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**Analysis of different technologies for
CO₂ capture and their application in the
Cement Industry.**

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Abstract

CO₂ is the main greenhouse gas responsible for global warming. It is emitted from a range of sectors like power generation, transport and industries. Due to this problem, a major effort has been done in the develop of strategy for its control and CO₂ Capture and Storage (CCS) has been recognized as an effective option.

Absorption, adsorption, membranes, cryogenic distillation and calcium looping are the main post-combustion technologies for CO₂ capture. The cement manufacturing is one of the major industrial emission sources of CO₂ and still needs technical developments for implementing CCS. Therefore, this project studied the capture of CO₂ from the flue gas coming from Ciments Molins, an industry with a capacity of 825,000 t/year of cement. The absorption technology was selected to be simulated and designed with Aspen HYSYS®.

For the design of the absorption tower, it was started with the variation of lean amine flow rate, observing that the higher the flow, the greater the CO₂ sequestration. Since an optimal separation was not reached, it was decided to change other factors such as the number of equilibrium stages and the diameter. By increasing each of them the degree of separation of CO₂ increased. However, being aware of the need to design towers with feasible dimensions, a diameter of 4 m and 15 stages was fixed. The influence of the amine stream temperature was also studied since it had an important effect on the separation. From these results the desired efficiency (75%) was achieved with an amine flow rate of 150,000 kmol/h at 45°C. On the other hand, for regeneration tower design, the effect of the number of stages was studied. A greater number of stages and greater heat, more separation was obtained. Moreover, there was a point where this trend did not continue. Since varying only these parameters the desired regeneration was not achieved, the pressure was changed, demonstrating that the greater the pressure, the greater the regeneration of the amine. From these results and observing that the greater heat also manifested a greater CO₂ separation, a 15-stages tower, a pressure of 202.6 kPa and a heat duty of 310E10 kJ/h were established.

With the proposed process, the CO₂ recovered would be 39,460.12 kg/h compared with the 33,755.55 kg/h released by the production of the required energy for the process. It is important to mention that this process could be further optimized, being possible from the environmental point of view.

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1. Introduction

The increasing worldwide demand for energy bound to a strong dependence of fossil fuels has considerably intensified the concentration of greenhouse gases (GHG) in the atmosphere, reaching alarming levels (Siqueira et al., 2017).

One of the major greenhouse gases is Carbon Dioxide (CO₂). It is the main responsible for global warming due to its relative high concentration in atmosphere which enhances the natural greenhouse effect. This greenhouse effect is based on the fact that solar radiation passes largely unhindered through the atmosphere, heating the earth's surface. In turn, energy is re-emitted as infrared, much of which is absorbed by CO₂ and water vapor in the atmosphere, which thus acts as a blanket surrounding the earth. Without this mechanism, the average surface temperature would plummet to about -21°C, but the accumulation of CO₂, and other contaminants, in atmosphere is getting too thick the blanket and overheating the earth because less energy (heat) escapes into space (Anderson et al., 2016). The atmospheric concentration of CO₂ has increased from 280 ppm, in the mid-1800, to nearly 407 ppm in 2017 (NOAA, 2018), and caused almost 1°C increase in mean earth temperature, from preindustrial levels. This temperature rise, only between 1901 and 2010, led to a 20 cm increase in global mean sea level due to the melting of the poles (Aminu et al., 2017).

According to the Synthesis Report (SYR) of the Intergovernmental Panel on Climate Change (IPCC), CO₂ emissions from fossil fuel combustion and industrial processes contributed about 78% to the total GHG emission increase between 1970 and 2010. Total annual anthropogenic GHG emissions have increased by about 10 Gt CO₂-eq between 2000 and 2010. This increase directly came from the energy (47%), industry (30%), transport (11%) and building (3%) sectors. Globally, economic and population growth continue to be the most important drivers of increases in CO₂ emissions from fossil fuel combustion, and this trend seems not change in the near future (IPCC, 2015).

As shown in Figure 1, this greenhouse gas is emitted from a range of sectors like power generation, transport and industries such as power plants, iron and steel, refining, petrochemical, cement manufacturing, ammonia production, hydrogen production and sour gas sweetening (Zhao et al., 2017). Due to this problem, in the last years, several studies have

been made about mitigation strategy of CO₂ (Kumar et al., 2018) and CO₂ Capture and Storage (CCS) has already been recognized as an effective option (Arias et al., 2016).

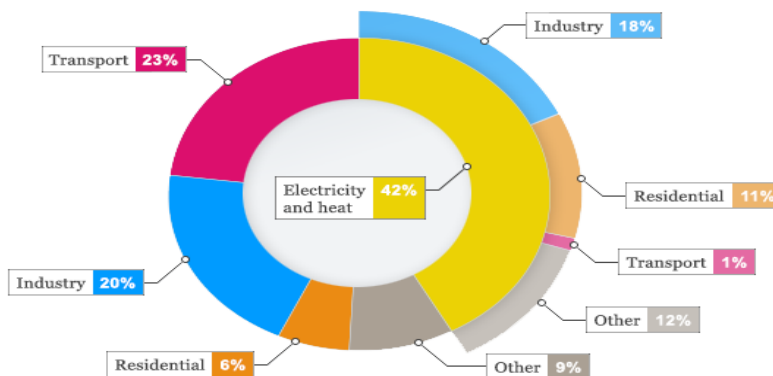


Figure 1. World CO₂ emissions by sector (Cottrell, 2016).

The technologies for CCS consist in the separation of CO₂ emitted by industry and energy sources and its transportations to a place for storage and its long-term insolate from the atmosphere. In fact, this is an emerging technology of geopolitical importance, with the main objective to mitigate the negative effects of global warming. In order to meet the 2 °C scenario of the International Energy Agency (IEA), CCS must be developed and deployed to become material within just one decade. The IEA advises on how CCS should be applied in various regions throughout 2030 and 2050, emphasizing its application in sectors like power generation and industry (Arias et al., 2016).

Depending the step to remove the CO₂, there are three main methods for it (Kanniche et al., 2010): pre-combustion capture, that is, to capture CO₂ in a synthesis gas after conversion of CO into CO₂; post-combustion capture, which corresponds to capture CO₂ in the exhaust gases once the fuel has been fully burned with air, and capture in oxy-combustion, consisting of combustion in oxygen with recycling of exhaust gases (composed mainly of CO₂ and water) and purification of the CO₂ flow, to eliminate incondensable gases.

Post-combustion corresponds to the most widely applicable option in terms of industrial sectors. Moreover, it shows the essential advantage of being compatible to a retrofit strategy (i.e. an already existing installation can be, in principle, subject to this type of adaptation) (Brunetti et al., 2010). That is the reason why this study is based on the most important post-combustion technologies for CO₂ capture.

2. Objectives

Due to the increasing amount of CO₂ emissions to the atmosphere, greenhouse gas which is the main cause of global warming, it is imperative to study and improve alternatives in order to mitigate this environmental problem. Thus, this work will be based on the analysis of different technologies for CO₂ capture. The specific objectives of this project are:

- To review of the most important applicable technologies for post-combustion CO₂ capture.
- To select the industrial process for the CO₂ capture as well as the post-combustion technology that will be used for it.
- To simulate and design the technology for the practical industrial process, by using the Aspen HYSYS[®] software.

3. Results and Discussion

3.1. Technologies for CO₂ Capture

The main processes for CO₂ post-combustion separation are described below. Each of these processes are based on different separation principles. The choice of the technology suitable for the specific separation is, thus, related on different parameters like economics, stream conditions, product target and, also, on design considerations (Brunetti et al., 2010).

3.1.1. *Absorption process*

Absorption could be both physical and chemical. Physical absorption depends on solubility of CO₂ in the solvent and it is preferred at higher pressures. The solvent only interacts physically with the dissolved gas and the separation occurs with mass transfer occurring at the gas-liquid interface. Here a solvent is used as an absorbent with thermodynamic properties which favored CO₂ absorption over the other components. Some commonly used physical solvents are methanol and glycol ethers (Ebner & Ritter, 2009), selexol, purisol and rectisol (Sreedhar et al., 2017). On the other hand, processes where the solvent chemically reacts with the dissolved gas are referred to as chemical absorption processes. For these applications alkanolamines are commonly used as reactive absorbents. To be employed as an absorbent, a solvent should have high reactivity and absorptivity with CO₂, high stability

under extensive thermal and continuous chemical exposure, low vapor pressure, easy regeneration, low environmental impact and low cost.

