

# The Calcium-Looping (CaCO<sub>3</sub>/CaO) Process for Thermochemical Energy Storage in Concentrating Solar Power Plants: A critical review

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## Abstract

Energy storage based on thermochemical systems is gaining momentum as potential alternative to molten salts in Concentrating Solar Power (CSP) plants. Several systems have been proposed in the last years, mainly based on hydroxides, organic compounds, carbonates, metal redox, hydrides, ammonia or sulfur. This work is a detailed review about the promising integration of a CaCO<sub>3</sub>/CaO based system, the so-called Calcium-Looping (CaL) process, in CSP plants with tower technology. The CaL process relies on low cost, widely available and non-toxic natural materials (such as limestone or dolomite), which are necessary conditions for the commercial expansion of any energy storage technology at large scale. A comprehensive analysis of the advantages of this process and challenges to be faced for it to reach a commercial scale is carried out. The review includes a deep overview of reaction mechanisms and process integration schemes proposed in the recent literature. In addition, the technological maturity and potential of the process is assessed. The direction towards which future works should be headed is discussed.

## 1. Introduction

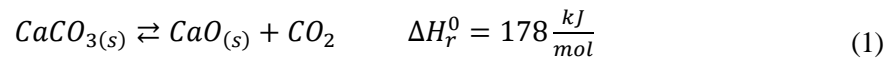
Concentrated Solar Power (CSP) has a great potential within the future energy scenario [1]. Achieving efficient, cheap and environmental friendly energy storage stands however as a main challenge to achieve a massive deployment of CSP plants [2–4].

Nowadays the installed CSP capacity throughout the world is around 5 GWe (~245 plants), while approximately 7 GW are under construction or planned to be commissioned from 2020 [5,6]. Currently, over 40% of commercial CSP plants around the world incorporate thermal energy storage (TES) systems while this percentage rises up to 83% for those planned and under development [5,7]. Energy storage is typically based on a two-tank TES system to use the sensible heat stored in molten salts [5]. Despite the full commercial scale reached, molten salts-based

systems suffer from several drawbacks that penalize the performance of CSP plants such as salt corrosiveness [8,9], limited power cycle efficiency because of the salts maximum working temperature ( $\sim 560^{\circ}\text{C}$  to avoid salt degradation) [10] and a significant energy consumption to keep the molten salts up to  $\sim 220^{\circ}\text{C}$  to avoid salt solidification [11].

As alternative to molten salts-based systems, other energy storage systems are being proposed in the last years based on: i) sensible thermal energy storage (TES) [10,12,13]; ii) latent heat storage using phase change materials (PCMs) [14,15] and iii) thermochemical energy storage (TCES) [16,17]. TCES relies on reversible chemical reactions by using the heat provided from CSP (or other sources) to carry out the endothermic reaction. The stored energy is then release through the exothermic reaction. Several reversible reactions have been proposed as TCES, mainly based on carbonates [18,19], hydroxides [20], metal redox [21], sulfur [22], hydrides [23], methanol [24] or ammonia [25].

One of the most promising TCES systems relies upon the calcination-carbonation reaction of  $\text{CaCO}_3\text{-CaO}$  (Eq. (1)). Limestone, which is the second most abundant material on Earth after water, can be employed for this purpose. In the so-called Calcium Looping (CaL) process, direct solar radiation is used to carry out the endothermic calcination reaction releasing  $\text{CO}_2$  and  $\text{CaO}$  as products that are stored separately. Storage conditions and time depends on the energy demand [26]. When energy is needed, the stored products are brought together to carry out the exothermic carbonation reaction which releases the stored energy.



The CaL process presents several benefits in comparison with molten salts such a higher energy storage density and its feasibility to work at significantly higher power cycle temperatures [18]. Moreover,  $\text{CaO}$  precursors such as limestone or dolomite have a very low cost and are wide available and environmental friendly [27–29], which are necessary conditions for the massive deployment on a large scale of any energy storage technology.

In the last years several reviews have been published regarding the integration of TCES in CSP plants. Pardo et al. [17] published a comprehensive review on high-temperature TCES. The authors reported a comparison of energy density for many systems as well as the technical disciplines involved in the development of TCES systems. Similarly, Prieto et al. [30] and Carrillo et al. [31] analyzed the characteristics of a large number of potential TCES systems from both technical and environmental criteria including cost, state-of-the-art of the technology, efficiency, etc. André et al. [32] also assessed the use of high-temperature TCES systems in CSP plants highlighting the importance of the cost of raw materials for large scale applications. Gil, Medrano

et al. [12,33] developed an extensive review on TES/TCES including a deep analysis on the specific properties of each system as well as a large number of case studies. Kuravi et al. [4] published a more generic review on energy storage for CSP, which addressed a comparison between sensible, latent and TCES systems. Mahlia et al. [34] analyzed the state-of-the-art of energy storage by thermal, electrical or mechanical energy storage systems. Several metal oxides (redox) systems were assessed in [35] where experimental data were reported for redox-based TCES. Moreover, a few extensive reviews on CSP plant components and performance can be found in the recent literature [36,37]. However, up to the authors knowledge, no extensive review on the integration of  $\text{CaCO}_3/\text{CaO}$  systems in CSP plants has been yet published.

## 2. The Calcium-Looping process for thermochemical energy storage

The CaL process is a promising thermochemical energy storage technology to be used in concentrated solar power plants [38–42]. Figure 1 shows a conceptual scheme of the CaL process integration in a CSP plant as TCES system. The process starts with the decomposition of  $\text{CaCO}_3$  to produce  $\text{CaO}$  and  $\text{CO}_2$  according to the endothermic calcination reaction. The kinetics of calcination is mainly dependent on the temperature and the  $\text{CO}_2$  partial pressure in the calciner [28,43]. After heat recovery, the  $\text{CaO}$  and  $\text{CO}_2$  streams are stored for their use afterwards as a function of energy demand. In the power production mode, the reactants are sent to the carbonator reactor, where the stored energy is released through the reverse carbonation reaction.

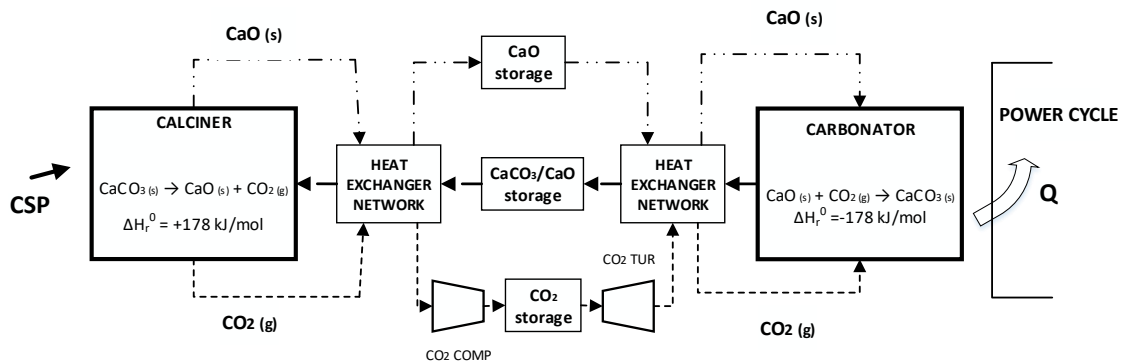


Figure 1: CSP-CaL conceptual scheme. Adapted from [44].

Energy storage based on the CaL process was conceptually proposed in the late 1970s [38,45,46]. A number of studies have been reported since regarding Ca-based materials behavior for TCES [8,42,47]. The intrinsic potential of the CaL process for energy storage has been also considered to increase the flexibility in non-renewable power plants. The CaL process has been widely investigated for post-combustion  $\text{CO}_2$  capture in fossil fuel power plants using the carbonation reaction [48,49]. According to [50–52], the  $\text{CO}_2$  capture efficiency, and therefore the overall plant

performance, could be improved by integrating CaO/CaCO<sub>3</sub> vessels for energy storage. As in CSP plants, this allows decoupling carbonation for CO<sub>2</sub> capture and CaO regeneration by calcination of the partially carbonated solids.

This section analyzes the potential of the CaL process for thermochemical energy storage from several chemical, physical and engineering aspects considered in the general criterion proposed by Wentworth et al. [53]. First, the CaL process presents the huge advantage of low price, wide availability and harmlessness towards the environment of natural CaO precursors such as limestone or dolomite [27–29], which is crucial for a massive sustainable development of energy storage systems at large scale. Another key advantage of the CaO/CO<sub>2</sub> system is its high energy density, which allows maximizing the storage capacity. As can be seen in Figure 2, the theoretical energy density of the CaO/CO<sub>2</sub> system (around 3.2 GJ/m<sup>3</sup>) is one of the largest among the TCES systems considered in literature. An alternative choice with larger energy density based also on a calcination/carbonation reaction is the SrO/CO<sub>2</sub> system (see Figure 2) [19]. Nevertheless, the too high turning temperature of this system and the high cost of the raw material (SrCO<sub>3</sub>) - \$580/tonne [54] - as compared to a price around \$10/tonne or less for natural limestone [55] hinders the practical feasibility of the use of this system in CSP plants.

