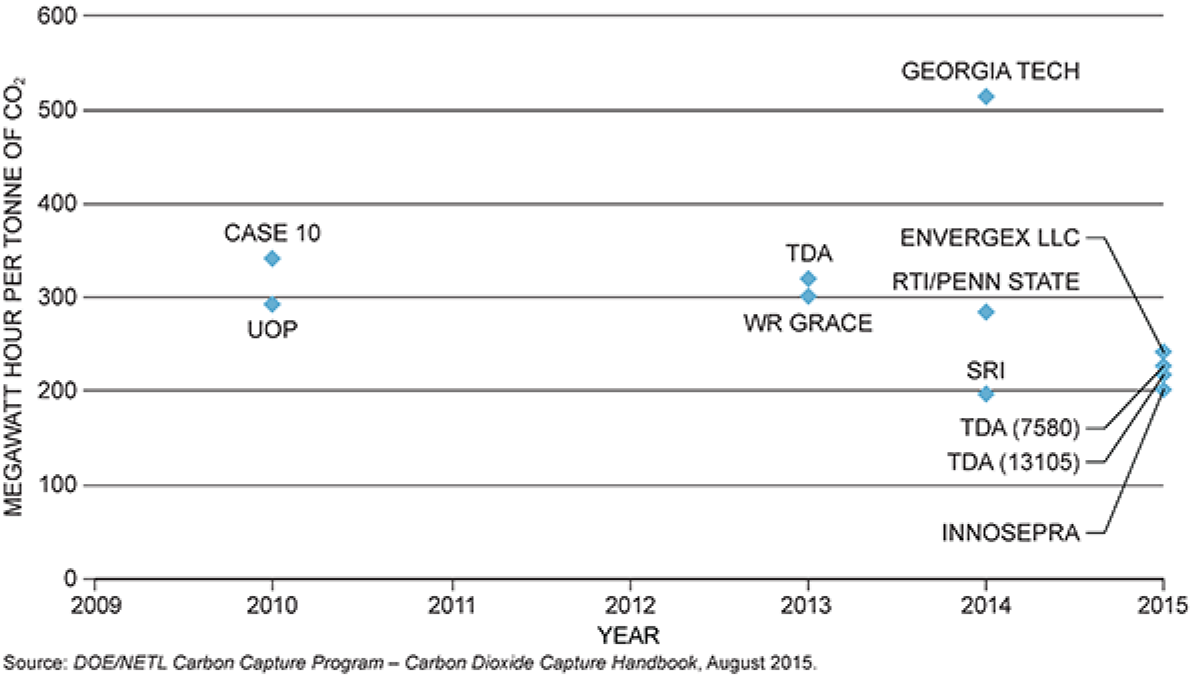
The removal of CO_2 from gas streams via adsorption is not a new concept. Throughout the manned space missions, solid sorbents have been used to remove CO_2 at low concentrations (<1%) from air. Regenerable sorbents have been employed since the 1990s in the space shuttle and for the International Space Station.

Cryogenic air separation uses sorbent material to remove water vapor and CO_2 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_2.

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_2 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_2 from the steam methane reformer syngas for injection in the West Hastings oil field for enhanced oil recovery. The CO_2 separation takes place upstream of the existing PSA process for capturing H_2.[10]

To advance sorbents as a viable CO_2 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_2 loading capacity, and high selectivity for CO_2. CO_2 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_2. Figure F-2 shows the progress for sorbent-based capture to reduce the parasitic load.[11]



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*

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_2 capture capacity. Following testing at the center, NETL continued sorbent work to improve material characteristics, although the group's current CO_2 capture work is focused on membrane material development.

- 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_2 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_2 sorbent for pre-combustion syngas at the NCCC consistently demonstrated the capability to remove more than 90% CO_2. TDA also tested a combined WGS/CO_2 sorbent system with an innovative heat management component. When parameters were adjusted to achieve 90% CO conversion in the WGS stage, the overall CO_2 capture rate was greater than 95%. TDA scaled up testing from bench- to small-pilot-scale (0.1-MW) with a CO_2 sorbent (without water gas shift) process, again demonstrating high CO_2 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_2 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_2 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_2 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_2 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 CO_2 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]

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	InnoSepra, 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	RTI International	Bench-Scale, 1 tonne 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

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

TSA systems being tested are provided in the following list. TSA is where CO_2 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_2 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.

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

Opportunities for adsorbent CO_2 capture include enriching natural gas from wells with high CO_2 content, coal or biomass gasification, CO_2 recovery from food and dry ice industries, and CO_2 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_2 from high CO_2 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 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_2 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_2 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 CO_2 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 CO_2 separation with the sorbent extracting the remainder to achieve 90% capture.[17]

C. Challenges and Research Needs for Adsorbents

CO_2 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_2 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_2 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

- 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 CO_2 capture since sorbents should selectively bind only CO_2. 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_2 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 CO_2 capture capacity than other sorbents. The MOF can be used in CO_2 capture from exhaust gas, but it is also applicable to CO_2 capture from other process streams such as CO_2-methane separations following anaerobic digestion.[19]

The leading materials for CO_2 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.[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 CO_2.[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.
- InnoSepra, LLC is developing a novel sorbent-based process consisting of a flue gas purification step, a moisture removal step, and a CO_2 adsorption step. Also, the CO_2 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 CO_2 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_2 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_2 capture processes, the use of membranes for large CO_2 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_2 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 pressure 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+.

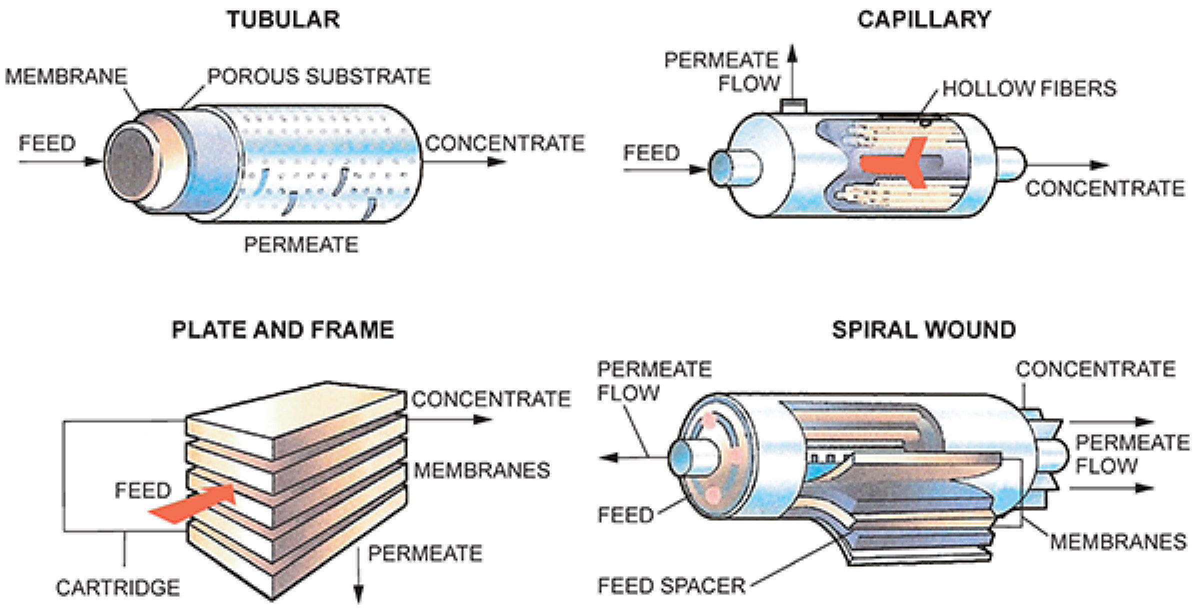
Several significant challenges for membrane CO_2 capture technologies result in a less favorable cost compared to other technologies. CO_2 permeability and permeance of gas separation membranes is lower than desired resulting in large membrane areas and higher capital costs due to a larger footprint 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-1m-2Pa-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]

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.

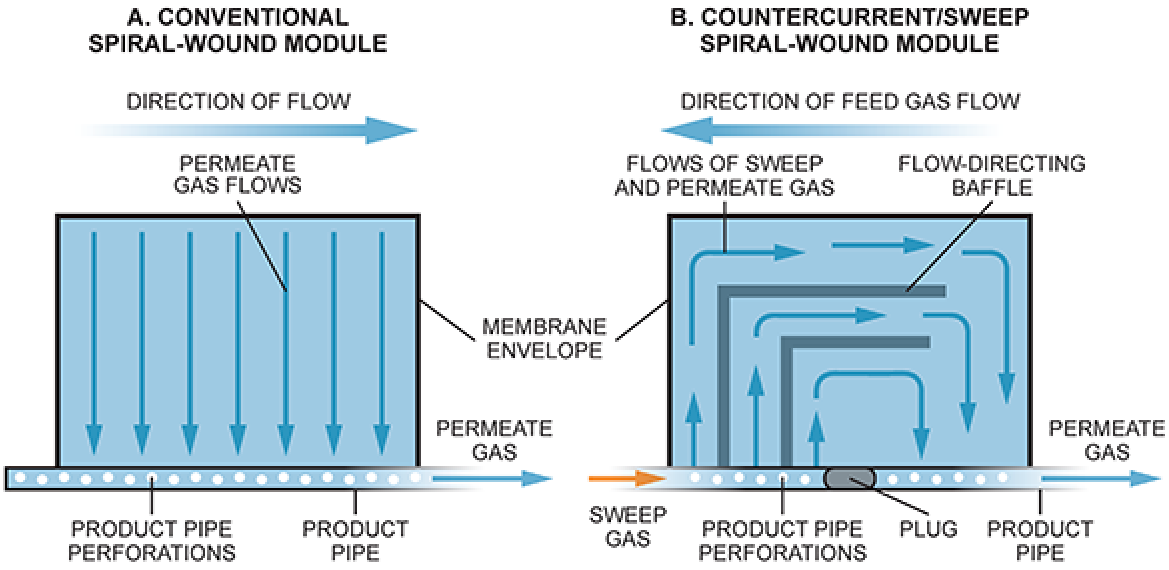
Or, membrane modules can be made with thin sheets of polymer arranged in spiral wound fashion. The feed gas enters the module and flows between the membrane leaves. The retentate flows over the leaves and exits the other end whereas the permeate spirals inward to a central core collection tube. Refer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



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*

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.

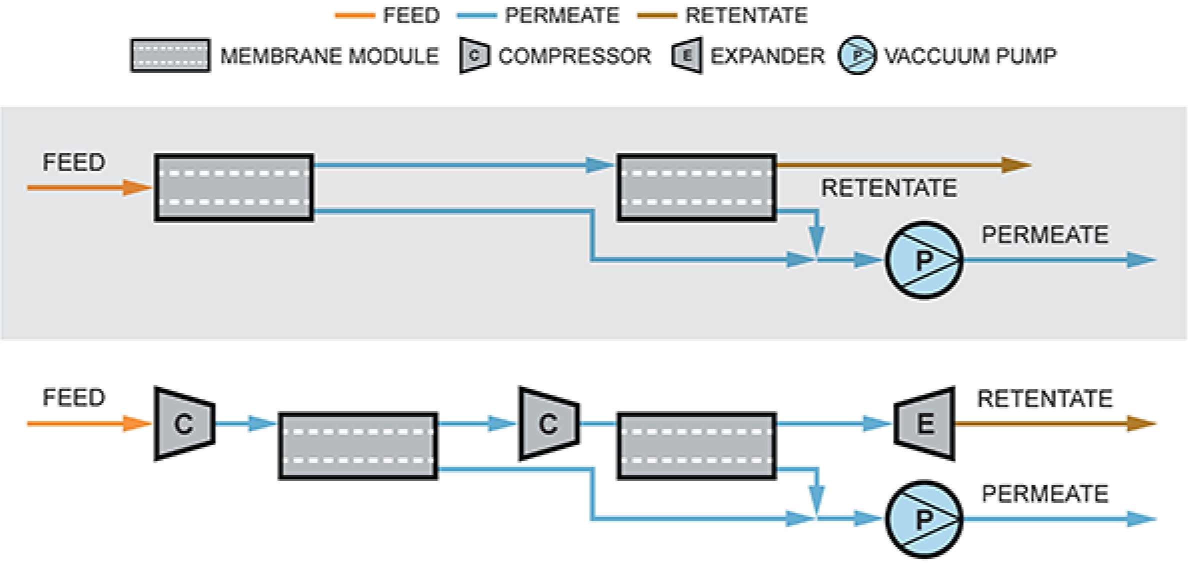


Source: *DOE/NETL Carbon Capture Program – Carbon Dioxide Capture Handbook*, August 2015.

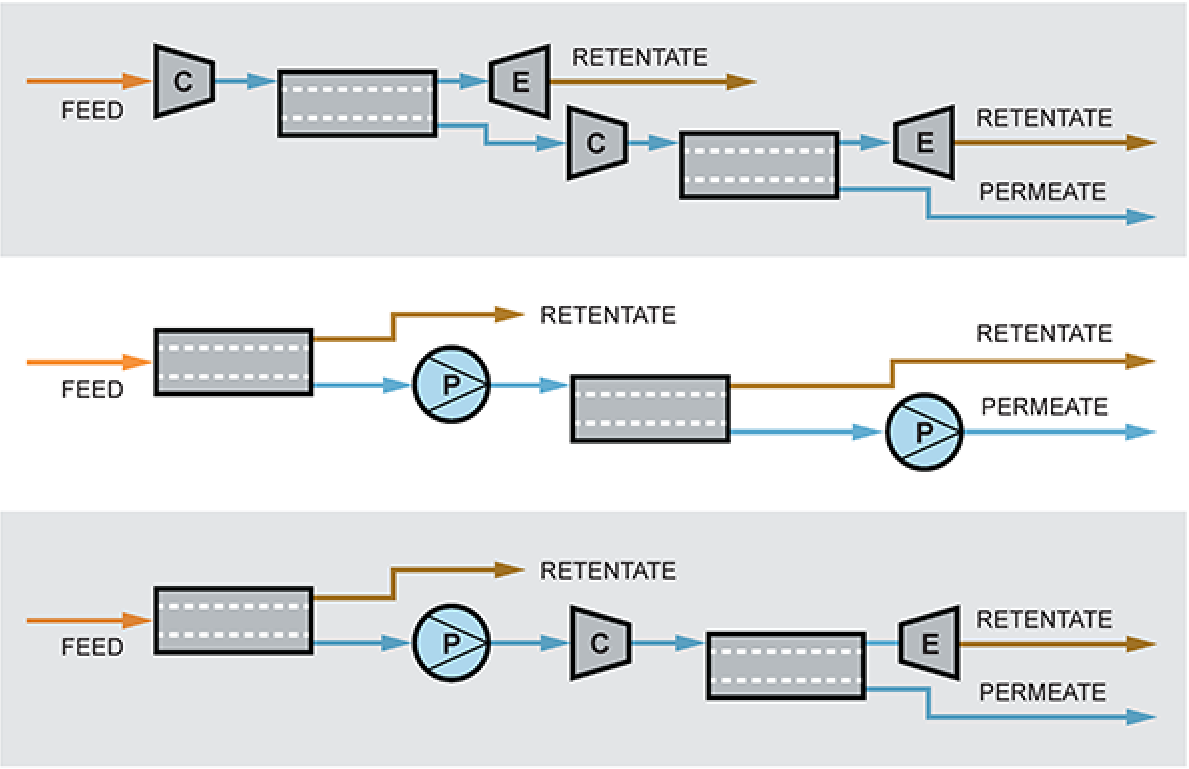
Figure F-4. *Spiral-Wound Membrane Module Flow Patterns*

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.



