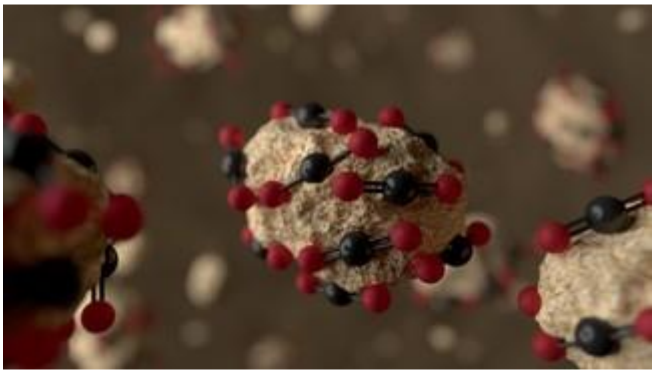

Carbon capture using wastes from marble industry

André João Ornelas Aguilar

Thesis to obtain the Master of Science Degree in

Chemical Engineering

Supervisor: Prof. Dra. Ana Paula Soares Vieira Dias (IST)

Examination Committee

Chairperson: Prof. Dr. José Manuel Félix Madeira Lopes
(IST)

Supervisor: Prof. Dra. Ana Paula Soares Vieira Dias (IST)

Members of the committee: Prof. Dr. João Fernando Pereira Gomes (ISEL)

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Abstract

The planet faces huge climate problems due to Greenhouse gases, specifically CO_2. In this context, and with the goal of solving this problem, CO_2 capture was studied in post-combustion conditions.

The geological sorbents studied were: marble, dolomite and limestone. The carbonation and decarbonation were followed using thermogravimetric analysis. The sorbent material references used were commercial CaO and $CaCO_3$.

Marble has the highest capture activity in the beginning, showing the habitual decay behavior, due to sinterization. The initial calcination temperature had a significant role in the sorbent stability. The calcinated sample at 850ºC was the most stable.

To minimize the sinterization the prepared sorbents were doped with Cerium and Nickel, hoping that the doping oxides reduced the contact between the formed grain boundaries of CaCO3, reducing the degradation of the sorbents properties. The doped sorbents revealed to be more stable.

It was studied the kinetics of carbonation, for the geological sorbents at temperature ranging between 600-750ºC. The obtained results revealed that marble possessed the highest activation energy, when compared with the other sorbents.

The results revealed that the wastes from the marble industry have potencial to be used in the capture of CO2, solving two environmental problems: What to do with marble wastes and the capture of CO2 in coal-fired power plants

Keywords: CO_2 capture, Carbonation, Geological Sorbents, Marble, Kinetics, Sinterization

Resumo

O mundo actual debate-se com graves problemas climáticos devido aos gases com efeito de estufa, nomeadamente o dióxido de carbono. Neste contexto, e com o objectivo de contribuir para a mitigação do problema, estudou-se a captura de CO_2 em condições de pós-combustão.

Estudaram-se sorventes de origem geológica: mármore, dolomite e calcário. A carbonatação e descarbonatação foram seguidas recorrendo à termogravimetria. Foram usados como materiais sorventes de referência CaO e $CaCO_3$ comerciais.

O mármore foi o sorvente com maior capacidade de captura inicial, mostrando o habitual decaimento devido à sinterização. A temperatura de calcinação inicial teve um papel preponderante na estabilidade do sorvente, assim send, a amostra calcinada a 850ºC foi a mais estável.

Para minimizar a sinterização prepararam-se sorventes dopados com cério e níquel, esperando que os óxidos dopantes reduzissem o contacto entre os limites de grão do $CaCO_3$ formado reduzindo assim a degradação das propriedades dos sorventes. Os sorventes dopados revelaram-se mais estáveis.

Estudou-se a cinética da carbonatação para os sorventes de origem geológica na gama de temperaturas 600-750ºC. Verificou-se que o sorvente derivado do mármore apresentava uma energia de activação superior à dos restantes sorventes.

Os resultados mostraram que os desperdícios de mármore, resultantes das indústrias de pedras ornamentais, tem potencialidades para serem usados na captura de CO_2 permitindo a resolução de dois problemas ambientais: o que fazer com os desperdícios de mármore e a captura de CO_2 em centrais termoeléctricas.

Palavras-Chave: Captura de CO_2 **,** Carbonatação, Cinética, Mármore, Sinterização, Sorventes

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CC - Carrying Capacity ($g_{CO2}/g_{sorbent}$)

E_{aux} - Auxiliary energy in a coal-fired power plant

E_{gross} - Generated electricity from the turbines in a coal-fired power plant

E_{net} - Domestic consumption of the electricity in a coal-fired power plant

k - kinetic constant of the carbonation reaction (s^{-1})

$m_{adsorbed\ CO2}$ - mass of CO2 adsorbed in the Nth cycle (mg)

$m_{fresh\ sorbent}$ - mass of the sorbent (mg)

MM_{CaO} – Molar weight of CaO (g/mol)

MM_{CO2} - Molar weight of CO_2 (g/mol)

NO_x – Mono-nitrogen oxides

P_{CO2} - Work pressure (Pa)

$P_{CO2,\ eq}$ - Equilibrium pressure at temperature work (atm)

P_T - Atmospheric Pressura (Pa)

$Q_{v,CO2}$ – CO_2 flow rate in the gas stream (L/h)

$Q_{v,N2}$ – N_2 flow rate in the gas stream (L/h)

SO_x – Sulphur oxides

T - Absolute temperature (K)

X - Conversion of CaO

Xu - Ultimate conversion of CaO

y_{CO2} – CO_2 molar fraction in the gas stream

ΔE - Energy Penalty

η_{CCS} - Efficency of a coal-fired power plant with CCS

$\eta_{net,CCS}$ - Net efficency of a coal-fired power plant with CCS

$\eta_{net,ref}$ - Net efficency of a coal-fired power plant without CCS

η_{ref} - Efficency of a coal-fired power plant

List of Acronyms

BET – Brunauer–Emmett–Teller theory – Determination of specific surface area

CCS – Carbon Capture and Storage

CD-CA-14 – Cadomin limestone – Commercial calcium aluminate cement

EGR – Enhanced gas recovery

EOR – Enhanced oil recovery

FGD – Flue Gas Desulphurizer

FTIR – Fourier Transform Infrared Spectroscopy

GHG – Greenhouse gases

IGCC – Integrated Gasification Combined Cycle

IL's – Ionic Liquids

KT-CA-14 – Katowice limestone – Commercial calcium aluminate cement

LHV – Low heating value

MEA – Monoethanolamine

PEI – Polyethyleneimine

PSA – Pressure swing adsorption

SEM – Scanning Electron Microscope

TEPA – Tetraethylenepentamine

TSA – Temperature swing adsorption

XRD – X-ray diffraction

1. Introduction

1.1 Thesis Scope and Motivation

There is not a single doubt about it, the succession of climate events indicate that the whole planet is in danger, and if nothing is done then mankind could face the worst consequences of all of humanity's history.

Firstly, some analysis of what is really contributing to this massive change has to be done. First of all, NASA, created a model to test the assumptions and causes of global warming, as shown in figure 1:

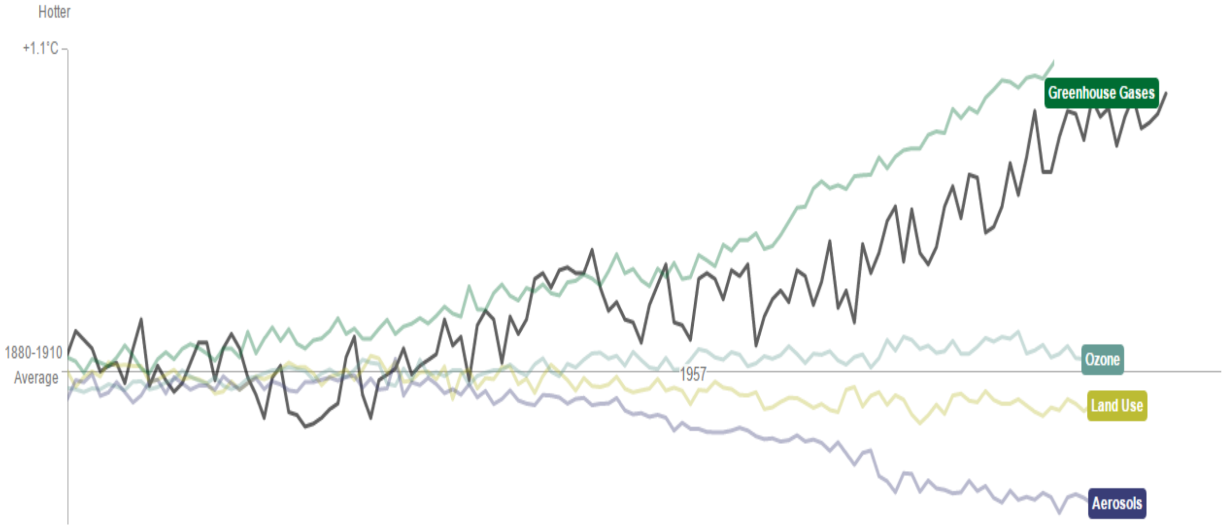


Figure 1 – NASA model: Variation of temperature increasing through the time (1880-2005): Black – Observed temperature increasing; Grey – Influence of Ozone; Blue – Influence of aerosols; Light Brown – Influence of excessive land use [1]

These four causes are the major contributors to the increasing temperatures and they are all referred as human factors. As shown in figure 1, the ozone, the excessive land use, and the aerosols do not have that much influence when they are compared with greenhouse gases. Although the aerosols and the excessive land usage contributed to lower the temperature, the sum of all factors dictate the alarming increase of the global average temperature. And for that reason, all the efforts should be focused on reducing the CO_2 emissions.

According to IPCC (Intergovernmental Panel to Climate Change), the rising of the average global temperature in more than 2ºC could have catastrophic consequences, such as floods, extreme heat waves, and so on. For this reason, the mission is to reduce this rising temperature between now and

2100. To achieve that goal, the GHG (Greenhouse Gases) should be reduced by between 40% and 70% until 2050, and carbon neutrality must be achieved until the end of the century, at least. [2]

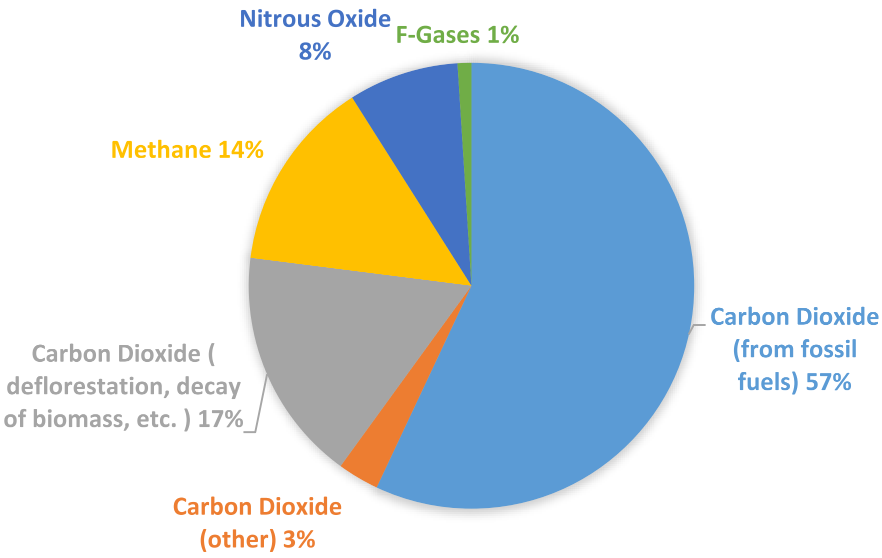


Figure 2 - Greenhouse Gas emissions from human activities in 2007, adapted from [3]

As mentioned above, almost 80% of GHG emissions from human activities are CO_2, and these emissions are the main problem nowadays. As shown in figure 2, more than half of GHG are from the extensive usage of fossil fuel [3], and it seems not to stop for the next 20-30 years. Countries like the USA and China contribute with more than 40% for the global emissions [3] and since the world population is estimated to grow exponentially, rise the demand of the fossil fuels is expected too. Therefore, if nothing is done, the emissions of GHG will increase, and that could lead to a series of catastrophic events.

The CO_2 atmospheric concentration has been followed over the past fifty years, as shown in figure below:

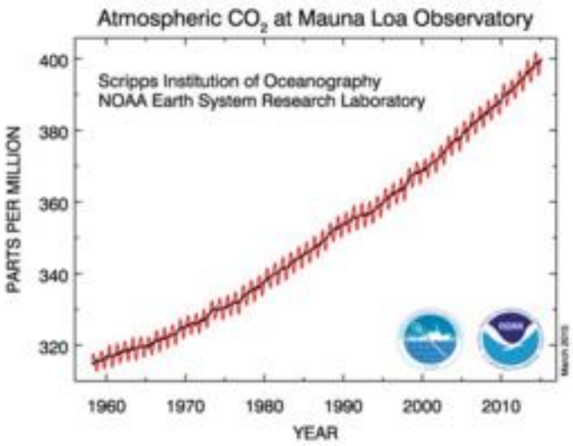


Figure 3 – Evolution of the CO_2 concentration (ppm) in the atmosphere, from 1960 to today, measured in the Manua Loa observatory [4]

By the year 1958, Keeling started measuring the CO_2 atmospheric concentration and the obtained value was 313 ppm [4]. But through the years Keeling kept registering these values and started to become more concerned, because the concentration kept rising at fast rate, breaking the carbon cycle, which means, that the CO_2 that was release from anthropogenic sources was higher than the planet could take. Looking carefully to figure 3, it is easy to understand that the concentration of the atmospheric CO_2 is above the 400 ppm, value way above the normal ones that have been contributing for these massive changes.

Because all the reasons mentioned, many technologies have been studied and developed in order to control all of the emissions caused by human activities. Amongst these, one shows great potential with dealing with these massive emissions, which is the Carbon Capture and Storage (CCS), which relies in the capture, transport and sequestration of CO_2 [10] and could deal with 80-90% of the emissions. For this reason, this subject will be scrutinized.

1.2 Objective

The main objective of this work is to evaluate the performance of different sorbents, for the capture of CO_2 from marble wastes and other geological sources that exists in Portugal. Through a series of experiments, it will be studied different reaction temperatures and CO_2 molar fractions and the respective calcination temperature of the samples in order to perform long cycles, to come closer to perform the capture under industrial conditions. The objective, through different experiments, is to improve the capture of CO_2 and to optimize these parameters.

Also, the kinetic of the carbonation reaction of the calcium looping cycle will be studied, in order to obtain some kinetic constants and activation energies to compare with the literature and to understand what could possibly be the main issues of this cycle.

1.3 Thesis Outline

There can be found five main chapters in this master thesis. In chapter one it is discussed the main issues of CO_2 emissions and why it is important to find a solution to this phenomena.

In chapter two it is presented an extensive literature review about the technologies relating to the capture of CO_2. To deconstruct this entire subject it is mentioned the necessity of the Carbon Capture and Storage and then it is focused on the existent technologies. First, it mentions the three main ways to capture CO_2, but since this thesis focus on post-combustion only this point will be emphasized. For the post-combustion technologies there is a brief explanation about all the existent technologies and then they are compared between them, to evaluate the potential of each type of technology. It is done a briefing about the after of capturing CO_2, since the storage and transport of CO_2 could lead to other thesis. It is studied the energy penalty of the most used technologies nowadays. Then, it is briefed the characterization of the used sorbents for this purpose and it is focused in detail the system used for this entire master thesis, the calcium looping cycle, where it is mentioned the most important issues about this technology. Finally, since the main source of the experiments is marble, it is done a briefing about the marble industry in Portugal.

For chapter three, it is shown all the materials used to achieve the purpose of this thesis, and also it is mentioned the main technique used to study the performance of the sorbents, the thermogravimetric analysis (TGA).

Initially, for the fourth chapter, it is applied a kinetic model to the obtained data for the different sorbents and then it is focused on the CO_2 adsorption tests.

Finally, for chapter five, it is presented the principal results and some conclusions and criticisms to the entire work. Some guidelines for future works are also mentioned.

2 Literature Review

The United Nations [5] estimates that the world population will reach 9 billion by 2040. Consequently, the energy demand will increase 37% by 2040 [7], hence increasing the consumption of fossil fuels. Therefore, it will contribute to generate even more greenhouse gases, especially the CO_2. These emissions have a negative effect in the atmosphere and contributes significantly to global warming.

Having said that, it is known that, in the future, fossil fuels will continue to be mankind’s main power source, generating even more CO_2.

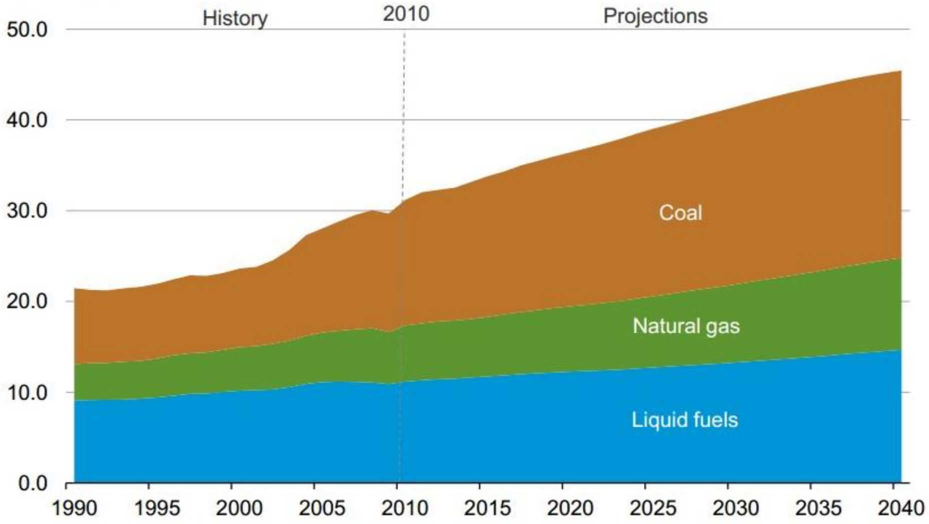


Figure 4 - World energy-related carbon dioxide emissions by fuel billion metric tons [4].

According to Figure 4, it is possible to see that coal will continue to be the main source of CO_2 emissions. In order to reverse this tendency, some efforts have been made by the EU-15, where Portugal is included [8], to decrease these emissions. The main target for 2020 is to reduce by 20% these emissions, but it seems it’s not going to be possible to reach it. Looking at this scenario, the scientific community, since the beginning of the century, have been working in technologies, such as carbon capture and storage (CCS), in order to be able to use these types of fuels without compromising the environment and the future of the planet. This thesis will focus on the main advantages of these types of technology, and it is going to be discussed, in detail, the post-combustion system, since it is the best way to solve the problem proposed. Furthermore, it will give special attention to the sintering of the particles, because it is the main problem nowadays, which does not let this type of technologies be effective. And, finally, it will be discussed the problem of the “Energy Penalty “of the CCS technologies, which composes a barrier that compromises the energy efficiency. All of these subjects are about to be discussed below.

2.1 Carbon Capture and Storage (CCS)

These types of technologies could have an important role in reducing CO_2 emissions. Currently there are some that are capable of capturing and reducing by 80-90% the emissions from power plants that burn fossil fuels [9].

In terms of operational steps, the CCS technology comprises three steps:

- Capture of CO_2 from power plants
- Transport and compression of CO_2 via pipeline
- Underground injection and geologic sequestration (storage) of CO_2 into deep underground rock formations

2.1.1 CO_2 capture

In order to complete the cycle of the CCS, it is important to have an effective capturing process of the exhaust gases of the power plants. The main step of this operation consists in capturing the CO_2 that is diluted in the vapor stream, which contains essentially water vapor, nitrogen and CO_2. In order to obtain a pure stream with CO_2, only, it is necessary to separate all of the compounds. This CO_2 must be suitable, for further storage. [9]

The capture of CO_2 is subdivided in three major groups:

- Post-combustion
- Pre-combustion
- Oxyfuel-combustion

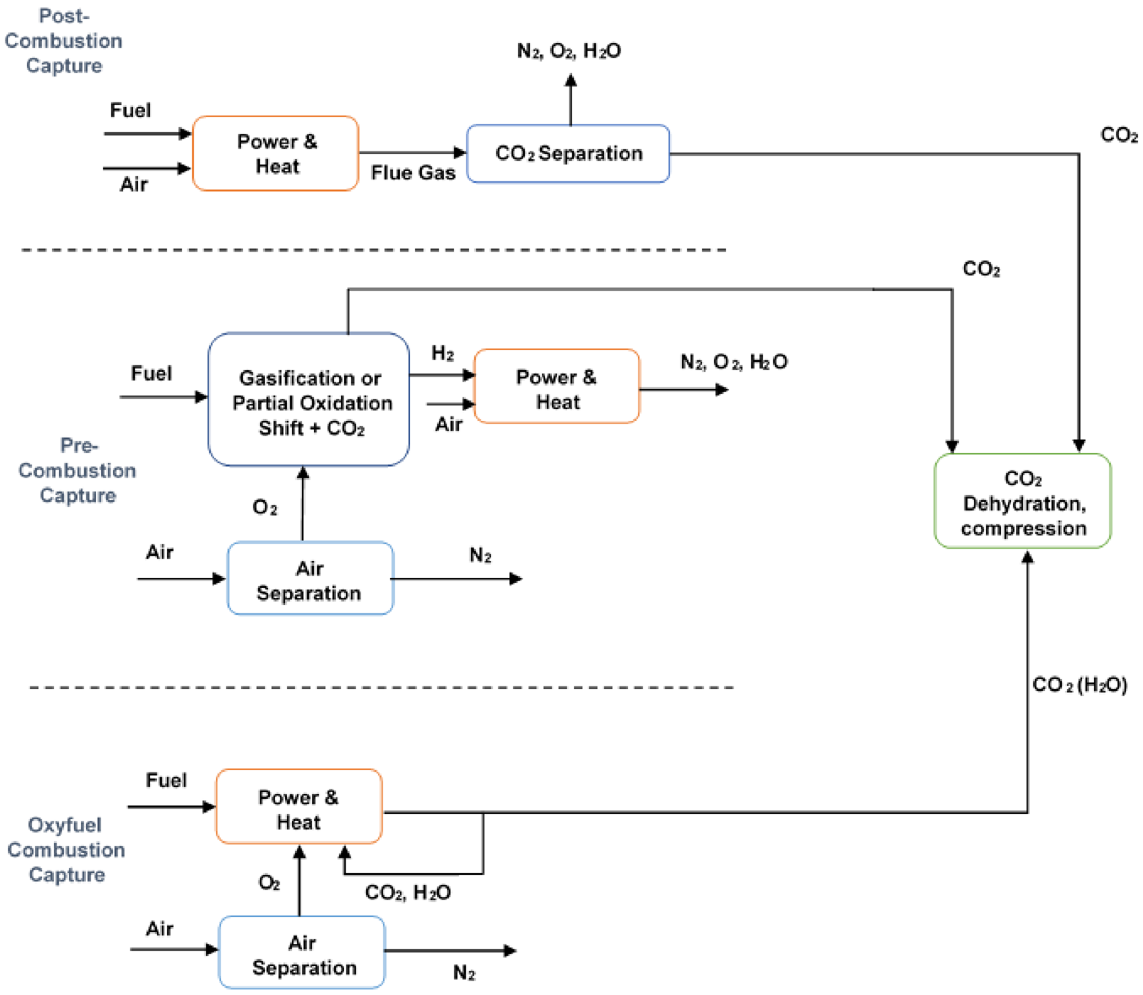


Figure 5 - Overview of CO2 capture approaches, adapted from [7]

According to figure 5, it is possible to understand that, the main goal is to obtain a high-pure CO_2 stream for further transportation and storage. For that purpose, it will be focused in detail the post-combustion, since it is the most common and easiest to apply to industrial conditions.

2.1.2 Pre-combustion

This method of capturing, consists in removing the CO_2 from the fuel (e.g. fossil fuels), before the combustion take place. The first step consists in steam reforming, where the fuel is reformed in syngas, producing carbon monoxide (CO) and hydrogen (H_2). This reaction occurs at high temperatures. After this step the syngas reacts with steam (H_2O) to generate CO_2 and more H_2 and CO_2. The CO_2 is separated of H_2 and is compressed and stored. The H_2 generated by these reactions can be used as the fuel in a gas turbine, to generate power; transport fuel or other purposes. [11]

This process is more efficient than the post-combustion setups, because the waste gas has a higher pressure, a high CO_2 concentration and the separation is easier, when these systems are compared. On the other hand the reactions that occur in pre-combustion, require technologies that are not as accessible as the post-combustion ones. [12]

The method illustrated in figure 5 is called IGCC (Integrated Gasification Combined Cycle), because CO_2 is captured before the syngas is used to burn and produce power. [13]

2.1.3 Oxyfuel-combustion

Oxyfuel-combustion uses pure oxygen (O_2), after cryogenic distillation of air, to burn a fuel. When the fuel is burned it generates a stream with steam and almost pure CO_2. After that, the stream condensates, leaving CO_2 for compression and further transport and storage. [11]

It has the highest efficiency of the three methods, almost 100%. But sometimes the stream is not suitable to compress after the condensation, due to presence of gases such as: SO_x, NO_x. The main causes could be the oxygen feed or an air leakage. These contaminants should be removed completely in order to avoid environmental problems in the storage of CO_2 in deep saline reservoirs. [8]

Although this process is highly efficient, the cryogenic distillation requires high energy consumption due to the high pressures and very low temperatures. Nowadays this process has industrial applications, but is not the one that is mostly used. [11]

2.1.4 Post-combustion

The post-combustion capture is the technology which is mostly used in the industry, since it is easier to retrofit into the existent facilities. This means that is possible to develop and upgrade the process without interfering in the power plant’s fundamentals. On the other hand, the major disadvantage found in facilities that use post-combustion technologies is the energy penalty associated with it, subject that will be discussed further on. [14] Having said this, it is easy to understand that these technologies are being developed at high speed in order to stop global warming.

The main goal is to produce a stream of CO_2, free from acidic gases and other gases such as NO_x and SO_x. [15] For this purpose there are many routes to perform it, such as:

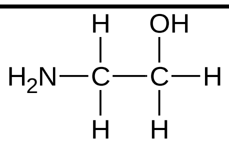
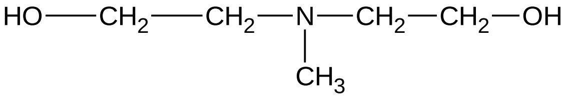
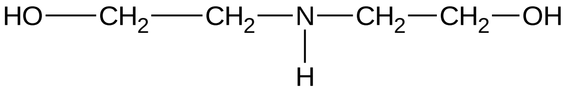
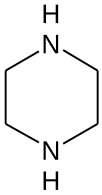
- Chemical absorption
- Adsorption processes
- Cryogenic separation
- Membrane-based separation using thin polymeric films
- Biological capture using Microbial/ Algal Systems [15,21]

Chemical absorption is the most wildly-spread technology in terms of industrial application, for capturing CO_2. It refers to a gas-liquid contacting and separating equipment. The lean solution contacts in countercurrent in the gas stream, to absorb the components in the gaseous phase which enters in the bottom of the absorber. After the solution passes through the absorber it can be called a rich solvent, because it contains the desired components, as shown in fig.6.

