

Role of looping-calcination conditions on self-reactivation of thermally pretreated CO₂ sorbents based on CaO

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Abstract

The conversion of thermally pretreated CaO along successive carbonation/calcination cycles has been investigated, as affected by looping-calcination conditions, by means of Thermogravimetric Analysis (TGA). Sorbent samples have been subjected in-situ to a thermal preheating program based on Constant Rate Thermal Analysis (CRTA) by virtue of which decarbonation is carried out at a low controlled rate, which is able to promote self-reactivation in the first carbonation/calcination cycles. Our observations support a pore-skeleton model according to which solid-state diffusion in the first carbonation stages, which is enhanced by thermal pretreatment, gives rise to a soft skeleton with increased surface area. Yet, the results show that self-reactivation

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is hindered as looping-calcination conditions are harshened. Increasing the looping-calcination temperature and/or the looping calcination time period favors sintering of the soft skeleton and eventually self-reactivation is precluded. A model is developed that retrieves the main features of multicyclic conversion of thermally pretreated sorbents in the first cycles based on the balance between surface area gain due to promoted solid-state diffusion carbonation and surface area loss due to sintering of the soft skeleton in the looping-calcination stage, which can be useful to investigate the critical looping-calcination conditions that nullify self-reactivation. The proposed model allows envisaging the behavior of the sorbent performance as a function of the pretreatment conditions.

Introduction

The Ca-looping (CaL) process, based on the carbonation reaction of CaO to capture CO₂ and the subsequent decarbonation of CaCO₃ to regenerate the sorbent, is at the basis of a promising postcombustion capture technology whose suitability has been demonstrated by sustained CO₂ capture efficiencies over 90% in large pilot-scale plants.¹⁻³ In practice, carbonation/decarbonation of CaO is carried out in two interconnected fluidized bed reactors through which the material is continuously circulated. In the carbonator, CaO particles become carbonated at contact with the postcombustion gas containing CO₂ in a vol% of around 15%. The carbonated particles are driven to the calciner where they are decomposed by calcination at high temperature, which produces a concentrated stream of CO₂ suitable to be compressed and transported for sequestration. By taking into account the tradeoff between the reaction equilibrium driving force and the reaction kinetics, carbonation is carried out at optimal temperatures of around 650°C. On the other hand, decarbonation in the CO₂ rich atmosphere of the calciner requires application of temperatures above 900°C, which are accomplished by burning coal with a stream of pure O₂ (oxyfired combustion).^{1,4}

Thermogravimetric analysis (TGA) studies show that carbonation of CaO solid particles

progresses through two well differentiated phases.^{5,6} A first kinetically-controlled reaction takes place quickly on the surface of the particles until a thin layer of CaCO_3 (between 30 and 50 nm thick⁶) is developed. Then, CO_2 sorption becomes controlled by solid-state diffusion of CO_2 through this carbonate layer and the reaction rate is slowed down. In practical applications most of the CO_2 sorption is restricted to the fast carbonation phase since the sorbent particles must react with CO_2 at low concentrations and over short contact times.⁷ An abundant and inexpensive material to be used as CaO precursor is natural limestone.⁷⁻¹⁰ Typically, CaO is derived from limestone by preheating it up to a temperature high enough to ensure that decarbonation is complete but quickly in order to avoid the sintering of CaO grains after decomposition. Yet, nascent CaO derived from a quick CaCO_3 decarbonation is prone to be significantly sintered, which decreases the surface area available for fast carbonation causing a drastic drop of CaO conversion in the first carbonation/calcination cycles. Even though the loss-in-conversion problem may be circumvented by high solid circulation rates,⁷ it is recognized that enhancing the regenerability of CaO would favor the efficiency of the Ca-looping technology.⁹

A proposed method to stabilize multicyclic CaO conversion consists of thermal pretreatment of natural limestones.¹¹⁻¹⁷ By exposing the sorbent to isothermal calcination at high temperature for a prolonged period of time, the sorbent activity in the first carbonation/calcination cycles may actually increase, a phenomenon referred to as self-reactivation.¹² Conversion reaches a maximum value at a certain number of cycles (usually $N < 20$) after which it decreases with the cycle number at a slow rate. An added benefit of thermal pretreatment is the increase of mechanical strength of the sorbent,¹⁸ which enhances its resistance to attrition and thus minimizes the loss of material due to elutriation at high gas velocities in the CO_2 postcombustion capture process. Self-reactivation of thermally pretreated sorbents has been explained by the formation during pretreatment of a hard and stable skeleton in which solid-state diffusion carbonation is enhanced in the first cycle. A quick decarbonation following an enhanced solid-state diffusive carbonation stage leads to

a renovated porous skeleton with increased surface area for the next carbonation.^{9,19} In agreement with this mechanism, it has been reported that self-reactivation is significantly enhanced if the sorbent is subjected to carbonation periods of prolonged duration and under atmospheres of high CO₂ vol%, which promote solid-state diffusion.¹³

Self-reactivation has been analyzed as affected by a wide range of experimental variables such as temperature and duration of the pretreatment, presence of additives/impurities in the sorbent skeleton, pre-grinding, pre-hydration and looping-carbonation conditions.¹²⁻¹⁴ Alonso et al.²⁰ have recently revisited the suitability of thermal pretreatment as a method to stabilize the conversion of limestones used in pilot-scale plants for CO₂ capture. In contrast with results reported by other authors, these limestones failed to exhibit self-reactivation after thermal pretreatment despite that the concentration of impurities (possibly hampering self-reactivation according to other works^{13,14}) was low and pretreatment conditions were sufficiently harsh to induce deep sintering for the development of a stable skeleton.²⁰ As suggested by Alonso et al.,²⁰ a possible reason for this discrepancy was the use of relatively short carbonation periods in their experiments (10 min), which would hamper carbonation in the solid-state diffusion phase. A further relevant issue that will be closely examined in the present manuscript is the conditions under which looping-calcination is carried out.

Looping-calcination conditions used in TGA tests on pretreated sorbents are similar in the different reported studies: around 10 min under 100%N₂ at 800-850°C in^{12-14,16} and 30 min under 100%N₂ at 750°C in.^{11,17} Likely, increasing the looping-calcination temperature might compromise self-reactivation since it would enhance sintering of the nascent CaO soft skeleton. Looping-calcination conditions to be expected in practice would be harsh due to the presence of CO₂ in the calciner, which requires to increase the calcination temperature above 900°C for efficient decarbonation to take place.¹ In this regard, looping-calcination conditions employed by Alonso et al.²⁰ (10 min at 950°C in a 10% CO₂/90% air vol/vol atmosphere) are more realistic than those employed in previous works showing self-reactivation. High looping-calcination temperatures and the presence of CO₂ would enhance the sintering of the porous

soft skeleton developed after solid-state diffusion as might be inferred from experimental measurements on the BET surface area of nascent CaO subjected to high temperatures in CO₂ enriched atmospheres.²¹⁻²³ To further investigate this argument, we analyze in the present manuscript the effect of varying looping-calcination conditions (temperature and time duration) on the multicyclic conversion performance of CaO derived from sorbents pretreated in-situ under a controlled preheating program.

Materials and methods

In our experiments we have used a Q5000IR TG analyzer (TA Instruments) provided with an infrared furnace heated with halogen lamps, which allows for a very fast change of temperature between cycles (up to 500°C/min for linear heating range), and with a high sensitivity balance (<0.1 μg) characterized by a minimum baseline dynamic drift (<10 μg). Ca(OH)₂ from Sigma-Aldrich (puriss. p.a.) has been used as CaO precursor free of impurities. After placing the sorbent (around 10 mg) in the balance, it is preheated in-situ up to 900°C by means of a controlled program in a dry air/CO₂ atmosphere (15% CO₂ vol). Benchmark conditions of subsequent carbonation/calcination cycles consist of carbonation at 650°C (85% dry air/15% CO₂ vol/vol) and calcination at 850°C (dry air), both stages for 5 minutes (a shorter period than those used in TGA analysis reported in previous works on thermal pretreatment usually above 10 min^{11-17,20}). Further tests were performed varying the looping-calcination temperature between 700°C and 950°C and the calcination time period between 1 min and 15 min.

The conventional preheating program consisted of a linear preheating program (20°/min). A novel preheating program applied (as regards the CaL process) was based on a technique known as Constant Rate Thermal Analysis (CRTA), which is an useful technique to derive materials with controlled texture and microstructure.²⁴⁻³³ During the CRTA pretreatment, the evolution of temperature is controlled by means of a feedback mechanism allowing the

reactions to occur at a small and constant prefixed rate selected by the user. By virtue of this program, similar reaction rates for each grain of the sample are achieved, which minimizes the influence of mass and heat transfer phenomena typically associated to thermal decomposition reactions.

A relevant issue concerning TGA tests regards the heating/cooling rates to pass from carbonation to calcination and viceversa. The use of an infrared halogen furnace in our TGA runs allowed us for heating/cooling the sample very quickly ($300^{\circ}\text{C min}^{-1}$) minimizing the duration of the transitional periods. An alternative technical approach used by Alonso et al.²⁰ is to employ a two zones furnace set to different temperatures that can be moved up and down by means of a pneumatic piston with respect to the balance. Otherwise, heating rates typically employed in conventional TGA instruments (of about $50^{\circ}\text{C min}^{-1}$ or even smaller³⁴) lead to excessively long transitional periods, which might have a nonnegligible influence on the multicyclic conversion data. For example, in ref.¹⁵ TGA tests are carried out between 850°C (calcination in N_2) and 650°C (carbonation in $15\%\text{CO}_2/85\%\text{N}_2$) but the heating/cooling rate (20°C/min) would lead to 10 min transitional periods. This problem has been usually circumvented in previous studies^{11-14,16,17,35} by testing the multicyclic capture of the pretreated sorbent when subjected to carbonation/calcination cycles isothermally (the temperature during cycling is fixed to a value in the range $750\text{-}850^{\circ}\text{C}$) and changing the gas between an inert gas for calcination and a $\text{CO}_2/\text{air}(\text{N}_2)$ mixture with a high CO_2 vol% (above 25%) for carbonation. Consequently, the pretreated sorbent is subjected to relatively low looping-calcination temperatures, which would minimize sintering of the soft skeleton, whereas looping-carbonation is carried out at a high temperature in a high CO_2 vol% atmosphere favoring solid-state diffusion.

