Pilot-scale calcination of limestone in steam-rich gas for direct air capture

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Abstract

A novel polygeneration concept, which has been proposed recently, comprises a fuel-cell calciner integrated system in order to produce electricity and lime which can be used for direct air capture (DAC) to remove CO_2 from the atmosphere. However, the scalability of the integrated system needs to be further studied. In this work, calcination of limestone under steam-rich conditions simulating flue gas from a solid oxide fuel cell (SOFC), and subsequent ambient carbonation has been explored. Limestone was calcined under two steam concentration (21% and 35% vol) conditions in a 25 kW_{th} pilot-scale bubbling fluidised bed (BFB), and then exposed to ambient air to evaluate DAC performance. Samples were characterised in order to quantify the hydration and carbonation conversions over time and, therefore, their DAC capacity. It was observed that steam reduces calcination time, confirming its catalytic effect, while the calcination temperature remained the same regardless of the steam composition at the same CO_2 partial pressure. Moreover, increasing steam concentration during calcination affected the material performance and DAC capacity at ambient conditions positively. Therefore, these findings demonstrate that limestone calcined under typical SOFC afterburner exhaust conditions is suitable as a DAC sorbent.

Keywords: calcination; steam; CO_2 capture; direct air capture; limestone

1 Introduction

In order to achieve the Paris Agreement target, reached at the 21st Conference of the UNFCC parties, of maintaining the mean global temperature rise below 2° C when compared to pre-industrial levels, a portfolio of technologies needs to be deployed [1]. These technologies include bioenergy with carbon capture and storage (BECCS) [2], direct air capture (DAC) and enhanced weathering of minerals, among others [3,4]. However, these carbon-negative technologies are still expensive and in early stages of development [5–8].

The reversible carbonation/calcination cyclic reaction of Ca-based materials (Eq. 1) has been widely researched for a variety of natural processes and applications such as production of cement, deployment in the iron and steel industry, water treatment, and desulphurisation. More recently, calcium looping (CaL) has been explored as a promising second-generation carbon capture technology, which employs the reaction of Ca-based materials with CO_2 [9]. It is aimed at the decarbonisation of large point sources such as power generation and industrial plants [10]. This technology comprises two interconnected fluidised beds and a Ca-based solid material being looped between the reactors. In the reactor called the carbonator, CaO reacts with the CO_2 present in a flue or fuel gas stream and forms calcium carbonate. The saturated sorbent is then circulated to another reactor (calciner) in order to regenerate sorbent at high temperature and to produce a concentrated CO_2 stream.

$$CaCO_3 \leftrightarrow CaO + CO_2 \qquad \Delta H^0 = +177.8\, kJ/mol \qquad \text{(Eq. 1)}$$

It has been suggested in several studies that injecting steam during carbonation and/or calcination has a positive effect on carbonation conversions over a number of capture/regeneration cycles at laboratory [11,12] and pilot plant scale [13]. Manovic and Anthony [14] investigated the effect of steam on carbonation for a variety of calcined limestones using a thermogravimetric analyser (TGA) and concluded that steam enhances sorbent conversion during the diffusion-controlled step (through the carbonate product layer). Donat et al. [11] also reported that steam injection during carbonation in a small bubbling

fluidised bed (BFB) raises carbonation conversion due to the minimisation of diffusion resistance. Further experiments were performed by Symonds et al. [15], which showed increased CO_2 capture capacity when steam (17% vol) was present in a BFB carbonator.

With regard to the effect of steam addition during calcination, it has been typically considered as an effective method of lowering the sorbent decomposition temperature by means of reducing CO_2 partial pressure in the calciner [16]. Namely, it has been suggested that steam is adsorbed onto the CaO surface faster than CO_2, which implies a weaker bond between CaO and CO_2, thus, lowering the calcination temperature [17]. Also, experimental observations showed that the decomposition rates are more rapid when a small amount of steam was introduced in the calciner [18–20]. This phenomenon was initially linked to the enhancement of thermal conductivity in the calciner [20]. However, Wang et al. [17] hypothesised a catalytic effect of steam in $CaCO_3$ decomposition. Moreover, steam addition during calcination increases lime performance in the subsequent carbonation cycles [12,21,22]. It has been reported that porosity and surface area were reduced in the presence of steam [23]. This caused a shift towards larger pores when steam was present in the reactor, inducing steam-enhanced sintering, which led to a decrease of surface area and conversion [22–26]. Also, it has been reported that steam injection during calcination has a negligible effect on the subsequent carbonation when compared to steam injection during carbonation or carbonation and calcination simultaneously [27]. It has also been suggested that there is a synergistic effect when steam is introduced to both carbonator and calciner [12]. Donat et al. [11] indicated that the carbonation conversion was highest when steam was added to both carbonator and calciner, as opposed to injecting steam either during calcination or carbonation only.

