

Demonstration of steady state CO₂ capture in a 1.7 MW_{th} Calcium looping pilot

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ABSTRACT

Calcium looping, CaL, is rapidly developing as a postcombustion CO₂ capture technology because its similarity to existing power plants using circulating fluidized bed combustors, CFBC. In this work we present experimental results from a pilot built to demonstrate the concept at the MW_{th} scale. The pilot plant treats 1/150 of the flue gases of an existing CFBC power plant (“la Pereda”) and it has been operated in steady state for hundreds of hours of accumulated experimental time. The pilot includes two 15 m height interconnected circulating fluidized bed reactors: a CO₂ absorber (or carbonator of CaO) and a continuous CaCO₃ calciner operated as an oxy-fuel CFBC. Operating conditions in the reactors are resembling those expected in large CaL CO₂ capture systems in terms of reactor temperatures, gas velocities, solid compositions and circulation rates and reaction atmospheres. The evolution of CO₂ capture efficiencies, solid properties (CO₂ carrying capacity and CaO conversion to CaCO₃ and CaSO₄) have been studied as a function of key operating conditions. It is demonstrated that CO₂ capture efficiencies over 90% are feasible with a supply of active CaO slightly over the molar flow of CO₂ entering the carbonator. Closure of carbon and sulphur balances has been satisfactory during steady state periods. A basic reactor model developed from smaller test facilities seems to provide a reasonable interpretation of the observed trends. This should facilitate the further scale up of this new technology.

INTRODUCTION

Postcombustion Calcium Looping technology has the theoretical potential to achieve a substantial reduction in energy penalties (Shimizu et al. 1999, Abanades et al. 2005, Romeo et al. 2008, Romano et al. 2009, Hawthorne et al. 2009, Yongping et al. 2010, Lasheras et al. 2011, Martínez et al. 2011a, Lisbona et al. 2010, Zhao et al. 2013) and cost (Abanades et al. 2007, Li et al. 2008, Romeo et al. 2009, Zhao et al. 2013) respect to more developed postcombustion and oxyfuel combustion systems. This is because CaL is the only CO₂ postcombustion technology able to generate additional power from the additional heat input required to drive the sorbent regeneration reaction (calcination of CaCO₃). Both carbonation and calcination reactions are carried out at very high temperatures (around 650°C for carbonation and over 900°C for calcination in a rich atmosphere of CO₂). The basic concept of postcombustion calcium looping, CaL, is represented in Figure 1 and was first proposed by Shimizu et al. (1999). Other Calcium looping processes concepts using combustion systems (Abanades et al. 2005, Ramkumar et al. 2010, Martínez et al. 2011b, Abanades et al. 2011, Edwards and Materic 2012, Junk et al. 2012) or precombustion systems (see review by Harrison, 2008) are being developed worldwide, but they are much less developed than the processes represented in Figure 1. This is by far the concept that has experienced the fastest developing pace, because the strong similarities and synergies with existing combustion technology in circulating fluidized beds, including recent oxyfired CFB developments (Myöhänen et al. 2009).

As indicated in Figure 1, the CO₂ is captured from the flue gas of an existing power plant using CaO particles as a sorbent (at 650°C) and calcining the resulting CaCO₃ in a different unit to regenerate CaO while producing a rich stream of CO₂. In the most standard configuration, both the carbonator and calciner are large scale circulating fluidized bed reactors, CFBs, operating at velocities between 3-5 m/s to allow compact reactor designs. There is a need in this particular CaL concept of an Air Separation Unit to oxy-burn a substantial flow of coal in the calciner and supply the energy needed for CaCO₃ decomposition. It should be evident from Figure 1 that the calciner

resembles a full oxyfired new power plant system, where highly suitable heat sources for a new steam cycle are available. In particular, the energy used for the endothermic calcination reaction is fully recovered in the carbonator at a temperature around 650°C. Furthermore, large make up flows of limestone to compensate for modest absorption capacity of highly cycled particles of CaO are economically feasible (Abanades et al. 2004), since fresh particles of CaO can be generated in the calciner by feeding a certain make up flow of crushed limestone (usually a very low cost material). This flow of limestone also purges inert materials (coal ashes and CaSO₄), and the integration of the rich purge of CaO with a cement plant or other large scale used of CaO (e.g.: desulfurization sorbent in the existing power plant) allows for an even larger flow of sorbent make up (see review by Dean et al. 2011).

As recently noted by Sanchez-Biezma et al. (2012), great progress has been achieved in different projects around the world developing CaL. The most aggressive scale up of the technology has been pursued under the EU funded “CaOling” project (www.caoling.eu), that relied first in a demonstration of the concept in lab scale pilots with continuous solid circulation (Alonso et al. 2010, Charitos et al. 2010, Rodriguez et al. 2011a, Rodríguez et al. 2011b, Charitos et al. 2011). Also part of CaOling project was the design, commissioning and operation of a 1.7 MWth pilot in la Pereda (Spain) to test the postcombustion Ca-looping concept under a real industrial environment. This pilot entered operation in January 2012, establishing successfully the solid circulation system components and obtaining the first results operating in dynamic and continuous mode (Sanchez-Biezma et al. 2012). Other developing efforts in Germany have also achieved positive results in large pilots: the 1 MWth pilot in Darmstadt (Galloy et al. 2011, Plötz et al. 2012) and in 0.2MW in Stuttgart University (Hawthorne et al. 2011, Dieter et al. 2012). There is also a wider R&D community publishing valuable results at laboratory scale and small pilot level (see review by Blamey et al. 2011) and the IEAGHG created in 2009 a Network on High Temperature Solid Looping (www.ieaghg.org) where these actors meet regularly to discuss progress of the different variants of the CaL technology. Therefore, postcombustion CaL is now an established “promising

technology” that faces similar credibility challenges than other emerging capture options. The main challenge is of course to progress in the experimental demonstration of the concept at increasing scale and realistic conditions, validating the benefits expected and overcoming the obstacles that may appear in the path towards large scale demonstration.

This paper is intended to contribute to the process of scaling up of this postcombustion CaL technology. We describe briefly the CaL test facility of La Pereda and the experimental method to reach steady state operation. We then present the experimental results from the pilot and how the closure of carbon and sulphur balances is achieved during continuous operation in air mode calcination as well as in oxy-combustion calcination mode. We then apply a modelling approach successfully used for the interpretation of experimental results from smaller pilots (Alonso et al. 2010, Rodríguez et al. 2011a, Alonso et al. 2011, Charitos et al. 2011) that should be valuable for scaling up purposes.