Experimental results

Figure 1 shows two examples of thermograms illustrating in detail the evolution of temperature, sample mass and sample mass derivative as a function of time during the CRTA preheating program. Firstly, the temperature is linearly increased ($20^\circ/\text{min}$), which leads to parallel dehydroxilation/carbonation at a quick rate when the temperature reaches a value around 400°C . Subsequently, decarbonation, which is initiated at a temperature of about 810°C , is controlled to take place at the small prefixed rate (mass variation rate of $\sim 0.4\%/\text{min}$). 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. After preheating the sorbent under this program, the resulting skeleton has suffered appreciable sintering due to prolonged slow decarbonation in the CO_2 enriched atmosphere as can be inferred from BET surface area measurements and SEM analysis (Fig. 2) of samples treated in a microwave oven by replicating the preheating temperature program used in the TGA tests. In contrast, the linear preheating program, wherein decarbonation takes place at a fast rate near the end of the preheating period, yields a relatively porous skeleton with a higher surface area (see Fig. 2) but that would be prone to be appreciably sintered in the looping-calcination stage of the subsequent cycles.

The thermograms plotted in Fig. 1 correspond to samples subjected in-situ to the same CRTA preheating program and cycled after at different looping-calcination temperatures. Note the reproducibility of the mass evolution during preheating in different experiments, which allows to accurately control the initial state of the sample prior to the carbonation/calcination cycles. As seen in Fig. 1, the evolution of sample mass along the cycles indicates the occurrence in our experiments of notable self-reactivation when looping-calcination is carried out at 700°C . Yet, self-reactivation is precluded for a looping-calcination temperature of 950°C . This remarkable feature will be analyzed in detail in our work.

Figure 3 shows data on the multicyclic CaO conversion X_N of linearly and CRTA preheated samples subjected to the same looping carbonation/calcination conditions (carbonation-

tion at 650°C in 85% air/15% CO₂ vol/vol and calcination in air at 850°C, both for 5 min). As can be seen, CaO conversion in the first cycle X_0 is notably decreased for the CRTA-preheated sorbent as might have been expected from its relatively small BET surface area (Fig. 2). Conversion as a function of time during the 1st carbonation/calcination cycle for both sorbents is shown in Fig. 4a. It is seen that the CRTA thermal pretreatment promotes carbonation in the diffusive phase, which yields a contribution to conversion in this phase X_{D1} roughly equal to conversion in the fast phase X_{K1} while it is $X_{D1} \ll X_{K1}$ for the non-pretreated sorbent. A rapid decarbonation after the promoted solid-state diffusion would thus yield a porous skeleton with a relatively higher surface area leading to an increase of conversion in the 2nd cycle as seen in Fig. 3. Nonetheless, self-reativation under the looping-calcination conditions applied in this case (temperature $T_{s0} = 850^\circ\text{C}$, and time period $t_{s0} = 5$ min) does not extend beyond the 3rd cycle. Data obtained on the ratio of conversion in the diffusive carbonation phase to conversion in the fast phase ($r_N = X_{DN}/X_{KN}$) are plotted in Fig. 4b. This plot shows that self-reativation in the first cycles occurs in parallel to a decrease of r_N with the cycle number. As a main difference with the CRTA preheated sorbent, the role of diffusive carbonation for the linearly preheated sorbent is not relevant in the first cycle ($r_N \simeq 0.2$). In this case, the initial soft skeleton after preheating would be susceptible to suffering progressive sintering in the successive looping-calcinations whereas surface area regeneration due to solid-state diffusion is negligible, which causes a drastic decrease of X_N with N along the first cycles. As the surface area is gradually decreased with N , conversion in the fast phase decreases and thus r_N increases with N in contrast with the decreasing trend of r_N observed for the CRTA preheated sorbent. Interestingly, r_N conforms for both sorbents to the same trend for $N \gtrsim 20$. At this cycle number, the effect of the preheating program on renovating the active skeleton by enhanced solid-state diffusion would be lost even though the total conversion is kept at a larger value than for the nonpretreated sorbent.

Data on the CaO multicyclic conversion for CRTA preheated samples and subjected to different looping-calcination temperatures ($700^\circ\text{C} < T_s < 950^\circ\text{C}$) plotted in Fig. 5a demon-

strate a strong effect of T_s on self-reactivation. While decreasing the looping-calcination temperature below 850°C enhances self-reactivation, increasing it above $T_s = 900^\circ\text{C}$ nullifies it completely. Figure 5b shows that the decline of self-reactivation is directly correlated to a change of trend of r_N . Self-reactivation is only observed as long as r_N decreases with N . For the highest looping-calcination temperatures r_N increases with N from the first cycle and self-reactivation does not occur.

Data on fast carbonation conversion X_{KN} and diffusive carbonation conversion X_{DN} are plotted in Fig. 6. Figure 7a shows a comparison on the evolution of conversion with time for the 10th carbonation/calcination cycle and for different values of the looping-calcination temperature T_s . Data on the maximum rate of conversion measured in the fast phase indicating the skeleton reactivity (dX_{KN}/dt) are plotted in Fig.7b as a function of the cycle number. Note in Figs. 6a and 7b that the values of conversion X_{KN} and rate of conversion dX_{KN}/dt for the 1st carbonation ($N = 1$) are approximately the same for all the tests since the samples have been subjected to the same pretreatment. Therefore, the skeleton to be carbonated for the first time should be similar in all the tests. The values of X_{KN} and dX_{KN}/dt are however greatly affected already in the 2nd carbonation ($N = 2$) by the looping-calcination temperature T_s used to regenerate the carbonated sorbent. As T_s is increased the values of X_{KN} and dX_{KN}/dt are markedly decreased for $N \geq 2$. In contrast, the results demonstrate that X_{DN} is approximately independent of T_s (see Fig. 6b). Interestingly, Fig. 7b shows that dX_{KN}/dt is mainly enhanced after the looping- calcination, which indicates that the reactivity of the hard skeleton obtained from thermal pretreatment is rather small as compared to the reactivity of the soft skeleton developed after this 1st calcinations. This enhanced reactivity is kept approximately constant with the cycle number for $T_s < 850^\circ\text{C}$. Harsher calcination conditions would lead to a reduction of the surface area by sintering and to a decrease of the soft skeleton reactivity as seen in Fig. 7b from the decrease of dX_{KN}/dt with N for $N > 2$ and $T_s > 850^\circ\text{C}$. Thus, it may be inferred that the main effect of increasing the looping-calcination temperature T_s for sorbent regeneration is

to decrease the surface area and reactivity of the nascent CaO soft skeleton by promoting its sintering. Unfortunately, the tiny amounts of sorbent used for the TGA tests (about 10 mg) prevented us from performing a physisorption analysis of the samples cycled at different calcination temperatures to further confirm this argument (a mass between 200 and 300 mg is typically needed to obtain sufficiently robust physisorption results). Nevertheless, we carried out a through SEM study which served to uphold the conclusions driven from the TGA results. Representative SEM micrographs obtained for samples subjected to just 1 cycle and 10 times cycled are shown in Figs. 8 (1 cycle) and Fig. 9 (10 cycles). As may be observed, a high looping-calcination temperature (950°C) produces a visible sintering of the soft skeleton that would have been regenerated after diffusive carbonation promoted by thermal pretreatment. Thus, the benefit of thermal pretreatment as regards self-reactivation is nullified if the sorbent is regenerated by high calcination temperatures. Presumably, this explains why Alonso et al.²⁰ did not observe self-reactivation of thermally pretreated samples, which were subjected to looping-calcination temperatures of 950°C for 10 min in a 10% CO_2 /90% air vol/vol atmosphere.

Further tests have been performed in our experimental program to look at the effect of prolonging the sintering time period during looping-calcination. Figure 10 shows that increasing the looping-calcination time period t_s produces a similar effect to increasing the looping-calcination temperature T_s . As t_s is prolonged up to 15 min, CaO conversion in the fast carbonation phase X_{KN} is notably decreased whereas carbonation in the diffusive phase X_{DN} is practically unaffected. A main conclusion from our work is therefore that thermal pretreatment induced self-reactivation is conditioned to the application of not too high looping-calcination temperatures nor too long calcinations for diffusion promoted regeneration of the sorbent skeleton to be effective. As T_s is increased above 850°C and the sintering period t_s is prolonged above 15 min, the skeleton regenerated after calcination available for fast carbonation in the next cycle becomes markedly sintered, which precludes self-reactivation.

