The Calcium-Looping technology for CO_2 capture: On the important roles of energy integration and sorbent behavior

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ABSTRACT:

The Calcium Looping (CaL) technology, based on the multicyclic carbonation/calcination of CaO in gas-solid fluidized bed reactors at high temperature, has emerged in the last years as a potentially low cost technology for CO_2 capture. In this manuscript a critical review is made on the important roles of energy integration and sorbent behavior in the process efficiency. Firstly, the strategies proposed to reduce the energy demand by internal integration are discussed as well as process modifications aimed at optimizing the overall efficiency by means of external integration. The most important benefit of the high temperature CaL cycles is the possibility of using high temperature streams that could reduce significantly the energy penalty associated to CO_2 capture. The application of the CaL technology in precombustion capture systems and energy integration, and the coupling of the CaL technology with other industrial processes are also described. In particular, the CaL technology has a significant potential to be a feasible CO_2 capture system for cement plants. A precise knowledge of the multicyclic CO_2 capture behavior of the sorbent at the CaL conditions to be expected in practice is of great relevance in order to predict a realistic efficiency from process simulations. The second part of this manuscript will be devoted to this issue. Particular emphasis is put on the behavior of natural limestone and dolomite, which would be the only practical choices for the technology to meet its main goal of reducing CO_2 capture costs. Under CaL calcination conditions for CO_2 capture (necessarily implying high CO_2 concentration in the calciner), dolomite seems to be a better alternative to limestone as CaO precursor. The proposed techniques of recarbonation and thermal/mechanical pretreatment to reactivate the sorbent and accelerate calcination will be the final subjects of this review.

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1. Introduction

Carbon dioxide (CO_2) capture and storage, or CCS, is a process in which CO_2 is separated from industrial and energy-related sources, compressed and transported to be stored underground or used in other applications such as Enhanced Oil Recovery (EOR).[1-3] CCS is recognized as a necessary technology for meeting greenhouse gas emissions reduction targets. Among the different techniques under study, the Calcium Looping (CaL) technology is a potentially low cost 2nd generation technology emerged in the last years.[4, 5] The process is based on the use of CaO as a regenerable sorbent through carbonation/calcination cycles as schematized in Figure 1. Thus, CO_2 present in the flue gas stream (in a volume concentration of ~15%) is captured by partial carbonation of the CaO particles in a fluidized bed reactor (carbonator) operating at 650ºC under atmospheric pressure. This temperature ensures a low value of the equilibrium CO_2 concentration (around 1% vol) and, at the same time, a fast enough reaction kinetics for carbonation to take place in short residence times, which allows efficiently reducing the concentration of CO_2 in the gas leaving the carbonator reactor.[6] The partially carbonated particles are subsequently circulated into a second reactor (calciner) where calcination of $CaCO_3$ to regenerate the sorbent is carried out at temperatures typically above 930ºC under a highly concentrated CO_2 environment of (between 70% and 90% vol). The CO_2 gas exiting the calciner is thus ready for condensation, compression and transport. The high temperatures needed for efficient calcination at practical rates is achieved by burning fuel in the calciner under a flow of pure O_2 (oxycombustion) in order to avoid CO_2 dilution.[7-9]

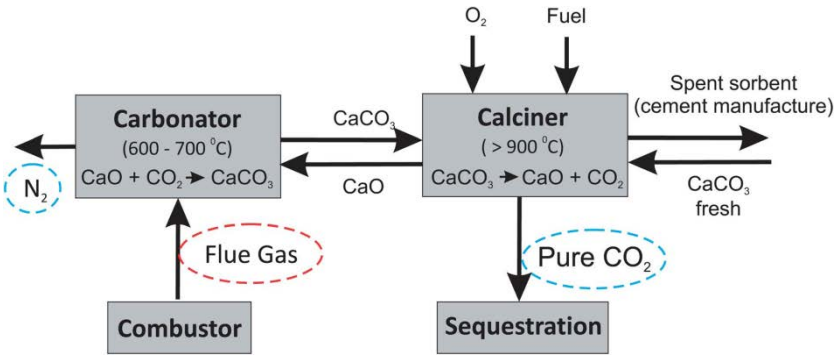


Figure 1. Schematic representation of the CaL process for CO_2 capture from post-combustion flue gas. Reproduced with permission from reference [29]. Copyright 2013, Journal of Materials Chemistry A.

The CaL technology is being currently validated with success in pilot-scale coal fired plants of 1-2 MWth.[8] The process is typically initiated by precalcining a batch of limestone ($CaCO_3$) under air in the calciner, where the net production of CO_2 is only due to this initial calcination step. Then, both the temperature and the CO_2 concentration in the calciner are increased by starting operation in the oxycombustion mode. The produced CaO is taken to the carbonator

after which the carbonated solids obtained are circulated back to the calciner to regenerate CaO in the oxycombustion mode. One of the main issues of this process is CaO deactivation and the loss of fine sorbent particles generated by attrition that cannot be captured by cyclones. Therefore, it is necessary to periodically feed the calciner with a make-up flow of fresh limestone, which increases the demand of heat at the calciner.[10-13] This inconvenience would be somewhat compensated by the low cost of natural limestone and the use of the purged CaO in other applications such as the cement industry or for desulphurization.[14-16] However, it is recognized that the high consumption of fuel and oxygen in the calciner imposes an important energy penalty to the technology, and that enhancing the multicyclic activity of CaO would significantly improve the industrial competitiveness of the CaL technology.[9, 17-20]

A novel CaL concept aimed at minimizing the need of a large make up flow of fresh limestone is based on the recarbonation of the partially carbonated particles exiting the carbonator using the high CO_2 concentration gas stream available from the calciner (Figure 2). Multicyclic carbonation/recarbonation/calcination lab-scale tests suggest that the incorporation of a recarbonator would effectively enhance the capture efficiency and reduce the cost of the technology by reducing the required makeup flow of fresh limestone and thus the heat demand in the calciner.[21-25]

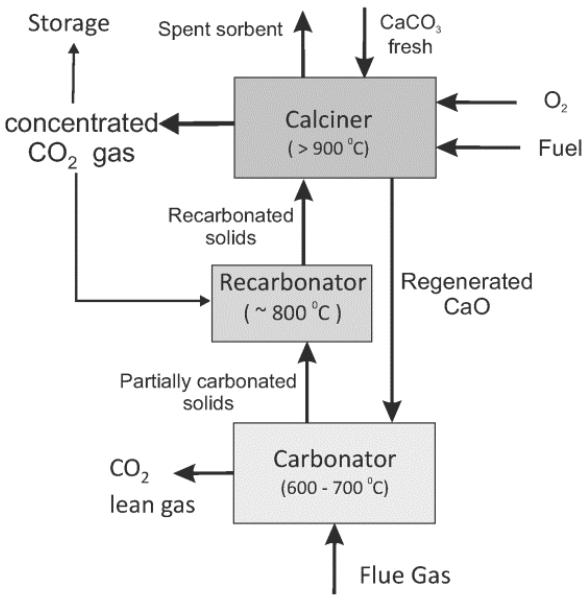


Figure 2. Schematic representation of the Ca-looping process for post-combustion CO_2 capture modified by introducing an intermediate recarbonator reactor. Reproduced with permission from reference [25]. Copyright 2014. Applied Energy.

In this manuscript we will review the main results published in the last 10 years on the effects of precalcination, carbonation and calcination conditions, as well as the effect of introducing a

recarbonation stage on the CO_2 capture performance of natural limestone and dolomite in the CaL process. Even though there are many works published in the literature focused on the synthesis of CaO based sorbents with enhanced carbonation activity,[26-29] most of the sorbents proposed are not compatible with the absolute necessity of reducing costs for the technology to be developed at the commercial level. Thus, a part of this review will be focused on analyzing the role of operating conditions on the multicyclic CO_2 capture capacity of the low cost natural precursors of CaO, namely limestone and dolomite. As will be seen, lab-scale results suggest that a modification on the operating conditions, within the constraints of the CaL process, could bring about a significant improvement of the CO_2 capture capacity of CaO from these natural precursors.

A further relevant aspect of the CaL technology that would contribute to improve the industrial competitiveness of the process is the minimization of energy penalties. Different schemes of the CaL process were originally proposed to match the need and supply of energy stream within the loop.[30] Some of these possibilities have been later developed further, such as the use of a solid heat carrier between the combustion chamber and the calciner in an indirect heat exchange; the use of biomass in a joint combustor/carbonator reactor; or the use of pressurized fluidized beds. The employ of solid carriers was developed by Lisbona et al.,[31] and later by the combination of CaL and chemical looping. The use of biomass in a joint combustor/carbonator reactor has been developed in a 300kWth pilot plant in Spain,[32] reaching 550h in combustion and in situ CO_2 capture mode. By integrating the CaL in biomass power plants, the fluidized bed combustor may serve at the same time as carbonator operating at a temperature about 700°C to maximize both biomass combustion and CO_2 capture. As regards the use of pressurized fluidized beds, it has not received much interest. Just one work has explored the economic viability of this option, which reports and efficiency of 40.7% and develops an economic model.[33] As conclusion, the estimated cost per metric ton for CO_2 captured was $23.7 (Canadian dollars), which is below the cost of the amine scrubbing technology (39-96 $/t$CO_2$ avoided).

The reduction of the energy demand in the CaL process has attracted the attention of many researchers. In general, these works could be divided in two main options to minimize the capture energy penalty. On one hand, we find some works aimed at reducing the energy requirements of the capture cycle within the loop. On the other, there are studies whose main goal is to recover the energy of the capture system by retrofitting the existing power plant or by defining a new power plant that produces additional power.

The present review is organized as follows. Section 2 is devoted to review the methods proposed to reduce the energy demand of the process by internal integration. In section 3 we discuss the process modifications aimed at optimizing the overall efficiency by means of

external integration. The possibility of using the CaL technology in precombustion capture systems and energy integration is described in section 4. The integration of CaL technology with other industrial processes will be the subject of section 5. In the next sections we turn to review results obtained on the CO_2 sorbent behavior at CaL conditions for post-combustion CO_2 capture with particular emphasis on natural limestone and dolomite. A review on the effects of recarbonation and thermal/mechanical pretreatment for sorbent reactivation at CaL conditions will be the final subjects of review.

2. Reduction of the energy demand by internal integration

The most recent proposals for internal heat integration in the CaL process to reduce energy requirements follow two different strategies (i) to recover energy in the loop itself using a basic CaL layout and (ii) to modify the traditional configuration of the cycle in order to avoid the oxyfuel combustion step. Among the works focused on the first approach, Martínez et al.[34] analyzed different options to recover energy from the solids which leave the calciner prior to enter the carbonator. The proposed layouts are oriented towards reducing the energy requirements in the calciner which accounts up to a 37% of the total amount of heat in the capture system.[35] Different configurations were studied to raise the temperature of the solid sorbent stream fed to the calciner by internally integrating available heat flows. This reduction in the calciner energy input may lead to a decrease in coal and oxygen consumptions which are the cause of the main energy penalties. The use of a mixing seal valve to transfer heat between particles is one of the most interesting proposals. In this device, solids exchange heat directly, although this mixture leads to a reduction of the fraction of active CaO in the particle population flowing from the seal valve to the carbonator. Also, the inclusion in the CaL system of an additional circulating fluidized bed, acting as a heat recovery device, was proposed to exchange heat from the gas leaving the calciner to the solids leaving the carbonator.

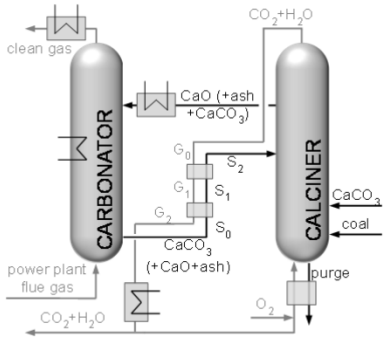
A further modification of the process would consist of the inclusion of a cyclonic preheater (Figure 3a) to transfer energy from the gas leaving the calciner to the solids that reacted in the carbonator.[18] Several cyclonic heat exchangers consisting of different number of steps were modelled. The results obtained from the simulation of a CaL system with a two-step cyclonic preheater showed a power of 127 MW transferred to the solids. This internal heat exchange leaded to a 13.3% of reduction in the mass ratio of coal consumed to CO_2 captured as compared to the ordinary configuration (0.39 kgcoal/kgCO_2 vs 0.45 kgcoal/kgCO_2). Furthermore, oxygen needs for oxyfuel combustion were reduced in a similar proportion (11%). The energy efficiency of the cycle, quantified as the ratio of the heat flow available for integration in a steam cycle to the thermal heat supplied by the coal in the calciner, was also assessed and the study showed that there was no significant energy penalty associated.

The CaL system including a mixing seal valve was thoroughly analyzed by Martínez et al.[36] In this configuration, the solids can directly exchange heat albeit the mixing of the particles reduces the fraction of active CaO entering the carbonator. Either a fraction of the flue gas from the power plant or a fraction of the CO_2 stream exiting the calciner might be used to fluidize the seal valve (Figure 3b). These options were assessed by Martínez et al.[36], and the independent use in the returning channels of both gas streams was finally proposed. The mass ratio of consumed coal to captured CO_2 was 0.38 kgcoal/kgCO_2 (15.5%), and the oxygen consumption decreased by a 14.5% similarly to the reductions obtained with the cyclonic preheater.

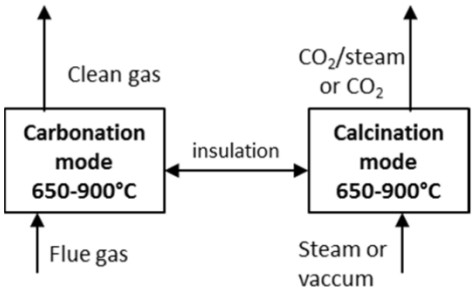
With the same target of reducing the process irreversibilities and limiting energy penalty of the process, Kim et al.[37] propose a process with multiple stages which operates at different temperature levels. In each stage the sorbent is recirculated between an absorber and a regenerator (Figure 3c). The concept is analogous to that presented elsewhere for amine scrubbing.[38] In this case there is an intra-stage heat integration from the high temperature carbonator to medium temperature regenerator. Thus, the high temperature energy availability for an additional steam cycle is reduced, which would decrease the size and the capital cost of the new power plant. This configuration has been suggested for other sorbents such as K_2CO_3, Na_2CO_3 promoted MgO and Li_4SiO_4 for the low (30-200°C), medium (300-500°C) and high temperature (550-750°C) stages.[37] Heat integration is proposed directly between hot and cold sorbent particles of different stages, and indirectly using heat transfer media for the intra-stage integration. For a capture efficiency of 85% and natural gas as a fuel in the high temperature regenerator, researchers reported a net electrical efficiency in a power plant associated with this high temperature looping of 34.9% for an adjusted three-stage process. That means an efficiency penalty of 9.5% in the power plant. There is an important room for improvement in this scheme as integration has not been completely defined, and operating conditions were not optimized.

One of the main penalties associated to the CaL cycle is the need of an air separation unit to obtain pure O_2 for calcination by oxy-fuel combustion. Different modified CaL schemes have been proposed lately to overcome this disadvantage. The process called “HotPSA” works with pressure swing absorption.[39-41] The main target is to drive both the carbonation/calcination reactions near equilibrium by maintaining the temperature in a small range and modifying the pressure to affect the CO_2 partial pressure. The temperature range in both reactors is between 650 and 900°C for carbonation and calcination reaction rates to be high enough. The calciner needs steam injection (Figure 3d) or depressurization to reduce the CO_2 partial pressure. The advantages of this process would include a long life for the sorbent by the reduction of loss of fast carbonation reactivity due to sintering as well as the elimination of oxy-fuel combustion (avoiding additional coal, oxygen and ASU consumption, and oxy-fuel CO_2 compression). This

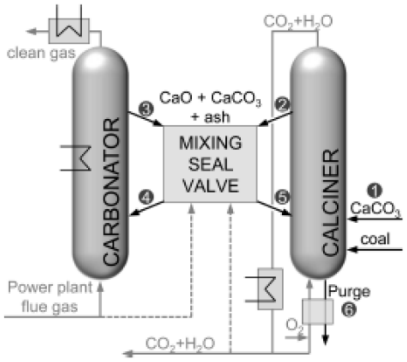
leads to some options for recovering the waste heat not used in the calcination and the flue gas energy in a new steam cycle to compensate energy penalties.



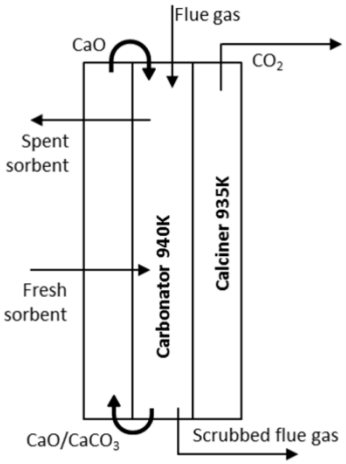
a) Cyclonic preheater scheme (adapted from reference [18])



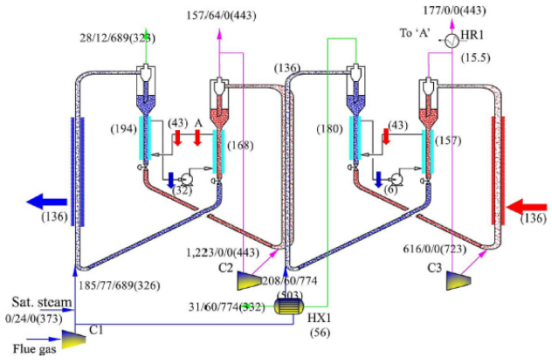
d) HotPSA process (adapted from reference [39])



b) Mixing seal valve scheme (reproduced from reference [36])



e) Endex Ca-Looping process (adapted from reference [40])



c) Two-stages process scheme (reproduced from reference [37])

Figure 3. Configurations for internal energy integration. Reproduced with permission from references [18], [36], [37], [39] and [40].

