Impact of load changes on the carbonator reactor of a 1.7 MW_{th} calcium looping pilot plant

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Abstract

This work analyses the performance of a Calcium Looping (CaL) carbonator reactor that captures CO₂ from a power plant operating under large load changes. Several experimental campaigns have been conducted in La Pereda 1.7 MW_{th} CaL pilot plant where the carbonator inlet flue gas velocity varied between 2.0 and 5.3 m/s, leading to large changes in the particles entrainment rate and the solids inventory. These tests showed that CaL systems using circulating fluidized bed reactors are highly flexible. Modest gas velocities translate into high CO₂ capture efficiencies because circulation rates equivalent to CaO/CO₂ molar ratios ~10-12 can still be maintained, while carbonator solids inventories are relatively large. Under high carbonator gas velocities, a sorbent with high CO₂ carrying capacity is necessary to guarantee high CO₂ capture efficiencies. In these conditions, the recirculation of a fraction of the exiting particles towards the bottom of the carbonator proved to be useful for moderating the solids circulation rate between reactors, increasing the particles residence time in the carbonator and sustaining high CO₂ capture efficiencies. For load increases, staging the flue gas entering the carbonator helped to sustain high CO₂ capture efficiencies thanks to maintaining the solids inventory at the bottom of the reactor.

Keywords: CO₂ capture; Calcium looping; Carbonator; Flexibility; Part-load

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1. Introduction

Future energy scenarios are expected to be largely dominated by renewables with the participation of other low-carbon technologies to complete the energy mix [1]. Amongst these, fossil fuel power generation systems equipped with CO₂ capture and storage (CCS) are considered as important options that can secure the supply of low-carbon electricity [1, 2]. In this context, CCS systems coupled to power plants need to be able to operate flexibly to respond rapidly to fluctuations in the electricity demand.

Calcium looping, also known as carbonate looping or CaL, is a CO₂ capture technology that relies on the reversible carbonation-calcination reaction of a CaO-based sorbent [3]. In its post-combustion variant, two circulating fluidized bed (CFB) reactors interconnected to facilitate the transport of solids between each other are usually employed [4-10]. In this process, the carbonator reactor receives a continuous flow of CaO particles from the calciner, which react with the CO₂ contained in the flue gas at ~650°C to form CaCO₃. As a result, a CO₂-depleted gas leaves the carbonator, while a stream of carbonated solids flows towards the calciner. The CO₂ sorbent is then regenerated by calcination of the CaCO₃ solids at high temperatures (around 900-920°C) inside this reactor, which are typically achieved by oxy-combustion of a fuel. The resulting CO₂-rich gas stream is compressed, purified and ultimately stored, whilst the CaO stream is returned to the carbonator to allow the continuous capture of CO₂. A make-up flow of fresh limestone is supplied to the system to compensate for the deactivation of the CaO sorbent over subsequent calcination-carbonation cycles [11]. In addition, a purge is taken out in order to extract deactivated solids and inerts (ash and CaSO₄) that would otherwise accumulate in the system.

CaL systems can achieve CO₂ capture efficiencies of 90% (or higher) with a low energy penalty, as a large fraction of the energy supplied to the calciner can be efficiently recovered in a steam cycle to generate additional electricity [12-22]. The CaL process has experienced rapid progress due to the resemblance of the carbonator and calciner to commercial CFB reactors. Thereby, this technology has been recently demonstrated in several pilot plants in an industrial-relevant environment at MW scale [6-8, 10, 23].

Despite significant progress made in this field in recent years and the importance of highly flexible CO₂ capture systems, research into the flexible performance of CaL systems has so far received little attention.

The studies already published mainly focus on analysing schemes and/or integration options to facilitate the flexibility of CaL plants [24-28]. Few works investigate the dynamics of the system, e.g., the response of the carbonator and calciner reactors after changes in the associated power plant load [29] (which can be analysed using available 1-D dynamic reactor models [29, 30]). In fact, no experimental studies have been carried out on the flexible performance of CaL systems with changes in load.

