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## Operation of a 25 kWth calcium looping pilot-plant with high oxygen concentrations in the calciner --Manuscript Draft--

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<b>Abstract:</b>	<p>Calcium looping (CaL) is a post-combustion CO<sub>2</sub> capture technology suitable for retrofitting existing power plants. The CaL process uses limestone as a cheap and readily available CO<sub>2</sub> sorbent. While the technology has been widely studied, a few possible options are available that could be applied to make it more economically viable. One of these is to increase the oxygen concentration in the calciner to reduce or eliminate the amount of recycled gas (CO<sub>2</sub>, H<sub>2</sub>O and impurities); therefore, decreasing or removing the energy necessary to heat the recycled gas stream. Moreover, there is a resulting increase in the energy input due to the change in the combustion intensity; this energy is used to enable the endothermic calcination reaction to occur in the absence of recycled flue gases. This paper presents the operation and first results of a CaL pilot plant with 100% oxygen combustion of natural gas in the calciner. The gas coming into the carbonator was a simulated flue gas from a coal-fired power plant or cement industry. Several limestone particle size distributions are also tested to further explore the effect of this parameter on the overall performance of this operating mode. The configuration of the reactor system, the operating procedures, and results are described in detail in this paper. The reactor showed good hydrodynamic stability and stable CO<sub>2</sub> capture with capture efficiencies of up to 70% with a gas mixture simulating the flue gas of a coal-fired power plant.</p>
<b>Author Comments:</b>	The comments present in the manuscript have been addressed, as well as new images have been added and some past images have been improved.
<b>Additional Information:</b>	
<b>Question</b>	<b>Response</b>

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Dear Editor,

Please find attached our manuscript entitled "Operation of a 25 kWth calcium looping pilot-plant with high oxygen concentrations in the calciner", which we would like to submit for publication in Journal of Visualized Experiments as an original research paper.

In this manuscript, the operational protocol to run our 25kWth calcium looping unit, comprising a CFB and a BFB, is described for the burning of fuel in high oxygen concentrations in the calciner. Several experiments are described to show the optimisation process of this protocol to reach the highest capture rate possible. Also, different particle sizes are investigated in our unit to show the effects of this parameter in the overall efficiency.

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. All authors have approved the manuscript and agree with its submission to the Journal of Visualized Experiments.

Yours sincerely,

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**TITLE:**

Operation of a 25 kW<sub>th</sub> Calcium Looping Pilot-plant with High Oxygen Concentrations in the Calcliner

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**KEYWORDS:**

Calcium looping, pilot plant experiments, CO<sub>2</sub> capture, operational procedure, oxy-fuel calcination, capture efficiency.

**SHORT ABSTRACT:**

This manuscript describes a procedure for operating a calcium looping pilot-plant for post-combustion carbon capture with high oxygen concentrations in the calciner in order to reduce or eliminate the flue gas recycle.

**LONG ABSTRACT:**

Calcium looping (CaL) is a post-combustion CO<sub>2</sub> capture technology that is suitable for retrofitting existing power plants. The CaL process uses limestone as a cheap and readily available CO<sub>2</sub> sorbent. While the technology has been widely studied, there are a few available options that could be applied to make it more economically viable. One of these is to increase the oxygen concentration in the calciner to reduce or eliminate the amount of recycled gas (CO<sub>2</sub>, H<sub>2</sub>O and impurities); therefore, decreasing or removing the energy necessary to heat the recycled gas stream. Moreover, there is a resulting increase in the energy input due to the change in the combustion intensity; this energy is used to enable the endothermic calcination reaction to occur in the absence of recycled flue gases. This paper presents the operation and first results of a CaL pilot plant with 100% oxygen combustion of natural gas in the calciner. The gas coming into the carbonator was a simulated flue gas from a coal-fired power plant or cement industry. Several limestone particle size distributions are also tested to further explore the effect of this parameter on the overall performance of this operating mode. The configuration of the reactor system, the operating procedures, and the results are described in detail in this paper. The reactor

showed good hydrodynamic stability and stable CO<sub>2</sub> capture, with capture efficiencies of up to 70% with a gas mixture simulating the flue gas of a coal-fired power plant.

## INTRODUCTION:

CO<sub>2</sub> emissions and the resulting global warming are critical environmental issues that have attracted a large amount of research in the past years. Carbon capture and storage (CCS) has been acknowledged as a potential technology for reducing CO<sub>2</sub> emissions to the atmosphere<sup>1,2</sup>. The most challenging part of the CCS chain is the capture of CO<sub>2</sub>, which is also the most costly stage<sup>3</sup>. In consequence, there has been a focus on developing new technologies for CO<sub>2</sub> capture from power plants and other industrial facilities.

CaL as a post-combustion CO<sub>2</sub> capture technology, was first proposed by Shimizu *et al.*<sup>4</sup> CO<sub>2</sub> is captured by a CaO-based sorbent at 600–700 °C in a reactor called a carbonator, and released by subsequent calcination at 850–950 °C (in a calciner) according to **Eq. (1)**, to produce a high-purity CO<sub>2</sub> stream suitable for sequestration<sup>5,6</sup>. The CaL cycle utilises fluidized beds, which represent an optimal configuration for this process, since they allow for large amounts of solids to be circulated easily from one reactor to the other<sup>4,7,8</sup>.



This concept has been demonstrated at pilot scale by various groups and with different configurations and scales, such as the 0.2 MW<sub>th</sub> pilot in Stuttgart, the 1 MW<sub>th</sub> pilot in Darmstadt, the 1.7 MW<sub>th</sub> pilot in La Pereda and the 1.9 MW<sub>th</sub> unit in Taiwan<sup>9-16</sup>. Although this process has been proven, there are still possibilities for increasing its thermal efficiency, such as by modifying the standard operating conditions and changes in the design of the reactor configuration.

The use of heat pipes between the combustion and calciner has been studied instead of oxy-combusting fuel in the calciner: The results for the CO<sub>2</sub> capture performance are comparable with those of a conventional CaL pilot-plant, however, this process has higher plant efficiencies and lower CO<sub>2</sub> avoidance costs<sup>17</sup>. Martínez *et al.*<sup>18</sup> investigated the heat integration possibilities in order to preheat the solid material entering the calciner and to reduce the heat needed in the calciner. The results showed 9% reduction in the coal consumption when compared with that of the standard case. Other studied possibilities for heat integration have also considered internal and external integration options<sup>19</sup>.

One of the main problems of the CaL cycle from the economic point of view is to supply the energy needed in the calciner by means of fuel combustion<sup>20</sup>. Increasing the oxygen concentration in the calciner's inlet is proposed in order to reduce or even avoid the need of CO<sub>2</sub> recycle to the calciner. This alternative reduces the capital costs (reduced size of calciner and air separation units (ASU)), which can significantly improve the competitiveness of this process. The drastic change in the combustion conditions can be attained by exploiting the endothermic calcination reaction and the large CaO/CaCO<sub>3</sub> flow circulating

from the carbonator operating at lower temperatures (neither advantage is available with the oxy-combustion technology).

This work aims to develop a standard operating procedure for running a CaL pilot plant with a Circulating Fluidized Bed (CFB) carbonator and a Bubbling Fluidized Bed (BFB) calciner with 100% O<sub>2</sub> concentration in the calciner's inlet. Several experimental campaigns have been run during the commissioning of the pilot plant to ensure proper operation as the oxygen concentration increased. Also, three limestone particle size distributions (100–200 µm; 200–300 µm; 300–400 µm) were studied to investigate how this parameter affects the elutriation of particles and capture efficiency in this operating mode.

## **PROTOCOL:**

### **1. Material Preparation**

1.1. Sieve the limestone (~ 50 kg of raw material) to the desired particle size distribution (300–400 µm or another distribution depending on the experiment) using a mechanical shaker. Put the sieved material in pots next to the calciner for feeding during the test.

1.2. Prepare the material in batches to be introduced into the reactor. The batches are generally 0.5 L or 1 L (1 L of limestone is roughly 1.5 kg), but this can vary depending on the operating parameters.

### **2. Start-up Procedure**

CAUTION: Extremely high temperatures are used here. Suitable PPE such as gloves, eye glasses, laboratory coat and safety shoes are required.

#### **2.1. Heat-up of Reactors**

2.1.1. Start the low flow of N<sub>2</sub> in the carbonator (60 L/min) and calciner (20 L/min) as well as the loop-seals (10 L/min) in the rotameters.

2.1.2. Turn on the carbonator transformers manually. Set the temperature of all electrical preheaters of the carbonator at 600 °C.

2.1.3. Start acquiring data (for gas temperatures and pressures, use the recording button in the software). The data include temperatures, pressures and gas composition of both reactors. In **Figures 1 and 2**, screenshots of the data acquisition system are shown.

