Experimental Characterization of Sorbents for Direct Air Capture of Carbon Dioxide

by

Thiago Stangherlin Barbosa

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Graduate Supervisory Committee:

Klaus Lackner, Chair
John Cirucci
Gary Dirks

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ABSTRACT

Climate change poses a serious challenge humankind. Society's reliance on fossil fuels raises atmospheric CO_2 concentrations causing global warming. Already, the planet has warmed by 1.1 °C making it nearly impossible to heed the advice of the IPCC (2022) and prevent warming in excess of 1.5 °C by 2050. Even the current excess of CO_2 in the atmosphere poses significant risks. Direct air capture (DAC) of CO_2 offers one of the most scalable options to the drawdown of carbon. DAC can collect CO_2 that is already diluted into the atmosphere for disposal or utilization. Central to most DAC are sorbents, i.e., materials that bind and release CO_2 in a capture and release cycle. There are sorbents that cycle through a temperature swing. Others use a moisture swing, or a pressure swing or combinations of all of them. Since DAC is still a nascent technology, advancement of sorbents is an important part of DAC development. There is a nearly infinite combination of possible sorbents and form factors of sorbents that can be deployed in many different variations of DAC. Our goal is to develop a methodology for characterizing sorbents to facilitate rational choices among different options. Good sorbent characteristics include high capacity, fast sorption and desorption kinetics, low energy need for unloading, and longevity. This work presents the development of a systematic approach to evaluate sorbents from the milligram to tonne scale focusing on the important characteristics mentioned above. The work identified a good temperature swing sorbent whose characterization moved from the mg to kg scale without loss in performance. This work represents a first step in systematizing sorbent characterization for rational sorbent development programs.

ACKNOWLEDGMENTS

I would like to express my deep gratitude first to my family, especially to my mother who has been supportive of my dreams. She was always there during the best and the most difficult times.

The work presented in this dissertation represent not just a step to obtain the title of Doctor of Philosophy in environmental engineering, but a giant step for myself built on years of education towards the dream to make a significant positive impact in the world. It also represents a small step for humankind`s knowledge towards solving one of the greatest challenges of our century, climate change.

The seeds of making a difference in the world started during my years of undergraduate studies at the Universidade de Caxias do Sul in the south of Brazil, where I had the privilege to study with some of the most inspiring Professors of my life. They build the foundation which lead me to believe I could do more and go further on my mission of making the world a better place. One year of my undergraduate studies (towards the end) was performed at the University of Oklahoma (OU). There are several different subjects an undergraduate in environmental engineering can take to specialize. During this year in Oklahoma (2013) I took a class named Global Climate Change IPCC with Professor Dr. Michael Richman at the National Weather Center which is part of the University. This class went deep in understanding the IPCC report 2015, which at the time was still in its draft version. Understanding of how complex and serious climate change is, I decided that my life goal is to dedicate myself to help find a solution to this complex problem.

At Arizona State University, I have started my PhD research at first on renewable energies, which is a logical pathway to solving climate change. Until I had the great privilege to take a class named Carbon Storage with Dr. Klaus Lackner. At his class I fully understood how important, necessary, and essential direct air capture and storage is for solving climate change.

I have continued my work towards renewable energies, until the covid-19 pandemic hit and shook the world. This resulted in a lack of funding towards my PhD studies and the first name that came to my mind was Dr. Lackner. I started working with the Center for Negative Carbon Emissions towards a different approach to solving climate change. This change was one of the best things that have ever happened in my life. Dr. Lackner is the best mentor and one of the best human beings I had the chance to meet. He is the smartest and most humble person I know. Moreover, the Center has an outstanding team which made the work very enjoyable and productive. I have to express my deep gratitude to Dr. Lackner and the entire team. I want to say an especial thank to Jason Kmon and Allen Wright for guidance in the laboratory and their unique skill in building and fixing anything; John Cirucci for its inspirational work and guidance in several experiments and discussions about our projects; to Travis Johnson for organizing all the financial support that made my work possible.

Finally, I would like to thank the Arizona State University for its progressive and inclusive approach and for bringing great minds together to solve the most important problems of our century. It has been a true privilege to be part of ASU, and this is just the beginning. A lot more needs to be done in the following decades to solve climate change.

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SUMMARY

Climate change is one of the greatest challenges of humankind for this century. As long as societies rely on fossil carbon for most of the energy that is so vital to societal functions, the release of carbon dioxide to the atmosphere will keep raising the global average temperature of the planet, which already is 1.1 ˚C higher than it was in preindustrial times[1]. With continued growth and development, global energy demand continues to increase despite advances in energy efficiency. Several renewable energy technologies show great promise for a transition away from fossil fuels. However, it is nearly impossible to change the world's energy matrix in a short period of time while keeping the world economy stable and society functional. According to the IPCC's Sixth Assessment Report AR6 (2022)[1], global warming should not exceed more than 1.5 ˚C relative to preindustrial times to avoid tipping points and potentially catastrophic change[1,3]. The globe is only 0.4 °C from breaching this limit and at current rates of emission would cross this line in less than fifteen years. Most likely it will be necessary to lower CO_2 concentration in the atmosphere and remove about 1,000 Gt of CO_2 from the atmosphere.

Carbon dioxide removal can be applied to point sources, or it could be directly removed from the air. The latter is commonly referred to as direct air capture (DAC). Point source CO_2 capture takes advantage of more concentrated and often very large CO_2 streams, for example at a fossil fuel power plant or other CO_2 emitter. Point source capture can be important and efficient in mitigating specific CO_2 emissions but cannot solve climate change by itself because much of the CO_2 released is diluted in the atmosphere. A large

portion of CO_2 emissions are distributed, small mobile sources in the transportation sector. The CO_2 is quickly released to the atmosphere and mixed. This makes DAC essential for solving climate change.

Since the DAC concept has been created by Lackner *et al*[14,15], it has become a growing field with several demonstration scale facilities close to industrial deployment. However, there are still important challenges to be addressed before reaching economic feasibility and achieving a scale that can effectively contribute to solving climate change. A major driver of capital and operational cost lies in the chemicals that bind and desorb CO_2, i.e., the DAC sorbent. Sorbents can be a major driver of cost due to the energy needs for regeneration (CO_2 desorption), the speed with which they can take up and release CO_2, performance limitations due to weather and engineering design; and how many cycles of absorption and desorption they last (sorbent's lifetime).

There is a great variety of chemical structures that can collect CO_2 with different DAC techniques: temperature, moisture, pressure swing, and one-time CO_2 capture. Beyond the chemistry there are form factors and engineering designs that can enhance CO_2 kinetics and minimize energy requirements. The methodologies to screen and scale a sorbent are dispersed in the literature and there is not a standard methodology which can apply to large classes of sorbents.

This work presents a standard methodology to screen moisture swing, temperature swing and one-time capture sorbents and the scalability of moisture and temperature swing sorbents from the mg scale to the kg scale. One temperature swing sorbent candidate TSB 03 maintained its high kinetics and capacity from the milligram (mg) scale to the kilogram (kg) scale with a potential for the tonne scale. Several experiments have been performed on the milligram, gram, and kilogram scale under dry and steam regeneration; a variety of form factors in which enhanced even further its kinetics as it scales. A model exercise demonstrated that the sorbent TSB 03 has the potential to absorb up to 3,000 kg CO_2/tonne of sorbent per day with an optimal form factor and engineering design.

Sorbents and their form factors will continue to evolve and better ones will be discovered. There is a need to continue to test, screen and improve sorbents to reach scalability in their diverse characteristics. This standard methodology results and modeling exercise can be used to advance DAC efforts on reaching economic feasibility and improving the CO_2 removal from the atmosphere on the timescale needed to solve climate change.

1. INTRODUCTION

1.1 Climate Change

Climate change is among the most difficult challenges that need to be overcome to maintain economic and social growth. The main contributor to climate change is the emission of carbon dioxide from the combustion of fossil fuels. It will require drastic reductions in carbon emissions and quite likely a prolonged phase of carbon drawdown to return to safe levels of carbon dioxide concentrations in the atmosphere.

Fossil fuels have been an important component in the development of today’s society. Beginning with the industrial revolution fossil fuels allowed exponential economic growth, increasing quality of life and ever an ever-larger life expectancy around the globe. However, the unabated CO_2 accumulation in the Earth`s atmosphere as the waste product of fossil fuel combustion threatens the Earth’s ecological balance and the stability of humanity`s economic and social growth that was achieved with access to vast quantities of affordable energy.

The recent IPCC report AR6[1] presents models of multiple scenarios that are based on different assumptions about policy and international developments. These models include the socio-economic impacts of managing climate change. SSP1, SSP2, SSP3, SSP4 and SSP5 assume different levels of mitigation, adaptation, and negative emissions. From a climate perspective SSP1 is the best and SSP5 the worst-case scenario. These social-economic scenarios were combined with the RCP scenarios of the previous IPCC Assessment Report AR5[3] RCP scenarios are characterized by different levels of climate forcing measured in W/m^2 by anthropogenic greenhouse gases. These scenarios are labeled by the amount of forcing by the end of the 21st century.

The new social-economical models can be described as follows[4,5]:

SSP1: This is the most sustainable scenario with few challenges to mitigation and adaptation: This scenario assumes a policy emphasis on sustainability, a continuous transition to renewable energies, a significant effort on negative carbon emissions, on reducing inequality, focus on low material production and human well-being. In this scenario the world makes significant efforts to meet the sustainable development goals[4,5].

SSP2: This model assumes an intermediate level of challenges to mitigation and adaptation. In this scenario the response to social, economic, and technological challenges is not fast enough. There is uneven growth worldwide with some countries lagging on economic and technological development. There is little effort to meet the sustainable development goals. There are some improvements on environmental protection but overall, there still is significant environmental degradation with inefficient response to environmental needs and energy demand[4,5].

SSP3 – Regional rivalry. This model includes high challenges to mitigation and adaptation. In this scenario there is a major political driving force on the rise of nationalism decreasing worldwide cooperation. As a consequence, there is less effort on the sustainable development goals, fragmentation of the world economy with less investments into and attention to solving the climate crises, education, human development, renewable energies and carbon capture[4,5].

SSP4 – Inequality – low challenges to mitigation and high challenges to adaptation: On this scenario there is high economic and technological growth with a diversified energy source on renewables, carbon-based economy and carbon capture. However, the economic growth and human development is highly unequal making adaptation to climate change a difficult challenge for poor countries fighting for resources[4,5].

SSP5 – high challenges to mitigation and low challenges in adaptation – In this scenario the economy grows worldwide with a more even social society with investments in education, health, and technological growth. However, there is an intense usage of fossil fuels and energy sources to satisfy the high energy demand associated with higher living standards[4,5].

In order to overcome the challenges of climate change, there is an urgent need of strong commitments from the private and public sector. Political trends need to follow a pathway on mitigation and adaptation. If the opposing trends prevent the necessary steps to solve climate change, the society can become nonfunctional with inequality, wars, and economic crises. A scenario that does not address climate change is unlikely to deliver stability and prosperity.

These scenario assumptions are then combined with emissions scenarios. The figure 1 presents a combination of some of these scenarios. For example, SSP1-1.9 represents the SSP1 scenario with 1.9 W/m^2 and similarly, we have SSP1-2.6, SSP2-4.5, SSP3-7.0 and

SSP5-8.5. The SSP5-8.5 scenario presents the greatest threat and or the biosphere and the humankind. This is the current World trend, in which there is a continuous increase on the fossil-fuel based development with very little global effort to shift to renewables and negative carbon emissions. This resulting increase in atmospheric CO_2 concentration can drastically shift the ecological world balance (IPCC, 2022). With the rising temperature, there is a high probability of sea-level rise, drowning major cities; ocean waters will become more acidic (carbon dioxide dissolves in water forming carbonic acid) changing the ocean`s ecological balance; an increase in forest fires in terms of frequency and acreage; changes in rainfall patterns; major effects in water availability and food production. Not only will the ecological balance change, but the quality of life will also change, resulting in major effects on the economy.

Since the beginning of the industrial revolution from the year 1830 until today the climate has warmed by about 1.1 °C. The atmospheric concentration of CO_2 increased from 280 ppm to 416 ppm. This is an increase of 1,030 Gt of CO_2 in the atmosphere. Total emissions were approximately twice as much, about 2,000 Gt CO_2 since the beginning of the industrial revolution. Roughly 50% of these emissions were absorbed by the ocean and the biosphere[6]. The planet has already warmed 1.1 ˚C since the beginning of the industrial revolution. According to the IPCC[3], in order to prevent a severe climate crisis, the planet must not warm by more than 1.5 °C from before the industrial revolution. Since warming is approximately proportional to cumulative CO_2 emissions, this gives humanity approximately 30 years to solve this exponentially growing problem. After that negative emissions become unavoidable.

The transition to renewable energies is a logical pathway to stopping climate change. However, the transition needs time to change our infrastructure and economy built relying on fossil fuels. In addition, even if the world were able to change the energy matrix to renewables overnight, the planet could still warm to dangerous levels and there would remain a serious risk of climate damages. For example, ocean rise will not stop unless CO_2 concentrations in the air are lowered. Thus, there is an urgent need to remove at least some of the carbon that humans emitted since the industrial revolution a large fraction of which resides in the atmosphere. One of the few ways to remove the diluted carbon is through direct air capture (DAC). DAC is therefore an important option, as removal of carbon from the environment at very large scale is becoming unavoidable.

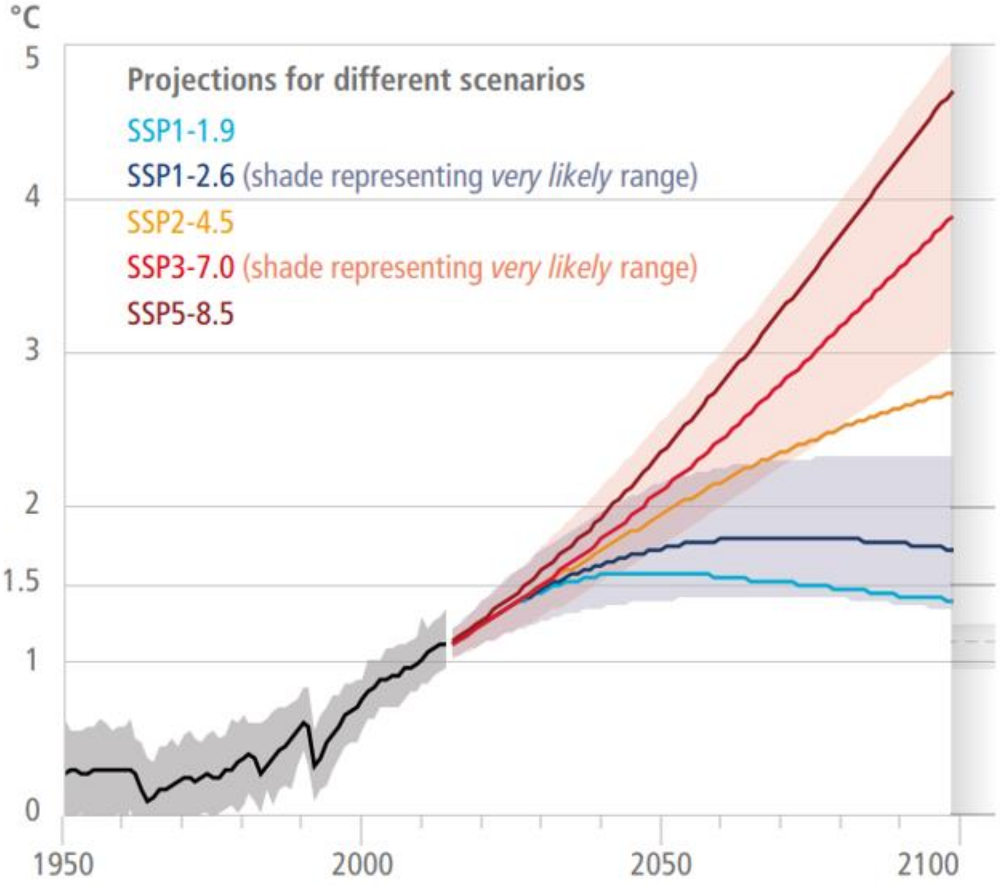


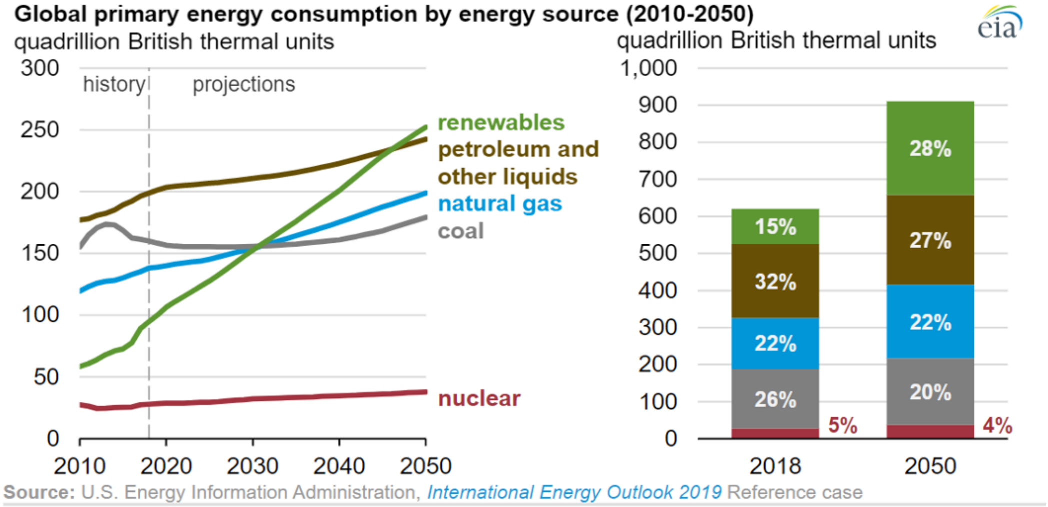
Figure 1– IPCC Ar6 20221 Model Scenarios of Average World Global Warming in °C.

1.2 Need for Carbon Removal

Currently the World demands 1,300 Mtoe (Mega tonnes of oil equivalent) (figure 2) per year or 17 TW (Tera Watts) of primary energy[7]. Of this energy, 84% come from fossil fuel sources: 33% oil, 27% coal and 24% natural gas[7]. This results in total CO_2 emissions of 36

GT per year. The world is currently rapidly increasing its use of renewable energy sources. However, at the same time it greatly increases its energy demand, thus demand for fossil fuels is also increasing. Global energy demand is expected to grow by 47% by 2050[10,11]. Despite a projected sharp increase in the renewable energies of 165% increase by 2050 when compared to 2020 levels, liquid fuels will still increase by 28% (natural gas by 16% and coal by 10%)[10,11]. The world currently has an estimated 1.65 x 10^{12} barrels of known oil reserves and it current has a consumption rate of 3.54 x 10^{10} barrels/year[12]. Thus according to these estimates there is about 47 years left of oil reserves. Despite several discussion in which the shift to renewable energies need to happen it a very short period of time (10 – 30 years), such a abrupt change it is nearly impossible as our energy systems infrastructure and economy rely on fossil fuels.

The SSP-RCP scenarios need negative carbon emissions to mitigate Global Warming[1]. The political and economic decisions on the SSP scenarios will determine the intensity of carbon capture and storage. The most likely scenario would be a middle ground in which the world will steadily transition to renewable energies and have a medium scale effort in carbon capture and removal to allow a stable economy for this transition. If the carbon capture and removal needs are too intense, the rate of the growth on this technology would not be feasible. Thus the solution for the problem is a balance between technological development, energy demand, human society quality of life growth and carbon capture and storage development in which we can bend the curve and keep the planet from warming above 1.5 °C by the end of the century[3]. Considering a reasonable time window to shift to renewable energies, the world is already too late to stay below 1.5 °C warming. In order to keep the climate stable, it is necessary to remove at least 1,000 GT of CO_2 from the atmosphere by 2050[3]. As the world has already emitted 135 ppm above the 280 ppm, direct air capture or similar technologies become necessary, even if were able to avoid or capture all the emissions from other sources in the world, these would not be enough to solve climate change.



Source: U.S. Energy Information Administration, *International Energy Outlook 2019* Reference case

Figure 2 – Global Primary Energy Consumption by Energy Source (2010-2050).

1.3 Close the Carbon Cycle with Renewable Energy

A large portion of carbon dioxide emissions is generated in the combustion of fossil fuels outside the large point sources. Carbon dioxide emissions from airplanes, ships or heavy trucks would be difficult to capture at the source. It also would be difficult to eliminate the use of hydrocarbon fuels in these applications. Furthermore, even for the large point sources, it can be difficult to avoid the consumption of carbon-based fuel. For example, it is expected that the use of natural gas or similar fuels will be necessary for a long time to back up intermittent renewable energy. Long term storage of energy is best accomplished in liquid fuels. Furthermore, steel plants and cement plants deploy processes that take advantage of carbon in the process. Therefore, there is a growing interest in developing methods for extracting the carbon directly from the environment. One of the most important is the removal of carbon dioxide from the air, i.e., direct air capture.

Carbon dioxide can be extracted from the atmosphere with a concept called direct air capture (DAC). Specific chemicals known as sorbents have affinity for CO_2 and this can be utilized combined with engineering processes to remove CO_2 directly from the atmosphere. Such process can buy time for a transition for renewable energies. Moreover, CO_2 can be converted to renewable natural gas, CH_4 and hydrocarbons as liquid fuel. Carbon dioxide through DAC can be captured utilizing renewable energies, converted to renewable natural gas and renewable liquid fuels, closing then the carbon cycle. Ultimately more carbon dioxide needs to be stored than utilized creating a negative carbon emissions scenario to remove about 1,000 Gt of CO_2 as discussed in the previous subchapters. The utilization of CO_2 to close the carbon cycle as a renewable energy source can add market value to store carbon dioxide.

1.4 Direct Air Capture (DAC)

Direct air capture is a concept created by Lackner *et al* (1995; 1999)[14,15] referring to capturing CO_2 directly from the air where it is highly diluted. Direct air capture can compensate for past or concurrent CO_2 emissions. The atmosphere is a well-mixed fluid in which carbon dioxide once released quickly mixes homogenously. Currently the CO_2 concentration into the atmosphere is 415 ppm[1] a concentration that is very small and dilute for a gas into the atmosphere, making it challenging to remove it, but this concentration is sufficient to unbalancing the Earth's climate, a concentration 48% above that before the industrial revolution.

The extraction of CO_2 directly from the atmosphere started with the concept as as tool to manage carbon dioxide instead of changing the energy matrix rapidly, which is not economic feasible[15]. The technical approach investigated utilized $Ca(OH)_2$ solutions. which can effectively absorb CO_2 just by simple bubbling air into it. The reaction is exothermic releasing a substantial amount of energy, 114 jK/mole, forming a stable mineral, calcium carbonate[15]:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O + 114\ kJ$$ [15]

However, the energy to cycle back to CO_2, i.e., to make a CO_2 swing is substantial as it requires calcination that consumes 180 kJ/mol[15]. The study noted that for every mole of CO_2 generated in the combustion of coal, one obtains 475 kJ of heat[15]. Thus, the energy to capture back CO_2 from the air can be held to a fraction of the energy obtained from CO_2.

However, such engineering process will require other energy consuming processes such as drying of the wet sorbent, making feasibility a difficult goal. Nevertheless, this study showed a pathway to be developed to reach feasibility for direct air capture. Nowadays a number of industries have demonstration scale facilities close to a feasible price for CO_2 and a number of different research and development efforts using different technical approaches are underway. The chemical compounds that bind CO_2 are known as sorbents.

There are many sorbent candidates that can operate with much lower energy inputs than calcium hydroxide, which is a good example of a temperature swing. In a temperature swing, CO_2 is pumped to higher pressure by absorbing it at a low temperature and releasing it at much higher partial pressure at high temperature. Amine-based sorbents and others require far less energy to perform a variation of regeneration cycles, including temperature, pressure, and moisture swings. At present DAC is still too expensive, but its development is moving rapidly as could be one of the most important solutions to solve climate change.

Once the need for negative carbon emission scenarios was widely accepted, direct air capture became an essential tool for addressing climate change. According to the IPCC report 2022[1] even if we replace all our energy sources with renewable sources and reduce CO_2 emissions to zero as fast as possible, the planet would still warm to above 1.5 °C until the end of the century[3]. In most scenarios stabilizing the climate requires negative carbon emissions to remove on the order of 1,000 gigatons of CO_2 before the end of the century[1].

DAC is a unique technology to stabilize the world's climate, because it addresses a number of important aspects:

1) *The ability to capture CO_2 emissions from mobile and distributed sources*[16,24]: About half of the total CO_2 emissions are from smaller and mobile sources such as cars, airplanes, buses, and the transportation sector in general[24]. These mobile sources mostly use fossil fuels and lack the capability to capture the CO_2 at the source. The CO_2 once emitted will quickly mix in the atmosphere homogenously and is best captured with DAC. Despite other alternatives such as electric vehicles, it will take a long time to convert the transportation sector to 100% renewable energies. Most of the energy source to charge electric vehicles are from fossil fuel generated electricity. Thus, DAC becomes an essential solution for offsetting the CO_2 emissions of the transportation sector.
2) *The production of synthetic fuels*[24]: CO_2 can be captured not only for storage but also to be converted into a usable product. One of the most promising scenarios is the use of CO_2 in the production of renewable synthetic fuels. CO_2 can react with H_2 forming CH_4 creating a renewable form of natural gas. It is also possible to form carbon monoxide, methanol, or formic acid from carbon dioxide and hydrogen. These small molecules can be converted to longer carbon chains forming DME, diesel and synthetic gasoline[24]. Energy cost is the main challenge for capturing and converting CO_2 efficiently into synthetic fuels, but there are feasible technological pathways. These technologies are helped by the rapidly dropping price of intermittent renewable energy. Essentially it is possible to close the carbon cycle through the air. Carbon is released during fuel combustion. It then captured back with DAC and used to produce new

fuels whose carbon is then released back into the atmosphere in a continuous, sustainable cycle.

3) *The ability to capture carbon near remote CO_2 storage sites*[24]: CO_2 storage sites are located in particular geological formations and in most cases are located far from industrial sources of CO_2. Remote storage sites become accessible by taking advantage of the fact that the CO_2 on earth is well mixed[16,24]. This flexibility eliminates the need for large CO_2 pipelines creating a high financial cost and preventing CO_2 leakage[24].
4) *CO_2 leakage insurance*[16,24]: CO_2 storage sites are considered safe to store CO_2 for thousands of years with a high degree of confidence. However, the potential of CO_2 leaks can add risks to the feasibility of the project[24]. Thus, a CO_2 capture capacity that can offset potential leaks greatly minimizes the risks associated with the project, enhancing feasibility of the overall process.

DAC can be performed with different scientific techniques. Most of them involve sorbents that are regenerated by various means. Typical examples include sorbent cycles that involve thermal, pressure, moisture swings or a combination of these systems such as temperature-vacuum swing and even temperature-vacuum swing with added moisture on the desorption cycle. In all cases the idea is that sorbents can rapidly load up with CO_2 in the ambient air and release it rapidly in a regeneration step. Regeneration can take advantage of heat, pressure, or moisture or a combination of these to provide the necessary driving force. Different materials known as sorbents (solid or liquid) have different chemical and physical properties that can perform thermal, moisture, pressure swing and one time CO_2 capture sorbents.

1.5 Advances of DAC Towards Industrialization

As discussed in the previous sections, DAC is essential for solving climate change and it must be deployed at a large enough scale to have a significant impact on reducing the effects of climate change. It needs to remove on the order of 1,000 Gt of CO_2 by 2050, resulting in 36 Gt CO_2/year for the next 28 years, while the world transitions to renewable energies. Less conservative estimates consider the removal of 20 Gt/year by 2050 in order to prevent the warming above 1.5 °C[25], thus it is possible to assume the range is between 20-36 GtCO_2/year to be removed directly from the atmosphere. Currently the total CO_2 emissions in the world is 36 Gt CO_2/year, thus there is a need to have enough DAC to offset current CO_2 emissions.

The development of DAC has made substantial progress since the first published paper on the subject in 1995 by Lackner *et al.*[14] During the 27 years of development, from a first concept paper there are several full-scale DAC operations trying to reach economic feasibility. The metric utilized to reach the feasibility is the cost per tonne of CO_2 captured. The ideal cost to reach feasibility on DAC is ~ 50 $USD/t-$CO_2$ other indicates it needs to be only < 100 $USD/t-$CO_2$.

Nowadays there are 19 DAC plants operating worldwide, capturing more than 10,000 tons of CO_2/year or 0.01 Mt CO_2/year. These companies have potential to achieve industrialization of DAC. The companies operate with different sorbents in which lead to different engineering process on absorb/adsorb and desorb CO_2. As discussed on previous section, the sorbent and its form are essential determining the engineering system, energy of operation mainly related to the regeneration (or desorption) step of the process.

Carbon Engineering is a Canadian company building a new air capture facility in Texas USA. They have proposed the world's largest DAC capture system planning to capture 500 kt CO_2/year[24]. This facility aims to achieve a levelized cost of 170 \$USD/t-CO_2[24]. Carbon engineering system is bases on a liquid (or aqueous) sorbent as potassium hydroxide. This sorbent requires high temperature for regeneration (desorption of CO_2) and thus can be classified as high temperature aqueous solution sorbent (HT aqueous solution)[21,24]. The main reactions of the system are[21]:

$$CO_{2(g)} + 2\ KOH_{(aq)} \rightarrow H_2O_{(l)} + K_2CO_{3(aq)} - 95.8\ \text{kJ/mol}^{21}$$

$$K_2CO_{3(aq)} + Ca(OH)_2 \rightarrow 2KOH_{(aq)} + CaCO_{3(s)} - 5.8\ \text{kJ/mol}^{21}$$

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} +179\ \text{kJ/mol (calcination)}^{21}$$

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)}^{21}$$

Carbon Engineering HT aqueous solution require 900 °C for sorbent CO_2 desorption, been one of the main limiting parts of the process[21,24]. Nevertheless, the company according to their published paper in 2018[21], is aiming for a levelized cost of 94-232 \$USD/t-CO_2 based on their TEA model assuming an industrial plant of 1 Mt-CO_2/year capture. Recently the company claimed to be able to achieve 80 – 140 USD/t CO_2 captured, purified and compressed to 150 bar[24] at > 1 Mt CO_2/year captured. However as there is a large demand for heat and the heating is provided by natural gas, their DAC plant would co-capture 0.5 ton of CO_2 per tonne of CO_2 captured[24]. The reported costs in the literature are based on total captured CO_2 without taking into account the net CO_2 to be captured offsetting this 50% decrease in efficiency. If this is taking into account, it would greatly increase the cost of net-captured CO_2[24]. Carbon engineering is still working on other possible scenarios such as utilizing electricity for heating.

Climeworks is a Swiss company that started with special amine functionalized cellulose sorbents[24]. These solid sorbents can be regenerated at a desorption temperature of about 100 °C. The company operates utilizes fans to push air through the contactors requiring on average 250 kWh_{el}/tCO_2 captured mainly for the fans and control systems[24,32]. In addition, the system needs heat for the regeneration process on average 1750 kWh_{th}/tCO_2 of low-grade or waste heat[24,32]. A full cycle time of their system takes 4-6 h with an output of 99.9% pure stream of CO_2[24,32]. The company was founded in 2009 and also built a partnership with Audi and Sunfire working on a pilot plant that captures CO_2 and converts into synthetic diesel[24]. The company constructed in 2017 a commercial scale DAC plant commercializing CO_2 capture for greenhouses. Another DAC unit was installed in Iceland to permanently fix CO_2 in a mineralization process 700 m underground[24]. The company is the first to offer a CO_2 online subscription to offset personal CO_2 emissions. The company estimates that at large-scale plants the cost of CO_2 capture will be 80 USD/tCO_2[24].

Another company that operates at lower temperature for regeneration is Global Thermostat. It utilizes an amine-based polymer sorbent with a regeneration temperature is on average 90 °C[24,32]. The total cycle time is 30 minutes with a very short regeneration time of 100 s. The company utilizes saturated steam at sub-atmospheric pressure as direct heat transfer fluid to desorb CO_2 to achieve such fast desorption process. In addition, they are able to recover 50% of the heat utilized for regeneration. Their system utilizes an average of 205 kWh_{el}/tCO_2 electricity and 1,290 kWh_{th} as thermal energy[24,32].

Antecy is a company founded in 2010 located in Netherlands (which now works in partnership with Climeworks) operates at 90 °C desorption temperature using low-grade heat[24]. The company utilizes a K_2CO_3 composite sorbent[24]. This slightly lower temperature when compared to Climeworks is due to the utilization of air evacuation utilizing water to reduce the pressure[24].

The company Carbon Collect with partnership with the Center for Negative Carbon Emissions and the Arizona State University is currently developing an engineering design that captures CO_2 without forcing air through the sorbent. This system relies on the natural energy of the wind to provide CO_2 to the sorbent for the absorption step of the process. This processed is named passive direct air capture (PDAC)[25]. The engineering design is named MechanicalTree^{TM} for its resamblance with a natural tree. The mechanical tree is designed to work with various sorbents. Currently, in the year 2022, the company and the CNCE are installing its full-scale pilot plant at ASU Tempe campus. The pilot plant aims to capture 84 kg/CO_2/day. The idea is this engineering process operates in clusters of 12 MechanicalTrees, capturing a total of 1 tonne CO_2/day[25].

Fasishi *et al* (2018)[24] evaluated a TEA classifying the temperature swing systems into HT DAC (high temperature for regeneration DAC) and LT DAC (low temperature for regeneration DAC) and projecting its costs as the DA scale cumulative increase its capacity. The HT DAC system was based on Carbon Engineering data and general process and LT DAC was based on Climeworks, Global Thermostat data, basing their analysis in a general LT DAC system process.[24] Their model analyzed the levelized cost of CO_2 (LCOD) in the period 2020 to 2050 as the DAC system scales[24]. They have assumed the DAC scaling as a 100 % base scenario and a 50% conservative scenario. The CO_2 capture assumed for the base case scenario was 1.5 Mt CO_2/year and reaching 15,356 Mt CO_2/year from the year 2020 to the year 2050[24]. For the conservative scenario the CO_2 capture was 1.5 Mt CO_2/year and reaching 7,678 Mt CO_2 respectively from the year 2020 to 2050, essentially half of the scaling up from the base case scenario[24]. As a result the model prediction for LT DAC base case scenario from a cost of 781 USD/tCO_2 decreased the cost with scale to 90 USD/tCO_2 captured[24]. Considering the conservative scenario LT DAC from the cost of 781 USD/tCO_2 decreased to 213 USD/tCO_2 captured[24]. Same scenarios were performed to model the HT DAC systems. The HT DAC systems costs went from 815 USD/tCO_2 in the year 2020 to 222 USD/tCO_2 with the conservative model and from 815 USD/tCO_2 to 93 USD/tCO_2 with the base model[24]. Thus based on thus model the LT DAC system reaches a slightly lower cost as it scales based on this particular TEA. The costs of both HT DAC and LT DAC demonstrate a tendency for feasibility. However there are other important factors to be considered. The LT DAC system as it has a much lower heat energy for regeneration when compared to HT DAC system (~100 °C vs. 900 °C), the LT DAC systems can feasibly use heat waste for its energy source and energy from solar or wind as its renewable energy sources. HT DAC systems as it is nowadays needs a substantial amount of natural gas or fossil fuel energy source for its regeneration energy, making more challenging when considering the net CO_2 captured and stored. In addition, LT DAC system rely mainly on solid sorbents in which has a greater variety of chemical and form factors compositions in which shows a pathway for continuing improvement, utilizing similar already developed engineering systems for DAC.

A study conducted by Ozkan *et al.*[25] projected the area necessary to capture 20 Gt CO_2/year based on the Climeworks and Carbon Engineering CO_2 absorption rates and the size of theirs engineering systems at industrial scale. Based on this study Climeworks would need a total of 2.4 million plants[25] to capture 20 Gt CO_2 with a total area of 1,920 km^2. Carbon Engineering would need about 9,980 plants[25] to capture the same amount resulting in a total area of 1,996 km^2. This area seems very large as the article compares it with the size of New York City and represent about 2.5 times the size of the city. However, putting it into a different perspective, the corn plantation in the U.S. is 371,097 km^2 Thus for both companies this represent an equivalent area of 0.5 % of the U.S. corn plantation to solve climate change with DAC. From this perspective and accounting to world`s capability of building industries, this is already a technological achievable goal. Nevertheless, there are still important challenges regarding the economic and energy feasibility of the processes in which needs to be addressed in a relatively short period of time to prevent the world from warming above 1.5 °C on average from the pre-industrial levels.

1.6 Challenges of DAC Towards Industrialization

Despite all the advances in DAC technology and the establishment of 19 operating plants worldwide, the capture of CO_2 with DAC at 0.01 Mt CO_2/year in 2022 is still very small. To resolve climate change, one needs to capture between 20-36 Gt CO_2/year by DAC by 2050 to prevent global temperatures to rise above 1.5 $^{\circ}$C as discussed in previous sections. Thus, there is a need of scaling up several million-fold.

A study by Ozkan *et al* (2022)[25], shows the three main areas necessary to improve DAC in which can drive economic feasibility: 1) contactors (facilitate air contact with the sorbent); 2) sorbents and 3) regeneration. All three issues are tightly coupled to the physical nature of the sorbent. In other words, sorbent development is at the core of driving DAC costs down. Sorbent chemistry and sorbent form factor are the main drivers of contactor design and the energy required for regeneration very much depends on the sorbent's binding energy with CO_2, its tolerance to temperature and water and the temperature or water requirements for breaking the bond between the sorbent and the CO_2. Thermal swing sorbents must be heated to release the CO_2; moisture swing sorbents release CO_2 in the presence of moisture, there is no need of heating for regeneration, the water equilibrium provides the energy for absorption and desorption. The development, deployment and maintenance of sorbents becomes one of the highest costs for DAC technologies. The capital costs can be high as the sorbent is a central part of the process and there is a need of hundreds of kg in a hypothetical DAC pilot plant. In addition, the operational costs can be greatly affected by the type of sorbent utilized. A sorbent that needs high temperature for regeneration and/or much time for it, will drive the operational costs significantly.

Sorbents characteristics such as cycle time, loading capacity, rate of degradation (how many cyles it lasts) and energy required for regeneration are key components driving DAC costs[17]. The optimization between the sorbent`s loading capacity and cycle times, for instance, can maximize the economics of DAC process[17]. The kinetics of a sorbent decreases as the sorbent approaches to its upper limit capacity. Thus evaluating the kinetics of a sorbent will determine the optimal cycle times. In addition, sorbent`s form factors and characteristics are influenced by weather conditions, wind velocity, temperature and humidity levels. Thus, understanding the detailed characteristics of a variety of different sorbents is essential for optimizing DAC and achieve the economic feasibility necessary to operate on the scale to solve climate change. One of the key findings according to Azarabadi and Lackner (2019)[17] was that the rate of degradation of a sorbent is very important. A sorbent must survive tens if not hundreds of thousands of loading and unloading cycles to assure economic feasibility of DAC[17]. The higher the cost of the sorbent the more cycles it needs to survive. However, as lifetimes of sorbents become very long, the cost of capital as reflected in the discount rate will limit the economics of more expensive sorbents.

As sorbent`s are key of any DAC engineering project design, optimization, and energy requirements, sorbent development becomes a key piece in making DAC economic feasible. There are many chemical combinations to be tested under many different form. One can expect a continuous evolution of better sorbents. To compare among different sorbents it becomes important to define standards tests that all sorbents can be subjected to. The sorbents need to be systematically tested, characterized, screened, and scaled up to compose this key component on engineering design and economics. There is a need to standardized procedures for screening sorbents, for comparing sorbents and for evaluating their potential starting with early laboratory samples to considerations of how to best scale to full production.

It is the goal of this thesis, to lay the groundwork for such intercomparisons and evaluations of sorbents as they are developed.

2. DAC SORBENTS

2.1 Introduction

A critical component of a direct air capture system is the sorbent. Sorbents that have been developed in the past were designed for very different applications. For example, in flue gas scrubbing[33] the concentration of CO_2 is two orders of magnitude higher than it is in direct air capture. On the other extreme, removing CO_2 from air with sorbents has been practiced in the past to produce CO_2 free air, for example for air liquefaction. This contrasts with direct air capture which aims to optimize capture rates than the cleanliness of the rejected air stream. Lastly, removal of CO_2 from submarines and space craft tends to operate at an order of magnitude higher CO_2 concentrations. Moreover, these applications are not seriously constraint by economic concerns.

Given the novelty of the direct air capture application, it is not surprising that sorbent development for direct air capture is still nascent, and methodologies for measuring their performance and characterizing their most important parameters are still in flux. Our goal with this thesis is to develop a systematic approach to characterizing sorbents as they are developed. Since the range of possible sorbents is very large and the issues that need to be considered range widely and depend on the goal of the development effort, the thesis aims to initiate the development of the methodology and will, by necessity, focus on a few exemplary issues that will need to be worked out.

Not all direct air capture technologies rely on sorbents. For example, at ASU researchers are investigating actively pumping membranes that provide a different method of separating CO_2 from background air. Other researchers investigated a technology named electrochemical CO_2 capture which works as a fuel cell capturing CO_2 as carbonate and bicarbonate[31]. Nevertheless, the vast majority of attempts to collect CO_2 from ambient air rely on sorbents. Sorbents are a natural choice, as there is little energy expenditure associated with bringing air in contact with the sorbent. The process of binding CO_2 is exothermic and releases energy, it is the regeneration of the sorbent and the associated concentration of the recovered CO_2 that requires energy. The high dilution of CO_2 in air favors processes that minimize work that needs to be done on the bulk air. As a result, any efforts in heating, cooling, drying, moisturizing, pressurizing, or expanding the air must be minimized. This makes a sorbent that simply takes CO_2 out of the passing air an obvious choice.

DAC sorbents are chemical structures that can be liquid or solid. They have the ability to bind (absorb or adsorb) CO_2 directly from ambient, atmospheric air. For this binding to occur, the affinity of the sorbent to CO_2 must be high enough that it can readily bind CO_2 at a partial pressure of 40 Pa or less under ambient temperature conditions. On the other hand, if the sorbent is to be used more than once, its affinity to CO_2 cannot be so high as to prevent its ready removal. Desorption of the collected CO_2 must happen without too much effort or energy input. Desorption can be induced by heat, or moisture or a drop in partial pressure of CO_2, or a combination of these approaches.

The chemical structure of the sorbent determines if it is a moisture-swing, thermal-swing or pressure-swing sorbent. Some thermal swing solid sorbents such as calcium or magnesium oxides or hydroxides, bind CO_2 very tightly as carbonates. For example, $CaCO_3$ desorbs CO_2 at around 900 °C (calcination point). For a sorbent that is used once and then sequestered with the CO_2 this is acceptable. However, if the sorbent is to be recycled, such a high energy penalty poses a serious obstacle. One-time capture also differs from recycling of sorbent in another important aspect. If the sorbent is to be discarded, then the time to loading is less critical than in other designs. Rather than aiming for minutes to hours to complete the loading stage, one-time sorbents may be exposed to open air for months or even years.

Another category of thermal swing sorbents operates at lower desorption temperatures, ~ 100°C (temperature of desorption will depend on the sorbent). These sorbents require less energy for desorption and offer a likely energy feasibility for faster cycles (minutes to hours) of sorption and desorption of CO_2, accumulating CO_2 to be stored or utilized.

Moisture swing sorbents are also usually fast cycles in order of minutes to hours. The cyclability of sorption and desorption of CO_2 on moisture swing sorbents can be cycled with low water vapor (dry environment, usually < 50% relative humidity) in which the sorbent will bind CO_2 in form of carbonate and bicarbonate and desorbed with a high water-vapor environment (usually >50 % relative humidity) or the sorbent can be desorbed with liquid water. The variation of the humidity level for absorption and desorption will vary with the sorbent’s chemistry.

For all sorbents unloading of CO_2 is facilitated by lowering the pressure of the gases it is in contact with. Pressure swings that drive the CO_2 partial pressure well below ambient conditions are demanding, because the CO_2 partial pressure of 40 Pa is already very small, and pumping costs rapidly escalate in such designs. On the other hand, moisture swings and thermal swings are helped by extracting gases at a pressure below the equilibrium conditions in the regeneration chamber. As a result, many practical designs combine vacuum extraction, heating and wetting to obtain a hybrid regeneration process that combines all features into one design.

The chemical and physical properties of a sorbent must also consider the selectivity of the sorbent. Clearly, sorbents need to favor CO_2 sorption greatly over that of N_2 and O_2, which together are 2500 times as abundant than CO_2. Another important consideration is the selectivity of the sorbent relative to H_2O. Many CO_2 sorbents also bind H_2O, which in the atmosphere is far more prevalent than CO_2. However, the interactions with H_2O are further complicated by the fact that many sorbents may contain water and release it to the atmosphere during CO_2 collection. This is certainly the case for many aqueous solutions that act as CO_2 sorbents, and it also is the case for moisture swing materials. Therefore, the interaction of CO_2 sorbents with H_2O can range from systems that consume large amounts of water that are discharged to the atmosphere during CO_2 collection, to sorbents that co-produce copious amount of water. Neither extreme is desirable, as the energetic cost of producing the water is high and a loss of water, particularly in arid regions, is typically not sustainable. If water is consumed, water quality requirements can result in substantial costs, unless the process can accommodate water with impurities present. If water is collected, the quality of this water may have economic implications.

However, the possible release of H_2O from the sorbent while itself harmless points to another issue. Sorbents must not release unwanted materials into the environment. Releases could include wastes from water purification, or incidental release of volatiles from organic sorbent materials. Such volatiles may have been introduced in the production process or are the consequence of degradation in the open environment. Exposure to UV light and high temperatures could result in such issues. The combination of UV and oxygen provides a chemical environment conducive to producing unintended decay products.

Another important aspect of a sorbent relies not just on its chemistry but on the form it is presented. A sorbent can be presented as a large block, as small particles, or very fine powder particles. It can have complex shapes which may include hierarchical structures to maximize contact with air. It can be highly porous or arranged in small fibrous structures. A sorbent can also be supported by a composite structure in form of beads, fibers, sheets, filter materials or larger and complex shapes. The form factor of the sorbent can greatly influence the kinetics and capacity as it changes the efficiency in which the air contacts the sorbent and allows it to bind CO_2. For instance, a sorbent with the same chemistry in a large particle form or in a fine powder form differs greatly in kinetics. Very small sorbent particles have a much higher surface area, greatly improving the air contact with the sorbent and thus kinetics and even effective loading capacity are improved as all material can be readily accessed. Sorbents in form of beads, fibers, sheets and more complex sorbent structures can give the sorbent an easier scalability of practical application and innovative engineering design systems.

Sorbent development is ongoing to achieve and improve carbon capture technical and economic feasibility. The ideal sorbent needs: high capacity, fast kinetics, free energy of binding that readily allows CO_2 to be absorbed from the atmosphere[16] yet readily releases it during regeneration, withstand many cycles (on the order of 100,000 cycles) on its lifetime, and be economic viable[17]. It must be highly selective for CO_2 and not release volatiles or other unwanted species into the environment. There is a specific balance between the number of cycles and the cost. If the economy of scale progresses, a sorbent can be replaced more often and thus require less cycles proportionally.

2.2 Types of Sorbents

As is typical for a nascent set of technologies, there is a wide range of options that are currently considered. This section aims to outline some of the major groups of sorbents that are of practical interest. Sorbent choices range from liquids to solids and involve different process designs. In this project we are focusing on characterizing solid sorbents. Therefore, the following description is largely confined to the discussion of solid sorbents. Future work will have to broaden this discussion and also include liquid sorbents.

2.2.1 Temperature Swing and Temperature-vacuum Swing Sorbents

Temperature swing sorbents can sorb CO_2 under ambient temperature and desorb CO_2 at a higher temperature. This temperature differential makes the CO_2 swing operate as a temperature pump in which removes CO_2 directly from the air and allow to be stored or utilized.

The first temperature swing concept was discussed by Lackner et all (1999)[15] as he also discussed the concept of removing CO_2 directly from the air as an option to solve climate change[15]. The concept introduced by Lackner et all (1999) presented two main possible ways: 1) calcium and magnesium oxides rocks can bind slowly CO_2 forming calcium and magnesium carbonates[14,15]:

$$CaO + CO_2 \text{ -> } CaCO_3 + 179\ \text{kJ/mole}$$

$$MgO + CO_2 \text{ -> } MgCO_3 + 118\ \text{kJ/mole}$$

or 2) calcium and magnesium hydroxides solutions can also bind CO_2 forming calcium and magnesium oxides[15]:

$$Ca(OH)_2 + CO_2 \text{ -> } CaCO_3 + H_2O + 114\ \text{kJ/mole}$$

$$Mg(OH)_2 + CO_2 \text{ -> } MgCO_3 + H_2O$$

However, the energy requirements for converting $CaCO_3$ back to CO_2 is substantial as it and it requires calcination at ~ 900 ˚C.

$$CaCO_{3\,(s)} \text{ -> } CaO_{(s)} + CO_{2\,(g)}\ +180 \text{ kJ/mole}$$

The energy requirement for calcination of $MgCO_3$ is somewhat lower,

$$MgCO_3 \text{ -> } MgO + CO_2 +118 \text{ kJ/mole}$$

and the temperature of calcination is around 500 ˚C. However, carbonation of MgO or $Mg(OH)_2$ is comparatively slow, and therefore quite challenging.

