

1 **Effect of heat pretreatment/recarbonation in the Ca-looping**
2 **process at realistic calcination conditions**

3 J. M. Valverde^a, P. E. Sanchez-Jimenez^b, L. A. Perez-Maqueda^b

4 ^a Faculty of Physics. University of Seville. Avenida Reina Mercedes s/n, 41012 Sevilla, Spain

5 ^b Instituto de Ciencia de Materiales de Sevilla (C.S.I.C.-Univ.

6 Seville), Americo Vespucio 49, 41092 Sevilla, Spain

Abstract

Even though an increasing number of pilot-scale plants are demonstrating the potential efficiency of the Ca-looping technology to capture CO₂ at a commercial level, a still standing matter of concern is the loss of carbonation reactivity of the regenerated CaO by calcination, which is expected to be particularly marked at realistic conditions necessarily implying a high CO₂ partial pressure in the calciner. In this work, we address the effect of previously reported strategies for sorbent reactivation, namely heat pretreatment and the introduction of a recarbonation stage before regeneration. Both techniques, either combined or separately, are shown to favor the carbonation reactivity albeit CaO regeneration is usually carried out at low CO₂ partial pressure in lab-scale tests. Novel results reported in this paper show the opposite when the sorbent is regenerated by calcination at high CO₂ concentration, which is arguably due to the diverse mechanisms that rule decarbonation depending on the CO₂ concentration in the calciner atmosphere. Dynamic and reversible adsorption/desorption of CO₂ is thought to govern decarbonation during calcination at high CO₂ partial pressure, which would be hindered by the introduction of a recarbonation stage before carbonation. Moreover, carbonation in the fast phase is severely hampered as a result of the marked loss of reactivity of the surface of CaO regenerated under high CO₂ partial pressure. On the other hand, heat pretreatment and harsh calcination conditions lead to a notable enhancement of diffusion, which would favor the process efficiency. In these conditions, diffusion controlled carbonation becomes a significant contribution to CaO conversion, which is notably increased by prolonging the carbonation stage. Heat pretreatment allows also reducing the calcination temperature at high CO₂ partial pressure while still achieving full decarbonation in short residence times.

29 I. INTRODUCTION

30 The multicyclic carbonation/calcination of CaO is at the basis of the Ca-looping (CaL)
31 technology, which has recently emerged as a potentially viable process for post-combustion
32 and pre-combustion CO₂ capture applications at a commercial level [1–4]. Natural limestone,
33 as a widely available and cheap CaO precursor, is currently used in pilot-plants up to 1.7
34 MW_{th} demonstrating the efficiency of the CaL technology [3, 4]. Practical constraints such
35 as the low concentration of CO₂ in the flue gas ($\sim 15\%$ vol) for carbonation, short residence
36 times, and high CO₂ partial pressure in the calciner determine the optimum values of the
37 carbonation temperature (around 650°C) and the minimum temperature at the calciner for
38 fast enough decarbonation $T_{calc} \simeq 950^\circ\text{C}$ [3–7], which is about 50°C higher than the reaction
39 equilibrium temperature under CO₂ at atmospheric pressure [8]. A main source of process
40 inefficiency is thus the energy requirement to heat the solids in the calciner [9–12]. Moreover,
41 sorbent regeneration at such high calcination temperatures leads to a loss of the carbonation
42 reactivity of the regenerated CaO. Similarly to other chemical looping based processes [13–
43 15], the progressive loss of reactivity as the number of cycles builds up further hampers the
44 efficiency of the technology [16, 17].

45 Developing methods and modified/synthetic CaO precursors to mitigate the irreversible
46 loss of CaO carbonation reactivity as the number of carbonation/calcination cycles builds
47 up is a current subject of great interest [18–22]. Multicyclic thermogravimetric analysis
48 (TGA) tests show that carbonation of CaO particles proceeds along two different phases
49 [23, 24]. Carbonation of the CaO surface occurs firstly by means of a kinetically-driven fast
50 mechanism after which carbonation turns to be controlled by a much slower diffusion pro-
51 cess of CO₃²⁻ mobile ions and counter-current diffusion of O²⁻ anions through the CaCO₃

52 product layer [25, 26]. As generally believed, short residence times below a few minutes
53 in the practical application constrain carbonation to occur mostly in the fast phase on the
54 CaO surface, which becomes progressively reduced due to material sintering by calcination
55 at high temperature. A technically and economically feasible technique for sorbent reactivation
56 would consist of subjecting the partially carbonated solids exiting the carbonator to
57 additional carbonation in an intermediate reactor operated at high CO₂ concentration and
58 high temperature before entering into the calciner [19, 27, 28]. Accidental recarbonation
59 would also occur in recently proposed techniques aimed at reducing the energy consumption
60 in the calciner such as the introduction of a cyclonic preheater [9] to transfer heat from the
61 hot gas leaving the calciner to the particles exiting the carbonator or a mixing seal valve
62 [12] where the solids from the carbonator and calciner exchange heat. Another method pro-
63 posed for sorbent reactivation is heat pretreatment [18, 29]. Isothermal preheating of CaO
64 at high temperature ($\gtrsim 900^{\circ}\text{C}$) for a prolonged period of time leads to a CaO skeleton with
65 very poor reactivity in the fast carbonation phase of the first cycle. However, reactivation
66 is seen to occur in subsequent cycles provided that calcination conditions are not harsh.
67 In a recent study [28], it has been shown that the combination of heat pretreatment and
68 recarbonation yields a high and stable value of CaO conversion. TGA results evidenced that
69 diffusion controlled carbonation in the recarbonation stage is markedly enhanced in the heat
70 pretreated CaO, which gives rise to a highly porous and reactive CaO skeleton left behind
71 by irreversibly desorbed CO₂ during calcination.

72 A critical issue that besets the practical usefulness of most lab-scale investigations on the
73 effect of either reactivation techniques or modified sorbents is that insufficiently fast heat-
74 ing/cooling rates of common furnaces prevent from carrying out carbonation/calcination
75 tests at realistic conditions. In practice, the solids are quickly circulated between the car-

76 bonator and the calciner and regeneration in the calciner takes place in a high CO_2 partial
77 pressure environment. Experimental studies indicate however that the presence of CO_2 at
78 high concentration during calcination may have a dramatically adverse effect on the carbona-
79 tion reactivity of the regenerated CaO [5, 30–32]. In the present work we report experimental
80 results from multicyclic TGA tests with a particular focus on the effects of recarbonation
81 and heat pretreatment on the CaL process at realistic conditions necessarily implying a high
82 CO_2 partial pressure during decarbonation and short transition periods between stages.

