Direct Capture of CO₂ from Air & Scale-Up it for Sustainable Developments

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Abstract: Environmentalists and climate specialists today recognize need for techniques that remove CO_2 from atmosphere to mitigate changes to the global climate caused by over a century of expanding anthropogenic CO_2 emissions. Traditional modes of carbon capture; such as *pre-combustion* and *post-combustion* CO_2 capture from large point sources can help to slow the rate of increase of atmospheric CO_2 concentration. However, 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 use of chemical sorbents that are cycled through sorption and desorption for CO_2 removal from ultra-dilute gases such as air. This paper provides a historical overview of the field of DAC, along with an exhaustive description of the use of chemical sorbents and its alternative uses, applications in CO_2 Capturing.

When developing technologies, there are number of steps includes; the development of commercial process, optimization of process, scale-up from the bench to a pilot plant, and from the pilot plant to the full scale process. Reasons for these critical steps include; understanding potential waste streams, examination of macro-processes, process interactions, process variations, process controls, development of standard operating procedures, etc. 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, concluded that many new materials could play role in emerging DAC techniques**.**

Index Terms **:–** CO₂, Air-Pollution, DAC, MOFs, Kyoto Protocol, Global Warming, Scale-UP, & Sustainable Development.

I. INTRODUCTION

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 pre-combustion and post-combustion 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 ultra-dilute gases such as air as shown below in **Fig. 1**, (Choi, Dress & Jones, 2009).
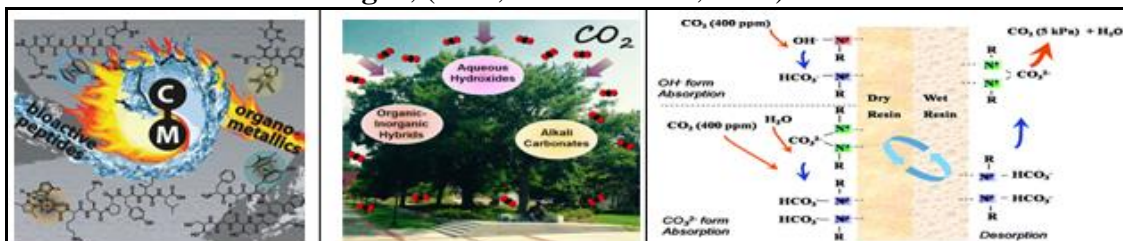

Figure 1:- The use of Chemical Sorbents that are cycled through Sorption and Desorption Cycles for CO₂ removal from AIR**.**

Forecasts indicate that fossil energy sources will remain the backbone of power generation worldwide in the coming decades, see **Fig. 2**. While the relative share of fossil power generation is expected to shrink slightly in future, absolute value of power generation from fossil fuels is expected to increase significantly. This also means that the total CO_2 emissions from power generation are very likely to grow, despite worldwide efforts to reduce greenhouse gas emissions. However, if Carbon Capture and Storage (**CCS**) or preferably Carbon Capture, Utilization, and Storage (**CCUS**) are implemented along with the maximizing of efficiency levels in power generation, there is still a chance to achieve CO_2 emission reduction targets and thus the assumed

maximum allowable increase in global warming. According to the International Energy Agency (**IEA**), CCS can play an important role, contributing to 14 percent of the global cuts in CO_2 emissions required by 2050 in accordance with the maximum 2°C global warm-up scenario, (Baciocchi, Storti & Mazzotti, 2006)**.** 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 applied by Zeman (2008).
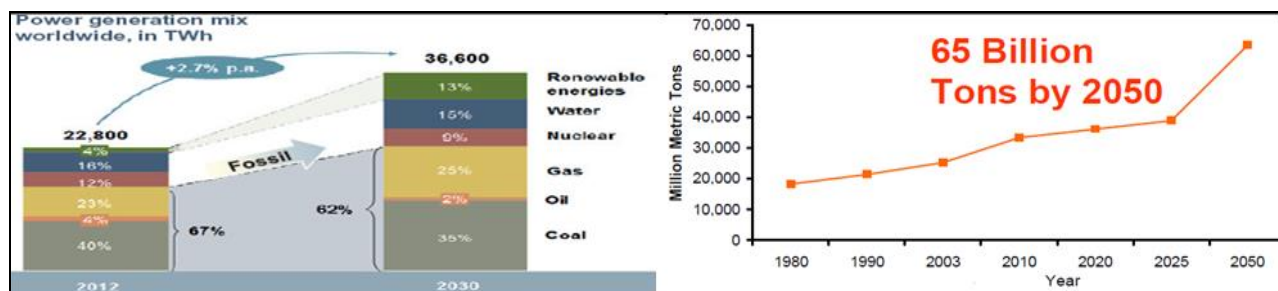

Figure 2:- Forecasts indicate that fossil energy sources will remain the backbone of power generation worldwide in the coming decades & World Carbon dioxide Emission in Million Metric Tons, (Aaron & Tsouris, 2005).