[Insert Figure 1 and 2 here]

2.1.4. Turn on the calciner gas preheaters. Turn on the heater around the calciner to 600 °C measured inside the BFB via a thermocouple.

Note: Data such as temperature, pressures and gas composition are already being acquired as stated in step 2.1.3.

2.1.5. Put 3 L of the sieved limestone into the BFB in the calciner. First open the top valve, introduce the material in the down-pipe and close the top valve, then open the bottom valve so that the material flows into the reactor.

2.1.6. Heat the material in the BFB to above 650 °C (by the electrical heater around the calciner).

Note: This usually takes ~ 1 h, during this time check the data acquisition and the pressures in the fluidized beds.

[Insert Figure 3 here]

## 2.2. Start combustion in calciner

2.2.1. Increase the oxygen concentration in the calciner from 0 to 40% vol, making sure that the concentration is stable before starting the combustion.

2.2.2. Start the stoichiometric flow of natural gas manually using a rotameter making sure that the combustion is stable.

Note: The natural gas flow should be increased carefully. Check that the data show an appropriate level of combustion reaction.

2.2.3. Increase the oxygen concentration in the calciner in 20% vol increments by adjusting the natural gas flow rotameter to ensure stoichiometric combustion.

Note: This process should be performed with extreme care. If any suspicion arises that the combustion is not occurring as expected from the preliminary calculations then stop the flow of natural gas and switch the oxygen flow to nitrogen for safe operation. Identify the source of this discrepancy. The overall duration of this process is about 1 h.

2.2.4. Achieve 100% oxygen concentration natural gas combustion.

Note: The temperature and gas composition data should be carefully followed throughout all the testing, but especially when the combustion is taking place in 100% oxygen.

2.2.5. Add limestone in 0.5 L increments until there is 7 L in the fluidized bed. Calcine all the material in the fluidized bed of the calciner (the estimated calcination temperature is 800–850 °C for the batch present in the calciner and the calciner temperature for the following batches).

2.2.6. Increase the flow of N<sub>2</sub> in the carbonator to start the circulation. Check the circulation view port regularly to ensure proper circulation.

2.2.7. Calcine all the available limestone circulating in the rig before starting the CO<sub>2</sub> capture.

### 3. Stable Operation

3.1. Manually switch the carbonation gas from N<sub>2</sub> to 15% vol CO<sub>2</sub> using the rotameter, which allows the calcined limestone to begin capturing CO<sub>2</sub>.

3.2. Adjust the flows in the calciner manually using the rotameters to achieve a stable 930–950 °C temperature in the calciner by regulating the flow of natural gas (NG) and oxygen (within the optimal fluidization regime). The O<sub>2</sub> flow is usually 100% with enough bed material, but it is adjusted throughout the experiment.

3.3. When the material starts to decline in activity (above 5% CO<sub>2</sub> concentration at the exit of the carbonator, which is acquired continuously by the software as described in step 2.1.3), add more limestone.

### 4. Shut-down Procedure

4.1. Manually turn off the natural gas flow using the rotameter and decrease the oxygen flow, and switch the gases in both reactors to N<sub>2</sub>. Turn off all the heaters (calciner and carbonator).

4.2. Allow the temperature of the inventory of the rig to decrease (normally overnight), and empty the reactors when they are at room temperature.

4.3. Weigh the extracted solids and perform a standard sieve analysis. Characterize the material: porosimetry, composition (X-ray fluorescence spectrometry, XRF)<sup>21,22</sup> and microscopic structure (scanning electron microscopy, SEM).

### REPRESENTATIVE RESULTS:

The experimental set-up is shown in **Figure 3**. The plant comprises two interconnected fluidized-beds. Namely, the carbonator is a CFB with 4.3 m height and 0.1 m internal diameter (ID); while the calciner is a BFB with 1.2 m height and 0.165 m ID. The solid transport from one reactor to the other is controlled by two loop-seals fluidized with nitrogen. Both reactors are fed a mixture of gas through a preheating line, and both are electrically heated; moreover, the calciner is fed with natural gas in order to produce by combustion the heat needed for the endothermic calcination and to heat the circulating sorbent. The carbonator distributor plate has 8 nozzles, each of them with twenty 2 mm holes, while the calciner has 20 nozzles with six 1 mm holes each.

The results from three different experiments are discussed in this section. These tests provide an overview of the process of running the pilot plant from air (~ 20% vol O<sub>2</sub>) to 100% vol O<sub>2</sub> at the calciner inlet. This work also explores the results of using different particle size distributions in this operational mode to see if this parameter has an impact on



the overall performance of the system. The limestone used in this study has a minimum content of 98.25% CaCO<sub>3</sub>.

**Experiment 1:** Flue gas (15% vol CO<sub>2</sub>) with limestone (200–300 µm) 30% vol O<sub>2</sub>

This first test with the limestone fraction 200–300 µm was performed to test the rig with limestone circulating between the two reactors within the rig as a starting point for performance optimization. During this test, a capture efficiency of 45% was achieved (**Figure 4**). This capture efficiency,  $E_{carb}$ , was calculated using the following formula<sup>23</sup>:

$$E_{carb} = \frac{F_{CO_2} - F_{carb}}{F_{CO_2}} \quad (2)$$

Where  $F_{CO_2}$  is the molar flow rate of CO<sub>2</sub> entering the carbonator and  $F_{carb}$  is the molar flow rate of CO<sub>2</sub> leaving the carbonator.

[insert figure 4 here]

The inferior capture efficiency during this experimental run was caused mainly by the insufficient supply of heat to calcine all the limestone residing in the BFB. This caused a decrease of the CaO/CaCO<sub>3</sub> ratio in the carbonator feed. Another probable reason was the deactivation and carry-over of the lime particles from the calciner, which reduced the total bed inventory and the amount of sorbent present in the system. After the experiment, a material balance of the inventory of the reactor was performed (**Table 1**). A shift towards smaller fractions can be observed, because of the attrition of the material in both fluidized beds.

[insert table 1 here]

**Experiment 2:** Flue gas (15% CO<sub>2</sub>) with limestone (100–200 µm) 100% O<sub>2</sub>

In this test, the main aim was to use of smaller limestone particles in order to investigate their possible beneficial effect on the system performance. The secondary aim was to provide more heat to the calcination process in the BFB calciner by combusting the natural gas in highly concentrated oxygen, ideally up to 100% at the inlet.

In this experiment, we successfully tested the possibility of using pure O<sub>2</sub> at the inlet of the calciner, which offers the possibility of completely eliminating the recycle of off-gas needed for a standard oxy-fuel process. This is made possible by the heat consumption in the form of a circulating fluidized bed material and the continuous calcination reaction.

The use of smaller particles did not have a beneficial effect on the carbonation process, most likely because of the higher contact area between particles and the gas. However, there is some controversy in this matter as smaller particles have shown decreased reactivity due to higher content of impurities<sup>24</sup>. Almost all the added limestone that was < 150 µm was very quickly elutriated from the calciner to the downstream cyclone. Therefore,

it was very difficult to maintain the necessary inventory of lime in the rig needed to achieve higher capture efficiency. The results of the capture efficiency are in **Figure 5**.

[insert figure 5 here]

The balance of the inputs and outputs of the solids was performed after the test (**Table 2**), and it was discovered that most of the material introduced into the rig during the experiment ended up in the calciner cyclone. This was probably the main cause of the low measured capture efficiency during this test.

[insert Table 2 here]

To conclude, we successfully tested the use of pure O<sub>2</sub> at the inlet of the calciner in order to completely eliminate the recycle of the off-gas needed for a standard oxy-fuel process. This is possible due to the heat sink provided in the form of circulating fluidized bed material and the continuous calcination reaction. However, the small particle size distribution (100–200 µm) was not beneficial for the capture process, due to the elutriation of the particles. It was extremely difficult to maintain the bed inventory needed to obtain a higher capture efficiency. Therefore, we decided to investigate the use of bigger particles in the next experimental campaign.

### **Experiment 3: Flue gas (15% CO<sub>2</sub>) with limestone (300–400 µm) 100% O<sub>2</sub>**

During this trial, the performance of the fraction 300–400 µm was tested so as to reduce the high material losses from the fluidized bed of the calciner as seen in previous runs. This was expected to enable retention of the necessary lime/limestone inventory needed for its efficient circulation and carbon capture. Due to use of an appropriate amount of sorbent circulating in the rig and sufficient heat provided by the combustion of natural gas in pure oxygen (releasing 18 kW), a stable capture efficiency of ~ 70% was achieved for more than 3 h; this is a very good result when considering the relatively short carbonator reactor tube and the consequent short contact time between the sorbent and CO<sub>2</sub>. The concentration of CO<sub>2</sub> at the outlet of the carbonator was maintained below 5% vol, and fresh limestone (in 0.5 L batches) was added to the calciner when the concentration of CO<sub>2</sub> at the outlet of the carbonator exceeded this value. A stable experimental run was achieved with optimized conditions.