In the desorber the solution will be recovered. The hot rich solvent enters in the top of desorber, to recover the CO_2. This column could have structure packing or horizontal trays. The main goal of the partial condenser is to obtain a stream of CO_2 as pure as possible, and to assure the reflux to the column. In terms of the reboiler, the goal is to have a high temperature, for the steam to serve as a stripper fluid and most of all, to break the chemical bonds formed in the absorber column. [17]

The process shown in figure 6, uses primary, secondary and tertiary amines to capture CO_2. The most common ones are Monoethanolamine (MEA) and Methyldiethanolamine (MDEA). For this purpose, these new technologies use a mixture of amines, but their formulation is not known. In Table 1 is summarized the main amines used:

Table 1 – Chemical Structure of used amines for CCS [15]

Amine	Acronym	Structure
Monoethanolamine	MEA	 $H_2N-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-H$
Methyldiethanolamine	MDEA	 $HO-CH_2-CH_2-\underset{CH_3}{N}-CH_2-CH_2-OH$
Diethanolamine	DEA	 $HO-CH_2-CH_2-\underset{H}{N}-CH_2-CH_2-OH$
Piperazine	PIPA	

These amines are recycled through the process, but a small part of them are released into the atmosphere or degraded. These emissions have strict rules due to their toxicity and danger. Some of the released chemicals are: aldehydes and nitrosamines. Furthermore, MEA is highly corrosive and the corrosion rate depends on the amount of O2 used. At an industrial scale, it is possible to reduce CO_2 emissions by 85%, by using this type of technology. [17, 18]

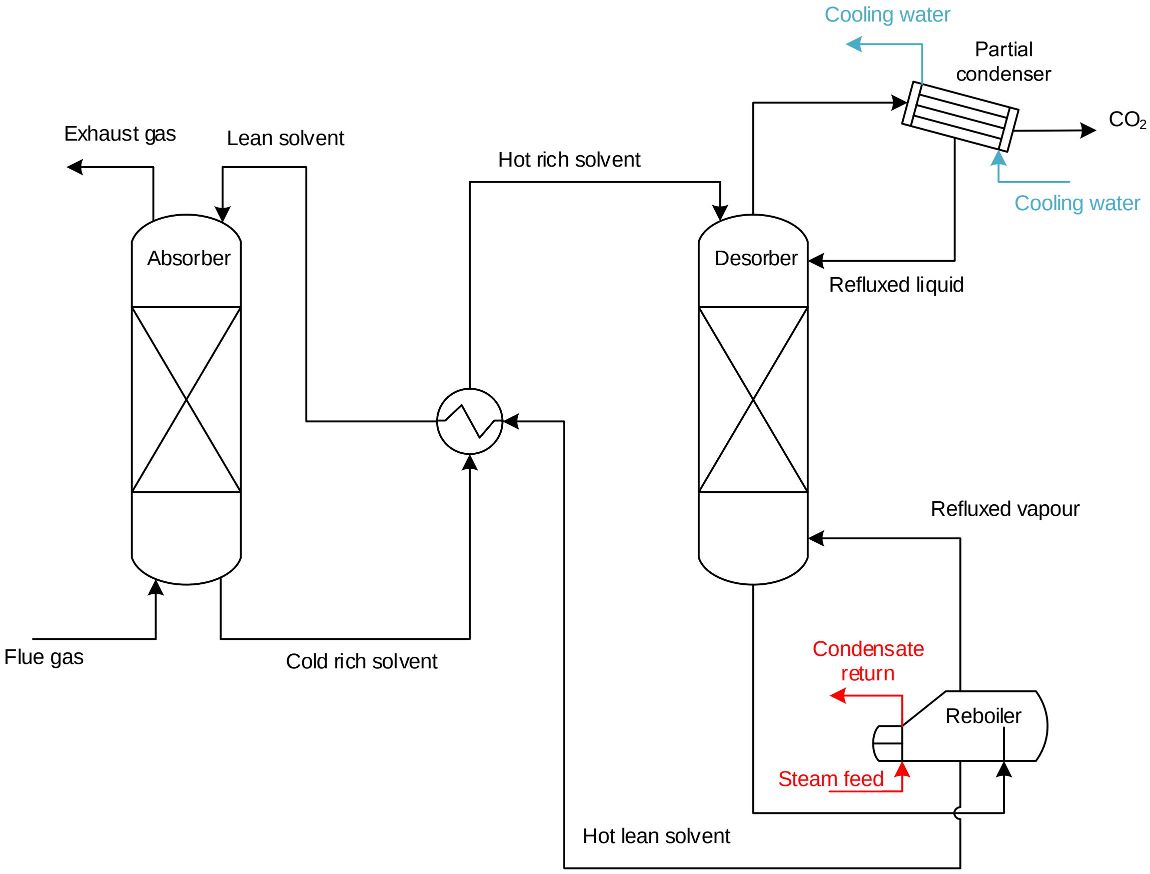
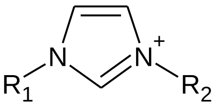
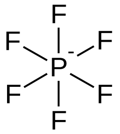
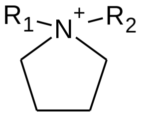
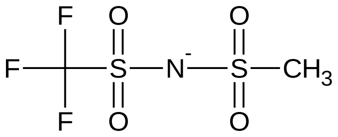
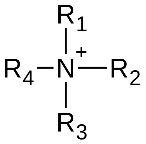
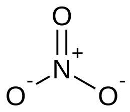


Figure 6 – Chemical absorption process for amine based CO_2 capture, adapted from [14]

Recently, a new technology - Ionic Liquids (ILs) - has been in development. It has a great potential in terms of chemical absorption. Inside ILs there are two distinct groups: organic cations an organic/inorganic anions, as shown on Table 2. It possesses a high chemical and thermal stability, low vapor pressure and they are excellent solvents for a range of polar and non-polar compounds. It is easier to separate CO_2 from ILs, because ILs are energetically favorable. Due to the low vapor pressure, it is possible to achieve high capture efficiencies and it becomes possible to recover and re-use ILs without loses, during the process. Since ILs are chemically and thermally stable, they only decompose at a high temperature (T>300°C), avoiding side reactions and equipment corrosion. Although it is a promising technology, these liquids are very expensive and require advanced technologies to develop it. [13, 19, 20].

Table 2 - Structure of Ionic Liquids, cations and anions

Cation	Structure	Anion	Structure
Imidazolium		Hexafluorophosphate	
Pyrrolidinium		Bis(trifluorophoshate)imide	
Quaternary Ammonium		Nitrate	

To obtain CO_2, through separation of the exhaust gases, it could be used Membranes. These are porous and selective material, as shown in Figure 7. The separation driving force is the partial pressure through the membrane. It is reached by the compression of the flue gas, by one of the sides of the material or by creating vacuum in the opposite side. Selectivity and permeability are the two main parameters to evaluate the membrane. The selectivity can be determined by the CO_2 output over the main composing feed gas. When the membrane has high selectivity it means that is possible to achieve a pure stream of CO_2. Permeability refers to a carried gas quantity given a differential pressure. This parameter allows to determinate the membrane superficial area, given an amount of CO_2.

Comparing with existing technologies, it does not need the use of steam and chemical reactants to perform the separation. However, one of the biggest challenges is to keep a high selectivity, considering that CO_2 concentration and pressure are very low. Besides, the feed gas needs a pre-treatment, several membranes to perform the desired separation and the recycle of the gaseous stream. These membranes are build using polymers such as polyamides and polyacetylenes [20, 21].

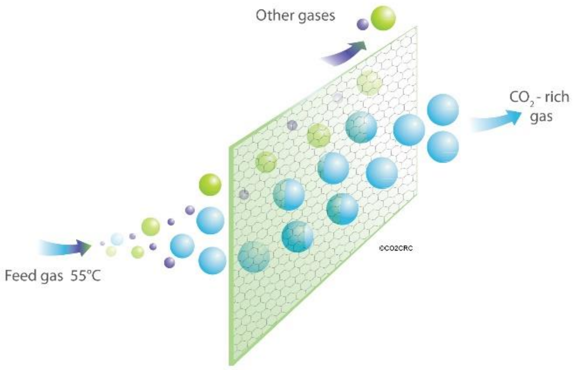


Figure 7 – CO_2 capture using polymeric membranes. [22]

The **Cryogenic Distillation** involves, most of all, the separation of these compounds: H_2, N_2, O_2, Ar, CH_4 and CO_2. According to Figure 8, it has to pass through several stages of compression, cooling and further separation in order to promote the final distillation. Higher temperatures require more energy to separate CO_2 efficiently, that's why cryogenic distillation, at high pressure is the best way to perform it. This method allows a stream with 99% of purity and guarantees a CO_2 recovery of 90%, from all the mixed gases, for a temperature of 22.5°C and a pressure of 60 bar for the distillation column, allowing it for use and storage. Furthermore, the energy penalty associated is the lowest, when compared with other ways to perform the cryogenic distillation. Although it presents a high selectivity, by using this method, the operational costs are almost unbearable, making the cryogenic distillation one of the least used, for CO_2 capture. [26]

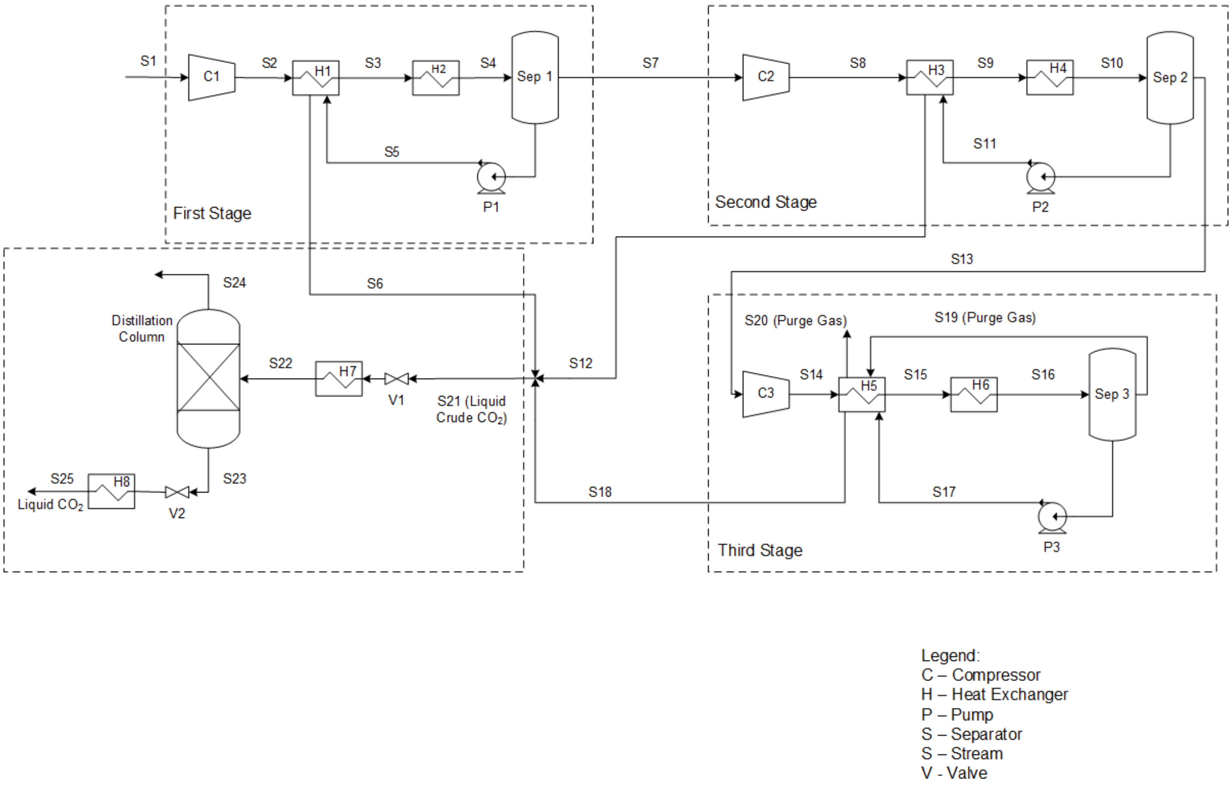


Figure 8 – Scheme of a cryogenic distillation, adapted from [23]

The **Biological** way of capturing CO_2 is sustainable and renewable because it makes use of photosynthetic microbes. They have the ability to capture the sunlight in order to use that energy to store CO_2 in a useful way for the anthropogenic activities, such as bio-fuels, medicines and food additives.

One of the main resources to make it useful is to use algae. These ones are capable of storing more biomass that the microbes, for further use and most of all they produce useful molecules for industrial synthesis, for many purposes. However, it still has some scale-up problems that have to be overcome. About 300 species are suitable for culture and use in oceanic environments, for direct capture of CO_2, from the burning of fossil fuels. To perform it, there are two types of microalgae culture that can be used: open ponds and photobioreators. The big issue involving these two is water usage, and it is limited by the annual sun irradiation and the environment. Although it has to have a moderate environment to work, there are many water losses through evaporation which complicates water replacement at the desirable rate. Making this process not that efficient. [24]

The **adsorption processes** are related to gas-solid processes, where the solid surface, adsorbs the CO_2, through a change of temperature or pressure, regenerating the surface (sorbent), after. These regeneration processes could be through TSA (Temperature Swing Adsorption), by increasing the temperature or by PSA (Pressure Swing Adsorption), by lowering the pressure, as shown in figure 9.

In terms of the materials, it could be used materials such as microporous, mesoporous, zeolites, activated carbon, MOF's (Metal-organic Frameworks) and the main one, in this thesis, carbonaceous materials (marble and derivatives). These ones are capable of capturing CO_2 and SO_2 at the same time, and some of them have low cost regeneration. Furthermore, they are accessible (e.g. Marble) and cheap. Although they have commercial potential, these materials are exposed to multiple regenerations through the cycles, which decreases the carrying capacity (capture efficiency) and subsequently their regeneration. Therefore, the main focus is the thermal stability and sintering of the particles, in order to overcome these problems.

Furthermore, the released heat in exothermic reactions is very high, in solid systems, which creates operational problems that should be solved before the scale-up. So, if it is desired to apply this type of technology at an industrial scale, it should be controllable and stable. [16, 20, 25, 26]

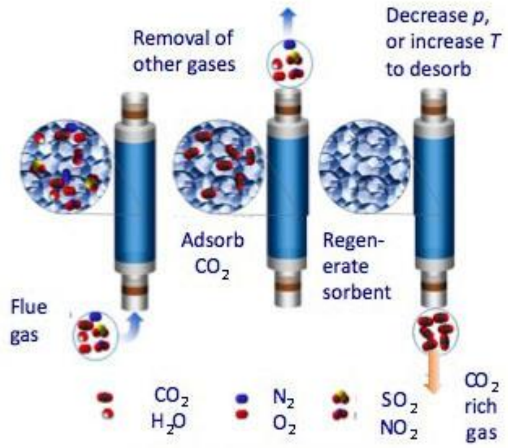


Figure 9 - Regeneration through TSA and PSA, in adsorption processes. [27]

In the table below (table 3) it is summarized the most important technologies and their advantages/disadvantages mention over this topic.

Table 3 - An overview of Post-Combustion technologies, adapted from [10, 24, 25, 28]

Post-Combustion Technology	Application Level	Strengths	Weaknesses	Commercialization Potential
Alkanolamines (Primary, Secondary and Tertiary	Commercial	- Tested Capability - Can be retrofitted easily	- Corrosion - Chemical degradation	Very High
NH_3 & Derivatives (Chilled)	Pilot Scale	- High CO_2 Capacity - Simultaneous SO_x and NO_x reaction to form useful byproducts	- Higher volatility - Higher regeneration losses	High
Ionic Liquids	Reasearch	- High CO_2 Solubility - No gas cooling needed	- High material cost - Higher viscosity	Low
Zeolites	Laboratory	- Capture CO_2 and SO_2 - Enhanced CO_2 adsorption	- High regeneration Temperature - Lower adsorption capacity	Moderate
Sodium Carbonate (Na_2CO_3)	Pilot Scale (Power Plant)	- Low capital& Operating costs - 90% CO_2 Removal	- Thermal instability	Moderate
Calcium Carbonate& Derivatives	Pilot Scale	- Versatile Process & Materials - Thermal, chemical, and mechanical stabilities under extensive cycling	- Limited capture at high pressure - Low selectivity	Moderate
MOF (Metal-Organic Frameworks)	Laboratory	- Low regenerate costs - High CO_2 capture potential	- Thermal stability to be established - Active at higher pressure	Low
Polymeric Membranes (Thin Film)	Bench Scale (1 m^2 area)	- No phase changes - Improved permeability/ selectivity	- Degradation susceptibility - Affected by flue gas impurities	Moderately high
Inorganic Membranes (Porous& Nonporous)	Laboratory	- High temperature stability	- High operation temperature - Adverse effect of steam	Low
Cryogenic Distillation	Pilot Scale	- 90% CO_2 Removal - High efficiency capture	- Operational costs	Moderate
Biological Capture	Laboratory	- Direct capture from the sources - Ability to store CO_2 at useful way	-Scale-up problems -Too many losses by evaporation	Low

2.1.5 CO_2 Transport

The CO_2 transport is done by the three states of the matter: solid, gaseous and liquid. Commercially, it is only done by liquid and gaseous phase, making use of pipelines and industrial ships. The solidification of CO_2 requires a high amount of energy, that's why is not common to transport in that state.

At atmospheric pressure the transported gas occupies great volume in the vessels. That's why it is compressed, to a pressure between 100 and 800 bar, via pipeline. In terms of legislation, the CO_2 has to be 95% (V/V) pure and should contain a small percentage of N_2. To transport CO_2 by ship, the gas has to be liquefied, to be according to the legislation. In the liquid state, it can be transported by tank truck or railways, but is not a good option due to great amount of CO_2 to transport.

To answer to all capture necessities, the transport infrastructures of CO_2 have to be bigger and have to have an extended network, comparing, with the ones that exist nowadays. In terms of associated costs, compression and liquefaction are the most expensive ones. However, the most economical (distance covered) and safest transport vehicle is by ship, although it has the issues mentioned above. [10]

2.1.6 CO_2 Storage

The third and last stage of this cycle is CO_2 storage. This stage is limited by the storage site and by storage conditions. According to figure 10, the main ways to store CO_2, geologicaly, are: Deep saline aquifers, Unmineable coal beds and Depleted oil and gas reservoirs:

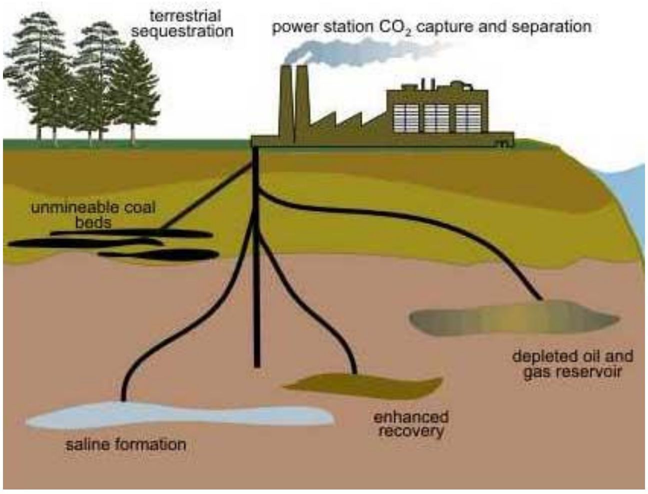


Figure 10 – CO_2 Capture through geologic sequestration. [30]

In order to sequestrate CO_2 safely and efficiently, these sites should attend to the follow physical properties, for the storage rocks: porosity, permeability, injectivity, accessibility, capacity and storage security. [29]

Deep saline aquifers are carbonate and sandstone formations, very porous that are distributed bellow the terrestrial and oceanic zones. These formations contains brackish water (not proper for human consumption), where it can be displaced the CO_2. To ensure that all the stored CO_2 remains in the reservoir, at high pressure and density, stable and without the possibility of evading, it should be put at a depth of 800m or higher. [31] In terms of storage potential, these reservoirs could store up to 10000 Gton[1] of CO_2 [34], more than enough to sequestrate, for example, the total emissions of 2014 which was approximately 40 Gton [31, 32].

One of the other options to store is by EOR (Enhanced Oil Recovery) or by EGR (Enhanced Gas Recovery). EOR is done in 3 phases: primary, secondary and tertiary. They consist in injecting CO_2 in the operational reservoirs, in order to rise oil mobility and to extract even more. Furthermore, the CO_2 remains sequestrated in the reservoir without consequences. The figure 11 , shows schematically how EOR works:

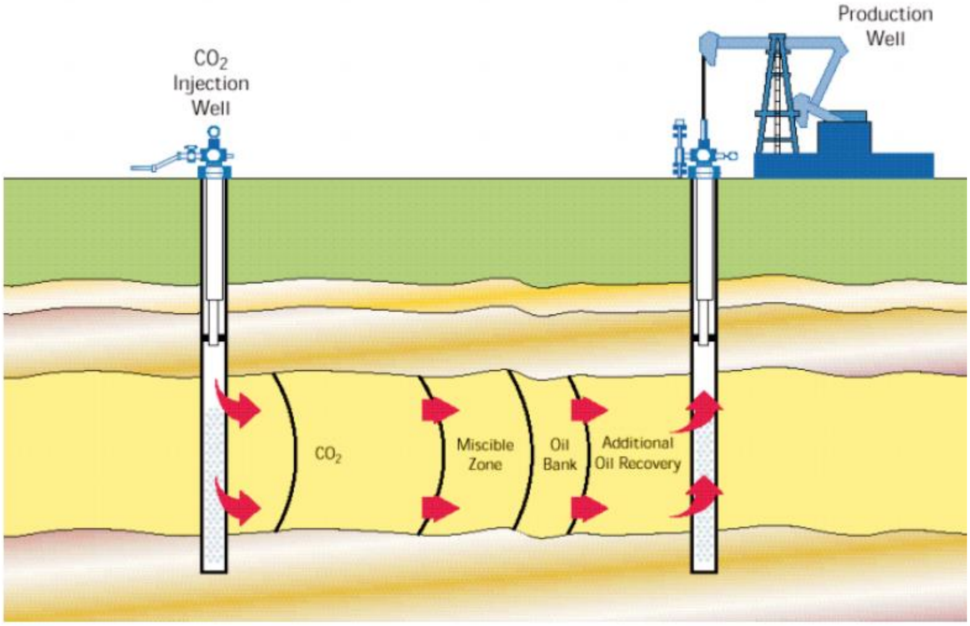


Figure 11 - Schematics of EOR. [33]

Towards EGR, it consists in injecting CO_2 on the base of the gas reservoir, to make natural gas float over CO_2 until the top, once CO_2 is heavier (1,8 g/cm^3) than natural gas (0,7 g/cm^3). Comparing this method with EOR, it can be said that the potential is not that high due to the low recovery of the natural

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[1] 1 Gton = 10^9 ton

gas. In terms of storage potential, it is estimated that these methods can store up until 920 Gton of CO_2 [29, 33, 34, 35].

The unmineable coal beds have a CO_2 storage potential with associated benefits. The coal beds could be gas reservoirs due to existence of fractures and microporous where natural gas (methane essentially) is adsorbed to the surface. Since CO_2 has a higher affinity than natural gas, eventually it will be displaced by CO_2, allowing the recovery of natural gas afterwards. Relatively to storage potential, it could store up until to 15 Gton. [32, 34]

Therefore, these procedures mentioned above could be a possible solution to enhance the recovery of value product and at the same time a way to store CO_2 without damaging the ecosystems, increasing the value of the companies.

2.2 Industry Issues – The " Energy Penalty "

The Energy Penalty is an important subject nowadays, due to the enormous energy waste that is done around of all power plants. Therefore, some efforts have to be done in order to use all the energetic potential. In first place is important to explain the definition of Energy Penalty. It refers to the generated power that was lost by installing CCS technology in a power plant and generally is considered the difference between centrals with (η_{ref}) and without CCS (η_{CCS}), in terms of thermodynamic performance. Equation 1, translates what was mentioned above:

$$Energy\ Penalty = \Delta E = 1 - \frac{\eta_{CCS}}{\eta_{Ref}} \tag{1}$$

In this topic it will be focused the coal-fired power plants, follow by the two post-combustion technologies for CO_2 capture: amines and the calcium looping cycle, where it is going to be shown the integrated process via flow sheet.

In terms of the power plant, it is composed essentially of a boiler, a turbine and of the flue gas of the boiler, it contains a flue gas desulphurizer (FGD). The coal is burned in the firebox that is engaged to the boiler. The released heat, generates steam that is going to be used to make the turbines work, to generate power. Burning coal generates essentially SO_x and CO_2, and that's why after the boiler is a FGD, in order to purify the stream. The remaining gas is composed for CO_2, which is going to be captured afterwards, with the chosen technology.

The coal-fired power plants with Ultra-Supercritical Steam Cycle (US-CSC) are being develop, and pilot-scale facilities show that is possible to achieve a net power of 50%, with the lowest energy penalty when compared with the existing ones nowadays. It is estimated that the US-CSC is going to be commercialized by 2020. [36]

Before discussing the two types of post-combustion in the energy penalty, it is important to mention the coal-fired power plants issues and main problems, related to the subject. The coal-fired power plant generates electricity, burning coal, generating vapor and making the turbines work. All the generated electricity from the turbines, in the end of the process is called "*gross output* "(E_{gross}). However, the electricity for domestic consumption is the "*net power*" (E_{net}), because in terms of CCS technologies it is necessary to subtract the energy for capturing and compressing the CO_2, besides the steam capture and the auxiliary energy (E_{aux}) for the returned heat, for the power plant. [36] All the topics mentioned above, are described in the figure below:

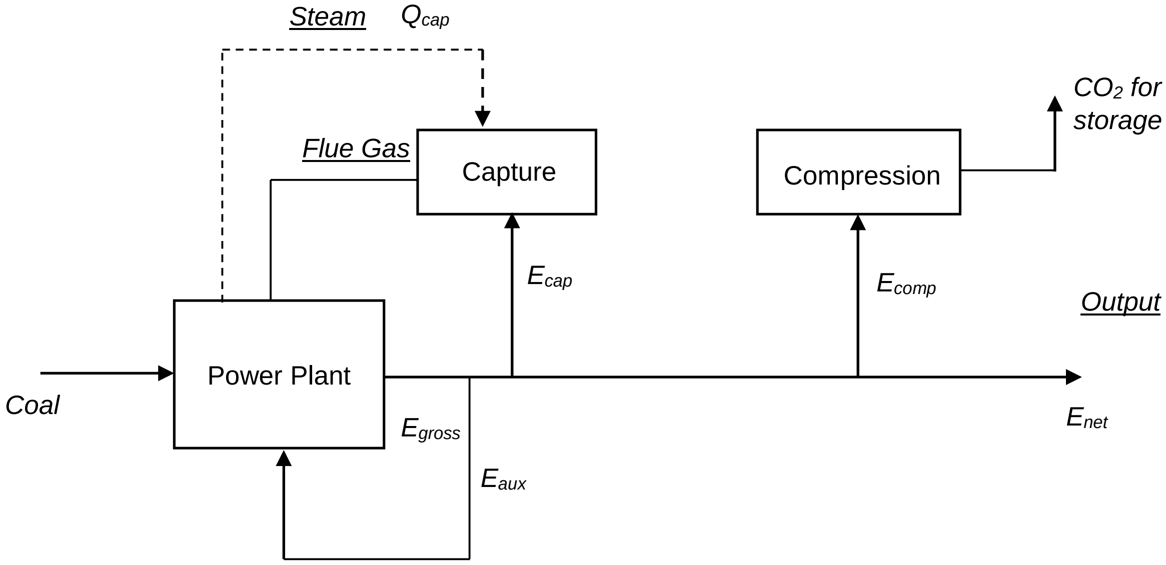

Figure 12 - Coal-fired Power Plant – Energy Schematics [36]

As mentioned above, the energy penalty depends on the efficiencies. These efficiencies are related with the *net power* of the central and the low heating value (LHV) of the coal. They are calculated by the equation 2:

$$\eta_{net} = \frac{E_{net}}{LHV} \tag{2}$$

The net efficiency of a coal-fired power plant with CCS technologies ($\eta_{net,ref}$) and without that ($\eta_{net,CCS}$), depend of the topics mentioned above.

However, this efficiency is affected by the LHV of the fuel. In this case, the fuel for the power plant is coal. In the table above it is show the composition of a standard coal:

Table 4 - Coal composition in dry basis [36]

%C	%H	%N	%O	%S	%Ash	%H_2O	LHV (kJ/kg)
72.04	4.08	1.67	7.36	0.65	14.20	8.10	25372

The type of coal used influences the energy penalty. The coal can be one of two types: hard coal or brown coal (lignite). This last one has a low LHV, for that reason, the most used is hard coal. According to [34], the types of coal don't influence the energy penalty at all. Since coal has a significant percentage of humidity, the pre-drying of the coal can reduce the energy penalty by 3%.

