Large-scale high-temperature solar energy storage using natural minerals

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## ARTICLE INFO

ABSTRACT – – –

The present work is focused on thermochemical energy storage (TCES) in Concentrated Solar Power (CSP) plants by means of the Calcium-Looping (CaL) process using cheap, abundant and non-toxic natural carbonate minerals. CaL conditions for CSP storage involve calcination of $CaCO_3$ in the solar receiver at relatively low temperature whereas carbonation of CaO is carried out at high temperature and high CO_2 concentration to use the heat of reaction for power production by means of a CO_2 closed power cycle. Under these conditions, large CaO particles derived from limestone to be used in industrial processes are rapidly deactivated due to pore-plugging, which limits the extent of the reaction. This is favored by the relatively small pores of the CaO skeleton generated by low temperature calcination, the large thickness of the $CaCO_3$ layer built upon the CaO surface and the very fast carbonation kinetics. On the other hand, at CaL conditions for CSP storage does not limit carbonation of CaO derived from dolomite (dolime). Dolime is shown to exhibit a high multicycle conversion regardless of particle size, which is explained by the presence of inert MgO grains that allow the reacting gas to percolate inside the porous particles.

1. Introduction

It is widely accepted that the massive deployment of power generation from renewable energy sources is one of the essential measures urgently needed to mitigate global warming [1]. Among the different renewable energies, concentrated solar power (CSP) offers the possibility of large scale electricity generation and relatively low cost energy storage in the form of heat for base load power generation. Nowadays, commercial CSP plants are capable of generating electrical power overnight from the sensible heat stored in molten salts [2–5]. In order to reach a large scale deployment stage, CSP with energy storage needs from cheaper massive energy storage technologies to compete against fossil fuel power plants [6–9]. In this context, *Thermochemical energy storage* (TCES) is being currently investigated as a possible alternative to CSP storage in molten salts. TCES basically consists of using the high temperatures achievable in CSP (up to ~1000 °C in CSP with tower technology) to carry out an endothermic chemical reaction. The by-products of the reaction are separately stored and brought together to carry out the reverse exothermic reaction on demand. Main general advantages of TCES systems are the high energy density potentially attainable and the possibility of storing energy in the long term [10–13]. Among diverse alternatives currently under research, the

Calcium-Looping (CaL) process based on the calcination/carbonation of $CaCO_3$ offers a great potential as it relies on the use of extremely cheap, widely abundant and non-toxic materials such as natural carbonate minerals [14].

The Calcium-Looping (CaL) process has been widely investigated in the last few years for CO_2 capture in coal fired power plants [15]. CO_2 capture is performed in this process by the exothermic carbonation reaction of CaO (Eq. (1)).

$$CaO_{(s)} + CO_{2(g)} \rightleftarrows CaCO_{3(s)}; \Delta H_r^0 = -178 kJ/mol \qquad (1)$$
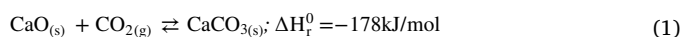
The reaction takes place inside a high temperature fluidized bed reactor (T~650 °C) wherein the post-combustion flue gas at atmospheric pressure carries a CO_2 concentration around 15% by volume. Once CaO particles are carbonated, they are transported into a second reactor (calciner) where CaO is regenerated by calcination under high CO_2 partial pressure and high temperatures (T~950 °C). Thus, CO_2 at high concentration can be extracted from the calciner to be compressed and sequestered or stored for other uses. The CaO particles regenerated from calcination are recirculated into the carbonator to be used in a new cycle.

The use of the CaL process in CSP plants for TCES was early proposed in the late 1970s [16–18] and has gained renewed interest in

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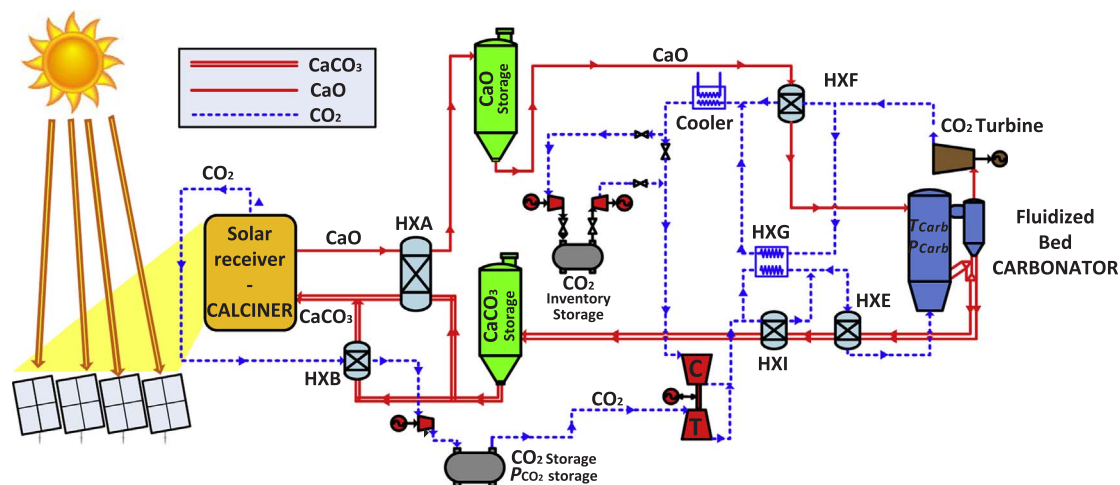 *E-mail address:* jmillan@us.es (J. Manuel Valverde).

