

Technology and Applied R&D Needs for Carbon Capture: Beyond 2020



**Resource Document for the Workshop
on Carbon Capture: Beyond 2020**

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**TECHNOLOGY AND APPLIED R&D NEEDS FOR
CARBON CAPTURE: BEYOND 2020**

**Resource Document for the
Workshop on Basic Research needs for
Carbon Capture: Beyond 2020**

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ABBREVIATIONS, ACRONYMS, AND INITIALISMS

ASU	air separation unit	NCCC	National Carbon Capture Center
bmim	1-butyl-methylimidazolium	NETL	National Energy Technology Laboratory
Btu	British thermal units	NGCC	natural gas combined cycle
CAP	chilled ammonia process	PC	pulverized coal
CCS	carbon capture and storage	PES	polyethersulfone
CHA	chabazite	PSA	pressure-swing adsorption
CLC	chemical looping combustion	PSDF	Power Systems Development Facility
CLG	chemical looping gasification	PSF	polysulfone
CO ₂	carbon dioxide	psia	pounds per square inch absolute
COE	cost of electricity	PZ	piperazine
dca	dicyanamide	SC	supercritical
DDR	Deca-dodecasil 3R	SLM	supported liquid membranes
dhtp	2,5-dihydroxyterephthalate	SNG	substitute natural gas
DOE	Department of Energy	SubC	subcritical
emim	1-ethyl-3-methylimidazolium	tdtdp	trihexyltetradecylphosphonium
EOR	enhanced oil recovery	Tf ₂ N	bis(trifluoromethylsulfonyl)imide
EPRI	Electric Power Research Institute	USC	ultrasupercritical
FAU	faujasite	WGS	water-gas shift
GPU	gas permeation unit	ZIF	zeolitic imidazolate framework
hmim	1-hexyl-3-methylimidazolium		
hmpy	1-hexyl-3-methylpyridinium		
IGCC	integrated gasification combined cycle		
IL	ionic liquid		
IM	imidazolate		
MEA	monoethanolamine		
MFI	mordenite framework inverted		
MHI	Mitsubishi Heavy Industries		
MOF	metal-organic framework		
MW	megawatt		
MWH	megawatt hours		

1.0 Introduction

A large body of evidence demonstrates that global temperatures are rising. Eleven of the past 12 years rank among the 12 warmest since the 1850s, when temperature began to be regularly recorded [1]. Many attribute this recent global warming to human influence on atmospheric composition, particularly the increase in carbon dioxide. Over the past several hundred years, atmospheric CO₂ concentrations have steadily increased from the pre-industrial level of 280 to over 370 ppm. The increases in CO₂ concentrations are attributed primarily to burning of coal, oil and natural gas for electrical generation, transportation, industrial and domestic uses (e.g. cement manufacturers). In 2007, human activities emitted roughly 37 GtCO₂ to the atmosphere, 85% of which came from combusting fossil fuels as a primary energy source and the balance from changes in land cover [2, 3]. Roughly one-third of the 37 GtCO₂ emitted in 2007 came from the United States and China [4]. If unabated, atmospheric CO₂ levels will continue to increase rapidly and, within 50 years, may exceed concentrations needed to protect sensitive ecosystems and avoid flooding in low-lying coastal areas. To address this challenge, a multi-pronged approach is needed to decrease CO₂ emissions which include efficient production and use of energy, solar power, wind energy, biomass utilization, switching to fuel sources with lower or negligible emissions, and carbon capture and storage (CCS).

Carbon capture involves the separation of CO₂ from an effluent stream and compressed to a liquid or supercritical state for transportation by pipeline. It is then injected into geologic reservoirs (e.g., oil and gas fields, deep saline aquifers) where the geologic structure and processes are expected to store the CO₂ for thousands of years. CCS is currently high on administrative and legislative agendas worldwide. In July 2008, the G8 leaders called for 20 CCS demonstrations announced globally by 2010. Since then, many countries have invested significant sums to initiate commercial-scale demonstrations and began developing policies to address legal and regulatory concerns about geologic storage. Capture standards for new facilities have been proposed in legislation in Europe and the United States. These proposals would set a performance standard (either in unit of CO₂ per unit of energy or as a percentage-based reduction in overall CO₂ emissions).

In the United States, the majority of 2008 emissions from stationary sources came from the electricity sector, primarily from coal-fired power plants [5]. A wide variety of industrial facilities also emit CO₂ as a by- or co-product of the industrial processes inherent to their industry, such as ethanol fermentation, oil and gas refining, chemical (including ethylene and ethylene oxide) production, hydrogen production, as well as others such as pulp and paper, iron and steel, ammonia and fertilizer, and cement manufacturing. CO₂ in exhaust streams is present to various extents, at various temperatures and pressures, and with various other constituents (e.g. NO_x, SO₂). Such a variety suggests that different markets for CO₂ capture technologies might exist and that number of different technologies to capture CO₂ will be necessary. A cost-effective technology that is flexible and robust to these different applications, however, is likely to be valued and more desirable than a niche-market counterpart.

A typical taxonomy separates CO₂ capture into three categories: (1) post-combustion, (2) pre-combustion, and (3) oxy-combustion capture [5]. Post-combustion capture separates CO₂ from exhaust gases. Using coal as a fuel, pre-combustion capture entails gasifying the coal prior to combustion in a process that produces a readily capture-able stream of CO₂. The technology used for carbon capture in pre-combustion is similar to that used in the hydrogen industry. Oxy-combustion capture produces a relatively pure stream of CO₂ and water vapor by burning the coal in pure oxygen, where nitrogen is separated from air prior to combustion. Processes that seek to capture 90% or more of the CO₂ in the exhaust stream are being developed, but it is equally if not more important that this treated stream be composed as much as possible of the exhaust stream that would otherwise be emitted. The gigatons of CO₂ that need to be captured necessitate the reuse of any capture material. It is further crucial to consider how the capture technology can scale with the exhaust stream and the amount of CO₂ being emitted. Similarly, the

physical space needed for the capture technology is important; roughly doubling the size of the facility that produces the CO₂. Furthermore, the potential for retrofits to the old fleet of coal-fired power plants and new-build installations of CO₂ capture technology will vary regionally, and provide incentive for technology development for both retrofits and new-builds. Importantly, current capture systems require large amounts of energy to operate. This decreases net efficiency and contributes significantly to CO₂ capture costs. Depending on the nature of the point source, cost estimates range from as low as roughly \$20/tCO₂ to nearly \$100/tCO₂ [5, 6]. Technological advances driven by multi-disciplinary fundamental research offer a path forward leading to novel materials and processing methods that will greatly improve capture efficiencies and lower cost.

This document provides the factual background for the basic science and research needs for CO₂ capture technologies to support the BES Basic Research Needs Workshop for Carbon Capture: 2020 and Beyond. This workshop will identify key basic research directions that could provide transformative breakthroughs needed for meeting future requirements for carbon capture. The intent of this document is to provide a broad-based overview of current technologies used for carbon capture – focusing primarily on materials used for carbon capture and alternative gas separation pathways – and to better define the requirements necessary to achieve fundamental breakthroughs that propel carbon capture technology into the next decade. This overall reference will not only provide background for participants in the workshop, but also a template for future technology development going forward.

2.0 Carbon Capture Technologies

There are commercially-available CO₂ capture technologies that are currently being used in various industrial applications and being tested for power plant capture in pilot and demonstration projects. However, in their current state of development these technologies are not ready for broad-based implementation on coal-based power plants for two primary reasons: 1) they have not been demonstrated at the scale necessary for power plant application, and 2) if successfully scaled-up, they would not be cost effective at their current level of process development. Other major technical challenges associated with the application of existing CO₂ capture technologies to coal-based power plants include auxiliary power requirements, energy efficiency, energy integration, flue gas contaminants, water use, CO₂ compression, and oxygen supply for oxy-combustion systems. A broad portfolio of research pathways are being investigated in three technology approaches for CO₂ capture – post-combustion, pre-combustion, and oxy-combustion. A key point is that the majority of the technology options being considered are still in the laboratory and bench-scale stage of development.

DOE has conducted systems-analysis studies that show currently available CO₂ capture technologies are expensive and energy-intensive, which would seriously degrade the overall efficiency of both new and existing coal-based power plants [7]. Figure 1 presents the impact of current state-of-the-art CO₂ capture technologies on the normalized cost of electricity (COE) and net efficiency of new coal-based power plants. For example, a subcritical pressure, air-fired power plant equipped with an amine-based solvent CO₂ capture process is estimated to have an 81 % higher COE and 14.6 % lower efficiency than a similar plant without CCS. Three major conclusions can be drawn from the DOE analysis:

- For all CO₂ capture cases, the COE is significantly higher than baseline costs.
- Plant efficiencies are substantially degraded in all processes as a result of large parasitic energy consumption associated with the CO₂ capture.
- It is important to develop new advanced CO₂ capture technologies in order to maintain the cost-effectiveness of U.S. coal-based power generation.

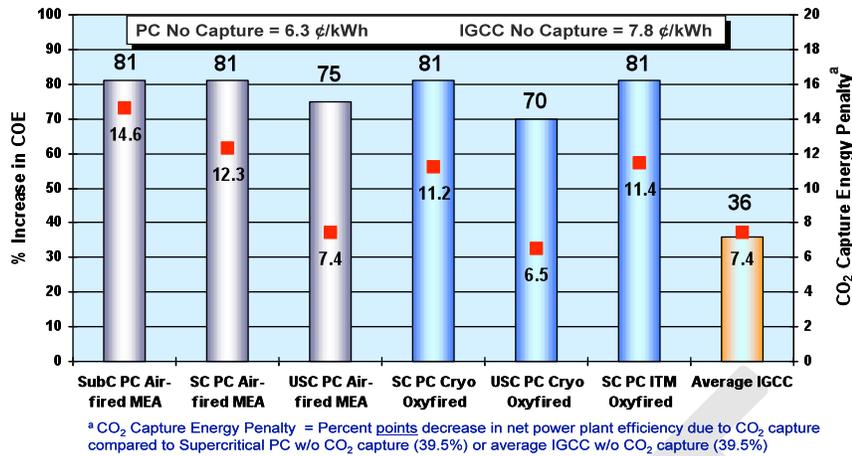


Figure 1. Impact of current state-of-the-art CO₂ capture technologies on the normalized cost of electricity and net efficiency of new coal-based power Plants (PC: pulverized coal; SubC: subcritical; SC: supercritical; USC: ultrasupercritical).

2.1 Post-Combustion CO₂ Capture

Post-combustion CO₂ capture offers the greatest near-term potential for significantly reducing CO₂ emissions since these technologies can be retrofit to the existing fleet of coal-fired power plants, which will likely produce the bulk of coal-fired CO₂ emissions for the foreseeable future. Post-combustion CO₂ capture involves the separation of CO₂ from the combustion flue gas, purification, and compression in preparation for geological storage or beneficial use such as enhanced oil recovery. It is primarily applicable to conventional coal-fired, oil-fired or gas-fired power plants, but could also be applicable to integrated gasification combined cycle (IGCC) and natural gas combined cycle (NGCC) flue gas capture. As shown in Figure 2, in a typical coal-fired power plant, fuel is burned with air in a boiler to produce steam that drives a turbine/generator to produce electricity. Flue gas from the boiler consists mostly of nitrogen, water vapor, and CO₂. Separating CO₂ from this flue gas is challenging for several reasons: a high volume of gas must be treated (~2 million cubic feet per minute for a 550 MW plant); the CO₂ is dilute (between 12 and 14 % CO₂); the flue gas is at atmospheric pressure; trace impurities (particulate matter, sulfur oxides, nitrogen oxides, etc.) and oxygen can degrade chemical scrubbing agents; and compressing captured CO₂ from near atmospheric pressure to pipeline pressure (about 2,200 psia) requires a large auxiliary power load.

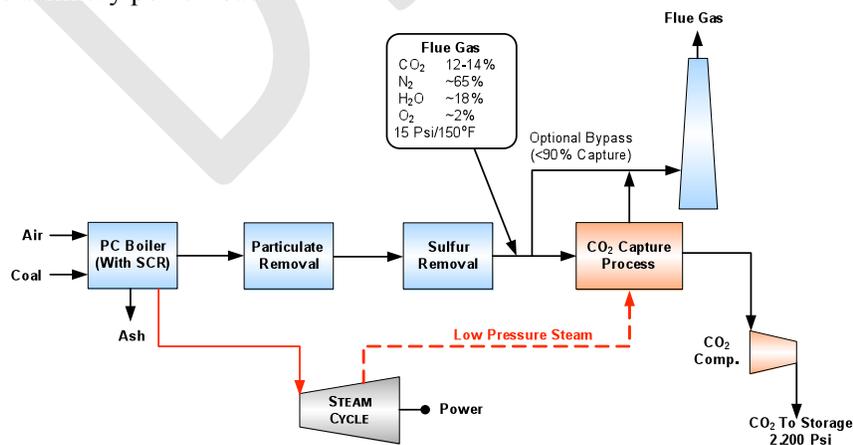


Figure 2. Block diagram illustrating a power plant with post-combustion CO₂ capture.

2.1.1 Currently Available Post-Combustion Capture Technologies

Amine-based chemical solvents, such as aqueous monoethanolamine (MEA), have been utilized for more than 60 years for removal of acid gases (CO₂ and H₂S) from natural gas streams and food-grade CO₂ production. This experience consists of several small (two to 320 ton/day) capacity capture plants that supply CO₂ for the food and beverage industry and a few large (800 to 1,000 ton/day) capture plants that use the CO₂ for enhanced oil recovery (EOR) [8, 9]. MEA scrubbing is capable of achieving high levels of CO₂ capture (90 % or more) for post-combustion applications, but it has not been demonstrated at the larger-scale necessary for coal-fired power plants (e.g., approximately 10,000 tons/day CO₂ production from a 500-MW coal-fired power plant). Although AES's coal-fired Warrior Run and Shady Point power plants are equipped with MEA scrubbers developed by ABB Lummus, they were designed to process a relatively small percentage of the plants' flue gas. At Warrior Run, the MEA system removes CO₂ from only about three to five percent of the flue gas (150 to 200 tCO₂ per day) that is subsequently used for the food processing industry.

Current amine solvents are corrosive; susceptible to degradation by trace flue gas constituents (particularly SO_x); and necessitate significant amounts of energy, in the form of low-pressure steam, for sensible heating, heat of reaction, and stripping for CO₂ regeneration. As shown in Figure 2-1, installing the current state-of-the-art MEA post-combustion CO₂ capture technology on new conventional subcritical (SubC), supercritical (SC), and ultrasupercritical (USC) coal-fired power plants would increase the COE by about 75 to 80 %. Further, the large quantity of energy required to regenerate the MEA solvent would reduce the net efficiency of new SubC and SC coal-fired power plants by more than 12 %.

Amines chemically react with CO₂ via reversible reactions to form water-soluble compounds. Despite the low CO₂ partial pressure in combustion flue gas, amines are capable of achieving high levels of CO₂ capture due to fast kinetics and strong chemical reactions. However, the absorption capacity for today's commercially available amines is chemically limited with two moles amine for each mole of CO₂ being required. In addition, typical amine solution concentrations are limited by viscosity and corrosion. Therefore, current amine systems use a solution that is between 20 and 30 % amine with the balance being water. Although the 70 to 80 % water present in the solution helps control the solvent temperature during the absorption exotherm, the water, with its high heat capacity, necessitates significant amounts of sensible heating and stripping energy upon CO₂ regeneration. Various vendors offer different designs of amine systems. In general, depending on the amount of heat integration, anywhere from ~1,500 to more than 2,000 British thermal units (Btu) per pound of CO₂ captured is required in the form of low pressure steam (approximately 45 psia) to regenerate the solvent to produce a concentrated CO₂ stream at a pressure of approximately 25 psia.