Direct heat transfer exchange between combustor/calciner or calciner/carbonator has been developed in the Endex configuration.[42] This process involves direct thermal coupling of the

carbonator and the calciner. In this configuration it is assumed that the endothermic process in the calciner will occur at a higher temperature than that of the carbonator, which can be achieved by maintaining the calciner pressure lower than that of the carbonator. In the Endex system, the endothermic reaction is driven directly by the heat released by the exothermic one. The rate of heat transfer has an exponential component due to the temperature dependence of the endothermic reaction rate. This configuration proposes a completely different system layout (Figure 3e) in which the carbonator is housed inside the calciner, and the entire unit is thermally insulated without the need for additional heat in the system. Due to the system characteristics, an important control parameter is the sorbent mass flow rate. The pressures and temperatures of the reactors are considerably lower than in the ordinary CaL, being just 0.048 bar for the carbonator and 0.002 bar for the calciner.[40] This process cannot be compared in energy terms with the conventional CaL. Exergy-based analysis has been performed in order to compare both processes,[40] and also to assess the entropy generation of the sub-processes of the Endex configuration.[43] The energy requirements of operation at very low pressures and the increase of power demand in CO_2 compression may hinder the potential advantages of this configuration.

Another possible scheme consists of a sequential capture of SO_2 and CO_2 using deactivated/spent CaO for flue gas sulphation at 900°C before being injected to the carbonator.[14] This option implies a complete modification of the power plant. Flue gas at high temperature has to be introduced to the sulphation reactor at 900°C, thus it is not possible to recover heat from flue gases before this reactor. Energy has to be recovered between sulphation and carbonation (650°C) reactors and from the clean gas after the carbonation. Moreover, the energy released in the exothermic reaction within the carbonator and from the CO_2 exiting the calciner at high temperature (~930ºC - 950°C) have to be recovered.

3. Optimizing the overall efficiency by external integration

The traditional approach for external heat integration was proposed by Romeo et al.[44] They designed a highly integrated system in which the energy released by the CaL process was integrated in a supercritical steam cycle. From then, a supercritical steam cycle with single reheat has been the preferred system to integrate the recovered heat from the CaL. The state of the art of these power plants includes steam conditions of 250 bar and 540-560 °C and net efficiency of 44%.[45] Such parameters could increase the overall system efficiency and reduce the specific CO_2 emissions ($kgCO_2/kWh_e$).

Energy sources in the CaL process come mainly from three high-temperature flows: the exothermic heat from the carbonation reaction (Q_{carb}), the flue gas stream leaving the carbonator ($Q_{flue\ gas}$) and the CO_2 stream leaving the calciner ($Q_{CO2\ out}$); and two low-temperature streams: the CO_2 stream through the compression ($Q_{CO2\ comp}$) and the purge flow (Q_{purge}). Also, heat from

the coolers in the ASU compression step (Q_{ASU}) and heat from the particles circulating from the calciner to the carbonator ($Q_{solids\ CL\ to\ CR}$) have the potential to be used. The works analyzed take advantage of these streams to define the bottoming steam cycle, although not all of them make use of the whole set of streams listed. Table 1 summarizes the energy sources used in each work.

Table 1. Energy sources

Reference	High temperature sources				Low temperature sources		
	Q_{carb}	$Q_{flue\ gas}$	$Q_{CO2\ out}$	$Q_{solids\ CL\ to\ CR}$	Q_{purge}	$Q_{CO2\ compression}$	Q_{ASU}
Romeo 2008 [44]	X	X	X		X		
Romeo 2009 [20]	X	X	X	X	X	X	
Hawthorne 2009 [46]	X	X	X			X	
Romano 2009 [47]	X	X	X			X	
Yang 2010 [48]	X	X	X				
Lisbona 2010 [49]	X	X	X	X	X	X	
Martínez 2011 [50]	X	X	X		X	X	
Vorrias 2013 [51]	X	X	X		X	X	X
Lara 2013 [52]	X	X	X	X	X	X	
Lara 2014 [53]	X	X	X	X	X	X	

In Romeo et al.,[44] an initial supercritical steam cycle was first defined and then modified to take advantage of the energy flows of the CaL cycle, with the aim of avoiding the need for an extra boiler. The supercritical cycle was divided into five zones (Reheat, In-boiler, Economizer, High- and Low-pressure feedwater heaters) depending on their temperature levels. This system reduced the reference plant CO_2 emission from 0.781 $kgCO_2$/net-kWh to a value of 0.122 $kgCO_2$/net-kWh, and obtained a net efficiency of 37.04 %; which translates to an energy penalty of 7,89 efficiency points (see Table 1).

To complement this option, an exergy analysis was presented to assess the conventional CaL process with a different integration point of view.[54] It took advantage of the vast amount of high quality energy to retrofit the power plant or to develop a new steam cycle. Romeo et al. used the pinch and the exergy analysis to define an optimum window for the integration of a CaL process and their retrofit in a coal power plant.[54] The waste heat from the CO_2 capture was used to produce steam in the original power plant. The exergy recovered as high pressure steam should be around 70% of the total exergy; while the exergy for reheating the steam amounts 25%. The low temperature heat released in the intercoolers pertaining to CO_2 compression may be used to reduce the steam bleed to low pressure regenerative heaters.

Several researches calculated the effect of the CaL process when applied to power stations on their efficiency. An overview of the integration results obtained in different works is summarized in Table 2. The drop in efficiency reported is between 6 and 8 efficiency points.[30, 55] Other works have reported energy penalties of 7.5 eff-points for a capture efficiency in the carbonator of 70% or 10.4% eff-points for a capture efficiency in the carbonator of 90%.[50] Hawthorne et al. modeled the CaL process and its integration taking into account also the available heat of the CO_2 compression unit.[46] In this case, the reference power plant is a 1052 MW_e coal-fired plant, and the energy penalty after integration is 6.4 percentage points. Due to the high temperature (high exergy) of the CaL cycles, the optimization of the integration with a power plant is an essential subject that has to be studied in detail.

Table 2. Net power and net efficiencies comparison

Reference	Reference plant		Capture plant		Reference + capture + integrated plant			
	Net power (MW)	Efficiency (%)	CO_2 capture efficiency (%)	Amount of heat recovered (MW)	Net power (MW)	Efficiency (%)	Energy penalty	CO_2 avoided cost (€/ton)
Romeo 2008 [44]	427,5	44,93	85,00	--	619,80	37,04	7,89	15,77
Romeo 2009 [20]	500[×]	40,32	--	--	--	--	--	13,20
Hawthorne 2009 [46]	1052,0	45,60	80,00	1624,0	1533,00	39,20	6,40	--
Romano 2009 [47]	630,8	44,18	97,04	--	452,40	37,35	6,83	--
Yang 2010 [ɣ] [48]	600,0	40,60	85,00	906,6	846,00	36,80	3,80	28,90
Lisbona 2010 [49]	500,0	38,11	--	--	709,50	32,33	5,78	15,80[¥]
Martínez 2011 [50]	350,0	36,00	70,00-90,00	--	--	--	8,30-10,30 [x]	--
Vorrias 2013 [·] [51]	304,15	39,05	94,00	524,0	428,2	34,09	4,96	--
Lara 2013 [52]	474,0	38,23	85,00	838,9	714,50	32,04	6,19	--
Lara 2014 [53]	474,0	38,23	85,00	841,9	738,10	33,06	5,17	--

[×] Gross power

[ɣ] Only case 4 shown

[¥] For generic natural limestone, 6€/ton CO_2 and low attrition

[·] Only case A shown

[x] Range w/o including a cement plant

Some works have analyzed possible integrations of the CaL process in a reference power plant. Yang Yongping et al.[48] studied for a 600 MW_e one-reheat power plant the integration of five cases depending on the use of the recovered heat: i) to replace extracted steam from the turbines; ii) to replace part of the boiler heat load; iii) to replace the extracted steam from the turbines and part of the boiler heat load; iv) to build a heat recovery steam generator and produce steam to drive new turbines; v) to replace the extracted steam in the new steam cycle.

375 The option of using the heat in a HRSG and drive new turbines was selected as the best
376 efficiency option (penalty of 3.8 efficiency points), the largest power output (net 846 MW_e) and
377 the lower cost of CO_2 avoided (28.9 €/tCO_2). This analysis also showed that although case iv
378 was not the one with largest total heat recovery, the efficiencies do not follow the same trend.
379 These efficiencies depend both on the amount of heat and the type of thermal energy use. The
380 option that replaces part of the boiler heat load showed the worst results in net power, efficiency
381 and costs. The rest of the options need a detailed analysis since replacing bleeding from the
382 steam turbine requires additional developments.
383 A similar scheme was proposed by Vorrias in 2013.[51] They used as a reference a 330 MW_e
384 lignite power plant with a supercritical single reheat boiler. In this scheme, concentric L-valves
385 were used as solid recirculation heat exchangers. As in previous papers, a secondary steam cycle
386 with single reheat is used to take advantage of the energy released by the CaL process. In the
387 high temperature section, the design included a split of the steam production in the carbonator
388 and calciner sections. The last one included the single reheater. In the low temperature section,
389 part of the energy from CO_2 compression and ASU coolers is integrated in the steam cycle as
390 low pressure heaters. There is no detailed information about the temperature profiles but a final
391 potential heat for district heating is described. This agrees with the fact that in this CCS option
392 there is huge amount of low temperature waste energy available. The energy content of the
393 purge is used to increase the oxygen and recirculated CO_2 temperatures. One of the important
394 novelties of this work is the analysis of the influence of lignite pre-drying on fuel consumption
395 and capture efficiency showing no effect on the carbonator capture efficiency.[51] Fuel pre-drying
396 decreased the fuel demands in the calciner and the CaL system was smaller (less additional
397 power production) and more efficient. Both are important advantages as this scheme would
398 require less capital and operational costs. In case that there is no heat exchange between solids,
399 the effect on the overall efficiency was small but the system was considerably bigger. An
400 evaluation of the CaL technology as a retrofit option showed higher overall net electrical
401 efficiency when compared to chemical absorption with MEA or oxy-fuel combustion power
402 plants. The energy penalty of the CaL process was below 5 efficiency points (Table 2) versus
403 the 7.8 of MEA or 5.85 of oxy-fuel combustion. The only disadvantage of this CaL scheme is
404 that the size of the overall system is higher than the other post-combustion processes, 82% than
405 MEA and 53% than oxy-fuel. For a new built power plant with CCS based on the CaL process
406 the overall efficiency increased up to 34.04% including the capture process.
407 The carbonation conversion of the sorbent and the heat requirements at the calciner are key
408 variables that influence the performance of CaL systems. Several studies have been devoted to
409 analyze the influence of the capture cycle parameters in the global system, considering not only
410 the capture step but their energy integration, to determine the CO_2 avoided costs. Romeo et al.
411 recommended avoiding operating conditions with low-recirculation rates and purge percentages

over 5% to optimize the cost per tonne of CO_2 avoided.[20] In this work, the minimum CO_2 avoided cost, Table 2, is obtained for a molar CaO/CO_2 ratio of 5 and a purge of 1.5%. In this analysis, heat recovery steam generators take advantage of the flue gas from carbonator at 650°C and from calciner at 930°C. A solid-gas heat exchanger is used to reduce the purge temperature down to 180°C. Intercooling CO_2 compression heat is used in low-pressure heat exchangers in the condensate section of the steam cycle.

The effect of the decay of carbonation conversion with increasing number of carbonation/calcination cycles was addressed in Romeo et al.[12] and Lisbona et al.[49], which maintain the same heat integration scheme. Romeo et al.[12] studied the competitiveness of CaO based synthetic sorbents with enhanced sorption behavior as compared to natural limestone. Simulations calculated the maximum price for enhanced sorbents to achieve a reduction in CO_2 removal cost under different process conditions (solid circulation and make-up flow). The results obtained in this study may be used as an assessment tool of new sorbents to understand what prices would be competitive as compared to natural limestone in the CaL capture systems. After analyzing the requirements of limestone and enhanced sorbents, on the basis of their multicyclic sorption capacity and the pair purge-CaO/CO_2 ratio, the possible use of sorbents other than natural limestone was assessed. In Lisbona et al.,[49] doped limestone, dolomite and synthetic sorbents were simulated within the system. In most cases, the increased cost of sorbent synthesis and/or limestone modification leads to a significant increase of the cost of the system operation and therefore CO_2 capture cost. Any comparison among sorbents will be accurate only if both chemical and economic considerations are taken into account in the study. Lisbona et al. present a common basis for sorbent comparison, including the influence of attrition processes in the model.[49] The integration of the sorbent cost and its chemical and mechanical performance were studied for different options. The aim was to compare the CO_2 avoided cost as a function of average conversion of solid population and cost for different sorbents. Despite improved conversion results, the unit cost of the sorbent is crucial to maintain the CaL concept economically attractive. Moreover, it must be remarked that most of lab-scale studies reported in the literature on the multicyclic CO2 capture behavior of synthetic sorbents are carried out under not realistic CaL conditions. As will be seen in the second part of this review, the behavior of a sorbent may change dramatically when CaL operating conditions are changed.

The work of Martínez et al. determined the operating conditions in a CaL cycle that minimize the energy penalty when implemented in an existing power plant with 36% net efficiency.[50] To evaluate energy penalties associated with the capture system, a reference plant consisting on the existing subcritical one and a new hypothetical supercritical power plant with the same fuel input as the calciner was assumed. Different integration possibilities were studied depending on the operating conditions in the CaL cycle. The highest thermal efficiencies were obtained for the cases with lowest make-up flow; in which the modest activity of the sorbent is compensated by

449 high-solids flow between reactors to maintain the desired carbonation efficiency, which agrees
450 with the results obtained by Romeo et al.[20]
451 Wang et al. simulated in Aspen Plus an integration of the CaL cycle using $Ca(OH)_2$ as sorbent
452 with different cases: one ideal case which is not very realistic, an industrial case and one acid
453 case to determine the effect of $Ca(OH)_2$ on the removal of all acid gases present in flue gas.[56]
454 For the ideal case, a minimum energy penalty (additional thermal energy input into the system)
455 of 5.8% is showed for an indirect-fired calciner and a minimum CO_2 compression energy of 75
456 kWh/tonne. One additional efficiency gain could be achieved by modifying the ASU
457 consumption from 200 to 167 kWh/tonne O_2. The industrial case included non-ideal heat
458 transfer and increases the CO_2 compression and ASU consumption. In this case the energy
459 penalty ranged from 13 to near 16% for a 100% heat extraction efficiency and indirect-fired
460 calciner. Considering the use of coal in the calciner, the penalty ranged from 16 to more than
461 24% depending on the coal.
462 Usually, researchers have focused on coal-fired power plants for application the of CaL process.
463 Flue gas CO_2 concentrations range between 10-17 vol%; much higher than in NG power plants
464 where typical CO_2 volume concentration in flue gas is around 3-5%. In spite the lower CO_2
465 partial pressure of NG combined cycle, the outlet temperature of the gas turbines around 600°C
466 makes interesting the analysis of the possibilities of integration of the CaL cycle into NGCC
467 power plants.[57, 58] Moreover, the lower CO_2 partial pressure reduces the carbonator temperature
468 down to 600°C. The CaL cycle could be located directly after the GT before any Heat Recovery
469 Steam Generator without incurring in exergy losses due to temperature changes. The scheme for
470 the integration of the energy streams in a bottoming cycle will be different to the usual HRSG in
471 NGCC or the previous coal-fired power plants.[57] Berstad et al. (32) reported several simulations
472 with/without heat integration within the CaL and using a standard/advanced/super-critical steam
473 cycle as bottoming cycle to take advantage of the energy streams in the CCS.[57] Assuming a
474 reference NGCC efficiency of 58.1%, the application of MEA chemical absorption reduces in
475 8.6 points the efficiency. In spite of the use of advance/super-critical steam cycle the design
476 with CaL cycle reduced the efficiency between 10.0-11.5 eff-points. Again, it was shown that
477 the use of internal heat integration reduces the size of the overall installation, in this case around
478 12%. Authors concluded that the CaL process is not competitive for NGCC in comparison with
479 MEA chemical absorption. Nevertheless, in a later work with synthetic sorbents the authors
480 claimed an efficiency loss of only 5.0 points for super-critical turbine (7.1 and 6.8 for natural
481 limestone and synthetic CaO/MgO).[58] The main variables affecting the power plant efficiency
482 were the internal heat recuperation and the CO_2 recycle temperature. To increase the process
483 flexibility the configuration included two HRSG and a primary and a secondary steam cycle and
484 a reduction of the calciner temperature to 900°C.

