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Calcium looping sorbents for CO₂ capture

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Abstract

Calcium looping (CaL) is a promising technology for the decarbonation of power generation and carbon-intensive (cement, lime and steel) industries. Although CaL has been extensively researched, some issues need to be addressed before the deployment of this technology at commercial scale. One of the important challenges for CaL is decay of sorbent reactivity during capture/regeneration cycles. Numerous techniques have been explored to enhance natural sorbent performance, to create new synthetic sorbents, and to re-activate and re-use deactivated material. This review provides a critical analysis of natural and synthetic sorbents developed for use in CaL. Special attention is given to the suitability of modified materials for utilisation in fluidised-bed systems. Namely, besides requirements for a practical adsorption capacity; a mechanically strong material, resistant to attrition, is required for the fluidised bed CaL operating conditions. However, the main advantage of CaL is that it employs a widely available and inexpensive sorbent. Hence, a compromise must be made between improving the sorbent performance and increasing its cost, which means a relatively practical, scalable, and inexpensive method to enhance sorbent performance, should be found. This is often neglected when developing new materials focusing only on very high adsorption capacity.

Keywords: CO₂ capture, calcium looping, sorbent, limestone, synthetic sorbent, sorbent modification method

Highlights

- The extensive literature on Ca Looping sorbents and their properties has been reviewed
- Currently, there is a lack of experiments on doped sorbents in realistic systems
- Most complex methods of sorbent modification appear to be prohibitively expensive for CCS
- A major challenge of all sorbent modification processes is their scalability

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1 **1. Introduction**

2 The CO₂ concentration in the atmosphere has risen from 280 ppmv in 1750 to 400
3 ppmv in 2015 which is the highest level in the past 650,000 years [1]. According to
4 the Intergovernmental Panel on Climate Change (IPCC) [2,3], this increase in CO₂
5 concentration is the main cause for an increase of 0.74 ±0.18°C in global
6 temperature; it is also a probable reason for a rise of 0.18-0.59 m in sea level over
7 the past century. The energy market still depends heavily on relatively cheap fossil
8 fuels, which, added to the expected increase of 37% in energy demand by 2040 [4],
9 means that fossil fuels will continue to be used during this century and possibly
10 beyond. Hence, it is necessary to find mitigation options for CO₂ emissions.

11 Carbon capture and storage (CCS) is a potential mitigation option, which consists of
12 capturing the carbon dioxide present in a stream in order to transport it and store it
13 in a safe location [5,6]. A diverse range of CCS technologies has been investigated
14 and a number of demonstration projects have been started or planned [7], although
15 currently the dominant CO₂ mitigation strategies are pre-combustion, oxy-fuel and
16 post-combustion techniques [8].

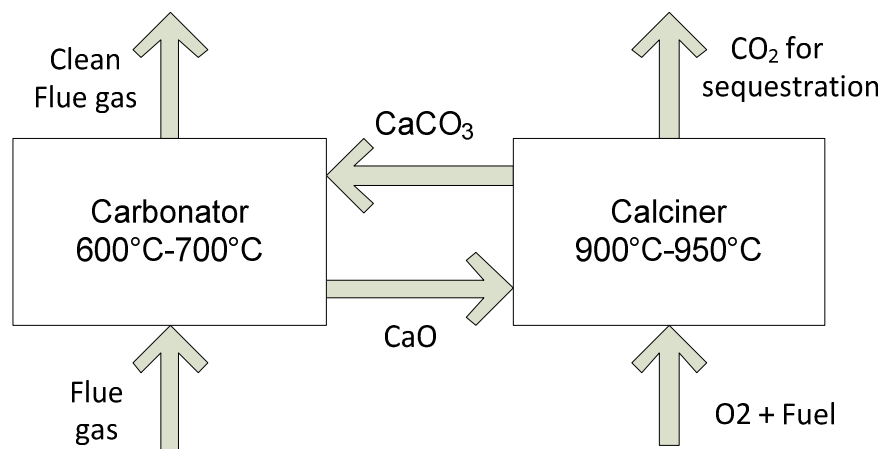
17 The CCS technology that is closest to the market is post-combustion amine
18 scrubbing, with solvents such as monoethanolamine (MEA) [9]. There are some
19 problems associated with this process such as solvent degradation, cost, and the
20 corrosive nature of the solvent [10–16]. Another technology that is close to the
21 market is oxy-fuel combustion, where fuel is burned in a mixture of O₂ and recycled
22 CO₂, but the drawback of this technology is the energy required to run the air
23 separation unit (ASU) to produce the oxygen needed for combustion [17]. However,
24 significantly the first large-scale deployment of CCS, an amine-based technology
25 started its operation in October 2014 at SaskPower's Boundary Dam Power Station
26 (Canada) with a lignite fired boiler [18]. Nonetheless, the relatively slow
27 deployment of CCS technologies, is mainly caused by their high efficiency and
28 economic penalties [19,20], but also to the lack of policies [21,22]. Therefore, these
29 are drivers that have triggered the development of alternative CCS technologies
30 such as second- and third- generation carbon capture technologies aiming at lower
31 efficiency and economic penalties.

32 One viable solution arising from this development is calcium looping (CaL), which is
33 based on the reversible carbonation of lime. This second-generation technology
34 [23] is attracting a vast amount of R&D resources with numerous demonstration
35 projects throughout the world [24].

36 This work reviews the CaL process in general, taking into account its challenges,
37 mainly sorbent reactivity decay and attrition in fluidised bed (FB) reactors. Then, it
38 examines current research in the area of sorbent testing and modification starting
39 with natural sorbents (limestone) and naturally-derived sorbents (dolomite among
40 others) and discusses their properties over extended numbers of cycles. As the
41 reactivity of these sorbents suffers from a drastic decrease while in continuous
42 operation, enhancement options, such as hydration, are also discussed along with
43 more complex methods that have been proposed to produce sintering- and attrition-
44 resistant sorbents with an emphasis on preparation methods. Finally, reactivation of
45 “spent” sorbent and its re-use are also discussed. The main objective of this study
46 is to provide recommendations for economically viable sorbent modifications and
47 treatments of different types of sorbents and their suitability for utilisation in
48 commercial-scale equipment.

49 2. Process description

50 CaL was first proposed as a post-combustion carbon capture technology by
51 Shimizu et al. in 1999 [25]. The schematic diagram of CaL application for post-
52 combustion CO₂ capture is shown in Figure 1.



53

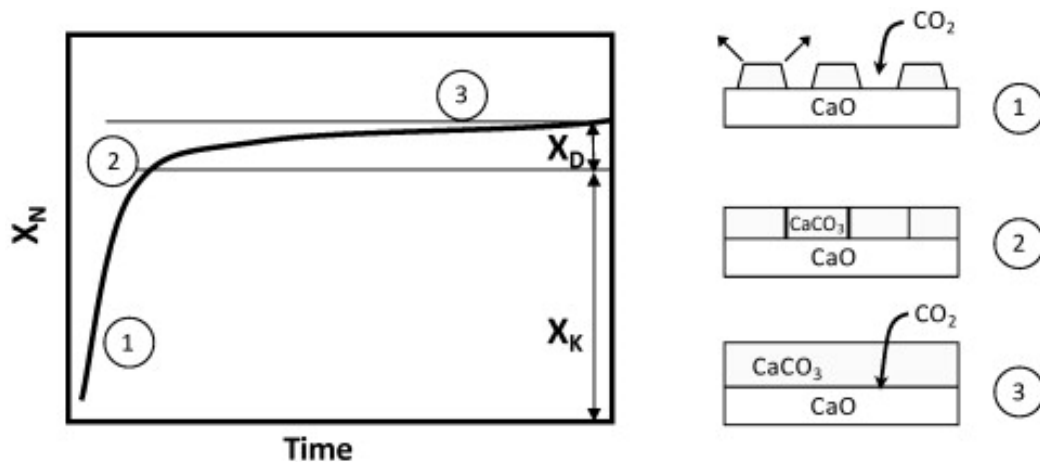
54 **Figure 1:** Schematic diagram of calcium looping process for post-combustion CO₂
55 capture.

56 In this process the solid sorbent cycles between two interconnected FBs. The flue
57 gas enters the carbonator where a CaO-based material reacts with the CO₂
58 present, resulting in formation of CaCO₃ (saturated sorbent). This carbonation
59 reaction occurs at a fairly rapid rate between 580-700 °C [25–27], which is suitable
60 for practical operation, with a trade-off between reaction kinetics and the equilibrium
61 driving forces [28,29]. This reaction has two stages: (i) an initial, relatively fast
62 stage, controlled by the chemical reaction kinetics, followed by (ii) a much slower
63 stage, which is limited by the diffusion of the reactants through the formed CaCO₃
64 product layer, which is postulated to be critical when it reaches a thickness of
65 around 50 nm [30]. The two-stage mechanism of the carbonation reaction can be
66 seen in Figure 2, which shows the sorbent conversion as a function of reaction time
67 obtained in a TGA [31]. Where X_N is the CaO molar conversion in each cycle, X_K is
68 the molar conversion under fast reaction regime and X_D the molar conversion under
69 diffusion controlled regime.

70 It is important to define the “maximum” carbonation conversion of any sorbent as
71 the moles of CO₂ that reacted in the period of fast reaction compared to the
72 stoichiometry of complete CaO to CaCO₃ conversion [32]. Subsequently, the CO₂-
73 saturated sorbent is transferred to the calciner, in which sorbent is regenerated at
74 high temperatures and the concentrated CO₂ stream is produced. This calcination
75 reaction is typically performed at temperatures above 900°C due to the chemical
76 equilibrium and (practical) reaction rate requirements, while maintaining sintering at
77 a reasonably low level [33]. Since calcination is an endothermic reaction, heat
78 needs to be supplied, which is typically achieved by burning a fuel in this chamber
79 using pure O₂ in order to obtain a highly concentrated CO₂ stream at the end of the
80 process [25,34]. Finally, the regenerated sorbent is transferred to the carbonator to
81 start the cycle again.

82

83



84

85 **Figure 2:** Schematic illustration of sorbent conversion during carbonation [31]

86 This technology has various advantages when compared to other carbon capture
 87 options such as amine scrubbing:

- 88 – Relatively low efficiency penalty, from 7 to 8% [35,36] with the capture step
 89 responsible only for 2 to 3% primarily due to oxygen requirement [37]
- 90 – Use of limestone, a widely available, inexpensive [38] and environmentally
 91 benign sorbent [20]
- 92 – The cost of CO₂ avoided has been calculated to be \$29–50/t-CO₂, which
 93 accounts for around 50% less than for amine scrubbing [39–43]

94 One of the major challenges of this technology is the relatively fast sorbent
 95 reactivity decay resulting in a residual activity of 8-10% after about 20 or 30 cycles,
 96 due to sintering during calcination [32]. This phenomenon has attracted research
 97 aimed at improving the performance of natural sorbents, and synthesising sorbents
 98 with enhanced properties.

99 **3. Reactivity decay over cycles**

100 It is common knowledge that CaO-based sorbents decay in activity is inevitable.
 101 The main causes for this decrease of reactivity are sintering and attrition. These
 102 phenomena are described in depth in this section with the mechanisms and
 103 theories that explain particle behaviour during cycling.

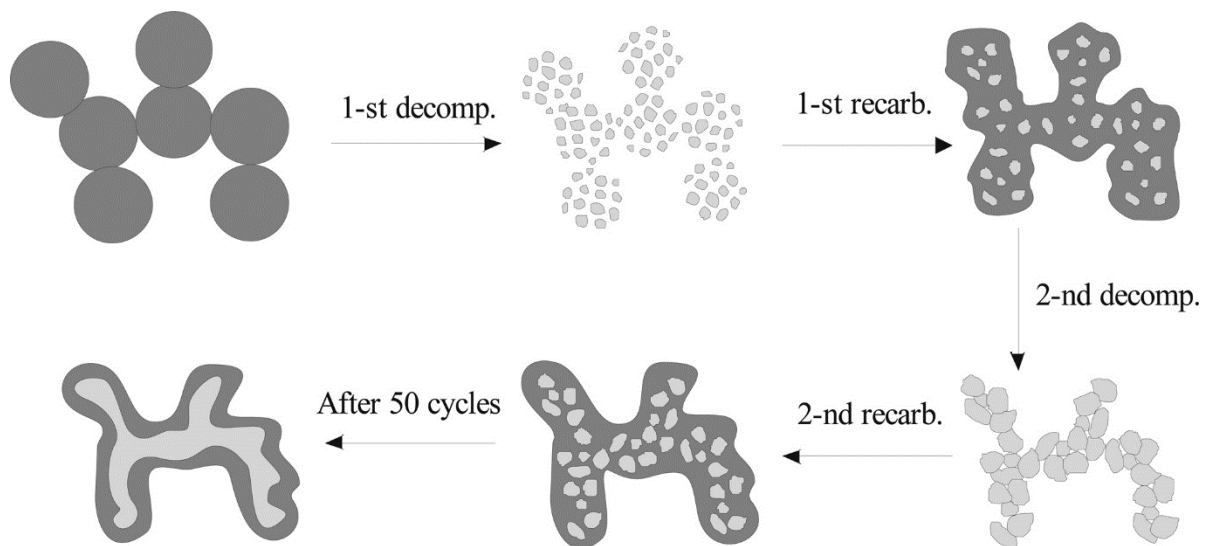
104 3.1. Sintering

105 Sintering is the change in pore shape, pore shrinkage and grain growth that
106 particles of CaO endure while heating. This phenomenon rises at higher partial
107 pressures of steam and CO₂, and also with impurities [44]. It has been discovered
108 that the sintering that contributes to the reactivity decay occurs mainly during the
109 calcination of such particles [45]. However, some of the decay can be connected to
110 closure of small pores on the carbonation that do not reopen subsequently [46]. The
111 deactivation rate escalates when increasing temperature in the calcination step with
112 lower reactivity associated with higher temperatures [47].

113 There have been several studies that have proven the bimodal pore size
114 distribution created upon calcination [30,45]. During calcination, small pores are
115 formed due to the CO₂ release; however, larger pores are not only present in the
116 initial material but are also formed caused by sintering, which driven by the
117 minimization of surface energy, swings smaller pores to larger pores.

118 It has also been perceived by several studies [48–50] that increasing carbonation
119 time results in a sorbent with higher reactivity towards CO₂. The effect of this longer
120 carbonation has been investigated by Álvarez and Abanades [30]. They suggested
121 that although the larger pores were accessible through pores with smaller opening,
122 they were closed at the surface. Presumably, if the slow carbonation solid diffusion
123 reaction occurs for longer periods, the solid bulk enlarges in order to fill the larger
124 pores in a more substantial way. This leads to a higher CaO reactivity in the next
125 calcination. On the other hand, this longer carbonation step could be unpractical
126 when talking about industrial operation.

127 A schematic way of understanding this sintering phenomenon can be found in
128 Figure 3 [51]. In this diagram the course of several calcination/carbonation cycles is
129 shown. In the first calcination, a highly porous and reactive CaO is produced. The
130 first carbonation is not complete due to pore blocking; some of these pores do not
131 open in the following calcination. This pattern is repeated until a substantially less
132 reactive sorbent is recovered after a high number of cycles.



