

# Constant rate thermal analysis for enhancing the long-term CO<sub>2</sub> capture of CaO at Ca-looping conditions

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## Abstract

Experimental results are reported on the (Ca-looping) multicyclic CO<sub>2</sub> capture of CaO and nanosilica/CaO composites derived from Ca(OH)<sub>2</sub> and nanosilica/Ca(OH)<sub>2</sub> dry mixtures subjected in-situ to linear and Constant Rate Thermal Analysis (CRTA) preheating programs in either air or air/CO<sub>2</sub> atmospheres. By means of CRTA preheating the rates of the reactions taking place during pretreatment are kept at a constant and small value along the entire process. In agreement with a pore skeleton model, previously proposed in the literature for explaining the behavior of natural limestones thermally pretreated, our results suggest that air/CO<sub>2</sub>-CRTA pretreatment yields a thermally stable hard skeleton of poorly reactive CaO on which a soft skeleton of reactive CaO would be supported. The sorbent subjected to this preheating program exhibits a reactivation in the very first carbonation/calcination cycles, after which CaO conversion decays slowly with the cycle number. In contrast, linearly or air-CRTA preheated sorbents show a significant decrease of CaO conversion within the first cycles. In the latter case, CaO multicyclic conversion fits well to a model where it is assumed that the progressive reduction of surface area as the number of carbonation/calcination cycles is increased obeys to sintering of the preheated sorbent skeleton as it is subjected to repeated calcinations during cycling. In the former case, CaO conversion data conforms to the prediction by a model in which the loss of surface area is mainly due to sintering of a nascent CaO soft skeleton regenerated in the diffusive carbonation phase, which is enhanced by the air/CO<sub>2</sub>-CRTA pretreatment. As regards the effect of nanosilica, the results indicate that it slows down CaO sintering during pretreatment, which hinders the development of a stable CaO skeleton thus hampering reactivation and stabilization of conversion. On the other hand, as CaO sintering is also lessened during looping calcination, nanosilica is useful to increase the absolute values of CaO conversion.

## I. INTRODUCTION

Technologies based on the Ca-looping (CaL) process are being currently implemented for an efficient capture of  $\text{CO}_2$  from postcombustion flue gas as well as for enhancing steam methane reforming by  $\text{CO}_2$  on-line capture [1–3]. The CaL process involves the carbonation reaction of  $\text{CaO}$  to capture  $\text{CO}_2$  and the subsequent calcination of  $\text{CaCO}_3$  to regenerate the sorbent in order to be reused in a subsequent cycle. By taking into account the tradeoff between the reaction equilibrium driving force and reaction kinetics, carbonation is carried out in practice at temperatures around  $650^\circ\text{C}$ . In the calciner,  $\text{CaCO}_3$  decomposes to yield  $\text{CaO}$  and a pure, dry stream of  $\text{CO}_2$ , which is compressed and transported for sequestration. Oxyfired combustion, by burning coal with pure  $\text{O}_2$ , is carried out in the calciner in order to supply the necessary heat for decarbonation and to produce a sufficiently high concentrated stream of  $\text{CO}_2$  suitable for purification and compression [4]. Decarbonation of  $\text{CaCO}_3$  at practical rates is typically carried out at temperatures above  $900^\circ\text{C}$ .

Carbonation of  $\text{CaO}$  occurs in two well differentiated phases. In a first carbonation stage,  $\text{CO}_2$  is rapidly chemisorbed on the free surface of the  $\text{CaO}$  particles. After a thin layer of  $\text{CaCO}_3$  (between 30 and 50 nm thick [5]) covers the free surface of the sorbent particles,  $\text{CO}_2$  sorption turns to be controlled by a much slower phase characterized by solid-state diffusion of  $\text{CO}_2$  through the solid  $\text{CaCO}_3$  layer. The most interesting phase for post-combustion  $\text{CO}_2$  capture purposes is fast carbonation since typical gas velocities are high and  $\text{CO}_2$  concentration is low. Ideally, the sorbent should react fast toward a maximum conversion and maintain it as the number of carbonation/calcination cycles is increased [6, 7]. Yet, a major inconvenient for the technological use of the CaL process is the loss of fast capture capacity by  $\text{CaO}$  as the number of cycles is increased, which is mainly due to sintering of  $\text{CaCO}_3$  at the high calcination temperatures. Sintering of the nascent  $\text{CaO}$  after decarbonation causes a progressive decrease of the active surface area available for fast  $\text{CO}_2$  capture. Most natural limestones exhibit a residual capture capacity that remains constant after a large number of carbonation/calcination cycles, which is just about 0.06 (grams of  $\text{CO}_2$  sorbed/grams of  $\text{CaO}$ ) [8]. Even though such a small value of the residual capture capacity is efficiently compensated by high solid circulation rates in pilot scale plants [6] and the spent sorbent could be used in a number of applications such as cement manufacture [9], it is recognized that enhancing the residual fast capture capacity

of Ca-based sorbents at a low cost would represent a substantial improvement of CaL based technologies [10].

Besides of natural limestone a cheap and abundant material which has been considered for its use in the CaL process is dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) [11, 12]. Since MgO does not suffer carbonation [13], the stoichiometric capture capacity of calcined  $\text{CaCO}_3 \cdot \text{MgCO}_3$  is just 0.46 as compared to 0.79 of  $\text{CaCO}_3$ . However, the presence of  $\text{MgCO}_3$  in dolomite, with a higher melting point than  $\text{CaCO}_3$ , mitigates material sintering and serves to disperse CaO, which leads to an enhancement of the long term multicyclic fast capture [1, 14, 15]. A current area of research is focused on the formulation of synthetic/modified sorbents to improve the thermal stability and thus the durability of limestones during repeated carbonation/calcination cycles [16, 17]. For example, one of the nanosilica/CaO composites analyzed in this work exhibits an enhanced fast and residual  $\text{CO}_2$  capture capacity [18]. Hydration of the spent CaO is another efficient and relatively cheap approach to reactivate natural limestones as shown by pilot-scale tests [1, 19, 20] even though it may cause a decrease of the mechanical strength of the sorbent, which would enhance particle attrition and consequently loss of material due to excessive elutriation [21]. An alternative reactivation strategy to enhance the multicyclic capture capacity of Ca-based sorbents consists of subjecting the sorbent to a preheating treatment [22–26], which will be the subject of the present manuscript.

Thermal activation of natural limestone was first examined by Manovic and Anthony [23], who observed a beneficial effect of a pretreatment consisting of a prolonged exposure of the sorbent to isothermal calcination under a  $\text{N}_2$  atmosphere. For example, the capture capacity of limestones preheated for 6 h at  $1000^\circ\text{C}$  increased with the number of carbonation/calcination cycles. A separate study [27] indicated that the chemical composition of the sorbent played also an important role in determining the CaL sorbent performance after thermal pretreatment. Doping a high purity limestone with  $\text{Na}_2\text{CO}_3$  produced a drastic loss of activity with increasing cycles despite thermal pretreatment. On the other hand, when doped with  $\text{Al}_2\text{O}_3$ , the activity of the doped limestone was actually augmented. Florin and Harris [25] have also observed a reactivation of pure CaO derived from nanosized  $\text{CaCO}_3$  after high temperature preheating treatment at  $900^\circ\text{C}$  and  $1100^\circ\text{C}$  for 12h in air. Albrecht et al. [22] showed that, after more than 1000 carbonation/calcination cycles, the capture capacity of CaO and MgO/CaO composites was substantially improved when they were initially preheated at  $1100^\circ\text{C}$  for 5 h as compared to calcination at  $900^\circ\text{C}$  for 3 h or at

1100°C for 2 h. The atmosphere under which thermal pretreatment is performed influences the long-term capture capacity of limestones. Manovic et al. [24] observed that preheating limestone in a CO<sub>2</sub> atmosphere is more effective than doing it in air. The efficiency of pretreatment has been attributed to recrystallization of CaO by deep sintering leading to the formation of a hard stable skeleton, which was promoted if pretreatment was conducted in a CO<sub>2</sub> atmosphere [24]. Ozcan et al. [26] found also that the stability of several CaO-based sorbents was favored by thermal pretreatment in a CO<sub>2</sub> enriched atmosphere (CO<sub>2</sub> vol % above 50%). This is in accordance with previous studies reported in the literature [28, 29] showing that sintering of nascent CaO is greatly accelerated by isothermal heating in the presence of CO<sub>2</sub>. On the other hand, the works reported by Arias et al. [10, 30] and Chen et al. [31] indicate that the gain of activity of thermally pretreated sorbents would be due to the enhancement of carbonation due to solid-state diffusion on the deeply sintered skeleton. After a quick decarbonation, the release of CO<sub>2</sub> captured during the promoted diffusive carbonation phase would give rise to a porous soft skeleton with a promoted surface area available for carbonation in the next carbonation. Besides of improving the CO<sub>2</sub> capture efficiency, a further benefit offered by thermal pretreatment would be increasing the mechanical strength of the sorbent [23], which would prevent excessive sorbent elutriation from the reactor as due to particle attrition [32, 33].

In our work we subject CaO-based sorbents in-situ to accurately controlled preheating programs in which the increase of temperature is either linear or based on constant rate thermal analysis (CRTA) [34, 35] and under either air or air/CO<sub>2</sub> atmospheres. During the CRTA pretreatment, the evolution of temperature is controlled for the reactions taking place during preheating to be kept at a small and constant prefixed value. The CRTA technique has been specially useful in the past to minimize the mass and heat transfer phenomena that accompanies thermal decomposition processes [34–38]. Our main scope is to investigate whether a preheating treatment based on CRTA has any effect on the multicyclic capture performance of CaO and nanosilica/CaO composites as compared to a linear preheating program and depending on the presence of CO<sub>2</sub>.

