

16th International Conference on Greenhouse Gas Control Technologies, GHGT-16

23rd -27th October 2022, Lyon, France

Advanced CO₂ capture systems based on Calcium Looping for deep decarbonization of flue gases

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Abstract

CO₂ capture efficiencies in post-combustion Calcium looping (CaL) systems are usually reported to be around 0.90, mainly due to the operation of the carbonator at temperatures around 650 °C and the restrictions imposed by the CO₂-CaO equilibrium. This work analyzes a solution to increase the CO₂ capture efficiencies, by reducing the temperature in the solid entrainment upper part of the circulating fluidized carbonator. To overcome known CaO conversion limits in such region, an additional small flow of Ca(OH)₂ is fed to the cooled solid entrainment region of the carbonator. Thus, the dense bed, where most of the CO₂ is captured, is operated at standard conditions but the full CaL process includes a small hydrator to treat a small fraction of the purge of CaO-rich solids and to provide the necessary flow of Ca(OH)₂. A second approach also discussed in this work involves similar actions but carried out after the carbonator cyclone, where the cooling is facilitated by the absence of the circulating solids. In this case, the flue gas leaving the CFB carbonator is put in contact with Ca(OH)₂ in a second carbonation entrainment zone. These two CaL configurations can reach CO₂ capture efficiencies of 0.99. Experimental work characterizing the fast carbonation kinetics of Ca(OH)₂ powders in the entrainment zones has been completed. Mass and energy balances have been solved to discuss feasible process configurations. Net energy efficiencies of 0.342 and 0.345 have been estimated for the two CaL configurations, which result into a decrease of only 0.021 and 0.018 net points respect to a standard CaL system with a CO₂ capture efficiency of 0.90.

Keywords: Calcium Looping; Ca(OH)2; high-CO2 capture efficiency.

1. Introduction

Post-combustion CO_2 capture by Calcium looping (CaL) is a technology that has developed rapidly in the last years thanks to the use of circulating fluidized bed (CFB) reactors for carbonation and calcination reactions[1,2]. Capture efficiencies in the carbonator have been typically targeted to around 90%, but the CO_2 -CaO equilibrium allows for a deeper decarbonization. For example, for a temperature of 550 °C, the capture efficiencies can be above 99% for a typical flue gas with a $15\%_v$ CO₂. However, reducing the carbonator temperatures leads to a poorer performance of the sorbent, as CO_2 carrying capacity of CaO is known to decrease with the temperature[3–5]. Moreover, operating the carbonator at reduced temperatures would increase the energy demand in the calciner and lead to thermal inefficiencies in the steam cycle used to produce power by recovering high grade heat from the CaL system.

This work presents a potential solution, that allows increasing the CO_2 capture efficiencies by using a small flow of $Ca(OH)_2$ as an additional sorbent in a high-efficiency carbonator [6]. $Ca(OH)_2$ is known to react much faster and reaches high carbonation conversions compared with CaO. Indeed, experimental studies have shown that carbonation

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conversions around 0.6 can be achieved in less than 4 s at temperatures around 600 °C[7,8]. Thus, several processes have been proposed by integrating hydrators in the calcium loop to exploit advantages of $Ca(OH)_2$ as CO_2 sorbent [7], [9], [10]. However, the extensive use of $Ca(OH)_2$ in CaL systems comes with important penalties, which include the cost and energy inefficiencies linked to hydrators, the reduction of the energy output in the carbonator due to the lower carbonation enthalpy of $Ca(OH)_2$ (72 kJ/mol_{Ca(OH)2} vs 176 kJ/mol_{CaO} at 650°C) and the poor fluidization characteristics of $Ca(OH)_2$ powders (i.e. highly cohesive particles,...). A solution to avoid these drawbacks is to minimize the flow of $Ca(OH)_2$ fed into the carbonator, so it is used it as a "polishing" agent in the CaL process [6].

