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Evaluation of the Environmental Impact of Introducing CCS Technologies in the Cement Industry

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SCHOOL OF SCIENCE & TECHNOLOGY

A thesis submitted for the degree of

Master of Science (MSc) in Energy Systems

DECEMBER 2015
THESSALONIKI – GREECE

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ABSTRACT

Cement is an industrial product, which is closely correlated with the economic development of a country and at the same time liable for massive amounts of energy consumption and CO_2 emissions emanating during its production. In view of a global and unprecedented climate change, a crucial, yet underdeveloped, component of the toolkit for emissions reduction, is the application of carbon capture technologies, which constitute the arrest of carbon dioxide at its source, in order to prevent its emission to the atmosphere. Taking the above issues into consideration, this report analyzes the life cycle of cement in a conventional cement plant, detecting the processes which are more energy-intensive and produce more greenhouse gas emissions and scrutinizes the application of two post-combustion capture technologies, namely monoethanolamine scrubbing and calcium looping, in order to evaluate their added environmental impact and ultimately assess their effectiveness as CO_2 mitigation strategies.

ACKNOWLEDGMENTS

Seeing this dissertation to an end seemed a tedious, and at times impossible, process, which required dedication, tenacity and patience. As such, I feel the need to express my sincere gratitude and utmost respect to my supervisor, Dr. Eleni Heracleous, for her valuable support, comments and punctuality in responding to my ceaseless questions and worries. Via this small message, I would also like to thank my parents and brother, who have aided me throughout all my studies, including this MSc programme, by all means imaginable and available. Last but not least, every word, every sentence that the reader sees here as result, is owed to an incredible inspiration infused to me by my loving girlfriend, Katerina; you are the best I could have ever hoped for, thank you for being beside me.

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INTRODUCTION

Within the context of a changing climate and an endangered environment, mainly led by the extensive use of fossil fuels, which continuously undermine its quality, several measures and policies have been identified, with the potential to reduce greenhouse gas emissions and provide a more sustainable future for mankind. Cement industry, being an intrinsically high emitter of carbon dioxide, is also held accountable for environmental degradation and there are respective requirements for cement plants to reduce their carbon footprint. Out of the many mitigation technologies proposed for application to the cement industry, carbon capture and storage (CCS) has been deemed by many parties as a viable alternative solution.

Part A of the present project includes a thorough literature review, tackling various subjects in thorough detail. At first, the cement manufacturing process is described, so that the reader is acquainted with the complexities and the nature of cement production, from raw material quarrying to final product. This will serve as a useful tool for the next section, which analyzes, again with the use of supporting arguments, the reasons why cement is correlated with great amounts of energy consumption and pinpoints the sources and magnitude of CO_2 emissions stemming from cement production.

The reader, after being introduced to the aforementioned concepts, is informed on the several CO_2 mitigation technologies that have been proposed for the cement industry, such as: i) increasing the thermal and electric efficiency (waste heat recovery, plant optimization, etc.), ii) substitution of conventional fossil fuels and use of alternative fuels (with details on selection criteria, suitable materials, advantages and disadvantages), iii) clinker substitution by means of introduction of additives, as well as the limits of its implementation.

Next subject on the literature review is the concept of carbon capture, where three different technologies, suitable for application to the cement industry, are presented, namely post-combustion capture with MEA scrubbing, post-combustion capture with calcium looping (CaL) and oxy-fuel combustion. Within this section, the process of each technology is described and the three technologies are scrutinized in terms of benefits and drawbacks, as well as current limits to implementation. The present project also contains a quantitative comparison of the three technologies based on key performance indicators, i.e. raw material and energy consumption, energy recovery potential, CO_2 footprint, emissions reduction and energy penalty and some estimations found in the literature regarding capture costs. The literature review concludes with a summary of current barriers (technical, economic, etc.), impeding the wider implementation of CCS in the cement industry, as well as proposed future actions that will provide the means for the development of carbon capture technologies.

Having pinpointed the problem and acknowledged its importance, the present thesis focuses, in the second part, on the environmental assessment of two post-combustion capture technologies, namely MEA scrubbing and calcium looping, by considering the life cycle of a conventional cement plant and juxtaposing its energy consumption and global warming potential figures against two identical plants, where the aforementioned technologies have been retrofitted. The goals of this study were multiple; i) to detect which processes consume more energy and produce more CO_2 emissions, ii) to expose the additional requirements in terms of mass and energy for the two carbon capture technologies, iii) to compare the cases, in order to verify their impact to the environment, as well as their potential for CO_2 abatement. In this context, life cycle inventories were compiled for the three cases, containing detailed information regarding mass and energy input, as well as emissions output, which yielded pie charts for fossil fuel consumption by type, energy consumption by process and contribution to GWP. Finally, the main visual aid for comparison of the cases is the cumulative graphs, constructed in a way that facilitates the evaluation of each technology and the assessment of their effectiveness.

PART A: LITERATURE REVIEW

1.1 HISTORICAL REVIEW OF CEMENT

Ever since civilizations started building structures, demand for a material that would bind stones into a solid, formed mass emerged. The origins of such binding agents date back to primitive civilizations, such as Assyrians and Babylonians, which started using clay, to form robust stone walls. Some 2600 years, ago, the Egyptians took this technique to the next level, using a mixture of lime, clay, sand and water. The next development came by the Romans, around the first century, who added volcanic soil (pozzolana) from the region of Pozzuoli, near Naples. This mixture comprised 60 to 90% clay and 10 to 40% lime and was capable of hardening under the presence of water **[1]**. Cement production was reportedly slowed down during the Middle Ages, with significant information being lost **[2]**, but was reinvigorated during the early stages of the industrial revolution, where, in 1817, Louis Vicat determined the required proportions of limestone and silica, which, after burning and grinding, produced a hydraulic binder. Seven years later, in 1824, Joseph Aspdin developed a patent for "Portland cement", having refined the composition proposed by Vicat. The term "Portland" was given, because the material's colour bore a striking resemblance to an oolitic limestone quarried on the isle of Portland in Dorset, England. Nowadays, about 99% of all cement used today is Portland cement **[3]**, otherwise termed Ordinary Portland Cement (OPC), which is a predetermined and carefully proportioned combination of limestone ($CaCO_3$), sand (SiO_2), clay and other materials (eg: Al_2O_3, Fe_2O_3, TiO_2).

1.2 CEMENT MANUFACTURING PROCESS

The procedure of manufacturing cement, according to the Cement Sustainability Initiative **[4]** consists of 10 basic steps, namely: i) quarrying raw materials, ii) crushing, iii) prehomogenization and raw meal grinding, iv) preheating, v) precalcining, vi) clinker production in the rotary kiln, vii) cooling and storing, viii) blending, ix) cement grinding and x) storing in the cement silo. The process is depicted in figure 1.

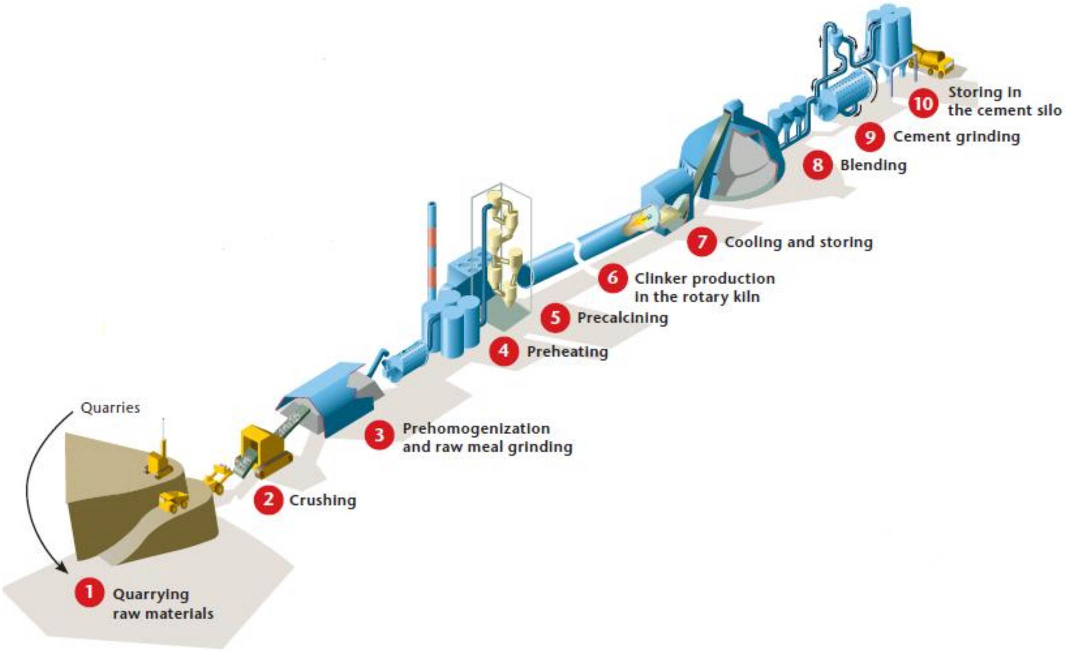

Figure 1: Cement manufacture at a glance [5]

The first step involves extraction of raw materials, required for the production of cement. The basic materials required are calcium carbonate ($CaCO_3$), extracted from naturally occurring calcareous deposits (limestone, marl or chalk) and small amounts of silica (SiO_2 - extracted from clay or sand), alumina (Al_2O_3 - extracted from bauxite) and iron oxide (Fe_2O_3 - extracted from iron ore), which are used, subject to product requirements, to adapt the chemical composition of the raw mix. In order to keep transportation costs at a minimum, cement plants are usually located nearby quarries.

The next steps involve routing of the quarried minerals to primary and secondary crushers, where they are broken into 10 cm-large pieces, mixing of different raw materials to maintain the required chemical composition and initial milling, before being reduced to a fine powder, to provide the so-called "*raw meal*" **[4, 6]**. This step is very crucial, in order to ensure high cement quality, therefore chemists are assigned with the task to monitor and control the chemistry of the raw meal **[4]**.

Subsequently, during the preheating phase, the raw meal is passed through a series of vertical cyclones, where it comes into contact with swirling hot exhaust gases at 800 °C, which rise from the kiln. Throughout this phase, thermal energy is gained from the hot flue gases and the raw meal is preheated, so that the following chemical reactions in the kiln occur faster and more efficiently, in terms of energy savings.

The most critical stage during the cement manufacturing process is the calcination, taking place in a steel cylindrical rotary kiln (figure 2), typically 60 to 90 metres long and up to 6 metres in diameter **[7]**, with a slight inclination, to allow for materials to slowly reach the other end.

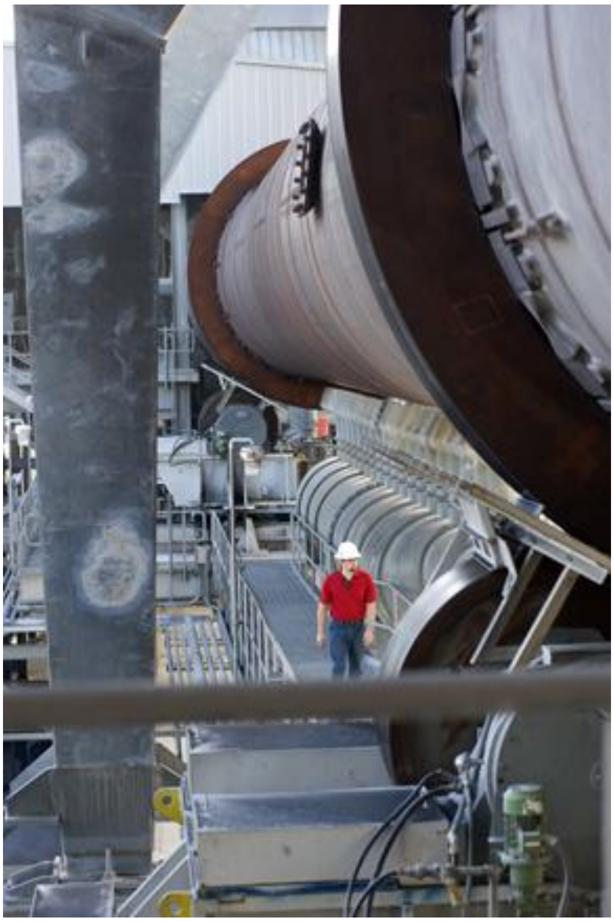

Figure 2: Rotary cement kiln [8]

During this stage, fuel is fired directly into the kiln to reach temperatures of up to 1450 °C. There are two basic ways that a raw meal will enter the kiln; it will either be wet, hence forming a slurry, or dry, in powder form **[9]**. Their main difference, apart from the fact that, in each case, a different type of kiln is required, is in terms of heat and electricity consumption, since the dry process utilizes more electricity, but significantly less thermal energy than the wet process **[10]**. A summary of the reactions occurring inside the kiln, with the respective rise in temperature, is shown in figure 3.

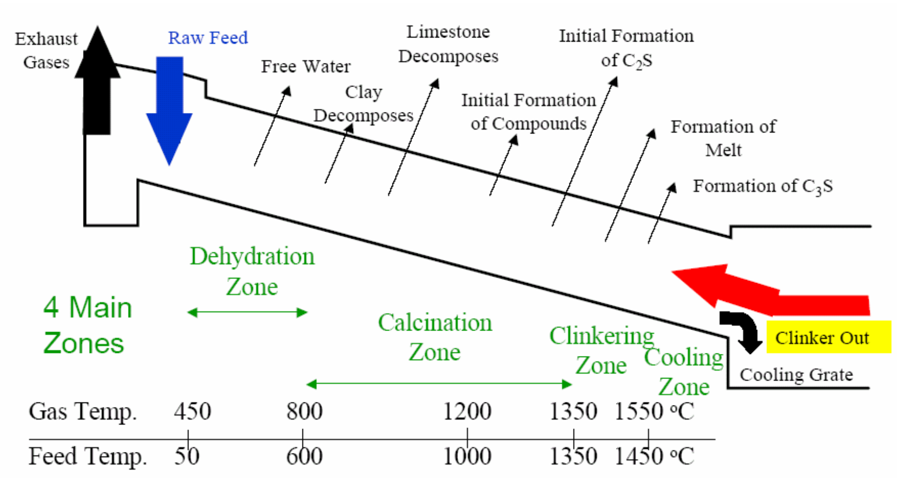

Figure 3: Summary of kiln reactions - wet process [11]

As seen in the image above, the procedure is divided into 4 main zones, progressively hotter, through which the material slides and tumbles, as the kiln rotates. Firstly, in the dehydration zone, water residues, if any, evaporate and clay starts to decompose, at a temperature between 100 to 300 °C. In the calcination zone, combustion of the raw meal causes a chemical reaction called decarbonation, where the CO_2 contained in the limestone is released at a temperature range between 30 and 900°C. The corresponding chemical equation is as follows: $CaCO_3 \rightarrow CaO + CO_2$. Subsequently, compounds such as silicon dioxide (SiO_2), iron(III) oxide (Fe_2O_3) and aluminum oxide (Al_2O_3) are introduced into the mix and firstly, when temperature rises above 800 °C, the formation of belite takes place, according to the following chemical equation: $CaO + SiO_2 \rightarrow CaO.SiO_2$. In the next phase, termed liquid phase, another set of reactions take place, when the temperature exceeds 1200 °C:

$$(CaO)_2.SiO_2 + CaO \rightarrow (CaO)_3.SiO_2$$

$$(CaO)_3.(Al_2O_3) \rightarrow C_3A$$

$$(CaO)_4.(Al_2O_3).(Fe_2O_3) \rightarrow C_4AF$$

The end product discharged from this zone, takes the form of hard nodules, typically 3 to 25 mm in diameter, and is called clinker (figure 4). It is composed mainly of four major compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) **[12]**.

Figure 4: Clinker [13]

Immediately after intense heating, the clinker granules are sent to a grated cooler, where incoming combustion air (at 100-200 °C) is entrained and then redirected to the kiln, to reduce the energy loss from the system **[8]**. Upon cooling, the clinker is firstly stored in silos and then mixed with gypsum (calcium sulphate), to control the setting time of the product and possibly other cementitious components (blastfurnace slag, coal fly ash, natural pozzolanas, etc.) or inert materials (limestone), depending on the type of cement produced **[4]**. All the constituents are ground in a cement grinding mill, yielding cement in the form of a fine and homogenous grey powder. Finally, the cement is stored in silos before being dispatched either in bulk, or in paper sacks.

1.3 ENERGY CONSUMPTION AND EMISSIONS IN THE CEMENT INDUSTRY

1.3.1. CEMENT PRODUCTION AND ECONOMIC DEVELOPMENT

Cement is a fundamental industrial product for infrastructure and building construction, providing the basis for concrete, which is "*second only to water in total volume produced and consumed annually by society*" **[14]**. Cement is also very closely interrelated with the economic development of a country, as increased industrialization, stemming from economic expansion (mainly in developing countries) tends to lead in corresponding increases in cement consumption **[15]**. A striking visual representation of this phenomenon is observed in figure 5, where emerging nations, such as China, South Korea and Saudi Arabia display an excess cement demand, compared to countries with similar gross domestic product, hence proving the level of investments taking place.

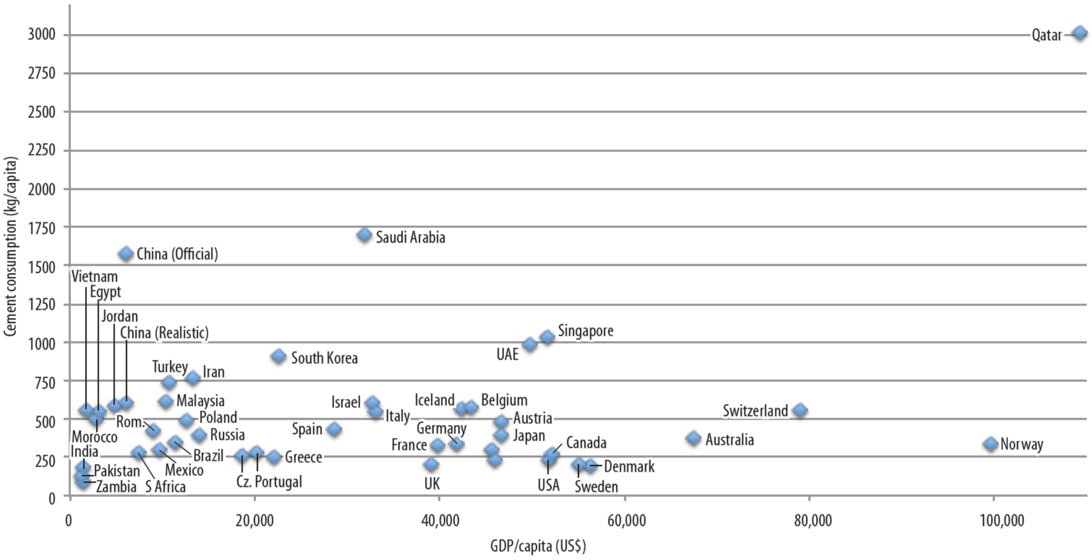

Figure 5: Cement consumption vs. GDP [15]

In 2014, the world cement production amassed 4.3 billion tons, the breakdown of which can be seen in figure 6. In the same context, future trends, portrayed in figure 7**,** reveal that cement production and consumption on a global scale is forecast to rise as well. Namely, a forward expansion to almost 5.9 billion tons is expected by 2025.

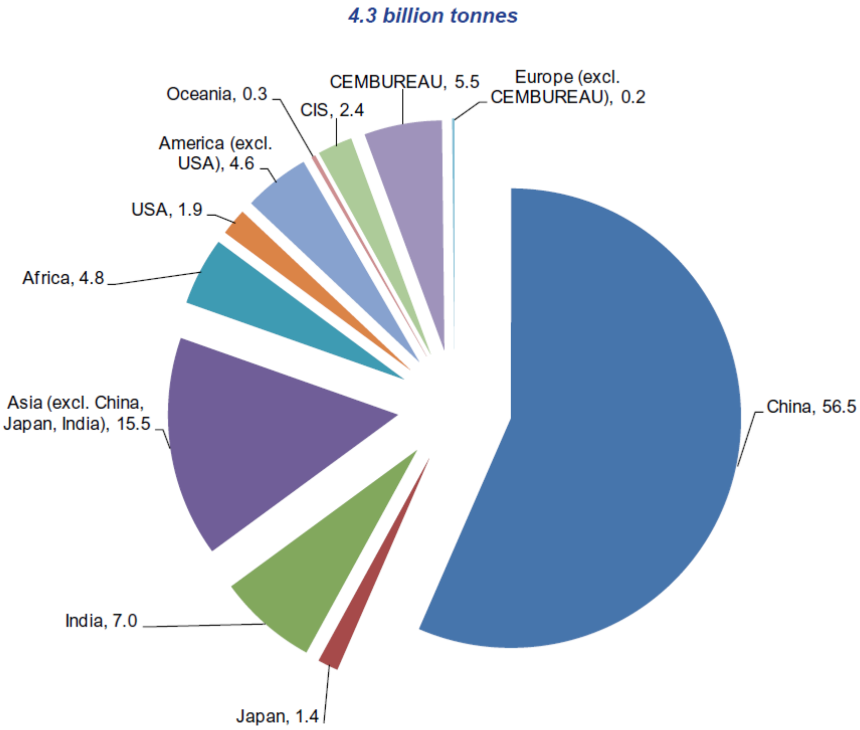

Figure 6: World cement production 2014 by region & main countries, % [16]

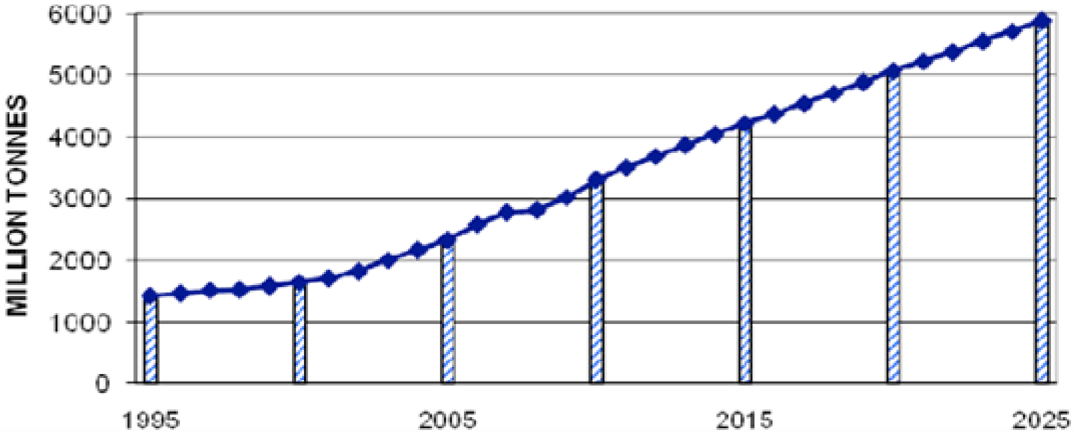

Figure 7: World: forecast cement consumption to 2025 [17]

1.3.2.CEMENT MANUFACTURING: AN ENERGY-INTENSIVE INDUSTRY

It is more than evident that cement manufacturing is an energy-intensive industry. Findings of a report published by the International Energy Agency **[18]** show that the cement industry, along with other non-metallic minerals, consumes around 10% out of the total global energy use corresponding to the industrial sector (figure 8) and, more specifically, among the industrial processes within this percentage, cement manufacturing is the most expensive in terms of energy consumption **[19]**.

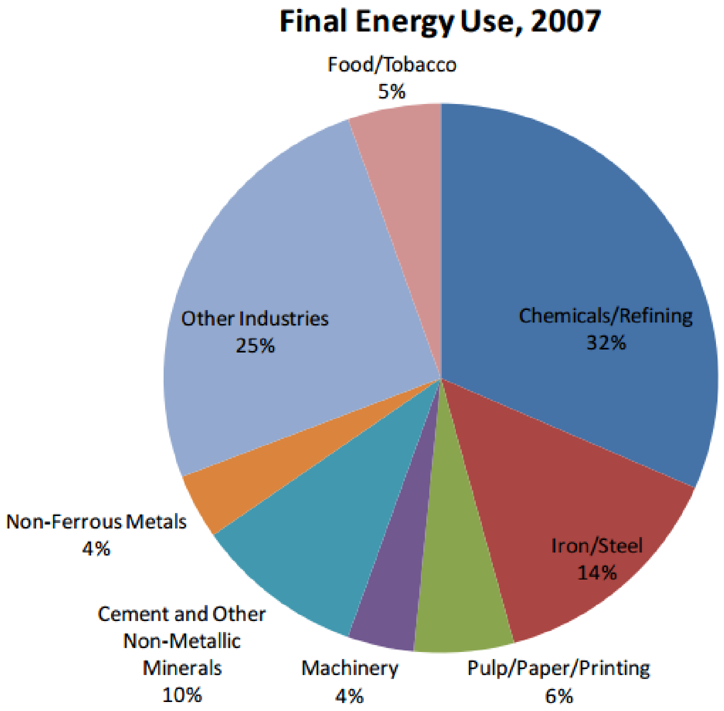

Figure 8: Industrial energy by subsector, 2007 [18]

Reportedly, around 50-60% of cement production costs is attributed to energy consumption **[20]**. In the same direction, the European Cement Association has stated that, subject to cement variety and process used, each ton of cement produced requires 60-130 kg of fuel oil (or its equivalent) and approximately 105 kWh of electricity **[21]**. Furthermore, a study conducted by CIPEC **[22]** in 2006, found in Madlool et al. **[23]**, reveals that, among others, coal, petroleum coke and electricity prevail as energy sources used for cement manufacturing (figure 9).

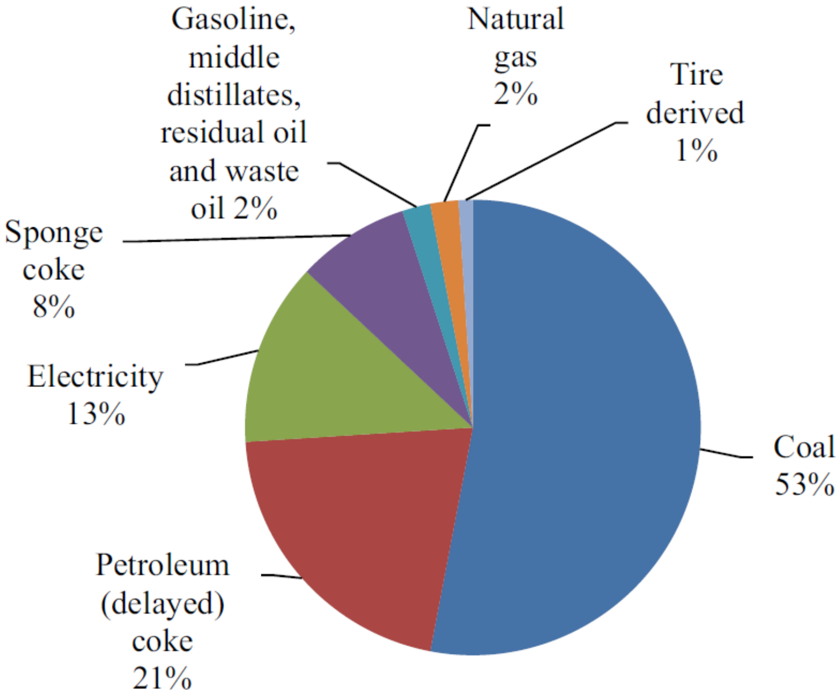

Figure 9: Total energy for cement manufacturing sector by energy source [22]

Out of the previously distinguished steps in cement manufacturing, thermal energy has been found to account for around 80% of the primary energy use, while the remaining 20% is attributed to electricity **[24]**. A breakdown of heat and electricity consumption, in terms of energy flows, is depicted in figure 10.

