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Full Length Article

Calcium looping performance under extreme oxy-fuel combustion conditions in the calciner

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ABSTRACT

Calcium looping (CaL) for post-combustion CO_2 capture is an emerging technology that has developed rapidly due to its similarities with existing circulating fluidized bed combustion boilers. This work presents an alternative calciner configuration as it is applied in La Pereda CaL pilot plant, the aim of which is to minimize or altogether eliminate the need to recycle CO_2 during the oxy-fuel combustion of coal in the calciner. The strategy underlying this configuration is to reduce the heat demand in the calciner, and hence the energy penalty of the whole CaL system. After undergoing several modifications, the pilot was able to operate under O_2-rich conditions in a series of experiments with a coal thermal input of up to 2.0 MW_{th} in the calciner and 75 $O_2\%_v$ in the oxidant. No hot spots were detected in the calciner reactor in these conditions due to the thermal ballast effect produced by the circulating solids from the carbonator. This new operation mode in the calciner in no way undermined the performance of the carbonator and CO_2 capture efficiencies close to the maximum limit permitted by the equilibrium were achieved during the experimental campaigns. In short, the results of this work indicate that it may well be possible to operate the calciner of a CaL system using pure oxygen.

1. Introduction

Calcium looping (CaL) is a CO_2 capture technology that uses CaO as sorbent for the capture of CO_2 [1]. The flue gas coming from a power plant meets a stream of CaO particles in the carbonator reactor where the CO_2 is captured as $CaCO_3$ at temperatures of around 650 °C. The CO_2-lean flue gas produced is separated from the partially carbonated particles before it is emitted to the atmosphere. This stream of particles is then diverted to the calciner in order to decompose the $CaCO_3$. The regenerated CaO particles are then recycled to the carbonator thereby closing the loop. The energy needed in the calciner for calcination and heating up the gas and the stream of solids can be supplied by burning coal under oxy-fuel conditions at temperatures close to and above 900 °C [2]. As a result, the CO_2 captured from the flue gas fed into the carbonator and the CO_2 released during the combustion of coal in the calciner is obtained in a highly concentrated stream ready for purification and compression.

The most advanced CaL configuration relies on circulating fluidized bed (CFB) reactors [2–7]. An important advantage of this kind of systems is its large gas throughput that makes it possible to use compact reactors. Its similarities with commercial CFB combustors and comparable operating conditions have led to the rapid development and scaling up of CaL post-combustion CO_2 capture systems to TRL6 over the last decade [2–7]. The experience acquired in these pilots has revealed that there are no major barriers to CaL, which is a viable and potentially competitive alternative technology [8].

Compared to other CO_2 capture technologies, CaL requires a large thermal energy input into the whole system. However, because the high temperatures at which both reactors operate, it is possible to recover a large fraction of the fuel thermal input into the calciner by producing additional power from a new steam cycle. In fact, the CaL system can be regarded as an oxy-fired power plant that repowers the existing plant while the CO_2 produced is being captured. The process is also highly power-efficient as several works in the literature have estimated overall energy penalties of around 7–9 net points compared to power plants without CO_2 capture [8–15]. A large fraction of these energy penalties is related to the consumption of energy needed to produce the oxygen fed into the calciner for fuel combustion. As a consequence, more sophisticated process schemes have been proposed to eliminate the need for oxy-combustion in the calciner. Some of these novel concepts employ a high temperature combustor chamber from which the heat needed in the calciner is transferred through metallic walls or heat pipes or alternatively from a stream of hot solids circulating between the combustor and the calciner [16–20]. Despite the low energy penalties expected from these new process configurations, they are still at an early stage of development and need to overcome several obstacles

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Notation

E_{carb}	CO_2 capture efficiency
$E_{carb,eq}$	maximum CO_2 capture efficiency allowed by the equilibrium
$E_{carb,norm}$	normalized CO_2 capture efficiency
f_a	fraction of active particles in the carbonator bed
f_{carb}	fractional carbonation conversion
f_{calc}	fractional calcination conversion
F_{Ca}	molar flow of calcium circulating between reactors in relation to the cross sectional area of the carbonator, mol/m^2 s
F_{CO2}	molar flow of CO_2 entering the carbonator in relation to the cross sectional area of the carbonator, mol/m^2 s
F_0	make-up molar flow of limestone in relation to the cross sectional area of the carbonator, mol/m^2 s
G_{sCB}	solid flow circulation rate from the carbonator to the calciner in relation to the cross sectional area of the carbonator, kg/m^2 s
G_{sCC}	solid flow circulation rate from the calciner to the carbonator in relation to the cross sectional area of the calciner, kg/m^2 s
k_s	constant reaction rate, s^{-1}
n_{Ca}	total inventory of calcium in the carbonator bed, mol/m^2
Q	heat stream, kW
T_{CC}	average calciner temperature, °C
T_{CB}	average carbonator temperature, °C
u_{CC}	calciner gas velocity, m/s
u_{CB}	carbonator gas velocity, m/s
W_{CC}	total inventory of solids in the calciner, kg/m^2
W_{CB}	total inventory of solids in the carbonator, kg/m^2
X_{ave}	maximum CO_2 carrying capacity of the sorbent
XS	Molar sulphate content of the particles
ν_i	volume fraction of gas species
τ_{active}	active space time, s
φ	gas-solid contacting effectivity factor

before they can be scaled up for commercial purposes (e.g. the need for high temperature alloys for the heat exchangers, large heat transfer areas, large solid circulation rates, high temperature solid classification devices, etc.).

