

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

Table of Contents

1. Introduction	1
2. Process description	2
3. Reactivity decay over cycles.....	4
3.1. Sintering	5
3.2. Attrition.....	6
4. Natural material-based sorbent.....	7
4.1. Limestone.....	7
4.2. Dolomite	10
4.3. Other natural materials	10
5. Enhancement of natural sorbents	12
5.1. Calcium hydroxide.....	12
5.2. Doping.....	13
5.3. Thermal pre-treatment.....	17
5.4. Chemical treatment	19
6. Synthetic sorbents	24
6.1. Sorbents from organic-acid precursors	24
6.2. Sol-gel combustion synthesis.....	27
6.3. Precipitated calcium carbonate (PCC)	30
6.4. Dry mixture and coating	31
6.5. Granulation	33
6.6. Nanomaterials.....	39
7. Reactivation of spent sorbent.....	41
7.1. Hydration	41
7.2. Re-pelletisation technique.....	43
7.3. Extended carbonation time and re-carbonation	45
8. Conclusions	47
9. References	48

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.

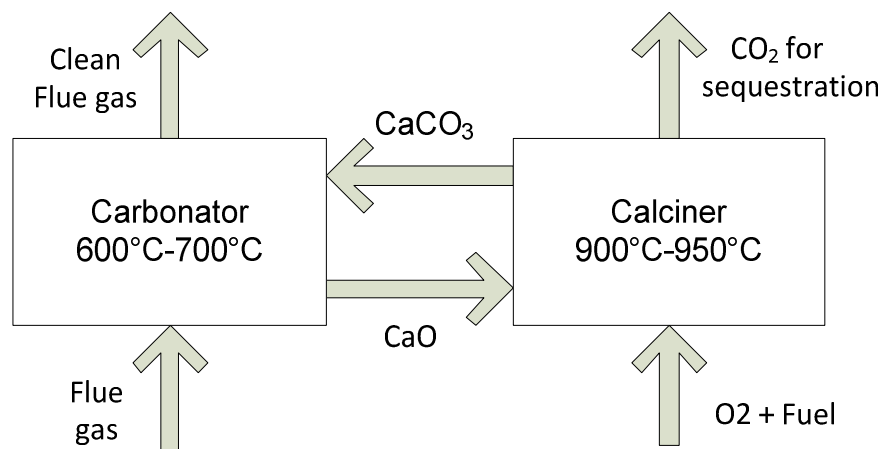


Figure 1: Schematic diagram of calcium looping process for post-combustion CO₂ capture.

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.

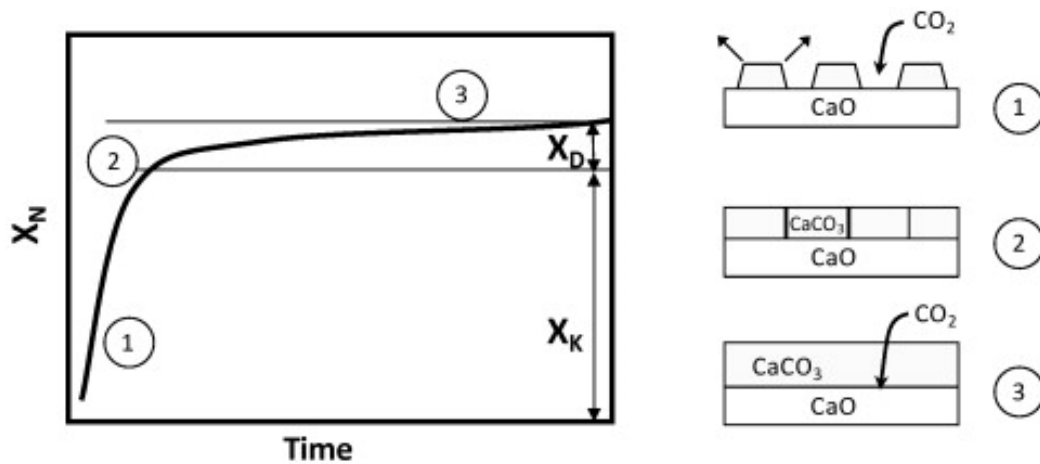


Figure 2: Schematic illustration of sorbent conversion during carbonation [31]

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.

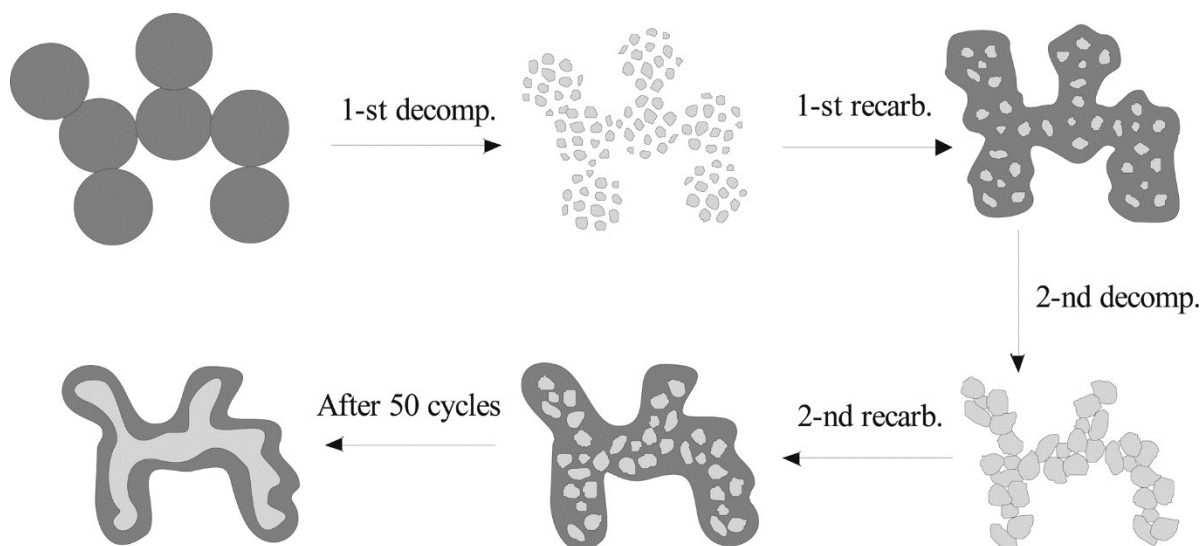


Figure 3: Transformation of the lime-based sorbent structure during carbonation/calcination (CaCO₃ phase is dark grey, CaO phase is light grey) [51]

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].

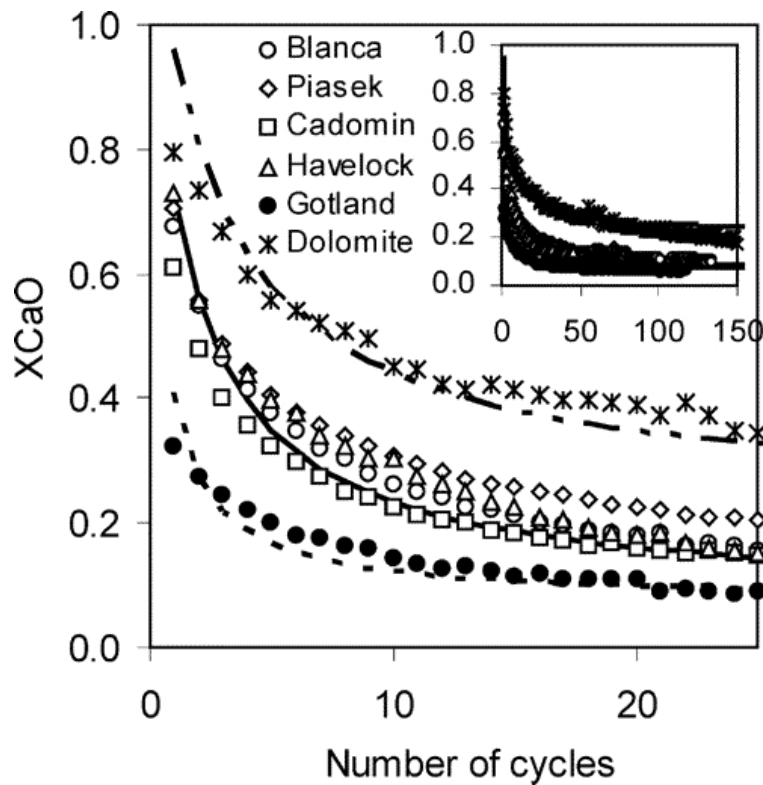


Figure 4: Conversion vs. number of cycles for experiments carried out with different types of limestone. Particle size 0.4-0.6 mm. Calcination temperature 850°C, 10 min; carbonation temperature 650°C, 10 min; pCO₂ of 0.01 MPa [59]

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].

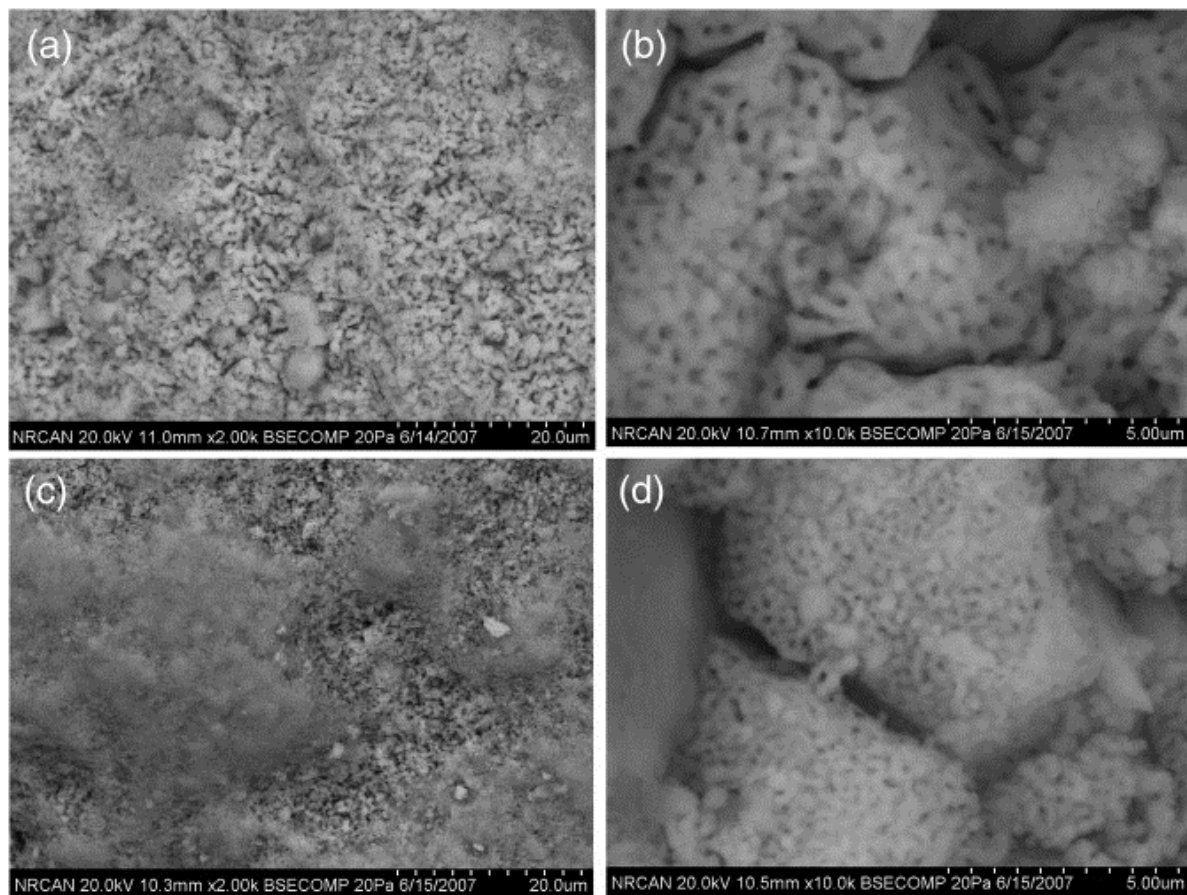


Figure 5: SEM of surface area of samples from carbonator: (a, b) after 3 cycles; (c, d) after 25 cycles [29]

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.