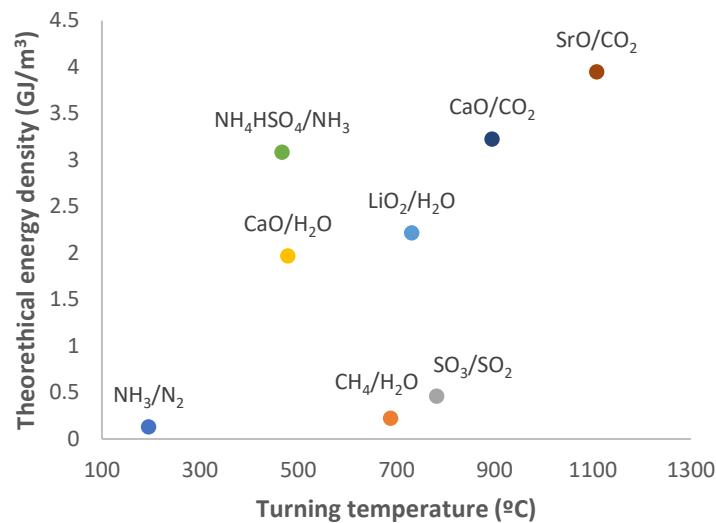


Figure 2: Theoretical energy density and turning temperature of some thermochemical energy storage systems. Adapted from [41].

There is not a unified consensus in the literature to define the energy density of a TCES system in practice. Some works [30,50,56] report values for the energy density of the CaL system in the range of 0.9-2 GJ/m<sup>3</sup> by considering gas and solids vessels and/or the possibility that carbonation is not fully achieved in the carbonator [57]. For the sizing of the solids storage tanks, which conditions capital costs of the energy storage system [58], it is necessary to consider the particles

porosity and the packing density of solids. To this end, Ortiz et al. [57] proposed a novel expression which can be generally applied to gas-solid TCES systems. The solids tank size is highly influenced by the CaO conversion. The CO<sub>2</sub> tank volume is also a critical factor to account for the energy density. As reference value in the CSP-CaL integration scheme, the CO<sub>2</sub> should be stored at a pressure higher than 75 bar under ambient temperature (25°C) at liquid state to reduce the vessel size. Hence, the energy density of the system mainly depends on CaO conversion and CO<sub>2</sub> storage conditions. According to CSP-CaL process simulations under typical conditions, a realistic value of the energy density of the entire system is in the range of 0.39-0.9 GJ/m<sup>3</sup> depending on CaO conversion [57]. These values are higher than energy storage density of a molten salt system (0.4 GJ/m<sup>3</sup>) by considering a two-tank configuration [59].

Contrary to molten salts-based systems, the CaL process presents the great advantage that reactants and products can be stored in the long term at ambient temperature. A main issue may be that CaO is highly reactive with ambient H<sub>2</sub>O to produce calcium hydroxide -Ca(OH)<sub>2</sub>-, which is important issue to consider since the formation of Ca(OH)<sub>2</sub> can modify the carbonation behavior [60,61]. In fact, Ca(OH)<sub>2</sub> shows a higher reactivity towards carbonation as compared to CaO. Thus, the introduction of an intermediate CaO hydroxylation reactor has been proposed to enhance CaO reactivity in the application of the CaL process for CO<sub>2</sub> capture in fossil fuel power plants [60,62]. Importantly, it is required to avoid any presence of CO<sub>2</sub> in the CaO storage tank to avoid unwanted carbonation of CaO [63], which would reduce the energy release to the power cycle. A solution could be to store the CaO under pure N<sub>2</sub> atmosphere even though it must be also remarked that the kinetics of carbonation at ambient temperature, although thermodynamically favorable, would be extremely slow [64].

In addition, the CaL process for TCES has the advantage of a high reaction turning temperature. The equilibrium temperature when pure CO<sub>2</sub> at atmospheric pressure is used in the reactors is T~895°C [65]. Moreover, carbonation for generating heat is extremely fast in the range of 650-1000°C depending on the CO<sub>2</sub> partial pressure [66]. This would allow achieving a highly efficient generation of electricity and would overcome the current CSP temperature limitation of T~550-600°C imposed by the degradation of molten salts at higher temperatures [10,13,67]. Higher efficiencies could be achieved by increasing the maximum temperature provided by the CSP plant [68]. Pressurized carbonation over atmospheric pressure is desirable for increasing the efficiency of the power-cycle direct integration as it allows carbonation at higher temperatures and faster rates [7,69].

The calcination reaction must be fast enough for calcination to be fully achieved in reasonably short residence times. Tests on several types of solar calciners have been reported in the literature [70–73]. According to thermochemical equilibrium [63], calcination only occurs fast under a

pure CO<sub>2</sub> atmosphere at temperatures above T~950°C [74]. At this temperature, a high energy input is required to increase the solids temperature up to the reaction one. Alternatively, calcination could be carried out in an easily separable gas from CO<sub>2</sub>, e.g. superheated steam [75]. Thus, calcination of MgCO<sub>3</sub> under superheated steam is an already available technology [76] at the commercial level (Catalytic Flash Calcination, CFC). The LEILAC project [77] aims at using CFC to calcine CaCO<sub>3</sub> for cement production with the important benefits that it occurs at a fast rate and releases pure CO<sub>2</sub> ready for compression and storage after condensation of H<sub>2</sub>O [17]. Calcination temperatures under superheated steam are considerably decreased to ~700-750°C [78], which is an important advantage to reduce the receiver radiation losses. Furthermore, the reactivity of CaO regenerated by calcination under superheated steam is notably enhanced [79], which would serve to boost the efficiency of the CSP-CaL integration. In addition, superheated steam for calcination in the solar reactor would be directly available from in-situ generation of superheated steam in solar receivers, which is already a mature technology [36]. On the other hand, a higher energy penalty is expected by carrying out calcination under superheated steam because of the solar energy consumption to bring the water (after separation) up to the calcination temperature. Moreover, lab-scale tests show that calcination under superheated steam reduces the mechanical strength of the formed CaO, which may lead to excessive attrition of the particles [80].

Another possibility to reduce the calcination temperature is by reducing the CO<sub>2</sub> partial pressure introducing Helium in the calciner. Calcination under He occurs fast at T~725°C [81] because of the He high thermal conductivity and CO<sub>2</sub> diffusivity in He. Nevertheless, Helium/CO<sub>2</sub> separation poses a technological challenge. Finally, carrying out calcination under pure CO<sub>2</sub> but below atmospheric pressure would lead also to a remarkable decrease of the calcination temperature [63].

While the particle receiver and conveying high-temperature solids are technological challenges for the development of the CSP-CaL integration, other components are already developed on an industrial scale mainly by the cement and lime industry [82–84]. This is further analyzed in section 5.

One of the main drawbacks of the CaL process is the multicyclic deactivation of the regenerated CaO [49,85,86]. CaO conversion is highly dependent on the carbonation-calcination conditions as discussed in section 3.

## **2.1 CSP-CaL related projects**

Thermochemical energy storage, solar calcination and high-temperature solar receivers are increasingly being investigated in many research projects. As mentioned above, the CSP-CaL process has a number of advantages which are fully aligned with the goals of current research

lines on CSP plants, namely: i) increasing the plant efficiency; ii) LCOE reduction; iii) increasing dispatchability and iv) improving sustainability and environmental impact [87]. Several projects (recently finished or on-going) related to the CSP-CaL integration are summarized in Table 1. More information about the projects can be found

Table 1: Summary of 2.1 CSP-CaL related projects

<i>Project /Acronym</i>	<i>scope</i>	<i>Funded by</i>	<i>Reference</i>
SOCRATCES: Solar calcium-looping integration for thermo-chemical energy storage	CSP-CaL integration	European Union's Horizon 2020	[88]
Carbon Dioxide Shuttling Thermochemical Storage Using Strontium	TCES based on SrCO <sub>3</sub> / SrO	ELEMENTS (DOE, USA)	[89]
Regenerative Carbonate-Based Thermochemical Energy Storage System for Concentrating Solar Power	TCES for CSP based on carbonate and silicate sorbents	ELEMENTS (DOE, USA)	[90]
Demonstration of High-Temperature Calcium-Based Thermochemical Storage System for use with Concentrating Solar Power Facilities	CSP-CaL integration	APOLLO (DOE, USA)	[91]
SOLPART: High temperature Solar-Heated Reactors for Industrials Production of Reactive Particulates	Solar calcination	European Union's Horizon 2020	[92]
TCSPower: Thermochemical Energy Storage for CSP Plants	TCES for CSP based on Ca(OH) <sub>2</sub>	European Union's Horizon 2020	[93]
CSP2: Concentrated solar power in particles	Particles as HTF in CSP plants	European Union's Horizon 2020	[94]

### 3. Materials

This section discusses in detail physical and chemical key aspects related with materials and reactions used in the CaL process, which highly conditions the efficiency of using it for TCES.

Remarkably, one of the key advantages of the CaL process is the low price, wide availability and environmental sustainability of natural CaO precursors. Nevertheless, the reactivity to carbonation in short residence times on CaO drops with the number of calcination-carbonation cycles, mainly due to CaO sintering and pore-plugging depending on the conditions [40]. Several CaO precursors, process conditions and techniques such as thermal [8,95] or mechanical [96] pretreatments are being investigated with the final goal of mitigating CaO deactivation. A comprehensive review on the multicyclic stability, conversion enhancement methods and reaction kinetics of CaO-based sorbents was published by Salaudeen et al. [97].

