Calcium-looping for post-combustion CO_2 capture. On the adverse effect of sorbent regeneration under CO_2

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Abstract

The multicyclic carbonation/calcination (c/c) of CaO solid particles at high temperature is at the basis of the recently emerged Calcium-looping (CaL) technology, which has been shown to be potentially suitable for achieving high and sustainable post-combustion CO_2 capture efficiency. Despite the success of pilot plant projects at the MW_{th} scale, a matter of concern for scaling-up the CaL technology to a commercial level (to the GW_{th} scale) is that the CaO carbonation reactivity can be recovered only partially when the sorbent is regenerated by calcination at high temperatures (around 950°C) as required by the CO_2 high concentration in the calciner. In order to reactivate the sorbent, a novel CaL concept has been proposed wherein a recarbonator reactor operated at high temperature/high CO_2 concentration leads to further carbonation of the solids before entering into the calciner for regeneration. Multicyclic thermogravimetric analysis (TGA) tests demonstrate the feasibility of recarbonation to reactivate the sorbent regenerated at high calcination temperatures yet at unrealistically low CO_2 partial pressure mainly because of technical limitations concerning low heating/cooling rates. We report results from multicyclic c/c and carbonation/recarbonation/calcination (c/r/c) TGA tests at high heating/coling rates and in which the sorbent is regenerated in a dry atmosphere at high CO_2 partial pressure. It is shown that that at these conditions there is a drastic drop of CaO conversion to a very small residual value in just a few cycles. Moreover, the introduction of a recarbonation stage has actually an adverse effect. Arguably, $CaCO_3$ decomposition in a CO_2 rich atmosphere is ruled by CO_2 dynamic adsorption/desorption in reactive CaO (111) surfaces as suggested by theoretical studies, which would preclude the growth of the regenerated CaO crystal structure along these reactive surfaces and would be intensified by recarbonation. Nevertheless, the presence of H_2O in the calciner, which is also adsorbed/desorbed

dynamically in CaO reactive planes, would shield CO_2 adsorption/desorption thus mitigating the deeply detrimental effect of CO_2 on the carbonation reactivity of the regenerated CaO structure. Oxy-combustion, which produces a significant amount of H_2O, is currently used in pilot-scale plants to raise the temperature in the calciner although alternative techniques are being explored since it represents an important penalty to the CaL technology. Our study suggests that steam injection would be necessary in a dry calciner environment to avoid a sharp loss of CaO conversion if the sorbent is regenerated at high CO_2 partial pressure.

I. INTRODUCTION

The Ca-looping (CaL) technology, based on the multicyclic carbonation/calcination (c/c) of CaO at high temperatures, has recently emerged as an economically viable process for post-combustion CO_2 capture [1–3]. In this process, CO_2 present at low concentration in the high velocity flue gas stream is captured by partial carbonation of solid CaO particles. The carbonated particles are then circulated into a second fluidized bed reactor where CaO is regenerated by calcination to release a stream of concentrated CO_2 ready for transport and storage. Taking into account the practical constraints in the carbonator reactor (CO_2 concentrations about 15% vol and short residence times) the optimum carbonation temperature is around 650°C, which leads to fast enough carbonation kinetics and still low CO_2 equilibrium concentration ($\simeq 1\%$) to assure a high CO_2 capture efficiency. On the other hand, the carbonated solids must be heated up under a typically high CO_2 partial pressure in the calciner environment to temperatures above 900°C to shift the reaction towards decarbonation and to complete it in short residence times [3, 4]. In order to heat the solids

up to the required temperature for regeneration, the technique currently used in pilot-scale plants is to burn fuel in the calciner using pure oxygen (oxy-combustion) [3], which entails a significant energy consumption and thus an important penalty of the CaL technology [5]. A current subject of research is focused on the development of alternative methods, such as the recovery of heat from the solids and gaseous streams leaving the calciner, to reduce fuel consumption and minimize the additional energy cost in the air separation unit required for oxy-combustion [5–7]. In regards to the material employed as CaO precursor, the best placed candidate is natural limestone due to its low cost, wide availability and synergy with the cement industry [8]. As in other chemical looping based processes [9–11] a matter of concern to scale up the CaL technology is the progressive loss of gas-solid reactivity after re-generation, which would make it necessary to re-introduce in the cycle considerable amounts of fresh limestone further increasing the demand of heat at the calciner and the overall cost of the technology [12, 13]. Another line of active research to improve the competitiveness of the CaL technology is thus oriented towards the development of methods and modified CaO precursors to mitigate the limestone irreversible loss of CO_2 capture capacity as the number of c/c cycles builds up [14–21].

Process simulations and economic analysis on the CaL technology [2, 6, 12, 15, 22, 23] are usually carried out by assuming a sorbent deactivation rate and residual CaO conver-sion inferred from thermogravimetric analysis (TGA) multicyclic tests. However, a critical issue that besets lab-scale tests is that, although calcination is carried out at high temper-atures (up to 950°C), technical limitations hinder testing the effect of sorbent regeneration at high CO_2 partial pressure. Due to typically low heating/cooling rates of conventional furnaces ($\lesssim 25$°C/min), the partially carbonated sorbent would suffer an appreciable recar-bonation when the CO_2 concentration is abruptly increased until the temperature reaches

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a sufficiently high value for the reaction equilibrium to be shifted towards decarbonation, which may take about 10 - 15 minutes [24] whereas, in the practical situation, the sorbent is rapidly circulated (at velocities of a few m/s) between reactors. Recarbonation was in fact early proposed by Salvador et al. [25] to reactivate limestone derived CaO and has been recently revisited as the basis of a novel CaL concept [15]. In this alternative concept, the partially carbonated solids would be transported before calcination to a recarbonator reactor wherein carbonation would be further intensified at high temperature (around 800°C) in a high concentration CO_2 atmosphere. TGA tests show that the residual capture capacity of limestone subjected to carbonation/recarbonation/calcination (c/r/c) cycles is substantially increased as compared to ordinary c/c cycles [15]. Process simulation results suggest that this alternative concept would bring about a significant efficiency improvement to the CaL technology by significantly minimizing the amount of solids to be purged [22]. Moreover, the combination of recarbonation with heat pretreatment has a synergistic effect leading to a high and stable CO_2 capture capacity [26]. Yet, sorbent regeneration in TGA c/r/c tests has been carried out under a low CO_2 partial pressure [15, 26], which might influence the results importantly. In spite of failing to resemble practical conditions in some other aspects, TGA [24], tube furnace [27], and batch fluidized bed [28] tests clearly indicate that the presence of CO_2 in the calciner at high concentration may lead to a regenerated sorbent with a marked loss of reactivity, which would make it necessary large amounts of fresh sorbent makeup. In the present manuscript, we report multicyclic TGA tests in which carbonation/calcination cycles are carried out at realistic CaL conditions and the temperature between stages is quickly shifted (300°C/min). As will be seen, the presence of CO_2 at high concentration during calcination has a dramatic effect on the regenerated sorbent reactivity. Moreover, in contrast with results inferred from TGA tests performed by calcination in air, it will

be shown that the introduction of a recarbonation stage accentuates even more the loss of carbonation reactivity. Theoretical arguments based on ab initio modeling and atomistic simulations are used to analyze the obtained results suggesting that the governing CO_2 adsorption/desorption mechanism during decarbonation enhances the preferential growth of the regenerated CaO crystal structure in poorly reactive oriented surfaces. In the light of the physico-chemical mechanisms that rule $CaCO_3$ decomposition further analysis is devoted to get a fundamental understanding on the significant effects caused by H_2O and SO_2 (also present under realistic calcination conditions) on the CaO surface carbonation reactivity.