For this purpose, a high CO_2 capture efficiency carbonator is proposed which basic scheme is presented in Figure 1 left. Typical circulating fluidized bed carbonators present a dense zone at the bottom of the reactor, where there is an intense mixing of solids that results into extremely high heat transfer coefficients and a homogeneous temperature. After that, there is a typical entrainment zone where solids particles move upwards with the gas towards the reactor exit before being separated in a cyclone. The idea behind the concept shown in Figure 1 is to reduce the temperature in the entrainment zone taking advantage of the reduced mixing of solids and, thus, avoiding the limits imposed by the CO_2 -CaO equilibrium. Among other options, the cooling in this zone be achieved by rearranging the heat exchangers in the CFB carbonator and by feeding the make-up flow of limestone and $Ca(OH)_2$ at the inlet of the entrainment zone, as schematically shown in Figure 1. The solids coming from the calciner, composed mainly by CaO, are fed into the bottom dense bed of the reactor. In this zone, rich-CaO particles react under the same conditions as a standard CFB carbonator (i.e. residence time of a few minutes, CO_2 concentration, temperature,....) and capture a large fraction of the CO_2 fed into the reactor. Therefore, most the heat available in the carbonator can be extracted in this zone at standard CaL temperatures.

Then, additional CO_2 is captured mainly by the $Ca(OH)_2$ fed at the inlet of the entrainment zone. The residence time of the solids in this zone is only of a few seconds. However, the fast $Ca(OH)_2$ carbonation rates allows for high sorbent conversions despite the lower temperatures and CO_2 concentrations in this zone. As example, Figure 1 right shows an experimental result obtained in a drop tube furnace[8] aimed to test the $Ca(OH)_2$ performance under such carbonation conditions. As can be seen in this graph, it is possible to reach the CO_2 concentration allowed by the equilibrium at the exit of the reactor using $Ca(OH)_2$ as sorbent with gas-solid contact times of only 4s and modest $Ca(OH)_2/CO_2$ ratios.



Figure 1. Left) Scheme of a high CO₂ capture efficiency circulating fluidized bed carbonator. Right) Experimental result obtained in a drop tube reactor [8].

The objective of this work is to analyze the implications of the integration of the high CO_2 capture efficiency circulating fluidized bed carbonator in a Calcium Looping system including a small hydrator to produce the $Ca(OH)_2$. As discussed in the next sections, two different integration schemes have been studied. Mass and energy balances have been solved to identify the main key operational parameters.

2. Process description and model assumptions

For comparison purposes, a standard CaL system has been included in this work. A basic scheme of this reference case (Case 1) is shown in Figure 2. In this process, the flue gas containing the CO_2 is fed into the carbonator, together with a flow of CaO-rich solids coming from the calciner. Thus, the CaO reacts with the CO_2 at temperatures around 650°C to form CaCO₃. Then, the stream of carbonated solids is separated from the CO_2 -lean gas and directed to the calciner. CaO sorbent is regenerated in this reactor by calcination of the CaCO₃ producing a CO_2 -rich flue gas stream ready to be sent to the compression and purification unit. The heat demand in the calciner is supplied by burning fuel using pure oxygen coming from an air separation unit. A make-up flow of fresh limestone is supplied to the system and a purge is taken out in order to maintain the activity of the CaO sorbent and to extract deactivated solids.



Figure 2. Scheme of the CaL reference system and specifications of the main streams involved (Case 1).

A basic scheme of the integration of a high CO_2 capture efficiency CFB carbonator in the CaL system is shown in Figure 3 (Case 2). In this case, a small fraction of the purge leaving the calciner is sent to a hydrator to produce $Ca(OH)_2$ from the reaction of CaO with liquid H₂O. The stream of hydrated solids is fed into the carbonator at the inlet of the entrainment zone together with the make-up flow of limestone. After that, the carbonated solids and the make-up flow of limestone are separated in the CFB cyclone and sent to the calciner to regenerate the CaO and close the loop.



Figure 3. Scheme of the CaL with a high CO_2 capture efficiency CFB carbonator system and specification of the main streams involved (Case 2).

