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**CAPTURE AND CONVERSION STUDIES OF
CARBON DIOXIDE INTO CHEMICAL PRODUCTS**

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*It is not knowledge, but the act of learning, not possession but the act of getting there,
which grants the greatest enjoyment.*

- Carl Friedrich Gauss

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ABSTRACT

The carbon capture and storage (CCS) and carbon capture and utilization (CCU) have been considered internationally as potential measures to reduce the atmospheric emissions of carbon dioxide by large industrial sources.

This study focuses on a theoretical analysis of the several options given by the CCS and CCU, and experimental work of mineral carbonation using an alkaline industrial waste, the grits, formed during the Kraft process in the production of paper pulp. The experimental tests were carried out at Chemical Process Engineering and Forest Products Research Centre (CIPQPF), Department of Chemical Engineering of University of Coimbra.

The route of the indirect mineral carbonation was adopted, composed by two steps: first the extraction of calcium from the grits and second the precipitation of calcium carbonate. In a first approach, four possible extraction solvents were analyzed (HNO_3 , CH_3COOH , NaOH and NH_4Cl) to determine which solvent exhibited the best performance of the extraction of Ca from the grits. Among them, only HNO_3 and CH_3COOH have shown significant results with extraction efficiencies of 79.4 and 73.2%, respectively, after 2 h at 30 °C. Kinetic tests conducted with the two solvents demonstrated that initially the rate of the extraction process of Ca was very fast, stabilizing after 60 minutes. Since the nitric acid is a corrosive acid and with high associated costs, the acetic acid was selected for dissolution of grits and extraction of calcium.

A *Box-Behnken* design with three factors (temperature, concentration of CH_3COOH solution and solid/liquid ratio) having three levels was used to determine the optimal conditions of the extraction step. From the Pareto chart, it was possible to conclude that the acetic acid concentration and the solid-liquid ratio were the factors that demonstrated results with a significant statistical level, contributing positively and negatively to the efficiency of Ca extraction, respectively. The analysis based on the response surface methodology and the desirability functions allowed to found the following optimal conditions: acetic acid concentration of 2M, solid/liquid ratio of 30 g/L and temperature of 45°C with an efficiency approximately of 77%.

In the second step, carbonation experiments for the precipitation of CaCO_3 were performed contacting the Ca-rich liquor, obtained from the extraction step operated under optimal conditions, with a flux of pure CO_2 gaseous in a stainless inox reactor. These experiments were planned according to a *Box-Behnken* design with two factors (temperature and the pressure inside the reactor) at three levels. The statistical analysis of the results demonstrated that the only variable with a significant statistical level was the quadratic effect of the temperature, contributing negatively to the carbonation efficiency. Therefore, the ranges of the levels selected for the 2 factors do not produced a desired variability in the carbonation efficiencies. However, the response surfaces and desirability functions led to optimal conditions of 30 °C and 30 bar, reaching a carbonation efficiency of 74%, corresponding a CO_2 sequestration capacity of 460 kg CO_2 /ton of grits, however and since the solubilization of the grits with acetic acid leads to a release of CO_2 due to the presence of Ca in the form of carbonates, the value of the CO_2 sequestration capacity decreases for a value of 220 kg CO_2 / ton grits instead of the previous value, still the decrease, the value presented shows good potential for purposes of mineral carbonation.

Keywords: CO_2 sequestration; Solvent extraction; Mineral carbonation; Grits; Calcium carbonate.

RESUMO

A captura e armazenamento de carbono (CAC) e a captura e utilização de carbono (CCU) são consideradas internacionalmente como potenciais medidas de mitigação para a redução de emissões atmosféricas de dióxido de carbono geradas em grandes fontes industriais.

Este estudo incide sobre uma análise teórica das várias opções das tecnologias de CAC e CCU, e uma parte experimental sobre a carbonatação mineral utilizando um resíduo industrial alcalino, os grits, formados durante o processo Kraft na produção de pasta de papel. A parte experimental do estudo foi realizada no Centro de Investigação para os Processos Químicos e Produtos da Floresta (CIEPQPF) do Departamento de Engenharia Química da Universidade de Coimbra.

Foi adotada a via de carbonatação mineral indireta composta por duas etapas: a etapa de extração de cálcio e a etapa de carbonatação originando um precipitado de carbonato de cálcio. Numa primeira abordagem foram analisados quatro possíveis solventes de extração (HNO_3 , CH_3COOH , NaOH e o NH_4Cl), de forma a determinar qual dos solventes teria um melhor desempenho na fase de extração de cálcio dos grits. De entre os quatro solventes apenas o HNO_3 e o CH_3COOH se destacaram com eficiências de remoção de 79,4 e 73,2 %, respetivamente, depois de 2 horas de operação a 30 °C. Testes cinéticos com os dois solventes demonstraram que inicialmente a cinética de dissolução do resíduo era muito rápida, estabilizando após 60 minutos. O HNO_3 teve um melhor desempenho sobretudo nas eficiências registadas, contudo como é um ácido de natureza corrosiva e com custos associados elevados, optou-se pelo CH_3COOH como solvente de extração de Ca dos grits.

Um planeamento *Box-Behnken* com três fatores (temperatura, concentração da solução de CH_3COOH e razão sólido/líquido, S/L(g/L)) com três níveis foi utilizado para determinar as condições ótimas da etapa de extração. A partir da análise estatística dos resultados, tendo como base o diagrama de Pareto, foi possível determinar quais os fatores que mais influenciam a extração de Ca. A concentração de ácido acético e a razão sólido-líquido foram os únicos fatores que demonstraram resultados com significância estatística, contribuindo positivamente e negativamente para a eficiência de extração de Ca, respetivamente. As

análises baseadas na metodologia da superfície de resposta e função de “desirability” permitiram encontrar as condições ótimas: concentração de ácido de 2M, temperatura de 45°C e razão sólido/líquido de 30g/L com uma eficiência de extração de cerca de 77 %.

Na segunda etapa, foram realizadas experiências de carbonatação para a precipitação de carbonato de cálcio, fazendo reagir o licor rico em cálcio, obtido na etapa de extração sob condições ótimas, com uma corrente gasosa de CO₂ num reator de pressão feito de inox. Essas experiências foram planeadas de acordo o projeto do tipo Box-Behnken com dois fatores (temperatura e pressão no interior do reator). A análise estatística dos resultados demonstrou que a única variável com significado estatístico era o efeito quadrático da temperatura, contribuindo negativamente para a eficiência de carbonatação. Deste modo, conclui-se que os intervalos de variação dos fatores selecionados não permitiram obter a variabilidade desejada para a eficiência de carbonatação. Contudo, foi possível obter condições ótimas de 30°C e 30 bar, com eficiências de carbonatação na ordem dos 74 %, correspondendo uma capacidade de sequestro de CO₂ de cerca de 460 kg CO₂/ton de grits. Contudo e devido a solubilização dos grits com ácido acético ocorre libertação de CO₂ essencialmente devido à presença de Ca na forma de carbonatos no resíduo, o valor da capacidade de sequestro de CO₂ diminui para 220 kg CO₂/ ton grits em vez do valor anterior. Após a redução do valor da capacidade de sequestro de CO₂, o valor apresentado demonstra um bom potencial para a carbonatação mineral.

Palavras-chave:

Sequestro de CO₂; Extração por solvente; Carbonatação mineral; Grits; Carbonato de cálcio.

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ACRONYMS

CCS – Carbon Capture and Storage

IPCC – International Panel of Climate Change

NOAA – National Oceanic and Atmospheric Administration

GHG – Greenhouse gases

UNFCCC – United Nations Framework Convention on Climate Change

COP – Conference of Parties

BECCS – Bioenergy with Carbon Capture and Storage

I&D – Investigation and Development

EOR – Enhanced Oil Recovery

FAAS – Flame Atomic Absorption Spectroscopy

SEM – Scanning Electron Microscope

XRD – X-Ray Diffraction

IGCC – Integrated Gasification Combined Cycle

RD&D – Research, Development and Deployment

IEA – International Energy Agency

DOE – Department of Energy (USA)

UN – United Nations

CEE – Calcium Extraction Efficiency

CE – Carbonation Efficiency

DOE – Design of Experiments

1. INTRODUCTION

1.1. Motivation

Since industrial revolution that the levels of carbon dioxide concentration in the atmosphere has been increasing at an alarming rhythm (Andres et al. 1999; Canadell et al. 2007; Metz, Meyer, IPCC 2014). Before the industrial revolution the global medium concentration of CO₂ in the atmosphere was approximately 280 ppm, although the recorded variations of CO₂ between the glacial epochs and the hotter interglacial epochs, the CO₂ concentration in the atmosphere has maintained a certain pattern during the latest 800 000 years, based on the ice cores (NOAA). The actual CO₂ concentration presents a value of 410 ppm approximately registered at the observatory of NOAA, Hawaii in Mauna Loa.

The biggest drivers for this increase can be attributed mainly to the fast economic and population growth that has been observed in the last decades. Economic sectors, like energy production, industries and transports together with the poor management and the intense exploration of the soil mostly deforestation for agriculture use or other ends are the main sectors responsible for the increase of CO₂ in the atmosphere. Between 1970 and 2010 the CO₂ emissions represented about 78 % of the total greenhouse gases (GHG) results of the fossil fuel combustion. Despite the environmental policies adopted, the annual global rate of CO₂ emissions between the periods of 1970 to 2000 and the period of 2000 to 2010 increased from 0,4 GtCO₂ to 1 GtCO₂ (IPCC 2014).

In 1997, the Kyoto protocol entered into force, the first international protocol with the aim to reduce the GHG for the all the signatory's countries or parties. This protocol only requests to the parties to adopt policies and measures on mitigation related to the emissions of GHG. Under the protocol, the parties had to monitor their actual emissions and track the main sources. Kyoto protocol also set emission reduction targets for 36 industrialized countries and the European Union (UNFCCC). More recently in 2015 came into place a new accord, the Paris Climate Accord that had as main objective enhance the global response to the effects of climate change, by delimitating the average global temperature increases below the 2 °C when compared to the pre-industrial levels. The last conference, the COP 25 held

in December of 2019 in Spain, had as main objective to define the further steps in the UN climate change progress. This conference help establish the building blocks beyond 2020, the year in which parties must submit the new national climate action plans (UNFCCC).

Of all the GHG, the water vapour has the greater portion in terms of affecting the greenhouse effect (Randall et. al., 2007), with approximately 75 % including clouds, carbon dioxide 20 % and the minor GHG 5 % (Lacis et. al., 2010). However, the water vapour concentration in the atmosphere is extremely variable and instable essentially due to the water cycle involving processes like precipitation, condensation and evaporation. Water vapour is the only GHG that humans cannot interfere at all, or by other words, humans cannot increase or decrease its concentration on the atmosphere and for this reason water vapour is not accounted for purposes of climate change mitigations. Even though the water vapour contributes substantially for the amplification of the heat-trapping by the molecule CO₂. The carbon dioxide is considerable the most relevant of the GHG mainly to its high atmospheric concentration and because at normal conditions CO₂ and like others GHG doesn't precipitate and condensate from the atmosphere while water vapour does it (Lacis et. al., 2010).

In a range of potential mitigation measures for the carbon dioxide reduction, the carbon capture and storage technology (CCS) is a viable option with a great potential and flexibility to achieve a significant decrease in the emissions of CO₂. Referenced by international entities as the example of IPCC (Intergovernmental Panel on Climate Change) as a considerable potential measure in the reduction and mitigation of CO₂ emissions. The CCS is a technology that consists of separation and capturing of CO₂ generated from stationary sources, gas transport to a long-term storage location, geological or oceanic storage. The storage of CO₂ may involve risks such as leakage, contamination of underground water, or even geological disasters. CO₂ capture and utilization (CCU) strategy is currently more attractive than CCS, for example, via mineral carbonation which offers the advantage of producing a final product (carbonates) with a market value.

In this study, the mineral carbonation process will be discussed in detail. The mineral carbonation involves the lixiviation of Ca or Mg ions from a silicate or an industrial alkaline residue in an aqueous medium, and the subsequent reaction between the dissolved CO₂ and the oxides of the respective ions which generates the carbonates. These carbonates generated are stable and insoluble in long-term and can be deposited at mining sit of silica for example or can be reutilized in the construction sector (Bruce G. Miller 2011).

Carbonation through industrial alkaline residues has an added value to the concept of CCS since it adds the possibility of the waste valorization, avoiding its disposal in landfills. The solid industrial residues used in carbonation are generally alkaline, inorganic and rich in Ca or Mg and can be provided by several different industries most commonly from steel, aluminium, cement and paper pulp industries.

In the present work, the indirect carbonation experiments were carried out by using the grits, an industrial alkaline residue from the paper pulp industry, an industry with a great impact on Portuguese economic and owner of an extensive forest area. This type of waste is formed during the Kraft process in the production of paper pulp and it exhibits a high concentration of calcium making it the predominant alkaline component with an advantage since is known to carbonate faster than Mg (Huijgen and Comans 2003). The experimental carbonation process adopted involves, firstly, the extraction of Ca from the waste (grits) dissolving it in an extracting solvent and as last step, the solution with the extracted components reacts with CO₂ originating stable calcium carbonates.

1.2. Objectives

The general objective of the research work reported in this dissertation was to study the mineralization process of carbon dioxide for the production of calcium carbonate by using an alkaline industrial waste. In order to achieve this goal, the following specific objectives have been identified:

- A review on the carbonation processes and the CCS technologies.
- Chemical characterization of the grits;
- Solvent screening to extract calcium from the grits;
- Analyse of effect of operating variables on the extraction and carbonation processes;
- Optimization of extraction and carbonation conditions using statistical methodologies based on the surface responses and desirability functions;

1.3. Thesis Structure

This work is organized in 6 chapters:

- Chapter 1: Introduction which is composed firstly by the motivation of the study, objectives and thesis structure;
- Chapter 2: Literature Review where an explanation of the various theoretical foundations about CCS technologies is presented, with a greater incidence in the processes of mineral carbonation and its current state and the main works developed.
- Chapter 3: State of Art where the current literature on the mineral carbonation process is discussed and the operating conditions and efficiencies reported in several works are summarized;
- Chapter 4: Materials and Methods, where is described in detail the materials involved in the laboratory experiments as well as the description of the methods used.
- Chapter 5: Results and Discussion, where are presented and discussed the results achieved in all the experiments;
- Chapter 6: Conclusions and suggestions for future works.

2. THEORETICAL FUNDAMENTALS

2.1. Carbon Capture and Storage

In recent years, there are many concerns about how to solve the problem of climate change. Climate change is a variety of environmental problems, but with a common cause, the impact of the anthropogenic activities. After the industrial revolution, carbon dioxide emissions and others GHG increased in an alarming rhythm essentially from fossil fuel combustion and industrial processes (Ethedde et al. 1996). According to IPCC, the main greenhouse gases are water vapour, carbon dioxide, methane, nitrous oxide, ozone, chlorofluorocarbons and hydrofluorocarbons. This study focuses on carbon dioxide, an odourless and colourless gas that have a major importance in biogeochemical carbon cycle.

The amount of CO₂ present in the atmosphere is 410 ppm, according to the NOAA Global Monitoring Division, three quarters of the emissions are due to the burning of fossil fuels and the remain is due to changes in land use (IPCC, 2014). Globally the responsible driving forces of the increase of CO₂ emissions are basically economic and population growth.

To achieve the targets established by COP 21, a conference dedicated to climate change, CCS fits into the range of mitigation solutions in view of the reduction of GHG emissions. The carbon capture and storage have been suggested and evidenced with a great potential to reduce GHG emissions according to IPCC and the International Energy Agency (IEA).

The first applications of CCS technologies were during the 1970s and 1980s, in processes that involved the routinely separation of CO₂, such as in the processing of natural gas and in the production of fertilizers. In 1996, in the North Sea, the first commercial-scale unit of CCS started, and as a CO₂ storage location, a saline formation was used under the sea (Furre et al. 2017; Baklid, Korbøl, and Owren 1996). Until then, the only form of CO₂ injection would be through enhanced oil recovery, where geological formations have been drilled through wells since the 1970s (Blunt, Fayers, and Orr 1993).

CCS have three major components, as first component the capture that includes the separation of CO₂ from exhaust gases produced at large industries such as coal, natural gas,

cement, power plants and refineries. The second component of CCS is transport, once separated, the CO₂ is compressed and transported via pipeline, trucks or ships to an appropriate storage location, whether ocean or geological storage. And the last and third component is storage, that involves the injection of CO₂ at great depths, and depending on the storage location, the depth at which it can be injected varies, as for example in geological storage, it should be at a depth of at least 1 km (CCS Institute 2017).

CCS has several advantages such as the integration in existing energy systems and without changing the system itself. CCS is a viable option for the decarbonization of emissions in industries such as cement production and can generate negative emissions by the combination with low-carbon bioenergy, most known by BECCS (Bioenergy with carbon capture and storage), is a process that includes the cultivation of plants, the harvest for energy generation and the capture of the released CO₂ for later underground storage. BECCS is an attractive technology basically due to the cost-optimisation perspective of an integrated assessment models. (Bui et al. 2018).

Carbon capture and storage systems are already implanted and working all over the world as shown in Figure 2.1. In 2017, seventeen large-scale CCS facilities were operating globally, with four more arriving in 2018. All CCS facilities together have a CO₂ capture capacity of 37 million tons per year, giving CCS technology the ability to decarbonize the industrial sector, reducing large-scale emissions from numerous industrial sources (CCS Institute 2017).

However, these technologies also have associated disadvantages in all the process of CCS. For example, the most common is the leakage problem in the pipelines. This problem could seriously impact the human's life and health, through the exposure of concentrations of CO₂ greater than 7 % by volume in air. The impacts of geological storage, mainly due to leakage, could include lethal effects on plants and subsoil animals and the contamination of ground water. In ocean storage the same happens and there is an increase in acidity at the injection site by more than 0.4 in pH, which can be harmful especially for surfaces ocean organisms (IPCC 2005). CCS is an energy-intensive process since consumes additional energy and can lead to a further emission of CO₂ (Pan et al. 2012).

To minimize these problems, monitoring is necessary for a good management of stored CO₂. Other techniques have also demonstrated a good efficiency in the management

of stored CO₂, such as the seismic surveys, which were developed in oil and gas industries (Gale et al. 2001).

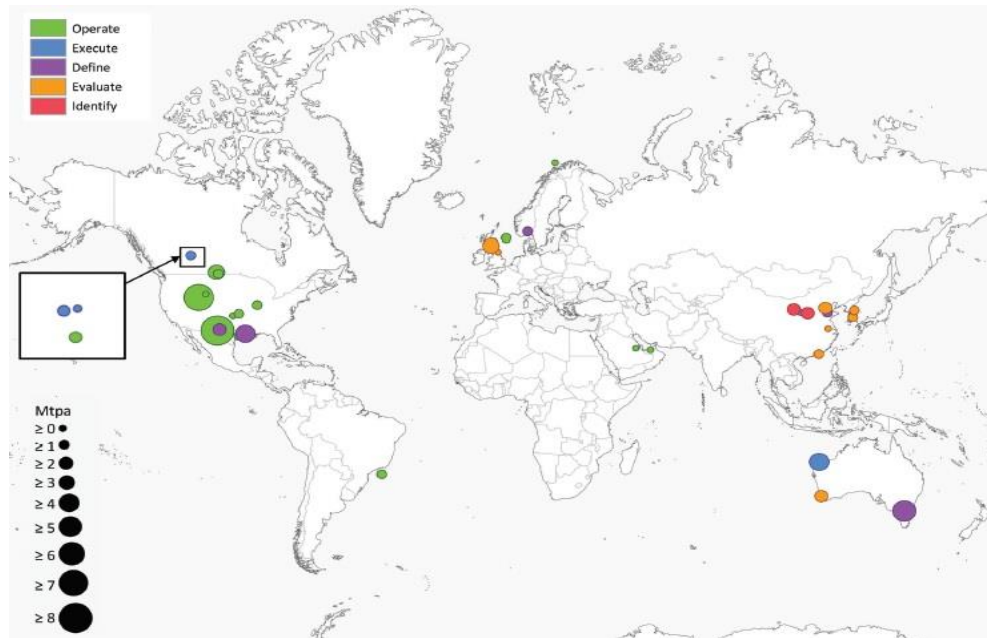


Figure 2.1. CCS integrated commercial projects worldwide. Circle size represents the CO₂ capture capacity of the project and the colour demonstrates the lifecycle of the project (Bui et al. 2018).

2.1.1. Capture of CO₂ technologies

The capture of CO₂ from the exhaust gases of industrial processes has been applied for over 80 years (Kohl and Nielsen 1997). Nowadays, the application of CO₂ capture can be sourced from large point sources as fossil fuel power plants, fuel processing plants mainly in the iron, cement, steel and chemicals industries. It may come from small sources, such as the transportation, residential and commercial sector but it can be more challenging and expensive.

