A Technical Review of Direct Air Capture using Inorganic Sorbents.

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Abstract

Spearheaded by the industrial revolution anthropogenic CO_2 emission has been on the rise since the 18th century AD. This upsurge in the CO_2 concentration has led to the increase in global temperatures and has elicited climate change whose complete repercussions are yet unknown. There is unanimity of the scientific community on the fact that the continuous rise of CO_2 has to be subdued in order to curb the global increase of temperature. Reductions in the concentration of the carbon dioxide can be brought about by capture of CO_2 emitted by large point sources and CO_2 capture directly from the atmosphere. The capture of carbon dioxide is carried out by the help of sorbents that bind to the CO_2 and then separating this CO_2 by regenerating the sorbent which is again cycled through the same procedure. In this review we shall focus our attention on the inorganic sorbents utilized for direct capture of carbon dioxide from the ambient air. We shall do a comprehensive in-depth study and comparison of the efficacy of different sorbents, their industrial designs while taking a brief look at the limited array of technoeconomic analyses present on Direct Air Capture. However, it is important to note that development must be done to produce newer next generation materials to deploy DAC as a climate change mitigation technology on an industrial scale and to make a move towards achieving net zero emissions.

Keywords – Direct Air Capture, CO_2 capture, Climate change mitigation technology, inorganic sorbents, Technical Analysis

1. Introduction

Economic progress fuelled by the industrial revolution has generated unparalleled developments in various stages of human life. Man has been successful in increasing life expectancy and the standard of living in the last century. Tremendous development in industry, energy, transport, agriculture, communication and many more sectors were achieved during this period. However, this progress has been achieved at the cost of diminishing the health of the environment around us. Propelled by the increase in greenhouse gas (GHG) emission, global warming and climate change have started to affect the daily lives of people. This excessive emission of greenhouse gases mainly CO_2 is the main source of global climate change. An ever-increasing population coupled with the exponentially growing need of energy suggests that complete reduction in fossil fuel usage is not possible in the short term. The atmospheric concentration of carbon dioxide

has risen from the preindustrial level of 280 ppm to 415 ppm in 2021. According to the recent COP26 Summit there is an increasing consensus that CO_2 emissions generated by human activity need to be curbed to prevent further global temperature increase, and constrain global average temperature increase to less than 2 degrees Celsius above the pre-industrial level and to pursue efforts to limit temperature increase even further to 1.5 degrees Celsius rise[1]. A change of this magnitude however requires an overhaul of historic proportions for energy policies and investment of the order of $16.5 trillion, as estimated by International Energy Agency[1]. Hence, CO_2 capture and sequestration has become an absolutely unavoidable in order to achieve negative emissions.

Traditionally carbon dioxide capture commonly resolved CO_2 emissions from large point sources. These stationary sources include iron or steel industry, cement factories, huge chemical plants, oil refineries, power stations, etc. The CO_2 emitted from these point sources may be captured during the precombustion or the postcombustion processes in these factories. The precombustion method is commonly employed for the electricity production plants. This precombustion method is one of the easiest and relatively cheaper method for

CO_2 separation. This is because of the relatively higher concentration of CO_2 in the input stream to the separation process which lies between 15 to 60%. Comparing this with postcombustion carbon capture the postcombustion capture is more difficult. This is because the concentration of CO_2 has decreased to 4% by volume for natural gas plant and about 13% for coal- fired combustion unit. This decrease in concentration coupled with impurities like NO_x and SO_2 can create problems for the processes. The presence of sulphur dioxide can be destructive considering their reactivity towards amine moieties which are commonly used for carbon capture in postcombustion method. Hence a pre-treatment of flue gas by desulphurization is required. Although CO_2 capture has proven its effectiveness there are major disadvantages that need to be paid attention to. However, it is worth noting that postcombustion capture is significantly easier as compared to Direct Air Capture considering the fact that the concentration of post combustion is at least 4% by volume whereas the concentration of CO_2 in the air is nearly 400 ppm.

We shall be discussing the different sorbents and processes utilised to extract CO_2 from the ambient air and a comparison between different methods by weighing in on their advantages and disadvantages.

