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Carbon Capture from Point Source Emissions and Direct Air Capture

An Overview and Comparison of Carbon Management Approaches

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Carbon Capture from Point Source Emissions and Direct Air Capture

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Abstract

This report provides an overview of the status, technologies, considerations, and performance of carbon capture from concentrated and dilute sources. It is intended to be a resource for understanding developments, opportunities, and challenges in carbon capture.

There are a variety of technologies for capturing CO_2 from carbon-containing gas streams. This report provides a summary of each of the different carbon capture methods for point-source capture and for direct air capture including CO_2 capture via solvent, sorbent, membrane, and cryogenic processes. The applicability of each capture method to different gas streams along with the benefits and challenges of each technology are reported.

Section 1 reports on the current status of carbon capture including technology and deployment landscape, disposition of CO_2, incentives, and potential deployment.

Section 2 focuses on point-source capture technologies with specific focus on solvents, sorbents, membranes, cryogenic, and CO_2 purification approaches along with examples of each technology and their applications. Considerations for CO_2 capture from a range of emission sources are discussed.

Section 3 provides an introduction to direct air capture with both solvent and sorbent based capture approaches considered. Descriptions and discussion of technologies, materials, energy consumption, applications, benefits, and challenges are included.

In Section 4 a comparison between direct air capture and point-source capture is performed, with materials, process, applications, scale, performance, and economics considered. Similarities and differences are identified in equipment, chemistries, and technologies, to inform scaling different technologies and their deployment potential.

Keywords

Direct Air Capture, DAC, Carbon Capture and Storage, Point Source Capture, CO_2

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Section 1: Introduction

Report Structure

Carbon dioxide can be removed from a gas stream where it is present. However, different streams may be at different conditions and concentrations. For example, fermentation off-gas contains >95% CO_2 while ambient air contains 0.04% CO_2. As a result, there is a wide range of different technologies and approaches for removing CO_2. This report assesses the status of carbon capture technologies over the range of applications where carbon capture has been proposed or applied. For each application, there are several technological solutions that have been proposed, tested, or are in operation. This work aims to provide an understanding of considerations for applying carbon capture and how these technologies are designed to be optimized for each application.

Chapter 1 introduces the background and motivation for carbon capture. This includes the status of emissions sources and considerations for how or why carbon capture could be applied for each source. Discussions of the impact of carbon capture focus on the overall impact on energy consumption and production, as well as the application-specific considerations of capacity factors, source of energy, and life-cycle analysis.

Chapter 2 focuses on carbon capture from point-sources. Considerations for applying carbon capture at a stationary source will be discussed. Technology options for capturing CO_2 are presented including separation via liquid solvent, solid sorbent, cryogenic, membranes, and CO_2 purification processes. Each of these classes of technologies is presented in detail with further discussion of the applicability, limitations, current research, and current status.

Chapter 3 provides an overview of direct air capture (DAC) technologies, where CO_2 is captured directly from the atmosphere. Key technology considerations for both solid and liquid phase systems including sorbents, air contactors, and regeneration strategies is presented alongside discussions about how these factors come together in the system designs of some of the leading DAC companies.

Chapter 4 compares carbon capture from point-source emissions to DAC. These comparisons focus on the difference in technologies, equipment, materials, processes, performance, scaling, economics, deployment, and impact.

Carbon Capture, Transport, and Storage Background

Carbon dioxide in the atmosphere acts as a greenhouse gas that absorbs heat which would otherwise be radiated from the surface of the earth to space. Increased concentration of CO_2 in the atmosphere leads to reduced heat radiation from earth, changing the overall energy balance of the earth and contributing to changing climate. Carbon capture and storage (CCS) is the removal of CO_2 from gas streams and subsequent permanent storage, or sequestration, of the CO_2, typically in suitable subsurface geological formations.

Intergovernmental Panel on Climate Change (IPCC) reports have consistently identified the need for rapid decarbonization in all sectors to avoid the most drastic effects of climate change [1]. CCS provides one of the few pathways to decarbonization of energy, electricity, and industry and the only mechanism for removing CO_2 from fossil fuels use that makes up more than 80% of global energy use today [2].

Carbon capture refers to a suite of different technical approaches and applications that are used for removing CO_2 from CO_2-containing streams. Mechanisms that have been proposed or commercialized for carbon capture include variations of each of the major approaches used in all gas separation processes. These include liquid solvents, solid sorbents, membranes, and cryogenic approaches.

Liquid solvent approaches make use of a circulating solvent with an affinity for CO_2. Once the solvent is contacted with the CO_2-containing gas stream, the CO_2 absorbs into or reacts with the solvent. The CO_2-rich solvent is then pumped to a regeneration column where it is heated, purged with steam, reduced in pressure, or some combination of the three to regenerate the solvent and produce high-purity CO_2.

Solid sorbent approaches use a high surface area adsorbent material with an affinity for CO_2 to preferentially adsorb CO_2 from a CO_2-containing stream. Similar to solvent processes, the solid material is then heated, purged with steam, reduced in pressure, or some combination of these steps to regenerate the solid sorbent and produce high-purity CO_2.

Membrane-based processes use a CO_2-selective membrane that preferentially permeates CO_2 from the feed side to the permeate side. The partial pressure on the permeate side has to be lower than on the feed side, which can be accomplished through pressurizing the feed and/or applying vacuum on the permeate side.

Cryogenic processes involve a phase change with CO_2 forming a solid or liquid when the gas stream is cooled sufficiently. The dense-phase CO_2 can then be readily removed from the other gas-phase components.

For each CO_2 capture technology, the separation of CO_2 from a gas stream requires energy. The energy can be in the form of electrical energy – generally used for powering fans, pumps, and compressors – or thermal energy – generally used for heating solvents or sorbents for regeneration. The quantity and source of the energy provided is vital for understanding the efficiency, cost, and impact of the process.

The temperature, pressure, humidity, and impurities of the gas stream greatly influence technology selection and capture costs. For example, capture from concentrated streams, such as 40 bar natural gas with 20% CO_2, consumes less energy penalty and smaller hardware than capture from less concentrated streams such as ambient pressure, natural-gas combined cycle (NGCC) power plant exhaust with 4% CO_2. Even more dilute streams such as atmospheric air with 420 ppm (0.04%) CO_2 require even more energy and much more gas flow to capture the same quantity of CO_2. The density of CO_2 in each of these streams varies from 15 kg CO_2/m^3 for the natural gas to 0.07 kg CO_2/m^3 for the NGCC flue gas to 0.0007 kg CO_2/m^3 in ambient air. As a result, to process fluid containing one tonne of CO_2 from each of these streams would require 68 m^3 of natural gas for the natural gas processing, 14,000 m^3 of NGCC flue gas, or 1,350,000 m^3 of ambient air.

In addition, the energy required for regenerating sorbents and solvents is generally much lower for gases with high CO_2 partial pressure than for gases with low CO_2 partial pressure. This is because CO_2 can be captured from high partial-pressure CO_2 streams by sorbents and solvents with lower affinity for CO_2. These materials with lower affinity for CO_2 require only mild heating or pressure changes to liberate the captured CO_2. In contrast, materials with strong affinity for CO_2, such as those required for capturing CO_2 from air, require larger temperature and pressure swings for regeneration. Similarly, capture with membranes can be performed at lower pressure and less surface area for high concentration sources. Cryogenic systems that rely on cooling the entire gas stream until CO_2 forms a dense phase have much energy consumption for chilling the stream approximately proportional to the amount of gas processed.

Once the CO_2 is captured through any of these methods, it may need to be further processed, such as through dehydration, purification, and pressurization before being transported, used, or stored. The purity and pressure requirements for the CO_2 product are based on the requirements of the transportation and final disposition of the CO_2. The contaminants of most concern vary based on the expected use or disposition of the CO_2 as well as the transportation method. Pipeline transportation usually has strict guidelines on oxygen and moisture, and more lenient requirements for other components. This is because oxygen and moisture can lead to pipeline corrosion. Other co-constituents, such as nitrogen and other non-condensable species can also be problematic for CO_2 pipeline operation causing lower density and two-phase flow in unexpected locations. CO_2 for subsurface injection requires low oxygen concentration if injected into oil-bearing formations. The presence of oxygen in natural gas or petroleum reservoirs can cause microbial growth and bio-fouling of subsurface pores, increasing subsurface pressures or slowing CO_2 injection rates. CO_2 for food-grade use has more stringent requirements on hazardous chemicals including metals and oils, and generally has the highest level of stringency.

The captured CO_2 can be stored or utilized either locally or transported to a suitable site. CO_2 transportation is usually determined based on the quantity of CO_2 being transported. For small quantities, CO_2 is usually transported in liquid tanker trucks. CO_2 can also be transported by ship or rail as liquified or supercritical CO_2 in cooled, pressurized vessels. For large quantities (millions of tons per year of CO_2) over a long distance, pipelines are the generally the most economical method of transportation.

The largest sinks for CO_2 are geologic including former oil and gas reservoirs, saline aquifers, and reactive geologic formations such as basalt. Subsurface sequestration of CO_2 can be accomplished in subsurface pore space by displacing water, petroleum, or natural gas. CO_2 stored at depth is generally buoyant, so requires stratigraphic trapping in porous layers of rock capped by impermeable layers to prevent mobility or leakage of the stored CO_2.

Point Source Capture Introduction

Carbon dioxide is present in gaseous emissions from many different industries and processes. CO_2 is most commonly a product of combustion from carbon-containing fuels. This can include combustion of fossil fuels such as natural gas, coal, and petroleum, biomass or bio-derived fuels, or carbon-containing fuels formed from synthesis reactions. CO_2 is also formed or processed from non-combustion sources in many industrial processes such as CO_2 liberation from limestone in cement kilns, CO_2 evolution during aluminum smelting, CO_2 that is naturally occurring in natural gas wells, or biogenic CO_2 from biological processes such as fermentation.

Carbon capture is most easily deployed to capture CO_2 from large, stationary point source emitters of CO_2. Global CO_2 emissions of 36 Gt CO_2 annually come from both stationary sources, such as industry and power generation, and mobile or distributed sources, such as from buildings or transportation. In 2022, 68% of global anthropogenic CO_2 emissions came from either industry or power generation, which represent the large, stationary sources for which point source carbon capture is best suited. The streams that are easiest to capture from are streams with CO_2 at high concentration of CO_2 and high pressure. CO_2 transportation and geologic CO_2 storage are most economical when performed at large scale of millions of tonnes per year.

Capture from existing facilities must be co-located with the facility. While some plants are near geologic storage, other plants do not have adequate geologic resources nearby for large-scale carbon sequestration. The energy for carbon capture is often supplied as a combination of thermal energy and electrical energy. Industrial and power producers of CO_2 often have steam generation on site that can be used to supply the thermal energy for carbon capture. Industrial infrastructure and utility systems including water treatment, cooling water, and electrical supply can often be used to reduce the capital expenditure for greenfield facilities. However, the operation of the carbon capture facility is linked to the operation of the source of emissions. Plant lifetime, capacity factor, availability, seasonal operation, and location are all determined by the emitting facility.

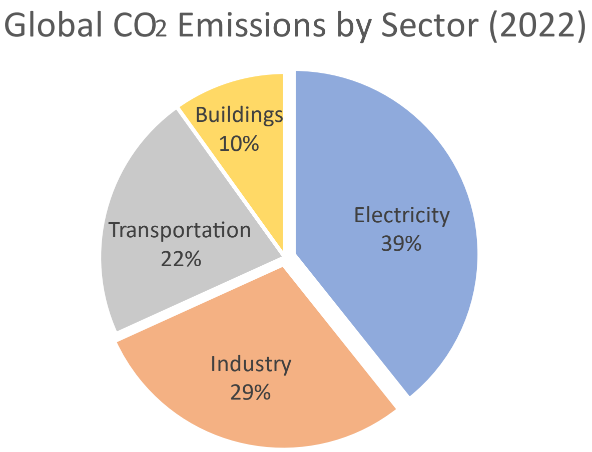

Figure 1-1
Sources of global CO_2 emissions. Data from [3]

Carbon capture is most commonly thought of as being proposed for capture from power generation flue gas streams, commonly referred to as post-combustion capture. As electricity generation makes up 39% of all CO_2 emissions, this offers one of the few ways to decarbonize the largest emitting sector. Power generation emissions are generally either from coal or from natural gas combustion, and each has different properties. In each case, the post-combustion carbon capture unit is generally located after all emissions control technologies prior to the stack.

Coal flue gas tends to be between 12 and 14% CO_2 with 2-3% oxygen, and a wide range of values for the criteria pollutants of SOx, NOx, particulates, and trace metals. Flue gas from natural gas fired gas turbines and combined cycle power plants tends to have much lower concentrations of CO_2 between 3.5-4.5% CO_2 and higher concentrations of oxygen near 12-13%. Criteria pollutants such as SOx are introduced mainly from mercaptan odorant added to NG streams and are much lower concentration than from coal combustion. Metals, particulates, and other components are generally not present in the flue gas composition.

There are other processes for generating electricity from fossil fuels and capturing the resulting CO_2. Oxy-combustion is the combustion of fuel with pure oxygen to produce a stream of nearly pure CO_2. The CO_2 stream would then be dehydrated, purified, and compressed for storage or transportation. Several oxy-combustion processes are under development.

Integrated Gasification Combined Cycle (IGCC) power plants are also proposed to be outfitted with carbon capture. Gasification is the conversion of a solid fuel into syngas, which can then be combusted for power generation. The syngas stream may be processed at high pressure to remove CO_2 prior to the combustion. This is referred to as pre-combustion carbon capture. Syngas production through gasification or natural gas reforming is also used for non-power applications such as hydrogen generation and chemical synthesis. The carbon in syngas can be converted from carbon monoxide to carbon dioxide through the water-gas-shift reaction which favors hydrogen and carbon dioxide products at low temperatures and water and carbon monoxide products at elevated temperatures. Conversion of carbon monoxide to carbon dioxide is usually proposed to be performed prior to CO_2 capture to allow a higher proportion of the carbon to be removed from the syngas stream.

While both oxy-combustion and pre-combustion carbon capture entail options for reducing CO_2 emissions from power plants, they are power-plant designs that have integrated power generation with carbon capture. The overall power production process is beyond the scope of this report but the carbon purification portion of each facility as described by the gas separation of CO_2 from the remaining gasses is described in Section 2.

Carbon can be captured or removed from other industrial streams as well. Most emissions are the result of fuel combustion and are similar to the emissions streams described for coal and NGCC power plants. Natural gas boilers tend to have higher CO_2 concentrations than NGCC flue gas with CO_2 concentrations up to 10% and oxygen concentrations as low as 3%. Cement kilns use fuel combustion to heat calcium carbonate which releases CO_2 both from the fuel combustion and the calcium carbonate decomposition. Iron and steelmaking similarly have CO_2 emissions from both the fuel combustion and the carbon used for reducing iron oxides into elemental iron. CO_2 concentrations can reach up to 20% in each of these cases. There are significant co-constituents in each flue gas including particulates, sulfur compounds, and metals. Capture from these industrial sources is likely to involve significant gas cleanup prior to entering the CO_2 capture unit.

Some industrial streams have much higher CO_2 concentrations. Fermentation processes, such as from ethanol production or brewing release a near-pure stream of CO_2 with water vapor that can be captured in its entirety by condensing out the moisture. Naturally occurring CO_2 can also exist at high concentrations. CO_2 is extracted from naturally occurring geologic formations for re-injection underground for enhanced oil recovery. CO_2 concentrations in natural gas production wells can also reach up to 70% CO_2. To produce a product natural gas that can meet pipeline and end-use specifications the CO_2 is often removed from natural gas streams. This CO_2 can either be vented to the atmosphere or purified and compressed for geologic reinjection. Because the quantity of produced gas is high, the pressure of produced natural gas is high (30-60 bar) and the CO_2 concentration can be high as well (typically 8-60%), these applications represent the largest CO_2 capture processes in operation today.

Energy for PSC

The energy for carbon capture is generally supplied as a combination of electrical energy and thermal energy. Higher partial pressure sources of CO_2 require less energy for capture than lower partial pressure streams.

Capture from natural gas streams is often accomplished with either solvent systems or membranes that use the high pressure of the feed gas to perform the separation at very low energy consumption. High pressure feed allows CO_2 to permeate through membrane systems to ambient pressure or to be captured in solvent systems for pressure-swing regeneration with mild heating.

Capture from flue-gas streams is best studied for power generation applications. The energy for capturing CO_2 from power plant flue gas using aqueous amine solvents and compressing it to 150 bar for pipeline transportation is on the order of 2.3-3.6 GJ/t CO_2 as thermal energy supplied at approximately 130 °C (165 °F) for the reboiler duty and an additional electrical auxiliary load of 120-130 kW/t CO_2 captured which includes CO_2 compression. The range in thermal load is primarily a function of the solvent chemistry and the process configuration.

The thermal energy consumption in the reboiler is to generate steam used for stripping the CO_2 from the solvent in the regeneration or stripping column. Stripping steam acts to heat the solvent and to provide a counter-current sweep gas that helps liberate CO_2 from the solvent. Higher pressure regenerators can be operated at higher temperatures. This higher pressure regeneration can occur within a small equipment, and create a CO_2 product that requires less compression but also generally requires more thermal energy supplied at a higher temperature. Recuperative heat exchangers are used in all solvent systems to reduce the thermal requirement of the reboiler.

The thermal energy requirement can be provided through extractions from the steam cycle, or from a standalone steam generation unit such as a boiler or combined heat and power (CHP) plant. To achieve high capture rates, the flue gas from the boiler or CHP would have to be recovered as well. The impact of the thermal energy on the host plant and the overall system depends on the source of that energy. Generally, steam extraction from a steam cycle is the most efficient source of thermal energy as the extraction can be designed to supply steam only at the temperature required. The high- and intermediate- pressure steam cycle components are mainly unaffected and the steam is extracted only from the low-pressure steam. For systems that have dedicated steam generation, such as CHP or standalone boiler, there is less work extracted from the steam prior to being used to supply thermal energy, so the overall efficiency of the plant is lower. For example, the Shell Cansolv carbon capture with aqueous amines applied to the NETL reference case [4] for a NGCC would yield a net HHV efficiency of 53.6% for the base NGCC without CCS, 47.7% for the NGCC with CCS and thermal energy supplied from steam extraction, 45.0% for the NGCC with CCS with thermal energy supplied from CHP, and 43.4% for the NGCC with CCS and the thermal energy supplied from a standalone boiler [5].

The impact of energy usage in a carbon-capture process depends on the source of energy and the CO_2. For industrial and utility applications, the CO_2 source and the energy source are usually the same. However, for some applications standalone boilers or CHP plants are used to generate thermal energy. Where CO_2 and energy are co-produced, such as in electric power generation from carbon-fuel combustion, the energy for CO_2 capture is supplied by either increasing the fuel consumption or reducing the output of the industrial or utility system. The decrease in output has the impact of making the existing facility less productive than the design condition without CCS. For power generation, this reduction in output is generally referred to as the energy penalty or parasitic load on the plant. Energy penalties have the dual impact of both reducing the efficiency of the plant, which increases the operating cost, and reducing the maximum output of the plant, which decreases the production over which the capital cost can be amortized. Significant research has been invested into reducing the energy penalty of carbon capture systems through different capture and regeneration configurations, process intensification, novel chemistries, and thermal integration. A discussion of these options is presented in Section 2.

Incentives for PSC

Point source capture of CO_2 requires a significant capital investment in addition to the energy for capture that must be supplied. Economic operation has been incentivized through a series of different approaches including prices on carbon emissions, direct investment in carbon capture projects, selling produced CO_2 or using it for EOR, only being allowed permits if operating with carbon capture, and tax credits for CO_2 captured.

In the United States, the 45Q tax credits were increased from \$50/t to \$85/t CO_2 captured in 2022 [6]. This pricing is near the levelized cost of CO_2 capture for NGCC plants, higher than the cost of CO_2 captured from coal plants, and significantly higher than the cost of capture from ethanol facilities. Since the announcement of the higher tax credit, CO_2 transportation, sequestration, and capture facilities on primarily ethanol facilities have been proposed and are proceeding.

Mandates for carbon capture have also been proposed, including the draft EPA regulation 111 which calls for the implementation of carbon capture by 2030 on any coal plants expected to retire after 2040 and by 2035 for most natural gas burning power plants [7].

Direct Air Capture Introduction

Direct air capture and sequestration is an engineered method of atmospheric carbon removal. Over the past few years, there has been significant interest public and private interest in quickly advancing both engineered and natural methods of carbon removal. Negative emissions technology (NET) is another frequently applied term to methods of atmospheric carbon removal.

Carbon removal methods have been identified as an essential method for limiting atmospheric CO_2 concentrations and global warming, and current IPCC models for limiting global warming reflect the increasingly important role of carbon removal [1]. The first primary business case for deploying direct air capture is the potential of DAC to offset any source of emissions, especially small and mobile sources of CO_2 emissions such as transportation, buildings, and agriculture. While alternative energy sources will enable the decarbonization of many of these sources over the coming decades, the cost of decarbonization can exceed \$1000/ton in many cases. An alternative strategy for decarbonizing these sources is to offset their emissions using centralized carbon removal technologies. As technologies scale and renewable energy becomes more affordable, these offsets will be a key enabler in enabling a net-zero CO_2 economy.

