

Research needs targeting direct air capture of carbon dioxide: Material & process performance characteristics under realistic environmental conditions

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(Received 2 September 2021 • Revised 4 October 2021 • Accepted 6 October 2021)

Abstract—The extraction of CO₂ from ambient air, or direct air capture (DAC), is a crucial negative CO₂ emissions technology with great potential for contributing to the mitigation of global warming and climate change. However, nearly all published research on DAC has been conducted under indoor temperature conditions: 20 to 30 °C. In contrast, the future global implementation requires DAC to be operational across a wide expanse of geographical areas, in which the local temperatures can vary between –30 to 50 °C. Similarly, the absolute humidity can vary from ~0 to 84 g/m³ in various locations. Due to the massive amount of air that would be processed, it may be impractical to preheat or dehumidify the air before the CO₂ separation. Therefore, it is important to develop DAC materials with good performance at realistic outdoor conditions, especially at sub-ambient conditions: –30 to 20 °C. In addition to material development, system-level studies at sub-ambient conditions are also needed for the DAC processes to reach optimal designs, which may be very different from those at ambient conditions. In this perspective article, we first assess the literature to identify the technical gaps that need to be filled for DAC to be applicable at realistic outdoor conditions. We then suggest additional research directions needed for DAC to be viable under varied conditions from the perspective of materials and system designs. For materials, we discuss the expected physical and chemical property changes for the sorbents when the temperature or humidity reaches extremes within their range, and how that will impact performance. Similarly, for system design, we indicate how varied conditions will impact performance and how these changes will impact process optimization.

Keywords: Direct Air Capture, CO₂ Capture, Sub-ambient, Humidity

1. INTRODUCTION

The atmospheric CO₂ concentration has risen rapidly since the industrial revolution. Over the last two centuries, it has increased from ~280 ppm to the current 410 ppm, which is higher than at any point in the past 800,000 years [1]. This has led the average global temperature to increase by 1.2 °C since the pre-industrial era [2]. If unchecked, this trend can lead to disastrous consequences for human health and well-being and the global ecosystem, in the form of extreme weather events [3], loss of species diversity [4,5], rising sea level [6], and ocean acidification [7]. To curb the increasing atmospheric CO₂ concentration, society is increasingly turning to renewable energy, but this transition will take decades. In parallel, CO₂ capture from flue gases has been widely studied to reduce CO₂ emissions from point sources such as power plants [8-11]. In addition to flue gas CO₂ capture, oxy-combustion [12,13] and chemical looping [14,15] are also proposed as alternatives for CO₂ mitigation. However, these methods are not able to mitigate CO₂ emissions from smaller and more distributed sources such as vehicles and airplanes. Moreover, these capture methods, which produce “avoided emissions,” can only decelerate the increase of atmospheric CO₂ concentration but cannot make it decrease. Hence, they are

not sufficient for reversing the increasing global temperature. To meet the goals set by the Paris Climate Agreement of limiting the global temperature increase to 2 °C, preferably 1.5 °C, above the pre-industrial level, negative emission technologies, those that provide for the direct removal of CO₂ from the atmosphere, are required. The removal of CO₂ from the atmosphere by chemical means, known as direct air capture (DAC), is one such approach. Related approaches, such as bioenergy with carbon capture and storage (BECCS), can also produce negative emissions [16].

DAC technology seeks to directly separate CO₂ from the air. In 2016, Sanz-Pérez et al. [17] published a thorough review of DAC approaches, where eight different types of approaches for DAC were elaborated, including (1) aqueous hydroxide sorbents [18], (2) solid alkali carbonates [19], (3) organic-inorganic hybrid sorbents [20], (4) supported amine materials [21] (5) electrochemical approaches [22], (6) direct mineralization [23], (7) membrane approaches [24], and (8) photocatalytic CO₂ conversion [25]. Recently, additional research efforts have also been dedicated to (9) approaches involving biological technologies [26] and (10) approaches combining DAC and CO₂ utilization [27]. Among these approaches, some are still in their infancy and relatively further away from commercialization, such as (5)-(10). Other approaches, such as (1) and (2), are relatively mature but rely on strong bases such as NaOH and KOH solutions, which require significant energy and/or high temperature for regeneration or can result in equipment corrosion. Therefore, solid sorbent-based approaches with milder

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regeneration conditions such as (3) and (4) have attracted the most research attention. Consequently, the use of this kind of sorbent and their corresponding processes will be the focus of this perspective.

Due to the much lower concentration of CO₂ in air (~0.04% or 400 ppm) than in flue gases (~5-15%), the optimal sorbent materials for DAC may have significantly different properties than sorbents for flue gas CO₂ capture. Sorbents showing desirable CO₂ uptake and kinetics at flue gas concentrations may not be applicable to ultra-dilute conditions due to slower kinetics and lower CO₂ uptakes. This is mainly because the lower CO₂ concentration in air requires relatively strong binding between the sorbent and CO₂ to achieve a substantial amount of CO₂ uptake. However, the binding cannot be excessively strong so as to hinder regeneration. Candidate materials that have shown promise for DAC include zeolites, metal organic frameworks (MOFs), and supported amine materials, among others. The review of these types of materials, in the context of practical utilization, will be the focus of this perspective.

Among the DAC research reported so far, a gap exists between the conditions under which the technologies were studied and their real-world application. Most of the CO₂ adsorption studies to date have been conducted at room temperature or above. On the contrary, very few reports have been conducted within the temperature range of -30 to 20 °C at 400 ppm, and these reports are limited to measuring CO₂ isotherms with little insight into material kinetics or recyclability. The future global implementation of DAC necessitates the coverage of a broad geographical area, and globally the local temperatures can vary between about -30 to 50 °C. In fact, ~70% of the land in the world has an annual average temperature below 20 °C [28].

For DAC to have a significant impact on the global climate, it likely has to cover a vast expanse of geographical areas. To meet the goal of limiting the global temperature increase to 2 °C, it has been estimated that DAC must be deployed at a rate such that 10 billion metric tons of CO₂ are removed per year by ~2060. By 2100, 20 billion metric tons of CO₂ must be removed per year [29]. To attain such a large amount of annual CO₂ capture, it is foreseeable that DAC plants may need to be installed in polar regions as well as temperate and tropical zones. This means that research on DAC at sub-ambient conditions needs to be conducted to ensure the feasibility of implementing DAC units in some of the coldest regions in the world where the marginal utility of the land for other human activities is low. In the context of the discussion presented here, sub-ambient refers to temperatures below typical indoor air temperatures, or roughly <20 °C.

Another gap is that most research conducted so far has been mainly focused on CO₂ adsorption under dry conditions, near zero relative humidity. This also limits the impact of the research on real-world applications of DAC because the absolute humidity can vary from ~0 to ~84 g/m³ around the globe (but it is effectively never 0 g/m³). Due to the significant amount of air to be processed, it may be impractical to preheat or dehumidify the air before the CO₂ separation. Therefore, it is essential to develop DAC materials with acceptable performance in the presence of humidity at realistic outdoor conditions.

Hence, to promote the global implementation of DAC, it is nec-

essary to study the performance of CO₂ sorbent materials as well as sorption systems under realistic temperature and humidity conditions. This perspective article reviews the limited published studies related to sub-ambient DAC and humid DAC to identify where research efforts are required to hasten the global implementation of DAC. The perspective also reviews research indirectly related to sub-ambient DAC and humid DAC with the purpose of elucidating the effects of temperature and humidity on both the material and process aspects of DAC, allowing for suggestions about what sorbent materials and what process configurations might be promising for DAC at sub-ambient and/or humid conditions. In Section 2, a literature review of current studies directly or indirectly related to sub-ambient temperature DAC is presented to identify technological gaps, as well as to summarize the influence of varying temperature on sorbent material performance and process operation. In Section 3, a similar literature analysis is conducted for DAC under humid conditions. Section 4 discusses DAC that specifically targets humid sub-ambient temperature conditions. In Section 5, suggestions for future research are made to enable the application of DAC around the world despite the great variations in global temperature and humidity.

2. INFLUENCE OF SUB-AMBIENT TEMPERATURE ON DAC PERFORMANCE AND CURRENT KNOWLEDGE GAPS

Because both the thermodynamic and kinetic properties of sorbent materials strongly depend on temperature, the change in adsorption temperature can have considerable impacts on the performance of DAC materials, and consequently on DAC process operation. In this section, research findings that provide insights into how sub-ambient temperatures can influence the performance of DAC sorbent materials and processes are summarized. Section 2.1 focuses on the influence of temperature on thermodynamics and CO₂ uptake of sorbent materials; Section 2.2 focuses on the influence of temperature on the adsorption kinetics; Section 2.3 discusses the influence of sub-ambient temperature on the system operation; Section 2.4 discusses the implications of sub-ambient temperature on equipment design and plant construction.

2.1. Influence of Temperature on Thermodynamics and CO₂ Uptake

The thermodynamics of CO₂ sorption on the sorbent materials is important to consider when designing sorbent materials for sub-ambient DAC, because the thermodynamics directly impact the amount of sorbent material needed to capture a target mass of CO₂. Several investigations have been conducted to study CO₂ adsorption in the sub-ambient temperature range, but only a few materials have been found to possess desirable CO₂ capacities. Table 1 summarizes materials studied so far that have shown CO₂ uptakes higher than 0.5 mmol/g at 400 ppm in the temperature range between -50 °C to 25 °C.

