

1     **Limestone calcination at Calcium-Looping conditions for CO<sub>2</sub>**  
2     **capture and Thermochemical Energy Storage in the presence of**  
3             **H<sub>2</sub>O: In-situ XRD analysis.**

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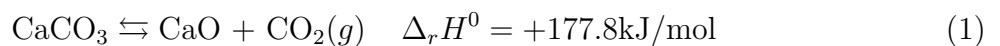
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**Abstract**

This work reports an in-situ XRD analysis on the calcination/carbonation behavior of natural limestone ( $\text{CaCO}_3$ ) as affected by the addition to the calciner of  $\text{H}_2\text{O}$  at a very small concentration under relevant Calcium-Looping (CaL) conditions for  $\text{CO}_2$  capture in coal fired power plants (CFPP) and Thermochemical Energy Storage (TCES) in Concentrated Solar Power plants (CSP). Previous studies have demonstrated that the presence of steam in the calciner at high concentration yields a significant increase of the reaction rate. However, a further undesired consequence is the serious deterioration of the CaO mechanical strength, which would lead to particle attrition and mass loss in any CaL process based on the use of circulating fluidized beds. Results presented in this manuscript on the time evolution of the wt% and crystallite size of the phases involved in the calcination/carbonation reactions indicate that the calcination rate is still notably increased by the presence of  $\text{H}_2\text{O}$  at very small concentrations whereas the reactivity toward carbonation and crystal structure of the formed CaO are not essentially affected, which suggests that neither the CaO mechanical strength is impaired. Thus, the benefit of using steam for calcination in the CaL process could be still retained while at the same time particle attrition would not be promoted.

**I. INTRODUCTION**

The calcination/carbonation reaction of limestone ( $\text{CaCO}_3$ )



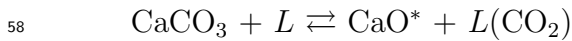
26 lies at the heart of a vast number of industrial applications and natural processes. This  
27 reaction plays an important role in the production of building materials, iron and steel,  
28 fertilizers, food processing, disinfection, water treatment, desulphurization, plastics, glass,  
29 sugar refining, pharmaceuticals, etc. As a result, it has been one of the most widely inves-  
30 tigated gas-solid heterogeneous reactions despite of which the physicochemical mechanisms  
31 behind it are not fully understood yet [1–8].

32 Generally, some relevant properties of the CaO derived from calcination are its porosity,  
33 reactivity, crystal structure and mechanical strength, which are critically determined by the  
34 environmental conditions under which the reaction evolves. Thus, archaeological studies  
35 show that the calcination of limestone or dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) in ancient Roman ovens  
36 was carried out under high  $\text{CO}_2$  concentration to produce deterioration resistant and high  
37 mechanical strength mortar [9]. Recently, limestone and dolomite calcination under su-  
38 perheated steam at reduced temperatures has become a commercial technology to produce  
39 enhanced CaO and MgO based fertilizers and cement products with a higher reactivity, low  
40 crystallinity and high friability [10]. Heat conductivity of the gases present in the calciner  
41 environment and  $\text{CO}_2$  diffusivity has long been identified as critical physical properties that  
42 greatly influence the kinetics of calcination [11, 12]. Thus, the calcination rate of limestone  
43 is significantly increased at reduced temperatures under Helium (with a rather high thermal  
44 conductivity and  $\text{CO}_2$  diffusivity as compared to air) without any significant effect on the  
45 structure and reactivity of the produced CaO [13]. Similarly, calcination is significantly  
46 promoted under superheated steam at high concentrations, which was originally attributed  
47 to the enhancement of thermal conductivity in the calciner atmosphere [12] although more  
48 recent works suggest that  $\text{H}_2\text{O}$  plays a critical catalytic role on  $\text{CaCO}_3$  decomposition [14].  
49 As a consequence of such chemical action, crystallinity, mechanical strength and reactivity

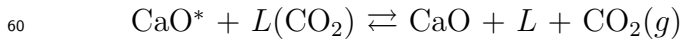
50 of the resulting CaO are fundamentally affected [10, 11, 15]. The enhancement of CaO sin-  
51 tering and crystallite size growth as due to the presence of H<sub>2</sub>O in the calciner environment  
52 at high concentration is a well known effect widely reported in the literature [16–20].

53 Recent studies [6, 21] have shown that limestone calcination is initiated by a topotactical  
54 chemical decomposition of CaCO<sub>3</sub> into a metastable CaO\* phase, which subsequently trans-  
55 forms into the stable CaO form lime. Accordingly, the reaction mechanism would consist of  
56 a two steps process:

### 57 1. Chemical decomposition



### 59 2. Desorption/structural transformation



61 Here  $L$  represents an active site in the solid where calcination occurs,  $L(\text{CO}_2)$  denotes a  
62 molecule of CO<sub>2</sub> that remains physically adsorbed after chemical decomposition. The CaO\*  
63 metastable phase appears as a pseudomorph from calcite (CaCO<sub>3</sub>) before the stable form  
64 lime (CaO) nucleates [6]. Figure 1 shows the crystallographic unit cells of the three phases  
65 (CaCO<sub>3</sub> calcite, CaO\*, and CaO lime) that would be expectedly involved in the calcination  
66 reaction [6, 21]. The hexagonal rhombohedral calcite structure (space group R $\bar{3}c$ , 167) yields  
67 after chemical decomposition a cubic metastable CaO\* structure (space group Fm $\bar{3}m$ , 225)  
68 as a dilated pseudomorph of lime (same space group that CaO\* ) which appears afterwards.

69 On the other hand, thermochemical data shows that the relationship between the CO<sub>2</sub>  
70 partial pressure  $P$  in the calcination atmosphere and temperature  $T$  for the reaction to be  
71 at equilibrium is given by [16, 22, 23]

$$P \approx A \exp(-20474/T) \quad (2)$$

72 where  $A = 4.134 \times 10^{12}$  Pa. In regards to kinetics, experimental measurements at high  
 73  $\text{CO}_2$  partial pressures near the equilibrium partial pressure show a significant slow down  
 74 of the reaction [8, 24]. Under these conditions, calcination is severely hindered by  $\text{CO}_2$   
 75 desorption and the exothermicity of the  $\text{CaO}^* \rightarrow \text{CaO}$  transformation step, which makes it  
 76 necessary to increase the calciner temperature well above the equilibrium temperature (or,  
 77 equivalently, increase  $P_{eq}$ ) for the reaction to occur sufficiently fast in applications wherein  
 78 the calciner is operated under high  $\text{CO}_2$  partial pressure [24]. If the concentration of  $\text{CO}_2$  in  
 79 the calcination environment is not high, the  $\text{CO}_2$  desorption and structural transformation  
 80 step occurs extremely fast and does not limit the reaction kinetics [6, 21].

### 81 **A. The Calcium Looping process**

82 In the past few years the Calcium-Looping (CaL) process, based on the cyclic calcina-  
 83 tion/carbonation of limestone, has come onto scene with a high potential to mitigate  $\text{CO}_2$   
 84 emissions. The integration of the CaL process into coal fired power plants has been already  
 85 successfully demonstrated at the pilot scale (1-2  $\text{MW}_{th}$ ) level [25–27]. In this process (Fig.  
 86 2a), early proposed by Shimizu et al. [28], the  $\text{CO}_2$  loaded flue gas ( $\sim 15\%$   $\text{CO}_2$  vol con-  
 87 centration) is used to fluidize a bed of CaO particles at temperatures around  $650^\circ\text{C}$ , which  
 88 leads to fast carbonation of the CaO solids. The carbonated particles are then circulated  
 89 into a second reactor wherein CaO is regenerated by calcination at temperatures typically  
 90 close to  $\sim 950^\circ\text{C}$ .  $\text{CO}_2$  concentration in the calciner must be necessarily high in order to ex-  
 91 tract it as pure as possible for compression and the subsequent storage. For this reason, the

92 calciner temperature has to risen well over the equilibrium temperature, which is  $T \simeq 896^\circ\text{C}$   
93 under pure  $\text{CO}_2$  at atmospheric pressure. To this end, a practical solution is to burn fuel in  
94 the calciner using pure  $\text{O}_2$  (oxy-combustion), albeit this method poses a significant energy  
95 penalty to the process [29]. Moreover, additional  $\text{CO}_2$  is released by oxy-combustion and  
96 the reactivity of the regenerated  $\text{CaO}$  is drastically impaired due to enhanced sintering un-  
97 der high temperatures/high  $\text{CO}_2$  concentration [17], deactivation by ashes and irreversible  
98 sulphation [25].

99 A further emerging application of the CaL process is Thermochemical Energy Storage  
100 (TCES) in Concentrated Solar Power (CSP) plants, which was proposed in the late 1970s  
101 [30] but still remains at the concept stage [31, 32]. Remarkably, the calcination/carbonation  
102 conditions under which the solids would be cycled in the CaL-CSP integration to maximize  
103 the global efficiency differ radically from those used in the CaL process for  $\text{CO}_2$  capture.  
104 Thus, according to a recently proposed integration scheme [32], carbonation in the CaL-CSP  
105 integration would be carried out at high temperatures ( $>\sim 850^\circ\text{C}$ ) under high  $\text{CO}_2$  partial  
106 pressure whereas the solids would be preferably calcined in the solar receiver at the lowest  
107 possible temperature in order to reduce technological risks and cost by using commercial  
108 metallic receivers (Fig. 2b). Electricity would be produced on demand in a gas turbine by  
109 the  $\text{CO}_2$  in excess over the stoichiometric ratio not used for carbonation and carrying the  
110 heat of this exothermic reaction. Solar energy would provide the heat for the endothermic  
111 calcination reaction, which could be performed at a fast enough rate at temperatures around  
112  $725^\circ\text{C}$  by using He or superheated steam in the calciner [33].