Low-cost, broadly available carbon removal technologies could play a major role in enabling a net-negative annual flux of CO_2 into the atmosphere for two primary reasons. First, to achieve net-zero greenhouse gas emissions, it is more practical to offset highly potent but extremely dilute global warming constituents such as methane and fluorocarbons with an equivalent quantity of CO_2 that matches their annual global warming potential. While DAC is a challenging gas separation because CO_2 is only present at approximately 420 parts-per-million (ppm), the separation of other global warming gases present at part-per-billion (ppb) or part-per-million (ppt) quantities represents a substantial further dilution in concentration.

The second primary motivation for enabling net-negative annual CO_2 emissions is that there is a high likelihood that the IPCC recommendation of limiting global temperature rise to no more than 1.5 °C will be exceeded. Once a net-zero emissions systems has been achieved, the possibility of offsetting historical emissions to ultimately drawdown atmospheric and ocean CO_2 concentrations can be explored. While such net-negative carbon removal scenarios are decades away, decades of development and scaling will likely be necessary for technologies to be at the cost and scale required.

The viability of any specific DAC technologies as well as the broader market will heavily depend on the extent to which the costs for removing tons of CO_2 are able to decline in the coming years. While the U.S. Department of Energy (DOE) through their carbon negative shot, has set an nth of a kind removal cost of less than \$100/ton [8], significant scientific, engineering, manufacturing, and energy system improvements need to be realized for such a target to be achieved. Thus, there is a need for research and development at all stages such that the science and engineering breakthroughs that have the potential to meaningfully reduce capture costs are in fact realized and brought to market.

Second, the most promising technologies must advance sufficiently in scale such that cost reductions through economies of scale can be realized. It should be expected that pilot and demo-scale carbon removal costs will be significantly higher than first of a kind commercial-scale operations, which will in turn be significantly higher than nth of a kind costs. Significant reductions in capital and materials costs can be realized as key equipment such as fans, contactors, compressors, and adsorbents are scaled up, and engineering and technology improvements are realized. As of mid-2023, a first-of-a-kind commercial facility is currently under construction by 1PointFive, which is using a licensed version of the Carbon Engineer technology discussed in Section 3. Their public projections estimate removal costs of approximately \$300-425/ton for this initial deployment [9]. As technologies matures, the supply chain is established, project and commercial risk is reduced and financing costs fall, it is anticipated that costs will continue to fall. As of early-2022, the projections for the Carbon Engineering technology indicates that costs between \$250-\$350/ton may be realized as total carbon removal capacity is scaled to 70 Mtpy by 2030 [9].

Energy for DAC

While technology improvement and scale will unquestionably reduce capture costs, the cost of net removal of CO_2 from the atmosphere can differ dramatically from the cost of capture. As such, DAC processes cannot be evaluated without consideration of the impacts of a multi-decade energy transition. Under nearly all foreseeable technology scenarios, DAC will require significant quantities of energy, either thermal energy, electrical energy, and likely both, to capture a ton of CO_2. The CO_2 and other greenhouse gas emissions that result from the energy production processes will diminish the efficacy of carbon removal processes. It has been shown that the use of fossil-fuel energy sources without carbon capture to power a DAC process would likely have no beneficial impact and could potentially be a net generator of CO_2 emissions [10]. The responsible deployment of carbon removal technologies must depend on the availability of sufficient low-carbon energy for their operations.

Detailed life-cycle analysis (LCA) of DAC operations is required to accurately assess the ratio of captured carbon to net removed carbon. To better control the availability of low-carbon electricity, some DAC technology and project developers are choosing to optimize their processes with this need in mind, including through the integration of geothermal energy or onsite CCS. If energy is sourced from the greater grid, net carbon removed will depend heavily upon the carbon intensity of the broader grid.

Few detailed LCA studies have been performed on DAC systems. One that has been completed on the Climeworks process shows the importance of the carbon intensity of energy supplied to the system. At the geothermal locations currently being pursued, the net removal efficiency is calculated to be more than 90%. For the same technology supplied with electricity from the current U.S. grid mix carbon intensity of 0.42 kg CO_2e/KWh, the net removal would be only 12% [10]. To illustrate the importance of net removal to overall economics, a system that has a capture cost of \$400/t captured and a net removal of only 12% would have an overall cost of CO_2 removed from the atmosphere of over \$3,000/t.

As the costs of solar and wind energy have drastically fallen over the past decade, there are locations, seasons, and times in which renewable energy production is being curtailed owing to localized overproduction. It can be envisioned, and it has been proposed, that emerging energy technologies such as DAC can cycle operations to consume energy only when an excess of low-cost, low carbon energy is available. The primary advantage of this approach would be the ability to purchase energy at very low costs relative to operations that are investing in independent 24/7 production. If the most energy intensive DAC operations such as absorbent regeneration can be effectively timed to align with curtailed energy, significant cost reductions can be potentially realized. However, such an approach would also reduce the capacity factor of the broader facility.

Commercial scale DAC installations are anticipated to require significant capital investment that will be recovered over decades of nearly continuous use. The ability of large capital projects to achieve high capacity factors is a major factor in achieving reasonable capital costs for a project, and so until low-cost, low-carbon energy is broadly available, DAC technology developers will need to find the optimum balance between high capacity factor operations to reduce capital costs and sourcing low-cost, low-carbon energy to ensure reasonable operating costs and favorable net-removal rates.

While energy is a major factor in the life-cycle analysis of DAC operations, it is not the only factor. DAC facilities are anticipated to utilize significant quantities of steel, cement, and plastic, and the emissions associated with the manufacturing and end-of-use disposal of this equipment is significant. Second, large quantities of the solid or liquid materials are used and replenished over the lifetime of a DAC facility. The raw materials and energy required to manufacture adsorbents is anticipated to be a major factor in both the cost and carbon intensity of running a DAC process. The manufacturing process for many adsorbents utilizes fossil fuels as both raw materials and energy source, and disposal methods such as incineration could enable the carbon embodied within adsorbents to end up in the atmosphere itself. A recent life-cycle analysis of the Climeworks process indicates that approximately a third of the CO_2 emissions from their process would result from manufacturing and replacing the adsorbent material. The useable lifetime of adsorbents is thus a major driver of not only the cost of a DAC process, but of its efficiency as well.

Direct Air Capture Commercial Incentives

Significant incentives for developing and deploying carbon removal technologies, especially DAC, has arisen over the past five years. In 2018, California's Low Carbon Fuel Standard was updated to allow for DAC as an offset in calculating the carbon intensity for transportation fuels sold in California. It further allowed flexibility for DAC operations by allowing DAC processes to disconnected from the fuel manufacturing process [11]. In combination with the tax credits available under IRS section 45Q, by 2019 the incentives for DAC were approximately $200-250/ton, significantly greater than the 45Q incentives alone available for point source capture process. While the LCFS carbon price has now dropped to below $100/t [12], the 45Q tax credits for DAC were increased to $180/t in 2022 [6] yielding an overall incentive for DAC of more than $250/t removed.

Simultaneously, a handful of corporations especially in the technology and financial sectors have publicly committed to net zero 2030 emissions targets. Encompassing scope 1, 2, and 3 emissions, carbon removal began to be viewed as an important technology to enable complete decarbonization of emissions, with leaders such as Microsoft and Stripe committing to purchasing engineered carbon removals at prices well above traditional carbon offsets. Over the past few years, a growing number of corporations have individually and collectively committed to purchasing high quality carbon removals to incentive development and investment in a range of engineered and natural carbon removal technologies. The primary difference between these and prior offset purchases has been the willingness of buyers to pay a premium for methods of carbon removal that are viewed to be durable and of high quality, and buyers have expressed a willingness to pay a premium in the early stages of technology development that reflects the true cost of technologies that are neither fully developed nor scaled. For example, in 2021 Stripe committed to paying $2,054/ton for early CO_2 removed via Heirloom's DAC process.

While the technology, financial, and consulting sectors have played a major role in developing the carbon removal space through their designed use of advanced market commitments, the aviation sector including Airbus and United Airlines has also committed to purchasing large volumes of DAC offsets. The full decarbonization of aviation is a pressing concern to the industry owing to challenges with achieving high sufficiently high energy densities with liquid fuel alternatives such as hydrogen or batteries, and the costs and limited availability of sustainable aviation fuels (SAF). Alternative fuels, SAF and carbon removal are all viewed as essential technologies by the aviation sector in achieving their requirements under CORSIA, an international treaty that mandates reductions in the carbon emissions of the aviation industry, as well as specific net-zero commitments made by individual airlines.

Direct Air Capture Governmental Incentives and Initiatives

Research and development funding for carbon removal technologies such as DAC has increased substantially since a 2018 report by the US National Academies of Science, Engineering, and Medicine (NASEM). A range of funding opportunities from the US Department of Energy have targeted both early-stage funding and later stage development projects. In 2023, the first funding opportunity for four anticipated DAC hubs was released by the DOE [14]. With anticipated public support of approximately $3.5B, the objective of the DAC hubs is the co-location of multiple DAC technologies to reach cumulative removal capacities of 1M tpy at each site.

Governmental support for reducing carbon intensity with carbon capture and carbon removal has expanded significantly and are currently playing a major role in spurring deployment of DAC in the United States. In the United States, the passage of the Inflation Reduction Act (IRA) modified section 45Q to incentives DAC with sequestration to $180/ton, while point source capture incentives were increased to $85/ton. A 2022 analysis from Oxy Low Carbon Ventures indicated that such government policies would likely result in a near doubling of DAC facilities they would plan have in operation by 2035 from 70 to 135 plants each capturing one million tonnes per year [9].

Industries and governments around the world have rapidly begun to support carbon capture hubs over the past few years. By focusing early deployments at concentrated sites, transportation and infrastructure costs can be significantly reduced compared to discrete deployments. Carbon capture hubs for point source capture have been proposed around the world, including Singapore, the United Kingdom, the Netherlands, Norway, and several locations around the United States. These hubs were primarily chosen for their existing concentration of point source emitters, proximity to geologic storage, and the need to deploy CCS technology to enable the decarbonization of heavy industry.

Because DAC is not restricted to being collocated with existing infrastructure, one of the primary advantages of DAC is the ability to site deployments at locations that are optimized for the needs of the technology, the availability of energy, and the accessibility of sequestration or utilization. In the United States, four geographically distinct DAC hubs expected to be funded through the IRA and will enable a variety of climatic and energy conditions to be effectively surveyed and early learnings to be captured. In Chapter 2, a range of CCS technology options are presented because the best performing technology is dependent upon the conditions of the gas stream being utilized. Similarly, owing to the diverse range of climatic and energy conditions around the world, it is anticipated that a suite of DAC technologies will likely be required that are optimized for a range of deployment conditions.

Section 2: Point Source Capture

Overview of Point-Source Capture

Carbon capture from concentrated sources has been proposed for a range of applications and been used commercially for decades. The CO_2 emitted by industrial processes can range from nearly pure CO_2 with concentrations above 95% to dilute streams with concentrations below 5%. Similarly, the pressures of the CO_2-containing streams can vary widely from atmospheric pressure streams discharged to the atmosphere to tens of atmospheres for gas processing or intermediate process streams. The temperatures of these streams can also vary from ambient conditions to hundreds of degrees. Different separation methods are best suited for different ranges of compositions, pressures, and temperatures.

The industries and sources for CO_2 that have been considered for CCS include: emissions streams from carbon-fuel combustion, natural-gas processing, oil refining, chemical production, steam methane reforming, cement, iron and steel, fermentation, oxy-combustion products, and syngas streams. Each stream has different compositions, conditions, and considerations. In addition, streams that are internal to a process versus emitted to the atmosphere have different requirements for how much CO_2 needs to be removed and the acceptable levels of co-constituents in the remaining gas.

Streams that are intended to be used as a product, such as natural gas, hydrogen, or syngas, are often at elevated pressures as the product is produced or delivered at elevated pressures. Removal of CO_2 from these streams is often required to meet product specifications or allow downstream processes to operate efficiently. The purity of the removed CO_2 is normally not a primary consideration as the primary focus is the purification of the product. The economics of carbon capture from these intermediate or product streams is dependent on the sold product more than the captured CO_2, and so these have been the first applications for which carbon capture has been adopted. Most product streams that have CO_2 co-constituents are already processed to remove the majority of CO_2 to product specifications.

Streams that are emitted to the atmosphere, such as flue gas, are at atmospheric pressure. Capture of CO_2 from these streams is driven by reduction in CO_2 emissions and/or through the creation of a CO_2 product stream. Carbon removal rate is based on the desired level of emissions reduction and the quantity of CO_2 that can be used or sold from the process. The purity of CO_2 produced is often critical as it must be sufficient purity to be transported, stored geologically, or otherwise sequestered from atmospheric release. Almost all CO_2-containing emissions streams do not yet have carbon capture deployed. Discussions of deploying carbon capture mainly focus on capturing carbon from these emissions streams.

The processes that are used to separate CO_2 from gas streams, whether CO_2 removal from products to meet product specifications or from flue-gas and other atmospheric emissions are broadly similar. There are several main methods of point source capture of CO_2 that are in operation or are being technically pursued: liquid Solvents, Membranes, solid Sorbents, and Cryogenic approaches are the most commonly considered and operated. CO_2 capture can also be performed on nearly-pure CO_2 streams through dehydration and compression or through compression and cryogenic purification. The benefits and challenges of each capture approach as well as the stream conditions and concentrations for which each is best suited are presented in this chapter.

Solvent-based systems use a physi- or chemi- solvent with an affinity for CO_2 to contact a CO_2-containing gas stream. The solvent preferentially absorbs the CO_2 from the gas stream in an absorption column before being heated up in a regeneration column to release the CO_2 product. Solvents with weak affinity for CO_2 are generally referred to as physi-solvents as the bond between the CO_2 and the solvent is a physical bond while solvents with a strong affinity for CO_2 are generally referred to as chemi-solvents due to the chemical bond formed. Solvent-based processes are the most technically mature CO_2 capture technology for point source capture over a range of applications.

Membrane systems use a thin membrane layer that selectively allows one species (such as CO_2) to permeate through the membrane while preventing the permeance of other species (such as nitrogen or methane) from a high pressure or high concentration stream to a low pressure or low concentration stream. Membrane-based processes are generally best deployed in high-pressure applications and to produce CO_2 from concentrated product streams.

Solid sorbent based processes use a high surface-area solid material with a selective affinity for CO_2 in contact with a CO_2 containing gas stream. The CO_2 is selectively absorbed onto the solid sorbent, and the sorbent material is subsequently regenerated through thermal-swing, vacuum-swing, or other methods to produce the product CO_2 stream.

Cryogenic systems use the phase change of CO_2 to separate it from a gas stream through chilling the gas stream. Below the triple point pressure of CO_2, (5.3 bar, 74 psia) CO_2 forms a solid, while above this pressure CO_2 can form a liquid. For capture of streams with partial pressure of CO_2 below the triple point pressure, solid formation, handling, and processing must be considered. Above the triple-point pressure, cryogenic CO_2 purification is commonly used to achieve high-purity CO_2 product.

Nearly-pure CO_2 streams are also used as a source of CO_2 for CCS and require only minimal processing. For streams that are nearly-pure that are produced through fermentation or certain chemical processes, CO_2 compression and CO_2 purification through dehydration or cryogenic purification may be all that is required to produce food-grade CO_2, liquid CO_2, or CO_2 for pipeline transportation. These are the same purification processes and techniques that can be used to process the nearly-pure products of other processes for carbon capture including point source capture, direct-air capture, or oxy-combustion processes.

Technology overviews for point-source carbon capture via these broad classes of separations incorporating the status, benefits, challenges, and considerations for each class of capture is described in the sections that follow.

Solvent-based CO_2 Capture

Solvent-based capture of CO_2 is a technically mature point-source carbon capture approach for elevated-pressure streams and the most technically mature for atmospheric-pressure streams, including streams that are emitted to the atmosphere.

There are two main types of solvent-based process: physical and chemical-solvents. Physical solvents, such as propylene or methanol, absorb CO_2 through the high solubility of CO_2 compared to the other species in the CO_2-containing stream. The CO_2 is then desorbed from the physical solvent by lowering the pressure of the system, often in conjunction with increasing the temperature. Chemical solvents, such as aqueous amines, absorb CO_2 by reacting with CO_2 to create a chemically-bound form of CO_2, such as carbamate. This chemical reaction can be reversed at elevated temperatures to produce CO_2 in a stripping column.

The main difference between the two types of solvents is the affinity for CO_2. Because of the chemical reaction in chemi-solvents, they can exhibit higher affinity and selectivity for CO_2. This makes them more effective at capturing CO_2 from atmospheric or lower pressure streams and streams with low CO_2 partial pressure. Because they are effective at capturing CO_2, even at low partial pressures, pressure swing is not an effective method of regeneration. Instead, chemi-solvents are most often regenerated through thermal swing regeneration. In thermal regeneration, the solvent carrying absorbed CO_2 is heated and pumped to a stripping column where steam generated in the reboiler is used as a stripping gas and to further heat the solvent to break the chemical bonds and liberate the CO_2. As the temperature of operation is critical for effective stripping, these columns often operate at elevated pressures (around 1.5-3 bar) to control the steam temperature from the reboiler. The maximum temperature of the system is often determined by the maximum temperature the chemi-solvent can withstand before experiencing thermal- or thermal-oxidative degradation. For many amine-based systems this is around 110-130°C (230-266°F).

Physi-solvent systems, on the other hand, generally have a lower affinity and lower selectivity for CO_2. The affinity for each species is based on its solubility in the solvent, but there are no selective chemical reactions to supplement this selective absorption process. Because of the lower affinity, physi-solvent based processes are generally applied in elevated pressure applications and for gas streams with higher concentrations of CO_2 and for separation of species with significant differences in their solubilities. For example, the two main uses of physical solvent-based CO_2 capture are separation of CO_2 from elevated pressure syngas streams containing mainly CO_2, and H_2 and separation of CO_2 from elevated-pressure natural gas streams with CO_2 content above around 8%.

Both processes rely on similar process steps and configurations. A generalized process is shown in Figure 2-1.

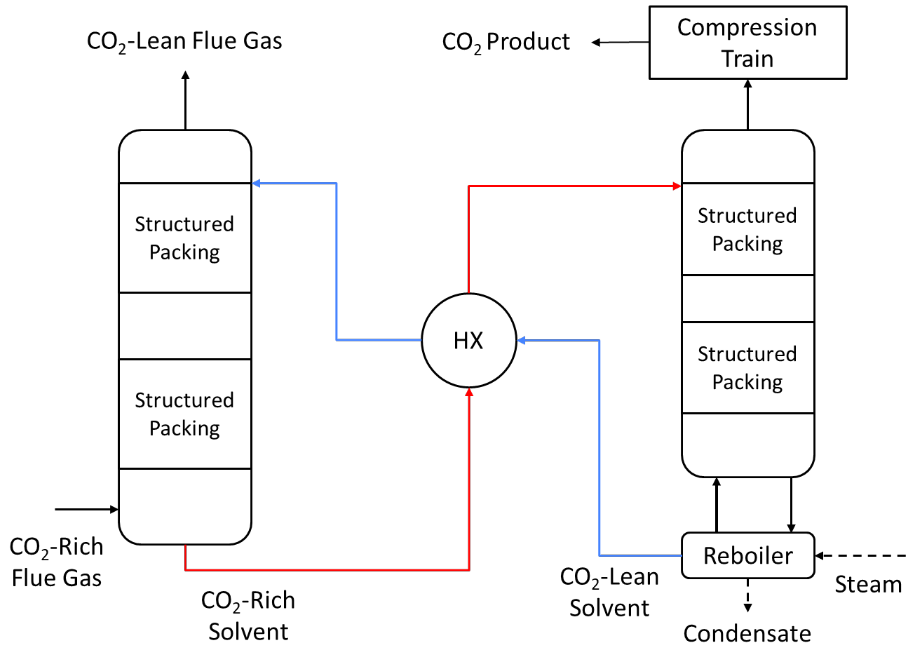

Figure 2-1
Generic Process Flow Diagram for solvent-based carbon capture process.

Solvent-based processes can be modified to absorb CO_2 from a wide range of CO_2 concentrations. At low CO_2 partial pressures, a stronger affinity for CO_2 is required to allow sufficient CO_2 absorption to regenerate efficiently in the stripper. The difference in CO_2 loading between the rich and lean solvent is known as the working capacity of the solvent and determines the amount of CO_2 that can be produced with each circulation cycle of the solvent. Higher working capacity is beneficial as the quantity of CO_2 capital cost of the heat exchanger and stripper are directly related to the volume of solvent processed and the energy requirement for the process increases with increased solvent flow due to additional thermal energy requirement and higher pumping load. Because solvents that can capture from lower partial-pressure streams have higher affinities for CO_2, the stripping unit must operate with higher thermal energy to increase steam flow rate and to increase the temperature in the stripper to liberate the CO_2. For systems with adsorption from high CO_2 partial pressure streams, low CO_2 affinity associated with physi-sorbent systems can be utilized. These systems tend to have lower overall energy penalty because they do not have chemical bonds that need to be overcome through higher-temperature thermal energy.