II. MATERIALS AND METHODS

The material used in our experiments is a natural limestone (Matagallar quarry, Pedrera, Spain) of high purity ($CaCO_3$ 99.62%, $SiO_2 < 0.05\%$, $Al_2O_3 < 0.05\%$, MgO 0.24%, Na_2O 0.08%). CO_2 capture multicyclic tests were carried out using a Q5000IR TG analyzer (TA Instruments) provided with a furnace heated by infrared halogen lamps and equipped with a high sensitivity balance (<0.1 μg) characterized by a minimum baseline dynamic drift (<10 μg). By means of infrared heating the sample is heated/cooled at a very fast rate ($300°C$ min^{-1}). As will be seen below, this is a critical parameter when calcination in c/c tests is to be performed in a CO_2 rich atmosphere, which requires shortening the duration of the transitional period up to reach the calcination temperature in order to avoid significant recarbonation of the solids before decarbonation is started.

As a general initialization procedure, a limestone sample was decarbonated prior to cycling by subjecting it in-situ to a linear heating program ($20°$/min) up to $850°C$ in air. Subsequent c/c cycles consisted of carbonation at $650°C$ (85% air/15% CO_2 vol/vol) and calcination either in air at $850°C$ (mild calcination conditions) or under a high CO_2 con-

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centration atmosphere (70% CO_2/30% air vol/vol) at diverse temperatures (between 900°C

and 950°C). Normally, both carbonation and calcination stages were kept for 5 minutes

each. On the other hand, c/r/c cycles were performed by subjecting the sample to a 3 min

recarbonation stage (10% air/90% CO_2 vol/vol) at 800°C in between the carbonation and

calcination stages. The mass used in all the tests was fixed to 10 mg in order to dismiss

any possible influence of mass transfer related effects on the reaction rate [29]. Likewise,

particles of small size were selected (volume weighted mean 9.5 μm) enabling us to discard

potential effects on the reaction rate caused by diffusion resistance through the pore network

inside the particles, which might be relevant for large particles [30, 31].

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows examples of thermograms (TGs) obtained from c/c tests in which cal-

cination was carried out in a CO_2 enriched atmosphere at 900°C and 950 °C, respec-

tively. The concentration of CO_2 for which the carbonation reaction would be at equi-

librium (at atmospheric pressure) may be calculated from the equation $[CO_2 \text{ vol}\%]_{eq} \simeq$

$4.137 \times 10^9 \exp(-20474/(T+273))$ derived elsewhere from the regression of thermochemical

data [30]. Thus, the minimum temperature to shift the reaction towards decarbonation in a

70% vol CO_2 environment (as used in our multicyclic tests) would be about 870°C. The TG

displayed in Fig. 1a demonstrates however that decarbonation does not occur sufficiently

fast at 900°C as to be completed in short residence times. The low decarbonation rate

precludes full sorbent regeneration in 5 minutes until a number of c/c cycles is reached for

which CaO conversion in the carbonation stage decays below $\simeq 0.2$. According to our tests,

the minimum temperature to achieve near complete decarbonation in 5 min from the 1st

cycle is about 950° as seen in Fig. 1b, which is consistent with results from large pilot-scale

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[3] and batch fluidized bed [28, 32] tests clearly evidencing that temperatures 30-50°C in excess of 900°C are necessary to attain fast enough sorbent regeneration in the calciner. The decline of $CaCO_3$ decarbonation rate with increasing CO_2 partial pressure (especially significant at high CO_2 concentrations) is a well documented observation yet it lacks a satisfactory explanation in regards to the driving physicochemical mechanism [4, 30, 33–38]. Empirical results seem to indicate that decarbonation in CO_2 is governed by a complex process involving a two-stage process consisting of the chemical decomposition of $CaCO_3$ to yield CaO and adsorbed CO_2 followed by CO_2 desorption as early depicted by Hyatt et al. [33] from observations on single calcite crystals calcination. Accordingly, the initial CaO lattice would acquire a metastable rhomboedral structure (as corresponds to calcite) when CO_2 leaves the $CaCO_3$ cell after which a well-crystallized cubic CaO lattice would nucleate from the metastable CaO. At low CO_2 partial pressures the desorption process is kinetically irreversible, but at high CO_2 partial pressures there would be a dynamic and reversible CO_2 adsorption/desorption process limiting the rate of decarbonation [34, 37]. As will be argued from the analysis of our experimental results and review of empirical/theoretical works this complex decarbonation process would also hamper the surface carbonation reactivity of the regenerated sorbent.

The inset of Fig. 1a illustrates a characteristic feature of multicyclic TGA tests that appears intensified in previous reports [24] when calcination is performed under CO_2, which is the enhancement of carbonation during the transitional heating period at increased CO_2 concentration until the temperature reaches a sufficiently high value to reverse the reaction. A precise determination of the CO_2 concentration and temperature evolution in practice during the transition between carbonation and calcination would be desirable in order to replicate these conditions by means of TG analysis. Ideally, the change of temperature in

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TGA multicyclic tests should be quick in order to mimic the practical process in which the sorbent is circulated at high velocities between the carbonator and the calciner. Otherwise, relatively low heating rates as typical of conventional TG furnaces ($\lesssim 25°/\text{min}$) leads to transitional periods of around 10 - 15 min in which the sorbent suffers a notable recarbonation [24], which is not representative of the practical situation. As will be seen, the existence of a recarbonation stage before calcination has important consequences on the multicyclic CaO conversion performance. The fast change of temperature allowed by infrared heating ($300°\text{min}$) in our tests serves to constrain the transitional period interval to about 30 seconds, which allows studying the effect of calcination at high CO_2 concentration on the carbonation reactivity of the regenerated sorbent by means of TG analysis at conditions close to practice.

Multicyclic c/c conversion data at the end of the 5 min carbonation stage are plotted in the inset of Fig. 1b for regeneration by calcination in air at 850°C (5 min) and in 70%CO_2/30% air at 950°C (5 min). As inferred from the data, severe calcination conditions have a quite detrimental effect on the multicyclic conversion in the fast carbonation stage. CaO conversion at the end of the 5 min carbonation stage reaches a value of just $X \simeq 0.05$ after only 10 cycles, which is just about half the residual value of conversion derived from c/c TGA tests performed in a wide diversity of conditions involving calcination at temperatures up to 950°C yet under low CO_2 partial pressure [15, 39]. It seems therefore clear that the very presence of CO_2 at high concentration in the calciner brings about a serious drawback to the efficiency of the CaL technology, which cannot be overlooked in the analysis and search of operation parameters to optimize the efficiency of post-combustion commercial plants mostly relying on the assumption that the sorbent has a residual conversion close to 0.1 [2, 15, 22].