The process started with the standard procedure; *i.e.*, first the reactor was heated up to 700 °C, then 2.9 L of limestone was added into the calciner and heated up. The temperatures and gas concentrations in the calciner are shown in **Figure 6**. Note that the numbers below correspond to those steps in **Figure 6**. 1) The air flow was replaced by a flow mixture of 40% O<sub>2</sub> and 60% N<sub>2</sub> and the combustion of natural gas in the fluidized bed was initiated (9.1 kW). The limestone in the fluidized bed was heated above 800 °C and 3 more batches of limestone (1 L) were added to the calciner. 2) While the limestone was calcining in the fluidized bed, the circulation of the lime/limestone was started by flowing preheated N<sub>2</sub> through the carbonator (at a velocity of 2.5 m/s at 650 °C). An additional 0.9 L limestone

was added and a fresh O<sub>2</sub> cylinder was connected to the inlet of the calciner. 4) After reconnecting the oxygen, the combustion was initiated again, this time in an inlet O<sub>2</sub> concentration of 70% (and 30% N<sub>2</sub>), which led to a consumption of 14 kW of natural gas to reach an O<sub>2</sub> concentration at the outlet of ~ 5% (in wet gas). 5) Pure O<sub>2</sub> was introduced at the calciner inlet, which led to the heat release of 18 kW into the calciner, and the carbonation was initiated in the carbonator by injecting 15% of CO<sub>2</sub>. The efficiency of the carbonation (**Figure 7**) was the highest yet on this reactor design (~ 70%). 7) The gas velocity flowing through the BFB of the calciner had to be lowered to 0.30 m/s (required by the desired temperature) to maintain the temperature of about 930 °C generated by the combustion of natural gas in pure O<sub>2</sub> (while maintaining the O<sub>2</sub> concentration in the off-gas to an industrially acceptable level below 5% vol).

[insert figure 6 here]

The temperature in the fluidized bed was maintained constant during the test by regulating the flow rate of natural gas and consecutively adjusting the flow rate of O<sub>2</sub> to achieve a calciner velocity of ~ 0.30 m/s. During the constant operation, the following energetic balance was observed: In the calciner, the oxygen was preheated to only 300 °C for safety reasons; hence, providing 0.5 kW in latent heat. Around 15.5 kW was released by the combustion of natural gas in the fluidized bed, but only 5.3 kW was needed for a continuous calcination (when no fresh material was added), 3.6 kW to cover the latent heat of the off-gas and ~ 7 kW for heating the circulating adsorbent and to cover the heat losses. In the carbonator, 3.2 kW was provided by preheating the gas (to 350 °C), and 5.4 kW was released by the carbonation process. Almost 5 kW was carried out of the carbonator as latent heat of the off-gas and 3.6 kW needed to be dissipated by heat losses to cover the heat released by the exothermic reaction while maintaining the temperature at 650 °C. When the carbonation process starts (and is effective), the temperature in the carbonator approaches 700 °C, which shifts the attainable thermodynamic equilibrium concentration of the outlet gas to higher values. This theoretical minimum concentration, dependent on the carbonator temperature, is depicted alongside the concentration measured during testing in **Figure 7**.

The carbonation process was initiated with ~ 6.7 L of limestone present in the rig. An additional 0.54 L at the beginning of the carbonation (13:45 in **Figure 7**) resulted in the decrease of residual CO<sub>2</sub> in the gas below 5% vol, and this level was maintained throughout the test by additions of 0.5 L limestone batches (when the concentration of CO<sub>2</sub> at the exit of carbonator exceeded 5%). The time intervals between the additions of fresh limestone to the calciner were 15, 20, 50, 45 and 50 min. Therefore, we concluded that a stable operation requires the addition of fresh sorbent corresponding to 0.5 L (750 g) of limestone approximately every 50 min, which is equivalent to a make-up ratio ( $F_0/F_{CO_2}$ ) of 6%, as described elsewhere<sup>25</sup>. The make-up ratio in these experiments was mainly influenced by the limestone (reactivity decay and elutriation). The value of this parameter was chosen based on the CO<sub>2</sub> concentration at the carbonator outlet, *i.e.*, adding more limestone when it reached a 5% vol CO<sub>2</sub>.

Based on the sieving analysis, we conclude that the original limestone fraction was retained mostly in the rig circulation, while particles mostly < 250  $\mu\text{m}$  were carried over to the calciner cyclone. These particles resulted predominantly from the breakage/attrition of larger particles.

#### **FIGURE AND TABLE LEGENDS:**

**Table 1:** Weight balance of the material inputs and outputs for 200–300  $\mu\text{m}$  limestone with 30%  $\text{O}_2$ .

**Table 2:** Balance of recovered material and its sieve analysis for 100–200  $\mu\text{m}$  limestone with 100%  $\text{O}_2$ .

**Table 3:** Mass balance of solids and sieve analysis of the inputs (limestone) and outputs (other) for 300–400  $\mu\text{m}$  limestone with 100%  $\text{O}_2$ .

**Table 4:** Molar balance estimate (10% humidity of the raw limestone, 75% wt of the output in calcined state) for 300–400  $\mu\text{m}$  limestone with 100%  $\text{O}_2$ .

**Figure 1:** Screenshot of temperature and pressure data acquisition for both reactors.

**Figure 2:** Screenshot of temperature data acquisition for the preheating system.

**Figure 3:** Schematic of the 25  $\text{kW}_{\text{th}}$  CaL (CFB carbonator and BFB calciner). 1: carbonator; 2: calciner; 3: lower loop-seal; 4: upper loop-seal; 5: carbonator cyclone; 6: calciner cyclone.

**Figure. 4:** Concentration of  $\text{CO}_2$  at the carbonator inlet and outlet and the capture efficiency ( $E_{\text{carb}}$ ) for 200–300  $\mu\text{m}$  limestone with 30%  $\text{O}_2$ .

**Figure 5:**  $\text{CO}_2$  concentration at the carbonator inlet and outlet and the corresponding capture efficiency ( $E_{\text{carb}}$ ) for 100–200  $\mu\text{m}$  limestone with 100%  $\text{O}_2$ .

**Figure 6:** Temperature of the BFB of the calciner and the temperature and composition of the off-gas at its exit.

**Figure 7:**  $\text{CO}_2$  concentration at the carbonator inlet and outlet and the corresponding capture efficiency ( $E_{\text{carb}}$ ) for 300–400  $\mu\text{m}$  limestone with 100%  $\text{O}_2$ . The mass and molar balances of the inputs and outputs of solids from the rig are given in **Table 3** and **Table 4**.

#### **DISCUSSION:**

The operation of the calciner with an inlet of 100% vol oxygen is achievable, based on exploiting the endothermic nature of the calcination reaction, as well as the fact that the solids circulate between the two reactors at different temperatures. This operating mode aims to make the CaL process more economically promising by reducing capital and operating costs. As the recycle of flue gas (mainly  $\text{CO}_2$ , water vapor and unreacted  $\text{O}_2$ ) is

reduced or even eliminated, the heat consumed to preheat this stream is lower. Therefore, less oxygen is needed and a smaller ASU would be required. As the gas flow would be lower in this configuration, the size of the calciner would be smaller for the same fluidization velocity.

A standard methodology was developed to ensure the safe operation of the high-oxygen concentration in the calciner. The results showed a capture efficiency of up to 70% in some of the performed experiments. Also, different particle size distributions were used in this reactor configuration (carbonator as a CFB; calciner as a BFB). The distributions were: 100–200  $\mu\text{m}$ ; 200–300  $\mu\text{m}$ ; 300–400  $\mu\text{m}$ . For the smallest distribution (100–200  $\mu\text{m}$ ), however, there were elutriation issues and the majority of the bed inventory was found in the calciner's cyclone catch-pot. The best results were achieved with the largest particle size distribution (300–400  $\mu\text{m}$ ): an  $E_{\text{carb}}$  of  $\sim 70\%$  was maintained throughout the experiment with a make-up ratio of about 6%.

This protocol was improved by minimizing the electrical heating provided to the gas and calciner when the natural gas is being combusted, in order to protect the tubes from electrical discharges caused by the heating elements. Also, it has been noted that the  $\text{O}_2$  concentration increase can be achieved more rapidly than in initial experimental campaigns, from 20% vol to 60% vol and 100% vol. It is important to highlight that the most critical steps in this process are the start of the combustion and the increase of the oxygen concentration, which can cause increased temperatures that will turn off the natural gas source if the temperature goes higher than 980  $^{\circ}\text{C}$ . Also, the material make-up is a concern as it can lower the temperature of the reactor and stop the combustion process, and therefore, it should be added in small batches.