Models on multicyclic CaO conversion

Non-pretreated sorbents

The decay of conversion exhibited by nonpretreated CaO as it is subjected to repeated carbonation/calcination cycles is essentially due to the progressive sintering suffered by the initial relatively soft skeleton during the looping-calcination stages.^{5,36} A simple and reliable equation to describe the relative decrease of the surface area S of nascent CaO subjected to high temperatures is the German-Munir model^{37, 21-23,38-40}

$$\frac{\Delta S}{S_0} = (K_s t_s)^{1/\gamma_s} \quad (1)$$

for $\Delta S/S_0 < 0.5$. Here S_0 is the initial surface area, K_s is the sintering rate constant, which increases with temperature T following an Arrhenius relationship, and γ_s is a characteristic exponent, which for nascent CaO sintered in an inert dry atmosphere takes a value of $\gamma = 2.7 \pm 0.3$ independent of the temperature and type of precursor. Assuming that in the looping-calcination stage of the i th cycle there is a decrease of surface area $\Delta s_i = s_{i+1} - s'_i$ and neglecting the surface area gain during the preceding carbonation/decarbonation stage ($s'_i \simeq s_i$), it may be written

$$\frac{s_{i+1}}{s'_i} = 1 - a \quad (2)$$

$$\frac{s'_i}{s_i} \simeq 1 \quad (3)$$

where $a = (K_s t_s)^{1/\gamma_s}$ will be the so-called sintering factor and the surface area is made nondimensional with the sorbent initial surface area S_0 . Taking into account that CaO conversion after N cycles (X_N) is proportional to the surface area available after the $(N-1)$ th cycle, it is

$$x_N = s_N = \prod_{i=0}^{N-1} \frac{s_{i+1}}{s_i} = (1 - a)^N \quad (4)$$

where $x_N = X_N/X_0$. Wang and Anthony⁴¹ have already proposed Eq. 4 following a similar derivation and an analogous power-law equation was previously derived by Abanades and co-workers from a different mechanism.⁴² Yet, the power-law decay of x_N with N predicted by Eq. 4 is too drastic as compared to results obtained on nonpretreated limestones subjected to long-series carbonation/calcination cycles.³⁶

As empirically observed for supported metal catalysts subjected to prolonged sintering periods,⁴³ the rate of sintering of an aged skeleton should decrease as the number of cycles builds up. By assuming that the sintering factor decreases in each cycle proportionally to the surface area, and still considering that the gain of surface area due to solid-state diffusive carbonation is negligible, the surface area gain/loss balance equations would be

$$\frac{s_{i+1}}{s_i} = 1 - as_i \quad (5)$$

$$\frac{s'_i}{s_i} = 1 \quad (6)$$

$$s_N - 1 = \sum_{i=0}^{N-1} s_{i+1} - s_i = -a \sum_{i=0}^{N-1} s_i^2 \quad (7)$$

By approximating the sum of finite variations to an integral of infinitesimals ($ds = -as^2 di$), s_N can be easily obtained by integration, which leads to

$$x_N = \frac{1}{1 + aN} \quad (8)$$

Eq. 8 provides good regression coefficients to multicyclic conversion data.⁴¹ However it predicts, after a large number of cycles, an asymptotic approach of conversion to zero, which is against empirical observations revealing the existence of a residual value of conversion $x_r > 0$ at large N .³⁶ Continuing the parallelism with the sintering of supported metal

catalysts, Grasa et al.³⁶ assumed that the sintering rate tends to zero as s_i approaches a residual value s_r . Under this assumption, it is

$$s_{i+1} - s'_i = -k(s_i - s_r)^2 \quad (9)$$

$$s'_i - s_i = 0 \quad (10)$$

$$s_N - 1 = \sum_{i=0}^{N-1} s_{i+1} - s_i = -k \sum_{i=0}^{N-1} (s_i - s_r)^2 \quad (11)$$

where k is the so-called deactivation constant. Integrating the differential approximation of Eq. 11 ($ds = -k(s - s_r)^2 di$), it is obtained

$$x_N = x_r + \frac{1}{kN + (1 - x_r)^{-1}} \quad (12)$$

which fits satisfactorily³⁶ to most of experimental data reported for nonpretreated limestones subjected to long-series carbonation/calcination cycles yielding values of the residual conversion $x_r \sim 0.1$ and of the deactivation constant $k_r \sim 0.5 - 2$.

Even though the surface area evolution of nonpretreated limestones would be mainly governed by sintering of the initial soft skeleton, intermediate solid-state diffusive carbonation/decarbonation stages might lead to a small gain of surface area. In order to take into account explicitly the possibility of a surface area gain in each cycle, Eq. 12 could be alternatively derived from the surface area gain/loss balance equations

$$\frac{s_{i+1}}{s'_i} = 1 - \frac{a}{1 + a(1 + i)} \quad (13)$$

$$\frac{s'_i}{s_i} = 1 + \frac{b}{1 + bi} \quad (14)$$

$$x_N = \prod_{i=0}^{N-1} \frac{s_{i+1}}{s_i} = \prod_{i=0}^{N-1} \left(1 - \frac{a}{1 + a(i + 1)}\right) \prod_{i=0}^{N-1} \left(1 + \frac{b}{1 + bi}\right) \quad (15)$$

where a regeneration factor $b \ll a$ is introduced. Using the known values of the definite products of the sequences $1 - a/(1 + a(1 + i))$ and $1 + b/(1 + bi)$ from mathematical analysis, it is

$$x_N = \frac{1 + b N}{1 + a N} \quad (16)$$

which is equivalent to Eq. 12 ($s_r = x_r = b/a$, $k = a^2/(a - b)$). According to this alternative mechanism, the sintering/regeneration rates are gradually reduced with the cycle number as the soft initial skeleton ages and loses activity. A residual activity $x_r = b/a$ is reached for $N \gg 1$. In this limit, the ratio of gain to loss of surface area is equilibrated ($|s_{i+1} - s'_i|/|s'_i - s_i| \rightarrow 1$ for $i \gg 0$).

Thermally pretreated sorbents

According to the pore skeleton model, thermally pretreated sorbent would be structured in a hard inward skeleton of low reactive CaO surrounded by a softer layer of reactive CaO with a network of small pores.¹² The hard skeleton is developed during thermal pretreatment and would serve to keep the pore structure essentially stable as the material is repeatedly subjected to carbonation/calcination cycles, whereas the external soft skeleton builds up during each recarbonation and renovates after the subsequent rapid decarbonation. Multicyclic CaO conversion of pretreated sorbents would be thus ruled in the first cycles by the balance between surface area variations of the outward soft skeleton. Arias et al. have suggested that the surface area gain leading to self-reactivation is essentially due to extended periods of carbonation by solid-state diffusion.^{9,19} Since the initial surface area of severely sintered sorbents is considerably reduced by pretreatment, fast carbonation in the first cycles would be impaired in favor of solid-state diffusion. In agreement with this picture, our experimental results show that the ratio of conversion in the diffusive phase to conversion in the fast phase $r_i = X_{Di}/X_{Ki}$ is relatively large for the CRTA preheated samples as compared

to the nonpretreated (linearly preheated) sorbent (Fig. 5). Arguably, the relative gain of surface area $(s'_i - s_i)/s_i$ would scale with the cycle number similarly to r_i for which a simple power law equation $r_i = b/(i + 1)^q$ can be proposed. The exponent q would be $q > 0$ for thermally pretreated sorbents in order to reproduce the progressive reduction of the relative gain of diffusive carbonation with the cycle number as seen in our experimental results (Fig. 5). As looping-calcination conditions become harsher, q would approach to zero since X_{Di} would grow proportionally to X_{Ki} . Thus, the gain of surface area due to solid-state diffusive carbonation would be given by

$$\frac{s'_i}{s_i} = 1 + \frac{b}{(i + 1)^q} \quad (17)$$

Arias et al.^{9,19} have followed a similar approach by introducing an additional term x_{DN} to conversion standing for diffusive carbonation, which was assumed to be proportional to the total conversion, $x_{DN} \approx x_N k_D$, where k_D is a proportionality constant. The model proposed by Arias et al.^{9,19} served to describe an increase of conversion with the cycle number for sufficiently large values of k_D and small values of x_0 . Yet, the existence of a maximum value of conversion after a few number of cycles as typically featured in results obtained for pretreated sorbents¹²⁻¹⁴ and seen in our experimental results (Fig. 5), could not be explained from the model. A possible reason of that is that X_{DN} actually decreases in the self-reactivation interval while X_N increases (see Figs. 5 and 6). Thus, the proportionality constant k_D would be a decreasing function of the cycle number. This important feature is taken into account in Eq. 17 by introducing the exponent $q > 0$.

As regards the surface area loss associated to sintering during looping-calcination, and since the soft skeleton is renovated after each decarbonation, it would be $\Delta s_i/s_i < 0.5$. This allows us to use the German-Munir model (Eq. 2) to take into account sintering in this stage. Altogether, Eqns. 2 and 17 lead to

$$x_N \simeq (1-a)^N \prod_{i=0}^{N-1} (1+b)^{\frac{1}{(i+1)^q}} = (1-a)^N (1+b)^{\sum_{i=0}^{N-1} \frac{1}{i+1^q}} \quad (18)$$

where it has been used $(1+b)^{1/(1+i)^q} \approx 1+b/(i+1)^q$ for $b < 1$. The finite sum in the exponent of Eq. 18, which is a special function so-called Harmonic-Number function $H(N, q) = \sum_{i=1}^N 1/i^q$, fits well to a power law equation $H(N, q) \simeq N^\beta$, with $\beta \approx e^{-q}$. In this way, the model yields a simple analytical equation for the multicyclic CaO conversion of pretreated sorbents,

$$x_N = (1-a)^N (1+b)^{N^\beta} \quad (19)$$

In the case of thermally pretreated sorbents showing self-reactivation, the regeneration factor b would be larger than the sintering factor a and it would be $q \simeq -\ln \beta > 0$ as the surface area gain due to diffusive carbonation is lessened with the cycle number (Eq. 17). However, if looping-calcination conditions are harshened, the sintering factor would be increased and the surface area gain could be counteracted by its loss in the looping-calcination stage. As the number of cycles builds up, the soft skeleton cannot be fully renovated due to the decline of solid-state diffusion. The progressive aging of the soft skeleton would cause a transition to a mechanism determined by the gradual attenuation of its sintering rate as for nonpretreated sorbents. Equation 19 would serve therefore to describe self-reactivation in the first cycles as usually reported in experimental studies on thermal pretreatment.¹²⁻¹⁴

Analysis of experimental results

As may be seen in Fig. 3 multicyclic conversion data on the nonpretreated (linearly preheated) sorbent can be pretty well fitted by Eq. 16 for $a = a_0 = 0.164$ and $b = 0.024$ (looping-calcination conditions: $T_{s0} = 850^\circ\text{C}$ and $t_{s0} = 5$ min). As expected in this case, it is $b/a \ll 1$ since most of carbonation occurs via fast carbonation and, thus, regeneration of

the soft skeleton due to solid-state diffusion is negligible. According to the German-Munir model, the sintering factor a of the initial skeleton would be given by $a = (K_s t_s)^{1/\gamma_s}$ where $\gamma_s \simeq 2.7$. Using $a = a_0 = 0.164$ and $t_s = t_{s0} = 5$ min, it would be $K_{s0} \simeq 10^{-3} \text{ min}^{-1}$ which fits to the experimental data reported by Borgwardt on the sintering rate of nascent CaO derived from limestone (see Fig. 4 in ref.²¹).