Typically, the particle size of CaO precursors considered for the CaL process is in the range 20-250µm [98,99]. The porous CaO formed upon calcination results in a friable solid [100] and therefore attrition of particles with the number of cycles can be a problem that must be properly addressed. Alonso et al. [101] analyzed the attrition of limestone derived CaO in a CaL prototype-scale setup assessing the predominant mechanism (fragmentation, decrepitation or abrasion)

depending on the particles properties. A review of attrition studies and modelling can be found in [100]. The use of fine particles is gaining interest due their the large surface to volume ratio which minimizes pore-plugging and as consequence enhance the multicycle CaO conversion [40,98]. However, interparticle adhesion forces prevail in fine cohesive powders ( $d_p < 30\mu\text{m}$ ) over hydrodynamics and gravitational forces [102], which causes agglomeration, channeling and plugging phenomena that hamper flowability [103].

The CaL process as post-combustion CO<sub>2</sub> capture system [48], where most of the CaL research has been focused in recent years, necessarily involves carbonation under low CO<sub>2</sub> partial pressure (imposed by the low CO<sub>2</sub> concentration in the flue gas exiting the power plant) whereas calcination must be carried out under high CO<sub>2</sub> concentration at temperatures around 950°C. These conditions lead to a severe drop of CaO conversion with the number of cycles due to sintering of the regenerated CaO, reaching a residual value of just around  $X=0.07-0.08$  for carbonation residence times of about 5 min [104]. In addition, CaO deactivation is further enhanced in the post-combustion application by irreversible CaO sulphation and ashes due to in-situ coal oxy-combustion [105,106]. However, CaL conditions for TCES may be different to those employed for CO<sub>2</sub> capture. Since the concentration of CO<sub>2</sub> entering the carbonator is not imposed, carbonation conditions can be chosen to minimize the negative impact of CaO deactivation due to sintering while at the same time the thermoelectric efficiency is enhanced. On the other hand, pore plugging can be enhanced and CaO reactivity hampered, especially for large particles, at carbonation conditions involving high temperatures/high CO<sub>2</sub> concentration. Regarding reaction kinetics in the CaL process as TCES system, interested readers are referred to detailed works reported elsewhere [7,41,66,107].

### **3.1 Multicyclic CaO deactivation**

Multicycle CaO deactivation is a major drawback of the CaL process. CaO conversion as the number the cycle increases strongly decays up to approach a low residual value typically after around 20 cycles [105], mainly due to CaO grain sintering [108] or pore plugging [8] depending on calcination/carbonation conditions and the CaO precursor used [109].

CaO deactivation could be partially compensated by adding periodically a certain amount of fresh limestone to the process. Due the low cost of limestone (~10 €/tonne), introducing a make-up flow of fresh material seems interesting from a techno-economic point of view [110,111]. In addition, the sintered CaO-rich purged stream could be used in the cement industry to increase the profitability of the process, improving even the cement properties [112,113].

CaO conversion plays a fundamental role in the CaL process efficiency [18]. According to the review on TCES systems carried out by Prieto et al. [30], the CaL system could be a viable option to be integrated in CSP plants though CaO deactivation can be a drawback. An important effect



of CaO deactivation is that a larger size of equipment is required because of the massive presence of non-reacting solids in the system. The lower the CaO conversion the higher the amount of inert solids that must be preheated and cooled through the plant, with the consequent loss of thermal efficiency. This effect is more critical when considering solids storage at ambient temperature (facing long-term storage) due the large temperature changes along the cycle (the reactors would operate at  $T > 800^{\circ}\text{C}$  and storage would be at ambient temperature). Thus an increase of CaO residual conversion from  $X=0.07$  to  $X=0.5$  would enhance the thermoelectric efficiency by more than 10% points [18] while by considering high-temperature solids storage the same increment of residual conversion would increase the thermoelectric efficiency by just 2-3% points [57]. Considering the energy density of the system such increment of the residual CaO conversion would result in an energy density enhancement from 0.26 to 0.89 GJ/m<sup>3</sup> [57]. Hence, improving the CaO multicycle conversion has many advantages, which justifies the focus of researchers on this issue during the last years. Table 2 shows residual CaO conversion values reported in the literature which were obtained from lab-scale calcination-carbonation tests for several CaO precursors tested under different conditions.

Table 2: Values of residual effective CaO conversion ( $X_r$ ) at different CaL conditions reported in the literature for TCES. Effective CaO conversion is defined as the ratio of CaO converted to total mass of sorbent including inert solids if existing such as MgO in dolomite.

Materials		Process conditions		residual effective CaO conversion ( $X_r$ )	Ref.
CaO precursor	Average median diameter	Calcination	Carbonation		
Limestone	>45 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$ 5 min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.18 ( $X_{20}$ )*	[40]
	<45 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$ 5 min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.41 ( $X_{20}$ )*	[40]
	3.19 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$ 5 min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.51	[114]
	>160 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$ 5 min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.21 ( $X_{20}$ )*	[115]
	>160 $\mu\text{m}$	950 $^{\circ}\text{C}/\text{CO}_2$ 5 min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.18 ( $X_{20}$ )*	[115]
	>200 $\mu\text{m}$	1000 $^{\circ}\text{C}/\text{CO}_2$	850 $^{\circ}\text{C}/\text{CO}_2$	0.13 ( $X_{11}$ )*	[116]
	>200 $\mu\text{m}$	1000 $^{\circ}\text{C}/\text{CO}_2$	850 $^{\circ}\text{C}/\text{CO}_2$ Pressurized 3 bar	0.07 ( $X_{11}$ )*	[116]
	45–160 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$ 5 min + intermediate step 300 $^{\circ}\text{C}/\text{He}/2$ min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.15 ( $X_{50}$ )*	[47]
Dolomite	>45 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$ 5 min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.42 ( $X_{20}$ )*	[40]
	<45 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$ 5 min	850 $^{\circ}\text{C}/\text{CO}_2$ 5 min	0.41 ( $X_{20}$ )*	[40]
	>160 $\mu\text{m}$	725 $^{\circ}\text{C}/\text{He}$	850 $^{\circ}\text{C}/\text{CO}_2$	0.47 0.32 (two samples)	[8]

		5 min	5 min		
	>160 $\mu\text{m}$	950°C/CO <sub>2</sub> 5 min	850°C/CO <sub>2</sub> 5 min	0.39 (X <sub>20</sub> ) <sup>*</sup>	[115]
	>200 $\mu\text{m}$	1000°C/CO <sub>2</sub>	850°C/CO <sub>2</sub>	0.20 (X <sub>11</sub> ) <sup>*</sup>	[116]
	>200 $\mu\text{m}$	1000°C/CO <sub>2</sub>	850°C/CO <sub>2</sub> Pressurized 3 bar	0.15 (X <sub>11</sub> ) <sup>*</sup>	[116]
Marble	>45 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.16 (X <sub>20</sub> ) <sup>*</sup>	[40]
	<45 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.40 (X <sub>20</sub> ) <sup>*</sup>	[40]
	11.17 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.27	[114]
Chalk	7.12 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.38	[114]
Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> /CaCO <sub>3</sub>	>160 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.41 (X <sub>20</sub> ) <sup>*</sup>	[115]
	>160 $\mu\text{m}$	950°C/CO <sub>2</sub> 5 min	850°C/CO <sub>2</sub> 5 min	0.18 (X <sub>20</sub> ) <sup>*</sup>	[115]
ZrO <sub>2</sub> /CaCO <sub>3</sub>	>160 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.46 (X <sub>20</sub> ) <sup>*</sup>	[115]
	>160 $\mu\text{m}$	950°C/CO <sub>2</sub> 5 min	850°C/CO <sub>2</sub> 5 min	0.37 (X <sub>20</sub> ) <sup>*</sup>	[115]
	>200 $\mu\text{m}$	1000°C/CO <sub>2</sub>	850°C/CO <sub>2</sub>	0.33 (X <sub>11</sub> ) <sup>*</sup>	[116]
	>200 $\mu\text{m}$	1000°C/CO <sub>2</sub>	850°C/CO <sub>2</sub> Pressurized 3 bar	0.22 (X <sub>11</sub> ) <sup>*</sup>	[116]
Steel Slag	<300 $\mu\text{m}$	675°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.63	[117]
	<300 $\mu\text{m}$	675°C/He 5 min + intermediate step 150°C/ He/2 min	850°C/CO <sub>2</sub> 5 min	0.82	[117]
CaO/SiO <sub>2</sub> 70%/30%	-	725°C/He 5 min + intermediate step 300°C/He/2 min	850°C/CO <sub>2</sub> 5 min	0.25 (X <sub>50</sub> ) <sup>*</sup>	[47]
CaO/SiO <sub>2</sub> 90%/10%	-	725°C/He 5 min + intermediate step 300°C/He/2 min	850°C/CO <sub>2</sub> 5 min	0.23 (X <sub>50</sub> ) <sup>*</sup>	[47]
CaAc	139 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.56 (X <sub>30</sub> ) <sup>*</sup>	[118]
CaMgAc	267.6 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.53 (X <sub>30</sub> ) <sup>*</sup>	[118]
CaMg50Ac	220.9 $\mu\text{m}$	725°C/He 5 min	850°C/CO <sub>2</sub> 5 min	0.69 (X <sub>30</sub> ) <sup>*</sup>	[118]
Limestone pre- treated thermic ally under: a) superheated steam (650°C) b) He (725°C) c) N <sub>2</sub> (760°C) d) CO <sub>2</sub> (960°C)	1-10 $\mu\text{m}$	725°C/He 5 min + intermediate step 150°C/He/2 min	850°C/CO <sub>2</sub> 5 min	a) 0.45 b) 0.49 c) 0.50 d) 0.49	[8]

CaO residual conversion (X<sub>r</sub>) calculated according to equation proposed in [119]

\* CaO conversion at Y<sup>th</sup> cycle (X<sub>Y</sub>) which is close to the residual value

Regarding carbonation kinetics it is well-known that carbonation occurs through two consecutive well differentiated phases. The first phase takes place on the free surface of the CaO particles by nucleation and growth of a CaCO<sub>3</sub> layer and it is governed by the kinetics of the reaction between CaO and CO<sub>2</sub> [120]. The end of the fast phase takes place when a product layer of a certain thickness is formed depending on the carbonation temperature [121,122], which makes inaccessible a large fraction of CaO in the interior of the particles to direct carbonation [121]. Further carbonation is controlled by the solid-state counter-current diffusion of CO<sub>3</sub><sup>2-</sup> and O<sup>2-</sup> ions through the carbonate product layer, which leads to a much slower kinetics [120].

