MEETING THE
DUAL CHALLENGE

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

CHAPTER FIVE –
CO_2 CAPTURE

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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 ferroalloy manufacturing; oil and gas processing; and pesticides, fertilizers and other agricultural chemical manufacturing, and bioethanol fermentation.

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

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

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[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.

program that includes collaboration from public and private sources in addition to durable funding mechanisms and stable legal and regulatory frameworks.

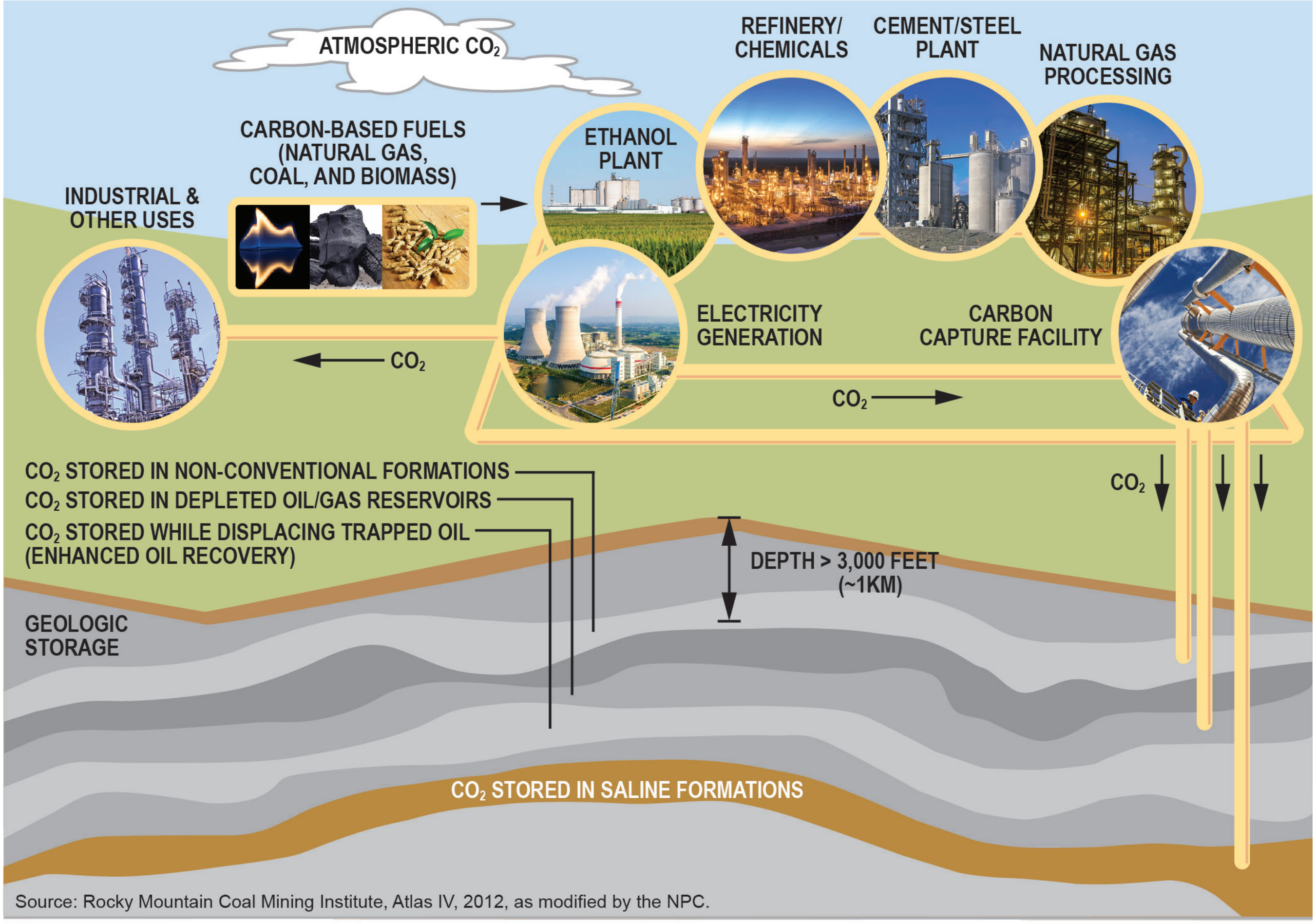
II. WHAT IS CO_2 CAPTURE?