Load-following operation of CaL systems coupled to flexible power plants entails frequent variations in the flue gas flow rate and, therefore, in the carbonator inlet gas velocity. This has direct hydrodynamic effects on this reactor and on the entire system, leading to changes in the solids circulation rate and the bed inventories of the reactors, which in turn impact on the residence time of the particles inside the carbonator and calciner and ultimately, on CO₂ capture efficiency. At high carbonator gas velocities, the entrainment rate achieved in the reactors is frequently higher than the solids circulation rate needed to achieve the targeted level of CO₂ capture efficiency. This mismatch can be counteracted by recycling a fraction of the solids entrained back towards the same reactor, so that the amount of solids circulating towards the opposite reactor matches the flow required [28, 31, 32]. However, there is a threshold in the case of low gas velocities beyond which the entrainment rate is below the required values, thus decreasing capture efficiency in the carbonator and also affecting the hydrodynamic stability of the CaL system. In these cases, Ylätaalo *et al.* [28] proposed a strategy to sustain the stability of CaL operation, which has also been investigated by Haaf *et al.* [32]. This consists in mixing the flue gas arriving from the power plant with a recycled fraction of the CO₂-lean gas exiting the carbonator (or with air) before it enters the carbonator. This approach ensures that the gas velocity at the inlet of this reactor is high enough to guarantee a stable solids circulation between the reactors. However, it also reduces the CO₂ concentration in the gas at the carbonator inlet, which affects the kinetics of the carbonation reaction (it is a first-order reaction with respect to the CO₂ concentration) and hence, it could lead to a decrease in CO₂ capture efficiency. Besides, the maximum CO₂ capture efficiency attainable would also be lower as the inlet CO₂ concentration in the flue gas would be closer to the equilibrium value.

Other alternatives may be considered to minimise the effects of an increase in the flue gas load when this exceeds the design values. In these cases, a fraction of the flue gas (equivalent to the increase in load)

could be emitted directly to the atmosphere after bypassing the carbonator to keep the gas velocity at the reactor inlet constant. However, this would be at the expense of a reduction in overall CO₂ capture efficiency. Another option is to use a sorbent of large average particle size when working at high flue gas velocities in order to limit the solids circulation rate between the carbonator and calciner and ensure that a sufficiently high solids inventory is maintained inside the reactors. However, load changes are often required to take place within a very short period of time, and replacing the total inventory of a CaL system is not a practical solution in these cases. Also, the coarse sorbent particles will undergo attrition and there will always be a fraction of fine particles in the system that will contribute to increasing the solids circulation rate when high carbonator inlet gas velocities are employed.

The study presented here reports on the experimental investigations carried out in the 1.7 MW_{th} CaL pilot plant of La Pereda in order to contribute to a better understanding of flexible CaL systems. Several tests were conducted to evaluate the flexibility of the interconnected circulating fluidized bed reactor system at different carbonator gas velocities (i.e., flue gas loads). The performance of the CaL plant was assessed during steady state operation under full- and part-load conditions, as well as during transient operation. Moreover, an alternative strategy based on flue gas staging to improve the flexibility of CaL systems and hence, to sustain an adequate level of CO₂ capture efficiency at different loads, was tested at this facility. Its practical scalability to future large CaL capture systems is also discussed on the basis of the results obtained.

2. Experimental

Several purpose-designed test campaigns were carried out in La Pereda 1.7 MW_{th} CaL pilot plant. This facility consists of two interconnected CFB reactors with a height of 15 m and internal diameters of 0.65 and 0.75 m for the carbonator and the calciner, respectively. A high-efficiency cyclone is located at the exit of each riser to separate the solids from the gas stream. The solids leaving the reactors are then directed to a loop seal through a standpipe. The loop seals are key elements for ensuring the flexible operation of the pilot plant, as they allow the solids circulation between reactors to be decoupled from the entrainment of solids in the risers. For this purpose, each loop seal has two exits, each of which is

equipped with a mechanical valve, so that the solids stream arriving from the cyclone can be split into a flow that is directed back to the same reactor (internal recirculation) and to a flow that is sent to the opposite riser (external circulation).

