

1     **High and stable CO<sub>2</sub> capture capacity of natural limestone at**  
2     **Ca-looping conditions by heat pretreatment and recarbonation**  
3                                     **synergy**

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## Abstract

The Ca-looping (CaL) process, based on the multicyclic carbonation/calcination of limestone derived CaO, has emerged recently as a potentially economically advantageous technology to achieve sustainable postcombustion and precombustion CO<sub>2</sub> capture efficiencies. Yet, a drawback that hinders the efficiency of the CaL process is the drastic drop of limestone capture capacity as the number of carbonation/calcination cycles is increased. Precalcination of limestone at high temperatures for a prolonged period of time has been proposed as a potential technique to reactivate the sorbent, which is however precluded by regeneration temperatures above 850°C and low CO<sub>2</sub> concentrations in the carbonator to be found in the practical situation. Under these conditions, heat pretreatment leads to a stable yet very small CaO conversion. On the other hand, the introduction of a recarbonation stage between the ordinary carbonation and calcination stages has been shown to decelerate the rate of sorbent activity decay even though this favorable effect is not noticeable up to a number of above 10-15 cycles. The present manuscript demonstrates that the synergetic action of heat pretreatment and recarbonation yields a high and stable value for the multicyclic conversion of limestone derived CaO. It is foreseen that recarbonation of heat pretreated limestone would lead to a reduction of process costs especially in the case of precombustion applications. Even though sorbent purging will always be needed because of ash accumulation and sulphation in postcombustion CO<sub>2</sub> capture applications, the stable and high multicyclic CaO conversion achieved by the combination of these techniques would make it necessary to a lesser extent.

## 27 I. INTRODUCTION

28 The carbonation reaction of CaO at high temperature constitutes the basis for emerging  
29 technologies in precombustion and postcombustion CO<sub>2</sub> capture applications [1–3]. Nor-  
30 mally, CaO particles react in a fluidized bed reactor (carbonator) with CO<sub>2</sub> present at low  
31 concentrations in the inlet gas stream at atmospheric pressure. Partially carbonated parti-  
32 cles are then circulated into a second fluidized bed reactor (calciner) where a pure stream of  
33 CO<sub>2</sub> ready for transport and storage is produced and the sorbent is regenerated for its use  
34 in a new cycle. By taking into account the tradeoff between the reaction equilibrium driv-  
35 ing force and the reaction kinetics, the optimal carbonation temperature is around 650°C  
36 whereas calcination must be carried out at temperatures above 850°C to assure complete  
37 decarbonation in the CO<sub>2</sub> rich atmosphere of the calciner [4].

38 Carbonation of CaO particles proceeds along two well differentiated phases as demon-  
39 strated by multicyclic thermogravimetric analysis (TGA) tests. The reaction takes place by  
40 means of a kinetically-driven mechanism in a first fast carbonation phase, which ends after a  
41 30-50 nm CaCO<sub>3</sub> layer thickness is developed on the surface of the solid [5]. Carbonation is  
42 then controlled by diffusion of CO<sub>2</sub> in the solid, which is a much slower process [5, 6]. Given  
43 the constrain imposed by short residence times in practical applications, most of carbona-  
44 tion in the Ca-looping (CaL) technology would take place in the fast phase, which depends  
45 essentially on the CaO skeleton porosity. A main drawback of the CaL technology is that  
46 sintering of the CaO skeleton regenerated during the calcination stage causes a progressive  
47 loss of conversion in the fast phase as carbonation/calcination cycles build up [5, 6]. This  
48 requires a continuous purge of the spent sorbent in the process that must be counterbalanced  
49 by fresh limestone, which increases further the demand of heat at the calciner [7, 8].

50 A current direction of research to improve the regenerability of natural limestones is the  
51 formulation of synthetic CaO-based sorbents [9, 10]. Nonetheless, taking into account the  
52 interplay between sorbent cost and multicyclic conversion improvement [7, 11], the low cost  
53 and wide availability of natural limestone ensures that it is still the most suitable candidate  
54 as CaO precursor to ensure the industrial competitiveness of the CaL technology. Other  
55 strategies have been explored to mitigate the loss of limestone multicyclic activity such as  
56 hydration to reactivate the sorbent [1, 12], heat pretreatment [1, 13, 14] and recarbonation  
57 [15, 16]. Manovic and Anthony [14] proposed heat pretreatment as a suitable technique to  
58 improve the CaO activity during multicyclic carbonation/calcination. TGA tests demon-  
59 strated that some natural limestones actually exhibited an increase of conversion with the  
60 cycle number if they had been pre-subjected to long periods of isothermal heating at high  
61 temperatures. Heat pretreatment is a well known process used for hardening a crystalline  
62 solid just by creating structural dislocations caused by thermal stresses. In addition, the in-  
63 crease of structural defects density would lead to an enhancement of solid-state diffusion [17].  
64 A careful analysis of the thermograms derived from TGA tests shows indeed that reactiva-  
65 tion of thermally pretreated limestones is essentially due to the enhancement of carbonation  
66 in the solid-state diffusion phase [18–20]. When the carbonated sorbent is regenerated at  
67 moderate calcination temperatures the porosity of the resulting CaO skeleton is enhanced,  
68 which leads to a promotion of fast carbonation in the subsequent cycle. However, most of  
69 early TGA studies were carried out isothermally (at temperatures in the range 750-850°C)  
70 by switching the gas between an inert gas for calcination and a gas mixture containing a high  
71 CO<sub>2</sub> partial pressure for carbonation as corresponds to conditions in practice [13, 14, 21–25].  
72 More recent tests show that calcination temperatures above 850°C are sufficiently high to  
73 prevent reactivation of heat pretreated sorbents carbonated under low CO<sub>2</sub> partial pressure

