

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. Introduction

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

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

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

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

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

2. Process description

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

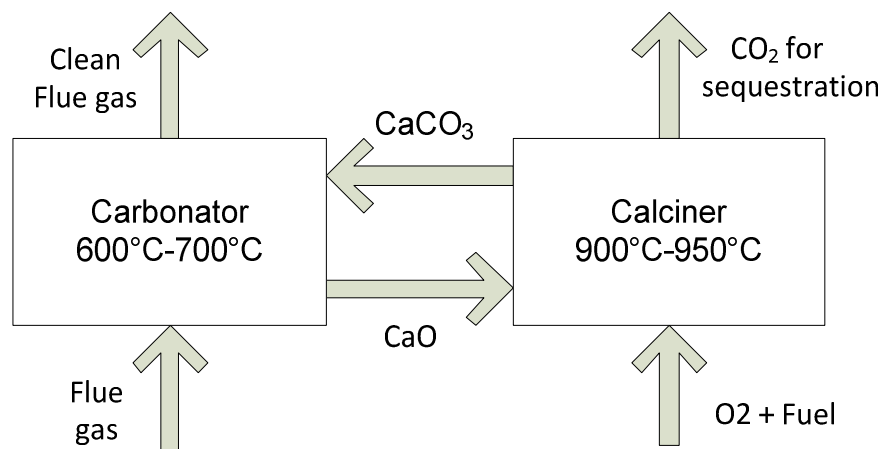


Figure 1: Schematic diagram of calcium looping process for post-combustion CO₂ capture.

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

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

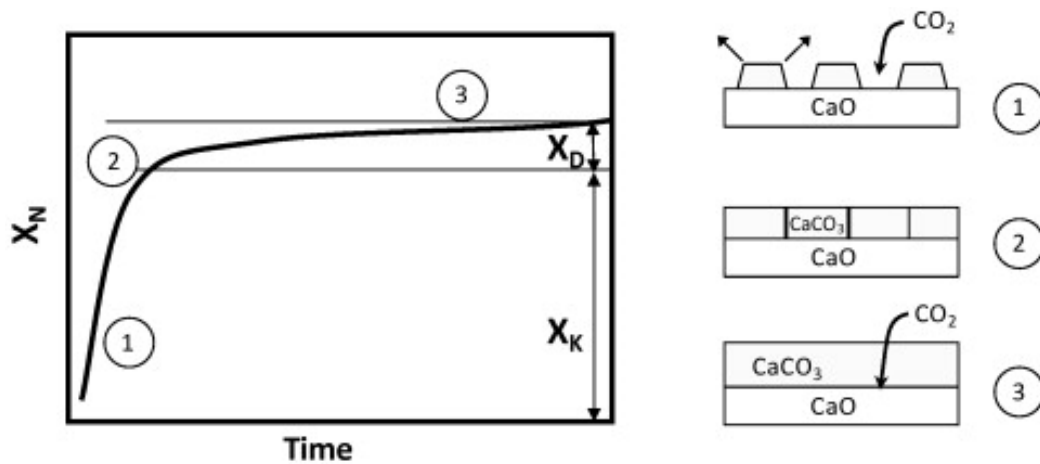


Figure 2: Schematic illustration of sorbent conversion during carbonation [31]

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

- Relatively low efficiency penalty, from 7 to 8% [35,36] with the capture step responsible only for 2 to 3% primarily due to oxygen requirement [37]
- Use of limestone, a widely available, inexpensive [38] and environmentally benign sorbent [20]
- The cost of CO_2 avoided has been calculated to be \$29–50/t- CO_2 , which accounts for around 50% less than for amine scrubbing [39–43]

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

3. Reactivity decay over cycles

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

3.1. Sintering

Sintering is the change in pore shape, pore shrinkage and grain growth that particles of CaO endure while heating. This phenomenon rises at higher partial pressures of steam and CO_2 , and also with impurities [44]. It has been discovered that the sintering that contributes to the reactivity decay occurs mainly during the calcination of such particles [45]. However, some of the decay can be connected to closure of small pores on the carbonation that do not reopen subsequently [46]. The deactivation rate escalates when increasing temperature in the calcination step with lower reactivity associated with higher temperatures [47].

There have been several studies that have proven the bimodal pore size distribution created upon calcination [30,45]. During calcination, small pores are formed due to the CO_2 release; however, larger pores are not only present in the initial material but are also formed caused by sintering, which driven by the minimization of surface energy, swings smaller pores to larger pores.

It has also been perceived by several studies [48–50] that increasing carbonation time results in a sorbent with higher reactivity towards CO_2 . The effect of this longer carbonation has been investigated by Álvarez and Abanades [30]. They suggested that although the larger pores were accessible through pores with smaller opening, they were closed at the surface. Presumably, if the slow carbonation solid diffusion reaction occurs for longer periods, the solid bulk enlarges in order to fill the larger pores in a more substantial way. This leads to a higher CaO reactivity in the next calcination. On the other hand, this longer carbonation step could be unpractical when talking about industrial operation.

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

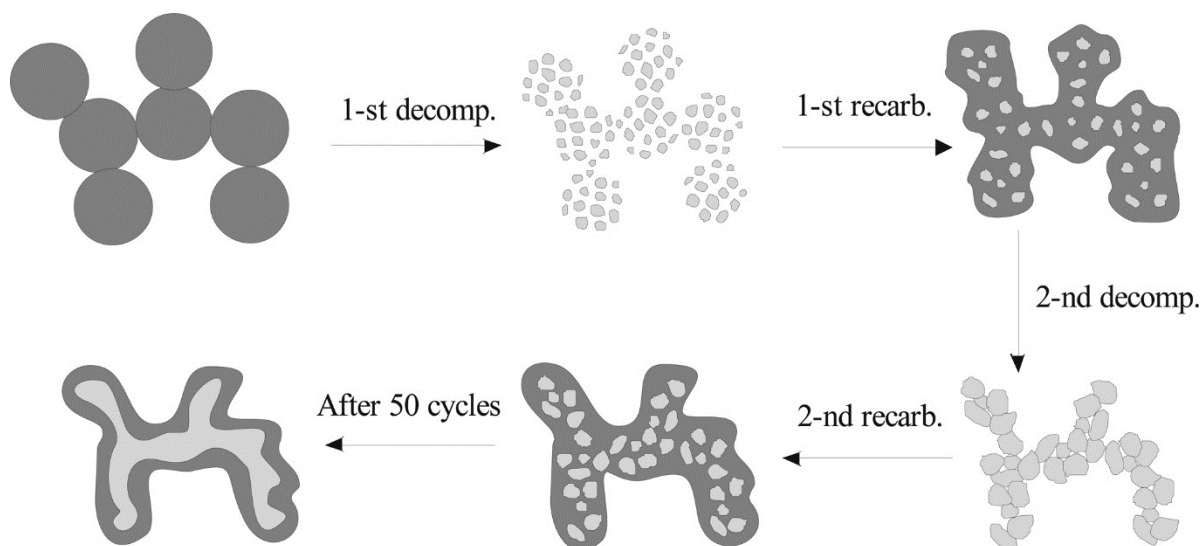


Figure 3: Transformation of the lime-based sorbent structure during carbonation/calcination (CaCO₃ phase is dark grey, CaO phase is light grey) [51]