The energy requirements to swing CO_2 thermally with the calcium and magnesium oxides and calcium and magnesium hydroxides can make the process economically or energetic challenging. Despite these challenges there is a company Carbon Engineering (CE) in which implemented a similar process utilizing hydroxide solutions[21]. The sorbent solution utilized to drive the process is a potassium hydroxide solution (KOH). The chemical reactions is at follows[21]:

$$CO_{2(g)} + 2\ KOH_{(aq)} \text{ -> } H_2O_{(l)} + K_2CO_{3(aq)} – 95.8 \text{ kJ/mol}^{21}$$

$$K_2CO_{3(aq)} + Ca(OH)_2 \text{ -> } 2KOH_{(aq)} + CaCO_{3(s)} – 5.8 \text{ kJ/mol}^{21}$$

$$CaCO_{3(s)} \text{ -> } CaO_{(s)} + CO_{2(g)} +179 \text{ kJ/mol (calcination)}^{21}$$

$$CaO_{(s)} + H_2O_{(l)} \text{ -> } Ca(OH)_{2(s)}^{21}$$

This cycle process has energy benefits but a large energy penalty, which drives the overall cost for DAC, is still a challenge. There is a need for sorbents with a lower binding energy of CO_2, high absorption kinetics and capacity, but lower energy intensively to desorb CO_2.

Amines and polyamines on solid supports have been developed as a lower energy intensive temperature swing sorbent[16]. The amines can be grafted or impregnated on a solid polymerical and porous material[16,]. The desorption process occurs ~ 100 °C. The actual regeneration temperature depends on the sorbent and the desorption process. In some implementations this process can occur in a few minutes. The sorbent can be easily regenerated under dry or steam heat regeneration.

Moisture affects many sorbents in complex ways. For example, in a dry environment the amines react with CO_2 forming carbamate on primary amine site and carbamic acid on a secondary amine site[16] as follows:

$$2R^1R^2NH + CO_2 <-> (R^1R^2NH_2^+) (R^1R^2NCOO^-) <-> (R^1R^2NH) (R^1R^2NCOOH)^{16}$$

During moist conditions the amine reacts with CO_2 forming bicarbonate as follows[16]:

$$2R^1R^2NH + CO_2 + H_2O <-> (R^1R^2NH_2^+)(HCO_3^-)^{16}$$

The presence or lack of moisture therefore can affect the sorption part of the cycle as well as the desorption part.

A more complex analysis on the thermal swing process on amine and polyamine based sorbents mechanism can be observed on the figure 3 below. It indicates that amine based sorbent, have a few driving forces operating in the formation of carbamate, bicarbonate or carbonate species absorbing and desorbing CO_2[20]: 1) At lower temperatures (~ambient) the equilibrium of the reaction will be driven to the amine binding CO_2 and forming carbamate, in opposite way as temperature are elevated (~ 100 °C) the equilibrium will tend to desorb CO_2 and the carbamate will be back to amine, releasing CO_2 (desorbing CO_2 or regenerating the sorbent); 2) Water will drive the reaction to the formation of bicarbonate and by drying the system will drive the reaction to the formation of carbamates. 3) Increasing the pH will drive bicarbonate to carbonate formation and the opposite, by decreasing the pH in the bicarbonate range, the equilibrium will tend to the formation to bicarbonates. It is important to note that for carbamate and carbonate CO_2 binding it is required 2 moles of amine for 1 mole of CO_2 (2:1 ratio) and in bicarbonate form 1 mol of bicarbonate for 1 mol of amine (1:1 ratio)[20]. This indicates two important factors if the sorbent absorb CO_2 in the bicarbonate form: a) the sorbent capacity can theoretically double in the bicarbonate form b) the desorption will occur more rapidly[20].

Temperature-vacuum swing (TSVA) is a system design for temperature swing sorbents in which the sorbent is absorbed/adsorbed under ambient temperature like a regular temperature swing process and the desorption process besides the temperature increase for desorption, the systems apply vacuum simultaneously in which increases desorption rates and deliver a more pure CO_2[29]. The company Climeworks DAC plan operates under the TSVA system[29].

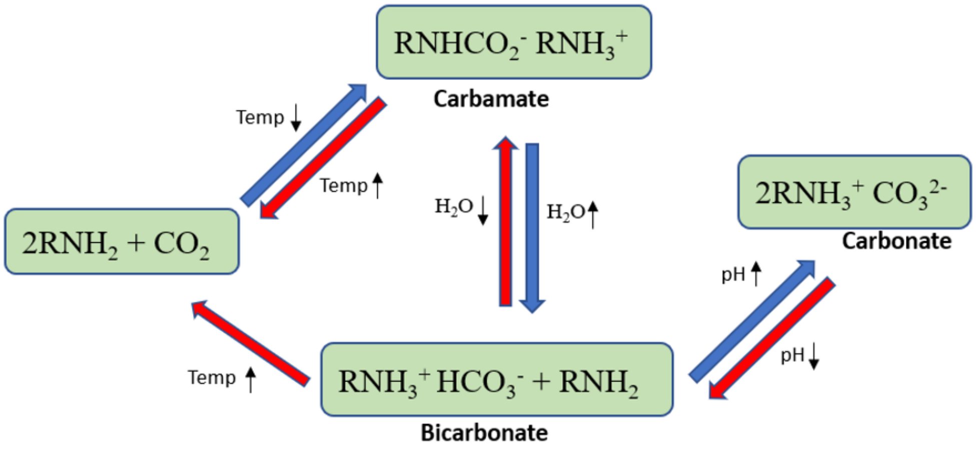


Figure 3 - CO_2 Absorption Using Amines and the Equilibrium Driving Forces of the Reaction[20](Modified).

2.2.2 Moisture Swing Sorbents

Moisture swing sorbents are chemical structures that bind CO_2 in a dry environment and release CO_2 in a wet environment. The concept was first introduced by Lackner[23]. These sorbents are typically ion exchange resins (IER) with a highly cross-linked structure that has specific advantages when compared to thermal swing sorbents[22]. Thermal swing sorbents are very efficient with high kinetics but introduce a considerable energy penalty of 130 to 200 kJ/mol and advanced amine materials in the order of 70 to 100 kJ/mol[22]. The high temperature regeneration process on thermal swing materials also creates challenges on how many cycles the sorbent can withstand without degradation[22]. The moisture swing process proposed by Lackner[22] has a lower energy consumption of 50 kJ/mol of CO_2, demonstrating moisture swing sorbents can have a significant advantage cost if the sorbent has a high kinetics as the thermal swing sorbent. However, one of the limitations of this process is it will be highly dependent on the dry region in the world, as it can be low energy intensive to make the sorbent wet in order to desorb CO_2, but it would be expensive to make the sorbent dry. A naturally dry environment is necessary to maintain the expected low energy cost. Roughly half of the exergy required to concentrate the CO_2 is derived from the evaporation of water into dry air. If the air is nearly saturated in water, a moisture swing is not possible.

The common chemistry on a moisture swing sorbent is the quaternary ammonium cation that is attached to polymer matrix of the ion-exchange resin, figure 4. Many of these resins are commercially available and the charge of the quaternary ammonium is often balanced by a chloride ion. To cycle CO_2 through the moisture swing process, the chloride needs to be replaced by OH^-, HCO_3^- or CO_3^{2-}. If the resin is in Cl^- form, an ion exchange protocol needs to be applied to the Cl^- ions to be exchanged with OH^-, HCO_3^- or CO_3^{2-} (see subchapter 4.1.1). Once the quaternary ammonium is active in one of these three forms, the affinity of CO2 to the sorbent is controlled by the available moisture and a moisture swing occurs. Figure 5 presents the cycles in which from an initial state on hydroxide state (on the top left of the figure 5), under a dry environment the resin will bind CO_2 on the hydroxide sites by reacting and forming bicarbonate (HCO_3^-), even at the low ambient partial pressure of CO_2. While not practical, it is theoretically possible to let the sorbent dry in the absence of CO_2 and form a mixture of bicarbonate and hydroxide. In the figure this is referred to as the dry-and-empty state. As the CO_2 pressure is raised to ambient conditions, the resin loads up to be fully in the bicarbonate form, which is labeled dry-and-full (of CO2). These first two stages are the CO_2 adsorption stages. In practice, they will occur concurrently and at any given moment the amount of free hydroxide is very small. The next step is the desorption stage when CO_2 needs to be released from the sorbent to complete the objective of a moisture pump to remove CO_2 from the air. By providing water or moisture, the resin transitions into the full-wet stage. The result of this transition is that the equilibrium partial pressure over the system increases about 500-fold and CO2 can now be released at a much higher partial pressure moving the system into the wet-empty state. Exposing the empty resin to ambient air to dry begins the next cycle[22]. Thus, the sorbent is ready to absorb CO_2 again and continue the cycles of adsorption and desorption.

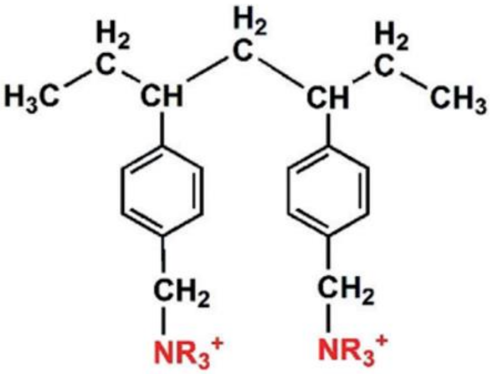


Figure 4 - Chemical Structure of an Ion-exchange Resin. $-NR_3^+$ Denotes the Quaternary Ammonium Cation[16].

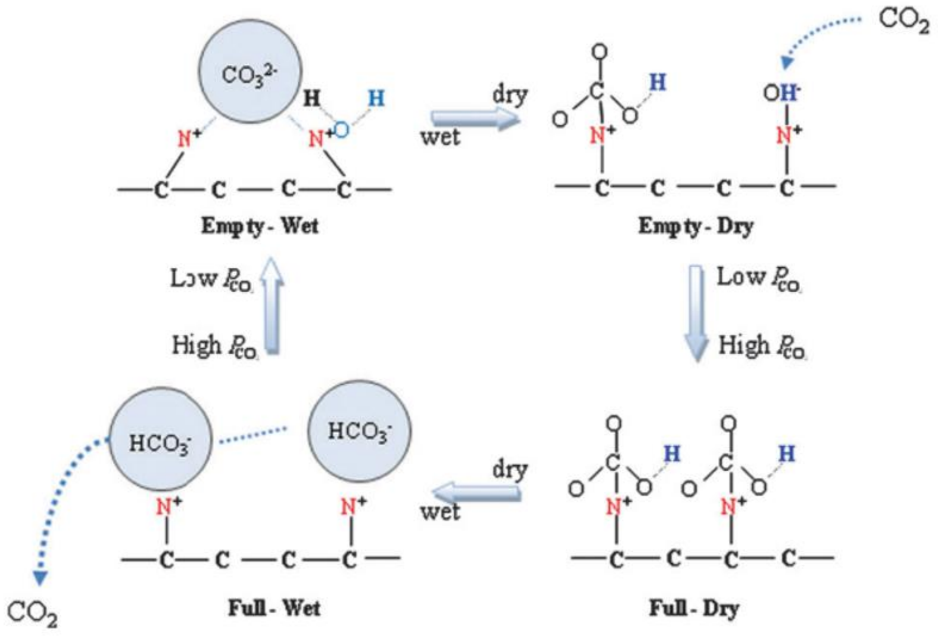


Figure 5– Moisture-swing Sorbent for CO_2 Capture from Ambient Air[16,22].

2.2.3 Pressure Swing Adsorption (PSA) Sorbents

Pressure swing sorbents will bind CO_2 under ambient conditions pressure and desorb CO_2 after reducing the total pressure below 40 Pa. The pressure swing is not commonly utilized without being combined with temperature or moisture swing processes as the absorption and desorption rates and the total equilibrium capacity tend not to be as high as the other two techniques[30]. The CO_2 partial pressure in the atmosphere is very low making a stand-alone PSA process alone challengingly expensive. Typical sorbents used for pressure swing are metal organic frameworks (MOFs) which have great performance under high pressure CO_2 with advantages due to their flexibility in shape and due to their highly porous structure, but with disadvantages in handling gas mixtures and humidity. The need to produce high pressure CO_2 can increase significantly the costs of a DAC plant. Another good sorbent for pressure swing is activated carbon with high capacity under high CO_2 partial pressures but it is sensitive to humidity and high temperatures.

2.2.4 One-time CO_2 Capture Sorbents

One-time CO_2 capture is a concept that differs from the swing process concept. The goal of this process is to capture the CO_2 once in a stable mineral form and not desorb it. In other words, the sorbent is used once. The concept is very similar to the first thermal swing process presented by Lackner[14] and discussed on the subchapter 2.1.1. Temperature swing sorbents based on calcium and magnesium hydroxides or calcium and magnesium oxides found in certain mineral rocks can slowly absorb CO_2 in a stable form as calcium and magnesium carbonate. There are several synthetic materials which use rocks with a fraction of its composition from mineral rocks with such properties. The approach of one-time capture is to utilize solid sorbent materials with a strong binding of CO_2 to permanently sequester the carbon. As discussed previously, it is necessary a very high temperature to displace CO_2 from such materials as calcination at 900 °C is necessary. On the first concept Lackner et al[14] on this first thermal swing approach have presented this type of materials as a possible solution for capturing back carbon dioxide released from fossil fuels and that the absorption kinetics was too slow and new approaches need to be taken to speed up the kinetics to match how fast we release CO_2 from burning fossil fuels. However, for the one-time capture approach, the time is not the main concern as this is not going to be the "one technique" to solve climate change. Furthermore, many of these materials will gradually carbonate with little or no effort needed to drive the process forward.

This approach takes advantage of the many materials which can slowly capture CO_2 in the course of decades of its lifetime. The diversity and variety of such materials can absorb a substantial amount of CO_2 from the atmosphere on the next decades. For instance, cement composition is 62-65 % CaO, assuming the slow absorption rate of 30 kg CO_2/tonne/decade (ballpark for this type of material, see subchapter 7.1 for more details) and assuming all cement produced in the world has the same production rate for the next 30 years of 4 billion tons cement/year, this cement can account for the absorption of 0.4 Gt of CO_2. Assuming the cement has 60 % of its mass CaO and the conversion of CaO to $CaCO_3$ requires 1 mol of CO_2, the CO_2 capture potential of cement is 47% of its mass. Thus, with the slow rate presented of 30 kg CO_2/tonne/decade, only about 0.3% of the total mass of the cement in 30 years will capture CO_2. Different form factors could potentially enhance kinetics of this process. As 47% of the cement mass can be utilized to capture CO_2, the cement has the potential to remove 56.4 Gt of CO_2 in the next 30 years. This is a very substantial amount as the total global year CO_2 emissions is 36 Gt, just cement with a fast capture rate could potentially offset almost 2 years of current total emissions.

Thus, the one-time capture concept is relevant and a more detailed methodology will be presented in this dissertation to screen different one time capture sorbents and its different form factors and weather effects that can enhance kinetics.

2.3 Characteristics of a Good Sorbent

In the development of better sorbents, one aims to improve properties of available sorbents in many different ways. To make rational choices between different sorbents, it becomes important to identify the characteristics of a sorbent that make them more or less useful. Without a clear metric it is difficult to advance these materials. On the other hand, sorbent optimization involves trade-offs among many different parameters, which are also affected by the specifics of a DAC technology. The following is a brief summary of some of the more important parameters that will need be considered in any analysis.

2.3.1 Capacity

Capacity of a sorbent is defined in general terms in how much CO_2 a given sorbent can absorb. Sometimes capacities are cited in terms of how many sites exist in the sorbent that can bind CO_2. However, from a practical perspective one needs to measure the amount of CO_2 that can be loaded on a sorbent that is in a nominally empty state, i.e., in equilibrium with the conditions that prevail under regeneration (desorption) conditions to a state that is in equilibrium with nominal ambient conditions in open air. In practice, the capacity in operation is likely to be less than that, because sorbent cycles typically do not wait for equilibrium conditions to be achieved.

We can therefore define several forms of capacity. A stoichiometric capacity, which is based on a particular reaction and assumes that this reaction goes to completion. This capacity may depend on the choice of reaction (for example, does one assume the formation of carbonate or bicarbonate when measuring the stoichiometry), but it is independent of ambient conditions.

By contrast, an equilibrium capacity, depends on the conditions the sorbent is exposed to during regeneration and under ambient conditions. Both can be varied, resulting in different measures of capacity. At a minimum it is necessary to specify these conditions, but they could vary dramatically with process design changes.

Lastly, it is possible to consider a dynamic capacity which measures the sorbent's change in carbon loading in a particular cycle. Here the kinetic properties of the sorbent will play an important role, and the dependence on dynamic designs becomes even more important.

The nominal equilibrium capacity has defined above is subject to the actual ambient conditions, which may differ from nominal conditions at different times of the day, different seasons, and weather conditions.

The capacity that relates to DAC must also account for the amount of CO_2 that is present in the atmosphere. How much CO_2 can a sorbent collect at ambient CO_2 partial pressure. Currently, the CO_2 concentration in the atmosphere is about 420 ppm. The unit to measure a sorbent`s capacity is usually normalized by the sorbent's mass. For example, a sorbent with a significant capacity will have > 1mmol CO_2/g of sorbent. Depending on the characteristics of a given sorbent, weather conditions mainly temperature and humidity can affect a sorbent's equilibrium and thus change the total capacity at the given environmental conditions. Another form to evaluate the capacity of a given sorbent is normalizing by the sorbent surface area for example mmol CO_2/m^2. This normalization is useful for system that may have different packing densities of sorbent and thus, a system can be evaluated as its total CO_2 absorbed for open area of the system (or sample) in contact with the ambient air.

2.3.2 Kinetics

Kinetics describes how fast a sorbent can uptake and bind CO_2 in the absorption/adsorption process and how fast it desorbs CO_2 at a given regeneration system in which is a function of the CO_2 binding energy to the sorbent. Despite capacity be one of the most important characteristics of the sorbent, kinetics evaluation is essential. A sorbent can have a high capacity of > 1 mmol CO_2/g but with a very slow kinetics in which compromises its feasibility as its scales. For example, considering a hypothetical sorbent "A" with 0.2 mmol CO_2/g with an absorbing 0.1 mmol/g (half of its capacity in which usually the kinetics is the highest) in 10 minutes versus a hypothetical sorbent "B" with 2 mmol of CO_2 in which absorbs 1 mmol CO_2 in 3 hours or 180 min (period of time in which the kinetics is the highest). Assuming the desorption rate is the same for both sorbents (usually sorbent B would take longer because it has more capacity), sorbent A would absorb about 1.8 times more CO_2 by cycling faster than sorbent B. And this without assuming the difference of time on the desorption rate in which sorbent A would likely also desorb faster than sorbent B promoting an even greater total CO_2 absorbed.

Kinetics characteristics evaluation it is an essential parameter to evaluate the period of time the sorbent`s absorption and desorption rate are the fastest. As the sorbent reaches closer to its maximum equilibrium capacity kinetics proportionally slows down. The opposite occurs on sorbent`s desorption rate. As the sorbent goes from fully loaded with CO_2 to be closer to be empty, the desorption rate slows down. Thus the absorption and desorption kinetics curves are essential to evaluate the optimal cycle times of a sorbent in order to maximize the total CO_2 captured over a period of time. Kinetics of a given sorbent can also be influenced for a number of factors: temperature, air to contact to the sorbent, wind or air velocity and humidity levels. These factors need to be evaluated in order to characterize the sorbent for a given engineering system design for direct air capture or passive direct air capture.

Kinetics must consider the uptake rate per unit time and mass (or alternatively surface area) of a sorbent under different conditions. Temperature, moisture level, and loading state of the sorbent all affect the kinetics. Kinetics is in part driven by reaction rate limitations, and in part by transport limitations of CO_2 into the bulk of the sorbent material or through the air side boundary layer of forming on the surface of the sorbent. This latter limitation suggests that air flow speed can have a strong impact on uptake rates. As result, kinetics issues must consider reaction rates, and various limitations from transport. This implies it is not solely determined by the chemistry of the material and its bulk properties but also by its form factor.

2.3.3 Binding Energy

Binding energy of a sorbent is an important parameter in order to evaluate a sorbent`s capability on absorbing CO_2 at atmospheric CO_2 partial pressure in which characterizes a DAC sorbent and its energy requirement for unbind CO_2 or desorb it. For a temperature swing sorbent the binding energy is important determining the temperature necessary for CO_2 desorption. The binding energy for DAC sorbents needs to be larger when compared to a flue-gas sorbent once the CO_2 concentration in the atmosphere is far less[22]. The minimum binding energy for DAC sorbents is 20 kJ/mol CO_2[22,23], almost three times larger than an ideal flue gas capture sorbent that is about 8 kJ/mol CO_2[22]. The binding energy of sorbents vary and it will determine the amount of energy required to desorb CO_2 through heat if the sorbent is thermal swing or by water equilibria if the sorbent is moisture swing. For instance IEM sorbents has a heat of sorption of -30 kj/mol with a regeneration temperature of ~ 300 K; amine based sorbent -90 kj/mol with regeneration temperature of 300-400 K; Na-based solid sorbent a range between 500-1,000 K of regeneration and -130 kJ/mol of heat of sorption; NaOH liquid sorbent 1,100 – 1,400 K regeneration temperature and 110 kJ/mol of heat of sorption and; Ca-based(solid) 1,200 K for regeneration temperature and -180 kJ/mol of heat of sorption[22,23,26,27,28].

The ideal sorbent for DAC needs to have a binding energy that is strong enough to keep CO_2 absorbed/adsorbed into its structure at the ambient temperature and a desorption with low energy intensity. For temperature swing, amine based sorbents are an example of lower energy for regeneration. Another example of lower energy for regeneration are moisture swing sorbents in which the water concentration drives the energy for regeneration under ambient temperature.

2.3.4 Form Factors

A sorbents capability to sorb and desorb CO_2 is not only driven by its chemistry. The form in which a sorbent is presented will make a significant difference in the air to contact with the sorbent and the application of a sorbent in an engineering system.

At first a sorbent can be liquid or solid. Solid sorbents present a more diverse possibilities of form factors. Solid sorbents can be on the form of small particles such as beads, fine powders, fine fibers, thin sheets or more complex structures in the form of filters.

Particle size on a solid sorbent increases surface area in which most of the cases enhances sorbent`s $CO_2$ absorption kinetics and in some cases capacity as more sorbent`s active sites are in contact with the ambient air and thus CO_2. Depending on the practical engineering application sorbent`s with a very small particle size can be utilized as long as there is a form of containment or the sorbent is utilized into a composite material that holds the sorbent in place such as fibers, filters or specific pouches with meshes opening sizes smaller than the sorbent`s particle size. There are several pouches materials in which can be utilized to contain sorbent particles and provide sufficient air to contact with the sorbent. A balance of ideal opening area and particle size in which the pouch contains the sorbent and at the same time allow maximum air flow to the sorbent is the strategy to be applied for this specific form factor.

Sorbent`s fine particles can also be sprinkled into adhesive sheets in which can hold the sorbent in place providing better air to contact with the sorbent, differing for a packed sorbent structure.

Another strategy on solid sorbents is to create more complex frame structures with specific geometries in which can hold the sorbent in place and provide better air to contact to the sorbent, better turbulence of air, enhancing sorbent`s kinetics.

Sorbent`s form factors are essential to maximize a sorbent`s kinetic and capacity potential and apply it on larger scales as we move from the bench scale testing into larger samples to finally move into an engineering system pilot plant in which can lead to an industrial development.

2.3.5 Longevity

Sorbent`s longevity is basically the lifetime of a sorbent operating under a specific engineering process. Temperature, moisture and pressure swing sorbents operate under cycles of absorption and desorption. These cycles can change a sorbent's equilibrium capacity, chemical composition and physical structure over a number of cycles. A study conducted by Azarabadi & Lackner (2019)[17] demonstrate that a sorbent's market value is greatly affected by its longevity. This study shows that for a sorbent be economically viable, it needs to last tens to hundreds of thousands of loading and unloading cycles. The longevity of the sorbent will be also dependent on the optimized cycle times in which are dependent of its capacity, kinetics and the engineering system design. DAC plants with forced air will depend on the air flow-rate utilized and PDAC will rely on wind velocity for this optimization. Ideally, the sorbent cycle times will operate on the timeframe the absorption kinetics is the highest. However, this can minimize a sorbent's lifetime as more cycles per time will be performed. Depending on the aging mechanism, this means a sorbent may collect more or less CO_2 over its lifetime if cycle times are kept short. The model developed on the Azarabadi & Lackner (2019)[17] study can evaluate the cycle times optimization for economics as well in order to the sorbent outstand the necessary number of cycles to reach economic feasibility and not just maximum absorption of CO_2 on a given time. However, it requires a detailed characterization of the degradation mechanisms, and the DAC process design.

2.3.6 Costs

Azarabadi & Lackner (2019)[17] developed a techno-economic analysis focused on sorbents for DAC. On this study they demonstrated the most important characteristics to value a sorbent based on CO_2 market price are: a) cycle time, b) loading capacity and c) rate of degradation[17]. Cycle time is defined as the sum of the time necessary to load CO_2 and the time needed to unload (absorption and desorption of CO_2)[17]. These times will vary depending on the sorbent's kinetics of absorption and desorption and the engineering decision on the optimal or ideal cycle time for the given environmental or systems operational design. Loading capacity as has been already discussed on subchapter 2.3.1, it is how much CO_2 a sorbent can absorb/adsorb per absorption/adsorption cycle, usually represented in mmoles CO_2/ g of sorbent. This is an important parameter that jointly with the sorbent's kinetics, the engineering system total CO_2 capture on a giving time and the evaluation of the number of cycles a sorbent can perform without significantly degradation will be evaluated in order to determine the optimal cycle times as the study by Azarabadi & Lackner (2019)[17] predicts. The rate of degradation is defined based on the sorbent`s loss of mass composition or loading capacity in which can be determine for many environmental and engineering processing factors[17]. The rate of degradation is the main parameter to evauate the longevity of a sorbent discussed on the previous subchapter.

Ozkan *et al* (2022)[25] conducted a TEA study in which demonstrate an economic of scale for a DAC technology of solid sorbents based on generic DAC system that mimics climeworks. From an initial total capital cost of 1,027 USD/tCO_2, the adsorbent cost was 988 USD tCO_2, 96% of the cost. With the economics of scale, the total capital cost went down to 13.9 USD/tCO_2 in which the sorbent accounts for 25% of the total[25]. This study demonstrates how impactful is the sorbent to a DAC industrial plant. This does not take into account that the sorbent determines the energy of the regeneration, engineering design choices, longevity, total amount of CO_2 captured on a given time. This shows that most of the efforts to make DAC economic feasible needs to be on sorbent characterization and sorbent development. The ideal sorbent will continue to evolve, it is unlikely to be found the ultimate sorbent. It is also very likely different sorbent`s will be utilized on different regions of the World as the weather can have major influence on the sorbents characteristics.

2.3.7. Supply Chains

As DAC aims to have a significant role on solving climate change and the need to remove 20-36 Gt CO_2 from the atmosphere is a large but achievable number as DAC scales, there is a proportional need to scale the development and production of sorbents in an unprecedent rate. As an example, the company Climeworks uses an amine-based sorbent, with the aim to capture 1% of global annual emissions or 0.36 Gt CO_2 per year, the scale production of amines as the sorbent needs to increase by more than one order of magnitude[29]. Thus, if we considered the need to capture 36 Gt CO_2 the amine production needs to increase by three orders of magnitude. And this considering one type of sorbent for one specific engineering design. This increase of magnitude can take many years to be develop and the time to solve climate change is getting shorter. As there are many possible sorbents with high performance, there is an urgent need to characterize a great number of sorbents in the shortest period of time possible and demonstrate that its production is scalable. Once it is scalable the world needs to significantly increase production to solve climate change. Nevertheless, sorbents need to concomitantly evolve their performance and kinetics and continuously be characterized and improved. As it will take years to scale sorbent production it is likely this scale will be a dynamic industry as sorbent's will continue to be improved. There is an urgent need to develop a standardized methodology that screen sorbents and show its step-by-step scalability.

2.4 Methodologies to Characterize Sorbents to Overcome DAC Challenges

Sorbents are key to the capital and operational cost of a DAC plant and are at the core of the engineering design. There are many chemical structures known and unknown that have a high affinity for CO_2. They can load up with CO_2 in contact with ambient air, and can be regenerated via temperature, pressure, or moisture swings. In some cases, on may collect the CO_2 and dispose of it together with the sorbent in one-time CO_2 capture. Sorbents can be screened on a mg to g scale but can perform very differently on larger scales, with different form factors and when submitted to different weather or climate conditions: wind, temperature, humidity levels. As of today, there is no standard procedure laid out in the literature to evaluate sorbent kinetics under the ambient air conditions to screen sorbents on mg to kg scale under different environmental conditions. As sorbents needs to continue to be developed in order to obtain higher kinetics, lower energy intensive regeneration temperature and time, long longevity, there is a need to characterize sorbents that are already developed and new sorbents specifically optimized for DAC.

A good sorbent needs to have 1) fast kinetics on absorbing/adsorbing and desorbing CO_2; 2) high equilibrium capacity; 3) low energy requirements for CO_2 desorption (regeneration of the sorbent; 4) the impact of water on the sorbent process must be positive or at least not detrimental. How water is absorbed or desorbed or how it helps or hinders the sorbent kinetics and capacity matters.

A sorbent also can perform differently when presented in different form factors as the air contact can be improved. This suggests that the ability to shape the sorbent structure or to embed into an appropriate support structure is of great interest. Sorbents also can perform well on a bench scale but poorly as one scales from mg to g to then kg and tons of grams.

There is a vast variety of chemical compositions available and to be created which have affinity for CO_2 and could be characterized as good sorbent candidates. Most of the DAC systems operate the absorption process at ambient conditions. Ambient conditions vary in different locations and seasons as a function of the weather patterns of each region. The weather characteristics is an important layer of interaction on the different sorbent characteristics. In addition, accounting that each good sorbent candidate can have different form factors in which can improve capacity and kinetics, there is an almost infinite amount of combinations of sorbent, form factors and weather conditions that can drive capacity kinetics and determine the engineering design of DAC systems. For new sorbent creation and form factor designs for human interpretation or the use of advance algorithms or artificial intelligence (AI) there is a need for a vast amount of data in a variety of sorbents and form factors. This data can be only generated through standard experimentation and screening of many sorbents. Much research has been done on characterizing in detail one single sorbent, there is a need to have a systematic procedure to screen many sorbents in a short period of time and then scale the characterization of the best performers.

The work presented in this thesis aims to develop and demonstrate a standard systematic methodology to screen and characterize temperature swing and moisture swing sorbents for practical DAC designs. This includes the design and advancement of experimental apparatus and and experimental protocols that can be applied to a wide range of different sorbents.

We begin with a first approach to screening temperature and moisture swing sorbents on a mg scale (1-10 mg). This makes it possible to gain a first measure of performance of novel materials that are only available in small quantities. The experiments are to consider capacity of the sorbent in ambient air and show that we can successfully discharge the sorbent. These experiments will also shed light on the effect water has on the behavior of the sorbent and its stability in the presence of oxygen.

This first stage is followed by a second stage that can screen sorbents and small-scale form factors on a g scale (0.1-2.0 g). At this stage we can see the impact of shape and form factor on the behavior of the sorbent, and extent the characterization to a broader set of parameters. One important outcome of this project will be that it begins to standardize performance measurements. Characterization at this scale is well suited to sorbent synthesis at the lab scale and must be designed with rapid screening in mind. The best performers among these early candidate sorbents are then incorporated into more complex and heavier sample on the tens of grams scale (1-100 g). They then can be tested on a larger system, a wind tunnel for sorption and in a regeneration device that aims to mimic real sorption systems. The wind tunnel then can also evaluate different weather conditions: wind velocities, temperature, and humidity levels. The wind tunnel is also used to evaluate more complex form factors that can be utilized for design of a pilot-scale prototype that can efficiently absorb CO_2. Once the form factor and the sample perform satisfactorily on the wind tunnel the sample and form factor can be scaled to a kg scale (100 – 3,000 g). Now we are on the scale of a small bench scale prototype which for many designs can look very similar to an operational DAC system. Therefore, one may expect multiple designs for testing systems that reflect different strategies for an operational DAC system. For example, for many designs that have been studied by the ASU group we are focused on passive flow designs. These have been referred to as synthetic or artificial trees. As a result, we are referring to a small regenerator system designed for a passible system as artificial sapling regenerator reactor. However, these systems can easily be extended to cover a larger set of applications.

These bench scale systems can evaluate the sorbent's capacity and kinetics with ambient air indoors and outdoors. As the screened sorbents can scale from the mg to 1 kg, this is 1-million-fold increase in scale. A sorbent and its form factor that can demonstrates considerable performance is very likely a suitable candidate to a full-scale pilot plant that will need in the order of hundreds to tons of sorbent.

As sorbents continue to evolve, it is essential to continue characterization. The data obtained is crucial to developing specific models and algorithms to be used in a combination with artificial intelligence to speed up the sorbent's development design. The combination of these tools can exponentially enhance the velocity necessary to evolve sorbents that can lead to the economic feasibility of DAC and thus play a key role on solving climate change.

This standard methodology on sorbent characterization is explained in detail on chapter 3. Furthermore, this work will demonstrate modeling exercises on a hypothetical full scale pilot plant based on the wind tunnel results. The model exercise will also indicate possible engineering designs that can use the maximum kinetics capability of a thermal swing sorbent on absorbing and desorbing CO_2.

2.5 Interfacing Sorbent Development and Sorbent Characterization

New sorbents are being developed continuously in order to approach the ideal characteristics already discussed on previous chapters: fast kinetics, high loading capacity, low energy for regeneration, high longevity. In addition, there is a great number of known chemical compositions and sorbents in already in the market performing a variety of water, wastewater, and air pollution treatment as ionic exchange materials in which has affinity with CO_2. Each of the chemical compositions can be utilized under a great variety of form factors enhancing carbon capture kinetics, giving an almost infinite number of combinations that can lead to a better economics for DAC. In addition, in order to develop new sorbents, there is a need for a large amount of data on each of these characteristics. Today, these data are scarce and not at all standardized in the existing literature. Simple and complex (AI) models algorithms can be used as an interface to the development of new chemical compositions, form factors and engineering designs in the continuous evolution of sorbents. However, for either human creativity or analyzing and improving models, there is a need of more and better data. Thus, it is necessary to develop a standard system in which sorbents can be characterized in great number in a short period of time starting from a fast screening on small samples on the mg scale and go up to scales of g, kg and finally prototype development on hundreds of kg. The interface between the great number of sorbents that first need to be characterized and then be improved through and again re-characterized in an iterative process is critical to a continuous improvement process. Such a systematic approach will lead to a progressive decrease in carbon capture cost and drive the industrialization of carbon capture and storage. The focus on sorbents is important, because sorbents are a main driver of costs and material for DAC.

2.6 Accuracy and Reproducibility

At present, data on characterization of many types of sorbents are scarce. Moreover, the data generated from different research institutes utilize different techniques for sorbent characterization, variation on the amount of sorbent mass evaluated, variety of form factors in which it is difficult to compare among different sources. Very often the accuracy and reproducibility of results is not known. For instance, it is necessary to first define accurately the characteristics that might be of interest to various research programs. For example, sorbent capacity can be very different depending on the experimental condition as there can be different definitions for capacity as already discussed on subchapter 2.3.1. Secondly the experimental design, form factor and initial environmental conditions must be the same. Only by standardizing these approaches results can be accurately reproduced and compared. The work presented in this dissertation presents a consistent definition on sorbent characteristics on different scales and a consistent experimental protocol. Results are shown to be reproducible with little variability on duplicate results for each method presented. There is a little variability regarding small variations on the initial environmental state of the sorbent before its desorption and absorption experiments. As the ambient humidity, temperature and CO_2 concentration have fluctuations there was small variations on the sorbent`s equilibrium. Temperature and CO_2 had minor fluctuations in certain times of the day, humidity present a greater variation in which is highly dependent on weather conditions and weather seasons. On future work the samples need to be kept on an environmental chamber in which maintain the exact same moisture, temperature, and CO_2 concentration for a sorbent`s initial state, before it is submitted to its characterization.

2.7 Scale of Characterization Effort

The characterization of sorbents needs to be fast at first and manage a great quantity of sorbents to address the diverse number of possible chemical compositions with affinity to CO_2. Over time accuracy will become more critical as the difference between good sorbents become smaller. However, in the early stages it is important to develop fast screening technologies. This fast screening can be operated on a mg scale of sorbent ideally with a characterization in 1-4 hours of experimentation (time usually it takes for a good temperature swing sorbent). Moisture swing sorbents can take longer depending on how many and how long the cycles of absorption and desorption the sorbent will be submitted, it usually takes a maximum of 24 hours. This first effort will be evaluating mainly the kinetics, capacity and how the sorbent reacts with different levels of humidity. The next step is to evaluate small samples on g scale in which can be evaluated on a variety of small-scale form factors evaluating under a relatively low air flow rate, its interaction under different humidity levels and in more detail the absorption and desorption kinetics. The sample selected on the first two scale systems can then be evaluated on tens of g on a more complex system evaluating temperature, wind velocity, relative humidity on the effect of sorbent`s kinetics and loading capacity. This system allows also a bigger and more complex form factor sample. The selected sorbent and form factor then is ready to be tested on a kg scale device and test the absorption on real outdoors ambient conditions. This evaluation will promote from the mg to kg scale 1-million-fold scale. If the selected sorbent still have an equivalent kinetics and capacity performance under this scalability is very likely to be able to perform in a next step of scale a tone scale, about one thousand-fold more. This is a crucial characterization effort in order to develop new sorbents and form factors and this methodology will be discussed in more detail on the next chapter.

3. EXPERIMENTAL CHARACTERIZATION OF SORBENTS FOR DIRECT AIR CAPTURE OF CARBON DIOXIDE

Sorbents are the key for most DAC processes. The variety of sorbents presents many distinct characteristics that can be explored under different environmental and engineering design conditions. The requirements for DAC sorbents are very different than those for sorbents deployed in flue gas scrubbing. For example, DAC sorbents needs slightly higher binding energies to successfully draw CO_2 out of a much more dilute stream. On the other hand, sorption kinetics can be slower as air side transport limits rates much more dramatically than in a flue gas stream. Stability in air, and in the presence of water play an important role. Release of volatiles requires much more stringent limits than in flue gas scrubbing. DAC techno-economic feasibility is still a challenge and sorbent kinetics, loading capacity, durability, energy requirements for regeneration are the key to solving these problems. Among the many different characterization methodologies in the literature, there is no standard methodology able to screen several temperature and moisture swing sorbents under different mass scales from the mg to the kg scale. Screening small mass samples on the mg scale is common among the literature, especially in TGA experiments, to show capacity. There is a significant lack on standardized kinetics evaluation of sorbent absorption and desorption on a second per second timescale. Beyond screening mg scale samples, many of these sorbents and their form factors do not maintain the same kinetics and capacity as mass scales move up to grams and kilograms. There is little agreement on how to determine or predict the longevity of sorbents, or their stability in the presence of typical impurities in the air. This chapter outlines these issues and begins the development of a systematic standard methodology to screen sorbents and evaluate their scalability to larger sizes and account for sorbent form factors variations that can enhance kinetics and capacity. It is a central goal of this thesis to start the development of a standard methodology for the evaluation of air capture sorbents.

The methodologies regarding the characterization of a sorbent at different scales of deployment has been developed with a combination of systems created for specific applications to characterize temperature and moisture swing sorbents. These systems operate on the mg sample size to the scale of tonnes of sorbents with specific functionalities. Figure 6 represents how the combination of these systems operates: 1) the first stage in this system in the figure is named Moisture Swing Closed System Device (MSCSD) and Temperature Swing mg Scale Device (TSMSD) in which has the capability for fast screening temperature and moisture swing sorbents at the 1-10 mg scale. It has a dynamic or steady humidity control capability; 2) second the CO_2 sorption open flow system (CAOFS) designed to test 0.1-1 g scale sorbents in a continuous open flow air. This system also allows humidity control through a dew point generator (DPG); 3) a wind tunnel system to test 1-100 g scale under representative air flow velocities and with appropriate form factor. This system allows humidity and temperature control of the samples; 4) a bench scale reactor to test 0.1-3 kg sorbent scale. This system allows evaluate desorption and absorption carbon capture sorbents for indoor and outdoor CO_2 absorption experimentation methodology, giving one step for a pilot plant scale; 5) and finally, full scale pilot plant which will be able to test at the 0.1-1 tonne scale. Combined these systems can first, fast screen sorbent, following to a more complex analysis of sorbent mass, size, volume, form factor and weather interactions: wind velocity, temperature and humidity.

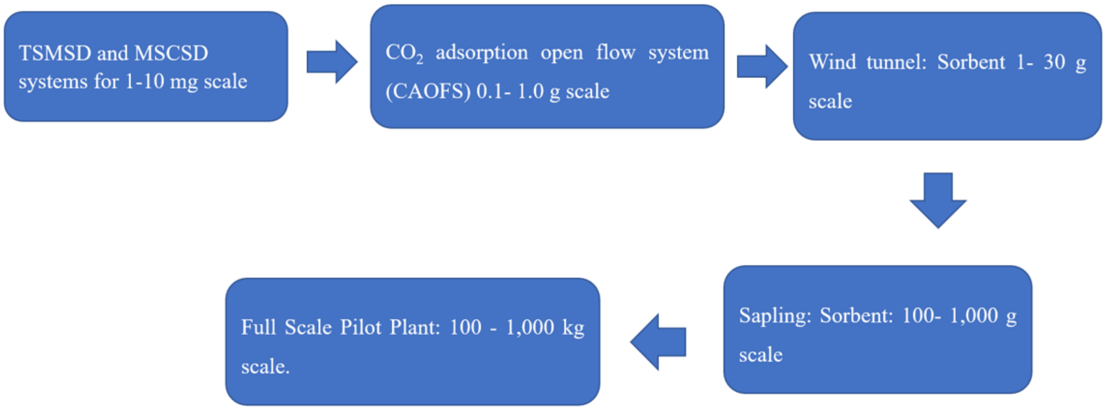


Figure 6 - Experimental Methodologies for Characterization of Sorbents for Direct Air Capture of Carbon Dioxide

3.1 Moisture Swing Closed System Device (MSCSD) and Temperature Swing mg Scale Device (TSMSD) – Methodology

This system has been developed with the main purpose of screening a great number of sorbents in a relatively short period of time. Typical experiments on temperature swings require a total time of 1 – 4 hours and moisture swing sorbents 1-24 hours depending on the cycle times for sorption and desorption of CO_2. For temperature swing sorbents this system evaluates the CO_2 sorption per time on a per second analysis. In addition, the system also evaluates the water vapor concentration in parts per thousand (ppt) on the same timescale as CO_2. The data obtained allow the evaluation of the a) sorbent kinetics; b) sorbent total CO_2 capacity on a mass basis; c) closed environment humidity change (the sorbent might absorb or desorb water); d) change in sorbent capacity over many cycles, even though this system has not been developed to test a sorbent on the ideal thousands of cycles, it can run many cycles to determine if there is a change in the sorbent`s capacity and kinetics over time; e) different small scale form factors such as sorbent on different pouches with different properties in which can enhance sorbent`s CO_2 absorption.

Screening systems for small scale sorbent`s moisture swing and temperature swing are not standardized on literature. Different approaches have been developed more focused on temperature swing sorbents mainly utilized TGA to determine total sorbent capacity. This chapter shows the system developed to evaluate small sorbent scales 1-1,000 mg range for moisture swing sorbents and 1-10 mg range for temperature swing sorbents. This system has a unique capability to evaluate in a close loop system a sorbent CO_2 absorption on a per second timescale, allowing the analysis of its kinetics of sorbing and desorbing CO_2. The system was first created for a moisture swing sorbent and it has a programming system to vary humidity level on specific cycle times determined by the experimental settings. For moisture swing sorbents the system can log the variation of CO_2 sorption and desorption. The system was then adapted for a temperature swing process in which the CO_2 desorption occurs in a separate system (oven for dry heat and CSDS system for steam heat regeneration) and then the sorbent is inserted on the MSCSD/TSMSD system to evaluate the CO_2 sorption data. The humidity level can be set constant or varying to evaluate the temperature swing sorbent.

The moisture swing closed system device (MSCSD) is presented in figure 7 and figure 8. The sorption portion will occur during the dry phase that is operating ~ 5 ppt of H_2O according to the moisture swing process described in subchapter 2.2. The desorption process will occur when the system is operating at high moisture content ~ 25 ppt of H_2O. The system will alternate between different water vapor concentrations at a stipulated cycle time under the control of lab view software. The system is composed by 1) a pump that starts the ambient air circulation after closing the loop system. 2) A small DPG that controls the moisture content in the system. This small dew point generator will alternate the dew point temperature to vaporize water (high moisture phase) and condensate it (dry state). The corresponded temperature will be proportional to the amount of water set in ppt. 3) the air at the given moisture content will then pass through the sample chamber. There are 3 types of sample chamber we can use in our system: a) a tubular sample chamber for small samples, b) a squared sample chamber for big flat sheet samples and c) a stainless steel sample chamber for an upflow large sample. 4) air flow will then pass through the IRGA which determines the values for CO_2 and H_2O concentration similar to those in previous systems and the data will be logged on the laptop (9) with the Licor software. 5) A signal controller that will give the signal to the dew point generator alternates times between heating and cooling according to what the lab view software cycle times command. The system parts 1,2,3,4,5 and 9 are to operate on a closed setting as the valves (8) are closed). By opening the valves 8 the system can operate with the parts 6 and 7. 6) This part comprises an air tank free of CO_2 which can flush out all the CO_2 from the system and set a zero CO_2 starting point. 7) An added bubbler system that comprises a small bucket on a plate heater. This bucket will be filled with DI water and when is hot it will generate steam and with combination with the CO_2 free air it can make the sample free of CO_2 as a starting point.

The same apparatus from the MSCSD can operate for small sample mass scales for temperature swing processes. The instrument/system/method is then called “Temperature swing mg Scale Device” (TSMSD). For this purpose, first the sample needs to be submitted in a different apparatus for either a dry or steam heat regeneration (or desorption). For dry heat regeneration the sample can be submitted to the oven at the desired temperature and time. For steam heat regeneration the sample is submitted to the CO_2 Desorption system device (CDSD) (described in detail in section 3.2). Once the regeneration is complete, the sample needs to be rapidly inserted into the TSMSD system. Before the sample is inserted, the system can establish a constant moisture content baseline between 5 to 25 ppt. Usually the baseline will be dry at 5 ppt, but it will depend on the experimental goals. A second possibility is to adjust the system to vary humidity in order to experiment a hybrid on moisture and temperature swing.