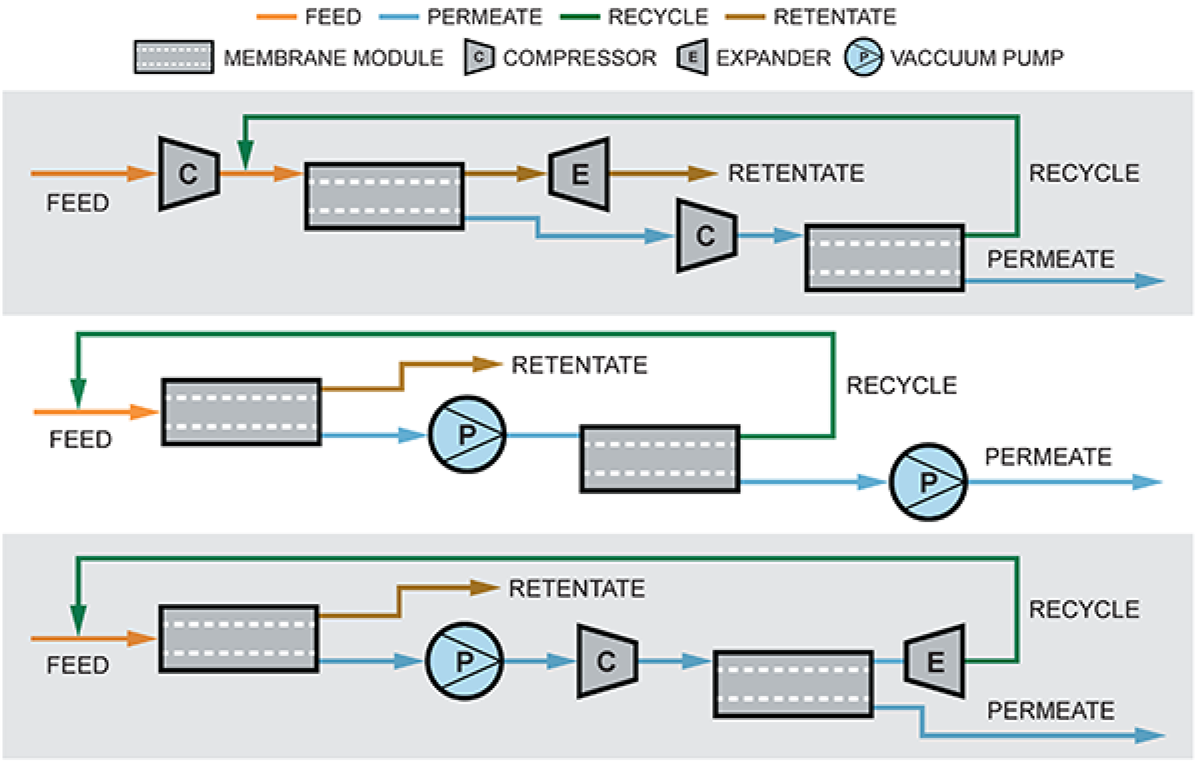
SERIAL STRIPPER CONFIGURATION



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 andSerial 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*

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_2 permeate away from the membrane surface, the permeate side has near zero CO_2 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_2 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 CO_2 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_2 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_2 selectivity at subzero temperatures to efficiently separate CO_2 from flue gas. Testing at NCCC focused on development and scale-up of the novel PI-2 membrane material featuring significantly higher CO_2 flux than commercially available material. The PI-2 module achieved 10 times the normalized CO_2 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_2 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^2 of membrane area. Capture was from a high CO_2 content flue gas of 17 mol% wet basis. The test results showed that 70 mol % CO_2 purity can be easily achieved in a single stage.[23]

The dense metal H_2-selective membrane technology that allows production of CO_2-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_2 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 NCCC[26] 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]

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

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	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
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-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
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

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*

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.[28] 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_2 Membrane.

For FOA 1791 AOI 2, EPRI will perform an initial engineering design and cost estimate of a Post-Combustion CO_2 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.[29]

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_2 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_2/N_2 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_2 from flue gas streams (aka CO_2 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_2 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_2 capture through phase change has been proposed and developed as a means of removing CO_2 from power plant flue-gas streams.

There are several major advantages of cryogenic CO_2 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_2 is pumped to pressure as a liquid minimizing compression energy, and the energy consumption per ton of CO_2 captured overall is low. Drawbacks include difficulties associated with solids formation and handling and large heat transfer areas with tight temperature approaches.[30] 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_2 capture processes come in many forms such as a thermal swing process, an inertial carbon extraction system, cryogenic CO_2 capture external cooling loop, and cryogenic CO_2 capture compressed flue gas.

A thermal swing process freezes CO_2 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_2 capture has energy efficiency advantages that stem from ease of liquid-solid separation and this process pressurizes the CO_2 when it is a liquid as opposed when it is a gas. Another advantage is that other gas impurities are separated from the gas.[31]

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_2 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_2 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, SOx, NOx, and mercury.[32]

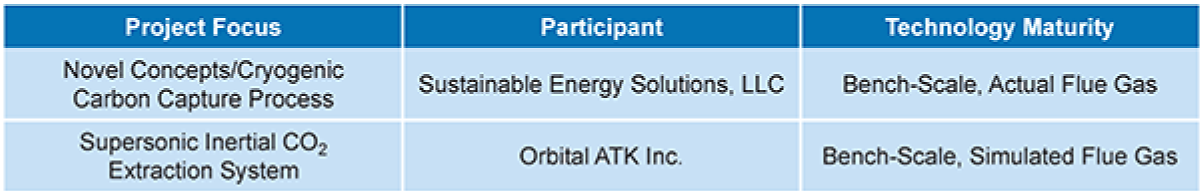
CCC is a retrofit, post-combustion method that uses phase change to separate CO_2 and other pollutants from gases. CO_2 is cooled to a low temperature (about -140°C) that it de-sublimates, or changes from a gas to a solid. The solid CO_2 is separated from the remaining light gases, melted, pressurized, 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).[33] Cryopur, EReiE and others have performed pilot tests and GE has done simulation work to evaluate the technology.[34] SES's cryogenic process was part of the demonstration of the first project to collect cement kiln CO_2 for utilization in concrete production. Emissions from the Cementos Argos' Roberta cement plant near Calera, Alabama, were captured by SES. The captured CO_2 was transported and used in concrete operations equipped with CarbonCure's CO_2 utilization technology. This project was an extension of the Team CarbonCure's participation in the NRG COSIA Carbon XPRIZE Challenge.[35]

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_2 avoided (~\$30/tonne captured) with no plant integration. Using existing plant infrastructure should reduce the cost further.[36]

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.[37] 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).[38]



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

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

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_2, 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_2 removal pretreatment steps are to remove the two species that would form a solid as they are chilled at atmospheric pressure. For cryogenic CO_2 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.

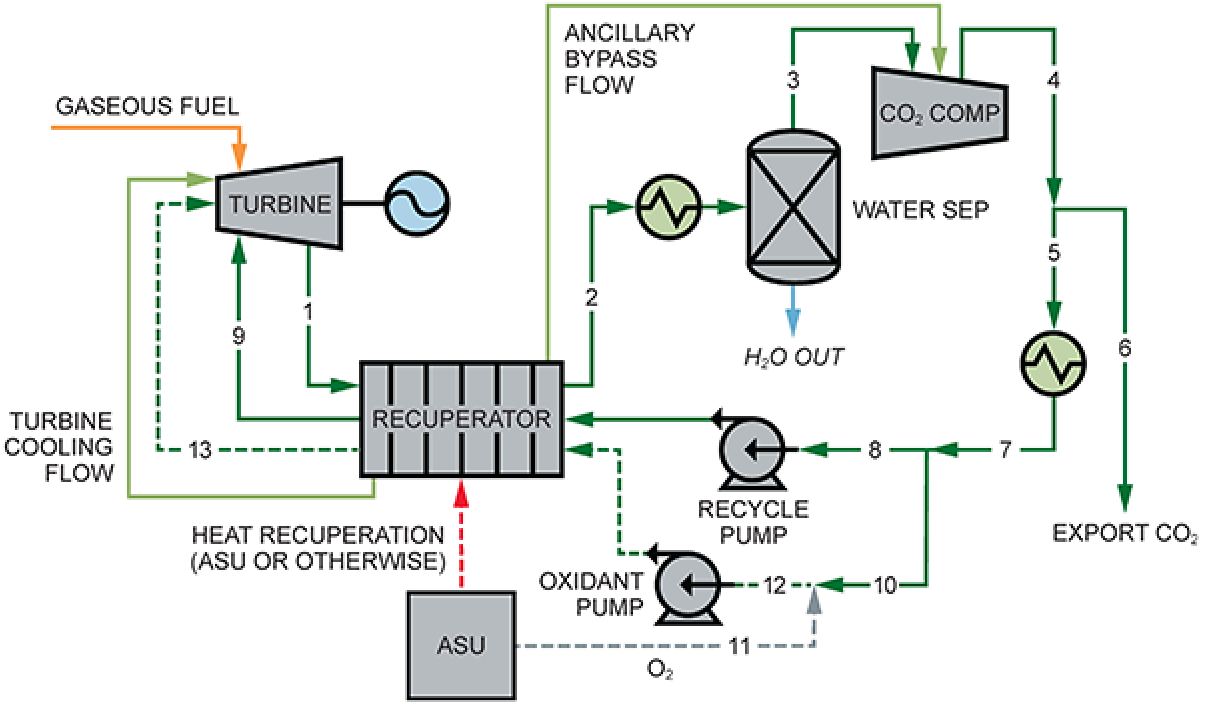
For all cryogenic systems, thermal integration and temperature management is required to minimize the energy consumption of the process. Thermal recuperation that uses the available cooling potential in cold internal streams or products to cool incoming gas or internal streams has to be carefully designed to minimize the exergy loss due to internal heat transfer or rejection to the environment. An idealized cryogenic CO_2 capture process could be envisioned in which there is no lost work from 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.[39]

A challenge for using cryogenics for flue gases is that CO_2 does not form a liquid at atmospheric pressures. Pure CO_2 gas forms a solid (dry ice) when it is cooled to -78.5 C (its sublimation point). So, cryogenic separation of CO_2 from flue gas is possible, but the formation of solids makes it difficult.[40] 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.[41]

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_2 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_2 as a working fluid in a highly recuperated manner. At the core of the cycle is a supercritical CO_2 loop, where high-pressure CO_2 passes through a turbine, is cooled to remove water and impurities, and then is re-pressurized and reheated in a heat 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.

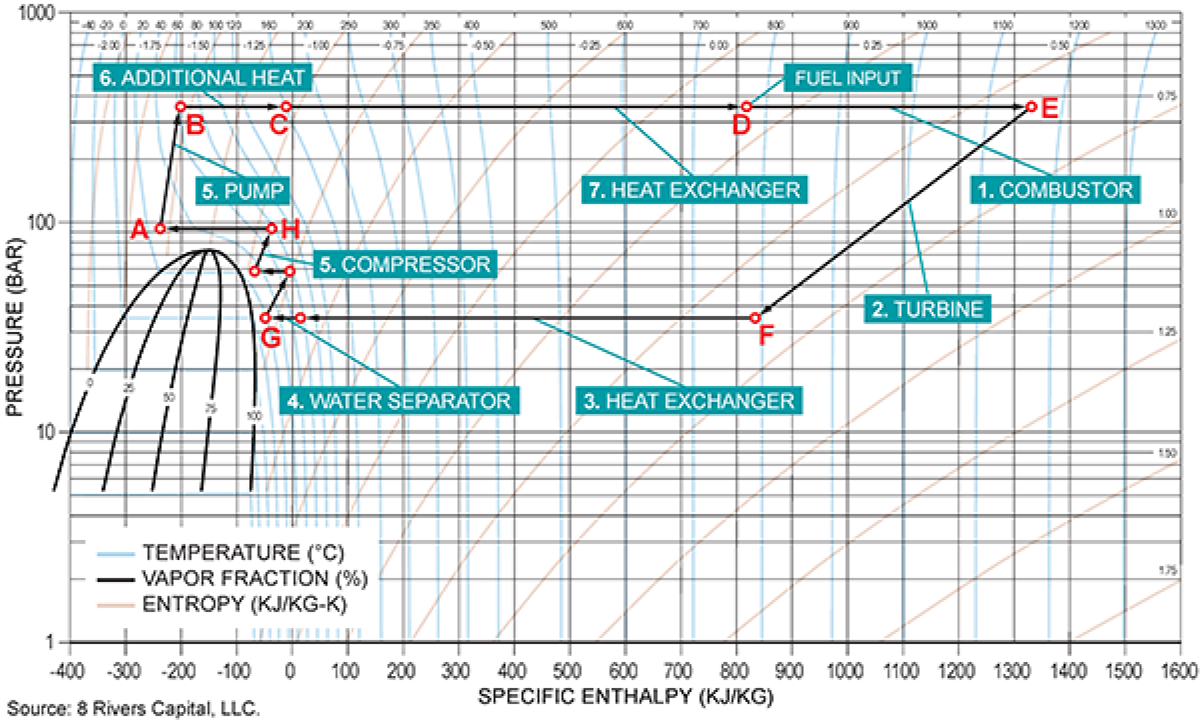


* ASU = air separation unit

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*

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.[42] Points on this diagram represent the conditions of the CO_2 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.



Source: 8 Rivers Capital, LLC.

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

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_2. Within this dome CO_2 is a mixture of both gas and liquid. At conditions to the left of the dome, CO_2 is liquid. At conditions to the right, CO_2 is a gas. Above the top of the dome, CO_2 becomes supercritical. In the supercritical realm, CO_2 does not undergo a “phase transition” (changing from liquid to gas, and vice versa); instead, CO_2 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_2 to circa 110 bar pressure
- B-C: Heating of recycled CO_2 (45% proportion) and oxidant stream in recuperative heat exchanger (stage 1 and 2) recovering low grade heat from turbine exhaust flow
- C-D: Heating of recycled CO_2 and oxidant stream in recuperative heat exchanger (stage 3) recovering
- D-E: Primary combustor heat input from oxy-combustion and sCO_2 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_2/H_2O vapor) in recuperative heat exchanger (stages 3, 2, and 1)
- G-H: Multi-stage compression of recycle CO_2 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 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.[43]

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-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_2 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_2 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_2 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_2 Storage	A synthetic catalyst is designed with the same function as carbonic anhydrase, an enzyme in the human lungs that helps to separate CO_2 from the blood. The catalyst can be used to quickly capture CO_2 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_2.	Lawrence Livermore National Laboratory	$3,632,000
Composite Membranes for CO_2 Capture	Development of an enhanced membrane by fitting MOFs, into hollow fiber membranes. Analyzing MOFs based on their permeability and selectivity toward CO_2. The composite membrane would be highly stable, withstanding the harsh gas environment found in coal exhaust.	Georgia Tech Research Corporation	$998,928
CO_2 Capture with Liquid-to-Solid Absorbents	Development of a unique CO_2 capture process in which a liquid absorbent changes into a solid upon contact with CO_2. Once in solid form, the material can be separated and the CO_2 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_2. 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_2. This technology cuts both the energy requirements and cost of CO_2 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_2, and/or liquid fuel with zero CO_2 emissions. An iron-based oxygen carrier is used to generate CO_2 and H_2 from syngas in separate, pure product streams by means of a circulating bed reactor configuration. The end products of the system are H_2, 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_2 Capture Technologies*

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Appendix G

CO_2 ENHANCED OIL RECOVERY CASE STUDIES

I. INTRODUCTION

Carbon dioxide (CO_2) enhanced oil recovery (EOR) has proven to be technically and economically viable in a variety of fields in the United States and abroad. The tools and knowledge to select and characterize reservoirs for CO_2 EOR application and to design successful projects are well established.

Three CO_2 EOR project examples are documented in this appendix. Case studies of the Denver Unit in the Permian Basin of West Texas, the Bell Creek Field in the Powder River Basin of Montana, and the Northern Niagaran Pinnacle Reef Trend in the Michigan Basin of Michigan are highlighted.