CO₂ 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 as decided, described and documented in Kyoto Protocol Agreement (1998). 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 34650 million metric tons of CO_2 in 2011. As a result, the atmospheric concentration of CO_2 has risen from the preindustrial value of 280 ppm to 401 ppm in 2015 and, it is estimated that global surface temperature will likely increase anywhere from 0.3 to 4.8°C relative to 1986–2005 data **Fig. 3**, which showing the Greenhouse Gases and their possible effects in future.
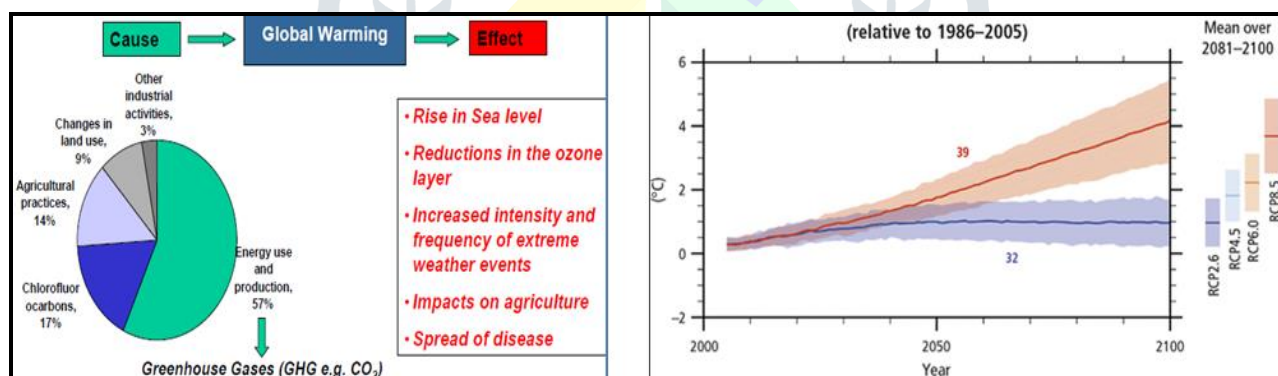

Figure 3:- Causes and Effects of Global Warming as average surface temperature change from 2006 to 2100 determined by multi-model simulations. All changes are relative to 1986–2005. Time series of projections and a measure of uncertainty (shading) are shown for scenarios RCP2.6 (**blue**) and RCP8.5 (**red**), (Hansen, Ruedy, Sato, & Lo, 2010).

I.   RESEARCH METHODOLOGY

Global warming and climate change concerns are intensifying global efforts to reduce the concentration of greenhouse gases such as carbon dioxide (CO_2) in our atmosphere. Increasingly, attention is focusing on the need to remove CO_2 from the flue gases released by several processes in countless industries including power, chemicals and steel. Carbon capture is a key strategy in meeting today's CO_2 emission reduction targets. 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. As shown in **Fig. 4**, by a review of papers published by 1300 climate experts, 97% of them support the anthropogenic origin of climate change by Keith (2009).
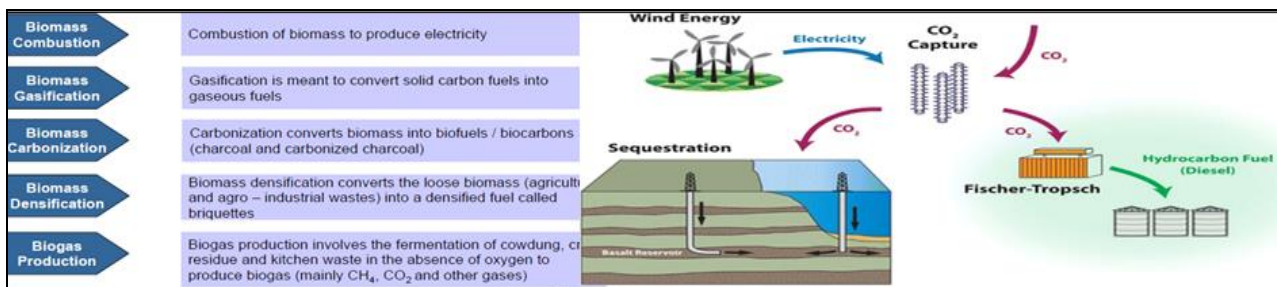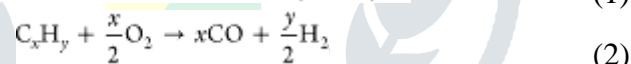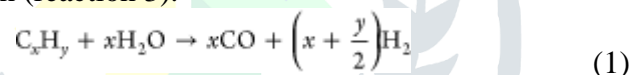
Figure 4:- Schematic of potential air capture operation proposed using Lackner's anionic-exchange resin where capture, sequestration, and potential synfuel production are collocated at a remote location.