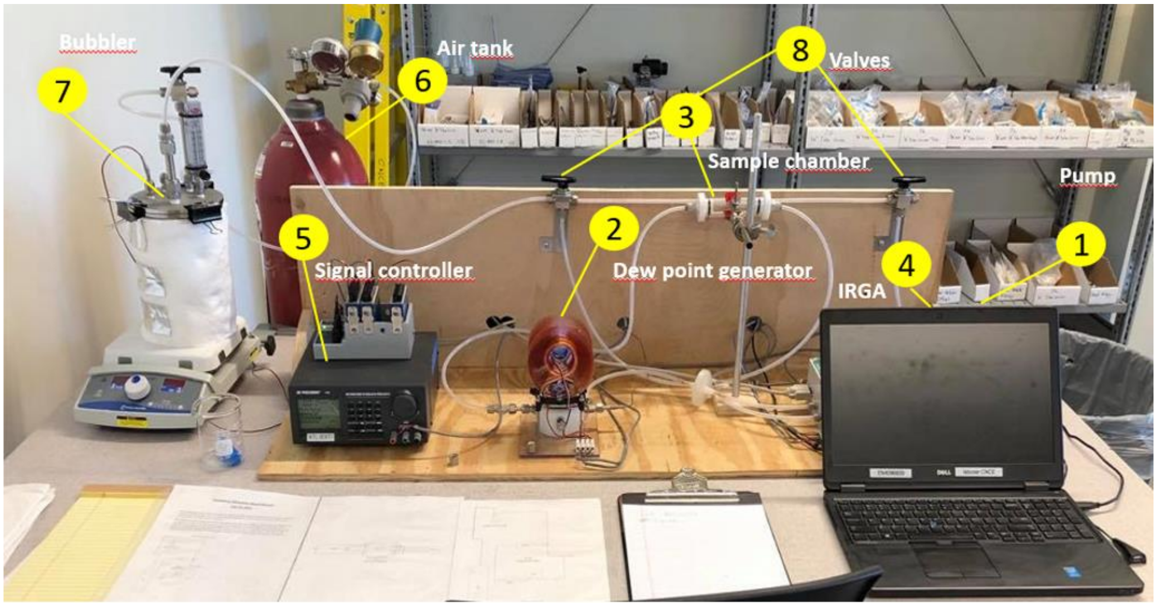


Figure 7 – Closed System for Moisture Swing and Temperature Swing

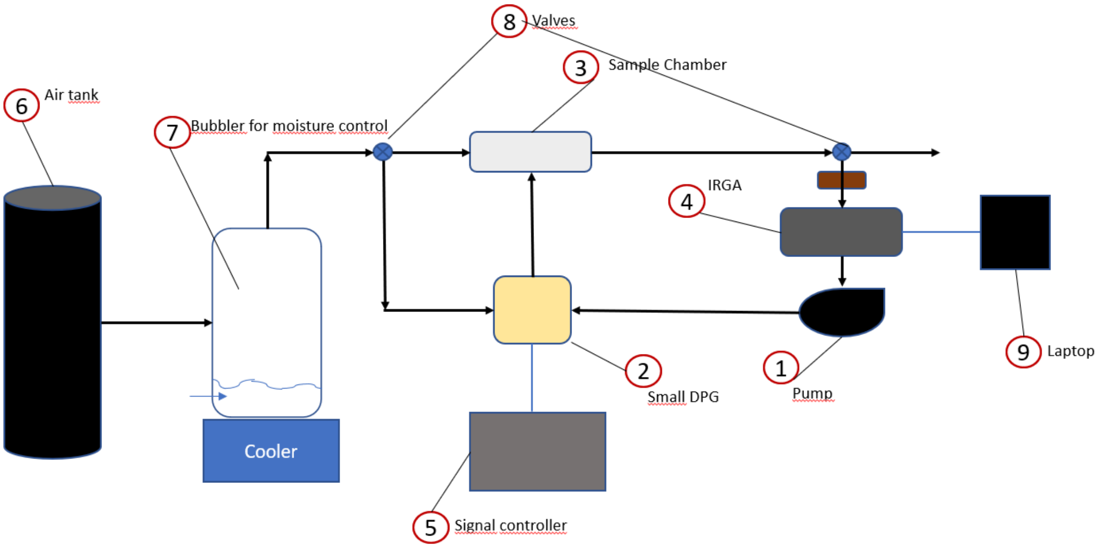


Figure 8 – Closed System for Moisture Swing and Temperature Swing Diagram

In the following sections we discuss several apparatus designs for measuring behavior of different sorbents. We begin with designs and test protocols for evaluating the performance of sorbents on the milligram scale. The first design will look at a moisture swing sorbent, the second is designed for measuring the uptake rate of any sorbent under ambient conditions.

Detecting the change in CO_2 concentration in a small chamber filled with air that includes a few hundred ppm of CO_2 is a very powerful way of measuring the removal of miniscule amounts of CO_2 from the gas phase. A detectable change of 1 ppm in a 100 cm^3 sample of air, is equivalent to roughly 4 nmol of CO_2. In other words, a milligram sample of a sorbent that can absorb a millimole of CO_2 per gram, could lower the CO_2 concentration in such a chamber by 250 ppm as it loads up with CO_2.

Based on such a measurement principle, one can design very sensitive detectors for characterizing sorbent materials on the milligram scale.

3.1.1 MSCS Experiment Protocol

The MSCS experiment protocol can evaluate different sorbents form factors utilizing different chambers. The most common sample chamber is the tubular chamber to evaluate 1 mg – 1,000 mg sample size. The sample size to be on the detectable range of the apparatus needs to be able to cycle between 0 – 5,000 ppm accurately and this cyclability will depend on the capacity, kinetics, cycle time (defined by the experiment) of the sorbent. This need to be determined by the knowledge or initial guess of the experimenter. The step-by-step protocol to the MSCS experiment is as follows:

1) Prepare your sample on the selected form factor. This preparation needs to ensure that the sample is well contained and cannot contaminate the experimental system. For instance, a powder sample usually needs to be inside sealed bag that with pores smaller than the powder particle size, but that still allows air and water vapor to flow through the sorbent. A 53 µm polyester mesh is commonly used in the lab for this purpose and it is able to hold in place most of the sorbents > 53 µm.
2) Once the sample is prepared it needs to be left for a minimum of 12 hours (or one overnight) in open air in order to allow the sorbent to equilibrate with the atmosphere and be “fully” loaded with CO_2. This time will vary depending on how fast the sorbent is or on the humidity of the environment. A second variance of this step is to leave the sample in a controlled dry environment in order to load with CO_2.
3) This step consists of getting the apparatus prepared for the experiment.
    a. Verify the dew point generator water level: open the water reservoir located at the bottom of the DPG. Remove all the water by tipping it over on a paper towel.
    b. Fill 1.5 mL of water using a syringe and close the reservoir.
    c. Open the lab view file “mother board”. There, choose the humidity level for absorption and the humidity level for desorption. Absorption for moisture swing needs to be drier than desorption, usually with a big difference in

moisture level between both. A typical value for absorption is 5 ppt of H_2O and for desorption 25 ppt of H_2O. Next set the desired cycle times: the cycle time will determine the absorption and desorption cycles. For example, if you choose 30 minutes, the system will run 30 minutes absorption and 30 minutes desorption and repeat accordingly until the experiment finishes. Typical values of cycle times are: 30, 60, 120 and 240 minutes. This choice will vary depending on the sorbent and on experimental objectives.

   d. Before starting the labview software insert your sample into the sample chamber.
   e. Open the LiCor software. Click on start logging data. Typically choose 1 data point per second. Starting logging data before the start of the system so that no data be lost and the not useful data can be eliminated later during data analysis and compilation.
   f. Start the labview system and press “clear” and “enter” the voltage controller immediately.
   g. Turn on the pump

4) The time the experiment runs will be determined according to the experimental objectives. Typically, the system needs around 4 full cycles (absorption and desorption) to equilibrate and to have a repeatability of the data. Once the experiment is finished there a step-by-step process to finish the experiments:
   a. Stop the login of the data to prevent any weird data points before you do any of the following steps.

    b. Turn off the labview software and immediately click on “clear” and “enter” on the voltage controller. Double check if the voltage signal is all “zero”.
    c. Turn of the pump
    d. Remove your sample

3.1.2 TSMSD Experiment Protocol

The TSMSD experiment protocol is similar to the moisture swing, since the apparatus is the same. Nevertheless, the method is slightly different. The sample size for thermal swing sorbents are usually on the range of 1-10 mg as the desorption process does not occur on the same system and the volume of CO_2 is limited by the 145 mL of air volume inside of the system, thus unless the sorbent has really low capacity, the sample mass needs to be very small to prevent emptying the CO_2 from the closed system. The steps 1 and 2 about the sample preparation is the same the subchapter 3.1.1 on the MSCS protocol. On Step 3 is slightly different:

3) Getting the apparatus prepared before inserting the sample
    a. Verify the dew point generator water level: open the water reservoir located at the bottom of the DPG. Remove all the water by tipping it over on a paper towel.
    b. Fill 1.5 mL of water using a syringe and close the reservoir.

c. Open the lab view file “mother board”. There choose the humidity level for absorption. As this is a thermal swing experiment, varying humidity usually is not the goal. Thus, a fixed humidity it is usually chosen between 5 and 25 ppt of H_2O. In order to hold the humidity constant, both humidity boxed needs to have the same value. For example if 5 ppt of H_2O is the desired constant humidity both boxes on the labview needs to be 5. The cycle times here will be irrelevant so leaving the regular 30 minutes would be enough. There is also the possibility of combining moisture and thermal swing tests if the experiment assumes a hybrid thermal and moisture swing sorbent. For this case the humidity settings can vary the same method utilized on the MSCS system.

d. On the thermal swing methodology, the desorption is not performed on the same apparatus. For thermal swing sorbents there is two ways for desorption: dry heat or steam heat desorption (desorption or regeneration). Thus, before the sample be inserted into the TSMSD apparatus it needs to be determined the type of desorption method. In the case of dry heat desorption, the sample needs to be inserted into the oven under the experimental determined temperature characteristic of the sorbent and the time of desorption. Commonly the sorbents are heat at 100 ºC during 1 hour. If the desorption is steam the sample needs to be inserted into the CSDS system (see methodology on subchapter 3.3.1). The CSDS system will graph the desorption process and the sorbent will release CO_2 until the CO_2

level comes back to the initial point showing that the sorbent is fully unloaded.

e. Open the LiCor software. Click on start loging data. Typically choose 1 data point per second. Starting to log in the data before the start of the system allow no data to be lost and the not useful data can be eliminated later on the data analysis and compilation.
f. Turn off the pump to minimize the air exchange with the ambient;
g. Open the sample chamber and quickly insert the sample immediately after the desorption. Close quickly the sample chamber. During these quick steps, hold your breath to prevent the high CO_2 concentration breathing to be release into the sample and into the apparatus.
h. Turn on the pump.

The absorption process will be complete once the CO_2 inside of the system stops dropping. Once it does, the step of stopping the experiment is the same steps 4.a to 4.d.

3.1.3 MSCS and TSMSD Results Compilation and Analysis

Figure 9 represents an example of the plotted raw data logged by the TSMSD experiment in which CO_2 in ppm and H_2O in ppt. The primary Y-axis shows the variation per second of CO_2 in ppm, starting from 460 ppm and dropping continuously to 353 ppm. The secondary Y-axis shows the water vapor was initially started on the dry mode controlled by the dew point generator at ~ 1 °C, initially maintaining the water vapor in 6.25 ppt of H_2O. The sorbent was passed first through a CO_2 desorption on the oven for 1 hour. Immediately after the sorbent was inserted in the chamber, the water rapidly increased to 7.5 ppt, but a few seconds went back to 6.25 as the dew point generator keeps working on condensing the water vapor released by the sorbent in order to maintain the system dry. This is a closed system with a limited amount of air and thus a limited amount of CO_2, thus once the CO_2 stop varying reaching a steady 353 ppm it means the sorbent is fully loaded with CO_2 and the 107 ppm drop represents the absorbed CO_2. Figure 10 presents the calculated data of CO_2 absorption in µmoles of CO_2 per g of sorbent. Considering that the system has 145 mL of air, atmospheric pressure 0.96 atm and temperature 295 K, there are 5.75×10^{-3} moles of air inside of the system and thus 5.75×10^{-9} moles of CO_2 per one unit of ppm presented on the data output. A spreadsheet model was created based on these calculations in which the initial CO_2 measurement in ppm, for example 460 ppm, is converted to 2.65×10^{-6} moles of CO_2, which is then normalized by the sorbent mass (3.2 mg) totaling 828 µmoles of CO_2 per g of sample. Thus 828 µmoles/g is considered the zero point on time zero in which no CO_2 has been absorbed yet. As the CO_2 is absorbed 460 ppm goes down and thus the zero point 828 µmoles/g calculated value declines and this decline is accounted as the positive inclination of the zero point until its max value of CO_2 absorbed by the sorbent when its fully loaded, according to figure 10 it is 196 µmoles CO_2/g.

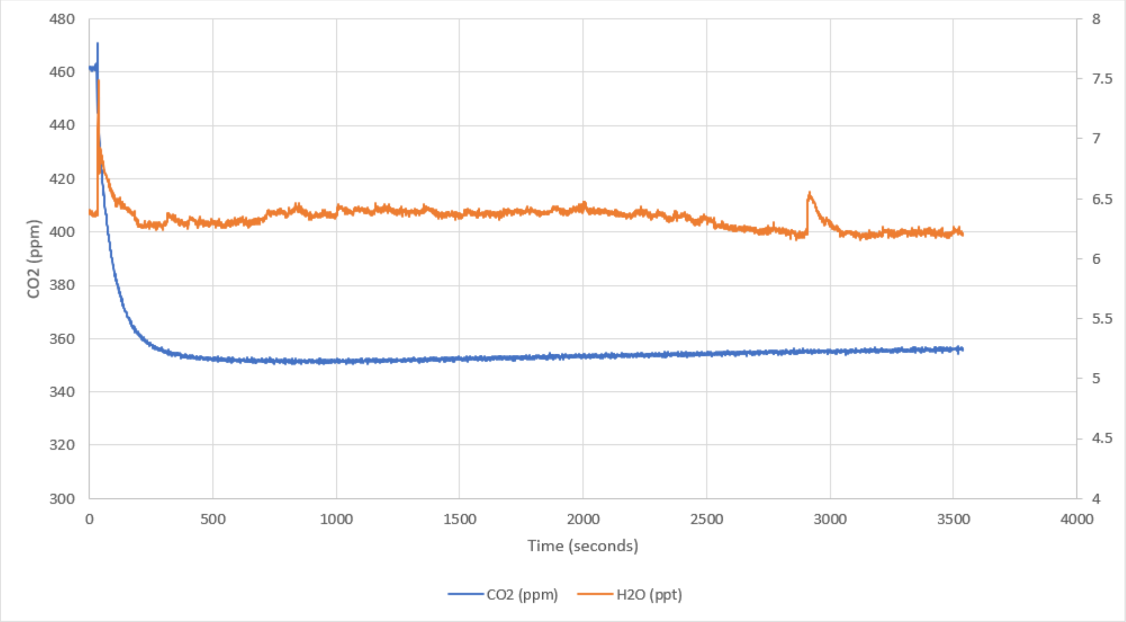


Figure 9 – TSMSD Results for Sorbent TSB 03 Absorption after Dry Heat Regeneration, Raw Data Results.

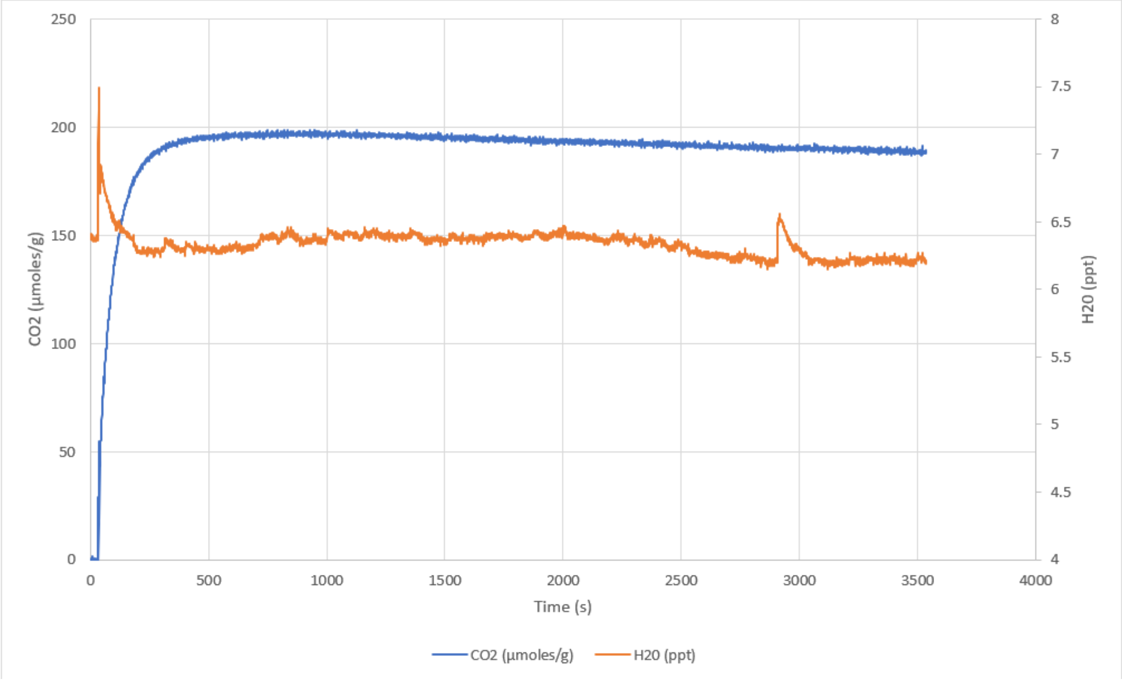


Figure 10 – TSMSD Results for Sorbent TSB 03 Absorption after Dry Heat Regeneration, Calculated Results.

Figure 11 is an example of a moisture swing experiment using the MSCS system. The sorbent PA318L after having been submitted to an ion exchange between Cl^- and HCO_3^- (protocol in detail on subchapter 4.1.1). Once the ion exchange was successfully completed, the sample was dried under vacuum and left for 12 hours in open air. After that we assume the sample is fully loaded with CO_2 for the starting point. The experiment was set to vary the humidity from 5 ppt of H_2O to 25 ppt of H_2O every 120 minutes, having then 120 minutes for absorption and 120 minutes for desorption. The orange lines (figure 11) represent the water variation starting to dry during 120 minutes and the CO_2 represented by the blue line following the drying trend, CO_2 inside of the board is quickly absorbed indicating the sorbent was not completely full of CO_2. The next 120 minutes the dew point generator goes from 1 °C to 30 °C vaporizing the water and increasing the humidity from 5 ppt to 25 ppt of H_2O. The CO_2 follows the trend, desorbing when it is wet going from 460 ppm to 4,000 ppm according to figure 10. Utilizing the same calculation model described for the TSMSD experiment this desorption represents 67 µmoles of CO_2 per gram of sorbent (figure 12). The next 120 minutes the system comes back to the dry mode in which the dew point generator goes from 30 °C back to 1 °C and the water vapor from 25 ppt to 5 ppt. As a result, the sorbent absorbs back the 67 µmoles of CO_2 released into the closed system. This cycle keep repeating until the experiment is considered finished. In this case the figure shows 4 full consistent cycles of CO_2 absorption and desorption.

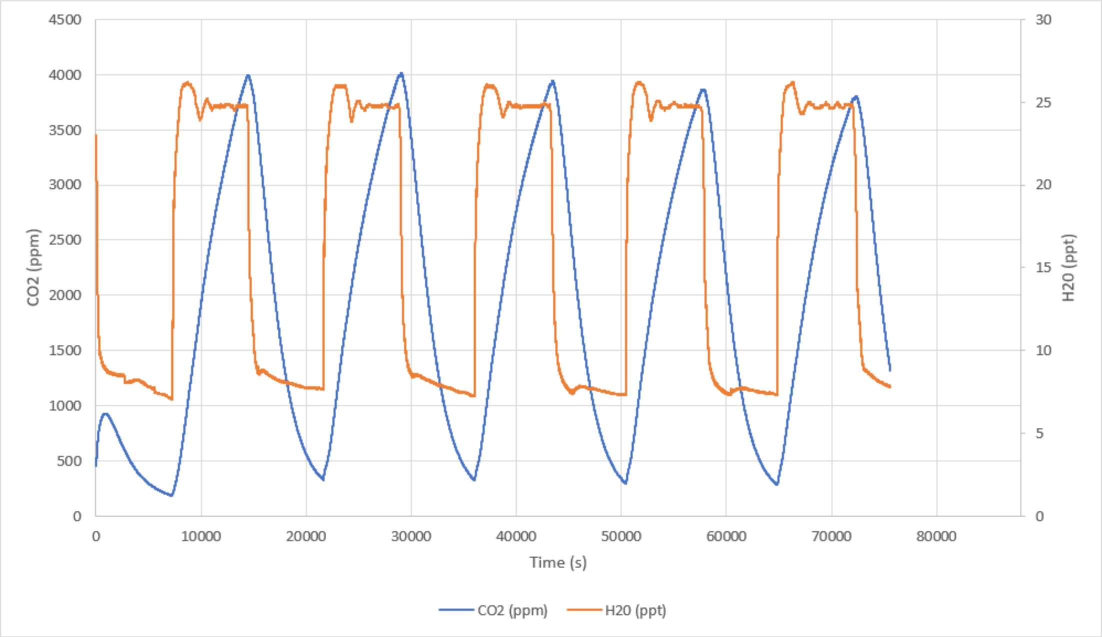


Figure 11– Raw Data Sorbent PA318L after HCO_3^- Ion Exchange Cycling 5 ppt to 25 ppt of H_2O with 120 min Half-cycle Times

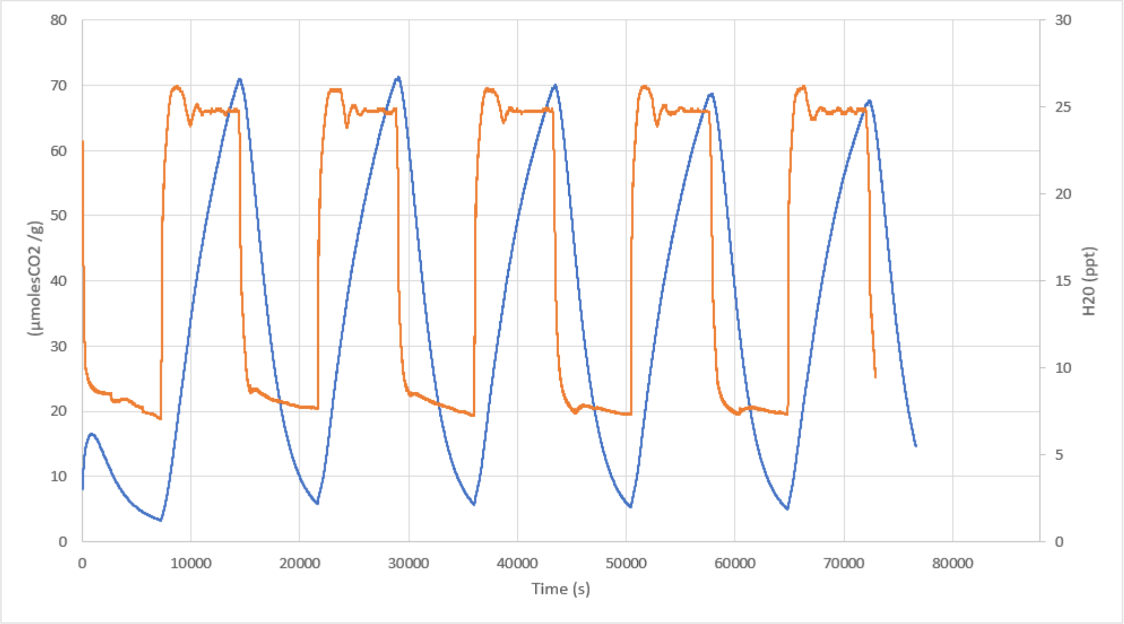


Figure 12 – Calculated Data Sorbent PA318L after HCO_3^- Ion Exchange Cycling 5 ppt to 25 ppt of H_2O with 120 min Half-cycle Times

3.1.4 TSMSD and MSCS Data Duplication

The methodology TSMSD and MSCS has proven to be reproducible. Figures 12 and 13 present a duplicate experimental data set respectively to the absorption and desorption of the MSCS experiment utilizing PA318 resin after been ionic exchanged with HCO_3^- (ionic wash protocol is described on subchapter 4.1.1). The samples were prepared with 0.2g sample weight, inserted on a 53 µm polyester mesh. The experiment was set with 120 minutes half cycles between absorption and desorption and a variation on humidity on 5 ppt H_2O for the absorption period and 25 ppt of H_2O for the desorption period. Evaluating the error based based on a duplicate results it is possible to notice on figure 14, there is little variation on the data, representing a reliable methodology. For the desorption presented on the figure 14, the duplicated data also show little deviation. Thus the results show the experimental method is reliable and precise. The absorption and desorption processes occur inside of the closed system, in which enhances accuracy.

For TSMSD methodology shown on figure 15 the absorption of CO_2 after the dry heat regeneration had an averaged standard deviation of 8.38 µmoles CO_2/g, higher when compared to the moisture swing sorbent. This is to the fact of certain steps on the TSMSD methodology increased the change of error. For instance the desorption process does not occur inside of the TSMSD apparatus. The sorbent dry heat regeneration occurred on the oven with 100 ºC for 1 hour. Once the desorption time is elapsed, the sample has to quickly manually be removed from the oven and inserted on the apparatus (in which should be running and ready on the desired humidity. These steps increases the chance of error, because this particular sorbent has a very fast kinetics on absorbing CO_2 and a few seconds in between experiments can increase the chances of error. Another room for error is if the researcher breathe on the sample while doing the transfer from the oven or CDSD system to the TSMSD apparatus. Humans breathe out about 50,000 ppm and this can load partially the sorbent if the researcher does not hold his/her breathe on the process. Nevertheless, the error was minimal with an average standard deviation of ± 8.4 µmoles CO_2/g. It is also noticeable a slight decline on the curve related to the second experiment. This shows a minor leak on the system.

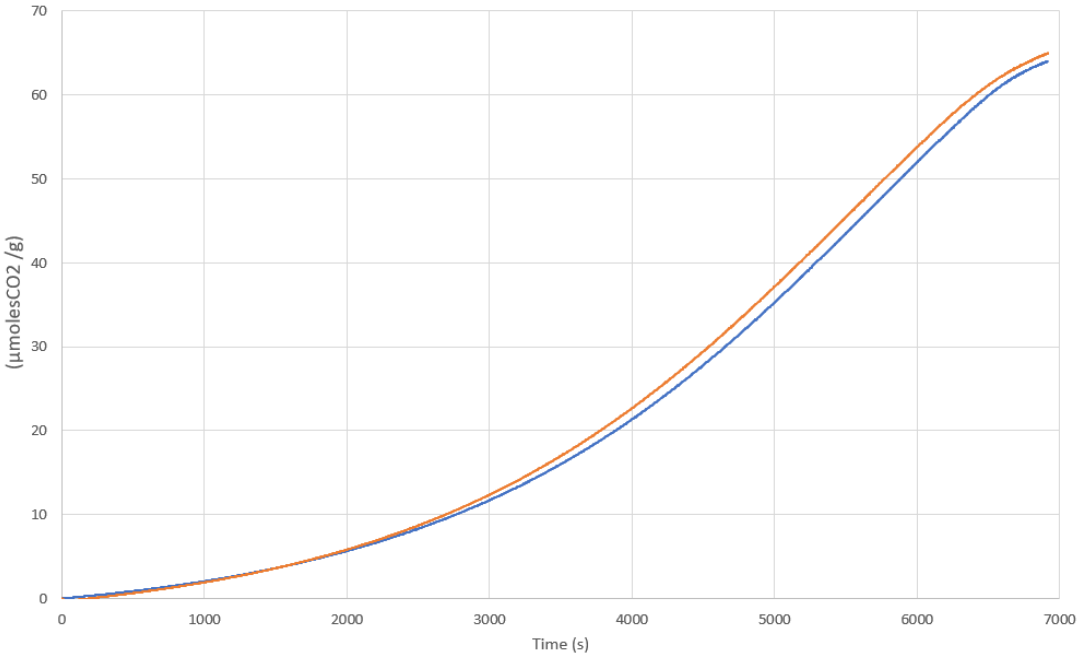


Figure 13 – MSCS CO_2 Absorption Curve Data Duplication

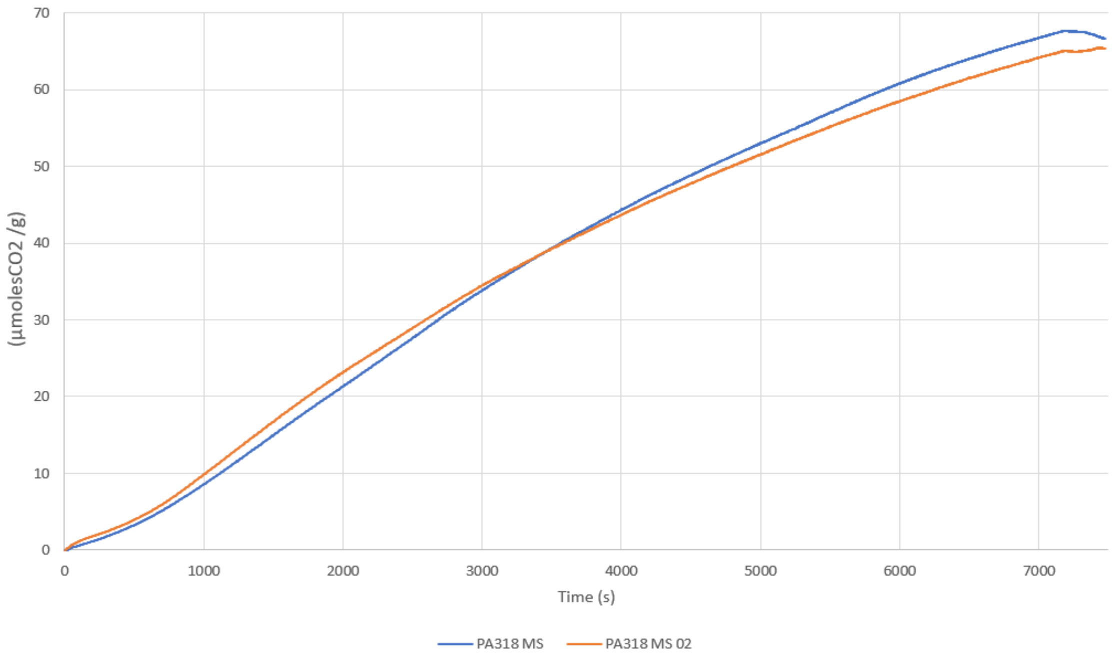


Figure 14 – MSCS CO_2 Desorption Curve Data Duplication

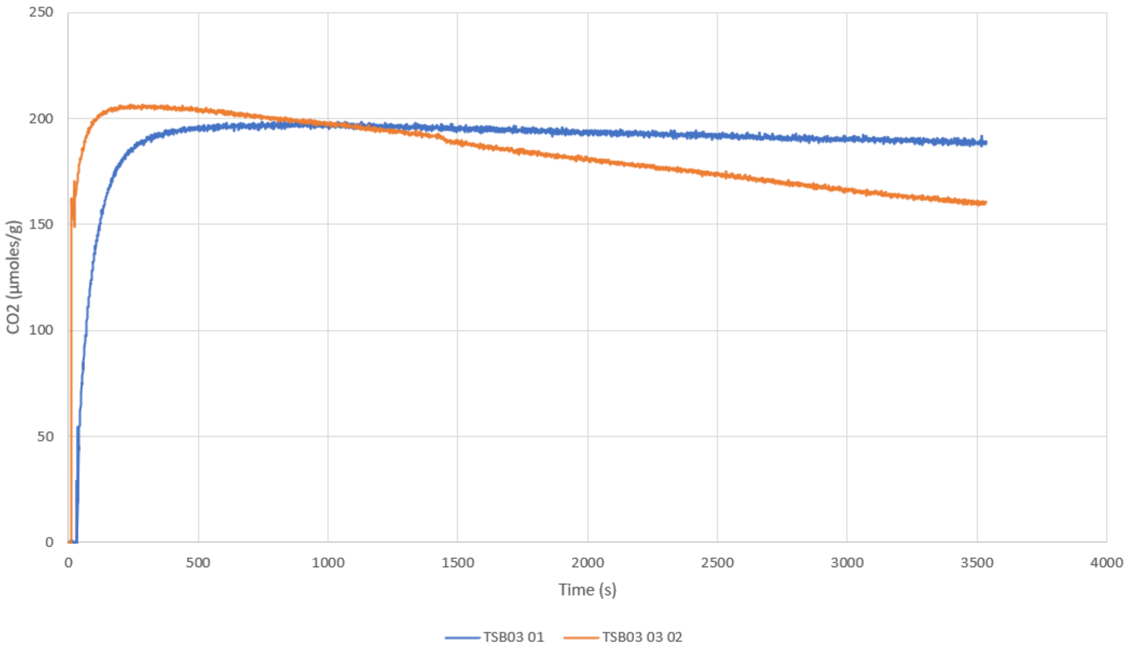


Figure 15 – TSMSD CO_2 Absorption Curve Data Duplication Error Bars

3.1.5 TSMSD for Fast Screening Thermal Swing Sorbents

TSMSD systems can be used to fast-screen sorbent materials on small mass scales. Figure 16 shows the sorbents named under a code TSB 03, TSB 04, TSB 05 and TSB 08. The sorbents were tested with 3-5 mg of weight respectively. The system operated at 5 ppt of H_2O with an initial concentration of CO_2 of ~415 ppm (ambient laboratory CO_2). It is possible to observe TSB 03 had a remarkable kinetics reaching 77% (period of time in which the kinetics was the highest) of its total loading in just 118 s with 150 µmoles CO_2/g of sorbent, and 100% of its loading in 500 s with a total of 195 µmoles CO_2/g. The sorbent TSB 04 had the second highest capacity reaching 150 µmoles CO_2/g after 3500 s; sorbent TSB 05 had the second fastest kinetics under 500 s but with considerable lower capacity when compared with sorbents TSB 03 and TSB 04 with a total of 50 µmoles CO_2/g; and lastly sorbent TSB 08 is a clear example of a sorbent with no capacity on absorbing CO_2.

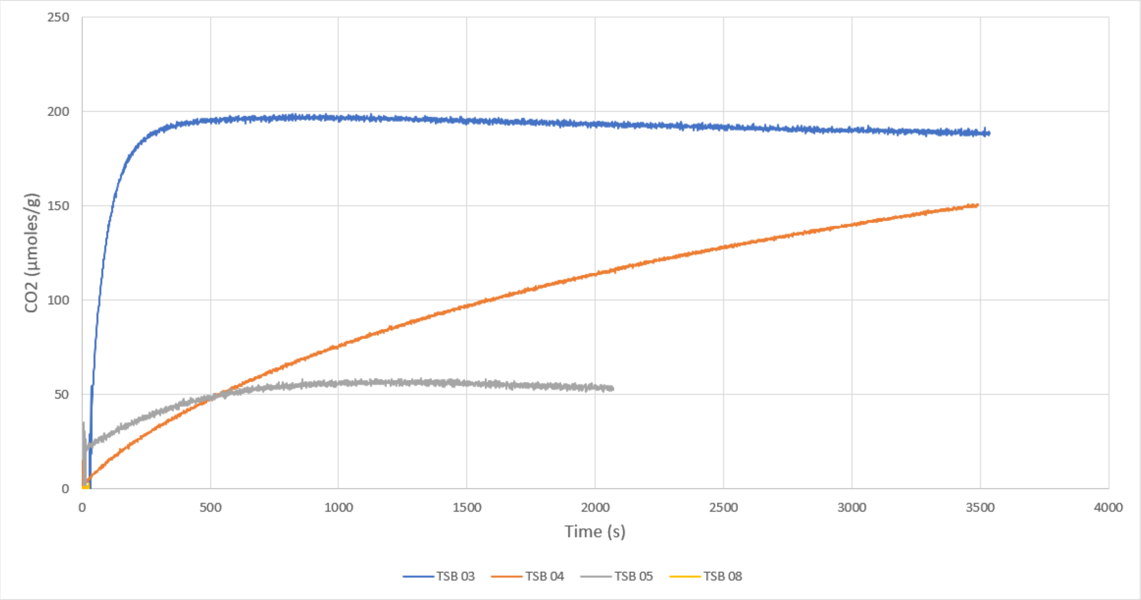


Figure 16 - TSMSD Results Screening and Characterizing Temperature Swing Sorbents

3.1.6 MSCSD for Fast Screening Moisture Swing Sorbents

Just like the TSMSD system the MSCSD experimental method can be used to fast-screen moisture swing sorbents. Figure 17 and 18 present the screening data of three moisture swing sorbent candidates. All the sorbents were submitted by a bicarbonate ion exchange method discussed on the subchapter 4.11. The experimental settings applied were a variation on the humidity between 5 to 25 ppt of H_2O vapor on half cycles of 120 minutes (120 minutes at 5 ppt and 120 minutes at 25 ppt of H_2O. Figure 17 presents the absorption cycle in which the system is operating at 5 ppt H_2O, after the 120 minutes half cycle the fastest kinetics and capacity was the sorbent PA318 MS followed by CBR 03 and snowpure. The sorbent CBR 03 had a lost on performance at 6,000 s in which the sorbent snowpure ended up with a slightly higher capacity at the end. The total CO_2 absorbed respectively to PA318 MS, snowpure and CBR03 were 64, 34 and 28 µmoles of CO_2/g of sorbent.

Figure 18 presents the desorption part of the experiment, once the sorbent is fully loaded with CO_2 from the desorption phase, the humidity is increased to 25 ppt of H_2O. All the sorbents obtained a desorption rate faster than the absorption rate. Considering the first 1200 s time mark the desorption is 4.2, 38 and 16 times faster than the absorption respectively to PA318 MS, snow pure and CBR 03. The thermal swing sorbent analyzed on subchapter 3.2 shown that the desorption was 48 times faster than the absorption under the steam heat desorption process.

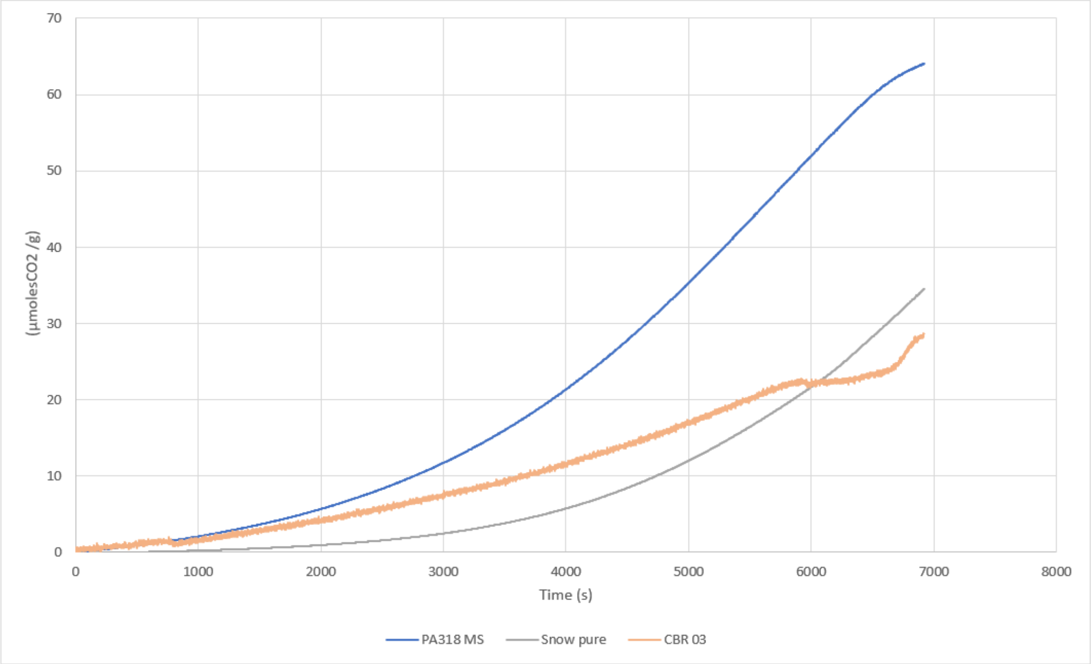


Figure 17– Moisture Swing Screening Sorbents, CO_2 Absorption Data

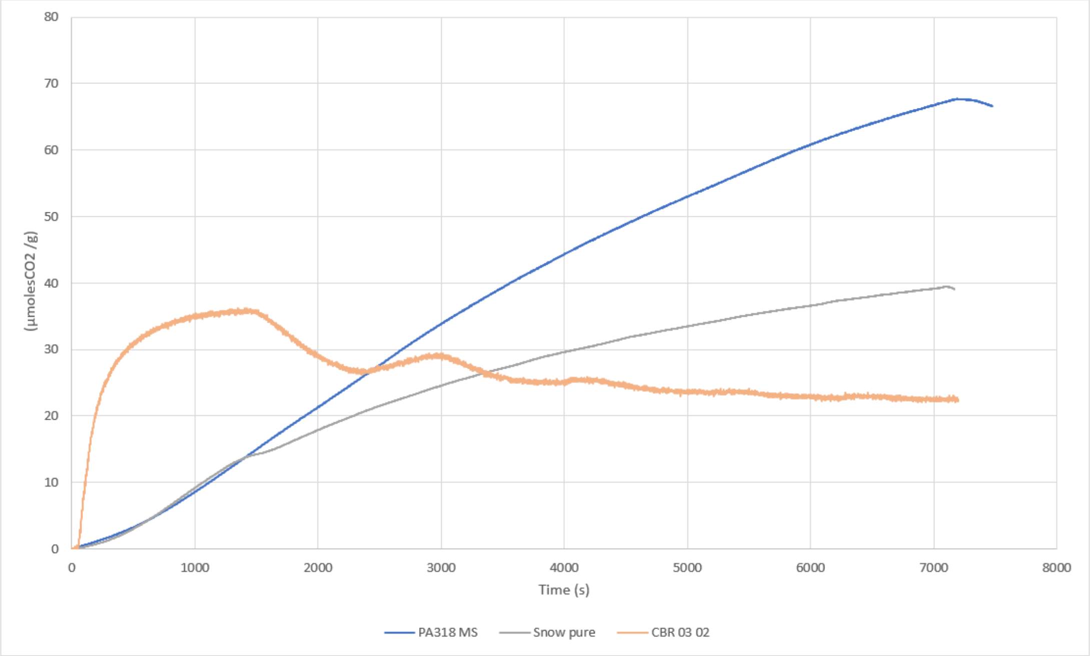


Figure 18 – Moisture Swing Screening Sorbents, CO_2 Desorption Data

3.1.7 MSCSD and TSMSD Methodologies Sources of Inaccuracy and Room for Improvement

The MSCSD methodology has a high accuracy as demonstrated in the previous subchapter on its duplicate result. The high accuracy of this test is due to the fact the moisture swing occurs in a closed environment, in which absorption and desorption is performed on the same apparatus. Differences in accuracy on a test can be found depending on the initial equilibrium state of the sorbent. When the sorbent is prepared the standard procedure is to leave the sorbent in open air on a bench in the lab for ~ 12-24 hours. Although the laboratory temperature is very stable at 22 °C, unexpected temperature fluctuations can occur. Humidity in the lab environment can fluctuate depending on environmental conditions and depending on the sorbent the initial equilibrium state can shift. The CO_2 concentration in the laboratory can also fluctuate in different hours of the day. These variations can change the accuracy of the results on the same sorbent, even if they are not significant for fast-screening, they need to be taken into consideration.

For the TSMSD system the same sources of error for MSCSD can occur. In addition, this system has a slightly higher chance of error because the desorption part of the experiment is not performed in the same apparatus. For dry heat desorption the sample is put into an oven and for steam heat desorption the sample is prepared at the CSDS system. After releasing the CO_2, the sample is then transferred to the TSMSD system. This transfer is performed manually and the time to transfer from one apparatus to the other may differ. However, CO_2 absorption will start before the sample has been transfered. In addition, if the researcher breathes out close to the sample during this transfer, the error can be even bigger as human breath contains more or less 5% of CO_2. Thus, this transfer needs to occur as fast as possible and without breath out on the sample. This part is still rudimentary and needs improvement in an integrated and automated system which will minimize these errors. Nevertheless, the duplicate results show overall a small margin of error in the system as-is.

This system can be improved to a fully automated system with many samples in a row to be tested. This needs mechanical and software design improvements. For temperature swing samples a heating system can be integrated into the process to have the desorption occur on the same system without an external apparatus. If the variation of temperature is added to the closed system, the software must be improved so that it includes logging temperature data. In addition, the software cycles of absorption and desorption can only perform an exact cycle time for both on the moisture swing system. A different cycle time for absorption and desorption can be useful on characterizing the sorbents.

3.2 CO_2 Sorption Open Flow System (CSOFS)

The CO_2 sorption open flow system has been developed to experiment on sorbents at the 0.1-1.0 g scale. The system can evaluate the CO_2 sorption on temperature swing sorbents with a fixed humidity level or moisture swing sorbents by changing the humidity manually on a larger dew point generator. This apparatus can evaluate essential characteristics of a sorbent: a) CO_2 sorption of a sorbent on a per second basis for temperature swing sorbents and CO_2 sorption and desorption for moisture swing sorbents. The main difference between this system and the MSCSD and TSMSD is the size of the sample to be evaluated and the evaluation of the sorbent on a)\ open flow continuous setting with a specific air flow rate, evaluating sorbent kinetics under different flow rates and the total sorbent loading capacity at the experimental given condition; b) evaluation of bigger sample form factors that can be for example: sorbent in different pouches; sorbent on adhesive, small 3 D printed form factors for sorbent; c) the assembly of the CO_2 steam desorption system chamber immediately after the sample total desorption been empty with CO_2. This allows the evaluation of a sorbent after steam regeneration which can absorb quantities of water that can increase or decrease sorbent`s kinetics and capacity; d) the ability to screen many g scale samples and compare with the mg scale results evaluating the first step of scale. The selected samples can then be tested on the next scale with tens of g in a wind tunnel.

The literature present ssystems with a controlled CO_2 concentration mixed usually with only nitrogen gas to evaluate a flow through very small samples in the mg scale. Compressed tanks with controlled CO_2 concentrations are expensive for testing many sorbents. The CSOFS system created an inexpensive system which uses ambient air flow over the sorbent and it can control the humidity of the system with a dew point generator. The system can also vary the air flow rate with mass flow controllers. In addition, the system differs from most of the systems in literature for having the capability to test sorbents on the gram scale.

The CO_2 sorption open flow system (CSOFS) (figure 19, figure 20) has been developed in order to obtain the CO_2 adsorption or absorption rate of a given sorbent after it has been submitted to dry or steam heat regeneration. The system is an open flow design and is composed by 1) A compressed air tank which is filled with ambient air. The air needs to be stored in order to maintain a constant CO_2 concentration in the air at that given moment in time. It has been observed in the lab area that the CO_2 concentration can vary at different times of the day. By introducing a tank, the experiment can operate at a constant CO_2 concentration. 2) A dew point generator (DPG) which controls the water vapor concentration based on the dew point temperature. This allows us to have a very dry setting at $\leq$ 5 ppt H_2O and up to a very high moist setting at ~ 25 ppt of H_2O. 3) two mass flow controllers that allow us to run two samples at the same time. The mass flow controller will maintain the flow at a constant flow rate. The DPG can support a maximum of 2 L air/min, thus each mass flow controller or both combined must not exceed this value. Most of the experiments are set at a constant 0.5 L air/min for the CO_2 sorption analysis. 4) two tubular sample chambers which allow us to hold the sample while the air flows through and CO_2 binding to the sorbent if it has capacity. 5) A special purpose sample chamber that is used for very fast CO_2 sorption. This chamber is part of the CO_2 Steam Desorption System (CSDS). The sample holder has been designed to be removable and it has 2 valves that make it possible to open and close the chamber. After the CSDS desorbs all the CO_2 with steam, the valves are closed to prevent any CO_2 sorption before the chamber is attached to the CSOFS system. Once attached to the CSOFS the valves are opened and the air flows from the tank through the sample, and CO_2 sorption start. 6) The air flow is then finally passed through an infrared gas analyzer (IRGA) which determines the CO_2 and H_2O vapor concentrations at ppm and ppt levels respectively. 7) The laptop converts the signals of the IRGA through the Licor software computing the amounts from the infrared signal.

