



**Politecnico
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CO₂ Capture and Sequestration Using Nanomaterials

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Abstract

Intense human activity over the last decades resulted in growing environmental concerns, including alarming carbon dioxide (CO₂) emission levels. CO₂ is a major anthropogenic greenhouse gas which principally results from excessive combustion of fossil fuels. To reach the targets imposed by governments worldwide in the Paris Agreement (2015), but especially to fight climate change, we propose to focus on different aspects of CO₂ capture and management, from the perspectives of materials science and computational chemistry. The main purpose of this research is to identify materials and processes (physisorption/chemisorption mechanisms) to accomplish sustainable CO₂ capture and sequestration. This means that we are not going to use energy for our processes, relying only on the materials chemistry. The first idea is to employ our prototype for indoor air quality. Hence, a vessel has been designed in order to accurately reproduce a closed environment. Usually, in closed environments, CO₂ has the ability to negatively influence human health and productivity. Thus, our plan is to reduce the concentration of CO₂ in closed environments, to prevent decrease in people cognitive functions. Computational techniques are used to determine which material has the best affinity for CO₂. Then, the results effectiveness is evaluated by means of experimental activities. The results indicate that the proposed sorbents can capture several thousands ppm of CO₂ in 24 hours under stationary diffusion conditions.

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Abbreviations

2MPZ	2-methylpiperazine
ADF	Annular dark field
ASC	Automatic self-calibration
BECCS	Bioenergy with carbon capture and storage
CB	Carbon black
CC	Carbon capture
CC	Climate change
CCFCV	Carbon capture fuel cell vehicle
CCUS	Carbon capture, utilization and storage
CFCs	Chlorofluorocarbons
CH₄	Methane
CNTs	Carbon nanotubes
CO₂	Carbon dioxide
DAC	Direct air capture
DEA	Diethanolamine
DFT	Density Functional Theory
EOR	Enhanced oil recovery
EVOH	Ethylene Vinyl Alcohol
GHG	Greenhouse gas
GO	Graphene oxide
GWP	Global warming potential
H₂SO₄	Sulfuric acid
H₃PO₄	Phosphoric acid
IEA	International Energy Agency

IPCC	The Intergovernmental Panel on Climate Change
K₂CO₃	Potassium carbonate
KMnO₄	Potassium permanganate
KOH	Potassium hydroxide
LCA	Life cycle assessment
LRN	Long rod nanoparticles
MEA	Monoethanolamine
MO	Molecular dynamic
MWCNT	Multiple walls carbon nanotubes
N₂O	Nitrous oxide
NOAA	National Oceanic and Atmospheric Administration
O₃	Ozone
OH	Hydroxy group
PC	Polycarbonate
ppm	Part per million
PZ	Piperazine
R&D	Research and development
rGO	Reduced graphene oxide
SRN	Short rod nanoparticles
STEM	Scanning transmission electron microscopy
SWCNT	Single wall carbon nanotubes
TEAM	Transmission electron aberration-corrected microscope
TEM	Transmission electron microscopy
TIT	Turbine inlet temperature
TRL	Technology readiness level
UNFCCC	United Nations Framework Convention on Climate Change
UV	Ultraviolet
VOC	Volatile organic compound

List of symbols

E	Young modulus
G	Gibbs free energy
ΔG	Gibbs free energy variation
H	Enthalpy
ΔH	Enthalpy variation
p_e	External pressure
p_i	Internal pressure
r_e	External radius
r_i	Internal radius
$R_{p0.2}$	Yield strength
s	Thickness
S	Entropy
ΔS	Entropy variation
SF	Safety factor
T	Temperature
T^*	Inversion temperature
UTS	Ultimate tensile strength
σ_{id}	Ideal stress
σ_r	Radial stress
σ_c	Circumferential stress
σ_z	Axial stress
σ_1	Stress along principal direction 1
σ_2	Stress along principal direction 2
σ_3	Stress along principal direction 3

1. INTRODUCTION

Natural phenomena combined with intense human activities have resulted in a sudden increase in carbon dioxide emissions. Data measurements show that CO₂ concentration in the atmosphere rose from 390 ppm (in 2012) up to 419 ppm (in 2022). Unfortunately, carbon dioxide is the most dangerous gas emitted by humans because it survives the longest in the atmosphere, causing a chain reaction of adverse effects on life.

Possible solutions to this huge problem might be multiple: like the conversion of green sources as solar energy, wind energy, mechanical vibration, etc. into electricity, or the implementation of carbon capture technologies to reduce the atmospheric concentration of CO₂ and also its emission.

This research project focuses on different aspects of CO₂ capture and management, from a material science perspective. The aim of this research is to identify materials, processes, and technologies to accomplish sustainable CO₂ capture and sequestration. With the word ‘sustainable’, it is meant a way to capture carbon dioxide using no energy but relying only on the materials chemistry. It also needs to be mentioned that this kind of technology is a key factor in order to reach carbon neutrality in the future. However, as for all new technologies, there are numerous obstacles to making CO₂ capture a reality.

The research activity has been carried out in the Bozlar Nanoscience Lab, at The University of Texas at Arlington, which has a long partnership with Politecnico di Torino. Furthermore, this project is in close collaboration with Princeton University. The primary goal of Bozlar Nanoscience Lab is addressing urgent societal needs, especially in the area of energy and the environment, by combining fundamental and applied research.

2. CLIMATE CHANGE

It would be hypocritical not to admit the unequivocal evidence that Earth is changing. A mutation toward the collapse of everything, and this is happening at an unprecedented rate. The human race is the criminal and it is ruining its home. The effects of human-caused global warming are occurring right now, they are irreversible if the timescale of people alive today is considered, and probably will get worse in the decades to come. Sudden and efficient solutions must be taken before reaching the point of no return.

At this purpose, sustainable energy and carbon capture technologies are playing an increasingly important role nowadays, especially in light of the rising environmental issues, as just mentioned above. Moreover, the fight against these environmental problems has become an increasingly active part of energy policymaking, even if the outcomes are not so encouraging.

Before digging into the core of the topic, highlighting scientific evidence and the current effects caused by the phenomenon, it might be interesting to start introducing Climate Change with some simple definitions, given by some of the most important authorities that keep track and deal with this crucial topic:

“Climate change refers to long-term shifts in temperatures and weather patterns. These shifts may be natural, such as through variations in the solar cycle. But since the 1800s, human activities have been the main driver of climate change.”

United Nations

“Climate change refers to a change in the state of the climate that can be identified by changes in the mean and/or the variability of its properties and that persists for an extended period, typically decades or longer. Climate change may be due to natural internal processes or external forcings such as modulations of the solar cycles, volcanic eruptions and persistent anthropogenic changes in the composition of the atmosphere or in land use.”

IPCC

“A change of climate which is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and which is in addition to natural climate variability observed over comparable time periods.”

UNFCCC

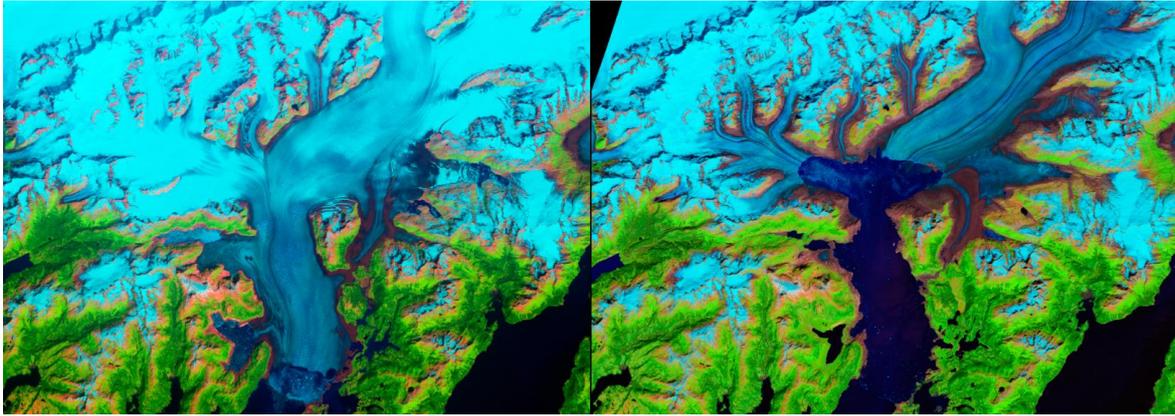


Figure 1 – Columbia Glacier melt, Alaska. Comparison shots of the same place at years of distance showing the effects due to Climate Change. Before (left) -July 28, 1986- and after (right) -July 2, 2014-.

Source: NASA (n.d.)[1]

Figure 1 and **Figure 2** are two of the several cases that could be shown in order to highlight the huge changes that our Earth is silently undergoing.

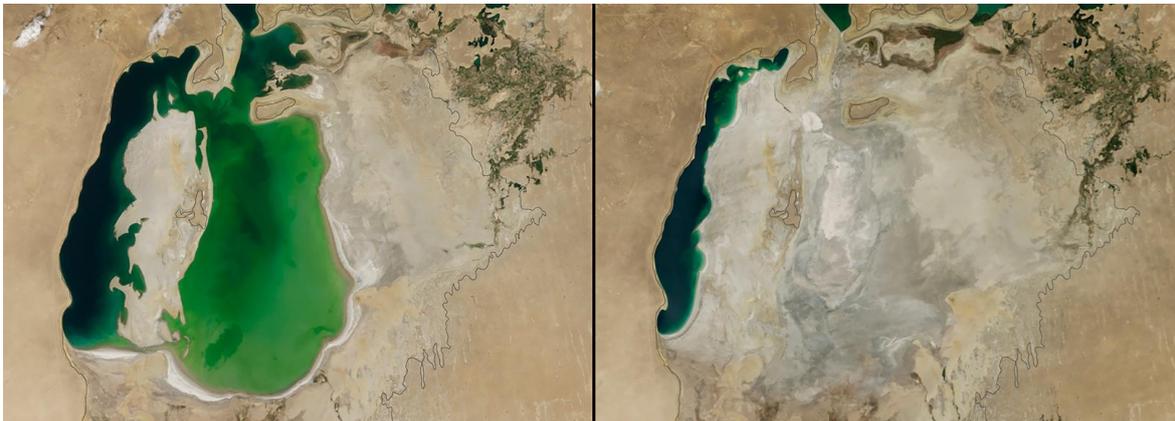


Figure 2 – Shrinking Aral Sea, central Asia. Comparison shots of the same place at years of distance showing the effects due to Climate Change. Before (left) -August 25, 2000- and after (right) -August 19, 2014-.

Source: NASA (n.d.)[1]

2.1 THE CAUSES OF CLIMATE CHANGE

The main responsible of Earth warming up is the Greenhouse Effect. Normally, this phenomenon is essential to life on our planet. However, anthropogenic emissions in the atmosphere are blocking and slowing heat loss to space, and a great part of this heat comes back to the surface. Carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄), chlorofluorocarbons (CFCs), and water vapor are the top five greenhouse gases.

In order to measure the contribution of each GHG, the ‘Global Warming Potential (GWP)’ concept should be introduced. The GWP is defined as the integration in a time period of the level of atmospheric damage that is produced by the emission of 1kg of a defined gas. The latter is expressed in relative terms with respect to CO₂ contribution. For this reason, the GWP of carbon dioxide will be the unity. Now, to better understand and quantify the dangerousness of these gases, the GWPs of each fundamental GHG aforementioned has been reported in the following table:

GHG	GWP over 100 years
CO ₂	1
CH ₄	28
N ₂ O	265
CFCs	[1,500-15,000]

Table 1 – Global warming potential of the most relevant GHGs.

It is immediately possible to notice the huge GWP of chlorofluorocarbons with respect to all the other gases, meaning that its impact is order of magnitude stronger. However, only a comparison of this value is not enough. At this purpose, in the following subchapters, each gas has been analyzed more in detail, giving an explanation on how it contributes to the enhancement of the greenhouse effect and the emissions by sector.

2.1.1 Carbon dioxide - CO₂

Among the whole GHGs, carbon dioxide is the most problematic one. GHGs have a certain lifetime in the atmosphere once emitted, and carbon dioxide is that one who lives longer than the others (in the range of 300-1000 years).

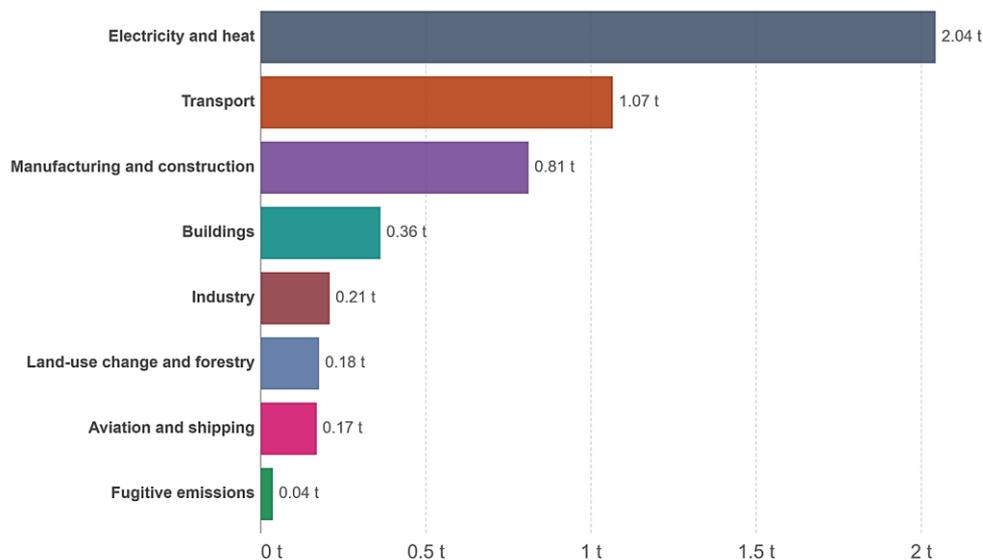


Figure 3 – Global CO₂ emissions per capita divided by sector, 2019; this is quantified in tons per person per year.

Source: CAIT Climate Data Explorer via Climate Watch

The graph shows that heat and electricity productions represent 42% of total carbon dioxide emissions. An important contribution is also given by the transportation sector, and manufacturing and construction field (respectively 22% and 17%).

2.1.2 Methane - CH₄

Methane is responsible for almost 25% of global warming. Once it is emitted into the atmosphere, the methane reacts generating the following negative effects:

- it oxidizes with the consequent production of CO₂ and water vapor,
- it reacts with radicals OH,

- it is the principal contribution to the ozone (O₃) formation at ground level, entailing a reduction in the air quality (this effect is responsible for approximately 1 million premature deaths every year).

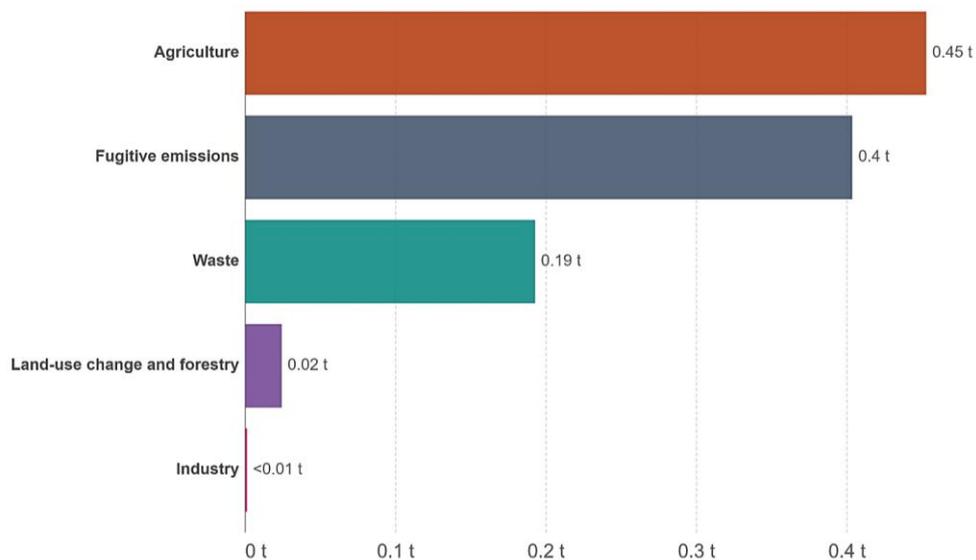


Figure 4 – Global CH₄ emissions per capita divided by sector, 2019; this is quantified in tons per person per year.
Source: CAIT Climate Data Explorer via Climate Watch

Agriculture and fugitive emissions are responsible for almost the entire emission of methane (~80%). The total emission in tons per person are quite small if compared to the ones of CO₂. However, as shown in **Table 1**, over a 100-year period, methane is 28 times more unsafe than carbon dioxide.

2.1.3 Nitrous Oxide - N₂O

This gas is basically inert when injected into the troposphere, and it is able to survive for a period of 120 years. Then, the nitrous oxide moves in the stratosphere where it neutralizes part of the ozone layer. It accounts for about 6% of global GHG emissions.