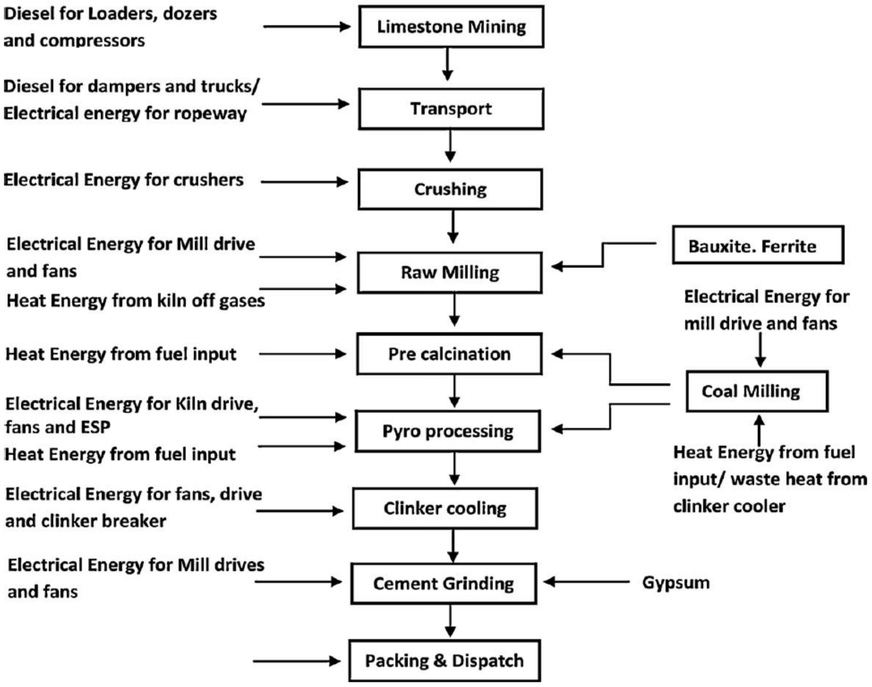

Figure 10: Electrical and thermal energy flow in a cement production process [10]

With respect to heat, the major energy-intensive process is the combustion of raw materials **[10, 25]**, which varies, depending on certain key determinants, which, in turn, are quantified in terms of specific energy consumption (MJ/ton of clinker). Firstly, the type of kiln technology (wet or dry process), has an impact on the quantity of heat required in a cement plant, as, the more humidity a raw meal contains, the more heat is needed to dry it **[25, 26],** namely from 3.4 GJ/ton for the dry process to 5.29 GJ/ton for the wet process **[23]**. Moreover, potential existence of pre-heater towers, consisting of vertical cyclone chambers, facilitates the recovery of heat, stemming from exhaust gases, thus yielding savings in energy consumption **[25]**. In the same context, clinker coolers retrieve hot air by heat exchange with the clinker, which can be redirected into the kiln, hence adding to the energy efficiency of the plant **[25]**. Finally, roughness of raw material and quality of fuel, which differ, depending on the country, may affect the specific energy consumption during cement production **[23]**, as, the harder the material and the lower the fuel quality, the higher the value of specific energy required in the process. In terms of statistics, Pardo, Moya and Mercier **[25]** mention that, in 2008, the weighted average thermal energy consumption totaled 3730 MJ/ton of clinker.

In alignment with table 1, there are three distinct processes during cement production, which consume the largest share of electricity, namely raw meal grinding (18 kWh/ton - 24%), kiln feed (22 kWh/ton - 29.3%) and cement grinding (23 kWh/ton - 30.7%).

Table 1: Electrical energy distributions in a cement industry [10]

Section/Equipment	Electrical energy Consumption (kWh/ton)	Share (%)
Mines, crusher and stacking	1.50	2.00
Re-claimer, raw meal grinding and transport	18.00	24.00
Kiln feed, kiln and cooler	22.00	29.30
Coal mill	5.00	6.70
Cement grinding and transport	23.00	30.70
Packing	1.50	2.00
Lighting, pumps and services	4.00	5.30
Total	75.00	100.00

Especially for the cement grinding process, other studies report a percentage between 38% **[25, 27]** and 40% **[28]**. Madlool et. al **[23]** also suggest that electricity consumption during cement production reaches 110 kWh/ton of cement. The World Business Council for Sustainable Development **[29]** converges with the latter, having found that the European electricity consumption was around 111 kWh/ton of cement in 2008. Sathaye et al. **[30]** have estimated that current state-of-the-art technologies, implemented in grinding, can reduce consumption to 75-80 kWh/ton of clinker, but still, as stated in Taylor, Tam and Gielen **[31]**, "*the energy efficiency of grinding is typically only 5 to 10%, with the remainder converted to heat*". Finally, according to the same authors, there can be massive variations in the consumption of electrical energy per plant.

1.3.3. CEMENT AND CO_2 EMISSIONS

As verified before, there are two facts in hand: global cement production displays an exponential growth and, at the same time, the cement manufacturing process is intrinsically energy-intensive. This combination evidently enhances the notion that emissions, associated with this specific industry, rise proportionately, leading to environmental degradation. The Cement Sustainability Initiative **[32]**, among others, has identified the substances which are emitted during the production of cement, namely particulate matter (cement kiln dust), nitrogen oxides (NO_x), sulphur dioxide (SO_2), carbon dioxide (CO_2) and carbon monoxide (CO). In addition, there may be emissions of volatile organic compounds, acid gases, trace metals and organic micro pollutants, but at much smaller, or even negligible, volumes. Table 2 indicates the typical exhaust gas compositions from a cement process, out of which CO_2 is found to have the biggest concentration, i.e. 14-33% **[33]**.

Table 2: Exhaust gases from cement process [34]

Component	**Concentration**
CO_2	14-33% (w/w)
NO_2	5-10 of NO_x
NO_x	<200-3000 mg/Nm^3
SO_2	<10-3500 mg/ Nm^3
O_2	8-14% (v/v)

From a macroscopic point of view, various sources deem the cement industry as one of the largest contributors of CO_2 emissions to the atmosphere. More specifically, in an analysis prepared by the World Resources Institute **[35]** in 2005, taking all greenhouse gas emissions attributable to human activities in consideration, the cement industry was shown to represent 3.8% of the total emissions. Focusing only on the CO_2 emissions globally, studies converge to the fact that cement manufacturing is responsible for approximately 5-7% of anthropogenic CO_2 emissions **[4, 35, 36, 37]**, which, as Barcelo et al. **[36]** emphasize, depends on the boundary conditions. This share is also illustrated in figure 11.

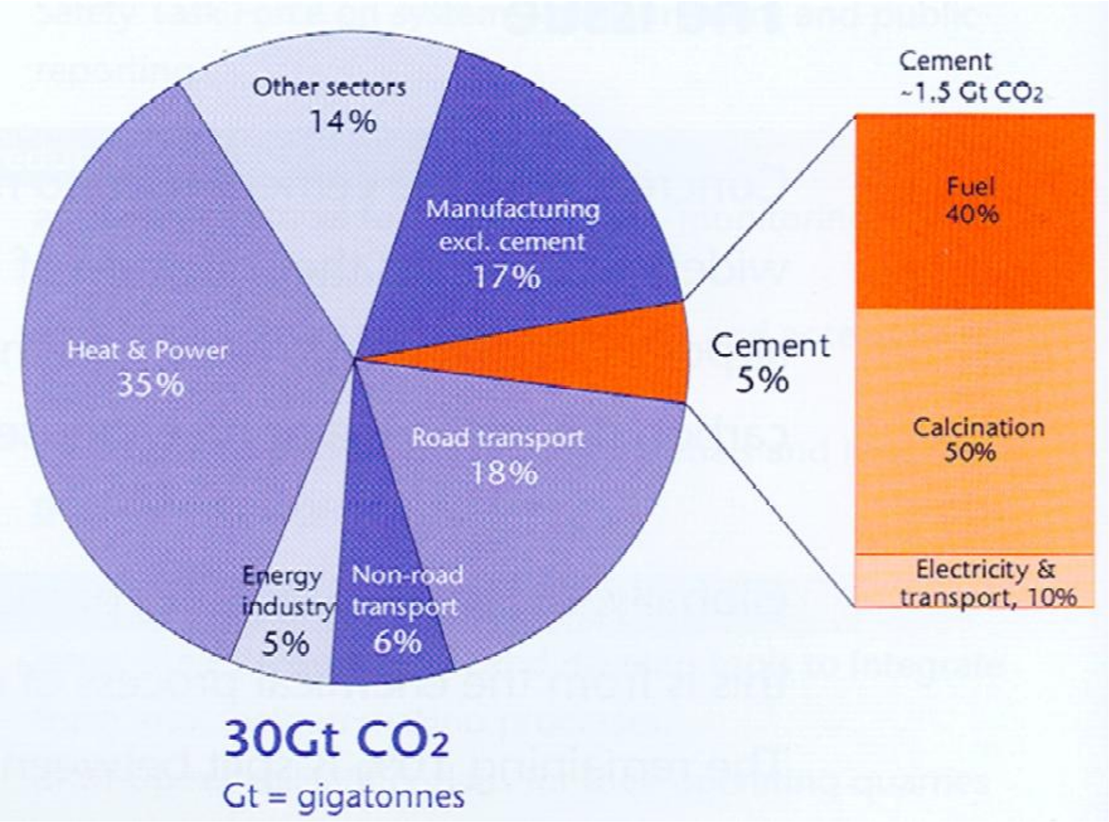

Figure 11: Global CO_2 production [38]

In terms of global annual emissions, CO_2 production from cement manufacturing processes was about 829 million metric tons, as found in Ali, Saidur and Hossain **[26]**. In their 2009 study, Barker et al. **[39]** maintain that the cement industry accounts for about 1.8 Gt of CO_2 emissions annually. On a European level, facts provided by Moya, Pardo and Mercier **[40]** reveal that the cement industry emitted 173.6 Mt of CO_2 in 2007, whereas in 2008, CO_2 emissions reportedly neared 2005 values (157.8 Mt CO_2). Studies by the Cement Sustainability Initiative **[14]** and Barcelo et al. **[36]** showed that, in 2006, global average gross CO_2 emissions were 866 kg per ton of clinker. According to the Cement Sustainability Initiative **[32]**, in 2010, the average specific CO_2 emissions amounted to 625 kg/ton of cementitious product, whereas Hasanbeigi, Menke and Price **[41]** argue that, during the cement manufacturing process, around 900 kg of CO_2 for every ton of cement produced are emitted. Finally, Ali, Saidur and Hossain **[26]** estimate that 1 ton of clinker yields 0.9-1 tons of CO_2, depending on the fuel type used, whereas Hoenig, Hoppe and Emberger **[42]**, having taken into account a modern technology and equipment, have found that 0.65-0.92 kg of CO_2 are emitted, as an outcome of producing 1 kg of cement.

CO_2 emissions linked to the cement industry are divided into two main categories: direct and indirect emissions. Direct emissions, according to the Cement Sustainability Initiative **[43]**, are emissions from sources that are owned or controlled by the cement plant. On the other hand, indirect emissions are "*a consequence of the operations of the cement plant, but occur* *at sources owned or controlled by another entity*" **[43]**. Firstly, direct CO_2 emissions stem from calcination of carbonates ($CaCO_3$ and $MgCO_3$), the chemical reaction that yields calcium oxide (CaO) and magnesium oxide (MgO), at approximately 50% **[26, 32, 37]**. Another 40% **[32, 36, 37]** originates from combustion of kiln fuels related to clinker production, and a minor, near-negligible percentage is attributed to combustion of non kiln fuels, fuels for on-site power generation and combustion of the carbon contained in wastewater **[43]**. The remaining 10% is mainly shared between two types of indirect emissions, i.e. external production of electricity consumed by cement producers and transport of inputs (raw materials, fuels) and outputs (cement, clinker) by third parties **[32, 43]**. Overall, the sum of CO_2 emissions during cement manufacturing is influenced by factors, such as type of production process, fuel used and clinker/cement ratio **[26]**.

Throughout the years, the cement industry has implemented various measures with the aim to reduce the energy consumption and associated emissions. As stated in Concretethinker **[44]**, since 1972, energy efficiency of the cement production process has been improved by 33%. In the same direction, figure 12 serves as evidence of the evolution of global absolute cement production in contrast with global absolute net CO_2 emissions. The Cement Sustainability Initiative **[14]** argues that a significant partial decoupling of economic growth (represented by cement production) and absolute CO_2 emissions. However, as noted by the same authors, "*wherever the growth of market demand for concrete and cement outpaces technical potential to reduce CO_2 emissions per tonne of product, absolute CO_2 emissions will continue to increase*."

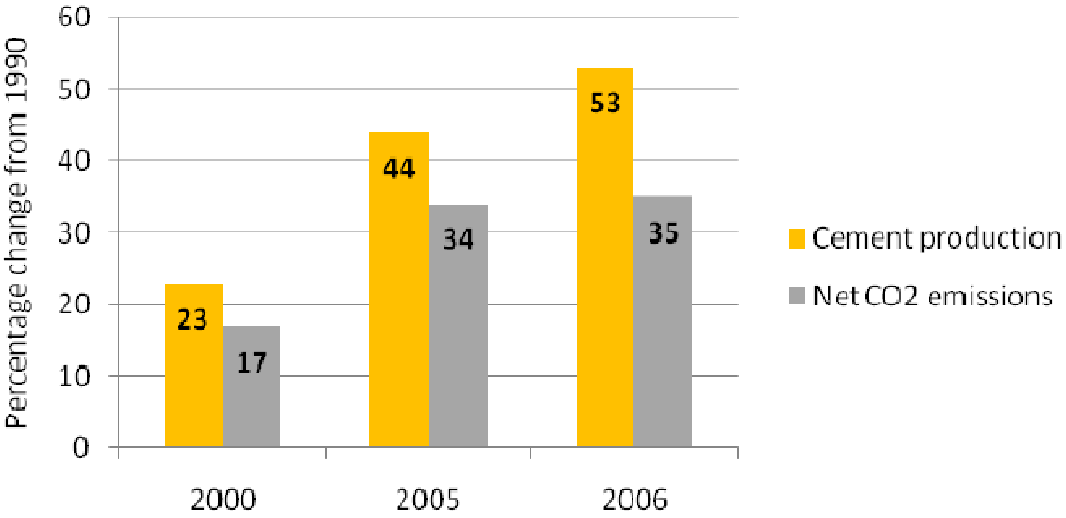

Figure 12: Partial decoupling of cement production from net CO_2 emissions over time [14]

Growing CO_2 emissions are linked with major economic and environmental threats, as **[37]** highlight. Such events have prompted, amongst others, the International Energy Agency

(IEA) and the World Business Council for Sustainable Development (WBCSD) to collaborate, in order to proactively research pathways that will embrace low-carbon energy usage. The overall policy objective has been set by IEA in 2008, according to which CO_2 emissions in 2050 must be half of the 2006 levels **[4]**. Specifically for the cement industry, the aforementioned organizations have compiled a roadmap, which outlines existing and potential technologies, along with related costs, timeline and potential that are capable of yielding the necessary industry-specific emissions reductions. The main levers upon which focus has been set are thermal and electric efficiency, alternative fuel use, clinker substitution and CCS **[4]**.

1.4 CO_2 MITIGATION TECHNOLOGIES FOR THE CEMENT INDUSTRY

1.4.1. THERMAL & ELECTRIC EFFICIENCY

Switching to Dry Process

As mentioned earlier, cement is manufactured by means of three distinct processes: wet, semi-wet and dry process, which correspond to the moisture content of the raw materials. In the wet and semi-wet processes, raw materials are directly fed to the kiln without any drying or preheating treatment **[37]**. These processes involve a supplementary amount of energy consumption, in contrast with the dry one, due to the increased temperature required to evaporate the water contained within the raw feed. According to the CSI's Getting the Numbers Right Protocol **[14]** energy consumption may be reduced by up to 50% and CO_2 emissions may be decreased by 20%, by switching to dry process with calciner. Wang et al. **[45]** also state that the dry manufacturing process, utilizing preheater and precalciner technology, "is currently considered the state of the art in cement production".

Waste Heat Recovery

The main sources of waste heat are the clinker cooler discharge and the kiln exhaust gas, which, according to Khurana et al **[46]**, waste up to 35% of total energy. Both sources can be manipulated in order to generate electricity, as described in [a critical review], via a steam turbine driven electrical generator, which "would offset a portion of the purchased electricity, thereby reducing the electrical demand" **[10]**. Schneider et al **[47]** have reported that such systems displayed the capacity to produce 30-45 kWh/ton of clinker in the big kilns. However, due to intrinsic losses and inefficiencies in the energy transfer, an appropriate efficiency estimation of the waste heat recovery steam generator is required **[10].** Other options include insulation of the external surface of cyclones and ducts, to reduce heat loss by convection and radiation through the hot kiln surfaces, as well as harnessing the thermal energy waste in order to preheat the raw meal before entering the clinkering grinding process, which leads to less required energy to evaporate the moisture content within it **[10]**. Since, according to **[40]** waste heat recovery is an emerging technology that is close to be cost-effective, there is a need for the public sector to diminish potential barriers that currently prevent full deployment of this technology, by means of market incentives and similar policies, which will eventually stimulate further research and development.

Plant Optimization & Maintenance

As Benhelal et al **[37]** suggest, an eminent approach towards lowering energy consumption and emissions, whilst keeping the quality and quantity of cement products at a high level, is plant optimization. In contrast with building new cement plants, where the most recently developed technologies are installed, improvements are an inevitable measure, to ensure that the machinery reaches its maximum potential operational efficiency. As pointed out by CSI **[4]**, when utilizing more efficient technologies, the producer gains a cost advantage through lower energy costs and efficiency is gradually increased, by adding new plants and upgrading old plants, an option also supported by **[45]**. CSI **[4]** also states that inefficient equipment and processes, such as long dry kilns and the wet production process, are gradually phased out by market and economic forces, as a consequence of more advanced technologies being commissioned. Representative examples are retrofitting of kilns, clinker coolers and cement mills and optimization of air to fuel ratio and air stream temperature. The latter method has been found to save 3-5% of energy consumption **[48]**. Overall, CSI **[4]** reports that by employing such actions, savings range from 0.2 to 3.5 GJ/ton of clinker.

In the same context, Madlool et al. **[10]** and Madlool et al. **[23]** have extensively reviewed energy efficiency measures regarding raw materials preparation, clinker production, finish grinding, product and feedstock changes, as well as general electric efficiency measures, which, according to the latter, were shown to yield thermal energy savings (from 0.05 to 3.4 GJ/ton of clinker) electrical energy savings (from 0.08 to 35 kWh/ton of clinker) and emission reductions (from 0.1 to 212.54 kgCO_2/ton of clinker). Representative excerpts of such measures are summarized in table 3.

Table 3: Summary of energy efficiency measures [10]

Energy savings in finish grinding			
Energy saving measure	**Energy/fuel saving (GJ/ton)**	**Electricity saving (kWh/ton)**	**Emission reduction (kgCO_2/ton)**
Vertical roller mill	0.2 - 0.29	10 - 25.93	8.82 - 26.66
High pressure roller grinding	0.09	8 - 28	1.8 - 6.3
Horizontal roller mill	0.3	27.78	4.33
High efficiency classifiers	0.04 - 1.62	2.8 - 3.7	0.4 - 1.4
General energy efficiency measures			
High-efficiency motors and drives	0.06	3 - 6	0.93
Adjustable/variable speed drives	0.1	6 - 8	1.68
High-efficiency fans	4E-04		
Energy efficiency measures for product and feedstock changes			
Blended cements	2.6 - 3.4		0.3 - 7.1
Limestone Portland cement	0.3	2.8	8.4
Low-alkali cement	0.19 - 0.5		4.6 - 12.1

Use of steel slag in kiln	0.19		4.9
Energy savings in clinker production			
Improved refractories for clinker making	0.12 - 0.4		
Energy management and process control systems	0.1 - 0.2	2.35	2.9 - 5.9
Increased number of pre-heater stages in rotary kilns	0.08 - 0.11		8.44
Energy savings in raw materials preparation			
Efficient transport systems	0.02	3.4	0.53 - 0.78
Raw meal blending	0.1	1.7 - 4.3	0.26
Raw meal process control for vertical mills	0.01	1.4 - 1.7	0.3 - 0.4

The same notion is maintained by Benhelal et al. **[37]**, as far as plant maintenance is concerned. The authors note that well structured and regular maintenance programs lead to more efficient processes, while Saxena **[49]** concludes that especially preventive maintenance can significantly contribute in curbing CO_2 emissions. Such measures entail regular leaking monitoring and control, corrosion control and reduction, periodical replacement of old motors and machines.

Finally, Benhelal, Zahedi and Hashim **[50]** have proposed a new process, the main novelty of which is the decomposition of CaCO3 and MgCO3 up to 90%, without any fuel consumption, where the required energy for the reactions is supplied by a hot stream of CO_2. This study showed that the novel process can reduce 2.3% of process fuel consumption, 66% of CO_2 emissions and decrease NO2 and SO2 as well.

1.4.2. ALTERNATIVE FUELS

Introduction

Use of alternative fuels essentially involves substitution of conventional fossil fuels (e.g. coal, petcoke) with fuels that are significantly friendlier to the environment, i.e. their combustion in the cement kiln is less carbon intensive. The predominant reasons for their growing popularity are the increasing fossil fuel prices, limited fossil fuel resources and environmental concerns **[51]** and use of wastes results in decrease in fossil fuel dependency, cement production costs and associated CO_2 emissions **[52]**.

Fuel Substitution

As stated in **[26]**, the degree of fuel substitution depends on the type of alternative fuel used. According to CSI **[4]**, the percentage of alternative fuel consumption in 2006 was 7%, whereas for biomass it was 3%. Review of the available literature, though, reveals that much higher substitution rates are possible. Taylor, Tam and Gielen **[31]** report that cement providers in Belgium, France, Germany, the Netherlands and Switzerland have achieved average substitution from 35% to more than 70% of the total energy used, while in other European countries, according to CSI's 2009 roadmap **[4]**, the average rate is over 50%. Lawrence **[53]** points out that cement plants derive 20-70% of their energy needs from alternative fuels. Finally, Ali Saidur and Hossain **[26]** and Taylor, Tam and Gielen **[31]** highlight that some individual plants have even reached a 100% fuel substitution, by use of appropriate waste materials. However, the latter authors argue that such high rates can only be accomplished in presence of a tailored pre-treatment and surveillance system.

Selection Criteria - Suitable Materials

Generally, according to Mokrzycki and Uliasz- Bocheńczyk **[54]**, alternative fuels are classified into the three main categories, namely gaseous (landfill gas, pyrolysis gas), liquid (solvents, waste oils, sewage sludge) and solid (animal meal, paper residues, discarded tyres, rubber wastes, plastics, textiles, agricultural residues).

Cement producers typically elect the type of alternative fuel, according to price and availability **[55]**, but fuel material characteristics should be considered as well **[10, 56]**. Typical selection criteria, as mentioned in **[55]** include: i) content of circulating elements (Na, K Cl, S), ii) toxicity, iii) ash composition and volatiles content, iv) calorific value (over 14 MJ/kg), v) chlorine and sulphur content (less than 0.2% and 2.5%, respectively), vi) physical properties (scrap size, density, homogeneity), vii) grinding properties, viii) humidity content, ix) moisture content, x) emissions released, xi) proportioning technology.

Kaddatz, Rasul and Rahman **[57]** investigated three alternative fuels, namely spent carbon lining (SCL), used industrial lubricants and used tires, and analyzed their suitability for use in a cement kiln. SCL was found to be a viable substitute, although its use increases carbon dioxide emissions and it had the worst performance, in terms of energy content. Used industrial lubricants were found to produce the required with 2 kg less fuel, compared to coal, but treating them for reuse was considered a more sustainable option. Used tyres were shown to produce 9% less CO_2 than pure coal and their combustion in the kiln was found to be a clean process, due to the very high temperature and long residence times, but handling and feeding of tyres was considered problematic, because it involves a high level of manual handling. In addition, studies by Rahman et al. **[55]** and Aranda Usón et al. **[58]** endorse the use of agricultural biomass, preferably in co-firing with coal, due to its carbon-neutral nature and its capability of reducing NO_x and SO_x levels **[59]**. In this case, seasonal availability and high fluctuation of calorific value constitute the major concerns **[55]**. Other, less optimistic, considerations have been made for the use of meat bone meal **[55, 58]**, municipal solid waste **[55, 58]**, plastic waste **[55]** and sewage sludge **[55, 58]**.

Benefits - Drawbacks

Various sources have cited the advantages that come along with usage of alternative fuels. Rahman et al. **[55]** report that alternative fuels are cheaper than fossil fuels, which prompts cement industries to produce the required thermal energy by using mixtures of both types of fuels in optimal proportions. This in turn leads into reduced clinker/cement production cost **[25]**. As mentioned in **[54]**, cement kilns are well suited for waste combustion, since they involve conditions such as high temperature, alkaline environment, oxidizing atmosphere and lack of incineration wastes **[54]**, which are favourable for the use of alternative fuels. Due to these prevailing conditions, a cement plant's kiln may function as an incineration plant and hence reduce emissions indirectly, as shown in figure 13. In the same manner, Habert et al. **[52]** explain that a direct reduction in CO_2 emissions can also be achieved, due to the fact that many alternative fuels are considered biomass and therefore carbon-neutral. Rahman et al. **[51]** also converge to the aforementioned statement, concluding that use of alternative fuels reduces the volume of waste disposal sites. Overall, introducing alternative fuels to the cement industry leads to preservation of non-renewable energy sources **[26, 51]** and decreased fossil fuel dependency **[25]**.