## II. EXPERIMENTAL MATERIALS AND PROCEDURE

The powder used as CaO precursor in our study has been  $\text{Ca}(\text{OH})_2$  from Sigma-Aldrich (puriss. p.a., >96%, <3%  $\text{CaCO}_3$ ). Nanostructured fumed silica powders (Aerosil-R974 and Aerosil-300 from Evonik [39]) have been used as additives. Aerosil-300 is a hydrophilic fumed silica with a specific surface area of  $300\pm 30 \text{ m}^2/\text{g}$  and moisture content (2 h at  $105^\circ\text{C}$ )  $\leq 1.5 \text{ wt } \%$ . Aerosil-R974 is based on a hydrophilic fumed silica after-treated with DDS (dimethyldichlorosilane) to render it hydrophobic, with a specific surface area of  $170\pm 20 \text{ m}^2/\text{g}$  and moisture content (2 h at  $105^\circ\text{C}$ )  $\leq 0.5 \text{ wt } \%$ . To make the nanosilica powder hydrophobic, hydroxyl groups on hydrophilic fumed silica surfaces are replaced by dimethylsilyl groups of silane, which yields low hydrogen bonding interaction. Powder mixtures were prepared by dry physical mixing of nanosilica and  $\text{Ca}(\text{OH})_2$  (1/6 weight ratio).

The  $\text{CO}_2$  capture performance (at conditions close to the CaL process) of CaO and nanosilica/CaO composites derived from  $\text{Ca}(\text{OH})_2$  and hydrophobic-nanosilica/ $\text{Ca}(\text{OH})_2$  dry mixtures has been reported in ref. [18]. In that study, the samples were preheated in air applying a linear heating program up to  $850^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . TGA results showed that the addition of hydrophobic-nanosilica served to increase the  $\text{CO}_2$  sorption rate in the fast stage as well as the residual capture capacity of CaO. A main effect of the hydrophobic-nanosilica is to improve CaO dispersibility, which allowed for a relatively larger number of small pores of the reactive surface being directly exposed to  $\text{CO}_2$ . The enhancement of mass/heat transfer yielded faster carbonation rates and relatively longer fast carbonation periods. Moreover, the additive improved the thermal stability of the sorbent and higher values of the residual capture capacity were obtained [18]. A further benefit of nanosilica additive is to improve the resistance of the calcined sorbent to high energy mechanical collisions [40], which bears similarity with the enhancement of compressive strength and abrasion resistance of high performance cement-based materials by the addition of nanosilica [41].

To carry out the thermal pretreatment and carbonation/calcination cycles in the new TGA tests reported in this manuscript, we have used a Q5000IR TG analyzer (TA Instruments). This equipment is provided with an infrared furnace, which allows for a very fast change of temperature between cycles (up to  $500^\circ/\text{min}$  for linear heating range), and with a high sensitivity balance ( $<0.1 \mu\text{g}$ ) characterized also by a minimum baseline dynamic drift ( $<10 \mu\text{g}$ ). Heating/cooling rates provided by this instrument are much higher

than the typically achievable by conventional TGA instruments (of about 50°C/min or even smaller [42]), which allows us to test the multicyclic sorbent performance at realistic carbonation/calcination temperatures without a significant effect on the sorbent of the transitional heating/cooling periods. Once the samples were placed in the TG balance, they were subjected in-situ to different types of preheating programs under either air or an air/CO<sub>2</sub> mixture (15% vol CO<sub>2</sub>). Initial masses of the tested samples were in the range 10-20 mg and the gas flow was kept at 100 cm<sup>3</sup>/min.

The ordinary pretreatment method consisted of heating the material from ambient temperature up to 900°C at a constant rate of 20°C/min. Figure 1 illustrates the evolution of weight and temperature in a typical TG diagram obtained during the linear preheating program under air. In this pretreatment, Ca(OH)<sub>2</sub> is dehydroxylated when the temperature reaches a value of  $T \simeq 350^\circ\text{C}$ . The CO<sub>2</sub> vol concentration in air is about 0.033% for which the carbonation reaction is at equilibrium at  $T \simeq 520^\circ\text{C}$  [1]. As long as  $T$  remains below this value, dehydroxylation and carbonation would occur in parallel. Yet, the carbonation kinetics is too slow for the reaction to be appreciated as the temperature raises quickly. Only when the temperature reaches a value of around 600°C we observe a small weight drop, which is due to decarbonation of CaCO<sub>3</sub> initially present as impurity in the sample. A thermogram corresponding to a linear preheating program carried out under a air/CO<sub>2</sub> atmosphere (15% vol CO<sub>2</sub> at atmospheric pressure) is shown in Fig. 2. In this case, the first appreciable increase of sorbent weight is due to simultaneous dehydroxylation/carbonation. Decarbonation is initiated at  $T \simeq 800^\circ\text{C}$ , which is the temperature at which the partial pressure of CO<sub>2</sub> at carbonation/decarbonation equilibrium equals the CO<sub>2</sub> partial pressure of the gas (0.15 atm). The rate of weight % variation is also plotted in Figs. 1 and 2 for these linear preheating treatments. It can be seen that dehydroxylation/carbonation and decarbonation rates conform to the typical sigmoid curve usually observed for solid-gas reactions rates. Note that the rate of decarbonation in the air/CO<sub>2</sub> atmosphere is significantly increased with temperature, reaching a maximum value around 845°C which is about 35%/min. As will be seen in our experimental results, the rate of decarbonation plays a main role in the CO<sub>2</sub> capture multicyclic performance of the sorbent.

During linear heating, the reaction rate is not a well-defined parameter at the place where actually the reaction occurs, i.e. on the reaction interface. Owing to temperature gradients, the temperature at each point of the sample is undetermined. In order to achieve a reaction

rate similar for each grain of the sample, the reaction interface must advance in each grain at the same rate, which may be pursued by means of an alternative heating method that yields slow and controlled decomposition rates. This heating method, in which the rate of decomposition is kept low and constant, was originally developed by Rouquerol [34, 35] and consists of the so-called *Constant Decomposition Rate Thermal Analysis* (CRTA). In contrast with linear heating, CRTA heating provides effective control of the reaction rate and hence better efficiency in the control of mass/heat transfer phenomena [36]. Koga and Criado [37] showed that CRTA under vacuum was useful to obtain reliable kinetic curves for decarbonation of  $\text{CaCO}_3$ . By maintaining decarbonation at a constant rate, the results were not influenced by mass/heat transfer phenomena. Application of CRTA in gas-solid chemical reactions has been used to control the texture and structure of some materials through the kinetic control of the thermal decomposition of their precursors [36, 38, 43]. The main novelty of our study is the use of the CRTA heating method to pretreat the sorbents to be subjected to carbonation/calcination cycles. A rapid increase of the decarbonation rate yields a great increase of the  $\text{CO}_2$  partial pressure, which might affect the texture and stability of the adsorbent thus influencing its  $\text{CO}_2$  capture capacity in the subsequent carbonation/calcination cycles. On the other hand, the CRTA pretreatment might have a diverse effect on the CaO texture as seen in a previous work where CRTA has been used to control the texture of hematite obtained from the thermal decomposition of goethite [38] and polymer degradation [44, 45].

Under the CRTA preheating program, the temperature was also raised up to  $900^\circ\text{C}$  but at a variable rate that was adjusted by a feedback mechanism in order to keep at a constant and prefixed small value (of about 0.3-0.4 %/min) the reaction rates. A typical thermogram obtained during CRTA preheating in air is shown in Fig. 3. As can be seen, dehydroxylation and decarbonation occur at a small and approximately constant rate. The small increase of weight observed just after dehydroxylation indicates a slight carbonation of the sample for  $T \lesssim 520^\circ\text{C}$  due to  $\text{CO}_2$  present in air. In contrast with the air-linear preheating program, the air-CRTA program allows carbonation to be observed in air by lowering down the rate of increase of temperature. As soon as the temperature reaches  $520^\circ\text{C}$ , the carbonation/decarbonation reaction is at equilibrium for the  $\text{CO}_2$  partial pressure in air, after which further increase of temperature causes the reaction to shift towards decarbonation of the previously carbonated CaO as well as of  $\text{CaCO}_3$  impurities initially

present. Figure 4 shows an example of a thermogram obtained for CRTA pretreatment in air/CO<sub>2</sub> (15% vol CO<sub>2</sub> at atmospheric pressure). Firstly dehydroxilation/carbonation, which take place in parallel, and subsequently decarbonation occur at the small and controlled prefixed rate. In order to maintain the rate of decarbonation constant, the temperature is kept approximately constant at a value slightly above 800°C for about 2 h. This is a main qualitative difference with the air/CO<sub>2</sub>-linear preheating program, wherein decarbonation took place at a quick rate at the end of the preheating period.

Once the material was preheated, carbonation/calcination cycles were carried out in the same conditions independently of the type of pretreatment employed. For carbonation, the temperature was decreased down to at 650°C (cooling rate 300°C/min) and the sorbent was subjected to a dry gas mixture (85% air/15% CO<sub>2</sub> vol/vol) for 5 minutes. Then, the material was calcined at 850°C (heating rate 300°C/min) for 5 minutes in a dry air atmosphere. After calcination, the temperature was decreased (cooling rate 300°C/min) to proceed again with carbonation in a new cycle.

### III. EXPERIMENTAL RESULTS

Figure 5a shows the CaO conversion measured along a total of  $N = 50$  carbonation/calcination cycles from different preheating treatments to which Ca(OH)<sub>2</sub> was subjected. CaO conversion, defined as grams of CaO converted/grams of CaO is related to the capture capacity  $X_N$  by  $\chi_N = X_N M_{CaO} / M_{CO_2}$  being  $M_{CaO} = 56$  g/mol and  $M_{CO_2} = 44$  g/mol the molecular weights of CaO and CO<sub>2</sub>, respectively. Generally, a higher conversion is obtained when the thermal pretreatment is performed in an air/CO<sub>2</sub> atmosphere, which is in qualitative agreement with previous results reported in the literature [24, 26]. As a novel result, it is seen that, even though the air/CO<sub>2</sub>-CRTA pretreatment gives rise to a relatively smaller conversion during the first cycles, it serves to improve the sorbent regenerability when it is subjected to multiple cycles, which allows to achieve a higher conversion at large  $N$ . Thus, the evolution of CaO conversion observed for the air/CO<sub>2</sub>-CRTA pretreatment resembles the trend of data reported in the literature for natural limestones when previously exposed to prolonged periods of calcination at elevated temperatures [22–26]. Note however that the air/CO<sub>2</sub>-CRTA preheating treatment carried out in our work takes a relatively short time as compared to the isothermal treatment of limestones at higher temperatures

in order to observe an analogous attenuation in the decay of conversion with the number of cycles [22–26].

