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Advancing Adsorption and Membrane-Separation Processes for the Gigaton Carbon Capture Challenge

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Abstract

Reducing CO₂ in the atmosphere and preventing its release from point-source emitters, such as coal and natural gas-fired power plants, is a global challenge measured in gigatons. Capturing CO₂ at this scale will require a portfolio of gas-separation technologies to be applied over a range of applications in which the gas mixtures and operating conditions will vary. Chemical scrubbing using absorption is the current state-of-the-art technology. Considerably less attention has been given to other gas-separation technologies, including adsorption and membranes. It will take a range of creative solutions to reduce CO₂ at scale, thereby slowing global warming and minimizing its potential negative environmental impacts. This review focuses on the current challenges of adsorption and membrane-separation processes. Technological advancement of these processes will lead to reduced cost, which will enable subsequent adoption for practical scaled-up application.

INTRODUCTION

Efficient capture of carbon dioxide (CO₂) from gas mixtures such as flue gas generated from coal- and natural gas-fired power plants, in addition to dilute gas mixtures such as air, will be an essential and potentially primary component of the portfolio of solutions available for mitigating CO₂ emissions. To prevent global climate change leading to irreversible damage to our environment and humanity, it is crucial to advance technologies of CO₂ capture to the extent that they become economically feasible and tractable to policy makers and our global society. The current state-of-the-art technology for point-source (e.g., power plants, refineries, cement manufacturing plants) CO₂ capture applications is chemical scrubbing using absorption-based separation processes. However, this technique has never been applied at the gigaton (Gt) scale, on which the world currently emits CO₂ (i.e., ~30 Gt CO₂ yr⁻¹). CO₂ capture must take place at this scale to help slow the increase in CO₂ concentration in the atmosphere and the subsequent global climate change. **Figure 1** shows the distribution of publications of the various gas-separation technologies (i.e., absorption, adsorption, and membranes) that have been applied to capture CO₂ from gas mixtures. This figure highlights the increase in political and government interest as it correlates to the increase in attention paid by the academic community, thereby demonstrating that addressing this gigaton challenge will require a mix of scientific and policy advancements at a global level. Since Roger Bottoms (1) filed the first patent in 1930 on “Processes for Separating Acid Gases,” absorption has continued to receive more attention from the scientific community compared with adsorption and membrane-separation processes. Capturing CO₂ at scale will likely take a portfolio of solutions, which is why particular attention is given to advancing adsorption and membrane technologies in the hope of discovering new pathways that might enable these processes to become more economically feasible. **Figure 1** clearly shows that governance in addition to increased funding opportunities are correlated with increasing research and publications associated with CO₂ capture.

Absorption via chemical scrubbing involves corrosive base chemicals with the potential to volatilize throughout the separation process and can lead to additional emissions. Also, the

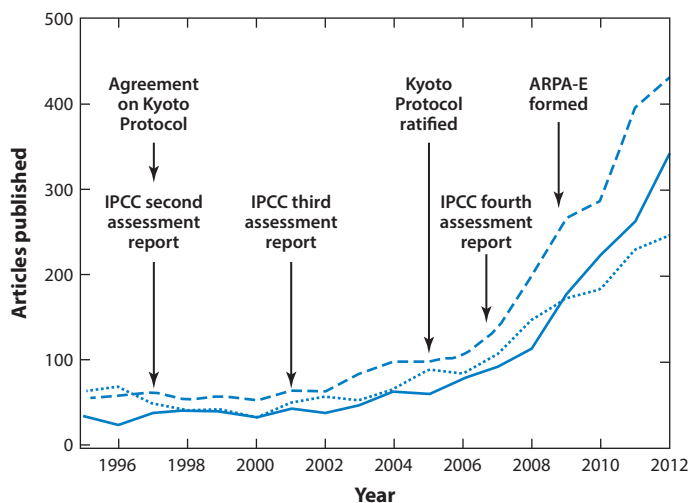


Figure 1

Numbers of articles published per year based upon absorption (*dashed line*), adsorption (*solid line*), and membrane-separation technologies (*dotted line*) with milestones associated with motivating research efforts. Abbreviations: ARPA-E, Advanced Research Project Agency–Energy; IPCC, Intergovernmental Panel on Climate Change.

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absorption process involving chemical scrubbing is expensive, making CO₂ capture an unattractive option in the absence of a carbon tax. The International Energy Agency reports an average of \$55 per tonne of CO₂ avoided (2). The cost of CO₂ avoided (3) is defined in Equation 1:

$$\text{Cost of CO}_2 \text{ avoided} = \frac{(\text{COE})_{\text{capture}} - (\text{COE})_{\text{ref}}}{(\text{CO}_2/\text{kWh})_{\text{ref}} - (\text{CO}_2/\text{kWh})_{\text{capture}}}, \quad 1.$$

where COE is the cost of electricity and *capt* and *ref* refer to the COE in a power plant with carbon capture and a reference power plant without carbon capture technologies, respectively. Any capture process has an energy requirement, and if the energy is hydrocarbon sourced, the process will lead to further CO₂ emissions. Hence, avoided emissions in which a comparison is made to a reference plant of the same type and size is the most commonly used measure. These costs typically include capture, solvent regeneration, and compression for pipeline transport, representing approximately 10%, 35%, and 55%, respectively, of the total energy requirements of the separation process (4).

Preventing global warming beyond 2°C will be unavoidable if mitigation action is not undertaken today. In fact, if gas-separation technologies for CO₂ capture can be advanced to become more economically tractable, the application of this approach may be broadened beyond point-source capture, potentially leading to greater impacts and deeper penetration of CO₂ reductions. In 2011, approximately 31 Gt of CO₂ was emitted worldwide (5). Business-as-usual practices, with 0.3%, 0.9%, and 2.3% increases in coal, oil, and natural gas, respectively (6), will lead to cumulative emissions of 1,790 Gt of CO₂ between 2000 and 2050. According to a study by Allen et al. (7), there is a 25% probability that the globe will warm beyond 2°C if the cumulative emissions during this time period are less than 1,000 Gt. This requires avoiding approximately 790 Gt of CO₂ during this time span. Mitigating CO₂ through capture at point sources is one method of several that will have to be employed in the coming years. Approaches associated with removing CO₂ directly from the atmosphere or engineering the carbon cycle, such as afforestation and cofiring with biomass, should also be considered for increased CO₂ reductions (8). It is also important to recognize the timescales associated with these strategies. Even if they were applied in a rigorous fashion overnight, there is still an existing warming trajectory that will take time to reverse (9). In the recent CCS Roadmap published by the International Energy Agency, the current scale of CCS must increase from millions of tons of CO₂ capture and storage per year to gigatons if CCS is going to comprise 17% of the portfolio of mitigation options to prevent 2°C warming. This requires a 1,000-fold increase in the number of capture and storage facilities. Currently, there are four in operation, with an additional nine under construction and expected to be operational by 2016 (10).

Several gas-separation approaches can be considered for CO₂ capture from both concentrated and dilute gas mixtures, including absorption, adsorption, and membrane separation. The catalytic conversion of CO₂ to fuel is one approach that results in a product (perhaps the only one) that scales with the CO₂ emissions. However, the production of useful hydrocarbons, such as ethylene and methanol, requires a hydrogen source and electrochemical reduction of CO₂. Both of these processes are energy intensive and will require noncarbonized energy resources to achieve a net reduction of CO₂. In addition, given that the fuel will be oxidized for energy generation, this concept at best may be considered a neutral, rather than CO₂-negative strategy. The development of electro- and photocatalysis to achieve efficient and affordable CO₂-to-fuel conversion is still at the early research stages and outside the scope of this review (11). Rather, focus will be paid to adsorption and membrane-separation approaches, primarily as they apply to point-source emissions, and consideration of their current status, including challenges that are preventing their readiness for scale-up to achieve impacts on the Gt scale.