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.

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



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*

- 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.

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

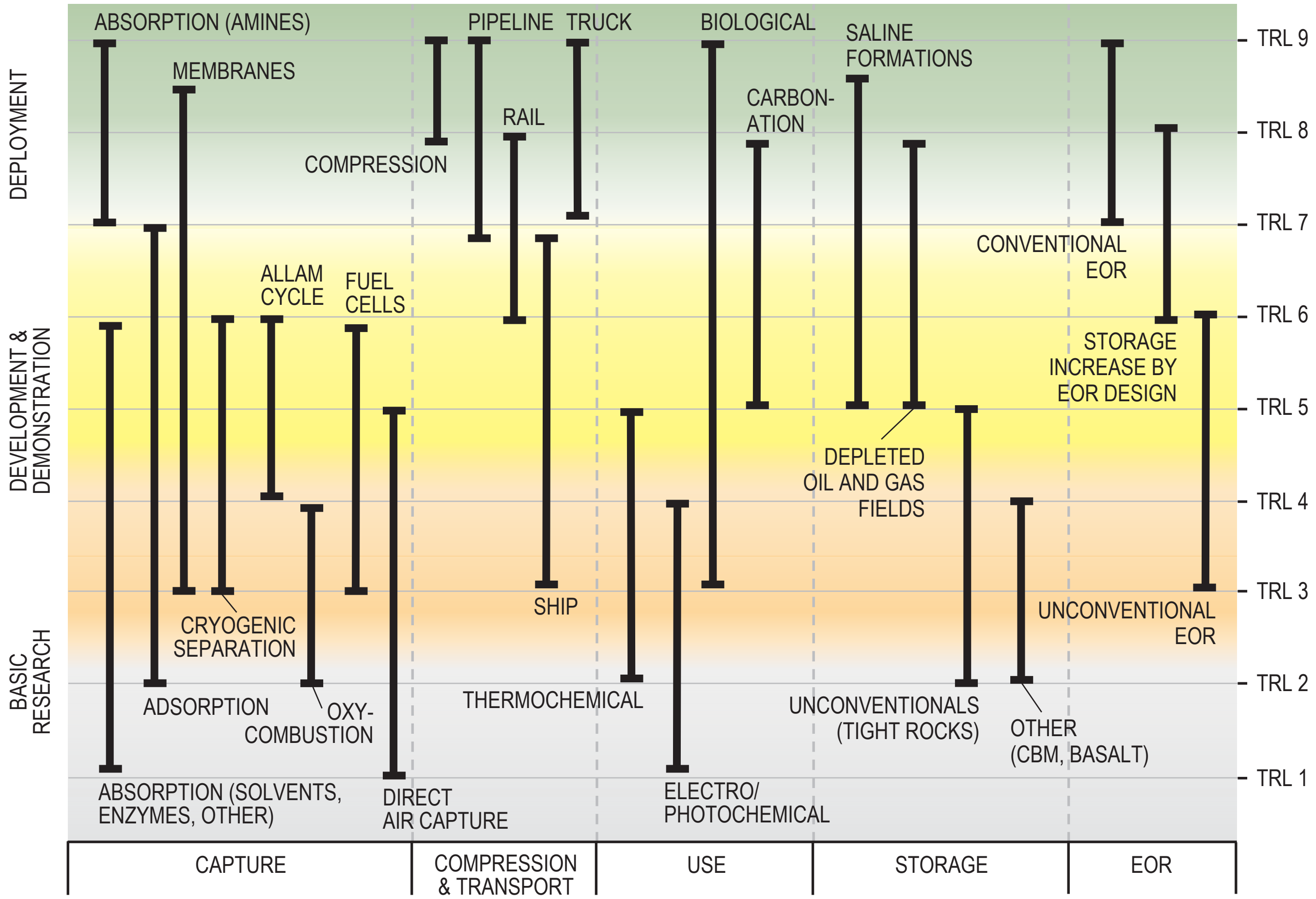


***Figure 5-2.** Technology Readiness Level (TRL) Ranges for CCUS Technologies*

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.

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%).

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).

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.

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*

Source: Air Products and Chemicals, Inc.

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

Source: Archer Daniels Midland Company.

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

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

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[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.

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 retrofitted to existing fossil-fuel power plants and other industrial emitters.