Figure 6 shows SEM images, mesopore size distributions (BJH method) and surface areas (BET method) measured for raw  $\text{Ca}(\text{OH})_2$  and  $\text{CaO}$  derived from the air/ $\text{CO}_2$  linear and CRTA preheating programs, which yield the more contrasting  $\text{CaO}$  multicyclic conversion behaviors (Fig. 5a). As may be seen, the air/ $\text{CO}_2$ -CRTA pretreatment gives rise to an initial skeleton which is sintered to a higher level than the initial skeleton arising from the air/ $\text{CO}_2$ -linear preheating program. Figure 7 shows the evolution of the weight gain (in %) as a function of time during the 1st carbonation/calcination cycle for  $\text{CaO}$  preheated according to the diverse programs used. As well known from previous studies [5, 46], it is seen that carbonation comprises two well differentiated phases, a first kinetically-controlled fast phase and a successive much slower phase controlled by solid-state diffusion of  $\text{CO}_2$  through the superficial carbonate layer. It is also observed that there is a direct correlation between conversion in the fast phase, which would be proportional to the surface area [8], and the total conversion. Accordingly, quick decarbonation in the air/ $\text{CO}_2$ -linear preheating program yields a highly porous skeleton with a relatively large surface area but also with a low resistance to sintering, which gives rise to a rapid decrease of conversion with the cycle number as seen in Fig. 5a. On the other side, slow rate-controlled decarbonation in the air/ $\text{CO}_2$ -CRTA program would produce an initial skeleton with a reduced surface area leading to a smaller conversion and lower carbonation rate in the fast phase. On the other hand, Fig. 7 demonstrates that this treatment promotes carbonation in the diffusive phase. Enhanced solid-state diffusion would lead, after quick decarbonation in the first calcination, to a soft porous skeleton supported on the initial hard skeleton and with a relatively increased surface area available for the next carbonation. These observations upheld the argument put forward by other authors [10, 30] on the main role of diffusive carbonation on the enhancement of the multicyclic conversion of thermally pretreated sorbents. It is worth to remark that most works showing even an increase of conversion with the cycle number after thermal pretreatment (self-reactivation) are based on TGA isothermal looping tests [14, 23, 24, 26, 27] (see [47] for a brief review), which comprise a mild calcination stage in an inert gas and a carbonation stage taking place in a high concentration  $\text{CO}_2$  atmosphere. Under these conditions diffusive carbonation is favored while sintering of nascent  $\text{CaO}$  in the calcination stage is minimized, which would contribute to enhance multicyclic

reactivation. Alonso et al. [47] have recently carried out looping TGA tests on thermally pretreated sorbents subjected to carbonation/calcination cycles under conditions closer to those expected for post-combustion CO<sub>2</sub> capture (low CO<sub>2</sub> concentration in the carbonation stage at  $T = 650^{\circ}\text{C}$  and high calcination temperature,  $T = 950^{\circ}\text{C}$ ). In spite that thermal pretreatments carried out in this work produced deep sintering on the sorbents, reactivation was not observed even in the case of isothermal pretreatment for a prolonged period in a CO<sub>2</sub> atmosphere (6h at  $1050^{\circ}\text{C}$ ). Looping carbonation/calcination conditions employed in [47] would not be as favorable as those used in previous works [14, 23, 24, 26, 27] to enhance surface area renovation by solid-state diffusive carbonation. Our study, carried out also under more realistic looping conditions, suggests that a small rate-controlled decarbonation during preheating might serve to improve the efficiency of pretreatment by further enhancing diffusive carbonation.

Let us now analyze the effect of the additive on the multicyclic conversion as related to the preheating program employed. Firstly, we will focus on the linear preheating program. Figures 5b to 5d show the multicyclic CaO conversion of nanosilica/CaO composites derived from linearly preheating the nanosilica/Ca(OH)<sub>2</sub> dry mixtures under air and air/CO<sub>2</sub> atmospheres. As reported elsewhere [18], the addition of hydrophobic nanosilica yields a notable increment of the multicyclic CaO conversion when pretreatment is made under ordinary linear heating in air (Fig. 5c). However, the composite derived from the mixture with hydrophilic nanosilica shows a notably worse performance as compared to the composite derived from the mixture with hydrophobic silica when air is used during preheating, and represents no improvement of the capture performance over the raw CaO (Fig. 5c). However, if preheating is carried out under an air/CO<sub>2</sub> atmosphere, the multicyclic conversion of the sorbent derived from the mixture with hydrophilic silica is enhanced whereas the presence of CO<sub>2</sub> during preheating increases only slightly the multicyclic conversion of the sorbent derived from the mixture with hydrophobic silica. It is thus inferred that the additive hydrophobicity plays a role on enhancing CaO conversion of the sorbents thermally pretreated under CO<sub>2</sub>.

Figures 8a and 8b show the effect of air/CO<sub>2</sub>-CRTA preheating on the multicyclic CaO conversion of the composite sorbents. As seen in the case of Ca(OH)<sub>2</sub>, the application of this pretreatment causes a decrease of CaO conversion in the first cycle as compared to the linear heating pretreatment. Note that CaO conversion is slightly increased in the very first

cycles for CaO and the hydrophilic-silica/CaO composite Reactivation induced by air/CO<sub>2</sub>-CRTA preheating in the first cycles can be more clearly appreciated in the inset of Fig. 8d where  $\chi_N/\chi_0$  is plotted for CaO and the composite sorbents ( $N \leq 10$ ). Interestingly, it is seen that nanosilica hinders reactivation, specially in the case of hydrophobic silica. As nanosilica hampers sintering during preheating, the initial CaO skeleton in the composite would be relatively softer as compared to pure CaO, which would impair diffusive carbonation and thus surface area regeneration necessary for reactivation. On the other hand, the use of hydrophilic silica would yield a relatively high CaO conversion in the first cycle while reactivation is still observed in the subsequent cycle. Accordingly, Fig. 9 demonstrates that the diffusive carbonation phase in the first cycle is also greatly enhanced for this composite sorbent when it is preheated by the air/CO<sub>2</sub>-CRTA program.

#### IV. MODELS ON THE CAO MULTICYCLIC CONVERSION

The typical decay of CaO conversion exhibited by natural limestones subjected to long series of carbonation/calcination cycles has been generally well fitted by the empirical equation [8]

$$\chi_N = \chi_r + \frac{1}{\kappa N + (1 - \chi_r)^{-1}} \quad (1)$$

where  $\chi_N$  is the conversion at the Nth carbonation. An important fitting parameter in Eq. 1 is the residual conversion  $\chi_r$ , which is achieved after a large number of carbonation/calcination cycles, whereas  $\kappa$  is the so-called deactivation constant, which gives an idea of the rate of CaO conversion decay. Experimental results obtained for natural limestones in a wide variety of conditions conformed well to Eq. 1 for similar values of the residual conversion in the range  $\chi_r \sim 0.075$ -0.08, while the deactivation constant showed a higher variability (typically between 0.5 and 2) [8]. Accordingly, a test on a natural limestone performed over 500 cycles (calcining at 850°C for 5 min and carbonating at 650°C for 5 min) yielded a residual value of conversion  $\chi_r = 0.075$  [8]. In these TGA experiments, the initial sorbent (CaO) was obtained by calcining natural limestone during relatively short time periods as compared with those employed in thermal pretreatments which leads to a trend of the multicyclic CaO conversion [22–26] that cannot be fitted to Eq. 1.

Equation 1 was derived from studies originally focused on the deactivation of supported

metal catalysts (mainly Ni/SiO<sub>2</sub>, Ni/AL<sub>2</sub>O<sub>3</sub>, Pt/AL<sub>2</sub>O<sub>3</sub> and Ag/AL<sub>2</sub>O<sub>3</sub>) caused by sintering induced loss of surface area [48]. The decrease of catalyst surface area  $S$  generally adjusts to the empirical rate equation [48]

$$-\frac{d S}{dt S_0} = k \left( \frac{S}{S_0} \right)^n \quad (2)$$

where  $S_0$  is the initial surface area,  $k$  is the sintering rate constant, and  $n$  is the so-called sintering order, which for typical catalyst systems may vary from 3 to 15 [48]. Equation 2 is known as the simple power law expression (SPLE) and can be rationalized from the assumption that the driving force for sintering is provided by surface energy [49]. Its usefulness is limited however to short sintering time lags. Otherwise,  $S$  approaches asymptotically to a limit or residual surface area  $S_r$  for long sintering periods. This is taken into account by the empirical general power law expression (GPLE) [48]

$$-\frac{d S}{dt S_0} = k \left( \frac{S}{S_0} - \frac{S_r}{S_0} \right)^m \quad (3)$$

The GPLE equation fits well to sintering rate data for small integer values of  $m$  of 1,2 or 3 (first, second or third order processes, respectively) depending on the prevalent sintering mechanism. It is suggested that first order processes are ruled by atomic migration, while second order process are determined by crystallite migration and agglomeration [48].

Assuming that in the CaL process the amount of CaCO<sub>3</sub> formed during each carbonation period is proportional to the available surface for reacting with CO<sub>2</sub> ( $\chi \propto S/S_0$ ), Grasa et al. [8] proposed to use the GPLE (Eq. 3) to account for the decay of CaO conversion as the number of carbonation/calcination cycles is increased. Underlying in this approach is the assumption that the initial pore skeleton suffers a progressive degradation during the calcination periods independently of re-carbonations taking place between successive calcinations. Thus, the sintering time would be proportional to the number of cycles  $t \propto N$ . Defining  $\chi_0$  as the first carbonation conversion and integrating, it is

$$-\int_{\chi_0}^{\chi_N} \frac{d\chi}{(\chi - \chi_r)^m} = \int_0^N \kappa dN \quad (4)$$

which leads to

$$\chi_N = \chi_r + \left[ \frac{1}{\kappa N(m-1) + (\chi_0 - \chi_r)^{1-m}} \right]^{1/(m-1)} \quad (5)$$

which conforms to Eq. 1 for  $\chi_0 = 1$  and  $m = 2$ . Thus, according to the exponent used in the literature to fit most experimental results of thermally untreated natural limestones ( $m \simeq 2$ ) [8], sintering of the initial CaO skeleton would conform to a second order process.