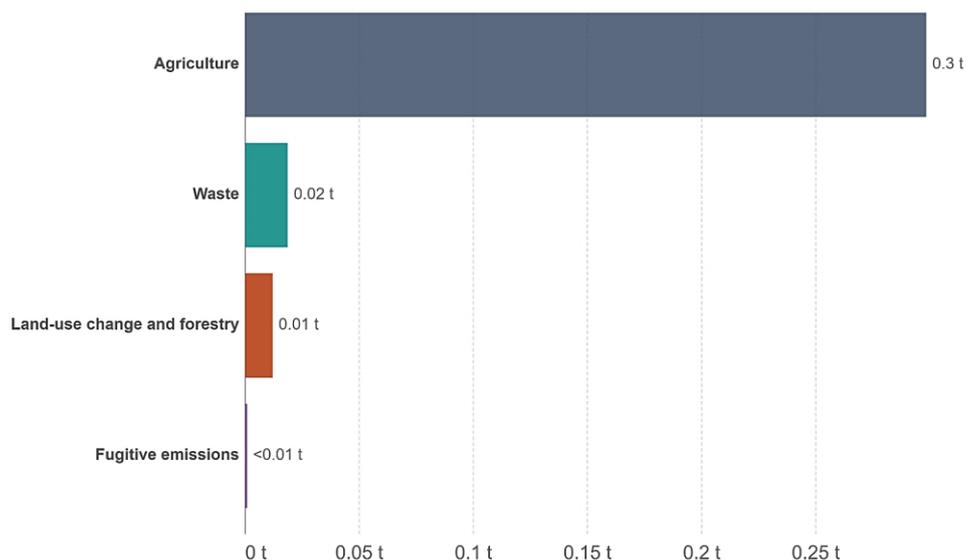


Figure 5 – Global N₂O emissions per capita divided by sector, 2019; this is quantified in tons per person per year.
Source: CAIT Climate Data Explorer via Climate Watch

Except for a small amount, nitrous dioxide emissions are due to fertilizers employed in the agriculture sector.

2.1.4 Chlorofluorocarbons - CFCs

In accordance with **Table 1**, chlorofluorocarbons have the largest GWP. It is responsible only for 2% of the global GHG emissions, and its impact is well known. CFCs have the capability to deplete Earth's atmospheric O₃ layer, which is a fundamental level in order to block strong sun UV rays.

Luckily, thanks to several legislations, the CFCs quantity in the atmosphere has drastically decreased in the last years.

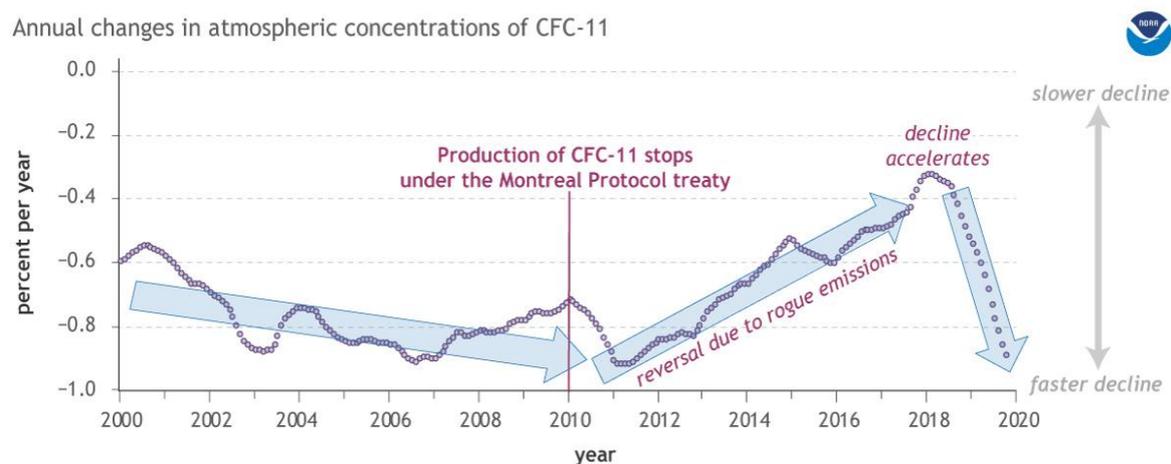


Figure 6 – This graph shows the annual changes in CFC-11 concentrations in the atmosphere from 2000 to 2020 as determined by analysis of samples from NOAA's monitoring network. This timeframe includes the steep reduction observed over the past two years, the 2010 worldwide agreement to limit new CFC-11 manufacturing, the following detection of new emissions that appear to be in violation of the moratorium, and the subsequent discovery of new emissions.
Source: NOAA Global Monitoring Laboratory and Climate (n.d.) [23]

2.1.5 Water Vapor

Water vapor is probably the most abundant greenhouse gas on the planet. It is responsible for about half of Earth greenhouse effect.

Its behavior is different from the other GHGs. Water vapor is not able to control Earth temperature. Nonetheless, the quantity of water vapor in the atmosphere is controlled by the temperature (due to condensation and evaporation phenomena). Essentially, it enhances the negative effects of the other GHGs, with a consequent increase in the global temperature, and thus leads to a higher amount of water vapor. Thus, water vapor acts as an indicator of the pollution level in the atmosphere.

2.2 SCIENTIFIC EVIDENCE THAT THE CHANGE IS HAPPENING

Scientific evidence for climate system warming is unequivocal [2]. Increasing magnitudes of warming raise the likelihood of severe, pervasive, and irreversible impacts [2]. This means that it is not a future problem, and decisions must be taken right now, in the present. Anyone can easily detect the most obvious evidence, like the rise in global temperatures. However, data give several other proofs:

- **Shrinking of the ice sheets, retreating of the glaciers, and reduction in snow cover** – from all around the globe, and satellite images can prove it, these phenomena are affecting areas like Greenland, Antarctic, Alaska (see **Figure 1**), Alps, Himalayas etc.;
- **Sea level rising** – the above mentioned evidences are mainly responsible for it; over the past century, the sea level increased worldwide by around 20 centimeters, and, unfortunately, the rate over the past two decades has roughly doubled and is slightly increasing each year [3];
- **Oceans temperatures are getting higher** (not only the air is warming up) – the ocean has absorbed much of this increased heat, which has warmed by more than 0.33°C the top 100 meters of water, since 1969 [4];
- **Higher oceans acidification** – considering a time period starting from the Industrial Revolution, which caused an abrupt CO₂ injection in the atmosphere (this gas is the major trigger, due to its absorption by the ocean), an increase of almost 30% in the acidity of surface ocean waters has been detected [5];
- **More extreme events globally** – since 1950, the number of recorded high temperature events has been rising while the number of recorded low temperature events has been falling, and, moreover, there have been more frequent events of heavy rain [6].
- **Longer wildfire season** – in most areas, due to the rise up of global temperatures, wildfire season have been longer and more severe, and deepening drought in the region has added to the risk of fires;
- **More heat waves and droughts** – the temperature is expected to rise during the years; if greenhouse gas emissions continue at their current rate, high heat events, that formerly happened only once every 20 years, are predicted to happen annually by the end of this century.



Figure 7 – Extreme events caused by Climate Change.

All these effects will continue to get worse if GHG emissions will not decrease. Nevertheless, those future effects depend on human activities, and if every person can reduce their own emissions, it should be possible to prevent some of the worst consequences.

According to NASA website (Global Climate Change [1]), the actual situation is the following:

Carbon Dioxide	419 [ppm]
Global Temperature	+ 1.01 [°C] since 1880
Artic Sea Ice Extent	-13% per decade since 1979
Ice Sheets	-427 billion metric tons per year
Sea Level	+ 4 [in] since 1993

Table 2 – Scientific measurements of the most relevant effects due to Climate Change – updated to 2022.

2.3 WORLD EMISSION SCENARIO

As previously said, anthropogenic emissions are worsening the Greenhouse Effect impact on the planet. However, what kind of anthropogenic activities lead to the actual situation? A significant portion of world emissions is due to power generation since, unfortunately, burning coal, oil, or gas still supplies the majority of the world electricity, causing the production of carbon dioxide and nitrous oxide (strong GHGs that cover the planet and trap the sun heat). Nevertheless, fossil fuels are also used in fields like transportation (22% of total GHG emissions in the European Union and 16% of the global ones) and food production (25% of the whole GHG emissions [7]). Then, it should be mentioned the deforestation process which, together with agriculture and other land use changes, is responsible for approximately a fifth of global GHG emissions [8].

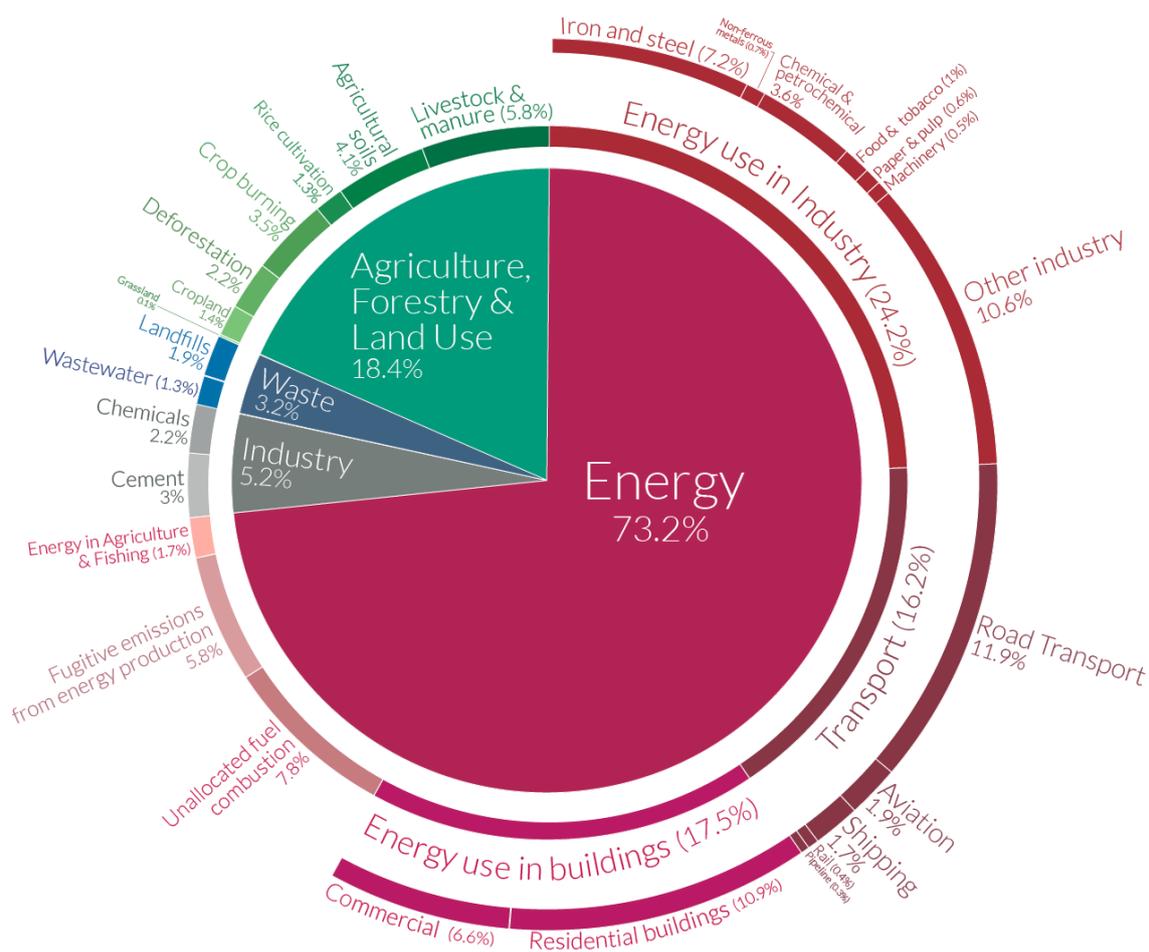


Figure 8 – Global greenhouse gas emissions by sector. The above picture is referred to 2016, during which the total amount of greenhouse emissions were 49.4 billion tons CO_{2eq}.

Source: Our World in Data (n.d.) [9]

Most of the attentions are now focused on carbon dioxide, as discussed in **Chapter 2.1.1**. For this reason, it is important to stabilize its concentration in the atmosphere. The web site ‘Our World in Data’ provides an excellent long-term trend of the atmospheric CO₂ concentration (expressed in ppm) over the last 800,000 years.

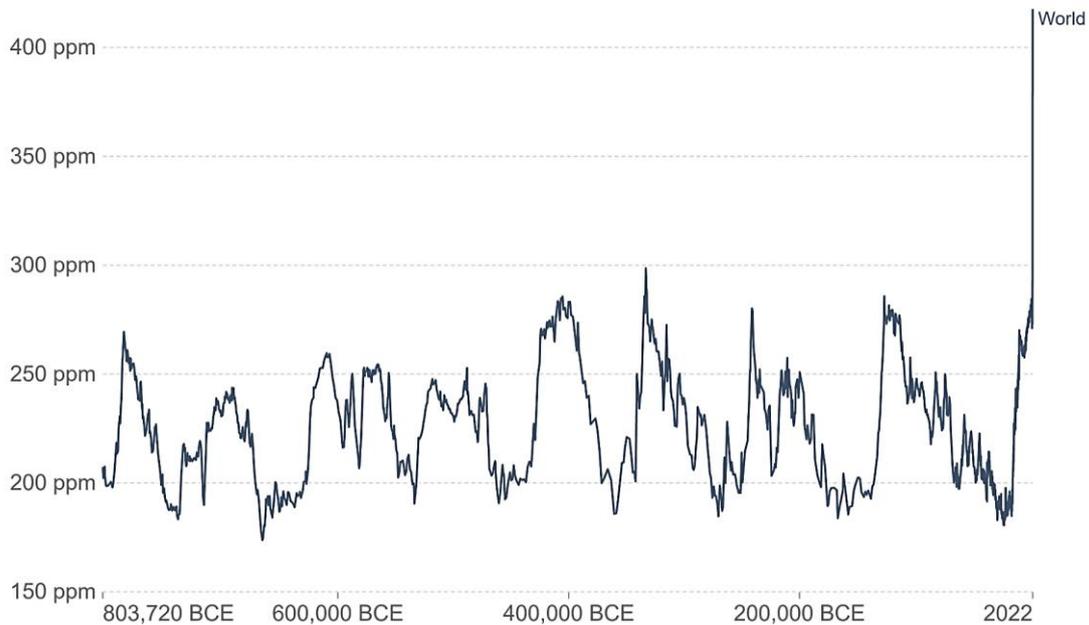


Figure 9 – Global atmospheric CO₂ concentration measured in part per million (ppm): this long-term trend has been made by using preserved air samples from ice cores.

Source: Our World in Data (n.d.) [9]

Consistent fluctuation in CO₂ concentration can be observed, due to changes in Earth’s orbit around the Sun, which are also known as Milankovitch cycles [9]. The period with the lowest value coincide with the onset of ice ages and the ones with the highest value with interglacial periods [9]. It needs to be pointed out that the concentration never went above 300 [ppm], until humans started working with fossil fuels (mostly for energy supply) with a consequent emission of large amounts of CO₂. Thus, today the Earth atmosphere has the biggest carbon dioxide concentration of its history with a value of 419.48 [ppm] (as confirmed by both sources: ‘NASA’ and ‘Our World in Data’ [1,9]).

At the end of the XX century, several governments started making decisions with the aim of controlling and reducing global emissions. To name some of the most important:

- **Kyoto Protocol (1997)** – the target was the limitation of GHG emissions compared to the ones in 1990, providing detailed methods and mechanisms on how to achieve the goals, to measure and to verify the data;
- **Doha Amendment (2012)** – it was created to establish the 2nd commitment period of the Kyoto Protocol;
- **Paris Agreement (2015)** – it replaced the Kyoto Protocol with the final aim to limit global warming well below 2 [°C], and below 1.5 [°C] above the pre-industrial levels.

Other targets have been set for the year 2030 or also, one of the most ambitious, the Net-Zero emissions by 2050 (even if the target year could vary in the countries, e.g. China Net-Zero target is set by 2060). It should be noted that the inclusion criteria may differ from country to country. Some of them, for example, may include international aviation and shipping in their Net-Zero commitment, whereas others do not. Alternatively, some may accept carbon offsets while others do not [9]. Then, even after decades, there are still no precise guidelines.

Moreover, even though several policies have been established in this field, according to the UNFCCC, the actual situation is still not enough in order to keep global warming to just 2°C above the pre-industrial level by 2035.

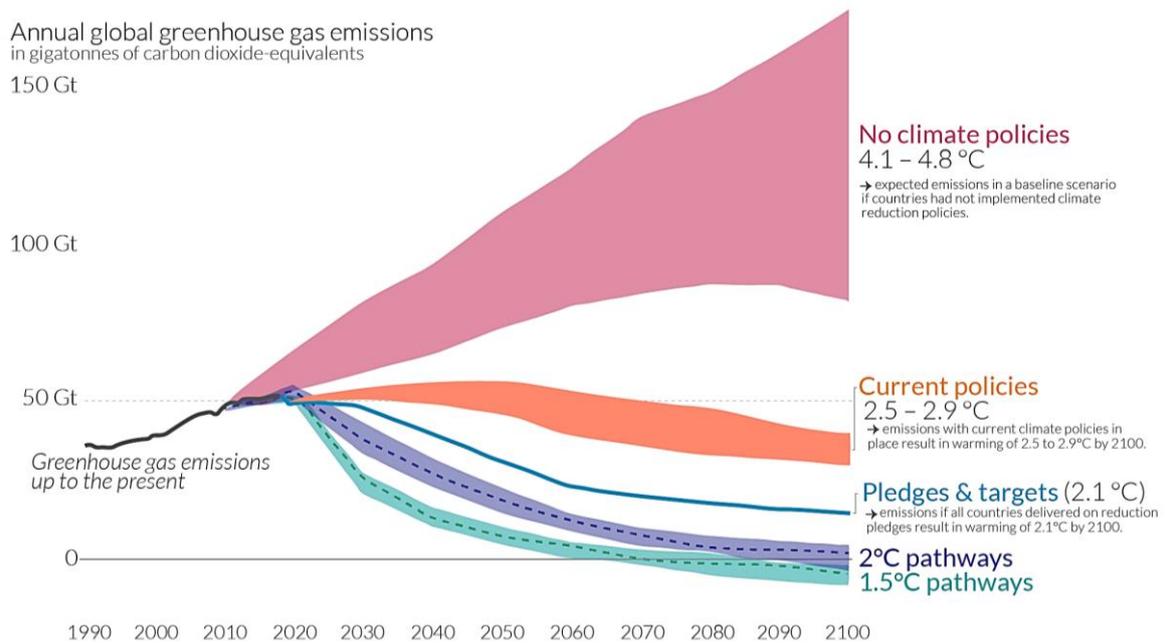


Figure 10 – Possible warming developments and GHG emissions: obviously each of these pathways has uncertainties in its prediction, and this uncertainty is represented by the shaded area; forecasts by 2100 and referred to pre-industrial level.