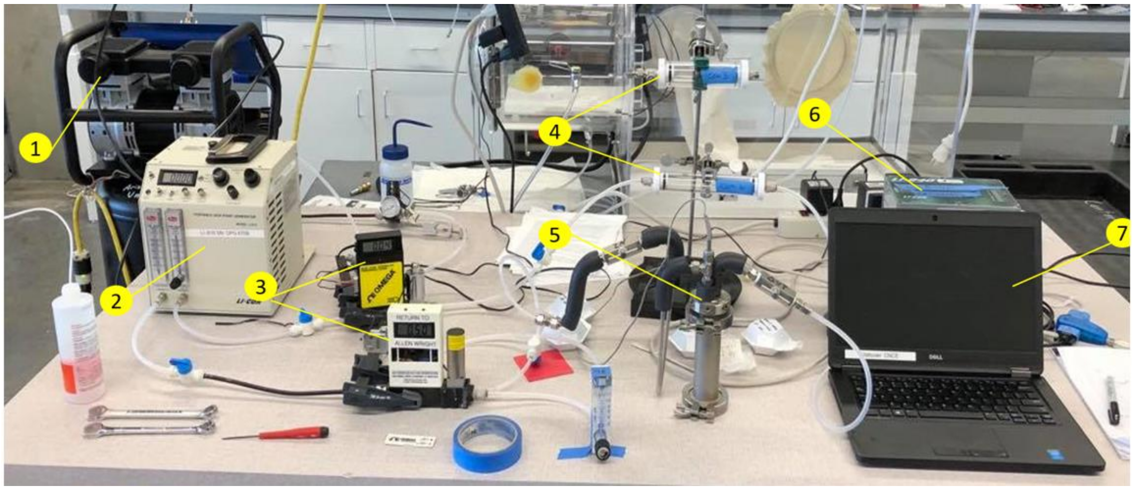


Figure 19 – CO_2 Sorption Open Flow System (CSOFS)

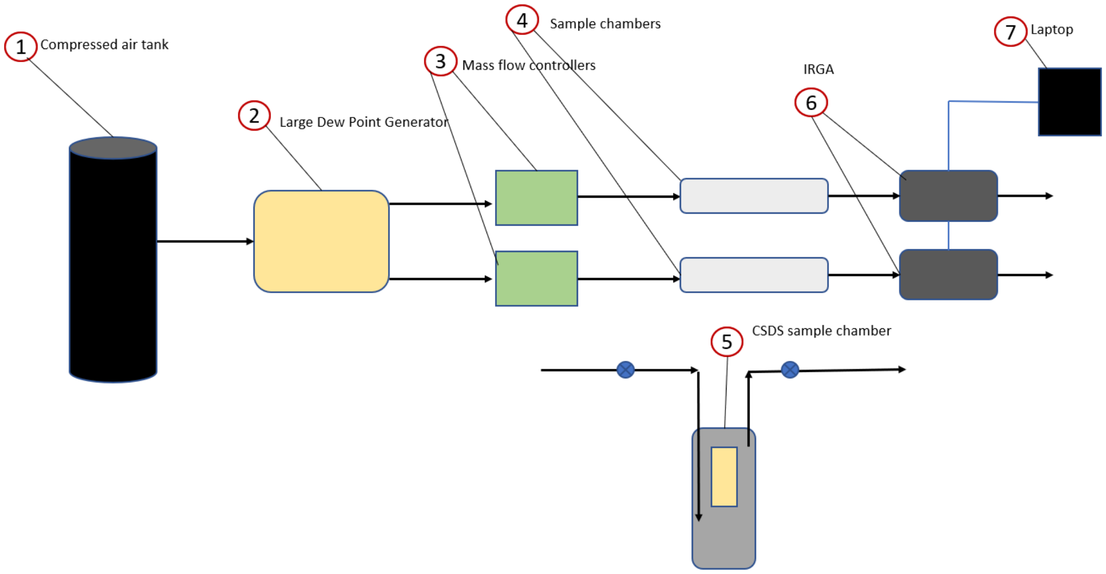


Figure 20 - CO_2 Sorption Open Flow System (CSOFS) Diagram

3.2.1 CSOFS Experiment Protocol

The CSOFS experiment is able to evaluate sorbents in the range of 0.1-1.0 g assuming the sorbent has a reasonable kinetics and capacity. If the sorbent has very low capacity the sorbent weight could be up to 2 g. The step-by-step experimental protocol is as follows:

1) The sample needs to be first prepared similarly to the MSCS and TSMSD experiment protocols described in subchapters 3.1.1 and 3.1.2. The sample needs to be prepared in a form that that ensures that the sorbent will not contaminate the system. As described on the MSCS items usually a 53 µm polyester mesh is commonly used in the lab for this purpose and it can hold in place most of the

sorbents > 53 µm. If the sorbent has smaller particle sizes the mesh needs to be less coarse to match the sorbent's particle size.

2) Once the sample is prepared, exactly as tin he MSCS protocol, the sample needs to be left for a minimum of 12 hours (or one overnight) in open air to allow the sorbent to equilibrate with the atmosphere and be "fully" loaded with CO_2. This time will vary depending on how fast the sorbent is or on the humidity of the environment. A second variance of this step is to leave the sample in a controlled dry environment in order to load with CO_2.
3) The third step is to prepare the system:
    a. Fill the compressed air tank by switching the valve to on. Typically it takes 6-10 minutes. The compressed air will stop filling once it reaches a selected pressure. Make sure to turn OFF the valve once it is filled. If the valve is left one, it will refill when the pressure drops to a selected specific pressure.
    b. Set the temperature of the dew point generator to the desired humidity level. The usual set point for a thermal and moisture swing sorbent is 4-5 ppt of H_2O with the DPG set point at ~ 0.5 ºC. The Humidity of the system will depend on the experimental objectives.
    c. Set the mass flow controllers to the desired air flow rate. Typical values are 0.5 and 1.0 l/min. The DPG cannot support more than 2.0 l/min. Thus one of the mass flow controllers or the sum of both cannot exceed 2.0 l/min.

    d. Turn the air flow valve of the compressed air tank to the air pass start passing through the system. It might take minutes to a few hours to the system reach the desired humidity level.

4) Once the 12+ hours has been passed and the sample is likely fully loaded of CO_2, the sample needs to pass through the thermal CO_2 desorption process. This methodology similar to the method used by the TSMSD explained on the subchapter 3.1.2, item 3.d. with a few differences:
5) For thermal swing sorbents there are two ways for desorption: dry heat or steam heat desorption (desorption or regeneration).
    a. Dry heat regeneration: insert the sample into the oven under the experimentally determined temperature characteristic of the sorbent and the time of desorption. Commonly the sorbents are heated at 100 ºC for 1 hour.
        i. Start logging the data at the CSOFS system to prevent any initial data loss;
        ii. Once the desorption time has elapsed move the sample immediately to the CSOFS sample chamber so the CO_2 sorption start to occur.
        iii. Once the sample is loaded: a) turn off the login data; b) turn off the air flow; c) turn off the DPG; d) remove your sample from the sample chamber.
    b. Steam heat regeneration: the sample needs to be inserted into the CSDS system (see methodology on subchapter 3.3.1). The CSDS system will graph the desorption process and the sorbent will release CO_2 until the CO_2

level comes back to the initial point showing that the sorbent is fully unloaded.

    i. Once empty of CO_2, a) close the air flow to the system; b) close both valves from the CSDS sample chamber to prevent any CO_2 absorption before the absorption process starts in the CSOFS system.
    ii. Disassemble the sample chamber from the CSDS system and move to the bucket of ice. Monitor the temperature until it reaches 25 °C.
    iii. Start logging the data at the CSOFS system to prevent any initial data loss;
    iv. Move the CSDS sample chamber and attach it to the CSDS system.

6) The CO_2 will drop and be continuously lower than the initial CO_2 until the sorbent is fully loaded with CO_2. Once the CO_2 is back to the initial level, it indicates the sorbent is fully loaded.
7) Once the sample is fully loaded with CO_2:
    a. turn off data logging;
    b. turn off air flow;
    c. turn off the DPG;
    d. remove your sample from the sample chamber.

3.2.2. CSOFS Results Compilation

The CSOFS system as its name already indicates it is an open airflow system. Figure 19 and figure 20 present the raw data in which the system was first set with continuous atmospheric air flow from the air tank starting at 450 ppm and the dew point generator was set close to 0 °C, starting the humidity in 4.5 ppt of H_2O. Once the sorbent is inserted into the system it CO_2 start to be absorbed quickly dropping the CO_2 concentration from 450 ppm to 60 ppm and its concentration continuous to be absorbed, increasing the CO_2 concentration that passes through the IRGA as the sorbent start to be fully loaded of CO_2. Once the concentration is the same as the initial, it indicates the sorbent is fully loaded. In order to convert this result in µmoles of CO_2 per gram of sorbent we need to consider first the amount of airflow in this case set in 0.5 l air/min considering 0.96 atm and temperature 295 K, the air flow is then $8.33\text{x}10^{-3}$ l air/s, $3.3\ \text{x}10^{-4}$ moles air/sec that result in $3.3\ \text{x}10^{-10}$ moles CO_2/sec per ppm measured in the system. Then, the CO_2 concentration consumed overtime is calculated with an integral, or accumulated CO_2 consumed over the experimental period of time (figure 22). Once the CO_2 concentration is the same as the initial it indicates the sorbent is fully loaded with CO_2 and the maximum capacity of the sorbent can be evaluated.

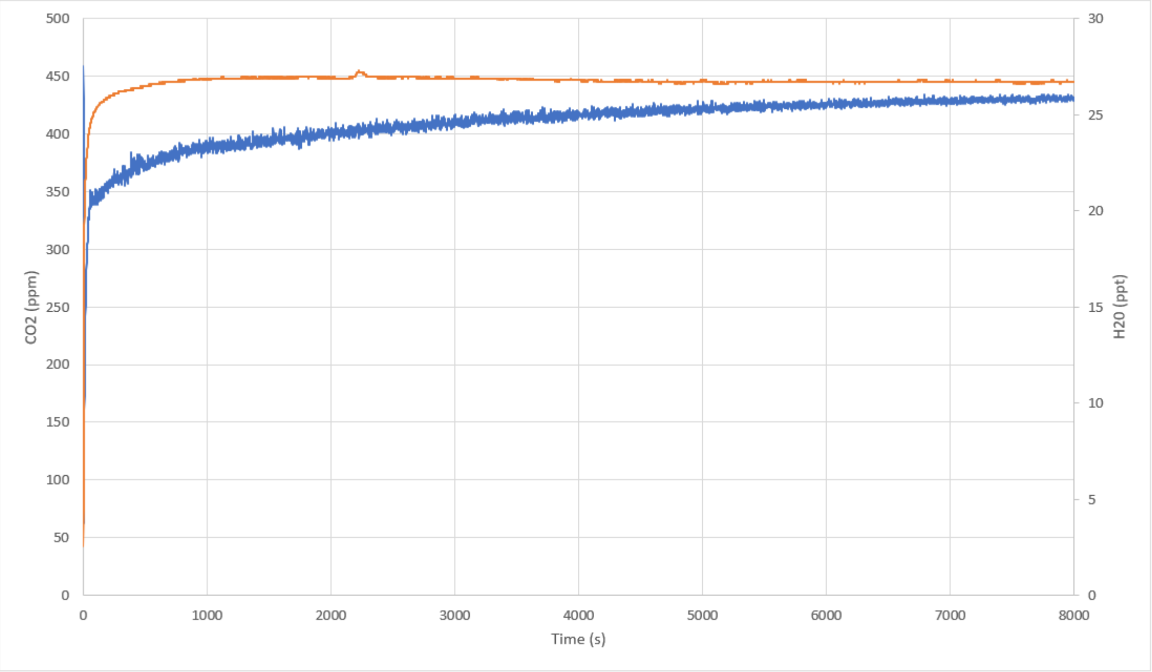


Figure 21- CSOFS Results Compilation, Raw Data.

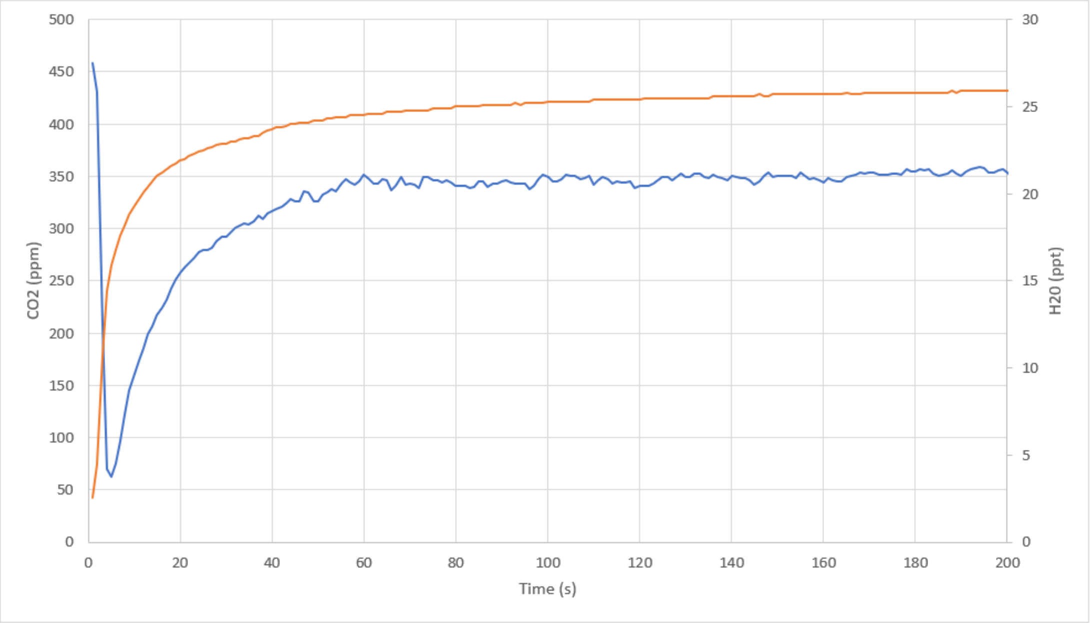


Figure 22 - CSOFS Results Compilation, Raw Data, under 200 s.

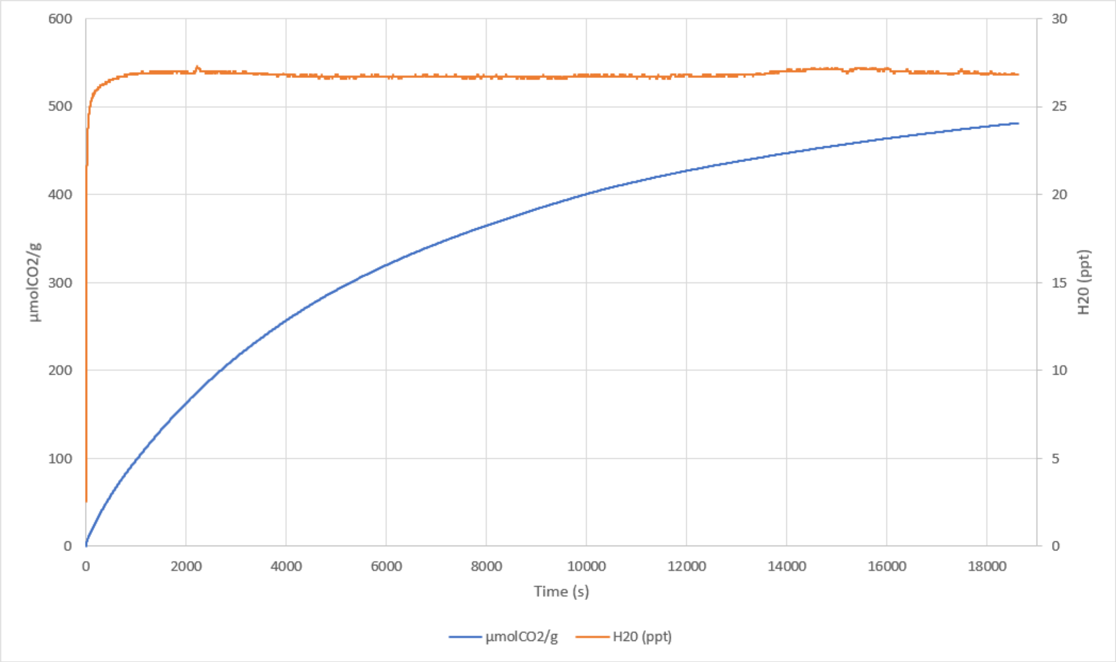


Figure 23 - CSOFS Results Compilation, Calculated Data.

3.2.3 CSOFS Sorbent Screening - Results CO_2 Absorption in CSOFS for 0.1 – 1.0 g Scale Testing

The CSOFS system can be used to screen a variety of sorbent candidates in relatively short period of time. Figure 24 and 25 present the calculated results of 7 temperature swing sorbent candidates. Figure 24 is a complete set of data points for all sorbents with a total time of 62,000 seconds once sorbents TSB 02 reaches its maximum capacity. Figure 25 present the same set of results but on a shorter timescale of 7,200 seconds in order to better evaluate the kinetics of the sorbents on ≤ 2 hours cycles. These figures indicates that sorbent TSB 02 has the higher capacity with 2,000 µmoles CO_2/g of sorbent when compared to 900 µmoles CO_2/g for sorbent TSB 01. However analyzing figure 25 on short timescales shows that sorbents TSB 01 and TSB 02 have similar kinetics. Sorbent TSB 01 kinetics is slightly faster from 0 to 2,500 seconds. Sorbent TSB 02 takes off to higher kinetics due to the fact it has more than twice the capacity of TSB 01. The remaining sorbents tested showed a range of kinetics and capacity from higher to lower in the order of TSB 03, TSB 04, TSB 05, TSB 06 and TSB 07. For all these experiments, the sorbents were tested inside of a polyester mesh bag with 53 µm porous size.

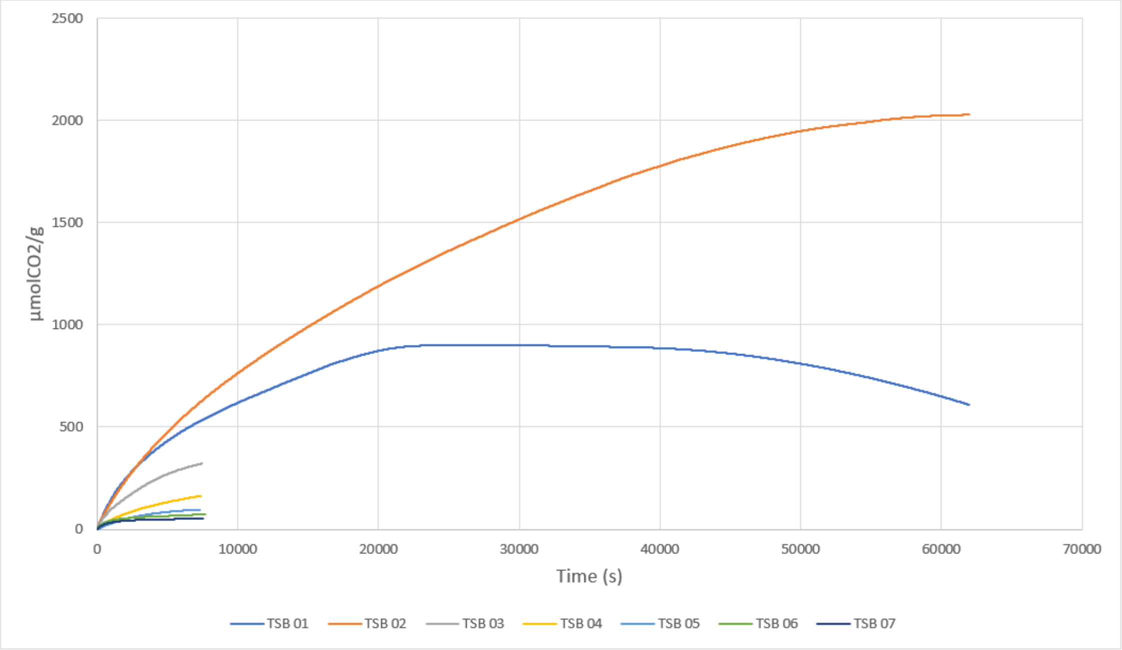


Figure 24 – CSFOS Results Screening Temperature Swing Sorbents under 62,000 S Timescale.

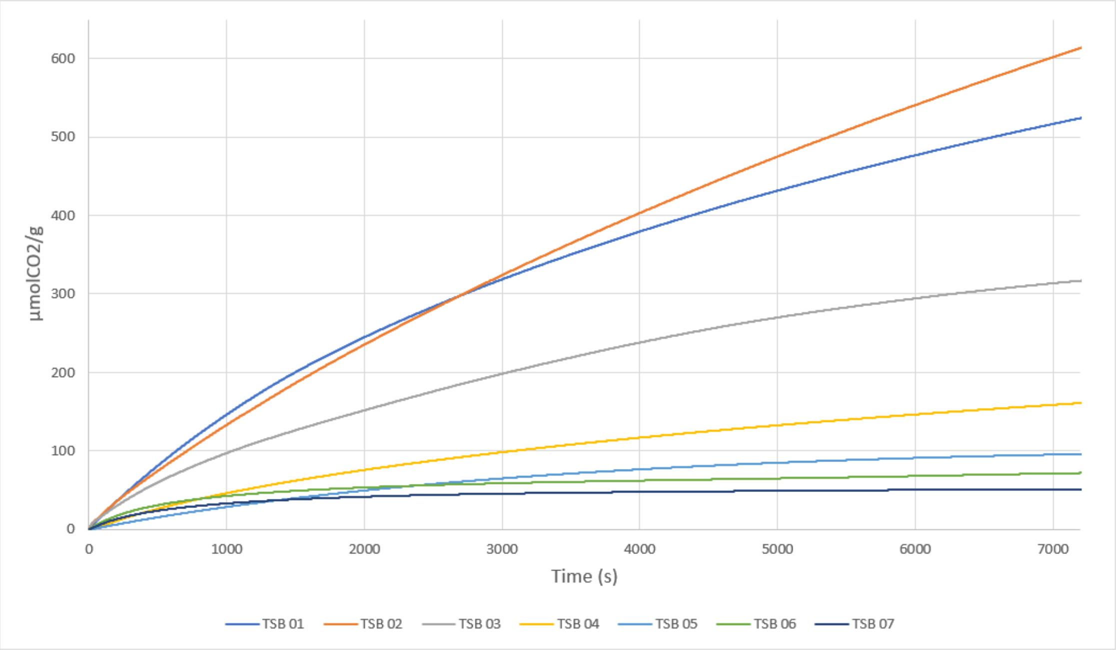


Figure 25 – CSFOS Results Screening Temperature Swing Sorbents under 7,200 S Timescale

3.2.4 CSFOS Methodologies Sources of Inaccuracy and Room for Improvement

The CSFOS system is mainly designed for temperature swings. Despite the fact that the dew point generator can control humidity, it does not automatically cycle it. Furthermore, the dew point generator can adjust moisture in a single pass, is very slow in changing the operating point. Moisture swing can be evaluated in the system if the variation of moisture is performed manually. When performing temperature swing the sources of inaccuracy are similar to the MSDS and TSMSD methodologies when the sample is performing absorption after dry heat desorption. The sample needs to be desorbed in the oven, which is a separate device. Therefore, the sample needs to be quickly inserted into the CSFOS system to prevent significant absorption before the system starts to log data. For samples after the steam heat regeneration in which the CSDS system is utilized, the CSDS sample chamber is removable. Thus, once the sample is empty of CO_2, the valves of CSDS sample chamber are closed, the sample is cooled down to ambient temperature and then attached to the CSFOS system. This minimizes the error that occurs on the absorption after dry heat regeneration. Sources of possible error on the absorption after the steam regeneration is how efficiently the researcher close the valves, cool down to the accurate temperature and carry the sample to be assembled effectively and efficiently to the CSFOS system. A new version of a CSDS and CSFOS system can be designed in which both systems are one. For this purpose, once the sample is empty of CO_2, the CSDS chambers need a fast-cooling system to ambient temperature and an effective dew point generator in order to keep the humidity into a desired experimental level. Another improvement on the system is to automate the dew point generator in order to alternate humidity levels on desired cycle times much like the MSDS and TSMSD methodologies. Moreover, the system can be automated to load many samples in order to screen faster. This system then can be replicated to evaluate a large number of samples in a shorter period of time like it is proposed for the future of the MSDS and TSMSD methodologies.

3.3 CO_2 Steam Desorption System (CSDS)

The CO_2 Steam Desorption System (CSDS) is a unique system to evaluate and screen sorbents desorption capacity and kinetics under steam or dry heat regeneration. Most of the data on literature present TGA analysis on desorption without an effective per second analysis in which allows to evaluate desorption kinetics. The system uses an unexpensive air compressed tank with mass flow controller using ambient air to flow through the sample. The steam heat regeneration evaluating kinetics is an unique setting, the ability to mass flow control the air, the water level for steam control and the temperature differential on the first 2 buckets and the last one are unique features that can enhance sorbent's desorption kinetics.

The CSDS system is an effective desorption system to screen and evaluate thermal swing sorbents capacity and kinetics on 0.1 – 1.0 g of sorbent mass scale. The system can be utilized to desorb CO_2 from a sorbent utilizing steam or operating dry, depending if water is added on the steam generator chamber (item 4 on figures 26 and 27).

According to figure 26 and figure 27 the CO_2 Steam Desorption System (CSDS) comprises: 1) compressed air tank from the ambient air to keep a constant CO_2 through the system; 2) mas flow controller to keep the flow in a desired rate in liters/min; 3) two DI water bucket that can submerge the two stainless steel chambers. 4) This first stainless-steel chamber is the steam generator chamber. The chamber is completely filled with DI water once the system starts. As the chamber is submerged into the bucket and it is heated the DI water in the chamber will evaporate and create a water vapor admixture to the gas with a partial pressure set by the water temperature. 5) The second stainless steel chamber is the sample chamber. This chamber will start free of water and the sample will be clamped in place in the upper part of the chamber. This chamber will be also submerged in water for heat transfer from the second bucket, maintaining the same temperature (for some experimental designs this temperature could be chosen differently depending on the experimental objectives) than the steam generator chamber. 6) There are two adjustable plate heaters for the first and second bucket. The temperature range of these hot plates varies between no heating to 250 °C, although the buckets hold water so the temperature of the water won`t surpass 100 °C. 7) The third bucket is filled with a mixture of liquid water and ice. This bucket will be used with the chamber after the sample chamber. 8) This last chamber needs to have a starting point free of water. This chamber is the water removal chamber in which it will condensate most of the steam that has already passed through the sample to prevent any excess water condensation to pass through the IRGA. 9) The IRGA model Li Cor LI-840 A10) The system currently has 4 thermocouples to measure temperature: on the hot water buckets (number 3) and on the stainless-steel chambers 4 and 5. 11 and 1213) The desktop computer convert the signals of the IRGA through the Li Cor LI-840 software computing the amounts from the infrared signal.

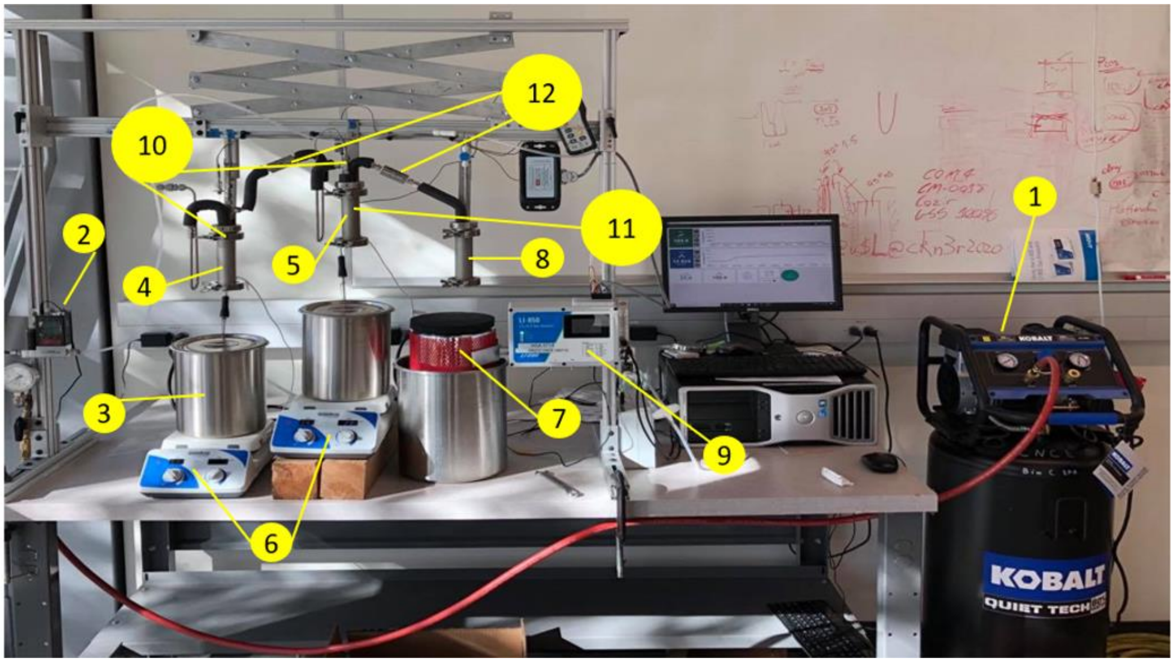


Figure 26 – CO_2 Steam Desorption System (CSDS)

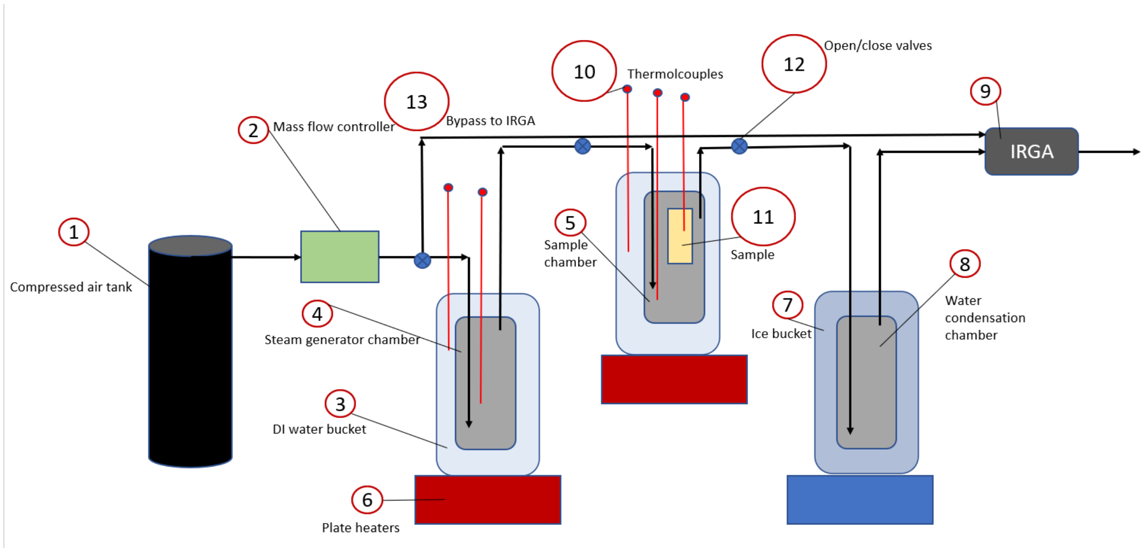


Figure 27 – CO_2 Steam Desorption System (CSDS) Diagram

3.3.1 CSDS Experimental Protocol

The CSDS methodology to obtain CO_2 steam desorption data before the system pass through the CO_2 absorption system TSMSD (1-10 mg sample size) or CSOFS (0.1-1.0 g sample size) systems step by step is as follows:

1) The process starts with the sample preparation, the same method utilized on the TSMSD and CSOFS since the sample is the same for both: The sample needs to be prepared in the specific form factor that ensures the sorbent will not contaminate the system. As described in the MSCS discussion, usually a 53 µm polyester mesh is used in the lab for this purpose and it is able to hold in place most of the sorbents > 53 µm. If the sorbent as smaller particle sizes the mesh needs to be less coarse according to the sorbent`s particle size.
2) Fill the compressed air tank turning on the filling valve. Once the tank is full make sure to turn the air filling valve to off much like the CSOFS system.
3) Fill the steam generator chamber with 70% of its volume with DI water.
4) Empty the water removal chamber (third chamber) if necessary.
5) Determine the flow rate on the mass flow controller (usually 0.5 l/min).
6) Turn the valves to bypass the main chambers.
7) Turn on the flow rate in order to flush well the system and have a steady starting point of CO_2.
8) Start heating the first 2 buckets of the system until the boiling point.
9) Fill the bucket of ice with half liquid water and half of ice.

10) Start logging the data to prevent any initial data loss.
11) Insert the sample on the sample chamber
12) Move all the chambers (using the 3 buckets movable parts) until the 3 chambers are submerged into the water.
13) Immediately move the valves to the airflow pass throughout the chambers and the system.
14) As the sorbent released CO_2 the system Li Cor LI-840 software will show an increase of its concentration and the rate will go down until the concentration becomes the same as the initial. Once the concentration is the same as the initial, it shows the sample is completely unloaded of CO_2.
15) Once the CSDS experiment has finished there are two possibilities:
    a. The sample chamber will be moved to the CSOFS system to obtain the absorption data. For this option
        i. Close the air flow rate.
        ii. Turn of the plate heaters
        iii. Close the sample chamber valves to prevent any CO_2 from start to be absorbed.
        iv. Move all the chambers from the buckets upward.
        v. Disassemble the sample chamber and move the bucket of ice (without removing the thermocouple) until the temperature drop to 25 °C.
        vi. Move the chamber to be inserted on the CSOFS system

b. The sample will be removed from the sample chamber and rapidly moved to the TSMSD system:
    i. Close the air flow rate.
    ii. Turn of the plate heaters
    iii. Close the sample chamber valves to prevent any CO_2 from start to be absorbed.
    iv. Move all the chambers from the buckets upward.
    v. Open the sample chamber and remove the sample.
    vi. Rapidly transfer the sample to the TSMSD system.

3.3.2 CSDS Results Compilation

The data output and compilation of CSDS system can be presented with the figures 25 and 26. Figure 24 present the graph of the raw data in which an initial sorbent sample starting fully loaded with CO_2 is exposed to steam heat desorption. The steam generator chamber was 70% filled with water and the air flow through the system was 0.5 l/min. On the figure 25 the raw data show the initial atmospheric CO_2 concentration on time zero with ~420 ppm and as the experiment starts the sorbent starts to quickly desorb CO_2 increasing the concentration read in the system from 420 ppm to 3,100 ppm and then the curve start to decline as the kinetics of desorption decreases as the sorbent unload CO_2 until be completed empty at the point that the CO_2 concentration in the system becomes the same as the initial on time zero. The data calculation and compilation to represent the data analysis in µmoles CO_2 / g of sorbent is performed similar to CAOFS: Considering 0.5 L/min of atmospheric air flow this represents 8.33×10^{-3} l air/s resulting in 3.3×10^{-4} moles air/sec resulting in 3.3×10^{-10} moles CO_2/sec/ppm. The integration of the accumulated CO_2 desorbed is then normalized for the sample mass, in the case of this experiment the mass of the sorbent was 0.2065 g. The result is then presented according to figure 29 in which the sorbent desorbed a total of 315 µmoles of CO_2/g, with most of the CO_2 desorbed on less than 100 s.

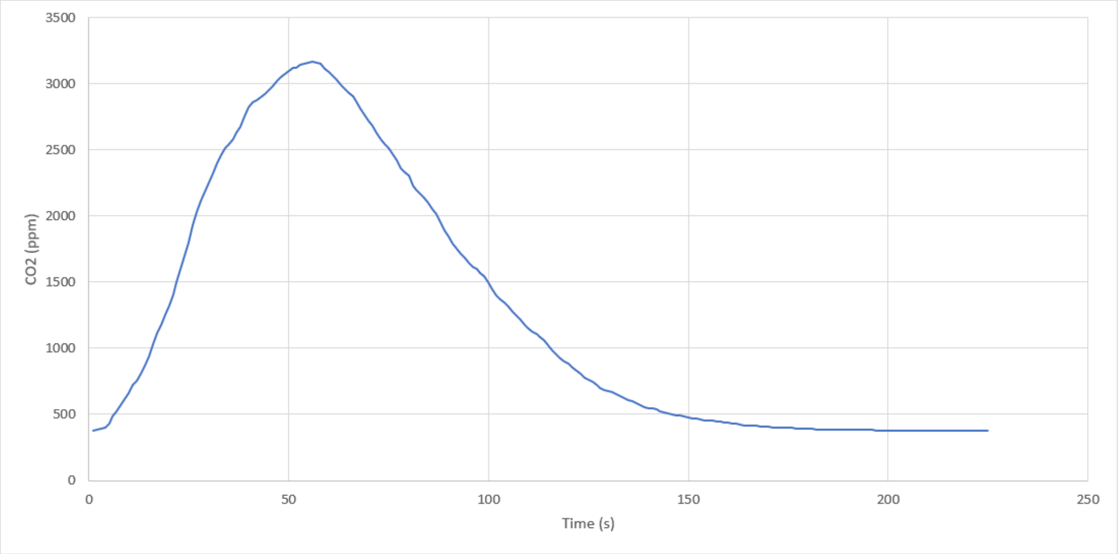


Figure 28 - CSDS Results Compilation, Raw Data

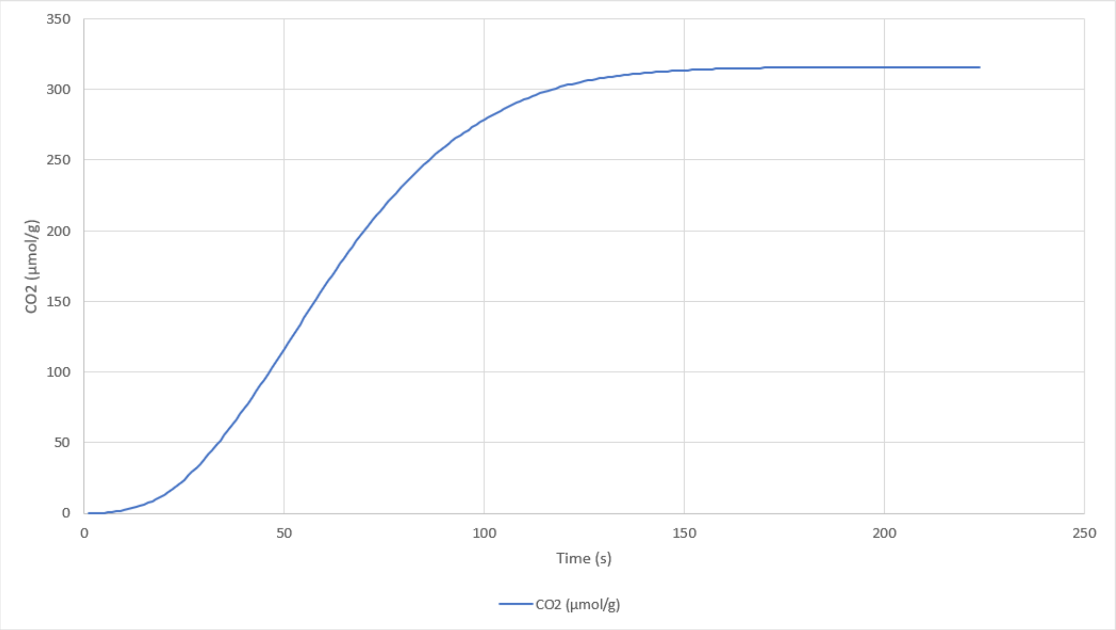


Figure 29 - CSDS Results Compilation, Calculated Data

3.3.3 CSDS Results Duplication

In order to determine to repeatability of the results produced with the CSDS methodology, two almost exact duplicate samples were prepared, running the experiment with the same settings. The sorbent TSB 03 with 0.3g of weight was inserted on the 53 μm polyester mesh. The CSDS system was prepared with 70% of the steam generator chamber full with DI water, the first 2 buckets with water at the boiling point and air flow rate at 0.5 l/min. The resulted obtained has demonstrated an average standard deviation of only 11.8 μmoles of CO_2/g. Thus the CSDS system has a very precise methodology with a low error margin (figure 27).

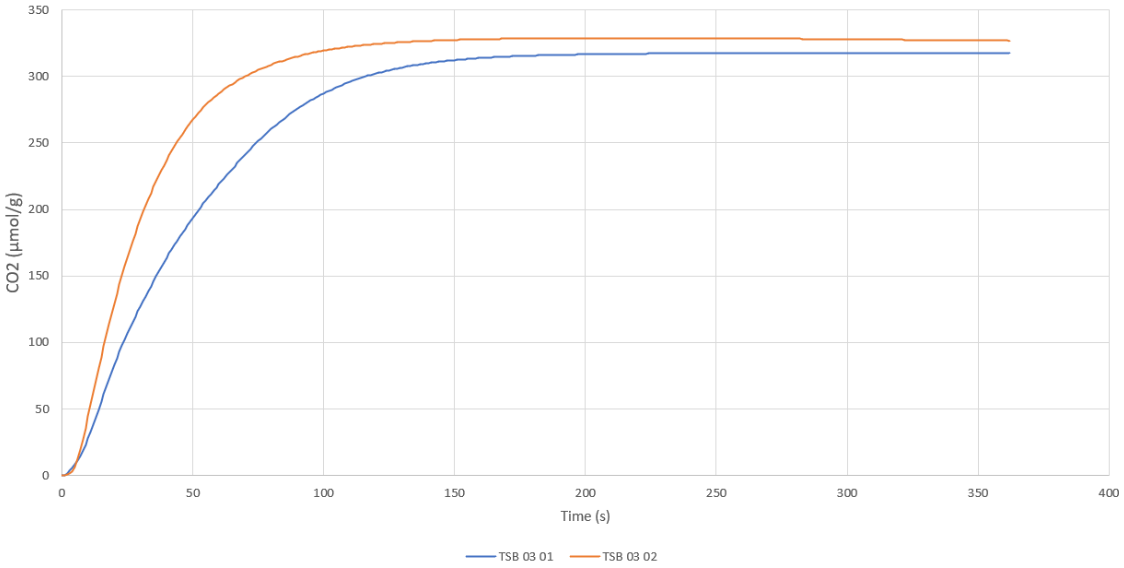


Figure 30 – TSB 03 Sorbent Stem Heat Desorption Data Duplication Error Range

3.3.4 CSDS Screening Sorbents

Analyzing the several data set of sorbent screening using the CSDS system operating with 0.5 L/min air flow rate, temperature of water at boiling point for the given atmospheric pressure (0.96 atm) and chamber 70% filled with water, all the sorbents tested desorbed with a very fast rate with all desorbing more than 80% of all the CO_2 in less than 500 s and all having its fastest part of the curve desorbing within 300 s. A more rudimentary system in the lab utilizing a beaker, DI water, plate heater with a metal plate to support the sample and a metal lid covering with a small whole to the steam pass through has been used. For the sample TSB 03 the rudimentary system has taken 3,600 s hour to desorb CO_2 while with the CSDS system under the given experimental conditions has taken only 300 s. A more detailed experimentation of the CSDS system under different water on the steam generator, flow rate and temperature needs to be evaluated in order to determine which are the main factors driving the enhancement rate.

Figure 32 shows the data frame under 300 s in which is the time the sorbents were in their fastest desorption rate. It is important to note that despite the fact on 300 s the TSB 02 has desorbed remarkably 1,250 µmoles CO_2/g, <85 s it was not the fastest desorbing sorbent, sorbents TSB 04 cr mlmb, TSB 07, TSB04 3fmb and TSB 03 were respectively faster on desorbing CO_2. Above 85 s most of the sorbents were >70% loaded and once they reach closer to its maximum capacity, the kinetics is greatly reduced. Thus the sorbents TSB 04 cr mlmb, TSB 07, TSB04 3fmb and TSB 03 show great promise in terms of kinetics and these if the capacity can be enhanced, can potentially be better than TSB 02 (figures 31 and 32). It is also important the note that the sorbent TSB 04 cr mlmb obtained an almost instantaneously desorption while all the other sorbents had between 15 to 50 seconds of delay before start desorbing CO_2 this is due to the fact this sorbent was on a powder form with particles in the nanoscale, this its surface area is considerable larger when compared to the other experimented sorbents.

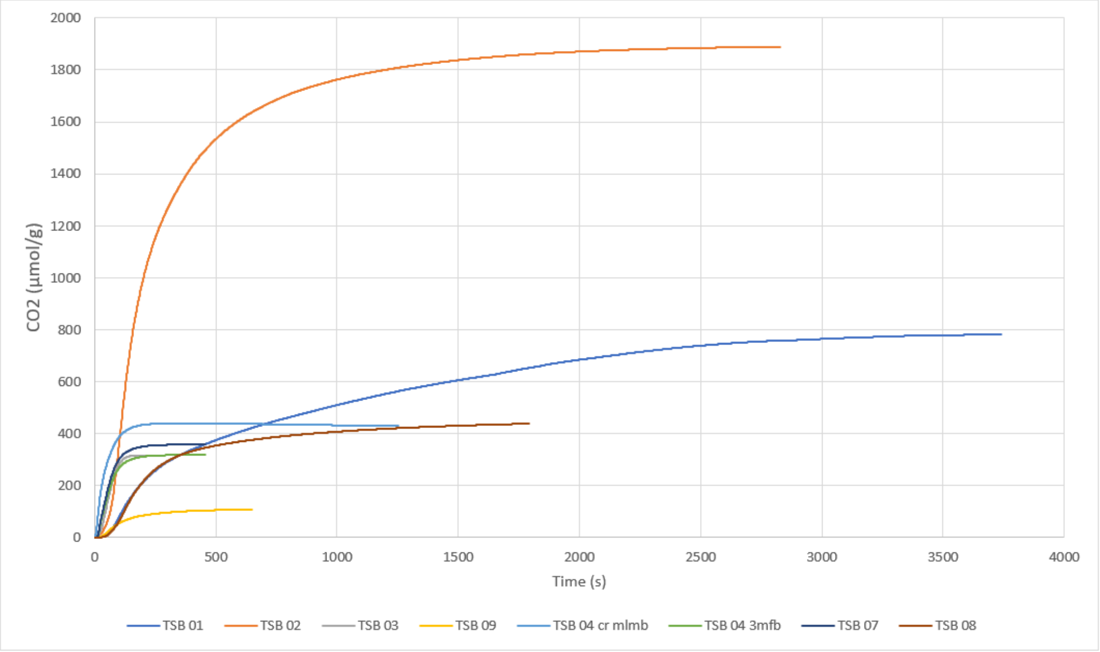


Figure 31– CSDS System for Screening Temperature Swing Sorbents

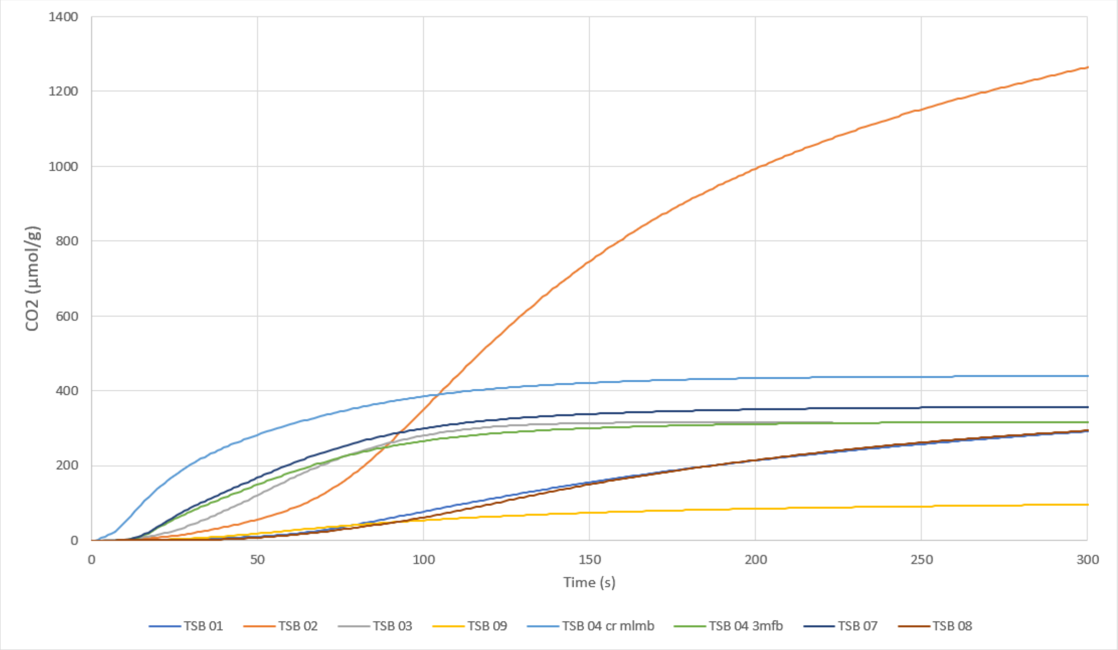


Figure 32 – CSDS System for Screening Temperature Swing Sorbents under 300 s.

3.3.5. CSDS Methodologies Sources of Inaccuracy and Room for Improvement

The CSDS sources of inaccuracy are more related to the researcher ability to operate the system precisely. The sample needs to be inserted once it is fully loaded of CO_2 much like in the MSCSD system. The sample is left about 12-24 hours in open air. Depending on the day ambient temperature, humidity and CO_2 concentrations may vary such that the initial equilibrium loading state can be different (this is especially critical for humidity variation). One strategy is to make the sample fully loaded by running the sample on the CSFOS system until it is completely full and then transfer it to the CSDS experiment. Fluctuations of the CO_2 concentration in the lab environment still can cause some variations, but overall, the methodology is quite accurate as discussed previously. Another source of human error is the time in which the sample is heating before changing the valves so that the air flow changes from bypassing the sample to pass through the sample. If the sample is heating for a specific period before the valves be turned and CO_2 passing through the sample, CO_2 will start to accumulate in the chamber and once the valve is turned, the airflow will carry a large amount of accumulated CO_2, giving a big jump on the data. This strategy can be on purpose if the intention is to heat the sample chamber to a certain temperature first, but in most cases the air flow pass through the sample while the sample is heating, before reaching the maximum temperature. Source of error can also be associated with the amount of water the steam regeneration chamber is filled. The same quantity needs to be evaluated in order to have a reproducible result. The amount of water on this chamber will be proportional to the amount of steam that will pass through the sample. For future improvements the system can be automated to go up and down; added a vacuum system in which aa temperature-vacuum desorption strategy can be evaluated on this small scale device.