A typical chemical absorption system is shown in Figure 2. This system consists of three components: solvent, absorber and stripper (Sreedhar et al., 2017). In this process, the flue gas enters the absorber at the bottom and flows upwards while the solvent solution goes downwards, forming a counter flow. Through the contact of these two streams, part of CO₂ in the flue gas is absorbed by the solvents. Then the solution with absorber CO₂ is pumped up to the head of the other column, the stripper, where is also a counter flow occurring with rich-loading solution flowing down the column and stripping steam generated in the reboiler upwards. With the heat from the stripping steam, chemical bonds between CO₂ and the solvent are broken so that CO₂ is carried up by the ascending steam towards the overhead condenser. Whilst the condensed steam is directed back to the stripper as a reflux, the product stream with high CO₂ purity (around 99%) is obtained. Then the product stream can be compressed for transportation to storage sites. At the bottom of the stripper, the amine solution which is termed as lean-loading solution is circulated back to the head of the absorber (Wanga et al., 2017). For this process operation pressure is around 1.0 bar and the temperatures in the absorber and stripper are generally in the range of 40-60 °C and 120 – 140 °C, respectively (Yu et al., 2012).

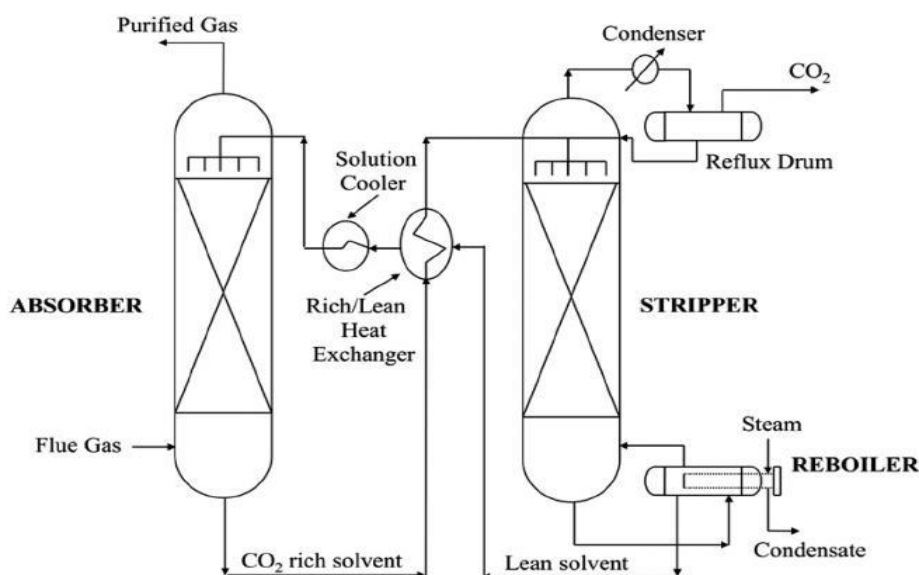


Figure 2. CO₂ absorption/stripping process (Bhosale & Mahajani, 2013).

Chemical absorption is suitable for diluting CO₂, but it requires a large amount of heat for absorbent regeneration, and a fair amount of the absorbent is lost due to acidic contents in the flue gas stream. Physical absorption requires less energy than chemical absorption and the properties of the physical sorbent makes it less susceptible to the impurities in the flue gas. However, it requires a high-pressure operation, is subject to corrosion issues and is only suitable for high CO₂ concentration sources (Nimmanterdwong et al., 2017).

Monoethanolamine (MEA) and diethanolamine (DEA) were the earliest and the most regularly employed absorbents because of their low cost, high reactivity and high rate of absorption. Methyldiethanolamine (MDEA), a hybrid of MEA and DEA has been used with some success because of its improved carbon dioxide loading capacity, higher corrosion and degradation resistance and reduced regeneration costs but a lower absorption rates.

Of all technologies, chemical absorption is considered one of the most suitable for CCS applications and this is a commercially available option. Although many solvents are tested for chemical absorption process, monoethanolamine (MEA) is undoubtedly the most extended solvent (Wanga et al., 2017).

3.1.2. Adsorption process

Adsorption is one of the promising technologies for CO₂ capture because its availability, low cost and high thermal stability (Nimmanterdwong et al., 2017). This process involves the selective uptake of CO₂ onto a solid surface, which is subsequently regenerated by lowering the pressure or increasing the temperature to release the adsorbed CO₂ (Rahman et al., 2017).

CO₂ adsorption can be achieved by using several adsorbents such as activated carbons, zeolites, amine immobilized mesoporous silica type of MCM-41, SBA-15, metal-organic frameworks (MOFs), microporous organic polymers (MOPs) and amine-grafted sorbents. The most important property of an adsorbent is its CO₂ adsorption (or equilibrium) capacity which depends strongly on the pore structure, the surface area and the degree and type of functionalization. In principle, an ideal sorbent should have high CO₂ adsorption capacity, high selectivity for CO₂ and it should also be economically regenerated without any significant cyclic performance loss (Ünveren et al., 2016). CO₂ capture is usually carried out at ambient pressures and chemical adsorbents with basic amine groups are most suitable.

Certain groups, such as alkylamines, can be attached to various porous solid materials enhanced the CO₂ sorption properties becoming suitable even for low pressure captures (Alesdsandro et al., 2010). These amine-based adsorbents are presently very popular for CO₂ capture applications since they provide high adsorption capacities, fast CO₂ adsorption rates and desirable desorption properties, such as easy regeneration (Ünveren et al., 2016). Polymeric adsorbents can also find applications for CO₂ capture. Amine attached or immobilized polymeric adsorbents have superior performances due to their high adsorption capacities and high adsorption rates for CO₂ for typical flue gas temperature range of 60 – 80° C (Drage et al., 2009).

For CO₂ capture by adsorption process, the most used technology in industrial scale is Pressure Swing Adsorption (PSA). It is a cyclic adsorption process, which allows continuous separation of gas streams. PSA is performed by periodic changes of pressure (Figure 3) aiming the optimization of contaminants removal and is considered viable for separation of CO₂ from flue gases containing about 5 – 15% v/v (Siqueira et al., 2017). This is a common process used for hydrogen purification.

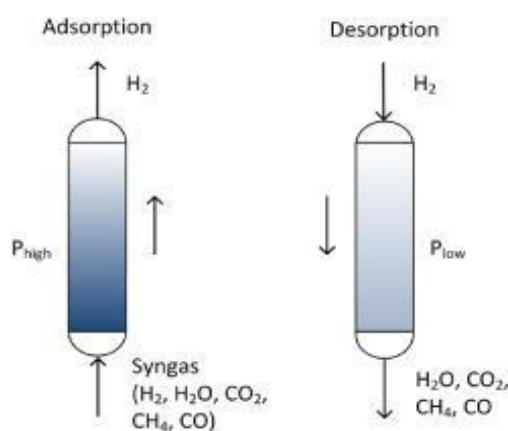


Figure 3. PSA - adsorption and desorption of impurities (Voldsund et al., 2016).

3.1.3. Membrane process

Membrane-based separation is an emerging promising technology with high maturity, and is considered to have one of the strongest cost-reduction potential (Wanga et al., 2017). Membrane technology has many benefits including, simplicity of operations, modular construction, small footprint, no hazardous by-product emissions and potentially lower

capital and operating costs (Baker et al., 2017), also, this technology does not require heat for regeneration (Turi et al., 2017).

Membrane material can be divided into two types: porous and non-porous. Porous membranes have interconnected pores which are larger than non-porous membranes which facilitate transport of gas molecules, but with no chemical interaction between the gas molecules and the membrane. The separation is based on molecular size of the gaseous mixture to be separated (Yeo et al., 2013). Porous membrane can be classified as micro-porous (< 2nm), meso-porous (2-50 nm) and macro-porous (> 50 nm) (Goyal et al, 2015). The last one, are usually preferred for the separation of gases with small molecular diameter, and exhibit high gas permeation. The main classes of micro-porous membranes employed are amorphous SiO₂, templated SiO₂ membranes, doped SiO₂ membranes and zeolite membranes (Sreedhar et al., 2017), these types of membrane are usually named as ceramic membrane (inorganic).

On the other hand, polymeric membrane (organic) are non-porous membrane, the gases follow the solution diffusion mechanism to pass through these membranes that occurs in five steps: absorption of gases on feed side, dissolution in the membrane, diffusion of the dissolved gases through the membrane, detachment from the membrane matrix and finally desorption of the gases from the permeate side of the membrane. Some of the polymeric material used are poly (arylene-ether), poly [1- (trimethylsilyl)-1-propyne], poly (dimethyl siloxane), polyether amine, polyimide and polyacrylates (Sreedhar et al., 2017).

Likewise, they have been designed and hybrid membrane which is aimed at utilizing the best of both materials (inorganic and organic membrane material) (Kang et al., 2015).