The particular carbonation depends on process conditions such as gas pressure, temperature, reactors atmosphere and CaO precursor which have an effect on the kinetics of the reaction and the formation of the CaCO<sub>3</sub> product layer [122] and therefore on CaO conversion at the end of the carbonation stage. For instance, as shown in the work by Benitez et al. [40], in which carbonation was carried out under pure CO<sub>2</sub> and T=850°C (after calcination at 750°C under pure He), most of the reaction in these conditions takes place mainly in a fast-initial phase controlled by the kinetics of the reaction on the surface of the CaO particles, with a subsequent negligible carbonation solid-state diffusion controlled phase (Figure 3). This information is highly relevant for the design of the process at industrial scale to optimize relevant parameters such as the solids residence time in the reactors. Data on the multicycle effective CaO conversion (defined as the ratio of CaO converted to total mass of sorbent) are shown in Figure 4.

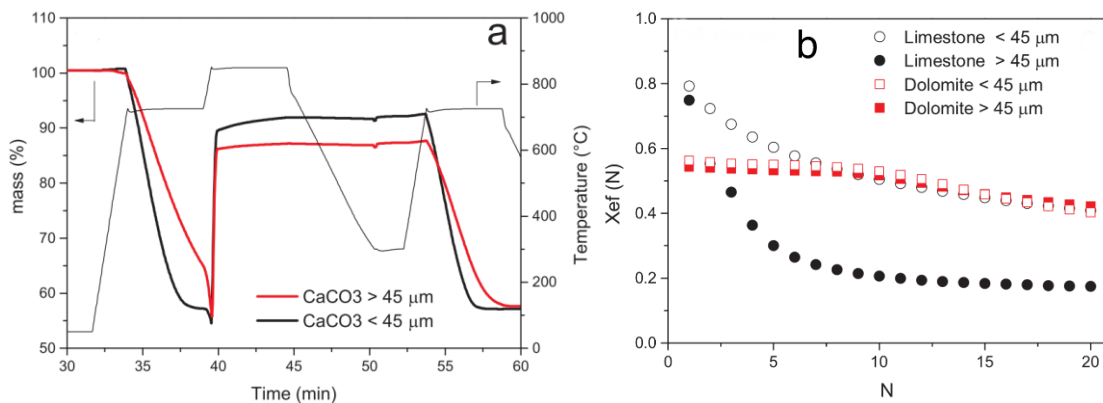


Figure 3: a) Time evolution of temperature and sample weight for the first calcination-carbonation cycle under carbonation at high temperature and pure CO<sub>2</sub> and limestone samples of different particle size. Calcination is carried out under helium atmosphere at 725°C while carbonation occurs under pure CO<sub>2</sub> at 850°C. b) Multicycle effective CaO conversion of limestone and dolomite samples of different particle size subjected to CaL cycles. Reproduced with permission from [40].

In addition to natural limestone, which is almost pure CaCO<sub>3</sub>, other CaO precursors have been proposed to improve the multicyclic CaO conversion. Dolomite [MgCa(CO<sub>3</sub>)<sub>2</sub>] is another abundant and low-price material which is decomposed into MgO and CaO upon calcination by a

two-stage process [104]. Despite the presence of MgO as inert material towards carbonation at the CaL specific conditions for TCES, which requires a higher energy consumption for solids conveying and higher thermal losses, the use of dolomite is a promising alternative to limestone due to the improved CaO conversion observed in multicyclic tests, the reduction in the calcination temperature to 900°C in short residence times and the possibility of using relatively large particles as pore-plugging is not a concern (see Fig 3b) [40].

As can be seen in Figure 3b, there is a rather different behavior in the CaL multicyclic performance between CaO precursors and particle size. For limestone, the multicycle conversion is strongly hindered for particles larger than 45  $\mu\text{m}$ , reaching a conversion after 20 cycles of around 0.18 (Figure 3b). However, for particles smaller than 45 $\mu\text{m}$ , the conversion is remarkably higher indicating that particle size poses a limitation to calcination/carbonation under these conditions [40]. The effect of particle size on the multicycle conversion of CaO is explainable from the relative thickness of the CaCO<sub>3</sub> layer built upon the CaO surface as compared to the size of the pores in the CaO skeleton formed after calcination and the carbonation kinetics in the fast reaction-controlled (FR) stage [40]. The thickness of this product layer can be increased over ~100 nm if the carbonation temperature and CO<sub>2</sub> vol concentration are increased as is the case at CaL conditions for thermochemical energy storage, leading to pore-plugging for relatively large CaO particles [40]. Pore plugging is further reinforced if calcination is carried out under relatively low temperatures, which gives rise to a CaO skeleton with small pores susceptible of being plugged during carbonation [40].

In the case of dolomite as CaO precursor, the conversion is not limited by pore plugging since the inert MgO grains provide a path for the CO<sub>2</sub> molecules to percolate inside the inner pores of the particles [40]. The presence of MgO grains notably mitigates sintering and aggregation of the CaO grains which leads to a markedly higher multicyclic performance [40,115] (see Figure 3b). Another possibility is using low price and abundant industrial waste materials such as steel slag as CaO precursor [117]. Results show that pore plugging is neither a limiting factor for the CaO derived from treated steel slag presumably due to the presence of inert oxides as happens for dolomite, which leads to high and stable effective conversion ( $X=0.63$ ) [117].

Sarrion et al. [115] analyzed different conditions for the CaL process as TCES system. Both calcination and carbonation reactions were performed under a pure CO<sub>2</sub> environment at 950°C and 850°C, respectively using sieved limestone of ~160  $\mu\text{m}$  particle size. Under these conditions, the multicycle CaO conversion evolves quite similarly to the case in which calcination was carried out under He, reaching a residual value of  $X\sim 0.2$ . Presumably, calcination under harsh conditions leading to a much larger pore size would serve to mitigate pore plugging, which was a severe limiting mechanism for calcination under He in the case of relatively large particles. In

comparison with calcination under He, using pure CO<sub>2</sub> for calcination and carbonation avoids the need to separate He from the released CO<sub>2</sub> in calcination, which reduces the complexity of the overall system. For dolomite, as in other works [40,116], a notably higher effective conversion was found with a residual value around  $X \sim 0.4$  [115]. In the same work composite Ca-based materials were tested using zirconia and alumina as additives. Figure 4 compares data on the multicycle effective CaO conversion for natural limestone, dolomite and the Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>/CaCO<sub>3</sub> and ZrO<sub>2</sub>/CaCO<sub>3</sub> composites.

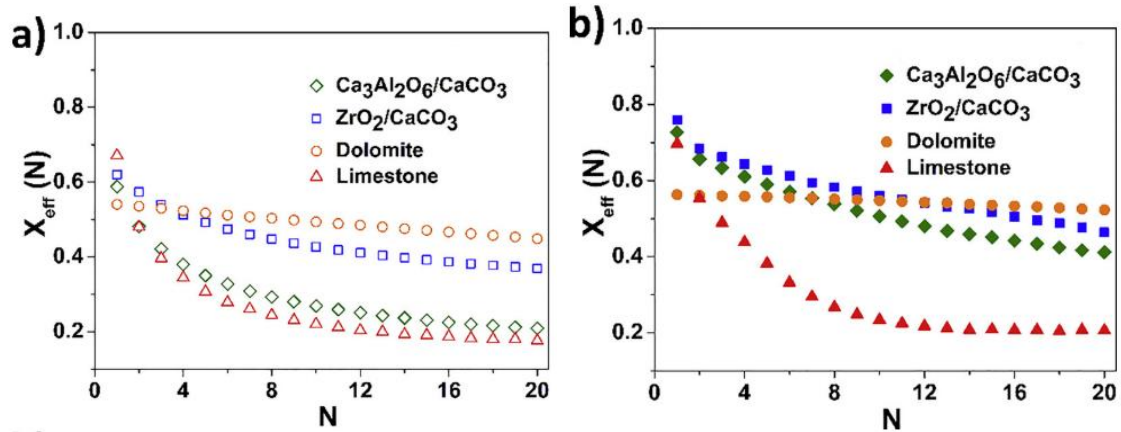


Figure 4: Multicyclic effective conversion for natural limestone, Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>/CaCO<sub>3</sub> composite, ZrO<sub>2</sub>/CaCO<sub>3</sub> composite and dolomite under: a) harsh calcination conditions (pure CO<sub>2</sub>, 950°C) and b) mild calcination conditions (pure He, 725°C). Reproduced with permission from [115].

As shown in Figure 4, both Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>/CaCO<sub>3</sub> and ZrO<sub>2</sub>/CaCO<sub>3</sub> composites show higher multicycle effective conversion than natural limestone, especially when tested under mild calcination conditions, although it is dolomite in both cases the CaO precursor with the highest multicycle effective activity. As can be seen, limestone behavior is quite similar under both CaL conditions while the composites and dolomite show sensible differences. Natural CaCO<sub>3</sub> minerals as marble and chalk have been also tested as CaO precursors for the CaL process [114] showing similar performances to natural limestone.