Since carbonation reactivity of CaO in the fast phase depends critically on the available surface area, its gradual reduction as the number of c/c cycles increases is generally considered as the main cause leading to the progressive loss of multicyclic CaO conversion [1, 2, 40, 41]. However, if CaO conversion in the kinetically driven fast phase would be just a function of surface area of the regenerated sorbent, its residual value should be independent of the calcination atmosphere composition whereas our results show otherwise. The presence of CO_2 not only affects the rate of decomposition but also the carbonation reactivity of the surface along which the regenerated CaO lattice grows during decomposition. Before further discussing this critical issue, let us analyze whether the novel CaL concept consisting of the introduction on a recarbonation stage in between carbonation and calcination [15, 25] is useful to enhance the multicyclic CaO conversion also when the recarbonated solid is calcined under CO_2. Figure 2 shows the time evolution of sorbent weight % measured from c/r/c cycles applying mild calcination (Fig. 2a, 850°C in air) and severe calcination (Fig. 2b, 950°C in 70% CO_2/30% air) conditions for regeneration. In agreement with the results recently reported in [15, 26], it is observed that recarbonation does serve to moderate the progressive decay of conversion if the sorbent is regenerated by calcination in air. This is clearly seen in Fig. 3a where conversion data at the end of the carbonation stage from c/r/c and c/c multicyclic tests are plotted. However, recarbonation does not lead to a beneficial effect if calcination is performed under severe calcination conditions (Fig. 2b. In fact, multicyclic conversion data (Fig. 3) demonstrate the opposite. The multicyclic loss of CaO conversion in the carbonation stage is accentuated even more by the introduction of a recarbonation stage if sorbent regeneration is performed under CO_2.

X-ray Diffraction (XRD) analysis of limestone decomposition in air shows that $CaCO_3$ Bragg peaks totally disappear at calcination temperatures $T_c \gtrsim 800°$ after which further

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increase of temperature or calcination time leads to an increase of the CaO crystal coherence length (crystallite size) [42–45]. Likewise, crystallite size is promoted by multicyclic c/c [46] and high CO_2 partial pressure in the calcination environment [44, 47]. Empirical studies demonstrate that the specific surface area of CaO derived from limestone calcination is decreased as the crystallite size is increased following a common trend for a diverse variety of conditions such as varying calcination time and temperature, CO2 concentration in the calcination atmosphere, and presence of impurities/additives [43, 44, 48]. Surface area reduction seems thus to be closely linked to crystallite growth (and not merely due to crystallite agglomeration and closure of pores) as early claimed by Anderson et al. [49, 50] from results showing a correlated intensification of surface area reduction and crystal growth of oxide powders (CaO, MgO, and BeO) calcined in the presence of H_2O, which was particulary marked for CaO. This observation was ascribed to an increase of surface mobility brought about by dynamic adsorption/desorption mechanism of hydroxyl groups (negligible water chemisorption at the typical calcination temperatures is not a critical factor), which resembles (as pointed out by Borgwardt [51]) the CO_2 adsorption/desorption mechanism proposed elsewhere as the governing mechanism for calcination of CaO under CO_2 [30, 33, 34, 36, 37]. Besides of the progressive increase of CaO crystallite size as calcination conditions are harshened, a close look at XRD patterns of calcined limestone samples suggests also a preferential growth of the CaO cubic crystal structure along (100) oriented surfaces (more stable energetically [52]), which can be inferred from the relative increase of intensity and sharpness of Bragg (200) peaks as compared to (111) peaks [43–45, 53]. On the other hand, the first step for surface carbonation should consist of the adsorption of CO_2 molecules on the CaO surface, which is critically determined by the lattice structure [52, 54–58]. Theoretical ab initio atomic-scale studies on the interaction between adsorbed

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$_{205}$ CO_2 species and CaO indicates that $CaCO_3$ nucleation should take place by a localized

$_{206}$ mechanism [52, 54] in agreement with experimental observations by means of metastable

$_{207}$ impact electron spectroscopy (MIES) [59, 60], which further indicate that CO_2 chemisorp-

$_{208}$ tion takes place at regular O^{2-} sites of the surface from the interaction of CO_2 with O^{2-}

$_{209}$ surface anions to form carbonate (CO_3^{2-}) species in a fast process. According to the energy

$_{210}$ balance associated with $CaCO_3$ nucleation in the CaO lattice [54], a preferential growth of

$_{211}$ the CaO crystal structure along certain oriented surfaces might have a decisive role on the

$_{212}$ surface carbonation reactivity. $CO_2 + O \rightarrow CO_3$ substitutions in O sites of (111) oriented

$_{213}$ surfaces of CaO crystals turns to be the most likely mechanism for carbonation whereas

$_{214}$ CO_2 insertion is unfavorable in CaO (100) oriented surfaces because of strong structural

$_{215}$ instabilities [52, 54]. Now, in regards to crystal growth of the regenerated CaO structure in

$_{216}$ the presence of CO_2, and if dynamic CO_2 adsorption/desorption is the driving mechanism

$_{217}$ during calcination as inferred elsewhere [30, 33, 34, 36, 37], this process would involve the

$_{218}$ preferential insertion of CO_2 in the reactive CaO (111) surfaces according to ab initio mod-

$_{219}$ eling results [54]. It is thus conceivable that the CaO crystal structure growth is hindered

$_{220}$ along these reactive surfaces where CO_2 fast adsorbtion/desorption is taking place dynam-

$_{221}$ ically while the CaO crystal growth along poorly reactive (100) surfaces is unrestrained.

$_{222}$ Accordingly, XRD patterns indicate that the degree of crystallinity increases and suggest

$_{223}$ that the CaO cryltal structure evolves preferentially in the most stable (100) planes when

$_{224}$ calcination takes place in a CO_2 rich environment [44]. This mechanism would lead to a

$_{225}$ CaO crystal structure regenerated upon calcination under CO_2 with very low surface car-

$_{226}$ bonation reactivity. Altogether, surface area reduction by crystallite enlargement and the

$_{227}$ promoted growth of CaO crystal structure along CaO (100) surfaces (unfavorable for $CaCO_3$

$_{228}$ nucleation), would contribute to a drastic drop of CaO conversion after the first regener-

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ation with a rapid convergence in the next cycles to a very low value as demonstrated by our experimental results (Fig. 3). Generally, it can be said that an increase of regenerated CaO crystallite size, implying a surface area reduction and a selective growth along poorly reactive oriented surfaces, would lead to a steep drop of carbonation activity. In line with this argument, Beruto and Searcy already reported back in 1976 [61] that CaO stemming from $CaCO_3$ decomposition in vacuum showed an extremely high surface reactivity regardless of calcination temperature (as high as 1050°C). XRD patterns of this highly reactive and high surface area CaO exhibited a quite low crystallite size with very weak diffraction peaks of height independent of calcination temperature as opposed to CaO resulting from decomposition under CO_2 [62].