Status of Solvent-based CO_2 Capture

Solvent-based CO_2 capture has been proposed since the Bottoms cycle was patented in 1930 [15] and commercial for decades in gas-processing applications. Operation in gas-processing plants starting in the 1970's and some with service lives over 50 years have shown the robust operation and technical maturity of the technology approach. The largest solvent-based capture installations are for natural-gas processing applications using physical solvents with the largest installation being approximately 5 million tons per year of CO_2 capture at the Century plant – a natural gas-processing facility in the Permian basin of Texas that has been operating since 2010. There are hundreds of solvent-based CO_2 capture facilities in commercial operation worldwide with most of those using physical-solvent based processes.

Commercial physi-solvent systems for carbon capture for removal from high pressure streams include well established gas-processing solutions such as Linde Rectisol, Fluor Solvent^{SM} Process, Honeywell UOP Selexol Process, and Shell ADIP-Ultra solvent.

Chemi-solvent based processes using aqueous amines are the most mature technology for atmospheric-pressure CO_2 capture. These systems have been deployed in commercial demonstrations at more than 1 Mtpy scale in power applications on flue-gas streams from coal-fired power plants at both Petra Nova in Texas, U.S. and Boundary Dam unit 3 in Saskatchewan, Canada.

Start up in 2014	Start up in 2016, shut down 2020, restart announced
1.0 Mt CO_2/yr	1.4 Mt CO_2/yr
~139 MWe flue gas slipstream out of 730 MWe Coal	~250 MWe gross out of 650 MWe Coal
Shell Cansolv Aqueous Amine Process	Mitsubishi Heavy Industries Aqueous Amine Process
41 mile pipeline to Weyburn oil field EOR	82 miles pipeline for EOR
1.2 miles to Aquistore geological storage (minor)	West Ranch Oil Field, Texas

Figure 2-2
Simplified process flow diagram and adsorption/desorption configurations of Climeworks' sorbent-based direct air capture technology.

There are several other aqueous solvent-based CCS technologies that have been demonstrated at the 0.5-10 MW scales for coal or natural-gas fired flue gas at test facilities such as the Test Center Mongstadt (TCM) in Norway or the National Carbon Capture Center (NCCC) in Alabama, U.S. There are also more than 20 other chemi-solvent-based approaches ranging from non-aqueous or water-lean solvents, different amine chemistries, ionic liquids, and precipitating solvents or phase-change solvents. These solvent systems also have a range of different contacting methods including absorption towers with spray nozzles and internal packing, membrane-contactors, rotating packed-bed contactors, and different process configurations including multiple solvent loops, staged solvent feeds with variable CO_2 loading, solvent intercooling or solvent pump-around in the absorber, and settling tanks for phase change solvents. Similarly, thermal supply can be altered to include thermal supply from various points within the steam cycle of a host plant, a dedicated combined heat and power unit or steam generation unit, or solar thermal or geothermal power to supply the reboiler steam. Thermal integration options can be arranged with stripper configurations to minimize the energy consumption for the overall process via the use of flash stripping in conjunction with a stripping column, thermal recovery from other process steps such as compressor intercoolers or overhead cooler, and heat exchange networks that minimize approach temperatures.

Benefits, Challenges, and Considerations for Solvent-based CO_2 Capture

Some of the main benefits of solvent-based processes are the standard equipment, tunable chemistry, ability to pump the solvent between adsorption and regeneration columns each operating at optimal temperatures and pressures, and the ease of thermal heat integration with solvent-based processes leading to lower energy consumption. The tunable chemistry and ease of heat integration has led to a proliferation of different processes and configuration modifications. These can generally be categorized into two main areas: process intensification and thermodynamic improvements.

Thermodynamic improvements are changes to the steady-state operation that lower the overall energy consumption of the process. This can be accomplished through improved solvent chemistry, tighter thermal integration, staging adsorption or regeneration, managing thermal energy in the absorber or regenerator, decreasing water content in the solvent for regeneration either through phase separation or the use of water-lean solvents, and optimizing the operating conditions.

Process intensification increases the rate of one or more steps to decrease the size of the system required. This can include changing the adsorber to a rotating packed bed or membrane absorber with higher surface area and the ability to accommodate higher viscosity solvents, adding absorption promoters such as carbonic anhydrase (a bio-catalyst that increases CO_2 uptake rate). Process intensification is commonly used in conjunction with a chemistry or process that shows thermodynamic benefits but would otherwise not be possible due to the large size or slow reaction rate.

One of the main challenges associated with solvent-based systems is the degradation of the solvent and solvent management. Physi-solvents tend to not have significant degradation as they are not as chemically reactive. However, chemi-solvent systems using organic chemistries tend to have reactive groups that can be degraded through a number of different mechanisms. The main mechanisms are either the poisoning of the solvent through reaction with a component that cannot be regenerated and hence forms a heat-stable salt (such as sulfur compounds) or the thermo-oxidative degradation of the solvent. Solvents, and especially amine solvents, that experience elevated temperatures in the presence of oxygen are prone to rapidly breaking down as oxidizing reactions are accelerated at high temperatures. For most amine chemistries, this degradation threatens the viability of the process somewhere in the range of 120-135 C (268-275 F). For all amine solvents, system control to sustain low levels of degradation are expected and solvent maintenance is required to maintain the solvent performance.

Solvent maintenance is most commonly performed in a reclaimer. Thermal reclaimers can be operated in batch or continuous modes and distill a small tear stream of the solvent to volatilize the amine and water components and concentrate the degradation products to be removed from the system. Solvent makeup is also required to conserve the circulating quantity of solvent. Other reclaiming processes using other separation processes such as ion exchange resins have been proposed but are not as widely considered for these applications.

To avoid solvent poisoning, gas cleanup may be required prior to carbon capture. Some of the main components that can poison chemi-solvents are sulfur compounds and heavy metals. Sulfur can react with amines in a non-reversable manner to form heat-stable salts that are not regenerated in the regenerator or the reclaimer. To prevent the buildup of these salts and the reduction in active amine, generally sulfur is controlled to the single digit ppm levels prior to absorption. This can be accomplished through optimized operation of a wet flue-gas desulfurization (FGD) unit or through an alkaline water wash in a direct contact cooler (DCC) used to cool the flue gas entering the absorber. For NGCC applications, the sulfur content is usually low enough to not require additional control. For other industrial processes, such as waste-to-energy flue gas, additional gas cleanup may be required to prevent further degradation. While the exact degradation mechanisms are not well studied, the presence of certain metals in the solvent have been linked to increased degradation. This may be due to the metal acting as a degradation catalyst or carrying oxidizing components into the stripper increasing the rate of oxidative degradation. Further, the buildup of metals such as selenium and arsenic in the solvent circulation may lead to the classification of the solvent as toxic waste and the buildup of nickel, vanadium, and other components can increase corrosion of the metal in the circulation loop.

Membrane-based CO_2 Capture

Membranes are thin layers of material that allow selective permeance of one component or class of components from a stream of high concentration or high pressure to a stream of lower partial pressure. Membrane-based processes are deployed at large-scale in a number of industries including reverse osmosis (RO) membranes for water treatment and proton-exchange membranes for electrolysis. Membranes are also deployed commercially at large scale for CO_2 separation from natural gas streams with high content of CO_2.

Processes that are best suited for membrane separation are those with high partial pressure of the permeated component and processes where high removal of the permeated species is not a requirement. This is because the material flux through a membrane system is determined by 1) the permeance of the membrane 2) the driving force from the feed-side of the membrane to the permeate side of the membrane and 3) the surface area of the membrane. The driving force through the membrane is determined by the difference in partial pressures between the feed side and the permeate side. Because the feed-side partial pressure decreases as the permeated component is removed, deep removal with a membrane is more difficult to accomplish and may require very high surface areas or low permeate pressure to accomplish.

Membranes are typically constructed out of a supporting layer and an active layer. The purpose of the supporting layer is to create a highly permeable, non-selective, macro-porous support that functions as a backing for the thin, selectively permeable, active layer. Active layers of membranes can be selective for certain components based on solubility into the membrane material, diffusion through the membrane material, or size selectivity through uniform nanopores.

Solubility-diffusion membranes generally use a thin layer of polymer as a homogenous active layer that can absorb gas components into the membrane substrate. Once the gas components are absorbed, they diffuse through the thin polymer to the permeate side where they are desorbed into the lower partial-pressure environment. Membrane flux in solution/diffusion membranes can be tuned based on the active layer characteristics. Components are permeated based on both solubility into the membrane and diffusion through the membrane. Larger components tend to have greater solubility and slower diffusion while smaller components have lower solubility but more rapid diffusion through the membrane. Increasing the diffusion rate through the membrane can be used to make solubility the limiting step for the separation, while increasing the solubility into the membrane tends to make diffusion the limiting step.

The other main source of selectivity in membranes is size-based selectivity. Nano-filtration membranes use small holes that can only permeate some species wile excluding larger components. Zeolites and other structured materials that have micro-pores with uniform size distribution can also be used to selectively permeate smaller molecules. Flakes of size-selective components can also be inserted into a polymer substrate to create mixed-matrix membranes which combine characteristics from both size-selective and solution/diffusion membranes.

The permeance for each component through the membrane is determined by the physical properties of the membrane – material permeability for each component through the active-layer material and the thickness of the active layer. Thinner active layers generally allow faster diffusion through the membrane and higher permeability. They also allow the use of higher cost materials that may have improved properties such as higher selectivity or stability.

Membrane separation systems rely on high surface area systems to increase the material flux through the membrane. Membranes are arranged into modules with different geometries to maximize the surface area while minimizing the system size. The three main geometries are flat plate, spiral wound, and hollow fiber.

Flat plate or plate and frame configurations use a flat sheet of membrane material with flow paths for the feed on one side and the permeate on the other side. These layers can be stacked by adding an impermeable layer between each layer of membrane. To maintain structure and open flow channels with pressure differences between the two sides of the membrane, a porous spacer is used.

Spiral wound modules use a similar layer structure as flat plate configuration, with the alternating layers of membrane, spacer, and impermeable material wrapped around a central tube that can be used to introduce the feed, extract the permeate, or both. The spiral wound modules are generally housed within a cylindrical pressure vessel and can be made in sizes up to Spiral wound modules tend to have higher surface area per volume than flat plate configurations due to higher density packing of sorbent material into the module.

Hollow fiber membranes can the highest surface area per volume. Hollow fiber membranes are thin tubes, generally less than 1 mm in diameter, comprised of a support material and the active layer coated on either the inside or the outside surface of the membrane tube. The fibers are arranged in a bundle within a cylindrical housing with each end of the fiber in the headers of the housing. The feed is generally through the lumen-side of the fiber while the permeate is generally collected from the tube side of the fiber bundle.

The system size for membranes is achieved with a modular approach based on modules with set diameters. Common sizes for cylindrical membrane systems are 40 inches long with diameters of 8, 16, or 24-30 inches. Cylindrical housings can hold either spiral wound or hollow fiber membranes. Flat plates tend to be similar configurations to plate-and-frame heat exchangers with approximately 1 m^2 sheets stacked in layers to make up a single module.

Membrane systems are best suited for removal from streams with high partial pressure of CO_2. Deep removal of CO_2 to very low concentrations can be uneconomical as higher removal rates requires deeper vacuum to create the driving force required and larger surface area as mass flux with low driving forces are reduced. Because of this, membrane systems are sometime used in different configurations to maximize the pressure and concentration of CO_2 seen by the membrane.

For gas processing, one common configuration is the use of a membrane for bulk removal of CO_2 at high purity. Once the purity of the CO_2 has dropped to a low level, a solvent system can then be used to achieve a deeper level of removal.

For ambient pressure, lower concentration systems, such as CO_2 capture from flue gas, other configurations have been proposed. These include integrating membrane capture with exhaust gas recycle or selective exhaust gas recirculation processes. Exhaust gas recirculation is the reintroduction of exhaust gas back into the combustor. In natural gas combined cycle units, there is enough excess oxygen in combustion gases to enable this use as primary air. In systems with tighter fuel/oxygen stoichiometry, the recycled flue gas may be introduced as secondary air into the system. Selective exhaust gas recirculation preferentially recycles CO_2 to the combustor. The purpose of exhaust gas recirculation is to either increase the concentration of CO_2 entering the membrane unit, or to recycle additional CO_2 that would otherwise be uncaptured by the membrane unit. One configuration pioneered by MTR uses selective exhaust gas recirculation via a CO_2-permeable membrane that uses the inlet air as the sweep gas to achieve deeper levels of CO_2 capture than would be possible with a single membrane stage as shown in Figure 2-3.

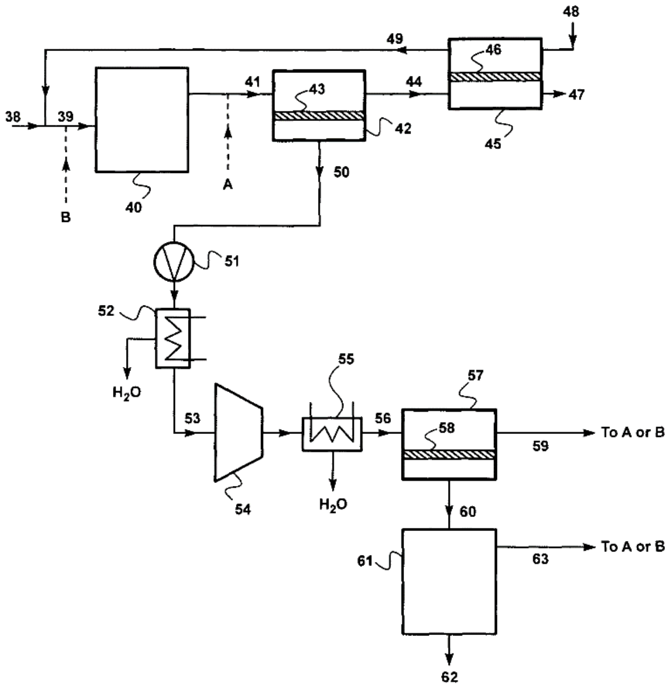

Figure 2-3
Schematic of MTR selective exhaust gas recycle configuration for CO_2 capture from combustion gas (from [16]).

Status of Membrane-Based CO_2 Capture

CO_2 capture via membranes is currently used for separation of CO_2 from natural gas streams and is being tested and developed for capture from flue-gas streams as well. Capture from natural gas streams with high concentrations of CO_2 have been ongoing since the 1980s. These systems are relatively high pressure (30-60 bar), high CO_2 partial pressure systems that remove CO_2 in order to achieve natural gas pipeline specifications – usually <2-3% CO_2 by volume.

The largest CO_2 sequestration based on membrane separation of CO_2 is based in the Petrobras floating production storage and offloading (FPSOs) platforms. These units on 21 FPSOs within the same production region captured and reinjected a total of 9.6 Mtpy of CO_2 in 2022 [17]. These units a mix of technologies incorporating both spiral wound and hollow-fiber membrane systems. They have been deployed over a period of about 10 years starting in 2010. Because of the modular nature of membrane systems, the modules are generally interchangeable with the same supporting structure and balance of plant remaining in place.

Systems for capture from flue-gas streams are currently under development. The most advanced systems for membrane capture are the Membrane Technology Research (MTR) and Air Liquid processes.

The MTR membranes have been tested at the 10 tpd scale at Test Center Mongstadt (TCM) in Norway on ~14% CO_2 flue gas and are expected to be tested at the 150 tpd (~10MW) scale at the Wyoming Integrated Test Center in 2025. The configuration for the 10MW testing does not have the sweep module, which means that the highest economic capture rate is limited to approximately 70% of the incoming CO_2 [18].

The properties of materials can also be modified based on the temperature of the material in the process. At colder temperatures, the polymers that make up the membrane vibrate more slowly, which reduces the open micro pore volume within the active layer. This slows down the diffusion of all components through the membrane but impacts the diffusion of larger molecular diameter molecules the most. This increases the selectivity of the membrane towards smaller diameter components. CO_2 has a smaller molecular diameter than nitrogen or oxygen, so that selectivity for CO_2 over other components can be enhanced at low temperatures. In addition, lower temperatures increase the solubility into membrane materials, which offsets some of the reduction in permeance from the reduced diffusivity.

Air Liquid has developed a capture method that makes use of the different material properties at low temperature. This can then be paired with cryogenic CO_2 purification as the CO_2-rich permeate stream is already at sub-ambient temperatures. The Air liquid process uses flue gas compressed to approximately 15 bar (215 psia) and cooled to below -40°C (-40°F) [19]. The cold temperature below the freezing point of water necessitates a moisture removal step prior to cooling to prevent solid ice buildup on heat exchanger surfaces. Mechanical energy from flue gas pressurization is recovered in a turboexpander and the expanded flue gas is used to cool the incoming flue gas to the chilled conditions. An integrated version of this technology was tested at the National Carbon Capture Center in 2019 at a scale of 0.3MW from coal-fired flue gas. The NCCC test showed continuous 90% capture at a purity of between 50% and 60% CO_2. The high capture rate is possible in part due to the high pressure of the feed flue gas. The low purity indicates a second stage of separation, such as a cryogenic purification would be necessary in a commercial process [19].

Benefits, Challenges, and Considerations for Membrane-based CO_2 Capture

Membrane systems are generally powered exclusively by pressure differential between the feed and permeate sides. There is no solvent or sorbent chemistry that needs to be maintained and no thermal cycling of materials of components. This requires only electrical or mechanical work and does not require thermal energy. For power generation and other point source emissions associated with fuel combustion for heat or steam generation, this means that no steam-cycle modifications are required. Conversely, the thermodynamic benefits of making use of lower-grade energy, such as thermal energy instead of electrical energy, cannot be realized.

Membrane systems can be operated robustly over a range of conditions with operational flexibility and no loss of efficiency. They are well suited for modular construction and operation with ease of operation due to the steady-state operation of the membranes and no circulating materials.

The membrane active layer can be degraded over time. Particle or precipitate accumulation can block surface area and inhibit mass transfer, small holes or defects can allow non-selective permeability, and co-constituents and oxidative degradation can change the membrane properties to inhibit permeance. Pressure cycling can also exacerbate cracks or tears in membrane materials or sealing structures. While membrane tend to have operational lifetimes of 3-7 years, applications with higher levels of contaminants tend to have shorter lifetimes and systems with fewer problematic co-constituents can have lifetimes of more than 10 years [20].

CO_2 capture through membranes is related to the partial pressure of the permeated species. High levels of CO_2 removal are difficult and uneconomical with single-stage or simple membrane configurations. Instead, membranes are best suited for bulk removal of CO_2 and can be paired with other removal systems or more complex configurations if deep removal levels are required.

The purity of captured CO_2 is also related to the selectivity of the membrane. Values of selectivity for CO_2 over other constituents such as nitrogen or oxygen are inversely proportional to the permeance of the material: generally, the higher the permeability through the system the less selective the material is. For single stage separations, to concentrate from 4% CO_2 to 90% CO_2 would require a selectivity of more than 200 and to achieve 99% CO_2 would require a selectivity of more than 2,000. Very few materials exhibit selectivities above 200, let alone 2,000 the permeance for CO_2 through such selective membranes would be very slow requiring large surface areas and large numbers of modules. As a result, secondary purification such as through cryogenic purification or multiple membrane stages are often applied to achieve the target CO_2 purity.

Sorbent-based CO_2 Capture

Solid sorbents tend to be highly-porous materials with surface chemistries that selectively react with CO_2 (chemi-sorbents) or geometries that have selective molecular attraction for CO_2 (physi-sorbents). To capture CO_2, sorbents are exposed to the gas stream containing CO_2, which selectively is adsorbed onto the sorbent. Once the sorbent is saturated with CO_2, it is regenerated, either through thermal swing, exposure to vacuum or a sweep gas, or a combination of these methods. Pressure swing adsorption (PSA) uses the difference between the high pressure adsorption and lower pressure regeneration to regenerate the materials. This is most effective for sorbents that have low CO_2 affinities so they can be effectively regenerated at lower partial pressures and is best paired with physi-sorbent materials. Thermal Swing adsorption (TSA) uses elevated temperature to regenerate the solvent is best paired with sorbent materials with higher affinity for CO_2 and is best paired with chemi-sorbent materials. The reason TSA is more effective with higher affinity materials is that the difference in loading as a function of temperature is a much steeper slope at high heats of adsorption than at low heats of adsorption. As the affinity of CO_2 to a sorbent is directly related to the heat of adsorption, materials with higher heats of affinities for CO_2 can have higher working capacities with smaller temperature changes than materials that more weakly adsorb CO_2. Processes that adsorb CO_2 at ambient pressures and lower concentrations (<20%) are generally better suited for temperature swing adsorption. Process that have higher partial pressure of CO_2 either due to high pressure or high concentration may be better suited for PSA applications.

There are many types of solid sorbent processes but they can generally be classified into either fixed bed processes or moving bed processes. In fixed bed processes the sorbent is housed within a vessel that cycles between absorption and regeneration. In moving bed processes the sorbent material is moved between an absorption region and a desorption region. Generally, PSA processes are better suited for fixed bed systems while TSA processes are better suited to moving-bed systems. This is because fixed-beds housed in pressure vessels can be rapidly cycled between high and low pressures but are difficult to heat and cool rapidly, have additional thermal mass to heat, and are difficult to recover thermal energy. Conversely, moving-bed systems are difficult to isolate and pressurize but are relatively easier to heat, cool, and perform heat recuperation. However, there are process intensification concepts that may improve the performance of TSA or temperature-vacuum swing adsorption (TVSA) cycles in fixed-bed configurations and several such concepts are being actively pursued.

