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Analysis of a process to capture the CO_2 resulting from the pre-calcination of the limestone feed to a cement plant

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Abstract

This work analyzes a new $CaCO_3$ pre-calcination method aimed at CO_2 production in a highly concentrated form. The method is based on the use of a very hot stream of CaO particles that transfer heat from a circulating fluidized bed combustor (CFBC) to the calciner (fluidized with CO_2). The aim of this work is to present a case study of the integration of the main units in the capture system: the CFB combustor, the fluidized bed calciner, and the CO_2 compressor for the application of the system to a reference cement plant. It is shown that it might be possible to avoid around 50% of the CO_2 emissions associated to the cement manufacture process.

CO_2 capture, cement plant, calcination

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1. Introduction

Global cement production grew from 594 Mt in 1970 to 2200 Mt in 2005 [1] and is projected to increase [2]. Nowadays, the cement industry generates approximately 5% of the global anthropogenic carbon dioxide emissions [3], making the cement industry an excellent candidate for implementing CO_2-emission mitigation strategies. Based on worldwide cement production, the average intensity of carbon dioxide emissions is 0.81 kg CO_2 per kg of cement and around 50% of cement-related greenhouse gas emissions result from fossil fuel combustion [3]. The remaining emissions are an inherent product of the process of the decomposition of $CaCO_3$ to CaO (the main precursor to cement) [2]. The fraction of CO_2 from $CaCO_3$ decomposition emitted from a cement plant increases as the thermal efficiency of the cement plant increases. In new highly efficient, cement plants almost 70% of the CO_2 emissions come from the decomposition of $CaCO_3$ to CaO. In this kind of cement plants, the potencial for improving energy efficiency is very limited [4, 5]. Even if efficiency could be increased, the overall fraction of CO_2 emitted from the cement plant due to the calcination of the raw feed would only increase from the current levels.

Cement production is a highly energy-intensive process. Cement making consists of three main steps: raw material calcination, clinker making in the clinker oven (kiln) and cement making. A large amount of energy is required for the calcination of the raw material and to reach the high temperatures (around 1400 ºC) required in the kiln. The theoretical energy consumption for producing cement is about 1.76 GJ (assuming reactants and products at 25 ºC) [6, 7], estimated based on the energy required to produced 1 ton of Portland cement clinker. In practice, energy consumption is higher, since energy is required to evaporate water and to compensate for the heat losses. Currently the best available technology (using a dry process with preheaters and a precalciner before the kiln) requires 3 GJ/t of cement manufactured from which, 1.99 GJ are required in the calcination of the raw material per ton of clinker product [6]. In cement plants, besides CO_2 emissions from energy consumption (supplied trough combustion of carbon-intensive fuels), the cement-making process also emits CO_2 from the calcining process.

The purpose of this work is to analyze a new process [8] aimed at substantially reducing CO_2 emissions from existing and new cement plants, but focusing only on the CO_2 evolving from limestone calcination. The process is briefly described below and a case study for integration into an existing cement plant is conducted afterwards using Aspen Hysis simulation software. The chosen configuration for simulation is a pre-calciner comprised of a CFB combustor, a fluidized bed calciner and a CO_2 compressor. Both, combustor and calciner have been designed as adiabatic reactors. Thermal integration of the system is performed, and a sub-critical Rankine cycle is used to obtain at least the energy to drive the CO_2 compression system.

2. Description of the new calcination process

The concept analyzed in this work is presented in Figure 1 and has also been described elsewhere [8]. The target of the process is to decompose the continuous stream of $CaCO_3$ into CaO to be fed to a cement plant and CO_2 to be purified and compressed for permanent geological storage. This can be achieved without using any chemical reaction of CO_2 absorption, by focusing only on the CO_2 arising from the decomposition of $CaCO_3$ to CaO (the CO_2 from combustion of the fuel in air is emitted). In the proposed process, the calcination and the combustion reactions take place in independent chambers. The necessary heat to sustain the calciner is supplied by a circulating stream of superheated CaO that is used as heat carrier between a circulating fluidized bed combustor and the fluidized bed calciner. Thus, the CO_2 released in the calcination of the $CaCO_3$ is obtained in a concentrated form, and is suitable for storage after purification and compression.