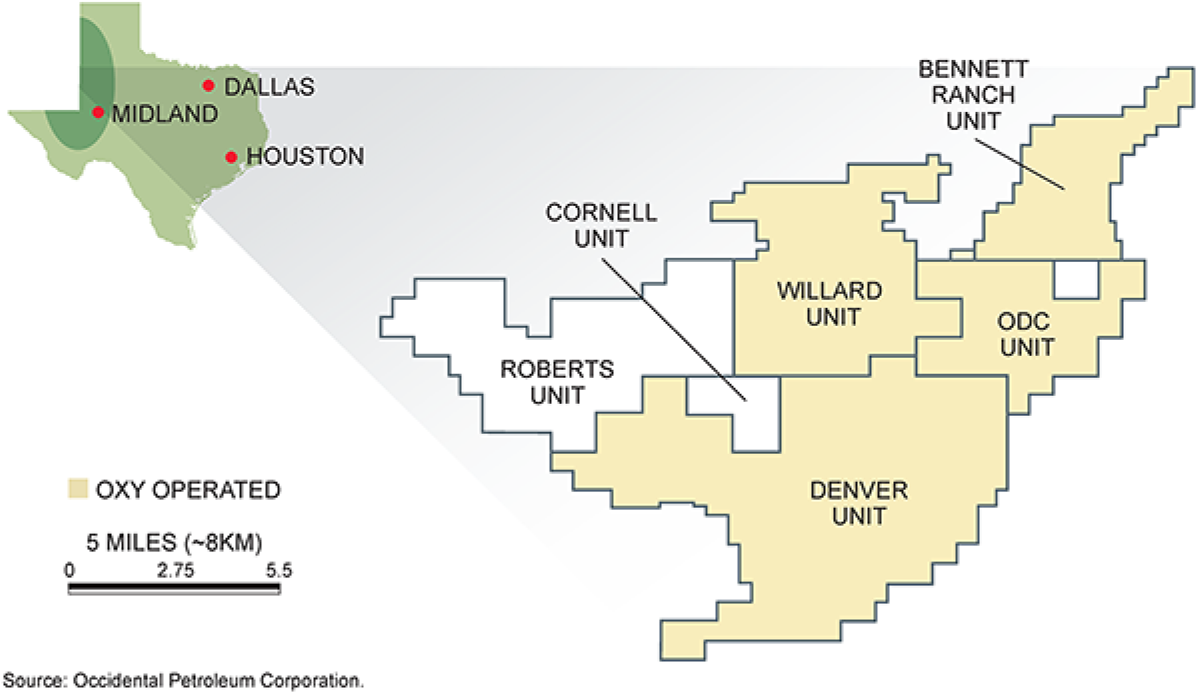
II. OXY PERMIAN DENVER UNIT

The Denver Unit is operated by Occidental Petroleum Corporation (Oxy) and has the distinction of being the largest CO_2 EOR project in the world. The unit comprises 27,000 acres and is the largest unit within the Wasson San

Andres field. Tertiary CO_2 EOR in the Denver Unit began in 1984 with the completion of the Cortez pipeline, which supplies CO_2 from southwest Colorado. Original hydrocarbons in place for this unit included 3.16 billion barrels of oil, including residual oil zone (ROZ) volumes, and 675 billion cubic feet of free gas. Currently, the field injects 420 million cubic feet per day (MMCF/D) of CO_2, including 200 MMCF/D of new CO_2 and 220 MMCF/D of recycled CO_2, into 609 active water-alternating-gas (WAG) injectors. The unit produces an average of 21,000 barrels of oil per day (BOPD), 249 thousand barrels of water per day, and 278 MMCF/D of gas from 1,130 active producers. As of 2018, the field has safely stored more than 2.8 trillion cubic feet, or 147 million metric tons (tonnes) of CO_2 incidental to oil production during the CO_2 EOR operation.

A. Geology

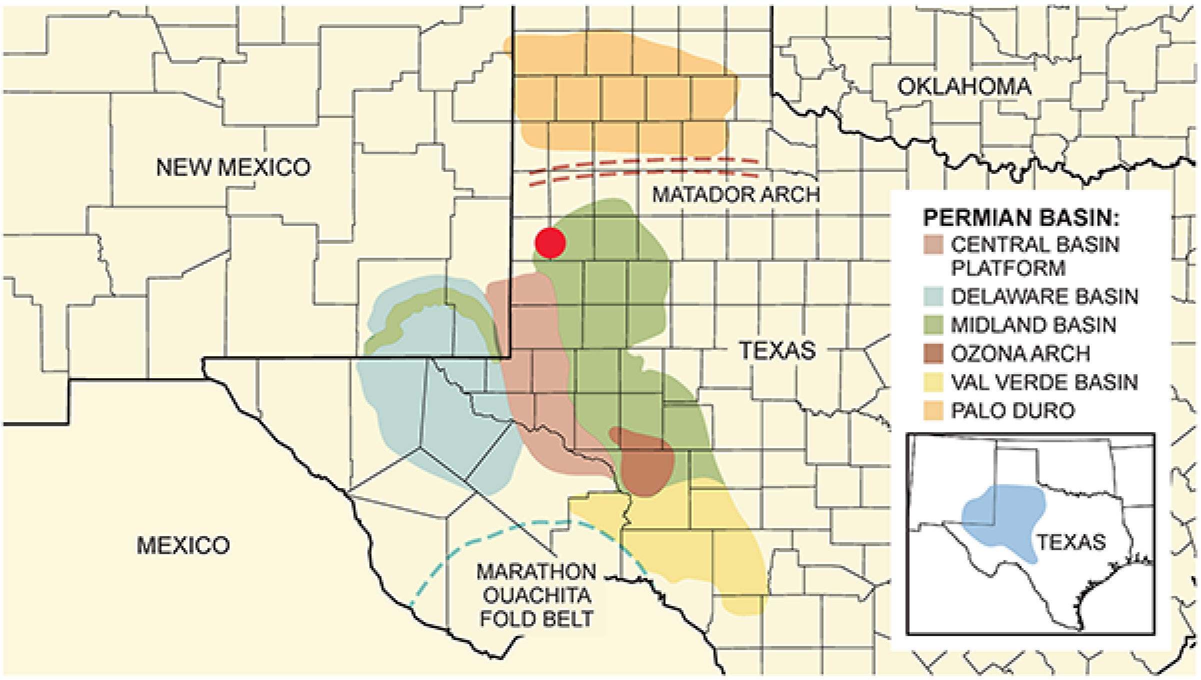
The Denver Unit is a subdivision of the Wasson field. It is located in the southern part of the oil accumulation area. The boundaries of the Denver Unit are indicated in the Wasson field map in Figure G-1.



Source: Occidental Petroleum Corporation.

Figure G-1. *Wasson Field Map*

Discovered in 1936, the Wasson field is located in southwestern Yoakum and northwestern Gaines counties of West Texas in an area called the Northwest Shelf. It is approximately 5 miles east of the New Mexico state line and 100 miles north of Midland, Texas, as indicated with the red dot in Figure G-2. The field extends over a productive area of about 62,500 acres.



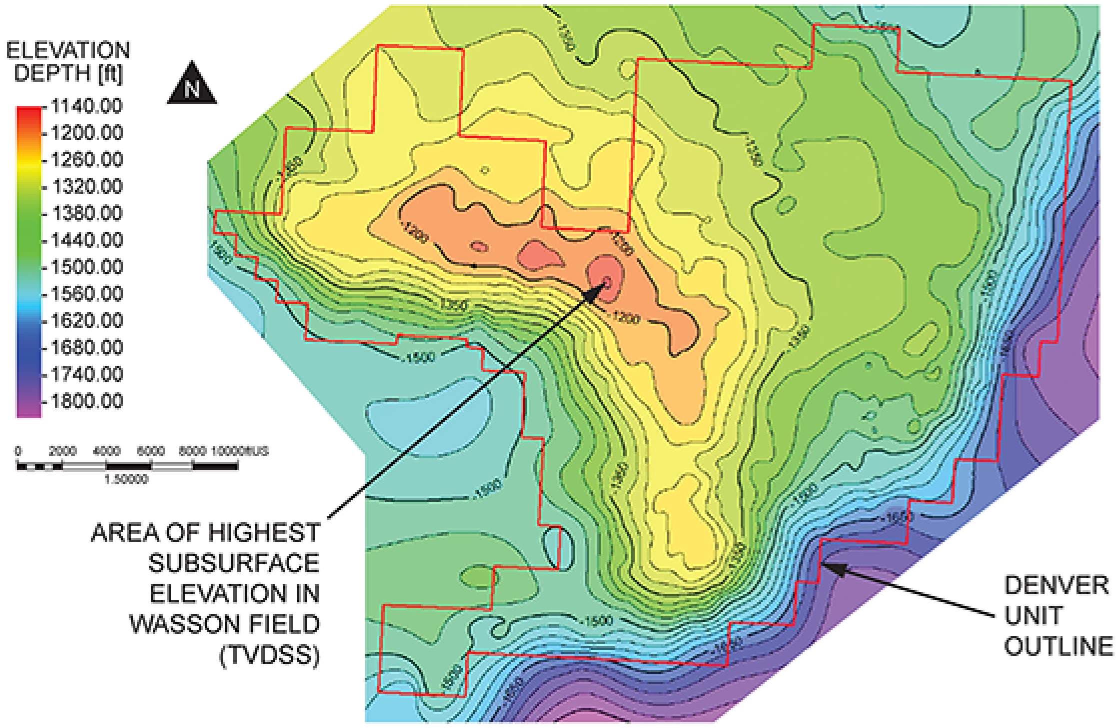
Source: Occidental Petroleum Corporation.

Figure G-2. *Permian Basin*

The Wasson field produces oil from the San Andres formation, a layer of permeable dolomites that were deposited in a shallow marine environment during the Permian period, some 250 to 300 million years ago. This depository created a wide sedimentary basin, called the Permian Basin, which covers the western part of Texas and the southeastern part of New Mexico. During the Permian period, this part of the central United States was under water. In the years following its deposition, the San Andres formation was buried under thick layers of impermeable rocks, and finally uplifted to form the current landscape. The process of burial and uplifting produced some unevenness in the geologic layers. Originally flat, there are now variations in elevation within the San Andres formation across the

Permian Basin. The relative high spots, such as the Wasson field, have become the places where oil and natural gas have accumulated over the ensuing millions of years.

The San Andres formation is of Guadalupian age and exhibits several fourth-order shallowing-upward cycles (G1-G9). Deposition of the San Andres occurred along a gently dipping carbonate ramp in an open marine environment, with rapid sea level changes due to cyclic icehouse conditions. Figure G-3 is an aerial view of the structure of the Denver Unit showing the depth of the top of the San Andres. The reservoir is overlain and capped by ~600 feet of tight anhydrite tidal flat deposits, which serve as the top seal for the San Andres in the Wasson field area. In effect, these deposits form the hard ceilings of an upside-down bowl or dome. Below this seal, the formation consists of permeable dolomites containing oil and natural gas.



Source: Occidental Petroleum Corporation.

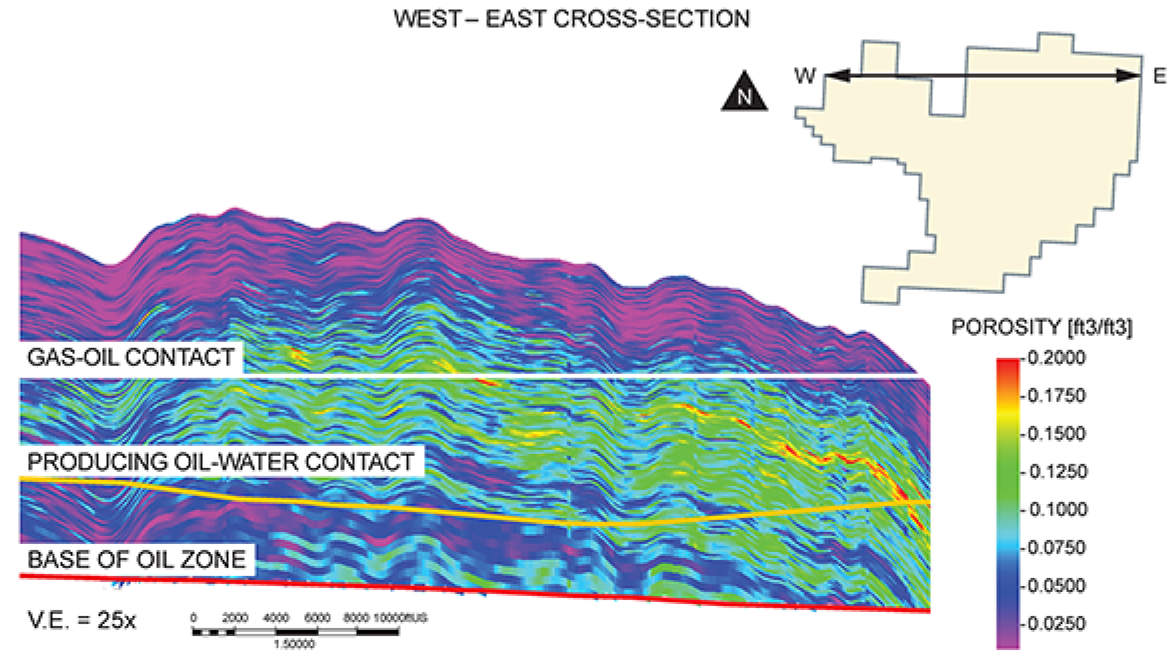
Figure G-3. *Structure Map on Top of San Andres Play*

The reservoir rock in the San Andres is composed of dolomitized limestone, mostly wackestone to grain-dominated packstone. Average porosity of the reservoir rock in the Denver Unit San Andres is 10%, with the most common pore type being intercrystalline. With nearly 6,000 million barrels of original oil in place (OOIP), the Wasson San Andres field is one of the largest oilfields in North America.

The colors in the structure map in Figure G-3 indicate changes in elevation, with red and orange being the highest levels (i.e., the horizon closest to the surface), and blue and purple being lowest levels (i.e., deepest below the surface). The detailed geology available on this map and others comes from over 1,700 well penetrations, logs and other data points collected throughout development of the field. As indicated in the structure map, the Denver Unit is located at the highest elevation of the San Andres formation within the Wasson field, forming the top of the dome. The rest of the Wasson field slopes downward from this area, effectively forming the sides of the dome. The elevated area formed a natural trap for oil and natural gas that migrated from below over millions of years. In the Wasson field, this oil and natural gas has been trapped in the San Andres formation for 50 to 100 million years. Over time, Wasson field fluids, including CO_2, would rise vertically until meeting the ceiling of the dome and then would follow it to the highest elevation in the Denver Unit.

The San Andres in the Denver Unit is divided into three zones based on fluid contacts: the gas cap, the main oil column, and the ROZ. Up until the late Tertiary, the San Andres in the Wasson field was filled past the spill point, with the San Andres outcropping in the west. During this time of subaerial exposure of the San Andres in the west, fresh water migrated from surface recharge zones and began moving eastward through the San Andres formation, forming a massive hydraulic head. Over time, the fresh meteoric water driven by the hydraulic head from the west swept large volumes of oil out of the Wasson San Andres oil column, leaving behind a ROZ with an average thickness of 200 feet in the Denver unit. Because the ROZ has oil saturations reduced to levels that are immobile relative to water, the residual oil requires tertiary recovery techniques to be mobilized.

Buoyancy dominates the mechanisms of oil and natural gas positioning in a reservoir. Gas, being lightest, rises to the top, and water, being heavier, sinks to the bottom. Oil, being heavier than gas but lighter than water, lies in between. The cross-section in Figure G-4 shows saturation levels in the oil-bearing layers of the Wasson field and illustrates this principle.



Source: Occidental Petroleum Corporation.

Figure G-4. *Wasson Field Cross-Section with Original Oil Saturation*

At the time of discovery, natural gas was trapped at the structural high point of the Wasson field, shown by the pink area above the white gas-oil contact line in Figure G-4. This interface is found approximately 5,000 feet below the surface (or at -1,325 feet subsea). Above the gas-oil interface is the volume known as a “gas cap.” The presence of a gas cap is evidence of the effectiveness of the seal formed by the upper San Andres. Gas is buoyant and highly mobile; if it could escape the Wasson field naturally through faults or fractures, it would have done so over the millennia.

Below the gas was an oil accumulation, which extended down to the producing oil-water contact (orange line in Figure G-4). The producing oil-water contact (POWC) was determined through early drilling to be the maximum depth where 100% of the fluid produced was oil. The ROZ at Wasson is important in that it represents an additional CO_2 EOR target that is accessible by the relatively inexpensive deepening of existing wells. The ROZ interval is estimated to contain 2.5 billion barrels of OOIP in the Wasson field. A commercial CO_2 EOR project in the ROZ is ongoing in the Denver Unit and in all other units except the Robertson Unit in the Wasson San Andres field.

B. Reservoir Development

1. Primary Production

The Denver Unit was discovered in 1936 by Shell Oil Company USA. The field produced from solution gas and gas cap drive (primary depletion) until it was unitized for waterflooding in 1964. Initial reservoir pressure was 1,850 psi, and initial solution gas/oil ratio, Rsi, was 450 standard cubic feet per barrel of oil. Cumulative oil production (on primary depletion) prior to waterflood was ~10% of the original oil in place above the POWC from approximately 716 producing wells.

