

1 **Ca-looping for postcombustion CO₂ capture: A comparative**
2 **analysis on the performances of dolomite and limestone**

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Abstract

The low cost and wide availability of natural limestone (CaCO_3) is at the basis of the industrial competitiveness of the Ca-looping (CaL) technology for postcombustion CO_2 capture as already demonstrated by $\sim 1 \text{ Mw}_t$ scale pilot projects. A major focus of studies oriented towards further improving the efficiency of the CaL technology is how to prevent the gradual loss of capture capacity of limestone derived CaO as the number of carbonation/calcination cycles is increased. Natural dolomite ($\text{MgCa}(\text{CO}_3)_2$) has been proposed as an alternative sorbent precursor to limestone. Yet, carbonation of MgO is not thermodynamically favorable at CaL conditions, which may hinder the capture performance of dolomite. In the work described in this paper we carried out a thermogravimetric analysis on the multicyclic capture performance of natural dolomite under realistic regeneration conditions necessarily implying high calcination temperature, high CO_2 concentration and fast transitions between the carbonation and calcination stages. Our study demonstrates that the sorbent derived from dolomite has a greater capture capacity as compared to limestone. SEM analysis shows that MgO grains in the decomposed dolomite are resistant to sintering under severe calcination conditions and segregate from CaO acting as a thermally stable support which mitigates the multicyclic loss of CaO conversion. Furthermore, full decomposition of dolomite is achieved at significantly lower calcination temperatures as compared to limestone, which would help improving further the industrial competitiveness of the technology.

29 I. INTRODUCTION

30 The Ca-looping (CaL) technology has recently emerged as a potentially feasible process
31 for postcombustion CO₂ capture [1–3]. As a main advantage over other technologies it
32 stands the low cost, wide availability and harmlessness towards the environment of natu-
33 ral limestone to be used as CaO precursor for CO₂ capture [4, 5]. In this process, CO₂ is
34 chemisorbed on the surface of CaO particles fluidized in a gas-solid reactor (carbonator)
35 by the postcombustion gas stream at atmospheric pressure and temperatures about 650°C.
36 The solids partially carbonated after typically short residence times (of a few minutes) are
37 circulated into a second gas-solid reactor (calciner) where CaO is regenerated by calcina-
38 tion at atmospheric pressure and a gas stream of highly concentrated CO₂ is retrieved for
39 compression and storage.

40 The CaL technology is being demonstrated in large-scale pilot plants (up to 1.7 MW_t)
41 showing efficient and sustainable CO₂ capture [3, 6]. A typical run commences by precalcini-
42 ng the initial inventory of limestone in air after which the calciner is set to oxy-combustion
43 mode and the circulation of solids in the loop is started. Burning fuel with pure oxygen
44 (oxy-combustion) ensures a high CO₂ concentration in the gas exiting the calciner and a
45 sufficiently high temperature (close to 950°C) to achieve complete CaO regeneration in short
46 residence times [3, 6–10]. However, oxy-combustion imposes an energy penalty (due to the
47 consumption of fuel and oxygen) and generates additional CO₂ [8, 11–13]. Moreover, the
48 carbonation activity of CaO regenerated at high temperature and under high CO₂ con-
49 centration suffers a marked drop, which is particularly intense in the first cycles [10, 14].
50 Other causes of decay of the sorbent capture capacity are irreversible sulphation due to SO₂
51 (present in the flue gas and produced in the calciner by oxy-combustion) and losses of fine

52 particles generated by attrition [3, 15]. It is thus necessary to feed the calciner periodically
53 with a makeup flow of fresh limestone to compensate for sorbent deactivation. As opposed
54 to the sorbent derived from calcination of the initial limestone inventory, CaO derived from
55 the makeup flow is obtained by calcination in a high CO₂ partial pressure environment.

56 Another naturally occurring mineral that can be used as CaO precursor is dolomite
57 (CaMg(CO₃)₂), which is also abundantly available at low price [1, 16, 17]. Arguably, the
58 irreversible decomposition of MgCO₃ would enhance the surface area of the calcined sorbent
59 [18], which should favor the CaO reactivity in the fast phase controlled by carbonation on
60 the surface of the solids. Moreover, the presence of MgO in calcined dolomite is expected
61 to increase the thermal stability of the sorbent and help mitigating the loss of CaO carbon-
62 ation reactivity, which is generally attributed to its superior resistance to sintering at high
63 calcination temperatures. The ultimate mechanism governing the thermal decomposition of
64 dolomite is however not well understood yet [19–21]. The Tamman temperature indicating
65 the initiation of sintering of MgO ($T_t \simeq 1276^\circ\text{C}$) [16] is only slightly above the Tamman
66 temperature of CaO ($T_t \simeq 1170^\circ\text{C}$) [16] being both values well over the typical calcina-
67 tion temperatures at CaL conditions. Thus, it is unclear why MgO should be resistant to
68 sintering while CaO is not. Furthermore, carbonation of MgO is not thermodynamically
69 favorable at CaL conditions [1, 22]. Hence, the stoichiometric CO₂ capture capacity (ratio
70 of mass of CO₂ chemisorbed to mass of CaO·MgO) of calcined dolomite at CaL conditions
71 is just 0.46 as compared to 0.79 for calcined limestone. Experimental results show accord-
72 ingly that the capture capacity of dolomite stays well below that of limestone after a certain
73 number of carbonation/calcination cycles [1] even though it must be remarked that most
74 lab-scale tests on dolomite or CaO·MgO synthetic composites do not mimic realistic CaL
75 conditions for postcombustion capture [23–26]. For example, Albrecht et al. [24] observed

76 that the presence of inert MgO served to increase the conversion of CaO after a very large
77 number of carbonation/calcination cycles (up to 1250). However, these cycles were con-
78 ducted isothermally at 750°C, subjecting the sample to a 25% CO₂/75% N₂ gas mixture
79 for carbonation during 20 min and calcining it under N₂ during 30 min. A first attempt to
80 compare the multicyclic capture performances of dolomite and limestone when subjected to
81 severe calcination conditions (940°C, 70% vol CO₂) has been recently made [27] by means
82 of a lab-scale bubbling fluidized bed (gas velocities of about 0.5 m/s). Results showed that,
83 despite of its lower Ca content, the sorbent derived from dolomite had a greater capture
84 capacity than limestone derived CaO. However, the sorbents were subjected in this study to
85 only 5 calcination/carbonation cycles in which carbonation was prolonged up to completion
86 and the materials were cooled down to ambient temperature between stages, which is not
87 representative of realistic CaL conditions.

88 Realistic CaL conditions for postcombustion capture necessarily involve short residence
89 times (of just a few minutes), low CO₂ concentration (about 15% vol) for partial carbonation
90 at around 650°C, high temperature (above 900°C) and high CO₂ concentration (above 70%
91 vol) in the calciner for sorbent regeneration and precalcination of the makeup flow of solids,
92 and very fast transitions between the carbonation and calcination stages (typically of a
93 few seconds) [15, 28]. Moreover, the dual fluidized bed in practice would be operated by
94 rapid gas flows (gas velocities in the range 5 - 10 m/s) in the fast fluidization regime [29]
95 characterized by a high mass/heat transfer efficiency, which is likely impaired in bubbling
96 beds (operated at small gas velocities) wherein gas-solids contacting effectiveness is hindered
97 by the development of gas bubbles [7, 30]. Mass/heat transfer inefficiency may be avoided
98 by means of TGA tests, which however usually fail to reproduce simultaneously the rapid
99 transitions between stages and high CO₂ partial pressure in the calcination environment.

100 According to process simulations [2, 11, 31, 32] the efficiency of the CaL technology is
101 extraordinarily dependent upon the sorbent capture performance. Thus, it is of paramount
102 importance to characterize it at realistic conditions in order to extract from simulations
103 useful information for the optimum design and operational parameters to scale-up the tech-
104 nology. In the present manuscript we show a comparative study on the multicyclic CO₂
105 capture behavior of natural dolomite and limestone by means of thermogravimetric analysis
106 (TGA) tests carried out at conditions closely resembling those to be expected in postcombus-
107 tion capture applications. The role of precalcination conditions and the effect of introducing
108 a recarbonation stage between carbonation and calcination stages will be a particular focus
109 of our study. The incorporation of a recarbonator reactor to the CaL process is thought
110 to improve its efficiency by minimizing the required makeup flow of fresh limestone and
111 the heat demand in the calciner [33–35] albeit in previously reported TGA tests demon-
112 strating the beneficial effect of recarbonation [33, 35, 36] the sorbent was regenerated by
113 calcination in air. More recent works have evidenced that the capture capacity of CaO
114 derived by precalcination of limestone in air and subsequently regenerated by calcination
115 at high temperature/high CO₂ concentration is actually hampered by the introduction of a
116 recarbonation stage [14, 37], which shed doubts on the usefulness of incorporating into the
117 technology an additional recarbonator reactor. As will be seen in this manuscript dolomite
118 and limestone respond in a very distinct way to recarbonation as a function of precalcination
119 conditions. Scanning Electron microscopy (SEM) analysis will be used in our study to gain
120 fundamental knowledge on the mechanisms governing the behavior of both natural CaO
121 precursors.

122 II. MATERIALS AND METHODS

123 The materials employed in our work are natural limestone of high purity (99.62% CaCO_3 ,
124 $\text{SiO}_2 < 0.05\%$, $\text{Al}_2\text{O}_3 < 0.05\%$, 0.24% MgO , 0.08% Na_2O) as received from Matagallar quarry
125 (Pedrera, Spain) and a purified natural dolomite ($\text{MgCa}(\text{CO}_3)_2$) purchased from Alfa Aesar
126 (CAS: 12001-27-3). X-ray diffraction (XRD) patterns measured in our work are shown in
127 Fig. 1. As may be seen, both samples are characterized by a high purity with only a minor
128 presence of CaCO_3 impurities in dolomite (as revealed by the small diffraction peak located
129 in the major calcite peak at $2\theta \approx 29.2^\circ$).

130 The multicyclic CO_2 capture behavior of limestone and dolomite samples has been ana-
131 lyzed by means of carbonation/calcination and carbonation/recarbonation/calcination cy-
132 cles carried out using a Q5000IR TG analyzer (TA Instruments). This instrument is
133 equipped with a furnace heated by infrared halogen lamps and a high sensitivity balance
134 ($< 0.1 \mu\text{g}$) with a minimum baseline dynamic drift ($< 10 \mu\text{g}$). Infrared heating allows fast
135 and controlled heating/cooling rates ($300^\circ\text{C}/\text{min}$) with rather small fluctuations ($< \pm 4^\circ\text{C}$).
136 In this way, the transition between the carbonation and calcination stages may be shortened
137 to tens of seconds in contrast with typical TGA tests carried out by using common furnaces
138 with low heating rates (usually below $25^\circ\text{C}/\text{min}$). This is a relevant issue when the sor-
139 bent is regenerated under high CO_2 partial pressure since during slow heating it will suffer
140 appreciable recarbonation until the temperature reaches a sufficiently high value (close to
141 900°C) to reverse the reaction towards decarbonation, which seriously affects its capture
142 performance [14].

143 Carbonation/calcination (carb/cal) cycles in our TGA tests consisted of 5 min carbona-
144 tion at 650°C (85% air/15% CO_2 vol/vol) and 5 min calcination at 950°C (70% CO_2 /30% air

145 vol/vol). For comparison, carb/cal tests were also carried out in which calcination was per-
146 formed at 925°C and 900°C under 70% CO₂/30% air vol/vol, and at 850°C in air. In regards
147 to carbonation/recarbonation/calcination (carb/recarb/cal) cycles, a 3 min recarbonation
148 stage at 800°C (10% air/90% CO₂ vol/vol) was introduced in between the carbonation and
149 calcination stages. TGA tests were initiated by subjecting the samples to different pre-
150 calcination programs in-situ. On one hand, precalcination was carried out by heating the
151 samples in air at a slow rate (20°C/min) up to 850°C with the goal of replicating the pre-
152 calcination conditions of the initial solids inventory in the practical application. On the
153 other hand, precalcination was performed by heating up the samples under high CO₂ par-
154 tial pressure (70% CO₂/30% air vol/vol) up to 950°C (925°C and 900°C in some tests) at
155 a fast rate (300°C/min), which was intended to mimic precalcination of the makeup flow
156 of solids periodically fed into the calciner at practice (due to technical limitations the heat-
157 ing rate was set to 20°C/min from ambient temperature up to 450°C, which is below the
158 reported decomposition temperatures for both materials [23]). The gas flow rate in all the
159 tests was kept small enough (100 cm³min⁻¹) as to neglect external mass transfer effects. A
160 fixed sample mass of 10 mg was employed in all the runs, which allows dismissing also any
161 effect of diffusion resistance through the sample on the reaction rate [38]. Particle size in
162 our samples was below 500 μm, thus intra-particle diffusion resistance can be disregarded
163 too [39, 40]. TGA tests were complemented with microscopy analysis of the cycled samples
164 by means of a ultra high-resolution Scanning Electron Microscope (SEM HITACHI S5200).