The possibility of capturing CO₂ directly from ambient air (Lackner 2003) has some complications, mainly due to the concentration of CO₂ in the atmosphere, which is approximately 410 ppm, a factor of about 100 lower than in flue gas. However, some companies like Climeworks, located in Zurich, Switzerland, focuses their products in CO₂ capture from the ambient air. In the Figure 2.2 shows one of their products that capture atmospheric CO₂ with a filter that bind the CO₂, as well as the moisture in the air which bond, the CO₂ bonded to the filter, can be dissolved at temperatures of 100 °C.

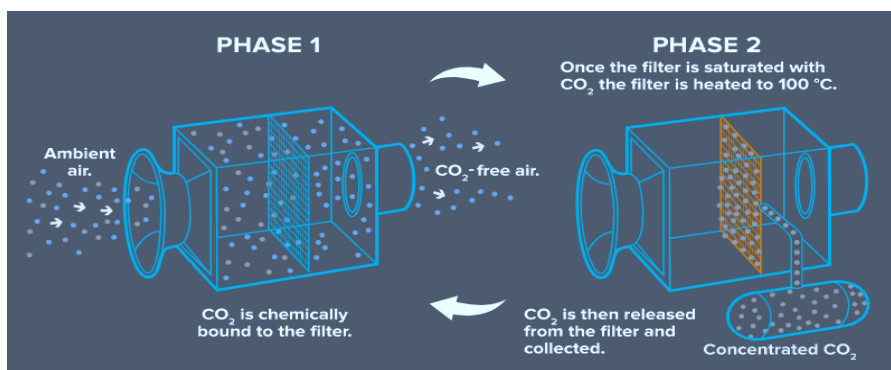


Figure 2.2. CO₂ capture system from atmospheric air produced in the company Climeworks AG

In terms of CO₂ capture costs the capture system is mentioned as the major cost factor for any type of sequestration and storage technology (Olajire 2013). An analysis of capture cost in a study (Bains et al. 2017) demonstrated that the purity of CO₂ in the flue gases from industries is closely correlated with capture costs. For example, an industrial process that presents a 95% purity of CO₂ in exhaust gases like ammonia, ethanol, hydrogen production, may only require dehydration and compression along with the associated capital cost for the capture system and the operational and maintenance costs results in an average cost of 14\$/MT (metric ton) of CO₂. For lower purities of CO₂ with concentrations of 3 %, the capture costs can increase about 100\$/MT of CO₂, this high capture costs are normally associated with natural gas and petroleum power plants. The achievement of low capture costs is a major factor to the development and promoting of CCS technologies.

One of the disadvantages in the CO₂ capture is about the installation of the capture equipment in plants. This equipment can be installed in new energy utilization plants or it may be retrofitted to existing plants. Such retrofits have disadvantages as constraints in the chosen site specifically in availability of land for the capture system, another issue is in the extension of the plant life that might be required to rationalise the expensive cost associated with the capture system and if the plant is old the energy efficiencies tends to be low and with the introduction of capture systems would impact the net output (IPCC 2005).

Capture systems can be divided into four major subsystems through fossil fuels and biomass: 1) CO₂ capture through exhaust gases from industrial processes; 2) Post-combustion capture; 3) Pre-combustion capture; 4) Oxyfuel combustion capture. In the Figure 2.3 shows the four simplified capture systems.

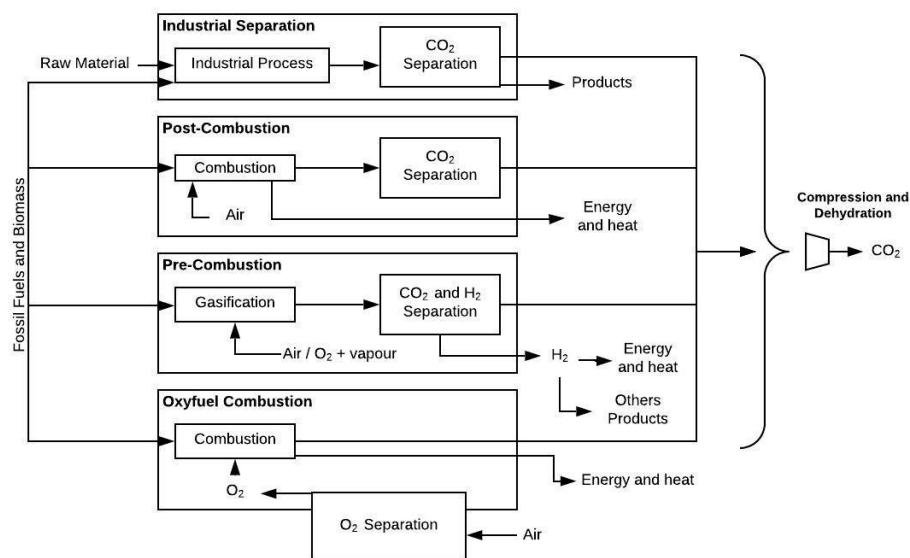


Figure 2.3. Simplified scheme of the capture systems (Adapted from IPCC, 2005)

CO₂ capture from flue gases in industrial processes has as main objective the separation of CO₂ from the flue gases produced mainly on a large-scale of fossil fuel combustion processes or on a smaller scale, biomass can be used as fuel. Several industrial processes involving process streams can capture CO₂ in large amounts and at lower costs. Some processes already have implanted CO₂ capture as in the purification of natural gas and in the production of hydrogen. But there are cases of some industries processes like cement and steel production which involves a large amount of CO₂ released into the atmosphere without any capture system. Capture in the industrial streams could not be the answer to the problematic of climate change, mainly due to the high volumes of CO₂ generated by combustion.

Post-combustion capture is the capture of CO₂ from the flue gases generated through combustion of fossil fuels and biomass. These flue gases are passed over equipment that separates most of the CO₂ in the stream. Since 1970s several post-combustion capture systems in a commercial scale were implanted using mostly monoethylene amine (MEA) process, providing CO₂ for industrial application (Rackley 2017).

The principal industries that generates CO₂ emissions through combustion systems are power plants, cement kilns and iron and steel production plants. In large-scale processes, the direct combustion of fuel with air in a chamber has been used for centuries to extract and use the energy from the fuel and is presented as the most economic technology in this area. The main systems of reference for post-combustion capture are at oil, coal and natural power

plants, the natural gas and coal plants are the types of high efficiency power plant, where the technology of CO₂ capture offers its best application (IPCC 2005).

Pre-combustion capture involves a gasification or reforming process that converts a solid or liquid fuel into a mixture of fuel gases known as “syngas” which is composed essentially by carbon monoxide (CO) and hydrogen (H). The carbon monoxide is then reacted in a catalytic reactor with steam to produce CO₂ and more hydrogen. Through chemical or physical absorption processes the CO₂ is separated, resulting in a high concentrated hydrogen fuel with various applications such furnaces, gas turbines, boilers and engines.

Pre-combustion capture can be implemented as Integrated Coal Gasification Combined cycle (IGCC) in power plants. IGCC systems generates electricity through the clean syngas (without possible contaminants such as particles, ammonia, mercury, sulphur, chlorides and other heavy metals) that gives a high efficiency to the gas turbine, while the produced heat is recovered to generates steam to power the steam turbines (Wagner et al. 2008). In contrast to post-combustion systems, the pre-combustion capture happens previously to the combustion, in other words the pre-combustion can occur at high pressures without the combustion-based pollutants like SO_x and NO_x. Today's, IGCC systems are the leading most effective power cycle when compared to the pre-combustion capture technologies. The most common separation technologies used in pre-combustion capture are physical absorption, pressure-swing adsorption and membrane capture processes (Carpenter and Long 2017).

Oxyfuel combustion capture is a process that involves the combustion of hydrocarbon fuel in a pure oxygen environment instead of air. When the combustion of fuel occurs in a pure oxygen environment, the flame temperature is extremely high and to moderate this temperature, a recycled stream of CO₂ and H₂O flue gas should be applied into the combustor (IPCC 2005). The main purpose of this systems is when implemented, as for example in a coal-fired power plant, it is to produce high concentration of CO₂ and water vapor in flue gas, making it possible to capture the CO₂ from the flue gas purely through low-temperature dehydration and desulfurization processes. The advantages in these systems encompasses a decrease in NO_x emissions, a high CO₂ purity and lower gas volumes due to increased density (Carpenter and Long 2017). However, oxyfuel presents some disadvantages such as high energy requirement due to the production of high purity O₂, and

the utilization of high temperatures generated by the combustion in an oxygen environment. Consequently the flue gas must be recycled in great amounts in order to maintain a reasonable level of temperature (Adams 2014).

CO₂ separation processes in capture systems

CO₂ capture systems have three distinguished technologies for gas separation: 1) Separation with sorbents or solvents; 2) Separation with membranes; 3) Separation by cryogenic distillation. These three technologies are represented in Figure 2.4.

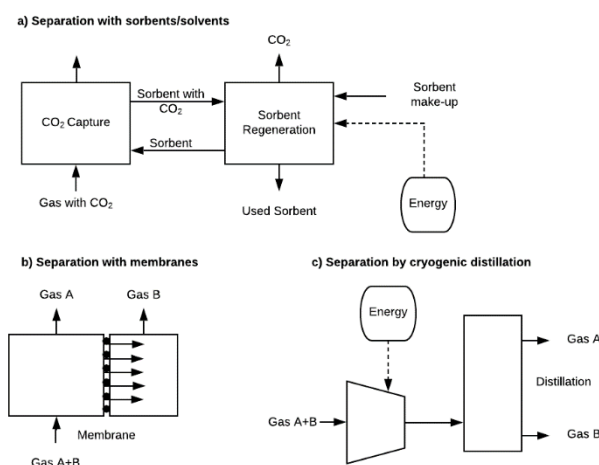


Figure 2.4. Separation processes used in CO₂ capture systems (Adapted from IPCC 2005)

Separation with adsorbents/solvents: The separation is attained when the gas stream that contains CO₂ contacts with a solid adsorbent or a liquid absorbent that allow the uptake of the CO₂. Once concentrated with the captured CO₂, the adsorbent is transported to a different vessel, passing to the next step the adsorbent regeneration where the CO₂ is released after being heated. The adsorbent after its regeneration is sent back to the capture step forming a cyclic process as is showed in the scheme (a) in Figure 2.4. The absorption into MEA is the most widely studied in CO₂ separation processes (Yang et al. 2008), which remove both CO₂ and H₂S from gas stream. One usual problem in these systems is that the stream of sorbent between the vessels is large because it must correspond to the high stream of CO₂ processed in power plant as an example.

The main disadvantages in these systems are due to the equipment sizes and the energy requirements at the solvent regeneration step which leads to a substantial efficiency penalty and an additional cost (IPCC 2005).

Separation with membranes: Membranes are manufactured materials of different types such as polymeric, ceramic and metallic which allows selective permeation of a gas through them, as shown in scheme (b) in Figure 2.4. The selectivity of the membrane is related to the nature of the material, affinity with the gas, molecular weight and size. However, the stream of gas through the membrane is typically due to the differential of pressure across the membrane. Separation by membranes is inexpensive when gas purity it is not essential. One of the problems in the use of membranes is associated with the low concentration of carbon dioxide presented in the fuels gases, which implies the need for a large amount of gases (Yang et al. 2008).

Separation by cryogenic distillation: A gas can turn into liquid phase through compression, cooling and expansion steps. In a liquid form the gas can be separated in a distillation column as it shows the scheme (c) in Figure 2.4. In the case of air, oxygen can be separated and applied in a range of CO₂ capture systems (oxyfuel combustion and pre-combustion) and, for its vital operation, a great flow of oxygen is needed (IPCC 2005). Cryogenic separation is generally used in commercial-scale streams with high CO₂ concentration (more than 90 %). One of the disadvantages of cryogenic separation is the quantity of energy required to proceeds the refrigeration process essentially in diluted streams. One of the advantages is that allows the direct production of liquid CO₂, which is a requirement in certain transport options.

2.1.2. CO₂ Transport

After captured the CO₂ is then transport to a storage site. The transport of CO₂ can occur in three states: gaseous, liquid and solid. Depending on which state and pressure conditions CO₂ presents, there are different ways to transport the gas, for example, a gas under atmospheric pressure conditions occupies a large volume so it will be needed a large facilities to transport it, for a less occupied volume gas should be compressed and then can be transported by pipeline. Other processes such as liquefaction, solidification and hydration can decrease even more the volume occupied by the gas.

For commercial purposes CO₂ can be transported using tanks, pipelines and ships for gaseous and liquid carbon dioxide. All these options are currently used. For a long-distance movement and for large amounts of CO₂, the best option to transport it's through pipelines. Currently pipelines are used in the transport of natural gas, oil for long distances in sea and in land. In western USA an extend over more than 2500 km of pipelines carries 50 MtCO₂ per year from natural sources to enhanced oil recovery (EOR) projects in west Texas (IPCC 2005).

Currently, CO₂ pipelines is a mature market technology with a great capacity to transport high amounts of CO₂. The transport of high quantity of CO₂ by ship occurs at lower temperatures and at much lower pressure than in pipeline transportation but in a minor scale. Another possible CO₂ transport is by truck but only for small quantities (Holloway et al. 2006). Pipelines are considered the most economical and efficient transport method for future commercial CCS (DOE 2010; Parfomak and Folger 2010). These transport systems require some consideration in the design, monitorization of possible leaks, and a protection against overpressure.

2.1.3. CO₂ Storage

CO₂ storage is the last step of CCS systems which includes the placement of CO₂ into a reservoir where it remains stored or sequestered permanently. Normally, the storage sites used for long-term CO₂ are in geological formations, in ocean, on land and through mineral sequestration. At a global perspective, annually it is released about 8,5 Gt of carbon into the atmosphere, and carbon storage is presented as a good mitigation solution which can store large volumes of Gt of CO₂ (Miller 2011). In Figure 2.5 is represented the carbon storage capacity versus the characteristic's storage time for various sequestration methods. In this figure is perceptible that mineral carbonation is the storage option with the highest levels of storage capacity and time.

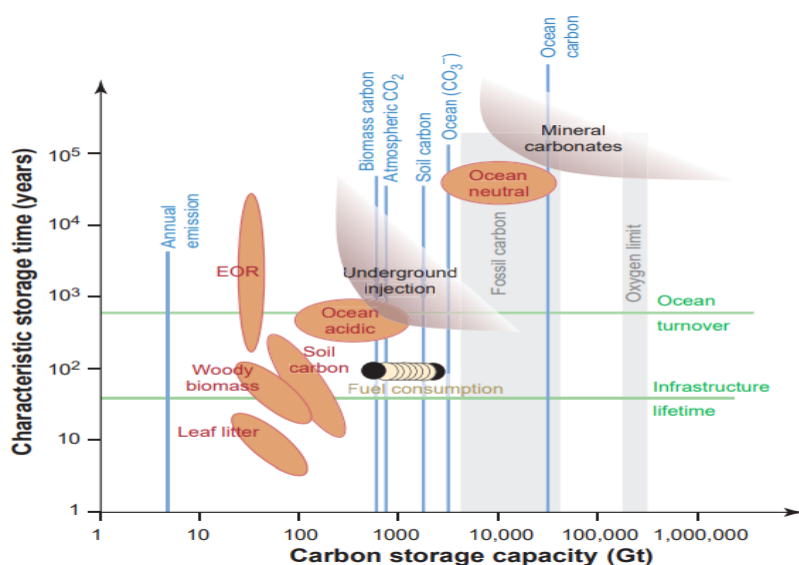


Figure 2.5. Storage capacities and times for various sequestration methods (Lackner 2003)

Geological Storage

Geological storage of CO₂ is a natural process that traps high volumes of CO₂ underground for millions of years and, as a result, carbonate minerals, oil, coal and natural gas are formed. The Earth's lithosphere is the largest carbon reservoir with near 10²³ g C in the forms mentioned before due to the natural carbon storage.

The CO₂ injection and storage has been applied for about 45 years within safe standards. Geological storage can provide a CO₂ retention of centuries, from the CO₂ captured in industries. The most common sites for geological storage are the geological formations known as sedimentary basins, that usually are used for trap oil, gas and CO₂ (J. Bradshaw et al. 2002; John Bradshaw and Dance 2005). A geological storage encompasses firstly the injection of CO₂ captured into rock formations at high depths. The main storage options are in saline formations, in EOR and in depleted oil or gas fields. These storage options are shown in Figure 2.6.

Saline aquifers are very porous sedimentary rocks and when compared with oil and gas reservoirs. Saline aquifers demonstrate a great performance to store high amounts of CO₂ and it is the more common storage site used (B. G. Miller 2011).

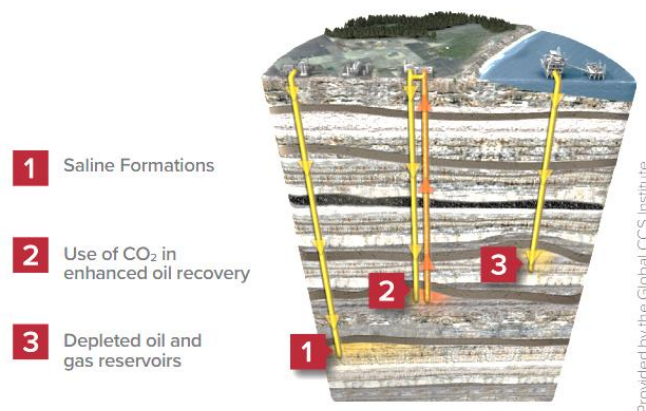


Figure 2.6. Geological Storage Options (Global CCS Institute, 2018)

An effective geological storage has some associated characteristics such as the existence of pores and cavities in the formation to provide capacity to store large amounts of CO₂, the pores need to be sufficiently connected to allow the movement and the containment of CO₂ and a caprock or an overlying rock formation with a low-permeability to prevent CO₂ releases (GlobalCCSInstitute 2018). Other important aspects to be considered at basin formations involve the tectonic activity, sediment type, and the geothermal and hydrodynamic activity.

It is estimated that 5000 years is the required period for all the CO₂ injected into the Weyburn Oil Field to dissolve or convert into carbonate minerals (Perkins et al. 2005). The first commercial-scale project of geological carbon storage was the *Sleipner Project* operated by a petroleum company the Statoil ASA in the North Sea at about 250 km offshore in Norway. The purpose of this project was to inject and store CO₂ into a saline formation at 800 m below the seabed, this operation initiated at October 1996, with an annual injection capacity of 1 MtCO₂. More recently at 2005, was been injected a flow of around 2700 tonnes of CO₂ per day (IPCC 2005).

EOR is a series of technics used to increase the capacity of oil to flow to a well through the injection of water, gases or chemicals into the reservoir. This technique provides a potential economic gain to the industry and creates an efficient option for CO₂ storage. Figure 2.7 demonstrates an EOR with CO₂ injection to recovery the oil.

The geological carbon storage is considered a promising technology to mitigate and reduce the CO₂ emission, mostly because of its development level making this technology

mature and due to the low costs associated (B. G. Miller 2011; Olajire 2013; Newell and Ilgen 2019)

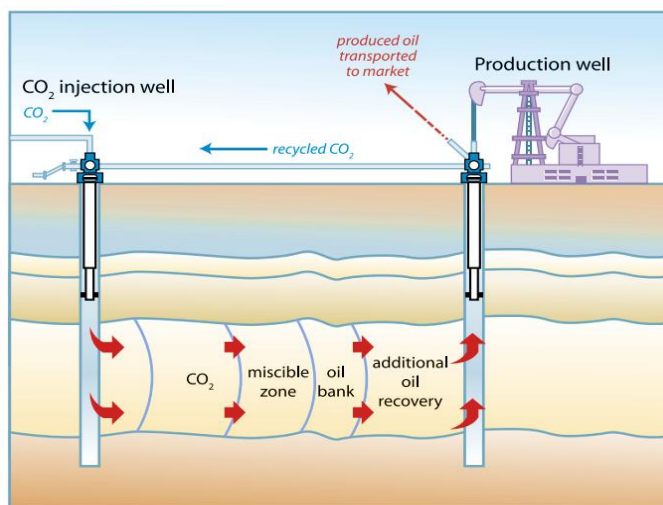


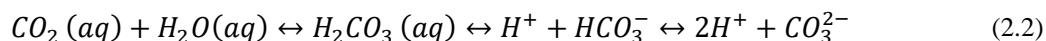
Figure 2.7. Injection of CO₂ for enhanced oil recovery (IPCC 2005).

Oceanic Storage

The first components in the global carbon cycle are the oceans, atmosphere, biosphere and the soils. With a coverage of 71% on the Earth's surface, the oceans have an average depth of 3800 m containing 50 times more carbon than the atmosphere and almost 20 times more carbon presented in plants and soils. The reason that oceans can support so much carbon resides in its large volume and in the chemistry of sea water with the atmospheric CO₂, that once dissolved form various ionic species. The oceans are an important sink of CO₂, taking up from atmosphere about 7GtCO₂/year during 1980 to 2000 (IPCC 2005).