Source: Our World in Data (n.d.)[9]

As a final comment, it can be said that with today’s climate and energy policies, there is a possibility to reduce warming relative to a world without climate policies. However, this is not enough to reach the best pathway and the target is still far from the actual situation.

3. CARBON CAPTURE, UTILIZATION AND STORAGE

After the ending of the previous chapter on Climate Change, aimed to give a clear background in which the idea of carbon capture is located, it should be easy to deduce that the technologies aimed to capture carbon dioxide are a hot topic, and the reasons are several. As already mentioned, CO₂ is a major anthropogenic GHG whose emissions are mainly due to the excessive use of fossil fuels. Therefore, an obvious solution might be to capture this harmful gas directly from the source, or from the atmosphere. This is where carbon capture technologies come into play.

Intergovernmental organizations like the IPCC, the UNFCCC and the IEA consider carbon capture and storage a fundamental strategy in order to reach the reduction level in CO₂ emissions and in global warming. Obviously, it should be coupled with other solutions like renewable energy systems, circular economics, hydrogen and improvement of energy efficiencies of existing technologies.

According to Einloft et al. [10], CCUS are technologies that can prevent more than 90% of carbon dioxide emissions generated from stationary energy resources. It also needs to be pointed out that, in these years, a great part of the efforts have been focused on these stationary energy resources. However, recently, new researches are focusing on the transportation field. Barrufet et al. [11], from Texas A&M University, are working on a way to capture the carbon dioxide and the water vapor from cars exhaust, and then utilize them in the food and agricultural systems. Schmauss et al. [12] are studying a system to use the captured CO₂ to power a fuel cell for heavy duty transportation, creating a carbon capture fuel cell vehicle (CCFCV).

In order to prove this growing interest in the topic, it has been decided to perform a research on the impact that it had on the scientific community. Thus, thanks to the website ‘Web of Science’ and using the key word ‘CO₂ capture’, the graph in **Figure 11** has been produced (Web of Science is a platform that gives access to numerous databases with reference and citation information from academic journals, conference proceedings, and other publications across a range of academic subjects).

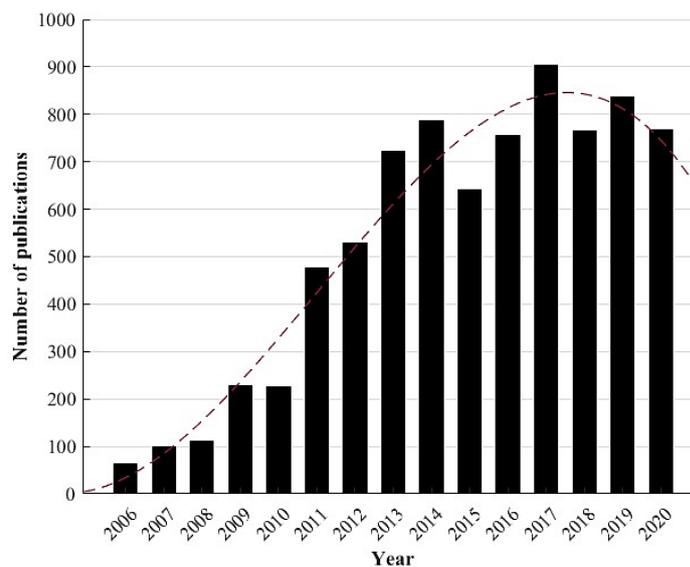


Figure 11 – Histogram highlighting the increasing trend in the number of scientific papers published on this topic between the years 2006 and 2020; it has been decided to also show the trendline (dotted line).

As expected, the graph shows a rising trend, with a significant increase in publications from 2010 to 2011. In 2011 there were more than 251 publications compared to those in 2010, which is an impressive growth. This could be linked to the emerging interest of governments, which also means more subsidies addressed to the research field. The second biggest growth in number of publications is from 2012 to 2013, corresponding to the entry into force of the Doha amendment (2012).

The name ‘carbon capture, utilization and storage (CCUS)’ suggests that more than one process is employed in this field. Indeed, it involves a portfolio of technologies aimed at separating the CO₂ from the stream, to catch it, and finally to transport and store it. However, CCUS is still far from large scale utilization. The reasons are several, but the cost is definitely the most significant drawback. The energy penalty globally paid in the working chain is still too big. An estimation is that one needs a carbon tax of almost \$70-100 per ton of CO₂ to recover the aforementioned costs [13]. It is also relevant to point out that among the whole CCUS procedures, the carbon dioxide capture is the most energetically demanding part, with an estimation of almost 70-80% of the entire costs [13]. Other drawbacks are the uncertain long term storage capacity and the possible danger that CO₂ transportation and storage can pose.

Plant type	Plant efficiency without CC ^a	Plant efficiency with CC
Coal, subcritical	33-39 %	23-25 %
Coal, supercritical	38-44 %	29-31 %
Coal, ultra-supercritical	43-47 %	34-37 %
NGCC ^b	45-51 %	38-43 %

Table 3 – Example of energy penalty for some post-combustion processes. ^a Plant efficiency is based on the fuel HHV (higher heating value); ^b NGCC refers to a natural gas combined cycle power plant.

Thus, it is clear that numerous efforts are now focused on R&D with the final target to minimize the energy penalty and the operating costs [14]. Moreover, since the carbon dioxide emitted in the atmosphere is in the order of gigatons [13], each improvement could be significantly helpful especially if obtained in the capture process.

3.1 OVERVIEW ON THE EXISTING INDUSTRIAL TECHNOLOGIES

Nowadays, all the CCUS installations around the world capture more than 40 [MtCO₂] every year [19]. Moreover, some of these installations started working in the first years of the 1970s [19]. The type of CO₂ generating plant and fuel utilized have a significant impact on the choice of a particular CO₂ capturing system. Basically, it is possible to classify carbon capture technologies in two macro-groups:

1. Combustion treatment,
2. Direct Air Capture (DAC).

3.2.1 Combustion Treatments

Usually, carbon dioxide is originated by a combustion process, and according to the kind of combustion, three different systems can be applied:

1. **Post-combustion** – it works with the exhaust gases, with a partial capture of the carbon dioxide from it;
2. **Pre-combustion** – the target is to remove the carbon dioxide content from fossil fuels before the ending of combustion process (it is typically more efficient due to the larger concentration of CO₂ even if the capital costs of the base gasification process are frequently higher);
3. **Oxy-combustion** – natural gas is combusted with nearly stoichiometric oxygen; a large portion of the CO₂ is recycled back to the combustor to limit the turbine inlet temperature (TIT).

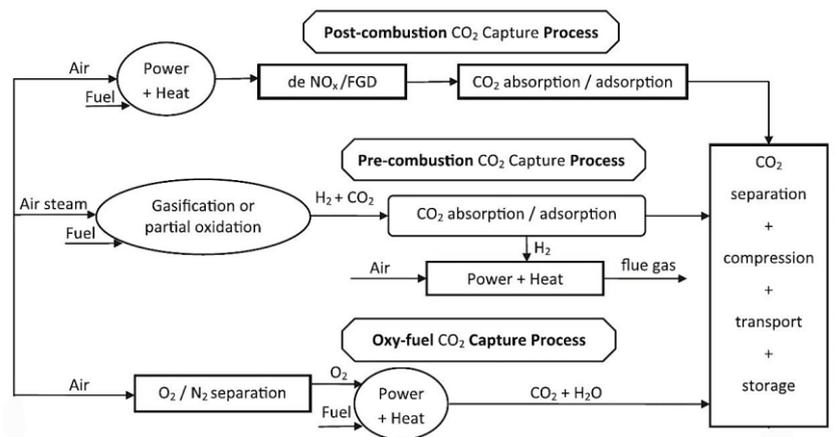


Figure 12 – Schematic illustration of the aforementioned CO₂ capture technologies [14].

3.2.1 Direct Air Capture

DAC belongs to the second macro-group of carbon capture technology. The basic idea is to extract carbon dioxide directly from the atmosphere. Then, the gas can be stored and also employed in other fields like agriculture, food processing or to manufacture synthetic fuels if combined with hydrogen. Furthermore, it should be mentioned that, according to IEA, DAC is expected to be a key process in the transition to a net zero energy environment.

This technology can work using two different methodologies:

1. **Solid DAC** – a solid sorbent is employed in order to capture CO₂; then, it is possible to release the gas by heating the sorbet or placing it under vacuum conditions;
2. **Liquid DAC** – in this case a liquid sorbet (e.g. potassium hydroxide, calcium carbonate) removes the carbon dioxide; the sorbent can be regenerated by means of high temperature techniques and reutilized again in the process.

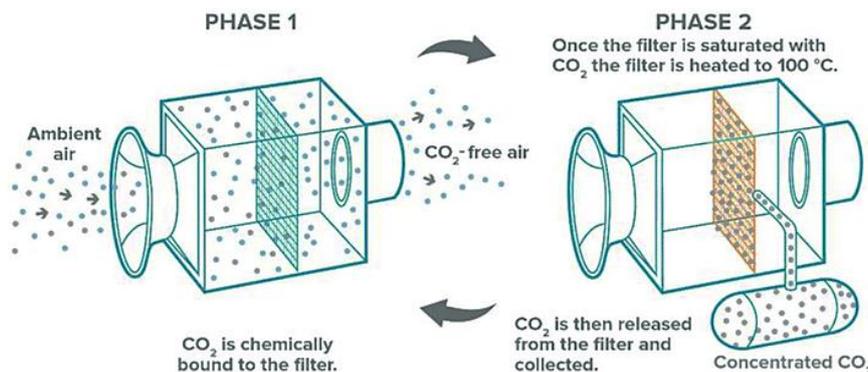


Figure 13 – Schematic representation of a solid DAC technology [18].

3.2 SEPARATION TECHNIQUES

The aim of this chapter is to identify the main separation techniques that can be employed in order to isolate the carbon dioxide from the primary stream. However, only adsorption and absorption processes will be examined in detail since they are the fundamental phenomena of the research activities of this project.

The following table reports a quick comparison of these techniques, highlighting their advantages and drawbacks.

PROCESS	PROS.	CONS.	REFERENCES
Cryogenic distillation	<ul style="list-style-type: none"> Well established process especially in industrial CO₂ capture. 	<ul style="list-style-type: none"> High energy demanding technique; Low operating temperatures; Suggested only for processes with CO₂ concentration larger than 90% v/v. 	[15]
Adsorption	<ul style="list-style-type: none"> The adsorbent can be reused since the process is reversible; High efficiency in the order of 85%. 	<ul style="list-style-type: none"> High temperatures are needed in the process; Big amount of energy for desorption of the carbon dioxide. 	[14]
Absorption	<ul style="list-style-type: none"> Most mature technique; Regeneration of the sorbent; High efficiency in the order of 90%. 	<ul style="list-style-type: none"> Large amount of heat (also meaning too much energy) required for absorbent regeneration; The effects on the environment still need to be identified; Carbon dioxide concentration affects process efficiency. 	[14]
Chemical looping	<ul style="list-style-type: none"> Carbon dioxide as primary product; During the combustion process, CO₂ does not mix with N₂; Low energy intensive. 	<ul style="list-style-type: none"> Still in R&D phase, with low TRL; No experiences in large scale projects. 	[17]
Membrane separation	<ul style="list-style-type: none"> It could reach a separation efficiency in the order of 80%; Already employed in the separation of other types of gases. 	<ul style="list-style-type: none"> Low fluxes; Fouling problem. 	[16]

Table 4 – Analysis of the main separation techniques for CO₂.

3.2.1 Absorption and Adsorption Processes

Essentially, they are two different kind of sorption processes. The main difference is that **adsorption** compounds adhere to the surface of the molecule (case of a solid sorbent), while **absorption** substances enter the bulk phase of what usually is a liquid.

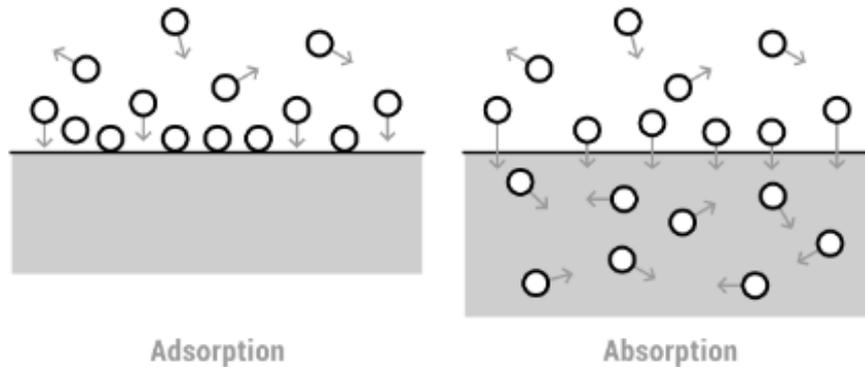


Figure 14 – Schematic representation of the conceptual difference between 'adsorption' and 'absorption' phenomena.

In order to carry out an overview of this operation, it has been decided to refer to the general sorption process. The latter usually involves chemical reactions, which can generally be expressed as follows:



where ' R_i ' are the reactants and ' P_i ' are the products. It is possible to define as '**sorbate**' the substance that gets attached and as '**sorbent**' the substance on which the sorbate gets attached to. A fundamental effect is that all these reactions have heat as a main product. Consequently, reconvertng the product to reactants requires thermal energy. Furthermore, sorption reaction can be of two types:

1. **Physisorption** – the bounding forces between sorbate and sorbent are weak as hydrogen bridge type or Van der Waals type;
2. **Chemisorption** – this time the bounding forces are very strong and due to covalent or ionic bonds.

Another important parameter to consider is the 'inversion temperature' T^* . In order to have the inversion of the reaction, this temperature needs to be guaranteed. It can be defined starting from the definition of Gibbs free energy:

$$\Delta G = \Delta H - T^* \Delta S = 0 \quad (2)$$

$$T^* = \frac{\Delta H}{\Delta S} \quad (3)$$

A reaction can be defined endothermic for temperature bigger than T^* , thus, products can be reconverted into reactants supplying thermal energy. On the other hand, for a temperature lower than T^* , an exothermic process takes place and heat is released by the reaction. Usually, the process from products to reactants, in which heat is required, is called desorption.

3.3 ACTUAL MATERIALS

The choice of the material sorbent is the core of each carbon capture technology, because without an adequate sorbent the capture would be not efficient. As mentioned in previous chapters, absorption and adsorption processes are used in this project. Therefore, the materials are referred to these two processes.

In the case of liquid sorbent for absorption, the typical sorbents are:

- Monoethanolamine (MAE),
- Diethanolamine (DEA),
- Potassium carbonate (K_2CO_3) – employed in DAC coupled with aqueous KOH.

In **Table 4**, it is reported that absorption is the most mature technique, and also according to Veawab et al. [27] and Aaron et al. [28] it is possible to reach efficiencies up to 90% with MEA sorbents such as aqueous alkanolamines. However, in the last years, materials like piperazine (PZ) and anion-functionalized ionic liquid received some attention. Yuan et al. [29], from The University of Texas at Austin, made a great study on semi-aqueous PZ for carbon capture applications, also highlighting the advantages and disadvantages of this sorbent: high absorption rate and capacity, good stability and low viscosity but it has a narrow solid solubility window which may limit its solubility. However, this issue can be settled by a partial substitution of the PZ with a different amine like 2-methylpiperazine (2MPZ) or changing water with a physical sorbent to solubilize the PZ. While anion-functionalized ionic liquids are still not very useful due to their high viscosity, low CO_2 capture capacity and not cost-effective.

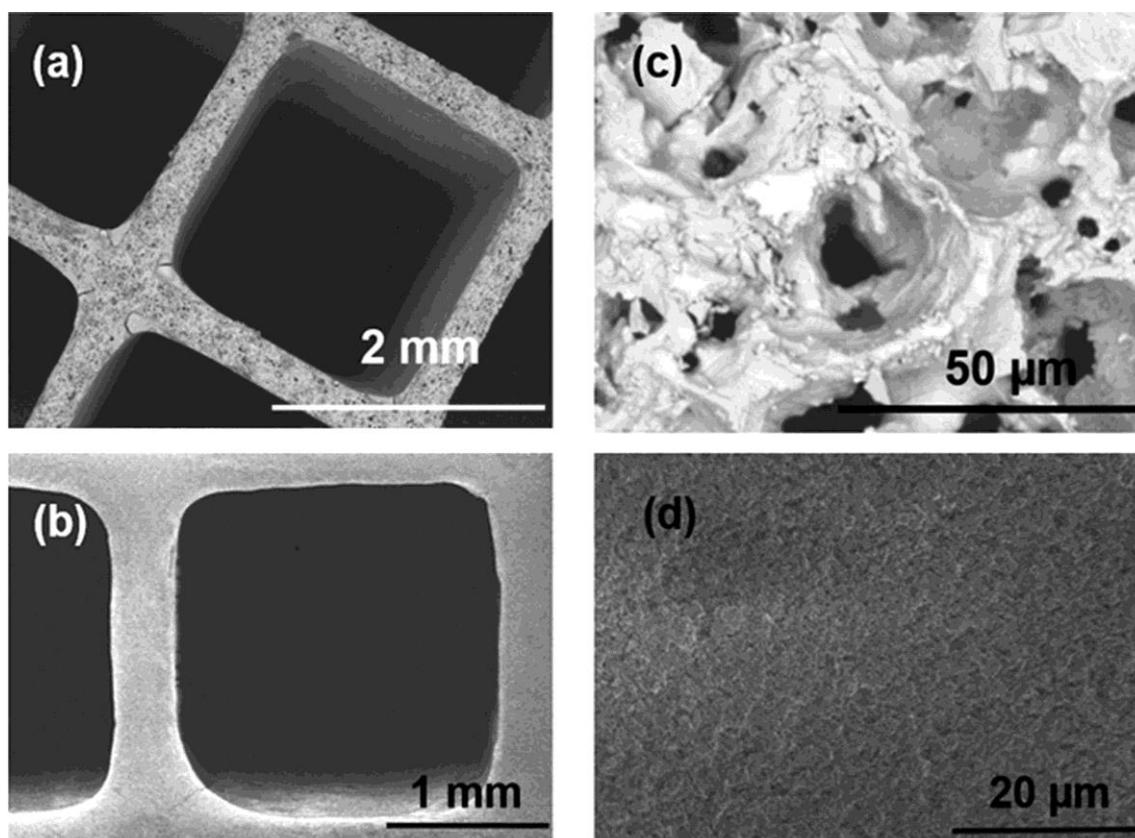


Figure 15 – Example of adsorbent: TEM low- and high-resolution pictures of development stages of Magnesium Oxide MgO - (a,b) mesh structure, (c,d) porous structure [30].