165 III. EXPERIMENTAL RESULTS AND DISCUSSION

166 A. CO₂ capture capacity

167 In order to take into account the presence of inert MgO in the sorbent derived from
168 dolomite, the appropriate parameter for practical purposes to characterize the sorbent per-
169 formance is the capture capacity, which is defined as the ratio of mass of CO₂ captured to
170 the mass of sorbent before each carbonation stage (including both CaO and MgO in the
171 case of dolomite). Figure 2 shows multicyclic capture capacity results from carb/cal tests in
172 which dolomite and limestone samples were precalcined in air and regenerated either in air at
173 850°C (Fig. 2a) or under 70%CO₂ at 950°C (Fig. 2b), respectively. As might be expected,
174 dolomite exhibits a lower capture capacity during the first cycles after precalcination in air
175 but it deactivates with the cycle number at a lower rate as compared with limestone. Under
176 these conditions (sorbent regeneration in air, Fig. 2a) limestone deactivation is not marked
177 and both sorbents exhibit a similar performance after the 5th carb/cal cycle. However, the
178 scenario is radically changed when the sorbents are regenerated under realistic (postcom-
179 bustion capture) calcination conditions (Fig. 2b). In this case, limestone suffers a drastic
180 drop of its capture capacity after regeneration and it falls below 0.05 in just 10 cycles. In
181 contrast, dolomite deactivates at a much lower rate. As a result, the capture capacity of
182 dolomite is twice that of limestone after 20 cycles.

183 The effect of recarbonation on the performance of both sorbents precalcined in air and
184 regenerated under high CO₂ concentration is illustrated by Figs. 3a and 3b. As can be
185 seen, recarbonation is actually detrimental for the carbonation activity of limestone cycled
186 under these conditions. Conversely, recarbonation does not cause an appreciable effect on
187 the performance of dolomite. Likewise, the behavior of dolomite is not essentially changed

188 by the conditions of precalcination as seen in Fig. 4 where capture capacity data are plotted
189 from carb/calc tests in which precalcination was carried out either in air at 850°C or under
190 70%CO₂ at 950°C. Contrarily, precalcination conditions play a relevant role on the multi-
191 cyclic behavior of limestone (see Fig. 4). Severe precalcination conditions cause a significant
192 drop of the capture capacity of limestone derived CaO in the 1st cycle but it serves to miti-
193 gate its progressive decay with the number of cycles. After 20 cycles, the capture capacity of
194 the limestone sample precalcined under high CO₂ concentration is about 0.08 as compared
195 to just 0.04 when limestone was precalcined in air. Still dolomite exhibits a neatly higher
196 capture capacity also when precalcination conditions are severe (see Fig. 5). Figure 6 shows
197 the effect of recarbonation on the performance of the sorbents precalcined and regenerated
198 under severe conditions. Interestingly, recarbonation has in this case a favorable influence on
199 the performance of limestone whereas the behavior of dolomite remains quite insensitive to
200 recarbonation up to the 10th cycle after which the capture capacity of the sorbent subjected
201 to recarbonation becomes only slightly hindered.

202 As a summary, TGA results demonstrate that dolomite exhibits a multicyclic capture
203 capacity which does not suffer remarkable variations with either sorbent recarbonation or
204 the conditions of precalcination. Conversely, the behavior of limestone is highly dependent
205 on both. Only if limestone is precalcined under severe conditions involving high CO₂ concen-
206 tration (similar to those of regeneration) and is subjected to an intermediate recarbonation
207 stage, its capture capacity may keep the pace with that of dolomite subjected to ordinary
208 carb/calc cycles as seen in Fig. 7. From the point of view of sorbent capture performance
209 at realistic CaL conditions, these results suggest that the use of natural dolomite for post-
210 combustion capture would yield an efficiency improvement of the CaL technology, which is
211 comparable to that of introducing a recarbonator reactor when using limestone (with the

212 added requirement, if limestone is employed, of precalcining under high CO_2 partial pressure
213 instead of air in order to avoid marked deactivation as seen in our work). An additional
214 gain of efficiency may be achieved by the possibility of calcining at lower temperatures. This
215 relevant issue will be discussed in detail in section IV. In regards to the sorbent behavior, it
216 is interesting to remark that the capture capacity of dolomite is practically insensitive to the
217 temperature of precalcination/regeneration in the range of temperatures between 900°C and
218 950°C as seen in Fig. 7, which stresses further the main role of MgO on avoiding sintering
219 and deactivation of CaO at high temperatures.

220 B. CaO conversion

221 Let us recall that, for practical purposes, the parameter used above to compare the mul-
222 ticyclic CO_2 capture performances of dolomite and limestone has been the capture capacity.
223 From a fundamental perspective it is also interesting to look at the CaO conversion defined
224 as the ratio of mass of CaO converted in each carbonation stage to the mass of CaO initially
225 present in the sorbent after calcination. In the case of limestone, CaO conversion is readily
226 obtained multiplying the capture capacity by the factor $M_{\text{CaO}}/M_{\text{CO}_2}$ where $M_{\text{CaO}} = 56$
227 g/mol and $M_{\text{CO}_2} = 44 \text{ g/mol}$ are the molecular weights of CaO and CO_2 , respectively.
228 For dolomite, the sorbent derived after calcination consists of $\text{MgO}\cdot\text{CaO}$. CaO conversion is
229 then obtained multiplying the capture capacity by the factor $(1 + M_{\text{MgO}}/M_{\text{CaO}})M_{\text{CaO}}/M_{\text{CO}_2}$
230 where $M_{\text{MgO}} = 40 \text{ g/mol}$ is the molecular weight of MgO . Figure 8 shows data on multicyclic
231 CaO conversion for both sorbents precalcined either in air (at 850°C) or under $70\%\text{CO}_2$ (at
232 950°C) and regenerated under severe conditions (note the log-log scale). Multicyclic CaO
233 conversion data reported in the literature is usually fitted by the semi-empirical equation
234 [41–43]

$$X_N = X_r + \frac{X_1}{k(N-1) + (1 - X_r/X_1)^{-1}}; \quad (N = 1, 2, \dots) \quad (1)$$

235 where N is the cycle number, X_1 is CaO conversion at the 1st cycle, k is a deactivation
 236 constant and X_r is the so-called residual conversion, which is asymptotically approached
 237 for a very large number of cycles. Most of TGA data obtained for natural limestones can
 238 be reasonably well fitted using Eq. 1 with a residual conversion between 0.07 and 0.08 and
 239 a deactivation constant k around 0.5 [41, 44]. Usually, process simulations and economic
 240 analysis on the CaL technology rely on these values to characterize the sorbent behavior
 241 [2, 12, 31, 33, 34, 45]. Yet, most lab-scale tests are not carried out under realistic (post-
 242 combustion capture) calcination conditions due to technical limitations as explained above.
 243 As may be seen in Fig. 8, CaO conversion data obtained in our work for limestone precal-
 244 cined and regenerated under high CO₂ concentration still converges towards a residual value
 245 ($X_r = 0.079$), which fits within the interval commonly reported for limestones precalcined
 246 and regenerated under low CO₂ concentration even though the deactivation constant ob-
 247 tained from our data is substantially higher ($k = 0.85$). In regards to the multicyclic CaO
 248 conversion of limestone precalcined in air and regenerated under high CO₂ concentration, in
 249 the first 10 cycles it follows a trend marked by a drastic drop which cannot be satisfactorily
 250 fitted by Eq. 1 (see Fig. 8). Under these conditions, Eq. 1 conforms well to the evolution of
 251 CaO conversion data only from the 10th cycle yielding a residual value of just $X_r = 0.034$.
 252 On the other hand, the behavior of CaO conversion for dolomite does not exhibit such a
 253 critical dependence on precalcination conditions and reaches a quite high residual value as
 254 compared to limestone. Note that, even after precalcination under severe conditions, CaO
 255 conversion for dolomite in the 1st cycle is about $X_1 = 0.794$ whereas for limestone it falls
 256 down to just $X_1 = 0.476$

258 Our TGA results indicate that the CaO skeleton derived from precalcining limestone in
259 air is highly reactive, yet when the sorbent is regenerated under high CO₂ concentration/high
260 temperature (a must for postcombustion capture) it suffers a drastic deactivation which is
261 additionally intensified by recarbonation. SEM pictures of limestone and dolomite samples
262 precalcined in air and subjected to carb/calc cycles under severe regeneration conditions
263 are shown in Fig. 9. Clearly, limestone derived CaO appears as markedly sintered. The
264 consequent reduction of its reactive surface area is in accordance with the significant drop
265 of the fast carbonation activity obtained from the TGA tests (Fig. 4a). On the other hand,
266 the cycled dolomite sample exhibits a much higher porosity. As inferred from TEM (in-situ)
267 and XRD analysis reported elsewhere [21] on dolomite crystals calcined at temperatures
268 in the range 500–1000°C, decomposition of dolomite occurs by de-mixing of a metastable
269 CaO·MgO precursor and the subsequent formation of pure CaO and MgO crystals via ori-
270 ented aggregation and sintering, which is favored by high ion diffusivity, although it must
271 be noticed that calcination in those tests was carried out in air and vacuum (we will come
272 back to this argument in section IV). In our SEM pictures, individual MgO grains seg-
273 regated from sintered CaO can be clearly identified (Fig. 9). MgO grains have a regular
274 size of around 100nm and appear to be rather resistant to sintering. In fact, these SEM
275 images of cycled dolomite samples show a striking resemblance with SEM images shown in
276 our previous work [46] of a CaO-based sorbent synthesized by impregnation of a calcium
277 nitrate solution on a nanostructured calcium silicate matrix (see Fig. 10), which acted as
278 a thermally stable support for CaO. Similarly, it may be argued that the thermal stability
279 and enhanced porosity provided by the nanostructured MgO skeleton in the case of cal-

280 cined dolomite allows the capture capacity of the dolomite derived sorbent to outweigh the
281 performance of limestone derived CaO, which is critically impaired when regenerated by
282 calcination under severe realistic conditions.

283 In some of the SEM images obtained in our work there is a marked segregation between
284 the MgO nanostructured grains and the sintered CaO skeleton. This is particularly notice-
285 able in the case of dolomite samples subjected to carb/recarb/carb cycles (precalcined and
286 regenerated under severe conditions) as may be seen in Fig. 11. Since diffusivity is enhanced
287 under the conditions of recarbonation (high temperature and high CO₂ concentration) [47–
288 49], it is likely that the segregation of MgO and CaO grains is promoted in accordance with
289 the mechanism reported elsewhere from in-situ observations [21]. This would lead to a loss
290 of efficiency of the MgO skeleton on enhancing the sorbent capture capacity, which can be
291 the reason for the observed slight decline of capture capacity performance of the dolomite
292 sample precalcined under severe conditions and subjected to a recarbonation stage (Fig.
293 6b). SEM pictures of cycled limestone and dolomite samples under diverse conditions can
294 be seen in Fig. 12 and show in general a higher porosity of the CaO skeleton for dolomite in
295 accordance with the higher conversion exhibited by this sorbent. Remarkably, MgO grains
296 are not visible in the surface of the cycled dolomite samples shown in Fig. 12. Figure 13
297 illustrate more clearly this phenomenon usually observed in the SEM pictures. Presumably,
298 repeated carbonation/calcinations on the surface of the particles and significant sintering
299 of the nascent CaO grains supported on the inert MgO skeleton would be responsible for
300 this segregation. As may be seen in these pictures, MgO grains have a tendency to migrate
301 towards the interior of the particles whereas sintered CaO grains build up onto the surface of
302 the particles. This kind of segregation is clearly observed in the representative photographs
303 on the right of Fig. 13, where the cross section of a fractured particle is featured.

304 IV. KINETICS OF LIMESTONE AND DOLOMITE CALCINATION

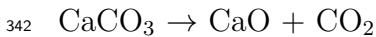
305 Simulations of the CaL technology at the industrial level show that the energy demand
306 in the calciner can reach a fraction near half the total energy required in the process [11] or
307 even higher if the detrimental effect on limestone performance caused by regeneration under
308 high CO₂% were taken into account. Many research efforts are thus currently devoted to
309 the development of innovative techniques to achieve a high calciner efficiency at a decreased
310 temperature and taking into account the short residence times imposed [15, 28]. Our goal in
311 this section is to carry out a comparative analysis of the decarbonation kinetics of limestone
312 and dolomite during calcination in our TGA tests.