The chemistry between the ocean surface water and the atmospheric CO₂ are determined by the chemical equilibrium between CO₂ and the existing carbonic acid in sea water, the partial pressure of carbon dioxide in the atmosphere and the rate of air/sea exchange. One main reaction is responsible for this transition, where carbonic acid which is an instable specie dissociates into bicarbonate ion (HCO₃) and subsequently forms carbonate ions (CO₃²⁻) and hydronium ion (H⁺) followed by the reaction 2.1 and 2.2.





Another major parameter in the reaction above is the pH since some ions species only appear or form in certain regions of pH as it is illustrated in the Figure 2.8

Despite the fact that the ocean is known as a high buffer system, the equilibrium of pH is mainly controlled by the concentration of the chemical species presented above which is significantly higher than the concentration of H^+ or OH^- (PMEL/NOAA 2015).

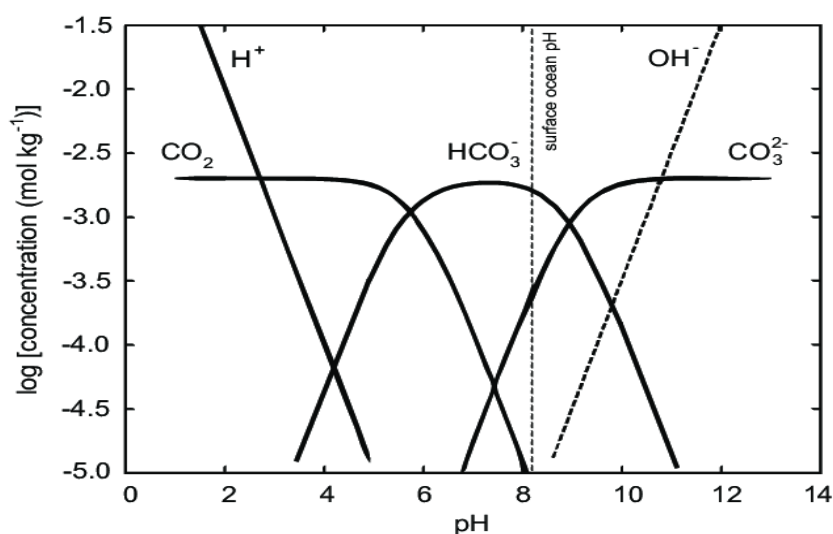


Figure 2.8. Carbonates species and the variation of pH when CO_2 reacts with water (Henriet et al. 2015)

In 1977 was introduced the first direct ocean sequestration of CO_2 , which involved the injection of liquefied CO_2 into deep Mediterranean Sea, where it would be isolated from the atmosphere for centuries. The effectiveness of this project depended on how long the CO_2 remains isolated from the atmosphere (Marchetti 1977).

Oceans are really a large sink for anthropogenic CO_2 emissions with a reported amount of near 39 000 Gt of carbon as carbonates and bicarbonates species. However, this uptake capacity is considered small (Lackner et al. 2010). Injecting CO_2 into deep ocean with a depth of 3000 m ensures a permanent storage, even with geomechanical perturbations. Below that depth the compressed CO_2 injected is denser than the seawater, making the CO_2 to sink to the bottom. Figure 2.9 shows a chart where it is visible the changes in the injected liquid CO_2 density with the depth. (B. G. Miller 2011).

Some studies (B. G. Miller 2011; Lackner et al. 2010) mention that an addition of 1000 Gt of carbon could destabilize and severely alter the ocean chemistry. Injecting CO₂ directly into the ocean would affect the deep-sea ecosystem near the point of injection, but since the knowledge of the deep-sea ecosystem is rudimentary, the impact assessment in these ecosystems are limited and preliminary. However, once injected CO₂ dissolve in seawater, disperses and ends in the ocean carbon cycle (IPCC 2005).

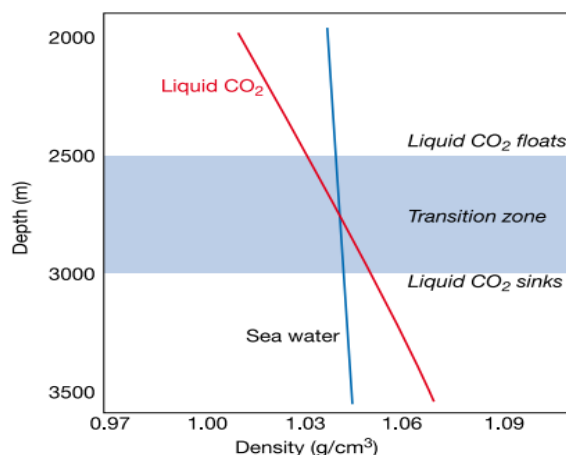
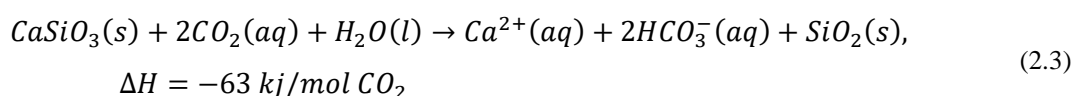
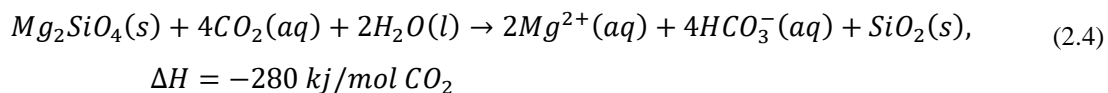


Figure 2.9. Variation of the density of liquid CO₂ with ocean depth. Between 2500 and 3000 m of depth a transition zone is marked that represents the change in CO₂ density. Below or in this transition zone the CO₂ sinks, mainly due to its high density greater than seawater density (IPCC, 2005).

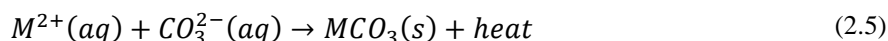
2.1.4. Mineral Carbonation

The last option of CCS technologies is the mineral carbonation, a natural process designated as weathering which consists firstly in the hydrolysis of alkaline mineral silicates with the rainwater leaching of ions such as calcium or magnesium. This first process is due to the reaction of atmospheric CO₂ with rainwater that forms a weak acid, carbonic acid that will eventually react with alkaline silicates, which can be found in great abundance in the earth's crust, leaching the Mg or Ca ions from silicate matrix in an exothermic reaction, as shown in reactions 2.3 and 2.4.





After leached, the calcium and the magnesium ions are carried by the rainwater to rivers and subsequently to the ocean, where these ions precipitate and form solid carbonates. This reaction is presented in the equation 2.5 where **M** represents an alkaline metal element such as Ca or Mg.



This chemical weathering is considered the main contributor to the geochemical carbon cycle (Pan, Chang, and Chiang 2012). Around 150 to 333 million tons of carbon are bound by silicate weathering per year assuming that each mol of Mg or Ca reacts with 1 mol of CO₂ (Hilley and Porder 2008).

Mineral CO₂ carbonation is a relatively new concept mentioned by Seifritz in 1990 which consists of using silicates to form carbonates, but it was only applied in detail at 1995 in Los Alamos National Laboratory (Lackner et al. 1995). In recent years, this concept has gained increasing interest worldwide, resulting in numerous published studies. Mineral carbonation is an accelerated form of weathering, based on the reaction of high concentrated CO₂ with metal oxide bearing materials to form insoluble and stable carbonates. The materials most appropriate in mineral carbonation are silicates rocks such as olivine and serpentine, and on a smaller-scale alkaline industrial residue from cement and steel industries can be used.

Pre-treatment Options

In order to increase mineral reactivity and efficiency through surface area, the pre-treatment of silicates and other alkaline materials must be done to increase carbonation rates. The pre-treatment options include mineral activation through thermal, mechanical and chemical processes or the combination of the three.

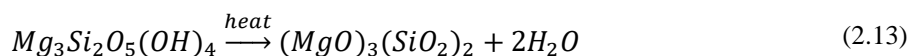
Mechanical pre-treatment

The available options of mechanical pre-treatment include grinding, crushing, abrasion and compression of the silicates or the alkaline materials. The aim of the mechanical grinding process is to destroy and disorder the mineral lattice thereby increasing the surface

area. Grinding is achieved by abrasion and the impact of the ore through the free motion of unconnected grinding equipment's such as rods or balls. The crushing process is usually carried out on dry materials with compression. The combination of crushing and grinding results in a reduction of the particle size to $< 300 \mu\text{m}$, a process important to release some valuable mineral grains (A. Sanna et al. 2014).

Thermal pre-treatment

The thermal pre-treatment removes hydroxyl groups and some chemical bounds resulting in some cases in a chemical transformation as, for example, chemical transformation to pseudo-forsterite when serpentine is used. The thermal activation of serpentine can be achieved at 630°C , in order to remove chemically bound water from the mineral lattice (W. O'Connor et al. 2001). Heat treatment or attrition grinding on serpentinite and olivine also appears to activate the minerals by creating a non-crystalline phase (W. O'Connor et al. 2002). Equation 2.13 illustrates the thermal pre-treatment of serpentinite.



Chemical pre-treatment

The chemical pre-treatment involved application of various acids and base. Sulphuric acid can be used in chemical activation increasing the specific surface area and removing adsorbed water. The acid treatments start with the leaching of magnesium or calcium ions from the material or silicate, resulting in the exposition of sub-micron pores that contributed to a significant increase of surface area. These chemical treatments do not increase the degree of the carbonation reaction, however, they allow to reach higher levels of conversion, mainly at lower temperatures, thus promoting a reduction in the necessary energy (Romanov et al. 2015).

Other pre-treatments

Other pre-treatments involve, for example, ultrasonic treatment and wet grinding in caustic solution, which do not allow to obtain high reactivity of the mineral. Studies performed in olivine with wet grinding, in a caustic solution of 1M NaOH and 1M NaCl,

proved to be insufficient to increase the mineral reactivity and the same results were achieved with ultrasonic treatment. (W. O'Connor et al. 2001).

The major obstacles found in pre-treatment options are associated to the high costs and intensive energy inputs. The reduction of particle size in both direct and indirect carbonation methods to increase the effective surface area requires high energy inputs. Krevor and Lackner 2009 estimated that 75% of the total energy costs of the process was due to the grinding of minerals to fine grain sizes. An alternative to reduce these energy costs may be the use of industrial alkaline waste, such as bottom ash and fly ash, which are presented as fine particles.

CO₂ sequestration by mineralization can occur in situ or ex situ. The in situ mineral carbonation consists of the injection of CO₂ into underground reservoirs to react with the alkaline minerals present in the geological formation, resulting in the formation of carbonates. The ex situ mineral carbonation is a chemical process with steps that requires rock mining and pre-treatment of the alkaline material. In general, an additional energy is required making difficult to compensate the energy released in the carbonation reaction (IPCC 2005).

CCS as geological storage is consider a good strategy for large sources of CO₂ while mineral carbonation is better for small and medium emitters representing about 10 to 15% of the total CO₂ emissions. However, mineral carbonation is a permanent and safe way to store captured CO₂ when compared to geological storage that requires monitoring (Sanna et al. 2012). Mineral carbonation has some disadvantages when compared to geological storage, mainly due to the costs associated and slow kinetic reactions.

In Situ Mineral Carbonation

In situ carbonation is a geological sequestration approach in which CO₂ is injected into reservoirs where CO₂ would react with the minerals present in the geological formation and eventually precipitate into various carbonate minerals, this process would improve the long-term stability of CO₂. There most suitable formations for this process are classified as sedimentary or igneous. Sedimentary formations can be marine, river and wind sandstones, evaporative carbonates, conglomerates and shale. The igneous formations can be mafic basalt, felsic granitic, ultramafic peridotite and ophiolites sequences. These formations have

crucial characteristics such as porosity and permeability which are good factors for CO₂ injection, temperature and pH which are critical parameters for the formation of the carbonates (Romanov et al. 2015).

The injection of CO₂ can lead to changes in the reservoir mainly due to dissolution of minerals at low pH and precipitation at high pH causing geomechanically implications in terms of stability of the reservoir mainly at permeability and porosity of the host rock (Kvamme and Liu 2009). Dissolution of minerals in the injection site can lead to the increase of porosity and permeability, while precipitation contrary to dissolution can lead to a decrease of the parameters but at some distance from the injection point (Romanov et al. 2015). Other issue involves also the drop of the pH to values of 4 or 5 mainly when the CO₂ is injected and dissolved, this acid reacts with mineral constituents in the host rock but also in the caprock formation, thus promoting potential leakage through existing faults and fractured zones (Rohmer, Pluymakers, and Renard 2016).

In situ mineral carbonation is a feasible option in terms of resources available and safety, however the transport and the costs associated represents the main barrier to its development and implementation (Holloway 1997; A. Sanna et al. 2014). The ideal concept of ex situ mineral carbonation requires some essential characteristics from the reservoir such as porosity, permeability and a low permeability caprock, and an injection of CO₂ at least or more 800 m, where the CO₂ presents a dense phase (Holloway 1997).

Ex situ Mineral Carbonation

Ex situ mineral carbonation consists in a series of processes which involves the reaction of metal oxide (Ca or Mg) bearing materials with CO₂ producing stables and insoluble carbonates (A. Sanna et al. 2014). However the slow reaction rates and material handling issues are an obstacle to a large-scale commercial application and due to the high costs of mineral carbonation (50-300\$/ ton CO₂) (Romanov et al. 2015). A study conducted by National Energy Technology Laboratory (NETL) indicates that a large-scale ex situ carbonation was impractical mainly due to the high costs associated of about 54\$/ton CO₂ and to the requirements of about 55 000 tons of mineral to carbonate daily CO₂ emissions from a 1 GW coal power plant (Connor et al. 2007).

Some of the advantages in the mineral carbonation is that provides a stable and leakage-free method for the injected CO₂ and there is a minimal or none necessity for

monitorization (Zevenhoven, Fagerlund, and Songok 2011) and feedstock are abundant and accessible such as olivine, serpentine and wollastonite.

Another feedstock available for mineral carbonation is the known alkaline industrial residues which presents high concentrations of Ca or Mg oxides. These silicates substitute materials are normally promptly available, at low cost and usually are produced near large CO₂ emissions sources. These materials are very reactive when compared to mineral silicates which can be an add-value to mineral carbonation (I. S. S. Romão 2015). Usually, the alkaline industrial residues presents moderates to low quantities of heavy metals such as Pb, Ni and Cd, which can be leached during the carbonation process resulting in a final stable product, the carbonates, eliminating potentials environmental impacts of these residues in landfills (Pan, Chang, and Chiang 2012). In the perspective of waste valorisation the carbonates produced by residues have a commercial use and value, as for example, it can be reused in constructive sector instead of being disposed into landfills decreasing its disposal.

Carbonates can be used in other sectors like construction, paper and pulp, pharmaceutical, agriculture and refractory metals. In Figure 3.1 is depicted the final use of carbonates, however in some cases their application can release CO₂ (Woodall et al. 2019).

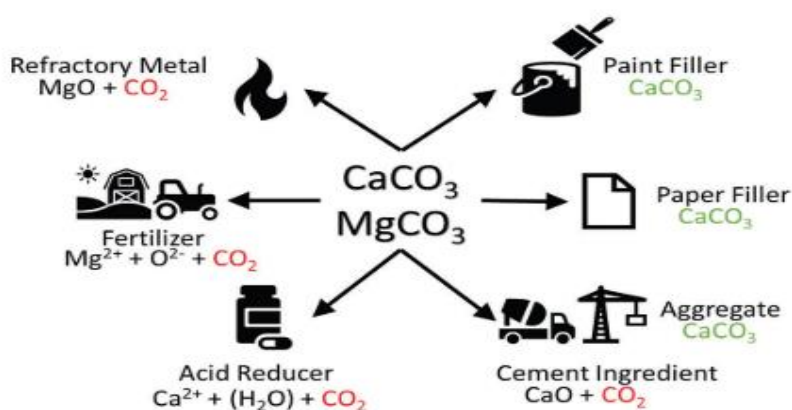


Figure 2.10. Utilization of mineral carbonates in industrial sectors and their respective final chemical form (Woodall et al. 2019).

The most common alkaline used in mineral carbonation are fly and bottom ashes from furnaces in steel industry, cement kiln dust and waste concrete from the cement industry, slags from steel and iron industry, mining waste and alkaline paper mill. The CO₂ capture capacity expressed in g per kg of waste depends on the oxides (CaO and MgO) or

hydroxides ($\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$) present in the residues (Romanov et al. 2015) as shown in Figure 3.2.

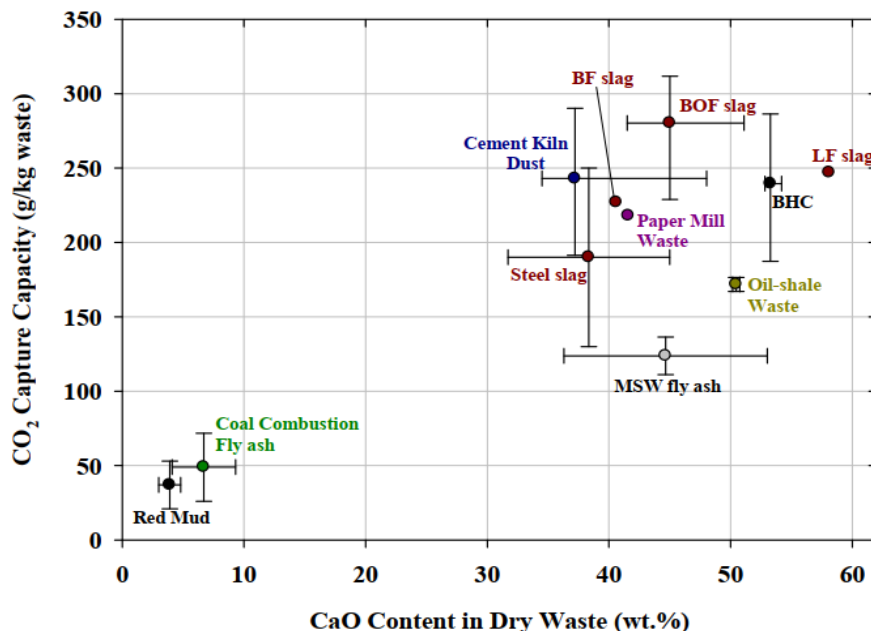


Figure 2.11. Actual CO₂ capture capacity versus CaO content in dry waste for several types of industrial residues (Pan, Chang, and Chiang 2012).

The ex situ mineral carbonation can be divided into two major categories, the direct carbonation route that consists in the directly reaction of CO₂ with the mineral in one step and the indirect carbonation route where the carbonation process is divided into various steps. Direct carbonation can be divided in two categories, dry carbonation (Gas/Solid) and aqueous carbonation and the indirect carbonation can be divided in three categories the acid

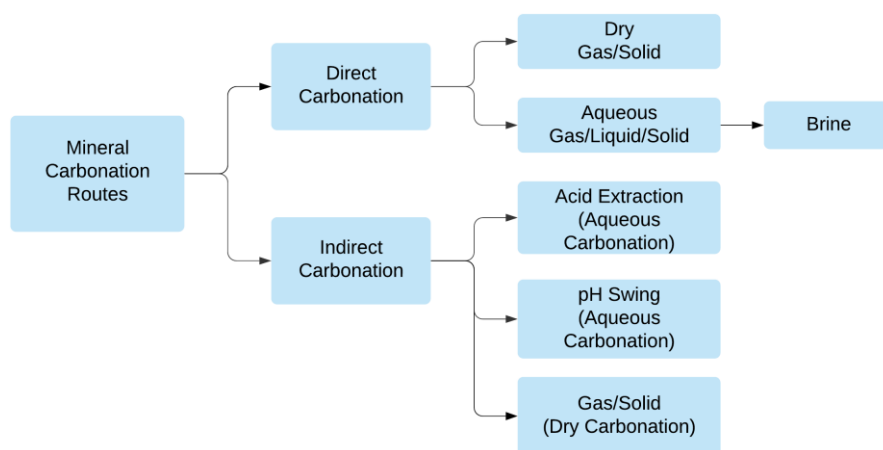


Figure 2.12. Principal routes in mineral carbonation.

extraction (aqueous), pH swing (aqueous) and dry carbonation or Gas/Solid. In Figure 3.3 is represented a simplified scheme of the routes of carbonation.

Direct Carbonation

The direct carbonation as mentioned before is performed in just one step or take place in a single reactor and can be achieved through a gas-solid or dry carbonation route and aqueous carbonation route. The simplicity of the process and the minimal use of reagents are the main advantages of this via (Ji and Yu 2018).