3.2. Attrition

The mechanisms for fragmentation/attrition can be divided into: primary fragmentation, which takes place when the sorbent is introduced into the reactor. It is mainly caused by thermal stresses and overpressures due to CO₂ release as part of the calcination reaction. Secondary fragmentation, which is caused by mechanical stresses from impacts between the particle and the reactor; and attrition by abrasion which is also due to mechanical stresses but generates finer fragments than secondary fragmentation [52].

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

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

4. Natural material-based sorbent

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

4.1. Limestone

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



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

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

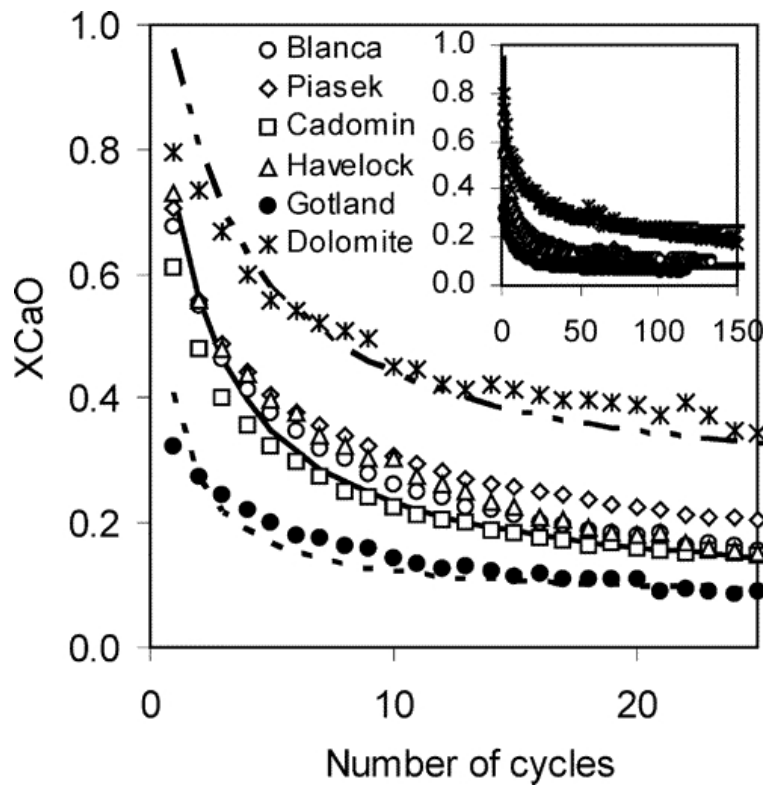


Figure 4: Conversion vs. number of cycles for experiments carried out with different types of limestone. Particle size 0.4-0.6 mm. Calcination temperature 850°C, 10 min; carbonation temperature 650°C, 10 min; pCO₂ of 0.01 MPa [59]

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

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

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

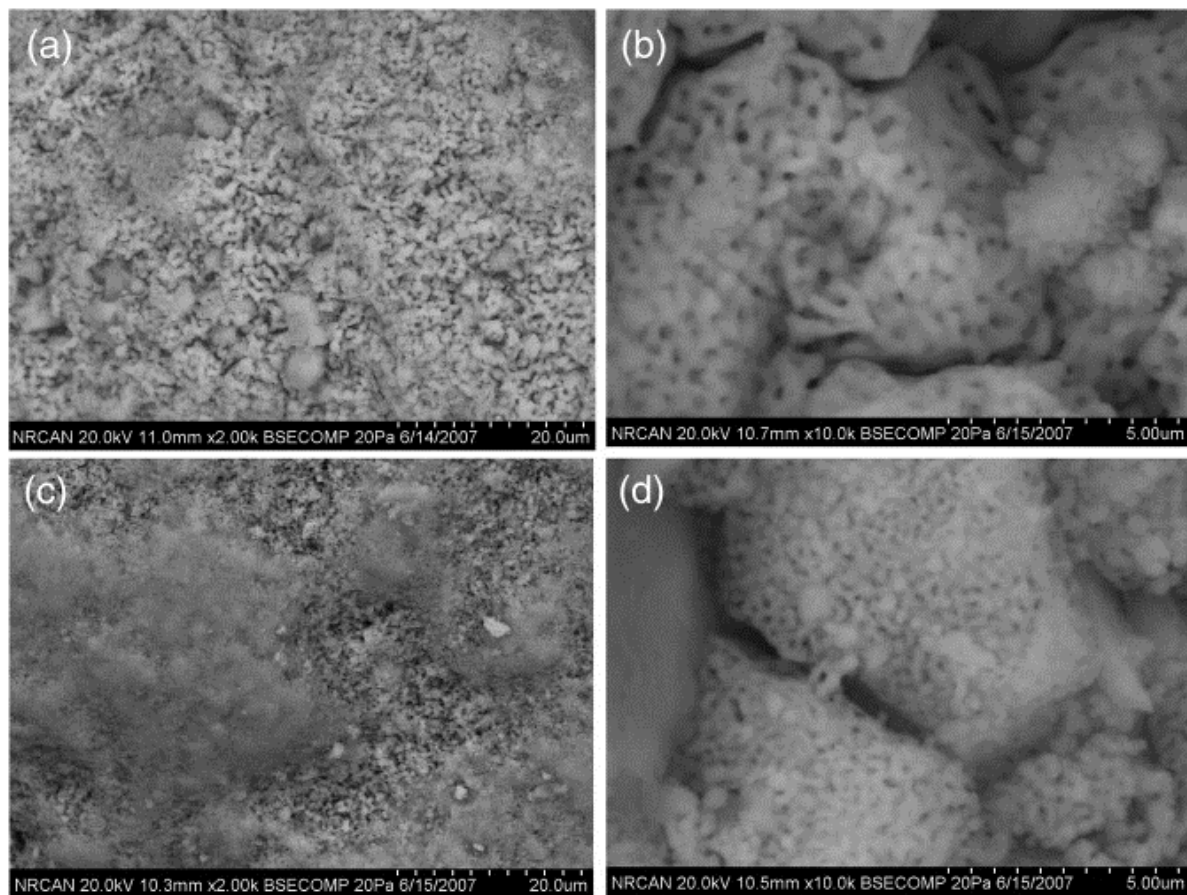


Figure 5: SEM of surface area of samples from carbonator: (a, b) after 3 cycles; (c, d) after 25 cycles [29]