Adsorption processes are also very effective, with an efficiency up to 85%. The usual materials employed in this process are:

- Molecular sieves,
- Activated carbon,
- Zeolites,
- Calcium oxides,
- Lithium zirconate.

One of the main target of the project is to find new sorbents (for both absorption and adsorption) to capture carbon dioxide, and graphene oxide is the most important one. All the aspects of graphene will be covered in **Chapter 4.1.2**.

3.4 CARBON UTILIZATION

At the end of the capturing process, the high carbon dioxide stream can go into geological storage or it can be utilized in different ways [14]. Basically, with ‘carbon utilization’, it is meant an industrial process able to turn the above mentioned stream into an economically valuable product with a CO₂ concentration higher than the atmospheric one [20]. There are two different possibilities: carbon dioxide is transformed by means of chemical reactions into materials or fuels; it is directly employed in activities such as enhanced oil recovery.

According to Aresta et al. [21], nowadays, carbon utilization technologies account only for 2% of emissions. Nonetheless, it is forecasted that chemical utilization is able to mitigate an annual amount of 700 [MtCO₂]. Thus, due to their huge potential, they can be an excellent business in the future, especially if it is possible to operate at large scale and have modest operating costs.

Hepburn et al. [20] propose a classification of 10 different pathways for CO₂ technologies: CO₂ chemicals, CO₂ fuels, microalgae, concrete building materials, CO₂ enhanced oil recovery (EOR), bioenergy with carbon capture and storage (BECCS), enhanced weathering, forestry, soil carbon sequestration and biochar.

4. CO₂ CAPTURE IN BOZLAR NANOSCIENCE LAB

After the theoretical background on Climate Change and carbon capture technologies, this chapter focuses on different aspects of the research project. As already mentioned in the introduction, the research activity has been carried out in the Bozlar Nanoscience Lab, at The University of Texas at Arlington. The primary goal of Bozlar Nanoscience Lab is addressing urgent societal needs, especially in the area of energy and environmental issues, by combining fundamental and applied research. Thus, the fundamental topics of the latter are: sustainability, human health and environment. Furthermore, the laboratory operates with nanomaterials, which are the core of each ongoing project.

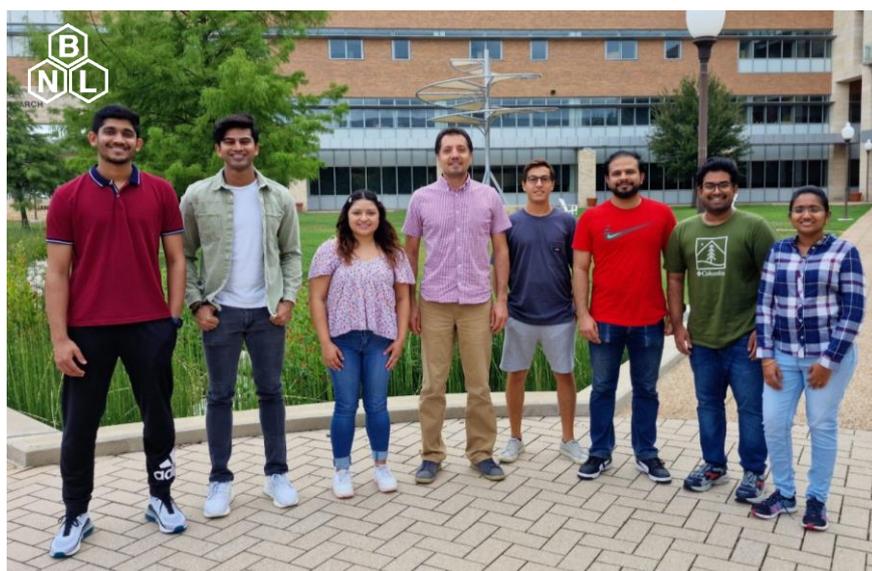


Figure 16 – BNL Team, Fall 2022, The University of Texas at Arlington.

4.1 NANOMATERIALS

With the term ‘nanomaterial’, it is usually meant a material with at least one external dimension that measures 100 [nm] ($100 \cdot 10^{-9}$ [m], 100 millionths of a millimeter or 100 billionths of a meter) or less, either with internal structures measuring 100 [nm] or less. Nanomaterials are everywhere. It is possible to have examples in nature like pollen and volcanic dust, and they are becoming a relevant product in today’s market [29].

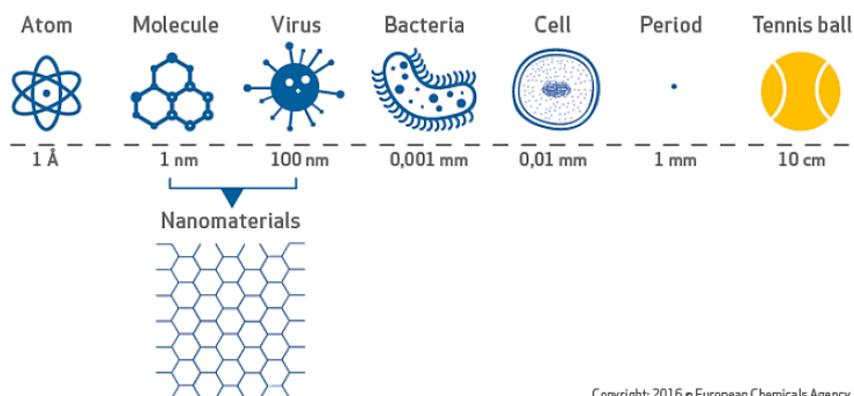


Figure 17 – Scale comparison to highlight nanomaterials dimensions [26].

There are different types of nanomaterials and they are usually classified according to their shape:

- **particle**: graphene and carbon black;
- **tube**: carbon nanotubes (CNTs), that can be single wall (SWCNTs) or multiple walls (MWCNTs);
- **rod**: that can be long rod nanoparticles (LRNs) or short rod nanoparticles (SRNs);
- **fiber**: natural (cellulose, keratin, etc.) or synthetic (polyurethane, polylactic acid, etc.).

Thanks to nanomaterials, it is possible to operate on the properties of a material, resulting in the enhancement of the latter: chemical and mechanical properties, electrical conductivity, thermal diffusivity, flammability, EMI shielding properties, etc. Each ongoing project in Bozlar Nanoscience Lab involves nanoparticles, and more precisely carbon-based nano-fillers. Among them, graphene is the most interesting one that has been employed in the project due to its great affinity with CO₂ after some dedicated chemical treatments.

4.1.1 Environmental Impact of Relevant Nanomaterials

Nanofillers are excellent materials with the ability to enhance the properties of the hosting matrix. Nonetheless, it is also fundamental to understand their environmental impact, especially in these last two decades. The idea of this study is that, even if one can create the perfect material, it will be useless if its production emits a relevant amount of pollution. Life cycle assessment (LCA) is the method to evaluate this impact. LCA is defined as a methodology aimed at assessing the environmental impact of a technology, process or service, and each stage is taken into consideration (raw material extraction, transport of raw material, manufacturing process, etc.). LCA for nanoparticles is more complicated than other cases, and several aspects are still not well known.

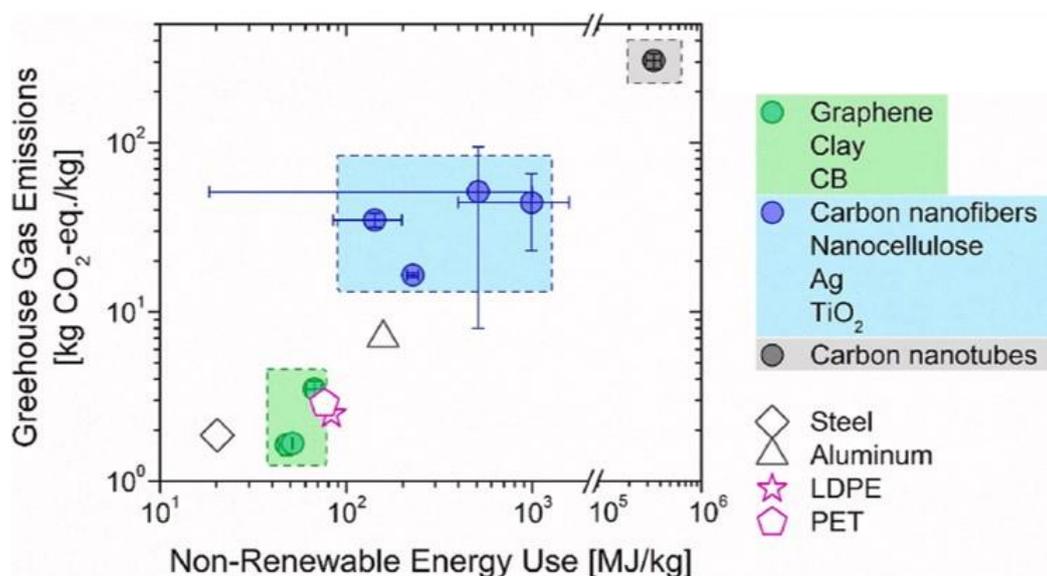


Figure 18 – Environmental impact of different nanoparticles highlighting that graphene, clay and carbon black (CB) are the most environmentally friendly materials to use, and carbon nanotubes (CNTs) the most pollutant [25].

Carroccio et al. [25] made a great study on this topic, and **Figure 18** reports the relevant outcomes in a graph comparing the greenhouse gas emissions in [kg CO_{2,eq}/kg] over the non-renewable energy used in [MJ/kg] to fabricate some of the most relevant nanomaterials. It is

immediately possible to highlight that the use of graphene, clay and carbon black (CB) entails the lowest environmental impact. On the contrary, CNTs are the least environmentally friendly. This is one of the reasons why graphene is employed in almost all the ongoing projects in the Bozlar Nanoscience Lab.

4.1.2 Graphene

It has already been mentioned that graphene is an important material used in the Bozlar Nanoscience Lab. For this reason, the aim of this chapter is to provide some fundamental information about this great nanomaterial in order to have a basic knowledge of it.

It might be interesting to start with a simple way to define graphene. It is a one atom thick layer of graphite (where graphite is that soft and crumbly material which pencils are made of) in which carbon atoms are arranged in a two-dimensional honeycomb structure. Thus, graphene is the basic structural element of graphite [31]. Every atom in a graphene sheet has a strong σ -bond with its three closest neighbors, resulting in carbon atoms having a sp^2 hybridization.

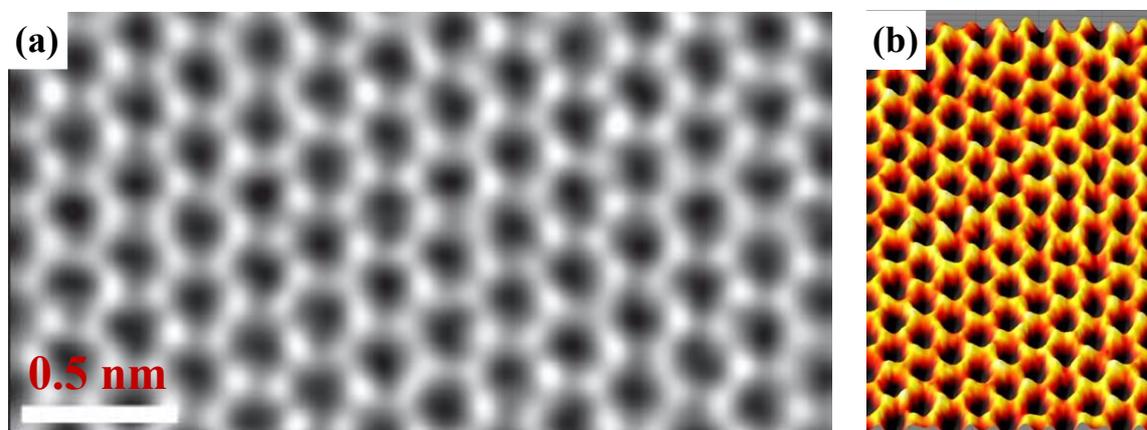


Figure 19 – (a) ADF-STEM image displaying the defect-free hexagonal lattice of graphene [32]; (b) TEAM 0.5 graphene picture showing individual carbon atoms, represented in yellow, of the honeycomb lattice [33].

However, graphene in its simplest form is very stable and it does not allow easy interactions. The field related to graphene physics is still one of the most active research area since not all the aspects are known, approximately the remaining 10-15% of its structure and properties need to be understood.

The typical classification of graphene is made according to the type of defects present in its layer. Thus, it is possible to distinguish the three following structures:

1. **Pristine Graphene** – it is the perfect layer of carbon atoms that are densely packed into a honeycomb configuration (**Figure 20**), nonetheless, this structure does not allow interaction because it is very stable;
2. **Graphene Oxide** – it is Pristine Graphene with the presence of oxygenated functional groups (**Figure 21**) as epoxy groups ($-\text{O}-$) and hydroxy groups ($-\text{OH}$), and it results in a higher level of interaction with other substances (the oxygenated functional groups break some bonds with a consequent reduction in the structural stability);
3. **Reduced Graphene Oxide** – it is Graphene Oxide with the addition of vacancies in the crystal lattice (**Figure 22**).

Between them, graphene oxide is the most investigated structure [31] and it is highly employed in several applications since it is able to tune the material characteristics.

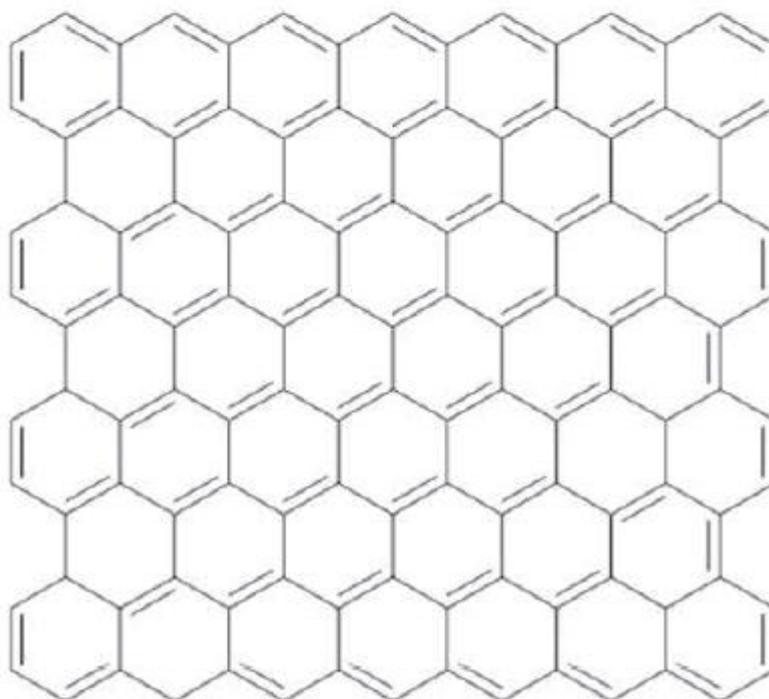
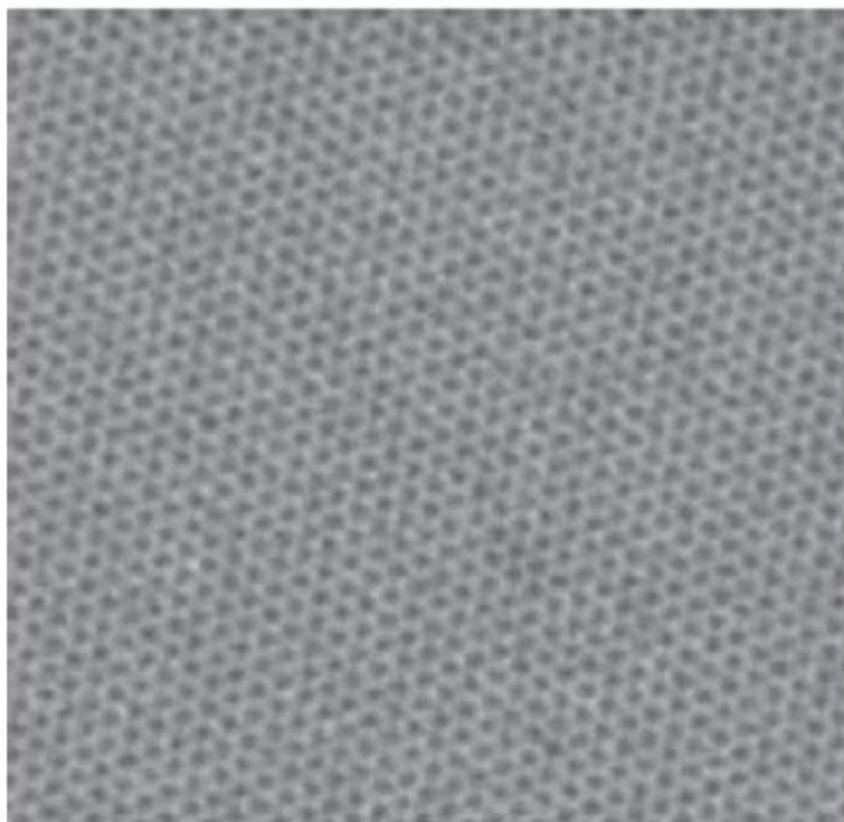


Figure 20 – Pristine graphene: TEM image at the top and atomic structure at the bottom [31].