74 [18, 26, 27]. Looping-calcination temperatures above 850°C lead to stable yet very low values  
75 of conversion for heat treated limestones [18, 27] whereas the minimum target value for the  
76 calcination temperature to ensure full decarbonation of the partially carbonated solids under  
77 practical constraints such as high CO<sub>2</sub> partial pressure (50 - 70 kPa) and short residence  
78 times (2 - 3 min) in the calciner [28] is around 870°C [4].

79 A feasible new CaL concept using low-cost natural limestone consists of the introduc-  
80 tion of a recarbonation stage under pure CO<sub>2</sub> (available from the calciner) and at high  
81 temperature (800°C) in between the carbonation and calcination stages [16]. According to  
82 this method, the partially carbonated CaO particles would be circulated before calcination  
83 to a recarbonator reactor wherein further carbonation would be intensified. TGA tests  
84 demonstrate that the residual conversion of limestone is increased by cyclic recarbonation,  
85 which would reduce the fresh sorbent make-up flow required and the heat demand in the  
86 calciner thus lowering the overall cost of the CaL capture process [16]. Recarbonation in  
87 pure CO<sub>2</sub> was firstly suggested in [15] for reactivation as evidenced from results derived us-  
88 ing a batch fluidized bed combustor. Nevertheless, thermogravimetric analysis (TGA) tests  
89 earlier reported in [15] failed to demonstrate reactivation, which is consistent with TGA  
90 results recently reported in [16] showing that reactivation is only noticeable after about  
91 15-20 cycles (see Fig. 3b of [16]). In the present manuscript we propose a modification of  
92 recarbonation as reactivation technique by combining it with heat pretreatment. As will be  
93 shown, the combination of both techniques leads synergetically to a further enhancement of  
94 the multicyclic CaO conversion, which reaches a high and stable value from the 2nd cycle.

## 95 II. MATERIALS AND METHODS

96 High purity natural limestone supplied to us by Segura S.L. (Matagallar quarry, Pedr-  
97 era, Spain) has been used in our tests as CaO precursor ( $\text{CaCO}_3$  99.62%,  $\text{SiO}_2 < 0.05\%$ ,  
98  $\text{Al}_2\text{O}_3 < 0.05\%$ ,  $\text{MgO}$  0.24%,  $\text{Na}_2\text{O}$  0.08%). Heat pretreatment was performed by subjecting  
99 the material to isothermal heating at  $950^\circ\text{C}$  for 12 h in dry air. Carbonation/calcination mul-  
100 ticyclic tests were carried out in a Q5000IR TG analyzer (TA Instruments). This equipment  
101 is provided with an infrared furnace heated with halogen lamps and with a high sensitivity  
102 balance ( $<0.1 \mu\text{g}$ ) characterized by a minimum baseline dynamic drift ( $<10 \mu\text{g}$ ). The use  
103 of an infrared halogen furnace in our TGA runs allowed us for heating/cooling the sam-  
104 ple very quickly ( $300^\circ\text{C min}^{-1}$ ), which serves to minimize the duration of the transitional  
105 periods thus allowing to test the multicyclic conversion of the sorbent at conditions close  
106 to CaL realistic conditions. As a general procedure, a sorbent sample (around 10 mg) was  
107 firstly subjected in-situ to a linear heating program ( $20^\circ/\text{min}$ ) up to  $850^\circ\text{C}$  in air prior to  
108 cycling. Benchmark conditions of subsequent carbonation/calcination (c/c) cycles consisted  
109 of carbonation at  $650^\circ\text{C}$  (85% air/15%  $\text{CO}_2$  vol/vol) and calcination at  $850^\circ\text{C}$  (air), both  
110 stages for 5 minutes. Carbonation/recarbonation/calcination (c/r/c) cycles were performed  
111 by subjecting the sample to a 3 min recarbonation stage (10% air/90%  $\text{CO}_2$  vol/vol) at  
112  $800^\circ\text{C}$  in between the carbonation and calcination stages.

## 113 III. EXPERIMENTAL RESULTS AND DISCUSSION

114 Figure 1 shows examples of thermograms obtained from multicyclic c/r/c tests carried  
115 out on raw and heat pretreated limestone samples. As may be seen, heat pretreatment leads  
116 to a relatively higher and more stable weight% gain of the sorbent along the carbonation