Recently, new concepts employing Ca-based sobents have been explored, such as integration of CaL with concentrating solar power for thermochemical energy storage [28]. Industrial waste streams, such as carbide slag, have also been studied, and it has been experimentally

84 demonstrated that simultaneous CO_2 capture and thermochemical energy storage can be
85 achieved [29]. Calcium hydroxide has been investigated as an efficient material for DAC
86 processes; however, it requires high energy in order to regenerate [30]. Lime has also been
87 suggested for DAC in a fluidised bed with solar energy used to provide heat needed for
88 regeneration [31]. Moreover, the concept of simultaneous power generation and CO_2 capture
89 from air using carbonate materials has recently been proposed [32]. In this process, the sorbent
90 regeneration step is performed by using the high-grade heat from a solid oxide fuel cell (SOFC).
91 SOFCs have been suggested for this process due to their high electrical efficiency [33–35], fuel
92 flexibility [36–40], and ability to co-generate high grade heat [41]. A key advantage of SOFCs
93 is that external reformer is not required in this technology [38]. The composition of the SOFC
94 off-gas depends on the fuel supplied, but for natural gas comprises mainly CO_2 and steam [38].
95 Then, steam is condensed, and concentrated CO_2 stream compressed, transported, and stored,
96 typically in geological formations [4]. Therefore, the proposed process possesses several
97 advantages, which include: generation of electricity and a concentrated CO_2 steam, as well as
98 CO_2 capture from air using Ca-based materials at costs which are competitive compared to
99 those of other DAC technologies [42]. This process has been demonstrated at laboratory scale
100 using a 2 kWe SOFC with a fixed-bed calciner, showing promising performance [43]. In order
101 to scale up the process, and explore the behaviour of the materials under realistic conditions, a
102 fluidised bed calciner, such as employed in the CaL cycle technology, was perceived as a most
103 suitable reactor choice.
104 In this work, calcination of limestone in steam-rich gas, simulating SOFC calciner conditions,
105 is explored at BFB pilot-scale. The aim is to evaluate the technical feasibility of the SOFC
106 calcination process and the effect of steam on calcination temperature and reaction time.
107 Furthermore, the performance of the lime produced under realistic SOFC calciner process
108 conditions, in order to be used for DAC, is tested. Finally, in addition to the practical

application of the proposed process, the fundamental aspects of the effect of steam on the performance of Ca-based materials in CO_2 capture processes are further explored. These are a key in order to evaluate potential of lime production under steam enriched conditions, such as those when the SOFC exhaust stream is used as a fuel and fluidizing gas.

2 Experimental

A detailed process diagram of the new concept for DAC by lime calcined using the high grade heat from SOFC is presented by Hanak et al. [32], and this study explores the calciner part of the integrated process. The experimental conditions during calcination were designed in order to simulate realistic gas composition from SOFC entering the calciner and conditions during combustion/calcination, primarily high concentration of steam. Finally, the DAC performance of limestone calcined under realistic conditions of the integrated process were tested by means of CO_2 capture from ambient air.

2.1 Pilot-scale calciner description

A 25 kW_{th} pilot-scale bubbling fluidised bed (BFB) reactor was used for the calcination experiments. This calciner was redesigned CaL pilot plant [44] and similar in the size to the CaL pilot plant at INCAR-CSIC [45]. The set-up of the calciner is shown in a schematic manner in Figure 1. The calciner is 1.2 m high with an ID of 0.165 m and was operated at atmospheric pressure. The distributor plate comprised 20 nozzles of 6 1-mm holes each. The fluidising gas was heated by electrically-heated pipes and the calciner was additionally heated by electrical heater and combustion of natural gas inside the bed. The electrical heater was used for start-up of the calciner to heat it up to 600-650 °C, which was the temperature enabling ignition and stable combustion of natural gas. In order to calcine limestone under the conditions simulating combustion of the surplus fuel from SOFC anode, the further temperature increase was

achieved by combustion of natural gas. Therefore, during the calcination regime, the heat supply required for calcination was a combination of electrical heating and methane combustion, simulating combustion of unreacted fuel and high grade heat supply from SOFC. The steam introduced into the calciner was produced via an in-house steam generator consisting of a water pressure vessel at 2 bar, a peristaltic pump (Masterflex, Cole Parmer) to adjust the flow rates, and two 1.2 kW heating tapes (OMEGA, UK), operating at 400-500 °C. Prior to installing the heating tapes, the pipe was wrapped with mica tape to avoid any potential electric discharge. The other gases were supplied to the calciner and their flow rates were measured by rotameters. The off-gas concentrations were measured by a Fourier Transform Infrared analyser (FTIR, Protea, model FTPA-002). The temperature through the steam generation system was continuously monitored throughout the experiments by an in-house system using K-type thermocouples and an in-house controller.