83 II. MATERIALS AND METHODS

84 Samples of a high purity natural limestone (CaCO_3 99.62%, $\text{SiO}_2 < 0.05\%$, $\text{Al}_2\text{O}_3 <$
85 0.05% , MgO 0.24%, Na_2O 0.08%) from Matagallar quarry (Pedrera, Spain) have been tested
86 in our work by means of a Q5000IR TG analyzer (TA Instruments), which is based on a
87 furnace heated by infrared halogen lamps and a high sensitivity balance ($<0.1 \mu\text{g}$) with a
88 minimum baseline dynamic drift ($<10 \mu\text{g}$). Heating/cooling rates (up to 500°C) achievable
89 by this instrument allow replicating CaL conditions at practice with a fast transition be-
90 tween carbonation and calcination stages and high CO_2 partial pressure in the calcination
91 stage. As a general initialization procedure, the limestone sample was decarbonated in-situ
92 by subjecting it to a linear heating program ($20^\circ\text{C}/\text{min}$) up to 850°C in air. Subsequent
93 carbonation/calcination (c/c) cycles were pursued by 5 min carbonation at 650°C (85%
94 air/15% CO_2 vol/vol) followed by 5 min calcination (70% CO_2 /30% air vol/vol) at 950°C .
95 In carbonation/recarbonation/calcination (c/r/c) cycles the sample was subjected to a 3
96 min recarbonation stage (10% air/90% CO_2 vol/vol) at 800°C in between the carbonation
97 and calcination stages. Heat pretreatment was carried out by subjecting the limestone sam-
98 ple to isothermal heating at 950°C for 12 h in dry air. Further tests were performed at

99 decreased calcination temperature (down to 880°C) and extended carbonation time (up to
100 10 min). The likely influence of mass transfer on the reaction rate has been avoided in our
101 tests by using a fixed mass of 10 mg in all the runs and small particle size. Undesired effects
102 due to diffusion resistance through the sample can be neglected for sample masses of about
103 10 mg as demonstrated elsewhere [33] by using four different TG analyzers including the
104 Q5000IR employed in our study. The height of the sample layer in the crucible (9.7 mm in
105 diameter) of this analyzer is just around 0.1 mm. Volume weighted mean particle size of the
106 natural limestone used in our experiments is 9.5 μm . Such small particle size allows us to
107 dismiss also effects related to intra-particle diffusion resistance on the reaction rate [8, 24].
108 Likewise, the possible effect of the superficial gas velocity over the sample on the reaction
109 kinetics was avoided by using a small gas flow rate of 100 $\text{cm}^3\text{min}^{-1}$ in all the runs, which
110 yielded a superficial gas velocity of the order of cm/s having no influence on the reaction
111 rate [33].

112 **III. EXPERIMENTAL RESULTS AND DISCUSSION**

113 Figure 1 shows the time evolution of sorbent weight % during the first 3 cycles of c/r/c
114 cycles for samples of raw (a) and heat pretreated (b) limestone demonstrating the strong
115 influence of the calcination conditions (850°C in air vs. 950°C under 70% CO_2 /30% air
116 vol/vol) on the carbonation reactivity of the sorbents after regeneration. A main effect of
117 sorbent regeneration at high CO_2 concentration is the marked decrease of carbonation reac-
118 tivity in the fast phase whereas diffusion-controlled carbonation is relatively promoted. In
119 addition to intensifying diffusion-controlled carbonation, sorbent regeneration at high CO_2
120 concentration leads to a significant enhancement of the recarbonation stage, which is also
121 controlled by diffusion [34]. However, in contrast with previously reported results obtained

122 from multicyclic tests in which the sorbent was regenerated in air [19, 28], recarbonation
123 does not serve to reactivate the sorbent regenerated under CO₂ leading on the contrary to
124 an even further drop of CaO conversion in the carbonation stage of the subsequent cycle.
125 This is clearly seen in Fig. 2 where data on the multicyclic CaO conversion at the end
126 of the carbonation stage as a function of the cycle number are plotted. The contrasting
127 effect of recarbonation depending on the CO₂ concentration in the calcination atmosphere is
128 particularly noticeable for the heat pretreated sample, which shows a high susceptibility to
129 diffusion-controlled carbonation and therefore suffers a relatively intense recarbonation. A
130 plausible explanation for the critical influence of the CO₂ partial pressure in the calcina-
131 tion atmosphere on the effect of recarbonation may be retrieved from the diverse mechanisms
132 that govern decarbonation as a function of the CO₂ partial pressure. During calcination at
133 CO₂ partial pressures much smaller than the equilibrium pressure decarbonation would oc-
134 cur by the irreversibly desorption of CO₂ [35, 36], which would give rise to a highly porous
135 CaO skeleton with enhanced surface area for fast carbonation. The porosity of the resulting
136 CaO skeleton would be enhanced by a precedent recarbonation stage, which would allow
137 subsequent decarbonation to occur deeper in the bulk of the solid thus leading to a further
138 gain of porosity in the resulting CaO skeleton. As might be expected, the favorable effect of
139 recarbonation is markedly promoted by heat pretreatment which enhances it. This picture
140 is changed however when decarbonation takes place in the presence of CO₂ at high con-
141 centration, which is governed by a dynamic and reversible adsorption/desorption process
142 of CO₂ [8, 35–38]. Atomistic simulations and ab initio modeling theoretical studies indi-
143 cate that CO₂ insertion in the CaO lattice would be only energetically favorable at high
144 temperature within the (111) oriented surfaces of the CaO crystal structure. Arguably,
145 CO₂ adsorption/desorption into these reactive planes would prevent the growth of the CaO

146 crystal structure along them thus compromising the reactivity of the regenerated sorbent to-
147 wards surface carbonation. On the other hand, the reversible adsorption/desorption of CO_2
148 into the CaO structure would involve intense distortions of the crystal lattice [39] causing
149 strong shear stresses and structural defects that help diffusion of mobile ions into the bulk
150 of the solid thus enhancing carbonation in the diffusion controlled carbonation phase and
151 recarbonation stage as seen in Fig. 1b.