485 Manovic and Anthony demonstrated experimentally the feasibility of a new approach to
486 eliminate the oxyfuel combustor: the combination of CaL with a chemical looping using CuO as
487 oxygen carrier. In their work, they developed, prepared and tested a composite material
488 consisting of CaO as CO_2 acceptor and CuO as oxygen carrier.[59] In the same work, three
489 alternative routes were proposed to implement the concept. Further techno-economic analysis
490 should determine the better integration option. Another experimental study carried out by Ridha
491 et al. compares the use of in-house developed composite CaO-CuO material with the use of a
492 mixed bed of CaO and CuO pellets.[60] The results showed a better performance of the mixture of
493 pure materials despite of the inherent advantages of composite materials.
494 We can conclude that the most important advantage of the high temperature CaL process is the
495 use of the high temperature streams that could reduce significantly the energy penalty associated
496 with CCS. As reported previously, there are several works in the literature that show and
497 quantify important penalty reductions. Nevertheless, it is essential to optimize the results
498 through a well stablished method. The pinch methodology, combined with economic and
499 exergetic analysis to optimize the design of the heat exchangers network is addressed in Lara et
500 al. where four configurations integrating the same amount of heat than the base case were
501 studied.[52] The design and analysis of these configurations to determine the optimum for the
502 system, according to energy, exergy and economic criteria were undertaken, and the cycle
503 efficiency was improved by the relocation of the heat exchangers. The results obtained in this
504 work are further distilled in the algorithm shown in Lara et al.,[53] aiming to provide a systematic
505 procedure for heat integration of this type of systems to find an energy and cost-efficient
506 solution for the heat exchanger network, to simplify the integration process. In this work, a
507 procedure based on pinch analysis was proposed and tested in two different cases. In both
508 scenarios the integration was designed to take advantage of all the available heat from the
509 process to power the bottoming supercritical steam cycle, thus quantifying the minimum energy
510 penalty (5.17 eff-points, Table 2). A sensitivity analysis for each process was also performed,
511 and the heat exchangers network obtained through the algorithm was the most economical one.
512 Finally, a future modelling challenge is the dynamic simulation of the CaL process. Recently,
513 some attempts have been done but it will be necessary to the flexibility of the capture systems in
514 a power plant load following scenario.[61]
515
516 **4. Energy integration of CaL in precombustion capture systems**
517
518 The CaL cycle provides a number of benefits when coupled with fuel gasification or reforming
519 as precombustion capture process. The heat released in the carbonation reaction is used to run
520 the endothermic in-situ steam reforming or the gasification reactions, leading to an overall
521 autothermic reaction. Another benefit derived from the presence of CaO is the shifting of the

equilibrium to greater hydrogen yields. The subsequent calcination of the $CaCO_3$ to regenerate the sorbent is however a significant problem still to be solved for precombustion CO_2 capture systems. The high temperature heat demanded in the calcination stage and the heat transfer mechanism is in practice quite problematic. Different configurations have been adopted to integrate the CaL process in a precombustion process for enhanced hydrogen production and minimize the energy penalty associated to sorbent regeneration. The basic configuration includes the application of oxycombustion of a solid fuel in the calciner itself to provide the energy required. Several studies have been focused in the integration of this CaL basic configuration with steam reforming of gaseous fuels (sorption enhanced reforming, CaL-SER) and solid fuel gasification.[62, 63]

4.1 Sorption enhanced reforming (SER) – CaL integration

Although the industrial process used to produce hydrogen, namely steam methane reforming, is a mature commercial technology, there are still a number of issues for further improvement. In particular, diverse reactor concepts, which combine several process stages within a single unit, are being investigated. Significant enhancement of the process is achieved by addition of a CO_2 sorbent to the reactor, which shifts the reversible reforming and water gas shift (WGS) reaction beyond their thermodynamic limitation.[64]

The complexity of CaL-SER processes relies in the fact that a single reactor is used to carry out hydrocarbon catalyzed reforming, carbonation and water-gas shift reaction. Potential energy savings associated to the autothermal overall reaction was initially estimated by Ortiz and Harrison in a 20%.[65] Experimental tests have proved the process in both small fixed-bed and fluidized bed reactors. Depending on reaction conditions of temperature, pressure and steam to carbon ratio, the content of hydrogen in the final gas is in the range 95-99%.[62, 63]

More recently, Connell et al. assessed from a techno-economic point of view the integration of CaL with a steam methane reforming plant.[66] Their results showed a 9% reduction of cost in the production of hydrogen (production rate of hydrogen 25579 kg/h) mainly related to the benefits obtained from the generation of electricity (189 MWe of net electric power) in a steam cycle driven by the waste heat released in CaL.

4.2. CaL enhanced gasification

The production of hydrogen from solid fuel gasification may be coupled to the CaL process for increasing the hydrogen content in the syngas. Under this scenario, WGS reaction with in situ CO_2 removal, sulphur and halide removal are integrated in a single reactor in the absence of WGS catalyst. The reactor is fed with the syngas from the gasifier after being cooled down.

559 Ramkumar and Fan conducted thermodynamic analysis which showed the positive effect of Ca-
560 based sorbents in the WGS reaction and in the purity of the obtained hydrogen (over 99%).[67]
561 They conducted also a number of experimental tests, which showed a worse behavior of the
562 sorbent for higher temperatures but a correct operation of the concept at near-stoichiometric
563 steam to carbon ratios without WGS catalysts. The waste heat from the CaL process would be
564 used to generate steam and co-produce electricity in a steam turbine. In the techno-economic
565 study presented by Connell et al.,[66] the extra produced net electricity power with respect to a
566 same-size coal-to-hydrogen plant without CaL CO_2 capture is estimated to be 319 MWe. The
567 same study points out that the reduction of the cost of hydrogen or electricity relative to the base
568 plant is found to be 12%.
569 Apart from these conventional gasification followed by syngas upgrading stage, a more
570 ambitious configuration was HyPr-RING (hydrogen production by reaction-integrated novel
571 gasification).[63] HyPr-RING was developed in Japan and the challenge was to carry out the in-
572 situ CO_2 capture in a coal gasifier reactor fed with coal, steam, and Ca-based sorbent. The CO_2
573 content in the produced syngas should directly react with CaO, thus enhancing the amount of H_2
574 produced via the WGS reaction. In the regenerator, the oxyfuel combustion of non-reacted coal
575 provided enough energy to regenerate the sorbent. An intermediate stage of hydration was
576 included to prevent sorbent degradation. The gasifier/carbonator operated at 600-700°C and 3
577 MPa, which resulted in slightly over 50% carbon conversion and around 90% H_2 in the syngas
578 corresponding to a cold gas efficiency above 77%. The regenerator was operated at 800°C and
579 0.1 MPa. Similar proposals for in-situ gasification with CaL CO_2 removal have also been
580 analyzed by Florin and Harris using biomass and low grade fuels.[68] This second concept (in-situ
581 gasification and CO_2 capture with CaO) has been demonstrated by Abanades et al. in the pilot
582 plants of INCAR.[69]
583
584 **4.3. Integrated gasification combined cycle (IGCC) – CaL integration**
585
586 Several researchers have investigated the utilization of syngas from gasification and CaL
587 upgrading process in electricity production. An advanced concept of power plants includes a
588 CaL gasifier/regeneration integrated with a combined Brayton/Rankine cycles, IGCC-CaL.
589 Connell et al. technically compared through simulations an IGCC CaL plant and a reference
590 case of IGCC plant with commercial CO_2 capture.[66] Both systems had the same gasifiers and
591 combustion turbines. The carbonator in the IGCC CaL operates at greater pressure compared to
592 hydrogen production gasification, because the pressure inlet to the turbine is greater to the
593 pressure specifications for high purity hydrogen. This results in a higher temperature
594 requirement in this reactor (700ºC). The syngas generated in this process does not require H_2O
595 removal since it serves as a diluent of the fuel to achieve the required heating value. A metallic

filter is required before the turbine inlet to retain possible solid particles. The calciner was exclusively fired by coal. Their results showed a reduction of costs of 12% in comparison with the base case. The proposed system processed 374 ton/h of coal, which generated a net power of 932.9 MW with CO_2 capture efficiency above 99% and a net efficiency near 33% HHV.

The exergy efficiency of the integrated concept was analyzed through detailed simulation by Siefert et al.[70] In the Brayton cycle, the air ratio was fixed in order to have a temperature of 1600K and a pressure of 1.62 MPa. In the Rankine cycle, superheated steam was introduced to high pressure turbine at 625°C and 20 MPa and reheated to the same temperature at 2MPa. The condenser operated at 0.02 MPa and a temperature spring form 136°C to 50°C. The proposed system gasifies 29 ton/h of coal and generates 112 MW of electric power (67MW Brayton cycle, 48 Rankine cycle, 3 MW fuel expander) which corresponds to an exergetic efficiency of 46.4%. The capture efficiency of the system is 66.6% and the normalized CO_2 emission rate is 0.23 kg CO_2/kWh.

An economic assessment of IGCC CaL coupled systems has been done by Cormos by analyzing the integration of CaL and a coal gasification plant, which consists of an oxygen-blown gasifier.[71] The power plant generates around 545-560 MW of net power presenting a net efficiency of 37% and a capture efficiency above 90%. The inclusion of the CaL technology increases between 24-42% the specific capital investment while O&M and LCOE costs are increased in the ranges 24-30% and 39-48%, respectively. Specific CO_2 emissions were estimated to be around 0.30-0.35 kg CO_2/kWh.[72]

4.4. Integrated Gasification Fuel Cell (IGFC) – CaL integration

Another advanced solid fuel based power plant coupled with CaL CO_2 capture is the integration of enhanced gasification and fuel cells. The removal of CO_2 prior entering the fuel cell reduces the content of CO and CO_2 and avoids carbon deposition while keeping a significant amount of methane in the gaseous fuel. This methane can be internally reformed in the solid oxide fuel cell (SOFC), which reduces cooling costs and parasitic loads. H_2S is also removed from the syngas without the need of being condensed and re-injected before entering the anode side of the SOFC. CO_2 and H_2S may be removed by lime inside or just after the gasifier which significantly reduce the size and consumptions of the equipment.

One of the first proposals in this direction was the ZEC process developed by Los Alamos National Laboratory.[63] Coal is hydrogasified to produce methane. Once the solid fuel is converted to methane, the gaseous fuel is subjected to a CaL-SER process as described above. Half of the produced hydrogen is used in the hydrogasification step and the remaining will produce electricity in a solid oxide fuel cell. The high temperature off-gas from the fuel cell is used to regenerate the spent sorbent. A system analysis estimated coal to electricity conversion

633 efficiency of 68.9% including CO_2 capture and compression. Although the project is no longer
634 pursued by ZECA, research on these topics has continued in the Cambridge University and
635 Imperial College. Dean et al. (40) gather those investigations done at laboratory scale on
636 different critical aspects.[63]
637 Based on promising experimental results on the field of CaL enhanced steam gasification of
638 coal, Xu et al. investigated the performance of the entire process consisting of two fluidized bed
639 reactors, a gasifier/carbonator and a regenerator.[73] Thermodynamic simulations of a similar
640 concept of SOFC fed with upgraded syngas were performed using Aspen Plus.[73] The obtained
641 syngas presented an amount of hydrogen above 95%. Considering the system heat balance, the
642 optimal operation conditions were 650°C and 3MPa in the gasifier and 900°C and 0.1 MPa in
643 the oxyfuel regenerator with a steam to carbon ratio of 3. The cold gas efficiency was 92.6%.
644 The integration of a SOFC- gas turbine (SOFC-GT) hybrid cycle with the enhanced gasification
645 process accounts for an equivalent power efficiency of CO_2 capture and compression of 61.9%.
646 Siefert et al. analyzed a system that integrates a CaL enhance gasifier with a solid oxide fuel cell
647 from an exergetic and economic point of view.[70] The SOFC operating parameters which
648 maximized the internal rate of return on investment were a pressure of 300 kPa, a current
649 density of 1.0 Acm^{-2}, an air stoichiometric ratio of 2.0 and a fuel utilization of 80%. The system
650 gasifies 29 ton/h of coal and has an AC power output of 143 MW (116 MW is generated by the
651 SOFC, 23 MW by the combined air compressor and exhaust expander and 9 MW by the fuel
652 expander). Near 70% of CO_2 is captured and sent to compression which corresponds to a
653 normalized CO_2 emission rate of 0.16 kg CO_2/kWh. The exergy efficiency was found to be
654 between 40-65% depending on the value of the SOFC operating variables which is much higher
655 than traditional IGCC-CCS concepts.
656
657 **4.5. Unmixed fuel processing**
658
659 Some approaches have tried to overcome the issue of high energy consumption in the
660 regeneration stage of the CaL process from substituting oxyfuel combustion in the calciner
661 reactor by an unmixed chemical combustion process.[74] The unmixed fuel process consists of
662 three coupled reactors: a gasifier/reformer, a sorbent regenerator and a reactor to oxidize an O_2
663 transfer material, which produces a high temperature/high pressure vitiated air. This technology
664 has the potential to eliminate the need for the air separation unit.
665 The concept was integrated and analyzed by Lisbona and Romeo,[31] which considered the
666 utilization of syngas obtained through CaL enhanced gasification of coal in a SOFC to produce
667 electricity, the inclusion of two gas turbines to take advantage of the energy contained in the
668 flue gases from afterburner and calciner and a steam cycle with steam produced from heat
669 recovery. The oxygen carrier used in the regeneration stage was FeO. The influence of steam to

carbon ratio in gasifier and regeneration reactor, pressure of the system, temperature for oxygen transfer material oxidation, purge percentage in calciner, average sorbent activity and oxidant utilization in fuel cell were analyzed. An electrical efficiency up to 73% was reached under optimal conditions and CO_2 capture efficiencies near 96% ensure a good performance for climate change mitigation targets.

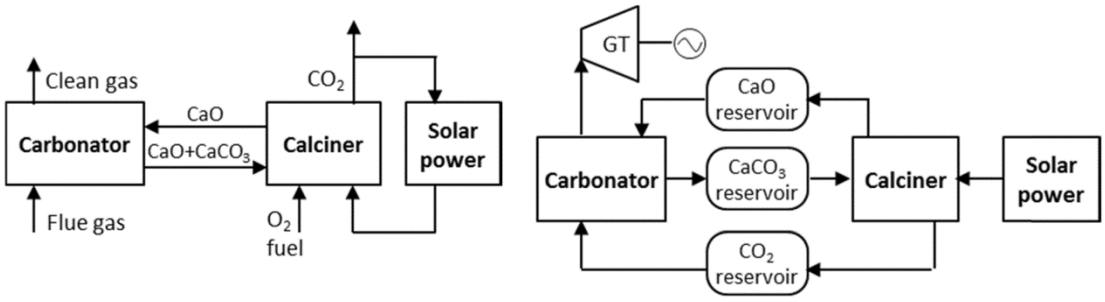
The application of this concept to in-situ enhanced biomass gasification has been more recently investigated by Rahman et al.[75] Instead of using a mixture of pellets, they have developed composite CaO/CuO materials and demonstrated experimentally the technical feasibility of the integration. Three sequences were simulated through testing. Two of them implied the use of composite materials and the third one used a mixture of separated CaO and CuO pellets. Results showed some difficulties related to reduction capacity loss in combining both materials in one pellet. Given the promising integration of both technologies using a dual loop, further research must be pursued especially through the testing of both types of pellets together.

Abanades et al. proposed the inclusion of a second chemical loop in which a reversible redox reaction between copper and oxygen takes place.[76] The technical solution consisted of three interconnected reactors; i) a sorption enhanced reformer where hydrogen is produced by catalyzed steam reforming of natural gas and CO_2 is captured simultaneously, ii) a regenerator of $CaCO_3$ using the heat released from the reduction of CuO with a gas fuel and iii) the oxidation of Cu to CuO with air. The high efficiency of heat transfer between calcination and copper reduction reactions allows moderating temperatures and saving energy. The proposed scheme is reported as one single reactor operating in batch mode switching between three operation modes: A) in which the fixed bed initially contains CaO and Cu to allow sorption enhanced reforming reaction (slightly exothermic); B) when the oxidation of Cu with nitrogen-rich air (under specific temperature and pressure to avoid CO_2 release) takes place; and C) performing $CaCO_3$ regeneration and reduction of CuO to Cu. In this last mode the reactor maintains a temperature between 800-900°C under atmospheric pressure or lower. Gases obtained in the B mode are sent to a gas turbine, whose electric efficiency is maximized by burning part of the hydrogen produced in the A mode to increase mass flow and temperature. Overall CO_2 capture efficiency is over 80% when 87% of H_2 is burnt in the gas turbine. Energy efficiency to hydrogen is 58% (H_2/CH_4). There is no complete heat integration so the overall energy efficiency of the process is not calculated but it is expected to be high since energy penalty processes have been avoided. The presence of solids in the calciner has to be optimized depending on the fed fuel to minimize the demand for additional heat. The calculations must be validated through experimental and modelling work.

5. Integration of the CaL technology with other industrial processes

The CaL technology may be also integrated with other industrial processes leading not only to a reduction of the CO_2 emissions but also to an improvement of the operation of those processes. This is the case of the concentrated solar power (CSP) generation and the paper and cement industries.

There are two ways in which CSP may be integrated with the CaL cycle. On one hand, CSP may be used to provide energy to the calciner for the regeneration reaction in order to reduce the fuel consumption associated with the CO_2 capture process (Figure 4a). On the other hand, the CaL cycle may be used as a thermal storage system to storage the unstable solar energy production for future use, thus avoiding the disadvantage derived from the production variability (Figure 4b). In regards to the former, Zhang et al. examined the energy efficiency of the CaL system when the calciner is driven by a combination of oxyfuel combustion and CSP.[77] In this system, a fraction of the CO_2 leaving the calciner is used as a heat transfer fluid in the solar collectors and then it is recycled to the regeneration reactor. Therefore, a reduction of the fossil fuel consumption in the calciner is obtained, entailing a decrease of the additional CO_2 generated and a diminution of the mass flow rate of fresh limestone.



a) b)

Figure 4. Calcium looping integration with concentrated solar power.