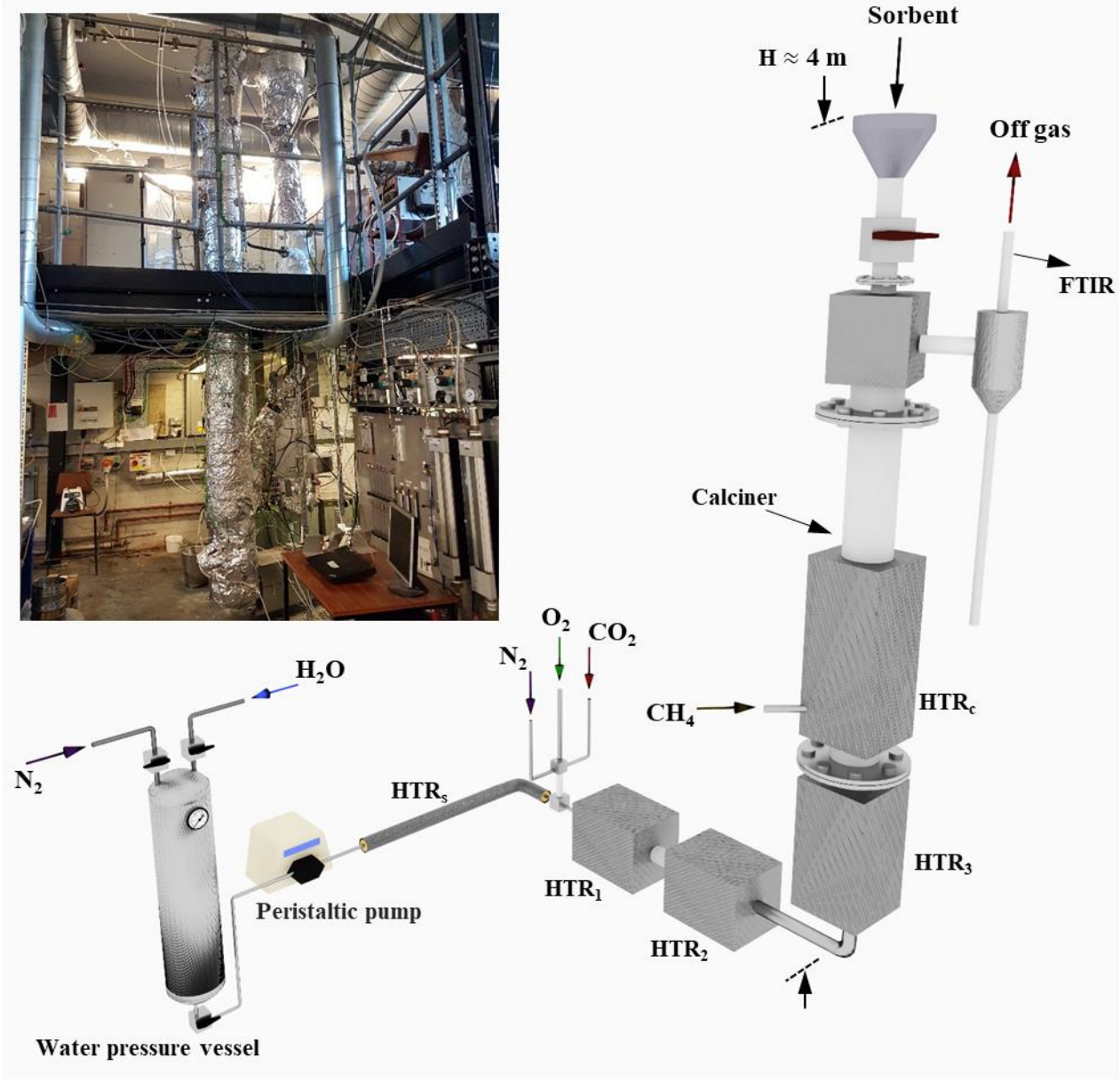

Figure 1: Photograph (top left corner) and schematics of the pilot-scale BFB calciner. The power of the calciner components are: preheaters (HTR_1 – 3 kW, HTR_2 – 3 kW, HTR_3 – 5 kW), steam line heating types (HTRs – 2 x 1.2 kW = 2.4 kW), calciner heater (HTR_C – 8 kW), and natural gas stream (9.6 L/min, CH_4 – ~3 kW).

2.2 Experimental procedure

Two sets of experiments were performed with different steam concentrations, while maintaining the same fluidisation velocity (0.25 m/s) and CO_2 concentration (35% vol). The

calciner was first commissioned, and several tests were performed in order to ensure stable steam supply, avoiding condensation, and operation near to steady state. Then, two tests, with different steam concentrations (21% and 35% steam), were performed two times in order to ensure reproducibility of experimental conditions and measured results. Considering the accuracy of the measuring equipment and repeatability, it was estimated that relative error of the results presented in this study is in the range of ±5%.