Figure 4 shows the time evolution of sorbent weight and rate of weight loss measured in our experiments during the 1st calcination stage at 850°C under air and 950°C under $70\%CO_2/30\%$air (after carbonation and carbonation/recarbonation, respectively). The rate of decarbonation is seen to be decreased if calcination in air is preceded by recarbonation, which is consistent with previous studies indicating a reduction of the decomposition rate with the $CaCO_3$ content of the partially carbonated sorbent as may be described from a shrinking core model under chemical reaction control [4]. In contrast, a noteworthy result shown in Fig. 4d is that the decarbonation rate at 950°C under CO_2 is significantly promoted when calcination is preceded by carbonation/recarbonation as compared to only carbonation. Besides of the already discussed very low carbonation reactivity in the fast phase observed in c/r/c tests for calcination under CO_2 at 950°, a peculiar feature seen in these TGs is the significant enhancement of the carbonation reactivity in the slow phase of the carbonation stage as well as in the recarbonation stage (both diffusion-controlled [63]) as can be seen in Fig. 2b. Analogously, previous studies show that the carbonation activity

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in the fast phase is low and carbonation in the diffusion controlled phase is enhanced for CaO samples subjected to prolonged heat pretreatment under harsh conditions [14, 64]. As argued above, a low surface carbonation reactivity in the fast phase would be due to promoted surface area reduction and preferential crystal growth along poorly reactive surfaces. On the other hand, the enhancement of diffusion controlled carbonation must be linked to a low resistance to diffusion of CO_3^{2-} mobile ions and counter-current diffusion of O^{2-} anions through the $CaCO_3$ product layer [65], which is most likely caused by a high density of lattice structural defects [66]. A correlation between the density of crystal imperfections and the carbonation rate in the diffusion controlled phase was already suggested by Bhattia and Pelmutter from experimental results on samples showing diverse degrees of crystallinity [67]. Since CO_2 insertions into the CaO structure should imply intense distortions of the crystal lattice [54], structural defects might be expected from the strong shear stresses caused by decomposition under CO_2 in the recarbonated structure, which would involve dynamic and reversible CO_2 adsorption/desorption at crystal sites in the bulk of the solid. These structural imperfections would accelerate decomposition as observed in our work by helping diffusion of mobile ions from the bulk of the solid. Structural defects that accelerate decarbonation of the sample subjected to c/r/c would at the same time enhance diffusion controlled carbonation as shown in Fig. 2b. Following this reasoning, it would be expectable that the decarbonation rate is decreased as the number of c/r/c cycles is increased since carbonation in the bulk of the solid is gradually reduced as the sorbent looses activity. Figure 5 shows the sorbent weight loss rate for c/r/c tests performed by regenerating it in air (850°C) and 70%CO_2/30%air (950°C), respectively. As may be observed, the maximum rate of decarbonation remains essentially constant for the sample subjected to c/r/c cycles calcined in air, yet it decreases with the cycle number for calcination in CO_2 in accordance with the

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above argument. Since dynamic CO_2 adsorption/desorption in the CaO crystal does not occur when calcination is performed in air, it is explainable that the decarbonation rate does not show a strong dependence with the cycle number (Fig. 5) neither diffusive carbonation activity is enhanced (Fig. 2a) for the sorbent subjected to c/r/c cycles regenerated in air.

In the light of Fig. 3, it might be concluded that recarbonation would be detrimental to the CaL technology efficiency under conditions necessarily implying calcination at temperatures around 950°C, high CO_2 partial pressure, short residence times and low CO_2 partial pressure for carbonation. One might wonder however whether the notable acceleration of decomposition observed when calcination under CO_2 is preceded by recarbonation (Fig. 4d) would allow lowering down the calcination temperature below 950°C while still achieving full sorbent regeneration under high CO_2 partial pressure. From the practical point of view, a potential decrease of the calcination temperature by means of recarbonation would expectedly mitigate the drastic decay of conversion in the fast carbonation phase while, at the same time, would improve the energy efficiency of the process. To further investigate this point, c/r/c multicyclic tests were carried out in our work at lower calcination temperatures and high CO_2 partial pressure. Figure 6 shows the time evolution of sorbent weight and rate of weight loss during the 1st calcination stage at 900°C and 925°C (preceded by carbonation/recarbonation) and at 900°C (preceded by carbonation) under $70\%CO_2/30\%$air. As can be seen, the recarbonation stage does not yield an acceleration of decarbonation at these reduced temperatures, which are insufficient to yield full decomposition in the calcination stage. In fact, the decomposition rate at 900°C after carbonation/recarbonation is slightly lower than the decarbonation rate at 900°C after just carbonation in accordance with the observed effect of recarbonation when regeneration was performed in air (Figs. 4a and 4b). Thus, calcination at temperatures of at least 950°C are also needed in c/r/c cycles

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to achieve a full sorbent regeneration from the 1st cycle in a high CO_2 partial pressure environment. TGs comprising the first c/r/c cycles are compared in Fig. 7 for calcination under 70%CO_2/30%air at 950°C and 900°C, respectively. In addition to the incomplete decarbonation at 900°C already seen, it is observed that diffusion-controlled carbonation and recarbonation are not enhanced in the 2nd cycle for the sample calcined at this reduced temperature in contrast with the behavior exhibited by the sample calcined at 950°C. This is consistent with the argument discussed above that dynamic adosorption/desorption of CO_2 (taking place at a high rate for 950°C) causes structural defects in the CaO structure regenerated at 950°C, which enhance decomposition and enhance diffusive carbonation. At lower temperatures, this dynamic process would not be fast enough for the internal stresses generated to be sufficiently intense as to provoke structural imperfections. Hence, recarbonation at this reduced temperature in the first cycle would not favor the decomposition rate nor the rate of diffusion-controlled carbonation and recarbonation in subsequent cycles.

Until now we have focused our work on the effect of the presence of CO_2 at high partial pressure in the calcination atmosphere for sorbent regeneration. However, the role of H_2O should be analyzed to assess the effect of sorbent regeneration under realistic calcination conditions. Water vapor would be present in the calciner if oxy-combustion is employed to raise the calcination temperature at vol concentrations typically around 20% [68, 69] or even at higher concentrations if steam is injected as proposed elsewhere to reactivate the sorbent [68, 70]. Unfortunately, technical limitations of our TGA apparatus prevent us for carrying out multicyclic tests in the presence of H_2O at these concentrations. However, useful conclusions may be derived from a review on works concerning $CaCO_3$ decomposition as well as multicyclic c/c tests carried out in the presence of H_2O/CO_2 during calcination. Even though the equilibrium temperature below which CaO hydration might proceed at atmo-

spheric pressure is far below the calcination temperature (at atmospheric pressure $Ca(OH)_2$ is fully decomposed for temperatures above $\sim 420°C$ [1, 18, 71]), the presence of H_2O is seen to have a strong effect on $CaCO_3$ decomposition, which is furthermore coupled to the effect of CO_2. Empirical observations [38, 50, 51, 68, 72, 73] demonstrate that the simultaneous presence of H_2O and CO_2 contribute synergistically to a reduction of surface area. Yet, and in contrast with the effect of CO_2, decomposition of limestone under H_2O is accelerated [35, 38]. Moreover, despite of surface area reduction, injection of steam during calcination is seen to increase the regenerated CaO carbonation reactivity [68, 70], which further proves that surface carbonation reactivity is not just determined by the specific surface area. In close similarity to the mechanism governing calcination under CO_2, H_2O dynamic adsorption/desorption was proposed as the driving mechanism during calcination under H_2O in the early works of Anderson et al. [49, 50], which has been upheld by more recent experimental observations using dynamic XRD analysis [35]. Moreover, experimental results suggest that H_2O adsorption occurs faster and to a higher extent than CO_2 adsorption, which would lead to a weakening of the $CaO \times CO_2$ bond. Thus, the presence of H_2O in calcination would catalyze decomposition of the crystal $CaCO_3$ lattice by shielding CO_2 adsorption [35]. It is thus plausible that the detrimental effect of calcination under CO_2 on CaO surface carbonation reactivity could be counterbalanced by H_2O dynamic adsorption/desorption as inferred from recent theoretical works [55–57]. Surface energy minima calculations by means of atomistic simulations analysis of CO_2/H_2O co-adsorption in CaO crystal surfaces show a particularly favorable affinity of the (111) surface for H_2O adsorption compared with the (100) surface with a preference of H_2O adsorption over CO_2 adsorption [55–57]. This is also in agreement with previously reported UPS and XPS measurements [58] on H_2O adsorption on faceted (100) and (111) crystals indicating a faster and more intense adsorption of H_2O as compared