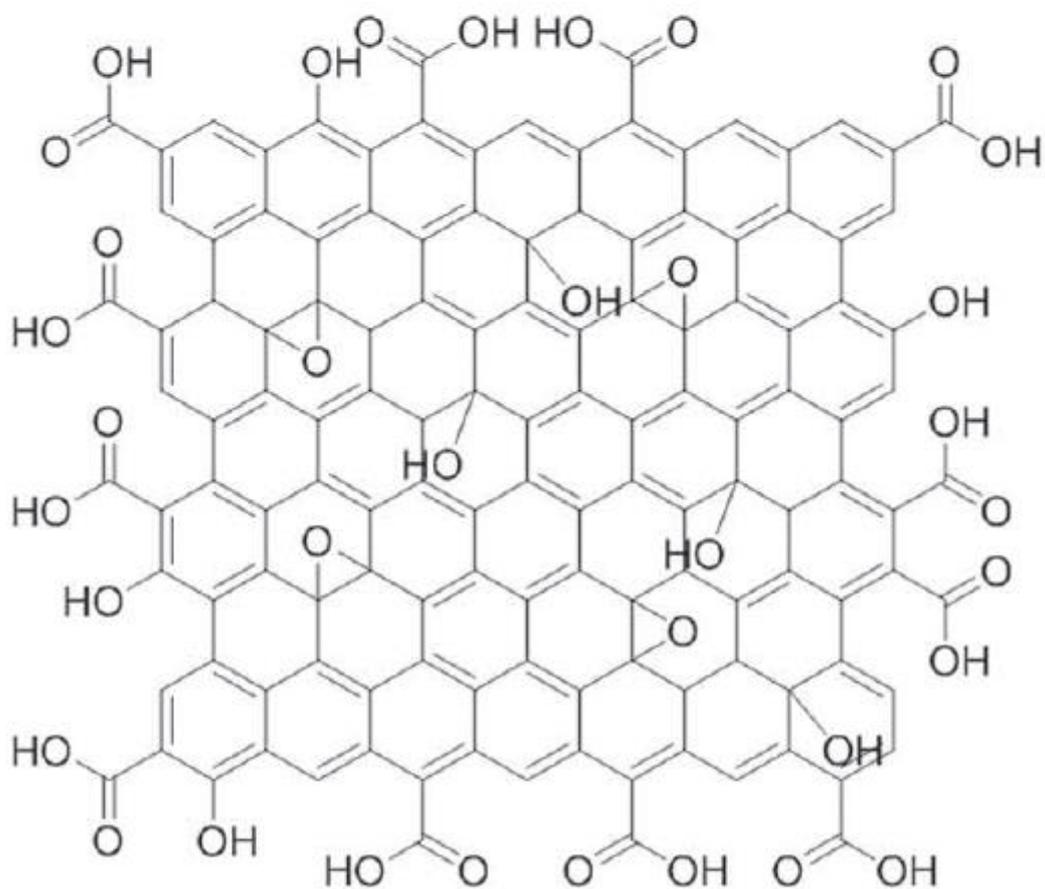
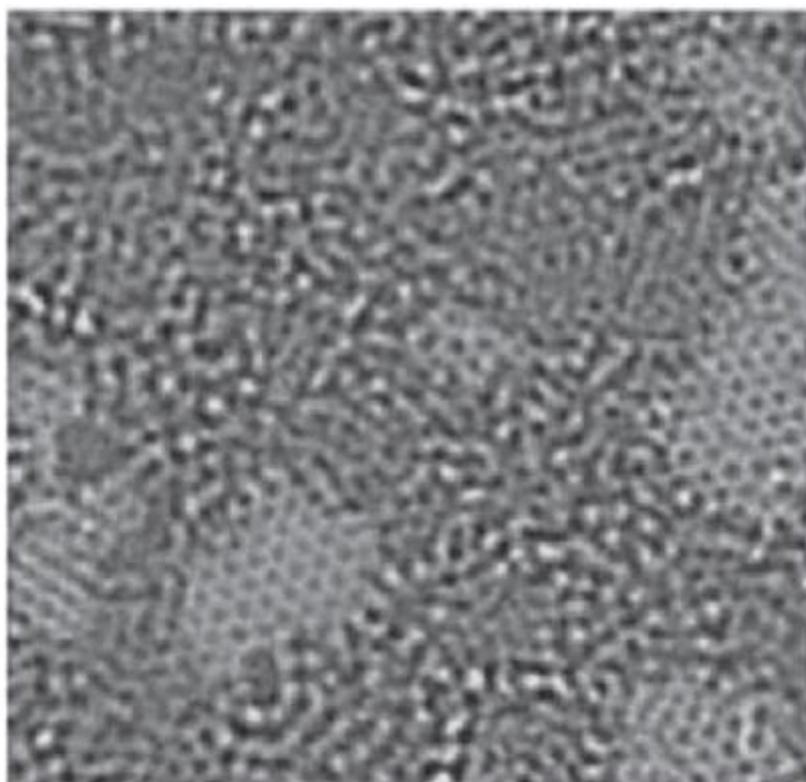


Figure 21 – Graphene oxide (GO): TEM image at the top and atomic structure at the bottom [31].

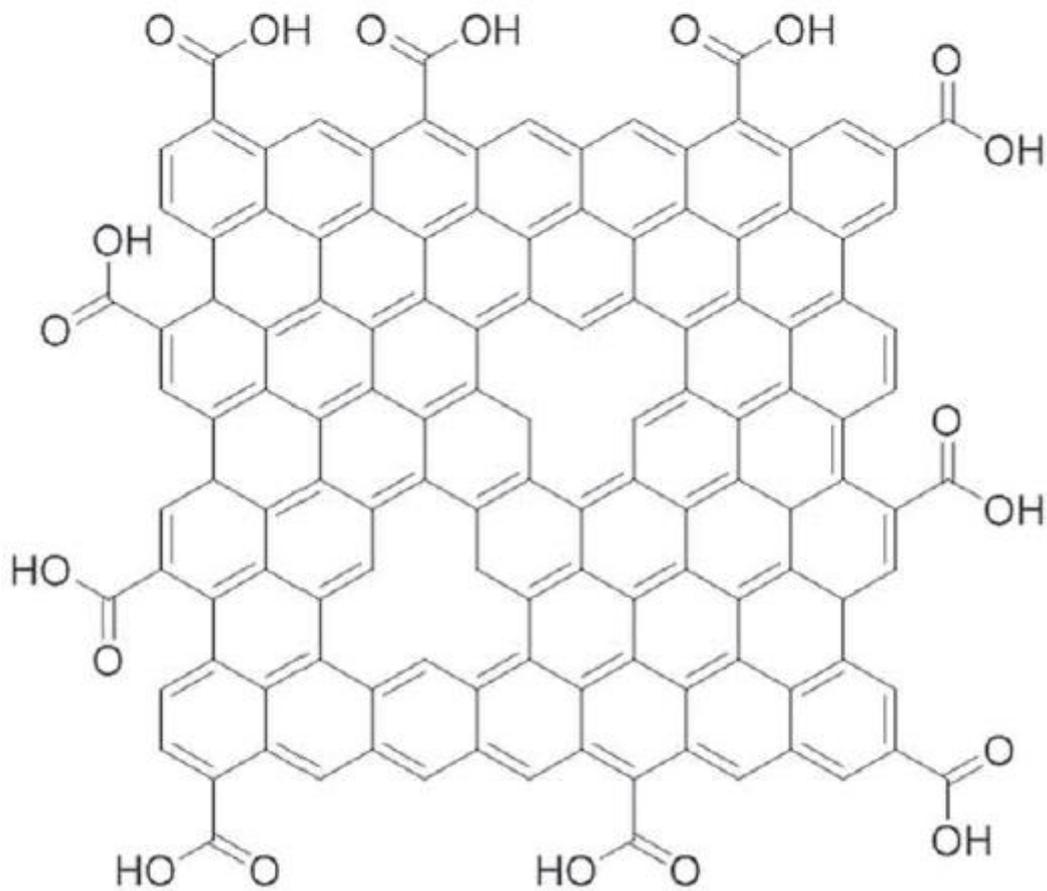
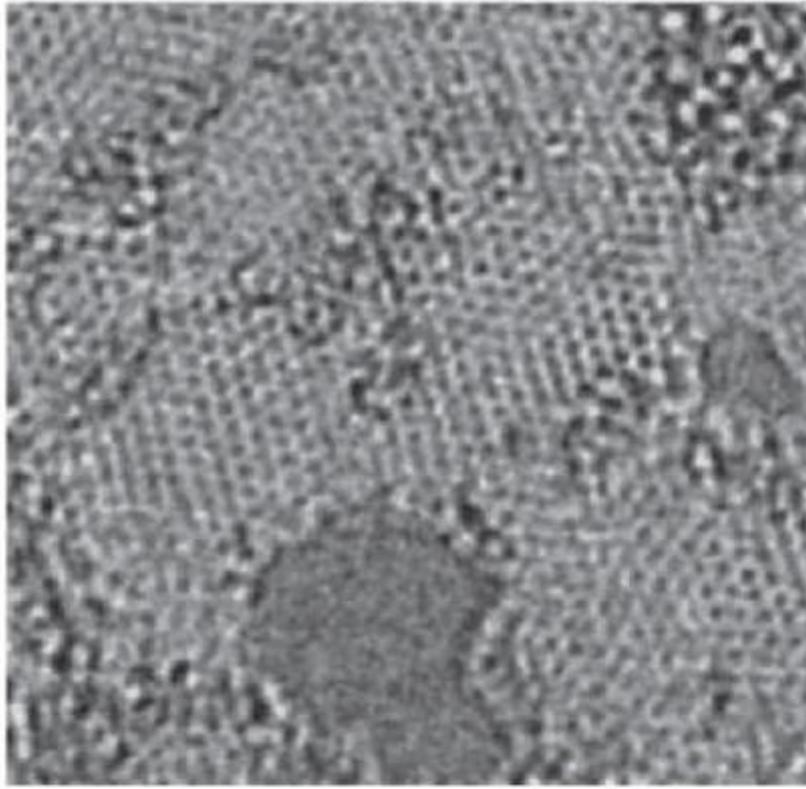


Figure 22 – Reduced graphene oxide (rGO): TEM image at the top and atomic structure at the bottom [31].

4.1.3 Graphene Synthesis

Now, it provides a brief description about the synthesis of graphene which is a peculiarity of the Bozlar Nanoscience Lab. This is a very delicate and difficult process and a lot of accuracy must be taken in order to avoid mistakes and the bad quality of the final result. For this reason, even if some procedures are known, it is not easy to reproduce and, consequently, the relevant information are not mentioned in the chapter.

The modified Hummers' method has been followed to prepare graphene oxide, which basically performs the graphite exfoliation thanks to strong oxidizing agents. In contrast to the standard Hummers' method, the modified one does not generate toxic gas and it is simple to manage the temperature level. The method requires the use of the following main chemicals:

- Sulfuric acid (H_2SO_4),
- Phosphoric acid (H_3PO_4),
- Potassium permanganate (KMnO_4),
- Graphite.

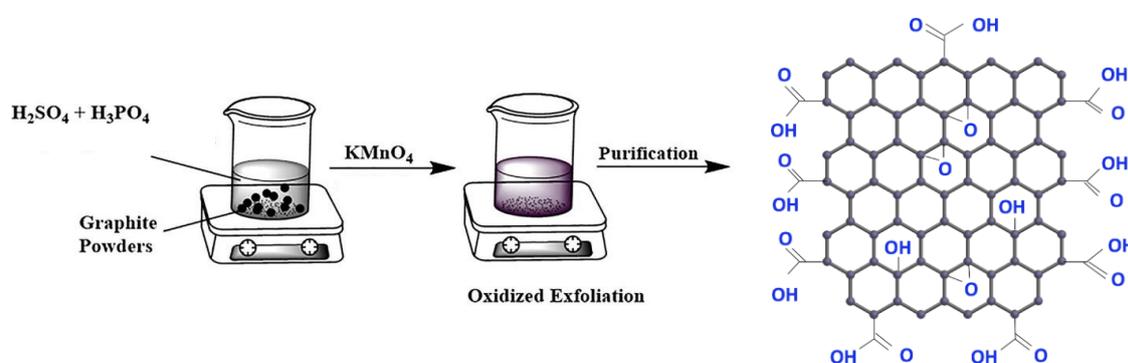


Figure 23 – Schematic representation of the Hummers' method for graphene synthesis.

The initial step demands a work of more than 12 hours. After that, the product will be quenched. Nonetheless, the product still has a great quantity of impurities and needs to be centrifuged several times before it is finally ready to be stored and then used (**Figure 24**).



Figure 24 – Part of the final product obtained from graphene synthesis.

4.2 PROJECT OVERVIEW

The target is to focus on different aspects of CO₂ capture and management, from the perspectives of materials science, taking advantage of nanomaterials qualities. The main purpose of this research is to identify materials and processes to accomplish sustainable carbon capture and sequestration. This means that there will not be energy consumption in the entire process, relying only on the materials chemistry. Liquid polymer sorbents and graphene sheets are the target materials to store carbon dioxide. The polymers saturated with CO₂, after solidification, will be used to produce other kind of plastic objects (e.g. bags, toothbrush, tires, etc.). The first idea is to employ the built prototype for indoor air quality since a closed environment is easier to reproduce and manage. Hence, a vessel has been designed in order to accurately reproduce a closed environment. Usually, in the latter, CO₂ has the ability to negatively influence human health and productivity. Thus, the plan is to reduce the concentration of carbon dioxide in closed environments, to prevent decrease in people cognitive functions. Nonetheless, the final idea is to move the sorbent outside (e.g. a large graphene sheet attached on a building wall) even if entailing a more complicated model, due to the addition of weather conditions and environmental factors that are not included in closed locations.

In this project, thanks to the colleague Dogukan Yazici, it has been possible to have a preliminary study based on computational calculations. Using computational techniques including, Density Functional Theory (DFT), it has been studied the electronic properties of the materials (Fermi Level, Density of States, and Charge Density Difference Analysis), as well as their ground states after adsorption and their capacity to capture CO₂. Moreover, it has been analyze the nature of the physical and chemical interactions of the different sorbent materials used. Then, another relevant point was to quantify the energetic requirements for the adsorption and desorption processes. Obviously, the results have been validated by means of experimental activities.

This project was started by Professor Michael Bozlar in collaboration with other researchers at Princeton University 3 years ago. Thus, there are proofs and experiences in this field showing that the idea works. For this reason, the first aim of the project has been to achieve and verify what they already have done.

Obviously, it is still a young project and a lot of aspects are unknown and should be investigated. Then the second part of the research focused on the improvement of the idea and on the exploration of new sorbents and nanomaterials suitable for this purpose.

4.3 CONTAINER DESIGN

The project started with the design of a new container to perform experiments, due to the not optimal configuration of the first and second prototypes (**Figure 25**). The basic idea has been to design a vessel in order to accurately reproduce a closed environment, which means to have an airtight system. Thus, a lot of efforts have been focused on connections of different components in order to make leakages negligible. The too thin structure of the previous prototypes has been the most important problem. For this reason, some small cracks appeared on the container surface after the carbon dioxide injection, which were potential sources of leakages. In order to avoid this problem, the optimal thickness has been evaluated and the whole calculations are reported in **Chapter 4.3.2**.

Then, it has also been decided to go from the cylindrical shape to a parallelepiped with a rectangular base shape.

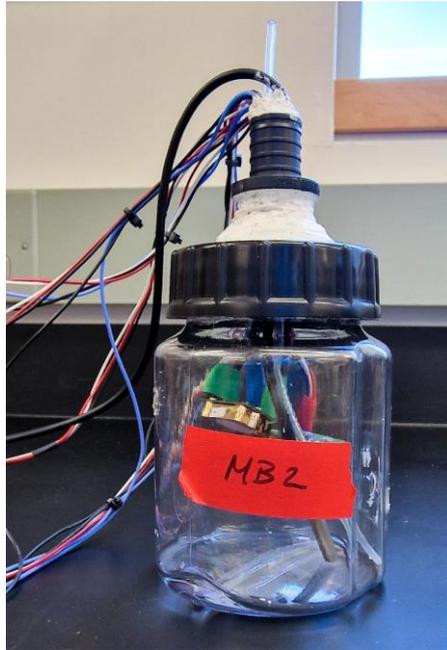


Figure 25 – Second experimental prototype.

The figure below shows the new container, that is the one utilized for the experiment sessions. It is characterized by three holes: one for the sensors' cables, one for injecting the CO₂ and one for the liquid polymer inlet.