In the first instance, 13% vol steam was mixed with 29% CO_2, and balanced with N_2. The calciner was heated up to 700 °C, then the limestone was introduced into the vessel, and heated until the temperature reached 700 °C again. The inventory of the bed was kept the same for both experiments for consistency purposes, i.e., 3 kg of limestone per experiment. At that point, 9.6 L/min of natural gas was fed into the calciner and combusted in 20.1 L/min O_2 in order to provide the necessary heat for the calcination. The steam and CO_2 concentrations at the outlet of the calciner, as measured by the FTIR, before calcination had started, were 21% and 35% vol, respectively, and this increase, compared to that at the inlet of the calciner, is a result of natural gas combustion ($CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$).

During the second experiment, 30% vol steam was mixed with 29% vol CO_2, and balanced with N_2. The flow rates of natural gas and O_2 were maintained the same as in the previous experiment in order to provide the same amount of heat for calcination. The steam and CO_2 concentrations at the outlet of the calciner, before calcination had started, were both 35% vol. When calcination was completed, i.e., when the CO_2 concentration at the outlet equalled the initial values before calcination, the calciner was cooled down using N_2 in order to avoid any carbonation and/or hydration of the already-calcined material.

It should be noted that gas composition in this study was selected assuming that the gas stream from SOFC anode with the excess of fuel is entering calciner. The model of the integrated process used to simulate the gas composition in calciner, considering the mass and heat

balance, is presented by Hanak et al. [32]. During the experiments, nitrogen was used to balance steam in order to mitigate risk of condensation in the reactor. The composition of the fluidising gas for both experiments is summarised in Table 1.

Table 1: Experimental gas concentrations

Experiment	**Steam (% vol)**	**CO_2 (% vol)**	**N_2 (% vol)**
21% steam	21	35	44
35 % steam	35	35	30

2.3 Material preparation and characterisation

Longcal limestone, supplied by Longcliffe Ltd., which has been used in our recent studies [46] as a typical natural source of high-purity calcium carbonate, contains minimum of 98.25% $CaCO_3$. The limestone was sieved to the desired particle size range (250 to 500 µm). A Pyris 1 TGA (Perkin Elmer) was used to determine the levels of hydration and carbonation of the samples after calcination in the BFB calciner as well as after their exposure to ambient air for DAC, by means of heating them to 900 °C at 30 °C/min in N_2. Also, the morphology of samples was characterised by a Philips XL30ESEM Scanning Electron Microscope (SEM) using an accelerating voltage of 20 keV. The samples were coated with gold before analysis in order to avoid electrostatic charging.

2.4 Direct air capture (DAC) tests

For the DAC experiments, the materials calcined in the BFB calciner were exposed to air by placing them in stainless steel trays (45 cm x 35 cm), forming a thin layer (~3 mm). Samples from the trays were taken after 7 and 14 days for characterisation by the TGA in order to assess their hydration and carbonation extents, i.e., DAC performance. The samples were denoted as CaO-DAC-21 and CaO-DAC-35, referring to 21% and 35% vol steam in the calciner, respectively. The ambient air temperature and humidity were continuously monitored through

the DAC experiment and can be found in Figure 2. It can be seen that the temperature and humidity profiles for both experiments are very similar with cyclic fluctuations through each day.

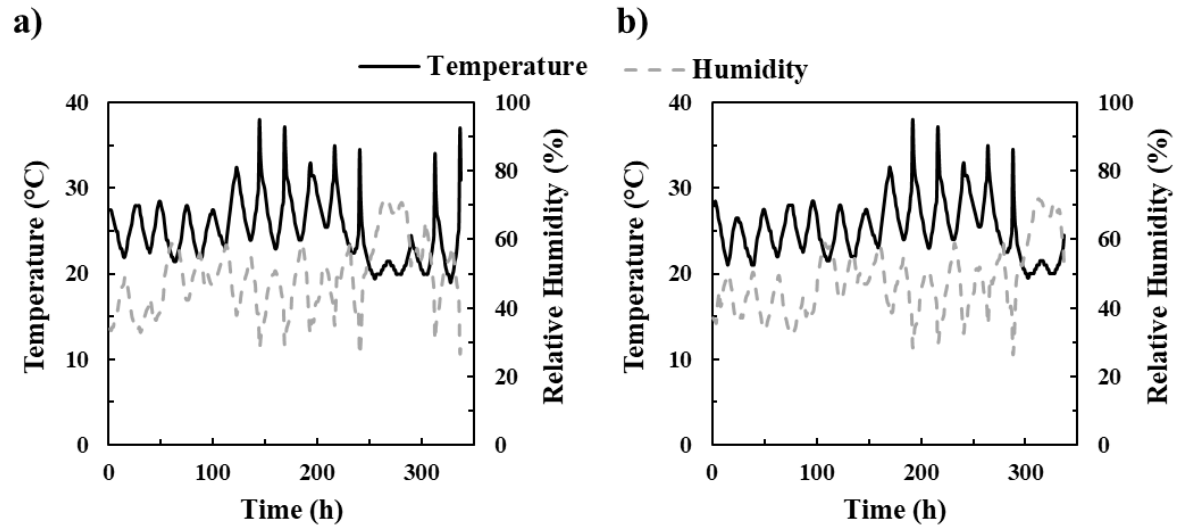

Figure 2: Temperature and humidity profiles for a) CaO-DAC-21, and b) CaO-DAC-35 tests.