2.1.2 Challenges and Technology Needs in Post-Combustion CO₂ Capture

There are several advanced post-combustion CO₂ capture technologies under development, including processes involving solvents, sorbents, and membranes. Challenges and needs for development of practical technologies are summarized in Table 1 and the paragraphs below.

Liquid Solvents: Post-combustion solvent-based CO₂ capture involves chemical or physical sorption of CO₂ from flue gas into a liquid carrier. Chemical absorption involves one or more reversible chemical reactions between CO₂ and an aqueous solution of an absorbent, such as an alkanolamine (e.g., MEA), hindered amine, aqueous ammonia, or a carbonate, to form water-soluble compounds. Although high levels of CO₂ capture are possible, the drawback of this approach is that significant amounts of energy are required in the regeneration step, which involves a temperature swing to break the absorbent-CO₂ chemical bond. Physical absorption is a bulk phenomenon where inorganic or organic liquids preferentially absorb a gaseous species from the gas mixture. Physical absorption is being used in

smaller-scale industrial applications. Although physical solvent regeneration is less energy-intensive than

Table 1. Post-Combustion Capture Advantages and Challenges

CO₂ Capture Technology	Description	Advantages	Challenges
<i>Liquid Solvent</i>	Solvent reacts reversibly with CO ₂ , often forming a salt. Solvent is regenerated by temperature swing, which reverses the absorption reaction (normally exothermic). Solvent is often alkaline.	<ul style="list-style-type: none"> • Chemical solvents provide fast kinetics to allow capture from streams with low CO₂ partial pressure • Wet-scrubbing allows good heat integration and ease of heat management (useful for exothermic absorption reactions) 	<ul style="list-style-type: none"> • Significant amount of steam required to reverse chemical reaction de-rates power plant • Energy required to heat, cool, and pump non-reactive carrier liquid (usually water) is often significant • Vacuum stripping can reduce regeneration steam requirements but is expensive
<i>Solid Sorbent</i>	When sorbent pellets are contacted with flue gas, CO ₂ is absorbed onto chemically reactive sites on the pellet by a reversible reaction. Pellets are regenerated by temperature swing, which reverses the absorption reaction.	<ul style="list-style-type: none"> • Chemical sites provide large capacities and fast kinetics, enabling capture from streams with low CO₂ partial pressure • Higher capacities on a per mass or volume basis than similar wet-scrubbing chemicals • Lower heating requirements than wet-scrubbing in many cases (CO₂ and heat capacity dependant) 	<ul style="list-style-type: none"> • Heat required to reverse chemical reaction (although generally less than in wet-scrubbing cases) • Heat management in solid systems is difficult, which can limit capacity and/or create operational issues when absorption reaction is exothermic • Pressure drop can be large in flue gas applications • Sorbent attrition
<i>Membrane</i>	Uses permeable or semi-permeable materials that allow for the selective transport and separation of CO ₂ from flue gas.	<ul style="list-style-type: none"> • No steam load • No chemicals 	<ul style="list-style-type: none"> • Membranes tend to be more suitable for high-pressure processes such as IGCC • Trade off between recovery rate and product purity (difficult to meet both high recovery rate and high purity) • Requires high selectivity (due to CO₂ concentration and low pressure ratio) • Good pre-treatment • Bad economy of scale • Multiple stages and recycle streams may be required

chemical systems, this technology is considered more practical for processing the high-pressure syngas generated at coal gasification plants since CO₂ solubility in physical solvents increases with partial pressure. Practical challenges in solvent-based CO₂ capture include large flue gas volume, relatively low CO₂ concentration, flue gas contaminants, and high parasitic power demand for solvent recovery. Technology needs include low-cost, non-corrosive solvents that have high CO₂ loading capacity, improved reaction kinetics, low regeneration energy, and resistance to degradation.

Solid Sorbents: Solid sorbents, including sodium and potassium oxides, zeolites, carbonates, amine-enriched sorbents, metal organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs), are

being explored for post-combustion CO₂ capture. A temperature swing facilitates sorbent regeneration following chemical and/or physical adsorption, but a key attribute of CO₂ sorbents is that less H₂O is present compared to solvent-based systems, thereby reducing the sensible heating and stripping energy requirements. Possible configurations for contacting the flue gas with the sorbents include fixed, moving, and fluidized beds. Challenges in the application of sorbent-based systems include solids circulation, sorbent attrition, low chemical potential, heat transfer, reactive flue gas contaminants, and the parasitic power and potential water demand for sorbent regeneration. Technology needs include low-cost, durable sorbents that have high selectivity, high CO₂ adsorption capacity, and ability to withstand multiple regeneration cycles.

Membranes: The potential of membrane-based CO₂ capture is generally viewed positively for high-pressure applications, such as IGCC, but not as promising for low-pressure combustion flue gas without further process enhancements. Usually, the selectivities of the membranes in one stage are insufficient to achieve the desired purities and recoveries, so multiple stages and recycle may be required in an actual operation, leading to increased complexity, energy consumption, and capital costs. CO₂ membranes could have an advantage if a lower rate of CO₂ removal (<90 %) is acceptable. Practical challenges to the use of membrane-based systems include large flue gas volume, relatively low CO₂ concentration, low flue gas pressure, flue gas contaminants, and the need for high membrane surface area. Technical needs for post-combustion membranes include low-cost, durable membranes that have improved selectivity, thermal and physical stability, and tolerance of contaminants in combustion flue gas.

2.2 Pre-Combustion CO₂ Capture

Pre-combustion capture is mainly applicable to gasification plants, where fuel is converted into gaseous components by applying heat under pressure in the presence of steam and sub-stoichiometric oxygen (O₂). A simplified process schematic for pre-combustion CO₂ capture is shown in Figure 3. By carefully controlling the amount of oxygen, only a portion of the fuel burns to provide the heat necessary to decompose the fuel and produce synthesis gas (syngas), a mixture of hydrogen (H₂) and carbon monoxide (CO), along with minor amounts of other gaseous constituents. To enable pre-combustion capture, the syngas is further processed in a water-gas shift (WGS) reactor, which converts CO into CO₂ while producing additional H₂, thus increasing the CO₂ and H₂ concentrations. An acid gas removal system can then be used to separate the CO₂ from the H₂. Because CO₂ is present at much higher concentrations in syngas (after WGS) than in flue gas and the syngas is at higher pressure, CO₂ capture is less expensive for pre-combustion capture than for post-combustion capture. After CO₂ removal, the H₂ can be used as a fuel in a combustion turbine combined cycle to generate electricity.

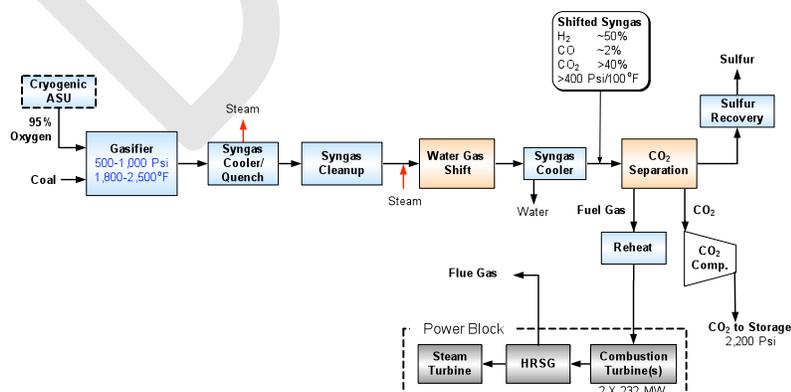


Figure 3. Block diagram illustrating a power plant with pre-combustion CO₂ capture.

2.2.1 Currently Available Pre-Combustion Capture Technologies

The current state-of-the-art CO₂ capture technologies that could be applied to IGCC systems – the glycol-based Selexol™ process and the methanol-based Rectisol® process – employ physical solvents that preferentially absorb CO₂ from the syngas mixture. There are multiple systems in use at commercial scale. For example, a Rectisol® system is used for CO₂ capture at the Dakota Gasification Company’s substitute natural gas (SNG) plant located in North Dakota, which is designed to remove approximately 1.5 million tons of CO₂ per year from the synthesis gas. The CO₂ is purified and sent via a 320-km pipeline and injected into the Weyburn oilfield in Saskatchewan. However, this experience is based on a gasification plant, not an IGCC plant. The advantage of physical solvents is that less energy is required in the solvent regeneration step, which involves a temperature increase and/or pressure reduction, leading to an energy penalty of about seven percentage points. Furthermore, although the COE for a base IGCC power plant is higher than a coal-fired plant, the high thermodynamic driving force for CO₂ capture and reduced CO₂ compression demands at IGCC facilities leads to an increase in COE of less than 40 % using Selexol™ technology, compared to 75 to 80 % for a conventional coal-fired power plant equipped with an MEA scrubber for CO₂ control, as shown in Figure 1.

The DOE systems analysis study assumes a WGS reactor combined with a two-stage Selexol™ process is used for CO₂ capture in IGCC applications. The WGS reactor is necessary to convert the CO in the syngas to CO₂. The first-stage Selexol™ process is used for hydrogen sulfide (H₂S) capture, and the second stage for CO₂ capture.

2.2.2 Challenges and Technology Needs in Pre-Combustion CO₂ Capture

There are several advanced pre-combustion CO₂ capture technologies under development, including processes involving solvents, sorbents, and membranes. Challenges and needs for development of practical technologies are summarized in Table 2 and the paragraphs below.

Table 2. Pre-Combustion CO₂ Capture Technology Advantages and Challenges

CO ₂ Capture Technology	Description	Advantages	Challenges
<i>Physical Solvent</i>	Solvent readily dissolves CO ₂ . Solubility is directly proportional to CO ₂ partial pressure and inversely proportional to temperature, making physical solvents more applicable to low temperature, high pressure applications (cooled syngas). Regeneration normally occurs by pressure swing.	<ul style="list-style-type: none"> • CO₂ recovery does not require heat to reverse a chemical reaction. • Common for same solvent to have high H₂S solubility, allowing for combined CO₂/H₂S removal. • System concepts in which CO₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems 	<ul style="list-style-type: none"> • CO₂ pressure is lost during flash recovery • Must cool down synthesis gas for CO₂ capture, then heat it back up again and re-humidify for firing to turbine • Low solubilities can require circulating large volumes of solvent, resulting in large pump loads • Some H₂ may be lost with the CO₂
<i>Physical Sorbent</i>	When sorbent pellets are contacted with syngas, CO ₂ is physically adsorbed onto sites and/or dissolves into the pore structure of the solid. Rate and capacity are directly proportional to CO ₂	<ul style="list-style-type: none"> • CO₂ recovery does <u>not</u> require heat to reverse a reaction. • Common for H₂S to also have high solubility in the same sorbent, meaning CO₂ and H₂S capture can 	<ul style="list-style-type: none"> • CO₂ pressure is lost during flash recovery • Must cool synthesis gas for CO₂ capture, then heat it back up again and re-humidify for firing to turbine

	partial pressure, making these sorbents more applicable to high pressure applications. Regeneration normally occurs by pressure swing.	be combined. <ul style="list-style-type: none"> System concepts in which CO₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems 	<ul style="list-style-type: none"> Some H₂ may be lost with the CO₂
<i>H₂/CO₂ Membrane</i>	A membrane material which selectively allows H ₂ or CO ₂ to permeate, used in gasification operations with concentrated streams of H ₂ and CO ₂ .	<u>H₂ or CO₂ Permeable Membrane:</u> <ul style="list-style-type: none"> No steam load or chemical attrition. <u>H₂ Permeable Membrane Only:</u> <ul style="list-style-type: none"> Can deliver CO₂ at high-pressure, greatly reducing compression costs. H₂ permeation can drive the CO shift reaction toward completion – potentially achieving the shift at lower cost/higher temperatures. 	<ul style="list-style-type: none"> Membrane separation of H₂ and CO₂ is more challenging than the difference in molecular weights implies. Due to decreasing partial pressure differentials, some H₂ will be lost with the CO₂. In H₂ selective membranes, H₂ compression is required and offsets the gains of delivering CO₂ at pressure. In CO₂ selective membranes, CO₂ is generated at low pressure requiring compression.
<i>Membrane/Liquid Solvent Hybrids</i>	Flue gas is contacted with a membrane, and a solvent on the permeate side absorbs CO ₂ and creates a partial pressure differential to draw CO ₂ across the membrane.	<ul style="list-style-type: none"> The membrane shields the amine from the contaminants in flue gas, reducing attrition and allowing higher loading differentials between lean and rich amine. 	<ul style="list-style-type: none"> Capital cost associated with the membrane. Membranes may not keep out all unwanted contaminants. Does not address CO₂ compression costs.

Liquid Solvent-Based Processes: Physical solvents are viewed as a potential approach for processing high-pressure, CO₂-rich streams, such as those encountered in IGCC systems that employ an upstream WGS reactor. However, solvent-based processes have several disadvantages, including loss of CO₂ partial pressure during the flash regeneration and requirement of a low operating temperature, thus requiring cooling of the syngas, followed by reheating to gas turbine inlet temperature. Novel, solvent-based processes are necessary that can produce high pressure CO₂ at elevated temperatures.

Potential process improvements include modifying regeneration conditions to recover the CO₂ at a higher pressure, improving selectivity to reduce H₂ losses, and developing a solvent that has a high CO₂ loading at a higher temperature. A physical solvent with acceptable CO₂ capacity at a higher temperature would improve IGCC efficiency.

Solid Sorbent-Based Processes: Pressure-swing adsorption (PSA) is currently used to separate hydrogen from CO₂ and other mixed gas streams. While PSA produces a highly pure hydrogen stream, it does not selectively separate CO₂ from other gases in the stream, and therefore does not produce a pure CO₂ product for storage. Solid sorbents for pre-combustion CO₂ capture from syngas must maintain a high adsorption capacity and be resistant to attrition over multiple regeneration cycles, and exhibit good performance at the high temperatures encountered in IGCC systems to avoid the need for syngas cooling.

Membrane Processes: Membrane-based CO₂ capture uses permeable materials that allow for the selective transport and separation of CO₂ from syngas. Different types of membrane materials are available including polymeric membranes, porous inorganic membranes, palladium membranes, and zeolite membranes. Membrane separation uses partial pressure difference as the driving force and is thus suitable for pre-combustion CO₂ capture. Several barriers must be overcome to reduce the cost and improve the performance of membrane systems. Methods must be found to improve separation and throughput and prevent membranes from becoming less effective over time. Thermal and hydrothermal stabilities of membrane need to be considered. Large-scale manufacturing methods for defect-free membranes and modules must be developed. Better methods are needed to make high-temperature, high-pressure seals using ceramic substrates.

2.3 Oxy-Combustion

Oxy-combustion systems for CO₂ capture rely on combusting coal with relatively pure oxygen diluted with recycled CO₂ or CO₂/steam mixtures. Under these conditions, the primary products of combustion are water and CO₂, with the CO₂ separated by condensing the water. Figure 4 shows the major systems for a power plant equipped for oxy-combustion. Oxy-combustion overcomes the technical challenge of low CO₂ partial pressure normally encountered in coal combustion flue gas by producing a highly concentrated CO₂ stream (~60 %), which is separated from H₂O vapor by condensing the H₂O through cooling and compression. An additional purification stage for the highly concentrated CO₂ flue gas may be necessary to produce a CO₂ stream that meets transportation and sequestration requirements. This purification step should have significantly less cost than a conventional post-combustion capture system due to the high CO₂ concentration and reduced flue gas volume.