Moreover, the energy required in the calciner is supplied by the combustion of coal, which can be conducted either in air-mode or under oxy-firing conditions (using O_2 and CO_2 stored nearby in tanks of liquefied gases). A continuous flow of fresh limestone can also be fed to the calciner, while a purge can be extracted from the bottom of the reactor using a water-cooled screw feeder. The facility has numerous temperature and pressure taps distributed at different locations to monitor the process. Continuous gas analysis of the main process streams is also available, and solid samples are taken regularly from the reactors using isokinetic probes. This allows the solids circulation rate between reactors to be measured experimentally, which is also calculated continuously by performing an energy balance (see the procedure in [33]). Furthermore, analyses of the solid samples are carried out in order to determine their composition ($CaCO_3$, CaO , $CaSO_4$ and ash content) and the average CO_2 carrying capacity of the sorbent.

Several experimental campaigns were carried out in La Pereda pilot plant under the conditions summarized in Table 1 to assess its flexible performance. Initial tests were carried out to evaluate the limits of the facility in terms of flue gas loads. For this purpose, several scenarios were tested using carbonator inlet gas velocities ranging from 2.0 to 5.3 m/s. Within this operational window, the entrainment rates, the pressure profile and the inventory of solids in the carbonator were determined. Once the limits were established, long-duration steady state experiments were conducted in the pilot plant to assess the performance of the carbonator. To this end, the inlet gas velocity to this reactor was varied in order to study the effect of two main variables that have a direct impact on CO_2 capture efficiency: the solids circulation rate and the carbonator bed inventory. For these tests, solids with a typical average CO_2 carrying capacity of between 0.13 and 0.20 were used. In all of the tests reported in this work, the calciner velocity was adjusted to balance the dual interconnected bed system and maintain stable operation.

Table 1. Range of the main variables during the tests conducted in the pilot plant.

Carbonator gas velocity	m/s	2.0-5.5
Carbonator inventory	kg/m ²	130-1300
Calciner gas velocity	m/s	2.6-5.9
Calciner inventory	kg/m ²	60-420
Solids circulation rate	kg/m ² s	2.6-13.4
Average particle diameter	µm	80-130
Normalised CO ₂ capture efficiency	-	0.50-1

Figure 1. Representation of flue gas staging in the carbonator reactor of La Pereda pilot plant.

In addition, flue gas staging is proposed and tested in this work as an alternative operational strategy to improve the flexibility of CaL systems. In this concept, which resembles the operation of commercial CFB boilers with air staging, a fraction of the total flue gas is diverted and injected at different heights into the carbonator to keep the velocity at the carbonator inlet constant, as schematically shown in Figure 1. Therefore, if the system is operating in a stable scenario and the load needs to be increased, this can be achieved by diverting the proportional amount of additional flue gas to secondary injection ports appropriately located along the carbonator. Clearly, the flue gas entering through the auxiliary ports bypasses part (or even all) of the lower dense solids bed inside the carbonator and hence, lower CO₂ capture efficiencies will be achieved for this fraction of gas. Nevertheless, the operating conditions in the

lower part of the carbonator (where most of the flue gas is injected) improve significantly compared to a scenario where there is no flue gas staging. The improvement thus achieved can offset these effects and contribute to keeping the overall CO₂ capture efficiency at a level similar to what it was before the increase in thermal load. Flue gas staging was tested in the carbonator of La Pereda 1.7 MW_{th} pilot plant using a secondary flue gas inlet located 2.8 m above the reactor grid (see Figure 1). All the tests started with the pilot plant operating at steady state and then, increases in the flue gas flow rate of 10, 20 and 30% were applied. The corresponding rise in the flue gas flow with respect to the initial steady state was bypassed using the secondary flue gas injection line shown in Figure 1. These conditions were maintained until a new steady state was reached. Then, the flue gas flow rate was reverted to the initial value and the bypass was closed to evaluate the plant's response. Sorbent particles with residual activity were used in all cases.