Polymeric membranes are usually operated under low temperature and possess better thermal stability as well as mechanical strength compared with ceramic membranes. On the other hand, ceramic membranes including silica and zeolite membranes give a better permeability-selectivity trade-off (Sreedhar et al., 2017).

The membranes used for CO₂ capture should possess (Brunetti et al., 2010): high CO₂ permeability, high CO₂/N₂ selectivity, thermally and chemically resistance and cost effective.

Membrane technology for gas separation could be classified into three types based on the method employed (Sreedhar et al., 2017). Non-dispersive contact via micro-porous membrane is generally used for post-combustion carbon separation (Xu & Hedin, 2014). It has several advantages such as flexibility in operating conditions and types of membrane contactors that could be employed. Other technology is CO₂ separation by gas permeation that occurs due to selectivity and permeability of a dense membrane for a particular gas combination in a mixture (Zhao et al., 2016). And the last one is supported liquid membranes (SLM), liquid is supported on the surface of a solid or could be filled inside the pores. The transport mechanism is diffusion. Some used solvents are monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA), selexol and rectisol (Sreedhar et al., 2017).

3.1.4. Cryogenic distillation

Cryogenic distillation process involves the separation of the gas mixture by fractional condensation and distillation at low temperature (lower than -73.3 °C) and high pressure (200 atm) (Olajire, 2010). This is a commercial process commonly used to liquefy and purify CO₂ from relatively high purity (> 90%) sources. This process shows promising potential and competitive energy figures for capture from syngas (in particular coal-derived). The CO₂ separation and compression work decreases with increasing CO₂ concentration in the feed (Voldsund et al., 2016). This technology could be an option if high efficiency is required and energy input is a key parameter. The efficiency of the process is 90-95% (Sreedhar et al., 2017).

The advantages of this technology are: liquid CO₂ is directly produced, thus making it relatively easy to store or send for enhanced oil recovery, also cryogenic separation can be easily scaled-up to industrial-scale utilization and this technology is relatively straightforward, involving no solvents or other components. On the other hand, the major disadvantages of this process are the large amount of energy required to provide the refrigeration for the CO₂ and the solidification under a low temperature, which causes several operational problems (Songolzadeh et al., 2014). This method is suitable only for concentrated CO₂ stream. For dilute stream, this technique is not economically sound and energetically viable (Maqsood et al., 2014).

3.1.5. Calcium looping (CaL)

This process utilizes the reversible chemical reaction between lime (CaO) and CO₂ in order to capture CO₂ from a gaseous stream. CO₂ reacts with CaO in an exothermic carbonation reaction to form CaCO₃ at temperatures in the range of 600 – 700 °C, the product CaCO₃ from the carbonator is then sent to a separate vessel called a calciner where the calcination reaction takes place at a high temperature (approximately 900°C), releasing high purity CO₂ suitable for transport to a sequestration site, then the CaO produced is sent back to the carbonator to complete the loop (Figure 4). As a result, CaL technology has the potential to be thermodynamically more efficient than a conventional CO₂ capture process using amines (Mantripragada & Rubin, 2017).

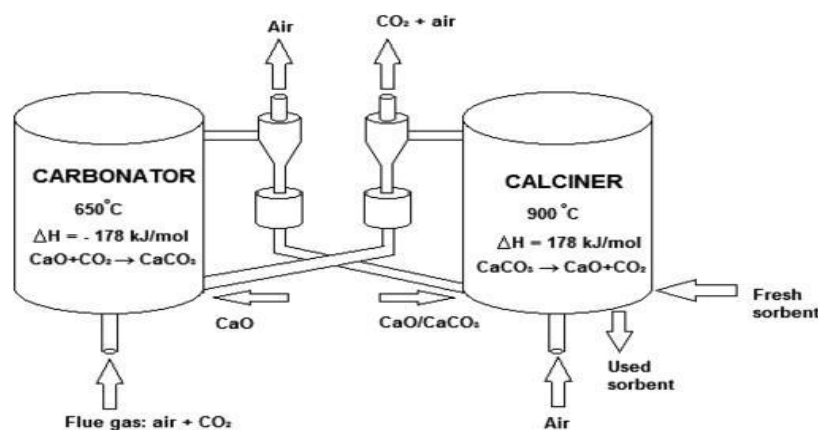


Figure 4. The calcium looping process (Cormos & Simon, 2015).

This CaL process has been successfully demonstrated up to 1 – 2 MW scale in operating conditions representative of the integration in coal-fired power plants, where flue gas has lower CO₂ concentration compared to cement kilns (De Lena et al., 2017). This technology has several advantages (Erans et al., 2016): use of limestone, a widely available, inexpensive and environmentally benign sorbent and most of the fuel chemical energy introduced into the calciner can be recovered as high temperature heat in the process. One drawback of this process is the need of a continuous make-up of fresh limestone to compensate the purge of solid from the CaL loop, which is needed to avoid build-up of coal ash and CaSO₄ originating from coal combustion in the calciner and keep a proper activity of the sorbent, which reduces with the number of carbon-calcination cycles (De Lena et al., 2017).

3.2. Study case and technology selection

3.2.1. Case of study: cement manufacturing

The cement industry is one of the largest industrial emission sources of CO₂, which contributes to 5% of the global CO₂ emissions and up to 30% of the industrial emissions. The cement industry still needs a lot of research studies and technical developments for implementing CCS. The European Cement Research Academy (EDRA) and the University of Mons (UMONS) established in 2013 a new Academic Chair with the purpose of studying the applicability of Carbon Capture and its Reuse for its specific application in the cement industry where the CO₂ content of the gas to treat is higher than for power plant flue gases (Dubois & Thomas, 2018).

A cement plant comprises the following steps: raw material preparation: crushing and milling, pre-heating, pre-calcining; kiln firing, clinker and additive mixing and cooling, cement milling and finally storage/packing (see Figure 5). The raw materials are crushed and milled into a fine powder before entering a preheater and being feed into a rotating kiln. Fuels are burned at the lower end of the kiln, allowing the materials to be heated to around 1500 °C, where they become partially melted. When the limestone (CaCO₃) reaches about 900 °C, it undergoes the chemical reaction known as calcination, whereby CO₂ is released and calcium oxide formed, before this converts to clinker. Then, the clinker or kiln product is cooled. Before packaging, appropriate additives or clinker substitutes are added to the clinker to form the end-product known as portland and cement (Bosoaga et al., 2009).

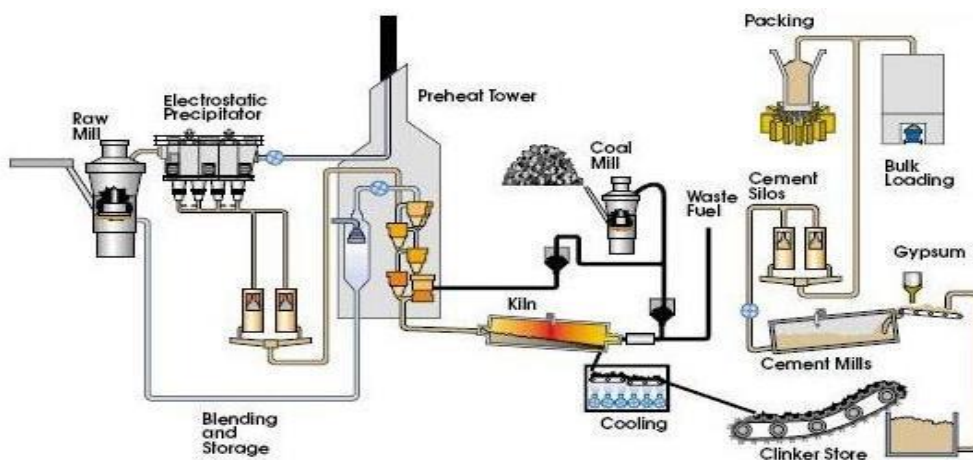


Figure 5. Cement manufacturing process (ZENITH, 2013)

In a cement plant, approximately 60% of CO₂ generated is coming from carbonate (limestone) calcination, while the remaining is coming from the fuel used to provide the process heat. Substantial efforts have been done already to reduce the CO₂ emissions for cement sector, increasing the energy efficiency and the use of alternative fuels and raw materials, but they are able to only partially contribute to the emission reduction targets (Cormos & Cormos, 2017). Therefore, to achieve significant cuts in CO₂ emissions in a cement production process, it is necessary to implement CCS techniques (De Lena et al., 2017).