3.4 Wind Tunnel

Sorbent's kinetics and capacity on DAC can vary significantly under different weather conditions. A sorbent's performance under small scales 1-10 mg and 0.1-1.0 g can perform very different from a sorbent of tens of grams. In addition, a larger sample can be composed with more specific more complex form factors in which can greatly affect sorbent's kinetics and capacity. The wind tunnel is a unique system developed to evaluate larger and heavier sorbent samples under different wind velocities, temperature, and humidity levels. This system can evaluate moisture and temperature swing sorbents.

This system has been created to evaluate moisture and temperature swing sorbents on a larger scale, a next step in scale after the CSFOS system. The wind tunnel operates as a closed system with a total of 561 L of volume. It has been developed to evaluate the CO_2 sorption utilizing of larger sorbent sample sizes (1-100 g scale) in a variety of form factors for temperature swing and moisture swing experiments. Considering the TSMSD and MSCSD systems are a closed system with 0.145 L, the wind tunnel represents about 3,900 -fold larger closed system scale. The wind tunnel main purposes on sorbent characterization are: a) evaluate larger samples 1-100 g kinetics and loading capacity; b) the effect of humidity for temperature and moisture swing sorbents on the kinetics and loading capacity; c) moisture swing sorbents experiments by varying water vapor performing absorption and desorption can be performed inside the wind tunnel; d) temperature effect on the sorbent`s kinetics and loading capacity, although the temperature control needs improvement for a more significant temperature change; e) the evaluation of a variety of wind velocities on the sorbent kinetics, evaluating the mass transfer- air to contact to the sorbent. In addition, wind direction on different parts of the sorbent can be evaluated. f) the evaluation of bigger more complex sample form factors in which can affect a sorbent`s kinetics. This evaluation can also more precisely analyze the CO_2 sorption kinetics by surface area of the bigger sample.

The wind tunnel has the capability to control the humidity and keep it constant or by varying it depending on the experimental objectives. If the experiment is moisture swing, it is possible to have the sorption (when is dry ~ 5 ppt of H_2O) and desorption data when is moist (~20-25 ppt of H_2O). The wind tunnel has the capability to run a variety of different wind velocities 0.5 – 12 m/s. The wind tunnel is an adaptation to a stock Omega WT-4401 tabletop tunnel. The main adaptations are an adapter for the exhaust of the original wind tunnel to an 8” diameter duct, configured to a close loop back to the intake of the wind tunnel; the conditioning chamber to control humidity and temperature and a tubing system to inject CO_2 as needed depending on the experimental objectives. According to the figure 33 and 34 the main components of the wind tunnel are: 1) Dayton 2 M191A fan or wind tunnel blower in which it`s speed is controlled by 2) a Dart 253G-200E potentiometer or speed controller and the wind speed can be read by 3) a hot wire anemometer TSI Velocicalc 9545-A and thus the wind speed can be set to the desired wind velocity. 4) The sample chamber made with acrylic material has its dimensions 110 x 110 mm xx 110 mm to support the sample. 5) is the conditioning chamber in which by cooling or heating the air environment it can condensate and remove water or it can be used to increase water vapor by injecting water though a nozzle by a Harvard 11 plus syringe pump. Connected to the conditional chamber are two Fisher scientific Isotemp 3013 chillers, one will be operating as a 7) “hot chiller” and the other as a 8) “cold chiller” .The hot chiller is maintained at 32 °C and the cold chiller at – 15 °C in order to maintain the temperature of the wint tunnel in balance at 24 °C. 8) is a water injector made with a Harvard 11 plus syringe pump, pumping water through a nozzle to inside of the conditioning chamber in order to increase the humidity on the wind tunnel experiment. 9) is a Dell i3 Laptop laptop with the same Li Cor LI-840 A software 10) are 2 thermocouples to read the temperature of the wind tunnel across the chamber and 11) the Li Cor LI-840A Infrared gas Analyzer that detects and inform the software the CO_2 concentration in ppm and the H_2O vapor in ppt.

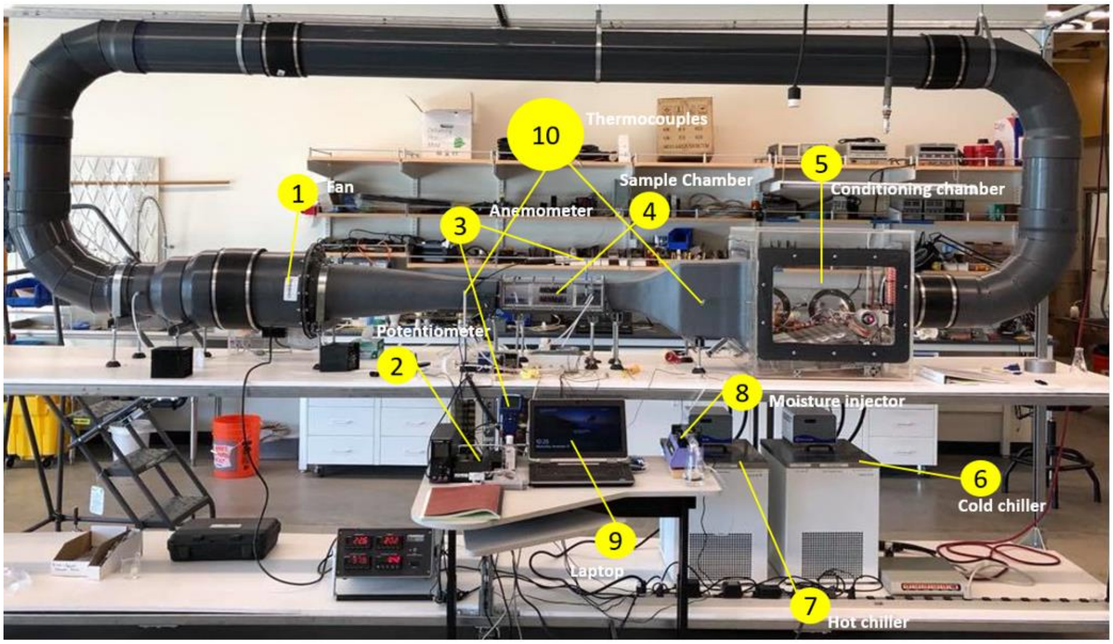


Figure 33– Wind Tunnel for CO_2 Sorption and Desorption Analysis

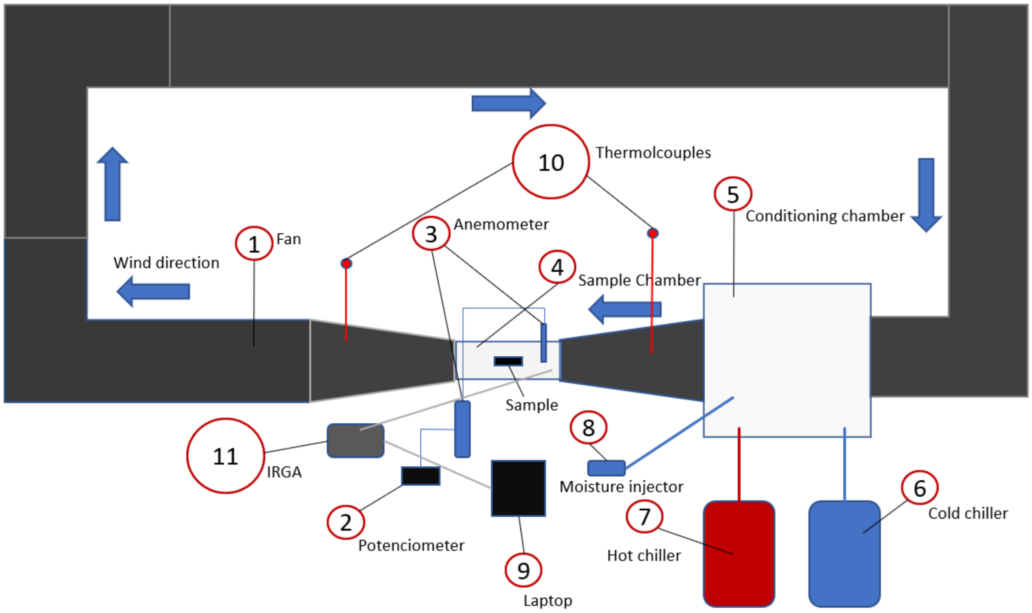


Figure 34 - Wind Tunnel for CO_2 Sorption and Desorption Diagram

3.4.1 Wind Tunnel for Moisture Swing

The wind tunnel has been originally designed to perform moisture swing by adding or removing water vapor utilizing the conditioning chamber. The sorbent also can be desorbed with liquid water, before it is inserted into the wind tunnel, to obtain the CO_2 sorption data and H_2O concentration as water vapor in ppt. The step-by-step procedure for wind tunnel experiments is:

1) Prepare sample and form factor. Leave the sample in open ambient air for ~ 12 hours (or more depending on the sorbent). This will allow the sorbent to be fully loaded with CO_2 to begin with.
2) There are 2 possibilities for desorption of the sample: water vapor desorption and liquid water desorption:
    a. Water vapor Desorption using high humidity: For this variation the wind tunnel can start on high humidity ~ 25 ppt of H_2O. Turn on the hot and cold chiller (32 and – 15 °C respectively). Make sure the coolant lines for both hot and cold chiller are closed from the conditioning chamber. Use the water injector through the nozzle until increase the humidity to ~ 25 ppt of H_2O. Maintain the high humidity level to the desired experimental time for desorption on the specific sorbent.
    b. Liquid water desorption: Once the sample is fully loaded with CO_2 from step 1, submerged the sample on DI water for the experimental desired

desorption time. If the goal is to evaluate the desorption, measure the pH over time is necessary to then be converted to how much CO_2 was released to the water.

3) CO_2 absorption, once the sample has been fully desorbed:
    a. Desorbed from water vapor: This method the sorbent is already inside the wind tunnel, and it is operating with high humidity. In order to start the absorption process, the humidity has to be reduced to a very dry environment. For this purpose, both valves from the hot and cold chiller need to be open. Once the cold chiller valve is circulating through the conditioning chamber, the water vapor from the wind tunnel start to condensate and thus humidity is drastically reduced. The humidity will reach a level ~ 3-4 ppt of H_2O. However in some cases the CO_2 sorption will be evaluated under a different humidity concentration, higher than 3-4 ppt of H_2O. If this is the case once the wind tunnel is very dry on the 3-4 ppt of H_2O range, both coolant valves from the hot and cold chiller needs to be closed. Then water volume needs to be injected with the water injector proportionally to the desired humidity level in the wind tunnel. Thus if the sorbent has good moisture swing properties, CO_2 inside the wind tunnel will start to decrease as the sorbent takes sorbs CO_2 during the experimental estipulate time. Once the stipulated absorption time has elapsed, if the goal of the experiment is to have multiple swing cycles, repeat the step 2.a and then 3.a as many times as it is desired by the experiment.

b. Desorbed from liquid water: On this method the sorbent is outside of the wind tunnel. The humidity level needs to be determined by the experimental objectives the same method explained on item 3.a. Once the experimental desorbing time has been elapsed:
    i. Start logging the data to prevent any data loss;
    ii. Open the wind tunnel chamber;
    iii. Quickly insert the sample;
    iv. Quickly close the wind tunnel chamber

4) Once the experiment is complete:
    a. Stop logging the data;
    b. Turn off the hot and cold chiller;
    c. Close both hot chiller valves and both cold chiller valves
    d. Remove the sample from the sample chamber
    e. Leave the wind tunnel chamber open to overnight to equilibrate with the atmosphere

3.4.2 Wind Tunnel for Thermal Swing

The temperature swing for the wind tunnel requires first a desorption method as the wind tunnel itself is not designed do thermally desorb a sorbent. There two settings to desorb a thermal swing sorbent: dry heat desorption or steam heat desorption. Once the sorbent is empty of CO_2, the wind tunnel can then be operated at the temperature, humidity, wind velocity for the specific sorbent for compute the CO_2 sorption data. The step-by-step experimental method for the wind tunnel thermal swing is:

1) Prepare the sorbent and form factor to be experimented. Leave the sorbent for a minimum of 12 hours (it varies depending on the initial sorbent absorption estimated time) on ambient air to initiate fully loaded with CO_2;
2) On the day of the experiment, set the wind tunnel on the temperature and humidity level desired and let it run at ~ 6 m/s until the temperature and humidity level are steady;
    a. First turn on the hot and cold chiller. Usually, these temperatures are 32 °C for the hot chiller and -15 °C for the cold chiller. This process may take 1 hour;
    b. Once the chillers temperature is stable, open both hot and cold chiller valves on the back of the conditioning chamber if the goal of the experiment is to keep the system very dry.
    c. IF the goal of the experiment is to operate in a certain humidity level. Use the water syringe with the nozzle to spray water and thus increase the humidity level at the expected range. On this case keep both hot and cold chiller valves closed.
3) Start the desorption process of the sample: using the oven at the sorbent`s desorption temperature or the steam regeneration system. The oven temperature will depend on the sorbent and steam regeneration system will most likely be at the

water boiling point for most cases. The desorption time will also depend on the sorbent’s characteristics and initial guess.

4) Once the temperature and humidity of the wind tunnel are steady, set the wind velocity to the desired level for the experiment.
5) Once the desorption time is complete, first start logging the data in order to not lose any important initial data points.
6) Quickly open and properly insert the sample at the sample chamber and close the chamber as fast as possible.
7) Wait the experimental setting desired time
8) Once the experiment is complete:
    a. Stop logging the data
    b. Turn off the hot and cold chiller
    c. Close both hot chiller valves and both cold chiller valves
    d. Remove the sample from the sample chamber
    e. Leave the wind tunnel chamber open to overnight to equilibrate with the atmosphere

3.4.3 Wind Tunnel Data Compilation and Analysis

The wind tunnel is a closed system much like the MSCSD and TSMSD systems and thus the calculation and analysis is quite similar. Figure 35 shows the raw data in which on this particular experiment the wind tunnel was set to have a starting point on continuous dry ~

3.5 – 4.0 ppt of H_2O (represented by the orange line on figure 35) more exactly starting at 3.6 ppt. The sample added has passed through a steam heat regeneration and thus added humidity to the system once it was inserted. The humidity then increase to 6.97 ppt of H_2O and slowing drops reaching 4 ppt of H_2O by the end of the experiment. The blue line on figure 35 represent the CO_2 concentration starting at 406 ppm on the beginning of the experiment and it drops to a minimum of 245 ppm as the CO_2 is absorbed by the sample. Once it reaches this minimum the CO_2 start to slightly increase as there is a leak rate of CO_2 from the outside ambient as the CO_2 partial pressure from outside becomes greater than the inside. The wind velocity used on this experiment was 6 m/s. The leak rate is proportional to the wind speed, and it has been mathematically corrected with blank runs for each wind speed experimented.

Figure 36 presents the calculated data of CO_2 absorption in µmoles of CO_2 per g of sorbent. Considering that the wind tunnel has 561 L of air, atmospheric pressure 0.96 atm and temperature 295 K, there are 22.25 moles of air inside of the system and thus 2.225×10^{-5} moles of CO_2 per one unit of ppm presented on the data output. A spreadsheet model was created much like for the MSCS and TSMSD systems based on these calculations in which the initial CO_2 measurement in ppm, example 406 ppm is converted to 9.04×10^{-3} moles of CO_2 in which is then normalized by the sorbent mass (14.17 g) totaling 638 µmoles of CO_2 per g of sample. Thus 638 µmoles/g is considered the zero point on time zero in which no CO_2 has been absorbed yet. As the CO_2 is absorbed 406 ppm goes down and thus the zero point 638 µmoles/g calculated value declines and this decline is accounted as the positive inclination of the zero point until its max value of CO_2 absorbed by the sorbent when its fully loaded.

Another form of evaluating data, especially for the wind tunnel results, is by surface area of the sample. The form factor utilized on this data set is a honeycomb frame named Hex B (see more details on chapter 5) The open surface (area in which the air can passthrough the sorbent) has a total of 7.23×10^{-3} m^2, thus accounting for this surface area the total capacity of this sample is 560 mmol CO_2/m^2 (figure 37). This is an important form for evaluating sorbents form factors as it is not normalized by the weight of the sorbent and thus it is possible to evaluate different sorbent packing densities heights total CO_2 absorption. For example: if a sorbent is packed with 5 mm vs 10 mm, the 10 mm will have more sorbent and thus if the result is normalized by weight, it will not show the total CO_2 absorbed difference among these two samples. If the sample is normalized by the surface area, this difference will be more evident, and it can be used the data can be used to extrapolate values for a bigger system using the same form factor.

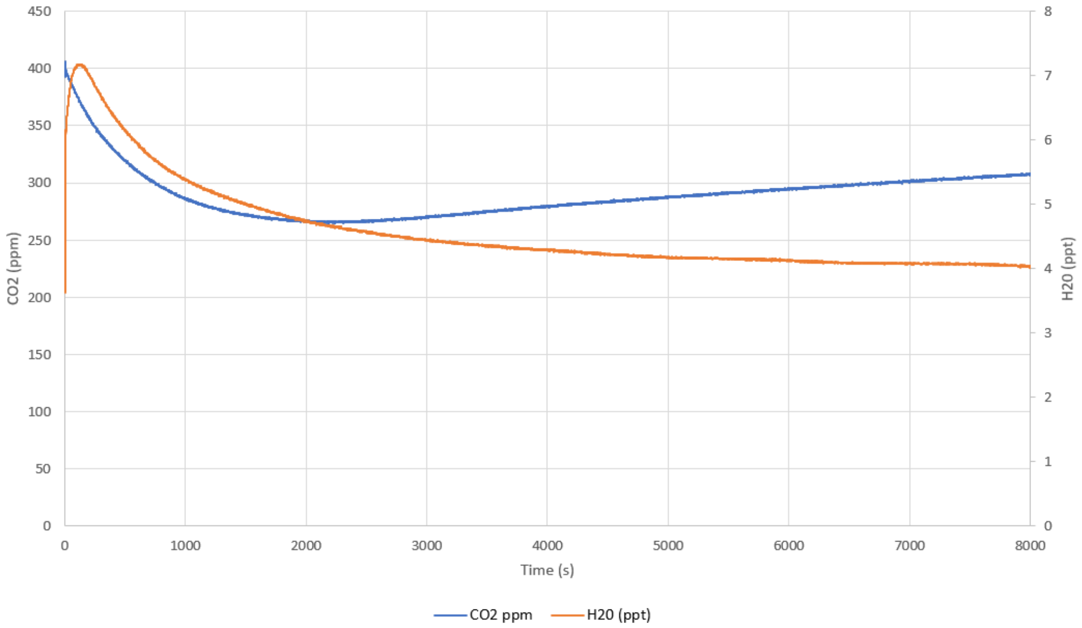


Figure 35 – Wind Tunnel Experiment at 6 m/s with 14.17 g TSB03 Sorbent Raw Data

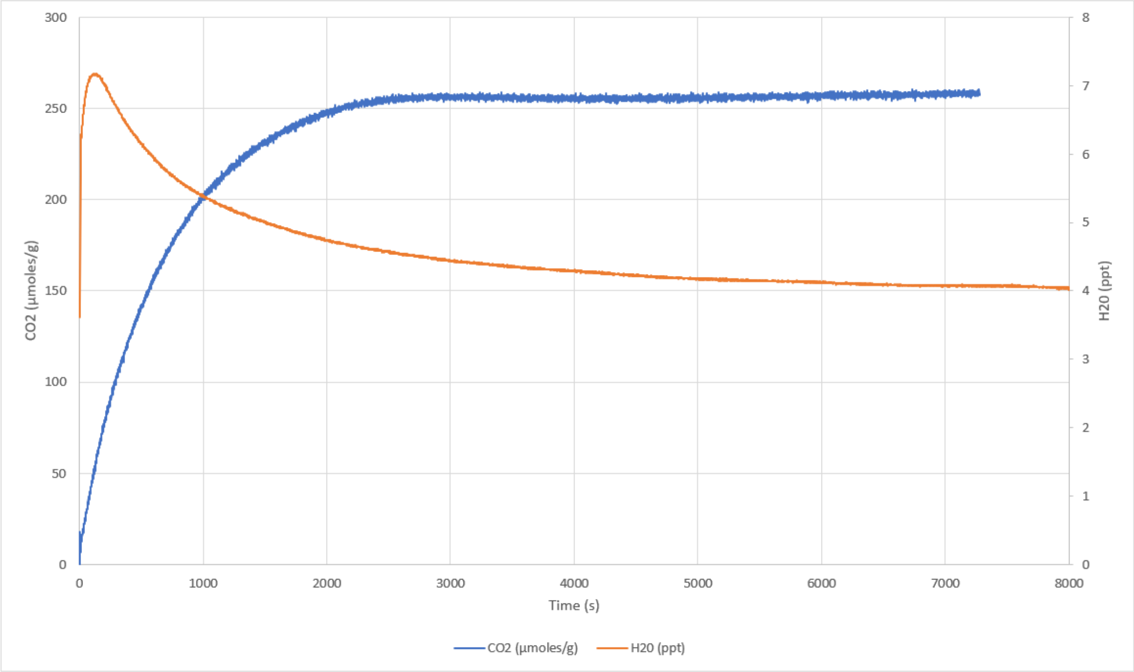


Figure 36 – Wind Tunnel Experiment at 6 m/s with 14.17 g TSB03 Sorbent Compiled Data

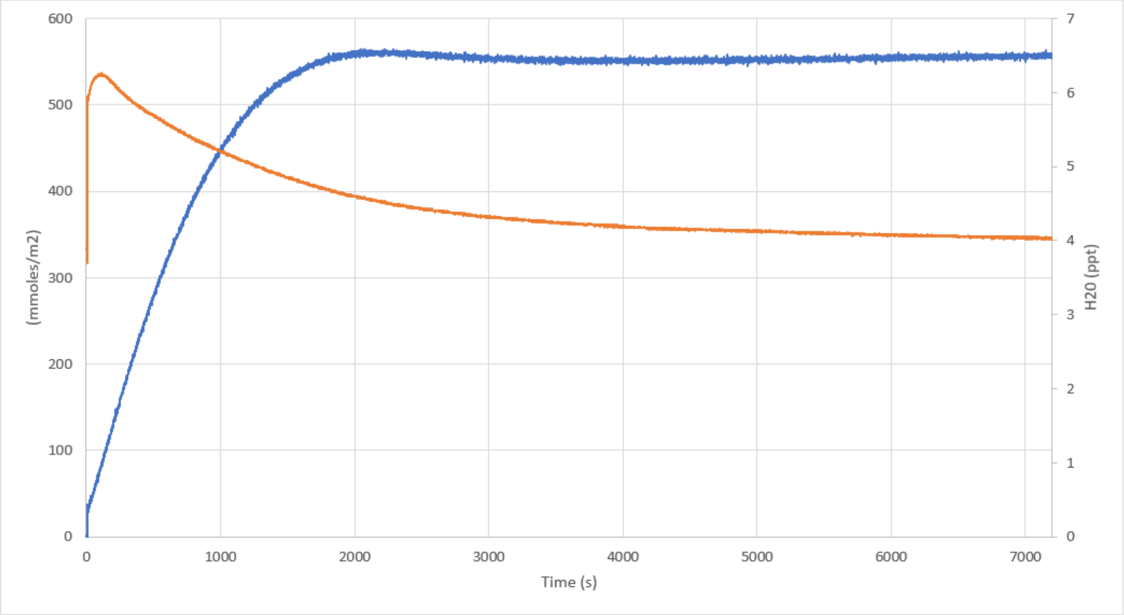


Figure 37– Wind Tunnel Experiment at 6 m/s with 14.17 g TSB03 Sorbent Compiled Data by mmol CO_2/m^2 of Surface Area.

3.4.4 Wind Tunnel Data Duplication

A duplicate experiment was prepared with 2 samples in the form factor Hex B (see chapter5 for details on hex B form factor). The sample 01 contained 14.17 g of the sorbent TSB 03 and the sample 02 15.01 g. Both samples were submitted to 1 hour steam heat regeneration and the wind tunnel was set on 6 m/s wind velocity at low humidity, starting at 3.5 ppt of H_2O. Figure 38 show the average and error bars of this experiment for the duplication. The average standard deviation for each second of data point was only 3.13 µmoles CO_2/g. Thus this methodology is reproducible with a very low margin of error.

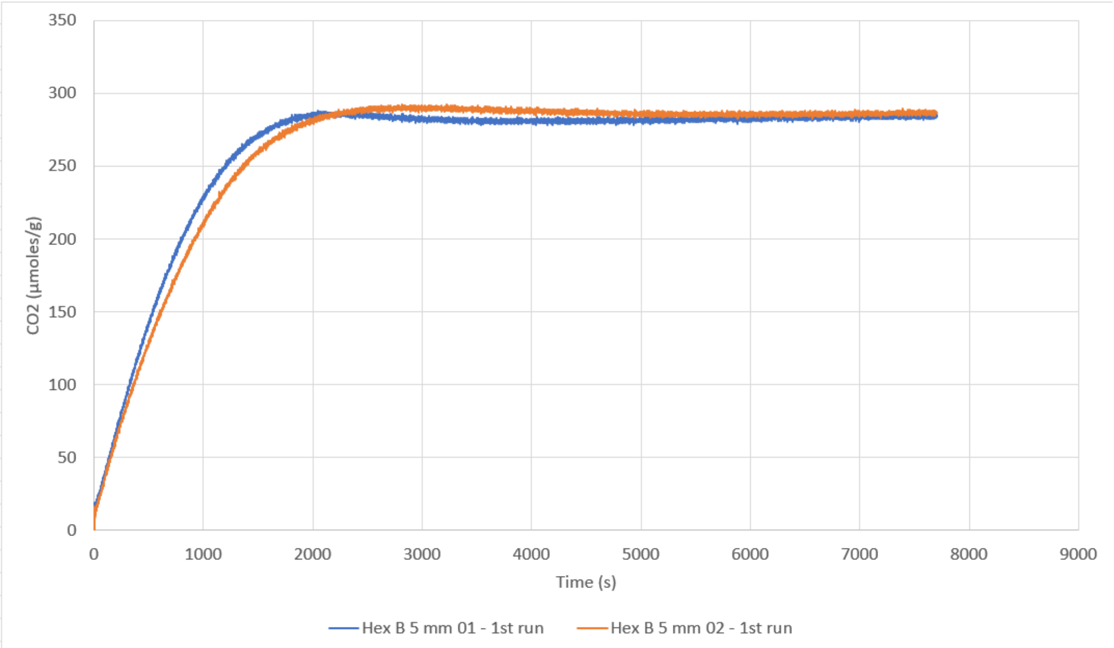


Figure 38 - Hex B 5 mm Duplicate Result at 6 m/s

3.4.5 Wind Tunnel Methodologies Sources of Inaccuracy and Room for Improvement

The wind tunnel temperature swing methodology has also a similar source of error than the TSMSD in which the desorption is performed in a separate apparatus before the sample be inserted into the wind tunnel for the absorption step. This time needs to be always consistent and as short as possible to prevent the sample absorption starts before the absorption inside the wind tunnel. Same situation if the wind tunnel is operating with the wet moisture swing methodology, in which the desorption process occurs out of the wind tunnel on liquid water and the sample needs to be inserted on the wind tunnel immediately. New features on the wind tunnel can be added in the future: a) a more efficient temperature change in which is still sensible to close to the ambient temperature; b) an automated humidity cycle as the humidity levels needs to be operated manually; c) a more fixed wind speed and the capability to vary wind speed over periods of time to simulate outdoor weather conditions.

3.5 Bench-Scale Regenerator Reactor (Sapling)

The Bench-Scale Regenerator Reactor (Sapling) has been created to evaluate the CO_2 uptake and desorption from a larger sorbent mass sample size and specific form factors as the systems increase scale. The TSMSD and MSMSD systems has the capability to evaluate mg sample size sorbents, the CSOFS system 0.1-1.0 g and the Wind tunnel 1-100 g sorbent mass. The Bench Scale Regenerator reactor can experiment on 100 – 3,000 g sorbent mass. Sorbents can perform very differently once it goes to a higher scale. For instance mg to kg scale is 1 million fold scale difference. If a specific sorbent can perform similarly in 1 million-fold scale it indicates it can be scalable to the industrial level. A hypothetical prototype would operate in the hundreds of kg of sorbent, thus 1 kg to a few hundreds is less than one thousand-fold scale. In addition specific form factors on much larger sample size can influence on the sorbent's kinetics. This unique system can effectively be an intermediate scale for a full-scale pilot plant. This system also has the capability to run temperature-vacuum swing CO_2 desorption simulating a large bench-scale experiment on specific sorbent`s and form factors characteristics before a pilot plant development. This system can be further improved and updated to test moisture swing sorbents.

This experimental apparatus is able to desorb the sorbent under steam and vacuum for the desorption process and a blower with 890 l air/min capacity for for CO_2 absorption from ambient air. Thus essentially the Sapling is originally designed for larger sample sizes thermal swing sorbents. The system can also be adapted for larger sample sizes moisture swing sorbents. Figure 39 show the front picture of the sapling reactor, the system is basically comprehend: 1) vacuum steam regenerator, this vessel will heat the water to the boiling point, under vacuum to generate the steam to desorb the sorbent. 2) The vessel has a metal box with 122 x 122 mm. The vessel will allocate the sorbent-sample-form factor to be experimented in which steam generated on the vacuum-steam vessel will react with the sorbent releasing CO_2. 3) The water freeze-out removes the water vapor and water from the steam generated removing the water from the system. 4) The infrared gas analyser (IRGA) will measure the CO_2 concentration in ppm and H_2O vapor in ppt. 6) Alicat flowmeter will monitor the air flow essential for the data compilation. 7) the O_2 gas analyzer will give the oxygen concentration. As the system is under vacuum, once the sample is desorbed, the water vapor is removed by condenser and the freeze out; and assuming all the other small concentration ambient air gas compositions does not interfere on the analysis; the gas then passing through the system will be 100% CO_2 + O_2. By knowing the O_2 % concentration, it is possible the determine the % of CO_2 and thus with the flow meter, it is possible to determine the CO_2 flow rate as its desorbed from the sorbent. 8) this flow meter will measure the has flow rate coming out of the system. 9) The vacuum compressor will evacuate all the air from the lines while the steam is desorbing CO_2 from the sample. 10) the -105 °C freeze out is designed to freeze the CO_2 desorbed by the sample and create a "CO_2 trap". 11) behind the vessel, there is a blower in which will blow ambient air at 890 l/min in order to perform CO_2 absorption in-situ (or inside of the laboratory), once the sample has been fully or almost fully free of CO_2 after the steam desorption process. A more detailed engineering design plant on the sapling reactor is presented on figure 40.

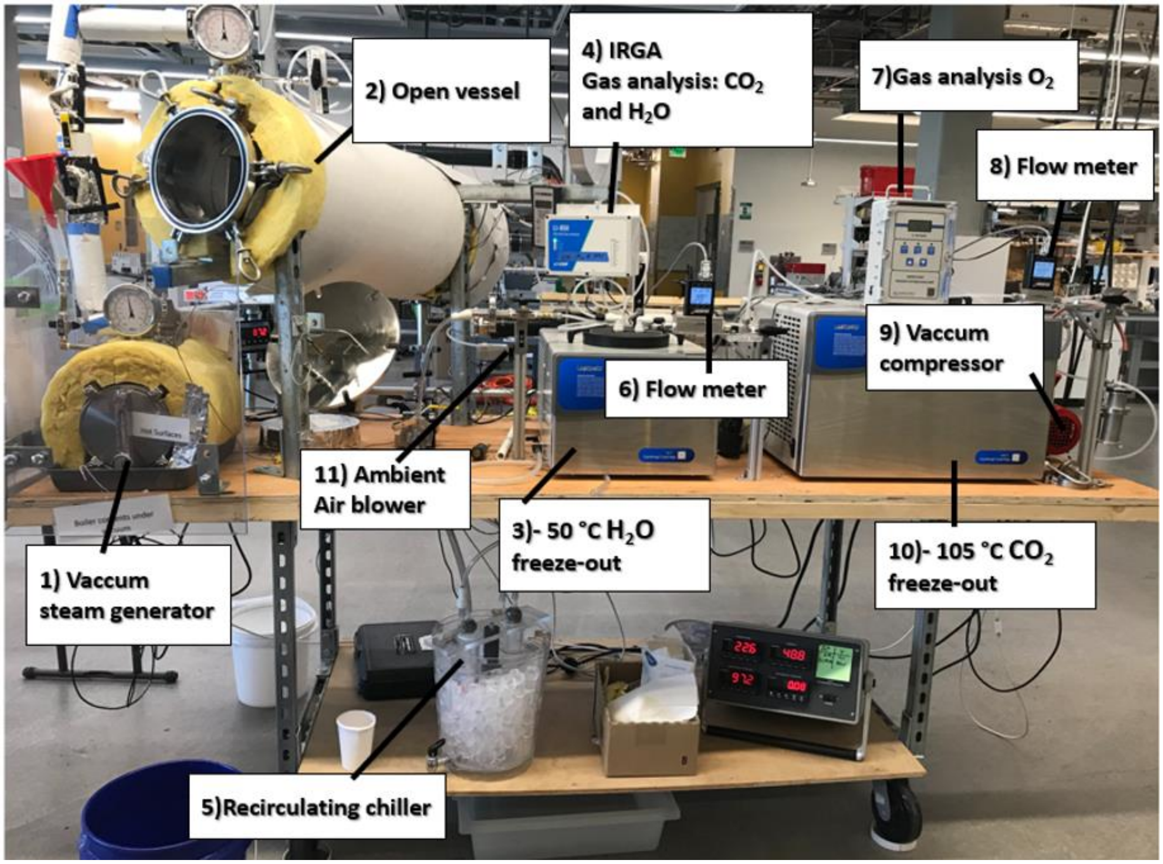


Figure 39 - Bench-Scale Regenerator Reactor System Picture (Sapling)

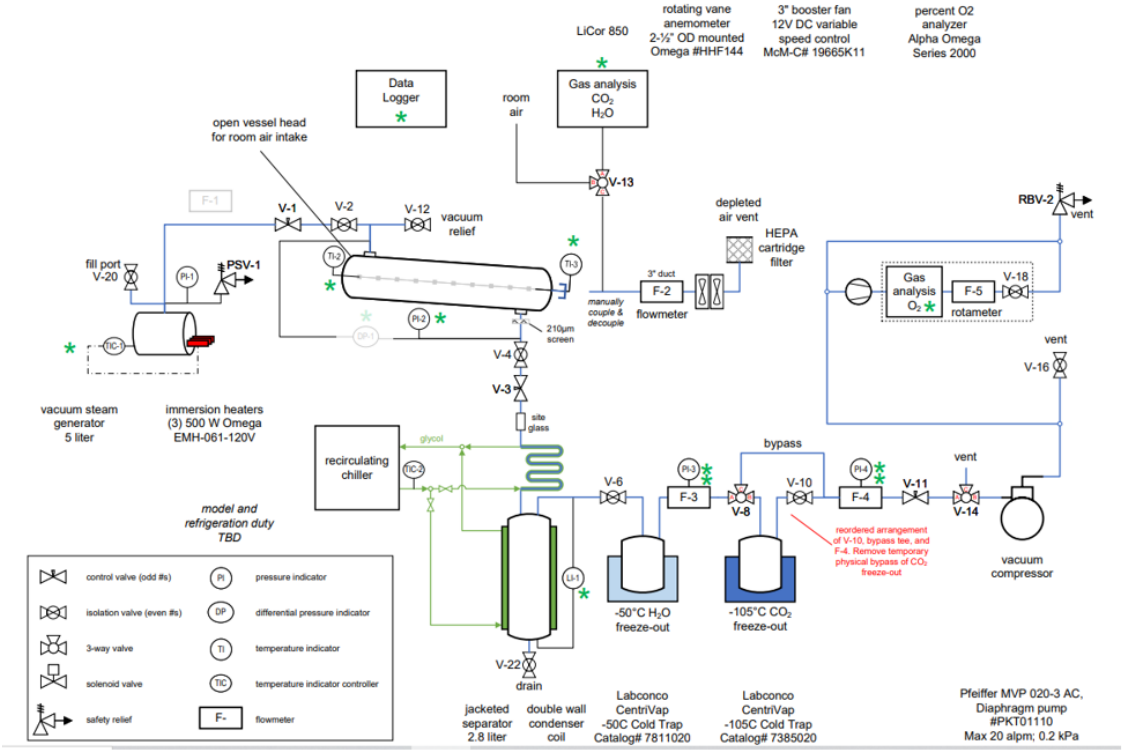


Figure 40 - Bench-Scale Regenerator Reactor Diagram (Sapling)

3.5.1 In-situ Experimental Protocol

In-situ experiments stands for experimentation occurring inside of the laboratory environment. The procedure starts with the sorbent fully loaded with CO_2 followed followed by a steam heat regeneration inside of the sapling reactor and a CO_2 absorption by blowing air through the vessel while its open This protocol has been written by John Cirucci. The step by step methodology is:

1) System preparation
    a. Close V-1, V-2, V-3, V-4, V-12
    b. Open V-6, V-8, V-10, V-11, V-20
    c. Turn on/commence cooldown of water FO and CO_2 FO (empty traps if necessary)
    d. Fill ice bath with ice and water (empty condensate trap if necessary)
    e. Fill vacuum steam generator to MAXimum level if below MINimum level: MIN level = ___ liters (heat element immersed - TBD); MAX level = 4 l
    f. Close V-20
    g. Confirm VS generator level is between MIN and MAX; set temperature and turn on heater
    h. Turn on gas analyzers (earlier as required to stabilize)
2) Capture Mode (in-situ case) [this can be performed concurrent with above “system preparation”]
    a. Open regenerator vessel head and insert (8) sorbent cassettes. Multipoint thermocouple rod should project through center of the sorbent/form factor
    b. Secure O-ring, close and clamp lid
    c. Manually connect inlet and outlet air line
    d. Turn on data logger
    e. Turn on booster fan

   f. Adjust fan voltage to achieve desired flow rate (nominal 500 lpm = 2.4 m/s thru 66mm diameter anemometer)
   g. Run to inlet equals outlet CO_2 concentration or desired earlier termination point.
   h. Decouple the inlet and outlet air lines; replace with caps.
   i. Turn off data logger

3) Pre-evacuation Mode
   a. Confirm cold traps are at operating temperatures
   b. Open V4, V6, V-10, V-12
   c. Turn on data logger
   d. Turn on vacuum compressor
   e. Slowly open V-11
   f. Slowly open V-3
   g. Observe vessel pressure PI-2
   h. When desired vacuum level is achieved, close V-3 and V-4
   i. Close V-12 and V-11
   j. Turn off vacuum compressor
   k. Observe if PI-2 for gross vacuum delay (leaks)
4) Vacuum Steam Regeneration Mode – Steam Feed
   a. Turn on data logger
   b. Confirm vacuum steam generator is at desired temperature and pressure
   c. Open V-2

    d. Slowly open V-1 to achieve desire steam flow rate

5) Vacuum Steam Regeneration Mode – Vacuum Withdrawal (this may preferentially commence immediately or after some period of steam heating)
    a. Turn on vacuum compressor
    b. Open V-10
    c. Slowly open V-11
    d. Open V-4
    e. Slowly open V-3
    f. Allow regeneration to continue to desired end point based on effluent flow rates, gas analyses, temperatures and pressures
6) Evaporative Cooling Mode
    a. Close V-2 and V-1; turn off steam generator (may maintain under vacuum to reduce headspace air for next runs)
    b. Continue evacuation to desired end point based on effluent flow rates, gas analyses, temperatures and pressures
    c. Close V-10
    d. Conclude experimentation.
    e. Close V-1, V-2, V-3, V-4, V-6, V-8, V-10, V-11, V-12, V-20
    f. Turn off: vacuum compressor, analyzers, data logger, cold traps
    g. Record water level in graduated condensate trap
7) Shutdown

    a. Break vacuum to regenerator (open air inlet plug) [add vacuum break valve – YESS, add valve]
    b. Turn off all energized equipment
    c. Empty condensate trap, ice bath
    d. After warming, empty -50°C trap

3.5.2 Ex-situ Experimental Protocol

Ex-situ experiments are to evaluate the absorption of CO_2 from an outdoor capture condition under the selected sorbent mass (large 100 g – 3,000 kg as the sapling reactor has been designed) and its selected form factor. The first step is to ensure the sorbent is empty of CO_2 to begin with, thus the sorbent needs to be processed through the desorption phase using the sapling regenerator. Thus, the sample needs to pass through the steps 1, 3, 4, 5 and 6 from the sub-chapter 3.5.1 (In-situ capture experiment). Once the sample is empty of CO_2 it is ready to start the capture procedure. This methodology has been written by John Cirucci. The methodology of the Ex-situ experiment follow the same steps from the in-situ capture except step 2 that need to be replaced by:

2. Capture Mode (ex-situ case)
    a. Expose sorbent and its form factor for direct air capture external under the selected design

b. Open regenerator vessel head and insert the sorbent/form factor. Multipoint thermocouple rod should project through center of the sorbent and it`s form factor;

c. Secure O-ring, close and clamp lid.

3.5.3 In-situ Experiment Data and Analysis

The sapling in-situ analysis is calculated similarly to the CSOFS system as the system is operating as an open system setting. The blower system on the sapling account for 924 l air/min of flow rate or 15.4 l air/s. This is equivalent to 0.6107 moles of air/s in which results in 6.107×10^{-7} moles of CO_2/s per unit of ppm computed by the IRGA. The raw data is shown on figure 41 in which the same way the CSOFS raw data is, CO_2 concentration drop rapidly in the first seconds as the air blows through the sorbent and it starts absorbing CO_2. CO_2 is then continuously absorbed during all the period of the experiment until the trend goes to the same as the original CO_2 concentration once the sorbent is fully loaded with CO_2. For a data representation of how much CO_2 has been absorbed one is calculating an integral (or the accumulated CO_2 absorbed) of this curve and converting the ppm of CO_2 values in µmoles of CO_2 and then normalizing by the sorbent weight resulting in µmoles of CO_2/g of sorbent represented on the figure 42.

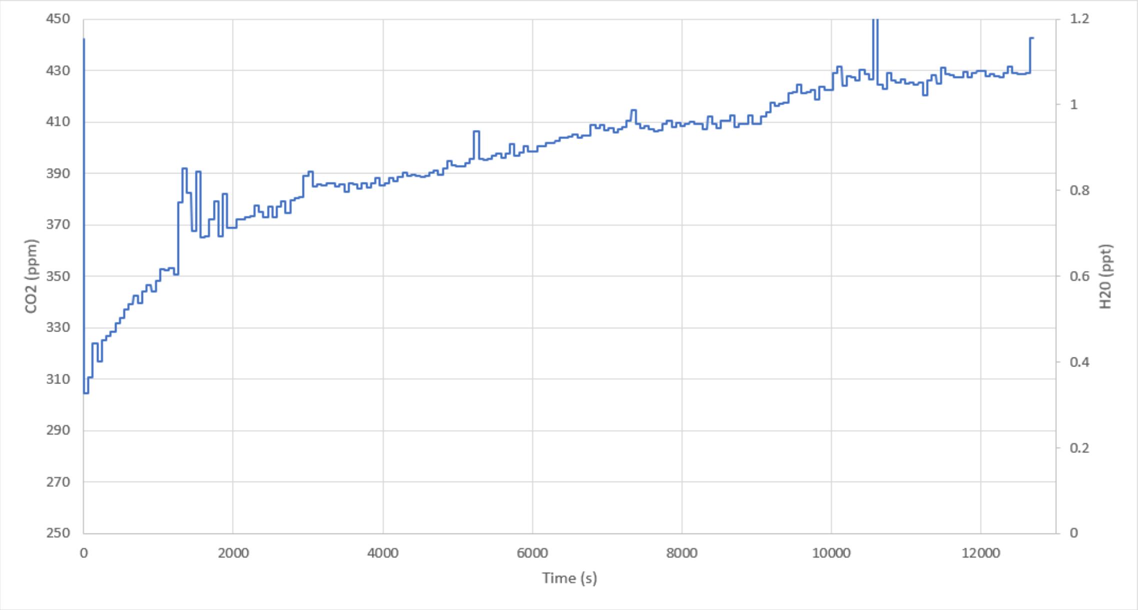


Figure 41– In-situ CO_2 Sorption Compiled Data

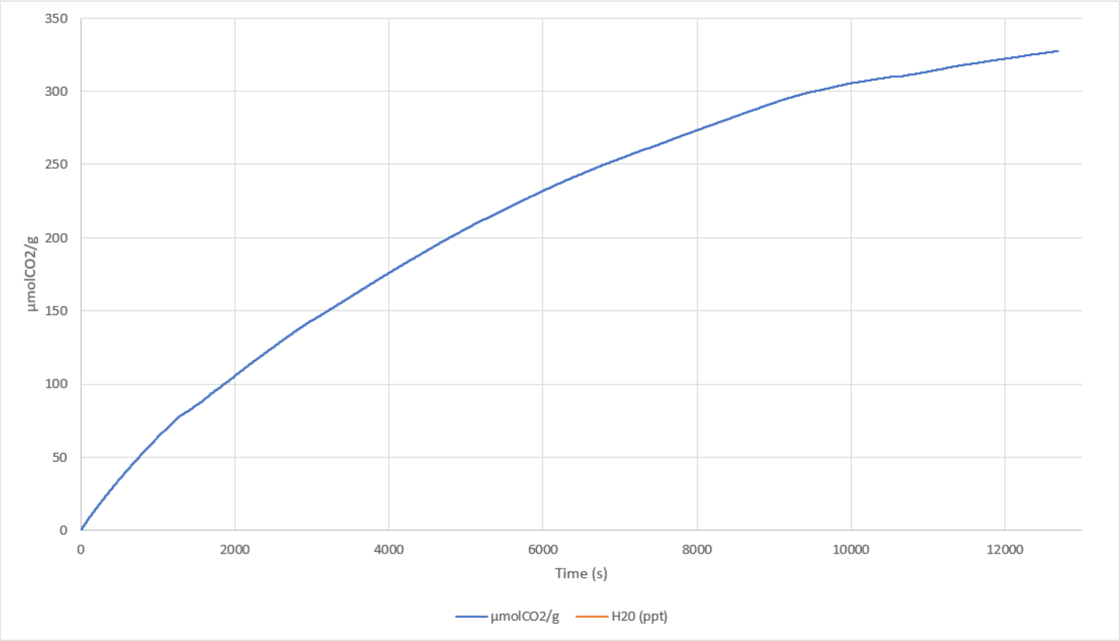


Figure 42 – In-situ CO_2 Sorption Compiled Data

3.5.4 Ex-situ Experiment Data and Analysis

The ex-situ experiments are an evaluation of the total amount of CO_2 absorbed by the sample by desorbing the CO_2 once the sample is fully loaded. First the sample needs to be left on open air for 12 – 48 hours (depending on the sample weight size and assumptions) to be considered fully loaded with CO_2. Then the sample needs to be experimented on the sapling reactor desorbing all the CO_2 with steam heat. Thus the sample needs to be positioning outdoors under the selected day of weather conditions. The absorption outdoor time is determined by the experimental objectives. Once the time of absorption for the sample in which is left outdoors under the selected experimental conditions (altitude, weather, location) has been elapsed, the sample needs to be carried to the sapling regenerator reactor for a second desorption. The second desorption will determine the amount of CO_2 absorbed by the determined capture time. As the sapling regenerator operates under vacuum, the flowmeters will be CO_2 + O_2. The O_2 meter will determine how much is left as CO_2. The sapling reactor operates in several regeneration cycles until the sample is fully desorbed. All the CO_2 flux logged into the system by the flow meters in each cycle needs to be accounted in order to calculate the total CO_2 desorbed by the experiment. The data can then be evaluated in many ways. 1) The percentage of CO_2 absorbed on the determined absorption time outdoors by knowing how much CO_2 has been desorbed on the first desorption when the sample was fully loaded compared to how much CO_2 has been desorbed after the outdoor absorption time. 2) total CO_2 absorbed in µmoles CO_2/g in order to compared with the CO_2 absorbed on the smaller scale systems; 3) Evaluate the CO_2 absorption time based on the wind velocity to compare with data generated on the wind tunnel and how the temperature and relative humidity affect the system. Outdoors there is a weather station monitoring monitoring wind speed, relative humidity and temperature.

3.5.5 Bench-Scale Regenerator Reactor Methodologies Sources of Inaccuracy and Room for Improvement

The bench-scale regenerator reactor sources of error for both in-situ and ex-situ methodologies are in how efficiently te steam-vacuum system is operated and how many cycles are consistently performed to desorb CO_2 and quantify it until it the sample is empty. The in-situ absorption is quite accurate as the blower maintain a constant air through the sample been log in with the IRGA and the absorption can start immediately after the CO_2 desorption. The ex-situ methodology there is more room for error. As the sample needs to be regenerated first and carry to outdoors to absorption under environmental conditions, the time to bag the samples and carry over to outdoor before the absorption time start to be counted, the sample can absorb CO_2 much like the other systems that operate the desorption in a different apparatus than the absorption.