Let us come back to the analysis of our experimental results. Except for the case of air/CO<sub>2</sub>-CRTA pretreatment, the decay observed in the CaO conversion seems to exhibit the main features of Eq. 5, namely a significant decrease in the first cycles followed by an asymptotic approach to a residual value when increasing the cycle number (Figs. 5 and 8). In accordance, experimental data is satisfactorily fitted by Eq. 5 using  $m = 2$  (Fig. 5) as for natural limestones. The values of the residual capture capacity  $\chi_r$  and deactivation constant  $\kappa$  obtained from these fits are shown in table I. It is seen that Ca(OH)<sub>2</sub>-derived CaO has a better capture performance than CaO derived from natural limestones (we remind that for limestones the residual conversion is  $\chi_r \simeq 0.075 - 0.08$  and the deactivation constant is  $\kappa \simeq 0.52$  [8]). The highest residual conversion and lowest deactivation constant are derived in the case of air/CO<sub>2</sub>-linear preheating (I). CRTA pretreatment in air does not yield a significant difference on the multicyclic conversion as compared to linear preheating in air. As regards the effect of the additive, the use of hydrophobic nanosilica yields a significant higher residual conversion either by linear preheating in air or in air/CO<sub>2</sub>. Hydrophilic silica does not give rise to a notable improvement of the residual conversion even though the deactivation constant is substantially decreased for air/CO<sub>2</sub>-linear preheating. Concerning the long-term conversion, the results suggest that air/CO<sub>2</sub>-CRTA pretreatment is the most effective method. This case, whose results obtained cannot be satisfactorily fitted by Eq. 5, needs however a special analysis.

As shown by our experimental results (Figs. 5 and 8) the multicyclic conversion of the air/CO<sub>2</sub>-CRTA pretreated sorbents follows a particular trend, which is mainly characterized by a small and approximately linear decrease of conversion along the carbonation/calcination cycles with a reactivation in the very first cycles. This behavior indicates that the evolution of the surface area is governed by a mechanism other than the progressive sintering of the initial CaO skeleton as it was assumed to derive Eq. 5. According to the pore skeleton model, thermally pretreated sorbents are structured in a hard inward skeleton of low reactive CaO surrounded by a softer layer of reactive CaO with a network of small pores. The hard skeleton would be formed during thermal pretreatment and would keep the pore structure essentially stable as the material is repeatedly subjected to carbonation/calcination cycles. Thus, CaO

CaO				
↓ Preheating	$\kappa$	$\chi_r$	$m$	$Rsqr$
Linear (air)	0.457	0.128	2	0.9995
Linear (air/CO <sub>2</sub> )	0.322	0.144	2	0.9933
CRTA (air)	0.392	0.103	2	0.9990

CaO/nanosilica(hydrophobic)				
↓ Preheating	$\kappa$	$\chi_r$	$m$	$Rsqr$
Linear (air)	0.424	0.213	2	0.9973
Linear (air/CO <sub>2</sub> )	0.316	0.204	2	0.9982

CaO/nanosilica(hydrophilic)				
↓ Preheating	$\kappa$	$\chi_r$	$m$	$Rsqr$
Linear (air)	0.409	0.110	2	0.9918
Linear (air/CO <sub>2</sub> )	0.253	0.169	2	0.9945

TABLE I. Fitting parameters of Eq. 5 to experimental data on the CaL multicyclic capture capacity of CaO and nanosilica/CaO composites derived from Ca(OH)<sub>2</sub> and nanosilica/Ca(OH)<sub>2</sub> (either hydrophobic or hydrophilic) preheated as indicated

conversion would be mainly determined just by the balance between changes of the outward soft skeleton during carbonation and decomposition in each cycle. As inferred from our observations and from the work of other authors [10, 30], enhanced carbonation in the solid-state diffusion by pretreatment would yield an increase of surface area. If looping calcination conditions are not harsh enough to provoke significant sintering of the CaO porous skeleton formed after decarbonation, the surface area at the end of the calcination stage would be still enlarged which would lead to an increase of conversion (self-reactivation). In our case, self-reactivation is observed also in the very first cycles (Fig. 8d). As the number of cycles is further increased the relative importance of carbonation due to solid-state diffusion is lessened and surface area regeneration becomes eventually outweighed by sintering of the nascent CaO during short-time looping calcination, which leads to a monotonous decrease of conversion with the cycle number.

A theoretical model which has been successfully used to interpret experimental results on the surface area loss of nascent CaO [29, 50–53] and other types of materials [49, 54, 55] when subjected to short-timed isothermal heating is the German-Munir model [49]. The model, which is based on the assumption that the dominant driving force during the initial stage of sintering is the curvature gradient at the necks of contacting grains, leads to the equation

$$\left(\frac{S_0 - S}{S_0}\right)^\gamma = K_s t_s \quad (6)$$

where  $t_s$  is the sintering time,  $K_s$  is the sintering rate constant, which includes the diffusion coefficient and surface tension, and increases with temperature  $T$  according to the law  $\Delta \log K \propto -1/T$  [50], and  $\gamma$  is a characteristic exponent which depends on the predominant mass transport mechanism. For plastic flow, it is  $\gamma = 1.1$ , for lattice diffusion  $\gamma = 2.7$ , for grain boundary diffusion  $\gamma = 3.3$  and for surface diffusion  $\gamma = 3.5$ . Measurements on the sintering rate of nascent CaO (produced by the rapid decomposition of small, dispersed particles of pure CaCO<sub>3</sub>, limestone and Ca(OH)<sub>2</sub>) indicated that the sintering rate constant depends on the type of precursor and temperature [50]. At  $T = 850^\circ\text{C}$ , it was  $K_s \simeq 10^{-5} \text{ min}^{-1}$  for nascent CaO derived from pure CaCO<sub>3</sub>,  $K_s \simeq 10^{-3} \text{ min}^{-1}$  for limestone-derived CaO, and  $K_s \simeq 10^{-2} \text{ min}^{-1}$  for Ca(OH)<sub>2</sub>-derived CaO (see Fig. 4 in [50]). On the other hand, values of  $\gamma$  were  $\gamma = 2$  for nascent CaO derived from pure CaCO<sub>3</sub>,  $\gamma = 2.3$  for limestone-derived CaO and  $\gamma = 2.7$  for Ca(OH)<sub>2</sub>-derived CaO (at  $T=900^\circ\text{C}$ ). From the results on the kinetics of the specific surface area reduction, the German-Munir model can be used to identify the mass transport mechanisms intervening in the sintering process. Equation 6 has provided a satisfactory phenomenological description of the surface area reduction during isothermal sintering, even in cases where the experimental conditions do not adjust to the physical model used to derive the equation [54, 55].

According to the pore-skeleton model the loss of activity observed in our experiments for air/CO<sub>2</sub>-CRTA pretreated sorbents would be mainly determined by sintering of the nascent CaO derived from the isothermal short-time calcination of the CaCO<sub>3</sub> formed during diffusive

carbonation. Thus, using the German-Munir equation, it can be written

$$S_0 - S_1 = S_0 (K_s t_s)^{1/\gamma} \quad (7)$$

$$S_1 - S_2 = S_1 (K_s t_s)^{1/\gamma} \quad (8)$$

$$\vdots = \vdots \quad (9)$$

$$S_{N-1} - S_N = S_{N-1} (K_s t_s)^{1/\gamma} \quad (10)$$

$$(11)$$

Summing up Eqs. 7 to 10 leads to

$$S_0 - S_N = (K_s t_s)^{1/\gamma} \sum_{i=0}^{N-1} S_i = S_0 (K_s t_s)^{1/\gamma} \sum_{i=0}^{N-1} \left[1 - (K_s t_s)^{1/\gamma}\right]^i \quad (12)$$

Since it is  $\sum_{i=0}^{N-1} x^i = (1 - x^N)/(1 - x)$ , and assuming that  $S_N/S_0 = \chi_N/\chi_0$  we obtain

$$\frac{\chi_N}{\chi_0} = \left[1 - (K_s t_s)^{1/\gamma}\right]^N \quad (13)$$

An equation similar to Eq. 13 has been already proposed by Wang and Anthony using also a discrete approach [56, 57]. An analogous power-law equation had been previously derived by Abanades and co-workers from a different mechanism [58, 59] which provided good fits to short-series of multicyclic conversion data on nonpretreated sorbents ( $N \leq 20$ ). A basic assumption of this approach is that after each decarbonation the nascent CaO arising from solid-state diffusion becomes regenerated and sintered in the rest of the calcination stage. Moreover, the relative increase of surface area in each cycle produced by enhanced solid-state diffusion, which would be relevant in the self-reactivation cycles interval, is neglected as compared to the relative loss of surface area due to sintering of the nascent CaO.

In order to fit our experimental data on  $\chi(N)$  to Eq. 13 we will use  $K_s = 10^{-5} \text{ min}^{-1}$ , as derived from Borgwardt's results on  $\text{CaCO}_3$ -derived nascent CaO (at  $T = 850^\circ\text{C}$ ), and  $t_s = 5 \text{ min}$  (calcination temperature and time employed in our carbonation/calcination cycles). With these values, Eq. 13 fits well to our data on the multicyclic conversion over the 50 cycles range for CaO derived from air/ $\text{CO}_2$ -CRTA pretreated  $\text{Ca}(\text{OH})_2$  (see Fig. 5). The best fitting parameter gives  $\gamma = 2.164$ , which is similar to the value of  $\gamma$  reported by Borgwardt on  $\text{CaCO}_3$ -derived nascent CaO at a similar calcination temperature and would point towards a sintering mechanism of the nascent CaO skeleton mainly ruled by lattice diffusion.

Figure 8 shows a comparison of the multicyclic conversion of CaO and nanosilica/CaO composites derived from air/CO<sub>2</sub>-CRTA pretreatment. As can be observed, the use of nanosilica yields a higher conversion, specially during the first cycles and for the case of hydrophilic silica. Nonetheless, Eq. 13 does not fit satisfactorily to the data over the whole range of 50 cycles. Assuming  $\gamma = 2.164$  as obtained for CaO, the sintering rate that would fit Eq. 13 to the data would be relatively higher ( $K_s \simeq 3.5 \times 10^{-5}$ ) in the first cycles and would tend to a similar value than for CaO ( $K_s \simeq 10^{-5}$ ) at large  $N$ . Since nanosilica prevents sintering the initial CaO skeleton produced by the air/CO<sub>2</sub>-CRTA pretreatment would be less stable. Thus, multicyclic conversion would be ruled by a mixing mechanism consisting of sintering of the nascent CaO generated in the outward porous skeleton but also by sintering of the initial skeleton as for non-pretreated sorbents.

