

Strategies to reduce CO₂ Emissions in the Cement Industry



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November 2018

The present study is associated to a research project with the purpose of exploring strategies to reduce CO₂ emissions in the cement industry, with focus on CO₂ capture through calcium looping cycle. It was developed with the support of CIMPOR's cement plant in Alhandra (CPA), Portugal, which provided process data. The current state of the environment impels the urgent mitigation of CO₂ emissions, and the cement industry plays an important role in it, since it produces CO₂ from both energy generation and raw material transformation. A sustainable cement production will only be possible with the implementation of several methods identified for CO₂ abatement, some of which are still under development^[1].

This work presents a preliminary analysis of the cement production process for determination of CO₂ emissions' quantity, and identification of strategies for its reduction, in general and in the case of CPA. The total CO₂ emission was obtained 840 kgCO₂/t_{Clinker}, which for cements represents approximately 59% from calcination of the raw materials, 33% from fuel combustion and 8% from electricity consumption. Two main sources of heat waste were identified: the gases conditioning tower (10MW) and the excess air stream from the clinker cooler (12MW); and two options for the carbon capture process feed stream were determined: the effluent stream from the pre-heating tower (340°C) and the effluent stream from the entire process, before the dedusting unit (130°C or 340°C).

Keywords: Cement Production, CO₂ Emissions, Alternative Fuels, Energy Efficiency, CO₂ capture, CIMPOR.

1 Introduction

The cement industry is responsible for 5% of the global anthropogenic CO₂ emissions^[2] and it is expected a 12% growth on cement production by 2050. Cement production emits CO₂ due to the raw material processing and to fuel combustion to provide energy for the endothermic reactions and to maintain a temperature up to 1500°C. 50% of emissions are estimated to be from the raw materials' calcination, 40% from fuel burning and 10% from electricity consumptions and transportation^[3].

The Cement Sustainability Initiative (CSI), part of the World Business Council for Sustainable Development (wbcSD) has identified four main levers for CO₂ reduction: Energy efficiency, via modern dry-process technology; the use of alternative fuels and biomass; the substitution of clinker with other mineral components; and carbon capture and storage^[3]. The intended target of CO₂ emissions for cement production, of an increase of only 4% by 2050^[4] despite the sector's growth, will only be attained with the implementation of strategies in all those four areas^[2]. CEMBUREAU's Roadmap on CO₂ mitigation estimates that a 32% reduction of emissions is possible with conventional means, but a reduction up to 80% is only possible with emerging technologies, on which CO₂ capture is included.

Reductions in CO₂ emissions can be considered at a global scale, accounting for emissions in the life-cycle of the product, or at the cement production center, where only direct emissions are accounted. The identification of strategies should take into account this difference, because a reduction

in a production center may not result in global reduction, or a strategy that reduces global emissions may not be beneficial for the production center or may be out of their responsibility.

The first step to develop strategies for CO₂ emission reduction is to acquire a deep understanding on the process and product specifications, so as to know what changes can be made to the process or product, and whether they would result in CO₂ mitigation. If the purpose is to reduce CO₂ emissions for the production center, then it is necessary to know how those emissions are accounted as well.

The CO₂ emissions in a production center are monitored and have an established determination method. In the case of CPA (CIMPOR's production center in Alhandra, Portugal), it follows the rules of TEGEE (translated: emission license on greenhouse effect gases), under the European Emission Trading System (EU ETS). These rules will be considered in the CO₂ accounting.

The present work intends to quantify CO₂ emissions on a cement's production center in Alhandra (CPA), Portugal, from the CIMPOR group. It also intends to review, based on knowledge of the process and product, different strategies for reduction of CO₂ emissions and conclude on the possibility of further investigation. For the specific case of CPA, it is intended to identify sources of potential optimization and possibilities of integration with the carbon capture process. This work is a preliminary analysis on CO₂ reduction strategies and data gathering that will assist future investigations.

2 Cement Production

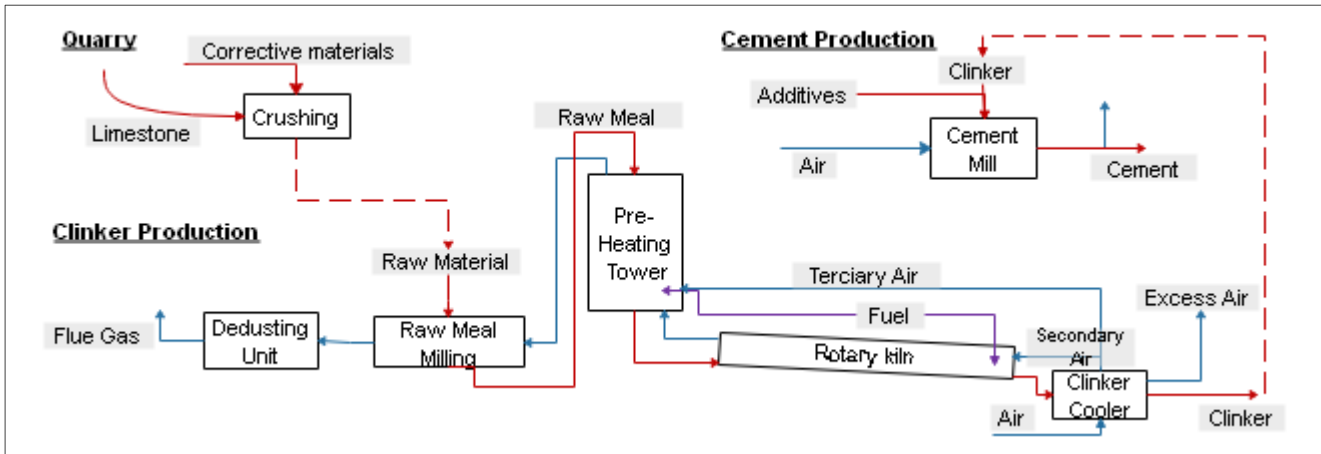
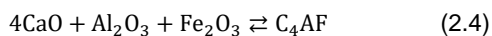
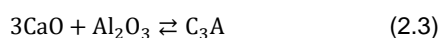
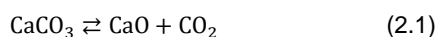