152 A further effect of recarbonation when the sorbent is regenerated at high CO_2 partial
153 pressure regards the high sensitivity of the decarbonation rate to temperature variations.
154 Ideally, the process efficiency would be benefitted from calcination temperatures as low as
155 possible to allow full decarbonation in short times. The TGs shown in Fig. 3 illustrate the
156 characteristics of carbonation/decarbonation kinetics when the calcination temperature is
157 decreased down to 900°C in c/r/c (Fig. 3a) and c/c (Fig. 3b) cycles. As observed above,
158 Fig. 3a demonstrates the substantially higher susceptibility of the heat pretreated sample
159 to carbonation in the diffusion controlled recarbonation stage. Even though the rate of
160 decarbonation for this sample at 900°C is decreased (reaching a maximum value of about
161 3 mg/min as compared to 9 mg/min for decarbonation at 950°C), decarbonation is almost
162 fully achieved in the 5 min period of the calcination stage. This is not the case however for
163 the raw limestone sample as may be seen in Fig. 3a. Despite that carbonation/recarbonation
164 levels are very low from the second cycle, decarbonation of this raw limestone occurs at a
165 quite slow pace, which further hampers carbonation in the next cycle. The detrimental
166 effect of recarbonation is further confirmed by inspection of Fig. 3b, showing the TGs
167 obtained by suppressing the recarbonation stage, and Fig. 4 where data on the multicyclic
168 conversion of heat pretreated samples are plotted as affected by recarbonation and the
169 calcination temperature. As may be seen, recarbonation leads to an acceleration of the loss

170 of multicyclic conversion when the sorbent is regenerated at high CO₂ partial pressure.

171 A remarkable feature observed in Fig. 3b is the overshoot exhibited by the sample
172 weight gain in the short transition period between the carbonation and calcination stages,
173 which is due to an accidentally occurring intense carbonation taking place from the end of
174 the carbonation stage at the point at which the CO₂ % is suddenly increased up to 70%
175 vol and until the temperature reaches a sufficiently high value (around 870°C [8]) to shift
176 the reaction towards decarbonation. This diffusion-controlled accidental recarbonation seen
177 in the carbonation/calcination cycles is further promoted in the heat pretreated sample
178 as compared with the raw limestone, which is consistent with the observed response to a
179 purposely introduced recarbonation stage and is attributable to the enhancement of diffusion
180 by heat pretreatment. Since it has been seen that recarbonation actually yields a detrimental
181 effect on the sorbent reactivity at realistic calcination conditions, our results suggest to
182 avoid recarbonation and keep accidental recarbonation as low as possible in the practical
183 application.

184 In regards to the effect of heat pretreatment on its own, and even though our results
185 show that decarbonation is faster for heat pretreated samples, the carbonation reactivity of
186 the regenerated CaO in the kinetically controlled fast phase is still very low. Nevertheless,
187 the relative contribution to CaO conversion of diffusion controlled carbonation is notably
188 promoted specially for the heat pretreated samples, which show a conversion in the diffusion
189 controlled phase more than twice that in the fast phase (the latter lasting just about 10 s,
190 see Fig. 3). Even though the susceptibility to diffusive carbonation is seen to be markedly
191 promoted in the first cycles for the heat pretreated sorbent, the effect of pretreatment is
192 progressively erased by the successive calcinations at severe conditions suffered in subsequent
193 cycles and the rate of diffusive carbonation is decreased with the cycle number as seen in

194 Fig. 5a showing the time evolution of CaO conversion in the 1st, 10th and 20th cycles
195 (calcination at 900°C, 70%CO₂). After 20 cycles the rate of diffusive carbonation for the
196 heat pretreated sample becomes similar to that of the raw limestone, which does not depend
197 on the cycle number as can be observed in Fig. 5b. Anyhow, the contribution of diffusive
198 carbonation to conversion at the end of the 5 min carbonation stage becomes significant
199 also for the raw limestone sample after just a few cycles. This behavior contrasts with the
200 commonly accepted conception that only the kinetically controlled fast carbonation phase
201 is relevant for the practical application, which stems from observations on the carbonation
202 kinetics of CaO derived from raw limestone calcination under low CO₂ partial pressure.
203 Indeed, if the sorbent is regenerated in air conversion in the 5 min carbonation stage of
204 subsequent cycles remains relatively high and mostly due to carbonation in the fast phase
205 for many cycles as seen from the TGs on the raw limestone derived CaO shown in Fig. 1a.
206 However, and since under realistic calcination conditions diffusion controlled carbonation
207 represents a significant contribution to conversion, an extension of the duration of this stage
208 would lead to a non negligible increase of conversion specially in the case of heat pretreated
209 samples with high susceptibility to diffusion and quick decarbonation rates from the 1st
210 cycle at temperatures close to the equilibrium temperature under high CO₂ partial pressure.
211 Figure 6a shows the TGs obtained at the 20th cycle for the heat pretreated sample subjected
212 to carbonation/calcination cycles in which calcination was carried out under 70%CO₂ at a
213 reduced calcination temperature (880°C, which is quite close to the reaction equilibrium
214 temperature $T_{eq} \simeq 870^\circ\text{C}$ under 70%CO₂ [8]) and extended time period (10 min). As
215 may be seen, an extension of the carbonation time produces a noticeable increase of CaO
216 conversion in the diffusion-controlled phase whereas the calcination temperature can be
217 decreased down to 880°C while still the decarbonation rate is high enough to achieve full

218 decarbonation in short residence times (below 5 minutes from the 1st cycle). As seen in
219 Fig. 6b, the CaO multicyclic conversion at the end of the carbonation stage is significantly
220 increased by either decreasing the calcination temperature or prolonging the carbonation
221 time mainly due to the enhancement of diffusion controlled carbonation, which is further
222 promoted as the calcination temperature is decreased.

223 IV. CONCLUSIONS

224 Experimental results are reported on the multicyclic CO₂ capture performance of lime-
225 stone derived CaO as affected by calcination conditions for sorbent regeneration and else-
226 where proposed sorbent reactivation techniques such as heat pretreatment and recarbon-
227 ation. Calcining under high CO₂ concentration as expected in practice yield markedly
228 contrasting effects to those reported from multicyclic tests in which sorbent regeneration is
229 performed under low CO₂ partial pressure. In fact, either recarbonation or the combina-
230 tion of recarbonation/heat pretreatment lead to an adverse effect under realistic calcination
231 conditions necessarily implying high CO₂ concentration. Thus, any modification of the CaL
232 technology which might cause a recarbonation of the partially carbonated solids at high
233 CO₂ concentration/high temperature should be carefully addressed taking into account the
234 detrimental effect of recarbonation when regeneration is carried out at high CO₂ partial
235 pressure. In these conditions, the reactivity in the fast carbonation phase of the regenerated
236 CaO is drastically reduced. On the other hand, the rate of diffusion-controlled carbona-
237 tion is significantly increased specially in the case of heat pretreated samples which show
238 a high susceptibility to diffusion and allow for a decrease of the calcination temperature.
239 Remarkably, diffusion-controlled carbonation turns to be a relevant contribution to CaO
240 conversion in carbonation stages lasting a few minutes, which might be of practical use to

241 improve the efficiency of the CaL technology. Even though short residence times for carbon-
242 ation are imposed by the practical application, a possible strategy to be explored in future
243 works taking advantage from the enhancement of diffusion controlled carbonation by heat
244 pretreatment/harsh calcination conditions could consist of recirculating the partially car-
245 bonated sorbent into the carbonator in order to prolong the carbonation time before taking
246 them to the calciner for regeneration.