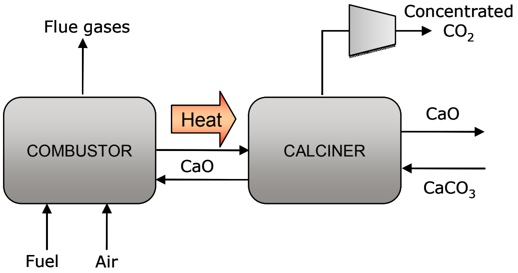


Figure 1. Scheme of the process proposed in this work to obtain a CO_2 concentrated stream resulting from the calcination of $CaCO_3$.

The process shown in Figure 1 can be integrated in a cement plant and take benefit of the high level of thermal integration typical in this energy intensive process and the experience in handling solid streams at very high temperatures.

The cement manufacture process of a conventional 3000 t cement/day plant is taken as a reference to calculate mass and heat balances and set the boundary conditions for a more detail analysis of the proposed precalcination process in the next sections. It is assumed that the reference cement plant uses a dry process with pre-heaters and a pre-calciner before the kiln. In the Figure 2 the main flows of the carbon balance involve in the cement manufacture process chosen as a reference are shown (more details can be found in references [6, 7]).

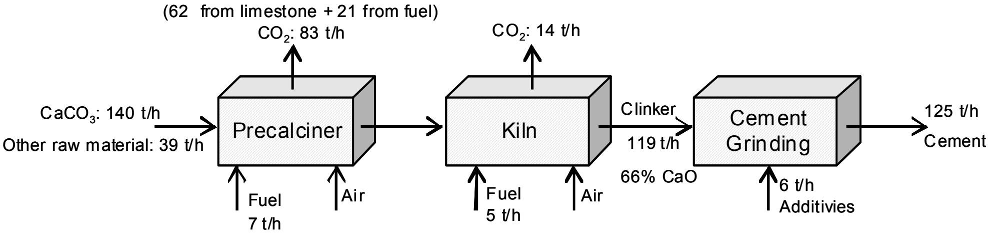


Figure 2. Scheme of the main mass flows of a high efficient cement plant that produces 3000 t of cement per day (125 t/h).

The fuel characteristics used in the calculation are compiled in Table 1, and correspond to a petroleum coke, a usual fuel in cement plants. In order to calculate the mass balance it is assumed that a modern cement plant requires an energy input of about 3 GJ/t of cement and about 60% of this energy is used in the precalciner to carry out the calcination [6, 7]. Since 1.99 GJ/t of clinker are required in the calcinations, around 140 t/h of limestone are required by the process with a clinker/cement ratio of 0.95. The composition of the clinker obtained has around 66% of calcium oxide, which is common in clinker compositions [7]. In the Figure 2 can be seen that a major fraction of carbon dioxide emissions (almost 64%) comes from calcining the limestone present in the raw material.

As mentioned above, the aim of the alternative process, outlined in the Figure 1, is to obtain the CO_2 emitted by the calcination process in the cement manufacture, in a pure form. Therefore, it is proposed to replace the pre-calciner of Figure 2 by a new arrangement that produces a pure stream of CO_2 as indicated in Figure 1.

The key feature of the proposed process is that high temperature CaO particles coming from a circulating fluidized bed combustor (CFBC) are brought into contact with the raw feed of $CaCO_3$. In the CFBC, petroleum coke (or another suitable fuel) can be burned at high temperatures (> 1000 ºC) in the presence of CaO. Thus, CaO particles are circulating between CFBC and precalciner reactor, transferring the heat required by the calcination reaction from the combustion chamber. Mass and heat balance calculations have shown [8] that there are operating windows to operate the system under realistic process conditions compared to similar high temperature applications of CFBCs in the power and mineral roasting industries. At some point in the recycled stream of CaO, there is a purge of CaO that is the actual product of the precalciner and directed to the kiln.