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

4.2. Dolomite

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

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

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

4.3. Other natural materials

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

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

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

Sorbent source (type of shell)	Initial CO ₂ capture capacity (wt %)
Chicken egg	60
Ostrich egg	45
Duck egg	61
Oyster shell	34
Clam shell	21

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

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

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

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

5. Enhancement of natural sorbents

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

5.1. Calcium hydroxide

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

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

5.2. Doping

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

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

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

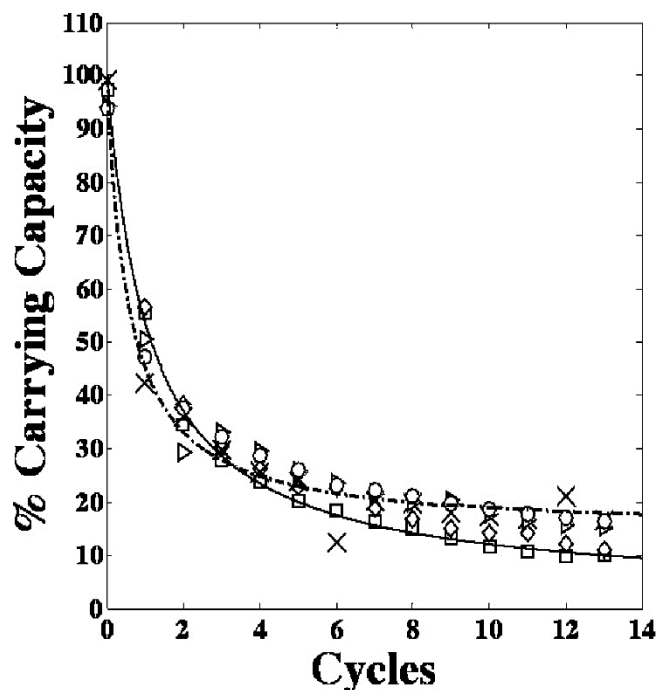


Figure 6: Carrying capacity (normalised) for Havelock limestone, plotted against the number of cycles: (—□—) un-doped, (---◇---) 0.159 mol% Mg(NO₃)₂, (---x---) 0.165 mol% MgCl₂, (▷) 0.138 mol% CaCl₂, (O) 0.15 mol% Grignard reagent [82]

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

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

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

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

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

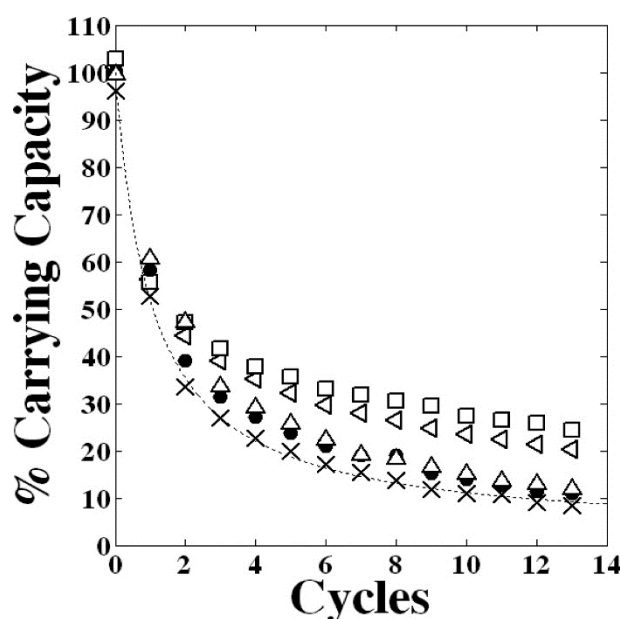


Figure 7: Carrying capacity (normalised) for Havelock limestone, plotted against the number of cycles: (x) undoped, (□) 0.167 mol% HBr, (sideways open triangle) 0.167 mol% HCl, (Δ) 0.164 mol% HNO₃, (●) 0.167 mol% HI [81]

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

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

Some metal-based dopants have been further investigated, such as γ - Al_2O_3 , SiO_2 sands and MgO . Sun et al. [88] also examined other dopants including TiO_2 and ZrO_2 . These materials were tested in a TGA and did not exhibit very promising results.

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

Table 2: Summary table of doping

Dopant	Method	Main findings	References
NaCl and Na_2CO_3	Quantitative wet impregnation	NaCl improved the sorbent by 0.15 in relative CO_2 capture capacity ($\text{gCO}_2/\text{g}_{\text{sorbent}}$) when compared to limestone in TGA after 13 cycles; Na_2CO_3 had no apparent effect. Doping with lower molarity is beneficial	[50]
NaCl and Na_2CO_3	Wet impregnation	Na_2CO_3 in small quantities had a positive effect increasing the carrying capacity by 0.14 $\text{gCO}_2/\text{g}_{\text{sorbent}}$ after 20 cycles. Lower molarity beneficial	[46]
KCl and K_2CO_3	Wet impregnation	KCl improved attrition resistance and reactivity by 0.15 $\text{gCO}_2/\text{g}_{\text{sorbent}}$ after 15 cycles when compared to limestone. Lower molarity beneficial	[80]
MgCl_2 , CaCl_2 and $\text{Mg}(\text{NO}_3)_2$	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