Let us now focus on the analysis of multicyclic conversion data obtained in our work for the CRTA pretreated sorbents in the first cycles where self-reactivation is observed for mild calcination conditions ($N \leq 10$). In this case the soft skeleton will be renovated in each carbonation and will arguably sinter during looping-calcination as it does the soft skeleton of the nonpretreated sorbent in the first calcination. Accordingly, the sintering factor a for this soft skeleton could be approximated to the sintering factor inferred for the nonpretreated sorbent. However, a necessary requirement to use the sintering factor a_0 inferred from conversion data on the nonpretreated sorbents is that looping-calcination conditions are not varied in the multicyclic experiment on the pretreated sorbents, Taking into account that K_s follows a dependence with temperature in accordance with an Arrhenius relationship ($K_s = A \exp(-\alpha/T_s)$), the sintering factor a for given values of T_s (in Kelvin) and t_s could be obtained as

$$a(T_s, t_s) = a_0 \left(\frac{t_s}{t_{s0}} \right)^{1/\gamma_s} \exp \left(-\frac{\alpha}{\gamma_s} \frac{T_{s0} - T_s}{T_{s0} T_s} \right) \quad (20)$$

where $\alpha \simeq 3 \times 10^3$ K for limestone-derived CaO.²¹ This leaves the regeneration factor b and the exponent β as the only free parameters in Eq. 19 to fit it to multicyclic conversion data on the CRTA pretreated sorbents at varying looping-calcination conditions. The best fit curves obtained in this way are plotted in Fig. 5 showing a good fit to the data. The best fit parameters b and $q = -\ln \beta$, and the sintering factor a obtained from Eq. 20, are represented in Figs. 11a-11b as a function of the looping-calcination temperature T_s and looping-calcination time period t_s . It is seen that the regeneration factor b , as well as the sintering factor a , increase with T_s and t_s . The increase of the regeneration factor b with

the looping calcination temperature T_s can be explained from the increase of the ratio of conversion due to diffusive carbonation to conversion due to fast carbonation with T_s at a given cycle number (Fig. 4b). However, the ratio b/a (Fig. 12) remains approximately constant ($b/a \simeq 1.5$) for $T_s \geq 770^\circ\text{C}$. The case $T_s = 700^\circ\text{C}$ can be considered as particular since decarbonation takes place very slowly at this looping-calcination temperature as seen in Fig. 7). On the other hand, q becomes close to zero for $T_s \simeq 900^\circ\text{C}$ ($t_s = 5$ min) and $t_s \simeq 15$ min ($T_s = 850^\circ\text{C}$) as self-activation is impaired as seen in our experimental results, following an exponential decay law with the sintering factor a (Fig. 12). Equation 19 may thus provide an useful tool to foresee the critical conditions at which thermal pretreatment loses efficiency in inducing self-activation.

Conclusions

In this paper we have analyzed self-activation of thermally pretreated CaO as affected by looping-calcination conditions. Thermal pretreatment has consisted of a Constant Rate Thermal Analysis (CRTA) program, which causes decarbonation to occur at a low prefixed value. This type of pretreatment induces self-activation of CaO during the first carbonation/calcination cycles by sintering the sorbent skeleton, which enhances carbonation in the solid-state diffusion phase. A series of multicyclic carbonation/calcination experiments have been made on CRTA pretreated samples subjected to varying looping-calcination conditions (temperature T_s and time period t_s). According to the pore-skeleton model, a soft porous skeleton is developed after quick decarbonation at the end of the first cycle with increased surface area available for enhanced fast carbonation in the next cycle. Conversion at a given cycle would be thus determined by a balance mechanism between the surface area gain due to enhanced diffusive carbonation and the loss of surface area of nascent CaO associated to sintering during looping-calcination. By assuming a German-Munir model for the surface area reduction of the nascent CaO in the calcination stage, data on multicyclic conversion

in the first cycles have been well fitted by a proposed equation based on this balance. Accordingly, the main effect of harshening looping-calcination conditions is to accelerate the sintering of the renovated soft skeleton. This causes a decrease of conversion in the fast phase whereas conversion in the solid-state diffusion phase is practically unaffected. As looping-calcination conditions are further harshened, the renovated soft skeleton is increasingly sintered during the calcination stage of the cycles and self-activation is eventually hindered. Self-activation is in our experiments fully precluded when the looping-calcination temperature is increased beyond 900°C ($t_s = 5$ min fixed) or for looping-calcination periods of 15 min ($T_s=850^\circ\text{C}$ fixed) whereas significant self-activation is observed for looping-calcination temperatures below 800°C or short looping-calcination periods of around 1 min. In order to assess the efficiency of thermal pretreatment on stabilizing the multicyclic CaO conversion for CO₂ capture from combustion gases it is thus important to analyze the restraint posed by the looping-calcination conditions, which will foreseeable be harsher than those used in most works showing self-activation of thermally pretreated sorbents.

Acknowledgement

This work was supported by the “Consejeria de Innovacion, Ciencia y Empresa (Junta de Andalucia)” within the European Regional Development Fund contracts FQM-5735 and by the Spanish Government Agency “Ministerio de Economia y Competitividad” (contracts FIS2011-25161 and CTQ2011-27626). The authors thank Dr. Francisco Varela from the Microscopy Service of the Innovation, Technology and Research Center of the University of Seville (CITIUS) for his assistance.

Supporting Information Available

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References

- (1) Blamey, J.; Anthony, E. J.; Wang, J.; Fennell, P. S. *Prog. Energ. Combust. Sci.* **2010**, *36*, 260–279.
- (2) Dean, C.; Blamey, J.; Florin, N.; Al-Jeboori, M.; Fennell, P. *Chemical Engineering Research and Design* **2011**, *89*, 836 – 855.
- (3) Sanchez-Biezma, A.; Ballesteros, J.; Diaz, L.; de Zarraga, E.; Alvarez, F.; Lopez, J.; Arias, B.; Grasa, G.; Abanades, J. *Energy Procedia* **2011**, *4*, 852 – 859.
- (4) Shimizu, T.; Hirama, T.; Hosoda, H.; Kitano, K.; Inagaki, M.; Tejima, K. *Chemical Engineering Research & Design* **1999**, *77*, 62 – 68.
- (5) Barker, R. *J. Appl. Chem. Biotechnol.* **1973**, *23*, 733 – 742.
- (6) Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J. C. *AIChE J.* **2009**, *55*, 1246–1255.
- (7) Abanades, J. C.; Anthony, E. J.; Lu, D. Y.; Salvador, C.; Alvarez, D. *AIChE J.* **2004**, *50*, 1614–1622.
- (8) Grasa, G.; Gonzalez, B.; Alonso, M.; Abanades, J. C. *Energ. Fuel.* **2007**, *21*, 3560–3562.
- (9) Arias, B.; Abanades, J. C.; Grasa, G. S. *Chem. Eng. J.* **2011**, *167*, 255–261.
- (10) Rodriguez, N.; Alonso, M.; Abanades, J. C.; Charitos, A.; Hawthorne, C.; Schefknecht, G.; Lu, D. Y.; Anthony, E. J. *Energy Procedia* **2011**, *4*, 393 – 401.
- (11) Albrecht, K. O.; Wagenbach, K. S.; Satrio, J. A.; Shanks, B. H.; Wheelock, T. D. *Ind. Eng. Chem. Res.* **2008**, *47*, 7841 – 7848.
- (12) Manovic, V.; Anthony, E. J. *Environ. Sci. Technol.* **2008**, *42*, 4170–4174.
- (13) Manovic, V.; Anthony, E. J.; Grasa, G.; Abanades, J. C. *Energy & Fuels* **2008**, *22*, 3258 – 3264.

- (14) Manovic, V.; Anthony, E. J.; Loncarevic, D. *Chemical Engineering Science* **2009**, *64*, 3236 – 3245.
- (15) Florin, N. H.; Harris, A. T. *Chemical Engineering Science* **2009**, *64*, 187 – 191.
- (16) Chen, Y.; Yang, J.; Dave, R. N.; Pfeffer, R. *Powder Tech.* **2009**, *191*, 206 – 217.
- (17) Manovic, V.; Anthony, E. J.; Loncarevic, D. *Ind. Eng. Chem. Res.* **2011**, *50*, 6933 – 6942.
- (18) Jia, L.; Hughes, R.; Lu, D.; Anthony, E. J.; Lau, I. *Industrial & Engineering Chemistry Research* **2007**, *46*, 5199 – 5209.
- (19) Arias, B.; Abanades, J. C.; Anthony, E. J. *Energy Fuels* **2011**, *25*, 1926 – 1930.
- (20) Alonso, M.; Lorenzo, M.; Gonzalez, B.; Abanades, J. C. *Energy & Fuels* **2011**, *25*, 5521–5527.
- (21) Borgwardt, R. H. *Chem. Eng. Sci.* **1989**, *44*, 53–60.
- (22) Borgwardt, R. H. *Industrial & Engineering Chemistry Research* **1989**, *28*, 493 – 500.
- (23) Stanmore, B.; Gilot, P. *Fuel Processing Technology* **2005**, *86*, 1707 – 1743.
- (24) Rouquérol, J. *Journal of Thermal Analysis and Calorimetry* **1970**, *2*, 123 – 140.
- (25) Rouquérol, J.; Ganteaume, M. *Journal of Thermal Analysis and Calorimetry* **1977**, *11*, 201 – 210.
- (26) Criado, J. M.; Macias, M.; Macias-Machin, A. *Solar Energy* **1992**, *49*, 83–86.
- (27) Perez-Maqueda, L.; Ortega, A.; Criado, J. *Thermochimica Acta* **1996**, *277*, 165 – 173.
- (28) Koga, N.; Criado, J. M. *Int. J. Chem. Kinet.* **1998**, *30*, 737–744.
- (29) Perez-Maqueda, L. A.; Criado, J. M.; Subrt, J.; Real, C. *Catalysis Letters* **1999**, *60*, 151 – 156.