With this methodology applied to this experimental rig, it is possible to test new synthetic materials, as well as materials improved via doping, thermal pre-treatment, chemical pre-treatment, *etc.*<sup>26</sup> This protocol allows these new sorbents to be tested under realistic conditions providing a standard methodology for sorbent comparison. However, there are some challenges when applying this concept at larger scale, such as the use of coal in the calciner under these operating conditions. The use of solid fuels would increase the difficulty in calciner operation due to the high temperatures, which can lead to ash agglomeration and eventually defluidizing phenomena<sup>27</sup>. This needs further study in order to determine the feasibility of this protocol; however, the concept was proved successful at pilot-scale in this work using natural gas.

Another limitation arising from this study is the duration of the tests, with  $\sim 3$  h of steady state operation per test; this is due to the heating process of the plant, which is a slow process. The average number of carbonation/calcination cycles experienced by a particle when circulating between reactors is not known. It is possible that the high oxygen concentration had a negative effect causing more sintering in the limestone particles. Further investigation of these challenges would help to assess the suitability of the protocol as a novel and feasible operating mode for CaL plants at a higher scale.

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## DISCLOSURES:

The authors have nothing to disclose.

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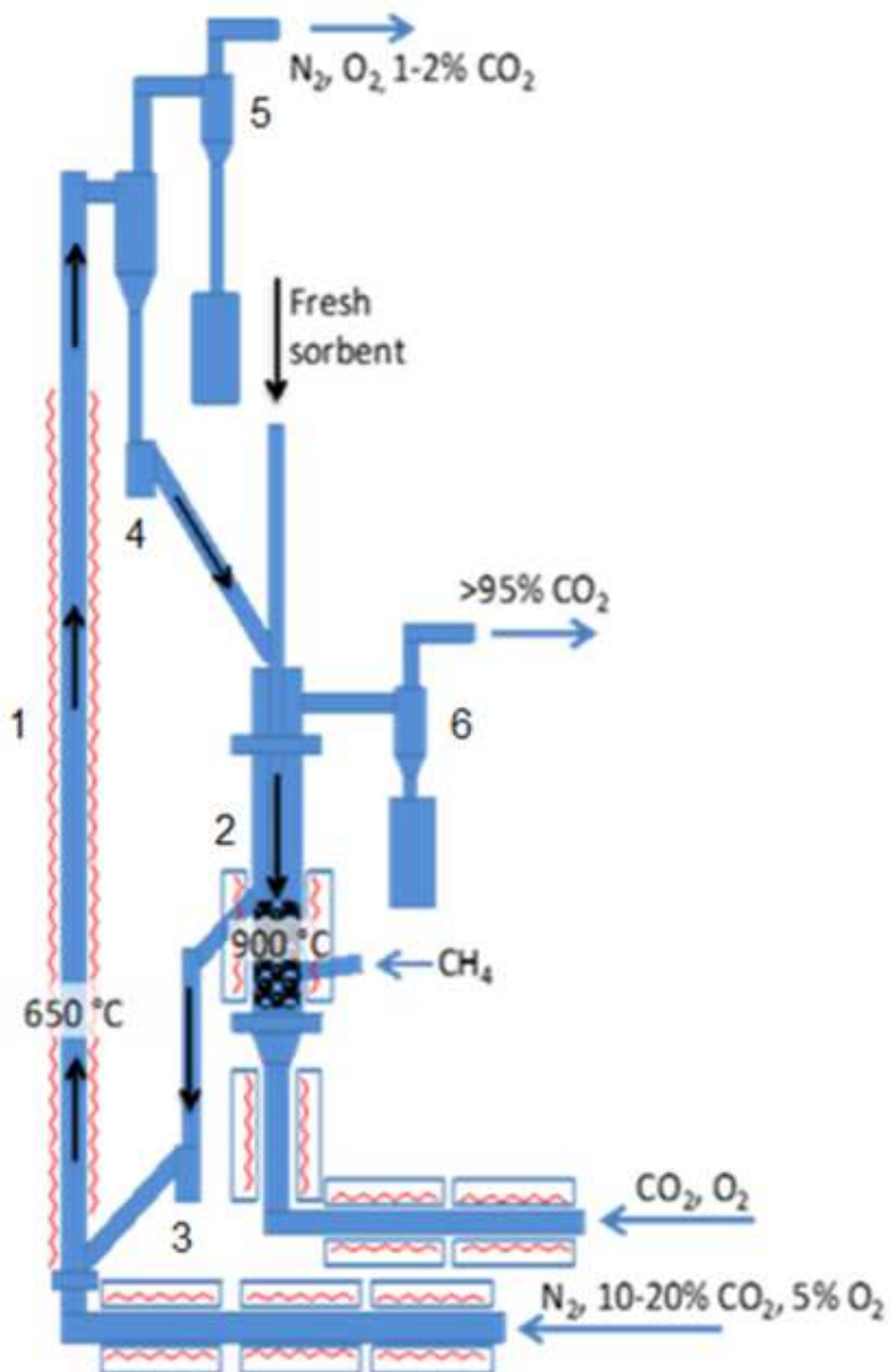
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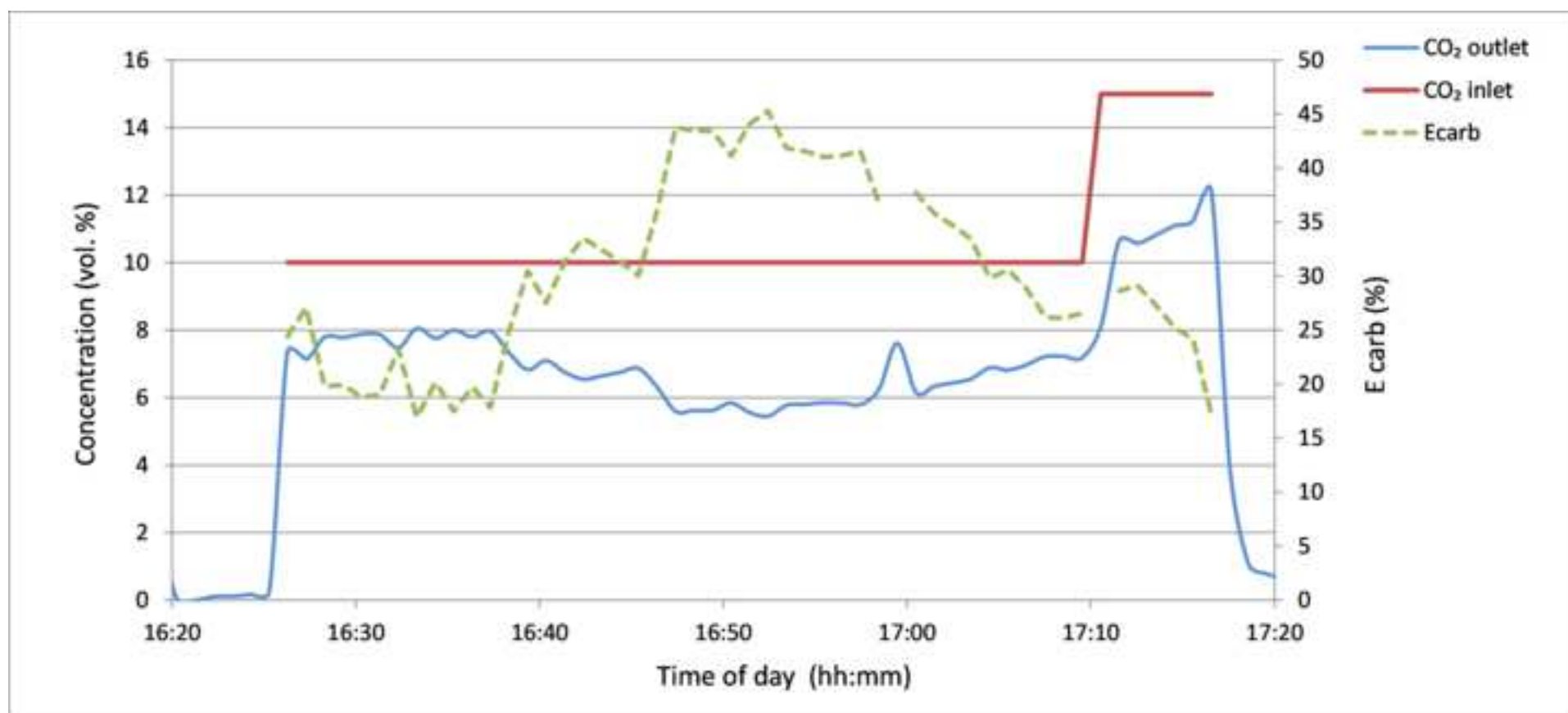
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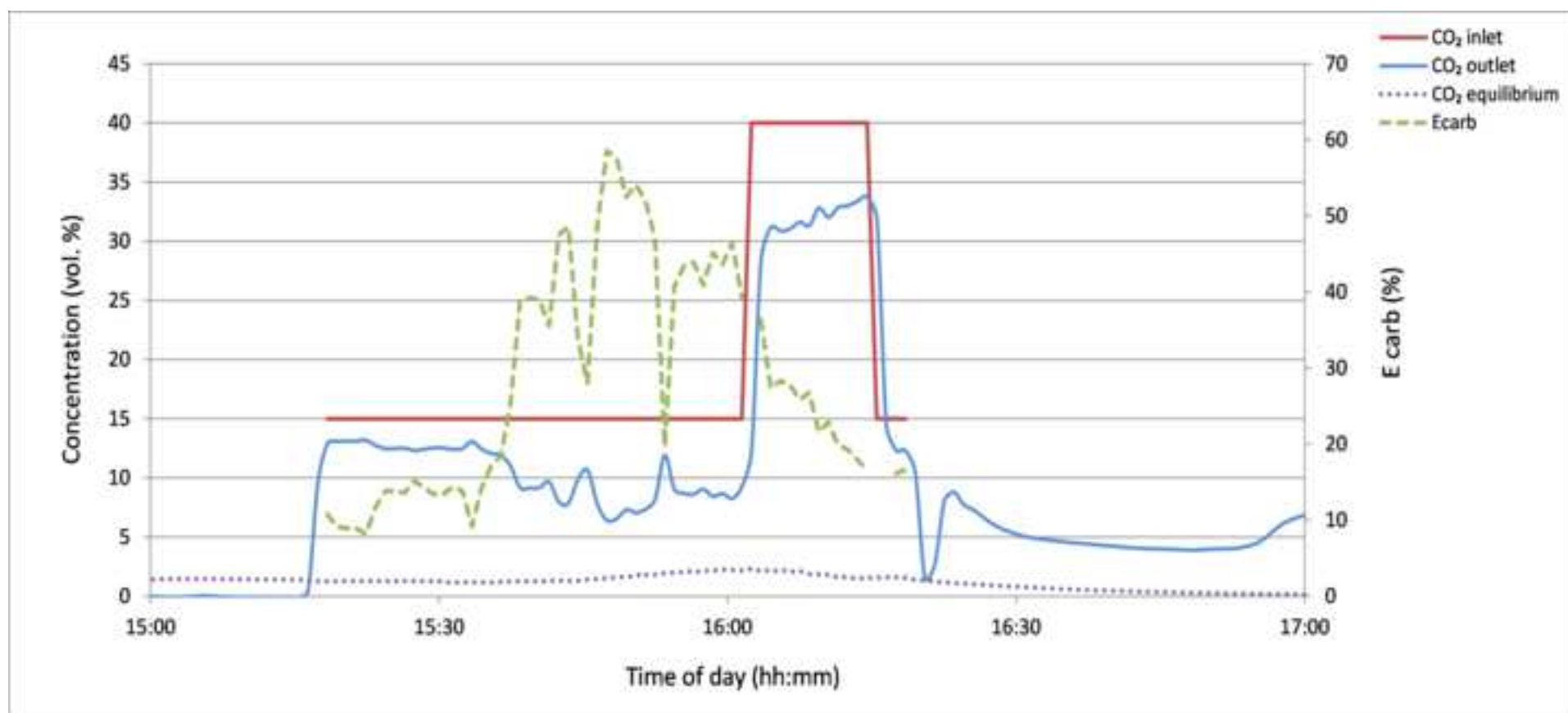