1.1 Rationale behind Atmospheric CO_2 extraction

The need for Direct Air Capture (DAC) was first realised in the 1990's and it was recognised as a climate change mitigation technology. However, the basic problem associated with DAC is that the concentration of CO_2 was around 0.04% by volume which was very low to design an industry level process. If one was to compare the costing difference between the capture of 1 ton of carbon dioxide of a postcombustion facility of a power station and an air capture facility it is quite evident that the cost of operating an air
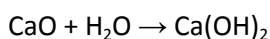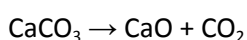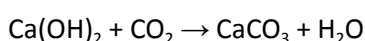
capture facility would incur higher costs for the same volume of output. However, there are some advantages of the DAC facility over the postcombustion process. A postcombustion facility has to be constructed near the exhaust of the factory to scrub off the CO_2 and then release the remaining gases into the atmosphere. Whereas a Direct Air Capture facility can be built anywhere, that is it can be built in places having low cost of real estate as the location of the plant does not affect the efficacy or the operability in any way. There is also no need of pre-treatment of the gases entering into the process considering the concentration of SO_2, NO_x or

mercury which may affect the sorbents is negligible. Also building a DAC facility is the only way yet known to achieve negative emissions. The postcombustion and precombustion methods are just instruments to delay the adverse effect of CO_2 emissions.

However, we are a long way from achieving negative emissions in the near future without significant investment from governments all around globe. Significant research work is yet to be conducted on the sequestration of CO_2 which is captured. This CO_2 capture technology coupled with sequestration can achieve carbon negative goals and a cyclic process can be obtained. Risks and uncertainties related with sequestration that needs attention are expenses, elicited seismicity and spillage or discharge of the sequestrate. Due to lack of research and the risks associated with sequestration in the short-term this process is not viable right now. However, the captured CO_2 can be utilised for other purposes like creation of carbon neutral hydrocarbons (CNHC's), as intermediates for pharmaceutical products[2] or used for the production of biofuels.

Sorbents for Direct Air Capture

Direct Air Capture (DAC) deals with air that contains very low concentration of CO_2 about 400 ppm. Flue gas capture typically can be operated by using physisorbent and chemisorbent materials as well[3]. But since the concentration of the CO_2 component is very low physisorbent materials are disregarded. Hence, chemical sorbents are used for DAC. These chemicals have a strong affinity for carbon dioxide. The typical work flow for DAC is the capture of CO_2 by using sorbents. These chemicals are then treated to release a pure stream of CO_2 and the sorbents are regenerated. Then these sorbents are again used for further capture of CO_2 and hence a cyclic process is formed. Traditionally, organic amines embedded inside porous supports are used as sorbent to capture CO_2 from the atmosphere[4]. However, the challenge related with utilizing amines as sorbents are the amine loss during evaporation in regeneration and the low amine utility ratio[5].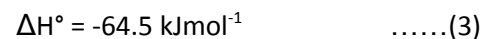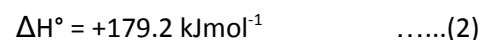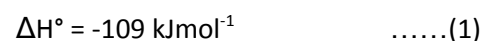 Hence, it is quite important to explore into other inorganic options to be used for Direct Air Capture. In this article we shall look into the developments in inorganic sorbents utilized for Direct Air Capture application.

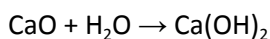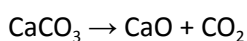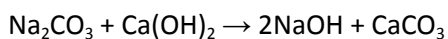**2.1 Causticization using Aqueous Hydroxide Sorbents**

One of earliest examples which was considered to be a possible solution for direct air capture was to use calcium hydroxide and react it with atmospheric CO_2[6]. Calcium hydroxide was known to have high affinity to react with CO_2 by releasing some amount of heat. Calcium hydroxide pools can be reacted with the atmospheric CO_2 and they precipitate out calcium carbonate[6]. This precipitated calcium carbonate is further separated, dried and ignited to about 700 °C[6]. This process is commonly known as calcination where calcium oxide and carbon dioxide (CO_2) are formed. Thus, a concentrated stream of CO_2 is obtained[6]. The sorbent calcium hydroxide is regenerated by adding water to the calcium oxide formed and thus closing the cycle[6].