313 As seen in Fig. 14 limestone and dolomite follow very similar decarbonation kinetics
314 when calcined in air by slowly increasing the temperature up to 850°C. In agreement with
315 observations reported in the literature [50, 51], we see that decarbonation of dolomite in air
316 occurs in one stage and starts at about 600°C analogously to limestone. Figure 15 illustrates
317 the kinetics of limestone calcination under 70%CO₂ by quickly increasing the temperature up
318 to 950°C. As may be seen, the presence of CO₂ hinders severely decarbonation of limestone
319 as widely reported in the literature [39, 52–58]. Since CaCO₃ decarbonation is heavily
320 influenced by the thermodynamic equilibrium the presence of CO₂ displaces it to higher
321 temperatures but also slows down it markedly. Decarbonation is seen to start in Fig. 15
322 at about 900°C (around 30°C above the thermodynamic equilibrium temperature under
323 70%CO₂ at atmospheric pressure [39]) and only progresses at a sufficiently fast rate to
324 be fully attained in a short residence time if the calcination temperature is raised above
325 925°C in accordance with pilot-scale tests results [3, 7–10]. As compared to limestone,
326 the kinetics of dolomite calcination under 70%CO₂ shows radically different features as

327 may be observed in Fig. 16. In agreement with previous works [50, 51], decomposition of
328 dolomite under high CO₂ concentration is seen to occur mainly by two stages. Irreversible
329 MgCO₃ decomposition occurs in a first stage whereas the second stage involving CaCO₃
330 decomposition is initiated at around 650°C, which is well below the equilibrium temperature
331 for pure CaCO₃ decomposition. As shown in Fig. 16, decarbonation of dolomite is fully
332 achieved in a time period below 5 minutes at a calcination temperature of just 900°C.

333 The thermal decomposition of dolomite via a single step at low partial pressures of CO₂
334 and along two distinct stages at high CO₂ partial pressures observed in our work is a well
335 documented phenomenon, yet the mechanism responsible for this behavior is still a subject
336 of debate [19–21, 23, 51, 59–61]. Experimental studies have shown that the intermediate
337 products between stages in the decomposition process under CO₂ are MgCO₃, CaCO₃ and
338 MgO while the final products were CaO and MgO. Thus, it is usual to represent the process
339 by means of the reactions

340

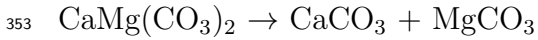


343

344 De-mixing of Ca²⁺ and Mg²⁺ cations in the 1st stage (half-decomposition) is thought
345 to yield the nucleation and growth of MgO crystals resistant to sintering and the con-
346 comitant formation of CaCO₃ through the diffusion of its constituents within the lattice.
347 Solid-state diffusion (of cations in the lattice and of CO₃²⁻ across the reacting interface) are
348 thus believed to be the rate-limiting factors of half-decomposition. As a matter of fact, it
349 is reported that the half-decomposition temperature is considerably decreased by grinding
350 the dolomite sample [51], which is known to decrease the resistance to solid-state diffusion

351 [48, 49]. An alternative more compact representation of the reaction is [59]

352



354

355 being MgCO_3 thermodynamically unstable at relatively lower temperatures [23], which
356 gives rise to the two-stage decomposition process. In accordance with this formulation we
357 see that the 1st weight loss (Fig. 16) occurs within the temperature range 400–500°C, which
358 conforms to the equilibrium temperature of MgCO_3 decomposition at a CO_2 partial pressure
359 of 0.7 atm [23] (70% vol concentration at atmospheric pressure in our tests). Nonetheless,
360 half-decomposition is generally observed at higher temperatures [60] in experiments usually
361 carried out at low heating rates ($\sim 10^\circ\text{C}/\text{min}$). In our tests, 1st chemical decomposition
362 is triggered just when the heating rate is increased to $300^\circ\text{C}/\text{min}$, which suggests that the
363 heating rate plays a relevant role on the mechanism of the process. On the other hand, Fig.
364 16 shows that $\text{MgO}\cdot\text{CaCO}_3$ decomposition would be started at temperatures well below the
365 equilibrium temperature for pure CaCO_3 decomposition ($T_{eq} \approx 870^\circ\text{C}$) whereas the kinetics
366 of $\text{MgO}\cdot\text{CaCO}_3$ decomposition would be significantly enhanced as compared to limestone
367 decomposition under CO_2 .

368 Figure 17 illustrates the kinetics of CaCO_3 and $\text{MgO}\cdot\text{CaCO}_3$ decomposition during CaO
369 regeneration in the 1st carb/calc cycle. As opposed to the contrasting behaviors exhibited
370 by limestone and dolomite calcination, it is observed that the calcination kinetics for both
371 sorbents is similar in this regeneration stage under high CO_2 concentration. Decarbonation
372 commences at about 850°C and proceeds at a quick rate, which is still faster for the dolomite
373 derived sorbent. Arguably, desorption of CO_2 at high CO_2 partial pressure would be favored
374 across the boundaries between different phases. The CaCO_3/CaO transformation experi-

375 enced by both sorbents during regeneration would be thus governed by a similar mechanism
376 with the MgO grains serving as a stable nano-structured support for the dolomite derived
377 CaO and favoring solid-state diffusion.

378 V. CAO REGENERATION AND SINTERING

379 The loss of multicyclic CaO conversion is usually explained from the marked sintering
380 suffered by the CaO skeleton regenerated by calcination at high temperature [41, 43]. The
381 point at which sintering begins in ceramic materials occurs at the Tammann temperature,
382 which, as a rule of thumb, is considered as half their melting temperature. As seen in our
383 SEM pictures, CaO grains of dolomite samples subjected to repeated carb/cal cycles exhibit
384 indeed notable sintering, yet MgO grains appear resistant to sintering. This is a puzzling
385 observation if one takes into account that the Tammann temperatures of both oxides are not
386 very different ($T_t \simeq 1170^\circ\text{C}$ for CaO and $T_t \simeq 1276^\circ\text{C}$ for MgO) [16] and both are well over
387 the calcination temperature at CaL conditions. However, the main reason for the sintering
388 dissimilarity of both oxides must be sought in their different multicyclic history. The essential
389 issue is that CaO undergoes repeated carbonation and regenerations whereas MgO remains
390 as an inert oxide. It may be therefore hypothesized that most of CaO sintering occurs
391 during the CaCO_3/CaO transformation in each cycle. Figure 18 shows limestone derived
392 CaO conversion data from carb/calc cycles in which the calcination stages were prolonged
393 to 3 hours. As may be seen, and despite the excessively long calcination periods, CaO
394 conversion is not remarkably decreased as compared to conversion in the tests with short
395 calcination stages (5 min) mimicking practical conditions, which supports the argument
396 that sintering and deactivation occurs mostly in the nascent CaO during the CaCO_3/CaO
397 transformation and not after CaO has reached its stable form.

398 Empirical measurements reported in a wide number of works indicate that the sintering
399 of CaO is greatly accelerated when CO₂ is present in the calcination atmosphere at high
400 concentration [42, 57, 62] whereas the CaCO₃ decarbonation rate suffers a drastic decline
401 [39, 52–58]. Gaining understanding on the physicochemical mechanism behind this behav-
402 ior should be a main scientific focus of studies on the CaL process since it determines the
403 multicyclic sorbent performance and therefore has a great influence on the efficiency of the
404 technology. Decarbonation of CaCO₃ is initiated by the chemical decomposition of CaCO₃
405 to yield CaO and CO₂ adsorbed, which is afterwards desorbed [39, 52]. At low CO₂ partial
406 pressures, the process is rate limited by the chemical decomposition stage since desorption is
407 very fast [39]. In the case of high CO₂ partial pressure however, CO₂ desorption is severely
408 hampered and would limit the decarbonation process [56]. Empirical studies indicate that
409 the presence of CO₂ at high concentrations in the calcination atmosphere leads to a reversible
410 CO₂ desorption/adsorption dynamic process [53, 56] that would slow down decarbonation.
411 In the pioneer work of Hyatt et al. [52], experimental measurements on the rate of cal-
412 cite crystals calcination lead the authors to formulate the hypothesis that the nascent CaO
413 lattice acquires a metastable rhombohedral structure (similar to the original CaCO₃) when
414 CO₂ is desorbed, after which the stable CaO cubic lattice nucleates from the transforma-
415 tion of the metastable CaO, which acts as bridge for the reaction. Later results from XRD
416 analysis upheld the idea that a distorted metastable phase of CaO was formed during de-
417 carbonation of calcite [63, 64] although little could be concluded about its crystal structure.
418 A more recent study [65] has shown from diverse advanced characterization techniques that
419 the CaCO₃/CaO transformation starts by the formation of a mesoporous structure made up
420 of rod-shaped (metastable) CaO nanocrystals on each rhombohedral cleavage face of the cal-
421 cite pseudomorph. These CaO nanocrystals undergo oriented aggregation driven by van der

422 Waals attractive forces to minimize surface energy. Aggregated nanocrystals become after-
423 wards sintered as decomposition progresses. Oriented aggregation and sintering reduces the
424 surface area and porosity of the metastable structure by closing the mesopores between the
425 rod-shaped CaO nanocrystals, which results in the formation of macropores through which
426 CO₂ can easily escape to complete the transformation by the nucleation of stable CaO cubic
427 crystals [65]. Chemical decomposition was observed to control the kinetics of the process
428 during most of the CaCO₃/CaO transformation in these experiments [65], which were car-
429 ried out in vacuum and air. Under these conditions there is no significant resistance against
430 CO₂ diffusion to migrate outside the metastable CaO structure. However, the resistance for
431 CO₂ to escape the metastable CaO mesoporous structure by diffusion would be impaired
432 under a high CO₂ partial pressure in the environment outside the solid, which would favor
433 re-adsorption of CO₂. It is well known that adsorption of CO₂ on solid surfaces gives rise to a
434 significant increase of the surface energy and therefore enhances the attractive force between
435 the solids [66]. Thus, it may be expected that, in the presence of CO₂ adsorbed onto the
436 surfaces of metastable CaO nanocrystals, their aggregation is promoted, which would favor
437 their subsequent sintering. In regards to decarbonation during regeneration of MgO·CaCO₃,
438 it may be argued that the presence of inert MgO nanocrystals between the CaO metastable
439 nanocrystals would reduce their attractive forces, thus counteracting the effect of high CO₂
440 partial pressure by preventing their adhesive aggregation and subsequent sintering. As the
441 number of cycles progresses, the cumulative aggregation and sintering of CaO nanocrystals
442 in each CaCO₃/CaO transformation would lead to a segregation between the sintered
443 CaO skeleton and the resistant to sintering MgO grains as observed from our SEM analysis.
444 Moreover, this argument may explain why sintered CaO is mostly seen on the surface of
445 cycled dolomite particles since it is there where most of CaO carbonation/regeneration takes

446 place in short residence times. Further research must be devoted in future works to explore
447 the fundamental mechanism of CaCO_3/CaO transformation at high CO_2 pressure but it
448 seems clear that the multicyclic loss of CaO conversion when subjected to repeated carb/cal
449 cycles is determined by the evolution of metastable CaO formed during the CaCO_3/CaO
450 transformation in each regeneration stage. From the practical point of view, it would be
451 interesting to devise feasible strategies to tailor this transformation by minimizing aggrega-
452 tion and sintering of metastable CaO nanocrystals. Presumably, this is the role played by
453 the MgO inert grains in natural dolomite.

454 **VI. INFLUENCE OF SORBENT PERFORMANCE ON THE CAL TECHNOLOGY EFFICIENCY**

455

456 Leaving aside the question on the fundamental mechanism that governs limestone and
457 dolomite decompositions under high CO_2 concentration, our results suggest that the use
458 of dolomite in the CaL technology would allow decreasing the temperature of the calciner
459 significantly. In regards to limestone, process simulations [8] show that the minimum cal-
460 cination temperature to achieve an acceptable calciner efficiency would be above 930°C
461 whereas the calciner efficiency would be severely hampered if the temperature is decreased
462 to 900°C , which agrees with our observations on the kinetics of limestone decarbonation
463 under high CO_2 concentration. On the other hand, our results indicate that a sufficiently
464 high calciner efficiency would be attainable at 900°C if natural dolomite is used, which de-
465 composes quickly at this reduced temperature under a high CO_2 concentration environment.
466 According to process simulation results [11] a decrease of the calcination temperature from
467 950°C to 900°C (while maintaining a high calciner efficiency) may bring about a substantial
468 reduction of costs. Particularly, the amounts of coal and oxygen needed for oxy-combustion

469 to raise the calciner temperature and the additional CO₂ produced by oxy-combustion,
470 which represent an important penalty for the technology [13, 28], would be lowered. Process
471 simulations [13, 45] indicate that the ratio of the mass of coal needed for oxy-combustion
472 to the mass of CO₂ captured would be decreased by a 10% if the calciner temperature is
473 decreased from 950°C to 900°C in the ordinary CaL configuration. If limestone is used,
474 the calciner temperature should be kept at 950°C and a similar 10% reduction would be
475 possible by incorporating a cyclonic preheater to transfer heat from hot gas leaving the cal-
476 ciner to the solids coming out from the carbonator, which has been proposed as a feasible
477 innovation to improve the industrial competitiveness of the technology [13]. Process simu-
478 lations indicate also that a low calciner to carbonator inventory ratio (of about 0.2) would
479 be only possible for limestone by calcining at 950°C (which yields a high calciner efficiency)
480 whereas a decrease of the calciner temperature to 900°C would require increasing this ratio
481 to about 1.2 [13]. Since full decarbonation at realistic CaL conditions could be efficiently
482 attained at 900°C for dolomite, it may be expected that the use of dolomite would allow
483 for a considerable reduction of the solids inventory in the calciner further decreasing the
484 energy penalty of the technology. Process simulations also show that the CaO/CO₂ molar
485 ratio (R) can be substantially decreased by a decrease of the calcination temperature for a
486 constant purge flow of solids (f) and if the capture efficiency (η) is kept constant as would
487 be possible by using dolomite. For example, for $f = 3\%$ and $\eta = 0.85$, it would be $R \simeq 10$
488 at 950°C and $R \simeq 7.5$ at 900°C [13]. The amount of solids purge and make-up flows have a
489 relevant influence on the process performance [12, 31]. Large purge flows lead to a dramatic
490 increase of the heat demand for calcination and hence the cost for oxygen production and
491 auxiliaries consumption is raised. Thus, the cost of CO₂ avoided tonne (tCO₂) is minimized
492 at relatively low purges. At an optimum CaO/CO₂ molar ratio of $R = 5$ and only $f = 1\%$

493 purge the estimated cost is around 14/tCO₂ whereas an increase of the purge flow in the
494 calciner (as would be required by enhanced deactivation) to 2.5% would increase the tCO₂
495 avoided cost by ~ 1 /tCO₂ [31].