Figure 2-1 – Simplified process diagram of cement production, raw material extraction, clinker production and cement milling

The main raw material for the cement production is limestone, mineral rock extracted from quarries. The main constituents necessary for the process, presented in the oxide form, are CaO , SiO_2 , Al_2O_3 e Fe_2O_3 , which exist in many different compounds and crystalline forms in the raw materials. For example, calcium exists mainly in the carbonated form, CaCO_3 . The raw material mixture needs defined proportions of these elements, and therefore, additional materials, rich in each element, need to be added to the extracted limestone in order to achieve the desired composition. Examples of those materials are: different grades of limestone, with a higher CaCO_3 content, sand, rich in SiO_2 , bauxite for Al_2O_3 , and pyrite ash for Fe_2O_3 .

The main constituent of cement is clinker (Ck), a mineral rock produced from the sintering process of the raw material mixture, composed of different crystalline phases, the main being¹: C_3S , C_2S , C_3A e C_4AF . The thermal treatment is performed in a cyclone tower and a rotary kiln. The tower consists of several cyclones placed in series and/or parallel, that promote direct contact in counter-current of the raw meal and the hot gases from the kiln, for pre-heating and partial decarbonization (equation 2.1) of the raw meal. After that, the materials are introduced in the rotary kiln where sintering occurs, promoting the formation of the clinker phases (equations 2.2 to 2.4). The heat source to the process is combustion, performed in a pre-calciner (PC), located in the cyclone tower, and in the main burner (MB), located inside the rotary kiln.



The clinker is immediately cooled after leaving the rotary kiln, in direct contact with atmospheric air, in order to preserve its properties. The cooling air is then used further in the process: part of it is fed to the rotary kiln (secondary air), it is used to supply air to the pre-calciner (tertiary-air), and the rest, not necessary for the process (excess air), is cooled by indirect contact with atmospheric air and sent to the atmosphere. The hot gases effluent from the cyclone tower, are used for the milling of the raw meal, dedusted and sent to the flue-gas stack.

The BAT² for clinker production is the dry-process route with a suspension pre-heater consisting of a cyclone tower with 4-5 stages equipped with a pre-calciner, and a grate clinker cooler. Alhandra's plant has two different lines of production, both dry-processes with a cyclone tower, but one is equipped with a satellite cooler, and has a production of 3969 t/day³, and the other one has a grate clinker cooler and a pre-calciner, with a production of 2653 t/day³. Alternative fuels are used in both lines. Clinker annual production is 50%³ from each production line and a typical clinker composition is presented in Table 2-1.

Table 2-1 – CPA's Clinker composition

Clinker Phase	C_3S	C_2S	C_3A	C_4AF	$\text{CaO}_{\text{livre}}$
%	74.6	5.8	5.6	11.3	1.7

Cement is produced by milling of clinker with gypsum and other additives, depending on the type of cement. Cement quality is regulated by the European Standard EN197-1 [5], that defines the type of materials and the range in which they can be included in each cement. Alhandra's plant produces the following types of cement: CEM I 52,5R, CEM I 42,5R, CEM II/A-L 42,5R, CEM II/B-L 32,5N and CEM IV/B(V) 32,5R. Their material composition is presented in Table 2-2³.

¹ The phases designation follows cement industry nomenclature in which: C=CaO, S=SiO₂, F=Fe₂O₃, A=Al₂O₃.

² Best Available Technology

³ Annual average of 2017

Table 2-2 – Material composition of cements produced in CPA in wt%

Type of Cement	Clinker	Limestone	Gypsum	Fly Ash
CEM I 52,5R	94	1	5	0
CEM I 42,5R	92	3	5	0
CEM II/A-L 42,5R	79	16	5	0.1
CEM II/B-L 32,5N	63	32	5	0.1
CEM IV/B(V) 32,5N	54	0	3	43

Since the clinker production is a very complex process, controlling the rotary-kiln conditions is not a straight-forward task, and the operating conditions have, inherently, some degree of variability, and so does the clinker produced. The conditions depend on the raw materials composition and granulometry, on the temperature profiles and residence time in each equipment, the gases flow and its O₂ and CO₂ content and on other minor volatile constituents [6]. Clinker quality will depend not only on the proportion between each phase but also on its allotropic form, which will be influenced by temperature and the presence of some minor solid constituents.