Within the DOE-funded project “Regenerative Carbonate-Based Thermochemical Energy Storage System for Concentrating Solar Power project”, a synthetic sorbent with an almost constant CaO multicycle CaO conversion of  $X=0.3$  was proposed although the high costs of the material could be a severe limitation to the process feasibility [123].

Benitez et al. [47] assessed the multicyclic performance of inexpensive CaO/SiO<sub>2</sub> composites synthesized from rice husk. The proposed composites, with 70 and 90% content of CaO, present a notably enhanced effective conversion compared with natural limestone particles larger than 45 μm due the mitigation of pore-plugging, which can be explained from the porous structure and uniform CaO/SiO<sub>2</sub> dispersion obtained by the biotemplate synthesis method used [47]. In another work, Sánchez-Jiménez et al. [118] assessed the performance of acicular calcium and magnesium

acetate precursors prepared by a simple, cost-effective and easily scalable technique from limestone and dolomite treated with acetic acid. The calcium magnesium acetates (CMA) (which consists of a mixture of hydrated calcium acetate and hydrated CMA in different ratios) showed a stable porous structure with uniformly dispersed MgO nanoparticles dispersed over the CaO grains making them more resistant to pore-plugging and reducing sintering, which leads to a highly stable multicyclic effective conversion (see Table 2).

#### **4. CSP-CaL process schemes**

Process integration plays a key role on the adaptation of the CaL technology to a CSP plant. Despite that the CaL technology was already conceptualized for solar energy storage in the late 1970s [53], process integration schemes have not been explored in detail until a few years ago.

Edwards et al. [124] proposed a CSP-CaL integration scheme in which the heat produced in the carbonator reactor is used for power generation through a CO<sub>2</sub>/air open cycle. Figure 5 shows a flow diagram of this configuration. CaCO<sub>3</sub> particles are assumed to attain complete decomposition in the calciner after which CaO particles and CO<sub>2</sub> are passed through a network of solid-gas and solid-solid heat exchangers to preheat the solids entering the calciner. CO<sub>2</sub> is stored under pressure at low temperature while the solids are stored at ambient conditions. In the carbonator side, the compressed CO<sub>2</sub> is mixed with compressed air (at carbonator pressure) and then passed through a preheating process before entering the carbonator, where it reacts with the preheated CaO solids. In this scheme, the CO<sub>2</sub> entering the carbonator is assumed to react completely with the CaO particles according the carbonation reaction. Thus, a pure air stream would be released from the carbonator and carried to a gas turbine for power production after which it is released to the atmosphere.

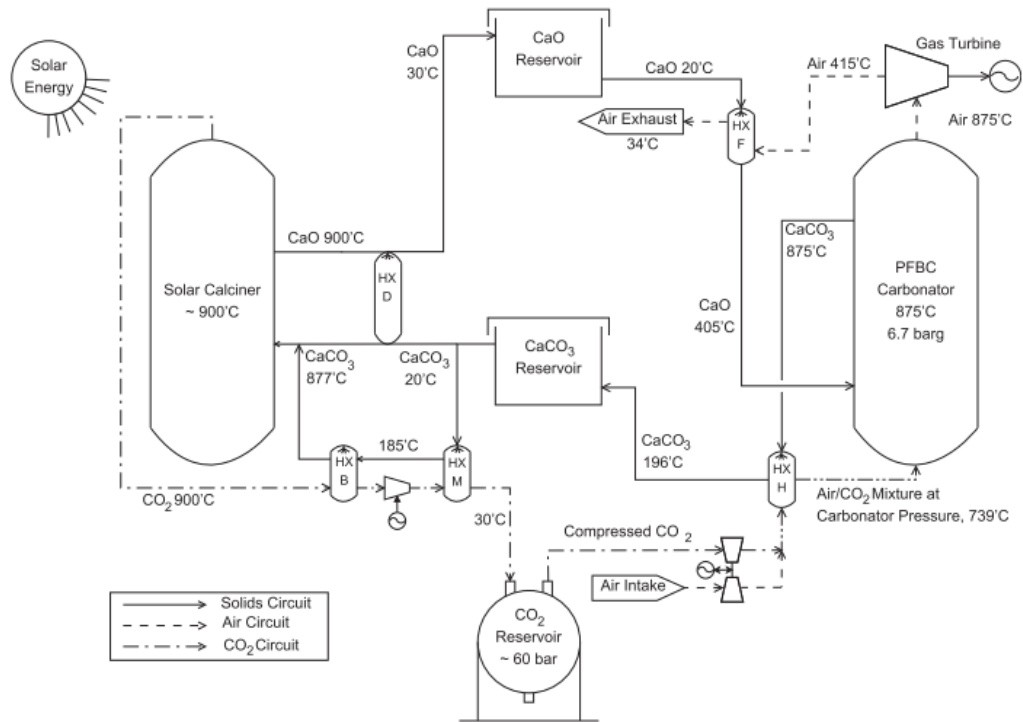


Figure 5: Flow diagram of a CaL-air open Brayton cycle integration for energy storage in CSP plants. Reproduced with permission from [124].

However, the reaction thermodynamic equilibrium [63] poses a critical drawback to this scheme. At a given temperature carbonation would occur until the CO<sub>2</sub> concentration reaches a threshold value for which the reaction reaches thermodynamic equilibrium. Therefore, the effluent gas vented to the atmosphere cannot be free of CO<sub>2</sub>. For example, when a 15% v/v CO<sub>2</sub> stream is introduced into the carbonator at pressurized conditions (i.e. 6 bar) and  $T \sim 850^\circ\text{C}$ , the minimum CO<sub>2</sub> concentration in the gas stream exiting the carbonator is around 8% (CO<sub>2</sub> vol% for the reaction to reach thermodynamic equilibrium at 850°C) [44]. Moreover, ideal equilibrium conditions are not fully achievable in practice and the CO<sub>2</sub> vol% in the effluent gas would be even higher. Thus, an open Brayton cycle is not appropriate for free CO<sub>2</sub> emissions in the CSP-CaL plant.

As alternative to the open Brayton cycle to circumvent this important limitation, a regenerative CO<sub>2</sub> closed Brayton cycle was proposed by Chacartegui et al. [18,44]. In this configuration (Figure 6) a pure CO<sub>2</sub> stream enters the carbonator with a molar rate well above the stoichiometric needs for carbonation. The excess CO<sub>2</sub> that leaves the carbonator is used as heat carrier fluid to remove the heat released during carbonation and delivered to a gas turbine for power production. After passing the turbine, the CO<sub>2</sub> is circulated through the regenerator as a previous step to be compressed again for a new cycle. The integrated plant performance was determined as an average over a 24h period. A daytime period  $\Delta t_{sun}$  is considered during which the solar thermal power entering the calciner is constant. Different operations in “sun” and “night” modes were

considered and a Solar Multiple (SM) equal to 3 was assumed. Importantly, the plant performance does not consider losses in the solar field and receiver. A more realistic value of the solar-to-electric efficiency should be calculated by considering the solar calciner performance in practice.

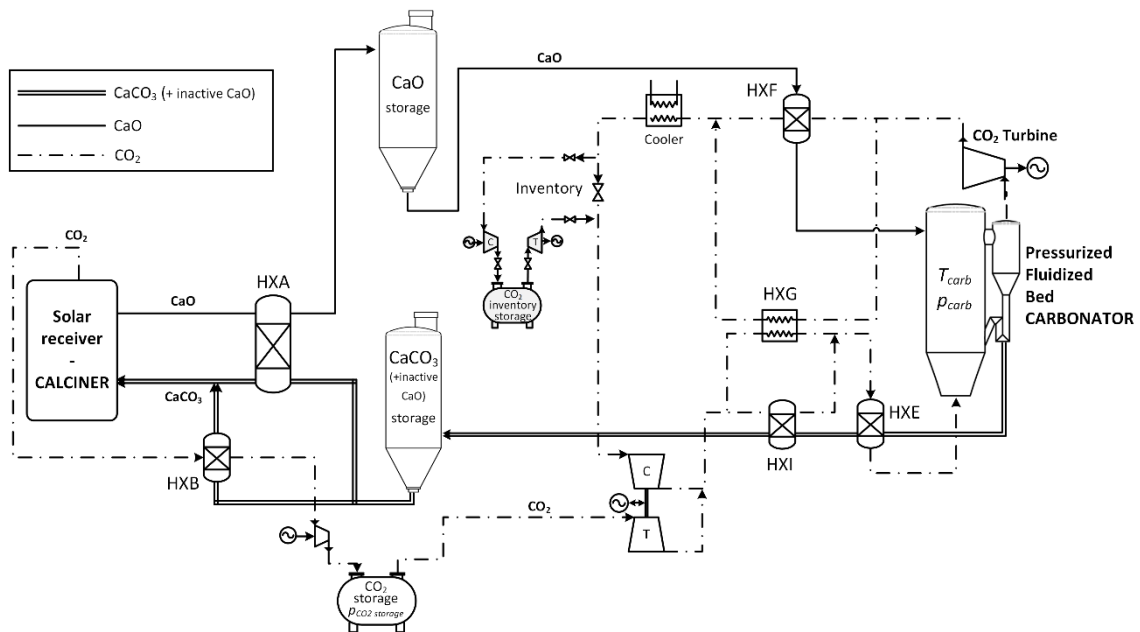


Figure 6: CaL-closed Brayton cycle integration for energy storage in a CSP plant [18]. Reproduced with permission from [44].