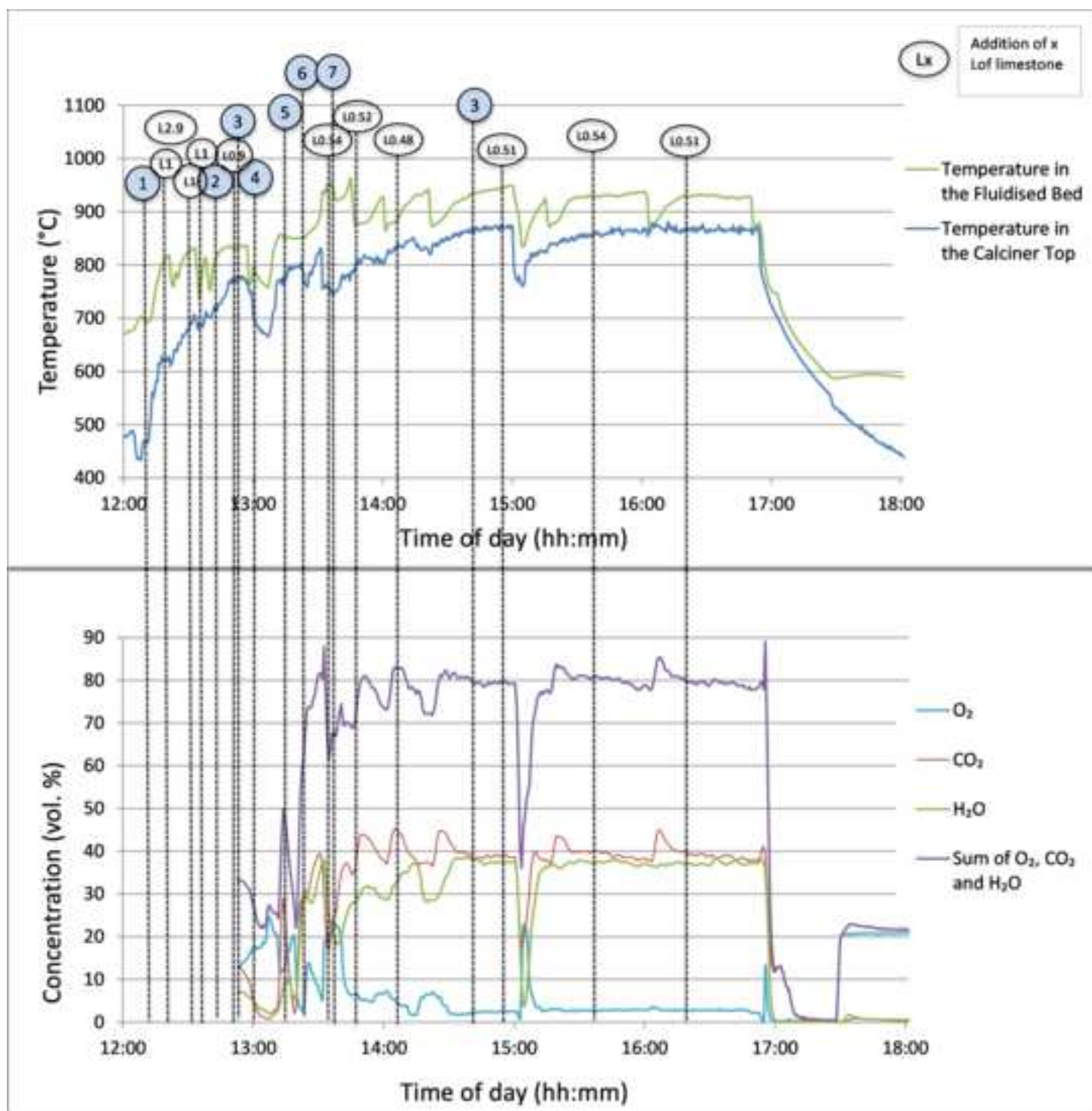




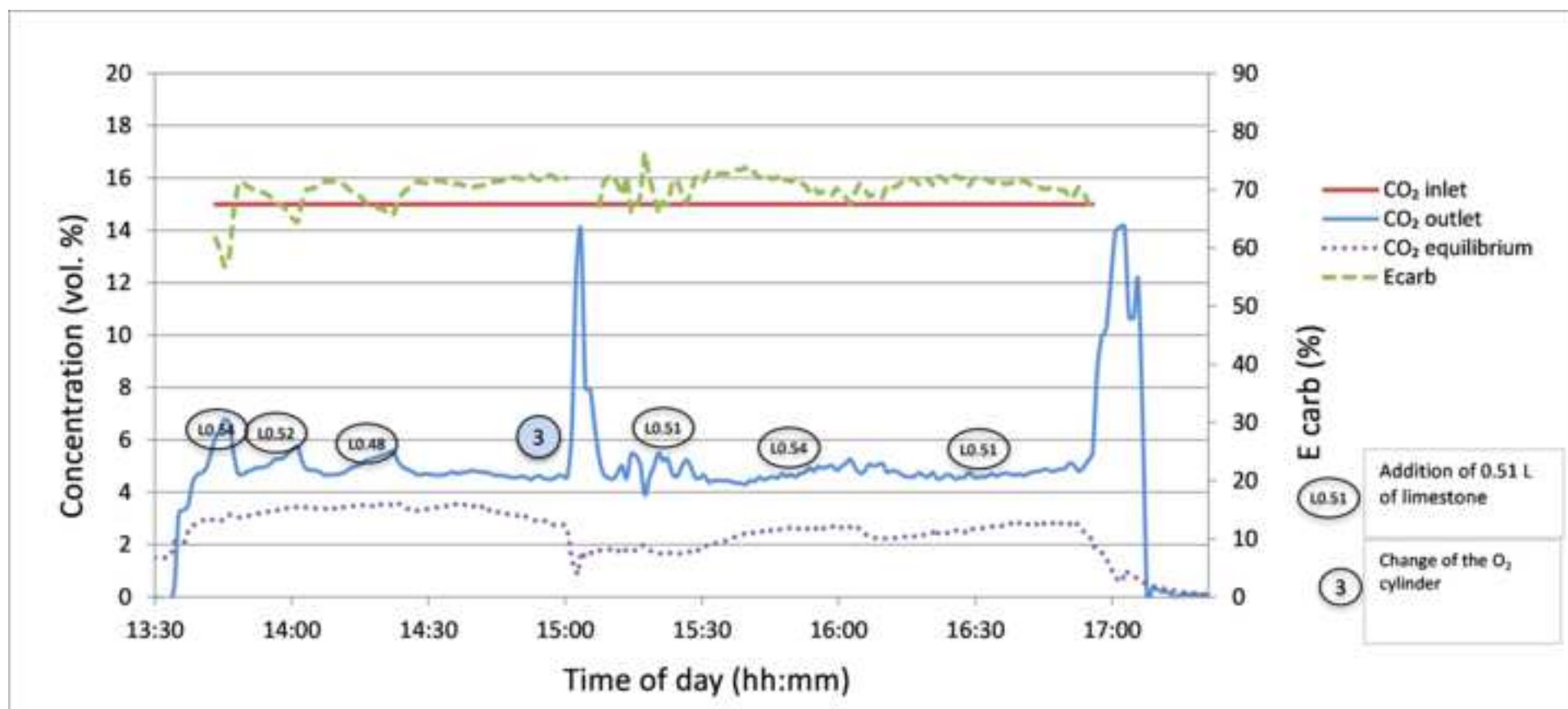












Fraction	Limestone in	Calciner+Carbonat or	Cyclone Calciner	Cyclone Carbonator
Total mass (g)	9100	5000	500	20
250-300 µm	22%	24%	2%	0%
212-250 µm	47%	41%	6%	18%
150-212 µm	28%	34%	24%	18%
0-150 µm	3%	1%	69%	65%



Fraction	Limestone	Carbonator	Calciner	Cyclone calciner
Total mass (g)	19000	1200	2700	8700
>212-212 µm	0%	21%	2%	0%
212-150 µm	18%	39%	73%	5%
150-125 µm	40%	22%	13%	32%
125-63 µm	41%	18%	12%	60%
0-63 µm	2%	0%	0%	3%

Cyclone carbonator
360
39%
42%
10%
9%
1%

Fraction	Limestone in	Carbonator	Calciner	Cyclone calciner	Cyclone Carbonator
Total mass (g)	14000	1900	4200	2000	120
>355 µm	21%	16%	4%	0%	0%
300-350 µm	43%	45%	38%	1%	1%
250-300 µm	33%	26%	48%	3%	0%
212-250 µm	2%	4%	9%	7%	1%
150-212 µm	0%	3%	1%	35%	14%
63-150 µm	0%	5%	0%	41%	46%
0-63 µm	0%	0%	0%	12%	38%

Fraction	Limestone in	Carbonator	Calciner	Cyclone calciner	Cyclone Carbonator
Total mol	130	31	66	32	2
>355 µm	27	5	2	0	0
300-350 µm	56	14	25	0	0
250-300 µm	4	8	32	1	0
212-250 µm	2	1	6	2	0
150-212 µm	0	1	1	11	0
63-150 µm	0	2	0	13	1
0-63 µm	1	0	0	4	1

Difference (out – in)
0
-20
-17
-2.6
6.9
13
16
4.1

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Longcal limestone	Loncliffe	Longcal SP52	n/a
Mechanical Shacker	SWECO	LS24S544+C	Mechanical siever to separate particles
Oxygen	BOC	n/a	BOC cylinders
Nitrogen	BOC	n/a	BOC tank
Carbon dioxide	BOC	n/a	BOC tank
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The introduction has been modified accordingly in the revised manuscript. Adding the following text:

"The use of heat pipes between the combustion and calciner has been studied instead of oxy-combusting fuel in the calciner, the results for the CO<sub>2</sub> capture performance were comparable with those of a conventional CaL pilot-plant, however, this process has higher plant efficiencies and lower CO<sub>2</sub> avoidance costs<sup>17</sup>. Martínez et al.<sup>18</sup> investigated the heat integration possibilities in order to preheat the solid material entering the calciner and to reduce the heat needed in the calciner. The results showed 9% reduction in the coal consumption when compared with that of the standard case. Other possibilities for heat integration are also studied considering internal and external integration options<sup>19</sup>. One of the main problems of the CaL cycle from the economic point of view is to supply the energy needed in the calciner by means of fuel combustion<sup>20</sup>."

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1) Line 66 – how much limestone is sieved? 1L, 2 Kg, etc. Please use a specific example to describe the entire protocol section. For example, write the entire protocol for experiment 1, "Flue gas (15% vol. CO<sub>2</sub>) with Longcliffe limestone (200–300 µm) 30% vol O<sub>2</sub>" while showing results from all 3 experiments in the representative results.

This has been changed to:

"1.1. Sieve the limestone (around 50 kg of raw material) to the desired particle size distribution (300-400 µm or some other choice depending on the experiment) using a mechanical shaker. Put the sieved material in pots next to the calciner for feeding during the test."