3 Results and discussion

3.1 Calcination in BFB calciner

During the calcination tests, the initial CO_2 partial pressure was the same for both experiments and the material inventory was maintained the same in order to enable direct comparison of the temperature profiles and reaction times. The reaction started at near equilibrium temperature as the material decreased the temperature of the calciner substantially when introduced. The heat produced by combustion of natural gas was utilised for the endothermic calcination process. The CO_2 and steam concentrations measured during the pilot-plant calcination experiments with 21% and 35% vol steam are presented in Figure 3. It can be seen that the CO_2 concentration increases when the calcination temperature is reached due to CO_2 being released as $CaCO_3$ decomposes. When calcination was completed, the CO_2 concentration decreased to the initial value. The calcination started at 835 °C for both experiments, as expected, since the

CO_2 partial pressure was the same. Therefore, the effect of the steam concentration on the calcination temperature was negligible under these conditions and on the onset of calcination. The key difference between both experimental campaigns was the duration of the calcination reaction, which dropped from 110 min for 21% vol steam to 70 min for 35% vol steam. Therefore, higher steam concentration increases the rate of the calcination reaction. These results imply that steam present during calcination has a catalytic role, which has been suggested previously and is in agreement with the literature data [17]. The mechanism of this catalytic effect can be related to the fact that calcination is a reversible reaction and adsorption of H_2O molecules at the active sites of limestone during calcination weakens the CaO-CO_2 bounds [17]. These findings also imply practical benefits of steam presence at elevated concentrations, such as those when the SOFC afterburner gas is used for calcination, and in addition to lowering the CO_2 partial pressure, steam acts as a catalyst and can significantly reduce required residence time of the material in the BFB calciner, which increases its capacity and efficiency. However, it should be noted that steam is believed to affect the attrition and elutriation rates of the material in the fluidised bed. It has been suggested that exposure to steam during calcination weakens particle structure and enhances particle attrition [27]. This is caused by the chemical effect of high steam concentrations on the CaO structure [19]. On the other hand, steam injection has shown other benefits when injected in the calciner, such as the improvement of the multicycle CO2 carrying activity of lime-based materials using standard CaL conditions [11,12]. Finally, by using simulated SOFC gas for calcination, this study demonstrates the technical feasibility of the integrated SOFC-calciner process proposed for power generation with simultaneous lime production for DAC.

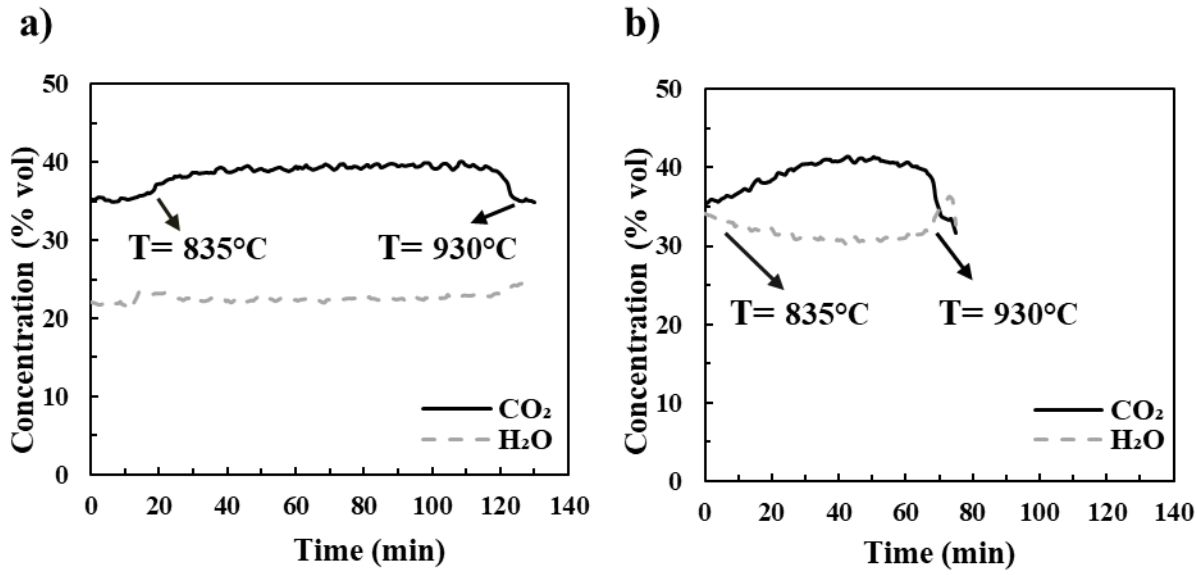

Figure 3: Gas concentrations measured by FTIR at outlet of the BFB calciner for a) 21% vol steam, and b) 35% vol steam.