Furthermore, it is possible to conclude that the power plants that work on higher pressures and temperatures of the generated vapor, have a lower energy penalty. Since the working temperatures and pressures are high it is possible to take advantage of the steam cycle. So it is possible to have a high number of steam extractors at high, medium and low pressure over the power plant, producing more energy and lowering the energy penalty. The power plants with the highest energy output tend to have lower energy penalty. The generated vapor, could be integrated in the process, using for example, in the desober reboiler for the amine aqueous solution. [37]

As expected, the pre-drying of the coal associated with energetic integration of process shows the best results in terms of energy penalty, about 11%. However the investment and the capital costs associated are very high. [37]

2.2.1 Energy Penalty for coal-fired power plants – using amines

In terms of using amines, there are some considerations that are important. The use of this technology leads to a capital investment, in terms of equipment: a partial condenser, a reboiler, two stripping columns and storage tanks. Furthermore, it is needed some extra space to allow a high regeneration of the amines and high cycles of compression for the electricity production hours (very low). Since the electricity is produced 24h a day, the periods in which the electricity has low peaks is when the amine solution is stored in the tank, to economize, in order to avoid even more energy penalty. [38]

It is known that 92% of the energy penalty is due to the solvent regeneration and the CO_2 compression. The most expensive equipment is the reboiler, due to the high *heat duty*. The use of vapor determines the profitability of the CO_2 capture, and that's why it is the bottle neck of this process. The new power plants with CCS make use of US-CSC, integrating the produced vapor in the process, using it in the regeneration of the solvent (reboiler). [37] Furthermore, the regeneration time of the lean amine and the time of permanence of the solution in the storage tanks, avoids by 37% the energy penalty. [38]. Figure 13, shows a coal-fired power plant with a CCS technology (amines).

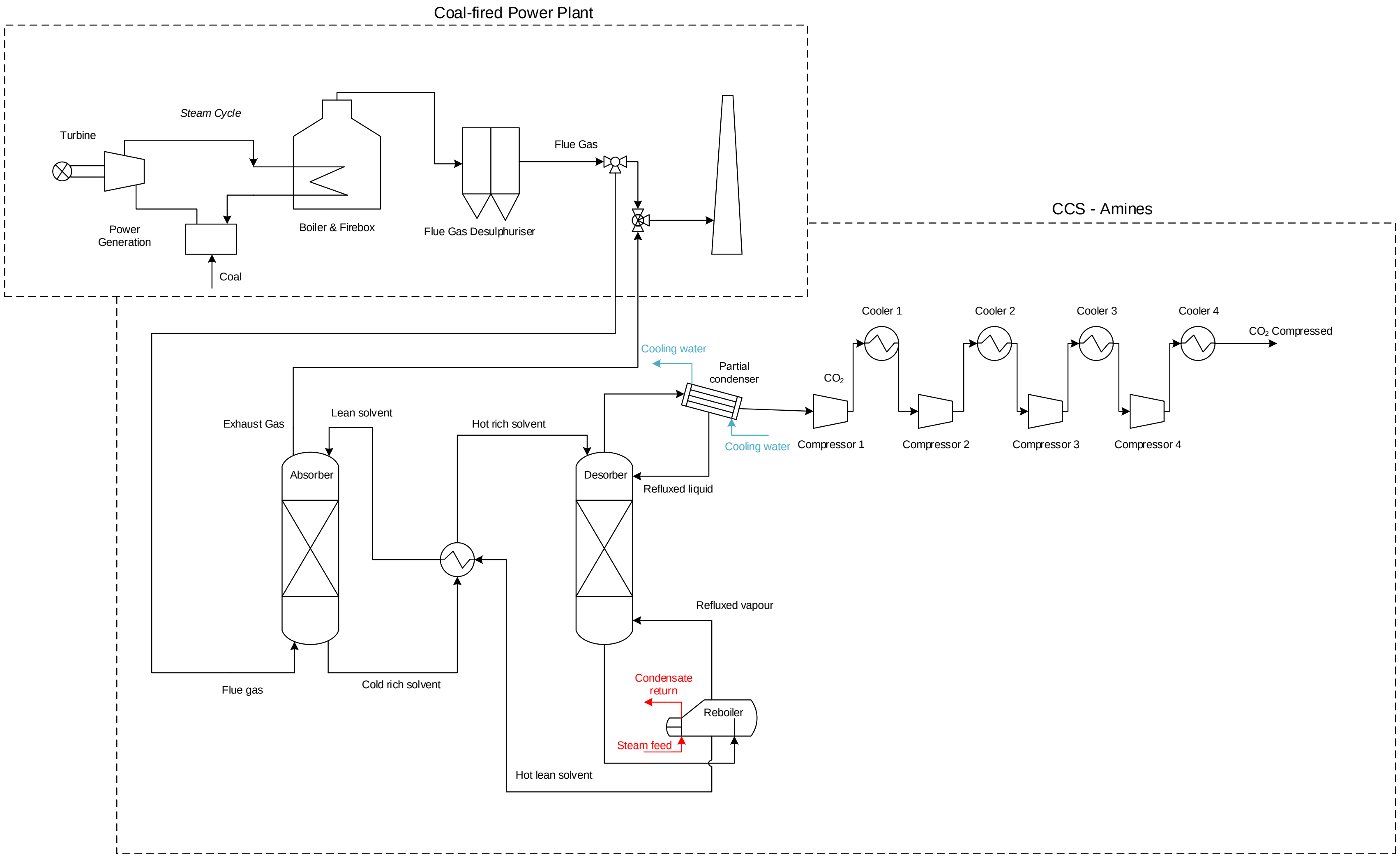

Figure 13 - Coal-fired power plant, using CCS technology (amines). [36]

2.2.2 Energy Penalty for coal-fired power plants – using the calcium looping cycle

The biggest challenge, concerning the use of this technology, is the loss of activity of the sorbent very quickly (carbonation – $CaCO_3$). The number of cycles is very low (carbonation/calcination), leading to a high energy penalty, although the sorbent is very accessible and cheap (e.g. marble).

To be possible to make this technology even more promising, it is necessary to take advantage of the released heat from the flue gas and from the exothermic reaction (carbonation) in order to minimize the energetic costs associated to the sorbent regeneration, as shown in figure 14. Using the heat for this purpose, minimizes the energy penalty in 3%. Although it seems a low value, at industrial scale and over time it can contribute significantly to a higher efficiency during the life-time of the power plant. One of the other factors that contributes for the energy penalty is the difference between the temperature of the carbonator and the calcinator. This difference can reach up to 300 °C. The higher the temperature gap is, the higher the energy penalty will be, and that's why it is necessary to find a balance between these reactions. Furthermore, the amount of solids in circulation in the system must be adjusted, because most of the energy spent is for the sorbent regeneration. Therefore, the scientific community is spending lots of time to find a sorbent that is easier to regenerate and that does not lose activity quickly. Once that's done, it will be, for sure, one of the tools to capture CO_2.

One of the most promising aspects of using this technology is the fact that its possible to use the heat from the flue gas and the released heat from the carbonation reaction in the steam cycle of the power plant, to generate even more energy. [39]

The following figure, illustrates the combined power plant with the calcium looping cycle. It is necessary to mention that this cycle will be discussed later on.

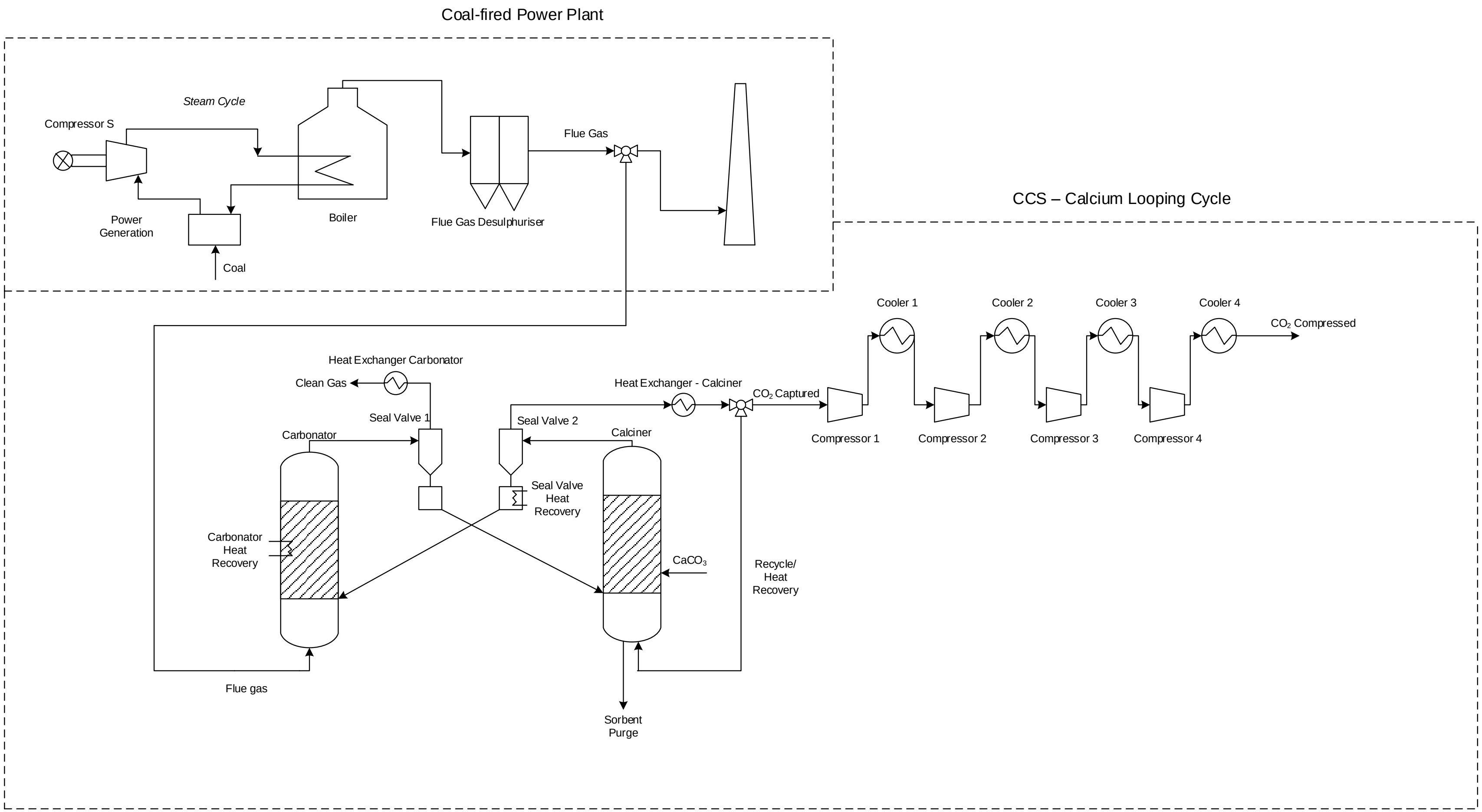

Figure 14 - Coal-fired power plant, using CCS technology (Calcium Looping Cycle) [36]

2.3 Sorbents

The success of CO_2 capture, relies on the sorbents and their performance. For that purpose, this chapter will present a review of the most used sorbent for adsorption processes in the post-combustion CCS technologies. It is known that these sorbents are used for adsorption and they can be divided in three major groups: organic adsorbents, inorganic adsorbents and hybrid adsorbents (they are composed by organic and inorganic bonds). Since this thesis is focused on marble, it will be given special attention to the inorganic adsorbents.

In terms of inorganic adsorbents, they can be split in two groups: the chemical sorbents and the physical sorbents. In terms of chemical sorbents, the most common used one is the metal based sorbent (single metal), which is the main focus of this thesis. For the physical sorbents, it is used activated carbon and zeolites essentially, but this chapter will focus only on the last one.

2.3.1 Physical sorbents

2.3.1.1 Zeolites

What are zeolites? Zeolites are microporus crystalline solids with well-defined structures. They have tetrahedral structures - AX_4 – where A is Si or Al and X is O. They contain porous which in turn may have cations, water and/or other molecules. Some of them are found in nature in the form of minerals, which are extracted intensively. It is known that their pores have unique properties and that's why they are used in gas separation (CO_2 in this case). In the literature they are referred as a molecular sieve.

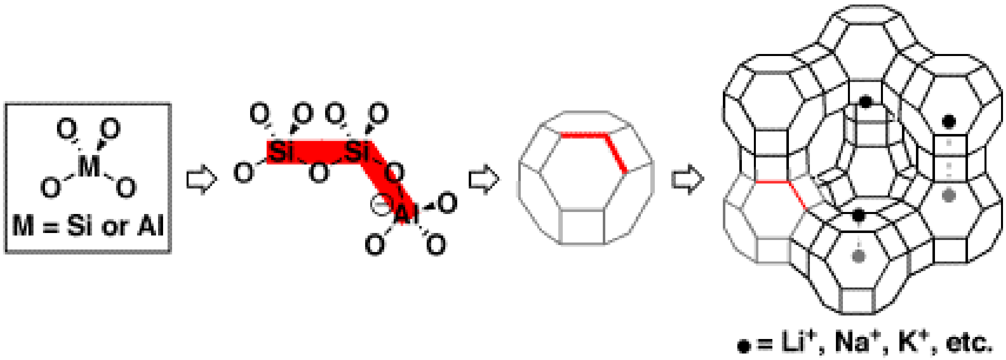

Figure 15 - Zeolite basic structure and Zeolite-Y 3D representation. [41]

Figure 15 shows the 3D representation of zeolite-Y and it is possible to see the cages, cavities or channels, that have the right size for the small molecules to get in. In terms of diameter they are between 3 and 10 Å. [40]

Throughout the literature [41, 42] it is possible to conclude that the fraction of occupied pores at room temperature starts to rise from P_{atm} until P=10 bar, reaching a fraction of 0.9. For higher temperatures it is possible to observe a decline of the fraction of occupied pores. For example, at 150°C the fraction is about half of the value for the environment temperature ≈ 0.45. The key to make an efficient CO_2 capture lies in the Si/Al ratio. It is demonstrated that a low Si/Al ratio corresponds to an efficient capture, which means that the framework have in the extremities more cations, introducing more electronegativity in the framework, allowing more exchanges between the cations in the pores. Normally these cations are alkaline metals (e.g. Li or Na), although some experiences used K, Rb and Cs. The presence of these cations generates electrostatic interactions with CO_2. Comparing the used metals, it is possible to conclude that Li and Na have a better performance than the rest, reaching carrying capacities of 3.9 mmol/g for NaX and 1.17 mmol/g for NaY, respectively. These two zeolites presents different results due to their Si/Al ratio. As expected, NaX possesses a high CC, due to their low ratio, when compared with NaY. The obtained results in the literature [41] suggests that the CC decreases with the increase of the temperature, for the same zeolite. In the other hand the enthalpy of adsorption for low Si/Al ratios is higher because, the CO_2 adsorption to the substrate is higher. Therefore, it is spent more energy to desorb the molecules, although the amount of molecules are high. For a Si/Al ratio of 1, the heat of adsorption is 45 kJ/mol and for a Si/Al ratio of 2.4 is 40 kJ/mol [42]. The CC of the refered zeolites, can be found in the annex – Table A3.

One other issue of using zeolites for capturing CO_2 is linked to the presence of water vapor in the flue gas, which inhibits the gas adsorption. This happens due to the water polarity and the cations affinity (zeolites). Although these zeolites are hydrophilic, the flue gas need a previous treatment, such as drying, to prevent the catalytic activity inhibition.

The size of the pores has a great role in the CO_2 adsorption, especially when the pressure is at stake. The high CO_2 adsorption is associated to a high zeolite volume and a large pore size. It is shown that the available space to adsorb CO_2 decreases with the increasing of the cation size (Na, Ca, K, Rb, Cs), for pressures above of the atmospheric. For the same pressure the CC differs largely. [43] For pressures above the atmospheric, it reaches the equilibrium and the CC are higher when compared with low pressure. Furthermore, it was demonstrated that at a high pressures (10 bar) the zeolites can operate, without being damaged. In the annex can be found the Figure A1 the CC of mixtures containing CO_2, N_2, CH_4 for the various cations and temperatures.

Relatively to the zeolite regeneration through to the cycles, the literature suggests that it is easily made and even at the end of many cycles, the capacity of adsorption remains the same and it can be applied at industrial scale, using the heat of the processes to regenerate through TSA, making the process economically viable. [43]

2.3.1.2 **Zeolites Functionalization**

Once it is add functional groups to the zeolites, it cannot be considered as a doping method but it is called functionalization. One of the used materials to functionalize zeolites are amines. The most used zeolites to functionalize, are referred in the literature [42]: MCM-41 and SBA-15 essentially. In terms of amines, the most referred ones are: PEI (Polyethyleneimine), TEPA (Tetraethylenepentamine), DEA and MEA.

Zeolites and amines are in a proportion of 50 %(m/m) in terms of blending and they present an average CC of 3 mmol/g. When compared with zeolites without the functionalization, the increase of the temperature increases the CO_2 capture. The optimum temperature for this task is situated in 75°C. Due to the adsorption be an exothermal reaction and since the pores are not accessible for the amines at low temperatures, the CC drops more than 50% for room temperature.

The equation 3 ilustrates the functionalization of the amines.

$$2\,(RNH_2) + CO_2 \leftrightarrow \underset{Carbamate}{RNHCO_2{}^{-}RNH_3{}^{+}}$$

$$RNH_2 + CO_2 + H_2O \leftrightarrow \underset{Bicarbonate}{RNH_3{}^{+}HCO_3{}^{-}} \overset{RNH_2}{\longleftrightarrow} \underset{Carbonate}{\left(RNH_3{}^{+}\right)_2 CO_3{}^{2-}} \tag{3}$$

For the functionalization Zeolites and amines are in a proportion of 50 %(m/m) in terms of blending and they present an average CC of 3 mmol/g. When compared with zeolites without the functionalization, the increase of the temperature increases the CO_2 capture. The optimum temperature for this task is situated at 75°C. Due to the adsorption be an exothermal reaction and since the pores are not accessible for the amines at low temperatures, the CC drops more than 50% for room temperature.

Although the zeolites without amines are affected by the humidity which leads to a decreasing of the CC, the presence of water favors the equilibrium for the zeolites with amine functionalization. Which means that the formation of bicarbonate is favored, leading to an increase of CO_2 capture. The only thing where these two groups of zeolites are in concordance is in the diameter of the pores. Higher the diameter, higher the CC, for the same used functional group.

It was referred above, that higher temperatures favor the CC for the zeolites with amines, but at the same time it is a disadvantage due to the possible evaporation of the solvents and the possibility of the occurrence of secondary reactions between CO_2 and the amine groups that can form stable product such as urea, decreasing the spots of adsorption [42]. For these reasons, the regeneration has to be done through PSA instead of TSA to avoid the problems mentioned before. One of the big issues presented for this method, is the existence of one of the intermediaries that is highly toxic: carbamate. This is one of the limitations of the impregnation of the zeolites with amines. In the annex is possible to find in figure XX3 some zeolites, solvent used and their carrying capacities.

2.3.2 Chemical sorbents

2.3.2.1 Metal-based adsorbents

In terms of metal-based adsorbents, we will focus on Ca, which is the main focus of the entire thesis. However, it has to be referred that the most used metals belong to the first and second groups of the periodic table. But transition metals and lanthanides can be used too. They can be found in aqueous solutions. Therefore it is possible to dope the matrix to give certain properties to the material: to enhance the CC, the resistance to friction or even the loss of activity of the sorbent. Some of the most used metals are: Ni, Fe, Cu, Zr, Ce, Sr, Al, and Ti. [45, 46, 47]

The CaO emerges as a potencial adsorbent for CO_2 capture, due to its great adsorption capture, for being very common in the environment (e.g. minerals – limestone, marble, dolomite and biological sources), for being very cheap and accessible, but, the most important thing, is the calcium looping cycle, mentioned further on in this thesis.

To understand this process, it is necessary to look at the generic reaction that occurs between the adsorbent and the CO_2:

$$MO(s) + CO_2(g) \rightarrow MCO_3\ (s) \tag{4}$$

Looking at the equation 4 it can be concluded that 1 mol of MO stoichiometriclly adsorbs 1 mol of CO_2, resulting in a carbonate form. Since the oxide metal used is the CaO and looking to the molecular weight of the compounds, it is known that the theoretical amount adsorved of CO_2 is 0.78g per gram of adsorbent.

One of the biggest challenges so far is the CC of the sorbents. Therefore, the key to solve the problems of CO_2 capture is in the used materials. So, there are many factors that have been studied and are still in progress to synthetize and perpetuate a sorbent capable of resist to the harshest conditions. The parameters are: size of the particles, superficial area, porosity and the composition of its precursors. [45, 46] Furthermore, the sinterization and the sorbent regeneration have some drawbacks in the physical properties of the sorbent, topics to discuss further in this thesis.

2.3.2.2 Doping

As a consequence of the drawbacks mentioned above and since our objective is to increase significantly the activity of CO_2 capture, it has been used metals to dope the inorganic materials. In this chapter is presented the main methods and a briefing of what is done with it:

(1) Dope limestones/marbles with aqueous solution of $Mg(NO_3)_2$, $Ni(NO_3)_2$, $KMnO_4$ [48]
(2) Dope limestones/marbles whit aqueous solutions of metals, such as: Ce, Cr, Ni, Co and Cu, through co-precipitation, that modificates the crystalline structure. [49]
(3) Sorbent production through organometallic precursors [50]

Through the years, it has been verified that the doping processes, improve significantly the carrying capacity of CO_2 when comparing the matrix without the doped material. Furthermore, it was verified that, initially, the CC of the commercial $CaCO_3$ was higher than the same material that has been doped. However, through multiple cycles, the activity of CO_2 capture remains the same for the doped material and for raw material drops 50% when compared with the initial values.

About (1), there are used other aqueous solutions such as Na_2CO_3, NaCl to impregnate the inorganic material (e.g. marble), with a concentration between 0.002 and 0.01M. This method consists in mixing the inorganic material with an aqueous solution and, after that evaporates, it to obtain the powder. It can be called quantitative wet impregnation. After synthetizing the sorbent it is possible to pass to the experience. Most of these impregnated sorbents are used in a FBR (Fluidized Bed Reactor), where the flue gas pass, as was explained previously. When compared with the TGA (Thermogravimetric Analysis), the biggest advantage of FBR is the solid recovery, as mentioned before. Generally, it is observed that the CC through the multiple cycles remains constant and stable. According to [48], the nitrate salts present better results than the chloride salts and higher the salt concentration, higher the CC through the time, when compared the matrix without the salt. The figure A2 in the annex demonstrates one of possible results, using these aqueous salts.

The second method (2) comprises the co-precipitation using nitrate precursors and from this group: Ce, Cr, Cu, Mn, Co, the most promising one is Ce, due to his great CO_2 capture, although Mn presents great results as Ce. Other of the great aspects of using this type of doping, is the tolerance to the sulfation through cycles without losing activity. The associated results to the tests can be found in the annex, Table A5.

Finally, for the third method (3) is about using organometallic precursors. The main goal is to obtain CaO through some chemical compounds and operational steps. In the equation below (5) it is possible to see the necessary steps to accomplish the objective:

$$Ca(Y) \xrightarrow[2.\,\Delta\ (450\text{-}560°C)]{1.\Delta\ Dehydration\ (50-200℃)} CaCO_3 \xrightarrow{\Delta\ (710-750℃)} CaO \tag{5}$$

The starting material is mentioned as Ca(Y), where Y is the correspondent compound, which can be found in the table below (5), along with some important properties for the CO_2 capture.

On equation 5, it is shown, that $CaCO_3$ is obtained through 2 steps. First is the dehydration of CaY between 50-200°C and then the thermal decomposition occurs between 450-560°C, after that it occurs decarboxylation between the temperatures mentioned above, resulting in the formation of CaO. After these thermal events, the experience goes under the calcium looping cycle, and the key for an efficient

CO_2 capture is in the times of carbonation and calcination. According to [50], the precursors with a great heat of combustion, have a high surface area and larger pore volume, leading to a high CO_2 capture. During the $CaCO_3$ formation, it is formed a layer in the sorbent with microporous characteristics, difficult the CO_2 diffusion in the formed layer, which means that the diffusion resistance in the solid phase is higher than the gaseous phase. In the table 5 can be found some compounds and theirs characteristics:

Table 5 – Organometallic precursors formula and heat of reaction [50]

Y – Chemical formulation	Coumpound	Heat of Reaction (J/g)
$Ca(C_2H_5COO)_2$	Calcium Propionate	3830
$Ca(CH_3COO)_2$	Calcium Acetate	2490
$Ca(CH_3COCHCOCH)_2$	Calcium Acetonate	2160
$Ca(COO)_2$	Calcium Oxalate	340
$Ca(C_7H_{15}COO)_2$	Calcium 2-ethylhexanoate	183

2.4 Calcium Looping Cycle

Time flies and there’s a necessity to find new technologies capable of capturing CO_2 in order to stop climate change. For that reason, calcium looping cycle emerges as an opportunity to annihilate this critical problem. According to equation 6, it consists in a reversible reaction between calcium oxide (CaO) and calcium calcium carbonate ($CaCO_3$), using CO_2 and other raw materials (e.g. marble, dolomite, limestone).

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3\ (s) \tag{6}$$

One of the great aspects of this technology is the abundance of raw materials. Furthermore, these sorbents, mentioned above, are very cheap. For this reason this process has been under study for over 20 years and there are some pilot-scale installations for CO_2 capture. [51]

As mentioned before, this technology is post-combustion and it makes use of the flue gas, from many sources. In figure 16 is from the combustor. Therefore, in the first stage it consists in reacting the sorbent (CaO) with the flue gas at ≈700°C, to form the $CaCO_3$. This stage happens in the carbonator. After the first stage, the sorbent ($CaCO_3$) goes to the calcinator to be regenerated (CaO). In this second stage, the sorbent goes under a thermal transformation at ≈900°C, where a pure stream of CO_2 and CaO is released, that is sent to the carbonator to react again with the flue gas. The CO_2 stream, as mentioned above, comes pure after the calcination reaction and it is compressed and cooled for further storage. The gaseous mixture (N_2 and other gases such as O_2, SO_x, H_2O) and the CaO deactivated are purged, as shown below in figure 16.