A particular set of process conditions in the pre-calciner of Figure 1 has been simulated with Aspen Hysys, enclosing all the necessary components to purify and compress the CO_2 stream obtained from the calciner, taking benefit of the high temperature streams obtained in the process in order to heat up the air fed to the combustor chamber as well as the fuel and limestone feeds to the process, also extracting the necessary power in a sub-critical Rankine cycle to drive compressors and auxiliary equipment. The objective in the simulation was to design a pre-calciner system self-sufficient in terms of fuel demand and electricity consumption to deliver a compressed CO_2 stream and a CaO stream to be fed to the kiln. The incorporation of this system in a cement plant might require a new design of the full cement plant to ensure a better heat integration in the whole process. However, this exercise of integration with the rest of components in the cement plant is outside the scope of the present work.

The CFB combustor and pre-calciner system substituting the calciner in the reference cement plant (3000 t/day) has been simulated in a process flowsheet (see Figure 3) that comprises the CFB combustor, the $CaCO_3$ pre-calciner, the CO_2 compressor and pump up to 100 bar and a sub-critical Rankine cycle extracting heat from gas streams. These units are described below in more detail:

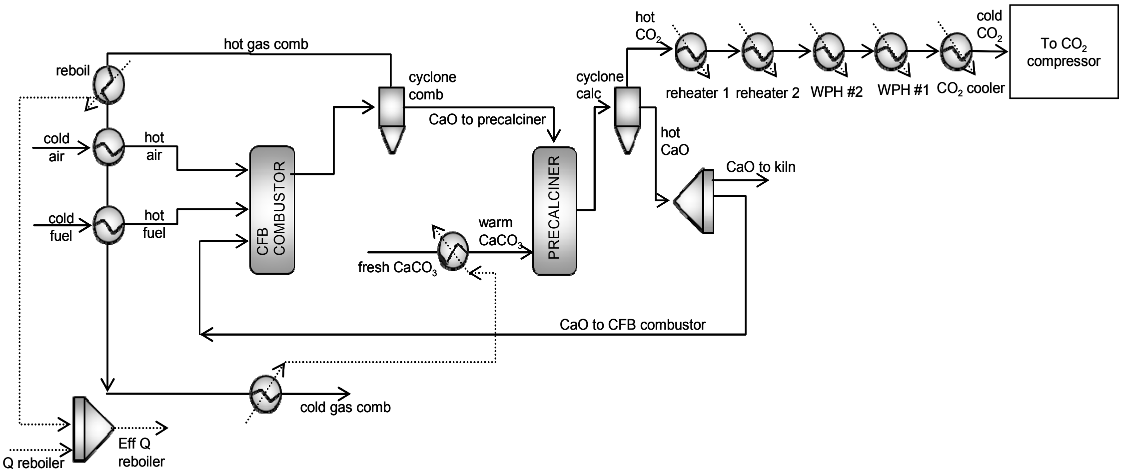


Figure 3. CFB combustor and precalciner flow diagram proposed to capture the CO_2 resulting from the pre-calcination of the fresh limestone in the cement manufacture process.

The aim of the CFBC is to heat up the solid material coming from the precalciner at 950 ºC (required temperature for rapid rate and full calcination) to temperatures close to 1050 ºC. At this temperature, fuel burns in an air-fired CFBC. From the mechanical and material point of view, these high temperature CFBCs are well established technology up to operating temperatures of 1150 ºC for alumina calcination and other mineral ore roasting processes [9]. The combustor has been designed as an adiabatic 125 MW unit. A large flow of CaO is required to transfer the necessary heat from the combustion chamber to the calciner when the ΔT between these reactor is moderate. For CFBCs reactors, solids fluxes can be as high as 10-50 kg/m^2s [9, 10], but large scale CFB boilers usually operate at the lower end of this range. The required solid flow circulating between the combustor and calciner to produce 125 t of cement per hour is about 4000 t/h. This large amount of solids indicates a solid circulation rate around 30 kg/m^{2}s referred to 6 m/s characteristic gas velocity in the CFB combustor. As indicated above, petroleum coke, a usual fuel in cement plants, has been used to provide the energy to the combustor. The fuel characteristics are compiled in Table 1. The heat balances in the combustor reaction considers two chemical reactions: coke combustion and CaO sulfation (SO_2 retention has been shown to be effective up to 1050 ºC, according to Anthony et al [11]). Three streams are fed to the combustor according to the arrangement shown in Figure 3: preheated fuel (250 ºC), preheated air (625 ºC) and a recycled stream coming from the pre-calciner (950 ºC). The combustor outlet is separated in the cyclone in gas and solid streams. The gas stream (hot gas comb in Figure 3) will be used not only in the reboiler for steam generation, but also for preheating the fuel, air and fresh $CaCO_3$ streams. On the other hand, the superheated CaO stream goes to the pre-calciner (see Figure 3). Finally, the gas stream leaves the system as exhaust gas at 130 ºC (cold gas comb in Figure 3).