Fig. 1. Calcium-Looping thermochemical energy storage system for concentrated solar power plants. The integration scheme is developed in Ref. [14], where the interested reader may find additional details.

the last years [11,14,19,20]. Fig. 1 shows an example of CaL-CSP integration scheme recently proposed with potentially high global efficiency [14,21]. The system essentially consists of a power unit, a solar calciner, a carbonator, a CO_2 compression-storage system and two reservoirs for both CaO and $CaCO_3$ storage. The process starts with calcination of $CaCO_3$ particles in a fluidized bed reactor (calciner) using concentrated solar energy as the source of heat. Once calcination occurs, sensible heat of the reaction products (CaO and CO_2) is recovered by heat exchangers before storing them separately. Conditions and time of storage can be adapted to power demand. When needed, CaO and CO_2 are circulated to the carbonator where the heat used for calcination is recovered through the carbonation reaction enthalpy. This heat is carried by the excess CO_2 not participating in the carbonation reaction to a gas turbine where electricity is generated in a closed cycle. According to process simulations [14], maximum efficiency CaL conditions for the integration into CSP plants according to this scheme are obtained when carbonation of CaO takes place at high temperature (above 850 °C) and under high CO_2 partial pressure. It must be remarked that these CaL carbonation conditions are radically different from the optimum conditions corresponding to the CaL process for CO_2 capture.

A potential improvement of the CaL-CSP integration consists of using He in the calciner for reducing the calcination temperature by the enhancement of thermal conductivity of the gas mixture and the great increase of CO_2 diffusivity in He [22,23]. The CO_2/He gas mixture exiting the calciner could be separated by selective membranes currently available at commercial scale [24], allowing the storage of CO_2 in compression tanks and the recirculation of He to be used in the calciner environment. The use of He in the calciner helps the calcination reaction to be fully achieved in short residence times at temperatures of just around 700 °C [21], which would make possible the use of relatively cheap solar receivers based on metal alloys in the calciner. Despite the high price and limited availability of He, it must be taken into account that this gas would be used in a closed loop. Further techno-economic analysis should be carried out in future works to assess the effect of possible He losses and membrane separation inefficiency.

Natural limestone (almost pure $CaCO_3$) is a widely available, low-cost (~10$/ton) and non-toxic CaO precursor that would help further reducing the cost of the CaL-CSP integration. However, a main potential drawback for the use of natural limestone at industrial scale is the rapid deactivation as widely observed in previous works [25,26] under CO_2 capture conditions. Agglomeration and sintering of the regenerated CaO grains under harsh calcination conditions needed for CO_2 capture drastically reduces the CaO surface area available for carbonation in

short residence times. Most of the strategies proposed to use CaO based sorbents for CO_2 capture involve doping and other treatments to counteract CaO sintering, but the compromise between improving the sorbent performance and the final cost of the technology necessarily requires the use of cheap natural carbonates [27]. On the other hand, a recent work has shown that carbonation/calcination conditions in the CaL process for CSP storage process yield a much higher residual conversion for natural limestone and dolomite derived CaO as compared to CO_2 capture conditions [21], which would lead to a high efficiency of the CaL-CSP integration. In the present work, we explore the influence of a critical parameter on the performance of natural carbonates under CaL-CSP conditions such as particle size. Generally, particle size plays a relevant role in industrial processes based on circulating fluidized beds (CFBs) relying on the efficiency of open cyclone exchangers for separation of the particles from the gas streams to transport solids between different reactors [14]. The collection efficiency of commercial cyclones drops dramatically for particles under ~10 μm in size [28]. Furthermore, the particles trajectories and residence time in the cyclones depend critically on their size. Thus, the typical particle size lower limit to ensure an acceptable efficiency of cyclones is around 50 μm [29].

Most of the investigations focused on the effect of particle size on CaO conversion during carbonation have been carried out under CO_2 capture conditions [30–32]. Under these conditions, the main limitation to carbonation concerning particle size is the diffusion of CO_2 molecules through the pores of the CaO particles. Intraparticle pore diffusion hinders carbonation for particles larger than about 300 μm [33,34]. Taking into account the limitations imposed by elutriation in commercial cyclones and pore diffusion the optimum particle size used in CaL pilot scale plants to capture CO_2 is in the range 100–300 μm [35–38].

Another important phenomenon that might limit gas-solid reactions concerning particle size is pore-plugging if the pore size is not sufficiently large and carbonation conditions lead to a very fast buildup of a thick $CaCO_3$ product layer on the surface of the CaO particles. At the harsh calcination conditions used in the CaL cycle to capture CO_2 for sorbent regeneration (high temperatures and high CO_2 concentration), the CaO structure becomes quite sintered with large pores (usually above ~100 nm) [39,40] as compared with the thickness of the carbonate layer built up on the surface (~40–60 nm) [41] during the chemically controlled fast reaction phase. Thus, pore-plugging rarely poses a limitation for carbonation under CaL conditions for CO_2 capture. In the present work, we investigate whether pore plugging might limit carbonation of natural carbonates in the CaL process at conditions for CSP storage detailed above. Under these conditions,