There are many different solid-sorbent processes configurations being developed for CO_2. Fixed-bed systems include beds of packed sorbent particles, monolith structures, laminate sorbent structures, hollow-fiber contactors, coated honeycomb structures, and simulated moving beds. Moving-bed systems include cascading bead systems, fluidized beds, and rotating monolith structures. The sorbents proposed have ranged from physi-sorbents such as activated carbons, zeolites, activated alumina, porous polymer networks (PPNs) and metal-organic frameworks (MOFs) to chemi-sorbents including amine-impregnated silicas, amine-appended MOFs, carbonate materials, and beads of encapsulated solvents.

Moving bed systems are either based on moving sorbent particles or a moving sorbent monolith. Moving sorbent monoliths are rotating wheels of structured sorbent similar to rotary heat exchangers. These beds rotate through different regions where adsorption, regeneration, and other process steps can take place. Advantages of a rotating monolith structure are that the structured sorbent avoids the solids handling and attrition of other moving bed systems. The open honeycomb structure permits low pressure drop through the system, fast flow, and fast cycle times. Heating is accomplished through direct steam injection and cooling through water vapor evaporation from the sorbent prior to adsorption. Challenges for the process involve difficulty in creating sealing systems that can prevent leakage between CO_2 product and inlet flue gas maintained at different pressures. In addition, the moisture from direct steam injection has to be removed from the solid sorbent and the heating requirement associated with the drying can be significant. Active R&D to reduce the moisture condensation onto the sorbent material is ongoing.

Moving bed systems have been developed using both fluidized bed and cascading bed geometries. In fluidized bed systems the sorbent particles are circulated in the absorber by the upward flow of carbon-containing gas. Within each fluidization stage the sorbent is well mixed and the gas stream flows through it. Sorbent stages can be arranged in a counter-current arrangement with the fresh sorbent introduced at the top of the moving bed and transported sequentially to lower beds. In a cascading moving bed the sorbent movement is controlled by gravity and the gas velocity is insufficient to fluidize the sorbent particles. Fluidized and moving-bed designs have better heat transfer than fixed bed designs due to the opportunity to embed heat transfer tubes within the adsorption chamber. This is important during adsorption as the heat of adsorption released when CO_2 is adsorbed onto sorbent surface can be significant and lead to a temperature rise sufficient to prevent further CO_2 adsorption. In most sorbent processes with CO_2 concentration higher than 3-4%, the removal of heat during adsorption is the limiting factor in adsorption. At lower CO_2 concentrations, such as dilute sources or direct air capture, the gas flow is sufficient to remove the heat of adsorption.

Drawbacks of moving-bed systems are mainly associated with the sorbent handling. Mechanical sorbent attrition is a major source of degradation and fine particles that can clog or build up on process equipment. Solid particle transportation is often accomplished through pneumatic transport with carrier gas used to lift particle to hoppers that can then be fed by gravity into adsorption or regeneration vessels. The use of carrier gas increases the energy penalty for the system and can result in loss of CO_2 product or working capacity. Pressure management and sealing in moving bed systems is also challenging to control during operation.

Status of Sorbent-Based CO_2 Capture

Sorbent-based gas separation has a number of commercial applications. Most sorbent-based separations are performed to remove a certain component from a gas stream. This can include removal of VOCs from a flue-gas stream through an activated carbon bed, air-separation in a rapid PSA process, CO_2 separation from H_2 streams in H_2 purification PSA systems, moisture removal via dehydration using silica or zeolites regenerated thermally or through dry gas purge, and moisture and CO_2 removal from inlet air to cryogenic processes to prevent frosting on heat exchanger walls.

For pressure-swing adsorption systems, the partial pressure of the incoming CO_2 is the primary factor in the economics. PSA for CO_2 separation from H_2 gas at elevated pressures is commercially operating at hundreds of plants worldwide and at scales up to 400,000 Nm^3/hr, primarily on steam methane reformers (SMR) and refinery systems [21, 22]. The operation generally swings between the elevated pressure adsorption at 20-60 bar and near atmospheric regeneration. In these processes, the product H_2 is not adsorbed while CO_2 and other components are removed through the PSA process. As such, the CO_2 purity during regeneration is not optimized and often low purity CO_2 is vented after capture. The largest system currently operating for H_2 production and CO_2 product is the vacuum swing adsorption system for in Port Arthur, Texas which utilizes fixed beds to capture CO_2 for enhanced oil recovery at a rate of approximately one million tons per year [23].

CO_2 capture from atmospheric pressure streams with concentrations between 3-20% CO_2 to produce a concentrated CO_2 product through sorbent-based processes have been tested at small scale with several installations at the 5-30 tpd scale.

Svante's Veloxotherm process is the most commercially advanced rotating solid sorbent system with the largest operational installation in Saskatchewan, Canada at the 30 tpd (10,000 tpy) scale on flue gas from a once-through steam generator [24]. This process uses a monolith of solid sorbent that rotates through different sections of a gas contactor, exposing the sorbent to different conditions in each section. The sorbent rotates through exposure to flue gas (adsorption), steam (desorption), and other streams for drying and cooling as shown in Figure 2-4.

Figure 2-4
Schematic and cutaway of Svante Solid-sorbent rotating bed process. Image courtesy of Svante

Kawasaki Heavy Industries has developed a moving-bed carbon capture system named Kawasaki Carbon Capture (KCC). The process uses gravity to let the sorbent particles flow from one chamber to the next. In the topmost chamber, the sorbent is contacted with flue gas to remove CO_2. In the second chamber, the sorbent is exposed to low-grade heat in the form of direct steam to regenerate the sorbent and produce CO_2. In the final chamber, the sorbent is dried by exposure to warm, dry air and then cooled to be readied for CO_2 absorption. A pilot unit of the technology was demonstrated at the 10 tpd scale in Japan as a fixed bed system and 3 tpd scale in the moving bed system. A similar-size unit is being constructed at the Wyoming Integrated Test Center (ITC) for capture from coal-derived flue gas [25].

Benefits, Challenges, and Considerations for Sorbent-based CO_2 Capture

Solid sorbent systems have been considered promising for thermal-swing adsorption due to the potentially lower energy consumption than similar solvent-based processes. Within the regenerator, the thermal loads are smaller than for solvent systems due to the absence of water vaporization which is one of the major components of solvent system regeneration. The theoretical thermal energy consumption for solid sorbent materials is lower than for aqueous solvent based processes, but the process difficulties have prevented the realization of this improved performance.

Sorbent systems also rely on thermal energy for heating. Heat recovery through sorbent-sorbent heat exchange is difficult with either a heat transfer fluid required as intermediary or transport on either side of a heat-transfer surface. In each case the temperature approach is much higher than liquid-liquid heat exchange. This leads to large thermal loads for heating and cooling sorbent systems.

For all solid sorbent systems the purity of CO_2 product is reduced for 2 reasons. First, there is co-adsorption of nitrogen and oxygen on sorbent sites which is then released during regeneration, and second, flue gas remains in the interstitial spaces between and within particles when they are brought to the regeneration chamber. To counteract this, often there is a purge gas such as steam or vacuum pulled on the system to reduce the interstitial gas quantity. In addition, the first cut of produced gas may be recycled to avoid reducing the purity of the CO_2 product. Even with these steps, cryogenic purification may be required to achieve pipeline specifications, especially for oxygen.

The direct introduction of steam to the sorbent helps to strip additional CO_2 from the sorbent and can reduce the heating step of the process. However, the sorbent will have significant water condensation onto the surface and into the pores of the material. This water will have to be removed in additional process steps, adding both time to the overall cycle and energy consumption for the drying step.

Cryogenic CO_2 Capture

CO_2, like all gases, enters the dense phase when sufficiently cooled. Cryogenic CO_2 capture uses this phase change to separate CO_2 from the other gas-stream components. Above the triple point pressure of CO_2 (5.3 bar), CO_2 can form a liquid when it is cooled. Below this triple point pressure, it cannot form a liquid, which is why dry ice sublimates directly from solid to gas at atmospheric pressure.

One of the main benefits of cryogenic systems is the purely physical separation. There are no chemical components that need to be cycled, pumped, protected, or managed. Further, the separation occurs at the boundary between the gas and dense-phase interface instead of within the dense phase and does not rely on diffusion through or into a dense phase such as a solvent, sorbent, or membrane. Gas-phase diffusion is orders of magnitude faster than dense-phase diffusion, so surface area required for cryogenic separations can be much smaller than for other separation methods. The potential for lower surface area, and hence potentially lower capital cost separations has driven interest in cryogenic separation processes.

CO_2 forms a solid along the vapor-solid equilibrium curve. This relation between the temperature and maximum vapor pressure of CO_2 can be used to calculate the remaining CO_2 in the gas phase at a given temperature. For an ambient-pressure system, initial CO_2 solidification for 14% CO_2 occurs at -100C, with 90% removal at -120C and 99% removal at -135 C. For a 4% CO_2 flue gas, initial CO_2 solidification would occur at -111C with 90% capture at -128C and 99% capture at -142 C [26]. Cooling the flue gas to the cold temperatures required for CO_2 removal and providing sufficient chilling to overcome the energy release during phase change are primary energy drivers of the process.

Three major approaches to cryogenic CO_2 separation will be presented in this section: capturing CO_2 in a modified distillation column, capturing CO_2 within a cold slurry, and capturing CO_2 it as a solid.

ExxonMobile has developed and patented the Controlled Freeze Zone (CFZ) process for removal of CO_2 from natural gas with high concentrations (>50%) of $CO_{2.}$ The CFZ process is a modified distillation column designed to counter solid CO_2 formation within the column. When high-CO_2 concentration natural gas is separated in a distillation column, the methane remains primarily in the gaseous phase while higher hydrocarbons and CO_2 condense to form a liquid. At the top of the column, the liquid phase is mainly liquid methane with some CO_2 and other co-constituents. At the bottom of the column the CO_2 partial pressure is above the CO_2 triple point pressure and liquid CO_2 can be formed. In the middle, the methane in the liquid phase would normally evaporate leaving primarily CO_2 which would normally form a solid. As solids formation inside of a conventional distillation column would clog and prevent efficient operation, a controlled freezing zone is instead introduced. In this zone, the CO_2-rich liquid that is nearing solidification is sprayed in an open spray tower configuration onto a tray of slightly warmed liquid. The CO_2 forms solid particles that are then melted in the liquid layer. This three-part column has been successfully operated at large scale in the Shute Creek gas processing plant for more than 10 years [27].

Other cryogenic approaches rely on cooling flue gas to produce a solid CO_2 product. To prevent solid CO_2 formation on heat exchange surfaces, Sustainable Energy Solutions (SES), has developed a process the call Cryogenic Carbon Capture (CCC)that uses a cold direct contacting liquid to cool the flue gas below the solidification point and precipitate solid CO_2 onto the surface of the liquid droplets to form a slurry. This liquid slurry is then physically separated to recover most of the contacting liquid from the solid CO_2. A further distillation step at pressure is required to recover the remainder of the contacting liquid and produce CO_2 at high purity. The chilling is provided through refrigerant loops with heat integration throughout to maintain a small temperature approach through the cycle.

Carbon America is developing an alternate process that uses solid CO_2 frosting onto heat exchanger surfaces to remove the CO_2. This Frosting Carbon Capture (FrostCC) process compresses flue gas and cools it to near the solidification temperature. The compressed, cool flue gas then enters frosting heat exchangers where the solid CO_2 forms on the walls of the heat exchangers. The cold, remaining flue gas is expanded in turboexpanders to further chill it before flowing through the cold side of the frosting heat exchangers. Solid CO_2 is periodically melted off the heat exchangers as a liquid to be collected.

Status of Cryogenic CO_2 Capture

Cryogenic gas separation is the dominant method of separating oxygen from nitrogen in air separation units with thousands of plants operating worldwide and at scales of up to millions of tons per year. These plants use the difference in boiling point between oxygen and nitrogen to perform the separation. The incoming air is first dehydrated and has CO_2 removed, usually via zeolite unit. This dehydrated, CO_2-free air is then chilled to the condensation points of oxygen (-183C) and nitrogen (-196C) and distilled to produce oxygen at purities between 95% and 99.5%.

The largest CO_2 capture facility in commercial operation for separating CO_2 from natural gas streams is the Shute Creek facility that uses the CFZ technology described above. This plant has been in operation since 2010 with a current capacity to capture 7 Mtpy from a 65% CO_2 natural gas stream, making it the largest operating single carbon capture facility. This facility is the only major cryogenic carbon capture unit in operation. This is due in part to the CFZ requirement of high CO_2 concentration in the natural gas feed. The CO_2 produced in the CFZ process is either sold for EOR or vented. Over the life of the facility, more than half of the CO_2 captured has been vented to the atmosphere.

Other cryogenic processes are early stage and in the TRL 5-6 range. The SES process has tested their cryogenic unit at the 1 tonne per day scale in a skid-mounted test unit on a variety of applications including cement and coal-fired flue gas [28]. Their proposed next step is an integrated 30 tpd unit expected to be tested in 2025 at a cement kiln. FrostCC has developed their technology at bench scale and are in the process of building their first pilot unit at ~2 tpd scale to be tested at the National Carbon Capture Center on NGCC flue gas.

Benefits, Challenges, and Considerations for Cryogenic CO_2 Capture

Capture in the dense phase has several benefits. Separation based on phase change does not require a separation material or chemicals, which eliminates the chemical handling, management, maintenance, and incoming gas stream conditioning. Systems with no separation material also do not require diffusion of CO_2 into the dense phase as the CO_2 is collected on the surface of the heat exchange medium. Diffusion in the gas phase is approximately 2 orders of magnitude faster than diffusion through liquid or solid phases, which increases the mass transfer rate and reduces the required surface are and residence time of the gas, which may reduce equipment size and capital costs. The CO_2 product can also be pressurized in the dense phase as a liquid, which requires much less energy than compression in the gaseous phase. As the CO_2 is already a liquid, additional cryogenic CO_2 purification, if required, has minimal energy consumption. Cryogenic systems also are mainly powered by electrical energy instead of thermal energy, which makes them independent of the source of CO_2 as no thermal integration is required. The energy for capture and equipment cost is dominated by the flue gas cooling. To achieve deeper levels of carbon removal, slightly lower temperatures are required. However, the incremental cost of capture tends to decrease at higher capture rates reaching an optimum capture efficiency around 98% for capture from gas streams with CO_2 concentrations in the 10-15% range.

Cryogenic systems also face serious research challenges to be scaled for operation. Pilot operation of cryogenic systems are often unrepresentative of full-scale operation due to the difference in thermal losses to the atmosphere at small scales and large scales. This makes small scale, integrated tests difficult to perform, and not representative of the potential benefits at commercial scale. Some of the issues associated with cryogenic technologies include the solids handling for processing solid CO_2. New operational modes for variations on existing equipment are being tested. Long term testing and testing in integrated systems will be vital as material buildup at cold temperatures, such as water-ice or dry-ice formation, will be slow and may occur only under certain conditions. To prevent this formation, significant pretreatment in the form of dehydration and the removal of other condensable species prior to entering the CO_2 separation portion of the unit is required. To achieve a moisture frost point below the CO_2 frost point, moisture must be removed to a frosting temperature of near -100C, or less than 1 ppm moisture. This can be accomplished more easily at elevated pressure and at temperatures near 0C through a desiccant system such as zeolite bed, liquid desiccant, or by allowing targeted frosting on specially designed heat exchangers.

CO_2 Purification

Streams with more than ~80% CO_2 or with CO_2 mainly diluted with water vapor can make use of CO_2 purification rather than CO_2 separation to achieve the desired CO_2 product. CO_2 separation refers to the removal of CO_2 from a stream while CO_2 purification refers to the removal of other components from a CO_2-containing stream. While both have the intended product of a high-purity CO_2 stream, the mechanism can be significantly different.

The most common form of CO_2 purification is dehydration. This is generally performed on streams that have very high concentrations of CO_2 with mainly moisture as the primary co-constituent. This is common from some industrial processes including fermentation header gas from ethanol production and as a byproduct from some industrial processes including steam-methane reforming (SMR). Bulk moisture can be removed during CO_2 compression through condensing compressor intercoolers. However, condensation can only occur at sub-critical pressures of below 73.8 bar (1072 psia) and down to the available cooling temperature. To remove sufficient moisture for CO_2 pipeline transportation and injection often additional steps must be performed. Pipeline moisture specifications vary around 500 PPM but can be as low as 20 PPM [29]. The selection of dehydration techniques is based large part based on the degree of moisture removal required.

Solvent-based dehydration uses a liquid desiccant such as Tri-Ethylene Glycol (TEG) to selectively adsorb moisture from the CO_2 compression train at a pressure just below the critical pressure of CO_2. The TEG is then heated and flashed to atmospheric pressure or purged with a dry gas to reduce the moisture content in the TEG prior to being re-introduced into the moisture adsorption column. The degree of moisture removal is determined by the pressure of the stream to be dehydrated and the degree of heating and purge in regeneration. Typical moisture content after TEG dehydration ranges from 100-500 ppmv.

For more complete dehydration solid sorbents are used. These tend to be zeolite-based for achieving very low moisture content. Zeolites have strong affinity for moisture and will remove moisture down to single-digit PPM levels from compressed gas streams. The zeolite beds are occasionally regenerated by heating and purging with dry gas.

CO_2 purification which contains other gas species can also be accomplished through cryogenic separation. While cryogenic carbon capture from near-atmospheric streams results in solid CO_2, concentrated CO_2 streams can be compressed to above the triple point of CO_2 and liquified through refrigeration. The non-condensable species such as nitrogen and oxygen are partitioned primarily into the vapor phase while the CO_2 is mainly in the liquid phase. A multi-stage distillation can achieve the desired purity of the CO_2 product. The higher the CO_2 purity, the more CO_2 will be lost along with the removed non-condensable gases in the overhead stream.

The energy consumption of the cryogenic process is relatively low because the mass and heat capacity of the produced liquid CO_2 is closely matched with the mass and heat capacity of the incoming stream to be liquified. A refrigerant loop is required to supply the low-temperature chilling.

Cryogenic CO_2 purification units are commercial units that can be purchased from a range of manufacturers in a range of sizes. For larger applications, such as purification of an oxy-combustion stream, a custom size will likely be required. These systems are very similar to air separation units (ASUs) that are commercial at the megaton scale and operate at the temperatures required to make liquid oxygen approximately 77K (C,F), which are significantly colder than the temperatures required to condense liquid CO_2 at elevated pressure (K,C,F, Pressure).

Considerations for Point Source Capture

Point source capture of CO_2 may be implemented with two main purposes: to remove CO_2 from a gas stream or to produce a CO_2 product. Historically, CO_2 removal from streams has been used for the purification of streams rather than the production of CO_2: removal of CO_2 from natural gas to produce natural gas that can be sold, transported, and used; removal of CO_2 from hydrogen streams to purify the hydrogen product; or removal of CO_2 from air to allow ASUs to operate with frosting. CO_2 production at high purity is generally for industrial gas production for enhanced oil recovery or other uses, or food grade CO_2, both of which were produced from high-purity sources

Carbon capture from existing facilities impacts the capture unit and the host site. The carbon capture unit must operate flexibly to capture the emitted flue gas stream through daily and seasonal variations related to the unit operation and capacity factor. For the host facility, the utility load to support the carbon capture unit must be considered. While the major component of this utility load is the energy for carbon capture, other utilities such as cooling water and water treatment must also be considered.

Energy for Point Source Capture

Capture from point-source emissions requires energy to perform the gas separation and to compress the produced CO_2. Generally, the energy to perform the separation is primarily thermal energy for solvent- and temperature swing sorbent-based systems and electrical energy for membrane-, pressure-swing sorbent, and cryogenic- based processes. The mechanical work to compress the product CO_2 is often provided via electrical motor or steam-driven driver.

The energy required for compressing CO_2 is based on the purity of the CO_2 to be compressed and the pressure at which it is regenerated. Solvent systems have pressure of regeneration that are determined by the temperature of regeneration – the maximum temperature the solvent can withstand without degradation determines the steam pressure and hence the stripper operating pressure. Operating pressures of 1.3-2.7 bar are typical for solvent applications. For PSA systems with high-pressure feed, the CO_2 product can be produced at ambient pressure. However, for ambient-pressure feed, pressure swing adsorption systems and membrane systems rely on low pressure of roughly 0.15-0.3 bar, which requires larger compressors and more compression energy.

The thermal energy requirement can be provided through extractions from the steam cycle, or from a standalone steam generation unit such as a boiler or combined heat and power (CHP) plant. To achieve high capture rates, the flue gas from the boiler or CHP would have to be recovered as well. The impact of the thermal energy on the host plant and the overall system depends on the source of that energy. Generally, steam extraction from a steam cycle is the most efficient source of thermal energy as the extraction can be designed to supply steam only at the temperature required. The high- and intermediate- pressure steam cycle components are mainly unaffected and the steam is extracted only from the low-pressure steam. For systems that have dedicated steam generation, such as CHP or standalone boiler, there is less work extracted from the steam prior to being used to supply thermal energy, so the overall efficiency of the plant is lower. For example, the Shell Cansolv carbon capture with aqueous amines applied to the NETL reference case [4] for a NGCC would yield a net HHV efficiency of 53.6% for the base NGCC without CCS, 47.7% for the NGCC with CCS and thermal energy supplied from steam extraction, 45.0% for the NGCC with CCS with thermal energy supplied from CHP, and 43.4% for the NGCC with CCS and the thermal energy supplied from a standalone boiler [5].