However, the appeal of oxy-combustion is tempered by a few key challenges, namely the capital cost and energy consumption for cryogenic air separation unit (ASU) operation, boiler air infiltration that dilutes the flue gas with N₂, and excess O₂ contained in the concentrated CO₂ stream. Flue gas recycle (~70 to 80%) is also necessary to approximate the combustion characteristics of air since currently-available boiler materials cannot withstand the high temperatures resulting from coal combustion in pure O₂. Consequently, the economic benefit of oxy-combustion compared to amine-based scrubbing systems is limited. As shown in Figure 1, construction of a new supercritical (SC) oxy-combustion coal-fired power plant equipped with a commercially-available cryogenic ASU would increase the COE by about 80% and reduce the net plant efficiency by more than 11 % points, as compared to a new SC air-fired, coal-based power plant without CO₂ capture. The parasitic power requirement for cryogenic O₂ production and CO₂ compression alone would increase the COE by nearly 60 %.

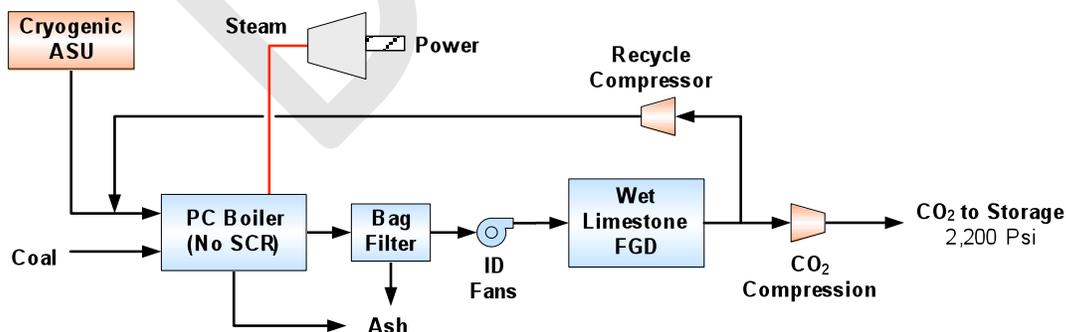


Figure 4. Block diagram illustrating power plant with oxy-combustion CO₂ capture.

2.3.1 Chemical Looping Combustion

Chemical looping combustion (CLC) is an advanced coal oxy-combustion technology that involves the use of a metal oxide or other compound as an oxygen carrier to transfer O_2 from the combustion air to the fuel, avoiding direct contact between fuel and combustion air, as shown in Figure 5.

The products from combustion (CO_2 and H_2O) are kept separate from the rest of the flue gases. Chemical looping splits combustion into separate oxidation and reduction reactions. In one potential configuration, chemical looping is carried out in two fluidized beds. The metal oxide (e.g., iron, nickel, copper, or manganese) releases the O_2 in a reducing atmosphere and the O_2 reacts with the fuel. The metal is then recycled back to the oxidation chamber where the metal oxide is regenerated by contact with air. The advantage of using the CLC process is that the CO_2 is concentrated once the H_2O is removed and not diluted with N_2 gas. Another advantage of CLC is that no separate ASU is required and CO_2 separation takes place during combustion.

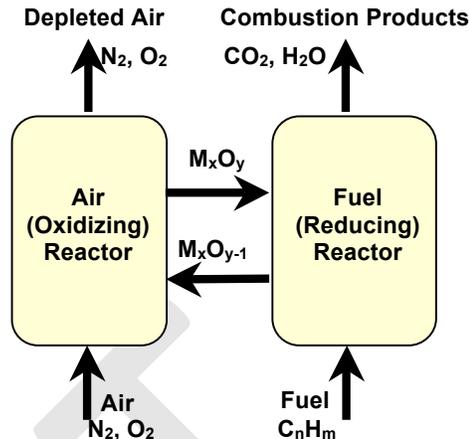


Figure 5. Schematic of chemical looping combustion process.

A related area of research is chemical looping gasification (CLG). In this system, two or three solid particle loops are utilized to provide the O_2 for gasification and to capture CO_2 . A loop, similar to that of CLC, is used to gasify the coal and produce syngas (H_2 and CO). A second solid loop is used in a WGS reactor. In this reactor, steam reacts with CO and converts it to H_2 and CO_2 . The circulating solid absorbs the CO_2 , thereby providing a greater driving force for the WGS reaction. The CO_2 is then released in a calcination step that produces nearly-pure CO_2 for further compression and sequestration.

2.3.2 Challenges and Technology Needs in Oxy-Combustion

Oxy-Combustion: The characteristics of oxy-combustion have not yet been fully developed. Oxy-combustion flame characteristics, burner and coal-feed design, and analyses of the interaction of oxy-combustion products with boiler materials are all areas in need of more research. In addition, because oxy-combustion produces a high- CO_2 flue gas that contains H_2O , excess O_2 , N_2 , SO_2 , NO_x , Hg , and other contaminants, flue gas purification technologies are needed. Companies such as Air Products are currently developing cryogenic purification schemes to remove these contaminants [10]. For oxy-combustion and IGCC to be cost-effective power generation options, a low-cost supply of pure O_2 is required. Although a cryogenic ASU can be used to supply high-purity O_2 to the boiler or gasifier, this commercially-available technology is both capital and energy intensive. Novel production technologies are needed to reduce the cost of O_2 production.

Chemical Looping Combustion and Gasification: Both CLC and CLG are in the early stages of process development [11]. Bench and laboratory-scale experimentation is currently being conducted. Projects in this pathway are advancing the development of chemical looping systems by addressing key issues, such as solids handling and O_2 carrier capacity, reactivity, and attrition. Table 3 provides a summary of the technical challenges for chemical looping technologies.

Table 3. Oxy-Combustion Advantages and Challenges

CO₂ Capture Technology	Description	Advantages	Challenges
<i>Oxy-Combustion</i>	Fossil fuel is combusted with pure oxygen diluted with recycled fuel gas. The combustion product is primarily CO ₂ and water.	<ul style="list-style-type: none"> • The combustion products are CO₂ and water. The relatively pure CO₂ is easily separated thus making the sequestration process less expensive. 	<ul style="list-style-type: none"> • Low cost oxygen supply is required. Currently very high cost. • High cost of CO₂ recycle • Develop processes to convert existing air fired furnaces to oxygen fired. • High temperatures can degrade boiler materials • Requires high temperature materials in new construction
<i>Chemical Looping</i>	Uses metal oxide or other compound as an O ₂ carrier to transfer O ₂ from the combustion air to the fuel, avoiding direct contact between fuel and combustion air.	<ul style="list-style-type: none"> • CO₂ and H₂O kept separate from the rest of the flue gases • ASU is not required and CO₂ separation takes place during combustion. 	<ul style="list-style-type: none"> • Undeveloped technology still conceptual and bench scale • Ash separation is problematic • Attrition-resistant metal oxide carriers required during multiple cycles

2.4 Cryogenic Separation

Cryogenic separation utilizes the attributes of a relatively clean flow stream where all flue gases except N₂ and CO₂ have been removed prior to cooling [12]. This process aims at setting the operational conditions at the triple point of CO₂ (-56.6 °C and 5.17 bars) so that CO₂ will condense while N₂ remains a gas. Once all of the other gases and particulates have been completely removed, the remaining gas is transported to a cryogenic vessel where the temperature and pressure are changed in such a way as to cause CO₂ to liquefy leaving N₂ as a gas. This process allows the N₂ to escape through an outlet at the top of the cryo-vessel while the highly concentrated liquid CO₂ can be collected at the bottom. A similar method commonly termed “refrigeration under pressure” also produces CO₂ from a mixture with N₂ but uses more intense pressurization and somewhat higher temperature compared to cryogenic distillation.

Cryogenic separation (distillation) has one distinct advantage over most other separation processes; its product is liquid CO₂, which is ready for transport via pipeline or tanker for storage. In addition to being ready for transport, the CO₂ recovery is very high (CO₂ purity after distillation can exceed 99.95%). The cryogenic process is however very energy intensive, wherein the energy required to keep the system cool (commonly using liquid N₂), makes the current process cost ineffective. The other limitation is that NO_x, SO_x, H₂O and O₂ must all be removed from the flue gas prior to cryo-processing. Refrigeration under pressure offers many of the same benefits to cryogenic separation, with similar drawbacks. The cost for cooling under pressure is lower, but more energy is required to pressurize the gases.

2.5 Status of CO₂ Capture Technology Field Testing

2.5.1 Amine-Based Solvent Processes.

With the potential of large-scale power plant CO₂ mitigation on the horizon, technology developers have begun to develop advanced next generation amine solvents. Two leading developers are Fluor

Corporation, with the development of the Econamine FG PlusSM technology, and Mitsubishi Heavy Industries (MHI), with the development of a line of hindered amines and structured packing [13, 14] The optimizations are focused primarily on extensive thermal integration of the CO₂ capture plant with the power plant and the development of improved solvent formulations with lower stripping steam requirements and lower solvent circulation rates than MEA. The following are some examples of the design improvements:

- Improved solvents (higher reaction rates, higher CO₂ capacity, and lower corrosion and degradation).
- Split flow configuration (flash regeneration and steam stripping).
- Absorber intercooling (higher reaction rates, smaller absorber size, lower rich solvent loading).
- Integrated steam generation.
- Structured packing (lower pressure drop and smaller absorber size).

It is important to point out that these technology improvements are still in the development stage and have yet to be demonstrated at power plant scale. To date, no commercial scale of Econamine FG PlusSM plants are operating, but it is being offered commercially by Fluor. A commercial 160 ton/day CO₂ capture plant using MHI's KS-1 technology has been in operation since 1999 at the Petronas Fertilizer Corporation in Malaysia, where the CO₂ is captured from reformer flue gas [8, 9] MHI is currently conducting pilot-scale, slip-stream testing (~10 ton/day CO₂ capture) at a coal-fired power plant in Matsushima, Japan. MHI's next step is to conduct full-scale testing (~500 ton/day CO₂ capture) demonstration at a coal-fired power plant.

2.5.2 Aqueous Ammonia-Based Solvent Processes.

In addition to various chemical amines, aqueous ammonia can be used as a solvent for CO₂ capture that relies upon a temperature swing to cycle between ammonium carbonate and ammonium bicarbonate. This has a significantly lower heat of reaction than amine-based systems, resulting in energy savings, provided the absorption/desorption cycle can be limited to this mechanism. Ammonia-based absorption has other advantages over amine-based systems, such as the potential for high CO₂ capacity, lack of degradation during absorption/regeneration, tolerance to O₂ in the flue gas, low cost, and potential for regeneration at high pressure. Alstom [14] developed the chilled ammonia process (CAP), in which the flue gas is cooled to less than 20°C to optimize the ammonium carbonate reaction with CO₂ and minimize ammonia slip. The resultant ammonium bicarbonate precipitates out of solution as a solid and is subsequently heated to approximately 80°C in the regenerator where the CO₂ is liberated. The ammonia carbonate is then recycled back to the absorber.

An ammonia solvent-based CO₂ capture process [Yeh and Pennline, U. S. patent 7,255,842, August 14, 2007] recently licensed by Powerspan Corporation (ECO₂TM) does not require additional flue gas cooling. Therefore, the process operates at a slightly higher temperature than the CAP process and the ammonium bicarbonate remains in solution. Ammonia slip is controlled via integration of the ECO₂TM process with the ECOTM multi-pollutant control system. Powerspan is currently conducting a 1-MW pilot test at FirstEnergy's R.E. Burger Power Station in Ohio.

2.5.3 National Carbon Capture Center. The DOE Office of Fossil Energy, EPRI, and Southern Company are responding to the need for developing cost-effective CO₂ capture technology for coal-based power generation with the addition of the National Carbon Capture Center (NCCC) at the Power Systems Development Facility (PSDF). The PSDF is an engineering-scale demonstration site for advanced power system components located adjacent to Alabama Power's coal-fired Plant Gaston in Wilsonville, Alabama. The PSDF-NCCC can test multiple projects in parallel with a wide range of test equipment sizes leading up to pre-commercial equipment sufficient to guide the design of full commercial-scale power plants. The PSDF-NCCC will be capable of testing pre-, post-, and oxy-combustion technologies. The backbone of the pre-combustion CO₂ capture technology development will be a high-pressure

flexible facility designed to test an array of solvents and contactors. For R&D projects that have been successfully tested at bench-scale in a research lab, the PSDF-NCCC will provide a 1,000 lb/hr flue gas slipstream for screening tests. For technologies that have been successfully tested at the screening-scale, two pilot test beds have been designed, a 5,000 lb/hr (0.5-MW equivalent) slipstream and a 10,000 lb/hr (1.0-MW equivalent) slipstream.

3.0 Materials for Carbon Capture

CO₂ capture systems use many of the known technologies for gas separation which can be integrated into the basic systems for CO₂ capture highlighted in Section 2. Much of this technology centers on the sorptive or separation properties of liquid solvents, solid sorbents or membranes. The state of our knowledge and technologic needs for each of three areas are summarized in this section.

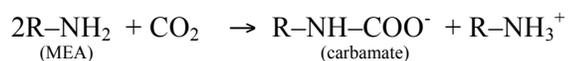
3.1 Liquid Absorbents

The idea of separating CO₂ from flue gas started in the 1970s – not out of concern about greenhouse gas emissions but as a source of potential economically valuable CO₂, mainly for enhanced oil recovery. Taking a cue from industries that needed to remove acid gas impurities (e.g. H₂S and CO₂) from their flow steam, the power industry started to explore the use of chemical adsorbents, specifically monoethanolamine (MEA) solvent, to capture CO₂. MEA is an organic chemical belonging to the family of compounds known as amines. As the first technology of choice for CO₂ capture, amine scrubbing was evaluated in 1991 [16] and was deemed to have unacceptable energy use and costs (materials cost; energy penalty due to water usage and regeneration processing). However, it had been successfully applied to gas [17] and coal-fired plants [18] at a small scale in the early 80s. Despite the cost and inefficiency, amine scrubbing is now a key technology for post-combustion capture. It is expected that new coal-fired power plants may also use post-combustion CO₂ capture by amine scrubbing with ultrasupercritical boiler cycles. Therefore intensive research on the fundamental materials and processes of that build upon amine chemistry will provide a certain, large, payoff.

3.1.1 Amine Scrubbing

CO₂ removal by absorption/stripping with aqueous amine is well-understood and heavily used. A continuous scrubbing system is used to separate CO₂ from a gaseous stream. The system consists of two key components, an absorber in which the CO₂ is absorbed into a solvent, and a regenerator (or stripper), in which CO₂ is released in concentrated form and the original solvent is recovered [19]. CO₂ is absorbed from a fuel gas or combustion gas near ambient temperature into an aqueous solution of amine with low volatility. The amine is regenerated at 100–120 °C by stripping with water vapor produced in a steam-heated reboiler. The hot lean solution is used to preheat the cold rich solution in a cross-exchanger. Water is condensed from the stripper vapor leaving pure CO₂. Chemical absorption systems tend to be more efficient than physical absorption systems because the process is accompanied by a chemical reaction that enhances the over all mass transfer from the initial gas phase to the liquid phase. Despite the cost and inefficiency, currently hundreds of power plants remove CO₂ from natural gas, hydrogen, and other gases with low oxygen. In CCS, the CO₂ would be captured and compressed to 100–150 bar for geologic sequestration.

The process chemistry is complex, but the main CO₂ absorption reaction taking place is given as [20]:



MEA regeneration involves the application of heat to the products formed in this reaction to liberate CO₂ leaving MEA as a product. There is a sizeable energy penalty for the heat required to regenerate the solvent because substantial energy is needed to heat the water/amine solution and break bonds in the carbamate. This heat requirement significantly reduces the net efficiency of the power plant. Pure MEA (with R = HO – CH₂CH₂) is an unhindered amine that forms stable carbamate; hence, only half a mole of CO₂ is absorbed per mole of amine, as depicted in this reaction. For hindered amines (where R is a bulky group; e.g. KS-1), the carbamate formed is not stable, and an alternate reaction leads to higher theoretical capacity of one mole of CO₂ per mole of amine [21, 22]. The drawback is that CO₂ uptake via hindered amines is very sluggish.