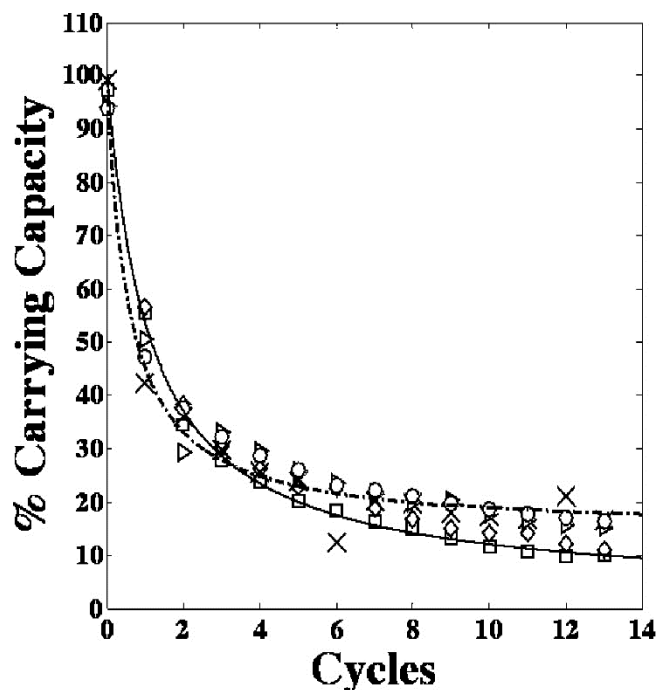


Figure 6: Carrying capacity (normalised) for Havelock limestone, plotted against the number of cycles: (—□—) un-doped, (---◇---) 0.159 mol% Mg(NO₃)₂, (---x---) 0.165 mol% MgCl₂, (▷) 0.138 mol% CaCl₂, (O) 0.15 mol% Grignard reagent [82]

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.

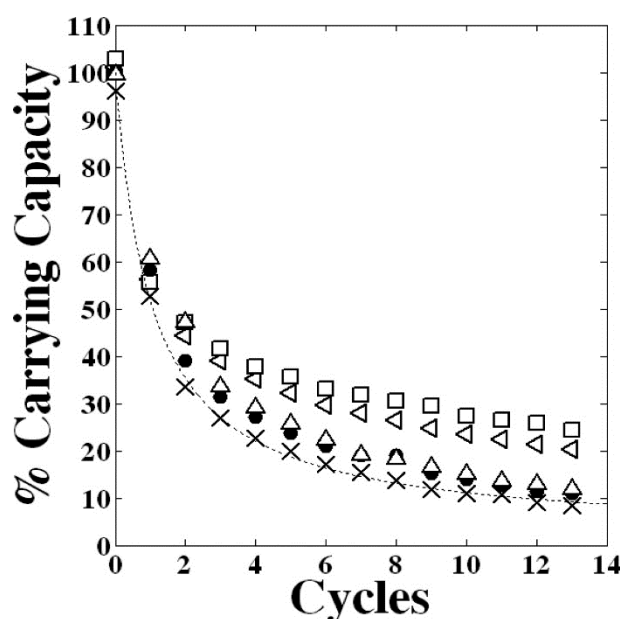


Figure 7: Carrying capacity (normalised) for Havelock limestone, plotted against the number of cycles: (x) undoped, (□) 0.167 mol% HBr, (sideways open triangle) 0.167 mol% HCl, (Δ) 0.164 mol% HNO₃, (●) 0.167 mol% HI [81]

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.

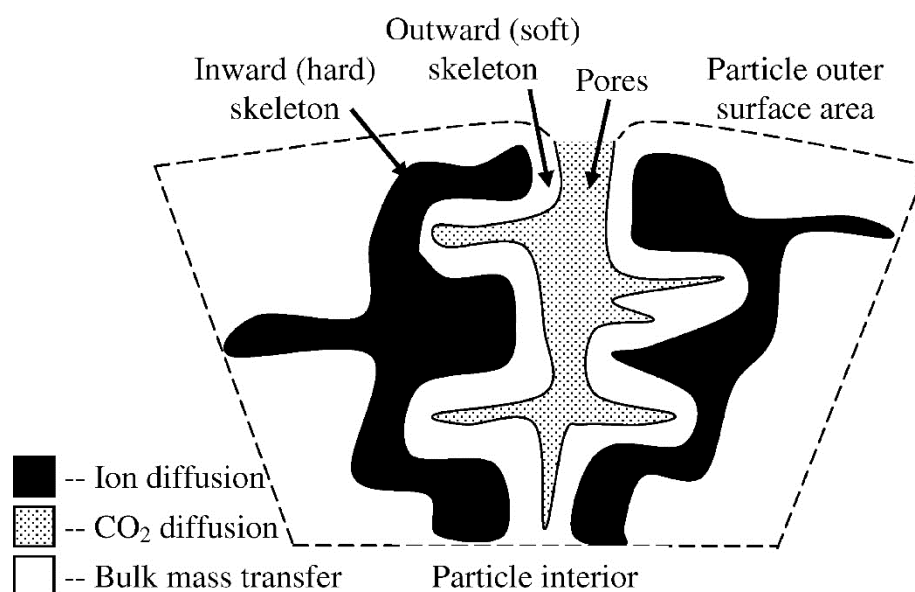


Figure 8: Schematic representation of proposed pore-skeleton model [89]

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).

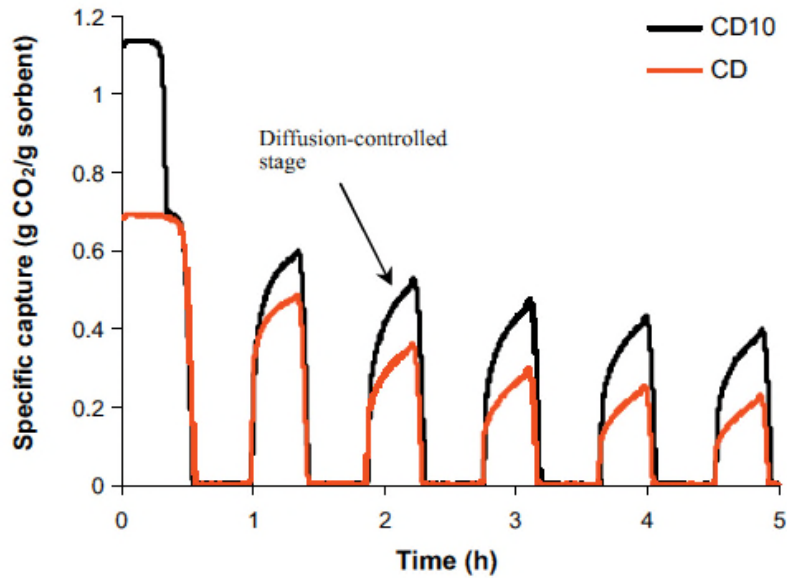


Figure 9: Carbon capture profile as a function of time. Calcination at 850°C in N₂ for 5 min and carbonation at 650°C in 15% CO₂ for 20 min [100]

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.

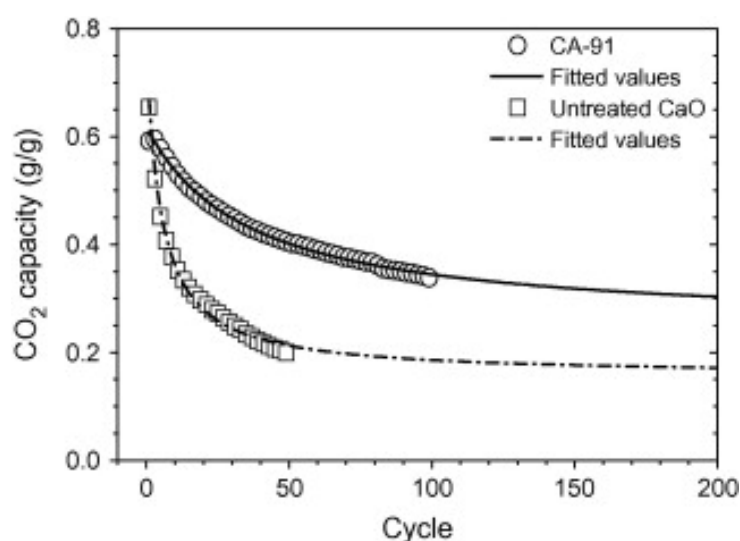


Figure 10: Evaluation of the long-term cycles of sample CA-91 (with 9% Al_2O_3) and untreated CaO in TGA (carbonation 650°C for 30 min in 20% CO_2 ; calcination at 850°C for 10 min in 20% CO_2) [102]

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.

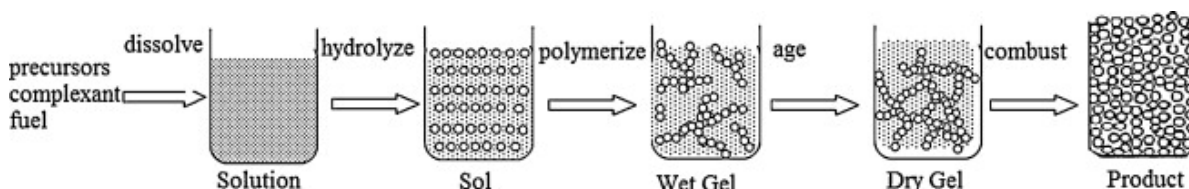


Figure 11: Manufacturing steps of the standard sol-gel combustion process [111]

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 .