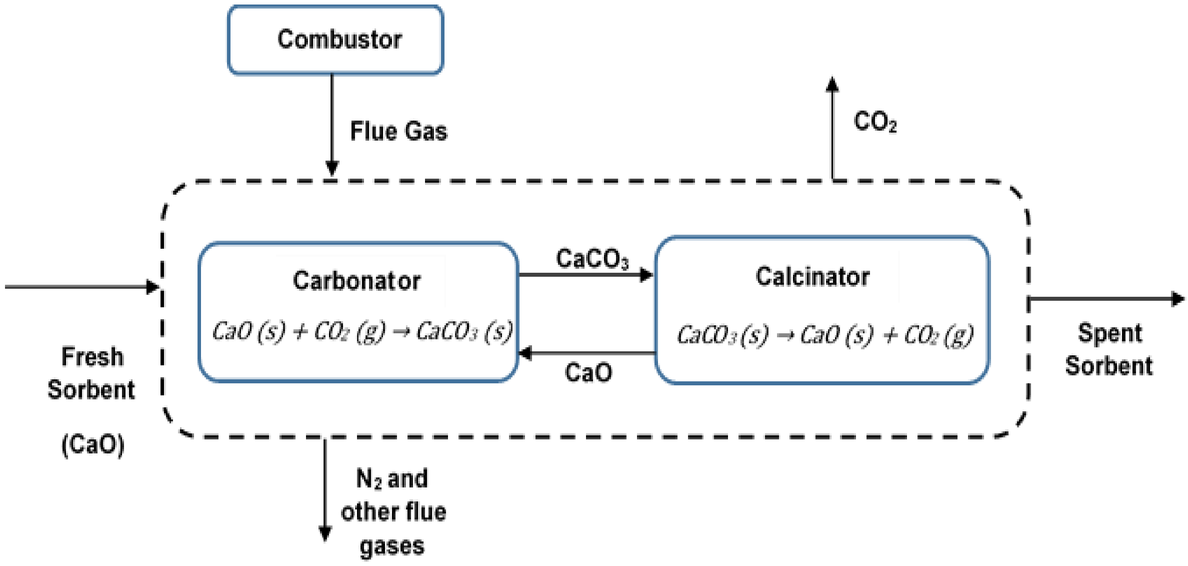

Figure 16 – Calcium Looping Cycle Scheme

2.4.1 Kinetics

To evaluate the calcium looping cycle performance, one of the methods that is mostly used is the Thermogravimetric Analysis (TGA), which is used through multiple cycles. Therefore, the objective is to see the evolution of the weight sample, as shown in figure 17

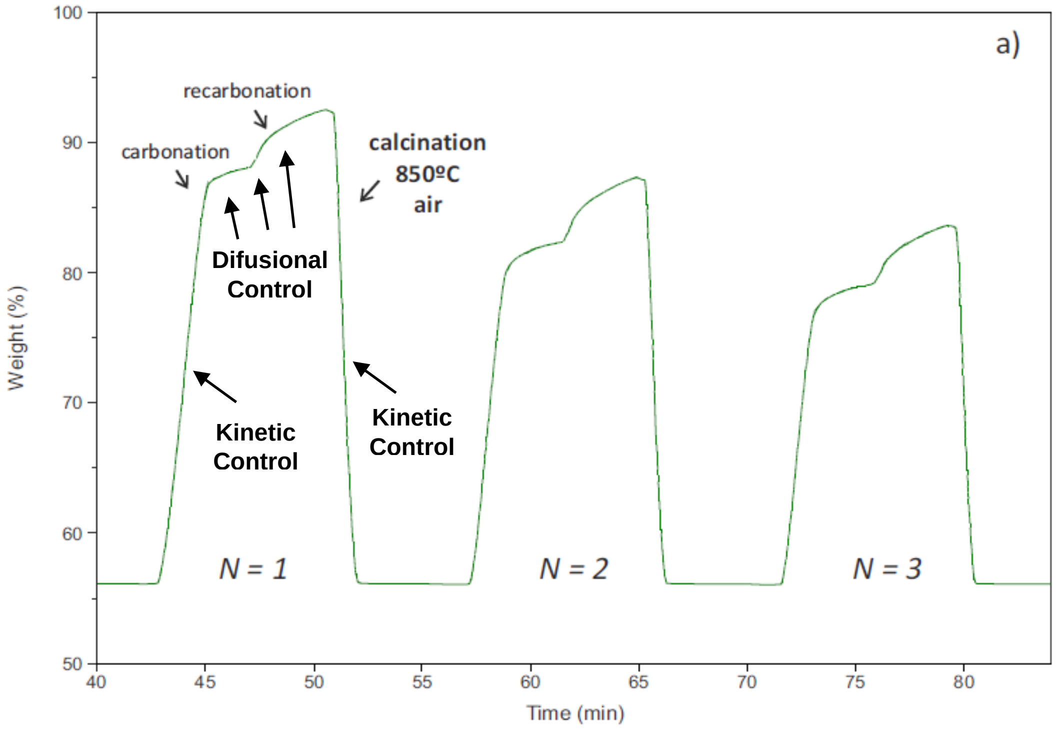

Figure 17 - Control mechanisms for the complete Calcium Looping Cycle, adapted from [53]

Looking carefully at figure 17, for a full calcium cycle, this concerns essentially two main reactions: carbonation and calcination. Concerning about carbonation, it happens in two stages: the first stage is about the solid-gas reaction in the interface (CO_2/sorbent), forming a $CaCO_3$ layer over the sorbent and it has kinetic control. It is characterized by high reaction velocities and its slope is practically infinite. The second stage of carbonation is recarbonation and looking at figure 17, it is possible to observe that the reaction velocity is very low and it has diffusional control. In recarbonation it occurs the $CaCO_3$ densification and for that reason the available pores for the reaction, close. Therefore, the diffusion of CO_2 molecules is limited, due to the layer formed early, as shown below in figure 18. The diffusion can occur in two ways: direct reaction between CaO and the CO_2 present in the pores or CO_2 diffusion through a layer of $CaCO_3$, which is surrounding CaO, followed by immediate reaction with CaO. [56]

Concerning calcination, it occurs just in one step and it has kinetic control, as shown in figure 17. In this phase the sorbent is regenerated at high temperatures, as mentioned above in Operational Conditions. CO_2 is released and the particles increase their size, due to the physical aggregation. Then, the available superficial area decreases and another cycle begins. [55] Furthermore, it is confirmed that the carrying capacity depends on the initial reaction phase, but overall it is not affected by the reaction partial pressure. [56]

The reaction order of the carbonation reaction, according to [54] is first order and it is related with CO_2 concentration. Through multiple cycles, it is possible to observe that the maximum conversion decreases, which makes the sorbent performance difficult. Finally, along the cycles, the carrying capacity does an asymptote, which means that have been created an equilibrium between the pore volume and superficial area loss, during thermal sinterization. Therefore, it is a consequence of solid-state diffusion mechanism. For calcination, it is known that for 850°C, the reaction is first order, take into account $CaCO_3$. Since it possesses kinetic control, the increase of the system total pressure, increases the reaction time, independently of CO_2 partial pressure. This reaction is affected by the particle size, due to external diffusional limitations. Higher the size of the particle, smaller the superficial area, which leads to a limitation in terms of heat and mass transfer and it decreases the reaction rate. Since the calcination reaction has less reaction steps, it occurs faster than carbonation. On the other hand, the reaction is incomplete.

2.4.2 Pore-Blockage and Sinterization

Actually, one of the biggest issues in the calcium looping cycle, is the sintering phenomena in the sorbent during the multiple cycles of carbonation/calcination. Furthermore, the sorbent activity, i.e. CO_2 capture, decreases quickly between cycles, reaching up to less than 10% of its initial capture activity. [55]

According to Stendardo et al, [56] one of the hypothesis for this phenomenon is the occurrence of the reaction in the exterior layer of the particle (sorbent), initially. Therefore, it is established a thin layer front, that moves progressively, which leads to a thick layer formation, during the reaction.

Stanmore et al., [57] refers that sinterization is favored largely for high temperatures and for long duration cycles with high temperatures. Furthermore, the presence of H_2O and CO_2 accelerates the process. What is the main factor? Mainly, the carbonation rate of the sorbent, which leads to sinterization and to pore closure. During sinterization there is an adjacent growth grain between particles, as shown in figure 18.

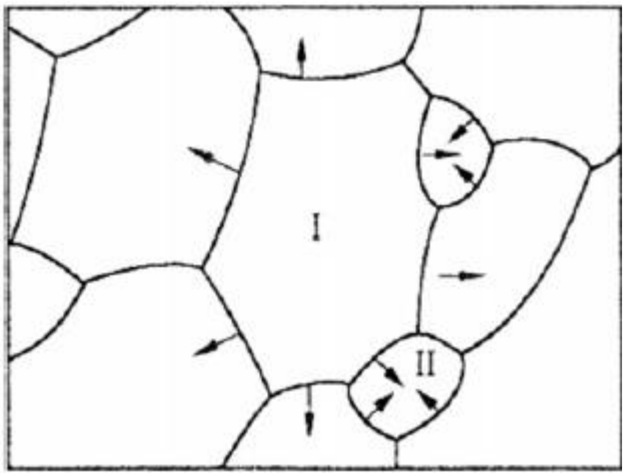

Figure 18 – Schematic diagram of the CaO grain boundary migration under high-temperature reactions. [58]

These grains grow indefinitely, once these materials take advantage of the other neighbor's grains to grown too. Therefore, the distance between centers decreases, leading to pore blockage which decreases the available superficial area for the adsorption reaction. According to [51], the superficial area can reach the value of 0 if the sinterization occur at 1050°C or higher. For that reason the temperature is a very sensitive parameter, when we are talking about the calcium looping cycle. The pore size is largely affected by the number of cycles. The normal size of these pores is 30-100 nm, but for harsh conditions could reach up to 17 nm, which is a critical factor for the capture activity. In figure 19 and 20, it is possible to see the evolution of the sorbent through cycles and the pore distribution.

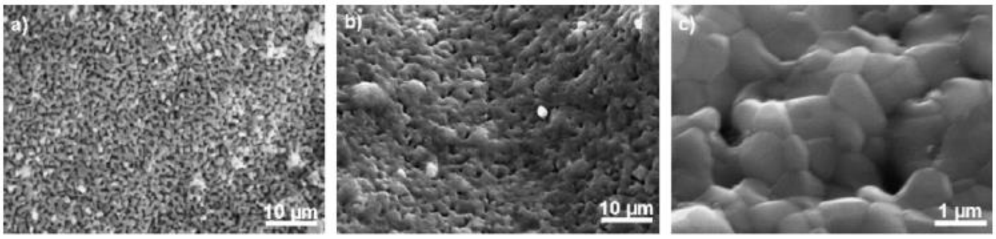

Figure 19 – SEM images of CD-CA-14 pellet particle surface obtained in different stages during carbonation/calcination cycles enhanced by steam reactivation and prolonged carbonation: (a) Calcined pellet, (b,c) carbonated after 30 cycles. [60]

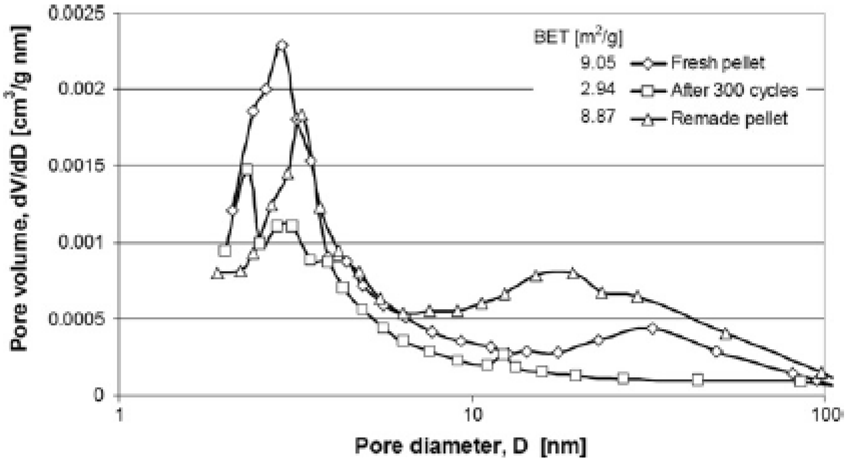

Figure 20 – Results of nitrogen phyisorption tests of CD-CA-14 pellets: (i) Fresh pellet; (ii) After 300 carbonation/calcination cycles; (iii) After hydration, reshaping and calcination. [61]

Looking closer at figure 20 it confirms what has been said above. The multiple cycles of carbonation/calcination deteriorate the sorbent and the capture behavior, which leads to a decrease of the available pores, as shown through the nitrogen physisorption tests. Furthermore, the superficial area decreases with the increase of the number of cycles, as shown in figure 19. Consequentially, the pore diameter increases, due to phenomena explained above. According to bibliography [57], in the first moments of reaction, the superficial area loss is the most significant change in the reaction and it is severely affected by the presence of CO_2 and water vapor (major components in the flue gas).

Stanmore et al. [57], studied the rates of sinterization of these materials: limestone, $CaCO_3$ and $Ca(OH)_2$ and they concluded that the limestone possesses the highest sinterization rate, due to the presence of different ions in the natural rock. Therefore, the introduction of these ions leads to an introduction of irregularities in the crystalline structure, which leads to interstitial diffusion of the CO_2 molecules.

2.4.3 Sorbent Sulphuration

Other factor that has a great influence in the calcium looping cycle and forces the presence of a FGD in integrated united, is the presence of SO_2. The presence of this gas in the flue gas mixture makes two secondary reactions with the main compounds of the calcium looping cycle:

$$CaO + SO_2 + {}^1/_2\, O_2 \leftrightarrow CaSO_4 \qquad (7)$$

$$CaCO_3 + SO_2 + {}^1/_2\, O_2 \leftrightarrow CaSO_4 + CO_2 \qquad (8)$$

Both are reversible and these reactions are extremely exothermic. According to Stanmore et al. [57], the sulphuration of the sorbent occurs when the CO_2 concentration is above of the decomposition pressure. During the calcination step, the presence of SO_2 is harmful to the cycle once $CaSO_4$ as a molar volume larger than $CaCO_3$ which increases even more the pore blockage, decreasing drastically the CO_2 uptake. Other great problem is temperature, once it is the limiting step in these reactions. During carbonation, for temperatures like 700°C, the $CaSO_4$ formation is limited and ceases after a few minutes. However, for temperature above 900°C, it keeps reacting indefinitely.

2.4.4 Particle size and Attrition

According to Chen et al. [59], it was expected that the particle size would affect extensively the carbonation rates. However, there has not been found a direct correlation between these two factors, therefore, they can be considered independent variables. For example, an extensive porous network affects directly the carbonation rates. About the particle size, those who have a poor microstructure with a small amount of pores, have small rates of carbonation. For this reason, the sorbent that possesses a high porosity, have more carbonation activity and higher conversions.

Attrition and particle fragmentation have an important role in calcium looping cycle. Concerning particle fragmentation, it can occur in two ways: internal stress due to thermal shock that the particles are exposed and the accumulated internal pressure. The other, is the increasing of the particle rugosity. For the first issue, the main issue is the particle sulphuration, e.g. the formed layer in the sorbent. The second problem is attributed to material nature, therefore, it is not a specific problem. For these reasons, it should be reinforce the need of a FGD for an integrated unit. [59] The particle attrition is related to carbonation and sulphuration reactions and once the particles are under harsh conditions it deteriorates and deactivates. According to [59], CaO is more friable than $CaSO_4$, therefore it deteriorates faster. However, the attrition tends to decrease exponentially, through the reaction in a FBR, although it has to take into account: the fluidization conditions, operational temperature, the solid amount and bed height. For these reasons, the first fifteen minutes of reaction can determinate the success of the calcium looping cycle.

2.4.5 Hydration and the effect of steam on CaO-based sorbents

The hydration reaction of the sorbent is described by equation 9 and it is exothermic. Furthermore, this reaction is reversible and the dehydration reaction is endothermic, for that purpose this scheme of three steps has been used to try to solve some of the problems associated to calcium looping cycle (equation 11), specially the kinetic limitations, mentioned above. [54]

$$CaO + H_2O \leftrightarrow Ca(OH)_2 \tag{9}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{10}$$

$$CaCO_3 \leftrightarrow CaO + CO_2 \tag{11}$$

This mechanism is very promising, and some studies are trying to understand how the hydration influences the posterior carbonation reaction and the sorbent structure, after regeneration (equation 10). Furthermore, the hydration made through vapor is the most efficient one, according to Manovic et al. [61], since the water excess does not have to be removed, plus there is no sorbent loss with the reactant liquid, because its only vapor being used.

In experimental terms, many temperatures are used for saturated vapor and respective times of hydration. These factors have an influence in the sub sequential calcium looping cycle. Manovic et al. [60] shows that for different sorbent sizes, the carbonation activity increases more than 70%, just in 10 cycles, which leads to an activity extension, until the sorbent has lost all of its activity. (Figure A3 and Figure A4 – Annex). For this sequence of reactions, the calcination/carbonation temperatures follow the same temperature ranges, for short amount of cycles (N=10: 650-750°C for carbonation and 800-900°C for calcination, as shown in the annex, figure A3. In terms of longer operational cycles (N=400), as shown in the annex, figure A5, shows that the use of vapor (hydration) increases the carrying capacity in ≈30%, when compared with carbonation. For short cycles (N=60), the hydration increases the CC in ≈90% and obviously the activity of capture is higher, once the sorbent has not been under longer and harsh cycles.

As expected, the available volume of the pores for CO_2 adsorption, after hydration increases and the size of the pores decreases in the surface, as shown in figure 20. When compared with the fresh sorbent, the superficial area is lower, but along the reaction, the available volume is two times high and for that reason, it is normal that the CC increase as shown in figures A4 and A5 in the annex.

2.4.6 Progressions on sintering problems

To fight the sintering problems, new studies were made, in order to find new materials capable of handling higher temperatures and sintering resistant. Therefore, these materials should possess certain characteristics. In addition to being highly resistant to sintering, these sorbents must have a destination, otherwise it will generate even more waste. One of the new materials used is the spacers, and not all spacers are suitable for further reutilization for producing cement, one of the possible destiny of these materials. Furthermore, the particle size of the sorbent and of the spacer, must be equal, in order to provide a homogeneous mixture and mainly to prevent particle sinterization, as shown in figure 21, for a).

According to Zhao et al., [52] the polymorphic spacers are capable of getting through these problems, once it inhibits the sinterisation. It prevents the densification of $CaCO_3$, maintaining the pores available for CO_2 diffusion, followed by calcination.

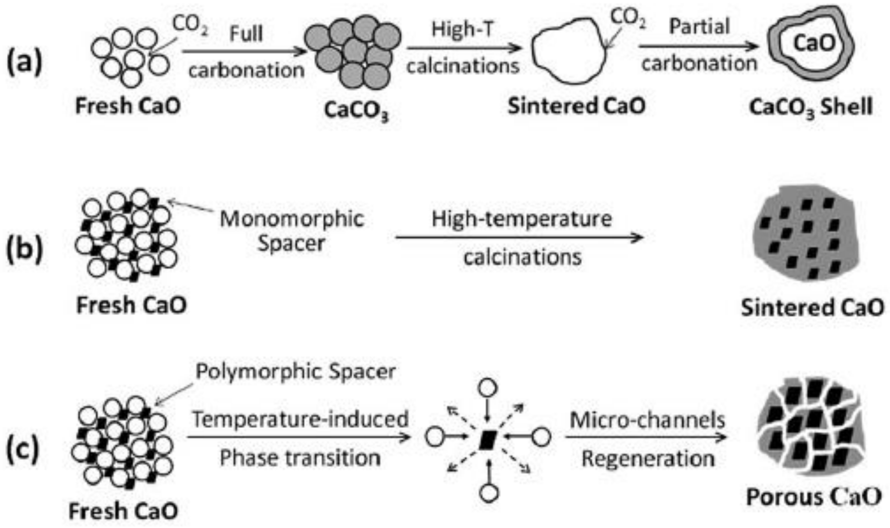

Figure 21 – Schematic presentation of sintering and strategies for stabilization: (a) Deactivation of the CaO sorbent due to sintering, (b) Effect of monomorphic spacers, and (c) Effect of polymorphic spacers [52]

In figure 21 it is possible to observe three possible stages for sintering, in the calcium looping cycle. In a) and b) it is possible to see that at high temperatures, the mentioned problem occurs, which leads to sorbent deactivation and lowering drastically the carrying capacity. However, in a) at the recarbonation temperature (800°C), there is phase transition where there is volume expansion, which allows a further sorbent regeneration and CO_2 diffusion through pores. Therefore, the capture activity remains constant, which allows the existence of a microstructure well established, avoiding the grain boundaries as described in figure 17. However, through multiple cycles, the porosity decreases and the sorbent starts agglomerating, decreasing the CC. The CC between cycles, lowers 0.1%, reaching a value of 0.522 $g_{CO2}/g_{Sorbent}$ after 15 cycles, which is above the average carrying capacities [52].

2.4.7 Operational Conditions

In relation to the operational conditions, it is known that the calcium looping cycle is performed under atmospheric pressure and operational the temperatures for these cycles are extremely high (T>600°C), which means that the energetic needs are very high between cycles. Therefore, it is required an energetic integration, as shown above.

The recarbonation temperature is situated between 700-900°C and this reaction is endothermic. Considering these temperature conditions, it has to be found a balance between the increasing of the reaction rate with the increase of the temperature and the increasing of the sintering rate, which leads to the sorbent deactivation. Furthermore, at the industrial scale, it has to be conceived a system, capable of handling the great amount of heat released, due to the fact that the carbonation reaction is exothermic. In the annex, in table A3 it can be found some of the performed experimental conditions.

2.5 Marble Industry in Portugal

This ornamental rock (marble) exists in the Estremoz/Vila Viçosa/ Borba triangle, as shown in figure 22. It possesses unique characteristics, and therefore, it is wanted across the globe. The main markets are the Chinese and the Saudi Arabian.

Portugal is the 9th biggest producer of marble in the world, according to [71]. In 2012 it was extracted 2.75 Mton of the material. The Asian market leads the marble industry, with the highest shares belonging to China and India, 1st and 2nd place respectively. [71]

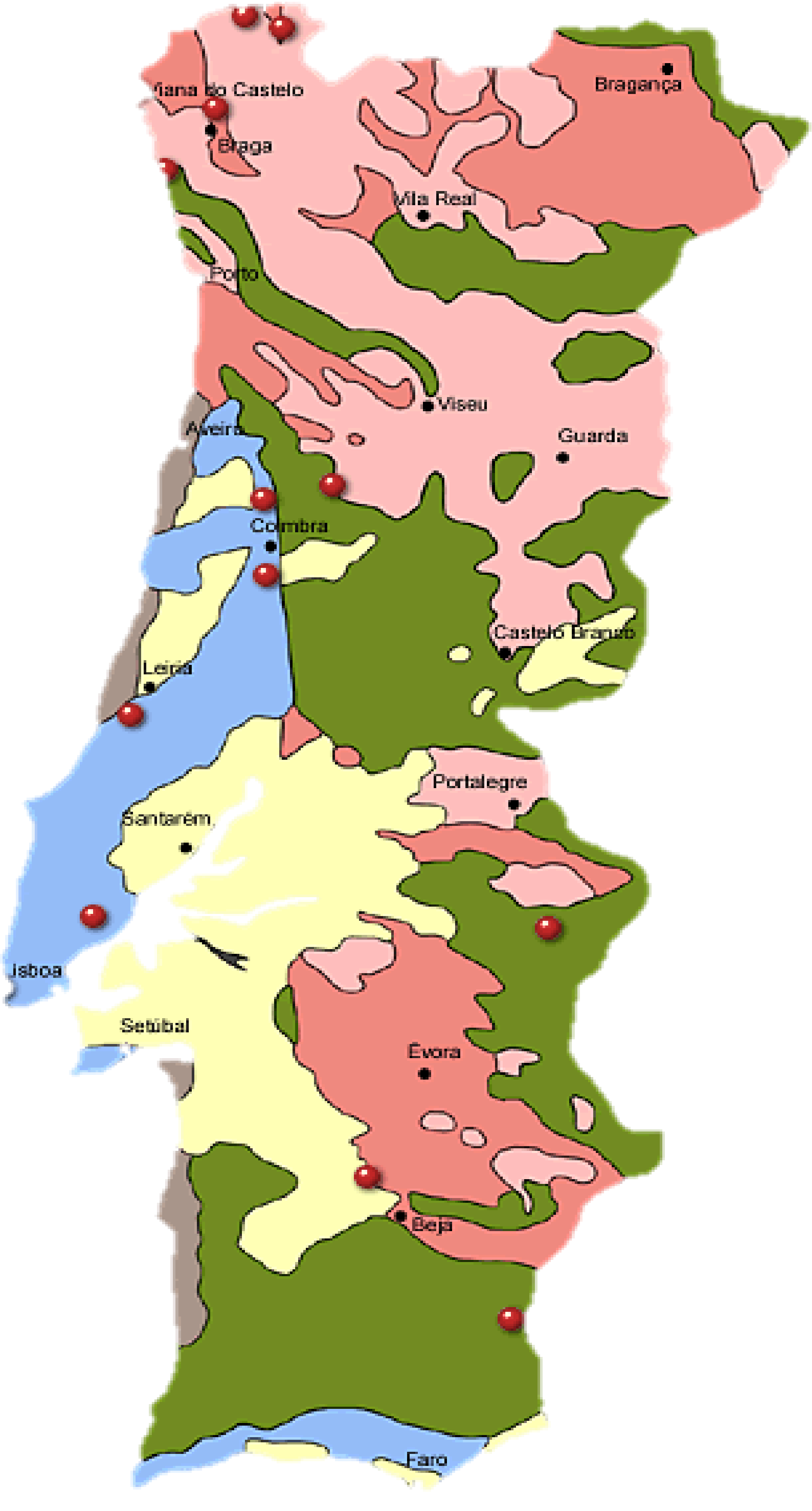

Figure 22 – Distribution of the rock types across Portugal: Grey – Sands; Yellow – Clays, Sandstones, Conglomerates; Blue – Limestones, Marls, Sandstones; Light pink – Granites; Green – Schists, Marbles, Quartzites; Dark Pink – Gneisses, Micaschists, Metamorphic schists. [70]

About Portugal, it is known that marble is inserted in the segment structure. This industry, and what it produces, represent about 31% of the national production of ores. Inside of that segment, this rock is the leader, selling over 77.1M€, in a total of 140.2M€ of extracted rocks. It means that, marbles and limestones, own over 50% of the market, which shows the importance of this industry in Portugal. The Portuguese districts that have the majority of the marbles and limestones reservoirs are: Santarém. Évora and Leiria. [70,72] However, [71] demonstrates that the Alentejo region is the biggest rock ornamental center and for that reason there are some efforts to do, so that it becomes possible to promote the growth of this industry.

Through a SWOT analysis it was possible to detect weaknesses, threats and positive aspects about the marble industry in Portugal. The quality of the Portuguese marble is one of the strong arguments, because it is known around the world. Furthermore, the exclusive composition of the Portuguese marbles, make them one of the most wanted. In terms of threats, the emergent markets have a competitive price, when compared with the rest of the marble industries. Furthermore, with the development of new materials, there are substitute materials for the marble, which is the major threat. In terms of weaknesses, the dimension of the Portuguese rock companies and their poor publicity are the major obstacle towards the growth of these industries. [71]

3 Materials and Experimental methods

For this part of the thesis, it will be described all the experimental methods and the raw materials used. It will also mention, as it was referred, the preparation of sorbents (treatment). All of this, with the intention of getting the best sorbents for CO_2 capture. Furthermore, there is a briefing about the used technique for preparing the sorbents - wet impregnation. And for the final part of this chapter, some of the characterization techniques, used for evaluating the behavior of the prepared sorbents, will be mentioned.

3.1 Raw Materials

Since the objective of this thesis is to study the capture activity using marbles and since Portugal is a rich geological source it was decided to use marble and other sources of calcium carbonate ($CaCO_3$). The only one that is not from Portuguese sources, is the pumice, which has a commercial source. All of them are listed in table 6. The limestone used has two sources: Alentejo and Alcobaça. The marble, also come from Alcobaça. Finally, the used dolomite for these studies, come from Vila Viçosa.

Table 6 - Geologic calcium carbonate sources used in the experimental work

Geologic Calcium Carbonate Sources		
		
Marble	Limestone	Dolomite

For a better understanding of the natural sorbents, it was decided to use the commercial calcium carbonate and calcium oxide. Both of the reactants are found in table 7.

Table 7 - Chemical compounds used as sorbents to compare with the natural sorbents

Coumpound	Molecular Formula	Purity (%)	Molecular Weight (g/mol)
Calcium oxide	CaO	95	56,1
Calcium carbonate	$CaCO_3$	99,5	100,1

Along the experimental work, there were some adjustments and it was observed that, putting some nitric acid (HNO_3) in the suspension, would eliminate some of the impurities of the natural sorbent. The information about the acid is on table 8. Essentially

Table 8 – Acid used to prepare the sorbents

Coumpound	Molecular Formula	Purity (%)	Molecular Weight (g/mol)
Nitric Acid	HNO_3	65	63,01

In order to get the best sorbents, i.e. sintering resistant and capable of maintaining constant the capture activity, it was decided to dope the natural samples with the metals listed below: Magnesium, Nickel, Cerium, Lanthanum and Zirconium, due to their enhancement capture activity, as shown above in section 2.3.2.2. [49, 50] The salts used to dope the natural sorbents and the commercial $CaCO_3$ and CaO, are in table 9.

Table 9 – Chemical coumpounds used to dope the sorbents

Coumpound	Molecular Formula	Purity (%)	Molecular Weight (g/mol)
Magnesium nitrate hexahydrate	$Mg(NO_3)_2.6\ H_2O$	99	256,41
Nickel (II) nitrate hexahydrate	$Ni(NO_3)_2.\ 6\ H_2O$	98	290,91
Cerium (III) nitrate hexahydrate	$Ce(NO_3)_3.\ 6\ H_2O$	99.5	434,22
Lanthanum (III) Oxide	La_2O_3	99.9	325,82
Zirconyl nitrate hydrate	$N_2O_7\ Zr$ aq.	99.5	231,23

3.2 Experimental Method

For this section it will be shown the used methods to perform the CO_2 capture. Therefore, it will focus on the preparation of the sorbents for further capture, i.e. wet impregnation, with explanative figures of the adopted methods. Furthermore, there is some briefing about the characterization techniques used, to evaluate the performance of sorbents and their behavior after and before the capture cycles.

3.2.1 Experimental Conditions

Before doing all the experimental measures in the TGA, it was necessary to find the optimum conditions that could lead to the best results in terms of CO_2 capture. For this purpose, there were carried five experimental calcination temperatures: 600°C, 650°C, 700°C, 725°C and 750°C. All of these chosen temperatures were taken in account, through the bibliography. For the flow rate of N_2 and CO_2 there were made some adjustments, during the experimental period of finding the right parameters. Finally, for the calcination temperature, it was chosen according to the consulted bibliography and the lowest temperature that could avoid thermal problems and side reactions. It is necessary to refer that, to find the optimum conditions, it was decided to perform the carbonation for 60 minutes and the calcination for 15 minutes in just one cycle. The experimental conditions used to evaluate the sorbent performance can be found in table 10.