The precalciner unit is also a CFB connected to the CFB combustor. This reactor is operated adiabatically at 950 ºC and the $CaCO_3$ endothermic calcination takes place. The energy required for this chemical reaction is provided by the hot solids coming from the combustor at 1050 ºC. This means that no additional fuel has to be supplied to this unit for the calcination process. Although it has not been considered in this scheme, recycled CO_2 could be used to fluidise this reactor because at this very high temperature (950 ºC) fast and complete $CaCO_3$ calcination is achieved even under pure CO_2 atmosphere. For lower calcinations temperatures or faster calcinations rates, superheated steam could be also recycled as fluidizing gas to the calciner, in order to reduce partial pressures of CO_2 in the calciner. The stream leaving the calciner reactor is separated into a eventually pure CO_2 gas stream (hot CO_2 stream) and a solid stream (hot CaO stream in Figure 3) that is partially recycled to the CFB combustor (CaO to CFB combustor stream) and also taken to the clinker production facility (CaO to kiln stream in Figure 3). Because of the high energy requirements of the precalciner, only 2% of the solids leaving this reactor are extracted from the circulating solids and directed to the kiln to be used in the cement production. The remaining 98% of the solids are used as energy carriers. Regarding the solids composition, they are mainly comprised of CaO (95.5 %), $CaSO_4$ (4.4 %) and fuel ashes (0.1 %). This composition can be considered as appropriate for cement production [5].

The mass flows and temperatures of the main streams in the CFB combustor and precalciner of Figure 3 can be seen in Table 1.

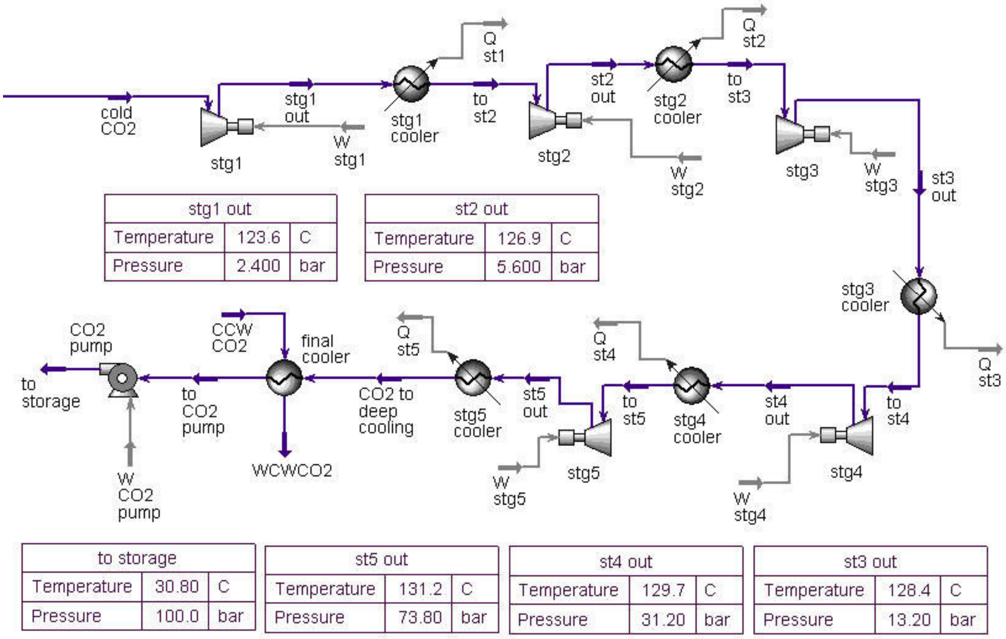
Table 1. Fuel composition and mass flows and temperatures of the main streams of the CFBC and pre-calciner system of the case study (Figure 3) for a standard cement plant that produces 125 t/h of cement.