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ $\Delta H° = -109 \text{ kJmol}^{-1}$ ……(1)

$CaCO_3 \rightarrow CaO + CO_2$ $\Delta H° = +179.2 \text{ kJmol}^{-1}$ …...(2)

$CaO + H_2O \rightarrow Ca(OH)_2$ $\Delta H° = -64.5 \text{ kJmol}^{-1}$ ……(3)

This process was only successful due to selective reaction property of the calcium hydroxide towards the ultra-dilute CO_2 present in the atmosphere[6]. However, since the

binding energy of the calcium hydroxide and CO_2 is high the regeneration process becomes more difficult and higher temperatures in the range of 700-800 °C are required to thermally decompose the calcium carbonate into calcium oxide and carbon dioxide[6]. Also considering the fact that the calcium hydroxide is mixed with water during the carbon capture process it is worth noting that the solubility of calcium hydroxide in water is low as a result increasing the amount of water and the time required for carbon capture[6]. Hence, due to the energy and low solubility factor this process is not economically viable to be pursued at a large scale.

The problem of low solubility of calcium hydroxide in water can be solved by using the Kraft's process for carbon dioxide capture[6]. In this process instead of using calcium hydroxide, sodium hydroxide is used to capture the carbon dioxide from the ambient air[6]. The reaction between sodium hydroxide and CO_2 is also spontaneous and exothermic.

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + H_2O \rightarrow Ca(OH)_2$
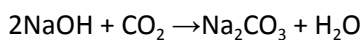
Even after overcoming various difficulties the process is not efficient enough to be utilized in an industrial scale. This is again due to the huge energy requirement during the calcination process.

Experiments were also conducted by substituting the NaOH by KOH. KOH can be a viable replacement as KOH can also act as an absorber for CO_2. Bandi, Specht and coworkers analyzed the utility of KOH as an absorber by using 1.5M solution of KOH kept in a 2-meter-long packed column[7]. It was

Initially the CO_2 is reacted with sodium hydroxide to precipitate out sodium carbonate and water is formed as the by-product[6]. This sodium carbonate which is precipitated is further treated to a process known as Causticization. During Causticization the sodium carbonate is further reacted with calcium hydroxide to give calcium carbonate and sodium hydroxide[6]. The regenerated sodium hydroxide is cycled back to absorb more CO_2. The calcium carbonate formed is passed through a calciner at around 700°C to undergo decomposition to form quick lime (CaO) and carbon dioxide[6]. The CaO which is formed is added to water to give calcium hydroxide which is then cycled back to react with more sodium carbonate[6]. This Kraft's method was already in use in the paper industry for a long time[6]. Here we use sodium hydroxide which is soluble in water to counter the low solubility problem that was encountered earlier when we used calcium hydroxide to absorb the CO_2.

$\Delta H° = -109.4$ kJmol^{-1} ....(4)

$\Delta H° = -5.3$ kJmol^{-1} ....(5)

$\Delta H° = +179.2$ kJmol^{-1} ....(6)

$\Delta H° = -64.5$ kJmol^{-1} ....(7)

successful in capturing 70% of CO_2 from the ambient air[7]. The K_2CO_3 formed is reacted with H_2SO_4 to give CO_2 as the main product and potassium sulphate as the by-product. [7]An electrodialysis unit which has a cation exchange membrane is used to separate KOH and sulphuric acid from potassium sulphate[7]. However, the drawback related to using KOH as the absorbent is that KOH is more expensive than NaOH[7]. This is one of the reasons why there are scant examples of them is research papers.

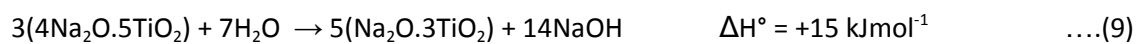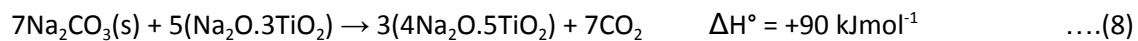## 2.2. Industrial design considerations for capturing CO_2