496 An additional important aspect to be carefully addressed in future TGA studies on lime-
497 stone and dolomite at realistic CaL conditions is the irreversible sulphation of the sorbent
498 due to the presence of SO₂ either in the flue gas in the carbonator or in the calciner due
499 to oxy-combustion, which causes a notable decay of CaO conversion [10, 27, 67]. The main
500 factor limiting CaO sulphation reactivity is pore blocking [68–70]. Sulphation is essentially
501 favored by sintering and hence sulphation conversion is observed to increase with the cycle
502 number in multicyclic carb/cal tests [9]. Since CaO sintering is mitigated in the dolomite
503 derived sorbent, sulphation would be presumably minimized by the use of dolomite as com-
504 pared to limestone. Moreover, the possibility of lowering down the calciner temperature
505 would allow decreasing the generation of SO₂ in this reactor, which would serve to further
506 mitigate deactivation of the sorbent as caused by sulphation thus allowing for a reduction
507 of the makeup of fresh solids to counterbalance the purge flow of the solids deactivated.
508 Moreover, as seen in our work (Fig. 2b), the capture capacity of dolomite is substantially
509 higher than that of limestone for the initial solids inventory precalcined in air, which would
510 allow further decreasing the amount of purged solids while the capture efficiency is kept at
511 a high level [31]. On the other hand, our results show (section III A) that, for the solids
512 precalcined under high CO₂ concentration, the multicyclic capture behavior of dolomite in
513 ordinary carb/calc cycles is similar to that of limestone when an intermediate recarbonation
514 stage is introduced with the goal of reducing the amount of purged solids to a minimum
515 required for desulfurization as proposed elsewhere [33–35]. Simulations of a large-scale sys-
516 tem indicate that a bubbling recarbonator reactor with a cross-sectional area of between 80

517 and 100 m², expanded bed height of 2 m, and inlet gas velocities of 0.6 - 0.9 m/s would
518 be needed for this purpose [71]. According to simulations, by introducing a recarbonator
519 reactor, the make-up flow of limestone would be as low as 0.07 kg limestone per kg coal as
520 compared to 0.35 kg limestone per kg coal predicted in the ordinary CaL configuration [33],
521 which would lead to a significant reduction in energy consumption and coal/oxygen for oxy-
522 combustion (albeit it must be reminded that these simulations were based on the assumption
523 of a sorbent behavior inferred from TGA tests in which the samples were regenerated un-
524 der low CO₂ concentration [33, 35]). Since, as observed in our work, the performance of
525 dolomite subjected to ordinary carb/calc cycle is similar to that of limestone subjected to
526 carb/recarb/calc cycles, the reduction of costs by using dolomite instead of limestone could
527 be estimated from the costs involving the incorporation of an additional recarbonator reac-
528 tor to reactivate the limestone derived CaO, which should be re-assessed by considering the
529 sorbents behavior under realistic regeneration conditions. A potential issue related to the
530 use of dolomite in the CaL technology is its friability as suggested in some works [27], which
531 may be due to the development of intense residual stresses inside the porous matrix of the
532 solid during decomposition [19] also leading to decrepitation phenomena observed in TGA
533 tests [59, 72]. Particle fragmentation would occur however only during dolomite decompo-
534 sition and not in the sorbent regeneration stage. Accordingly, the rate of generation of fine
535 particle fragments in lab-scale fluidized bed tests [27] has been observed to be significant
536 just in the first calcination.

537 VII. CONCLUSIONS

538 A main conclusion of our study is that natural dolomite can be an advantageous alterna-
539 tive to limestone as sorbent precursor for postcombustion CO₂ capture by means of the CaL

540 technology. TGA tests carried out under realistic sorbent regeneration conditions (high CO₂
541 concentration, high temperature and quick transitions between carbonation and calcination
542 stages) show that the capture capacity of limestone derived CaO is critically influenced by
543 precalcination conditions and an intermediate recarbonation stage. The capture capacity
544 of CaO derived from precalcining limestone in air suffers a drastic drop in the first cycles.
545 Moreover, the introduction of a recarbonation stage, which is intended in practice to mini-
546 mize the need for a makeup flow of fresh limestone fed to the calciner, would actually have
547 an adverse effect on the capture capacity of the sorbent derived from precalcining the initial
548 inventory of limestone in air. SEM analysis of CaO derived from limestone precalcined in
549 air and regenerated under high CO₂ concentration/high temperature show that it suffers
550 marked sintering. The multicyclic stability of CaO may be enhanced if precalcination is
551 carried out under the same conditions as those used for regeneration, which leads also to a
552 favorable effect of recarbonation. On the other hand, the behavior of the sorbent derived
553 from dolomite is quite insensitive to either precalcination or recarbonation conditions and
554 shows a neatly higher capture capacity as compared to limestone at realistic calcination
555 conditions. The predictability of dolomite behavior, regardless of precalcination and recar-
556 bonation conditions, can be a further advantage over the strong dependence of limestone
557 performance on these conditions, which may vary uncontrollably in any modification of the
558 process. For example, proposed innovations of the CaL technology such as the addition of
559 a cyclonic preheater to transfer heat from the hot gas leaving the calciner to the particles
560 exiting the carbonator [13] will lead to recarbonation of the partially carbonated solids. In
561 this case, and if the makeup flow of fresh limestone fed to the calciner is minimized, the
562 activity of the sorbent precalcined in air might be further hindered. SEM analysis demon-
563 strates that, after a number of carbonation/calcination cycles, MgO and CaO grains in

564 the dolomite samples become segregated with resistant to sintering MgO grains migrating
565 towards the interior of the particles and a CaO layer building up on their surface. The
566 improved stability provided by the inert MgO skeleton would serve to significantly enhance
567 the multicyclic CaO conversion and sorbent capture capacity at realistic CaL conditions for
568 postcombustion CO₂ capture. An additional potential advantage brought about by the use
569 of dolomite would be its much faster decomposition under CO₂ as compared to limestone,
570 which would allow reducing notably the temperature of the calciner that imposes the main
571 energy penalty to the technology.

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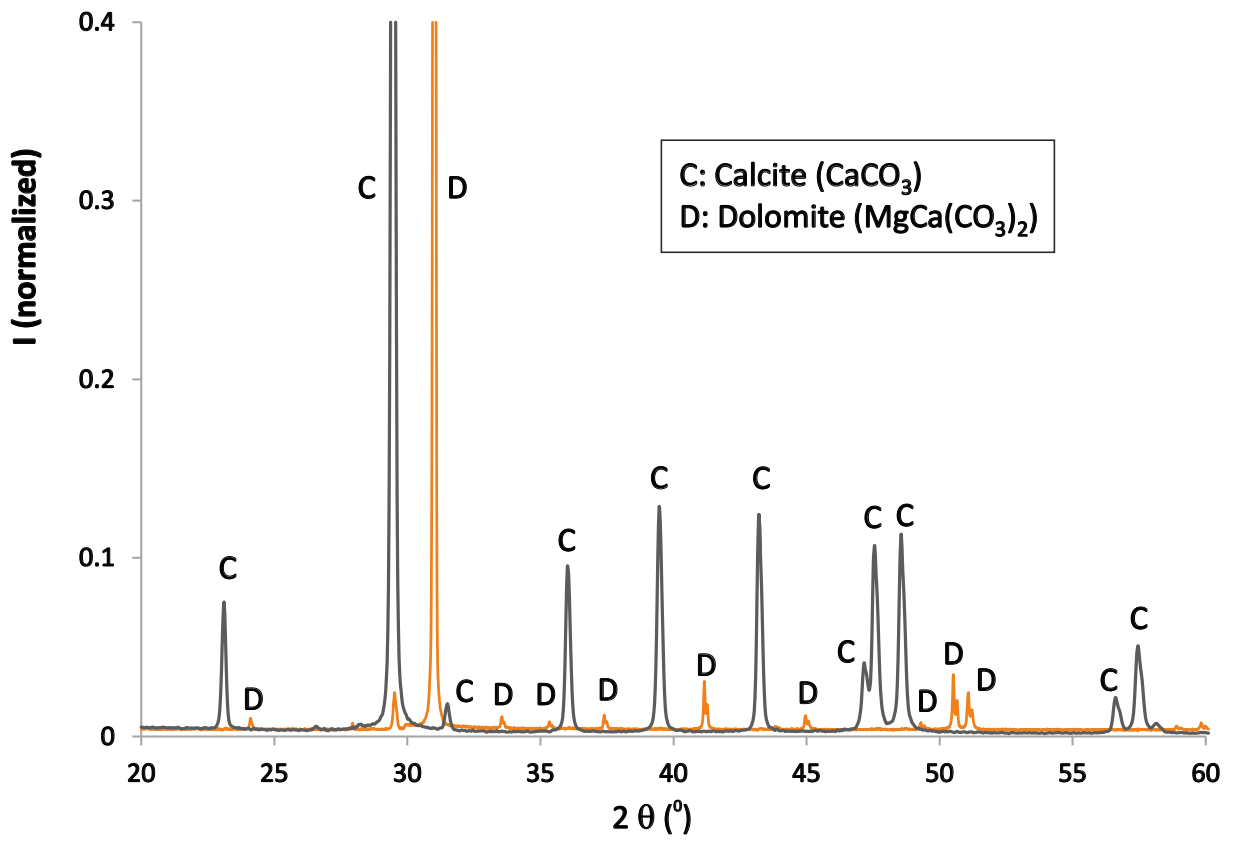


FIG. 1: X-Ray diffractograms measured for samples of dolomite and limestone used in our study (obtained using a Bruker D8 Advance powder diffractometer, Cu-K α). Values of Intensity are shown normalized to the maximum.

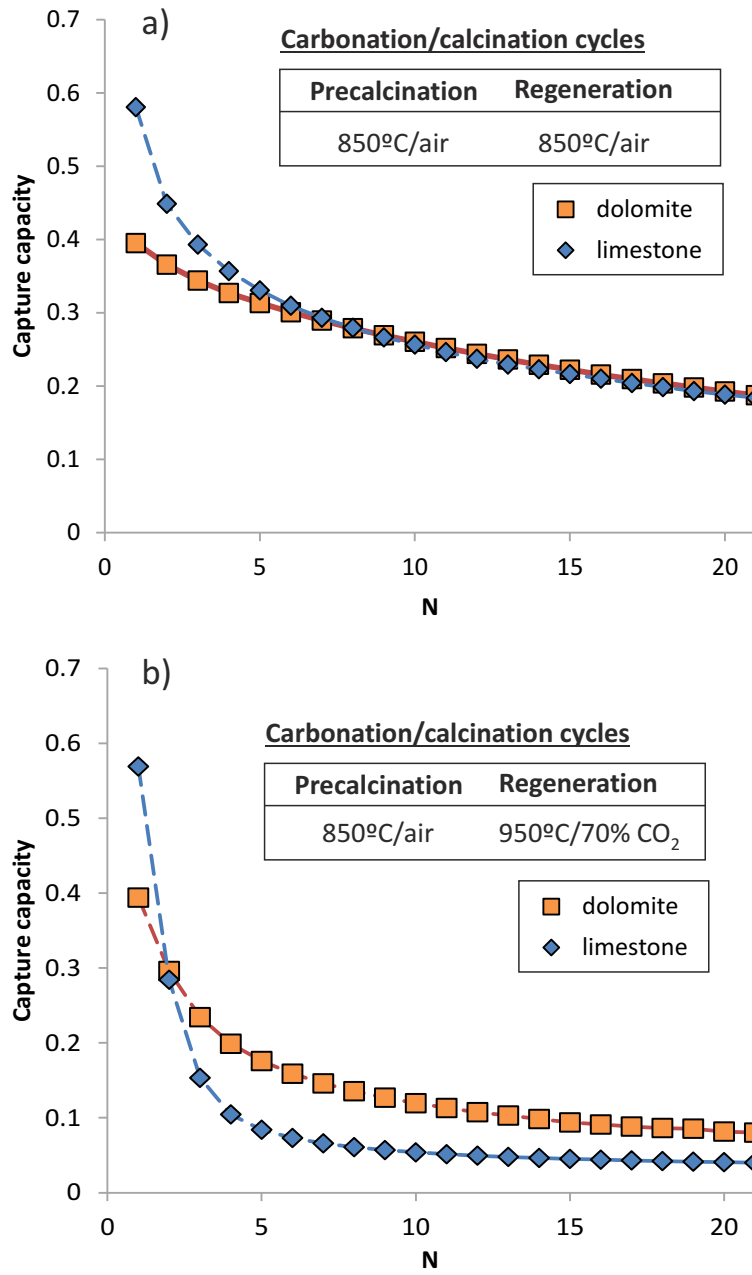


FIG. 2: CO₂ capture capacity as a function of carbonation/calcination cycle number for dolomite and limestone samples precalcined in air and regenerated by calcination either in air at 850°C (a) or under 70%CO₂ at 950°C (b).