EXPERIMENTAL

The pilot is only briefly summarized here as it has been described in detail elsewhere (Sanchez-Biezma et al. 2011). The calcium looping reactor system is made up of two interconnected CFB reactors of 15 m height with an internal diameter of 0.65 in the carbonator and 0.75 in the calciner. The reactors are connected to high efficiency cyclones: the cyclone of the carbonator separates the flue gas lean in CO₂ from the partially carbonated solids; the calciner cyclone separates the concentrated CO₂ stream leaving the oxyfired combustor from the solids rich in CaO. Solids fall by gravity from the cyclones to double loop seals, that are bubbling fluidized beds allowing for the control of the solid circulation between reactors. Part of the solids coming to each loop seal return to the reactor from which the solids are coming (internal solid circulation) and the rest circulates to the other reactor (from carbonator to calciner or from calciner to carbonator). The relevance of this internal solid circulation streams to maintain certain solids inventories in the reactors has been discussed elsewhere (Charitos et al. 2010, Diego et al. 2012).

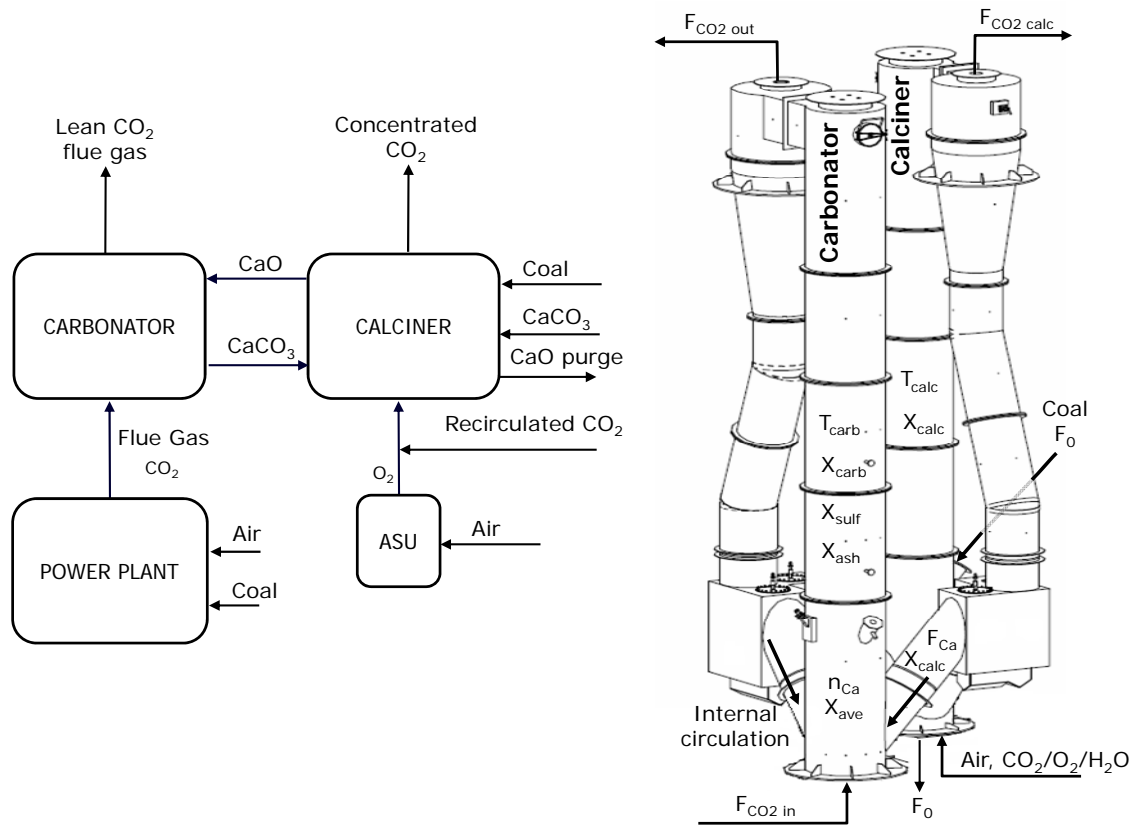


Figure 1. General scheme of a power plant incorporating a Ca-looping system and schematics of the “la Pereda” pilot plant facility, with the main mass flows and operating variables involved in the test campaigns.

The calciner is able to operate under air combustion or under oxy-fuel combustion conditions, using O₂ and CO₂ coming from tanks of liquefied gases. The carbonator is equipped with removable cooling bayonet tubes which allow variable heat extraction from the reactor under different conditions of temperature, solid circulation flows and different intensity of the exothermic carbonation reaction of CaO. Flue gas from the power plant is blown to the carbonator with a fan. There is a continuous limestone and coal feeding system connected to the calciner which allows working in a steady state combustion and sorbent feeding modes. There is also a continuous solid removal system in the calciner made up with a water cooled screw feeder. Instrumentation including temperature, pressure and continuous gas analysis from different points is available. Many other ports are available for solid sampling and local solid circulation rates measurement with

isokinetic probes. Subsequent analysis of such solids samples (in terms of particle size distribution, chemical composition and reactivity towards CO₂ capture and SO₂ capture) are carried out in the lab, using thermogravimetric equipment described elsewhere (Gonzalez et al. 2008).

The calciner has been run aiming at full conversion of CaCO₃ to CaO in all test discussed in this work. This has been possible by allowing a sufficiently high calcination temperatures (20-30°C over the limit given by the equilibrium of CO₂ on CaO at the exit of the calciner) and a certain O₂ excess at the exit of the combustion-calciner reactor (over 5% vol) to ensure high coal combustion efficiencies in the calciner. Optimization of combustion conditions of the calciner in order to reduce this level of O₂ is considered outside the scope of the present work. We focus in this work on investigation of the carbonator reactor operated with a steady state flow of CaO as indicated in Figure 1.