Figure 2 is a plot of the minimum work (calculated from the combined first and second laws of thermodynamics) required for a given percent capture and CO₂ purity from gas mixtures with



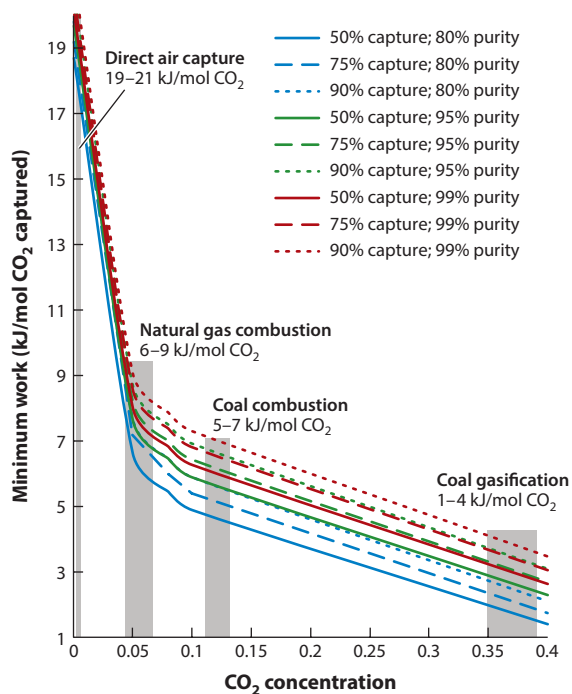


Figure 2

Minimum work required for CO₂ capture based upon initial gas concentration, percent capture, and final purity of CO₂.

a known starting CO₂ concentration (11). The minimum work sharply increases as CO₂ becomes more dilute in a gas mixture, ranging from the most concentrated source, fuel gas from coal gasification, to flue gas from coal and natural gas oxidation, respectively, down to the very dilute system of CO₂ in the troposphere. Hence, it becomes obvious that efforts toward implementing CO₂ controls should begin at existing point-source emitters, such as coal and natural gas-fired power plants. However, if a carbon tax is in place, a better solution may be to reconsider how electricity is currently generated from coal and natural gas. For instance, in a carbon-constrained world, separating CO₂ from the fuel gas of a gasification process (precombustion capture) may be cheaper and less energy intensive compared with retrofitting existing coal and natural gas power plants with CO₂ controls (postcombustion capture) (11).

In addition, the final purity is important because the CO₂ will have to be compressed for pipeline transport. The addition of 5–20% N₂ in a binary mixture of CO₂ and N₂ decreases the gas density from 681 kg m⁻³ down to 343 kg m⁻³, which adds an additional 0.5 kJ mol⁻¹ CO₂ in additional compression energy. Hence, the desired purity as a consequence of capture must be optimized along with the distance and energy limitations associated with compression for pipeline transport and potentially CO₂ sequestration (11).

In the process of discussing adsorption and membrane technologies, we attempt to establish the current challenges that must be overcome to apply these technologies at the scale required to achieve significant reductions in CO₂ emissions. Additionally, we provide a thorough description of these gas-separation processes so that a beginner in this field can become engaged in pursuit of solutions, because addressing the gigaton carbon capture challenge will require a broad mix of backgrounds, ranging from engineering to policy to the fundamental sciences.

Precombustion capture:

the separation of CO₂ from fuel gas following a gasification process, but prior to H₂ combustion, with typical CO₂ partial pressures of 0.4 to 0.45 atm

Postcombustion capture:

the separation of CO₂ from flue gas following a combustion process, with typical CO₂ partial pressures of 0.08 to 0.15 atm

IMPORTANCE OF WORKING CAPACITY

The working capacity of a sorbent is defined as the difference in the amount sorbed at the adsorption and desorption pressures (130). A fresh adsorbent will always adsorb more than a sorbent that has been exposed to flue gas on multiple cycles because it would be too energy intensive to completely regenerate a sorbent to its original condition at the start of a new cycle. The adsorption capacity of the sorbent would be the total capacity of the sorbent in its fresh state. Current research typically focuses on CO₂ capacity at a specific partial pressure (i.e., 0.15 bar). The more useful evaluation is to consider the CO₂ adsorption isotherm and present the working capacity for a differential partial pressure (i.e., 0.03 to 0.15 bar).

ADSORPTION-BASED SEPARATION

Equilibrium Behavior and Capacity

To make adsorption-based technology efficient and cost effective for CO₂ capture, an ideal adsorbent should have the following characteristics: (a) high working capacity, (b) high selectivity, (c) fast adsorption and desorption kinetics, (d) chemical stability, and (e) recyclability (see sidebar, Importance of Working Capacity). Solid adsorbents for CO₂ capture can generally be divided into three categories according to their working temperatures: high-temperature (>400°C), intermediate-temperature (200–400°C), and low-temperature (<200°C) adsorbents (15). Based upon chemical reactions, high- and intermediate-temperature adsorbents (e.g., layered double hydrides, metal oxides, and alkali-metal carbonates) may not necessarily be appropriate for postcombustion capture (in which CO₂ is removed from flue gas after hydrocarbon combustion) because flue gas applications often take place at relatively low temperatures (50–150°C). However, these adsorbents may be effective for precombustion capture applications, where CO₂ is removed from a fuel gas stream prior to hydrogen combustion. The gas conditions typical for pre- and postcombustion capture are listed in **Table 1**. In this case, coal flue gas refers to postcombustion capture and coal gasification fuel gas and post-water-gas shift gas refers to the precombustion regime. Coal gasification or natural gas reforming produces fuel gas, which is composed mainly of H₂ and CO, of which the H₂ is subsequently separated from the fuel gas and burned directly in a gas turbine. Following gasification, the fuel gas is reacted with steam between 250–400°C through a water-gas shift reaction, thereby generating additional H₂ and oxidizing CO to CO₂ (16, 17). Several low-temperature adsorbents have been developed for CO₂ capture, such as activated carbon, zeolites, metal organic frameworks (MOFs), and amine-modified materials. The major challenges associated with post- and precombustion capture, in addition to the equilibrium CO₂ capacities of typical adsorbents, are discussed.

The interaction between a CO₂ molecule and the pore surface of a given adsorbent material dictates whether the adsorption mechanism is physical or chemical. Physical adsorbents (i.e., physisorbents) capture CO₂ by a physical interaction primarily based upon a charge attraction. More specifically, the selective adsorption of CO₂ over N₂ is based upon CO₂-surface van der Waals interactions, as well as pole-ion or pole-pole interactions between the CO₂ quadrupole and the surface ionic or polar sites. These interactions are normally very weak, resulting in low heats of adsorption, typically ranging from 10 to 15 kJ mol⁻¹ (11). Hence, physisorbents can be regenerated by applying minimal energy and can therefore be readily implemented using pressure swing adsorption (PSA), a competitive technology for postcombustion CO₂ capture that is discussed in greater detail in the section titled Beyond Material Properties.

Selectivity: the characteristic of a material to adsorb/interact with one compound over a second, i.e., CO₂ over N₂

Physisorption: sorption process where the primary mechanism of selection is a charge

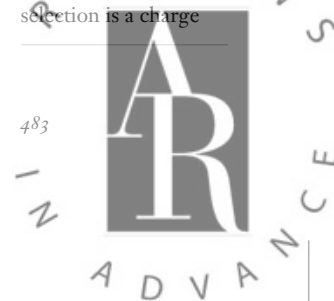


Table 1 Gas mixture compositions and physical conditions relevant for potential membrane applications

		Coal flue gas (4, 12)	Coal gasification fuel gas (4, 12)	Post water-gas shift (13, 14)
Mixture composition	N ₂ (vol.%)	70–80	1–6	–
	CO ₂ (vol.%)	11–13	1–13	30–40
	O ₂ (vol.%)	~6	–	–
	H ₂ O (vol.%)	6–12	2–28	6–15
	H ₂ (vol.%)	–	21–30	40–60
	CO (vol.%)	–	40–63	<4
	H ₂ S (ppm)	–	1,000–13,500	<500 ^a
	NH ₃ (ppm)	–	50–800	–
	NO _x (ppm)	200–800	–	–
	HCl (ppm)	1–250	500–600	<10 ^a
	SO ₂ (ppm)	200–4,000	–	–
	SO ₃ (ppm)	0–20	–	–
	Hg (ppb)	1–7	–	–
Particulate matter (g m ⁻³)	5–20	8–17	<0.1 ^a	
Temperature (°C)		60–150	500–1,800	250–550
Pressure (bar)		~1	24–70	20–80

^aPost acid-gas scrubbing.

However, the major challenge in applying physisorbents is the existence of combustion water in flue gas, which may be detrimental to the CO₂ selectivity in the case of zeolites, activated carbons, and MOFs, in particular, owing to the competitive adsorption of water with CO₂. For example, water uptake as low as 0.8 wt% can significantly compromise the CO₂ capacity of zeolitic materials, owing to the stronger dipole-ion interaction between water and the adsorbent compared with the quadrupole-ion interaction of CO₂ (18). Water is shown to negatively affect CO₂ adsorption on activated carbons in particular. For instance, the CO₂ capacity of a yeast-based activated carbon was found to decrease from 4.8 mmol g⁻¹ (25°C, 1 bar) under dry conditions to 3.5 mmol g⁻¹ (25°C, 1 bar) with preadsorbed water (19). Another study reported a decrease in CO₂ adsorption at 25°C on coconut shell-based activated carbon in the presence of water (20).