The impact of energy usage in a carbon-capture process depends on the source of energy and the CO_2. For industrial and utility applications, the CO_2 source and the energy source are usually the same. However, for some applications standalone boilers or CHP plants are used to generate thermal energy. Where CO_2 and energy are co-produced, such as in electric power generation from carbon-fuel combustion, the energy for CO_2 capture is supplied by either increasing the fuel consumption or reducing the output of the industrial or utility system. The decrease in output has the impact of making the existing facility less productive than the design condition without CCS. For power generation, this reduction in output is generally referred to as the energy penalty or parasitic load on the plant. Energy penalties have the dual impact of both reducing the efficiency of the plant, which increases the operating cost, and reducing the maximum output of the plant, which decreases the production over which the capital cost can be amortized. Significant research has been invested into reducing the energy penalty of carbon capture systems through different capture and regeneration configurations, process intensification, novel chemistries, and thermal integration.

Energy for CO_2 capture has been reported based on baselining studies such as the NETL Bituminous baseline rev 4a [4]. However, recent work with Front-End Engineering Design (FEED) studies that have developed more detailed designs for real plants and applications tend to show a higher energy consumption and higher capital cost than the baselining studies.

Capture Rate for Point Source Capture

CO_2 can be removed to any level. However, the equipment cost and energetic cost of capture generally increases as the capture rate increases beyond a certain point. CO_2 capture from flue gases has focused on 90% capture in large part due this being identified as target capture rate by the DOE for hundreds of millions of dollars in grants to technology developers. Recently, the target capture rate has been reassessed to include higher capture rates. This reflects the understanding that incremental increases in capture rate are often economical compared to other CO_2 mitigation options such as using direct air capture to recapture the remaining CO_2.

Higher capture rates can be accomplished by either approaching equilibrium more closely during the capture step, or by pushing the equilibrium further by changing the capture material or the regeneration step. To have close approach to equilibrium, the surface area for the gas contacting must be increased, resulting in greater capital cost. To change the regeneration condition, the pressure or temperature of the regeneration must be pushed to more extreme conditions increasing the energy consumption of the process. To achieve deep decarbonization of over 99% capture, often both greater surface are and deeper regeneration are required.

High capture rates over 99% have been proposed in order to achieve net-zero power plants where the quantity of CO_2 exiting the plant in the flue gas is equal to the quantity of CO_2 that entered the plant in the inlet air. To achieve net-zero, a NGCC plant would require 99% CO_2 capture while a coal power plant would require 99.7% CO_2 capture. Costs for reaching these low levels of CO_2 emissions have been studied and incremental costs for this level of removal approach the same cost ranges as direct air capture, making it a potentially viable pathway to further reducing CO_2 emissions.

Section 3: Direct Air Capture

Introduction to DAC

Direct air capture (DAC) is a carbon management technology that utilizes ambient air as the source of CO_2. Technical similarities and differences to point-source capture technologies will be directly compared in section 4, but the ability of DAC to offset the CO_2 from any source has been a major factor in its growth over the past few years. As companies and governments have started looking at long-term horizons for achieving net-zero emissions targets, DAC as a form of carbon removal has the potential to not only offset emissions from hard to decarbonize sectors, but to also contribute to proposed carbon removal efforts.

The core technology of any separation system is the inclusion of material with the ability to effectively capture CO_2 from air and to efficiently release it in a concentrated form. The materials requirements for DAC system push the limits of materials and absorption science today, and the widely adopted target of sub $100/ton DAC will likely only be possible with significant absorbent, process engineering, and manufacturing advancements.

Dozens of concepts for DAC have emerged over the past few years. To effectively create a DAC system, mass and energy transfer challenges most be effectively solved. Solid adsorbent systems generally have a mass transfer advantage over liquid-based systems, while liquid systems have advantages with respect to creating continuous unit operations adopted from current industrial approaches. Here, within these broad categories, we present a general framework for understanding each approach alongside a discussion of specific technologies and their technical and competitive differentiation.

DAC Systems Utilizing Solids Adsorbents

Owing to their favorable mass transfer and regeneration properties, many solid adsorbent based systems are presently under development for DAC. While the most advanced systems and developed systems are presently at TRL 7, the early-stage R&D happening now will be a key to long-term cost reductions in these systems. Here, we discuss the most important considerations in understanding and evaluating DAC unit operations and then highlight with a few examples how these principles have come together in the systems currently under development by a selection of companies.

Solid Adsorbents

The foundational technology of a solid-phase DAC system is the adsorbent material. In general, a DAC adsorbent is a high-surface area solid that is replete with functional groups that enable it to capture high concentrations of CO_2 from air, approximately 420 ppm. The adsorption of such a minor constituent of air is possible owing to the nature of CO_2 itself. CO_2 is a gas with both high polarizability and while it does not possess a permanent dipole, has a large quadrupolar moment. These attributes allow it to preferentially adsorb on solid surfaces using physical adsorption mechanisms. However, the affinity of physical adsorbents for CO_2 at 400 ppm and near ambient temperatures, especially in the presence of gaseous H_2O, is low, and thus chemical adsorption mechanisms are generally required for DAC processes to be effective. CO_2 is a reactive molecule, and as an electrophilic, acidic species has an affinity to chemically adsorb to solid surfaces replete with nucleophilic or basic moieties including amines and hydroxides.

The most common class of DAC adsorbents are porous materials including zeolites, metal-organic frameworks (MOFs), activated carbons, and metal oxides (e.g. silica and alumina). High concentrations of CO_2 binding sites within these materials are generally desired, and approaches such as the inclusion of amines, hydroxides, carbonates and bicarbonates have been widely pursued. In general, CO_2 adsorbed within the pores of such materials can be regenerated at low-temperatures (80° - 150° C). For many porous solids, the presence and coadoption of water vapor can present significant challenges. Other challenges include short operational lifetimes and high manufacturing costs with limited supply. Early DAC companies such as Climeworks and Global Thermostat have built their technologies around proprietary solid adsorbent technologies, and dozens of DAC startups over the past few years are utilizing porous solids in their systems. One major challenge for these companies, however, is that there is no effective off-the-shelf adsorbent material that can be effectively used for DAC systems and thus significant investment in materials development, testing, and manufacturing is necessary at this point for new DAC entrants.

To overcome these limitations, several DAC startups are focusing on utilizing materials that are widely available and inexpensive. Oxides and hydroxides of calcium and magnesium are among the most promising materials for DAC because they are highly reactive with CO_2, tolerant to H_2O, widely available at the kiloton scale, and significantly cheaper than porous sorbents to manufacture. However, these materials are not without their own challenges. Unlike porous solids, the reaction of these materials with CO_2 produces very stable carbonates and bicarbonates, and temperatures exceeding 900 °C are required to effectively regenerate them. While materials such as calcium hydroxide can be mined from limestone, low-carbon or zero-carbon lime is not yet widely available. Lastly, the lack of internal porosity creates challenges for accessing the full adsorption capacity of these materials without expensive processing steps.

Significant R&D on new adsorbent materials for DAC has occurred over the past few years. One of the primary objectives of most researchers has been to increase the effective rich-to-lean cycling (i.e. working) capacity of adsorbents. Adsorbents with large working capacities offer several process benefits. Systems utilizing higher capacity sorbents require less frequent regeneration. For non-continuous processes, higher utilization rates of the contactor will result in reduced capital costs per ton CO_2. Furthermore, there is generally an energetic penalty associated with the sensible energy of heating the sorbent (and potentially the system that contains it). For systems with a large thermal mass, adsorbents with large CO_2 capacities can significantly reduce regeneration energy.

The capacity of materials reported for DAC capture generally range between 0.4-1 mol/kg, with recent reports of materials with capacities approaching 4 mol/kg. With any promising material, a thorough testing process is necessary to evaluate its competitiveness. First, while most materials are tested at a single average adsorption temperature (20 °C ± 5 °C), one of the major challenges of DAC is the highly variable adsorption operating conditions. Unlike flue gases which are generally captured at a consistent temperature, DAC systems must be capable of dealing with daily and seasonal temperature variations. In general, higher temperatures will decrease adsorbent capacity while lower temperatures will increase adsorption capacity. However, for adsorbents that chemically react with CO_2 such as amines or hydroxides, cool temperatures may dramatically reduce adsorption kinetics resulting in overall drop in performance.

Achieving high purity CO_2 from a DAC process is a major process challenge. One of the primary advantages of high-capacity adsorbents is their greater selectivity for CO_2 relative to other gases. While N_2 is the primary constituent of air, effective DAC adsorbents generally exhibit a very high CO_2:N_2 selectivity. While more dilute than N_2 in air, contamination of purified CO_2 with O_2 can have a significant impact on downstream transportation and sequestration options. Lastly, the effects of water vapor can have a significant impact on the viability of a promising adsorbent for use in a DAC system.

First, H_2O has the potentially to rapidly degrade the active sites of many adsorbent materials. For physical adsorbents like zeolites, water will generally preferentially bind over CO_2. Given the large volumes of air that needs to be processed and the high concentration of H_2O, complete gas stream dehydration is unlikely to be a viable option for protecting water sensitive materials under most scenarios, but the use of zeolites in combination with dehumidification is a strategy for DAC presently under development.

Second, since a 70% relative humidity gas stream streams at 20 °C contains approximately 40 times more H_2O than CO_2, adsorbents will frequently be saturated with both CO_2 and H_2O under DAC adsorption conditions. Porous materials can exhibit extremely high capacities for adsorbing H_2O, in excess of 10 mol/kg, a capacity far higher than their CO_2 capacity. H_2O generally adsorbs in porous materials with an enthalpy of 30-50 kJ/mol. As adsorbents are cycled between adsorption and desorption conditions, the desorption of adsorbed H_2O can contribute significantly and unexpectedly to the energy requirements for a DAC process.

All DAC adsorbents will need to develop specific process steps that minimize the impact and costs of H_2O. For example, the removal of H_2O from zeolite pores requires significantly higher temperatures than would be required for removing just CO_2, and so DAC processes utilizing zeolites can be expected to require a regeneration temperature of 200 – 300°C. Here, the advantages of zeolites including their low cost, mechanical stability, and wide availability are offset by the need for significant quantities of high-temperature thermal energy.

Chemical adsorbents are also susceptible to degradation under DAC conditions including by CO_2, O_2, H_2O, as well as trace impurities in air such as acidic species. One of the primary challenges for many amine-functionalized adsorbents is their limited stability window. Degradation processes can occur during both adsorption and desorption, and so a detailed understanding and testing of any chemical adsorbents is required to develop a process that minimizes per cycle degradation rates. There are few reliable reports in the literature about adsorbent lifetimes, which represents a major research need. However, when comparing adsorbents, the cost of adsorbent per ton of CO_2 captured is critical for understanding overall system performance and process economics.

If adsorbents are utilized outside of their stability window, sudden loss in performance can be observed. However, even inside of their stability window, most adsorbents will exhibit a slow and continuous loss in performance over their lifetime. A detailed process and technoeconomic analysis should seek to understand not only the initial capacity of the sorbent, but what the final capacity of an adsorbent can be before it needs to be replaced. In this analysis, the costs of replacing adsorbent, which can be substantial, should be less than the operational inefficiencies associated with using partially degraded sorbent. Important factors in this analysis include the cost and amount of energy required per cycle, the replacement cost of the adsorbent bed, and the life-cycle implications of manufacturing and disposing of adsorbent materials. In general, inexpensive adsorbents would favor being replaced more frequently than expensive adsorbents.

The integrated amount of CO_2 captured by a batch of adsorbent during its useful lifetime is a simple metric for comparing these values. For example, an adsorbent with a starting capacity of 1 mol/kg may be replaced at a capacity of 0.6 mol/kg. Assuming the sorbent lost capacity at an approximately linear rate over its lifetime, ~28,400 cycles would be required for the sorbent to capture 1 ton of CO_2.

The 2018 NASEM report on DAC indicates that adsorbent is one of the primary drivers of DAC costs, contributing as much as 80% of overall DAC costs for mid-range systems. Analyzing scenario 2, DAC capture costs were estimated to be approximately $88, with sorbent accounting for $70 of those costs. Based upon the input parameters, a kg of sorbent was estimated to capture approximately 700 kg of CO_2 in its estimated six-month lifetime. While the breakdown of sorbent costs to other capital and operating costs will heavily depend on technology selection, driving the useable lifetime of adsorbents towards or past 1 ton CO_2/kg is a major factor in the cost reductions assumed by the NASEM report [30].

Adsorption Contactor

Owing to the highly dilute nature of CO_2 in air, relative to point source capture technologies, significantly greater volumes of gas are processes in DAC systems. The density of CO_2 in air is 0.0007 kg/m^3 , which is about 100 times more dilute than the CO_2 in NGCC flue gas and more than 20,000 times more dilute than the CO_2 in some natural gas streams. A DAC system that removes 50% of the CO_2 in ambient air would need to process 2,800,000 m^3 of air per ton of captured CO_2, which is roughly 180 times more gas than is required to capture a ton of CO_2 from a natural gas power plant.

The fraction of CO_2 removed from air under various process conditions will determine exactly how much volume of air needs to be processed to collect 1 ton of CO_2. Higher capture fractions can reduce volumetric flow requirements significantly. For example, a system that removes 80% of CO_2 will require 1,800,000 m^3/air to be processed for each ton of CO_2 captured. Capture fraction is heavily influenced by fundamental adsorption kinetics, adsorption temperature, bed design, and bed depth, and so technoeconomic modeling can play a key role in optimizing the necessary design parameters to minimize costs.

One of the primary impacts of adsorbing rom an ultra-dilute stream is that the time required for an adsorption bed to reach saturation will be dramatically increased. If one's goal is minimize adsorption step time, the velocity of air through DAC systems should be maximized to minimize capital costs. However, for non-laminar flow systems, pressure drop across the adsorption bed dramatically increases at high gas velocities, as dictated by the Ergun equation. Thus, capital cost savings that can be realized by increasing gas processing speed are offset by additional operating expenses owing to the increased electrical energy required to flow air at high velocities.

Several innovative designs that balance these competing factors have been developed, and detailed examples of processes developed by Global Thermostat and Climeworks are discussed below. It should be noted that the properties of the adsorbent material heavily influence the contactor and process design and thus it may be difficult to adapt a process designed for one material to a different material. The processability of the adsorbent, adsorbent stability, adsorbent cost, and adsorbent regeneration method all have an influence on contactor design.

In contrast to system designs that actively process air over the adsorbent materials, other DAC companies are developing passive system designs. The CapEx and OpEx associated with moving air during adsorption are substantial. Some systems are seeking to reduce these costs by developing high surface contactor arrays that allow air to flow over materials unassisted. It would be expected that for such processes, the time required to saturate the adsorbent materials with CO_2 will be significantly increased. As such, to achieve a particular capture rate, the footprint of the facility and the amount of adsorbent required to be in active use would be significantly larger for these passive designs. Passive adsorption designs are generally paired with low-cost materials, such as calcium or magnesium hydroxides, but other approaches such as the use of ion-exchange membranes have also been proposed. One important consideration in passive designs is that without a structured contactor, the penetration of air into a deep adsorbent bed would be disfavored. Thus, passive contactors generally need to be highly structured, which can significantly increase both materials and capital costs.

Lastly, DAC systems are frequently differentiated by whether they pursue a batch process with stationary beds or moving bed configuration that circulated adsorbent between adsorption and regeneration processes. Systems that can effectively cycle adsorbent between adsorption and desorption phases will more effectively utilize balance of plant equipment such as fans, compressors, and heat exchangers. However, moving adsorption beds are generally significantly more complex, can potentially causes mechanical attrition of adsorbent, or may require more extensive and expensive adsorbent processing into structured bed configurations. Stationary and moving bed configurations are being developed for both active and passive contactors designs.

Adsorbent Regeneration Processes

Adsorbent regeneration processes are the primary energy consuming process of any DAC system. While energy may be expended moving air during adsorption, CO_2 has a natural affinity for adsorbent materials and thus adsorption is an energetically spontaneous process. Thus, energy must be provided into the system to separate CO_2 from the adsorption media, a process known as desorption. The primary methods of regeneration include temperature swing, temperature-vacuum swing, and electrochemical swing.

The primary method by which DAC systems are regenerated is through the introduction of thermal energy into the system. High temperature fluids are the primary mechanism for delivering heat within carbon capture systems, however alternatives such as resistive heating or radiative heating have also been proposed or are in early stages of development.

For most systems that utilize hot fluids, the primary challenge becomes effectively extracting heat from the fluid. To minimize the volume of thermal fluid that is required by the system, it is desirable to maximize the heat that can be extracted. The primary method of achieving this is by effecting a phase transition within the regeneration bed, allowing the latent heat of the transition to be utilized for the desorption process. This is the primary advantage of utilizing a steam to water condensation process as the method of desorption. However, many promising DAC sorbents are not amenable to direct contact with steam. For such materials, heat must be transferred through heat exchangers, which can increase the cost and thermal mass of adsorption beds significantly. As the stability of adsorbents to direct steam contact is a major impediment for many promising DAC sorbents, the use of hot gases besides steam is frequently proposed by researchers.

The primary obstacle to utilizing hot gases such as CO_2 that do not experience a phase transition is that that useable heat can only be extracted from the sensible heat change of the working fluid. For example, the heat capacity of CO_2 at 130 C is 41.3 J/mol•K. In contrast, the latent enthalpy for H_2O condensation is approximately one thousand times greater at 40 kJ/mol. Thus, a nearly one thousand times increase in fluid volumes is required to utilize non-condensing gas as the source of heat for a solid sorbent system. While flowing hot CO_2 through an adsorption bed is frequently proposed, the fan/booster energy and time required to heat a bed using only CO_2 appears to be a major impediment to its practical implementation.

The primary source of energy required for adsorbent regenerations plays a critical role in determining the best method for sorbent regeneration. As discussed in Section 1, the net removal rate will be heavily influence by the carbon intensity of energy and power production that goes into a DAC process. While point source capture methods generally have existing heat and steam sources on-site owing to combustion of fossil fuels, the direct integration of DAC systems with renewable power production is highly desirable. Heating methods that can directly utilize renewable sources of energy will likely be well suited for many DAC system designs. Concepts that have been proposed include the use of electrically driven heating elements to either directly or indirectly heat adsorbent beds. For example, designs have been proposed that integrate resistive heating elements into adsorbent beds without the need for heat exchanger. Other designs utilize heat exchangers with adsorption bed, which needs to be considered in the overall capital cost considerations of the design but can unlock additional energy efficiency by utilizing heat pumps to generate hot working fluids. Lastly, low-carbon energy sources that directly produce steam, such as geothermal and nuclear power plants have the potential to effectively integrate with DAC processes that require steam.

A steam condensation process operating with a heat exchanger is an effective way of quickly delivering heat to any material not suitable for direct steam contact. However, the use of heat exchangers has two primary drawbacks. First, the heat exchanger can contribute significantly to the capital cost of the bed. The thermal conductivity of porous solids is low and so a high surface area contact is required to effectively transfer heat without unacceptable temperature gradients within the adsorbent. Second, the thermal mass of the heat exchanger cannot be significant if a temperature change of the adsorbent bed and its internals is required for operation. This is one of the primary advantages of a moving bed configuration, which requires only the adsorbent material itself to cycle in temperature reducing the sensible energy required for each adsorption.

To improve the efficiency of temperature swing processes, a combined temperature-vacuum swing adsorption (TVSA) process is often utilized. The primary advantage of TVSA is the ability to effectively regenerate sorbents at lower temperatures. As the adsorbent is heated, CO_2 is released by the material and the partial pressure of CO_2 in the bed increases. As adsorbent loading as determined by both the temperature and partial pressure of CO_2, very high temperatures are required to maximize the lean loading of CO_2 within the sorbent. By utilizing a vacuum swing, the partial pressure of CO_2 within the system is dramatically reduced allowing the adsorbent to be effectively regenerated at low to moderate temperatures.

Reducing regeneration temperatures reduces not only the sensible energy requirements for regeneration but can often impact the reliability of the adsorbent materials. For carbon capture technologies, process efficiency is heavily determined by the stability of the sorbent under desorption conditions. For example, the ~120 °C temperature limit for the widely used carbon capture absorbent MEA is related to its unacceptable degradation rate at higher regeneration temperatures [31]. For DAC sorbents, the most efficient combinations of temperature and vacuum regeneration need to be surveyed so that the sorbent can demonstrate a large working capacity under cycling conditions with acceptable rates of sorbent decomposition and attrition.

The final advantage in utilizing vacuum for regeneration is its ability to increase CO_2 product purity, as developing a process that meets the required CO_2 purity specifications is an additional consideration for solid adsorbents. In contrast to liquid solutions that have minimal void spaces, the void spaces within solid adsorbent beds contain residual air which has the potential to drastically reduce the final CO2 purity if not effectively purged from the system prior to desorption of CO2 from the media. With TVSA, the pressure of the bed can be reduced prior to heating, improving final product purity.