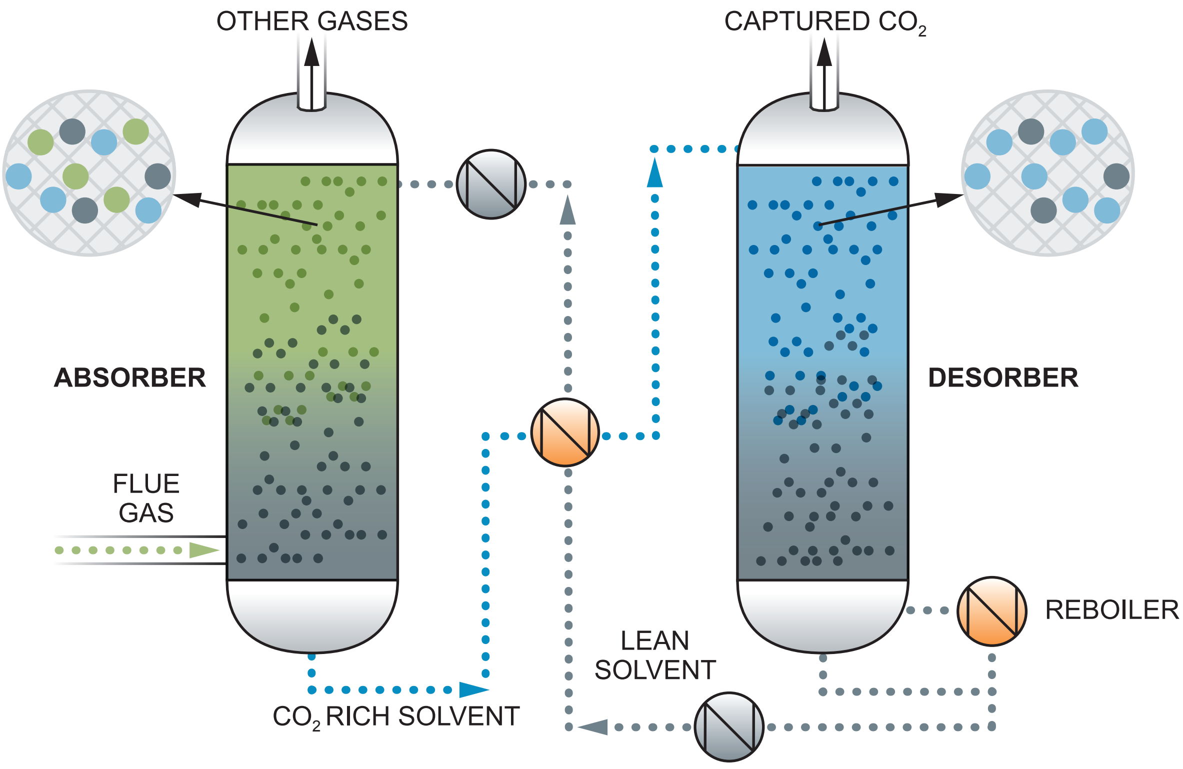
A specific technology may have a marketplace advantage over other technologies given variable factors such as cost, operability, environmental footprint, CO_2 concentration in the feed gas stream, purity of CO_2 required in the outlet stream, and other practical aspects. However, even if a capture approach 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