As discussed above, the heat exchangers in the carbonator are re-arranged to enhance the cooling of the entrainment and to operate it at lower temperature than the dense bed. One of the main disadvantages of this configuration is the increase of the heat demand in the calciner due to the lower temperature of the carbonated solids leaving the CFB carbonator. Therefore, the outlet temperature in the carbonator is a parameter to be optimized in order to avoid equilibrium restrictions while minimizing the energy penalty in the calciner.

Another process configuration has been analyzed in this work (Case 3). The strategy behind this configuration is to avoid the cooling of the main stream of carbonated solids. In this case, the CFB carbonator operates as in a standard CaL system but includes a second entrainment after the cyclone (see Figure 4). This zone could be a flue gas duct and a second cyclone that allows for a gas-contact time of a few seconds. In this case, the Ca(OH)₂ and a fraction of the make-up flow are mixed with the flue gas leaving the CFB carbonator at the inlet of the entrainment zone. As shown in the next section, the mixing of these streams with the flue gas could be sufficient to cool down this zone without additional heat exchangers. After reaction, the solids are separated in a second cyclone and sent to the calciner with the main stream of carbonated solids leaving the CFB carbonator.



Figure 4. Scheme of the CaL system with high CO_2 capture efficiency and specification of the main streams involved (Case 3).

3. Results and discussion

Mass and energy balances have been solved using simplified assumptions to facilitate the comparison between the different cases. A flue gas flow of 12 kmol/s and a composition of $15\%_v \text{CO}_2$, $2.5\%_v \text{O}_2$ and $10\%_v \text{H}_2\text{O}$ is considered as input in the CaL system. This is produced in a power plant with a total power of 360 MW_e and a net power efficiency of 0.45. Biomass free of sulfur and ashes is used as fuel in the calciner (with a composition of $50\%_w \text{C}$, $5\%_w \text{t}$, $5\%_w \text{t}$, $35\%_w \text{t}$, $0, 10\%_w \text{t}$ H₂O and a PCS=21 MJ/kg). This reactor operates at 910 °C by burning the fuel using oxygen produced in an air separation unit with a 95% purity. The flow of oxidant is adjusted to have an O₂ content of $2\%_v$ in the CO₂-rich flue gas. The calciner has been solved as a conversion reactor by assuming a full conversion of the CaCO₃ to CaO. For all the cases, a make-up flow of fresh limestone of 0.1 mol_{CaCO3}/mol_{CO2} is fed into the CaL system to achieve a CaO sorbent with a maximum carbonation conversion system of 0.15 mol_{CaCO3}/mol_{CaO}. It has also been assumed that there are no losses of fines through the cyclones and all the solids leaves the CaL system through the purge.

The mass balance in the carbonator has been solved assuming two reaction zones: the dense bed and the entrainment zone. Both zones have been solved as a conversion reactor. A CO₂ capture efficiency (E_{carb}) in the dense bed of 0.90 has been considered for the three cases. A feeding rate of calcined solids into the carbonator with a F_{Ca}/F_{CO2} ratio of 10 has been fixed. This would translate into CaO carbonation conversion of 0.090 mol_{CaCO3}/mol_{CaO} which is reasonable considering the maximum carbonation conversion of the sorbent of 0.15 mol_{CaCO3}/mol_{CaO}.

Regarding the entrainment zone in the carbonator, a conservative residence time of the solids of 5s has been considered. For simplification purposes, the conversion of the CaO leaving the carbonator dense bed has been considered as negligible in the entrainment zone due to the low gas-contact times. On the other hand, it has been assumed that the Ca(OH)₂ reaches a carbonation of 0.5 accordingly to experimental information available[8]. For the cases using Ca(OH)₂, the flow of sorbent has been adjusted to reach a CO₂ capture efficiency of 0.99, corresponding to a CO₂ concentration in flue gas emitted to the atmosphere of $0.17\%_v$. The temperature at the outlet of the entrainment zone has been fixed at 565 °C to minimize the cooling the carbonated solids and to avoid equilibrium restrictions (CO_{2eq} concentration at 565 °C=0.15%_v).