Results have shown that water may be either beneficial or detrimental to CO₂ adsorption on MOFs, depending on the type of MOF and the amount of water adsorbed. For instance, in some cases, a small amount of water (approximately 4 wt%) may become coordinated within the matrix of open-metal site MOFs, thereby enhancing CO₂ adsorption by providing additional interaction sites (21, 22). The interaction mechanism likely occurs through a carbonate formation between CO₂ and water; otherwise, the water would be in direct competition with CO₂. Hence, design of an adsorbent in which water is adsorbed and becomes more basic, and thus more likely to react with the acidic carbon atom of CO₂, would lead to a cooperative effect between water and CO₂ uptake. Another route to designing adsorbents selective to CO₂ is to create hydrophobic surfaces (23, 24); however, the additional surface groups have the potential to occupy CO₂ adsorption sites and/or pore volume, thereby reducing the potential CO₂ capacity. Outside of these efforts, preremoval of water from the flue gas may be a necessary step in the case of physical adsorption approaches for CO₂ capture.

Physical adsorption is an inherently exothermic process. Therefore, the management of heat in an adsorption process can be crucial for maximizing a sorbent's working capacity. Several approaches have been considered to date, which include the installation of heat-transfer equipment into the sorption columns or the use of materials that dissipate heat readily (25). In contrast to physisorbents, chemisorbents exhibit high isosteric heats of adsorption with superior selectivity. Furthermore, chemisorbents are able to achieve higher CO₂ adsorption capacity at relatively lower CO₂ partial pressures compared with physisorbents by introducing basic pore-surface functionalities to react with acidic CO₂. Nevertheless, the major disadvantage of chemisorbents involves the energy-intensive regeneration step, which requires thermal swing adsorption (TSA), a time-consuming process technology.

Amine functionalization seems to be a promising solution given the number of studies indicating enhanced capacity for amine-modified adsorbents under humid conditions. The mechanism of uptake in this case closely resembles an absorption process involving CO₂ dissolution. The diffusion of CO₂ molecules into the amine matrix is expected to be slow, which may limit the application of these adsorbents in a dynamic adsorption system owing to insufficiently slow diffusion kinetics. Amines react with CO₂ through a zwitterion (26) and/or a base-catalyzed hydration (27) mechanism, where the first mechanism is generally accepted in the case of primary or secondary amines, whereas the second mechanism is known to occur in the case of tertiary or sterically hindered primary or secondary amines in the presence of water. The overall stoichiometries for the two mechanisms are 0.5 and 1 mol CO₂ mol⁻¹ amine, respectively. Owing to the nature of the amine-CO₂ reaction, the presence of water may enhance the CO₂ adsorption capacity of the amine-functionalized adsorbents. For instance, the hyperbranched aminosilica prepared by *in situ* polymerization of aziridine on SBA-15 exhibited an enhanced CO₂ capacity of 5.55 mmol g⁻¹ (25°C, 0.1 bar) under humid conditions compared with 3.11 mmol g⁻¹ under dry conditions (28). More recently, polyethyleneimine and tetraethylenepentamine supported on mesoporous silica capsules with diameters of approximately 400 nm showed a CO₂ capacity of 6.6 mmol g⁻¹ (75°C, 1 bar), which increased to 7.9 mmol g⁻¹ in the presence of water (29). However, the densely packed amine groups can significantly reduce the adsorbent surface area in some cases. For example, *in situ* polymerization of aziridine to form hyperbranched amine in SBA led to a decrease in the N₂ BET surface area from 870 to 45 m² g⁻¹ (28).

In addition to postcombustion capture, precombustion CO₂ capture for gasification applications may also play a role in the portfolio of capture solutions in a carbon-constrained future. The elevated feed pressure (approximately 35 bar) and the relatively high CO₂ concentration (20–40%) collectively provide an optimal environment for a PSA separation process (30). The high CO₂ partial pressure leads to a reduction in the size of the capture system compared with postcombustion technologies, as well as a subsequent decrease in capital cost (31, 32). Adsorbent design requirements for precombustion capture include high cyclic working capacity, high CO₂/H₂ selectivity, and high CO₂ recovery (33). MOFs exhibit a high CO₂ capacity at elevated pressures; for example, both MOF-200 and MOF-210 hold the record at 54.5 mmol g⁻¹ at 25°C and 50 bar, owing to ultrahigh BET surface areas and pore volumes (i.e., 4,530 and 6,240 m² g⁻¹ and 3.59 and 3.60 cm³ g⁻¹, respectively) (34). It would be more relevant to investigate the performance of these MOFs at the higher temperatures of the fuel gas (**Table 1**), in which a pressure as high as 50 bar would be of interest. Also, the high cost of MOF synthesis may limit their applications at scale. The typical retail price for commercialized MOFs ranges from \$10 to \$15 per gram of material, compared to a commercially available activated carbon, which may range from \$0.05 to \$2 per gram. Scaling up the synthesis process is a necessity that will reduce the costs of the starting materials but might require specially developed synthetic techniques and hence result in additional synthetic cost (35). Zeolites, which have a promising CO₂ capacity between 0.1–0.15

Chemisorption:

sorption process where the primary mechanism of selection is a chemical interaction, such as in an amine-CO₂ reaction forming a carbamate bond



Table 2 CO₂ adsorption capacity of selected adsorbents for postcombustion capture

Adsorbents	Adsorption temperature (°C)	CO ₂ partial pressure (bar)	^a CO ₂ capacity (mmol g ⁻¹)	References
Carbon-based	25	1	1.5–4.8	38–45
	25	1	(1.0–3.5)	19, 20, 46
	25	0.1	0.7–1.5	38–45
Zeolite-based	25–32	1	0.75–5.71	47, 48
	20–40	0.1/0.15	0.32–3.81	47–49
Metal organic frameworks	25	1	≤4.5	15
	25	0.1	0.1–5.95	35, 50
AMM ^b	75	1	2.0–4.95	38
	25	0.05–0.15	0.4–5.77	47
	25	0.05–0.15	(0.5–14.03)	47

^aCO₂ capacities shown in parentheses were measured under humid conditions.

^bAmine-modified adsorbents.

bar, have shown limited adsorption of CO₂ at elevated pressures (e.g., 7.4 mmol g⁻¹ for zeolite 13X at 25°C and 32 bar) (36). Activated carbons might be promising adsorbents for precombustion applications because of their low cost and reasonable capacity at precombustion conditions. The highest uptake reported to date is 23 mmol g⁻¹ for Maxsorb at 25°C and 30 bar (37). A summary of capacities and operating conditions for typical sorbent groups is found in **Table 2**.

Furthermore, the stability of these adsorbents under realistic flue gas conditions, e.g., in the presence of other acid gas impurities, such as SO_x (i.e., SO₂ and SO₃) and NO_x (i.e., NO and NO₂), has yet to be investigated; therefore, the potential competition of these acid gases with CO₂ uptake is currently unclear. In addition, the adsorbent properties, both working capacity and diffusion kinetics, must be properly considered within a given dynamic adsorption process for the adsorbent technology to be practical. Most of the adsorption literature focusing on material design is based upon equilibrium adsorption capacities, rather than the kinetics of adsorption. In fact, there exists very limited data on mass-transfer resistance and subsequent diffusion limitations, which are required to accurately model a full adsorption process for optimization of material properties with a given process configuration.

Adsorption Dynamics

For adsorption separation processes, in addition to the adsorption isotherms, an accurate description of the mass transfer between the CO₂-containing gas and the porous adsorbent particle is essential when it comes to the design of an optimal coupled material and process for CO₂ capture. Physical adsorption is a very rapid process, and its rate is generally controlled by mass-transfer resistances rather than by the intrinsic rate of equilibration at the active surface. In other words, in almost every physical adsorption process, diffusion is the rate-limiting step. A porous adsorbent in contact with a fluid phase offers three distinct resistances to mass transfer: external film resistance and intraparticle diffusional resistances (composed of macro- and mesopore resistance), as shown in **Figure 3**.