3.1.2 Challenges and Technology Needs in Amine Absorption

Further development of this technology will provide more efficient systems to reduce energy cost, large single absorbers, heat exchangers, and compressors to reduce capital cost, and more robust solvents to reduce makeup costs and secondary environmental impact. MEA processing of CO₂ offers a number of distinct advantages including (a) easy retrofitting – i.e. end-of-the-pipe treatment, (b) effective for dilute CO₂ streams between 3 and 15%, (c) functions well at ordinary temperature and pressure power plant conditions, (d) produces a high-purity reaction product - >98%, and (e) is commercially available [19]. The disadvantages include the substantial energy penalty due to the heat required to regenerate the solvent, loss of solvent due to physical losses, entrainment, vaporization, chemical degradation, and corrosion particularly when O₂ content are high.

Research opportunities leading to improved amine solvents exhibiting better energy performance may be realized by targeting key issues related to their physicochemical properties:

1. Greater thermal stability of the solvent will permit solvent regeneration at greater temperature and pressure. Alkanolamines and other hydrophilic amines typically degrade at 120–130 °C. Cyclic aliphatic diamines such as piperazine are stable up to 150 °C. Other useful structures could be identified that are thermally stable.
2. Greater capacity will reduce the inefficiency of heating and cooling the solvent. Greater solvent concentration increases capacity but also increases viscosity which increases the cost of the cross exchanger. Greater capacity can be achieved by manipulating the volume of CO₂ to volume of absorber ratio. Anhydrous solvents are probably not practical because there is always water in these systems.
3. Greater CO₂ absorption/desorption rates will allow smaller driving force and more reversibility in the absorber. Piperazine provides the fastest rate of the known amines. Other amine structures or enzymes could be used to accelerate CO₂ absorption.

Reduced capital and energy costs will come with amines other than MEA, but there cannot be major improvement since the existing designs already provide about 50% thermodynamic efficiency. Concentrated piperazine (PZ) is a thermally-resistant solvent with a high heat of CO₂ absorption that claims to reduce power loss to 0.24 MWH/tCO₂ by operating the stripper at 150°C. [23] Vacuum stripping or solvents with a lower heat of absorption will not get the full impact of thermal swing stripping and will require more energy [23] Solvents with greater capacity, such as KS-1, minimize sensible heat losses from heating and cooling the circulating solvent. Solvents with a faster rate of CO₂ absorption, such as methyldiethanolamine/PZ, allow for adequate absorber performance with more dissolved CO₂ in the rich and lean solvent, resulting in reduced energy use by the stripper [23].

Improved solvent systems must have low makeup cost, reliable operating characteristics, and minimum impact on the environment. These objectives may be satisfied by meeting these criteria:

1. Slow rate of thermal and oxidative degradation with nontoxic, easily separated degradation products

2. Low volatility at lean conditions, preferably no volatility so that a water wash is unnecessary.
3. Commercially available in large quantities at low cost (less than \$10/lb)
4. Environmentally benign components and degradation products
5. Easily reclaimed from coal flue gas impurities such as sulfate, fly ash, metal, gypsum.
6. Compatible with inexpensive material of construction such as carbon steel and polymers.
7. Preferably two phase (gas and liquid). Additional liquid and solid phases can result in unreliable systems.
8. Non-foaming.

MEA is subject to oxidative and thermal degradation, [24, 25] but it is the least expensive amine and its losses are expected to be less than \$5/tCO₂. Impacts of SO₂, NO_x, and fly ash on solvent degradation will be minimized by efficient upstream equipment and a polishing scrubber. Oxidative degradation can be minimized by additives such as free radical scavengers [25]. Thermal degradation can be minimized by operating the stripping systems at lower temperature (e.g. 100 °C). Volatile amine emissions in the clean gas are easily avoided by a water wash section at the top of the absorber. Advanced amines such as proprietary hindered KS-1, piperazine [24], and ethyldiethanolamine [26] are resistant to degradation but are more expensive and will require more complex gas pre-treating to avoid economic losses from process upsets and the effects of SO₂, NO_x, and fly ash. More expensive solvents, such as ionic liquids, will be more economically sensitive to process upsets and other impurities, even if they are otherwise stable.

Recently, an innovative CO₂ capture system based on the formation of amidinium or guanidinium alkylcarbonate salts with good reactivity and high absorption capacity has shown interesting promise [27-31] This CO₂ capture system consists of an alcohol and a strong amidine (or guanidine) base. Compared with aqueous solution systems, the low specific heat and reduced hydrogen bonding in alkylcarbonate salts result in less energy intensive CO₂ release [32]. Unfortunately, volatilization of alcohol, as well as the recombination of CO₂ with volatilized species (i.e., alcohol and/or base) can lead to loss of organic solvent and increased operating costs associated with preventing CO₂ recombination losses during desorption. Hence, there remains a strong need to develop alternative technologies and approaches for the efficient and reversible capture of CO₂ without incurring loss of volatiles (e.g., alcohols, water).

3.1.3 Alternative Liquid Sorbents

Ionic liquids (ILs) are a class of compounds showing significant potential for CO₂ separation applications. Ionic liquids are organic salts molten below 100 °C whose cations, substituents, and anions can be varied virtually at will to tune their chemical and physical properties. Examples of typical cations and anions of ILs are shown in Figure 6. ILs act much like good organic solvents, dissolving both polar

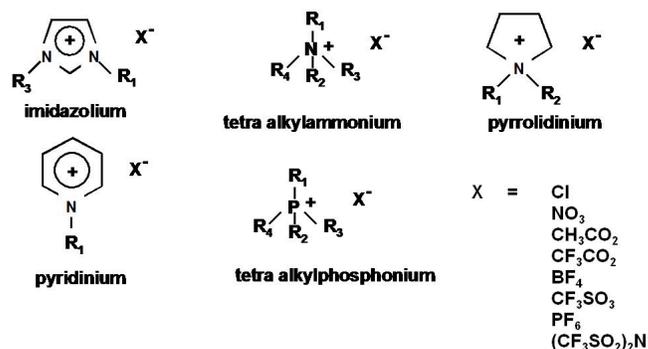


Figure 6. Examples of typical ILs [33].

and non-polar species. In many cases, they have been found to perform much better than commonly used solvents. Perhaps the most intriguing feature of these compounds is that, while they are liquid in their pure state at or near room temperature, they have essentially no vapor pressure. *They do not evaporate*, and so they cannot lead to fugitive emissions. Many of these compounds are liquids over incredibly large temperature ranges, from below ambient to well over 300 to 400 °C, which suggests they could be used under unique CO₂ processing conditions [33-35].

For use in CO₂ separations, the tunability of ILs is invaluable. There are virtually endless possibilities for cations, anions, substituents, and functional groups that can be incorporated into ILs. As a result, there are innumerable combinations possible, providing the opportunity to optimize physical and chemical properties for specific applications like CO₂ capture.

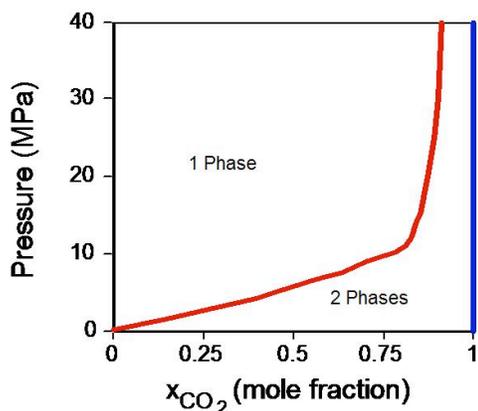


Figure 7. Phase diagram of CO₂ with 1-butyl-3-methylimidazolium hexafluorophosphate [36].

The solubility of CO₂ in an ionic liquid was first measured in 1999 [35], as shown in Figure 7. The discovery that CO₂ had significant solubility within ILs led to the idea of using ILs as a sorbent for separating CO₂ from other gases [37].

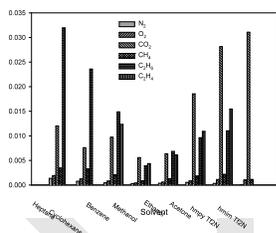


Figure 8. Solubility of CO₂ in various solvents at a partial pressure of 1 atm and temperature of 298.15 K [38].

The simplest way to separate CO₂ from other gases would be taking advantage of the difference in the physical solubility of the different gases in the ILs. Numerous investigations have shown the solubility of CO₂ in various different ILs increases with increasing pressure, reaching values as high as 20 or 30 mole % at 10 bar of partial pressure at 25 °C. As expected, CO₂ solubility decreases with increasing temperature. By comparison, the solubility of gases such as N₂ and O₂ in ILs tends to be quite low. This is shown clearly in Figure 8, where the solubility of various gases are shown at room temperature and 1 bar of partial pressure in common solvents and two ILs [37]. Clearly, the selectivity (solubility of CO₂/solubility of N₂ or O₂) is higher for the ILs than the common solvents.

3.1.4 Challenges and Technology Needs for ILs

Performing CO₂ separations using differences in physical solubilities in ILs would be best suited for applications where the CO₂ partial pressure is relatively high. An example would be separation of CO₂ from hydrogen or syngas produced from gasification of a fossil fuel or biomass (followed by reverse water gas shift).

The capacity of ILs for CO₂ using physical dissolution is too low for performing separation from post-combustion flue gas where the partial pressure of CO₂ is only 0.1 – 0.14 bar. In this case, ILs can be designed to have much greater affinity for CO₂ by incorporating functional groups that react with CO₂. Tethering an amine to the cation [39], first showed high capacity for CO₂, with chemistry similar to conventional amines, where two cation-tethered amines are required for each CO₂. Since the solubility of other gases, such as N₂ and O₂ is still low, this means excellent selectivity. Subsequently, it has shown that by tethering the amine to the anion, only one amine functionalized IL is required to complex one CO₂ molecule [40]. With 1:1 stoichiometry and since no added water is required, it is possible to achieve high CO₂ capacity, even on a volumetric basis, even though the IL is higher molecular weight than conventional amines. More importantly, by choice of the anion and cation, it is possible to tune the enthalpy of reaction. As a result, systems-modeling shows that it should be possible to achieve a 30% reduction in the parasitic energy requirements for the post-combustion CO₂ capture system using functionalized ILs compared to aqueous MEA [41]. One potential challenge with functionalized ILs is that there have been numerous reports that their viscosity increases substantially when they complex with CO₂ [42], rendering them unsuitable for a conventional absorber/stripper process system. This increase in viscosity also occurs with conventional amines; however, the dilution of conventional amines with water, which has a low viscosity of just 1 cP at ambient conditions, ameliorates this problem. Rather than diluting the ILs with a low viscosity solvent, one can solve this problem with appropriate tailoring of the chemistry [43]. Therefore, there are now functionalized ILs that react with CO₂ and have high CO₂ capacity but that do not increase in viscosity.

The potential benefits of IL sorbents over conventional aqueous amines include:

- extremely low volatility
- the opportunity to regenerate the IL sorbent over a wider range of temperatures in order to minimize parasitic energy loss
- elimination of the need to dissolve the sorbent in water
- less energy loss in the regeneration step to evaporation of water since the sorbent is not an aqueous solution
- potentially lower corrosion, in part due to the low water content
- significantly lower parasitic energy losses, as demonstrated by systems modeling
- the potential to even further tune the ILs for CO₂ capture applications by choice of anion, cation and functional groups

There are a number of challenges, providing opportunities for research, associated with the use of ILs for CO₂ capture applications.

1. Most importantly, these compounds are new and not available commercially in bulk quantities. In particular, functionalized ILs suitable for post-combustion CO₂ capture are still in the laboratory development stage. As a result, significant effort would be needed to produce commercial quantities at reasonable prices.
2. In addition, the functionalized ILs developed to date contain amine functionality so they would still be susceptible to poisoning by SO₂. Therefore, the use of ILs for post-combustion CO₂ capture would not eliminate the flue gas desulfurization step. By contrast, many non-functionalized ILs suitable for CO₂ separations by physical solubility differences are completely tolerant to SO₂. In fact, SO₂ is very soluble in them so simultaneous CO₂ and SO₂ removal might be possible. Other unknowns include tolerance to other impurities in pre- or post-combustion flue gas, long term stability and exact corrosion rates.
3. Finally, for functionalized ILs that react with CO₂, we lack any sort of fundamental molecular-level understanding of the reaction mechanism and the kinetics.

3.1.5 Ionic Liquid-Supported Membranes

Polymer-based membranes are being investigated as an alternative separation material because they are less energy intensive, undergo no phase change in the process, and typically provide low-maintenance operations. Polymer membranes have been used successfully in a number of industrial applications, including air separation. Recently published systems analysis and feasibility studies demonstrate that membranes are a technically and economically viable option for CO₂ capture from flue gas exhaust in coal fired power plants [44-46]. Membrane performance is dictated by the membrane permeance (pressure normalized flux) and selectivity for the components of interest. In the case of flue gas separation, the CO₂ permeance and the selectivity for CO₂ over N₂ are of primary interest. Commercially available membranes for CO₂ separation from air have low CO₂ permeance characteristics, ca. 100 GPU (1 GPU = 10⁻⁶ cm³cm⁻²s⁻¹cmHg⁻¹). All else equal, the membrane area required for a given application scales linearly with the permeance for a given gas flux through the membrane. Thus, a ten fold increase in permeance equates to a ten fold decrease in the membrane area required to achieve the same productivity. Reduced membrane area requirements also translate into smaller membrane footprint requirements and correspondingly better system economics. In a recent study, Merkel et al. have shown that the optimal membrane selectivity for separation of CO₂ from flue gas is in the range of 20 to 40 and that increasing membrane permeance is *the* critical factor to reduce capture costs [47]. For example, they show that for a given process scheme, a system comprised of a membrane with a selectivity in the aforementioned range and CO₂ permeance of 1000 GPU results in a cost per ton of CO₂ captured of ~\$32 (Figure 9)

A 4-fold increase in CO₂ permeance to 4000 GPU decreases this cost by nearly 50% to ~\$18. While the reduction of separation cost versus gas permeance is nonlinear, it is clear that a permeance of 10,000 GPU would result in a cost per ton of CO₂ captured of less than \$10. This is a *significant* reduction compared to both the benchmark amine technology and the current membranes under development for this application. Realization of such a high permeance membrane would be a transformational achievement resulting in a membrane based separation

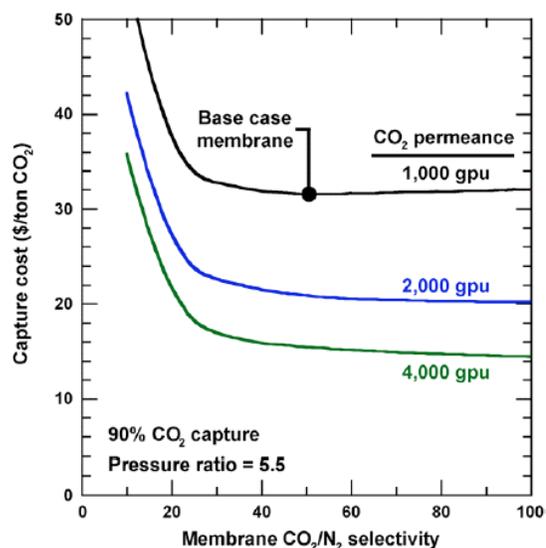


Figure 9. Effect of membrane CO₂/N₂ selectivity on the cost of capturing 90% of the CO₂ in flue gas for membranes with a CO₂ permeance of 1000, 2000, and 4000 gpu

technology for post combustion CO₂ capture that would *exceed* the current DOE targets (\$20-25 per ton of CO₂; <35 % increase in COE) in sensational fashion. Production of a membrane with a selectivity of at least 20 and a permeance of at least 10,000 GPU is the goal. One way achieve this goal these high permeances and selectivity is a combination of ILs and membranes.