The $Ca(OH)_2$ is produced in a standard hydration reactor using liquid water [11]. This reactor is operated as an adiabatic reactor using an excess of water to maintain the temperature at 100 °C without heat recovery. Under these conditions a full CaO conversion to Ca(OH)₂ has been assumed.

The main stream specifications for the three cases are summarized in the tables shown in Figures 2, 3 and 4. For the standard CaL system (Case 1 of Figure 2) with a CO₂ capture efficiency of 0.90, a flow of 283 kg/s of flue gas leaves the carbonator with a CO₂ concentration of $1.7 %_{v}$. In addition, a stream of carbonated solids of 1079 kg/s at 650 °C is produced and sent to the calciner. A biomass flow of 32.7 kg/s is burnt in the calciner to fulfill the energy demand of 686 MWth. The make-up flow of limestone fed into the system is of 18 kg/s and a purge of 10.1 kg/s is removed from the CaL system.

To achieve an E_{carb} of 0.99 in Case 2, a flow of 20.3 kg/s of Ca(OH)₂ is needed. To produce this amount of sorbent, a flow of 18.2 kg/s of calcined solids (less than a 2% respect to stream flowing directly from the calciner to the carbonator) is fed into the hydrator with 13.6 kg/s of liquid water. As discussed in the previous section for Case 2, the make-up flow of limestone at ambient temperature is fed at the inlet of the entrainment zone in the CFB carbonator with the Ca(OH)₂ coming from the hydrator at 100 °C. Despite the cooling effect of these two streams, it is necessary to extract 90.6 MW_{th} in the entrained zone in order to operate at 565 °C. A free-CO₂ gas flow of 282 kg/s with a 0.17% v leaves the carbonator and is emitted to the atmosphere. On the other hand, a carbonated solids flow of 1123 kg/s at 565 °C is produced and sent to the calciner. As results of the lower temperature of the carbonated solids and the higher amount of CaCO₃ produced in the carbonator, the heat demand in the calciner increases up to 826 MW_{th} which is 20% higher respect to the reference case.

	Case 1	Case 2	Case 3
Ecarb	0.90	0.99	0.99
Calciner thermal input (MWth)	686	826	715
Power available CaL (MWth)	667	747	643
Gross efficiency steam cycle	0.45	0.45	0.45
CPU consumption (MW _e)	70.0	80.2	74.6
ASU consumption (MWe)	36.1	43.1	37.7
Auxiliaries consumption (MWe)	15.0	16.8	14.5
Net power produced CaL (MW _e)	179.1	196.2	162.5
Thermal input power plant (MWth)	800.0	800.0	800.0
Net power produced power plant (MW _e)	360	360	360
Net efficiency power plant with CaL	0.363	0.342	0.345
Specific CO ₂ emissions (kg/kwh _e)	52.8	5.1	5.4

Table 1. Summary of the main key operation performance parameters.

In Case 3, the CFB carbonator operates under the case conditions as the reference case and the gas and solids leave the reactor at a temperature of 650 °C. Then, the flue gas is mixed with the Ca(OH)₂ and the make-up flows at the inlet of the second entrainment zone. For the operation conditions used in this example, only a fraction of the make-up flow (5.1 kg/s) is fed directly into the CFB carbonator to maintain a temperature of 565 °C in the second entrainment zone. For other conditions (i.e., F_0/F_{CO2} ratios, carbonation efficiencies in the CFB carbonator, etc.), other splits of the makeup flow or strategies (i.e. installation of heat exchangers in this zone, spray with liquid water to reduce the temperature, etc.) would be needed to operate this zone at the target temperature. A flow of solids of 39.7 kg/s is produced in this zone which is separated from the gas in the second cyclone before being sent to the calciner. The heat demand in the calciner for this configuration is only 715 MW_{th} (a 4% higher respect to the reference case) as a large fraction of the carbonated solids enters the calciner at the standard temperature of 650 °C.