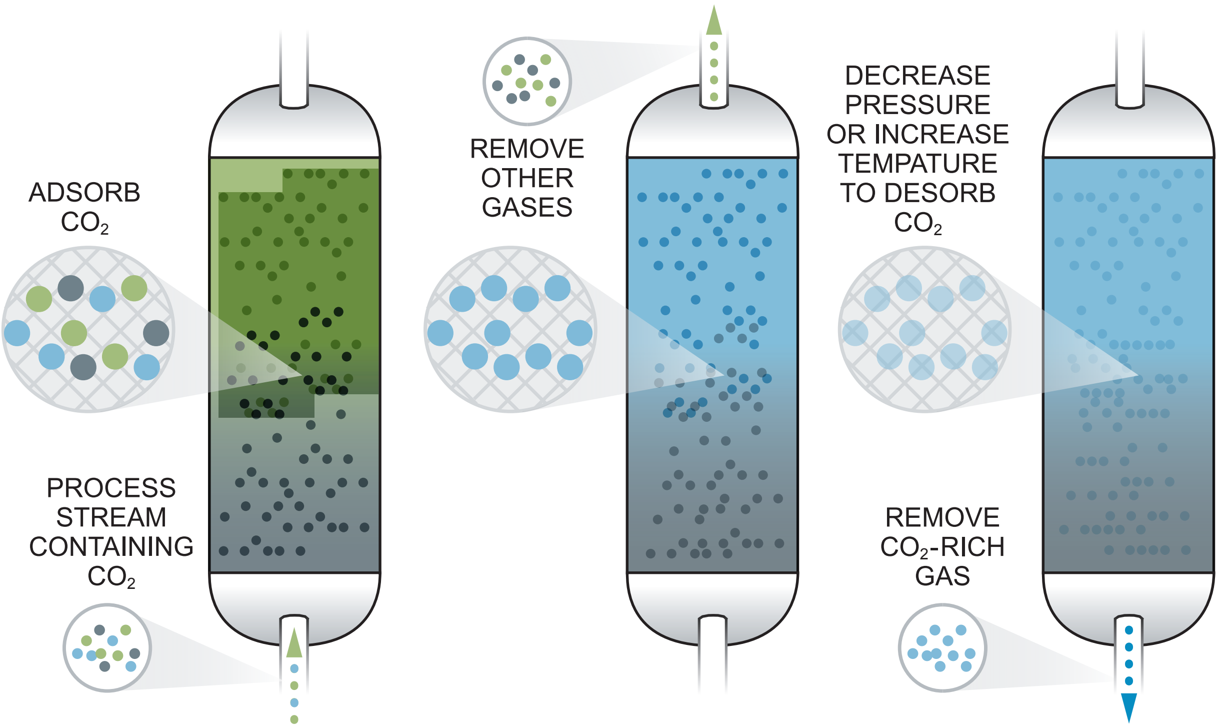
Absorption refers to the uptake of CO_2 into the bulk phase of another material, such as dissolving CO_2 molecules into a liquid solution. This is different than adsorption where CO_2 molecules adhere to the surfaces of another material (Figure 5-10).

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



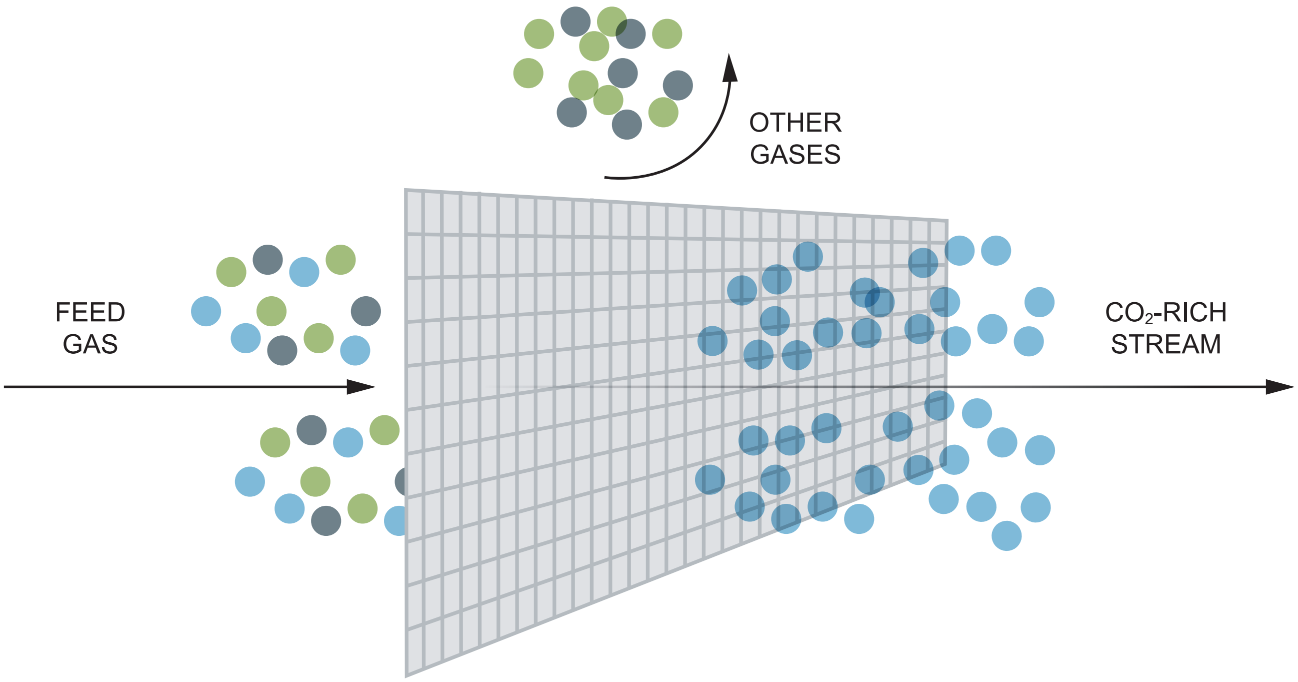
Source: CO2CRC.

