CHEMICAL REVIEWS

Review

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Direct Capture of CO_2 from Ambient Air

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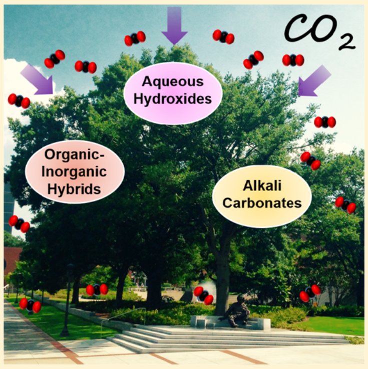

ABSTRACT: The increase in the global atmospheric CO_2 concentration resulting from over a century of combustion of fossil fuels has been associated with significant global climate change. With the global population increase driving continued increases in fossil fuel use, humanity's primary reliance on fossil energy for the next several decades is assured. Traditional modes of carbon capture such as precombustion and postcombustion CO_2 capture from large point sources can help slow the rate of increase of the atmospheric CO_2 concentration, but only the direct removal of CO_2 from the air, or "direct air capture" (DAC), can actually reduce the global atmospheric CO_2 concentration. The past decade has seen a steep rise in the use of chemical sorbents that are cycled through sorption and desorption cycles for CO_2 removal from ultradilute gases such as air. This Review provides a historical overview of the field of DAC, along with an exhaustive description of the use of chemical sorbents targeted at this application. Solvents and solid sorbents that interact strongly with CO_2 are described, including basic solvents, supported amine and ammonium materials, and metal−organic frameworks (MOFs), as the primary classes of chemical sorbents. Hypothetical processes for the deployment of such sorbents are discussed, as well as the limited array of technoeconomic analyses published on DAC. Overall, it is concluded that there are many new materials that could play a role in emerging DAC technologies. However, these materials need to be further investigated and developed with a practical sorbent−air contacting process in mind if society is to make rapid progress in deploying DAC as a means of mitigating climate change.

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Received: March 9, 2016
Published: August 25, 2016

DOI: 10.1021/acs.chemrev.6b00173
Chem. Rev. 2016, 116, 11840−11876

1. INTRODUCTION

1.1. CO_2 Emissions and Related Problems

Global temperatures have been registered since the late 19th century by many institutions, and as early as the 1980s, the Goddard Institute for Space Studies (GISS) realized that a global warming was on course. Their most recent data show a global temperature increase of at least 0.8 °C since 1951, with the increase continuing into the 21st century.[1,2] In parallel, there has been a strong increase in the release of greenhouse gases over the past century of human activity, with carbon dioxide being the most important such gas. CO_2 emissions to the atmosphere continue to steadily increase every year, reaching a recent value of 34 650 million metric tons of CO_2 in 2011.[3] As a result, the atmospheric concentration of CO_2 has risen from the preindustrial value of 280 ppm to 401 ppm in 2015.[4] The Intergovernmental Panel on Climate Change (IPCC) has reported that the excessive emissions of greenhouse gases (GHG) to the atmosphere, mainly CO_2, are the primary source of modern global climate change and the consequent global warming of the Earth.[5] Despite some political opposition to the hypothesized human origin of modern climate change, the scientific community maintains an almost unanimous agreement on this topic. As shown by a review of papers published by 1 300 climate experts, 97% of them support the anthropogenic origin of climate change.[6]

The last report published by the IPCC (Fifth Report) in 2013 and 2014 projects data for the end of the 21st century using several scenarios.[5,7] It is estimated that the global surface temperature will likely increase anywhere from 0.3 to 4.8 °C relative to 1986–2005 data (Figure 1). All the scenarios consider the continuation and aggravation of side-effects of global warming, including the shrinking of the Arctic sea ice cover, the decrease of the global glacier volume, and the rise of the sea level, among other consequences.

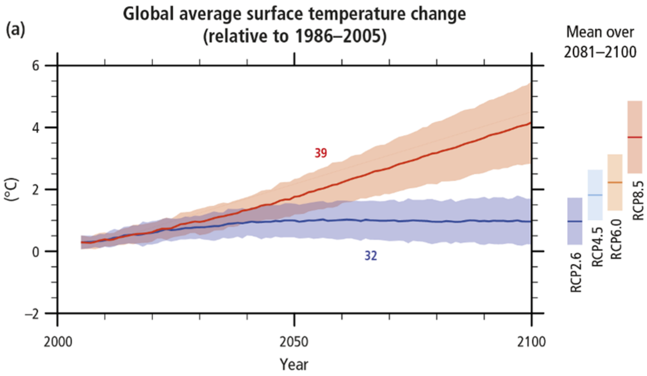


Figure 1. Global average surface temperature change from 2006 to 2100 determined by multimodel simulations. All changes are relative to 1986–2005. Time series of projections and a measure of uncertainty (shading) are shown for scenarios RCP2.6 (blue) and RCP8.5 (red). The mean and associated uncertainties averaged over 2081–2100 are given for all RCP scenarios as colored vertical bars at the right-hand side of each panel. The number of Coupled Model Intercomparison Project Phase 5 (CMiP5) models used to calculate the multimodel mean is indicated. Reprinted with permission from ref 5. Copyright 2014 IPCC.

For these reasons, global awareness regarding the large volumes of CO_2 being continuously released to the atmosphere has risen during recent years, leading to increased efforts to reduce its environmental impact, including utilization of both preventive and remediation methods. Preventive strategies are related to the promotion of renewable energies and energy efficiency programs, while remediation approaches have been more linked to implementations in current thermal power stations and other industrial facilities that produce massive CO_2 discharges. Many industrialized countries even agreed to pursue reductions in GHG emissions by 5.2% in the Kyoto Protocol,[8] with carbon capture and storage (CCS) techniques being proposed as an emerging technology to effectively minimize CO_2 discharges.[9]

1.2. Processes for Reducing CO_2 Emissions

Despite all the efforts aimed at minimizing CO_2 emissions, tens of billions of tons are still released every year. Thus, CO_2 capture was proposed by the IPCC as a technology necessary to restrain the growth of the atmospheric CO_2 concentration.[9] Conventional CO_2 capture has commonly addressed CO_2 emissions from large stationary sources, such as fossil-fuel-based power stations, cement plants, oil refineries, and iron or steel industry installations, as examples. According to the different processes where carbon capture can be implemented, three main technologies are described.

1.2.1. Precombustion. Precombustion technologies are typically used when starting from natural gas or syngas (CO and H_2). Several processes can be used to create suitable feeds for energy generation as well as CO_2 separation, including steam reforming (reaction 1), as well as gasification of pulverized coal (IGCC), coke, or oil residues (reaction 2). The reaction between CO and water, the water gas shift reaction, yields a gas stream composed of primarily CO_2 and hydrogen (reaction 3). The removal of CO_2 yields a high-purity H_2 stream available for electricity production. CO_2 capture is relatively easy in these cases because its concentration ranges between 15 and 60%. On the other hand, the first steps of fuel preparation for coal gasification and steam reforming are challenging and expensive.[9]

$$C_xH_y + xH_2O \rightarrow xCO + \left(x + \frac{y}{2}\right)H_2 \tag{1}$$

$$C_xH_y + \frac{x}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2 \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

1.2.2. Capture During Combustion. Two main technologies are used for capture during combustion, oxy-fuel combustion and carbonation–calcination. Oxy-fuel processes carry out the combustion with pure oxygen instead of air. A part of the combustion gases is typically recirculated in such processes. The flue gas volume is considerably reduced by the use of oxygen instead of air, and the CO_2 concentration is concomitantly increased (up to 90%). However, these technologies are not yet highly favored because of the high cost of the air separation needed to obtain pure oxygen.

1.2.3. Postcombustion. CO_2 can also be captured from flue gas released after combustion. A number of technologies can be used for this approach because existing combustion facilities do not need to be modified. Typically, the flue gas needs to be previously desulfurized to a great extent—which is compulsory by law in most countries. The main disadvantage of this approach is the reduced CO_2 concentration, which ranges from ~4 vol % for a natural gas combined cycle processes to 13–15 vol % for a coal-fired combustion plant.[9−11] Impurities such as SO_2 and NO_x are also a problem for many separation processes; for example, because of their reactivity toward amines, which are the compounds commonly used for postcombustion CO_2 capture, amine-based separation processes require flue gas pretreatment to significantly reduce the concentrations of these strongly acidic gases.

To date, large-scale postcombustion CO_2 separation processes have been mainly based on liquid amine absorption techniques. Aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) have been successfully used to capture carbon dioxide on a large scale. Despite their proven efficacy in capturing CO_2, absorption processes still entail major drawbacks.[12] The most important problems are related to the corrosive properties of liquid amines,[12] the amine losses incurred during the operation, and, significantly, the energy consumption in the regeneration process.[13] Therefore, in recent years many efforts and significant funding have been focused on the development of alternative processes for CO_2 capture, such as cryogenic, adsorption, or membrane-based technologies.[14−16]

Carbonation−calcination uses the carbonation reaction between quicklime (calcium oxide, CaO) and CO_2 to produce limestone (calcium carbonate, $CaCO_3$).[17] Calcium carbonate is then introduced in a calcination reactor, where the opposite process is performed. Calcination yields regenerated quicklime and a gas stream enriched in CO_2. The main advantages of this technology are the low cost of the initial limestone used and its reactivity toward both CO_2 and SO_2. Thus, no desulfurization step is needed prior to carbonation−calcination. However, the high temperature used during the carbonation (650 °C) and calcination reactions (900 °C) as well as material attrition are a significant economic drawback. The carbonation step is commonly performed with flue gas, in a postcombustion CO_2 capture setup.[18] Nevertheless, it can also be applied to precombustion, for example, during coal or biomass gasification (Table 1).[19]

Table 1. Typical Pressures, Temperatures, and CO_2 Concentrations of the Different Gas Streams Used in CCS Technologies[10]

	syngas (precombustion)	oxy-fuel combustion	flue gas (postcombustion)
pressure (atm)	>5	>50	1
temperature (°C)	>100	<50	<100
CO_2 concentration (vol %)	∼35	>90	4−14

1.3. Reduction of CO_2 Emissions vs Negative Carbon Technologies

Given the slow realization that the last century of carbon dioxide emissions has significantly impacted the climate, society has continued to use fossil fuels at an ever-expanding rate over the past few decades. Although the IPCC recognized the need for rapid and immediate reductions in fossil fuel use in 1990,[20] the rate of anthropogenic CO_2 emissions has continued to expand rapidly, with little slowdown in sight. While the use of noncarbon energy technologies is quickly growing, the growth does not match the pace of a growing global population's energy demands. As such, there appears to be little probability of a slowing of CO_2 emissions, globally, in the near future. In fact, the latest IPCC report from Working Group III suggests that society has reached a point where it is very likely that stabilizing the atmosphere at twice the preindustrial level will require negative CO_2 emissions in the later part of this century, as can be seen in Figure 2.[21] To this end, the recent climate talks in Paris have identified the need for rapid deployment of "negative carbon technologies," technologies that can remove CO_2 from the atmosphere.[22] Additionally, the report from the National Research Council (NRC) on Climate Intervention also concluded that research and development of negative carbon technology is warranted.[23] This is in contrast to the conventional CO_2 capture technologies described above, which, even if widely deployed, would only slow the rate of increase of the global atmospheric CO_2 concentration.

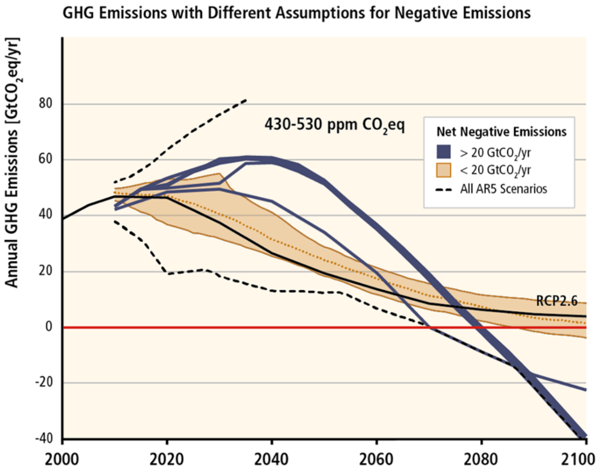


Figure 2. Development of total GHG emissions for scenarios reaching ∼450 to ∼500 (430−530) ppm of CO_2eq in 2100 with and without net negative CO_2 emissions larger than 20 Gt of CO_2/year. Ranges are given for the 10th−90th percentile of scenarios. All approaches that extend below the red line require substantial negative emissions. Reprinted with permission from ref 21. Copyright 2014 Cambridge University Press.

This Review describes the advances made in the direct extraction of CO_2 from ambient air using sorbents, or direct air capture (DAC), as one of the few potential "negative carbon" technologies. The history of DAC from a climate perspective is first presented, followed by the identification of an array of sorbents and processes that have been examined for their utility in extracting CO_2 from the atmosphere. A brief discussion of nonsorbent-based approaches to DAC is also included. Finally, an overview of the feasibility and cost of DAC processes is presented.

2. CAPTURING CO_2 FROM AIR

2.1. Rationale and Role in Atmospheric CO_2 Reduction

There has been much discussion of the benefits and need of direct air capture (DAC), a concept that was first introduced for climate change mitigation by Lackner in 1999[24] and is now broadly defined as the direct extraction of CO_2 from ambient air.[25] The subsequent decade following the introduction of DAC as a climate change mitigation technology produced many commentaries and analyses in an effort to educate the broader community that DAC is (or is not) an important and viable option for reducing greenhouse gas levels.[26−45] Now, in the second decade of its existence, a shift to more experimental work as well as a marked increase in publications relevant to DAC can be observed (roughly 25 publications in the first decade, with ~100 publications in the subsequent half decade). DAC is a rapidly growing environmental technology, with an increasing number of academics shifting their attention to developing materials and processes for this technology along with several start-up companies pushing this technology from the lab scale to the demonstration and pilot scale.

Many of the perceived advantages of DAC have been summarized in detail in previous reviews, most often with the comparisons in direct relation to conventional CO_2 capture technologies separating CO_2 from large point sources before atmospheric emission.[46,47] To briefly reiterate, a prominent advantage of DAC is the fact that it has the potential to address emissions from distributed sources as well as point sources. When considering that roughly half of annual CO_2 emissions are derived from these distributed sources, it is obvious why something other than solely point-source capture must be considered to truly impact anthropogenic emissions. Additionally, DAC processes are not location-specific, meaning capture facilities can be set up anywhere, and furthermore the processes do not have to contend with the high concentrations of contaminants in flue gas (SO_x, NO_x, mercury, etc.) that cause degradation of performance of the sorbents used in flue gas capture processes. It should be noted that, although DAC is generally evaluated in comparisons against flue gas capture, they are two different technologies with differing end goals, whereby DAC is meant to skim or extract CO_2 from the atmosphere while flue gas capture is meant to scrub or purify CO_2 from an exhaust gas. Additionally, the environmental community is increasingly not considering DAC and conventional CO_2 capture from large point sources as either/or technologies, with many suggesting their development in parallel. The scale of the CO_2 emissions problem is sufficiently vast that all technologies that can reduce emissions or extract CO_2 from air should be pursued with vigor to identify those that scale most effectively and offer the most compelling economics. As noted earlier, there is now a growing consensus that negative carbon technologies are needed to address the scale of the current problem.[22]

While there are many advantages and compelling arguments in favor of DAC technologies, there are many areas of uncertainty that require further exploration. The NRC report states that further investigations of long-term storage and sequestration of CO_2 are of critical importance, as there are environmental risks and uncertainties associated with CO_2 sequestration including cost, long-term monitoring, potentially induced seismicity, and leakage.[23] An alternative option to sequestration—especially in the short term while these uncertainties are further investigated—is utilization, which offers another incentive to developing DAC technologies due to a potentially beneficial end use. While use of captured CO_2 is a viable short-term goal that may allow emerging DAC technologies to mature, it is not a long-term option as a means of CO_2 disposal unless CO_2 can be economically converted back to a fuel.

2.2. CO_2 Utilization

DAC has potential carbon feedstock advantages in addition to its environmental benefits. With the increasing possibility of CO_2 use as a chemical feedstock for the synthesis of value-added products, the ability of DAC technology to provide a route to on site CO_2 generation anywhere on the globe for utilization applications is advantageous.[48] The most commonly investigated approaches are the direct capture of CO_2 from the air and subsequent conversion to produce fuels.[29,49−53] However, other avenues of use are also possible, including chemical conversion to produce synthetic intermediates for pharmaceuticals[54] or other value-added chemical products as well as feeding greenhouses or algae installations for agricultural or biofuel production. The key point to be made is that while DAC coupled with CO_2 sequestration is being explored as a carbon negative technology, it may also be used for synthesis of value-added products in the near term (which, however, would have minimal impact on climate change), with an ultimate end goal of geological sequestration once the above uncertainties are addressed.

2.3. DAC through Sorbent-Based Processes

The main focus of this Review is on processes proposed for DAC based on technologies employing reversible sorbents that can be cycled many times to capture and release CO_2. Additionally, a brief discussion of other avenues for DAC is presented in section 6. While sorbents studied for flue gas capture applications have included both physisorbent and chemisorbent materials,[15,16] it has been suggested that physisorbent materials such as zeolites, activated carbons, or metal−organic frameworks (MOFs) typically perform poorly at low CO_2 partial pressures, offering very small CO_2 uptake and low CO_2 selectivity.[55] As air capture deals with an extremely low CO_2 concentration (ca. 400 ppm today), roughly 350 times lower than that found in a typical coal-based flue gas, chemisorbent materials have proven to be much more effective for DAC processes.[46,56]

3. AQUEOUS HYDROXIDE SORBENTS

3.1. Causticization with Alkali and Alkali-Earth Hydroxides

Because of the ultradilute nature of CO_2 in the atmosphere, chemical sorbents with strong CO_2-binding affinities are typically employed for CO_2 capture. One common example, as proposed by Lackner in 1999 as the initial DAC "strawman",[25] is the use of a calcium hydroxide solution, which is known to have a high binding energy with carbon dioxide to form calcium carbonate. Pools of calcium hydroxide, either passive or agitated, provide one of the simplest concepts in which CO_2 from air can be captured with calcium carbonate precipitating and accumulating. Calcium carbonate must then be separated and dried and must undergo a process known as calcination at temperatures above 700 °C to form calcium oxide with the release of the captured CO_2 as a concentrated stream. Calcium hydroxide is finally regenerated in a slaking process via hydration of calcium oxide, therefore closing the cycle.[25]

$$\begin{aligned} &Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \\ &\quad \Delta H^\circ = -109\ \text{kJ mol}^{-1} \end{aligned} \tag{4}$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H^\circ = +179.2\ \text{kJ mol}^{-1} \tag{5}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H^\circ = -64.5\ \text{kJ mol}^{-1} \tag{6}$$

The substantial binding energy of CO_2 with calcium hydroxide leads to a majority of the energy input into this process going toward the regeneration of the sorbent, a trade-off required for the selective binding of the ultradilute CO_2. The drying and calcination of calcium carbonate to release CO_2 both require energy and provide the largest component of the energy penalty for calcium hydroxide systems. The calcination of calcium carbonate requires 179 kJ/mol of CO_2, while the thermodynamic minimum required energy for conversion of calcium carbonate to calcium oxide is only 109.4 kJ/mol. Additionally, the solubility of calcium hydroxide in water is very low, limiting the hydroxide concentration present to bind CO_2. Although efficient in capturing CO_2, the energy penalty for calcium hydroxide regeneration and other disadvantages, such as the low solubility, made the point of attack for future research improvements the identification of a better sorbent.[25,57] Despite the significant drawbacks of this first process from an energetic perspective, the process served as an effective "strawman" by starting the environmental community thinking about DAC as a potential climate change mitigation technology.

The Kraft process has become a very influential system for CO_2 capture from air with caustic solutions; it has been used in the paper industry since 1884 and involves the use of a sodium hydroxide solution to extract cellulose from wood. The same principles for the use and recycling of the sodium solution also can be applied for CO_2 capture.[58] Sodium hydroxide still allows for sufficiently strong binding of CO_2 and is therefore just as effective as calcium hydroxide with the added benefit of the carbonate formed being highly soluble in water. Through reaction of sodium carbonate with calcium hydroxide, calcium carbonate precipitates and sodium hydroxide is regenerated in a process known as causticization. The NaOH solution is limited to 1 mol/L due to the use of calcium at higher NaOH concentrations resulting in the precipitation of unwanted calcium hydroxide. The exchange of carbonate ions from sodium to calcium has been calculated to be very efficient, with a theoretical efficiency of 96%,[31] although experimental values have not reached efficiencies close to the theoretical limit. The precipitated calcium carbonate is then separated and in a kiln undergoes the aforementioned calcination process to form lime (CaO) and carbon dioxide, which can be transferred and compressed. To complete the cycle, calcium hydroxide is regenerated by hydration in a slaker and reused.[27] A schematic of this process is demonstrated in Figure 3. While the calcination of calcium carbonate requires 179 kJ/mol (reaction 9), the thermodynamic minimum required energy for conversion is still 109.4 kJ/mol (reaction 7), as this is the enthalpy of the reaction for NaOH absorbing CO_2 from the air. Therefore, large energy requirements are still present due to the energy required for causticization being well above the calculated thermodynamic minimum.[31,57]

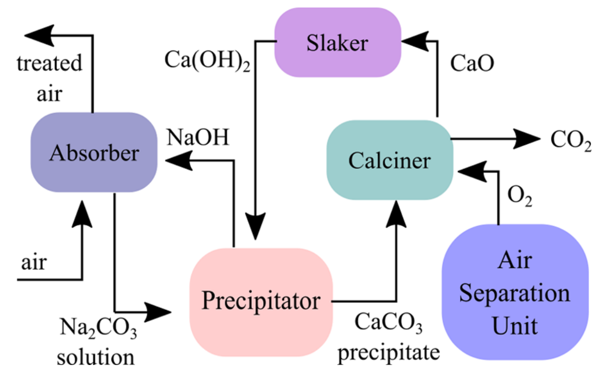


Figure 3. Scheme of a process for DAC based on the Kraft process often used in the pulp and paper industry. Figure adapted from the American Physical Society report on direct air capture of CO_2 with chemicals.[59]

$$\text{Absorber: } 2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad \Delta H^\circ = -109.4 \text{ kJ mol}^{-1} \tag{7}$$

$$\text{Causticizer: } Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \quad \Delta H^\circ = -5.3 \text{ kJ mol}^{-1} \tag{8}$$

$$\text{Calciner: } CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H^\circ = +179.2 \text{ kJ mol}^{-1} \tag{9}$$

$$\text{Slaker: } CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H^\circ = -64.5 \text{ kJ mol}^{-1} \tag{10}$$

While most processes such as the Kraft process utilize NaOH as the CO_2 sorbent, KOH is also a viable alternative to NaOH and could be used to capture CO_2 by the aforementioned methods. However, with KOH being more expensive than NaOH, limited examples are available in the literature. Weimer, Schaber, and co-workers examined the use of KOH by using a 2 m packed column and a 1.5 M solution of KOH to sorb ~70% of the CO_2 in ambient air.[60] The potassium carbonate produced was subjected to acidification with sulfuric acid or $KHSO_4$ to release the captured CO_2 and produce potassium sulfate. KOH and sulfuric acid were then regenerated in an electrodialysis unit with cation-exchange membranes.