3.1.6 Challenges and Technology Needs for ILs and Polymer Membranes

Unlike traditional organic media, the properties of ILs may be adjusted via chemical alteration of the cation or anion to produce application specific compounds. Thus, the potential exists to tune the IL such that one of the ions (cation or anion) functions as a complexing agent for the desired sorbate, tremendously increasing the sorption capacity of the IL. Recent studies on ILs indicate that the combination of subtle (*e.g.*, changing cation substitution patterns) and gross (*e.g.*, changing the anion type) modifications enables very precise tuning of the IL solvent properties [48]. Changes in solvation properties are possible in this way, thus enabling the rational design of application specific ILs. These so-called “task specific” ILs can also be “tuned” to absorb very high quantities of a specific gas, *e.g.* CO₂. For example, Davis and co-workers reported the synthesis of an IL containing an amine functionality that was capable of absorbing 0.5 mol of carbon dioxide per mole of IL (approx. 6 mL/g IL) [39].

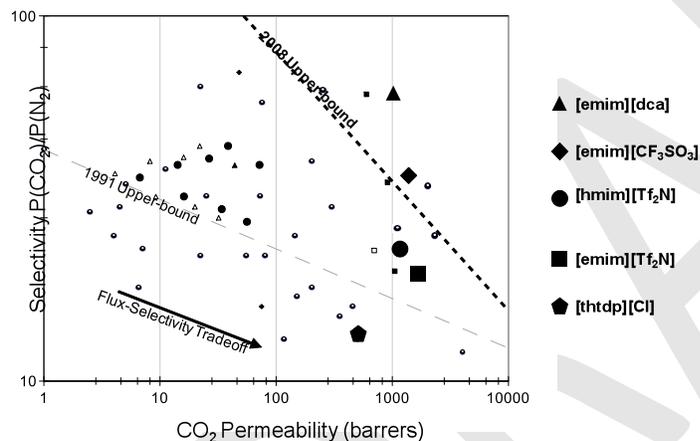


Figure 10. (Left) Robeson plot of ionic liquids used as SLMs and representative polymers (small circles) [52]. (Right) plot of selectivity vs. permeability for CO₂/N₂ separations. Ionic liquids exceed the “upper bound” observed for polymer membranes.

Previous research has demonstrated that supported liquid membranes (SLMs) containing ILs can be prepared and used for gas separations [39, 49, 50]. We have demonstrated that relatively stable SLMs could be made by impregnating commercially available micro-porous hydrophilic polymeric (polyethersulfone (PES)) or ceramic (Alumina Anodisc[®]) substrates. These membranes exhibited a combination of high permeability [51] and selectivity for carbon dioxide as shown in Table 4 and Figure 10 [49]. Further, Condemarin et. al. recently reported exceptional long term stability of SILMs in mixed gas testing [53]. All these data demonstrate the significant potential of IL-SLMs for CO₂ capture from flue gas.

The ability of materials to perform a particular separation in a membrane format is frequently represented on Robeson plots of selectivity vs. permeability [54]. For the separation of CO₂ and N₂, several emim-containing ILs have demonstrated performance well above that represented by the so-called Robeson upper-bound observed for dense polymers, *including commercial ones* (Figure 10, Table 4). They also have demonstrated excellent stability in chemically challenging environments as well as thermal stability

over a broad temperature range (sub-ambient to > 200 °C). As a result, this class of materials has separation performance characteristics that demonstrate their potential as a medium for the removal of CO₂ from flue gas. The industrial implementation of this class of exciting materials has not yet been realized for this application due to low productivity (permeance) and the mechanical stability limitations inherent to the IL-SLM format.

Table 4. Gas transport properties of various supported ionic liquid membranes. Some unpublished data recently obtained by the Noble group is also included [55] (PES: polyethersulfone; PSF: polysulfone).

Ionic Liquid	Support	CO ₂ Permeability (Barrer)	CO ₂ /N ₂ selectivity	Reference
[emim][Tf ₂ N]	PES	960	21	Scovazzo[53]
[emim][CF ₃ SO ₃]	PES	920	35	Scovazzo[53]
[emim][dca]	PES	610	61	Scovazzo[53]
[thtdp][Cl]	PES	350	15	Scovazzo[53]
[H ₂ NC ₃ H ₆ mim][Tf ₂ N]	nylon	80	-	Myers[56]
[hmim][Tf ₂ N]	PSF	860	-	Llconich[57]
[bmim][BF ₄]	PES	2500	55	Zhao[58]
[C ₆ mim][Tf ₂ N]	PES	700	23	Voss[50]
[C ₆ mim][Tf ₂ N]	PES	650	22	Voss[50]
[emim][Tf ₂ N]	Anodisc	1628	36	Noble[55]
[emim][dca]	Anodisc	946	58	Noble[55]

Thus, the key challenges hindering the realization of a transformational separations technology based on IL membranes for flue gas application are:

1. The achievement of a mechanically stable, commercially viable IL membrane platform that retains the chemical stability, thermal stability, and permselectivity characteristics that have been demonstrated in this class of materials.
2. Realization of such a platform in concert with the development of a fabrication/coating technology to enable preparation of very thin, high permeance, defect-free selective layer films ($\leq 1 \mu\text{m}$) on a suitable support. The ultimate game changing technology resulting from the successful achievement of those goals would be a chemically, mechanically, and thermally robust IL-based membrane system with a permeance of > 10,000 GPU and a selectivity of at least 20 under industrially relevant operating conditions (see Figure 9) that will *exceed* the current DOE targets (\$20-25 per ton of CO₂; <35 % increase in COE) in sensational fashion.
3. A commercial process for removal of smoke and oxides of sulphur from flue gases

3.2 Solid Adsorbents

New classes of solid adsorbents are being investigated to complement the existing arsenal of ionic liquid adsorbents and transport-controlling membranes. These new hybrid materials consist of metal ions with well-defined coordination geometry linked to organic bridging ligands.

3.2.1 Metal-Organic Frameworks (MOFs)

Over the past decade, metal-organic frameworks (MOFs) have emerged as a new class of microporous solids exhibiting record surface areas of up to 5200 m²/g, as well as tunable pore sizes and surface chemistry [59]. MOFs, also known under the names such as porous coordination polymers, are typically

crystalline powders obtained from a high-dielectric solvent by reaction of a metal salt with a multitopic organic bridging ligand capable of linking the metal cations into a porous three-dimensional network structure. Subsequent heating under dynamic vacuum or treatment by supercritical drying [60] evacuates the solvent molecules from the pores of the structure without destroying the network connectivity and crystallinity. Owing to their exceptionally high surface areas, these materials can exhibit tremendous capacities for compressed gas storage, delivering the highest known storage densities for CH₄, C₂H₂, CO₂, and cryogenic H₂ [61]. A high surface area is also beneficial for CO₂ capture, where it can ensure a high loading capacity and, assuming good permeability, rapid adsorption as a result of the large gas-solid interface. Most importantly, however, MOFs offer the possibility of using the power of synthetic chemistry to tailor the nature of their internal surfaces and thereby adjust the CO₂ adsorption selectivity.

MOFs are of potential utility for capturing CO₂ under a variety of scenarios. Of particular interest is capture from the flue gas emitted by fossil fuel power plants using a pressure and/or temperature swing adsorption process. They are additionally of interest for applications in natural gas sweetening, in the efficient capture of O₂ from air for oxyfuel combustion, and in precombustion capture of CO₂ from the higher pressure (50-60 bar) synthesis gas obtained upon coal gasification. For this last application, further research into methods for integrating MOFs within membranes is essential. Finally, it should be noted that MOFs are also of possible value for the transport of compressed CO₂ gas subsequent to capture [61c].

For adsorptive separations, differences in size and/or electronic properties can be utilized. The major separation issue for a flue gas with an overall pressure of 1 bar is the separation of CO₂ (ca. 15-16 % by weight) from N₂ (70-75%), ideally in the presence of water vapor (5-7%) and O₂ (3-4%). Separations can be achieved on the basis of the smaller kinetic diameter of CO₂ (3.30 Å) compared with N₂ (3.64 Å), but it should be kept in mind that the small pore sizes required may severely impede gas permeation. Typically, CO₂ is preferentially adsorbed over N₂ because it has a greater polarizability (29.1 x 10⁻²⁵ cm³ vs. 17.6 x 10⁻²⁵ cm³) and quadrupole moment (-13.4 x 10⁻⁴⁰ Cm² vs. -4.7 x 10⁻⁴⁰ Cm²). For a high selectivity to be achieved, the adsorbent should have a large heat of adsorption for CO₂ compared with the other gases; however, increases in selectivity will also come with a penalty in the energy required to release the CO₂ and regenerate the adsorbent.

Structural Considerations: The following are some structural issues worthy of consideration in attempting to design MOFs suitable for CO₂ capture from flue gas.

Surface area. As mentioned, the very high surface areas of MOFs can be an advantage for achieving a high gravimetric CO₂ adsorption capacity. Surface areas in excess of 4000 m²/g have been reported for a number of MOFs [62]. When making comparisons of surface areas, however, one must be careful to ensure that the values have been calculated correctly [63]. Of course, it is also important that the exposed surface area within a MOF have a strong affinity for CO₂ if a high loading capacity is to be achieved at the relevant partial pressure of 0.1 bar.

Pore size. MOFs featuring small pore openings can serve to give selectivity for CO₂ over N₂ by restricting access to the larger N₂ molecules. For example, Mn(HCO₂)₂ with 4.5-Å zig-zag channels exhibits a 10-fold selectivity for adsorbing CO₂ over N₂ or CH₄ at 1 bar and 195 K [64]. To obtain narrow pores, one can utilize short bridging ligands, such as formate in this example, or rely upon interpenetration, wherein two or more distinct networks are interwoven. Another means of using pore size for gaining selectivity is by taking advantage of the temperature-dependent dynamics of substituents on the bridging organic ligand (e.g., *t*-butyl groups) positioned near the pore openings [65]. In all of these cases, it will be important to measure the kinetics of flue gas permeation. Indeed, it is not yet clear, but it may in fact prove necessary to have quite large pore openings (of ca. 10 Å diameter or greater) to ensure rapid permeance of the flue gas.

Framework flexibility. Certain MOFs can exhibit a structural flexibility in which the framework retains connectivity while undergoing a breathing motion, typically involving a volume change of 50-85%, in response to a gas or liquid [66]. For example, Cr(OH)(BDC) (MIL-53(Cr)) flexes upon interaction with CO₂, resulting in a contraction of the framework at pressures of 1-4 bar. On increasing the pressure of CO₂ to ca. 6 bar, the structure expands and the pores widen to adsorb more CO₂ [67]. Since no equivalent effect occurs for CH₄, a comparison of single-gas isotherms suggests a very high selectivity for CO₂ over CH₄. The results of breakthrough experiments performed with CO₂/CH₄ mixtures at 10 bar and 303 K show that selectivity is indeed observed in the mixed gas system, although it is not as high as predicted from the single-gas isotherms [68]. In general, it is not clear if this mechanism is truly viable for performing gas separations, since once one of the gas components triggers pore opening, all of the gases may then be permitted entry.

Affinity of the Surface for CO₂. Given the low partial pressure of CO₂ in a flue gas (ca. 0.1 bar), it is essential that the internal MOF surface have a high selectivity for binding CO₂ preferentially over N₂. At least two methods for accomplishing this are now well-established.

Exposed metal cation sites. Owing to the greater polarizability and quadrupole moment of CO₂, variations in the charge distribution on the MOF surface can provide an excellent means of achieving selectivity over N₂. In particular, the large positive charges created upon desolvation and exposure of a metal cation embedded within the surface can afford a strong induced dipole interaction with CO₂. A range of MOFs of this type have been created and evaluated for hydrogen storage applications, [69] and many of the same materials are of potential interest for CO₂ capture. Of the examples tested to date (see Figure 11), [70] the most promising by far are the isostructural compounds M₂(dhtp) (M = Mg, Co, Ni, Zn; H₂dhtp²⁻ = 2,5-dihydroxyterephthalate). [71] These MOFs contain one-dimensional hexagonal channels that are lined with a high concentration of exposed M²⁺ cations, each capable of binding a CO₂ molecule in an end-on fashion (see Figure 12). [71b] Within this series, Mg₂(dhtp) exhibits the best performance in terms of uptake capacity (23.6 wt % or 5 mmol/g of CO₂ at 0.1 bar and 296 K) and the heat of CO₂ adsorption (-47 kJ/mol). This MOF has also been utilized in the quantitative separation of CO₂ over CH₄ in breakthrough experiments, where it was further shown that after loading the CO₂ can be readily removed by heating at 80 °C [71c]. The ability to obtain an isostructural family of compounds with different metal cations is potentially important here, since variation of the charge density at the exposed metal site provides a powerful means of adjusting the CO₂ adsorption enthalpy to match with that needed for a specific power plant design.

Surface functional groups. Coating MOF surfaces with polar functional groups can provide another means of gaining selectivity for CO₂ adsorption. In particular, substituents on the organic bridging ligands, including chloro (-Cl), bromo (-Br), fluoro (-F), nitrile (-CN), nitro (-NO₂), and amino (-NR₂) groups can enhance the

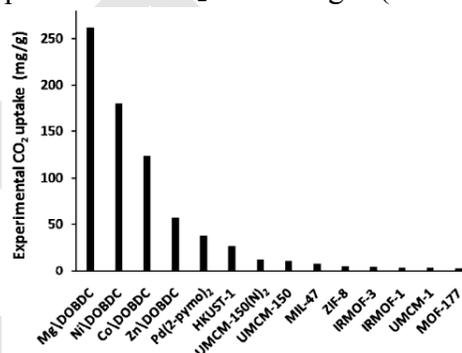


Figure 11. Comparison of CO₂ uptake capacities for selected MOFs at 0.1 bar and 293-298 K [70]. Note that DOBDC = dhtp.

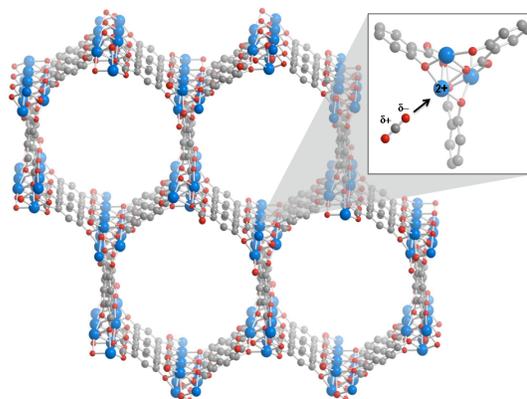


Figure 12. A portion of the crystal structure adopted by the MOFs M₂(dhtp) (M = Mg, Co, Ni, Zn), wherein open M²⁺ cation sites lead to a preferential binding of CO₂ over N₂.

electronic interaction with CO₂. Amine groups are perhaps most noteworthy here, since aqueous solutions of ethanolamine are currently used commercially for CO₂ scrubbing. In general, alkylamine groups will react reversibly with CO₂ to form either carbamates via nucleophilic attack of the lone pair of the amino group on the C atom of CO₂, or ammonium bicarbonate. By functionalizing a MOF surface with dangling alkylamine groups it should therefore be possible to create a solid adsorbent with a very high CO₂ binding selectivity. Importantly, it should be possible to adjust the strength of the interaction with CO₂ by varying the R groups of the amine. Indeed, aromatic amino groups are much less basic, and accordingly have a relatively weak interaction with CO₂.