Most of the materials shown in Table 1 are zeolites or MOFs. Most of these materials show an increasing CO₂ uptake as temperature decreases, following a typical thermodynamic trend, such as zeolites 13X and 5A [32]. The type, composition and form of the materials all influence their CO₂ uptake. For example, Palo-

Table 1. Summary of materials showing CO₂ uptakes higher than 0.5 mmol/g between –50 °C to 25 °C

Material	T, °C	CO ₂ uptake at 400 ppm, mmol/g	Reference
SIFSIX	0	1.5	Shekhah et al. [30]
$^3[(\text{Cu}_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\text{Me}_2\text{trzpba})_4)]$	0	0.62	Lincke et al. [31]
5A	0	0.68	Wang et al. [32]
13X	0	0.45	Wang et al. [32]
5A	–25	1.36	Wang et al. [32]
13X	–25	0.78	Wang et al. [32]
5A	–45	2.19	Wang et al. [32]
13X	–45	1.37	Wang et al. [32]
Porous sodium-impregnated and N-doped carbon sorbents (SNSs) --SNS2-20	0	0.9	Kim et al. [33]
13X crystal	0	1.58	Pini [34]
13X pellet	0	0.91	Pini [34]
LTA zeolite	0	1.17	Palomino et al. [35]
45.8% NbOFFIVE-1-Ni@PA	0	2.2	Guo et al. [36]
Proprietary, poly(styrene) functionalized with primary amine	–10	0.85	Elfving et al. [37]
50% PEI (mw 800)/SBA-15	–5	1.2	Miao et al. [38]
50% TEPA/SBA-15	–5	2.3	Miao et al. [38]

mino et al. found that the adsorption energy of CO₂ increases as the Al/Si ratio in the LTA zeolite increases [35]. As a consequence, the CO₂ uptake, especially at ultra-dilute conditions, increases with increasing Al content. In another example, Pini demonstrated that the 13X crystals showed higher CO₂ uptake under the same conditions as 13X pellets, likely due to the presence of binder in the pellets [34]. Thermodynamic, isotherm data are routinely published using single component sorbates. Indeed, the above CO₂ sorption data are all under dry conditions.

The most well-studied solid sorbents for DAC under ambient and warmer conditions are supported amine materials. Materials of this class are effective in a range of humidity, making them versatile candidates for incorporation into DAC processes. Furthermore, DAC companies like Climeworks, with knowledge and expertise in amine-based sorbents, have operated in cold weather climates such as Switzerland and Iceland. Despite this, data describing the fundamental behavior of supported amine materials for CO₂ adsorption at sub-ambient conditions are rare from the current literature [38]. Nevertheless, it is still worthwhile reviewing the literature at ambient and elevated temperature conditions concerning the behavior of these materials to understand the influence of temperature on the CO₂ uptake thermodynamics and kinetics to help guide the screening and design of materials with desirable CO₂ uptakes for sub-ambient DAC.

Table 2 lists an array of supported amine materials and their corresponding CO₂ uptake at 400 ppm available across a range of varying temperatures. However, a large fraction of the papers in the current literature present CO₂ uptake as isotherms from 0 to 1 bar on a linear scale, making it almost impossible to read the

CO₂ uptake values at 400 ppm. Hence, Table 2 only includes literature with clearly presented CO₂ uptake at 400 ppm. As shown in the table, most sorbents showed decreasing CO₂ uptake as the temperature increased. However, some supported poly(ethyleneimine) (PEI) materials showed an increase followed by a decrease in CO₂ uptake with increasing temperature [39,40]. This is rationalized by the trade-off between kinetics and thermodynamics, where sorption kinetics are enhanced as temperature is increased by enhanced mass transfer through the PEI, even while thermodynamic capacities are decreased [41]. Based on this observation we note that many measured sorption capacities for supported aminopolymer materials do not represent true thermodynamic equilibria, with slow polymer chain motions at lower temperatures leading to very slow kinetic approaches to equilibrium. The effect of varying temperature on adsorption kinetics will be further discussed in Section 2.2.

From Table 1 and Table 2, the following summary represents the current stage of development of sub-ambient temperature DAC, along with useful trends to guide future research on material development:

1. Very few materials studied so far have shown promising CO₂ adsorption performance at sub-ambient temperatures, and most of these materials are zeolites or MOFs studied in the absence of humidity, which is known to harm the uptake on these materials. More candidate materials need to be identified for performance in the range of –30 to 25 °C.

2. Most supported amine materials studied to date show increasing CO₂ capacity with decreasing temperature at ambient and above-ambient temperature ranges (>25 °C; exceptions include

Table 2. Influence of temperature on CO₂ uptake of supported amine materials at 400 ppm

Sorbent material	Low T, °C	Uptake, mmol CO ₂ /g adsorbent	High T, °C	Uptake, mmol CO ₂ /g adsorbent	Curve type	T with max CO ₂ uptake, °C	Maximum uptake, mmol CO ₂ /g adsorbent	Reference
45.8% NbOFFIVE-1-Ni@PA	0	2.2	75	0.2	decreasing	0	2.2	Guo et al. [36]
2.62 g PEI/g SiO ₂ (hierarchical silica with bimodal meso-/macroporosity)	30	2.3	60	1.5	increasing and decreasing	50	2.6	Kwon et al. [39]
mmen-Mg ₂ (dobpdc)	25	2.2	75	0	decreasing	25	2.2	McDonald et al. [42]
Proprietary, poly(styrene) functionalized with primary amine	25	0.4	50	0.13	decreasing	25	0.4	Elfving et al. [43]
Proprietary, poly(styrene) functionalized with primary amine	-10	0.85	90	0.07	decreasing	-10	0.85	Elfving et al. [37]
FS-PEI-33 (PEI 25000)	25	1.1	85	0.03	decreasing	25	1.1	Goeppert et al. [40]
FS-PEI-50 (PEI 25000)	25	1.6	85	0.02	increasing and decreasing	35	1.7	Goeppert et al. [40]
mmen-Mg ₂ (dobpdc)	25	3	69	0	decreasing	25	3	Darunte et al. [44]
linear PPI (1,000 g/mol)/SBA-15 sample	25	1.7	75	0	decreasing	25	1.7	Pang et al. [21]
35 wt% PGA-50 on SBA-15	35	0.26	75	0	decreasing	35	0.26	Sujan et al. [45]
35 wt% branched PEI (800) on SBA-15	35	0.98	75	0.13	decreasing	35	0.98	Sujan et al. [45]
50% PEI (mw 800)/SBA-15	-5	1.2	75	0.3	increasing and decreasing	45	1.6	Miao et al. [38]
50% TEPA/SBA-15	-5	2.3	75	0.3	decreasing	-5	2.3	Miao et al. [38]

materials with large loadings of polyamines). Furthermore, the three studies [36-38] that extended to the sub-ambient temperature range (-10 °C, -5 °C and 0 °C,) show monotonically increasing CO₂ uptake with decreasing temperature, even within the sub-ambient range. This observation may suggest the opportunity to utilize sorbents ruled out for ambient temperature DAC due to their low CO₂ capacity, as they may show higher CO₂ uptake at sub-ambient temperatures. However, most current research is only conducted at ambient and above ambient temperatures, and therefore more investigation of materials at sub-ambient temperatures is required to assess if meaningful increases in CO₂ uptake can be achieved.

3. Some of the measured capacities do not represent true thermodynamic equilibria. Therefore, the measured CO₂ uptake of the sorbent materials needs to be considered together with their

kinetic behavior. As will be discussed below, some sorbents may show promising CO₂ uptake at sub-ambient temperature, but only after excessively long adsorption periods.

2.2. Influence of Temperature on CO₂ Adsorption Kinetics

As mentioned, the CO₂ uptake of the sorbent materials needs to be considered together with their kinetic behavior to determine their viability for sub-ambient DAC. However, literature review indicates that only one study has been conducted so far on the kinetics of CO₂ adsorption on supported-amine materials at sub-ambient temperatures [38]. The objective of this section is therefore to review the current literature on CO₂ kinetic studies conducted at ambient or above-ambient temperatures to identify the relations between CO₂ adsorption kinetics and temperature on different types of adsorbents to guide future material screening for sub-ambient CO₂ adsorption. A goal is to identify candidate mate-

Table 3. Summary of kinetic studies on the temperature dependence of the kinetics of supported amine CO₂ adsorbents

Material	CO ₂ concentration	Lowest T, °C	Time to reach half capacity, s	Capacity, mmol/g	Highest T, °C	Time to reach half capacity, s	Capacity, mmol/g	KT factor	Reference
SBA-15/TEPA60	10%	30	130	2.7	75	72	3.5	17	Zhao et al. [46]
1 g PEHA on 1 g KIT-6	10%	20	180	1.8	70	180	3.3	10	Liu et al. [47]
PME-PEI(50)	100%	50	492	2.3	75	21	4.1	140	Heydari-Gorji et al. [48]
PME-PEI(30)	100%	25	132	2.7	75	14.4	2.3	35	Heydari-Gorji et al. [48]
TRI-PE-MCM-41 (tri amine is 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane)	5%	25	20	2	70	18	1.4	-5	Serna-Guerrero et al. [49]
PEI-PE-MCM-41	5%	25	4000	3.9	70	100	1.9	56	Serna-Guerrero et al. [49]
PEI-functionalized SBA-15 (branched PEI 1200, 33 wt% deposit)	5%	15	25	2	35	17	1.9	12	Ge et al. [50]
MMT	100%	25	132	0.52	100	48	0.06	-14	Stevens et al. [51]
MMT CTAB	100%	25	120	0.2	100	7.2	0.03	11	Stevens et al. [51]
MMT N2	100%	25	840	0.18	100	240	1.7	43	Stevens et al. [51]
MMT CTAB N2	100%	25	600	0.24	100	32	2.4	64	Stevens et al. [51]
wet-grafted W-AG-150A	70%	25	5,700*	1.5	75	240*	1.7	57	Anyanwu et al. [52]
50% PEI (mw 800)/SBA-15	400 ppm	-5	4,800	1.2	75	300	0.3	13	Miao et al. [38]
50% TEPA/SBA-15	400 ppm	-5	2,100	2.3	75	300	0.3	-1	Miao et al. [38]

*when calculating the KT factor for wet-grafted W-AG-150A, the time required to reach 90% maximum capacity was used because it was impossible to read the time required to reach half maximum capacity from the plot

rials that are expected to maintain relatively fast adsorption kinetics at sub-ambient conditions.