The advantages of utilizing vacuum need to be balanced against its disadvantages. First, the degree to which vacuum assisted regeneration is applied will have significant impacts on process viability. While weak or moderate vacuums generally show promising technoeconomics, but vacuum assisted desorption introduces a number of additional challenges for system developers. At increasingly deep vacuum levels, the molar volume of gases increases substantially. This dramatically increases the size and thus CapEx of the vacuum system. As CO_2 must be effectively transported away from a DAC site, any CO_2 that is produced under vacuum conditions will require additional stages of compression to bring it to transportation conditions. Additionally, systems that operate under vacuum, especially deep vacuum, need to be composed of materials suitable for the differential pressures they will experience. Thus, thicker components and tighter seals will be required, increasing the CapEx and manufacturing costs of adsorbent beds. Lastly, the energy required by the vacuum and compression itself needs to be factored into the overall economics.

If materials are steam stable, the use of steam can provide a stripping force that is an effective substitute for vacuum regeneration. While steam stripping will produce CO_2 at sub-ambient partial pressures, the total pressure of the gas will remain near ambient reducing system CapEx costs and thermal mass. Water vapor is effectively separated from CO_2 during the compression process, and so while steam stripping will increase compressor size and energy consumption, for steam stable materials the advantages can be significant. However, steam that is taken up in the material during the desorption process will be evaporated to the environment during adsorption. This contrasts with many solid adsorbent systems which effectively produce CO_2 from the environment because they also capture H_2O during adsorption. In regions with constrained water resources, the net gain/loss of water may be an important consideration if the viability of a particular DAC technology.

While thermal energy is an effective medium for desorption, there are many challenges to its practical implementation for any system. Thus, there is significant interest in developing alternatives to heat in adsorbent regeneration. While at early stages of development, researchers have demonstrated the potential for CO_2 adsorbents to capture and release CO_2 using electrochemical processes. Verdox is the most prominent example of an electroswing approach, in which reduced quinone molecules are assembled onto electrodes with the ability to directly interact with passing gas molecules. Electrophilic CO_2 molecules chemically bind with the reduced quinone molecules and are released upon depolarization of the electrode. Long-term challenges for this approach are similar to alternative approaches, including adsorbent capacity, selectivity, stability, and systems engineering.

Deployment Status and Technology Discussions

Owing to the favorable incentive landscape for R&D and commercialization since 2020, dozens of companies developing DAC systems or relevant technologies have recently emerged, joining established companies such as Global Thermostat and Climeworks. As of early 2023, deployment up to TRL 7 are in operation, including the ORCA plant by Climeworks in Iceland. Currently, a 36,000 typ facility, Mammoth, is under construction in Iceland.

In mid-2023, there are over two dozen companies working on bench scale or prototype systems. In addition to startups, DAC technology efforts have been announced by several major industrial and energy technology companies including GE and Baker Hughes. Owing to the rapid evolving nature of the field and the lack of detailed information of many of these efforts, a summary of some more established efforts and their application to the forementioned principles is provided below. Rather than provide a comprehensive summary of all technologies, our objective is to show examples of how the principles of adsorbent, contactor, and regeneration come together to develop novel systems.

Global Thermostat

The starting point for Global Thermostat's direct air capture system is the use of cordierite support with laminar channels. Here, the laminar channels give Global Thermostat the ability to achieve very high gas velocities, as much as 5 m/s with very low pressure drops because gas flow is laminar rather than turbulent. Cordierite is an effective base because it is widely used as the base for automotive catalytic converters, and so it is a low-cost material with known monolith manufacturing techniques. The use of monoliths is an important aspect in developing a laminar flow system. An additional benefit of cordierite as a monolith material is its low coefficient of thermal expansions, a critical property for a temperature swing-based process.

Cordierite is not a porous material and on its own would have a low affinity for adsorbing CO_2 and is not readily amenable to functionalization. Thus, to develop an effective DAC adsorbent, Global Thermostat coats its cordierite supports with a wash coat of porous materials, such as alumina. The high surface area alumina contains the necessary pore volume to retain functional groups such as polyethyleneimine (PEI), a polymeric amine that exhibit excellent CO_2 capacities and has low vapor pressure. The primary downsides of PEI include slow adsorption kinetics and poor oxidative stability, and so key process developments of Global Thermostat have included the development of process steps to overcome these challenges. PEI is reported to lack stability under dry adsorption conditions and so Global Thermostat has developed a steam stripping method for effectively regenerating their adsorbent and reducing materials degradation rates. This is accomplished by the implementation of a moving bed system, that allows monoliths to be effectively circulated from adsorption to desorption zones within their system. The use of steam provides both heat and a stripping fluid for their regeneration process, however it is expected that the process overall would evaporate significant quantities of H_2O to the environment.

Climeworks

Based in Switzerland, Climeworks is presently the most advanced DAC company utilizing solid sorbents, working presently on the construction of a 36,000 tpy facility in Iceland. This project, Mammoth, represent a 10X scaleup over its ORCA demonstration. Working in partnership with CarbFix, a geologic sequestration company, Iceland's geothermal energy potential and onsite sequestration opportunities have enabled Climeworks to demonstrate the technology in a region well suited for carbon removal deployments. In 2021, Climeworks announced a partnership with Svante related to adsorbent and contactor joint development. As adsorbents and contactor designs are evolving, the technology description that follows is meant to provide a case study on how the principle described were applied in the development of early systems.

With origins to ETH Zurich, the starting point for Climeworks development was the potential of amine-functionalized cellulosic materials to capture CO_2 from air with a saturation capacity of approximately 0.5-.7 mol/kg. In contrast to the ceramic supports of Global Thermostat, cellulose fibers were not readily amenable to monolith formation that could enable laminar flow. Instead, Climeworks developed a fixed bed contactor. To effectively manage pressure drop and air handling energy, the incoming air stream is diverted through multiple beds inside each assembled contactor. By diverting a fast-moving incoming gas stream into parallel streams, gas velocities through each bed are minimized and a short bed depth of approximately 10 cm is effective at capturing approximately 50-60% of the incoming CO_2.

Climeworks uses a batch adsorption-regeneration process, and so upon saturation of a contactor bed, it enters a regeneration process. Early demonstrations of the technology utilized heat exchangers embedded withing each adsorbent bed to heat the system to a regeneration temperature of approximately 100 ˚C. Regeneration was aided using vacuum, which first purged the void spaces from each bed to increase product purity and lowered the required regeneration temperature. In an early demonstration, the heat for regeneration was provided by a co-located incineration process and in Iceland it is provided by geothermal power.

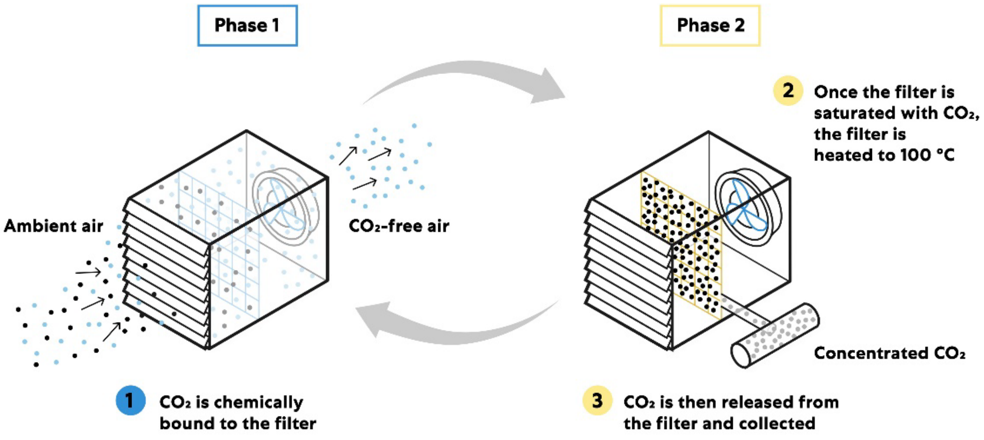

Figure 3-1
Simplified process flow diagram and adsorption/desorption configurations of Climeworks' sorbent-based direct air capture technology.

In 2021, Climeworks and Svante announced a collaboration on adsorbent technologies. One potential area of collaboration revolves around the integration of Svante's contactor design into a DAC system. In contrast to an unstructured packed bed, a structured bed design has the potential to significantly reduce pressure drop in a DAC system. Alternative bed design and contactors also have the potential to enable alternative regeneration strategies, including the use of steam for desorption heat and stripping as an alternative to a TVSA process with indirect heat transfer.

Heirloom

Heirloom is a California based DAC company spun-out of work initially done at the University of Pennsylvania. In contrast to Global Thermostat and Climeworks, Heirloom is utilizing readily available reactive minerals such as CaO and $Ca(OH)_2$ to capture CO_2. By utilizing a mineral adsorbent, Heirloom avoids many of the commercialization obstacles that specialized materials can bring including limited availability and high materials prices, especially at early stages of development.

Heirloom's system design, however, must overcome the inherent limitations of utilizing hydrated lime. First, $Ca(OH)_2$ is not an intrinsically porous material. In general, reactive hydroxide species near the outside of crystallites will be able to effectively capture CO_2, but any functional groups within the bulk will not react. Thus, it is necessary to process they sorbent into forms that have maximum external surface area. While pores can be introduced into hydrated lime, such processing techniques can dramatically increase materials costs and are not as widely available as bulk lime. As small diameter crystallites are unsuitable for integration into a system owing to their ability to be entrained by flowing gases, Heirloom's initial approach is to formulate lime into sheets that both provide high external surface area and allow for ordered assembly of contactors.

As lime is a low-cost material to manufacture but also has a limited useable lifetime, approximately 10-20 cycles, Heirloom's approach to contactor design is not focused on maximizing adsorbent cycling rate. Rather, Heirloom uses a passive collection approach, which should enable them to save significantly on the capital and energy costs associated with actively moving air through adsorption bed. However, such an approach would be at the expense of site intensity as more adsorbent will need to be always deployed to harvest CO_2 at rates comparable to competing technologies.

The second primary disadvantage of utilizing lime-based adsorbents is their need for high temperature regeneration. Lime reacts with CO_2 to form calcium carbonate. With an appropriately design reactor, calcium carbonate can evolve a high purity stream of CO_2 amenable to compression. Heirloom has recently announced a partnership with Calix on the development of electric kilns, originally developed for the cement and lime industries. In lime and cement production, the decomposition of calcium carbonate (lime) has a significant carbon footprint because of both the process emissions (the released CO_2) and the combustion of fossil fuels to fire the kilns. Heirloom's approach is to avoid fossil fuel related emissions by utilizing renewable energy for its electric kilns, while its process emissions will originate directly from the air. There are significant similarities between this approach and the Carbon Engineering approach described below.

DAC Systems Utilizing Liquid Absorbents

Significantly fewer liquid phase DAC systems are presently under development in contrast to solid phase technologies under development. While the mass transfer of air into the solvent presents a major challenge, the most advanced liquid phase approaches to DAC have been able to build upon established industrial technologies. As of mid-2023, a 500ktpy DAC plant, the largest in the world, is under construction in Texas utilizing Carbon Engineering's liquid-phase technology.

Absorbents

As discussed in Chapter 2, physical solvents have the ability to absorb sufficient quantities of CO_2 at high pressure and/or sub-ambient temperatures. For air, the cost of either cooling or pressuring air to have sufficient solubility in physical absorption mechanism-based solvent would be economically non-competitive. The use of strong bases dissolved in a liquid solvent is necessary to develop an economically viable DAC process.

The most advanced liquid-phase DAC process, currently being developed by Carbon Engineering, utilizes a 1M solution of aqueous potassium hydroxide (KOH) as the primary absorbent. Hydroxides are strong bases and thus have a high affinity for chemically reacting with CO_2 to form carbonate and bicarbonate anions. Similar to the solid phase efforts using $Ca(OH)_2$, the primary advantages of NaOH and KOH is their low-cost, broad availability, and excellent stability. For these benefits, system developers must develop strategies to effectively decompose metal carbonates, a process that requires temperatures in excess of 900 °C.

While industrial carbon capture process favor using amines for CO_2 capture, the use of amines for DAC processes is at an early stage of development. The primary advantage of amines is their ability to be regenerated at significantly lower temperatures than hydroxide solvents. However, amines are expected to have inferior absorption kinetics and CO_2 working capacities. Hydroxides are also impervious to oxidative degradation, a major drawback for organic bases. Recently, academic researchers have proposed potential liquid absorbents for DAC, and several companies have also emerged working on proprietary liquid absorbents for DAC processes. The success of these approaches will likely depend upon their ability to overcome these traditional challenges so that the advantages of a reduced regeneration energy requirements can be realized.

Absorption Contactor

One of the primary considerations of liquid-phase approaches must be how solve the mass transfer challenge inherent to capturing 420 ppm CO_2. One advantage of permanently porous solids is their very high internal surfaces areas (100-4000 m^2/g), which affords excellent contact between adsorption sites and the air. In contrast, the surface area of a liquid solution is limited to the liquid area directly exposed to the air. An early report on the feasibility of DAC compiled by the American Physical Society (APS) assumed a very simple open contactor for passive adsorption [https://www.aps.org/policy/reports/assessments/upload/dac2011.pdf]. The capital costs and land areas of such an approach were rightly assumed to be substantial. However, the learnings form decades of experience in structured packings for absorption beds, when effectively applied to the mass transfer problem was shown to be able to substantially improve upon these early assumptions [https://www.sciencedirect.com/science/article/pii/S1876610211003894].

To develop an effective contactor for a liquid absorption process, several features have been developed. First, to achieve significant mass transfer areas, structured packing beds wetted with thin films of hydroxide solution can be effectively deployed. A structured bed is thus amenable not to passive absorption, but to an active process that features a minimal pressure drop. To reduce the costs of the bed, which polyvinylchloride (PVC) materials have been developed by Carbon Engineering, which substantially reduce the cost versus traditional metal packings. The pumping energy of circulating liquid through the bed is reduced through the development of a pulsed flow process, that allows liquid absorbent to flow through the bed. In contrast to solid sorbents, liquids are easily transported from absorption to regeneration processes with minimal losses to energy or attrition.

In the state-of-art Carbon Engineering design, the movement of liquid through the bed is cross-flow with respect to the movement of air through the bed. The depth of the contactor is a major consideration in its overall design, enabling approximately 60% of CO_2 from air to be absorbed across a depth of approximately 7 m. The high solubility of CO_2 in the KOH solution is a key enabler of this moderate bed depth. If liquid absorbents with a reduced solubility for CO_2 are proposed, one impact may be on the need to develop a deep contactor to achieve similar removal rates. In a detailed technoeconomic analysis published by Carbon Engineering, the cost of the contactor is expected to represent approximately 10 % of total DAC costs. Thus, the energy benefits of an easier to regenerate absorbent will need to be offset by potentially significantly increased contactors costs. [https://www.cell.com/joule/pdf/S2542-4351(18)30225-3.pdf]

The loss of water/solvent from the contactor is a major consideration for liquid systems. The large surface area affords significant opportunities for evaporation, and the availability of water will be a consideration in the deployment of the Carbon Engineering technology. If non-aqueous solvents are developed or if volatile additives such as amines are utilized for DAC, the evaporation of volatile components must be factored into both the cost and environmental implications of deploying the technology.

Absorbent Regeneration Processes

In the chemical looping process of Carbon Engineering, the first step in regeneration is a salt metathesis is which aqueous sodium carbonate solutions are reacted with calcium hydroxide solutions to produce calcium carbonate precipitate and potassium chloride solution. The primary advantage of this is the low-energy separation of CO_2 (as carbonate) from water, reducing the energy penalty of evaporating water in the thermal regeneration process. Next, carbonate is fed into a fluidized bed calciner. Operating at temperatures of approximately 900 ˚C, the calciner decomposes carbonate into calcium oxide and CO_2. The pure CO_2 stream is cooled, dehydrated, and compressed for subsequent transportation. Calcium oxide is then slacked with water and returned to the salt metathesis process, completing the chemical looping cycle.

The need for high-temperature calcination is a major challenge for any hydroxide-based absorption process, and Carbon Engineering has published a comprehensive review of producing the requisite low-carbon thermal energy. It has been proposed that a parallel carbon capture and sequestration process can be deployed that allows pure CO_2 to be produced from O_2 using an oxyfuel combustion process. In this scenario, approximately 32% of the CO_2 sequestered by the Carbon Engineering process would be attributable to the fossil fuel capture process and 68% of the carbon would originate from the air. As discussed in Chapter 1, DAC deployments must develop low-carbon energy strategies.

Here, the onsite availability of firm, low-carbon energy provides a reliable path to high-capacity factors, but with the drawback of potential increasing fossil fuel extraction to power the process, and accurate figures on fugitive methane emissions will be an important component to any LCA of a process that utilizes fossil fuels for DAC.

The second strategy for regeneration is the use of electrically driven calciners that can utilize renewable energy. Electrical calciners are under development for a range of industries, including lime and cement, but full-scale systems are still a few years aways. Like other approaches that utilize renewable electrical energy, the 24/7 availability is a major consideration. If renewable energy is not stored, energy intensive operations must either be halted during periods of high-carbon intensity, which can create significant process challenges. If DAC operations are powered by fossil fuel power production, the net carbon removal will be significantly impaired.

Amine based liquid absorbents will offer the advantage of significantly reduced regeneration temperatures versus hydroxide solutions. As in industrial capture applications with alkanolamines, liquid absorbents can be regenerated in a stripping column. In contrast to solids, the heat transfer characteristics of liquids are very favorable. Large portions of the sensible energy provided to the liquid can be reclaimed using heat exchangers, as is done for acid gas scrubbing systems, and a narrow temperature differential can be utilized between the steam temperature and the final stripping temperature. The key, however, is to develop absorbents that can effectively demonstrate a working capacity for CO_2 under DAC conditions.

Finally, electrochemical regeneration of liquid absorbents has the potential to significantly reduce the energy required to regenerate liquid absorbents. DAC startups including Mission Zero have indicated that their approach to regeneration is based upon an electrochemical approach. While the details of any such approach will depend heavily on the nature of the proprietary sorbent, one potential approach for DAC is to utilize acidity changes to release CO_2 and regenerate sorbent. Both carbonates and carbamates will react with acid produced by electrolysis or electrodialysis process to liberate gaseous CO_2. This CO_2 can be captured and compressed. Fresh base can be regenerated by the addition of hydroxide from the balancing electrolysis process, closing the chemical loop.

Section 4: Applications and Comparisons

Applications and Requirements

Carbon capture to mitigate the accumulation of atmospheric CO_2 is technically feasible from both concentrated CO_2 streams and from dilute streams. A large number of technologies are required to capture CO_2 emissions owing to the highly variable set of conditions CO_2 is produced every day, and the best abatement option will depend heavily on the size, location, and specifics of how CO_2 is produced.

Presently, large quantities of CO_2 are separated from the chemicals and fuels produced every day. Much of the CO_2 that is already being separated is released into the atmosphere as the lowest cost method of disposal. For industries that are already capturing CO_2, sequestration credits such as those offered by 45Q present an attractive additional revenue stream. For the natural gas, ethanol, and ammonia industries, sequestering the CO_2 that is separated as routine part of their operations is an attractive path forward.

The CO_2 that is generated from fossil fuel combustion for heat and power operations, however, requires cost effective capture and storage technologies to be developed. Point-source capture technologies are being primarily developed to address current and anticipated future regulatory needs. Carbon emissions are regulated by a patchwork of regulations around the world, including emissions caps and carbon taxes. From large industrial emitters, it is anticipated that at least 90% of current emissions will need to be abated under most regulatory schemes, and technologies are generally developed to meet this minimum capture target. In general, the cost per ton to capture 90% of CO_2 from a point-source facility will be less than the cost per ton to capture 100% of the CO_2 emissions from that same site.

However, under a net-zero regulatory environment, 100% of emissions from every site will need to be abated. Recently, there has been work on developing point-source capture technologies optimized to capture 99% or more of CO_2 emissions from flue gas. While technically feasible, the marginal cost for capturing the lowest concentration emissions can be higher than for DAC due to the impact the design for capture at low concentrations has on the bulk capture system.

CO_2 that is not captured at its generating point enters the atmosphere and contributes to global warming and ocean acidification. It is desirable to capture it during the combustion process because the concentration of CO_2 is generally 100 times the atmospheric concentration of CO_2. However, large quantities of CO_2 are produced under circumstances that are not readily amenable to onsite capture. It is neither practical nor cost-effective to capture the CO_2 that is produced from most small, mobile, or natural sources. As discussed below, a reasonable capture capacity is required to achieve sufficient economies of scale on the necessary capture, compression, and transportation equipment. One of the appeals of direct air capture, is that be by aggregating the capture of this CO_2 into large, centralized facilities, the emissions from many challenging sources of CO_2 can be removed from the air at a reasonable cost.

Because it is more expensive to remove CO_2 directly from the air than from a large point-source emitter, the incentives for storing CO_2 produced via DAC processes are larger, currently $180/ton of CO_2 removed under IRS section 45Q. Carbon removal processes such as DAC will be critical in achieving a net-zero or net-negative economy because it is a technology that has the potential to abate the emissions of industrial sectors for which electrification, point-source capture, or other abatement strategies are either not practical or significantly more expensive than nth-of-a-kind carbon removal deployments. For DAC, the cost and permeance of capture and storage are the major criteria. In contrast to point-source capture that will generally be required to achieve specific reduction targets (e.g. at least 90%), DAC systems only need to be optimized to achieve the lowest possible cost of CO_2 removal. While point-source capture generally is benchmarked by the quantity of CO_2 captured and stored, DAC is benchmarked by the net-removal of CO_2 from the atmosphere. Because net-removal needs to factor in the life-cycle emissions of building and operating the DAC facility, the volume of CO_2 stored will always be greater than the volume of CO_2 removed.