This project will study the capture of CO₂ from the flue gas coming from Ciments Molins, this is a cement manufacturing plant in Catalunya, Spain with a capacity of 825,000 t/year of cement. The composition of the flue gas to be treated was deduced from the emission inventory data reported by the cement plant that are published in “Registro Estatal de Emisiones y Fuentes Contaminantes” (PRTR, 2017). The flows of the most representative compounds were taken from this inventory for the case study according to the bibliography (Lecomte et al., 2010). The Table 1 summarizes these data.

Table 1. Composition of the flue gas to treat.

Components	Mass Flow (kg/h)
CO₂	52,625.57
CO	118.72
NO₂	73.86
O₂	18,750.00
N₂	145,833.33

3.2.2. *Technology selection*

Amine scrubbing using aqueous monoethanolamine is the most mature technology for post-combustion carbon capture that can be quickly deployed (Yuan & Rochelle, 2018). In specific, this aqueous amine solvent ensures high absorption efficiency due to their reactivity with CO₂ (Prentza et al., 2018), and it has been extensively used because of the rapid reaction rate and low cost of the raw material (Kim et al., 2012). Also, this technology has been developed for power generation plants characterized by the generation of large volumes of flue gas. These are the reasons why it has been selected for being studied in this work.

With this technology it is possible to achieve a high CO₂ removal efficiency (95-99%), However, because the large flows that are treated, which will involve the use of large equipment to achieve those efficiency, it was decided to establish a more realistic efficiency close to 75%, which is acceptable for this cement company, since they currently buy carbon offset.

A carbon offset is a credit for greenhouse gas reductions achieved by one party that can be purchased and used to compensate (offset) the emissions of another party. Carbon offsets are typically measured in tones of CO₂-equivalents (or CO₂e) and are bought and sold through a number of international brokers, online retailers and trading platforms.

Therefore, any reduction that can be made with respect to CO₂ emissions would represent a benefit for the company since it would decrease its demand with respect to carbon credits as long as the proposed process is viable.

3.3.Simulation and design process

Aspen HYSYS[®] is an interactive process engineering and simulation program. It is a powerful software for simulation of chemical plants and oil refineries. It includes tools for estimation of physical properties and liquid-vapor phase equilibrium, heat and material balances, and simulation of many types of chemical engineering equipment (Shukor et al., 2016).

The CO₂ capture process from a flue gas coming from Cements Molins was studied with an Aspen HYSYS[®] software. According to this, the conditions, parameters, models and methodology used in the simulation are explained below.

3.3.1. Component list

This was the first step in building the Aspen HYSYS[®] model. This list contains all the components presented in the process. The Table 2 shows the species involved in the simulation.

Table 2. Component list.

Components
CO₂
CO

Components
NO₂
O₂
N₂
H₂S

The H₂S was not present in the flue gas, but due to the thermodynamic package utilized, was necessary including it on the list. On the other hand, the solution used for CO₂ absorption was constituted by MEA at 30% mass, water 65% mass and 5% mass of CO₂. The percentages used for MEA and CO₂ were established according to the bibliography (Øi, 2007). 5% of CO₂ was considered a necessary requirement because the process is designed with regenerated amine so it will always contain traces of CO₂ that should be considered to approximate the process as much as possible to the reality.

3.3.2. *Property package*

After defining the components list, it was necessary to associate with a fluid package. Aspen HYSYS[®] provides three property packages designed specifically for Acid Gas Cleaning. They are: Acid Gas – Chemical Solvents, Acid Gas – Physical Solvents and Acid Gas – Liquid Treating. In this case, because of the utilization of MEA, a chemical solvent, the first package was selected.

The reactions and chemistry for this case are automatically generated by Aspen HYSYS[®] using the thermodynamics and calculation models in the Acid Gas Property Package, and the component list associated (AspenTech, 2018).

3.3.3. *Simulation environment*

In the simulation environment, you will find a blank page on which to build the model (AspenTech, 2018). In this case, an absorber, a regenerator and a heat exchanger were the equipment utilized to simulate the CO₂ capture process.

3.3.4. *Absorption tower simulation*

To define the specifications of the absorber, a bibliographic review of similar processes was carried out. The following conditions were established for a base case from which several variations were made to optimize and adjust the process to the flue gas treated in this work. The Table 3 shows the values used.

Table 3. Specifications for absorption tower base case (*Øi, 2007*).

Parameter	Value
Inlet gas pressure	101.3 kPa
Inlet gas temperature	40 °C
Lean amine pressure	101.3 kPa
Lean amine temperature	40 °C
Lean amine flow	100,000 kmol/h
MEA content in lean amine	30% mass
CO₂ in lean amine	5% mass
Number of stages in absorber	10
Diameter	2 m

The absorption tower was designed with perforated plates because cross-flow plates are the most common type of plate contactor used in absorption columns (Sinnott & Towler, 2009). Moreover, tray towers can offer high efficiency performance, usually with low to moderate pressure drop (Watson, 1999). The spacing chosen will depend on the column diameter and operating conditions. Close spacing is used with small-diameter columns and where head room is restricted. For columns above 1 m diameter, plate spacing of 0.3 to 0.6 m will normally be used (Sinnott & Towler, 2009). In this case, large flows are treated thus a diameter greater than 1 m will be required, so it was decided to use the suggested spacing of greater value (0.6 m).

Once the results of the base case were obtained, sensitivity analyzes were made with the intention of study the effect generated in the process by the variation of certain parameters such as lean amine flow rate, number of stages, diameter of the absorption tower and temperature of the lean amine stream. Figure 6 shows the order in which the parameters of the absorption process were varied.

First, the lean amine inlet flow rate was varied. Then, for each one of the flows studied, the effect on the CO₂ removal efficiency with the variation of the stages was evaluated. For the smaller flow rates, the diameter of the tower was varied. And finally, the temperature was changed to reach the established efficiency.

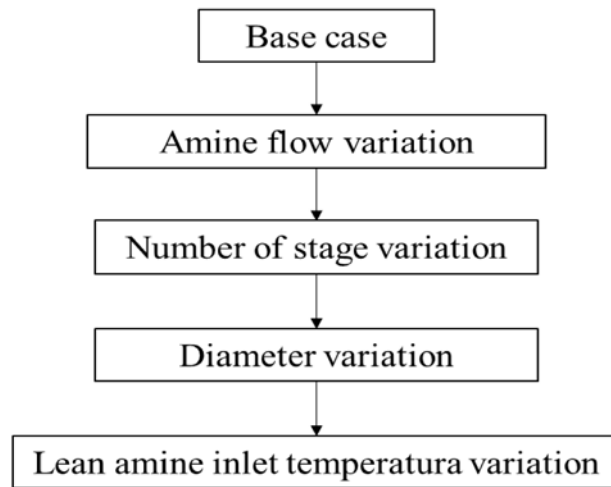


Figure 6. Parameters variation order for absorption tower optimization.

The selection of the final conditions for the absorption tower was based on those with which it will be possible to reach CO₂ removal efficiency equal to or greater than 75% utilizing the smallest equipment.

3.3.5. Regeneration tower simulation

The same procedure used for the absorber tower was established for the amine regeneration tower, from which a sequence of variations was made to obtain the optimal design conditions.

Table 4 shows the initial values used.

Table 4. Specifications for amine regenerator tower base case (*Øi, 2007*).

Parameter	Value
Rich amine temperature	105 °C
Rich amine pressure	101.3 kPa
Number of stages in the regenerator	10
Diameter	2.5 m
Heat duty	200,000,000 kJ/h
Reflux	Full reflux
Reboiler Temperature	120 °C
Condenser pressure	101.3 kPa
Reboiler pressure	101.3 kPa

The regenerator tower was also designed with perforated plates and with spacing between them of 0.6 m. From this, a series of variations were made. Figure 7 shows the sequence of these changes.

First, the number of stage was varied simultaneously with heat. From the previous result, the optimal number of stages was established and proceeded to study the effect on the CO₂ recovery the variation of the condenser pressure and the reboiler pressure with heat.

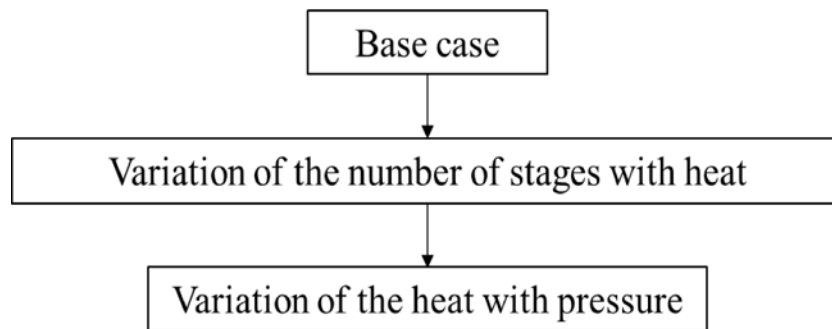


Figure 7. Parameters variation order for regeneration tower optimization.