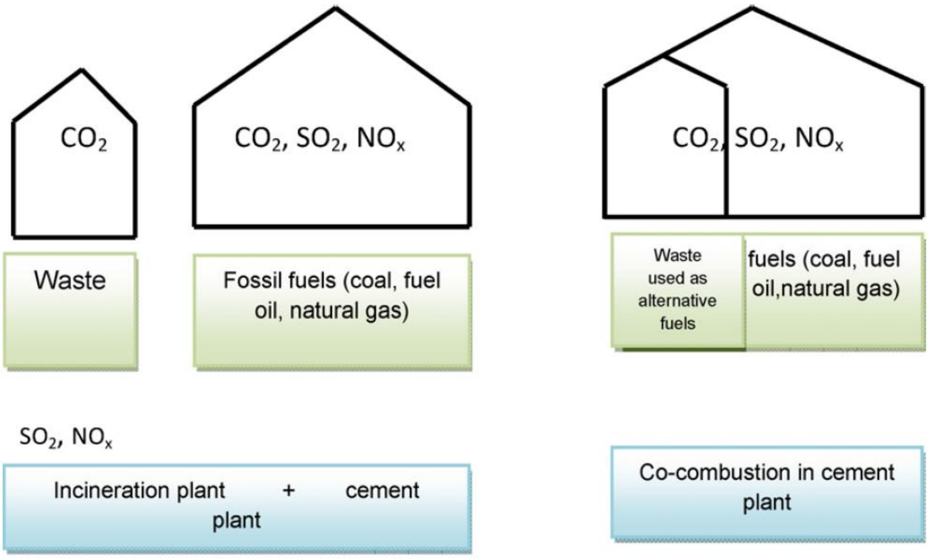

Figure 13: Benefits of co-combustion of alternative fuels in a cement plant [53]

Alternative fuel usage is associated with certain barriers and limitations as well. Rahman et al. **[55]** report that the transfer from conventional to alternative fuels presents challenges attributed to the intrinsically different behaviour of alternative fuels, namely "...poor heat distribution, unstable precalciner operation, blockages in the preheater cyclones, build-ups in the kiln riser ducts, higher SO_2, NO_X, and CO emissions, and dusty kilns" which need to be addressed. Schneider et al. **[47]** also point out that different characteristics of the alternative fuels can change the temperature profile of the kiln, which in turn affect the quality of the clinker produced, in terms of burning grade, granule porosity and crystal size of clinker phases. Ashes produced by alternative fuels present another technical impediment, which, as emphasized in **[37]**, can create unusual components into the kiln (e.g. phosphorous) that may alter the early strength and setting times of the produced cement. Consequently, Benhelal et al. **[37]** indicate that production processes and materials have to be precisely monitored and also some parts of the process need to be adjusted. In addition, CSI **[4]** suggests that political and legal barriers are far greater than technical ones; greater fuel substitution is impeded by i) lack of proper waste management legislation, that will restrict landfilling and allow treatment of alternative fuels, ii) inadequacy of local waste collection networks, iii) potential of alternative fuels to increase with high CO_2 costs, hence rendering their usage economically impracticable, iv) low social awareness of the concept of co-processing waste fuels in cement plants.

R&D Needs and Goals

Aranda Usón et al. **[58]** have indicated that, by coupling the cement industry with the waste management sector, it becomes feasible to alleviate greenhouse gas emissions and conserve fossil fuels and natural resources. However, as stated by CSI **[4]**, materials with the potentials to be used as alternative fuels must be identified and classified and further research and development regarding their processing and use needs to be carried out, to enable widespread expertise in using high volumes of these materials.

1.4.3. CLINKER SUBSTITUTION

Description

Another effective strategy that results in CO_2 emissions abatement is the reduction of the amount of clinker, which is the main component in most types of blended cement **[4]**. This is achieved by introducing additives into the cement blend, the production of which is far less energy intensive, owing to the lower clinker requirements per ton of cement **[31]**. As a consequence, the clinker/cement ratio will be lowered **[26]** and emissions from energy consumption in the kiln and process emissions from clinker production will be reduced **[31]**. Reportedly, the corresponding global potential for the reduction of CO_2 emissions was estimated at 5% of the total emissions associated with cement manufacturing **[26]**, however Bosoaga, Masek and Oakey **[34]** suggest that the proportion may be as high as 20%.

Global clinker factor

Under normal circumstances, the most common cement type (Ordinary Portland Cement) may contain up to 95% clinker **[4]**, but generally the clinker-to-cement ratio (also known as clinker factor) can vary widely **[4]**, due to fact that it depends on the type and volume availability of clinker substitutes, cement standards and the cement market **[47]**. The available literature suggests that the clinker factor is prone to a continuous decrease. More specifically, the global average in 2003 was 0.85, 0.75 in South America and 0.92 in North America **[37, 47]**. In Europe, a gradual reduction was observed, from 0.79 in 1990 to 0.76 in 2006 **[14]**, where the world average was 0.78 **[4]**. Finally, in 2010, the world average clinker factor was 0.77. Based on a study conducted by Pardo, Moya and Mercier **[25]**, the long term expectations, by extrapolating this trend, are that the ratio may decrease to 0.7 by 2030.

Representative examples of such additive materials are ground granulated blast furnace slag, fly ash, natural or artificial pozzolanas and limestone. Blast furnace slag is a by-product of iron and steel industries, which comprises silicates, alumina-silicates and calcium-alumina-silicates **[37]**. Its inclusion in the feed reduces the demand for limestone, improves the burnability of the raw material and hence lowers CO_2 emissions, due to limestone decomposition **[37]**. Fly ash, which is a residue from coal-fired power stations **[4]** also contributes to the reduction of raw materials and energy requirements, as well as the improvement of the durability of concrete **[37]**. Moreover, partial substitution of clinker with pozzolanas (a natural volcanic material) has a positive impact on the workability, strength and chemical resistance of the final product along with reduction of the energy requirements of the process **[4]**. Finally, an innovative type of clinker, proposed by Barcelo et al. **[36]** may aid towards changing the current landscape of blended cements. Generically referred to as BCSAF (belite-calcium sulfoaluminate-ferrite), this clinker requires far less limestone in its formulation and significantly less fuel to burn, whereas the concrete performance obtained is similar to contemporary Portland cements. In addition, keeping the clinker content unchanged, this clinker type can result in a 20-30% reduction in CO_2 emissions per unit of clinker used **[36]**.

Limits to implementation

Review of the relevant literature exposed several limitations to the implementation of clinker substitution. Apparently, a very important impeding factor is the regional availability of the substituting materials **[4, 31]**; notably, Taylor, Tam and Gielen **[31]** report that pozzolana, being a volcanic material, can only be obtained in specific locations. As a result, potential long-distance transportation would nullify the notion of energy saving and, taking the low value of the product into account, would not be a viable option. Other criteria that restrain the expansion of the aforementioned constituents are properties of substituting materials and the intended application of the cement, their rigorously increasing prices and externalities, such as national standards for Portland and composite cements and market acceptance, with respect to construction contractors and customers **[4]**. In order to combat this situation, CSI **[4]** has suggested a research and development toolkit, which entails documented assessment of proposed material properties, that will help towards accurate tailoring of intended cement applications.

1.5 CARBON CAPTURE IN THE CEMENT INDUSTRY

1.5.1. INTRODUCTION

An interim measure that is currently considered a critical component of low-carbon energy technology portfolios **[60]**, is carbon capture and storage (CCS). CCS is a procedure capable of capturing up to 90% of the CO_2 emissions produced by use of fossil fuels in industrial processes **[61]** and preventing carbon dioxide to reach the atmosphere. It is divided into three steps, namely capture and separation of carbon dioxide from other flue gases, transportation, utilizing media such as pipeline networks, ships or vehicles and, lastly, secure storage in depleted oil and gas fields or saline aquifer formations **[61]**. For the purposes of the present thesis, the aspects of transportation and storage are not scrutinized, although it is fairly evident that capture technologies only have value when the full chain of CCS is available.

Carbon capture may be performed via three different pathways: pre-combustion, post-combustion and oxy-fuel combustion. Pre-combustion systems involve conversion of fuels (regardless of their phase) into a mixture of carbon dioxide and hydrogen, by means of gasification or reforming. However, process conditions appear more favourable in refineries, chemical plants and electricity production through integrated gas combined cycle (IGCC) plants **[61]**. Applicability of this technology is considered irrational, firstly due to the explosive properties of hydrogen, thus hindering its use in cement kilns, secondly due to its combustion and radiation properties, which would require radical modifications to the clinker burning process **[42]** and thirdly, because only the CO_2 from fuel combustion will be captured, excluding the largest proportion of CO_2, which is released by limestone calcination **[62]**. As such, it is out of the scope of the present work.

Moreover, post-combustion capture, is a process where CO_2 is withdrawn from the rest of the flue gases after combustion of the carbonaceous fuel by means of absorption in a suitable solvent **[61]**. Alternative methods of CO_2 separation after combustion include membrane filtration, adsorption/desorption processes and cryogenic separation. Finally, during the oxyfuel combustion procedure, fuel is combusted in an oxygen-rich environment, diluted with recycled flue gas, rather than air being entrained to the system **[61]**. The oxygen required for the process is removed from the air via an air separation (ASU) unit, while a flue gas recirculation facility is also needed to introduce the gases in the combustion chamber, as previously mentioned. As stated in **[42]**, retrofitting of oxy-fuel technology systems is extremely challenging, however this process is a predominant option for new plants. The three systems are represented schematically in figure 14.

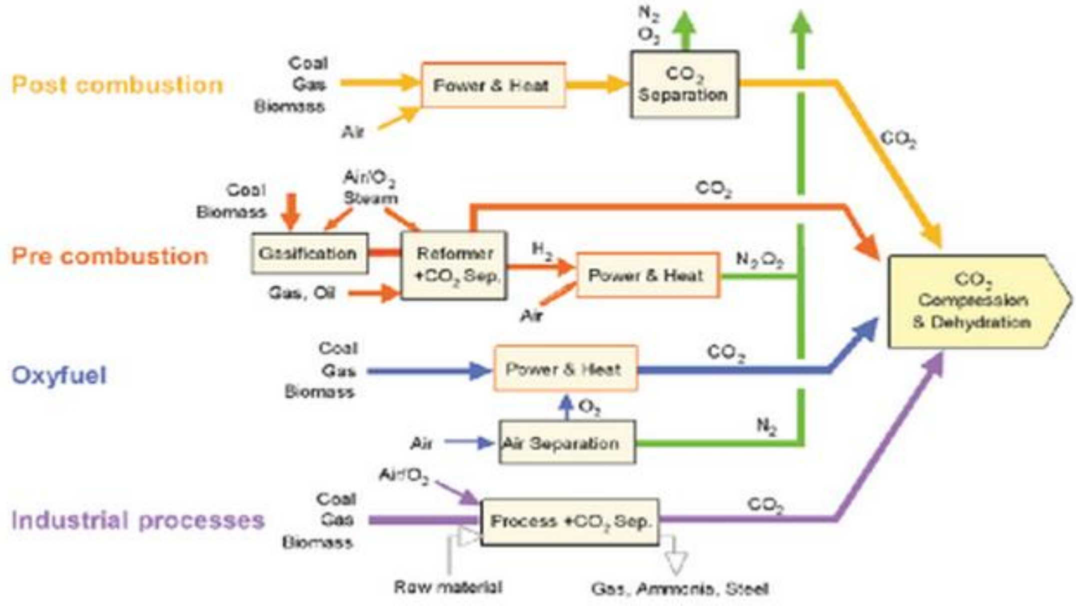

Figure 14: Capture technology diagram [63]

1.5.2. POST-COMBUSTION CAPTURE: MEA/AMINE SCRUBBING

Process Description

Post combustion capture by amine scrubbing and especially with the use of monoethanolamine (MEA) is an end-of-pipe technology, already employed in chemical and oil & gas industries **[34, 64]** for the sequestration of carbon dioxide from the flue gases. In order for this technology to be fully integrated into a plant's cement production process, the following equipment is required, according to the description by Bosoaga, Masek and Oakey **[34]** and Barker et al. **[39]**:

i) a Selective Non-Catalytic Reduction (SNCR) unit, fitted between the preheater and the raw mill, to reduce NOx in compliance with MEA process requirements
ii) a wet limestone Flue Gas Desulfurization (FGD) unit, fitted to remove SO_x from the flue gas stream
iii)a CO_2 capture unit based on MEA solvent separation (absorber, stripper along with auxiliary equipment)

and, on a second level, the following units, to ensure electrical efficiency and continuity of the CCS chain:

i) a coal-fired Combined Heat and Power (CHP) plant or independent steam generators, connected to the grid, in order to a) generate the required steam for MEA stripping and b) provide the necessary electrical power for the amine absorption and the CO_2 compression

plant. The CO_2 emitted during this process is also captured and mixed with the cement plant flue gas before the FGD.
ii) a CO_2 compression plant, where the captured stream of carbon dioxide is purified, dried and compressed to pipeline pressures of 110 bar, prior to transportation.

According to figure 15, flue gases stemming from the precalcining procedure and the combustion occurring in the rotary kiln, after introducing heat to the pre-heater, are directed to a preliminary cleaning system, where dust, NO_x and SO_x are arrested.

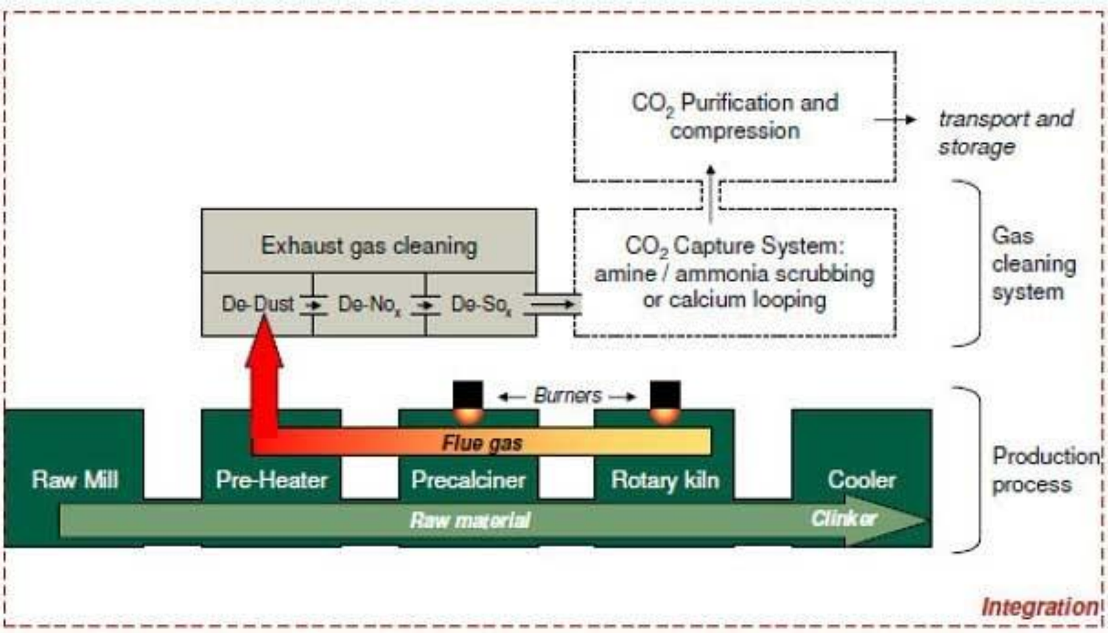

Figure 15: Block diagram of post-combustion technology applied at a cement plant [65]

Afterwards, the CO_2 stream is funneled to the CO_2 capture system, where the actual scrubbing process takes place as per the following steps, mentioned in **[42]**:

i) An aqueous alkanolamine solution is contacted in an absorber column with flue gas from combustion processes containing CO_2.
ii) The basic amine reacts with the acidic CO_2 vapors to form a dissolved salt. The purified flue gas exits the absorber.
iii) The CO_2-rich amine solution is regenerated in a stripper column (desorber), where the pressure is reduced and/or the temperature increased to roughly 120 °C in order to release the CO_2 and to yield a concentrated gas stream.
iv) Lean solution is cooled and returned to the absorber so that the process is repeated in a closed loop.

A representative schematic diagram of the closed-loop amine scrubbing process is depicted in figure 16.

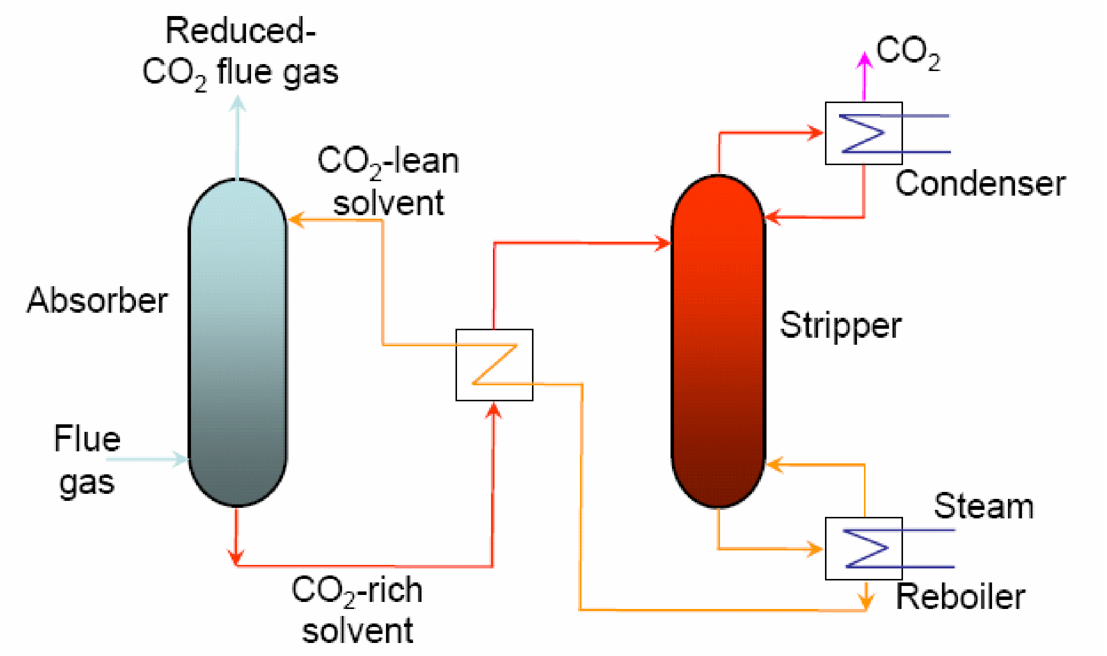

Figure 16: Schematic diagram of liquid solvent scrubbing [42]

Advantages & Challenges

Post-combustion capture by amine scrubbing appears promising, on one hand, for application to the cement industry, from the perspective that it is commercially available, as it is already implemented in other industrial sectors and does not require fundamental alterations to the clinker burning process **[42, 62, 66]**. Furthermore, amine scrubbing has been shown to be very efficient in abating CO_2, namely up to 98% **[4, 42]**. The aforementioned traits, according to Hoenig, Hoppe and Emberger **[42]**, make the amine scrubbing technology a noteworthy candidate to install in new kilns and retrofit existing cement kilns. However, it is very demanding in terms of energy consumption. As stated in **[67]**, a typical cement plant with 1 Mt/year capacity yields a flue gas stream comprising CO_2 at approximately 30%, or 0.26 kg/MJ of coal input. When amine scrubbing is employed, 1 kg of CO_2 is separated from the stream by consuming 3.5 to 4.5 MJ of heat. Consequently, thermal energy and electricity consumption are increased, by 1000-3500 MJ/t clinker and 50-90 kWh/t clinker, respectively **[68]**. This amounts to an overall rise in primary energy consumption, estimated at more than 3 MJ/kg CO_2 avoided, according to Hasanbeigi, Price and Lin **[68]**. Another restricting factor to direct implementation of this technology is the degradation of amine absorbents by oxygen and contaminants, such as SO_2 and NO_2 **[42, 67]**. The presence of such impurities can increase corrosion and poison the absorption solvent **[42]**, which renders the installation of the FGD and SNCR units utterly indispensable, in order to keep SO_2 and NO_2 concentrations at minimal levels (10 ppmv and 20 ppmv at 6% O_2, respectively **[67]**. Finally, a minor setback that should nevertheless be taken into account is the cement industry's practically nonexistent experience at handling and processing liquid chemical processes, as well as operating liquid solvent-based systems **[62]**. Overall, as of 2012, investment costs estimated by Hasanbeigi, Price and Lin **[68]** are set roughly at a region between \$130 to \$443 million and operations are expected to cost \$13 to \$96/t cement, excluding the costs attributed to transport and storage of CO_2. In the same context, Hoenig, Hoppe and Emberger **[42]** report that production costs will amount to approximately 45 €/t CO_2 at a 3,000 t/day cement kiln, whilst rates from power plants already using MEA technology are set between 21.6 to 55.1 €/t CO_2 avoided. Concise information regarding the amine scrubbing technology implementation in the cement industry is summarized in table 4.

Table 4: Maturity of chemical absorption technology [42]

Technology used in other sectors		Power generation Chemical industry Oil and gas industry
Technology applicable to		
	Existing clinker burning process	No
	Modified clinker burning process	• Waste heat recovery system for sorbent regeneration needed • SO_2 abatement (<10 ppm) required • NO_2 abatement (<20 ppm) required
Abatement efficiency		>98%
Energy efficiency penalty		Very high (due to additional energy demand of sorbent regeneration)
Impact on		
	Kiln operation	limited
	Product quality	no
	Other emissions	No (minor reduction of other acid flue gas components)
	Production costs	• ~45 €/t CO_2 for MEA technology at a 3,000 t/day cement kiln [106] • examples from other sectors (MEA technology) from 21.6 to 55.1 €/t CO_2 avoided [101] • Investment costs, not currently given for cement production, will be a

		significant cost driver
Advantages		• Already commercially available • Can be applied to modified plants
Challenges		• The most expensive technology at present • Very big size of equipment

1.5.3. POST-COMBUSTION CAPTURE: CALCIUM LOOPING CYCLE

Process description

The calcium (or carbonate) looping cycle is an alternative post-combustion capture technology, which is based on the separation of CO_2 from flue gases by use of lime (CaO) as solid sorbent, in order to form limestone ($CaCO_3$) **[34]**. The CaL concept makes use of the reversible carbonation reaction: $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$ **[67]** in dual fluidized bed reactors, where calcium oxide (CaO) reacts with carbon dioxide to form calcium carbonate ($CaCO_3$) in the carbonator and the reverse reaction occurs in the calciner, where a rich-CO_2 stream is produced and the CaO is regenerated for subsequent carbonation cycles **[34, 67, 69]**. Hence, CO_2, as part of the combustion flue gases stemming from the cement kiln, enters the carbonator, where it reacts with CaO particles at atmospheric pressure and temperature around 650 °C **[34]**. Subsequently, the newly formed $CaCO_3$ particles are directed to the calciner vessel, where they are decomposed into CaO, which in turn is recycled in the carbonator and a CO_2 concentrated stream. **[67, 69]**. This process occurs in an oxygen-rich atmosphere at temperatures over 900 °C **[67]**. The aforementioned process can be visualised in the simplified flow diagram provided in figure 17.

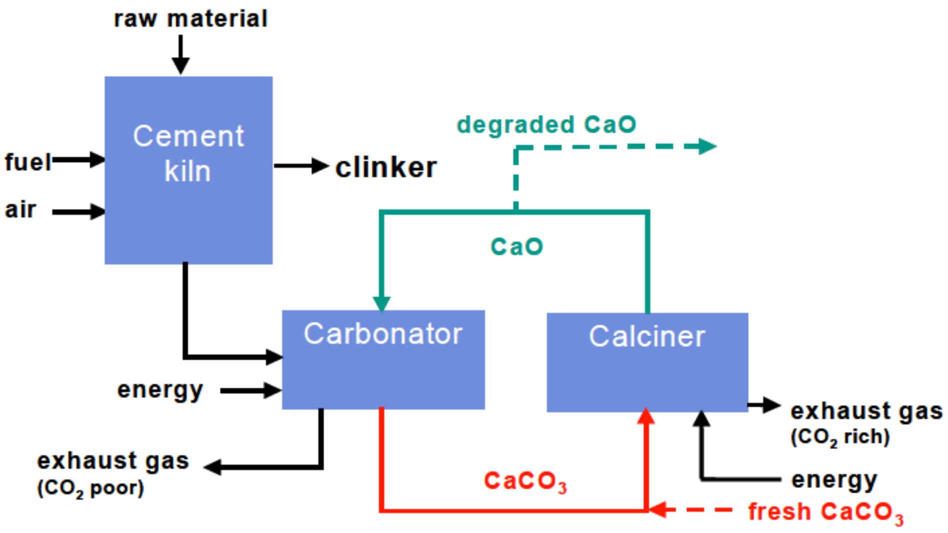

Figure 17: Simplified flow diagram of calcium looping applied at clinker making process [11]

Due to the fact that the calciner operates with pure oxygen, so as to achieve a high CO_2 concentration (>95%) **[67]**, an ASU is required, in order to supply oxygen in the capture system, for sorbent regeneration **[62]**. In addition, it is of utmost significance to keep the reactivity of CaO at high levels, since the sorbent does not fully react with CO_2. As such, part of the calciner's exit solid stream is continuously replaced (purged) and the purge stream can be fed to the cement kiln as raw material, for clinker formation **[62, 67]**. It should also be noted that, due to the high temperature profile of the exhaust streams, a waste heat recovery block would prove beneficial, in order to generate power from waste heat and offset consumption stemming from operation of additional process equipment, air separation and CO_2 compression systems **[62]**. Finally, as in the case of amine scrubbing, a CO_2 purification and compression unit is installed, along with a subsequent pipeline and injection unit, in order to remove impurities from the CO_2 stream, compress it and inject it to pipelines for transport **[62]**. Naranjo, Brownlow and Garza **[62]** proposed the following process blocks, for the integration of CaL technologies to a cement plant (figure 18).

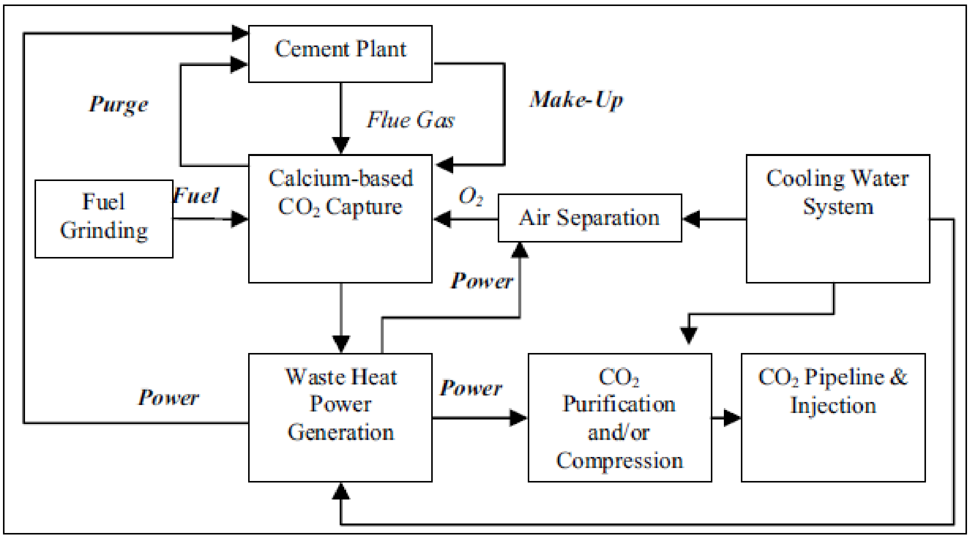

Figure 18: Calcium-based CO_2 capture technologies integrated to a cement plant [62]

Overall, several assessments **[34, 62]** have rendered CaL as a noteworthy option for retrofitting existing kilns and in the development of new oxy-firing kilns, drawing from similar experience of application in power plants. In addition, synergies of cement plants with power plants have also been considered, as deactivated sorbents from the power plant can be reused as secondary raw meal in the clinker making process **[34]**. However, complexity of the incorporation of the carbon capture system to the plant, as well as the waste heat recovery potential require further optimization and analysis **[62, 67]**, mainly in terms of efficiency maximization of the power production by means of waste heat recovery and the extent of CO_2 purity, which currently poses an impediment, due to the increased presence of oxygen in the stream **[62]**.