3 CO₂ Emissions in Cement Plant

3.1 Raw materials and calcination

The CO₂ emissions from raw materials are calculated from the composition analysis of the prepared mixture. This composition is not universal, and depends on the target for clinker phase composition, on the production unit specifications and on the fuels used. An example of this composition is shown in Table 3-1. The loss on ignition (L.O.I) is the method used to determine the CO₂ emission factor (EF_{CO₂}) from the raw meal. From the total LOI, it is deduced the water evaporated from both humidity and clay components, and the organic carbon, which is not accounted as emission [7], to obtain the value of CO₂. Alternatively, a LOI analysis in the temperature range between 500°C and 975°C may be performed.

Table 3-1 – Raw meal composition (%wt) example from CPA and CO₂ emission factor (kgCO₂/t_{rawmeal})

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	L.O.I. (total)	CO ₂ EF _{CO₂} (kg/t)
43.34	12.77	3.67	2.1	1.06	0.33	35.47	33.77

The weight raw-meal-to-clinker ratio used was determined by plant data, for CPA's kiln 7, which has the value of 1.5.

3.2 Fuel combustion

In CPA, as in most of cement plants nowadays, alternative fuels (AF) derived from waste materials are used in addition to petcoque. Refuse-derived fuel (RDF) is a broad term, used for many types of non-hazardous wastes, from municipal or industrial sources, but in this work, it refers to

paper, plastic and fabrics derived from municipal waste. Other types of RDF are automotive shredded residues (ASR), tires and biomass residues, which in this case are derived from the olive oil and animal feed industry. The properties of these fuels are presented in Table 3-2. The combustible composition refers to both the fixed carbon and the volatile matter of Proximate Analysis, meaning, all components that oxidize and become part of the gas phase.

Table 3-2 – Properties from fossil and alternative fuels used in the CPA and CO₂ emission factors

Property	Petcoke	Coal	ASR	Tires	RDF	Animal waste	Olive Pomace
Total fuel basis							
LHV (kcal/kg)	7677	4266	6869	5647	5203	4145	4147
Humidity (%)	5	16	2	2	3	3	10
Combustible (%)	94	66	76	79	87	75	82
Ash (%)	0	18	22	19	10	22	8
Combustible Part of the fuel (%)							
C	87	77	89	68	59	57	55
H	4	3	8	9	8	8	7
O	1	20	1	19	31	22	35
N	2	1	0	2	1	12	3
S	7	0	2	0	0	1	0
Cl	0	0	0	2	1	1	0
Biogenic Carbon	0	0	27	20	52	100	100
CO ₂ Emission Factors							
EF _{CO₂} (kg/kg)	3.0	1.9	1.6	1.8	0.9	0	0
EF _{CO₂} (kg/Gcal)	391	436	278	263	175	0	0

The thermal emission factor of each fuel is determined by the fuels' carbon content and the lower heating value (LHV), according to equation 3.2, where MW refers to the molar weight, V to the combustible part of the fuel, C to the carbon content of the combustible part of the fuel and B to the biogenic carbon fraction, all in weight percentage. The results of the emission factor are also presented in Table 3-2. These emission factors should not be used for calculations of CO₂ concentration in the flue gas, since they don't account the biogenic carbon.

$$EF_{CO_2}(\text{massic}) = \frac{C \times V \cdot MW_{CO_2}}{100^2 \cdot MW_C} \left(1 - \frac{B}{100}\right) \quad (3.1)$$

$$EF_{CO_2}(\text{thermal}) = \frac{C \times V \cdot MW_{CO_2}}{100^2 \cdot MW_C} \left(1 - \frac{B}{100}\right) / LHV \quad (3.2)$$

In Figure 3-1 the CO₂ emission factors are represented, where effective CO₂ is the total, including the biogenic carbon, and the accounted is the one calculated with equation 3.2. It's possible to conclude that the use of alternative fuels instead of petcoque results in an effective CO₂ emission reduction. However, a reduction to a great extent is only possible because biogenic carbon is not accounted.