117 stages of the cycles. The weight% evolution for the pretreated sorbent in the two first  
118 cycles is shown in detail in Fig. 2. Carbonation of the heat pretreated CaO skeleton in  
119 the first cycle is seen to exhibit two main distinctive features. As reported in previous  
120 works [27], the pretreated sorbent activity in the kinetically driven fast phase (phase I in  
121 Fig. 2) is very low while diffusive carbonation is relatively intense. On the other hand,  
122 we observe that carbonation in the diffusion-controlled recarbonation stage is remarkably  
123 enhanced. After calcination, the sorbent activity in the fast carbonation phase of the 2nd  
124 cycle is markedly promoted (see Fig. 2). As a result, CaO conversion at the end of the  
125 carbonation phase is increased from just  $X_1 \simeq 0.12$  in the 1st cycle up to  $X_2 \simeq 0.37$  in the  
126 2nd cycle. The multicyclic conversion remains practically stable around this value for the  
127 following c/r/c cycles (up to 100 cycles were performed). In contrast, the c/r/c cycled raw  
128 limestone still shows a decay with the cycle number which is especially noticeable in the first  
129 10 cycles. Data of multicyclic conversion are plotted in Fig. 3 for the raw and pretreated  
130 limestones subjected to c/c and c/r/c tests (data reported elsewhere by Arias et al. [16]  
131 are also plotted for comparison). As shown in [16], our results indicate that introducing an  
132 intermediate recarbonation stage serves to mitigate the rate of conversion decay exhibited  
133 by the raw limestone subjected to ordinary c/c cycles even though the improvement is not  
134 remarkable up to a number of above 10 - 15 cycles.

135 We noticed that the heat pretreated sample had a great tendency to hydrate and carbon-  
136 ate just in contact with ambient atmosphere as seen in the XRD patterns depicted in Fig.  
137 4 showing that CaO had almost completely converted overnight into  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$ .  
138 The weight drops observed in the TGA test during the initial linear heating period of an  
139 overnight pretreated sample as due to dehydration (at about  $400^\circ\text{C}$ ) and decarbonation (at  
140 about  $600^\circ\text{C}$ ) indicated that it consisted of a 77.3%wt of  $\text{Ca(OH)}_2$ , 17.7%wt of  $\text{CaCO}_3$  and

141 just 4%wt was left of CaO. Multicyclic c/r/c conversion data for this sample are also plotted  
142 in Fig. 3. The results show that overnight pre-hydration/carbonation yields a remarkable  
143 reactivation in the 2nd cycle. Conversion reaches in subsequent cycles values well above  
144 those obtained for the raw and soon after pretreated sorbents. Yet, the sorbent activity is  
145 decreased with the cycle number and, after about 30 cycles, it becomes somewhat smaller  
146 than the stable value of conversion exhibited by the soon after pretreated sample.

147 The enhancement of conversion for the raw limestone is even more marked in the exper-  
148 iments performed in our work than in those reported by Arias et al. [16], which might be  
149 explained by the higher CO<sub>2</sub> vol% that we use in the carbonation stage (15% in our tests  
150 vs. 10% in [16]) and the lower calcination temperature (850°C in our tests vs. 900°C in  
151 [16]). A lower CO<sub>2</sub> vol% would lead to a smaller conversion [2] since most of carbonation  
152 occurring in the kinetically driven phase conforms to a first order kinetic law being pro-  
153 portional to the difference between the actual CO<sub>2</sub> concentration and the equilibrium CO<sub>2</sub>  
154 concentration ( $\simeq 1\%$  at 650° and atmospheric pressure). On the other hand, calcining at a  
155 higher temperature would promote further sintering of the regenerated CaO skeleton thus  
156 hampering fast conversion in the next cycle. As may be seen, the data reported in [16]  
157 exhibit an appreciable scatter as compared to ours, which might be due to vibrations caused  
158 by the vertical displacement of the two-zones furnace used in their specially designed TG  
159 analyzer (originally reported in [29]) to allow for a rapid change of temperature between  
160 cycles resembling practical conditions. In our tests, this requirement is helped by infrared  
161 heating, which allows for quick transitional periods between stages.

162 In order to assess whether the combination of heat pretreatment and recarbonation would  
163 lead to a reduction of the cost of CO<sub>2</sub> avoided in practice several parameters involved have  
164 to be considered, namely the improvement of the maximum average capture capacity of



165 the CaO solid population ( $X_{ave}$ , depending on the increment of residual conversion), the  
166 sorbent purge flow ( $f$  defined as the percentage of sorbent leaving the process), and the  
167 CaO/CO<sub>2</sub> molar ratio ( $R$ ). A systematic procedure to carry out this study is detailed in [7].  
168 The applicability of postcombustion CaL technology in coal-fired power plants is critically  
169 determined by the irreversible formation of CaSO<sub>4</sub> due to the presence of SO<sub>2</sub> in the flue  
170 gas (a simulated flue gas of 0.45% SO<sub>2</sub> is shown to lead to a significant drop of the CO<sub>2</sub>  
171 capture capacity just after 2-3 cycles in multicyclic TGA tests [30]). Since CaO with low  
172 carbonation activity still has a strong sulphation capability, a feasible strategy is to use  
173 purged sorbent with low carbonation activity for the capture of SO<sub>2</sub> from the flue gas before  
174 it enters the carbonator [31, 32]. Arias et al. [16] estimated that the residual conversion  
175 of c/r/c cycled raw limestone is sufficiently high as to reduce the amount of purged CaO  
176 to the amount usable for SO<sub>2</sub> capture thus minimizing the quantity of CaO going to waste.  
177 This estimation was made using a residual conversion  $X_r$  between 0.15 and 0.2 obtained  
178 from their multicyclic c/r/c experiments on raw limestone (as compared to about 0.07-0.08  
179 for limestones subjected to ordinary c/c cycles [29]). Taking into account the percentage of  
180 residual conversion improvement attained for heat pretreated limestone subjected to c/r/c  
181 cycles, this same amount of purge flow could be kept (as needed to de-sulfurize the flue gas)  
182 while reducing the CaO/CO<sub>2</sub> molar ratio, which would allow to downsize the system thus  
183 cutting down further the cost of the process. The influence of  $X_{ave}$  on the CO<sub>2</sub> avoided  
184 cost can be estimated from the industrial scale simulation of the CaL process integrated  
185 with a power plant reported in [7]. CO<sub>2</sub> avoided cost data inferred from this simulation are  
186 graphically presented versus sorbent price and depending on  $X_{ave}$ . Figure 5 reproduces the  
187 results originally reported in [7] for values of  $X_{ave} = 32\%$  and  $67\%$ , low CaO/CO<sub>2</sub> molar ratio  
188 ( $R = 1.5$ ) and different values of purge flow in the calciner (1% and 2.5%). Following the