Figure 5-6. *CO_2 Capture by Absorption*



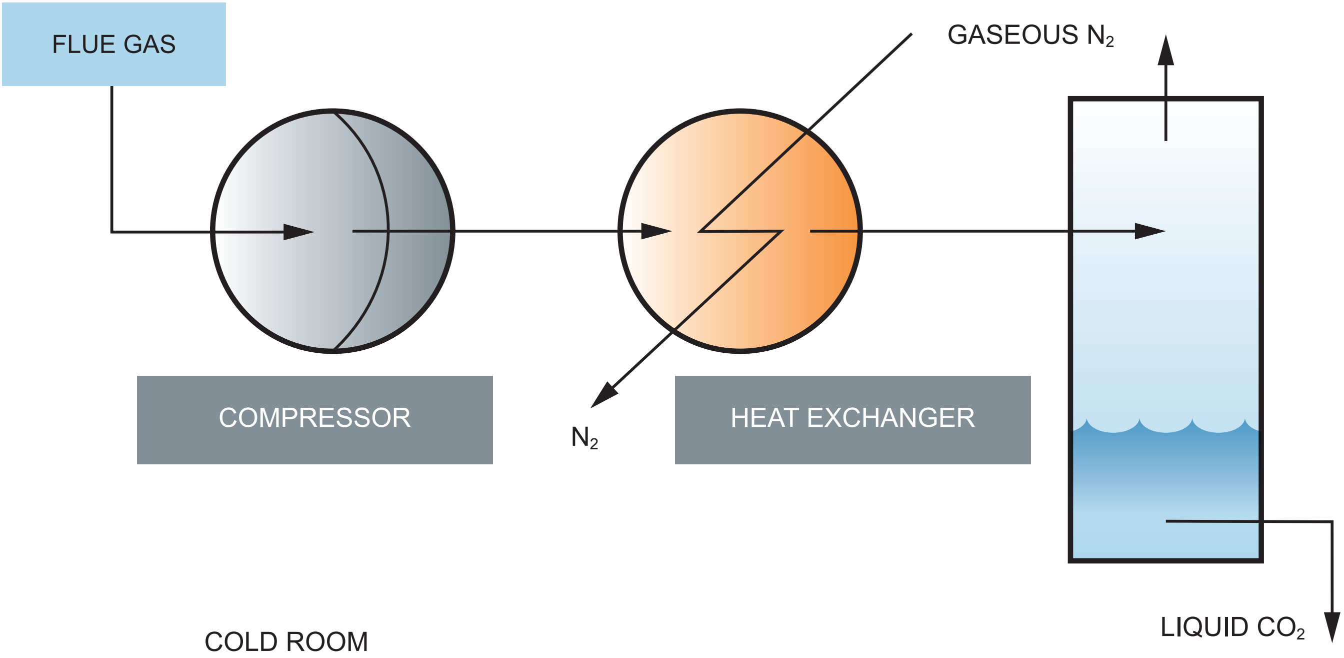
Source: CO2CRC.

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*

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.