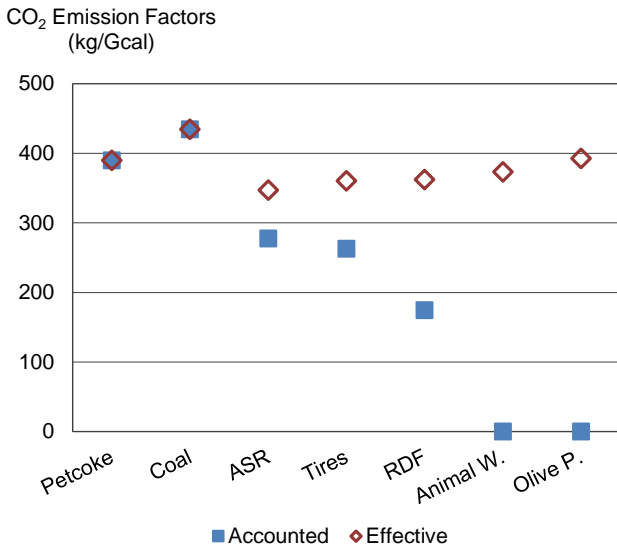


Figure 3-1 – CO₂ emission factors for each fuel used in CPA

The fuel mix used in the production center varies with the wastes availability, and they are only fed to the kiln if the system is stable. For CPA's kiln 7, the maximum thermal substitution (TS) recorded recently was of 59% in total [pre-calciner (PC) and main burner (MB)]. The target for fuel split is for 60% of heat to be provided by the PC. Local TS is higher on the PC as well, with values up to 65%, while on the MB is 55%. Theoretically, the specific heat consumption (HC) of the kiln varies with the type of fuel used, since they have different temperatures and oxygen needs for their ignition. However, a statistical analysis on CPA data shows that for TS rates ranging from 18 to 59%, HC only varied 0,6%⁴, and no correlation was observed between the two variables. Being so, the average value of 841 kcal/kg_{ck} may be used to predict CO₂ emissions from different fuel mixes.

The specific CO₂ emission from combustion was determined by equation 3.3, in which f represents each fuel, Q_f its mass flow, and P_{ck} the clinker production. The data used were daily totals from CPA, for 67 days of stable production, with different cases of fuel substitution. The results are presented in Table 3-3. The average obtained was of 262 kg_{CO2}/ton_{ck}, and there was a maximum CO₂ saving due to biogenic carbon of 30%. The high values of StDev are due to the great variability of fuel mixtures that are used. Values of accounted CO₂ (Figure 3-1) have a greater variability for different fuels than the effective CO₂, which results in greater variability for the values of Emission reduction than for the values of CO₂ Emission (Table 3-3).

$$CO_2 \text{ Emission} = \frac{\sum_f EF_{CO_2}(\text{massic}) \times Q_f}{P_{ck}} \quad (3.3)$$

⁴ Calculated as $3 \times \text{StDev} / \text{Average}$, where StDev.p is Excel's standard deviation function, and both functions are applied to the same data sample.

Table 3-3 – CO₂ emissions due to fuel combustion in CPA cement plant

	CO ₂ Emission (kg/ton _{ck})	Emission Reduction (%)	Total Thermal Substitution (%)
Maximum	344	30	59
Average	262	19	42
Minimum	224	3	3
StDev (%)	26	90	70

3.3 Electricity consumption

Electricity consumption has a carbon footprint associated, since its production generates CO₂. However, this emission is accounted by the power plant that produces it, not by the consumer. Therefore, electricity consumption is an indirect emission of cement production, that does not account for CPA's emissions license (TEGEE). It is relevant, however, in terms of Life Cycle Assessment (LCA), and shall be quantified in this section.

By annual statistics, specific electricity consumption for intermediary products was determined for each process stage: crushing and milling of the raw materials, milling of petcoke, clinker burning and cement milling. Based on the proportions between these products, it is possible to determine the total electricity consumption, specific of each final product, clinker and cements. The results are presented in Table 3-4 and Figure 3-2.

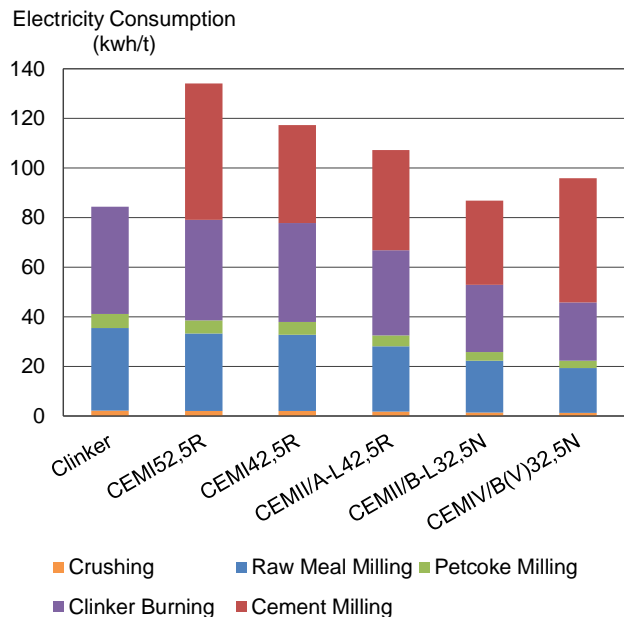


Figure 3-2 – Electricity consumption of each stage of production, for clinker and cements produced in CPA

The CO₂ emission associated with electricity depends on its generation process. For legal purposes, the value of 0.47 kg_{CO2}/kWh^[8] is the standard and will be used in this work. However, due to the use of alternative fuels and energy

efficiency optimization in power plants, this value tends to decrease. Therefore, for a more detailed estimation, an investigation of the supplier of electricity and its emission factor should be made. The total CO₂ specific emission from electricity consumption is presented in Table 3-4.

Table 3-4 – Total specific electricity consumption of each CPA product, contribution of each stage of the process and CO₂ emission factor due to electricity consumption

Product/ Process Stage	Clinker	CEM I 52,5R	CEM I 42,5R	CEM II/A-L 42,5R	CEM II/B-L 32,5N	CEM IV/B(V) 32,5N
Electricity Consumption (kWh/t)						
Total	84.4	134.1	117.2	107.3	86.9	95.8
Electricity consumption per process stage (%)						
Crushing	3	2	2	2	2	1
Raw Meal Milling	39	23	26	25	24	19
Petcoke Milling	7	4	4	4	4	3
Clinker Burning	51	30	34	32	31	25
Cement Milling	-	41	34	38	39	52
CO ₂ Emission Factors (kg/t)						
Total	40	63	55	50	41	45

3.4 Total Specific Emissions

Based on the CO₂ emission factors previously presented, it is possible to determine the total specific CO₂ emissions, for clinker and each type of cement. For this total, the average value of emissions from combustion (Table 3-3) was used. The results are presented in Table 3-5.