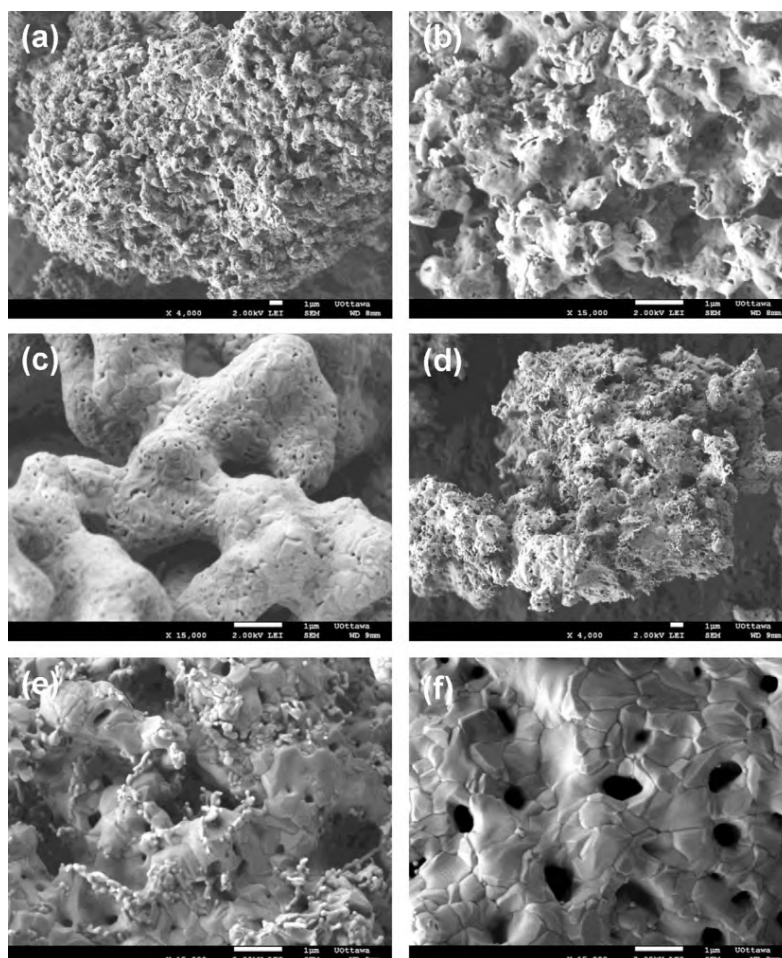


Figure 12: SEM images of CaO SG (sol gel) and pure CaO . (a) and (b) CaO SG mild conditions; (c) pure CaO mild conditions; (d) and (e) CaO SG under severe conditions; (f) pure CaO under severe condition [112]

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

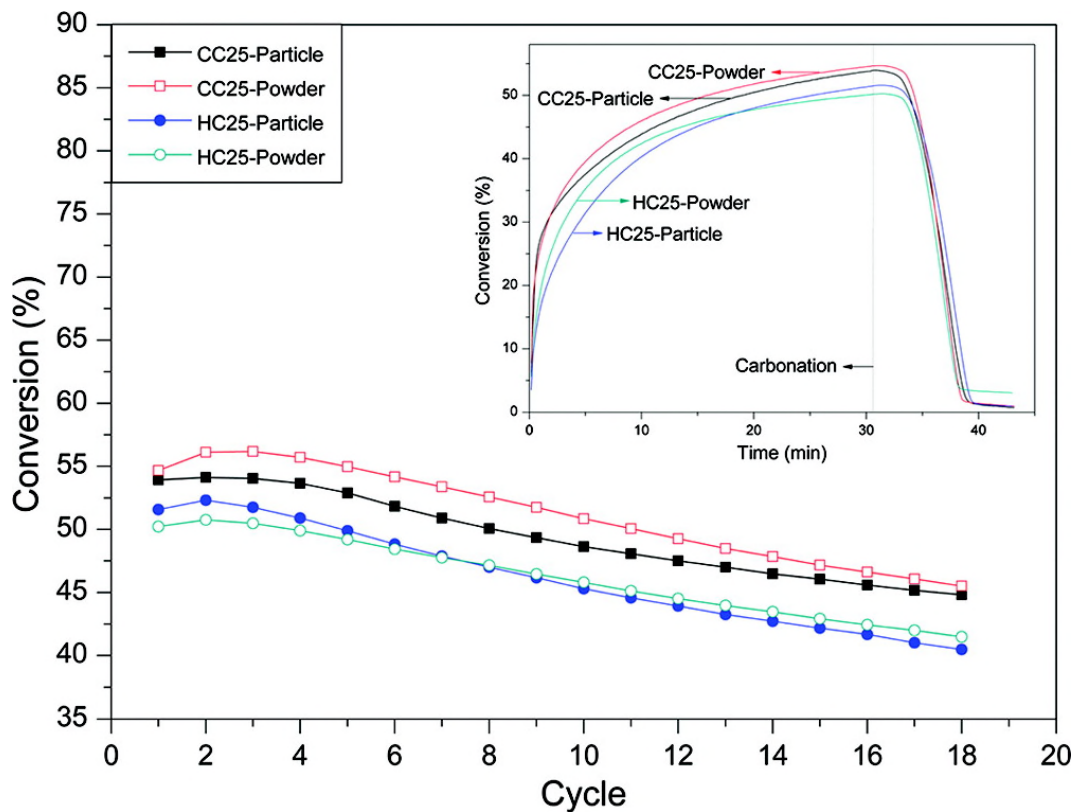


Figure 13: CaO conversion of original extruded particles and crushed limestone (CC - reagent calcium hydroxide used as a precursor, HC - commercial hydrated lime used as a precursor [132])

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].

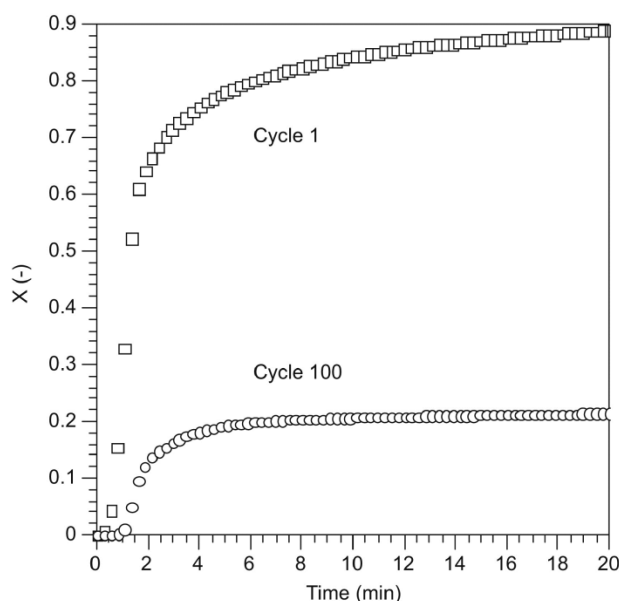


Figure 14: Conversion (X) for nano- CaCO_3 in the first carbonation and 100th carbonation [140]

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.

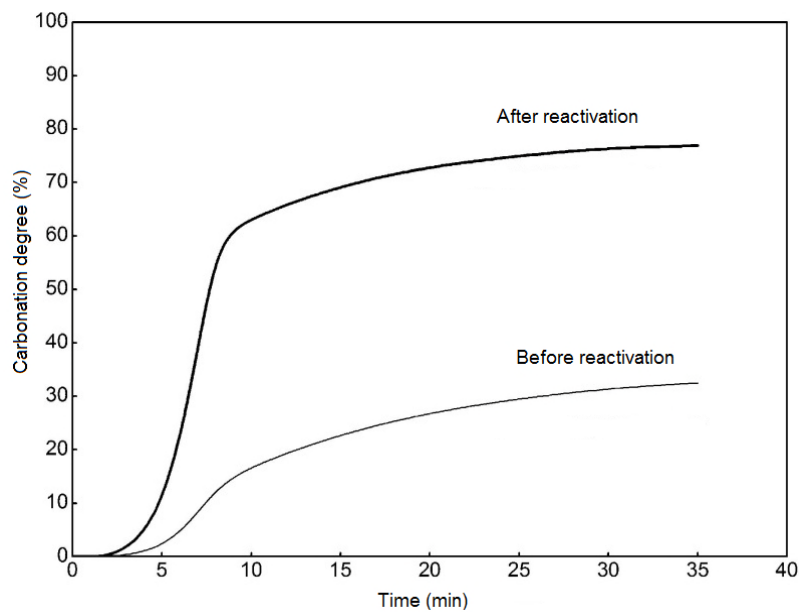


Figure 15: Effect of hydration on sorbent activity (after the first cycle in tube furnace) [155]

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].

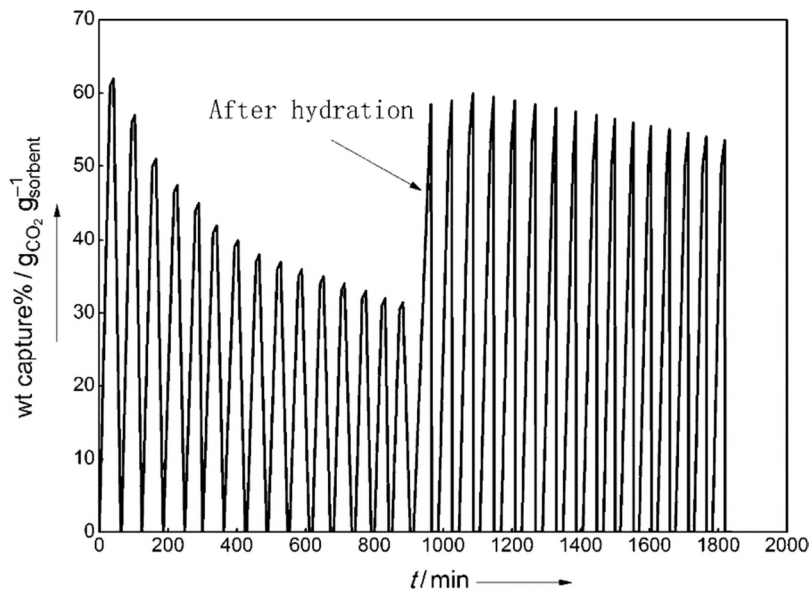


Figure 16: Effect of hydration on decay rate of CO₂ sorption of CaO sorbent (the hydration was performed after the 15th cycle) [150]