The selection of the final conditions for the regeneration tower was based on those with which it will be possible to reach a CO₂ recuperation near to 100% with the minimal energy consumption.

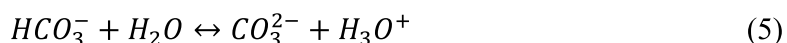
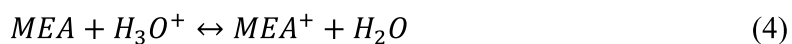
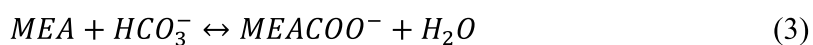
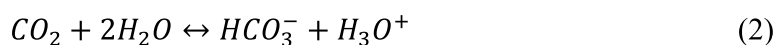
3.3.6. Heat exchanger simulation

A heat exchanger was placed between the absorption tower and the regeneration tower to increase the temperature of the rich amine stream to 105 °C as suggested in the literature. The specified pressure drop was insignificant to simplify the simulation process.

3.3.7. Absorption tower design

The flue gas enters to the absorber from the bottom and contacts counter-currently the lean amine aqueous solvent that enters to the absorption column from the top. Under a regime of diffusion and reaction phenomena, CO₂ is absorbed by the lean solvent which finale exits the column from the bottom with CO₂ loading. The free of CO₂ gas leaves the absorber from the top of the column.

In MEA system, CO₂ is solubilized in the liquid phase either in a carbamate, carbonate or bicarbonate form. The following reversible reactions occur in the MEA system (Øi, 2007):



According to these equations, two moles of MEA are necessary to absorb one mole of CO₂. The Figure 8 shows the stream arrangement for the absorption tower that has been simulated.

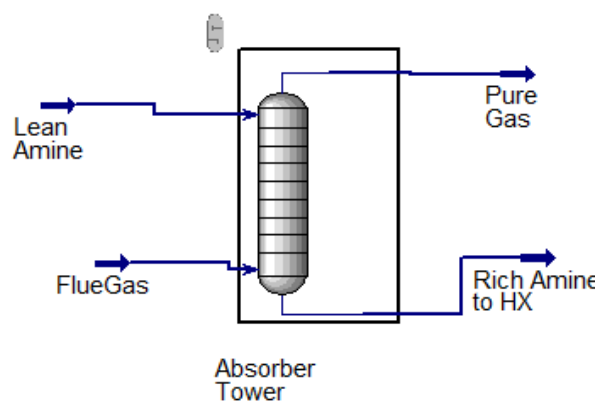


Figure 8. Absorption tower.

The results obtained from the base study were presented in Table 5.

Table 5. Absorption tower base case results.

Composition	Flue Gas	Lean amine	Pure Gas	Rich Amine to HX
CO (kg/h)	118.72	0.00	118.70	0.02
CO ₂ (kg/h)	52,625.57	118,686.23	34,629.97	136,681.83
N ₂ (kg/h)	145,833.33	0.00	145,816.40	16.93
O ₂ (kg/h)	18,750.00	0.00	18,745.90	4.10
NO ₂ (kg/h)	73.86	0.00	0.00	73.86
H ₂ O (kg/h)	0.00	1,542,921.01	8,488.02	1,534,432.99
MEA (kg/h)	0.00	712,117.39	16.41	712,100.98
H ₂ S (kg/h)	0.00	0.00	0.00	0.00
Flow Rate (kg/h)	217,401.48	2,373,724.64	207,815.4	2,383,310.71

Composition	Flue Gas	Lean amine	Pure Gas	Rich Amine to HX
Temperature (°C)	40.00	40.00	40.84	41.93
Pressure (kPa)	101.30	101.30	101.30	101.30

In this case, the CO₂ absorption efficiency was 34.19% with the cement manufacturing conditions. For this work the main objective is to reach at least an 75% of efficiency, that is the reason why, the design conditions utilized for this base case was modified.

At the beginning, lean amine flow rate variations were studied, because the increase of the amine solution leads to more efficient removal of CO₂ due to the spread of liquid on the plates surface and an increase in the effective interfacial area between liquid and gas (Dey & Aroonwilas, 2009). It also results in a higher liquid mass transfer coefficient and shortens the residence time of solution in the tower, because more fresh solution would be in contact with the gas which improve the degree of the absorption reaction (Liu et al., 2016).

As it was expected, solution flow rate has an impact on CO₂ removal as shown in Figure 9. A greater amine flow rate results in an increase of CO₂ removal. However, even doubling the initial flow rate and maintaining the same flue gas composition, the increase in the efficiency is very low. Varying the flow rate between 100,000 kmol/h and 450,000 kmol/h the improvement in efficiency is only 10%.

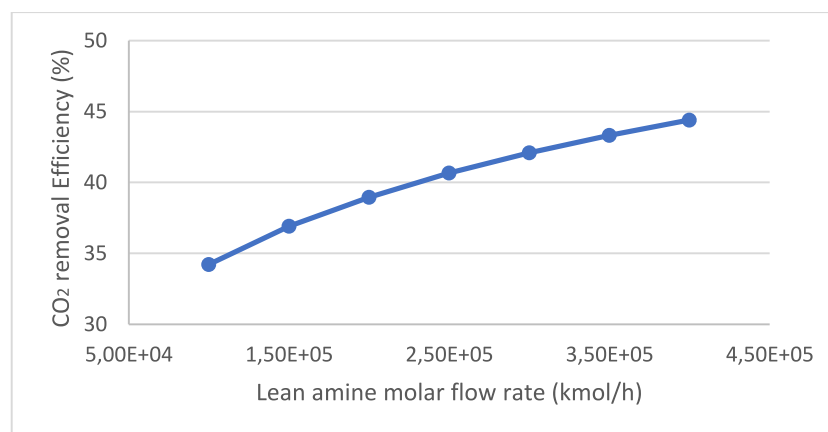


Figure 9. Effect of lean amine flow rate on CO₂ absorption performance.

CO₂ solubility in MEA solution is finite under specific temperature and pressure conditions, so it exists a limit of increasing solution flow rate after MEA concentration is determined. In

fact, if acid gas loading in the solution is high (optimal is between 0.2 and 0.4), CO_2 effective absorption capacity cannot reach the expected value because 1 mol of amine can only react with 0.5 mol of CO_2 at the case of stoichiometric ratio, so a certain amount of CO_2 must remain in the lean solution (Liu et al., 2016).

According to the bibliography, the lower lean amine solution flow rate is, the more obvious the effect of increasing solution flow rate on improving CO_2 absorption is. But for a high flow rate of MEA solution, there is no remarkable effect of such enhancement (Liu et al., 2016). This is in agreement with this case, that is why in addition to an increase in the amine flow rate, it is necessary to consider other factors to increase absorption efficiency.

After amine flow rate variations, it was decided to study the effect of the variation of the number of the stages of the tower on the efficiency of the absorption for each flow studied previously. The Figure 10 shows the results obtained.

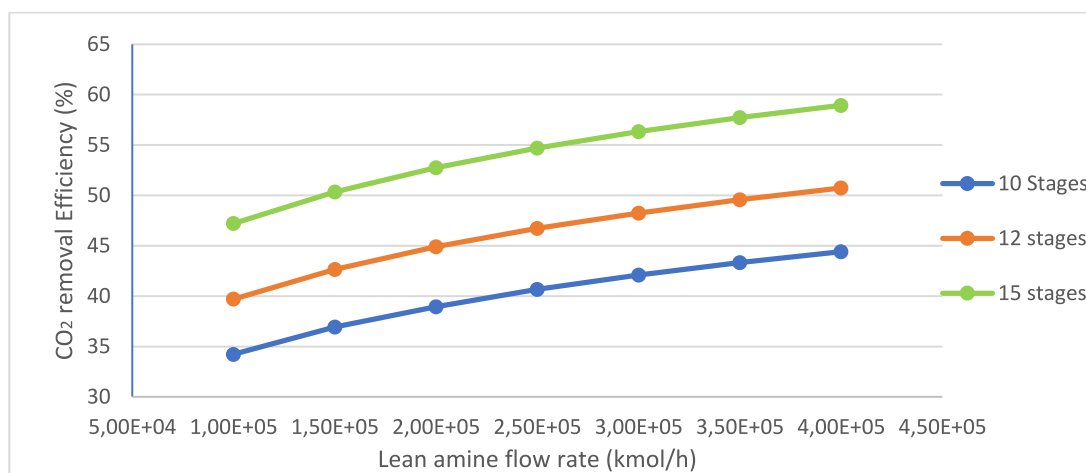


Figure 10. Effect of the number of stages on CO_2 absorption performance.