Overall, the results shown here correspond to more than 650 h of operation time accumulated in the 1.7 MW_{th} pilot plant of La Pereda, providing valuable information to support the discussions and conclusions on CaL flexible systems presented below.

3. Results and discussion

The results shown in this paper focus on the effects that the flue gas load has on the carbonator reactor. This is because, as mentioned in the Introduction, direct changes can be expected in this reactor as a result of variations in its gas velocity, which affects the circulation of solids between the reactors and the carbonator inventory and therefore, the CO₂ capture efficiency. However, the gas velocity in the calciner can be maintained constant independently of the thermal load in CaL systems by changing the composition of the oxidant (as already demonstrated elsewhere [34]), which therefore minimises the impacts on this reactor.

As pointed out above, tests were carried out to analyse the impact of the carbonator gas velocity on two of the most important variables affecting the CO₂ capture efficiency: the circulation of particles between the reactors and the solids inventory in the carbonator. Figure 2 depicts the changes in the entrainment of solids in kg/m²s referred to the carbonator as a function of the gas velocity at the carbonator inlet ($u_{\text{gas in CB}}$)

in La Pereda 1.7 MW_{th} pilot plant. In order to facilitate the interpretation of the results, these experiments were carried out with the internal recirculation of solids closed in both the carbonator and calciner but with the external solids circulation between the reactors fully open. Therefore, the entrainment rate resembles the solids circulation rate between the reactors.

Figure 2. Representation of the solids entrainment rate (black dots) as a function of the carbonator inlet gas velocity in La Pereda 1.7 MW_{th} pilot plant (average particle diameter = 85 μm). The grey dotted line shows the calculated solids circulation rate between reactors necessary to achieve 90% CO₂ capture efficiency assuming the conditions mentioned in the text.

As can be seen in Figure 2, the gas velocity at the carbonator inlet has a significant effect on the solids entrainment rate, which varies between 3.4 and 13.4 kg/m²s in the range of velocities tested (between 2.0 and 5.3 m/s). A grey dotted line has been included in this graph in order to give a rough estimation of the solids circulation needed between the reactors to achieve a 90% CO₂ capture efficiency in the carbonator. This has been calculated assuming that the flue gas has a CO₂ inlet concentration of 14% vol. and the increase in the carbonate content of the particles between the reactors is 0.07 points. As can be seen, the entrainment rate of solids from the carbonator is high enough to achieve the targeted CO₂ capture efficiency (90%) when the gas velocity is around 2-3 m/s. However, gas velocities below these values would lead to a lower CO₂ capture efficiency due to an insufficient solids circulation rate between the

reactors, which could also cause instability in the operation of system. In contrast, the entrainment rate of the solids in the carbonator is higher than the solids circulation rate required between reactors for gas velocities greater than 2-3 m/s. In these cases, any excess of entrained solids over the required values could be recirculated back into the same reactor by using the internal recycle provided by the double-sided loop seals.

An additional evaluation of the impacts of the gas velocity on the inventory of solids in the carbonator reactor is presented in Figure 3. This graph shows two representative solids pressure profiles measured in the carbonator of La Pereda pilot plant for very different inlet gas velocities (2.7 and 5.3 m/s). As can be seen, there is no dense bed when the carbonator is working at 5.3 m/s, and the pressure profile is fairly flat with the solids distributed along the height of the reactor. The total bed inventory within the carbonator is around 180 kg/m², as can be inferred from the pressure measurements. A reduction in the carbonator inlet gas velocity down to 2.7 m/s has a significant effect on the carbonator solids profile and bed inventory. As can be seen, a dense bed is formed in the lower part of the reactor. The carbonator bed inventory is substantially higher in this case, amounting to around 850 kg/m². A further analysis of these results by using a hydrodynamic model of the dual interconnected fluidized bed system is considered outside the scope of this work. However, these initial tests indicate that the entrainment of solids from the carbonator is sufficient to fulfil the CaO requirements for the range of velocities studied. Furthermore, they also show that low solids inventories can be expected at high carbonator gas velocities.