Advantages & Challenges

Post-combustion CO_2 capture utilizing carbonate looping technology demonstrates certain conceptual benefits and as Atsonios et al. **[69]** maintain, it seems to be the most appropriate capture technology for integration in the cement industry, for several reasons. Firstly, the cement industry is inherently familiar with handling and processing of CaO-bearing materials **[69]** and utilization of the CaO sorbent proves advantageous, in the sense that its reuse reduces the waste stream **[64, 68]** and the purge CaO stream is available for use in cement production, as it is compatible with the cement raw meal **[69]**, thus yielding 50% less CO_2 emissions from the cement plant **[68]**. In this context, natural limestone reserves are conserved and cement plants with such reserves situated nearby can be self-sustainable, in terms of limestone supply to the carbon capture system **[64, 68]**, hence diminishing the cost of limestone required for the enhancement of the circulating solids capture ability **[69]**. Furthermore, implementation of CaL offers the potential of waste heat recovery, in the form of high pressure steam dissipated from the capture unit, which can be used for power production, thus reducing its CO_2 footprint **[67]**. In addition, according to Naranjo, Brownlow and Garza **[62]**, the same plant fuel can be used to operate the CO_2 capture system, which is likely to decrease associated costs. Finally, Dean et al. **[70]** report that use of the fluidized bed technology in both carbonator and calciner vessels is beneficial, as it already established and deployed on a large scale.

On the contrary, there are several issues hindering large-scale application of CaL technology, that need to be addressed. As mentioned before, tracking of oxygen and other inert gases in the CO_2-rich stream creates the necessity for a CO_2 purification unit, and, due to i) health & safety reasons (explosion avoidance), ii) technical reasons (corrosion) and iii) increase in storage capacity, limitations for gaseous components are rather stringent **[69]**. As such, research and development is required in order to deliver a CO_2 stream that meets the specifications and is ready for pipeline transportation, and for such settings, the costs are expected to be significant **[62]**. Another concern, highlighted by Atsonios et al. **[69]**, is the effective removal of the heat produced inside the carbonator, which is hampered, due to the geometry of the carbonator and the high heat fluxes observed at its bottom region. To counteract this setback, the authors, in line with the CALMOD project (a large-scale CaL test facility) **[71]** have proposed bed material coolers, in order to decrease the temperature of the calcined sorbent, before it enters the carbonator, so that the amount of heat extracted from the carbonator and the carbonator itself operates in stable conditions, in turn. Finally, according to Atsonios et al. **[69]**, in order for CaO to be used as raw material for cement production, there must be limitations to ash and CaSO4 concentrations (30% and 10% wt. respectively), according to Bosoaga, Masek and Oakey **[34]** and Weimer et al. **[72]**, as presence of SO_3 in the purge stream disrupts the kiln's operation, leading to clogging; and the source of this is the composition of the fuel which is introduced in the calciner; thus it affects both the performance of the carbon capture system and the quality of the CaO exiting the calciner **[69]**.

1.5.4. OXY-FUEL COMBUSTION

Process description

Carbon capture using oxy-fuel technology (figure 19) relies on fuel combustion in the presence of pure oxygen, separated from ambient air before entering the kiln, and recycled flue gas, which results in a final flue gas stream consisting mainly of CO_2 and water vapor, which facilitates the procedure of purification **[61]**.

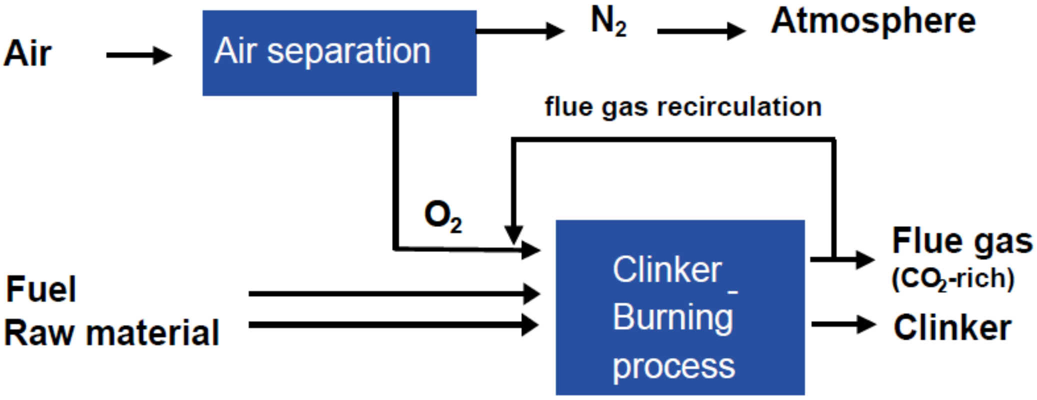

Figure 19: Oxy-fuel technology with flue gas recirculation [11]

Integration of this technology in the cement industry may be implemented with two different approaches: the full and the partial oxy-fuel concept. By applying the first concept, both the precalciner and the rotary kiln are operated under oxy-fuel conditions **[66]** and almost all generated CO_2 can theoretically be captured **[73]**, as, reportedly, CO_2 concentrations in over 80% (compared to 20-30% in a conventional process) **[67]**. The required additional installations for the oxy-fuel kiln, as depicted in figure 20, according to the International Energy Agency **[73]**, are the following:

i) rotary kiln burner for oxy-combustion

ii) cryogenic ASU: nitrogen is removed from ambient air, remaining oxygen (95 mol% O_2 with 2 mol% N_2 and 3 mol% Ar, as per **[39]**) is mixed with recirculated CO_2 (forming the oxidizer) and supplied to precalciner and kiln firing and cooling gas premixing. Estimated oxygen demand for a typical 3,000 tpd cement plant is 30 to 35 tph.

iii) exhaust gas recirculation system: around 50% **[34, 39]** of CO_2-rich flue gas produced in the precalciner is stripped from heat, dust and water vapor and directed to the burners.

iv) gas-gas heat exchanger: used to extract heat from the flue gas leaving the preheater and increase the drying potential of the exhaust air in the cooler.

v) condensing unit

vi) two-stage clinker cooler: first stage is operated with recycled flue gas, second with ambient air, while the air leaving the cooler may be used for raw material drying or fuel preparation.

vii) CO_2 purification unit (CPU): needed to enrich the carbon dioxide stream and prepare it for transport and storage.

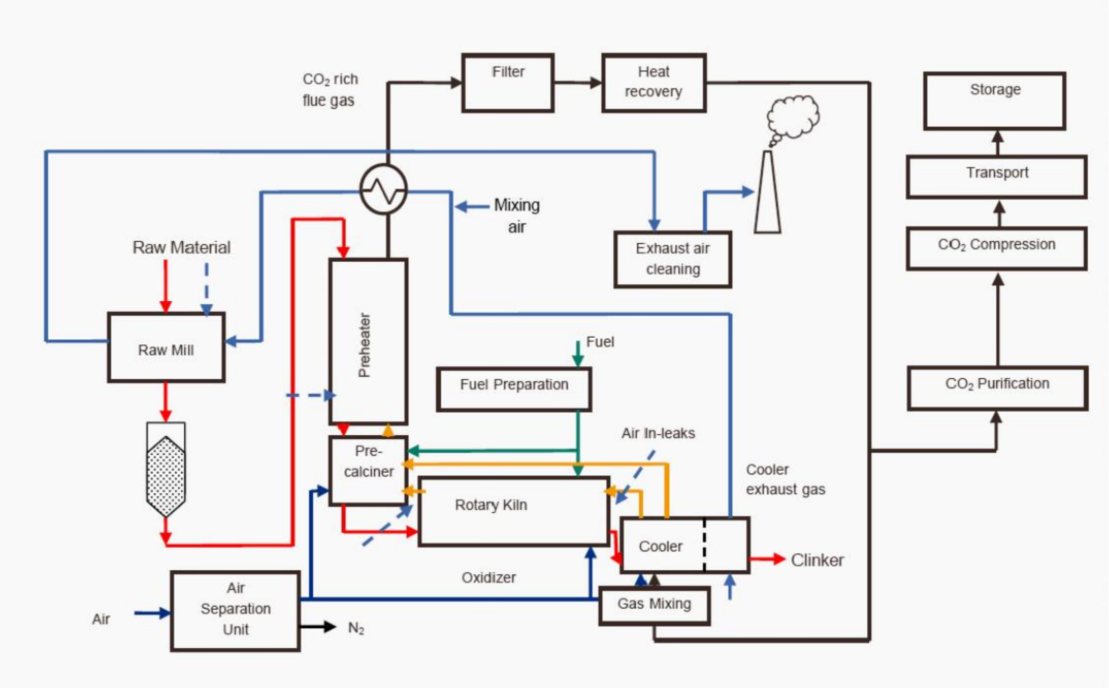

Figure 20: Block diagram of full oxy-fuel CCS technology applied at a cement plant [66]

As fuel and raw material are introduced into the burning process, part of the flue gas is mixed with the pure oxygen, in order to raise the feed temperature and also adjust the temperature in the kiln **[64, 67]**. The International Energy Agency **[73]** reports that this changed gas atmosphere, under full oxy-fuel conditions, has an impact an all plant units, as different gas properties (heat capacity, emissivity, density) affect heat transfer, combustion, material and gas capacity streams, clinker formation and eventually product quality. In addition, Vatopoulos and Tzimas **[67]** state that oxygen concentration should be kept at levels between 30-35% v/v at maximum, in order to avoid excessive damage to the cement kiln, due to the increased oxygen presence. Regardless, Hoenig, Hoppe and Emberger **[42]** state that air intrusion is extremely challenging to prevent, in order to establish combustion under oxy conditions, as the entire plant has to be sealed or else operated with excess pressure.

In the context of partial oxy-fuel combustion, a CO_2 stream is recovered at the end of one of the dual preheaters, after fuel is combusted under oxy-fuel conditions in the precalciner only **[73]**. The same authors have described the process blocks of the cement plant configuration depicted in figure 21, as following; in the same manner as in full oxy-fuel, a mixture of oxygen from the ASU and recycled flue gas enter the calciner. In this case, two preheaters are installed, both of which send the preheated raw material to the precalciner and subsequently to the rotary kiln; preheater 1 is operated with flue gases from the kiln, which can also be used for raw material drying, whereas preheater 2 receives the flue gases from the precalciner. Tertiary air stemming from the cooler is provided to the calciner and can also be utilized for preheating, drying or even power generation.

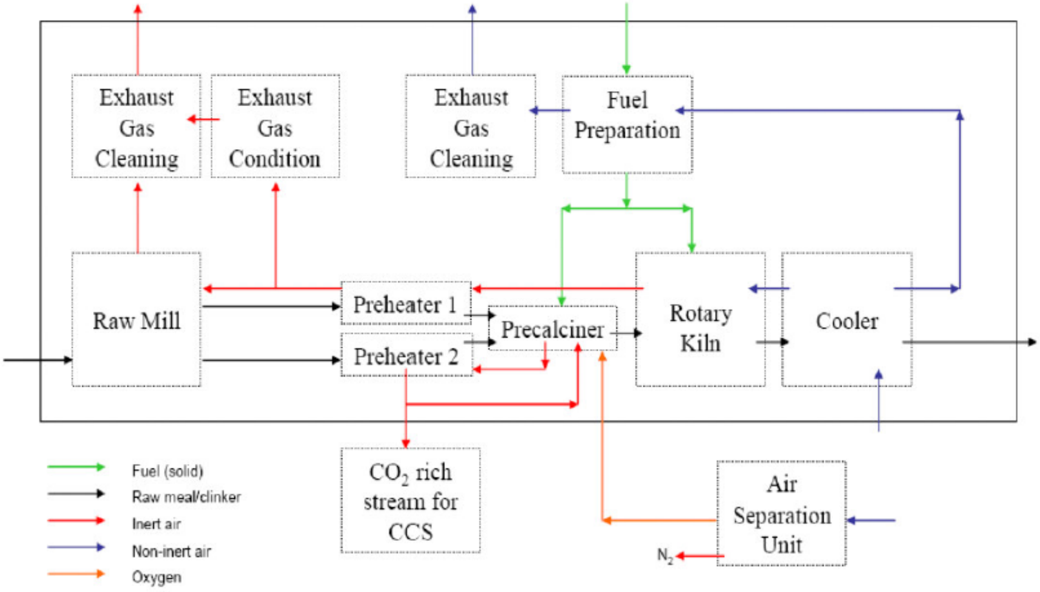

Figure 21: Block diagram of proposed partial oxy-fuel CCS technology applied at a cement plant [66]

The International Energy Agency **[73]** also explains that this specific technology exploits the fact that most (approximately 60%) of CO_2 emissions stem from the decarbonation procedure occurring in the calciner and the respective fuel input (60% of total fuel input). With the rest of the process units functioning conventionally, there is no requirement to improve the seals (as in the full oxy-fuel case) and the product quality is not affected. This concept has garnered attention for retrofitting, due to minimal interventions in kiln plant design and operation **[73]**, however the downside of this technology lies to the higher energy demands in the main burner, which, combined with expected losses from the CO_2 purification unit, yields a lower capture rate (60%, compared to >85% of full oxy-fuel **[73]**).

Advantages & Challenges

Considering the aforementioned traits of both oxy-fuel combustion technology aspects, there are certain advantages that arise. Vatopoulos and Tzimas **[67]** indicate that oxy-fuel combustion technology reduces overall energy consumption and its use leads to a negative energy plant for a cement plant. In this context, Hasanbeigi, Price and Lin **[68]** report that overall energy requirements drop by 75 to 84 MJ/t cement, fuel use is reduced by 100 to 200 MJ/t clinker, compared to conventional processes and this in turn reduces CO_2 emissions from 454 to 726 kg CO_2/t cement. Regarding emissions, the International Energy Agency **[73]** and Hasanbeigi, Price and Lin **[68]** point out that, if partial oxy-fuel combustion is used, approximately 60% of generated CO_2 emissions can be abated, whereas in the case of full oxy-fuel combustion (in both precalciner and kiln) this percentage rises to almost 100%, even though technical uncertainties are associated with this approach. Moreover, Bosoaga, Masek and Oakey **[34]** highlight that the main advantage of the process is the low oxygen consumption, "*with only 1/3 of the amount of* O_2 *needed per tonne of* CO_2 *captured compared to a coal-fired boiler*". Furthermore, Hoenig, Hoppe and Emberger **[42]** note that the cement industry can benefit from the fact that oxygen production by air separation is already a state-of-the-art technology. The authors also mention that, since the flue gas has a high CO_2 concentration (around or above 80%), CO_2 capture from flue gas is not necessary. Finally, Hasanbeigi, Price and Lin **[68]** and Hoenig, Hoppe and Emberger **[42]** cite certain experiments conducted with oxygen enrichment in kilns, which have managed to increase the kiln capacity.

As expected from a technology that has not yet reached its full potential and readiness level, oxy-fuel combustion comes with drawbacks as well. Hasanbeigi, Price and Lin **[68]** report that this process increases electricity use by 92 to 96 kWh/t clinker, attributed mainly to the CO_2 separation, purification and compression facility and the ASU. The authors also maintain that the previously mentioned drop in CO_2 emissions would be partially offset by the respective increase in electricity use, which is associated with CO_2 emissions ranging between 50 and 68 kg CO_2/t cement. One of the main challenges that currently encumbers the wider application of the technology is the excessive degree of retrofitting necessary to take place at the cement plant, in order to comply to the requirements of the oxy-fuel technology. As such, measures must be taken to hedge against air intrusion in the raw mill, preheater and kiln, resulting in contamination of the CO_2-rich flue gas **[39]**. Also, new processes, such as the ASU (requiring power in the range between 200-240 kWh/t O_2 **[39]**) and the flue gas recirculation must be installed. Due to different flue gas flows and enthalpies, owed to the changed atmosphere inside the combustion chamber **[39]**, a different clinker cooler efficiency is needed **[34, 42]**. The above factors lead to oxy-fuel combustion being predominantly considered an option for new plants **[42]**. In addition, there still are specific technology gaps that need to be bridged; the impact of the O_2/CO_2 atmosphere on calcination, sintering and product quality must be further investigated, as their effects are currently unknown **[39, 42, 67]**. In addition, the thermal load and the high flame temperatures (in excess of 3500 °C **[39]**) produced during oxy-fuel combustion **[42]** will probably augment deterioration of the cement kiln wall and its refractory durability **[39]**. Finally, Mott Macdonald **[66]** suggest that oxy-fuel combustion technology, applied at a cement plant, may generate wastes, which will require handling and disposal. Specifically, the authors report that the main waste considered is condensed water, containing acidic components, which would oblige the cement plant to neutralize them before discharge or reuse. Overall, Hasanbeigi, Price and Lin **[68]** have estimated the additional investment costs for application of oxy-fuel technology to a new facility, excluding costs related to CO_2 transport and storage, to range from \$495 to \$540 million, whereas operational costs are expected to increase by \$10 to 13/t cement for a facility producing 2.2 milliont/yr.

1.5.5. EVALUATION OF CCS TECHNOLOGIES

Introduction

After having thoroughly reviewed the three main carbon capture technologies in the previous sections, this part of the report attempts a quantitative comparison, based on specific performance indicators mentioned in **[67]**, to elucidate the manner in which the performance of a cement plant is altered, when it incorporates these technologies. These are: i) raw material consumption (kg of limestone per kg of clinker), ii) energy consumption (energy consumed per kg of clinker produced), iii) energy recovery potential (potential recovery in terms of high pressure steam for power generation and of low pressure steam for heat integration), iv) CO_2 footprint and reduction in CO_2 emissions (CO_2 emitted per kg of clinker produced), v) CO_2 capture energy penalty, compared to consumption of a cement plant applying conventional processes and vi) cement plant costs, compared to a cement plant without CO_2 capture.

Raw material & energy consumption

With respect to specific raw material consumption, Vatopoulos and Tzimas **[67]** have found that the conventional plant consumes 1.5 kg per kg of clinker produced, whereas the application of carbon capture technologies has a negligible effect on this figure. In terms of energy consumption, the authors had the following findings, reproduced in table 5.

Table 5: Energy consumption results [67]

Technology	No capture	Oxy-fuel combustion	Amine scrubbing	CaL
Energy consumption	**kJ/kg clinker**			
Fuel	2918.08	2985.67	2918.33	4874.65
Electricity clinker plant	522.00	522.00	522.00	522.00
ASU	0.00	84.49	0.00	111.15
MEA scrubber	0.00	0.00	3508.18	0.00
FGD	0.00	8.25	37.82	11.06
CO_2 purification	0.00	212.19	191.63	206.78
CO_2 compression	0.00	43.90	241.02	260.07
Sum	**3440.08**	**3856.51**	**7418.98**	**5985.70**

By observing this table, it becomes evident that the specific energy consumption, compared to the conventional plant, increased in all capture scenarios, namely 45% in the case of amine scrubbing, 18% in the case of CaL and 12% in oxy-fuel combustion. These differences are also depicted in figure 22.

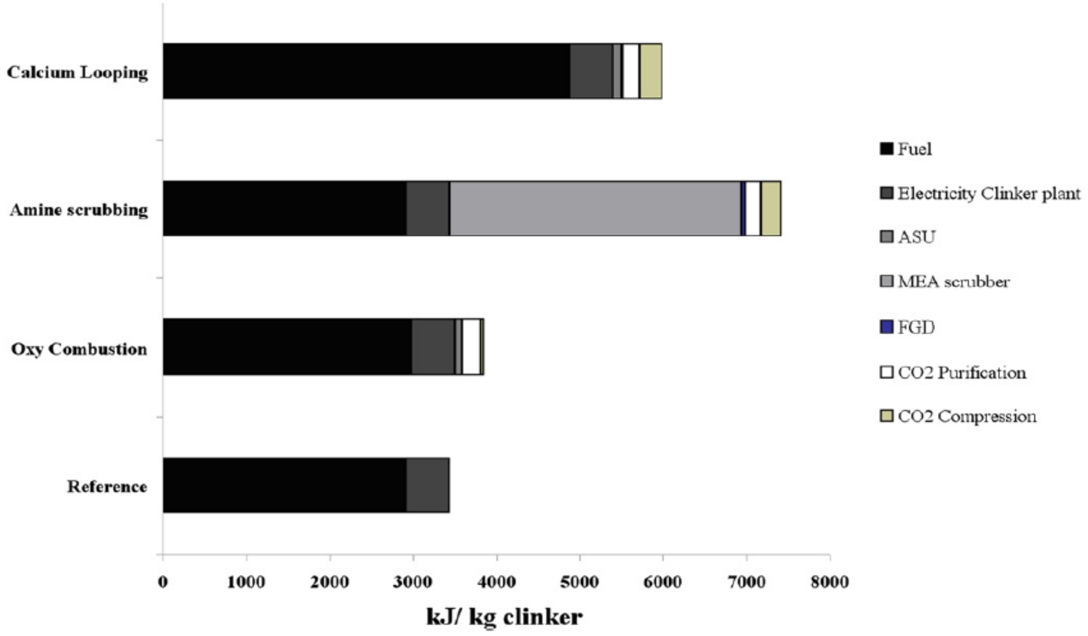

Figure 22: Energy intensity in kJ/kg of clinker produced [67]

According to the authors, the increase in the case of MEA is owed to the heat demand of the desorber reboiler, while in CaL, the main sources of energy consumption are the additional fuel on which the calciner operates and the additional oxygen produced in the ASU and provided to the calciner. On the other hand, oxy-fuel combustion was found to require significantly less energy, as the energy consumed in the ASU to produce oxygen is less than the savings in fuel consumption **[67]**. The difference between post-combustion capture and oxy-fuel combustion in terms of energy consumption is also validated from a study by the International Energy Agency **[74]**, the results of which are summarized in table 6.

Table 6: Summary of cement plant performance with and without CO_2 capture [74]

	Unit	**Base case (no capture)**	**Post combustion capture**	**Oxy-fuel combustion**
Fuel and power				
Coal feed	Kt/y	63.3	291.6	72.1
Petroleum coke feed	Kt/y	32.9	32.9	27.1
Total fuel consumption (LHV basis)	MW	96.8	304.0	97.8
Average power consumption	MW	10.2	42.1	22.7
Average on-site power generation	MW	-	45.0	0.7
Average net power consumption	MW	10.2	-2.9	22.0
CO_2 emitted and captured				
CO_2 captured	Kt/y	-	1067.7	465.0
CO_2 emitted on-site	Kt/y	728.4	188.4	282.9
CO_2 emissions avoided at the cement plant	Kt/y	-	540.0	445.6
	%	-	74	61
CO_2 associated with power	Kt/y	42.0	-11.8	90.8

import/export				
Overall net CO_2 emissions	Kt/y	770.4	176.6	373.7
CO_2 emissions avoided, including power import and export	Kt/y	-	593.8	396.8
	%	-	77	52

Evidently, without taking into account the on-site power generation potential, post-combustion capture consumes 42.1 MW, whereas oxy-fuel combustion requires significantly less power (22.7 MW).

Energy recovery potential

In terms of energy recovery potential, Vatopoulos and Tzimas **[67]** analyzed the heat duties and temperatures of streams targeted for heat integration and hence found that CaL displayed the highest potential. Reportedly, the CL process had 3.8 times more energy recovery potential than the oxy-fuel combustion and 11.5 times than more MEA (figure 23).

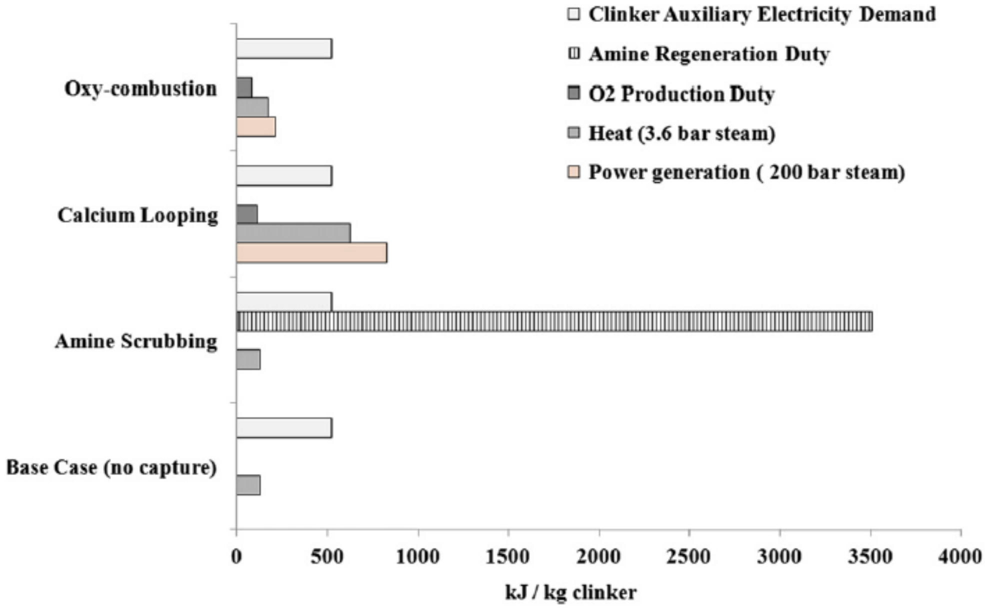

Figure 23: Energy recovery potential of capture technologies [67]

This result was attributed to the resulting high temperature CO_2 and flue gas streams. The power generation potential, as seen in the figure, would be able to cover the energy of the ASU and the electricity duty of the auxiliary clinker production unit. In the MEA scenario, the available waste heat (125 kJ/kg clinker) can satisfy only 4% of the energy required to operate the amine regeneration boiler (3508 kJ/kg clinker) by being recovered as low pressure steam

[67]. The results for the oxy-fuel combustion scenario also displayed a certain potential for power generation from waste heat, which, in this case, could also cover the ASU. From the same point of view, Barker et al. **[39]** showed that post combustion capture offers a great potential for power generation (45 MW), while the respective contribution of oxy-fuel combustion capture is trivial, at 0.7 MW (table 6).

CO_2 footprint - emissions reduction - capture energy penalty

In terms of carbon footprint, i.e. the amount of CO_2 which is not captured by the technologies under consideration, Vatopoulos and Tzimas **[67]** found that post-combustion technologies display a similar performance (CaL and amine scrubbing reduce specific CO_2 emissions by a factor of 6.8 and 6.7, respectively), whereas, if oxy-fuel combustion is applied, this factor reduces to 3.6 (figure 24).