Concerning the performance of the carbonator reactor, previous experience from small test facilities in continuous mode (Alonso et al. 2010, Rodríguez et al. 2011a, Charitos et al. 2011) have been used to define the experimental methodology to measure and characterize the main variables that affect the performance of the carbonator as a chemical reactor:

- The inventory of solids in the carbonator (n_{Ca} in Figure 1) is determined continuously through the measurement of the pressure difference between the plane above the distributor and the exit of the reactor. Occasional test where the fluidization has been switched off and the solids have been extracted from the carbonator have confirmed the direct relationship between bed ΔP and the solid inventory (the contribution of the acceleration of the circulating solids to the ΔP in the carbonator is negligible)
- The average carbonator reactor temperature (T_{carb} in Figure 1). The carbonator reactor displays a certain axial temperature profile due to the effect of the bayonet tubes, the exothermic character of the carbonation reactor (more intense in the dense bottom part of the carbonator) and the arrival of high temperature solids from the calciner (at between 830°C-920°C). Internal solid circulation (within the reactor through solid convective flows and

through the recirculating solids from the cyclone-double loop seal system) can drastically reduce this difference of temperature to 20-30°C, so that an average temperature in the reactor can be calculated.

- The molar flow of CO₂ entering the carbonator with the flue gas (F_{CO_2in} in Figure 1). The inlet concentration of CO₂ changes little during the experiments (between 12%-12.5%v) as these correspond to the flue gas composition of the power plant. These concentrations are measured continuously, as well as the mass flow of flue gas entering the carbonator reactor.
- The average composition of the solids arriving to the carbonator and their activity towards CO₂ and SO₂ capture (X_{carb} and X_{sulf} in Figure 1). This cannot be monitored continuously but frequent solid sampling from suitable entry and exit ports is feasible using isokinetic probes. Chemical analysis of the solids samples taken during each experiment is carried out in order to determine the CaO, CaCO₃ and CaSO₄ content. The solids samples are also tested in a TG equipment described elsewhere [Rodríguez et al. 2011a] to determine the CO₂ carrying capacity and the carbonation reaction rates.
- The molar circulation rate between carbonator and calciner reactors (F_{Ca} in Figure 1). As will be discussed later, when the system is operating in stationary state, this variable can be estimated by two methods in parallel: the closure of the carbon balance and the closure of the heat balance in the carbonator. The total solid circulation rate through the risers can also be measured using a suction probe in isokinetic conditions at the exit of the riser. The carbonator riser is 15 m height and solids are largely disengaged from the gas at this height. Therefore, upwards solid circulation at that point are close to total solid circulation.

. The test campaigns carried out in the pilot plant add up to more than 1800 hours of operation of the interconnected reactors in combustion mode in the calciner. A total of 380 hours have been achieved in CO₂ capture mode (with capture efficiencies between 40-95%), out of which 170 hours have been achieved in CO₂ capture mode with stable oxyfuel combustion of coal in the calciner.

Table 1 summarizes the main range of operating conditions used during CO₂ capture tests in the pilot.

Table 1 Range of operating conditions and the main variables involved during CO₂ capture tests in “la Pereda” 1.7MW_{th} pilot plant.

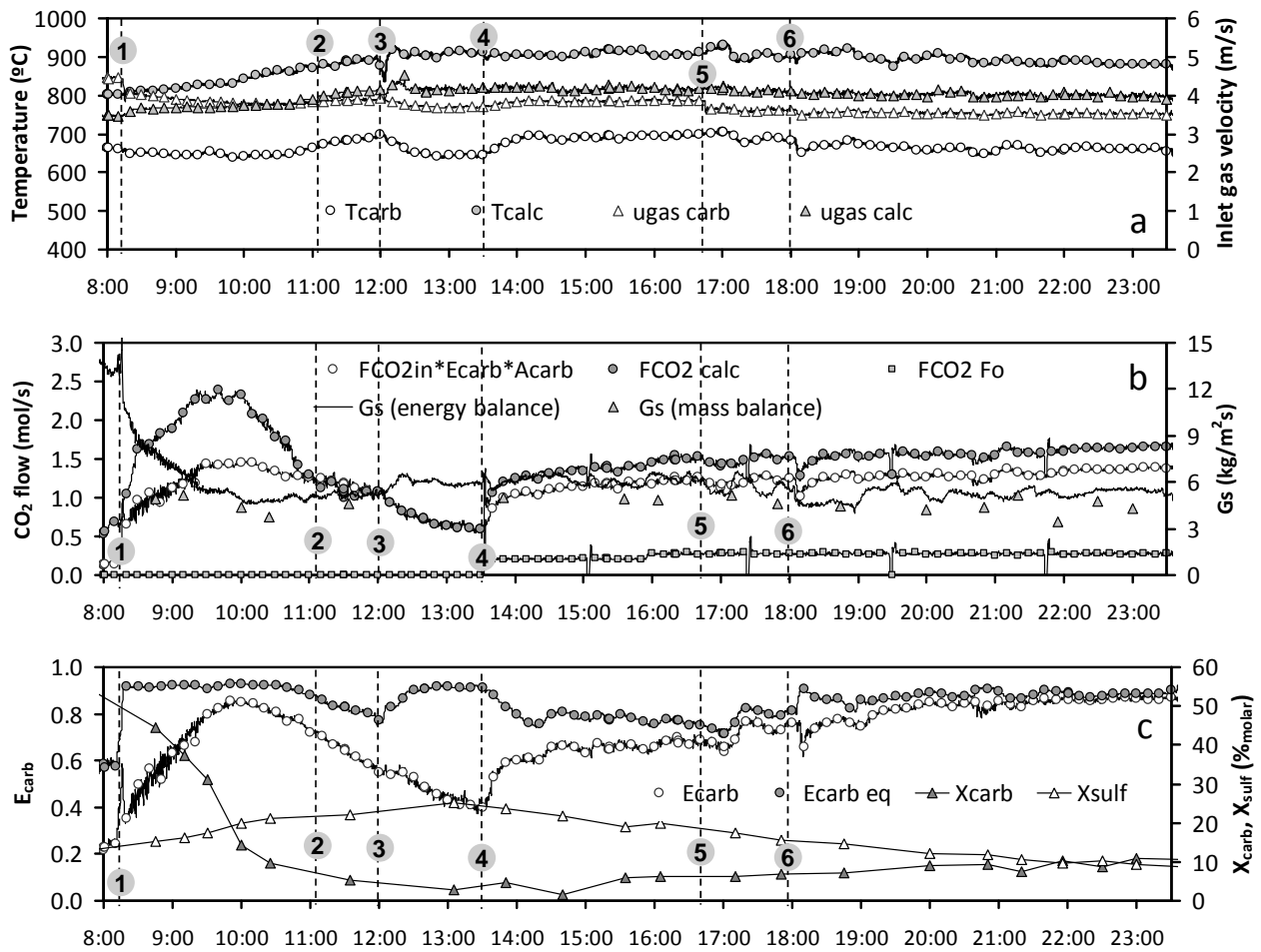
Carbonator temperature (°C)	T_{carb}	600-715
Carbonator superficial gas velocity inlet (m/s)	$u_{gas\ carb\ in}$	2.0-5.0
Inlet CO ₂ volume fraction to the carbonator	$v_{CO_2\ carb\ in}$	0.12-0.14
Inlet SO ₂ concentration to the carbonator (ppm _v)	C_{SO_2}	100-250
Inventory of solids in the carbonator (kg/m ²)	W_s	100-1000
Maximum CO ₂ carrying capacity of the solids	X_{ave}	0.10-0.70
Calciner temperature (°C)	T_{calc}	820-950 °C
Inlet O ₂ volume fraction to the calciner	$v_{O_2\ calc\ in}$	0.21-0.35
Inlet CO ₂ volume fraction to the calciner	$v_{CO_2\ calc\ in}$	0-0.75
CO ₂ capture efficiency	E_{carb}	0.4-0.95
SO ₂ capture efficiency	E_{sulf}	0.95-1.00