Design Considerations

Because of the different requirements of DAC systems and point source capture systems, the technologies to perform the capture have different designs. Each system is optimized to the intended application, which leads to diverse system and component designs. For processes that have shared components between the different applications, the equipment may still look significantly different or have different operating regimes. Some of the major design considerations for major equipment and how it differs between capture from concentrated and dilute sources is presented in this section.

The components with the greatest differences are the gas/liquid contactor, separation material, regeneration, and CO_2 post-processing.

Gas Contactor

Capturing CO_2 from a gas stream generally requires diffusion of the CO_2 into a dense-phase separation material, such as a solvent, sorbent, or membrane. This diffusion is generally proportional to the surface area of the contacting times the driving force of the component being captured from the gas stream into the dense-phase medium. For systems with small driving force, such as DAC from air at 420ppm, the surface area of the system must be much larger than for systems with high driving force.

In addition to the surface are for capture, the gas flow through the gas contactors is determined by the concentration of the CO_2 in the gas stream and the capture efficiency.

The large volume of air that is required to capture a ton of CO_2 limits the feasibility of preconditioning such as temperature or humidity control. The introduction of additional processing steps is likely to increase the pressure drop of the DAC process, increasing air handling costs significantly for any process that requires pretreatment. Second, the absolute volume of air that must be treated presents significant challenges as significant additional energy will be required to either heat, cool, or dehumidifier approximately 2 million m^3 air per ton of CO_2 captured.

In contrast, the higher concentration of CO_2 in flue gas streams enables and sometimes requires pretreatment prior to CO_2 capture. To maximize the absorption capacity of most solid materials, reducing the gas temperature to approximately 40 °C is preferred. By reducing the temperature of the flue gas, the absorption capacity of the solvent or sorbent media is generally significantly improved. However, the flue gas needs to remain sufficiently buoyancy and so temperature reductions below 40 °C are not practical.

Heat evolution during adsorption is a significantly greater challenge for point source capture than direct air capture, while mass transfer is a greater challenge for DAC than flue gas capture. As the concentration of CO_2 rises in the gas stream, the rate at which the material can capture CO_2 will increase. CO_2 capture is an exothermic process. While DAC systems require minimum active cooling, significant bed temperature increases will result in point-source capture. In general, heat is transferred into integrated cooling pipes within the absorption bed. The significantly improved heat transfer characteristic of liquid solvents versus porous solids is one of the primary advantages of using liquids for point source capture.

Separation Material

The CO_2 separation material is the most critical component of a carbon capture system. The performance and chemistry of this material is what determines the system size, operating conditions, and ultimately performance and energy consumption of the system designed around the material properties.

Separation materials for point source and DAC have different requirements. Air has lower CO_2 concentration than point-source emissions, but each has different co-constituents and associated issues. Point-source emissions often have co-constituents, such as sulfur compounds, that may poison or react with separation material irreversibly. To prevent the poisoning of chemical separation materials and buildup of heat-stable salts that cannot be regenerated generally a sulfur removal wash that reduces sulfur composition to single digit ppm levels is required.

A large number of solvent and sorbent options are available for point source capture because the higher concentration of CO_2 in point source capture enables significant process flexibility. Point source gas streams can be cooled and/or pressurized to enable optimal conditions during separations, such as through the use of chilled solvents such as methanol, chilled flue gas in cryogenics, or pressurized flue gas for membranes. However, due to the large quantity of gas processed these materials and processes are not suitable for DAC.

New system designs using amine solvents or porous solids are under development for both point-source capture and DAC. One of the major differences between DAC and point-source capture is the cycle time of the sorbent material. Owing to the high concentration of CO_2 in flue gases, sorbent media are generally quickly saturated and fast cycling processes (as little as 1 minute per cycle) can be developed.

For DAC, sorbent saturation is determined heavily by how quickly CO_2 can be introduced across the sorbent, and hour to multi-day cycle times are likely. For point-source capture systems, hundreds of thousands of cycles of the media are required for multi-year operations. In contrast, DAC absorbents with a lifetime of tens of thousands of cycles would suffice for multi-year operations in some process designs. Because DAC sorbent captures less CO_2 per year than a point-source capture systems, sorbent costs per ton of CO_2 captured are much higher for DAC. Thus, extending the useable lifetime of both point-source and DAC capture materials, through both materials and process innovations, is a major research need.

Regeneration

Regenerating the separation material is generally accomplished through increasing the temperature or lowering the pressure so that the equilibrium loading of CO_2 in the separation material is higher during the capture conditions than they are during the regeneration conditions. This difference in loading is what drives the separation process. For gas streams with high concentration of CO_2, the difference in equilibrium loading is easy to achieve with very gentle regeneration conditions. For example, some pressure-swing adsorption processes use a high pressure (>30 bar) absorption coupled with ambient pressure regeneration. In this case, the regeneration is accomplished only by exposure to ambient pressure. However, for systems that capture CO_2 from dilute sources such as air, the separation material has such a high affinity for CO_2 a more extreme regeneration condition may be required in order to regenerate the CO_2.

For example, carbonate materials are considered for a range of DAC approaches including solvent-based systems and sorbent-based systems. Calcium carbonate, (limestone) decomposes to liberate its carbon dioxide at temperatures in excess of 600 ˚C (1100 ˚F) and usually around 900 ˚C (1650 ˚F). Achieving these temperatures requires the use of direct-firing natural gas in oxy-combustion systems with carbon capture from the combusted natural gas as well as the evolved CO_2. Research into alternate methods of supplying high-grade heat such as electrically fired calciners are in early stages of development.

In contrast, most near-commercial solvent and sorbent-based processes for point source CO_2 capture are performed with amine chemistries. Amines reversibly react with CO_2 in aqueous environments, and are then regenerated in stripping columns at temperatures around 110-130 °C (230-266 °F). The maximum temperature of the system is determined by the degradation rate of the separation material.

Supplying thermal energy at lower temperatures has several benefits. Lower temperature heat can be supplied by thermal integration with other systems such as low-pressure steam systems or process heat. Low temperature heat also has less of an energetic impact on the overall system as less work could be extracted from low-pressure steam than can be extracted from high-pressure steam. Low-grade heat can also be supplied through other sources of low-carbon thermal energy such as geothermal, integration with nuclear energy, solar-thermal with storage, or heat pumps. Higher temperature heat is mainly supplied through the less efficient processes of direct combustion or electric resistance heating.

Low temperature regeneration of DAC processes is also possible. Generally, this is performed with solid sorbent systems with a range of chemistries including amines and CO_2-surface interactions. The regeneration then occurs at a significant vacuum (<0.2 bar) and/or with a steam purge rate several times greater than the CO_2 production rate. This steam purge is required to lower the partial pressure of CO_2 in the regeneration chamber but also requires energy to produce, resulting in a higher energy penalty than a comparable system with small steam purge rate.

CO_2 Post-processing

As the capture material is regenerated, CO_2 is produced from the separation process. CO_2 must be processed prior to transportation, storage, or use. The degree of purification and compression is dependent on the separation process and the required purity at export conditions.

Liquid solvents generally produce CO_2 with few impurities except the solvent itself, which is generally H_2O. Water is among the easiest and least expensive impurities to separate from CO_2 as it can normally be integrated into the CO_2 compression process described below.

CO_2 produced from solid adsorbent beds will generally have higher concentrations of hard to separate light gases such as N_2 and O_2. Oxygen in particular presents significant problems for pipeline corrosion, and O_2 concentrations below 100 ppm are often required for pipeline transportation. For comparable systems, O_2 contamination of CO_2 is a greater challenge for DAC than for PSC because the O_2 level in flue gas is generally less than 5% O_2.

Additionally, DAC beds are generally optimized to have significant void fractions to minimize pressure drop and thus air handling energy. The air that remains in those void spaces as the regeneration process begins can significantly reduce downstream product purity, and thus steps such as vacuum or sweep gas purges can be utilized to increase final product purity. However, these process steps are difficult to implement in practice owing to the challenges of effectively sealing commercial-scale adsorption beds to prevent leaks. Moving bed configurations are especially prone to leaking under even modest vacuum pressures.

Both PSC and DAC system designs should account for the impacts that co-adsorbed and void spaces gases will have on initial product purity, and when necessary, account for the gas of additional CO_2 purification.

The selectivity of the most advanced carbon capture membranes is generally not sufficient to meet purity specifications. The permeate of a single stage membrane with a selectivity of 40 capturing from a 10% CO_2 gas stream would contain approximately 75% CO_2. Thus, multiple stages of compression and generally a cryogenic purification process are required for membrane-based carbon removal processes.

Compression is a critical aspect of purifying and transporting captured CO_2. At a high-level, CO_2 must be brought from its initial pressure to approximately 150 bar. With a compression ratio of 2.3, approximately six stages of compression would be required to compress a CO_2 stream with a CO_2 pressure of 1.1 bar to 150 bar.

The total pressure of the gas produced by a reboiler in amine-scrubbing processes is approximately 1.3-2.7 bar. This stream is typically more than 50% water vapor by mass and water dropout is performed in the overhead condenser and compressor intercooling. To remove trace water, CO_2 is typically passed through a tri-ethylene glycol absorber dehydration unit at approximately 70 bar, just below the critical pressure of CO_2. This can reduce the moisture content of CO_2 to below 100 ppm. Once the CO_2 stream is fully dehydrated, CO_2 is brough to its final delivery pressure with additional stages of compression.

For CO_2 streams contaminated with light gases such as N_2 or O_2, after the initial stages of compression, purification is performed through cryogenic distillation. Once the gas stream is above the triple point of CO_2, the gas stream can be cooled to liquify the CO_2 and distill out the N_2 or O_2 gases to produce high quality CO_2.

Gases such as N_2, O_2, and H_2O will increase the cost of compressing CO_2 in its initial stage. First, as CO_2 concentration decreases, the size of the compressor increases, increasing compressor capital costs. Second, while contaminating gases can be removed, doing so increases the energy required during the compression process. There are specific regeneration processes for which compression costs may be substantial and should be specifically evaluated.

The use of vacuum in regeneration can significantly increase compression costs. Vacuum pressures dramatically increase the volume of the gas that enters the compressor, which is a major factor in determining compressor size and capital costs. DAC processes that rely upon deep vacuum would dramatically increase the size, number of stages, and energy use of a compressor. Furthermore, as total pressure falls, the concentration of water vapor in the gas stream rises. A low-pressure, steam stripping process would result in a product stream containing mostly H_2O, resulting in significant CapEx and OpEx compression costs.

Compression results in a significant increase in the temperature of the stream being compressed. As compression efficiency decreases at higher gas temperatures, compression costs need to factor in the costs associated with interstage cooling processes. Significant quantities of low-grade heat result from the compression process. It is theoretically possible to utilize the heat that results from compression in other stages of a carbon capture process. It would highly desirable to utilize energy in the sorbent or solvent regeneration process. However, highly efficient compression processes generally do not produce heat above 50 °C, and so this heat can only be practically utilized if it is further heated. For example, for DAC processes it has been proposed to utilize heat pumps to heat waste heat streams to a temperature that is useful for sorbent regeneration.

Application Considerations

The faster than expected deployment of grid-scale renewable energy such as solar and wind represents the beginning phase of a multi-decade transition to a net-zero economy. To achieve proposed net-zero, pathways for eliminating or reducing and offsetting all emissions sources would need to be developed. For many applications, the primary energy source must transition from fossil fuels to renewables. However, there are scale-up, deployment, and cost challenges related to utilizing only solar and wind combined with energy storage to fully decarbonize the electrical grid. Modeling scenarios indicate that the lowest cost pathway to net-zero is to rely upon fully dispatchable forms of low-carbon energy production such as nuclear and fossil fuels such as natural gas or coal combined with carbon capture for approximately 30% of our primary energy needs [Jenkins].

Presently, there is significant momentum behind electrifying fuel consuming machines and appliances. The carbon intensity of electric cars, heat pumps, and induction stoves will reflect the carbon intensity of the electrical energy going into them. As a decarbonization strategy, the elimination of small and mobile sources of CO_2 if feasible may be a lower cost decarbonization strategy than alternatives such as onsite carbon capture. One of the major use cases of point source carbon capture technologies is to ensure that a dispatchable source of carbon-free electricity is available to power this transition. As such, carbon capture collocated with electricity generation competes with alternative forms of carbon-free electricity generation such as nuclear, hydroelectric, geothermal, and grid-scale storage combined with intermittent renewable sources such as solar and wind.

Currently, the US electricity grid has a coverage intensity per kilowatt hour of around 0.42 kg CO_2 /MWh, with significant regional, daily, and seasonal variations in carbon intensity. Consumer appliances such as electric vehicles will in general only utilize energy for the grid for a small portion of each day, enabling smart devices that can be optimized to preferentially consume electricity only when low-cost and/or low-carbon intensity electricity is available.

It has been proposed that industrial facilities such as DAC facilities can similarly be designed for intermittent operations. While such operations are theoretically possible, they face significant headwinds. Owing to the significant capital investment required in a DAC facility, decades of continuous operation are generally required to sufficiently amortize the upfront capital investment. Intermittent operation of major pieces of capital equipment will significantly increase the cost per ton of capture. The most advanced demonstrations of DAC facilities are being designed for high-capacity factor operations through the use of onsite, dispatchable, low-carbon power: either onsite carbon capture to enable low-carbon fossil fuel production (Carbon Engineering) or geothermal heat and power (Climeworks).

It should be noted that intermittent operation is also a major consideration in the deployment of carbon capture for electricity generation. In areas with high renewable penetration, fossil fuel generating facilities are generally curtailed during periods of significant renewable energy production owing to their higher generating costs. As such, many of facilities for which carbon capture is required generally have capacities significantly below the 90% capacity factor that is commonly assumed in technoeconomic modeling. At lower capacity factors, the CapEx for the system cannot be amortized over as many operating hours. This increases the importance of CapEx in determining the cost per ton of CO_2 captured at low capacity factors. At high capacity factors, the energy cost tends to dominate the operating cost of the facility. Increasing heat integration and process modifications to reduce OpEx through additional equipment and higher CapEx may be favored at high capacity factors. For both DAC and point-source capture, the lowest cost technology option will depend heavily on the facility capacity factor, with different designs or design considerations for each type of operation.

Over the past decade, significantly more attention has been paid to the potential for integrating carbon capture technologies on industrial technologies beyond electricity generation. In contrast to fossil fuel power stations, the onsite heat and power operations of industrial facilities generally have high-capacity factors, bypassing the challenges of capturing CO_2 from large but dispatchable sources. Second, while fully electrified alternatives are under development, it is expected that fossil fuels will be required to provide the necessary process heat for carbon intensive industrial operations such as cement, metals, and refining operations.

Throughout the world, there are regions with high concentrations of industrial activity. To reduce the cost of early carbon capture deployments, developing carbon capture hubs centered on areas with multiple major point-source emitters is currently underway. Because the cost of CO_2 transportation per ton decreases as pipeline capacity increases, significant savings in transportation and sequestration costs is anticipate with these hubs. Furthermore, the availability of onsite heat and power for carbon capture operations may result in energy savings and cost reductions versus other early deployment locations. Finally, it has been proposed that carbon utilization technologies can be co-located at carbon capture hubs to provide an alternative path to sequestration for the captured CO_2.

The cost-savings that can be realized by aggregating the capture and sequestration process for multiple facilities into a centralized facility is one of the primary incentives behind developing DAC technologies and facilities. For small or diffuse sources of greenhouses for which transitioning to electricity is not practical or viable, offsetting the emissions of those sources by capturing an equivalent volume of CO_2 from the atmosphere is likely to be the most cost-effective option for achieving net-zero. Thus, DAC competes with other carbon removal and offsetting techniques including nature-based offsets and ocean-based CO_2 capture. One of the primary benefits of DAC is that monitoring and verifying the permeance and additionality of other carbon removal techniques is more challenging when compared to DAC, reducing the uncertainty associated with DAC based carbon offsets.

Impact of Scale

Carbon capture for global climate impact requires large-scale removal of CO_2 at the megaton scale and above. The impact of scaling technologies varies by applications and designs. Technology scale can be achieved by either scaling individual components to large size or scaling manufacturing to allow modular buildout. Fossil power plants are most efficient at large size due to both lower thermal losses and higher efficiency components and also lower capital costs per MW and operating costs per MWh generated. Conversely, solar PV has developed lower costs due to buildout of manufacturing capacity to allow rapid production and installation of modular solar panels. However, even in cases where solar module prices are extremely low, the lowest cost installations are still clustered around central equipment such as inverters and grid connections.

As surface area to volume ratio decreases with size, cost can decrease and efficiency increase. Rotating equipment such as turbines, fans and compressors are most efficient and lowest cost at large scales. The increased efficiency is due to the larger percentage of flow that passes through the central region of the rotating machinery, and reduced flow in contact with the casing, bypassing the blades, or used for sealing. Tanks, columns, and other large components have lower unit cost at large scale due to less material required per volume treated. This holds true for ducting, piping, tanks, vessels, and some types of heat exchange. Other components, such as controls, instrumentation, foundations, and electrical systems have even less sensitivity to size and are nearly the same total cost across a range of sizes. For this equipment, spreading the cost over a larger quantity of CO_2 captured results in a lower capital cost per ton of CO_2 captured.

DOE NETL maintains their Quality Guidelines for Energy System Studies (QGESS) library of resources for costing different components and plants. Scaling exponents are generally listed to allow relative costing based on scaling parameters such as heat duty, flow rates, or the amount of CO_2 captured. The range of exponents for the major equipment found in carbon capture facilities ranges from around 0.6 to 0.8, meaning that for a doubling in size, the cost of the component would increase by $2^{0.6} = 1.5$ or $2^{0.8} = 1.74$. This would result in a relative cost reduction of between 13% and 25% from the linear scaling cases. The impact is even greater at larger scaling values and tends to lead to units and equipment that is as large as can be reasonably manufactured and transported.

For carbon capture the component cost is not the only reason to seek large scale: the climate-relevant sinks for carbon dioxide are geologic. Geologic storage requires CO_2 compression, transportation, and injection. Compressors are, as discussed above, most efficient and lowest cost at large scales. Transportation via pipeline requires the construction of a pipeline of a fixed diameter. The installation cost per mile is nearly linear in the diameter of the pipe [32]. As the volume that can be transported is proportional to the square of the diameter and the cost is proportional to the diameter, larger pipelines are more economical per ton of CO_2.

Geologic CO_2 storage also requires significant effort regardless of the amount of CO_2 stored. Fixed costs such as geologic surveys, monitoring wells, plume imaging, and long-term monitoring remain similar at small and large-scale injections and are determined by the expected extent of the CO_2 plume. A single CO_2 injection well can inject more than a million tons of CO_2 per year [32], with injection rates below a million tons per year not making the best use of existing infrastructure and capacity.

The economics of large-scale capture are best seen in capture from utility scale power plants or large industrial emitters such as natural gas facilities that have emissions on the megaton scale for each unit. However, not all point-source emissions are large-scale. Point-source capture from small-scale sources such as commercial or residential boilers are not well suited for carbon capture due to their small size of capture and the relatively higher cost per ton of CO_2 removed. Instead, DAC processes, which have lower efficiency and higher cost than similarly sized point-source capture processes, may be better suited to capture CO_2 that is emitted from small, distributed point source emissions.

DAC processes can be designed for optimal-scale installation as there is not a requirement for capturing a certain percentage of an existing gas stream. This optimal scale may be constrained by geologic storage resources, availability of energy or water, land use, or economics. Another factor that might limit the scale of DAC at the very-large scales is the localized decrease in ambient CO_2 concentrations near DAC facilities. While this impact is not significant for smaller scale installations, multi-megaton scale installations may experience localized CO_2 concentration decreases on calm days without significant atmospheric mixing.

Cost and Performance

Carbon capture facilities from both point sources and from the atmosphere have only limited cost and performance information available. While some industrial capture such as from natural gas processing are commercially operational, most cost estimates are based on baselined paper studies or a limited number of FEED studies. However, the baseline studies can have significant differences from FEED studies and each may differ significantly from actual construction and real-world performance. Due to the lack of reliable cost and performance numbers, a wide range of values have been claimed by various developers and presented in literature.

Cost Ranges

Carbon capture is less expensive from higher concentration sources, at elevated partial pressures, and at large scale and more expensive from dilute sources, at low partial pressures, and at small scale. This holds true for both CapEx and OpEx – for a given gas stream the lowest cost option optimizes both capital and operating costs. As a result, capture from streams with higher energy consumption, such as direct air capture, tend to also have higher capital costs while capture from streams that require lower energy consumption, such as natural gas processing, have associated lower capital cost.