To make evaluations about the energy profile and to measure the economic viability, various absorber designs were analyzed to absorb a large volume of CO_2 when ambient air is passed through it under pressure. An ideal design would be such that it would allow maximum absorption of CO_2, that is have maximum surface area and the pressure drop when air is passed through it would be minimum. Physical separation procedures are commonly used techniques in chemical engineering. But the very low concentration of CO_2 coupled with the burden of removing non-carbon dioxide components makes the process unachievable. Another established method of separating out the ultradilute component could be cryogenic separation method. In this method the temperature is reduced to such an extent that the CO_2 solidifies and the pressure is kept at a constant 1 atmosphere. Considering the low concentration of carbon dioxide, the temperature has to be lowered to -160°C. After cooling at such low temperature fractional distillation can be carried out to get a pure CO_2 stream. This can be achieved at the laboratory but a process like this in the large scale is unattainable. Energy estimate for such a process may lie in hundreds of GJ/tCO_2. Separation of the CO_2 based on its molecular size can be carried out by membranes. Such polymeric membranes are being developed for their use in flue gas-based industries. However, to apply such a membrane to direct air capture application on an industrial level would require tremendous surface area of the membrane because the air which will be passed contains very low amount of CO_2. Physisorption was a viable option for precombustion or post-combustion but applying it to DAC would be impractical due to the fragmentary energy recovery during temperature-swing or pressure-swing processes.

Due to these economic and energy factors, using the chemisorption process for carbon capture from ambient air is the most economically feasible option. In chemisorption, the acidity of CO_2 is utilized to separate it from the air. Aqueous hydroxide solutions with pH in the vicinity of 13 and concentration between 1 to 6 mol/L are used for this purpose[8]. The prevalent method used in industry to capture a gas is by using tower filled with packing materials and dripping the solution down the tower while the gas is blown from bottom of the tower[8]. Contactor design for CO_2 capture from air after studies reveal dimensions different from traditionally used towers, due to the dilute nature of CO_2 a packed column with relatively short length and very large cross-section is best choice[8]. Baciocchi and coworkers have conducted experiments with one such packed column[9]. A 2.8 meter long and 12-meter-wide column packed with packing material was used, the pressure drop was 100 Pa/m and the solution used was 2 molar sodium hydroxide solution[9]. The CO_2 concentration at the input was 500 ppm and at the output the concentration was reduced to 250 ppm[9]. It was determined that the unavoidable calcination contributed the most to the 12-17 GJ/tCO_2 energy requirement depending on the system that was used[9]. Spray towers can be possible substitutes to the packed column towers that are used for DAC[10]. The spray creates a large surface area for interaction between air and liquid. It also avoids the cost of large packed towers but this spray has its own share of energy losses[10]. One of the main components that decides the reactor design is drop coalescence. A reduction in flow rate causes decrease in coalescence, which in turn reduces the CO_2 capture rate[10].

3. Direct Causticization method

In the Direct Causticization approach for DAC, the sodium hydroxide is reacted with CO_2 similar to the Kraft's process and sodium carbonate along with water are formed as the products[6]. This sodium carbonate is further causticized by reaction with $Na_2O.3TiO_2$ and releases CO_2 into the product stream with the formation of $4Na_2O.5TiO_2$[10,11]. The formed sodium penta-titanate, $4Na_2O.5TiO_2$ is then hydrolyzed to give sodium hydroxide and sodium tri-titanate as the products which are recycled to be used again in the causticization unit[11].

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad \Delta H° = -109.4 \text{ kJmol}^{-1} \qquad ....(4)$$

$$7Na_2CO_3(s) + 5(Na_2O.3TiO_2) \rightarrow 3(4Na_2O.5TiO_2) + 7CO_2 \qquad \Delta H° = +90 \text{ kJmol}^{-1} \qquad ....(8)$$

$$3(4Na_2O.5TiO_2) + 7H_2O \rightarrow 5(Na_2O.3TiO_2) + 14NaOH \qquad \Delta H° = +15 \text{ kJmol}^{-1} \qquad ....(9)$$

The reaction between sodium tri-titanate and sodium carbonate requires 90 kJ per mole of energy which when compared to the lime causticization process (179 kJ) is lesser even though the temperature range required for this reaction lies between 800 – 900 °C[10,11]. Also, in this process of causticization by titanates requires dry and anhydrous sodium carbonate to extract CO_2 by reaction with sodium tri-titanate[10,11]. Hence, an extra separation procedure is required to remove the precipitated sodium carbonate and make it anhydrous. This is also responsible for the increase in the cost of this process.

After reviewing the different Direct Air Capture processes involving aqueous hydroxide sorbents many flaws and disadvantages in the processes were observed. Lower energy efficiency, larger regeneration temperatures, water loss and problems with solubility are some of the major problems encountered. However, these processes improved the perception of Direct Air Capture from an inconceivable idea to a difficult but tangible concept. The impression of the public started to change regarding the process and researchers, scientists and engineers started to ponder over the problem in hand. In the decades continuing studies were published and experiments were conducted to find solution to the problem. A startup company known as Carbon Engineering from British Columbia; Canada has concentrated their attention to improving DAC processes by utilizing liquid alkali sorbents.