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to CO_2 [35]. Interestingly, atomistic simulations show that, at high temperature, only the (111) surface remains active with an intensified affinity for adsorption of H_2O as compared to CO_2 [57]. In accordance with ab initio modeling predictions [54], adsorption of either H_2O or CO_2 is not favorable in the rest of surfaces at high temperature [57]. These studies suggest that, in the absence of H_2O, CO_2 adsorption will take place in the (111) surfaces whereas increasing H_2O partial pressures will hinder CO_2 adsorption. Arguably, H_2O adsorption during decomposition of $CaCO_3$ would thus allow the growth of the regenerated CaO crystal structure along reactive (111) surfaces otherwise restrained by CO_2 adsorption, which would result in a CaO surface structure with higher carbonation reactivity. In regards to the practical application, this implies that the presence of steam in the calciner (either generated by oxy-combustion or injected) would mitigate the drastic loss of CaO conversion due to a high CO_2 partial pressure in a dry atmosphere as seen in our work. TGA tests recently reported [68, 70] in which calcination is performed in a high CO_2 partial pressure atmosphere with the simultaneous presence of H_2O show accordingly that steaming in the calcination stage yields an improvement of the carbonation reactivity. Since the presence of H_2O/CO_2 promotes synergistically further surface area reduction, it is explainable that the presence of H_2O would have a detrimental effect on the regenerated CaO carbonation reactivity above a critical concentration as seen from TGA tests [70]. According to this argument, it is also foreseeable that the presence of steam during calcination, and in the absence of CO_2, does not yield an increase of the CaO carbonation reactivity as seen in the results from TGA tests reported in [74]. It can be thus inferred that the production of H_2O by oxy-combustion in the calciner currently employed in pilot-scale plants mitigates the adverse effect on the CaO carbonation reactivity arising from calcination under CO_2. This should be taken into account if oxy-combustion is replaced by more energetically efficient heating

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methods currently under investigation [5, 6], which would lead to a drastic loss of CaO conversion unless steam is injected in the calciner. If the temperature is decreased to shift the reaction equilibrium towards carbonation, atomistic simulations analysis (at T=627°C similar to carbonation temperature in the CaL process) indicate that reactive (111) surfaces can present an hydroxylated layer (dissociative H_2O adsorption) with an energetically favorable interaction between the hydroxide and carbonate species [57]. The favorable interaction between hydroxide and carbonate species would promote CO_2 chemisorption in these sites thus intensifying the reactivity towards carbonation as seen from TGA tests in which steam is injected in the carbonation phase [28, 68, 70].

As discussed above, theoretical and experimental works indicate that the surface carbonation reactivity of CaO regenerated by calcination is determined by an interplay between the growth of the CaO crystal lattice along certain oriented surfaces depending on the competition between the adsorption/desorption mechanisms of H_2O and CO_2 species, which is particularly favorable at high temperatures in the (111) surfaces that remain reactive towards carbonation. SO_2 will be also present in the calciner due to fuel oxy-combustion and represents a further relevant source of inefficiency for the CaL technology due to the irreversibility of sulphation at the calcination temperature [1, 28, 32, 75]. The main factor limiting CaO sulphation reactivity is pore blocking, hence sulphation is basically promoted by the increase of pores size due to sintering. Wider pores allow accommodating large volume sulfate ions, thus intensifying the surface sulphation reactivity [72, 76, 77]. Accordingly, sulphation conversion is seen to increase with the cycle number in multicyclic carbonation/calcination tests [28]. The beneficial effect of calcining under CO_2 towards sulphation was early reported by O'Neil et al. [76] and a similar favorable consequence is expected from the presence of H_2O [28]. Thus, although the presence of CO_2 and H_2O during calcination in the absence of SO_2

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leads to contrasting effects on the carbonation reactivity (arguably related to preferential crystal growth), both H_2O and CO_2 would contribute to an increase of the sulphation reactivity of the regenerated CaO since sintering is synergistically enhanced in the presence of both gases [51]. As a result, the generation of SO_2 by oxy-combustion would nullify the favorable effect of H_2O on the surface carbonation reactivity as suggested by multicyclic carbonation/calcination tests with calcination under oxy-firing conditions [28, 32]. In order to further assess the multicyclic CaO conversion performance under realistic calcination conditions it is thus necessary to analyze in further depth the complex interplay between the effects of CO_2, H_2O and SO_2 on the porosity and crystal structure of the calcined solids, which determine their reactivity towards carbonation.

IV.   CONCLUSIONS

TGA tests reported in the literature in which the sorbent is regenerated by calcination at temperatures up to 950°C (but under low CO_2 partial pressure) show that the conversion of limestone derived CaO decreases gradually as the number of cycles builds up and converges towards a residual value close to 0.1. Process simulations and economic analysis of the CaL technology at a commercial level are usually carried out based on these results, which further suggest the suitability of a novel CaL concept to enhance the multicyclic CaO conversion based on the introduction of an intermediate reactor between the carbonator and the calciner wherein the partially carbonated solids would be additionally carbonated at high CO_2 partial pressure and relatively high temperature. On the other hand, it is well known that the presence of CO_2 in the calcination atmosphere has a catalyzing effect on crystallite growth. Moreover, CaO resulting from decarbonation under CO_2 would show a preferential growth of the crystal structure along (100) oriented surfaces, wherein insertion of CO_2 for $CaCO_3$

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nucleation is energetically unfavorable at high temperatures, whereas the growth along still reactive (111) oriented surfaces is impaired. Yet, low heating/cooling rates of common furnaces prevent lab-scale tests for replicating carbonation/calcination (c/c) cycles under realistic conditions involving high CO_2 partial pressure for sorbent regeneration and short transition periods between stages. In our work we have analyzed the multicyclic carbonation performance of limestone subjected to c/c and carbonation/recarbonation/calcination (c/r/c) cycles in a TG analyzer under conditions implying carbonation at low CO_2 partial pressure and calcination at high CO_2 partial pressure as well as very quick heating/cooling rates. Our results indicate that the drop of CaO conversion is greatly magnified in the first cycles because of the very presence of CO_2 at high concentration in the regeneration stage. As a result, CaO conversion falls after only a few cycles to a value just about half that of residual conversion generally assumed from TGA tests in which calcination is carried out at high temperature but at low CO_2 partial pressure. Moreover, our results demonstrate that the introduction of a recarbonation stage yields an adverse effect further accelerating the decay of CaO conversion. Recarbonation leads to an intensification of diffusion controlled carbonation, which suggests that structural defects are developed due to intense bulk stresses caused by CO_2 adsorption/desorption during decarbonation at high temperature. Nonetheless, the presence of H_2O in the calciner would counteract the deeply adverse effect of CO_2. Arguably, highly favorable dynamic adsorption of H_2O in the CaO structure would compete with CO_2 adsorption thus allowing the crystal lattice to grow along reactive surfaces. The production of H_2O in the calciner of pilot-scale plants by fuel oxy-combustion would therefore serve to mitigate the, otherwise intense, loss of carbonation reactivity by regeneration under CO_2. Steam injection in the calciner should be thus necessary if oxy-combustion is replaced by potentially more efficient techniques to raise the temperature currently under

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investigation. Further multicyclic carbonation/calcination tests should be pursued in future works to quantify the effect of the simultaneous presence of CO_2, H_2O in the calcination stage at realistic CaL conditions for post-combustion capture.