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

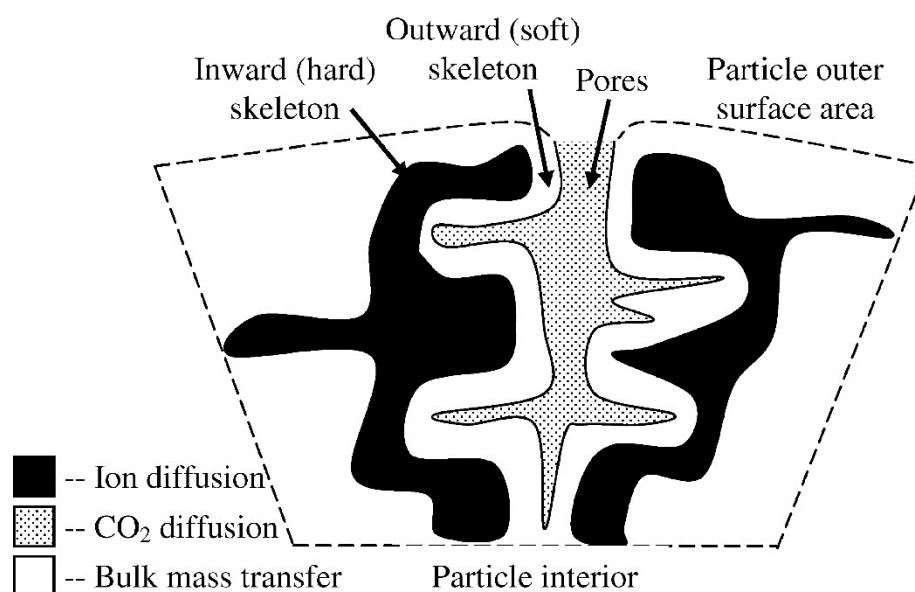


Figure 8: Schematic representation of proposed pore-skeleton model [89]

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

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

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

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

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

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]

5.4. Chemical treatment

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

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

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

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

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

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

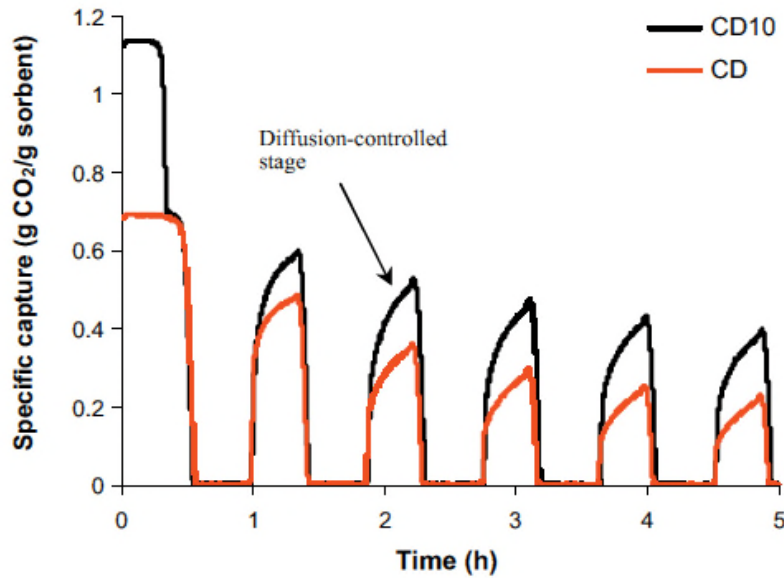


Figure 9: Carbon capture profile as a function of time. Calcination at 850°C in N₂ for 5 min and carbonation at 650°C in 15% CO₂ for 20 min [100]

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

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

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]

6. Synthetic sorbents

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

6.1. Sorbents from organic-acid precursors

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

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

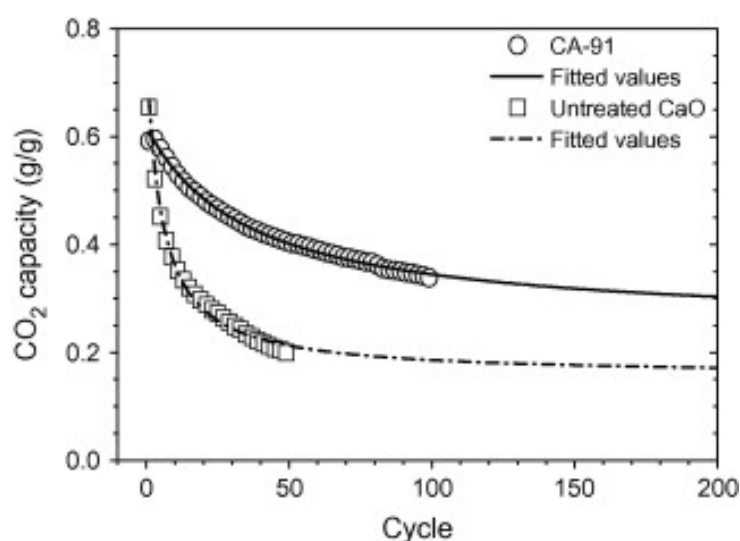


Figure 10: Evaluation of the long-term cycles of sample CA-91 (with 9% Al_2O_3) and untreated CaO in TGA (carbonation 650°C for 30 min in 20% CO_2 ; calcination at 850°C for 10 min in 20% CO_2) [102]

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

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

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

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

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

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

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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6.2. Sol-gel combustion synthesis

This method was first proposed by Luo et al. [109] for CaO-based sorbents and their work was extended in a subsequent study [110]. It included the following procedure: Predetermined quantities of La(NO₃)₃·6H₂O or Al(NO₃)₃·9H₂O and Ca(NO₃)₂·4H₂O were added to distilled water with a weight ratio of CaO to La₂O₃ of 80:20 and the mole ratio of water to metal ions of about 40:1. Citric acid was added, stirred and dried to form the sol, which was then left at ambient temperature for 18 h to form a gel. The gel was dried, and then calcined in a muffle furnace at 850°C for 2 h. Sorbents generated in this study showed better performance than those containing mayenite (Ca₁₂Al₁₄O₃₃) in their structure due to the effect of La₂O₃ in delaying sintering and absorbing extra CO₂ in the process. However, the problem of loss in reactivity was still present.

The process is illustrated in Figure 11.