- (30) Perez-Maqueda, L.; Dianez, M. J.; Gotor, F. J.; Sayagues, M. J.; Real, C.; Criado, J. *Journal of Materials Chemistry* **2003**, *13*, 2234 – 2241.
- (31) Criado, J. M.; Perez-Maqueda, L.; Dianez, M. J.; Sanchez-Jimenez, P. E. *Journal of Thermal Analysis and Calorimetry* **2007**, *87*, 297 – 300.
- (32) Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A.; Crespo-Amoros, J. E.; Lopez, J.; Perejon, A.; Criado, J. M. *Analytical Chemistry* **2010**, *82*, 8875 – 8880.
- (33) Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A.; Perejon, A.; Criado, J. M. *Polymer Degradation and Stability* **2011**, *96*, 974 – 981.
- (34) Lu, D. Y.; Hughes, R. W.; Anthony, E. J.; Manovic, V. *J. Environ. Eng.* **2009**, *135*, 404–410.
- (35) Lysikov, A. I.; Salanov, A. N.; Okunev, A. G. *Ind. Eng. Chem. Res.* **2007**, *46*, 4633 – 4638.
- (36) Grasa, G. S.; Abanades, J. C. *Ind. Eng. Chem. Res.* **2006**, *45*, 8846–8851.
- (37) German, R. M.; Munir, Z. A. *Journal of the American Ceramic Society* **1976**, *59*, 379 – 383.
- (38) Milne, C. R.; Silcox, G. D.; Pershing, D. W.; Kirchgessner, D. A. *Industrial & Engineering Chemistry Research* **1990**, *29*, 139–149.
- (39) Fuertes, A. B.; Alvarez, D.; Rubiera, F.; Pis, J. J.; Marban, G. *Chemical Engineering Communications* **1991**, *109*, 73 – 88.
- (40) Perez-Maqueda, L.; Criado, J.; Real, C. *J. Am. Ceram. Soc.* **2002**, *85*, 763 – 768.
- (41) Wang, J.; Anthony, E. J. *Ind. Eng. Chem. Res.* **2005**, *44*, 627 – 629.
- (42) Abanades, J. C. *Chem. Eng. J.* **2002**, *90*, 303–306.
- (43) Bartholomew, C. H. *Applied Catalysis A: General* **1993**, *107*, 1 – 57.

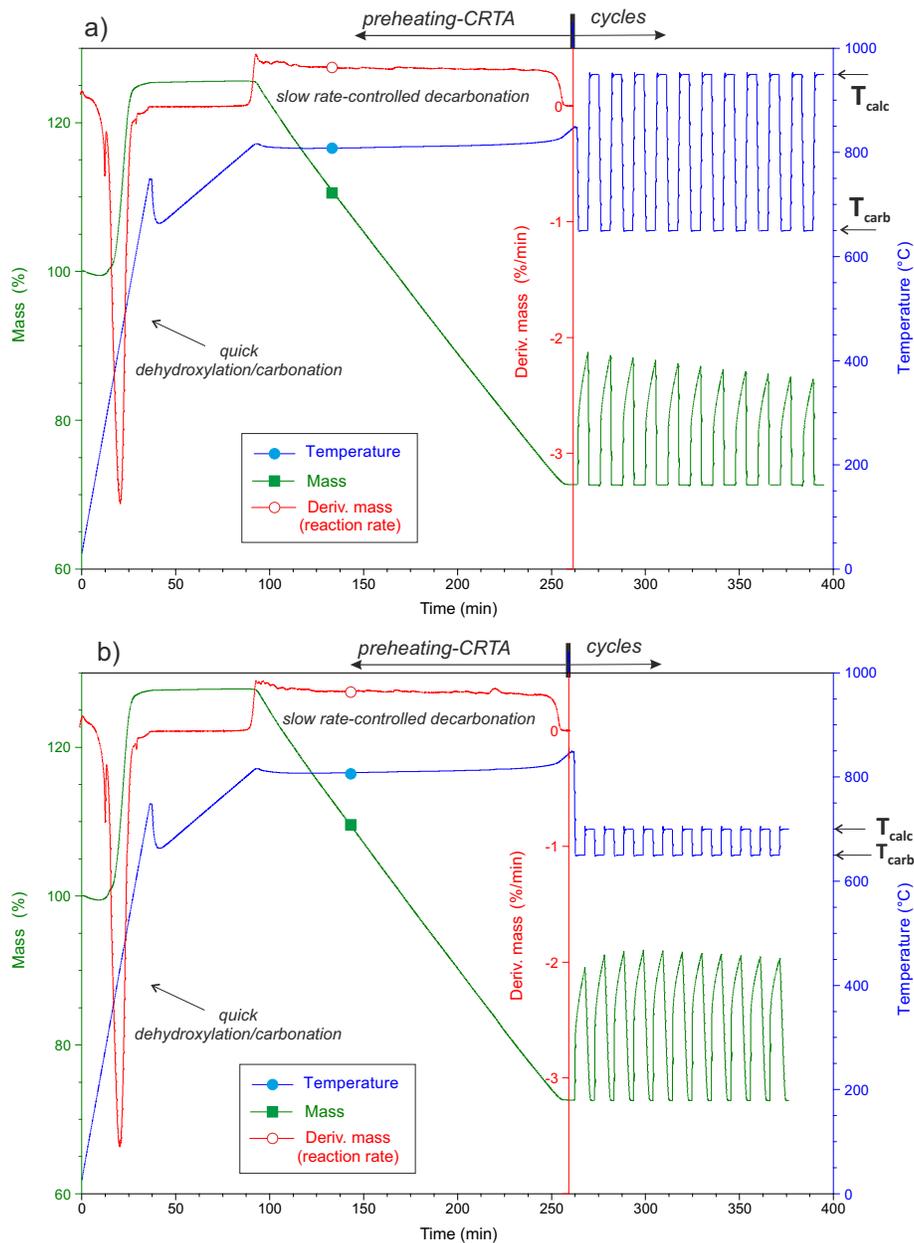


Figure 1: Thermograms showing the evolution of temperature, sample mass % and mass % derivative (reaction rate) during CRTA preheating of $\text{Ca}(\text{OH})_2$ samples (9.573 mg in (a), 10.296 mg in (b)) in an air/ CO_2 atmosphere and carried out as pretreatment before the carbonation/calcination cycles are initiated. The occurrence of dehydroxylation/carbonation at a quick rate and decarbonation at a slow controlled rate are indicated. Carbonation/calcination temperatures (T_{carb} and T_{calc} are indicated) In (a) looping-calcination is carried out at 950°C and in (b) at 700°C .

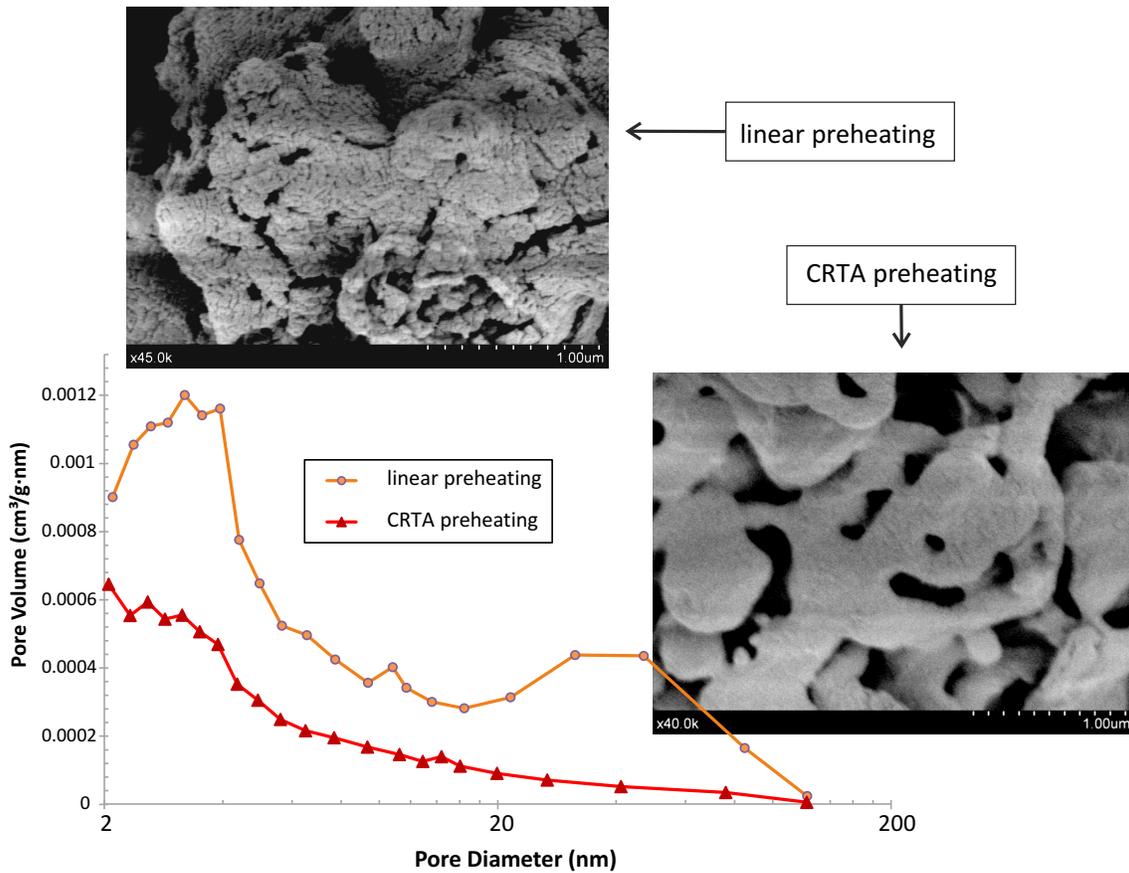


Figure 2: BJH Desorption dV/dD Pore Volume and SEM pictures of sorbent samples after being subjected to different preheating treatments: linear preheating ($BET=9.04 \text{ m}^2/\text{g}$) and CRTA preheating ($BET=3.87 \text{ m}^2/\text{g}$).