The detailed integration of the heat available in the carbonator and streams leaving the CaL into a steam cycle to produce power is not included in this work. However, the net power efficiency of the system has been estimated assuming that the gas and solid streams leaving the CaL can be cooled down to a temperature of 150 °C. Under this assumption, the total power available in the CaL to be transferred to the steam cycle is of 667, 747 and 643 MWth for Cases 1, 2 and 3, respectively. The reduction of the ratio between the power transferred to the steam cycle and the thermal input in the calciner for the Cases 2 and 3 is mainly due the energy penalty linked with the hydrator. Approximately, a thermal power loss of 34 MW_{th} is calculated in this reactor as the hydration heat is not recovered (104 kJ/mol_{Ca(OH)2}). To estimate the power produced in the CaL steam cycle, a gross efficiency of 0.45 has been considered. A specific power consumption of 200 kWh_e/t_{O2} and 120 kWh_e/t_{CO2} has been considered for the air separation and CO₂ compression and purification units [12]. In addition, a power consumption of 5% respect to the gross power produced has been considered for the auxiliaries used in the CaL system [13].

The main parameters of this basic analysis are summarized in Table 1. For the reference case, a net power efficiency for the whole system of 0.363 has been estimated which is agreement with the data available in the literature for standard post-combustion CaL system[14]. For the Case 2, the net efficiency drops to a value of 0.342 which is mainly due to the penalties associated to the higher CO_2 capture efficiency, the hydration step and the higher energy demand in the calciner. Meanwhile the Case 3, the net efficiency is improved up to a value of 0.345 mainly due to the reduction of the heat demand in the calciner. Based on the results presented in this work, it can be concluded that the process configurations proposed seem to be a promising option to increase the CO_2 capture efficiency in CaL system.

4. Conclusions

A new Calcium Looping configuration to increase the CO_2 capture efficiency in the CFB carbonator has been analyzed in this work. For this purpose, the temperature in the solid entrainment upper part of the circulating fluidized bed is reduced to avoid the CO_2 -CaO equilibrium restrictions. In addition, a small flow of $Ca(OH)_2$ is used as an additional "polishing" sorbent. Experimental results indicate that this sorbent can achieve high carbonation conversions in the short gas-contact times expected in the entrainment zone of the CFB thus allowing to reach the minimum CO₂ concentration allowed by the equilibrium. To produce Ca(OH)₂, the CaL system includes a small hydrator to treat a fraction of the solids leaving the calciner. A disadvantage of this configuration is the cooling of the main stream of solids leaving the CFB that increases the heat demand in the calciner. To avoid this, a second configuration has been analyzed. This uses the $Ca(OH)_2$ to capture the CO_2 contained in the flue gas leaving the CFB carbonator in a second entrained zone. These two configurations with CO₂ capture efficiencies of 0.99 have been analyzed to treat a flue gas produced in a power plant with a thermal input of 800 MWth. In both cases, the fraction of the calcined solids sent to the hydrator is less than a 2% of the total flow of solids between the calciner in the carbonator. For the first case, including the cooling of the entrained zone of the CFB carbonator, a heat demand in the calciner of 826 MW_{th} has been calculated. This results into an increase of around 20% respect to a reference CaL case with a CO₂ capture efficiency of 0.90. For the case without cooling in the CFB carbonator, the heat demand is only of 715 MW_{th}. The analysis presented in this work yields net power efficiencies of 0.342 and 0.345 for the two cases analyzed, respectively. These values compare reasonably well with a reference CaL case with an efficiency of 0.363.

Acknowledgements

The authors acknowledge the financial support provided by the Spanish Ministry of Science and Innovation under the R&D Program Oriented to Challenges of the Society (RTI2018-097224-B-I00) and by the Spanish Ministry of Economy and Competitiveness (PTI+ TransEner TRE2021-03-005). Further experimental work to test the concept at TRL7 is now planned under the CaLby2030 (GA 101075416) Horizon Europe project (2022-2026).

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