Dry routes (Gas-Solid)

The gas-solid or dry carbonation route consists in the reaction of gaseous carbon dioxide with a solid mineral source. The simplicity and the possibility of recycling the heat from the exothermic reaction are the main advantages of this route, however the reaction rates are too slow making this route not viable for an industrial scale (Huijgen and Comans 2005)

In 2010, a method to sequester CO₂ as mineral carbonate was patented by DaCosta, Fan, and Russell. A direct dry process for silicate rocks such as olivine, serpentine or wollastonite with grain sizes of 2,5 to 60 mm, consisting of the removal of carbon dioxide from flue gases through a bed of finely ground of metal silicates was developed. Then, the CO₂ reacted with particulate material to produce carbonates. Results showed that after 30 min the storage capacity was 0.12 g CO₂ per g of olivine for temperatures in a range of 100 to 500 °C and with a flue composition of 10 % CO₂ and 8.3 % of H₂O. It was also observed that in absence of moisture, the CO₂ stored decreased when 5% or 20% of CO₂ stream was used. Water vapor proved that can be useful to convert oxides into hydroxides which can then be carbonated. The equations 3.1 and 3.2 demonstrate the sequence.



The process demonstrate that is able to work in a dry environment, where vapor water present in flue gas is enough to convert oxides into reactive hydroxides and subsequently form carbonates in 30 minutes, which is an added value to an industrial scale. However a

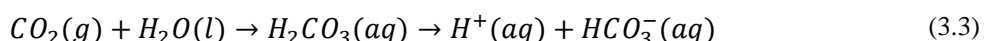
large amount of mineral would be required to sequester a tonne of CO₂ due to the low efficiency.

A study performed by Kwon et al. 2011 concluded that water has a major role in direct carbonation. In this study, the mineral source was olivine due to its thermodynamic stability and the capacity to form stable carbonates. The experimental results demonstrated that water vapor had a major role in CO₂ carbonation rates.

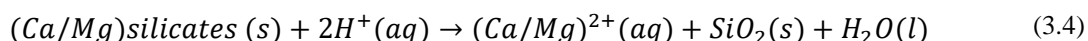
More recently, a study performed by Altiner 2018 with Turkish fly ashes revealed a potential of using these industrial residues in gas-solid carbonation under different CO₂ pressures and at ambient temperature. As a main result, it was observed that the amount of CO₂ sequestered in carbonates increased with the increasing of CO₂ pressure and carbonation time. About 14.25 g of CO₂ was captured per 100 g of residue in the form of calcite. The maximum efficiency was 43.41% under 5 bar of CO₂ pressure for 15h. This study provides an alternative to sequester CO₂ using fly ash under low CO₂ pressures and at ambient temperature.

Aqueous routes (Gas/Liquid/solid)

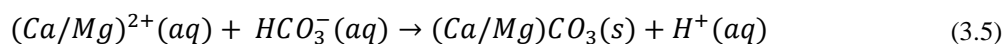
Direct aqueous carbonation can be separated in three coexistent mechanisms in just one reactor. The first mechanism is when CO₂ dissolves in water and forms carbonic acid resulting in a slightly acidic environment as demonstrated in equation 3.3.



The protons of hydrogen (H⁺) presented enables to leach Ca or Mg from the matrix of the alkaline material as shown in equation 3.4.



The Ca or Mg cations and the bicarbonates ions precipitates into carbonates, as evidenced in equation 3.5.



The Albany Research Centre (ARC) was the pioneer in direct aqueous carbonation, leading numerous experiments using serpentine at many pressures (> 200 bar), temperatures (> 300°C) and reaction times of 24 h or more (W. K. O'Connor et al. 2005). However, the obtained efficiency in this process was relatively low. This study developed an economic

evaluation with an initial cost estimate of \$69/ ton of CO₂. To minimize this cost, mineral pre-treatment and reactor design could be the answers. However, for a 1GW coal-fired power plant it will be required 55 000 ton mineral/day to carbonate 100% of CO₂ emissions, this results favour an in-situ methodology (W. K. O'Connor et al. 2005).

Another study based on aqueous direct carbonation investigated the possible explanation for the low efficiencies achieved and the substantial energy waste in heat activated serpentine (Benhelal et al. 2019). In this research, the discovery of side reactions that occurred in direct aqueous carbonation increased the energy penalty and subsequently decreased efficiency rates mainly due to the consumption of dissolved magnesium to precipitate the magnesium silicate hydroxide phase and the crystalline serpentine. Magnesium dissolved in another competitive reaction must react with CO₂ to precipitate magnesite instead of the precipitates mentioned above. These side reactions have a crucial impact on the efficiency of aqueous direct carbonation and on the produced magnesite with a reduction of 40 % or more. To reduce this impact on efficiency and cost, kinetic and thermodynamic issues of magnesite precipitation and other products should be investigated (Benhelal et al. 2019).

Brine Application

Ferrini et al. 2009 proposed a modified method for direct aqueous carbonation to produce nesquehonite (MgCO₃·3H₂O) through the reaction of a flux of CO₂ with magnesium brine solution (MgCl₂) at relatively ambient temperatures (20 ± 2°C). The rate reaction presented is considered fast due to the fact that after 10 minutes the carbonation was almost completed.

Carbonation via magnesium brine at 20°C is a simple and stable method to trap CO₂ using rejected brine and could be applied in sources of CO₂ emission. Potential sources of brine include seawater, evaporated saline deposits or waste flows such as desalination sub products and water generated in oil and gas industries (Romanov et al. 2015).

Another approach of brine application was developed by Calera in a demonstration plant at the gas power plant in USA (Zaelke et al. 2011). This process consists of introducing brine into a reactor, where CO₂ is put in contact with the brine resulting in the CO₂ dissolution in water, forming carbonate and bicarbonate ions. Due to the decrease in pH, protons are removed to precipitate carbonates. Although brines have large amounts of

cations, such as Ca or Mg (Constantz et al. 2011), their adaptation to the Calera process requires a high amount of energy and alkaline residues, making this operation unsustainable on a large scale.

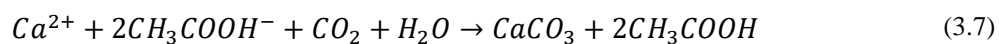
Indirect Carbonation

Indirect mineral carbonation involves normally more than one step that can lead to an increase of the speed of carbonation step (Romanov et al. 2015). Typically, an indirect method had a minimum of two steps, the first step or stage involves the extraction of reactive components such as Mg^{2+} or Ca^{2+} from the alkaline material source with acids or other solvents, and the second step is the reaction between the reactive components extracted with CO_2 in gaseous or aqueous phase in order to form carbonates. The formed carbonates are stable and can be consider pure, since there is a removal of impurities in the first step known as dissolution or extraction phase (A. Sanna et al. 2014).

Acid Extraction

The use of acids to extract reactive components can enhance the rate and the number of ions that can be leach form the mineral or material matrix. In this section, it will be analysed the several studied acids used in the dissolution step.

Kakizawa et al. 2001 proposed a new disposal process for CO_2 captured from sources such as power plants, where CO_2 can be sequestred in the form of calcium carbonate. In this process, acetic acid was used to extract calcium from wollastonite rocks and was composed by two steps: the dissolution and the carbonation as shown in the equations 3.6 and 3.7.



The conditons of the extration involved the reaction between 13.46 g of wollastonite and 50 g of a solution of acetic acid in an extraction column at a temperature of 60 °C and at atmospheric pressure. The extration rate achieved was 48% at 250 minutes. Another result noticed in this study was the linear relationship between the extration ratio and the intial particle size, suggesting that the reaction was essentially determinated by the total surface area of the wollastonite particles.

A study performed by Teir, Revitzer, et al. 2007 about the dissolution of natural serpentinite in acids at room temperature demonstrated that strong acids have a great impact on the extraction step. The acids tested were H_2SO_4 , HCl , HNO_3 , HCOOH and CH_3COOH . Sulphuric acid was the most efficient at extracting magnesium, followed by HCl , HNO_3 , HCOOH and CH_3COOH . A significant amount of iron in serpentinite was extracted and the apparent activation energies calculated for the dissolution step were 68 kJ/mol for H_2SO_4 , 70 kJ/mol for HCl and 74 kJ/mol for HNO_3 .

Alexander et al. 2007 studied the effect of particle size (61-163 μm) in the dissolution of magnesium from serpentine with sulfuric acid (1-5M) for a reaction duration of 1 to 6 hours. The results showed that the acid concentration was the main factor in the leaching process. The extraction rate increased for particles sizes lower than 125 μm .

Van Essendelft and Schobert 2009 tested four acids (sulphuric acid, oxalic acid, orthophosphoric acid and EDTA) as leaching agents in serpentine. This study involved a kinetic study of Mg leaching with grinding at simultaneous. The most important result in this research is that grinding is unable to keep surfaces refreshed under the conditions applied, or by other words grinding action increases the leaching of magnesium by breaking down and thinning the silica layer. However, grinding action increases the diffusion through silica instead of exposing the fresh area surface. The combination of physical and chemical methods can lead to a greater increase in kinetics reaction, for example, the fastest kinetic reaction happens with untreated, natural and non-chrysotile containing serpentine. In this study, they concluded that strong acids have a great effect than mixtures of acid and organic agents.

A patent developed by Maroto-Valer et al. 2009 reports a process for sequestering carbon dioxide, which involves a reaction between a silicate based material and an acid to create a suspension. The suspension reacts with CO_2 to form carbonates, silica and at final stage there is a potential of regenerating the acid in liquid phase or suspension. Sulfuric acid, nitric acid, phosphoric acid and acetic acid were tested. The group of materials or minerals in this process have the formula $\text{X-SiO}(\text{OH})$ where X can be Mg, Ca, Fe^{2+} , Fe^{3+} , Ni, Al, Zn and Mn.

Another feedstock available for mineral carbonation is the industrial alkaline residues as source of Ca or Mg. Mun et al. 2017 tested several acids with the same concentration (0.1 M) on blast furnace slag and waste cement under atmospheric conditions

in order to determine the efficiency on mineral carbonation. The acids tested were HCl, CH₃COOH and NH₄Cl. The most efficient acid was NH₄Cl, and waste cement was the most suitable for mineral carbonation based on the maximum calcium concentration (2400 mg/L) and selectivity (99%). The concentration of acid has a great influence on the calcium extrated ratio, with a linear relationship, only dependind on the used acid.

Irfan, Usman, and Rashid 2018 tested four solvents including acids and bases in dissolution step of concrete waste. The solvents used were propionic acid, NaOH, HNO₃ and NH₄Cl. The results showed that NaOH and propionic acid was not able to extract a significant amount of calcium when compared to HNO₃ and NH₄Cl. Nitric acid was the most efficient in leaching the calcium. An explanation for the differences performances found for nitric acid and ammonium chloride is related to their pK_a values. HNO₃ has a low value of pK_a of -1.4, while NH₄Cl presents a high value of 9.24.

pH Swing

The pH swing process is multistep process which consists firstly of the dissolution of Ca or Mg from the alkaline material or mineral and the precipitation of carbonate in the following steps. Since the first step, known as dissolution step, requires a low pH while the precipitation of carbonates requires a higher pH value, this separation has led to the development of pH swing routes and two-steps in the indirect carbonation.

Teir et al. 2007 studied the precipitation of magnesium carbonate on an aqueous solution from serpentinite. The serpentinite was dissolved with 4M of HCl or HNO₃ at 70 °C and then CO₂ gas was introduced and bubbled into the solution. The alkalinity of the solution was controlled for the precipitation of magnesium carbonates by adding NaOH. The optimal solution pH for precipitation of the magnesium carbonate was at 9. At this pH was achieved the highest purity of carbonate, highest amount of CO₂ fixed as carbonate and the highest conversion of magnesium ions into hydromagnesite. However, the high requirements of NaOH and acid utilized in the overall process makes this application economically unfeasible.

Wang and Maroto-Valer 2011 utilized a serpentine mineralization process through a mixture of nitric and hydrochloric acid as leaching agent, This process has already been studied by Lin et al. 2008, a pH swing method that involves the preparation of Mg(OH)₂ from serpentine, since raw materials based on magnesium hydroxide have better

performances in terms of kinetics reaction than magnesium silicates materials. In the study purposed by Lin et al. 2008, the magnesium ions were leached with HCl. In a first approach, the addition of NaOH increased the solution pH at 8 promoting the precipitation of SiO_2 , then to precipitate the $\text{Mg}(\text{OH})_2$ was added more NaOH to increase the solution pH to 11. The conversion of hydromagnesium was reported to be more than 90%..This is a process that involves three steps to the final carbonate product.

Hemmati et al. 2014 studied a carbon dioxide mineralization pH swing on a magnesium silicate rock and their solid products including silica, iron hydroxide and magnesium carbonates. The iron hydroxide generated in the process have different crystalline properties, and their formation depends strongly on the pH of the reaction. In the dissolution experiments 4 g milled mineral ore with 10 – 56 μm was reacted with 100 ml of 1M HCl solution at 80 °C and atmospheric pressure for 6 hours. For the carbonation was prepared 1M of Na_2CO_3 solution used as the CO_2 source. In this process, it was added 1M NaOH to increase the pH (pH initial = 0.56) in two steps to obtain the two first precipitates: the first precipitate occur at a pH of 5 and is consisted mainly in crystalline $\text{Fe}(\text{OH})_3$ and Fe_2O_3 , the second was formed with a pH of 9 and was essentially amorphous $\text{Fe}(\text{OH})_2$ and Fe_2O_3 , and the third was formed spontaneously due to the addition of Na_2CO_3 with a complete carbonation when the value of pH was 10 and was mainly magnesium carbonate. The last precipitate had different crystalline structures depending on the carbonation temperature. For a temperature of 0 °C the main product was hydromagnesite, for a temperature of 60 °C the main carbonate product was dypingite and at a temperature range of 10 to 50 °C, nesquehonite was the dominant product. For 1 tonne of CO_2 3.74 tonnes of mineral ore are required. The efficiency achieved was 73.6%.

More recently, a study performed by A. Sanna et al. 2017 used sodium hydrogen sulphate (NaHSO_4) to leach Mg from lizardite-rich serpentinite to form MgSO_4 and then reacting this last product with CO_2 to form carbonates in the form of MgCO_3 and Na_2SO_4 through a pH swing process. This work demonstrated that NaHSO_4 is a good leaching agent under the conditions applied and that a decrease in the concentration of the leaching agent leads to a decrease in the dissolution efficiency. The optimal dissolution efficiency was 69.6 % in 3 hours of dissolution reaction and the optimal carbonation efficiency was 95.4 %. The process based in NaHSO_4 was able to sequester 223.6 g CO_2/kg .

Munz et al. 2009 proposed a three-step carbonation process using a flow-through stirred reactor without the need for chemical additives, such as acids or bases. The process consists firstly in the dissolution of olivine with CO₂ and water at 130 °C, secondly in the precipitation of magnesite at a temperature of 250 °C and at last the precipitation of silica. Experimental conditions were in a range of pressure of 100 – 150 bar and a range of temperature of 130 – 250 °C. The precipitation of magnesite and silica has different dependences on pH and in temperature, magnesite precipitation occurs at high temperatures of 180 – 250 °C.

Gas/Solid

Aqueous processes demonstrated a reasonable chemical kinetics but with considerable energy costs. A dry process with slow kinetics but with low energy costs could be an alternative. In Finland, an indirect method for gas-solid carbonation of Ca or Mg hydroxide/oxide was considered. Zevenhoven et al. 2008 proposes two routes that consisted of two- and three-step processes for the carbonation of magnesium silicate. The main differences between the 2 routes is that the two-stage is limited by the temperature and CO₂ pressure, allowing for the formation of a stable MgCO₃, while in the three-stage the temperature and CO₂/H₂O pressure ratio were the most important factors. The both systems operates at the same temperature (>500 °C) and CO₂ pressure (>10 bar). The process involves at first the formation of reactive magnesium oxide/hydroxide in an atmospheric pressure, and then carbonation at high pressures allowing a reasonable carbonation reaction kinetics. To make this route possible in large-scale, kinetics in each reactor must be fast enough and the heat produced must be enough to compensate the energy inputs. The results demonstrated, that for a specific combination of temperatures in each reactor, an operation at a negative or zero-energy input can be achieved for a certain carbonation reactor pressure and degree of carbonation conversion.

2.1.5. Carbon dioxide utilization

In this section, several applications and products derived from CO₂ utilization are described. CO₂ has a diversified application and can be used directly, such as dry ice, fire extinguisher, solvents, refrigerants, process fluid and welding medium; however, these

small-scale applications have no significant impact on reducing CO₂ emissions. It can also be used indirectly to enhance industrial processes, such as in enhanced oil recovery, enhanced gas recovery and in enhanced geothermal systems, or even as a feedstock in the production of chemicals and fuels.

There are two main categories of CO₂ utilization: the physical and the chemical. In the physical utilization, the CO₂ molecule keeps pure or dissolved in a solution without reacting chemically. In the chemical utilization, the bonds of the CO₂ molecule break in an exothermic or endothermic reaction and can lead to the conversion of various chemicals, such as synthetic fuels or components needed for other products. In Table 2.1 can be seen several examples of both categories in the utilization of CO₂ based on the review prepared by Rafiee et al. 2018.

The routes presented above have differences in terms of research demands. The physical CO₂ utilization is a mature industry with low demand in research, while chemical CO₂ utilization is a developing field with a substantial demand for research. These routes depend mostly on the market trends, the energy prices and the climate change mitigation policies (Rafiee et al. 2018).

Table 2.1. Examples of CO₂ utilization in chemical and physical approaches.

CO ₂ Utilization Categories	
Chemical	Physical
Syngas production	Dry ice
Methanol production	Fire extinguisher
Dimethyl ether (DME) production	Solvent
Urea production	Refrigerant
Dimethyl carbonate (DMC) production	Process fluid
Polyurethane	Welding medium
Fischer-Tropsch gas-to-liquid (FT-GTL) products	Enhanced Oil Recovery (EOR)
Methane production	Enhanced Gas Recovery (EGR)
Chemical looping dry reforming	Enhanced Geothermal Systems (EGS)
Mineralization	
Other products (ethers, esters, and acids):	
- Polyethylene esters	
- Furan-2,5-dicarboxylic acid	
- Cyclic carbonates (N-bromosuccinimide (NBS) and benzoyl peroxide (BPO))	
- Ethylene carbonate (EC) and propylene carbonate (PC)	

2.2. The production process of grits

The alkaline industrial residue used in this study is generated during the chemical recovery step using the Kraft chemical pulping process. The pulping process has as main objective to separate the individual fibres presented in the wood chips by chemical or mechanical methods which is represented in the Figure 2.13.

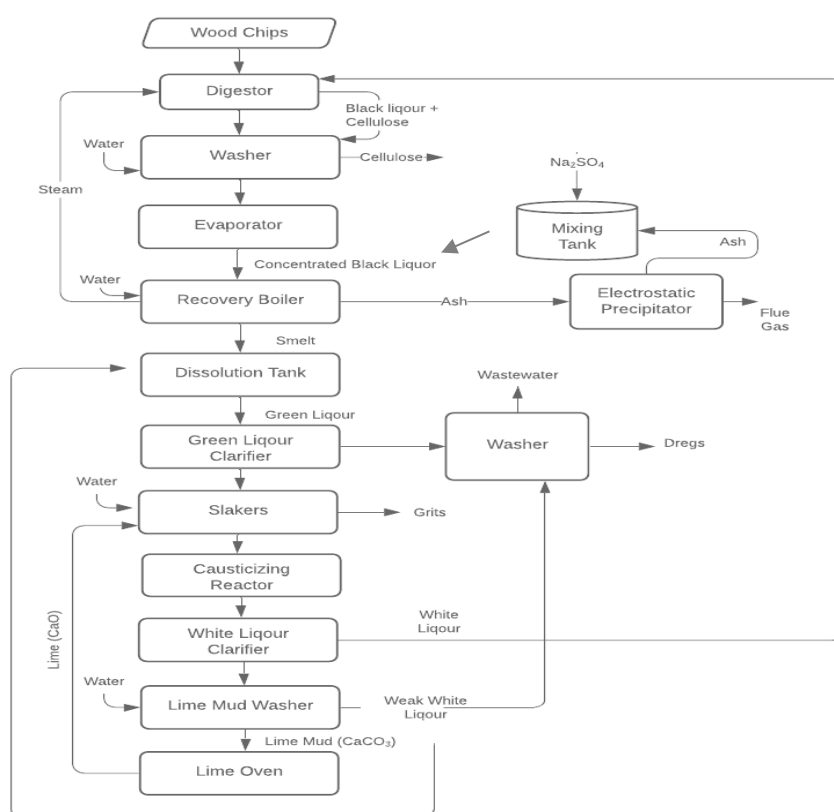


Figure 2.13. Kraft Process in pulp paper production (Adapted from Martins et al. 2007)

The manufacture of the pulp and paper can be carried out via the Kraft process (sulphate) or the Sulphite process. The Kraft pulping process is the method used to produce the chemical pulp, where the chemicals sodium hydroxide (NaOH) and sodium sulphite (Na₂S) are used to digest the wood chips (cooking process) at elevated temperatures and pressures. The Sulphite process is similar to Kraft pulping, except that different chemicals are used in the cooking liquor. The causticizing process is part of the chemical recovery energy, in which chemicals are recovered, mainly to convert sodium carbonate (Na₂CO₃) back to sodium hydroxide (NaOH). The recycling and reuse of several streams present in the kraft process leads to the build-up of non-process elements (e.g. K, Mg, Ba, Fe, Al, Cu, Ni,

Cr and Zn) and the accumulation of these elements in the pulp mills have significant problems in the equipment's which can lead to a decrease in the process efficiency's. To minimize these problems, the non-process elements are purged from the chemical recovery cycle in the form of dregs and in the form of slaker grits (Watkins et al. 2010).

