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The Calcium looping process for low CO_2 emission cement plants

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Abstract

The aim of this work is investigating the application of the Calcium looping process in cement plants with CO_2 capture. A novel configuration with oxyfuel calciner and a carbonator integrated in the raw meal suspension preheater has been assessed by means of process simulations. The results obtained show a high potential of the proposed process, with equivalent avoided CO_2 emissions (i.e. accounting for credits associated to electric power export) of about 94%, vs. 76% obtained for a competitive oxyfuel cement plant.

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1. Introduction

Cement production is the largest industrial source of carbon dioxide emissions, responsible for about 7% of the total CO_2 emission from large stationary sources. In cement plants, about 60% of the total CO_2 emissions arise from the calcination of the $CaCO_3$ in the raw meal feed (the remaining portion resulting from fuel combustion). Therefore, carbon capture and storage is the only option to significantly reduce the emission from cement plants.

Calcium looping is one of the most promising technologies for CO_2 capture in future short-medium term plants featuring the combustion of fossil fuels. Ca-looping is a regenerative process which takes advantage of the capacity of Calcium Oxide-based sorbents in capturing the CO_2 from combustion gases by means of sequential carbonation-calcination cycles. The process is carried out in two interconnected reactors operating at nearly atmospheric pressure. In the first one (the carbonator), CO_2 is removed from

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the gaseous phase at high temperatures (600-750°C) by Calcium Oxide, forming solid Calcium Carbonate according to the exothermic carbonation reaction ($CaO + CO_2 \rightarrow CaCO_3$). In the second reactor (the calciner), the sorbent is regenerated according to the reverse endothermic reaction, sustained by oxycombustion of a carbon containing fuel. Thus, a highly concentrated CO_2 stream is released from the calciner, ready for sequestration after proper purification.

A first option for cement plant emission reduction by Ca-looping process is to use the CaO-rich purge stream extracted from a power plant utilizing the Ca-looping process as a feed stream of the cement plant [1]. In this way, CO_2 emission can be strongly reduced (well above 50%) with very limited modifications to the cement plant, because of both the avoided calcination of the feed (which is largely already calcined) and the reduced fuel input required. On the other hand, a large power plant needs to be present relatively close to the cement plant to transport this large amount of solids from the power to the cement plant. A second option is integrating the Ca-looping process in a stand-alone cement plant. This can be done by treating the flue gas in a carbonator placed either at the "end of pipe", as already proposed in some works in the literature and object of a demonstration plant in Taiwan [2], or integrated within the raw meal suspension preheater. According to this second layout, the risers of the preheater are modified to work partly as carbonator reactors by including heat transfer surfaces and handle modified solid and gas flow rates. Such a configuration is object of a recent patent application from the authors [3-4].

The aim of this study is to present the first results of the integration of the Ca-looping process in a stand-alone cement plant, in a configuration where the process reactors are integrated in the raw meal preheating section. Energy efficiency and CO_2 emissions are discussed and compared with those obtained for a plant with oxyfuel combustion, which represents the reference technology generally considered for CO_2 capture in cement plants.

2. Plant description

The configuration of the innovative cement plant with CO_2 capture by CaL process is shown in Fig. 1. Clinker is produced in a rotary kiln typical of state-of-the-art-plants, where the pre-calcined raw material is heated up to 1400-1450°C to initiate the reactions for clinker formation. Heat is provided by combustion of pet-coke at the hot end of the kiln. Hot combustion gases and solid species flows counter-currently in the kiln: solids move towards the hot end of the kiln thanks to its rotation around a slightly sloping axis, while gases flow in the opposite direction. The hot clinker exiting the kiln is cooled down in the clinker cooler by direct contact with ambient air. The combustion gases exit the kiln at around 1000-1050°C from the opposite side and cooled down by preheating the raw meal (i.e. the raw material for cement production, mainly constituted by $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3). Raw meal preheating is typically performed in a suspension preheater, where hot gas and cold solids are sequentially contacted in risers and separated in cyclones. While gas and solids flow co-currently in each riser, the preheating process is basically counter-current, since the solids entering at the top of the system descend through the preheater and are heated up, while the hot gas stream flows upwards and releases heat to the solids. In conventional cement plants, hot gases flowing through the preheater also include the gas from the pre-calciner, resulting from the combustion of part of the total fuel input (about 60% of the total) and from the CO_2 of the decomposed limestone. In the proposed plant configuration, only the kiln flue gas is cooled in the suspension preheater, since limestone calcination is performed in a separate oxy-fired calciner.