Table 3-5 – Total specific CO₂ emission for clinker and cements production

Product/ Emission type	Clinker	CEM I 52,5R	CEM I 42,5R	CEM II/A-L 42,5R	CEM II/B-L 32,5N	CEM IV/B(V) 32,5N
CO ₂ emission (kg/t)	840	813	792	684	479	542
Direct (%)	Calcination	61	59	59	59	59
	Combustion	35	33	34	34	34
Indirect (%)	Electricity	5	8	7	7	8

As expected, cement's CO₂ emissions due to electricity consumption are small compared to direct emissions an average of 8%. Because of that, the proportion of each type of emission is approximately the same for each cement, even though the totals are different. Being so, it is possible to characterize different types of cement's emissions as being on average 59% due to calcination of raw meal, 33% to fuel combustion and 8% to electricity consumption. Since most of the emissions are the direct ones due to clinker production, the clinker content of each cement is the decisive factor on their total CO₂ emissions, as it can be verified in Figure 3-3.

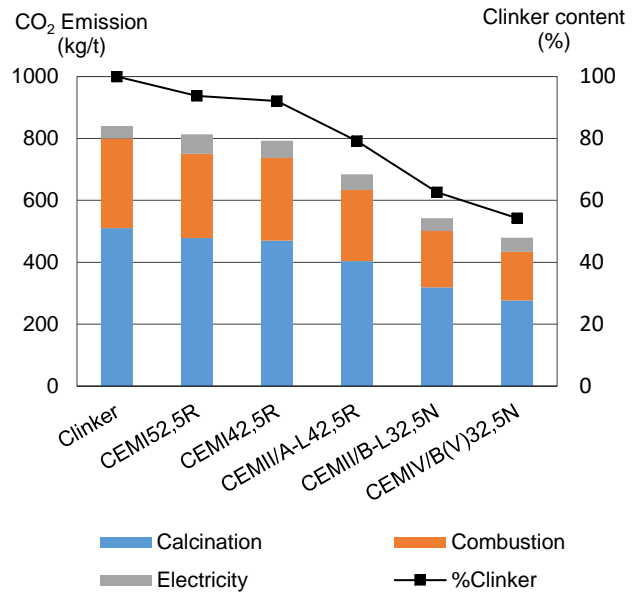


Figure 3-3 – Comparison of CO₂ emissions of each cement with its clinker content

4 Energy Optimization Options

Clinker production is an inherently integrated process, but there's still some wasted heat. In order to investigate possible waste heat applications, it is necessary to quantify its temperature and heat potential. This analysis was performed with process data from online measurements of 17 days of continuous and stable production.

4.1 Gas Conditioning Tower

There is a maximum temperature of 190°C for the gas that can go through the dedusting unit before the flue gas stack. A Gas Conditioning Tower (GCT) is used to cool those gases by water spraying if needed. The effluent gases from the pre-heating tower are around 340°C, therefore, when not integrated with the raw meal milling process, the use of the GCT is imperative, but when the milling occurs, it is only used occasionally. This operation, although necessary, represents a waste of process heat. The process effluent's flow, at the end of the line, is on average 266310 Nm³/h, with a StDev of 6%. But since the GCT is upstream, the flow at that point is less altered by false air.

The waste heat is determined by equation 4.1, which describes the heat balance to the stream, considering only the water's latent heat, where $\Delta H_{\text{vap,H}_2\text{O}}$ is the enthalpy of vaporization of water and $Q_{\text{H}_2\text{O}}$ is the water's mass flow. The results are presented in Table 4-1, in which the case 'with milling' corresponds to periods only with water addition to the GCT. It should be noted that for the case without milling, the stream temperature is measured right after the GCT, and so, although the table states 192°C, the stream will cool below the 190°C limit before entering the dedusting unit.

$$\text{WasteHeat} = \Delta H_{\text{vap,H}_2\text{O}} \times Q_{\text{H}_2\text{O}} \quad (4.1)$$

Table 4-1 –Cases of the use of GCT, characterization of the gas fed to the dedusting unit and waste heat associated

	With Milling	Without Milling
Stream into GCT (°C)	339	
Water Flow (m ³ /h)	3.9	14.6
Waste Heat (MW)	2.7	10.2
Wasted Heat (kcal/kg _{ck})	20.3	76.2

4.2 Excess Air

Another source of wasted heat is the excess air from the clinker cooler, which also needs to be cooled to be dedusted, in this case, below 130°C. This flow has the mean value of 189173 Nm³/h, with a StDev of 18%. Table 4-2 presents the temperature values for the excess air, in o and out of the air cooler. The excess air out of the clinker cooler has a great variability in temperature due to process' characteristics, but since it's possible to regulate the cooling air, this variability is eliminated in the outlet air from the cooler.