The grits present a high calcium concentration since grits are formed during the slaking process in which the lime (CaO) reacts with green liquor (NaOH , Na_2S and Na_2CO_3) in the slaker unit. The grits contain calcite (CaCO_3) with 23.5 % of mass, pirssonite ($\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) with 18.6 % mass, portlandite ($\text{Ca}(\text{OH})_2$) with 11.8 % mass, larnite (Ca_2SiO_4) with 28.4 % and brucite ($\text{Mg}(\text{OH})_2$) with 4.1 % mass of the grits (Martins et al. 2007).

As the grits have as a dominant species calcite and pirssonite with approximately 42% of mass, during the dissolution of the grits for Ca extraction in an indirect carbonation process the carbon dioxide release must be minimized, in order not to compromise the capacity CO_2 sequestration.

3. STATE OF ART ON CO₂ SEQUESTRATION BY MINERALIZATION

As a conclusion of the review on mineral carbonation, the materials and operational conditions used in the mineral carbonation process reported in several published works were summarized in Tables 3.1 and 3.2. Table 3.1 shows a wide variety of silicate rocks that can be utilized in the indirect or direct route of the mineral carbonation with its respective mineral and chemical composition. In Table 3.2, a more specific analysis was done about the industrial alkaline wastes used in mineral carbonation with their respective carbonation route with some relevant parameters (particle size, temperature, pressure and extracting agents). The composition of the wastes is predominantly based on oxides of magnesium and calcium. The alkaline industrial wastes most reported by the literature are those produced by the steel industry, such as the blast furnace slag and the steel making slag, the cement industry and the coal industry specially the fly ashes. Information listed in Table 3.2 has a great relevance to the present work, since the material used in the experiments is an industrial alkaline waste generated by the pulp and paper industry, the grits. To the best of our knowledge, there are no carbonation studies using this type of waste.

Table 3.1. Silicates rocks and their chemical formula used in mineral carbonation.

Silicate Rock	Mineral Composition and Chemical Formula	Chemical Composition (%)	CO ₂ Storage Capacity (kg / kg CO ₂)	References
Olivine	(Mg, Fe) ₂ SiO ₄	MgO: 49.3	0.06 – 0.18 g CO ₂ /g olivine	Kwon et al., 2011
	92% Forsterite (Mg ₂ SiO ₄)	CaO: 0.01		
	8% Fayalite (Fe ₂ SiO ₄)	Fe ₂ O ₃ : 8.3		
		SiO ₂ : 42.1		
Serpentinite		MgO: 48.1	70 % (CO ₂ Sequestration Capacity) ^a	Sanna et al., 2014
	84% Forsterite (Mg ₂ SiO ₄)	CaO: 0.4		
	6% Enstatite (MgSiO ₃)	Fe ₂ O ₃ : 7.7		
		SiO ₂ : 41.9		
Serpentinite	Mg ₃ Si ₄ O ₁₀ (OH) ₂	Mg: 23.22	70 % (Carbonation Efficiency)	I. S. Romão et al. 2016
	90% Serpentine (Antigorite and Lizardite) 5% Talc	Ca: 0.09		
		Fe: 5.71		
		Si: 19.51		
Serpentinite	83% Serpentine	Mg: 21.8	86 % (Leaching Efficiency)	Zhao et al., 2015
	(Mg ₃ Si ₂ O ₅ (OH) ₄)	Ca: 0.34		
	Impurities: 82% Magnetite (Fe ₃ O ₄)	Fe: 10.10		
		Si: 11.60		
Wollastonite	CaSiO ₃	CaO: 48.3 SiO ₂ : 51.7	0.34 kg CO ₂ / kg CaCO ₃	Teir et al., 2005
Basalt	-	CaO: 9.4 MgO: 6.2	7.1 ton rock/ ton CO ₂	Lackner et al. 1995
Feldspar	CaAl ₂ Si ₂ O ₈	Mg: 4.8 Ca: 10.3 Fe: 3.1	9 % (Reaction Efficiency to carbonate)	O'Connor et al. 2005
Pyroxene	CaMg ₃ Si ₂ O ₆ + (Fe, Al)	Mg: 6.9 Ca: 15.6 Fe: 9.6	33 % (Reaction Efficiency to carbonate)	O'Connor et al. 2005
	73% Diopside; 11% Forsterite	MgO: 20.6	30 % Mg Extracted	Sanna et al., 2014
	7% Enstatite; 5% Anorthite	CaO: 17.2		
	3% Lizardite; 1% Actinolite	Fe ₂ O ₃ : 6.3		
		SiO ₂ : 49.3		

Table 3.1. Silicates rocks and their chemical formula used in mineral carbonation (continuation).

Silicate Rock	Mineral Composition and Chemical Formula	Chemical Composition (%)	CO ₂ Storage Capacity (kg / kg CO ₂)	References
Amphibole	59% Actinolite; 27%	MgO: 12.1	29 % Mg Extracted	Sanna et al., 2014
	Prehnite	CaO: 14.9		
	10% Clinocllore; 3.7%	Fe ₂ O ₃ : 9.3		
	Epidote	SiO ₂ : 45.9		
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	CaO:0.01 MgO: 34.69	No carbonation observed	Wu et al. 2001

^a Sequestration capacity is the CO₂ that can be sequestered using olivine, considering the Mg dissolved (77,4%) and the carbonation efficiency (90%). (70% = 77,4% * 90% = 70%)

Table 3.2. Overview of the industrial alkaline residues used in mineral carbonation.

Industrial alkaline residue	Carbonation Method	Waste Composition (%)	CO ₂ Storage Capacity (kg waste / kg CO ₂)	References
Blast furnace slag (Steel Industry)	Indirect (Particle Size: < 10 µm)	CaO: 40.6	4.4	Eloneva et al. 2008
	CH ₃ COOH extraction (50 g/L; T=70°C)	MgO: 10.4		
	(Particle Size: 75- 150 µm)	CaO: 41.84	361	Chu et al. 2019
	ABS extraction: 3.25 (ABS/BFS); T=50°C	MgO: 6.74		
	Indirect (Particle Size: 48 - 1700 µm)	CaO: 38.3	3,802	Liu et al. 2018
	ABS extraction	MgO: 10.2		
Steel making slags	Indirect (Particle Size: 250 – 350 mm)	CaO: 45.84	-	Mun et al. 2017
	Analysis between solvents (100 g/L; T=25°C)	MgO: 3.62		
	Direct (Particle Size: < 38 µm - 2mm)	CaO: 31.7	0.25	Huijgen et al. 2005
	T=100 °C; P=19 bar	MgO: 6		
	Indirect (Particle Size: 125 - 250 µm)	CaO: 45.9	86 % (Conversion of Ca to CaCO ₃)	Eloneva et al. 2008
	CH ₃ COOH extraction (T=30 - 70 °C)	MgO: 3.7		
	(Particle Size: 50 - 1000 µm)	CaO: 44.9	96 % (Ca extracted 50-74 µm)	Said et al. 2015
	Ultrasonic w/NH ₄ Cl extraction (20 g/L)	MgO: 1.6		
	Indirect (Particle Size: 75–150 µm)	CaO: 38.44	85 % (Mg dissolution efficiency)	Dri et al. 2013
	ABS extraction (T=25 - 90°C; 50g/L)	MgO: 8.96		
Coal fly ash	Direct (Particle Size: 320; 116; 54 µm)	CaO: 12.5; 18.5; 24.8	27.05 kg CO ₂ /ton waste	Ukwattage et al. 2015
	pCO ₂ :10MPa; T > 120°C	MgO: 10.7; 5.5; 13		
	Direct (Particle Size: < 0.212 mm)	CaO: 31.95	180 kg CO ₂ /ton waste	Mazzella et al. 2016
	P=1 - 15 Bar; T=45°C	MgO: 1.896		
	Indirect (Particle Size: 1.25 – 4.5 µm)	Ca: 42.28	31.06 kg CO ₂ /ton waste	Han et al. 2015
	50g/L (DW/FA); Carb. (Tamb; Pamb)	Mg: 11.88		

Table 3.2. Overview of the industrial alkaline residues used in mineral carbonation (continuation).

Industrial alkaline residue	Carbonation Method	Waste Composition (%)	CO ₂ Storage Capacity (kg waste / kg CO ₂)	References
Alkaline paper mill waste	Direct (Particle Size: 1 – 100 µm) T=30 - 60°C; PCO ₂ =10 - 40 bar	CaO: 83.2 wt% MgO: 0.35 wt%	218 kg CO ₂ /ton waste	Pérez-lópez et al. 2008
Waste cement	Indirect (Particle Size < 0.75 mm) Analysis between solvents (100 g/L; T=25°C)	CaO: 37,95 MgO: 1,98	0.07 (NH ₄ Cl) 0.19 (HCl and CH ₃ COOH) 0.19 (HCl and CH ₃ COOH)	Mun et al. 2017
	Direct (Particle Size: 10 – 100 µm) pCO ₂ =3.0 MPa; T=323K	Ca: 27.3	270 kg CO ₂ /ton waste	Iizuka et al. 2004
MSWI bottom ash (Municipal Solid Waste Incinerator)	Direct (Particle Size: 4 mm) pCO ₂ =1 – 20 bar; Tamb	CaO: 16.3 MgO: 2.6	24 L CO ₂ /kg waste	Rendek & Germain, 2006
MSWI fly ash	Direct (Particle Size: < 212 µm) T=21°C; P=3 bar	CaO: 36.26	7 – 10 % w/w of CO ₂	Hills et al. 2007
Red mud	Direct (Particle Size: 0.1 – 160 µm) Ambient Conditions	Fe ₂ O ₃ : 54.26 Al ₂ O ₃ : 12.20 CaO: 0.23	70.2 kg CO ₂ /ton waste	Chandra et al. 2010
	Direct (Particle Size: 5 – 50 µm) P=3.5 bar; Room temperature	Fe ₂ O ₃ : 31.88 Al ₂ O ₃ : 20.10 TiO ₂ : 21.20 CaO: 2.99	53 kg CO ₂ /ton waste	Yadav et al. 2010
Nickel mine waste	Indirect (Particle Size: 75 - 150 µm) HCl Extraction (T=100°C)	Fe ₂ O ₃ : 86.85 Al ₂ O ₃ : 2.47 MgO: 1.06 CaO: 0.10	327.2 kg CO ₂ /ton waste	Razote et al. 2019

4. MATERIALS AND METHODS

4.1. Materials

The calcium source used in all experiments was grits, an alkaline waste produced by Kraft pulp mills. The waste samples were collected in a pulp mill located in the center region of Portugal. The samples were previously dried at 40 °C and then ground to a particle size less than 0.5 mm. Figure 4.1 shows images of the original grits and the grits after the pre-treatment. All chemicals and reagents used in this study were of analytical degree. In Table 4.1 are listed all chemicals used during the experiments with their main properties.

Table 4.1. Reagents used throughout the laboratorial experiment with their respective CAS, chemical formula, purity, density, molecular weight and supplier.

Reagents	CAS	Chemical Formula	Purity (w/w)%	Density (g/cm ³)	Molecular Weight (g/mol)	Provider
Sodium Hydroxide	1310-73-2	NaOH	100	2,13	39,99	EKA
Ammonium Chloride	12125-02-9	NH ₄ Cl	99,5	1,53	53,49	SIGMA
Nitric Acid	7697-37-2	HNO ₃	65	1,40	63,01	Fluka
Acetic Acid	64-19-7	CH ₃ COOH	100	1,05	60,05	VWR Chemicals
Hydrochloric Acid	7647-01-0	HCl	37	1,2	36,458	Fluka
Caesium Chloride	7647-17-8	CsCl	-	1,17	168,4	Fluka
Carbon Dioxide	124-38-9	CO ₂	100	0,00198	44,01	Nippon Gases

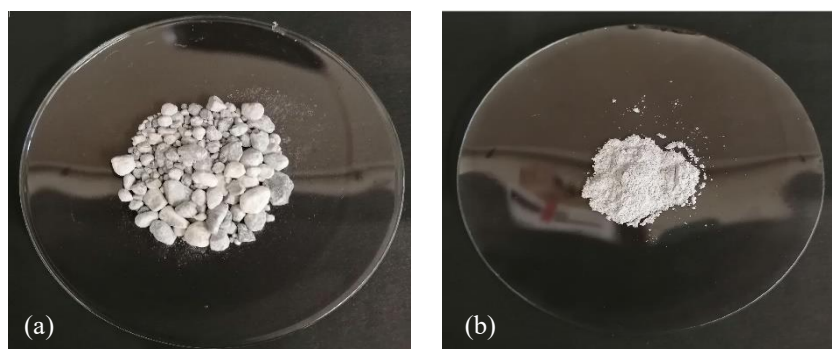


Figure 4.1. Grits: (a) grits at normal size and without pre-treatment; (b) grits after pre-treatment.

4.2. Characterization of grits samples

In order to determine the calcium concentration in the grits, two replicate samples were subjected to acid digestion. Thus, 0.5 g of grits were put in contact with 2,5 ml of 37% HCl and heated on a steam bath at 90°C until the volume has been reduced. After digestion reaction, the solution was filtered with a 0.47 µm filter with the aid of a kitasato flask and a vacuum pump, then the solution was diluted to obtain a final calcium concentration in the range of 0 to 1.5 mg/L for analysis. The concentration of Ca in each sample was determined through Flame Atomic Absorption Spectroscopy (FAAS) technique, model ContrAA 300.

4.3. Dissolution Experiments

The carbonation approach adopted in this study is an indirect method consisting of two steps. In the first step the main objective is to extract the maximum amount of calcium from the waste with an extract agent or solvent. In the second step, the mother liquor rich in Ca reacts with CO₂ to form a calcium carbonate precipitate. This second step will be analysed in detail later. In Figure 4.2 is schematically represented the experimental step-up where the dissolution step is circumscribed at red with all the respective inputs and outputs of required chemicals.

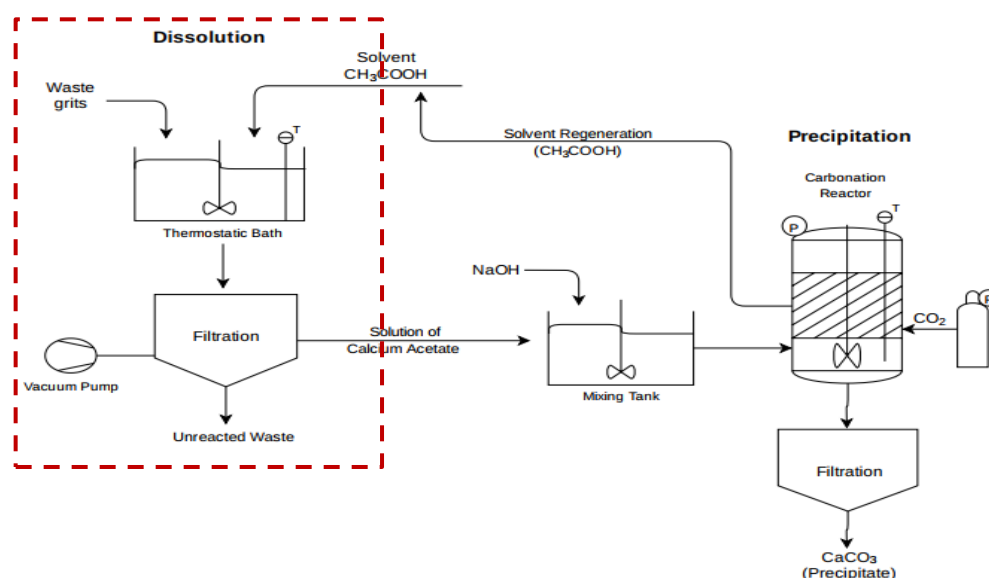


Figure 4.2. Experimental Setup

Initially, to screen the best solvent for the extraction step of Ca from the grits, four solvents were tested, namely acetic acid (CH₃COOH), nitric acid (HNO₃), ammonium

chloride (NH_4Cl) and sodium hydroxide (NaOH). All these solvents are mentioned in the literature as good extraction agents for several types of wastes, from steel waste to cement waste (Irfan et al. 2018; Sun et al. 2011; Eloneva et al. 2008). However, for the grits, there is no available information on which solvent is best to use, hence the reason for this first analysis.

The dissolution tests for each solvent were conducted by pouring a certain amount of grits in flasks containing solvent of known volume. The suspensions were stirred in a thermostatic water bath for 2 h. Then, the solution samples were filtered under vacuum using a filter of $0.47\ \mu\text{m}$ and after diluted for further analysis. The experimental conditions were the following: solid/liquid ratio of 50 g of grits per 1 L of solvent, solvent concentration of 2 M and temperature of $30\ ^\circ\text{C}$.

The calcium extraction efficiency (CEE) was calculated using Equation 4.1, where the calcium concentration final and initial are expressed as mg Ca/kg grits. The average concentration of Ca, $\overline{[Ca]}$ was calculated by Equation 4.2, and the standard deviation, σ by Equation 4.3 with $[Ca]_i = x_i$.

$$\text{CEE (\%)} = \frac{[Ca]_{\text{final}}}{[Ca]_{\text{initial}}} \times 100 \quad . \quad (4.1)$$

$$\text{Average, } \overline{[Ca]} = \frac{1}{N} \sum_{i=1}^N x_i \quad . \quad (4.2)$$

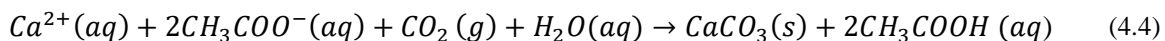
$$\text{Standard Deviation, } \sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \mu)^2} \quad . \quad (4.3)$$

Depending on the acidity of the solvent, there will be a different behavior throughout the extraction reaction. In the case of the use of acetic acid and nitric acid as a solvent, the concentration of calcium ions increases in the solution, but the pH of the solution decreases, a drawback for the carbonation step. In these cases, is necessary to add a base to increase the pH for values in the range approximately from 8 to 9 to ensure the precipitation of the carbonates. Using ammonium chloride, as the extraction reaction proceeds ammonia is generated increasing the pH of the solution, so that it is not necessary to add a base for the next step, the carbonation. All of the solvents tested can be regenerated at the last phase of the carbonation process (Mun et al. 2017).

For the kinetic study, Ca extraction was analysed with time using the two best solvents. The kinetic experiments were performed using the dissolution waste methodology explained above, in which 6 samples were collected in 5, 10, 20, 30, 60 and 90 minutes during the extraction process to obtain the reaction behavior over time. After filtration, each solution sample was diluted and analyzed by FAAS.

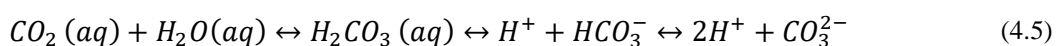
4.4. Mineral carbonation experiments

The second step known as precipitation step or carbonation, requires the reaction between the Ca-rich solution obtained in the extraction process and a pure stream of CO₂ to form carbonates as represented by Equation 4.4.



The experimental set-up used in the carbonation experiments is shown in Figure 4.3. In these experiments, carbon dioxide was bubbled through the calcium acetate solution for 90 minutes with a magnetic stirring of 650 rpm, at desired pressure and temperature. To ensure the precipitation of the calcium carbonate, for each sample of 35 ml of salt acetate solution was initially added 10 ml of 1 M NaOH to increase the pH above 8 or 9. In this first attempt, it was not possible to get a significant increasing in the pH due to buffer capacity of the acetate solution. Thus, only the addition of 10 ml of 5M NaOH allowed to obtain precipitate during the carbonation tests.

Equation 4.5 depicts the chemical reaction when CO₂ reacts with water and the subsequently formed species, where the amount of each specie depends on the solution pH, as shown in Figure 2.8.