When an adsorbent shows a well-defined bimodal pore-size distribution, the intraparticle diffusional resistance is divided into the diffusional resistance of the micropores within the microparticles, the diffusional resistance of the meso- and macropores, and a possible barrier resistance at

Mesopores: pores between 2 and 50 nm in diameter

Micropores: pores less than 2 nm in diameter

Macropores: pores greater than 50 nm in diameter



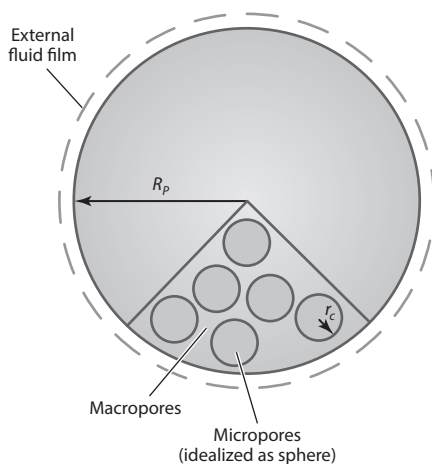


Figure 3

Three mass-transfer resistances in a composite adsorbent pellet. Abbreviations: r_c , microparticle radius, R_p , particle radius.

the pore mouth of the microparticle. The relative importance of these resistances varies widely, depending on the system and the conditions. The dominant resistance may be either macropore or micropore diffusion or a combination of the resistances previously discussed.

According to the International Union of Pure and Applied Chemistry classification, pores may be subdivided into ultramicropores (<0.7 nm), micropores (0.7–2 nm), mesopores (2–50 nm), and macropores (>50 nm) (51). Transport in meso- and macropores can occur through four distinguishable diffusion mechanisms: molecular diffusion, Knudsen diffusion, Poiseuille flow, and surface diffusion (52). In the micropore, where the pore diameter and the diameter of the diffusing molecule are comparable, the molecule never escapes the force field of the adsorbent surface, and the diffusing molecules jump between adsorption sites, just as in surface diffusion. Micropore diffusion is an activated process and depends strongly on both the CO_2 concentration and temperature. In an equilibrium-controlled cyclic adsorption process, the dominant resistance is often macropore diffusion, whereas in a kinetically controlled process, the major resistance to mass transfer is micropore diffusion (53).

In a cyclic adsorption process, the adsorption kinetics can be described using two particle models, namely the pore diffusion model and the linear driving force (LDF) model. In the pore diffusion model, diffusion within the macro- and micropores along with mass transfer through the film surrounding a given particle are all considered. However, in the LDF model, all of the mass-transfer resistances (i.e., external film, macropore, and micropore) are combined into a single mass-transfer coefficient term, k_i , as shown in Equation 2. The LDF model can be written as

$$\frac{\partial q_i}{\partial t} = k_i(q_i^* - q_i), \quad 2.$$

such that q_i^* is the equilibrium value of the solid-phase concentration of component i corresponding to the concentration of the adsorbate in the fluid phase. The overall LDF coefficient can be estimated from

$$\frac{1}{k_i} = \frac{R_p^2}{3k_f c_i} + \frac{R_p^2}{\Omega_i \varepsilon_p \left(\frac{D_c}{\tau}\right) c_i} + \frac{r_c^2}{\Omega_i D_c}, \quad 3.$$

Diffusivity: the rate of transfer of the solute under the driving force of a concentration (or pressure) gradient

such that the terms on the right-hand side represent the external film, macropore, and micropore resistances, respectively. R_p is the particle radius, k_f is the external film resistance, Ω_i depends upon the cycle frequency, ε_p is the particle porosity, τ is the particle tortuosity, D_e is the effective macropore diffusivity, r_c is the microparticle radius, and D_c is the micropore diffusivity. The effective macropore diffusivity accounts for the contributions from molecular D_m , Knudsen D_k , and surface diffusion D_s contributions (52, 56) by

$$\frac{1}{D_e} = \frac{1}{D_m} + \frac{1}{D_k + \frac{1 - \varepsilon q_i^*}{\varepsilon} D_s}. \quad 4.$$

More explicitly, the value of Ω_i shown in Equation 3 depends on the frequency of cycling in a cyclic adsorption process that matches the LDF solution with the exact solution obtained from application of the pore diffusion model (53–55). However, for most equilibrium-controlled separation processes, an estimate of $\Omega_i = 15$ is adequate. In an equilibrium-controlled separation process, the pore diffusion model is of secondary importance because the LDF model is adequate for describing the mass-transfer resistance to the solid particle. However, in a kinetically-controlled separation process, micropore diffusivity is strongly concentration dependent if the assumption of constant diffusivity in the micropores is not valid. For these processes, either the LDF correlation should be calibrated for each specific system using experimental data (57) or a full micropore diffusion model must be developed that includes the concentration dependence of micropore diffusivity (58–60).

Conventional adsorbents, in the form of pellets, consist of small microporous crystals held together with a clay-based binding material (52). As previously discussed, these adsorbents have macropore and micropore mass-transfer resistances within the particle, which makes rapid cycling of the cyclic adsorption processes a challenge. The reduction in cycle time typically results in poor cycle performance owing to mass-transfer limitations. However, in an equilibrium-based separation process, low mass-transfer resistance is usually desirable to carry out an adsorption process with a shorter cycle time with increased productivity. One option for reducing the mass-transfer resistance is to reduce the pellet size; however, a decrease in pellet size will lead to an increase in the pressure drop along a packed column and may also result in significant gas maldistribution and gas channeling, which is explored in greater detail in the **Supplementary Material** (follow the **Supplemental Material link** from the Annual Reviews home page at <http://www.annualreviews.org>) (56). In addition, performing rapid PSA cycles to significantly improve cycle productivity may lead to the fluidization of small adsorbent pellet particles. An alternative approach to reducing mass-transfer resistance and pressure drop is the use of novel structured adsorbents in the form of monoliths (25, 61). This is traditionally done in the catalysis community to reduce pressure drop and related operating and maintenance costs of the process.

MEMBRANE-BASED SEPARATION

Membranes have several advantages compared with absorption and adsorption separation processes for CO₂ capture, including a relatively small footprint, reducing the capital costs; no regeneration requirements, thereby reducing the complexity in designing heat-exchange systems; no solvent requirements, making them more environmentally friendly; and higher efficiency of separation owing to a lack of phase change. In general, membranes can be classified based on material (e.g., polymeric, ceramic, or metallic), transport mechanism (e.g., Knudsen diffusion, molecular sieving, or solution-diffusion), or gas selectivity (e.g., CO₂-, H₂-, O₂-, or N₂-selective). To choose an appropriate membrane for effective separation, an understanding of the mixture



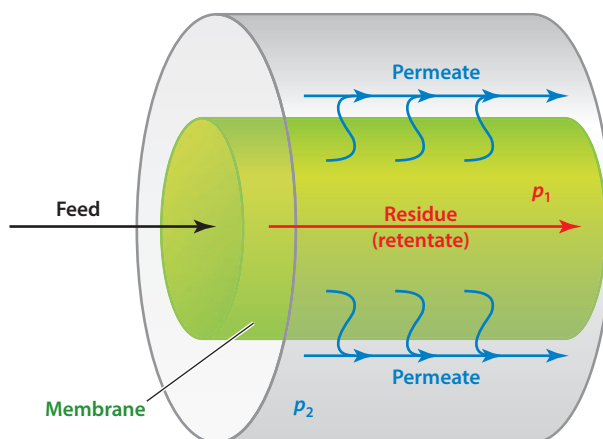


Figure 4

Schematic of simplified membrane gas-separation system (adapted from Reference 11) such that p_1 is feed (or retentate) pressure and p_2 is permeate pressure.

streams, such as gas composition, temperature, and pressure, is critical. Based on the gas mixture properties shown in **Table 1**, CO_2 - or N_2 -selective membranes would be suitable for capturing from postcombustion flue gas applications, whereas H_2 - or CO_2 -selective membranes would be useful for precombustion capture. This review focuses on CO_2 -selective polymeric membranes for application to postcombustion CO_2 capture and H_2 -selective metallic membranes for application to precombustion CO_2 capture. Metallic membranes are particularly beneficial in precombustion capture because of their workability at high temperatures.

Figure 4 shows a simplistic schematic of a membrane-separation process illustrating relevant gas streams. In general, the high-pressure side of the membrane is termed the feed stream, whereas the low-pressure side is termed the permeate stream. The residue (or retentate) is the remainder of the feed stream that does not pass through the membrane. The total feed and permeate pressures in this case are p_1 and p_2 , respectively.