189 procedure described in [7] and using our multicyclic conversion results, it may be estimated  
 190  $X_{ave} \sim 40\%$  for the c/r/c raw limestone and  $X_{ave} \sim 60\%$  for the c/r/c heat pretreated  
 191 limestone. According to Fig. 5, the roughly similar increase of  $X_{ave}$  due to the combination  
 192 of heat pretreatment and recarbonation would bring about a significant reduction of the  
 193 cost of CO<sub>2</sub> avoided for incremental sorbent costs up to around 40 €/ton as compared to 5  
 194 €/ton for raw limestone (using a purge flow of 2.5%). A decrease of the purge flow down to  
 195 1% would allow the incremental sorbent cost to be further increased up to 90 €/ton while  
 196 still achieving a reduction of the cost of CO<sub>2</sub> avoided. The possibility of increasing sorbent  
 197 cost while still keeping the cost of CO<sub>2</sub> avoided low by means of c/r/c cycling would make  
 198 it interesting to investigate the behavior of synthetic sorbents showing reactivation when  
 199 subjected to c/c cycles similarly to heat pretreated limestone. A significant example is the  
 200 case of CaO/mayenite polycrystalline composites, which exhibit reactivation when subjected  
 201 to c/c cycles even under severe calcination conditions [33]. Arguably, solid-state diffusion  
 202 of CO<sub>2</sub> in these composites is enhanced across the interface between CaO and mayenite  
 203 crystallites, which would presumably lead to a high and stable value of CaO conversion when  
 204 the sorbent is subjected to c/r/c cycles as seen in our work for heat pretreated limestone.

205 The minimum amount of fresh limestone make-up flow which is required to reach a sus-  
 206 tained high level of CO<sub>2</sub> post-combustion capture efficiency has been assessed in a very  
 207 recently work [34] in order to have an accurate estimation on the effect of CaSO<sub>4</sub> and inert  
 208 solids accumulation. The study allows quantifying the reduction of limestone make-up flow  
 209  $F_0$  (relative to the CO<sub>2</sub> molar flow that enters the carbonator  $F_{CO_2}$ ) as a function of the  
 210 reactivation level achieved in a c/r/c process configuration. According to the simulation  
 211 results, a 90%CO<sub>2</sub> capture efficiency would be reached for a ratio  $F_0/F_{CO_2} = 0.08$  if the  
 212 residual sorbent conversion is increased up to  $X_r = 0.12$  whereas this ratio is reduced to

213  $F_0/F_{CO_2} = 0.03$  for  $X_r = 0.3$ . The achievement of a high residual conversion by introducing  
214 an intermediate recarbonation stage can be thus expected to have a notable impact on the  
215 efficiency of  $CO_2$  post-combustion capture (even though the costs related to the recarbon-  
216 ation reactor should be also considered). Combining heat pretreatment and recarbonation  
217 would be thus a useful strategy to be explored in order to notably minimize the limestone  
218 make-up flow required. In particular, heat pretreatment/recarbonation of limestone would  
219 be specially attractive for post-combustion applications allowing for a low percentage of  
220 purge flow as in the case of high quality coal (with low sulfur and ash content). On the  
221 other hand, the efficiency of precombustion applications (such as steam methane reforming  
222 enhanced via pre-combustion  $CO_2$  capture [35]) would be neatly benefitted from a stable  
223 and highly active sorbent since in these applications the gas to be processed is  $SO_2$  free and  
224 purging due to sulphation is not required.