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

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

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

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

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

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

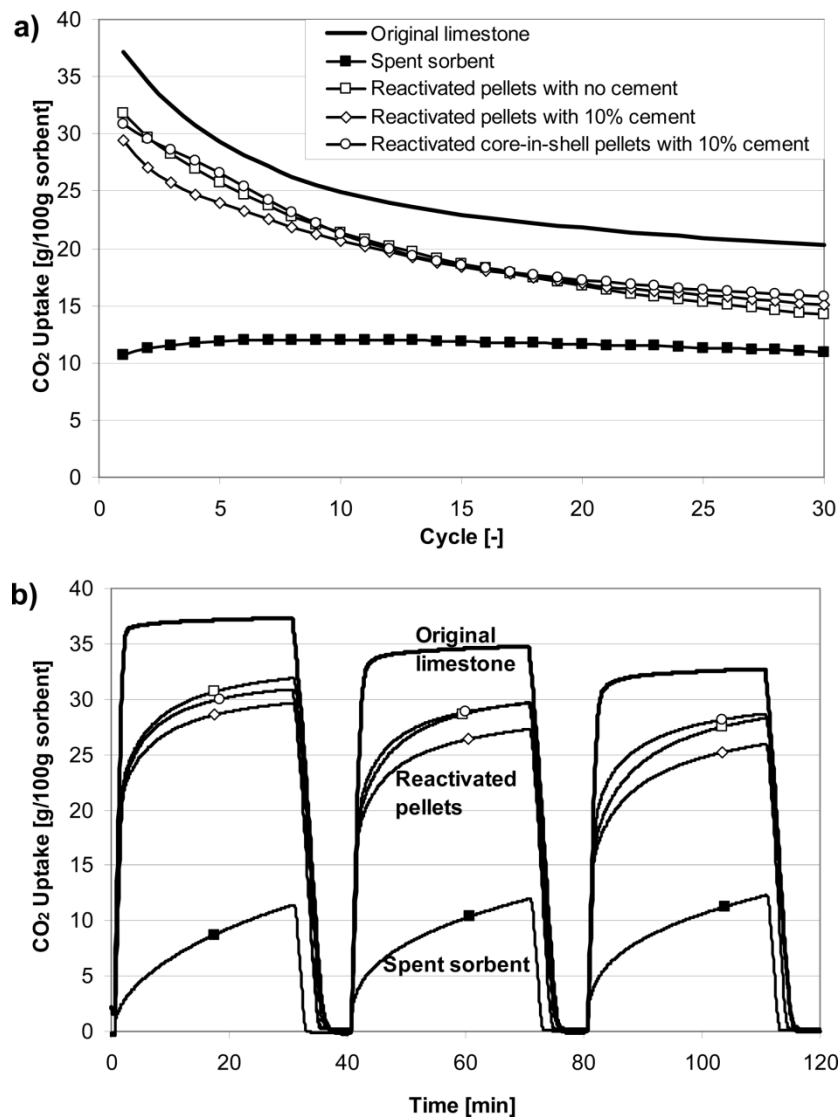


Figure 17: CO₂ capture performance of tested sorbents: (a) CO₂ capture capacity during 30 cycles, and (b) conversion profiles during the first three cycles. Conditions: carbonation in 50% CO₂ (N₂ balance) for 30 min, calcination in 100% N₂ for 10 min, isothermally at 800°C [167]

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.

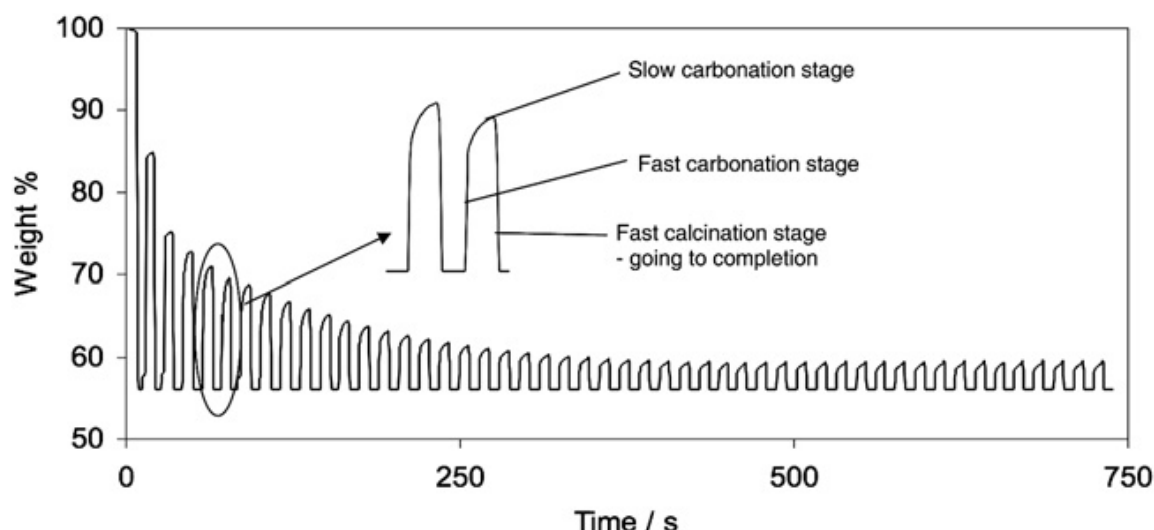


Figure 18: Repeated calcination/carbonation cycles of limestone in a TGA [32]

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.

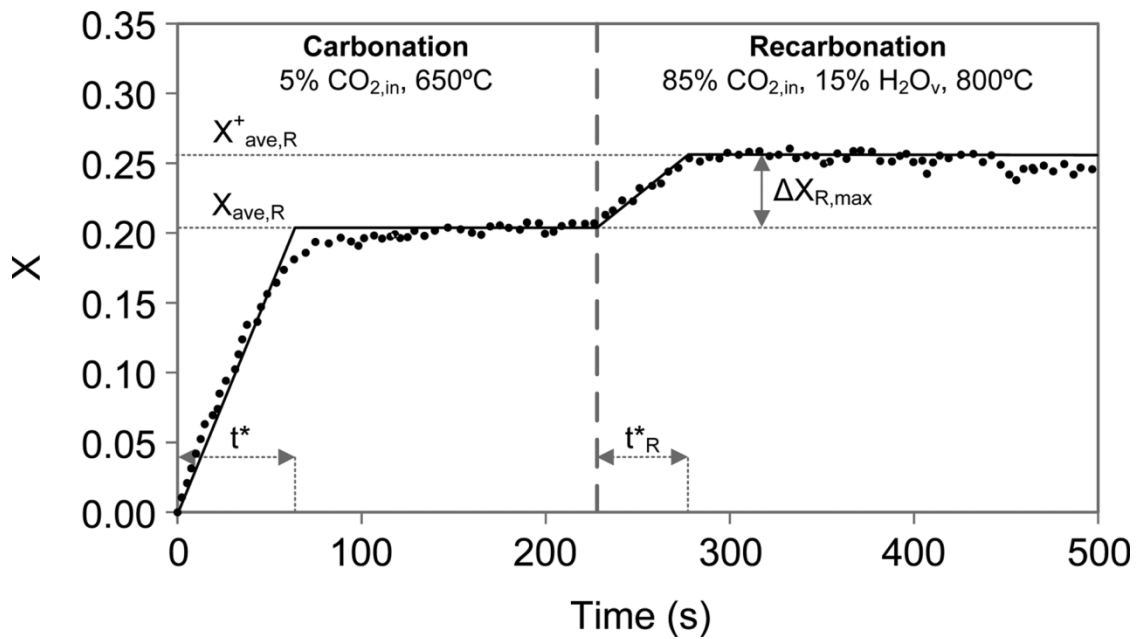


Figure 19: Example of a typical conversion versus time curve during carbonation and recarbonation stages [168]

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.

9. References

- [1] IEA. CO₂ emissions from fuel combustion. 2015.
- [2] Nakicenovic N, Swart R. IPCC, Intergovernmental panel on climate change: Special report on emissions scenarios. Cambridge: 2000.
- [3] Watson RT, Albritton DT. IPCC, Climate change 2001: Synthesis report A. Contribution of working groups I, II and III to the third assessment report on intergovernmental panel on climate change. Cambridge: 2001.
- [4] IEA. World energy outlook. London: 2014.
- [5] Fan L-S. Chemical looping systems for fossil energy conversions. John Wiley & Sons; 2011.
- [6] Herzog H, Eliasson B, Kaarstad O. Capturing greenhouse gases. Sci Am 2000;282:72–79.
- [7] Rackley SA. Carbon Capture and Storage. Elsevier; 2010.
- [8] Li F, Fan L-S. Clean coal conversion processes-progress and challenges. Energy Environ Sci 2008;1:248-267. doi:10.1039/b809218b.
- [9] MacDowell N, Florin N, Buchard A, Hallett J, Galindo A, Jackson G, Garrido A, Jackson G, Adjiman CS, Williams CK, Shah N, P Fennell. An overview of CO₂

capture technologies. *Energy Environ Sci* 2010;3:1645-1669. doi:10.1039/c004106h.

[10] Supap T, Idem R, Tontiwachwuthikul P, Saiwan C. Analysis of monoethanolamine and its oxidative degradation products during CO₂ absorption from flue gases: A comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations. *Ind Eng Chem Res* 2006;45:2437–2451. doi:10.1021/ie050559d.

[11] Veawab A, Tontiwachwuthikul P, Chakma A. Investigation of low-toxic organic corrosion inhibitors for CO₂ separation process using aqueous MEA solvent. *Ind Eng Chem Res* 2001;40:4771–4777.

[12] Aaron D, Tsouris C. Separation of CO₂ from flue gas: A review. *Sep Sci Technol* 2005;40:321–348. doi:10.1081/SS-200042244.

[13] Chi S, Rochelle G. Oxidative degradation of monoethanolamine. *Ind Eng Chem Res* 2002;41:4178–86. doi:10.1021/ie010697c.

[14] Goff GS, Rochelle GT. Monoethanolamine degradation: O₂ mass transfer effects under CO₂ capture conditions. *Ind Eng Chem Res* 2004;43:6400–6408. doi:10.1021/ie0400245.

[15] Fytianos G, Ucar S, Grimstvedt A, Hyldbakk A, Svendsen HF, Knuutila HK. Corrosion and degradation in MEA based post-combustion CO₂ capture. *Int J Greenh Gas Control* 2016;46:48–56. doi:10.1016/j.ijggc.2015.12.028.

[16] Li K, Leigh W, Feron P, Yu H, Tade M. Systematic study of aqueous monoethanolamine (MEA)-based CO₂ capture process: Techno-economic assessment of the MEA process and its improvements. *Appl Energy* 2016;165:648–659. doi:10.1016/j.apenergy.2015.12.109.

[17] Xiong YQ, Luo P, Hua B. Energy consumption analysis of air separation process for oxy-fuel combustion system. *4th Int Conf Chem Eng Adv Mater* 2014;1033-1034:146–150. doi:10.4028/www.scientific.net/AMR.1033-1034.146.