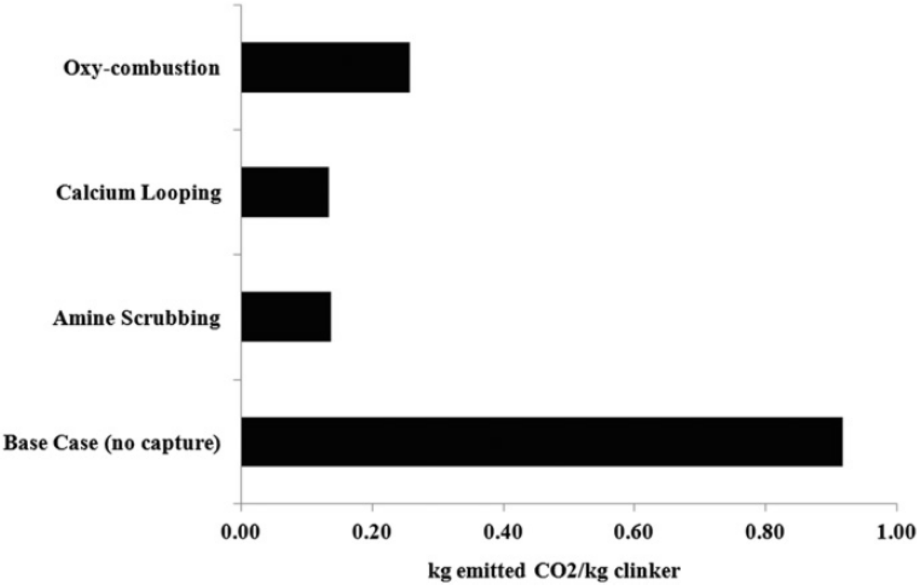

Figure 24: Specific CO_2 emissions of carbon capture technologies [67]

The decreased capture efficiency, according to the authors, is mainly owed to the fact that by electing a partial oxy-fuel combustion configuration, CO_2 is only captured at the precalciner; alternatively, if a full oxy-fuel combustion system was considered, as mentioned before, the capture efficiency would display an abrupt increase. It should also be noted that this study considered only the direct avoided CO_2 emissions, as fuel use in supporting units (ASU, CO_2 purification, steam boilers etc.) and electricity production by waste heat recovery, which would offset the produced CO_2 emissions, were not taken into account. Table 6 serves as supporting evidence, since post-combustion capture application was found to emit 188.4 kt/year, where, on the other hand, oxy-fuel combustion capture is associated with a higher amount of CO_2 emissions, namely 282.9 kt/year **[39]**. The International Energy Agency **[74]** has also indicated that the CO_2 capture potential is greater in post-combustion technology

(1067.7 kt/year) than in oxy-fuel combustion (465 kt/year). In the same direction, CO_2 avoidance of amine scrubbing at the cement plant was found to be as high as 74%, whereas oxy-fuel combustion capture, applied only at the precalciner, abated only 61% of total CO_2 emissions (table 6).

Another vital performance indicator which was considered for the comparison of the highlighted carbon capture technologies is the carbon capture energy penalty, which, according to Vatopoulos and Tzimas **[67]** is defined as "*the additional energy required as an input to the clinker process in order to capture the* CO_2". As such, oxy-fuel combustion was found to be the least energy-intensive option, namely 81% less than amine scrubbing (figure 25), whereas CaL stands in between, being 43% less energy-intensive than MEA. Reportedly, this result is associated with the lower capture efficiency of oxy-fuel combustion, as well as its lower fuel requirements per ton of clinker in the clinker making process **[67]**.

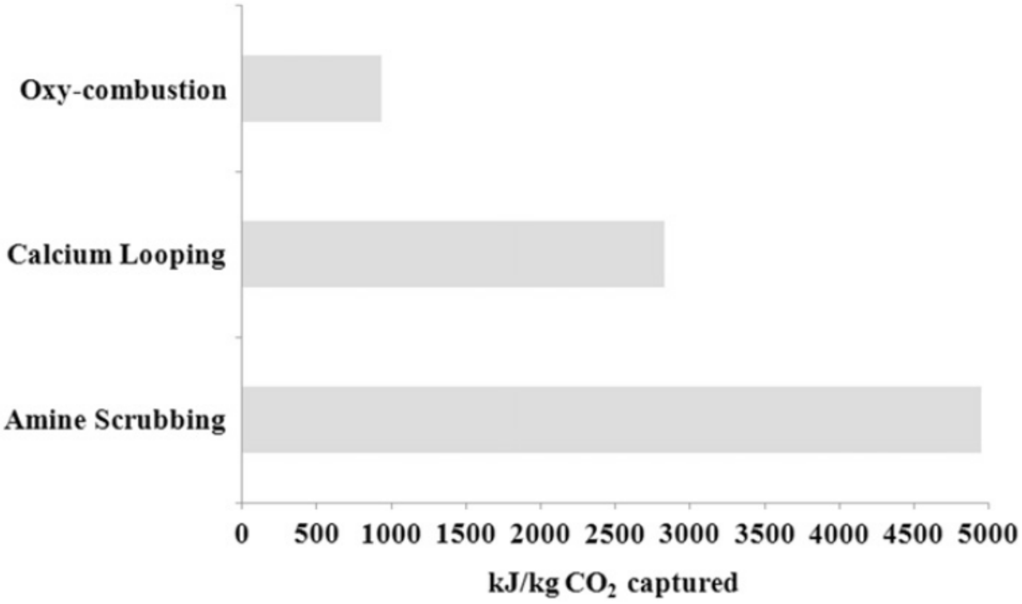

Figure 25: Specific CO_2 capture energy penalty [67]

Carbon capture costs

As far as costs of applying carbon capture to the cement industry are concerned, there is scarce literature available, since there is significant uncertainty **[66]**. Mott Macdonald **[66]**, taking into account transportation and storage costs, estimated an avoided cost to society of 45-60 €/tCO_2, with the range reflecting new build versus retrofit. Regarding post-combustion capture by amine scrubbing, Mahasenan, Dahowski and Davidson **[75]** estimated the capture cost at about \$50/tCO_2. **[76]** evaluated the performance of MEA retrofitted at a 1.4 Mt/y cement plant in Norway and set the total cost per capture at 46 €/tCO_2. In addition, Mott Macdonald **[66]** indicated that, for a 1Mt/y plant, sited in the UK, the cost per tonne of CO_2

emissions avoided, in case of retrofitting the plant with MEA, was 107.4 €/t. Barker et al. **[39]** have dignified this high cost to three aspects, namely i) lower economies of scale, ii) the need to install an FGD unit and iii) the relatively high costs associated with solvent regeneration, with respect to provision of steam from CHP plants.

Review of the available literature highlighted the fact that, due to the extent of the required modifications on existing cement kilns, costs for oxy-fuel combustion capture cannot be accurately defined at the moment. For example, Zeman and Lackner **[77]** set a minimum limit for a novel REO (reduced emission oxygen) kiln at \$15-18/tCO_2 captured, assuming a 1.4 Mt/y cement plant, but admitted that this stage of research does not allow for feasible cost estimations. Mott Macdonald **[66]**, in the same sense as with the MEA scenario, estimated the cost of CO_2 emissions avoided at 42.4 €/tCO_2, excluding transport and storage costs, which overall is substantially lower than the case of post combustion capture. On this subject, Barker et al. **[39]** have pointed out that oxy-fuel combustion displays a conceptual advantage, since oxygen is only required for the CO_2 that originates from fuel combustion and not for the respective stream that stems from mineral decomposition, thus deeming the technology suitable for application at cement plants.

1.5.6. CURRENT BARRIERS - FUTURE ACTIONS

Pilot projects

Experimental investigation of the performance of the aforementioned technologies being implemented on cement plants, is still at a very early stage, as, apart from project announcements, pilot projects have not yet commenced. On the contrary, regarding the power sector, several projects have been commissioned, such as the 1.7 MW_{th} pilot plant at La Pareda by ENDESSA in Spain, the 1 MW_{th} at TU Darmstadt Germany, the 200 kW_{th} pilot at IFK University of Stuttgart, as well as a 1.9 MW_{th} pilot plant currently under construction in Taiwan at ITRI, all of which are testing the application of post combustion capture by CaL. In the same context, oxy-fuel combustion technology, although appearing as a prominent candidate for CO_2 capture at cement kilns **[42]**, is currently under demonstration at small-scale power plants and results obtained may be helpful towards application to future cement plants **[42]**, so its application lies still on a conceptual level. Furthermore, the Verein Deutscher Zementwerke is preparing a similar project, in order to delve into the parameters defining oxy-fuel technology. More specifically, research objectives are threefold: i) to evaluate plant and process requirements and limits of the oxy-fuel technique, ii) to assess impacts on energy balance, clinker quality and plant operation and to determine the composition of the flue gas subject to oxy-fuel enrichment **[42]**. Developments are only noticed in the field of amine scrubbing, as Heidelberg Cement has commissioned a pilot cement plant in Brevik, Norway (figure 26), where, among other experimental work packages, an amine-based solvent (termed S26) is currently scrutinized by Aker Solutions for post-combustion capture. Recent (2014) testing results yielded a low build-up of degradation products and stable performance above 90% capture, after approximately 2700 hours of operations **[78]**. Heat requirements for solvent regeneration were found as low as 2.7 MJ/kgCO_2 and a further reduction to 2 MJ/kgCO_2 is expected, from the time when heat integration with CO_2 compression is made available **[78]**.

Figure 26: Aker's pilot at Brevik cement factory [78]

Technical barriers

From a technical perspective, application of carbon capture technologies to the cement industry is not likely to be commercially available before 2020 **[4]**. Before that time, research and development efforts are needed, so that practical experiences are gained and potential bottlenecks can be overcome. The current status of post-combustion capture, although a state-of-the-art in other industry sectors **[11]**, dictates specific requirements for further investigation, such as: i) less energy intensive solvent regeneration by use of new solvents **[73]**, ii) integration of capture plant with waste heat recovery **[73]**, iii) waste solvent disposal with respect to clinker chemistry **[34, 73]** and process operation, iv) further investigation of CaL **[73]** and the scale-up of demonstrations **[34, 67, 79]**. Issues also exist in the current status of oxy-fuel combustion capture, such as: i) reduction of electricity demand by low-energy oxygen supply **[73]**, ii) produced clinker quality **[39, 42, 67, 73]**, iii) refractory durability of kiln due to increased flame temperature **[33, 43]** and iv) sealing aspect in long-term operation **[39, 73]**.

Hoenig, Hoppe and Emberger **[42]** highlight potential objectives of future research projects, the most important of which are: i) to contribute to the development of capture technologies for new and existing cement plants, ii) to influence developments in equipment from various suppliers, by means of joint CCS projects and iii) to regularly assess CCS projects from scientific, economic and political aspects. In this context, Mott Macdonald **[66]** have estimated a learning rate of 1% per year for amine scrubbing and oxy-fuel combustion, for the period between 2030 and 2050. Therefore, such objectives, if fulfilled, will lead to a more thorough understanding of the capture technologies, with the ultimate goal being the seamless integration of carbon capture in the cement industry. Also, CSI's forecast **[4]** is that kilns with a capacity of less than 4,000-5,000 tpd will not be equipped with CCS and that retrofits will not be common. CSI also estimates that CCS would be commercially available in 2025.

Economic and other barriers

Besides from technical barriers, the economic framework shall be decisive for application of CCS to cement plants in the future **[4, 42]**. The 2009 rate of abating carbon dioxide ranging from 20-75 €/tCO_2 captured **[4]**, is expected to drop at a target value in the order of 20-30 €/tCO_2 **[42]**, through gradual technical and scientific evolution, in order to make CCS a more viable option. It should be noted that the aforementioned wide value range corresponds to the very different values given for individual technologies in the literature. Other parameters that will play a significant role in the near future are:

i) the political support, through research funding, government incentives and the promotion of CCS as a valuable tool of a comprehensive climate change strategy **[4, 42]**,

ii) the willingness of property owners to cooperate, in order to obtain relevant permits and approvals for CO_2 transport and storage sites, as well as the local residents' approval of proposed projects in their communities **[4]**.

iii) dedicated education and information campaigns to raise awareness of public and stakeholders about CCS **[4]**.

iv) future climate policy should become apparent **[42]**. In such case, where the political backbone is supportive and social acceptance is achieved, according to CSI **[4]**, it is probable that, after 2020, CCS will become commercially implemented.

PART B: LIFE CYCLE ASSESSMENT OF CEMENT PRODUCTION EMPLOYING CARBON CAPTURE TECHNOLOGIES

2.1 GENERAL

Life cycle assessment (LCA) is a technique that assesses a product's life cycle from the point of raw material acquisition (cradle) through to production, use, recycling and disposal (grave), in terms of environmental aspects and potential environmental impacts, i.e. environmental consequences throughout the phases the product undergoes. In each stage, it encompasses input in terms of mass and energy and output in terms of generated waste and emissions to the environment, which serves as a valuable decision making tool for material selection or environmental strategy planning.

Life cycle assessment comprises four basic stages, namely:

i) goal and scope definition (ISO 14040): LCA's aim and method, system boundaries, and functional unit are defined.

ii) inventory analysis (ISO 14041): input and output data, in terms of mass, energy and emissions are identified for each product phase, with correlation to the elected functional unit.

iii) life cycle impact assessment (ISO 14042): inventory data are converted into environmental impacts of the product's life cycle by characterization factors corresponding to each material/emission.

iv) interpretation of results (ISO 14043): aforementioned converted data are compared against benchmark values for each impact category and their effect on the environment is evaluated, followed by estimations on potential corresponding improvements.

2.2 LCA GOALS

The literature review presented in the first part of this study can be summarized in the following key points:

i) cement is a significant industrial product, closely correlated with the economic development of a country.

ii) Cement manufacturing is an energy-intensive industry (thermal energy is consumed during combustion of raw materials, while great amounts of electricity are consumed during processes such as cement grinding).

iii) Cement industry is a serious contributor to GHG emissions (mainly CO_2).

iv) Out of the CO_2 mitigation technologies presented earlier on, post-combustion capture of CO_2 by chemical absorption (MEA scrubbing) is seemingly considered a promising CO_2 abatement measure, since it is already commercially available, even though it is the most expensive technology at present. Furthermore, post-combustion carbon capture by calcium looping displays the greatest potential in terms of compatibility, due to the nature of the sorbent, which, after its use, can serve as raw material for cement production.

v) there is a lack of environmental studies - and especially life cycle assessments - exploring the implementation of carbon capture & storage in cement production **[80]**.

In view of the above key points, the present study analyzes the life cycle of cement in a conventional cement plant (CCP) and, keeping the input and output of the cement manufacturing process constant, quantifies the additional input required and output produced for the application of amine scrubbing and CaL, each in contrast with the base case. This procedure sought to reach the following goals:

i) to verify the predominant causes, due to which cement production affects the environment;

ii) to detect the processes within cement production which are more energy-intensive and produce more GHG emissions;

iii) to evaluate the environmental impact of two different types of post-combustion capture technology when installed at a cement plant;

iv) to juxtapose the post-combustion capture cases with the CCP scenario, in order to elucidate the differences between cases and ultimately assess the value and effectiveness of post-combustion capture technologies as a CO_2 mitigation strategy.

2.3 LCA SCOPE DEFINITION

In order to reach the aforementioned goals, focus was set on the individual processes associated with cement production, by quantifying total inputs (raw material, energy) and outputs (in terms of CO_2 emissions) of each system that participates in the manufacturing procedure. For the conventional case, a cement plant in Thessaloniki, Greece was considered. For the post-combustion capture scenarios, since the cement manufacturing process is assumed to remain unadulterated, as already stated by Garcia-Gusano et al. **[80]** and Volkart, Bauer and Boulet **[81]**, respective inventory was kept constant, thus, each post-combustion capture case encompasses the data for conventional cement manufacturing and the additional inputs and outputs from the respective capture unit. The functional unit utilized for the assessment was 1 kg of ordinary Portland high-strength cement, type CEM II 42.5, which is the most common cement type destined for concrete manufacturing in Greece **[82]**.

2.3.1 System boundaries

The system boundaries of the LCA of all cases are described schematically in figures 27-29. All assessments are a cradle-to-gate analysis of the cement manufacturing process, commencing from extraction of materials and ending to production of cement. The carbon capture cases do not include CO_2 compression, transport and storage, i.e. these processes are not included in the system boundaries of the carbon capture cases.

It is easily observed that the typical cement manufacturing process is divided into 5 basic processes, which are namely raw material extraction, transportation, raw meal preparation, clinker formation and cement production. Within the boundaries of this procedure, every process requires certain resources, such as diesel oil, electricity, petroleum coke, and materials that are added to form the end product, i.e. 1 kg of cement. As expected, each process and resource utilized also result to a specific level of CO_2 emissions. The inventory analysis contained in the following pages withholds more detailed information on the life cycles of each product and individual processes participating in the cement production.

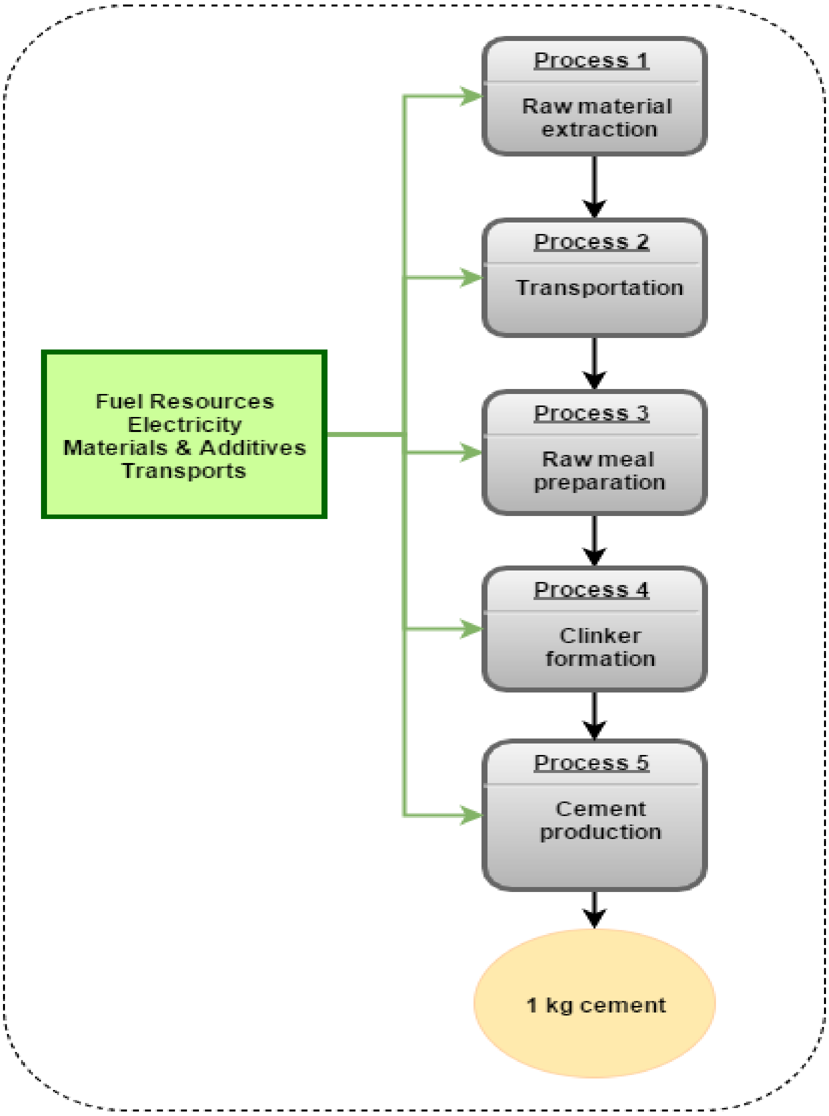

Figure 27: System boundary of CCP

Concerning the actual cement making process, the second scenario remains unscathed and, in accordance with Hoenig, Hoppe and Emberger **[42]**, the minor changes imposed on the plant configuration and especially in the clinker burning process do not have a significant effect on the total product quality. The main difference with the first scenario lies in the installation of two additional process blocks depicted in figure 28, i.e. a coal-fired CHP plant and a MEA scrubbing CO_2 capture unit. Garcia-Gusano et al. **[80]** cite that, due to the fact that the cement process emits great amounts of CO_2 - and hence the MEA unit will in turn filter these great amounts - "*huge quantities of low pressure steam are needed for* CO_2 *solvent regeneration*". As such, the CHP plant is used to provide heat in the form of steam for the regeneration of MEA. It also produces sufficient electricity to cover the requirements of the clinker formation and cement production processes, and the surplus is delivered to the grid, while it is assumed that this excess electricity will displace electricity from the mix fuel, reducing the respective demand. The fuel mix used in Greece for electricity production was assumed **[83]**. Finally, CO_2 produced during coal combustion within the CHP plant premises is assumed to be directed to the CO_2 capture unit.

Regarding the post-combustion CO_2 capture unit, as Garcia-Gusano et al. **[80]** suggest, it is placed in the clinker formation unit, after the flue gas cleaning, where concentrations of carbon dioxide are approximately 20%. Although CO_2 emissions in the part between the cyclones and the raw mill are higher, great proportions of cement kiln dust (CKD) are present, thus incapacitating post-combustion capture at this point **[81]**. In addition, the unit, apart from the absorber and desorber columns, explained in earlier chapters of this study, comprises an SCR unit, which utilizes ammonia (NH_3) in order to transform NO_x contained in the flue gas stream into N_2 and water **[80]**. Moreover, a FGD unit, consuming wet limestone is assumed, in order to further purge the flue gas stream from SO_x **[80]**.

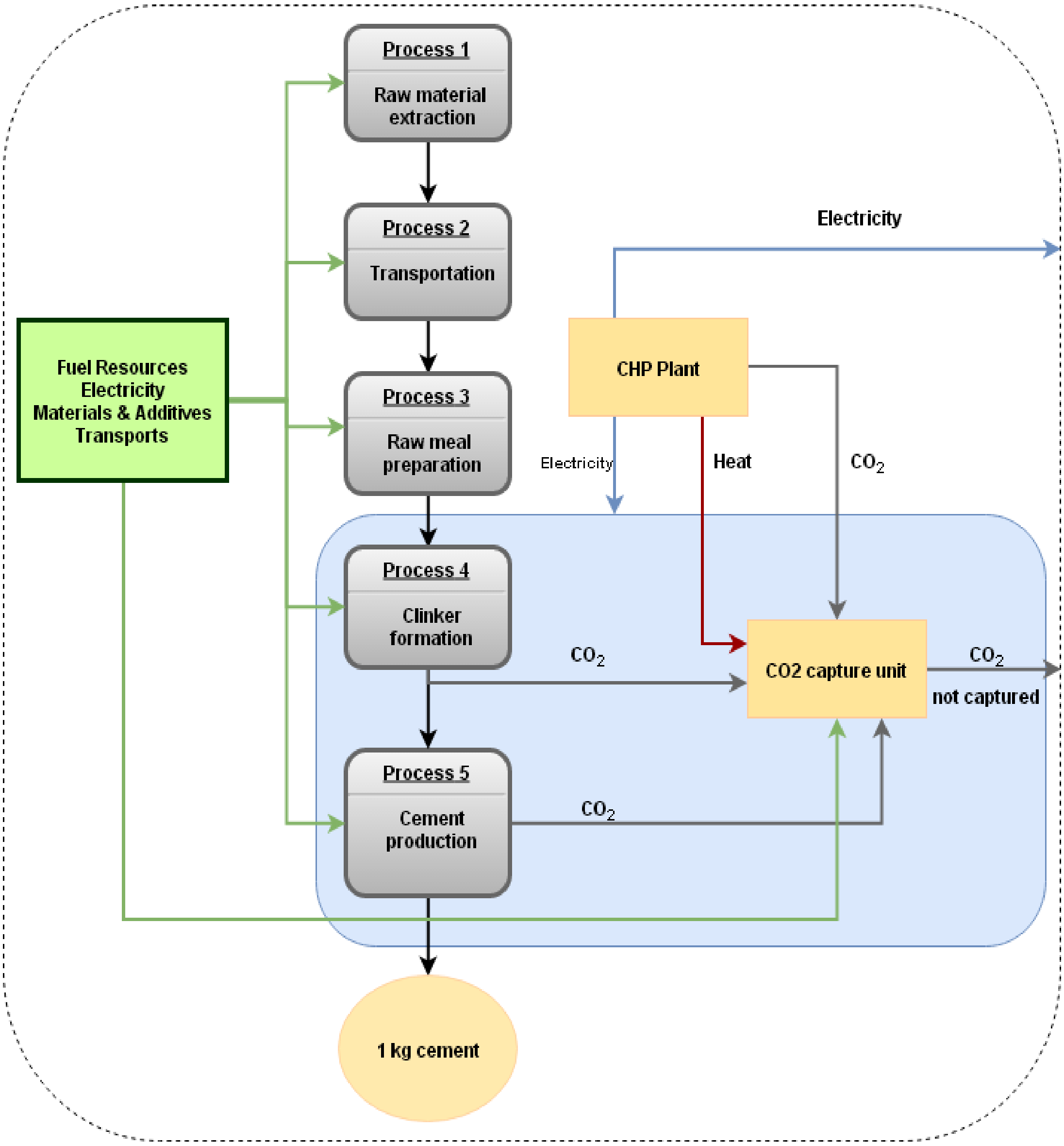

Figure 28: System boundary of cement plant with MEA scrubbing for CO_2 capture

The third case encompasses the conventional process for cement manufacturing, as well as a CaL capture unit for carbon capture. In accordance with the second case, the cement manufacturing process remains unchanged and the CO_2 emissions are directed towards the capture unit. As already stated in the first part of this report, the reversible carbonation reaction occurs in an oxygen-rich atmosphere in order not to dilute the desorbed CO_2. Thus, an ASU has been considered for the provision of oxygen into the calciner, in order to regenerate the sorbent and decompose $CaCO_3$. The additional energy required to cover the heat demands of the capture unit is assumed to be provided by petroleum coke, which has already been grinded in order to be fed to the unit. In addition, due to the high temperature profile of the exhaust streams, a waste heat recovery unit has been considered for the conversion of waste heat exiting the capture unit into electricity by means of a steam cycle, that will energize the ASU and the cement plant, while the rest of the power generated is supposed to drive the CO_2 compression and purification units, which, in this case, are shown to be outside the system boundary. In order to be consistent with the case of MEA capture, this additional electricity is assumed to be fed to the grid, replacing fossil-based electricity. Finally, the purge stream of CaO is supposed to be fed into the cement kiln, in the form of raw material, to aid the clinker formation process.