3.2 Direct air capture (DAC) results

After each pilot-plant calcination, the materials were tested in the TGA to assess the completeness of the calcination and possible hydration and/or re-carbonation during the cooling down step and discharging the inventory of the calciner. The TGA results from the calcined samples are shown in Figure 4 (solid lines), and the hydration and carbonation conversions are presented in Table 2. It can be seen that both samples were almost completely calcined after each test, regardless of the steam concentration, which was expected based on the CO_2 profiles presented in Figure 3, and there was no significant difference between the TGA decomposition curves. The small mass loss observed between 550-700 °C can be attributed to ambient carbonation of the CaO-based sorbent during the discharge process and/or presence of some non-calcined material.

After the pilot-plant calcination tests, the samples were exposed to air in order to investigate their hydration and carbonation conversions, i.e., DAC performance, over a prolonged duration. In Figure 4a, the weight losses for CaO-DAC-21 sample during heating to 900 °C are

shown. These data correspond to the DAC capacity of the material after 7 and 14 days. It can be seen that during the first week the material was mainly hydrated by moisture from the air which reacts with the CaO surface. Some carbonation can be also seen during that period, but it was negligible when compared to the hydration conversion. The corresponding TGA profile is shown for CaO-DAC-35 sample in Figure 4b. It appears that the sample which was exposed to the higher steam concentration during calcination carbonates faster at the beginning, i.e., carbonation conversions after 7 days are 8% and 36% for CaO-DAC-21 and CaO-DAC-35, respectively. However, after 14 days the carbonation conversions were very similar at around 53-55%. This suggests that steam present during calcination has a positive effect on the material at the beginning of the air capture process, increasing the rate of carbonation when the steam concentration was higher. It should be noted that DAC by lime, as considered in this study, is a long process that takes weeks/months if not aided by forcing air through the material. Therefore, it may not be economically feasible to increase the steam concentration in the calcination gas for a rise in reaction rate during a short period of DAC. However, depending on the application of this technology, namely, the source of the fluidising calcination gas, the gas can be inherently rich in steam, which is the case for the integrated SOFC calciner. In this case, the re-carbonation during DAC would be faster during the initial stages, which can enable more frequent recycling of the material to the calciner, depending on other thermodynamic and economic parameters of the proposed DAC process.

It can be inferred that a higher steam concentration during the calcination reaction aids the air capture performance of the material. However, it has been previously suggested that steam enhances sorbent sintering during calcination [23]. This is believed to be caused by the formation of OH^- ions, which support the growth of CaO crystals causing the surface area to decrease. However, the same phenomenon can favour the increase of the particle's mean pore size and mitigate the reactivity decay over the cycles [11,12]. Therefore, the carbonation may

be promoted by improved accessibility of CaO in the particles. As the steam addition during the reaction affects sorbent morphology, the pore structure is believed to be more stable [47]. This, perhaps, removes the delay in the first stage of the carbonation reaction (kinetically-controlled) and raises the reaction rate in the second stage of the reaction (diffusion-controlled). All of these effects are expected to increase the carbonation kinetics of CaO. However, it should be noted that previous studies have claimed that steam has a greater impact on sorbent reactivity when injected during carbonation, while a less significant effect has been found when steam is injected during calcination [12].