The free water level as defined by capillary pressure data in the Wasson field is approximately 200 feet deeper than the POWC, and it will be referred to throughout this appendix as the Paleo free water level, or PFWL. The ROZ lies between the POWC and the PFWL. This ROZ oil is a legitimate target for CO_2 EOR, but it was avoided during primary depletion and waterflood recovery because it contains no mobile oil and produces only water.

2. Waterflood

Waterflooding works most efficiently with regular patterns over a large area. The Wasson field was originally developed as numerous leases held by individuals and companies. To improve efficiency, a number of smaller leases were combined (or unitized) into larger legal entities (units), which can be operated without the operational restrictions imposed by the former lease boundaries. In 1964, six such units were formed at Wasson to enable waterflooding; the largest of these is the Denver Unit (see Figure G-1).

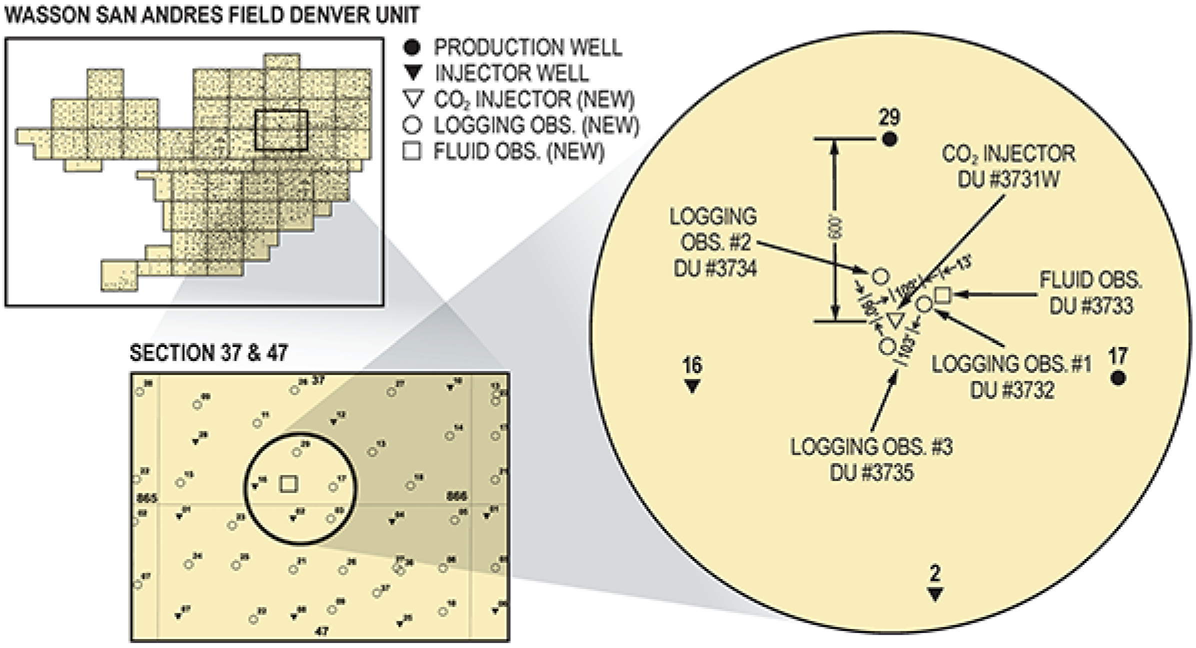
CO_2 flooding of the Denver Unit began in 1983 and has continued and expanded since that time. The experience of operating and optimizing the Denver Unit CO_2 flood over three decades has created a strong understanding of the reservoir and its capacity to store CO_2.

At the beginning of the waterflood, reservoir pressure was approximately 700 psi. The producing gas/oil ratio at the beginning of the waterflood was approximately 4,400 standard cubic feet per barrel. The water injection project began with an injection rate of 550,000 barrels of water per day, for an injection throughput rate of 3% of the hydrocarbon pore volume per year. As reservoir pressure increased, the first clear signal of waterflood response was a dramatic decline in the producing gas/oil ratio, followed by an increase in oil production. At its peak, Denver Unit oil production was 150,000 BOPD under waterflood with 800 producers and 300 injectors.

3. CO_2 Enhanced Oil Recovery

a. Main Oil Column CO_2 EOR History

In 1978, a pilot program was implemented to evaluate the potential of enhanced oil recovery through CO_2 injection at the Denver Unit. The objectives were to assess interactions, if any, of CO_2 and water injection into a carbonate reservoir, measure CO_2 mobility compared to water, assess vertical and horizontal sweep, and determine residual oil saturation to CO_2 injection. The pilot consisted of an injector, a fluid observation well, and three logging observation wells placed about 100 feet from the injector. The configuration of the pilot wells is shown in Figure G-5.

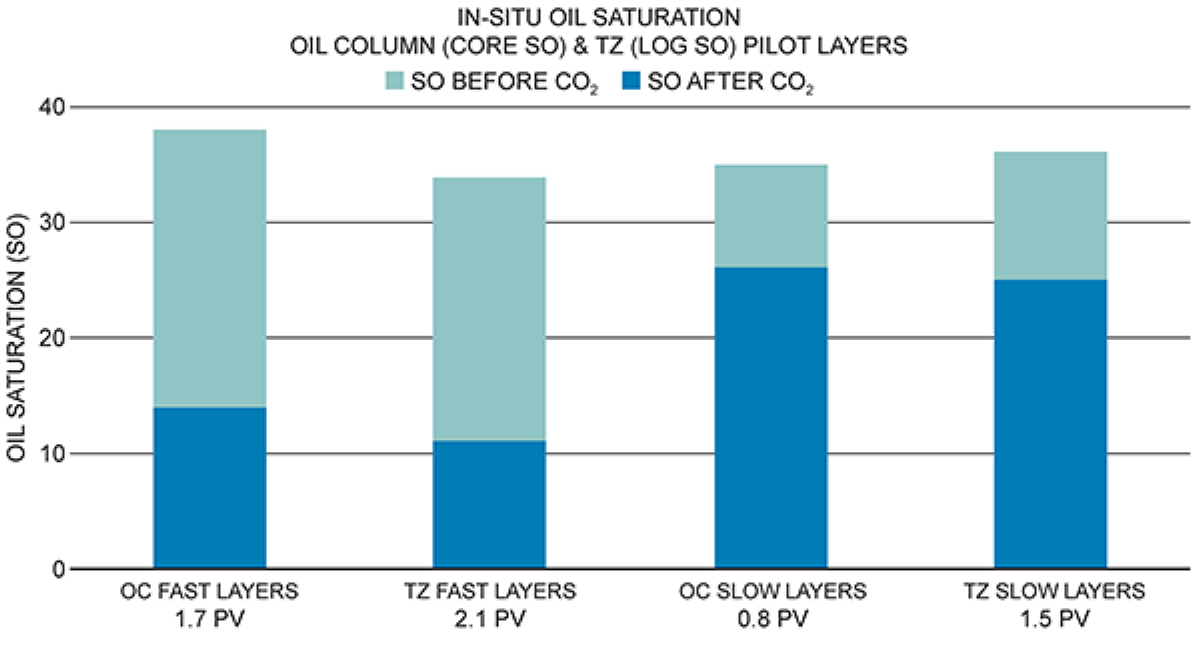


Source: Occidental Petroleum Corporation.

Note: Distances are bottomhole locations.

Figure G-5. *Denver Unit CO_2 Flood Pilot*

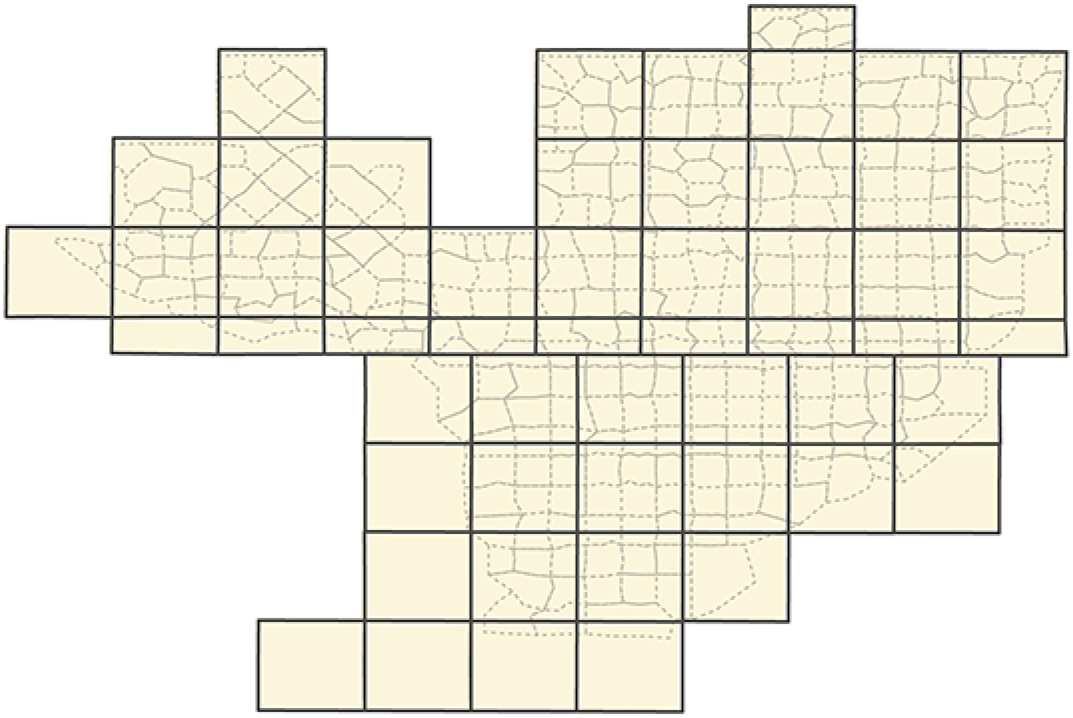
A biweekly logging program was conducted at the observation wells to monitor the advancement of water in the pre-CO_2 injection brine flush, then of the oil bank and the CO_2. Pressurized cores were collected after the brine flush and again after a cumulative volume of 132 MMCF or 44% of the pilot area's pore volume was injected. The measured residual oil after waterflood and after the CO_2 flood are shown in Figure G-6. The pilot demonstrated that CO_2 enhanced oil recovery can range from 9% to 24% of the original oil in place, or 25% to 63% of the oil remaining after waterflood for the Denver Unit San Andres reservoir.



Source: Occidental Petroleum Corporation.

Figure G-6. *Residual Oil Saturation after CO_2 Injection from the Denver Unit CO_2 EOR Pilot*

In 1984, upon completion of the Cortez Pipeline, CO_2 from the McElmo Dome CO_2 field in southwestern Colorado was transported to the Denver Unit at an initial CO_2 injection rate of 300 MCF/D. The CO_2 project was implemented in phases, with the eastern and southern areas starting first. The initial project authorization called for a 40% hydrocarbon pore volume (HCPV) of CO_2 to be injected into all areas. As the CO_2 flood was implemented in each area of the field, patterns were standardized to 80-acre inverted nine-spots (~20 acres per well). Continuous CO_2 injection was used initially in the eastern portion of the unit, and WAG injection was done in the southern area to compare the two methods and determine the best injection process to be used for the remaining expansion areas. A 20% HCPV of continuous CO_2 injection followed by WAG injection was found to work best for the San Andres reservoir at the Denver Unit. Over a 5-year period from 1984 to 1989, the Denver Unit CO_2 project expanded from the sweet spot on the eastern side of the field, to the south and west to complete the CO_2 flood development. Figure G-7 presents the Denver Unit CO_2 flood patterns.

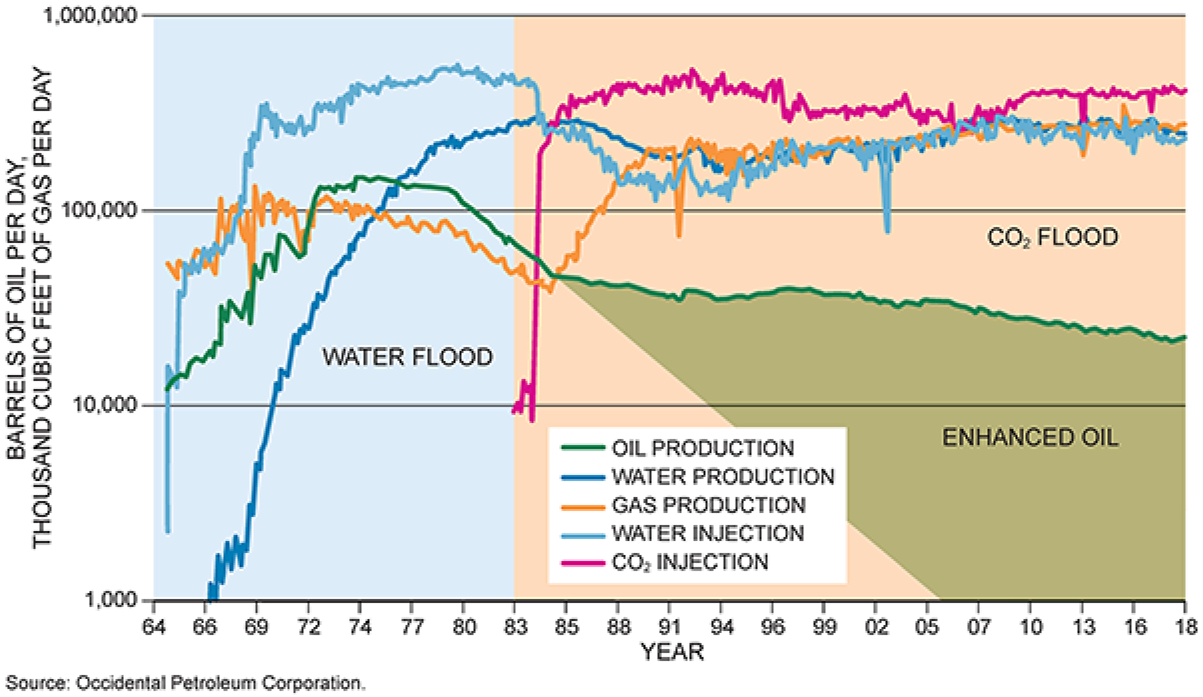


Source: Occidental Petroleum Corporation.

Figure G-7. *Denver Unit CO_2 Flood Patterns Outline*

Cumulative enhanced oil recovery from the Denver Unit through 2018 is ~11% of the original oil in place. Associated CO_2 storage in the reservoir is more than 2.8 trillion cubic feet or 147 million tonnes. The peak oil response rate was

40,000 BOPD, and current production is approximately 21,000 BOPD. Figure G-8 depicts the Denver Unit historical production and injection data.



Source: Occidental Petroleum Corporation.

Figure G-8. *Denver Unit Historical Production and Injection*

b. TZ/ROZ Development

In 1992, a pilot program was developed to assess CO_2 EOR viability in the reservoir interval below the producing oil-water contact at the Denver Unit, typically referred to as the transition zone (TZ). The operator tested CO_2 recovery over a 75-feet interval below the POWC, where sponge core data indicated that residual oil saturation was above the irreducible level after a waterflood.

The pilot was a success, and full field ROZ development began as CO_2 supply became available, due to the mature main oil column (MOC) patterns being placed on the WAG injection scheme. The early TZ projects involved deepening existing injectors and producers to only 75 feet below the POWC, and TZ injection and production streams were commingled with the MOC. As full field TZ development continued, based on early successes, injectors and producers were deepened through both the TZ and ROZ, stopping short of the base of the zone. Drilling dedicated TZ/ROZ injectors was sometimes necessary to avoid preferential injection into the CO_2-flushed MOC, thereby giving the TZ/ROZ a higher chance of success technically and economically. However, the producers remained commingled with the MOC.

The TZ/ROZ CO_2 enhanced oil recovery behaves just like CO_2 EOR in the MOC, with incremental oil being produced from a previously water swept zone, because the TZ/ROZ interval had simply been waterflooded naturally over geologic time.

C. Denver Unit Facilities and Closed Loop Process

New CO_2 is delivered to the Wasson field via the Permian pipeline delivery system. Once CO_2 enters the Denver Unit, it becomes part of a closed loop system within three main EOR processes and becomes stored incidental to the overall EOR operation. These processes include CO_2 distribution and injection, produced fluids handling, produced gas processing, and water treatment and injection. These processes are described in the following three sections.