Modeling CO₂ Adsorption and Transport in MOFs : Molecular-level modeling is playing an important role in improving our understanding of CO₂ adsorption and transport in MOFs. Molecular simulations based on classical mechanics and statistical mechanics can predict uptake amounts of CO₂ and other small gases in MOFs, heats of adsorption, selectivity for mixtures, diffusion coefficients, and detailed molecular-level information on where molecules sit within the MOF pores and how they move. Quantum mechanical (QM) calculations can provide information on binding of CO₂ to strong adsorption sites, as well as energetic and other information that can be fed into Monte Carlo simulations, but the QM methods do not directly predict adsorption isotherms. The application of these methods to adsorption and diffusion in MOFs has recently been reviewed [72].

Initial work in the field focused on modeling one material at a time, testing the ability of simulations to predict adsorption isotherms in agreement with experiment, and using simulation results to obtain additional insights beyond those available from experiment. Currently, there is a shift to screening larger numbers of materials. Figure 3 shows that simulated isotherms for CO₂ in MOF-177, IRMOF-1, and IRMOF-3 are in excellent agreement with experimental data [73]. It should be noted that the simulation results were not fit in any way to this data; nevertheless, they are able to capture the complex shapes of these isotherms essentially quantitatively. The CO₂ isotherm in IRMOF-1 shows an unusual inflection at 298 K, which grows into a distinct step as temperature is decreased. Further analysis of the results shed additional light on the cause of the inflection and steps and showed that the pore-filling pressure shifts toward the bulk condensation pressure with increasing pore size [73].

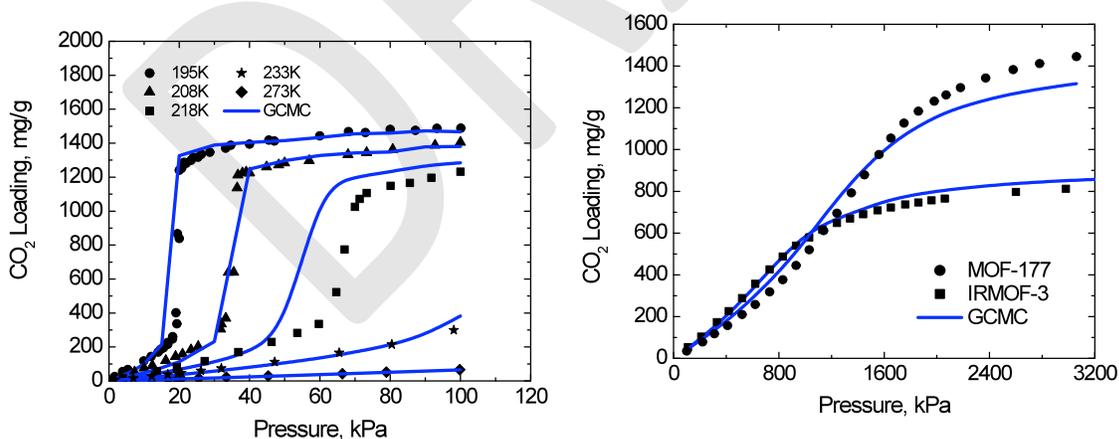


Figure 13. Left: Comparison of adsorption isotherms for CO₂ in IRMOF-1 at various temperatures from grand canonical Monte Carlo (GCMC) simulations (lines) and experiments (symbols). Right: Comparison of adsorption isotherms for CO₂ in MOF-177 and IRMOF-3 at 298 K from GCMC simulations and experiments.

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Researchers have recently begun to compare CO₂ uptake across families of different MOFs. For example, Yang et al. [74] investigated the effects of organic linker, pore size, pore topology, and electrostatic fields

on the adsorption of CO₂ in nine different MOFs. They found that the enthalpy of adsorption plays an important role at low pressures, so that there is a correlation between CO₂ uptake and the adsorption enthalpy. At higher pressures, CO₂ uptake correlates with the material surface area and free volume. A similar trend was observed by Yazaydin et al. [70], who examined a more diverse group of 14 MOFs and reported experimental uptake at conditions relevant for flue gas capture in addition to results from molecular simulation. The simulation results were in good agreement with experiment, especially in ranking the MOFs for CO₂ uptake at 0.1 bar (representative of flue gas conditions). For example, the simulations correctly predicted the top 5 MOFs for uptake of CO₂ at 0.1 bar in agreement with experiment [70]. It should be emphasized that good agreement between simulation and experiment relies on careful characterization of the materials used in the experiments. Simulations model adsorption in the “perfect” MOF crystal structures reported from single-crystal x-ray diffraction. If powder samples used for adsorption measurements differ from these structures, one should not expect good agreement between simulation and experiment. Deviations could include partial collapse of the MOF upon solvent removal, residual solvent molecules in the MOF pores, or unreacted molecules from the MOF synthesis.

3.2.2 Zeolitic Imidazolate Frameworks (ZIFs)

Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal-organic frameworks that consist of a tetrahedral cation coordinated by an organic imidazolate (IM) bidentate ligand, or substituted derivative thereof [75]. In the large majority of ZIFs that have been synthesized to date the central cation is Zn²⁺, although several examples of ZIFs containing Co²⁺ can be found in the literature [75-77]. ZIFs carry their “zeolitic” moniker not from any *chemical* similarity to silicon-based zeolites, but rather due to their *structural* analogy: the Zn-IM-Zn bond angle in a ZIF is nearly identical to the Si-O-Si in conventional zeolites (Figure 14) [75]. This correspondence leads to the formation of similar three-dimensional structures for both compounds, containing large pore regions, interconnected by (typically) more constricted entrances (apertures) (Figure 15). Yet in contrast to traditional zeolites, ZIFs offer tremendous potential for design and modification, allowing for control of the physical (pore size, aperture diameter) and chemical properties by functionalization of the organic IM linker [78]. This flexibility opens entirely new possibilities that are inaccessible using traditional zeolite chemistry.

Like the MOFs counterparts, ZIFs form stable, three-dimensional, crystalline microporous solids. Due to their porous nature and large interior pores, ZIFs possess very low density, and extraordinarily high surface areas, often in excess of 1000-2000 m²/g [77, 78]. Furthermore, recent studies indicated that ZIFs may display very good selectivity for CO₂ [77-80]. Both the capacity and selectivity of the ZIFs can be influenced and tailored by proper functionalization of the IM linker [77, 78]. This was recently demonstrated in an isostructural series of ZIFs of formulae Zn(nIm)(Lbim) (nIm⁻ = 2-nitroimidazolate; Lbim⁻ = 5-L-benzimidazolate where L is a variety of functional groups) [[80]. Thus, at 1 bar and 298 K, the CO₂ uptake selectivity was found to vary along the series: L = NO₂ (ZIF-78) > CN, Br, Cl (ZIF-82, -81, -69) > C₆H₅, Me (ZIF-68, -79) > H (ZIF-70) > BPL carbon (Figure 16). Most notably, the uptake capacity for the nitro-functionalized structure (ZIF-78) is nearly three times that

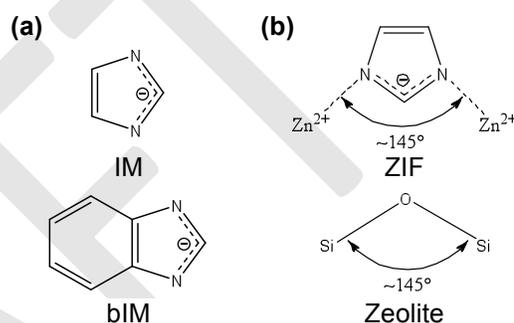


Figure 14. (a) Structure of an imidazolate anion [top], and a benzyl-substituted imidazolate [bottom]. (b) Comparison of ZIF and zeolite structures, showing a similar bond angle; adapted from Ref. 59.

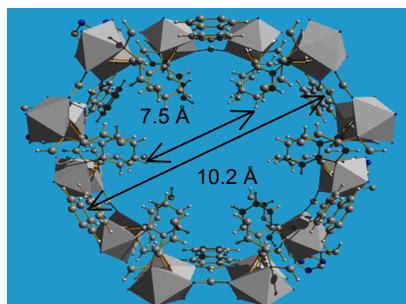


Figure 15. ZIF-68, with a large cavity and smaller aperture. Aperture sizes range from 0.7 – 13 Å in various ZIFs.

of commercial BPL carbon, with more than twice the selectivity over N₂.

While selective adsorption serves as one mechanism for potential gas separation, the unique structure of ZIFs, containing large pores with small apertures, provides an additional pathway for gas separation: kinetic separation [81, 82]. The controllable aperture diameter of ZIFs means that it may be possible to design a ZIF with an aperture sized to allow the passage of one gas, while excluding (partially) the flux of a second gas.

The performance of ZIFs as selective adsorbents for carbon dioxide ultimately depends on their specific interactions with the CO₂ molecules. Although little direct experiment data (such as neutron or x-ray diffraction) exists to date, molecular simulations yielded some insight about the predominant interaction mechanisms [82, 84]. These simulations employ empirical interaction potentials, and the results depend somewhat sensitively on the exact force field employed. In such simulations, the most favorable adsorption site for the CO₂ is found to be in the small cages of the ZIF [84]. At low pressures the predominant interaction is between CO₂ and the polar substituents of IM, localizing in the small pores made by the polar groups [83]. The electrostatic interactions of the CO₂ with the framework atoms is quite significant, and cannot be neglected at or below ambient pressures; at much higher pressure (above those likely applicable for flue gas separation) the effect of electrostatic interaction seems to become of secondary importance [85].

ZIFs exhibit impressive thermal stability [75], up to 500 °C, which is moderately higher than for prototypical MOFs [77, 78]. Yet it is the chemical and solvent stability of ZIFs that strongly differentiates them from most other MOFs, displaying excellent resistance to many common solvents [75]. For example, a group of ZIFs were shown to be resistant to 7 days of refluxing in both benzene and methanol [77, 80]. Another ZIF, ZIF-8, was resistant to 7 days of exposure to 50 °C water, and even to 24 hours in 0.8M NaOH at 100 °C [75]. The enhanced chemical stability of ZIFs facilitates their post-synthetic functionalization, allowing for modulation of the CO₂ capacity and selectivity [86]. The unusual solvent resistance of ZIFs has been attributed to either unusually strong metal-ligand bonds, or the hydrophobic nature of the ZIF ligands protecting the sensitive metal-ligand bonds to hydrolysis [75]. Some support for the latter hypothesis is given by subsequent experimental work on water adsorption, where it was shown that ZIF-8 is extremely hydrophobic [87]. In fact, the ZIF displays almost no water adsorption until the condensation point is reached. Note that in this work, in contrast to that of Park et al., this later work found a few additional peaks in the powder XRD spectrum after exposure to water at 50 °C for 24 hours, suggesting that although their solvent resistance is good, the ZIFs are far from inert [87].

3.2.3 Current Limitations in CO₂ Capture by MOFs and ZIFS

It seems clear that it will be feasible to develop MOFs with truly outstanding levels of performance in the separation of CO₂ from mixtures with N₂. Their eventual use on the enormous scale required for CO₂ capture from power plant flue gases, however, still presents a number of serious challenges. Some of the issues to consider are economical, with uncertainties arising, for example, in the availability of materials and the ultimate costs of manufacture of MOFs if they are to be produced on such an enormous scale. Other challenges involve fundamental science. For example, little is currently known about the necessary physical and chemical properties of the sorbent that would be required for utilization in a practical flue gas separation system. While these properties would depend on the detailed structure of the separation

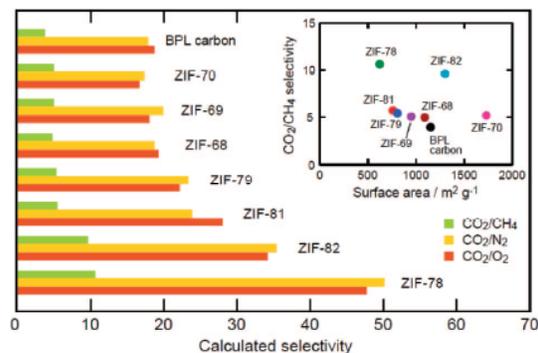


Figure 16. Selectivity for CO₂ binding over CH₄, N₂, and O₂ in selected ZIFs adopting the *gme* structure type and having a variety of surface functional groups.

system, even order of magnitude estimates would be extremely useful. In particular, estimates for the following are required: capacities (translated into laboratory measurable units, such as mmol CO₂ / g or mmol CO₂ / L of sorbent at a given pressure or temperature), adsorption selectivity for CO₂ over other relevant flue gases, transport diffusion constants for CO₂ through the sorbent, and heat of CO₂ adsorption, are essential for guiding future synthetic work.

Our fundamental understanding of the interaction of MOFs and ZIFs with CO₂ and other flue gases, in particular N₂ is still limited. Experimental efforts to probe these interactions via either diffraction studies or spectroscopic (IR, perhaps even NMR) methods may provide valuable insight that is not currently available. Additional insights can also be gained through computational techniques, including molecular simulations and electronic structure methods. These computational efforts are somewhat hindered by the fact that different empirical force fields have yielded different results, and the weak intermolecular interactions between the framework and adsorbate are difficult to probe using common density functional theory techniques. On the other hand, it remains particularly difficult to predict the CO₂ uptake in MOFs that contain open metal sites or other strongly interacting functional groups. The models typically used in current simulations are based on a classical “force field” model and do not take into account orbital interactions and thus are generally not expected to perform well for strong binding sites.

In addition to the above-mentioned fundamental problems, there are some practical issues that need to be resolved before MOFs and ZIFs can be used effectively for CO₂ capture:

Performance in the Presence of Water. The management of water will be an important factor for the industrial application of MOFs in CO₂ capture. Unless rigorously dried, most industrial gas streams contain some amount of moisture, and untreated flue gas contains 5-7% water vapor by weight. Ideally, a MOF suitable for CO₂ capture should be stable to the sustained presence of water vapor at this level. Although many MOFs are unstable to water, a growing number are held together by very strong metal-ligand bonds and can survive even extreme hydrothermal conditions [87]. Importantly, the MOFs displaying a high water stability include Mg₂(dhtp), HCu[(Cu₄Cl)₃(BTri)₈], and most ZIFs [71, 80, 89]. In addition, since water has a large dipole moment, it will tend to adsorb to charged sites on a MOF surface preferentially over CO₂, potentially interfering with CO₂ capture. In general, many more measurements on MOFs using mixed gas streams that include water vapor are needed to probe what effects water will have. Interestingly, however, there are indications that certain MOFs may actually perform better in the presence of water [89].

Stability Towards Impurities. In natural, synthesis, and especially flue gas streams, there are impurities that can be acidic, such as SO₂, H₂S, HCl, and NO_x, and could potentially be corrosive to MOFs. Ideally, a MOF would be stable to exposure to any potential flue gas impurities; although certain of these gases may already be removed in power plants due to environmental legislations. Further measurements on the impact of such trace gases on MOFs are needed.

Gas Diffusion Rates. Most of the work on MOFs to date has focused on thermodynamic aspects of their performance. Equally important, however, is the kinetics of how a flue gas will permeate a MOF. Very few measurements of this type have yet been carried out, and many more are needed. Similarly, very little experimental or theoretical data exists for diffusion of CO₂ in ZIFs. Wang et al. noted that slow diffusion seems present during gas absorption (although this is not quantified), which they attribute to the effect of constricted pore apertures [79]. A handful of simulation studies have looked at diffusion in ZIFs and found that it could be up to an order of magnitude slower than in typical MOF systems [83, 84]. The decreased diffusion was attributed to the smaller pores in the ZIF system, as well as steric hindrance due to substituents on the IM linkers. It would seem that experimental measurements of gas diffusion in ZIF systems are crucially important in order to evaluate whether the observed diffusion rates are sufficient for practical applications, or whether the ZIFs can be altered in a way to increase the diffusion

rates without sacrificing gas adsorption capacity or selectivity.

Scalability. It is not yet clear whether the existing solvo-thermal synthetic procedures, used in both MOF and ZIF synthesis, can be applied to the extremely large scales that would be required for use in a flue gas separation system. Although this pathway has so far been scaled to the gram scale, it is likely that additional research would be required to achieve kilogram scale, and beyond.