[18] Idem R, Wilson M, Tontiwachwuthikul P, Chakma A, Veawab A, Aroonwilas A, Gelowitz D. Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the Boundary Dam CO₂ capture demonstration plant. *Ind Eng Chem Res* 2006;45:2414–2420. doi:10.1021/ie050569e.

[19] Bhowan AS, Freeman BC. Analysis and status of post-combustion carbon dioxide capture technologies. *Environ Sci Technol* 2011;45:8624–8632. doi:10.1021/es104291d.

[20] Dean CC, Blamey J, Florin NH, Al-Jeboori MJ, Fennell PS. The calcium looping cycle for CO₂ capture from power generation, cement manufacture and

hydrogen production. Chem Eng Res Des 2011;89:836–855.
doi:10.1016/j.cherd.2010.10.013.

[21] Hamilton RH, Herzog H, Parsons JE. Cost and U.S. public policy for new coal power plants with carbon capture and sequestration. Energy Procedia, 2009, p. 4487–94.

[22] Blyth W, Bradley R, Bunn D, Clarke C, Wilson T, Yang M. Investment risks under uncertain climate change policy. Energy Policy 2007;35:5766–5773. doi:10.1016/j.enpol.2007.05.030.

[23] Markewitz P, Kuckshinrichs W, Leitner W, Linssen J, Zapp P, Bongartz R, Schreiber A, Müller TE. Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂. Energy Environ Sci 2012;5:7281–7305. doi:10.1039/c2ee03403d.

[24] Hanak DP, Anthony EJ, Manovic V. A review of developments in pilot-plant testing and modelling of calcium looping process for CO₂ capture from power generation systems. Energy Environ Sci 2015;8:2199–2249. doi:10.1039/C5EE01228G.

[25] Shimizu T, Hiramata T, Hosoda H, Kitano K, Inagaki M, Tejima K. A twin fluid-bed reactor for removal of CO₂ from combustion processes. Chem Eng Res Des 1999;77:62–68. doi:10.1205/026387699525882.

[26] Alonso M, Rodríguez N, Grasa G, Abanades JC. Modelling of a fluidized bed carbonator reactor to capture CO₂ from a combustion flue gas. Chem Eng Sci 2009;64:883–891. doi:10.1016/j.ces.2008.10.044.

[27] Lasheras A, Ströhle J, Galloy A, Eppele B. Carbonate looping process simulation using a 1D fluidized bed model for the carbonator. Int J Greenh Gas Control 2011;5:686–693. doi:10.1016/j.ijggc.2011.01.005.

[28] Valverde JM. A model on the CaO multicyclic conversion in the Ca-looping process. Chem Eng J 2013;228:1195–1206. doi:10.1016/j.cej.2013.05.023.

[29] Lu DY, Hughes RW, Anthony EJ. Ca-based sorbent looping combustion for CO₂ capture in pilot-scale dual fluidized beds. Fuel Process Technol 2008;89:1386–1395. doi:10.1016/j.fuproc.2008.06.011.

[30] Álvarez D, Carlos Abanades J. Determination of the critical product layer thickness in the reaction of CaO with CO₂. Ind Eng Chem Res 2005;44:5608–5615. doi:10.1021/ie050305s.

[31] Arias B, Abanades JC, Grasa GS. An analysis of the effect of carbonation conditions on CaO deactivation curves. Chem Eng J 2011;167:255–261. doi:10.1016/j.cej.2010.12.052.

1080 [32] Blamey J, Anthony EJ, Wang J, Fennell PS. The calcium looping cycle for
 1081 large-scale CO₂ capture. *Prog Energy Combust Sci* 2010;36:260–279.
 1082 doi:10.1016/j.pecs.2009.10.001.

1083 [33] Yin J, Qin C, Feng B, Ge L, Luo C, Liu W, et al. Calcium looping for CO₂
 1084 capture at a constant high temperature. *Energy & Fuels* 2014;28:307–318.
 1085 doi:10.1021/ef401399c.

1086 [34] Valverde JM, Sanchez-Jimenez PE, Perejon A, Perez-Maqueda LA. CO₂
 1087 multicyclic capture of pretreated/doped CaO in the Ca-looping process. Theory and
 1088 experiments. *Phys Chem Chem Phys* 2013;15:11775–11793.
 1089 doi:10.1039/c3cp50480h.

1090 [35] Hanak DP, Biliyok C, Anthony EJ, Manovic V. Modelling and comparison of
 1091 calcium looping and chemical solvent scrubbing retrofits for CO₂ capture from coal-
 1092 fired power plant. *Int J Greenh Gas Control* 2015;42:226–236.
 1093 doi:10.1016/j.ijggc.2015.08.003.

1094 [36] Romano MC. Modeling the carbonator of a Ca-looping process for CO₂
 1095 capture from power plant flue gas. *Chem Eng Sci* 2012;69:257–269.
 1096 doi:10.1016/j.ces.2011.10.041.

1097 [37] Abanades JC, Anthony EJ, Wang J, Oakey JE. Fluidized bed combustion
 1098 systems integrating CO₂ capture with CaO. *Environ Sci Technol* 2005;39:2861–
 1099 2866. doi:10.1021/es0496221.

1100 [38] Mantripragada HC, Rubin ES. Calcium Looping Cycle for CO₂ Capture:
 1101 Performance, Cost And Feasibility Analysis. *Energy Procedia* 2014;63:2199–2206.
 1102 doi:10.1016/j.egypro.2014.11.239.

1103 [39] Zhao M, Minett AI, Harris AT. A review of techno-economic models for the
 1104 retrofitting of conventional pulverised-coal power plants for post-combustion capture
 1105 (PCC) of CO₂. *Energy Environ Sci* 2013;6:25–40. doi:10.1039/c2ee22890d.

1106 [40] Abanades JC, Grasa G, Alonso M, Rodriguez N, Anthony EJ, Romeo LM.
 1107 Cost structure of a postcombustion CO₂ capture system using CaO. *Environ Sci*
 1108 *Technol* 2007;41:5523–5527. doi:10.1021/es070099a.

1109 [41] Cormos CC. Economic evaluations of coal-based combustion and
 1110 gasification power plants with post-combustion CO₂ capture using calcium looping
 1111 cycle. *Energy* 2014;78:665–673. doi:10.1016/j.energy.2014.10.054.

1112 [42] Cormos CC. Assessment of chemical absorption/adsorption for post-
 1113 combustion CO₂ capture from Natural Gas Combined Cycle (NGCC) power plants.
 1114 *Appl Therm Eng* 2015;82:120–128. doi:10.1016/j.applthermaleng.2015.02.054.

1115 [43] Romeo LM, Abanades JC, Escosa JM, Paño J, Giménez A, Sánchez-
 1116 Biezma A, Ballesteros JC. Oxyfuel carbonation/calcination cycle for low cost CO₂

1117 capture in existing power plants. *Energy Convers Manag* 2008;49:2809–2814.
 1118 doi:10.1016/j.enconman.2008.03.022.

1119 [44] Borgwardt HR. Sintering of nascent calcium oxide. *Chem Eng Sci*
 1120 1989;44:53–60. doi:10.1016/0009-2509(89)85232-7.

1121 [45] Sun P, Grace JR, Lim CJ, Anthony EJ. The effect of CaO sintering on cyclic
 1122 CO₂ capture in energy systems. *AIChE J* 2007;53:2432–2442.

1123 [46] Fennell PS, Pacciani R, Dennis JS, Davidson JF, Hayhurst AN. The effects
 1124 of repeated cycles of calcination and carbonation on a variety of different
 1125 limestones, as measured in a hot fluidized bed of sand. *Energy and Fuels*
 1126 2007;21:2072–2081. doi:10.1021/ef060506o.

1127 [47] Blamey J, Paterson NPM, Dugwell DR, Fennell PS. Mechanism of particle
 1128 breakage during reactivation of CaO-based sorbents for CO₂ capture. *Energy and*
 1129 *Fuels* 2010;24:4605–4616. doi:10.1021/ef100476d.

1130 [48] Baker R. The reversibility of the reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$. *J Appl Chem*
 1131 *Biotechnol* 1973;23:733–742.

1132 [49] Sun P, Lim CJ, Grace JR. Cyclic CO₂ capture by limestone-derived sorbent
 1133 during prolonged calcination/carbonation cycling. *Am Inst Chem Eng*
 1134 2008;754:405–410. doi:10.1002/aic.

1135 [50] Salvador C, Lu D, Anthony EJ, Abanades JC. Enhancement of CaO for CO₂
 1136 capture in an FBC environment. *Chem Eng J* 2003;96:187–195.
 1137 doi:10.1016/j.cej.2003.08.011.

1138 [51] Lysikov AI, Salanov AN, Okunev AG. Change of CO₂ carrying capacity of
 1139 CaO in isothermal recarbonation-decomposition cycles. *Ind Eng Chem Res*
 1140 2007;46:4633–4638. doi:10.1021/ie0702328.

1141 [52] Coppola A, Scala F, Salatino P, Montagnaro F. Fluidized bed calcium
 1142 looping cycles for CO₂ capture under oxy-firing calcination conditions: Part 1.
 1143 Assessment of six limestones. *Chem Eng J* 2013;231:537–543.
 1144 doi:10.1016/j.cej.2013.07.113.

1145 [53] Coppola A, Montagnaro F, Salatino P, Scala F. Attrition of Limestone During
 1146 Fluidized Bed Calcium Looping Cycles for CO₂ Capture. *Combust Sci Technol*
 1147 2012;184:929–941. doi:10.1080/00102202.2012.663986.

1148 [54] Coppola A, Montagnaro F, Salatino P, Scala F. Fluidized bed calcium
 1149 looping: The effect of SO₂ on sorbent attrition and CO₂ capture capacity. *Chem Eng*
 1150 *J* 2012;207-208:445–449. doi:10.1016/j.cej.2012.06.149.

1151 [55] Abanades JC, Rubin ES, Anthony EJ. Sorbent cost and performance in CO₂
 1152 capture systems. *Ind Eng Chem Res* 2004;3462–3466. doi:10.1021/ie049962v.