To understand the influence of pH on the development of carbonates, Figure 2.8 exemplifies the various carbonates species when CO₂ reacts with water in a general way. For a lower pH than 4 the main species are CO₂ aqueous, carbonic acid (H₂CO₃) and ions of H⁺, to a pH between 4 and 7 the main species are bicarbonate and carbonic acid, and for a higher pH than 8 carbonates and ions of OH⁻ are the dominant species.



Figure 4.3. Experimental Installation of the carbonation step (1 – Pressure relief valve; 3,8 – Valve; 2 –Three-way valve; 4,5,9 – Manometer; 6 – CO₂ input; 7 – CO₂ bottle; 10 – Carbonation reactor; 11 – Magnetic stirrer with heating plate)

To increase the pH solution is added approximately 2 ml of NaOH turning the solution pH suitable to increase the amount of carbonates. In this case more calcium carbonate can be formed in the solution. After the stabilization of pH, the solution was filtered and then the filter was weighted and dried at 105 °C during the night in an oven. The filtered solution is once more filtered, but with a filter of 0.47 μm for the analysis in the FAAS to measure the calcium that didn't react in the solution. The filter once dried is weighted again and the precipitate in the filter was sent to XRD and SEM analyses. The addition of NaOH has a fundamental role in the presented form of the precipitate and it is likely that the precipitate is mostly calcite. If the NaOH was suppressed, the precipitate will be mostly aragonite (Eloneva 2008). Images of the obtained samples after the carbonation step can be seen in Figure 4.4.

At the end of the carbonation step, acetic acid is regenerated and can be recirculated into the first step of this method, as showed in Figure 4.2.

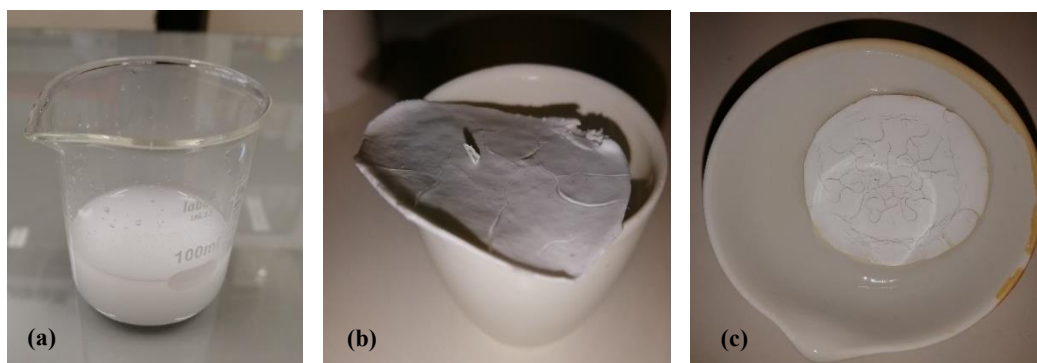


Figure 4.4. Procedure after the carbonation process: (a) Solution after carbonation and pH stabilization; (b) Filter after the filtration of the solution represented in (a); (c) Filter after being dried at 105 °C overnight in an oven.

4.5. Experimental Design

To obtain optimal conditions for the extraction and carbonation experiments, multiple linear regression models were developed from design of experiments (DOE), enabling to relate response variables with input variables (factors). In the case of study addressing the calcium extraction from the waste, a factorial design with three levels and three factors was performed. The levels of the factors used in the experiments are shown in Table 4.2. This DOE approach led to a matrix with 30 experimental runs, including already the two replicates.

Table 4.2. Levels of factors used in the experimental design for the extraction studies

Factor	Level		
	-1	0	1
X1: Temperature (°C)	25	50	75
X2: Solid/Liquid Ratio (g/L)	20	60	100
X3: Acetic Acid Concentration (M)	0,5	1,25	2

The optimization approach and the statistical analysis was carried out through the application of the software *STATISTICA*. Considering the general multivariate regression (Equation 4.6), a quadratic model, given by Equation 4.7, was used for describing the behaviour of the extraction percentage of Ca as function of the operating variables.

$$y = f(X_1, X_2, X_3) = \beta_0 + \sum_{i=1}^N \beta_i X_i + \sum_{i=1}^N \beta_i X_i^2 . \quad (4.6)$$

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_1^2 + \beta_3 X_2 + \beta_4 X_2^2 + \beta_5 X_3 + \beta_6 X_3^2 . \quad (4.7)$$

The three factors X_1 , X_2 and X_3 are the independent variables, where X_1 represents the temperature in °C, X_2 the solid/liquid ratio in g/L and X_3 the acetic acid concentration in mol/l. The response variable, y , is Ca extraction efficiency (CEE).

The experimental design adopted in the analysis of the carbonation process was based on a design with three levels and two factors, as shown in Table 4.3. Thus, a matrix with 18 experimental runs, including 1 replicate, was considered.

Table 4.3. Levels of factors used during experimental design

Factor	Level		
	-1	0	1
X1: Temperature (°C)	30	60	90
X2: Pressure (bar)	10	20	30

A quadratic multivariate model, given by Equation 4.8, was employed for interpreting the behaviour of the carbonation efficiency percentage as functions of the temperature and pressure.

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_1^2 + \beta_3 X_2 + \beta_4 X_2^2 \quad (4.8)$$

The factors X_1 , X_2 are the independent variables, where X_1 represents the temperature in °C and X_2 the pressure in bar. The response variable, y , is the carbonation efficiency (CE) calculated through the Equation 4.9.

$$CE (\%) = \frac{[Ca_{initial}] - [Ca_{final}]}{[Ca_{initial}]} \times 100 . \quad (4.9)$$

5. RESULTS AND DISCUSSION

5.1. Characterization of the waste

Table 5.1 shows the content of inorganic species in the grits allowing to know levels of possible impurities, such as the Fe, Mg, Na, which can interfere in the carbonation process. The variability in the concentration of inorganics found in grits is due to the recovery process of the chemical liquor in Kraft pulp mills. The average calcium concentration measured by acid digestion is of $418\,088 \pm 32\,802$ mg/kg. This value is of the same order of magnitude found by Cabral et al. 2008.

Table 5.1. Elementary concentration on grits

Element	Elementary concentration on grits (mg/kg)				Measured values
	[1]	[2]	[3]	[4]	
Ca	346 200	$417200 \pm 72\,400$	388 500	$331\,333 \pm 3\,786$	$418088 \pm 32\,802$
Na	64 400	$10\,400 \pm 3\,700$	13 200	$35\,033 \pm 586$	
Mg	9 200	$3\,600 \pm 1\,800$	-	$4\,910 \pm 114$	
Fe	10 300	$2\,200 \pm 1\,300$	-	-	

¹Martins et al. 2007; ²Cabral et al. 2008; ³Rogério et al. 2020; ⁴Watkins et al. 2010

5.2. Calcium Extraction Experiments

5.2.1. Solvent Selection

In order to screen the best solvent to extract calcium from the grits, four solvents (acid acetic, ammonium of chloride, nitric acid and sodium hydroxide) were tested, under the same conditions, namely solid/liquid ratio, contact time, temperature and acid concentration.

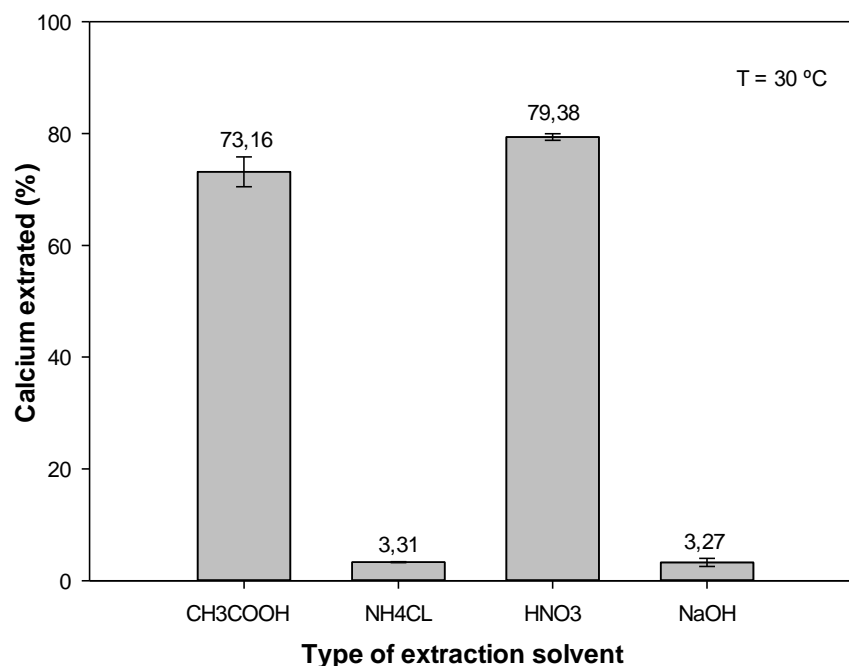


Figure 5.1. Calcium extraction efficiency for different solvents tested (S/L ratio=50 g/L; Time=2 h; Temperature=30 °C, Acid concentration = 2 M)

Figure 5.1 allows analysing of which tested solvents is better for extracting calcium from the grits. Among the tested solvents and for the same extraction conditions, only two achieved extraction efficiencies higher than 70 %. The highest extraction efficiency (79.38 %) was achieved with nitric acid, on account of being a stronger acid than acetic acid, and the other solvents. The use of sodium hydroxide and ammonium chloride led to very reduced extraction efficiencies, between 3.2 and 3.4 %. According to the literature, these solvents have showed a low performance when compared to the others extraction solvents employed in this study. However, a greater efficiency was achieved, with values of 40 to 60 % approximately, in the case of the dissolution of concrete and cement residues (Mun et al. 2017; Faisal et al. 2018).

5.2.2. Analysis of kinetics of calcium extraction

Figure 5.2 shows the kinetics of Ca extraction for the best performing solvents, acetic acid (Figure 5.2a) and acid nitric (Figure 5.2b).

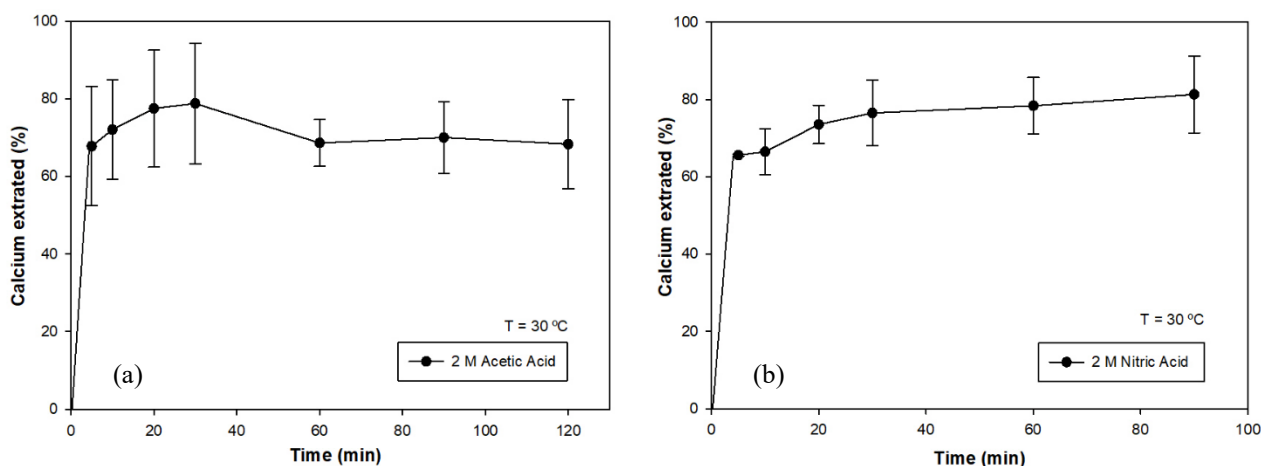


Figure 5.2. Kinetics of calcium extraction from grits (a) with acetic acid and (b) with nitric acid.

Analysing Figure 5.2, it can be concluded that the extraction kinetics for both solvents is initially very fast. After 5 minutes of reaction, an efficiency higher than 60 %, is reached. Process stabilization or equilibrium conditions are achieved practically after approximately 60 minutes. Henceforward, the subsequent extraction experiments were conducted during 1 h. Among the two solvents, the nitric acid demonstrated to be the best extractant agent with efficiencies around 80 % at 60 minutes of reaction. However, the nitric acid has a corrosive behaviour and due to its high cost, the acetic acid was selected as the best solvent. Acetic acid is a weaker and cheaper acid than the nitric acid and for the purpose of this work, it has a potential to be a good calcium extractant.

5.2.3. Study of calcium extraction using the experimental design

The experimental design of the calcium extraction process depends on the temperature, solid/liquid ration and acetic acid concentration. The dependent variable (response variable) is the calcium extraction efficiency. The experimental results based on a *Box-Behnken* design are shown in Table 5.2.

Table 5.2. Experimental conditions utilized during the extraction step in grits with acetic acid and the respective efficiencies. The efficiency shown in the table is an average of the replicas.

Run	Temperature (°C)	Solid/Liquid Ratio (g/L)	Concentration CH ₃ COOH (M)	Average of the Extraction Efficiency (%)
1	25	20	1.25	61.22
2	75	20	1.25	59.89
3	25	100	1.25	25.48
4	75	100	1.25	25.78
5	25	60	0.50	26.92
6	75	60	0.50	23.43
7	25	60	2.00	69.40
8	75	60	2.00	64.54
9	50	20	0.50	47.18
10	50	100	0.50	11.26
11	50	20	2.00	76.57
12	50	100	2.00	48.02
13	50	60	1.25	52.81
14	50	60	1.25	51.59
15	50	60	1.25	49.16

An analysis of variance (ANOVA) of the results, by using the software *STATISTICA*, was performed in order to describe the behaviour of the response variable, CEE, as function of independent variables (X_1 – temperature; X_2 – solid/liquid ratio and X_3 – Acid concentration). Thus, it was possible to obtain the quadratic model represented by Equation 5.1.

$$y = 22,27879 + 0,54881 X_1 - 0,00599 X_1^2 - 0,26154 X_2 - 0,00149 X_2^2 + 33,15075 X_3 - 2,94413 X_3^2 \quad (5.1)$$

The regression coefficients, β , are provided by the software, as well as the coefficient of determination or R squared, R^2 and the adjusted coefficient of determination, R^2_{adj} , which these two last are statistical parameters important to provide a measure of how the observable results are replicated by the statistical model. The determination coefficient of 0.98222 and an adjusted coefficient of determination of 0.96889 found indicates a goodness

fit, as shown in Figure 5.3. In fact, analyzing Figure 5.3, a good agreement between the predicted and the observable values is noticeable.

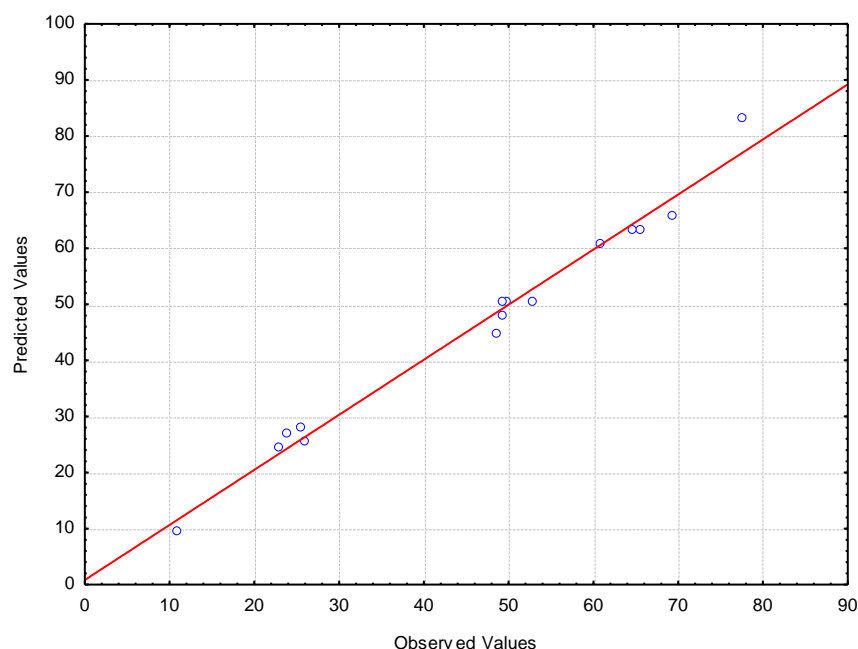


Figure 5.3. Relationship between the predicted values and the observed values.

The Pareto chart depicted in Figure 5.4 can also be obtained by the software and demonstrates the interaction effects of the variables or factors with a 95 % confidence level. The relevant variables are the ones that overpass the red line ($p < 0.05$). The level of statistical significance is only relevant when its value is lower than 0.05, which means that the variable with $p < 0.05$ is statistically relevant to the model, or by other words, that it has a significant influence on the response of the system, in this case, the calcium extraction efficiency.

According to the information shown in Figure 5.4, the concentration of acetic acid appears as the variable with the most significant effect on the CEE, in a positive way, while the solid/liquid ratio is the second most important variable, contributing negatively. The temperature did not produce a significant effect on the removal of calcium from grits, contrary to some studies reported by the literature for other wastes where this variable exhibits a relevant influence on the extraction process of calcium or magnesium.

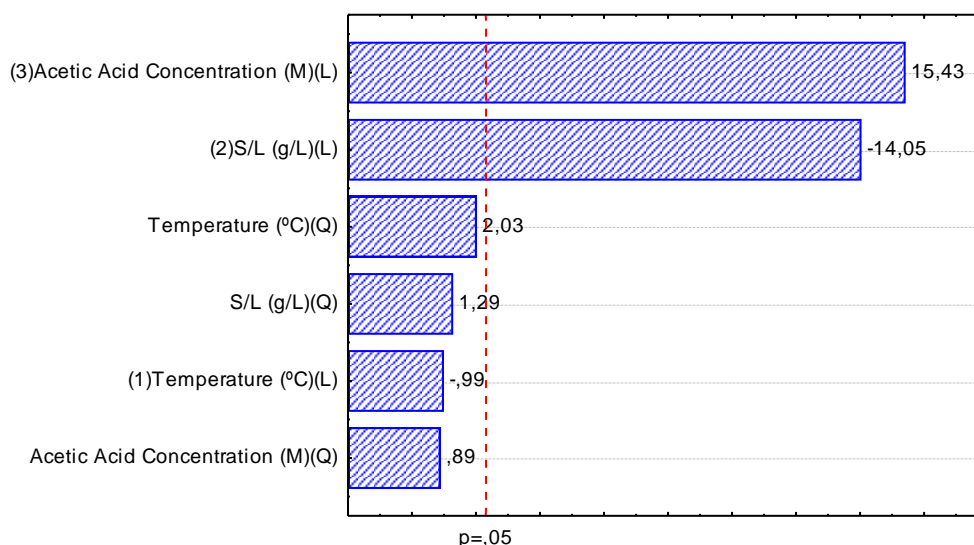


Figure 5.4. Pareto Chart of the calcium extraction experiments with acetic acid.

Surface graphs in 3D (Response surface plots) were generated by the multivariable model (Equation 5.1), a useful tool mainly to identify regions that determine optimal conditions of the extraction process. Therefore, it was possible to elaborate nine surface graphs, but only three will be presented, and the others six can be consulted in the Annex B. In all the plots, on the z axis are represented the CEE, the only dependent variable, while on the x and y axis two of the three independent variables can be assigned. Thus, it is possible to ascertain the real impact of the variables studied on the efficiency in this step of the carbonation.

Response surface at constant acetic acid concentration

In Figure 5.5(a), the CEE behaviour is plotted as function of variables solid/liquid ratio and temperature, keeping the acetic acid concentration constant at the value of 2 M. For these conditions, the efficiency values vary in the range of 40 to 80%, increasing mainly due to the decrease of the solid/liquid ratio, which is expected, since with a smaller mass of grits and an acetic acid concentration of 2 M, the maximum tested concentration, obviously the efficiency increases.