With large energy penalties still in place for aqueous hydroxide solutions, baseline designs will be useful for economical and energetic evaluations. Many types of sorption units have been assessed, analyzing the need for the processing of such large volumes of air and the need to limit the pressure drop. The efficiency of the sorber and the diffusion of CO_2 will be important design factors. The common method industrially for sorbing a gas into solution is to use towers filled with packing material and dripping a solution down the tower while blowing the gas up from the bottom of the tower.[28] Contactor designs for CO_2 capture for air reveal dimensions different from traditional packed towers; due to the dilute nature of CO_2, relatively short columns with very large cross sections have been reported to be the most beneficial.[28] One example provided by Baciocchi et al. is the use of packed columns.[27] A 2 M sodium hydroxide was used to reduce an inlet CO_2 concentration of 500 ppm to an outlet value of 250 ppm. An absorber was designed to allow for a 100 Pa/m pressure drop and a liquid-to-gas ratio of 1.44, leading to the use of a column 2.8 m in height and 12 m wide.[27] It should be noted that, in the process, water loss was a large energy penalty, as the moisture present before calcination in a kiln must be removed. Zeman and co-workers, in their system, showed how significant the water loss can be, with an average mass loss of 90 g of H_2O/g of CO_2 captured.[33] Additionally, kilns should be operated using pure oxygen rather than air to avoid the difficult separation of CO_2 from nitrogen once calcination is compete. It was determined that the unavoidable calcination of calcium carbonate contributed the most toward the 17 or 12 GJ/t of CO_2 energy requirements, depending on which system was used, and contributed 4.5 GJ/t of CO_2.[27]

Others have examined the feasibility of spray towers rather than packed towers or open, stagnant pools as the component of the system that contacts the air. The spray provides a large surface area for air−liquid contacting and a means to maintain a low pressure drop. Additionally, the spray avoids the cost of large packed towers, but in return, creation of the spray incurs its own energy losses.[32] A simplistic estimate of the cost and

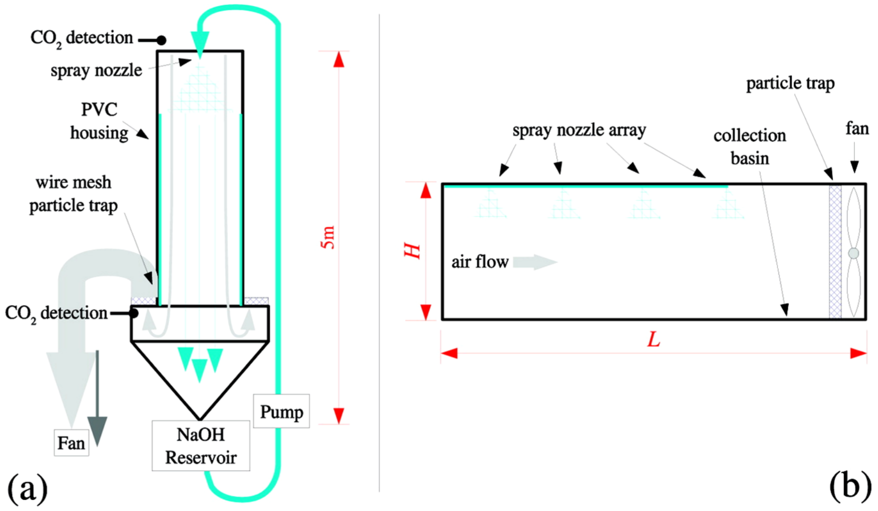


Figure 4. (a) Diagram of prototype spray tower contactor for DAC with aqueous sodium hydroxide solutions. (b) Representation of a channel in a full-scale contactor. Multiple channels would be arranged side-by-side and contained in a hanger-like structure. Reprinted with permission from ref 32. Copyright 2008 American Chemical Society.

energy requirements was provided by Keith and co-workers,[28] whose main goal was to show that air capture can indeed be realized with current technologies. These estimates have been expanded upon to look at factors such as drop coalescence in more sophisticated models. A model by Stolaroff et al., using a 1.3 M NaOH solution, monitored the effective CO_2 capture using a 450 ppm inlet CO_2 concentration. A diagram of their design is shown in Figure 4. The spray was found to reduce the concentration by only 17 ppm with another 17 ppm removed by the air passing through the wetted walls of the system. The 17 ppm loss due to the spray can be converted to a CO_2 absorption rate of 3.7 mmol/L of solution/pass. As previously mentioned, water loss can be a detrimental part of these systems, and this was addressed by examining evaporative water loss at different NaOH concentrations. For a ∼1 M solution of NaOH, at 15 °C and 65% relative humidity, 20 mol of H_2O/mol of CO_2 would be lost if 30% of the CO_2 was captured through the process. However, by increasing the NaOH concentration to ∼7 M, water loss was eliminated.[32] When dealing with a spray tower, coalescence is also a major factor and will drive reactor design. Flow rates must be decreased to reduce coalescence, which ultimately reduces the CO_2 capture rate. As the height of the contactor increases, efficiency decreases quite rapidly due to spray efficiency.[32] Keith and co-workers used this technology to create the startup company Carbon Engineering, which is discussed in further detail in section 7.

3.2. Alternative Causticization Processes

Additional causticization methods have also been investigated due to the drawbacks of traditional methods using calcium hydroxide in the Kraft process, namely, the large energy demand, limited efficiency, and limit of 1 M concentrations for regenerated NaOH solutions. Nonconventional methods can be derived from the pulp industry as their recovery systems for NaOH can also be used for CO_2 capture. One such method is autocausticization, where the reaction product is water-soluble and is maintained as a caustic solution throughout the entire pulping cycle. Using borates, particularly sodium metaborate ($NaBO_2$), is one such method studied in the pulp industry. Initial eqs (reactions 11 and 12) revealed a stoichiometry that would only produce one mole of CO_2 for every two moles of sodium metaborate present, which would be unfavorable, as this would double the inorganic content required. The stoichiometry was later corrected (reactions 13 and 14) to reveal that only one equivalent of sodium metaborate was necessary and regeneration of the borate was achieved when reacted with water. This new finding rejuvenated interest in the process; however, high energy requirements remain (high temperatures at or above 900 °C).[61,62]

$$2NaBO_2 + Na_2CO_3 \rightarrow Na_4B_2O_5 + CO_2 \tag{11}$$

$$Na_4B_2O_5 + H_2O \rightarrow 2NaOH + 2NaBO_2 \tag{12}$$

$$NaBO_2 + Na_2CO_3 \rightarrow Na_3BO_3 + CO_2 \tag{13}$$

$$Na_3BO_3 + H_2O \rightarrow NaOH + NaBO_2 \tag{14}$$

Additional methods involve direct causticization, when the reaction product is insoluble and the decarbonizing agent is separated from the hydroxide solution and not carried through the remaining pulping cycle. One such technique is the direct causticization of sodium carbonate using titanium dioxide,[36,63] which, depending on reaction conditions, leads to a variety of sodium titanates as products. The main decarbonization reactions are those between Na_2CO_3 and $Na_2O{\cdot}3TiO_2$, as seen in reactions 15 and 17. The reactions between Na_2CO_3 and $Na_2O{\cdot}3TiO_2$, whether the reaction occurs above or below the melting point of Na_2CO_3, have an overall reaction enthalpy of 90 kJ/mol. Therefore, with a 90 kJ/mol reaction enthalpy, the titanate process requires half the energy when compared to causticization with lime (179 kJ/mol) but still requires high temperatures between 800 and 900 °C. Sodium trititanate and NaOH can be regenerated and recycled by hydrolysis at temperatures near 100 °C.

$$\begin{aligned} &7Na_2CO_{3(s)} + 5(Na_2O{\cdot}3TiO_2) \\ &\quad \rightarrow 3(4Na_2O{\cdot}5TiO_2) + 7CO_2 \\ &\quad \Delta H = +90 \text{ kJ mol}^{-1} \end{aligned} \tag{15}$$

$$Na_2CO_{3(s)} \rightarrow Na_2CO_{3(l)} \quad \Delta H = +25 \text{ kJ mol}^{-1} \tag{16}$$

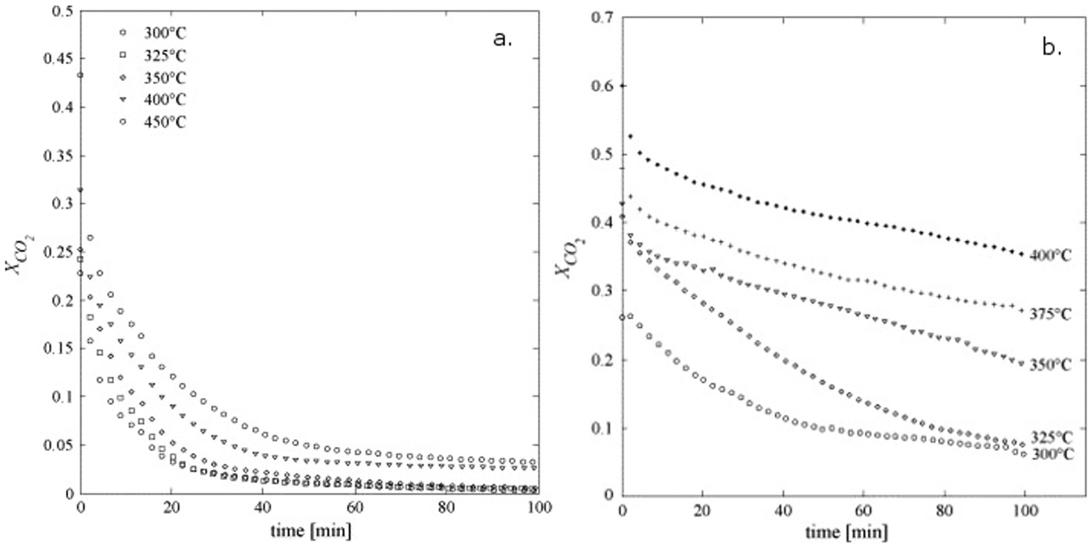


Figure 5. Extent of CO_2 captured by the carbonation of CaO, defined as $1 - ([CO_2]_{outlet}/[CO_2]_{inlet})$ as a function of time operating at various temperatures using (a) synthetic air containing 500 ppm of CO_2 and (b) synthetic air containing 500 ppm of CO_2 and 50% H_2O. Reprinted with permission from ref 64. Copyright 2007 Elsevier.

$$7Na_2CO_{3(l)} + 5(Na_2O{\cdot}3TiO_2) \rightarrow 3(4Na_2O{\cdot}5TiO_2) + 7CO_2 \quad \Delta H = +65\ \text{kJ mol}^{-1} \tag{17}$$

$$3(4Na_2O{\cdot}5TiO_2) + 7H_2O \rightarrow 5(Na_2O{\cdot}3TiO_2) + 14NaOH \quad \Delta H = +15\ \text{kJ mol}^{-1} \tag{18}$$

One major difference between traditional causticization and the titanate process is that dry, anhydrous sodium carbonate is required. Therefore, the ability to extract sodium carbonate that is soluble in the sodium hydroxide solution adds more processing steps. This extraction process has been studied using multistep crystallization techniques. For example, temperature swing allows for sodium carbonate decahydrate to precipitate from a hydroxide solution. Subsequent heating in a high-concentration NaOH solution lowers the solubility of sodium carbonate and leads to precipitation of anhydrous sodium carbonate.[36,63] An energy analysis by Mahmoudkhani and Keith revealed a heat requirement comparable to that of the aqueous amine-based liquid postcombustion CO_2 capture process, which is a benchmark process for large point sources such as coal-fired power plants, at ~130 kJ/mol of CO_2.[36] While aqueous hydroxides are still being examined for CO_2 removal from air and improvements to the process have emerged, there are still many areas where the technology may be further improved. The high energy demands, the high regeneration temperatures, and the operation of kilns under pure oxygen are just a few of the drawbacks that have made some researchers skeptical that this is a viable technology for implementation. Nonetheless, as discussed in section 7, at least one company has focused significant resources in optimizing processes employing liquid alkali sorbents.

4. SOLID ALKALI CARBONATES

4.1. Bulk Alkali Carbonates

The idea of using solid inorganic bases rather than solutions for ultradilute CO_2 removal has mainly been studied by Steinfeld and co-workers.[34,39,64−66] Thermodynamic, kinetic, and thermogravimetric analysis of a Ca-based cycle were initially examined, as this approach provides a conceptually straightforward path to CO_2 capture from air. The carbonation rates of CaO and $Ca(OH)_2$ were studied using a thermogravimetric analysis (TGA) with 500 ppm of CO_2 concentration, with and without the presence of water vapor to study the effect of moisture on carbonation rate. For CaO, carbonation temperatures between 300 and 450 °C led to an initial 44% decrease of the 500 ppm of CO_2 concentration within the first minute, with a significant reduction in CO_2 uptake afterward, as can be seen in Figure 5a. Temperatures below 300 °C led to essentially no carbonation, while temperatures in excess of 450 °C thermodynamically favored the reverse reaction, calcium carbonate decomposition to CaO and CO_2. In the presence of water vapor, the extent of carbonation was found to increase up to 80% after 100 min and proceeded at a rate ~22 times faster in the initial 20 min of reaction. This is attributed to adsorption of CO_2 on the surface by OH^- groups. The effect of water vapor on CO_2 uptake for CaO is demonstrated in Figure 5b. The use of $Ca(OH)_2$, as expected, followed a similar trend, but the carbonation reaction proceeded at a faster rate with a higher degree of conversion, both with and without the presence of moisture. The carbonation of $Ca(OH)_2$ required slightly lower carbonation temperatures, 200−425 °C.[64,65]

The employment of Na-based rather than Ca-based thermochemical cycles was also examined by Steinfeld and co-workers, as the Na-based cycles are the favorable processes in solution.[34] Three Na-based cycles were tested for CO_2 capture from air: (1) a four-step $NaOH/NaHCO_3/Na_2CO_3/Na_2O$ cycle, (2) a three-step $NaOH/NaHCO_3/Na_2CO_3$ cycle, and (3) a two-step $Na_2CO_3/NaHCO_3$ cycle. Thermogravimetric runs carried out at low CO_2 concentrations of 500 ppm allowed for examination of reaction extents based on the choice of CO_2 sorbent, NaOH or Na_2CO_3. NaOH carbonation at 25 °C, as was applied in cycles 1 and 2, was found to reach only 9% conversion after 4 h. Likewise, Na_2CO_3 carbonation in water-saturated air during cycle 3 was determined to reach only 3.5% conversion after 2 h. The closing of the cycles was studied in thermal decomposition experiments using $NaHCO_3$, as was employed in all three hypothetical cycles, as well as Na_2CO_3, which was applied in cycle 1. $NaHCO_3$ was found to reach completion after heating at 90−200 °C for 3 min, while Na_2CO_3 reached completion after heating to 1000−1400 °C for 15 min. On the basis of thermogravimetric analyses of the three Na-based cycles, the significantly slow reaction rates during carbonation and subsequent large mass flow rates rendered the process inefficient.

As the Ca-based processes led to increased sorption of CO_2 from the air, additional reactor studies were performed in which solar power was applied to accomplish both the calcination and carbonation steps.[39,65,66] The solar reactor contained a fluidized bed of reacting particles that were directly exposed to high-flux solar radiation, providing effective heat and mass transfer and eliminating the need for transportation of solids. A schematic of the reactor setup used is shown in Figure 6. Carbonation of CaO occurred between 365 and 400 °C, while $CaCO_3$ calcination required temperatures between 800 and 875 °C. To increase the kinetics of CO_2 capture by CaO, as previously noted, water vapor was introduced during carbonation. The solid sorbent was tested under multiple cycles with a continuous 500 ppm of CO_2 stream and was shown to maintain its sorption capacity. Each cycle revealed a 1.3 s residence time for complete removal of CO_2 from the continuous 500 ppm stream. The thermal energy input for the complete $CaO-CaCO_3$ thermochemical cycle was calculated to be 10.6 MJ/mol of CO_2 captured if carbonation occurred at 375 °C and calcination occurred at 875 °C. The energy input for the Ca process was quite high compared to wet scrubbing with alkali metal hydroxide solutions, as was expected due to the additional energy required to heat ambient air to 375 °C prior to carbonation.[39,65,66]

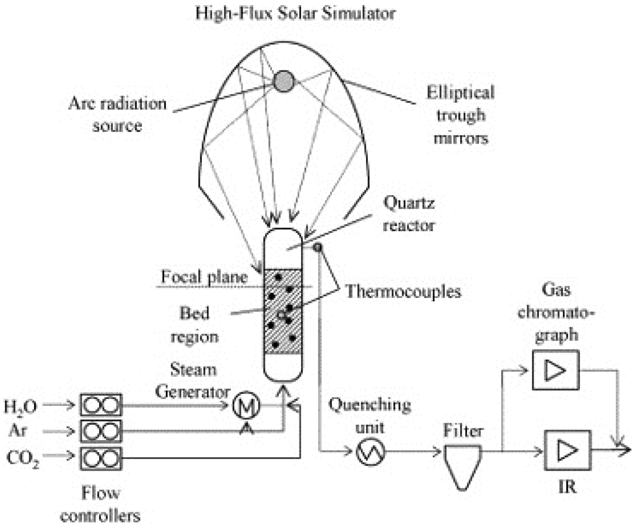


Figure 6. Experimental setup for CO_2 capture via carbonation of CaO using solar power for calcination and carbonation steps. Reprinted with permission from ref 39. Copyright 2009 Elsevier.

4.2. Supported Alkali Carbonates

Creating hybrid solid sorbents through the impregnation of alkali carbonates within porous matrices has also been studied, as the solid supports may increase the exposed alkali surface area and thus increase carbonation rates. An early example involved the production of methanol using hydrogen and CO_2 that had been adsorbed from the air.[50] Hydrophobic microporous hollow fiber membranes were utilized in which the small fiber diameter (200−500 um) provided a high surface-to-volume ratio for a liquid KOH phase maintained in the hydrophobic channels. The membranes were designed so that the KOH solution and air flowed orthogonally and the mass transfer therefore occurred as gas diffused through the membrane pores to the alkali solution. Subsequent electrolysis of the K_2CO_3 formed led to the release of CO_2, and the cycle could then be repeated.

Later studies on alkali sorbents loaded into porous matrices were aimed directly at the sorption of CO_2 from the atmosphere. Porous carbons that were loaded with both CaO and MgO were synthesized via pyrolysis of poly(ethylene terephthalate) (PET) and dolomite (DOL) mixtures.[67] Removal of 2 000 ppm of CO_2 from dry air was measured for PET containing 0, 17, 50, and 70% dolomite. Under dry conditions at 20 °C, CO_2 uptakes were low and peaked at 0.22 mmol/g for the 70% dolomite sample. Although uptakes were low, the addition of dolomite substantially increased the CO_2 sorption capacity despite the low micropore area and volume. Under humid conditions, the sorption capacity increased as a function of the amount of water added, with the highest value reported being 0.48 mmol/g. The increase in sorption under humid conditions was again reported to be due to the formation of a water film on the surface of the sorbent, which acted as a solvent for CO_2 sorption and subsequent reaction with the sorbent material. No new carbonate phases were detected by powder X-ray diffraction (PXRD) under dry conditions, but humid conditions led to detection of $CaCO_3$ by PXRD, as shown in Figure 7, potentially due to carbonation of newly formed $Ca(OH)_2$. The sorption levels by the hybrid materials exceeded those of the pure dolomite and showed that there was an advantage to using supported Ca materials. However, to be considered for DAC technologies, new methods to improve performance are needed, as the CO_2 sorption is still quite low.

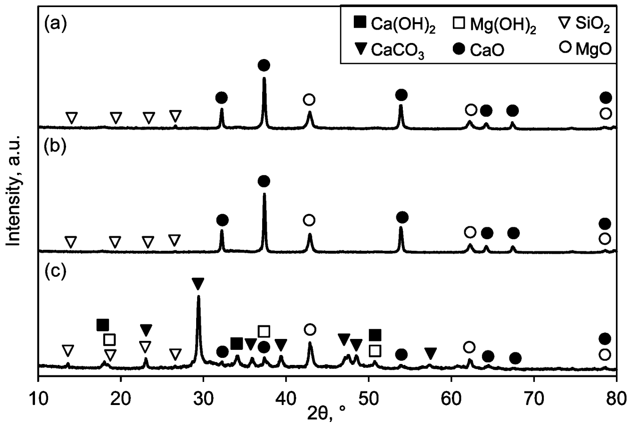


Figure 7. XRD patterns of the MgO/CaO-loaded carbon material prepared from a PET/DOL (50:50) mixture, measured for the (a) virgin material, (b) dry material exposed to air containing CO_2 gas, and (c) prehumidified material exposed to air containing CO_2. Reprinted with permission from ref 67. Copyright 2013 American Chemical Society.