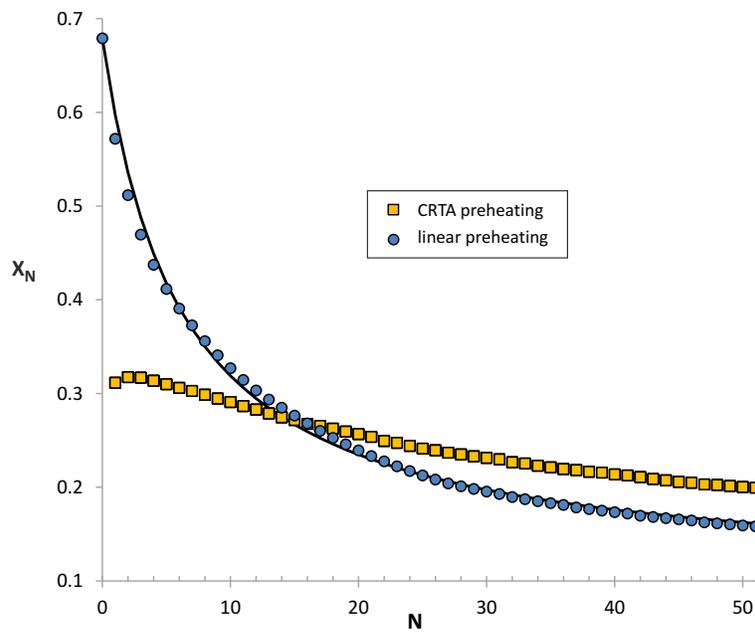


Figure 3: Multicyclic conversion of CaO derived from in-situ linear and CRTA preheating programs. The solid line is the best fit curve of Eq. 16 to the data ($a = 0.164$, $b = 0.024$). Looping calcination conditions: $T_{s0}=850^{\circ}\text{C}$, $t_{s0}=5$ min.

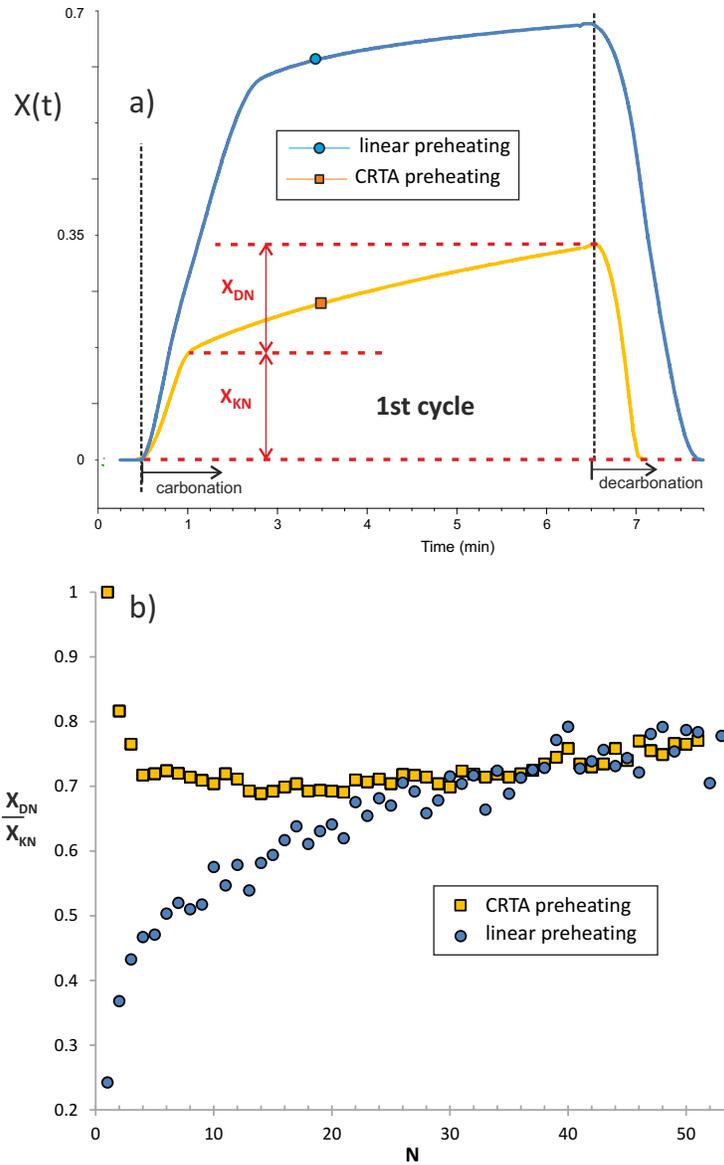


Figure 4: a) Conversion as a function of time in the 1st carbonation/calcination cycle for CaO samples derived from in-situ linear and CRTA preheating programs. The border between the fast and slow carbonation phases is delineated. b) Ratio of conversion in the solid-state diffusion phase to conversion in the fast phase as a function of the carbonation/calcination number for CaO samples subjected to linear and CRTA preheating programs. Looping calcination conditions: $T_{s0}=850^{\circ}\text{C}$, $t_{s0}=5$ min.

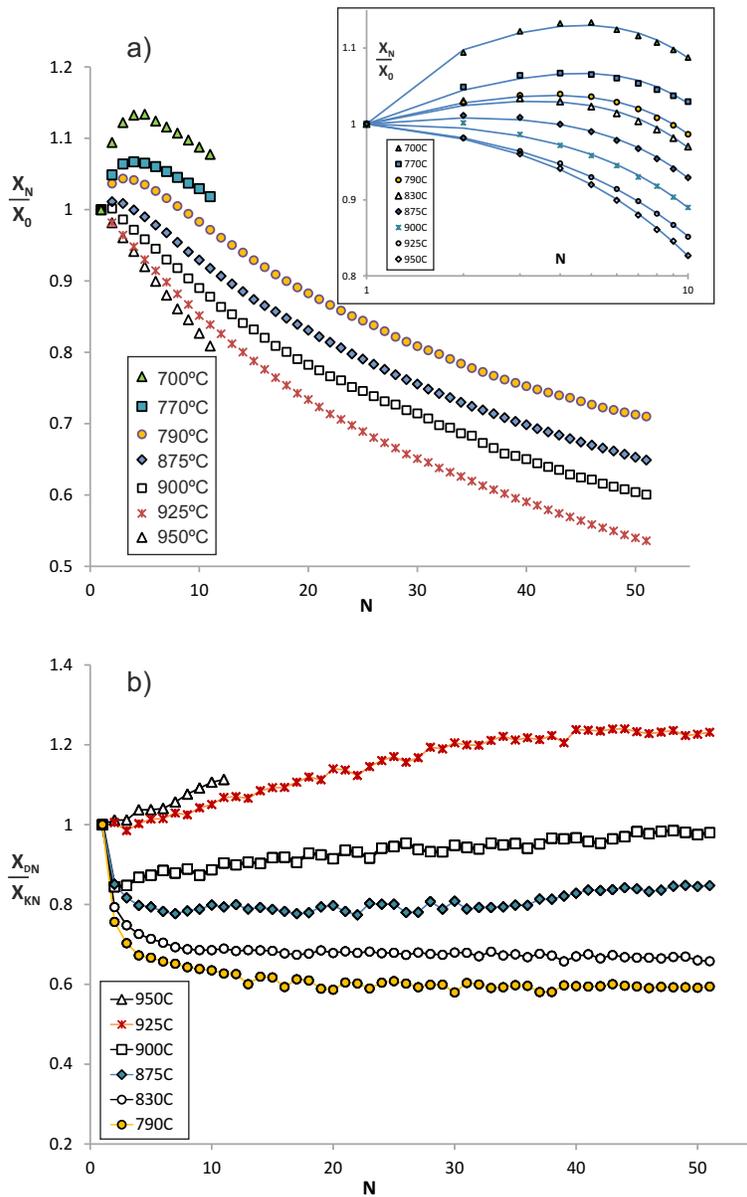


Figure 5: a) Multicyclic conversion of CaO derived from in-situ CRTA preheating and for different looping-calcination temperatures T_s as indicated ($t_s = 5$ min). The inset is a zoom of the self-reactivation interval ($N \leq 10$) where the solid lines are obtained from the best fits of Eq. 19 to the data as detailed in section ($X_0 \simeq 0.3$). b) Ratio of conversion in the solid-state diffusion phase to conversion in the fast kinetically controlled phase ($r_N = X_{DN}/X_{KN}$) as a function of the carbonation/calciation number.

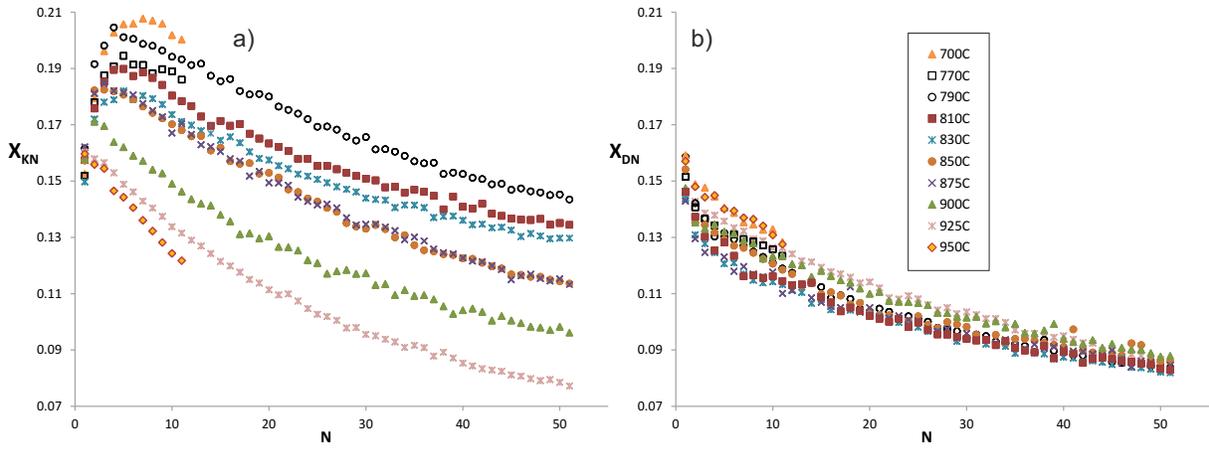


Figure 6: a) CaO conversion in the fast kinetically controlled phase X_{KN} as a function of the carbonation/calciation number. b) CaO conversion in the solid-state diffusion phase X_{DN} as a function of the carbonation/calciation number. Data are shown for different looping-calciation temperatures as indicated ($t_s = 5$ min).