Table 10 – Experimental conditions used to perform the cycles of carbonation/calcination in TGA

Reaction	Parameter	Value
Carbonation	Temperature (°C)	750
	Time of Reaction (s)	1800
	CO_2 Flow Rate (% V/V)	20
	N_2 Flow Rate (% V/V)	80
Calcination	Temperature (°C)	850
	Time of Reaction (s)	1800
	CO_2 Flow Rate (% V/V)	20
	N_2 Flow Rate (% V/V)	80
Heating Rate (°C/min)		50
Cooling Rate (°C/min)		25

3.2.2 Sorbent Preparation

In terms of sorbent preparation, since our raw materials are rocks and minerals, they had to be crushed in an agatha mortar, until they have the right granulometry to be used in all desired techniques. Some of them were also sieved in plates with a 75 µm mesh, just to guarantee the suitable grain size.

3.2.2.1 Wet Impregnation

The intention of using this kind of technique is to change the crystalline network of the calcium carbonate samples, in order to provide better conditions to resist the harsh conditions of the flue gas.

The technique used for this purpose was ***wet impregnation***. Firstly, the samples (sorbents) and the respective salts were weighted. Then, the salt was dissolved in deionized water, under vigorous agitation and heating. Finally, when the salt was totally dissolved in water, the sample (e.g. marble) was added to the solution, creating a suspension. The suspension was under agitation and a high temperature in a hot plate, to evaporate until it was dry. In the follow figure it is possible to see some phases of the prepared sorbent

Figure 23 – Different phases of the prepared sorbent – experimental procedure

Since the beginning of the experimental process, all of the sorbents were prepared in a molar ratio of 1:0.1 (calcium carbonate sample: salt), although there were made some changes, due to the obtained results. Even so, more than 90% of the prepared sorbents, were made through this chemical route. The prepared sorbents depend essentially on the following parameters: type of salt used, molar ratio between the sample and the salt, type and concentration of acid used.

Through the experimental work, it was decided to add to some samples nitric acid, since the samples are from nature, they have many other ions and impurities. Therefore, to eliminate them, in order not to interfere with the doped structure.

After obtaining the dry sorbent from the flask, they were all crushed in a mortar, until it was obtain a powder, i.e. with the necessary granulometry. After milling, the samples were under calcination in a muffle. To evaluate the performance of the sorbents, they were calcinated at three different temperatures: 750°C, 850°C and 950°C for about 3h, with a heating rate of 10°C/min. The objective of the calcination is to convert the calcium carbonate into calcium oxide and to eliminate some of the impurities that are still present, through thermal degradation. Overall, it was decided to put under investigation, the samples that were calcinated at 850°C, after some analysis in TG and the consulted bibliography. The figure below, shows the before of the calcination, for the sorbents prepared through wet impregation:

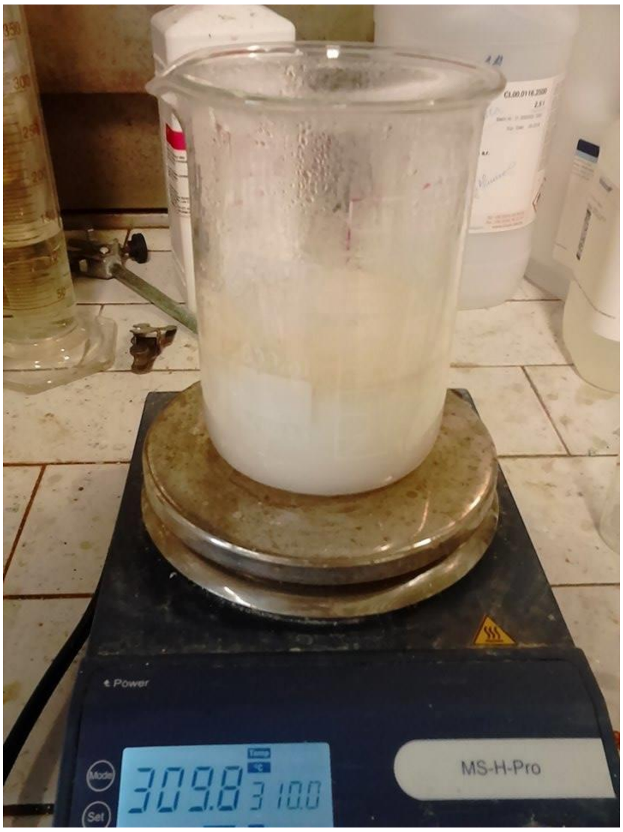

Figure 24 – Sorbent obtained through wet impregnation – before calcination

3.2.2.2 **Sorbent Groups**

In order to evaluate correctly the behavior of these materials, it was decided to divide them into five distinct groups, for a better understanding of the various behaviors and phenomenon. Therefore, the groups are:

- Group A: Commercial calcium carbonate and calcium oxide
- Group B: Geologic sorbents: marble, limestone, pumice and dolomite
- Group C: Doped commercial calcium carbonate and calcium oxide
- Group D: Doped geologic sorbents: marble, limestone, pumice and dolomite
- Group E: Doped geologic sorbents with acid treatment (HNO_3)

To compare the performances of the different sorbents, it was decided to test the commercial ones (Group A) to see the differences in terms of behavior with Group B, through the thermograms and the other characterization techniques used. With these two groups, it was determined the optimum temperature for calcination, i.e. the calcinated samples that presented the best results in terms of adsorption capacity and the ability to maintain constant the capture activity. After concluding that, all the adsorption tests were performed, with the doped samples. It is necessary to say that the nitrate precursors are the best ones to prepare the sorbents, and for that reason the majority of used salts are nitrates. Finally, to amplify and optimize the obtained sorbents, it was decided to do an acid treatment to the samples, i.e. after the addition of the natural sorbent, in order to eliminate impurities.

3.2.3 CO_2 Adsorption Tests – Thermogravimetric Analysis (TGA)

The core of the experimental work are the CO_2 adsorption tests, i.e. the thermogravimetric analysis of the prepared samples through calcination. The thermogravimetric technique is used to evaluate the weight loss through thermal and gas oscillations that are previously programmed. It can measure at the same time the weight loss and temperature oscillations as a function of time, as shown in figure 25.

These adsorption tests are performed under cycles and they are composed by the two main reactions described in the literature review: calcination and carbonation. The calcination reaction occurs under an inert atmosphere, i.e. N_2 (100% v/v), with an average temperature between 800 and 850°C for about 30 minutes. For the carbonation reaction the flue gas is composed by CO_2 (15% v/v) and N_2 (85% v/v), just to be closer from the real composition of the industrial flue gases and the reaction was programmed to occur for 30 minutes too. It is necessary to say that these parameters were chosen after performing some cycles with different time and temperature reactions and after an exhaustive bibliography research.

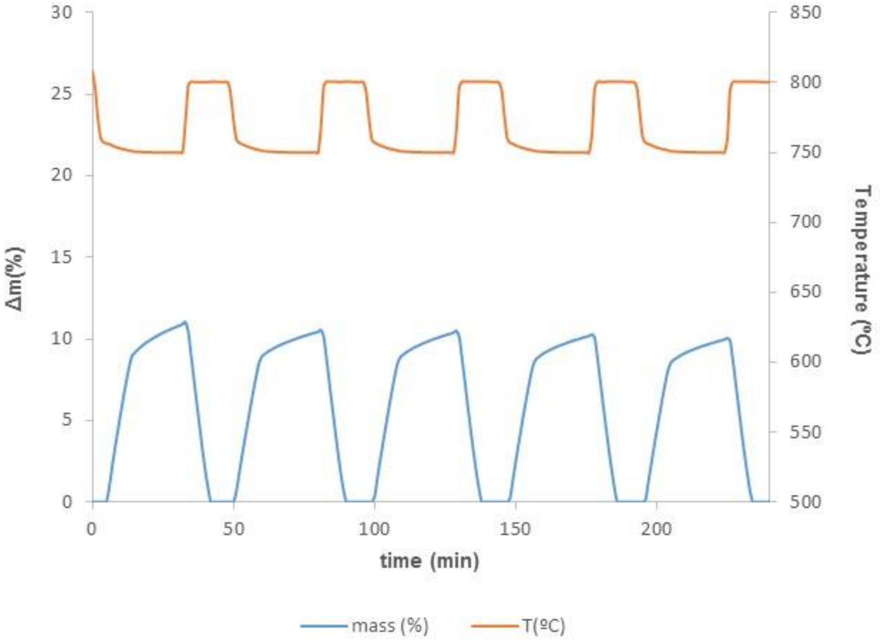

Figure 25 - Specific thermogram from the adsorption tests: thermal profile

Looking carefully to the figure, it is possible to visualize a red and a blue line. The blue line corresponds to the mass evolution through the successive cycles. As mentioned above in the literature review, the carbonation reaction is where the sample gains weight, by reacting with the CO_2 in the surface of the calcium oxide and for that reason is possible to observe the CO_2 uptake under successive cycles and the stability of the sorbent, through them. As for the carbonation reaction, its temperature is the lowest, 700ºC (red line). The calcination reaction, is where the pure CO_2 stream is released, desorbed from the sorbent surface. So, the weight loss (blue line) takes place under high temperatures, and the calcium oxide is available, again, to react with the flue gas to form the calcium carbonate and so on.

To evaluate these mentioned parameters, it was used a thermobalance STA 409 PC from Netzsch. First of all, the sample is weight in an analytical scale, inside the crucible. Then, the crucible is put inside the thermobalance for further reaction. Once it is inside, the experimental parameters are computed with the desired values. In the figure below, it is possible to observe the experimental settings:

Figure 26 - TGA apparatus: Thermogravimetric balance from Netzsch (left), Mass debitometer (middle), specific mortar where it is put the sample (right)

The used gases were measured using a bubble flow meter, because the flue gas has to have an approximate composition of the real industrial conditions. For that purpose, the rotameter was calibrated in order to obtain the desired values and to not allow further oscillations in the gas composition. The computer is connected to the analyzer, which programs and control the temperature. This analyzer contains a high-precision scale combined with an electric furnace. The furnace provides the heating energy and the tap water provides the necessary energy to cool down the sample.

4 Results and Discussion

4.1 Kinetics study and modelation

To evaluate the behavior of the used sorbents for CO_2 capture, it was decided to study the kinetic parameters, and it was decided to estimate the activation energy in order to compare with the literature and to try to understand what influences the capture activity.

First of all, it is important to mention some concepts about the capture activity. Regarding the thermogravimetric analysis, it is important to define the carrying capacity of the sorbent in order to provide some results and the respective conclusions. Carrying capacity is defined as the amount of CO_2 captured per mass of the fresh sorbent in the Nth cycle: $g_{CO2}/g_{sorbent}$

$$Carrying\ Capacity_N = \frac{m_{adsorbed\ CO_2,N}}{m_{fresh\ sorbent}} \tag{12}$$

In equation 12, the *Carrying Capacity,* is the amount of adsorbed CO_2 in grams per mass of fresh sorbent, N is the number of the cycle, the $m_{adsorbed\ CO_2}$ is the mass of CO_2 adsorbed in the Nth cycle and it is given by the mass of the sorbent at cycle N minus the mass of the sorbent after the calcination of the N-1 cycle. Finally, the $m_{fresh\ sorbent}$ is the mass of the sorbent in miligrams and it is given by the initial mass of the sample plus the sorbent mass, after the thermal treatment, before the carbonation reaction.

In order to estimate these parameters it was important to define the carbonation temperature reaction and the CO_2 molar fraction in order to evaluate the sorbent performance. It was decided to fix the carbonation temperature to optimize the CO_2 molar fraction, and the used temperature was 750ºC. For this purpose, the CO_2 and N_2 rotameters were calibrated. The respective calibration curves can be found in the annex A1. The CO_2 molar fraction was calculated according to equation 13:

$$y_{CO_2} = \frac{Qv_{CO_2}}{Qv_{CO_2} + Qv_{N_2}} \tag{13}$$

Where y_{CO_2} is the molar fraction of CO_2, Qv_{CO_2} is the CO_2 flow rate (L/h) and Qv_{N_2} is the N_2 flow rate also in L/h. It was decided to perform the kinetic experiments for three species: Dolomite, commercial Calcium oxide, and of course the main study subject, marble. For each of these sorbents it was used four CO_2 flow rates which corresponds to each molar fraction as shown below in figure 27.

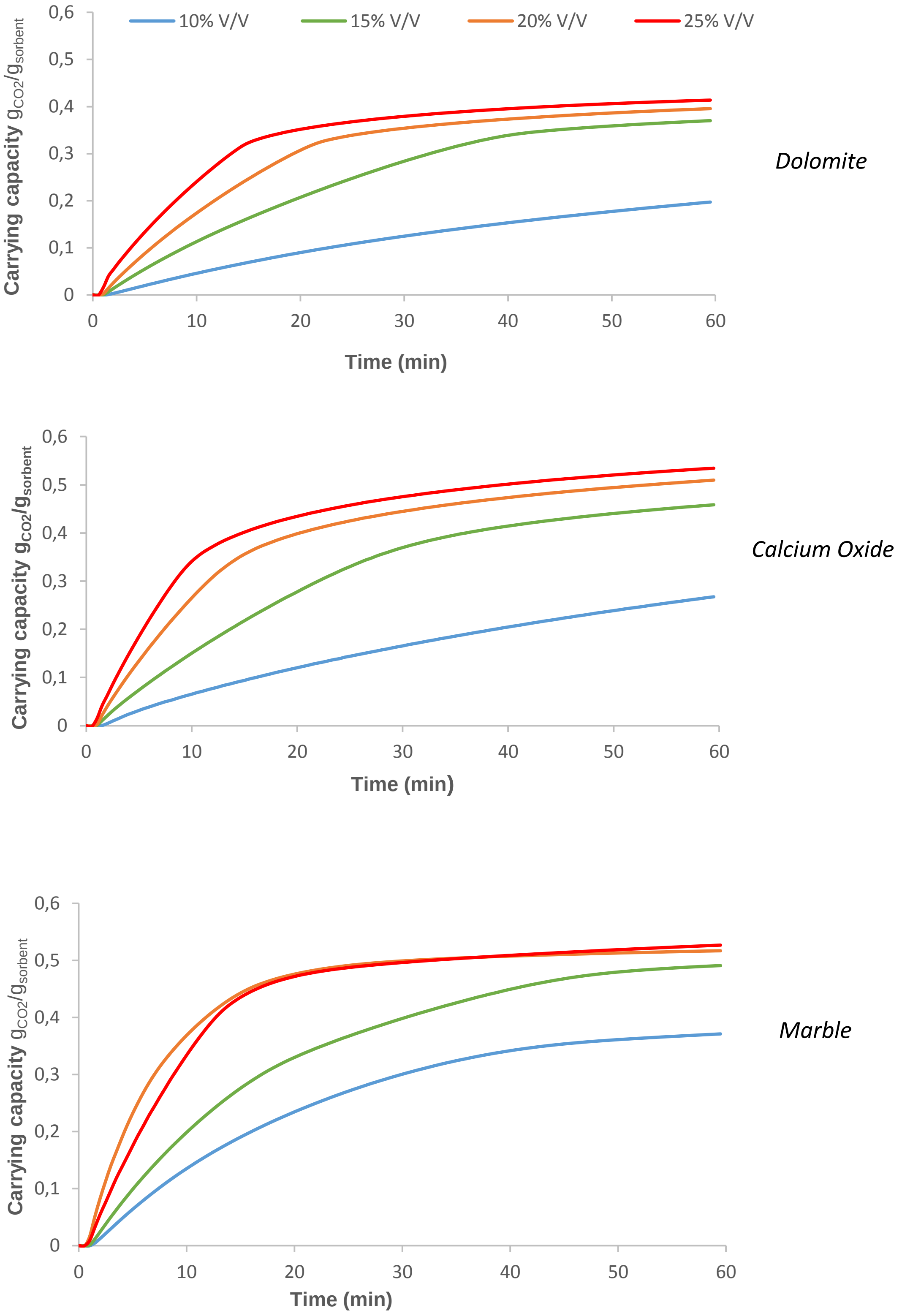

Figure 27 – Carrying Capacity of the samples at different CO_2 flow rates at 750°C

In the three experiments, the same result was obtained, higher the molar fraction of CO_2, higher the CC of the used sorbents and materials. It is possible to observe that the sorbent is satured for molar fractions above 20%, because the CC remains constant, which means that above 20% is indifferent to use more CO_2. Increasing the flow rate of CO_2 is a waste of energy.

The main goal is to recreate the industrial conditions as well as possible, and for that reason it was supposed to use 15% of CO_2 in the flue gas for the main experiments, since it is the average composition of the flue gas of a coal-fired power plant [73]. However it was decided to use 20% (V/V) since these sorbents shown potential to capture CO_2 at higher rates, at this temperature. It is important to remind that for each temperature the molar fraction has a different influence and for high temperatures, the CC can be affected by other factors. Since there does not exist data for marble, it is possible to conclude that it has the same behavior of the other sorbents, and it shows potential to be recovered for this purpose.

After choosing the CO_2 molar fraction it was investigated which temperature of reaction was most suitable to perform the long tests, and to determine the desired kinetic parameters there were tested five different temperatures for the carbonation reaction: 600ºC, 650ºC, 700ºC, 725ºC and 700ºC, taking into account the collected data in the annex (Table A2). For these reactions, the sorbent suffered some thermal pre-treatment for about fifteen minutes at 800ºC, and the carbonation reaction took one hour, with a heating rate of 50ºC/min and cooling rate of 25ºC/min between the isothermal steps.

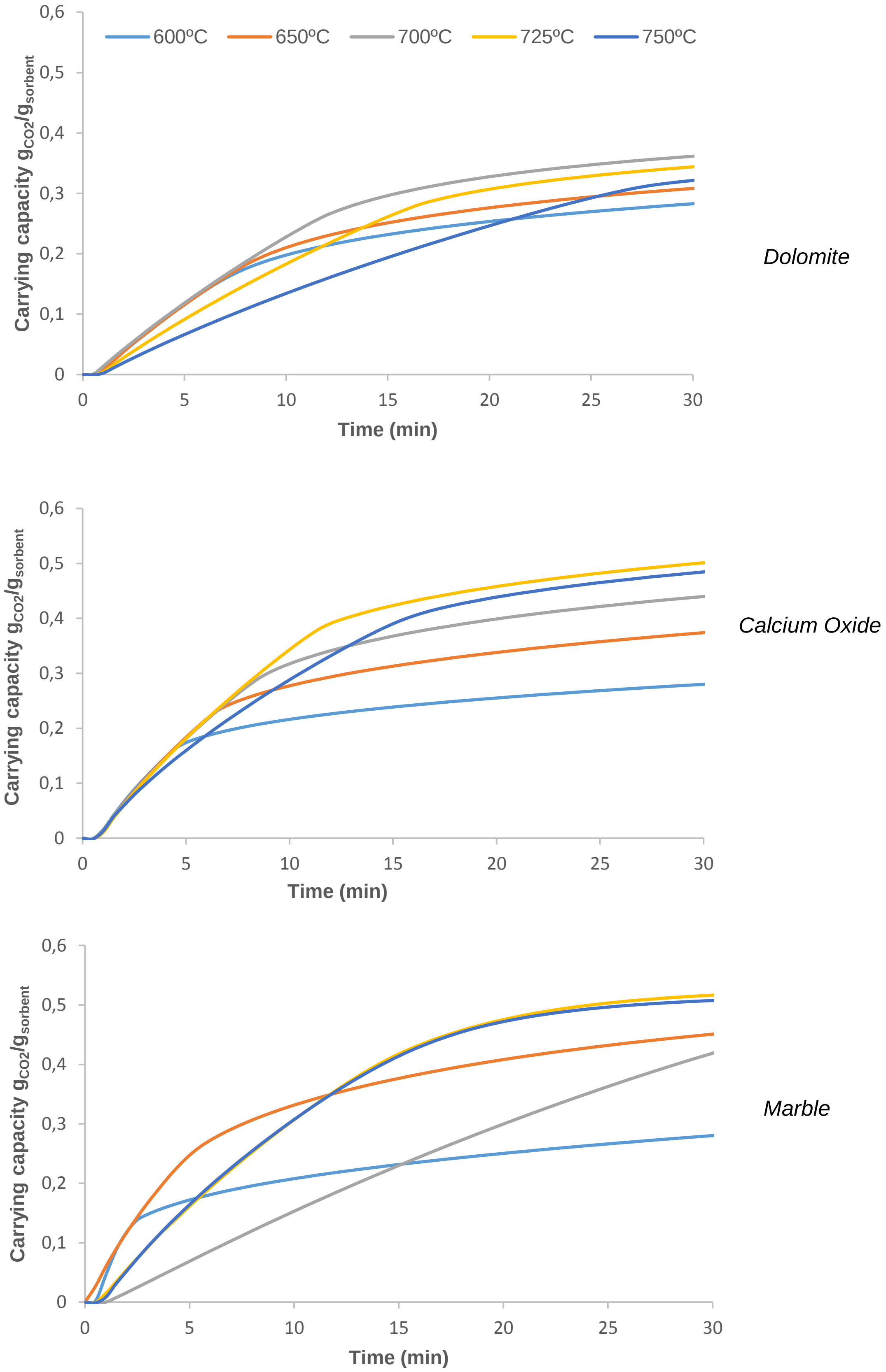

Figure 28 - Carrying Capacity of the samples at different temperatures for a molar fraction of CO_2 of 0.20

According to [74], the CC increases with the increasing of the temperature and it is precisely what happens, looking to figure 28. Looking carefully at figure 28, for calcium oxide the difference between the five temperatures is not high and between them the increasing of the carrying capacity is very low. About the temperature chosen for the long experiments (750ºC), it is possible to conclude that it was a good choice and it presents two well defined regions of the carbonation reaction, although this temperature is not mention in table A3. However, working with low temperatures, e.g. 700ºC, could prevent some sintering problems, since the rate of sintering of the particles increases with the increase of the temperature and affects the sorbent morphology.

For dolomite, it is possible to see that it has the same behavior of the calcium oxide and since it had been choosen to work with the same temperature for all the long experiments, this temperature suits perfectly and it presents good results of carrying capacity. Although the dolomite shows a lower carrying capacity, when compared with calcium oxide and marble, it possesses an advantage: the presence of MgO. This compound serves as an inert and it does not interfere in the CO_2 capture. Furthermore, it is a structural stabilizer, i.e. it can provide enough space for the diffusion of CO_2 through the cycles [75]. Although the dolomite possesses MgO, it can be affected by the sintering phenomena for temperatures above 700ºC. However it is possible to achieve a balance between the calcination/carbonation in terms of carrying capacity for several cycles [75].

For marble, there is no literature available. It can be observed that it has almost the same behavior of dolomite and calcium oxide. The carrying capacity of marble is not affected by the increasing of the temperature, from 650ºC. In terms of the sintering phenomena, it is known that the Taman temperature - the temperature at which the mobility and reactivity of the molecules in a solid becomes appreciable. It is approximately half the melting point in kelvin – is 938 K (665ºC) [76]. So it means that it can have long-term repercussions, for multiple calcination/carbonation in the carrying capacity, although the best results belong for temperature above the Tamman temperature. Therefore, the chosen temperature (750ºC) is a good temperature for CO_2 capture, despite the presented issues.

After this initial explanations, it is possible to proceed to the kinetic study of these three sorbents. For this parameters estimation it was used the Lee model and it was based in [77].

$$\frac{dX}{dt} = k\left(1 - \frac{X}{Xu}\right) \tag{14}$$

Where X is the conversion of CaO, Xu is the ultimate conversion of CaO and k is the kinetic constant in (s^{-1}). This differential equation was integrated between 0 and X and between 0 and t, in order to obtain the expression below (equation 15):

$$X = \frac{Xut}{(Xu/k) + t} \tag{15}$$

The author introduced constant b and considered it as the time taken to achieve half of the ultimate conversion. Therefore, for t=b, X=Xu/2. Substituting this relation in the equation 15 it is possible to obtain the expression of the ultimate conversion (equation 16):

$$Xu = kb \tag{16}$$

Finally, the substitution of the equation 16 on the equation 15, leads to the equation 17, presented below. It gives the conversion of CaO as a function of time:

$$X = \frac{kbt}{b+t} \tag{17}$$

The determination of the kinetic parameters is achieved through the data fitting, after the linearization of the equation 17:

$$\frac{1}{X} = \frac{1}{k}\left(\frac{1}{t}\right) + \frac{1}{kb} \tag{18}$$

Through equation 18, it is possible to obtain the kinetic pararameter (k). These determinations were made, after collecting the data from the thermogravimetric analysis. The objective was to perform the carbonation reaction, for the established five different temperatures, as shown below in figure 30. The collected data presents the evolution of the sample weight through time, which allowed the calculation of X:

$$X = \frac{m_{sample\ t=t}}{m_{sample\ t=0}} \times \frac{MM_{CaO}}{MM_{CO_2}} \tag{19}$$

Where, $m_{sample\ t=t}$ is equal to the mass of the sample at t=t minus the mass of the sample at t=t+1 in mg, $m_{sample\ t=0}$ is equal to initial mass of the sample plus the maximum weight lost at the initial calcination step. It is important to refer that the calculation of X starts (t=0) for the maximum weight loss, i.e the most negative value in the thermogram, as shown below in figure 29:

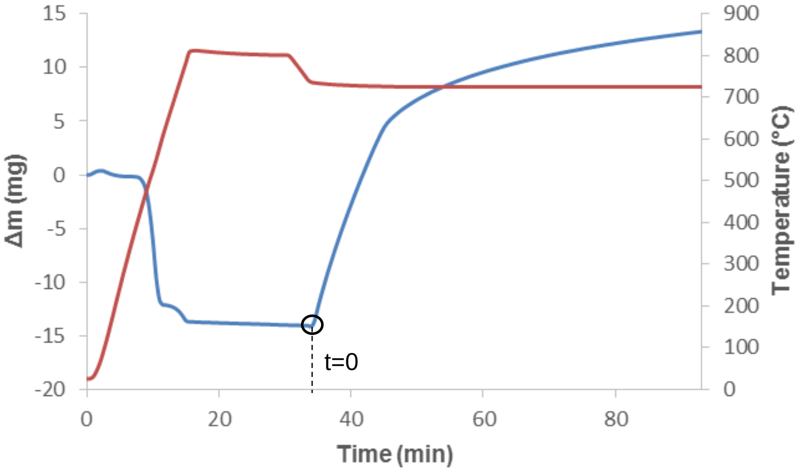

Figure 29 – Thermogram of the commercial calcium oxide: Carbonation temperature=725°C. Exemplification of the maximum of weight loss

Since the k has the unit of s^{-1} the model is only valid for reactions with first order. According to Sun et al. [74], for low CO_2 partial pressure driving force, the carbonation reaction is first order, therefore it can be written as:

$$P_{CO_2} - P_{CO_{2,eq}} \leq 10\ kPa \tag{20}$$

Where P_{CO_2} is the work pressure in Pa and $P_{CO_{2,eq}}$ is the equilibrium pressure at work temperature in Pa. The P_{CO_2} is calculated through the equation 21:

$$P_{CO_2} = y_{CO_2} \times P_T\ (Pa) \tag{21}$$

Where y_{CO_2} is the molar fraction of CO_2 in the flue and P_T is the work pressure in Pa. In this case, all of the experiments were made at atmospheric pressure. The equilibrium pressure was calculated through the equation 22:

$$P_{CO_{2,eq}} = e^{\left(7.079 - \left(\frac{8308}{T}\right)\right)} (atm)\ \text{[78]} \tag{22}$$

Where T is the absolute temperature (K). Since the carbonation reaction is isothermic, the T was calculated as the average of all of experimental temperatures, since (t=0) until the end of the experiments. The obtained results are shown in table 11.