247 V. ACKNOWLEDGEMENTS

248 This work was supported by the Andalusian Regional Government Junta de Andalucia
249 (contracts FQM-5735 and TEP-7858), Spanish Government Agency Ministerio de Econo-
250 mia y Competitividad and FEDER funds (contracts FIS2011-25161 and CTQ2011-27626).
251 One of the authors (PESJ) is supported by the Juan de la Cierva program of the Spanish
252 Ministerio de Economia y Competitividad.

253 VI. REFERENCES

-
- 254 [1] J. Blamey, E. J. Anthony, J. Wang, and P. S. Fennell, “The calcium looping cycle for large-
255 scale CO₂ capture,” *Prog. Energ. Combust. Sci.*, vol. 36, no. 2, pp. 260–279, 2010.
- 256 [2] M. C. Romano, “Modeling the carbonator of a Ca-looping process for CO₂ capture from power
257 plant flue gas,” *Chemical Engineering Science*, vol. 69, pp. 257 – 269, 2012.
- 258 [3] B. Arias, M. Diego, J. Abanades, M. Lorenzo, L. Diaz, D. Martinez, J. Alvarez, and
259 A. Sanchez-Biezma, “Demonstration of steady state CO₂ capture in a 1.7 MWth calcium

- 260 looping pilot,” *International Journal of Greenhouse Gas Control*, vol. 18, pp. 237 – 245, 2013.
- 261 [4] J. Ströhle, M. Junk, J. Kremer, A. Galloy, and B. Epple, “Carbonate looping experiments in
262 a 1MWth pilot plant and model validation,” *Fuel*, vol. 127, no. 0, pp. 13 – 22, 2014. Fluidized
263 Bed Combustion and Gasification CO₂ and SO₂ capture: Special Issue in Honor of Professor
264 E.J. (Ben) Anthony.
- 265 [5] R. T. Symonds, D. Y. Lu, V. Manovic, and E. J. Anthony, “Pilot-scale study of CO₂ capture
266 by cao-based sorbents in the presence of steam and SO₂,” *Industrial & Engineering Chemistry
267 Research*, vol. 51, no. 21, pp. 7177 – 7184, 2012.
- 268 [6] I. Martinez, G. Grasa, R. Murillo, B. Arias, and J. C. Abanades, “Kinetics of calcination
269 of partially carbonated particles in a ca-looping system for CO₂ capture,” *Energy & Fuels*,
270 vol. 26, no. 2, pp. 1432 – 1440, 2012.
- 271 [7] A. Coppola, F. Scala, P. Salatino, and F. Montagnaro, “Fluidized bed calcium looping cycles
272 for {CO₂} capture under oxy-firing calcination conditions: Part 1. assessment of six lime-
273 stones,” *Chemical Engineering Journal*, vol. 231, pp. 537 – 543, 2013.
- 274 [8] F. Garcia-Labiano, A. Abad, L. de Diego, P. Gayan, and J. Adanez, “Calcination of calcium-
275 based sorbents at pressure in a broad range of {CO₂} concentrations,” *Chemical Engineering
276 Science*, vol. 57, no. 13, pp. 2381 – 2393, 2002.
- 277 [9] A. Martinez, Y. Lara, P. Lisbona, and L. M. Romeo, “Operation of a cyclonic preheater
278 in the Ca-looping for CO₂ capture,” *Environmental Science & Technology*, vol. 47, no. 19,
279 pp. 11335–11341, 2013.
- 280 [10] A. Martinez, Y. Lara, P. Lisbona, and L. M. Romeo, “Energy penalty reduction in the calcium
281 looping cycle,” *International Journal of Greenhouse Gas Control*, vol. 7, pp. 74 – 81, 2012.

- 282 [11] Y. Lara, P. Lisbona, A. Martinez, and L. M. Romeo, "Design and analysis of heat exchanger
283 networks for integrated ca-looping systems," *Applied Energy*, vol. 111, pp. 690 – 700, 2013.
- 284 [12] A. Martínez, Y. Lara, P. Lisbona, and L. M. Romeo, "Operation of a mixing seal valve in
285 calcium looping for CO₂ capture," *Energy & Fuels*, vol. 28, no. 3, pp. 2059 – 2068, 2014.
- 286 [13] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, and L. F. de Diego, "Progress in chemical-
287 looping combustion and reforming technologies," *Progress in Energy and Combustion Science*,
288 vol. 38, no. 2, pp. 215 – 282, 2012.
- 289 [14] H. Tian and Q. Guo, "Investigation into the reactivity of calcium sulfate with gaseous and
290 solid fuels and thermodynamic analysis of carbon deposits and sulfur evolution in chemical-
291 looping combustion system," *International Review of Chemical Engineering*, vol. 1, no. 1,
292 pp. 51 – 57, 2009.
- 293 [15] H. Tian and Q. Guo, "Recent advances on preparation and characteristics of oxygen carrier
294 particles," *International Review of Chemical Engineering*, vol. 1, no. 4, pp. 357 – 368, 2009.
- 295 [16] L. M. Romeo, Y. Lara, P. Lisbona, and A. Martinez, "Economical assessment of competitive
296 enhanced limestones for CO₂ capture cycles in power plants," *Fuel Processing Technology*,
297 vol. 90, no. 6, pp. 803 – 811, 2009.
- 298 [17] P. Lisbona, A. Martinez, and L. M. Romeo, "Hydrodynamical model and experimental results
299 of a calcium looping cycle for CO₂ capture," *Applied Energy*, vol. 101, pp. 317 – 322, 2013.
- 300 [18] V. Manovic and E. J. Anthony, "Thermal activation of CaO-based sorbent and self-reactivation
301 during CO₂ capture looping cycles," *Environ. Sci. Technol.*, vol. 42, pp. 4170–4174, 2008.
- 302 [19] B. Arias, G. S. Grasa, M. Alonso, and J. C. Abanades, "Post - combustion calcium looping
303 process with a highly stable sorbent activity by recarbonation," *Energy Environ. Sci.*, vol. 5,
304 pp. 7353 – 7359, 2012.