- 1153 [56] Chen S, Xiang W, Wang D, Xue Z. Incorporating IGCC and CaO sorption-
 1154 enhanced process for power generation with CO₂ capture. *Appl Energy*
 1155 2012;95:285–294. doi:10.1016/j.apenergy.2012.02.056.
- 1156 [57] Romeo LM, Lara Y, Lisbona P, Escosa JM. Optimizing make-up flow in a CO₂
 1157 capture system using CaO. *Chem Eng J* 2009;147:252–258.
 1158 doi:10.1016/j.cej.2008.07.010.
- 1159 [58] Jia L, Hughes R, Lu D, Anthony EJ, Lau I. Attrition of calcining limestones in
 1160 circulating fluidized-bed systems. *Ind Eng Chem Res* 2007;46:5199–5209.
 1161 doi:10.1021/ie061212t.
- 1162 [59] Grasa GS, Abanades JC. CO₂ Capture Capacity of CaO in Long Series of
 1163 Carbonation/Calcination Cycles. *Ind Eng Chem Res* 2006;45:8846–8851.
 1164 doi:10.1021/ie0606946.
- 1165 [60] Arias B, Grasa GS, Alonso M, Abanades JC. Post-combustion calcium
 1166 looping process with a highly stable sorbent activity by recarbonation. *Energy*
 1167 *Environ Sci* 2012;5:7353–7359. doi:10.1039/c2ee03008j.
- 1168 [61] Wang J, Manovic V, Wu Y, Anthony EJ. A study on the activity of CaO-based
 1169 sorbents for capturing CO₂ in clean energy processes. *Appl Energy* 2010;87:1453–
 1170 1458. doi:10.1016/j.apenergy.2009.08.010.
- 1171 [62] González B, Alonso M, Abanades JC. Sorbent attrition in a
 1172 carbonation/calcination pilot plant for capturing CO₂ from flue gases. *Fuel*
 1173 2010;89:2918–2924. doi:10.1016/j.fuel.2010.01.019.
- 1174 [63] Chen H, Zhao C, Yang Y, Zhang P. CO₂ capture and attrition performance of
 1175 CaO pellets with aluminate cement under pressurized carbonation. *Appl Energy*
 1176 2012;91:334–340. doi:10.1016/j.apenergy.2011.09.032.
- 1177 [64] Arias B, Diego ME, Abanades JC, Lorenzo M, Diaz L, Martínez D, Alvarez J,
 1178 Sánchez-Biezma A. Demonstration of steady state CO₂ capture in a 1.7MW_{th}
 1179 calcium looping pilot. *Int J Greenh Gas Control* 2013;18:237–245.
 1180 doi:10.1016/j.ijggc.2013.07.014.
- 1181 [65] Sánchez-Biezma A., Paniagua J, Diaz L, Lorenzo M, Alvarez J, Martínez D,
 1182 Arias B, Diego ME, Abanades JC. Testing postcombustion CO₂ capture with CaO in
 1183 a 1.7MW_{th} pilot facility. *Energy Procedia* 2013;37:1–8.
 1184 doi:10.1016/j.egypro.2013.05.078.
- 1185 [66] Ströhle J, Junk M, Kremer J, Galloy A, Epple B. Carbonate looping
 1186 experiments in a 1 MW_{th} pilot plant and model validation. *Fuel* 2014;127:13–22.
 1187 doi:10.1016/j.fuel.2013.12.043.

- 1188 [67] Dieter H, Hawthorne C, Zieba M, Scheffknecht G. Progress in Calcium
1189 Looping post combustion CO₂ Capture: Successful pilot scale demonstration.
1190 Energy Procedia 2013;37:48–56. doi:10.1016/j.egypro.2013.05.084.
- 1191 [68] Manovic V, Anthony EJ. Parametric study on the CO₂ capture capacity of
1192 CaO-based sorbents in looping cycles. Energy & Fuels 2008;22:1851–1857.
1193 doi:10.1021/ef800011z.
- 1194 [69] Manovic V, Charland JP, Blamey J, Fennell PS, Lu DY, Anthony EJ.
1195 Influence of calcination conditions on carrying capacity of CaO-based sorbent in
1196 CO₂ looping cycles. Fuel 2009;88:1893–1900. doi:10.1016/j.fuel.2009.04.012.
- 1197 [70] Li YJ, Zhao CS, Duan LB, Liang C, Li QZ, Zhou W, Chen HC. Cyclic
1198 calcination/carbonation looping of dolomite modified with acetic acid for CO₂
1199 capture. Fuel Process Technol 2008;89:1461–1469.
1200 doi:10.1016/j.fuproc.2008.07.008.
- 1201 [71] Chrissafis K, Dagounaki C, Paraskevopoulos KM. The effects of procedural
1202 variables on the maximum capture efficiency of CO₂ using a carbonation/calcination
1203 cycle of carbonate rocks. Thermochim Acta 2005;428:193–198.
1204 doi:10.1016/j.tca.2004.10.010.
- 1205 [72] Valverde JM, Sanchez-Jimenez PE, Perez-Maqueda LA. Ca-looping for
1206 postcombustion CO₂ capture: A comparative analysis on the performances of
1207 dolomite and limestone. Appl Energy 2015;138:202–215.
- 1208 [73] Itskos G, Grammelis P, Scala F, Pawlak-Kruczek H, Coppola A, Salatino P,
1209 Kakaras E. A comparative characterization study of Ca-looping natural sorbents.
1210 Appl Energy 2013;108:373–382. doi:10.1016/j.apenergy.2013.03.009.
- 1211 [74] Deshpande N, Yuh B. Screening of multiple waste animal shells as a source
1212 of calcium sorbent for high temperature CO₂ capture. Sustain Environ Res
1213 2013;23:227–232.
- 1214 [75] Sacia ER, Ramkumar S, Phalak N, Fan LS. Synthesis and regeneration of
1215 sustainable CaO sorbents from chicken eggshells for enhanced carbon dioxide
1216 capture. ACS Sustain Chem Eng 2013;1:903–909. doi:10.1021/sc300150k.
- 1217 [76] Ives M, Mundy RC, Fennell PS, Davidson JF, Dennis JS, Hayhurst AN.
1218 Comparison of different natural sorbents for removing CO₂ from combustion gases,
1219 as studied in a bench-scale fluidized bed. Energy & Fuels 2008;22:3852–3857.
1220 doi:10.1021/ef800417v.
- 1221 [77] Shan SY, Ma AH, Hu YC, Jia QM, Wang YM, Peng JH. Development of
1222 sintering-resistant CaO-based sorbent derived from eggshells and bauxite tailings
1223 for cyclic CO₂ capture. Environ Pollut 2015;208:546–552.
1224 doi:10.1016/j.envpol.2015.10.028.

- 1225 [78] Wu SF, Beum TH, Yang JI, Kim JN. Properties of Ca-base CO₂ sorbent
1226 using Ca(OH)₂ as precursor. *Ind Eng Chem Res* 2007;46:7896–7899.
1227 doi:10.1021/ie070135e.
- 1228 [79] Hughes RW, Lu D, Anthony EJ, Wu Y. Improved long-term conversion of
1229 limestone-derived sorbents for in-situ capture of CO₂ in a fluidized bed combustor.
1230 *Ind Eng Chem Res* 2004;43:5529–5539. doi:10.1021/ie034260b.
- 1231 [80] González B, Blamey J, McBride-Wright M, Carter N, Dugwell D, Fennell P,
1232 Abanades JC. Calcium looping for CO₂ capture: Sorbent enhancement through
1233 doping. *Energy Procedia* 2011;4:402–409. doi:10.1016/j.egypro.2011.01.068.
- 1234 [81] Al-Jeboori MJ, Nguyen M, Dean C, Fennell PS. Improvement of limestone-
1235 based CO₂ sorbents for Ca looping by HBr and other mineral acids. *Ind Eng Chem*
1236 *Res* 2013;52:1426–1433. doi:10.1021/ie302198g.
- 1237 [82] Al-Jeboori MJ, Fennell PS, Nguyen M, Feng K. Effects of different dopants
1238 and doping procedures on the reactivity of CaO-based sorbents for CO₂ capture.
1239 *Energy & Fuels* 2012;26:6584–6594. doi:10.1021/ef301153b.
- 1240 [83] Sun R, Li Y, Liu H, Wu S, Lu C. CO₂ capture performance of calcium-based
1241 sorbent doped with manganese salts during calcium looping cycle. *Appl Energy*
1242 2012;89:368–373. doi:10.1016/j.apenergy.2011.07.051.
- 1243 [84] Chen H, Zhao C, Yu W. Calcium-based sorbent doped with attapulgite for
1244 CO₂ capture. *Appl Energy* 2013;112:67–74. doi:10.1016/j.apenergy.2013.06.002.
- 1245 [85] Manovic V, Fennell PS, Al-Jeboori MJ, Anthony EJ. Steam-enhanced
1246 calcium looping cycles with calcium aluminate pellets doped with bromides. *Ind Eng*
1247 *Chem Res* 2013;52:7677–7683. doi:10.1021/ie400197w.
- 1248 [86] González B, Blamey J, Al-Jeboori MJ, Florin NH, Clough PT, Fennell PS.
1249 Additive effects of steam addition and HBr doping for CaO-based sorbents for CO₂
1250 capture. *Chem Eng Process Process Intensif* 2015;103:21-26.
1251 doi:10.1016/j.cep.2015.09.019.
- 1252 [87] Reddy EP, Smirniotis PG. High-temperature sorbents for CO₂ made of alkali
1253 metals doped on CaO supports. *J Phys Chem B* 2004;108:7794–7800.
1254 doi:10.1021/jp031245b.
- 1255 [88] Sun P, Grace JR, Lim CJ, Anthony EJ. Investigation of attempts to improve
1256 cyclic CO₂ capture by sorbent hydration and modification. *Ind Eng Chem Res*
1257 2008;47:2024–2032. doi:10.1021/ie070335q.
- 1258 [89] Manovic V, Anthony EJ. Thermal activation of CaO-based sorbent and self-
1259 reactivation during CO₂ capture looping cycles. *Environ Sci Technol* 2008;42:4170–
1260 4174. doi:10.1021/es800152s.