Table 11 – Determination of the reaction order, using the difference of pressures

T(ºC)	P_{CO2} - $P_{CO2, eq}$ (Pa) - Marble	P_{CO2} - $P_{CO2, eq}$ (Pa) - Dolomite	P_{CO2} - $P_{CO2, eq}$ (Pa) – Calcium Oxide
750ºC	-15319	-15320	-15315
725ºC	-8732	-8733	-8734
700ºC	-3115	-3114	-3116
650ºC	5609	5612	5612
600ºC	11580	11589	11588

Looking carefully at table 11 it is possible to observe that the only temperature that does not respect equation 22 is 600°C, for all the three sorbents. Obviously, the values of CO_2 partial pressure are equal, since the experiments were made at the same temperature. Therefore, the temperatures used to fit the data were 750ºC, 725ºC, 700ºC and 650ºC. However, for marble it was decided to use only the first three, since 650ºC presented a different behavior. It is very important to refer that this approximation of the reaction order is not the most correct one. By evaluating these parameters it is possible to conclude that the molar fraction of CO_2 interferes with order reaction. Higher the molar fraction could mean a reaction with zero order. The chosen temperature has an even high influence in the reaction order, that the molar fraction, because normally for temperature above 700ºC, the reaction is first order [74].

In figure 30 there are the various curves for each temperature and sorbent, through the data fitting using equation 18, to obtain the slopes in order to calculate after, the kinetic parameters:

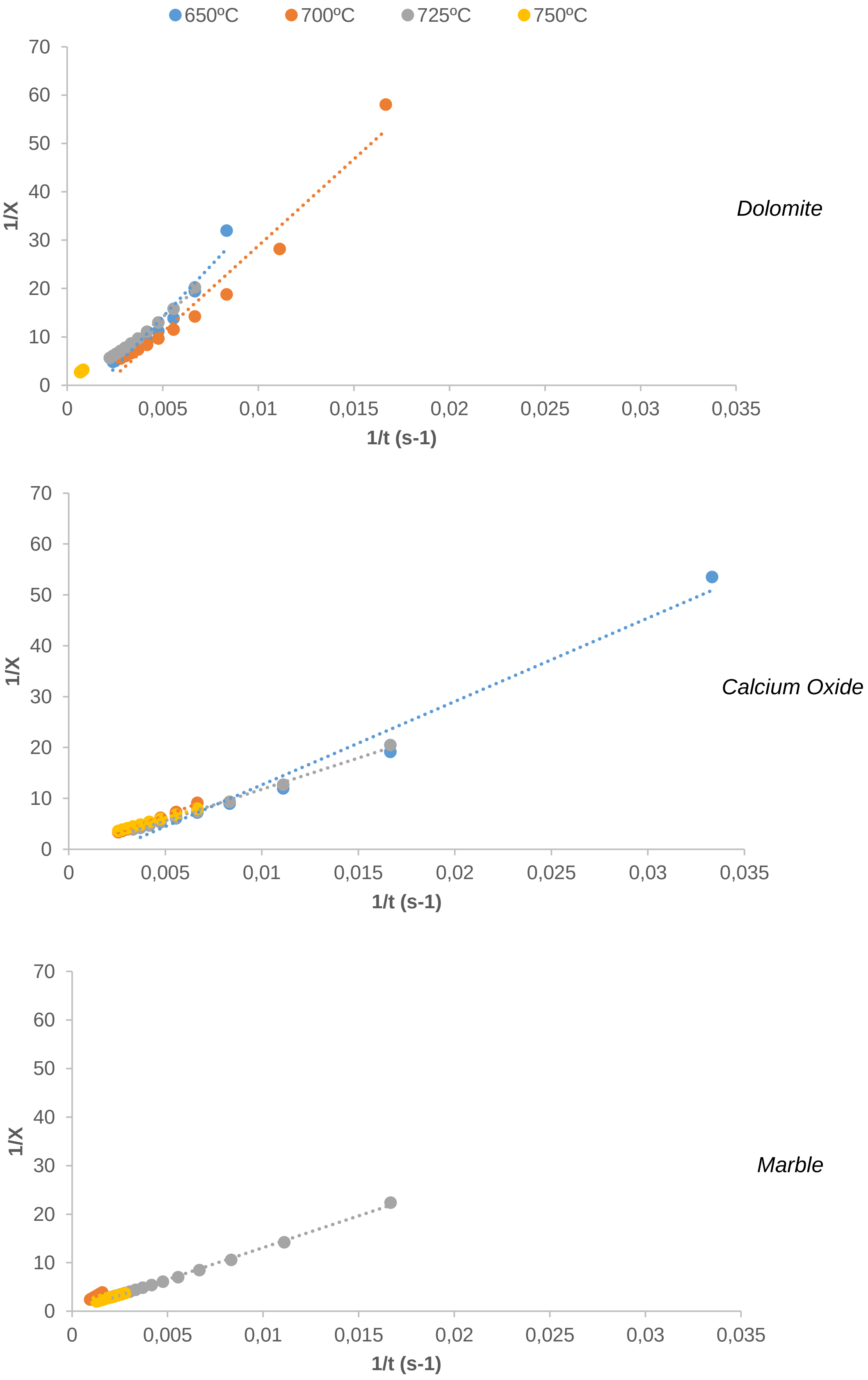

Figure 30 - Data fitting into linear regression equation for the kinetic region

It is important to mention that the data used to fit, corresponds graphically to number 1, the kinetic region, as shown in the figure above.

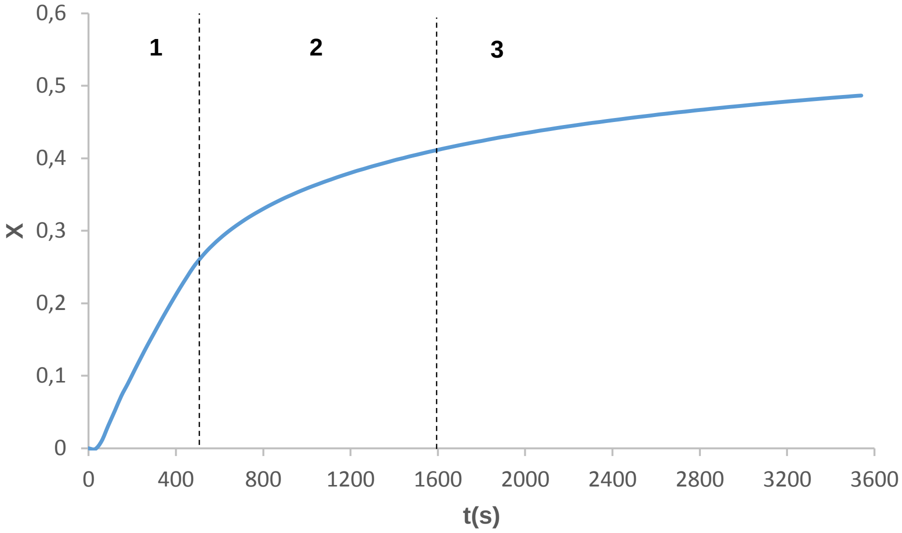

Figure 31 - Explanation of the different regions of the carbonation reaction. Sorbent - Dolomite; Temperature of reaction: 650ºC. 1 – Kinetic region, 2 – Transition region, 3 – Diffusional region

This model divides the kinetic region in two parts: the lower part of the curve and the upper part of the curve, near the transition region. For this part of the thesis it was chosen to work only with the lower part of the curve of the kinetic region, since the obtained results were coherent. However, looking at the upper part of the curve, the obtained results were not that good and didn't follow the results of the lower part, which means that it could be an inversion of the reaction order or even the external diffusion limitation.

To estimate the kinetic parameter k, it was necessary to use the Arrhenius equation. This equation is a function of time and uses the natural logarithm of k and the inverse of the absolute temperature. These plots are shown in figure 32:

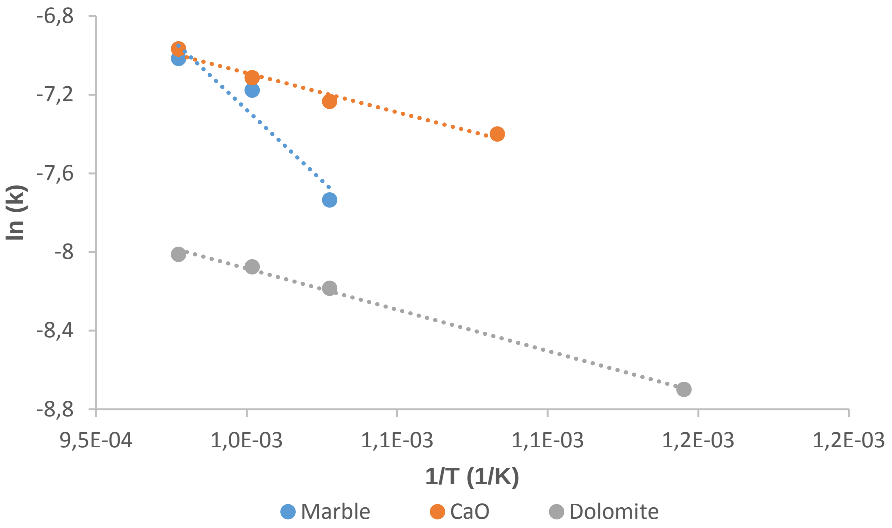

Figure 32 - Determination of the Activation energy through the Arrhenius plot for each sorbent

In the tables below there are all the results summarized of the Arrhenius plot for each sorbent and their respective temperature.

Table 12 – Arrhenius plot results for Calcium Oxide sorbent at the kinetic region

T(ºC)	Calcium Oxide			
	k (s^{-1})x10^{-5}	Ea (kJ/mol)	k$_0$ (s^{-1})	R^2
750ºC	94	33.3	0.05	0.970
725ºC	81			
700ºC	72			
650ºC	61			

Table 13 - Arrhenius plot results for Dolomite at the kinetic region

T(ºC)	Dolomite			
	$k\ (s^{-1})\times10^{-5}$	Ea (kJ/mol)	$k_0\ (s^{-1})$	R^2
750ºC	33	34.9	0.02	0.996
725ºC	31			
700ºC	28			
650ºC	17			

Table 14 - Arrhenius plot results for Marble at the kinetic region

T(ºC)	Marble			
	$k\ (s^{-1})\times10^{-5}$	Ea (kJ/mol)	$k_0\ (s^{-1})$	R^2
750ºC	98	119.7	1234	0.917
725ºC	100			
700ºC	103			
650ºC	-			

Looking carefully to the obtained results in tables 12, 13 and 14 for the three sorbents and comparing the results from the literature, it is possible to say that the correlation coefficients are reasonably good, therefore the kinetic parameters obtained are plausible. In terms of the activation energy for the sorbents obtained, there are only values for calcium oxide and dolomite since marble has never been studied before. For dolomite in [74] and [79] the values found were Ea=24±6 kJ/mol and for calcium oxide 29±4 kJ/mol. Also for calcium oxide in [77] it was obtained a value of 65.6 kJ/mol. Comparing these results, they are at the same order of magnitude, therefore the obtained values are plausible.

4.2 CO_2 adsorption tests – Evaluation of the performance and their behavior

The main goal of this thesis is to evaluate and to compare different sorbents in terms of capturing CO_2 through several cycles. For the first part it will be evaluated the different geological sources, then it will be discussed the calcination temperature of the samples and their influence in the capture activity and the morphology, although the morphology of the samples are not presented and discussed in this thesis. Another important aspect is the fact that the majority of the sorbents used for the cycles were calcinated at 850ºC. The calcination temperatures are discussed in the topics below.

4.2.1 Geologic sorbents

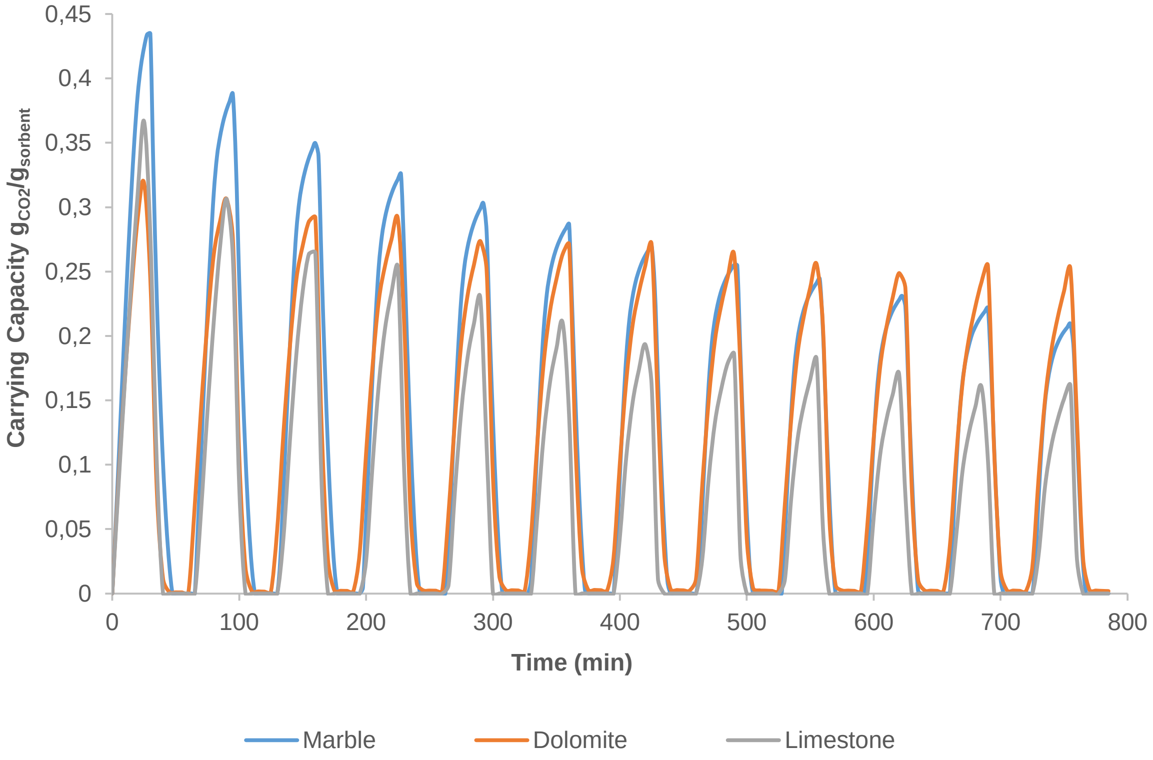

Figure 33 – Carrying capacity for the chosen geological sources: Marble, Dolomite, Limestone and Pummice

Looking at figure 33 it is possible to conclude that limestone and dolomite have lower capture capacities initially: 17% and 25% respectively, but through the cycles the CC of marble and limestone lowers more than 50% while dolomite has a diminution of 20% approximately. Dolomite has inert coumpounds in its composition such MgO and since MgO does not participate in the reaction, could act as a spacer preventing the growing of the grain boundaries, which could lead to a constant CC. As mentioned above, marble has a high activation energy, therefore it could present some diffusional limitation which reflects in the results shown in figure 33. The CC decreases at high rate, and for that reason, doping this sample could lead to better results.

Paying attention to figure 33, it is possible to observe that through the cycles, the carbonation has two well-defined regions: kinetic and diffusional. And one has predominance over other as the cycles proceed. In the figure 34(below) it is presented the scheme of the carbonation regions:

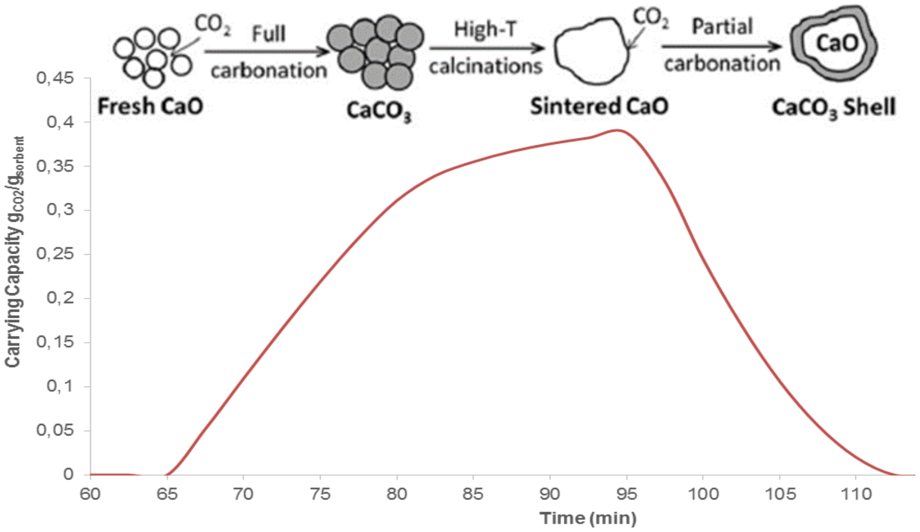

Figure 34 – Scheme of the carbonation/calcination cycle for the third cycle of calcinated marble at 850ºC

Through the cycles the tendency is to increase the duration of the diffusional stage, since the formed layer tends to increase through the cycles due to carbonation reaction. It is known that the size of particles has a great influence in the carbonation reaction. For smaller particles of CaO, the tendency is to have a bigger layer formed, therefore the passage of the CO_2 molecules become more difficult and leads to the diminution of the CC. The grain boundaries through the cycles tend to be bigger and lead to the closing of the mesopores, therefore the reaction rate lowers due to the formation of the $CaCO_3$ layer has shown above in figure 34. To evaluate these behaviors it had to be done some morphology evaluations to confirm this facts.

The calcination temperature of the sample has an impact in the carrying capacity of the sorbents. For that reason it was performed long cycles for calcinated marble at four different temperatures: 750ºC, 850ºC, 950 ºC and 1100ºC and for non calcinated marble, in order to evaluate the behavior. They are shown in figure 35.

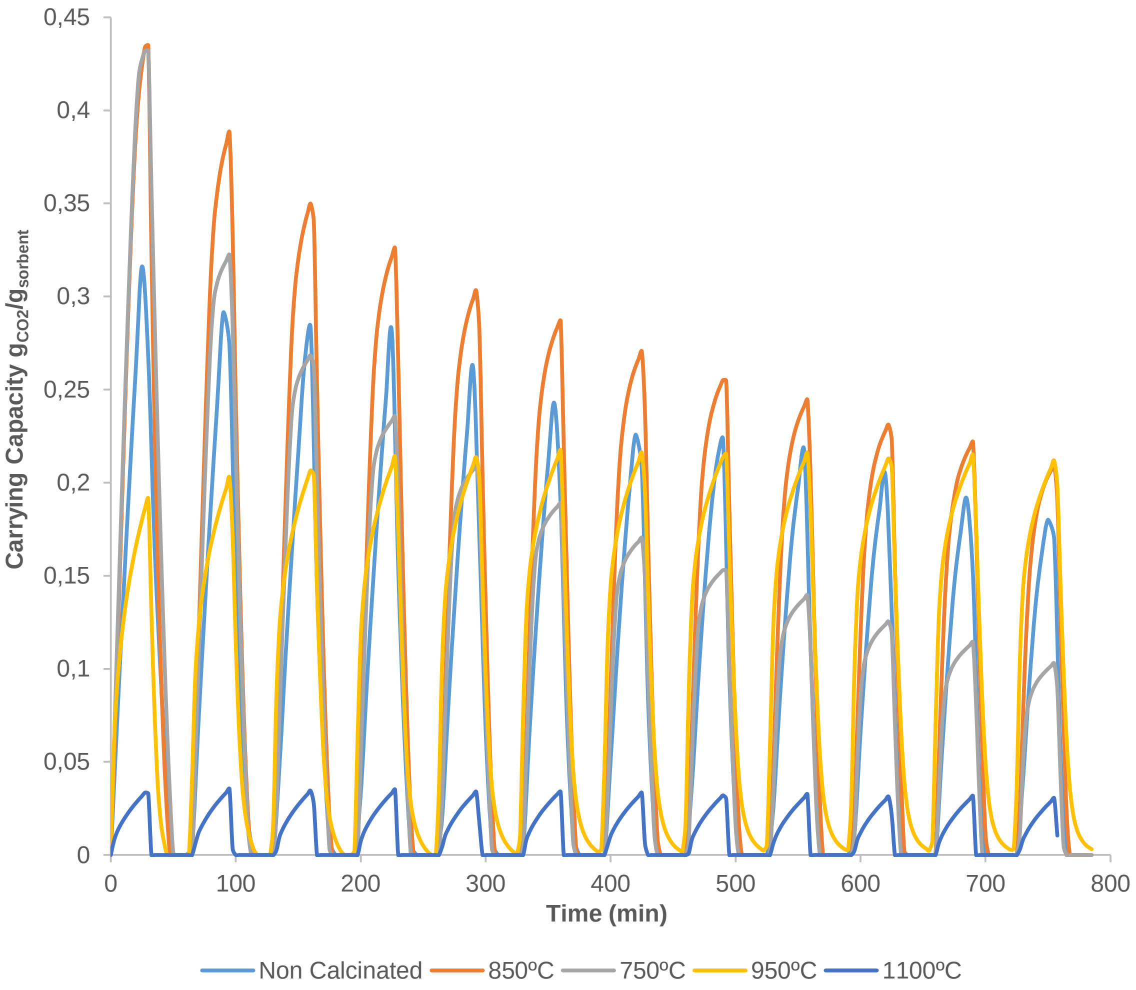

Figure 35 – Carrying capacity of calcinated and non-calcinated marble

There are many factors that influence these results. First of all, using high calcination temperatures leads to lower carrying capacities. As mentioned above, the tamman temperature of $CaCO_3$ is approximately 650ºC which means that higher temperatures could lead to sinterization and consequently lower CC. For the highest calcination temperature (1100ºC) the CC does not pass from 0.05 $gCO_2/g_{Sorbent}$ although it remains constant through the cycles. Since the particles could be already agglomerated due to high temperature it could be one of the reasons of the predominance of the diffusion region. The behavior of 950ºC is similar to 1100ºC although its CC is four times higher than 1100ºC. In the end of the cycles, the calcination temperature of 950ºC presents the same values of the work calcination temperature: 850ºC, therefore it could be work in further works. For 750ºC the initial values of CC are high, but as the cycles proceed the decay is very high. Comparing the initial and the final value of the CC for 750ºC it has a diminution of 75%. The chosen calcination temperature to work (850ºC) has potential in terms of CC, although it suffers diminution it is not harsh as 750ºC and these results could improve in presence of metals. Finally, the non-calcinated marble could be used raw, for capturing CO_2 since it presents good results and the decay of the activity it not high when compared, for example, with the calcination temperature of 750ºC.

The main factors that influence the behavior of the capture of CO_2 for the calcinated sorbents at different temperatures are the amount of CO_2 adsorbed naturally in the sorbent, the presence of H_2O and the amount of $CaCO_3$ that was not converted in CaO. But, to evaluate it, some characterizations had to be done, such as XRD or FTIR. The increasing of the calcination temperature leads to the aggregation of the particles as mentioned above, which leads to bad results.

4.2.2 Commercial calcium carbonate and calcium oxide

To compare the different samples it is necessary to study the main sources and for that reason it was decided to perform some tests with commercial calcium oxide and calcium carbonate to compare it after. In the figure below it is possible to see the behavior of CaO in different cases.

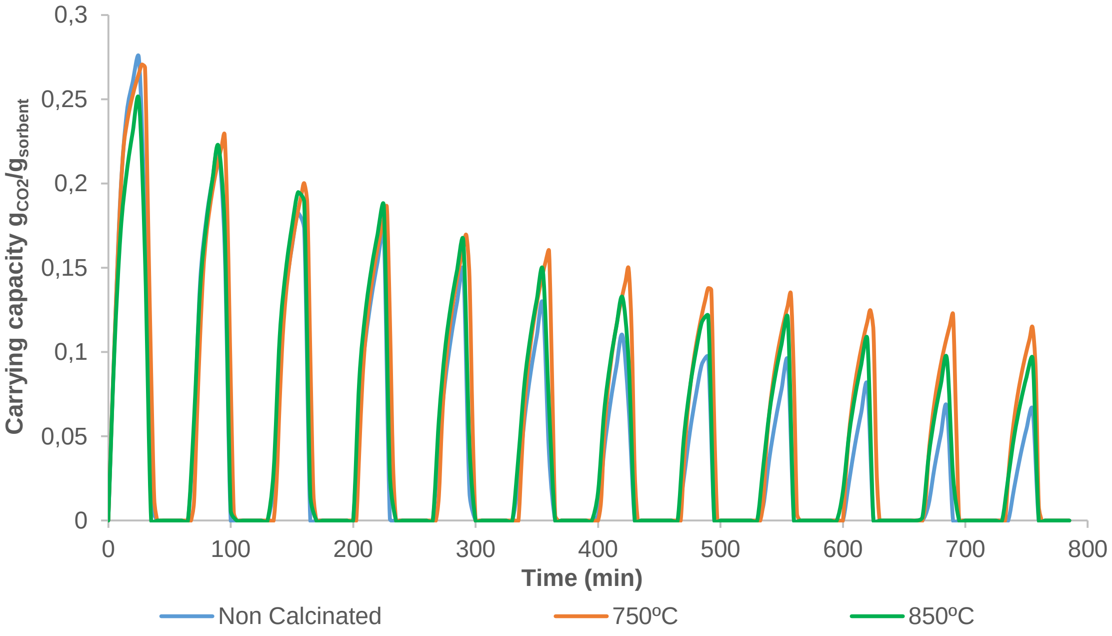

Figure 36 – Carrying capacity of non-calcinated and calcinated commercial CaO

For calcium oxide, it is possible to see, in figure 36, that for the first cycle the sorbents present almost the same CC. Even the non-calcinated CaO shows higher CC than the calcinated ones. But through the cycles, the non-calcinated loses more that 50% of activity and presents much lower slopes, which means that the diffusional region tend to predominate over the kinetic region. Comparing the two calcination temperatures of CaO, 750ºC and 850ºC there are no bigger differences between then, although 750ºC presents better results. It is important to refer that the calcination time used is too high, since it has more than enough time to desorb. Therefore, the diminution for 15-20 min is more than enough to perform the experiments.

In figure 37, the obtained results for $CaCO_3$ are presented:

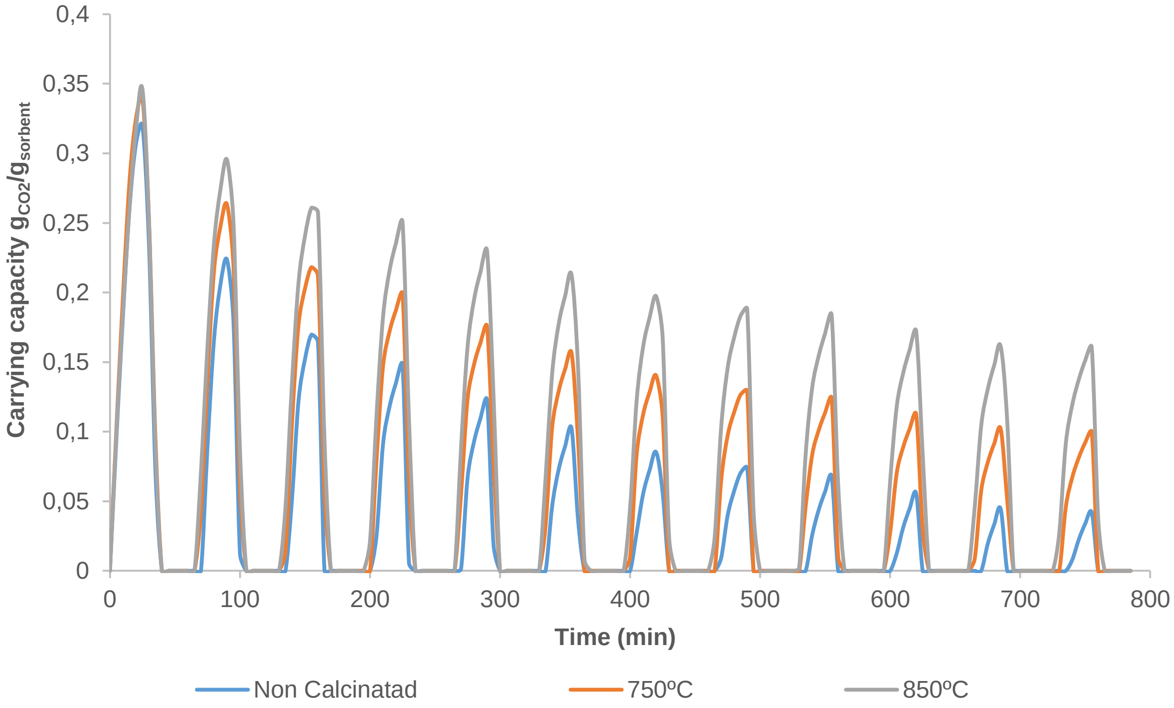

Figure 37 - Carrying capacity of non-calcinated and calcinated commercial $CaCO_3$

For this sorbent the difference between the different CC is more visible. Initially the non-calcinated and the calcinated samples have the same CC, ranges from 0.28 and 0.34 $gCO_2/g_{Sorbent}$. However through the cycles it is possible to see an accentuated diminution of the CC for the non-calcinated sample and for 750ºC. For both, the decrease of the activity is higher than 50% which leads to a conclusion that the chosen temperature (850ºC) to perform the kinetic experiments was the right one. The same result is verified in marble, since it possesses great amounts of $CaCO_3$. The sample calcinated at 850ºC possesses more kinetic activity than the others, since it has a high slope and through the cycles does not present an accentuated diffusional behavior as the others.