RESULTS AND DISCUSSION

As mentioned above the focus of this paper is on steady state results, but it may be of interest to discuss first the main transitions in the system from the start up to the steady state periods. A typical experimental run starts with the calcination of a batch of limestone in the facility, that is used initially as a heat carrier to transfer heat from the reactors (where the start up propane burners operate) to the rest of the installation. Once the initial batch of solids are calcined, the calciner is switched to oxy-fuel combustion mode. After that, fresh limestone is fed to the calciner only to adjust the activity of the sorbent and compensate for attrition losses, while solids are removed to keep constant the total inventory in the system and to avoid the accumulation of inert solids (CaSO₄ and ashes). Figure 2 presents a typical experiment from the onset of the calcination of the initial total solid inventory in the system to the steady state period in oxyfuel combustion-calcination mode. The main events are highlighted in the Figure and summarized in the auxiliary table included in the Figure. During this particular test, the inlet gas velocity was kept between 3.6-3.9 m/s in the carbonator and between 3.8-4.2 m/s in the calciner.

The initial period corresponds to the calcination of the solids present in the system, and this process can be followed using several parallel approaches. The first one is by determining the composition of the solids extracted periodically from the system. Figure 2a shows the carbonate and sulfate molar composition of the solids taken from the carbonator reactor at different times. During this period of the experiment, the carbonate content of the solids in the carbonator dropped from 54 to 5%w between 8:00 and 11:00. It can be also observed that the sulfate accumulates in the system as there is no extraction of the solids from the reactors during this period.

Another approach to follow the calcination period is by comparing the CO₂ released by calcination in the calciner and the CO₂ captured in the carbonator. Figure 2b shows the comparison of both terms along the experiment. During the initial 3 hours, there is a net production of CO₂ in the calciner due to the calcination of the carbonate present in the initial inventory of solids (see in Figure 2b). However, it can be seen in Figure 2b that once the batch of solids is completely calcined, the CO₂ produced by calcination becomes equal to the CO₂ capture in the carbonator. During this initial period, the net amount of CO₂ released in the carbonator calculated from the difference between the CO₂ calcined and captured is about 7.2 kmol. This value matches the amount of CO₂ that should be produced by the calcination of the initial batch of solids present in the system (that has an initial carbonate content of 54 %w). The agreement between both values also indicates that the total inventory of solids in the system can be estimated sufficiently accurately using pressure measurements in the facility. The CO₂ produced in the calciner increased above the CO₂ captured in the carbonator from 13:30 due to continuous addition of fresh limestone into the system from that point.



Event	Time	Description
1	8:05	Start of calcination of the batch of solids and feeding of flue gas
2	11:00	End of calcination of the batch of solids
3	12:00	Switch to oxy-combustion mode
4	13:30	Continuous limestone feeding
5	16:50	Modification of carbonator inlet gas velocity
6	18:00	First solid extraction from the calciner

Figure 2. Example of a typical experimental run in la Pereda pilot plant.

Attending now to the CO₂ capture efficiency, E_{carb} , this is quite low (below 0.4) at the beginning of the calcination period (see Figure 2c) due to the low amount of CaO present in the system. But, as the calcination progresses and the CaO content in the solids increases, E_{carb} rises to a value close to that limited by the equilibrium. The equilibrium CO₂ capture efficiency ($E_{\text{carb eq}}$) shown in Figure 2c has been calculated using the average temperature in the carbonator.

The temperature of the calciner and the efficiency of the calcination also changes with time in the first few hours of this experiment (Figure 2a). As the initial batch of solids is being calcined, the

temperature of the calciner increases progressively until it reaches a value above 900 °C. This trend in the calciner temperature tends to cause an increase in the temperature of the solids arriving to the carbonator, thus increasing the temperature of this reactor and reducing the equilibrium CO₂ capture efficiency. In these conditions it is necessary to adjust the heat transfer area provided by the bayonet tubes to stabilize the carbonator temperature at the target temperature in the experiment. At 12:00, the calciner was switched to oxy-combustion mode by supplying a mixture of O₂/CO₂.

At 13:30, the X_{ave} of the sorbent had decreased to a residual value of 0.067 after more than five hours without adding fresh limestone into the system. Thus, a continuous flow of limestone was set up at this point to increase the activity of the sorbent circulating in the system. This flow of fresh limestone increased progressively the X_{ave} up to a value 0.18 at 23:00. The addition of the limestone also increases progressively the inventory of solids in the system, which reaches a maximum value of 900 kg/m² at 18:00 in the carbonator reactor. From this point, solids were removed using the ash extraction system in order to maintain the inventory of solids below this value in this particular experiment. During this period, the increase of X_{ave} and the inventory of solids led to an increase of the CO₂ capture efficiencies, which almost reaches the maximum CO₂ capture efficiency limited by the equilibrium from 20:00. The addition of fresh limestone and the extraction of solids also reduced the CaSO₄ content to around 5 mol%.