As mentioned, the CaL process may be used as a thermochemical storage system integrated with the concentrated solar power generation. It has the advantages of operating at high temperatures and having significant energy density compared to most sensible and latent storage technologies. However, besides the development of a solar calciner, there are some challenges to be faced since high carbonation activities and high pressure in the carbonator are required. Edwards et al. determined that the optimal sorbent activity should be in the range 20% – 40%

743 and the carbonator should operate at 800 – 900 ºC at 2.8 – 9.1 bar to achieve plant efficiencies
744 between 40% - 46%.[78]
745 Regarding the paper industry, Sun et al. analyzed the possibility of using lime mud,[79] which is a
746 solid waste resulting from the causticization reaction in alkali recycling process, as sorbent in
747 the CaL cycle. Results showed a stable carbonation conversion of 21% from 2 to 100 cycles.
748 Better results were obtained when a pre-wash was carried out to reduce the chlorine content,
749 thus avoiding its negative effect on sintering and carbonation conversion. In this case, a 36%
750 carbonation conversion was obtained after 100 cycles. Also the effect of hydration of the CaO
751 derived from both the lime mud and the pretreated lime mud was analyzed obtaining a further
752 enhancement of the capture capacity, especially in the first cycles.
753 The integration of the cement industry and the CaL technology has been broadly studied since
754 the production of cement is one of the industrial sectors with the biggest carbon footprint and
755 makes use also of limestone as a raw material for the clinker manufacture. Moreover, the CaL
756 retrofitting capacity makes this integration a promising combination not only for future designs
757 but also for existing cement plants. Different degrees of integration may be achieved depending
758 on the aspects coming into play: i) Most proposed schemes focus on the integration of mass
759 flows (Figure 5a); the CO_2 generated in the cement plant is captured in the CaL cycle and the
760 purged sorbent is directed to the cement plant to feed the precalciner or the rotary kiln.[80-82] ii) In
761 other studies, the heat flows are also involved (Figure 5b). Romeo et al. proposed an integration
762 scheme in which a fraction of the waste heat from the CaL cycle was used to preheat the air
763 entering the cement plant.[83] The whole system comprises a power plant and a cement plant,
764 from which the CO_2 is captured, the CaL process, and a steam cycle to make use of the surplus
765 energy from the capture system and the cement plant. Results showed that this synergy may
766 permit 94% of CO_2 avoided emissions with an interesting cost, 12.4 €/tCO_2. iii) Lastly, even the
767 sharing of a reactor has been proposed.[84, 85] Rodríguez et al. presented a scheme in which the
768 CaL calciner and the cement plant precalciner are the same reactor and the flue gas from the
769 rotary kiln is directed to the carbonator (Figure 5c).[84] They compared this system with the use of
770 an oxy-fired precalciner obtaining higher CO_2 capture efficiency, 99% and 89% respectively,
771 and avoided CO_2 cost, 23 \$/tCO_2 and 16 \$/tCO_2 respectively. Romano et al. proposed a
772 configuration with an oxyfuel calciner, shared by CaL and cement plant, and a carbonator
773 integrated in the raw meal suspension preheater process (Figure 5d).[85] Results showed a CO_2
774 capture efficiency of 95.4% with this scheme.
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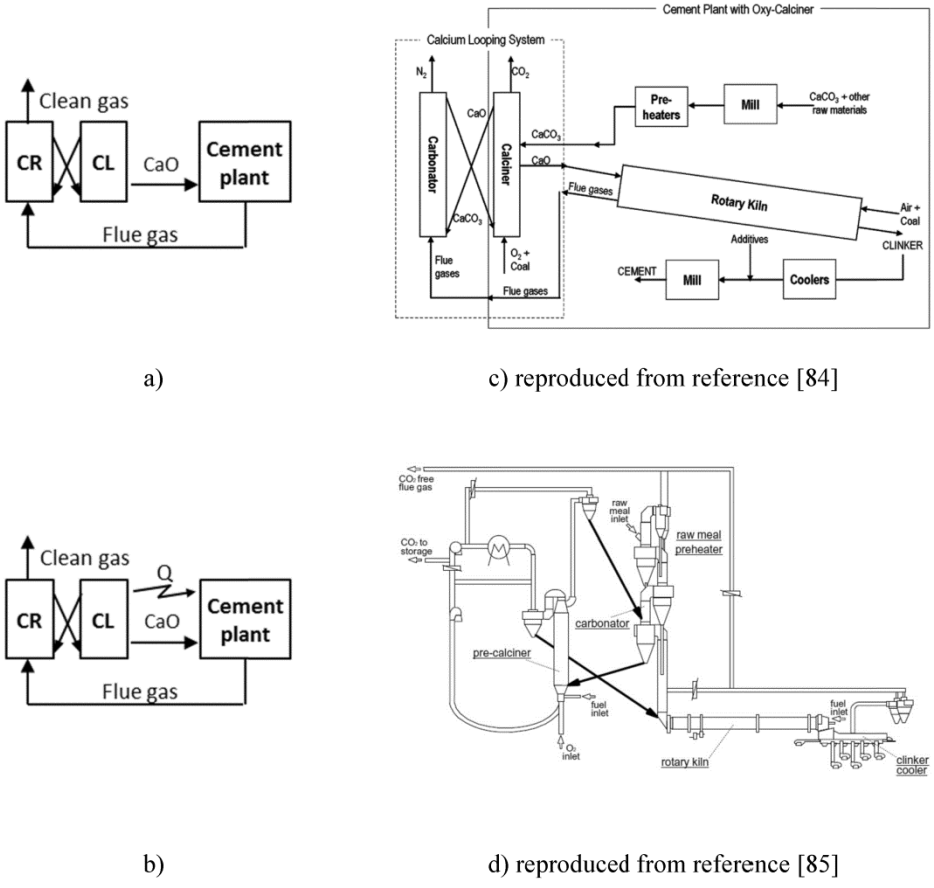

Figure 5. Calcium looping integration with cement plants. Reproduced with permission from references [84], [85].

Using the purged sorbent from the CaL calciner to feed a cement plant has the advantage of reducing the CO_2 generated in the cement manufacture. The CO_2 from the calcination and that generated in the combustion required to provide the energy for this reaction is avoided. Moreover, the raw material costs and the energy consumption of the ensemble cement plant and CaL process are reduced. However, the demands imposed on cement composition may limit this potential synergy. Dean et al. analyzed the limiting factors taking part.[63] Purged material consists mainly of CaO, a less significant fraction of ashes, calcium sulphate and trace elements released from fuel. Regarding the later, the maximum sulphur content of the ordinary portland cement is about 2.5% - 3% to avoid the expansion and cracking of the cement paste upon hydration and a reduction of the strength properties. Repeated exposure of trace elements contained in the fuel to the calciner environment over a long series of cycles may cause undesired effects on cement properties. Furthermore, attrition and agglomeration may affect the cement production since fines may be entrained and coarser particles may reduce the material burnability. Atsonios et al. analyzed the effect of different fuels on purge sulphur content concluding that the use of petcoke leads to an undesirable proportion of this compound.[80] They

proposed an intermediate gasification step as a petcoke pretreatment method to reduce the sulphur presence in the purge.

The use of other CO_2 capture technologies, mainly amine scrubbing and oxy-fuel combustion, in combination with cement manufacture has also been analyzed and compared with the use of the CaL technology.[80, 82, 84-86] The CaL energy consumption per kg of captured CO_2 has been calculated to be 0.43 – 0.68 times higher than that of the oxy-fuel combustion and 0.61 - 1.89 times lower than that of the amine scrubbing.[86] The CaL process has the highest energy recovery potential, 3.8 times higher than that of the oxy-fuel combustion and 11.5 times higher than that of the amine scrubbing.[82] Regarding CO_2 capture efficiency, the best results are obtained with the CaL technology, 90% - 100%, against a 63% - 89% in the case of the oxy-fuel combustion and around 85% for the amine scrubbing.[80, 82, 84-86] As a conclusion, the CaL technology has a significant potential to be a feasible CO_2 capture system for cement plants.

6. Lab-scale test results on the multicyclic CaO capture capacity at CaL conditions

A precise knowledge of the multicyclic carbonation reactivity of the Ca-based sorbent is of paramount importance to assess the CO_2 capture efficiency and cost of the CaL technology. The reaction kinetics and CO_2 capture capacity of Ca-based sorbents are usually evaluated by means of thermogravimetric analysis (TGA) lab-scale tests. Realistic CaL conditions to be expected in practice involve: i) short residence times (on the order of a few minutes), ii) low CO_2 concentration (about 15% in volume) for carbonation at temperatures around 650ºC, iii) high temperature and high CO_2 concentration in the calciner for sorbent regeneration and precalcination of the makeup flow of solids (temperatures above 930ºC and CO_2 vol% of at least 70% in volume, respectively) and iv) very fast transitions between the carbonation and calcination stages (of just a few seconds).[13, 87] The fluidized bed carbonator and calciner reactors would be operated in the fast fluidization regime, which ensures an optimum transfer of heat and mass. TGA tests provide optimum mass and heat transfer by using limestone samples of very small mass (just about 10 mg) at contact with the gas. However, the common furnaces usually employed in TGA tests to assess the multicyclic sorbent behavior are characterized by low heating rates (of about 10ºC/min) between the carbonation and calcination stages that are not representative of the real process.[88] The use of TG analyzers based on infrared heating by halogen lamps allows varying the temperature at a very fast and controlled rate (300ºC/min for heating and cooling), thus shortening the transitions between the carbonation and calcination stages to just tens of seconds, which adjusts better to conditions to be expected in the real application.[89, 90]

A common observation from TGA tests is that carbonation takes place in two well differentiated phases (Figure 6). In a first fast carbonation stage, CO_2 is chemisorbed on the available free

surface of the CaO particles until a thin layer of $CaCO_3$ (40-50 nm thick) is formed. Carbonation continues in a second relatively slower stage characterized by diffusion through the solid $CaCO_3$ layer.

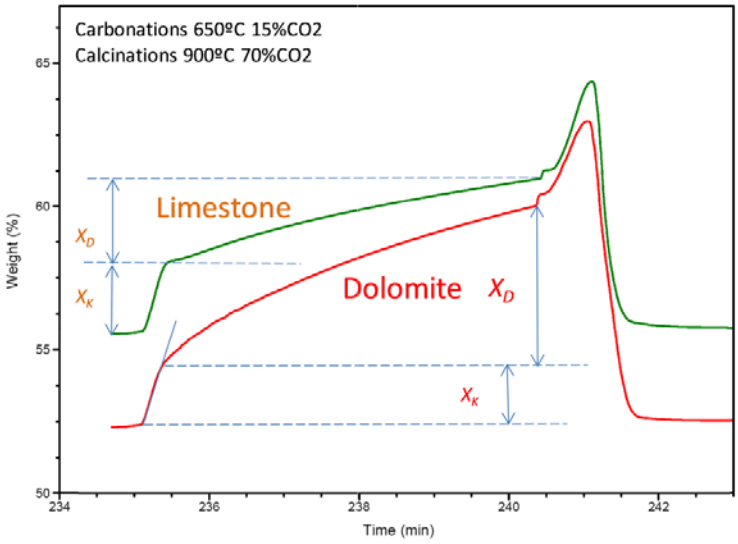

Figure 6. Time evolution of sorbent weight % during a carbonation/calcination cycle for limestone and dolomite measured by TGA[91] showing in the detail the existence of a fast carbonation phase and a relatively slower phase during carbonation (carbonation for 5 min at 650ºC under 15% CO_2; calcination for 5 min at 900ºC under 70% CO_2. Cycle number 20). The overshoot at the end of the carbonation stage is due to a short recarbonation under high CO_2 partial pressure at the transition to calcination stage that takes place while the temperature has not reached yet the equilibrium temperature.

It is usually believed that most of carbonation taking place in residence times of a few minutes occurs in the fast carbonation stage, which is driven by the reaction kinetics.[92] However, TGA tests carried out under calcination environments of high CO_2 partial pressure show otherwise.[91, 93-95] As may be seen in Figure 6, carbonation in the solid-state controlled diffusion phase (X_D as compared to X_K in the fast phase) represents a significant contribution to the overall carbonation. The substantial relevance of diffusion controlled carbonation when calcination is carried out at realistic conditions of high CO_2 partial pressure remains yet to be taken into account in the formulation of carbonator models to scale-up the technology.[7]

Ideally, the sorbents should react fast toward an optimum capture capacity and maintain it independently of the number of calcination/carbonation cycles. However, the multicyclic conversion of CaO decays progressively with the cycle number, mainly due to the decrease of available surface area as a consequence of material sintering during calcination at high temperature.[4, 17, 96, 97] CaO conversion is defined as the ratio of mass of CaO converted in each carbonation stage to the mass of CaO initially present in the sorbent after calcination. TGA tests show that the CaO multicyclic conversion in short residence times can be described by the following expression:[98]

$$\frac{X_N}{X_1} = \frac{X_r}{X_1} + \left[\frac{1}{k(N-1) + (1 - X_r/X_1)^{-1}}\right]; (N = 1, 2 \ldots) \qquad (1)$$

where N is the cycle number, X_1 is CaO conversion in the first cycle, k is the deactivation constant and X_r is the residual conversion, which is asymptotically approached after a large number of cycles.

7. The multicyclic CO2 capture capacity of natural limestone at CaL conditions

Limestone stands as the most suitable CaO precursor to guarantee the industrial competitiveness of the CaL technology.[12, 15] However, the porous skeleton obtained from calcination of limestone suffers severe sintering usually attributed to lattice diffusion at the high temperatures of calcination, which causes a progressive reduction of the CaO surface area with the cycle number, and therefore an irreversible loss of CaO conversion.[99, 100] TGA tests involving calcination at 950ºC under low CO_2 concentration show that multicyclic CaO conversion decays with the cycle number and converges to a residual value X_r = 0.07-0.08.[21, 92, 101, 102] The presence of CO_2 at high concentration in the calcination environment produces a significantly marked drop of conversion for CaO derived from limestone precalcined in air, with values around 0.05 after few cycles.[33, 89, 90, 103] It has been proposed that a progressive growth of the regenerated crystal structure along preferential surfaces, which are more stable but less favorable for $CaCO_3$ nucleation, could play a role on the loss of multicyclic CaO conversion.[104-106] On the other hand, empirical results seem to indicate that decarbonation in CO_2 is a complex process involving a two-stage reaction mechanism, which consists of the endothermic chemical decomposition of $CaCO_3$ to yield CO_2 and adsorbed CO_2, followed by CO_2 desorption and exothermic structural transformation of CaO from a metastable CaO* form to the stable phase.[107] Thus, at low CO_2 partial pressures, desorption of CO_2 is fast, but at high CO_2 partial pressures and high temperatures hindered desorption of CO_2 and the exothermicity of CaO structural transformation would hamper calcination.[108]

Figure 7 compares multicyclic CaO conversion data obtained for limestone samples precalcined at 850ºC (heated at 20ºC min^{-1}) in air and at 950ºC (heated at 300ºC min^{-1}) under 70% CO_2 and 30% air vol/vol. The former conditions would replicate precalcination of the initial batch of limestone in the practical application, while the latter mimic precalcination of the fresh makeup of limestone introduced in the calciner to compensate for sorbent losses and deactivation. Subsequent carbonation/calcination (carb/cal) cycles consisted of 5 minutes of carbonation at 650ºC under 85% air and 15% CO2 (vol/vol), and 5 minutes of calcination at 950ºC under 70% CO2 and 30% air (vol/vol).

The CaO derived from precalcination at 950ºC under high CO_2 concentration presents a low conversion in the first cycle as compared to the CaO obtained from precalcination in air, which has a higher porosity. Moreover, it is clear from Figure 7 that precalcination conditions have an important influence on the multicyclic behavior of the sorbent. The sample precalcined in air presents a drastic drop of conversion after the first cycle,[89] whereas the conversion of the sample precalcined under high CO_2 concentration decays at a lower rate. Consequently, conversion of the latter is higher from the fourth cycle. While Equation 1 is not able to provide a good fit to the conversion data of the sorbent precalcined in air, the sample precalcined under high CO_2 concentration is well fitted by this equation yielding a residual value of 0.079, which is similar to the residual value of conversion for samples regenerated under low CO_2 partial pressure. Yet, regeneration under CO_2 yields a larger deactivation rate.

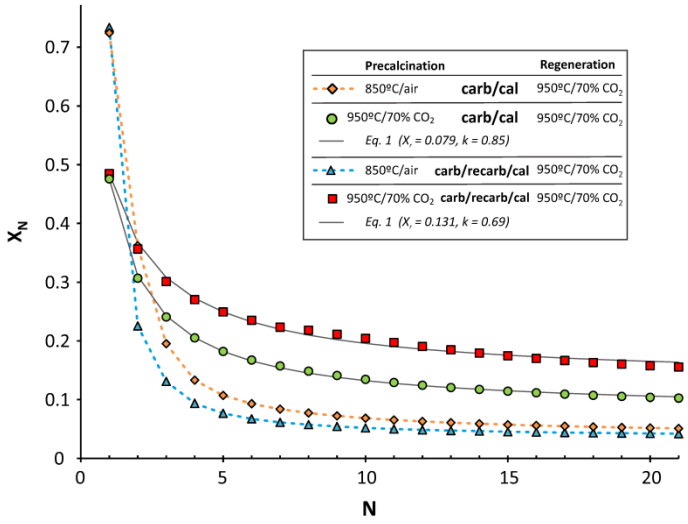

Figure 7. CaO conversion at the end of the carbonation stage (X_N) as a function of the cycle number (N) for samples of raw limestone subjected to carbonation/calcination (carb/cal) and carbonation/recarbonation/calcination (carb/recarb/cal) cycles. Precalcination and regeneration conditions are indicated. The solid lines are the best fits from Eq. (1). Reproduced with permission from reference [25]. Copyright 2014. Applied Energy.

Figure 7 also shows the effect of introducing a recarbonation stage aimed at reactivating the sorbent. In carb/recarb/cal cycles, 3 minutes of recarbonation in 10% air and 90% CO_2 (vol/vol) at 800ºC were introduced between the carbonation and the calcination stages.[25] Interestingly, the effect of recarbonation depends on the precalcination stage. Thus, the recarbonation stage accentuates the drop of CaO conversion if precalcination is performed in air. On the other hand, recarbonation improves the conversion of the sample precalcined under high CO_2 concentration, with an enhanced residual conversion, obtained fitting the data with Equation 1, of X_r=0.131.