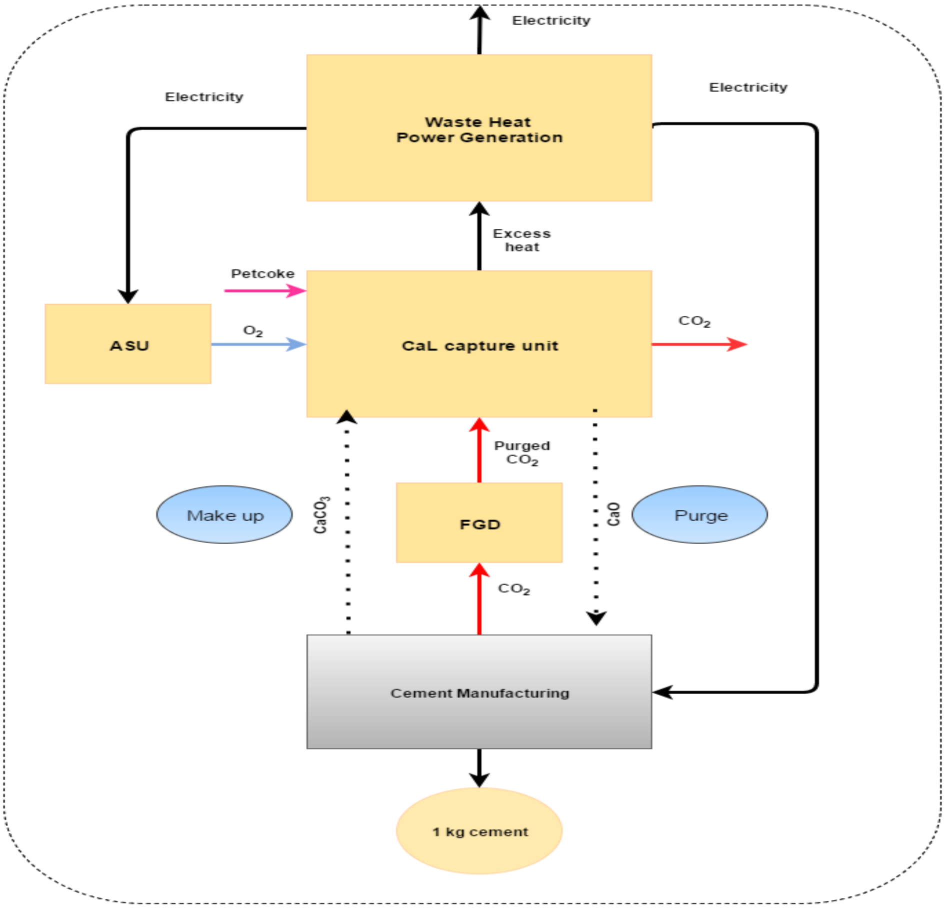

Figure 29: System boundary of cement plant with CaL for CO_2 capture

2.3.2 Data Acquisition - Assumptions

Life cycle inventory data for the CCP was acquired from Lambrou **[82]**, the assumptions of which can be found in Appendix 1. The respective inventory data for the MEA scrubbing capture unit was taken from Garcia-Gusano et al. **[80]**, while the data for the CHP plant was extracted from Mayer-Spohn and Blesl **[84]**. The system boundary was based on a respective representation by Volkart, Bauer and Boulet **[81]**. In addition, the ECOINVENT database **[83]** was used, in order to extract data for the electricity fuel mix of Greece, and the lifecycle inventories of MEA and ammonia. Due to lack of similar LCA studies of CaL application to the cement industry, inventory data was extracted from a study by Vatopoulos and Tzimas **[67]**, which, amongst other aspects, investigates the various components of a CaL capture unit, applied to a cement plant, in terms of energy consumption. The configuration of the cement plant with CaL CO_2 capture was based on a respective system boundary found in Naranjo, Brownlow and Garza **[62]**. All inputs and outputs considered for the analysis were transformed in line with the required functional unit, i.e. 1 kg of cement.

2.3.3 Life Cycle Impact Assessment Categories

The input and output data collected during the Life Cycle Inventory step of the study were categorized to two environmental impact categories: energy consumption, expressed in MJ/kg cement, and Global Warming Potential (GWP) expressed in kg CO_2 eq/kg cement. The former category reflects the fossil energy that is consumed in the production of cement with and without CO_2 capture. The GWP is an environmental impact category which demonstrates the impact of the specific lifecycles to the global warming phenomenon, i.e. the amount of greenhouse gases emitted during the processes. Since it is a relative measure, it is expressed in terms of carbon dioxide (the factor of which is 1, given that it is used as a reference), and the unit used is termed carbon dioxide equivalent (CO_2eq). This ability of greenhouse gases is dependent on a specified time horizon and, the larger the GWP, the more a given gas heats the atmosphere relative to carbon dioxide over that time period **[85]**. The present analysis entailed the effect of three greenhouse gases, namely carbon dioxide, methane (CH_4) and dinitrogen oxide (N_2O) over a period of 100 years, with the use of the following formula:

$$\boldsymbol{CO_2 + 21 * CH_4 + 315 * N_2O}$$

the factors of which are consistent with the indicative values given in IPCC's fourth assessment report **[86]**. Investigation of the individual processes constituting the three cases revealed that methane and dinitrogen oxide have a very small contribution to emissions, compared to carbon dioxide, hence their respective amounts were neglected for the formulation of the GWP of each case.

2.4 INVENTORY ANALYSIS

2.4.1 Case 1: CCP

The base case scenario, the inventory of which was extracted from Lambrou **[82]**, entails cement manufacturing without any use of post-combustion capture systems. The annual production figures of the CCP considered for this case are displayed in table 7.

table 7: Annual production figures of CCP [82]

Cement plant capacity	
Cement production	2 Mt
Days in operation	345
Annual energy consumption	
Electricity	150,000,000 kWh
Petroleum coke	120,000 ton
	1,039,305,600 kWh

The flow chart (figure 30) displayed below depicts the inflows and outflows of materials, energy and CO_2 emissions. According to the findings of Lambrou **[82]**, 0.8077 kg clinker are required to produce 1 kg of cement. Background life cycle processes are also included, such as the transportation of petroleum coke for the process of clinker formation and the inclusion of quarrying and/or transport of constituents required for the production of cement, such as pozzolana, gypsum and fly ash. The inventory for the base case is also summarized in table 8.

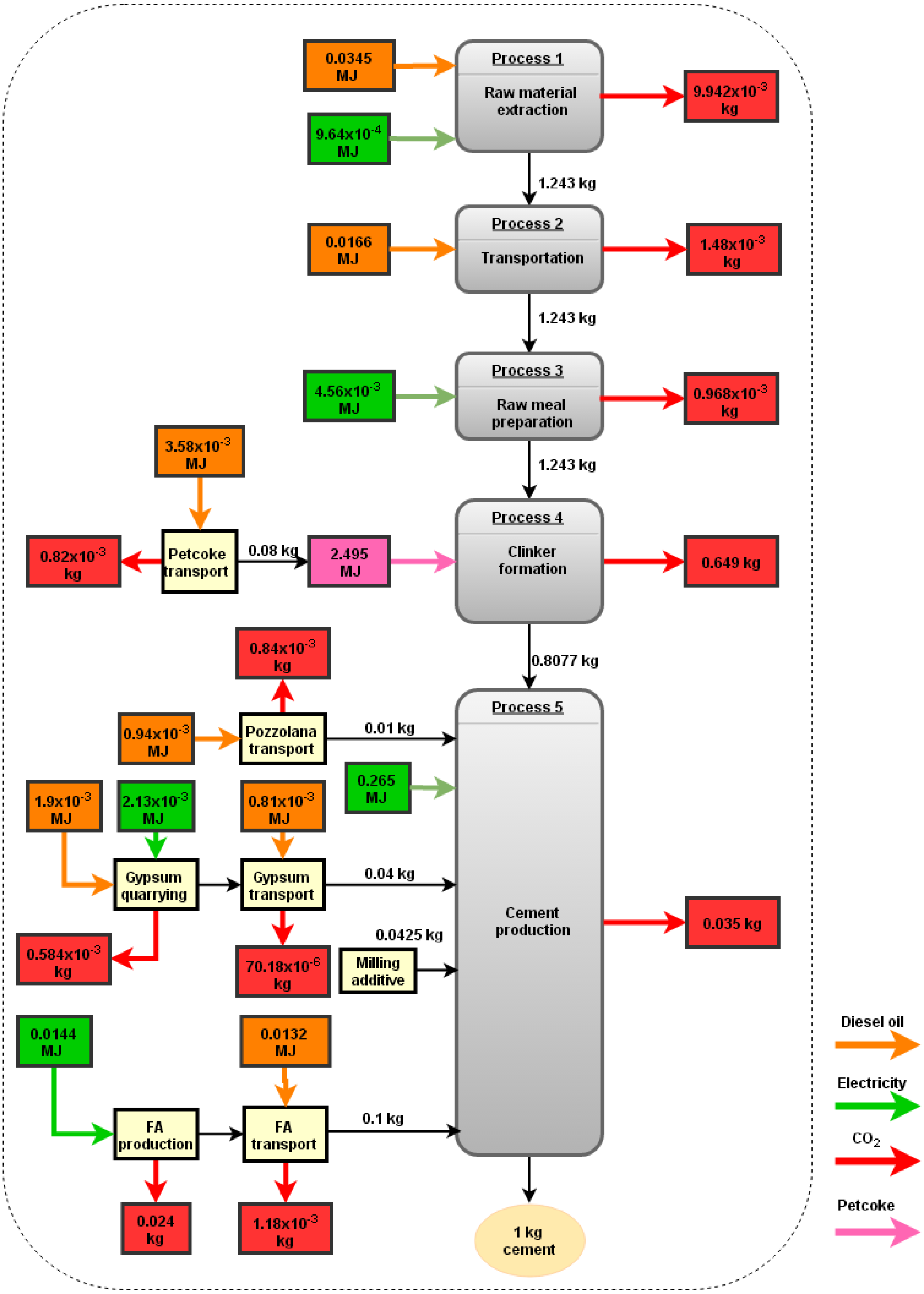

Figure 30: Input/output flow chart - CCP

table 8: LCI for 1 kg cement [82]

Input	
Energy (MJ)	
Diesel oil	0.07153
Electricity	0.287054
Petcoke	2.495
Raw Materials (kg)	
Shale	0.233
Limestone	0.699
Additives	0.311
Gypsum	0.04
Fly ash	0.1
Pozzolana	0.01
Milling additives	0.0425
Water	0.25
Output (kg)	
CO_2	0.7243
CH_4	0.001448
N_2O	1.23E-05

2.4.2 Case 2: Cement plant with MEA scrubbing

In this case, the CCP considered for the previous scenario is retrofitted with a post-combustion capture unit utilizing MEA scrubbing technology. The respective flow chart (figure 31) offers a visualization of the mass and energy balance of this scenario in thorough detail.

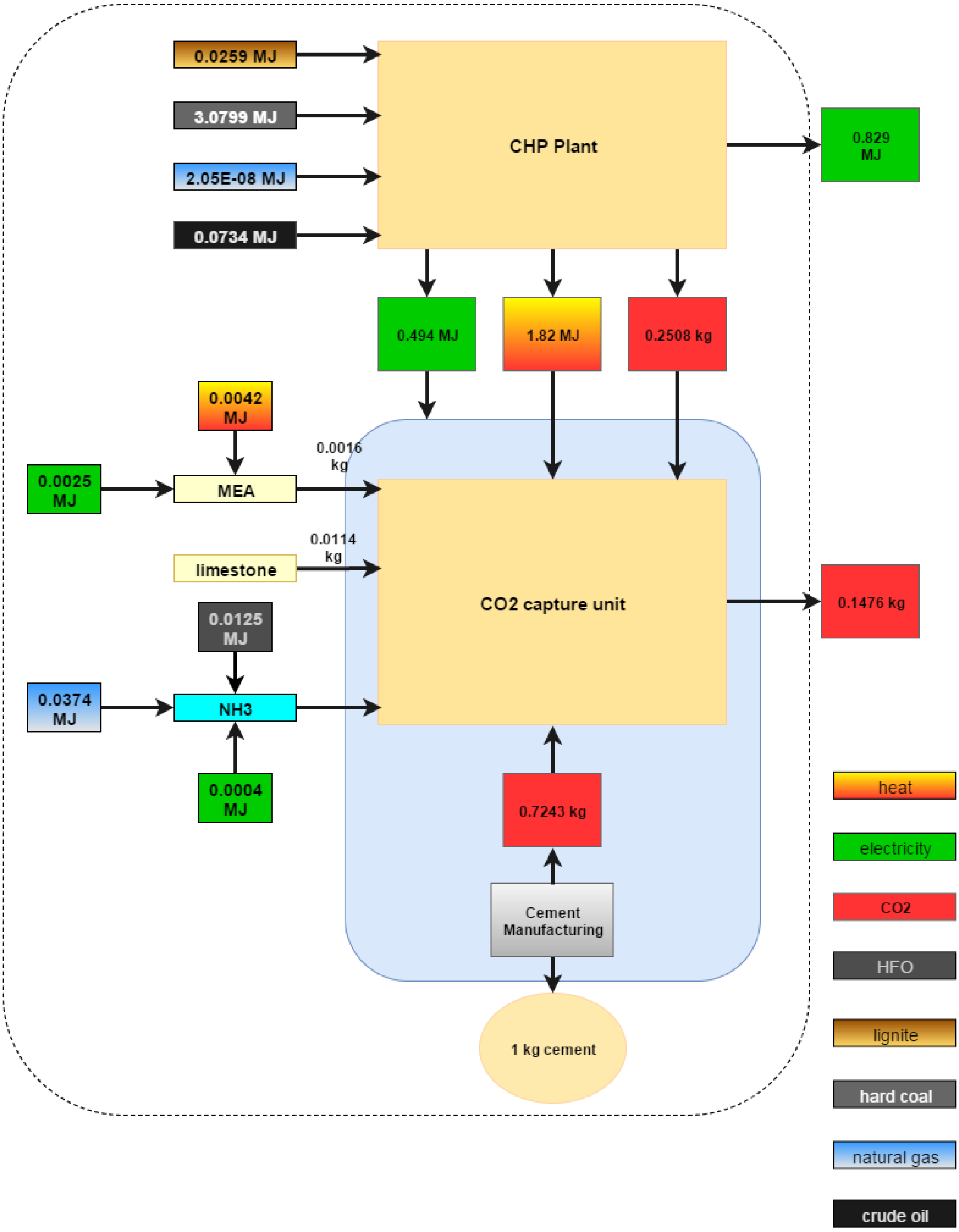

Figure 31: Input/output flow chart - cement plant with MEA

The life cycle inventory of the CCP is kept constant and the emissions produced are directed to the capture unit. For the purposes of the additional energy supply of the cement plant, a hard coal-fired CHP plant with backpressure turbine, with a net electrical efficiency of 38% and a thermal efficiency of 59% was considered, according to Mayer-Spohn and Blesl **[84]**. Its lifecycle inventory is displayed in table 9.

table 9: LCI of coal-fired CHP for 1 kWh electricity production [84]

Input	
brown coal kg)	0.00405
hard coal (kg)	0.351
natural gas (Nm3)	0.00129
crude oil (kg)	0.00465
Output (kg)	
CO_2	0.682
CH_4	0.00195
N_2O	0.0000296
Heat (MJ)	4.95
Electricity (kWh)	1

The CHP plant supplies both the cement plant, along with its processes, and the capture unit with electricity and the surplus produced is assumed to displace electricity from the fuel mix in Greece, displayed in table 10.

table 10: Fuel mix of Greece for the production of 1 kWh [83]

Input (kg)	
lignite	1.22
hard coal	0.004571
natural gas	0.048462
crude oil	0.037832
Output (kg)	
CO_2	0.005127
CH_4	5.52E-06
N_2O	1.45E-07

The CHP plant also provides the capture unit with the heat required for the MEA regeneration and all the emissions, stemming from the CHP plant due to combustion of the various fuels depicted in the flow chart, are also directed to the capture unit. Concerning the capture unit, the additional lifecycle inventory for the production of 1 kg cement with the use of MEA scrubbing was extracted from Garcia-Gusano et al. **[80]** and can be observed in table 11. The carbon capture efficiency of the MEA scrubbing unit was calculated at 84.9% and the result was deduced by the data mentioned in table 6. The calculation procedure can be found in Appendix 2**.**

table 11: LCI for the MEA capture unit per kg cement [80]

Input	
Raw materials (kg)	
MEA	0.0021
NH_3	0.0016
Limestone	0.0011
Energy (MJ)	
Heat	1.82
Electricity	0.204
Output (kg)	
CO_2	0.0024
CH_4	1.92E-08
N_2O	2.45E-08

As also seen in the chart, lifecycle inventory of background processes, such as provision of MEA, limestone and ammonia for the capture unit is also included, the inventory of which is found in tables 12-13. Specifically for limestone required for the FGD, it is assumed that its supply is incorporated in the raw material quarrying process block of the base case. Further assumptions regarding the production of MEA and ammonia can be found in Appendix 3.

table 12: LCI for the production of 1 kg MEA [83]

Input (MJ)	
Electricity, medium voltage, production UCTE, at grid	1.1988
Heat, natural gas, at industrial furnace >100 kW	2
Output (kg)	
CO_2	0.0265
Products (kg)	
MEA	1

table 13: LCI for the production of 1 kg ammonia [83]

Input (MJ)	
Natural gas, at consumer (EU)	23.4
Heavy fuel oil, at regional storage	7.683
Electricity, medium voltage, production UCTE, at grid	0.25
Output (kg)	
CO_2	1.46
CH_4	1.20E-05
N_2O	1.53E-05
Products (kg)	
NH_3	1

2.4.3 Case 3: Cement plant with CaL

In this case, the base case cement plant is retrofitted with a post-combustion capture unit utilizing CaL technology. The flowchart (figure 32) provides a visual aid of the mass and energy balance of this scenario. The procedure followed for the deduction of the mass and energy inputs can be found in Appendix 4.

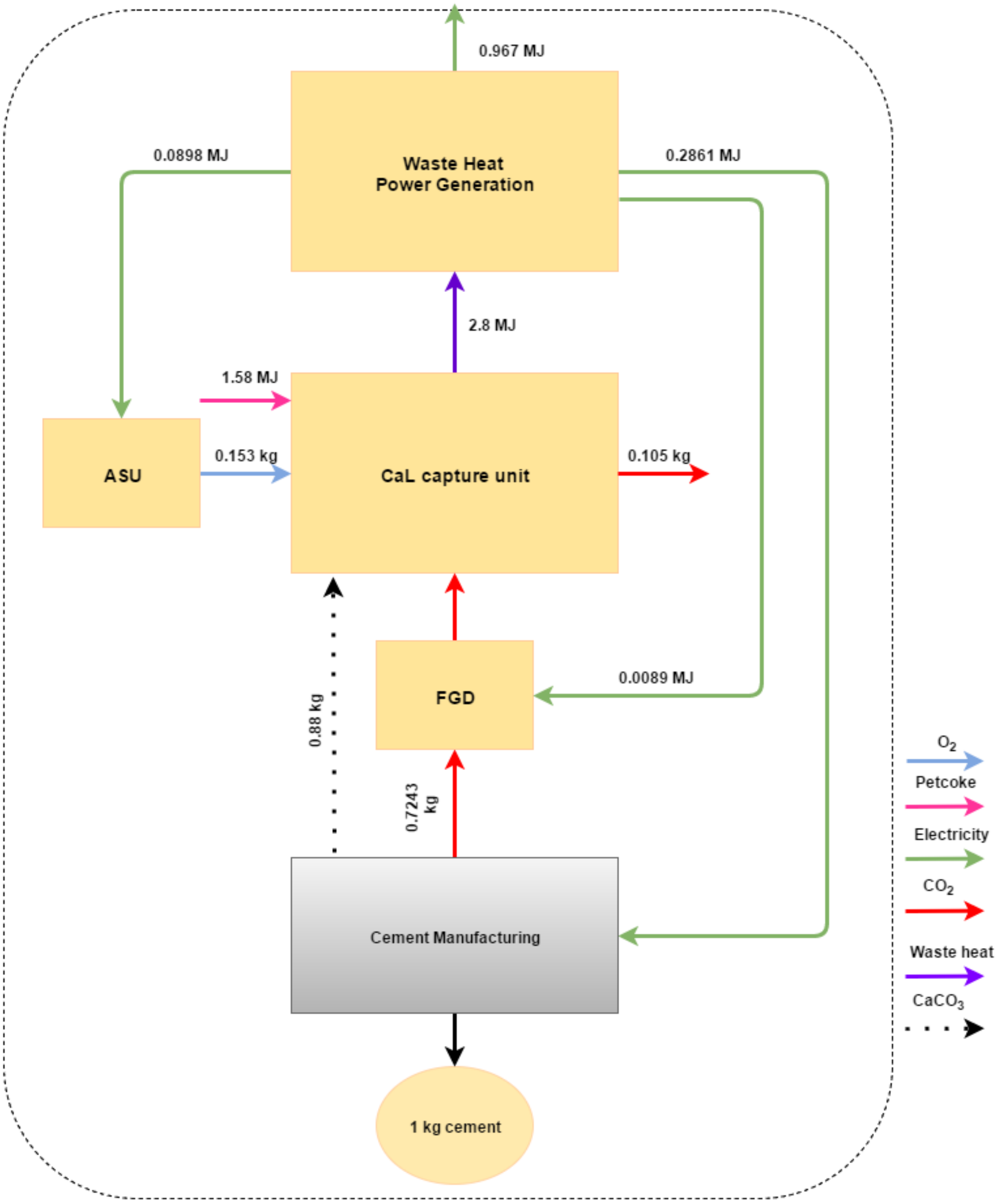

Figure 32: Input/output flow chart - cement plant with CaL

As previously mentioned, all CO_2 emissions produced are directed to the CaL unit, which is assumed to have a capture efficiency of 85% **[67]**. The waste heat produced from the capture process is funneled to a waste heat recovery unit, which produces electricity by means of a steam cycle and redirects the produced power to the ASU, the FGD and the cement plant. The electricity has a surplus which is exported to the grid, replacing fossil-based electricity. The heat required for the capture unit is assumed to be provided by petcoke, which is fed into the calciner vessel. The oxygen provided by the ASU is assumed to have a purity of 95%, as per Atsonios et al. **[69]**. In addition, the purge stream of CaO exiting the carbonator vessel is assumed to enter the cement kiln as raw material to suit the purposes of clinker formation, while the surplus limestone required for the calciner vessel is assumed to be extracted from the same process block for conventional cement manufacturing, namely the raw material quarrying process. The additional lifecycle inventory for the production of 1 kg of cement with the use of CaL can be found in table 14.

table 14: LCI for the integrated CaL capture unit (including FGD, ASU and WHR systems) per kg cement

Input	
Raw materials (kg)	
Limestone	0.88
Oxygen	0.153
Energy (MJ)	
Petcoke	1.58
Heat	0.0089
Electricity	0.0898
Output	
CO_2 (kg)	0.105
Electricity produced from WHR (MJ)	0.7267
Heat produced from WHR (MJ)	0.5249

2.5 ENVIRONMENTAL IMPACT ASSESSMENT

2.5.1 General

Having collected all the appropriate inventory, respective tables were formed, including inputs and outputs for the three aforementioned cases. All serve as basis for the comparison of the cases, which was done in terms of fossil fuel consumption by fuel type, energy consumption by process and contribution to GWP. Tables 15-17-19 contain a breakdown of energy input by process block and fossil fuel type, as well as the fuel consumption corresponding to the electricity use (with respect to the fuel mix in Greece). These tables were compiled using all the previously presented inputs and after making the appropriate transformations from kilograms to MJ for each fossil fuel employed in the processes. The low heating values considered for each fuel can be found in Appendix 5. In addition, tables 16-18-20 include information regarding GWP, which is at the same time equal to the CO2 emissions associated with each process.

2.5.2 Case 1: CCP

The energy requirements for the CCP are depicted in table 15. This case entails mainly two types of fuel (diesel and petcoke) for direct use, whereas the rest of the categories are attributed to the electricity fuel mix of Greece, which dictates the quantities of fuels used to provide power to the cement plant.

table 15: Energy input - CCP

Energy Input - Base Case (MJ/kg cement)				**Secondary Fuel for Electricity Production**				
Process	**Diesel**	**Petcoke**	**Electricity**	**Lignite**	**Hard coal**	**NG**	**Crude oil**	**Total Energy Consumption**
Raw material extraction	0.0345		0.001	0.0057	0	0.0005	0.0004	0.0411
Transportation	0.0166							0.0166
Raw material preparation			0.0046	0.0269	0.0001	0.0023	0.0021	0.0314
Clinker formation	0.0036	2.495						2.4986
Cement grinding	0.0169		0.2815	1.6601	0.0085	0.144	0.1272	1.9567

Total	**0.0715**	**2.495**	**0.2871**	**1.6927**	**0.0087**	**0.1468**	**0.1297**	**4.5445**

As seen from the chart (figure 33) the conventional cement manufacturing process is especially demanding in terms of petroleum coke, which is combusted during clinker formation, where a high temperature profile is required. The second most used fuel is lignite, which corresponds to the fuel mix consumed in Greece for electricity production, as lignite power plants constitute the main source of power locally. The rest of the fuels, such as diesel, used in raw material quarrying and transportation, have negligible values.

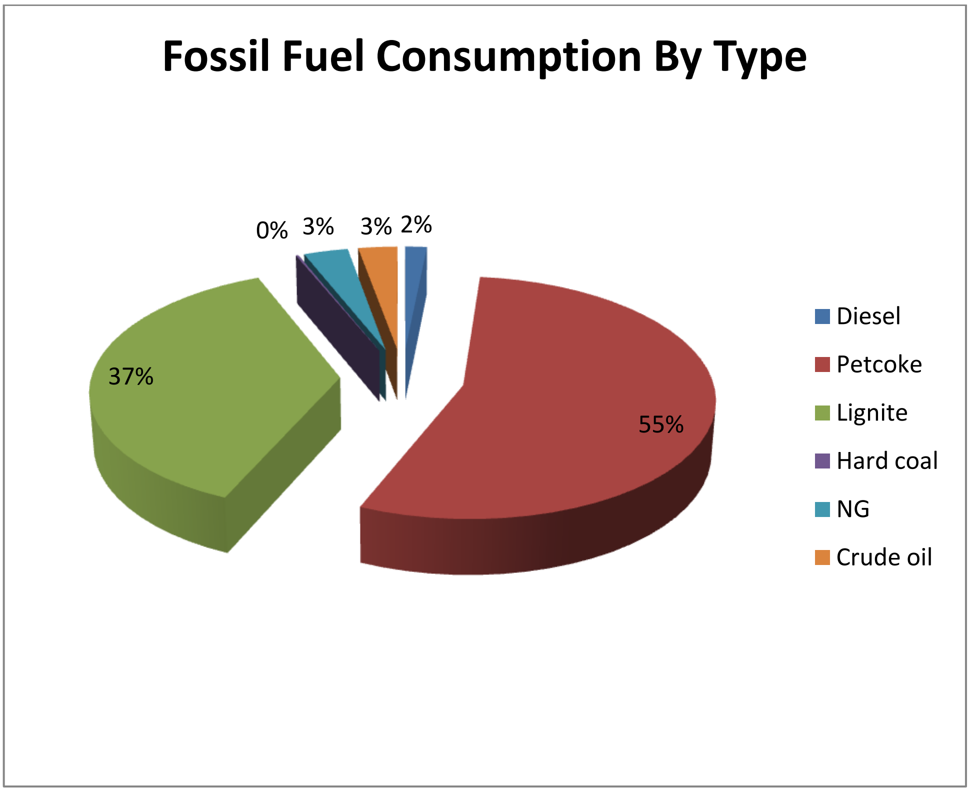

Figure 33: Fossil fuel consumption by type - CCP

A simple observation of the energy consumption chart (figure 34) elucidates the fact that cement production is an energy demanding procedure. Specifically, concerning the CCP, the process of clinker formation requires 2.5 MJ per kg of cement produced (55% of total energy consumption), whereas cement production requires nearly 2 MJ/kg cement (43% of total energy consumption). This was previously justified in the literature review, as clinker is formed with the use of excess amounts of heat, while, in order for the final product to be formed, there is a high demand of electricity from the grinder to operate.