	Mass fraction
C	0.8221
H	0.0311
S	0.0550
O	0.0050
N	0.0190
Moisture	0.0652
Ash	0.0026
Calorific value (MJ/kg)	32.65

Stream	*Flow (t/h)*	*T (ºC)*
Hot air	162	625
Hot Fuel	14	250
CO_2 in Hot gas comb	41	1050
CaO to CFB combustor	4048	950
CaO to precalciner	4050	1050
Warm $CaCO_3$	140	178
Hot CaO	4126	950
CaO to kiln	78	950
Cold CO_2	62	45

The hot CO_2 stream obtained in the precalciner chamber is directed to the compression unit. The CO_2 compressor has been designed as a multi-stage turbocompressor with intermediate cooling and is represented in Figure 4. This is a common arrangement for CO_2 compressors. The final pressures in any stage have been selected in order to have outlet gas temperatures below 135 ºC. The inlet temperature for every stage has been fixed to 45 ºC and the adiabatic efficiency has been considered 75%. Although it has not been considered in this model, the intermediate coolers could be shell and tube heat exchangers and the compressed CO_2 thermal energy could be used for preheating the water used in the Rankine cycle. After the fifth compressor stage, a pump is used because the CO_2

is a liquid at that high pressure. The compression and pumping power up to 100 bar has been calculated and a value of 6.2 MW was obtained. In Figure 4 is shown the temperature and pressure of the CO_2 stream after each stage of compression and cooler.



stg1 out		
Temperature	123.6	C
Pressure	2.400	bar

st2 out		
Temperature	126.9	C
Pressure	5.600	bar

to storage		
Temperature	30.80	C
Pressure	100.0	bar

st5 out		
Temperature	131.2	C
Pressure	73.80	bar

st4 out		
Temperature	129.7	C
Pressure	31.20	bar

st3 out		
Temperature	128.4	C
Pressure	13.20	bar

Figure 4. Detailed scheme of the multi-stage CO_2 compressor.

A sub-critical Rankine cycle, shown in Figure 5, is used to obtain the required power for compression. A steam turbine of three bodies is used. In the high pressure body (HPT1), steam is fed at 540 ºC and 172 bar coming from the reboiler and the superheater. The steam leaves the first body at 353 ºC and 42 bar and is driven to the first reheater. There, the steam temperature rises up to 540 ºC and the steam is fed to the medium pressure body (MPT). The steam leaves this unit at 320 ºC and 8.1 bar. After that, the steam is conducted to a second reheater where it is heated up to 430 ºC and later expanded in the low pressure body (LPT). When the steam leaves this last step, the temperature has dropped up to 38.6 ºC, the pressure is 0.068 bar and the vapour fraction yields 0.921. Finally, this partially condensed stream (LPT outlet stream) is driven to the condenser where it is completely condensed. The condensed water is compressed from 0.068 bar to 13 bar in the condensate pump (CP pump) and driven to the first water preheater (WPH 1). The warm water leaves the first water preheater at 170 ºC and goes to the main pump (MP pump) where the pressure is increased up to 196 bar. The pressurised water is again preheated in the second water preheater (WPH2) up to 250 ºC and finally fed to the reboiler where the water is evaporated again and converted into superheated steam at 540 ºC and 172 bar. The net cycle power is the sum of the partial power produced in the three steam turbines minus the energy required for pumping. The total power extracted from this cycle is 10.4 MW with cycle efficiency 41.6 %, clearly higher than the efficiency obtained in pulverised fuel (PF) power stations with subcritical Rankine cycles because turbine steam extractions for water preheaters have been avoided and a second reheater has been included. The power obtained in the Rankine cycle could be used to produce electricity and provide the energy for the CO_2 compression system, the CO_2 pump and the Rankine cycle pumps. In addition, there are 4.2 MWe that could be used to provide energy in other plant locations.