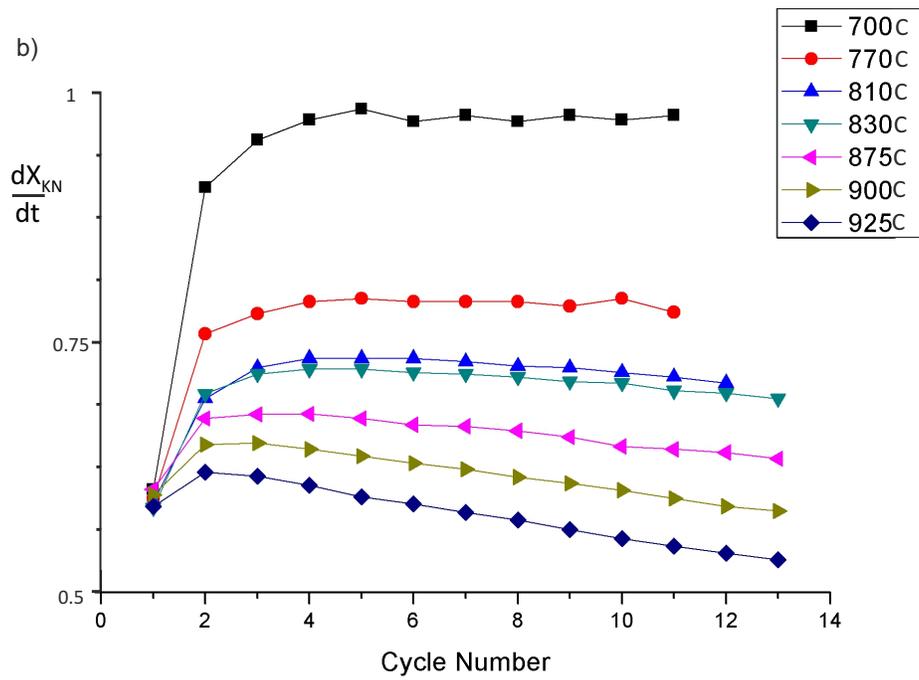
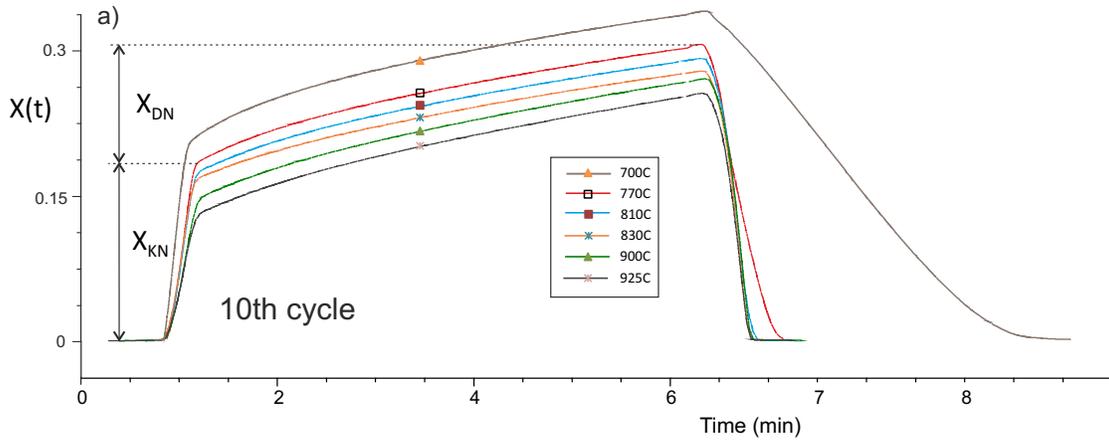


Figure 7: a) Evolution of conversion with time during the 10th carbonation/calcination. Looping-calcination conditions: T_s variable as indicated and $t_s=5$ min. Conversion in the diffusive phase X_{DN} and in the fast phase X_{KN} are indicated for $T_s = 770^\circ\text{C}$. b) Maximum rate of conversion in the fast phase as a function of the cycle number for different values of T_s .

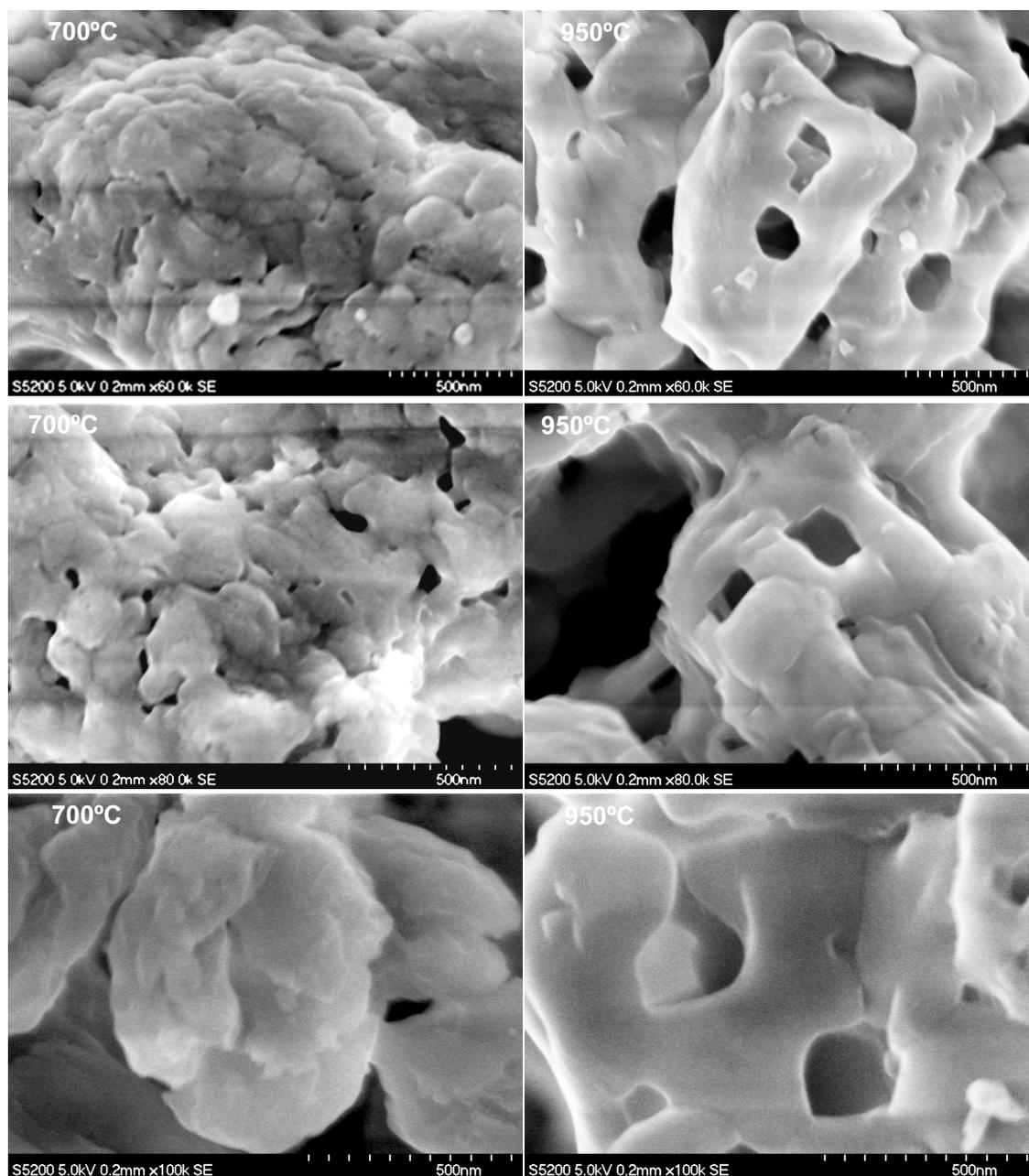


Figure 8: SEM micrographs of CRTA-preheated samples after 1 carbonation/calcination cycle for different looping-calcination temperatures (700°C and 950°C as indicated) and $t_s=5$ min.