1. CO_2 Distribution and Injection

New CO_2 is combined with recycled CO_2 from the Denver Unit CO_2 Recovery Plant (DUCRP) and sent through the main CO_2 distribution system to various CO_2 injectors throughout the field.

New CO_2 and recycled CO_2 are combined and sent through the CO_2 trunk lines to injection manifolds. These manifolds are complexes of pipes that have no valves and do not exercise any control function. At the manifolds, the CO_2 is split into multiple streams and sent through distribution lines to individual WAG skids. Currently, the Denver Unit has 16 injection manifolds and 609 injection wells. As of 2019, 420 million standard cubic feet of CO_2 is injected each day, of which approximately 47% is new, and the balance (53%) is recycled.

Each injection well has an individual WAG skid located near the wellhead (typically 150 to 200 feet away). WAG skids are remotely operated and can inject either CO_2 or water at various rates and injection pressures, as specified in the injection plans. The length of time spent injecting each fluid is a matter of continual optimization, designed to maximize oil recovery and minimize CO_2 utilization in each injection pattern. The WAG skid control system consists of a dual-purpose flow meter used to measure the injection rate of water or CO_2, depending on what is being injected as defined from a control center.

2. Produced Fluids Handling

As injected CO_2 and water move through the reservoir, a mixture of oil, gas, and water (referred to as “produced fluids”) flows to the production wells where the fluids mixture is produced to the surface. Gathering lines bring the produced fluids from each production well to satellite tank batteries. The Denver Unit has 1,120 production wells, and production from each is sent to one of 32 satellite tank batteries, each containing a large vessel that performs a gas-liquid separation. Each satellite battery also has well test equipment to measure production rates of oil, water, and gas from individual production wells.

The gas phase, which is approximately 80% to 85% CO_2, is transported by pipeline to DUCRP for processing.

The water/oil (liquid) mix is sent to one of six centralized tank batteries, where the oil is separated from the water. Produced oil is metered and sold; the water is sent to a water treatment facility. Any gas released from the liquid phase rises to the top of the tanks, as part of the closed loop system, and is collected by a vapor recovery unit, which compresses the gas and sends it to DUCRP for processing.

3. Produced Gas Processing

The hydrocarbon natural gas and CO_2 gas mixture separated at the satellite and centralized tank batteries goes to the DUCRP where the natural gas, natural gas liquids (NGL), and CO_2 streams are separated. The natural gas and NGL move to commercial pipelines for sale. The remaining CO_2 is recycled within the closed loop system through the CO_2 distribution system for reinjection around the field, where it becomes trapped in the reservoir.

D. Monitoring

Oxy reports the amount of anthropogenic CO_2 it receives at the Denver Unit under Subpart RR of the Environmental Protection Agency's (EPA) Greenhouse Gas Reporting Program, in order to quantify the amount of CO_2 that is stored during CO_2 EOR operations. The Denver Unit has in place a monitoring, reporting and verification plan, which describes the operations, the monitoring program, and its CO_2 material balance quantification process. This plan has been approved by the EPA.

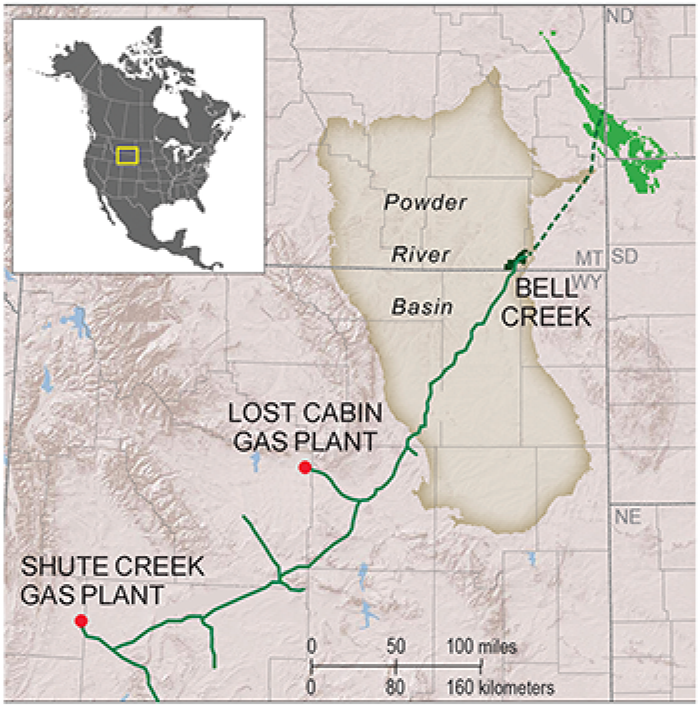
E. Summary

CO_2 EOR has successfully enhanced the recovery of hydrocarbons from the well characterized natural geologic trap in the Denver Unit while inherently storing CO_2 in that same geologic system continuously since CO_2 EOR operations were begun in 1984. To date, more than 2.8 trillion cubic feet, or 147 million tonnes of CO_2 have been stored in the reservoir of the Denver Unit. This project encompasses CO_2 EOR and associated storage in not only the main oil column of the field, but also in the transition zone and residual oil zone areas with equal success.

III. DENBURY BELL CREEK FIELD

The Bell Creek oil field is in southeastern Montana near the northeastern edge of the Powder River Basin (Figure G-

9). The Bell Creek unit is operated by Denbury Resources. The field has been under CO_2 flood since May 2013, and under some form of development for nearly 60 years prior to that. Oil has been produced in the field via primary, secondary (waterflood), and now tertiary (CO_2 EOR) recovery methods. The cumulative recovery prior to CO_2 flooding is 135 million barrels (38.2% of original oil in place). CO_2 flooding through 2018 has recovered nearly 6 million barrels of incremental oil production through injection of more than 180 billion cubic feet of CO_2 (10 million tonnes).

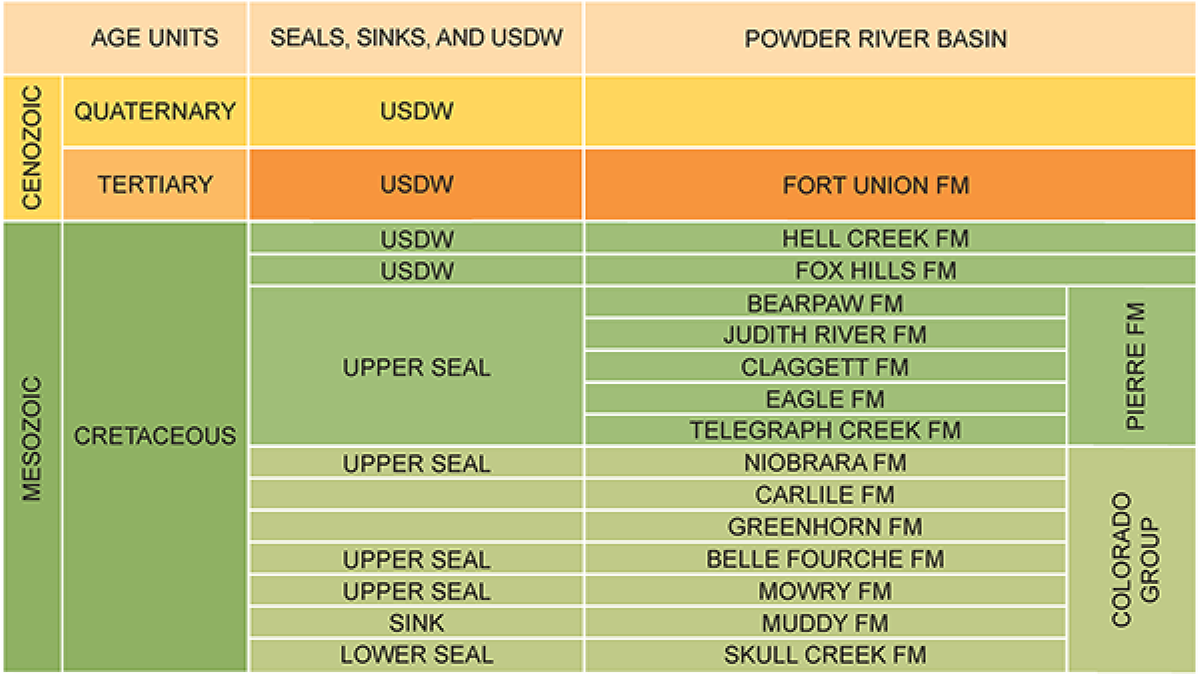


Source: Denbury Resources.

Figure G-9. *Regional View of Bell Creek in Relation to Lost Cabin Gas Plant*

A. Geology

The producing formation in Bell Creek is the Lower Cretaceous Muddy (Newcastle) formation at a depth of 4,300 to 4,500 feet. The Muddy formation is characterized by clean, high-porosity (25% to 35%), and high-permeability (100 to 1,175 md) sandstones deposited in a nearshore marine environment. The Muddy formation in Bell Creek features an updip facies change from sand to shale that serves as a trap. The estimated original oil in place is 353 million barrels distributed between three main pay sands: B10, BC20, and BC30. The field is split up areally into phases that are stratigraphically defined in most cases by erosional channels and reservoir quality transitions. The primary seal for the formation is provided by the overlying Mowry shale formation. On top of the Mowry shale are several thousand feet of low-permeability shale formations, including the Belle Fourche, Greenhorn, Niobrara, and Pierre shales, which provide redundant layers of protection in the unlikely event that the primary seal fails (Figure G-10).



AGE UNITS		SEALS, SINKS, AND USDW	POWDER RIVER BASIN	
CENOZOIC	QUATERNARY	USDW		
	TERTIARY	USDW	FORT UNION FM	
MESOZOIC	CRETACEOUS	USDW	HELL CREEK FM	
		USDW	FOX HILLS FM	
		UPPER SEAL	BEARPAW FM	PIERRE FM
			JUDITH RIVER FM	
			CLAGGETT FM	
			EAGLE FM	
			TELEGRAPH CREEK FM	
		UPPER SEAL	NIOBRARA FM	COLORADO GROUP
			CARLILE FM	
			GREENHORN FM	
		UPPER SEAL	BELLE FOURCHE FM	
		UPPER SEAL	MOWRY FM	
		SINK	MUDDY FM	
		LOWER SEAL	SKULL CREEK FM	

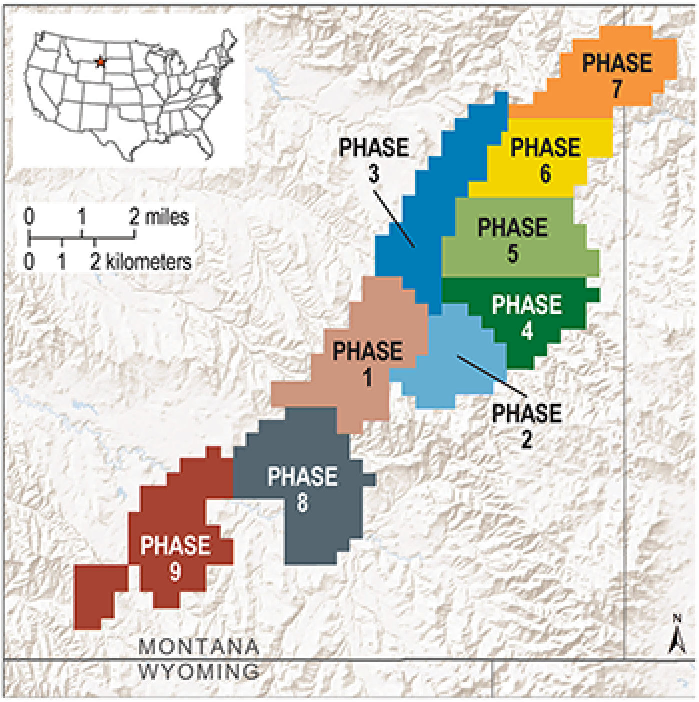
Source: Denbury Resources.

Figure G-10. *Geologic Description of Reservoir and Overlying Formations*

The reservoir is subnormally pressured with an initial reservoir pressure of only 1,200 pounds per square inch (psi) (hydrostatic pressure for this horizon would be 2,100 psi). The CO_2 miscibility pressure is estimated at 1,342 psi, as per slim tube and PVT study results. The field is currently operated at 3,100 psi to keep CO_2 in the dense phase and the EOR process largely miscible. The pressure is well below the fracture pressure of the reservoir and overlying seal. This operating pressure also allows the wells to flow, reducing the requirement for artificial lift.

B. Reservoir Development

Bell Creek CO_2 flood was developed in nine phases that covered the areal extent of the unit (Figure G-11). The initial development areas (Phases 1 through 4) were developed at 80-acre pattern spacing with five-spot pattern orientation (injector located in the center of four producers). A combination of previous existing wells and new drills were used to complete the patterns, and most of the OOIP in each of the phases is covered with patterns.



Source: Denbury Resources.

Figure G-11. *Phases of Development at Bell Creek*

The central injector in each pattern is set up to inject either CO_2 or water. The producers do not have artificial lift equipment because the field is kept at elevated reservoir pressure and therefore the wells flow naturally. The field achieved this elevated reservoir pressure through fill-up with water injection once the injection wells were in place.

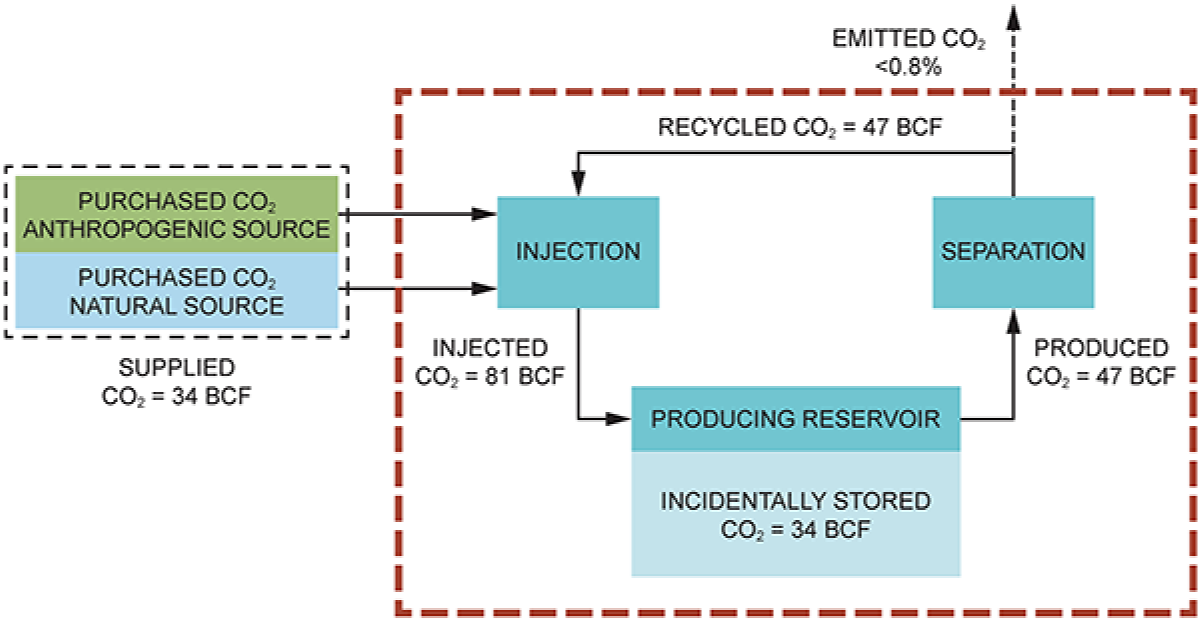
Phases 5 and 6 are the most recent developments. They are also completed with five-spot patterns but are more widely spaced at 160 acres. The Phase 5 development recently responded to CO_2 injection, and the Phase 6 development is underway with first injection expected to start in Q1 of 2019. Phases 5 and 6 are more centrally located in the field and represent the areas with some of the highest expected recoveries (and best rock qualities). Additional development phases will be brought online as compression capacity becomes available.

C. CO_2 Supply

The CO_2 for field injection is from the ExxonMobil LaBarge gas plant and the ConocoPhillips Lost Cabin gas processing plant in Wyoming. Total CO_2 delivered to the field is approximately 115 million cubic feet per day. The Lost Cabin facility initially generated about 50 million cubic feet per day, but declined to a rate of 35 million cubic feet per day by the end of 2018. The CO_2 is transported to the site via a 232-mile pipeline and is compressed to 2,200 psi for injection. New CO_2 acquired to date is more than 180 billion cubic feet. New CO_2 acquisition is scheduled to continue at declining rates as the field matures and full development is reached. An ultimate CO_2 volume of 220 billion cubic feet (12 million tonnes) is estimated to remain in the field at project completion.