133

134 **Figure 3:** Transformation of the lime-based sorbent structure during
 135 carbonation/calcination (CaCO_3 phase is dark grey, CaO phase is light grey) [51]

136 3.2. Attrition

137 The mechanisms for fragmentation/attrition can be divided into: primary
 138 fragmentation, which takes place when the sorbent is introduced into the reactor. It
 139 is mainly caused by thermal stresses and overpressures due to CO_2 release as part
 140 of the calcination reaction. Secondary fragmentation, which is caused by
 141 mechanical stresses from impacts between the particle and the reactor; and attrition
 142 by abrasion which is also due to mechanical stresses but generates finer fragments
 143 than secondary fragmentation [52].

144 Interestingly, it has been stated that the attrition rate is higher during the first cycles
 145 and then subsequently decreased [53,54]. Nonetheless, attrition becomes a more
 146 significant problem when dealing with pilot-scale FBs. 30% of the initial limestone
 147 was recovered in the cyclone after 3 cycles (<0.1 mm) and 60% after 25 cycles,
 148 whilst the initial particle size was 0.4-0.8 mm [29].

149 Attrition is highly dependent of the experimental set-up. Namely, it depends on the
 150 gas velocities, size and configuration of the plant. This phenomenon becomes even
 151 more important when exploring new sorbents. There should be a shift in research
 152 from only studying reactivity decay caused by sintering to a complete analysis of
 153 any new synthetic material including attrition investigations.

154 **4. Natural material-based sorbent**

155 The use of natural materials ground to a particle size distribution, suitable for FB
156 operation, is the easiest and cheapest way of obtaining a solid CO₂ carrier due to
157 its availability and possible re-use for the cement industry [55]. Reactivity decay is
158 caused mainly by sintering, which decreases the specific surface area with
159 increasing number of cycle number resulting in a loss of capacity. Other causes of
160 deactivation include poisoning of the material through sulphation/sulphidation
161 reactions and ash fouling [20,56]. This can be reduced by boosting the Ca to C ratio
162 in the carbonator or increasing the purge flow of spent sorbent in order to get more
163 fresh sorbent into the reactor [57].

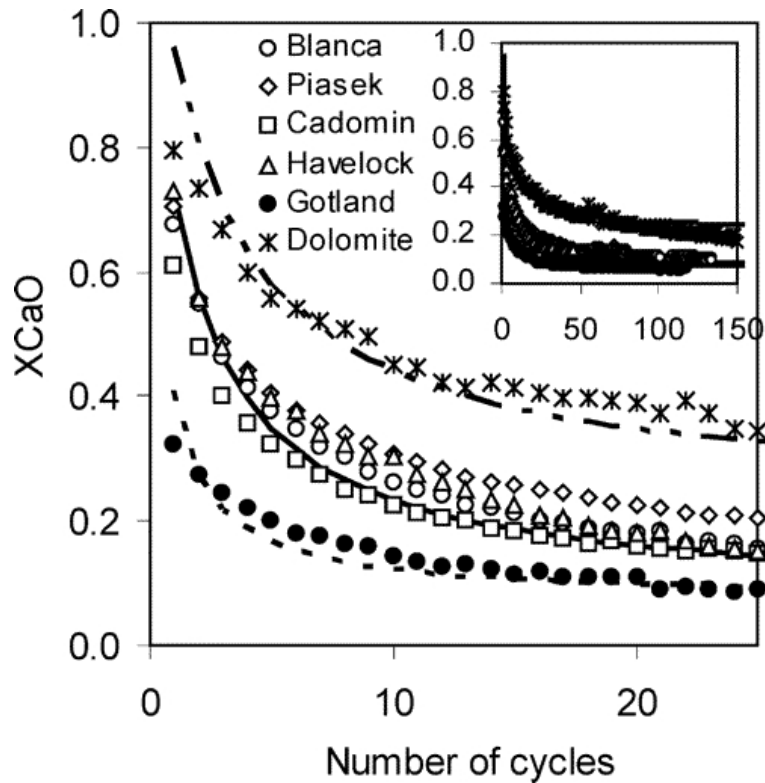
164 4.1. Limestone

165 The reversible carbonation of lime is shown in the following reaction:



166 Most of the investigations performed on natural limestone reactivity for CO₂ capture
167 in calcination/carbonation cycles were executed using either a thermogravimetric
168 analyser (TGA); or less frequently a bubbling FB [50,58], where the sorbent stays in
169 the same reactor as opposed to being transported between two reactors. Although
170 these tests are suitable for sorbent screening purposes, the results are less useful
171 for numerous reasons; for example, they neglect particle attrition during solid
172 circulation as well as phenomena such as reactions with sulphur or ash
173 components.

174 In general, studies on the reactivity of natural limestone show qualitatively the same
175 decay over a number of cycles. Grasa and Abanades [59] tested different types of
176 limestone from different locations (Blanca from Spain, Cadoming and Havelock
177 from Canada, Piasek from Poland and Gotland from Sweden) and a dolomite
178 (approx. 50% MgCO₃) using a TGA. The results presented in Figure 4 show that
179 the decay in carbonation capacity after a number of cycles is a common feature in
180 all types of limestone and for all process conditions. Further investigations with
181 TGAs showed that residual limestone conversion converges to a value of X_r= 0.07-
182 0.08 [34,60,61].



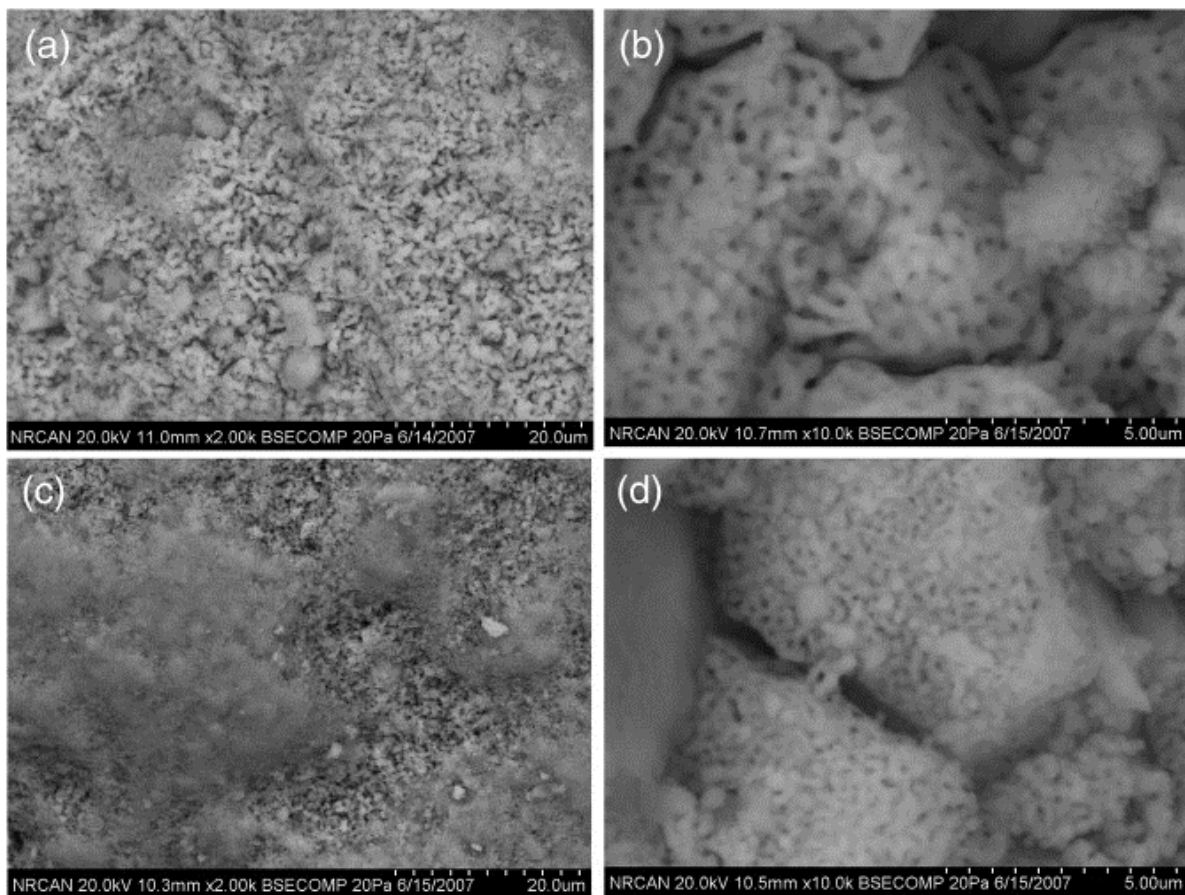
183

184 **Figure 4:** Conversion vs. number of cycles for experiments carried out with different
 185 types of limestone. Particle size 0.4-0.6 mm. Calcination temperature 850°C, 10
 186 min; carbonation temperature 650°C, 10 min; pCO₂ of 0.01 MPa [59]

187 The attrition mechanisms of limestone under FB CO₂ capture conditions are
 188 complex [62]. Chen et al. [63] explored the most important factors that contribute to
 189 attrition in the carbonation reaction and concluded that they are (from most to least
 190 important): carbonation temperature; carbonator superficial gas velocity; exposure
 191 time; and pressure. For calcination, the key attrition parameter is temperature, with
 192 attrition rate increasing with higher temperatures. It was also noted that CO₂
 193 release in this reaction had a more important role than thermal stress. Jia et al. [58]
 194 studied attrition in a small pilot-scale circulating FB reactor and concluded that even
 195 with the limited number of limestone samples tested the results varied considerably
 196 with the type of limestone used. Another important finding was that elutriation of
 197 fines is more pronounced during the first few carbonation/calcination cycles and
 198 then decreases over cycles [52].

199 Arguably, the first demonstration of CO₂ capture in a FB reactor using limestone-
 200 derived sorbent at the pilot plant scale was performed by Lu et al. [29] using a 75
 201 kWth dual FB reactor. The authors found that the capture efficiency dropped from
 202 90% in the first cycle to 72% after 25 cycles, which they attributed to sintering.

203 Figure 5 shows how the micro-porosity of the sample decreased while the macro-
204 porosity increased when the sorbent was subjected to capture/regeneration cycles.
205 As a result of attrition, 50% of the original sorbent was recovered in the cyclones as
206 fines. Finally, the authors concluded that attrition, sulphation and process
207 optimisation needed further investigation in order to understand their influence on
208 the process. More, larger and more realistic pilot plant tests have been performed
209 subsequently; these experiments include 1800 h in the 1.7 MW_{th} unit at CSIC
210 (Spain) [64] with 170 h of stable operation and CO₂ capture close to the equilibrium
211 at a given temperature [65]. Similarly, in Darmstadt University of Technology a 1
212 MW_{th} plant ran during different testing campaigns demonstrating constant CO₂
213 capture in the carbonator of approximately 85% when maintaining 660°C in the
214 carbonator [66]. In IFK (Stuttgart), a 200 kW_{th} plant has run for over 600 h with a
215 capture level above 90% [67].



216

217 **Figure 5:** SEM of surface area of samples from carbonator: (a, b) after 3 cycles; (c,
218 d) after 25 cycles [29]

219 Manovic and Anthony [68] performed a parametric study of CO₂ capture using
220 limestone-based sorbents. The parameters included sorbent particle size,
221 impurities, limestone type, temperature, CO₂ concentration, carbonation/calcination
222 duration and heating rate. It was found that increasing the carbonation
223 temperatures had a negative outcome on long-term sorbent reactivity. The effect of
224 particle size on CO₂ carrying capacity was negligible and the differences
225 encountered were likely due to differences in the content of impurities in different
226 particle size samples. It was also discovered that prolonged carbonation time has a
227 negative impact on sorbent reactivity accelerating its decay. Manovic et al. [69]
228 carried out further investigations on the effect of calcination conditions. This work
229 concluded that high temperatures and CO₂ partial pressures that would be
230 encountered in real systems had a negative effect on the sorbent carrying capacity,
231 which is due to the change in the particle morphology caused by sintering.

232 4.2. Dolomite

233 Dolomite (CaMg(CO₃)₂), which contains about 20% MgO and 30% CaO [70], is
234 another naturally occurring material that can be used as a sorbent for CaL
235 technology, although it is less common than limestone. MgO does not undergo
236 carbonation under typical CaL conditions [71] and, therefore, the stoichiometric
237 capture capacity of calcined dolomite is just 0.46 compared to 0.79 for lime.

238 Although dolomite shows a lower initial CO₂ uptake, it exhibits a higher residual
239 activity (after 20-30 cycles). The reasons for this are that the porosity of the sorbent
240 is preserved by the unreacted MgO and less sintering occurs due to its higher
241 melting point. Valverde, Sanchez-Jimenez and Perez-Maqueda [72] have shown
242 this better performance of dolomite in a TGA under realistic sorbent regeneration
243 conditions (70% vol CO₂ and 950°C).

244 Itskos et al. [73] performed a study in a TGA and concluded that the effect of
245 sulphation on CO₂ capture activity for dolomite was not significantly different than
246 for limestone.

247 4.3. Other natural materials

248 Deshpande and Yuh [74] studied the use of animal products as a CaL sorbent.
249 They tested five different materials: eggs (chicken, duck and ostrich) and sea shells

250 (oyster and clam). The samples were treated with acetic acid and crushed. The
 251 study concluded that using these materials in CaL cycles is cost-effective, but it is
 252 unlikely that these residues can be produced in the quantities needed for the
 253 commercial deployment of CaL. Moreover, they exhibited higher capacity after
 254 water hydration techniques were employed for regeneration of spent sorbent. The
 255 results for the initial CO₂ capture activity can be seen in Table 1.

256 **Table 1:** Waste animal initial CO₂ capture capacity (%) [74]

Sorbent source (type of shell)	Initial CO₂ capture capacity (wt %)
Chicken egg	60
Ostrich egg	45
Duck egg	61
Oyster shell	34
Clam shell	21

257 Sacia et al. [75] investigated pre-treatments using solutions of 1 and 2 M acetic acid
 258 and regeneration using pure water, 0.5 M, 2 M, 5 M, 50%, and glacial acetic acid,
 259 with regenerations performed every 5 cycles. The natural material used in this work
 260 was oyster shells. The authors concluded that the pre-treated samples behaved
 261 better in a TGA (from around 30% conversion in the 5th cycle in untreated shells to
 262 50% conversion in the best case, 1 M for 15 min). Moreover, the regeneration of the
 263 natural material was also successful, especially with 2 M acetic acid. It was also
 264 suggested that acetic acid regenerations tend to renew the initial porosity of the
 265 sorbent.

266 Chicken eggshells and mussel shells have been compared to limestone in a study
 267 performed by Ives et al. [76]. It was found that the CO₂ uptake of the eggshells and
 268 mussel shells was very similar to that of the limestone investigated (Purbeck) over
 269 50 cycles. Therefore, there was no clear advantage of using these natural sorbents
 270 rather than limestone from the reactivity point of view. Shan et al. [77] have also
 271 examined eggshells mixed with bauxite tailings (BT) to see how the latter impacted
 272 the ability to capture CO₂. They found that the addition of BT was beneficial to the
 273 process with a carbonation conversion of 55% after 40 cycles.