113 The use of steam in diverse ways has been widely studied in the last years to improve  
114 the CaL performance for  $\text{CO}_2$  capture [15, 25, 34–38]. Thus, it has been observed that  
115 the intermediate hydration of  $\text{CaO}$  at relatively low temperatures ( $\sim 200 - 400^\circ\text{C}$ ), with

116 the formation of  $\text{Ca}(\text{OH})_2$ , leads to a significant reactivation of the sorbent [25, 34, 35,  
117 38]. Nevertheless, the mechanical strength of the hydrated sorbent is severely impaired,  
118 which causes the generation of very fine particle fragments by attrition that cannot be  
119 recovered and are therefore lost, thus negating the benefit of reactivation. The multicycle  
120  $\text{CaO}$  activity can be also enhanced by the presence of steam (at vol % typically in the range  
121 5 - 40%) in the carbonator and/or the calciner [15, 36, 37]. Experimental observations  
122 show that steam in the calciner leads to the formation of large yet relatively stable pores  
123 thus mitigating  $\text{CaO}$  deactivation with the number of cycles [15, 37]. On the other hand,  
124 some studies have shown a relevant increase of the calcination rate in the presence of  $\text{H}_2\text{O}$   
125 at high concentration [11, 12, 14, 39]. It has been suggested that  $\text{CO}_2$  desorption would  
126 be enhanced by the more favorable adsorption of  $\text{H}_2\text{O}$ , which would catalyze in this way  
127 the calcination reaction [14].  $\text{H}_2\text{O}$  dynamic adsorption/desorption was already proposed  
128 as the driving mechanism for calcination under  $\text{H}_2\text{O}$  in the early works of Anderson et  
129 al. [18, 40]. Atomistic simulations analysis of  $\text{CO}_2/\text{H}_2\text{O}$  co-adsorption in  $\text{CaO}$  crystal  
130 surfaces show a preference of  $\text{H}_2\text{O}$  adsorption over  $\text{CO}_2$  adsorption [41–43], which agrees  
131 with previously reported UPS and XPS measurements [44]. The efficiency of the CaL  
132 process in both  $\text{CO}_2$  capture and TCES applications would benefit notably from a reduction  
133 of the calcination temperature. Nevertheless, a detrimental side effect of calcination under  
134 steam is a reduction of the mechanical strength of the resulting  $\text{CaO}$  solids. MacIntire and  
135 Stansel [11] early observed that limes derived from calcination in steam were exceedingly  
136 pulverous as demonstrated by their decidedly greater tendencies to remain in suspension.  
137 Promoted fracturing of the particles resulting from calcination under steam is also reported  
138 in the recently developed Catalytic Flash Calcination (CFC) Technology [10].

139 The energy efficiency of the CaL process would benefit notably from a reduction of the

140 calcination temperature [29] as might be achieved by the use of steam albeit the enhancement  
141 of particle fracturing would be a drawback. In the work reported in the present manuscript,  
142 we tested the presence of steam at very small concentration in the calciner on the rate  
143 of limestone calcination and CaO reactivity by means of in-situ XRD analysis. This study  
144 served us also to investigate the crystal structure of the formed CaO, which is closely related  
145 to its mechanical strength. As will be seen, the use of steam at very small concentrations  
146 in the calciner still leads to a significant reduction of the minimum temperature to achieve  
147 full calcination in short residence times without causing any relevant change on neither the  
148 structure nor the reactivity of the resulting CaO.

## 149 II. EXPERIMENTAL MATERIAL AND METHODS

150 In this work we have used a powdered natural limestone of high purity (99.6% CaCO<sub>3</sub>)  
151 from Matagallar quarry (Pedrera, Spain). Volume weighted mean particle size is 9.5  $\mu\text{m}$   
152 as measured by laser diffractometry (Malvern Mastersizer 2000 instrument). Thus, the  
153 influence of intra-particle diffusion resistance on the reaction rate, which would be relevant  
154 only for particle sizes above  $\sim 300 \mu\text{m}$  [23, 45], can be neglected.

155 In situ XRD tests have been carried out by means of the experimental setup depicted in  
156 Fig. 3. The powder sample of mass around 150 mg is placed over a 0.01 m diameter porous  
157 ceramic plate inside the reaction chamber, which is operated at atmospheric pressure. A  
158 controlled gas flow is passed at the same rate in all the runs (1000 scc/min) downwards and  
159 across the powder, which facilitates a homogeneous distribution of the gas in the powder  
160 thus promoting gas-solid contacting efficiency and mass/heat transfer. Pure N<sub>2</sub>, He and CO<sub>2</sub>  
161 are employed under dry and wet conditions to test the sample calcination behavior. H<sub>2</sub>O  
162 was added to the dry gas by bubbling the gas flow in distilled water at ambient temperature



163 using a SYCOS H (Ansyco, Germany) accurate humidity controller, which yields a H<sub>2</sub>O  
164 vol. concentration in the wet gas of 0.03%. For calcination tests under N<sub>2</sub> and He, the  
165 temperature was increased at a rate of 10°C /min from ambient to 725°C as representative  
166 of conditions to be expected in the CaL process for CSP energy storage. XRD scans during  
167 the temperature ramps were registered each 25°C at constant temperature in the range  
168  $20^\circ < 2\theta < 60^\circ$  (0.03°/step, step time of 0.2 s and tube conditions of 40 kV and 40 mA). On  
169 the other hand, for calcination tests under CO<sub>2</sub>, the temperature was increased up to reach  
170 a target calcination temperature above 900°C as corresponding to CaL conditions for CO<sub>2</sub>  
171 capture. This high temperature was kept constant for a given time period while XRD scans  
172 were continuously recorded as calcination evolved. Additionally, the carbonation behavior  
173 of the samples was tested in-situ readily after calcination. To this end, the temperature was  
174 set to 850°C and CO<sub>2</sub> was introduced in the reaction chamber after which XRD scans were  
175 continuously registered as carbonation evolved.

176 In situ XRD analysis has been carried out by means of a Bruker D8 Advance powder  
177 diffractometer provided with a fast response/high sensitivity detector (Bruker Vantec 1), ra-  
178 dial Soller slits and 60 mm Gobel mirrors (Bruker, Germany). Cu K<sub>α</sub> radiation (0.15405 nm  
179 wavelength) has been employed with parallel Johansson geometry in the incident beam. The  
180 instrument is equipped with an Anton Paar XRK 900 high temperature chamber specially  
181 designed for high temperature gas-solid reactions. Dead volumes are avoided to achieve a  
182 homogeneous filling with the reaction gas and temperature gradients across the sample are  
183 minimized. The temperature of the sample is accurately measured by means of a pair of  
184 NiCr/NiAl thermocouples placed close to the sample holder. Corundum, LaB<sub>6</sub> and silicon  
185 standards were employed in a wide range of diffraction angles to correct instrumental contri-  
186 butions for structural adjustments and resolution. The recorded XRD scans were analyzed

187 by using the software TOPAS 5 (Bruker) [46], which allowed us to accurately obtain the wt%  
188 and coherent crystal length (crystallite size) of the different phases involved in the reaction  
189 by means of Rietveld refinement [47] and Le Bail methods [48], respectively. Rietveld and  
190 Le Bail refinements were performed using the fundamental parameters method. Zero error  
191 ( $2\theta$ ), sample displacement, and absorption and lattice parameters of the phases were allowed  
192 to vary in order to search for the best fittings. The background was fitted by a fourth-order  
193 Chebychev polynomial. Lorentz and polarization geometric factors for the measurement  
194 configuration were used. The crystallite sizes were calculated using the best combinations  
195 of Gaussian and Lorentzian functions. The robustness of the data derived was checked from  
196 the values of several fitting indicators such as the goodness-of-fit and residual factors (Rwp  
197 and RBragg) [47].

### 198 III. RESULTS AND DISCUSSION

199 Figure 4a shows the time evolution of  $\text{CaCO}_3$  wt% during the calcination tests carried  
200 out under dry  $\text{N}_2$  and He atmospheres. As reported in previous works [12, 13, 33], it is seen  
201 that the calcination rate is significantly enhanced under dry He as compared to  $\text{N}_2$ , which  
202 can be explained by the notably higher thermal conductivity and  $\text{CO}_2$  diffusivity in He.  
203 The thermal conductivity of He at temperatures around  $700^\circ\text{C}$  is  $\lambda \simeq 350 \text{ mW}/(\text{m K})$  [49]  
204 whereas it is  $\lambda \simeq 60 \text{ mW}/(\text{m K})$  [49] for  $\text{N}_2$ . On the other hand, because of the very low He  
205 molecular weight,  $\text{CO}_2$  diffusivity in He is rather high ( $D \simeq 0.7 \times 10^{-2} \text{ m}^2/\text{s}$  at atmospheric  
206 pressure and room temperature) as compared to  $\text{CO}_2$  diffusivity in  $\text{N}_2$  ( $D \simeq 0.16 \times 10^{-2}$   
207  $\text{m}^2/\text{s}$ ). These values would increase with the 1.5 to 1.8 power of temperature [50]. Thus, the  
208 remarkable enhancement of heat and mass transfer when calcination is carried out under  
209 He would allow it to occur at a faster rate. In our tests we observe that calcination is

210 completely attained at 700°C under He whereas the temperature must be further increased  
211 about 25°C to achieve full calcination under N<sub>2</sub>. On the other hand, as seen in Fig. 4a, the  
212 rate of carbonation of the CaO resulting from calcination is not influenced by the type of  
213 gas, either He or N<sub>2</sub>, under which calcination was performed.