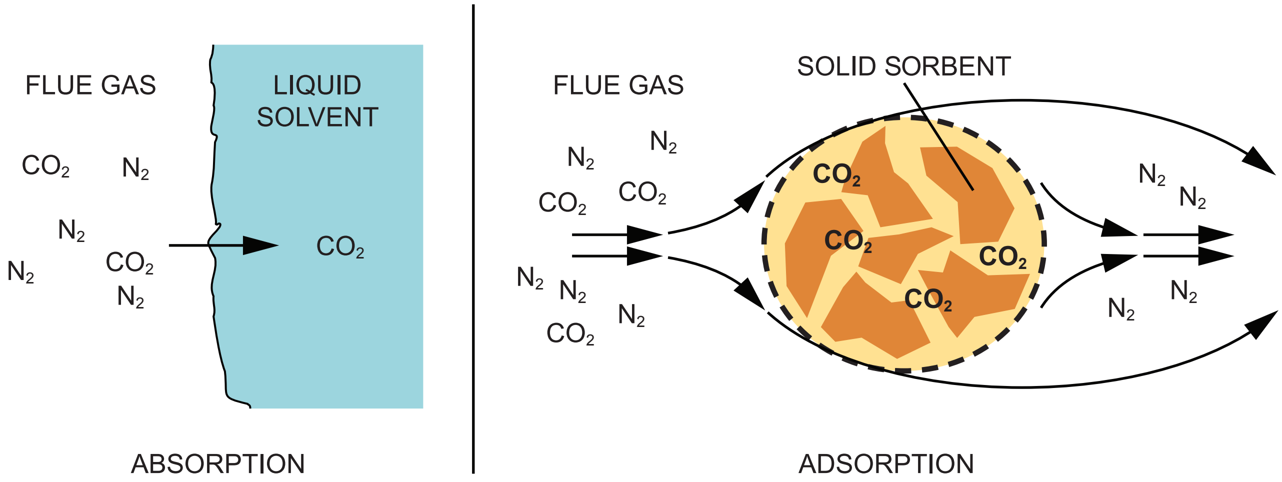


Figure 5-10. *Mechanisms of CO_2 Absorption and Adsorption*

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.

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.

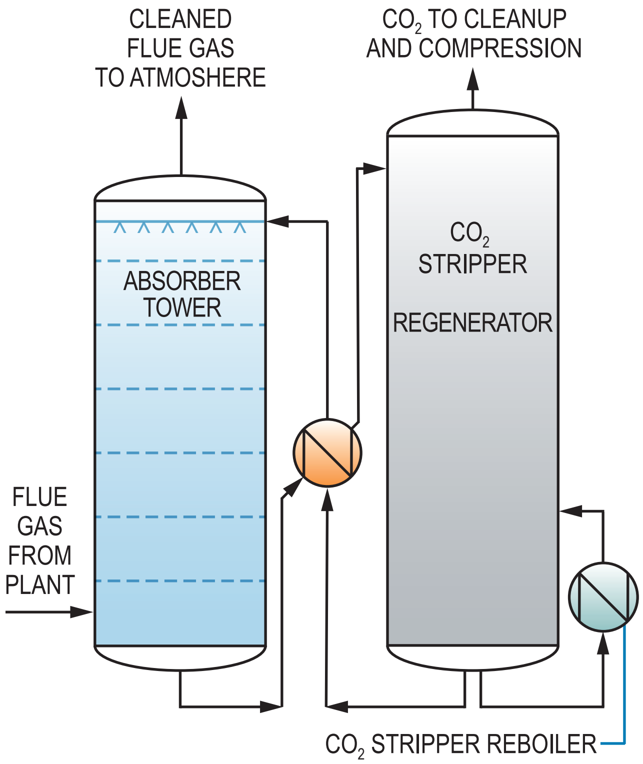


Figure 5-11. Conventional Absorption-Regeneration Process

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

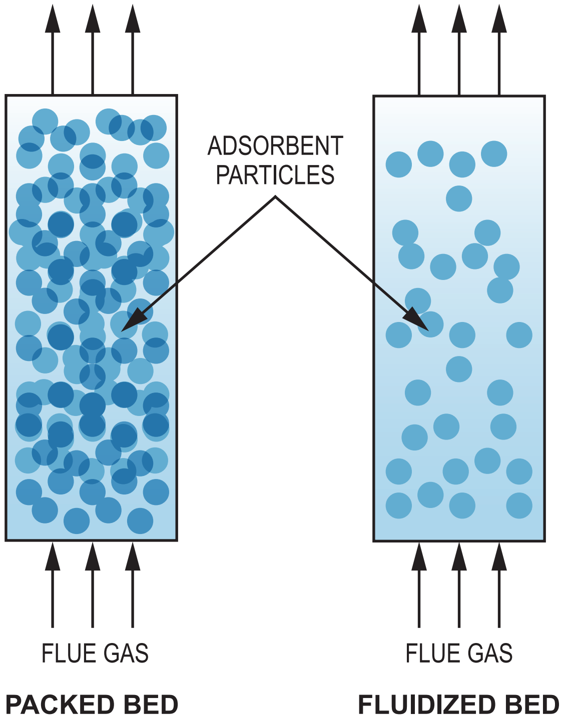


Figure 5-12. *The Packed Bed and Fluidized Bed Adsorption Processes*

adsorbent selectively adsorbs more CO_2 relative to the other constituents passing through the column.