- 305 [20] S. Choi, J. H. Drese, and C. W. Jones, “Adsorbent materials for carbon dioxide capture from
306 large anthropogenic point sources,” *ChemSusChem*, vol. 2, pp. 796–854, 2009.
- 307 [21] A. M. Kierzkowska, R. Pacciani, and C. R. Müller, “CaO-based CO₂ sorbents: From funda-
308 mentals to the development of new, highly effective materials,” *ChemSusChem*, vol. 6, no. 7,
309 pp. 1130–1148, 2013.
- 310 [22] J. M. Valverde, “Ca-based synthetic materials with enhanced CO₂ capture efficiency,” *J.*
311 *Mater. Chem. A.*, vol. 1, p. 447–468, 2013.
- 312 [23] R. Barker, “Reversibility of the reaction $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$,” *J. Appl. Chem. Biotechnol.*,
313 vol. 23, pp. 733–742, 1973.
- 314 [24] G. Grasa, R. Murillo, M. Alonso, and J. C. Abanades, “Application of the random pore model
315 to the carbonation cyclic reaction,” *AIChE J.*, vol. 55, no. 5, pp. 1246–1255, 2009.
- 316 [25] S. K. Bhatia and D. D. Perlmutter, “Effect of the product layer on the kinetics of the CO₂-lime
317 reaction,” *AIChE Journal*, vol. 29, no. 1, pp. 79–86, 1983.
- 318 [26] Z. Sun, S. Luo, P. Qi, and L.-S. Fan, “Ionic diffusion through calcite (CaCO₃) layer during
319 the reaction of cao and {CO₂},” *Chemical Engineering Science*, vol. 81, pp. 164–168, 2012.
- 320 [27] C. Salvador, D. Lu, E. Anthony, and J. Abanades, “Enhancement of CaO for CO₂ capture in
321 an FBC environment,” *Chemical Engineering Journal*, vol. 96, no. 1–3, pp. 187–195, 2003.
- 322 [28] J. M. Valverde, P. E. Sanchez Jimenez, and L. A. Perez Maqueda, “High and stable CO₂
323 capture capacity of natural limestone at ca-looping conditions by heat pretreatment and re-
324 carbonation synergy,” *Fuel*, vol. 123, p. 79–85, 2014.
- 325 [29] J. M. Valverde, “A model on the CaO multicyclic conversion in the Ca-looping process,”
326 *Chemical Engineering Journal*, vol. 228, p. 1195–1206, 2013.

- 327 [30] D. Y. Lu, R. W. Hughes, E. J. Anthony, and V. Manovic, “Sintering and reactivity of CaCO_3 -
328 based sorbents for in situ CO_2 capture in fluidized beds under realistic calcination conditions,”
329 *J. Environ. Eng.*, vol. 135, no. 6, pp. 404–410, 2009.
- 330 [31] V. Manovic and E. J. Anthony, “ CO_2 carrying behavior of calcium aluminate pellets under
331 high-temperature/high- CO_2 concentration calcination conditions,” *Industrial & Engineering*
332 *Chemistry Research*, vol. 49, no. 15, pp. 6916 – 6922, 2010.
- 333 [32] V. Manovic, J.-P. Charland, J. Blamey, P. S. Fennell, D. Y. Lu, and E. J. Anthony, “Influence
334 of calcination conditions on carrying capacity of CaO -based sorbent in CO_2 looping cycles,”
335 *Fuel*, vol. 88, pp. 1893–1900, 2009.
- 336 [33] M. Alonso, Y. Criado, J. Abanades, and G. Grasa, “Undesired effects in the determination of
337 CO_2 carrying capacities of CaO during TG testing,” *Fuel*, pp. –, 2013.
- 338 [34] Z.-S. Li, F. Fang, X.-Y. Tang, and N.-S. Cai, “Effect of temperature on the carbonation
339 reaction of CaO with CO_2 ,” *Energy & Fuels*, vol. 26, no. 4, pp. 2473–2482, 2012.
- 340 [35] D. Beruto, L. Barco, and A. W. Searcy, “ CO_2 -catalyzed surface area and porosity changes in
341 high-surface-area CaO aggregates,” *Journal of the American Ceramic Society*, vol. 67, no. 7,
342 pp. 512–516, 1984.
- 343 [36] D. Beruto, A. W. Searcy, and M. G. Kim, “Microstructure, kinetic, structure, thermodynamic
344 analysis for calcite decomposition: free-surface and powder bed experiments,” *Thermochimica*
345 *Acta*, vol. 424, no. 1–2, pp. 99 – 109, 2004.
- 346 [37] E. P. Hyatt, I. B. Cutler, and M. E. Wadsworth, “Calcium carbonate decomposition in carbon
347 dioxide atmosphere,” *Journal of the American Ceramic Society*, vol. 41, no. 2, pp. 70–74, 1958.
- 348 [38] J. Khinast, G. Krammer, C. Brunner, and G. Staudinger, “Decomposition of limestone: The
349 influence of CO_2 and particle size on the reaction rate,” *Chemical Engineering Science*, vol. 51,

350 no. 4, pp. 623–634, 1996.

351 [39] R. Besson and L. Favergeon, “Atomic - scale study of calcite nucleation in calcium oxide,”

352 *The Journal of Physical Chemistry C*, vol. 117, no. 17, pp. 8813 – 8821, 2013.