Table 4-2 – Excess air stream characterization and waste heat associated

	Inlet	Outlet
Temperature Average (°C)	285	105
Temperature Deviation (%) ⁴	50	26
Flow Average (t/h)	245	
Flow Deviation (%)	18	
Wasted Heat (MW)	13	
Wasted Heat (kcal/kg _{ck})	94	

The wasted heat was estimated by a heat balance between the inlet and outlet streams of the air cooler, described in equation 4.2, where Q_{Air} is the stream flow and \bar{C}_p is an averaged value, for the temperature interval ΔT , of the air's heat capacity.

$$\text{WasteHeat} = Q_{Air} \bar{C}_p \Delta T \quad (4.2)$$

4.3 Fuel Humidity

The use of fuels with humidity for combustion constitutes a reduction in the energy that is provided to the system. That reduction is accounted for when considering the LHV of the fuel tested with its water content, therefore, the process is provided with the necessary heat, but more fuel is used, since part of its calorific potential is being consumed in the evaporation of water.

The wasted heat (WH) is defined by equation 4.3 as the heat consumed to evaporate the water content (%H), with $\Delta H_{vap, H_2O}$ being the water's enthalpy of vaporization, on a basis of mass of dry fuel. The wasted heat is compared to the total heat potential of the fuel, also in a dry basis (LHV_{dry}).

$$\text{WH (\%)} = \frac{\%H \times \Delta H_{vap, H_2O} \times \frac{1}{1 - \%H/100}}{\text{LHV}_{dry}} \quad (4.3)$$

The results presented in Table 4-3 show that the heat wasted in water evaporation is only between 0.2 and 2.2 % of the fuel's heat potential. For this small amount, a unit to previously dry the fuels may not be justifiable for the fuels

already used in CPA but adding a fuel drier unit would make possible the use of other alternative fuels, with a much higher water content.

Table 4-3 – Heat waste due to fuel humidity, for each fuel used in CPA

Wasted Heat	Petcoke	Coal	ASR	Tires	RDF	Animal W.	Olive P.
kcal/kg _{dry fuel}	34	112	11	12	18	21	65
%	0.4	2.2	0.2	0.2	0.3	0.5	1.4

5 Feed Stream Options for the Carbon Capture Process

Carbon capture is one of the strategies to reduce CO₂ emissions. It consists of an end-of-pipe process which removes CO₂ from the flue gas for future usage or storage. The capture process considered in this project is the calcium-looping cycle. After the kiln and pre-heater, where all the CO₂ is produced, there are several options for the streams to feed to the capture process, illustrated in Figure 5-1, and which will be described below.

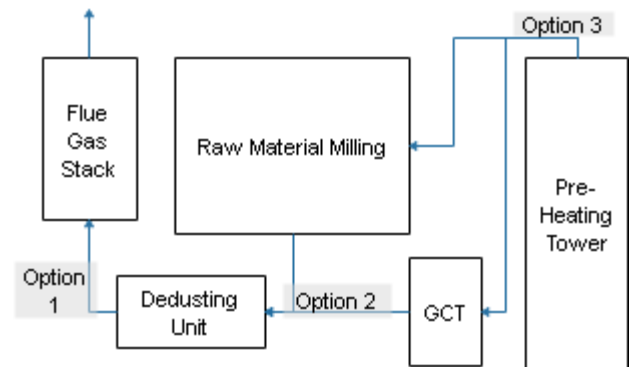


Figure 5-1 – Options for the stream to feed the carbon capture process: 1-Gas to flue gas stack, 2-Gas before dedusting unit, 3-Effluent from pre-heater

The straightforward option for the stream is the process effluent, that goes to the flue gas stack (option 1). This option has the advantage of not interfering with the upstream process and there is already a complete characterization of that stream available, since its temperature, flow and compositions are monitored. However, this stream was cooled down, which constitutes a heat waste, and to feed a calcium-looping cycle capture process the stream would have to be re-heated up to 600-650°C^[9]. Therefore, it is worth to consider other options upstream.

To avoid the waste heat of the TCG cooling, the stream could be fed to the capture process before being dedusted (option 2). Without the temperature limitation, there would be no need to cool the stream, and its heat potential would be used for the capture process. Without being dedusted, the flow would transport particles to the capture reactor, which may be of a different composition and granulometry from the material particles used to capture the CO₂. Its influence on the process would need to be investigated.

Table 5-1 –Options for feed stream to the carbon capture process, for each regime, with milling (A) and without it (B)

Stream	Gas to flue gas stack		Gas before dedusting Unit		Effluent from pre-heater
	1		2		
Option					3
Regime	A	B	A	B	
Temperature (°C)	124	165	130	339	339
Flow (Nm ³ /h)	266310				~199733
CO ₂ (%)	17.6				~31.33
H ₂ O (%)	10.2				-
SO ₂ (mg/Nm ³)	36				-
Particles (g/Nm ³)	1.25E-4		>1.25E-4		~78.6
Advantages	No changes to existing process		No GCT waste		Stability
Disadvantages	Heat waste in TCG		Two very different regimes		New gas stream for milling. More dust.