Many industrialized countries even agreed to pursue reductions in GHG emissions by 5.2% in the Kyoto Protocol (UN Kyoto Protocol, 1998)**,** with carbon capture and storage (**CCS**) techniques being proposed as an emerging technology to effectively minimize CO_2 discharges. 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, as shown in **Fig. 4**. According to the different processes where carbon capture can be implemented, three main technologies are described by National Research Council, (2015)**,** as per the choice of strategy on the source of the gas.

Pre-combustion technologies; combining upstream gasification of fuel with pre-combustion separation of the CO_2, are typically used when starting from ***NATURAL GAS*** or ***SYNGAS*** (CO and H_2). Hot flue gas is fed to the Pre Combustion Capture (PCC) plant, where it first enters the pH-controlled Direct Contact Cooler (DCC). In addition to cooling the flue gas, the DCC also removes sulfur dioxide to prevent the downstream amine loop from forming particulates. If necessary, an additional module for removing fine particles/aerosols could be included in the DCC to mitigate amine losses at the top of the absorber column.

Several processes could 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).

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

$$C_xH_y + \frac{x}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2 \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

Capture (Oxy-fuel) during Combustion; to create mainly steam and CO_2, which can be easily separated from the flue gas. Two main technologies are used for capture during combustion, oxy-fuel combustion and carbonation calcinations. Oxy-fuel processes carry out the combustion with pure oxygen instead of air. CO_2 absorption after leaving the blower, the flue gas is fed to the bottom of the absorber column where CO_2 is removed by the **PostCap^{TM}** blue technology in a counter-current flow. High-performance packing is installed in order to ensure efficient mass transfer and to minimize the column diameter and pressure drop. Due to the absorption enthalpy, the temperature in this section increases and this has the effect of lowering the overall process efficiency. A gravity-driven inter-stage cooler is installed between the absorption beds in order to increase the general performance of the plant. The upper section of the absorber column features the advanced emission control system.

Post-combustion; where CO_2 could be scrubbed from the flue gas following the combustion. Many chemical applications rely on CO_2 scrubbing. Oxy-fuel technology could be an ideal way to increase the efficiency of combustion processes in new power plants. Apparently, the post-combustion capture (PCC) should be targeted specifically at flue gas in existing power plants, typically using a solvent to chemically absorb the CO_2 from the flue gases after the combustion process. For the regeneration**, t**he hot, rich solution enters the upper section of the desorber column and flows downwards counter-current to the vapour, which is generated in the re-boiler. CO_2 should be stripped off the amine solution at this stage. After leaving the desorber column, the CO_2 stream saturated with water could be cooled in the overhead condenser. Condensate and CO_2-rich gas are separated in the reflux drum and the condensate should be fed back to the desorber column. Steam could be used to provide the regeneration heat in re-boiler. The hot steam condensate should be sent back to battery limit, as process flow-chart, chemical's detailed with steps-wise numbers are shown in **Fig. 5**.
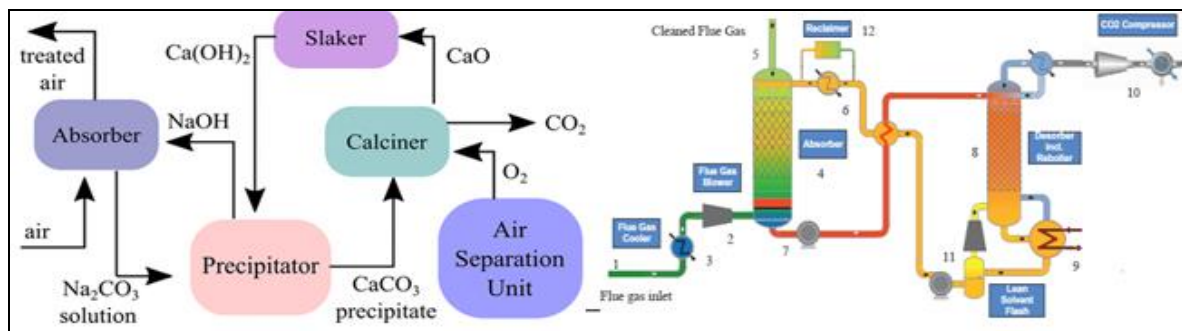
Figure 5:- Direct air capture of CO_2 with chemicals & Simplified flow diagram of the PostCap™ process.