Cost studies tend to have more variable results than performance-based analyses due to the number of factors that can be incorporated into costing numbers. Cost estimate ranges are commonly referred to based on the Association for the Advancement of Cost Engineering (AACE) estimate class with class 4 or class 3 being the most common estimate ranges. AACE Class 4 estimates are intended to provide feasibility assessments and have a range of potential costs ranging from -30% to + 50% of the reported number while AACE Class 3 estimates require significantly more engineering and generally are produced after a FEED process and indicate a range of potential costs between -20 to +30% of the reported number. In practice, these cost estimation tools applied to baseline studies may significantly under-represent the actual cost of technology for several reasons outlines below.

Carbon capture baselines, such as the DOE NETL Cost and Performance Baseline for Fossil Energy Plants rev 4a [4] make several assumptions that may not hold true in actual operation. Cost for these units is based on the assumption of new-build units with carbon capture integrated into the initial design. For example, all thermal loads are able to be supplied through steam-cycle extractions at optimal conditions within the steam cycle. For the FEED studies that are being performed and units that are expected to be installed are mainly retrofit installations. Retrofit installations have several issues that raise the cost relative to greenfield construction.

Design of retrofit carbon capture must take into account the existing infrastructure at the host utility or industrial plant. This includes siting of the carbon capture unit, reduced integration opportunities, and increased ducting or pipe runs with associated higher pressure drops and capital costs. Steam cycles are designed for tight pinch points and optimal use of thermal energy. Extracting energy from the steam cycle decreases the efficiency of the overall process more than if the steam cycle were designed for that extraction. Further, the steam extraction may not be viable from the host plant, either because the steam may not be available or because the steam turbine may be configured in such a way that extraction is not feasible or economic. Designs that use steam generation from other sources, such as from a standalone boiler or from a combined heat and power unit are commonly considered in options analysis to facilitate host-plant operation while the carbon capture unit is in operation. These standalone power generation options have the impact of lowering the efficiency of the process relative to steam extraction and the reported baseline study values. Design parameters for baseline studies can also be optimistic including cooling water temperature and availability. Design conditions for real operation tend to be based on near-maximum temperatures which can result in higher flow rates, larger equipment, lower efficiencies, and reduced performance.

Reported costs in direct air capture are even more scattered than for point source capture. Cost analyses have shown ranges of values that differ by more than an order of magnitude. This is due in part to the early stage of development of the technology, lack of available resources on actual performance, and strong dependence on the assumptions involved. Cost claims directly from developers can also be unreliable, especially at early stages, as they may be manipulated to look promising to investors or to attract funding from programs with overly optimistic cost targets.

A representative reported range of costs for carbon capture from a variety of sources is shown in Figure 4-1. While these costs rely on a series of assumptions both about the technology performance and the deployment environment, they can be used to understand the scatter in potential costs. Actual costs, especially for DAC, may be significantly higher than presented in this plot.

DAC costs are difficult to benchmark due to several factors. The technology is relatively recently developed, there are no large-scale plants in operation, and there are very few cost studies publicly available. Two cost studies have been published by the DOE – a liquid-solvent benchmark study based on the Carbon Engineering design [34] and a solid sorbent benchmark study [33]. The costs for these different technologies range from \$300-\$486/t CO_2 for the solvent case depending on the size of the system to \$936-\$1,489/t CO_2 for the solid sorbent case. In both studies, the energy for CO_2 capture is produced via an NGCC with carbon capture or with carbon-free electricity. For the solid sorbent study, the same system powered by electricity with carbon intensity of the current US electric grid would be a net CO_2 emitter.

Other cost estimates are available from company presentations and claims. Climeworks is currently selling CO_2 removal subscriptions at approximately \$1100/t CO_2. Costs for the Carbon Engineering DAC technology are reported to be between \$300-425/t CO_2 for the million ton per year plant currently being developed [9].

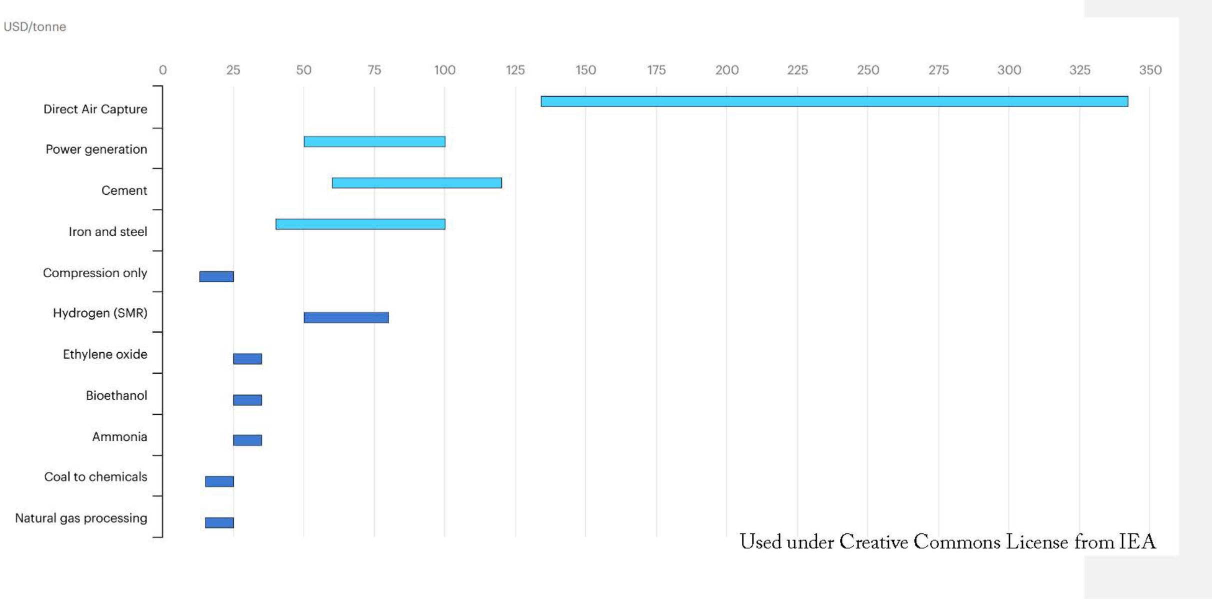

Figure 4-1
Representative costs for CO_2 capture from a range of different sources at concentrated (dark blue) and dilute (light blue) CO_2 concentrations [42]. Used under Creative Commons License from IEA.

Cost numbers are a function of capital cost, performance, deployment environment, and economic assumptions. For most technologies, the capital cost represents the largest single component of the cost of capture. The capital cost results from DOE baseline studies for CCS from coal and NGCC plants, recently completed FEED studies, and DOE baseline studies for DAC based on solid sorbent and solvent cases is shown in Figure 4-2. Most of these carbon capture studies are for solvent-based processes as shown in the blue clusters and orange DOE baseline study results.

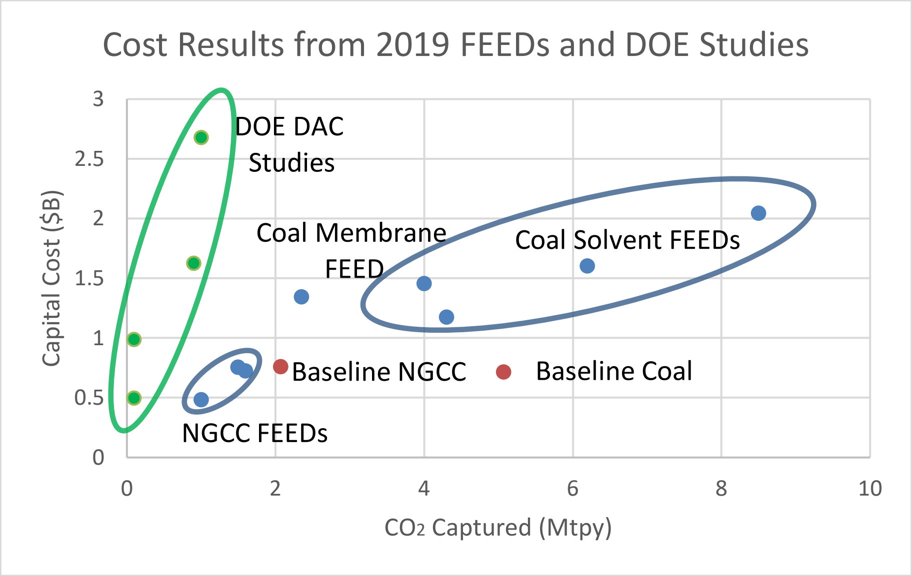

Figure 4-2
Capital costs for CCS plants as reported from recent DOE-funded FEED studies, and DOE baseline studies for natural gas, coal, and DAC capture [4,33,34,35,36,37,38,39,40,41].

Performance Ranges

The energy for carbon capture is important not just for the economics of the process but for the net carbon reduction and climate impact. The energy for carbon capture from concentrated or high pressure sources such as natural gas processing, ammonia production, or ethanol are primarily for the compression and dehydration steps.

For capture from sources in the 3-20% CO_2 range, the current state of the art is solvent-based aqueous amine technologies. The main energy requirement is for the thermal load for solvent regeneration – which can range from 2.4-3.65 GJ/t CO_2 produced, and the auxiliary load for the compressors, pumps, and other equipment which can range from 0.1-0.2 MWh/t CO_2 captured. Most of this electrical auxiliary load is used to power the CO_2 compressor train. The primary source of the reboiler energy is either steam extraction from the steam cycle or from a standalone steam generating unit. For the standalone units, which can be either gas-fired boiler or combined heat and power unit, the CO_2 produced in that steam production must also be accounted for and captured.

Depending on the source of the thermal energy, CCS can result in either an increase in fuel consumption or a decreased power output. The overall impact on a power plant that is equipped with CO_2 capture is expected to be a reduction in net power exported by approximately 20-25% for the coal-fired power plant. For a NGCC with lower CO_2 content, the energy consumption is higher per ton of CO_2 captured but has a lower overall impact on the plant performance. A reduction in net power produced of between 10-12% can be expected for NGCC units.

The main components that impact this range in performance are the solvent used, the amount of heat integration and the source of steam. Systems can often achieve higher efficiency with higher capital cost. A typical example is a heat exchanger – greater heat exchange area results in greater efficiency but also higher cost. Systems that are optimized for lowest cost can have a range of costs and performance ranges as they are designed for lower capital/higher operating cost or for higher performance/lower capital cost operations.

For DAC, reported performance values are sparsely reported. The two main DOE baseline studies for solid sorbent and liquid solvent systems report overall energy consumption of the process that are much higher than for point-source capture cases. For the solid sorbent case, a reported electrical load of 4.4 MWh/t CO_2 captured from the air is reported [33]. Self-reported performance estimates at commercial scale and with significant R&D advances of approximately 2 MWh/t CO_2 have been reported for other solid-sorbent based processes [43].

For a solvent-based DAC process based on the Carbon Engineering approach, DOE estimates an energy consumption of 13 GJ/t CO_2 captured supplied as natural gas HHV. This is not comparable to the low-grade heat thermal requirements for solvent-based PSC processes as the energy quality in the fuel is much higher than the energy quality of the low-pressure steam. For each of the major DAC approaches, the energy consumption can be considered approximately several times higher than for capture from concentrated sources.

When the net power produced by a power plant is reduced, or if the carbon capture unit has an external power requirement the power must often be procured. The source and carbon intensity of that replacement power must be considered. In a DAC system, this energy can have a significant impact on the net capture rate of the process.

Energy and LCA

The energy consumption of DAC and PSC is important for three main reasons: the cost of providing the energy; the availability of the energy; and the impact of the producing the energy on net CO_2 removal.

For point source capture, the goal is to dramatically reduce the carbon intensity of energy produced from fossil fuel sources. Traditionally a 90% reduction target has been used by organizations such as the DOE, though 95% is becomingly increasingly common. The challenge with achieving only 90% reduction with point source capture is that the final 10% of emission remain to be abated to achieve net-zero energy systems. Because of this, there has been recent development of new technologies that can achieve higher capture rates. The challenge associated with higher capture rates from PSC are that the deeper removal results in higher cost per ton for the entire amount of CO_2 removed in the PSC. In an optimized system, the marginal cost for reducing CO_2 from power plants down to zero emissions is expected to be lower than DAC [44]. Zero emissions occurs at 99+% capture for NGCC and 99.7% for coal.

The impact of energy on PSC from electric generation units is also seen in the reduction of electricity produced from these plants. This is often referred to as the parasitic load as it is a reduction in energy produced due to both steam extraction and additional auxiliary power requirements for CCS. The parasitic loads for CCS plants can range from 11% to over 40% in recent FEED studies. Because of the parasitic effects of CCS, the cost of power increases because the operating costs and capital costs for the base plant remain similar while the electricity produced decreases. The makeup power to overcome the power shortfall must then be provided by other sources including renewables and low-carbon electricity but also dispatchable power with associated carbon emissions. In a fully decarbonized energy system, the CO_2 capture parasitic load results in a larger overall fleet of dispatchable power production. The energy consumption in PSC plants is by far the largest factor in the LCA of the CCS unit.

The impact of DAC can be measured by how much CO_2 is permanently removed from the atmosphere. This is determined by the size of the capture system, the capacity factor, and the carbon removal efficiency. The size of the system determines the maximum CO_2 capture rate while capacity factor determines the how often the system is running. The removal efficiency is determined by life-cycle analysis as the net removal of CO_2 from the atmosphere for each gross ton of CO_2 captured from the air in the DAC unit. This removal efficiency is important to quantify in order to understand the climate impact of a given plant or technology.

The main component of the LCA is the energy consumption of the DAC. CO_2 removal efficiency is driven by the energy consumption of the plant and the carbon intensity of the electricity used to provide that energy. For electrically driven systems, the carbon intensity of the electricity consumed to circulate the air, regenerate the separation material, and compress the CO_2 can be significant. For current baseline solid-sorbent systems, this electricity use has been calculated to be on the order of 6 MWh/t CO_2 captured [33]. However, the carbon intensity of the 6 MWh electricity consumed must be considered in the net CO_2 captured. At the current U.S. grid intensity of around 0.42 t/MWh, this would result in a net increase in atmospheric CO_2. In fact, the CO_2 intensity of electricity consumed in the process must be less than 0.16 t CO_2/MWh to achieve no net CO_2 emissions and must be much lower than that in order to have a significant climate benefit for the system analyzed.

Other analysis has shown that the carbon removal efficiency can be greater than zero for state-of-the-art solid sorbent systems. For carbon intensity of electricity at the U.S. grid average, the Climeworks system is expected to have a net removal efficiency of around 12% [10]. This means that for every 1000 kg (gross) of CO_2 capture by the process, 120 kg (net) of CO_2 would be removed from the atmosphere. The impact of the low removal efficiency is that a one million tpy plant would only achieve 120,000 tpy net removal. The capital cost of that DAC plant and the operating cost would not change, but the net CO_2 impact would be approximately eight times lower than if it was supplied by zero-carbon energy. Because of this, the cost of DAC would be eight times higher using this current carbon-intensity electricity than it would in a zero-carbon electricity system. This makes the cost and impact of DAC variable as it is dependent on the deployment environment and assumptions.

LCA is an important tool to understand the impact of DAC. Overly optimistic assumptions such as wide availability of low-carbon electricity may lead to much lower claimed costs for DAC systems than would be obtained from a more comprehensive approach.

To achieve lower-cost DAC, high carbon removal efficiencies are required. This means deploying in environments with high availability of low-carbon electricity or making use of low-carbon energy resources. One way to make use of low-carbon resources is by using fossil fuels with carbon capture as the source of the electricity or energy. This is what is assumed for the DOE baseline studies on DAC. It is also the basis for the oxy-fired calcining approaches such as Carbon Engineering which use natural gas combustion with pure oxygen to supply the heat for CO_2 release from calcium carbonate and to provide a near-pure stream of CO_2 that can be co-sequestered with minimal additional CO_2 emissions.

Deployment Potential and Impact

Point-source capture and direct air capture are complementary approaches for achieving net-zero greenhouse gas emissions. Presently, 68% of CO_2 emissions originate from large-scale emissions sources such as power generation and industrial facilities. PSC thus has the potential to drastically reduce the CO_2 emissions from the most carbon intensive sectors of the economy. In aggregate, PSC can dramatically reduce CO_2 emissions because these facilities produce hundreds of thousands to millions of tons of CO_2 per year. For the most promising sites, the large size, high concentration of CO_2, and ability to reduce costs with process and heat integration with the existing facilities can enable capture costs significantly lower than what are possible with DAC and costs that are competitive to other carbon abatement solutions.

However, capture cost estimates are dependent upon a high-capacity factor for the industrial facility and its carbon capture equipment for 10-30 years. PSC capture facilities require significant capital investment to deploy, and the risk of significant technology or market shifts stranding these investments is a major hurdle in their development. Additional practical considerations that may ultimately prevent the deployment of PSC at otherwise promising facilities. For example, a lack of nearby suitable CO_2 storage facilities may dramatically alter the cost or timeline for deploying capture technologies on existing facilities. Additionally, the availability of sufficient space for the CO_2 capture equipment can further limit the ability of existing industrial facilities to deploy PSC technologies.

Approximately one-third of CO_2 emissions originate from sources for which on-site capture is not practical because they are mobile or small, diffuse sources of CO_2 such as buildings and agriculture. It is anticipated that electrification will significantly reduce these CO_2 emissions, but carbon removal such as DAC are anticipated to play a critical role in achieving net-zero for those use cases in which electrification is either not practical or is more expensive than DAC. The total addressable market for DAC will depend heavily on the removal costs that fully mature and scaled technologies can achieve. If DAC costs remain above $200/ton, DAC capacity of 1-5 Gtpy are likely to be cost competitive to alternative abatement strategies. If costs are below $200/ton, DAC would likely be the lowest cost abatement strategy for more than 10 Gtpy of CO_2 emissions. It is anticipated that DAC will play a critical role in offsetting the emissions of greenhouse gases that are not CO_2 such as methane and nitrous oxides. Owing to their ultra-dilute concentrations and the highly diffuse nature of many of their emissions, DAC is one of the most promising approaches for offsetting the impacts of these potent greenhouse gases.

Beyond net-zero, carbon removal is essential under overshoot emissions scenarios, in which negative annual emissions are required to reduce atmospheric CO_2 concentrations. Under this scenario, DAC capacity will depend on the extent and rate at which CO_2 needs to be removed from the atmosphere.

Concluding Thoughts

Fossil fuels remain a large component of our energy system. Point source capture of CO_2 is the only technology that significantly reduces CO_2 emissions from carbon-containing fuel combustion. Recent consensus reports have indicated that point-source capture and other carbon emissions reduction techniques are insufficient to achieve decarbonization targets and that Negative Emissions Technologies (NETs) are required [1]. DAC is one of the most promising NET technologies because it is well suited for large-scale implementation. However, it must overcome performance and deployment hurdles to achieve low-cost CO_2 reduction. Some of these barriers have hard limits on them due to thermodynamics.

Major considerations for Point Source Capture and Direct Air Capture are:

1) PSC from high-pressure, higher purity streams such as ethanol production and natural gas processing are currently mature technologies with low cost. Capture from intermediate concentration streams such as power-plant flue gas has higher cost and is less technically mature though had been demonstrated at scale in several applications worldwide. Capture from air is technical less-mature and needs to be scaled up by many orders of magnitude to achieve climate-relevant scales.

2) Geologic storage of CO_2 is the primary and most mature climate-relevant sink for CO_2. While geologic storage is not well distributed across the globe, there are significant geologic reservoirs that can be used for storing CO_2 from PSC or DAC. It is likely that DAC and PSC deployments will be located close to geologic reservoirs.

3) PSC from concentrated sources has lower capital costs and lower energy requirements than from lower-concentration sources such as DAC. Highly concentrated streams need less contacting area, equipment, and less energy

for performing the separation. Dilute sources have much greater gas-contacting area, which necessitates more equipment and more energy for air contacting in addition to greater energy requirements during material regeneration. This difference is fundamental to the different gas streams and is independent of the technologies used.

4) In a changing energy landscape, sources of point-source emissions such as electrical generating units are likely to have reduced operation due to the increased proliferation of variable-renewable generation. Reduced capacity factors are likely to increase the cost of carbon abatement from fossil-fired power plants. Industrial facilities are likely to have higher long-term capacity factors and PSC applied to these facilities may provide a lower cost for carbon abatement than from power generation.

5) Due to the high energy consumption and goal of reducing atmospheric CO_2, finding the energy for DAC is one of the greatest challenges for the technology. Utilizing exclusively low-carbon electricity may result in low capacity factors, reducing the quantity of CO_2 captured and increasing the cost. Conversely, DAC powered by higher carbon-intensity energy sources may result in net CO_2 emissions or low net CO_2 removal efficiency. As a result, the deployment environment and energy system surrounding a DAC installation are critical inputs to the performance of a DAC plant. A comprehensive Life Cycle Analysis of DAC is necessary to understand the actual cost of CO_2 removed from environment.

6) DAC to achieve global and regional CO_2 emissions targets requires abundant, low-carbon energy. To scale DAC and advance development, it is important to initiate deployment in regions or areas with available low-carbon energy.

There are a wide range of technologies in operation or under development for both PSC and DAC. For PSC, CO_2 is emitted under a range of concentrations, pressures, and temperatures for which solvents, sorbents, cryogenics, or membranes are best suited. For DAC, the climate coupled with the availability and carbon intensity of energy, electricity, water, and materials will determine the technologies that are best suited for a given region.

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