In addition to dolomite, other alkali metal sorbents can be included in porous structures to increase the CO_2 sorption capacity from air or ultradilute CO_2 mixtures. Composites of potassium carbonate and γ-Al_2O_3, for example, were shown to be promising candidates for CO_2 capture from flue gas and were therefore analyzed for CO_2 capture at lower concentrations.[68] With a potassium loading equivalent to 21−23% potassium carbonate, the potassium carbonate/γ-Al_2O_3 composites reached a sorption capacity between 4.0 and 4.9 wt % after exposure to ambient air. Two routes of CO_2 sorption were identified by in situ PXRD and sorption tests, leading to formation of $KHCO_3$ (through formation of an intermediate $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ phase) and $KAlCO_3(OH)_2$ dispersed along the alumina surface. Capacities showed good repeatability for over 80 cycles of CO_2 sorption with regeneration temperatures between 250 and 300 °C.

Potassium incorporated within mesoporous γ-Al_2O_3 was also investigated and compared to benchmark amine-based γ-Al_2O_3 sorbents under dilute (1%) and ultradilute (400 ppm) CO_2 capture conditions.[69] While most studies use direct wet impregnation of K_2CO_3 onto the porous substrate, potassium acetate was dispersed and calcined under an inert N_2 atmosphere to create the supported potassium species in this study. Samples of γ-Al_2O_3 impregnated with 5 and 10 wt % potassium, denoted AlK5 and AlK10, respectively, were synthesized, and PXRD patterns indicated the presence of potassium carbonate (K_2CO_3), potassium bicarbonate ($KHCO_3$), and $KAl(CO_3)(OH)_2$ species formed on the support. A slight decrease in Brunauer−Emmett−Teller (BET) surface area from 223 to 167 m^2/g was observed when going from the bare support to 10% potassium loading. The CO_2 capacities using 1% CO_2 in helium were 1.19 and 1.28 mmol/g for AlK5 and AlK10, respectively, after 12 h of contact with the CO_2 streams at 25 °C (Figure 8a). The uptakes were comparable or slightly better than benchmark γ-Al_2O_3 substrates containing impregnated or covalently grafted amines. For air capture conditions (400 ppm), the AlK5 and AlK10 sorbents exhibited CO_2 uptakes of 0.86 and 0.78 mmol/g, respectively, which were significantly lower than a sorbent based on 35 wt % poly(ethylenimine) (PEI) loaded on γ-Al_2O_3, which exhibited a CO_2 uptake of 0.95 mmol/g (Figure 8b). All the materials could be regenerated at 250 °C with no significant loss in capacities for multiple cycles. Overall, these first-generation materials were slightly inferior to benchmark amine adsorbents (vide infra), but more comparisons between inorganic and amine-based sorbents are warranted. Additionally, studies using humid air, which have so far not been reported, are needed for these materials.

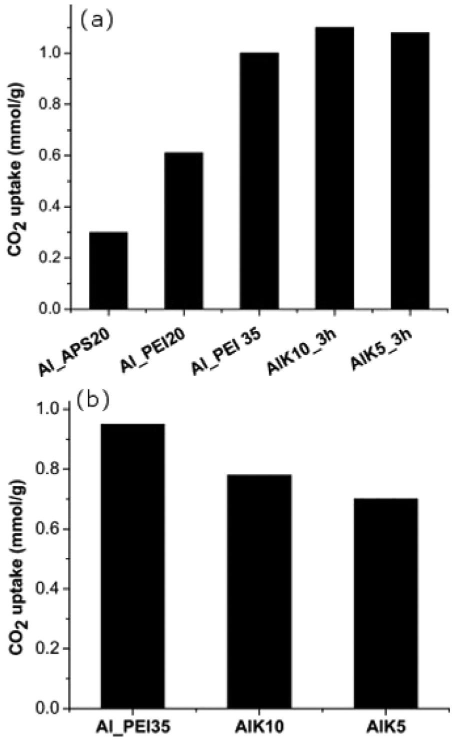


Figure 8. Comparative CO_2 uptakes for potassium-incorporated γ-alumina (AlK) and amine-based benchmark sorbents on γ-alumina at (a) 1% CO_2 and (b) 400 ppm of CO_2. See Figure 10 for APS and PEI structures. Reprinted with permission from ref 69. Copyright 2015 Elsevier.

While it has been shown that the active sorbent used to bind CO_2 has a large impact on a supported material's CO_2 sorption properties,[16] the nature of the supporting phase can affect the dispersion of the active sorbent as well as the chemical properties of the sorbent. To this end, exploration of different support materials with the same active, CO_2-sorbing phase is a useful way to identify possible synergistic effects. Like γ-Al_2O_3, Y_2O_3 has also been shown, in higher gaseous CO_2 concentrations, to be a promising support material for CO_2 sorption.[70] Y_2O_3 containing 26 wt % potassium was synthesized by wet impregnation and was exposed to ambient air, resulting in a CO_2 sorption capacity of 0.64 mmol/g with regeneration temperatures between 150 and 250 °C. The CO_2 capacity of the hybrid potassium carbonate/Y_2O_3 was very similar to that of the potassium carbonate/γ-Al_2O_3 composites despite the higher potassium loading for the Y_2O_3 samples (26 wt % vs 12% for γ-Al_2O_3). Additionally, while higher regeneration temperatures led to higher cyclic sorption capacities with γ-Al_2O_3 as a substrate, differences in thermal stability between the K−Al and K−Y phases led to a loss in capacity for Y_2O_3 samples as regeneration temperatures exceeded 250 °C.

The carbonation behavior of potassium carbonate impregnated within activated carbon has also been analyzed. Potassium carbonate was impregnated onto a porous carbon support with potassium levels ranging from 5 to 25% to determine the effect of potassium loading on CO_2 uptake characteristics.[71] A hybrid potassium sorbent was shown, under humid conditions, to undergo hydration reactions where the unstable products $K_2CO_3 \cdot 1.5H_2O$ and $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ were initially formed. Thereafter, the final product $KHCO_3$ was rapidly produced. As the hydration reactions were the rate-controlling steps for CO_2 adsorption, the water concentration had a large impact on the sorption process. Increasing the water content led to an increase in hydration reaction rates and therefore an overall increase in the CO_2 uptake rate. Besides the importance of the water concentration, it was shown that more K_2CO_3 was converted to $KHCO_3$ in sorbent materials with lower K_2CO_3 loadings or under reaction conditions with high temperature and low water concentration.

Lu and co-workers studied the effect of the support on CO_2 sorption using K_2CO_3 as the active component at a slightly elevated CO_2 concentration relative to ambient air.[72] The supports utilized were activated carbon, zeolite 5A, zeolite 13X, and silica aerogel, and the gas-phase conditions simulated typical submarine conditions, with 5000 ppm of CO_2, 1.8% H_2O, and N_2 balanced at ambient temperature. All supports were prepared with theoretical loadings of 30% potassium but ranged from 11 to 38% potassium and had CO_2 capacities of 0.87, 1.18, 0.34, 0.53, and 0.15 mmol/g for the activated carbon, Al_2O_3, zeolite 5A, zeolite 13X, and silica aerogel supports, respectively. On the basis of potassium loadings, Al_2O_3 showed the highest capacity while activated carbon as a support showed the highest potassium conversion efficiency. Regeneration studies of the sorbents showed that all supports could be completely regenerated, but lower temperatures, 100−200 °C, were sufficient for activated carbon and silica aerogels while temperatures of up to 350 °C were required for the remaining supports due to the amount of water sorbed and the conversion of byproducts. Due to the formation of intermediate $KAl(CO_3)_2(OH)_2$ on the Al_2O_3 supports, which necessitates higher regeneration temperatures, activated carbon was determined to be the best support studied, as the potassium utilization efficiency approached 100% and the regeneration required the lowest temperatures.

As most studies involve the use of one substrate and one active component, more comparative studies of sorbents at lower CO_2 concentrations are needed, which will lead to a better understanding of the CO_2 capture properties of supported alkali hydroxides. The synergistic effects of the solid support and the alkali carbonate have been clearly demonstrated with the aforementioned studies, and additional studies at relevant concentrations will help improve sorption levels, as they are currently close to substrates impregnated with amines.

5. ORGANIC−INORGANIC HYBRID SORBENTS

One of the oldest approaches for separation of CO_2 from gas streams is via application of aqueous amine solutions. This approach is practiced commercially for CO_2 removal from CO_2-rich natural gas streams, as one example, and is now used in submarines to purify breathing air. By far the largest number of reports describing investigations of sorbents for DAC have focused on the use of solid-supported amine materials. In supported amine materials, a chemical reaction between CO_2 and the amines takes place, creating strong bonds and allowing for significant uptakes even at low CO_2 partial pressures.[73,74] Accordingly, the heat of sorption and the selectivity toward CO_2 are higher than for physical sorbents. This feature makes organic−inorganic hybrid materials based on amines highly suitable for direct air capture.

According to Caplow[73] and Danckwerts,[74] the mechanism of the CO_2−amine reaction under anhydrous conditions requires one CO_2 molecule and two primary (reaction 19) or secondary amine moieties (reaction 20) to give an ammonium carbamate. Thus, the maximum CO_2/N ratio achievable by chemical reaction with amine sorbents under such conditions is 0.5 mol of CO_2/mol of N. The molar CO_2/N ratio is usually considered as the amine efficiency. It is important to note that when performing this calculation, the overall CO_2 uptake is assigned only to chemisorption with the amines, with any contribution of physisorption on the remaining silica surface being disregarded. Thus, low amine-loaded sorbents might present spurious values above the theoretical maximum of 0.50 mol of CO_2/mol of N, especially at high CO_2 partial pressures.

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^- \quad (19)$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NHCOO^- \quad (20)$$

When moisture is present, a reaction yielding ammonium carbonate or bicarbonate (depending on the pH) has been observed (reaction 21). This reaction is furthermore the only reported possibility of a strong, chemical interaction between CO_2 and tertiary amines (reaction 22), as these groups do not react in the absence of water or other protic species like alcohols,[75] although the latter are much less frequently described. As seen from the above reactions, the maximum achievable CO_2/N ratio via chemical reactions under humid conditions is 1.0 mol of CO_2/mol of N, double that of the corresponding anhydrous conditions.

$$CO_2 + R_1R_2NH + H_2O \leftrightarrow \underbrace{R_1R_2NH_2^+HCO_3^-}_{\text{bicarbonate}} \leftrightarrow \underbrace{R_1R_2NH_2^+CO_3^{2-}}_{\text{carbonate}} \quad (21)$$

$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+HCO_3^- \leftrightarrow R_1R_2R_3NH^+CO_3^{2-} \quad (22)$$

Amine-containing sorbents have been previously divided into three classes:[47,55,76] (i) class 1 sorbents, prepared by impregnating amines into the pores of a support, (ii) class 2 sorbents, consisting of amines covalently bonded to the walls of porous materials, and (iii) class 3 sorbents, where amine monomers have been polymerized in situ, resulting in polyamine structures tethered to the walls. Figure 9 shows schematic examples of these three classes of materials.

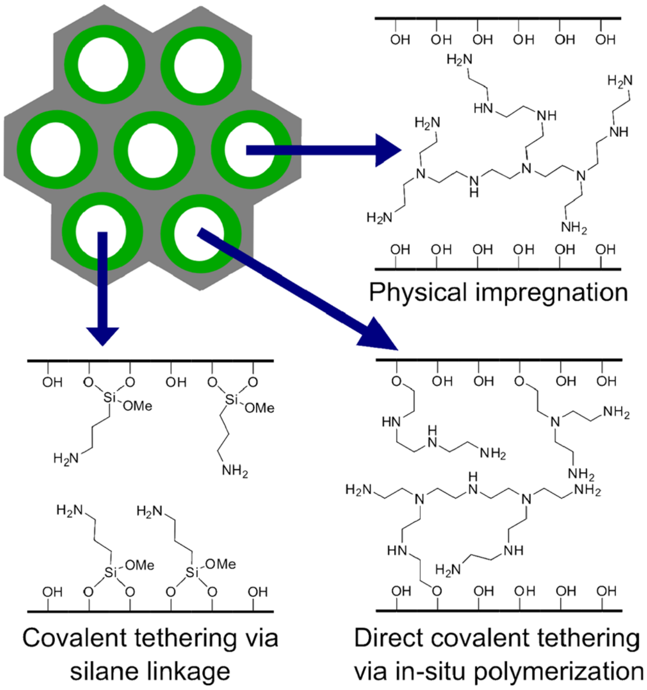
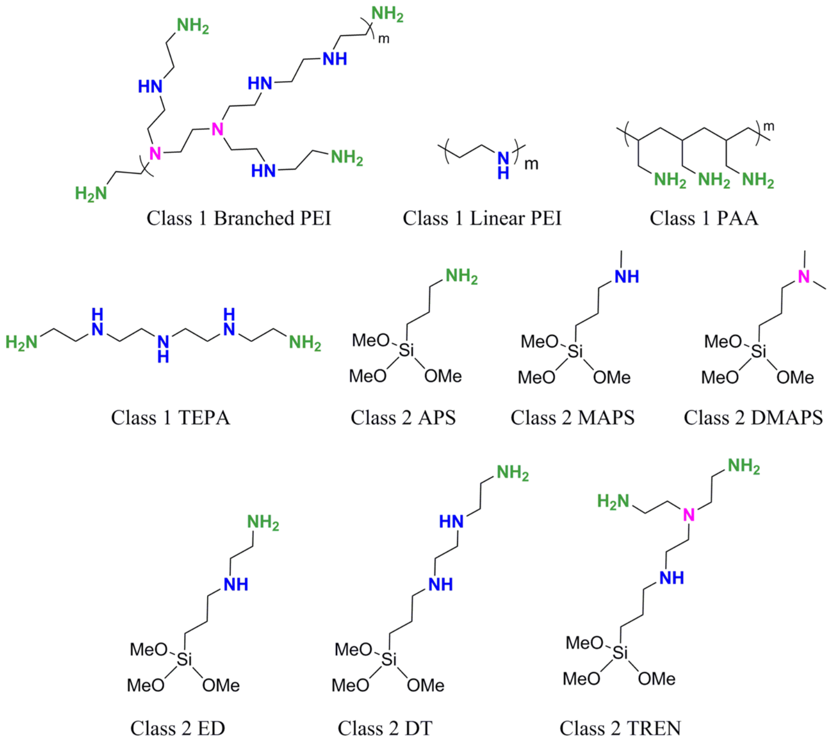


Figure 9. Schematic representation of the three main routes used for functionalization of porous supports with amine moieties. Reprinted with permission from ref 84. Copyright 2014 Georgia Institute of Technology.

Several combinations of class 1−class 2 sorbents have been proposed as a way to improve the properties of amine-based CO_2 sorbents.[77−82] Recently, these materials have been proposed to form a new class 4, with an aminosilane-grafted silica surface and an additional impregnated layer consisting of physically impegnated aminopolymer clusters enclosed by a net of aminosilanes.[83]

When physical sorbents are studied, the CO_2 uptake can be easily related to textural properties. For example, pore diameter plays a major role in the sorption properties of microporous sorbents.[85−87] However, when using mesostructured materials,



Class 1 Branched PEI
Class 1 Linear PEI
Class 1 PAA
Class 1 TEPA
Class 2 APS
Class 2 MAPS
Class 2 DMAPS
Class 2 ED
Class 2 DT
Class 2 TREN

Figure 10. Molecular structures of commonly used amines for class 1 and class 2 DAC sorbents.

which are commonly employed to support amine species for CO_2 sorption, pore diameters are much larger and confinement effects are less important. For a wide range of mesostructured materials, it has been shown that the combination of surface area and gas-surface interaction (measured by means of the *C* parameter of the BET equation) correlates with the CO_2 uptake.[88] When amines are present in the sorbent material, chemical sorption plays a critical role in CO_2 capture, especially when the CO_2 concentration is <1 vol %. In these cases, the CO_2 uptake is mainly determined by the amine loading and is less dependent on the surface area.

The capture of CO_2 from air using amine-modified materials for environmental purposes was first described by Global Thermostat in a 2007 patent application[89] with the patent issuing in 2013.[89,90] A number of contactors and sorbents were registered, including amines "bound to the surface of a large surface area porous substrate". Jones and co-workers, who work collaboratively with Global Thermostat, proposed specific systems to fulfill the objective of capturing CO_2 from air in 2009.[91] Namely, sorbent materials referred to as hyperbranched aminosilicas (class 3 materials—see Figure 11)[92] were applied to the extraction of CO_2 from simulated air (400 ppm of CO_2), following the good results obtained under flue gas conditions,[92] and patented after a short time.[93]

Working in parallel, Sayari and co-workers described the use of amine-grafted (class 1) materials for CO_2 removal from ultradilute gases such as ambient air in 2010.[94,95] In 2011, the field began to take off, with multiple authors reporting the use of different types of supported amine sorbent materials for DAC. Jones and co-workers explored the use of grafted,[79] impregnated,[79,96] and hyperbranched[97] aminosilicas for sorption of CO_2 from simulated air. Custom-made amines were also prepared by Jones and co-workers[98,99] to maximize the amount of primary amines, which were thought to have higher heats of CO_2 adsorption than secondary or tertiary amines and therefore were hypothesized to provide the highest CO_2 uptake under ultradilute conditions. Olah, Prakash, and co-workers employed commercial fumed silica impregnated with PEI for direct air capture in 2011.[100] That same year, Stuckert and Yang reported that zeolites performed well for DAC under dry conditions, but amine-modified silica performed better in the presence of moisture, where the zeolite physisorbent did not offer selectivity for CO_2 over H_2O.[101] Also in 2011, Steinfeld and co-workers applied a temperature-vacuum swing process (TVS), studying the influence of relevant variables such as the relative humidity, desorption temperature, and desorption pressure using amine-grafted silica gel.[102] They also developed a unique type of supported amine material that year, a poly(aminosilane) grafted nanofibrillated cellulose material.[103]

Later on, in 2012, Global Thermostat patented a detailed air contactor capable of working with many sorbent media, including supported amines like the ones reviewed in this section.[104] Additional structures and techniques were then proposed.[105] In both cases, a typical temperature swing adsorption (TSA) cycle was described, with desorption being achieved by an inert gas flow. Nevertheless, in a later patent by the same company, a steam flow was proposed as a substitute of inert gas to obtain more concentrated CO_2 in a more efficient way.[106]

In the extensive body of work currently describing the use of supported amine materials in direct air capture, solid amine sorbents based on porous oxide supports are among the most common sorbents. The existing literature using such materials is presented below in two sections, organized according to the earlier-described classification (section 5.1, class 1 sorbents; section 5.2, class 2 and 3 sorbents), while the use of other, nonoxide support materials is addressed in section 5.3. Bare and amine-modified MOF materials are discussed separately in section 5.4. Figure 10 and Figure 11 depict the types of amines that have been most commonly loaded onto porous solids for

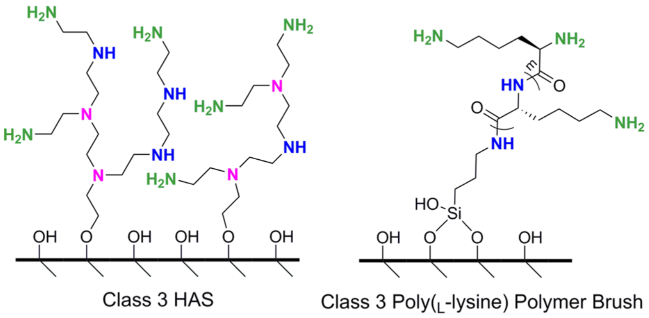


Figure 11. Molecular structures of class 3 amine sorbents for DAC.

use as CO_2 sorbents. Among polymeric or oligomeric amines, these include branched poly(ethylenimine) (PEI), linear poly(ethylenimine) (PEI-ln), poly(allylamine) (PAA), and tetraethylenepentamine (TEPA). Additionally, a number of different amines have been used as impregnating agents in studies of flue gas and pure CO_2 capture. Some examples are linear molecules, such as diethylentriamine, triethylenetetramine, pentaethylenehexamine, and 1,6-diaminohexane,[81,107−111] and cyclic amines, such as hexamethylenimine, piperazine, and 4-amino-2-hydroxy-6-methylpyrimidine.[112] However, as a consequence of the poor results obtained in higher concentrated CO_2 streams, there are not many applications of these amines for DAC.

Among aminosilanes used in class 2 sorbents, aminopropyl trimethoxysilane (APS), methylaminopropyl trimethoxysilane (MAPS), dimethylaminopropyl trimethoxysilane (DMAPS), *N*-[3-(trimethoxysilyl)propyl] ethylenediamine (ED), *N*-(3-trimethoxysilylpropyl) diethylenetriamine (DT), and *N*-(3-trimethoxysilylpropyl) triethylenetetramine (TREN) have been most commonly studied. Figure 10 shows the molecular structures of these aminosilanes.

5.1. Amines Physically Adsorbed on Oxide Supports

The impregnation procedure, whereby a chemical species is deposited into the pores or on the surface of a solid support, is a highly versatile procedure that allows almost any species to be loaded onto a given material, since no chemical reaction is typically involved in the process. A variety of amine-containing species have thus been loaded onto porous oxide supports. However, given that temperature swing adsorption (TSA) processes have been most commonly applied to direct air capture, relatively low volatility amine species have been primarily studied to limit sorbent degradation and amine loss during sorbent regeneration. Low molecular weight, branched poly(ethylenimine) (PEI) has been the primary amine-containing polymer used by numerous researchers to sorb CO_2 because of its large density of amine groups and good stability under TSA or vacuum swing adsorption (VSA) conditions.[15,16] The utility of smaller amines, such as those used in solution separation processes like monoethanolamine, have also been explored in solid sorbents.[100,107,108] Unfortunately, their low boiling points (typically ranging from 140 to 245 °C) resulted in considerable evaporation and amine loss using practical temperature swings.[110] Other linear amines such as tetraethylenepentamine (TEPA) and pentaethylenehexamine (PEHA) usually show some leaching or amine loss as well,[113−115] although not as much as the lower molecular weight compounds.[110]

The first use of poly(ethylenimine)-impregnated oxide sorbents for direct CO_2 capture from air was reported by Choi, Gray, and Jones.[79] A commercial silica was impregnated with 45% PEI, reaching a CO_2 uptake of 2.36 mmol/g from simulated ambient air (400 ppm of CO_2 in Ar, room temperature). However, a 30% loss in the CO_2 uptake was registered after 4 cycles. With the aim of obtaining adsorbents with better performance, PEI was combined with other compounds and then impregnated into the supports. Mixtures of PEI with 3-aminopropyltriethoxysilane (APS) or tetrapropylorthotitanate (TT) were compared to the sorbent impregnated only with poly(ethylenimine). PEI-APS and PEI-TT mixtures achieved similar CO_2 uptakes in the first cycle but increased the kinetics of CO_2 sorption, as seen in the reduction of adsorption half-time compared to the sorbent loaded with just PEI (see Figure 12). The use of the mixtures also provided better thermal and cyclic stability. A then-unknown interaction of the additives with PEI was likely the origin of the improved stability. A recent report on such class 4 materials has shed some light into this matter. Hydrogen bonds between PEI and the organosilane as well as between PEI and the silica surface have been suggested as the cause of their higher resistance to degradation by liquid/vapor H_2O and by air-oxidation.[83]

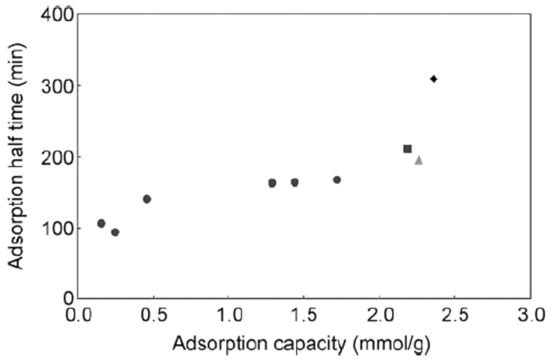


Figure 12. CO_2 adsorption capacity and adsorption half-time of ♦ PEI/silica, ▲ A-PEI/silica, and ■ T-PEI/silica compared to those of class 3 sorbents ●. Reprinted with permission from ref 79. Copyright 2011 Wiley.