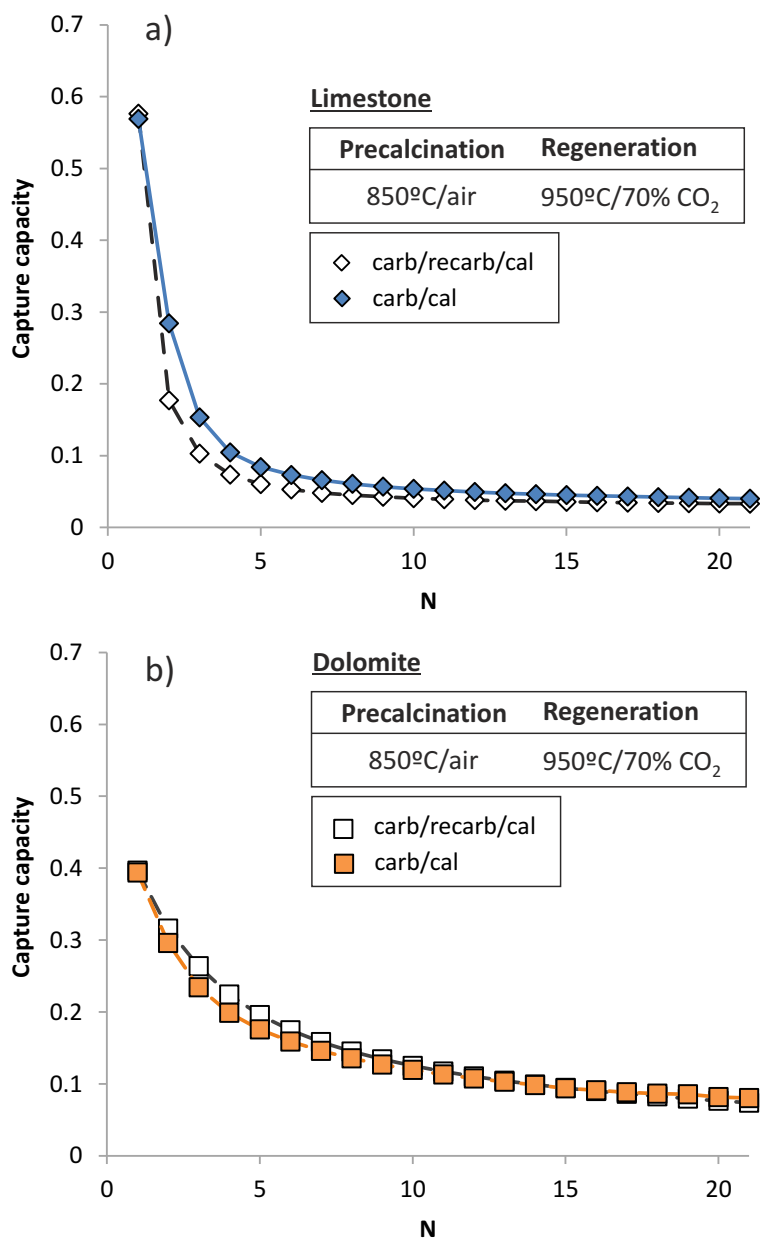


FIG. 3: CO₂ capture capacity as a function of cycle number for limestone (a) and dolomite (b) samples subjected to carbonation/calcination and carbonation/recarbonation/calcination cycles (as indicated), precalcined in air and regenerated by calcination under 70%CO₂ at 950°C.

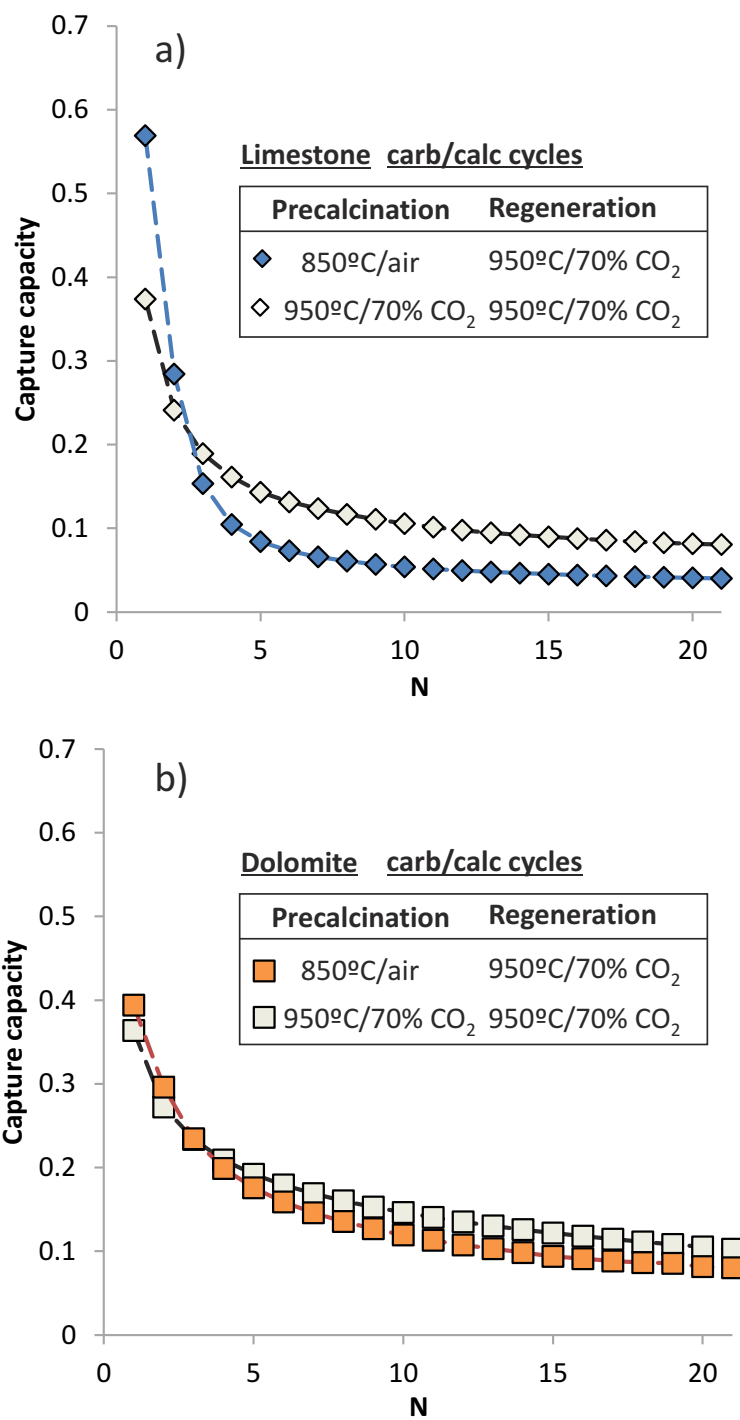


FIG. 4: CO₂ capture capacity as a function of cycle number for limestone (a) and dolomite (b) samples precalcined under different conditions (as indicated) and subjected to carbonation/calcination cycles (regenerated by calcination under 70%CO₂ at 950°C).

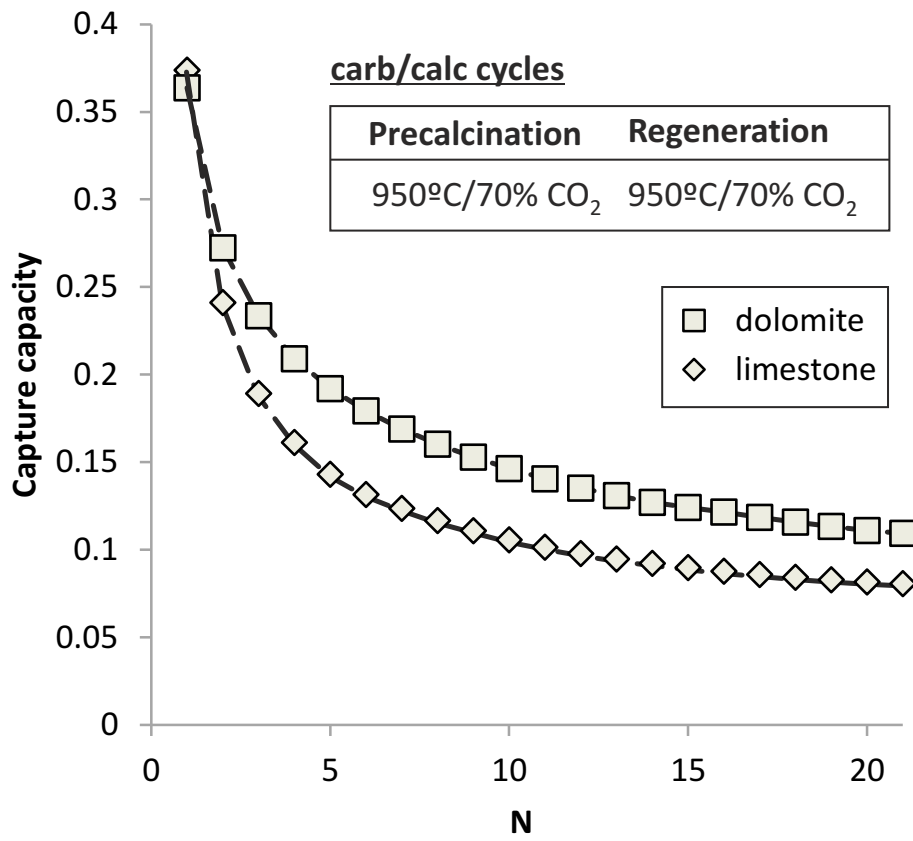


FIG. 5: CO₂ capture capacity as a function of cycle number for limestone and dolomite samples subjected to carbonation/calcination cycles, precalcined and regenerated by calcination under 70%CO₂ at 950°C.

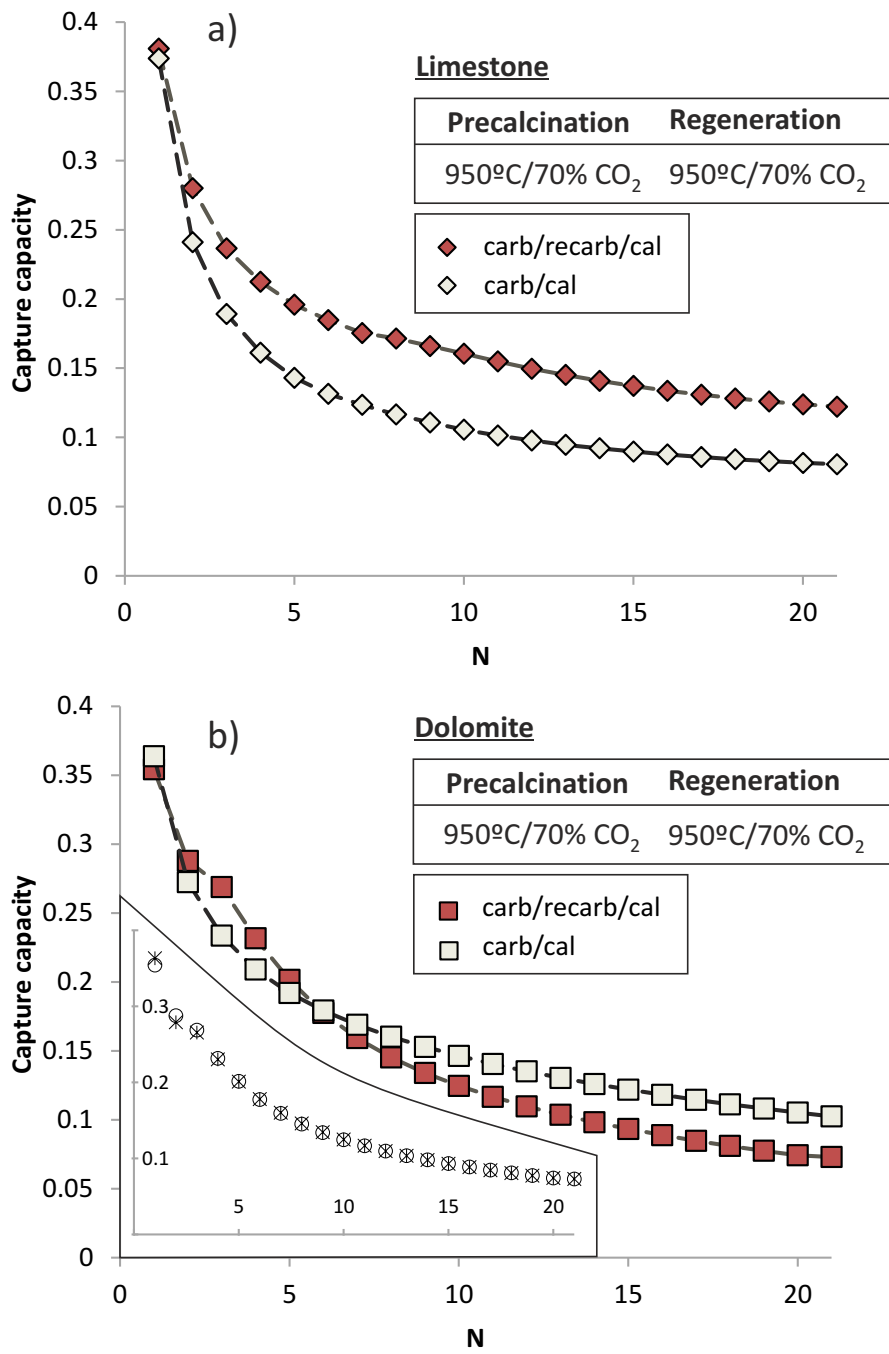


FIG. 6: CO₂ capture capacity as a function of cycle number for limestone (a) and dolomite (b) samples subjected to carbonation/calcination and carbonation/recarbonation/calcination cycles (as indicated) precalcined and regenerated by calcination under 70%CO₂ at 950°C. The inset in b) is a plot of data obtained from tests on different samples of dolomite and same conditions (carb/recarb/calc) to demonstrate results reproducibility.