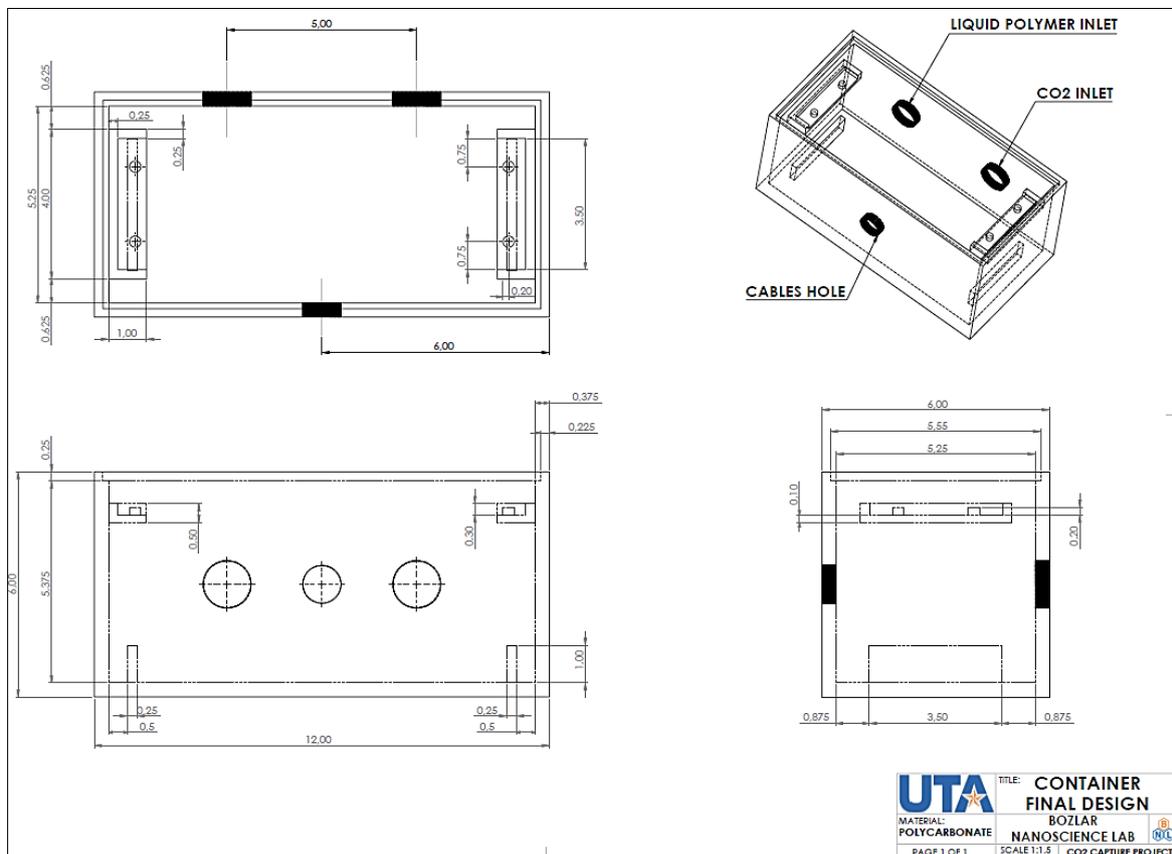


Figure 26 – 2D drawing of the final design of the container.

Figure 27 is a component realized with the aim of holding a mesh, that will clutch the graphene sheet when needed. The mesh selected is made of nylon due to its compatibility to carbo dioxide. This means that the mesh properties will not be affected, as well as the gas concentration in the experimental container.

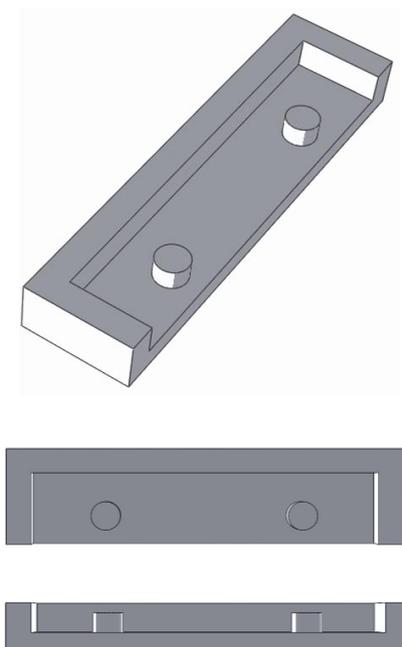


Figure 27 – Mesh holder 3D drawing.

The container dimensions has been designed considering the idea to contain a bicker and petri dishes with a diameter of 9 [mm] and the sensors for the carbon dioxide concentration, temperature and relative humidity. Furthermore, in order to optimize the space inside the vessel, it has been decided to have a single sensor able to measure all the three physical quantities aforementioned. The characteristics of this latter are highlighted in **Chapter 4.3.4**.

4.3.1 Materials

Polycarbonate (PC) has been chosen as material for the vessel. PC is a high-performance thermoplastic polymer characterized by organic functional groups connected together by carbonate groups (-O-(C=O)-O-).

2D Structure	Chemical Formula
	$C_{16}H_{18}O_5$

Table 5 – Polycarbonate 2D structure and chemical formulation.

Due to its thermoplastic characteristics, it is easy to work, shape and thermoform. It is also considered as one of the most important engineering polymer. However, since the project involves the use of carbon dioxide inside the container and a good airtight environment, the first reason of the choice of PC has been its low permeability (see **Table 6**) to this gas compared to other polymers, but also its cheap price.

CO₂ permeation	Density	E	UTS	R_{p0.2}
[cm ³ ·mm/(m ² ·day·bar)]	[g/cm ³]	[GPa]	[MPa]	[MPa]
400-800	1.2	2.2	65	60

Table 6 – Carbon dioxide permeation, density and mechanical properties of PC (average properties).

In the figure below, it is possible to see the polycarbonate sheets used for the container’s walls.

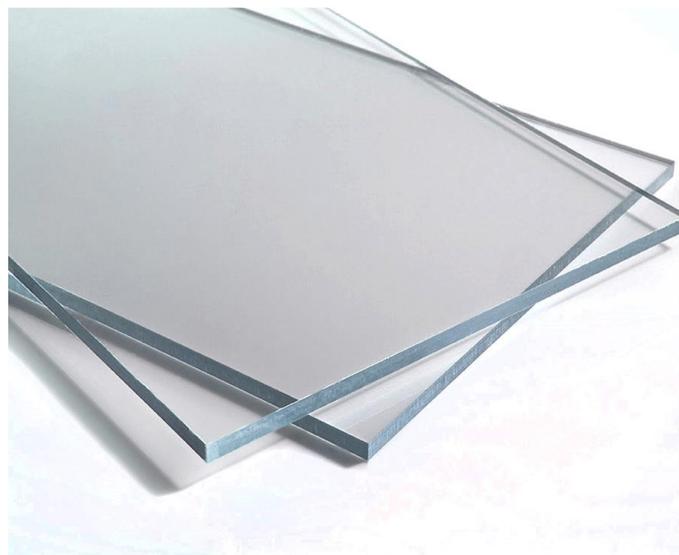


Figure 28 – Polycarbonate sheets utilized for the container construction.

A further idea has been the use of Ethylene Vinyl Alcohol (EVOH) resin in the junctions between different pieces. The reason is that EVOH offers outstanding gas (oxygen, carbon dioxide, nitrogen, and helium) barrier properties and maintain this barrier property over a wide range of humidity values. In **Table 7**, it is possible to notice that the permeability coefficient for carbon dioxide at room temperature of the resin is four order of magnitude lower than the one of PC.

Material	Permeability Coefficient for CO₂
	[cm ³ ·mm/(m ² ·day·bar)]
Polycarbonate (PC)	400-800
Ethylene Vinyl Alcohol (EVOH) [24]	0.01-0.08

Table 7 – Comparison between the permeability coefficients of PC and EVOH.

4.3.2 Thickness Evaluation

For this calculations, the container has been modelled as a cylinder with external radius ‘d_e’ equal to the length of the longer side of the rectangular section, undergoing an internal pressure

‘ p_i ’. In order to evaluate the thickness, the worst possible conditions have been considered, that is the case in which there is the maximum concentration of CO₂ inside the container. Considering a maximum concentration of 10 million ppm of CO₂, the internal pressure will be equal to 1.1 [MPa] (~ 11 [atm]).

Then, according to static structural mechanics, it has been assumed to have a static safety factor equal to 2:

$$SF = \frac{R_{p0.2}}{\sigma_{id}} = 2 \quad (4)$$

After that, it has been supposed to have thick walls, which means that ‘ $s/r_i > 0.1$ ’. Therefore, applying the Lamè theory, it is possible to evaluate the principal stresses that have been reported in Table 5:

Radial stress, σ_r	Circumferential stress, σ_c	Axial stress, σ_z
$-p_i$	$p_i \cdot \frac{r_e^2 + r_i^2}{r_e^2 - r_i^2}$	it has a value between the previous two stresses
σ_3	σ_1	σ_2

Table 8 – Principal stresses of the container.

After that, they have been used to find an equation for the ideal stress ‘ σ_{id} ’ as a function of the thickness ‘ s ’. Furthermore, the calculations need to be performed on the internal circumference since it is the most stressed part. At the end, thanks to the Tresca criterion, it has been found an equation for the ideal stress to further substitute in (4) and, finally, the thickness ‘ s ’:

$$\sigma_{id} = |\sigma_1 - \sigma_3| = |\sigma_c - \sigma_r| = p_i \cdot \frac{r_e^2 + r_i^2}{r_e^2 - r_i^2} + p_i = 2p_i \cdot \frac{r_e^2}{r_e^2 - r_i^2} \quad (5)$$

$$r_i = \sqrt{r_e^2 - \frac{4p_i r_e^2}{R_{p0.2}}} \quad (6)$$

$$s = r_e - r_i \quad (7)$$

ppm of CO ₂	internal pressure, [MPa]	thickness, [mm]
10 ⁵	0.111355	0.930
10 ⁶	0.201355	1.684
10 ⁷	1.101355	9.353
10 ⁸	10.101355	107.133

Table 9 – Thickness variation at different CO₂ concentration inside the container.

These results are also displayed in a diagram form in the figure below.

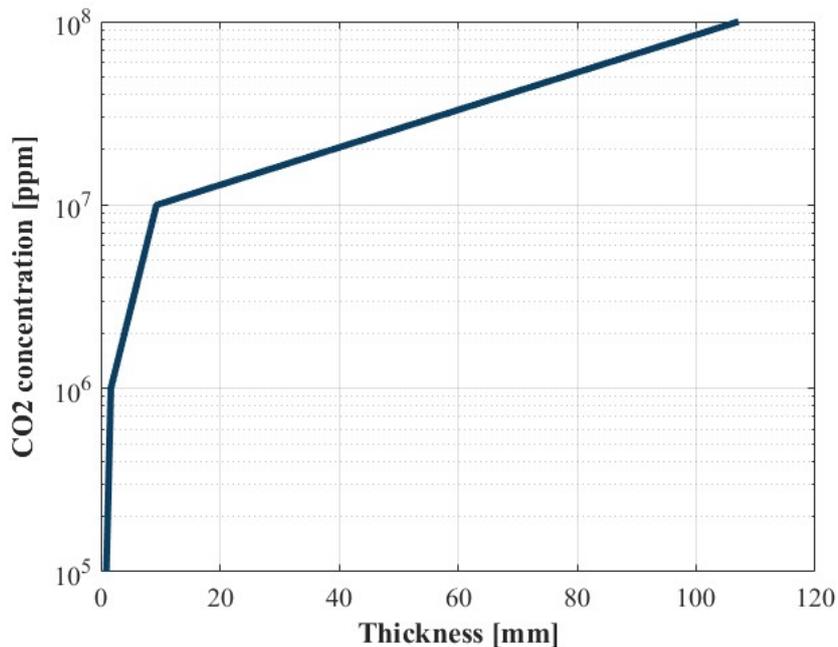


Figure 29 – Graphical representation of the thickness variation at different CO₂ concentration levels.

4.3.3 Valves

The choice of the valves has been one of the most important part of the container design. This is due to the need to have almost null leakages in the experimental box. As already mentioned, the final aim is to measure the variation of CO₂ concentration, and since the latter is measured in part per million (ppm), every source of leak matters. According to **Figure 26**, two are the inlet holes: one for the carbon dioxide and one for the polymer sorbent.

For the injection of carbon dioxide, it has been decided to utilize a one-way valve. Usually, this type of valve is realized with a mobile body (it might be a sphere, a cylinder, a plate, etc.) that translates within a special chamber. The movement of this body may be due to the only fluid forces, or to the combined action of the fluid pressure and a spring. In this way, after the CO₂ flow stops, the spring can act to the mobile body and close the inlet hole avoiding the gas to escape from this component.

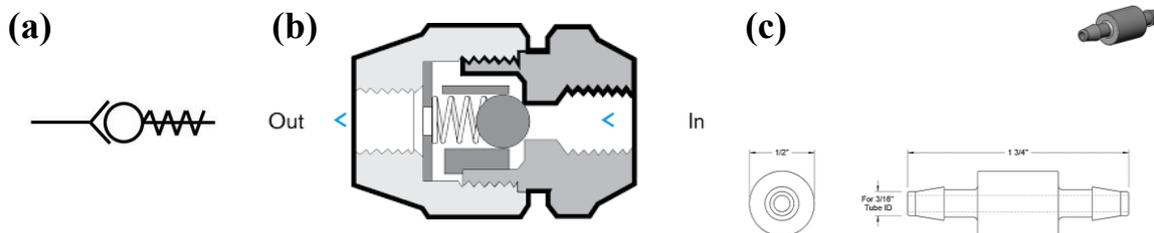


Figure 30 – One way check valve icon (a); Valve schematic representation (b); 2D drawing of the chosen valve (c.)

While for the polymer, it has been chosen two different valves suitable for the use of viscous liquids which are characterized by a similar operating principle: ball valve, butterfly valve. In **Table 10** are reported some of their principal features. At the end, it has been decided to use the ball valve. The ball inside the valve has the same aim as the sphere inside the check valve, or better to avoid the escape of carbon dioxide from the injection site. At the same time, it is also possible to regulate the amount of sorbent added in the vessel.

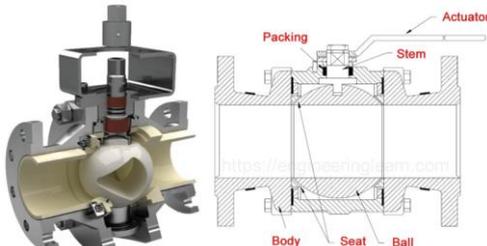
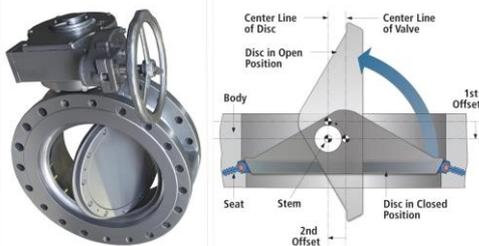
Ball valve	Butterfly valve
It can handle viscous liquids and slurries	Quick shut-off
Well suited to shut-off applications	Simple design so cheaper solution
It can handle up to 400 [°C] and 1,000 [bar]	It suffers in high temperature and high corrosive environments
Possible materials: metal, plastic or metal with ceramic	It generates a pressure drop
	

Table 10 – Principal characteristics of the ball valve and butterfly valve.

In addition to these components, Teflon tape (**Figure 31**) has been used around all the threads of the vessel. The tape works as a deformable filler and thread lubricant, helping to seal the joint without hardening or making it more difficult to tighten. It also protects the threads of both pieces from direct contact with each other and physical wear and helps seal and prevent leaks from the connection.



Figure 31 – Teflon tape (a); example of application around a valve's thread (b).

Other junction components were required to make some connections between the valve, the container and the different tubes.



Figure 32 – Adapters for auxiliary connections.

4.3.4 Sensors

In an experimental analysis, it is fundamental to capture the correct physical quantities in order to have a good description of what is happening and a good understanding of the phenomenon. Therefore, sensors must be included in all experimental set-ups. A sensor is a device able to detect the interested physical quantity, that will be then plotted in a digital or analytical way.

For this project, the physical quantities of interest that have to be measured are the following:

- CO₂ concentration expressed in ppm,
- Temperature,
- Relative humidity.

It could happen that in most cases space is one of the most relevant issue. At this aim, it has been decided to find and buy a sensor able to measure all the three quantities.

Measured Quantity	Working Range	Accuracy	Temperature Dependency
ppm of CO ₂		at 25 °C and 1,013 mbar	
	0 ÷ 10,000 ppm	± (100 ppm + 5% of the MV)	± (1 + CO ₂ concentration ppm/1,000) ppm/°C
RH		at 25 °C and 20...80 %RH	
	0 ÷ 95 %RH	± 3 %RH	
Temperature		at 25 °C	
	- 40 ÷ 60 °C	± 0.5 °C	
Ambient Pressure		at 25 °C	
	700 ÷ 1,100 mbar	± 2 mbar	± 0.015 mbar/K

Table 11 – Sensor specifications.

In **Table 11**, some relevant information are shown, that are the working range, the accuracy and the dependency from temperature. While in **Figure 33** there is a picture of the sensor, also highlighting its size compared to a coin.

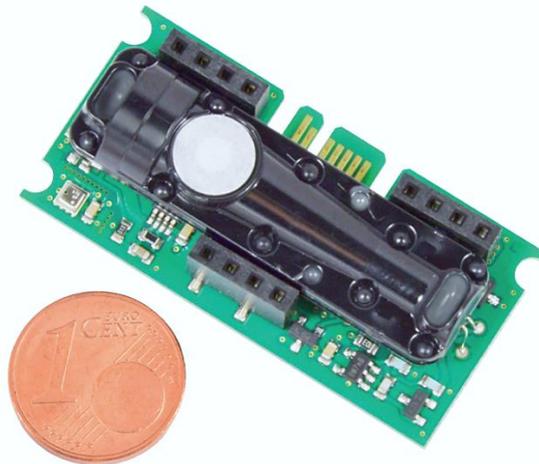


Figure 33 – E+E sensor for carbon dioxide concentration, temperature, relative humidity and pressure measurements.

As for all electronics devices, the calibration process is fundamental in order to have a correct data acquisition. When the sensor is activated for the first time, a period of minimum 7 days is needed so that the algorithm can find its initial parameter set for ASC (automatic self-calibration). Furthermore, the sensor has to be exposed to fresh air for at least 1 hour every one or two days, and during this period the sensor may not be disconnected from the power supply, otherwise the calibration procedure needs to be restarted.

4.3.5 Tubing

Pipes are a fundamental part of the set-up since they need to transport the CO₂ and the liquid sorbent from the source to the container. They are located at both inner and outer side. For this reason, an important characteristic is their resistance to carbon dioxide, or better they need to interact with the gas as little as possible. Thus, 6 [mm] polyurethane tubing (**Figure 34**) have been utilized, which can easily work with high CO₂ concentrations and pressures.