4. Solid Inorganic Bases

Previously, liquid alkali hydroxides were being used as sorbents to capture CO_2 from the ambient air. However, research was conducted by Nikulshina, Steinfeld and co-workers on the concept of using solid inorganic bases for DAC[12–15]. Lackner and Zeman had suggested the use of calcium hydroxide as the primary material to absorb CO_2 from the air[6]. A comparative study was done by Nikulshina and coworkers between CaO and $Ca(OH)_2$ regarding their CO_2 absorption properties under various conditions[12,13]. Thermogravimetric analysis of CaO and $Ca(OH)_2$ for their rates of the carbonation reaction was conducted under dry and humid conditions[12,13]. It is essential to conduct experiments in ultradilute concentration of CO_2 to completely understand the real-world implications of the use of such methods. Hence the input stream used contained about 500 ppm of CO_2 concentration. When CaO was tested carbonation temperature lies between 300 – 450 °C. These temperatures led to a primary lowering of 44% of the 500 ppm CO_2 concentration in the first minute with more

decline in the level of CO_2 as the time passed by[12,13]. Subjecting the CaO to temperature below 300 °C led to virtually no carbonation reaction. When subjected to temperatures above 450 °C the reaction is unfavored as the formation of CaO and CO_2 from $CaCO_3$ is preferred[12,13]. Experiments were also carried out in the presence of water vapor. An improvement in the extent of carbonation of the tune of 80% after 100 minutes was observed[12]. Also, the reaction took place about 22 times quicker than the one in dry condition for the first 20 minutes of the reaction[12]. The adsorption of CO_2 on the OH^- group can be the reason for this increased rate of reaction[12]. Similar kinetic and thermogravimetric (TGA) analysis was conducted for $Ca(OH)_2$ and the reaction rates were determined. It was found out that the carbonation reaction rates were higher for $Ca(OH)_2$ for both with and without water vapor[12]. The carbonation temperature also lied in the range of 200-425 °C. Utilization of the sodium based thermochemical cycles instead of using calcium based thermochemical cycles was tested by Steinfeld and coworkers[15]. After the TGA analysis of the sodium based thermochemical cycles for DAC considerably slower reaction rates of the process was observed[15]. This reason coupled with the large mass flow rate rendered the process to be inefficient.

## 5. Use of Porous Matrices with Alkali Sorbents

Studies regarding various parameters were previously conducted with liquid and solid sorbents for the capture of CO_2 from the ambient air. It is essential for the sorbents to be in direct contact with the ambient air. We know that chemisorption and physisorption are surface phenomena. As a consequence, increasing the exposed alkali surface to the ambient air is also vital for the process to take place quickly. An increased surface area of contact ensures quicker absorption and better utilization of the sorbent earmarked for the absorption purpose which in turn increases

the efficiency of the process and the cost of the procedure decreases. One of the industrial design considerations paying special importance to surface area of contact was the spray-based absorption[10]. Another way to increase the surface area of contact is by employing porous matrices as support and impregnating sorbent solution into the pores such that the exposed surface area of the aqueous alkali solution increases with the ambient air[16]. Large surface area to volume ratio is provided by microporous fiber membranes with internal diameter of the pores lying between 200-500 μm[16]. Liquid alkali sorbent solution of required concentration is percolated into the pores of this support[16]. The design of the membrane is done in such a way that the alkali solution and the incident air is flowed in a perpendicular direction to each other ensuring that the absorption of the CO_2 takes place smoothly. The alkali carbonate is formed from which CO_2 is extracted by electrolysis and the alkali is restored.