Kinetic studies have been reported in the current literature correlating the rate of CO₂ adsorption as a function of multiple variables including temperature, CO₂ concentration, as well as material type and morphology, among other factors. Table 3 summarizes the studies on the temperature dependence of the kinetics of various types of supported amine CO₂ adsorbents. Note that most studies were conducted with CO₂ concentration ranging from 5 to 100%, as kinetic studies using 400 ppm CO₂ are rare in the current literature [38]. Therefore, the conclusions drawn from these studies may not be directly transferrable to the kinetic behavior of DAC.

Most studies summarized in the table reported CO₂ adsorption kinetics by plotting the adsorption capacity as a function of time. In some work, various kinetic models were proposed, showing relatively close matches with the experimental kinetic data. However, most of these models were only verified above 25 °C. Because rigorous, quantitative kinetic studies are not routinely reported in the literature, an alternate method that utilizes the limited kinetic data available is needed to correlate uptake rates for different types of sorbents operating under varied conditions. The kinetic-temperature (KT) factor is introduced here to measure the dependence of CO₂ adsorption kinetics on temperature, as defined in Eq. (1). T₁ and T₂ are the lower and higher temperatures where the kinetic

experiments were conducted; q stands for the CO_2 adsorption capacity; $t_{0.5}$ stands for the time required for CO_2 uptake to reach half of the maximum capacity; R is the molar gas constant. The KT factor is defined to roughly represent the activation energy of permeation [53], and it has the same units as energy. A more detailed derivation of the KT factor is provided in the supplemental material. A larger KT factor entails a faster increase in kinetics with increasing temperature. A KT factor of 0 means that kinetics are independent of temperature. Note that the KT factor is only used to qualitatively describe the dependence of adsorption rate on temperature and is not intended for precise quantitative calculations.

$$KT = \frac{\ln\left(\frac{q(T_2)}{q(T_1)}\right) - \ln\left(\frac{t_{0.5}(T_2)}{t_{0.5}(T_1)}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} R$$

By studying the dependence of the KT factor on the experimental conditions in Table 3, the following trends of the influence of temperature on the adsorption kinetics can be summarized:

1. Amines with higher molecular weight such as PEI tend to exhibit large KT factors, which means that the CO_2 adsorption kinetics of PEI-based sorbent materials benefit greatly from increasing temperature and suffer considerably with decreasing temperature. This trend correlates with the discussion above about polymer chain mobility and amine site accessibility, which drive amine adsorbents containing polymeric amines to often have adsorption capacity maxima at elevated temperatures. Conversely, amines with lower molecular weights such as tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA) and 3-aminopropyltriethoxysilane (APTES) show less significant dependence on temperature. Some sorbents have negative KT factors, and this is mainly caused by the reduction in CO_2 capacity as temperature increases. The time required for CO_2 uptake to reach a certain proportion of the maximum capacity still decreases with increasing temperature in the cases with negative KT factors.

2. When PEI is used as the sorbent material, higher PEI loading increases the KT factor. For example, Heydari-Gorji et al. found that when the PEI loading was increased from 30 to 50 wt% on PME (pore-expanded MCM-41 washed by ethanol), the KT factor increased from 35 to 140 [48]. The major cause for this

phenomenon is that increasing the PEI loading over a certain value significantly reduces the adsorption kinetics at lower temperature but has relatively little influence on adsorption kinetics at higher temperature. This is likely due to the large polymeric chains of PEI blocking each other due to slow chain mobility; thus the amine active sites, at lower temperatures and higher loadings, prevent the CO_2 from reaching the amine groups below the surface.

3. The synthesis procedures and resulting porous structures of the supported amine materials have great influence on the CO_2 adsorption kinetics at different temperatures. For example, Stevens et al. [51] discovered that by intercalating montmorillonite (MMT) with hexadecyltrimethylammonium bromide (CTAB), the CO_2 adsorption kinetics at 100°C increased ten times, while the CO_2 adsorption kinetics at 25°C were almost unaffected. This causes the KT factor of CTAB-intercalated sorbent samples to have a greater KT factor than samples not treated by CTAB. Thus, sorbent designs that enhance porosity and accessibility of binding sites can greatly facilitate the implementation of DAC. Unlike the method used above [51], which mainly enhanced CO_2 adsorption kinetics at elevated temperatures, strategies that can enhance adsorption kinetics at sub-ambient temperatures are also needed.

2.3. Influence of Temperature on Process Operation

The influence of sub-ambient temperature on the performance of sorbent materials will undoubtedly impact the operation of the DAC processes. It is therefore important to understand such influences in order to adjust the operating parameters of DAC processes to suit the specific operating temperature to optimize the process performance. This section reviews the most widely studied operating mode of DAC and summarizes how its operation can be influenced by a decrease in adsorption temperature.

Various process modes have been considered for DAC, including temperature swing adsorption (TSA), temperature vacuum swing adsorption (TVSA), pressure swing adsorption (PSA), and moisture swing adsorption (MSA). Among these, PSA is shown to be unrealistic by modeling studies because it requires an unreasonably high level of vacuum during the desorption phase [37]. Similarly, if pressurizing the inlet feed, the low CO_2 concentration makes the process energetically costly [54]. TSA utilizes increased temperature to desorb the CO_2 , but the purity of desorbed CO_2 from a TSA process is often limited, with one report suggesting lim-

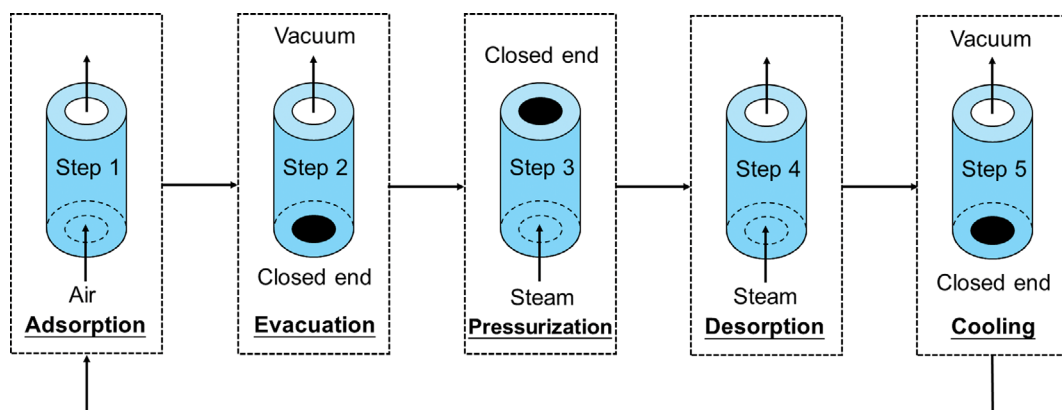


Fig. 1. Process flow diagram of TVSA [56].

its around 20% [55]. Therefore, the most widely studied system configuration for solid sorbent-based DAC is TVSA.

A typical TVSA process has five steps in an adsorption-desorption cycle [56], as described by Sinha et al. The flow diagram of TVSA process is shown in Fig. 1. The first step is adsorption, where air is passed through the contactor bed for CO₂ adsorption. The second step is evacuating the contactor by a vacuum pump. In the third step, the contactor is filled by steam back to 1 atm. The fourth step is desorption by flowing steam continuously through the contactor to increase the temperature for CO₂ to be desorbed (both direct and indirect heat transfer modes have been studied and deployed). The fifth step is cooling the system by applying vacuum to the contactor again to allow some of the condensed steam to evaporate to remove heat. Similar processes with indirect steam heating are also known.

The TVSA process is a complex process with numerous parameters to adjust to allow the system to reach the optimum operating conditions. Sinha et al. [56] discussed the influence of adjusting the air flow rate for the adsorption step, the steam flow rate for the desorption step, and the duration of these two steps on the energy consumption and economic performance of the overall DAC system. Stampi-Bombelli et al. [57] analyzed DAC via a steam-assisted TVSA process and studied the performance as functions of the duration of each step of the cycle, the evacuation pressure during the desorption, and the use of steam purge during desorption. They reported that a tradeoff existed between the thermal energy consumption and the electrical energy consumption of the process. Zhu et al. [11] studied the design of a steam-assisted TVSA process and investigated the effects of air velocity during adsorption, the steam velocity during desorption, the durations of adsorption and desorption, and the temperature and pressure of the desorption phase on the process performance. The authors observed a tradeoff between the daily CO₂ productivity and energy consumption per unit amount of CO₂ captured. Wilson et al. [58] studied DAC using TVSA with a faujasite zeolite, and the influences of desorption temperature, gas space velocity during adsorption, and the bed length. They concluded that increasing the desorption temperature increased the thermal energy required but decreased the electrical energy per ton of CO₂ captured.

From these studies we note that the design of a TVSA process has the following features:

1. Many operating parameters that can be adjusted during the whole process to alter its performance. Most of these parameters can be optimized to achieve desired performance characteristic(s). For example, the duration of the adsorption step should neither be too long nor too short and the optimum duration varies with other parameters such as the type of the adsorbent used in the process.

2. Numerous tradeoffs exist in the optimization, such as the consumption of thermal energy vs. the electrical energy per unit amount of CO₂ captured; the CO₂ productivity per unit time and the energy consumption per unit amount of CO₂ captured.