4.2.3 Doped geological sorbents

Once the main issue of the chosen calcination temperature is detected, it is time to evaluate the influence of metals in the sorbent. For marble it was decided to dope with Cerium (Ce) and Nickel(Ni) in a molar proportion of 1:0.1 (Marble:Metal) and after the doping the samples were calcinated at 850ºC. The obtained thermogram is shown below in figure 38:

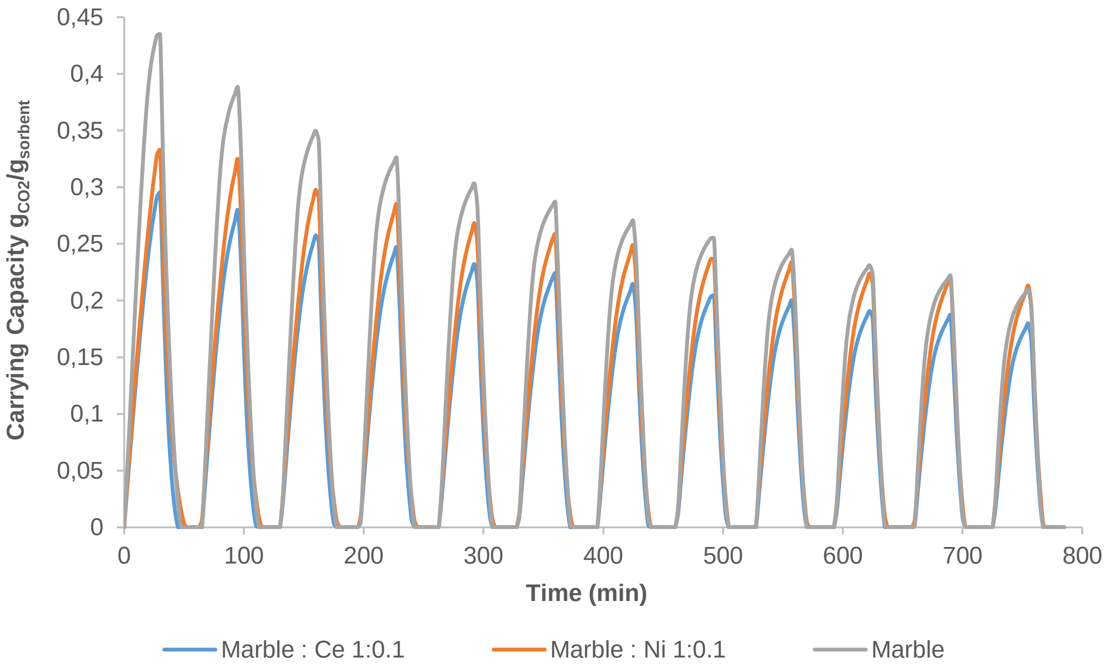

Figure 38 - Carrying capacity of doped marble samples calcinated at 850ºC

The introduction of metals in these samples introduces modifications at the morphological level, which cannot be evaluated. However these results in terms of CC show greater stability when it used metals. Comparing Ce and Ni, both present stable results when compared with marble without doping. Furthermore it is possible to see that for the last cycle marble and marble with Ni achieve the same CC, therefore it can be considered a plausible sorbent for capturing CO_2. The presence of this metals can be considered as spacers, between the CaO particles and for that reason the CC remains stable through the cycles, between 0.32 and 0.26 $gCO_2/g_{Sorbent}$ for the samples doped with Ni and between 0.29 and 0.21 $gCO_2/g_{Sorbent}$. The time to desorb the CO_2, one more time, is too much.

4.2.4 Geologic sorbents (marble) with acid treatment

After doping the marble samples, it was decided to investigate the influence of an acid treatment using HNO_3, since marble could contain some impurities that could affect the final result. Although the right way to evaluate it, should be through characterization of the samples, e.g. XRD or FTIR. The figure below compare the used metals to dope the samples and the sample without the metal.

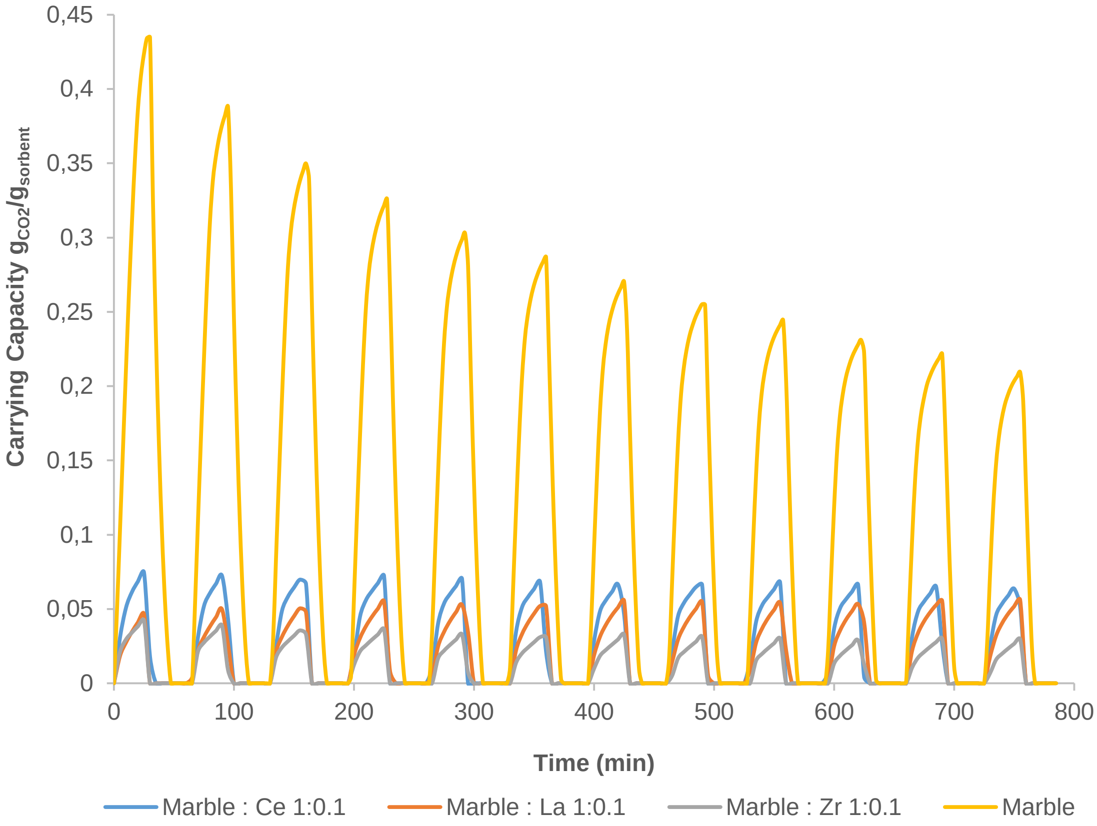

Figure 39 - Carrying capacity of doped marble samples calcinated at 850ºC with HNO_3 treatment

In figure 39 it is visible that using HNO_3 to treat the samples is not the best solution, because the difference in terms of CC is higher than 90%. In the first cycle, marble without metals presents a carrying capacity of 0.44 $gCO_2/g_{Sorbent}$ and marble doped with Ce and with an acid treatment is 0.075 $gCO_2/g_{Sorbent}$. It is important to mention that it was not performed a long cycle with marble treated with HNO_3 and without metals, therefore it could have been interesting to evaluate and compare it. As mentioned above, marble presents some diffusional limitations, therefore the doping of the samples could improve the results. However, this method with the acid treatment solves the decay of CC, because for the three samples the CC remains constant, but the capture activity is too low for what is desirable and for that reason it is not a good solution to apply at other scale

4.2.5 Doped calcium carbonate and calcium oxide

Since it was used metals to dope the marble, it was decided to repeat the same procedure for the commercial calcium oxide and calcium carbonate. First it is presented the calcium oxide samples in the figure 40:

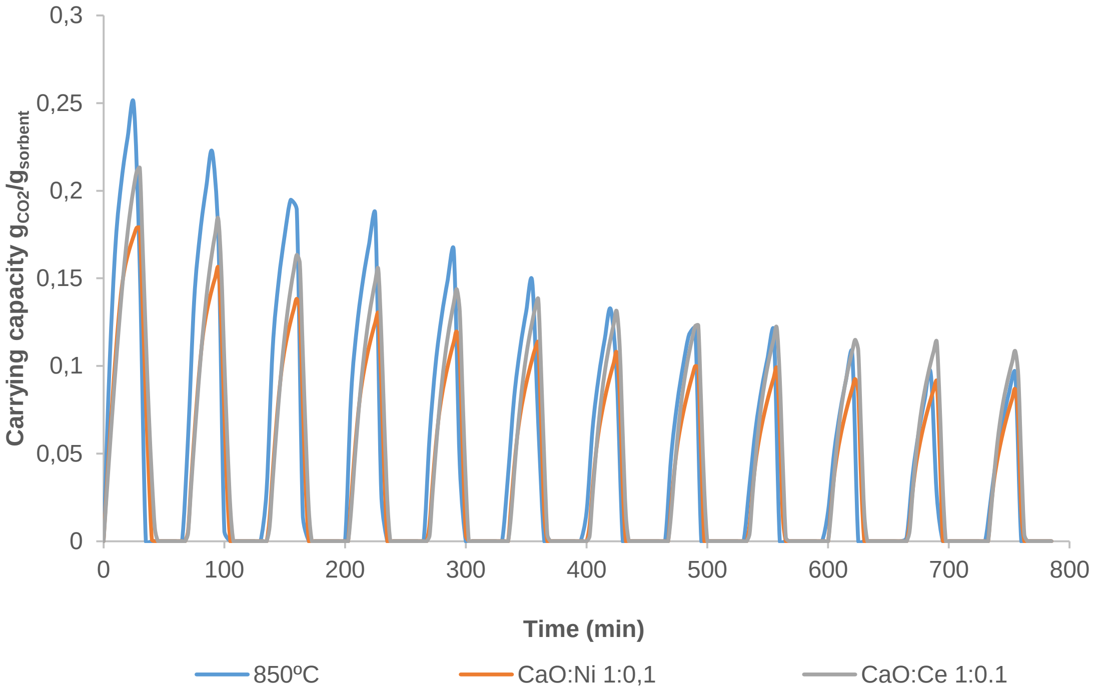

Figure 40 - Carrying capacity of doped commercial calcium oxide samples calcinated at 850ºC

One more time it is confirmed the same behavior in terms of carrying capacity for the calcium oxide. It is verified that in the last cycle (12th) the sample doped with cerium presents higher CC than the sample without the metal. The same is not verified for the sample doped with Ni, since it presents the lowest value of the evaluated three. One more time, the absence of characterization in terms of SEM, does not help to confirm the fact that Ce could act as spacer between the particles, and for that reason manages to maintain the CC almost constant through the cycles. Once again, the time of calcination is too high. In terms of the behavior of the carbonation region it was decided to fragmentize the cycles shown in figure 40 to observe the evolution of these regions. The individual cycles can be observed in figure 41.

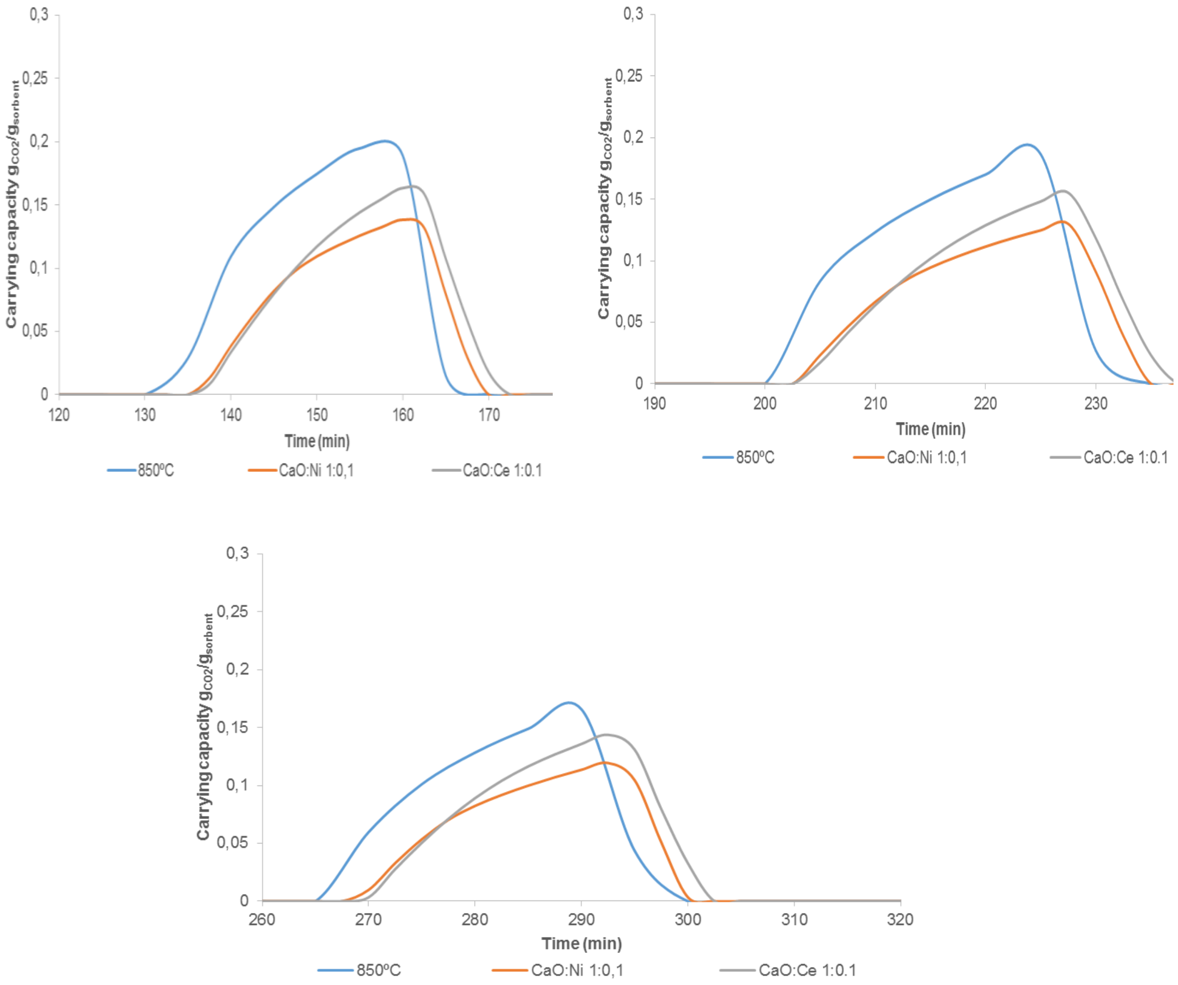

Figure 41 – Evaluation of the regions of the carbonation reaction for doped commercial calcium oxide samples calcinated at 850ºC. Left – 2nd cycle, Right – 3rd cycle, Middle-4th cycle

Since these carbonation/calcination cycles are too long, and since more than 10 cycles were performed, it was decided to show the 2nd, the 3rd and the 4th cycles, since the cycles follow the tendencies shown in the figure above. For the second cycle of the non-calcinated sample it is possible to see that it has the two well-defined regions: kinetic and diffusional. This cycle presents a great slope when compared with the third and the fourth cycle. For the third cycle, the two regions are also well defined, but the kinetic region has a short duration when compared with the previous cycle. Finally for the fourth cycle there is mist behavior between the kinetic and diffusional. For the doped samples, the kinetic region is well-defined for the 2nd cycle, but for the rest it starts to show some behavior between the kinetic and the diffusional. Although that behavior applies better to the samples doped with Ce than with Ni.

Since the chosen temperature of the calcination temperatures of the samples was 850ºC, it was decided not to evaluate the graphics in the annex A2 and A3. Since it is shown other experiences with CaO and these metals with different calcination temperatures of the samples.

For the final group of sorbents, it is shown in the figure below the behavior of the calcium carbonate sorbents doped and non-doped:

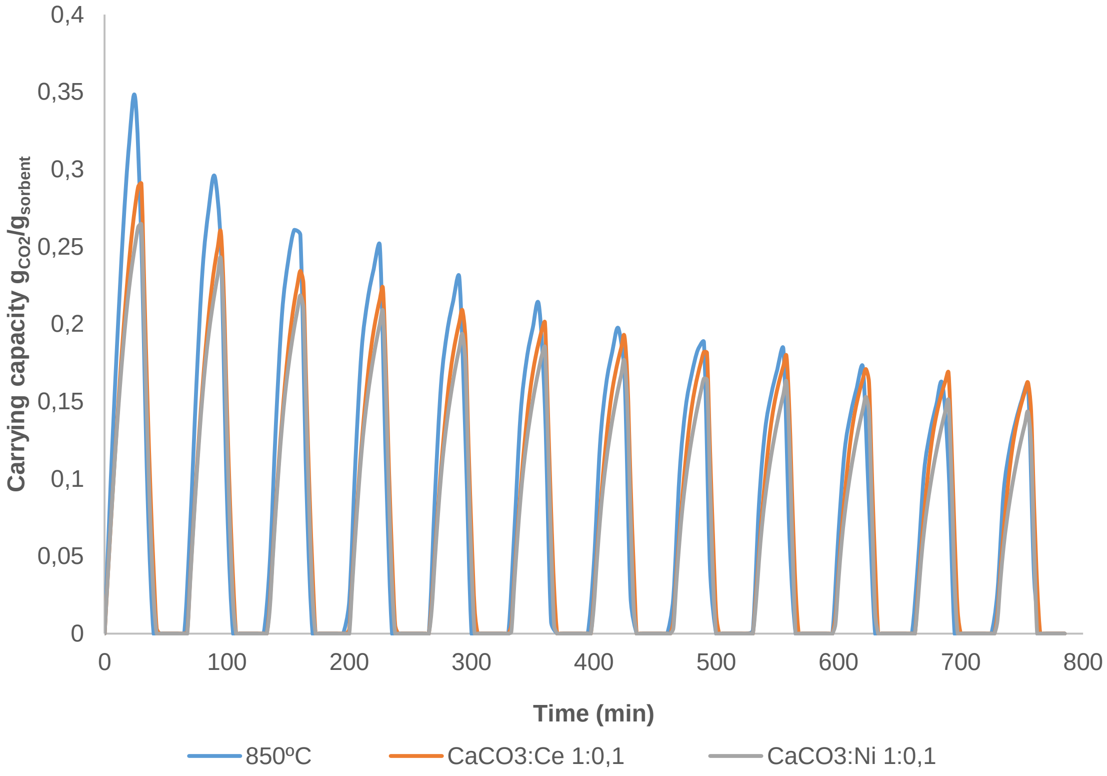

Figure 42 - Carrying capacity of doped commericial calcium carbonate samples calcinated at 850ºC

Looking carefully at figure 42, these group of sorbents present, again, the same behavior of marble and calcium oxide sorbents. As mentioned before, these sorbents are exposed to high temperatures which leads to sinterization of the sorbent and consequently the diminution of the carrying capactity, which it is not what is wanted. The samples doped with Ce present great results, since it has an almost constant CC and even in the last cycle, presents high CC than the sample without metal. As for the sample of Ni presents the same behavior of Ce, although it's CC is lower than the rest.

Through the cycle and looking carefully at the thermogram, the diffusional region tends to be more extensive than the kinetic, which influences the CC through the cycles.

In the annex A4 and A5 there are the two groups of samples evaluated in the thermogram, for the reasons mentioned before.

Finally, in the figure 43, it is summarized the best results obtained for all the sorbents.

Table 15 - Summary of the best results for the sorbents

Sorbent	Calcination Temperature	CC 1st Cycle	CC 12th Cycle	% Decreasing Activity
CaO	750ºC	0.27	0.11	60%
CaO : Ce (1:0.1)	850ºC	0.21	0.11	48%
Marble	850ºC	0.43	0.21	51%
Marble	950ºC	0.19	0.21	-10%[2]
Marble : Ce (1:0.1)	850ºC	0.3	0.18	40%
Marble : Ni (1:0.1)	850ºC	0.33	0.21	36%
$CaCO_3$	850ºC	0.35	0.16	54%
$CaCO_3$: Ce (1:0.1)	850ºC	0,29	0.16	45%
Dolomite	850ºC	0.32	0.25	22%

---

[2] For this sorbent, the activity increased

5 Summary & Conclusions

The main purpose of this thesis was to study a new type of sorbent (marble) and other sorbents, using the calcium looping cycle, through thermogravimetric analysis. First of all, it was determined and optimized the experimental conditions in order to determine the kinetic parameters and to perform the long cycles. In terms of the kinetic parameters, the obtained results have the same order of magnitude, for dolomite and commercial calcium oxide. For marble, it was obtained the very first values, since this sorbent has never been studied. As mentioned, it presents a high activation energy, which means that it possesses diffusional limitations, which are demonstrated in the thermograms. However, the lack of morphologic analysis, does not reinforce it, and that is one of the negative points. Also, the determination of the reaction order, was made using an approximation, and in future works, to determine it, it should be performed for each temperature reaction, for different CO_2 molar fractions.

Another aspect that could have been optimized in the long cycles, was the calcination time chosen. As shown through the entire thesis, it is possible to observe that the CC remains constant and equal to zero, for too long and reducing it, could allow to perform more cycles and perhaps the obtained results could improve. In terms of the carbonation reaction, the used temperature for the three sorbents, was not the best temperature for capturing the CO_2, as observed in chapter 4. However, it was decided to work in the harshest conditions, because those ones are more proximate from the industrial conditions. One criticism to this experiments, was the CO_2 molar fraction used to perform the long cycles, because the average composition of the flue gases is 0.15 and not 0.20, and that could provide more realistic results in terms of CO_2 capture, because the main goal is to get close as possible of the industrial conditions.

The use of metals, such as Cerium and Nickel to dope the different samples, showed great results in terms of CC, because the main purpose was achieved: get the capture activity constant through the cycles and avoid the sintering phenomena. However, it was not possible to prove that the sample has not suffered particle aggregation. For that purpose, it should have been used a SEM analysis. Also, the use of an acid treatment in sorbents, does not show the best results as expected, because the CC was too low.

Another important aspect of this entire work is the temperature calcination of the samples. The chosen temperature for all the samples was 850ºC, however it should be done some work in terms of XRD (X-ray diffraction) and FTIR to analyze the presence of other compounds that influence the results in order to understand better the obtained thermograms.

In general, the obtained results for marble were quite good and it is great material to work with. This raw material is abundant and the use of marble wastes could solve other environmental problem associated with this industry. For future considerations, in order to get close to the real industrial conditions, the flue gas should contain, not only N_2 and CO_2 but also water vapor and SO_2. Since SO_2 reacts with CaO it should be interesting to evaluate through morphologic analysis and TGA the influence of these chemicals in CO_2 capture.

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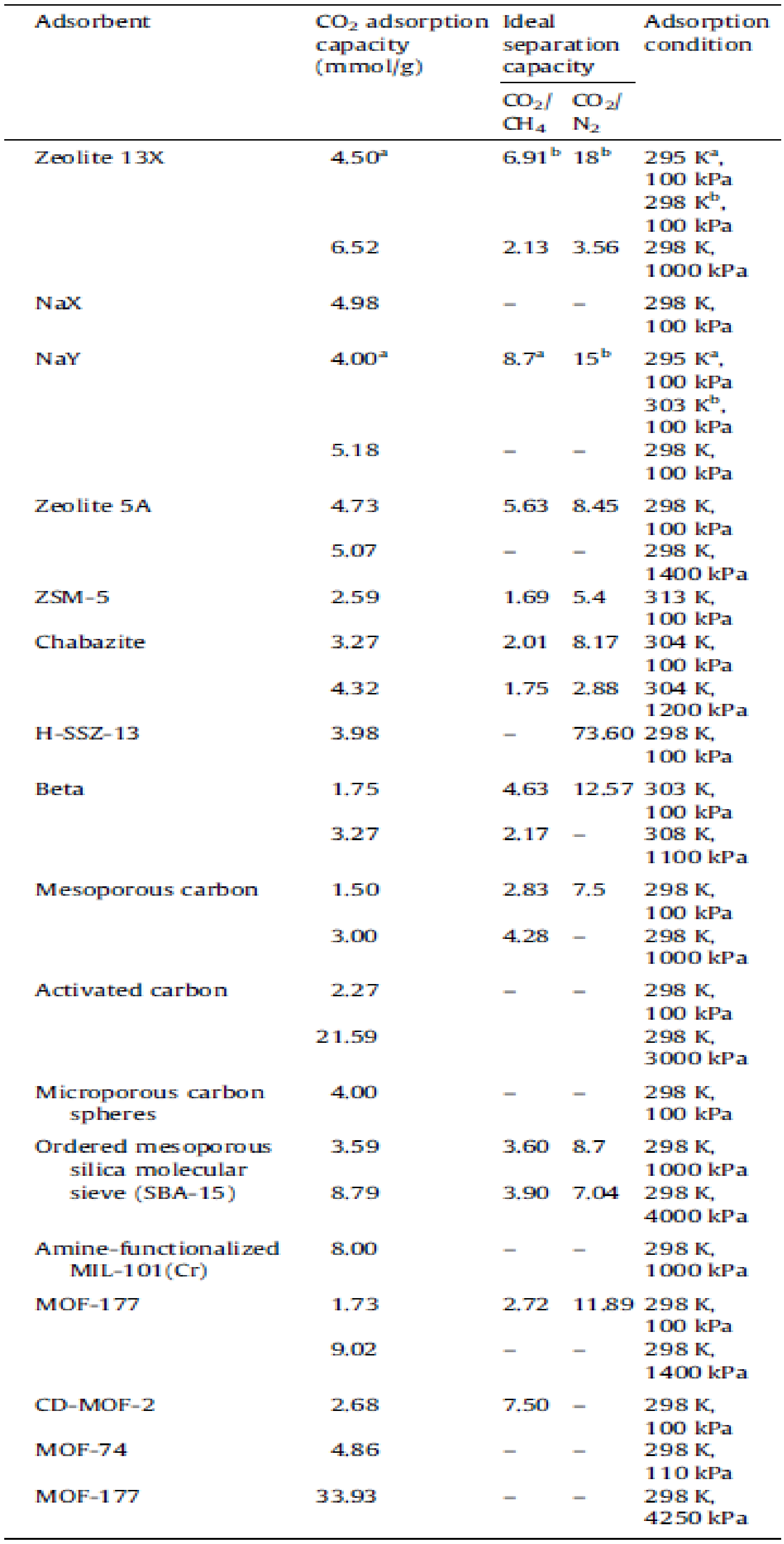
7 Annex

Table A 1 - CO_2 adsorption properties of various micro and mesoporous materials, from literature [43]