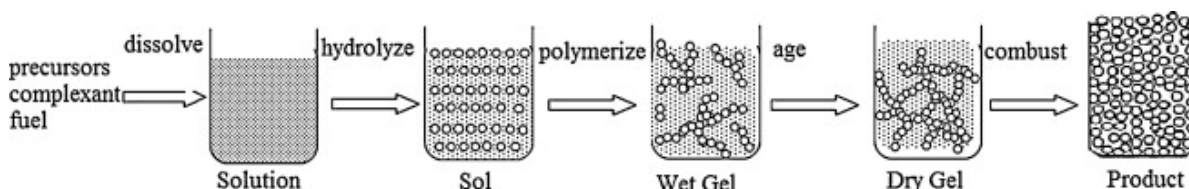


Figure 11: Manufacturing steps of the standard sol-gel combustion process [111]

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

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

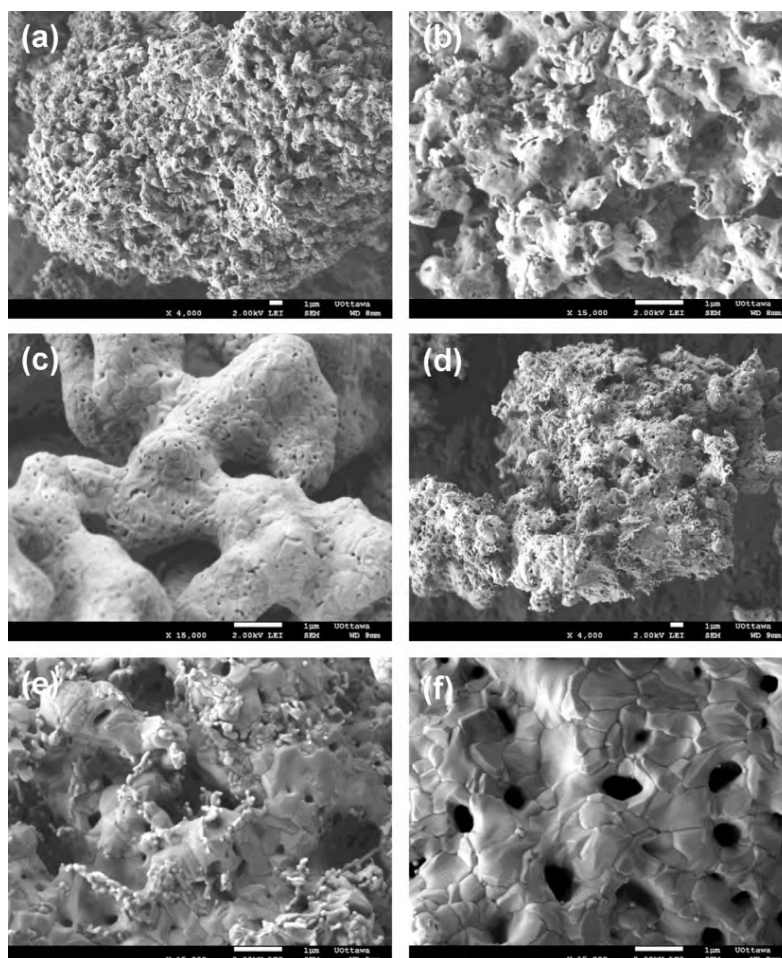


Figure 12: SEM images of CaO SG (sol gel) and pure CaO . (a) and (b) CaO SG mild conditions; (c) pure CaO mild conditions; (d) and (e) CaO SG under severe conditions; (f) pure CaO under severe condition [112]

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

Angeli, Martavaltzi and Lemonidou [113] used triethanolamine (TEA) as a 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 formation of TEA-ion complexes ensured that the dispersion of Ca and Al formed a coral-like structure. The sorbent showed higher stability than previous sorbents [32]. Nonetheless, the high temperatures in calcination and the presence of CO_2 increased sintering.

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

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

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

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	Calcination 850°C in 100% N ₂ (%vol) Carbonation 650°C in 15% CO ₂	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	Calcination 800, 850, 900, 930°C in 100% N ₂ (%vol) Carbonation 650, 700°C in 100% CO ₂	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	Calcination 800°C in 100% N ₂ (%vol) Carbonation 690°C in 15% CO ₂	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	Calcination 850°C in 100% N ₂ (%vol) Carbonation 650°C in 15% CO ₂	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

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

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

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

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]

6.4. Dry mixture and coating

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

Ca₂SiO₄ reacts with CO₂ during the carbonation while SiO₂ acts as an inert support. The results showed a CaO conversion of 41% in the 13th cycle at 800°C in 15% CO₂ [119]. MgO has also been physically mixed with Ca(CH₃COO)₂ using a ball mill and calcined afterwards, showing great stability and CO₂ capacity of 43% after 50 carbonation/calcination cycles [107]. Luo et al. [121] added La₂O₃ and CaCO₃ with dry physical mixing. This sorbent showed slightly better performance than natural limestone. However, such marginal improvements are likely to be overshadowed by cost issues, which may make this technique impractical for large-scale projects.

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

Peng et al. [125] developed another methodology for nano/micron-particle coating called self-assembly template synthesis (SATS) which followed a procedure to coat micron-Al₂O₃ with nano-TiO₂. The material was synthesised with SATS as well as prepared by wet impregnation with CaO (80 wt%) and Al₂O₃ (20 wt%) and limestone obtained from calcium acetate monohydrate. These three resulting sorbents were tested in a TGA at 700°C with 10% vol CO₂ for carbonation and pure N₂ for calcination to represent mild conditions and at 900°C in pure CO₂ to represent more realistic calcination conditions. The SATS sorbent exhibited much better CO₂ capture capacity in both mild and extreme conditions with approximately 0.47 gCO₂/gsorbent after 30 cycles in comparison with 0.27 gCO₂/gsorbent for the CaO. Peng et al. [126] performed tests in a batch FB with the same materials. The findings agree with the results mentioned before with a CO₂ capture capacity of 0.78 molCO₂/molCaO after 10 carbonation/calcination cycles.