3. Some variables influence the performance monotonically. For example, to maximize the efficiency and economic benefits, the weight of the gas/solid contactor (dead weight) should be minimized; the CO₂ capacity of unit amount of adsorbent should be

maximized; the lifetime of the sorbent material should be as long as possible.

4. In a typical TVSA process using supported amines as sorbents, the electrical energy consumption is typically only one quarter of the thermal energy consumption. Therefore, reducing the cost of thermal energy supply by using cheap and/or renewable heat sources can lead to significant economic benefits. Apart from heating by steam or hot gas, electricity can also serve as the thermal energy source by Joule heating, and such a process is often known as electrical swing adsorption (ESA) [59-61]. Because the ESA process uses electricity, a high-quality energy form, to provide heating at relatively low temperatures, its second-law efficiency is usually only 1-6% [59]. Nevertheless, electricity is easier to transport than heat, and hence the ESA technique may become viable in the future when cheap renewable electricity becomes available, enabling the deployment of DAC plants far from industrial heat sources.

TVSA systems intended for sub-ambient temperatures share most of the features listed above with ambient systems. However, the operating modes of the sub-ambient plants may need to differ from those used at ambient temperatures. This is fundamentally due to the differences in chemical properties of the sorbents. On the one hand, a given sorbent material may show dramatic change in performance when used at sub-ambient temperature; on the other hand, in some cases, sub-ambient temperatures may require the use of totally different sorbents from ambient temperature operations. Process studies on sub-ambient DAC are not available in current literature. However, by reviewing process studies conducted at ambient temperature as well as DAC material studies, we surmise that the following changes may occur when DAC processes are shifted from ambient to sub-ambient temperature operations:

1. Most sorbent materials show reduced kinetics at sub-ambient temperature, which means that the adsorption phase will take longer to reach pseudo-equilibrium or the desired working capacity. This will result in reduced CO₂ productivity, ultimately resulting in larger plant sizes and capital costs to attain the same CO₂ annual productivity as a corresponding ambient DAC plants.

2. For many sorbent materials, the equilibrium CO₂ uptake increases with decreasing temperature, resulting in higher CO₂ productivity per cycle. Consequently, keeping other operating parameters constant, a smaller amount of contactor substrate and sorbent materials need to be heated during desorption to produce an equivalent amount of CO₂, leading to savings in thermal energy. However, to maintain relatively fast CO₂ adsorption kinetics, the CO₂ uptake of the materials optimized for sub-ambient DAC may not be higher than the CO₂ uptake of the materials optimized for ambient DAC. Additionally, lower temperature operation may necessitate larger temperature swings to induce desorption, leading to higher energy costs.

3. It is also possible that the sub-ambient operation will result in a reduction in desorption temperature if suitable sorbents are chosen. This is because, as discussed above, at sub-ambient temperatures, sorbents with weaker binding energies with CO₂ such as physisorbents, can potentially be used. These sorbents tend to have lower desorption temperatures. Instead of desorbing at 80-100 °C,

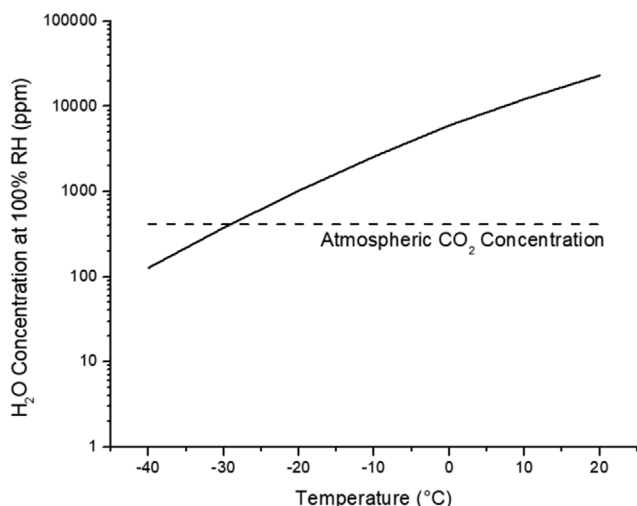


Fig. 2. Absolute moisture concentration at the dew point.

as most ambient amine sorbents do, these sorbents might be regenerated at 50 °C, for example. This may result in more options for heating, such as the heat provided by heat pumps or solar power, and the exergy efficiency of sorbent regeneration may be greatly enhanced.

Apart from TSA, the use of MSA for DAC applications has been discussed in the literature. However, MSA does not show promise for sub-ambient temperature DAC because these processes rely on the vaporization of water as the driving force for CO₂ desorption. Typically, 12 to 37 moles of water need to be vaporized for the desorption of 1 mole of CO₂ [62]. At sub-ambient conditions, the capacity of air to hold water is very limited, as shown in Fig. 2, making the use of MSA less feasible for sub-ambient DAC.

2.4. Influence of Temperature on the Equipment Design

Temperature affects not only the sorbent materials and the optimal process operating parameters, but also the equipment used for capturing CO₂. Hence, it is important to review the influence of the decrease in environmental temperature on the instrumentation of DAC. The materials used in the DAC equipment and supporting infrastructure vary considerably, ranging from cement to metal alloys to polymer composites. It is known that daily and seasonal fluctuations of temperature combined with inherent humidity and solar radiation variations may induce degradation of polymer-based materials, not only in both warm/mild and humid/dry climate regions but also in those of cold and extreme cold conditions [63]. For example, metals, alloys, and plastics become brittle at very low temperatures [64], which may preclude them from use in certain regions. Other challenges will be potentially associated with buildup of static charge, choice of lubricants to protect equipment, insulation of heated units and electric wires and cables. Extreme cold conditions may lead to temporary shutdowns of the plant for maintenance at shorter intervals, adding to the cost of the DAC technology.

Choice of materials for use in DAC processes that are resistant to extreme or varied temperature conditions may benefit from knowledge transfer from other disciplines (e.g., coating industry, aviation). For example, coatings repelling water [65] and prevent-

ing freezing [66] at the surface of materials may be useful additions to integrate into DAC materials development. Currently used de-icing methods involve mostly chemical and mechanical approaches that may not be feasible for some DAC plants. Furthermore, to date, DAC prototypes and plants mostly rely on using steam for regeneration of the sorbents. Obviously, in cold environments, additional insulation of piping will be a necessity and the cold weather adaptations, along with heat losses, will add to overall costs. The type of modifications needed will depend on the temperatures experienced by the region in which a DAC plant is operating.

The sub-ambient DAC field is only at a nascent stage of development. With few experimental sub-ambient laboratories available for materials and process development, and few low temperature DAC deployments, little has been published about specific challenges of DAC under such conditions. Nonetheless, other industries have developed sophisticated processes and operations for cold climates, and adaptation of best practices from other fields will undoubtedly be pursued.

3. INFLUENCE OF HUMIDITY ON DAC PERFORMANCE AND CURRENT KNOWLEDGE GAPS

Besides temperature, another crucial factor that can induce a significant difference in CO₂ adsorption performance and DAC process operation is humidity. In this section, the influence of humidity on the performance of DAC materials and processes is discussed. Section 3.1 focuses on the influence of humidity on the performance of zeolite and MOF materials; Section 3.2 summarizes the influence of humidity on the performance of supported amine materials; Section 3.3 discusses the changes in process operation induced by the presence of moisture. This section mainly focuses on DAC with humidity at ambient temperature, as DAC with humidity at sub-ambient temperature will be elaborated in Section 4.

3.1. Influence of Humidity on the Performance of Physisorbents

For many physisorbent materials considered for DAC applications such as zeolites and MOFs, moisture is undesirable because it competes with CO₂ for adsorption sites, and the desorption of water consumes a large amount of extra energy [67-70]. This section presents a literature review of the influence of humidity on the performance of zeolite and MOF materials to thoroughly examine these effects. Although research reports on the use of physisorbents for DAC at humid conditions are limited in number, there is an abundance of papers on flue gas CO₂ capture under humid conditions and insights can be gained from these studies. Zeolites such as 5A and 13X are two prototypical CO₂ adsorbents showing compromised CO₂ uptake under humid conditions due to their similar or higher affinity to water molecules than CO₂ [71,72]. Several well-known MOFs also have shown strongly inhibited CO₂ uptake in the presence of water. Degradation and permanent losses in CO₂ capacity due to exposure to moisture have also been observed for some MOFs. For instance, studies focusing on the effect of humidity in M/DOBDC MOFs revealed a 40% loss in dry gas CO₂ uptake for Ni/DOBDC and 15% for Co/DOBDC after regeneration from hydration at 70% relative humidity CO₂/N₂ gas and room temperature compared to their pristine state [73]. Therefore,

such materials are likely ruled out for DAC under humid conditions unless further modification to protect them from water is applied [70]. Interestingly, it was reported that HKUST-1 retains its CO₂ capacity at low water loadings of 3.4 mol/kg at 0.1 atm CO₂ pressure and 25 °C, although it loses almost all of its CO₂ capacity when the water loading of the material is 25.4 mol/kg due to the nature of competitive adsorption [68,74]. However, given that HKUST-1 can reach a water uptake of 25 mol/kg even at 10% relative humidity at 25 °C, it is hard to expect HKUST-1 to be

applicable to DAC in humid environments. Along with HKUST-1, MIL-101(Cr), zirconium-based UiO-66, and microporous copper silicate SGU-29 all showed minimal change in CO₂ uptake within certain ranges of humidity due to the favorable interaction between adsorbed water and CO₂ gas molecules and the absence of apparent competitive adsorption between H₂O and CO₂ [67]. MIL-100(Fe) showed among the most notable improvements in CO₂ uptake induced by the presence of water [70]. Also, CO₂ adsorption of MIL-100(Fe) at 25 °C and 0.2 bar of CO₂ under 40%