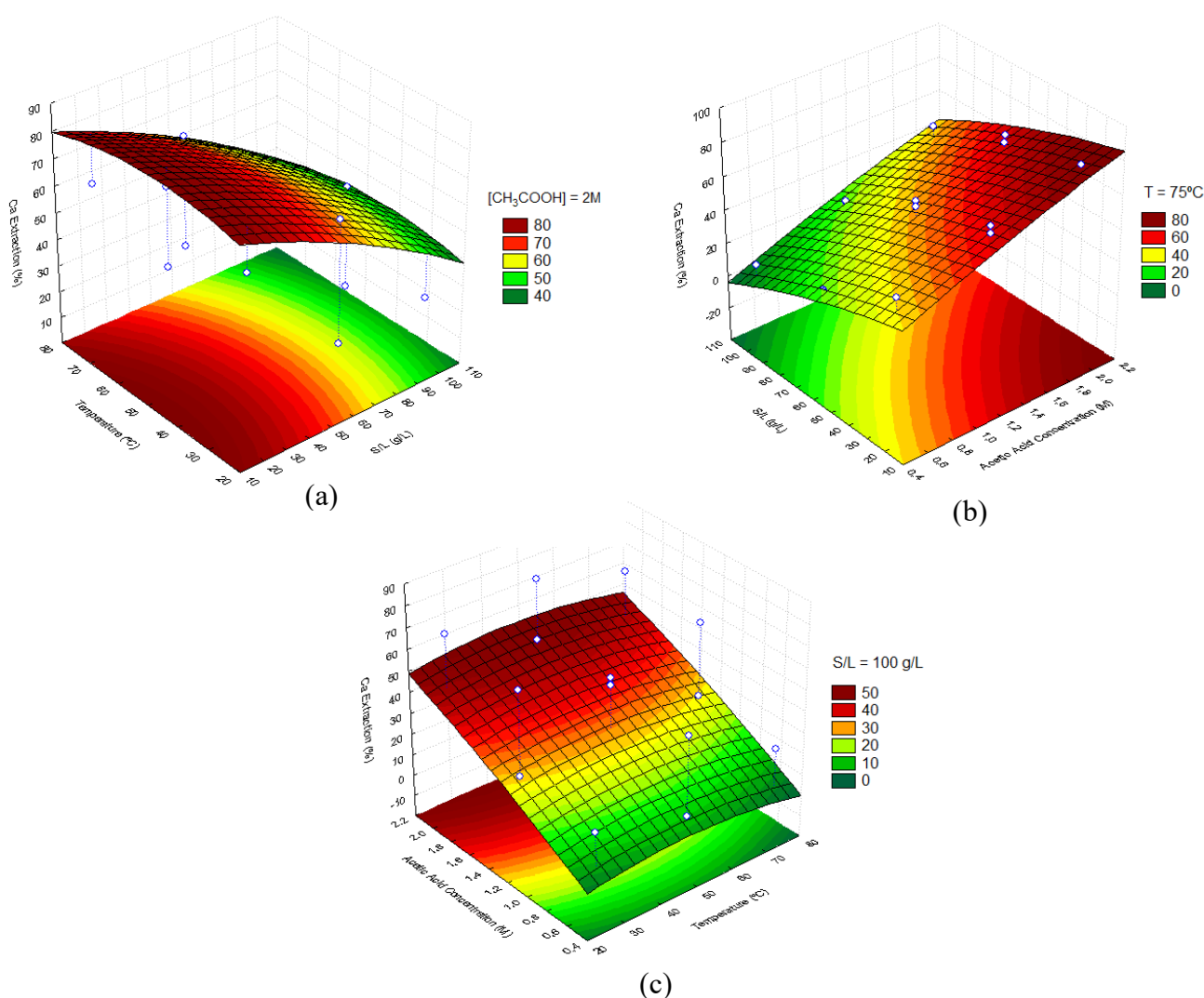


Figure 5.5. Surface graphs of the experimental design: (a) Ca extraction efficiency versus solid/liquid ratio and temperature, with the acetic acid concentration constant at 2 M; (b) Ca extraction efficiency versus acetic acid concentration and temperature constant at 75°C; (c) Ca extraction efficiency versus acetic acid concentration versus temperature and a solid liquid ratio constant at 100 g/L

In the Annex B are presented the other plots for different constant acetic acid concentrations (Figure A3), and among them, for a concentration of 1.25 M (an intermediate concentration tested) the CEE varied between 20 to 60 %. For a lower concentration of 0.5 M, the CEE was within in the range 0 - 40 %. A reduction approximately of 40 % in the CEE was found when the acid concentration decreased of 1.5 M (maximum variation tested), which is a significant variation, only due to the acetic acid concentration, meaning so far that this variable has a great influence on the Ca extraction step as was shown in the Pareto chart.

Response surface at constant temperature

In Figure 5.5(b), the CEE behaviour is represented as function of variables acetic acid concentration and solid/liquid ratio, keeping the temperature constant at 75 °C. The CEE increases from 0 to 80% with the increase of acetic acid concentration and the decrease of solid/liquid ratio.

The response surfaces for other constant values of temperature tested (Figure A2a at 25 °C and Figure A2b at 50 °C) are shown in Annex B. For a temperature of 50 °C, the CEE is within in the range 20 - 80 % while for a temperature of 25 °C CEE is between 0 to 80%. In the face of these outcomes, it is noticeable that the changes in the temperature variable, with a maximum tested variation of 50 °C, do not interfere at all in the Ca extraction efficiency.

Response surface at constant solid/liquid ratio

Finally, in Figure 5.5(c), the CEE behaviour is plotted as function of variables acetic acid concentration and temperature, keeping the solid/liquid ratio constant at 100 g/L. For these conditions, the CEE values are in the range of 0 to 50%, a range lower than that observed previously, mainly due to the higher solid / liquid ratio. An increase in this variable decreases the efficiency of Ca extraction.

Other response surfaces for constant solid/liquid ratio values of 60 and 20 g/L, are shown in Figures A1a and A1b, respectively. For 60 g/L, the efficiency ranged from 20 to 70 % and for 20 g/L, the efficiency varied between 40 and 80%. These results confirm that the solid/liquid ratio variable has a great influence on the Ca extraction step on the grits. A decrease of this variable results in an increase of efficiency, for example, with the maximum variation tested of 80 g/L the efficiency may vary until 40%.

Optimal Conditions

The response surfaces show that the highest values of CEE were found for low solid/liquid ratios. The optimal extraction conditions can be obtained through the analysis of the profiles of predicted by the multivariate quadratic model (Equation 5.1) and the desirability function using the *STATISTICA 7.0 software*. In Figure 5.6 is represented each independent variable and their respective region of maximum efficiency, the blue layer represents the peak of efficiency provided by the model at a value of 77.2 %.

The desirability function is limited between 0 to 1, where 0 means an efficiency of 11.13% and 1 means an efficiency of 77.02 %, based on the observable results. For the purpose of optimal conditions, this function search in every variable what is their value when the function is equal to 1 in the profile of predicted values. Therefore, the optimal conditions obtained occurred for the following conditions: a solid/liquid ratio of 30 g/L, a temperature of 45 °C and an acetic acid concentration of 2 M with an efficiency of 77 %.

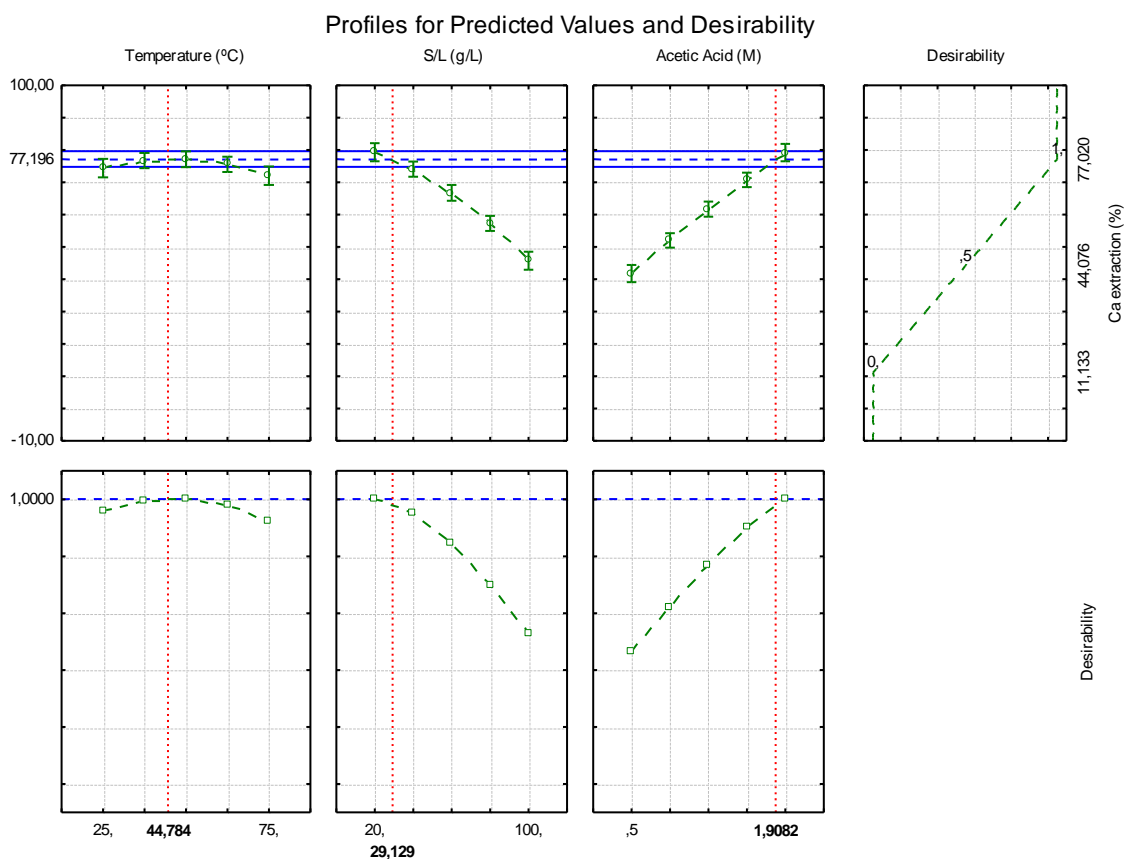


Figure 5.6. Profiles of predicted values and desirability function for the optimal conditions in the Ca extraction reaction.

Validation of the statistical model

To validate the multivariate model, three additional experiments were carried out, with two replicas, with the aim to test new conditions that were not previously analysed by the experimental design. For the first experiment, the chosen values were a temperature of 40 °C, a solid/liquid ratio of 40 g/L and an acetic acid concentration of 1 M, which these values are between the lower and medium levels of the factors tested. The other experiment was performed at a temperature of 60 °C, a solid/liquid ratio of 80 g/L and an acetic acid

concentration of 1.5 M, standing between the medium and the higher level of the factors tested. The last experiment was to validate the optimal conditions provided by the software.

Table 5.3. Experimental validation of the statistical model and for the optimal conditions.

Run	T (°C)	S/L (g/L)	Acetic Acid (M)	Observable Values	Predicted Values	Error (%)
				Ca Extraction	Ca Extraction	
				Efficiency (%)	Efficiency (%)	
1	40	40	1	58.26 ± 2.16	52.00	10.75
Optimal	45	30	2	84.92 ± 1.04	78.99	6.99
2	60	80	1.5	48.94 ± 0.97	46.75	4.47

Table 5.3 shows the experimental extraction conditions of the new tests and the values predicted by the model. For the experiments 1 and 2 the relative error was 10.75 % and 4.47 %, respectively. The experiment corresponding to optimal conditions presented an error of 6.99 %. Based on the validation experiments, it can be concluded that the model can provide a good prediction of the behaviour of calcium extraction from the grits under different operating conditions.

5.3. Mineral carbonation studies

The precipitation experiments are the last step of the carbonation method used in this study, with the main objective to produce carbonates, mostly calcium carbonate. To perform this reaction, carbon dioxide will be needed, and there are two options: for an industrial scale, exhaust gases obtained after the capture of CO₂ is used, thus creating this way a sustainable system or for a laboratorial scale, a bottle of CO₂ may be used. In the precipitation experiments, the reaction between CO₂ and the calcium acetate solution produced in the Ca extraction step, was performed in a reactor with only two variables controlled, the temperature and the pressure inside the reactor.

The calcium acetate solution obtained in the last step, under optimal conditions, has other species contained in the grits, especially Fe, Na and Mg which can precipitate in the form of carbonates. Thus, as first analysis, all of these elements, including Ca, were quantified in the solution and their concentrations can be seen in Table 5.4.

Table 5.4. Element concentrations in the grits and in the calcium acetate solutions.

Element	mg/kg grits	mg/L
Ca	424 514.85 \pm 5204.93	12 788.51 \pm 156.80
Mg	3 001.35 \pm 9.4996	90.42 \pm 0.29
Fe	138.31 \pm 1.6447	4.17 \pm 0.050
Na	1 112.30 \pm 20.285	33.51 \pm 0.61

The impurities found in the acetate solution exhibit very low concentrations when compared to those of calcium. These concentrations were around 100 times or less, there is still the possibility of finding these impurities in the precipitate of calcium carbonate.

Experimental Design

The carbonation experiments were planned using a *Box-Behnken* design with 2 factors leading to 9 runs. The two factors correspond also to the two variables controlled inside the reactor which are the temperature expressed in °C and the pressure expressed in bar. The main response variable is the carbonation efficiency (CE). For the experimental design were carried out 18 carbonation tests including already one replicate. As inputs in the software *STATISTICA* were used the average values between the two replicates. The results are summarized in Table 5.5.

Table 5.5. Experimental design of the carbonation stage

Runs	Temperature (°C)	Pressure (bar)	Carbonation Efficiency (%)
1	30	10	72.17
2	30	20	70.85
3	30	30	72.32
4	60	10	62.54
5	60	20	64.85
6	60	30	65.96
7	90	10	67.42
8	90	20	65.56
9	90	30	71.96

The statistic treatment of the experimental results allowed to find a polynomial quadratic order model (Equation 5.2) for the correlation of the independent factors

(temperature and pressure) with the response variable (CE). The model will be useful for analysing the behaviour of the carbonation reaction when faced with the variation of the tested variables and to determine the optimal conditions.

$$y = 93.09004 - 0.80458 X_1 + 0.00622 X_1^2 - 0.52166 X_2 + 0.01642 X_2^2 \quad (5.2)$$

where, y means CE, X_1 the temperature and X_2 the pressure. Figure 5.7 shows the comparison between the predicted efficiency and the observable efficiency values.

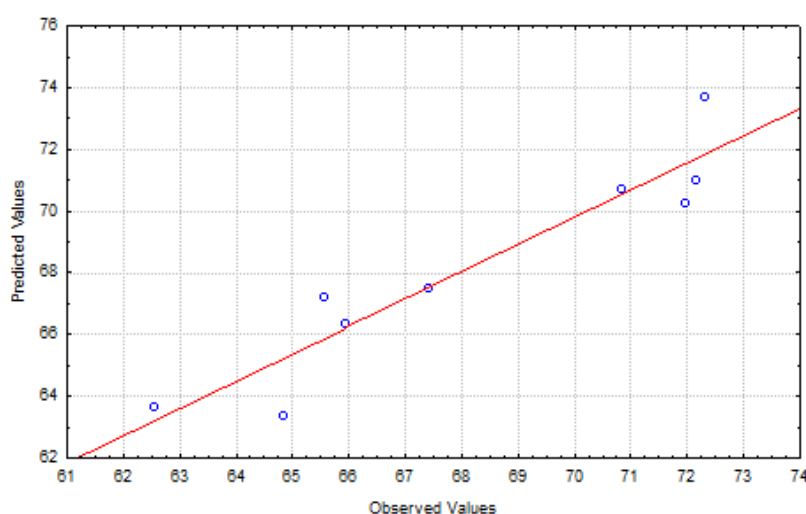


Figure 5.7. Observed carbonations efficiency values versus predicted carbonation efficiency values.

The achieved coefficient of determination, R^2 of 0.8840 and the adjusted coefficient of determination, R^2_{adj} of 0.7681 indicate a satisfactory agreement between experimental data and predicted values.

The Pareto chart shown in Figure 5.8 was obtained through the software and in general shows the most statistically significant variables in their linear (L) and quadratic (Q) mode with a 95 % confidence level. The variables are considered statistically significant when p is lower than 0.05.

The major influence factor for the carbonation efficiency is the quadratic effect of temperature (X_1^2) with a negative contribution. All other variables do not affect the efficiency and all the linear variables are non-relevant at a statistical point, which means that the levels of factors tested were not enough to reproduce a significant impact on the carbonation reaction. However, the levels of factors tested played an important role in achieving the objective in this stage of the work, the precipitation of calcium carbonate.

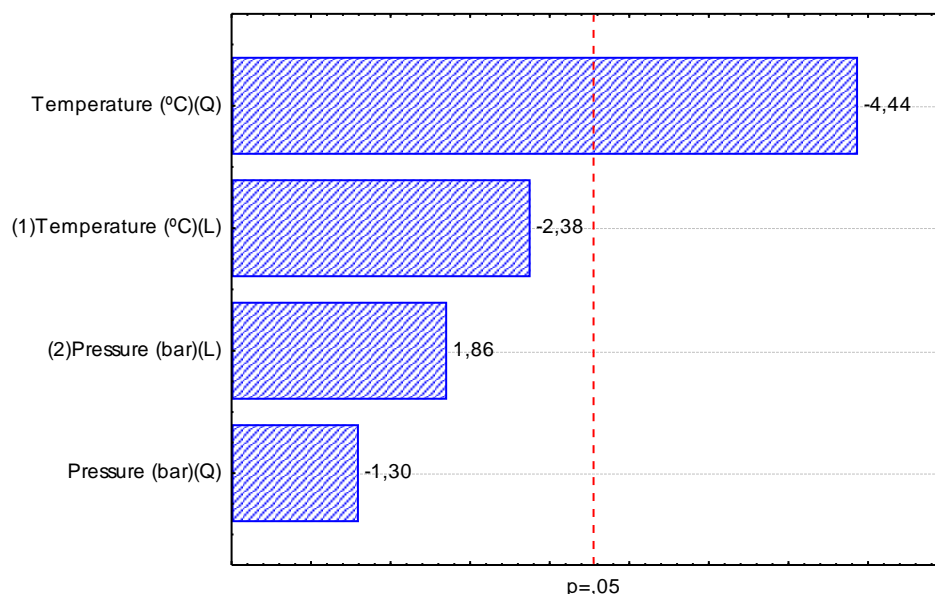


Figure 5.8. Pareto Chart

For a more detailed analysis of how the carbonation efficiency changes, altering the levels of the factors studied, a surface response and a contour graph represented in Figure 5.9 were generated.

In Figure 5.9, it is visible that the highest efficiency was achieved at high pressures (> 20 bar) and low temperatures ($< 35^{\circ}\text{C}$). The decreased efficiency due to the temperature can be attributed to decreased solubility of $\text{Ca}(\text{OH})_2$ and CO_2 at higher temperatures. The results demonstrate that the levels of factors used do not cause any pronounced curve in the response surface behaviour, or by other words, the difference between the maximum CE and minimum CE achieved is quite low, about 6 %, meaning that the range of the factors studied are in a good zone to precipitate CaCO_3 which the minimum efficiency is of 64%. However, a wider range could be better to understand the behaviour of the factors for the worst and better scenarios.

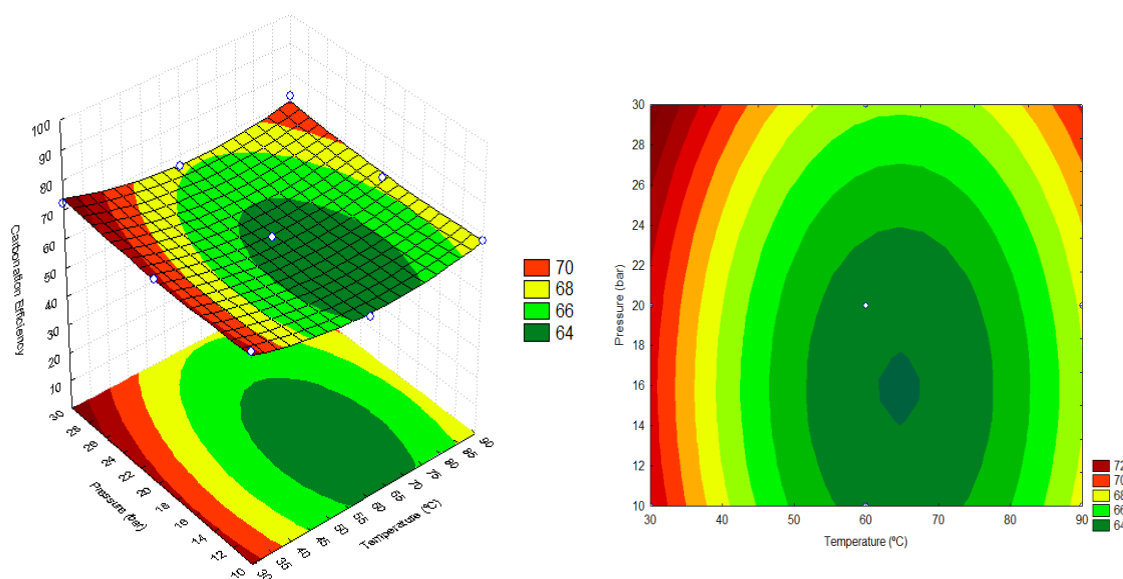


Figure 5.9. Surface plot (left) and contour plot (right) of experimental design.

Optimal Conditions

The optimal conditions were obtained by the *STATISTICA 7.0 software* through the analysis of the profile of predicted values and the desirability function.