Mesoporous alumina was also used as a support by Jones and co-workers.[96] Higher amine efficiencies were obtained compared to silica under a 10% CO_2 feed stream. Unfortunately, this result was not repeated with air, where the amine proximity was likely playing a more important role at such an ultradilute concentration. Nevertheless, the most important application of alumina was found to be its stability when steam-stripping was used as a regeneration method. The employment of this technique is favored by some as a way to obtain a relatively concentrated CO_2 stream, because stripping with inert gases, as commonly done in laboratory studies during regeneration, only redilutes CO_2. However, the most commonly used amine−silica materials are known to degrade to some extent in the presence of steam.[116−119] In contrast, Jones and co-workers found that PEI-loaded alumina was highly stable under steam-stripping conditions.[96] Moreover, even when some γ-alumina was transformed into bohemite, its presence did not significantly reduce the CO_2 adsorption performance of the sample under DAC conditions.[120]

From the idea that primary amines typically have higher heats of adsorption than secondary amines,[16,55] this same group prepared a low molecular weight poly(allylamine), PAA, for use as an alternative amine polymer to PEI.[99] The resulting

Table 2. Amine-Impregnated Oxide Supports Used for Direct Air Capture; Amine Loadings, CO_2 Uptakes, and Amine Efficiencies Are Presented[a]

support	amine	T (°C)	CO_2 (ppm)	amine loading (mmol of N/g of sorbent)	adsorption capacity (mmol of CO_2/g of sorbent)	amine efficiency (mmol of CO_2/mmol of N)	method	ref
commercial silica	PEI	25	400	10.5	2.36	0.22	TGA	79
	PEI+AP	25	400	10.7	2.26	0.21	TGA	79
	PEI+TP	25	400	10.5	2.19	0.21	TGA	79
MCF	PAA	25	400	7.24	0.86	0.12	TGA	99
	PEI	25	400	10.7	1.74	0.16	TGA	99
	PEI-lnH	25	400	11.4	1.05	0.09	TGA	99
Zr-SBA-15	PEI	25	400	8.3	0.85	0.10	TGA	134, 135
γ-alumina	PEI	25	400	11.2	1.74	0.16	TGA	96
SBA-15	PEI	25	400	9.2	1.05	0.11	TGA	96
commercial silica	TEPA	35	400	10.1	2.50	0.25	TGA	138
fumed silica	PEI-H	25	420	33%	1.18		IR	100
		25	420	33%	1.77[b]		IR	100
		25	420	50%	1.71		IR	100
		25	420	50%	1.41[b]		IR	100
SBA-15	PEI	75	400		0.51		TPD	133
γ-alumina	PEI	30	400	8.5	1.96[c]	0.25	IR	120
fumed silica	PEI-H + PEG	50	360	9.8[d]	0.68	0.07[d]	TGA	123
SBA-15	PEI + PEG200	30	400	5.75	0.79	0.14	TGA	130
fumed silica	PEI-ln	25	400	50%	2.34		IR	137
	PEI	25	400	50%	2.44		IR	137
	PEI-M	25	400	50%	1.69		IR	137
	PEI-H	25	400	50%	1.67		IR	137

[a] MCF, silica mesocellular foam; PEI, branched PEI (M_W = 800 Da); PEI-M, branched PEI (M_W = 1 800 Da); PEI-H, branched PEI (M_W = 25 000 Da); PEI-ln, linear PEI (M_n = 423 Da); PEI-lnH, linear PEI (M_W = 2 500 Da); PAA, poly(allylamine); PEG, poly(ethylene glycol) (M_W = 400 Da); TGA, thermogravimetric analysis; IR, infrared analyzer; TPD, temperature-programmed desorption. [b] 67% relative humidity (RH) at 25 °C. [c] 50% relative humidity at 30 °C. [d] Amine efficiency calculated with equation given in the paper. Amine loading calculated from CO_2 uptake and efficiency.

polymer was linear, contained only primary amines, and was estimated to have a Mn of 1130 Da. It was impregnated onto a mesocellular silica foam, and its performance was compared to that of linear and branched poly(ethylenimine). PAA achieved CO_2 uptakes and amine efficiencies similar to those of linear PEI, where all amines are secondary. However, the most interesting outcome was the much better performance obtained with branched PEI even though 23−25% of the amines are tertiary[121,122] and thus useless for CO_2 capture in the absence of moisture (or other protic compounds such as alcohols). In this case, the better performance of branched PEI was ascribed to the higher accessibility of its primary amines, located at the ends of all the polymer branches. Nonetheless, poly(allylamine) showed a fair cyclic stability and a CO_2 uptake up to 0.86 mmol/g,[99] and it is hypothesized that structurally tuned all-primary-amine polymers such as PAA or poly(vinylamine) might offer advantages over PEI.

In the selection of different amines, Olah, Prakash, and co-workers stated that secondary amines were the best compromise between reactivity and energy requirements during regeneration.[123] Actually, secondary amines have played major roles in industrial processes for acid gas separation since the 1980s.[124] This topic of primary versus secondary amines has also been investigated with tethered amines, so it will be further discussed in section 5.2. Olah, Prakash, and co-workers also worked with poly(ethylenimine), loading fumed silica with 33 and 50% PEI. CO_2 uptakes of 1.18 and 1.71 mmol/g were registered at 25 °C, respectively.[100] It is interesting to note that the CO_2 uptake of the bare support was negligible under the same conditions due to the ultralow concentration of CO_2. On the contrary, previous reports with either pure or 15% diluted CO_2 showed that SBA-15 silica did adsorb selectively this component rather than nitrogen or oxygen[115] due to specific gas−solid interactions.[125,126] In this regard, these data make clear the importance of amines for CO_2 capture under ultradilute conditions using silica-based materials.

Olah, Prakash, and co-workers also used mixtures of PEI and poly(ethylene glycol) (PEG) to obtain sorbents with enhanced air capture performance.[123] Following the long-known improvement of CO_2 sorption by amines mixed with PEG,[127] an optimum mix of 10% PEG, 42.5% PEI, and 47.5% fumed silica yielded the best CO_2 uptake under the conditions employed, 0.68 mmol/g. The combined use of PEI with organosilanes[80] or even with nonamine molecules[77,78] has been also applied to enhance CO_2 capture from flue gas. These mixtures were claimed to improve the arrangement of PEI, resulting in scattered aggregates rather than a compact layer,[128] allowing for high amine efficiencies even in highly amine-loaded materials.[129] Recently, the coaddition of PEI and two different kinds of poly(ethylene glycol), with M_W 200 (PEG200) and M_W 1000 (PEG1000), was investigated.[130] Both PEG species had a positive effect on the CO_2 uptake and amine efficiency of PEG−PEI−SBA-15 sorbent compared to their non-PEI counterpart. PEI−SBA-15 showed a net uptake of 0.63 mmol of CO_2/g, with an amine efficiency of 0.10 mol of CO_2/mol of N. The addition of PEG200 and PEG1000 yielded CO_2 uptakes

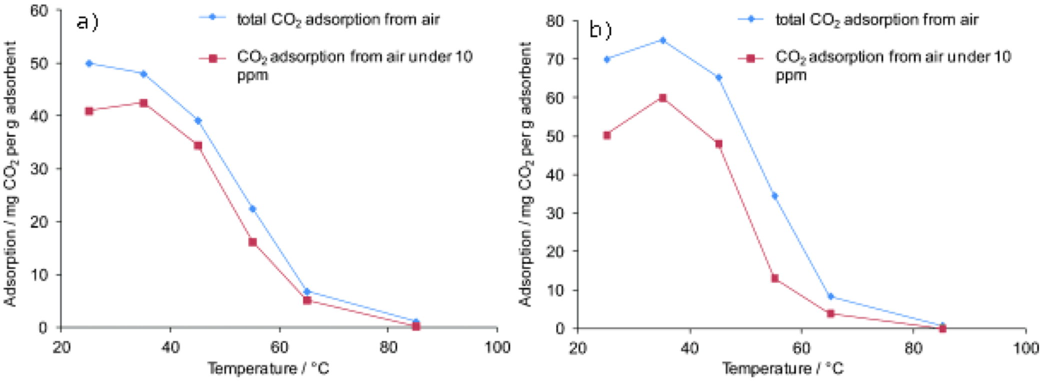


Figure 13. CO_2 uptake as a function of temperature on (a) fumed silica-PEI (33) and (b) fumed silica-PEI (50). Reprinted with permission from ref 137. Copyright 2014 Wiley.

of 0.79 and 0.71 mmol of CO_2/g, with amine efficiencies being 0.14 and 0.13 mol of CO_2/mol of N. Both PEG chemicals yielded better CO_2 uptakes when the PEG loading was low (and, hence, the amine loading higher). Additionally, PEG200 showed higher amine efficiencies for highly PEG-loaded samples. Thus, on the basis of the results shown, the positive effect of PEG observed with higher CO_2 concentrations seems to be maintained for direct air capture.

Since 2002, when Song and co-workers first published on the synthesis of mesoporous silica impregnated with PEI for CO_2 capture from flue gas,[131,132] class 1 amine sorbents have grown to become very popular for numerous CO_2 separation applications. Ten years later, in 2012, the Song group starting applying similar materials to air capture. In their first DAC work, a material composed of 50% PEI impregnated in SBA-15 was exposed to air overnight in a DRIFTS cell. Fourier transform infrared (FTIR) spectra were collected to demonstrate the proof of concept that CO_2 in air would interact with and bind to their sorbent.[133] Indeed, several distinctive bands commonly attributed to adsorbed CO_2 appeared in the IR spectra. Additionally, the CO_2 uptake was measured with simulated air at 75 °C via temperature-programmed desorption (TPD), with a resulting capacity of 0.51 mmol/g.

Porous supports have also been subject to modification to produce adsorbents with better performance. As an example, Jones and co-workers synthesized SBA-15 incorporating different amounts of aluminum, titanium, zirconium, and cerium to modify the acid/base properties of the supports.[134,135] After impregnating the obtained supports with PEI, all of them showed a higher CO_2 uptake from air compared to the impregnated SBA-15 silica. The best material was prepared by incorporating a moderate amount of zirconium and achieved a CO_2 uptake in air of 0.85 mmol/g. In a continuation to this study, it was determined that the change in textural and morphological properties derived from the metal incorporation was more significant to the CO_2 adsorption properties than the presence of the metal itself.[136] Namely, a modified SBA-15 silica with higher pore volume, larger mesopores, and less microporosity than conventional SBA-15 showed the best CO_2 properties after its impregnation with PEI. Conversely, the loading of Zr into the modified SBA-15 structure did not yield significant benefits.

Olah, Prakash, and co-workers investigated the effect of the kind of poly(ethylenimine) employed (i.e., linear, branched, low or high molecular weight) on the CO_2 uptake from air.[137] The use of linear PEI (M_W = 423 Da) and low molecular weight branched PEI (M_W = 800 Da) yielded higher CO_2 uptakes than were obtained by samples containing higher molecular weight PEI (M_W = 1 800 and 25 000 Da), as seen in Table 2. This behavior was found for PEI loadings of both 33 and 50%, revealing that linear or low molecular weight PEI materials are advantageous, similar to what was found in studies targeting flue gas.[137] On the other hand, linear PEI with M_W of 423 Da was previously shown to have leaching problems.[110] Thus, it is no surprise that branched PEI (M_W = 800 Da) has been widely used throughout the literature for CO_2 capture applications, providing a good balance of capacity, kinetics, and stability.

Apart from PEI, other amines have been used, as previously stated. In the case of tetraethylenepentamine (TEPA), different amounts of this molecule, from 26 to 45%, were used by Brilman and Veneman to impregnate two different porous silicas (CARiACT Q-10 and Davisil-646).[138] An amine loading of 38% was shown to be the optimum, leading to a CO_2 uptake of 2.50 mmol/g. Also as noted above, these sorbents are not expected to be stable under practical operating conditions.

5.1.1. Effect of Temperature.

The sorption temperature is also a key parameter for CO_2 capture from air. For class 1 materials, Song and co-workers noticed the curious behavior in their early work on flue gas that the optimum CO_2 uptake occurred at somewhat elevated temperatures.[131,132] This counterintuitive trend was ascribed to the competition of thermodynamic factors (better sorption at low temperature) and kinetic factors (better diffusion of CO_2 through polymeric PEI layers at elevated temperature and higher reaction rate).[131,132] This trend has been reproduced by many authors studying these materials over the past decade of work, mostly studying flue gas. Jones and co-workers studied mesocellular silica foams impregnated with 39% PEI, registering CO_2 uptakes at 25, 50, and 75 °C. The maximum CO_2 uptake was observed 50 °C.[99] Olah, Prakash, and co-workers found a different trend for 33%-PEI-loaded fumed silica. The CO_2 uptake underwent a decrease for increasing temperatures from 25 to 85 °C, showing the highest value at 25 °C (see Figure 13a).[137] When the amount of PEI loaded was increased to 50%, the total CO_2 uptake was higher, and it occurred at a temperature of 35 °C, as seen in Figure 13b.[137] Interestingly, the CO_2 uptake was negligible at 85 °C in both cases. Consequently, the temperature swing necessary between adsorption and desorption for this type of material might only be 50−60 °C.

Table 3. Grafted Oxide Supports Used for Direct Air Capture; Amine Loadings, CO_2 Uptakes, and Amine Efficiencies Are Shown[a]

support	amine	T (°C)	CO_2 (ppm)	amine loading (mmol of N/g of sorbent)	adsorption capacity (mmol of CO_2/g of sorbent)	amine efficiency (mmol of CO_2/mmol of N)	method	ref
PE-MCM-41	DT	25	400	7.9	0.98	0.12[b]	TGA	94
PE-MCM-41	DT	25	300	7.9	0.90	0.11[b]	PB	94
PE-MCM-41	DT	25	300	7.9	1.19[c]	0.15[b]	PB	94
PE-MCM-41	DT	25	300	7.9	1.40[d]	0.18[b]	PB	94
PE-MCM-41	DT	30	400	7.9	0.61	0.08	TGA	149
PE-MCM-41	DT	30	400	7.9	0.54[e]	0.07	TGA	149
PE-MCM-41	DT	(+5)−(−5)	400[f]	7.9	1.16	0.15	TGA	149
MCF	APS	25	400	2.70	0.54	0.20	TGA	142
MCF	MAP	25	400	2.41	0.17	0.07	TGA	142
SG	ED	25	400−440	2.48	0.40	0.16	TGA	102
SG	ED	25	400−440	2.48	0.44[g]	0.18	TGA	102
SBA-15	AZ	25	400	9.9	1.72[h]	0.17	MS	97
SBA-15	LY	25	400	5.18	0.60	0.12	TGA	98

[a] MCF, mesocellular foam; SG, silica gel; APS, aminopropyl organosilanes; MAP, methylaminopropyl organosilanes; ED, ethylenediamine organosilanes; DT, diethylenetriamino organosilanes; AZ, aziridine in situ polymerization; LY, Z-(L-lysine) in situ polymerization; TGA, thermogravimetric analysis; PB, packed bed. [b] Amine efficiency calculated from amine loading and CO_2 uptake. [c] Relative humidity 26%. [d] Relative humidity 64%. [e] Relative humidity 73%. [f] Outdoor air used. [g] Relative humidity 40%. [h] Fully humidified conditions.

5.1.2. Influence of Moisture. Olah, Prakash, and co-workers also studied the influence of moisture on the CO_2 uptake.[100] Namely, the performance of fumed silica impregnated with 33% PEI experienced an increase in CO_2 uptake from 1.18 to 1.77 mmol/g when using 25 °C dry and humid air (relative humidity of 67%), respectively. On the contrary, the sorbent with 50% PEI suffered a decrease in CO_2 uptake from 1.71 to 1.41 mmol/g under the same two conditions. This different behavior was ascribed to the dissimilar arrangement of PEI in the interparticle space of the two materials. When the organic loading was low, PEI was well-dispersed on the surface, thus allowing access to most or all of the amine groups. In contrast, highly loaded samples hindered the diffusion of CO_2 and the uptake efficiency decreased. In addition, water was claimed to possibly have a negative effect on the adsorption uptake, blocking the access to the amine groups via oversaturation of the materials with water (PEI is very hydrophilic),[100] as also proposed by Belmabkhout and Sayari using higher concentrations of CO_2.[139] Another possible explanation is the absence of an appropriate environment existing in the sorbent for the formation of carbonate and bicarbonate species.[140]

Another study by Brilman and Veneman showed no differences in the CO_2 breakthrough curves obtained in dry or wet air (relative humidity of 80%) with 38%-impregnated TEPA.[138] Clearly, more studies are needed in this respect in direct air capture, as the effect of moisture on the CO_2 uptake of amine−silica materials has already yielded different results in flue gas sorption as well. As examples, in the area of CO_2 capture from flue gas, increases between 24 and 61% have been reported for impregnated materials in the presence of humidity.[115,141]

5.2. Amines Covalently Tethered to Oxide Supports

Aminopropyl (APS) and diethylenetriamine (DT) silanes (see chemical structures in Figure 10) are by far the compounds most often used to modify porous oxide supports via grafting for applications in CO_2 capture. An extensive list of amine-grafted materials applied to air capture is shown in Table 3, including their CO_2 adsorption properties.

Functionalization with DT for air capture purposes was first applied by Sayari and co-workers over pore-expanded MCM-41 (PE-MCM-41) in 2010.[94] A low-pressure CO_2 isotherm revealed a CO_2 uptake of 0.98 mmol/g at 25 °C and a relative pressure corresponding to 400 ppm of CO_2. Dynamic analysis in packed bed with simulated air (N_2, O_2, and CO_2) showed an analogous result, achieving a CO_2 uptake of 0.90 mmol/g. Moreover, the amount of N_2 or O_2 adsorbed was negligible compared to that of CO_2, thus inferring a very high selectivity to CO_2 over these two common components in air.[94] According to Calleja and co-workers, the use of postcombustion gas mixtures with 15% CO_2 revealed a similar high selectivity toward carbon dioxide.[115] Interestingly, a high selectivity seems to be maintained when using highly diluted CO_2, which is very promising for air capture purposes.

Because of the presence of both primary and secondary amines in the diethylenetriamine organosilane, the role of different amine types of CO_2 capture from air was not easy to infer from this first paper on class 2 sorbents. With the aim of revealing the role of amine structure on CO_2 adsorption efficiency, organosilanes containing only one amine group at a common amine loading were prepared and evaluated. Primary amines were shown by Jones and co-workers to possess an efficiency value of 0.20 mol of CO_2/mol of N using a 400 ppm of CO_2 feed, while the use of secondary amines yielded an efficiency of just 0.07 mol of CO_2/mol of N (see Table 3).[142] Moreover, an efficiency of up to 0.30 mol of CO_2/mol of N was achieved for primary amines by increasing the organic loading. Thus, CO_2 dilution was shown to have a strong effect on the amine efficiency of secondary amines but not as significant an effect on primary amines. This different behavior was ascribed in that work to the higher heat of adsorption for primary amines.[142] This was later shown not to be an enthalpic effect but rather an entropic effect, as the experimentally measured heats of adsorption for the primary and secondary amines were found to be similar at low coverage.[143] The effect of amine loading on the hydrophilicity of the adsorbent was also studied, finding a positive correlation for primary amine loading and water adsorption. On the contrary, the presence of secondary amines made the materials more hydrophobic.[142] Thus,

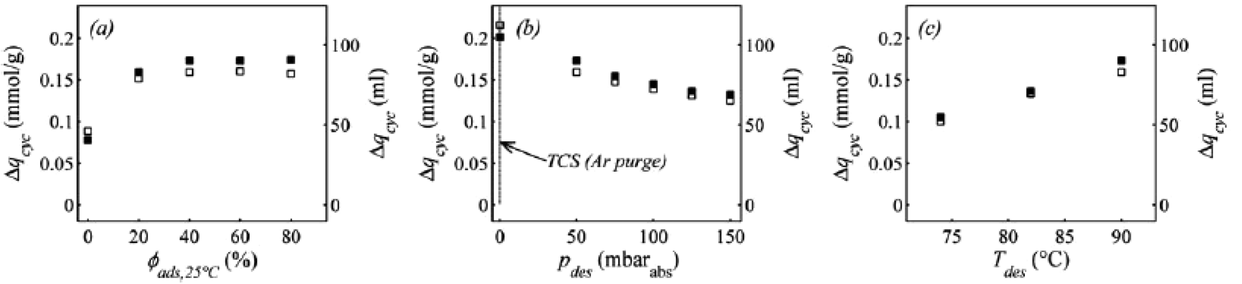


Figure 14. Variation of cyclic CO_2 sorption (open symbols) and desorption (closed symbols) as a function of (a) sorption humidity, (b) desorption pressure, and (c) desorption temperature for ethylenediamine-grafted silica in nonequilibrium conditions ($\phi_{ads,25°C}$ = 40%; p_{des} = 50 mbar; and T_{des} = 90 °C when not stated otherwise). Reproduced with permission from ref 102. Copyright 2011 The Royal Society of Chemistry.

primary amines may be even more beneficial for CO_2 adsorption compared to secondary amines when moisture is present. Interestingly, Choi and co-workers reported comparable efficiencies for primary and secondary amines under pure CO_2 (0.28 and 0.24 mol of CO_2/mol of N, respectively).[144] This further shows that the CO_2 partial pressure plays a key role in determining the amine efficiency for different amine types.