Table 4. Effects of moisture on CO₂ capture on various physisorbents

Materials	Adsorption conditions	Equipment	CO ₂ uptake (mmol/g)	Method	CO ₂ capacity loss (%)	Reference	Study aim
5A	100% CO ₂ 25 °C	SAP	1.53 mmol/g at 4.4 kPa and 1.0 mmol/g water loading	Pre-humidification	52 (0.738 mmol/g at 4.56 kPa and 3.4 mmol/g water loading)	Wang et al. [32]	CO ₂ capacity loss due to the presence of water
13X	100% CO ₂ 25 °C	SAP	1.41 mmol/g at 4.32 kPa and 1.0 mmol/g water loading	Pre-humidification	87 (0.1769 mmol/g at 4.962 kPa and 9.4 mmol/g water loading)	Wang et al. [32]	CO ₂ capacity loss due to the presence of water
Mg/DOBDC	16.7% CO ₂ / N ₂ at 25 °C	FB (fixed bed)	5.36	Adsorption (16.7% CO ₂ /N ₂) after regeneration (16.7% CO ₂ /N ₂ with 70% RH)	84	Kizzie et al. [73]	CO ₂ capacity loss after regeneration
Co/DOBDC	16.7% CO ₂ / N ₂ at 25 °C	FB	3.04	Adsorption (16.7% CO ₂ /N ₂) after regeneration (16.7% CO ₂ /N ₂ with 70% RH)	15	Kizzie et al. [73]	CO ₂ capacity loss after regeneration
Ni/DOBDC	16.7% CO ₂ / N ₂ at 25 °C	FB	2.86	Adsorption (16.7% CO ₂ /N ₂) after regeneration (16.7% CO ₂ /N ₂ with 70% RH)	39	Kizzie et al. [73]	CO ₂ capacity loss after regeneration
Zn/DOBDC	16.7% CO ₂ / N ₂ at 25 °C	FB	1.65	Adsorption (16.7% CO ₂ /N ₂) after regeneration (16.7% CO ₂ /N ₂ with 70% RH)	78	Kizzie et al. [73]	CO ₂ capacity loss after regeneration
HKUST-1	0.1 atm CO ₂ at 25 °C	SAP (surface area physisorption)	≅0.6 at 3.4 mmol/g water	Pre-humidification	100 (≅0 at 25.4 mmol water loading)	Liu et al. [74]	CO ₂ capacity loss due to the presence of water
UiO-66	0.2 bar CO ₂ / N ₂ at 25 °C	FB	≅0.80	Adsorption under 40% relative humidity gas after pre- humidification at 40% relative humidity	Minor difference (within experimental error)	Soubeyrand- Lenoir et al. [70]	CO ₂ capacity loss due to the presence of water
MIL-100(Fe)	0.2 bar CO ₂ / N ₂ at 25 °C	FB	2.39 (40% higher than dry condition)	Adsorption under 40% relative humidity gas after pre- humidification at 40% relative humidity		Soubeyrand- Lenoir et al. [70]	CO ₂ capacity increase due to the presence of water

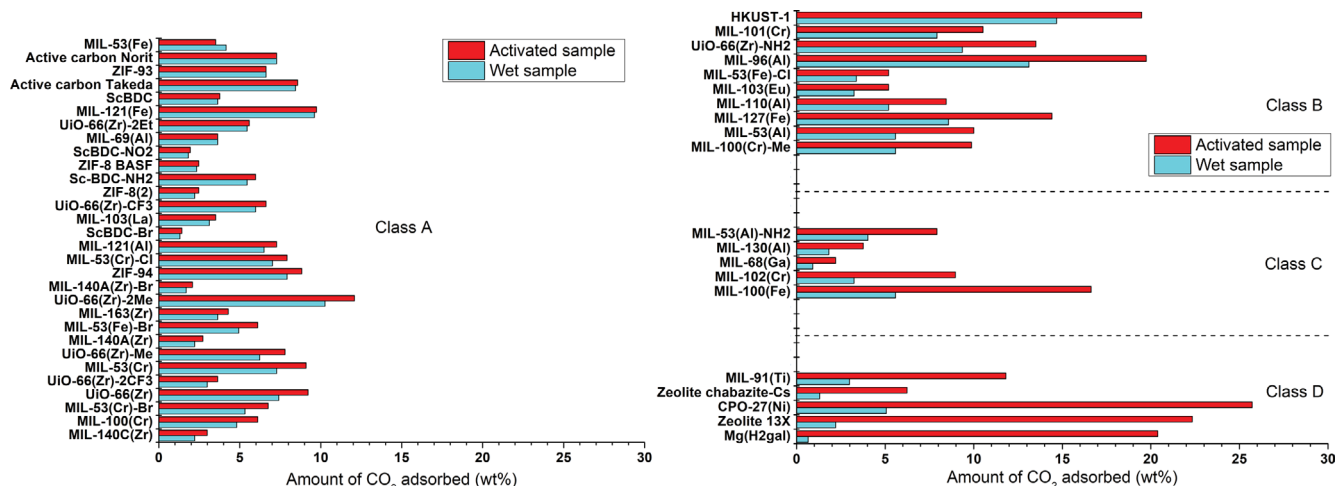


Fig. 3. Summary of the effects of adsorbed water on CO₂ uptake obtained for 43 MOFs and 4 reference materials [67].

relative humidity after pre-equilibration under a relative humidity of 40% exhibited a five-fold increase in CO₂ uptake, 105 mg of CO₂/g of sorbent, compared to the dry condition due to water displacement, where water acted as microporous pockets that induce CO₂ to sorb. Table 4 summarizes the effect of moisture on CO₂ adsorption of those physisorbents.

Besides the materials discussed above, Chanut et al. screened 43 metal-organic frameworks (MOFs) to investigate the effect of water on CO₂ adsorption [67]. In that study, the materials were first placed above liquid water in an airtight chamber for two days where the relative humidity reached 100%, leading to complete prehumidification. Then, the samples were partially dried in N₂ at 303 K for 8 h to evacuate the weakly adsorbed water on the outer surface and in the pores. After partial drying, pure CO₂ was introduced into the sample to measure the CO₂ uptake at 25 °C, and the result is listed as the CO₂ uptake on “wet samples” in Fig. 3. The desorption was carried out by flowing dry N₂ through the sample bed at elevated temperatures. After several adsorption and desorption cycles, where the desorption temperature of each cycle was higher than the previous one, the water was gradually desorbed. At the last cycle, when water was almost totally desorbed, the CO₂ uptake was measured for each sample and the results are given as the CO₂ uptake on the “activated samples” in Fig. 3. After the measurement, they classified the materials into four categories depending on their CO₂ uptake behavior after hydration and 30 of them were characterized as the class where the reduction of CO₂ uptake was less than 25%, as shown in Fig. 3. For each adsorbent, the blue bars correspond to the CO₂ uptake on the wet sample, which is determined from the first adsorption step during consecutive adsorption and desorption cycles, and the red bars correspond to the uptake of CO₂ adsorbed on the sample in its most activated state, which is determined from the last adsorption step during the same consecutive adsorption and desorption cycles. From top to bottom, adsorbents least affected by humidity are classified as A and most affected are classified as D. Adsorbents listed in class A have CO₂ adsorption capacities reduced by less than 25%, class B between 25 and 50%, class C between 50 and 75%, and class D by more than 75%.

In general, physisorbent materials that have high selectivity to CO₂ may be considered promising sorbents for DAC processes since less energy is required for regeneration compared to chemisorbents [75]. However, as discussed above, the CO₂ capture performance of most physisorbents is dramatically reduced by moisture in the air. This is because the permanent dipole moment of H₂O makes the moisture interact with the sorption sites more strongly than CO₂, which has a quadrupole interaction with charges in the physisorbent materials [76]. Thus, significant decreases in CO₂ capture performance are routinely experimentally observed from physisorbent materials in the presence of humidity, such as MOFs, zeolites, and related materials [75,77-79]. Furthermore, the adsorption of large quantities of water from humid air not only reduces the CO₂ uptake of physisorbents, but in the case of some MOF sorbent materials, the sorbent structures are degraded when exposed to water for long periods [80-82]. For example, HKUST-1 and Mg-MOF-74 were degraded and their CO₂ uptake was dramatically decreased by 34% and 68%, respectively, after exposure to water vapor at 40 °C and 75% relative humidity for 14 days [78]. Nevertheless, it has been shown that properly controlling the structures of amine-appended MOFs can enhance their moisture stability. For example, Mg₂(dobpdc) with amines inserted into its pores has been demonstrated to possess exceptional stability under some humid conditions [83-85]. However, these amine-containing sorbents may no longer qualify as physisorbents, and they also may possess significant kinetic resistance in some operating conditions [44]. In addition, SIFSIX MOFs have also shown some moisture tolerance, making them possible candidates for DAC in humid environments [86].

It can be concluded from these studies that materials working with minimal or no negative impact of humidity on their properties should be given priority for study of DAC at humid, sub-ambient conditions. However, the CO₂ sorption challenge at 400 ppm CO₂ concentration is a demanding one, requiring the highest affinity sorption sites in most adsorbent materials. To this end, one may expect that the array of water-tolerant CO₂ sorption materials at elevated CO₂ concentrations may not correlate directly in describing performance under humid DAC conditions. For this

reason, targeted humid studies at ultra-dilute CO₂ concentrations are needed. To deploy physisorbents for use in DAC processes under humid conditions, control of pore size and/or modification of the pore chemistry may be required to enhance the water resistance. For example, zeolites or MOFs can be modified with a hydrophobic surface or shell so that they selectively reject water vapor [75]. While this approach may aid CO₂ sorption for a few cycles, over extended cycling approaching pseudo-steady-state operation, one may still expect significant water uptake. Another strategy to circumvent the competitive effect of water suggested by Kolle et al. is to use kinetic separation, where the adsorption stage ends while the water adsorption front is still at the entrance of the adsorption bed [87,88]. This strategy may be worthwhile if water and CO₂ are fully desorbed in each cycle, but it will falter if water remains on the sorbent after CO₂ desorption, as the water loading will progressively build over cycles to equilibrium values. Indeed, one of the most common errors made in studying humid CO₂ sorption using breakthrough studies is starting with a dry bed, running just a few cycles that offer CO₂ breakthrough but stop when water has only penetrated the front of the bed, and falsely concluding that the sorbent is water tolerant, offering little or no water/CO₂ competition during adsorption.