Figure 34 – Polyurethane tubing: excellent resistance to CO₂ and it can handle high pressures.

4.3.6 Construction

The construction process started from the polycarbonate sheets, already shown in **Figure 28**. Their start dimensions were 12 [in] × 12 [in] (304.8 [mm] × 304.8 [mm]), and since these sizes were different from the desired ones for the container, some adjustments were required. In order to perform these operations, it has been proposed to use the machines available in the FabLab (university’s workshop). All the straight cuts have been performed by means of the ‘Band Saw’ machine (**Figure 35**).



Figure 35 – FabLab tools for straight cuts: Band Saw machine plane with polycarbonate sheet (a), blades utilized in the machine to perform different type of cuts.

While in **Figure 36** is represented the second machine used to make the holes to fit the different valves.

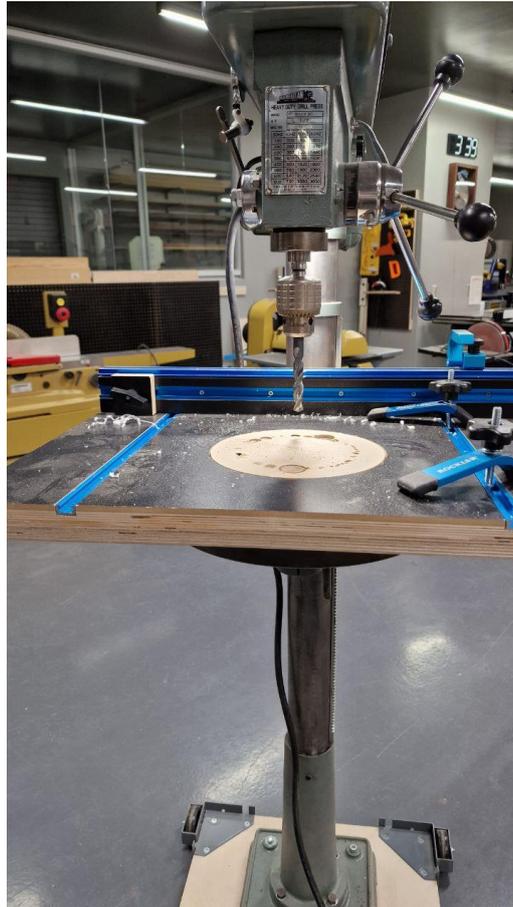


Figure 36 – FabLab's drilling machine.

Obviously, for safety reasons, it has been required to attend some preparatory courses in order to use the two machines.

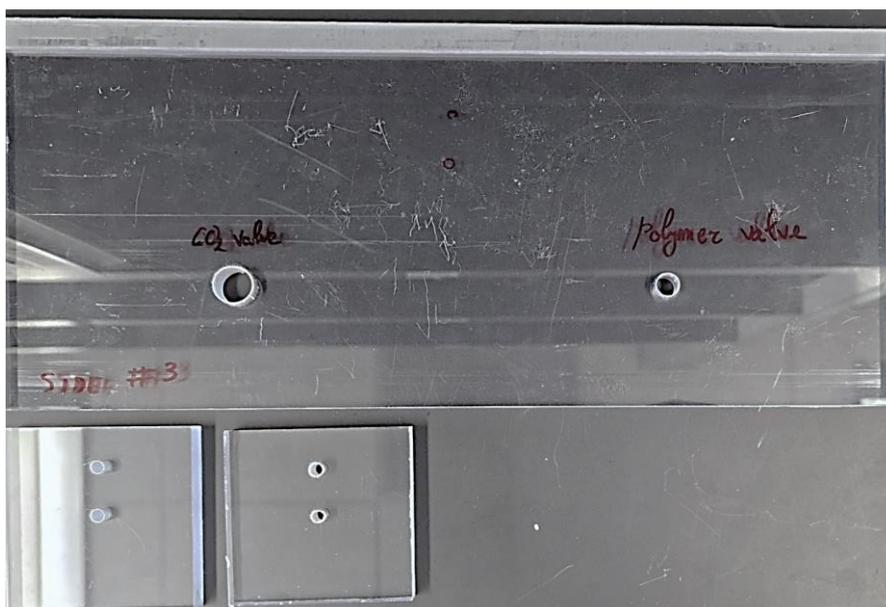


Figure 37 – Some on the final polycarbonate sheets after the manufacturing processes.

4.4 INDOOR AIR QUALITY

As mentioned in the ‘Project Overview’, the idea is to start performing experiments to treat indoor air quality. Therefore, what is found in literature represents a further reason and incentive to work in this field and have excellent results.

Nowadays, people spend a very long time indoors (~90%), consequently, the environment in a building has an important role in people overall well-being, especially in light of the ability of building to influence human health positively or negatively [22]. Hence, several building designs are expected to have good energy efficiency and environmental performance, also involving indoor air quality.

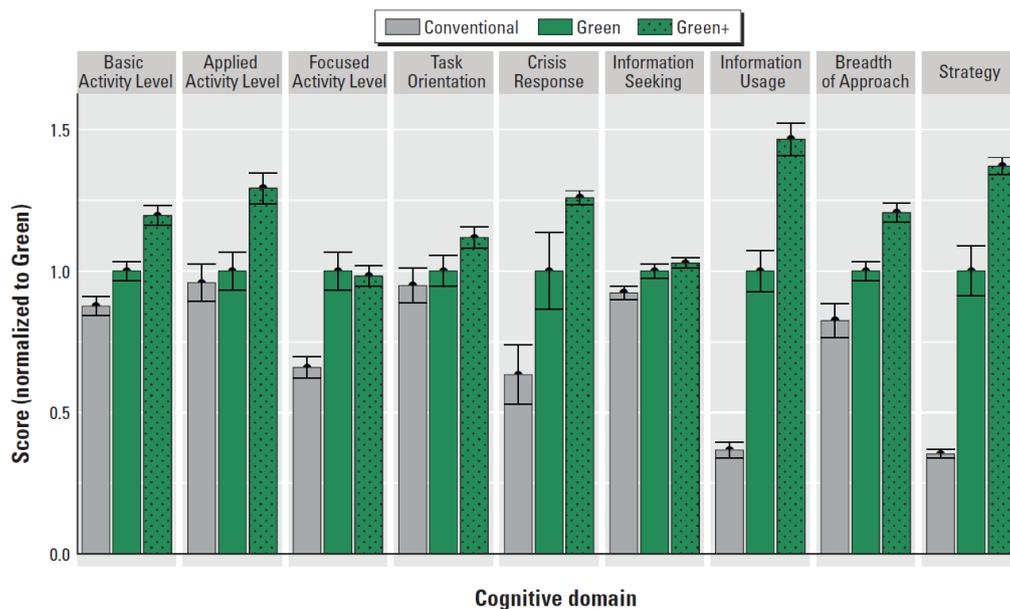


Figure 38 – Graph highlighting the cognitive function scores for the three cases considered (i.e. Conventional, Green and Green+ conditions) normalized to the Green conditions [22].

Allen et al. [22] carried out a great and interesting study on closed environments (i.e. office), proving how a not polluted air results in higher people productivity with lower energy consumed. Moreover, carbon dioxide is one of the major causes of reduction in workers cognitive function and decision making.

What Allen et al. [22] have done is to compare three type of indoor environments:

1. **Conventional** – high concentration of volatile organic compounds (VOCs);
2. **Green** – small concentrations of VOCs;
3. **Green+** – environment with high ventilation rate able to also remove CO₂.

From **Figure 38**, it is easy to detect the big improvement obtained with respect to Conventional closed environments, in the order of 60% for Green case, and up to 100% for Green+ case. Thus, these kind of green buildings can offer higher cognitive function levels, spending less energy and improving workers welfare.

5. COMPUTATIONAL METHODS

In this chapter, it has been provided a brief description of the computational method performed, as previously mentioned, by a colleague that is also working on this project. With theoretical calculations, it will be determined with which material it is easier to remove CO₂ from the environment. Then, the effectiveness of these theoretical calculations has been validated by means of the experimental activities. Nonetheless, in this work only graphene has been utilized and other sorbents are the target for a future work.

5.1 THEORETICAL PROCEDURE

The interaction of the CO₂ molecule with the materials used in the experimental environment will be simulated using Plane-wave basis sets based on the first-principal calculation method Density Functional Theory through the Quantum Espresso open source code.



Figure 39 – Logo of the open source code employed in the computational part.

The optimizations of the Graphene structure to be used for CO₂ adsorption was simulated through Graphite. The lowest energy configuration and super-cell dimensions obtained by successive optimizations of the graphite structure led to the formation of the Graphene surface. The electronic properties of the graphene surface were determined without any molecular adsorption. Analysis methods such as Density of States provided information about the characteristic structure of the surface. At the same time, the results of Raman Spectroscopy, pioneered by Quantum Espresso open-source code, were helpful to measure the correspondence of the created Graphene surface to the experimental data. After obtaining a suitable graphene surface, CO₂ adsorption has been performed and the nature of the interaction has been investigated with the help of the same analysis methods and methods such as Charge-Density Difference. The comparability of the adsorption energy can give information as the effects of the graphene surface compared to other materials used in the experimental environment. In this way, the suitability of the materials used in the Indoor Air Quality study for the process can give an idea even before the experiment.

5.2 RESULTS

Now, some of the results given as output by Quantum Espresso are shown and explained. As described in **Chapter 4.1.2**, graphene in its simplest form (Pristine graphene) is very stable and usually does not interact with external molecules, except if great temperatures and/or pressures are applied. For this reason, graphene oxide is preferred because of the presence of oxygenated group that increase the interactivity with other molecules (carbon dioxide in this case). Thus, the

first step has been to simulate these two configurations of graphene and evaluate their adsorption energies.

In the theoretical explanation part of this chapter, it has been mentioned that the starting point is the graphite structure, because graphene is the fundamental element of graphite. After the Pristine graphene structure was achieved, the graphene oxide was modeled using one hydroxy and epoxy group attached to the Pristine graphene. This was done because, in terms of adsorption energy evaluation, it is possible to simulate the behavior of graphene oxide by only adding one of the different type of oxygenated groups, entailing a reduced computational cost and time for the simulation. All these possibilities are shown below.

In **Figure 40**, it is represented a monolayer of Pristine graphene with a molecule of CO₂ showing that no interactions happened between the two components.

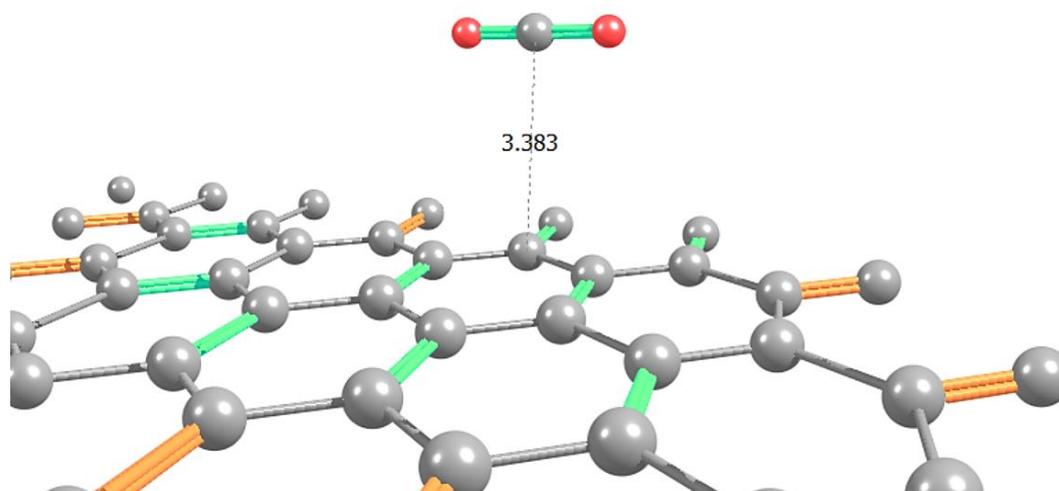


Figure 40 – Monolayer of graphene and CO₂ molecule without any interaction; 3.383 is the interatomic distance among the carbon dioxide and the graphene layer expressed in angstrom $1[\text{Å}]=10^{-10}[\text{m}]$.

In **Figure 41**, it is displayed a graphene layer bonded with an hydroxy group. The numbers are the interatomic distances among the different atoms in angstrom [Å].

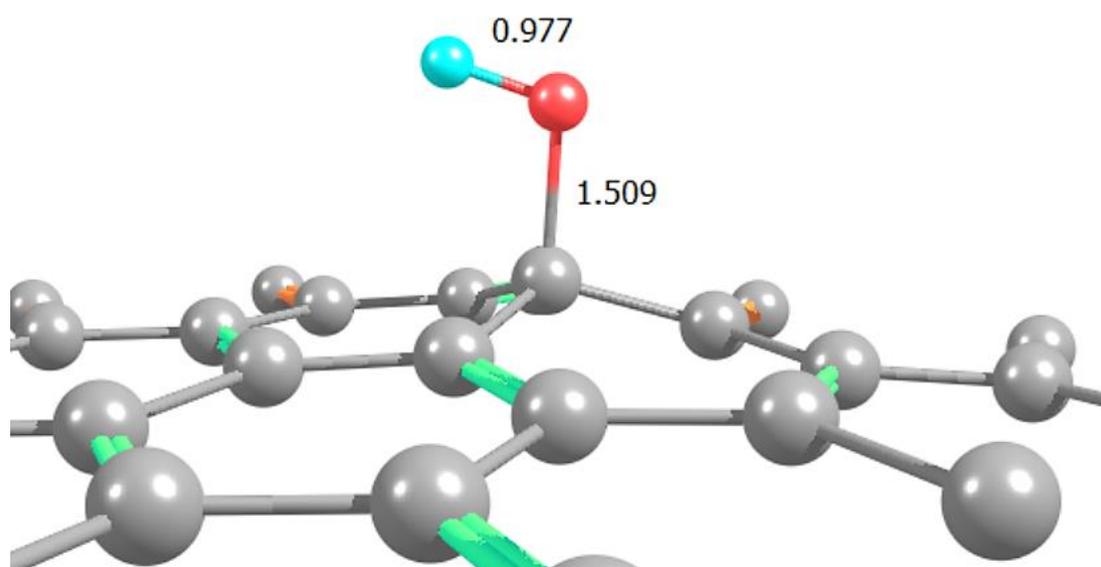


Figure 41 – Monolayer of graphene with a hydroxy group attached to it: the numbers represent the interatomic distance between each atoms expressed in angstrom $1[\text{Å}]=10^{-10}[\text{m}]$.

In **Figure 42** both epoxy and hydroxy groups are bonded with the monolayer of graphene, resulting in a better capacity of the entire molecule to interact with carbon dioxide.

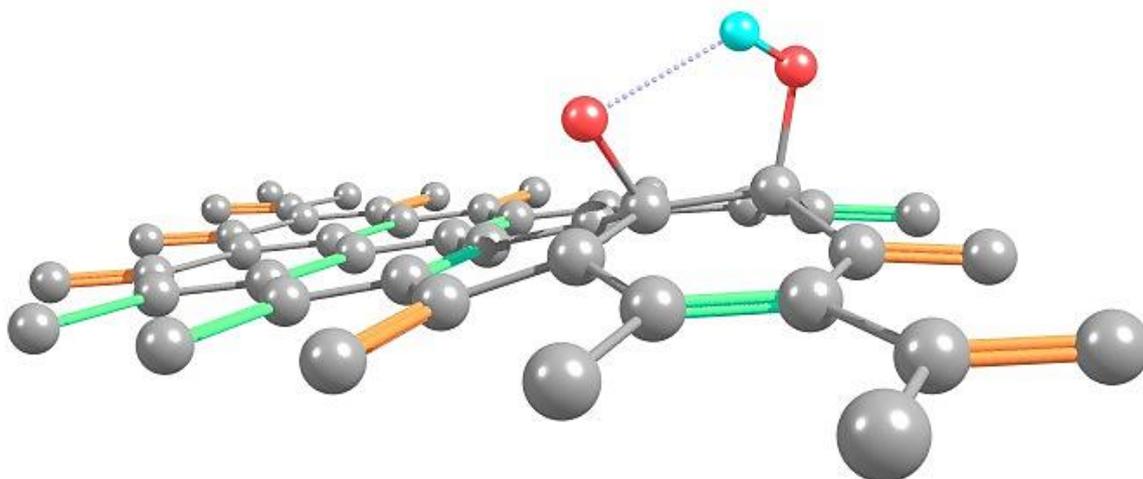


Figure 42 – Monolayer of graphene oxide composed by an epoxy and hydroxy group, with a little distortion of the crystal lattice.

In **Figure 43 (a)** and **Figure 43 (b)**, two different possibilities of bonds with a carbon dioxide molecule are reported. It should be highlighted how distorted the crystal lattice is in the second figure, entailing that the structure is not at its minimum energy.

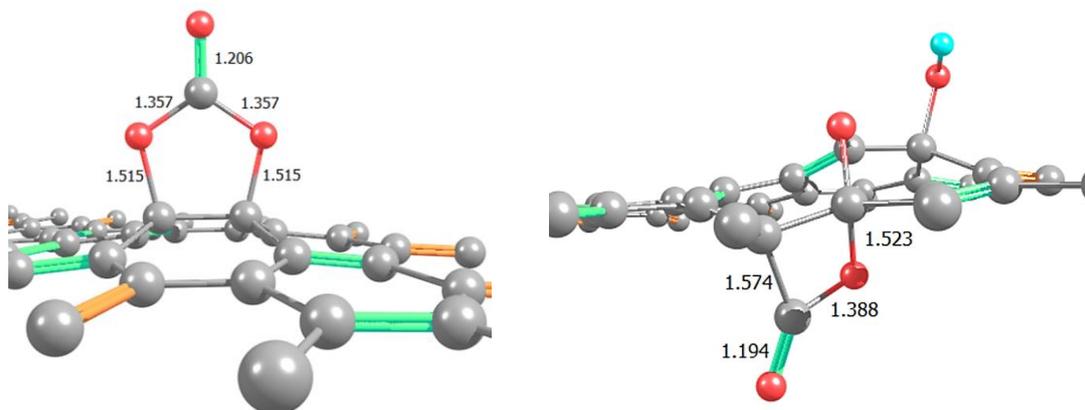


Figure 43 – Different possibilities of bonds between the carbon dioxide molecule and the oxygenated groups, with two distinct final configurations characterized by two different energy levels: the numbers represent the interatomic distance between each atoms expressed in angstrom $1[\text{Å}] = 10^{-10}[\text{m}]$.