214 The time evolution of CaCO<sub>3</sub> wt% during calcination tests carried out under N<sub>2</sub> and  
215 He atmospheres under dry and wet conditions is shown in Figs. 4b-c. Interestingly, the  
216 presence of H<sub>2</sub>O in the calcination atmosphere, even at the very small concentration used in  
217 our tests (0.03 vol %), yields a noticeable acceleration of calcination for both gases. Thus,  
218 calcination proceeds at a similar rate under wet N<sub>2</sub> than under dry He and becomes almost  
219 completed at 700°C . In the case of wet He, the reaction rate is further increased and it  
220 is fully attained completely at about 680°C . As may be seen in Figs. 4b-c the presence  
221 of H<sub>2</sub>O at the small concentration of our tests does not lead to any significant effect on  
222 the reactivity toward carbonation of the CaO resulting from calcination. Figures 4b-c show  
223 that CaO carbonation occurs through two well differentiated stages as well known from  
224 previous studies [27]. A first reaction controlled phase takes place until a CaCO<sub>3</sub> layer is  
225 built upon the surface of the CaO particles. This stage is rather fast at the carbonation  
226 temperature of our experiments and is followed by a much slower phase limited by solid state  
227 diffusion of ions across the CaCO<sub>3</sub> product layer. The rate of carbonation in the solid-state  
228 diffusion controlled phase is therefore determined by the diffusion coefficient, which mainly  
229 depends on the solid crystal structure and the presence of impurities. Thus, the similar  
230 carbonation rate observed in our tests of the CaO resulting from calcination under dry and  
231 wet conditions (Figs. 4b-c) suggests that the crystal structure of the solids is not affected by  
232 the presence of H<sub>2</sub>O at the small concentration used in our experiments. This observation is  
233 consistent with crystallite size data inferred from the in-situ XRD analysis (Figs. 5a-b). This

234 suggests that the remarkable influence of H<sub>2</sub>O observed on the calcination rate is not due  
235 to a catalyzing effect of the H<sub>2</sub>O molecules on CO<sub>2</sub> desorption as was suggested in previous  
236 works from calcination tests under higher H<sub>2</sub>O concentrations. Indeed, such chemical action  
237 would have led to a CaO structure with higher reactivity toward carbonation and promoted  
238 crystallite size not observed in our tests. Since the CaO crystal structure is not influenced  
239 by the small H<sub>2</sub>O concentration used in our tests, it might be expected that neither the  
240 CaO mechanical strength is compromised as would be the case if calcination was carried out  
241 under H<sub>2</sub>O at relatively higher concentrations. Although a direct link between crystallinity  
242 and mechanical strength cannot be generally established, such correlation has been recently  
243 reported elsewhere for the calcium based materials used in our work [51]. Thus, our results  
244 suggest that the addition of H<sub>2</sub>O at very small concentrations in the calciner would allow in  
245 practice reducing further the calcination temperature under He to about 680°C in the CaL  
246 process for CSP energy storage without compromising the mechanical strength of the CaO  
247 particles resulting for calcination.

248 Next we analyze the effect of the presence of H<sub>2</sub>O in the calciner environment at CaL  
249 conditions relevant for CO<sub>2</sub> capture involving calcination under CO<sub>2</sub> at high concentration.  
250 Figure 6 shows the time evolution of in-situ XRD patterns continuously recorded for calci-  
251 nation at 925°C under dry and wet CO<sub>2</sub>. As may be seen, the presence of H<sub>2</sub>O, despite  
252 its very low concentration, has also a significant effect under these conditions. Thus, full  
253 decarbonation is achieved after just about 10 min in the case of wet CO<sub>2</sub> calcination whereas  
254 it takes more than 30 min to be completed under dry CO<sub>2</sub>. The time evolution of CaCO<sub>3</sub>  
255 wt% during calcination/carbonation tests carried out under dry and wet CO<sub>2</sub> at different  
256 temperatures (903, 911, and 925°C) is plotted in Fig. 7. At the lowest temperature (903°C  
257), which is just 7°C over the equilibrium temperature, calcination under dry CO<sub>2</sub> is not

258 even started after 2 h. However, the addition of H<sub>2</sub>O at the very low vol % used in our  
259 tests allows calcination to be initiated after an induction period of about 1.5 h, albeit at  
260 a very slow rate. By increasing the temperature to 911°C , calcination is observed to be  
261 started after about 70 min under dry CO<sub>2</sub> and proceeds at a very slow pace. At this same  
262 temperature, the induction period is shortened to just about 15 min under wet CO<sub>2</sub> and the  
263 reaction speed is multiplied by a factor of almost 3. At a temperature of 925°C the reaction  
264 speed is increased by a similar factor when H<sub>2</sub>O is present in the calcination chamber and  
265 calcination becomes fully attained after a few minutes, which is fast enough for practical  
266 purposes.

267 The above observations are consistent with results reported from thermogravimetric anal-  
268 ysis and pilot-scale tests indicating that the calciner temperature must be raised to about  
269 950°C under dry conditions and high CO<sub>2</sub> partial pressure to achieve complete calcination in  
270 just a few minutes of the fresh limestone makeup that must be periodically introduced in the  
271 reactor to counteract CaO deactivation with the number of CaL cycles [26, 27]. Injection of  
272 steam in the calciner at relatively high concentrations has been proven in previous works to  
273 improve the multicycle stability of the formed CaO [15, 37]. However, the chemical action  
274 of steam at high concentrations affects also the CaO structure so as to seriously impair its  
275 mechanical strength [11]. As seen in Fig. 7 the carbonation rate in the diffusion limited  
276 phase of the CaO formed at the conditions of our tests is not influenced by the presence of  
277 H<sub>2</sub>O, which suggests that neither the CaO structure is significantly altered under wet CO<sub>2</sub>  
278 calcination as compared to dry CO<sub>2</sub> . This is supported by data on the time evolution of  
279 CaCO<sub>3</sub> and CaO crystallite size showing no significant difference between dry and wet CO<sub>2</sub>  
280 calcination (Fig. 8). Thus, we may infer that the presence of H<sub>2</sub>O at the small concentration  
281 used in our tests leads to a significant acceleration of calcination allowing for a reduction

282 of the calcination temperature whereas the mechanical strength of the generated CaO is  
283 neither impaired at CaL conditions for CO<sub>2</sub> capture. As derived from CaL process simula-  
284 tions within the context of its application for CO<sub>2</sub> capture [29] a reduction of the calciner  
285 temperature by just 20°C while maintaining a high calciner efficiency might notably reduce  
286 the energy penalty of the technology. Thus, such temperature reduction would allow to  
287 cut down the amounts of coal and oxygen needed for oxy-combustion to raise the calciner  
288 temperature, which would also diminish the additional CO<sub>2</sub> produced by oxy-combustion.  
289 Simulations [29] indicate that the ratio of the mass of coal needed for oxy-combustion to  
290 the mass of CO<sub>2</sub> captured could be decreased by a 5% if the calciner temperature could be  
291 lowered from 950°C to 930°C. In the ordinary CaL configuration a low calciner to carbona-  
292 tor inventory ratio (of about 0.2) would be only possible by calcination at 950°C (yielding  
293 a high calciner efficiency) whereas a decrease of the calciner temperature to 930°C would  
294 require increasing this ratio to about 0.4 as the calciner efficiency becomes impaired [29].  
295 Thus, achieving efficient calcination at 930°C by using H<sub>2</sub>O at very small concentrations as  
296 suggested by our work would serve to reduce significantly the solids inventory in the calciner  
297 thus decreasing the energy penalty of the technology.