The definition of the number of stages is a fundamental point. It is related with the height of the tower. Usually this parameter is defined as a compromise between capital and operational cost and in general corresponds to the lowest number that assures the achievement of the purity requirements (Errico et al., 2016). Under this premise, the number of stages was varied between a short range, to study the synergic effect between the variation of the number of stages with the lean amine flow rate.

It is possible to observe that a greater number of stages the CO₂ removal efficiency increases. This is because in the staged approach, a tower is viewed as a collection of stages, and in each stage the gas and liquid phases are brought together and equilibrated until the two phases are in thermodynamic equilibrium. When this happens, solute begins to transfer from the gas to the liquid, in consequence, the concentration of solute decrease in the gas and increase in the liquid (Watson, 1999). Thus, with major equilibrium stages, more mass transfer will be.

However, as the objective is to design an absorption tower with the smallest possible dimensions, and seeing that varying the lean amine flow rate with the number of stages simultaneously does not reach the required efficiency, it was decided to study the effect of tower diameter, maintaining the same ideal to obtain the highest efficiency with the smallest possible diameter. Figure 11 shows simulation results varying tower diameter between values of 1.5 m and 6 m for the lowest flows and for each number of stages studied.

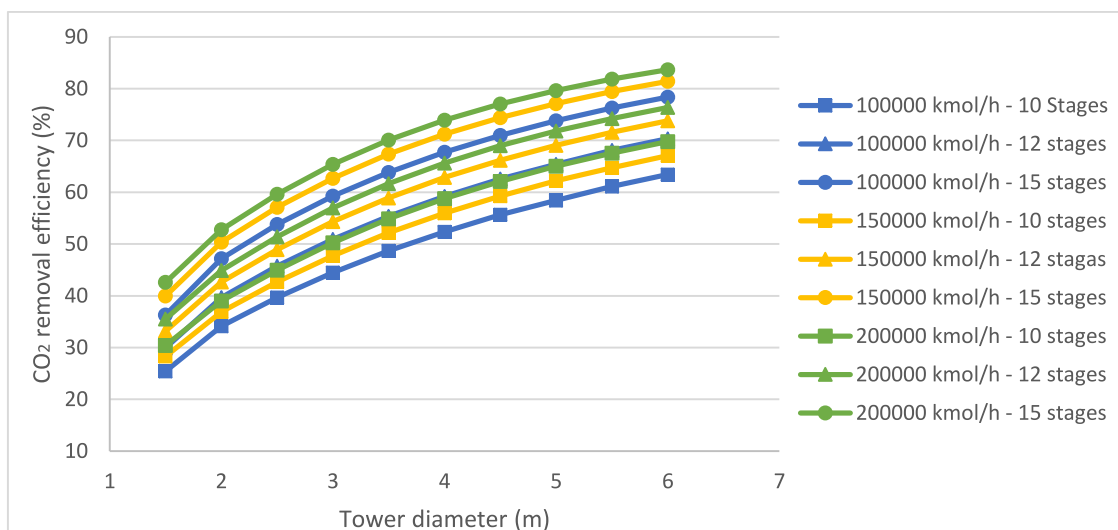


Figure 11. Effect of the diameter on CO₂ absorption performance.

It is observed that a major diameter, major will be de CO₂ absorption. This corresponds with the expected, because vapor flow velocity is dependent on column diameter and also a major diameter provides a major contact area between gas and liquid, which favor the mass transfer.

The lower flows used in the previous study were those utilized for the variation of the diameter. This was because the management of large flows will involve larger dimensions of the tower, which is intended to avoid for reduce costs. This is a very important point in

this work. In fact, because of the huge amount of exhausted gas from big industries, like power plants and cement manufacturing plants, the volume of absorber is generally quite large. For example, a 600 MW LGN- fired power plant using conventional MEA absorption process, the diameter and height of an absorber reported are 4.7 m and 44 m, respectively, whereas the stripper is about 25 m. These two main towers represent the 55% and 17% of the total capital cost (Yu et al., 2012). Therefore, the design of smaller towers will reduce costs.

In addition, it is important to mention that using the smallest flows, the efficiency value obtained is close to that established in this work. On the other hand, taking the example cited above (LGN- fired power plant), we sought to obtain the required efficiency (equal to or greater than 75%) with a diameter equal to or less than 4 m.

According to what is presented in Figure 11, with a flow between 150,000 kmol/h and 200,000 kmol/h and a 15-stage tower, the efficiency value is close to 75%. This suggests that, by making some improvements of another parameter in these two cases, it will be feasible to reach the established efficiency.

The inlet temperature of the amine solution influences the CO₂ removal efficiency. The absorber inlet liquid temperature was found to be one of the most important factors influencing the absorption performance (Prentza et al., 2018). Because of that, variations in temperature were studied. The Figure 12 shows the result obtained.

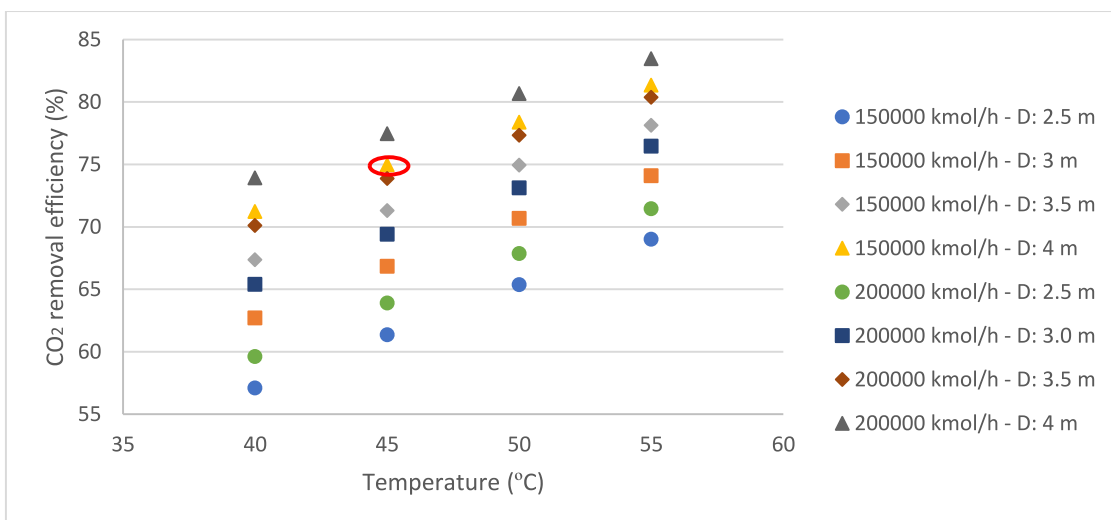


Figure 12. Effect of the temperature on CO₂ absorption performance.

The efficiency increases as temperature rise. This occurs because solution temperature rising would make solution viscosity decrease. It also promotes second-order reaction rate constant, which is more conducive to maintain a higher CO₂ absorption efficiency at the bottom section of the tower, where the reaction between MEA and CO₂ occurs at the initial stage. However, many other problems such as solvent evaporation, equipment corrosion, etc., would occur too when solution temperature is pretty high (Liu et al., 2016).

According with Liu et al., (2016) 40°C temperature is reasonable for MEA solution to achieve better stabilization, and that is the reason why the base case established in this work for the absorption tower was based on that temperature for the lean amine stream. However, for being an absorption process, a 6°C temperature difference between the inlets could improve the process. That is the reason why the case study that achieved the desired efficiency at 45°C is selected as the optimal one.

On the other hand, according to other studies, the variation of gas inlet temperature shows that it has no considerable impact on the absorption efficiency (Koronaki et al., 2017). Therefore, the variation of this parameter was not studied.

Finally, with the last analysis presented in Figure 12, the specifications of the absorption tower were defined, and they are presented in Table 6.

Table 6. Specifications of the absorption tower.

Parameter	Value
Inlet flue gas pressure	101.3 kPa
Inlet flue gas temperature	40 °C
Lean amine pressure	101.3 kPa
Lean amine temperature	45 °C
Lean amine flow	150,000 kmol/h
MEA content in lean amine	30% mass
CO₂ in lean amine	5% mass
Number of stages in absorber	15
Diameter	4 m

The results obtained from the simulation for these conditions are shown in Table 7.

Table 7. Results obtained from the absorption proposed design.