The desirability function is limited between 0 to 1, where 0 means an efficiency of 62.5 % and 1 means an efficiency of 72.3 %. In the profile of predicted values, the maximum efficiency reached is about 73.7 % when the desirability function value is at 1. For reaching this efficiency, temperature should be of 30 °C and pressure of 30 bar as shown in Figure 5.10.

Based on the average mass of the precipitate formed during the carbonation experiments and assuming this precipitate as 100% of CaCO_3 , the CO_2 sequestration capacity is 460 kg CO_2 /ton of grits. In the Table 3.2 is represented several residues with different Ca or Mg concentrations and with different vias of carbonation, the range of CO_2 sequestration capacity varies from 53 to 3800 kg CO_2 /ton of waste, meaning that the result from this study is reasonable and significant value, confirming that the method used was effective. The CO_2 sequestration capacity on the grits is greater than the value for paper mill residues (218 kg CO_2 /ton) presented on the Table 3.2, which indicate that the method used in this study ensures better results at CO_2 sequestration in these type of residues. However

the grits presents Ca mainly at the form of carbonates with approximately 42 % of its mass, this value is based on the literature (Martins et al. 2007), since its solubilization with acetic acid can lead to a release of CO₂ the value of the CO₂ sequestration capacity have a negative impact of 220 kg CO₂ per ton of grits, resulting in a CO₂ sequestration capacity of 240 kg CO₂/ton grits instead of the 460 kg CO₂/ ton grits.

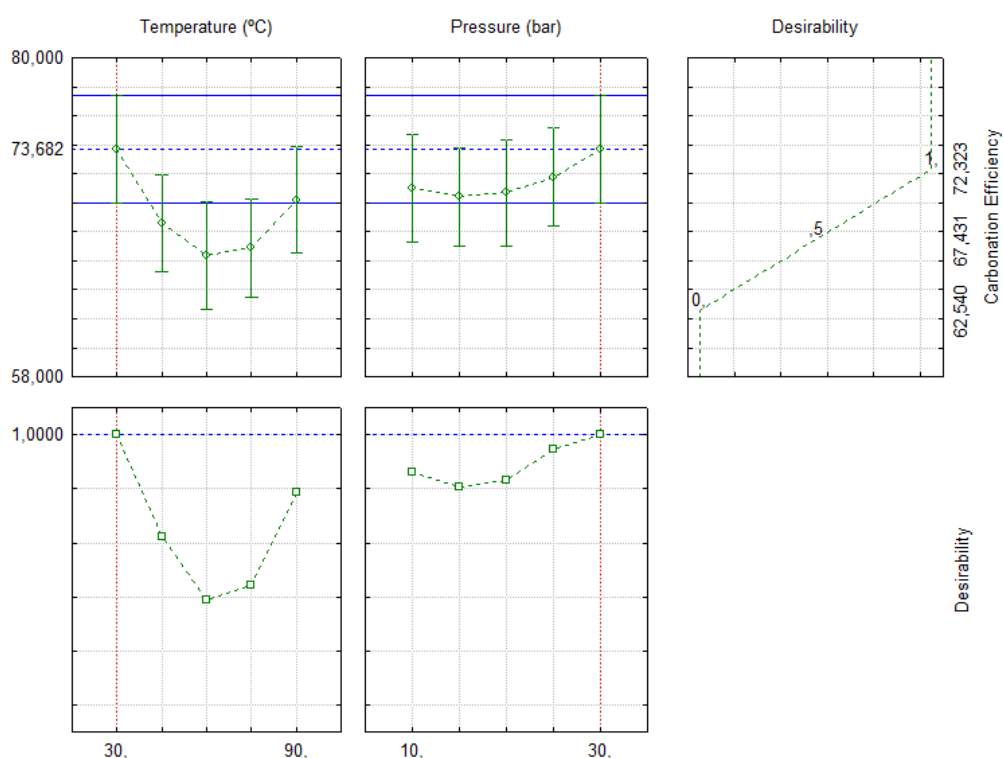


Figure 5.10. Profiles for predicted values and desirability

pH Analysis

The solution pH has a great influence on the carbonate precipitation reaction. The amount of carbonates species in an aqueous solution varies with pH, for example, for pH less than 6, the dominant specie is CO₂ and carbonic acid, pH between 6 and 10 bicarbonate is the main specie and for pH values higher than 10, carbonate is the most dominant specie in the solution. In the performed experiments, the solution pH was measured at four stages. At first stage, it was measured the pH of Ca acetate solution, then was added 10 ml of NaOH was added to increase pH before the carbonation reaction. At third stage, the solution pH

was measured after the carbonation reaction, and at last stage and due to the pH decrease, 2 ml of NaOH was added to ensure carbonate specie is the major specie in the solution. In Figure 5.11 is represented the pH variation in the nine runs studied (which is shown in the legend of Figure 5.11 as 1 to 9 series, where each run is an average of the two replica) in the four stages previously described.

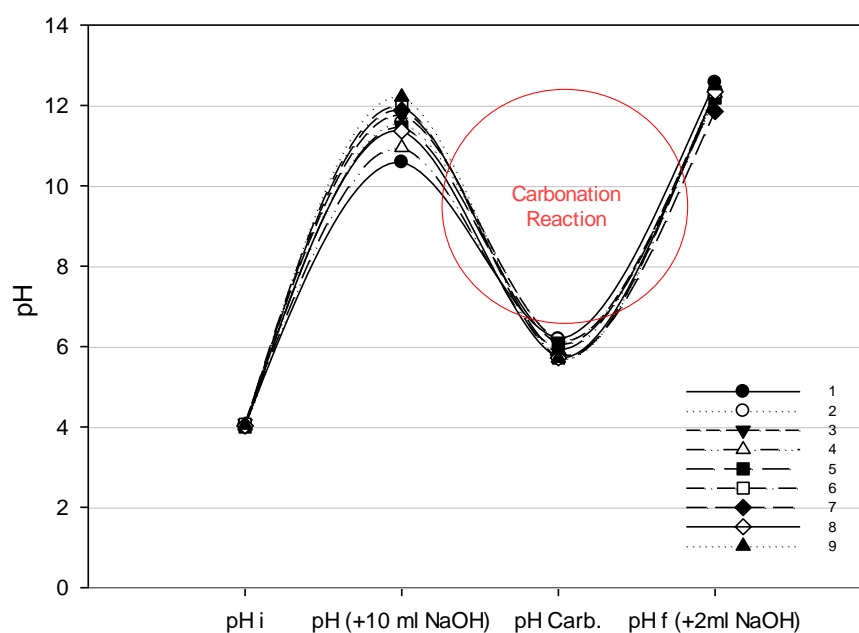


Figure 5.11. pH variation during the carbonation experiments

The calcium acetate solution exhibits an average pH value of 4, a very low value to ensure an efficient precipitation, hence the addition of NaOH to increase the pH to a value approximately of 11. After the carbonation, the solution has a pH of 6 due to the formation of carbonic acid, a product of the reaction between the water and the CO_2 leading to an enrichment of H^+ ions in the solution. This solution has as main species carbonic acid and bicarbonate and, to guarantee the carbonate specie as the dominant species, NaOH was added to increase the solution pH close to 12.

6. CONCLUSIONS AND FUTURE WORKS

6.1. Conclusions

In this work was studied the mineral carbonation by indirect route, composed by two steps: first the extraction of calcium from the grits, and second the precipitation of CaCO_3 . The principal objective was to find optimum conditions of both steps and demonstrate the potential of the grits as an alkaline industrial waste for mineral carbonation.

The characterization of the waste by acid digestion led to concentration of approximately $418\,088 \pm 32\,802$ mg of Ca/kg of grits, a promising value for purposes of mineral carbonation. A screening of solvents was carried out from four possible extractant agents (HNO_3 , CH_3COOH , NaOH and NH_4Cl), under the same operating conditions (solvent concentration of 2M, temperature of 30°C , solid/liquid ratio of 50 g/L and contact time of 2h). It was found that the acid nitric and the acetic acid had the best performances, with extraction efficiencies of 73.2 % and 79.4 %, respectively.

The kinetic studies conducted only with the nitric and acetic acids for 2 hours demonstrated that, after 5 minutes of the reaction the extraction, efficiencies were higher than 60% for the two solvents which means very fast-kinetic reactions. The stabilization of the extraction was achieved in 60 minutes. The nitric acid was the solvent that allowed to reach the higher efficiencies. However, this acid has a corrosive nature and due to its high costs, the acetic acid was selected for the subsequent extraction studies.

A *Box-Behnken* experimental design was applied for studying the extraction of Ca with acetic acid. This approach comprised 3 factors (temperature, solid/liquid ratio and acetic acid concentration) with 3 levels, where the extraction efficiency was considered the response variable. From statistical treatment of the results was demonstrated that only two factors had a significant statistical level, the acetic acid concentration and the solid/liquid ratio contributing positively and negatively for the extraction efficiency respectively. The optimal conditions were found by analysing the response surface and the desirability functions. The predictive capacity of the multivariate model was validated with operating conditions different from those tested in the experimental design. A maximum efficiency of

77 % was obtained for the conditions: S/L ratio of 30 g/L, temperature of 45 °C and acetic acid concentration of 2 M.

The analysis of the calcium acetate solution, obtained in the extraction step, showed that Mg, Fe and Na were the main impurities. Their concentrations were approximately 100 times lower than the concentration of Ca, with Mg as the most relevant, meaning that there is the possibility of finding these impurities in the final precipitate of CaCO_3 .

An experimental design with two factors (pressure inside the reactor and temperature) at three levels was used in the carbonation step, where the carbonation efficiency was the variable response. The results demonstrated that the only factor with significant statistical level was the quadratic effect of temperature, contributing negatively to the carbonation efficiency. The maximum carbonation efficiency predicted by a quadratic multivariate model was of 73.7%, under the conditions of 30 bar and 30 °C. The CO_2 sequestration capacity was 460 kg CO_2 /ton of grits, however the solubilization of the grits with acetic acid can lead to a release of CO_2 due to the presence of carbonates species in the grits resulting in a decrease of the value presented as the CO_2 capacity sequestration for a value of 220 kg CO_2 /ton of grits, which is a satisfactory value for purposes of mineral carbonation. Another important parameter in the carbonation step is the pH of the solution that needed to be controlled by adding NaOH before and after the carbonation reaction to guarantee the precipitation of calcium carbonate.

This work demonstrated that the grits is an industrial waste with potential for mineral carbonation, and with relatively low temperatures and pressures can be achieved high efficiencies in extraction and carbonation steps. The operating costs that can significantly contributes to economy of the overall process are the costs associated to the amount of acetic acid used in the extraction step and sodium hydroxide for pH control.

6.2. Future works

The principal objectives in this study were achieved, however some other studies with different approaches can be implemented, as for example, according to the following suggestions:

- Investigate the use of different solvents in the process of extracting calcium from thermally activated grits;

- Evaluate the effect of the particle size of the waste, since particles with reduced size have a larger surface area, promoting better extraction efficiencies;
- Study the effect of the stirring mainly in the carbonation step where is important to ensure an effective dissolution of CO₂ gas into the liquid;
- Improve the precipitation experiments with a more suitable reactor and study more parameters, such as CO₂ flow and promote an inert atmosphere with N₂ before introducing CO₂;
- Investigation of another route of mineral carbonation using the grits, such as direct or indirect without acid extraction to ensure that the grits is a good source of Ca for the purposes of mineral carbonation.

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ANNEX A

Analytical techniques

Flame Atomic Absorption Spectroscopy (FAAS)

The analytic determination by atomic absorption encompasses three major steps, first the sample is atomised, in other words, the sample is transformed in atomic vapor where the gaseous atoms remain on their fundamental state, then as a second step, the conditions to absorb radiation by the atoms from an appropriated source, like flame, are achieved. And as last step is performed the measurements of the absorbed radiation. The used oxidant/fuel in these analyses was air/acetylene respectively with flame temperatures around 2100 to 2400 °C.

ANNEX B

Response surfaces of experimental design applied to the Ca extraction step

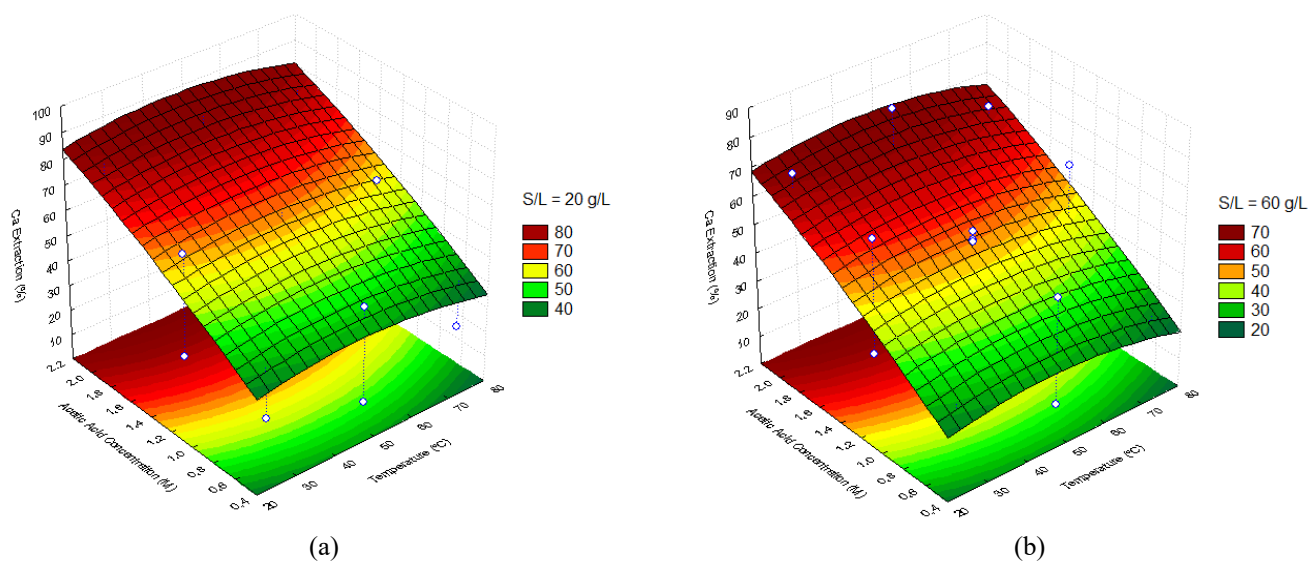


Figure B1. Surface graphs in Ca extraction step with temperature and acetic acid concentration as independent variables (X and Y axis respectively) and Ca extraction efficiency has dependent variable (Z axis), on the both graphs the remaining independent variable (solid/liquid ratio) maintain a constant value: (a) of 20 g/L; (b) of 60 g/L.

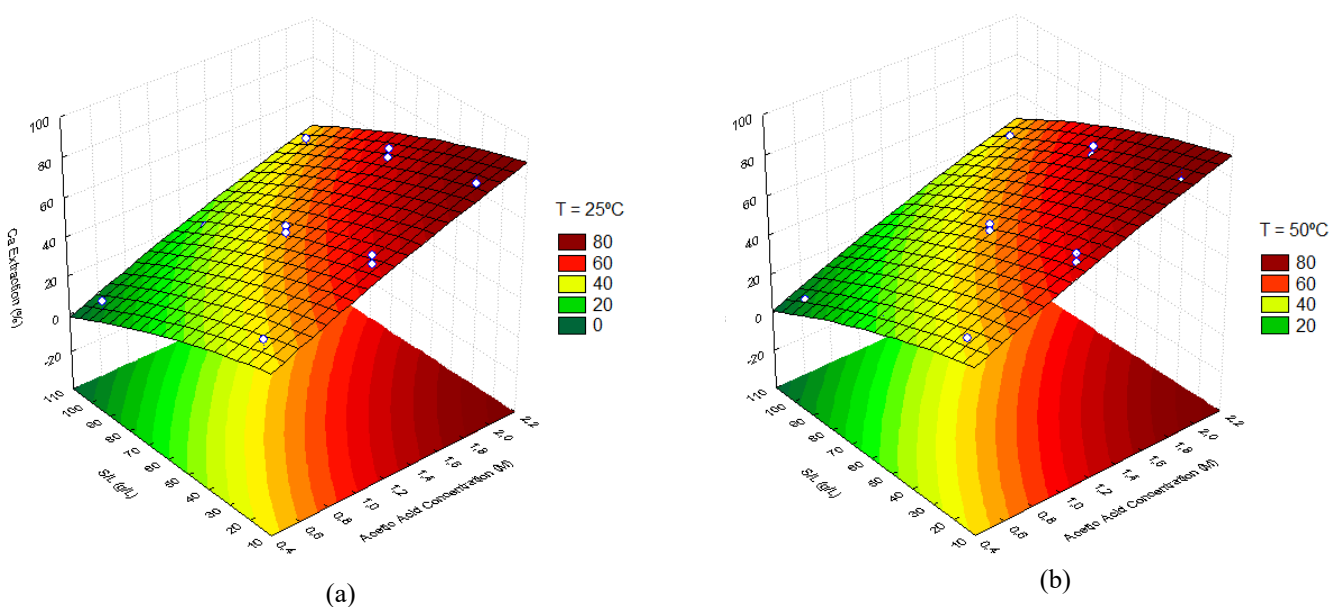


Figure B2. Surface graphs in Ca extraction step with acetic acid concentration and solid/liquid ratio as independent variables (X and Y axis respectively) and Ca extraction efficiency has dependent variable (Z axis), on the both graphs the remaining independent variable (temperature) maintain a constant value: (a) of 25 °C; (b) of 50 °C.

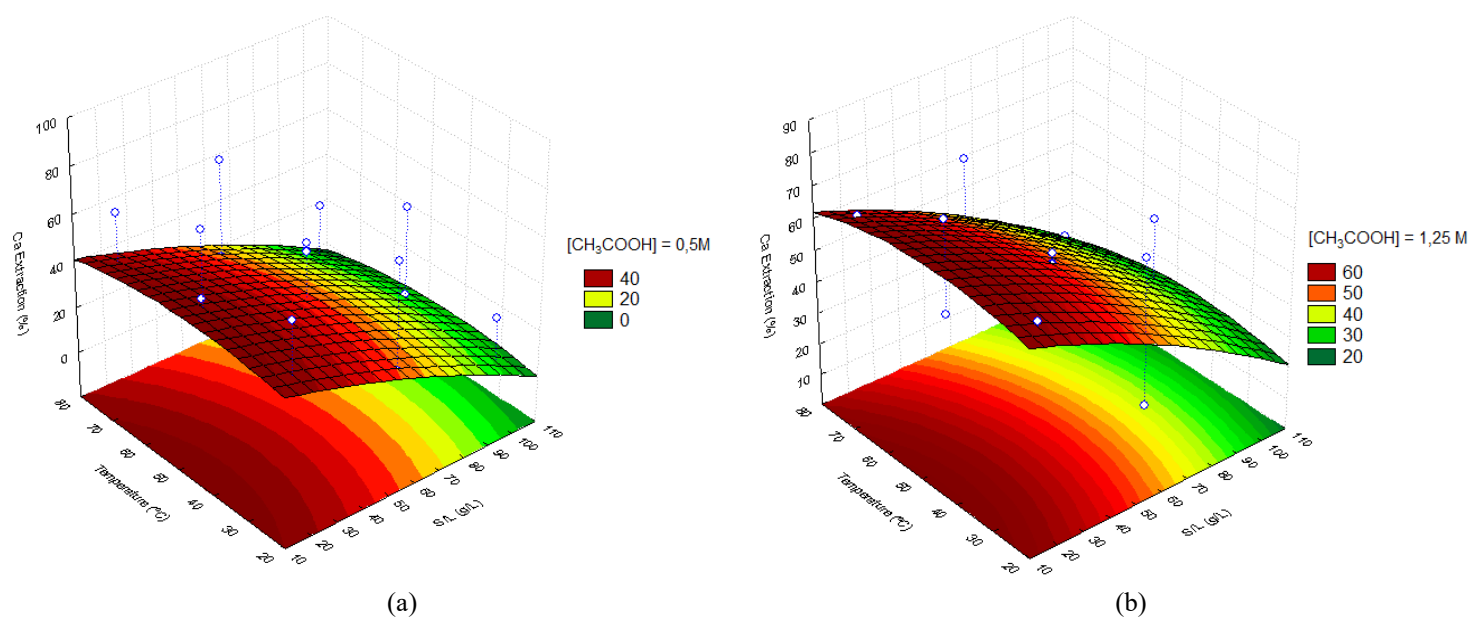


Figure B3. Surface graphs in Ca extraction step with temperature and solid/liquid ratio as independent variables (X and Y axis respectively) and Ca extraction efficiency has dependent variable (Z axis), on the both graphs the remaining independent variable (acetic acid concentration) maintain a constant value: (a) of 0,5 M; (b) of 1,25.