Focusing their research on primary amines, Jones and co-workers varied the length of the organic linker attaching an ending primary amine to the silica surface.[145] Linkers with 1−5 carbon atoms were considered. The low flexibility of methyl and ethyl linkers limited the interaction of two neighboring amines, essential for the reaction with CO_2 molecules. The resulting CO_2 uptake was even less than that by the bare support, indicating that these organosilanes did not significantly contribute to CO_2 adsorption when isolated. Propyl linkers, with more flexibility, allowed the interaction between amino groups, resulting in considerably higher CO_2 uptakes. However, further increase in the linker length (C4 and C5) did not yield significant changes in the CO_2 uptake. Aminopropyl functionalities were also created on a silica surface by postgrafting amination by the same research group. This technique consisted of the grafting of alkyl halide organosilanes and a subsequent conversion of the terminal halide groups to primary amines with ammonia.[146] Low-loaded materials presented similar CO_2 adsorption properties as aminosilane-grafted samples. Overall, it was inferred that postgrafting amination yielded amines that were slightly more spaced on the surface, which is potentially favorable for CO_2 adsorption in highly loaded materials but which can inhibit the necessary amine−amine pairing needed to bind CO_2 under dry conditions.

Most commonly, temperature swing (TSA) and, to a much lesser extent, pressure swing (PSA) adsorption/desorption processes have been applied to CO_2 capture with amine sorbents, targeting the maximizing of CO_2 uptake and amine efficiency. However, a diluted CO_2 stream is obtained after desorption when conventional inert gas stripping is applied, as noted earlier. To obtain a concentrated CO_2 stream, steam-stripping has been applied,[76,119,120] as well as vacuum in a TVS (temperature-vacuum swing) process.[102,139,147,148] The downside of this technique is that the obtained CO_2 capacities are typically lower, but this disadvantage can be offset by the much higher CO_2 purities obtained.

Following a TVS process, Steinfeld and co-workers studied the importance of the desorption temperature as a key parameter in the cyclic application of class 2 materials.[102] The use of ethylenediamine-grafted silica yielded CO_2 uptakes of 0.32 and 0.40 mmol/g when adsorbing at 25 °C and desorbing, respectively, at 74 and 90 °C. The amine efficiency of the ethylenediamine material, with one primary and one secondary amine in its structure, was 0.16 mol of CO_2/mol of N. Interestingly, this value was between the ones obtained by adsorbents with only primary and secondary amines (0.20 and 0.07 mol of CO_2/mol of N, respectively).[142] Despite attaining higher CO_2 uptakes with a higher desorption temperature, it was pointed out that it is not practical to perform cycles between equilibrium states.[102] Accordingly, nonequilibrium TVS cycles were performed. As expected, CO_2 capacities were smaller than those of the pseudoequilibrium experiments, as seen in Figure 14. On the other hand, the cycle time was reduced by a factor of 5. A stable capacity was registered after 40 cycles using the TVA process. This study also reported relatively high CO_2 uptakes at relative pressures as low as 10 mbar, thus inferring that isothermal vacuum swings without temperature increase would be unfavorable for air capture with these materials.

In 2013, Wagner et al. performed experiments using simulated air to study CO_2 sorption at 30 °C using DT-containing PE-MCM-41, reporting capacities up to 0.60 mmol/g.[149] Experiments under real outdoor conditions outperformed lab tests, achieving a CO_2 uptake of 1.16 mmol/g. This improvement was ascribed mainly to the lower sorption temperature used (ranging between +5 and −5 °C) due to Swedish winter outdoor conditions as well as to the fact that the equilibration time was also substantially increased from 3 h (lab experiments) to overnight sorption (outdoor tests). Regeneration in controlled conditions (100 °C, 2 h) with synthetic air yielded only a minor decrease in the CO_2 uptake after 4 cycles. Alas, real conditions had a dramatic effect on the cyclic adsorption performance. The decrease in the CO_2 uptake was so sharp that the CO_2 sorption capacity of the sample was negligible only after three cycles.[149] The long thermal desorption step was pointed out as the probable cause of the material degradation, with the authors suggesting amines possibly forming urea-like compounds through reaction with CO_2[150] even though the presence of moisture is advantageous in avoiding this side reaction.[151] Although it was not stated by the authors, amine oxidation processes are more likely to have played an important role,[152,153] as similar infrared bands as those detected by Wagner et al. at 1660 cm^{-1} had been previously described as an effect of air oxidation of amines.[152]

Class 3 materials are sorbents with amine monomers polymerized off the support surface in situ, yielding polyamine structures covalently bound to the walls. Jones' group made two contributions to this specific field in 2011. In the first, aziridine was used as a monomer to obtain hyperbranched aminosilica (HAS) materials with different loadings.[97] The highest nitrogen

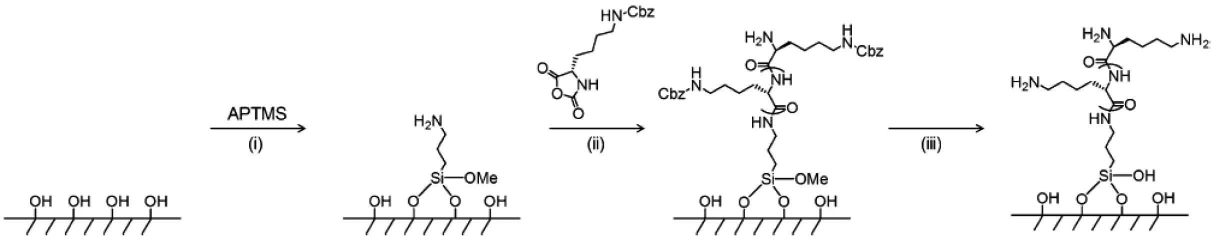


Figure 15. Preparation of poly(L-lysine) brush-mesoporous silica hybrids: (i) grafting of SBA-15 with 3-aminopropyl trimethoxysilane (APTMS), (ii) in situ ring-opening polymerization of Z-(L-lysine) N-carboxyanhydride (NCA), and (iii) deprotection of Z-protecting group and neutralization with $NaOH_{aq}$. Reprinted with permission from ref 98. Copyright 2011 Wiley.

Table 4. Polymers, Resins, and Other Solid Organic Materials Used for Direct Air Capture; CO_2 Uptakes, As Well As Amine Loadings and Amine Efficiencies (Where Applicable), Are Shown[a]

type	support	amine	T (°C)	CO_2 (ppm)	amine loading (mmol of N/g of sorbent)	adsorption capacity (mmol of CO_2/g of sorbent)	amine efficiency (mmol of CO_2/mmol of N)	method	ref
polymers	PPN-6-CH_2DETA	DETA	22	400	8.5	1.04[b]	0.12	VOL	161
	CB-*N*-g-PCMS-OH^-		15	400[c,d]		0.14		IR	167
	CB-g-*x*PCMS-OH^-		15	400[c,d]		0.14		IR	170
	PS-CC		15	400[c,d]		0.57		IR	172
	colloidal crystal		15	400[c,d]		0.36		IR	167
	HIPE		15	400[c,d]		0.50		IR	167
	pick-20%—silica-2%		15	400[c,d]		0.72		IR	173
resins	HP20/PEI-50	PEI	25	400	11.8	2.26	0.19	TGA	175
	proprietary		25	440		0.86		IR	185
NFC	AP-NFC	APS	25	506[e]	4.9	1.39	0.28	IR	103
NFC	AP-NFC	APS	23	400	4.2	1.11	0.26	IR	179
NFC	AP-NFC	APS	23	400[f]	4.2	2.13	0.51	VOL	179
	RFAS4	APS	30	400[g]	8.07	1.69	0.21	IR	184

[b]Adsorption capacities interpolated from IAST calculation from measured single-component CO_2, O_2, and N_2 isotherms. [c]Compressed laboratory air was used as gas feed. [d]Relative humidity 95%. [e]Relative humidity 40%. [f]Relative humidity 91%. [g]Relative humidity 4%. [a]DETA, diethylenetriamine; PEI, poly(ethylenimine) (M_n = 600 Da); APS, aminopropyl organosilanes; IR, infrared gas analyzer; VOL, volumetric method; TGA, thermogravimetric method.

loading achieved was 9.9 mmol of N/g, a value that exceeds most of those corresponding to grafted samples (as discussed above). A significant CO_2 uptake of 1.72 mmol/g under air capture conditions was registered at 25 °C, again surpassing all the results available for grafted sorbents. A representative sorbent of the HAS series also revealed a good stability over four sorption—desorption cycles. The high stability was assigned to the fact that amines were covalently tethered to the silica surface.

Another approach made by the same group in collaboration with Shantz consisted of the polymerization of Z-(L-lysine) over an aminopropyl-grafted silica surface.[98] Figure 15 depicts the unusual synthesis route followed. Amine contents obtained ranged from 2.76 to 5.18 mmol of N/g, representing a much lower value than that reached by aziridine polymerization. The CO_2 uptake of the highest loaded sample was only 0.60 mmol of CO_2/g, partially due to the low amine efficiency (0.12 mol of CO_2/mol of N). Nevertheless, lysine-polymerized sorbents achieved a stable CO_2 uptake after three cycles, although many more cycles would be needed for industrial application purposes.

In 2014 Giannelis and co-workers reported a new class 3 material[154] prepared using a similar multistep approach as discussed above whereby an alkyliodine was first grafted to a mesoporous silica foam support, followed by a cationic polymerization of 2-methyl-2-oxazoline and subsequent acid hydrolysis to produce a high density of a grafted linear PEI-like polymer composed of secondary amines with terminal primary amines. The reported sorption capacity for flue gas capture is the highest known to date: 11.8 mmol/g under conditions of 8% CO_2 with 18% RH at 25 °C. The presence of moisture greatly increased the capacity, as the dry CO_2 uptake was just 0.82 mmol/g. While nothing has been reported on this material for DAC, its impressive performance for flue gas capture suggests it may be a promising sorbent for further study.

5.2.1. Influence of Moisture.

Wagner et al. found little differences in the CO_2 uptake of DT-functionalized PE-MCM-41 with dry (0.61 mmol/g) and humid air (73% RH, 0.54 mmol/g) at 30 °C. Using a very similar material, Sayari and co-workers found an increase from 0.90 mmol/g in dry conditions to 1.19 and 1.40 mmol/g with 26 and 64% RH, respectively.[94] However, the same authors observed only a slight increase (ca. 7%) between the sorption uptake under dry conditions or in a stream with 27% RH when the gas mixture contained 5% CO_2.[95] Steinfeld found that ethylenediamine-grafted silica gel underwent a slight increase in the CO_2 uptake when comparing

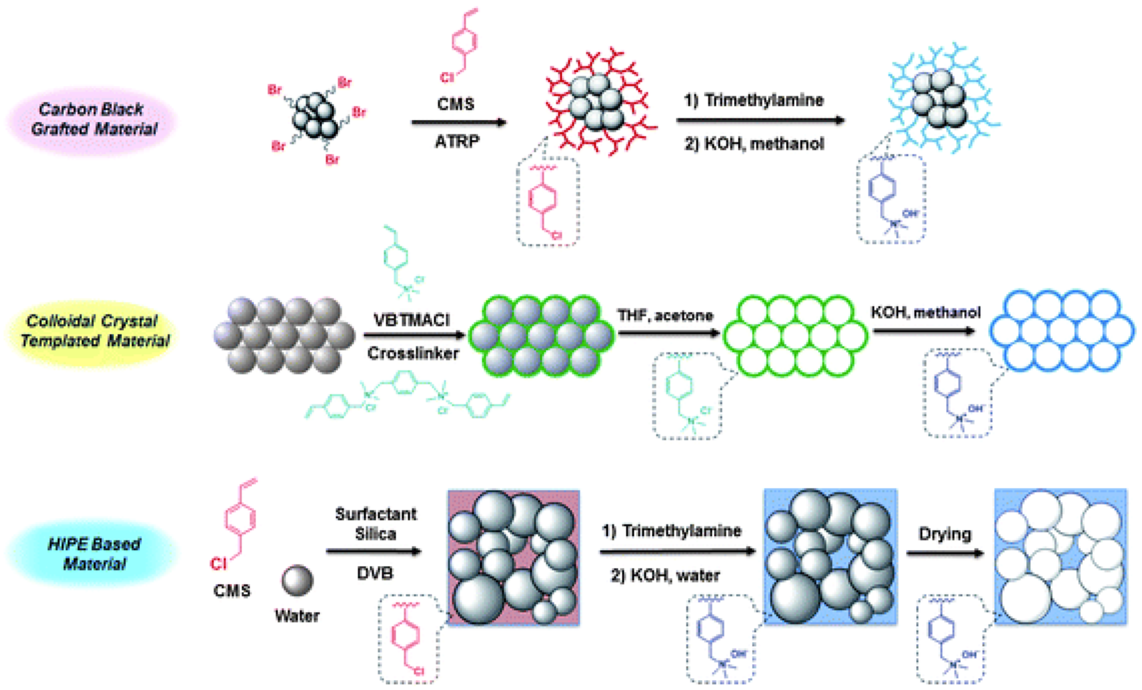


Figure 16. Synthetic protocols for polymer-grafted carbon blacks (top), colloidal crystal templated material (middle), and high internal phase emulsion (HIPE)-based material (bottom). Reproduced with permission from ref 167. Copyright 2013 Royal Society of Chemistry.

dry (0.40 mmol/g) and wet (0.44 mmol of CO_2/g) experiments in air capture at 25 °C. A further study by Jones and co-workers showed that the amine efficiency increase due to the presence of moisture was dependent not only on variables such as the support or the amine used but also on the amount of amine loading.[155] Namely, the grafting of SBA-15 with an APS coverage lower than that of the monolayer yielded the highest increase in the amine efficiency when comparing dry and humid conditions (30 °C, 0−0.01 bar CO_2). Higher APS loading coinciding to or exceeding that of the monolayer resulted in progressively smaller increases in amine efficiency, although the dependence with the pressure was different for the latter.[155]

As discussed in the earlier section on impregnated amines, there are not clear trends regarding the influence of water on CO_2 uptake under DAC conditions, and the complex binary sorption of CO_2 and H_2O merits further exploration.

5.3. Amines Supported on Solid Organic Materials

Supports other than silica and alumina have also been used for direct CO_2 capture from air. Carbon dioxide removal from enclosed spaces such as submarines or space cabins has been of interest before this technology was targeted toward reducing anthropogenic CO_2 emissions. As examples, activated carbon,[156] ion-exchange resins,[157] and polymers such as poly(methyl methacrylate) loaded with amines[158] have been used for this purpose. CO_2 inlet concentrations corresponding to confined environments (0.5−2%) were considered in these works. However, these values are significantly higher than the 0.04% existing in the atmosphere, so that these studies fall outside the scope of this Review.

In the last 30 years, significant progress has been made in the design of CO_2-responsive polymers,[159] with a number of them being applied to DAC in recent times. One straightforward route is to functionalize polymers with amines, selecting efficient reactions and high-surface-area starting polymers. Zhou and co-workers grafted linear amines over PAF-1, also known as PPN-6 (where PPN stands for porous polymer networks), with 4023 m^2/g surface and a pure CO_2 uptake of 1.3 mmol/g (22 °C, 1 bar).[160] PPN-6 grafted with diethylenetriamine (DETA) gave particularly good behavior, sorbing up to 1.04 mmol/g under DAC conditions (see Table 4) and showing a great selectivity of 3.6×10^{10} (400 ppm of CO_2, 21% O_2, balanced with N_2).[161] Additional interesting results were obtained by Zhou and co-workers in the following years, although they primarily studied flue gas−CO_2 adsorption.[162−166]

Carbon black has also been used as a support to obtain DAC-active materials by several methods. One method employed was to functionalize the carbon surface with atom transfer radical polymerization (ATRP) initiators (see Figure 16 top). There are three common methods to covalently bind ATRP initiators onto carbon materials: nitrene chemistry, acid oxidation, and Pschorr-type arylation. Nitrene chemistry was used to polymerize *p*-chloromethylstyrene (PCMS), yielding a hyperbranched polymer whose chloride groups were then transformed into quaternary ammonium hydroxide groups (sample CB-*N*-*g*-PCMS-OH^-).[167] Quaternary ammonium hydroxide groups are the preferred CO_2 sorption groups for a novel humidity swing process developed by Lackner (more on this below).[37,168,169] A CO_2 uptake of 0.14 mmol/g was achieved by the CB-*N*-*g*-PCMS-OH^- sample. Acid oxidation was also used after forming a divinylbenzene (DVB) polymer shell on the carbon black to increase ATRP efficiency. After obtaining quaternary ammonium hydroxide groups, sample CB-*g*-*x*PCMS-OH^- also showed a CO_2 uptake of 0.14 mmol/g, with faster adsorption and desorption rates compared to the previous sample.[170] Despite the adsorption capacities being modest and comparable to a reference Excellion membrane, the raw carbon black material showed no CO_2 uptake, so there was clearly an improvement achieved by the quaternary ammonium groups incorporated.

Inverse templating is another method to prepare highly porous polymeric structures (Figure 16, middle). When colloidal crystals are used, monodispersed particles (typically polymer latex or silica microspheres) leave interstitial spaces were the polymer is formed. The wide variety of particles, polymer monomers, and synthesis conditions that can be used suggests that a huge number of functional materials might be obtained.[171] Two of the best results in direct air capture yielded CO_2 uptakes of 0.36 and 0.57 mmol/g, respectively.[167,172] The idea of inverse templating was also applied using immiscible solutions of liquids through the so-called high internal phase emulsions (HIPEs) process (Figure 16, bottom). In the special case of Pickering-HIPE, the emulsion is stabilized by micro- or nanometer-sized particles that preferentially migrate to the interface between the two liquids. Thus, solid particles form shells that prevent coalescence by surrounding the dispersed phase, and a highly porous material is obtained with a significantly lower amount of surfactant.[173] With this technique, CO_2 uptakes up to 0.50 and 0.72 mmol/g were achieved.[167,173] Overall, the rational design of appropriate polymeric architectures led to increases in CO_2 uptake under DAC conditions by about a factor of 4. Nonetheless, these uptakes remain modestly below those obtained using conventional amine−CO_2 interactions, as discussed above.

All the data reported above using quaternary ammonium-based sorbents were obtained using a moisture-swing adsorption cycle originally developed by Lackner and coworkers.[169] In this process, immobilized quaternary ammonium cations are used with hydroxide, carbonate, or bicarbonate counteranions in various parts of the cycle. As depicted in Figure 17, CO_2 sorption is performed under dry conditions, where bicarbonate species are formed. When the material is wetted, CO_2 is desorbed due to the formation of carbonate species. This approach uses the energy released during evaporation, thus saving the energy-penalizing desorption step in temperature or vacuum swings. Although evaporation is spontaneous, it requires enthalpy, provided by the flowing of air through the sorbent, and entails high water losses between 12 and 37 mol per mol of CO_2.[174]

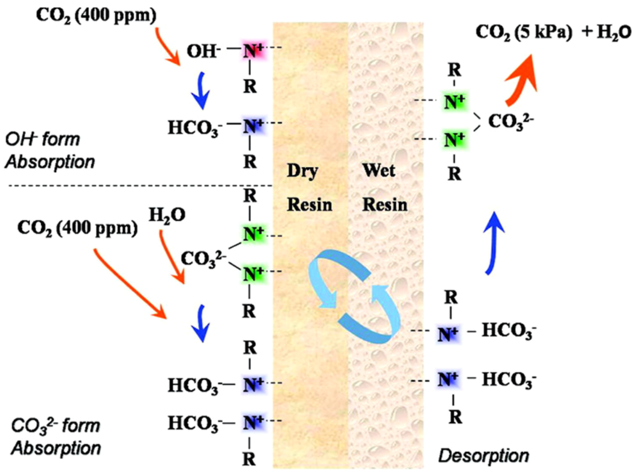


Figure 17. Schematic representation of a moisture swing process. Reprinted with permission from ref 168. Copyright 2011 American Chemical Society.

Amine-based anion-exchange resins have also been used under moisture swing conditions, being the original materials studied by Wang and Lackner for this process. They discovered that exchange resins dispersed in a thin polymeric film were capable of adsorbing CO_2 when dry and releasing it when wet. As an example, one of the tested resins was fully saturated with CO_2 at water vapor concentrations up to 0.5% at 23 °C, with half of the CO_2 being depleted upon increasing the moisture content to 1.8%,[168] yielding CO_2 uptakes in dry air of 0.86 mmol/g.

PEI impregnation was also studied as a way to increase CO_2 adsorption capacities in ion-exchange resins. A commercial nonpolar copolymer styrene−divinylbenzene adsorbent resin (Diaion HP20) was used. After impregnation with 50% PEI, it yielded a remarkable CO_2 uptake of 2.26 mmol/g at 25 °C,[175] which is close to the highest CO_2 loading reported to date under DAC conditions, i.e., 2.50 mmol/g, obtained by Brilman and Veneman.[138]

As early as 2010, Lackner and Global Research Technologies, LLC, described in a patent application the use of anion-exchange resins for DAC using humidity swings.[176] An analogous system was patented coupled to a greenhouse structure, using the enriched CO_2 stream to speed plants and/or algae growth.[177] Alternative contactors for air capture were developed by Lackner with the aim of maximizing energy efficiency during CO_2 removal.[178] In this case, the sorbent was regenerated by increasing its temperature in an enclosed compartment instead of using a hot gas stream; a heat exchanger was used to recover the heat contained in the sorbent after desorption, and a combination of humidity and thermal swings was proposed to optimize sorbent regeneration.