VI.   REFERENCES

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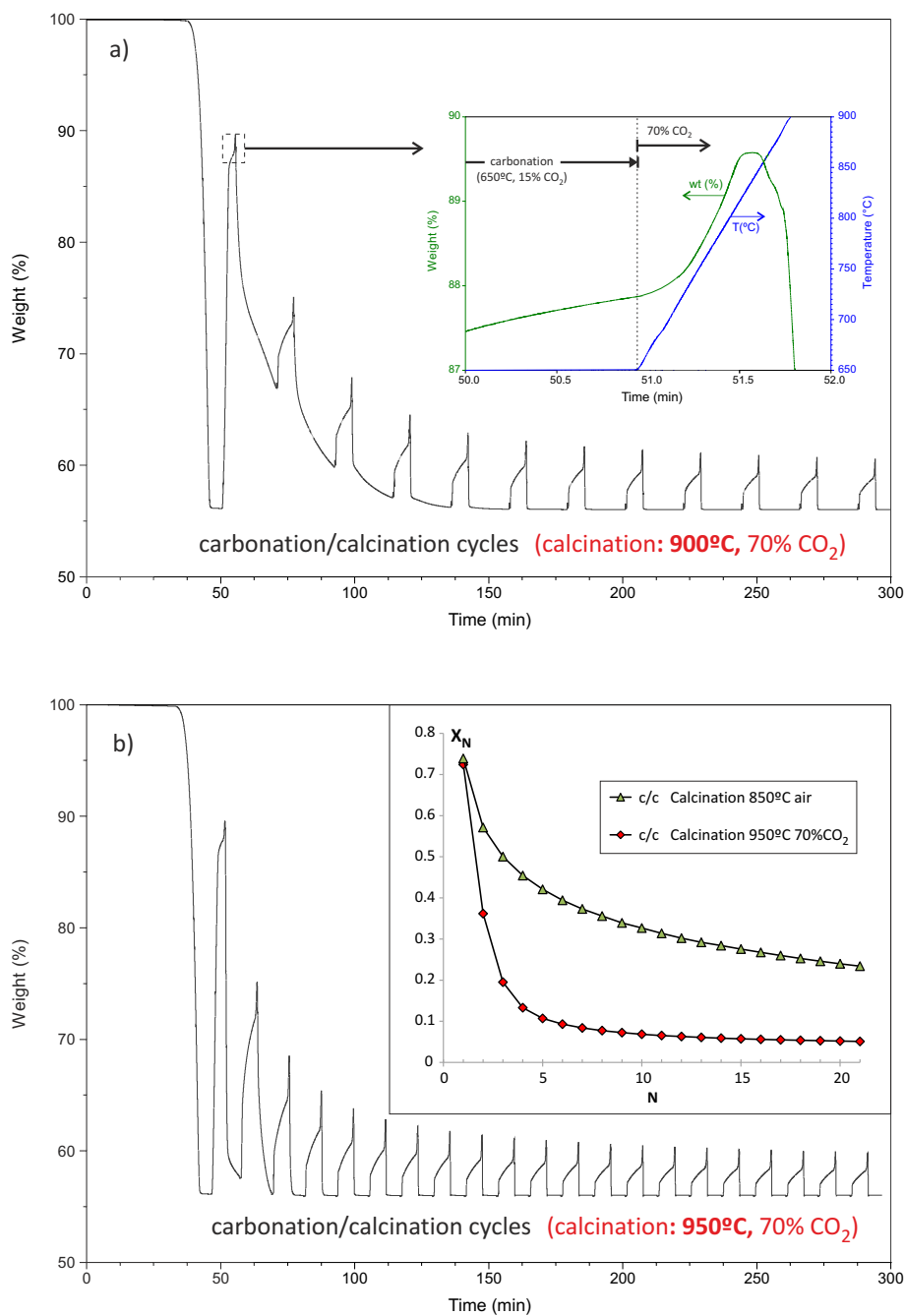
FIG. 1. Time evolution of sorbent weight % during carbonation/calcination cycles. Carbonation at 650°C for 5 min (15% CO_2/85% air vol/vol). Calcination at 900°C for 15min (a) and at 950°C for 5 min (b) in a 70%CO_2/30% air vol/vol atmosphere. The inset in a) is a zoom showing in detail the wt% and temperature time evolution during the transition period between the end of the carbonation stage and beginning of calcination (heating rate 300°C/min). The inset in b) shows data of CaO conversion measured at the end of the carbonation stage as a function of the cycle number for calcination in air at 850°C (5 min) and calcination in 70%CO_2/30%air at 950°C (5 min).