- 1261 [90] Albrecht KO, Wagenbach KS, Satrio JA, Shanks BH, Wheelock TD.
 1262 Development of a CaO-based sorbent with improved cyclic stability. *Ind Eng Chem*
 1263 *Res* 2008;47:7841–7848. doi:10.1021/ie8007743.
- 1264 [91] Manovic V, Anthony EJ, Grasa G, Abanades JC. CO₂ looping cycle
 1265 performance of a high-purity limestone after thermal activation/doping. *Energy &*
 1266 *Fuels* 2008;22:3258–3264. doi:10.1021/ef800316h.
- 1267 [92] Chen Z, Song HS, Portillo M, Lim CJ, Grace JR, Anthony EJ. Long-term
 1268 calcination/carbonation cycling and thermal pretreatment for CO₂ capture by
 1269 limestone and dolomite. *Energy & Fuels* 2009;23:1437–1444.
 1270 doi:10.1021/ef800779k.
- 1271 [93] Gupta H, Fan L-S. Carbonation–Calcination Cycle Using High Reactivity
 1272 Calcium Oxide for Carbon Dioxide Separation from Flue Gas. *Ind Eng Chem Res*
 1273 2002;41:4035–4042. doi:10.1021/ie010867l.
- 1274 [94] Li Y, Zhao CS, Chen H, Liu Y. Enhancement of Ca-based sorbent multicyclic
 1275 behavior in Ca looping process for CO₂ separation. *Chem Eng Technol*
 1276 2009;32:548–555. doi:10.1002/ceat.200800525.
- 1277 [95] Ridha FN, Manovic V, Macchi A, Anthony EJ. The effect of SO₂ on CO₂
 1278 capture by CaO-based pellets prepared with a kaolin derived Al(OH)₃ binder. *Appl*
 1279 *Energy* 2012;92:415–520. doi:10.1016/j.apenergy.2011.11.036.
- 1280 [96] Adánez J, Fierro V, García-Labiano F, Palacios J. Study of modified calcium
 1281 hydroxides for enhancing SO₂ removal during sorbent injection in pulverized coal
 1282 boilers. *Fuel* 1997;76:257–265. doi:10.1016/S0016-2361(96)00204-9.
- 1283 [97] Li Y, Zhao CS, Qu C, Duan L, Li Q, Liang C. CO₂ capture using CaO
 1284 modified with ethanol/water solution during cyclic calcination/carbonation. *Chem*
 1285 *Eng Technol* 2008;31:237–244. doi:10.1002/ceat.200700371.
- 1286 [98] Sun R, Li Y, Wu S, Liu C, Liu H, Lu C. Enhancement of CO₂ capture capacity
 1287 by modifying limestone with propionic acid. *Powder Technol* 2013;233:8–14.
 1288 doi:10.1016/j.powtec.2012.08.011.
- 1289 [99] Li Y, Sun R, Liu H, Lu C. Cyclic CO₂ capture behavior of limestone modified
 1290 with pyroligneous acid (PA) during calcium looping cycles. *Ind Eng Chem Res*
 1291 2011;50:10222–10228. doi:10.1021/ie2007455.
- 1292 [100] Ridha FN, Manovic V, Wu Y, Macchi A, Anthony EJ. Post-combustion CO₂
 1293 capture by formic acid-modified CaO-based sorbents. *Int J Greenh Gas Control*
 1294 2013;16:21–28. doi:10.1016/j.ijggc.2013.02.026.
- 1295 [101] Ridha FN, Manovic V, Macchi A, Anthony MA, Anthony EJ. Assessment of
 1296 limestone treatment with organic acids for CO₂ capture in Ca-looping cycles. *Fuel*
 1297 *Process Technol* 2013;116:284–291. doi:10.1016/j.fuproc.2013.07.007.

1298 [102] Zhang M, Peng Y, Sun Y, Li P, Yu J. Preparation of CaO-Al₂O₃ sorbent and
 1299 CO₂ capture performance at high temperature. *Fuel* 2013;111:636–642.
 1300 doi:10.1016/j.fuel.2013.03.078.

1301 [103] Li Y, Shi L, Liu C, He Z, Wu S. Studies on CO₂ uptake by CaO/Ca₃Al₂O₆
 1302 sorbent in calcium looping cycles. *J Therm Anal Calorim* 2015;120:1519-1528.
 1303 doi:10.1007/s10973-015-4480-9.

1304 [104] Li Y, Su M, Xie X, Wu S, Liu C. CO₂ capture performance of synthetic
 1305 sorbent prepared from carbide slag and aluminum nitrate hydrate by combustion
 1306 synthesis. *Appl Energy* 2015;145:60–68.

1307 [105] Wang K, Guo X, Zhao P, Zheng C. Cyclic CO₂ capture of CaO-based
 1308 sorbent in the presence of metakaolin and aluminum (hydr)oxides. *Appl Clay Sci*
 1309 2010;50:41–46. doi:10.1016/j.clay.2010.06.021.

1310 [106] Li CC, Wu UT, Lin HP. Cyclic performance of CaCO₃@mSiO₂ for CO₂
 1311 capture in a calcium looping cycle. *J Mater Chem A* 2014;2:8252-8257.
 1312 doi:10.1039/c4ta00516c.

1313 [107] Li L, King DL, Nie Z, Howard C. Magnesia-stabilized calcium oxide
 1314 absorbents with improved durability for high temperature CO₂ capture. *Ind Eng*
 1315 *Chem Res* 2009;48:10604–10613. doi:10.1021/ie901166b.

1316 [108] Zhao M, Bilton M, Brown AP, Cunliffe AM, Dvininov E, Dupont V, Comyn TP,
 1317 Milne SJ. Durability of CaO–CaZrO₃ sorbents for high-temperature CO₂ capture
 1318 prepared by a wet chemical method. *Energy & Fuels* 2014;28:1275–1283.
 1319 doi:10.1021/ef4020845.

1320 [109] Luo C, Zheng Y, Ding N, Zheng C. Enhanced cyclic stability of CO₂
 1321 adsorption capacity of CaO-based sorbents using La₂O₃ or Ca₁₂Al₁₄O₃₃ as
 1322 additives. *Korean J Chem Eng* 2011;28:1042–1046. doi:10.1007/s11814-010-0469-
 1323 z.

1324 [110] Luo C, Zheng Y, Ding N, Wu Q, Bian G, Zheng C. Development and
 1325 performance of CaO/La₂O₃ sorbents during calcium looping cycles for CO₂ capture.
 1326 *Ind Eng Chem Res* 2010;49:11778–11784.

1327 [111] Luo C, Zheng Y, Zheng C, Yin J, Qin C, Feng B. Manufacture of calcium-
 1328 based sorbents for high temperature cyclic CO₂ capture via a sol-gel process. *Int J*
 1329 *Greenh Gas Control* 2013;12:193–199. doi:10.1016/j.ijggc.2012.11.011.

1330 [112] Radfarnia HR, Sayari A. A highly efficient CaO-based CO₂ sorbent prepared
 1331 by a citrate-assisted sol-gel technique. *Chem Eng J* 2015;262:913–920.

1332 [113] Angeli SD, Martavaltzi CS, Lemonidou AA. Development of a novel-
 1333 synthesized Ca-based CO₂ sorbent for multicycle operation: Parametric study of
 1334 sorption. *Fuel* 2014;127:62–69. doi:10.1016/j.fuel.2013.10.046.

1335 [114] Wang B, Yan R, Lee DH, Zheng Y, Zhao H, Zheng C. Characterization and
 1336 evaluation of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier prepared by sol-gel combustion synthesis.
 1337 J Anal Appl Pyrolysis 2011;91:105–113. doi:10.1016/j.jaap.2011.01.010.

1338 [115] Wang B, Song X, Wang Z, Zheng C. Preparation and application of the sol-
 1339 gel combustion synthesis-made $\text{CaO}/\text{CaZrO}_3$ sorbent for cyclic CO_2 capture
 1340 through the severe calcination condition. Chinese J Chem Eng 2014;22:991–999.

1341 [116] Broda M, Müller CR. Sol-gel-derived, CaO -based, ZrO_2 -stabilized CO_2
 1342 sorbents. Fuel 2014;127:94–100. doi:10.1016/j.fuel.2013.08.004.

1343 [117] Luo C, Zheng Y, Xu Y, Ding H, Zheng C, Qin C, Feng B. Cyclic CO_2 capture
 1344 characteristics of a pellet derived from sol-gel CaO powder with $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$
 1345 support. Korean J Chem Eng 2015;31:1–5. doi:10.1007/s11814-014-0291-0.

1346 [118] Florin N, Fennell P. Synthetic CaO -based sorbent for CO_2 capture. Energy
 1347 Procedia 2011;4:830–838. doi:10.1016/j.egypro.2011.01.126.

1348 [119] Wang M, Lee CG, Ryu CK. CO_2 sorption and desorption efficiency of
 1349 Ca_2SiO_4 . Int J Hydrogen Energy 2008;33:6368–6372.
 1350 doi:10.1016/j.ijhydene.2008.07.114.

1351 [120] Valverde JM, Perejon A., Perez-Maqueda LA. Enhancement of fast CO_2
 1352 capture by a nano- SiO_2/CaO composite at Ca-looping conditions. Environ Sci
 1353 Technol 2012;46:6401–6408. doi:10.1021/es3002426.

1354 [121] Luo C, Zheng Y, Ding N, Wu Q, Bian G, Zheng C. Development and
 1355 performance of $\text{CaO}/\text{La}_2\text{O}_3$ sorbents during calcium looping cycles for CO_2 capture.
 1356 Ind Eng Chem Res 2010;49:11778–11774.

1357 [122] George SM. Atomic layer deposition: An overview. Chem Rev
 1358 2010;110:111–131. doi:10.1021/cr900056b.

1359 [123] Puurunen RL. Surface chemistry of atomic layer deposition: A case study for
 1360 the trimethylaluminum/water process. J Appl Phys 2005;97:121301-121335.
 1361 doi:10.1063/1.1940727.

1362 [124] Soria-Hoyo C, Valverde JM, van Ommen JR, Sánchez-Jiménez PE.
 1363 Synthesis of a nanosilica supported CO_2 sorbent in a fluidized bed reactor. Appl
 1364 Surf Sci 2015;328:548–553.

1365 [125] Peng W, Xu Z, Luo C, Zhao H. Tailor-made core-shell $\text{CaO}/\text{TiO}_2\text{-Al}_2\text{O}_3$
 1366 architecture as a high-capacity and long-life CO_2 sorbent. Environ Sci Technol
 1367 2015;49:8237–8245. doi:10.1021/acs.est.5b01415.

1368 [126] Peng W, Xu Z, Zhao H. Batch fluidized bed test of SATS-derived $\text{CaO}/\text{TiO}_2\text{-}$
 1369 Al_2O_3 sorbent for calcium looping. Fuel 2016;170:226–234.
 1370 doi:10.1016/j.fuel.2015.12.004.

1371 [127] Langereis E, Heil S, Knoops H, Keuning W, van de Sanden M, Kessels W. In
 1372 situ spectroscopic ellipsometry as a versatile tool for studying atomic layer
 1373 deposition. *J Phys D-Applied Phys* 2009;42:073001–1/19. doi:10.1088/0022-
 1374 3727/42/7/073001.

1375 [128] Manovic V, Anthony EJ. Screening of binders for pelletization of CaO-based
 1376 sorbents for CO₂ capture. *Energy & Fuels* 2009;23:4797–4804.
 1377 doi:10.1021/ef900266d.

1378 [129] Wu Y, Manovic V, He I, Anthony EJ. Modified lime-based pellet sorbents for
 1379 high-temperature CO₂ capture: Reactivity and attrition behavior. *Fuel* 2012;96:454–
 1380 461. doi:10.1016/j.fuel.2012.01.034.

1381 [130] Ridha FN, Manovic V, Wu Y, Macchi A, Anthony EJ. Pelletized CaO-based
 1382 sorbents treated with organic acids for enhanced CO₂ capture in Ca-looping cycles.
 1383 *Int J Greenh Gas Control* 2013;17:357–365. doi:10.1016/j.ijggc.2013.05.009.