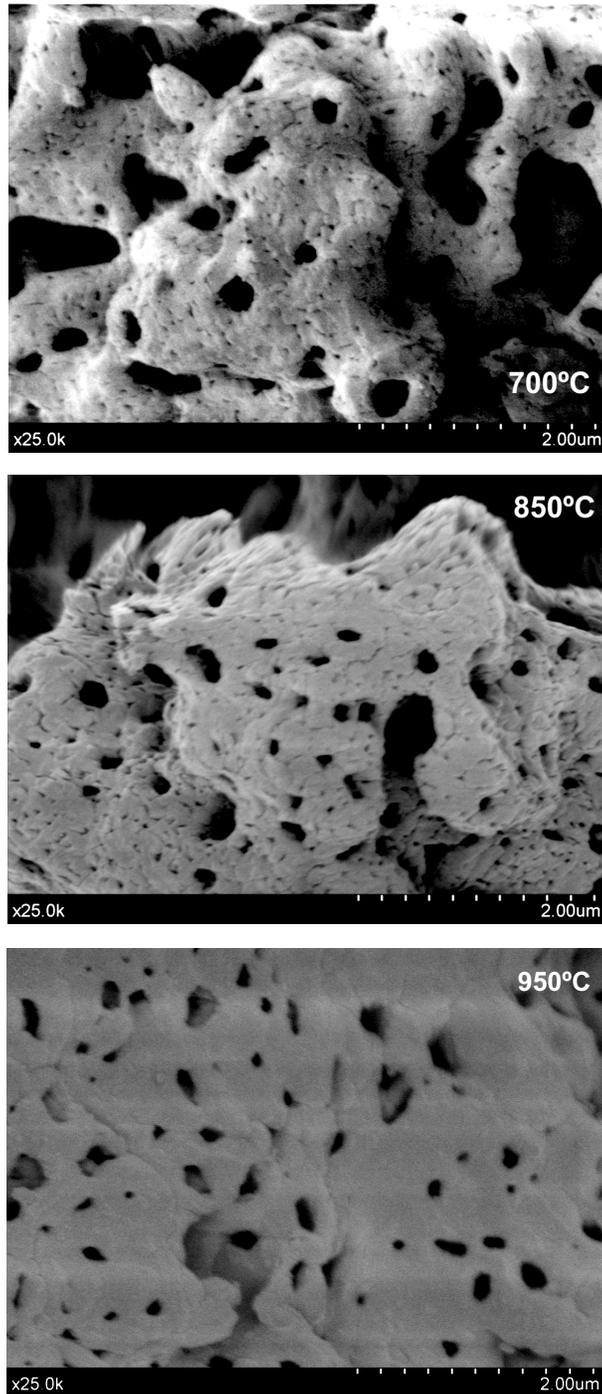


Figure 9: SEM micrographs of CRTA-preheated samples after 10 carbonation/calcination cycles for different looping-calcination temperatures (700°C, 850°C and 950°C as indicated) and $t_s=5$ min.

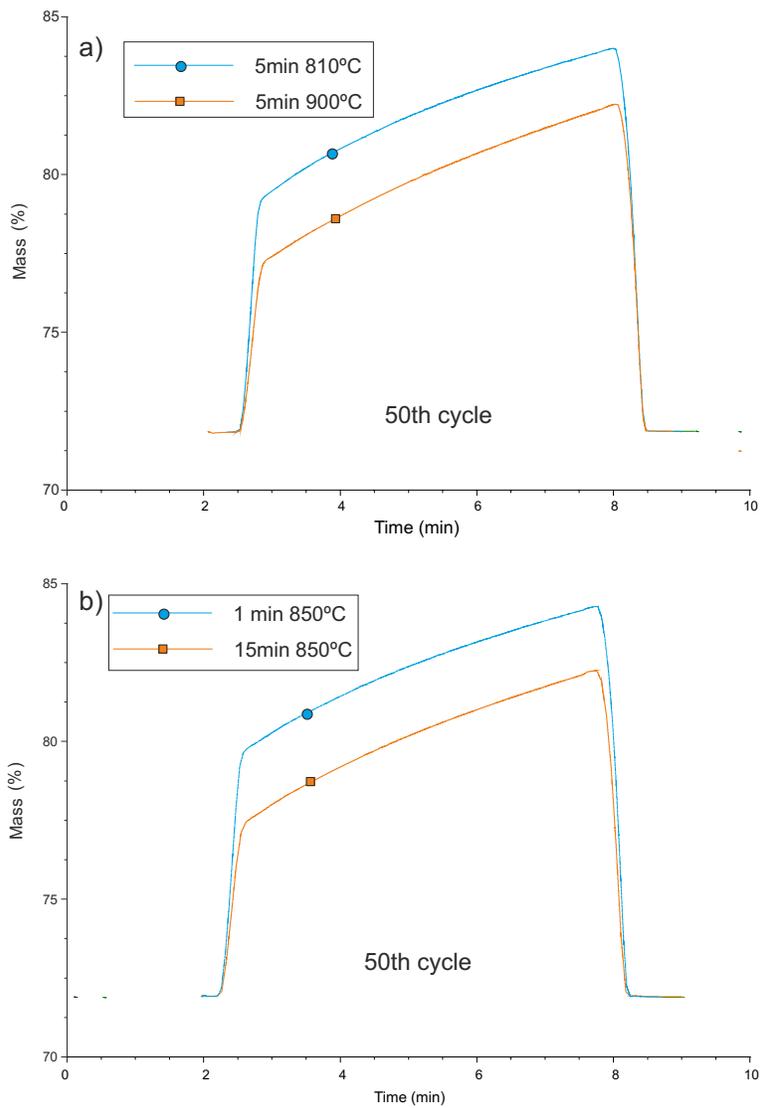


Figure 10: Mass gain % as a function of time in the 50th carbonation cycle for samples cycled under different looping-calcination temperatures (a) and time periods (b) as indicated.

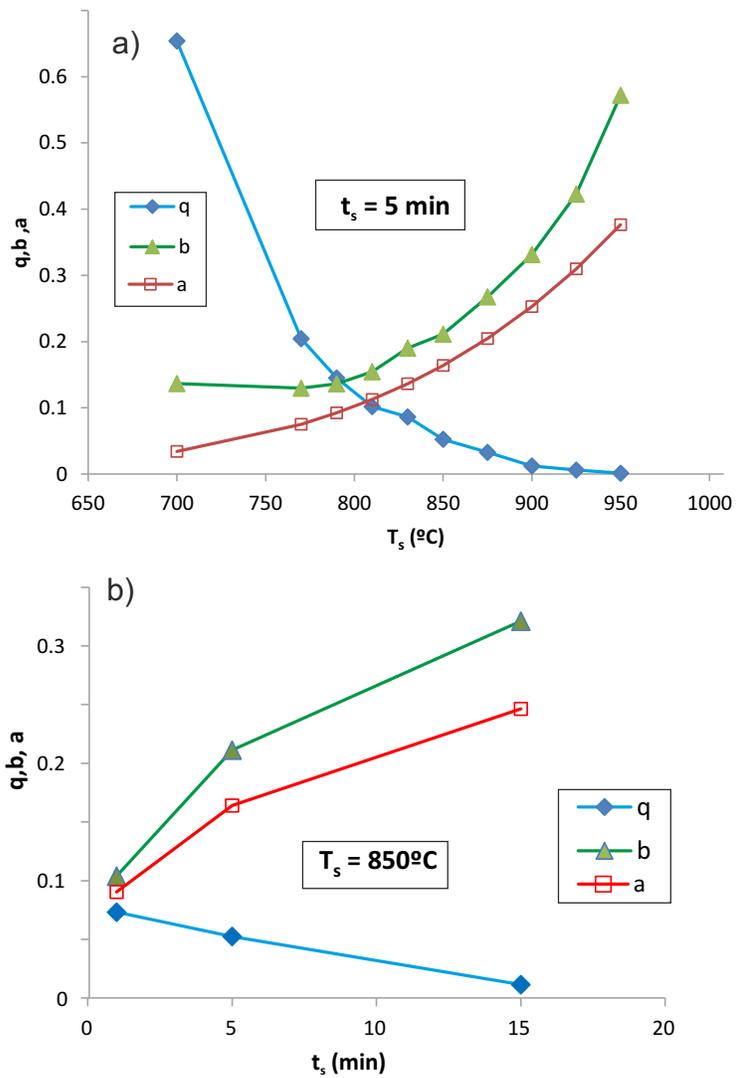


Figure 11: Best fitting parameters (b and $q = -\ln \beta$) of Eq. 19 to multicyclic conversion data in the first 10 cycles as a function of looping-calcination temperature T_s ($t_s=5$ min) (a) and looping-calcination time period t_s ($T_s = 850^\circ\text{C}$). Best fit curves for conversion using these parameters are plotted in Fig. 5.

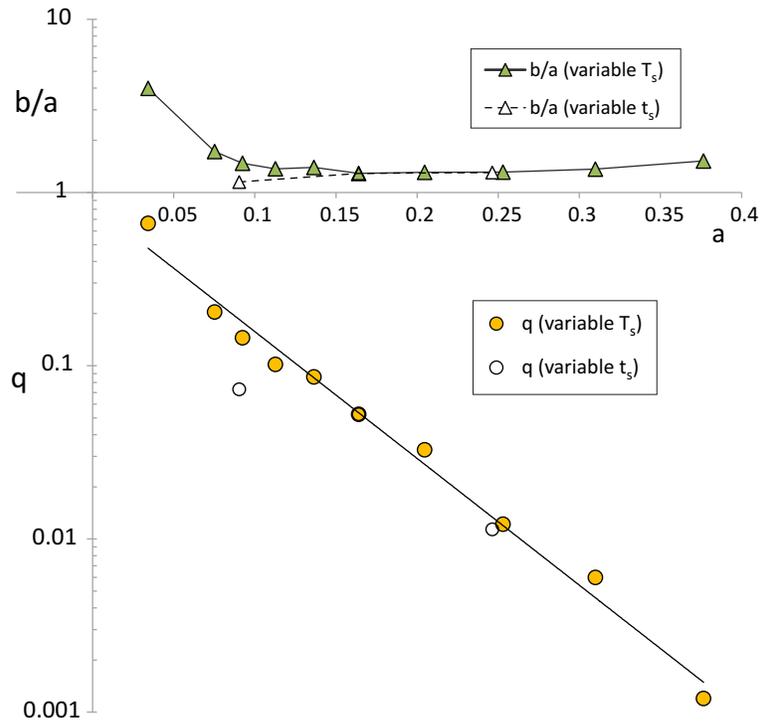


Figure 12: Ratio of the regeneration to sintering factors b/a and exponent $q = -\ln \beta$ obtained from the best fitting parameters of Eq. 19 to multicyclic conversion data in the first 10 cycles as a function of the sintering factor a calculated from Eq. 20. The solid line is an exponential decay fit to data on q ($q = 0.85 \exp(-16.9 a)$).