It is important to remark that heating rates typically employed in conventional TGA instruments (of about 50°C min<sup>-1</sup> or even smaller [42, 60]) are likely to give rise to non-negligible sorbent sintering in the transition between carbonation/calcination periods, which would affect the CO<sub>2</sub> capture performance measured in the TGA cycles and would make it difficult to interpret the results by using the German-Munir model. As can be appreciated in Figs. 1 to 4, the transition from calcination to carbonation and viceversa in our TGA cycles took place very quickly (in just 40 seconds) thanks to a rapid and stable temperature change allowed by the infrared furnace.

Equation 13 may be also derived by integrating the simple power law empirical expression (Eq. 2),

$$\int_{S_0}^S \frac{d(S/S_0)}{(S/S_0)^n} = - \int_0^{t_s} k dt \quad (14)$$

which leads to

$$\frac{S}{S_0} = (1 - (1 - n)kt_s)^{1/(1-n)} \quad (15)$$

For short-timed sintering and small sintering rate, Eq. 15 can be rewritten as

$$\frac{S}{S_0} \simeq 1 - kt_s \quad (16)$$

Using Eq. 15 for the sintering suffered by the nascent CaO during each calcination in the CaL process, and assuming  $\chi \propto S$ , it would be

$$\frac{\chi_N}{\chi_0} = \frac{S_N}{S_0} = \frac{S_1}{S_0} \cdot \frac{S_2}{S_1} \cdot \frac{S_3}{S_2} \cdots \frac{S_N}{S_{N-1}} = (1 - kt_s)^N \quad (17)$$

which is formally equivalent to Eq. 13 even though, in this case, the parameter  $k$  does not have a clear physical meaning whereas Eqs. 13-18 allows identifying the physical mechanism which rules the sintering process of the nascent CaO in each calcination.

Note that for short-time calcinations (as it is normally the case in practice for the CaL process) and very small sintering rates, Eq. 13 can be simplified for  $N(K_st_s)^{1/\gamma} < 1$  by the linear expression

$$\frac{\chi_N}{\chi_0} \simeq 1 - N(K_st_s)^{1/\gamma} \quad (18)$$

which fits to the approximately linear trend observed in our data on air/CO<sub>2</sub> preheated CaO (Fig. 5a). In the case of sorbents subjected to very long calcinations and very high temperatures, the hard skeleton would show a very stable pore structure ( $N(K_st_s)^{1/\gamma} \ll 1$ ). According to Eq. 18 would predict then a small but roughly constant conversion along the subsequent carbonation/calcination cycles as seen experimentally in some cases [23, 47]. Nonetheless, Eq. 13 does not explain self-reactivation, as observed in some cases of harshly preheated sorbents in an extended range of number of cycles and if looping carbonation/calcination conditions are favorable for surface area regeneration by carbonation due to solid-state diffusion [10, 23, 30]. In order to describe self-reactivation, a factor should be thus introduced accounting for this gain of surface area in each cycle. To this purpose, an linearized equation could be proposed similar to Eq. 16

$$\frac{S'_i}{S_i} \simeq 1 + k't_c \quad (19)$$

where  $k'$  would be an empirical constant related to the physical mechanism responsible for the increase of surface area of the soft skeleton and  $t_c$  is the carbonation time. Taking into account the balance between surface area gain due to regeneration and surface area loss due to sintering, it would be

$$\frac{\chi_N}{\chi_0} = \frac{S_N}{S_0} = \frac{S_1}{S_0} \cdot \frac{S'_1}{S_1} \cdot \frac{S_2}{S'_1} \cdot \frac{S'_2}{S_2} \cdots \frac{S'_{N-1}}{S_{N-1}} \cdot \frac{S_N}{S'_{N-1}} = (1 - kt_s)^N (1 + k't_c)^N \simeq (1 - Nkt_s)(1 + Nk't_c) \quad (20)$$

which might describe a growth of CaO conversion with the cycle number up to reach a maximum value of

$$\left(\frac{\chi_N}{\chi_0}\right)_{max} = \frac{(kt_s)^2 + (k't_c)^2 + 2kt_s k't_c}{4kt_s k't_c} \quad (21)$$

at a cycle number

$$N_0 = \frac{k't_c - kt_s}{2kt_s k't_c} \quad (22)$$

Thermally pretreated sorbents under very harsh conditions might show a gain of sorbent activity during a large number of cycles if  $k't_c \gg kt_s$ . In this limit,

$$\left(\frac{\chi_N}{\chi_0}\right)_{max} \rightarrow \frac{1}{2} + \frac{k't_c}{4kt_s} \quad (23)$$

$$N_0 \rightarrow \frac{1}{2kt_s} \quad (24)$$

Note that  $N_0$  would be very large since usually  $kt_s \ll 1$ . In practice, the relative gain of surface area in each cycle would decrease as the cycle number is increased since the relative importance of carbonation due to solid-state diffusion becomes diminished as the sorbent is cycled over. In order to account for this effect, a further elaboration of the model will be pursued in a separate work aimed to derive a general equation able to replicate the multicyclic conversion observed for thermally pretreated sorbents as affected by pretreatment/looping conditions and sorbent properties.

## V. CONCLUSIONS

Our work shows that CaO regenerability at conditions close to the Calcium-looping (CaL) process is improved by means of a relatively short-timed preheating treatment and carried out at a relatively low temperature, which is based on Control Rate Decomposition Thermal Analysis (CRTA) in an air/CO<sub>2</sub> atmosphere. By keeping decarbonation during preheating at a small and controlled rate, the drastic drop of conversion usually exhibited by non-pretreated sorbents in the first carbonation/calcination cycles is lessened. In the experiments reported in the present work the decarbonation rate is controlled for about 2 h at  $T \simeq 800^\circ\text{C}$  in a 85% air/15% CO<sub>2</sub> (vol/vol) atmosphere at a rate of about 0.4 %/min

(weight percentage variation per unit time). As inferred from our observations and in accordance to the pore skeleton model previously suggested by other authors, this pretreatment would yield a thermally stable hard skeleton of poorly reactive CaO supporting a soft skeleton of reactive CaO, which becomes regenerated in each cycle due to enhanced carbonation in the solid-state diffusion phase. A main difference between air/CO<sub>2</sub>-CRTA pretreatment and previously reported isothermal pretreatments leading to CaO stabilization is that, in the CRTA preheating program, carbonation/decarbonation reactions are controlled to occur at a constant and low rate. Air/CO<sub>2</sub>-CRTA pretreatment allows efficiently controlling of mass/heat transfer phenomena during carbonation/decarbonation, which has a relevant effect on the texture and structure of treated sorbent as demonstrated by other works. On the other hand, we have seen that the addition of nanosilica as dopant would hamper sintering of CaO during the air/CO<sub>2</sub>-CRTA pretreatment as it is also inferred from empirical observations on the specific surface area and crystallite size changes of calcined CaO/SiO<sub>2</sub> composites [61]. As a consequence, the initial CaO skeleton would be less stable and would have a higher porosity, which leads to a larger CaO conversion in the first cycle but also to a faster decay of it in subsequent cycles. According to our experimental results, the thermal stability provided by nanosilica is more effective in the case of a hydrophilic nanosilica as compared to a hydrophobic one.

## VI. ACKNOWLEDGEMENTS

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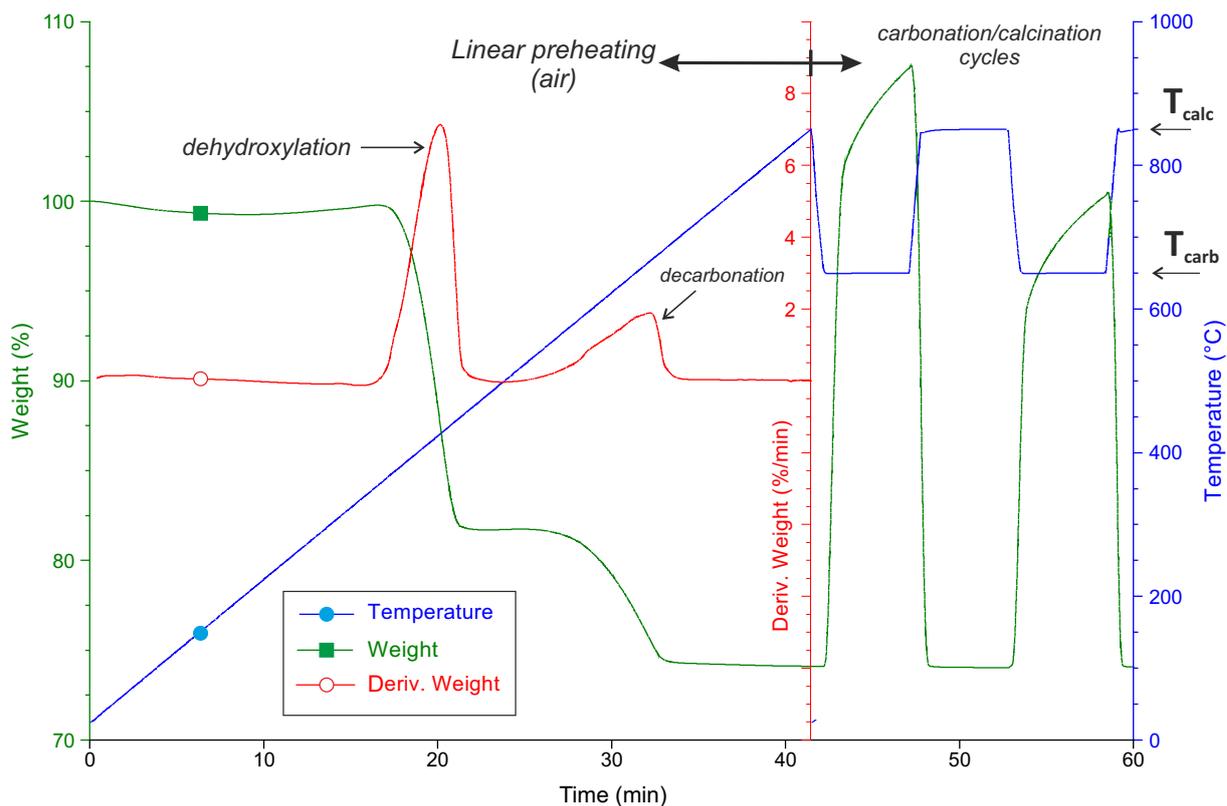


FIG. 1. a) Thermogram illustrating the weight and temperature variation during linear preheating of a  $\text{Ca(OH)}_2$  sample (18.551 mg) in air carried out as pretreatment preceding the carbonation/calcination cycles. The derivative of the weight % is also plotted showing in detail the variable reaction rates as indicated.