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

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

6.5. Granulation

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

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

Later, the acidification of these pellets was investigated [130] as an option to improve the performance of pelletised sorbent. Samples acidified with 10% acetic acid solution exhibited better behaviour than samples treated with acid vapours. However, the acid and the modification procedure are neither simple nor 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

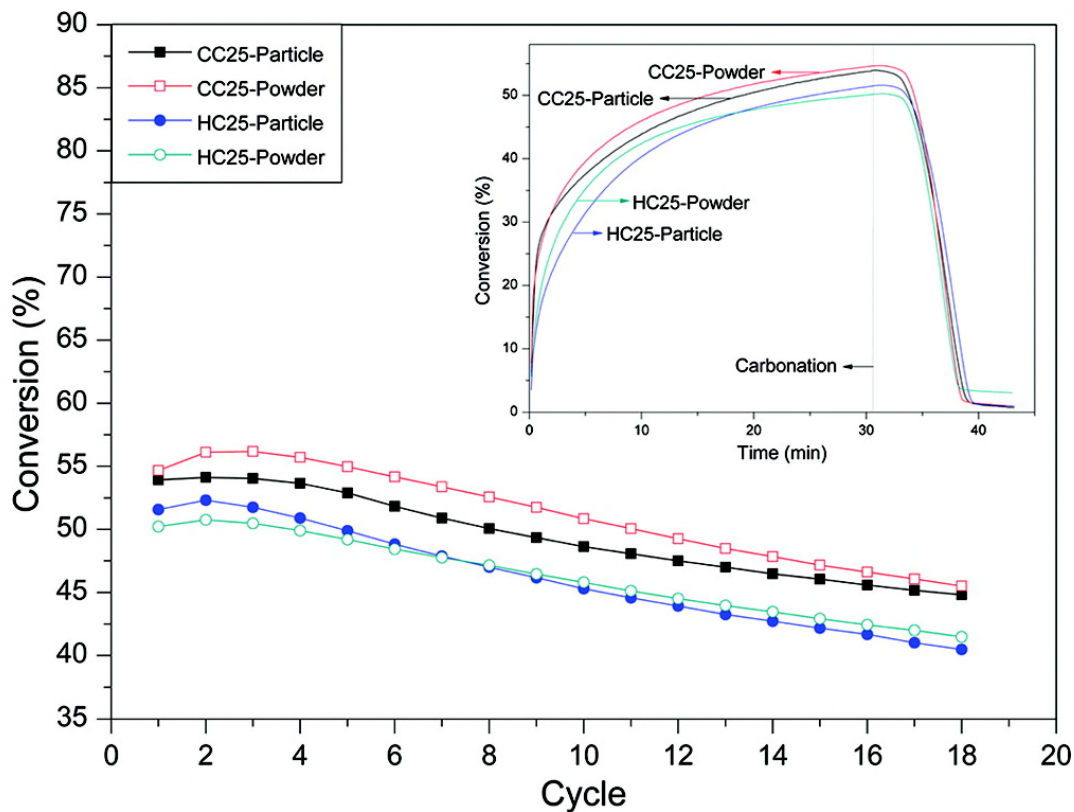


Figure 13: CaO conversion of original extruded particles and crushed limestone (CC - reagent calcium hydroxide used as a precursor, HC - commercial hydrated lime used as a precursor [132])

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

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

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

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

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

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

Table 8: Granulation summary table

Base material and/or binder and method	Reactor	Conditions	Main findings	References
Bentonites, calcium aluminate cements	TGA	Calcination 850°C in 100% N ₂ (%vol)	Bentonites enhanced sintering because of the formation of certain compounds Ca ₂ (SiO ₄) and Ca ₅ (SiO ₄) ₂ CO ₃	[128]
Extrusion through sieve		Carbonation 850°C in 100% CO ₂	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	
Calcium aluminate cement (10%)	TGA-reactivity	TGA: Calcination 800°C in 100% N ₂ (%vol)	Higher CO ₂ uptake in carbonation/calcination cycles than plain limestone. Higher resistance to attrition than plain material.	[129]
Mechanical pelletiser	Bubbling FB-attrition	Carbonation 800°C in 25% CO ₂ Bubbling FB: 2 h 800°C in continuous fluidisation	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	
Calcium aluminate cement (10%)	TGA	Calcination 850°C in 100% N ₂ or 920°C in 100% CO ₂ (%vol)	Acetification was a possible method of enhancing pellet performance, but attrition effects may have increased	[130]
Treated with acetic acid and commercial vinegar		Carbonation 650°C in 15% CO ₂	10% acetic acid solution enhanced morphology, while vinegar showed worse pore volume and surface area	
Extrusion through sieve			Tests performed under mild conditions and results showed marginal benefit with an increase of 0.1 g CO ₂ /g _{sorbent}	
Kaolin binder or Al(OH) ₃ binder (obtained from acid leaching of metakaolin)	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.	[131]
Acetification with acetic acid			Kaolin appears inadequate as a binder	
Commercial cement	TGA-reactivity	TGA: Calcination 900°C in 100% N ₂ (%vol)	Screw-extrusion particles displayed good attrition resistance and mechanical strength	[132]
Extrusion using a 16 twin-screw extruder	Friability tester-attrition	Carbonation 650°C in 15% CO ₂ Friability tester: 2000 and 4000 rotations	Preparation method had no effect on the chemical performance under the tested conditions with a marginal difference of around 2% conversion after 20 cycles	
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]

6.6. Nanomaterials

Nano- CaCO_3 was investigated with a TGA, which showed a residual activity double what regular limestone would present after 100 cycles. The conversion (X) is presented in Figure 14, which shows a residual conversion of 20% and a first-cycle conversion of 89% [140].

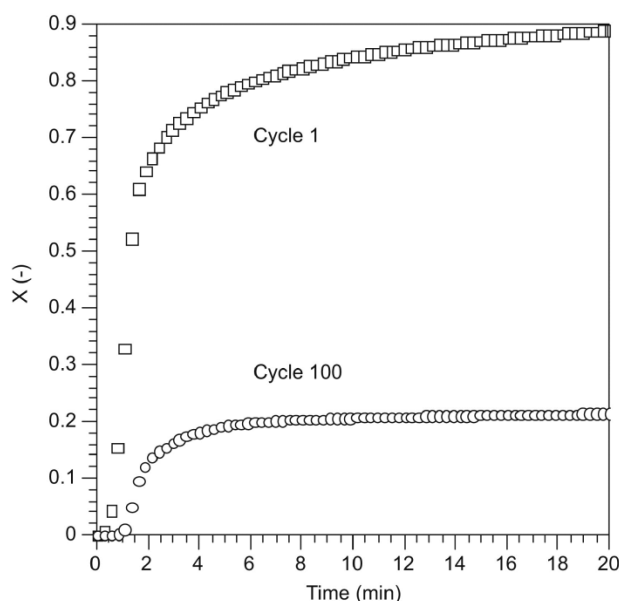


Figure 14: Conversion (X) for nano- CaCO_3 in the first carbonation and 100th carbonation [140]