D. CO_2 System Material Balance

A key element to demonstrating containment of CO_2 in an EOR process is through the identification of incoming, injected, and any emitted gasses. Figure G-12 illustrates this process and includes the values for the Bell Creek process in 2018. All values in the figure are in billion cubic feet.



Source: Denbury Resources.

Figure G-12. *Material Balance of the CO_2 System at Bell Creek*

The accounting of the system indicates that less than 0.8% of the CO_2 supplied to the Bell Creek EOR system is emitted to the atmosphere. The closed loop system allows for the gas to be produced, compressed, and reinjected for additional oil recovery.

E. PCOR Partnership

The Plains CO_2 Reduction (PCOR) Partnership, led by the Energy & Environmental Research Center (EERC) and supported by the Department of Energy, is working with Denbury Onshore LLC (Denbury) to determine the effect of a large-scale injection of CO_2 into a deep clastic reservoir for simultaneous CO_2 enhanced oil recovery (EOR) and associated or incidental CO_2 storage at the Bell Creek oil field.[1] Denbury owns and operates the field, while a technical team that includes Denbury, the EERC, and others conducts a variety of activities to determine baseline reservoir characteristics, build out the development plan, and frame out a testing program for monitoring strategies around the EOR activities. The partnership with PCOR should also extend the learnings from site characterization, risk assessments, and monitoring programs to applicability in other EOR or deep saline formation projects.

1. Site Characterization, Modeling, and Simulation

The more than 60 years of development and operational performance at Bell Creek offer a wealth of well, geologic, and dynamic production and injection data to build a thorough site characterization. This characterization is undertaken at a variety of levels from regional, field level, and phase level. These levels allow for different reference frames that may emphasize different characteristics.

Regional site characterization involves review of other Muddy fields in the Powder River basin and any characteristics of Bell Creek that may be transferrable. This level of analysis also involves reviewing the extent of the Mowry shale seal and other overlying shale layers. The field level characterization integrates the geologic information into a full field geomodel that honors the log, seismic, and core data. This geologic model covers the target Muddy formation and incorporates the stratigraphic features that may bank or trap CO_2.

The field level model is integrated with all the well perforations and dynamic data to build a simulation history match. Because the field is so large, this simulation history match is undertaken by development phase level. The first two phases (Phase 1 and 2) were completed as a connected geomodel as the pressure data indicate that the two phases communicate and exchange fluids. Integration of the dynamic data increases the likelihood of proper characterization and gives more clarity to the key drivers of success.

Site characterization is further enhanced by the gathering of pre-injection baseline information at the surface and near-surface levels to understand the fluctuations of natural CO_2 present in the soil, air, and water. The data gathered can help clarify whether CO_2 operations have impacted surface conditions. Site characterization is a foundational step in the progressing of a CO_2 EOR project that also confirms associated CO_2 storage.

Time and energy spent on this step can improve project economic viability while pointing to key early indicators of success or challenge.

2. Risk Assessment and Mitigation

Risk assessment plays an integral role in the formation of effective site characterization and monitoring plans.

Identification of risks helps the operator tailor the monitoring plan to areas with greatest uncertainty. Primary risks identified for the Bell Creek CO_2 project include wellbore leakage, out-of-zone fluid migrations, and early breakthrough or CO_2 channeling during the injection project.

Bell Creek has more than 450 wellbore penetrations that could provide potential pathways for CO_2 out of the target zone. Periodic collection and analysis of soil gas, surface water, and groundwater samples, along with continuous pressure monitoring at active injection and production wells, will allow for the early identification of potential injectivity or wellbore integrity issues. These anomalies can then be addressed via remediation activities, if necessary.

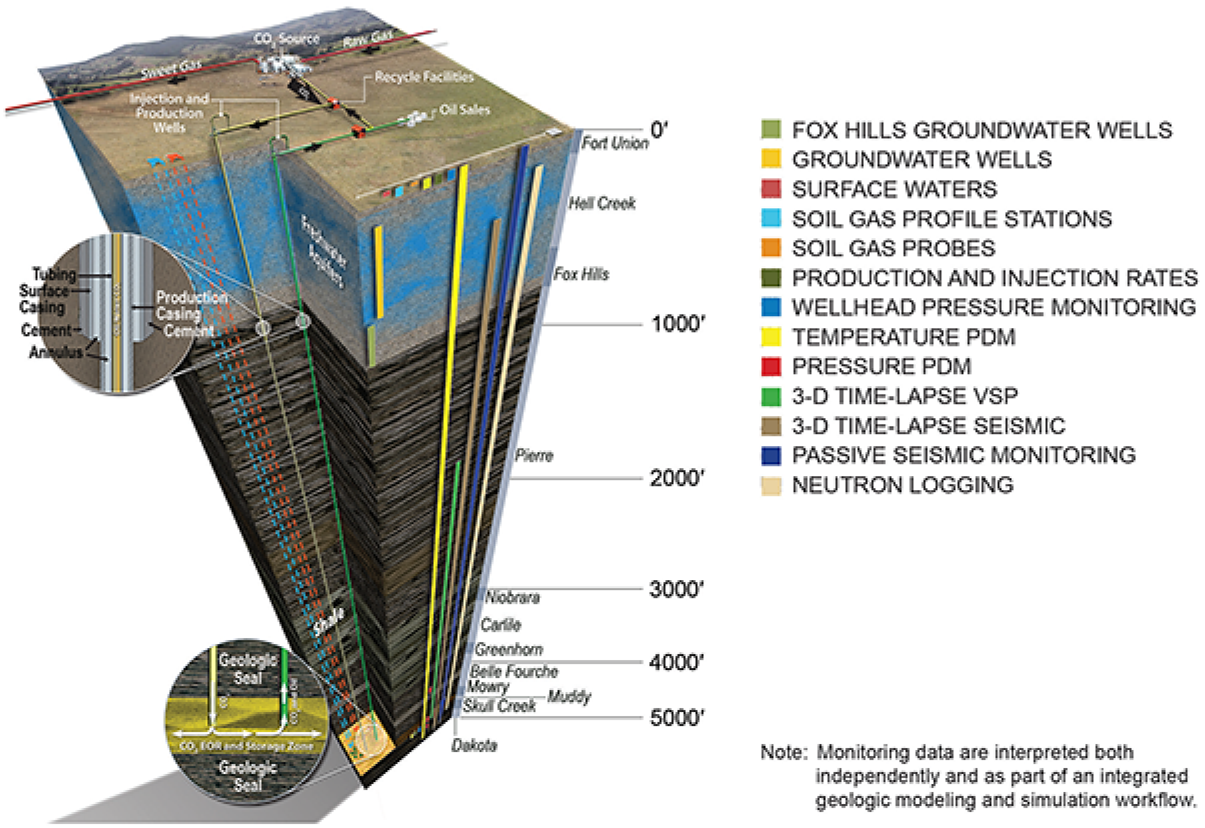
Out-of-zone flow, whether laterally or vertically, results in storage retention and economic challenges for the project. If CO_2 is not staying in the designated target zone, it is not being used effectively or economically. Early simulation work and detailed geomodeling enables a development team to build a plan that minimizes the likelihood of this occurrence. Incorporation of previous flood history (including waterflood and the polymer flood pilots) helps to increase the voracity of the modeling process. Baseline and periodic monitoring can provide early indicators to potential issues. The techniques used at Bell Creek include repeat 3D seismic surveys over time (also called 4D seismic), pressure and temperature data, and pulsed neutron lifetime (PNL) logs to quantify near wellbore fluid saturations.

Early breakthrough represents a challenge to flood’s economic performance as it limits contact of the CO_2 with the remaining oil saturation, thereby reducing the efficiency of the flood. Early breakthrough can be monitored with the same methods as out-of-zone flow with emphasis on production pressure, temperature and gas flow rates as key indicators. Early breakthrough risks can be somewhat mitigated by utilization of a WAG injection process, where water is injected in alternating cycles with CO_2 injection into the same well. The injected water cycles serve to “plug” off higher permeability zones and redirect the CO_2 to lower permeability zones with often higher residual oil saturations. WAG has been implemented in all phases of Bell Creek and supports better utilization of the CO_2 limited volumes that are available for injection.

3. Monitoring Plan

The monitoring plan for Bell Creek was developed to address findings from risk assessment and site characterization processes. A wide variety of techniques have been employed to test a range of technologies for this application. The plan includes a program of baseline monitoring followed by periodic repeat surveys and updates to test the integrity of the project.[2]

Monitoring techniques cover the range from surface to the reservoir formation at 4,500 feet (Figure G-13). Surface monitoring technologies include groundwater wells, surface water samples, and soil gas profile stations and probes. Surface monitoring data must identify and quantify baseline CO_2 concentrations (and fluctuations) under normal conditions so that any operational variances to this baseline may be detected. To date, no variances in baseline CO_2 concentrations have been observed as a result of Bell Creek CO_2 EOR flood operations.



Note: Monitoring data are interpreted both independently and as part of an integrated geologic modeling and simulation workflow.

Source: Energy & Environmental Research Center.

Figure G-13. *Illustration of Monitoring Techniques at Bell Creek*

Surface and subsurface monitoring is a standard practice of oil and natural gas operations, undertaken for a variety of reasons including economic, environmental, safety, and regulatory. While the partnership with PCOR at Bell Creek enabled testing of newer monitoring technologies, it did not change the fundamental focus of the monitoring activities—to ensure that the CO_2 injected stays in the reservoir and is used as efficiently as possible in the oil recovery process. The surface and subsurface monitoring techniques employed include wellhead pressure, production and injection rates, neutron logs, 3D seismic (initial and time-lapse), and one monitoring well. This combination of the data yields information on the areal and vertical location and characteristics of the CO_2 flood front and identifies production wells that are affected by CO_2 breakthrough at the wellbore.[3]

Many of the monitoring strategies utilized at Bell Creek and other typical oil and natural gas operations will have direct application in carbon capture, use and storage activities as well, whether it be associated or incidental storage resulting from CO_2 EOR operations, or dedicated CO_2 storage in deep saline formations.

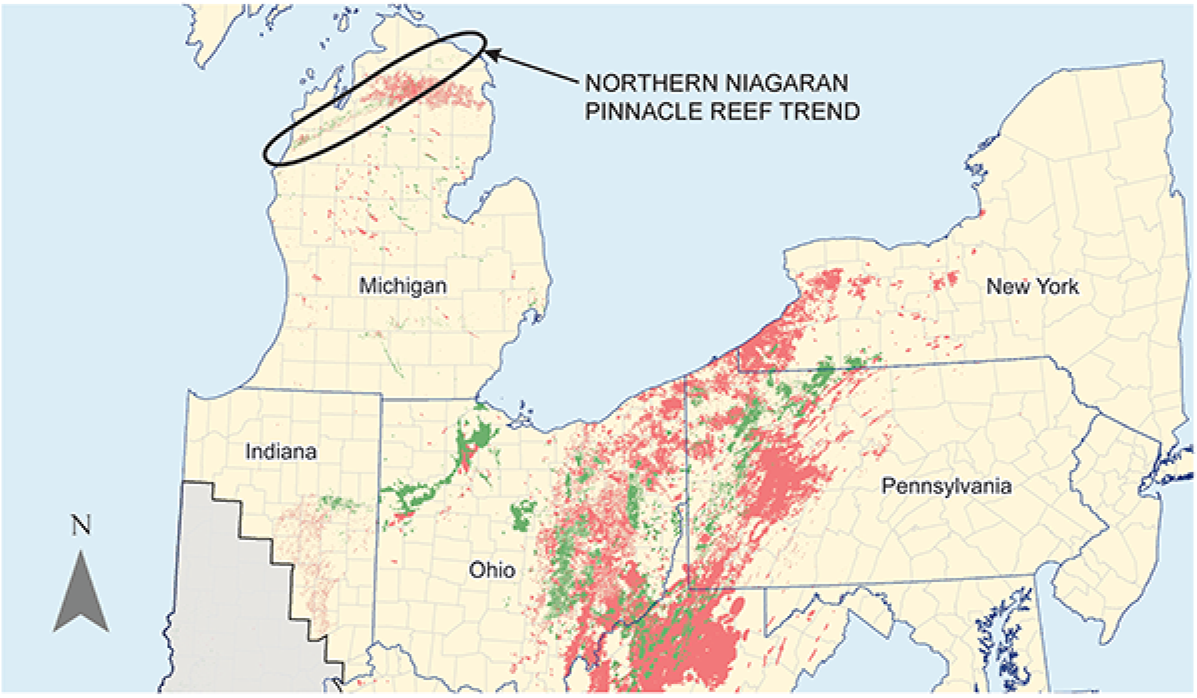
F. Summary

Denbury anticipates that the Bell Creek field will recover between 30 and 50 million barrels of oil through application of CO_2 EOR over the project life, for an incremental 8% to 14% of original oil in place[4] as a result of injection of more than 13 million tons of CO_2 over the project's life.

The project is providing a means to test and validate a range of site characterization, risk analysis, and monitoring techniques, methods and techniques that will be useful in ensuring the long-term and secure storage of CO_2 that is incidentally trapped as part of the project.

IV. CORE ENERGY MICHIGAN NORTHERN NIAGARAN PINNACLE REEF TREND

Core Energy LLC (Core Energy) operates an integrated CO_2 capture and EOR facility in the upper north portion of Michigan in what is known as the Northern Niagaran Pinnacle Reef Trend (NNPRT) (Figure G-14). The Core Energy facility includes equipment to capture CO_2 from various sources nearby, dedicated pipelines to deliver the CO_2 to the field and wells, a set of subsurface geologic reef formations, and equipment to process oil.



Source: Core Energy LLC

Figure G-14. *General Location of Core Energy Operations*

The Core Energy CO_2 EOR facility includes a total of 10 subsurface reef reservoirs that are in various stages of development. Core Energy has already produced 2.45 million barrels of oil and incidentally stored 46.08 billion cubic feet of CO_2 (2.42 million tonnes). The company estimates that as many as 250 million additional barrels of oil could be economically recovered through CO_2 EOR, and there is the potential to store hundreds of millions of tonnes of CO_2 through ancillary CO_2 EOR storage across the state of Michigan. Core Energy anticipates that it will be limited in the future by the amount of available CO_2, not by the amount of economically viable CO_2 EOR opportunities.