Figure 3. Pressure profile of the solids in the carbonator reactor of La Pereda 1.7 MW_{th} pilot plant at carbonator inlet gas velocities of 2.7 and 5.3 m/s (average particle diameter = 80 μm).

Moreover, several long-duration steady state tests were conducted to assess the flexible operation of the carbonator at different flue gas loads, focusing on the CO₂ capture efficiency achieved. To illustrate the general trends observed, three experiments with carbonator inlet gas velocities of 5.3, 3.6 and 2.6 m/s are shown in Figure 4. The graphs in this figure show the bed inventory in this reactor, the solids circulation rate and the normalised CO₂ capture efficiency (defined as the ratio between the experimental CO₂ capture efficiency and the maximum allowed by the equilibrium) achieved in the three scenarios analysed. Figure 4a depicts the steady state operation of the pilot plant with a gas velocity of 5.3 m/s at the carbonator inlet. In this test, the solids circulation between the carbonator and the calciner ($G_{s\text{ CB}}$, referred to the carbonator) is moderated by opening the internal recirculation valves in the loop seals, which yields an average $G_{s\text{ CB}}$ value of 6.2 kg/m²s. In this experiment, the carbonator is operating at an average temperature of 670°C, as a result of the relatively high solids circulation rate and the moderate heat extraction capacity in the reactor. A low bed inventory of 200 kg/m² is achieved in the reactor due to the high gas velocity, which limits the residence time of the CaO particles in the riser. Nevertheless, the inventory is made up of moderately active solids with an average CO₂ carrying capacity of 0.20, thus allowing the normalised CO₂ capture efficiency to vary in the range of 0.6-0.9, as shown in Figure 4a.

The results for a steady state at an inlet gas velocity of 3.6 m/s are depicted in Figure 4b, which corresponds to an intermediate flue gas load scenario. In this case, an average carbonator temperature of 660°C was maintained during the test. As can be seen, the lower operating gas velocity in the carbonator leads to a carbonator bed inventory of 630 kg/m², which is substantially higher than in the previous case. Besides, the solids circulation rate between the reactors also reduces and takes a value of ~4.9 kg/m²s without the need for internal recirculation. The normalised CO₂ capture efficiency is around 0.8, which is achieved using particles with an average CO₂ carrying capacity of 0.14. This lower particle activity explains the similarity between the CO₂ capture efficiencies of Figures 4a and 4b, despite the higher residence time of the particles in the carbonator during this test.

Figure 4. Representation of the carbonator bed inventory (W_{CB}), the solids circulation rate between the reactors ($G_{s CB}$) and the normalised CO₂ capture efficiency ($E_{CO2 norm}$) achieved during the steady state tests carried out in La Pereda pilot plant using a carbonator inlet gas velocity of (a) 5.3 m/s, (b) 3.6 m/s and (c) 2.6 m/s.

Finally, the steady state operation with a low carbonator inlet gas velocity (2.6 m/s) is represented in Figure 4c. As can be seen, the results are consistent with the main trends described above. The low gas velocity in the carbonator gives rise to a bed inventory as high as 900 kg/m² inside the reactor. The entrainment of solids diminishes substantially with respect to the previous scenarios depicted in Figures 4a and 4b, and a solids circulation rate between the carbonator and calciner of 2.8 kg/m²s is achieved with the internal recirculation in the loop seals fully closed. As a result, the carbonator operates at a lower temperature (615°C). Under these operating conditions, the residence time of the sorbent inside the carbonator is high. This makes it possible to achieve normalised CO₂ capture efficiencies close to 1 throughout the entire test, despite using solids with a moderate CO₂ carrying capacity of 0.13.