Thermograms corresponding to the different experiments above reviewed are shown in Figure 8. The higher conversion of the CaO precalcined in air in the first cycle, as observed in Figure 7, is due to its high reactivity in the fast carbonation phase, and its drastic drop in conversion can be associated to the high susceptibility of the soft CaO skeleton resulting from precalcination in air to sintering. On the other hand, the low reactivity in the first cycle of the CaO obtained from precalcination under high CO_2 concentration is explained by the enhancement of sorbent sintering under these conditions. However, precalcination under CO_2 mitigates the subsequent reduction of the CaO surface available for reaction.[109, 110] As stated above, the carbonation stage is seen to take place through two phases,[111] a reaction controlled phase on the surface of the CaO particles and a slower phase controlled by the solid-state diffusion of CO_2 into the material.[112, 113]

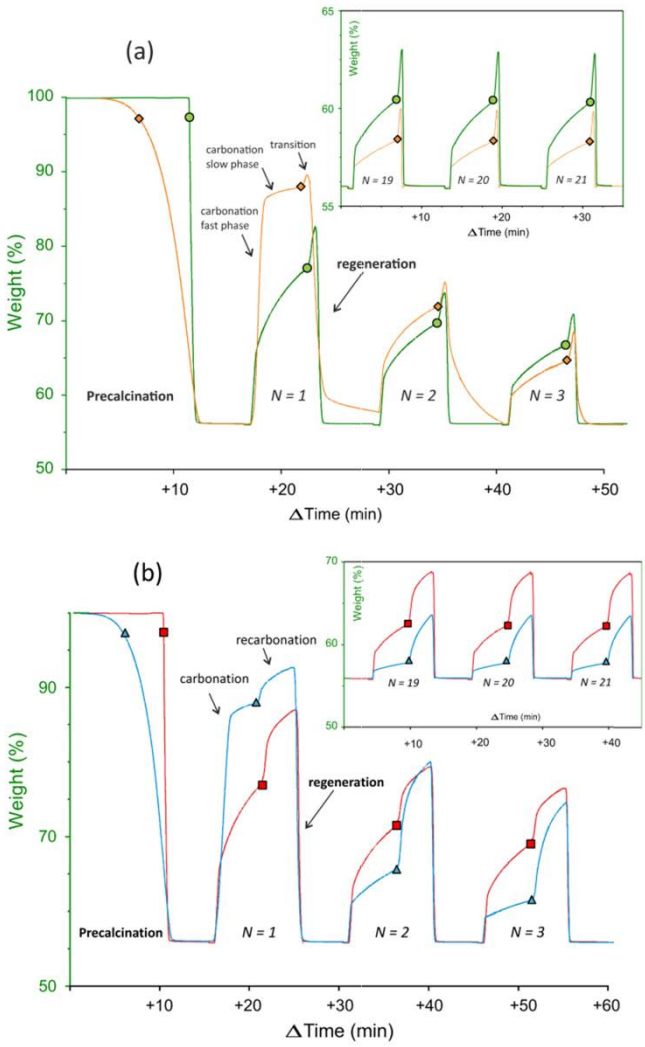

Figure 8. Time evolution of sorbent weight% during precalcination and the three first and last (inset) cycles for raw limestone. (a) Carbonation/calcination cycles of limestone slowly precalcined at 850ºC in air (orange line) and quickly precalcined at 950ºC under 70% CO_2 (green line). (b) Carbonation/recarbonation/calcination cycles of limestone precalcined at 850ºC in air (blue line) and at 950ºC under 70% CO_2 (red line). Carbonation at 650ºC for 5 min (15% CO_2/85% air vol/vol), calcination (regeneration) for 5 min at 950ºC (70% CO2/30% air vol/vol). Reproduced with permission from reference [25]. Copyright 2014. Applied Energy.

Note also in the thermograms shown in Figure 8a that carbonation in the diffusion controlled phase of the 1st cycle for the sample precalcined in air is negligible as compared to carbonation in the fast kinetically controlled phase. On the contrary, the diffusion controlled phase gains an extraordinary relevance after regeneration under high CO_2 concentration.

A similar behavior is observed in the thermograms of the carb/recarb/cal experiments shown in Figure 8b. Thus, diffusion controlled carbonation and recarbonation in the first cycle is more marked for the sample precalcined under high CO_2 concentration. As may be seen, the carbonation reactivity of the sample precalcined in air is severely reduced after only few cycles.

A possible mechanism proposed for product layer formation and growth establishes that $CaCO_3$ nucleates on CaO surface in islands with a critical size which depends on temperature controlled surface diffusion.[114, 115] Surface diffusion is considerable when the temperature is close to the Huttig temperature, $T_H \approx 690$ºC for CaO and $T_H \approx 260$ºC for $CaCO_3$. Thus, the intense carbonation observed in the recarbonation stage can be explained due to the high surface diffusion controlled reactivity at 800ºC and 90% CO_2 in vol.

Figure 9 illustrates SEM micrographs of samples subjected to 20 cycles under different precalcination and regeneration conditions. Thus, samples precalcined in air and regenerated under 70% CO_2 (Figure 9a), with very low CaO conversion, show large grains as compared with the grain size of the samples precalcined and regenerated under high CO_2 concentration (Figure 9b). Among these samples, those subjected to the intermediate recarbonation stage present smaller grain size (Figure 9c) than those subjected to carb/cal cycles. It may be seen that the CaO grains have a characteristic size that depends on the conditions of the experiments. CaO conversion in the fast kinetically controlled phase depends on the available surface area for carbonation and is therefore inversely correlated to grain size as shown in a recent work.[108]

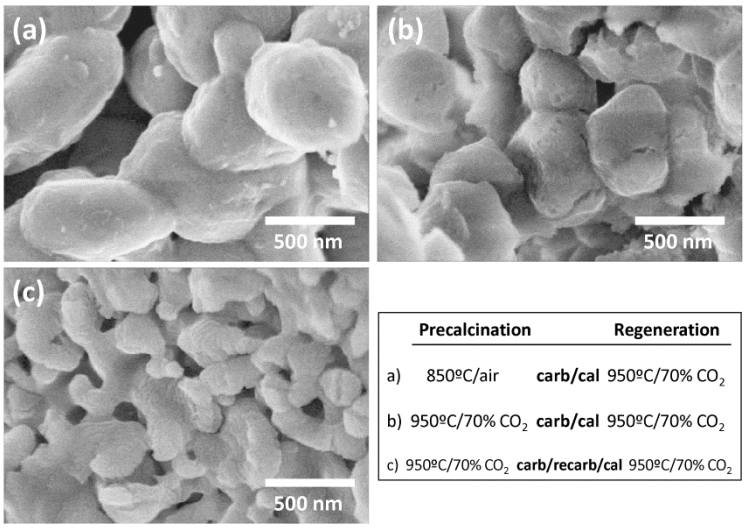

Figure 9. SEM pictures of limestone samples after being subjected to 20 carb/cal (a and b) and carb/recarb/cal cycles (c) under different precalcination and regeneration (calcination) conditions as indicated. Reproduced with permission from reference [25]. Copyright 2014. Applied Energy.

8. The multicyclic CO_2 capture capacity of natural dolomites at CaL conditions

Dolomite, $CaCO_3$•$MgCO_3$, is another natural and abundantly available material that has been considered as CaO precursor for the CaL technology.[4, 29, 116] Dolomite has a relatively lower stoichiometric capture capacity because carbonation of MgO is not thermodynamically favorable at CaL conditions.[4, 117] However, the irreversible decomposition of $MgCO_3$ that takes place during precalcination yields stable MgO inert nanograins that would serve to increase the available CaO surface area of the calcined sorbent thus favoring the CaO reactivity.[118] Moreover, due to its high resistance to sintering at high temperatures, the presence of inert MgO nanograins in calcined dolomite would increase the thermal stability of the sorbent, although the detailed mechanism of thermal decomposition of dolomite is still unclear.[119-121] Despite the potential advantages of using dolomite, experimental measurements reported in literature generally fail to show a superior performance of dolomite as compared to limestone. Yet, most lab-scale tests on dolomite or CaO•MgO synthetic composites do not mimic realistic CaL conditions.[122-125] The multicyclic capture performance of dolomite and limestone has been recently compared in TGA tests reproducing severe calcination conditions (950ºC, 70% CO_2 vol.). This work has shown that the sorbent derived from dolomite does have a higher residual capture capacity than CaO derived from limestone despite of the lower CaO content of dolomite.[126]

In order to assess the performance of dolomite as a suitable sorbent in the CaL technology for practical purposes, the presence of inert MgO in dolomite has to be taken into account. For this reason, the capture capacity, defined as the ratio of mass of CO_2 captured to the mass of sorbent before each carbonation stage (including both CaO and MgO for dolomite), is the appropriate parameter to be studied in a comparative analysis with limestone.[91] Figure 10a presents multicyclic capture capacity results from carb/cal test in which dolomite and limestone samples were precalcined in air and regenerated under high CO_2 concentration. As shown above in terms of conversion (Figure 7), CaO derived from limestone suffers a drastic drop of its capture capacity after regeneration. Dolomite however deactivates at a lower rate and after 20 cycles its capture capacity is almost twice that of limestone. Moreover, while limestone is affected by precalcination conditions, and recarbonation is detrimental for limestone precalcined in air (Figure 7), recarbonation does not produce an appreciable effect on the performance of dolomite. In general, the multicyclic behavior of dolomite is not significantly sensitive to the conditions of precalcination, even when precalcination conditions are severe (Figure 10b), which makes it rather predictable regardless of precalcination conditions. Only if limestone is precalcined under severe conditions (involving high CO_2 concentration) and subjected to recarbonation, its capture capacity may evolve similarly to that of dolomite (see Figures 7 and 10b). These results strongly suggest that natural dolomite would improve the CO_2 capture

efficiency at least to the same extent than the introduction of a recarbonator would do when using limestone.

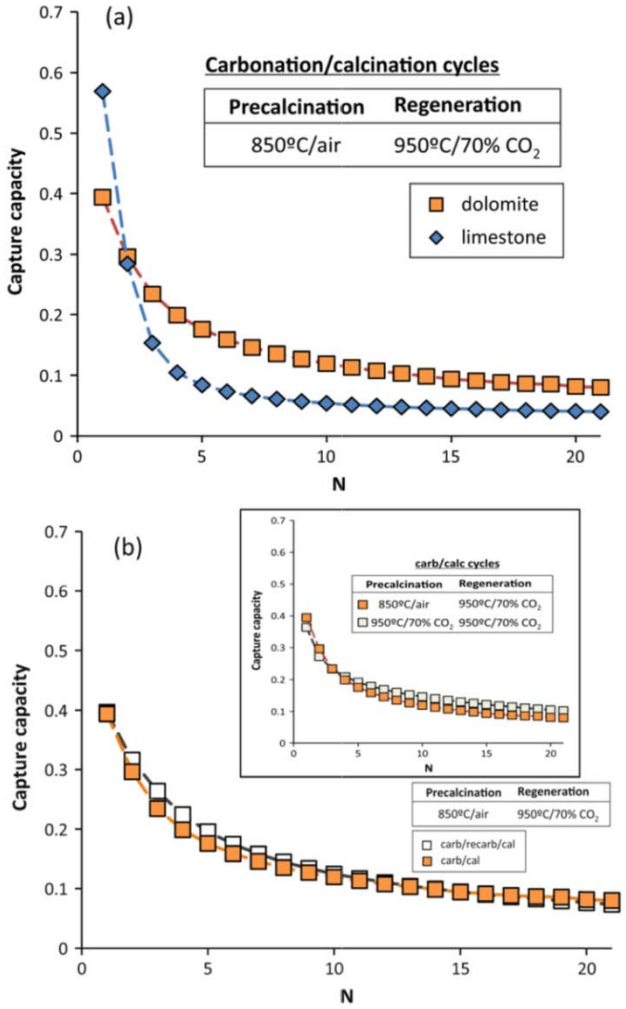

Figure 10. (a) CO_2 capture capacity as a function of carb/cal cycle number for dolomite and limestone samples precalcined in air and regenerated by calcination in 70%CO_2 at 950ºC. (b) CO_2 capture capacity as a function of cycle number for dolomite samples subjected to carb/cal and carb/recarb/cal cycles precalcined in air and regenerated by calcination under 70%CO_2 at 950ºC. The inset shows the CO_2 capture capacity for dolomite precalcined under different conditions and subjected to carb/cal cycles, calcined at 950ºC in 70% CO_2. Reproduced with permission from reference [91]. Copyright 2015. Applied Energy.

Figure 11a illustrates SEM micrographs of dolomite samples precalcined in air and subjected to carb/cal cycles under severe regeneration conditions. Remarkably, these samples show a higher porosity than limestone samples subjected to the same conditions (Figure 9). Individual MgO grains, with a size of about 100 nm, can be clearly observed, dispersed in the sintered CaO. Thus, the enhanced porosity and thermal stability provided by the MgO skeleton could be the responsible mechanism for the high capture capacity of dolomite in comparison with limestone. Note that a marked segregation of the MgO nanograins from the sintered CaO skeleton can be

observed for dolomite samples subjected to carb/recarb/cal cycles precalcined and regenerated in severe conditions (Figure 11b). Taken into account that diffusivity is enhanced by the recarbonation conditions,[127-129] the segregation of MgO and CaO grains would be expected to be promoted, in agreement with in situ observations.[121] This phenomenon causes a slight decrease in capture capacity of dolomite precalcined under severe calcination conditions when the intermediate recarbonation stage is introduced.

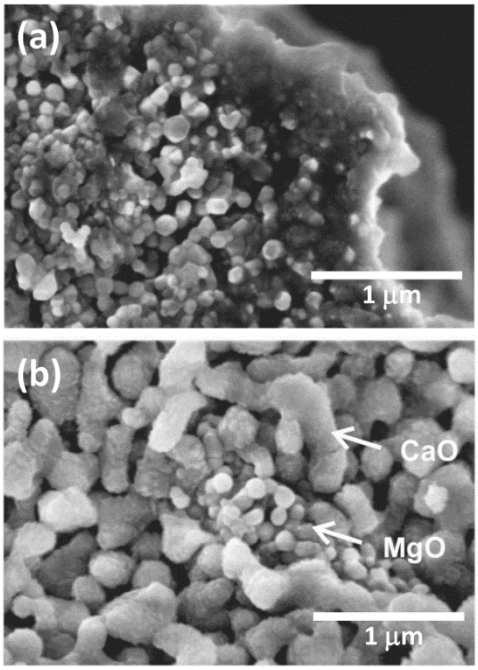

Figure 11. SEM pictures of dolomite samples (a) after being subjected to carb/cal cycles (precalcined at 850ºC in air and regenerated by calcination in 70% CO2 at 950ºC and (b) after being subjected to carb/recarb/cal cycled precalcined and regenerated by calcination under 70% CO_2 at 950ºC. Reproduced with permission from reference [91]. Copyright 2015. Applied Energy.

A further benefit of using dolomite instead of limestone in the CaL technology would be the possibility of reducing the calcination temperature. Figure 12 illustrates the kinetics of limestone calcination under 70% vol CO_2 by quickly increasing the temperature up to 950ºC. The presence of CO_2 hinders severely the decarbonation of limestone, as observed in many works.[6, 107, 130-133] Not only the thermodynamic equilibrium is displaced to higher temperatures but also decarbonation of $CaCO_3$ is markedly slowed down. As may be seen in Figure 12, limestone decarbonation starts at about 900ºC (30ºC above the thermodynamic equilibrium temperature under 70% vol CO_2 at atmospheric pressure).[6] The kinetics of dolomite calcination under 70% vol CO_2 shows different features as compared to limestone (Figure 13). Thus, decomposition of dolomite under high CO_2 concentration occurs in two stages.[134, 135] In a first stage, irreversible $MgCO_3$ decomposition takes place, whereas the second stage, involving

$CaCO_3$ decomposition, is initiated at about 650ºC, which is well below the equilibrium temperature for pure $CaCO_3$ decomposition. Moreover, decarbonation of dolomite is complete in less than 5 min at 900ºC. The two stages calcination of dolomite in environments of high CO_2 partial pressure has been widely reported in literature, but the mechanism of the reactions involved is still under debate.[91, 119-122, 135, 136]

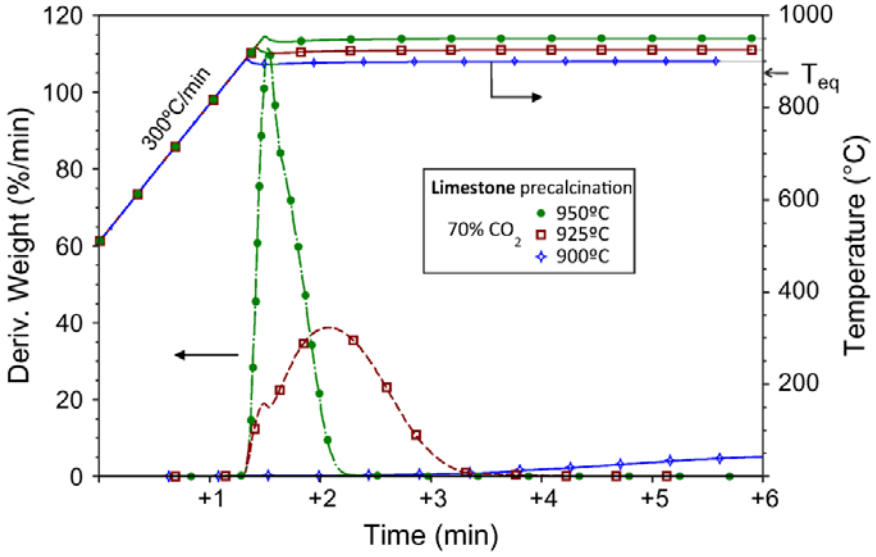

Figure 12. Time evolution of sample weight % derivative (absolute value) and temperature during decomposition of samples of limestone precalcined in-situ in the TGA tests under 70%CO_2 by quickly increasing the temperature up to 900ºC, 925ºC, and 950ºC (as indicated). The arrow in the temperature axis (right) indicates the thermodynamic equilibrium temperature (T_{eq} ≈ 870ºC). Reproduced with permission from reference [91]. Copyright 2015. Applied Energy.