The flue gas to be cleaned (1) is fed by a flue gas blower (2) into the absorption column (4), where it is counter-currently treated with a (regenerated or so-called "*lean*") washing agent instead of solvent (6). Prior to absorption, any useful heat in the flue gas should be recovered by means of producing steam for heating the re-boiler (9), before the flue gas is further cooled to absorption temperature in a flue gas cooler (3). During absorption, CO_2 could be captured in the solvent so that cleaned gas leaves the column at the top (5). The so-called "rich" solvent, saturated with CO_2, should be taken from the absorber's bottom (7) and heated up before being fed into the desorption column (8). There, the solvent could be regenerated by heat introduction by steam in the re-boiler (9), resulting in the release of water vapor and CO_2.

The steam should be condensed in a condenser at the top of the desorber column, so that the remaining CO_2 could be further treated - compressed in a usually multi-stage compressor (10) with intercoolers and/or liquefied - in a next step. The regenerated washing agent (lean solvent) leaves the bottom of the desorption column and is used for heating up the saturated solvent. After further cooling, the lean solvent (6) could be used again for capturing CO_2 in the absorption column. With the application of a lean solvent flash (11), the evaporation of the aqueous phase of the solvent at the bottom of the desorber should be supported by lowering the pressure in a flash drum. By doing this, thermal energy could be saved at the expense of electrical energy used for the generation of the vacuum by the flash gas compressor, leading to considerable advantages in the overall energy balance.

IV. RESULTS AND DISCUSSION

Putting captured CO_2 to good used like food-grade CO_2 in the production of food and beverages, to enhance oil recovery (EOR) and/or as a feedstock for the production of commodities like methanol or urea. Alternatively, it could be stored underground (sequestered) as a carbon abatement measure. The captured CO_2 should be further purified and liquefied for use in chemical or other industry processes. Demister used at pilot plant and test results shown in Fig. 6 in which the bars indicate the detection limits in ppb range during captured droplet's analysis, which varies due to the time period of sample taking at the Siemens **PostCap^{TM}** pilot plant.

The demister tests were also carried out during sampling 5, (see **Fig. 6**) with significantly increased gas load (F-factor 2.3 vs. 2.0 Pa0.5) and thus enforced entrainment upstream. The results was, that no solvent droplets were detected downstream of the demister. The bars in **Fig. 6** indicate the respective detection limit allocated to the time period for sampling. The emission of low-boiling degradation products depend on the stability of the solvent, i.e. its robustness towards degradation caused e.g. by oxygen or thermal stress. Concentrations of the by-products in the treated flue gas are usually very low, and emission limits vary from site to site. If necessary, respective washing steps could be applied as countermeasures.
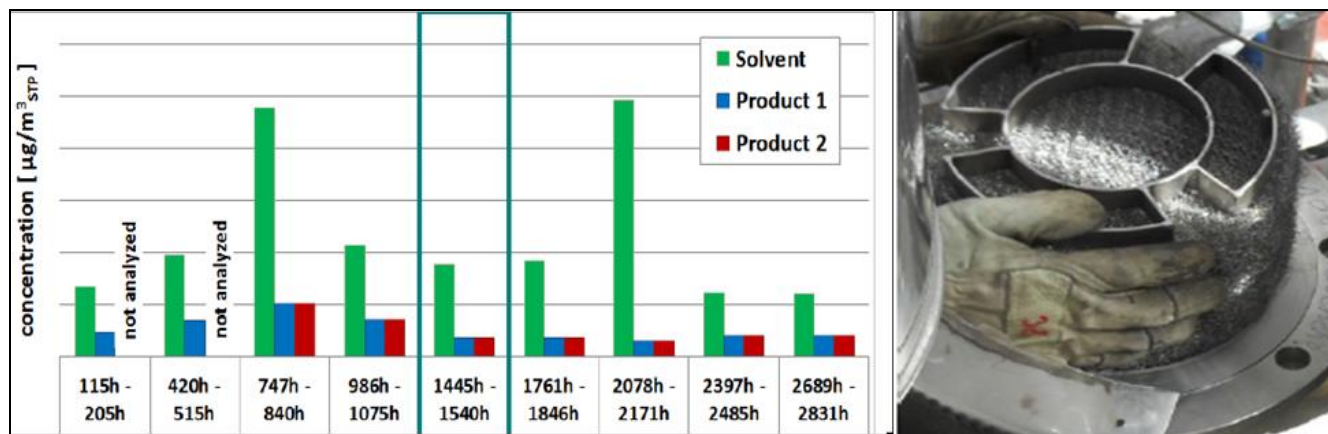
Figure 6:- Demister used at pilot plant and test results (***droplet analysis***), the bars indicate the detection limits in ppb range, CO_2 Captured at the metal organic frameworks (MOF) with period for taking a particular sample.