To compare the carbonator performance at different flue gas loads is not an easy matter, since several variables change at the same time when the carbonator inlet gas velocity is varied, as mentioned above (e.g., the solids circulation rate and bed inventories in the reactors, leading to different particle residence times in the risers). Therefore, a simple reactor model employed in previous works [4, 6, 8, 34, 35] has been used to interpret the performance of the carbonator under different flue gas loads. This model assumes that the carbonator behaves as a perfectly mixed reactor (CSTR) with respect to the solids and a plug flow reactor (PFR) with respect to the gas phase. Thus:

$$E_{carb} = k_s \phi \tau_{active} (\overline{v_{CO_2}} - v_{CO_2,eq}) \quad (1)$$

where E_{carb} is the CO₂ capture efficiency, k_s is the reaction rate constant, ϕ represents the gas-solid contact factor, v_{CO_2} is the molar fraction of CO₂ and $v_{CO_2,eq}$ is the molar fraction at equilibrium conditions. The last parameter is the active space time (τ_{active}), which can be calculated as follows (see references [4, 36] for more details):

$$\tau_{active} = f_a \frac{W_{Ca}}{F_{CO_2,in}} X_{ave} \quad (2)$$

where f_a is the active fraction of particles, W_{Ca} is the molar bed inventory of calcium in the carbonator, $F_{CO_2,in}$ is the molar flow of CO₂ at the reactor inlet and X_{ave} is the average CO₂ carrying capacity of the particles.

By considering the carbonator as a perfectly mixed reactor with respect to the solids, the fraction of active particles in the bed can be calculated as the fraction of solids with a residence time lower than t^* , which is the time required to increase the carbonate content of the particles from that achieved at the calciner exit (X_{calc}) up to X_{ave} :

$$f_a = 1 - e^{-\frac{t^*}{W_{Ca}/F_{Ca}}} \quad (3)$$

The characteristic reaction time (t^*) can be estimated using the X_{calc} and X_{ave} values measured in the samples taken from the reactors and the carbonation reaction rate:

$$t^* = \frac{X_{ave} - X_{calc}}{k_s \phi X_{ave} (\bar{v}_{CO_2} - \bar{v}_{CO_2,eq})} \quad (4)$$

This model has been applied to a set of experimental data obtained during tests carried out in the pilot plant at different carbonator inlet gas velocities. This is depicted in Figure 5, which represents the normalised CO_2 capture efficiency achieved in the carbonator as a function of the active space time calculated by the model (bold black line), whereas the experimental data are depicted in the figure as dots. The general trend predicted by the model agrees reasonably well with the experimental data, despite some dispersion.

Figure 5. Normalised CO_2 capture efficiency as a function of the active space time for tests carried out at different carbonator inlet gas velocities.

The active space time represented here is a key parameter for the design of the carbonator. It is largely affected by the hydrodynamic conditions in the reactor, since it depends directly on the carbonator calcium inventory and the molar flow of CO₂ entering the reactor (i.e., flue gas load), as well as on the calcium flow circulating between the reactors (see Eqs. 2 and 3). It also includes the effect of the characteristics of the sorbent (i.e., the average CO₂ carrying capacity).

As shown in Figure 5, the experimental results have been grouped into three different ranges of carbonator inlet gas velocities. Tests carried out at high gas velocities are characterised by low values of active space time and therefore, modest CO₂ capture efficiencies. This is due to the fact that high flue gas loads ($F_{\text{CO}_2,\text{in}}$) are associated with a high carbonator inlet gas velocity and, in turn, with a low inventory in this reactor, as a result of which the active space time is reduced (despite the increase in f_a due to the shorter residence time of the solids in the reactor, see Eq. 3). The effect is opposite when the carbonator velocity decreases, which leads to larger active space times and therefore, higher capture efficiencies. The negative effect of a high carbonator gas velocity on the inventory of solids can be compensated for by using highly active solids in order to increase the active space time and achieve high CO₂ capture efficiencies. On the other hand, moderate X_{ave} values could be used in scenarios where the thermal load is reduced. In these cases, larger bed inventories can be expected and high CO₂ capture efficiencies can be achieved by using solids that are less active.