225 To further investigate the role of the recarbonation stage additional tests were carried out  
226 in our work by alternating  $c/r/c$  and  $c/c$  cycles. The thermograms plotted in Fig. 6a are re-  
227 trieved from tests in which the samples were subjected to a 1st  $c/r/c$  cycle followed by 10  $c/c$   
228 cycles and 11  $c/r/c$  cycles. As seen before, it may be observed that carbonation during the  
229 1st recarbonation stage is enhanced for the heat pretreated sorbent, which yields reactiva-  
230 tion in the carbonation stage of the 2nd cycle. In contrast, carbonation in the recarbonation  
231 stage of the 1st cycle is not significant for the raw sorbent. If the recarbonation stage is  
232 eliminated in subsequent cycles, the conversion of both the heat pretreated and raw sorbents  
233 exhibit a similar characteristic decay with the cycle number. By reintroducing the recar-  
234 bonation stage in 12th cycle both sorbents are markedly reactivated. Note that although  
235 reactivation in the pretreated sorbent is more noticeable, carbonation in the recarbonation  
236 stage becomes appreciable also for the raw sorbent. This might be attributed to thermal

237 stresses to which the sorbent is subjected in the precedent  $c/c$  cycles lowering its resistance  
238 to diffusion. Ceramic materials usually experience internal failure when subjected to a sud-  
239 den change in temperature (thermal shock) or repeated cycling between two temperatures  
240 (thermal fatigue) depending on the rates of heating/cooling and material thermomechanical  
241 properties [36]. If the material is quickly heated/cooled and its thermal conductivity is low  
242 (as it is the case of ceramics in general) it experiences intense tensile/compressive stress  
243 that may lead to rupture. Thermal stresses can be further accentuated by the occurrence of  
244 exothermical/endothermical reactions such as calcination/carbonation. SEM micrographs  
245 of raw limestone previously subjected to 40  $c/c$  cycles (reported in [37]) show indeed cracks  
246 in the CaO crystalline structure, which are characteristic of brittle fracture in ceramics.  
247 Cracking of the crystal structure would facilitate  $\text{CO}_2$  diffusion through the solid [38] thus  
248 intensifying diffusion controlled carbonation in the recarbonation stage.

249 Data of conversion at the end of the carbonation stage obtained from our mixed  $c/c$  -  
250  $c/r/c$  tests are plotted in Fig. 6b, where data from full  $c/r/c$  cycling tests are replicated  
251 for comparison. After the 1st  $c/r/c$  cycle, conversion of the raw and pretreated samples is  
252 almost identical along the successive  $c/c$  cycles. When recarbonation is again introduced  
253 in the 12th cycle both samples exhibit a notable reactivation reaching values of conversion  
254 above those obtained for the fully  $c/r/c$  cycled sorbents. The relative increase of conversion is  
255 markedly important in the case of the heat pretreated sorbent but it becomes also remarkable  
256 for the raw sorbent, which can be a consequence of the enhancement of diffusion in the  
257 recarbonation stage of the 12th cycle caused by thermal stresses suffered during  $c/c$  previous  
258 cycling as discussed above. Thermal strains would be more intense for  $c/c$  cycling, which  
259 subjects the sorbent to higher temperature gradients as compared to  $c/r/c$  cycles. Hence,  
260 a practical recommendation for raw sorbent reactivation using  $c/r/c$  cycles would be to

261 subject it to recarbonation only when its activity is decreased below a critical value and  
262 thermal fatigue along the precedent c/c cycles allows for enhanced diffusion. As can be seen  
263 in Fig. 6b, conversion turns again to decay with the cycle number if the recarbonation stage  
264 is eliminated. This stage must be thus maintained to keep conversion at a high level.

265 Finally, it must be remarked that in TGA tests originally carried out to validate the novel  
266 CaL technology (based in c/r/c cycling [16]) the calcination atmosphere was air. In our work,  
267 we have employed similar calcination conditions to firstly reproduce the observed beneficial  
268 effect of recarbonation on the multicyclic behavior of a natural nonpretreated limestone  
269 and later on assess the influence of heat pretreatment. Nevertheless, it must be reminded  
270 that calcination is carried out in practice in a CO<sub>2</sub> rich environment (in fact the calciner  
271 is proposed as a source of CO<sub>2</sub> for the recarbonator [16]). Carbonation/calcination TGA  
272 tests [39] have shown that that the presence of CO<sub>2</sub> at high concentration in the calciner  
273 may have a great impact on the c/c multicyclic behavior of natural limestone. However,  
274 technical limitations prevent TGA tests from closely mimicking CaL conditions since the  
275 sorbent partially carbonated is prone to suffer further carbonation when the partial CO<sub>2</sub>  
276 pressure is increased for calcination until the temperature reaches a sufficiently high value  
277 to reverse the reaction towards decarbonation [39]. Thus, it would be difficult to further  
278 quantify the effect of a purposely introduced recarbonation stage. To this end, it would  
279 be desirable to have an accurate determination of the CO<sub>2</sub> concentration and temperature  
280 evolution in the transition between carbonation and calcination to be expected at practice,  
281 which can be determinant on the sorbent behavior. Ideally, the change of temperature in  
282 TGA multicyclic tests should be quick in order to better mimic the practical process wherein  
283 the sorbent is circulated between the carbonator and the calciner at high gas velocity. This  
284 critical issue will be the subject of a future work under preparation.