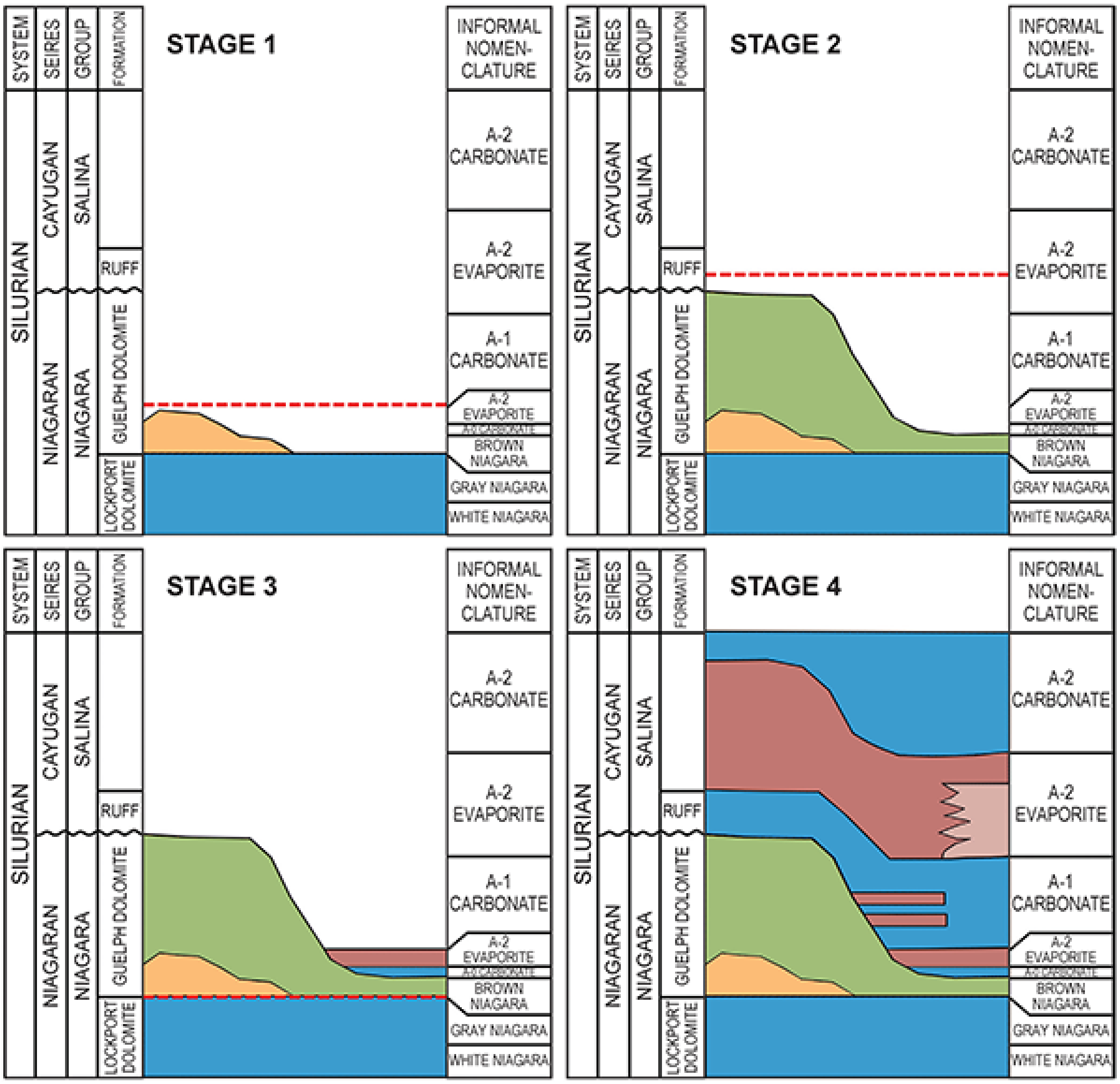
A. Geology

The NNPRT is part of an extensive paleo shallow shelf carbonate depositional system that forms a circular belt along the platform margin that rings the Michigan Basin. Most of the oil- and gas-producing reefs along the NNPRT are at depths of approximately 3,500 to 5,500 feet. While individual reef complexes are localized (averaging 50 to 400 acres in projected surface area), they may be up to 2,000 acres in total areal extent and 150 to 700 feet in vertical relief with steeply dipping flanks. Reef height, pay thickness, burial depth, and reservoir pressure increase toward the basin center.[5] Currently, there are approximately 800 fields in the NNPRT and another approximately 400 in the Southern Niagaran Pinnacle Reef Trend of the Michigan Basin.

The NNPRT is generally divided in the updip direction into gas, oil, and water-saturated zones. The reservoir facies consist primarily of porous and permeable dolomite and limestone. Some reefs are completely dolomitized, while others are essentially all limestone. Dolomitization of reefs increases as the reefs become shallower, and salt and anhydrite plugging of porosity occurs in the deeper reefs.[6]

Effective porosity intervals for the reservoir range from only a few feet to several hundred feet from reef to reef and location within the Trend. Porosity values extend to 35%, but typically average 3% to 12%; the best porosity and permeability are associated with dolomitized reef core and flank facies. The best reservoir rocks are characterized by well-developed intercrystalline and vuggy porosity with average permeability values of 3 to 10 millidarcies. Secondary porosity can significantly enhance permeability within the reservoir. The seals for the Niagaran reefs consist of a series of evaporites and salt-plugged carbonates that encase the flanks and top of the reefs, forming regional seals over the entire reef complex.

Figure G-15 illustrates the internal structure and geometry of reefs as well as their development cycle. This knowledge is important for predicting areas of best reservoir within the reef. The building of a Niagaran reef was initiated by carbonate mud-rich bioherm accumulation in warm, calm, shallow waters. The bioherm grew as sea level rose, following the prime conditions where biohermal organisms thrive (Stage 1). As sea level continued to rise, the reef core developed, dominated by corals and stromatoporoids. The wind direction during time of reef building was important because it created asymmetry within the reef.[7] The windward direction developed reef rubble where pieces of the reef core broke off and reduced in size by wave water impact. The leeward side developed a muddy detrital grain apron as fine-grained material sloughed off the reef (Stage 2). When relative sea level stabilized, stromatolitic algal caps formed over top of the reef and created an intertidal, depositional environment. Next, as sea level fell within the Michigan Basin, the reef complex was exposed (Stage 3), and the living reef was killed. Evaporites such as salt and anhydrites were deposited along the flanks of the reefs and diagenesis occurred within the reef core. As post-Niagaran sea level rose and fell, layers of carbonates and evaporites were deposited over the reef complex (Stage 4).



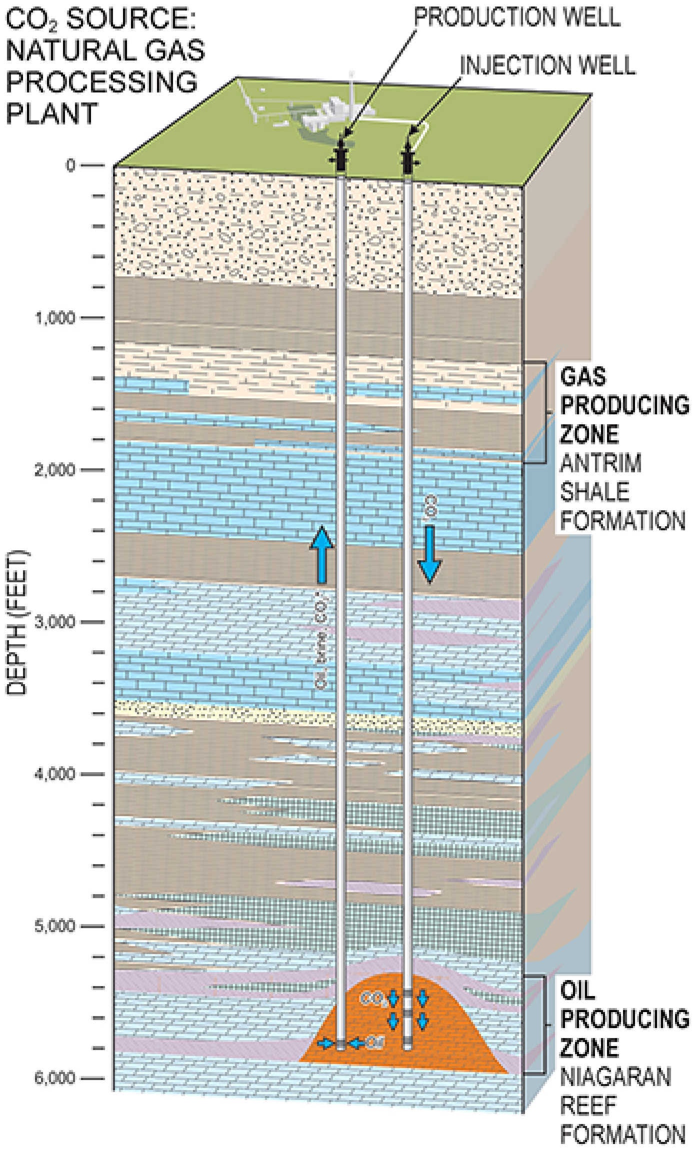
Source: Core Energy LLC.

Figure G-15. *Simplified Diagrams of the Stages of Niagaran Reef Development (Red dashed line denotes approximate sea level relative to reef growth.)*

B. Field Development

The NNPRT reefs were originally developed in the 1970s to 1980s and have undergone primary production and, in some cases, secondary recovery through water flood and other methods. After primary production in the reefs, secondary recovery methods were tried on a limited basis and abandoned due to limited success. In the late 1990s, CO_2 flooding was initiated in two reefs. In 2003, Core Energy was founded and took over operations in these two reefs. Since then the company has revitalized oil production from these reefs through application of CO_2 EOR.

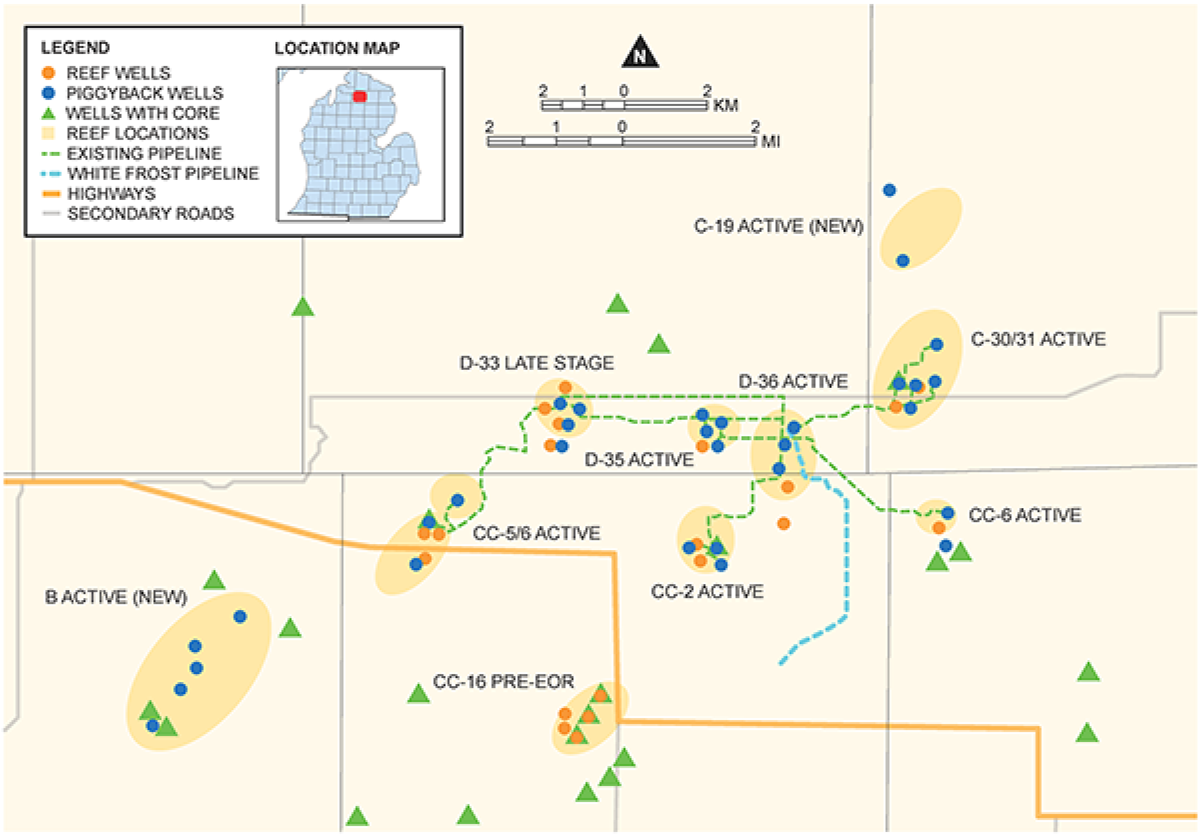
The drive mechanisms for the reef reservoirs under primary recovery is pressure depletion and the development of secondary gas caps. When CO_2 is injected into the reefs, it contacts the oil trapped in the pore space while simultaneously increasing the reservoir pressure from its depleted level toward the initial reservoir pressure. As contact and reservoir pressure increase, the minimum miscibility pressure for CO_2 in this oil is exceeded, and the CO_2 becomes miscible with the oil, improving its flow toward a designed production well. Figure G-16 illustrates the CO_2 EOR process in a reef field for a CO_2 injection well and the associated production well. Figure G-17 shows the reefs currently operated by Core Energy. Core Energy continues to explore and develop new reefs in the NNPRT.



Note: Not to scale.

Source: Core Energy LLC.

Figure G-16. *Simplified Diagram Illustrating CO_2 EOR Process in a Reef*



Source: Core Energy, LLC.

Figure G-17. *Active Reefs Operated by Core Energy*

C. CO_2 Supply

The original source of CO_2 for the Core Energy EOR Facility is a natural gas processing facility that treats gas produced from the Antrim Shale, as indicated at a depth of approximately 1,800 feet, also in Figure G-17. This source of CO_2 is expected to continue to be available and operating for another 10 to 20 years, depending on market conditions. Therefore, Core Energy is exploring options for new sources of CO_2, even as it exploits the flexibility inherent in the modular structure of its EOR facility to take as much CO_2 as it can from the current source.

D. Midwest Regional Carbon Sequestration Partnership

In 2005, Core Energy joined the Midwest Regional Carbon Sequestration Partnership (MRCSP). Research conducted under the auspices of the MRCSP effort have expanded Core Energy’s knowledge of the NNPRT geology and informed reservoir modeling for the reefs. This work demonstrates the integrity of the reef structures, informs the operational plans, and helped to create a data collection system to track the amount of CO_2 stored in the project as a result of CO_2 EOR operations.

E. Monitoring

As with other CO_2 EOR projects, permits for CO_2 injection have been issued under the Underground Injection Control Class II program of the U.S. Environmental Protection Agency. Early on, Core Energy reported the amount of CO_2 it receives under Subpart UU of the EPA’s Greenhouse Gas Reporting Program (GHGRP). In 2018, Core Energy opted into the GHGRP Subpart RR program so that it could quantify the amount of CO_2 storage achieved as a result of its CO_2 EOR operations.

As an initial step, Core Energy developed a monitoring, verification, and reporting (MRV) plan to describe the operations, the monitoring program, and its CO_2 material balance quantification plan. The MRV plan was approved in late fall of 2018, and Core Energy is assembling its first report, which is expected to be submitted in 2019.

F. Summary

The Core Energy CO_2 EOR Facility demonstrates the diversity and value of potential CO_2 EOR projects. The reefs have proven to be an excellent geologic setting for oil production and CO_2 storage. The use of oil fields that had been developed and depleted previously, or that have been completely abandoned, is an approach that can be repeated elsewhere in the United States. The revitalization of these fields further optimizes the natural resource, provides economic development, and ultimately stores CO_2 that would otherwise be emitted to the atmosphere. It is estimated that in northern Michigan alone, the reefs in the NNPRT could sequester several hundred million tonnes of CO_2.

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Appendix H

CO_2 ENHANCED OIL RECOVERY ECONOMIC FACTORS AND CONSIDERATIONS

Development costs are an important driver in the economics of carbon dioxide (CO_2) enhanced oil recovery (EOR) projects. These costs are difficult to generalize since they are highly dependent upon the type, size, and location of the project being developed, and the depth of the play.[1] Costs can also vary considerably due to well configurations and whether or not existing field wells and equipment can be repurposed for the CO_2 EOR application. Most CO_2 EOR plays have their own set of idiosyncrasies that can impact overall project economics in positive and negative ways.

There is, however, a broad set of costs that are common to most CO_2 EOR applications. These include:

- Cost of the supply of CO_2 for injection purposes

- Cost to drill a series of CO_2 injection wells and/or converting selected producing wells to injection wells
- Cost to install surface facilities needed to separate, measure, recycle, and transport the CO_2 into the subsurface
- Cost of added compression
- Cost to provide additional surface equipment that is needed.

In addition, there are other economic factors that impact overall CO_2 EOR profitability, particularly those associated with financing these types of projects. This appendix explores each of these factors and examines how the component costs vary and change CO_2 EOR project economics. The appendix borrows heavily from the work prepared by Godec in 2014 that surveys and discusses each of these important CO_2 EOR cost components.[2]

I. CO_2 ACQUISITION COSTS

Godec notes that CO_2 acquisition costs are a very important component of overall CO_2 EOR costs.[3] When coupled with their corresponding recycling costs (discussed later), CO_2 acquisition can account for 25% to 50% of all CO_2 EOR project costs. EOR projects generally acquire CO_2 in one of three different ways. First, the EOR project is integrated as part of a capture-transport-storage application that sources naturally occurring CO_2 and transports it to the EOR site, where it is then used in production operations. Most existing projects currently use this type of acquisition model. Second, EOR projects are part of an integrated project that includes an anthropogenic CO_2 source captured from either a power plant or industrial source and transported to the EOR site. Third, a project may acquire CO_2 from a pipeline, regardless of source, and then use that CO_2 for EOR purposes.

As will be discussed later, the nature of the source (natural or anthropogenic CO_2) and the industry structure can affect overall CO_2 commodity costs, as well as overall delivered CO_2 costs to an EOR site. Industry organization (i.e., if the CO_2 is provided as part of a vertically integrated application) can also affect the terms and conditions under which CO_2 is provided to a particular EOR site, as well as the manner in which that CO_2 is priced.