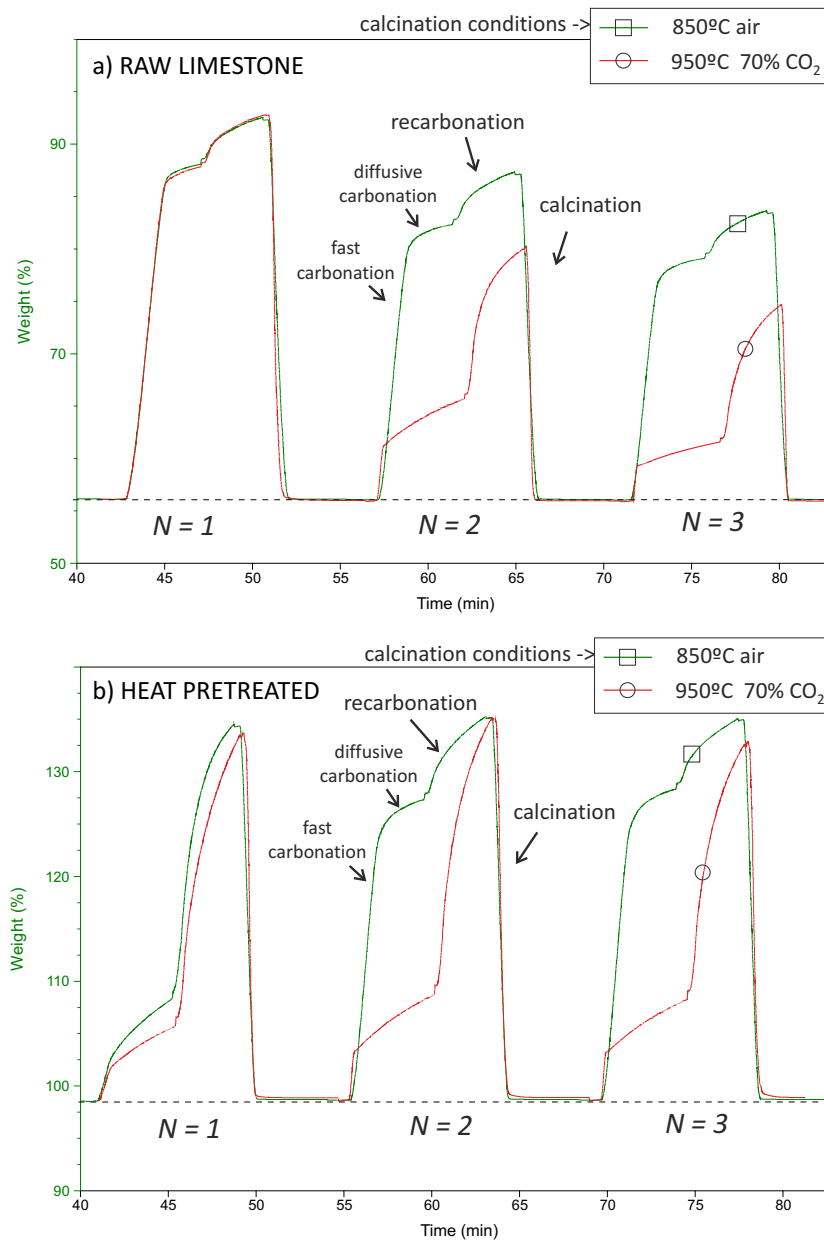


FIG. 1. Time evolution of sorbent weight % during the first 3 cycles of carbonation/recarbonation/calcination cycles for samples of raw and heat pretreated (950°C 12 h) limestone. Carbonation at 650°C for 5 min (15% CO₂/85% air vol/vol). Recarbonation at 800°C for 5 min (90% CO₂/10% air vol/vol). Calcination for 5 min at 850°C (air) and at 950°C (70% CO₂/30% air vol/vol) as indicated. These stages are indicated for the 2nd cycle.

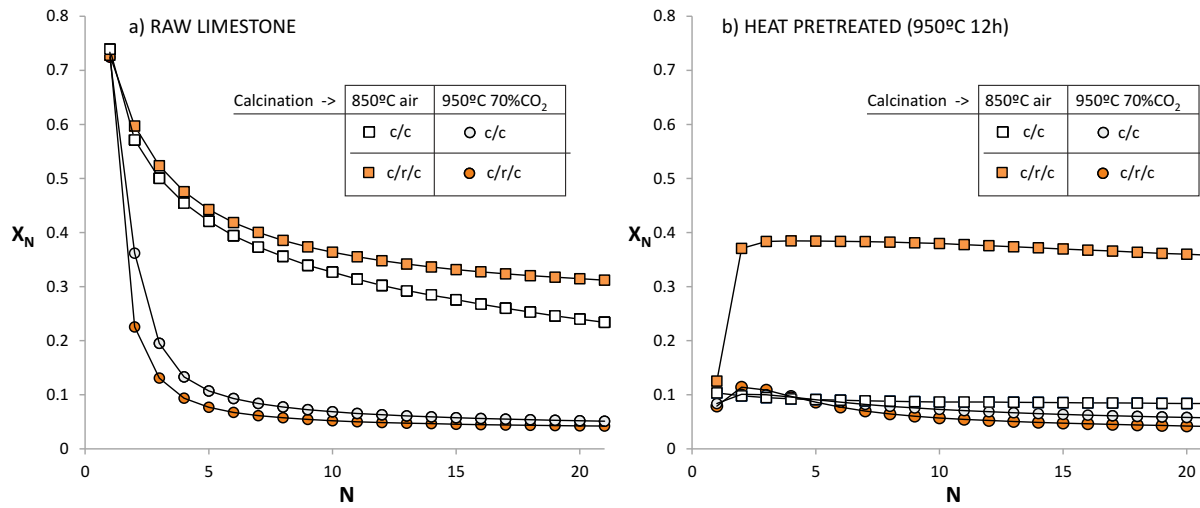


FIG. 2. CaO conversion at the end of the carbonation stage as a function of the cycle number for raw and soon after heat pretreated (950C for 12h) limestone samples subjected carbonation/calcination (c/c) and carbonation/recarbonation/calcination (c/r/c) cycles at different calcination conditions (as indicated).