There is also a possibility of further minimizing the energy requirements of the calciner in the oxy-fuel combustion-based CaL configuration, thereby enhancing the efficiency of the system and reducing the investment costs. A large fraction of the energy input into the calciner is needed to heat up the stream of solids arriving from the carbonator [21]. Increasing the operation temperature in the carbonator would thereby reduce the energy demand in the calciner. However, there is limited scope for increasing the carbonator operation temperature beyond 650 °C, as this would have a negative impact on the maximum CO_2 capture efficiency allowed by the equilibrium [22]. A possible solution to this problem would be to preheat the stream of solids leaving the carbonator before they enter the calciner. For this purpose, several high temperature heat sources inside the CaL boundaries can be used. The CO_2-rich gas stream leaving the calciner could be used to preheat the carbonated solids in suspension preheaters arranged as in the configuration employed in commercial cement plants [20,23,24]. A more challenging alternative would be to use the hot stream of solids leaving the calciner as this would require complex solid-solid heat exchanger solutions [25,26]. Yet, another alternative proposed recently [20] is to use an external flue gas at high temperature placed in direct contact with the particles as a heat source to preheat the carbonated sorbent.

An additional large fraction of thermal input to the calciner is needed to increase the temperature of the oxidant gas fed in for the coal combustion. Due to limitations imposed by temperature control, the maximum inlet oxygen concentration in oxy-CFB pilots has been up to 55%$_v$ [27]. Because of their similarities to these oxy-CFB combustors, a recycle of CO_2 has been considered for all the calciners of CaL systems so that the coal combustion is carried out with an oxygen concentration of around 30–40%$_v$ in the oxidant [8]. However, operating under higher oxygen concentrations may be feasible in the oxy-fired calciner of a CaL system as the large circulation of solids and the calcination of $CaCO_3$ particles can be expected to moderate the temperature profiles due to the thermal ballast effect of the cool solids arriving from the carbonator and to the endothermic character of the $CaCO_3$ decomposition reaction [28]. This has been confirmed theoretically by state-of-the-art simulations of large scale oxy-fired calciners [29]. Consequently, one way to reduce the coal and oxygen requirements in the calciner is to simply minimize or altogether eliminate the recycling of CO_2 to the oxy-fired calciner, which would translate into a reduction in thermal input of up to 20% [28]. Moreover, operating without a CO_2 recycle allows the use of compact calciner reactors with a reduced cross-sectional area, as depicted in Fig. 1. Despite these potential benefits, most of the tests carried out in pilot plants have employed only moderate oxygen concentrations in the oxidant fed into the calciner [6,30] and the information available for high O_2 concentrations refers to relatively short operations performed in laboratory pilot plants, where the small cross sections, non-adiabatic conditions and high volume-to-surface ratios do not facilitate the scalability of the results achieved which are linked to heat transfer phenomena in the bed [31,32].

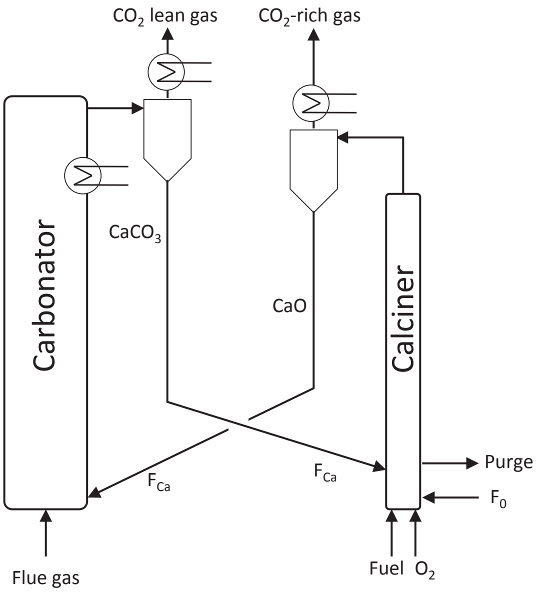

Fig. 1. Schematic diagram of a calcium looping system with the calciner operating under pure-oxygen.

In order to demonstrate the feasibility of operating the calciner of a calcium looping system under ultra-rich oxygen conditions at a relevant scale and to gain operational experience, we carried out several experimental campaigns in the quasi-adiabatic calciner of La Pereda pilot plant under the EU project “CaO2” [28]. For this purpose, several modifications were introduced so that the facility could operate safely under these new experimental conditions [28,33]. The objective of the present work is to present and analyze the main experimental results obtained during these experimental campaigns using O_2-rich concentrations in the calciner.