274 There is a clear advantage in the use of limestone and other natural materials, its
 275 low price, its availability and its direct use. However, one of the most important
 276 aspects and highlights of limestone use is that it is a highly researched material for

277 SO₂ and CO₂ capture. On the other hand, the decay in reactivity during the capture
278 cycles and attrition require make up of fresh material, which results in reduction in
279 the efficiency of the process and economic penalties. Also, the use of waste
280 materials as a natural source of Ca-based sorbents (marine shells and other
281 animal-derived materials) is a good example of re-use of those materials which
282 otherwise would require disposal and related costs. However, the performance of
283 these sorbents in cyclic FB operation needs to be further investigated, especially
284 taking into account that the particles are of irregular shape, which enhances their
285 attrition.

286 **5. Enhancement of natural sorbents**

287 Although limestone is the cheapest material for the CaL process, its challenges with
288 reactivity decay and attrition have led researchers to modify it to improve its
289 properties whilst maintaining a low cost. These techniques represent a midpoint
290 between the use of natural materials and utilisation of complex techniques for
291 synthesis of sorbents and such solutions are expected to be generally less costly
292 than the production of new sorbents.

293 **5.1. Calcium hydroxide**

294 Calcium hydroxide can be used as a sorbent for the CaL process. However, this
295 material is extremely fragile. Wu et al. [78] performed a study in which they showed
296 that calcium hydroxide has higher sorption capacity, with the maximum CO₂ uptake
297 at 650°C. They showed that the reason for the improved properties of the sorbent is
298 the formation of cracks during the hydration of the material, which results in higher
299 pore surface area and volume. This increased the conversion of CaO by 52% at the
300 20th cycle [79].

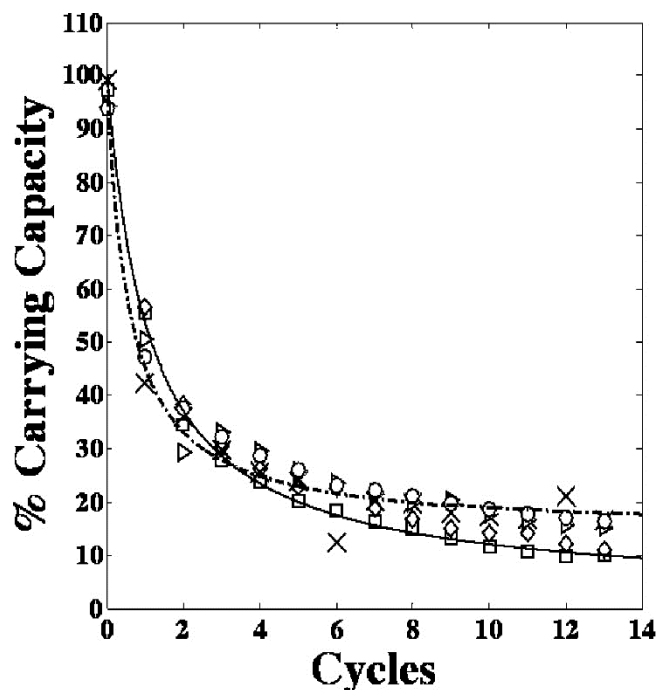
301 Although the morphological properties of calcium hydroxide derived lime are more
302 favourable than that of calcium carbonate derived CaO, the hydrated material is
303 typically soft and not suitable for direct utilisation in FB reactors. Therefore, some
304 type of granulation, extrusion or other treatment would be required, before its final
305 use under realistic CaL conditions. This step would increase the final price of the
306 material.

307 5.2. Doping

308 Researchers have also attempted to decrease the reactivity decay over the cycles
309 through doping of the material to avoid or postpone the sintering.

310 Salvador et al. [50] investigated the addition of sodium chloride (NaCl) and sodium
311 carbonate (Na_2CO_3) using wet impregnation. The addition of NaCl improved the
312 capture capacity, maintaining it at 40% of overall capacity over 13 cycles due to
313 positive changes in the pore structure. However, the addition of Na_2CO_3 had no
314 apparent effect on capture capacity. Both of these tests were performed using a
315 TGA. When the doped sorbents were tested in FB conditions, the sorption capacity
316 of both decreased as a result of pore blocking. These dopants were also studied
317 using a wet impregnation technique by Fennell et al. [46], which consists of pouring
318 a solution of known and very low molarity into the sorbent. Then the mixture is
319 stirred, sealed, decanted and dried. The samples were later tested in a small, hot
320 FB with dilution by sand addition to reduce temperature rises due to the exothermic
321 carbonation reaction. It appears that doping with small quantities of Na_2CO_3 showed
322 a small improvement in the carrying capacity. However, a higher dopant quantity in
323 the solution (more than 0.1 M) had a detrimental effect and decreased the carrying
324 capacity of the limestone sorbent [46].

325 Other tests with KCl and K_2CO_3 using wet impregnation were performed using two
326 types of limestone (Havelock and Imeco) [80]. González et al. [80] concluded that
327 doping with lower solution concentration (0.05 M) improved the performance of both
328 types of limestone. They also suggested that doping with KCl reduced attrition of
329 limestone due to the crystallisation of the dopant in the cracks of the particles. Al-
330 Jeboori et al. [81] performed experiments with other inorganic salts (MgCl_2 , CaCl_2
331 and $\text{Mg}(\text{NO}_3)_2$) and the Grignard reagent (isopropyl-magnesium chloride) [82]. All of
332 these dopants produced some improvement as shown in Figure 6, which is in
333 agreement with the results discussed above [46,80]. In summary, samples doped
334 with lower molarity solutions showed an increase and those with higher ones
335 showed a reduction in the carrying capacity.



336

337 **Figure 6:** Carrying capacity (normalised) for Havelock limestone, plotted against
 338 the number of cycles: (—□—) un-doped, (—◇—) 0.159 mol% Mg(NO₃)₂, (—×—)
 339 0.165 mol% MgCl₂, (▷) 0.138 mol% CaCl₂, (○) 0.15 mol% Grignard reagent [82]

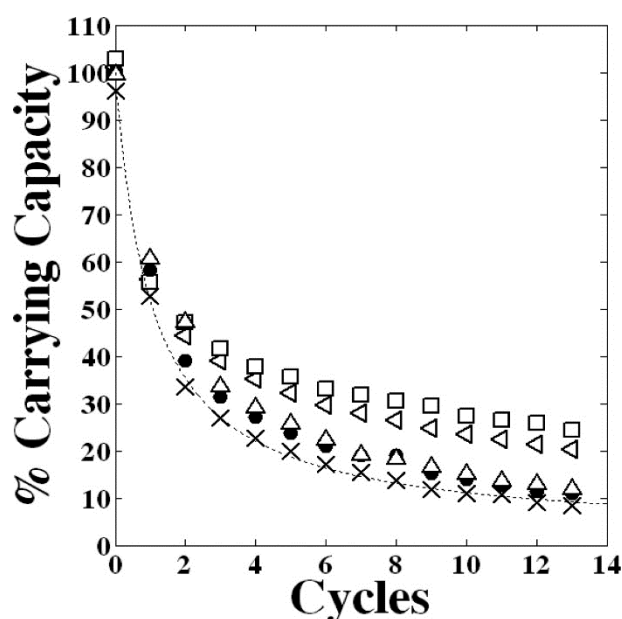
340 Manganese salts (Mn(NO₃)₂ and MnCO₃) also improve the cyclic carbonation
 341 conversion. In a study using wet impregnation, tests in a fixed-bed reactor and a
 342 TGA showed a residual carbonation conversion of Mn(NO₃)₂- and MnCO₃-doped
 343 sorbents of 0.27 and 0.24, respectively, after 100 cycles. Sun et al. [83] also
 344 showed that the sorbent retained an improved pore structure, pore volume and pore
 345 size. Mn(NO₃)₂-doped CaCO₃ achieves the highest cyclic carbonation conversions
 346 when the Mn/Ca molar ratio is 1/100 and the optimum molar ratio of Mn/Ca for
 347 MnCO₃-doped CaCO₃ is 1.5/100.

348 Another suitable doping material is attapulgite (Mg₅Si₈O₂₀(HO)₂(OH₂)₄•4H₂O). The
 349 microstructure of the modified particle was improved by the formation of Ca₂SiO₄,
 350 Al₂O₃ and Ca₃Al₁₀O₁₈; these compounds were distributed in the material, enhancing
 351 the resistance to sintering during multiple cycles [84]. In this work a technique of dry
 352 mixing followed by hydration was applied. The results showed that the hydration
 353 method exhibited 128% higher CO₂ capture performance than undoped limestone.

354 Manovic et al. [85] investigated doping of pellets (calcium oxide and calcium
 355 aluminate cement) with CaBr₂ in the presence of steam during carbonation and
 356 calcination; natural limestone was used as a material for comparison, and both

357 sorbents were tested in a TGA. The findings showed improved performance for
358 both pellets and limestone when doped with low quantities of bromide of 0.2 % mol.
359 The most improved parameter was the conversion rate during the diffusion-
360 controlled stage of carbonation. This type of dopant has been tested in other
361 studies in conjunction with steam addition. Al-Jeboori et al. [81] and Gonzalez et al.
362 [86] concluded that the effects of doping and steam addition were effectively
363 additive, at least at the levels tested.

364 Other types of dopants such as HCl, HNO₃ and HI have been tested with the
365 quantitative wet impregnation method, and all the halogen dopants exhibited an
366 increase in carrying capacity with Havelock doped with HCl and HBr from 0.135 to
367 0.259 mol % and HNO₃ from 0.102-0.205 mol %, and Longcliffe doped with HCl
368 and HBr from 0.102 to 0.189 mol% and HI from 0.15-0.245 mol% [81]. The carrying
369 capacity of Havelock (Canadian) limestone treated with these reagents can be seen
370 in Figure 7.



371

372 **Figure 7:** Carrying capacity (normalised) for Havelock limestone, plotted against
373 the number of cycles: (x) undoped, (□) 0.167 mol% HBr, (sideways open triangle)
374 0.167 mol% HCl, (△) 0.164 mol% HNO₃, (●) 0.167 mol% HI [81]

375 These results encouraged research into the use of other group 1A elements in
376 calcined limestone, such as Li, K, Rb and Cs. The capture performance of alkali
377 metal-doped CaO has been linked to the electro-positivity of the material [87]. The

378 material doped with 20% Cs for instance had higher sorption in the first cycle than
 379 the other materials.

380 Some metal-based dopants have been further investigated, such as γ -Al₂O₃, SiO₂
 381 sands and MgO. Sun et al. [88] also examined other dopants including TiO₂ and
 382 ZrO₂. These materials were tested in a TGA and did not exhibit very promising
 383 results.

384 Doping has been used as an enhancement technique due to the positive effects
 385 that some dopants have on the pore structure, pore volume and pore size. While
 386 this method is not excessively complex, the cost of the dopants should be taken
 387 into account when assessing its economic feasibility. Also, scale-up of the
 388 impregnation techniques is a challenge that has to be resolved before their use at
 389 pilot plant- or demonstration-scale due to the large amount of sorbent that would
 390 need treatment and, therefore, the required space. One especially feasible
 391 possibility is doping with sea water, due to its availability and low cost. This path
 392 would make doping a highly promising enhancement technique.

393 **Table 2:** Summary table of doping

Dopant	Method	Main findings	References
NaCl and Na ₂ CO ₃	Quantitative wet impregnation	NaCl improved the sorbent by 0.15 in relative CO ₂ capture capacity (gCO ₂ /g _{sorbent}) when compared to limestone in TGA after 13 cycles; Na ₂ CO ₃ had no apparent effect. Doping with lower molarity is beneficial	[50]
NaCl and Na ₂ CO ₃	Wet impregnation	Na ₂ CO ₃ in small quantities had a positive effect increasing the carrying capacity by 0.14 gCO ₂ /g _{sorbent} after 20 cycles. Lower molarity beneficial	[46]
KCl and K ₂ CO ₃	Wet impregnation	KCl improved attrition resistance and reactivity by 0.15 gCO ₂ /g _{sorbent} after 15 cycles when compared to limestone. Lower molarity beneficial	[80]
MgCl ₂ , CaCl ₂ and Mg(NO ₃) ₂	Wet impregnation	All dopants showed an improvement of around 10% after 14 cycles in carrying capacity when lower molarity solutions were used	[82]

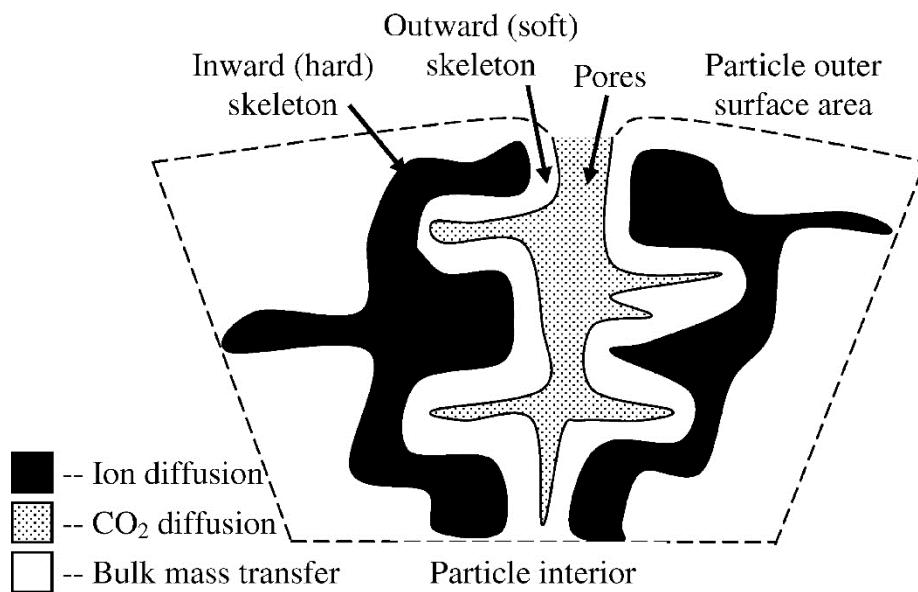
Mn(NO ₃) ₂ and MnCO ₃	Wet impregnation	Observed an optimal Mn to Ca ratio, improved capture capacity by 69% when compared to undoped limestone after 100 cycles	[83]
Attapulgite	Dry mixing and hydration	Hydration showed much better performance (128% increase when compared to limestone after 20 cycles) than natural limestone	[84]
CaBr ₂	Quantitative wet impregnation	Steam addition and doping have additive positive effects on the sorbent going from 22 gCO ₂ /100g _{sorbent} to 31 gCO ₂ /100g _{sorbent} after 11 cycles	[85] [81][86]
Halogen dopants	Quantitative wet impregnation	All of them showed improvement in capacity, especially 0.167% mol HBr which went from 10% carrying capacity of undoped limestone to 25% in the doped sorbent after 14 cycles	[81]
Group 1A elements	Wet impregnation	The performance has been linked to electropositivity with a sorption capacity of 50 wt%CO ₂ /wt%sorbent after 35 min	[87]
Other metal-based materials	Wet impregnation	Al ₂ O ₃ showed promising results from 0.2 CaO conversion to CaCO ₃ of 0.4 when a ratio of 1:1 CaO to Al ₂ O ₃ after 15 cycles	[88]

394

395 5.3. Thermal pre-treatment

396 There have been several studies that demonstrated that thermal pre-treatment was
397 a valid method to improve the conversion of CaO in long series of cycles [89–91]. A
398 theory to explain this behaviour was proposed by Lysikov, Salanov and Okunev
399 [51]. This was based on the formation of a skeleton of interconnected CaO caused
400 by repeated carbonation/calcination cycles; the skeleton acts as an outer reactive
401 CaO layer and stabilises the sorption capacity. Manovic and Anthony [89] followed
402 this work testing samples in a TGA up to very high temperatures (up to 1300°C)
403 under a nitrogen atmosphere. These tests demonstrated that particles were highly
404 sintered and carbonation occurred only on the surface of the solid particle. The
405 model suggests that the pre-treatment results in the formation of an internal
406 skeleton, which protects the integrity of the particle. When sorbents are preheated,
407 after the CaCO₃ decomposes, ion diffusion continues, stabilises the skeleton, but

408 the porous structure in the hard skeleton is able to maintain significant carbonation.
 409 This model is depicted schematically in Figure 8.