According to simulation results, a maximum efficiency is reached for a pressure ratio (PR) of the carbonator to the turbine outlet  $PR=3.2$  regardless of the value of CaO conversion [18]. Higher pressure ratios reduce the temperature at the turbine outlet which is detrimental since the temperature of the CaO particles entering the carbonator is decreased. On the other hand, the CO<sub>2</sub> flow rate needed in the power cycle reaches very high values when the pressure ratio is small. Therefore, the size of all heat exchangers can be reduced by increasing the pressure ratio. Low absolute pressures in the carbonator require high compression power and high expansion power in the intermediate turbine (linked to the CO<sub>2</sub> storage vessel), which leads to a net reduction of power consumption. The higher the carbonator pressures the higher the carbonation temperature may be from thermodynamic equilibrium with the consequent efficiency increase. Regarding the plant efficiency, first law efficiency of 40-46% and second law efficiency of 43%-48% were reported to be achievable by means of an optimized CSP-CaL scheme [18].

Three different integration schemes based on the closed Brayton cycle were compared by Alovio et al. [44]:

- i) a first scheme with the same heat exchangers than in Figure 5 but including the necessary adaptations derived from the use of a CO<sub>2</sub> closed Brayton. Results shown an



overall efficiency in the range of 34-35%, mainly depending on the carbonator pressure and temperature and the pressure ratio in the CO<sub>2</sub> turbine.

- ii) a modified scheme which includes a gas-gas regenerator in the carbonator side to improve energy integration (*HXG* in Figure 6). Results for this modified scheme showed an efficiency improvement of ~2% points regarding case i).
- iii) a second modified scheme optimized by a detailed pinch-point analysis (Figure 6). For a fixed CaO conversion of 0.2, the global net efficiency is increased by about 5% points over case i). The enhancement of heat recovery so achieved yields a relevant increase of the cycle performance, which would be further promoted as CaO conversion is increased.

In a more recent work Ortiz et al. [125] have explored other CSP-CaL integration schemes based on the scheme shown in Figure 6. The use of alternative indirect cycles was assessed for power production such as reheat Rankine cycle (with a calculated efficiency of 35.5%), a recompression supercritical CO<sub>2</sub> (sCO<sub>2</sub>) Brayton cycle (calculated efficiency of 32%) and a Combined Cycle, which showed the best performance. In the last case the results showed that the cycle performance was improved by decreasing the outlet turbine pressure up to reach a maximum value of 40.4% for operation under an inlet/outlet turbine pressure ratio of 3.6/1 [125]. Even though a CO<sub>2</sub> closed cycle direct integration would yield the best efficiency results additional studies regarding techno-economic feasibility should be pursued to further assess the applicability of these power cycle integrations in the CSP-CaL integration [125].

Further configuration schemes have been explored by considering high temperature solids storage [57]. The power cycle considered in this work was, as in previous cases, a regenerative CO<sub>2</sub> Brayton cycle. As simplified heat integration allows using CSP-CaL schemes provided with state-of-the-art equipment. The four novel schemes proposed were built with an increasing degree of complexity and therefore a higher investment cost but also a higher efficiency. The best one from an efficiency perspective is depicted in Figure 7.

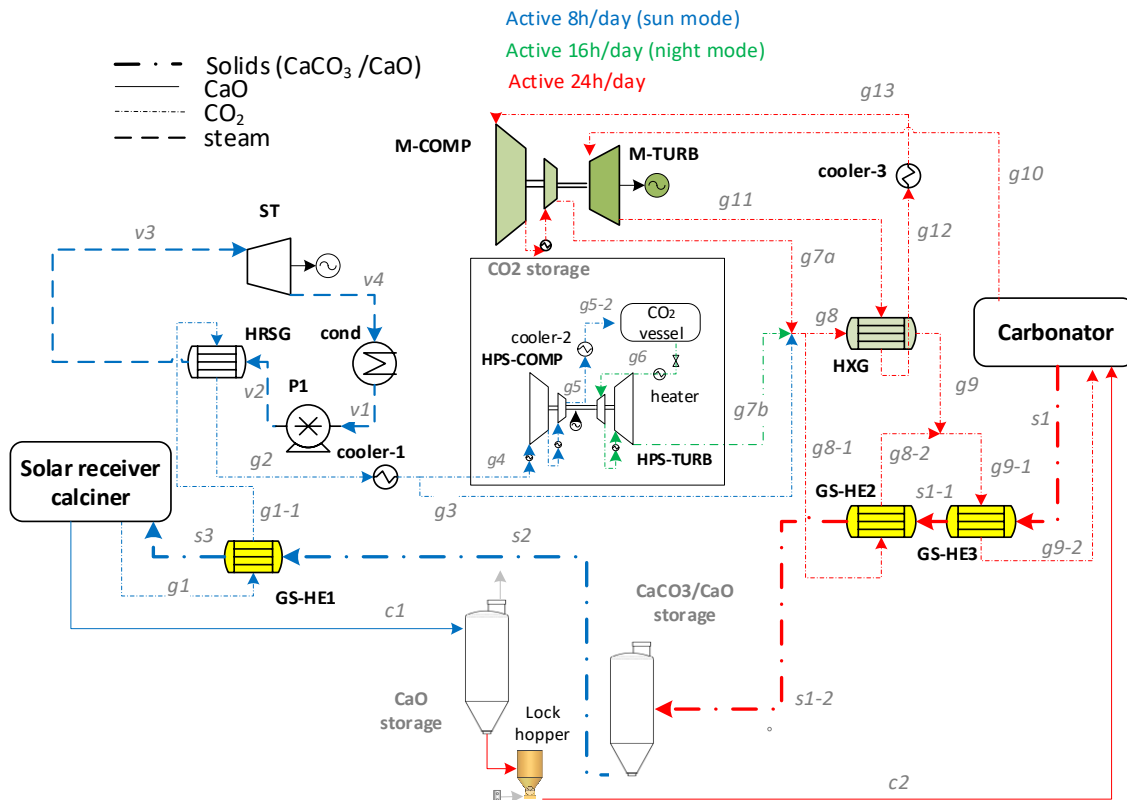


Figure 7: CSP-CaL integration scheme with high-temperature solids storage. Reproduced with permission from [57].

In the calciner side, the main novelty regarding previous schemes (Figure 6) is the removal of the solid-solid heat exchanger. CaO solids are directly sent to storage at high temperature while a part of the sensible heat of the released CO<sub>2</sub> is recovered by a gas-solid preheater (GS-HE1 in Figure 7) and a heat recovery steam generator (HRSG). On the carbonator side, GS-HE2 and GS-HE3 solid-gas heat exchangers are used to preheat the CO<sub>2</sub> stream. As in the previous scheme, an intercooled CO<sub>2</sub> compressor (2-stages in this case) was considered to reach the carbonator pressure. The scheme shown in Figure 7 could be operated by considering either atmospheric or pressurized carbonation without remarkably differences on the overall plant efficiency. By considering pressurized carbonation, results show a maximum in the overall efficiency near 40% at PR between 4 and 5. In any case, the optimum carbonation pressure would be dependent on technical issues such as the cost of a high-temperature lock hopper system or the sealed components for a specific facility [57]. From a sensitivity analysis, it was seen that the increase of either CaO conversion or Turbine Inlet Temperature (TIT) enhanced the overall plant efficiency by up to 2.7%. Further analysis showed that by increasing a 5% the reference isentropic efficiency value for the main CO<sub>2</sub> compressor (M-COMP) the overall efficiency was raised up to 44% [57].

Another CSP-CaL scheme was proposed by Karasavvas et al. [126]. For the calcination process, the total heat uptake in the calciner could be arguably accomplished by using CO<sub>2</sub> as the working medium. The high CO<sub>2</sub> temperature (above 950°C) could be accomplished in a solar heat exchanger previously to be introduced in the calciner. Both the entering CO<sub>2</sub> in the calciner and surplus produced by the calcination reaction will be at high temperature at the exit of the adiabatic calciner and will be used for energy production during the process taking place during sun hours in the day. For the carbonation process using the stored CaO earlier produced in the calciner, a parametric analysis considering the incoming stored CaO temperature (200-700 °C) was performed. Global efficiency calculated considering that the calciner worked for 12 hours in the day as the carbonator. Electric power was produced in the range of 1-5 MW at night with a global efficiency in the range ~28-31%.

## **5. Technology assessment and prospective**

This section is devoted to gather information on industrial and prototype-scale components to be integrated within the CSP-CaL scheme. The analysis is focused on the technologies with the greatest risks of scaling up such as solar calcination, heat exchange, material conveying and solid-gas separation.

### **5.1 Solar calcination**

Because of the high temperature needed for calcination (above 900°C), a solar tower configuration is the most appropriate to be used in the CSP-CaL integration. Currently, there are in operation around 5GWe of CSP, of which a 13% utilizes solar tower technology [127]. However, the trend of the CSP technology mix is changing. Among those under construction and under development 44% of the plants are solar towers [5]. A detailed study on the main characteristics of solar tower plants may be found in [127].