Steinfeld reported the use of nanofibrillated cellulose (NFC) as solid support for amines to promote the application of renewable materials.[103] Aminopropyl-modified NFC reached a CO_2 uptake of 1.39 mmol/g in compressed lab air with 40% relative humidity, with stable capacity after 20 cycles.[103] The influence of moisture on CO_2 uptake was later studied at temperatures between 10 and 30 °C and relative humidities of 20, 40, 60, and 80% at each adsorption temperature.[148] Important increments in CO_2 uptake were observed as a function of the relative humidity, as seen in Figure 18.[148] However, it is well-known that similar experiments performed with pure CO_2 produce smaller beneficial effects.[15,16] The explanation may lie in the slow diffusion of ultradilute CO_2 across the bulk of the sorbent.[179] According to these authors, in DAC conditions, humidity is necessary to achieve high efficiencies, because moisture yields diffusive intermediates that enhance the accessibility to all amine-active sites.[180] This

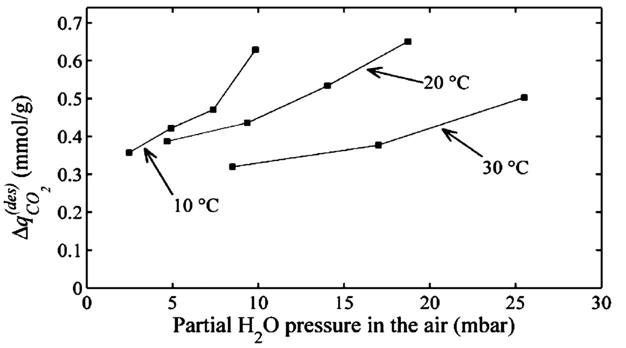


Figure 18. CO_2 desorption capacity in a TVS cyclic process as a function of temperature and H_2O partial pressure. Reprinted with permission from ref 148. Copyright 2012 American Chemical Society.

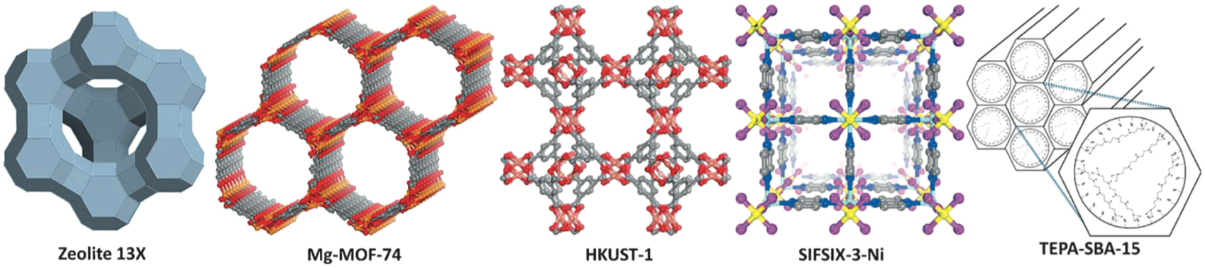


Figure 19. Range of physisorbents investigated by Zaworotko and co-workers. Reprinted with permission from ref 186. Copyright 2015 Wiley.

finding is consistent with other works on flue gas, where humid streams yielded faster CO_2 uptake and diffusion in fiber sorbents.[181]

A temperature-vacuum swing (TVS) process previously described was applied to avoid CO_2 dilution during desorption using the NFC materials.[102] CO_2 desorption capacities with TVS were up to 0.65 mmol/g under the best conditions reported (10 °C, 80% relative humidity).[148] The use of nanofibrillated cellulose as a macroporous support for amines was described in patent applications by Steinfeld, Gebald, and co-workers.[182,183] The choice of a macroporous support instead of a microporous (zeolites, MOFs, etc.) or a mesoporous material (silica, alumina, etc.) was aimed to reduce the CO_2 diffusion restrictions through the pores.

Finally, another set of amine-containing materials, RFAS, were prepared from a gel containing different amounts of resorcinol, formaldehyde, and 3-aminopropyltriethoxysilane (hence the acronym RFAS).[184] A CO_2 uptake of 1.69 mmol/g was observed under DAC conditions for RFAS4, the material with the highest amine loading.

5.4. Utilizing MOFs and their High Degree of Tunability

While the study of direct air capture systems has focused heavily on chemisorbents such as materials composed of amine-based groups tethered to or impregnated within oxide supports, there has been a recent resurgence in the examination of physisorbent materials. Compared to the elevated temperatures required to regenerate chemisorbents, often >100 °C,[186] physisorbents would require less energy for regeneration. However, there has been a general lack of suitable candidates in the literature for use with ultradilute gases.

One class of materials that has gained increased interest due to their versatility is metal−organic frameworks (MOFs). MOFs are highly ordered materials composed of metal atoms or clusters as nodes bridged by organic moieties. The ability to tailor the surface area and pore functionality of these crystalline materials has led to the use of MOFs in a variety of lab-scale adsorption and separation applications.[186−191]

To increase CO_2 capacities within MOFs in particular, the ability to fine-tune the pore size has been examined in numerous studies. Beyond just tuning the pore size, MOFs provide a means to incorporate additional reactivity, as seen in frameworks replete with open-metal sites. As opposed to other flexible polymeric structures where rearrangement occludes the reactive sites, the inherent rigidity in MOFs allows for the open-metal sites to remain available. A well-studied MOF with a high density of open-metal sites is MOF-74, which can be made with a variety of metal salts such as magnesium and cobalt.[192,193] The inclusion of open metal sites has led to high CO_2 capacities at ambient pressures and steep uptakes at very low concentrations. The Mg version of MOF-74, in particular, has been reported to have a CO_2 adsorption capacity of 0.38 g/g of sorbent when dry 100% CO_2 is used, and this is one of the highest capacities reported in the MOF literature.[194] The initial heat of adsorption was determined to be 39 kJ mol^{-1} for the Mg version and therefore reveals a moderate interaction between the metal sites and the CO_2.[195] While adsorption results show high capacities, humidity studies revealed regeneration and recyclability issues with MOF-74, as water competes with CO_2 for binding and leads to an overall decrease in the number of reactive sites, similar to other physisorbents such as zeolite 13X.[196,197] Therefore, if MOFs are to be utilized in direct air capture specifically, methods to tailor them for high CO_2 selectivity and stability in the presence of other competing guests must be developed.[198]

One such method to increase the CO_2 selectivity within MOFs, as previously stated, is through tuning the pore size of the MOF. Eddaoudi and co-workers have recently shown, using their MOF SIFSIX-3-M where M is copper, nickel, or zinc, that the metal used during synthesis can lead to slight changes in the unit cell and therefore increase CO_2 interactions.[186,199] All SIFSIX-3-M structures contain chains of $MSiF_6$ that are bridged by pyrazine moieties to yield a three-dimensional structure. The unit cell and ultimately the pore size distribution can be changed by simply adjusting the metal used, with the copper variant being the smallest and centered at 3.5 Å while Zn is the largest centered at 3.8−4.0 Å. When performing CO_2 studies for all MOFs, the copper variant, having the smallest pore size, exhibited very steep variable-temperature CO_2 adsorption isotherms. Additionally, the Q_{st} of CO_2 increased accordingly from 45 to 54 kJ/mol when going from the two extremes, zinc to copper. Even under competitive adsorption studies such as CO_2/N_2 = 10/90 or CO_2/H_2 = 30/70, the CO_2 adsorption behavior followed the same behavior as pure CO_2. Analysis of SIFSIX-Cu at 400 ppm and 298 K revealed an uptake of 1.24 mmol/g, an uptake substantially higher than the Zn analogue (0.13 mmol/g) due to the contracted pore size. Full desorption can also be performed under vacuum at 323 K. As this CO_2 uptake value is the highest reported for MOFs without unsaturated metal centers or amine functionalities, future work on how to tailor the pore chemistry to increase CO_2 capacities even more should be considered.[186,191,199]

As MOFs and their tunability have been shown to be useful for CO_2 capture from air, Zaworotko and co-workers recently surveyed a range of sorbents including the three MOFs SIFSIX-3-Ni, HKUST-1, and Mg-MOF-74.[186] These materials were studied along with more well-known zeolite 13X and TEPA-SBA-15, an amine-modified mesoporous silicate (Figure 19). Along with studying the performance of each material under air capture conditions, accelerated stability tests to simulate long-term storage and exposure to atmospheric water vapor were studied. All sorbents studied were evaluated via temperature-programmed desorption (TPD) on pristine activated samples that were exposed to the laboratory atmosphere for a prescribed time period. The average relative humidity and temperature were measured to be 49% and 23.4 °C, respectively. The cell was then heated to fully evacuate the host, and the He carrier gas was monitored with a mass spectrometer. TPD results showed that the chemisorbent TEPA-SBA-15 was far superior to all physisorbents tested by adsorbing the most CO_2 and the least amount of H_2O. TPD results revealed concentrations of 93% CO_2 and 7% H_2O. Of the physisorbents tested, SIFSIX-3-Ni was the top performer, with TPD results showing a composition of 8% CO_2 and 92% water. Behind SIFSIX-3-Ni were Mg-MOF-74, HKUST-1, and zeolite 13X.[186]

TPD results thus showed that all physisorbents adsorbed large amounts of water.[186] While the adsorption of water decreases the CO_2 uptake, MOFs in particular have shown susceptibility to structural degradation upon exposure to water vapor as well.[196,200] Therefore, not only are the TPD results of pristine samples important, but the recyclability will be equally important. Stability studies were performed at 40 °C and 75% humidity for up to 14 days. TEPA-SBA-15, zeolite 13X, and SIFSIX-3-Ni were both found to be stable after the 14 days, but HKUST-1 and Mg-MOF-74 were degraded. This degradation is not surprising, as previous literature results have shown similar behavior upon exposure to moisture for both MOFs.[201,202] The last physisorbent studied, SIFSIX-3-Ni, did exhibit a different PXRD pattern from the pristine sample after exposure, but upon regeneration at 110 °C, the PXRD pattern again matched the pristine sample.[186] Although the physisorbents studied were not as competitive as standard chemisorbents, the performance of SIFSIX-3-Ni shows how pore size and chemistry must continuously be addressed to improve the performance of MOFs. Overall, this study highlights the importance of water/CO_2 competitive adsorption, an issue often neglected by academic laboratories in studies of CO_2 capture despite the fact that most MOFs behave poorly in the presence of humidity or water.[203]

5.4.1. Amines Tethered to MOFs. With MOFs exhibiting such tailorability, one common method to increase CO_2 uptakes has been to incorporate open-metal sites within the frameworks, as noted earlier. As certain MOFs are formed, such as the previously mentioned MOF-74, vacant metal sites line the pore walls after guest solvent molecules are removed. While pristine samples have high CO_2 adsorption capacities, the materials are difficult to regenerate and the presence of moisture drastically decreases performance, as noted earlire. Because of the decrease in CO_2 capture performance in humid conditions with open-metal sites, a recent approach to improve the materials' performance has been to use the active metal sites for chelation of diamines, leaving free amines in the pores, which are known to be highly effective for CO_2 adsorption.

Initial inspiration for tethering amines to MOFs was derived from the use of amines in mesoporous silicas for catalysis and metal encapsulation.[204] Hydroxyl groups on the surface of mesoporous silicas require the use of alkoxysilane groups for tethering, while MOFs can have coordinately unsaturated metal sites for chelation. This initial study examined MIL-101(Cr), which has two types of mesoporous cages and a very large BET surface area of 4 100 m^2/g. Additionally, MIL-101(Cr) has a large number of potential open-metal sites (up to 3.0 mmol/g). After synthesis and purification of the MOF, upon CO adsorption, IR analysis revealed 1.0 mmol/g of open chromium sites, and it was therefore likely that residual ligand was present. Initial grafting of amines was performed using ethylenediamine, and follow-up CO studies revealed that all open-metal sites were utilized after amine tethering and therefore full grafting was obtained. IR spectra of the amine-grafted MOF revealed signature N−H stretches, and the BET surface area was reduced from 4 100 to 3 555 m^2/g. Importantly, the amines were confirmed to be thermally stable after degassing the MOF under a range of increasing temperatures up to 473 K. While the initial study on amine grafting in MOFs was evaluated using the Knoevenagel condensation reaction and metal-encapsulation studies, this set the path forward for utilization of amine-tethered MOFs in CO_2 capture.

The first report of modifying Mg-MOF-74 with amines was performed by Jones and co-workers and involved the use of ethylenediamine.[205] Functionalization of open-metal sites with amines provided a regenerative functional sorbent with improved stability under practical operating conditions. As multiple configurations of diamine-functionalized MOF-74 are possible, four different possibilities were examined using density functional theory (DFT) calculations and ranged from 1 to 18 ethylenediamine molecules per unit cell. Using TGA to analyze the weight gain after functionalization, refluxing MOF-74 in toluene/ethylenediamine solution led to ~3 ethylenediamine molecules per unit cell. The surface areas and pore volumes of the bare and amine-functionalized MOF-74 also confirmed the number of amines tethered within the MOF. The CO_2 adsorption capacity and regenerability of bare MOF-74 and amine-functionalized MOF-74 were evaluated by monitoring the CO_2 uptake over four cycles of adsorption−desorption using 400 ppm of CO_2 balanced with Ar on a TGA. The CO_2 adsorption results were compared with two benchmark materials, PEI-impregnated silica and diamine-grafted silica, as shown in Figure 20. PEI-impregnated silica was found to have the highest initial capacity, but degradation or leaching of the amine led to a decrease in CO_2 adsorption from 2.36 to 1.65 mmol/g after four cycles. The surface-grafted amine sorbent, however, exhibited robust stability but very low uptakes due to the low number of available amine sites. Bare MOF-74 adsorption capacities resembled PEI-impregnated silica in that the CO_2 adsorption capacity started at 1.35 mmol/g but dropped 20% after four cycles due to the material's limited

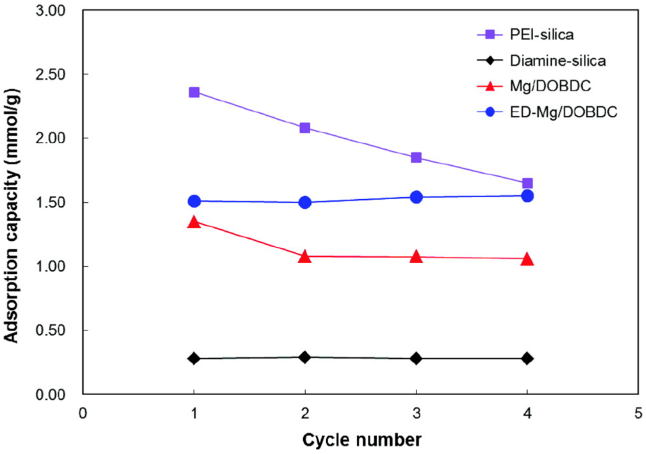


Figure 20. Changes in CO_2 capacity for amine-functionalized MOF-74 versus different hybrid sorbents as a function of adsorption cycle. Reprinted with permission from ref 205. Copyright 2012 American Chemical Society.

stability. Amine-functionalized MOF-74 exhibited an initial adsorption capacity of 1.51 mmol/g, exceeding that of the parent framework. Additionally, the adsorbent proved to be stable and fully regenerable under the employed moderate adsorption−desorption conditions. This initial study showcased how amines tethered to MOFs can not only help increase CO_2 adsorption capacities but can also help make more stable, practical materials.

While Mg-MOF-74 showed promising increases in CO_2 uptake as amines are tethered to the support, Long and co-workers, in parallel, developed a much more versatile MOF-74 derivative with a larger pore size.[206] As the channels in the original MOF-74 were relatively narrow, ∼11 Å in diameter, more amine molecules might be tethered within the pores if diffusion through the channels was more effective. To help aid amine diffusion, an expanded analogue of MOF-74, labeled M_2(dobpdc), was synthesized using a biphenyl variant of the original linker. Channels within the new framework were increased from ∼11 to ∼18 Å by increasing the linker size, and the BET surface area was found to increase accordingly from 1 490 to 3 270 m^2/g for the Mg versions of both frameworks. The alkylamine-functionalized Mg_2(dobpdc) was obtained by activating the bare framework and suspended in hexanes with an excess of *N,N*′-dimethylethylenediamine (MMEN). Tethering of MMEN to the available Mg sites led to a decrease in BET surface area from 3 270 to 70 m^2/g and enhanced the stability of the parent material, with no observable degradation upon exposure to air. At 25 °C, the amine-functionalized material displayed an extremely high affinity for CO_2 at very low partial pressures. The material adsorbed 2.0 mmol/g of CO_2 at partial pressures of CO_2 equal to 390 ppm or atmospheric levels. Its CO_2 uptake at 1 bar even exceeded the amount of N_2 adsorbed at 77 K. While CO_2 uptakes revealed high uptake values, the 2.2 mmol/g of CO_2 adsorbed at 1 bar did not equal the theoretical 3.4 mmol/g calculated based on the amount of amine present. Therefore, while CO_2 uptakes increased compared to the original Mg-MOF-74, additional capacity improvements might still be achieved, in principle. Furthermore, TGA analysis was used to evaluate MMEN-Mg_2(dobpdc) as a regenerable adsorbent through the cycling of simulated air containing 390 ppm of CO_2. Despite the low concentration of CO_2, a percent mass change equivalent to ∼1.05 mmol of CO_2 was obtained after only 60 min. Upon regeneration of the sorbent under flowing N_2 at 150 °C for 30 min, 10 cycles were repeated with no loss of capacity.

While the CO_2 isotherms for MMEN-Mg_2(dobpdc) revealed high uptakes at low pressures, a step in the isotherms existed at low pressures that moves to higher pressures as the adsorption temperature increases. Using X-ray diffraction studies on the isostructural MMEN-Mn_2(dobpdc) framework due to its greater crystallinity, detailed structural information on how CO_2 binds was obtained.[207] The initial configuration of the tethered MMEN was as expected before exposure to CO_2 with one amine bound to the open Mn^{2+} sites and the other amine exposed on the surface of the framework. Upon exposure to CO_2, the CO_2 was found to insert into the Mn−N bond, resulting in a carbamate with one of the O atoms binding to Mn. The second O atom revealed a close interaction with the N of a neighboring amine, resulting in chains of ammonium carbamate. Therefore, a structural transition leading to ion pairing between bound carbamates and neighboring ammonium groups is responsible for the cooperative insertion of CO_2 and the sudden uptake of a large amount of CO_2 or step in the isotherm. The proposed adsorption mechanism is illustrated in Figure 21.

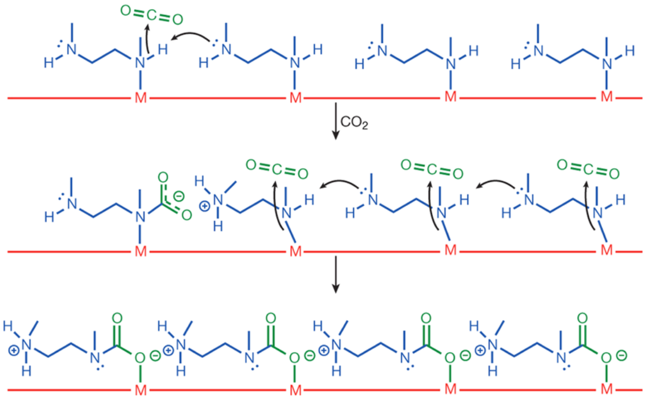


Figure 21. Mechanism for CO_2 insertion for MMEN-M_2(dobpdc) as ammonium carbamate is formed and initiates the cooperative adsorption of CO_2 by a chain reaction. Reprinted with permission from ref 207. Copyright 2015 Macmillan Publishers Ltd.

Because of this mechanism of CO_2 adsorption, the steps in the isotherm should therefore be manipulated by varying the amine−metal bond strength. To examine this manipulation of the isotherm, a series of isostructural compounds of MMEN-M_2(dobpdc) where M = Mg, Mn, Fe, Co, Ni, and Zn were synthesized.[207] CO_2 isotherms were subsequently measured at 25, 40, 50, and 75 °C for all sorbents and are reproduced in Figure 22. With the exception of the Ni compound, all showed steep steps in the isotherms that shifted at higher temperatures. Step positions occurred in the order Mg < Mn < Fe < Zn < Co, which is in agreement with the stability of the octahedral metal complexes. The Ni−N bond is exceptionally stable and prevents carbamate insertion, yielding a normal Langmuir-type adsorption. With such steep transitions in CO_2 isotherms, MMEN-Mn_2(dobpdc) and MMEN-Mg_2(dobpdc) were tested in a simulated temperature swing adsorption process due to their adsorption at lower partial pressures of CO_2. During the cooling phase, 15% CO_2 in N_2 was flowed over the samples while 100% CO_2 was used during the heating phases. Cycling data with MMEN-Mg_2(dobpdc) was obtained by adsorption at 70 °C and desorption at 120 °C, highlighting that, by using small changes in temperature, a large working capacity can be obtained. Again, exposure to water at 40 or 100 °C revealed no changes in the CO_2 isotherm, demonstrating the stability of the sorbents.