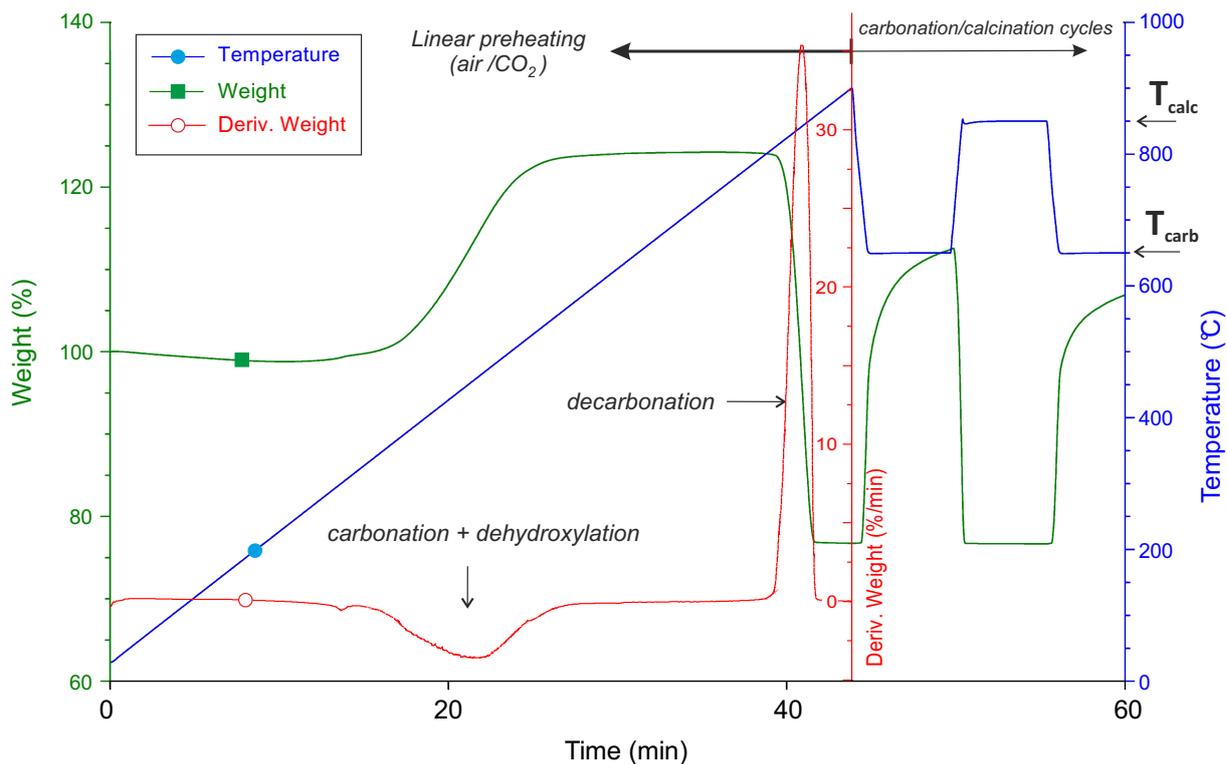


FIG. 2. Thermogram illustrating the weight and temperature variation during linear preheating of a (hydrophilic)nanosilica/Ca(OH)<sub>2</sub> sample (9.009 mg) in an air/CO<sub>2</sub> atmosphere (15% CO<sub>2</sub> at atmospheric pressure) carried out as pretreatment preceding the carbonation/calcination cycles. The derivative of the weight % is also plotted showing in detail the variable reaction rates.

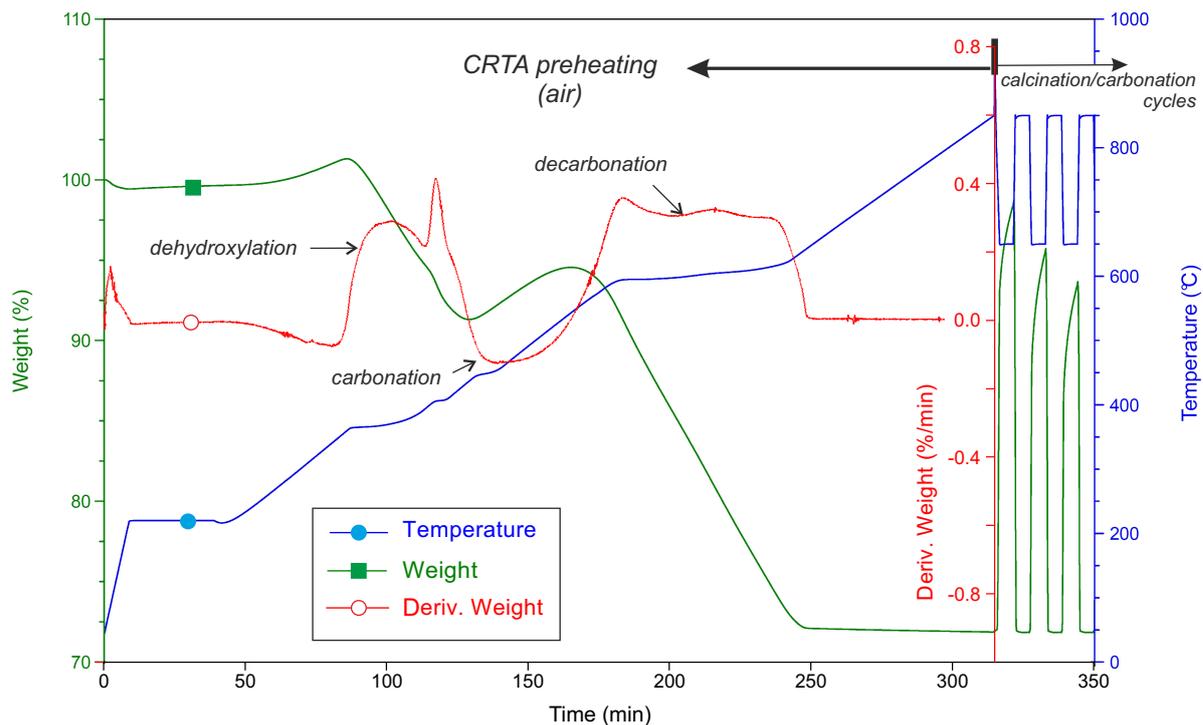


FIG. 3. Thermogram illustrating the weight and temperature variation during CRTA preheating of a  $\text{Ca}(\text{OH})_2$  sample (17.530 mg) in air carried out as pretreatment before the carbonation/calcination cycles are initiated. The derivative of the weight % is also plotted showing in detail similar and small reaction controlled rates.

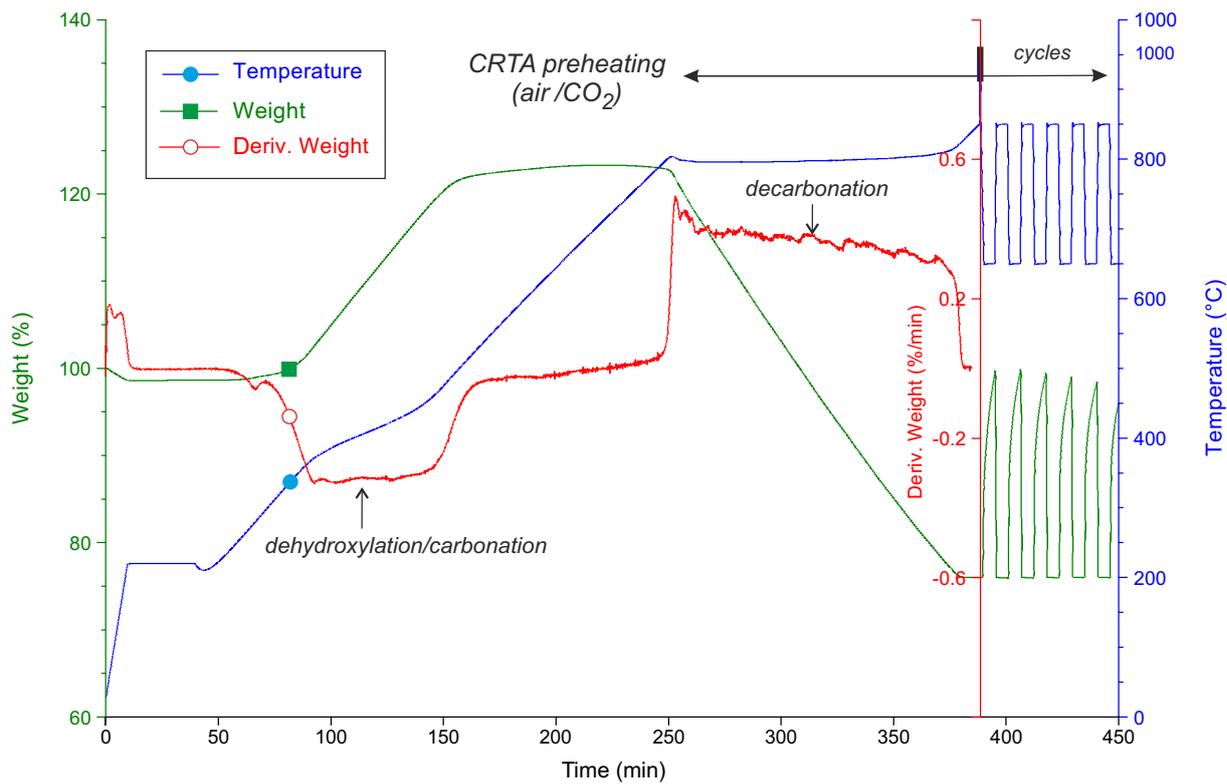


FIG. 4. Thermogram illustrating the weight and temperature variation during CRTA preheating of a hydrophilic-nanosilica/Ca(OH)<sub>2</sub> sample (8.771 mg) in a air/CO<sub>2</sub> atmosphere (15% CO<sub>2</sub> at atmospheric pressure) carried out as pretreatment before the carbonation/calcination cycles are initiated. The derivative of the weight % is also plotted showing in detail the occurrence of reactions at small controlled rates.