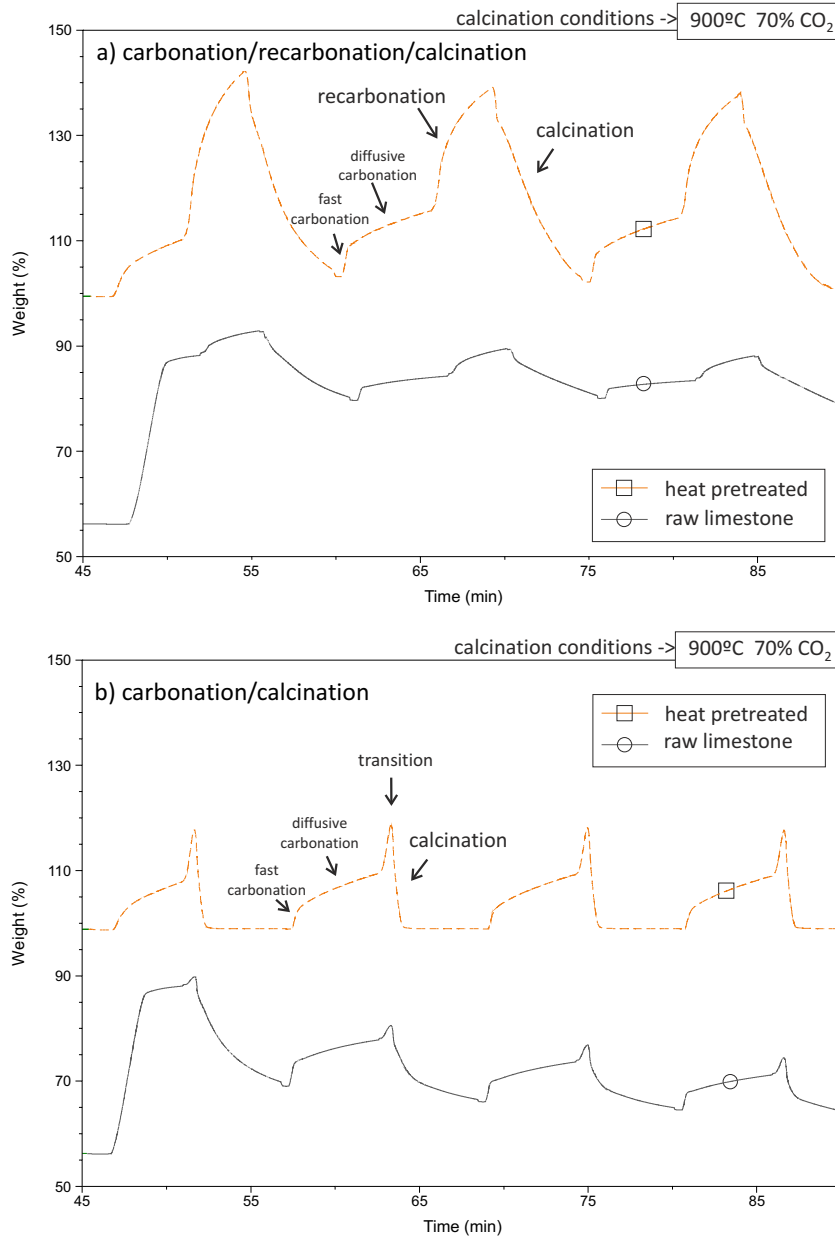


FIG. 3. Time evolution of sorbent weight % during the first cycles of carbonation/re-carbonation/calcination (a) and carbonation/calcination cycles (b) for samples of raw and heat pretreated (950°C 12 h) limestone. Carbonation at 650°C for 5 min (15% CO₂/85% air vol/vol). Re-carbonation at 800°C for 5 min (90% CO₂/10% air vol/vol). Calcination for 5 min at 900°C (70% CO₂/30% air vol/vol) as indicated.

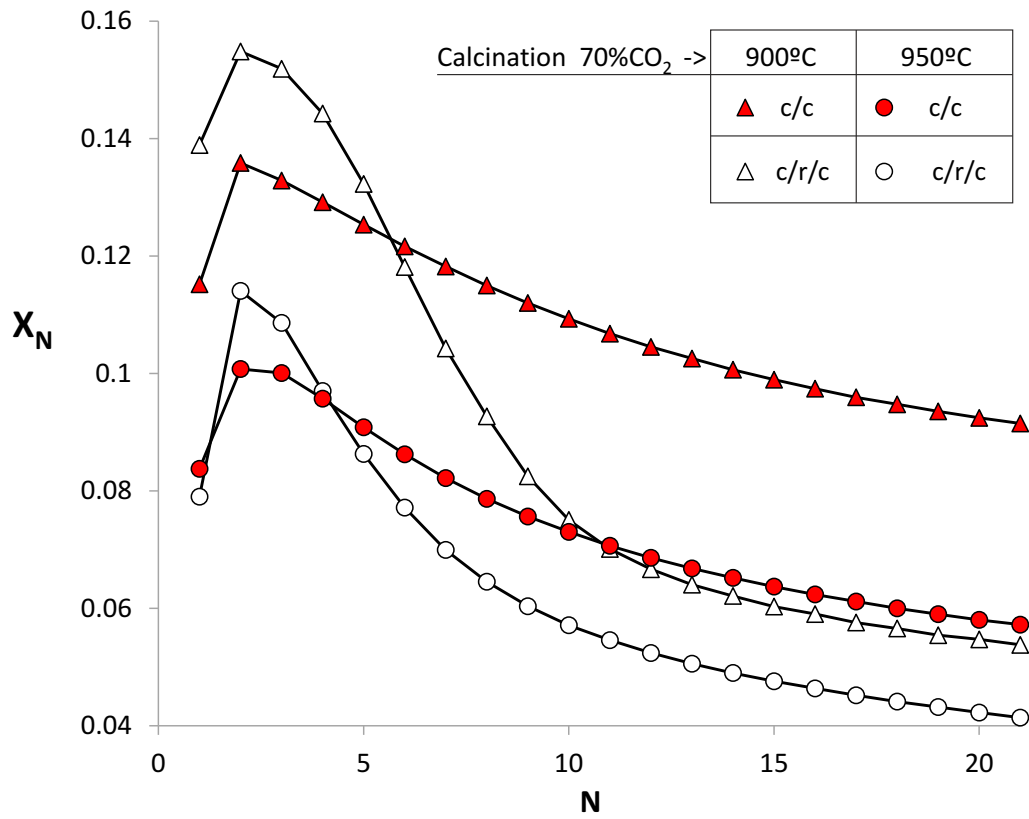


FIG. 4. CaO conversion at the end of the carbonation stage as a function of the cycle number for soon after heat pretreated (950°C for 12h) limestone samples subjected carbonation/calcination (c/c) and carbonation/recarbonation/calcination (c/r/c) at different calcination temperatures (as indicated) under 70% CO₂.