The preheated raw meal exits the bottom stage of the suspension preheater and is sent to the oxyfuel pre-calciner, where limestone is decomposed to CaO and CO_2. About 55% of the resulting calcined raw meal is sent to the rotary kiln, while the remaining portion is re-injected in a proper position of the suspension preheater, where CaO can act as sorbent of the CO_2 contained in the kiln flue gas. In this way, about 30% of this CaO is carbonated back to $CaCO_3$ in this carbonation section (a high carbonation level was assumed considering the small particle size and the large flow of fresh limestone) before returning to

the pre-calciner, where it is released in the concentrated CO_2 stream. Therefore, the concentrated CO_2 stream released from the oxy-fired pre-calciner contains (i) the CO_2 from raw limestone calcination, (ii) the CO_2 from the oxyfuel combustion of the calciner fuel and (iii) the CO_2 initially contained in the kiln flue gases and captured in the carbonation section by the CaO sorbent. It must be highlighted that the carbonation section of the preheater line can require modifications of the conventional geometry to allow proper gas-solid contact times and include heat exchange surface for the absorption of the heat of the carbonation reaction. In particular, the carbonation section needs to be kept at a temperature of around 650°C to have proper reaction kinetics and chemical equilibrium leading to high CO_2 capture.

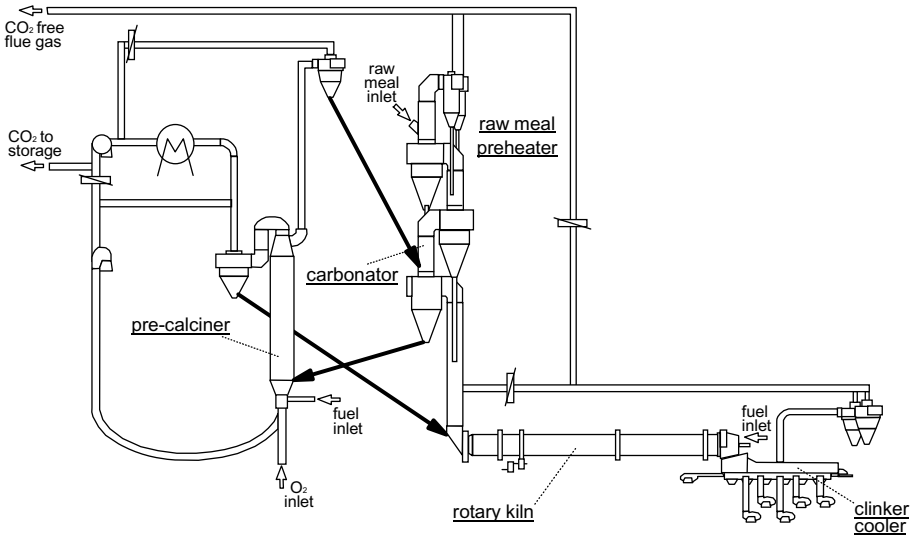

Fig. 1. Configuration of the innovative cement plant with CO_2 capture by Ca-looping process

3. Results

Mass and energy balances were calculated by means of the in-house process simulation code GS. The main results of the innovative plant proposed are resumed in Table 1 and compared with benchmark plants without CO_2 capture (first column) and with CO_2 capture by partial oxyfuel combustion (second column). The oxyfuel plant refers to a case similar to the CaL plant shown in Fig. 1, but no CaO is recycled to the suspension preheater to create a carbonation section in this case. Therefore, CO_2 generated in the kiln by fuel combustion and residual calcination is eventually emitted to the atmosphere. Such a configuration avoids some important drawbacks resulting from a full oxyfuel process (i.e. where also the combustion in the kiln is performed with a CO_2/O_2-based oxidant), which would suffer from high air in-leakages in the kiln, leading to low expected purities of the final CO_2.