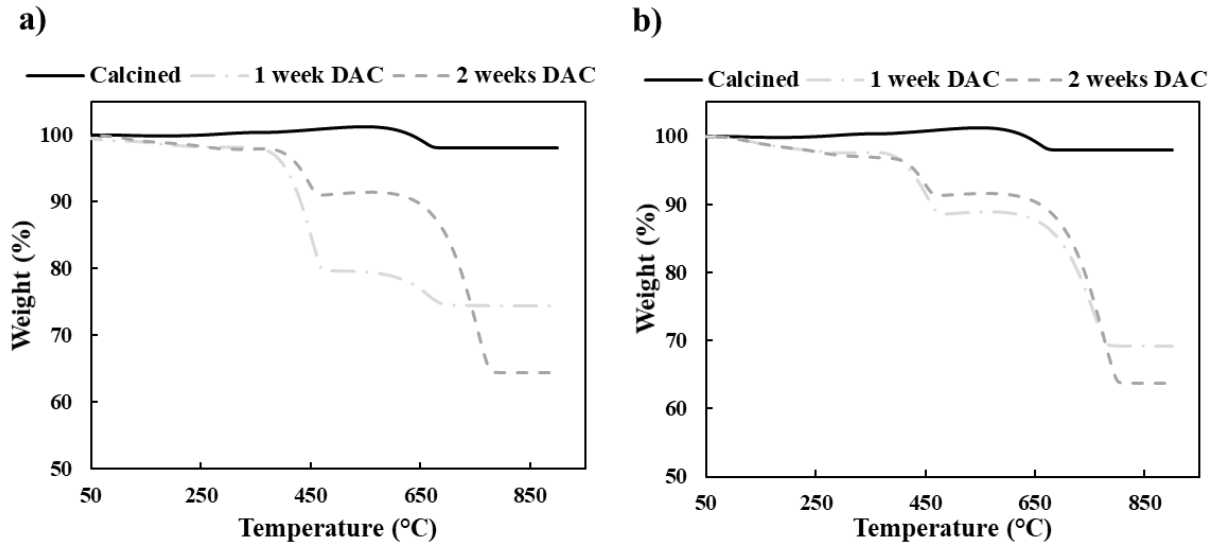

Figure 4: Re-carbonation experiments for: a) CaO-DAC-21, and b) CaO-DAC-35 calcined materials. Note: X_h and C_{carb} refer to hydration and carbonation conversions, respectively.

Table 2: Hydration and carbonation conversions for DAC experiments*

Sample	Xh (%)	Xcarb (%)
CaO-DAC-21-1week	79	8
CaO-DAC-21-2week	34	53
CaO-DAC-35-1week	41	36
CaO-DAC-35-2week	31	55

* Note: Xh and Xcarb refer to hydration and carbonation conversions, respectively

Figures 5 and 6 show selected SEM images of the CaO-based materials calcined under different steam concentration conditions, as well as corresponding samples after exposure to air for prolonged durations. It can be seen that the increase in steam concentration during the calcination aids the development of a more resistant structure due to larger pores and a more open pore structure. These results are in agreement with the previous findings by Donat et al. [11] and Coppola et al. [48]. It can also be observed how the morphology of the material changes during hydration/re-carbonation by air. A very porous structure is characteristic for the calcines presented in Figures 5b and 6b, changing to a compact structure presented in Figures 5f and 6f due to the formation of a carbonate layer which fills the pores.

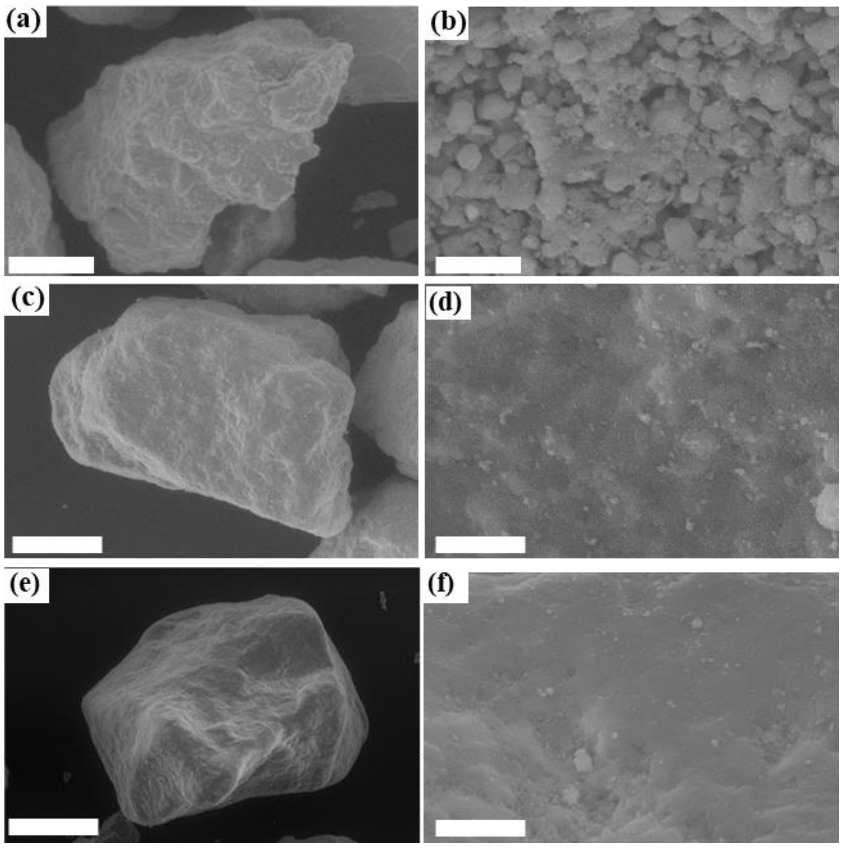

Figure 5: SEM images of particles after the 21% vol steam calcination test and exposure to air: a) and b) calcined material; and material after c) and d) one week of re-carbonation, and e) and f) two weeks of re-carbonation. The bars are 250 µm for a), c), and e); and 10 µm for b), d) and f).