At the end, it has been calculated the adsorption energies of Pristine graphene and graphene oxide:

Structure	Adsorption energy [eV]
Pristine Graphene	- 0.15
Graphene Oxide	- 0.72

Table 12 – Adsorption energy comparison for Pristine graphene and graphene oxide.

The results in **Table 12** are expected values.

It can be noticed that the adsorption energy of graphene oxide is almost 5 times bigger than the one of the other structure. Furthermore, the values are negative with means that there is interaction:

- Pristine graphene can have physisorption phenomena since its adsorption energy is lower in absolute value than 0.5 [eV],
- Graphene oxide will have chemisorption of the carbon dioxide molecules (stronger type of bond).

Therefore, it can be said that the results confirm what is said in literature, or better that, due to their different structures, graphene oxide tends to interact with external particles more than Pristine graphene.

6. EXPERIMENTAL ACTIVITIES

The following chapter is going to describe the whole procedures used in order to carry out each experimental activities before the final discussion on the obtained results.

After the theoretical research and the container design, the experimental activities represent the last component of the project chain. Thanks to this activities, it is possible to acquire all the data needed to understand if the idea is working, and if not, to identify the problem (it could be in the container set-up, in the sorbent, in the sensors, etc.). In this project, it has been performed tests in two different phases: the first to test the container airtightness and the second to acquire data. Consequently, the tests can be divided according to their target in:

1. Preliminary tests,
2. Experimental procedures.

6.1 PRELIMINARY TESTS

The aim of this part is to prove the airtightness of the container, which means that no leakages should be detected. The sensor is inserted into the vessel and let it work for at least 12 hours. Obviously, in this step only the CO₂ concentration is measured. After this time period, all the collected data are analyzed and the container has passed the test only if the data show a constant trend.

Before starting all the experiments, preliminary or acquisition tests, the sensor need to be exposed to the ambient air for more or less 5 hours in order to have the auto-calibration. Furthermore, it is fundamental to not forget this part otherwise the data acquisition might be compromised, and to not remove the power supply to the sensor or the auto-calibration process has to be repeated again.

6.2 EXPERIMENT PROCEDURES

The steps have been designed in order to have stationary experiments, meaning that the container conditions need to be stable. It is mandatory to follow exactly the correct order:

1. Closure of the container;
2. Stabilization of the ambient inside the container;
3. Injection of the liquid sorbent;
4. Wait for equilibrium;
5. Carbon dioxide injection;
6. The experiment will be conducted in 48-72 hours.

Once the membrane or the liquid sorbent is inserted into the vessel, it is very important that the CO₂ is carefully injected into the chamber at a magnitude of 5,000 [ppm]. Two different sensors have been employed in order to have a more reliable data acquisition. It also needs to be pointed out that one sensor acquired data every 10 seconds, while the second one every 60 seconds.

In the case in which a graphene sheet is employed to adsorb the carbon dioxide, the procedure changes. In this new situation, the solid sorbet will be in the vessel from the beginning. There are no possible ways to insert the graphene sheet inside the container without avoiding opening the cover, entailing a loss in the working concentration.

The sensors were connected to a device, named 'photon' (**Figure 44**), able to directly upload the acquired data, having therefore the possibility to get constant monitoring of the experiments.

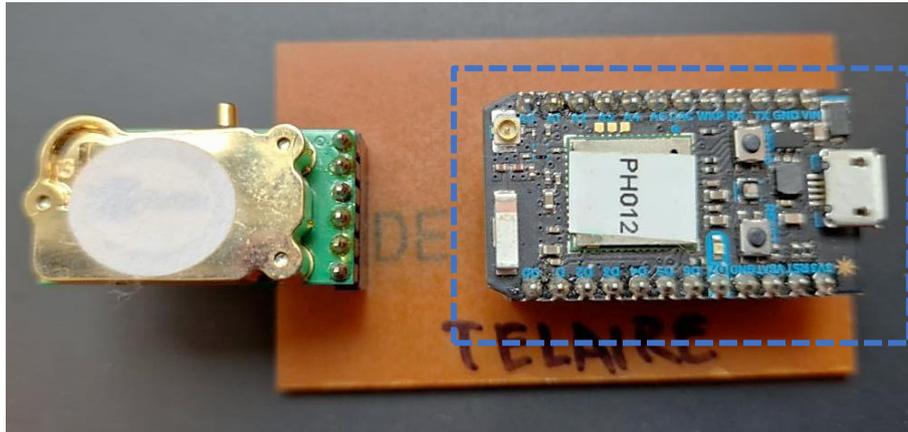


Figure 44 – Picture of the 'photon' microprocessor coupled with a Telaire T6371 CO₂ sensor used in the initial measurements.

At the end, all the acquired data have been processed and plotted in order to be analyzed. They are discussed in the next chapter.

7. RESULTS

This chapter represents the end of the experimental activity carried out at The University of Texas at Arlington in the Bozlar Nanoscience Lab. Now, all the acquired data are reported and commented, starting from the ones related to the initial leakage tests all the way to the final measurements performed with graphene oxide sheets. Thus, the chapter has been divided into two sections to separately discuss the two parts just mentioned.

However, before continuing with the results discussion, it needs to be pointed out that these are just initial measurements and a lot of work must be done. The main target, for now, has been to gain confidence with the topic, the built set-up and the materials used as sorbents. All the information about the future works is reported in the final chapter.

7.1 LEAKAGE TESTS

These tests have been crucial since the target is to have an airtight environment in order to have very accurate measurements. All leakages, even the smallest ones, impact the data acquisition entailing results not reliable at 100%.

The first two leakages test were not successful. In the first one (performed on October 26th, 2022), due to a not perfect closure of the cover, a drop of almost 1400 [ppm] has been detected after only 9 hours. Nonetheless, the new solution adopted to solve this issue was not good enough. In the second attempt (performed on October 28th, 2022), the container lost a quantity of almost 1000 [ppm] of carbon dioxide after 12 hours. The previous two quantities were too high if compared to the concentration of 5000 [ppm] injected to perform the tests.

Test	CO ₂ lost in ppm	Experiment duration in hours
October 26 th	1400	9
October 28 th	1000	12
November 3 rd	500	15
November 18 th	200	15

Table 13 – Performed leakage tests highlighting the ppm of CO₂ lost from the experimental container.

The third leakage test (performed on November 3rd, 2022) had better results. The graph reporting the CO₂ concentration against the time has been plotted in **Figure 45**. It has been chosen to report the error band due to the sensor accuracy that in this case is ± 30 [ppm]. In experimental data acquisitions, it is always fundamental to report error band since sensors cannot reproduce exactly the detected physical quantity. Moreover, two different sensors have been employed in the measurements, with the aim of detecting malfunctions in the acquisitions (this idea has been utilized in all the tests performed).

From the graph below, it is possible to notice that the trend is not perfectly horizontal, which means that the container still has few leaks. However, now the amount of CO₂ lost is almost three time smaller than the first test and two times the one in the second test, but it is not enough. Again, some adjustments to the container has been made and a new test performed.

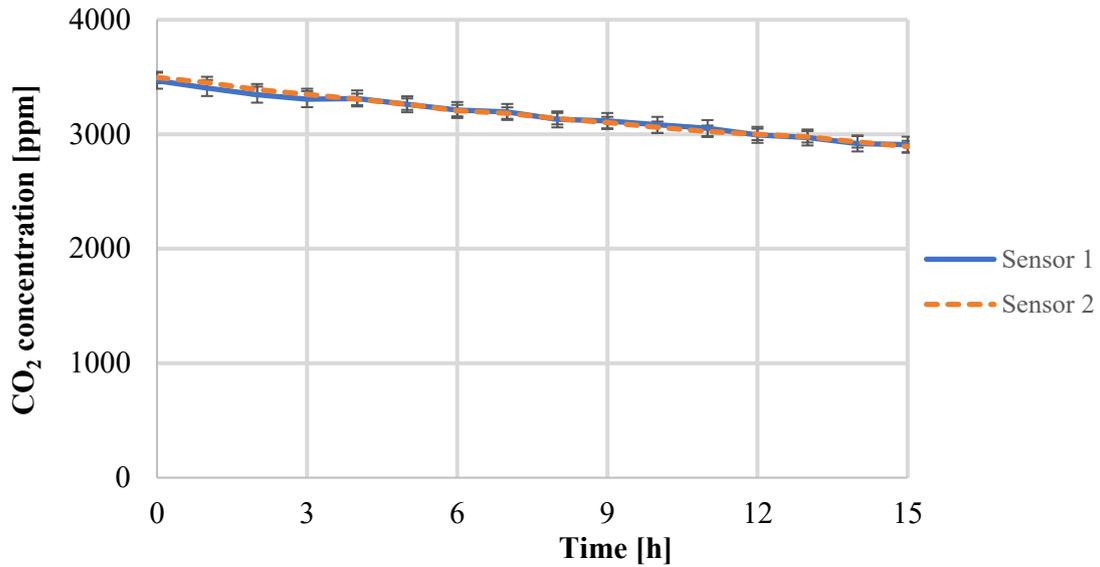


Figure 45 – Leakage test performed on November 3rd, 2022: measurements from two independent sensors are shown (orange and blue lines).

7.2 RESULTS FROM EXPERIMENTAL ACTIVITIES

As already mentioned in the ‘Project Overview’ (**Chapter 4.2**), the project was started a few years ago and some data are already available. Due to privacy and copyright reasons, it is not possible to show the exact data obtained by Professor Bozlar and his team from Princeton University. However, it has been possible to report an approximate trend, that is the one in **Figure 46**, which represent the starting point of the experimental activities. The outcomes indicate that the proposed sorbents can capture several thousands ppm of CO₂ in 24 hours under stationary diffusion conditions. Thus, at first, the data acquired needs to be compared to these results.

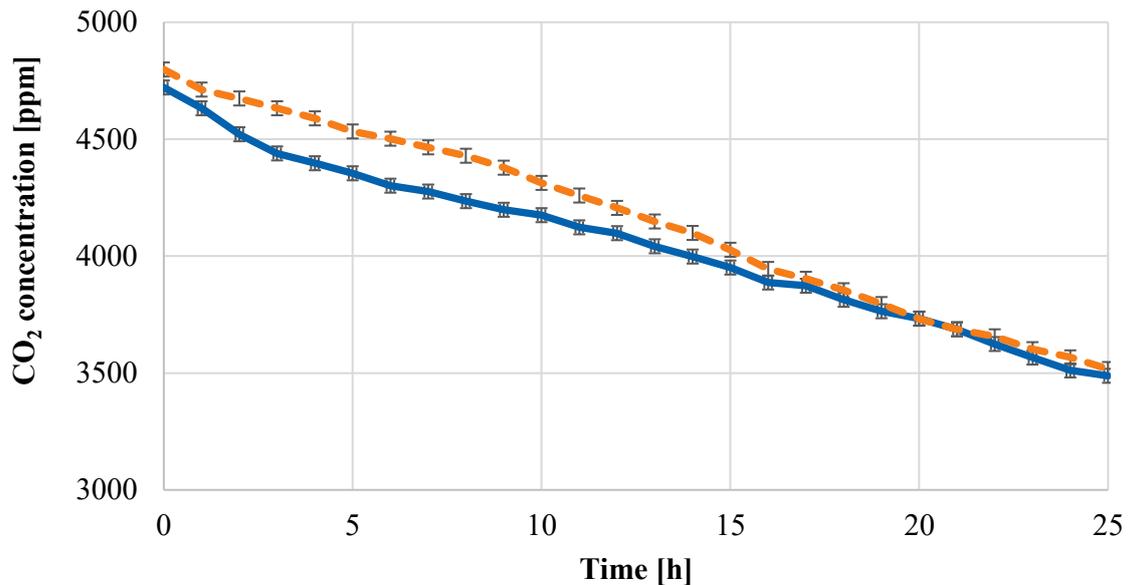


Figure 46 – Typical behavior of the CO₂ concentration in the presence of a sorbent: measurements from two independent sensors are shown (orange and blue lines).

Among the several materials available to capture carbon dioxide from the atmosphere, it has been chosen graphene oxide as a starting point (**Figure 47**).

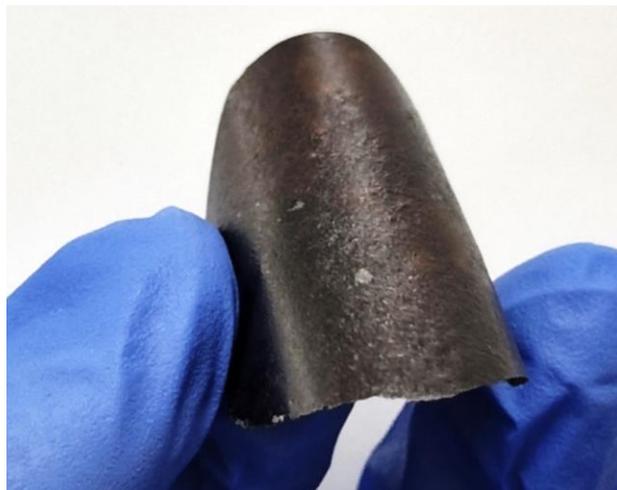


Figure 47 – Example of graphene oxide sheet used to adsorb carbon dioxide.

Nonetheless, it may be mentioned that different types of amino groups were included in the material. The basic idea is to let the different amino groups react with epoxy and/or hydroxy groups present in the graphene oxide in order to have a higher reactivity. In this way, the molecules of carbon dioxide are more prone to create stable and strong bonds with the solid sorbent. In **Figure 48** it is shown three different typologies of bonds that can be created between the amino group and the graphene oxide, according to Herrera-Alonso et al. [34].

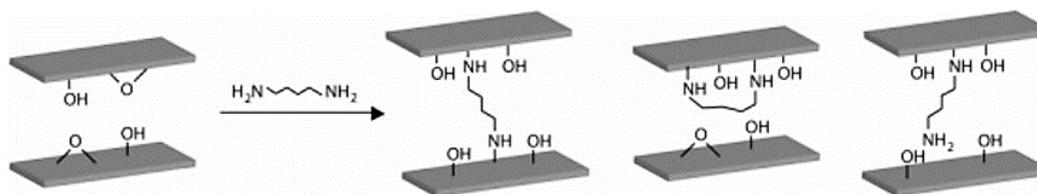


Figure 48 – Three different way of the amino group to chemically bond with the graphene oxide [34].

In order to test the efficiency of the amino group, different concentrations have been used in different graphene sheets: 1 [mg/ml] and 3 [mg/ml]. Nonetheless, these concentrations were not enough in order to have significant results.

8. CONCLUSIONS AND FUTURE WORK

In this work it has been highlighted that nowadays intense human activities resulted in growing environmental concerns, including alarming carbon dioxide (CO₂) emission levels. CO₂ is a major anthropogenic greenhouse gas which principally results from excessive combustion of fossil fuels. For this reason, emissions target has been set by governments worldwide to fight climate change. This is why the project proposes to focus on different aspects of CO₂ capture and management, from the perspectives of materials science and computational chemistry. The principal carbon capture technologies with main sorbents have been discussed. Among them, the project idea fall in the direct air capture technologies.

The first idea is to employ the prototype for indoor air quality. Hence, a vessel has been designed in order to accurately reproduce a closed environment and also to solve some issues detected in the previous prototype. Usually, in closed environments, CO₂ has the ability to negatively influence human health and productivity. Thus, our plan is to reduce the concentration of CO₂ in closed environments, to prevent decrease in people cognitive functions.

All the details related to the container design have been described: starting from the basic idea and the CAD design to the sensors utilized to detect carbon dioxide concentration inside it, to the manufacturing processes, to the optimal thickness evaluation and valves employed to inject CO₂ and liquid sorbents. This part involved knowledge about static structural mechanics, valves functions and characteristics, electronic and electrical circuits for the choice and connection of the sensors.

The idea of computational techniques is used to determine which material has the best affinity for CO₂. Then, the results effectiveness needs to be evaluated by means of experimental activities. However, due to lack of time, these techniques have been employed only to prove that they can work and it is possible to use them in the project for future work.

At the end, the whole procedures and test were explained and analyzed in order to have a good understanding of the experimental activities carried out.

It has been proved that the computational methods worked. We were able to verify, thanks to the evaluation of the adsorption energy, that Pristine graphene is a more stable structure than graphene oxide, that is what is reported in literature. Then, it has been proved that the container is almost airtight meaning that the leakages are almost negligible and are not going to compromise the data acquisition. Moreover, thanks to graphene oxide sheets bonded with amino groups are able to adsorb thousands of ppm of carbon dioxide.

The future work will consist of trying different amino groups bounded in the graphene oxide with different concentrations. Other nanomaterials like carbon black and metal organic frameworks (MOFs) are going to be tested as well as liquid sorbents such as piperazine. We will also try to include graphene oxide in piperazine and in liquid sorbents (polymers might be a possible material). The actual experiments are performed in stationary conditions and a possible future work could also be (this is for the case of a liquid sorbent) to try mixing the liquid during the entire process.

Acknowledgments

A huge thanks goes to Professor Marco Simonetti and Professor Michael Bozlar that gave me this wonderful opportunity in the United States, and probably the best experience of my life.

I am also thankful to my parents and my all family that supported me during these month in a place far far away from home.

Thanks to my friends for always believing in me and encouraging me.

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