Adsorbent	CO_2 adsorption capacity (mmol/g)	Ideal separation capacity		Adsorption condition
		CO_2/ CH_4	CO_2/ N_2	
Zeolite 13X	4.50^a	6.91^b	18^b	295 K^a, 100 kPa 298 K^b, 100 kPa
	6.52	2.13	3.56	298 K, 1000 kPa
NaX	4.98	–	–	298 K, 100 kPa
NaY	4.00^a	8.7^a	15^b	295 K^a, 100 kPa 303 K^b, 100 kPa
	5.18	–	–	298 K, 100 kPa
Zeolite 5A	4.73	5.63	8.45	298 K, 100 kPa
	5.07	–	–	298 K, 1400 kPa
ZSM-5	2.59	1.69	5.4	313 K, 100 kPa
Chabazite	3.27	2.01	8.17	304 K, 100 kPa
	4.32	1.75	2.88	304 K, 1200 kPa
H-SSZ-13	3.98	–	73.60	298 K, 100 kPa
Beta	1.75	4.63	12.57	303 K, 100 kPa
	3.27	2.17	–	308 K, 1100 kPa
Mesoporous carbon	1.50	2.83	7.5	298 K, 100 kPa
	3.00	4.28	–	298 K, 1000 kPa
Activated carbon	2.27	–	–	298 K, 100 kPa
	21.59			298 K, 3000 kPa
Microporous carbon spheres	4.00	–	–	298 K, 100 kPa
Ordered mesoporous silica molecular sieve (SBA-15)	3.59	3.60	8.7	298 K, 1000 kPa
	8.79	3.90	7.04	298 K, 4000 kPa
Amine-functionalized MIL-101(Cr)	8.00	–	–	298 K, 1000 kPa
MOF-177	1.73	2.72	11.89	298 K, 100 kPa
	9.02	–	–	298 K, 1400 kPa
CD-MOF-2	2.68	7.50	–	298 K, 100 kPa
MOF-74	4.86	–	–	298 K, 110 kPa
MOF-177	33.93	–	–	298 K, 4250 kPa

Table A 2 - Operational conditions for calcination and carbonation reactions - references

Reference	Calcination			Carbonation		
	T(°C)	Q_{gas} (mL/min) or %(V/V)	t (min)	T(°C)	Q_{gas} (mL/min) or %(V/V)	t (min)
43	900	100 % - N_2	10	650	15 % - CO_2/N_2 balance	30
44	920	100 % - CO_2	5	800	100 - CO_2	25
44	950	100 % - CO_2	10	650	15 - CO_2/ 85 - N_2	60
48	950	100 % - CO_2	10	700	15 - CO_2/ 85 - N_2	60
50	850	100 % - N_2	10	700	15 - CO_2/ 85 - N_2	20
50	850	85 % -air 15 % -CO_2	5	650	85 % air 15 % - CO_2	5
52	900 - 950	85 % - air 15 % - CO_2	5	650	70 % - CO_2 30 % - air	5
56	900	100 % - N_2	10	650	15 % - CO_2 N_2 balance	30
57	950	100 % - CO_2	10	700	15 % - CO_2 85 % - N_2	60
58	950	100 % - CO_2	-	700	20% -CO_2 N_2 balance	30
59	850	100 % - N_2	30	650	20 % -CO_2 N_2 balance	30
60	800	100 % - N_2	15	700	15 % - CO_2 N_2 Balance	100
61	800	100 % - N_2	13	700	15 % - CO_2 N_2 Balance	50
62	900	100 % - N_2	5	650	100 % - CO_2	30
63	800	100 % - N_2	6	800	100 % - CO_2	30
64	800	100 % - N_2	15	800	100 % - CO_2	15
65	900	15 % - CO_2 N_2 and He balance	5	650	15 % - CO_2 N_2 and He balance	10
66	900	45-55 % - CO_2 N_2 balance	15	630	13,5% - CO_2 N_2 balance	15
43	800	100 % - CO_2	3	650	15 % - CO_2 air balance	5

Table A 3 – CO_2 adsorption properties of some zeolites and zeolite-like materials at low pressure, adopted from [42]

Zeolites/Si/Al ratio	CO_2 adsorption temperature (K)	Adsorption capacity at 0.1–0.4 bar (mmol/g)	N_2 adsorption capacity at 0.9–1.6 bar (mmol/g)	CO_2/N2 capacity molar ratio
NaX/1	298	3.9	0.264 – 0.46	11-8.5
NaX/1	323	1.43 - 2.49	-	-
LiX/1	303	4.6	-	-
NaY/2.4	323	0.45 - 1.17	-	-
CsY/2.4	333	0.86 - 1.2	-	-
KY/2.4	333	0.75 – 1.6	-	-
Silicalite/∞	334	0.16 – 0.45	0.1	1.6
H-ZSM-5/30	313	0.7 – 1.5	0.23	3
Li-MCM-22/15	333	0.68 - 1	-	-

Table A 4 – CO_2 adsorption capacity of amine-impregnated adsorbents, adapted from [42]

Support	Amine	Amine loading (wt%)	Capacity (mmol/g)	CO_2/N_2	Experimental Conditions	
					CO_2 concentration (%)	T(ºC)
MCM-41	PEI	50	2.1	0.18	10	75
MCM-41	PEI	50	2.84	0.27	13 (13% H_2O)	75
SBA-15	PEI	50	3.18	0.27	15	75
KIT-6	PEI	50	1.95	0.17	5	75
Monolith	PEI	65	3.75	0.25	5	75
As-synthesized SBA-15	TEPA	50	3.25	0.28	10	75
As-synthesized MCM-41	TEPA	50	4.54	0.34	5	75
As-synthesized SBA-15	TEP + DEA	50(20% TEPA, 20% DEA)	3.77	0.38	5	75

Table A 5 - Relative weight change after Carbonation and/or Sulfation and Regeneration. [a]After Carbonation, [b]After Carbonation and Regeneration, [c]After Carbonation/Sulfation, [d]After Carbonation/Sulfation and Regeneration, [e]After Sulfation, adapted from [49]

Sorbent	**Wt% increase[a] (g g^{-1})**	**Wt% increase[b] (g g^{-1})**	**Capacity for CO_2 uptake[a] (g g^{-1})**	**Wt% increase[c] (g g^{-1})**	**Wt% increase[d] (g g^{-1})**	**Capacity for CO_2 uptake[d] (g g^{-1})**	**Wt% increase[e] (g g^{-1})**
Mn/Ca	47	0.3	47	66	25	41	30
Ce/Ca	44	0.1	44	46	5	41	8
Cr/Ca	40	0.8	40	36	12	27	13
Co/Ca	26	0.2	26	27	10	17	16
Cu/Ca	24	0.05	24	24	6	18	8

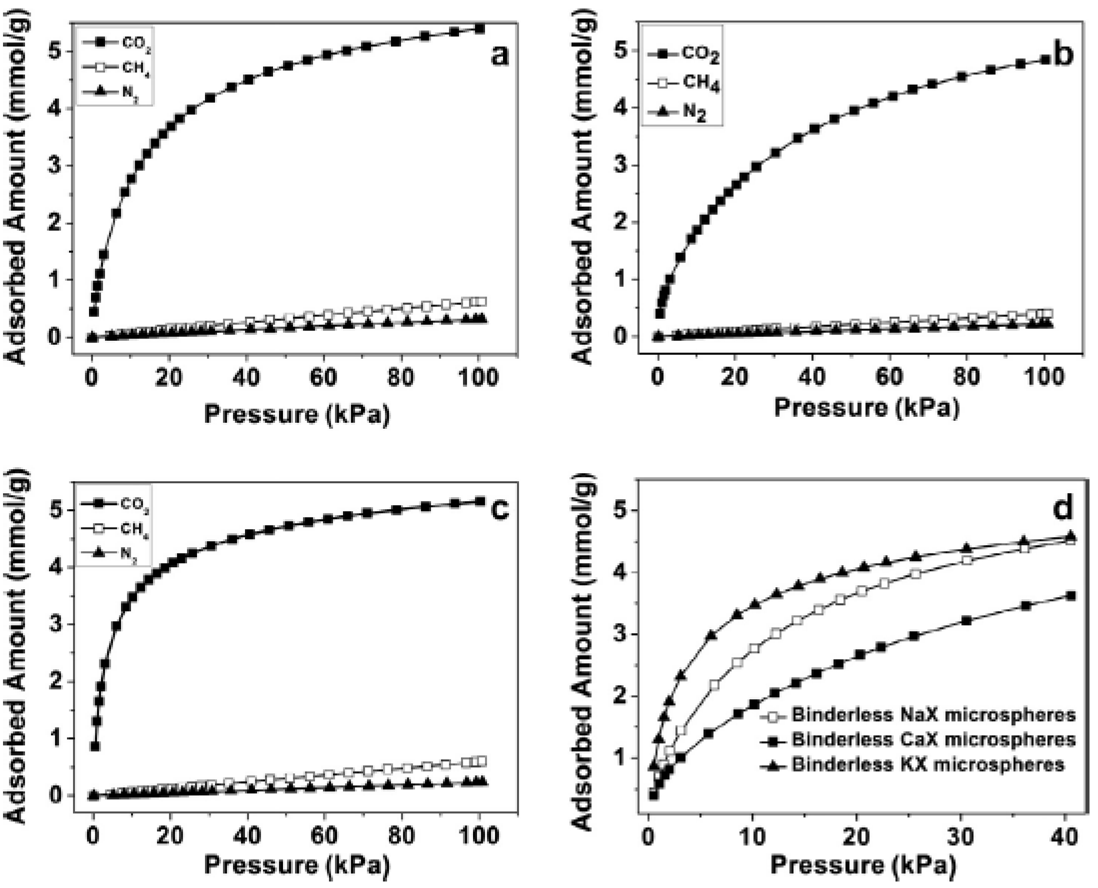


Figure A 1 - CO_2, CH_4 and N_2 adsorption isotherms on binderless NaX(a), CaX(b), KX(c) microspheres at 298 K and ambient pressure and CO_2 adsorption isotherms at pressure region under 298 K on NaX, CaX and KX binderless Zeolite X microspheres (d). [40]

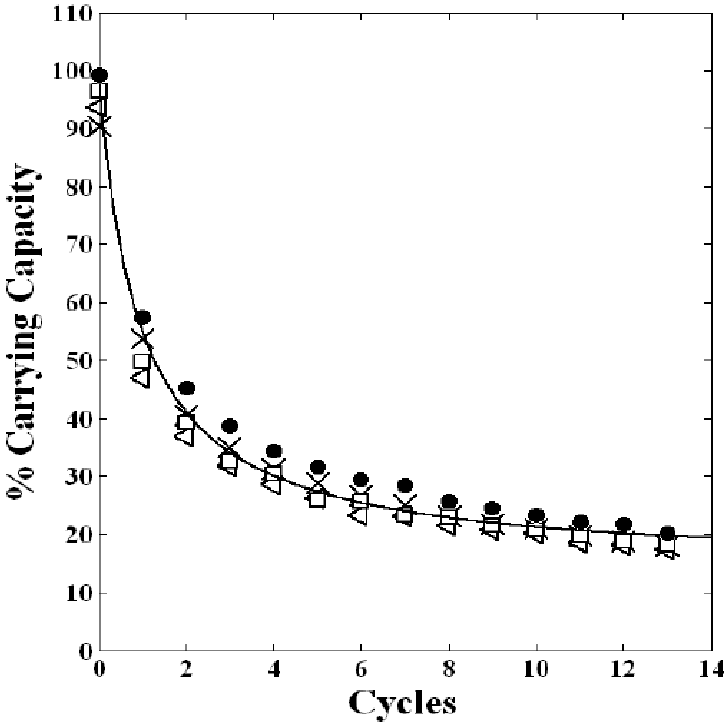


Figure A 2 – Carrying capacity for Purbeck limestone, plotted against the number of cycles: (X) undoped; (Δ) 0,165 mol-% $MgCl_2$; (○) 0,138 mol-% $CaCl_2$; (●) 0,190 mol-% $Mg(NO_3)_2$

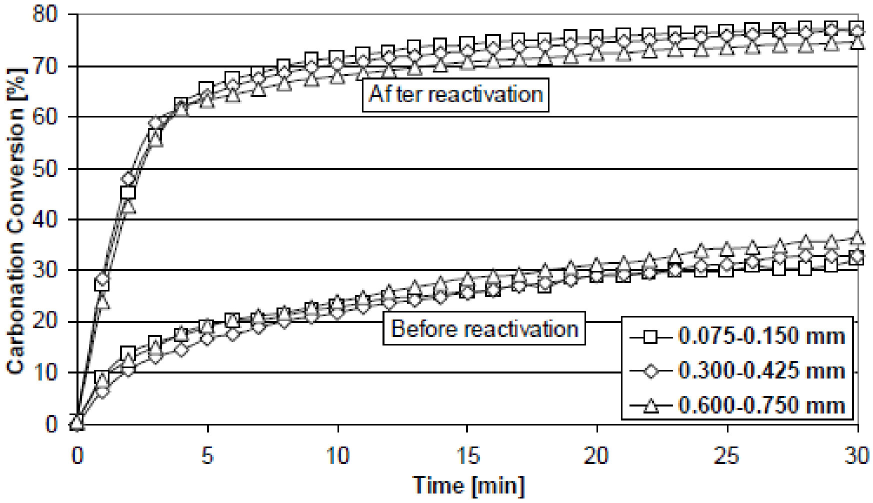


Figure A 3 – Steam reactivation effect on sorbent activity during carbonation in the TGA. Kelly Rock limestone; 20 cycles (20% CO_2, N_2 balance, 650°C, 30 min/ 100% N_2, 850°C, 30 min); reactivation by steam (saturated steam, 200°C, 30 min); and carbonation in TGA (15% CO_2, N_2 balance, 700°C) [61]

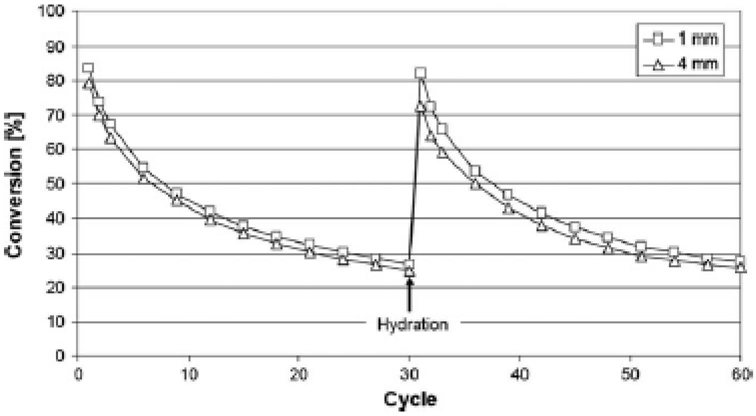


Figure A 4 – Conversions of KT-CA-14 pellets (1 and 4 mm pellets size) after 300 carbonation/calcination cycles in TGA, hydration and reshaping [60]

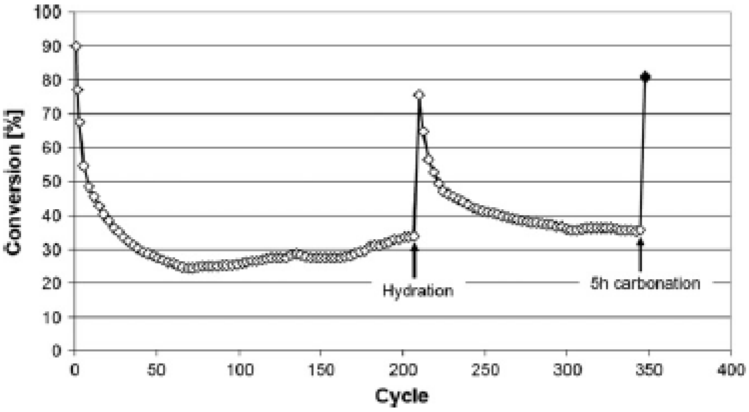


Figure A 5 – Conversions of CD-CA-14 pellets (1 mm) in a longer series of carbonation/calcination cycles after 300 carbonation/calcination cycles in TGA, hydration and reshaping [60]

A1 – Calibration of the Rotameters

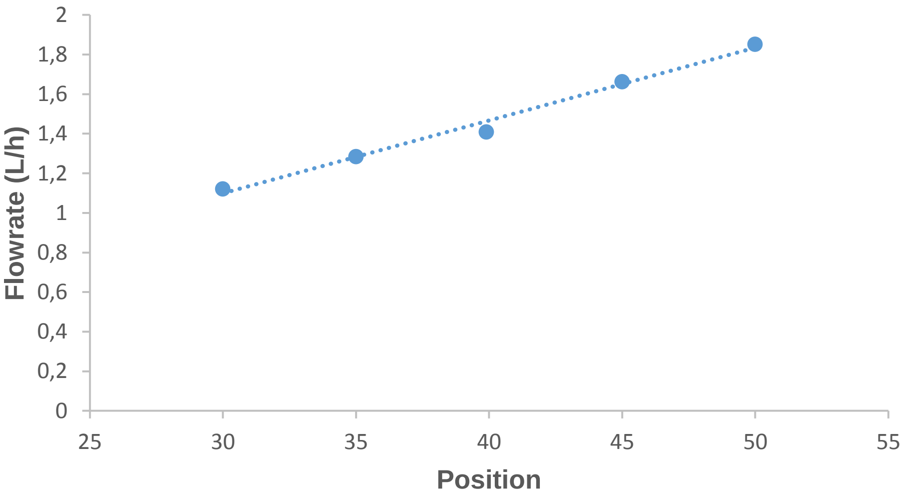


Figure A 6 - Calibration of the CO_2 rotameter. Linear regression: y=0,0368x – 0,0046, R^2=0,9886

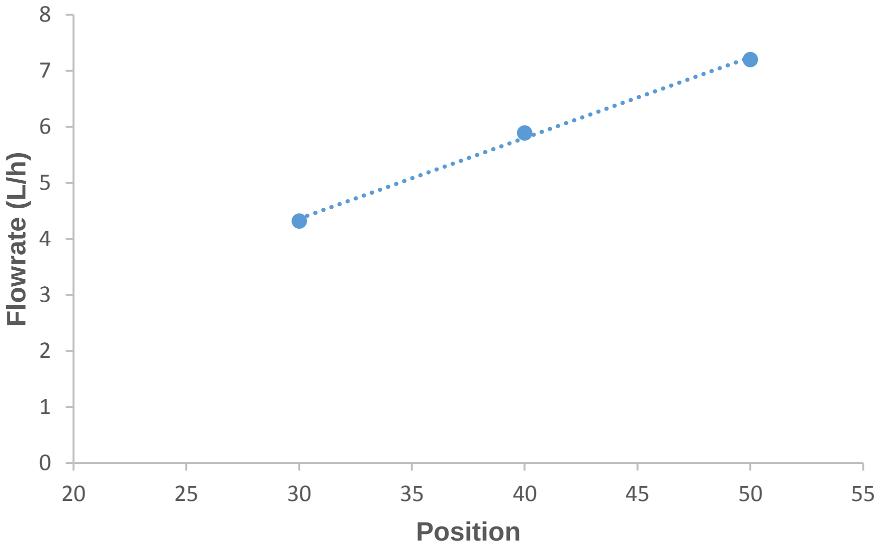


Figure A 7 – Calibration of the N_2 rotameter. Linear regression: y=0,144x + 0,0436, R^2=0,9973

A2 – CaO doped with Cerium at different temperatures

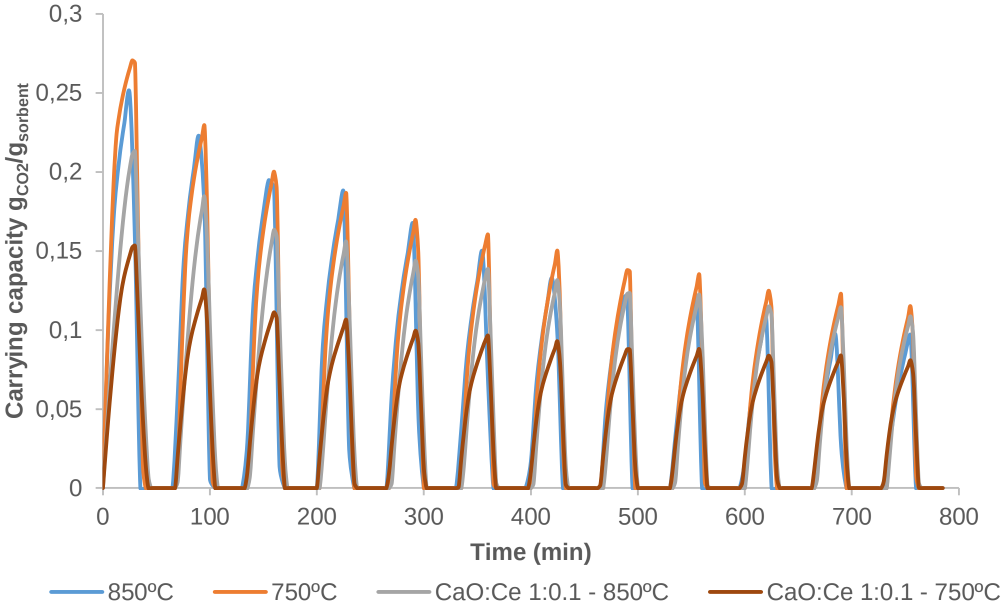


Figure A 8 - Carrying capacity of doped and non-doped commercial calcium carbonate samples calcinated at 850ºC and 750ºC

A3 – CaO doped with Nickel at different temperatures

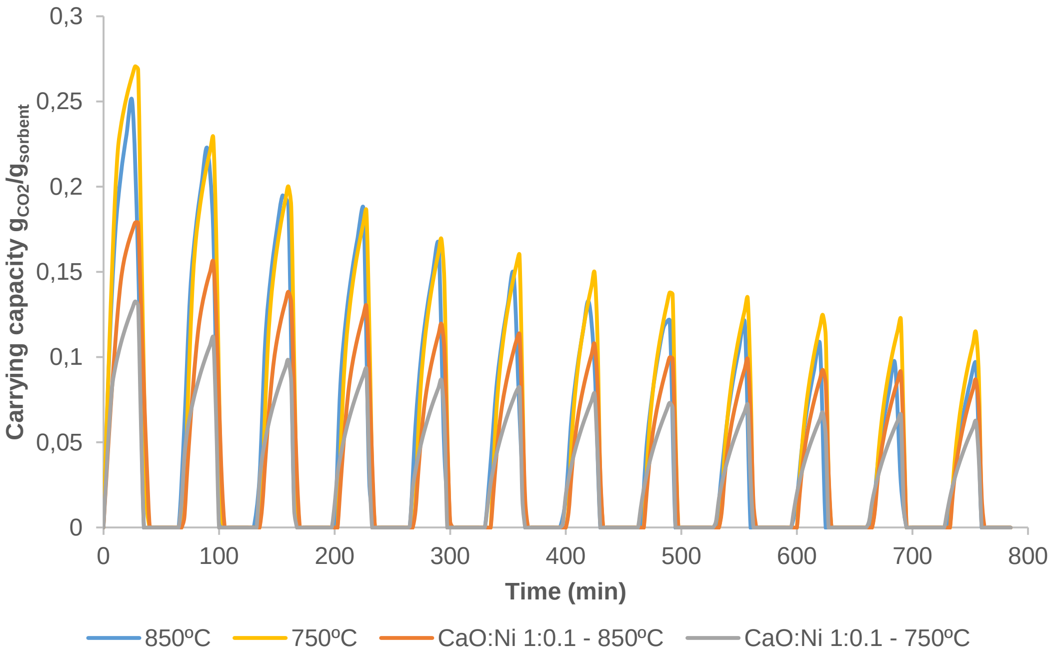


Figure A 9 - Carrying capacity of doped (Ni) and non-doped commercial calcium carbonate samples calcinated at 850ºC and 750ºC

A4 – $CaCO_3$ doped with Cerium at different temperatures

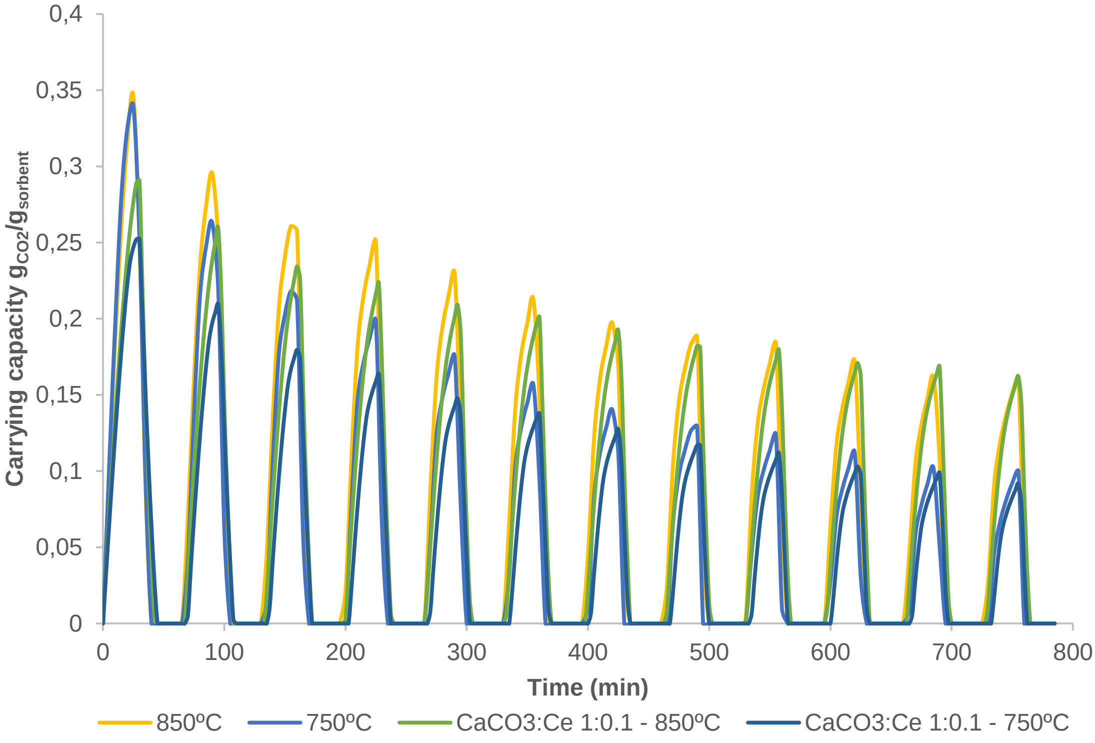


Figure A 10 – Carrying capacity of doped (Ce) and non-doped commercial calcium carbonate samples calcinated at 850ºC and 750ºC

A5 – $CaCO_3$ doped with Nickel at different temperatures

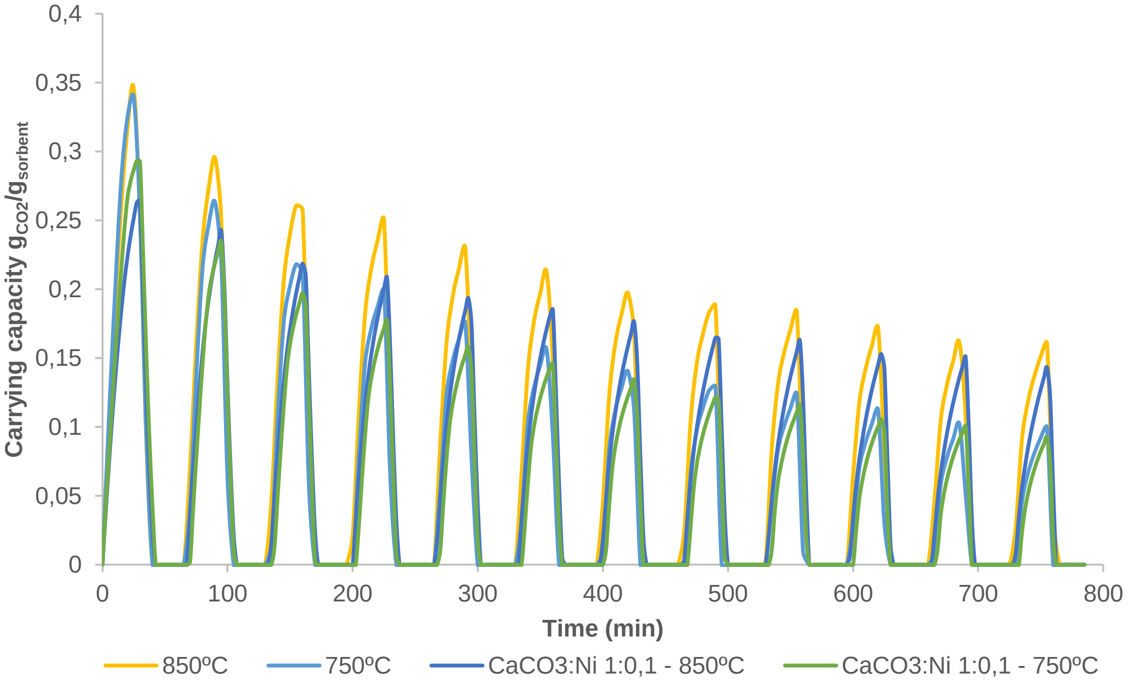


Figure A 11 - Carrying capacity of doped (Ni) and non-doped commercial calcium carbonate samples calcinated at 850ºC and 750ºC