## 285 IV. CONCLUSIONS

286 To summarize, the work reported in this paper shows that the synergetic combi-  
287 nation of heat pretreatment and recarbonation gives rise to a stable and high value  
288 of (limestone derived) CaO conversion in the carbonation stage of multicyclic carbon-  
289 ation/recarbonation/calcination tests. Our work evidences that solid-state diffusion is  
290 markedly enhanced during recarbonation of the heat pretreated limestone, which gives rise  
291 to a thermally stable CaO skeleton after decarbonation. This sorbent exhibits an almost  
292 constant value of conversion from the 2nd cycle substantially higher than the residual con-  
293 version of nonpretreated limestone, which is foreseen to allow reducing costs of the CaL  
294 technology. Nonetheless, it must be stressed that in our thermogravimetric analysis (as  
295 in previous works reported to validate the novel CaL concept based on recarbonation) the  
296 sorbent was cyclicly regenerated in air whereas the CO<sub>2</sub> partial pressure in the calciner is  
297 expected to be high in the practical application. Since calcination under high CO<sub>2</sub> partial  
298 pressure is expected to yield a pronounced intensification of sorbent sintering further tests  
299 should be performed wherein the calcination atmosphere in practice is more accurately  
300 mimicked in order to better assess the effect of recarbonation on the multicyclic sorbent  
301 behavior as well as the expectedly beneficial influence of heat pretreatment.

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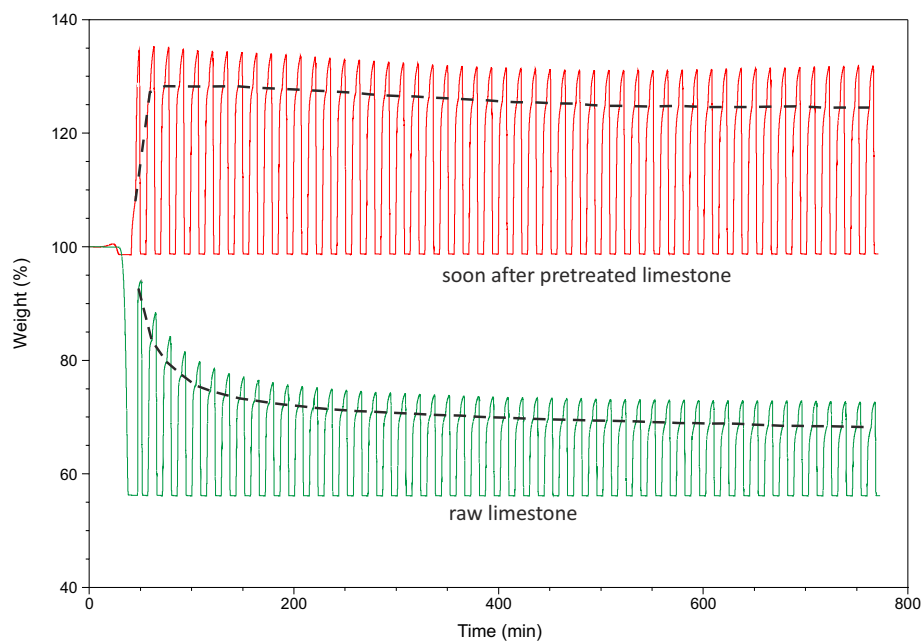


FIG. 1. Time evolution of sorbent weight % during 50 carbonation/recarbonation/calcination cycles from the TGA multicyclic test for soon after heat treated and raw limestones. The dashed lines are drawn joining the points at the end of the carbonation stage of each cycle.

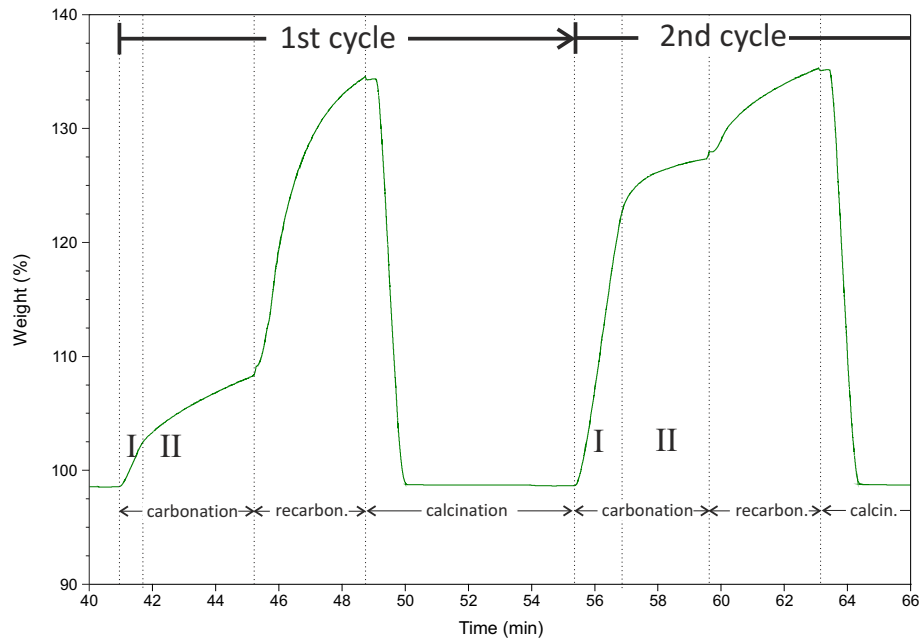


FIG. 2. Time evolution of weight % during the two first carbonation/re-carbonation/calcination cycles from the TGA multicyclic test for soon after heat treated limestone. Fast (I) and diffusion controlled (II) carbonation during the carbonation stages are indicated.