As stated above, after several hours of stable operation, the activity of the material circulating between reactors decays towards a residual activity. This concept of residual activity was first detected in thermogravimetric studies (Grasa et al. 2006, Lysikov et al. 2007, Chen et al. 2009) but has also been observed in continuous test of sufficient duration in stationary state (Charitos et al. 2011). It is important to confirm this general deactivation trend of the sorbent in the “la Pereda” pilot. An example of the steady state experiments conducted with this purpose was carried out during 12 hours without feeding limestone, allowing the sorbent activity to fall towards the residual value. Attrition losses were negligible during this test because the bed inventory was made up with what was left after calcination (in air combustion mode) of the large batch of fresh limestone. It is

already known (Jia et al. 2007, Gonzalez et al. 2010, Coppola et al. 2012) that attrition mainly takes place in the first calcination of the material. We confirmed that the attrition rate drastically reduces afterwards, as the particles “surviving” the first calcination are those with best mechanical properties and the internal sintering taking place during carbonation-calcination cycles further strengthen the particles. Attrition during calcination is highly dependent on limestone type and attrition conditions in CaL systems should be identical to those present in large scale CFBC systems. Figure 3a shows the evolution with time of the CO₂ carrying capacity (X_{ave}) of the solid samples extracted from the system during this test against the effective number of cycles. In this continuous and well mixed reactor system, the effective number of carbonation-calcination cycles of the solids has been calculated using the following equation:

$$N_{th} = \frac{\int_0^t F_{CO_2in} E_{carb}(t) dt}{n_{Ca,total} X_{ave}} \quad (1)$$

This number, N_{th} , is only an approximation that accounts for the number of times that the moles of CO₂ captured could carbonate the total inventory of Ca ($n_{Ca,total}$) up to its average CO₂ carrying capacity (X_{ave}) (see Charitos et al. 2011 for a more detailed methodology). In Equation 1, $E_{carb}(t)$ represents the instantaneous CO₂ capture efficiency, while $n_{Ca,total}$ stands for the total inventory in the system. X_{ave} is measured at different time points analyzing the samples taken from the system and its value is considered constant between these points. The product, $F_{CO_2in}E_{carb}(t)$, is calculated continuously through gas analysis, while the total calcium moles, $n_{Ca,total}$, are known through measurements of bed inventories and the chemical analysis of the solid samples.

As can be seen in Figure 3a, the drop in the CO₂ carrying capacity observed during this experiment is consistent with the deactivation curve (Grasa et al. 2006) when it is tested in a TGA in absence of SO₂ (shown as a solid black line in Figure 3a). Sulfation conversion of the solids increases with N_{th} , as the total inventory of material in the reactor system (including loop seals and standpipes)

progressively reacts with SO_2 . More than 95% of the SO_2 coming into the carbonator in the flue gas from the existing CFBC power plant (200-300 ppm_v during this period) and more than 95% of the sulfur in the coal feed to the calciner, is captured by the solids circulating in the CaL system.

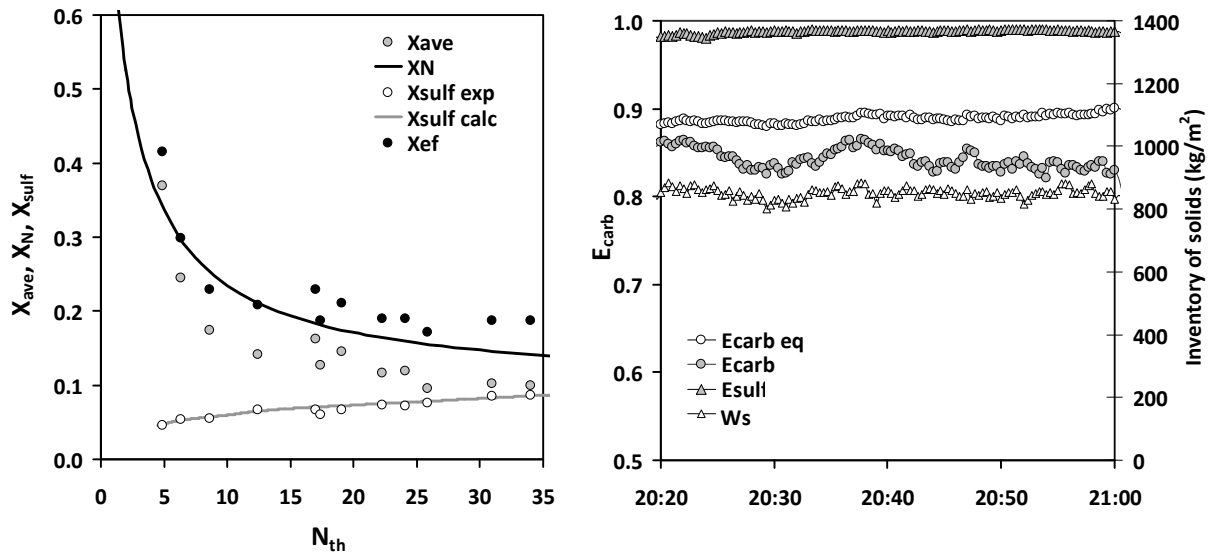


Figure 3. (a) Evolution of sorbent utilization with the average number of carbonation-calcination cycles of particles in the system and (b) CO₂ capture and SO₂ capture efficiencies when operating with solids with residual CO₂ carrying capacity of Figure 3a.

This is consistent with results recently reported by Arias et al. (2012) from experiments carried out in a 30 kWth pilot. Furthermore, by knowing the amount of Ca in the system and the SO₂ that is captured in the carbonator and calciner, the evolution of the sulphate conversion, X_{sulf} , can be calculated (shown as solid grey line in Figure 3a). Excellent closure of the SO₂ mass balance was achieved, as can be seen from the good agreement between experimental and calculated values. Figure 3a also shows the total sorbent utilization which is the sum of the CO₂ carrying capacity and CaSO₄ molar conversion. As can be seen in this Figure, the total sorbent utilization ($X_{ef} = X_{sulf} + X_{ave} = 0.19$) is higher than the expected and after 35 cycles the sorbent with a molar fraction of 0.086 in CaSO₄ is still able to achieve a molar carbonate conversion of 0.1. This qualitative trend (effective sorbent utilizations higher than expected) has been confirmed in other similar test and has economic

implications for the CaL systems as it will make more feasible to operate the system with low make up flows of fresh limestone.