3.2. Influence of Humidity on the Performance of Chemisorbents

Another possible strategy to capture CO₂ from humid air is deploying amine-containing solid adsorbents, which are often tolerant to moisture in the feed gas. It is generally known that the

CO₂ adsorption capacity of amine-based solid sorbents can be enhanced by the presence of moisture due to increased amine efficiency (mol CO₂/mol amine) made possible by the mechanisms of adsorption. In particular, if the sorbent can be tuned to shift adsorption from carbamate formation to bicarbonate formation, the amine efficiency can be theoretically enhanced from 0.5 (dry) to 1 (humid) [89-93]. However, this is not the sole way of enhancing CO₂ uptake, as some authors have also showed that the enhanced CO₂ capture capacity under humid conditions is attributed to the formation of more carbamate ion pairs in the presence of moisture [94-96]. The enhanced amine efficiency via the formation of bicarbonate under humid conditions has been primarily observed in the case of tertiary amine functionalized solid sorbents with low total sorption capacity [69,97], as these materials cannot form carbamates. Identification of bicarbonate formation is a challenge via conventional spectroscopic techniques, like FTIR, as demonstrated in the study that first showed the formation of bicarbonate on the primary amine-loaded mesoporous silica with low surface coverage under humid CO₂ conditions [98]. Methods to detect bicarbonate using solid state NMR have also recently been described [99]. It was also shown that water can enhance the long-term stability of amine-containing adsorbents by inhibiting the formation of urea at the expense of CO₂ adsorption sites [90]. In addition to enhanced amine efficiency, decreased amine efficiency under humid DAC conditions has also been reported. For example, Goeppert et al. reported decreased performance of PEI-

Table 5. Effect of humidity on the performance of chemisorbents for DAC

Support	Amine	Loadings	Adsorption conditions	Method	CO ₂ loading (mmol/g)	Pre-humidification	Cycles	Loss (%)	Reference
Polymer/silica monolith fiber	PEI (M _w =800)	25 wt%	380 ppm CO ₂ /N ₂ at 35 °C	FB (fixed bed)	0.62 (dry) 1.7 (humid)	yes	21 6	9.7 7	Sujan et al. [102]
PE-MCM-41	PEI (M _w =800)	40 wt%	400 ppm CO ₂ /N ₂ at 25 °C	FB	2.18 (dry) 2.92 (humid)	no	20 20	4.6 2.1	Sayari et al. [103]
SBA-15	Aminopropyltrimethoxysilane	4.3 mmol N/g	400 ppm CO ₂ at 30 °C	SAP (surface area physisorption)	0.85 (dry) 0.96 (humid)	no			Didas et al. [98]
Cellulose	3-Aminopropylmethyldiethoxysilane	4.2 mmol N/g	400 ppm CO ₂ at 23 °C	SAP	1.11 (dry) 2.13 (humid)	no			Gebald et al. [104]
Cellulose	3-Aminopropylmethyldiethoxysilane	4.2 mmol N/g	400 ppm CO ₂ at 50 °C	SAP	0.11 (dry) 1.42 (humid)	no			Gebald et al. [104]
MCF Silica	PEI (M _w =1,200)	63 wt%	420 ppm CO ₂ /N ₂ at 46 °C	FB	1.94 (dry) 2.52 (humid)	no			Wijesiri et al. [105]
Fumed Silica	PEI (M _w =25,000)	33 wt%	415 ppm CO ₂ /air 25 °C	FB	1.18 (dry) 1.77 (humid)	no			Goeppert et al. [100]
Polymer (TEGO Rad 2650)	NOHM-PEI	50 wt%	400 ppm CO ₂ /N ₂ at 25 °C	TGA (thermogravimetric analysis)/FB	1.05 (dry) 1.66 (humid)	yes			Rim et al. [106]

impregnated fumed silica materials, likely due to blockage of the access to amine groups by the adsorbed water [100]. As shown in Table 5, most of the DAC studies under humid conditions reported to date provide evidence for a synergistic, positive effect on CO₂ sorption capacity between moisture and CO₂ adsorption over amine-based solid sorbents. However, the heat capacity of the amine-based adsorbents increases as moisture adsorbed by the materials is increased and any water desorbed during regeneration will result in increased energy requirements for the regeneration process [101]. Such effects of moisture on process operation will be elaborated in Section 3.3.

3.3. Influence of Humidity on Process Operation

Humidity can have a significant impact on sorbent performance, as noted above, and this in turn greatly affects the process operation. Several papers on DAC process designs have discussed the influence of moisture on the process performance. Wurzbacher et al. [107] studied DAC using TVSA using diamine-functionalized silica gel, showing that the presence of humidity in air can allow the use of a higher desorption pressure (a weaker vacuum) to achieve the same level of CO₂ uptake. Wurzbacher et al. [108] also studied the concurrent separation of CO₂ and H₂O from air by TVSA using an amine-functionalized nanofibrillated cellulose sorbent. An energy analysis on the process showed that when the relative humidity in air varies from 20 to 80%, the heat consumption of the process changes between 493 to 640 kJ/mol CO₂. Although higher humidity in air leads to higher CO₂ uptake, the desorption of water consumes a significant amount of additional energy. In another study, Wurzbacher et al. [109] investigated the effect of moisture on a DAC TVSA process using the same type of amine-functionalized material, showing that a higher level of moisture in air has a positive effect on the purity of the CO₂ product because during the desorption step, the adsorbed water desorbs earlier than CO₂, creating a purge for the reactor and preventing the mixing of air and CO₂, which is desorbed subsequently. Wilson et al. [58] studied a DAC process using TVSA with a faujasite zeolite as the sorbent. Unlike solid-supported amine materials, the use of such zeolites requires water to be removed prior to CO₂ adsorption due to the preferential H₂O adsorption over CO₂ on zeolites. The authors calculated the energy consumption associated with water removal from air, indicating that the energy is significantly lower at lower DAC operating temperatures. Drechsler et al. [110] investigated the influence of water co-adsorption on the energy balance of solid sorbent-based DAC processes, showing that a well-designed desorption step can greatly reduce the co-desorption of water, reducing the thermal energy consumption. The operation of a counter-current adsorber can reduce the H₂O:CO₂ ratio in the product gas. In addition, part of the water desorption enthalpy can be recovered by recovering the condensation heat of vapor in a recompression unit. Elfving et al. [37] modeled various DAC processes including TSA, TVSA and PSA using polymeric amines as the sorbent material and studied the influence of cold temperatures (−10 to 0 °C) and humidity on the process performance. The study showed that at humid conditions, lower desorption temperatures can be used to achieve the same performance as dry conditions. The results showed that TSA can use a regeneration temperature of 50–60 °C when adsorbing either in dry cold

conditions or humid warm conditions.

From this literature review, we conclude that humidity has both positive and negative effects on DAC from a process perspective. When operating a DAC system in areas with high humidity, the following changes can be expected:

1. When using materials with low water resistance such as zeolites and MOFs, a drastic decrease in CO₂ uptake can be expected. This leads to a diminished CO₂ throughput per cycle that will significantly increase the capital and operating costs for capturing unit amount of CO₂. Some materials are so susceptible to water that they lose almost all their CO₂ capacity under humid conditions. For these materials to be used for DAC under humid conditions, pre-removal of water becomes necessary before CO₂ adsorption, which leads to additional thermal energy consumption. At warm and wet conditions, the energy consumption of water pre-removal can be so high as to essentially preclude these materials from DAC applications. However, as will be discussed in Section 4, at cold conditions, because the absolute humidity in air is much lower, pre-removal of humidity becomes more affordable, or even no longer necessary.

2. Unlike physisorbent, most amine-based chemisorbents have increased CO₂ uptake per unit mass of sorbent in the presence of humidity. Besides, the adsorbed water molecules appear to be acting as plasticizers, weakening inter/intra molecular hydrogen bonds and dipole-dipole interactions [111], thus enhancing mobility of PEI chains and CO₂ diffusion and resulting in improved adsorption kinetics [112–114]. These effects, in turn, lead to a higher CO₂ throughput per cycle or allow the use of higher desorption pressures/lower desorption temperatures to reach the same CO₂ uptake as under dry conditions.

3. For certain sorbent materials, water desorbs prior to CO₂ in the desorption step, creating a purging effect in the contactor that leads to a higher CO₂ product purity. This will reduce the energy consumption and costs associated with further CO₂ purification.

4. The co-adsorption of H₂O requires additional energy for desorption, which can significantly increase the energy consumption of the process. Furthermore, as discussed in Section 3.2, the heat capacity of the amine-based adsorbents increases as the moisture adsorbed by the materials increases, leading to even higher energy consumption.

For MSA, because this approach depends on the evaporation of water as the driving force for CO₂ desorption, it is most viable at dry and warm conditions. When the weather is humid, the driving force is limited, making the process less practical [62,115,116].