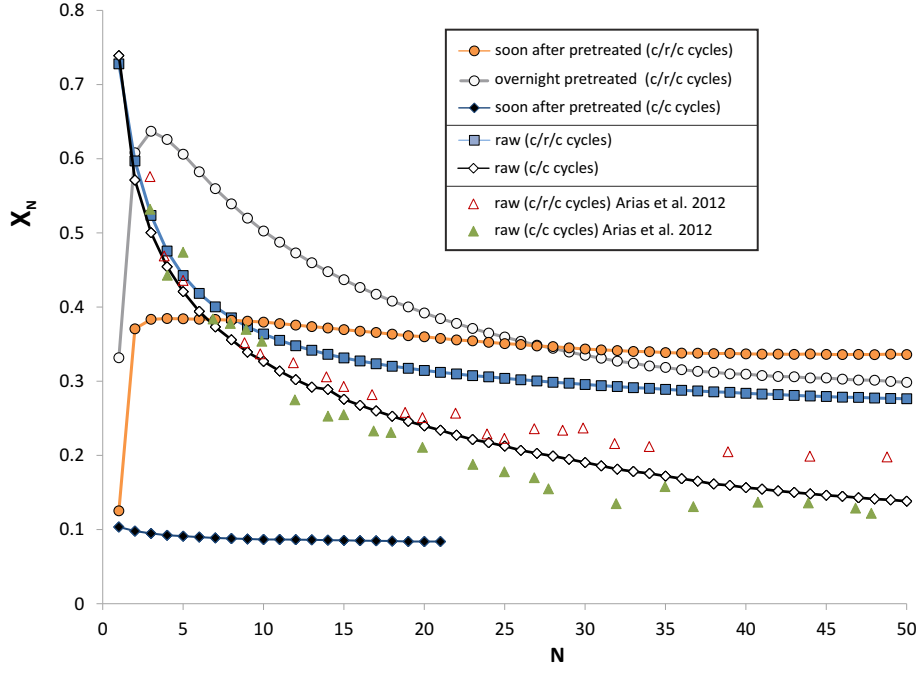


FIG. 3. Conversion at the end of the carbonation stage as a function of the cycle number for raw and heat treated limestones. Results from ordinary carbonation/calcination cycles and carbonation/recarbonation/calcination cycles are plotted (carbonation under 15%  $\text{CO}_2$  at  $650^\circ\text{C}$  and calcination in air at  $850^\circ\text{C}$  both stages for 5 min; recarbonation under 90%  $\text{CO}_2$  for 3 min). Conversion data reported by Arias et al. [16] are reproduced for comparison (carbonation under 10%  $\text{CO}_2$  at  $650^\circ\text{C}$  and calcination in air at  $900^\circ\text{C}$  both stages for 5 min; recarbonation under pure  $\text{CO}_2$  for 3 min).

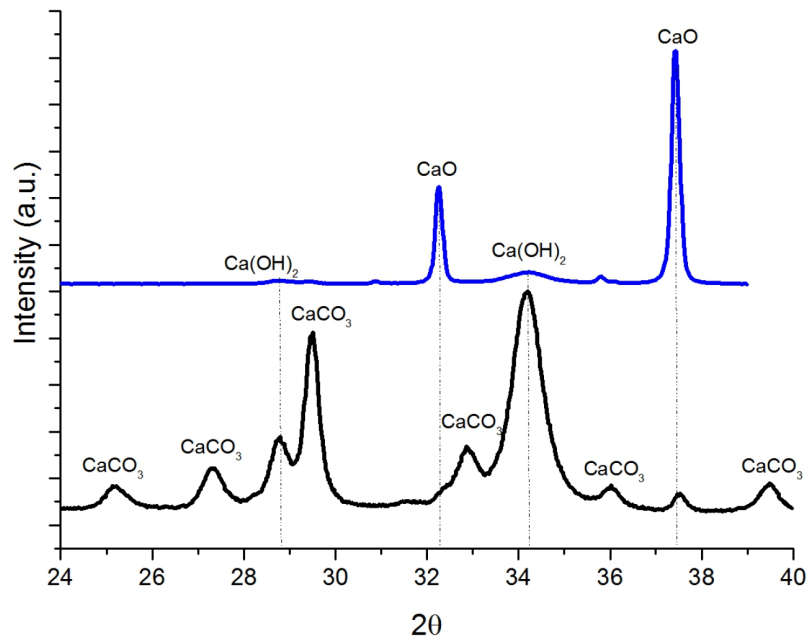


FIG. 4. XRD patterns of soon after (top) and overnight (bottom) heat treated (950°C for 12 h in air) samples.