298 As discussed above the effect of He on speeding up calcination as compared to N<sub>2</sub> can be  
299 explained by the enhancement of thermal transfer and CO<sub>2</sub> diffusivity. These gas physical  
300 properties promote the transfer of heat from the furnace to the self-cooling reactant due to  
301 the reaction endothermicity and evacuation of the CO<sub>2</sub> released far from the surface of the  
302 material. The effect observed in the present work of the addition of H<sub>2</sub>O in the calcination  
303 environment cannot be certainly attributed to a change of the physical properties of the  
304 calciner atmosphere, which would not be sufficiently modified by just a 0.03 vol % H<sub>2</sub>O  
305 concentration. Moreover, we have seen that calcination is enhanced also under wet He with

306 a higher thermal conductivity than H<sub>2</sub>O (at 700°C the thermal conductivity of H<sub>2</sub>O is 90  
307 mW/(m K) [52] whereas it is 350 mW/(m K) for He [49]). The results obtained on the CaO  
308 reactivity and crystallite size suggest also that neither H<sub>2</sub>O acts chemically by facilitating  
309 CO<sub>2</sub> desorption to speed up the CaO\* → CaO structural transformation. In fact, this step  
310 has been seen to limit calcination only at conditions near equilibrium and under high CO<sub>2</sub>  
311 partial pressure [6, 21]. Thus, it would be relevant in any case only for the tests carried  
312 out under pure CO<sub>2</sub> in our work. The presence of the phase CaO\* during calcination under  
313 CO<sub>2</sub> may be certainly inferred from a detailed analysis of the XRD patterns recorded for  
314 calcination under CO<sub>2</sub>. Figure 9a shows a zoom of an experimentally recorded XRD pattern  
315 around 29.1° where the main reflection peak of calcite (104) is located for calcination under  
316 dry CO<sub>2</sub> at 925°C. As may be observed, the experimentally recorded peak is slightly shifted  
317 with respect to the location of the theoretical calcite peak. A better fit is obtained by taking  
318 into account the presence of the metastable CaO\* phase, whose main reflection peak (111) is  
319 found around 29.3°. Figure 9b shows the goodness-of-fit parameter for the best Rietveld fits  
320 obtained with and without taking into consideration the presence of CaO\* during calcination  
321 under dry CO<sub>2</sub> at 925°C. Values of the goodness-of-fit closer to unity, which are indicative  
322 of better fits, are systematically obtained when the presence of the metastable CaO\* phase  
323 is allowed. CaO\* wt% data calculated during our calcination tests as a function of CaCO<sub>3</sub>  
324 conversion at diverse temperatures and under dry and wet CO<sub>2</sub> are shown in Fig. 10. As  
325 may be seen, CaO\* is detected although at quite low concentrations, and its wt% drops  
326 quickly with CaCO<sub>3</sub> conversion. Remarkably, for a given calcination temperature the CaO\*  
327 wt% evolution only depends on CaCO<sub>3</sub> conversion independently of whether calcination is  
328 carried out in the presence or absence of H<sub>2</sub>O. Thus, the evolution of CaO\* does not seem  
329 to be significantly affected by the presence of H<sub>2</sub>O at the conditions of our tests despite

330 the important effect that H<sub>2</sub>O has on the reaction kinetics. These results indicate that the  
331 fundamental mechanism by which the presence of H<sub>2</sub>O at the small concentration used in  
332 our tests accelerates calcination is not related to the catalysis of CO<sub>2</sub> desorption and CaO  
333 structural transformation, which is consistent with the absence of any effect of H<sub>2</sub>O observed  
334 above on the reactivity and crystallite size of the CaO that results from calcination.

335 On the other hand, the effect of H<sub>2</sub>O in the calciner at very low concentrations observed in  
336 our work could be rationalized from the unconventional physical approach to decomposition  
337 of alkaline-earth carbonates proposed by L'vov [4, 53], which has remained largely ignored  
338 in the field of thermal analysis. This mechanism assumes that decomposition is initiated by  
339 the congruent dissociative evaporation of CaCO<sub>3</sub> molecules. The main, rate-limiting stage  
340 would be the reaction of volatile CaCO<sub>3</sub> with H<sub>2</sub>O molecules, which would be present in  
341 the reactor environment even under dry conditions at residual concentrations ( $< \sim 10^{-4}$  vol  
342 %), resulting in the formation of low-volatility Ca(OH)<sub>2</sub> as reaction intermediate. Ca(OH)<sub>2</sub>  
343 vapor would rapidly condensate onto the solid and decompose afterwards into CaO and  
344 H<sub>2</sub>O. Since condensation of Ca(OH)<sub>2</sub> generates heat, part of this heat would go into the  
345 excitation of the H<sub>2</sub>O molecules released in the decomposition of the solid Ca(OH)<sub>2</sub>. The  
346 activated H<sub>2</sub>O molecules would interact more effectively with volatile CaCO<sub>3</sub> molecules as  
347 compared to inactivated H<sub>2</sub>O, therefore accelerating decomposition. The model foresees that  
348 a slight excess of H<sub>2</sub>O in the reactor over its residual presence under dry conditions would  
349 significantly reduce the decomposition temperature [53]. Thus, the significant effect on the  
350 calcination kinetics of very low H<sub>2</sub>O concentrations (0.03 vol %) observed in our work could  
351 find an explanation in this mechanism of intermediate Ca(OH)<sub>2</sub> formation. Moreover, this  
352 approach predicts that the influence of water vapor in the presence of CO<sub>2</sub> at high concen-  
353 tration on the calcination rate should be further magnified [53], which is consistent also with



354 our experimental findings. Remarkably, our work is to our knowledge the first experimental  
355 report published in the literature showing a relevant effect of very small amounts of water  
356 vapor on the kinetics of  $\text{CaCO}_3$  decomposition as early predicted by Lvov's model. Never-  
357 theless, such mechanism of intermediate hydroxide formation would involve the presence of  
358 crystalline  $\text{Ca}(\text{OH})_2$  as a metastable phase during the transformation [53], which we fail to  
359 detect at the conditions of our in-situ XRD tests.

#### 360 IV. CONCLUSIONS

361 The CaL process is being widely investigated in the last years for its applications to  
362 capture  $\text{CO}_2$  from coal fired power plants and thermochemical storage of CSP. In both  
363 applications, a reduction of the calcination temperature would greatly contribute to improve  
364 energy efficiency. Importantly, the conditions of calcination in both applications are rather  
365 diverse although a common requirement is that calcination must be completed in short  
366 residence times on the order of several minutes. Thus, calcination in the CaL process for  
367  $\text{CO}_2$  capture must be carried out under high  $\text{CO}_2$  concentration whereas, in the case of CaL-  
368 CSP conditions, calcination would be ideally carried out under a gas separable from  $\text{CO}_2$  that  
369 would allow at the same time a considerable reduction of the calcination temperature such  
370 as He due to its high thermal conductivity and  $\text{CO}_2$  diffusivity. Experimental observations  
371 reported elsewhere indicate that under these conditions calcination of natural limestone  
372 is quickly completed for temperatures around  $\sim 950^\circ\text{C}$  and  $\sim 725^\circ\text{C}$  under  $\text{CO}_2$  and He,  
373 respectively. Previous studies have also shown that the addition of steam at relatively  
374 high concentrations catalyzes calcination. Furthermore, the reactivity of the formed CaO  
375 is enhanced albeit the chemical action of  $\text{H}_2\text{O}$  affects critically the CaO crystal structure  
376 and impairs severely the CaO mechanical strength, which poses a serious limitation to the

377 practical use of steam in circulating fluidized beds. The in-situ XRD analysis shown in the  
378 present work demonstrates that the use of H<sub>2</sub>O at very small concentrations yields still a  
379 significant acceleration of the calcination reaction whereas the CaO reactivity and crystal  
380 structure are not essentially affected. These results have been obtained at CaL conditions  
381 relevant for both CO<sub>2</sub> capture and CSP energy storage and suggest the possibility of reducing  
382 in both applications the calcination temperature by about ~20°C without compromising the  
383 mechanical strength of the formed CaO.

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## 389 VI. REFERENCES

- 
- 390 [1] Boynton, R. S. *Chemistry and Technology of Lime and Limestone*; Wiley: New York, 1980  
391 For general practical information, the interested reader is recommended perusal of the first  
392 edition (1966).
- 393 [2] Towe, K. M. *Nature* **1978**, *274*, 239 - 240.
- 394 [3] Caceres, P.; Attiogbe, E. *Minerals Engineering* **1997**, *10*, 1165 - 1176.
- 395 [4] L'vov, B. V.; Polzik, L. K.; Ugolkov, V. L. *Thermochimica Acta* **2002**, *390*, 5 - 19.

- 396 [5] Beruto, D.; Searcy, A. W.; Kim, M. G. *Thermochimica Acta* **2004**, *424*, 99 - 109.
- 397 [6] Rrodriguez-Navarro, C.; Ruiz-Agudo, E.; Luque, A.; Navarro, A. B.; Ortega-Huertas, M.  
398 *American Mineralogist* **2009**, *94*, 578 - 593.
- 399 [7] Michele, P.; Loic, F.; Michel, S. *Thermochimica Acta* **2011**, *525*, 93 - 102.
- 400 [8] Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. *The Journal of Physical*  
401 *Chemistry C* **2015**, *119*, 1623-1641.
- 402 [9] Beruto, D.; Vecchiattini, R.; Giordani, M. *Thermochimica Acta* **2003**, *404*, 25 - 33.
- 403 [10] Sceats, M.; Horley, C. "System and method for the calcination of minerals", 2014 US Patent  
404 8,807,993.
- 405 [11] MacIntire, W. H.; Stansel, T. B. *Industrial & Engineering Chemistry* **1953**, *45*, 1548-1555.
- 406 [12] Berger, E. E. *Industrial & Engineering Chemistry* **1927**, *19*, 594-596.
- 407 [13] Valverde, J. M.; Medina, S. *ACS Sustainable Chemistry & Engineering* **2016**, *4*, 7090-7097.
- 408 [14] Wang, Y.; Thomson, W. J. *Chemical Engineering Science* **1995**, *50*, 1373 - 1382.
- 409 [15] Donat, F.; Florin, N. H.; Anthony, E. J.; Fennell, P. S. *Environmental Science & Technology*  
410 **2012**, *46*, 1262 - 1269.
- 411 [16] Stanmore, B.; Gilot, P. *Fuel Processing Technology* **2005**, *86*, 1707 - 1743.
- 412 [17] Borgwardt, R. H. *Industrial & Engineering Chemistry Research* **1989**, *28*, 493 - 500.
- 413 [18] Anderson, P. J.; Horlock, R. F.; Avery, R. G. *Proc. Br. Ceram. Soc.* **1965**, *3*, 33.
- 414 [19] Agnew, J.; Hampartsoumian, E.; Jones, J.; Nimmo, W. *Fuel* **2000**, *79*, 1515 - 1523.
- 415 [20] Fierro, V.; Adnez, J.; Garcia-Labiano, F. *Fuel* **2004**, *83*, 1733 - 1742.
- 416 [21] Valverde, J. M.; Medina, S. *Phys. Chem. Chem. Phys.* **2015**, *17*, 21912-21926.
- 417 [22] Barin, I. *Thermochemical data of pure substances*; Weinheim: VCH.: 1989.