The selection of the suitable demister is based on common rules and experience, but has to be ensured by experiments. 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· 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. As MOFs and their tunability have been shown to be useful for CO_2 capture from air, Bazzanella and Kramer (2019) recently surveyed a range of sorbents including the three MOFs SIFSIX-3-Ni, HKUST-1, and Mg-MOF-74. These materials were studied along with more well-known zeolite 13X and TEPA-SBA-15, an amine-modified mesoporous silicate with their analytical results are shown in **Fig. 7**.
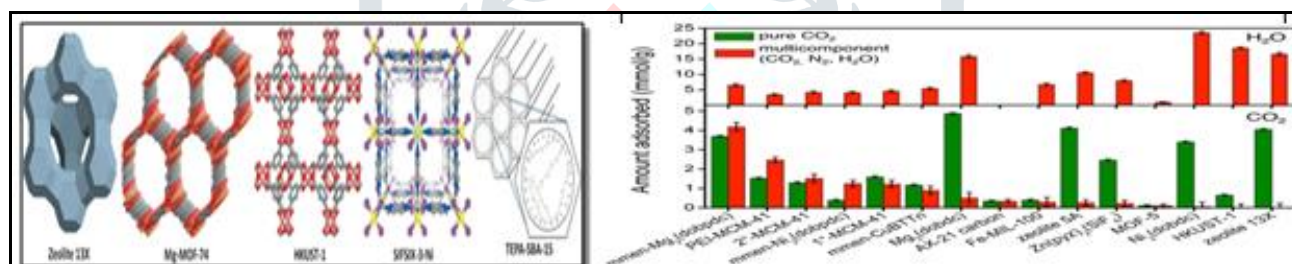

Figure 7:- Multi-component adsorption measurements for mixtures of CO_2, N_2, and H_2O at 40°C. The green bars represent the amounts of CO_2 adsorbed in a single-component isotherm at the same CO_2 partial pressure as the multi-component experiment. The red bars in the bottom (top) pane represent the amount of CO_2 (H_2O) adsorbed in the multi-component 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.

In order to minimize up-scaling risks, the same type of demister should be used for pilot tests as will be applied later for full-scale. At pilot plant scale, equipment should be validated and optimized with respect to design features. The absorber and desorber column internals in particular are essential for the efficient and reliable operation of the capture plant. The columns equipped with structured packings will be operated with the same packing type both for pilot plant and industrial scale; the packing height will basically be kept constant, whereas the cross-sectional area is increased.

The important performance parameter to be validated is the emission behaviour of the capture plant, mainly emissions of solvent and low-boiling degradation products (like NH_3) with the treated flue gas. Regarding solvent emissions, evaporation, aerosols and entrainment of droplets have to be considered. The formation of aerosols has to be prevented by appropriate technical measures. Solvent droplets carried out by entrainment have to be rejected by demisters. The post combustion carbon capture processes plants using chemical absorbtion and desorption as process principle, technological up-scaling risks could be minimized by thorough process design, supported by laboratory experiments, both for single unit operations and for complete process with the engineered plant are shown in **Fig. 8**.

Figure 8:- Typical lab equipment for investigation on property data to full scales CO_2 Capture Plant.

II. CONCLUSIONS

Liquid and solid sorbents based on alkali and alkaline earth metal oxides, hydroxides, sorbents based on supported amines, and tailored MOFs have been studied and reported. Opportunities exist for new materials that can capture CO_2 from ultra-dilute 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 would be provide the 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 ultra-dilute 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, techno-economic analyses of DAC processes as well. Overall, the field of DAC using sorbents is truly in its formative years, 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. The capture plant comprises main columns (two absorbers, one de-sorber, and two flue gas coolers) with an empty weight of up to 1,000 tons (prefabricated, steel, cylindrical shape).

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