4. DAC AT SUB-AMBIENT AND HUMID CONDITIONS

This section focuses on discussing humid sub-ambient DAC operations and identifying the associated technology gaps. While several papers have reported the influence of moisture for ambient temperature DAC, only one paper has discussed the influence of moisture under sub-ambient conditions [37]. Of course, humidity is greatly influenced by temperature. As shown in Fig. 2, with a decrease in temperature, the absolute humidity reduces dramatically. At 20 °C, 100% relative humidity corresponds to an absolute humidity of 2.3%; while at −20 °C, 100% relative humidity corre-

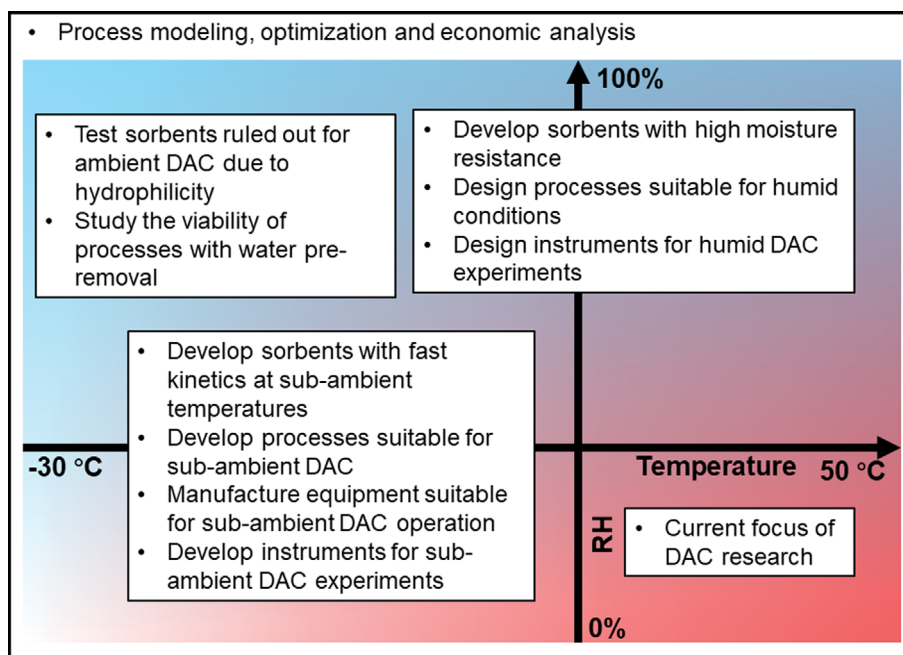


Fig. 4. Overview of research requirement for the global implementation of DAC.

sponds to an absolute humidity of 0.12%. This fact has significant impact on the material selection and process design for humid-sub-ambient DAC, creating some unique opportunities and challenges that do not apply to dry-sub-ambient, humid-ambient, or dry-ambient DAC. These opportunities and challenges are summarized below.

1. Due to the significantly lower absolute humidity at sub-ambient temperatures, sorbents that are ruled out for ambient-humid DAC, such as zeolites, may prove to be applicable for sub-ambient-humid DAC due to the much lower levels of absolute humidity.

2. For materials extremely sensitive to moisture, where even a minimal amount of moisture may compete with CO_2 for adsorption sites and hence drastically reduce the CO_2 uptake, the system can be designed to include pre-removal of moisture from air prior to CO_2 adsorption because the amount of moisture to be removed at sub-ambient temperatures is drastically lower than ambient temperatures.

3. Although the absolute humidity level decreases drastically at sub-ambient conditions, the presence of moisture in the air may still have significant impact on the process operation. Some challenges may be uniquely encountered at humid-sub-ambient conditions. For example, if the process has to go through freeze-thaw cycles due to the accumulation of water on the sorbents, the operational cycles may need to be altered significantly.

5. RECOMMENDATIONS ON FUTURE RESEARCH

Through the above literature review and analysis, we have identified the following areas where research efforts need to be dedicated to enable real-world implementation of DAC technologies. Note that this is not an exhaustive list, as new knowledge gaps will be identified as these topics are explored, undoubtedly. Fig. 4 gives

an overview of the required research efforts identified through the literature review. More detailed discussion of each aspect is provided in the sub-sections below.

5.1. Developing Sorbent Materials for Sub-ambient Temperature DAC

Due to the current lack of data under sub-ambient conditions and the considerable differences in kinetics and thermodynamics between ambient and sub-ambient DAC elaborated above, virtually all CO_2 sorbent materials studied so far for DAC applications need to be reevaluated for sub-ambient CO_2 capture applications, whether they have been shown as feasible candidates for ambient CO_2 capture or not. The tests should focus on various aspects of the material performance, including the kinetics, CO_2 uptake, regeneration energy requirements, durability, and recyclability. Besides existing materials, new sorbent materials also need to be developed for sub-ambient DAC. Below are some suggested general approaches for developing materials, conducting experiments, and presenting results for sub-ambient DAC:

5.1.1. Developing Sorbents with Good CO_2 Adsorption Kinetics

Much research attention needs to be paid to improving the kinetics of the adsorption at low temperatures. Existing studies have shown that supported amine materials with large amine molecules (e.g., oligomers and polymers) and higher loadings suffer greatly in regard to kinetics due to decreasing temperatures. To improve reaction kinetics, smaller amine molecules and perhaps lower loadings are recommended. In addition, the selection of support materials may also affect the reaction kinetics and hence need to be investigated.

5.1.2. Developing Sorbents with Both High CO_2 Capacity and Selectivity

Generally, materials for sub-ambient DAC do not need to have particularly strong binding energy with CO_2 because CO_2 capac-

ity tends to increase with decreasing temperature. However, useful materials should still offer high selectivity for CO₂ over N₂, O₂ and to the extent possible, H₂O.

5.1.3. Starting from Materials that Already Show Promise for Sub-ambient Temperature DAC

Due to the lack of data on CO₂ adsorption at sub-ambient temperatures, especially kinetic data, it is unclear which materials may be the best candidates for sub-ambient DAC. However, from the literature review conducted, when both thermodynamic and kinetic properties are considered, two types of sorbents seem to be promising for sub-ambient DAC. The first type includes zeolites, such as 5A and 13X, because they have been shown to possess promising CO₂ uptakes at temperatures between -45 to 0 °C. These materials have generally been ruled out for ambient temperature DAC because of their excessively strong hydrophilicity. However, at sub-ambient temperatures, the absolute humidity of air is much lower than at ambient temperature, rendering the zeolites potentially more feasible. The second type is supported amine materials, preferably materials with lower amine loadings and smaller amine molecules, to favor CO₂ adsorption kinetics. So far, only one report [38] has described these materials for CO₂ adsorption at sub-ambient temperatures, and therefore much research effort in this area is needed.

5.1.4. Conducting Experiments under Conditions More Relevant to Industrial Operation

Most research on CO₂ adsorption kinetics conducted so far uses CO₂ concentrations much higher than the ambient concentration (400 ppm). More kinetic studies with ambient air CO₂ concentrations, both at ambient and sub-ambient temperatures, are required for the further development of DAC technologies. Additionally, most sorbent materials studied are in powder form. For industrial operation, it is essential to shape the sorbent materials into sheets, fibers, or monoliths [102,117] to reduce the pressure drop to avoid compressing large quantities of air. Additional discussion on reducing the pressure drop of DAC processes can be found in a recent review article [118]. For sub-ambient and/or humid DAC, the pressure drop is not expected to differ significantly from ambient dry conditions, keeping other parameters constant. In general, additional research using industrially relevant operating conditions is needed, considering operation in all temperature and humidity ranges.

5.1.5. Presenting Results in a Way that Clearly Show the Applicability for DAC

When presenting CO₂ isotherms in research papers, logarithmic plots are recommended if the research intends to show the potential applicability for DAC because it is challenging to see the CO₂ uptake at 400 ppm on a linear scale isotherm plot ranging from 0 to 1 atm, which is the most common format reported.

5.2. Developing Processes for Sub-ambient Temperature DAC

In addition to materials and equipment development, another essential research topic to enable sub-ambient DAC is process simulation and techno-economic analysis. As discussed in Section 2.3, sub-ambient DAC operation induces significant differences in the sorbent performance. Consequently, thorough process simulation and economic analyses are needed to identify the optimum operating parameters, which may be significantly different from

those at ambient temperature. Below is a list of recommended topics of study in regard to process aspects for DAC processes to be extended to sub-ambient temperature ranges.

5.2.1. Modeling of the CO₂ and H₂O Diffusion behavior and Reaction Kinetics

Diffusion studies of the gaseous/vapor phase in the DAC process will form an important basis for subsequent process simulations and economic analyses because they will help elucidate the key rate limiting steps of the DAC processes [109]. While heat and mass transfer can be reasonably predicted at low temperatures for many systems, predictions of the reaction kinetics are more challenging, and therefore experimental data at sub-ambient temperatures should be used to construct kinetic models as the basis for subsequent process analysis.

5.2.2. Elucidating the Influence of Operating Parameters on Process Performance Metrics

The influence of various operating parameters on the system performance needs to be quantified for sub-ambient DAC to reach optimal operating conditions. These parameters include, but are not limited to, the duration of adsorption and desorption steps, the gas flow rate and steam flow rates during adsorption and desorption, the desorption temperature and the level of vacuum. The performance metrics include CO₂ purity in the product, percentage of CO₂ removal from air (relatively unimportant for DAC), CO₂ productivity per unit amount of sorbent material per unit amount of time, thermal and electrical energy consumption per unit amount of CO₂ product. In addition to the typical TVSA process, the ESA process may also become viable in the future when cheap and/or renewable electricity becomes available, and hence the feasibility of desorption using electricity should also be assessed and optimized based on different operating parameters such as temperatures (e.g., ambient or sub-ambient) and types of sorbent (e.g., physisorption or chemisorption).