- 418 [23] Garcia-Labiano, F.; Abad, A.; de Diego, L.; Gayan, P.; Adanez, J. *Chemical Engineering*  
419 *Science* **2002**, *57*, 2381 - 2393.
- 420 [24] Valverde, J. M. *Chemical Engineering Science* **2015**, *132*, 169–177.
- 421 [25] Blamey, J.; Anthony, E. J.; Wang, J.; Fennell, P. S. *Prog. Energ. Combust. Sci.* **2010**, *36*,  
422 260–279.
- 423 [26] Hanak, D. P.; Anthony, E. J.; Manovic, V. *Energy Environ. Sci.* **2015**, *8*, 2199-2249.
- 424 [27] Perejon, A.; Romeo, L. M.; Lara, Y.; Lisbona, P.; Martinez, A.; Valverde, J. M. *Applied*  
425 *Energy* **2016**, *162*, 787 - 807.
- 426 [28] Shimizu, T.; Hiramata, T.; Hosoda, H.; Kitano, K.; Inagaki, M.; Tejima, K. *Chemical*  
427 *Engineering Research & Design* **1999**, *77*, 62 - 68.
- 428 [29] Martinez, A.; Lara, Y.; Lisbona, P.; Romeo, L. M. *Environmental Science & Technology*  
429 **2013**, *47*, 11335-11341.
- 430 [30] Flamant, G.; Hernandez, D.; Bonet, C.; Traverse, J.-P. *Solar Energy* **1980**, *24*, 385 - 395.
- 431 [31] Edwards, S. E.; Materic, V. *Solar Energy* **2012**, *86*, 2494 - 2503.
- 432 [32] Chacartegui, R.; Alovio, A.; Ortiz, C.; Valverde, J.; Verda, V.; Becerra, J. *Applied Energy*  
433 **2016**, *173*, 589 - 605.
- 434 [33] Sarrion, B.; Valverde, J. M.; Perejon, A.; Perez-Maqueda, L.; Sanchez-Jimenez, P. E. *Energy*  
435 *Technology* **2016**, *4*, 1013–1019.
- 436 [34] Blamey, J.; Manovic, V.; Anthony, E. J.; Dugwell, D. R.; Fennell, P. S. *Fuel* **2015**, *150*,  
437 269 - 277.
- 438 [35] Blamey, J.; Paterson, N. P. M.; Dugwell, D. R.; Fennell, P. S. *Energy Fuels* **2010**, *24*,  
439 4605–4616.

- 440 [36] Symonds, R. T.; Lu, D. Y.; Manovic, V.; Anthony, E. J. *Industrial & Engineering Chemistry*  
441 *Research* **2012**, *51*, 7177 - 7184.
- 442 [37] Champagne, S.; Lu, D. Y.; Macchi, A.; Symonds, R. T.; Anthony, E. J. *Industrial &*  
443 *Engineering Chemistry Research* **2013**, *52*, 2241-2246.
- 444 [38] Phalak, N.; Wang, W.; Fan, L.-S. *Chemical Engineering & Technology* **2013**, *36*, 1451–1459.
- 445 [39] Asano, K.; Fujimoto, K.; Yamaguchi, Y.; Ito, S. Reactivity of Carbonates in Superheated  
446 Steam under Atmospheric Pressure. In *Inorganic and Environmental Materials*, Vol. 617;  
447 Trans Tech Publications: 2014.
- 448 [40] Anderson, P. J.; Morgan, P. L. *Trans. Faraday Soc.* **1964**, *60*, 930–937.
- 449 [41] de Leeuw, N. H.; Watson, G. W.; Parker, S. C. *The Journal of Physical Chemistry* **1995**,  
450 *99*, 17219-17225.
- 451 [42] Allen, J. P.; Parker, S. C.; Price, D. W. *The Journal of Physical Chemistry C* **2009**, *113*,  
452 8320-8328.
- 453 [43] Allen, J. P.; Marmier, A.; Parker, S. C. *The Journal of Physical Chemistry C* **2012**, *116*,  
454 13240 - 13251.
- 455 [44] Onishi, H.; Egawa, C.; Aruga, T.; Iwasawa, Y. *Surface Science* **1987**, *191*, 479 - 491.
- 456 [45] Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J. C. *AIChE J.* **2009**, *55*, 1246–1255.
- 457 [46] Bruker, A. *Bruker AXS GmbH, Karlsruhe, Germany Search PubMed* **2014**, .
- 458 [47] (Ed.), R.-A. Y. *The Rietveld Method*; IUCr Monographs on Crystallography 5; Oxford Uni-  
459 versity Press: New York, 1993.
- 460 [48] Le Bail, A. *Powder Diffraction* **2005**, *20*, 316–326.
- 461 [49] Vargaftik, N. B.; Yakush, L. V. *Journal of engineering physics* **1977**, *32*, 530–532.

- 462 [50] Cussler, E. *Diffusion: Mass Transfer in Fluid Systems*; Cambridge Series in Chemical Engi-  
463 neering Cambridge University Press: 1997.
- 464 [51] Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A.; Quintanilla, M.; Perez-  
465 Vaquero, J. *Applied Energy* **2014**, *125*, 264 - 275.
- 466 [52] Huber, M. L.; Perkins, R. A.; Friend, D. G.; Sengers, J. V.; Assael, M. J.; Metaxa, I. N.;  
467 Miyagawa, K.; Hellmann, R.; Vogel, E. *Journal of Physical and Chemical Reference Data*  
468 **2012**, *41*, 033102.
- 469 [53] L'vov, B. V. *Thermochimica Acta* **1997**, *303*, 161 - 170.

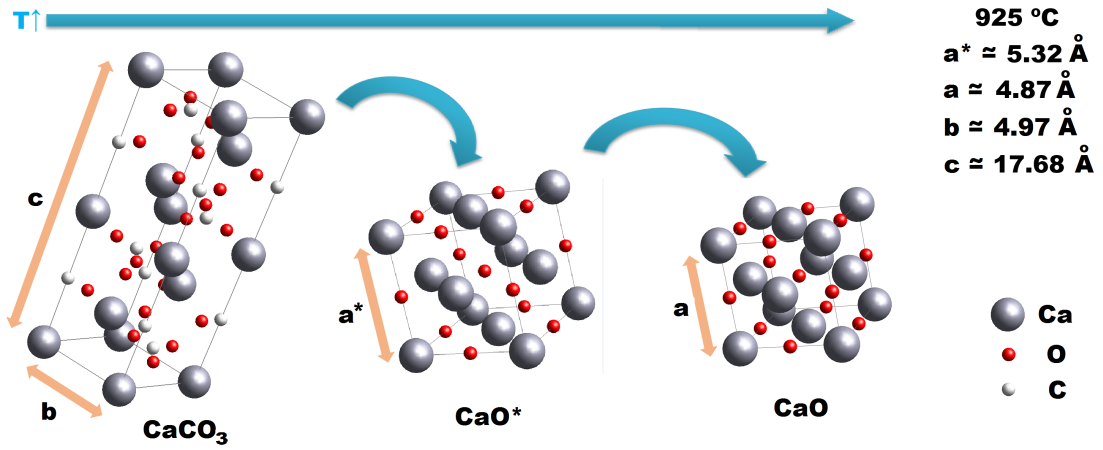


FIG. 1: Transformation during calcination of the hexagonal rhombohedral calcite structure (space group  $R\bar{3}c$ , 167) into a cubic metastable  $\text{CaO}^*$  structure (space group  $Fm\bar{3}m$ , 225) as a dilated pseudomorph of the final stable  $\text{CaO}$  form lime (same space group that  $\text{CaO}^*$ ). Cell parameters indicated are calculated for a temperature of  $925^\circ\text{C}$ . Adapted from [21].