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

Another attempt to use nano-sized calcium carbonate as a precursor for the sorbent was made by Wu et al. [142], and the results confirmed that nano-calcium carbonate is a better precursor than $\text{Ca}(\text{OH})_2$ and micro CaCO_3 . Wu and Zhu [143] coated the surface of nano- CaCO_3 with a nano- TiO_2 using a solution containing $\text{Ti}(\text{OH})_4$. The resulting material was heated and calcined, and TGA tests showed a constant reactive sorption capacity of 5.3 mol/kg after 10 cycles (under carbonation at 600°C in 0.02 MPa CO_2 partial pressure and calcination at 750°C using N_2). In comparison, the uncoated material showed a capacity of 1.6 mol/kg after the same

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

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

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

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

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

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

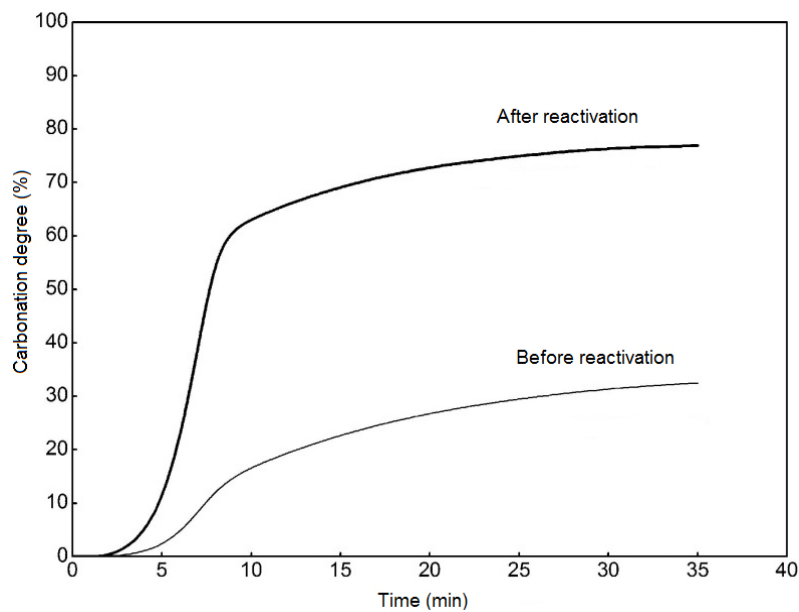


Figure 15: Effect of hydration on sorbent activity (after the first cycle in tube furnace) [155]

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

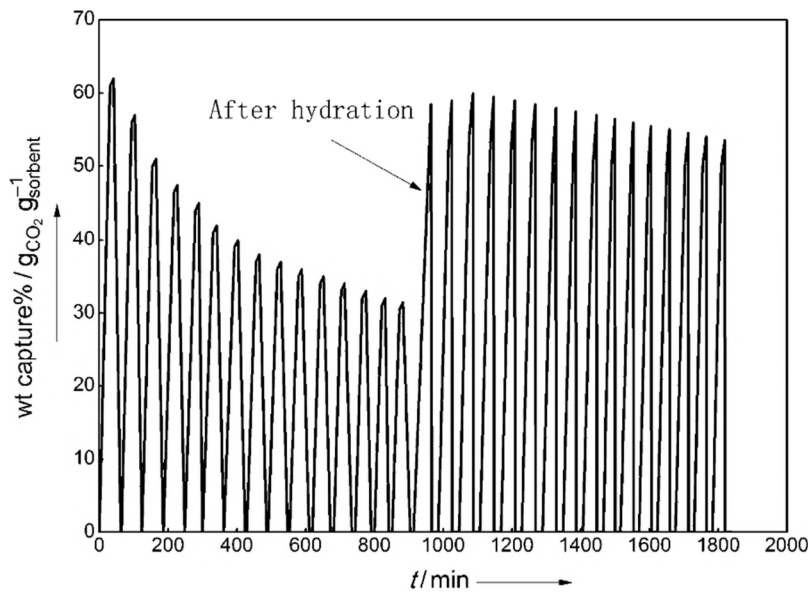


Figure 16: Effect of hydration on decay rate of CO₂ sorption of CaO sorbent (the hydration was performed after the 15th cycle) [150]