In a follow-up paper, Long and co-workers reported on the design and use of a high-throughput multicomponent adsorption instrument that allowed for the first reports of multicomponent $CO_2/H_2O/N_2$ adsorption on MOFs.[208] An array of MOFs, zeolites, mesoporous silicas, and activated carbons were evaluated for $CO_2/H_2O/N_2$ adsorption at conditions relevant to flue gas capture. A significant outcome from their study demonstrated that adsorption of CO_2 on mmen-Mg_2(dobpdc) in the presence of water increases the capacity from 3.7 to 4.2 ± 0.2 mmol/g at conditions of 40 °C, 113 mbar CO_2, 689 mbar N_2, and 19 mbar H_2O (in the case of water coadsorption). This can be seen along with the results of other materials tested in Figure 23. While data were not reported for ultradilute conditions corresponding to air capture, these findings provide further support that humidity will not

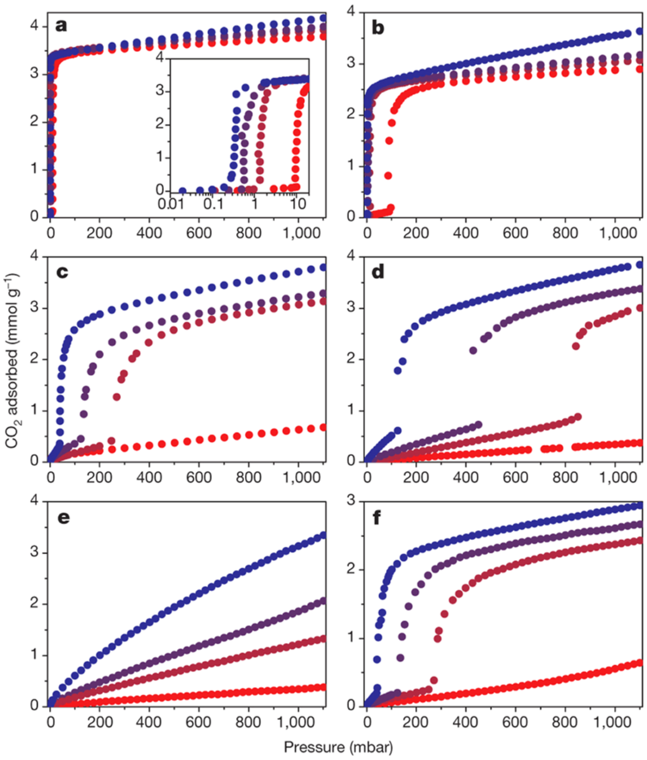


Figure 22. CO_2 sorption isotherms at 25 °C (blue), 40 °C (blue−violet), 50 °C (red−violet), and 75 °C (red) for MMEN-Mg_2(dobpdc) (a), MMEN-Mn_2(dobpdc) (b), MMEN-Fe_2(dobpdc) (c), MMEN-Co_2(dobpdc) (d), MMEN-Ni_2(dobpdc) (e), and MMEN-Zn_2(dobpdc) (f). Reprinted with permission from ref 207. Copyright 2015 Macmillan Publishers Ltd.

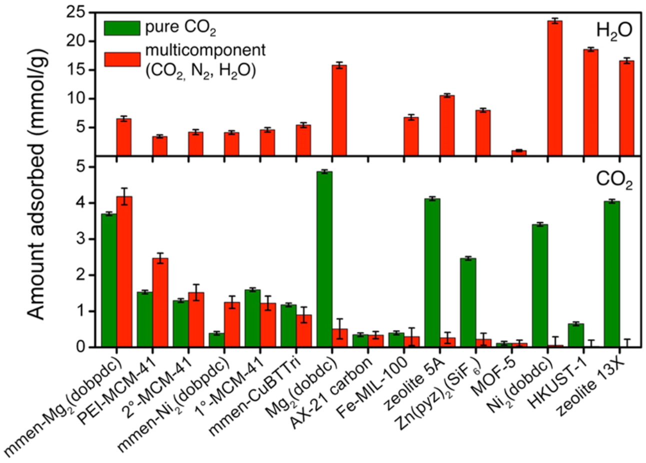


Figure 23. Multicomponent adsorption measurements for mixtures of CO_2, N_2, and H_2O at 40 °C. The green bars represent the amounts of CO_2 adsorbed in a single-component isotherm at the same CO_2 partial pressure as the multicomponent experiment. The red bars in the bottom (top) pane represent the amount of CO_2 (H_2O) adsorbed in the multicomponent experiment. All partial pressures of N_2 are between 679 and 698 mbar, of CO_2 are 112−178 mbar, and of H_2O are 10−29 mbar. Reprinted with permission from ref 208. Copyright 2015 American Chemical Society.

negatively impact the adsorption of CO_2 for these materials in DAC processes.

As the M_2(dobpdc) series of frameworks has shown high CO_2 uptakes at extremely low pressures using MMEN as the tethered amine, further studies have examined the use of additional amines such as ethylenediamine (EN) for CO_2 capture from air.[209] Formation of EN-Mg_2(dobpdc) led to a reduction in BET surface area from 3 270 to 1 253 m^2/g, a value much greater than that of 70 m^2/g with MMEN-Mg_2(dobpdc). The CO_2 capacity of EN-Mg_2(dobpdc) at 25 °C and 1 bar was 4.57 mmol/g with a capacity of 2.83 mmol/g at 0.39 mbar or atmospheric CO_2 levels, therefore surpassing MMEN-Mg_2(dobpdc). The CO_2 isotherms of EN-Mg_2(dobpdc) are much sharper than those of the MMEN version as well, and this is likely due to the easier accessibility of CO_2 with the presence of primary amines rather than secondary amines. To investigate the CO_2 capacity from the ambient air, TGA experiments monitoring mass change using temperature swing adsorption (TSA) were used. Treating EN-Mg_2(dobpdc) at 25 °C for 15 h allowed for saturation of the sorbent with 11.8 wt % CO_2, in accordance with the single-component CO_2 isotherms. Desorption was accomplished via heating at 150 °C for 2 h under the simulated air, and cycling experiments revealed only a 6% loss in capacity after the first five cycles. Stability under humid conditions for both the bare and EN-functionalized MOFs was tested by exposing to humidity, activating, and adsorbing CO_2. Water in the amine-functionalized MOF was again found to be more easily removed than the bare MOF with open-metal sites, allowing for more practical application.

MOFs have only recently begun to be tested for air capture applications, and the impregnation of MOFs with amines has led to exceptionally high CO_2 uptakes in some cases (see Table 5). The best MOF for CO_2 capture at low concentrations reported to date is EN-Mg_2(dobpdc) with a capacity of 2.83 mmol of CO_2/g of sorbent. While the fine-tuning of the pore size in the SIFSIX-M series of frameworks has led to an increase in CO_2 sorption, the limited amount of data available points toward impregnation of MOFs with amines as the most fruitful path for future studies. However, overall, very limited studies have been performed to date and more examples are needed to

Table 5. MOFs Used for Direct Air Capture; Amine-Tethered (If Applicable) And Experimental Conditions Are Noted As Well[a]

MOF	amine	T (°C)	CO_2 (ppm)	adsorption capacity (mmol of CO_2/g of sorbent)	method	ref
SIFSIX-3-Cu		25	400	1.24	vol.	191
SIFSIX-3-Zn		25	400	0.13	vol.	210
SIFSIX-3-Ni		23	400[b]	0.18	TPD	186
HKUST		23	400[b]	0.05	TPD	186
Mg-MOF-74		23	400[b]	0.14	TPD	186
Mg-MOF-74	EN	22[c]	400	1.51	TGA	205
Mg_2(dobpdc)		25	390	0.13[d]	vol.	206
Mg_2(dobpdc)	MMEN	25	390	2.0[d]	vol.	206
Mg_2(dobpdc)	EN	25	390	2.83[d]	vol.	209

[b] Approximate value. Samples exposed to lab atmosphere with an average T = 23.4 °C and 49% RH. [c] Approximate value. Room temperature denoted in manuscript. [d] Adsorption capacities interpolated from a pure CO_2 isotherm. [a] EN, ethylenediamine; MMEN, N,N′-dimethylethylenediamine; vol., volumetric; TPD, temperature-programmed desorption; TGA, thermogravimetric analysis.

identify robust structure−property trends using MOFs for DAC.

6. ALTERNATIVE APPROACHES FOR DAC

Apart from the sorbents described above, there are a number of alternative approaches to achieve DAC already proposed in the literature but not yet widely studied for this purpose. Examples include electrochemical approaches and mineral carbonation, as well as use of membranes and photocatalytic CO_2 conversion.

A few electrochemical approaches have been reported to aid in the direct CO_2 capture from air.[47] For example, electrochemical methods have been proposed as the driving force for the regeneration of depleted amine-containing solid sorbents[211] or caustic[31,212] and carbonate solutions.[213] In another example, CO_2 previously absorbed in KOH has also been transformed into useful chemicals such as using hydrogen generated electrocatalytically to make methanol.[50]

The reduction of CO_2 directly from the atmosphere electrochemically can be used to scavenge CO_2 from the air. Such a process starts from the electrochemical OH^-/H^+ generation,[214] with protons being produced in an anodic reaction using water (reaction 23), while hydroxyl groups are produced in its paired cathodic reaction (reaction 24). If air is supplied to the cathode, i.e., O_2 is present, hydroxyl groups are formed via the more favorable reaction 25. Subsequently, CO_2 from the air can react with hydroxyl groups, thus being captured in the aqueous solution.

$$2H_2O \xrightarrow{\text{electricity}} O_{2(g)} + 4e + 4H^+ \quad (23)$$

$$4H_2O + 2e \xrightarrow{\text{electricity}} 2H_{2(g)} + OH^- \quad (24)$$

$$O_2 + 4e + 2H_2O \xrightarrow{\text{electricity}} 4OH^- \quad (25)$$

Using ambient air as the feed gas with a current density of 2.0 mA/cm^2, Wang et al. successfully captured 0.158 mmol of CO_2 with an energy consumption of 383 kJ/mol.[215] This is an interesting result, because it achieves direct CO_2 capture with an energy consumption lower than 400 kJ/mol, considered a target to be achieved by these technologies.[216] Nevertheless, this technology is far from optimized and needs more development.

The abundance of silicate materials rich in metal oxides (mainly CaO, MgO, and FeO) and the ability of the latter to react with CO_2, yielding stable bicarbonates, has drawn attention to a process known as mineralization or mineral carbonation as a means of CO_2 sequestration.[9,217,218] When applied to reduce the CO_2 concentration in the atmosphere, mineralization should be treated as a carbon-storage technology, because it consists of irreversible chemical reactions aiming to fix CO_2 molecules permanently. Mineralization is thermodynamically favored, so it occurs spontaneously in nature, being called silicate-weathering. However, the natural process takes place on a geological time scale,[219] and therefore several methods have been proposed to accelerate it, with most of them being based on the use of previously enriched CO_2 streams.[9,218,220] Significant rate enhancements are expected to require substantial CO_2 enrichment from ambient conditions, making this approach less compelling for DAC.

Membrane technology has been successfully applied at laboratory scale to capture CO_2 from flue gas (ca. 12−15% CO_2),[221−223] as well as from lower CO_2 concentrations such as those found in enclosed spaces (0.52−0.60% CO_2).[224−226] However, there are few reports using this technology to remove CO_2 from air (0.04% CO_2). The use of up to 6% PEI impregnated membranes yielded a high CO_2/N_2 selectivity of 300 in one study.[227] When increasing the pressure up to 3 bar, >40% of the CO_2 fed was recovered, yielding a downstream with up to 0.80% CO_2. Compression of ultradilute gases is likely to be prohibitively energy-intensive, and this level of enrichment is quite modest, with sorption-based approaches offering much better performance to date.

Photocatalysis can serve as means of artificial photosynthesis, with photocatalytic reduction of CO_2 captured from ambient air coupled with photochemically produced hydrogen from water splitting yielding a sustainable way of closing the carbon cycle. While today this is not economically viable, the photocatalytic reduction of CO_2 is well-studied, with de Richter et al. recently publishing a comprehensive review on this topic.[228] Among other things, this review highlights that key parameters such as the irradiation wavelength, the specific rate of CO_2 reduction, and the quantum yield of the photoreactions, as well as other variables, still need to be determined and/or optimized.

Finally, there are other approaches to climate change mitigation that involve removal of CO_2 from the atmosphere but are formally outside the scope of this Review, which focuses on use of reversible sorbents for CO_2 capture. Some examples include the massive addition of limestone ($CaCO_3$)[229,230] or olivine (Mg_2SiO_4)[231−233] in rivers and oceans, capturing CO_2 from the atmosphere and at the same time reducing water alkalinity. The dissolution of silicate minerals has also been proposed coupled to electrolytic processes to enhance CO_2 air capture.[51,234] Finally, the use of autotrophic organisms has also been proposed as a way to capture CO_2 from air. Many approaches have been proposed, from planting 1 million trees in the Sahara and Australian deserts[235] to the use of other plants, algae, or bacteria to harvest sunlight and convert CO_2 into biomass.[236,237] Growth of biomass or reforestation on a massive scale has been discussed as a stand-alone approach,[235] as well as in combination with production and storage of biochar.[238] In general, these methodologies fall out of the scope of this Review and are not considered in detail here. Undoubtedly, the most effective way to reduce the atmospheric CO_2 concentration is via multiple parallel efforts to reduce CO_2 atmospheric concentration, including both chemical and biological approaches.

7. FEASIBILITY, ECONOMICS, AND DESIGN CONSIDERATIONS FOR DIRECT AIR CAPTURE PROCESSES

7.1. Thermodynamic Analysis of Feasibility

As stated previously, much of the initial literature on DAC centered on proposing various processes for air capture and analyzing their feasibility using thermodynamic-based arguments.[26,28,29,31,32,34,36,37] One metric that has been used to demonstrate the feasibility of DAC is to examine the thermodynamic efficiency of the air capture process. Comparing the second law thermodynamic efficiency—the ratio of the minimum thermodynamic energy required to the actual amount used in the process—is a way to evaluate how well DAC processes can work, as well as to see how they compare to traditional flue gas capture technologies. Using the free energy of mixing, it has been calculated that the theoretical minimum work required to separate CO_2 from a 400 ppm stream is ~20 kJ/mol of CO_2.[28,31,216,239] In contrast, the theoretical minimum work for the benchmark aqueous MEA-based flue gas capture process is 8.4 kJ/mol CO_2.[31] Due to the logarithmic nature of the dependency of the minimum work on partial pressure of CO_2, it can be seen that despite a 250-fold reduction in concentration, the minimum energy requirement does not scale accordingly. Real-world separation processes typically possess second law efficiencies in the range of 5−40%, and analyses of varying DAC technologies reported have determined that efficiencies in this range can be achieved (from 2 to 50% according to analyses by House et al.[216]).

Subsequently, Lackner published a thermodynamic analysis considering the minimum free energy change of a sorption reaction to take into account the irreversibility of a practical sorbent-based process.[240] This generated a more realistic minimum energy estimation of roughly 30 kJ/mol of CO_2. Despite the larger energy demand, it was estimated that the theoretical attainable efficiency for DAC can be over 90%, as opposed to roughly 45% for flue gas capture. This is explained by the fact that air capture processes are meant to skim CO_2 from the air, where a successful separation would reduce the outlet concentration of CO_2 by a factor of 2 (CO_2 extraction), while flue gas capture has much more stringent scrubbing requirements that result in roughly 15-fold reductions in concentration (flue gas purification). Lackner thus concluded that the potential for greater efficiencies with DAC closes the gap in energy requirements between the two processes and suggests that arguments of DAC being unfeasible due to large energy demands compared to flue gas capture may not be accurate. However, while these efficiencies are theoretically attainable, it is still very unlikely that a large-scale industrial process employing DAC technology would operate at such a high level of efficiency. Regardless, there is merit to Lackner's point of DAC being a skimming process versus the stricter requirements of flue gas scrubbing that should motivate additional researchers to explore the energy intensity of DAC processes. In this context, it should be noted that early on, comparisons were typically made to flue gas capture processes due to the relative maturity of such technologies, along with an implied competition between DAC and traditional carbon-capture approaches. Today, it is recognized that these approaches are not alternatives to each other, and in fact, both approaches are needed. However, for reduction of the atmospheric CO_2 concentration, for "negative carbon", only DAC technologies can provide an answer and conventional CO_2 capture is not relevant.

In 2014 Ruthven presented a study comparing the traditionally considered thermodynamic minimum work of separation to the "separative work" that was derived from ideal cascade theory.[241] He concluded that separative work derived from the "value function" provides a better estimate for separation costs and that the thermodynamic minimum work of separation does not reflect the actual work of separation for dilute feeds relevant to DAC. The value function used was derived from Ideal Cascade theory, which is rooted in the concept of a hypothetical idealized separation process from which all pressure drops, back-mixing, and other thermodynamic irreversibilities have been eliminated. This leads to a sequence of ideal separation stages with no back-mixing and equilibrium separation between the phases in each stage. The separative work derived from the equations expressing this system are assumed to provide a lower limit estimate of the actual work of separation for a real system. Therefore, this is not an absolute thermodynamic minimum but rather an estimate of what might possibly be obtained in an optimized separation process. From Figure 24, it can be seen that, at the extremes of very high and very low CO_2 concentrations, the separative work is substantially greater than the thermodynamic minimum. As CO_2 capture from flue gas represents a realm where the separative work and thermodynamic minimum are comparable, Ruthven argues that, based on these findings, DAC can be as much as 100 times more energy-intensive than CO_2 capture from a coal-fired power plant. However, a key assumption in this analysis is that the DAC process will be utilizing a physisorbent and will rely on a multistage process to achieve an efficient and cost-effective separation. Because cascade theory does not accurately predict separations in a single stage and because chemisorbents are chiefly used for DAC, as described in the earlier sections, this analysis does not hold for DAC processes with strongly adsorbing materials that would not use this iterative separation process.

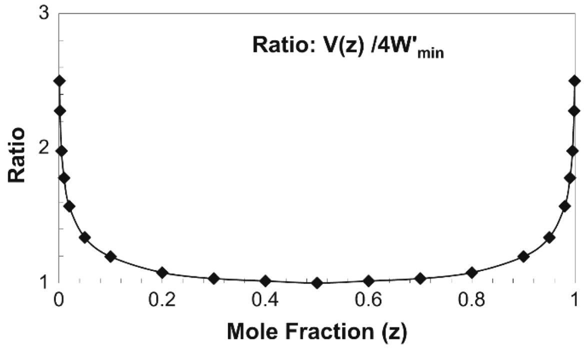


Figure 24. Plot demonstrating how the ratio of the modified separative work value function $(V'(z)/4)$ to the thermodynamic minimum work of separation $(W'_{\min})$ varies with CO_2 concentration (mole fraction (z)). Deviations from 1 indicate disagreements between the two methods. Reprinted with permission from ref 241. Copyright 2014 Elsevier.

More recently, Lively and Realff published a thermodynamic analysis of adsorption processes for a nonspecific sorbent in TSA and PSA modes as a function of adsorbate concentration and the adsorbent−adsorbate interaction strength.[242] The goal of this study was to both demonstrate the differences in thermodynamics of two different adsorption cycles and to examine the differences that new highly selective materials could make on a DAC process. It was found that the separation efficiency of a TSA process is optimized at dilute CO_2 concentrations and can become more thermodynamically efficient as the adsorbate affinity, or heat of adsorption, increases. This may initially seem counterintuitive, as higher heats of adsorption equate to a greater energy demand for desorption. However, this finding is rationalized by the fact that the adsorption step for a strongly adsorbing material is spontaneous, and so the energy required to desorb CO_2 is nearly independent of the adsorbate concentration, as the material can be considered nearly saturated regardless of feed concentration. Alternatively, one can think of this in the sense that, in a TSA system, the work, desorption, is being done on a concentrated product rather than on a dilute feed. The authors do note that this highly adsorbing material would have an upper bound on its adsorbate affinity, whereby some threshold would yield a desorption step that would be prohibitively energy-intensive. Figure 25 illustrates the results of these studies where four materials were evaluated with adsorption strengths ranging from physisorbing (ΔH_{ads} = −35 kJ/mol) up to chemisorbing (ΔH_{ads} = −65 kJ/mol). It can be seen that, for the material with the strongest adsorbate affinity, an optimal separation efficiency is obtained at concentrations on the order of CO_2 in ambient air, thus validating that chemisorbents are preferred for DAC. It is noteworthy that the adsorbate interaction strengths represented in this study are on par with oxide and MOF-supported amine materials, thus suggesting these classes of materials are suitable candidates for DAC applications.

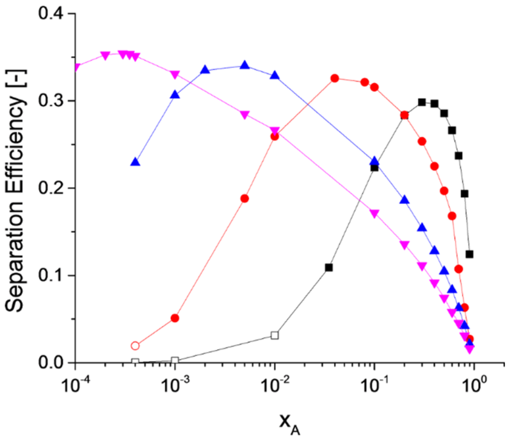


Figure 25. Optimal second law efficiency for a TSA process with varying adsorbate affinities as a function of adsorbate mole fraction in the gas feed. Magenta (▼): ΔH_{ads} = −65 kJ/mol; blue (▲): ΔH_{ads} = −55 kJ/mol; red (●): ΔH_{ads} = −45 kJ/mol; black (■): ΔH_{ads} = −35 kJ/mol. Closed points indicate processes capable of achieving x_A, product > 0.95, while open points indicate TSA processes not capable of achieving 95 mol % of A in the product stream. Reprinted with permission from ref 242. Copyright 2016 Wiley.

7.2. Design Considerations and Cost Estimates of DAC

Ultimately, the cost of DAC will determine the feasibility of its adoption and implementation in society. Generally, the cost of DAC has been compared to that of flue gas capture, both from a benchmarking perspective and the false notion that society should apply only one of these carbon capture technologies initially. Both of these technologies incur costs from the following: (i) capital investment, (ii) cost of capture (energy for operating the process), (iii) cost of CO_2 release and regeneration of the sorbent, and (iv) sorbent losses and maintenance of equipment. Depending on the intended fate of the captured CO_2, the following costs may also be considered: (v) CO_2 compression, (vi) transportation of pressurized CO_2, (vii) geological sequestration, and (viii) leakage monitoring and addressing unintended environmental impacts. The estimated cost for flue gas capture is on the order of \$30−100/t of CO_2, while estimates for DAC costs are more highly debated, with reports ranging from \$30−1000/t of CO_2. With this much uncertainty, it is important to understand the underlying specifications and assumptions that go into each cost estimate. Here we present an overview of these studies as well as discussion of different design prototypes for DAC. A chronological summary of cost estimates for DAC processes is presented in Table 6.