411 **Figure 8:** Schematic representation of proposed pore-skeleton model [89]

412 In the early cycles only the less reactive hard skeleton exists, but conversion
 413 increases as the soft skeleton develops. These studies showed that even if the pre-
 414 treated limestone exhibited lower initial sorption capacity, this capacity is
 415 augmented over many cycles owing to the softening of the hard skeleton. A
 416 drawback of this enhancement technique is that although the reactivity was
 417 increased, attrition of the particles rose substantially [92].

418 Thermal pre-treatment has not been successful in all types of limestone [91] and it
 419 is believed that it only works on certain varieties of the natural material. It is
 420 probable that different types of limestone require different conditions for the pre-
 421 treatment due to differences in impurity composition and internal structure [60].

422 With regard to synthetic materials, a study of precipitated calcium carbonate (PCC)
 423 in a slurry bubbling FB used an extra thermal pre-treatment stage for these particles
 424 [93].

425 There are clear advantages to this treatment; it is straightforward and inexpensive.
 426 However, it should be noted that it would require extra energy to heat up the
 427 amount of material needed before its final use. This can result in a decrease of the

428 power output of the power plant. Therefore, the heat integration techniques are
 429 applied, which would requires additional heat exchange systems.

430 **Table 3:** Summary table for thermal pre-treatment

Type of material	Temperature	Main findings	Reference
Kelly Rock, Cadomin, Graymont and Havelock limestone	1100°C	A model with skeleton changes is proposed to explain the reactivation of particles after pre-treatment in long series of cycles, the improvement was of 25% in carbonation conversion of untreated Kelly rock for the 24 h sample treated to 900°C after 30 cycles	[89]
Microna 3 (US limestone) and coarser limestone	1100°C	Material heated for 5 h was found to be more stable than that heated for 2 h with an increase of capacity ($\text{mmolCO}_2/\text{g}_{\text{sorbent}}$) from 7 to 7.4, which is more stable than the material calcined at 900°C after 80 cycles	[90]
La Blanca and Kelly Rock	1000-1200°C	No improvement in La Blanca possibly due to composition (high purity). Not all limestone types are suitable for thermal pre-treatment	[91]
Monodisperse carbonate particles (precipitated CaCO_3 with calcium nitrate and ammonium carbonate)	1100°C and 1300°C	Samples treated at 1100°C are not strong enough to resist sintering under test conditions, but samples treated at 1300°C had a stable carrying capacity of 12% after 200 cycles	[51]
Limestone and dolomite	1000°C	Pre-treatment resulted in benefit in terms of reactivity (improved by about 0.05 in CaO utilization efficiency after 1000 cycles) properties but attrition resistance and mechanical properties were decreased substantially	[92]

431

432 5.4. Chemical treatment

433 This refers to the treatment of limestone with a chemical agent in order to achieve
 434 superior properties. However, the effect on the sorbent may ultimately produce
 435 physical changes in the sorbent morphology.

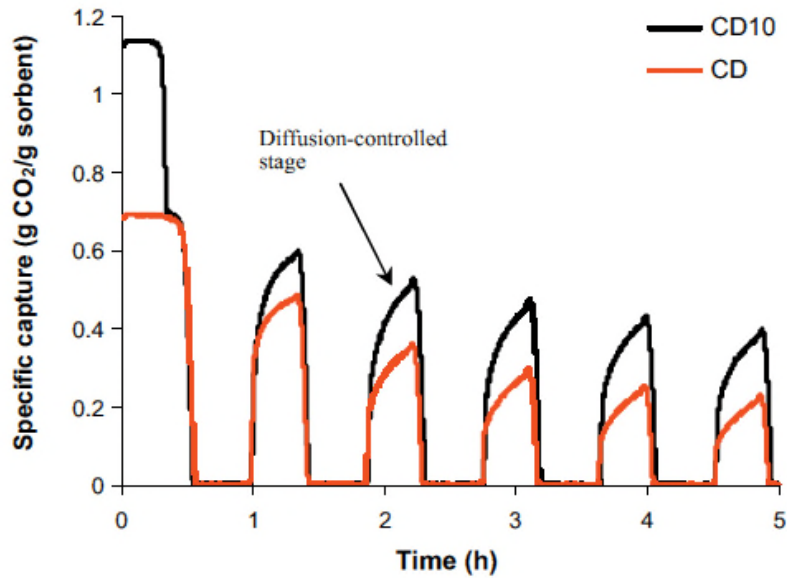
436 Limestone treated with acetic acid results in a modified sorbent with a high capture
437 capacity [70,94]. Natural limestone treated with a 50% acetic acid solution was later
438 tested in two FB reactors; the modified sorbent showed better sintering
439 performance and also more favourable pore area and volume [70].

440 Ridha et al. [95] used calcium aluminate pellets as a base material, the treated
441 synthetic material also exhibited improvement in performance. Treating dolomites
442 with acetic acid has also been studied because of the high sintering resistance of
443 the base material; industrial waste acid from acetate production has been proposed
444 for this treatment in order to reduce costs [70].

445 Other materials besides acetic acid have been proposed as modifying agents for
446 limestone. Ethanol-water solutions have been discussed, and were previously
447 studied for enhancing SO₂ capture, which resulted in increased porosity of the
448 treated material as a side benefit [96]. This particular treatment gave improved
449 capture capacity, which was increased as the ethanol concentration was raised
450 [97]. However, the high price of ethanol is a drawback for this treatment and further
451 studies need to be done to assess the potential of the procedure.

452 Propionic acid has been studied for sorbent chemical pre-treatment. In a small
453 molar ratio (4:1 CaO to propionic acid), the modified sorbent exhibited a capture
454 capacity of 0.24 after 100 cycles, approximately four times the capacity of natural
455 limestone [98].

456 Pyroligneous acid (PA) has also been investigated [99], revealing that it produces a
457 main phase of calcium acetate hydrate in the modified sorbent. PA-treated
458 limestone displayed a higher carbonation rate than natural limestone as well as
459 improved porosity. Figure 9 shows the effect of such a treatment (here CD10 is the
460 sample treated with PA and CD is the untreated limestone).



461

462 **Figure 9:** Carbon capture profile as a function of time. Calcination at 850°C in N₂
 463 for 5 min and carbonation at 650°C in 15% CO₂ for 20 min [100]

464 Formic acid has also been studied, showing results in line with those exhibited
 465 above with higher capture capacity [100]. In addition, Ridha et al. [101] carried out
 466 a study of various acid treatments, which showed that the reactivity over cycles was
 467 enhanced albeit that the activity was found to decline in a similar manner to that for
 468 natural-based sorbents.

469 Although this treatment presents reactivity benefits such as increased pore volume
 470 and pore surface area, it has two drawbacks the cost and availability of the acid;
 471 and the marginal increase in CO₂ uptake. It should also be noted that the final
 472 benefit of this procedure depends heavily on limestone type and origin, and the acid
 473 used. Moreover, this technique would increase the cost of the overall process
 474 significantly, which diverges with the main aim of trying to keep the capture costs
 475 low. It is expected that treated sorbent would react rapidly with SO₂, which would
 476 incur in sorbent poisoning and would eradicate the higher reactivity achieved by this
 477 treatment.

478

479

480

481

482 **Table 4:** Summary table of acid pre-treatment

Acid used for treatment	Material treated	Reactor	Conditions	Main findings	References
Acetic acid	Limestone	Twin fixed-bed reactor	Calcination 920-1100°C in 80% CO ₂ 20% O ₂ (%vol) Carbonation 550-750°C in 15% CO ₂	Treated sorbent had higher carbonation levels (0.4 carbonation conversion compared to less than 0.1 for untreated material after 20 cycles), better carbonation kinetics and delayed degradation	[94]
Acetic acid	Limestone	Twin fixed-bed reactor	Calcination 920-1100°C in 80% CO ₂ 20% O ₂ (%vol) Carbonation 550-750°C in 15% CO ₂	Treated sorbent had higher resistance to sintering due to smaller grain size and better pore structure with a conversion of the original limestone of 0.15 after 20 cycles and of the modified sorbent of 0.5 after 20 cycles	[70]
Acetic acid	Kaolin-derived Al(OH) ₃ pellets	TGA	Calcination 920°C in pure CO ₂ or 850°C in pure N ₂ Carbonation 650-700°C in 15% CO ₂	Pellets with acetified lime showed better performance than untreated pellets and limestone and also had higher porosity but poorer CO ₂ capture in the presence of SO ₂ (from 18% of the treated sample to 29.2 % of natural limestone after 5 cycles)	[95]
Acid waste from acetate production	Dolomite	Twin fixed-bed reactor	Calcination 850-1100°C in 80% CO ₂ 20% O ₂ (%vol) Carbonation 550-750°C in 15% CO ₂	Higher carbonation conversion than unmodified sorbent (from 0.2 to 0.45 after 20 cycles), improved sintering behaviour at high temperature, higher surface area	[70]
Ethanol-water solution	Lime (Calcined)	Twin fixed-bed reactor	Calcination 920°C in 80% CO ₂ 20% O ₂ (%vol) Carbonation 550-750°C in	Carbonation conversion of modified sorbent twice as high as lime from 0.25 in	[97]

	limestone)		15% CO ₂	the untreated sample to 0.51 in the ethanol treated sample after 15 cycles. Higher ethanol concentration in the solution enhanced resistance to sintering	
Propionic acid	Lime (Calcined limestone)	Dual fixed-bed reactor	Calcination 850-950°C in 100% N ₂ (%vol) Carbonation 650-700°C in 15% CO ₂	Modified limestone had faster carbonation rates and higher carbonation conversion (from 0.31 for the treated sample after 100 cycles to 0.08 for the untreated sample after 100 cycles) under realistic conditions. Modified sorbent was more resistant to sintering	[98]
PA	Limestone	TGA	Calcination 850-1000°C in 100% N ₂ (%vol) Carbonation 600-700°C in 15% CO ₂	Main component of the modified limestone was calcium acetate hydrate. Modified limestone had higher carbonation conversion (from 0.078 after 103 cycles for the untreated sample to 0.33 for the treated sample) and better pore structure	[99]
Formic acid	Lime (Calcined limestone)	TGA	Calcination 850°C in 100% N ₂ (%vol) Carbonation 650°C in 15% CO ₂	Sorbent morphology was insensitive to acid solution concentration. Liquid solution performed better, it captured 67.4 % more CO ₂ than the natural material after 20 cycles	[100]
Organic acids (acetic, vinegar, formic and oxalic acid)	Limestone	TGA	Calcination 850°C in 100% N ₂ (%vol) Carbonation 650°C in 15% CO ₂	The best organic acid treatment was with oxalic acid with 0.25 gCO ₂ /g _{sorbent} when compared to 0.13 gCO ₂ /g _{sorbent} of limestone after 20 cycles, but all of these treated sorbents exhibited better CO ₂ uptake than untreated	[101]

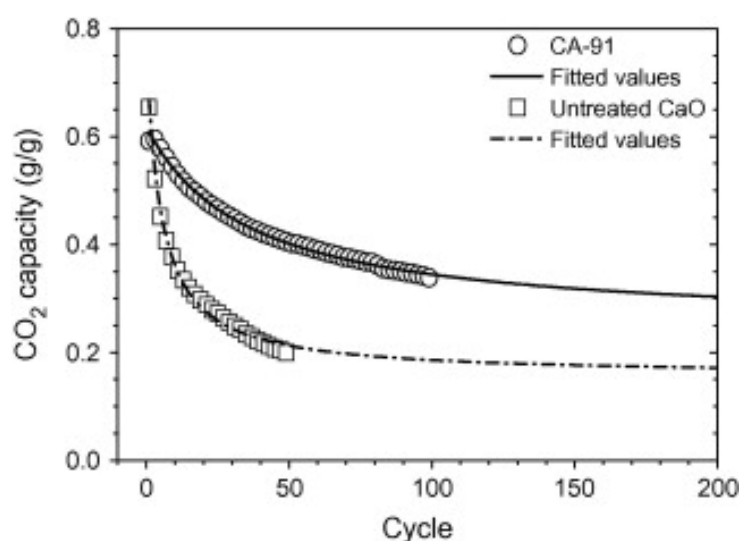
483 6. Synthetic sorbents

484 In this section, new methods for producing synthetic sorbents will be discussed and
485 their suitability for scale up, FB operation and cost will be assessed.

486 6.1. Sorbents from organic-acid precursors

487 Several complex procedures have been developed to synthesise new sorbents
488 using acid treatments; these sorbents often have alumina (Al_2O_3) or other similar
489 material as a support. The process comprises an active component integrated with
490 an inert support diluted in an acid solution [102,103].

491 Citric acid can be used for producing this type of material, for example. Aluminium
492 nitrate is dissolved in citric acid and calcium carbonate is added. The mixture is
493 then stirred, aged, dried, crushed, sieved, and heated in a four-step activation
494 procedure to obtain the $\text{Ca-Al}_2\text{O}_3$ sorbent [102]. The heating procedure appears to
495 favour the formation of the porous structure in synthetic sorbents due to the mild
496 conditions employed. The results of this study by Zhang et al. [102] revealed high
497 sintering resistance due to the formation of $\text{Ca}_3\text{Al}_2\text{O}_6$ and also an increased capture
498 capacity as shown in Figure 10.



499

500 **Figure 10:** Evaluation of the long-term cycles of sample CA-91 (with 9% Al_2O_3) and
501 untreated CaO in TGA (carbonation 650°C for 30 min in 20% CO_2 ; calcination at
502 850°C for 10 min in 20% CO_2) [102]

503 A modification of this method was proposed by Li et al. [103] using glycerol and
504 water instead of citric acid in an attempt to reduce reagent costs. The resulting
505 sorbent also exhibited better results than raw limestone. Li et al. [104] also
506 developed a similar technique using carbide slag instead of limestone, which
507 exhibited better CO₂ uptake results than carbide slag without modification .

508 A less expensive route for obtaining an alumina support utilises kaolin [105]. In this
509 study kaolin was calcined, the CaO was dispersed in water and ethanol and then
510 metakaolin was added at different ratios. Finally, the mixture was acid-activated
511 with hydrochloric acid, dried and calcined. The results exhibited higher carbonation
512 in the first few cycles, but the sintering of the particles was also higher than for
513 natural material.