One of the experiments conducted by Pietrzak, Morawski and coworkers was done by using CaO/MgO loaded onto a porous carbon support and tested as a possible absorbent material for Direct Air Capture[17]. In this experiment, research was conducted on the effect of temperature of gas removal, moisture, pore size and loading of oxide on the efficiency of absorption of the CO_2 molecules[17]. A mixture of polyethylene terephthalate (PET) and Dolomite (Dolostone) was pyrolyzed and porous carbon matrix was formed[17]. CaO and MgO were impregnated into the porous carbon matrix and dry air of 2000 ppm of initial concentration of CO_2 was passed through the pores. The effect of different dolomite concentration in the mixture of PET and dolomite was investigated to create porous carbon and it was determined that the addition of dolomite boosted the CO_2 sorption capability eventhough the pore volume decreased[17]. At 20 °C the CO_2 absorption peaked at 70%

concentration of dolomite inside the hybrid material[17]. Analysis was conducted for moist conditions and higher sorption capacity was encountered which increased as a function of amount of water vapor peaking at about 0.48 mmol/g[17]. The dissolution of CO_2 molecules into the water film formed due to the condensation of water vapor on the surface of the sorbent could be the reason for this increased absorption. This hybrid material showed better adsorption than using only dolomite as a support.

Another hybrid composite material was tested for its usability as a support and alkali

$$K_2CO_3 + H_2CO_3 \rightarrow 2KHCO_3$$
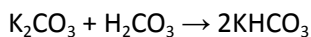
This potassium carbonate was previously used as a sorbent for flue gas CO_2 capture and was quite efficacious in its application and hence was studied as a possible solution to CO_2 capture from the ambient air[18]. Porous γ-Al_2O_3 was used as a support with K_2CO_3 and composition of the composite was tested under powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC), atomic absorption spectroscopy, transmission electron microscopy, low temperature nitrogen adsorption and thermogravimetry (TGA)[18]. When the potassium loading was equivalent to 21-23% potassium carbonate, a sorption capacity between 4.0-4.9% was reached[18]. No significant sorbent loss while the absorption and desorption cycle was observed with good repeatability upto 80 cycles. However, the biggest and the most important advantage of using this technique was that the regeneration temperature for CO_2 was between 250 to 300 °C[18]. The reduction in regeneration temperature was incredibly critical to mitigate costs as bulk of the energy input in the direct air capture process is required to regenerate the sorbent which is a compromise for the strong and selective binding property of the sorbent.

Amine based sorbents impregnated inside the porous matrix of hybrid support materials are used as a yardstick to compare the

carbonate was tested as a sorbent to be used for Direct Air Capture. Veselovskaya, Derevschikov and coworkers examined the utility of composite of K_2CO_3 and γ-Al_2O_3 for Direct air Capture[18]. The use of liquid sorbents like KOH and NaOH were already studied but its use was impractical due to the high regeneration temperatures required to extract the pure stream of CO_2[13]. Hence, compounds like potassium carbonates were suggested to be used as the sorbent. A viscous paste of aqueous potassium carbonate when reacted with CO_2 gives potassium hydrogen carbonate ($KHCO_3$).

......(10)

performance of the different carbon capture techniques. Analysis was conducted on the alkali metal (Potassium) embedded inside the mesoporous γ-Al_2O_3 and its efficiency was compared with the performance of the benchmark amine-based sorbents[19]. Under normal conditions the aqueous KOH or the K_2CO_3 is directly pervaded into the pores of the support material[18]. However, in this technique the potassium metal incorporated inside the γ-Al_2O_3 matrix is formed insitu by the calcination procedure of the already impregnated potassium acetate under inert conditions[19]. The resulting potassium-alumina sorbent composite formed is then directly tested for CO_2 capture under dilute (1%) and ultradilute (400 ppm) concentrations of carbon dioxide[19]. AlK5 is formed when 5% potassium by weight is added to the γ-Al_2O_3 support. Experiments were conducted for AlK10 and AlK5 for 1% concentration and 400 ppm concentration of carbon dioxide[19]. The materials inside the support were examined by powder X-ray diffraction (PXRD) and the existence of $KAl(CO_3)(OH)_2$, $KHCO_3$ and K_2CO_3 was noted[19]. The absorption of AlK10 was found out to be more than the absorption of AlK5 for the dilute condition of carbon dioxide under similar temperature. The intake of CO_2 for potassium-alumina sorbents was found to be better than the amine-based sorbents

under dilute (1%) concentration conditions at the same temperature[19]. However, the uptake of carbon dioxide by the polytheneimine (PEI) impregnated in $\gamma-Al_2O_3$ support showed better absorption of CO_2 than potassium-alumina sorbents under ultradilute (400 ppm) concentration of CO_2[19]. The uptake of AlK5 was 0.86 mmol/g and the uptake of AlK10 was 0.78 mmol/g whereas the uptake of 35% polyethylenimine embedded in $\gamma-Al_2O_3$ is about 0.95 mmol/g while using air containing 400 ppm of CO_2[19]. The regeneration temperatures of these materials was in the range of 250 °C with good repeatability.