Future improvements on the sapling reactor are to minimize any possible leaks on the system, update the system to large scale moisture swing tests and have a different blower in which can vary the air velocity on the sample chamber. Essentially the spling reactor could operate as a large scale open system wind tunnel with the necessary updates.

3.6 Sorbent and Form factor Analysis as it Scales

Sorbents can perform differently as it scales with greater mass and different form factors under different experimental settings. In order to standardize the systems and test a specific sorbent and its form factors under a step-by-step scale from the mg, g, kg scale it is necessary to compare the results from the TSMSD, CAOFS, wind tunnel and sapling reactor. Despite each system have a different air flow configuration, the sorbent more or less needs to perform a similar total capacity and reasonable kinetics on the larger scale in order to evaluate its feasibility on a real-world scenario. This chapter will evaluate the TSB 03 sorbent as it successfully scales about one million fold from the mg to the kg scale.

3.6.1 TSMSD, CSOFS and Wind Tunnel Using TSB 03 Thermal Swing Sorbent Absorption After Dry Heat Regeneration

To evaluate if a sorbent is scalable, a comparison among the different sample weight for the devices TSMSD (1-10 mg scale), CSOFS (0.1 -1.0 g scale), wind tunnel (1-100 g scale), sapling regenerator (100 g – 3,000g scale) was made. Figure 43 present the experimental result on the sorbent TSB 03 CO_2 absorption data after the sorbent`s dry heat regeneration. The experiments were performed in the TSMSD, CSOFS and wind tunnel. All the samples were regenerated with 1 hour on the oven under 100 °C. The figure 43 show the total capacity of this experiments is consistent with all 3 reaching ~ 200 µmoles/g of CO_2. The sample weights were 3 mg, 0.4 g and 25 g respectively to TSMSD, CSOFS and wind tunnel systems. Thus despite the order of magnitude be 8,333:1 between the TSMSD system and the wind tunnel, the total capacity is still very consistent. This experiment demonstrates the precision on this methodologies and the consistency on the sorbent TSB 03 when it goes to scale. It is very important to note on this experiment the kinetics among the different systems were vastly different. This is expected once the air flow rate to the amount of sorbent mass ratio is very different in each case. For instance, considering the wind tunnel operating at 6 m/s. The total cross-sectional area of the wind tunnel chamber is 1.44×10^{-2} m^2, which results in 5,184 l air/min. The CSOFS is operating at 0.5 l air/min and it has a cross-sectional area of 4.9×10^{-4} m^2, resulting in a velocity of 0.017 m/s. Thus, the wind tunnel has 353 times faster air velocity than the CSOFS system and 10,368 more volume of air per time passing through the sample. Evaluating the mass into this equation the amount of air per time per mass of sample (l air/min/g sample), the wind tunnel operating at 6 m/s has 207.36 lair/min/g of sorbent while the CSOFS system has 1.25 l air/min/g. Despite the TSMSD system be a small device, the pump generates a considerable velocity that still need to be precisely measured to compare.

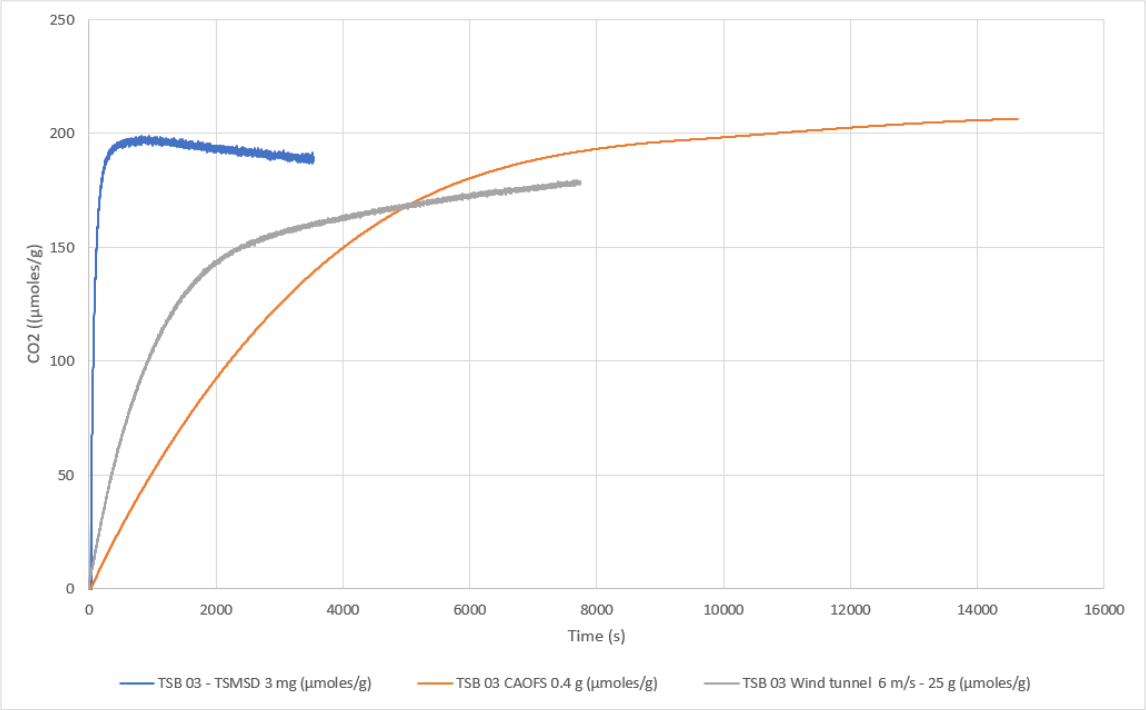


Figure 43 – TSB03 Adsorption at Different Experimental Scales after Dry Regeneration

3.6.2. TSMSD, CAOFS, Wind Tunnel and Sapling Reactor Using TSB 03 Thermal Swing Sorbent Absorption after Steam Heat Regeneration

Experimentation in the TSB 03 sorbent was also performed at the different system scales after steam heat regeneration. The TSMSD, CAOFS, wind tunnel and now also on the sapling reactor regeneration were used since the sapling reactor can only perform steam heat desorption and not dry heat desorption as it is designed now. The TSB 03 sorbent weight in each system was 3 mg, 0.3 g, 25 g and 1,000 g. respectively for the tests in

TSMSD, CAOFS, wind tunnel and sapling reactor. Comparing the different scales based on the sample mass TSMSD versus CSOFS has 1:100 mass scale ratio, TSMSD vs wind tunnel 1:8,333 and TSMSD versus sapling 1:333,333 ratio. Comparing CSOFS system versus the wind tunnel is 1:83 mass scale and CSOFS versus sapling reactor 1:3,333. Considering these differences in scale is important to observe on figure 44 the sample TSB 03 is scalable considering the 1 to 5 orders of magnitude difference among the systems. The sorbent capacity varied between 200 – 350 µmoles of CO_2/g among differences in the kinetics. These differences are due to the form factor, air velocity and water content in contact with the sorbent. For instance, the TSMSD experiment after the steam heat regeneration had a considerable amount of water after the steam heat regeneration. As a result, the 3 mg TSMSD sample had an initial uptake to 50 µmoles/g in the first 100 s and then a delay on absorption of 550 s. This delay is very likely due to the high water to sorbent mass ratio resulted from the steam heat regeneration as the sample mass was considerably small. The water fill the porous of the sorbent delay the CO_2 absorption. The CO_2 started to have room to be absorbed once the water was dried as the system was operating constantly at 5 ppt of H_2O vapor, reaching 274 µmoles of CO_2/g of capacity. The wind tunnel results for 6 and 0.8 m/s have reached a total of ~ 200 µmoles/g of capacity. For the TSMSD and wind tunnel results the desorption methodology does not have the capability to log in data to ensure the sorbent was fully unloaded of CO_2. Thus, the likely possibility of the sample not reaching ~ 300 µmoles CO_2/g is that the sample was not fully unloaded. Nevertheless, the wind tunnel at 6 m/s absorbed 200 µmoles/g of CO_2 in only 1200 s while the TSMSD, CSOFS sapling and wind tunnel at 0.8 m/s absorbed 187, 109, 74 and 58 μmoles CO_2/g respectively on the first 1200 s. Air flow velocity tested in the wind tunnel has a major effect in kinetics, this subject is more detailed explored on the chapter 5 of this document. The sapling reactor considering the same form factor utilized on the wind tunnel tests but with a longer length (115 mm wide and 8 mm height with a pack of 8 samples stacked with ~5 mm spacing in between) operated at 4.25 m/s velocity. It is noticeable the kinetics of sapling was an intermediate between the wind tunnel at 6 and 0.8 m/s, indicating the form factor length had little interference on the CO_2 absorption kinetics.

It is important to evaluate not just the wind velocity but the effective mass of air passing through the mass of sorbent. The CSOFS system 0.5 l/min with 0.4 g of mass result in 1.25 l/min/g; the wind tunnel at 5,184 l/min and 25 g sorbent mass result in 207.36 l/min/g; the sapling reactor with 890 l/min and 1,064 g of mass result in 0.836 l/min/g. Evaluating the effective amount of air for mass of sample is important to note on figure 44, the kinetics follow the trend in which wind tunnel at 6 m/s is the fastest followed by open flow device then followed by the sapling reactor. The TSMSD system after steam heat regeneration has a delay because of a different scenario on the mass of liquid water per mass of sample initially on the system. It is important to consider that the wind tunnel is a closed system with a total volume of 561 L. thus the same air is passing 10 times per min and loosing total CO_2 concentration each time, changing the CO_2 partial pressure adding dynamic to this analysis. The TSMSD system air velocity still needs to be precisely measured to be able to compare with the other systems.

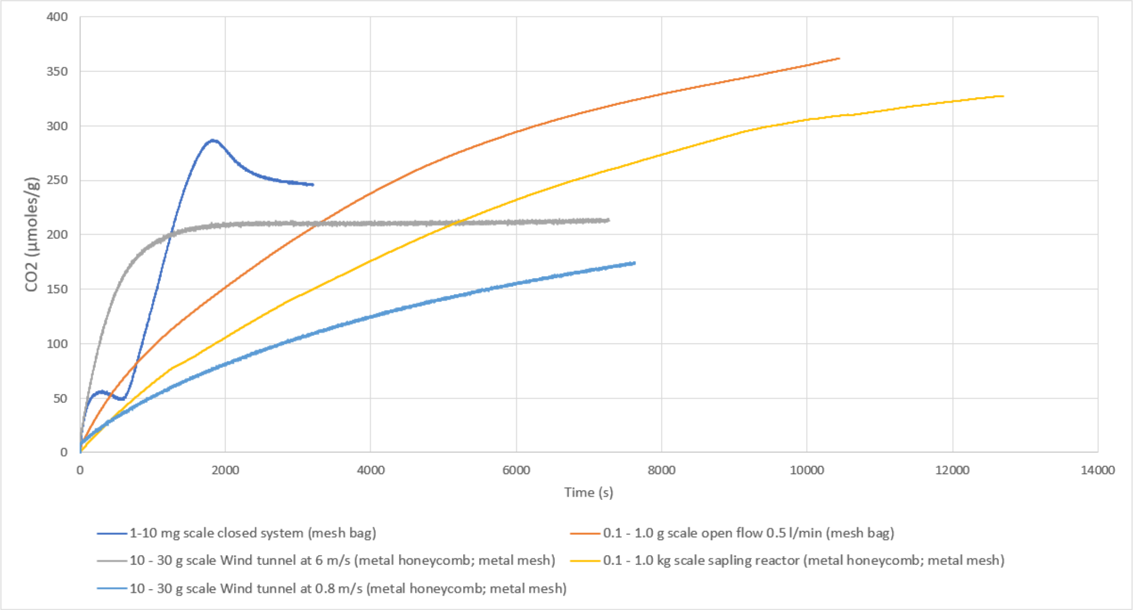


Figure 44 – TSB 03 Absorption at Different Experimental Scales after Steam Regeneration

3.6.3. Wind Tunnel under High and Low Wind Velocity Compared to Ex-situ Sapling Experiments

Experiments have demonstrated the effect of the wind velocity on the kinetics of thermal swing sorbents (more detailed wind velocity study on chapter 5). Higher wind velocities ~ 6 m/s increase significantly the absorption kinetics when compared to lower wind velocities. Utilizing the form factor assembly 03 and sorbent TSB 03, at 6 m/s the sample absorbed 200 µmoles of CO_2/g in just 1200 s while at 0.8 m/s the sample absorbed 57 µmoles of CO_2/g. The wind tunnel was operating at 27 °C with 3.5 ppt of H_2O as the humidity level and the sample size was 25 g. In order to evaluate the next scale level and under real weather condition, 5 sapling reactor ex-situ experiments were performed with different capture times: two experiments with 1 hour absorption time outdoors, one experiment with 1.5 hours and one experiment with 2 hours CO_2 capture time (review sapling ex-situ experimental method subchapter 3.5.2). Each day performed the weather was slightly different temperature and wind velocities. Table 1 shows the weather conditions from the experiments. The temperature varied between 26 to 33 °C with most days around 31 °C. The wind velocities varied between 0.82 to 1.91 m/s mean in each experiment. Evaluating the total CO_2 absorbed in each experiment on the determined capture times, figure 45 show this correlation with the wind tunnel experimental data. The green dots represent the ex-situ results total CO_2 absorbed. Experiments 2 and 5 had similar mean wind velocity of 0.8 m/s with the capture times 1.5 and 2 hours respectively. Observing on figure 45 correlating with the wind tunnel data at 0.8 m/s, it is possible to conclude the accuracy of this results as more or less the values are the same as the wind tunnel with small deviations probably due to the difference in temperature between the wind tunnel at 27 °C and the experiments 2 and 5 with 31 °C. This result demonstrate this particular sorbent and form factor is scalable to 1 kg of sorbent. Experiments 1, 3 and 4 had 1.07, 1.67 and 1.91 m/s wind velocity respectively all with 1 hour absorption cycle time. These results also represented on figure 45 show a trend on the graph between the low wind velocity at 0.8 m/s and the high at 6 m/s. It is also important to note experiment 3, despite wind velocity be slightly less than experiment 4, obtained slightly more CO_2 absorbed. This is very likely to the fact experiment 3 had slightly lower temperature, 26 °C while experiment 4 had 31.7 °C. Lower temperature tend to have a higher equilibrium capacity to the sorbent. For the TSB 03 sorbent and assembly 03 form factor, wind velocity is essential to enhance kinetics.

Table 1– Ex-situ Experiments Using TSB 03 Sorbent and Assembly 03 Form Factor.

Test		**1**	**2**	**3**	**4**	**5**
time, capture	h:mm	1:00	1:30	1:00	1:00	2:00
temperature, mean	**°C**	**32.9**	**31.5**	**26**	**31.7**	**31.3**
wind speed, mean	**m/s**	**1.07**	**0.82**	**1.67**	**1.91**	**0.83**

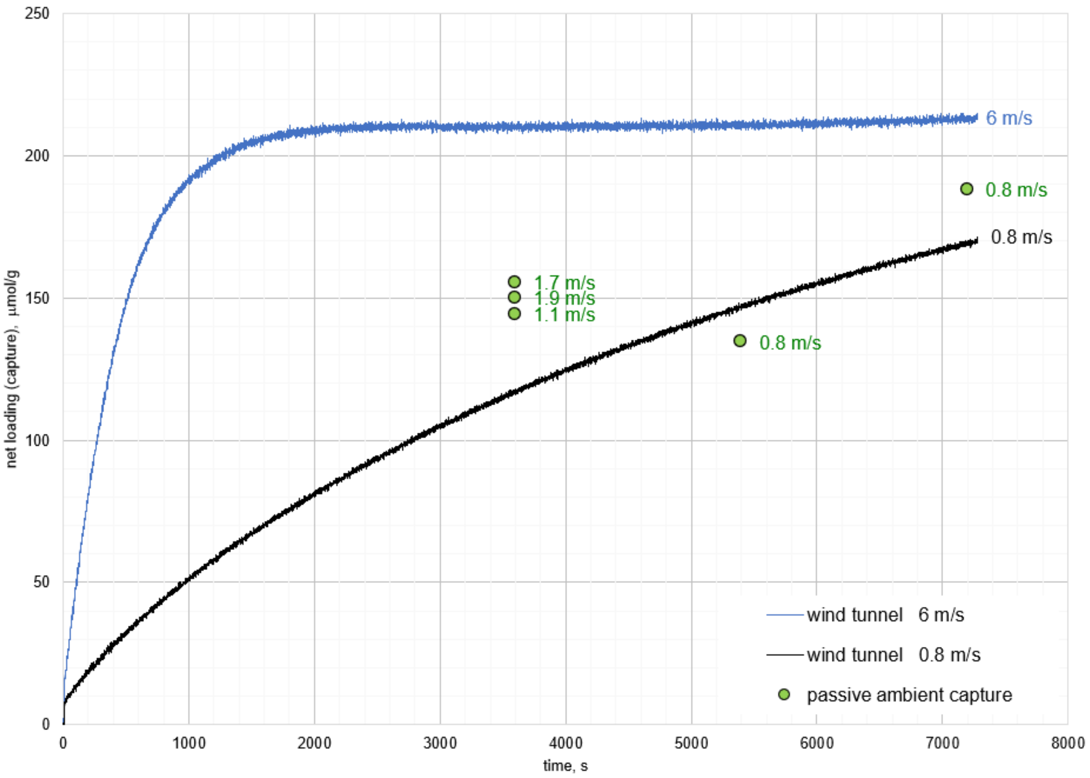


Figure 45 – Sorbent TSB 03 Assembly 03 Wind Tunnel and Sapling Ex-situ Experimental Results

3.7 Sorbent`s Longevity

As discussed previously longevity is an important characteristic of a sorbent to be evaluated due to the technical economic importance. A sorbent needs to outstand about 1,000 – 100,000 cycles of absorption and desorption in order to be economic feasible[17]. Despite we still under development of a methodology to test a sorbent this many cycles, we performed a few consecutive cycles for temperature and moisture swing sorbent.

Sorbent TSB 03, a temperature swing sorbent was tested on the wind tunnel at 6 m/s after steam heat regeneration 5 consecutive times with the form factor Hex B 5 mm (chapter 5 go in depth about this form factor). It can be observed there is a decline on the total capacity from the first run to the 5th run. From the first run to the second there was a 7.4% decline; from the second to the third 4.1 %, third to the fourth 5.4 % and fourth to the fifth 4.7%. For this first runs there is about 4-7% decline in each cycle (figure 46). However there is a possibility the sorbent will decline to a certain equilibrium capacity and keep itself stable for many cycles before significantly decline. A new methodology to test hundreds, thousands and even hundreds of thousands of cycles needs to be developed in order to have a better conclusion on the sorbent TSB 03. It is also important to notice there is not significant decline on the short timeframe, if the cycles were faster. For instance on 1,000 mark there are fluctuations between decline and increase on the kinetics ± 4-10% on each cycle. This shows the need for an improvement on a methodology to run many cycles in order to have a more clear conclusion.

Figure 47 shows the result of the moisture swing sorbent MTSB01 under 74 cycles of absorption and desorption utilizing the system MSCSD. Each cycle of absorption and desorption was 30 minutes with a total cycle time of 1 hour. It is possible to obsrve that despite the first tens of runs 9 full rins there was not decline on the performance, after 10 cycles there was a low but steady decline in the total capacity. The total decline on total capacity between the first few runs in equilibrium and the last was 31.8%. The total time of this experiments was 267,000 s or about 3 days. In order to test the sorbent for 10,000 cycles it will take about 1.1 years of continuous experimentation with the MSCSD system assuming the data log in does not crash and 100,000 cycles about 11 years of continuous experiment. Thus despite MSCSD system can run such many cycles in one moisture swing sorbent, there is a need of a faster, accelerated sorbent decay methodology to be developed in order to obtain data in a shorter period of time.

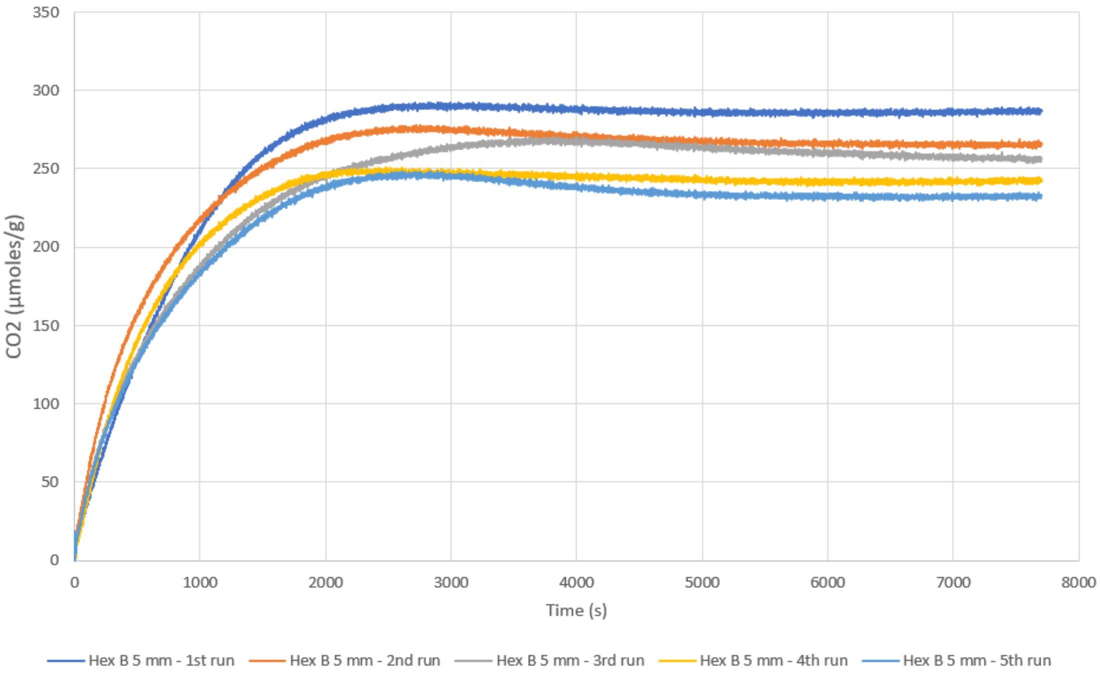


Figure 46 – Temperature Swing Wind Tunnel Results Hex B 5 mm Consecutive Runs

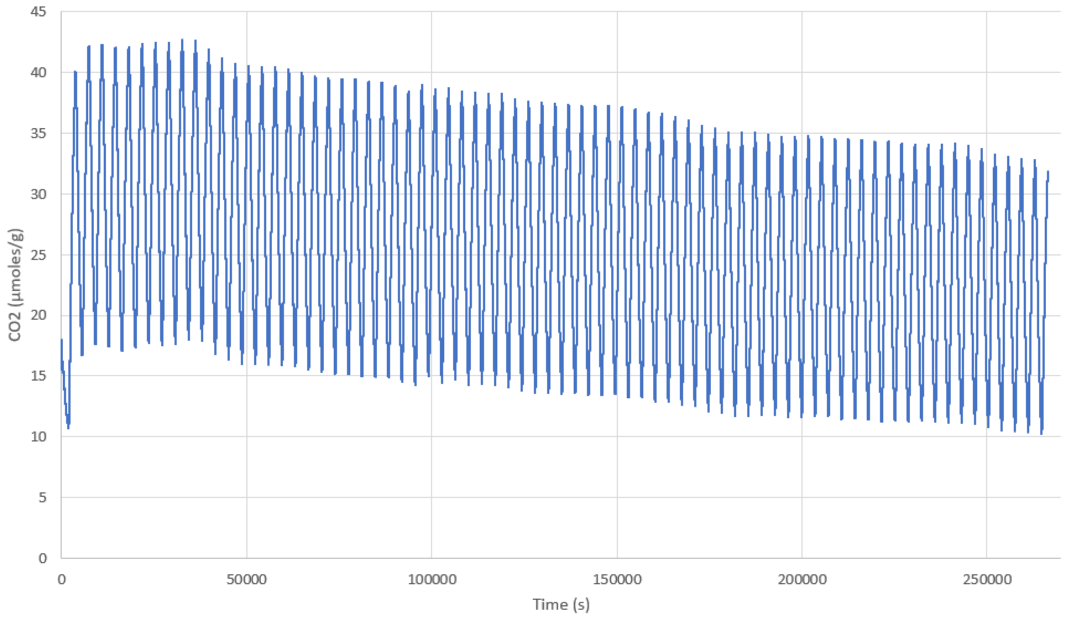


Figure 47 – Moisture Swing Sorbent Consecutive Runs at MSCSD System

4. TEMPERATURE AND MOISTURE SWING SORBENT ENHANCEMENT AND FORM FACTORS

4.1 Chemical-physical Enhancement

Sorbents can have their CO_2 sorption kinetics and capacity enhanced with chemical and/or physical pre-treatments such as: increasing surface area, ionic exchange washes. Increasing surface area has been shown to enhance both moisture and temperature swing sorbents kinetics and capacity; ion exchange is necessary for moisture swing sorbents since bicarbonate, carbonate and hydroxide are ions that need to be exchanged to replace ions that are typically bound to moisture swing resins as they are made. Very often these resins are delivered in the chlorine form, i.e., with chlorine ions ionically bound to its chemical structure. The capacity of moisture swing sorbents can also decrease over a certain number of moisture swing cycles, and by ionically exchange the capacity can be "recharged". Temperature swing sorbents that are based on amines can also benefit from ionic washes. As discussed in detail on subchapter 2.1, a temperature swing amine sorbent can potentially increase its capacity with a bicarbonate wash, as the ratio of amines to carbamate can double.

Sorbents can be selective, and the exchange is not always complete. Thus, it is necessary also to determine the selectivity of the sorbent when it exchange ions. In order to effectively ionically wash a moisture or temperature swing sorbent a protocol has been developed, assuming the sorbent has chlorine at first.

4.1.1 Ion Exchange and Ion Selectivity Protocol for Sorbents

This protocol has been developed with the focus on moisture swing sorbents that are initially bonded with chlorine. However it can be applied can also be applied for sorbents that are not initially bonded with chlorine in case moisture swing sorbents need to be recharged or temperature swing sorbents have its capacity enhanced, in this case the chlorine measurements can be ignored. The step by step on this protocol is as it follows:

Exchanging Chlorine to Bicarbonate, determining chlorine concentration and resin selectivity:

- Transfer the sample into the bicarbonate solution for titration right after the DI wash.
- Expose the sample to a 20 mM of bicarbonate solution in a 500 mL beaker) with 500 mL water volume for 12 hours.
    a. Wash the sample with DI water to remove any remaining salts in the surface.
    b. Pipette 100 mL of beaker 1 and transfer to a clean beaker (beaker 2).

c. Prepare beaker 2 for titration with 0.05M of NaOH solution to construct the pH curve. Once the upper pH limit has been reached, start titration with 0.05M of HCl until reach the lower pH limit. Take notes as the pH change occurs to construct a graph pH vs log(conc). The expected conversion point is pH = 8.3 where all CO_3^{2-} is converted to HCO_3^- and pH = 3.7 where all HCO_3^- is converted to H_2CO_3.
d. Pipette 100 mL of beaker 1 and transfer to a clean beaker (beaker 3). Titrate with Mohr`s (See Appendix) method to determine the Cl^- concentration.
e. Wash the sample (resin) with DI water to remove any remaining salts in the surface.
f. Repeat the steps a,b,c,d,e and f for about 3 cycles until chlorine is unable to be detected into the wash solution.
g. Based on the results determine the selectivity of the resin.

Figures, 48, 48 and 50 present an example of a commercial ionic resin with a quaternary ammonium functionality in which originally was with chlorine ions bonded to the ammonium functionality, in which was submitted to an experiment on the MSCSD operating with 30 minutes half cycles under 5 and 25 ppt of H_2O in order to perform the moisture swing cycles. Figure 48 present the sorbent on its original form, without any ionic exchange. Figures 49 and 50 present the data for the same sample after been submitted to the ionic exchange protocol. From figure 48 it the sorbent has shown almost no moisture swing as it is expected on been on the chlorine form, with variations on the raw data of just 14 ppm, corresponding within the IRGA`s error margin. After the bicarbonate exchange the raw data presented on figure 49 is clear the well-defined moisture swing with variations of 2,000 ppm in each swing. Figure 50 present the calculated data based on the mass of the sorbent (0.63 g) and total CO_2 inside of the closed system, accounting each absorption cycle with 47 µmoles CO_2/g of sorbent every 30 minutes and desorbed the same amount.

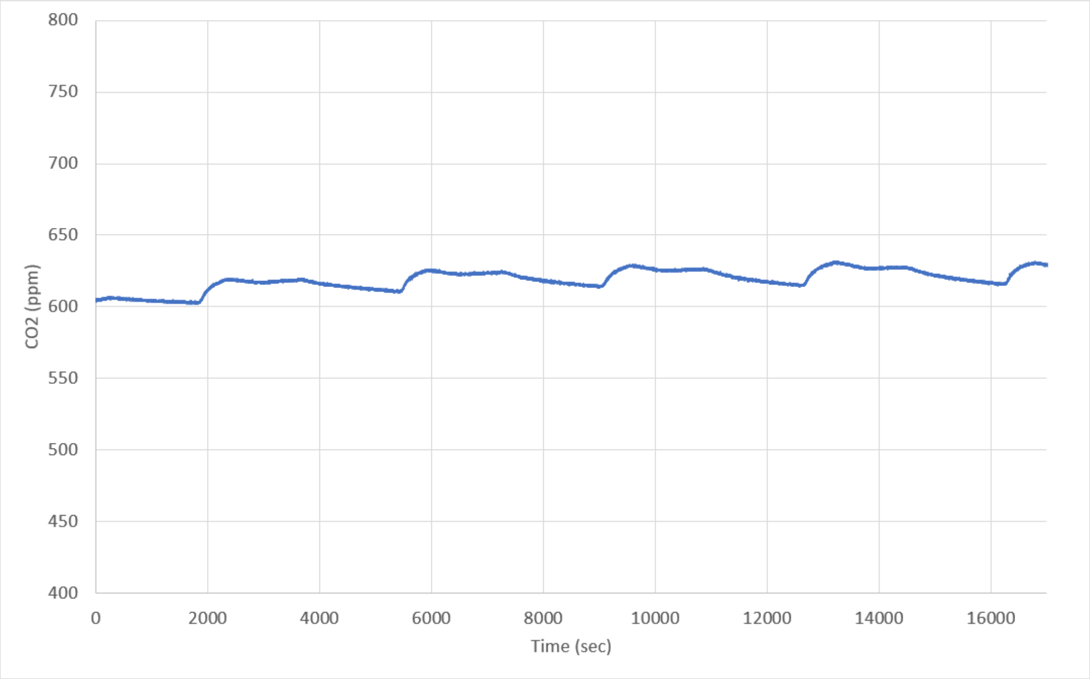


Figure 48 – Moisture Swing Sorbent before HCO_3^- Ionic Wash, Raw Data

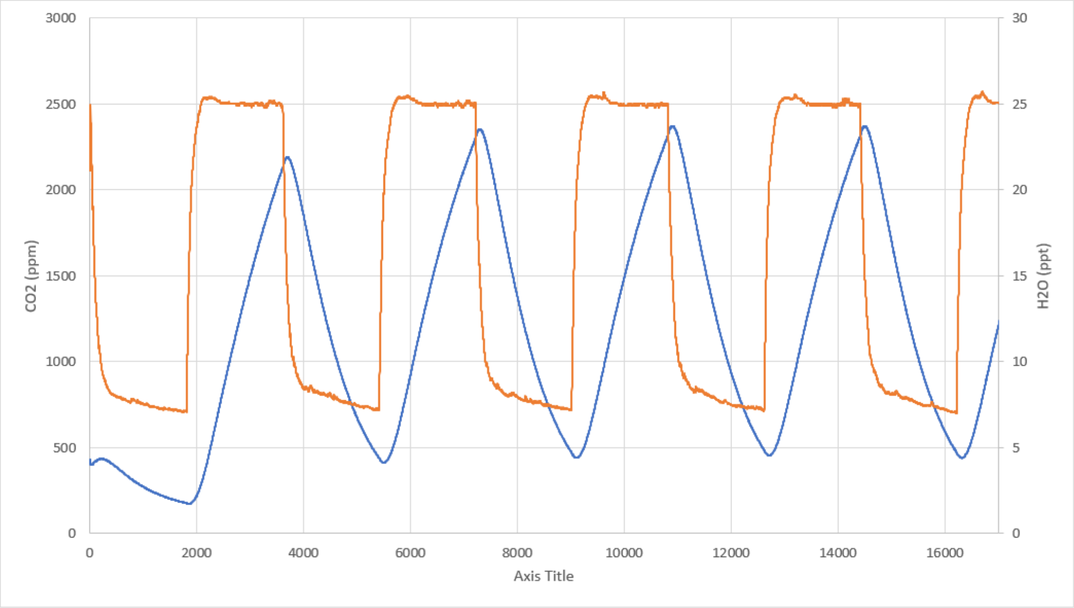


Figure 49 – Moisture Swing Sorbent after HCO_3^- Ionic Wash, Raw Data

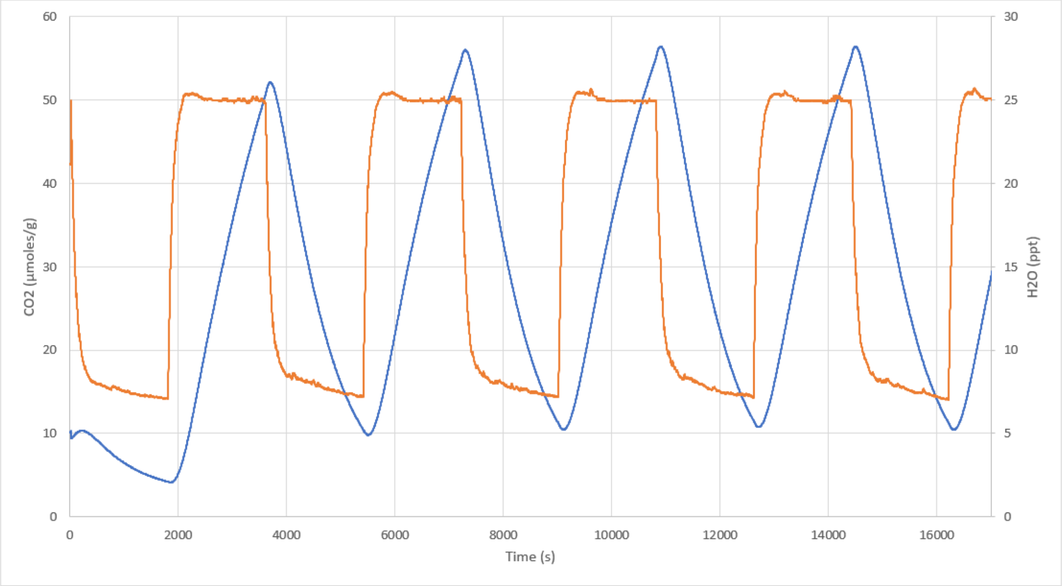


Figure 50 – Moisture Swing Sorbent after HCO_3^- Ionic Wash, Calculated Data

4.1.2 Enhancing Sorbent Surface Area

The physical strategy to mechanically reduce a sorbent particle size and thus increase surface area was performed utilizing a cryo mill 6870. Figure 51 shows the cryo mill in which the sorbent is filled on the sample chamber, the cryo mill is then filled with liquid nitrogen at – 196 °C. The sample is then passed throw cycles of 10 minutes pre-cooling, 20 minutes shaking and the cycle repeats itself for 3 times. The metal bar inside of the chamber mechanically breaks down the sorbent into smaller particles. At the end of the procedure the sorbent beads utilized were reduced from a few hundreds μm to nanometers. This procedure was able to greatly increase the sorbent`s surface area, having particles from hundreds of micrometers to a nanometer scale.

In order to evaluate if the higher surface areas on the sorbent after the cryo-mill, four experiments were performed, two with TSB03 beads on the CDSD and CSOFS system and two with TSB 03 after passed through the cryo mill procedure also on the CDSD and CSOFS systems to be able to compare. TSB03 beads were placed in a 53 μm polyester mesh and TSB03 cryo in a inside of a hydrophobic small porous bag (its porous sizes can contain the TSB03 in the nanometer powder form). The samples then were left on ambient air for 12 hours in order to be possibly fully loaded with CO_2 as a starting point. After the 12 hours each of the samples were experimented on the CSDS system. Figure 52 present the results of both samples CO_2 desorption under steam, with the experimental settings: 70% of steam generator chamber full with water; water of the 2 first buckets at the boiling point ~ 95 °C for our given temperature and pressure and the last bucket filled with water and ice ~ ° 0 C; and air flow rate at 0.5 l/min. The rate of desorption for both sorbents was very similar with TSB03 beads been slightly faster (probably due to the bigger mesh porous size) but with less total capacity than TSB03 powder form. TSB03 powder obtained 42 % more capacity than TSB03 beads, desorbing a total of 447 µmoles CO_2/g of sample while TSB03 beads desorbed 315 µmoles CO_2/g.

Once both samples were then empty of CO_2 the CDSD system chamber was than moved to the CSOFS system to obtain the absorption data. Figure 53 present the result of TSB03 beads versus TSB03 powder form absorption. TSB03 powder obtained 36 % higher kinetics on the 1200 s mark and 32 % higher capacity than TSB03 beads by the end of TSB03 beads experiment with 475 µmoles CO_2/g for TSB03 powder versus 361 µmoles CO_2/g for TSB03 beads. Thus overall the higher surface area on TSB03 was able to facilitate the CO_2 binding to the sorbent offering more active sites because of the greater surface area.

A similar test was made with a moisture swing sorbent PA318L on the beads form and on a powder form after the cryo-mill process. The experiment was performed with the MSCSD system with 240 min half cycles (240 min for absorption and 240 for desorption) by varying the humidity from 5 ppt for absorption, to 25 ppt for desorption. The powder sample had a significant enhancement on kinetics and capacity when compared to the beads sample. As observed on the figure 54, the PA318L powder form sorbent absorbed 41.8 and 132 µmoles/g respectively to 1,200 and 7,200 s time marks while PA318L beads form absorbed 16.1 and 87.2 µmoles/g respectively to 1,200 and 7,200 s time marks. This represents a 160 and 51 % absorption kinetics enhancement respectively to ,200 and 7,200 s time marks. Similarly, the desorption kinetics saw a significant improvement with the PA318L sorbent. The powder form desorbed 49.5 and 132.3 µmoles/g respectively to 1,200 and 7,200 s time marks while PA318L beads form absorbed 19.6 and 76.8 µmoles/g respectively to 1,200 and 7,200 s time marks. This represents a 152 and 72 % improvement on the desorption rate respectively to 1,200 and 7,200 s time marks. There is also an improvement on the sorbents total ability to take CO_2, or the total capacity. The powder form absorbed a total of 129 µmoles/g while the beads form absorbed a total of 92 µmoles/g. This represents a 40% improvement.

The results suggested an example of a good thermal and moisture swing sorbent when with a much smaller particle size, as a powder on the nanoscale, compared to a bead on 100-300 µm scale has a significant improvement on the kinetics and on the total capacity. This is very likely because of the large improvement on the sorbent`s surface area, improving the air delivering $CO_2$ more efficient and more accessible to the sorbent`s active sites.

Figure 51 – Cryo Mill 6870 to Reduce Particle Size

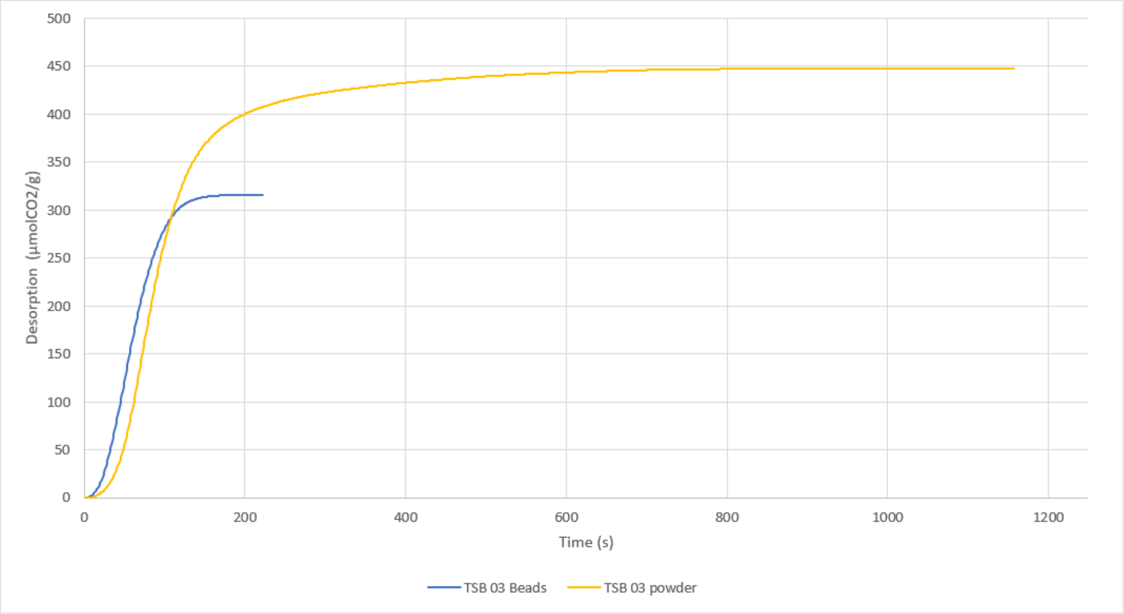


Figure 52 – TSB03 Beads Versus TSB03 After Cryo Mill Desorption

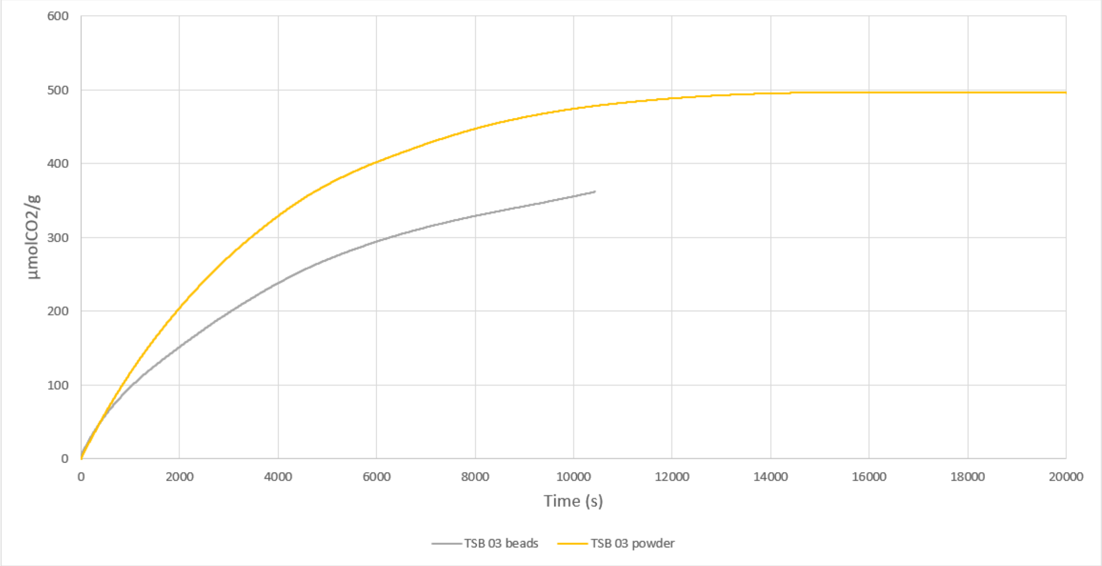


Figure 53 – TSB03 Beads Versus TSB03 After Cryo mill Absorption

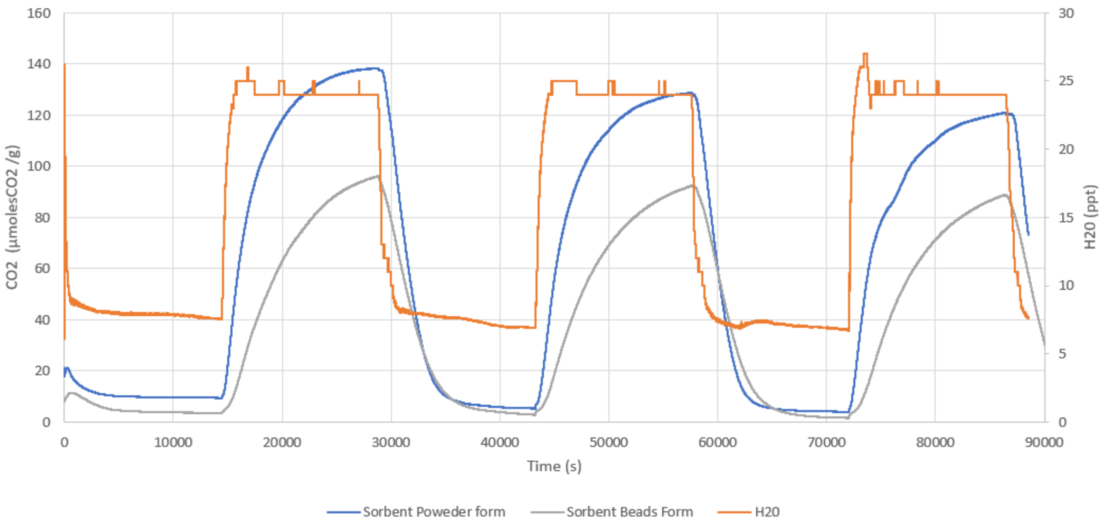


Figure 54 – PA318L Beads Versus PA318L Powder (after cryo mill) Absorption and Desorption

4.2 Form Factors Air to Sorbent Enhancement

4.2.1 CSOFS Form Factors Screening

After screening several sorbents another important factor on evaluating sorbents kinetics and forms that can lead a sorbent`s scalability is the form in each the sorbent will be composed. Several experiments were performed with the TSB 03 sorbent, a high kinetics and robust sorbent identified on the screening process. TSB 03 sorbent was composed in several form factors that can hold the sorbent in place and allow good air contact with the sorbent. The form factors utilized were: 1) several materials that were heat sealed in form of "bags" that can hold TSB 03 in place, allowing the air flow in but preventing the sorbent from been released to the environment. The materials were: spun-bound polypropylene; melt blown polypropylene, 3 M filter, 53 µm polyester mesh. 2) A sunscreen material with TSB 03 adhered with spray adhesive, with a possibility of making several layers as a "sandwich". 3) TSB 03 adhered on 3 different thickness 250, 25 and 12.5 µm.

Figures 55 and 56 present the CO_2 absorption data of all the form factors compiled as µmoles of CO_2 per g of sorbent over time. Taking a reference point of loading time of 1200 s, the highest to lowest was 1) TSB03 in 12.5 µm adhesive film with 225 µmoles CO_2/g; 2-3) the second and third faster are fairly draw for the 25 and 250 µm adhesive film with 193 µmoles CO_2/g at 1200 s; 3) TSB 03 in spun-bound polypropylene with 135 µmoles CO_2/g; 4) TSB 03 in melt-blown polypropylene with 126 µmoles CO_2/g, polyester mesh bag with 109 µmoles CO_2/g; 5) TSB 03 in 3 M filter bag 103 µmoles CO_2/g; 6) TSB03 sandwich with 3 layers with 57 µmoles CO_2/g and 7) TSB03 sandwich with 6 layers with 48 TSB03 sandwich with 3 layers.

The total capacities varied between 500 to 400 µmoles CO_2/g for most of the form factors results except the TSB03 sandwiches with slightly lower at 300 µmoles CO_2/g. The reason could be 1) the TSB03 sandwiches does not provide the ideal air to contact with the sorbent or 2) the adhesive utilized affected the sorbent`s capacity.

Despite the samples TSB03 in 12.5, 25 and 250 µm adhesive film have the higher kinetics on the first 1,200 s on moles of CO_2 per g of sorbent, this is likely to the fact the sorbent was less packed and more evenly spread out through the surface, facilitating the air to contact with the sorbent, it does not have the total effective CO_2 captured on a per surface area comparison with the samples inside the pouches. The sorbents TSB 03 12.5, 25 and 250 µm adhesive film had a total mass of 0.06111, 0.1085 and 0.1623 g of TSB 03 sorbent while the sample on fourth place for kinetics at 1200 s, TSB 03 in spun-bound polypropylene, had a total mass of 0.4857 g. Assuming these samples had a very similar surface area, calculating by its mass the total effective CO_2 absorbed was 13.7, 20.9, 31.6 and 66.0 µmoles CO_2 respectively for the samples TSB 03 12.5, 25, 250 µm adhesive film and TSB 03 in spun-bound polypropylene. Thus thinking in scale a form factor for a practical engineering perspective the sample TSB03 in spun-bound polypropylene can absorb more CO_2 per a given system area than the 12.5 µm adhesive film.