514 SiO₂ can be used as a support in a similar way to the alumina-based sorbents. In
515 such a study, 12 g of limestone was diluted in water and then added to a gelatinous
516 solution containing 0.72 g of type A gelatine and 45 g of water. Then the mixture
517 was added to an acidified sodium silicate solution, stirred, thermally treated and
518 activated by calcination at 600°C [106]. The resulting sorbent was then pelletised
519 due to the initial unsuitability for use in FBs. These samples showed an increase in
520 the carbonation conversion rate of 25% compared to natural sorbents after 50
521 cycles; this was believed to be related to the creation of a mesoporous silica
522 framework structure.

523 MgO has also been proposed as a support [107] showing slightly better
524 performance than natural dolomite, indicating that molecular level mixing of CaO
525 and MgO can be achieved with this methodology. Finally, in a recent study carried
526 out by Zhao et al. [108], the effect of ZrO₂ as an additive to improve stability was
527 studied. Ca(OH)₂ was mixed with hydrolysed zirconyl nitrate under vigorous stirring,
528 then aged, dried and calcined. The most durable composition under severe
529 calcination conditions (950°C and 100% CO₂) was 30% CaZrO₃/70% CaO powder
530 with a capture capacity of 0.36 g of CO₂/g sorbent in cycle 1, declining to 0.31 by
531 cycle 30.

532 In some of these studies the sorbents were exposed to heat treatment, which
533 caused an increase in the porosity of the resulting sorbent. Moreover, if additives or
534 supports were included in the solution the stability of the synthetic particles was

535 improved, which resulted in an increase of reactivity. However, further studies of
 536 these materials in FB environments need to be performed in order to investigate
 537 attrition resistance and to determine the performance of the particles in long series
 538 of cycles. Also, these techniques use some type of heat for the particle production
 539 (at high or low temperature) of the material before calcination, which will add extra
 540 cost to the process due to the high energy consumption before entering in the
 541 reactor. Moreover, the precursors needed are fairly expensive materials.

542 **Table 5:** Summary of synthetic sorbents derived from organic-acid precursors

Organic-acid precursor and support	Reactor	Conditions	Main findings	References
Citric acid with aluminium nitrate	TGA	Calcination 850°C in 100% N ₂ (%vol) Carbonation 600°C in 20% CO ₂	Activation of material with four-step heating (high energy consumption), better porous structure and higher sintering resistance than natural limestone (0.30 g/g after 200 cycles and 0.17 g/g after 200 for limestone)	[102]
Glycerol-water solution and aluminium nitrate hydrate (limestone)	Dual fixed-bed reactor	Calcination 850-950°C in 100% N ₂ or CO ₂ (%vol) Carbonation 650-725°C in 15% CO ₂	The modified structure was CaO/Ca ₃ Al ₂ O ₆ ; the CO ₂ uptake capacity after 50 cycles was six times higher (0.43 g/g) than natural limestone. The sintering resistance was higher than untreated sorbent	[103]
Glycerol-water solution and aluminium nitrate hydrate (carbide slag)	TGA	Calcination 850°C in 100% N ₂ (%vol) Carbonation 700°C in 15% CO ₂	Synthetic sorbent had 2.5 times higher CO ₂ capacity than carbide slag by the 20 th cycle. The sintering of new sorbent was higher due to the mechanical support of Ca ₃ Al ₂ O ₆	[104]
Ethanol-water solution and metakaolin	Twin fixed-bed	Calcination 850°C in 100% N ₂ (%vol) Carbonation 700°C in 15% CO ₂	Enhanced sintering of CaO and loss of sorption during cycles, higher conversion from 0.3 to 0.65 after 25 cycles	[105]
Gelatine-water with acidified sodium silicate then pelletised	TGA	Calcination 850°C in 100% N ₂ (%vol) Carbonation 650°C in 100% CO ₂	This method did not produce suitable particles for FB operation so they had to be pelletised. The carbonation conversion rate was 25% higher than limestone after 50 cycles	[106]
Aqueous solution of Ca and Mg acetates	TGA	Calcination 758°C in 100% He (%vol) Carbonation 758°C in 100% CO ₂	Higher conversion than dolomite (53 wt% CO ₂ after 50 cycles for the treated sample and 26 wt% CO ₂ for dolomite) due to molecular mixing of CaO and MgO	[107]
Ethanol with ammonium hydroxide solution and ZrO	TGA	Calcination 800°C in air (mild conditions)	The Zr-modified sorbents had more favourable performance. Under severe conditions the	[108]

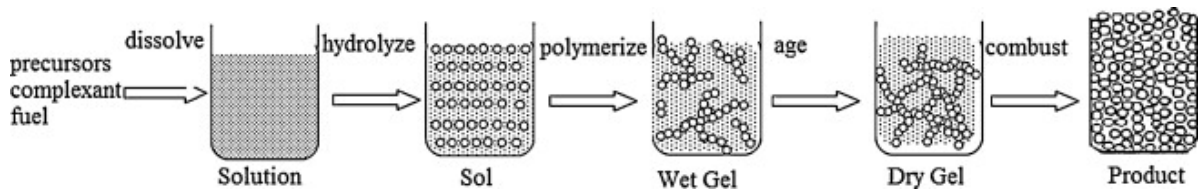
nitrate	100% CO ₂ (severe conditions) (%vol) Carbonation 650°C in 15% CO ₂	most durable composition was produced with a composition of 30% CaZrO ₃ /70% CaO
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543

544 **6.2. Sol-gel combustion synthesis**

545 This method was first proposed by Luo et al. [109] for CaO-based sorbents and
 546 their work was extended in a subsequent study [110]. It included the following
 547 procedure: Predetermined quantities of La(NO₃)₃.6H₂O or Al(NO₃)₃.9H₂O and
 548 Ca(NO₃)₂.4H₂O were added to distilled water with a weight ratio of CaO to La₂O₃ of
 549 80:20 and the mole ratio of water to metal ions of about 40:1. Citric acid was added,
 550 stirred and dried to form the sol, which was then left at ambient temperature for 18
 551 h to form a gel. The gel was dried, and then calcined in a muffle furnace at 850°C
 552 for 2 h. Sorbents generated in this study showed better performance than those
 553 containing mayenite (Ca₁₂Al₁₄O₃₃) in their structure due to the effect of La₂O₃ in
 554 delaying sintering and absorbing extra CO₂ in the process. However, the problem of
 555 loss in reactivity was still present.

556 The process is illustrated in Figure 11.

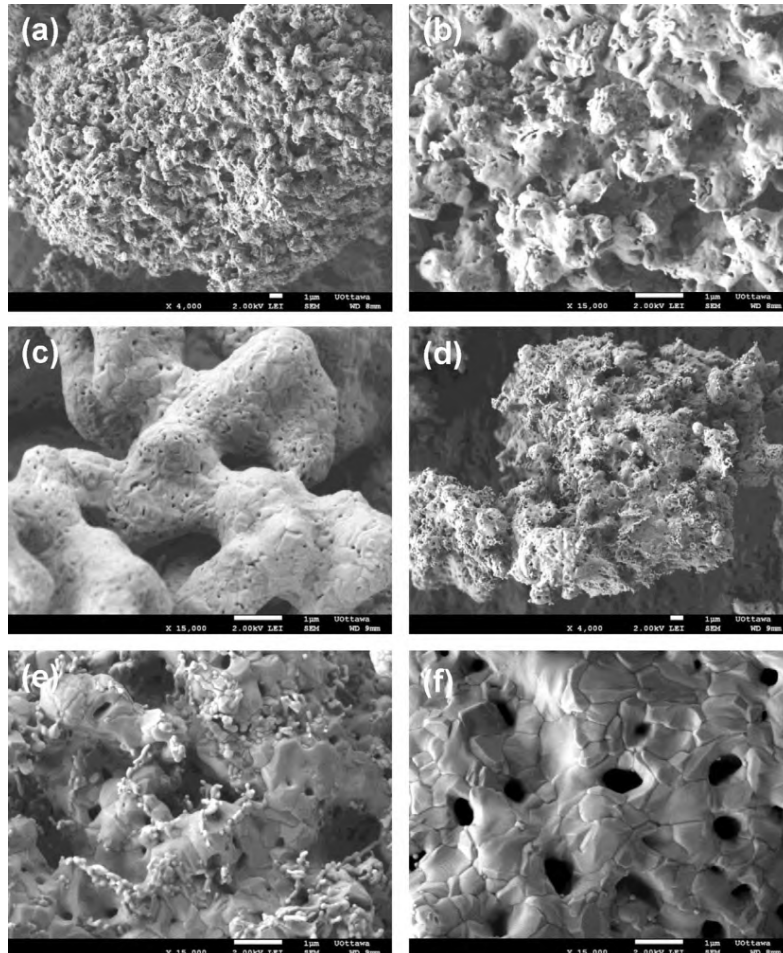


557

558 **Figure 11:** Manufacturing steps of the standard sol-gel combustion process [111]

559 Further studies were performed by Luo et al. [111] creating a simplified method.
 560 The main differences between the methods were that the duration of the process
 561 steps was shortened, and the amount of water used was significantly less. They
 562 concluded that the standard sol-gel method produced sorbents with high CO₂
 563 capture under mild calcination conditions (800°C under 100% N₂) and could
 564 maintain a quite high reactivity of 0.20 g CO₂/g sorbent after 20 cycles, under more
 565 realistic calcination conditions, 950°C under 100% CO₂. The porous microstructure
 566 was found to be favourable for the reaction and the sintering resistance was better
 567 than natural limestone.

568 Other materials have been prepared [112] following similar techniques containing
569 primarily two phases: $\text{Ca}_9\text{Al}_6\text{O}_{18}$ and CaO , and Figure 12 provides SEM images
570 comparing the pure CaO and the modified sorbent. It can be seen how the structure
571 of the sol-gel material is less sintered when compared to the pure CaO .



572

573 **Figure 12:** SEM images of CaO SG (sol gel) and pure CaO . (a) and (b) CaO SG
574 mild conditions; (c) pure CaO mild conditions; (d) and (e) CaO SG under severe
575 conditions; (f) pure CaO under severe condition [112]

576 The stability of this sorbent was attributed to the dispersion of $\text{Ca}_9\text{Al}_6\text{O}_{18}$ in the CaO
577 matrix, which eventually controlled sintering.

578 Angeli, Martavaltzi and Lemonidou [113] used triethanolamine (TEA) as a
579 complexing agent and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as metal precursors. The
580 formation of TEA-ion complexes ensured that the dispersion of Ca and Al formed a
581 coral-like structure. The sorbent showed higher stability than previous sorbents [32].
582 Nonetheless, the high temperatures in calcination and the presence of CO_2
583 increased sintering.

584 Different supports, such as Zr, can be used in sol-gel techniques [114–116]. These
 585 showed a similar CO₂ uptake than the other particles synthesised with this
 586 procedure.

587 Although the porosity and stability were increased using this method in all the
 588 studies mentioned, a number of issues need to be addressed before such
 589 approaches can be applied on a large scale, including the attrition properties, the
 590 effect of gaseous impurities (SO₂), and the cost and lack of availability of large
 591 quantities of the modified sorbent.

592 Recently, there have been efforts to mitigate attrition of the particles by producing
 593 pellets using extrusion equipment in order to increase mechanical strength. In a
 594 recent study by Luo et al., the high reactivity of the sol-gel CaO powder was
 595 retained and its cyclic durability was higher than limestone and sol-gel powder
 596 [117]. However, this process needs further study with regard to attrition and
 597 durability of this sorbent in a FB environment. It is likely possible that these
 598 materials would need besides the costly preparation process some type of
 599 granulation that would incur in a cost rise and even a more complex procedure.

600 **Table 6:** Summary table for sol-gel combustion method

Support precursor	Reactor	Conditions	Main findings	References
La(NO ₃) ₃ or Al(NO ₃) ₃	Twin fixed-bed	Calcination 850°C in 100% N ₂ (%vol) Carbonation 850°C in 100% CO ₂	La(NO ₃) ₃ as an additive showed better performance (0.58 g CO ₂ /g _{sorbent} after 11 cycles) than Al(NO ₃) ₃ (0.48 g CO ₂ /g _{sorbent} after 11 cycles) using SGCS (Sol-gel-combustion-synthesis method). The baseline CaO captured 0.2 0.58 g CO ₂ /g _{sorbent} after 11 cycles.	[109]
La(NO ₃) ₃	Fixed-bed reactor	Calcination 850°C in 100% N ₂ (mild conditions) or 950°C in 100% CO ₂ (severe conditions) (%vol) Carbonation 650°C in 100% CO ₂	Tested under realistic conditions and high CO ₂ concentrations, with 20% carbonation conversion after 25 cycles for CaO and 42% carbonation conversion for the the sol-gel derived sorbent	[110]

La(NO ₃) ₃	TGA	<p>Calcination 850°C in 100% N₂ (%vol)</p> <p>Carbonation 650°C in 15% CO₂</p>	Compared simplified method with standard sol-gel method, the latest gave better results with a 49% conversion for the standard after 20 cycles and a 28% for the simplified sol-gel method	[111]
Aluminium isopropoxide(Al(O-iPr) ₃)	TGA	<p>Calcination 800, 850, 900, 930°C in 100% N₂ (%vol)</p> <p>Carbonation 650, 700°C in 100% CO₂</p>	A phase of Ca ₉ Al ₆ O ₁₈ was formed stabilising the structure and controlling sintering; attrition of sorbents produced by this method was an issue. The cyclic sorption was of 58.9 wt % for the sol gel material and a 34.8 wt% for pure CaO after 32 cycles	[112]
Aluminium nitrate hydrate (TEA as complexing agent)	TGA	<p>Calcination 800°C in 100% N₂ (%vol)</p> <p>Carbonation 690°C in 15% CO₂</p>	The complexing agent ensured the uniform distribution of Ca and Al ion which increased the stability of the sorbent with a 81% conversion after 50 cycles compared to 53% of pure CaO	[113]
High aluminium-based cement	TGA	<p>Calcination 850°C in 100% N₂ (%vol)</p> <p>Carbonation 650°C in 15% CO₂</p>	Pelletised material was prepared to solve attrition challenges with promising results with 0.43gCO ₂ /g _{sorbent} after 50 cycles when compared to 0.09 g CO ₂ /g _{sorbent} of lime	[117]

601

602 6.3. Precipitated calcium carbonate (PCC)

603 Gupta and Fan [93] performed synthesis of CO₂ sorbents using PCC. The
 604 procedure bubbled CO₂ through a Ca(OH)₂ slurry. PCC achieved high capture
 605 capacity which was accredited to the low predisposition of meso-porous sorbents to
 606 pore filling and plugging. In TGA testing, almost complete regenerability of PCC
 607 was found during the first 2-3 cycles; however, the long-term reactivity under a
 608 large number of cycles was not studied.

609 The design of a slurry bubble column was proposed to produce precipitated calcium
 610 carbonate using Al(NO₃)₃.9H₂O and Ca(OH)₂ slurry [118]. TGA tests with this

611 sorbent were quite positive, showing a high conversion of 33% by the 33rd cycle.
 612 Nonetheless, FB reactor experiments showed that the inert support was not an
 613 effective component in comparison with normal PCC.