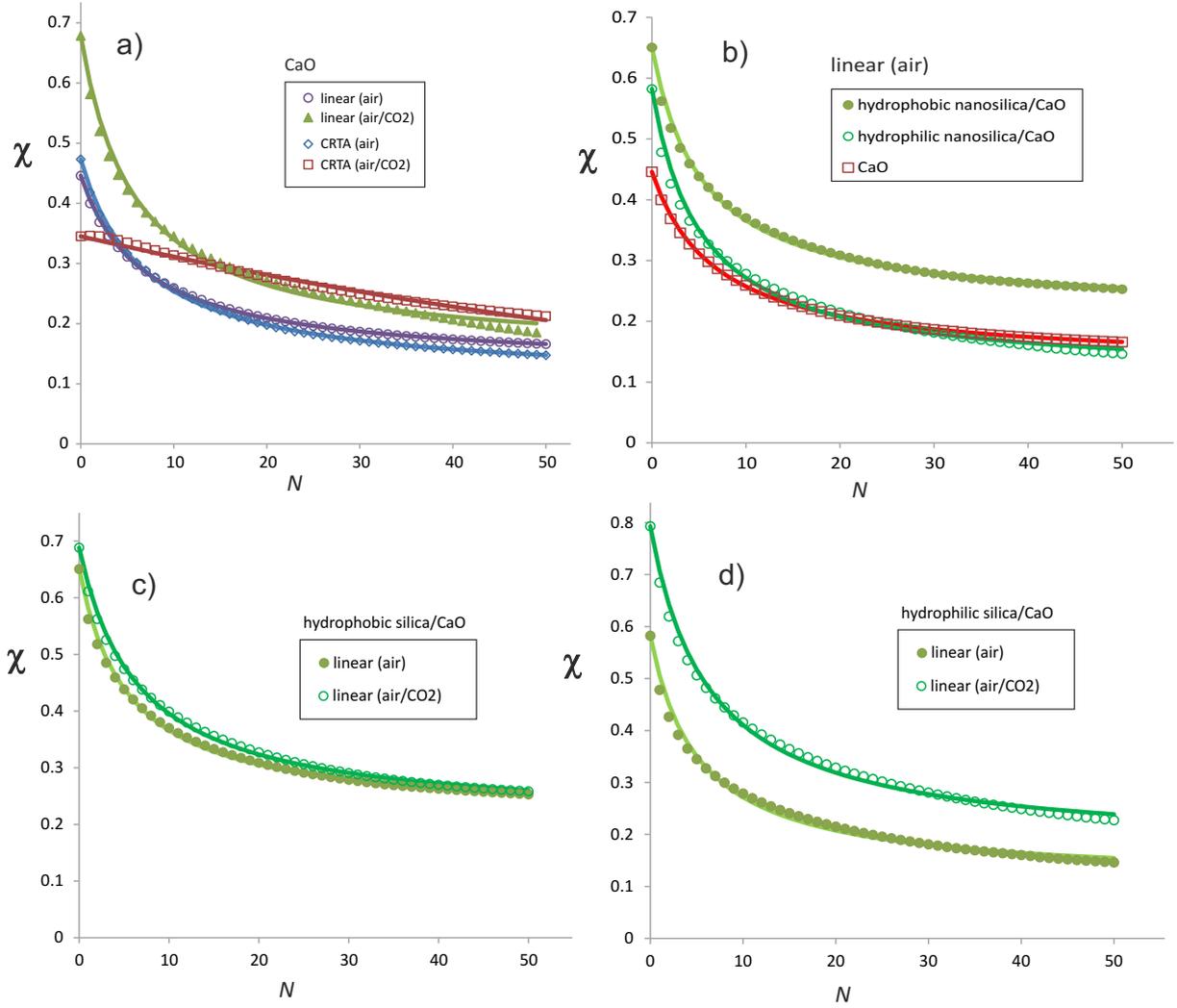


FIG. 5. CaO conversion of CaO and nanosilica/CaO composites derived from  $\text{Ca}(\text{OH})_2$  and nanosilica/ $\text{Ca}(\text{OH})_2$  dry mixtures subjected to linear and CRTA preheating programs under air and air/ $\text{CO}_2$  atmospheres as indicated. The solid lines are best fits curves of Eq. 5 to the data for the fitting parameters shown in table I. In the case of air/ $\text{CO}_2$ -CRTA pretreatment the solid line is the best fit of Eq. 13 to the data ( $K_s = 10^{-5}$ ,  $\gamma = 2.164$ ,  $R_{sqr} = 0.992$ ).

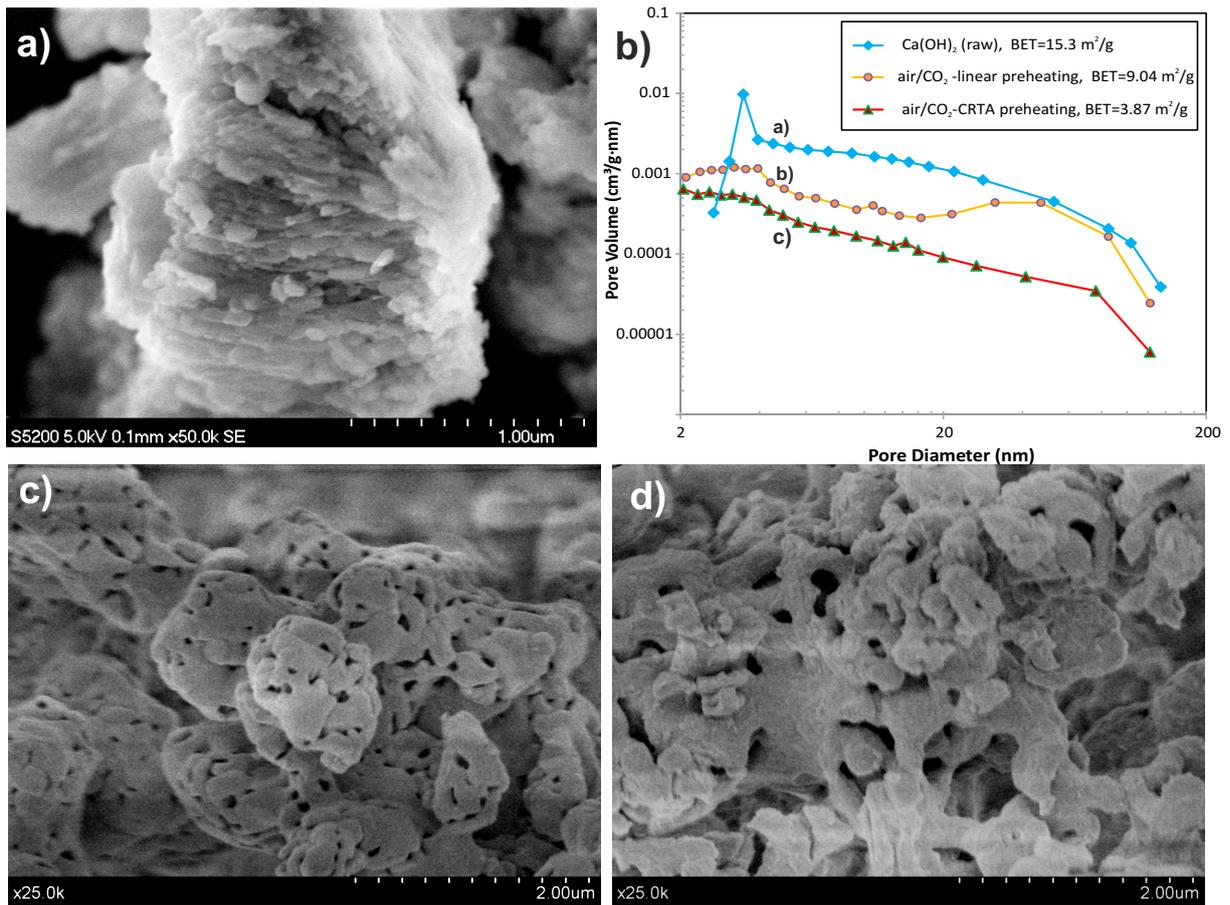


FIG. 6. SEM pictures of raw  $\text{Ca(OH)}_2$  used in this work (a) and  $\text{CaO}$  samples derived from preheating  $\text{Ca(OH)}_2$  up to  $900^\circ\text{C}$  under air/ $\text{CO}_2$  (15% vol  $\text{CO}_2$ ) by a linear program (c) and by a CRTA program (d) being afterwards cooled in air. b) BJH Desorption  $dV/dD$  Pore Volume of these samples with measured BET surface area as indicated (obtained by means of a TriStar II 3020 V1.03 physisorption analyzer operated by  $\text{N}_2$  sorption at 77 K).