The flux of gas component i , J_i , is proportional to the concentration gradient across the membrane, represented as

$$J_i = -D_i \left(\frac{dc_i}{dz} \right) = D_i \left(\frac{c_{i,1} - c_{i,2}}{z} \right), \quad 5.$$

such that D_i is the diffusivity of gas i ; $c_{i,1}$ and $c_{i,2}$ are the concentrations of gas i at the feed and permeate sides, respectively; and z is the membrane thickness. In membranes based on the solution-diffusion mechanism, the concentration of gas i within the membrane is related to the partial pressure of the gas in the feed mixture through the solubility coefficient S_i , represented by Equation 6, with units that are the reciprocal of the Henry's law coefficient:

$$c_i = p_i S_i. \quad 6.$$

Substitution of Equation 6 into Equation 5 yields

$$J_i = \frac{D_i S_i (p_{i,1} - p_{i,2})}{z}, \quad 7.$$

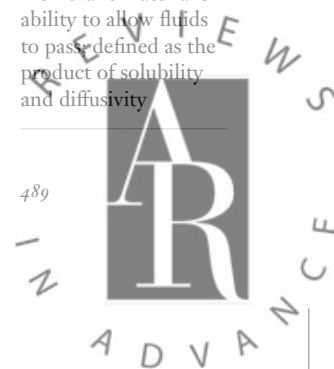
such that the product of the diffusivity and the solubility of component i is equivalent to its permeability, P_i , and the ratio of $D_i S_i / z$ is equivalent to a mass-transfer coefficient. Selectivity

Permeate: the fraction of a feed stream that permeates through the membrane

Retentate: the fraction of a feed stream that does not pass through a membrane

Solubility: a property of a membrane's material (or solute) to allow a solvent to dissolve and form a homogeneous phase

Permeability: a measure of a membrane material's ability to allow fluids to pass, defined as the product of solubility and diffusivity



Permeance: the degree to which a membrane material allows the permeation of a fluid and is equal to the quotient of the permeability and the membrane thickness; this is equivalent to the mass-transfer coefficient in the flux equation

Gas permeation unit (GPU): $1 \text{ GPU} = 10 \text{ Barrer cm}^{-1} = 7.5005 \times 10^{-16} \text{ m} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$

(i.e., separation factor) is defined as the ratio of permeabilities for a binary mixture. Reasonably high selectivity is critical to enhance membrane performance.

For the practical implementation of membranes in a CO₂ capture process, performance can be assessed based upon several different criteria. First, the membrane should have a reasonable permeability and selectivity to separate CO₂ directly or indirectly. The target selectivity may vary depending on the number of stages and other process conditions, but many feasibility studies have agreed that a selectivity (CO₂/N₂) of at least 20 to 200 and a permeance of 1,000–10,000 GPU is required to achieve at least 90% postcombustion CO₂ capture, at which point membranes may be more economical than amine-based absorption technology (62, 63). Only several of the current membranes have high selectivity, with the best-performing membrane currently known having a selectivity of 30–40 with a permeance of 1,500–1,600 GPU (64). An increase in the surface area may enhance permeability, which linearly corresponds to the cost of capture, indicating that either a high-permeability or a low-cost, high-surface area membrane is desired. Second, in addition to long-term stability, the membrane should be stable at the desired operating temperature, pressure, and chemical environment. Finally, the separation process should be scalable both technically and economically. Currently, the main challenge for large-scale implementation is that no single membrane technology has satisfied all of these requirements simultaneously.

Polymeric membranes have been developed widely for traditional industrial processes for decades, and CO₂-selective membranes have also been used for small-scale applications, such as natural gas purification. Glassy and rubbery polymers are typical membrane materials, with physical structures differentiated by their glass-liquid transition temperature, T_g . The glass-liquid transition is not the same as a phase transition between equilibrium states but rather is commonly defined based upon experimental observations, influenced by the thermal history of a given material. Polymers operating below T_g are rigid and brittle, whereas those operating above T_g are soft and flexible and are referred to as glassy polymers and rubbery polymers, respectively. In general, most rubbery polymers have a high permeability but a low selectivity, whereas glassy polymers exhibit a low permeability but high selectivity. Flexible rubbery polymers with high chain mobility tend to create large channels within the polymer matrix to facilitate molecular diffusion, leading to high permeability but potentially low selectivity. Glassy polymers are defined by rigid and regular microdomains that allow for limited diffusion of small molecules, providing high selectivity but relatively low diffusivity (65). Gas transport in polymeric membranes is also affected by several other polymer properties beyond T_g , such as morphology, free volume content, orientation, crosslinking structure, polymer polarity, thermal-processing history, average molecular weight, molecular weight distribution, composition, degree of crystallization, and types of crystallites. There have been extensive studies on poly(dimethylsiloxane) rubbery polymer membranes and glassy polymers, including polyacetylenes, poly[1-(trimethylsilyl)-1-propyne], polyimides, polyamides, polyarylates, polycarbonates, polysulfones, and cellulose acetates (65–68). Polyimides, in particular, are among the most extensively investigated polymer materials owing to their high selectivity and permeability compared with many other glassy polymers. However, these membranes typically fail to satisfy both the selectivity and permeance criteria simultaneously. They are limited by a well-known trade-off relationship, which was originally described by Robeson (69, 70). **Figure 5** shows the upper-bound relationship between CO₂ permeability and CO₂/N₂ selectivity. The data marked in yellow were published in and after 2010. This clearly shows that there have been significant recent efforts to improve membrane transport properties but that these efforts have led to only a minimal shift in the upper bound. In the case of porous membranes, the upper-bound relationship is correlated to the kinetic diameters of the gas components of a given binary mixture. In other words, as the pore size within the membrane decreases, the permeability decreases



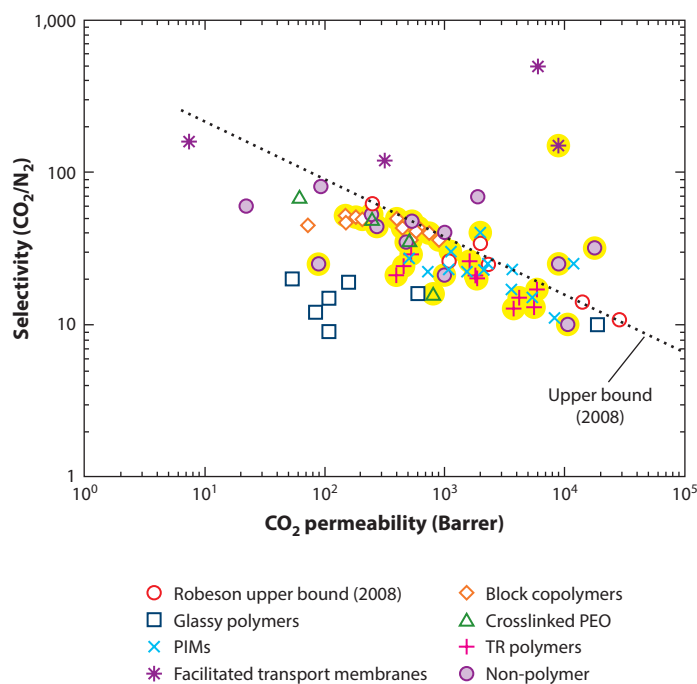


Figure 5

Trade-off relationship between CO_2 permeability and CO_2/N_2 selectivity, including traditional polymers and recent developments. The upper bound suggested by Robeson (2008) accounts for only traditional polymers, and the data marked in yellow are recently developed membranes published in or after 2010 (64, 70, 72, 75). Abbreviations: PEO, polyethylene oxide; PIMs, polymers with intrinsic microporosity; TR polymers, thermally rearranged polymers.

with increased selectivity. This implies that an ideal membrane would have an optimal, and likely narrow, pore size distribution, in the case of separation by size exclusion. Therefore, engineered uniform porous membranes may provide the true upper-bound limit beyond the traditional upper bound, as shown in the cases of carbon molecular sieves, block copolymers, mixed-matrix membranes, thermally rearranged polymers, and polymers with intrinsic microporosity (64, 66, 71). Facilitated transport membranes may lead to materials with properties lying even above the upper bound because amine-based carriers in the membrane may enhance CO_2 transport and subsequent CO_2 diffusion (64, 72). In recent studies, large-scale screening of nanoporous zeolites and MOFs showed promising permeability and selectivity that exceed the traditional upper limit substantially through enhanced solubility selectivity (73, 74). These new membrane materials are currently being investigated at the bench scale, and their cost may be an order of magnitude higher than that of commercial synthetic polymers (71). Challenges are associated with achieving high integrity of the porous structures without defects in fabrication and maintaining the optimal membrane properties in the presence of water (72).

Polymer membranes are often susceptible to high temperatures, requiring the gas to be cooled to less than 100°C prior to separation. In addition, trace acid gases are often present in the flue gas, as shown in **Table 1**, and may compromise the membrane's stability. For rigid polymers, a high partial pressure gradient may be created to enhance the separation efficiency, but this increase in feed pressure will ultimately lead to increased parasitic energy demand. Therefore, it is

Barrer: a non-SI unit of permeability; 1 Barrer = 3.348×10^{-19} kmol m (m⁻² s⁻¹ Pa⁻¹)

necessary to consider membrane material properties alongside the complete membrane-separation process to ultimately develop a separation strategy that is effective, but with a minimal energy requirement. Several process-level investigations indicate that membrane technology could be a major component of the portfolio of gas-separation solutions to CO₂ separation (62, 63, 64, 75).