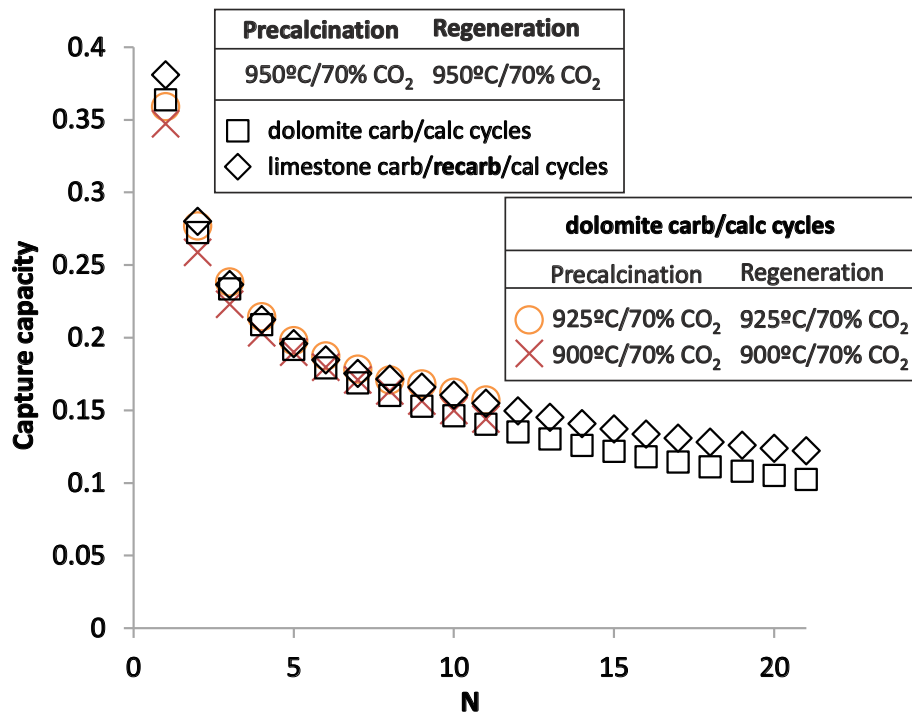
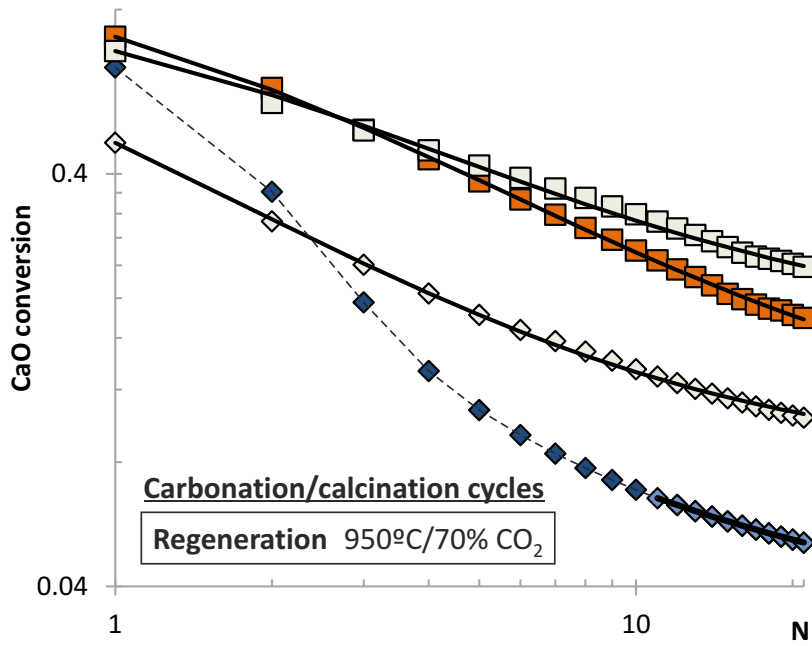


FIG. 7: CO₂ capture capacity as a function of cycle number for dolomite (carbonation/calcination cycles) and limestone samples (carbonation/recarbonation/calcination cycles) precalcined and regenerated by calcination under 70%CO₂ at 950°C.

Results for dolomite samples precalcined and regenerated under 70%CO₂ at 925°C and 900°C are also shown.



Precalcination 950°C/70% CO ₂			Precalcination 850°C/air		
	k	X_r		k	X_r
□ dolomite	0.478	0.166	■ dolomite	0.455	0.093
◇ limestone	0.853	0.079	◆ limestone	0.172*	0.034*

FIG. 8: CaO conversion as a function of cycle number (carbonation/calcination cycles) for dolomite and limestone samples regenerated by calcination under 70%CO₂ at 950°C and precalcined as indicated. The solid lines are drawn from the best fits of Eq. 1 to the data. The inset shows the best fitting parameters (deactivation rate k and residual conversion X_r). (*) In the case of limestone precalcined in air, Eq. 1 fits satisfactorily to the data only from the 10th cycle.

Carbonation/calcination cycles Precalcination 850°C/air Regeneration 950°C/70% CO₂

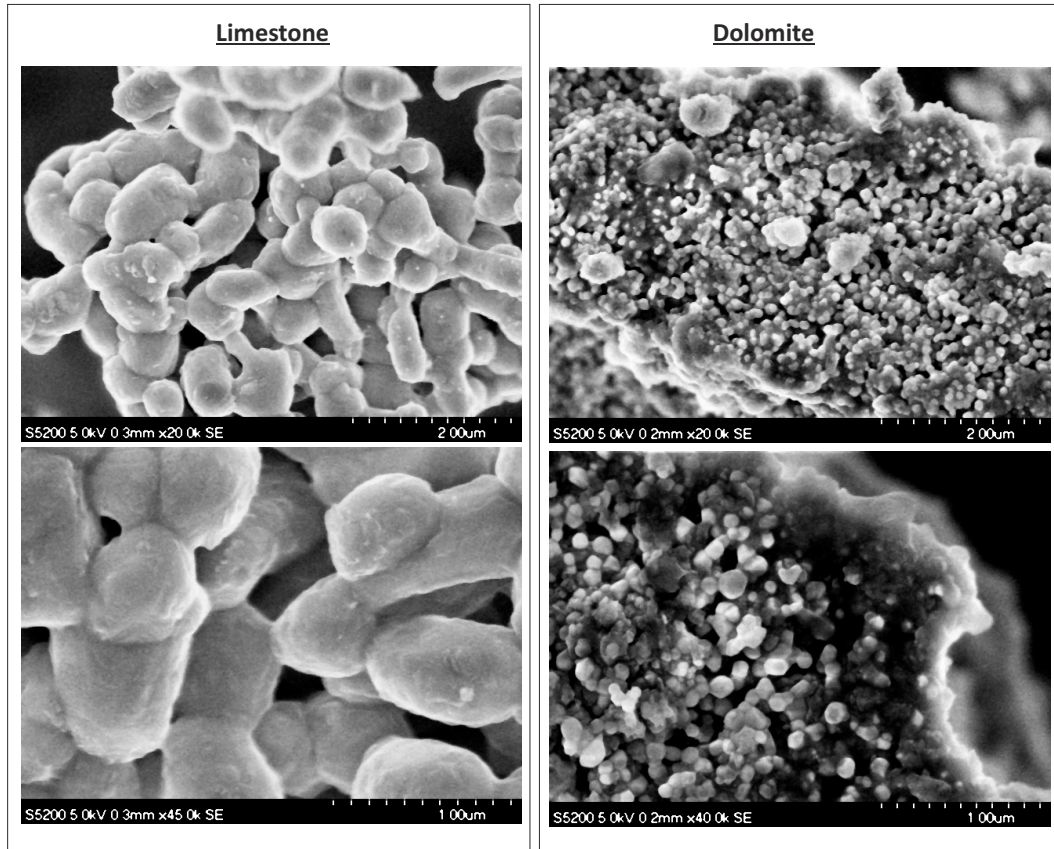


FIG. 9: SEM pictures of limestone and dolomite samples after being subjected to carbonation/calcination cycles (precalcined in air (850°C) and regenerated by calcination under 70%CO₂ at 950°C).

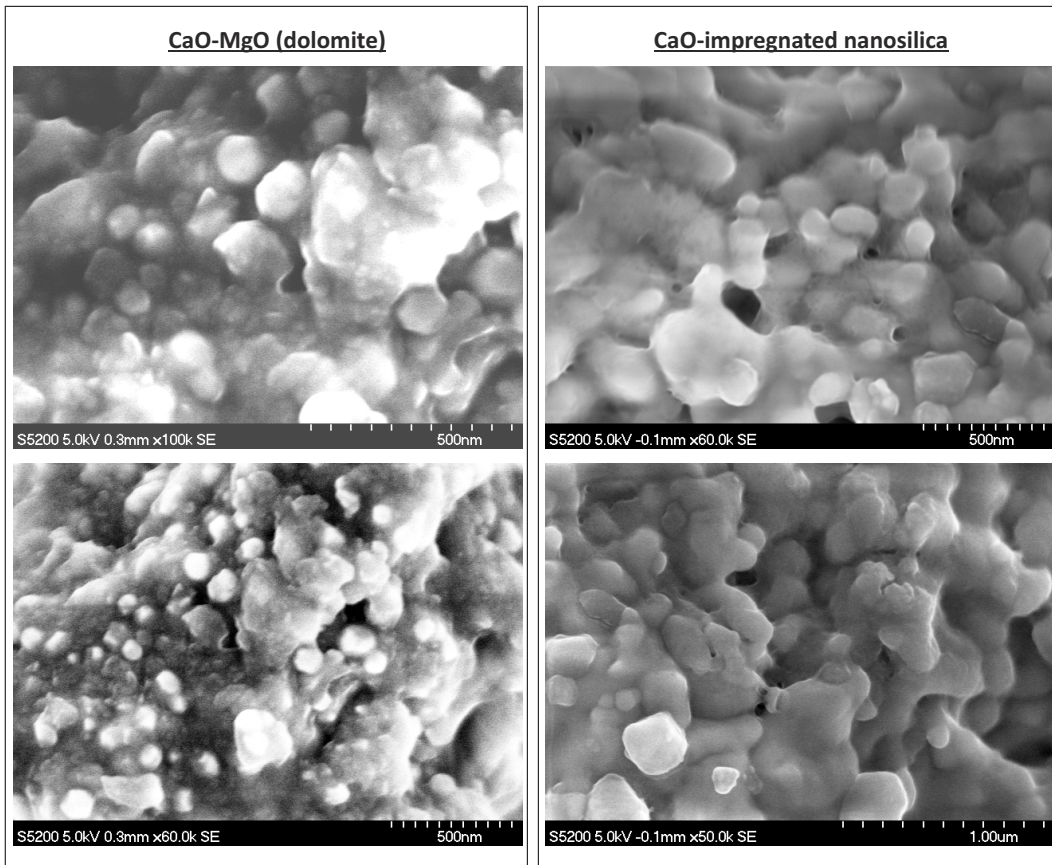


FIG. 10: SEM pictures of: a) dolomite sample after being subjected to carbonation/calcination cycles (regenerated by calcination under 70%CO₂ at 950°C and precalcined in air at 850°C); b) CaO-based sorbent synthesized by impregnation of calcium nitrate solution on a nanostructured calcium silicate matrix after calcination (reported in [46]).