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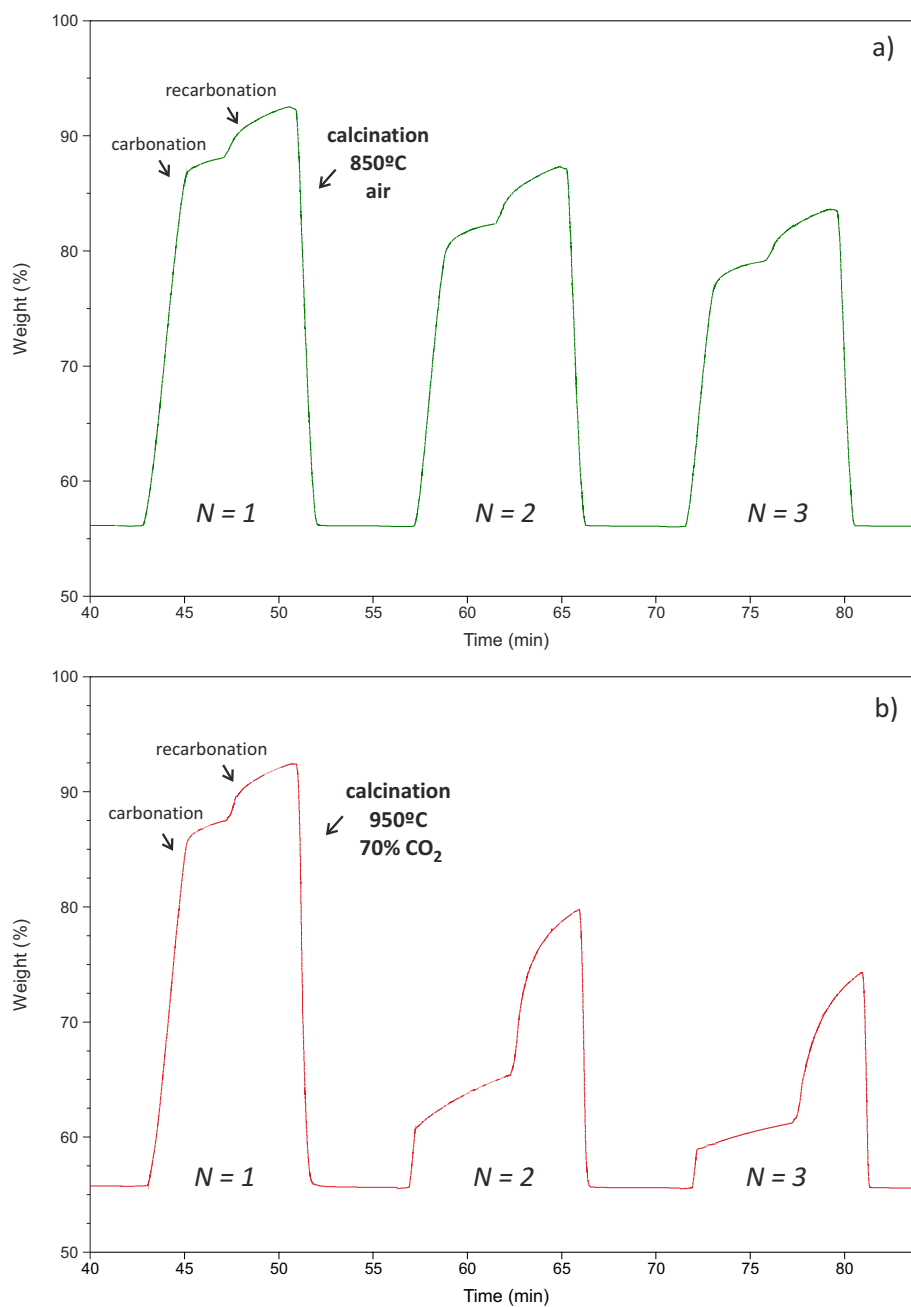
FIG. 2. Time evolution of sorbent weight % during carbonation/recarbonation/calcination cycles $N = 1, 2, 3$. Calcination at $850°C$ in air (a) and at $950°C$ in $70\%CO_2/30\%$air (b).
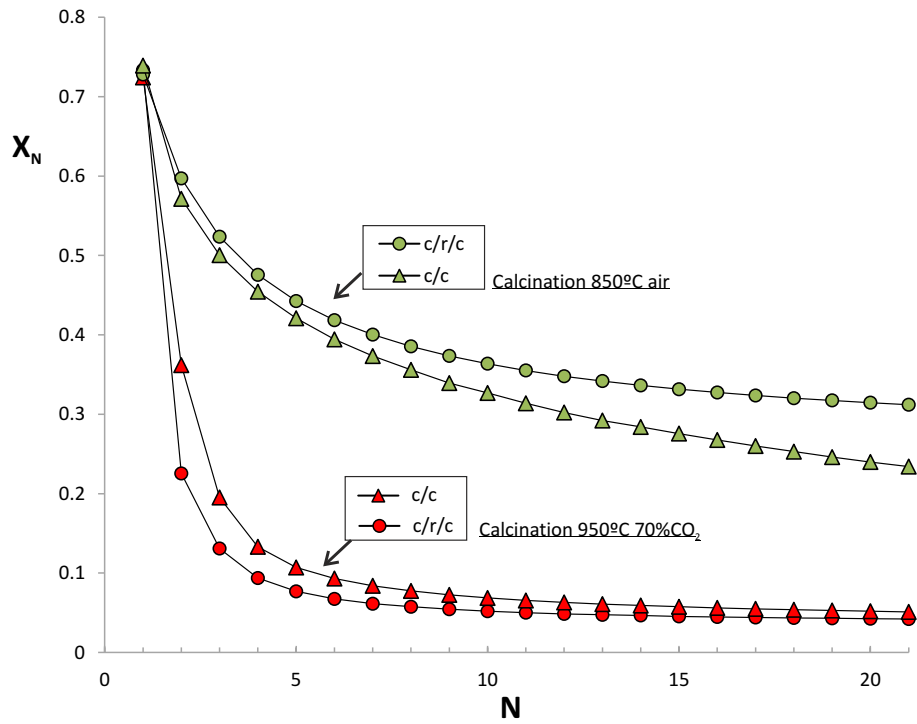
FIG. 3. CaO conversion at the end of the carbonation stage as a function of the cycle number for carbonation/calcination and carbonation/recarbonation/calcination cycles. a) Calcination in air at 850°C. b) Calcination in 70%CO$_2$/30%air at 950°C.
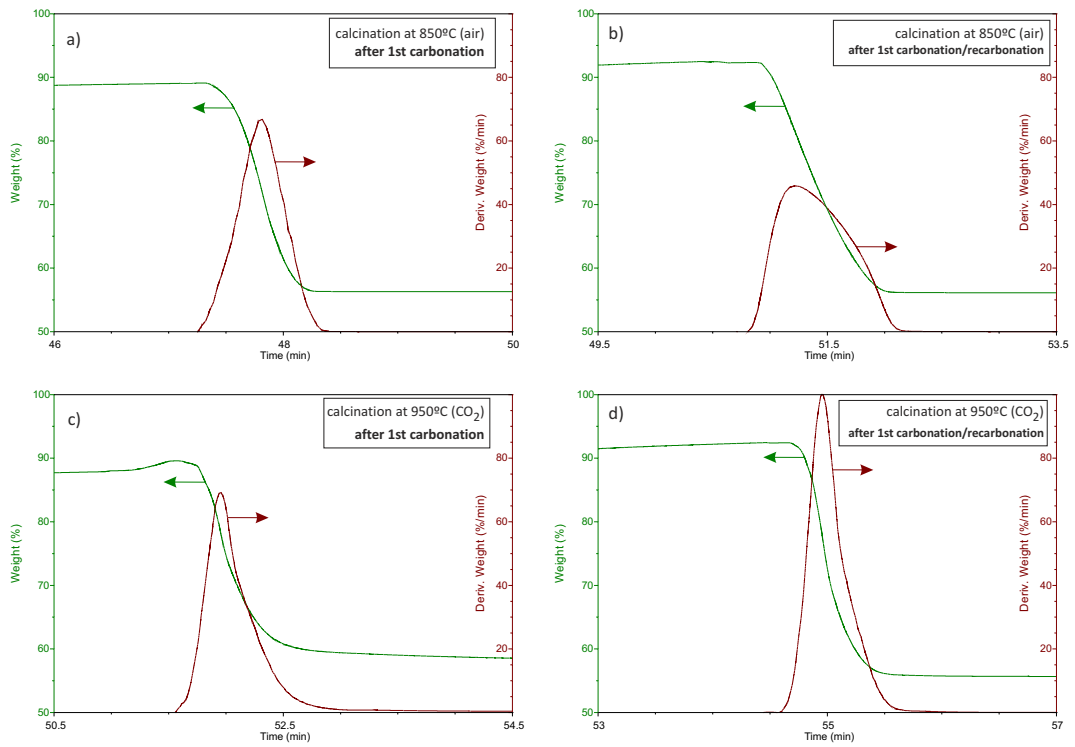
FIG. 4. Time evolution of sorbent weight % and rate of weight % loss during the 1st calcination stage at 850°C in air (a: after carbonation; b: after carbonation/recarbonation) and at 950°C in 70%CO_2/30%air (c: after carbonation; d: after carbonation/recarbonation).