1384 [131] Ridha FN, Manovic V, Macchi A, Anthony EJ. High-temperature CO₂ capture
 1385 cycles for CaO-based pellets with kaolin-based binders. *Int J Greenh Gas Control*
 1386 2012;6:164–170. doi:10.1016/j.ijggc.2011.11.006.

1387 [132] Qin C, Yin J, An H, Liu W, Feng B. Performance of extruded particles from
 1388 calcium hydroxide and cement for CO₂ capture. *Energy & Fuels* 2012;26:154–161.
 1389 doi:10.1021/ef201141z.

1390 [133] Sun J, Liu W, Hu Y, Wu J, Li M, Yang X, Wang W, Xu M. Enhanced
 1391 performance of extruded–spheronized carbide slag pellets for high temperature
 1392 CO₂ capture. *Chem Eng J* 2016;285:293–303. doi:10.1016/j.cej.2015.10.026.

1393 [134] Knight A, Ellis N, Grace JR, Lim CJ. CO₂ sorbent attrition testing for fluidized
 1394 bed systems. *Powder Technol* 2014;266:412–423.
 1395 doi:10.1016/j.powtec.2014.06.013.

1396 [135] Ridha FN, Lu DY, Symonds RT, Champagne S. Attrition of CaO-based
 1397 pellets in a 0.1MW_{th} dual fluidized bed pilot plant for post-combustion CO₂ capture.
 1398 *Powder Technol* 2016;291:60–65. doi:10.1016/j.powtec.2015.11.065.

1399 [136] Ridha FN, Wu Y, Manovic V, Macchi A, Anthony EJ. Enhanced CO₂ capture
 1400 by biomass-templated Ca(OH)₂-based pellets. *Chem Eng J* 2015;274:69–75.
 1401 doi:10.1016/j.cej.2015.03.041.

1402 [137] Erans M, Beisheim T, Manovic V, Jeremias M, Patchigolla K, Dieter H, Duan
 1403 L, EJ Anthony. Effect of SO₂ and steam on CO₂ capture performance of biomass-
 1404 templated calcium aluminate pellets. *Faraday Discuss* 2016 (Accepted Manuscript).
 1405 doi:10.1039/C6FD00027D.

- 1406 [138] Sun J, Liu W, Hu Y, Li M, Yang X, Zhang Y, Xu M. Structurally improved,
1407 core-in-shell, CaO-based sorbent pellets for CO₂ capture. *Energy & Fuels*
1408 2015;29:6636–6644. doi:10.1021/acs.energyfuels.5b01419.
- 1409 [139] Manovic V, Anthony EJ. CaO-based pellets with oxygen carriers and
1410 catalysts. *Energy & Fuels* 2011;25:4846–4853. doi:10.1021/ef2009748.
- 1411 [140] Florin NH, Harris AT. Reactivity of CaO derived from nano-sized CaCO₃
1412 particles through multiple CO₂ capture-and-release cycles. *Chem Eng Sci*
1413 2009;64:187–191. doi:10.1016/j.ces.2008.10.021.
- 1414 [141] Liu WG, Low NWL, Feng B, Wang G, Diniz Da Costa JC. Calcium
1415 precursors for the production of CaO sorbents for multicycle CO₂ capture. *Environ*
1416 *Sci Technol* 2010;44:841–847. doi:10.1021/es902426n.
- 1417 [142] Wu SF, Li QH, Kim JN, Yi KB. Properties of a nano CaO/Al₂O₃ CO₂ sorbent.
1418 *Ind Eng Chem Res* 2008;47:180–184. doi:10.1021/ie0704748.
- 1419 [143] Wu SF, Zhu YQ. Behavior of CaTiO₃/nano-CaO as a CO₂ reactive
1420 adsorbent. *Ind Eng Chem Res* 2010;49:2701–2706.
- 1421 [144] Purwanto A, Wang W-N, Okuyama K. Handbook of Atomization and Sprays:
1422 Theory and Applications. Springer US; 2011, p. 869–879. doi:10.1007/978-1-4419-
1423 7264-4_39.
- 1424 [145] Lu H, Khan A, Pratsinis SE, Smirniotis PG, Zu C-. Flame-made durable
1425 doped-CaO nanosorbents for CO₂ capture. *Energy & Fuels* 2009;23:1093–1100.
- 1426 [146] Liu W, Feng B, Wu Y, Wang G, Barry J, Diniz Da Costa JC. Synthesis of
1427 sintering-resistant sorbents for CO₂ capture. *Environ Sci Technol* 2010;44:3093–
1428 3097. doi:10.1021/es903436v.
- 1429 [147] Li L, King DL, Nie Z, Li XS, Howard C. MgAl₂O₄ spinel-stabilized calcium
1430 oxide absorbents with improved durability for high-temperature CO₂ capture.
1431 *Energy & Fuels* 2010;24:3698–3703. doi:10.1021/ef100245q.
- 1432 [148] Fennell P, Anthony EJ. End use of lime-based sorbents from calcium looping
1433 systems. *Calcium and Chemical Looping Technology Power Generation Carbon*
1434 *Dioxide Capture*, 2015, p. 153–67.
- 1435 [149] Wu Y, Blamey J, Anthony EJ, Fennell PS. Morphological changes of
1436 limestone sorbent particles during carbonation/calcination looping cycles in a
1437 thermogravimetric analyzer (TGA) and reactivation with steam. *Energy & Fuels*
1438 2010;24:2768–2776. doi:10.1021/ef9012449.
- 1439 [150] Yu FC, Phalak N, Sun Z, Fan LS. Activation strategies for calcium-based
1440 sorbents for CO₂ capture: A perspective. *Ind Eng Chem Res* 2012;51:2133–2142.
1441 doi:10.1021/ie200802y.

- 1442 [151] Yin J, Zhang C, Qin C, Liu W, An H, Chen G, Feng B. Reactivation of
1443 calcium-based sorbent by water hydration for CO₂ capture. *Chem Eng J* 2012;198-
1444 199:38–44. doi:10.1016/j.cej.2012.05.078.
- 1445 [152] Coppola A, Salatino P, Montagnaro F, Scala F. Reactivation by water
1446 hydration of the CO₂ capture capacity of a calcium looping sorbent. *Fuel*
1447 2014;127:109–115. doi:10.1016/j.fuel.2013.09.059.
- 1448 [153] Arias B, Grasa GS, Abanades JC. Effect of sorbent hydration on the average
1449 activity of CaO in a Ca-looping system. *Chem Eng J* 2010;163:324–330.
1450 doi:10.1016/j.cej.2010.08.009.
- 1451 [154] Han L, Wang Q, Ma Q, Guan J, Luo Z, Cen F. Hydration reactivation of CaO-
1452 based sorbent for cyclic calcination-carbonation reactions. *Proc. 20th Int. Conf.*
1453 *Fluid. bed Combust.*, 2010, p. 726–731.
- 1454 [155] Manovic V, Anthony EJ. Steam reactivation of spent CaO-based sorbent for
1455 multiple CO₂ capture cycles. *Environ Sci Technol* 2007;41:4435–4440.
1456 doi:10.1021/es0629458.
- 1457 [156] Wang J, Wu Y, Anthony EJ. The hydration behaviour of partially sulfated
1458 fluidized bed combustor sorbent. *Ind Eng Chem Res* 2005;44:8199–8204.
- 1459 [157] Fennell PS, Davidson JF, Dennis J., Hayhurst AN. Regeneration of sintered
1460 limestone sorbents for the sequestration of CO₂ from combustion and other
1461 systems. *J Energy Inst* 2007;80:116–119.
- 1462 [158] Materić BV, Sheppard C, Smedley SI. Effect of repeated steam hydration
1463 reactivation on CaO-based sorbents for CO₂ capture. *Environ Sci Technol*
1464 2010;44:9496–9501. doi:10.1021/es102623k.
- 1465 [159] Martinez I, Grasa G, Murillo R, Arias B, Abanades JC. Evaluation of CO₂
1466 Carrying Capacity of Reactivated CaO by Hydration. *Energy Fuels* 2011;25:1294–
1467 1301. doi:10.1021/ef1015582.
- 1468 [160] Anthony EJ, Jia L, Woods J, Roque W, Burwell S. Pacification of high calcic
1469 residues using carbon dioxide. *Waste Manag* 2000;20:1–13. doi:10.1016/S0956-
1470 053X(99)00305-0.
- 1471 [161] Jia L, Anthony EJ. Pacification of FBC ash in a pressurized TGA. *Fuel*
1472 2000;79:1109–1114. doi:10.1016/S0016-2361(99)00248-3.
- 1473 [162] Manovic V, Lu D, Anthony EJ. Steam hydration of sorbents from a dual
1474 fluidized bed CO₂ looping cycle reactor. *Fuel* 2008;87:3344–3352.
1475 doi:10.1016/j.fuel.2008.04.035.

- 1476 [163] Jia L, Wang J, Anthony EJ. Reactivation of fluidised bed combustor ash for
 1477 sulphur capture. Chem Eng J 2003;94:147–154. doi:10.1016/S1385-
 1478 8947(03)00048-2.
- 1479 [164] Lu DY, Hughes RW, Reid T, Anthony EJ. Hydration and pelletization of
 1480 CaCO₃-derived sorbents for in-situ CO₂ capture. Proc. 20th Int. Conf. Fluid. Bed
 1481 Combust., 2010, p. 569–575.
- 1482 [165] Manovic V, Anthony EJ. Reactivation and remaking of calcium aluminate
 1483 pellets for CO₂ capture. Fuel 2011;90:233–239. doi:10.1016/j.fuel.2010.07.054.
- 1484 [166] Manovic V, Wu Y, He I, Anthony EJ. Spray water reactivation/pelletization of
 1485 spent CaO-based sorbent from calcium looping cycles. Environ Sci Technol
 1486 2012;46:12720–12725. doi:10.1021/es303252j.
- 1487 [167] Diego ME, Arias B, Grasa G, Abanades JC. Design of a novel fluidized bed
 1488 reactor to enhance sorbent performance in CO₂ capture systems using CaO. Ind
 1489 Eng Chem Res 2014;53:10059–71. doi:10.1021/ie500630p.
- 1490 [168] Anthony EJ, Lu D, Salvador C. Pre-treatment of lime-based sorbents using
 1491 hydration. U.S Patent Application No.10/577,540.
- 1492 [169] Valverde JM, Sanchez-Jimenez PE, Perez-Maqueda L a. Calcium-looping
 1493 for post-combustion CO₂ capture. On the adverse effect of sorbent regeneration
 1494 under CO₂. Appl Energy 2014;126:161–171. doi:10.1016/j.apenergy.2014.03.081.

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