In options 1 and 2, two regimes would exist, for the case with and without raw material milling (regimes A and B, respectively), which would influence the stream's temperature, mass flow and water content. In option 1, the stream would be either 124°C or 165°C, with and without milling, respectively. In option 2, the temperatures' gap will be greater, since the stream won't be cooled without milling – the stream would be 130°C with milling and 339°C without it. As to the flow, the milling process will result in an average of 25% of excess air. The circuit of the gases through the GCT is less prone to false air, so there will be a difference between regimes as well, which will also be greater for option 2. The gases' water content will depend on the raw meal humidity.

The existence of regimes means that the capture process would need to be flexible - be able to process the inlet stream with different temperatures, flows and CO₂ content, which may result in a process under optimal conditions, less efficient.

There is a third option that would provide a constant stream, not dependent on the raw milling regimes, which is the pre-heater effluent (339°C). This option is the same as option 2 for the case without raw meal milling, and since the stream will no longer be used in the milling process, an alternative for it would need to be arranged. There's a percentage of raw meal feed to the cyclones that is transported by the gases, which depends on the cyclones' separation efficiency. A typical value for dust in the pre-heater effluent in CPA is 14,2% of the raw meal feed. For an average feed of 110,5 t/h, dust is approximately 78.6 g/Nm³. Besides stability, this option has the advantage of having a lower mass flow and higher CO₂ content (less false air), which results in a higher capture efficiency. It has a lower water content than option 1, which might be a disadvantage, since steam has proven to improve the calcium-looping cycle efficiency [9], but there are still other options available to humidify the stream.

Since only the stream into de flue gas stack is monitored, the characterization of the other streams will have to be done

with estimation methods, or by additional measurements in the plant. The data necessary is flow, temperature, content and composition of dust particles, gas content on CO₂, H₂O, SO₂ and on other components that may affect the capture process. Table 5-1 presents the characterization, advantages and disadvantages of each option.

6 Conclusions

In this work, CO₂ emissions in the Alhandra's cement plant (CPA) were determined. The values obtained are going to be compared with the averages of global cement production for the year 2016, provided by the "Getting the numbers Right" database [10]. Also, based on the process analysis, several considerations on how to apply CO₂ emissions strategies will be made, which will assist future investigations.

CEMENT PLANT DATA

The average thermal consumption for clinker production provided by the GNR database for a production line with a pre-calciner is 810 kcal/kg_{ck} [10], while the value obtained in CPA was 841 kcal/kg_{ck}, higher in 4%, which is not a significant difference. However, it suggests that there may be a way to improve energy efficiency.

As to alternative fuels' usage, the average thermal substitution (TS) is 17%, of which 11% is derived from mixed wastes, and 6% [10] from biomass. The average TS in CPA is 42% and a maximum of 60% has already been reached. TS average for EU28 is 44% [10], which is in accordance with CPA values. These values show that alternative fuels are not yet being used in all cement plants, or are being used at lower substitution rates, while CPA is already within the average of the EU.

GNR database also presents the type of fuels used. Of the fossil fuels used, 44% is petroleum coke and 41% is coal. As for alternative fossil fuels and mixed fuels, 36% are RDF with plastics and 18% tyres. The biomass fuels are 33% agricultural or organic waste and charcoal, 22% wood and 11% animal bone. CPA already uses most of these fuels, but there are still other options that may be explored.

The direct CO₂ emission for a clinker production line with pre-heater and pre-calciner is 837 kg_{CO2}/t_{ck} [10]. CPA's clinker emission factor, for direct emissions, is 798 kg_{CO2}/t_{ck}, approximately 5% lower than the GNR average, which is probably due to its higher alternative fuel usage. Considering the several types of cementitious products that exist, cement's clinker content is on average 75% and direct CO₂ emissions are 637 kg_{CO2}/t_{cement} [10]. This value is included in the range of values obtained for CPA's cements of 441-748 kg_{CO2}/t_{cement}.

As to power consumption, GNR database provides the average of 103 kWh/t_{cement} [10], which is included in the range of 87-134 kWh/t_{cement} obtained with CPA data of different cements.

Table 6-1 – Strategies to reduce CO₂ emissions in cement production – direct emissions in the cement plant

Product CO ₂ Emission Source	Clinker					Cement	
	Raw Material Calcination		Combustion for Thermal Energy			Clinker	
CO ₂ Emission Reduction Strategy	Decarbonated Materials	Clinker's Calcium Silicate Content	ENERGY EFFICIENCY			Alternative Fuels	Cement's Clinker Content
			Combustion Conditions	Optimum Heat Integration	Process Stability		
Source of reduction	↓EF _{Material} ↓Heat Demand	↓Demand (Heat and Material)	↓Heat Demand	↓Heat Demand ↓Waste Heat	↓Heat Demand	↓EF _{Fuel}	↓EF _{Cement}
Investigation Areas	Materials	Materials – Clinker performance Clinker Process	Clinker Process			Materials	Materials – Cement performance and Applications

STRATEGIES TO REDUCE CO₂ EMISSIONS

Raw material calcination is the main source of CO₂ emissions in cement production - based on CPA data, it results in 64% of direct emissions. Those emissions can be reduced in two ways: use of decarbonated raw materials and production of clinker with less calcium silicates (C₃S and C₂S).