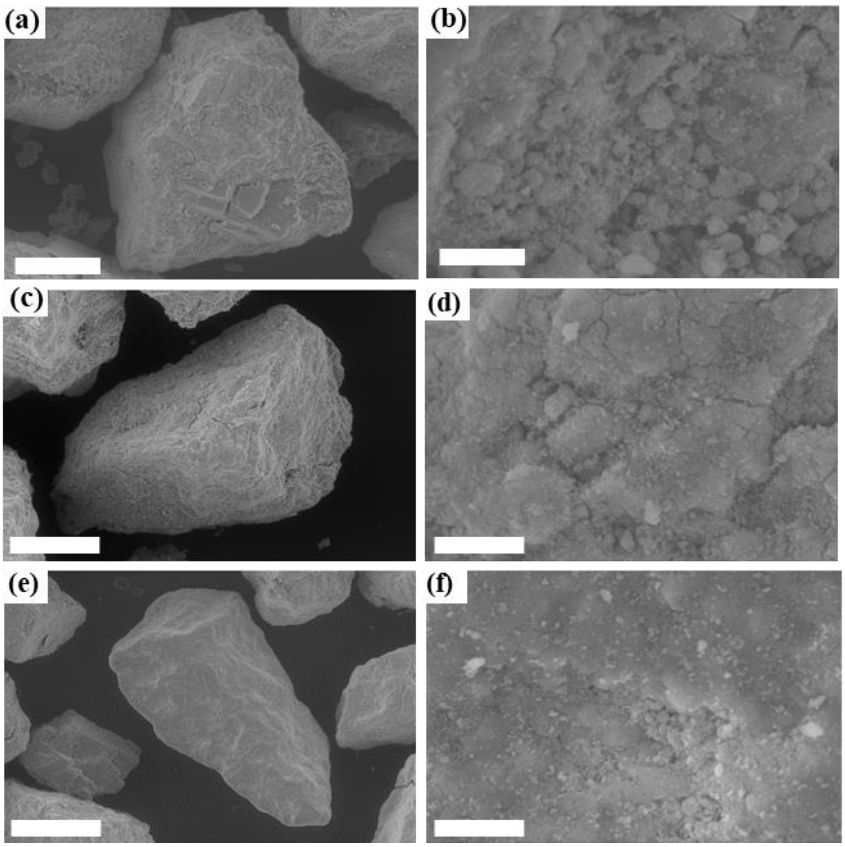

Figure 6: SEM images of particles after the 35% vol steam calcination test and exposure to air: a) and b) calcined material; and material after c) and d) one week of re-carbonation; and e) and f) two weeks of re-carbonation. The bars are 250 µm for a), c), and e); and 10 µm for b), d) and f).

The results presented in this paper clearly demonstrated technical feasibility of the calciner component of the integrated SOFC-calciner concept for lime production. Both catalytic role of stem and reducing calcination temperature due to lowering partial pressure of CO_2 plays a crucial role in further development of the concept considering that steam is inherently present in the system. This means higher efficiency of the technology, and concentrated stream of CO_2 is easily produced after steam condensation. Importantly, produced lime has superior morphology and performance in removing CO_2 from air when exposed to the ambient conditions. Therefore, the concept is carbon-negative ready, and demonstration of the calciner component of the concept is a driver for the further development of the concept, considering

that produced lime can be sold in market, but in the case it is needed, produced lime can be used to remove CO_2 from air.

4 Conclusions

Different steam-rich conditions (21% vol and 35% vol) were tested for the calcination of limestone at pilot scale using a bubbling fluidised bed (BFB) calciner, with 35% vol CO_2, and balance N_2, in order to evaluate the effect of steam and subsequent DAC performance of the calcined materials. It was found that steam had a significant effect on the duration of calcination, reducing carbonation time from 110 min in 21% steam to 70 min in 35% steam. However, the onset calcination temperature seemed unaltered when varying the steam concentration (around 835 °C). This suggests a catalytic effect of steam, which aids calcination near the equilibrium temperature. After calcination, the lime material was exposed to air in order to investigate its potential for DAC. It was found that the materials carbonated fairly quickly, exceeding 50% carbonation conversion after 14 days, which is of practical interest for utilisation at industrial scale. This also implies that the high levels of steam present during calcination promote the DAC performance of CaO-based materials. Moreover, the increased steam concentration during the calcination has a more positive effect in the first stage of the subsequent re-carbonation under ambient conditions. This is believed to be due to the fact that steam present during calcination alters the porous structure of lime, making it more stable and with larger pores. Therefore, CO_2 would encounter lower diffusion resistance when it reacts with CaO in the lime particles. In addition to further highlighting the effects of steam on calcination of limestone, these results also demonstrate the technical feasibility of calcination in a steam-rich gas stream such as that from a SOFC and suitability of the calcines for DAC, with a potential for power generation with negative carbon emissions.

Acknowledgments

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