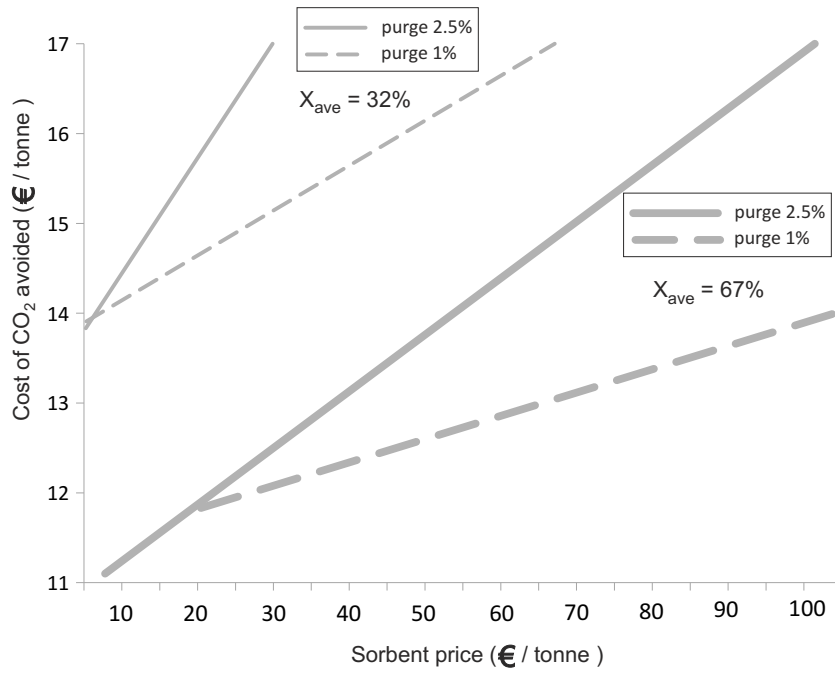


FIG. 5. CO<sub>2</sub> avoided cost estimated from the simulation of the capture process integrated with a power plant as a function of sorbent price for different values of the purge flow in the calciner and low CaO/CO<sub>2</sub> molar ratio ( $R = 1.5$ ). The figure shows the effect of increasing the maximum average capture capacity of the CaO solid population ( $X_{ave}$ ). Adaptation of Fig. 8 originally reported in [7].



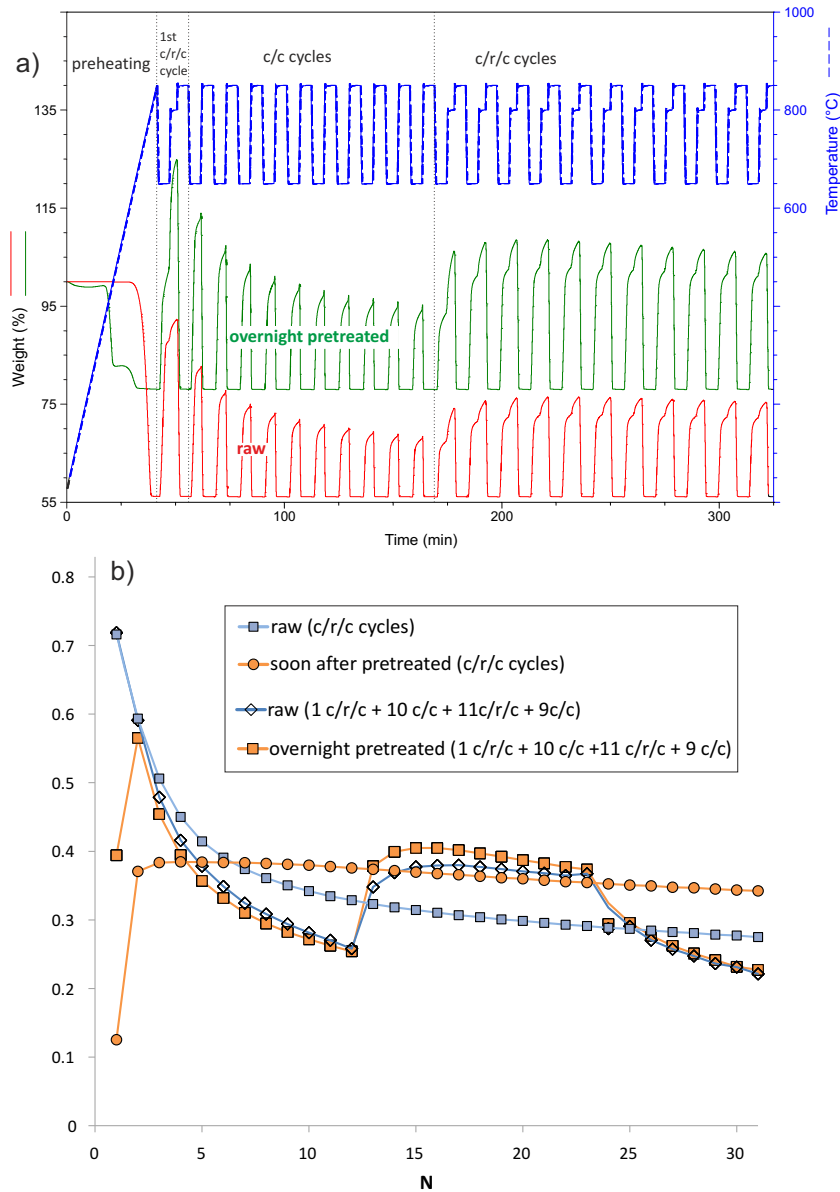


FIG. 6. a) Time evolution of sorbent weight % during a 1st carbonation/recarbonation/calcination cycle followed by 10 carbonation/calcination cycles and 11 carbonation/recarbonation/calcination cycles from the TGA multicyclic tests for heat treated and raw limestones. Evolution of temperature (right axis) is also shown. b) Conversion at the end of the carbonation stage as a function of the cycle number for raw and heat treated limestones obtained from these tests. Conversion values obtained from c/r/c multicyclic tests (shown in Fig. 3) are plotted for comparison