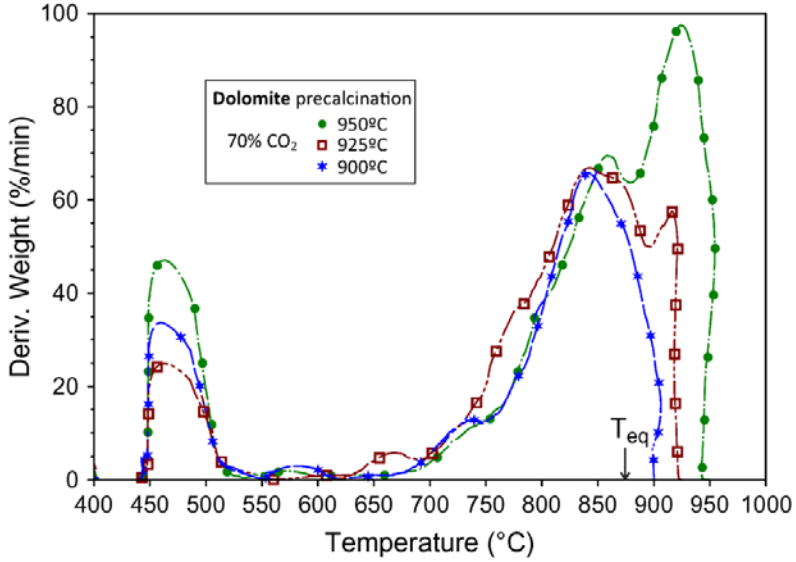

Figure 13. Derivative of sample weight % (absolute value) as a function of temperature during decomposition of samples of dolomite precalcined under 70% vol CO_2 in the TGA tests by quickly increasing the temperature up to 900ºC, 925ºC, and 950ºC (as indicated). The arrow in the temperature axis (horizontal) indicates the thermodynamic equilibrium temperature for calcite (T_{eq} ≈ 870ºC). Reproduced with permission from reference [91]. Copyright 2015. Applied Energy.

Some authors have shown experimentally that the capture capacity of dolomite is lower than that of limestone from the first carbonation/calcination cycles. However, most of these tests have been carried out at conditions far from realistic. On the other hand, it has been recently demonstrated that dolomite has a superior capture capacity (which also takes into account the inert MgO) as compared to limestone at realistic CaL conditions (implying high CO2 concentration, high temperature for calcination and quick transitions between carbonation and calcination stages).[91] Moreover, the capture capacity of limestone derived CaO is critically influenced by the conditions of precalcination and the inclusion or not of a recarbonation stage, while the behavior of the sorbent derived from dolomite is almost insensitive to precalcination and recarbonation conditions, which allow predicting the dolomite behavior on a more solid basis. The improved stability provided by the inert MgO skeleton, as stated above, is thought to enhance the multicyclic capture capacity of dolomitic CaO at realistic CaL conditions.. In addition, an further advantage of the use of dolomite would be its fast decomposition under CO_2 that would allow reducing the temperature of the calciner, which is the main energy penalty of the CaL technology.As regards the decomposition enthalpies of limestone and dolomite, they are 1.78 kJ g^{-1} and 1.63 kJ g^{-1}, respectively. Therefore, the use of dolomite in the CaL process would imply also a lower energy consumption in the calciner, where the main energy penalty to the technology is imposed. Moreover, differential thermal analysis (DTA) experiments have shown that the enthalpy to decompose dolomite can be reduced by mechanical milling, which is an industrial scalable process.[137]

9. Effect of thermal pretreatment of limestone on its multicyclic CO_2 capture behavior

Prolonged heating of the sorbent at high temperatures prior to its use in the CaL process was proposed as a feasible technique to improve the multicyclic conversion of CaO by Manovic and Anthony,[98] who observed a positive effect of thermal pretreatment on the multicyclic CO_2 capture behavior of CaO.[138-140] Recrystallization of CaO during thermal pretreatment, which leads to a hard stable porous skeleton, was proposed as the main cause of the high efficiency of the pretreatments on reactivation of the sorbent, especially under CO_2 enriched atmosphere.[139] Thus, experimental results showed that the capture capacity of the pretreated sorbent, although small in the first cycle, was in fact increased with the cycle number during the first 10-20 cycles up to reach a stable value over the residual capture capacity of non-pretreated natural limestone. Moreover, another advantage of thermal pretreatment would be the increase in the mechanical strength of the sorbent. The effect of thermal pretreatment became however a controverted issue since initial TGA tests carried out to show reactivation were not carried out at realistic CaL conditions. Reactivation was enhanced by the regeneration conditions applied, which involved

relatively low temperatures and low CO_2 partial pressures.[98] Further carbonation/calcination tests carried out by calcination at temperatures above 900ºC failed to confirm sorbent reactivation.[98, 141]

Figure 14 compares multicyclic CaO conversion data obtained for samples of heat pretreated (isothermal preheating in air at 950ºC for 12 h) and raw limestone subjected to carb/calc and carb/recarb/cal cycles in which sorbent regeneration is carried out at 950ºC under 70% vol CO_2. In carb/calc tests, heat pretreatment does not yield reactivation, and conversion after the first cycle is maintained at a small value. Equation 1 is able to fit the conversion data and a value of residual conversion is similar to that of raw limestone tested under the same conditions, with the disadvantage that conversion of the first cycle is just about 0.13. An even bigger drop of CaO conversion is observed if the heat pretreated sample is precalcined in air. A different behavior is observed when heat pretreatment, precalcination under high CO_2 concentration and recarbonation are combined. Then, a significant reactivation of CaO conversion is obtained from the second carb/recarb/cal cycle for the heat pretreated sample, which becomes higher than that of raw limestone subjected to carb/recar/cal cycles under the same conditions and remains higher with the number of cycles. Thus, the synergistic combination of heat pretreatment and recarbonation improves the multicyclic CaO conversion when precalcination and regeneration are performed under high CO_2 concentration.

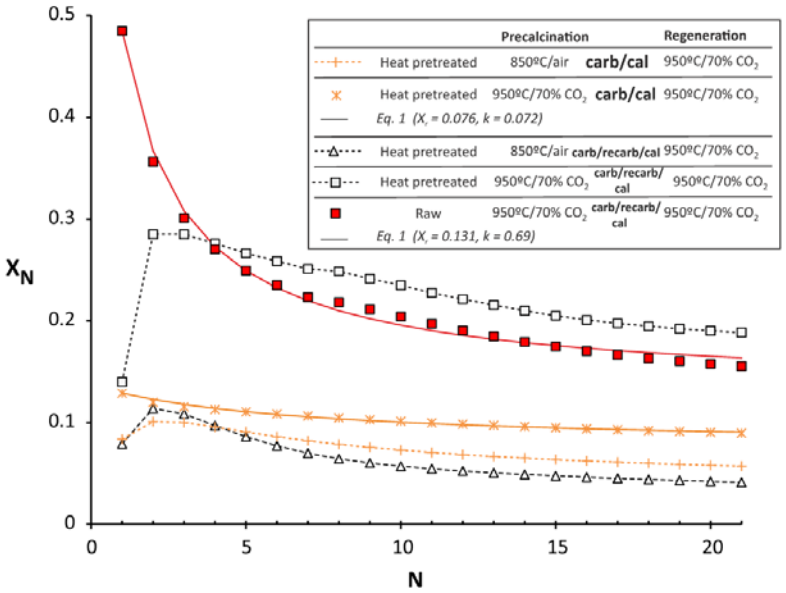

Fig. 14. CaO conversion at the end of the carbonation stage (X_N) as a function of the cycle number (N) for samples of heat pretreated and raw limestone subjected to carb/cal and carb/recarb/calc cycles. Carbonation at 650ºC for 5 min (15% CO_2/85% air vol/vol), calcination (regeneration) for 5 min at 950ºC (70% CO_2/30% air vol/vol) and recarbonation at 800ºC for 3 min (90% CO_2/10% air vol/vol). Different precalcination conditions are indicated. The solid lines are the best fits from Eq. (1). Reproduced with permission from reference [25]. Copyright 2014. Applied Energy.

10. Effect of mechanical pretreatment of limestone on its multicyclic CO_2 capture behavior

Mechanical milling is a common treatment used in the industry to favor chemical reactions by creating a high density of structural defects in the solid crystal structure, which serves to enhance solid-state diffusion.[142-144] The milling method to prepare materials with reduced crystallinity and enhanced reactivity is simple, relative inexpensive and is applicable to almost all kind of materials, with the possibility of scaling up to tonnage quantities of materials.[145-147]

Figure 15 shows the time evolution of sorbent weight % during carbonation/calcination cycles for samples of raw, milled, and annealed limestone. Limestone was milled in a centrifugal mill (working at 500 rpm) employing 100 cm^3 steel jar with 200 tungsten carbide balls 5.5 mm in diameter, and a sample-to-ball mass ratio of 1:40.[129] Thermal annealing was pursued by subjecting a limestone sample to a pure CO_2 atmosphere at 850°C for 12 h.

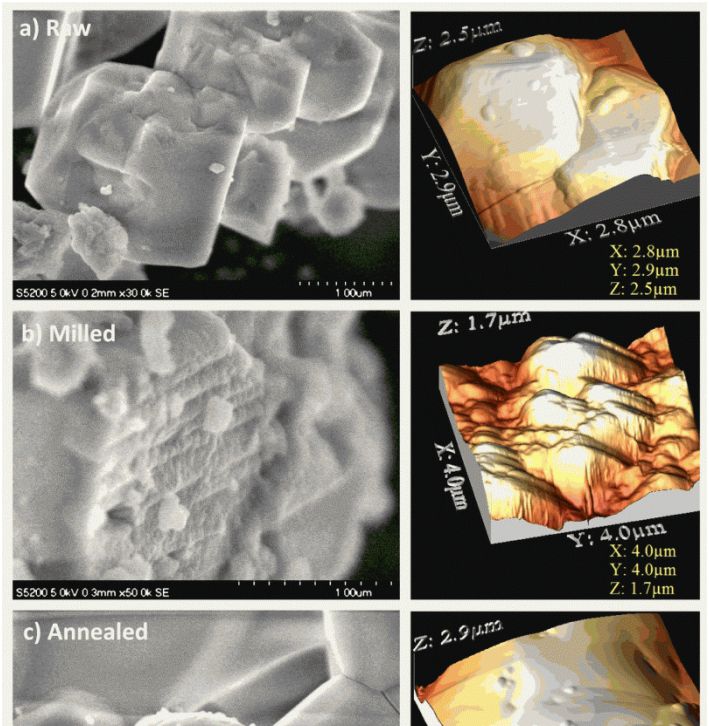

Figure 15. Scanning electron microscopy (SEM) and 3D scanning probe microscope (SPM) images of limestone particles from raw (a), milled (b) and thermally annealed (c) samples. SEM analysis was made by using a HITACHI Ultra High-Resolution S-5200 equipment. SPM images were obtained by using a Molecular Imaging Pico Plus system provided with AppNano ACT silicon tapping-mode rectangular cantilevers. Reproduced with permission from reference [126]. Copyright 2014. Environmental Science and Technology.

The increase of crystallinity degree induced by annealing enhances the resistance to solid-state diffusion thus playing the opposite role of milling.[148, 149] Figure 15 shows scanning electron (SEM) and scanning probe microscopy (SPM) images which demonstrate contrasting effects of milling and thermal annealing on the structure of the solids. In the milled particles, the structural damage is clearly appreciable, while the surface of the annealed particles appears smoothed.

In the carb/cal tests carried out to assess the effect of crystal structure sorbent regeneration was carried out by calcination under 70% CO_2 at 900ºC whereas the samples were precalcined in air. As can be seen, most carbonation in the first cycle occurs through the kinetically controlled fast phase and up to a similar extent for the three samples. Once the fast carbonation phase is ended, CaO conversion is controlled by diffusion and would be inversely correlated to CaO crystallite size.[150] In accordance to the expected effects of pretreatment on the crystallinity of the solids, it is seen in Figure 16 that carbonation in the diffusion-controlled phase is enhanced for the milled sample while annealing hinders it. This behavior is more apparent in the short transition between carbonation and calcination. The sharp overshoot observed in the weight gain is due to the enhancement of carbonation when CO_2 concentration is increased from 15% vol to 70% vol and until the equilibrium temperature is reached. Since surface diffusion becomes noticeable at temperatures close to the Huttig temperature, it would be promoted at high temperatures by structural defects that enhance the exposition of surface available in the sorbent for accelerated recarbonation in the transitory period.[129] Although the critical temperature for decarbonation under 70% vol CO_2 is about 870ºC,[6] it may be seen in Figure 15 that calcination at 900ºC does not yield a sufficiently fast regeneration of CaO derived from raw limestone.

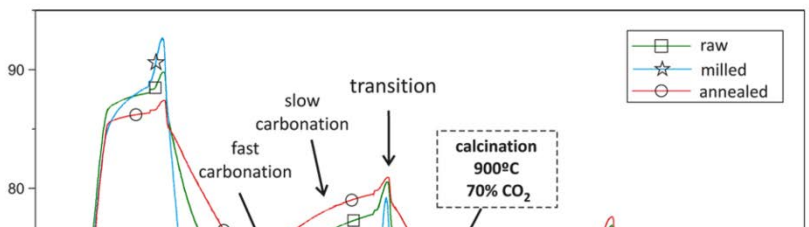

Figure 16. Time evolution of sorbent weight % during carbonation/calcination cycles for samples of raw, milled and annealed limestones. Carbonation at 650 °C for 5 min (15% CO2/85% air vol/vol). Calcination for 5 min at 900 °C (70% CO2/30% air vol/vol). Reproduced with permission from reference [126]. Copyright 2014. Environmental Science and Technology.

Decarbonation is even slower for the annealed sample with a higher crystallinity. On the other hand, decarbonation is fast and completed at 900ºC for the sorbent derived from milled limestone. The limiting mechanism of calcination under these conditions involving CO_2 desorption and structural transformation step would be enhanced by the structural damage caused by milling.[107, 116, 130, 132, 133]

A straightforward recommendation that may be extracted from this study is that the use of limestone with low crystallinity should be pursued in favor of highly crystalline solids. This would allow for a reduction of the calciner temperature of about 50ºC while maintaining high calcination efficiency.

Natural chalk, whose chemical composition is mainly $CaCO_3$ with minor presence of silt and clay, has been proposed also as a natural CaO precursor to be used in the CaL process not just for carbonation but also for SO_2 removal[151].CO_2 capture capacity and uptake of SO_2 were compared with that of limestone and dolomite in a fluidized bed. The sulfation was carried out at 850ºC in 0.18 vol% SO_2 and 5.2 vol% O_2 (N_2 balance) and the CO_2-capture tests were performed at 750ºC with calcination in pure N_2 followed by carbonation in 14 vol % CO_2 (N_2 balance).[151] Under these conditions, the uptake of SO_2 and CO_2 capture of chalk derived CaO were higher than those of limestone and dolomite derived CaO . A subject of great interest to be analyzed in future works would be whether natural chalk still maintains a superior capture performance as compared to limestone and dolomite under the severe calcination conditions typical of the CaL process.

11. Pilot-plant testing

Demonstration of the CaL technology in pilot-scale plants is required to optimize the process parameters and has been in fact one of the most significant fields of advancement of the technology. A number of test facilities have been built worldwide in the last five years. The interested reader on pilot-plant testing is referred to the very recently published Hanak's exhaustive review and references therein.[155] Here we give just a brief summary of the largest scale facilities that are currently demonstrating the efficiency of CO2 capture by means of the CaL process.

The pilot plant in La Pereda (Asturias, Spain) is a 1.7 MW_{th} facility designed to process approximately 1% of the flue gas produced in a 50 MW_{el} coal-fired commercial power plant. The pilot plant consists of two interconnected circulating fluidized bed (CFB) reactors operating at gas velocities of 3-5 m s^{-1}, with operating temperatures of 600-715ºC for the carbonator and 820-950ºC for the calciner, which is fired with coal.[8] The experimental facility at Darmstadt University of Technology is a 1MW_{th} pilot plant comprising two interconnected CFB reactors that are refractory lined. In this plant, the fresh limestone is pre-heated in the carbonator at 650ºC to minimize the fuel and oxygen consumption in the calciner. The fluidizing medium in the carbonator is a synthetic flue gas and oxygen-enriched air is used to fluidize the calciner.[152] The Industrial Technology Research Institute in Taiwan has erected a 1.9 MW_{th} pilot plant, which is integrated into a cement plant that is able to remove a tonne of CO_2 per hour. The system contains a bubbling fluidized bed reactor, a gas distributor and a moving bed calciner. The temperature in the carbonator is controlled by water-cooled steel jackets and the heat for calcination is obtained by oxy-combustion of diesel.[153]

The CaL technology has also been integrated with biomass combustion. Thus, a 0.3 MW_{th} pilot plant has been developed to capture CO_2 during the combustion of biomass in a fluidized bed operating in continuous mode. The pilot plant is located at a 655 MW_e coal power plant in Leon (Spain) and operates at temperatures around 700ºC both in the carbonator and in the calciner in order to maximize the combustion and CO_2 capture efficiencies. The use of biomass as a fuel in CCS systems (BIO-CSS) would allow producing power with negative emissions of CO_2[154]. The necessity of urgently developing BIO-CCS technologies is increasingly gaining importance as perspectives of keeping CO_2 concentration in the atmosphere below 450ppm in order to limit global warming to +2ºC from pre-industrial level are becoming more pessimistic.