H₂-selective polymer membranes are also a possibility, but dense metallic membranes are more advantageous for precombustion capture applications owing to their increased stability at high temperature and pressure conditions. Metallic membranes traditionally consist of H₂-selective palladium (Pd) membranes following a solution-diffusion mechanism in which hydrogen is catalytically dissociated on a metal surface, followed by the dissociated hydrogen atoms permeating through the metallic lattice and recombining to H₂ on the permeate side of the membrane. Pd and Pd-based alloys are commercially available to a small extent (76, 77). The performances of various Pd-based H₂-selective membranes have been described extensively in the literature and are known to produce high-purity H₂ streams (i.e., 99.99% to 99.9999%) (76, 78, 79). Because only hydrogen can be dissociated on the Pd membrane surface, the selectivity of the membrane toward H₂ is ideally infinite, but the practical selectivity (H₂/CO₂) is often estimated at 1,000 owing to defects in the material as well as potential leakage (80). The H₂ flux may also be derived from Equation 5 but is proportional to the gradient of the square root of the partial pressure difference across the membrane. The solubility of atomic H in a given metallic membrane is given by Sieverts' law, represented by

$$c_x = K_s \cdot p_{x_2}^{0.5}, \quad 8.$$

such that x_2 is the diatomic gas molecule and x is the dissociated atomic phase present in the metal. Substitution of Equation 8 into Equation 5 yields

$$J_{x_2} = \frac{D_x K_s (p_{x_2,1}^{0.5} - p_{x_2,2}^{0.5})}{2z}. \quad 9.$$

The gas permeability through the metallic membrane is half of the product of the solubility K_s and diffusivity D_x . Note that the factor of one half is included because the molecular permeation is equivalent to half of the atomic permeation. A recent study has suggested that N₂ may be separated using metallic membranes via a mechanism similar to H₂ separation. Because N₂ is the major product of coal- and natural gas-fired combustion processes, N₂-selective metallic membranes take advantage of the greater driving force of separation, given the higher partial pressure of N₂ compared with CO₂ in a postcombustion process. This approach would lead to CO₂ in the high-pressure retentate stream instead of the lower-pressure permeate stream, which may lead to savings in compression requirements for pipeline transport of CO₂ (81).

As in the case of polymer membranes, metallic membranes should also possess reasonably high permeability and selectivity. Although the mechanism in metallic membranes is slightly different from that in polymers, **Figure 6** shows a similar trade-off relationship between selectivity and permeability for a binary mixture of H₂ and CO₂. Note that the theoretical selectivity of metallic membranes is infinity, but in **Figure 6** it is reported as 1,000 if it was not specified in the literature. Note also that to compare the performance of metallic membranes to polymers, the units of Barrer were backed out based upon the reported H₂ flux values combined with a linear dependence on the pressure gradient. From **Figure 6**, it is clear that enhanced polymers and inorganic porous membranes lie beyond the upper-bound region determined by traditional polymer membranes. The properties of polymer membranes may be enhanced by surface modifications in which nucleophilic groups on glassy polymers present a higher affinity toward hydrogen, or by constructing a well-defined pore structure for optimal diffusivity selectivity, similar to the strategies for improving CO₂-selective polymer membranes. The inorganic porous membranes indicated in **Figure 6**



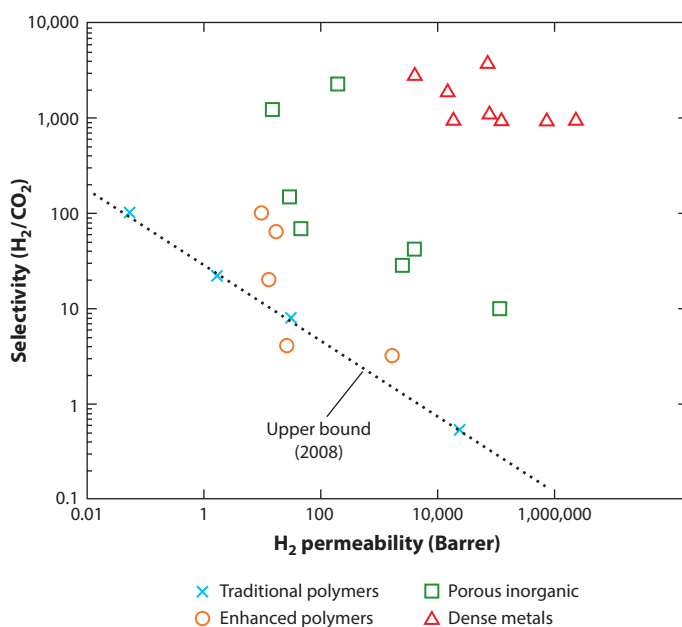


Figure 6

Trade-off relationship between H₂ permeability and H₂/CO₂ selectivity, including traditional polymer, inorganic, and metallic membranes (70, 84–100).

are composed of porous materials, such as zeolites and silica-based materials. The enhanced separation capacity of these inorganic membranes is due mainly to the improved diffusivity and selectivity, which leads to even greater capacities than those of enhanced polymers owing to the tunable pore structures, which are composed of ultramicro-, micro-, and mesopores. Because the transport of gas through the ultramicropores is an activated process, operation at high temperatures is beneficial for these systems. Benefits of these materials are their thermal stability and favorable economics. Known challenges include their low tolerance to water vapor and the lack of hydrothermal stability for zeolites, in particular (82, 83). Hydrogen permeation through metals combined with catalytic dissociation exhibit significantly higher permeability owing to increased solubility, compared with porous membranes, placing the metallic membranes in the upper-right quadrant of the selectivity-permeability trade-off plot, as shown in **Figure 6** (70, 84–100).

Scalability is the major issue for the application of Pd-based membranes, particularly because of the high cost of the precious metal. In the early stages of Pd membrane applications, pure Pd membranes with a thickness of a few tens of micrometers were considered, but later studies showed significant savings through deposition techniques, such that 1- μm layers of Pd were deposited on ceramic or metallic supports (83, 101). These composite membranes are known to exhibit improved permeance (17, 102). Another approach to lower the cost is the use of Earth-abundant metals, such as vanadium, niobium, or nickel, and their alloys as a major membrane component (78, 103). As an example, in 2010, the costs were approximately \$7 and \$8,000 per pound for vanadium and palladium, respectively (104). Palladium-based membranes for precombustion CO₂ capture applications have been studied extensively (16, 17, 105), but there have been no large-scale applications to date. Because Pd-based membranes were first developed for the generation of high-purity H₂ streams, primarily for H₂ fuel cell applications, they tend to have very high selectivity but relatively

low permeability. In fact, the purity requirement may be significantly reduced for gasification or natural gas-reforming applications in which CO₂ capture is the primary goal (77, 82, 83).

BEYOND MATERIAL PROPERTIES—PROCESS CONSIDERATIONS

Adsorption Processes

Adsorption-based separation processes are cyclic processes that alternate between adsorption and desorption modes of operation. Based on the regeneration technique, these processes are categorized as PSA and TSA. If the cycle switches between adsorption at above atmospheric pressure and desorption at vacuum conditions, then it is termed pressure vacuum swing adsorption (PVSA). In a vacuum swing adsorption (VSA) process, the pressure cycling takes place between atmospheric and subatmospheric pressures.

Several challenges exist in the design of an adsorption-based process for CO₂ capture. First, the relatively low concentration of CO₂ (i.e., **Table 1**) in the flue gas for postcombustion capture makes the separation of CO₂/N₂ challenging. Second, the throughput of flue gas from an existing power plant is significantly larger than from an existing gas-separation plant to which the adsorption technology would be applied traditionally. This sets stringent requirements on the size of equipment, such as columns, compressors, and vacuum pumps. To increase the productivity of the capture process plant, which results in a smaller plant size, a shorter cycle time is required. Third, in all existing physical adsorbents, CO₂ adsorbs more strongly than N₂ owing to its larger quadrupole moment. The quadrupole moments of CO₂ and N₂ have been reported in the literature as -13.71×10^{-40} and -4.91×10^{-40} Coulomb m⁻², respectively (11). Hence, CO₂ is recovered as the heavy product (extract). Conventional cyclic adsorption processes have been designed and optimized for the purification of the light component (i.e., the less strongly adsorbed component), which can be recovered as the adsorption product. However, in the case of CO₂ capture, the challenge is to recover the heavier product (i.e., CO₂) in high purity. This requires novel cycles that incorporate different steps for the enrichment of the more strongly adsorbed component (CO₂) in the desorption product while preventing the contamination of the adsorption product with CO₂. Finally, the challenge of combustion water lies in its competitive adsorption with CO₂ onto adsorbents, which reduces the adsorbent capacity. Because water possesses a strong dipole moment, it will always be preferentially adsorbed in the case of physical adsorption, because the primary mechanism is based upon a charge attraction of the adsorbate to the charge groups of the adsorbent.