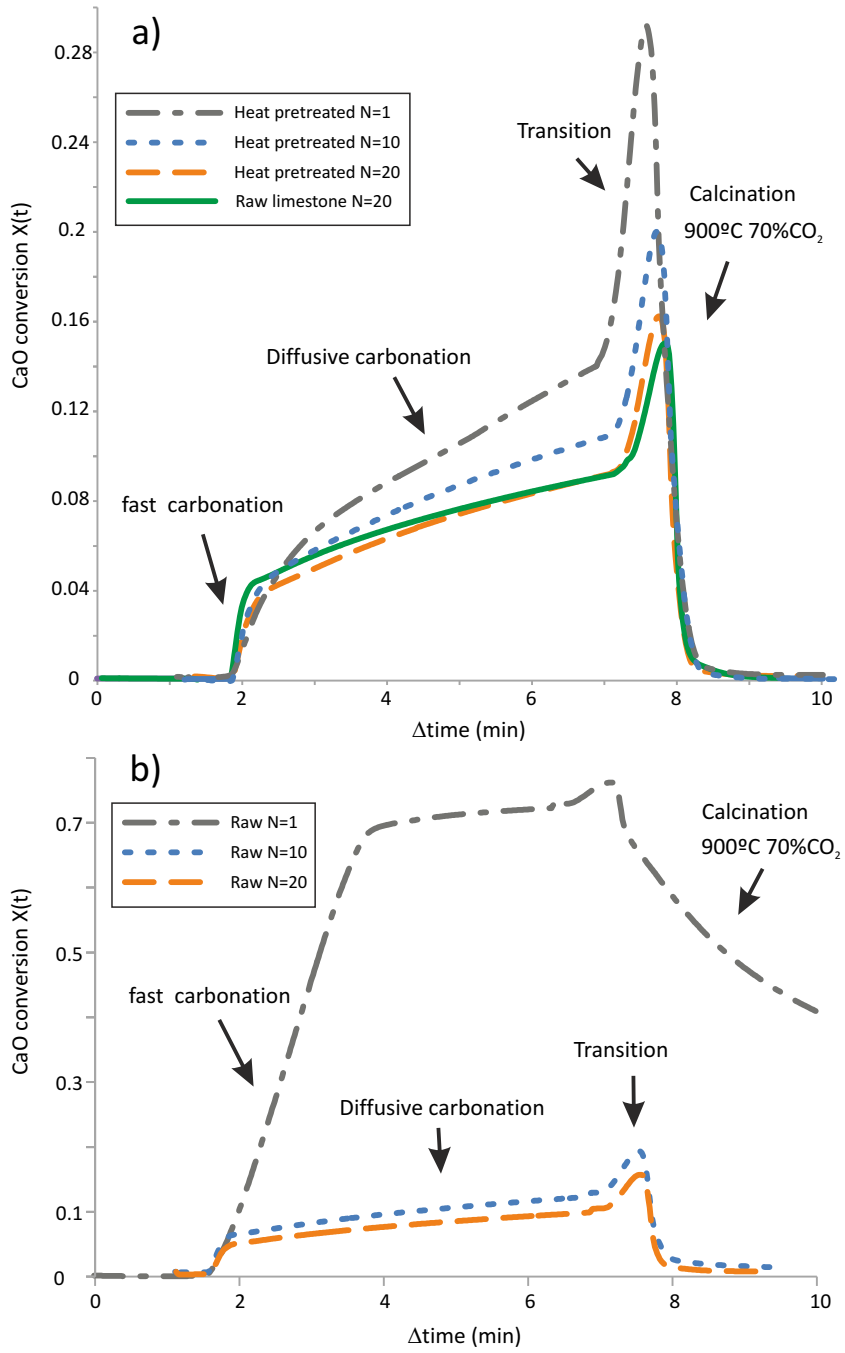


FIG. 5. Time evolution of Ca conversion during the 1st, 10th and 20th carbonation/calcination cycle for (a) heat pretreated (950°C 12 h) and (b) raw limestone samples. Carbonation at 650°C for 5 min (15% CO₂/85% air vol/vol). Calcination for 5 min at 900°C (70% CO₂/30% air vol/vol).

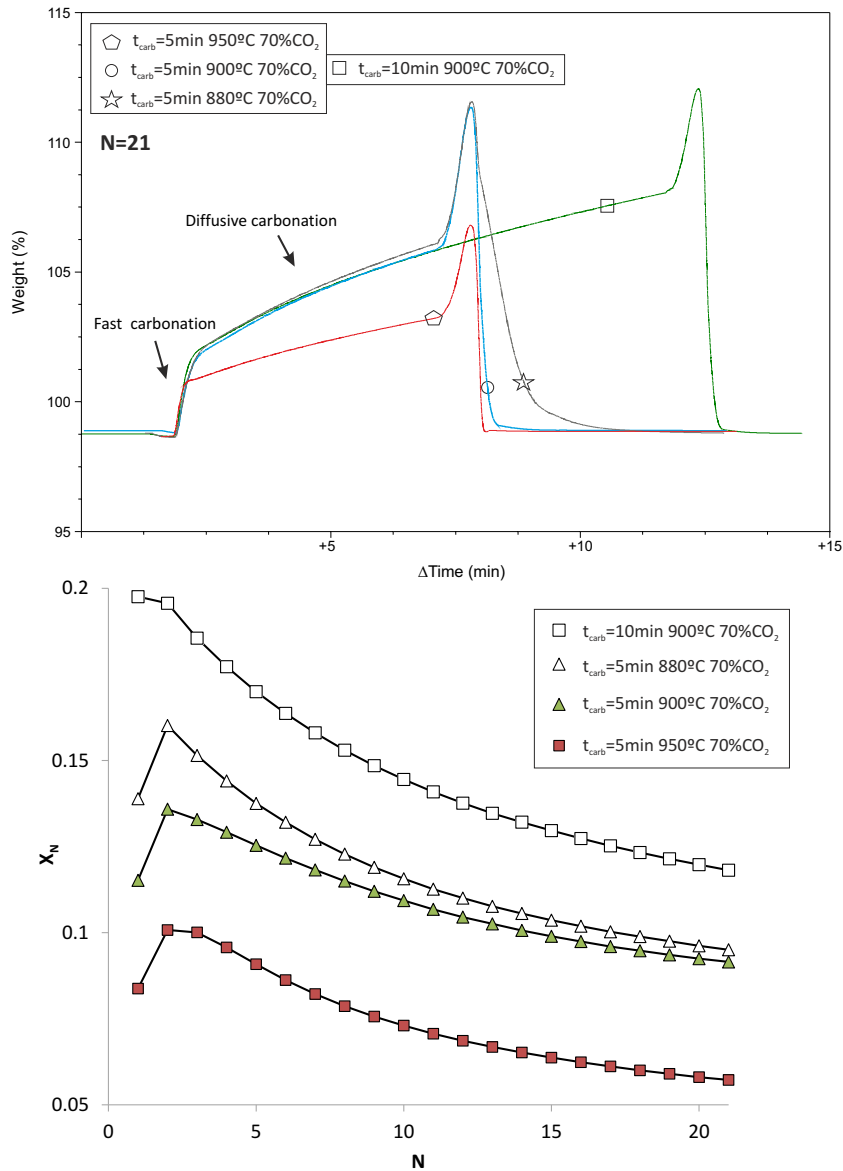


FIG. 6. a) Time evolution of sorbent weight % during the 20th carbonation/calcination cycle for the heat pretreated (950°C 12 h) limestone. Carbonation at 650°C for 5 min and 10 min (15% CO₂/85% air vol/vol) as indicated. Calcination for 5 min at 950°C, 900°C and 880°C (70% CO₂/30% air vol/vol) as indicated. b) CaO conversion at the end of the carbonation stage as a function of the cycle number at these conditions.