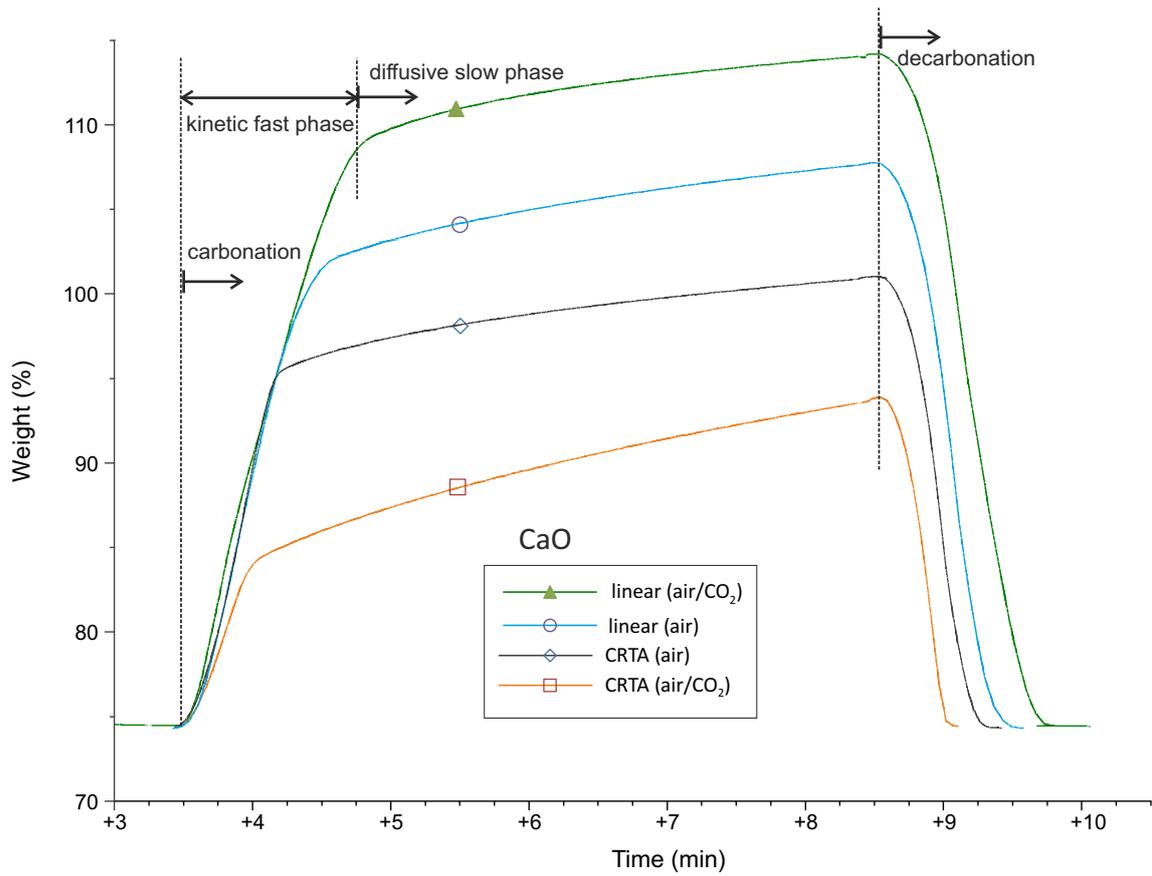


FIG. 7. Evolution of sorbent weight % as a function of time in the 1st carbonation/calcination cycle carried out after preheating  $\text{Ca}(\text{OH})_2$  under different programs as indicated. The border between kinetic fast carbonation and slow carbonation controlled by solid-state diffusion is indicated for the air/ $\text{CO}_2$ -linear preheating program

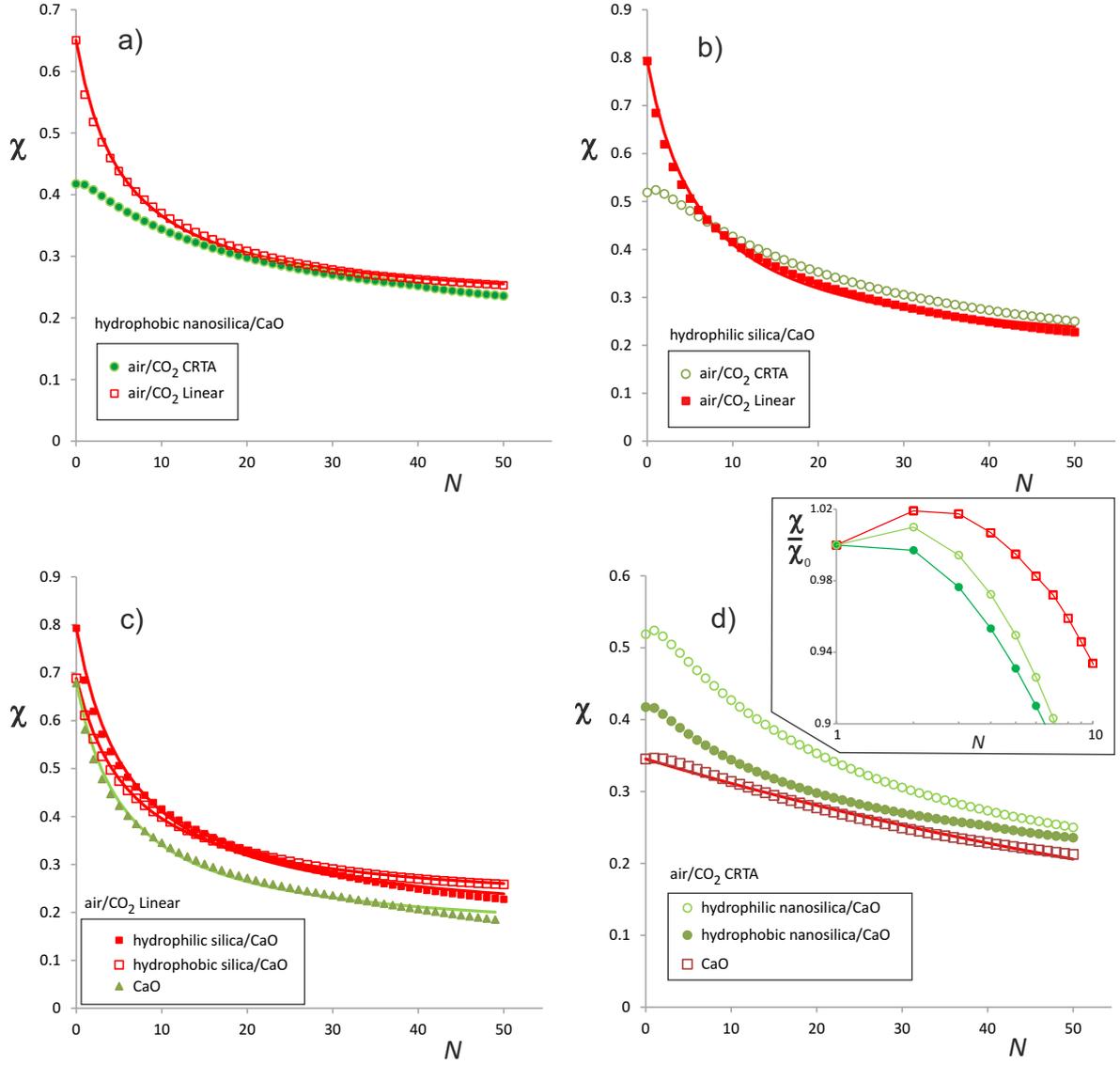


FIG. 8. CaO conversion of CaO and nanosilica/CaO composites derived from  $\text{Ca}(\text{OH})_2$  and nanosilica/ $\text{Ca}(\text{OH})_2$  dry mixtures preheated by CRTA and linear programs under either air or air/ $\text{CO}_2$  (15%  $\text{CO}_2$  vol concentration) atmospheres as indicated. The solid line are best fits curves from Eqs. 5 and 13. In the case of air/ $\text{CO}_2$ -CRTA pretreatment the solid line is the best fit of Eq. 13 to the data ( $K_s = 10^{-5}$ ,  $\gamma = 2.164$ ,  $R_{sqr} = 0.992$ ). The inset shows  $\chi/\chi_0$  for the first 10 cycles to illustrate sorbent reactivation of the sorbents pretreated by means of the air/ $\text{CO}_2$ -CRTA program.

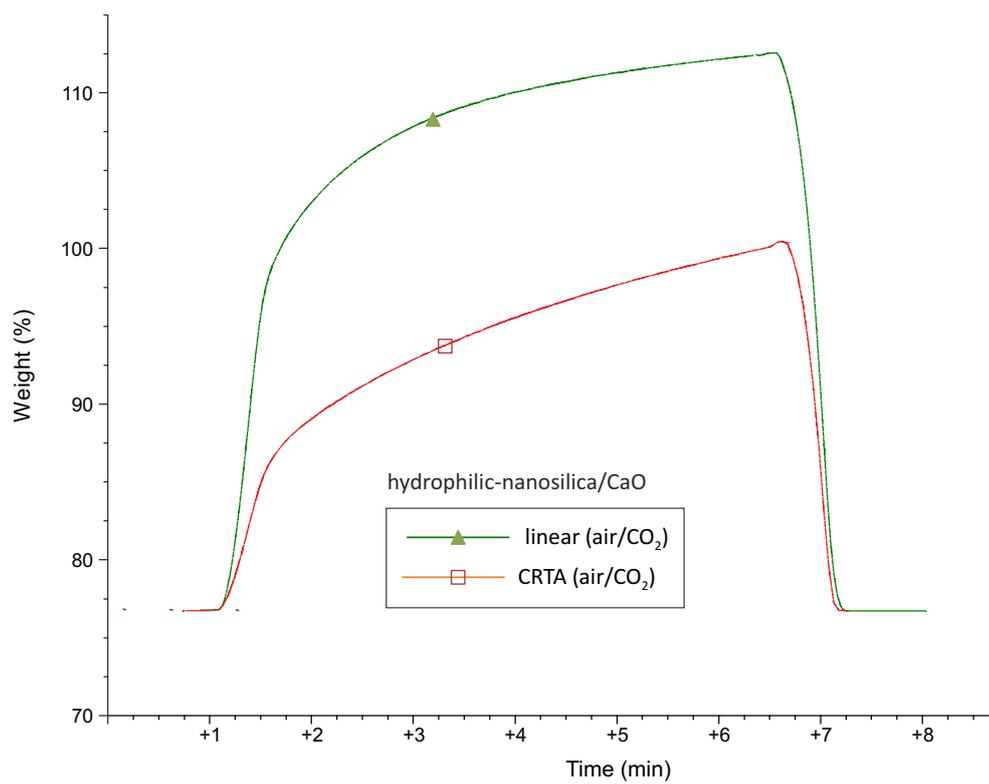


FIG. 9. Evolution of sorbent weight % as a function of time in the 1st carbonation/calcination cycle carried out after preheating hydrophilic-nanosilica/Ca(OH)<sub>2</sub> by means of linear and CRTA programs in air/CO<sub>2</sub> as indicated.