As shown in Table 1, the Ca-looping process allows capturing over 95% of the CO_2 produced in the plant, vs. about 82% of the oxyfuel plant. From another point of view, the specific emissions from the stack are equal to 94.9 g per kg of clinker produced, corresponding to 88.9% less than the reference plant without CO_2 capture and 52% less than the oxyfuel case. Such a high CO_2 capture level is obtained with a higher heat input, about 71% higher than the reference plant without capture and 35% higher than the oxyfuel cement plant. This increased fuel input leads to a large availability of waste heat which can be recovered by raising steam and generating electric power. Considering at first approximation a conversion efficiency of 43% from the heat recovered at temperature higher than 350°C and 30% for the lower

temperature heat (between 100 and 350°C), a gross power output of 1.22 kJ_e and 0.60 kJ_e per kg of clinker has been estimated for the CaL and the oxyfuel plants respectively. On a net basis, i.e. also including the auxiliary consumption from oxygen production (assumed equal to 200 kWh/t_{O2}) and CO_2 compression (112 kWh/t_{CO2}), a net export of 0.27 kJ_e/kg_{clk} has been obtained for the CaL case, vs. a net import of 0.10 kJ_e/kg_{clk} for the oxyfuel case. Considering also the additional CO_2 emission associated to the electric power import for the oxyfuel case and the avoided emission for electricity export to the grid for the CaL case, it is possible to calculate the equivalent CO_2 emission associated to clinker production. Assuming an average emission of 530 g/kWh, typical of the Italian power generation mix, the equivalent CO_2 emissions reduce to 54.4 g/kg_{clk} for the CaL cement plant and increase to 215 g/kg_{clk} for the oxyfuel plant. On the whole, the CaL cement plant allows reducing CO_2 emission by 93.8% with respect to the plant without CO_2 capture and by 75% with respect to the oxyfuel cement plant.

Table 1. Main results of the mass and energy balance of the Calcium looping cement plant and the benchmark plants without CO_2 capture and with CO_2 capture by oxyfuel combustion.

	State of the art cement plant w/o CO_2 capture	Oxyfuel calciner cement plant	Calcium looping cement plant
Fuel input, kJ_{LHV}/kg_{clk}	3230	4097	5531
Gross electric output, kJ_e/kg_{clk}	-	0.60	1.22
Auxiliaries, kJ_e/kg_{clk}	-0.21	-0.71	-0.95
Net power output, kJ_e/kg_{clk}	-0.21	-0.10	0.27
CO_2 capture efficiency, %	-	81.9	95.4
CO_2 emitted, g/kg_{clk}	854.6	199.2	94.9
CO_2 avoided, %	-	76.7	88.9
Equivalent CO_2 emission, g/kg_{clk}	884.8	214.7	54.4
Equivalent CO_2 avoided, %	-	75.7	93.8

4. Conclusions

A new plant configuration for the production of cement with CO_2 capture by Calcium looping process has been presented in this work. A distinctive feature of the process is the high integration level of the carbonator reactor in the suspension preheater of the cement plant. From the mass and energy balances, CO_2 avoided emission of 89% has been obtained, with a net power output of 0.27 kJ_e/kg_{clk}, estimated by simplified assumptions on the heat recovery steam cycle. If the CO_2 credits from electric power export are taken into account, the equivalent CO_2 emissions are reduced by 94% with respect to the reference plant without CO_2 capture vs. 76% obtained for a competitive oxyfuel cement plant. The application of the Ca-looping process in cement plants in a highly integrated configuration is hence extremely promising for future low emission cement plants and certainly deserves further investigations.

References

[1] Romano MC, Spinelli M, Campanari S, Consonni S, Cinti G, Marchi M, Borgarello E. The Calcium looping process for low CO_2 emission cement and power. *Energy Procedia* 2013; 37:7091–7099.

[2] Chang MH, Huang CM, Liu WH, Chen WC, Cheng JY, Chen W, Wen TW, Ouyang S, Shen CH, Hsu HW. Design and Experimental Investigation of the Calcium Looping Process for 3-kW_{th} and 1.9-MW_{th} Facilities. *Chemical and Engineering Technology* 2013; 39(9):1525–1532.

[3] Marchi MI, Cinti G, Romano MC, Campanari S, Consonni S. Improved process for the production of cement clonker and related apparatus (in Italian). *Patent application MI2012 A00382.*

[4] Marchi MI, Cinti G, Romano MC, Campanari S, Consonni S. Process and improved plant for the production of cement clinker (in Italian). *Patent application MI2012 A00383.*