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

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

7.2. Re-pelletisation technique

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

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

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

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

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

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

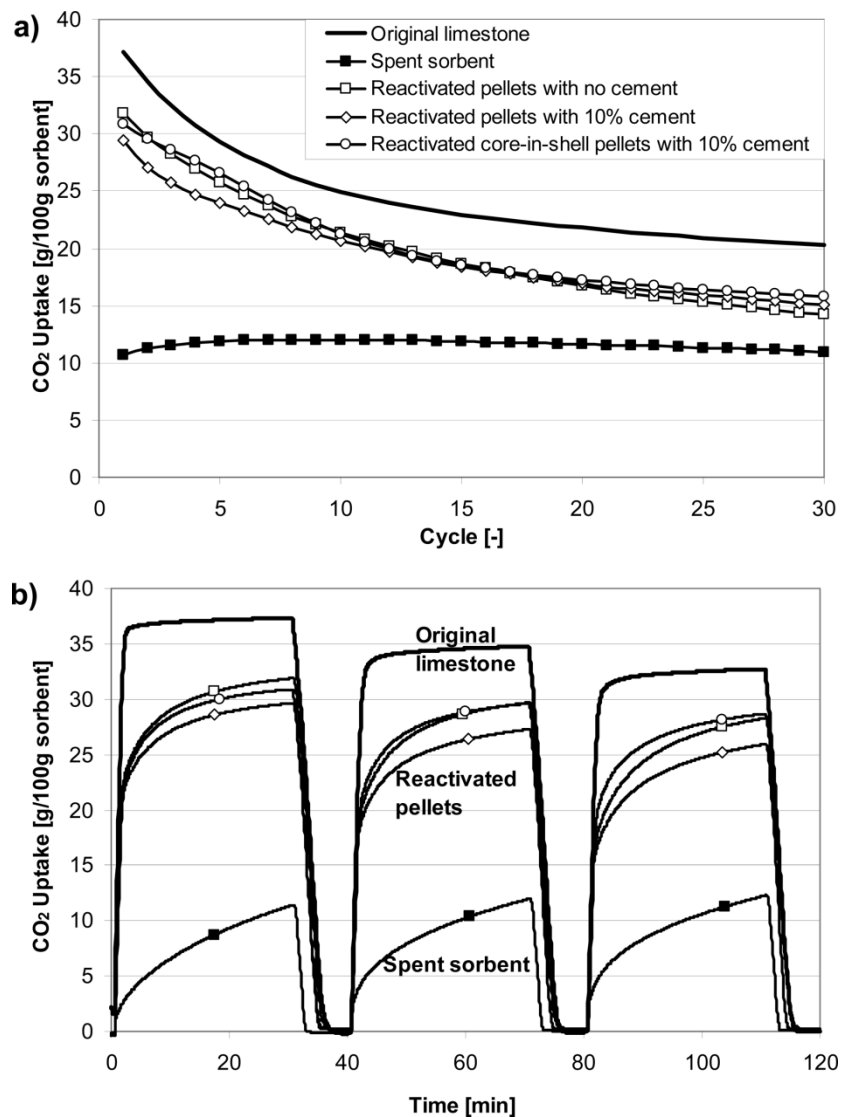


Figure 17: CO₂ capture performance of tested sorbents: (a) CO₂ capture capacity during 30 cycles, and (b) conversion profiles during the first three cycles. Conditions: carbonation in 50% CO₂ (N₂ balance) for 30 min, calcination in 100% N₂ for 10 min, isothermally at 800°C [167]

7.3. Extended carbonation time and re-carbonation

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

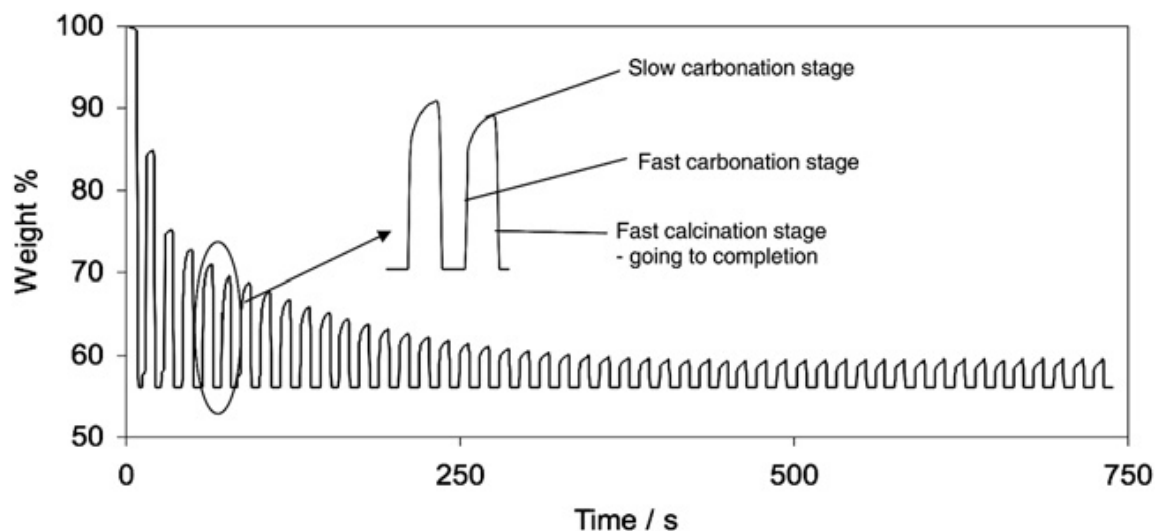


Figure 18: Repeated calcination/carbonation cycles of limestone in a TGA [32]

This phenomenon was first studied for energy storage where it was noted that if the slow diffusion stage was completed then the flow of CO_2 during calcination would increase porosity and increase the surface area for the next cycle [48].

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

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

Arias et al. [60] proposed incorporating this into the CaL scheme with a recarbonation reactor. This would keep a quasi-optimal carrying capacity by carbonating the solids with pure CO_2 from the calciner. This hypothesis was verified using a TGA, increasing the residual carrying capacity from 7% to 16%. The design of a reactor for this purpose was suggested recently [167], although the idea was first proposed by Salvador et al. in 2003 [50,168]. The results for the modelled recarbonator are displayed in Figure 19, which clearly indicates the increased conversion versus recarbonation time.

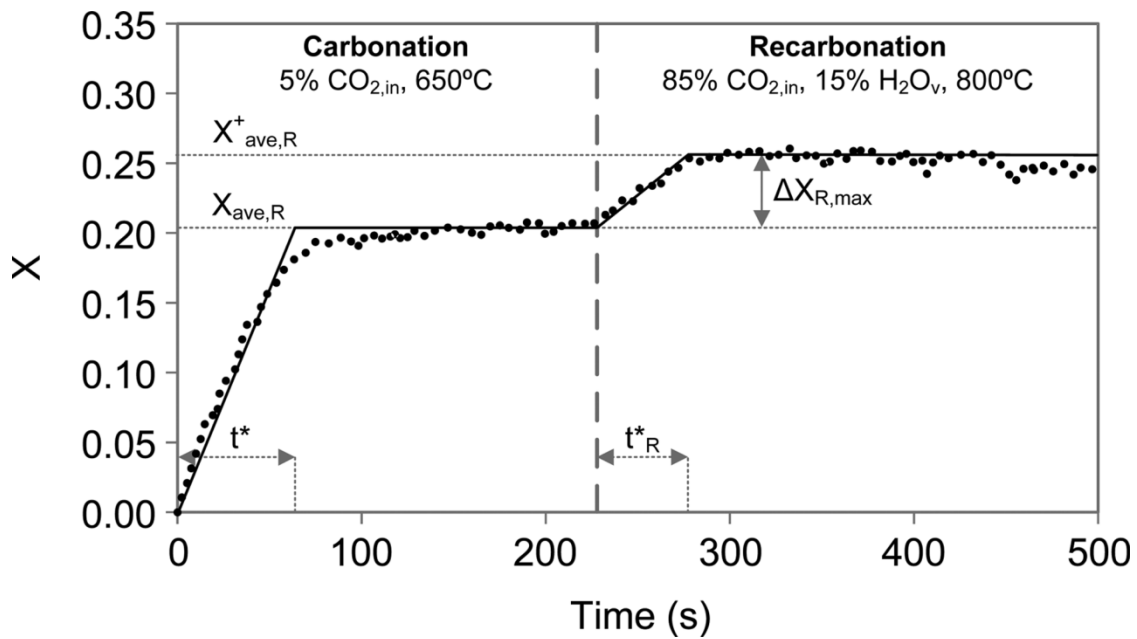


Figure 19: Example of a typical conversion versus time curve during carbonation and recarbonation stages [168]

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

8. Conclusions

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

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

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

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Calcium looping sorbents for CO₂ capture

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