Reversibility and Regeneration. Any flue gas separation system based on gas adsorption will need to be operated in a cyclic manner, using some mechanism (typically temperature or pressure swing) to regenerate the adsorption medium and release the adsorbate. While CO₂ adsorption in MOFs and ZIFs seems to be essentially completely reversible based on pressure swing, it is not yet clear whether the adsorption/desorption can be done over thousands of cycles without deterioration of performance. Ultimately this depends on the long-term stability of the frameworks, which need to be tested under conditions relevant to flue gas separations.

3.3 Membranes

Gas separation by membranes is highly desirable since separation by membranes is generally a low energy process. The selectivity of membranes can lead to highly pure streams and membrane based automated plants can remain in operation without requiring major maintenance. The CO₂ separation by membranes has been accomplished and is applied in natural gas processing industry. This section summarizes the status of gas separation membranes.

3.3.1 Types of Membranes

Both polymeric and inorganic membranes have been studied for gas separation. Inorganic membrane materials generally offer higher permeability and selectivity and better chemical and thermal stability than the polymeric membrane materials. However, polymeric materials can be more easily processed to thin, flexible membranes and to the modules with packing density. Polymer membranes are less expensive than inorganic membranes on the square footage basis. Although many polymer membranes have been investigated, only a limited number of polymer membranes are used industrially for gas separations [91]. These include rubbery polymers of poly (dimethylsiloxane), ethylene oxide/propylene oxide-amide copolymer, and glass polymers of cellulose acetate, polyperfluorodioxides, polycarbonates, polyimides, and polysulfone. Inorganic membranes studied for gas separation include amorphous and crystalline microporous silica, carbon and other ceramic membranes, metal membranes and crystalline metal oxide membranes [92]. Metal membranes are used in hydrogen purification in the semi-conductor industry and porous inorganic membranes have been used for large scale gas diffusion separation of uranium isotopes. There is currently a major industrial effort to develop crystalline ionic transport inorganic membranes for air separation and syngas production.

Membranes have potential for use in the post-combustion, pre-combustion and oxyfuel combustion processes for CO₂ capture. Oxygen semi-permeable mixed-conducting metal oxide ceramic membranes operated at temperatures above 700 °C are suitable for oxygen separation from air for oxyfuel combustion applications. Both H₂ and CO₂ selective membranes are considered for pre-combustion applications. The H₂ or CO₂ selective membranes operated at the high temperatures (above 700 °C) may be used in the membrane reactors for reforming reactions, and those in the temperature range of 300-500 °C are more suitable for use in the membrane reactors for water gas shift reaction, a key step in the pre-combustion process. Low temperature CO₂ selective membranes have also been considered for pre-combustion CO₂ capture but in principle the combined membrane separator/reactor process is not as efficient as the high temperature membrane reactor. Therefore thermally stable inorganic membranes are most suitable for pre-combustion and oxyfuel combustion CO₂ capture applications.

For post-combustion CO₂ capture, the membrane should be operated in the temperature range of 50-150°C, the temperature of flue gas leaving the flue gas desulfurizer (typically a wet-lime scrubber). This temperature range fits the operation conditions of both polymer and inorganic membranes. The flue gas contains roughly about 15% CO₂, 5% O₂, 70% N₂, 10% H₂O, and other impurities (see Fig. 2, Section 2). For post-combustion CO₂ capture, the membrane is used primarily to separate CO₂ from N₂. So CO₂ permeance, CO₂/N₂ permselectivity, chemical and mechanical stability, material processibility and membrane costs are the main considerations for selecting a membrane for post-combustion CO₂ capture.

Polymeric Membranes: A large number of polymer membranes have been studied for CO₂/N₂ separation including polyacetylenes, polyarylene ethers, polyarylates, polycarbonates, polyimides, polyprrolones and polysulfones [93, 94]. Most polymer membranes have CO₂/N₂ selectivity in the range from 5 to 50 and CO₂ permeability up to about 600 Barrer (2.0×10^{-12} mol/m·s·Pa) [95]. Many polymer membranes suffer from a chemical stability problem; in particular, CO₂ induced plastization [92]. The polyimide membranes appear most attractive for CO₂ capture due to their good physical properties and structural variability, ease of membrane formation, and desired gas transport properties. Polymer membranes with higher CO₂/N₂ selectivity have been reported, but mostly achieved through the mechanism of facilitated transport of CO₂. Recently Membrane Technology and Research Inc. (MTR) has reported a rubbery polymer membrane called “Polaris” (detailed composition and material not revealed [95]). The membrane exhibits a moderate CO₂/N₂ selectivity (about 50) but high CO₂ permeance (1000 GPU, or 3.3×10^{-7} mol/m²·s·Pa) [95]. Figure 17 compares selectivity and permeance of the Polaris membrane with other representative polymer or composite membranes for CO₂ capture, along with the desired range for membranes properties obtained by simulation of membrane separation process [95].

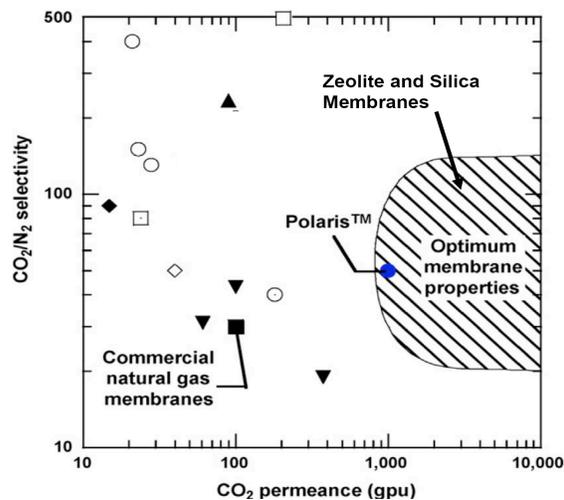


Figure 17. Comparison of CO₂/N₂ selectivity and CO₂ permeance of various polymer and composite membranes (points) with those of commercial membranes for acid gas removal from natural gas (full square), Polaris membrane (full circle), and microporous inorganic membranes (modified from [95]).

Inorganic Membranes: Inorganic membrane materials are known for their better chemical and thermal stability and higher perm-selectivity for gas separation than polymer membranes. The majority of inorganic membranes studied for CO₂ separation are microporous membranes including zeolite membranes, sol-gel derived or chemical vapor deposited silica or zirconia membranes, carbon membranes, organic modified silica membranes, and inorganic-polymer composite membranes such as mixed-matrix membranes. CO₂ and N₂ have a kinetic diameter respectively of 0.33 and 0.36 nm, very close to each other. However, the quadrupole moment for CO₂ is about 3 times larger than that for N₂ [96]. Thus, many inorganic membranes are perm-selective for CO₂ over N₂ due to preferential adsorption of CO₂ on the membrane material and, to much less extent, the smaller molecular size of CO₂ as compared to N₂. Sol-gel derived silica membranes and NaY and KY zeolite membranes show CO₂/N₂ selectivity up to 70-100 with CO₂ permeance in the range of $1-5 \times 10^{-7}$ mol/m²·s·Pa at room temperature. These microporous inorganic membranes already have CO₂/N₂ selectivity and CO₂ permeance in the desired range shown in Figure 17. However, these microporous inorganic membranes become essentially non perm-selective for CO₂/N₂ separation at high temperatures (>300 °C).

Gas/vapor permeation through microporous inorganic membranes is determined by adsorption and diffusion of the permeating species in the membrane pores [92]. At low temperatures the CO₂/N₂ permselectivity for these microporous inorganic membranes is mainly determined by the adsorption properties of the membranes for CO₂ and N₂. Their pore sizes are still too large to show any significant diffusion-controlled selectivity for CO₂ over N₂ [97, 98]. For MFI or FAU type zeolite membranes, with zeolite pore diameter respectively of 0.55 nm and 0.7 nm, the ratio of the molecular size to pore size, λ , is smaller than 0.75 for CO₂ and N₂. If one considers possible microporous defects, the average pore size of the membranes would be even larger than the zeolite pores, yielding a much lower value of λ . With λ in this range, these two zeolite membranes will offer essentially no diffusion-controlled selectivity for CO₂ over N₂. At high temperatures, adsorption diminishes and therefore the adsorption-controlled selectivity disappears for these microporous membranes. It is unlikely for other microporous membranes with a pore size larger than FAU type zeolite, such as metal organic framework materials, to exhibit better selectivity and permeance for CO₂/N₂ than those summarized above.

To improve the diffusion controlled CO₂/N₂ selectivity requires further reduction in the membrane pore size. Amorphous silica membranes obtained by the sol-gel method from acid catalyzed polymeric silica sol or by chemical vapor deposition at the intermediate temperature have an ultramicropore structure with pore diameter in the range of 0.3-0.4 nm. These membranes might offer high CO₂/N₂ selectivity at high temperatures if their thermal and hydrothermal stability can be improved. Efforts have been reported to improve the stability of the microporous silica membranes through surface modification or doping of a second metal to the silica framework. Recent work showed that thermally stable microporous silica membranes with a pore diameter of around 0.3 nm can be prepared by a high temperature chemical vapor deposition method [99]. However, the CO₂ permeance of the membrane is too low (about 2×10^{-10} mol/m²·s·Pa) which is expected from the membrane pore size.

Crystalline zeolite membranes with small pore size offer better chemical stability and more controlled more structure than the amorphous ultramicroporous silica membranes discussed above. Two 8-member-ring zeolites, CHA type (e.g. SAPO-34) and DDR type zeolites have recently attracted much interest as membrane materials for gas separation involving CO₂ [100]. SAPO-34 and DDR zeolites have a pore diameter of about 0.38 and 0.36x0.44 nm, respectively, slightly larger than the kinetic diameter of CO₂ and N₂. SAPO-34 membranes exhibit good separation properties for CO₂/CH₄ mixture separation [100]. However, presence of water in the gas stream has a negative impact on SAPO-34 membrane performance due to the hydrophilic nature of the SAPO-34 framework. DDR zeolite contains pure silica, and, similar to pure silica 10- or 12-member-ring MFI type silicalite and FAU-type dealuminized-Y zeolites, is highly chemically and thermally stable. A 5 μ m thick DDR zeolite membrane, possibly containing some microporous intercrystalline defects [94], has CO₂ permeance of about 3×10^{-7} mol/m²·s·Pa and CO₂/N₂ selectivity of about 30 at 25 °C [101]. The selectivity and permeance of these membranes can be improved if the membrane thickness is further decreased and the intercrystalline pores of membrane eliminated.

For microporous inorganic membranes there is a limit to improve the CO₂/N₂ selectivity while maintaining high permeance through pore size reduction. Dense, nonporous ceramic membranes are known for their infinitely large selectivity for O₂ over N₂, and high O₂ permeance at temperatures above 700°C. Research efforts on synthesis of dense Li₂ZrO₃ and Li₄SiO₄ membranes for high temperature separation of CO₂ were reported but these membranes exhibit a CO₂/N₂ selectivity of about 5 and CO₂ permeance of 10^{-8} mol/m²·s·Pa at 525 °C [102]. It is known that molten carbonate, such as Li₂CO₃/K₂CO₃, can conduct CO₃²⁻ at a very high rate at high temperatures. A metal-carbonate dual-phase membrane was prepared and shown to be able to separate CO₂ from mixture of N₂, CO₂ and O₂ [101]. However the permeation of CO₂ through the metal-carbonate membrane requires the presence of oxygen and the membrane suffers from a stability issue due to metal oxidation and metal-carbonate interaction. These problems can be addressed by replacing the metal phase with a mixed electronic-ionic conducting

metal oxide phase [102]. A dual-phase membrane consisting of a molten carbonate ($\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$) entrapped in a porous $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ support is perm-selective to CO_2 (with CO_2/N_2 selectivity well above 225) with CO_2 permeance of above $1.0 \times 10^{-8} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ at temperatures above 500°C . These membranes have potential for pre-combustion CO_2 capture applications, but much more work need to be done to improve the CO_2 permeance.

3.3.2 Theoretical and Experimental Studies on the Mechanism of Gas Separation

Development of membranes that create a step change in performance relative to existing materials presents two complementary challenges. First, a large search space of possible materials must be considered to select a small number of materials that are expected to yield high performance membranes. If the aim is to use zeolites to make a membrane, for example, the identity and chemical composition of the zeolite(s) to be studied must be chosen from among hundreds of possible candidate materials. Second, the physical issues that affect the practical performance of membranes that are fabricated into working devices must be understood and controlled. To continue with the example of a zeolite membrane, the crystal orientation and microstructure of a zeolite film is often decisive in membrane performance. In broad terms, theoretical studies are currently making valuable contributions in the first area (materials selection), while device performance issues are currently most effectively addressed experimentally. Below, the current status of these issues for several different classes of membranes is briefly reviewed.

Nanoporous membranes: The potential for crystalline nanoporous materials to overcome the fundamental selectivity/throughput tradeoff that exists for polymeric membranes is widely known. Extensive experience has been accumulated in fabrication of zeolite membranes [105]. MOFs represent a useful extension of the class of nanoporous materials that can be considered as membranes, but development of MOF membranes is at an early stage of development. Detailed theoretical models show promise for guiding materials selection of MOFs for membrane development [106]. The characteristics of molecular diffusion in nanoporous materials are critical to the performance of membranes grown from these materials, and most information about molecular diffusion in MOFs to date has come from theoretical studies. The development of theoretical models that combine quantum chemistry and force field-based calculations to accurately describe the subtle balance of dispersion forces and framework flexibility effects in MOFs has progressed rapidly in recent years, although this work has been hampered in some instances by the availability of reliable, reproducible experimental data. It appears likely that in the near future it will be possible to use theoretical methods to screen large numbers of MOFs to reliably select which materials have most promise as membrane materials.

When membranes are fabricated based on intergrown thin films of zeolites or MOFs, the microstructure of the resulting films can be critical in the effectiveness of the membrane. Significant progress has been made in controlling film microstructure for some zeolite films [105], but control of these issues for new materials remains a severe challenge. Theoretical models currently contribute little to this challenge.

An attractive alternative to making membranes from intergrown thin films of crystalline materials is to use polymer/filler composites as membranes. These so-called mixed matrix membranes are likely to play an important role in near term technologies because they can be used to manufacture membranes at large scales using minor variations on known approaches [107]. As theoretical methods are used to screen new nanoporous materials, it is becoming possible to consider which polymer/filler combinations will have desirable membrane properties and to focus experimental efforts on these materials [108]. Issues of particle size, particle dispersion, and the interface between filler particles and the polymer matrix are typically critical in the viability of mixed matrix membranes. A significant body of knowledge already exists associated with these issues for nonporous and zeolite filler particles [109]. The use of MOFs as filler particles is relatively new, so these important microstructure-related topics are not yet well understood for MOF/polymer composites.

Dense membranes for high temperature separations: Membranes to separate high temperature syngas can potentially play an important role in CO₂ mitigation within IGCC and other gasification processes. Theoretical approaches based on quantum chemistry calculations are beginning to play a useful role in materials selection for dense metal membranes using both crystalline and glassy metals [110]. Current theoretical approaches focus on predicting the throughput of hydrogen through these dense films. The response of metal films to gas contaminants such as S-containing species remains a critical issue for implementation of these devices, and this topic is currently only accessible via experiments. The fundamental mechanisms of membrane poisoning by these contaminants remain poorly understood; changing this situation could allow significant progress in the development of practical membranes.

Ceramic membranes also show promise for high temperature CO₂ separations. Progress has been made in testing devices made from lithium-based ceramics [111]. These experimental studies have revealed the main physical mechanisms that control CO₂ permeation through these ceramics. Little theoretical work is available on these mechanisms, so theory has not yet played a role in materials selection in this area.