It is interesting to note that the “deactivated” material ($N_{th}>35$) circulating between calciner and carbonator in Figure 3a is still able to capture CO_2 in the carbonator with an efficiency over 80%, as long as there is sufficient bed inventory in the reactor. This is shown in Figure 3b, that corresponds to an experimental period of 50 minutes at the end of the experimental run of 12 hours without addition of limestone when the CO_2 carrying capacity (X_{ave}) of the solids present in the system was around 0.10. Figure 3b also represents SO_2 capture efficiency in the carbonator at the same time period. In this figure we can see that SO_2 capture efficiency in the carbonator was kept well above 0.95. The high SO_2 removal obtained during the CO_2 capture tests in the pilot plant confirms the trends observed at laboratory scale and in the 30 kWth facility which indicated that CFB carbonator are excellent desulfurization units (Arias et al. 2012).

As indicated in Table 1, many other stationary state periods were tested using a range of operating conditions and operating in steady state. Figure 4 shows an example of one hour of operation in two such steady states, comparing the effect of the average activity of the solids, X_{ave} , on the normalized CO_2 capture efficiency ($E_{carb}/E_{carb\ eq}$) which is an indication of the carbonator reactor efficiency. In both experiments, the inventory of solids in the carbonator was kept at the same value and the inlet gas velocity to the carbonator was around 4.0-4.3 m/s. During the first steady state (shown in grey), the activity of the solids (X_{ave}) was around 0.11. Under these experimental conditions, the normalized CO_2 capture efficiency achieved was around 0.65, and increased to 0.90 during the second steady (shown in black) state when the activity of the sorbent is 0.21. This is consistent with previous works (Alonso et al. 2010, Charitos et al. 2010, Rodríguez et al. 2011a) that have shown that two of the most relevant operating parameters in a carbonator reactor are the inventory of solids in the bed and the average activity of the solids in such reactor. Therefore the trends observed during all stationary state periods such as the example in Figure 4 have been analyzed following the methodology reported in these references.

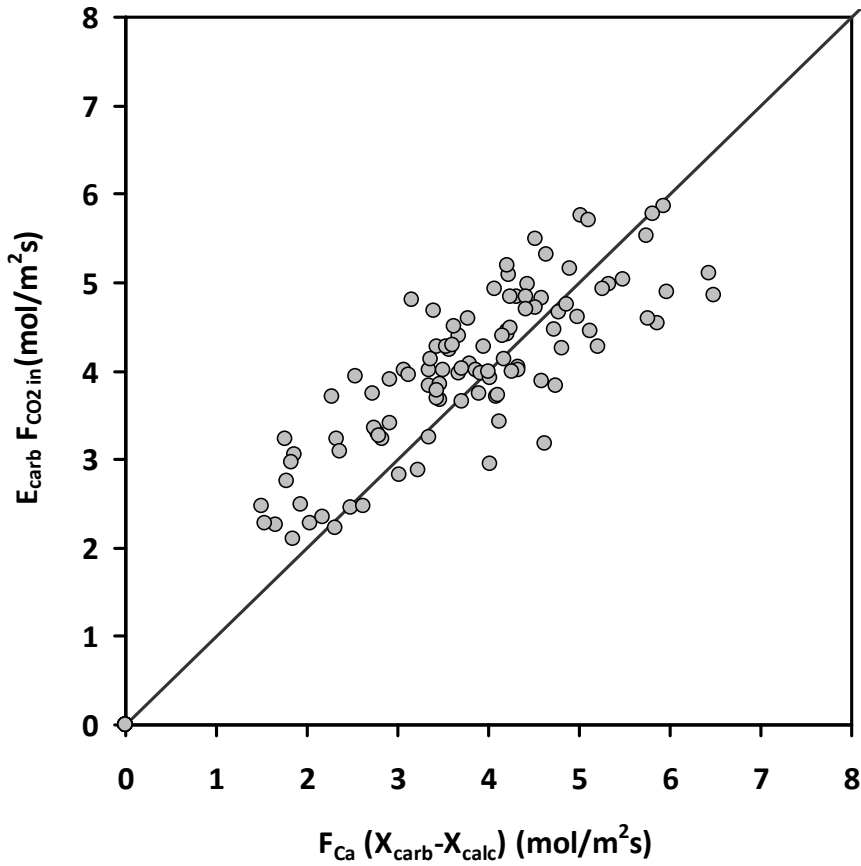


Figure4. Comparison of two steady states of one hour ($u_{\text{gas carb in}}=4.0-4.3$ m/s, average carbonator temperature= $660-690^{\circ}\text{C}$, $X_{\text{ave}}=0.11$ (grey), $X_{\text{ave}}=0.21$ (black)).

The CO_2 capture efficiency in the carbonator is defined as the amount of CO_2 captured respect to the CO_2 fed to the carbonator and can be calculated as follows:

$$E_{\text{carb}} = \frac{F_{\text{CO}_2\text{in}} - F_{\text{CO}_2\text{out}}}{F_{\text{CO}_2\text{in}}} \quad (2)$$

where F_{CO_2} is molar flow of CO_2 ($\text{mol}/\text{m}^2\text{s}$). In a steady state, the overall CO_2 mass balance of the system can be written and calculated using three approaches.

$$\left(\begin{array}{c} \text{CO}_2 \text{ reacting} \\ \text{with CaO in the bed} \end{array} \right) = \left(\begin{array}{c} \text{CaCO}_3 \text{ formed in the} \\ \text{circulating stream of CaO} \end{array} \right) = \left(\begin{array}{c} \text{CO}_2 \text{ removed} \\ \text{from the gas phase} \end{array} \right) \quad (3)$$

Each term of this equation can be calculated independently using experimental measurements available in the pilot plant, and the values can be compared to analyze the closure of carbon balances at steady state in the system. The CO₂ removed from the gas phase is the most reliable term in the mass balance of Eq. 3 as this can be calculated directly from the continuous measurements of flue gas fed into the carbonator and the gas composition entering and leaving the reactor. Additional sources of CO₂ in the carbonator from the combustion of unconverted fuel in the calciner are evaluated from small differences detected in the flow of oxygen after and before the carbonator.