It has become quite apparent that the support material used with the active sorbents have their own behavior of CO_2 adsorption. It is very important to study this behaviour and choose the correct combination of active sorbents and the support material. One of the techniques to find the appropriate support material for a specific absorbent is to test the different support materials by keeping the same active sorbent common to all of them[20]. Yttrium Oxide (Y_2O_3) similar to $\gamma-Al_2O_3$ has yielded competent results in flue gas carbon capture[21]. When tested under ambient air conditions, a composite of potassium (26% by wt) impregnated inside Y_2O_3 as a support material absorbed CO_2 to the tune of 0.64 mmol/g[21]. The regeneration temperature of the CO_2 had been reduced to a range of 150 to 200 °C[21]. A similar analysis was carried out on Y_2O_3 as the basis material with potassium carbonate as the active sorbent[21]. It was observed that there was not much of a difference in the absorption properties of carbon dioxide between K_2CO_3/ Y_2O_3 as a composite material and K_2CO_3/ γAl_2O_3 as a composite material[21].

The properties of the support material that are of paramount importance are its ability to disperse the active sorbent and providing more surface for the reaction to take place. Apart from this it is important for the support material itself to be a selective adsorber of CO_2. Activated Carbon is one of the materials which satisfactorily fulfills these properties. The implementation of activated carbon as a support material for the potassium carbonate as the sorbent material was investigated by Zhao, Guo and co-workers[22]. Wet impregnation of potassium carbonate inside the porous activated carbon with potassium levels between 5 to 25%[22]. The K_2CO_3 ultimately forms $KHCO_3$ however this reaction happens by two different routes both having distinct external conditions[22]. When the loading of K_2CO_3 is low, the temperature is high and the concentration of water is low the $KHCO_3$ is formed directly without any intermediate[22]. When the loading of K_2CO_3 is high, the temperature is low and the concentration of water is high the intermediate $K_4H_2(CO_3)_3.1.5H_2O$ and $K_2CO_3.1.5H_2O$ are formed which on further reaction form $KHCO_3$[22]. The regeneration temperature of carbon dioxide from $KHCO_3$ is between 150 °C and 200 °C[22].

In another research article Zhao, Guo and co-workers have compared various sets of support material for the same active sorbent K_2CO_3[5]. This comparison was conducted between Activated Carbon (AC), Al_2O_3, Zeolite 5A, Zeolite 13X and Silica Aerogel (SG) while K_2CO_3 was used as an active sorbent, whereas the experimental setup had ambient temperature and air containing 5000 ppm of CO_2[5]. The capacity of carbon dioxide capture at 30% potassium loading inside the supports were considered and the CO_2 sorption capacities for the Silica Aerogel, Zeolite 5A, Zeolite 13X, Activated Carbon and Al_2O_3 as supports were found out to be 0.15, 0.34, 0.53, 0.87 and 1.18 mmol/g respectively[5]. Here we can observe that Al_2O_3 when used as a support gave the best results for CO_2 capture whereas Activated Carbon when used as a support gave the highest bi-carbonation conversion efficiency[5]. Regeneration temperatures for CO_2 was determined and it was detected that when K_2CO_3 was used with Al_2O_3, Zeolite 5A or Zeolite 13X the

regeneration temperature lies in the vicinity of 350 °C[5]. However, the regeneration temperatures in the presence of Activated Carbon and silica aerogel as a support material were approximately 100 °C[5]. Owing to the high potassium conversion efficiency, great absorption characteristics and low regeneration temperatures Activated Carbon was determined to be the best support material for CO_2 capture[5].

More experimentation in the ambient air conditions (where concentration of CO_2 is in the vicinity of 400 ppm) are warranted. A comparative study of the pressure swing and temperature swing characteristics in different humid conditions must also be established. A better understanding of the synergistic effects between active sorbents and support materials will definitely improve the absorption levels in inorganic sorbents and improved regeneration temperatures can be achieved.