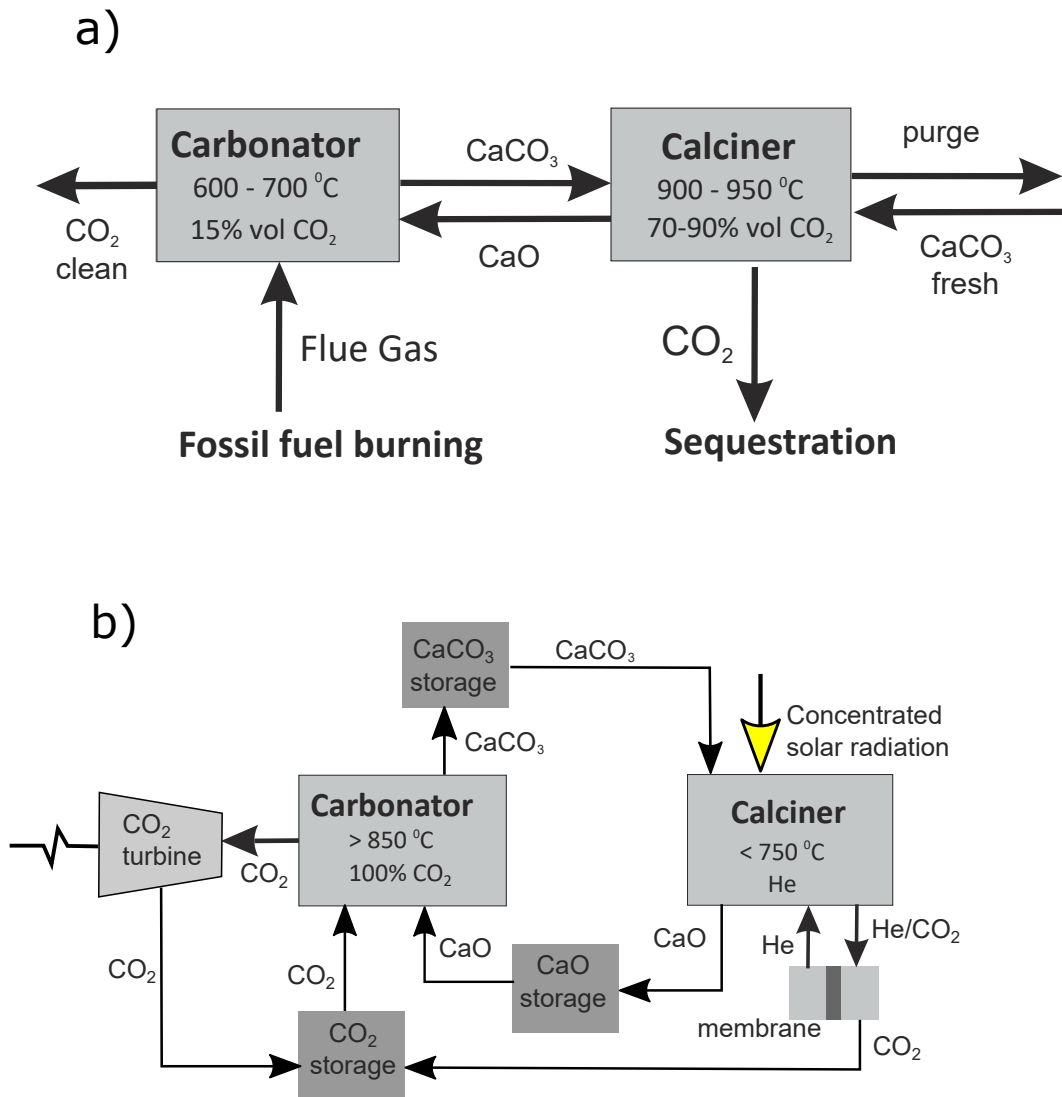


FIG. 2: Flow diagrams of the Calcium Looping process for CO<sub>2</sub> capture in fossil fuel fired power plants (a) demonstrated at the pilot scale (1 - 2 MW<sub>th</sub>) stage [26] and for Thermochemical Energy Storage in Concentrated Solar Power plants (b) currently at the concept stage [32].



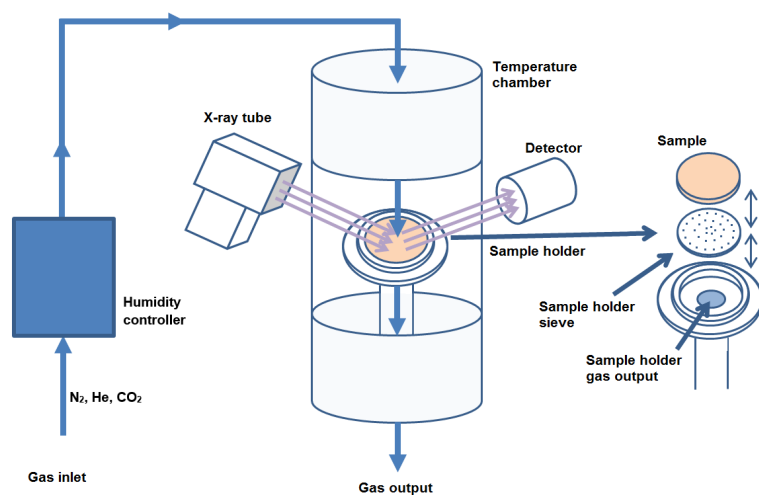


FIG. 3: Schematic layout of the experimental setup used in this work for limestone calcination/carbonation in-situ XRD analysis under different dry and wet gases.

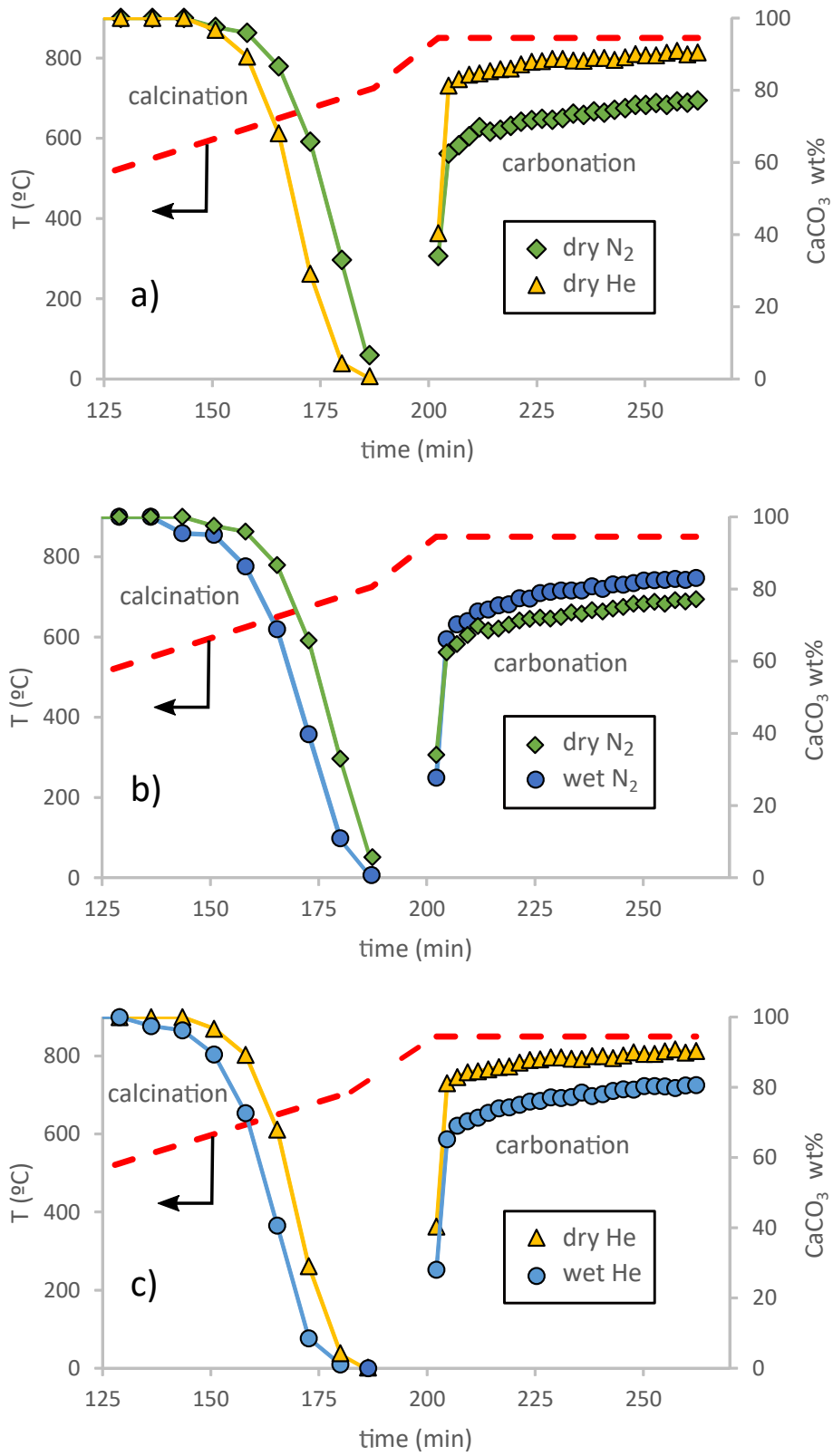


FIG. 4: Time evolution of temperature (left axis) and  $\text{CaCO}_3$  wt% during calcination/carbonation tests carried out under dry  $\text{N}_2$  and He (a), dry and wet  $\text{N}_2$  (b) and dry and wet He (c) atmospheres.