614 MgO was proposed as a support for the co-precipitation technique. Aqueous
 615 solutions containing Ca acetate and Mg acetate with 1 M Na₂CO₃ were precipitated,
 616 filtered, washed, dried and calcined. In this study several techniques for the addition
 617 of MgO were studied. The one that gave the worst performance was the co-
 618 precipitation technique which produced sorbents with less than 10% carrying
 619 capacity after 30 cycles [107].

620 The porosity of the material is increased by this procedure, but there is no in-depth
 621 study of the mechanical properties of the particles produced using this
 622 methodology, and it is expected that the particles are mechanically weak due to the
 623 production method. Also, the scalability must be carefully investigated in order to
 624 see if this method is economically feasible at large scale.

625 **Table 7:** Summary table for PCC

Method	Reactor	Conditions	Main findings	References
Slurry bubble column for PCC	TGA	Carbonation 550, 600, and 650°C in 100% CO ₂ Cyclic conversion: Calcination 700°C in 100% N ₂ (%vol) Carbonation 700°C in 100% CO ₂	Natural sorbents failed to carbonate completely. The PCC sorbent achieved 90% conversion in carbonation. The cyclic studies did not show relevant sintering in PCC at 700°C	[93]
Slurry bubble column for PCC	TGA	Calcination 900°C in 15% CO ₂ (%vol) Carbonation 650°C in 15% CO ₂	The highest capacity was the pure PCC with 20 gCO ₂ /g _{sorbent} (%) after 15 cycles	[118]

626 **6.4. Dry mixture and coating**

627 Dry mixing of two precursors is probably the simplest way of producing a synthetic
 628 sorbent for the CaL process. This has been studied for materials with Si as an inert
 629 solid support [119,120]. The calcium precursor and support are mixed in a ball-mill-
 630 like device, then pressed into a disc shape and calcined in N₂ atmosphere.

631 Ca_2SiO_4 reacts with CO_2 during the carbonation while SiO_2 acts as an inert support.
632 The results showed a CaO conversion of 41% in the 13th cycle at 800°C in 15%
633 CO_2 [119]. MgO has also been physically mixed with $\text{Ca}(\text{CH}_3\text{COO})_2$ using a ball mill
634 and calcined afterwards, showing great stability and CO_2 capacity of 43% after 50
635 carbonation/calcination cycles [107]. Luo et al. [121] added La_2O_3 and CaCO_3 with
636 dry physical mixing. This sorbent showed slightly better performance than natural
637 limestone. However, such marginal improvements are likely to be overshadowed by
638 cost issues, which may make this technique impractical for large-scale projects.

639 Coating is another technique that can be employed to produce suitable particles for
640 CaL. Atomic Layer Deposition (ALD) deposits thin films of functional materials using
641 sequential, self-limiting surface reactions allowing control of the thickness deposited
642 on the particle [122,123]. ALD was used to coat limestone particles with amorphous
643 silica [124]. The coated particles exhibited a stable capture capacity during tests.
644 This indicates that the nanosilica coating acts as a thermally stable support to
645 mitigate sintering of lime during the calcination stage.

646 Peng et al. [125] developed another methodology for nano/micron-particle coating
647 called self-assembly template synthesis (SATS) which followed a procedure to coat
648 micron- Al_2O_3 with nano- TiO_2 . The material was synthesised with SATS as well as
649 prepared by wet impregnation with CaO (80 wt%) and Al_2O_3 (20 wt%) and
650 limestone obtained from calcium acetate monohydrate. These three resulting
651 sorbents were tested in a TGA at 700°C with 10% vol CO_2 for carbonation and pure
652 N_2 for calcination to represent mild conditions and at 900°C in pure CO_2 to
653 represent more realistic calcination conditions. The SATS sorbent exhibited much
654 better CO_2 capture capacity in both mild and extreme conditions with approximately
655 0.47 $\text{gCO}_2/\text{gsorbent}$ after 30 cycles in comparison with 0.27 $\text{gCO}_2/\text{gsorbent}$ for the
656 CaO. Peng et al. [126] performed tests in a batch FB with the same materials. The
657 findings agree with the results mentioned before with a CO_2 capture capacity of
658 0.78 $\text{molCO}_2/\text{molCaO}$ after 10 carbonation/calcination cycles.

659 Dry mixture is the simplest and most inexpensive technique to incorporate a
660 support material into a CaO-based matrix. However, the enhancement in
661 performance was found to be marginal; therefore, unless other materials show a
662 greater improvement in conversion, this method is of limited benefits.

663 There is a clear advantage in using ALD, which is the extremely stable material
664 than can maintain a high reactivity over long series of cycles. Such high reactivity is
665 caused by the insertion of a thermally stable support that delayed sintering.
666 Nonetheless, there are several drawbacks to this technique. Namely, the process of
667 the ALD reaction, needed to coat the material, is very slow. This would be a major
668 limitation for the production of large quantities of this sorbent. Moreover, there are
669 several limitations on the materials that can be used as a coating agent (i.e. the
670 precursors have to be volatile, but not decompose) [127].

671 6.5. Granulation

672 Granulation of materials for utilisation in CaL is a method of incorporating a support
673 material into CaO to obtain a highly attrition-resistant material. However, such
674 treatments must not adversely affect the sorbent reactivity. Thus for example,
675 Manovic and Anthony [128] suggested that Na_2CO_3 and bentonite, although
676 possessing the required binding properties, are not suitable due to their sintering
677 and loss of CO_2 -capture capacity. XRD analysis revealed that local eutectic
678 mixtures were formed. The authors recommended the use of calcium aluminate
679 cement as it does not enhance sintering of the material. These cements also have
680 other benefits such as fast setting, good refractory properties, low cost and ready
681 availability.

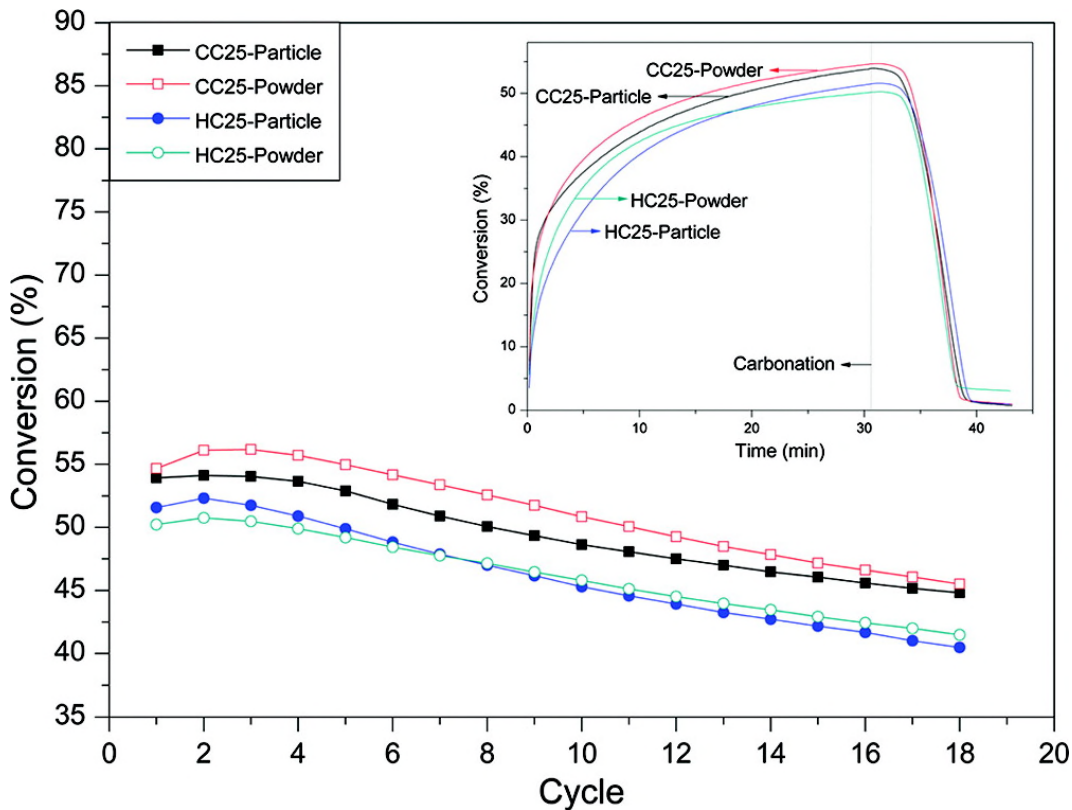
682 Pelletisation with calcium aluminate cements was further explored by Wu et al.
683 [129]. The particles were tested in a TGA with repeated carbonation/calcination
684 cycles at 800°C . Further, attrition tests were performed in an atmospheric bubbling
685 FB. The results showed better performance for the pelletised material with and
686 without the cement binder and higher attrition resistance during fluidisation in a
687 bubbling bed than regular limestone. Moreover, the particles containing the
688 aluminate cement showed more stable CO_2 carrying capacity over long-term cycle
689 tests.

690 Later, the acidification of these pellets was investigated [130] as an option to
691 improve the performance of pelletised sorbent. Samples acidified with 10% acetic
692 acid solution exhibited better behaviour than samples treated with acid vapours.
693 However, the acid and the modification procedure are neither simple nor
694 inexpensive and this technique, therefore, appears to offer marginal benefits. The

695 same group also proposed using kaolin as a potential precursor for $\text{Al}(\text{OH})_3$ (using
696 a leaching method) and raw kaolin for the pelletisation of acetified limestone [131].
697 This procedure displayed better results than the raw kaolin due to the dispersion of
698 $\alpha\text{-Al}_2\text{O}_3$ generated by the leached $\text{Al}(\text{OH})_3$ which enhanced the resistance and
699 stability of the sorbents and the accessibility of CO_2 to the interior of the pellets.

700 While granulation devices are usually used for this technique, extrusion equipment
701 can also be employed [132]. The samples in this study exhibited good attrition
702 resistance and mechanical strength; commercial cement from Kerneos Aluminate
703 Technology containing 37 wt% CaO and 39.8% Al_2O_3 was used as a binder and
704 also as a support material. The difference in CaO conversion between the samples
705 used in this investigation is shown in Figure 13. Carbide slag has also been used as
706 an initial material for extruded-spheronised pellets [133]. In this work the addition of
707 biomass and the use of cement with 50 wt% Al_2O_3 was studied as well as the effect
708 of calcination temperature and pellet size. The results demonstrated that cement
709 addition should be limited to 10 wt% in order to maintain a high CO_2 capture
710 capacity. Pellets doped with pre-washed rice husk showed better CO_2 uptake than
711 un-doped particles.

712



713

714 **Figure 13:** CaO conversion of original extruded particles and crushed limestone
 715 (CC - reagent calcium hydroxide used as a precursor, HC - commercial hydrated
 716 lime used as a precursor [132]

717 Knight et al. [134] have performed attrition tests with pellets prepared in
 718 CanmetENERGY, Canada. Experimental results suggested that cement-bound
 719 pellets underwent attrition to a similar or greater degree than natural limestone. The
 720 pellets that showed the best results were silica-coated. However, more tests need
 721 to be performed varying the size and humidity as well as further analysis on the
 722 kinetics, economics and environmental properties of such sorbents.

723 Ridha et al. [135] performed attrition tests in a pilot dual FB on calcium aluminate
 724 cement pellets (90 wt% lime, 10 wt% calcium aluminate cement) using Cadomin
 725 limestone from Canada and Spanish limestones. The results showed that around
 726 50% of the sorbent by mass was smaller than 250 μm . The authors concluded that
 727 the size distribution of the pellets indicated that the attrition tendencies were similar
 728 regardless of the type of limestone used.

729 Ridha et al. [136] noted that biomass was potentially a readily available and
 730 inexpensive material for increasing the porosity of the pelletised sorbent particles,
 731 and in their work the resulting sorbents demonstrated capture capacity of 0.41 g

732 CO₂/g sorbent (prepared with 10% powdered leaves) after 20 cycles with 15%
733 steam present. Before the addition of the templating material to the pelletiser, the
734 biomass was ground and sieved to < 30 µm in diameter. Pellets with leaves,
735 cardboard, date seeds and white soft wood were studied. The most promising
736 material was the one templated with leaves, which exhibited a 33.3% higher CO₂
737 capture than pellets without leaves. All the particles with biomass components
738 displayed better results than those without biomass. Erans et al. [137] studied flour
739 as a biomass-templating material in both TGA and bubbling FB. The synthetic
740 materials displayed better performance than limestone; however, BFB testing
741 proved that the attrition and fragmentation in biomass-templating materials is higher
742 than in calcium aluminate pellets.

743 Materials used for templating pellets have been further studied by Sun et al. [138]
744 where three different types of pellets were produced: non-shell pellets, core-in-shell
745 with cement shells, and core-in-shell pellets with cement and lime shells. These
746 samples were tested in a TGA (carbonation 650°C in 15 vol% CO₂, calcination
747 900°C in 100 vol% N₂). The most promising sample taking into account the capture
748 capacity and sorbent strength was the material with 10% lime added to the cement
749 shell, which demonstrated a capture of 0.165 gCO₂/gcalcined sorbent after 17
750 cycles. The authors suggested that adding lime to the inert shell in small quantities
751 had a beneficial effect in both the capture capacity and mechanical strength.

752 Granulation holds several benefits such as incorporation of a support material that
753 stabilizes the structure, the formation of pores during the pelletisation process, the
754 possibility of incorporating pore-forming materials for a more beneficial pore
755 structure. It is also a relatively easy to scale up technique that uses cheap materials
756 for its production process. One of the most important benefits of pelletisation is that
757 not only use of binders is enabled, but it allows combining oxygen carriers and
758 catalysts in order to make composite materials for the integration of CaL and
759 chemical looping combustion (CLC) [139].