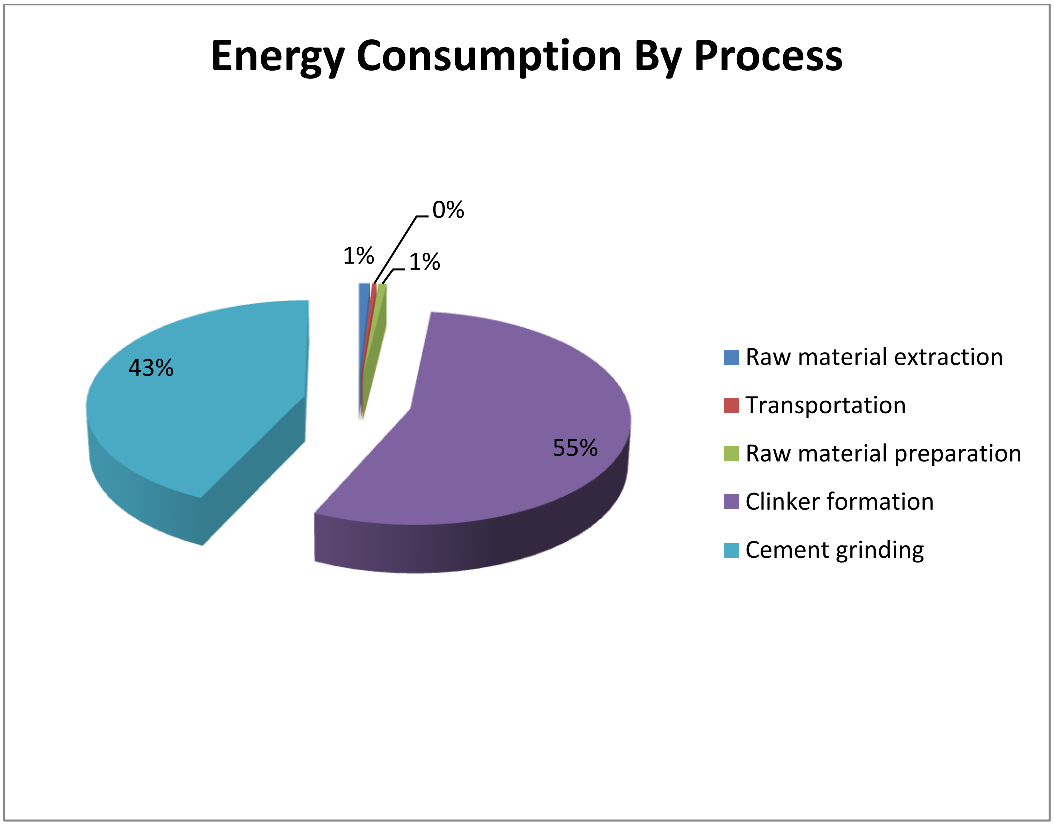

Figure 34: Energy consumption by process - CCP

Regarding the output of the CCP, figure 35 shows that there is a grave difference between processes in terms of contribution to GWP, as out of the overall 0.7243 $kgCO_2eq$ per kg of cement, the clinker formation is held accountable for 90% of the amount, namely 0.65 $kgCO_2eq$. The next biggest impact towards global warming is inflicted by cement production, with a contribution of 0.06 $kgCO_2eq$ (9%) due to the carbon dioxide emissions during the electricity production process. The rest of the processes have comparatively negligible amounts.

table 16: GWP of CCP

GWP - CCP ($kgCO_2eq$/kg cement)	
Process	**GWP**
Raw material extraction	0.009942
Transportation	0.00148
Raw material preparation	0.000968
Clinker formation	0.64982
Cement grinding	0.062074
Total	**0.724284**

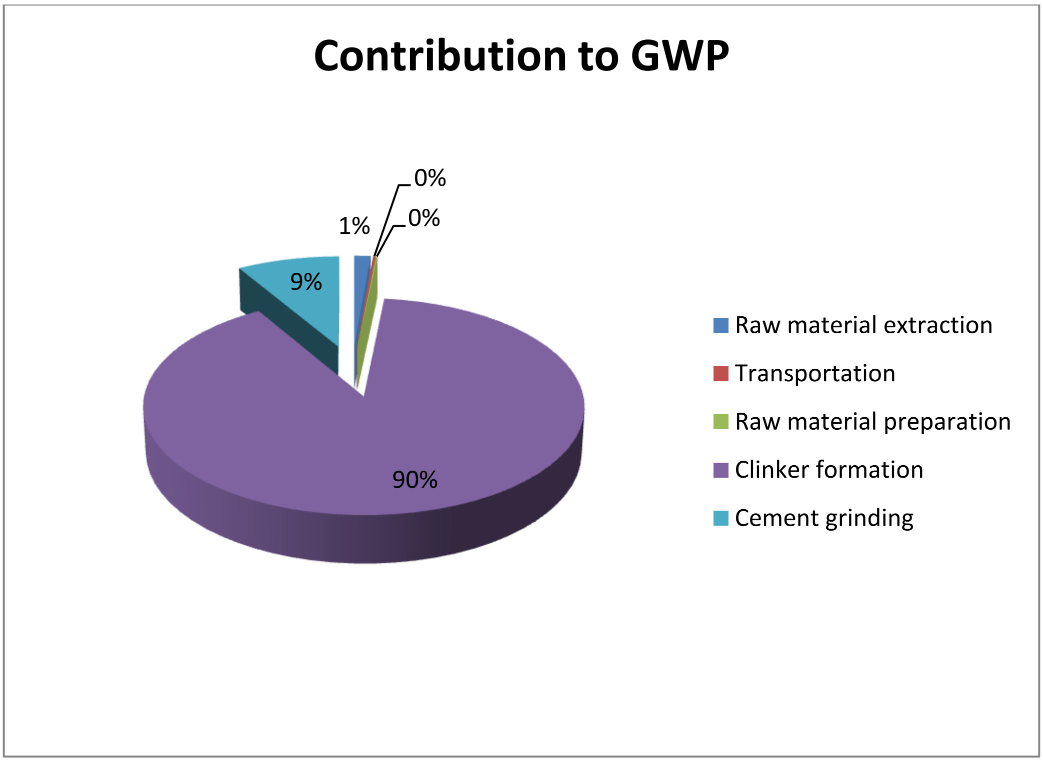

Figure 35: Process contribution to GWP - CCP

2.5.3 Case 2: Cement Plant with MEA scrubbing

In this case, it is worth mentioning that, since the CHP plant produces heat and electricity, the respective amounts take a negative value (table 17). The calculations for the surplus electricity that is fed back to the grid can be found in Appendix 6. It should also be noted that, since the CHP plant supplies the cement plant with the required electricity, every process covered by electricity produced by the CHP is not represented in the breakdown of secondary fuels, as this part of the table corresponds to electricity provided by the domestic electricity producer (PPC). Finally, due to their small contribution in terms of energy consumption and CO_2 emissions, the lifecycles of NH_3 and MEA, previously observed in the input table for MEA, are considered together as background LCI processes.

table 17: Energy input - cement plant with MEA scrubbing

Energy input - CC with MEA (MJ/kg cement)							Secondary Fuel for Electricity Production				
Process	Diesel	Petcoke	HFO	NG	Electricity	Heat	Lignite	Hard coal	NG	Crude oil	Total Energy Consumption
Raw material extraction	0.0345				0.000964		0.005684	2.93E-05	0.000493	0.000436	0.041142
Transportation	0.0166										0.0166
Raw material preparation					0.00456		0.026889	0.000138	0.002333	0.002061	0.03142
Clinker formation	0.00358	2.495									2.49858
Cement grinding	0.01685				0.28153						0.29838
Capture unit					0.204	1.82					2.024
CHP plant					-1.323	-1.82	0.025898	3.082921	0.018015	0.073482	0.057315
Background LCI processes			0.0125	0.0416	0.0029		0.001483	0.00131	0	0	0.056894
Unit total	0.07153	2.495	0.0125	0.0416	-0.82905	0	0.059954	3.084399	0.020841	0.075978	5.024332
Credits due to avoided electricity					0.829046		4.888608	0.02516	0.424093	0.374631	5.712492
Total	0.07153	2.495	0.0125	0.0416	0	0	-4.82865	3.059239	-0.40325	-0.29865	-0.68816

Judging by the pie chart (figure 36), this scenario differs from the base case, as it encompasses far more hard coal use (3.08 kg/kg cement - 53%), stemming from the increased electricity requirements of the capture unit, which are satisfied by the CHP unit. The second most consumed fossil fuel is petcoke, which remains unchanged (2.495 kg/kg cement) since the cement manufacturing process was not altered. Although more diverse, including more fuels (HFO, NG) used for the additional processes taking place for carbon capture, this pie chart lacks variety in percentages, as the rest of the fuels have comparatively insignificant contribution. Such examples include fuels associated with either background lifecycle processes (e.g. diesel for transportation of materials, heavy fuel oil for the production of ammonia) or their participation in the fuel mix is significantly less than other fuels (e.g. crude oil, natural gas).

The energy consumption, visualized in figure 37, is evidently augmented when carbon capture with amine scrubbing is applied. In addition to the already energy-demanding process of clinker formation (50%), the respective capture unit requires 1.82 MJ of heat (40% of the total energy consumption), in the form of steam, to regenerate the MEA solvent within the cycle.

This amount of heat is provided by the CHP plant, which requires resources that amount to 1% of the total energy consumption; however, since it covers the demand of the entire cement plant in electricity, a significant proportion of these resources is saved, due to surplus electricity produced being fed back to the grid in the form of credits, i.e. 0.829 credits due to avoided electricity (table 17).

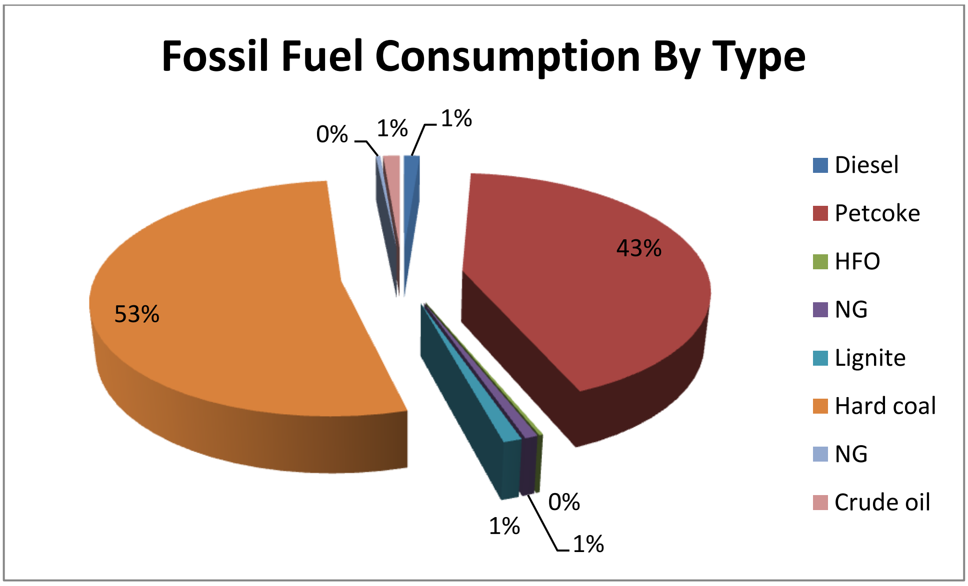

Figure 36: Fossil fuel consumption by type (cement plant with MEA)

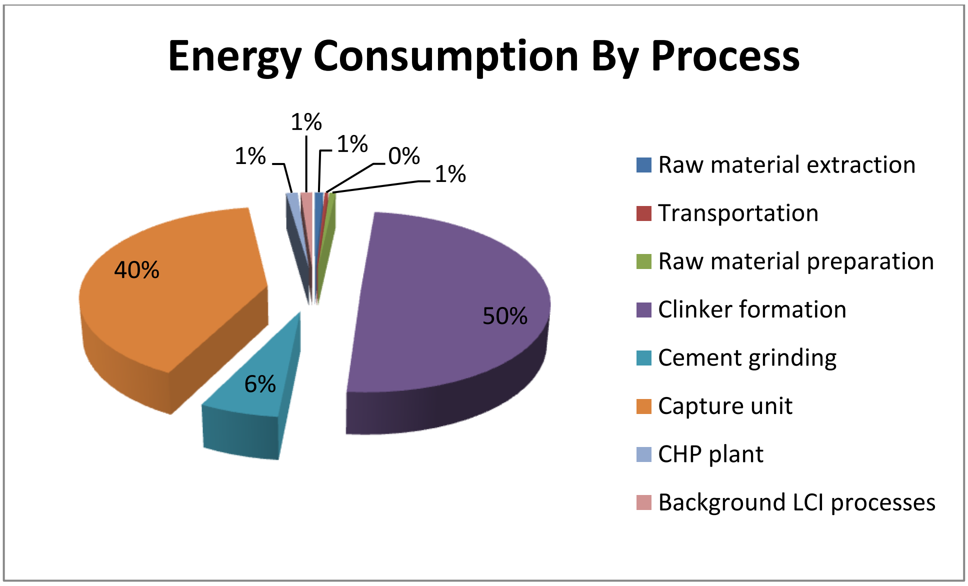

Figure 37: Energy consumption by process (cement plant with MEA)

Concerning the GWP table (table 18), it should be noted that the amount of CO_2 captured by the MEA scrubbing unit (taking its 84.9% efficiency into account) is depicted with a negative value (-0.83 $kgCO_2eq$), while the same stands for the emissions avoided due to the electricity that is fed back to the grid (-0.001 $kgCO_2eq$), which is subsequently translated into less fuel use from the fuel mix and thus less CO_2 emitted.

Regarding the contribution of each process to GWP (figure 38), it is evident that CO_2 emanating from clinker formation and the CHP plant has the greatest impact on GWP. More specifically, it is blatantly clear that clinker formation gains the lion's share, with 0.65 kg CO_2eq per kg of cement (67% of total GWP). The CHP plant comes second in GWP contribution, with 0.25 kg CO_2eq (26%), in order to cover the demand of the whole cement plant in electricity and the capture unit in particular in heat. Again, since the percentages of the rest of processes remain unchanged, their impact is insignificant, effect which is portrayed in the chart.

table 18: GWP of cement plant with MEA scrubbing

GWP - CC with MEA ($kgCO_2eq$/kg cement)	
Process	**GWP**
Raw material extraction	0.009942
Transportation	0.00148
Raw material preparation	0.000968
Clinker formation	0.64982
Cement grinding	0.062074
Capture unit	0.002396
CHP plant	0.250771
Subtotal	0.977451

CO_2 captured	-0.82986
Emissions avoided	-0.00118
Total	**0.146414**

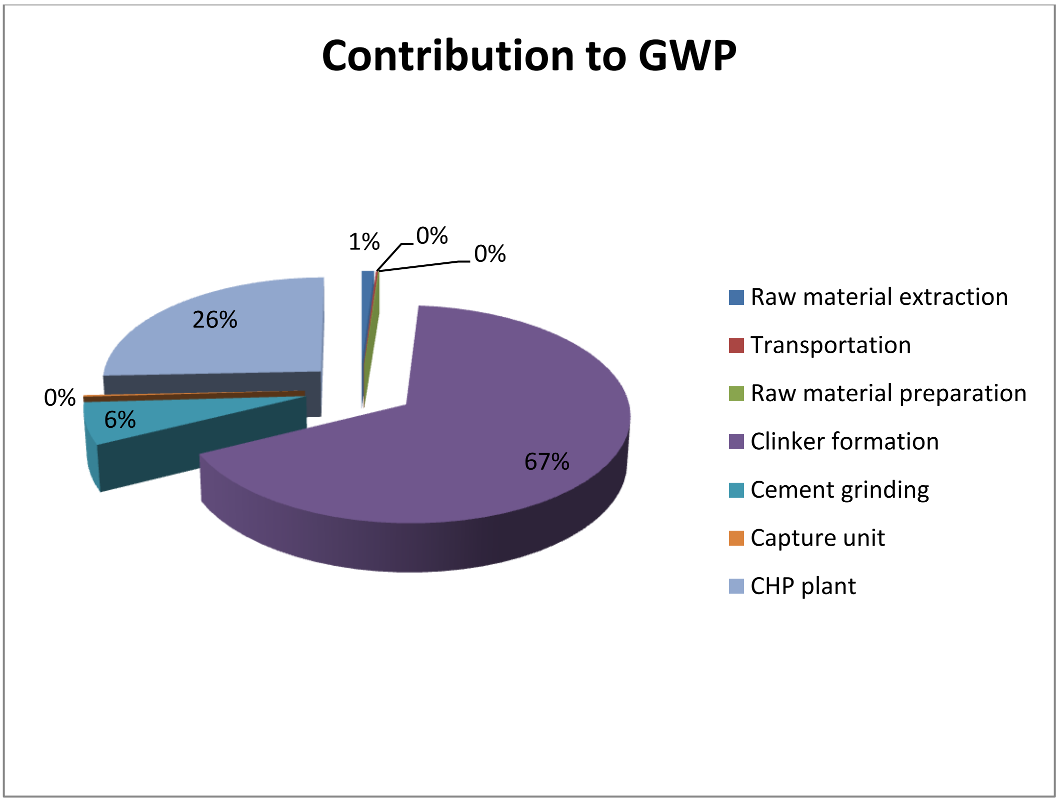

Figure 38: Process contribution to GWP - cement plant with MEA scrubbing

2.5.4 Case 3: Cement plant with CaL

The energy input for the cement plant, equipped with CaL for post-combustion capture, is depicted in table 19. In this case, input has been gathered for the ASU and FGD units. Moreover, this scenario involves power generation from waste heat, which is rejected from the carbonate looping unit and the amounts of electricity and heat exploited by the waste heat power generation unit are also found in the table. Finally, the procedure considered for the calculation of the credits attributed to avoided electricity, follows the same pattern with case 2.

table 19: Energy input - cement plant with CaL

Energy input - CC with CaL (MJ/kg cement)					**Secondary Fuel for Electricity Production**				
Process	**Diesel**	**Petcoke**	**Electricity**	**Heat**	**Lignite**	**Hard coal**	**NG**	**Crude oil**	**Total Energy Consumption**
Raw material extraction	0.0345		0.000964		0.005684	2.93E-05	0.000493	0.000436	0.041142
Transportation	0.0166								0.0166
Raw material preparation			0.00456		0.026889	0.000138	0.002333	0.002061	0.03142
Clinker formation	0.00358	2.495							2.49858
Cement grinding	0.01685		0.28153						0.29838
Capture unit		1.58							1.58
ASU unit			0.08978						0.08978
FGD unit				0.0089					0.0089
Waste Heat Power Generation unit			-0.7267	-0.52494					-1.25164
Unit total	0.07153	4.075	-0.34987	-0.51604	0.032573	0.000168	0.002826	0.002496	3.313163
Credits due to avoided electricity			0.349866		2.063043	0.010618	0.178972	0.158098	2.410731
Total	0.07153	4.075	0	-0.51604	-2.03047	-0.01045	-0.17615	-0.1556	0.902432

Concerning the different types of fossil fuel consumed (figure 39), petcoke displays an undisputed prevalence, with 1.58 MJ/kg cement being consumed on top of the initial 2.5 MJ required for clinker formation, which is translated to a substantial 97%. Apparently, due to this massive amount, the rest of the fuels do not have a significant contribution in the fuel mix.

Drawing from figure 40, there is a significant increase in terms of energy consumption from the CaL unit, compared to the conventional process. As already argued in the first part of this report, both the carbonator and calciner vessels require very high temperatures, so that the reversible reaction occurs in ideal conditions; subsequently, there is an equally amplified demand for heat, which eventually leads to an overall amount of 1.58 MJ/kg cement (35%). Apart from the capture unit, the clinker formation process, remaining once again unchanged, has the greatest contribution (2.5 MJ/kg cement, 55%) and the cement production contributes with another 6%, whereas, next to such percentages, the rest of the processes seem nullified.

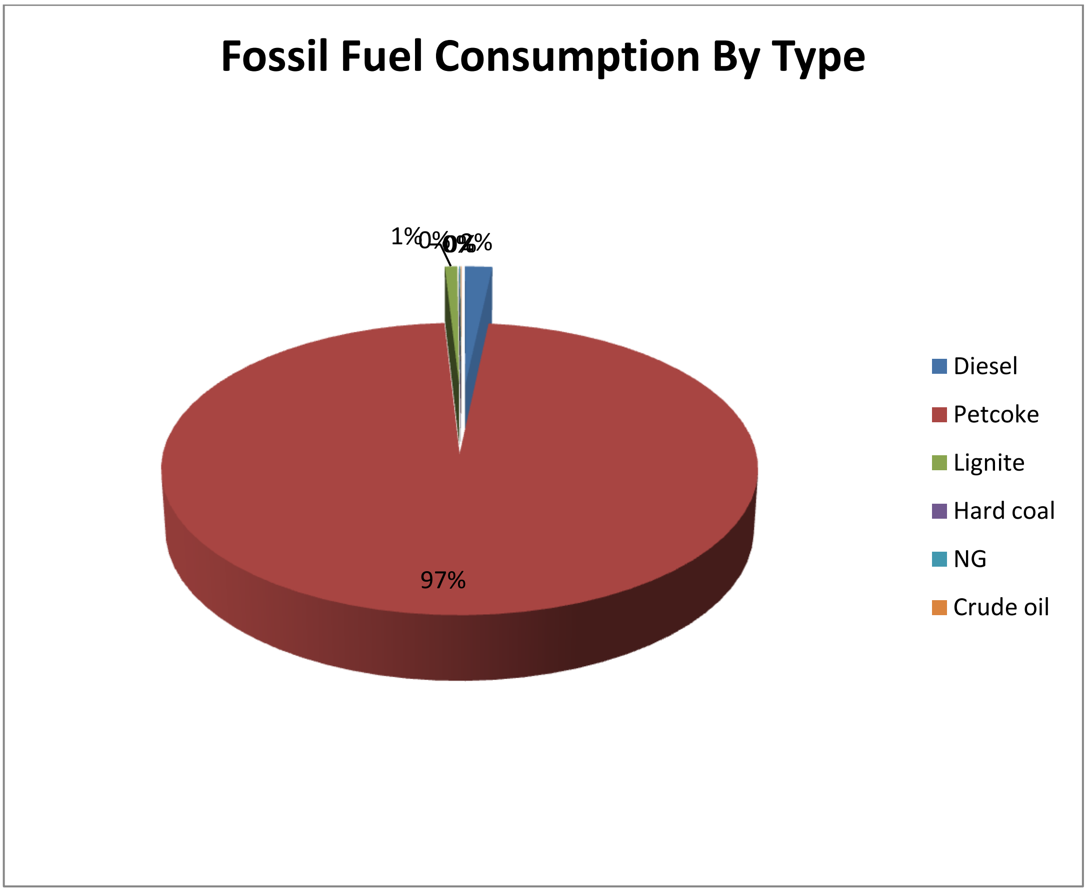

Figure 39: Fossil fuel consumption by type - cement plant with CaL

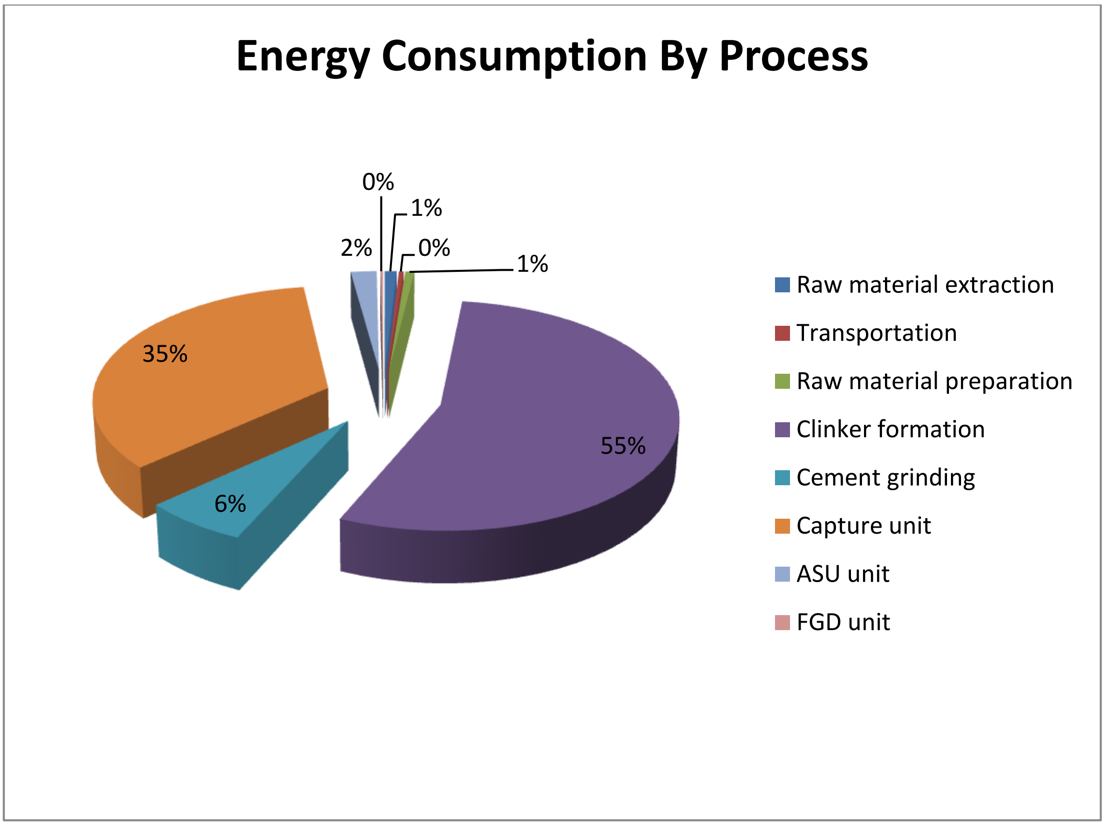

Figure 40: Energy consumption by process - cement plant with CaL

The respective CO_2 emissions - translated into GWP - of the cement plant considered in case 3 are shown in table 20. The amount captured from the CaL (0.7 kg CO_2eq) and the emissions avoided due to the electricity that is fed back to the grid are depicted with a negative value. The contribution of each process to GWP (figure 41) is apparently in tandem with the rest of the cases, as clinker formation occupies the greatest percentage (78%). In this case, the capture unit emits 0.105 kg CO_2eq per kg cement (13%), which is mainly owed to energy required for background processes, such as the operation of the ASU and the FGD. Finally, cement production displays a GWP contribution of 0.06 kg CO_2eq (8%), while the rest of the processes yield minuscule proportions.

table 20: GWP of cement plant with CaL

GWP - CC with CaL (kgCO_2eq/kg cement)	
Process	**GWP**
Raw material extraction	0.009942
Transportation	0.00148
Raw material preparation	0.000968
Clinker formation	0.64982
Cement grinding	0.062074
Capture unit	0.105
CO_2 captured	-0.7049
Emissions avoided	-0.0005
Total	**0.123894**

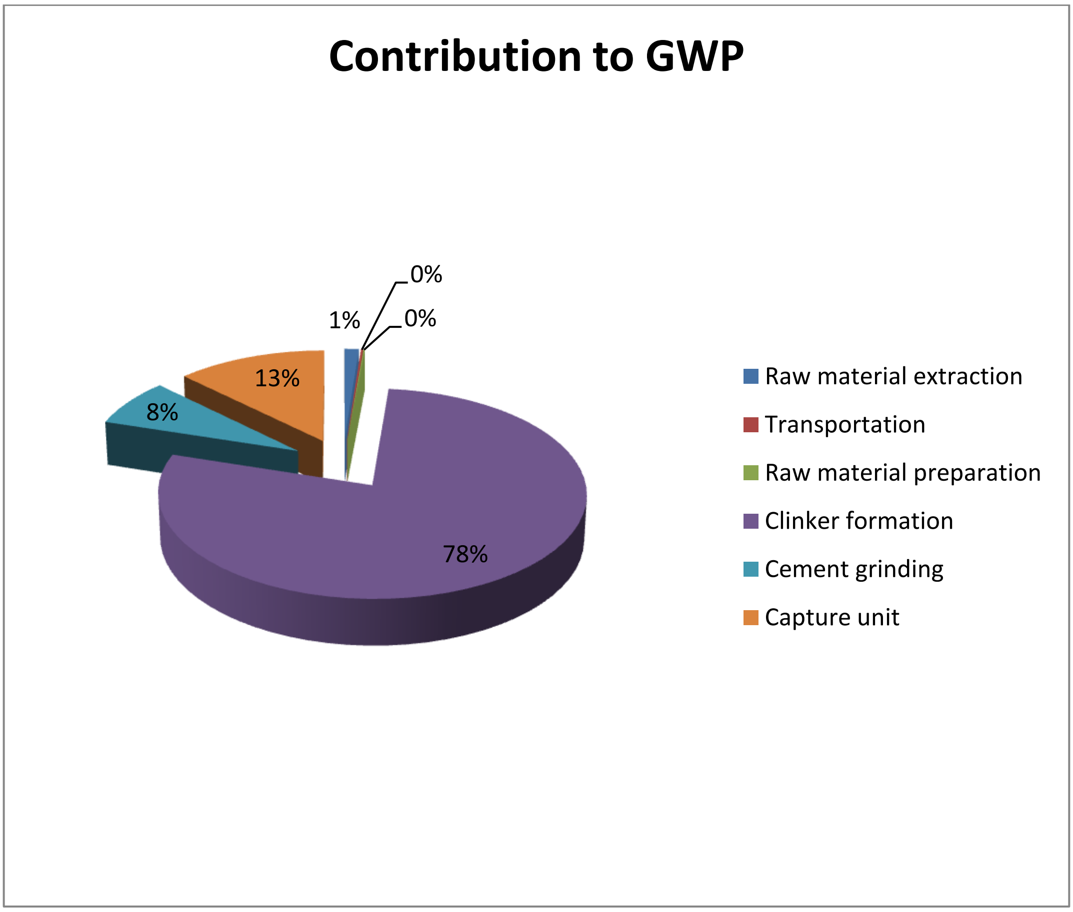

Figure 41: Process contribution to GWP - cement plant with CaL

2.6 COMPARISON

The cumulative graphs, depicted in figures 42-43, provide a useful visual aid, in order to comprehend the differences between the CCP and the two cases of post-combustion capture application.

