

Calcium-Looping performance of steel and blast furnace slags for thermochemical energy storage in concentrated solar power plants



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ABSTRACT

The Calcium Looping (CaL) process, based on the carbonation/calcination of CaO, has been proposed as a feasible technology for Thermochemical Energy Storage (TCES) in Concentrated Solar Power (CSP) plants. The CaL process usually employs limestone as CaO precursor for its very low cost, non-toxicity, abundance and wide geographical distribution. However, the multicycle activity of limestone derived CaO under relevant CaL conditions for TCES in CSP plants can be severely limited by pore plugging. In this work, the alternative use of calcium-rich steel and blast furnace slags after treatment with acetic acid is investigated. A main observation is that the calcination temperature to regenerate the CaO is significantly reduced as compared to limestone. Furthermore, the multicycle activity of some of the slags tested at relevant CaL conditions for TCES remains high and stable if the treated samples are subjected to filtration. This process serves to remove silica grains, which helps decrease the porosity of the CaO resulting from calcination in the mesoporous range thus mitigating pore plugging.

1. Introduction

The massive deployment of renewable energy technologies is an urgent need to limit global warming to 2 °C over pre-industrial values in 2100 as was agreed in the 21st Climate Change Conference COP21 [1]. A critical challenge is to find efficient, low cost and environmentally friendly energy storage technologies to manage the intermittency of solar and wind as main renewable energy sources. Concentrated Solar Power (CSP) is a rapidly growing technology wherein the implementation of large scale energy storage at relatively low cost would be feasible [2]. A relevant advantage of CSP is that energy can be massively stored in a primary form such as high-temperature heat usable for generating electricity on demand. The present paper deals with energy storage in CSP plants with central tower technology in which a number of heliostats are distributed on the ground to reflect direct solar radiation into a receptor placed at the top of a tower where temperatures up to about 1000 °C can be achieved.

In currently commercial CSP plants with energy storage, heat is transferred in the solar receptor to a fluid composed of a mixture of nitrate salts, usually sodium nitrate (NaNO₃) and potassium nitrate (KNO₃) in a 60/40 percent ratio (solar salt) of high heat capacity. The

solar salt is then transported into a hot salts tank where heat is stored as sensible heat (the energy density of solar salt is ~0.8 GJ/m³) [3]. Storage of heat using molten solar salts allows for about 15 h of autonomy in the absence of direct solar radiation [4]. However, the use of molten salts is hampered by their thermal decomposition at temperatures close to 600 °C [5]. Another inconvenient of molten salts is their relatively high freezing point, between 120 and 220 °C, which besides being a technological risk leads to relevant heat losses at night in deserted regions or high altitude areas where CSP technology allocation is more appropriate due to the elevated number of sun hours. A further drawback of solar salts is the impossibility of circulating them through standard conduction systems and valves because of their corrosiveness, which makes it necessary to use high cost materials [6,7].

An alternative to thermal energy storage (TES) as sensible heat for storing energy in CSP plants is thermochemical energy storage (TCES) [8,9] currently under research and development. TCES is based on the use of heat to carry out an endothermic reaction. When this energy is required, the separately stored by-products of the reaction are brought together to carry out the reverse exothermic reaction, which releases the previously used heat for power production on demand. Main advantages of TCES are the potentially high energy density as well as the

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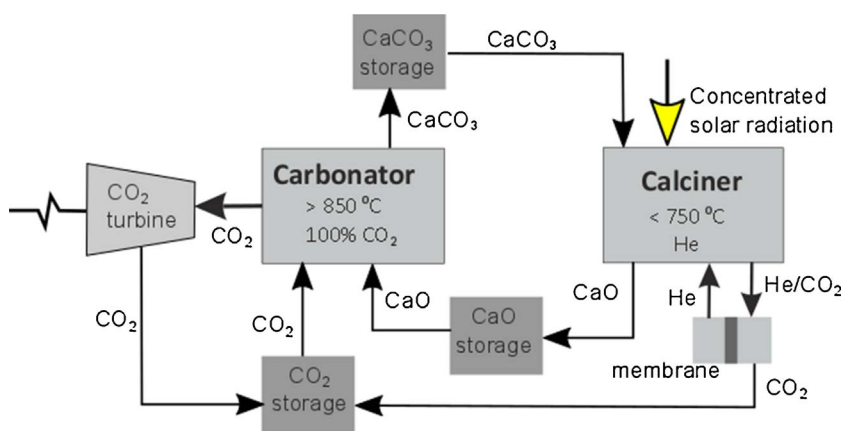


Fig. 1. Flow diagram for the integration of the Ca-Looping process in Concentrated Solar Power plants with central tower technology for thermochemical energy storage. A detailed description can be found in [12].

possibility of storing energy in the long term without losses. Moreover, in addition to the enthalpy of the chemical reaction, it is also possible to use the heat stored as sensible heat in the reaction products [4].

Among the diverse possibilities explored for TCES at large scale, one of the most promising technologies is the Calcium Looping (CaL) process, which relies on the carbonation/calcination reaction of CaO (Eq. (1)) [10].