760

761

762

Table 8: Granulation summary table

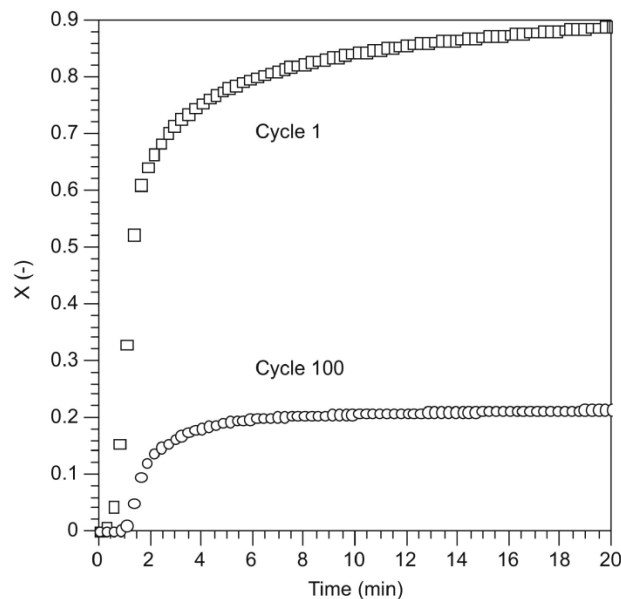
Base material and/or binder and method	Reactor	Conditions	Main findings	References
Bentonites, calcium aluminate cements Extrusion through sieve	TGA	Calcination 850°C in 100% N ₂ (%vol) Carbonation 850°C in 100% CO ₂	Bentonites enhanced sintering because of the formation of certain compounds Ca ₂ (SiO ₄) and Ca ₅ (SiO ₄) ₂ CO ₃ Calcium aluminate cements had very promising properties due to fast setting, good refractory properties and their low cost with a 42% conversion after 30 cycles	[128]
Calcium aluminate cement (10%) Mechanical pelletiser	TGA- reactivity Bubbling FB- attrition	TGA: Calcination 800°C in 100% N ₂ (%vol) Carbonation 800°C in 25% CO ₂ Bubbling FB: 2 h 800°C in continuous fluidisation	Higher CO ₂ uptake in carbonation/calcination cycles than plain limestone. Higher resistance to attrition than plain material. Cement stabilised the CO ₂ carrying capacity and increased resistance to sintering with 27 mg CO ₂ /100mg _{sorbent} after 90 cycles for the cement supported pellets and 18 mg CO ₂ /mg _{sorbent} for Ca(OH) ₂ pellets	[1290]
Calcium aluminate cement (10%) Treated with acetic acid and commercial vinegar Extrusion through sieve	TGA	Calcination 850°C in 100% N ₂ or 920°C in 100% CO ₂ (%vol) Carbonation 650°C in 15% CO ₂	Acetification was a possible method of enhancing pellet performance, but attrition effects may have increased 10% acetic acid solution enhanced morphology, while vinegar showed worse pore volume and surface area Tests performed under mild conditions and results showed marginal benefit with an increase of 0.1 g CO ₂ /g _{sorbent}	[130]
Kaolin binder or Al(OH) ₃ binder (obtained from acid leaching of metakaolin) Acetification with acetic acid	TGA	Calcination 920°C in 100% CO ₂ (%vol) Carbonation 650°C in 15% CO ₂	Pellets prepared with Al(OH) ₃ binders exhibited higher CO ₂ uptake than kaolin binder, but it was marginal of 0.05 g CO ₂ /g _{sorbent} after 30 cycles. Kaolin appears inadequate as a binder	[131]
Commercial cement Extrusion using a 16 twin-screw extruder	TGA- reactivity Friability tester- attrition	TGA: Calcination 900°C in 100% N ₂ (%vol) Carbonation 650°C in 15% CO ₂ Friability tester: 2000 and 4000 rotations	Screw-extrusion particles displayed good attrition resistance and mechanical strength Preparation method had no effect on the chemical performance under the tested conditions with a marginal difference of around 2% conversion after 20 cycles	[132]
Extruded-spheronised	TGA	Calcination 850°C in 100%	Pellets doped with pre-washed rice husk showed better	[133]

		N ₂ (%vol) Carbonation 650°C in 15% CO ₂	performance with 41.58% conversion for the 5% wt addition of rice husk after 25 cycles Cement addition should be limited to 10 wt%	
Crushed limestone Calcium aluminate cement pellets Pellets without binder	Air jet apparatus-attrition testing	Temperature 20±3 or 500±5°C Atmospheric pressure Times 0,1,5,12,24 and 36 (h) Superficial gas velocity(m/s) 10 (20°C, 500°C) or 0.457 (500°C)	Pellets experienced similar attrition to crushed limestone and were highly sensitive to humidity.	[134]
Calcium aluminate cement	Attrition testing Dual FB (0.1 MW _{th})	Velocity carbonator:2-2.6 m/s T _{carb} =650°C Velocity calciner 0.5-0.8 m/s T _{calc} =650°C	Pellets experienced similar attrition to limestone. 50% of particles were recuperated as fines	[135]
Biomass used for templating: cardboard, maple leaves, date seed and white soft wood Calcium aluminate cement as binder	TGA	Calcination 850°C in air Carbonation 650°C in 15% CO ₂ (15% steam in some tests)	Leaf-derived biomass pellets showed higher porosity than all the other types of biomass, increasing also the CO ₂ uptake. Optimal content 10% biomass with a 33.3% more CO ₂ captured than biomass-free pellets after 20 cycles. Tests with steam exhibited better performance of the biomass-templated sorbents	[136]
Biomass used for templating: commercial wheat white flour Calcium aluminate cement as binder Doped with sea-water	TGA	Carbonation 650°C in 15% CO ₂ Calcination 850°C in N ₂ Carbonation 650°C in 15% CO ₂ Calcination 950°C in 100% CO ₂ Carbonation 850°C in 90% CO ₂ Calcination 850°C in 20% CO ₂	The synthetic materials showed better performance than limestone under BFB conditions from 0.25 g/g for calcium aluminate pellets to below 0.1 g/g for limestone after 10 cycles	[137]
Calcium aluminate, rice husk as pore-forming material and inert or semi-reactive shells	BFB TGA	Calcination 900°C in 100% N ₂ (%vol) Carbonation 650°C in 15% CO ₂	The addition of limestone to the inert shell proved to be beneficial for the reactivity and improved the structure with a maximum with 60% lime added to the shell (0.293 g/g after 17 cycles) when compared to the inert shells (0.132 g/g)	[138]

764

765 6.6. Nanomaterials

766 Nano-CaCO₃ was investigated with a TGA, which showed a residual activity double
767 what regular limestone would present after 100 cycles. The conversion (X) is
768 presented in Figure 14, which shows a residual conversion of 20% and a first-cycle
769 conversion of 89% [140].



770

771 **Figure 14:** Conversion (X) for nano-CaCO₃ in the first carbonation and 100th
772 carbonation [140]

773 Liu et al. compared the capture performance from synthetic precursors including
774 nano-particles. All the samples were subjected to 9 carbonation/calcination cycles
775 in a TGA. The solids obtained from nano-sized precursors exhibited a slower decay
776 in conversion, which suggests that those materials are less susceptible to sintering
777 [141].

778 Another attempt to use nano-sized calcium carbonate as a precursor for the sorbent
779 was made by Wu et al. [142], and the results confirmed that nano-calcium
780 carbonate is a better precursor than Ca(OH)₂ and micro CaCO₃. Wu and Zhu [143]
781 coated the surface of nano-CaCO₃ with a nano-TiO₂ using a solution containing
782 Ti(OH)₄. The resulting material was heated and calcined, and TGA tests showed a
783 constant reactive sorption capacity of 5.3 mol/kg after 10 cycles (under carbonation
784 at 600°C in 0.02 MPa CO₂ partial pressure and calcination at 750°C using N₂). In
785 comparison, the uncoated material showed a capacity of 1.6 mol/kg after the same

786 number of carbonation/calcination cycles. These results suggest that the higher
787 melting point of the CaTiO_3 developed as the coating layer after calcination reduced
788 sintering.

789 An alternative method for producing nano-particles is flame spray pyrolysis (FSP),
790 in which precursor droplets are converted into solid nano-particles in flames. This
791 has been proposed as an inexpensive large-scale production method for various
792 types of reactive powders [144]. Different sorbents were produced using this
793 technique, doping the particles with silica, titanium, chromium oxide, cobalt oxide,
794 zirconia and ceria [145]. Nano- CaO exhibited increased capture capacity and the
795 performance of the sorbents generated by FSP was better than that of the sorbents
796 prepared from regular wet methods.

797 Liu et al. [146] investigated wet mixing of calcium and magnesium salts of D-
798 gluconic acid. The particles exhibited well-distributed CaO nano-particles coated
799 with MgO , which the authors suggested acted as a barrier to avoid sintering. The
800 TGA experiments displayed a constant CO_2 capture capacity over 24 cycles of 0.56
801 (650°C for 30 minutes for carbonation using 15% CO_2 in the flue gas, and
802 calcination at 900°C for 10 min in 100% N_2).

803 An alternative to the materials mentioned above was proposed by Li et al. [147]:
804 mixing a 2-propanol slurry containing $\text{Ca}(\text{CH}_3\text{COO})_2$ and MgAl_2O_4 particles. The
805 particles were then dried and calcined, and experiments were performed in a TGA
806 and fixed bed. Both experiments demonstrated the superior capture capacity of the
807 $\text{CaO}/\text{MgAl}_2\text{O}_4$, compared to CaO/MgO particles prepared with the same technique
808 and natural dolomite. The thermal and mechanical properties of MgAl_2O_4 added as
809 a support were beneficial for the particles as they interfered with the agglomeration
810 of the nano- CaO particles, which minimised the sintering.

811 The production of these materials has several benefits such as the advantageous
812 properties of supports (high melting point, stabilization of structure), as well as the
813 benefit of using nanoparticles on their own (slower decay in conversion). However,
814 these methods are difficult to scale up and much more expensive than using natural
815 limestone or granulated material; therefore, a compromise between durability, cost
816 and adsorption capacity has to be made. Attrition also has to be studied with such
817 materials, and generally the lack of attrition studies on new materials represents a

818 potential major limitation for determining their suitability for calcium looping
819 applications.

820 **7. Reactivation of spent sorbent**

821 Once the sorbent has been used for a long series of tests, the residual reactivity is
822 very low. For the CaL process to be feasible at commercial scale, a method should
823 be found to re-use the potentially very large quantities of spent sorbent, thereby
824 avoiding the necessity of disposal. Besides, the cost of synthetic sorbents is a
825 critical parameter for the feasibility of the technology making their reactivation even
826 more important [148].

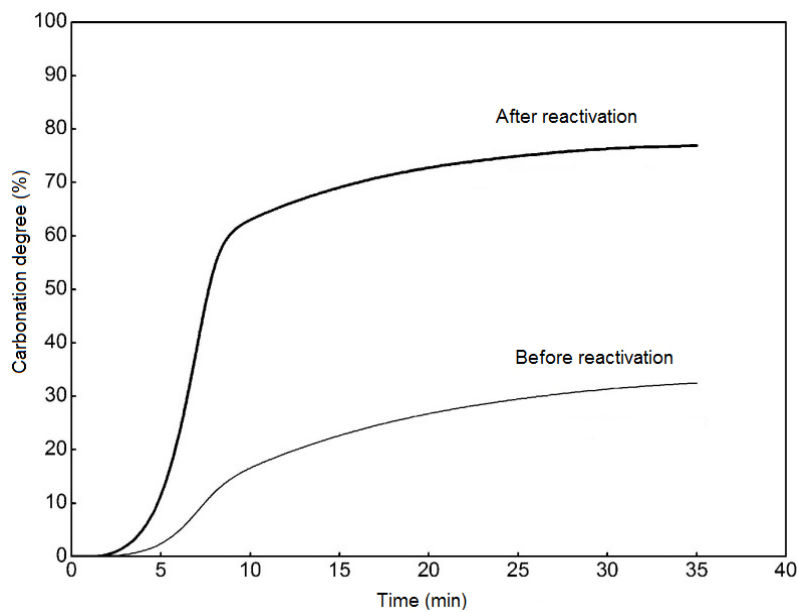
827 7.1. Hydration

828 Hydration can be used not only as a pre-treatment to make limestone more reactive
829 but also as a reactivation technique for spent sorbent. Hydration is beneficial due to
830 the formation of cracks in the CaO particles creating paths to the interior of the
831 particles and, therefore, improving CO₂ capture [149]. Another positive effect of
832 hydration is the formation of larger pores, which make the particles less susceptible
833 to pore blockage [150].

834 Reactivation can be achieved utilising water [151,152], water vapour or steam
835 [153,154]. Generally, calcination/carbonation reactors are not designed for
836 hydration. Therefore, a new vessel would be required so that the used sorbent can
837 be reactivated. The hydration reaction between CaO and water is exothermic,
838 which raises two considerations: the dehydration is endothermic, and the heat
839 produced in the hydrator needs to be integrated with the power plant or the process
840 in order to maintain overall efficiency [153]. It is also essential that the material that
841 needs to be hydrated comes from the calciner, due to the fact that the material from
842 the carbonator is likely to show minimal reactivation compared to calcined material
843 [88,155].

844 The most effective way of hydrating spent sorbent is water hydration [151,152].
845 Used sorbent reactivated with water for 1 min can reach 70% of the initial
846 conversion of natural sorbent. There are many factors that affect the hydration of
847 synthetic sorbents, but ultrasonic hydration could be a solution for reactivating this
848 type of material [151], which was first proposed by Wang, Wu and Anthony [156] to

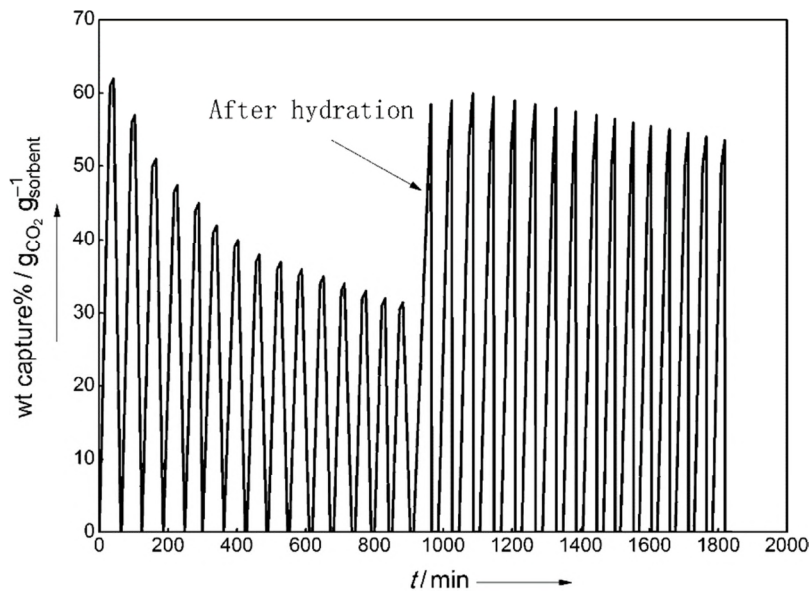
849 enhance hydration in sulphated sorbent. However, direct water hydration is far from
850 ideal due to the energy penalty caused by drying humid hydrated lime. Therefore,
851 steam hydration is proposed as the best method for reactivation [153,154]. Another
852 advantage of steam over water is that spent sorbent exhibited high reactivity
853 towards steam, allowing small pores to be produced. More investigations [155,157]
854 have been conducted with promising results using steam as the hydration
855 procedure as shown in Figure 15 and from an industrial point of view it seems more
856 likely that steam would be used rather than liquid water.



857

858 **Figure 15:** Effect of hydration on sorbent activity (after the first cycle in tube
859 furnace) [155]

860 However, the results seen in Figure 15 only demonstrated the effect of reactivated
861 lime during the first cycle after the hydration, while the most important parameter for
862 the CaL cycle is long-term reactivity. The results shown in Figure 16 indicate that
863 the improvement in the reactivity in the first cycle actually continues over a relatively
864 high number of cycles [150]. This is attributed to the enhanced rate of carbonation
865 in the diffusion-controlled regime [158].



