Integration of calcium looping technology in existing cement plant for CO$_2$ capture: Process modeling and technical considerations

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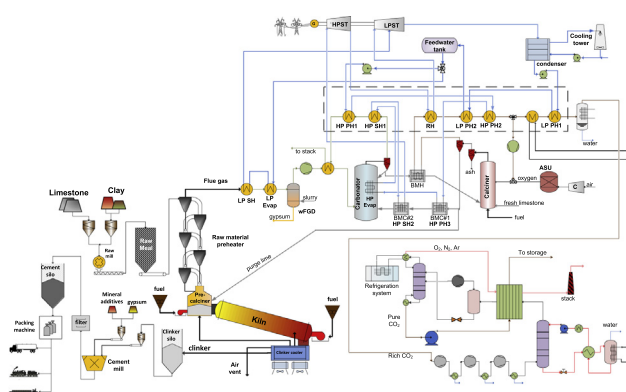[b] Laboratory of Steam Boilers and Thermal Plants, National Technical University of Athens, 9 Heroon Polytechniou Street, 15780 Zografou, Greece
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HIGHLIGHTS

- Process integration of cement plant with CaL including CO$_2$ purification and capture.
- Low S fuels are preferable for CaL system in terms of better performance.
- The CO$_2$ avoidance cost for the optimum case was 68.75 €/t CO$_2$.
- Net electricity production is estimated to be around to 426.66 kW h per ton clinker.
- CaL and MEA scrubbing are almost comparable in financial terms.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Cement sector is currently responsible for approximately 5% of the global CO$_2$ emissions. CO$_2$ originates principally from the raw meal calcination stage and conventional fuel (e.g. coal) combustion for the thermal needs of the process. Carbon capture and storage (CCS) is among the examined technologies for mitigating CO$_2$ emissions generated in a cement plant. A very competitive technology for CO$_2$ capture from flue gases appears to be Calcium Looping (CaL). The process is realized in a dual fluidized bed system where CO$_2$ is absorbed by CaO in the first reactor (carbonator), and the produced CaCO$_3$ is regenerated in the second oxy – fired reactor (calciner). During calcination, CO$_2$ is released from the sorbents, purified, compressed and finally led to storage. Among the advantages of CaL when compared against other CO$_2$ capturing technologies that could be applied in the cement industry, are the familiarity of the sector with the management (extraction, storage, feeding, etc.) of CaO-bearing materials and the prospect of reusing purge CaO in cement making as it is chemically compatible with cement raw meal.

This study describes the process modeling of the CaL implementation on a typical (no by-pass) five-stage preheater with pre-calciner cement plant as a retrofit option, in order to capture the CO$_2$ produced through the clinker production. The process simulations were performed with the commercial software ASPEN Plus™ in conjunction with house-built models for the CaL process itself. A detailed description of the process configuration of the CO$_2$ capture unit including its integration with the CO$_2$ purification scheme and the basic parameters for the clinker production line are presented. Simulation results revealed that high S content in the supplementary fuel affects negatively the CaL performance and the

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quality of purge CaO in terms of replacing limestone in the kiln feed. Using low-sulfur coal for a 90% capture rate, a total purge CaO utilization can be achieved along with a raw limestone substitution of 8% and a net electricity yield of 426.66 kWh/t clinker. The economic evaluation of the proposed concept was also performed, estimating that the cost for CO_2 avoidance equals approx. 68.75 €/t_{CO_2}. In terms of economic efficiency, CaL was found to be comparable to amine scrubbing. Give that CaL has not been examined so extensively as MEA, it has the potential for technical improvements in order to become more competitive by the adoption of novel concepts with smaller equipment cost.

1. Introduction

Following the power sector, cement industry is one of the industrial sectors with the highest GHG emissions globally, accounting for over than 5% of CO_2 emissions worldwide [1,2]. More than half of the total direct CO_2 produced during the cement manufacture process originates from the limestone calcination, while the remaining arises from the fuel combustion that is required for the pyro-processing of raw meal to clinker. Substantial effort has already been paid toward reducing the emissions in the cement industry such as utilizing alternative fuels with high biogenic content (e.g. SRF), and technical improvements in the clinker process in terms of lower fuel consumptions. Despite effective, such types of alternative paths have reached a plateau in further reducing GHG-related emissions. Therefore, CO_2 capture for storage (CCS) or utilization (CCU) could be considered as alternative end-of-pipe options for achieving a significant CO_2 reduction and more sustainable in economic terms processes on a long-term period.