Composition	Flue Gas	Lean amine	Pure Gas	Rich Amine to HX
CO (kg/h)	118.72	0.00	118.70	0.02
CO₂ (kg/h)	52,625.57	178,029.35	13,144.75	217,510.17
N₂ (kg/h)	145,833.33	0.00	145,809.67	23.66
O₂ (kg/h)	18,750.00	0.00	18,744.38	5.62
NO₂ (kg/h)	73.86	0.00	0.00	73.86
H₂O (kg/h)	0.00	231,4381.52	10,293.81	2,304,087.71
MEA (kg/h)	0.00	106,8176.09	23.26	1,068,152.83
H₂S (kg/h)	0.00	0.00	0.00	0.00
Flow Rate (kg/h)	217,401.48	3,560,586.95	188,134.57	3,589,853.87
Temperature (°C)	40.00	45.00	45.72	49.51
Pressure (kPa)	101.30	101.30	101.30	101.30

Due to the content of MEA present in the stream of purified gas it will be necessary to take corrective measures such as water washes to mitigate this emission (Øi, 2007). The water wash section could be part of the absorption tower. This consist of a top wash tray followed by a packed wash section. Most of the MEA in the absorber overhead gas is removed in the packed section just below the top wash tray through washing with cooled recirculating water (Thomas & Benson, 2016).

3.3.8. Regeneration tower design

In a regeneration tower or stripping tower, an absorber solute is removed from a liquid solvent by counter-current contact with vapor. Stripping and absorption are usually used together, with a stripping column regenerating the solvent from the absorber column (Sinnott & Towler, 2009).

The vapor and liquid are brought into contact on plates or packing. The condensate from the condenser is returned to the top of the column to provide liquid flow above the feed point (reflux), and part of the liquid from the base of the column is vaporized in the reboiler and returned to provide the vapor flow. The Figure 13 shows the stream arrangement for the regeneration tower that has been simulated.

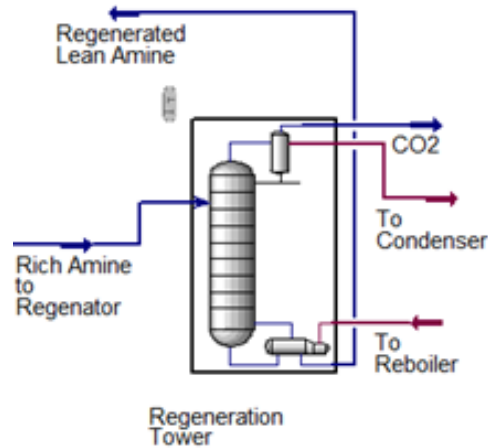


Figure 13. Regeneration tower

For the stripping process as well as for the absorption process, based on the bibliography, a case study was established. Primary amines like MEA are characterized by a high rate of reaction. However, compared to higher order amines, they require more heat for regeneration. CO₂ separation requires a continuous supply of heat to the installation for the sorbent regeneration. Using MEA, the desorption process requires 2-5 MJ of heat per 1 kg of separated CO₂ (Bochon & Chmielniak, 2015). According to this, and knowing that it is required to desorb at least 39,480.82 kg/h of CO₂, the amount of heat required was estimated, which would be close to 200E+06 kJ/h. This is the reason why this value was used as a starting point for the simulation. The results obtained from this study are presented in Table 8.

Table 8. Stripping tower base case results.

Composition	Rich Amine to regenerator	CO ₂ stream	Regenerated lean amine
CO (kg/h)	0.02	0.02	0.00
CO ₂ (kg/h)	217,510.17	22,313.51	195,196.66
N ₂ (kg/h)	23.66	23.66	0.00
O ₂ (kg/h)	5.62	5.62	0.00
NO ₂ (kg/h)	73.86	70.55	3.31
H ₂ O (kg/h)	2,304,087.71	268,983.73	2,035,103.98
MEA (kg/h)	1,068,152.83	76.37	1,068,076.45
H ₂ S (kg/h)	0.00	0.00	0.00

Composition	Rich Amine to regenerator	CO ₂ stream	Regenerated lean amine
Flow Rate (kg/h)	3,589,853.87	291,473.48	3,298,380.40
Temperature (°C)	105.00	100.00	103.40
Pressure (kPa)	101.30	101.30	101.30

The CO₂ recovery efficiency was 56.51% with the cement manufacturing conditions. For this case a recovery close to 100% was established to reach the established conditions for the lean amine stream that enters to the absorber, because this regenerated amine will be reused. Thus, the design conditions utilized for this base case was modified.

At the beginning, the number of stages required was studied. The Figure 14 shows the effect on the CO₂ recovery of the variation of the stages with heat used. It is possible to observe that the greater the number of stages and greater heat, more separation will be obtained. However, it is important to note that there is a point where the increasing of the number of stages for the same heat leads to a standstill in separation efficiency.

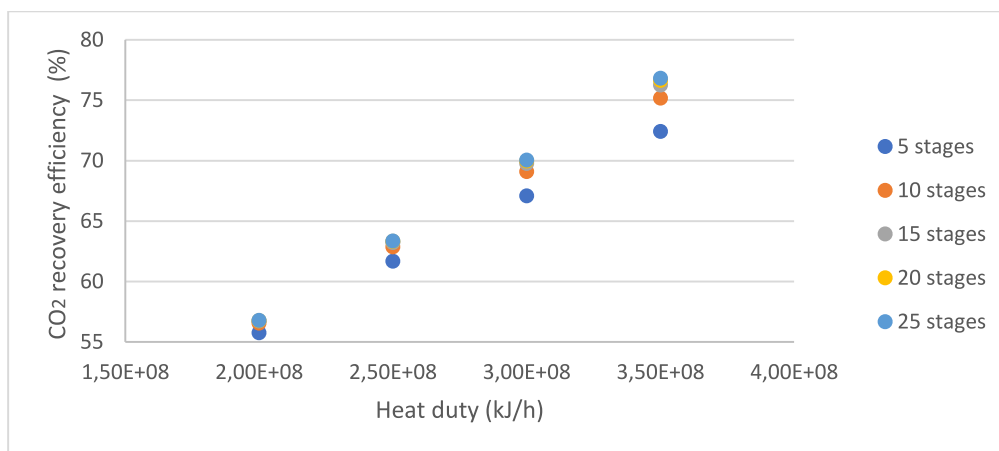


Figure 14. Effect of the number of stages on CO₂ recovery.

According to other studies in bibliography, the stages seem not influence both the reboiler heat and column diameter. One explanation is that when the packing height is low, the minimum required contact surface area is not reached yet, for this reason a higher duty is needed to guarantee the target removal. Once the minimum contact surface area is achieved the reboiler duty and the column diameter remain practically constant with the variation of the stages (Madeddu et al., 2018).

On the other hand, it is important to keep in mind that in the regeneration process of the amine, the heat is indispensable to break the bonds between the CO₂ and the amine. Therefore, for a rich amine flow established, a fixed heat will break a certain amount of bonds, thus if the same amount of heat is maintained and the number of stages is increased, the variation in the separation will be negligible.

From these results, observing that from 15 stages the separation was basically the same, it was decided to work with this value for the design of the regeneration tower.

Due to the fact that with these design conditions, the required recovery of CO₂ was not achieved, other factors were varied.

Generally, the stripper operates at a pressure higher than the atmospheric. The heat of absorption of CO₂ in MEA is almost two times the heat of vaporization water. Then, according to the Clausius-Clapeyron equation, the CO₂ vapor pressure increases more rapidly compared to H₂O vapor pressure. Therefore, the stripper must work at higher pressures compared to the absorber, in order to reach higher temperatures to favor the transfer of CO₂ over H₂O (Madeddu et al., 2018).

On the other hand, it is known that this process is carried out at low pressures, so it was decided to slightly increase the condenser and reboiler pressure between 202.6 kPa and 303.9 kPa (Øi, 2007) and observe how this parameter affected the recovery of CO₂ for an established range of heats. It is important to mention that the tower was designed to work without pressure drop, thus, the pressure of the column will correspond to the pressure established for the condenser and reboiler. The results are presented in Figure 15.

As it is observed, the pressure has a significant effect on the performance of the process. The pressure increases in the reboiler and condenser is accompanied by an increase in the temperature. As the temperature increases, the conditions become favorable for transfer of CO₂ to the gas phase and, hence, less steam is required to maintain the driving force for CO₂ transfer. Thus, it is favorable to operate the desorber at high pressure and temperatures as possible, however, the operating conditions in the desorber are limited by the fact that the degradation of MEA is accelerated with increasing temperatures so a temperature greater than 125 °C in the reboiler is not recommended (Movagharnjad & Akbari, 2011).