866

867 **Figure 16:** Effect of hydration on decay rate of CO₂ sorption of CaO sorbent (the
868 hydration was performed after the 15th cycle) [150]

869 However, it is interesting to note that Sun et al. [88] reported poor capture
870 performance after hydration; it was later found that if the hydrated sample was
871 exposed to temperatures above 750°C after reactivation, the beneficial effect was
872 effectively eliminated [159]. The carbonation of Ca(OH)₂ is faster than CaO
873 [160,161], so it has been suggested that the hydration vessel for post-combustion
874 operation should be positioned before the carbonator, taking special care in
875 selecting the carbonation temperature.

876 While the benefits of using hydration as a means to reactivate the sorbent are
877 numerous (e.g low price of water as a reactivating chemical, easy procedure and
878 scale up of the hydration technique and high reactivity of the treated sorbent), an
879 extra vessel would certainly increase the cost and complexity of the plant. Another
880 drawback for the technique is the high attrition of hydrated particles, which is a
881 challenge for FB operation [47,149,162]. An extra step (i.e. granulation or extrusion)
882 would be required to overcome the mechanically weak particles, which will incur in
883 a rise in price.

884 7.2. Re-pelletisation technique

885 The re-pelletisation process uses water to re-bind the pellets. There is a double
886 effect when using this method for reactivation purposes. The porosity of the
887 particles is increased and some unreacted CaO in the core is exposed at the

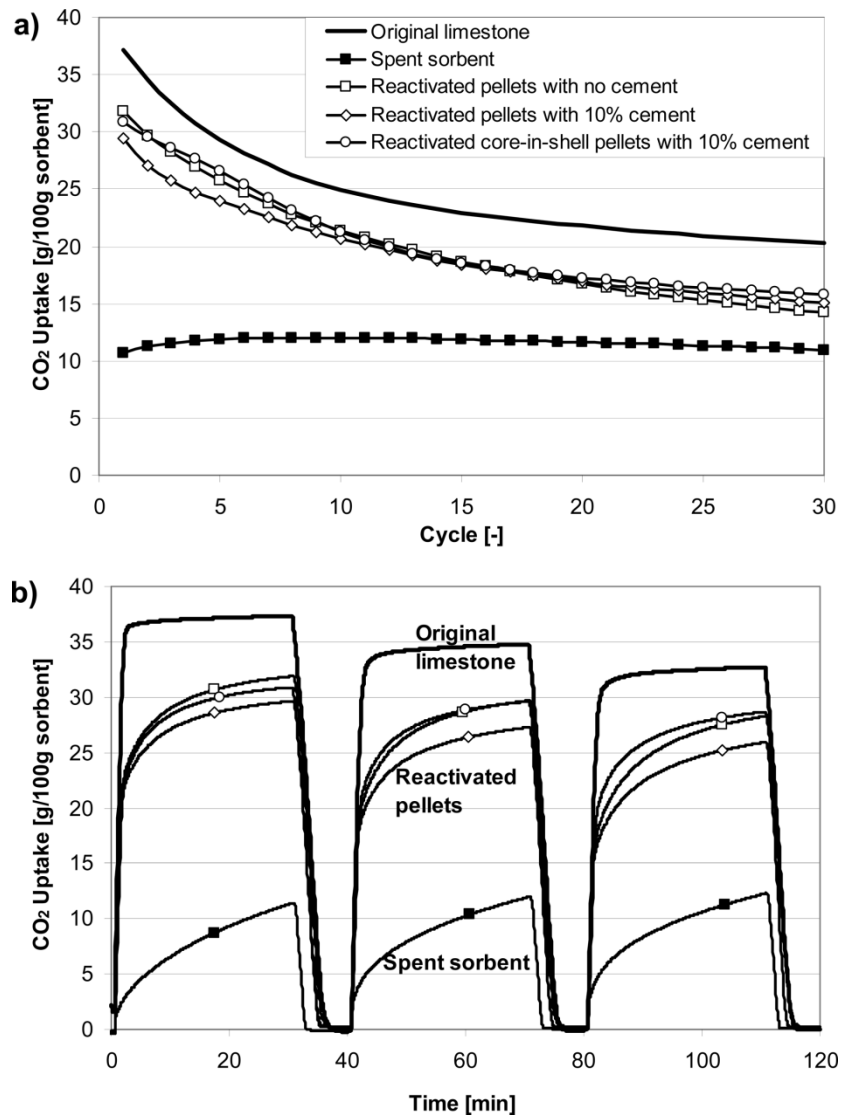
888 surface. Moreover, water used to re-pelletise the sorbent hydrates the material
889 increasing its performance further.

890 This phenomenon was first studied in the field for sulphur capture for flue gas
891 desulphurisation, where it was demonstrated that wet mixing was beneficial
892 compared to dry mixing for re-pelletisation of spent material [163].

893 This technique could be used for CaL. Lu et al. [164] proposed pelletisation of
894 hydrated lime as an acceptable solution for attrition of the hydrated material.
895 Manovic and Anthony [165] mixed calcined limestone with calcium aluminate
896 cement using extrusion through a sieve as a technique for obtaining pellets. These
897 pellets were cycled 300 times, under isothermal conditions at 850°C with 100% CO₂
898 for calcination and 100% N₂ for carbonation (using a tube furnace to make spent
899 sorbent). They were then removed following calcination, before being ground and
900 remade by addition of water and extrusion through a sieve. TGA tests showed that
901 the fresh pellets and the ones made with spent sorbent showed very similar results
902 exhibiting 33%-34% conversion after 30 cycles at 700°C in an atmosphere of 20%
903 CO₂, N₂ balance for carbonation, and 950°C in pure CO₂ for calcination.

904 The spent sorbent from a pilot plant was pelletised using a mechanical granulator
905 [166]. Three types of granules were made: with no binder; with 10% calcium
906 aluminate cement; and with a cement-free core, cement-containing mixture. This
907 last type of pellet was prepared in a two-step process. Spent sorbent with no
908 cement was hydrated, granulated and dried. Then, these pellets were added to the
909 vessel with cement to be pelletised forming a cement shell around the cement-free
910 pellet. The results for the pellets were then compared to the spent sorbent from the
911 power plant, showing improvement in reactivity. Although the reactivity was
912 increased, the pellets did not show the level of conversion seen in fresh limestone
913 due to sulphation during cycles, as can be seen in Figure 17.

914 As a reactivation technique remaking of pellets would be beneficial from the
915 economic perspective as the materials are cheap (deactivated material and water).
916 Moreover, the procedure would be easy to implement as it is the same as the
917 production method explained in the granulation subsection. It has a clear advantage
918 over hydration, as the material is hydrated and pelletised at the same time.
919 Therefore, the reactivity is increased but the material is less subjected to attrition.

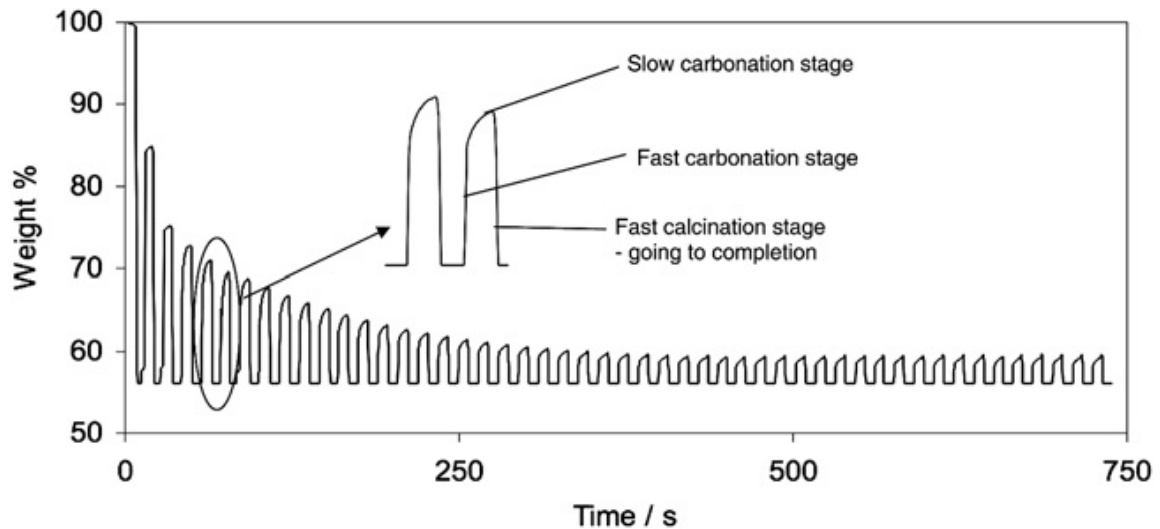


920

921 **Figure 17:** CO₂ capture performance of tested sorbents: (a) CO₂ capture capacity
 922 during 30 cycles, and (b) conversion profiles during the first three cycles.
 923 Conditions: carbonation in 50% CO₂ (N₂ balance) for 30 min, calcination in 100% N₂
 924 for 10 min, isothermally at 800°C [167]

925 7.3. Extended carbonation time and re-carbonation

926 To understand the benefits of this technique a more detailed explanation of the
 927 reaction of CaO with CO₂ is needed. The carbonation reaction has two stages: a
 928 fast kinetically-controlled stage and a slow diffusion-controlled stage as shown in
 929 Figure 18 [32]. The more time the solid spends in the slow diffusion stage, the more
 930 reactive the particle is in the next calcination due to the increasing volume of the
 931 particle which will result in a more porous structure, advantageous for the process.



932

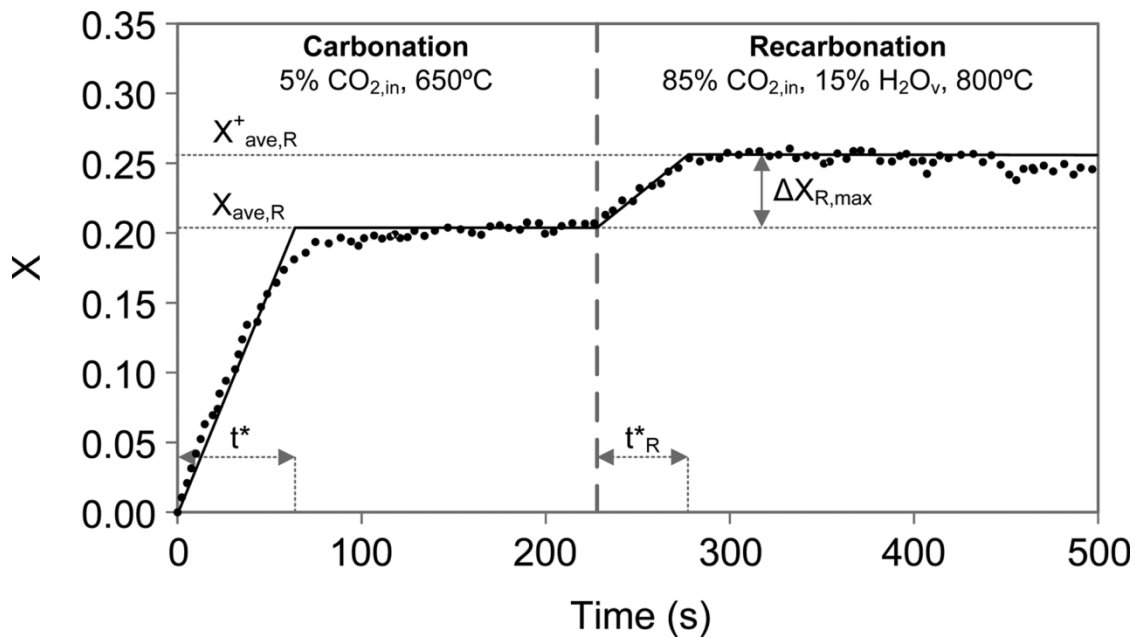
933 **Figure 18:** Repeated calcination/carbonation cycles of limestone in a TGA [32]

934 This phenomenon was first studied for energy storage where it was noted that if the
 935 slow diffusion stage was completed then the flow of CO₂ during calcination would
 936 increase porosity and increase the surface area for the next cycle [48].

937 In the CaL field this was first stated by Sun, Lim and Grace [49] where marginal
 938 increase in carbonation times had a positive outcome on the capture capacity over
 939 several cycles. Chen et al. [92] stated that extending the carbonation time
 940 substantially helped to recover some capture ability of the sorbents. Although this
 941 recovery decreased with increasing number of cycles, the samples that went to
 942 extended carbonation time showed better reactivity than the ones that did not.

943 Further work demonstrated that carbonation time has a robust effect on carrying
 944 capacity. If the carbonation time increased, the residual conversion also increased
 945 and then slowly decreased until both samples reached the same level [31].

946 Arias et al. [60] proposed incorporating this into the CaL scheme with a
 947 recarbonation reactor. This would keep a quasi-optimal carrying capacity by
 948 carbonating the solids with pure CO₂ from the calciner. This hypothesis was verified
 949 using a TGA, increasing the residual carrying capacity from 7% to 16%. The design
 950 of a reactor for this purpose was suggested recently [167], although the idea was
 951 first proposed by Salvador et al. in 2003 [50,168]. The results for the modelled re-
 952 carbonator are displayed in Figure 19, which clearly indicates the increased
 953 conversion versus recarbonation time.



954

955 **Figure 19:** Example of a typical conversion versus time curve during carbonation and recarbonation stages [168]
 956

957 Manovic and Anthony [68] have shown that recarbonation can have an adverse
 958 effect, further accelerating the decay of CaO conversion. This was confirmed in a
 959 recent publication where the authors suggested that this process leads to an
 960 intensification of diffusion-controlled carbonation, which causes defects due to
 961 intense bulk stresses [170]. Further studies need to be carried out regarding the
 962 potential of this process to better understand the effects on the sorbent due to the
 963 contradictory results that can be found in the literature.

964 **8. Conclusions**

965 Although limestone would be initially preferred as a CaL sorbent due to its low cost,
 966 ready availability and possible re-use as a feedstock for the cement industry, there
 967 are several drawbacks to its use: in particular, the reactivity decay caused by
 968 sintering, the potentially high attrition rate for many limestones, and vulnerability of
 969 limestone to sulphation in practical systems. A number of solutions have been
 970 reviewed in order to overcome these challenges. First, enhancement of natural
 971 sorbents can be achieved, reducing their reactivity decay by means of some simple
 972 procedures, such as using calcium hydroxide as a precursor, and thermal pre-
 973 treatment. In addition, novel synthesis methods have been developing during the
 974 past decade to obtain particles with upgraded properties. The techniques vary from

975 fairly simple procedures such as granulation and dry mixing to very complex
976 processes like sol-gel combustion synthesis and co-precipitation.

977 There is a need to study the scalability of these complex processes. The preferred
978 processes would be, at least at an initial stage of deployment, techniques that are
979 already proven in industry such as granulation or extrusion. Another important
980 factor is the cost of the material since one of the main advantages of CaL is the low
981 sorbent cost. The last important concern with respect to sorbents is the suitability of
982 the particles for use in FBs. Some of the methods presented here require
983 modifications to fine particles (nano-materials or PCC) in order for them to be
984 usable in a reactor of this kind. Consequently, the cost of granulation of this
985 material should be added to the overall process costs and evaluation, which risks
986 making such approaches prohibitively costly. Moreover, reactivation techniques
987 should also be carefully investigated to determine their appropriateness at
988 commercial scale as an alternative approach to preparing synthetic sorbents.

989 **9. References**

990

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