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13. References

1. Metz, B.; Davidson, O.; Coninck, H. D.; Loos, M.; Meyer, L., *Special report on carbon dioxide capture and storage, intergovernmental panel on climate change*, 2005.
2. Middleton, R. S.; Eccles, J. K. The complex future of CO_2 capture and storage: Variable electricity generation and fossil fuel power. *Applied Energy* **2013**, 108, 66-73.
3. Roddy, D. J. Development of a CO_2 network for industrial emissions. *Applied Energy* **2012**, 91, 459-465.
4. Blamey, J.; Anthony, E. J.; Wang, J.; Fennell, P. S. The calcium looping cycle for large-scale CO_2 capture. *Progress in Energy and Combustion Science* **2010**, 36, 260-279.
5. Romano, M. C. Modeling the carbonator of a Ca-looping process for CO_2 capture from power plant flue gas. *Chemical Engineering Science* **2012**, 69, 257-269.
6. García-Labiano, F.; Abad, A.; de Diego, L. F.; Gayán, P.; Adánez, J. Calcination of calcium-based sorbents at pressure in a broad range of CO_2 concentrations. *Chemical Engineering Science* **2002**, 57, 2381-2393.
7. Charitos, A.; Rodríguez, N.; Hawthorne, C.; Alonso, M.; Zieba, M.; Arias, B.; Kopanakis, G.; Scheffknecht, G.; Abanades, J. C. Experimental validation of the calcium looping CO_2 capture process with two circulating fluidized bed carbonator reactors. *Industrial & Engineering Chemistry Research* **2011**, 50, 9685-9695.
8. Arias, B.; Diego, M. E.; Abanades, J. C.; Lorenzo, M.; Diaz, L.; Martínez, D.; Alvarez, J.; Sánchez-Biezma, A. Demonstration of steady state CO_2 capture in a 1.7 MWth calcium looping pilot. *International Journal of Greenhouse Gas Control* **2013**, 18, 237-245.
9. Martínez, I.; Grasa, G.; Murillo, R.; Arias, B.; Abanades, J. C. Modelling the continuous calcination of $CaCO_3$ in a Ca-looping system. *Chemical Engineering Journal* **2013**, 215–216, 174-181.
10. Kunze, C.; Spliethoff, H. Assessment of oxy-fuel, pre- and post-combustion-based carbon capture for future IGCC plants. *Applied Energy* **2012**, 94, 109-116.
11. Lisbona, P.; Martínez, A.; Romeo, L. M. Hydrodynamical model and experimental results of a calcium looping cycle for CO_2 capture. *Applied Energy* **2013**, 101, 317-322.
12. Romeo, L. M.; Lara, Y.; Lisbona, P.; Martínez, A. Economical assessment of competitive enhanced limestones for CO_2 capture cycles in power plants. *Fuel Processing Technology* **2009**, 90, 803-811.
13. Ylätalo, J.; Ritvanen, J.; Tynjälä, T.; Hyppänen, T. Model based scale-up study of the calcium looping process. *Fuel* **2014**, 115, 329-337.
14. Chen, H.; Zhao, Z.; Huang, X.; Patchigolla, K.; Cotton, A.; Oakey, J. Novel optimized process for utilization of CaO-Based sorbent for capturing CO_2 and SO_2 sequentially. *Energy & Fuels* **2012**, 26, 5596-5603.
15. Rodriguez, N.; Alonso, M.; Abanades, J. C.; Charitos, A.; Hawthorne, C.; Scheffknecht, G.; Lu, D. Y.; Anthony, E. J. Sulfation and reactivation characteristics of nine limestones. *Energy Procedia* **2011**, 4, 393–401.
16. Sánchez-Biezma, A.; Ballesteros, J. C.; Diaz, L.; de Zárraga, E.; Álvarez, F. J.; López, J.; Arias, B.; Grasa, G.; Abanades, J. C. Postcombustion CO_2 capture with CaO. Status of

the technology and next steps towards large scale demonstration. *Energy Procedia* **2011**, 4, 852-859.
17. Arias, B.; Abanades, J. C.; Grasa, G. S. Enhancement of fast CO_2 capture by a nano-SiO_2/CaO composite at Ca-looping conditions. *Chemical Engineering Journal* **2011**, 167, 255–261.
18. Martínez, A.; Lara, Y.; Lisbona, P.; Romeo, L. M. Operation of a cyclonic preheater in the Ca-Looping for CO_2 capture. *Environmental Science & Technology* **2013**, 47, 11335-11341.
19. Rodriguez, N.; Alonso, M.; Grasa, G.; Abanades, J. C. Heat requirements in a calciner of $CaCO_3$ integrated in a CO_2 capture system using CaO. *Chemical Engineering Journal* **2008**, 138, 148-154.
20. Romeo, L. M.; Lara, Y.; Lisbona, P.; Escosa, J. M. Optimizing make-up flow in a CO_2 capture system using CaO. *Chemical Engineering Journal* **2009**, 147, 252-258.
21. Arias, B.; Grasa, G. S.; Alonso, M.; Abanades, J. C. Post-combustion calcium looping process with a highly stable sorbent activity by recarbonation. *Energy & Environmental Science* **2012**, 5, 7353-7359.
22. Diego, M. E.; Arias, B.; Alonso, M.; Abanades, J. C. The impact of calcium sulfate and inert solids accumulation in post-combustion calcium looping systems. *Fuel* **2013**, 109, 184-190.
23. Grasa, G.; Martínez, I.; Diego, M. E.; Abanades, J. C. Determination of CaO carbonation kinetics under recarbonation conditions. *Energy & Fuels* **2014**, 28, 4033-4042.
24. Diego, M. E.; Arias, B.; Grasa, G.; Abanades, J. C. Design of a novel fluidized bed reactor to enhance sorbent performance in CO_2 capture systems using CaO. *Industrial & Engineering Chemistry Research* **2014**, 53, 10059-10071.
25. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. Role of precalcination and regeneration conditions on postcombustion CO_2 capture in the Ca-looping technology. *Applied Energy* **2014**, 136, 347-356.
26. Chen, H.; Zhao, C.; Yang, Y.; Zhang, P. CO_2 capture and attrition performance of CaO pellets with aluminate cement under pressurized carbonation. *Applied Energy* **2012**, 91, 334-340.
27. Itskos, G.; Grammelis, P.; Scala, F.; Pawlak-Kruczek, H.; Coppola, A.; Salatino, P.; Kakaras, E. A comparative characterization study of Ca-looping natural sorbents. *Applied Energy* **2013**, 108, 373-382.
28. Sun, R.; Li, Y.; Liu, H.; Wu, S.; Lu, C. CO_2 capture performance of calcium-based sorbent doped with manganese salts during calcium looping cycle. *Applied Energy* **2012**, 89, 368-373.
29. Valverde, J. M. Ca-based synthetic materials with enhanced CO_2 capture efficiency. *Journal of Materials Chemistry A* **2013**, 1, 447-468.
30. Abanades, J. C.; Anthony, E. J.; Wang, J. S.; Oakey, J. E. Fluidized bed combustion systems integrating CO_2 capture with CaO. *Environmental Science & Technology* **2005**, 39, 2861-2866.
31. Lisbona, P.; Romeo, L. M. Enhanced coal gasification heated by unmixed combustion integrated with an hybrid system of SOFC/GT. *International Journal of Hydrogen Energy* **2008**, 33, 5755-5764.
32. Alonso, M.; Diego, M. E.; Pérez, C.; Chamberlain, J. R.; Abanades, J. C. Biomass combustion with in situ CO_2 capture by CaO in a 300 kWth circulating fluidized bed facility. *International Journal of Greenhouse Gas Control* **2014**, 29, 142-152.
33. MacKenzie, A.; Granatstein, D. L.; Anthony, E. J.; Abanades, J. C. Economics of CO_2 capture using the calcium cycle with a pressurized fluidized bed combustor. *Energy & Fuels* **2007**, 21, 920-926.
34. Martínez, A.; Lara, Y.; Lisbona, P.; Romeo, L. M. Energy penalty reduction in the calcium looping cycle. *International Journal of Greenhouse Gas Control* **2012**, 7, 74-81.

35. Rodriguez, N.; Alonso, M.; Grasa, G.; Abanades, J. C. Heat requirements in a calciner of $CaCO_3$ integrated in a CO_2 capture system using CaO. *Chemical Engineering Journal* **2008**, 138, 148-154.
36. Martínez, A.; Lara, Y.; Lisbona, P.; Romeo, L. M. Operation of a mixing seal valve in calcium looping for CO_2 capture. *Energy & Fuels* **2014**, 28, 2059-2068.
37. Kim, K.; Kim, D.; Park, Y.-K.; Lee, K. S. A solid sorbent-based multi-stage fluidized bed process with inter-stage heat integration as an energy efficient carbon capture process. *International Journal of Greenhouse Gas Control* **2014**, 26, 135-146.
38. Le Moullec, Y.; Neveux, T.; Al Azki, A.; Chikukwa, A.; Hoff, K. A. Process modifications for solvent-based post-combustion CO_2 capture. *International Journal of Greenhouse Gas Control* **2014**, 31, 96-112.
39. Yin, J.; Qin, C.; Feng, B.; Ge, L.; Luo, C.; Liu, W.; An, H. Calcium looping for CO_2 capture at a constant high temperature. *Energy & Fuels* **2014**, 28, 307-318.
40. Ball, R. Entropy generation analyses of Endex and conventional calcium looping processes for capture. *Fuel* **2014**, 127, 202-211.
41. Yin, J.; Qin, C.; An, H.; Liu, W.; Feng, B. High-temperature pressure swing adsorption process for CO_2 separation. *Energy & Fuels* **2012**, 26, 169-175.
42. Ball, R.; Sceats, M. G. Separation of carbon dioxide from flue emissions using Endex principles. *Fuel* **2010**, 89, 2750-2759.
43. Ball, R. Using the second law first: Improving the thermodynamic efficiency of carbon dioxide separation from gas streams in an Endex calcium looping system. *Applied Thermal Engineering* **2015**, 74, 194-201.
44. Romeo, L. M.; Abanades, J. C.; Escosa, J. M.; Paño, J.; Giménez, A.; Sánchez-Biezma, A.; Ballesteros, J. C. Oxyfuel carbonation/calcination cycle for low cost CO_2 capture in existing power plants. *Energy Conversion and Management* **2008**, 49, 2809-2814.
45. Bugge, J.; Kjær, S.; Blum, R. High-efficiency coal-fired power plants development and perspectives. *Energy* **2006**, 31, 1437-1445.
46. Hawthorne, C.; Trossmann, M.; Galindo Cifre, P.; Schuster, A.; Scheffknecht, G. Simulation of the carbonate looping power cycle. *Energy Procedia* **2009**, 1, 1387-1394.
47. Romano, M. Coal-fired power plant with calcium oxide carbonation for postcombustion CO_2 capture. *Energy Procedia* **2009**, 1, 1099-1106.
48. Yang, Y.; Zhai, R.; Duan, L.; Kavosh, M.; Patchigolla, K.; Oakey, J. Integration and evaluation of a power plant with a CaO-based CO_2 capture system. *International Journal of Greenhouse Gas Control* **2010**, 4, 603-612.
49. Lisbona, P.; Martínez, A.; Lara, Y.; Romeo, L. M. Integration of carbonate CO_2 capture cycle and coal-fired power plants. A comparative study for different sorbents. *Energy & Fuels* **2010**, 24, 728-736.
50. Martínez, I.; Murillo, R.; Grasa, G.; Carlos Abanades, J. Integration of a Ca looping system for CO_2 capture in existing power plants. *AIChE Journal* **2011**, 57, 2599-2607.
51. Vorrias, I.; Atsonios, K.; Nikolopoulos, A.; Nikolopoulos, N.; Grammelis, P.; Kakaras, E. Calcium looping for CO_2 capture from a lignite fired power plant. *Fuel* **2013**, 113, 826-836.
52. Lara, Y.; Lisbona, P.; Martínez, A.; Romeo, L. M. Design and analysis of heat exchanger networks for integrated Ca-looping systems. *Applied Energy* **2013**, 111, 690-700.
53. Lara, Y.; Lisbona, P.; Martínez, A.; Romeo, L. M. A systematic approach for high temperature looping cycles integration. *Fuel* **2014**, 127, 4-12.
54. Romeo, L. M.; Usón, S.; Valero, A.; Escosa, J. M. Exergy analysis as a tool for the integration of very complex energy systems: The case of carbonation/calcination CO_2 systems in existing coal power plants. *International Journal of Greenhouse Gas Control* **2010**, 4, 647-654.

55. Ströhle, J.; Galloy, A.; Epple, B. Feasibility study on the carbonate looping process for post-combustion CO_2 capture from coal-fired power plants. *Energy Procedia* **2009**, 1, 1313-1320.
56. Wang, W.; Ramkumar, S.; Fan, L.-S. Energy penalty of CO_2 capture for the Carbonation–Calcination Reaction (CCR) process: Parametric effects and comparisons with alternative processes. *Fuel* **2013**, 104, 561-574.
57. Berstad, D.; Anantharaman, R.; Jordal, K. Post-combustion CO_2 capture from a natural gas combined cycle by $CaO/CaCO_3$ looping. *International Journal of Greenhouse Gas Control* **2012**, 11, 25-33.
58. Berstad, D.; Anantharaman, R.; Blom, R.; Jordal, K.; Arstad, B. NGCC post-combustion CO_2 capture with Ca/carbonate looping: Efficiency dependency on sorbent properties, capture unit performance and process configuration. *International Journal of Greenhouse Gas Control* **2014**, 24, 43-53.
59. Manovic, V.; Anthony, E. J. Integration of calcium and chemical looping combustion using composite CaO/CuO-Based materials. *Environmental Science & Technology* **2011**, 45, 10750-10756.
60. Ridha, F. N.; Lu, D.; Macchi, A.; Hughes, R. W. Combined calcium looping and chemical looping combustion cycles with CaO–CuO pellets in a fixed bed reactor. *Fuel* **2015**, 153, 202-209.
61. Cormos, A.-M.; Simon, A. Assessment of CO_2 capture by calcium looping (CaL) process in a flexible power plant operation scenario. *Applied Thermal Engineering* **2015**, 80, 319-327.
62. Harrison, D. P. Sorption-Enhanced hydrogen production: A review. *Industrial & Engineering Chemistry Research* **2008**, 47, 6486-6501.
63. Dean, C. C.; Blamey, J.; Florin, N. H.; Al-Jeboori, M. J.; Fennell, P. S. The calcium looping cycle for CO_2 capture from power generation, cement manufacture and hydrogen production. *Chemical Engineering Research and Design* **2011**, 89, 836-855.
64. Barelli, L.; Bidini, G.; Gallorini, F.; Servili, S. Hydrogen production through sorption-enhanced steam methane reforming and membrane technology: A review. *Energy* **2008**, 33, 554-570.
65. Lopez Ortiz, A.; Harrison, D. P. Hydrogen production using sorption-enhanced reaction. *Industrial & Engineering Chemistry Research* **2001**, 40, 5102-5109.
66. Connell, D. P.; Lewandowski, D. A.; Ramkumar, S.; Phalak, N.; Statnick, R. M.; Fan, L.-S. Process simulation and economic analysis of the Calcium Looping Process (CLP) for hydrogen and electricity production from coal and natural gas. *Fuel* **2013**, 105, 383-396.
67. Ramkumar, S.; Fan, L.-S. Calcium looping process (CLP) for enhanced noncatalytic hydrogen production with integrated carbon dioxide capture. *Energy & Fuels* **2010**, 24, 4408-4418.
68. Florin, N. H.; Harris, A. T. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. *Chemical Engineering Science* **2008**, 63, 287-316.
69. Abanades, J. C.; Alonso, M.; Rodríguez, N.; González, B.; Grasa, G.; Murillo, R. Capturing CO_2 from combustion flue gases with a carbonation calcination loop. Experimental results and process development. *Energy Procedia* **2009**, 1, 1147-1154.
70. Siefert, N. S.; Chang, B. Y.; Litster, S. Exergy and economic analysis of a CaO-looping gasifier for IGFC–CCS and IGCC–CCS. *Applied Energy* **2014**, 128, 230-245.
71. Cormos, C.-C. Economic evaluations of coal-based combustion and gasification power plants with post-combustion CO_2 capture using calcium looping cycle. *Energy* **2014**, 78, 665-673.