Despite considerable growth in the practical applications of cyclic adsorption processes, the design and optimization of these processes are still predominantly carried out using experimental techniques or parametric studies (106–110). More importantly, heuristic or parametric studies cannot be expected to provide optimal process parameters that will maximize or minimize the desired objective(s) while fully meeting the design and operational constraints, because it is essentially impossible to test all of the combinations of design and operating variables.

Researchers have investigated different PVSA/VSA adsorption processes for postcombustion capture of CO₂ from coal-fired flue gas; however, in most of these studies, the heavy reflux step is used to enrich the feed stream with CO₂ and to remove the lighter component (N₂) prior to product collection. More specifically, in the heavy reflux step a fraction of the stream, which consists primarily of the heavy-product gas (CO₂), from the countercurrent depressurization step is recycled back to the column in order to enrich the feed end of the column with CO₂ and flush out N₂ (107–114). Although the heavy reflux step improves the performance of the cycle in terms of CO₂ purity, it unfortunately increases the energy consumption significantly.

Most of the optimization studies available in the literature consider single-objective optimization (e.g., minimization of energy or maximization of recovery) (115–120). However, the design of a PSA/VSA process involves multiple objectives, which are often in conflict. Note that in the case of multiobjective optimization, unlike in single-objective optimization, there may not be a unique optimum solution. Instead, there is an entire set of optimal solutions (i.e., a curve of solutions) known as a Pareto front or trade-off curve. In other words, moving along the Pareto curve results in the improvement of one objective at the expense of another.

By performing multiobjective optimization using a genetic algorithm, Haghpanah et al. (121, 122) have systematically analyzed most known PVSA/VSA cycles with zeolite 13X as the adsorbent for postcombustion CO₂ capture from dry flue gas containing 15% CO₂ in N₂. They considered two multiobjective optimization scenarios. First, they performed the maximization of purity and recovery to identify the optimal performance of the synthesized cycles and whether the configuration was able to satisfy the purity and recovery targets for CO₂ capture. Then, they considered the promising cycles for the minimization of energy and maximization of productivity optimization with the desired CO₂ purity and recovery as constraints.

Within the work of Haghpanah et al. (121), the effects of evacuation pressure and flue gas pressurization were investigated for a basic four-step cycle consisting of the following steps: feed pressurization, high-pressure adsorption, forward blowdown, and reverse evacuation, as shown in **Figure 7**. In the feed pressurization step, the column is supplied with the feed while the product end of the bed is closed. During the high-pressure adsorption step, the product end is then opened, and the adsorption of CO₂ takes place while N₂ is withdrawn from the product end. Following the high-pressure adsorption step, the column inlet is closed and then depressurized from the product-end pressure to an intermediate pressure. The main role of the forward blowdown step is to remove as much N₂ as possible to prevent the contamination of CO₂ with N₂ during the evacuation step. During reverse evacuation, the CO₂ product is withdrawn from the column by evacuating the column to a low pressure, P_L , from the feed end. To obtain the minimum energy required by the basic four-step PVSA cycle while simultaneously achieving the 90% purity-recovery constraint, the cycle must operate in the VSA mode with an evacuation pressure equal to 0.02 bar. This corresponds to a minimum energy of 149 kWh/tonne CO₂ captured (i.e., 11% energy penalty) at a productivity of 0.49 mol CO₂ m⁻³ adsorbent s⁻¹. However, Haghpanah et al. (121) also showed that if a higher evacuation pressure is required in the four-step cycle, then flue gas pressurization is required to meet the purity-recovery requirement, which results in a significant energy penalty. In addition, although feed pressurization was detrimental to the energy consumption, it led to improved process productivity. In another study, Haghpanah et al. (122) systematically evaluated six promising VSA cycles with a minimum vacuum level of 0.03 bar, which is an industrially achievable condition. The effect of light product pressurization, light reflux, heavy reflux, and pressure equalization was evaluated by performing purity-recovery and energy-productivity optimization. A four-step VSA cycle with light product pressurization, as shown in **Supplemental Figure 1**, is able to achieve the 90% purity-recovery requirements with a minimum energy consumption of 131 kWh/tonne CO₂ captured, which is equivalent to approximately 10% energy penalty, at a productivity of 0.57 mol CO₂ m⁻³ adsorbent s⁻¹. The minimum energy consumption required to achieve 95% purity with 90% recovery increases to 154 kWh/tonne CO₂ captured with a productivity of 0.44 mol CO₂ m⁻³ adsorbent s⁻¹.

Apart from PSA/VSA processes, several TSA processes have also been discussed in the literature. Note that TSA processes require long cycle times owing to slow cooling of the bed after thermal regeneration, which affects the productivity of the cycle. Lively et al. (123) proposed a hollow-fiber, sorbent-based, rapid temperature-swing adsorption system with low pressure drop and regeneration thermal requirements for postcombustion CO₂ capture, which is still



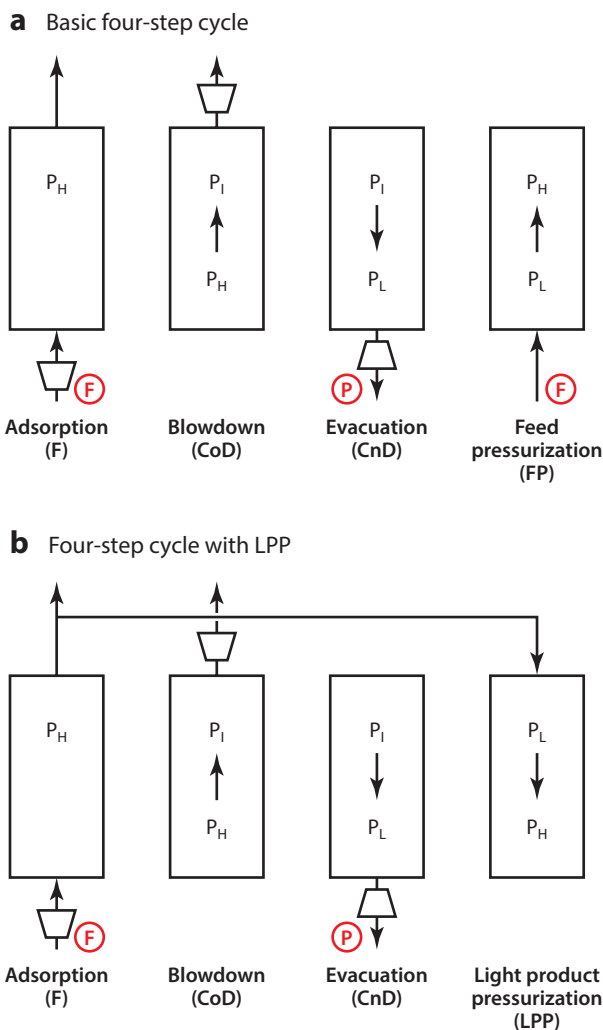


Figure 7

Basic four-step cycle and four-step cycle with light product pressurization (LPP). The steps in which feed introduction and product removal occur are shown as F and P, respectively.

under development (124). With the use of structured adsorbents with minimal mass-transfer resistance, in addition to new valve technology, the cycle times of PSA/VSA processes may be further improved over TSA processes.

In addition to the PSA cycle design, the choice of the adsorbent for CO₂ capture is another critical factor. Over the past decade, there has been an explosive growth of new materials suited for CO₂ capture. Among the available commercial adsorbents, activated carbon (107, 111) and zeolite 13X (110, 112, 121, 122) have received the most attention. Many new adsorbents under the family of MOFs and zeolitic imidazolate frameworks are being proposed as promising candidates for CO₂ capture (125). Recently, several studies have considered material screening for CO₂ capture as an attempt to identify several key adsorption material and/or process parameters that may be sensitive to determining an optimal combination of the two. However, one must couple

full process modeling and optimization with material properties, i.e., equilibrium and kinetic data. This important test is often missing in the literature and can help create more focused research and advanced development of CO₂ capture processes. Krishna & van Baten (126) examined the characteristics of a wide variety of MOFs, zeolitic imidazolate frameworks, and zeolites by considering adsorption selectivity and working capacity. Although both are important characteristics and show strong correspondence to process performance, as previously discussed, one must couple full process modeling and simulation with material properties. In another study, Krishna & Long (127) proposed the breakthrough time as a metric for MOF and zeolite screening. Harlick & Tezel (128) examined 13 zeolitic adsorbents, using the CO₂ pure-component adsorption isotherms and working capacity as the merits for selecting the promising adsorbents. Lin et al. (129) assessed hundreds of thousands of hypothetical materials by minimizing the parasitic energy on a power plant using a temperature-pressure-swing adsorption process for the capture unit while assuming equilibrium adsorption and desorption conditions. Recently, Maring & Webley (130) developed a simple PSA/VSA model for the quick screening of adsorbents. They have used the model to compare the performance of zeolite 13X, Mg-MOF-74, activated carbon, and a chemisorbent for postcombustion CO₂ capture. Although these are steps in the right direction, the methodologies are too simplified at this stage to provide reliable estimates of process performance. To evaluate the true potential of an adsorbent, rigorous simulation and optimization of the cyclic adsorption processes are required.