The results shown in Figures 4 and 5 demonstrate that CaL systems configured as dual circulating fluidized beds are highly flexible. They can operate over a wide range of gas velocities and accommodate reductions in the flue gas load of as much as 50% with respect to their original design conditions. Adjustment in the operating conditions (e.g., the make-up flow to modify the sorbent activity) may be required to compensate for the hydrodynamic changes occurring in the plant and, therefore, to maintain high CO₂ capture efficiencies over the entire range of flue gas loads. It is for this reason that CaL systems can be regarded as suitable options to be coupled to power plants that are required to operate flexibly in order to supply variable power needs at any given time.

Finally, flue gas staging was assessed in La Pereda pilot plant as a strategy to minimize the effects of changes to the flue gas load on the inventory of solids in the carbonator, as shown in Figure 6 for several

tests with an initial gas velocity at the carbonator inlet of 2.6 m/s. As discussed in the experimental section, the total flue gas flow rate was then increased (point 1 in the figure) by 10, 20 and 30% in cases a, b and c in the figure, respectively. In order to maintain a similar gas velocity at the carbonator inlet, a flue gas stream equivalent to the increase in the mass flow rate was bypassed and fed into the carbonator through a secondary inlet 2.8 m above the grid. These conditions were maintained until the system stabilised, and then the flue gas flow rate was reverted to the initial value and the bypass was closed (point 2 in the figure) in order to return to the original scenario. During these short experiments, the CO₂ carrying capacity of the sorbent remained constant and therefore, any change in the CO₂ capture efficiency can be mainly ascribed to modifications in the solids circulation rate between the reactors and the inventory of solids in the carbonator.

Figure 6. Evolution of the carbonator bed inventory (W_{CB}), the solids circulation rate between reactors ($G_{s\ CB}$) and the normalised CO_2 capture efficiency ($E_{CO_2\ norm}$) with time after a flue gas load increase of (a) 10%, (b) 20% and (c) 30% with flue gas staging.

Figure 6a shows the performance of the system after a rise in the flue gas velocity of 10%. The implementation of flue gas staging to maintain the carbonator inlet gas velocity constant allows the solids circulation rate to remain stable at around $5.0\ kg/m^2s$, without any major changes in spite of the higher flue gas load. The carbonator bed inventory also remains more or less constant at around $1100\ kg/m^2$. As a result, the normalised CO_2 capture efficiency maintains approximately the same values (between 0.70 and 0.85) throughout the test, as can be seen in the figure. Figure 6b shows the results of another experiment where there is an increase of 20% in the flue gas flow rate. In this case, stable conditions are achieved in the carbonator when flue gas staging is implemented, although slight variations appear in the solids circulation rate and the inventory of solids in the carbonator. Although the same gas velocity is maintained at the inlet of the carbonator, the gas velocity profile changes after the secondary injection point and a larger fraction of the solids above this height can be entrained from the reactor. Hence, there is a modest increase in the solids circulation rate from 4.6 to $5.8\ kg/m^2s$. As a result, the carbonator temperature increases by around $40^\circ C$ (up to $660^\circ C$). At the same time, the bed inventory in the carbonator decreases from 1200 to $1000\ kg/m^2$. The resulting conditions still allow a normalised CO_2 capture efficiency in the carbonator of 0.70-0.80, which is similar to that at the beginning of the test, as shown in Figure 6b. The results of an increase of 30% in the flue gas load are shown in Figure 6c. Larger changes are observed in this case, where a substantial increase in the solids circulation rate between the reactors of 50% takes place (up to $7.2\ kg/m^2s$), resulting in a substantial increase in the average carbonator temperature ($\sim 70^\circ C$, up to $695^\circ C$). Moreover, the carbonator inventory decreases from 800 to less than $400\ kg/m^2$. As a result, the normalised CO_2 capture efficiency drops sharply from 0.75 to 0.50 in the first 5-10 minutes after the increase in load.