72. Cormos, C.-C. Economic implications of pre- and post-combustion calcium looping configurations applied to gasification power plants. *International Journal of Hydrogen Energy* **2014**, 39, 10507-10516.
73. Xu, X.; Xiao, Y.; Qiao, C. System design and analysis of a direct hydrogen from coal system with CO_2 capture. *Energy & Fuels* **2007**, 21, 1688-1694.
74. Moghtaderi, B. Review of the recent chemical looping process developments for novel energy and fuel applications. *Energy & Fuels* **2012**, 26, 15-40.
75. Rahman, R. A.; Mehrani, P.; Lu, D. Y.; Anthony, E. J.; Macchi, A. Investigating the use of CaO/CuO sorbents for in situ CO_2 capture in a biomass gasifier. *Energy & Fuels* **2015**.
76. Abanades, J. C.; Murillo, R.; Fernandez, J. R.; Grasa, G.; Martínez, I. New CO_2 capture process for hydrogen production combining ca and cu chemical loops. *Environmental Science & Technology* **2010**, 44, 6901-6904.
77. Zhang, X.; Liu, Y. Performance assessment of CO_2 capture with calcination carbonation reaction process driven by coal and concentrated solar power. *Applied Thermal Engineering* **2014**, 70, 13-24.
78. Edwards, S. E. B.; Materić, V. Calcium looping in solar power generation plants. *Solar Energy* **2012**, 86, 2494-2503.
79. Sun, R.; Li, Y.; Liu, C.; Xie, X.; Lu, C. Utilization of lime mud from paper mill as CO_2 sorbent in calcium looping process. *Chemical Engineering Journal* **2013**, 221, 124-132.
80. Atsonios, K.; Grammelis, P.; Antiohos, S. K.; Nikolopoulos, N.; Kakaras, E. Integration of calcium looping technology in existing cement plant for CO_2 capture: Process modeling and technical considerations. *Fuel* **2015**, 153, 210-223.
81. Ozcan, D. C.; Ahn, H.; Brandani, S. Process integration of a Ca-looping carbon capture process in a cement plant. *International Journal of Greenhouse Gas Control* **2013**, 19, 530-540.
82. Vatopoulos, K.; Tzimas, E. Assessment of CO_2 capture technologies in cement manufacturing process. *Journal of Cleaner Production* **2012**, 32, 251-261.
83. Romeo, L. M.; Catalina, D.; Lisbona, P.; Lara, Y.; Martínez, A. Reduction of greenhouse gas emissions by integration of cement plants, power plants, and CO_2 capture systems. *Greenhouse Gases: Science and Technology* **2011**, 1, 72-82.
84. Rodríguez, N.; Murillo, R.; Abanades, J. C. CO_2 capture from cement plants using oxyfired precalcination and/or calcium looping. *Environmental Science & Technology* **2012**, 46, 2460-2466.
85. Romano, M. C.; Spinelli, M.; Campanari, S.; Consonni, S.; Marchi, M.; Pimpinelli, N.; Cinti, G. The calcium looping process for low CO_2 emission cement plants. *Energy Procedia* **2014**, 61, 500-503.
86. Kuramochi, T.; Ramírez, A.; Turkenburg, W.; Faaij, A. Comparative assessment of CO_2 capture technologies for carbon-intensive industrial processes. *Progress in Energy and Combustion Science* **2012**, 38, 87-112.
87. Ylätalo, J.; Parkkinen, J.; Ritvanen, J.; Tynjälä, T.; Hyppänen, T. Modeling of the oxy-combustion calciner in the post-combustion calcium looping process. *Fuel* **2013**, 113, 770-779.
88. Lu, D. Y.; Hughes, R. W.; Anthony, E. J.; Manovic, V. Sintering and reactivity of $CaCO_3$-based sorbents for in situ CO_2 capture in fluidized beds under realistic calcination conditions. *J. Environ. Eng.-ASCE* **2009**, 135, 404-410.
89. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. Calcium-looping for post-combustion CO_2 capture. On the adverse effect of sorbent regeneration under CO_2. *Applied Energy* **2014**, 126, 161-171.
90. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. Effect of Heat Pretreatment/Recarbonation in the Ca-Looping Process at Realistic Calcination Conditions. *Energy & Fuels* **2014**, 28, 4062-4067.

91. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. Ca-looping for postcombustion CO_2 capture: A comparative analysis on the performances of dolomite and limestone. *Applied Energy* **2015**, 138, 202-215.
92. Grasa, G. S.; Abanades, J. C. CO_2 capture capacity of CaO in long series of carbonation/calcination cycles. *Industrial & Engineering Chemistry Research* **2006**, 45, 8846-8851.
93. Alvarez, D.; Abanades, J. C. Determination of the critical product layer thickness in the reaction of CaO with CO2. *Industrial & Engineering Chemistry Research* **2005**, 44, 5608-5615.
94. Alvarez, D.; Abanades, J. C. Pore-size and shape effects on the recarbonation performance of calcium oxide submitted to repeated calcination/recarbonation cycles. *Energy & Fuels* **2005**, 19, 270-278.
95. Salvador, C.; Lu, D.; Anthony, E. J.; Abanades, J. C. Enhancement of CaO for CO2 capture in an FBC environment. *Chemical Engineering Journal* **2003**, 96, 187-195.
96. Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J. C. Capture of CO2 from combustion gases in a fluidized bed of CaO. *AIChE J.* **2009**, 55, 1246–1255.
97. Perez-Maqueda, L. A.; Criado, J. M.; Real, C. Kinetics of the initial stage of sintering from shrinkage data: Simultaneous determination of activation energy and kinetic model from a single nonisothermal experiment. *J. Am. Ceram. Soc.* **2002**, 85, 763-768.
98. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perejon, A.; Perez-Maqueda, L. A. Role of Looping-Calcination Conditions on Self-Reactivation of Thermally Pretreated CO2 Sorbents Based on CaO. *Energy & Fuels* **2013**, 27, 3373-3384.
99. Borgwardt, R. H. Sintering of nascent calcium-oxide. *Chemical Engineering Science* **1989**, 44, 53-60.
100. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perejon, A.; Perez-Maqueda, L. A. Constant rate thermal analysis for enhancing the long-term CO2 capture of CaO at Ca-looping conditions. *Applied Energy* **2013**, 108, 108-120.
101. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perejon, A.; Perez-Maqueda, L. A. CO2 multicyclic capture of pretreated/doped CaO in the Ca-looping process. Theory and experiments. *Physical Chemistry Chemical Physics* **2013**, 15, 11775-11793.
102. Wang, J.; Manovic, V.; Wu, Y.; Anthony, E. J. A study on the activity of CaO-based sorbents for capturing CO2 in clean energy processes. *Applied Energy* **2010**, 87, 1453-1458.
103. Manovic, V.; Charland, J. P.; Blamey, J.; Fennell, P. S.; Lu, D. Y.; Anthony, E. J. Influence of calcination conditions on carrying capacity of CaO-based sorbent in CO2 looping cycles. *Fuel* **2009**, 88, 1893-1900.
104. Allen, J. P.; Marmier, A.; Parker, S. C. Atomistic Simulation of Surface Selectivity on Carbonate Formation at Calcium and Magnesium Oxide Surfaces. *J. Phys. Chem. C* **2012**, 116, 13240-13251.
105. Besson, R.; Favergeon, L. Atomic-Scale Study of Calcite Nucleation in Calcium Oxide. *J. Phys. Chem. C* **2013**, 117, 8813-8821.
106. Besson, R.; Vargas, M. R.; Favergeon, L. CO2 adsorption on calcium oxide: An atomic-scale simulation study. *Surf. Sci.* **2012**, 606, 490-495.
107. Hyatt, E. P.; Cutler, I. B.; Wadsworth, M. E. Calcium Carbonate Decomposition in Carbon Dioxide Atmosphere. *J. Am. Ceram. Soc.* **1958**, 41, 70-74.
108. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. Limestone calcination nearby equilibrium: kinetics, CaO crystal structure, sintering and reactivity. *J. Phys. Chem. C* **2015**, 119, 1623-1641.
109. Borgwardt, R. H. Calcium oxide sintering in atmospheres containing water and carbon dioxide. *Industrial & Engineering Chemistry Research* **1989**, 28, 493-500.

110. Stanmore, B. R.; Gilot, P. Review—calcination and carbonation of limestone during thermal cycling for CO_2 sequestration. *Fuel Processing Technology* **2005**, 86, 1707-1743.
111. Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J. C. Application of the random pore model to the carbonation cyclic reaction. *AIChE Journal* **2009**, 55, 1246-1255.
112. Bhatia, S. K.; Perlmutter, D. D. Effect of the product layer on the kinetics of the CO_2-lime reaction. *AIChE Journal* **1983**, 29, 79-86.
113. Sun, Z.; Luo, S.; Qi, P.; Fan, L.-S. Ionic diffusion through Calcite ($CaCO_3$) layer during the reaction of CaO and CO_2. *Chemical Engineering Science* **2012**, 81, 164-168.
114. Li, Z.; Sun, H.; Cai, N. Rate equation theory for the carbonation reaction of CaO with CO_2. *Energy & Fuels* **2012**, 26, 4607-4616.
115. Li, Z.-s.; Fang, F.; Tang, X.-y.; Cai, N.-s. Effect of temperature on the carbonation reaction of CaO with CO_2. *Energy & Fuels* **2012**, 26, 2473-2482.
116. Kierzkowska, A. M.; Pacciani, R.; Müller, C. R. CaO-Based CO_2 sorbents: from fundamentals to the development of new, highly effective materials. *ChemSusChem* **2013**, 6, 1130-1148.
117. Chrissafis, K.; Dagounaki, C.; Paraskevopoulos, K. M. The effects of procedural variables on the maximum capture efficiency of CO_2 using a carbonation/calcination cycle of carbonate rocks. *Thermochimica Acta* **2005**, 428, 193-198.
118. Readman, J. E.; Blom, R. The use of in situ powder X-ray diffraction in the investigation of dolomite as a potential reversible high-temperature CO_2 sorbent. *Physical Chemistry Chemical Physics* **2005**, 7, 1214-1219.
119. Beruto, D. T.; Vecchiattini, R.; Giordani, M. Effect of mixtures of H_2O (g) and CO_2 (g) on the thermal half decomposition of dolomite natural stone in high CO_2 pressure regime. *Thermochimica Acta* **2003**, 404, 25-33.
120. Galai, H.; Pijolat, M.; Nahdi, K.; Trabelsi-Ayadi, M. Mechanism of growth of MgO and $CaCO_3$ during a dolomite partial decomposition. *Solid State Ionics* **2007**, 178, 1039-1047.
121. Rodriguez-Navarro, C.; Kudlacz, K.; Ruiz-Agudo, E. The mechanism of thermal decomposition of dolomite: New insights from 2D-XRD and TEM analyses. *American Mineralogist* **2012**, 97, 38-51.
122. Silaban, A.; Narcida, M.; Harrison, D. P. Characteristics of the reversible reaction between CO_2(g) and calcined dolomite. *Chemical Engineering Communications* **1996**, 146, 149-162.
123. Albrecht, K. O.; Wagenbach, K. S.; Satrio, J. A.; Shanks, B. H.; Wheelock, T. D. Development of a CaO-Based CO_2 sorbent with improved cyclic stability. *Industrial & Engineering Chemistry Research* **2008**, 47, 7841-7848.
124. Sultan, D. S.; Müller, C. R.; Dennis, J. S. Capture of CO_2 using sorbents of calcium magnesium acetate (CMA). *Energy & Fuels* **2010**, 24, 3687-3697.
125. Yang, X.; Zhao, L.; Yang, S.; Xiao, Y. Investigation of natural CaO–MgO sorbent for CO_2 capture. *Asia-Pacific Journal of Chemical Engineering* **2013**, 8, 906-915.
126. Coppola, A.; Scala, F.; Salatino, P.; Montagnaro, F. Fluidized bed calcium looping cycles for CO_2 capture under oxy-firing calcination conditions: Part 2. Assessment of dolomite vs. limestone. *Chemical Engineering Journal* **2013**, 231, 544-549.
127. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A.; Quintanilla, M. A. S.; Perez-Vaquero, J. Role of crystal structure on CO_2 capture by limestone derived CaO subjected to carbonation/recarbonation/calcination cycles at Ca-looping conditions. *Applied Energy* **2014**, 125, 264-275.
128. Sanchez-Jimenez, P. E.; Valverde, J. M.; Perez-Maqueda, L. A. Multicyclic conversion of limestone at Ca-looping conditions: The role of solid-sate diffusion controlled carbonation. *Fuel* **2014**, 127, 131-140.

129. Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. Relevant influence of limestone crystallinity on CO_2 capture in the Ca-Looping technology at realistic calcination conditions. *Environmental Science & Technology* **2014**, 48, 9882-9889.
130. Beruto, D.; Barco, L.; Searcy, A. W. CO_2-catalyzed surface-area and porosity changes in high-surface-area cao aggregates. *J. Am. Ceram. Soc.* **1984**, 67, 512-515.
131. Wang, Y.; Thomson, W. J. The effects of steam and carbon dioxide on calcite decomposition using dynamic X-ray diffraction. *Chemical Engineering Science* **1995**, 50, 1373-1382.
132. Khinast, J.; Krammer, G. F.; Brunner, C.; Staudinger, G. Decomposition of limestone: The influence of CO_2 and particle size on the reaction rate. *Chemical Engineering Science* **1996**, 51, 623-634.
133. Beruto, D. T.; Searcy, A. W.; Kim, M. G. Microstructure, kinetic, structure, thermodynamic analysis for calcite decomposition: free-surface and powder bed experiments. *Thermochimica Acta* **2004**, 424, 99-109.
134. Haul, R. A. W.; Heystek, H. Differential thermal analysis of the dolomite decomposition. *Am. Miner.* **1952**, 37, 166-179.
135. Caceres, P. G.; Attiogbe, E. K. Thermal decomposition of dolomite and the extraction of its constituents. *Minerals Engineering* **1997**, 10, 1165-1176.
136. Samtani, M.; Skrzypczak-Janktun, E.; Dollimore, D.; Alexander, K. Thermal analysis of ground dolomite, confirmation of results using an X-ray powder diffraction methodology. *Thermochimica Acta* **2001**, 367–368, 297-309.
137. Arai, Y., *Chemistry of Power Production*, Chapman & Hall, Glasgow, 1996.
138. Manovic, V.; Anthony, E. J. Thermal activation of CaO-based sorbent and self-reactivation during CO_2 capture looping cycles. *Environmental Science & Technology* **2008**, 42, 4170-4174.
139. Manovic, V.; Anthony, E. J.; Loncarevic, D. Looping cycles with CaO-based sorbent pretreated in at high temperature. *Chemical Engineering Science* **2009**, 64, 3236-3245.
140. Ozcan, D. C.; Shanks, B. H.; Wheelock, T. D. Improving the stability of a CaO-based sorbent for CO_2 by thermal pretreatment. *Industrial & Engineering Chemistry Research* **2011**, 50, 6933-6942.
141. Alonso, M.; Lorenzo, M.; Gonzalez, B.; Abanades, J. C. Precalcination of $CaCO_3$ as a method to stabilize cao performance for CO_2 capture from combustion gases. *Energy & Fuels* **2011**, 25, 5521-5527.
142. Baláz, P., *Mechanochemistry in nanoscience and minerals engineering*, Springer, Berlin, 2008.
143. Heitjans, P.; Indris, S. Fast diffusion in nanocrystalline ceramics prepared by ball milling. *Journal of Materials Science* **2004**, 39, 5091-5096.
144. Perejon, A.; Murafa, N.; Sanchez-Jimenez, P. E.; Criado, J. M.; Subrt, J.; Dianez, M. J.; Perez-Maqueda, L. A. Direct mechanosynthesis of pure $BiFeO_3$ perovskite nanoparticles: reaction mechanism. *Journal of Materials Chemistry C* **2013**, 1, 3551-3562.
145. Suryanarayana, C. Mechanical alloying and milling. *Progress in Materials Science* **2001**, 46, 1-184.
146. Kong, L. B.; Zhang, T. S.; Ma, J.; Boey, F. Progress in synthesis of ferroelectric ceramic materials via high-energy mechanochemical technique. *Progress in Materials Science* **2008**, 53, 207-322.
147. Perejon, A.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A.; Criado, J. M.; de Paz, J. R.; Saez-Puche, R.; Maso, N.; West, A. R. Single phase, electrically insulating, multiferroic La-substituted $BiFeO_3$ prepared by mechanosynthesis. *Journal of Materials Chemistry C* **2014**, 2, 8398-8411.
148. Kronenberg, A.; Yund, R.; Giletti, B. Carbon and oxygen diffusion in calcite: Effects of Mn content and P H_2O. *Phys Chem Minerals* **1984**, 11, 101-112.

149. Anderson, T. F. Self-diffusion of carbon and oxygen in calcite by isotope exchange with carbon dioxide. *Journal of Geophysical Research* **1969**, 74, 3918-3932.
150. Akgsornpeak, A.; Witoon, T.; Mungcharoen, T.; Limtrakul, J. Development of synthetic CaO sorbents via CTAB-assisted sol–gel method for CO_2 capture at high temperature. *Chemical Engineering Journal* **2014**, 237, 189-198.
151. Pacciani, R.; Muller, C. R.; Davidson, J. F.; Dennis, J. S.; Hayhurst, A. N. Performance of a Novel Synthetic Ca-Based Solid Sorbent Suitable for Desulfurizing Flue Gases in a Fluidized Bed. *Industrial & Engineering Chemistry Research* **2009**, 48, 7016-7024.
152. Strohle, J.; Junk, M.; Kremer, J.; Galloy, A.; Epple, B. Carbonate looping experiments in a 1 MWth pilot plant and model validation. *Fuel* **2014**, 127, 13-22.
153. Chang, M. H.; Huang, C. M.; Liu, W. H.; Chen, W. C.; Cheng, J. Y.; Chen, W.; Wen, T. W.; Ouyang, S.; Shen, C. H.; Hsu, H. W. Design and Experimental Investigation of the Calcium Looping Process for 3-kW(th) and 1.9-MWth Facilities. *Chem. Eng. Technol.* **2013**, 36, 1525-1532.
154. Alonso, M.; Diego, M. E.; Perez, C.; Chamberlain, J. R.; Abanades, J. C. Biomass combustion with in situ CO2 capture by CaO in a 300 kWth circulating fluidized bed facility. *International Journal of Greenhouse Gas Control* **2014**, 29, 142-152.
155. Hanak, D. P.; Anthony, E. J.; Manovic, V. A review of developments in pilot-plant testing and modelling of calcium looping process for CO2 capture from power generation systems. *Energy & Environmental Science* **2015**, 8, 2199-2249.