Membrane Processes

Similar to an adsorption process, achieving high purity and recovery with a membrane unit relies heavily on the membrane properties in addition to the process design and configuration. The main parameters that play a significant role in the performance of the membrane process are membrane permeance, selectivity, and the pressure ratio. Achieving a high CO₂/N₂ selectivity and high CO₂ permeance simultaneously in a membrane is a challenge because there is a trade-off between these two parameters, as discussed in the section titled Membrane-Based Separation. High permeability is desired to minimize the membrane surface area and the time required for separation, with high selectivity being the key parameter affecting the CO₂ purity. Note that although higher selectivity increases the CO₂ purity, the inherent tradeoff between permeability and selectivity means that high-selectivity membranes have low permeability and therefore require a very large membrane area. As previously discussed, it has been proposed that the optimum membrane should have selectivity in the range of 20 to 200 with a CO₂ permeance between 1,000 and 10,000 GPU (63). Baker and coworkers (63) showed that improving membrane permeance is more important than increasing selectivity to reduce the cost of postcombustion CO₂ capture. In addition, generating an appropriate pressure difference across the membrane to provide the required driving force for separation is another critical factor for achieving both high separation performance and minimum energy consumption. Baker and coworkers at Membrane Technology Research, Inc. discovered that the CO₂ driving force can be increased by enriching the CO₂ concentration in the feed up to 20% without impacting the combustion process significantly. In this process, as shown in **Figure 8**, the flue gas passes through a CO₂-selective membrane with air used as a sweep gas on the permeate side. This CO₂-laden air is then recycled back to the boiler to subsequently increase the concentration of CO₂ in the feed and the CO₂ partial pressure driving force across the membrane.

In general, three strategies have been considered in the literature for increasing the pressure difference between the feed and permeate streams: (a) compression of the feed, (b) use of vacuum on the permeate, and (c) a combination of these two. Applying vacuum conditions on the permeate side of the membrane results in reduced energy consumption compared with feed compression.



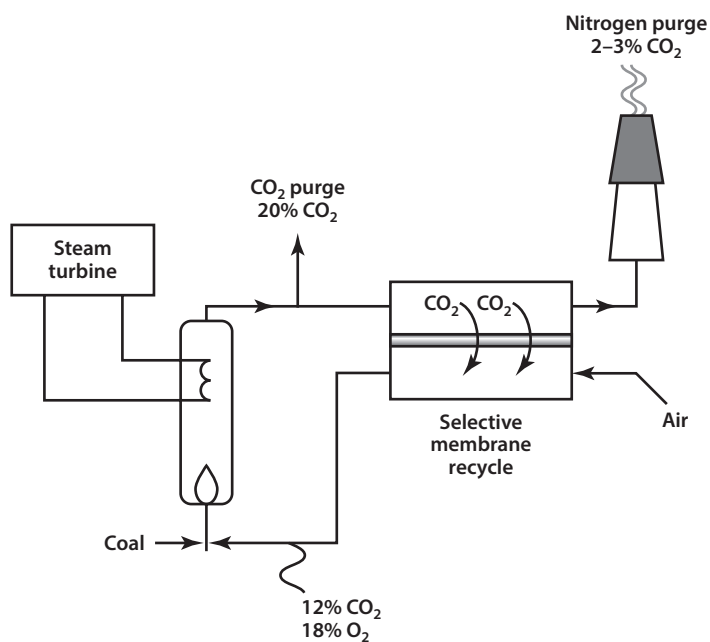


Figure 8

Schematic of the Membrane Technology Research process allowing for enhanced CO₂ flue gas partial pressure at no energy cost (image courtesy of Richard Baker, 2011).

The reason for this is that feed compression requires higher energy consumption because a feed compressor must pressurize a large volume of gas consisting primarily of N₂. However, there is a trade-off here because feed compression does result in a smaller membrane area. In other words, a higher pressure ratio (i.e., feed pressure divided by permeate pressure) increases the energy consumption but reduces the membrane area. In a practical membrane-separation process, the pressure ratios may range between 5 and 15 (63, 131).

Systematic parametric studies in the literature have shown that single-stage membrane processes are not able to achieve the desired purity-recovery requirements because the system performance is limited by the pressure ratio across the membrane. Recently, Zhai & Rubin (132) performed a comprehensive parametric study for different membrane configurations and showed that a two-stage membrane process with a sweep gas can satisfy the 95% purity and 90% recovery requirements with a 19% energy penalty. However, it is worth noting that detailed, multiobjective optimization is required to minimize membrane area and energy consumption simultaneously to evaluate the effect of the pressure ratio, selectivity, and permeability on the performance of membrane processes, which has yet to be carried out.

SUMMARY POINTS

1. The scale of CCS must increase from MtCO₂ y⁻¹ captured and stored to GtCO₂ y⁻¹ to prevent 2°C warming. To achieve reductions in CO₂ emissions on the order of 800 Gt by 2050, capture beyond point-source emissions must take place; however, first-stage reductions of CO₂ should begin at scale with the concentrated sources, such as coal- and natural gas-fired power plants.

2. The work required to capture CO₂ increases with the dilution of CO₂ in a given gas mixture, which is also a more sensitive parameter than the percent capture or purity of the CO₂ product stream.
3. Development of sorbents for CO₂ capture should seek high working capacity, which will reduce both energy and capital costs, while acknowledging that a high capacity is not, by itself, a solution, as mass-transfer kinetics will also play a role in capturing CO₂ at scale.
4. Because membrane-separation processes are absent regeneration, current technical limitations of membranes should be of particular focus. Inorganic porous and metallic membranes show enhanced performance beyond the Robeson limit.
5. Optimization is a powerful tool that may be used for any gas-separation process to determine the minimum energy required given a desired CO₂ purity and percent capture. This technique forces a strong coupling between a material properties and the process in which the material is housed for effective separation.

FUTURE ISSUES

1. How might the costs of CO₂ capture be reduced from \$55 ton⁻¹ CO₂ avoided so that industries can move forward with minimal carbon tax? Even incremental reductions to meet the current market demand (i.e., enhanced oil recovery and chemical feedstocks) can lead to greater cost reductions in the future owing to economies of scale.
2. Acid gases and trace metals are present in significant enough levels in coal-fired flue gas that they may compete with sorbents for selective CO₂ capture. To what extent this competition exists is still unknown.
3. Heat management for adsorption-separation processes will likely become a significant challenge at scale owing to the inherent exothermic nature of adsorption.
4. Owing to the thousands of tons of CO₂ that must be captured on a daily basis for a given power plant, how much do current technologies appreciate the importance of kinetics?

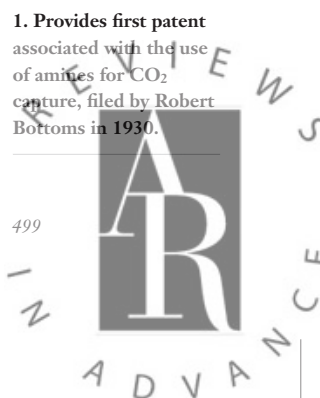
DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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4. Provides software that allows one to simulate exhaust from combustion and gasification processes for energy and cost estimates of emissions control technologies for CO₂, NO_x, SO_x, particulate matter, and mercury.

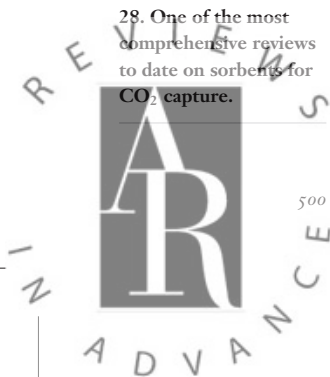
8. Report sponsored by the American Physical Society that estimates a direct air capture cost of ~\$600 ton⁻¹ CO₂ captured based upon current state-of-the-art absorption technologies.

11. Represents the only textbook on the subject to date.

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