It is also helpful to interpret the carbonator performance to compare the CO₂ carbonation efficiency (E_{carb}) with the maximum CO₂ removal efficiency achievable from the gas phase ($E_{\text{carb, eq}}$). This is estimated from the minimum CO₂ molar fraction ($v_{\text{CO}_2 \text{ eq}}$) allowed by the equilibrium (Baker, 1962) which is a function of the average temperature in the carbonator.

Under steady state conditions, when there is no accumulation of CaCO₃ in the carbonator bed, the fraction of CO₂ captured from the gas phase has to be the same as the CaCO₃ formed in the circulating stream of CaO. Thus, the following mass balance should be fulfilled:

$$E_{\text{carb}} F_{\text{CO}_2 \text{ in}} = F_{\text{Ca}} \times (X_{\text{carb}} - X_{\text{calc}}) \quad (4)$$

where F_{Ca} is the molar flow (mol/ m²s) of CaO entering into the carbonator, X_{carb} is the carbonate content of the solids leaving the carbonator and X_{calc} is the carbonate content of the solids coming from the calciner and entering the carbonator. If the solid circulation rate between reactors (G_s) is known, the molar flow (F_{Ca}) can also be obtained from the analysis of the samples taken from the reactors.

$$F_{Ca} = \frac{G_s (1 - X_{ash})}{PM_s} \quad (5)$$

Considering the calciner and carbonator as perfect mixed reactors, it can be assumed that the composition of the solid in these beds is the same as the one measured at the exit of the reactors. Then, the molar flow of CaO (F_{Ca}) can be estimated from the Equation (4) above and from the experimental determination of carbonate and ash content of the solids extracted from carbonator and calciner during the experiment. As was indicated above, another approach to calculate the mass flow of solids between reactors is to solve an energy balance to the carbonator. Since the pilot is refractory lined, heat losses are modest and can be calibrated. Therefore, it is possible to determine during steady state conditions the total solid circulation rate of solids arriving to the carbonator (G_s) from the calciner loop seal of Figure 1. All the terms in the heat balance can be estimated continuously from instrumentation available in the pilot plant and the measurements from the heat balance calibrated to correct systematic deviations. As an example, Figure 2c showed both the calculated solid circulation rate (G_s) through calciner during the experimental run from the heat balance and the same G_s calculated from Equations (4) and (5).

Figure 5 compares the two terms in the carbon balance of Equation 4 for all stationary states achieved in the operation of the plant in CO₂ capture mode. As can be seen from Figure 5, the CaCO₃ formed by carbonation and circulating in the stream of solids between reactors reasonably agrees with the CO₂ removed from the gas phase. The main source of uncertainty in this mass balance closure concerns the representativity of the values of X_{calc} and X_{carb} used in Eq 4.

The other relevant CO₂ mass balance closure expressed in Equation (3) is particularly useful for reactor design: this concerns the comparison of the flow of CO₂ captured from the gas phase and the flow of CO₂ reacting with the CaO particles present in the carbonator bed inventory at any particular time. This second term can be estimated as the product of two parameters, the amount of solids present in the bed and the average reaction rate of the solids.

$$F_{\text{CO}_2\text{in}} E_{\text{carb}} = n_{\text{Ca,active}} \left(\frac{dX}{dt} \right)_{\text{reactor}} \quad (6)$$

To close this mass balance, we have applied the carbonator model proposed by Alonso et al. (2009) and methodology used by Charitos et al. (2011) to interpret the experimental trend observed in the lab scale Ca-looping facilities. Parallel efforts to build more elaborate reactor models for the carbonator and calciner reactors are on going within the CaOling project (Ylätaalo et al. 2012).

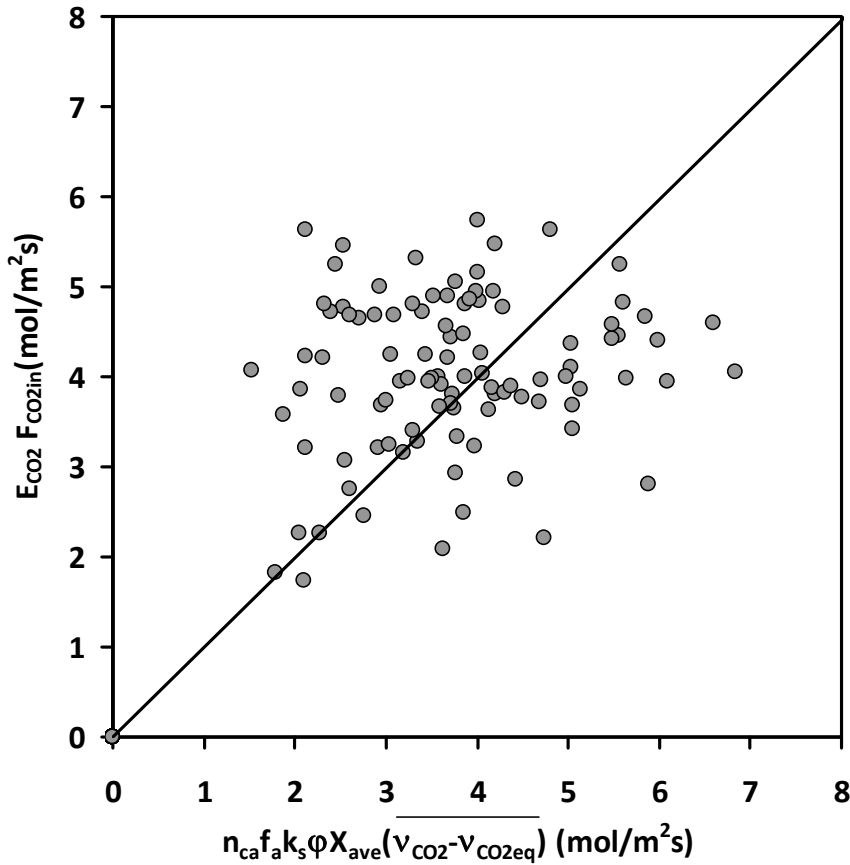


Figure 5. Comparison between the CO_2 removed from the gas phase in the carbonator and the increment in CaCO_3 flow between reactors.