2) Line 67 – what is desired material? Please use a specific example

This meant the sieved material in the previous sentence. This has been clarified.

"Put the sieved material in pots next to the calciner for feeding during the test."

3) Line 71 – add a "caution: extremely high temperatures. Use suitable PPE such as gloves, masks, eye glasses"

This has been added to line 71.

"2. Start-up procedure (caution extremely high temperatures. Use suitable PPE such as gloves, eye glasses, and laboratory coat and safety shoes)"

4) Line 76 – is the data acquisition done using a software? If yes, please mention what button is clicked on in the software to do this, or which menu items need to be selected. This is done by software. It has been modified in the text accordingly.

"2.1.3. Start acquiring data (for gas temperatures and pressure using the recording button in the software), these data include temperatures, pressures and gas composition of both reactors."

5) Line 81 – step 2.1.5 - which material? Please provide details

This refers to the sieved limestone mentioned throughout the protocol. This has been changed to:

"2.1.5. Put 3 L of the sieved limestone material into BFB the calciner. Note: first open the top valve, introduce the material in the down-pipe and close the top valve, after that, open the bottom valve so that the material flows into the reactor."

6) Line 112 – please replace "find an optimal heat balance.....". use a specific example This has been modified to clarify with the usual example. However, this is adjusted throughout the experiment depending on temperature, pressures, bed material etc.

"3.2. Adjust the flows in the calciner to achieve a stable 930–950 °C temperature in the calciner by regulating the flow of natural gas (NG) and oxygen (within optimal fluidization regime), usually it is 100% O<sub>2</sub> with enough bed material, but it is adjusted throughout the experiment"

7) Line 114 – do you keep monitoring the CO<sub>2</sub> concentration in the carbonator exhaust? How frequently? What do you use to monitor CO<sub>2</sub>?

This is acquired every second using the software mentioned in 2.1.3. This has been modified to:

"3.3. When the material starts to decline in activity (above 5% CO<sub>2</sub> concentration at the exit of the carbonator, this is acquired every second in step 2.1.3), add more limestone."

8) Line 122 – please cite references for each of these.

Two standards have been cited for XR Spectrometry and XRF for lime-based materials.

[21] ASTM C1271-99(2012), Standard Test Method for X-ray Spectrometric Analysis of Lime and Limestone, ASTM International, West Conshohocken, PA, 2012, [www.astm.org](http://www.astm.org)

[22] ASTM C25-11e2, Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime, ASTM International, West Conshohocken, PA, 2011, [www.astm.org](http://www.astm.org)

- Representative Results:

1) Line 134 – what is that (2)?

This is the equation number.

- Figure legends:

1) Figure 5, Table 3, table 4 – Please expand the legends to adequately describe the figures/tables. Each figure or table must have an accompanying legend including a short title, followed by a short description of each panel and/or a general description.