6. Economics Related with Direct Air Capture Technologies.

6.1. Comparison of DAC with CCS of Power Plant.

The CO_2 capture and sequestration by large immovable sources like petroleum facilities, cement factories, etc has been extensively studied along with Direct Air Capture. In CCS the concentration of CO_2 is greater than 5% (for simplicity purposes 10% concentration is considered for cost analysis) whereas the DAC happens at concentration as low as 0.04%. So, intuitively one might expect the cost and the energy of Direct Air Capture to be very high compared to the cost required for CCS. However according to Keith and co-workers the theoretical energy required for CO_2 capture from ambient air is only about 3.4 times the energy required to capture CO_2 from a facility with 10% CO_2 concentration output[8]. Further analysis by the thermodynamics point of view suggests that the CO_2 capture from air requires only about 1.8 to 2 times the energy required for CCS of a power plant with 10%

CO_2 concentration output[8]. This analysis completely changes the industrial perspective of approaching Direct Air Capture since one can consider even more reduction in costs and energy requirement considering the fact that DAC has huge advantages over CCS technique[8]. The first issue that affects the cost of a CCS of power plant is the downside of the real estate presence. A CCS facility has to be present in the vicinity of the power plants CO_2 output. A CCS facility of a power plant is restricted to be present at a geological position by 3 transportation requirements: fuel must be transported to the plant; CO_2 has to be transported from the captured site to the sequestration site and the CO_2 free energy product that is the petroleum produced/ electricity produced has to be transported to the consumer[8]. A DAC facility can be built at any place considering the fact that it derives its energy from natural resources and the capture facility is near a sequestration site. Direct Air Capture is also effective as it can remove CO_2 from all parts of economy with equal ease[8]. CCS of large point sources can remove CO_2 from that particular source only whereas DAC can reduce diffused CO_2 emissions from various small point sources where the cost of achieving reductions in emissions from the small point source itself will cost several thousands of dollars per ton of CO_2[8]. Hence, one can say over long-term application the cost of Direct Air Capture can be more or less equal to the cost of carbon capture by large point sources.

6.2. Cost Estimates for Different DAC Processes

Before performing a cost estimate analysis for the different procedures, one must understand that under different set of assumptions the final cost estimate may vary. According to Keith and co-workers the initial process of CO_2 capture by using NaOH solution and causticizing it with Lime and further calcination procedure results to an estimated cost requirement of at least $136 /t of CO_2[8]. However, by another set of

assumptions by Baciocchi, Mazzotti and co-workers for the same procedure of CO_2 capture by NaOH, causticization by lime and calcination resulted to estimates of the range $518-$568 per ton of carbon dioxide captured[9]. According to the assumptions made by Nikulshina, Mazzoti and co-workers the process of Direct Air Capture by carbonation of aqueous $Ca(OH)_2$ followed by calcination by a solar calciner and regeneration of the $Ca(OH)_2$ can cost at least $162 per ton of carbon dioxide[13]. From these examples one can understand that the fundamental assumptions and appropriation of the process can considerably affect the final cost estimates of the processes. There is a void of accurate cost estimates for the process and some researchers believe that the cost of DAC may as well be above $600 per ton of CO_2.

7. Conclusions

Carbon capture as a climate change mitigation technology had been popular from the 1990's. However, the public perception towards this technological wonder has not yet bettered. The general public and the governments of the world still have reservations regarding this method to tackle climate change. As a result, more awareness about the problems, solutions and the different techniques inside carbon capture technology needs to be raised. Due to the lack of accurate cost estimates the large-scale implementation of the technology for negative emissions is disputed. Conflicting opinions about the widespread utilization of this technology are present. Hence, the importance of a pilot-scale working model to establish accurate results of cost analysis is needed which can then be scaled further to even more large-scale facilities if the economics are favourable. Government support to climate mitigation technologies is extremely crucial for success in this area. In the last 2 decades studies were conducted on various materials that can operate under various conditions and provide a pure stream of carbon dioxide. Enhanced next-generation materials that can capture carbon dioxide efficiently and are able to regenerate the captured CO2 without any losses in energy or capture capacity are required. Primary information about the structure property relationship between the supports and the sorbents can make the process

more viable and cheaper. Also, there is necessity of newer and more efficient chemical engineering designs which can make the process more economically feasible. One can agree that carbon capture is truly in its initial phase and more research work is essential to tackle the grave dilemma of global warming. Hence the conclusion what one can draw from the debate over the cost estimates is that there is still a significant development that has to take place in order for the expenses of the process to reduce.

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