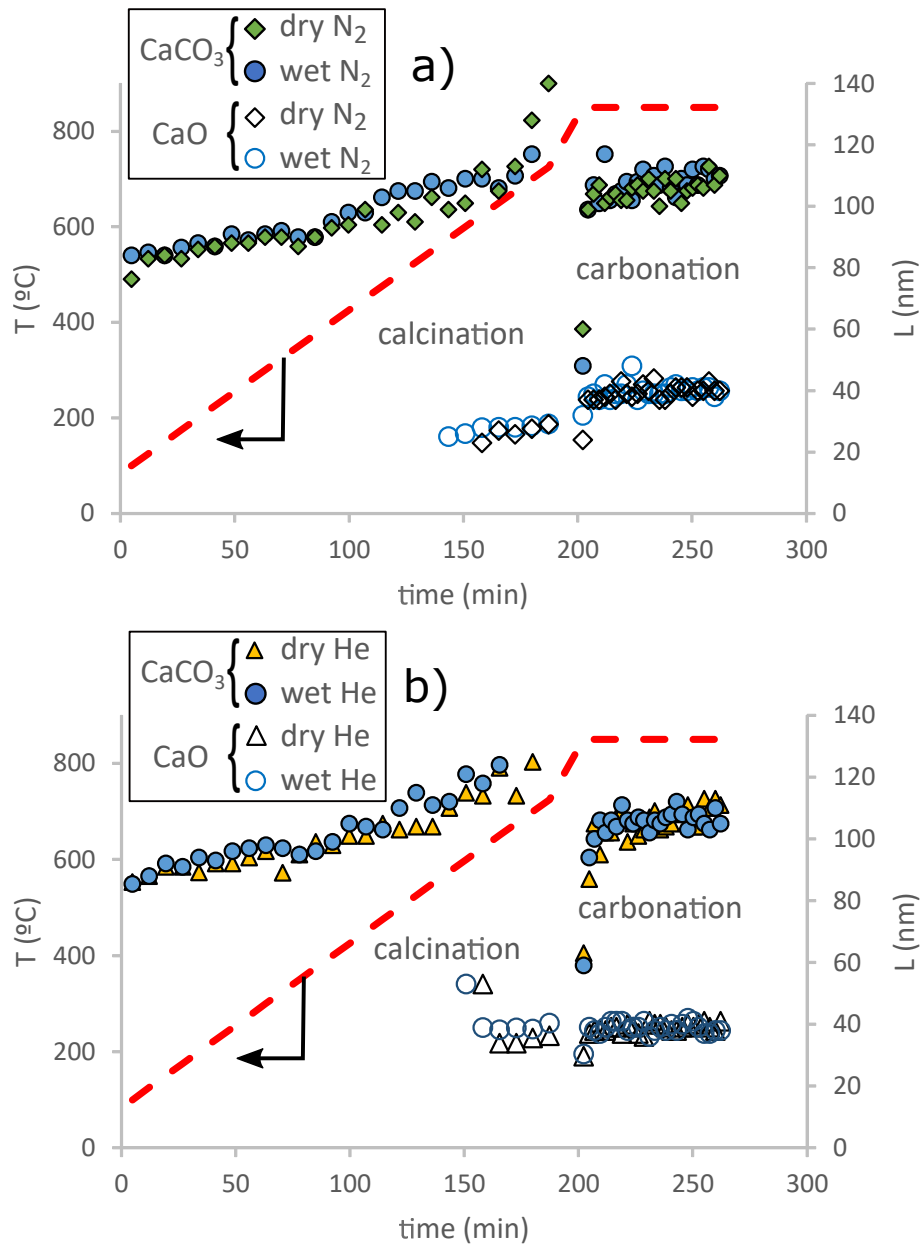


FIG. 5: Time evolution of temperature (left axis) and crystallite size (right axis) of  $\text{CaCO}_3$  and  $\text{CaO}$  during calcination/carbonation tests carried out under dry and wet  $\text{N}_2$  (a), and dry and wet  $\text{He}$  (c) atmospheres.

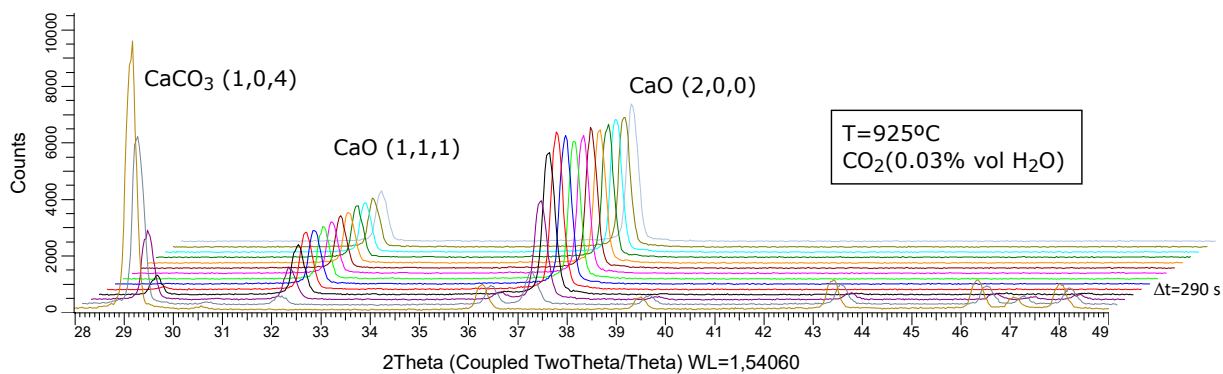
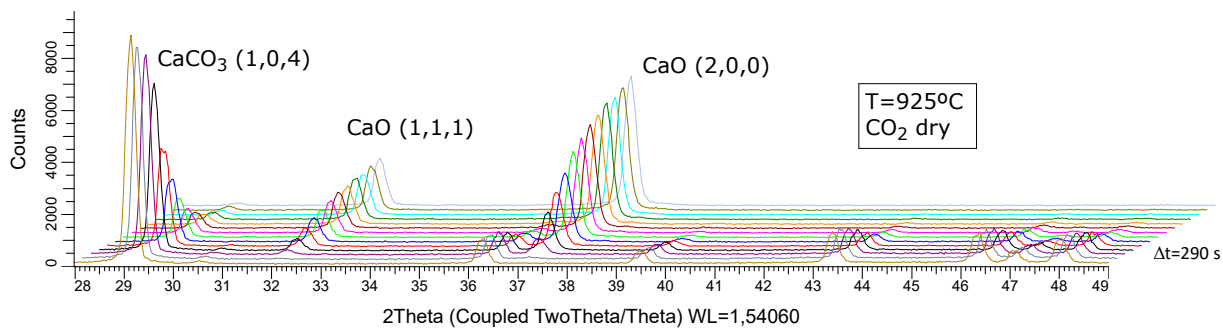


FIG. 6: Segments of the diffractograms recorded by in-situ XRD analysis during calcination of limestone at 925°C under dry and wet CO<sub>2</sub> (0.03 vol% H<sub>2</sub>O). Main Bragg peaks of calcite (CaCO<sub>3</sub>: Rombo.H.axes, space group R $\bar{3}$ c (163)) and lime (CaO: Cubic, space group Fm $\bar{3}$ m (225)) are indicated.

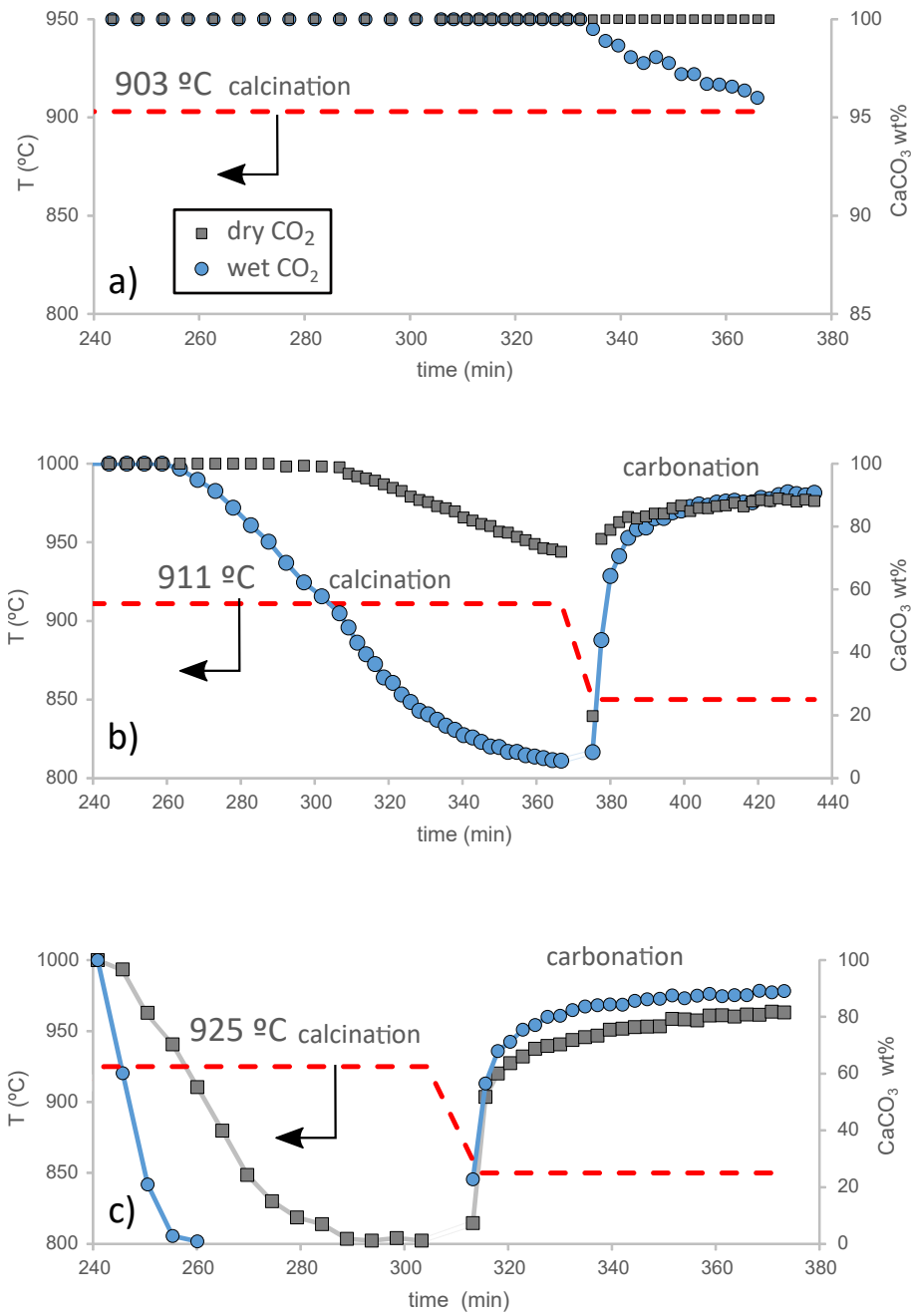


FIG. 7: Time evolution of temperature (left axis) and  $\text{CaCO}_3$  wt% during calcination/carbonation tests carried out under dry and wet  $\text{CO}_2$  at  $903^\circ\text{C}$  (a),  $911^\circ\text{C}$  (b), and  $925^\circ\text{C}$  (c).