The solar-to-electric efficiency of the integrated CaL-CSP plant will be highly dependent on the solar receiver performance and therefore a proper selection, configuration and sizing of the solar calciner is a crucial task that remains unsolved yet. Even though early calciner designs and prototypes were already drawn in the 1980s [45,46] the solar particle receiver technology remains immature although its development has been notably intensified in the last years. Heat transfer losses is a critical issue for the solar receiver design, especially when high temperatures in the receiver are considered as would be the case of solar calcination of CaCO<sub>3</sub> under pure CO<sub>2</sub>, which requires temperatures well over 900°C. Radiation losses are mainly dependent on the receiver temperature and should be mitigated by a proper design [128] whereas conduction losses can be reduced by improving thermal insulation. Thus, increasing the solar absorptance, decreasing the

thermal emittance and/or reducing conduction/convective heat losses are necessary to enhance thermal efficiency in the receiver [9].

Critical issues for the development of solar calcination receivers are: i) the need for enough solids residence time to reach the target temperature and allow for reaction completion; ii) choosing an adequate particle size for particles conveying, fluidization and separation; iii) proper managing of high gas flow-rates that must be used for the transport of the particles (especially in the case of fluidized beds); iv) avoiding possible deposition of particles in the optical window that may cause damage; v) operating under continue operation mode for scaling-up; vi) minimizing thermal gradients which would lead to heterogeneous calcination; and vi) particles attrition and agglomeration. Moreover, it must be considered for the reactor design that  $\text{CaCO}_3$  has a poor solar absorptance [45].

Solids residence time and mass flow are crucial parameters when designing the receiver for solar calcination. In the CSP-CaL integration, solar radiation is used to heat the particles up to calcination temperature. The particles residence time in the calciner must be long enough to reach full calcination. The temperature at which the particles enter the solar receiver depends on the CSP-CaL scheme. Since carbonation does not occur completely, typically a mixture of  $\text{CaCO}_3$  and  $\text{CaO}$  solids enters the solar calciner. Falling particle receivers [9,129,130], centrifugal particle receivers [45,131–133] and Fluidized Bed receivers [134,135] can be considered a feasible candidates to be used in the CSP-CaL integration. Table 3 compares the main characteristics of each of them. In a recent paper, Moumin et al. [133] summarized the solar calciners proposed in the literature.

Table 3: Receiver technology comparison.

		Particle receiver technology		
		Falling particle	Centrifugal receiver/ Rotary kiln	Fluidized Bed
CSP-CaL integration issues	Benefits	<ul style="list-style-type: none"> <li>-High solar irradiance</li> <li>- High thermal efficiency</li> <li>- Highly tested in the last years (MWth scale)</li> <li>-<math>T_{\text{max}} &gt; 1000^\circ\text{C}</math></li> <li>- Good scalability</li> <li>- Geometry similar than solar tower</li> <li>- Improved continuous operation mode</li> <li>- co-current or counter-current flow</li> </ul>	<ul style="list-style-type: none"> <li>-Core technology for calcination in cement industry</li> <li>-<math>T_{\text{max}} &gt; 1000^\circ\text{C}</math></li> <li>-Well-known preheaters coupling</li> <li>-adjustable residence time of particles</li> <li>- Improved continuous operation mode</li> <li>-good heat transfers</li> <li>- co-current or counter-current flow</li> </ul>	<ul style="list-style-type: none"> <li>- high thermal inertia improving the thermal regimen under short variations of solar radiation</li> <li>- Well-known technology at industry</li> <li>- high transfer coefficients</li> <li>- Direct and indirect heating configuration</li> </ul>
	Challenges	<ul style="list-style-type: none"> <li>- Window integration</li> <li>-Increasing the residence time (especially problematic for particles <math>&gt; 200\mu\text{m}</math>)</li> <li>- Particle attrition</li> </ul>	<ul style="list-style-type: none"> <li>- Scalability must be addressed because the focalized solar heating</li> <li>- Window integration</li> <li>-Thermal losses in rotary kiln mainly occurs by conduction <math>\rightarrow</math>improve thermal insulation</li> </ul>	<ul style="list-style-type: none"> <li>-total absorptance of the fluidized bed depends on both of particle's emittance and bed configuration</li> <li>- Beam-down technology development</li> <li>- Energy consumption for fluidization</li> <li>-Gas-solid separation</li> </ul>

Restrictions	- Low solar absorptance of CaCO <sub>3</sub> particles for direct irradiation - Direct heating is not possible because avoiding CO <sub>2</sub> losses	- Horizontal design which makes difficult is integration in solar tower at large scale.	- Geometry incompatibilities with solar towers
Tested for calcination	No	[45,46] [131] [132] [73] [133]	[45,46]

## 5.2 Carbonator

Gas-solid reactors are used in many industrial processes. In particular, fluidized beds (FB) are widely employed as they provide a large gas-solid contact surface, which promotes heat/mass transfer. FB reactors are found in a large number of applications in the environmental, chemical and process industries [136] and can be also potentially considered for the CaL process as TCES. In fact, the CaL process in its application for CO<sub>2</sub> capture was originally conceived by means of a twin FB reactor (calciner and carbonator) [137]. Most of the already constructed CaL pilot plants for CO<sub>2</sub> capture are based on FB reactors [98] and a large number of FB carbonator models can be found in the literature [138–141].

Fluidization efficiency is critically determined by particle size. In the case of fine cohesive powders (with particle size  $d_p < 30\mu\text{m}$ ) interparticle adhesion is dominant against hydrodynamics and gravitational forces [102], which causes agglomeration, channeling and plugging phenomena that impede uniform fluidization [103]. Several methods have been proposed to enhance fluidization of fine particles: Mechanical vibrations, application of magnetic, acoustic, electric or centrifugal fields, application of gas micro-jets or pulsated gas flow [103]. In addition, the use of fine cohesive powders in an industrial-scale process may be challenging due to the difficulty of capturing small particles from the effluent gas stream using conventional cyclones [83]. The collection efficiency of cyclones is limited for particles smaller than typically 20  $\mu\text{m}$  [82].

Fine particles provide a large surface to volume ratio, and for the CaL process bring about the important advantage of reducing the pore-plugging that hinders the multicycle CaO conversion at the conditions to be used for TCES as discussed above [40,98]. Downer (entrained flow) reactors are a well-known technology in the cracking industry [142] and can be an alternative to FBs reactors to handle fine particles. In a recent work a 1-D model of entrained flow reactor has been proposed for the carbonator reactor to capture CO<sub>2</sub> in cement kilns using the CaL process [99].

## 5.3 Heat exchangers

Optimizing heat integration in the CSP-CaL integration is crucial to achieve high efficiencies due to the high temperature differences between the calciner, the storage vessels and the carbonator. Because of the system characteristics, a gas-gas heat exchanger as regenerator would be needed

by considering a CO<sub>2</sub> close-loop for power production [44]. On the other hand, the CO<sub>2</sub> exiting the calciner at high temperature (>900°C) must be cooled previously to be compressed and stored. Similarly, solid-gas preheaters allow increasing the CO<sub>2</sub> temperature entering the carbonator (from the storage in which CO<sub>2</sub> is at low temperature) using heat from the CaCO<sub>3</sub> particles exiting the carbonator. Finally, solid-solid heat exchangers would further improve heat integration although they are not completely developed at commercial scale.

Gas–solid heat exchange can be carried out in either the open or close configuration. Direct contact within an open configuration is a well-known technology [82]. Solids heating could be performed in a suspension preheater where gas and solids enter into contact sequentially in risers and are separated by cyclones [57] as commonly used in cement plants for raw material preheating [143]. In suspension preheaters raw particles are maintained in suspension by the hot gas from the calciner.

In the case of the CSP-CaL integration in which CaO particles are preheated before entering the carbonator with the CO<sub>2</sub> exhaust stream [44,124], an indirect gas-solid heat exchanger is needed in the carbonator side to avoid direct contact between CaO and CO<sub>2</sub>, which could lead to undesired partial carbonation with the consequent reduction in the carbonation heat transfer to the power cycle. Indirect solid-gas heat exchange could be performed by using multiple heat transfer plates conveniently spaced to allow the flow of material to be heated inside [144]. An alternative high-temperature solid-gas heat exchanger was proposed by Al-Ansary et al. [145] in which particles circulate on the shell side through an arrangement of tubes while the CO<sub>2</sub> passes through the tubes. Moving packed-bed heat exchangers implementing shell-and-tube and finned shell-and-tube designs were investigated by Ho et al. [146]. Tests showed that the particle-side heat transfer coefficient could reach values up to ~100 W/m<sup>2</sup>-K. Regarding the solid-solid heat exchanger, a possible system would use two solid-gas indirect heat exchangers with one intermediate heat-transfer fluid recirculated within the bulk of both solids. Because of the high temperature needs, liquid-metals could be used as fluid transfer to this end.

#### **5.4 Solids conveying and gas separation**

Transport of the solids can be performed either by mechanical or pneumatic conveying or by gravity depending on the available space or the facility geometry [147]. Mechanical systems normally have a higher investment cost but a much lower operating cost than pneumatic transport [82].