2.6.1 Total Energy Consumption

In terms of total energy consumption (figure 42), it is worth observing that the CCP requires 2.85 MJ to produce 1 kg cement, without taking into account the consumption of fuels to produce the required electricity. The respective amount, calculating the amounts of secondary fuel, is 4.54 MJ. The same plant, equipped with a MEA scrubbing unit, has increased direct and indirect demands of 4.99 MJ/kg cement and 5.02 MJ/kg cement respectively (percentile changes of 75.09% and 10.79%).

The cement plant with CaL has a direct energy demand of 3.28 MJ/kg cement, which is higher than the base case (15.09%), but if the consumption of secondary fuels is counted in, then the indirect demand of the CaL plant is 3.31 MJ/kg cement, marginally lower than the base case (27.09% reduction). The latter phenomenon is owed to the amount of waste heat recovered from the capture unit, which is in turn reused in the cement plant.

Hence, without taking the electricity credits of each case into consideration, MEA scrubbing is apparently the most energy-consuming means of carbon capture. However, weighing in the effect of the credits, due to the fact that both the CHP plant and the waste heat recovery unit produce more electricity (per kg cement) than required by the entire cement plant, MEA scrubbing yields 5.71 credits, which, added to the indirect energy demand of the plant, result in a negative amount of energy consumption (-0.688 MJ/kg cement), which essentially means that the cement plant is more than self-sustainable. The respective credits in CaL amount to 1.32, thus presenting a less promising potential, however, by summation of the credits with the indirect energy demand, it is evident that the cement plant in case 3 is also more than self-sustainable (-0.349 MJ/kg cement). As such, despite its greater requirements in terms of energy, MEA scrubbing presents delivers better results than CaL overall.

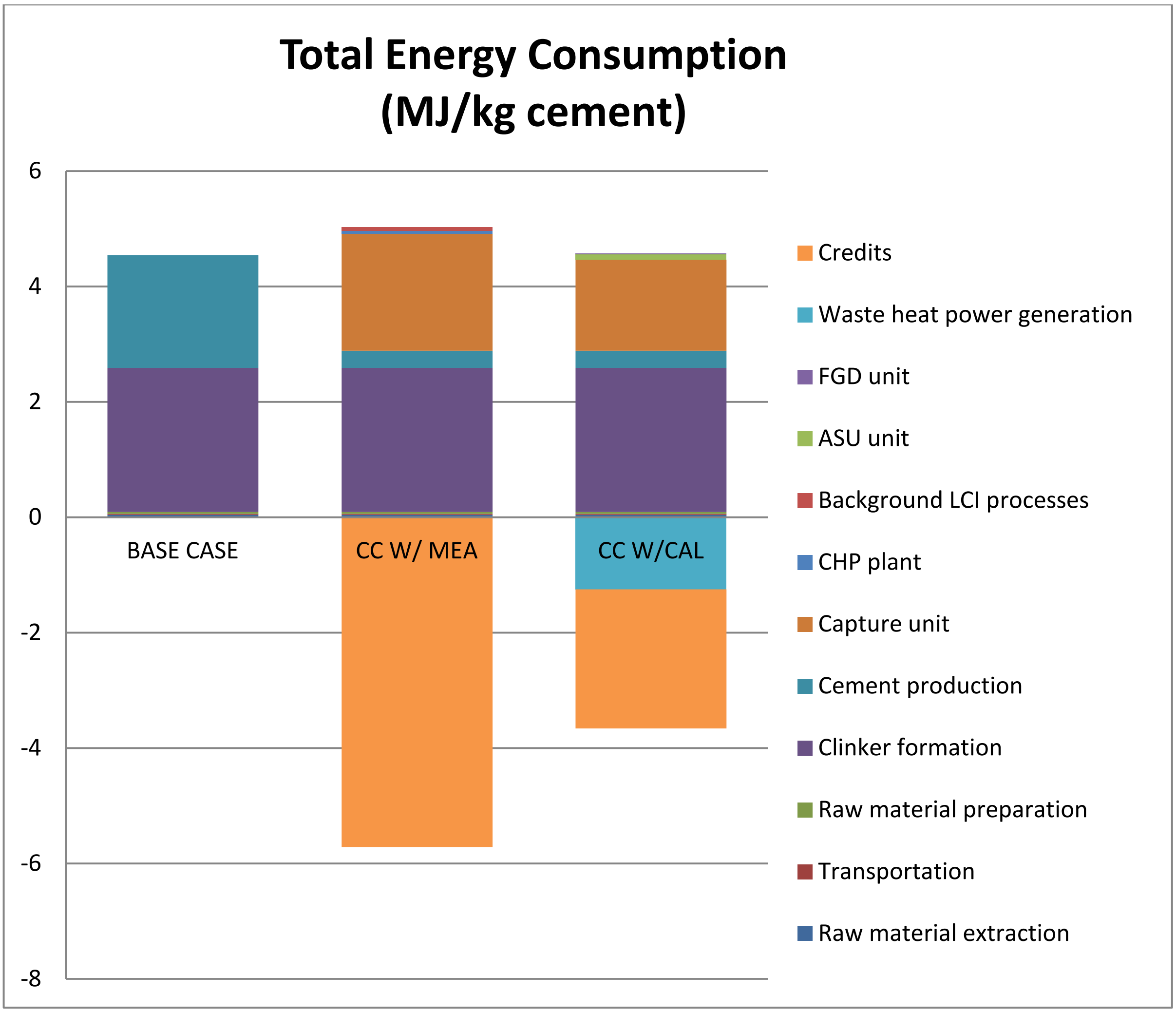

Figure 42: Comparison of total energy consumption

2.6.2 GWP

Juxtaposition of the three cases (figure 43) leads to the appreciation of the great amounts of CO_2 abated from the distinguished capture units. As such, the CCP emits 0.724 kg CO_2eq/kg of cement. The benefits of carbon capture are fairly evident; by application of MEA scrubbing in case 2, the CO_2 emissions are ostensibly nearing 1 kg CO_2eq/kg cement, which bodes well with the increased energy consumption of this case, attributed to the installation of the CHP plant and the capture unit. However, the amount captured by MEA (0.83 kg CO_2eq/kg cement) results in a significant decrease, thus leaving a mere 0.15 kg CO_2eq/kg cement to be emitted in the atmosphere (80% reduction in GWP). In the same context, application of CaL is equally beneficial, since cement plant 3 produces 0.96 kg CO_2eq/kg cement, but captures 0.83 kg CO_2eq/kg cement. As a result, 0.12 kg CO_2eq are emitted in the atmosphere (83% reduction in CO_2 emissions). Consequently, although MEA scrubbing presents a better performance in abating CO2 in terms of energy consumption, the GWP - and, by extension, the environmental impact - of CaL is significantly lower.

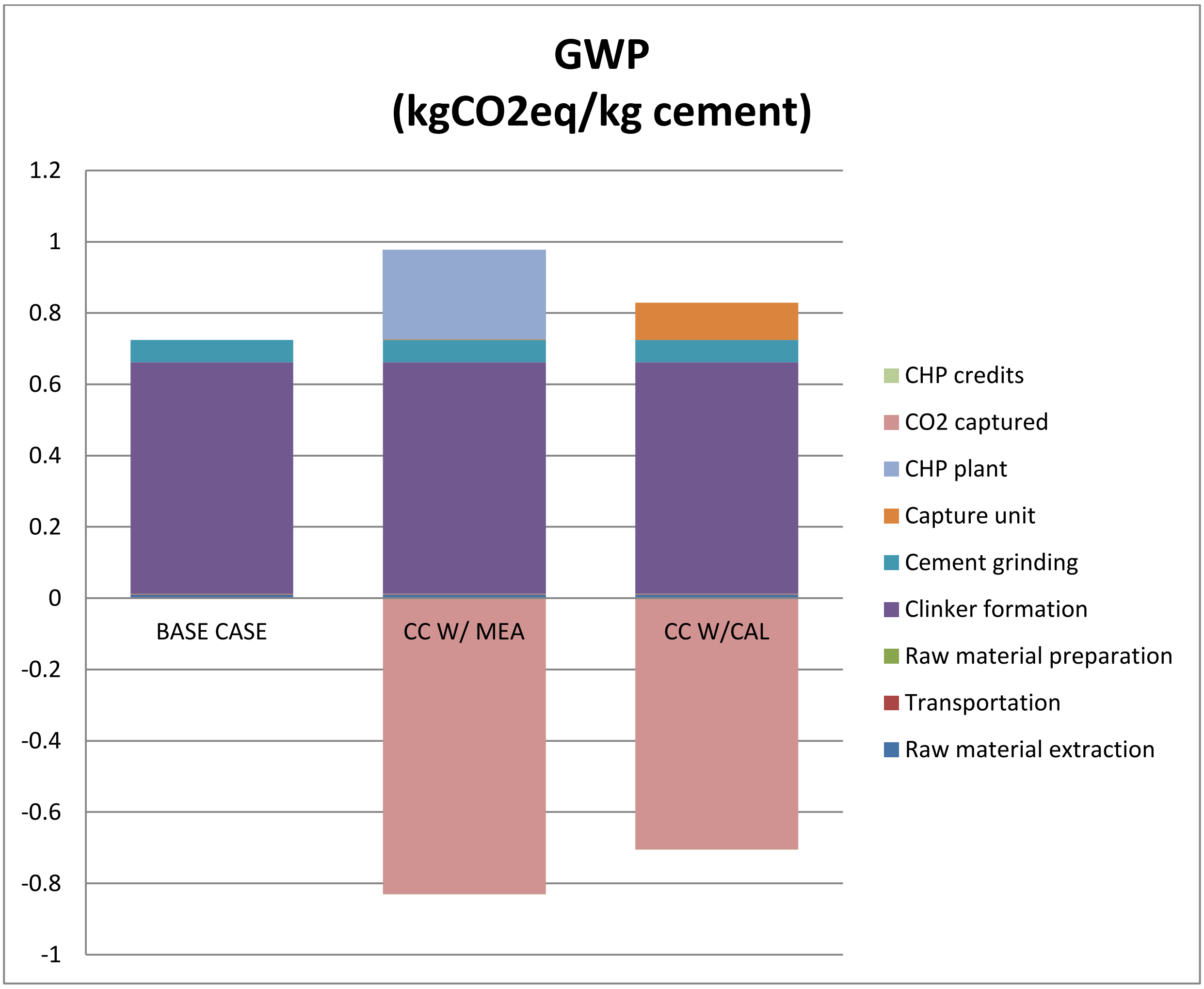

Figure 43: Comparison of GWP

PART C: CONCLUSIONS

In line with the literature review performed for the purposes of this study, when a country displays economic growth, aspects of this growth are translated into increased industrialization and construction. Thus, cement, being a fundamental product for infrastructure and construction, is closely correlated with the economic development of a country. Nonetheless, cement production in great volumes is associated with certain setbacks; cement manufacturing is an intrinsically energy-demanding process, which results in substantial quantities of carbon dioxide emitted to the atmosphere. The present thesis detected that these implications are attributed to two parts of the process, namely clinker formation and cement grinding. The former is a procedure which requires a high temperature profile in the kiln, in order for the raw material to be converted to clinker (a compound formed before cement takes its final form), hence appropriate amounts of fuel (most often petroleum coke) are necessary to maintain the needed temperature. Cement grinding, on the other hand, is a process within which clinker is ground into fine particles with the use of a ball-bearing mill, that requires a considerable amount of electricity in order to operate. Thus, the extensive amount of electricity consumed in a cement plant essentially corresponds to respective indirect fossil fuel consumption on behalf of the electricity provider, a procedure which also yields a certain environmental impact.

Drawing from the aforementioned implications, the present work was dedicated to the investigation of the environmental impact of the cement industry and recorded proposed measures for the amelioration of this impact. Firstly, a set of measures that improve the thermal and electric efficiency of the cement plant were examined. the application of which was found to result in significant savings in terms of fuel and/or electricity, as well as emission reductions. Afterwards, the issue of alternative fuel use and conventional fuel substitution was raised, where a variety of materials was investigated, with the main aim being the reduction of indirect emissions. Review of the available literature conceded the suitability of certain fuels for kiln combustion and revealed that appropriate alternative fuel usage may lead to decreased fossil fuel dependency, however there are still technical and political barriers, which currently impede the further expansion of this mitigation measure. Thirdly, the notion of introducing blended cement types, to partially substitute clinker, was evaluated. The research showed that the clinker/cement ratio and, by extension, energy requirements and carbon dioxide emissions are lowered, whilst cement properties are maintained at a similar level. However, there are several limitations to the implementation of such cement types, such as the regional availability of substituting materials and the market acceptance, which prevent the further application of these constituents.

The predominant CO_2 mitigation measure considered in this thesis for application to the cement industry is post-combustion carbon dioxide capture, a technology which encompasses separation of carbon dioxide from other flue gases, by means of absorption in a suitable solvent or sorbent and thereby prevents CO_2 from being emitted to the atmosphere. This specific technology was set as the main focus of this report, due to the fact that review of the available literature conveyed a potentially promising future, especially taking into account the gained knowledge from other industrial sectors, and secondly because significant quantities of carbon dioxide are abated with a great degree of efficiency, with certain compromises in terms of energy and cost. The most dignified cases of post-combustion capture are MEA scrubbing and CaL. The former utilizes MEA, which reacts with acidic CO_2 vapours to form a dissolved salt, which subsequently releases a concentrated CO_2 stream with the use of heat. Research on this concept revealed that, although MEA scrubbing is very efficient in abating CO_2, electricity consumption is increased. CaL, on the other hand, makes use of the reversible carbonation reaction, utilizing calcium oxide as a sorbent, to make up calcium carbonate when reacting with carbon dioxide. The reverse reaction takes place in the adjoining vessel, where the calcium carbonate particles are decomposed into the aforementioned substances at very high temperatures. This technology encourages reuse of spent CaO as raw material in cement manufacturing. Moreover, incorporation of a waste heat recovery unit in the system is reportedly beneficial for power production, where excess heat rejected from the capture unit would be used in a steam cycle for power production. On the contrary, its main hindrance is the fact that there is no practical experience of this application in the cement industry.

As a consequence of the aforementioned research results, in order to ascertain whether post-combustion capture is eventually suitable for application in cement production and in absence of similar work, a case study was established, where the lifecycle of a conventional cement plant, from raw material extraction to production of 1 kg of cement was compared with two identical plants, each equipped with one of the post-combustion capture technologies analyzed previously. Specifically, every case was scrutinized in terms of fossil fuel consumption, energy consumption by process and carbon dioxide emissions, translated into global warming potential. Firstly, this analysis managed to verify that the predominant causes, due to which conventional cement production affects the environment, are the processes of clinker formation and cement grinding, as they were found to be the two most energy-intensive processes, yielding at the same time the most CO_2 emissions, throughout cement manufacturing. Regarding post-combustion capture with MEA scrubbing, this assessment concluded that it has the largest energy penalty out of the three cases, due to the additional energy demand for the regeneration of the MEA solvent and the operation of the CHP plant, initially considered to cover the requirements of both the cement plant and the capture unit. However, the CHP plant was shown to produce excess electricity, assumed to be fed back to the grid, thus decreasing electricity production from fossil fuel use. In terms of CO_2 capture, this technology displayed great potential, as the amount of CO_2 emissions was abruptly decreased, in contrast with the conventional cement plant. Concerning CaL, the lifecycle assessment revealed that, due to the fact that both carbonation and calcination reactions take place in excessive temperatures, an augmented quantity of petcoke is used to provide the required heat. However, weighing in the effect of the electricity avoided due to the independence provided to the system by the waste heat power generation unit that was assumed in this case, the energy demand of the cement plant, equipped with CaL, is marginally lower than the benchmark case. In addition, CaL produced less credits than MEA scrubbing, but in terms of CO_2 capture capabilities, its performance was similar, mainly owing to the fact that the two cases were assumed to have the same capture efficiency. However, since the cement plant with CaL emits less CO_2 per kg cement, its environmental impact was significantly lower. Overall, within the particular restrictions and assumptions of this study, CaL was deemed more suitable for application to a cement plant.

This study took advantage of a valuable environmental analysis tool, namely life cycle assessment, in order to shed some more light to a still obscure - but yet intriguing - issue, such as carbon capture in the cement industry. Certain limitations, such as the absence of similar LCA studies for benchmarking, especially for CaL, restricted the scientific research to a specific depth, beyond which an uncharted area was unveiled. The author believes that, the great advantages of this technology, which lie in i) the exploitation of spent CaO, thus leading to savings in material and ii) its capture capabilities, in combination with its apparent independence in electricity consumption, are sufficient to consider CaL as a sensible choice for CO_2 abatement in this industrial sector. This thesis may serve as basis for further research pathways, which may examine similar case studies from a techno-economic point of view and acquire a more spherical perspective of the feasibility of this technology, with the objective to raise public awareness for carbon capture to a greater level.

NOMENCLATURE

ASU: Air Separation Unit

BCSAF: Belite - Calcium Sulphoaluminate - Ferrite

CaL: Calcium Looping

CCS: Carbon Capture and Storage

CCP: Conventional Cement Plant

CHP: Combined Heat and Power

CKD: Cement Kiln Dust

CIPEC: Canadian Industry Program for Energy Conservation

CPU: Carbon Purification Unit

CSI: Cement Sustainability Initiative

FGD: Flue Gas Desulphurization

IEA: International Energy Agency

IGCC: Integrated Gas Combined Cycle

LHV: Low Heating Value

MEA: Monoethanolamine

OPC: Ordinary Portland Cement

REO: Reduced Emission Oxygen

SCL: Spent Carbon Lining

SNCR: Selective Non-Catalytic Reduction

WBCSD: World Business Council for Sustainable Development

WRI: World Resources Institute

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Appendix 1: Assumptions for LCI of CCP [82]

- Transportation processes were simulated with respect to conditions in Germany, due to lack of respective entries for Greece in the software.

- The ratio of the raw material feed is assumed to be 25% shale and 75% limestone.

- Shale is assumed to be transported by lorry from the region of Efkarpia, at a distance of 4.5 kilometres from the cement plant.

- Limestone is assumed to be transported by lorry from the region of Drymos, at a distance of 17.5 kilometres from the cement plant.

- Gypsum, which constitutes 3-5% of the final product, is assumed to be transported by lorry from the port of Thessaloniki, at a distance of 13 kilometres from the cement plant.

- Pozzolana constitutes 1% of the final product and is assumed to be transported from Skydra by lorry, at a distance of 85 kilometres from the cement plant.

- Fly ash produced as waste from the power plant in Ptolemaida is assumed to be transported by lorry at a 120 kilometre distance from the cement plant.

- Input and output of background life cycle inventory processes (e.g. fuel mix breakdown for electricity) was assumed to be embodied in the inventory.

- Storing and packaging processes were omitted from the life cycle assessment.

Appendix 2: MEA CO2 capture efficiency calculation

Table: Summary of cement plant performance with and without CO_2 capture **[74]**

	Unit	Base case (no capture)	Post combustion capture	Oxy-fuel combustion
Fuel and power				
Coal feed	Kt/y	63.3	291.6	72.1
Petroleum coke feed	Kt/y	32.9	32.9	27.1
Total fuel consumption (LHV basis)	MW	96.8	304.0	97.8
Average power consumption	MW	10.2	42.1	22.7
Average on-site power generation	MW	-	45.0	0.7
Average net power consumption	MW	10.2	-2.9	22.0
CO_2 emitted and captured				
CO_2 captured	Kt/y	-	1067.7	465.0
CO_2 emitted on-site	Kt/y	728.4	188.4	282.9
CO_2 emissions avoided at the cement plant	Kt/y	-	540.0	445.6
	%	-	74	61
CO_2 associated with power import/export	Kt/y	42.0	-11.8	90.8
Overall net CO_2 emissions	Kt/y	770.4	176.6	373.7
CO_2 emissions avoided, including power import and export	Kt/y	-	593.8	396.8
	%	-	77	52

The cement plant considered for the base case emits 0.7284 kg CO_2/ kg cement. According to the same table, in the post-combustion capture case (with MEA) the additional coal required for the CHP plant is:

$$\frac{[(coal\ feed_{MEA}) - (coal\ feed_{base})]}{annual\ cement\ production} = \frac{(291.6 - 63.3) * 10^3 t}{10^6 t/year} = 0.23\ kg\frac{coal}{kg}cement.$$

Considering that the emission factor for coal is 2.3 kg CO_2/kg of coal combusted, this extra coal combustion emits:

$$0.23\ kg\frac{coal}{kg}cement * 2.3\ kg\frac{CO_2}{kg}coal = 0.529\frac{kgCO_2}{kg}cement.$$

Therefore the total CO_2 emissions for the case with post combustion capture equal 0.728 + 0.529 = 1.257 kg CO_2/ kg cement (or 1253 kt/y).

Given that, from the table, the captured emissions are 1.067 kg CO_2/kg cement, then

the capture efficiency of MEA is:

$$\frac{1.067}{1.257} * 100\% = 84.9\%$$

including conventional cement manufacturing and the CHP plant process.

Appendix 3: Assumptions for MEA - NH3 inventory [83]

MEA

- MEA, at plant, Europe (1 kg)

- Collection method: Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.

- Included processes: Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production, estimation of energy demand and infrastructure of the plant (approximation), solid wastes omitted.

- Average European processes for raw materials, transport requirements and electricity mix used.

- The multioutput process **"**ethanolamines, at plant**"** delivers 40% MEA; large uncertainty of process data due to weak data on production process and missing data on process emissions/geography not specified.

- Technology: Production from ethylene oxide with 95% process yield, inventory based on stoichiometric calculations, emissions to air and water estimated using mass balance, treatment of waste water in an internal waste water treatment plant assumed.

Ammonia

- Ammonia, steam reforming, liquid, at plant (1 kg)

- Transportations based on standard distances of Ecoinvent

- Infrastructure: proxy module used (chemical plant, organics)

- Manufacturing process starting with natural gas, air, electricity plus auxiliaries, energy transportation, infrastructure, land use, wastes and emissions into air and water

- Transportation of raw materials, auxiliaries and wastes is included; transport and storage of product not included

- Production assumed to be taking place under stable operation conditions

- Emissions to air assumed to be emanating in a high population density area; emissions to water assumed to be emitted into rivers

- Geography: European average values

Appendix 4: Deduction of mass and energy input in CaL

table 3, mass balance modelling results **[67]**

	kJ/kg clinker	**MJ/kg cement**
Limestone	1.09	0.88
O_2	0.19	0.153
CO_2 emissions	0.13	0.105

x0.8077/1000

deduction of additional petcoke consumed:

base case overall fuel consumption **[67]**: 2918.08 kJ/kg clinker

CaL overall fuel consumption **[67]**: 4874.65 kJ/clinker

thus, CaL petcoke consumption: 4874.65 - 2918.08 = **1956.57 kJ/clinker**

According to Lambrou **[82]**, 0.8077 kg clinker produce 1 kg of cement, hence

1956.57 * 0.8077/1000 = **1.58 MJ/kg cement**

table 5, energy consumption **[67]**

	kJ/kg clinker	**MJ/kg cement**
ASU	111.15	0.08978
FGD	11.06	0.0089
CO_2 purification	206.78	0.167
CO_2 compression	260.07	0.21

x0.8077/1000

According to energy recovery potential calculations, from Vatopoulos and Tzimas **[67]**:

electricity produced from waste heat: 899.67 kJ/kg clinker = **0.7267 MJ/kg cement**

heat produced from waste heat: 649.87 kJ/kg clinker = **0.5249 MJ/kg cement**

Appendix 5: Low Heating Values of fuels [87]

Fuel	**LHV (MJ/kg)**
Diesel	42.6
Petroleum coke	29.505
Brown coal (lignite)	17.4
Hard coal	23.9
Crude oil	43
Heavy fuel oil	39
Natural gas	38

Appendix 6: Calculation of electricity avoided

- From the input of the CHP plant, 0.351 kg coal produce 4.93 MJ heat, as the thermal efficiency of the plant is 59%.

- The capture unit requires 1.82 MJ heat, for 1 kg of cement.

- To produce 1.82 MJ heat, the CHP requires $\frac{0.351}{4.93} * 1.82 = 0.129$ kg hard coal/kg cement.

- These 0.129 kg coal/kg cement correspond to $\frac{0.128*3.6}{0.351} =$ **1.323 MJ** electricity produced by the CHP plant for 1 kg cement.

- The total electricity required for cement production with MEA scrubbing is 0.2871 + 0.204 + 0.0029 = **0.494 MJ**

- Hence, the surplus electricity that will be fed to the grid will be 1.323 - 0.4911 = **0.8290 MJ**