This has been modified accordingly:

"Figure 5: CO<sub>2</sub> concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (Ecarb) for 300–400 µm limestone with 100% O<sub>2</sub>"

"Table 3: Mass balance of solids and sieve analysis of the inputs (limestone) and outputs (other) for 300–400 µm limestone with 100% O<sub>2</sub>"

"Table 4: Molar balance estimate (10% humidity of the raw limestone, 75% wt. of the output in calcined state) for 300–400 µm limestone with 100% O<sub>2</sub>"

Also for Figure 2 and 3 Table 1 and 2, the titles have been modified:

"Fig. 2: Concentration of CO<sub>2</sub> at inlet and at outlet of the carbonator and capture efficiency (Ecarb) for 200–300 µm limestone with 30% O<sub>2</sub>"

"Figure 3: CO<sub>2</sub> concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (Ecarb) for 100–200 µm limestone with 100% O<sub>2</sub>"

"Table 1: Weight balance of the material input and outputs for 200–300 µm limestone with 30% O<sub>2</sub>"

"Table 2: Balance of recovered material and its sieve analysis for 100–200 µm limestone with 100% O<sub>2</sub>"

- Discussion:

1) Please expand your discussion to cover the following in detail and in paragraph form:

1) modifications and troubleshooting, and 2) critical steps within the protocol.

This paragraph has been added in order to cover these points.

"This protocol has been resolved by minimising the electrical heating provided to the gas and calciner when the NG is being combusted in order to protect the tubes of electrical discharges caused by the heating elements. Also, it has been noted that the O<sub>2</sub> concentration increase can be achieved more rapidly than initial experimental campaigns

going from 20 % vol to 60% vol and 100% vol. It is important to highlight also that the most critical steps in this process are the start of the combustion, the increase of the oxygen concentration, which can cause increased temperatures that will trigger the shut-off of NG off if the temperature goes higher than 980 °C. Also, material make-up is a concern as it can lower the temperature of the reactor and stop the combustion process, therefore, it should be added in small batches.”

- Figures:

1) Figure 1 – please label individual units, e.g., carbonator, calciner, top valve, bottom valves, etc

This figure has been labelled in the revised manuscript.

- Highlighting:

1) After you have made all of the recommended changes to your protocol (listed above), please re-evaluate the length of your protocol section. Please highlight 2.75 pages or less of text (which includes headings and spaces) in yellow, to identify which steps should be filmed to tell the most cohesive story of your protocol steps. Please see JoVE’s instructions for authors for more clarification. Remember that the non-highlighted protocol steps will remain in the manuscript and therefore will still be available to the reader.

Reviewers' comments:

**Reviewer #1:**

*Manuscript Summary:*

This work is focused on the Calcium-Looping process applied for post-combustion CO<sub>2</sub> capture. The present paper describes an operating procedure of a Calcium-Looping pilot plant (25 kWth) in which the calciner reactor works under 100% O<sub>2</sub> atmosphere. Several limestone particle sizes are tested. Results show that a stable CO<sub>2</sub> capture higher than 70% can be achieved when carbonator works under 15% v/v CO<sub>2</sub> (85% N<sub>2</sub>), simulating the flue gas of a Coal-Fired Power Plant (CFPP). This work proposes a realistic calciner operation since a high CO<sub>2</sub> concentration of CO<sub>2</sub> at calciner outlet is achieved, which is fundamental in the CaL process for post-combustion CO<sub>2</sub> capture

*Major Concerns:*

-According to the authors, the operation of the calciner at high O<sub>2</sub> concentrations is motivated by the possibility of reducing the size of calciner and the size of air-separation units. This seems to be a contradiction since a higher O<sub>2</sub> concentration at calciner inlet to avoid CO<sub>2</sub> recirculation could require high O<sub>2</sub> flow and therefore a high ASU size (and a higher energy consumption). Please clarify this issue.

This has been clarified in the discussion section:

“As the recycle of flue gas (mainly CO<sub>2</sub>, water vapour and unreacted O<sub>2</sub>) can be reduced or even eliminated, the heat consumed to preheat this stream will be lower. Therefore, less oxygen would be needed and a smaller ASU (Air Separation Unit) would be required.

As the flow gas will be lower in this configuration, the size of the calciner would be smaller for the same fluidization velocity."

-On the other hand, a 6% of limestone make-up flow seems high. This would increase the energy consumption in the calciner in comparison with a "conventional" calciner operating with CO<sub>2</sub> recycled gas stream and therefore it's not clear enough if 6% could improve the energy penalty of the process. please discuss.

The make-up ratio was found to be 6%, which is in accordance with the literature as it can be seen in reference [23] in the manuscript. However, it has not been claimed that this would be beneficial for the energy penalty of the process. The make-up ratio of these tests mainly depends on the material (reactivity decay and attrition), as well as the CO<sub>2</sub> being captured in the carbonator (it is explained in the protocol that more limestone was added every time the carbonator CO<sub>2</sub> outlet was above 5%).

This has been explained in the text as it follows:

"Therefore, it can be concluded that for stable operation it would be necessary to add fresh sorbent corresponding to 0.5 L (750 g) of limestone approximately every 50 minutes, which is equivalent to a make-up ratio ( $F_0/F_{CO_2}$ ) of 6%, as described elsewhere<sup>25</sup>. The make-up ratio in these experiments was mainly influenced by the limestone (reactivity decay and elutriation). The value of this parameter was chosen based on the CO<sub>2</sub> concentration at the carbonator outlet, i.e. adding a portion of limestone when it reached a 5% vol CO<sub>2</sub>."

#### *Minor Concerns:*

-More references could be added to introduction section,i.e. lines 48-49 would be more interesting if the authors describe the possibilities to achieve higher thermal efficiencies by means of modifications in operating conditions [references], changing reactors design [references] or modifying the CaL proceses integration [references], instead of use a lumped references [17-19].

The introduction has been modified accordingly in the revised manuscript. Adding the following text:

"The use of heat pipes between the combustion and calciner has been studied instead of oxy-combusting fuel in the calciner, the results for the CO<sub>2</sub> capture performance were comparable with those of a conventional CaL pilot-plant, however, this process has higher plant efficiencies and lower CO<sub>2</sub> avoidance costs<sup>17</sup>. Martínez et al. <sup>18</sup> investigated the heat integration possibilities in order to preheat the solid material entering the calciner and to reduce the heat needed in the calciner. The results showed 9% reduction in the coal consumption when compared with that of the standard case. Other possibilities for heat integration are also studied considering internal and external integration options <sup>19</sup>.One of the main problems of the CaL cycle from the economic point of view is to supply the energy needed in the calciner by means of fuel combustion<sup>20</sup>."

-Figure legends should be better explained, since there is no appreciable difference between figure 3 and figure 5.

This has been modified to:

"Figure 3: CO<sub>2</sub> concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (E<sub>carb</sub>) for 100–200 µm limestone with 100% O<sub>2</sub>"

"Figure 5: CO<sub>2</sub> concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (E<sub>carb</sub>) for 300–400 µm limestone with 100% O<sub>2</sub>"

*Additional Comments to Authors:*

N/A

## **Reviewer #2:**

*Manuscript Summary:*

The manuscript written by Erans et al. presented the operation and first results of a CaL pilot plant with 100% oxygen combustion in the calciner flue gas simulating the behaviour of a coal-fired power plant and developed a procedure in order to operate a Calcium looping pilot plant with high oxygen concentrations in the calciner. The result is important and interesting. However, this manuscript looks like a test report and much information is missing. This manuscript can be published in Journal of Visualized Experiments after the major revision.

*Major Concerns:*

N/A

*Minor Concerns:*

N/A

*Additional Comments to Authors:*

The specific comments are shown as follows:

(1) In the introduction, the new research progress about calcium looping technology is not enough.

The introduction has been modified accordingly, adding the text below.

"The use of heat pipes between the combustion and calciner has been studied instead of oxy-combusting fuel in the calciner, the results for the CO<sub>2</sub> capture performance were comparable with those of a conventional CaL pilot-plant, however, this process has higher plant efficiencies and lower CO<sub>2</sub> avoidance costs<sup>17</sup>. Martínez et al.<sup>18</sup> investigated the heat integration possibilities in order to preheat the solid material entering the calciner and to reduce the heat needed in the calciner. The results showed 9% reduction in the coal consumption when compared with that of the standard case. Other



possibilities for heat integration are also studied considering internal and external integration options<sup>19</sup>. One of the main problems of the CaL cycle from the economic point of view is to supply the energy needed in the calciner by means of fuel combustion<sup>20</sup>."

(2) The chemical components of the limestone used in the experiment are missing.

This has been included in the revised manuscript.

"The limestone used in this study has a minimum content of 98.25%  $\text{CaCO}_3$ ."

(3) All the presented figures are not clear. The authors should provide the enough clear figures.

The quality of the figures has been improved throughout the manuscript.