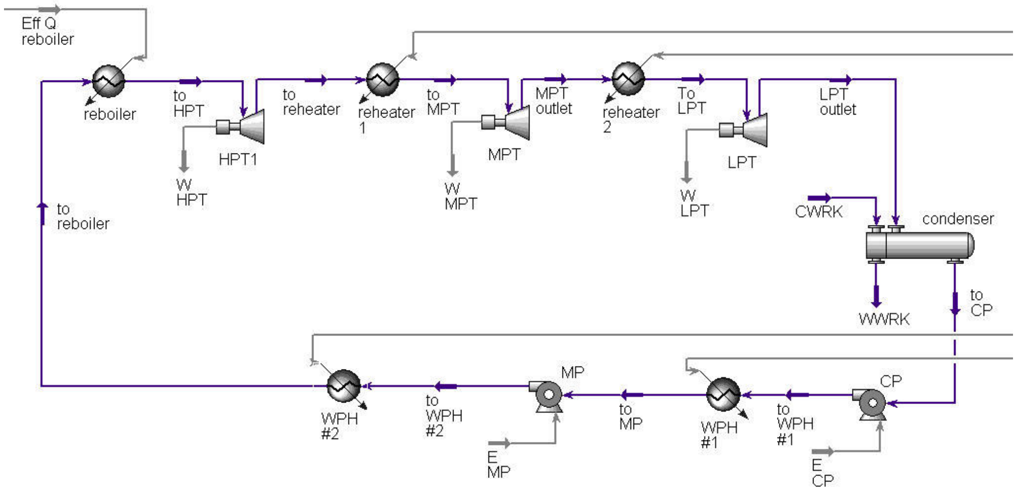


Figure 5. Scheme of sub-critical Rankine cycle.

When assessing the previous schemes it is necessary to highlight that the aim of the process is to achieve the calcination of $CaCO_3$ for the production of CaO to be used in the cement production process and not the production of power. Therefore, most of the energy produced in the combustor is transferred to the calciner and only the thermal energy of the gas streams is used for power generation. Appropriate energy integration is fundamental in order to produce extra power to compensate for the energy demand of the proposed plant and CO_2 compression systems. In addition, in this particular case study, it has been considered that the combustor and pre-calciner are independent units respect to the cement production facility and that the energy for preheating streams is obtained only from internal streams inside the proposed precalcination process. In a real plant, most likely, both sections (CaO combustor and pre-calciner section and cement production section) would be further integrated in order to save fuel or produce more power or cement. On the other hand, in this case study, the energy for the production of high pressure steam in the reboiler has been obtained using only the thermal energy of the hot gas leaving the combustor at 1050 ºC. The temperature of the gas leaving the reboiler is 800 ºC and it is finally exhausted up to 130 ºC in the air, fuel and $CaCO_3$ preheaters. The energy necessary for reheating the steam at the exit of the high pressure and medium pressure turbines is obtained from the thermal energy of the CO_2 stream leaving the pre-calciner at 950 ºC (hot CO_2 stream). After the gas has passed through both reheaters (reheater 1 and reheater 2 units) the CO_2 temperature is still 759 ºC. As the inlet temperature of the CO_2 stream in the compressor should be bellow 40 ºC, the stream leaving the reheaters is used to perform the preheating of water for the Rankine cycle. The final temperature of the CO_2 stream is 461 ºC but no more energetic integration has been considered.

3. Conclusions

The process analyzed in this work shows that it is possible to obtain a CO_2 concentrated stream from the calcination of limestone without a "CO_2 capture" reaction. This is possible when the combustor and calciner chambers are independent, and part of the heat generated in the combustor chamber is transferred to the calciner by high temperature CaO particles circulating between reactors. Aspen Hysys simulations have proven that the combustor and the calciner in this configuration can be designed as adiabatic reactors, and it is possible to recover the energy produced in the combustor to produce overheated steam. These theoretical calculations have shown that when a sub-critical Rankine cycle is used and a moderate thermal integration is performed, there is no energy penalty other than the penalty associated to CO_2 purification and compression. If the proposed process was built to substitute a conventional precalciner in standard cement plants (as seen in Figure 2), it would be possible to capture up to 53% of the CO_2 released in the cement manufacture process and avoid 43% of the CO_2 emitted in the original cement plant (according with data shown in Table 1).

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