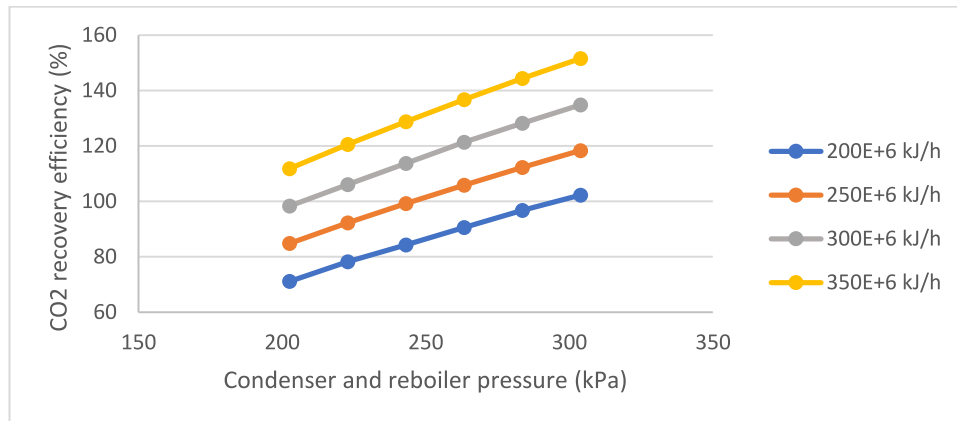


Figure 15. Effect of the pressure and heat on the CO₂ recovery.

At higher pressure, less heat will be required to reach a certain recovery. However, as mentioned above, the degradation of the amine must be taken into account, and since these processes are usually developed at a pressure of 202.6 kPa or less, it was decided to take this as a final value for the design. Therefore, with the results obtained from Figure 15, by using 300E+06 kJ/h, the desired recovery is almost reached. Performing other tests to determine more accurately the required heat, it was determined that with approximately 310E+06 kJ/h a little more of the recovery established is achieved.

Finally, with the last analysis presented, the specifications of the absorption tower were defined, and they are presented in Table 9.

Table 9. Specifications of the regeneration tower.

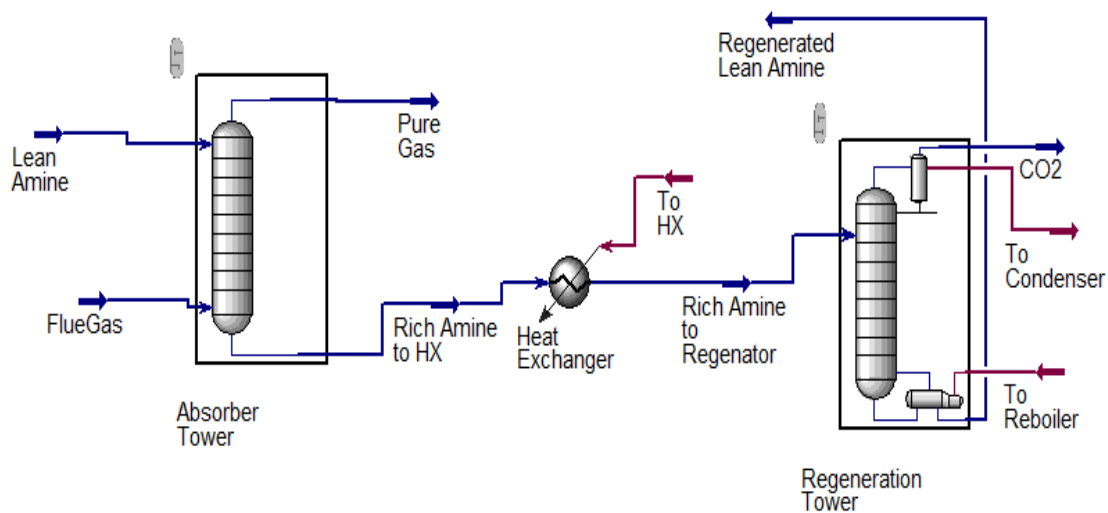
Parameter	Value
Rich amine temperature	105 °C
Rich amine pressure	202.6 kPa
Number of stages in the regenerator	15
Diameter	2.5 m
Duty	310,000,000 kJ/h
Reflux	Full reflux
Reboiler Temperature	120 °C
Condenser pressure	202.6 kPa
Reboiler pressure	202.6 kPa

The results obtained from the simulation for these conditions are shown in Table 10.

Table 10. Results obtained from the desorption proposed design.

Composition	Rich Amine to regenerator	CO ₂ stream	Regenerated lean amine
CO (kg/h)	0.02	0.02	0
CO ₂ (kg/h)	217,510.17	39,761.99	177,748.18
N ₂ (kg/h)	23.66	23.66	0.00
O ₂ (kg/h)	5.62	5.62	0.00
NO ₂ (kg/h)	73.86	70.04	3.82
H ₂ O (kg/h)	2,304,087.71	250,161.56	2,053,926.15
MEA (kg/h)	1,068,152.83	153.31	1,067,999.52
H ₂ S (kg/h)	0.00	0.00	0.00
Flow Rate (kg/h)	3,589,853.87	290,176.20	3,299,677.67
Temperature (°C)	105.00	121.80	118.80
Pressure (kPa)	101.30	202.30	202.30

The Figure 16 shows the final arrangement for the CO₂ capture process.

**Figure 16.** Final simulation arrangement.

It is important to mention the behavior presented by the CO and NO₂ in the process. Almost all the carbon monoxide escapes from the process by the Pure Gas stream. This occurs because this compound has a very slow reaction kinetic, which results in a slow absorption by MEA (Jamal, 2002). In contrast, the NO₂ is absorbed by the MEA solution. Depending

on the degree of purity with which CO₂ must be present, this portion of NO₂ must be removed or not. It should be noted that the fraction of this compound in the CO₂ stream is minimal. However, a preventive measure of the efficiency of the elimination of this compound in the stages prior to the treatment of the combustion gas would be the best strategy, because this also prevents the degradation of the amine.

On the other hand, in the process of absorption and regeneration part of the MEA and the water are lost by the gas outlet stream, that is why water and MEA make up must be injected to the lean amine stream regenerated in order to keep total circulating solvent flow rate constant and maintain the amine concentration.

Finally, it is interesting to study the amount of CO₂ hypothetically released to generate the thermal energy necessary for the desorption column. Assuming that the steam used in the reboiler to heat and generate the steam circulating inside the regeneration tower is produced through electricity provided by a power plant, it is possible to determine the amount of CO₂ released. According to the emission factor associated with energy, reported by the Generalitat de Catalunya (Generalitat de Catalunya, 2018), 392 g of CO₂ are generated per kWh of energy produced. For this case, an emission close to 33,755.55 kg CO₂/h is estimated. With the proposal process, the CO₂ recovered will be 39,460.12 kg/h, so the CO₂ removal balance would still be positive being, from the environmental point of view, a viable option.

It should be noted that the way in which this CO₂ separation process was designed is a first approximation. Other factors that can be studied in more detail to optimize the process and thus have lower energy expenditure. In addition, this study can be carried out by testing other absorbents with which the process could be further optimized.

4. Conclusions

The worldwide increasing temperature is one of the biggest threats that is facing the society. Numerous efforts have been made to mitigate this problem, however, with the economic development and population growth, the implementation of stricter policies to make an effective change is essential and CCS technologies have been developed becoming an effective solution.

Absorption, adsorption, membranes, cryogenic distillation and calcium looping are the technologies with greater development so far. The selection of one of them for an industrial process depends on economy, process conditions and product. A cement manufacturing plant was the industrial case selected because is one of the major CO₂ sources, in consequence, this is an important field where many studies should be done. The absorption process was chosen for the capture of CO₂ from flue gas from Cement Molins for been the most mature and already implemented. Thus, an absorption and desorption process using aqueous MEA solution was simulated with Aspen HYSYS[®].

For the design of the absorption tower it was noticed that the variation of the amine flow rate had a significant impact. When increasing the flow, the recovery of CO₂ was greater due to the solution is better spread on the plates, increasing the interfacial area of material exchange. A similar behavior is observed when increasing the diameter of the tower, because it also contributes to the increase of the interfacial area. On the other hand, the increase of the temperature of the amine flow rate also favors the CO₂ separation because it decreases the viscosity of the solution and promotes a second-order reaction rate constant.

In the regeneration tower the effect on the variation of the stages has a lower effect on the regeneration of the amine. However, the pressure manifested to have an important role in the process because when increasing the pressure, it increases the temperature which favored the conditions for the transfer of CO₂ to the gas stream. In addition, less heat is necessary to maintain the driving force for CO₂ transfer. Still, it is important to maintain the system at a temperature that does not generate degradation of the amine.

To conclude whether this option may be viable or not from the environmental point of view, it was compared the amount of CO₂ recovered with the released to produce the energy necessary for the process, observing that it recovers more than what it is released which makes it an interesting option to consider. However, the process can be further optimized so that the CO₂ recovered could be significantly improved.

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