These experiments indicate that flue gas staging may serve as a useful tool to accommodate moderate increases in the flue gas load with a minimal impact on the stability of the CaL system. It was found to be a suitable operation strategy for accommodating flue gas load changes of up to $\sim 20\%$ in La Pereda pilot

plant, without any major changes to the main process variables. However, optimized designs incorporating several flue gas injection points at different heights could contribute to maintaining a stable performance over a wider range of thermal load increases in large circulating fluidized bed carbonators.

4. Conclusions

The flexible performance of CaL systems was tested in La Pereda 1.7 MW_{th} pilot plant with special focus on the carbonator reactor. To this end, the hydrodynamic changes that occurred in this reactor as a result of modifications in the flue gas load were first assessed. It was seen that an increase in the carbonator gas velocity from 2.0 to 5.3 m/s leads to a rise in the particles entrainment rate from 3.4 to 13.4 kg/m²s, and to the gradual disappearance of the dense solids region at the bottom of the carbonator. The recirculation of a fraction of solids towards the bottom of the reactor (internal recirculation) is therefore necessary to decouple the circulation of solids between the carbonator and calciner from the flue gas load when the carbonator inlet gas velocity exceeds 2-3 m/s under the conditions employed in this work.

Moreover, the results obtained from several steady state tests confirm that the flexible operation of CaL dual CFB systems is possible over a wide range of flue gas loads. Reductions in the carbonator inlet gas velocity of up to 50% with respect to nominal conditions were successfully managed in the pilot plant, leading to the stable operation of the facility without the need for any substantial modifications to the operating procedure or the system. Nevertheless, modifications to the make-up flow may be needed in some cases to compensate for the hydrodynamic changes that occur in flexible CaL systems and to guarantee high CO₂ capture efficiencies. In addition, the implementation of flue gas staging was tested as a strategy to improve the flexibility of CaL systems. The results obtained indicate that this is a useful tool for buffering the hydrodynamic effects resulting from moderate changes to the carbonator flue gas load (up to 20% in the case of La Pereda pilot plant), thereby contributing to maintaining CO₂ capture efficiency. The effectiveness of this option could be further extended towards higher flue gas loads if a purpose designed secondary flue gas injection system were incorporated. This study provides an extensive database of experimental information that contributes to a better understanding of the operation of flexible CaL systems, which is key for the scaling up and deployment of this technology in future energy scenarios.

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378 **Nomenclature**

E_{carb}	-	CO ₂ capture efficiency
$E_{\text{CO}_2 \text{ norm}}$	-	Normalised CO ₂ capture efficiency
f_a	-	Active fraction of particles
$F_{\text{CO}_2, \text{in}}$	mol/s	Molar flow of CO ₂ at the carbonator inlet
$G_{s \text{ CB}}$	kg/m ² s	Solids circulation between reactors, referred to the carbonator
k_s	s ⁻¹	Reaction rate constant
t^*	s	Characteristic reaction time
$u_{\text{gas in CB}}$	m/s	Gas velocity at the carbonator inlet
W_{Ca}	mol	Molar bed inventory of calcium in the carbonator
W_{CB}	kg/m ²	Carbonator bed inventory
X_{ave}	-	Average CO ₂ carrying capacity of the particles
X_{calc}	-	Carbonate content of the particles at the calciner exit
Greek symbols		
ϕ	-	Gas-solid contact factor
τ_{active}	s	Active space time
v_{CO_2}	-	Molar fraction of CO ₂
$v_{\text{CO}_2, \text{eq}}$	-	Molar fraction of CO ₂ at equilibrium conditions

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