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

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[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.

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.

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

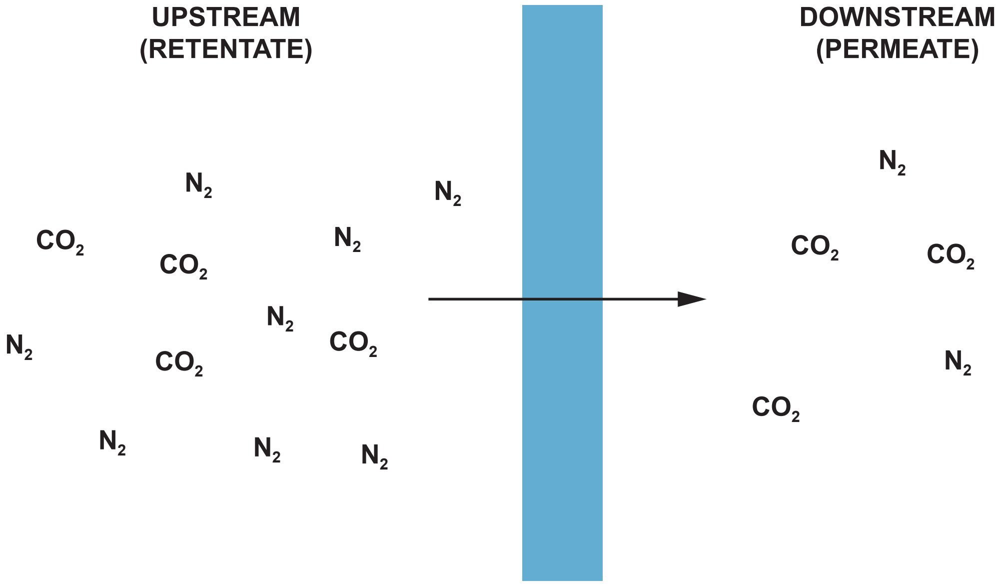

Figure 5-13. Separation Mechanism in a CO_2-Selective Membrane

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 1% 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

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[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.

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*

is generally less mature. Finally, cryogenic CO_2 capture is at the earliest stage of application but has theoretical potential across several 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.

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

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*

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]

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[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.

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

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[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).

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

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[14] Department of Energy/National Energy Technology Laboratory, "Cost of Capturing CO2 from Industrial Sources," January 2014.

[15] Perez-Fortes, M. "CO_2 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.

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.

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).

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]