3.3.3 Industrial Applications of Gas Separation Membranes

Membrane gas separation is one of the most significant new unit operations to emerge in chemical industry in the last 40 years. From tentative beginnings in the 1970's, commercial gas separation membranes have evolved to the point where they have gained industrial acceptance in many areas such as nitrogen production, hydrogen separation and natural gas upgrading (Figure 18). In virtually all areas where gas separation membranes are commercial today, they compete with established, well-developed technologies like cryogenic distillation, pressure swing adsorption (PSA) and liquid absorption. Selection of the best technology is always difficult because in practice the specifics of each application, such as product purity, feed composition, utilization patterns, turndown requirements, impurity levels, supply pressure, operating temperature and the relative cost of power and capital all have a significant impact on the selection of the optimal technology and process configuration. This section will highlight the two relevant areas where membranes have been most successful in industrial gas applications.

Membrane air separation is based primarily on the use of composite and asymmetric hollow fiber technology using polymers that permeate oxygen faster than nitrogen. This permits the design of relatively simple cycles that fundamentally require only a compressor and a membrane assembly; nitrogen is the retentate and is obtained at close to compressor discharge pressure while an oxygen rich gas is obtained as low pressure permeate. In principle, it is possible to use membranes to produce both oxygen and nitrogen. In practice, with current membrane properties, it is much easier to produce high purity nitrogen and hence membranes have been confined largely to nitrogen production.



Figure 18. A membrane plant for natural gas processing (courtesy MTR, Inc.).

In general, the O₂/N₂ selectivities of polymers used in air separation are in the range of 4 - 8 and the permeabilities are in the range of 1 – 20 Barrers. The effective skin thickness achieved in production is in the range of 500- 2000 Å. Small skin thicknesses are most desirable because they increase membrane productivity (P/t) and permit the use of higher selectivity (but lower permeability) materials. The thin “skin” is always supported on a porous layer which provides structural strength.

The simple, single stage process is best for producing low purity nitrogen while multi-stage processes are better suited at higher purities and large capacities. "Oxygen free" nitrogen can be produced using a hybrid system comprised of a membrane system plus a catalytic de-oxygenation system using hydrogen to remove the residual oxygen.

Oxygen production by membranes has to date seen only limited application and has been confined to small sizes and low purities. This is due to the following important factors:

- The cost of O₂ produced is high.
- Most traditional applications use high purity O₂, but current material selectivities and permeabilities are too low for high purity O₂ production.
- Oxygen is typically produced at low pressure and O₂ compression is expensive.
- The contaminants present in feed air (e.g. CO₂, H₂O) contaminate the product

To produce low cost oxygen at high purity, membranes with very high permeability and selectivity are required. The most common process used for membrane O₂ production is the simple, single stage process in which the O₂ rich permeate is obtained as the product. The lack of membrane materials which simultaneously possess high selectivity and very high permeability has stymied the commercial development of membranes for oxygen production. It is important to note that many industrial gas companies are developing oxygen transport membranes of the sort described above. For example some, such as Air Products are now in pilot scale testing on the tons per day level.

<http://www.airproducts.com/PressRoom/CompanyNews/Archived/2009/21May2009b.htm>

CO₂ Removal in Natural Gas Processing: The most widely practiced application of membrane processes in natural gas treatment is for CO₂ removal (Figure 19). Cellulose membranes have been used primarily for the past 20+ years and have been now increasingly applied for larger flow rate applications. Recent advances in membrane technology have introduced new commercial membranes in this market space. Specifically, rubbery CO₂ selective membranes (e.g. Polaris from MTR, Inc.) and glassy polymer membranes (e.g. polyimide, perfluoro) have recently been introduced in limited applications in the gas treatment market. These membranes are being tailored to address certain shortcomings of conventional cellulosic membranes such as membrane stability and requirement for substantial pretreatment.

Apart from CO₂ removal from natural gas, two other applications have gained significant traction in natural gas processing and treatment. Membranes are now successfully deployed for nitrogen removal from natural gas and numerous plants are now operating in the US. Also, new membranes have been applied successfully for the separation of heavy hydrocarbons and acid gases such as H₂S and CO₂ from

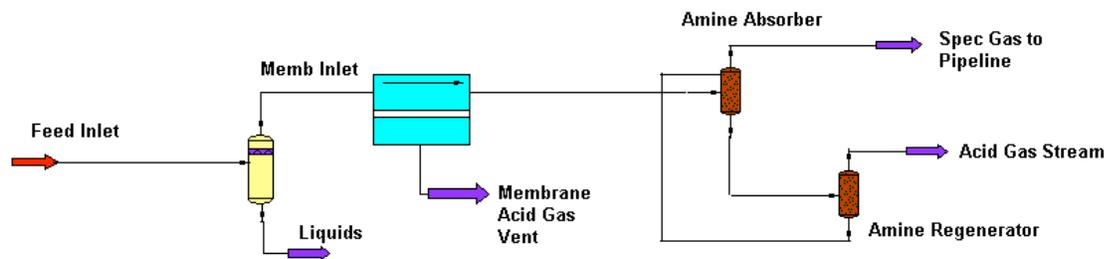


Figure 19. Hybrid membrane process for CO₂ removal from natural gas (Courtesy MTR Inc.).

fuel gas used to fuel gas engines and turbines. Fuel gas cleanup reduces emissions and increases operational efficiency of gas engines and turbines which are the work horses for moving natural gas in the pipeline grid. Table 5 provides a summary of typical application conditions for the use of membranes in natural gas processing.

Table 5. Application of membranes in natural gas processing

Application	Species Removed	Typical Flow MMSCFD	Feed Pr Psig	Temperature F
CO ₂ Removal	CO ₂	0.5 - 500	100 - 1500	0 - 150
N ₂ Removal	N ₂	0.2 - 50	100 - 1500	0 - 150
Fuel Gas Conditioning	C ₂ + hydrocarbons, H ₂ S, CO ₂ , Water	0.1 - 100	101 - 1500	0 - 150

4.0 Alternative Gas Separation Pathways

A brief summary is provided here of alternative pathways for CO₂ capture via hydrate formation, and catalytic-based chemical conversions.

4.1 Gas Hydrates

It is well known that CO₂, N₂, O₂ and H₂ are molecules which have the ability to combine with H₂O under proper temperature and pressure conditions to form a crystal known as gas or clathrate hydrate [112, 113]. Water molecules linked through hydrogen bonding enclose the CO₂ molecules in cavities and create guest/host (H₂O) arrangements known as gas or clathrate hydrate crystals (cubic structure). Recently, the use of hydrates for CO₂ capture from flue gas mixtures became of interest [114, 115]. The U.S. Department of Energy proposed a concept for a high-pressure process to recover H₂ and CO₂ from a shifted synthesis gas stream [116, 117]. However, very little data were presented. The hydrate process is able to concentrate a CO₂ containing stream. There remains the CO₂-lean stream, which cannot be treated through hydrate formation since it would be rich in either N₂ or H₂ and the required pressures would be very high. Thus, the hydrate process should be coupled with another, highly selective process for CO₂ capture.

4.2 Chemical Conversion

To date the efforts to convert CO₂ from the manufacturing sector into useful products have been rather limited. Thermodynamic considerations show that it is impossible to get more energy from CO₂ reduction products than needed to reduce CO₂ into products. As such, all approaches to CO₂ conversion to value added products employ energy from renewable sources, e.g. photocatalytic reduction, CO₂ as a solvent, CO₂ as a polymer precursor, etc.

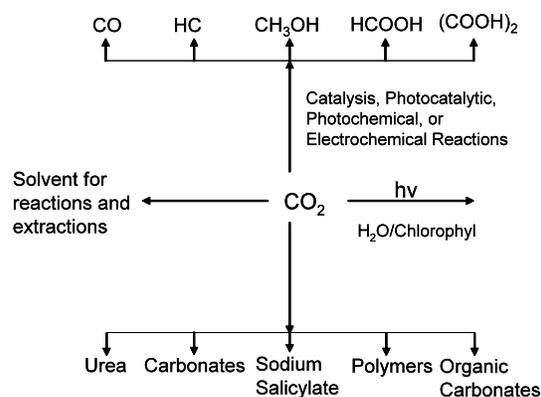


Figure 20. Conversion of CO₂ to various products.

The use of CO₂ as a reagent in organic synthesis is receiving renewed attention. Another highly desirable approach to convert CO₂ into useful products is artificial photosynthesis. In this scenario, CO₂ produced from various sources can be efficiently converted to hydrocarbons, alcohols of synthesis gas employing solar energy. This approach will create an artificial CO₂ cycle and reduce the need for CO₂ capture and sequestration. The photochemical CO₂ reduction employing homogeneous catalysts has been the subject of intense interest for a number of years now [118, 119]. However, the stability of CO₂ makes economical utilization of carbon dioxide as a feedstock for fuels or chemicals a formidable challenge.

Since CO₂ lies in a deep energetic well of stability, the reduction process will be energy intensive and for significant round-trip cycle efficiency requires a renewable energy input. The voltage and free energy required for several CO₂ reduction processes can be provided by using ‘direct’ electrochemistry with concomitant water splitting or by use of hydrogen as a chemical reductant. To create fuels or chemical feed stocks with C-2 or greater from CO₂, electrochemical reduction steps must be coupled to C-C bond formation chemistry. Two dominant pathways are identified that can potentially facilitate this type of reaction - direct electrocatalytic conversion where reactions occur between adsorbed species on a surface, typically metallic, that catalyzes reactions and electrochemically mediated processes using organometallic complexes.

A number of mechanistic pathways utilizing heterogeneous catalysis are available for conversion of CO₂ to useful feedstocks. The most direct and extensively studied of these involves hydrogenative conversion of CO₂ to methanol. Efficient heterogeneous catalysts based on metals and their oxides, in particular the combination of copper and zinc oxide have been developed for this conversion. Another mechanism, known as the Sabatier reaction or Sabatier process involves the reaction of hydrogen with carbon dioxide at elevated temperatures and pressures in the presence of a nickel catalyst to produce methane and water. Optionally ruthenium on aluminum oxide makes a more efficient catalyst [120]. CO₂ reduction to CO can be achieved by the reverse Boudouard reaction via the thermal reaction of carbon dioxide with carbon, or coal itself. This process has an advantage over the steam reforming of coal, which is somewhat less endothermic (31.3 kcal mol⁻¹), in that it allows for the recycling of CO₂. Another mechanistic pathway optimizes the use of natural gas resources (which generally contain 5 to 50 % CO₂) and concurrently converts CO₂ to *syngas* via reaction of CO₂ with natural gas or other hydrocarbon sources. This reaction is carried out commercially at temperatures around 800-1000 °C using catalysts based on nickel and other metals (Ni/MgO, Ni/MgAl₂O₄, Ni/Al₂O₃, Rh/NaY, Rh/Al₂O₃, etc) [121-123]. CO₂ is used as a feedstock reacted with ammonia under pressure with no catalyst present to produce urea [124]. This reaction is practiced in a large scale and currently close to 80 Mt of CO₂ is consumed annually.

5.0 Summary and Technical Challenges

As with the March 2009 workshop on carbon capture co-sponsored by BES and FE [125], several overall common scientific and technologic themes have been highlighted in this factual document that require near-term attention in order to stimulate transformative breakthroughs in mitigating carbon emissions. These include; (a) fundamental understanding of gas-host interactions, (b) need to measure and understand in greater detail key thermodynamic, kinetic, chemical and structural characteristics of the current suite of available materials, (c) discovery of entirely new materials for carbon capture and oxygen separation from air, (d) discovery of capture materials that can be regenerated with minimal energy use, perhaps through mechanisms other than thermal or pressure swings, and (e) implementation of new approaches to theory, modeling and simulation that accelerate the scale-up. A synergistic research portfolio involving novel experiments, synthesis, analytical and characterization methods in concert with molecular-level simulations is needed to fill key knowledge gaps in our fundamental understanding of materials properties and reaction chemistry. Science discovery should keep pace with the expected timeline for commercial deployment of capture and storage as outlined in Fig. 21 [126].

In the context of Basic Energy Sciences, five broad areas are defined that could afford new research opportunities to the materials and chemistry community. These are liquid absorbents, solid absorbents, membranes, gas hydrate separation and catalytic materials/reactions. Each of these has varying applicability to the three main carbon capture technologies currently being investigated – post-, pre-, and oxy-combustion.

Liquid absorbent-based CO₂ capture involves chemical or physical sorption of CO₂ from flue gas into a liquid carrier. Solvent-based systems, such as commercially available amine-based systems, are being used today for scrubbing CO₂ from industrial flue gases and process steams. However, scaling this type of CO₂

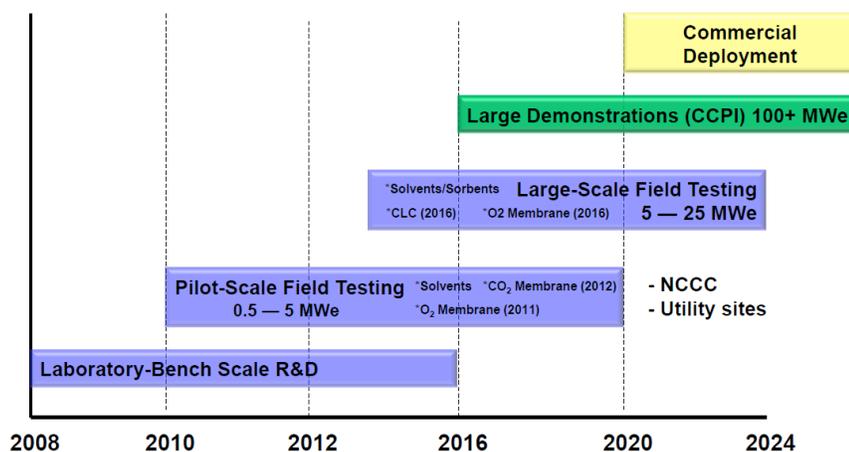


Figure 21. R & D timeline for commercial deployment of carbon capture [126].

capture methodology to the size required for processing large volumes of CO₂ has not been achieved. Research efforts on liquid absorbents need to focus on new solvents that are thermally stable to high temperatures, chemically stable in flue gas conditions, have a high CO₂ loading capacity, minimize regeneration energy, exhibit fast reaction kinetics, are non-corrosive and are cost effective. Scientific breakthroughs may be realized through exploration of new amine-based chemistry, novel ionic liquids and ionic-liquid supported polymeric membranes, especially for materials that can be regenerated with minimal parasitic energy.

Solid absorbents such as metal-organic and zeolite imidazolate frameworks have highly desirable properties such as microporosity, high surface areas, and exceptional thermal and chemical stability, making them potentially ideal for gas separation applications. Scaling to “real world” conditions is recognized as a major obstacle in the deployment of solid sorbents. Additionally, fundamental research is needed to identify new methods for releasing CO₂ from the solid sorbents (e.g. microwave, electrical or optical), and to develop novel functionalization schemes of the pore walls that improve thermal and chemical stability (particularly during pressure drops), diffusivity and sorptive selectivity.

Membranes for CO₂ separation are, in principle, simple to operate – i.e. no chemical reactions to track and no moving parts. Currently available membranes have a tolerance to high levels of wet acid gases, are compact and modular with a small footprint and require relatively low energy. However a number of technology challenges remain including the need to handle low flue gas CO₂ partial pressures, withstand the deleterious effects of particulate matter degradation of membrane performance and life, reduced cost and scale-up for large volumes of CO₂. For post-combustion capture, advanced membrane research targets include the design and synthesis of new materials that have high CO₂/N₂ selectivity and permeability which will require tailoring the pore size and distribution in ways that do not degrade gas

permeance, chemically stabilize membranes especially in the presence of SO₂, and control the microstructure and crystal orientation of thin-film membranes. For oxy-combustion materials that would allow for low cost separation of oxygen from air are needed.

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