Carb/recarb/calc cycles Precalcination and regeneration 950°C/70% CO₂

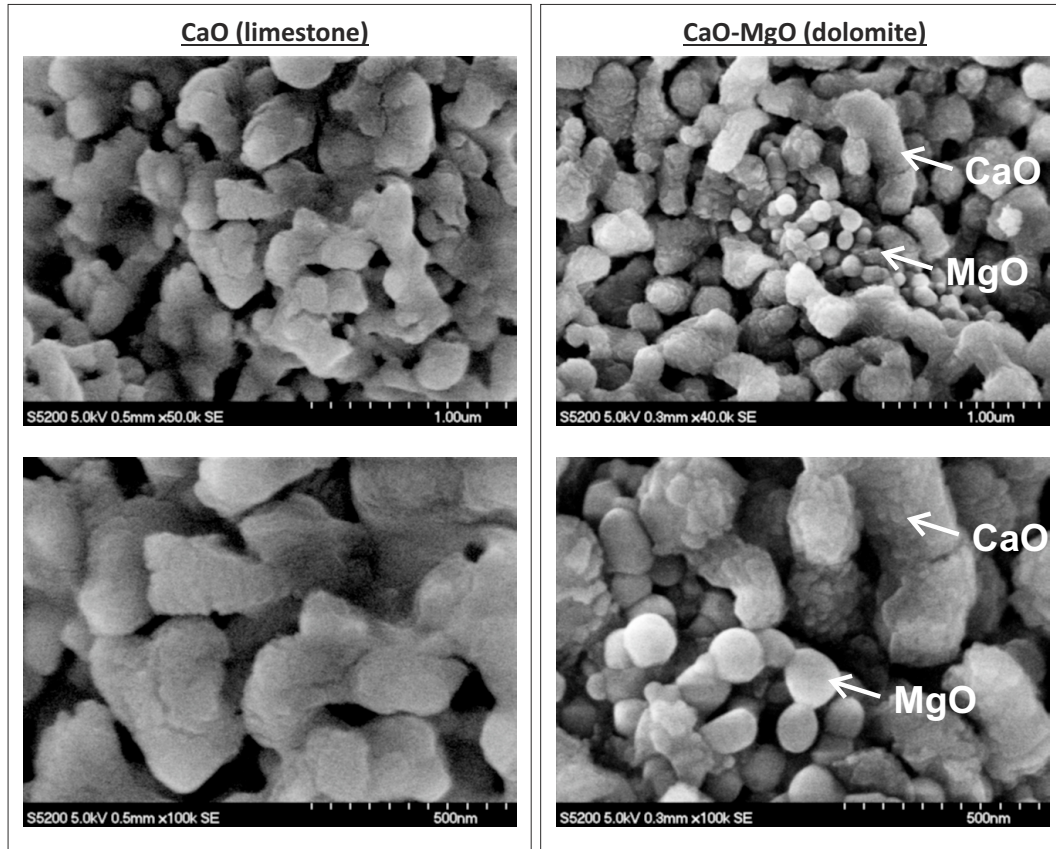


FIG. 11: SEM pictures of limestone and dolomite samples after being subjected to carbonation/recarbonation/calcination cycles (precalcined and regenerated by calcination under 70%CO₂ at 950°C).

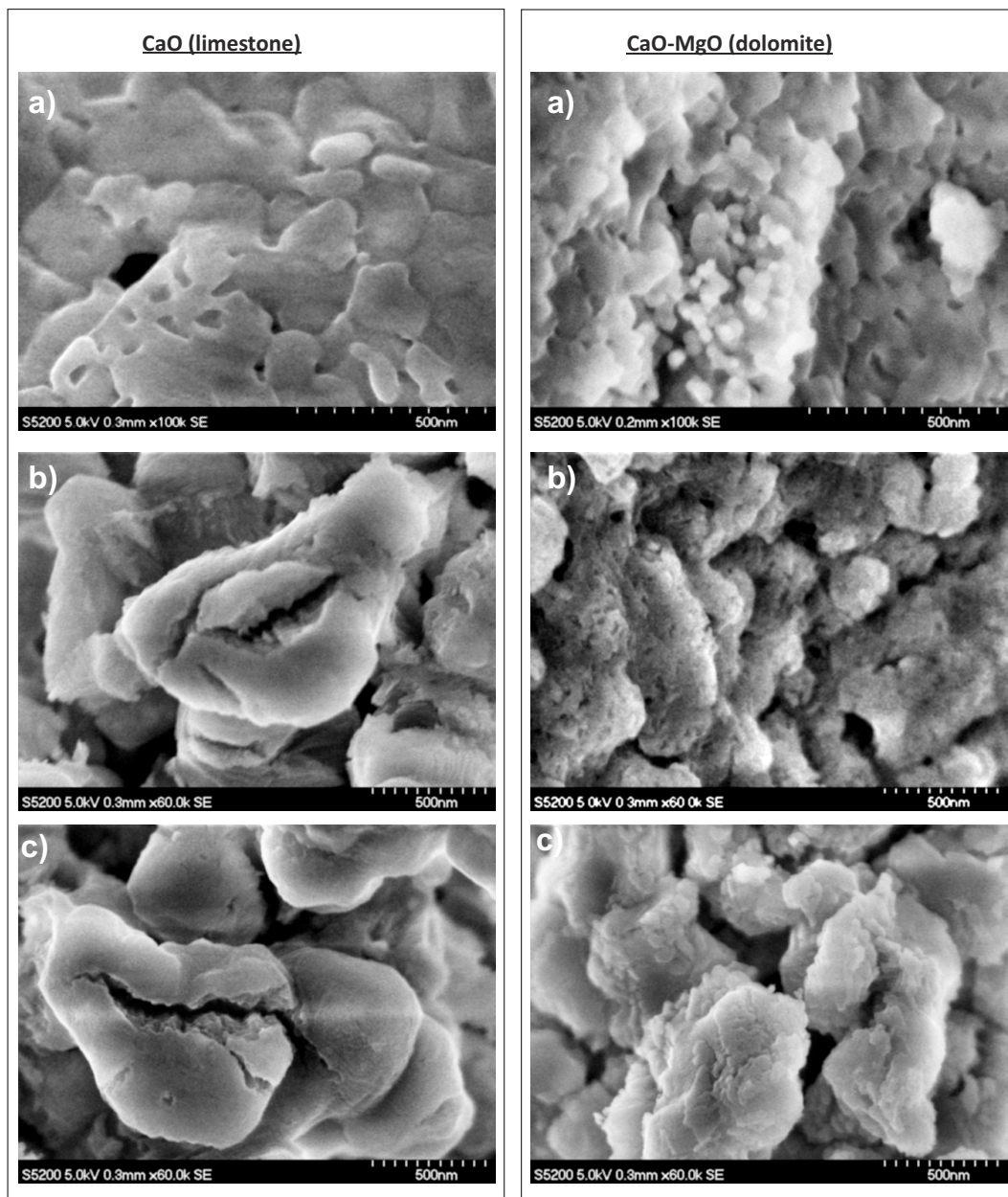


FIG. 12: SEM pictures of limestone and dolomite samples after being cycled under diverse conditions. a) Carbonation/calcination cycles (precalcined and regenerated by calcination in air at 850°C). b) Carbonation/recarbonation/calcination cycles (precalcined and regenerated by calcination under 70%CO₂ at 950°C). c) Carbonation/calcination cycles (precalcined and regenerated by calcination under 70%CO₂ at 950°C).

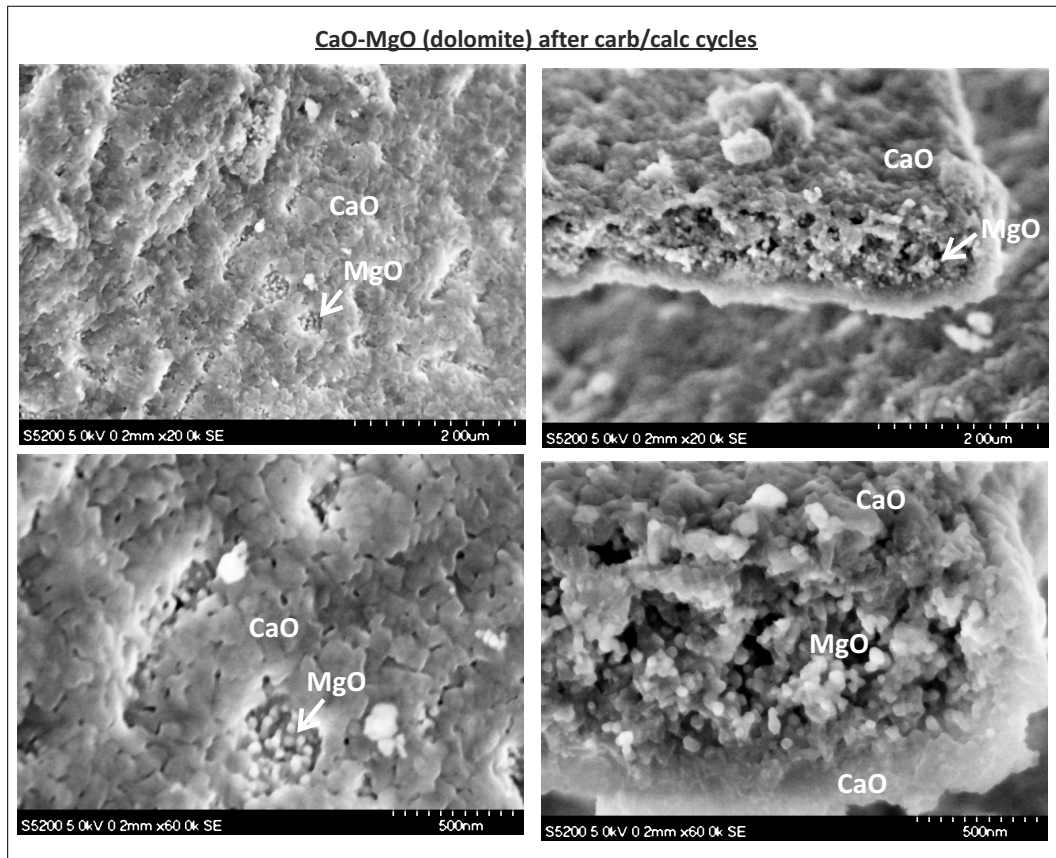


FIG. 13: SEM pictures of a dolomite sample after being subjected to carbonation/calcination cycles (precalcined and regenerated by calcination in air at 850°C).

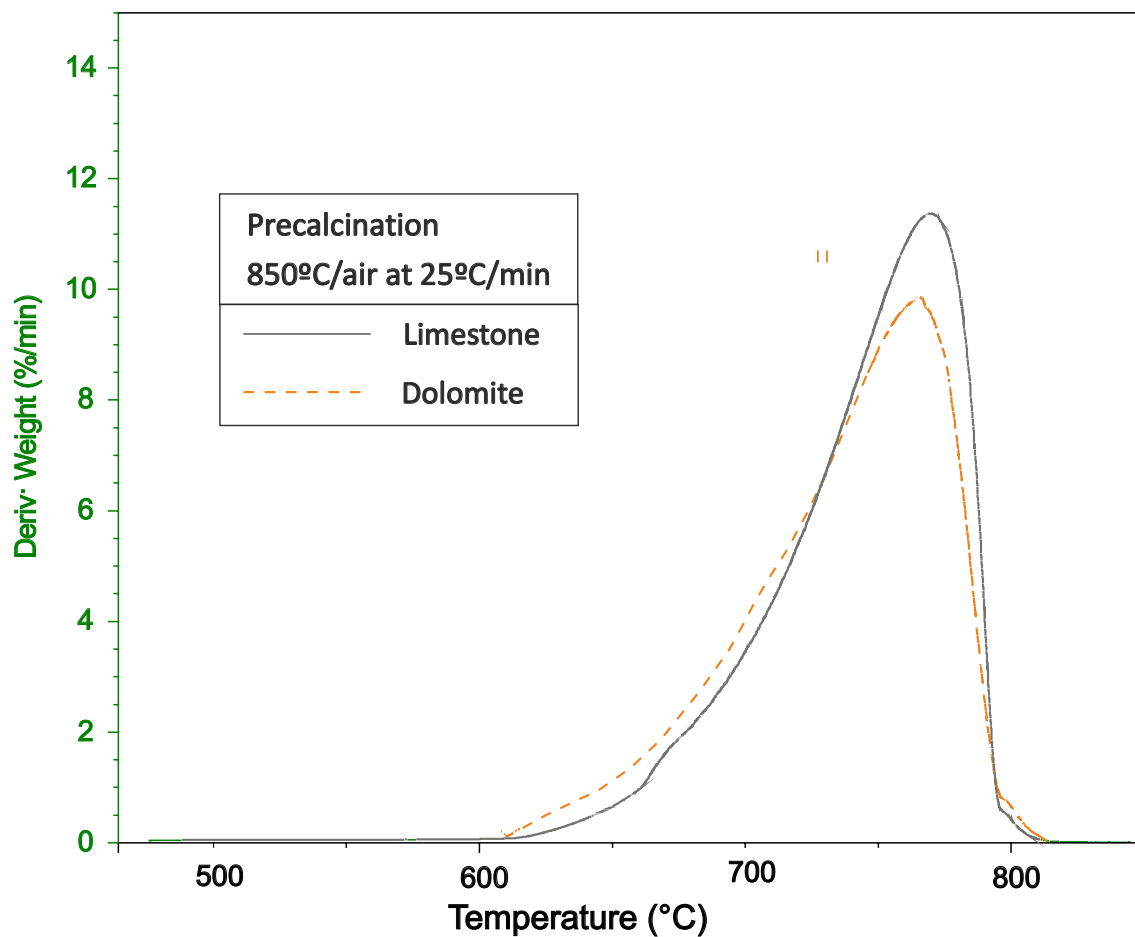


FIG. 14: Derivative of sample weight % (absolute value) as a function of temperature during decomposition of samples of dolomite and limestone precalcined in-situ in the TGA tests under air by slowly increasing the temperature up to 850°C).