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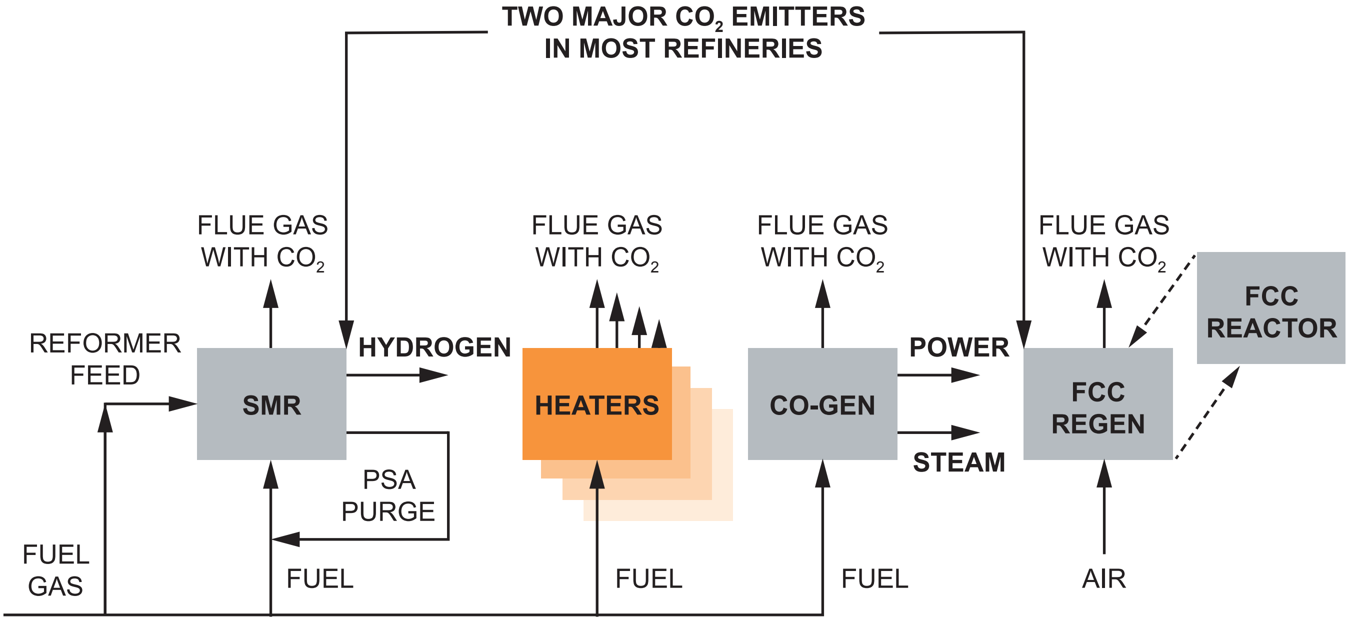
[17] Leeson, D., Mac Dowell N., Shah N., Petit, C., and Fennell, P. S. "A techno-economic analysis and systematic review of carbon capture and storage (CCS) applied to the iron and steel, cement, oil refining and pulp and paper industries, as well as other high purity sources," *International Journal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

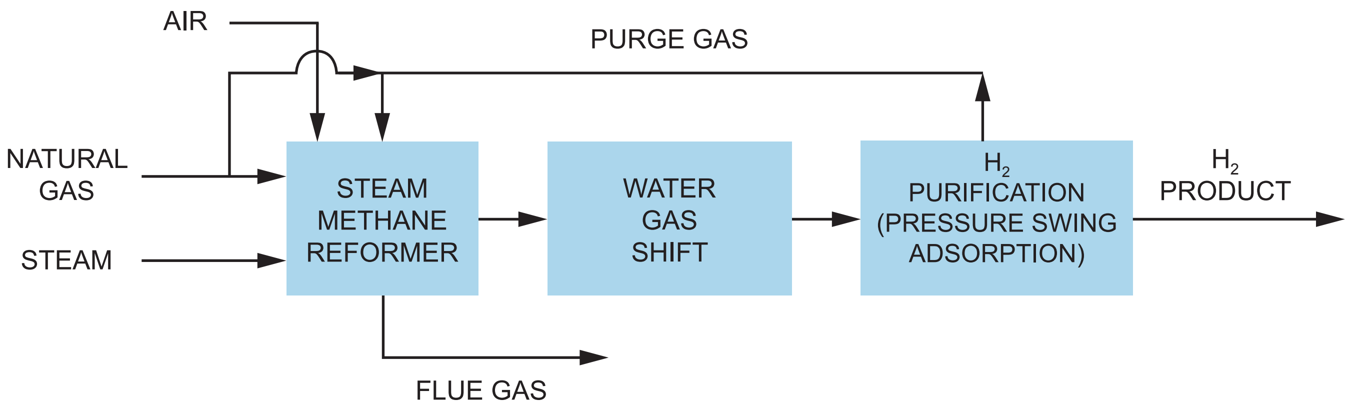
[18] Carbon Sequestration Leadership Forum, 2017.



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*



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

Figure 5-15. *Modern Hydrogen Plant*

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,

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[19] Sanchez, D. L., Johnson, N., McCoy, S. T., Turner, P. A., and Mach, K. J. (2018). "Near-term deployment of carbon capture and sequestration from biorefineries in the United States," *Proceedings of the National Academy of Science* 115(19):4875–4880.

[20] Hornafius, K. Y., and Hornafius, J. S. (2015). "Carbon negative oil: A pathway for CO_2 emission reduction goals," *International Journal of Greenhouse Gas Control* 37:492–503.

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

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[21] National Academies of Sciences, Engineering, and Medicine. (2019). Consensus Study Report, *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*. Washington, DC: The National Academies Press, https://doi.org/10.17226/25259.

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%).

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.

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*

- 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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