The energy density that can be potentially stored by the CaO/CaCO₃ system in terms of reaction enthalpy and density of the material (~3.2 GJ/m³) is much higher than the sensible heat stored by solar salts currently used in CSP plants (~0.8 GJ/m³) [3]. Limestone is a natural CaO precursor abundantly available at low price (~10 €/ton), non-toxic and with a high CaCO₃ content (close to 100%), albeit the CaO derived from its calcination may present a progressive deactivation with the number of cycles depending on reaction conditions [11].

Fig. 1 shows a simplified flow diagram of a possible configuration for the CaL-CSP integration recently proposed elsewhere [12,13], which is based in a closed CO₂ cycle for carbonation and power generation by means of a Brayton cycle. The process starts with the calcination of CaCO₃ in a calciner reactor using concentrated solar power as the heat source. Once the sensible heat from the streams exiting the calciner (CO₂ and CaO) is recovered, these products are stored separately. When required, the streams of CaO and CO₂ are transferred to the carbonator, wherein heat is recovered from the enthalpy of the carbonation reaction. In the carbonator, CO₂ reacts with CaO at conditions to shift the reaction towards exothermic carbonation to produce CaCO₃. The process is designed in such a way that the CO₂ mass flow rate entering in the carbonator is well above the stoichiometric need. Thus, the CO₂ in excess that exits the carbonator is used as fluid carrier to evacuate the heat released by carbonation and is looped through the closed power cycle for generation of electricity. The interested reader in further details is referred to [12,13] for a rigorous mass-balance model of the plant taking into account the flow rates of solids and CO₂ streams between the carbonator and calciner and the energy integration analysis. One of the main advantages of this integration is that the time and the conditions for storage are flexible and could be adjusted according to the energy demand [12,13].

The calcination stage has an important role on the global efficiency of the process because for storing the highest amount of energy in sun hours decarbonation has to be fast and at the lowest possible temperature. The latter would allow the use of relatively cheap commercial solar receivers based on metal alloys thus reducing the cost and technological risk of the technology [14]. A possible choice to this end is to carry out calcination under a gas that could be easily separated from the CO₂ generated in this stage as could be He by using membranes [15,16]. Moreover, the high thermal conductivity of He and high CO₂ diffusivity in this gas serves to speed up the calcination reaction [17].

This would help full calcination of the solids in short residence times at temperatures around 725 °C in the case of limestone [18]. However, the calciner technology is not yet fully developed. Small prototypes of solar chemical reactors have been proposed for the production of lime based on fluidized beds [19,20], rotary kilns [21,22] and cyclone atmospheric reactors [23]. In the CaL-CSP integration the effluent gas stream from the calciner must be cleared of particles before sending it to the membrane for He/CO₂ separation. Thus, a cyclone separator should be used for removing the particulates from the gas mixture.

According to process simulations the CaL-CSP integration may achieve a high thermoelectric global efficiency provided that the multicycle CaO conversion is kept above 0.5 after a large number of cycles [12]. In this integration scheme, the operation temperature in the carbonator would be around 850 °C or higher to optimize the thermoelectric efficiency and carbonation would be performed under pure CO₂. However, the global efficiency of the process decays notably if CaO conversion is decreased below 0.2 [12]. As shown in a recent work, the multicycle activity of limestone derived CaO is notably limited by pore plugging at these CaL conditions for particles of size above ~50 μm to be employed in practice [11]. The relatively low calcination temperature used at CaL conditions for CSP storage leads to a highly porous CaO skeleton. And these small pores become rapidly plugged by the thick layer of CaCO₃ that forms very quickly on the CaO particles' surface at the high temperature and high CO₂ concentration employed for carbonation [11].

The CaL process has been widely studied in the last years for CO₂ capture in fossil fuel power plants, which has been successfully demonstrated in large pilot-scale plants (1–2 Mwth) [24–26]. In this application the CaL process is carried out in two interconnected fluidized bed reactors. In the first one, carbonation of CaO solids takes place at temperatures near 650 °C under a ~15% CO₂ vol. atmosphere, which is the typical concentration of CO₂ in the flue gas. Then, the solids are circulated into a second reactor at temperatures between 900 and 950 °C under high concentration of CO₂ for the calcination stage. In that way, almost pure CO₂ can be extracted from this reactor for its subsequent compression and sequestration. After this stage, the re-generated CaO particles are circulated back into the carbonator for a new CaL cycle. Process conditions in the CaL cycle for CO₂ capture such as the high temperature and CO₂ concentration in the calciner lead to a drastic loss in the activity of CaO in short residence times as the number of cycles progresses. It must be stressed that the main limiting mechanism for the multicycle CaO activity at CaL conditions for CO₂ capture is diverse from that limiting the CaO activity at conditions for CSP storage. In the former case, the multicycle sorbent activity is hindered by the severe sintering of the regenerated CaO at the harsh calcination conditions, which yields a drastic loss of its surface area and therefore a drop of activity in short residence times [27–29].

Besides of limestone, an abundantly available Ca based material that could be used to store CSP by means of the CaL process is steel slag.

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