The reactor model used in the present work considers the CFB carbonator as a perfect mixed reactor for the solid phase and a plug flow reactor for the gas phase. For the average reaction rate of the solids, we assume that the particles react at a constant rate until they reach their maximum carbonate conversion (X_{ave}) and after that point the reaction rate is zero. This simplification of the

reaction rate is consistent with the experimental data available (see for example (Grasa et al. 2008)) and it has been shown to be accurate enough for the interpretation of the experimental data in the small facilities (Charitos et al. 2011). According to this assumption, the reaction rate of the particles depends on the CO₂ carrying capacity of the sorbent (X_{ave}) and the average CO₂ concentration in the carbonator and can be expressed as follows:

$$\left(\frac{dX}{dt} \right)_{\text{reactor}} = k_s \phi X_{ave} \left(\overline{v_{CO_2} - v_{CO_2eq}} \right) \quad (7)$$

where k_s is a constant reaction rate that depends on the limestone used and ϕ is a gas-solid contacting factor defined by Rodriguez et al. (2011). Once defined the reaction rate term, the active inventory of calcium can be defined taking into account the assumption of a perfect mixing reactor. According to this, the fraction of active solids in the carbonator (f_a) is that corresponding to the fraction of particles with a residence time lower than the time needed to increase the carbonate content from X_{calc} to X_{ave} (t^*).

$$n_{Ca,active} = n_{Ca} f_a = n_{Ca} \left(1 - e^{-\frac{t^*}{n_{Ca}/F_{Ca}}} \right) \quad (8)$$

The characteristic carbonation reaction time (t^*) can be calculated by determining X_{calc} and X_{ave} from the solid taken and using the reaction rate define in Eq 7 (see references Alonso et al. 2009 and 2010, Rodríguez et al 2011, Charitos et al. 2011). By combining Eqs. 7-8 into Equation 6, a simple expression can be obtained that links all the operating parameters in the Ca-looping with the CO₂ capture efficiency:

$$E_{carb} F_{CO_2 in} = n_{Ca} k_s \phi f_a X_{ave} \left(\overline{v_{CO_2} - v_{CO_2eq}} \right) \quad (9)$$

The apparent constant rate ($k_s \phi$) in Eq. 9 can be calculated as a fitting parameter by comparing the CO₂ capture from the gas phase and the CO₂ reacting with the CaO in the carbonator bed using Eq. 6. The constant rate (k_s) can be measured in TGA for the limestone used for the tests (an average value of 0.45 s⁻¹ consistent with other similar limestones as reported in Grasa et al. 2008).

Figure 6. Comparison between the CO₂ removed from the gas phase and the CO₂ reacting with CaO in the carbonator bed.

Figure 6 shows the final comparison between the CO₂ removed from the gas phase and the CO₂ reacting with CaO in the carbonator bed. As can be seen, there is only a rough closure of this mass balance, which can still be considered reasonable when taking into account the inherent uncertainties in the determination of the parameters of the involved in Equation 9. These are discussed in more detail in a previous work reporting data from a much smaller pilot (Rodriguez et al 2011). The qualitative similarities in the closure of the CO₂ mass balances represented in Figures 5 and 6 with those reported from a smaller pilot provides confidence about the scalability of these results in what refers to CO₂ capture in the carbonator reactor.

CONCLUSIONS

The results obtained in a 1.7MW_{th} pilot confirm that postcombustion calcium looping is a promising technology for CO₂ capture that can strongly benefit for scaling up purposed from existing knowledge on mature Circulating Fluidized Bed Combustion Technologies. CO₂ capture efficiencies over 90% have been achieved in a wide range of experimental conditions in the CFB carbonator, including continuous operation using solids with modest CO₂ carrying capacities. Closure of carbon and sulphur balances has been satisfactory during steady state periods lasting for

up to 380 hours of accumulated experimental time with CO₂ capture, including 170 hours with the calciner operating under oxy-fuel combustion mode.

A valuable data base of results have been acquired for model validation and scale up purposes, including test conducted in full oxy-combustion mode in the calciner. A basic reactor model has been used to interpret the results obtained. The apparent reaction rates and CO₂ carrying capacities of the materials in the system are in agreement with those found from smaller facilities. The positive experience in the 1.7 MW_{th} La Pereda pilot plant should facilitate the scale up of this new technology and provide the necessary confidence for the demonstration of Ca-looping technology making use of the available expertise in CFB combustion and parallel developments in related oxy-fuel combustion.

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NOMENCLATURE

A_{carb}	m^2	carbonator cross-section
E_{carb}		CO ₂ capture efficiency
$E_{\text{carb eq}}$		Maximum CO ₂ capture efficiency allowed by the equilibrium
E_{sulf}		SO ₂ capture efficiency
f_a		fraction of active particles in the carbonator bed
F_{Ca}	$\text{mol/m}^2\text{s}$	Ca molar flow circulating between reactors
$F_{\text{CO}_2\text{calc}}$	mol/s	molar flow of CO ₂ produced by calcination leaving the calciner
$F_{\text{CO}_2\text{FO}}$	mol/s	molar flow of CO ₂ produced by calcination of fresh limestone
$F_{\text{CO}_2\text{in}}$	$\text{mol/m}^2\text{s}$	molar flow of CO ₂ entering the carbonator
$F_{\text{CO}_2\text{out}}$	$\text{mol/m}^2\text{s}$	molar flow of CO ₂ leaving the carbonator
F_{O}	mol/s	make-up flow of limestone
G_s	$\text{kg/m}^2\text{s}$	solid flow circulation rate from carbonator to calciner
k_s	s^{-1}	constant reaction rate

n_{ca}	mol/m ²	total inventory of Ca in the carbonator bed
$n_{ca, total}$	mol	total inventory of Ca in the experimental facility
$n_{ca, active}$	mol/m ²	active inventory of Ca in the carbonator bed
N_{th}		average number of carbonation calcination cycles of CaO particles in the system
PMs	kg/mol	average molar weight of the solids
t^*	s	time required to increase the carbonate content from X_{calc} to X_{ave}
T_{calc}	°C	average calciner temperature
T_{carb}	°C	average carbonator temperature
u_{gas}	m/s	gas velocity
Ws	kg/m ²	total inventory of solids in the carbonator
X_{ash}		mass ash content of the solids
X_{ave}		average CO ₂ carrying capacity
X_{calc}		molar carbonate content of the solid in the calciner
X_{carb}		molar carbonate content of the solid in the carbonator
X_{ef}		total sorbent utilization
X_{sulf}		molar sulphate sulphate conversion of the solids
ΔP	mbar	pressure drop in the riser
ϕ		gas-solid contacting effectivity factor
v		volume fraction

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