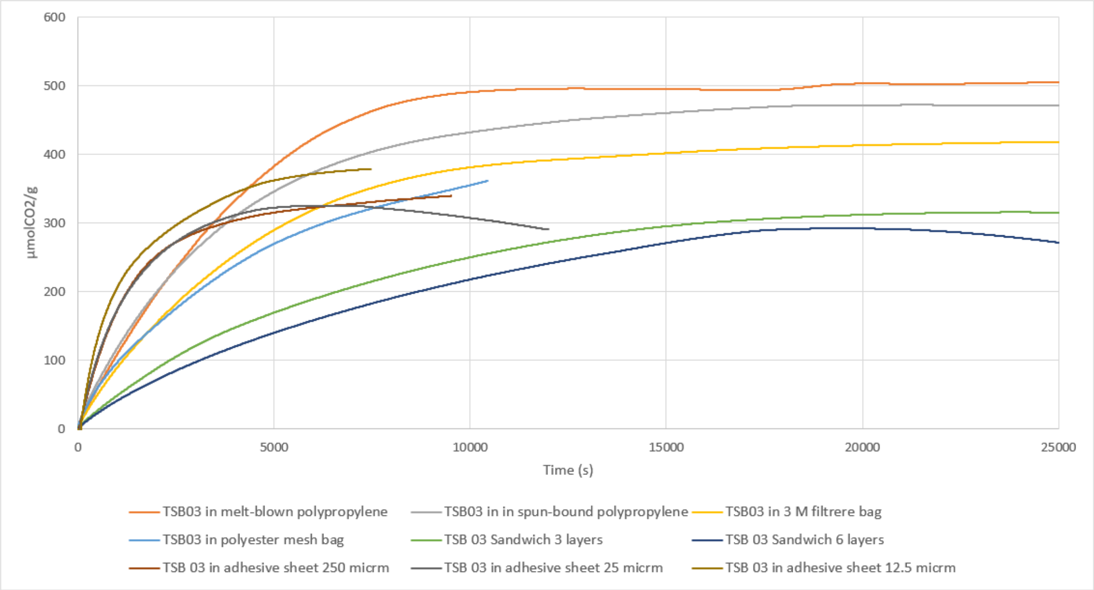


Figure 55 – CSOFS form CO_2 Absorption Sorbent Screening at Full Experimental Timeframe

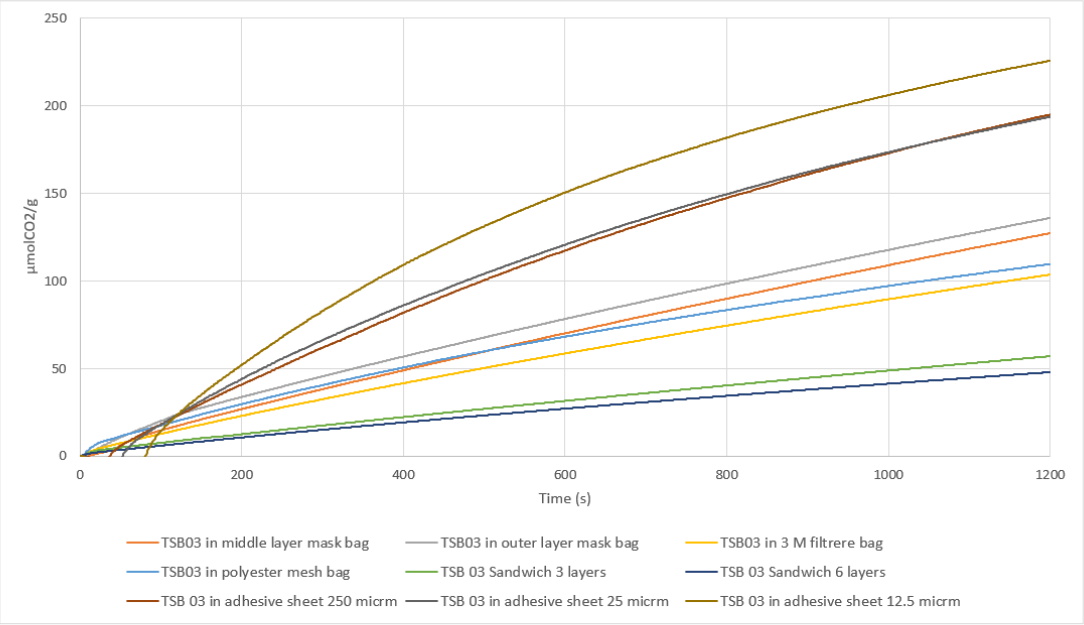


Figure 56 – CSOFS form CO_2 Absorption Sorbent Screening at 1200 s Experimental Timeframe

4.2.1 Wind Tunnel Thermal Swing Form Factors Screening

Based on the results obtained on the CSOFS form factors it has been realized that 1) the “bags” utilized do not significantly interfere with CO_2 absorption; 2) there is a need of a form factor in which the sorbent needs to be held in place with significant mass to account for a significant CO_2 capture by surface area. Thus, several variations of a more complex sample form factor were created for the sorbent TSB 03. The results are presented on figures 57 and 58.

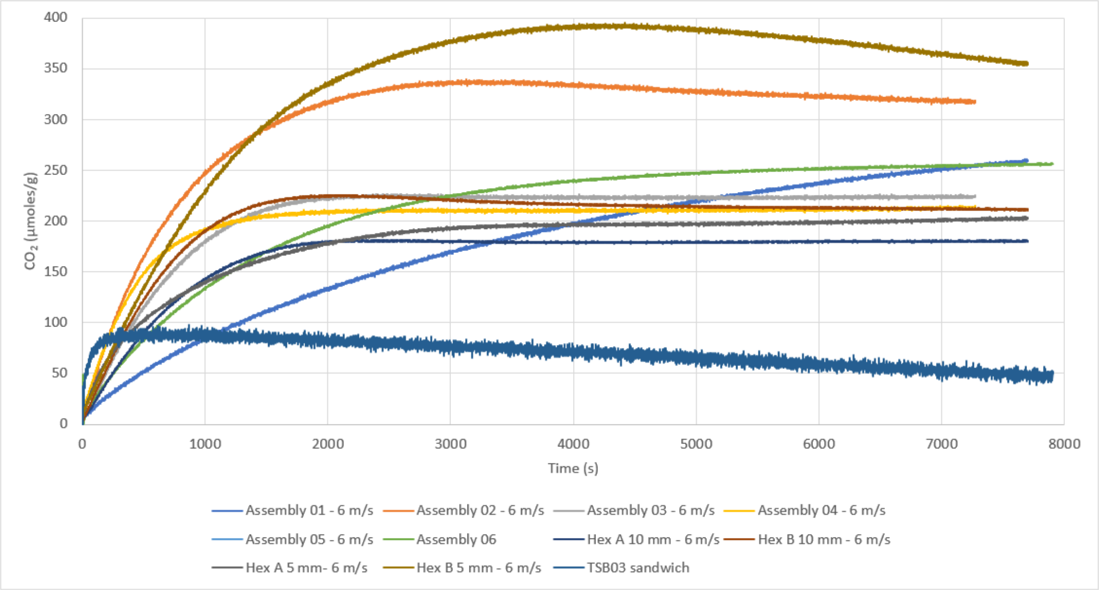


Figure 57 - Wind Tunnel Thermal Swing Form Factors Screening under 8000s.

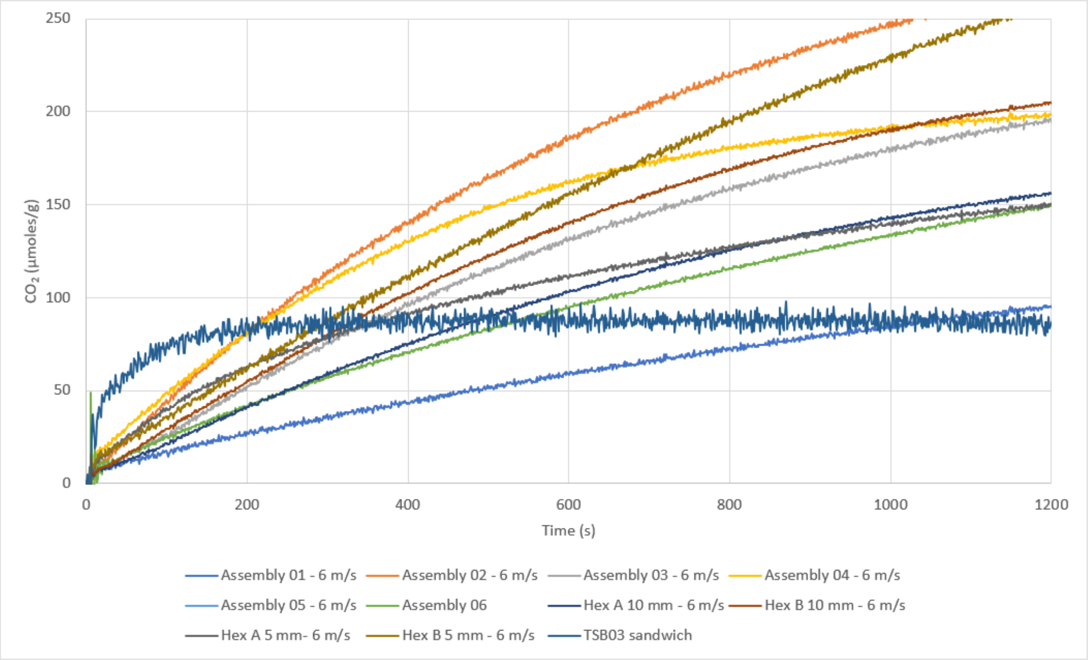


Figure 58 - Wind Tunnel Thermal Swing Form Factors Screening under 1200s

4.3. Amine Based Sorbent Dry Heat Regeneration Versus Steam Heat Regeneration

The experiments performed with TSB 03, a polyamine sorbent, demonstrate the effect of the water content in the sample leading to changes in performance kinetics and total capacity. The water can be adhered to the sorbent through humid air but mainly after the steam regeneration, liquid water accumulates on the solid structure of this particular sorbent. Several experiments have shown TSB 03 CO_2 absorption after steam heat regeneration has higher kinetics when compared to TSB 03 CO_2 absorption after dry heat regeneration. Figure 59 shows the results of two experiments performed in the wind tunnel with the TSB 03 sorbent using the form factor Hex A (see more details on the wind tunnel form factors on chapter 5). Both experiments the wind tunnel was operating at 6 m/s wind speed and under continuously dry condition at 4 ppt H_2O vapor. One experiment the CO_2 absorption was after 1 hour of dry heat regeneration at 100 °C and the other after steam heat regeneration at the water boiling point ~ 100 °C during also 1 hour, both with sample size of 29 g of sorbent. Analyzing the results on figure 59 under 1000 s, timeframe the kinetics is the highest, it is possible to conclude that there is a 37% increase on the adsorption kinetics at 1000 s time mark, with 104 µmols CO_2/g for dry heat regeneration experiment versus 143 µmols CO_2/g. Thus, the amount of water absorbed and adhered by the sorbent was beneficial for CO_2 absorption kinetics.

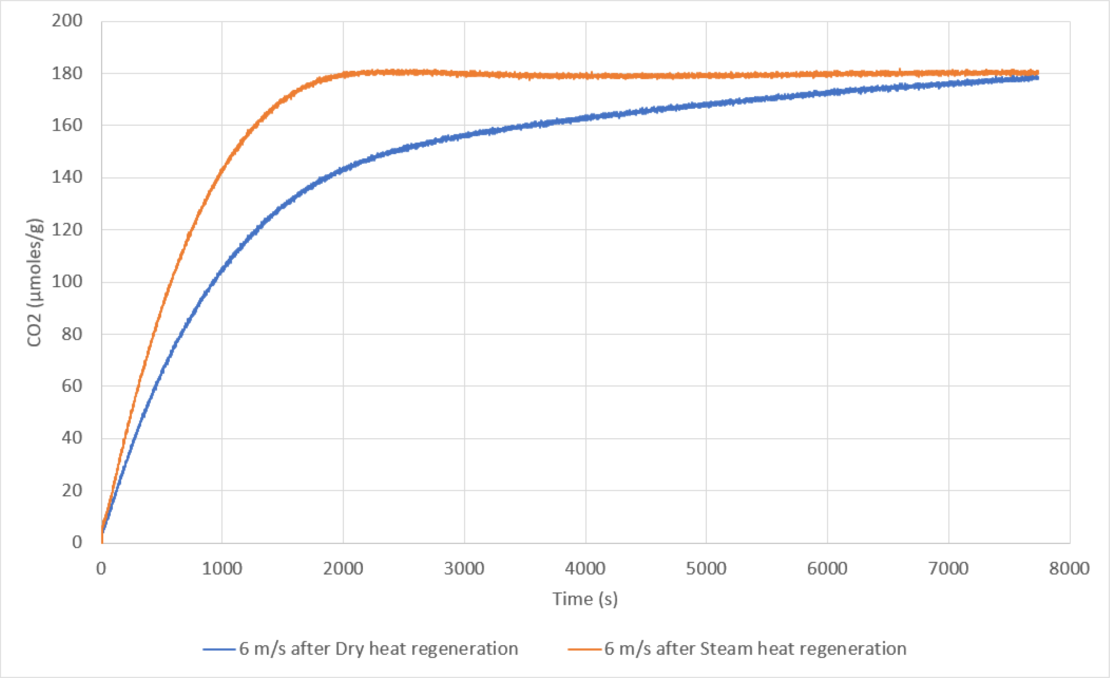


Figure 59 – TSB 03 Adsorption after Steam Regeneration Versus Dry Heat Regeneration.

The same concept of experiment was performed utilizing the TSMSD method with 3 mg of TSB 03 sorbent. One experiment was performed the CO_2 absorption after 1 hour of dry heat regeneration at 100 °C and the other after 1 hour of steam heat regeneration at ~ 100 °C. Figure 60 show both results. On this case the CO_2 absorption after the steam heat regeneration quickly absorbs 50 µmoles of CO_2/g on the first 170 s and then there is a delay of 459 s until the sorbent starts absorbing CO_2 again for 1,187s, reaching its maximum at with 245 µmoles of CO_2/g. This delay process was very likely due to the fact the water concentration on the sorbent was too high for the among of mass on this small system. The water was likely filling all the porous of the sorbent and not allowing the CO_2 absorption until the water was than dried since the system was operating continuously dry at 6.25 ppt of H_2O.

For the experiment on CO_2 absorption after dry heat regeneration there were no delays on the CO_2 absorption. There was a fast and sharp absorption kinetics in which the sorbent was fully loaded at 300 s, reaching 195 µmoles of CO_2/g.

These results suggest there is a balance on the water content on the sorbent that needs to be taking into consideration after a steam heat regeneration. The water concentration correlating with the sorbent mass ratio needs to have an equilibrium. Also the drying time of the water contained on the sorbents surface can be important on achieving high kinetics.

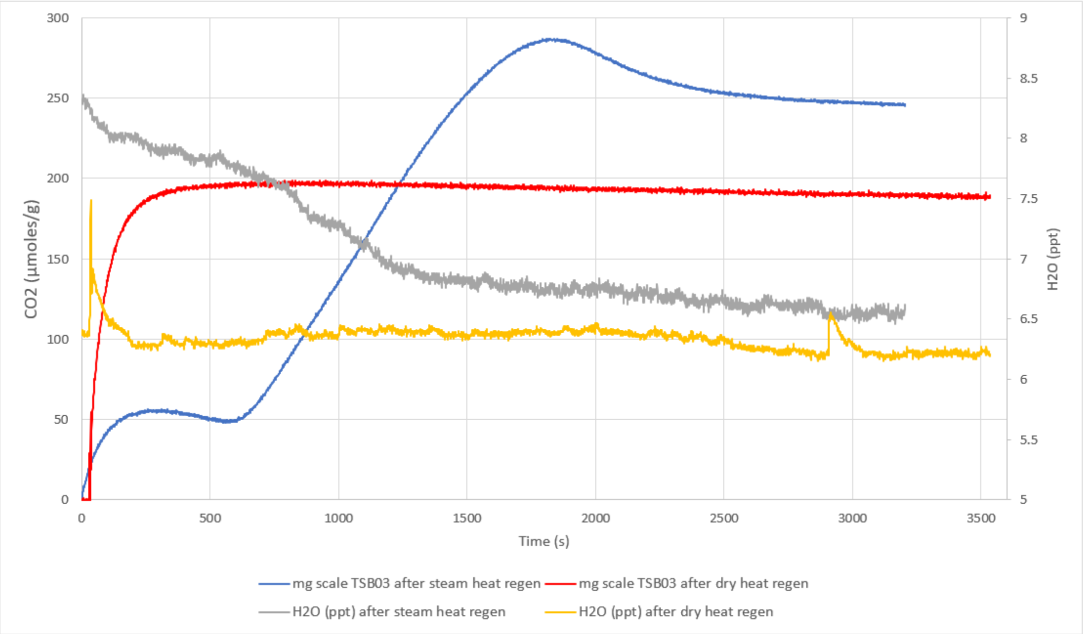


Figure 60 – TSB 03 Adsorption after Steam Regeneration Vs Dry Heat Regeneration on mg Scale

4.4 Amine Based Sorbent Adsorption and Desorption Kinetics and Capacity

TSB 03 has a very fast desorption rate. Figure 61 present the result of a 0.2065 g TSB 03 sample inside of McMaster-Carr mesh with 53 micron hole size and 24% open area submitted a steam heat desorption at 95 °C with air flowing at 0.5 l/min. TSB03 started loaded and desorbed 317 µmoles of CO_2/g and it was fulling desorbed in only 150 s (or 2.5 min) when the sample was free of CO_2. This sorbent present a very promise economic viability with this very fast rate of desorption since it needs heating for a short period of time and thus translates in far less energy input when compared with other sorbents. The adsorption of the same sample was completed in 7,200 s (or 120 min) when the sample reached 318 µmoles of CO_2/g, a bit higher than the desorption what indicates the sample was likely not completely loaded with CO_2 when was submitted to the steam desorption. The fastest absorption kinetics is below 1000 seconds. The desorption is 48 times faster than the absorption.

It has been observed that this accelerated rate is very likely related to the experimental settings in which there is an air flow rate of 0.5 L/min moving the steam through the sample and a temperature differential between the first 2 buckets at ~ 95 °C and the last bucket (ice bucket) of ~ 0 °C. With a more simple system for steam regeneration in which there was not air flow, just a bucker with steam and a metal cover with a small hole to the steam move through, the time to desorb TSB03 was ~ 1 hour versus 3.68 minutes on the CSDS system at the given conditions. Thus 16 times faster desorption utilizing the CSDS air-flow rate and the temperature delta.

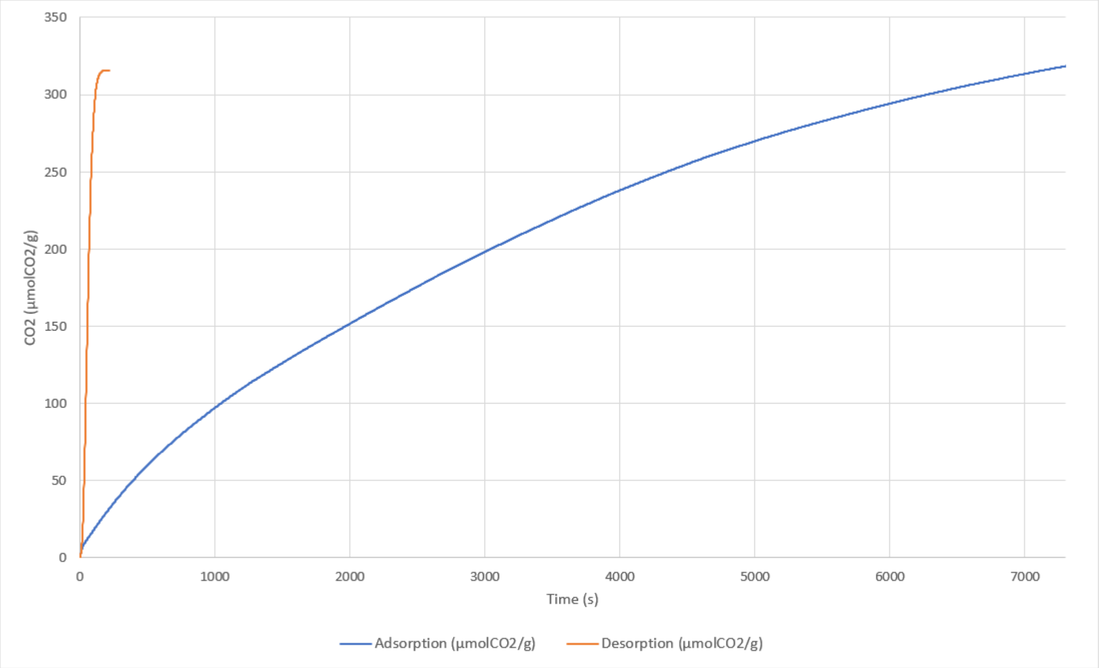


Figure 61– Adsorption Versus Desorption of TSB03 Inside McMaster-Carr Mesh with 53 Micron.

5. CO_2 ABSORPTION IN WIND TUNNEL UNDER DIFFERENT WIND VELOCITIES AND FORM FACTORS TO SCALE UP

The sorbent`s kinetics, capacity and overall performance does not rely only on its chemistry. Weather and environmental conditions can greatly affect sorbent performance and are key for scalability and economic feasibility. This study presents an effective form factor to hold the sorbent in place and enhance air contact to the sorbent. In addition, the form factors created were tested under various wind velocities in order to determine how it affect the sorbent kinetics on a thermal swing process. These tests were performed with larger sample size 15-30 g of sorbent on the wind tunnel.

5.1 Polyamine Temperature Swing Sorbent in Honeycomb Form Factor Versus Squared Packed Bed

In order to scale up direct air capture, it is necessary to have an effective form factor in which provides a structure to hold the sorbent in place and allow efficiently CO_2 sorption from the air by facilitating the air contact with the sorbent. The form factor utilized is in a form of a holder with a honeycomb structure with a polyester mesh on the top and bottom. The samples holders for the sorbent were prepared using a 3 D printed ABS 110 x 110 mm square plate with 10 mm height as a square (figure 62); and a honeycomb plate with 110 x 110 mm, 10 mm height and10 mm across section s with a total of 105 s named Hex A (figure 63). A McMaster-Carr mesh with 53 micron hole size and 24% open area were attached up and bottom of each plate using soldering iron to melt and attach the mesh to the edges of the plates and the TSB03 beads were filled inside.

This form factor can provide 1) a separation of the sorbent beads, minimizing the packing and allowing the air flow through the sample more easily; 2) an increase in the localized turbulence improving the contact with the sorbent even further; the polyester mesh on top and bottom allow the air pass through the honeycomb structure and with 53 µm of porous size, prevents this specific sorbent from passing through it, holding it in place.

In order to test the hypothesis in which the honeycomb structure can provide faster kinetics due to its improved air flow and localized turbulence, it has been performed experiments to compare the honeycomb structures with the sorbent packed in a open square frame, also with polyester mesh on the top and the bottom.

To evaluate this hypothesis both structures with sorbents were submitted to a dry heat regeneration and tested at the wind tunnel under 6 m/s wind velocity. According to figure 64 on the 2000 seconds (time where the kinetics is still in its maximum rate range) time mark, the TSB03 on square frame obtained 110 µmoles CO_2/g sorbent while the honeycomb sample obtained 144 µmoles CO_2/g. This is a 31% increase in the kinetics of CO_2 adsorption for this timescale what can potentially provide a significant capital gain on CO_2 absorption.

Figure 62 – 3 D Printed ABS 110 x 110 mm Square Frame with McMaster-Carr Mesh with 53 micron, Filled with TSB03 Beads

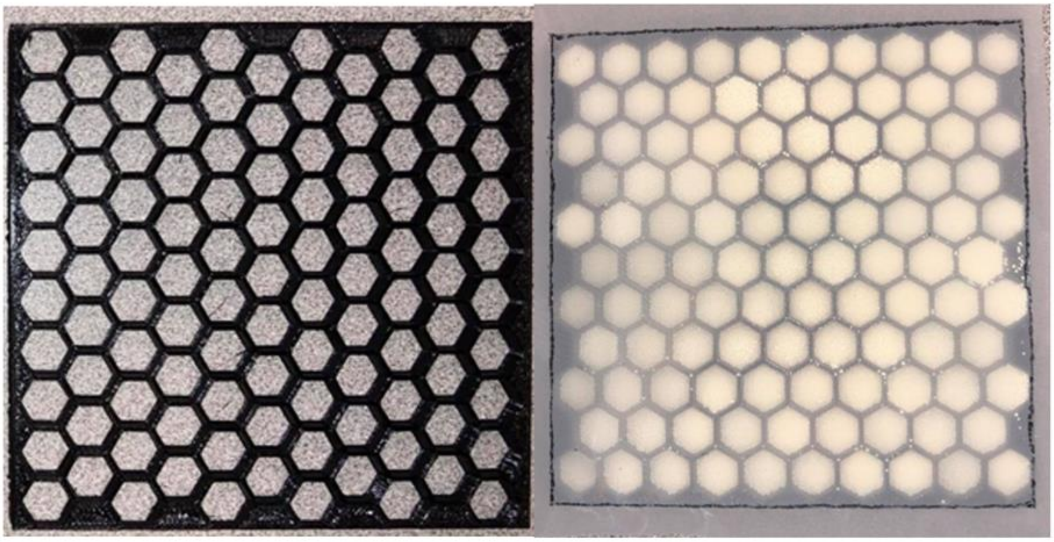


Figure 63 – 3 D Printed ABS 110 x 110 mm Honeycomb (10 mm height and 10 mm s Accreoss Section) Frame with McMaster-Carr Mesh with 53 Micron, Filled with TSB03 Beads

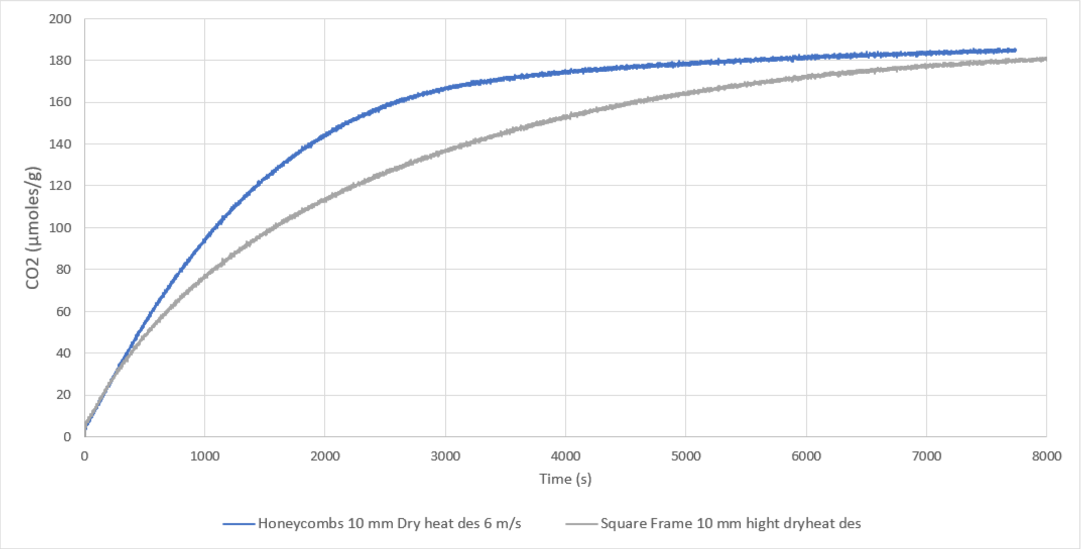


Figure 64 – Square Frames Filled with Beads vs Honeycombs Filled with Beads after Dry Heat Desorption.

5.2. Hex A Versus Hex B 10 mm Depth vs 5 mm Depth – Evaluating Different TSB03 Packing Densities

Based on the results obtained with Hex A, a new form factor has been developed with smaller hexagonal openings and both form factors evaluated with different packing densities: 10 mm and 5 mm heights to evaluate the kinetics, CO_2 capture efficiency on a per sorbent weight normalization and the CO_2 capture kinetics and capacity based on the form factor's surface area.

In order to promote even faster kinetics, the next hypothesis is to evaluate if the size of each s in a 110 x 110 mm plate can influence the localized turbulence and air contact with the sorbent once there is less sorbent in each hexagon and thus higher air/sorbent ratio and more CO_2 absorption by the sorbent. For this purpose, a plate named Hex B has been created with 5 mm across section in each hexagon (hexagon twice as small than Hex A). The Hex A plate has a total of 105 hexagons with a total surface area of 9,114 mm^2 while Hex B has 333 hexagons with 7,226 mm^2 surface area. For both Hex A and Hex B plate were 3 D printed with 5 and 10 mm heights in order to evaluate different sorbent packing densities (figures 65, 66 and 67).

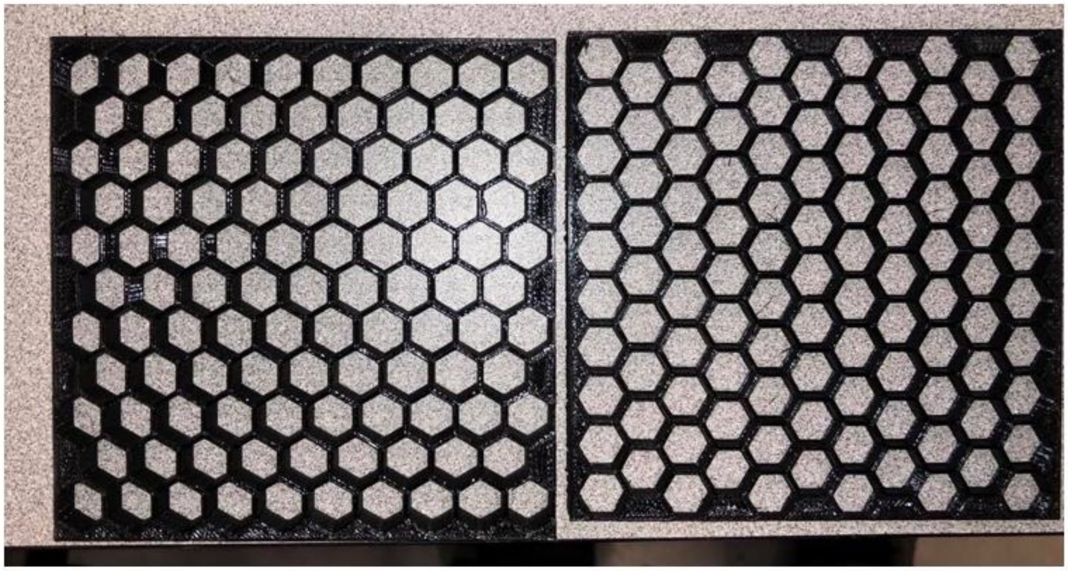


Figure 65 – Upper View of Hex A Honeycomb.

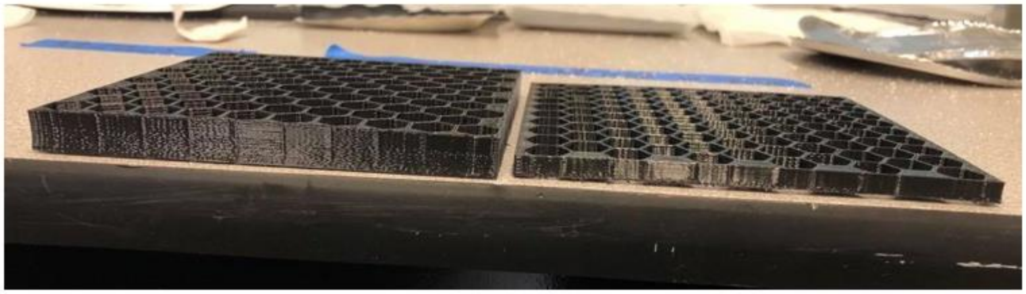


Figure 66 – Side View of Honeycombs with Different Heights, 10 and 5 mm.

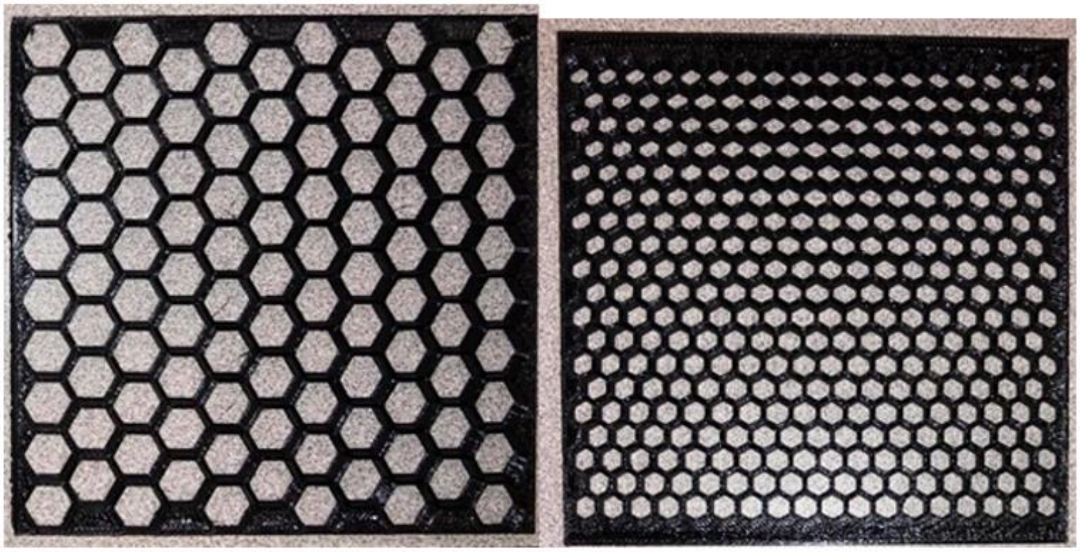


Figure 67 – Ppper View Comparing Honeycomb Hex A (Left Side) and Honeycomb Hex B (Right Side).

Absorption kinetics for TSB03 beads is a function of the windspeed, as faster the wind speed is, higher is the kinetics as it increases the air-contact with the sorbent. As observed and explained on the section honeycombs vs square frame, hexagons in the honeycombs increase the localized turbulence and thus increase absorption kinetics. It has been also evaluated how important is the size of each hexagon. Evaluating two different hexagons sizes, 10 mm across sectional area named Hex A and 5 mm across section hexagons named Hex B (twice as small as Hex A). Figures 68, 72 and 74 represent experiments performed on Hex A and Hex B after 1 hour steam regeneration under different wind velocities (2, 4 and 6 m/s) at the wind tunnel represented as µmoles of CO_2 per g of sorbent under 7,200 s timescale. For the wind speeds 4 and 6 m/s the absorption of CO_2 for Hex B was 32 % and 35 % higher in a CO_2 absorption per sorbent weight than Hex A in the 1000 s time mark respectively to 6 and 4 m/s wind velocities. For 2 m/s velocity Hex A and Hex B had almost identical CO_2 absorption kinetics. Thus the hexagon sizes are more important creating more localized turbulences at higher wind velocities and less important at lower wind speeds.

According to the figure 68, Hex B outperform Hex A on both 5 and 10 mm heights. Evaluating the absorption time at 1200 s or 20 min, Hex B 5 mm when compared with Hex A 10 mm obtained 71 % more CO_2 absorption in a per sorbent mass unit and Hex B 10 mm vs Hex A 10 mm 31 % at 6 m/s wind speed. Evaluating at 4 m/s the difference are still significant with 51.3 % for Hex B 5 mm vs Hex A 10 mm and 38% when for Hex B 10 mm vs Hex A 10 mm. When the wind speed is lower at 2 m/s the difference on absorption kinetics is minimum with Hex A this time outperforming Hex B for only 6 %. These results suggest smaller hexagons with a lower and higher packing density has a great effect on passive CO_2 absorption kinetics under higher wind velocities, more prominent on the lower packing density as the air flow can reach the sorbent more easily.

Nevertheless a fair evaluation to know the actual CO_2 been effectively uptake is on the units of absorption by surface area. The results just presented on figures 68-73 , give a good evaluation on the kinetics per mass of sorbent but not on the effective CO_2 absorbed. The figures 72-75 present the absorption in each as in mmol of CO_2 per m^2. For example, on figures 72 and 74 we observed Hex B 5 mm outperform in kinetics and capacity all the other form factors significantly because of the fact it has a) higher inner turbulence; b) the beads are more spread-out allowing more contact with the air and c) the 5 mm height give twice less mass density allowing more air to have contact with the sorbent. But when evaluating by effective CO_2 surface area all the “a” and “b” explanation are valid except “c”. The Hex B 10 mm height has more effective CO_2 uptake, it has a higher sorbent density, about 2 times more, however it has more sorbent per surface area, thus more total CO_2 absorbed. It absorbed a total of 800 mmol CO_2/m^2 for both 6 m/s and 4 m/s wind velocities. Hex B 10 mm obtained 47 and 54% higher kinetics than Hex A 10 mm respectively to 6 and 4 m/s wind velocities, demonstrating how effective is smaller hexagons on improving kinetics for passive direct air capture.

Figure 72 shows that Hex B 5 mm height had more sorbent loading per unit mass of sorbent on the 7200 s experiment timeframe. However figure 73, evaluating the first 100 s of this experiment shows that Hex A 5 mm and Hex 5 mm had a very similar initial kinetics but it differs after ~ 400 s. This suggest the difference on the absorption kinetics and capacity of this 2 samples is 1) related to how efficient it desorbed CO_2 as both experiments the desorption time was 1 hour under steam or 2) the Hex A offer more CO_2 transport limitations to the sorbent when compared to Hex B.

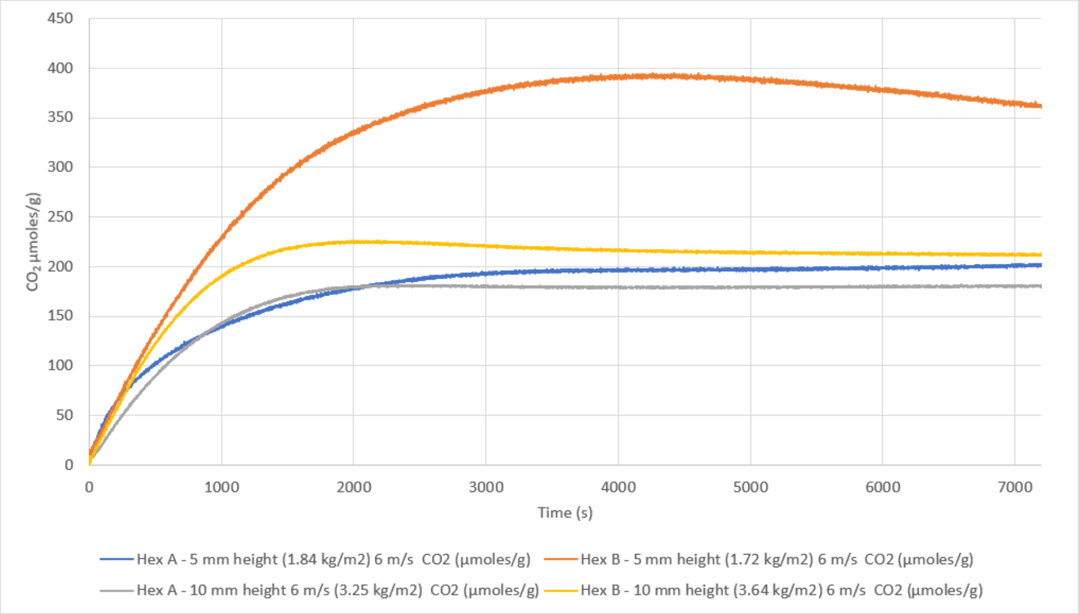


Figure 68 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in µmoles of CO_2 Per Gram of Sorbent at 6 m/s, 0 to 7200 s Timescale

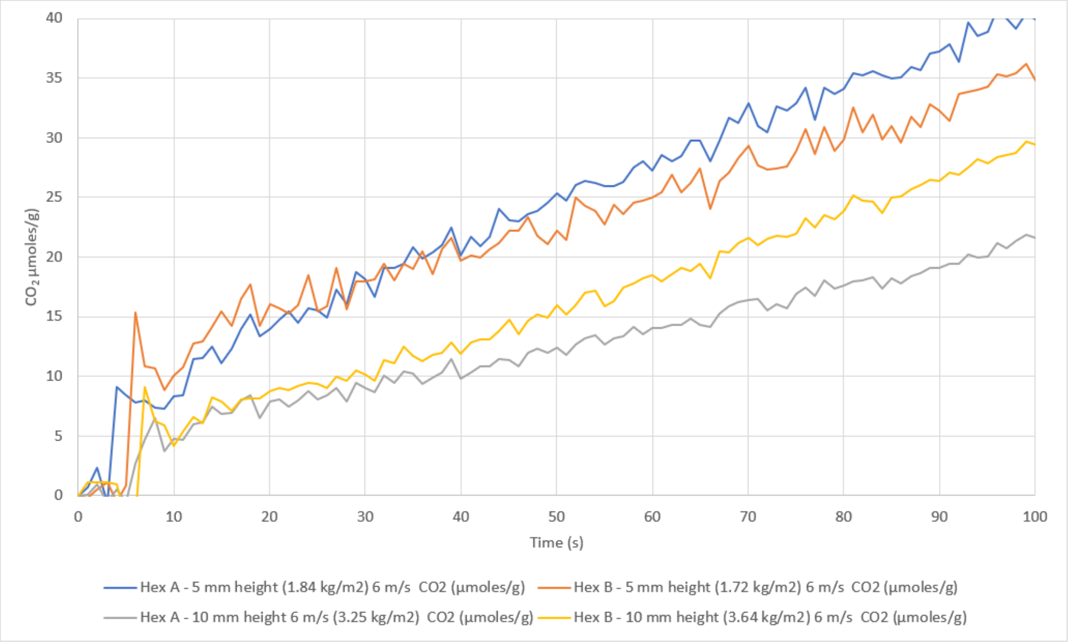


Figure 69 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in µmoles of CO_2 Per Gram of Sorbent at 6 m/s, 0 to 100 s Timescale

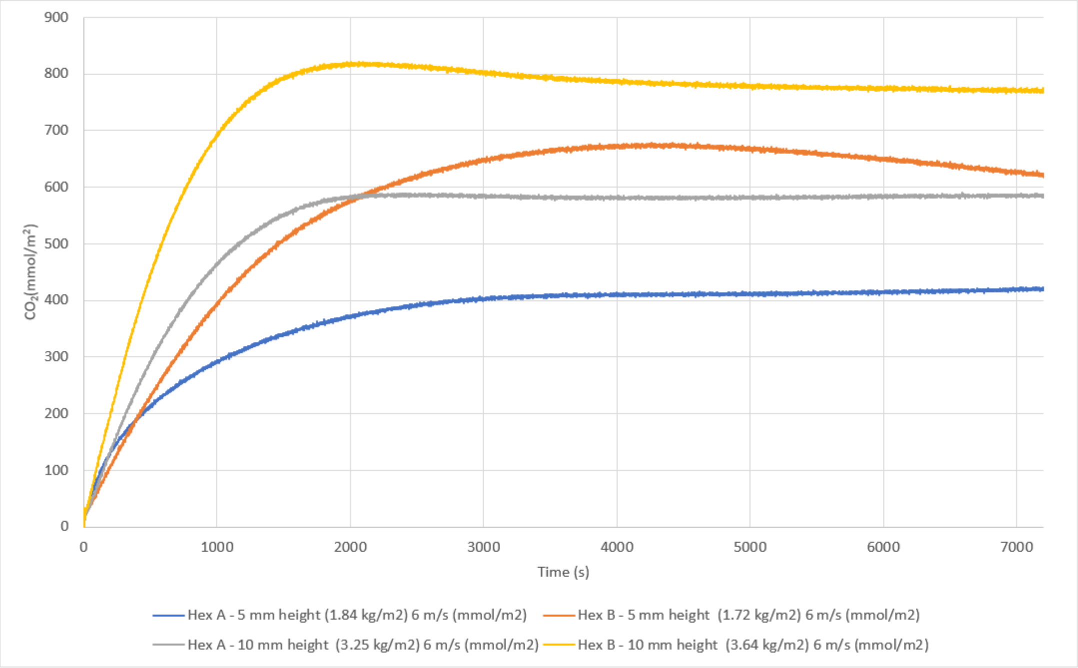


Figure 70 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in mmol of CO_2 Per Square Meter at 6 m/s, 0 to 7200 s Timescale

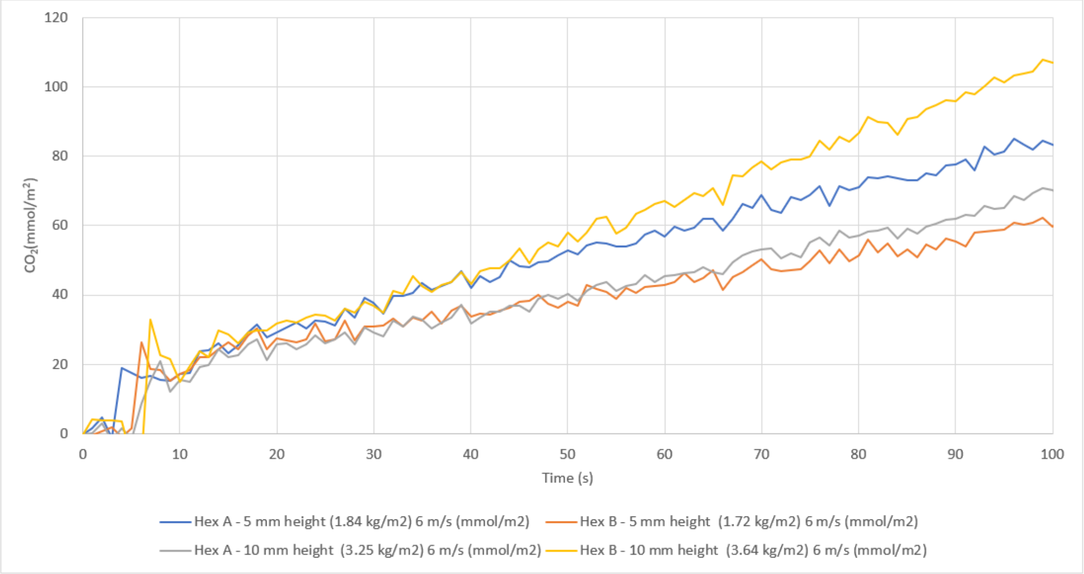


Figure 71 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in mmol of CO_2 Per Square Meter at 6 m/s, 0 to 100 s Timescale

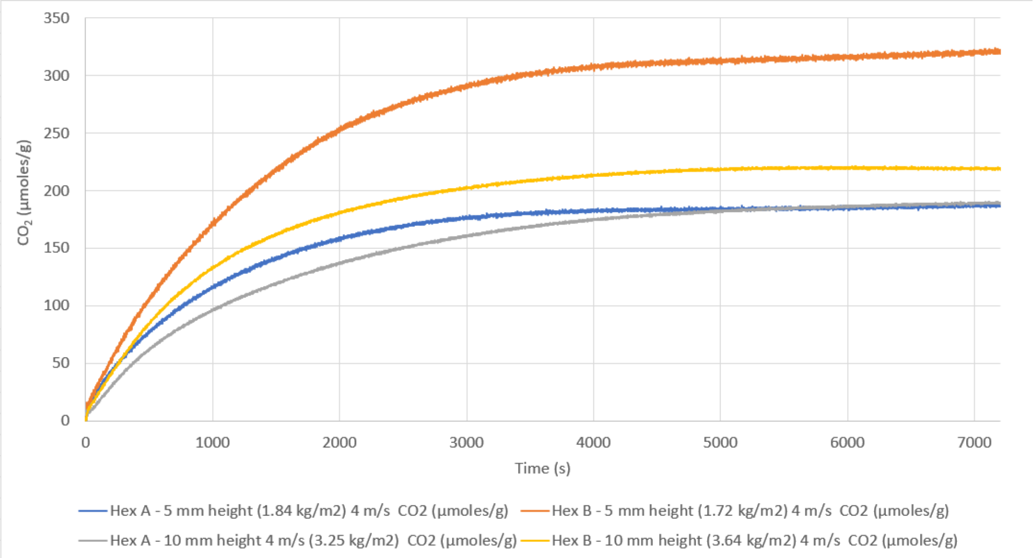


Figure 72 – Evaluation of Hex A and Hex B at 10 and 5 mm Height µmoles of CO_2 Per Gram of Sorbent at 4 m/s, 0 to 7200 s