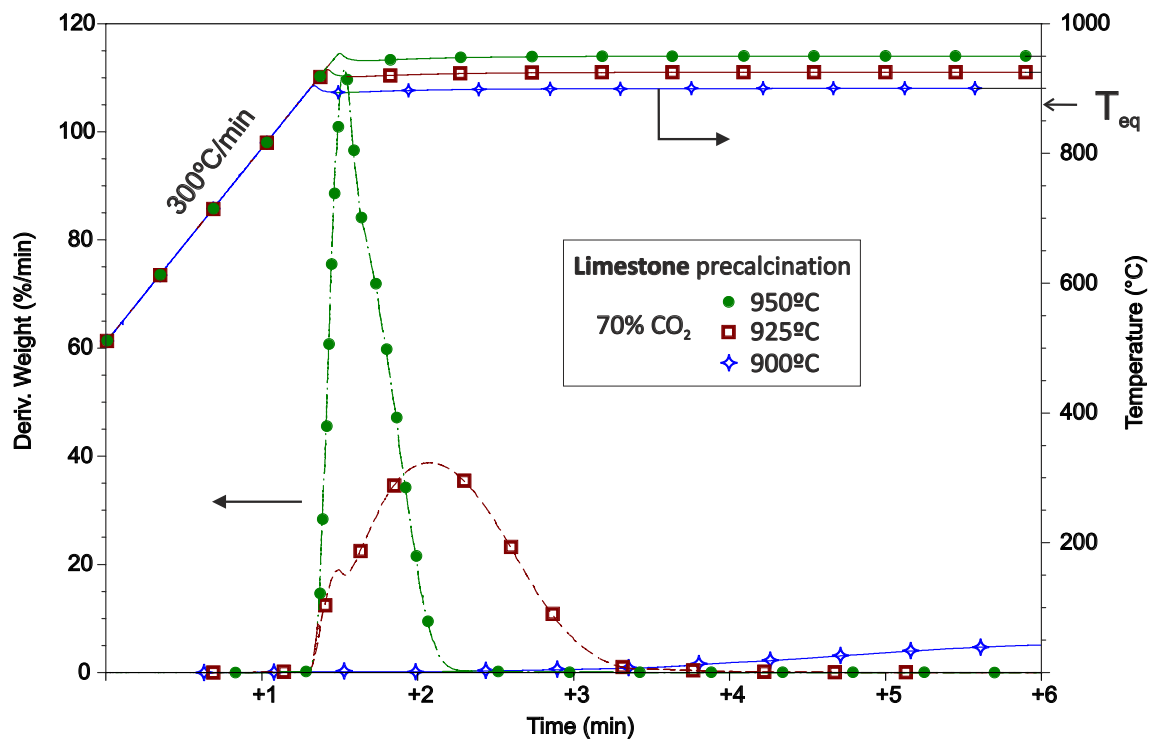


FIG. 15: Time evolution of sample weight % derivative (absolute value) and temperature during decomposition of samples of limestone precalcined in-situ in the TGA tests under 70%CO₂ by quickly increasing the temperature up to 900°C, 925°C, and 950°C (as indicated). The arrow in the temperature axis (right) indicates the thermodynamic equilibrium temperature ($T_{eq} \approx 870^\circ\text{C}$).

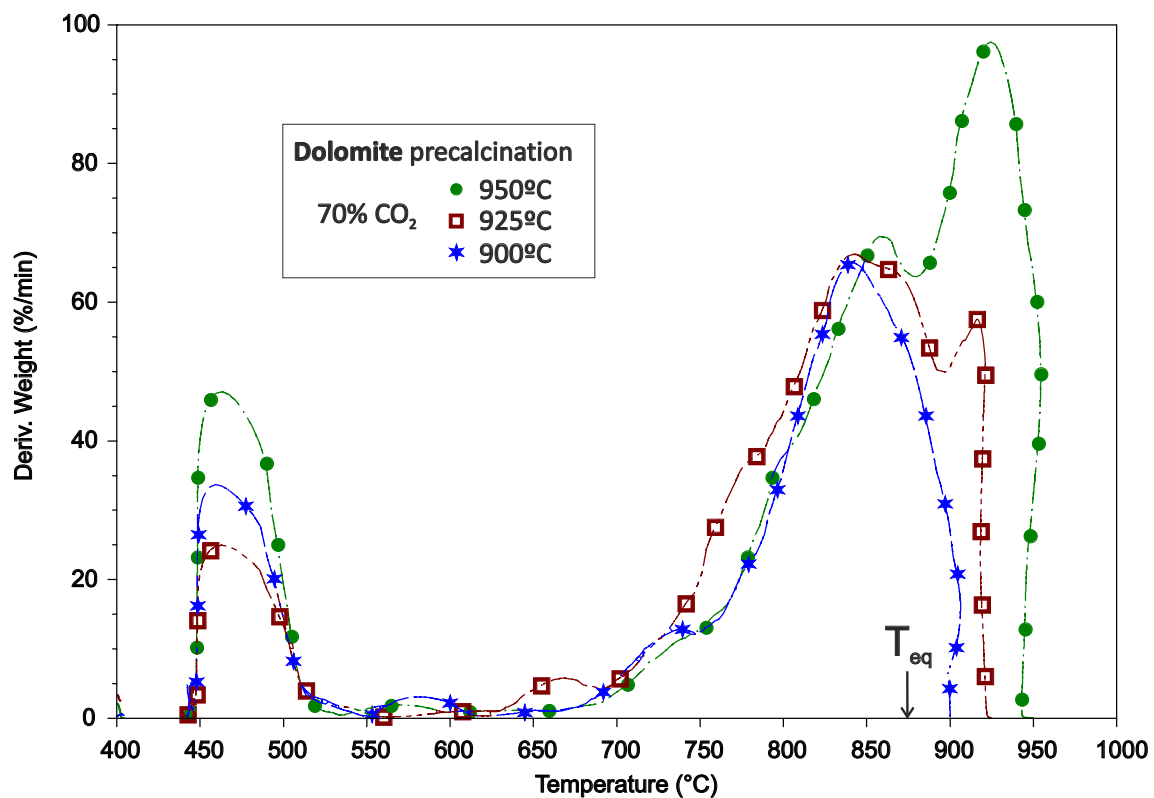


FIG. 16: Derivative of sample weight % (absolute value) as a function of temperature during decomposition of samples of dolomite precalcined under 70%CO₂ in-situ in the TGA tests by quickly increasing the temperature up to 900°C, 925°C, and 950°C (as indicated). The arrow in the temperature axis (horizontal) indicates the thermodynamic equilibrium temperature for pure calcite ($T_{eq} \approx 870^\circ\text{C}$)

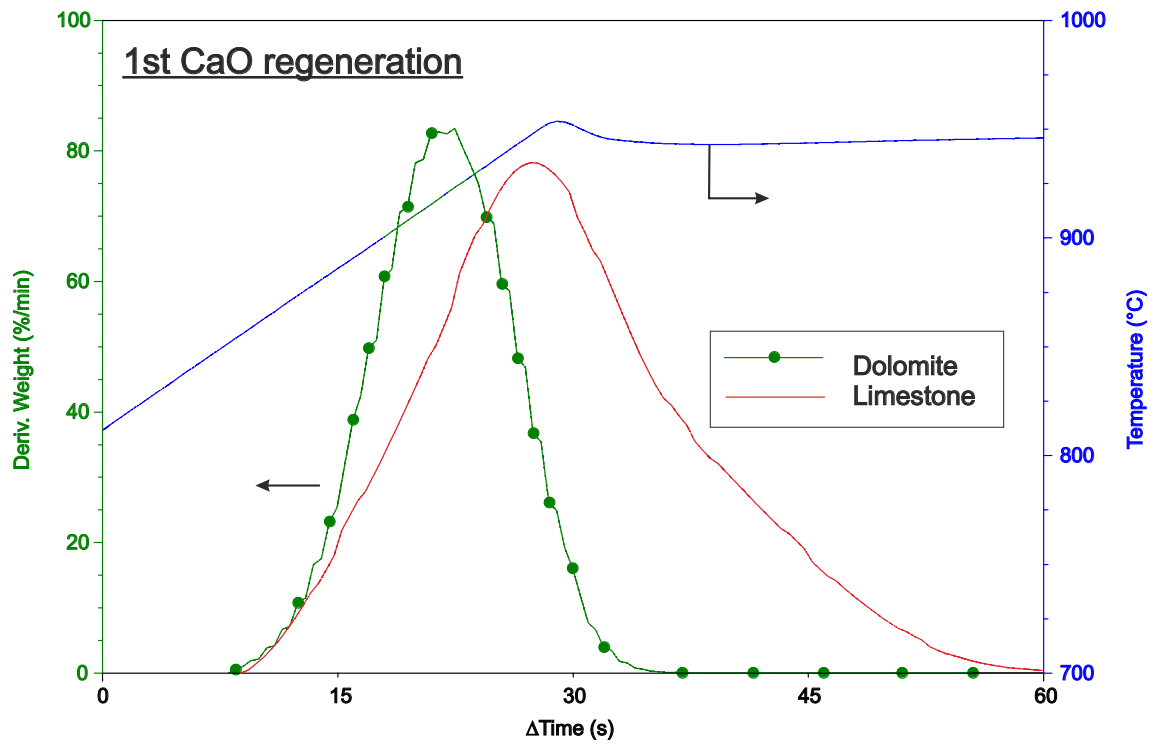


FIG. 17: Time evolution of sample weight % derivative (absolute value) and temperature for samples of limestone and dolomite during 1st regeneration (precalcined and regenerated at 950°C under 70%CO₂) as indicated).

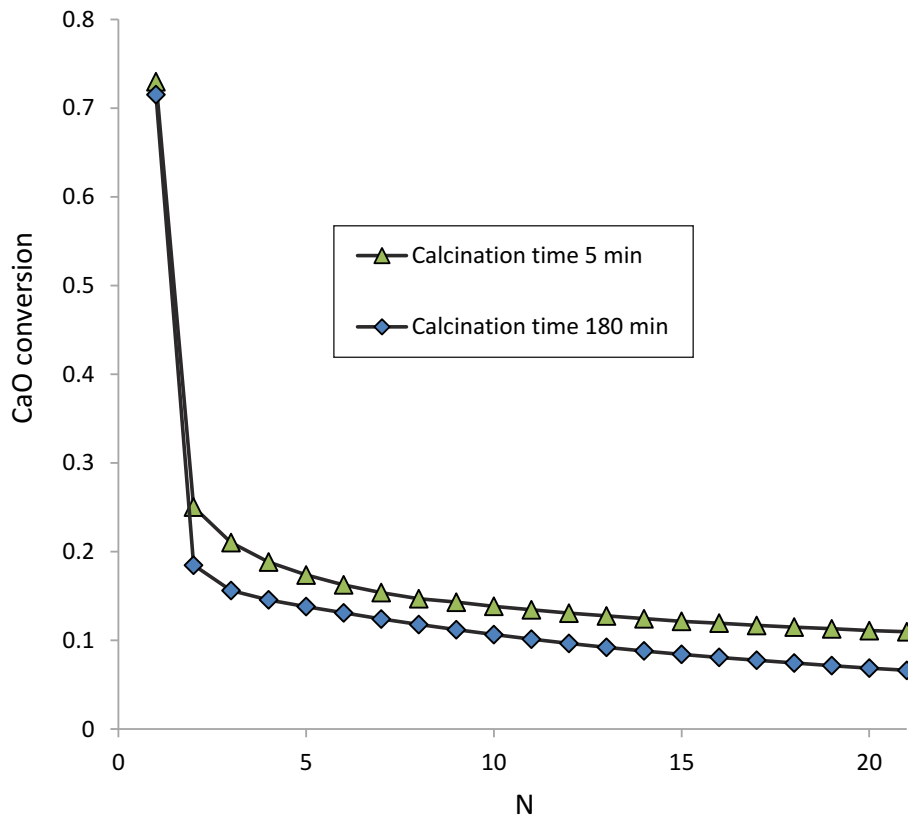


FIG. 18: CaO conversion as a function of cycle number (carbonation/calcination cycles) for limestone samples regenerated by calcination under 70%CO₂ at 925°C (samples precalcined in air at 850°C). Data are shown from tests with different durations of the calcination stages as indicated.