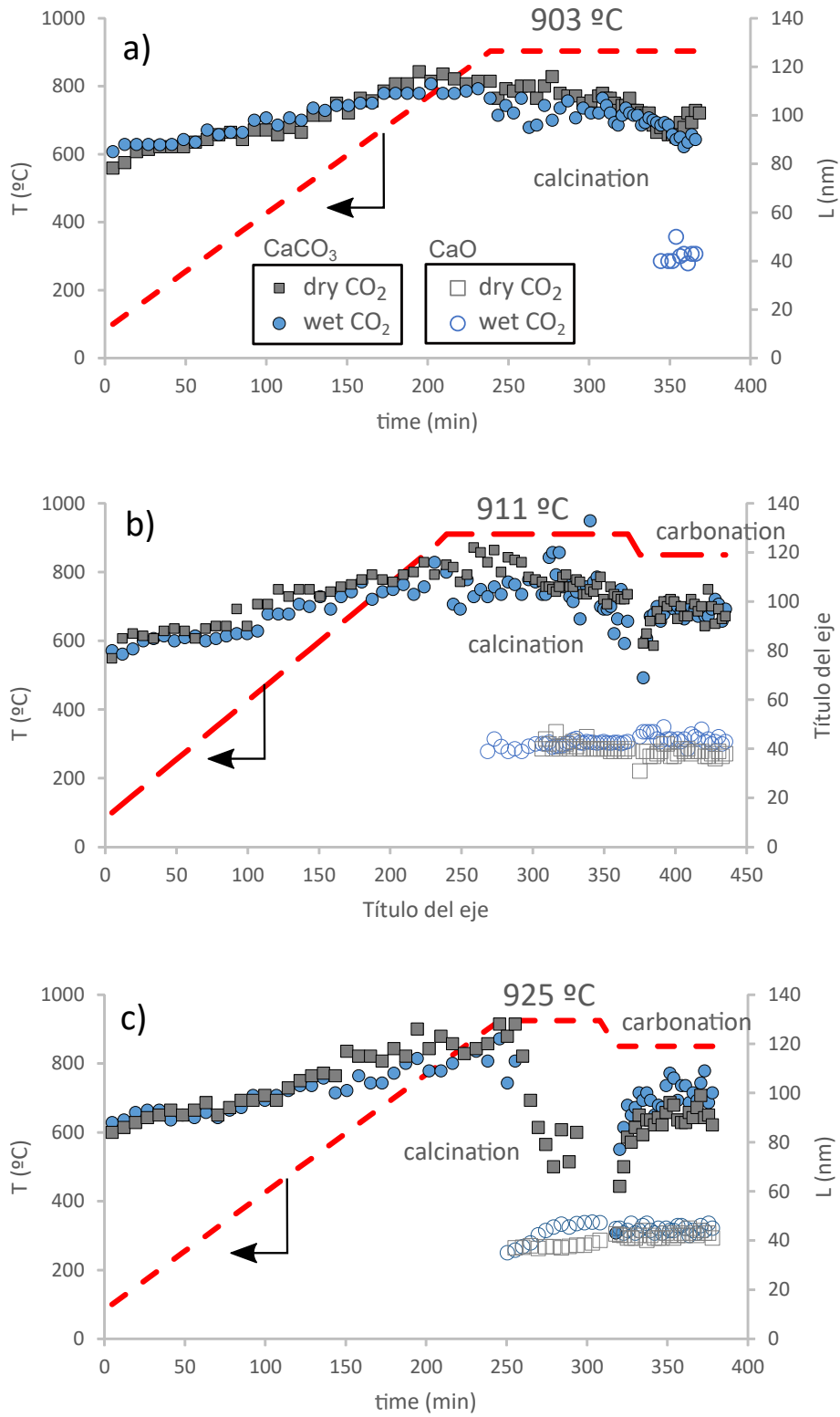


FIG. 8: Time evolution of temperature (left axis) and crystallite size (right axis) of  $\text{CaCO}_3$  and  $\text{CaO}$  during calcination/carbonation tests carried out under dry and wet  $\text{CO}_2$  at  $903^\circ\text{C}$  (a),  $911^\circ\text{C}$  (b), and  $925^\circ\text{C}$  (c).

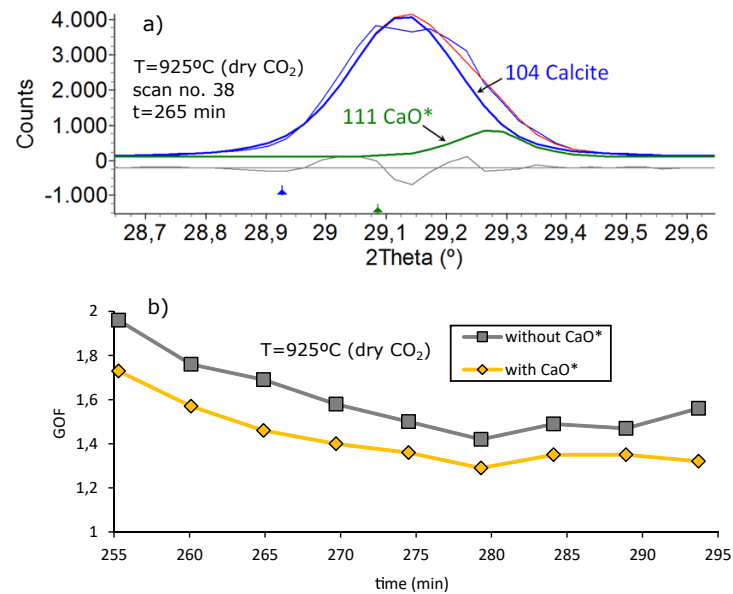


FIG. 9: a) Main Bragg reflection peak of calcite recorded (blue thin line) at scan 38 ( $t=265$  min) during calcination under dry  $\text{CO}_2$  ( $T=925^\circ\text{C}$ ), peak obtained from the best Rietveld fit (red thin line), which includes the contribution of calcite (blue thick line, 56.8% wt content) and  $\text{CaO}^*$  (green line, 4.2% wt content) reflection peaks. b) Goodness-of-fit parameter obtained for the Rietveld best fits to experimentally recorded XRD patterns with and without taking into consideration the presence of the metastable  $\text{CaO}^*$  phase during calcination under dry  $\text{CO}_2$  ( $T=925^\circ\text{C}$ ).

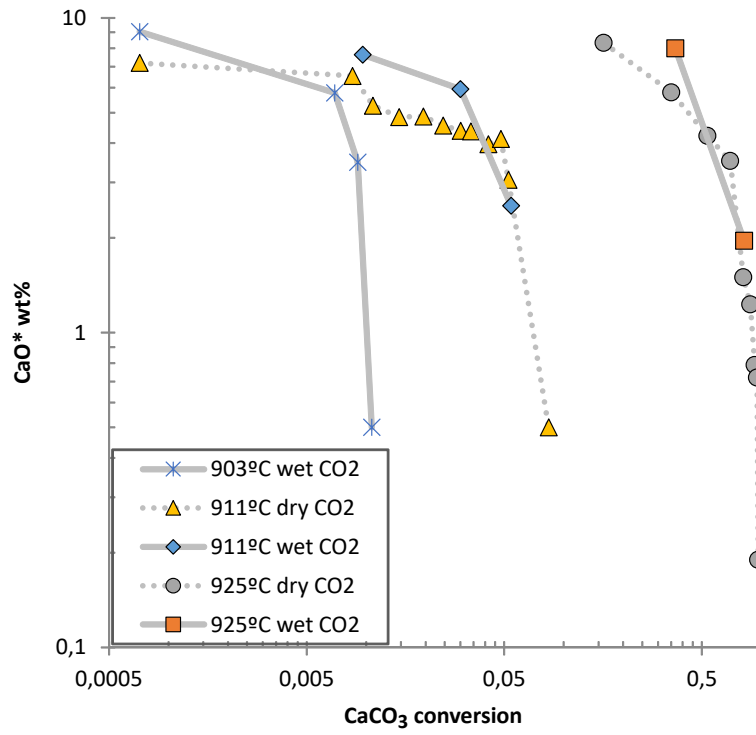


FIG. 10: Time evolution of CaO\* wt% as a function of CaCO<sub>3</sub> conversion during calcination under dry and wet (0.03% wt H<sub>2</sub>O) CO<sub>2</sub> at diverse temperatures as indicated (calculated by means of a Rietveld quantitative analysis).