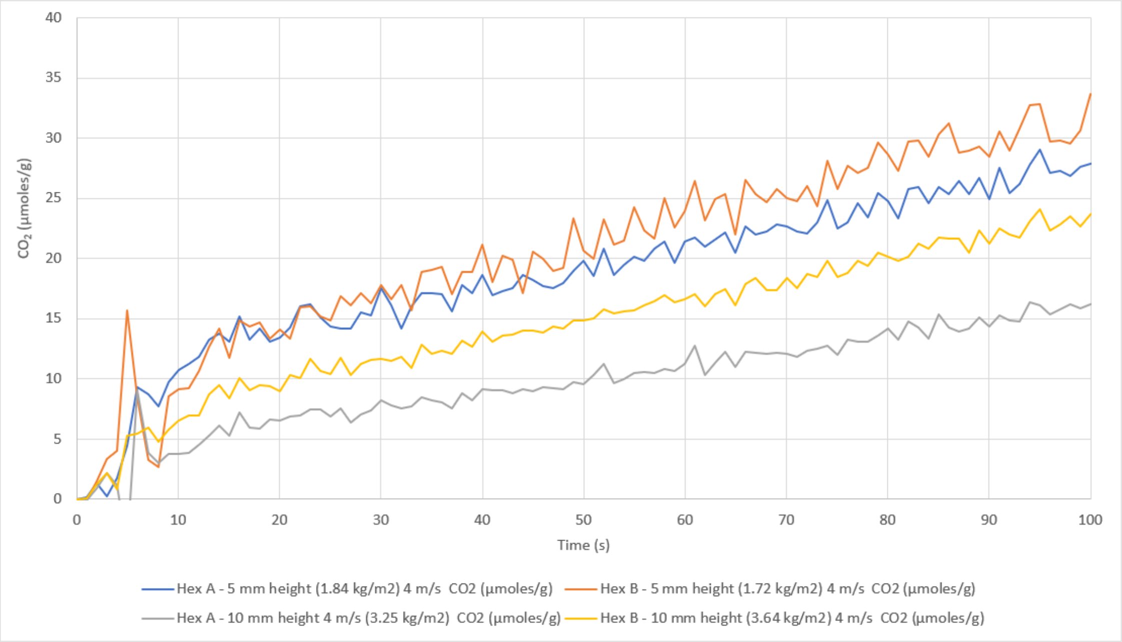


Figure 73 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in µmoles of CO_2 Per Gram of Sorbent at 4 m/s, 0 to 100 s Timescale

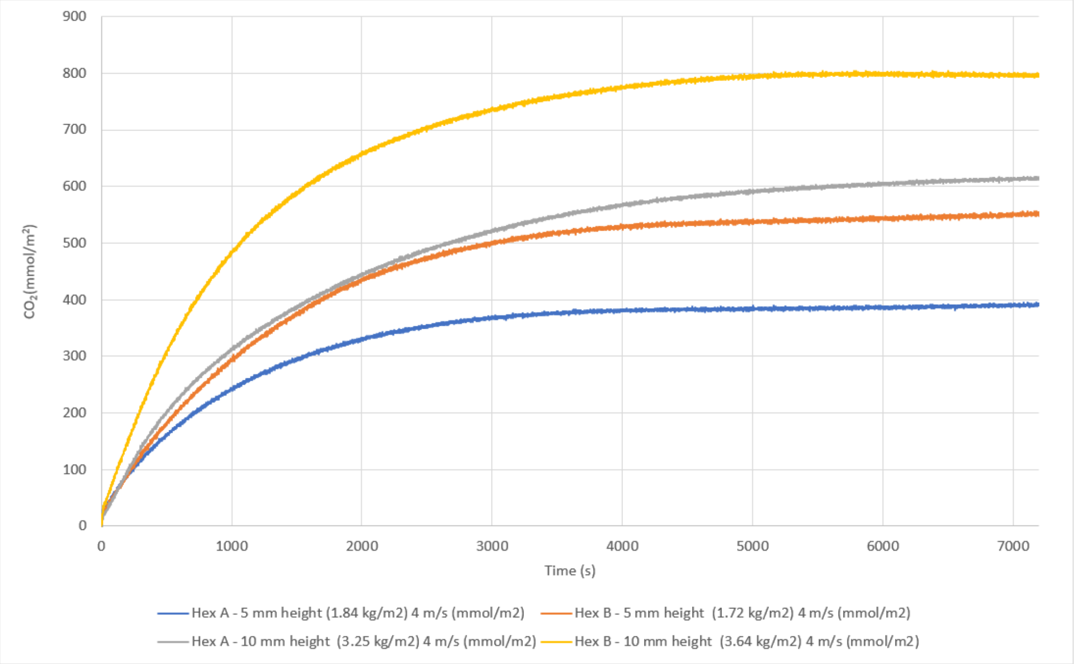


Figure 74 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in mmol of CO_2 Per Square Meter at 4 m/s, 0 to 7200 s

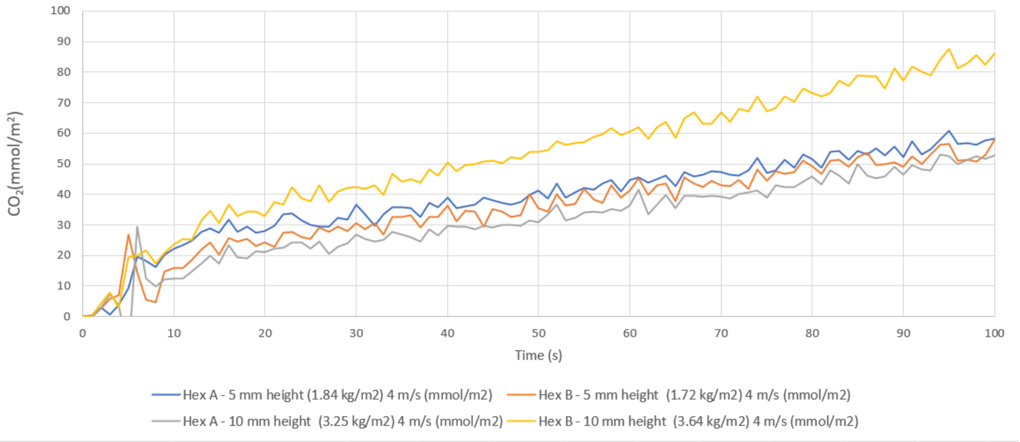


Figure 75 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in mmol of CO_2 Per Square Meter at 4 m/s, 0 to 100 s

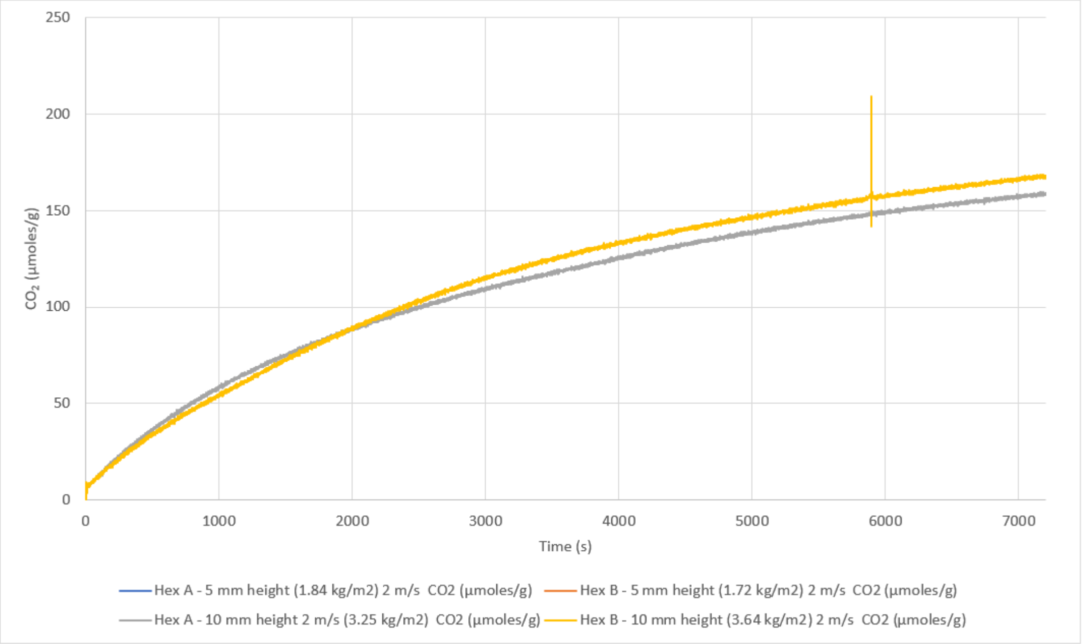


Figure 76 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in µmoles of CO_2 Per Gram of Sorbent at 2 m/s

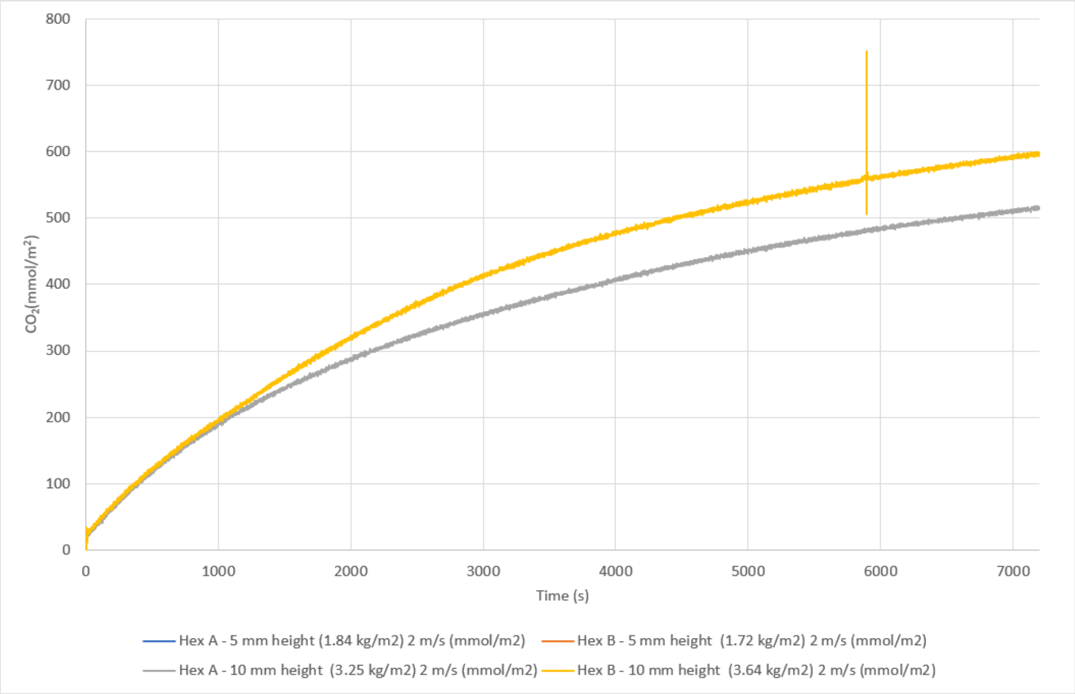


Figure 77 – Evaluation of Hex A and Hex B at 10 and 5 mm Height in mmol of CO_2 Per Square Meter at 2 m/s

6. MODELING: SIMULATION ON PROTOTYPE PROPORTIONAL TO SORBENT WEIGHT AND WIND SPEED

This chapter present a model exercise for a hypothetical large-scale prototype utilizing the data acquired on the wind velocities and form factor study. A second model exercise utilizes the data acquired on the systems TSMSD and CSDS for its remarkable kinetics. This second model idealize an engineering design can hypothetically keep that high kinetics.

Assuming a hypothetical full-scale prototype with a total surface area of 285 m^2, Hex A and Hex B Based on a proportional surface area calculation and packing density of the sorbent bead the maximum sorbent weight for Hex A is 925 kg and for Hex B 1,036 kg. These differences are attributed to the differences in electrostatic repulsion when more or less beads (more repulsion with more beads and less repulsion when less beads are packed per hexagon cell) are packed, thus the weight, surface area and electrostatic repulsion differences favors more total packed beads for Hex B. The model assumed a system operating on 20 minutes of absorption, 20 minutes of desorption, with a total cycle of 40 minutes operation time, operating 36 cycles per day. Utilizing the absorption results obtained on the wind tunnel for 20 minutes adsorption time on under different wind velocities the extrapolation model results is presented on figure 76. For both Hex A and Hex B, the absorption kinetics is influenced by the wind velocities, as higher are the wind velocities, faster is the absorption kinetics. However is expected to have an optimal wind velocity, it can be assumed that an extremely high wind velocity can be detrimental to the process and has lower CO_2 capture, although this hypothesis has to be evaluated. The total CO_2 captured for Hex A is 205, 138 and 85 kg CO_2/day respectively to 6, 4 and 2 m/s wind velocities. Hex B obtained 301, 214 and 91 kg/day respectively to 6, 4 and 2 m/s. Thus Hex B is 46, 37 and 7 % higher than Hex A respectively to 6, 4 and 2 m/s wind velocities. This trend indicates that the localized turbulence for Hex B is more prominent on higher wind velocities and less important on lower wind velocities.

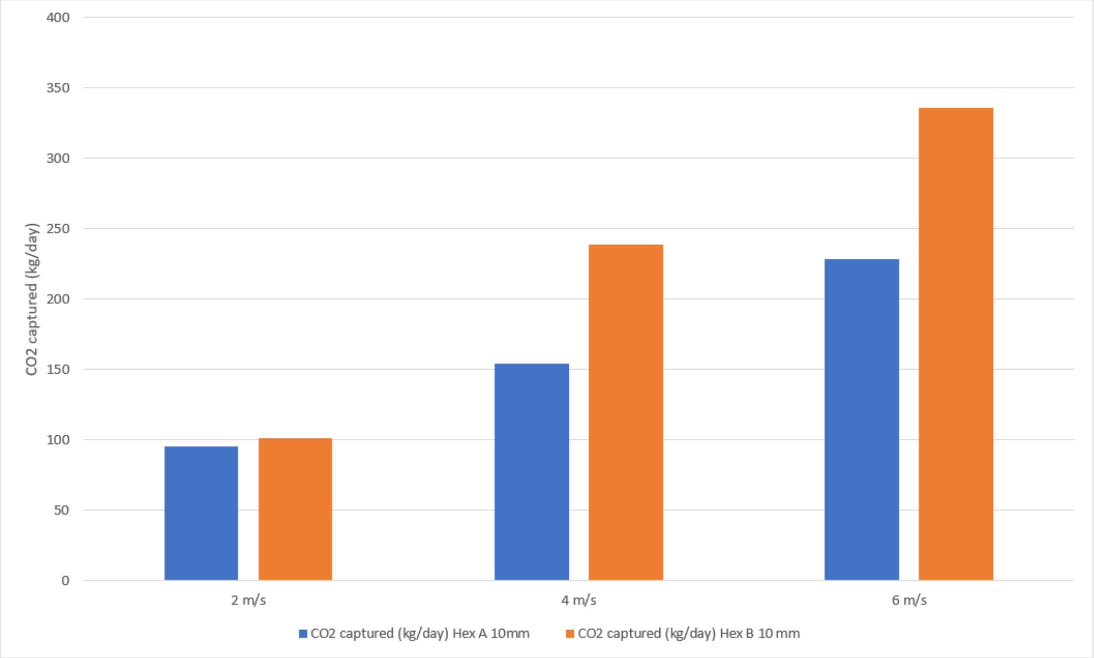


Figure 78 – Simulation Exercise Extrapolating the Wind Tunnel Data for a Hypothetical Pilot Plant.

A second model simulation has been developed utilize results from Hex B under different wind velocities, this time varying the absorption cycle times and assuming a hypothetical prototype with 1,036 kg of sorbent mass. This model has the main purpose is to demonstrate the maximum CO_2 capture in order to minimize capital cost and total cost.

The model maintained the desorption cycle fixed with 20 minutes and varied the absorption cycle times in 5, 10, 15, 20, 30, 60 and 120 minutes, completing multiple total cycle times (absorption + desorption) in the course of a day (figure 77). These resulted in 57, 48, 41, 36, 28, 18 and 10 total absorption + desorption cycles in a day. This simulation demonstrated the optimal absorption cycle time in which has higher CO_2 absorption per day is 20 minutes for all three wind velocities: 2, 4 and 6 m/s. The difference on absorption kinetics is more prominent on higher wind velocities at 6 m/s and less prominent as the wind velocity decreases. Wind velocity is variable in most places in the world, so this simulation become important in order to evaluate what is the ideal absorption time at given wind velocity considering the energy cost on the number of cycles in a day. For example, at lower wind speeds, would be more feasible to run longer absorption cycles on >60 minutes per day as the total absorption in the day is not significantly different at 2 m/s. In the other hand, in a windy day ~ 6 m/s, the optimum cycle time of 20 cycles per day would be ideal as it can capture 2.4-fold more CO_2 when compared to 2 m/s.

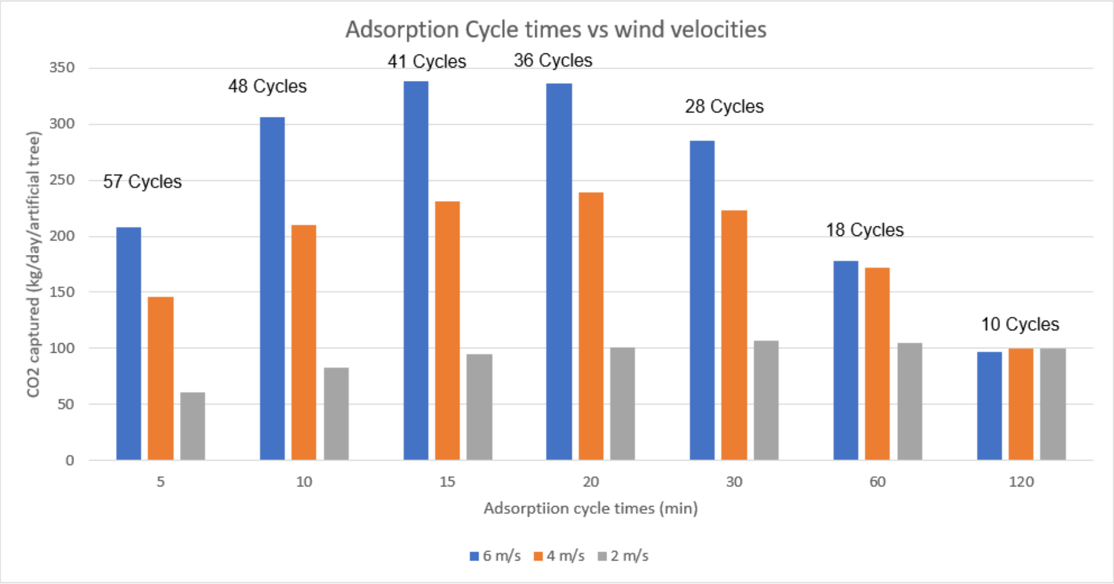


Figure 79 – Extrapolation Model for CO_2 Capture Using Polyamine Sorbent Maintaining 20 Minutes Desorption Time and Varying Absorption Time.

An ideal engineering design for a pilot plant could possibly exclude the wind velocity limitation on the same TSB 03 sorbent. It has been proven on this work the experimentation on the mg and g scale using the TSMSD system for absorption in which the sorbent absorbed all the CO_2 in less than 500 s and the desorption on the CSDS system in less than 150 s. (see subchapters, 3.1.4, 3.1.5 and 3.2.3). This fast absorption rate had a relatively small sample mass to a relatively high velocity and relatively high mass of air passing through the small sample size in which has its porous widely available to absorb CO_2. The CSDS system has a 0.5 l/min air flow and a temperature differential between the 2 first buckets at ~ 100 $^{\circ}$C and the bucket of ice and water ~ 0 $^{\circ}$C. The steam then pass throw the sample very efficiently, desorbing CO_2 rapidly. Evaluating the results of the fast absorption on the TSMSD it is important to note the fastest absorption kinetics is under 120 s before the curve slow down due to the sample get closer to its maximum capacity. During this time the sample absorbed 150 µmoles CO_2/g. Assuming then the CSDS system have only 150 µmoles CO_2/g to desorb, the system desorbed this amount in 57 s. Figure 78 present both absorption and desorption of CO_2 under this timescale conditions.

It is possible then to assume the sorbent TSB 03 can have an ideal engineering design pilot plant with a specific form factor in which the sorbent has it`s porous available to the amount of air necessary to have the same very fast absorption obtained on the TSMSD result. A scaled up system that can also desorb as fast as the CSDS system proportionally to the mass of sorbent utilized. This ideal design taking advantage of the possible very fast kinetics of the sorbent TSB 03 can lead to many very fast cycles of absorption and desorption in which will result on more overall CO_2 absorbed on a daily basis.

Creating a similar model exercise, assuming this hypothetical pilot plant, the total cycle time accounting for 150 s absorption and 57 s desorption would be 176 s. This will result in 491 total cycles per day. Assuming it is utilized 1,036 kg of sorbent, same as Hex B from previous model exercise, it is possible to absorb 3,357 kg CO_2 per day with the same sorbent. Figure 79 shows a visual comparison of the CO_2 absorbed per day between the ideal design not limited by wind velocity and the results obtained on a design dependent on the wind velocity. The ideal design obtain a 10-fold increase on capacity for the fast wind velocity at 6 m/s. This results shows the sorbent has enough capacity to reach economic feasibility and there are possible solutions to optimize the design in order to obtain a much faster absorption and desorption rate.

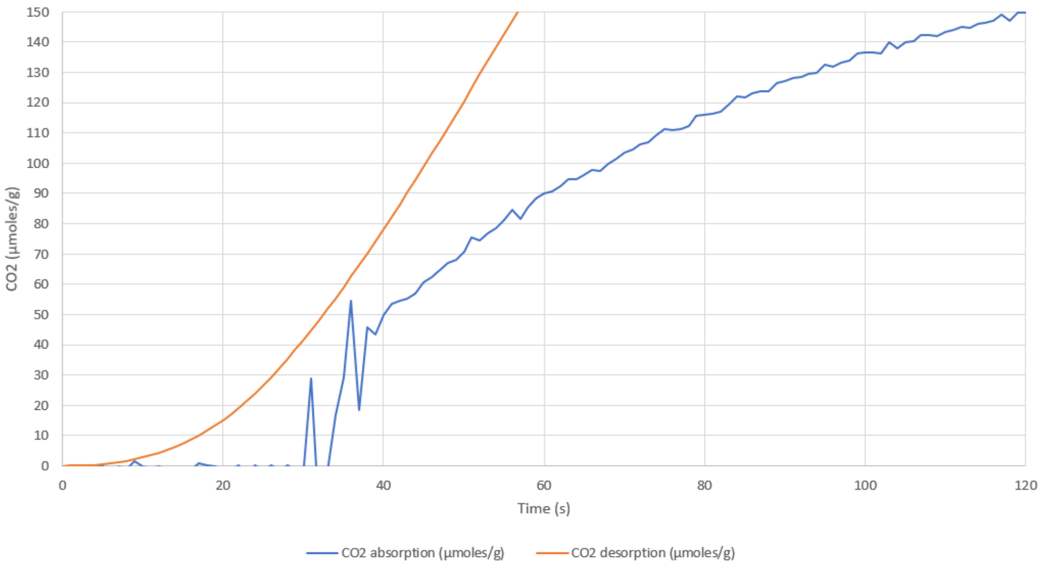


Figure 80 – TSB 03 Very Fast Absorption and Desorption Rates on TSMSD and CSDS Systems

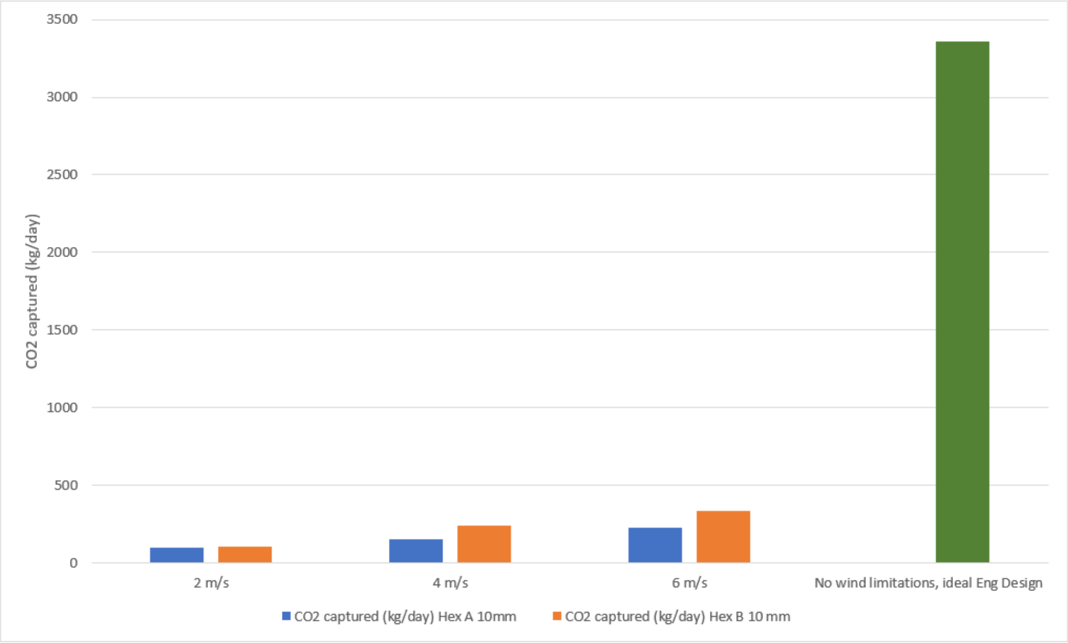


Figure 81 – Model Simulation Comparison of Wind Velocities Results and an Ideal Engineering Design with No Wind and Air Limitations for TSB 03 Sorbent Absorption and Desorption.

7. ONE TIME CO_2 CAPTURE SYSTEM (OCS)

One time CO_2 capture system concept has been presented in subchapter 2.4. Sorbents of one-time capture systems at ambient temperature are expected to have a very slow kinetics when compared to thermal and moisture swing sorbents. This is not a problem as the goal of this type of sorbent is to capture CO_2 continuously in a course of decades. The challenge is to evaluate the kinetics on a short period of time for a sorbent that need years and decades to be evaluated. In addition the slow kinetics of absorbing CO_2 imposes a challenge on a systems sensibility as a small drop of CO_2 concentration in a closed system can be due to the small error variations of a gas analyzer or small leak rates. In order to have an efficient system we developed a system apparatus in a close loop with a relatively small volume of air to a relatively large sample size. Thus, the sample uptake rates of CO_2 can be larger than the small error variations of the gas analyzer. The system has been developed to be very leak tight, and very small leaks can be corrected mathematically as needed. Effective data from one time capture sorbents can be evaluated in a course of 1 to 2 days with this system. The CO_2 absorption rate can be analyzed and mathematical extrapolation indicates how much CO_2 a particular sample can absorb in a course of decades.

The main components of the experimental system are: 1) Tubular sample chamber to fit ~ 100 g sample size, with 4 filter cartridges, 2 on the bottom and 2 above; 2) dew point generator to control the humidity; 4) infrared gas analyzer (IRGA) for CO_2 and H_2O vapor measurements; 5) laptop with the licor and lab view software 6) signal controller; 7) tubes to connect the air flow through the system; 8) 2 valves that allow the system to be open or closed (figure 80 and 81).

The methodology applied is to flow ambient air in an up-flow setting operating at high humidity content of 25 ppt of H_2O. The high humidity content can drive part of the calcium and magnesium oxide samples to be converted to calcium and magnesium hydroxides, which can enhance capacity and kinetics of the samples. The up-flow air velocity increases the air content retention time on the relatively high weight sample per total experimental volume, forcing more sample air content in which can result in higher CO_2 absorption. The system is mostly operating in a closed setting with a total of 380 mL of air volume looping around the system. The valves can be open in order to replenish any CO_2 consumed by the sample in order to re-establish a new baseline of continuous CO_2 adsorption.

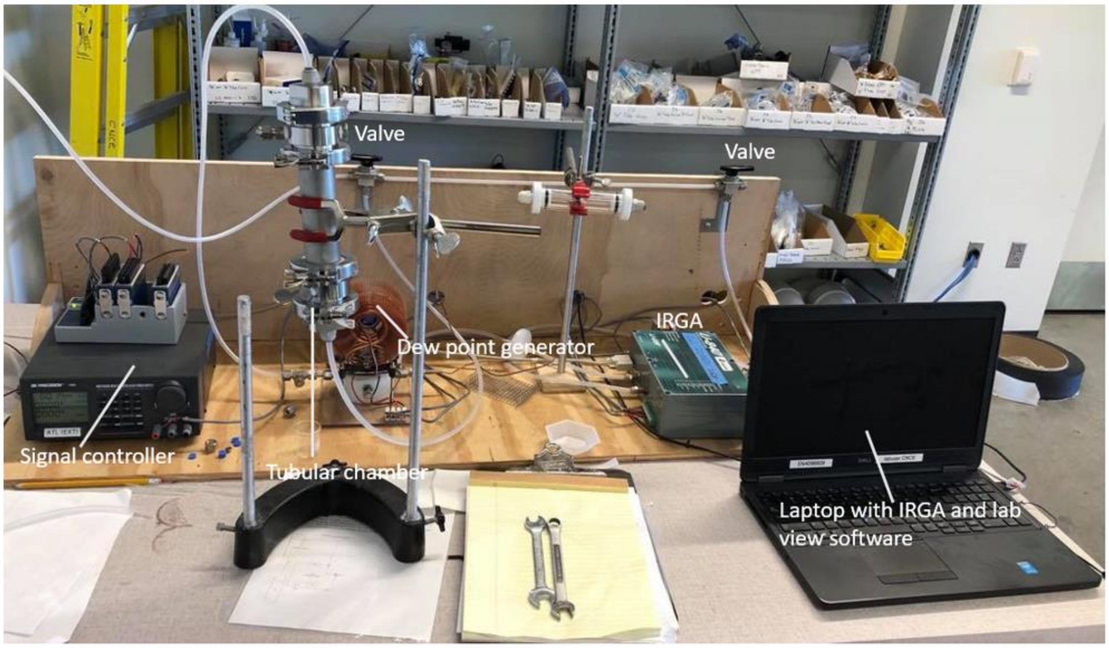


Figure 82 - One Time CO_2 Capture Sorbent Screening System

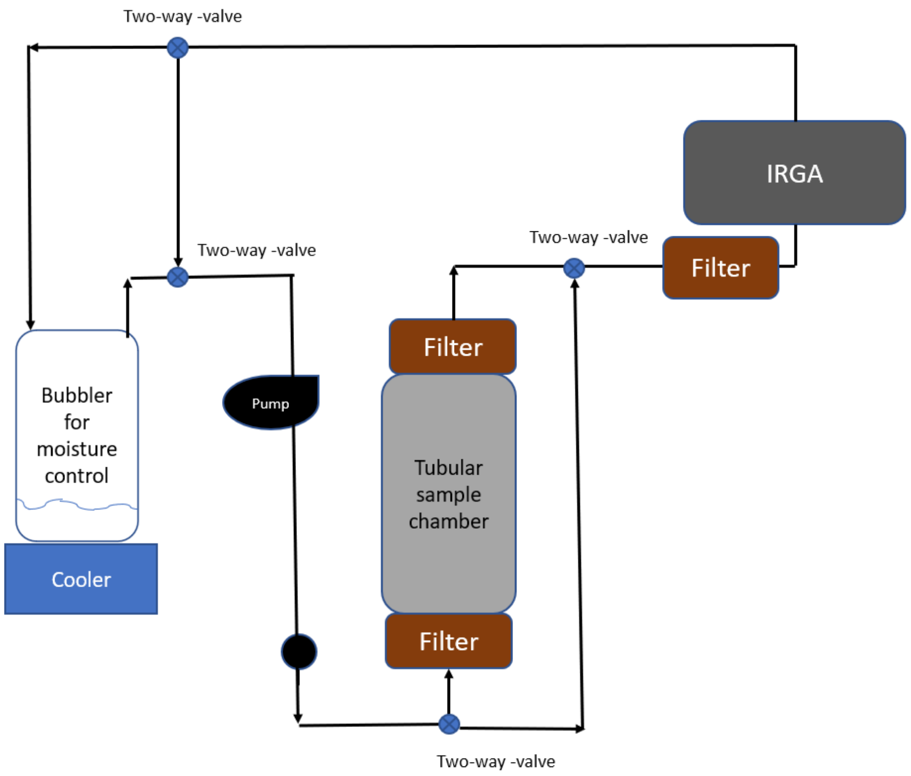


Figure 83 - One Time CO_2 Capture Sorbent Screening System Diagram

7.1 OCS System Results Compilation

The CO_2 started at 500 ppm and the sample adsorbed CO_2 rapidly from 500 ppm to a remaining of 41 ppm in the closed system (figure 82). The maximum adsorption was reached in about 35,000 s time mark or 9.7 hours. The rate of adsorption decreased significantly when the CO_2 reaches 200 ppm inside of the system. This rate of change happens more likely because as the CO_2 partial pressure from the ambient is much greater than the CO_2 partial pressure inside of the system creating a higher leaking rate of CO_2 entering the system and matching the rate of adsorption of the closed system. A second possibility (unlikely) is that the sample has achieved maximum capacity after 9.7 hours. Once the CO_2 reached the steady state of 41 ppm inside of the system, it maintains at this level what shows CO_2 bided strongly to the material and is not been released back to the system accomplishing the concept of one time capture. It is likely if injected CO_2 into the system the adsorption rate will be constant in the range of the time 0 to 10,000 seconds (2.7 hours) where the rate is constant and is not interfered by the greater difference of the CO_2 partial pressure outside and inside of the system.

Figure 83 present the compilation of the data presenting the CO_2 adsorption in nmoles of CO_2 per gram of sample through the experiment`s time. The result present an initial CO2 desorption of 25 nmoles of CO_2/g in the first seconds followed by the CO_2 adsorption maximum of 70 nmoles of CO_2 /g when the system reaches a steady state due to the differences in CO_2 partial pressures and CO_2 leaking rate into the system as previously explained. Considering that in a closed system the CO_2 adsorption rate better represented in the linear portion of this curve where there is minimum interferences of the CO_2 partial pressure differentials. The linear portion of the data selected was on the delta of 4,316 s to 10,038 s ranging from 14 to 43 nmoles of CO_2 /g (figure 84). This selected data curve is presented on figure 84. Accounting the rate of this curve and assuming it constant through time, this material has an adsorption rate of 0.005 nmol CO_2/g/s, or 158,800 nmol CO_2/g/year, or better represented as 70 kg CO_2/tonne/decade.

Based on the chemical composition of the material the CO_2 capture is likely be driven mostly by calcium oxides and magnesium oxides based on the following chemical reactions:

$CaO + CO_2$ -> $CaCO_3$ + 179 kJ/mole

$MgO + CO_2$ -> $MgCO_3$ + 118 kJ/mole

As this sample was submitted to 900 °F calcination process might be occurring converting calcium and magnesium carbonates into calcium and magnesium oxides increasing capacity and kinetics on this samples based on the following equations:

$CaCO_{3\,(s)}$ -> $CaO_{(s)} + CO_{2\,(g)}$

$MgCO_3$ -> $MgO + CO_2$

The experiment has been performed under high humidity at 25 ppt H_2O. The humidity can have favor the chemical reaction of magnesium and calcium oxides to calcium and magnesium hydroxides. The following reactions represent the conversion of calcium oxides to calcium hydroxide:

$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)}$

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

And for magnesium oxides:

$MgO_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)_{2(s)}$

$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$

Calcium and magnesium hydroxides have a higher kinetics when compared to its oxide forms. Thus as the samples are calcium and magnesium are converted to its hydroxide forms due to the high humidity flow the performance of the sample`s kinetics tends to be enhanced.

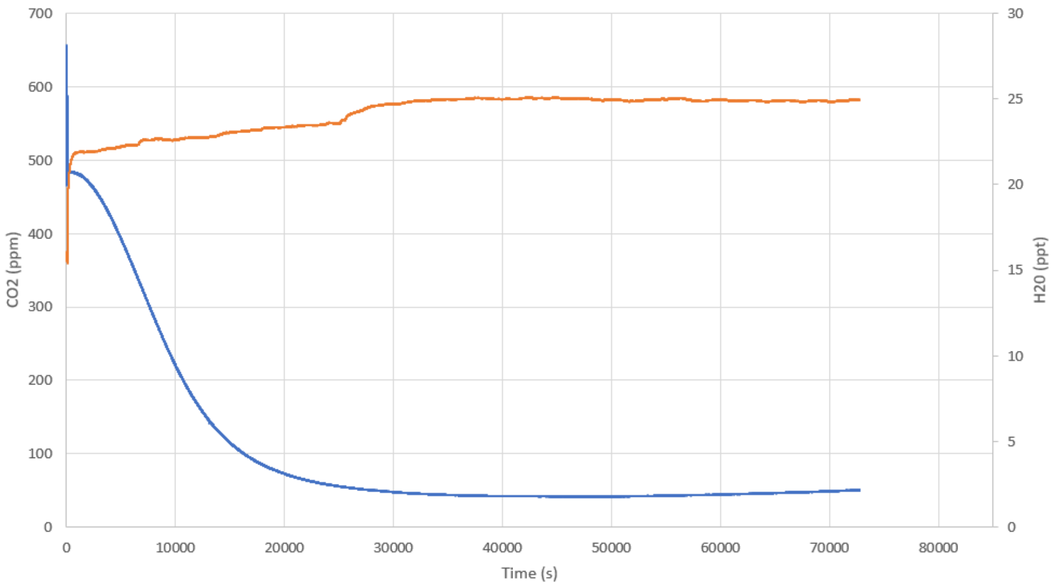


Figure 84 – One Time Capture STSB01 Sample Raw Data.

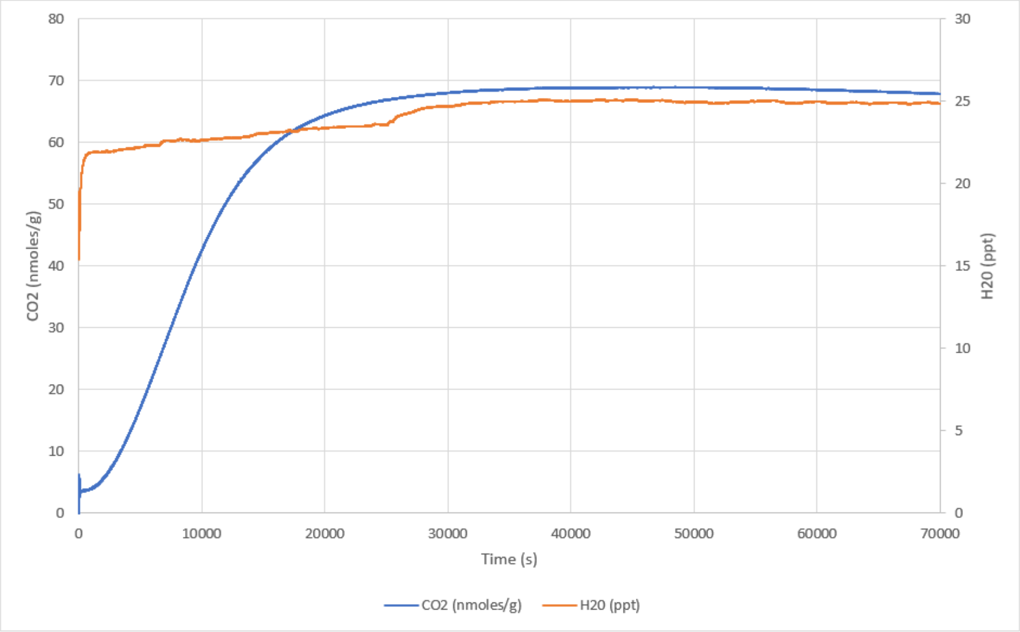


Figure 85 – One Time Capture STSB01 Sample Calculated Data

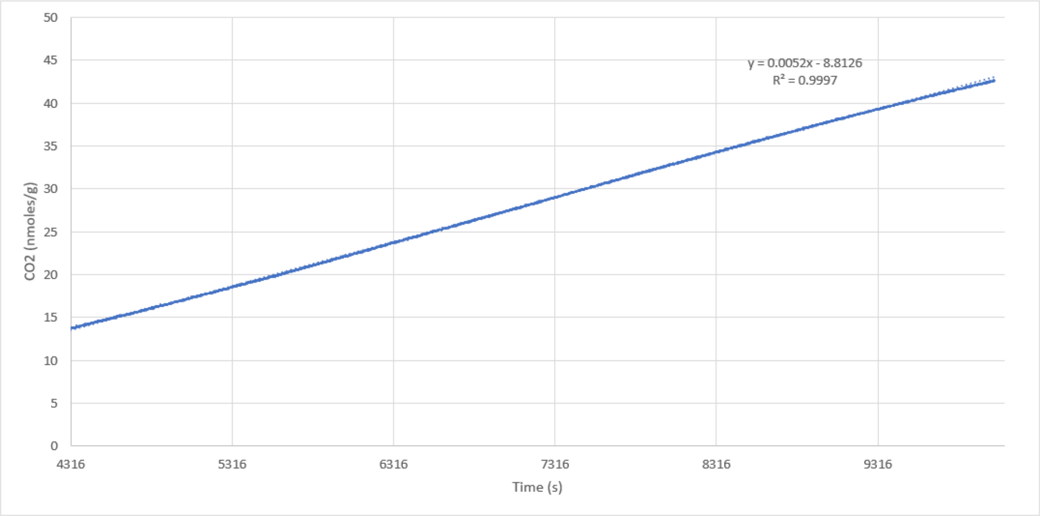


Figure 86 - One Time Capture STSB01 Sample STSB01 Linear Rate

7.2 OCS System Sorbent Screening and Data Analysis

One time capture sorbents as explained previously are slow by its nature and it differs from most of the other CO_2 capture methodologies for not having a swing cycle of sorption and desorption, rather only absorption to store CO_2. The data then is better represented on a decade range as explained on previously. By using the OCS system we were able to screen several samples candidates on the period of 1-2 days experiments and extrapolated the data for a decade range. The samples utilized had a total of 100 g as per methodology developed. Extrapolating the data we present it on figure 85 as kg CO_2/tone of sorbent per decade. Sorbents STB02 and STB01 presented the highest sorption capacity with 88 kg CO_2/tone/decade and 70 kg CO_2/tone/decade respectively. This represent a total of 8.8 and 7 % of the materials mass with room for CO_2 capture. Sorbent candidate STB07 also presented a significant performance of 30 kg CO_2/tone/decade and the remaining obtained low or non CO_2 absorption.

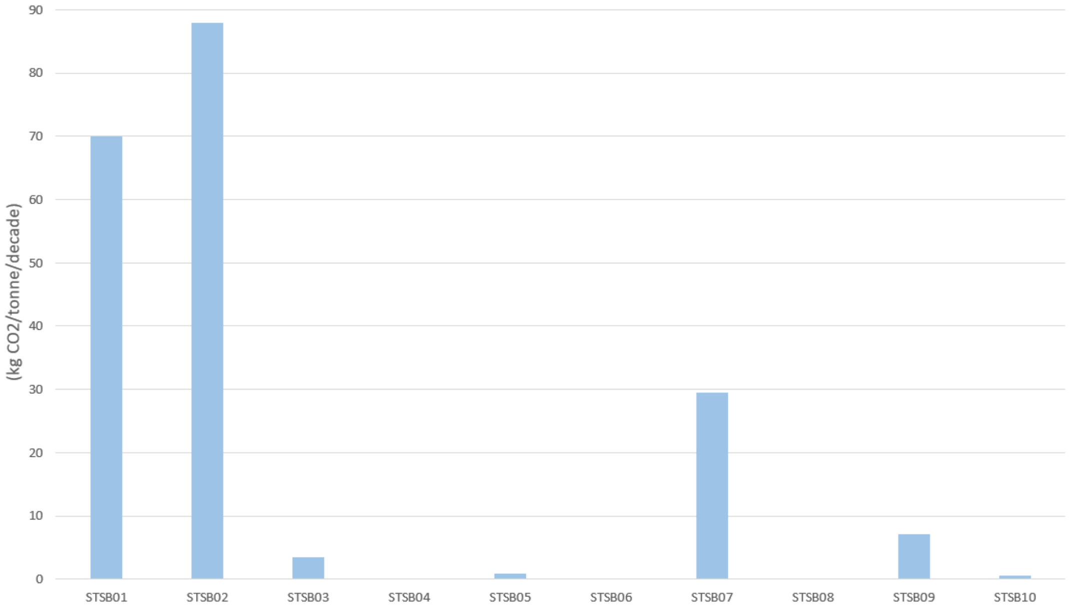


Figure 87 - One Time Capture Sample Screening Performance, Extrapolated Data for a per Decade Capture.

8. CONCLUSION

The work presented in this dissertation successfully introduced methodologies for characterizing DAC sorbents and demonstrated the results of applying these methodologies that can be used to characterize and screen temperature swing, moisture swing and one-time capture sorbents and the scalability of temperature and moisture swing sorbents. Temperature swing and moisture swing specific sorbents were characterized on key characteristics that represents a good sorbent: loading capacity, kinetics of sorption and desorption, effects of different humidity levels; sorbent scalability performance at mg, g and kg scales. The sorbent TSB 03, in particular, was able to demonstrate such characteristics with no significant loss in performance as one moved from scale to scale. The sorbent characterization was scaled from the mg to kg scale. This represents a one million-fold increase in size. This sorbent very likely can be utilized on an industrial scale as to reach the tonne scale is just 1 thousand-fold scale away.

A sorbent’s performance is highly influenced by its form factor. The same sorbent in a powder form has higher surface area and thus faster kinetics and effective capacity in both temperature and moisture swings. Specific geometric structures such as honeycombs can hold a sorbent in place for practical engineering scalability and create better air contact with the sorbent, thereby enhancing kinetics. This work also demonstrated that wind velocities have a large effect on a sorbent’s absorption kinetics of a temperature swing amine-based sorbent, especially considering a passive direct air capture scenario and the geometries considered. The higher the wind velocity, the faster is the absorption kinetics, although it has not been tested above wind velocities > 6m/s. Very high wind velocities might negatively affect the sorption kinetics, but there is as of yet no data to decide. A model exercise shows the importance of optimizing absorption cycle times to maximize CO_2 capture based on the current wind velocity condition. Such optimization will benefit the economics of a hypothetical DAC large prototype/plant. The optimal sorption cycle time for the sorbent tested is 20 minutes if the weather condition is 4-6 m/s wind velocity, cycling 36 times a day. If the wind velocity is 2 m/s, choosing 60 minutes-120 minutes absorption cycle times can bring economic benefits as there is minor difference on CO_2 total absorption in 10-18 cycles a day (in all the scenarios of this simulation the desorption was maintained fixed at 20 minutes). A second model simulation based on the very fast kinetics rates on the small-scale experiments for absorption and desorption of CO_2 shows a possible 10-fold increase on total CO_2 captured optimizing the same conditions on scale with a much faster cycle time. This pathway can be optimized on an engineering design that facilitates air-contact with the sorbent.

One time capture sorbent screening methodology was effective in selecting good sorbents showing a sorbent with 8.8% of its mass absorbing CO_2 in a course of a decade, with 88 kg CO_2/tone of material captured based on the extrapolation data calculations.

Overall, this dissertation presents a novel methodology to characterize a variety of types of sorbents, opening door for a great number of new dissertations for future work which can be built on the chapters presented.

9. FUTURE WORK

This dissertation has laid the groundwork for a wide-ranging set of methodologies. Much work remains to be done to flesh out the many new concepts that have been discussed in this dissertation. One important issue is the development of techniques that can accelerate data collection to study many different sorbents with many different form factors at the same time. This raises the question what is the shortest time possible to characterize a sorbent? In order to screen many sorbents in the shortest period of time, the fast-screening systems MSCS, TSMSD, CSOFS and CSDS need to be automated in order to load consecutive number of samples and need to be multiplied, many of these systems operating simultaneously. The data acquisition and part of its analysis can also be improved with specific algorithms, which can automatically calculate sorbents capacity and kinetics. The data acquired on specific sorbents and its form factors can become an important data library that can be used for more complex algorithms/Artificial Intelligence to iterate in order to create new and higher performance sorbents. The iteration between complex algorithms and sorbent characterization can be an important tool to the continuous evolution of sorbents.

Air contact with the sorbent TSB 03 and similar sorbents has a significant effect on absorption kinetics. Experiment on TSMSD and CSDS demonstrated a very fast rate. In the TSMSD system the high kinetics is likely related to the high air mass flow rate relating to the low sorbent mass for the particular system. The CSDS high desorption kinetics is due to the rate and quantity of steam passing through the sample enhancing heat transfer.

The data acquired in these particular experiments provides an opportunity and guidance for more extensive detailed work to be developed to scale this high performance on a specific engineering design.

More complex models can be developed to optimize sorbent cycle times, optimize sorbents for weather conditions, including wind velocity, temperature, humidity. These models which are fed uniform data from a unified characterization methodology can then be used to improve DAC economic performance and provide the basis for better DAC techno-economic assessments.

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