II. WELL DEVELOPMENT COSTS

Well development costs are an important component cost of any CO_2 EOR project. Well design and project requirements, in addition to well unit costs, drive overall well development costs for a given CO_2 EOR project.

Well requirements are based on initial assessments regarding how many, and what types of, wells will be needed in a given CO_2 EOR application. The produced water arising from a CO_2 EOR project will affect well requirements since additional wells will be needed to maintain reservoir pressure. There are some instances where existing onsite infrastructure can be repurposed for the CO_2 EOR application. For instance, formerly producing wells can sometimes be used as CO_2 injection wells depending on location and well integrity.

The number and type of injection wells needed for a CO_2 EOR project are difficult to generalize since they are custom tailored depending on the specific properties of each reservoir. Further, well-specific development costs will be a function of the type, location, number, and more importantly, the depth of all such wells. Well costs generally increase with depth and complexity.

Artificial lift requirements for CO_2 EOR producers present an additional cost compared to natural lift operations. This is because the volume and composition of produced fluids can change significantly over the duration of a CO_2 EOR project, requiring periodic changes to the artificial lift system. A waterflooded producer may produce oil with a low gas-oil ratio and a high water-oil ratio. After CO_2 injection begins, the same producer typically experiences an increasing gas-oil ratio and decreasing water-oil ratio. It is important that the artificial lift system be capable of efficiently removing produced fluids from the well across the full range of operating conditions.

III. SURFACE FACILITY COSTS – INJECTION/RECYCLING COSTS

CO_2 EOR projects require a unique set of surface facilities and equipment to capture, separate, and re-inject CO_2. The costs for these facilities can represent one of the more expensive sets of costs at a CO_2 EOR project. Surface facility costs are a function of the various plant component costs needed to facilitate a CO_2 EOR project, which in turn, are a function of the specific field being developed for CO_2 EOR purposes.

Equipment component requirements can be difficult to generalize since every EOR project is unique. There are, however, several common CO_2 EOR plant components that are required, including separation equipment (gas/liquid, water/oil, CO_2/hydrocarbon—even though some separation may occur in satellite locations), dehydration, and in some instances, hydrogen sulfide (H_2S) removal. The most substantive cost with a CO_2 recycling plant is typically the compression cost.

Recycling plant capital costs are a function of the scale at which the plant's capacity is developed. Higher plant capacities can potentially lead to some moderate scale economies as higher upfront costs are divided by more production and CO_2 volumes. Godec, for instance, identifies 30 million cubic feet per day of CO_2 as the threshold for lower recycling plant unit costs.[4] This threshold assumes standard temperatures (62°F) and pressures (14.696 pounds per square inch gauge).

The primary annual operations and maintenance (O&M) cost associated with a CO_2 recycle plant will be associated with operating the onsite compression. If this compression runs on natural gas, then recycling plant O&M costs will be dependent on commodity gas price changes. If the compression is run using electricity, then recycle plant O&M costs will be dependent on retail electricity prices.

In some instances, CO_2 EOR facility costs will need to include the costs of capturing, separating, and compressing natural gas liquids (NGLs). Again, Godec notes that the unit costs of these NGL recycle costs will be a function of scale, with higher recovery rates having lower unit costs than plants designed to recover a lower rates of NGLs.[5] Godec identifies a threshold recovery rate of 20 million cubic feet per day as being the point at which unit costs for NGL recovery can start to decrease, driven by the large capital costs associated with developing the necessary compression to collect and move the NGLs offsite to commercial NGL pipeline pressures. The O&M costs for any NGL recovery plant, if needed, will also be driven by compression-related costs and whether the compressor is being run on natural gas or retail electricity.

Last, the CO_2 EOR facilities require a system of pipes and manifolds to move CO_2, water, and hydrocarbons throughout the field. This distribution network, and its costs, will be comparable to a typical gathering system at a traditional oil and natural gas field. Fluid distribution costs will be driven by the level of pipeline capital investment required for the anticipated field operations. Pipeline capital costs will be a function of the pipe diameter and its wall thickness, which will differ from what is traditionally used for natural gas purposes at a production field given the higher operating pressures needed for CO_2.

IV. ADDITIONAL COMPRESSION COSTS

Most of the compression costs needed for a CO_2 EOR application would be included in the recycling plant costs noted earlier. There could be some instances, however, where the CO_2 arrives at the field locations at less than optimal pressures. A hypothetical example would be an instance where a former natural gas pipeline is repurposed for CO_2 transportation, but that CO_2 is moved as a gas at relatively lower pressures than is typical. For instance, Dismukes et al. examined opportunities for repurposing natural gas transportation lines for CO_2 transportation, but found few opportunities; however, they recognized that such opportunities are often very field-specific.[6] If such an application were utilized, additional onsite compression would be needed to raise the transported CO_2 pressures to those commonly used for injection purposes. The economics of this application would be based on the relative costs of repurposing an older natural gas transportation line and field-specific compression, versus using a newer line with booster pumps to provide pressure to the delivery location. To the extent that such applications are economic, it would likely be for relatively short distances.

V. SURFACE FACILITY COSTS – OTHER CO_2 EOR COSTS

There are many other miscellaneous field equipment costs that are required to complete a CO_2 EOR project, and these are typically associated with the scope and location of the project. Godec notes that any CO_2 EOR project will have a host of additional equipment costs (capital and operating) needed to run project equipment and its fluid management systems.[7,8] Some of this incremental equipment may include free water knockout, water disposal, other water treatment costs, and various pumps, and the electricity needed to run these pumps will need to be purchased.

Water treatment requirements can increase the capital and O&M costs associated with separation, filtering, pumping, and waste fluid injection. Retail electricity prices may impact additional fluid lifting costs, as well as the running of filtration systems, smaller pumps, heaters, and lighting. While these costs collectively are not considerable and do not rival CO_2 recycle plant costs, they can influence overall project economics.

Godec notes that other important costs include those associated with site, field, and well assessments. Other upfront capital expenditures include mechanical integrity reviews of existing/older wellbores and surface production equipment, pressure testing casing and replacing old tubing, installing new wellheads, installing new flow lines as well as addressing any specific localized environmental requirements.

VI. OTHER ECONOMIC FACTORS

The economic performance of a CO_2 EOR project will be a function of a number of factors that may be beyond the control of the oil and natural gas operator, or of any other market participant. These factors include commodity prices, recovery factors and decline rates, capital cost factors, industry structure, and government policies and incentives (the latter is not discussed in this appendix; see instead Chapter 3 in Volume II of this report). The levels, variability, and uncertainty of each of these factors can have considerable implications for CO_2 EOR adoption and the development of a CO_2 EOR-based carbon market.

A. Commodity Prices

Commodity prices can affect CO_2 EOR development in two different ways. The first is related to the absolute level of crude oil prices, since there is a positive relationship between EOR profitability and high oil prices. Higher oil prices directly improve EOR profitability. Lower crude oil prices may reduce the incentive to engage in these activities entirely, unless state or federal government incentives are offered.

The second is the relationship between EOR adoption decisions and the volatility of oil price movements. In some instances, oil price volatility on its own can create sufficient uncertainty about sustained project economics to discourage the development of CO_2 EOR projects. Some CO_2 supply contracts provide for a reduction in CO_2 price when oil price falls. This provides a buffering effect and may allow CO_2 floods to sustain operation during times of low oil prices.

CO_2 is, and will increasingly become more of, a tradeable commodity that will follow market trends as do other commodities. CO_2 credits are already traded on markets in the Mid-Atlantic region (through the Regional Greenhouse Gas Initiative) and in California, and the prices for these credits can take sharp turns depending upon market conditions and policy expectations.

B. Recovery and Decline Rates

Welkenhuysen et al. show that geologic uncertainty influences the oil producer's view of the economic threshold level for an EOR project.[9] The authors use a series of simulation models to predict producer decisions given changes in both crude oil prices and EOR-based production outlooks. The authors found that geological uncertainty is an important factor. It is likely more important than developing fixed revenue streams through a unit-tax credit like a carbon tax. The simulation modeling, conducted for potential applications in the North Sea, shows that crude oil prices and recovery factors have nonlinear impacts on EOR project profitability. The authors caution that assessing EOR project economics without a strong respect for residual geological uncertainty can lead to erroneous profitability and EOR adoption rate conclusions.

C. Capital Cost Sensitivity, Escalation, and Uncertainty

King et al. examined cost and profitability outcomes (on a net present value, or NPV, basis) using an integrated systems approach (integrated source-to-sink cost analysis) and found that under all scenarios, the profitability of a CO_2 EOR application using anthropogenic CO_2 was negative.[10] However, the negative profitability improves (less negative NPV cash flows) as costs are reduced. In fact, the authors note that if CO_2 acquisition and recycling costs are low enough, it is feasible that some CO_2 EOR projects could flip to positive NPV cash flows.

The ability to keep recycling costs down will largely be a function of how much existing/legacy field equipment, particularly wells, can be repurposed. If existing wells can be used for production and injection, it is likely that overall unit costs can be driven down. If existing in-field equipment can be reused, particularly piping and compression, overall field distribution costs may be lowered, as well. These are big “ifs” and underscore that: (1) cost estimates are usually a function of CO_2 EOR project specifics and can be difficult to generalize, and (2) there can be unknowns and uncertainties that can affect final costs that increase project risks and reduce profitability.

Cost escalation can also affect the profitability and economics of a CO_2 EOR project. While high oil prices are good for CO_2 EOR projects, they often drive higher drilling activity that often puts pressure on drilling and field service costs. Unanticipated cost escalation can have negative effects on overall CO_2 EOR profitability, even in high oil price environments. Increases in future recycling plant upgrade costs and other capital maintenance expenses can also negatively affect CO_2 EOR project economics.

Last, geography can have an important impact on capital costs for CO_2 EOR projects. Dismukes et al.,[11] King et al.,[12] and Dubois[13] show that having numerous anthropogenic CO_2 sources and EOR projects in close proximity to one another can reduce overall project capital costs and improve project economics, primarily by reducing expensive transportation and compression costs. Compression is the most significant operating cost in the transport of CO_2. Therefore, oil fields that are in close proximity to several anthropogenic sources, particularly lower-cost industrial capture sources, are likely to have greater profitability than those spread over larger areas.

D. Industry Structure

Roussanaly and Grimstad note that even though CO_2 EOR projects have existed in the oil and natural gas industry for more than four decades, recent proposals, which increasingly emphasize the CCUS benefits of such projects, can strongly influence business model decisions and profitability.[14] The authors note that if the CO_2 capture and transport activities are handled by an entity other than the oil field operator, potentially competing development objectives may arise.

Al Mazrouei et al. show that industry structure can have implications not only on profitability but also on EOR infrastructure in development decisions.[15] The authors employ simulation to establish that an integrated approach to EOR project development can result in outcomes quite different from, and better than, those achieved by multiple players acting independently. Thus, facilitating a competitive and healthy CO_2 EOR industry will be important for the efficient scale up of CO_2 EOR projects.

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ACRONYMS AND ABBREVIATIONS

ADM	Archer Daniels Midland Company
ANSI	American National Standards Institute
AoR	Area of Review
ARB	Air Resource Board (California)
ARPA-E	Advanced Research Projects Agency of the Department of Energy
BBA	Bipartisan Budget Act (2018)
BCF/D	billion cubic feet per day
BECCS	bioenergy carbon capture and storage
BEG	Bureau of Economic Geology (University of Texas)
BF	blast furnace
BOF	basic oxygen furnace
BLGCC	black liquor integrated gasification combined cycle
BLM	Bureau of Land Management
BOEM	Bureau of Ocean Energy Management
BOF	basic oxygen furnace
BSCF/D	billion standard cubic feet per day
BSEE	Bureau of Safety and Environmental Enforcement
BTU	British thermal unit
$CaCO_3$	calcium carbonate
CAG	CCUS Advisory Group
CAP	closure assurance period

CCPI	Clean Coal Power Initiative
CCS	carbon capture and storage
CCU	carbon capture and use
CCUS	carbon capture, use, and storage
CES	Clean Energy Standard
CFD	contract for difference
CFR	Code of Federal Regulations
CHP	combined heat and power
CO_2	carbon dioxide
CO_2e	carbon dioxide equivalent
COG	coke oven gas
CRI	Carbon Recycling International
DAC	direct air capture
DOE	Department of Energy
DOI	Department of the Interior
DOT	Department of Transportation
EAF	electric arc furnaces
EEZ	exclusive economic zone
EIA	Energy Information Administration
EOR	enhanced oil recovery
EPA	Environmental Protection Agency
ESP	Energy Saving Process
ETIA	Energy Tax Incentives Act
ETS	emissions trading systems
FCC	fluid catalytic cracking
FER&D	Fossil Energy Research and Development
FERC	Federal Energy Regulatory Commission
FLIGHT	Facility Level Information on Greenhouse gases Tool

FUTURE	Furthering carbon capture, Utilization, Technology, Underground storage, and Reduced Emissions Act
GDP	gross domestic product
GHG	greenhouse gas
GJ	gigajoule
GOM	Gulf of Mexico
GOR	gas oil ratio
GS	geologic storage
Gt	gigatonnes
H_2	hydrogen
HCPV	hydrocarbon pore volume
IEA	International Energy Agency
IEAGHG	IEA Greenhouse Gas R&D Programme
IGCC	integrated gasification combined cycle
IL-ICCS	Illinois Industrial Carbon Capture and Storage
IPCC	Intergovernmental Panel on Climate Change
IRS	Internal Revenue Service
ISO	International Standards Organization
ITC	Investment Tax Credit
K	Kelvin
kJ	kilojoule
kJ/mol	kilojoules per mole
LED	light-emitting diode
LNG	liquefied natural gas
LPG	liquefied petroleum gas
LVC	lean vapor compression
MDEA	methyldiethanolamine
MEA	monoethanolamine

MES	microbial electrosynthesis
µm	micrometer
MLA	Mineral Leasing Act
MLP	master limited partnerships
MMB/D	million barrels per day
MMBTU	million British thermal units
MMCF/D	million cubic feet per day
MMP	minimum miscibility pressure
MMscf	million standard cubic feet
MOF	metal-organic frameworks
MPRSA	Marine Protection, Research, and Sanctuaries Act
Mt	million tonnes
Mtpa	million tonnes per annum
MTR	Membrane Technology and Research, Inc.
MW	megawatts
MWe	megawatts-electric
MWh	megawatt hour
NASEM	National Academies of Sciences, Engineering, and Medicine
NCCC	National Carbon Capture Center
NEPA	National Environmental Policy Act
NETL	National Energy Technology Laboratory
NGCC	natural gas combined cycle
NGO	nongovernmental organizations
NIMBY	not in my backyard
NPC	National Petroleum Council
NPS	New Policies Scenario
NRAP	National Risk Assessment Partnership
NUMBY	not under my backyard

OCS	Outer Continental Shelf
OCSLA	Outer Continental Shelf Lands Act
OECD	Organisation for Economic Co-operation
OOIP	original oil in place
PCC	precipitated calcium carbonate
PEM	proton exchange membrane
PHMSA	Pipeline and Hazardous Materials Administration
PIM	porous inorganic membranes
PISC	post-injection site care
ppm	parts per million
PSA	pressure swing adsorption
psi	pounds per square inch
psig	pounds per square inch gauge
PTC	production tax credit
R&D	research and development
RCP	reinjection compression plant
RCSP	DOE’s Regional Carbon Sequestration Partnerships
RD&D	research, development, and demonstration
ROZ	residual oil zone
RPS	renewable portfolio standard
RTO	regional transmission organization
SACROC	Scurry Area Canyon Reef Operators
SDS	Sustainable Development Scenario
SDWA	Safe Drinking Water Act
SMR	steam methane reforming
SOA	state-of-the-art
SOE	solid-oxide reactor
SSEB	Southern States Energy Board

STB	Surface Transport Board
STEPS	Stated (Energy) Policies Scenarios
TCF	trillion cubic feet
TCM	Technology Centre Mongstad
TIFIA	Transportation Infrastructure Finance and Innovation Act
TRL	technology readiness level
TSA	temperature swing adsorption
UF	utilization factor
UIC	underground injection control
USDA	U.S. Department of Agriculture
USDW	underground sources of drinking water
USGS	U.S. Geological Survey
VSA	vacuum swing adsorption
WAG	water alternating gas