(4) The discussion is simple and the deep analysis is lacking. Some parts of the paper is just observations and reporting of results without any effort to explain the results. This will diminish the impact. Even if speculative, it is important to try to understand the results.

Some paragraphs have been added throughout the text to try to discuss the results in a more insightful manner.

The discussion has been modified to include more details about the results and limitations of this study:

"As a result of these experiments various conclusions can be drawn. Firstly, operation of the calciner with an inlet of 100% vol oxygen is achievable, which is enabled by the possibility of exploiting the endothermic nature of the calcination reaction, as well as the fact that the solids circulate between two reactors at different temperatures. This operating mode aims at making the CaL process more economically viable by means of reducing capital and operating costs. As the recycle of flue gas (mainly  $\text{CO}_2$ , water vapour and unreacted  $\text{O}_2$ ) can be reduced or even eliminated, the heat consumed to preheat this stream will be lower. Therefore, less oxygen would be needed and a smaller ASU would be required. As the gas flow will be lower in this configuration, the size of the calciner would be smaller for the same fluidization velocity.

A standard methodology for this type of operation was developed to ensure the safe operation of the high-oxygen concentration in the calciner. The results showed capture efficiency of up to 70% in some of the performed experiments. Also, different particle size distributions were used in this reactor configuration (carbonator as a CFB; calciner as a BFB). The distributions were: 100-200  $\mu\text{m}$ ; 200-300  $\mu\text{m}$ ; 300-400  $\mu\text{m}$ . For the smallest distribution (100-200  $\mu\text{m}$ ), however, there were elutriation issues and the majority of the bed inventory was found in the calciner's cyclone catch-pot. It was found that the best results were achieved with the largest particle size distribution (300-400  $\mu\text{m}$ ) with those particles an Ecarb of around 70% was maintained throughout the experiment with a make-up ratio of about 6%.

This protocol has been improved by minimising the electrical heating provided to the gas and calciner when the NG is being combusted in order to protect the tubes of electrical discharges caused by the heating elements. Also, it has been noted that the O<sub>2</sub> concentration increase can be done more rapidly than initial experimental campaigns going from 20 % vol to 60% vol and 100% vol. It is important to highlight also that the most critical steps in this process are the start of the combustion, the increase of the oxygen concentration, which can cause increased temperatures that will trigger the source of NG off if the temperature goes higher than 980 °C. Also, material make-up is a concern as it can lower the temperature of the reactor and stop the combustion process, therefore, it should be added in small batches.

This methodology can be applied for this experimental rig to test new synthetic materials, as well as materials improved via doping, thermal pre-treatment, chemical pre-treatment, etc.<sup>24</sup>. This protocol would allow these new sorbents to be tested under realistic conditions providing a standard methodology for sorbent comparison. However, there are some challenges when applying this concept at larger scale, such as the use of coal in the calciner under these operating conditions. The use of solid fuels would increase the difficulty in operation of the calciner due to the high temperatures, which can lead to ash agglomeration and eventually defluidizing phenomena<sup>25</sup>. This needs to be further studied in order to determine the feasibility of this protocol; however, the concept was proofed successfully at pilot-scale in the course of this work using NG . Another limitation arising from this study is the duration of the tests with around 3 h of steady state operation per tests; this is due to the heating process of the plant, which is an inherently slow process. Moreover we do not know the average number of carbonation/calcination cycles experienced by a particle when circulating between reactors. It is possible that the high oxygen concentration had a negative effect causing more sintering in the limestone particles. Further investigation of these challenges would help to assess the suitability of the protocol as a novel feasible operating mode for CaL plants at higher scale."

### **Reviewer #3:**

#### *Manuscript Summary:*

This manuscript presents experiments in a lab-scale calcium looping plant with a calciner that is fired with natural gas at high oxygen concentrations. The topic is highly relevant in the field of CO<sub>2</sub> capture from flue gases of power/industrial plants, since the calcium looping process has the potential of relatively low energy penalty compared with other post-combustion CO<sub>2</sub> capture technologies. The realization of high oxygen concentration (up to 100%) in the fluidization gas of the calciner has the advantage of minimizing (or even avoiding) a flue gas recirculation, so that the energy penalty caused by the recycle fan can be reduced (or avoided) leading to an improved efficiency of the process. The material provided by the authors is new and could be of high interest to readers working with fluidized bed reactors. The experimental procedure is well described, although a description of the experimental configuration is missing. There might be some concern regarding the visualization of the experiment, since there usually is limited visual access to such reactors. All in all, the content is highly recommended for

being published in JoVE with some modifications, as indicated below.

*Major Concerns:*

1) A detailed description of the experimental setup (including reactor dimensions, materials, instrumentation, control loops) should be given.

A detailed description of the experimental set up has been given in the representative results section:

"The experimental set-up is shown in Fig.1. The plant comprises two interconnected fluidized-beds. Namely, the carbonator is a CFB with 4.3 m height and 0.1 m ID; on the other hand the calciner is a BFB with 1.2 m height and 0.165 m ID. The solid transport from one reactor to the other is controlled by two loop-seals fluidized with nitrogen. Gases for both reactors are fed through a preheating line, both reactors are electrically heated; moreover, the calciner is fed with natural gas in order to generate the heat needed for the endothermic calcination. The carbonator distributor plate has 8 nozzles, each of them with twenty 2 mm holes, whilst the calciner has 20 nozzles with six 1 mm holes each."

2) The Figures are of very poor quality and should be improved.

The quality of the figures has been improved throughout the manuscript.

3) In the conclusions, the authors state that "operation of the calciner with an input of 100% vol oxygen is achievable". However, this has only been proven for natural gas as fuel, and a commercial calciner will hardly be fired with natural gas, but with coal. When firing with coal, there are other challenges related to ash softening at locally high temperatures, which might lead to agglomeration. This issue should be discussed in the paper.

We agree with the reviewer that this could be an issue. However, in this work, we wanted to prove this concept of running with high oxygen concentrations, but further work should focus on the study of solid fuels before this operating mode can be moved to higher scale.

" However, there are some challenges when applying this concept at larger scale, such as the use of coal in the calciner with under these operating conditions. The use of solid fuels would increase the difficulty in operation of the calciner due to the high temperatures, which can lead to ash agglomeration and eventually defluidizing phenomena<sup>27</sup>. This needs to be further studied in order to determine the feasibility of this protocol; however, the concept was proofed successfully at pilot-scale in the course of this work using NG."

4) The longest test presented was 3 hours. It is not clear whether this duration is an upper limit or whether longer test durations are possible. When defining a test procedure, it should be assured that the composition/activity of the sorbent has reached

a (semi) steady state. It would be interesting to know the average number of carbonation/calcination cycles that the sorbent experiences during one test.

The duration is an upper limit for these tests due to work policies at Cranfield University. The plant cannot be run overnight or in shifts. However, the plant was run 3 h under steady state, which are the results presented as part of this work. It is unknown what the average number of cycles is. This has been clarified in the text:

"Another limitation arising from this study is the duration of the tests with around 3 h of steady state operation per tests; this is due to the heating process of the plant, which is a slow process. It is also unknown the average number of carbonation/calcination cycles experienced by a particle when transferring from one reactor to another"

5) Has the reactivity of the used sorbents been analyzed? Are there any differences related to the oxygen concentrations? It can be expected the sintering might be promoted by high oxygen concentrations leading to reduced activity.

The reactivity of the sorbents has not been analysed. However, we agree with the reviewer and a statement has been made about this issue in order to clarify that this is a possibility that should be further studied.

"It is possible that the high oxygen concentration had a negative effect causing more sintering in the limestone particles. Further investigating these challenges would help to assess the suitability of the protocol as a novel feasible operating mode for CaL plants at higher scale."

#### *Minor Concerns:*

6) line 74: "Set all electrical..."

This has been changed to:

"Set the temperature of all electrical preheaters of the carbonator at 600 °C."

7) line 76: "...these data include temperatures..."

This has been changed to

"These data include"

8) line 102: At what temperature is the material being calcined?

The material is being calcined with the heating up process to speed up the start of the test but it is estimated that this would be around 800-850°C for the first batch and the calciner temperature for the fresh make-up of sorbent.

This has been clarified in the revised manuscript:

"2.2.5. Add limestone in 0.5 L increments until there is 7 L in the fluidized bed. Calcine all the material in the fluidized bed of the calciner (the estimated calcination temperature is 800-850° for the batch present in the calciner and the calciner temperature for the following batches)."

9) line 131: What does "100% limestone" mean here? Has the limestone not been calcined? Have there been experiments with less than 100% limestone?

The 100% has been deleted in the sentence. All tests are done with pure limestone.

10) The text in the tables needs to be adjusted.

The text has been adjusted in the revised manuscript.

*Additional Comments to Authors:*

N/A