The cases that were firstly investigated for CO_2 capture in cement industry are post-combustion capture techniques as for example amine scrubbing or oxyfuel technology [3–8]. Although amine scrubbing is a commercially mature technology, it is an energy intensive technique and there is lack of experience in gas/liquid processing in the cement sector. On the other hand, oxyfuel technology has lower specific energy requirements but it is not suggested for existing cement plants due to the fundamental modifications that are required to be made along the clinkering process [9,10].

In contrast to the two abovementioned approaches, Calcium Looping process (CaL) is a promising CO_2 capture technique with the prospect of a relatively small reduction of the total energy efficiency. The CaL process comprises of a dual fluidized bed (DFB) reactors (i.e. the carbonator and the calciner) with a continuous looping of Ca-bearing solids. The capture principle is based on the reaction of lime (CaO) with CO_2, forming calcium carbonate ($CaCO_3$) in the carbonator and the reverse reaction in the calciner, producing a rich-CO_2 gas stream and a quantity of calcined lime, which is active for further CO_2 absorption. Because of the endothermic nature of the calcination reaction, the simultaneous fuel combustion under oxy conditions in the calciner is required. In order to maintain the recirculating solids CO_2 carrying capacity (X_{max}) in high rates, fresh limestone is inserted in the calciner. To avoid unexpected accumulation of the solids in the CaL system, part of spent (purge) CaO is extracted after the calcination process. The concept of integrating the CaL technology with the cement industry for CO_2 capture has been investigated in several theoretical studies [4–6,11–16]. There is a general consensus that CaL process seems to be the most appropriate technology for CO_2 capture in cement industry since:

- cement industry is already familiar with the management (handling, storage, feeding, etc.) of CaO-bearing materials,

- has a low cost of fresh limestone that is required for the enhancement of the circulating solids capture ability,
- it allows for potential utilization of the purge CaO for the cement production as it is the chemically compatible with cement raw meal [17,18],
- there is room for recovery of the waste heat that is dissipated from the CO_2 capture unit.

Although the CaL technology has already been proved effective for the separation of CO_2 from flue gases in demo scale [19–21] especially in the power sector, there are several issues that need to be addressed before its large scale application, including those of process integration with a CO_2 purification unit prior to its compression, transportation and final storage. Even though a gas stream with high CO_2 concentration is produced in the calciner, it is not allowed to be transferred and stored unless gas purification takes place. The problem of O_2 tracking in the rich-CO_2 stream is observed for any oxy-fired case, regardless of the process under investigation. From experimental and numerical studies on both PC [22–24] and CFB [25–28] oxy-fired boilers, the specified oxygen to fuel equivalence ratio (λ) is specified between 1.1 and 1.2 and the corresponding O_2 concentration at the flue gas exit is around to 1.5% or even higher. On the contrary, very few experimental studies on oxy-calcination have been performed using coal so far and the reported oxygen excess at the exit of the reactor is reported to be more than 5% to ensure high fuel combustion efficiencies [20,29]. Hence, like in oxy-fuel cases [30–32] the implementation of CO_2 purification unit for the removal of oxygen and other inert gases is essential for the CaL technology, too. Primarily for H&S (explosion avoidance), technical reasons (mainly corrosion), [33–36] and increase in storage capacity [37] the limitations for condensable and non-condensable components are rather strict, making the gas treatment before compression compulsory.

For the case of CO_2 stream derived from the oxy calciner, according to the limitations shown in Table 1, H_2O and O_2 are the species that require intensive removal in order to meet the abovementioned specifications. Inert gases (Ar, N_2) are present in the CO_2 stream but their concentration is under 4%. Regarding the NO_x, there is not a justified conclusion about the impact of calcination reaction on the rate of their formation in the oxy-calciner. However, the NO_x emissions are expected to be low and around to 100 ppm [22,38]. Neither for the case of SO_x, is there a clear view about their production but in this study it is assumed that S originating from the fuel totally reacts with CaO sorbents forming $CaSO_4$.

Furthermore, another concern that is related to the large scale design of the CaL is the effective removal of the produced heat in the carbonator, due to reactor geometrical limitations and the high heat fluxes observed at the bottom region of the carbonator [29,39]. To overcome this, based on the detailed sizing and design of a large scale calcium looping facility carried out in the framework of the EU funded CALMOD project, bed material coolers are