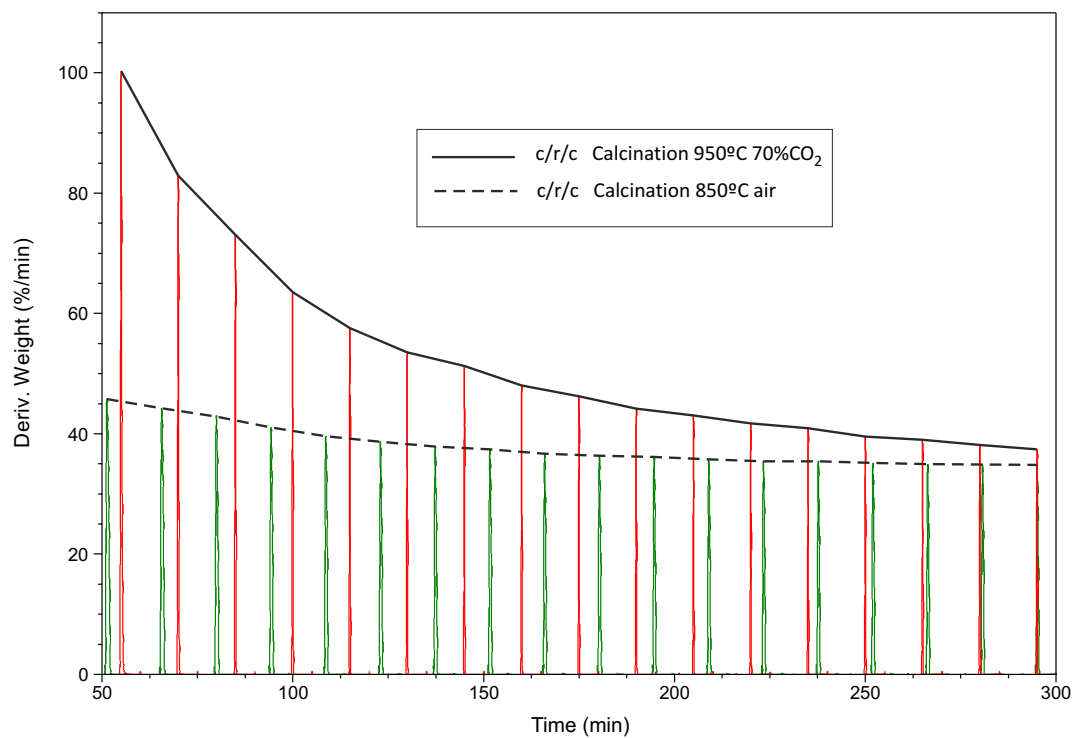
FIG. 5. Time evolution of rate of sorbent weight % loss during regeneration by calcination at 850°C in air and at 950°C in 70%CO$_2$/30%air in carbonation/recarbonation/calcination cycles. Values at maximum rates of each cycle are joined by lines.
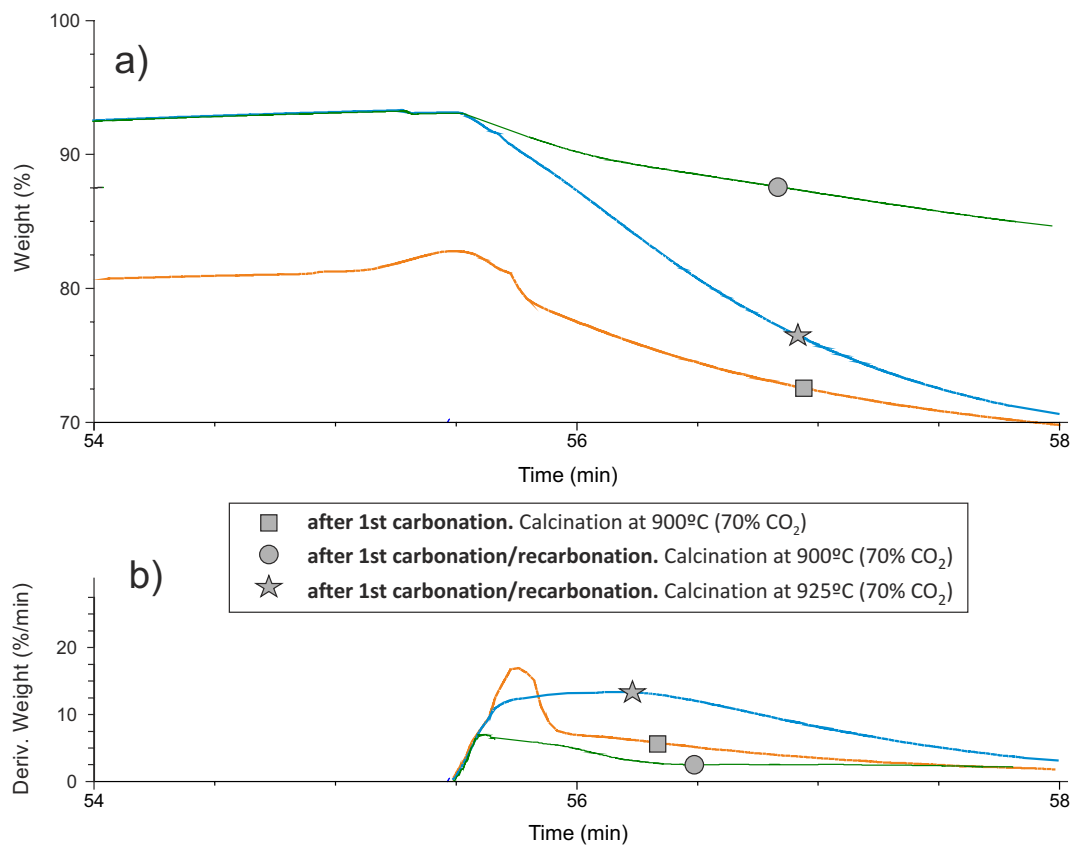
FIG. 6. Time evolution of sorbent weight % (a) and rate of weight % loss (b) during the 1st calcination stage under 70%CO$_2$/30%air after 1st carbonation (at 900°C) and after 1st carbonation/recarbonation (at 900°C, 925°C, and 950°C as indicated).
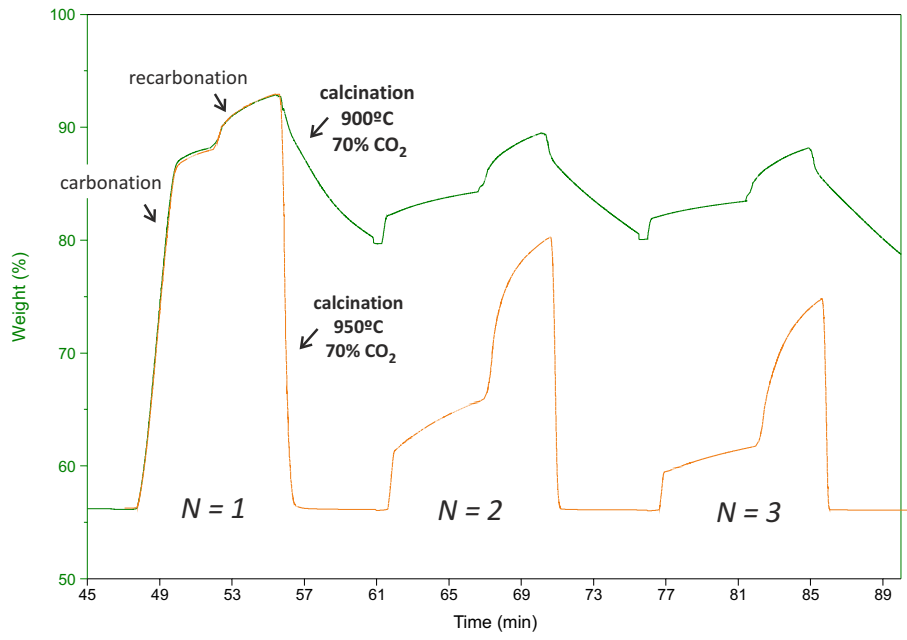
FIG. 7. Time evolution of sorbent weight % during carbonation/recarbonation/calcination cycles $N = 1, 2, 3$ for calcination in $70\%CO_2/30\%$air at $900°$C and at $950°$C as indicated.