Examples of decarbonated materials are ashes from lignite or coal, blast furnace slag, concrete crusher sand and demolition waste [11]. For a cement plant, the use of these materials will always result in a CO₂ emission reduction: not only from calcination, but also from fuel, since calcination is a highly endothermic reaction. However, these material's availability is limited, and indirect emissions associated with its transport, from a life-cycle point of view, could result in a net increase of carbon emissions.

Clinker resistance properties are mainly due to C₃S and C₂S phases, and the content on these constituents greatly influences the amount of CO₂ emissions, not only from calcination of materials, but also from fuel combustion, since they are formed at very high temperatures (up to 1500°C). Cements' European norm doesn't specify a range of clinker's content on each of these phases, only a minimum content of 67% for the total of C₃S and C₂S [5]. CPA's clinker content on these phases is 80.4%. So, theoretically, a way to reduce carbon emissions is to produce clinker with less C₃S and C₂S content. In practice, however, changes would have to be made to cement production, in terms of clinker content and granulometry, and the kiln's operational conditions would also need to be changed in order to achieve a different clinker phases' ratio, which could result in a less thermal efficient process. Therefore, it is not straightforward to predict the feasibility and the impact to CO₂ reductions of this strategy.

The second main source of CO₂ emission is fuel combustion, which is greatly dependent on the type and quantity of fuel substitution. It is due to the increasing use of alternative fuels that the typical value of 40% of emissions being due to combustion tends to decrease. In CPA only 36% of direct emissions are due to fuel combustion. No solid fuel has zero CO₂ emissions, but due to the present legislation, biogenic carbon is considered to be carbon neutral, which means that theoretically, it is possible to have zero accounted emissions from fuel combustion, when only biofuels or

biowastes are used. However, fuel substitution is limited by practical/operational issues:

Alternative fuels are usually harder to ignite, need more time and/or a higher temperature to burn, and have a different demand for oxygen. It is necessary for the combustion chamber to have the right dimensions, and combustion air needs to be adjusted, so to provide enough residence time. The change in combustion air may also influence cyclone's separation efficiency. The other limiting factor is the fuels' content in minor constituents: volatile elements, like sulfur and chloride, that tend to accumulate in the system; potassium and sodium, which affect the volatility of other elements, and phosphorus, which affects cement's quality.

Another way to reduce fuel combustion related emissions is by reducing thermal energy consumption. That can be done by either lowering the energy required or by optimizing operational conditions. The former can be achieved by the already mentioned clinker composition change. Since C₃S is the phase that forms at the highest temperature and that demands more CaO, lowering its content in clinker would result in thermal energy reduction necessary for CaCO₃ calcination and to maintain the system at a higher temperature. Optimization of operational conditions requires a complete knowledge of the complex interactions between gas and material flows on residence times, temperature profiles, material transport and thermal losses, which will reflect on combustion efficiency and clinker quality.

Since electricity emission from cement milling represents only an average of 3% of total emissions, the CO₂ emission associated to cement is proportional to its clinker content. Clinker substitution – incorporating other materials with hydraulic properties into cement – is another strategy to reduce CO₂ emissions. The Cements' European Standard already defines cements based on the type of materials that compose it and defines a range of clinker that each should contain, therefore, studies on clinker substitution should follow those guidelines. In order to reduce clinker content and still achieve the same mechanical properties, changes need to be made either on clinker quality or on cement's granulometry. Another way to implement clinker-substitution strategy is by using the adequate cement for each application. There may still be a tendency to use cement with quality above the needed. An example of that was the use of

CEMI42,5R, which was possible to replace in some applications with CEMII/A-L42,5R, that has the same resistance but less clinker content, and therefore emits 14% less CO₂.

Although clinker production is an inherently integrated process, there is still the possibility to make use of the process waste heat. In this preliminary analysis, two main sources of waste heat were identified: the excess air from clinker cooler, with a flow of 245 t/h at 285°C, which corresponds to 13MW of heat wasted; and the effluent gas from clinker production, with 266310 Nm³/h and 339°C, which represents a waste up to 10MW. These streams could be used for steam production/power generation and for drying of fuel and raw materials. They can also be integrated with the CO₂ capture process in a way that the total heat demand of both processes is lower than the non-integrated option.

The options identified for streams to feed the carbon capture process are the effluent gas from the process, before going to the flue gas stack, before going to the dedusting unit, or before going to the raw material milling process. Each of these options have advantages and disadvantages, presented in Table 5-1, depending on their temperature, flow water and particle content. There is the need to acquire more information about the process, namely, to quantify the dust collected in the final dedusting unit and the exact gas flow of the effluent of the pre-heating tower. The choice of the best option is dependent on the definition of the conditions of the carbon capture process.

With the present work, a strategy for future investigations on developing specific methods to reduce the CO₂ emissions in cement plants, and in particular, on Alhandra's plant, can be made. As a final thought, it is possible to state that investigation of strategies are mostly on the area of material science or process analysis on a very complex level. Decisions on what strategies should be investigated further should take into account the phenomenon's involved, either of material quality or process, it's correlation with other strategies, and consider whether there are resources available to accurately quantify them.

Acknowledgments

Thanks are owed to Alhandra's production center (Cimpor) for sharing knowledge of the process and for the data provided.

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