5.2.3. Constructing Comprehensive Optimization Models for Process Economics

All the performance metrics used to analyze sub-ambient DAC processes ultimately lead to the economic performance, i.e. the capital and operating costs per unit amount of CO₂ product. Comprehensive economic models need to be built to allow the process to achieve minimal costs.

5.3. Developing Materials and Processes for DAC at Humid Conditions

Another aspect of research required for widening the application of DAC is to screen and develop CO₂ adsorbents that can withstand humid operations in a broad temperature range. Many climates have tremendous temperature spans, sometimes of over 50 °C, seasonally. The current literature suggests several types of materials that can be used for CO₂ capture at humid conditions. However, when the CO₂ concentration is reduced to 400 ppm, these materials may not be effective for CO₂ capture anymore and hence more research is needed to develop new materials. Below is a list of suggested approaches for developing sorbents and designing processes for DAC at humid conditions, both at ambient and sub-ambient temperatures.

5.3.1. Classify DAC Sorbents According to their Moisture Tolerance

When studying DAC sorbents, attention should be paid to

quantifying their moisture tolerance so that they can be implemented in geographical areas with the most suitable climate. Here we present a potential way to categorize DAC sorbent materials based on their compatibility with moisture. Category A includes materials that benefit from moisture either in CO₂ uptake or kinetics, such as many supported-amine materials. Category B includes materials whose performance is not significantly affected by moisture. Category C consists of materials whose performance is compromised under high humidity but still acceptable when humidity is low, hence eligible for DAC in cold environments or relatively dry areas. Category D includes materials that are extremely vulnerable to humidity that pre-removal of water is necessary in most circumstances, including sub-ambient temperatures. Each category of materials has their own niches of application and should be used in specific types of geographical areas to achieve optimal performance.

5.3.2. Designing Materials and Processes that can Benefit from Moisture

For DAC implementation in areas with high absolute humidity, the materials and processes should be designed properly, so that the overall performance of the process can be enhanced rather than compromised by the presence of moisture. Amine-based materials are good candidates for such applications because their CO₂ capacity usually increases in humid conditions. Besides, the materials and processes can be designed to take advantage of the purging effect of water vapor during desorption to increase the CO₂ product purity in some cases. The difference in adsorption kinetics for CO₂ and H₂O in certain materials can also be utilized to design processes where the adsorption stage is terminated before the sorbents adsorb too much H₂O. To achieve these goals, the process design and the selection of sorbent materials should be considered together.

5.3.3. Studying the Viability of Water Pre-removal at Sub-ambient Temperatures

As mentioned in Section 4, the absolute humidity decreases significantly with decreasing temperature. Therefore, some materials that cannot be used for ambient humid DAC due to strong hydrophilicity may be applicable at sub-ambient temperatures, such as zeolites 13X and 5A. On the other hand, due to the smaller amount of water to be removed, it may be economically viable to remove the water from the air before injecting the air into the DAC units. Sorbents that can selectively adsorb water at sub-ambient temperature and can be regenerated with low energy consumption are hence worth investigating. The choice of whether to use sorbents resistant to moisture or sorbents that demand prior water removal should be assessed in process economic models. It is expected that every viable sorbent material will have a specific window of practical operation, from a temperature and humidity perspective, with the most versatile sorbents having the broadest window.

5.3.4. Accounting for the Changes in Process Structure Caused by Moisture

When modeling DAC processes under humid conditions, it is important to note that moisture may induce changes in the whole process structure. For example, when zeolites are used as the sorbent, an additional water removal and sorbent regeneration system

may need to be added. These changes in process structure need to be considered prior to fine-tuning the operating parameters. For some sorbents, there may exist multiple feasible process structures, such as one with water pre-removal and another without water pre-removal. In such cases, all possible processes structures need to be assessed to compare their performance to identify the best process.

5.3.5. Linking the Operating Parameters to an Economic Model

For performance optimization, the ultimate goal should be to maximize the economic benefits of the overall process. To achieve this, the process model needs to be constructed such that the influence of adjusting operating parameters can be directly reflected by the changes in the process economic performance. Most approaches of process modeling and economic studies discussed in Section 5.2 for sub-ambient DAC are also applicable to humid DAC. However, the presence of moisture introduces new variables into the optimization process, and these variables need to be considered carefully. If water needs to be removed prior to the CO₂ adsorption, the level of removal is a design parameter because total removal may be costly and unnecessary. If total water removal is not needed, the duration of the adsorption and desorption phases need to be carefully quantified to minimize the influence of water co-adsorption. The optimum desorption temperature may be different with different moisture levels in the air. At sub-ambient temperatures, some sorbents are anticipated to withstand moisture, but they may have inferior performance in other aspects compared to sorbents sensitive to moisture. Therefore, comparisons need to be performed between these two types of sorbents by considering their respective overall economic benefits.

5.4. Equipment Development for Sub-ambient DAC: Lab Scale vs. Pilot or Plant Scale

As mentioned in Section 2.4, sub-ambient DAC technology is at the beginning of implementation for both the lab scale and pilot scale studies. The concept of achieving a climate-positive sub-ambient DAC facility starts in the laboratory. One of the essential factors to developing a lab-scale sub-ambient DAC process is to mimic actual outdoor operation under extreme cold, in contrast to the outdoor pilot plant scale where nature provides such conditions. While it is possible to generate a sub-ambient testing environment in a lab, the creation of a cold environment can become difficult when the process is scaled up to the sub-pilot or pilot scale. For laboratory studies, measurement of single component sorption isotherms at sub-ambient temperatures is straightforward with commercial equipment. However, measurement of binary or ternary isotherms, especially with condensable components like water, is not as simple. Furthermore, kinetic study of CO₂ and H₂O uptake at sub-ambient conditions requires suitable instrumentation for breakthrough studies with fine control of temperature and humidity. Laboratory experiments of this type are essential because they will determine whether additional processing of the cold air will be necessary (e.g., dehumidification) and will give insight into possible process designs. For pilot scale systems, equipment that can operate in extreme cold will need to be deployed, and if initial results are promising and if low cost, sub-ambient DAC appears practical, the supply chains for the specialized equipment will need to be developed.

6. CONCLUDING REMARKS

DAC is a crucial technology that needs intensive research focus to reduce the increasing atmospheric CO₂ concentration and global temperature. Current DAC research has only considered operation at or near indoor ambient conditions, despite the fact that DAC technologies will be deployed outdoors in varied climates. In particular, there are scant studies that consider DAC at sub-ambient temperatures and under humid conditions, which are crucial to real-world implementation. We reviewed the existing literature on DAC technologies relevant to operation at sub-ambient temperatures or humid conditions to identify the technology gaps that should be closed by future research studies. Current DAC technologies are reviewed by focusing on two aspects: sorbent material design and process development.

For DAC at sub-ambient temperatures, materials with faster CO₂ adsorption kinetics are required, since kinetics are generally slowed at cold temperatures. For amine-loaded materials, large amine molecules and high amine loadings may result in significant decreases in adsorption kinetics at lower temperatures, and hence these materials may be disfavored for sub-ambient temperature DAC. Most materials tend to show higher equilibrium CO₂ uptake with decreasing temperatures, making it potentially possible to use materials previously ruled out for ambient temperature applications due to their low CO₂ uptake or unfavorable competition with water adsorption. Two classes of materials appear to be promising for sub-ambient temperature DAC: molecular sieves, such as zeolites or MOFs, and supported amine materials with small amine moieties and moderate amine loadings. For the process operation of sub-ambient DAC, the duration of each cycle may need to be longer due to reduced kinetics. However, because materials with weaker bonding with CO₂ can be used at sub-ambient temperatures, it is probable that a lower regeneration temperature can be deployed for sub-ambient operations, with potential for lower desorption energy costs. This means that more options for providing heat can be considered and the exergy efficiency of the process may be improved.

The development of DAC at humid conditions also demands much research effort. Current literature data show that most physisorbents such as zeolites tend to be too hydrophilic to be promising candidates for DAC at humid conditions. Therefore, physisorbents that can selectively adsorb CO₂ without adsorbing H₂O need to be discovered or developed. On the other hand, most chemisorbents show enhanced CO₂ uptake at humid conditions, making them good candidates for humid DAC. The presence of moisture may have significant influence on the process design because drying may become necessary prior to CO₂ adsorption if unselective physisorbents are used. For materials sensitive to water, such as many MOFs and zeolites, the performance of processes with pre-removal of water and without pre-removal of water needs to be compared to achieve an optimal process design. For DAC at humid-sub-ambient conditions, sorbents ruled out for humid-ambient DAC due to their excessive hydrophilicity may become viable because the absolute humidity in air decreases drastically with decreasing temperature. This fact also makes the option of moisture pre-removal more practical at sub-ambient tempera-

tures due to the much lower quantity of water that needs to be removed.

For equipment design, the whole DAC system, including the sorbent beds and the regeneration system, needs to be able to withstand cold temperatures. In addition, the development of experimental laboratory equipment enabling the study of sub-ambient DAC from kinetic and competitive adsorption perspectives is also needed to facilitate sorbent material screening and process scale-up of sub-ambient DAC technologies. The study of DAC at sub-ambient temperatures is a largely unexplored research subject that will require expertise and contributions from different disciplines. To this end, much research is needed to hasten the development and commercialization of polar DAC technologies.

ACKNOWLEDGEMENTS

The authors thank Jason Lee for providing the initial sub-ambient CO₂ adsorption database and the Georgia Tech Direct Air Capture Center, DirACC. The authors also thank David Elenowitz for fruitful discussions concerning all aspects of DAC. The authors furthermore acknowledge all researchers who have contributed to the development of DAC technology to date. This research was supported by National Energy Technology Laboratory of the U.S. Department of Energy, under award no. DE-FE-FE0031952, and Zero Carbon Partners, LLC.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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