7.2.1. Aqueous Alkaline Systems. Upon the inception of the study of DAC for climate change mitigation, the initial "strawman" technology focused on using alkaline materials for CO_2 capture. As such, when the American Physical Society put forth their initial technology assessment of DAC in 2011, they used the aqueous NaOH system as their benchmark for estimating the cost and feasibility of the technology for a one million tons of CO_2 per year air capture facility.[59] The process is shown in Figure 3 and consisted of a two-loop hydroxide−carbonate system that operated with closed, countercurrent flow. This hydroxide solution flowed over and wetted a stainless steel packing, creating a fluid film where reaction of CO_2 occurs. It was estimated that the net cost of air capture using this process would be on the order of \$600/t of CO_2. It should be noted that, compared to many of the costs estimated in Table 6, this was a rather technically rigorous estimate, whereas many costs listed in Table 6 are derived from less-detailed assessments. In this regard, one key need in the development of

Table 6. Cost Estimates for DAC; Total Cost unless Otherwise Noted

year−ref	steps in proposed process	cost (\$/t of CO_2)
2003−Zeman[243]	aqueous NaOH solution, causticization with lime, calcination	25−75
2006−Keith et al.[28]	aqueous NaOH solution, causticization with lime, calcination	136
2006−Nikulshina et al.[29]	aerosol-type carbonator using aqueous $Ca(OH)_2$, solar calciner, conventional slaker	162−200 (solar calciner only)
2008−Stolaroff et al.[32]	aqueous NaOH spray tower prototype, proposed parameters for optimization	96 for base case, 53−127 based on optimization (total cost of capture only, excludes regeneration)
2009−Lackner[37]	anionic exchange resin, regenerate with humidity swing	200, estimated to drop to ∼30 in the long term
2011−APS[59]	aqueous NaOH solution, causticization with lime, calcination	610
2011−House et al.[216]	unspecified process, calculation based on minimum work of separation	1000
2011−Simon et al.[244]	unspecified process, generic air capture process characterized by energy and water use and capture footprint	293−863
2012−Kulkarni and Sholl[239]	amine-functionalized monolith contactor with temperature swing adsorption, regenerate with low-pressure steam	95 (excludes capital cost)
2012−Holmes and Keith[245]	aqueous NaOH solution, causticization with lime, calcination	60 (total cost of capture only, excludes regeneration)
2013−Mazzotti et al.[246]	aqueous NaOH solution, causticization with lime, calcination-optimized APS benchmark system plus system with two alternate packings	518−568
2014−Zeman[247]	aqueous NaOH solution, causticization with lime, calcination-optimized APS benchmark system	309

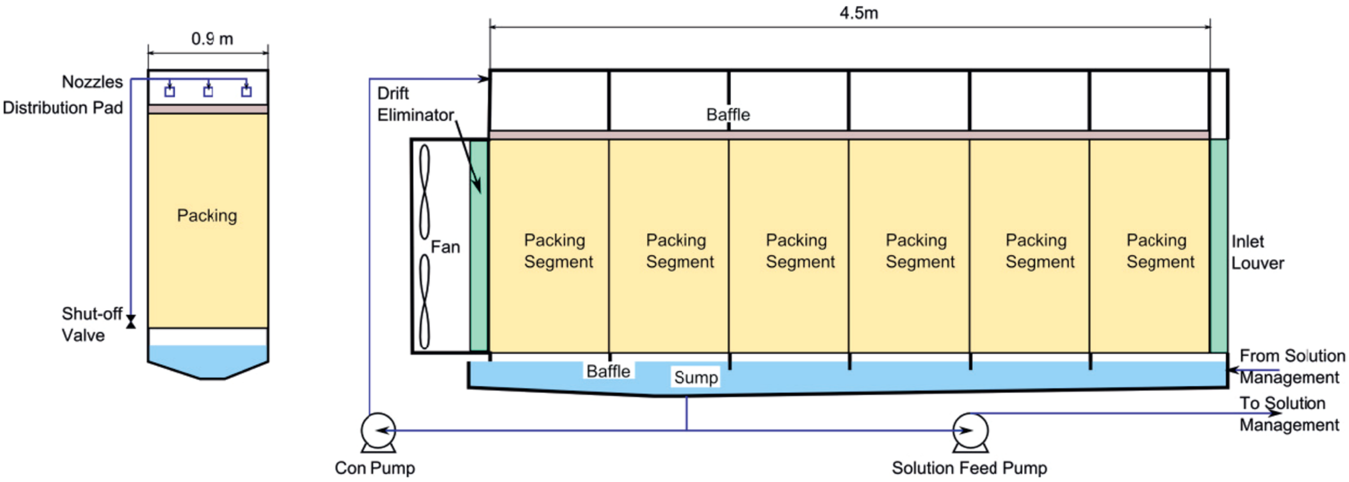


Figure 26. Carbon Engineering's air contactor design with cross-flow and slab geometry. Reprinted with permission from ref 248. Copyright 2013 Elsevier.

DAC processes is an array of more rigorous technoeconomic analyses of different DAC processes.

Subsequent to this report, several studies were published with new cost estimates based on optimizing parameters of the aqueous hydroxide process. Mazzotti et al. published a study that focused on optimizing the design of the front-end section of the system.[246] New correlations relating mass transfer and pressure drop to the air and liquid flow velocities were developed and implemented to optimize performance based on the air and aqueous NaOH velocity and fraction of CO_2 captured. Three different packings were evaluated—two previously considered in the APS's case study along with one new packing that has been optimized for postcombustion CO_2 capture. Optimization of this system yielded a reduction in costs by 10−20%, where the best system achieved a cost of \$518/t of CO_2 using the new CO_2 capture-specific packing. It was concluded that, despite the potential reductions in cost afforded by system optimization, costs were still too high to be a competitive mitigation strategy in comparison to flue gas capture.

In response to the APS report, Holmes and Keith, who are associated with the independent air capture company Carbon Engineering (CE), presented their system design for an aqueous hydroxide air−liquid contactor with vastly improved economics.[245] On the basis of CE's engineering studies, they reported a total cost for the air contactor alone at \$60/t of CO_2, a 4-fold reduction from the APS report's estimate of the contactor costing \$240/t of CO_2. Holmes and Keith suggest the deviation arises not from a difference in costing methodology, which in fact was the same, but from differences in fundamental design choices. While the system described in the APS report consisted of a closed, counter-flow scrubber column, CE chose a contactor based on a cooling tower design that consisted of an open contactor with cross-flow and a slab geometry. This means that air passed through a downward-flowing aqueous hydroxide solution in an orthogonal direction and that the overall contactor was thin along the direction of air flow compared to the overall height and length of the unit. A schematic representation is illustrated in Figure 26. In fact, the APS report suggested that a design like the one used by CE would be significantly cheaper but ruled it out due to technical risks associated with an open system such as solution losses from misting (also called drift) or reaction with atmospheric particulates, as well as uncertainty in the ability of a cross-flow system providing good contact between the air and sorbent.[59] In a follow-up report from Holmes et al., results from an outdoor prototype with >1 000 h of operation were presented.[248] The main achievement from this was the validation of their cross-flow contactor design. An intermittent liquid flow technique that was developed and is under patent review[249] was also demonstrated to effectively reduce the required liquid pumping requirement to 10% of the full manufacturer's specifications, thus allowing for a reduction in the fluid pumping requirement. Additionally, over the entire course of operation, no degradation to the system was measured and extensive sampling of the air was carried out to measure loss of liquid via drift droplets. During normal operation, OH concentrations were found to be <5% of OSHA regulated indoor respiratory requirement. One key outcome that identified needed improvements was related to the observation of absorption underperformance compared to engineering analysis for "high-performance solutions" (optimized solution concentrations). It was hypothesized that this was due to a liquid distribution artifact introduced by their specific prototype design, which identified a good target for further optimization. The result of this artifact, should it not be addressed, would be a larger energy requirement for fan operation that would then increase the cost of the contactor. While CE has demonstrated an air contactor system that performs capture at costs lower than those estimated in the APS report, they have yet to disclose or demonstrate their regeneration process and the associated costs from it. This demonstration will be valuable, as some critics of aqueous hydroxide processes note that regeneration is likely to be the most energy- and cost-intensive step in the process.

In 2014 Zeman published a follow-up study to the APS report and Mazzotti et al.'s subsequent optimization,[247] which further reduced the cost estimates from the APS's initial value of \$610/t of CO_2 to \$309/t of CO_2. In successive iterations, the following scenarios were considered and evaluated for cost of capture: (i) electricity from coal with CCS, (ii) electricity from an NGCC facility, (ii) NGCC with CCS, (iii) efficient heat integration, (iv) low-cost natural gas, (v) onsite NGCC with use of waste heat for drying, and (vi) switching from stainless steel to a plastic packing material. All of these scenarios reduced the cost of DAC, with the use of NGCC with CCS and

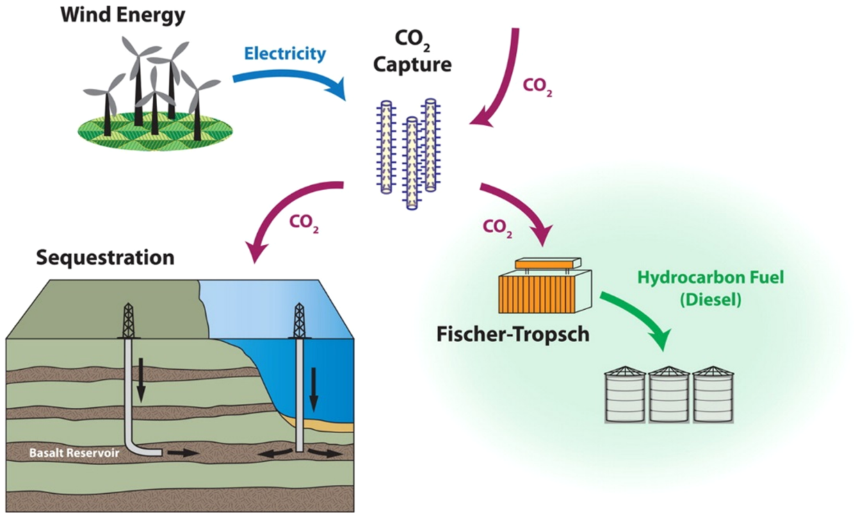


Figure 27. Schematic of potential air capture operation proposed using Lackner's anionic-exchange resin where capture, sequestration, and potential synfuel production are colocated at a remote location. Reprinted with permission from ref 253. Copyright 2013 American Chemical Society.

switching to plastic packing being the biggest drivers for cost reduction, coming in at estimates of \$437 and \$413/t of CO_2, respectively. Therefore, the ultimate optimization of an onsite NGCC facility with CCS combined with heat integration and the use of plastic packing material yielded an avoided cost of \$309/t of CO_2. Noteworthy in this analysis are the following considerations: all of Zeman's optimizations were based on the APS and Mazzotti's design principle of a counter-flow contactor, and the plastic packing material considered by Zeman (Brentwood Industries CF1900) is still more expensive than the packing used by Carbon Engineering (Brentwood Industries XF12560), with costs of \$350/m^3 and \$256/m^3, respectively.

In light of this discussion, some of the key components affecting cost estimates for DAC in the context of Zeman's study can be considered, as the suggested cost breakdowns for the net cost of capture for aqueous hydroxide systems have demonstrated that the major expenses result from capital costs, with the biggest contributor being the packing material.[247] Additionally, fugitive emissions and the cost of electricity are also key components to the pricing of this technology. In the APS report,[59] Mazzotti et al's follow up,[246] and Holmes and Keith's air-contactor cost discussion,[245] it was assumed that electricity would be purchased from the grid at costs of \$71–80/MWh.[250] Additionally, House et al.'s cost analysis of DAC, while modeled on an unspecified nonspontaneous separation process, also considered traditional coal-derived electricity when suggesting the DAC cost would be on the order of \$1000/t of CO_2.[216] Therefore, the main takeaway from the discussion of the APS report followed by subsequent follow-up studies is that there is clearly room for improvement and cost reduction for DAC, but it is also important to understand all of the underlying assumptions of the process and how optimistic its assertions are for supplying electricity and avoiding fugitive emissions.

7.2.1.1. Aqueous Alkaline Systems with Axial Compression. The impact of increasing inlet CO_2 concentration during operation of an unoptimized aqueous hydroxide system[27,59] has been investigated through the proposed implementation of axial compression. In two publications, Chan et al. used process modeling to assess the feasibility of adding axial compression to a DAC system for enhanced CO_2 recovery. The authors examined the trade-offs between additional energy penalties due to compression versus offset energy consumption due to increased capture capacity.[251,252] An analysis examining the energy requirements and CO_2 throughput for a reference DAC system (aqueous process only) and that same system coupled with axial compression to the inlet air stream suggest that axial compression both reduces the energy required to capture CO_2 and increases the annual throughput of CO_2. Analysis demonstrated that the benchmark system recovered 88 Mt of CO_2/year while the addition of axial compression increased recovery to 1.8×10^6 Mt of CO_2/year. At the same time, the total energy required decreased from 1.24 GJ/t of CO_2 for the benchmark system to 0.96 GJ/t of CO_2.[252] The authors acknowledge that, while these metrics are great improvements, they still do not compare with conventional postcombustion capture, as well as that further studies should explore coupling axial compression to existing industrial technologies.

7.2.2. Solid Sorbent Systems. While Lackner's initial propositions for DAC were based on an aqueous hydroxide system as a "strawman",[25] he subsequently deemed them perhaps too energy-intensive in the regeneration step and thus transitioned to a sorbent-based approach in designing an air capture system.[37] The process outlined by Lackner in 2009 was based on the premise of constructing portable capture units that could be transported in a standard shipping container. The sorbent material of choice was an anionic-exchange resin that adsorbs CO_2 in a dry state and releases it using a moisture swing, as depicted in Figure 17. The modular design would consist of multiple chambers in sets of 6 that would rotate between one chamber interacting with the environment to adsorb CO_2 and the remaining 5 chambers going through different stages of regeneration. Wind energy is considered as a source for electricity, and as such, it is estimated that initial costs for a prototype would be on the order of \$200/t of CO_2, with the majority of the cost resulting from regeneration of the sorbent. Over time, it was suggested that improvements to the process could be implemented that would bring the cost down to \$30/t of CO_2. One such improvement is an increase in surface area per unit of resin by a factor of 10 that could decrease the amount needed by an equivalent factor or more, depending on additional improvements in CO_2 uptake rate due to a reduction in fiber thickness. It should be noted that these cost estimates were done at a much less rigorous level than those described above and that there is more uncertainty in the numbers presented by Lackner than for those around the processes related to the APS and subsequent follow-up studies.

More recently, Lackner and others have started to explore the potential of implementing their resin-moisture swing technology coupled with synfuel production and sequestration in remote locations.[253,254] This concept is illustrated in Figure 27, where a remote offshore location with substantial winds can generate sufficient energy to collect ~75 Mt of CO_2 per year for sequestration below the seafloor or generation of synfuel through Fischer−Tropsch processes. In their first analysis of this concept, the Kerguelen Plateau in the southern Indian Ocean was proposed as a viable location due to steady and constant winds (8−14 m/s) as well as temperatures and humidities (0−10 °C, 80−90% RH, respectively) throughout the year.[253] An additional factor in the choice of location is the prevalence of Large Igneous Provinces (LIPs)—massive extrusions or intrusions of igneous rock that are believed to be most effective for sequestration. Due to the less-than-optimal climate of this location, an initial analysis via bench-scale laboratory experiments verified that sufficient CO_2 could be captured and released in this type of climate, as well as that the air collectors could be sufficiently dried through the naturally occurring high wind speeds. It is noted that the cost of establishing and operating colocated infrastructure would be considerable. Initial estimates are on the order of \$9−10B for installed capital including wind turbine farms, transmission lines, power stations, and substations, and an additional \$10B for drilling, pipeline, and storage infrastructure. Operating costs of the system are also important when considering the viability of the system. The authors suggest that *if* a net cost of \$50/t of CO_2 could be achieved, processing 75 Mt of CO_2 per year would cost \$3.5B. However, if the energy harvested from the plateau were solely dedicated to fuel production, it is estimated that 47 TWh of wind energy could be converted to 770 M gallons of diesel, with a commercial value of \$3B. It was acknowledged by the authors that substantial estimates for operating costs are difficult to establish.

An alternate solid sorbent system extensively discussed in section 5 is based on amines supported on porous oxide supports. While these systems are the most widely studied experimentally, on the laboratory scale, the cost estimates regarding their use have not been widely disclosed. In 2012 Kulkarni and Sholl developed and analyzed process models to assess the viability of DAC technologies using aminosilica sorbents on structured cordierite monolithic contactors.[239] Similar to Lackner's design, a contactor unit was considered with dimensions such that it could fit in a standard shipping container for ease of transportation. Two processes were considered: the first was TSA based solely on diurnal temperature swings, for which multiple locations in the U.S. were considered and accounted for by analyzing weather data from the National Climatic Data Center (NCDC). In this approach, no external heat was added to the process for sorbent regeneration. The second process was TSA that used low-quality steam to supply the heat for desorption and also to act as a purge gas. Ultimately it was found that a steam-assisted desorption process greatly outperformed solely diurnal operation, with CO_2 recoveries on the order of 2−4 kg/unit/year for diurnal processes vs recoveries of 1−3 t/unit/year for a steam-based process. In estimating operating costs for a TSA process using steam for desorption, multiple scenarios were considered with regard to the source and purpose of the steam: (i) dedicated steam generated specifically for the DAC process, (ii) purchased steam, and (iii) waste steam were considered for electricity sources ranging from conventional coal all the way to wind, hydro, and solar thermal. Figure 28 demonstrates the cost of DAC based on different assumptions of electricity source and working capacity of the sorbent. On the basis of experimental data for a sorbent material with a working capacity of 1 mmol of CO_2/g, which is a large but not unreasonable swing capacity for DAC sorbent based on supported amines, it was determined that it would cost \$95/t of CO_2 using natural gas derived electricity and dedicated steam. It should be noted that this cost estimate does not include capital costs, and so the total cost of capture for a process with these specifications would be higher. Considering the breakdown of energy requirements, it was found that the total energy required is dominated by sensible heating of the monolith and adsorbent (roughly 70% of energy demand). Therefore, reduction in the thermal mass of the monolith contactor as well as increasing working capacity were identified as key areas that could further reduce the cost of DAC with amine monolith systems.

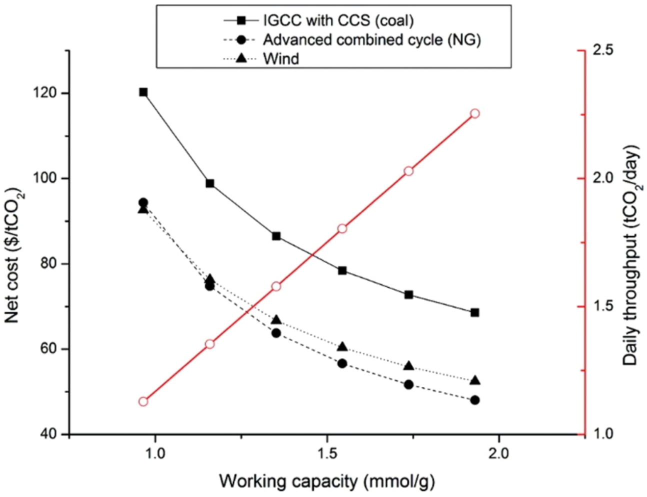


Figure 28. Cost of DAC (black, solid) and daily throughput of CO_2 (red, open) for aminosilica adsorbents supported on a monolithic contactor as a function of increasing working capacity. Reprinted with permission from ref 239. Copyright 2012 American Chemical Society.

Today there are multiple companies pushing process research and development in this field. As discussed in section 5, Global Thermostat is developing technology based on porous amine sorbents supported on a monolithic contactor.[89,93,104,106] Climeworks is a spinoff from the work performed at ETH Zurich by Steinfeld and co-workers. This company has initially focused on developing portable units utilizing their amine-based nanocellulose materials and has partnerships with Audi and Sunfire.[182,183,255−258] Infinitree uses the humidity swing process proposed by Lackner[176−178,259] and is further developing technology developed by Kilimanjaro Energy and Global Research Technologies for purposes of greenhouse enrichment. Unlike Carbon Engineering, very little technical data describing their processes is available in the open literature, and process systems analyses of their respective approaches would be helpful in pushing the field of DAC forward.

8. CONCLUSIONS

Environmentalists and climate specialists today recognize the need for technologies that remove CO_2 from the atmosphere to mitigate changes to the global climate caused by over a century of expanding anthropogenic CO_2 emissions. The concept of DAC using sorbents was introduced by Lackner in 1999, and in the ensuing decade and a half, a wide array of approaches employing different sorption materials have been described. In particular, the last five years have seen a rapid expansion of reports using various chemisorbents for CO_2 capture from ultradilute gas streams such as ambient air. Liquid and solid sorbents based on alkali and alkaline earth metal oxides and hydroxides, sorbents based on supported amines, and tailored MOFs have been studied. Opportunities exist for new materials that can capture CO_2 from ultradilute gas streams and operate under all humidity levels to play a role in emerging DAC technologies. In parallel, fundamental knowledge about sorbent structure−property relationships that will provide the fundamental basis for rational design of air capture sorbents needs to be developed further. However, these sorbents should not be developed in isolation from practical processes, as the ultradilute nature of the gas stream will require highly efficient gas/sorbent contacting strategies for any such process to be economically feasible. There is a need for additional, thorough, technoeconomic analyses of DAC processes as well. Overall, the field of DAC using sorbents is truly in its infancy, and there remains much room for improvement of sorbents and processes, which should be developed quickly if rapid deployment to slow global climate change is to be implemented.

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Notes

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ACKNOWLEDGMENTS

The authors thank the array of researchers who have contributed to the accumulated knowledge on CO_2 capture using sorbents in our group at Georgia Tech, including Jason Hicks, Jeff Drese, Eric Ping, Genggeng Qi, Hyung-Ju Kim, Praveen Bollini, Miles Sakwa-Novak, Ratayakorn Khunsupat, Sunho Choi, Wen Li, Yasutaka Kuwahara, Watcharop Chaikittisilp, Nick Brunelli, Yanfang Fan, Fateme Rezaei, Sumit Bali, Adam Holewinski, Matthew Potter, Simon Pang, Eric Moschetta, Lalit Darunte, Jason Lee, Chunjae Yoo, Hyuk-Taek Kwon, and Bo Hu. McMahan Gray and Daniel Fauth at NETL are acknowledged for collaborating in our first work on postcombustion CO_2 capture using amine sorbents. This work was supported by UNCAGE-ME, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award no. DE-SC0012577.

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