Screw conveyors have been considered for CaL applications [148]. At a commercial-scale, with large volumes of solids circulating through the calciner side, the solids load will vary due to changes in the solar irradiation making the screw conveyors mechanically inefficient [98]. Screw

conveyors were used in the Carina European project [149,150] to feed  $\text{CaCO}_3$  into the calciner. The flow rate of solids through the calciner was properly controlled by using the screw conveyors but the temperature range remains a challenge for this system [149]. As a reference, the 1 MWth CaL prototype plant at Darmstadt [150] uses a screw conveyor to control the solids mass flow rate. No difficulties were reported regarding the particles transport despite the small median particle diameter ( $\sim 36 \mu\text{m}$ ) used in the plant. In Arias et al. (2017) [151] screw feeders were also used for a particle size of  $\sim 50\text{-}80 \mu\text{m}$ ). Although Ca-based materials with a particle size below  $30 \mu\text{m}$  are common in cement plants, instabilities were reported due to blockage of the stand-pipes with such fine materials. Particles with average size higher than  $70 \mu\text{m}$  were recommended [151]. In a more recent paper [152] the minimum particle size was reduced to  $50 \mu\text{m}$  above which a continuous and controlled solids flow was allowed. OLDS elevator, which are a type of vertical screw conveyor [153], employs a circular casing rotating around a stationary screw or helix with a small parasitic power consumption [130]. These systems can operate a high temperature (around  $700^\circ\text{C}$ ) [153], and seems a suitable option for the CSP-CaL integration.

Since  $\text{CO}_2$  and  $\text{CaO}$  are stored separately, solid-gas separation after calcination is fundamental in the CSP-CaL integration. The same occurs in the power production side, where  $\text{CO}_2$  exiting the carbonator and headed to the turbine must be free of particles. The most common method to separate particles from a gas stream is by cyclones, which are based on centrifugal separation. Thus, particles are forced out against the outer wall and then eliminated through an aperture at the bottom of the unit. Cyclones allow a high separation efficiency (95-100%), they are robust and allow operating under high-temperature with low energy requirement. However, the use of cyclones for small size particles [14], typically lower than  $20 \mu\text{m}$ , is not feasible. A post-cyclone was proposed by Ray et al. [69] to improve the efficiency when working with fines. The post cyclone consists of a cylindrical annular shell located on top of the vortex finder. Both experiments and simulations indicate a 50% decrease in emission of  $<5 \mu\text{m}$  size particles.

## 5.5 Storage system

The storage capacity of the CSP-CaL plant should be properly designed to meet the energy release plant criteria as a peaker, intermediate or baseload. Despite that one of the main advantages of TCES systems is the possibility of storing energy in the long term, the CSP-CaL plant could be operated under a solar multiple SM, defined as the ratio of the solar thermal power to the power block design thermal input, similar to that in current CSP plants ( $\text{SM} \sim 2\text{-}3$ ) [154]. By considering the higher energy storage density of the CaL system in comparison with molten salts [57], a high-temperature CaL storage system of similar size could allow storing energy for longer periods, even days, than the current 16 hours storage period in commercial molten salts-based CSP plants

[5]. Remarkably the CSP-CaL plant can be also considered as a long-term (even seasonal) energy storage system.

According to Purutyan et al. [155], the material's flow properties have to be considered in the design of the particle vessel apart from the bulk density, particle size distribution, angle of repose, etc. In the CSP-CaL integration, these properties might change over time after repeated calcination-carbonation cycles and as a function of temperature [156]. Among the solids storage vessel operating requirements to consider are its capacity, discharge rate and frequency, mixture and material uniformity, material friability, pressure and temperature differences, safety and environmental concerns, and construction materials [155]. CO<sub>2</sub> storage tanks are a well-known at the commercial scale.

## **6. Economic issues**

This section is devoted to a brief discussion on the cost of the CaL process for TCES, which has not been yet studied in detail. Because of the early stage of experimental researches at pilot scale, carrying out a sufficiently accurate cost estimation at a commercial scale is not possible. Project contingencies at this stage of development can be up to 70% [157]. However, several estimations are found in the literature about costs of the CaL process for CO<sub>2</sub> capture that may be translated to its application for TCES and for solid particles receivers.

As previously discussed, the CaL process has been widely investigated as post-combustion CO<sub>2</sub> capture system. This includes several techno-economics analyses where the capital and operational cost of the CaL process has been assessed. These values can be used as references for the CaL-TCES application since the process is essentially the same for both applications (the difference resides mainly on the reactors operating conditions). According to Mantripraga et al. [158], the carbonator and calciner reactors comprise the highest cost of plant together with the cost of solids handling systems. Several authors estimated the capital cost of the calciner and carbonator from CFB reactors costs from exponential functions by using volume flow rate of flue gas, reactor volume or heat input to the calciner as scaling parameter [158–160]. Hanak et al. [55] concluded that specific total capital requirement for the CaL process (retrofitting a coal-based power plant) is around 2100-2300 €/kWe. A detailed method for estimating the cost of the main CaL process equipment is provided in [161].

One of the main advantages of the CaL process is the reduced cost of limestone if used as CaO precursor (~10 \$/ton) [55] as compared with the molten-salts costs (~1000 \$/ton) [162]. This highly influences the variable O&M costs of the plant facing the need of material reposition [110]. On the other hand, the system complexity and the auxiliaries consumption for the CaL process (mainly the CO<sub>2</sub> compression and the solids conveying) makes it difficult the comparison with molten salt-based systems.



Bayon et al. [58] developed a techno-economic analysis comparing a number of 17 gas-solid systems for TCES. Eight systems were identified as competitive with molten salts, among which was the CaL process. For the comparison, the total storage cost included feedstock, vessels, pumps, compressors, particles conveyor and labor. Importantly, it did not include reactors cost. The authors indicated that cost of the CaL process was one of the lowest (~54 \$/kWh) but the carbonate-based systems present a high parasitic energy consumption by auxiliary equipment. Thus, for the CaL process, the parasitic energy was calculated as 48.7%. This figure reflects a poor integration of the process, which could be highly enhanced by following the schemes reviewed in section 4.

Santosh et al. [123] assessed the cost of the CaL process for TCES by using a highly stable synthetic sorbent ( $X \sim 0.3$ ), estimating a total cost of the system in 47 \$/kWh. Since a main part of costs is due to CO<sub>2</sub> compression, a series of inexpensive vinyl tanks was considered as alternative to storage the CO<sub>2</sub> at atmospheric pressure. This solution, which highly penalizes the energy density of the system, could be profitable though (the estimated cost was 42.5 \$/kWh). The authors indicated that a reduction of up to 19.5 \$/kWh could be achieved by using specific pieces of equipment however commercially unavailable yet.

It must be noted that the SunShot Initiative (USA) [163] contemplates a target cost of 15 \$/kWh for storing energy in CSP plants, which is quite below these estimations. Thus, it follows that additional research is absolutely needed on the CSP-CaL integration aimed at reducing auxiliaries energy consumption to enhance the profitability of the CaL system as compared with molten salts because of the reduced cost of the feedstock.

One major issue when analyzing the CaL-CSP integration is the particle receiver cost. Estimating this cost is a complicated task because of the lack of maturity of these systems as discussed in section 5.1 of this review. Ho [9] performed a sizing and cost analysis for a falling particle receiver at commercial scale (460 MW<sub>th</sub>). The calculated total cost of the particle solar receiver was 125 \$/kW<sub>t</sub>, of which, the cost of receiver, tower and particle elevators were 44.91 \$/kW<sub>t</sub>, 57.07 \$/kW<sub>t</sub> and 2.64 \$/kW<sub>t</sub>, respectively. Further efforts are necessary to better estimate the CaL process cost as TCES in CSP plants, especially regarding the solar receiver (calciner). This should include a scaling-up analysis from a pilot to commercial scale based on challenges and solutions found in prototypes testing. Once the first prototypes at pilot scale are developed a more accurate cost estimation should be pursued to properly assess the profitability of the system under several CSP technology future scenarios.

## 6. Conclusions

Dispatchability is a major technological challenge of CSP plants. As a possible solution the CaL process is a promising thermochemical energy storage system to store solar energy using as raw materials natural limestone or dolomite, which are abundant, low cost and non-toxic. These are necessary conditions for any large scale energy storage technology to be commercially developed.

Several international projects are concerned with the CSP-CaL integration. Traditionally, the usefulness of the CaL process to store energy has been underrated because of the multicyclic CaO deactivation commonly reported in lab-scale tests aimed at investigating the CaL process for CO<sub>2</sub> capture, which has already reached a large pilot-scale demonstration stage. However, recent studies are showing that CaO deactivation is highly dependent on the calcination and carbonation conditions (pressure, temperature, gas composition) particle size and the type of CaO precursor. In contrast to the CaL process for CO<sub>2</sub> capture, CaL conditions and particle physical properties for energy storage are flexible and may be tuned to optimize multicyclic effective conversion and process efficiency in a synergistic way. Thus, CaL conditions involving carbonation under pure CO<sub>2</sub> at high temperature can be found for which the residual multicycle conversion of limestone derived CaO is as high  $X=0.5$  provided that fine particle are employed (particle size < 45 $\mu$ m) to avoid pore plugging. In addition, the low price of natural CaO precursors would allow replacing periodically the solids by fresh materials.

Several CSP-CaL integration schemes have been proposed in the recent literature where some options such as the temperature of the storage tanks and different levels of complexity are considered. Remarkably, some of the equipment and systems to be employed in the CSP-CaL plant are well-known from the lime and cement industries (reactors, vessels, conveying systems, heat exchangers). Global plant efficiencies over 45% have been reported yet without considering the efficiency of the solar receiver as calciner which is a critical exclusive component of the technology that remains to be developed. Finding an optimized-design of the solar receiver as calciner is the main technological challenge of the process since its efficiency is critical for the overall performance of the plant. Several specific designs have been proposed in tested without finding a final solution that satisfies the main requirements of the equipment: scalability, high thermal efficiency and particles residence time long enough to complete the reaction. Advance in the solar receiver definition as well as analyze the economic viability of the process remains as main tasks to critically evaluate the huge potential of the CaL process as energy storage system in CSP plants.

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