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Calcium looping in solar power generation plants

Susan E.B. Edwards *, Vlatko Materić

Industrial Research Limited, Lower Hutt 5040, New Zealand

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Abstract

The use of a calcium looping based process as a thermal storage and transportation system for concentrated solar power plants is proposed in this work. This system exploits the reversible calcination–carbonation reaction of limestone and lime. Concentrated solar heat is used to calcine $CaCO_3$, which is then released as required by carbonating the resulting CaO. The $CaO/CaCO_3$ system has a high energy density and its high temperature operation allows the use of a gas turbine for power production. This paper presents a first order evaluation of the potential of this application of calcium looping, with particular consideration given to carbonation activity of the sorbent. A model including a solar calciner and a pressurised fluidised bed carbonator feeding a gas turbine in an open Brayton cycle has been developed. Results from the model indicate that electric efficiencies of 40–50% could be achieved with sorbent carbonation activities between 15% and 40%. Higher sorbent activity levels do not affect efficiency but would lead to lower capital costs. According to the model, CaO activity levels above 17% lead to significant reductions in the required storage volume over existing systems, such as molten salts. In principle, high efficiency and smaller footprint solar thermal power plants are possible with calcium looping. Such plants would have no process use of water and could be used as baseload, variable demand load or microgrid systems.

Keywords: Solar thermal power plant; Calcium looping; Calcium looping thermal storage; $CaO/CaCO_3$; Model

1. Introduction

Growing concern about the levels of carbon dioxide in the atmosphere has generated increasing interest in renewable energy sources to replace the dependence on fossil fuels. A significant proportion of fossil fuels are used in power generation, in both base load and peak load plants. In order to significantly reduce the production of carbon dioxide, renewable energies need to provide the equivalent of both base load and peak load power. Most renewable energy technologies are fundamentally cyclic or intermittent and there is a need to develop technologies that will allow power to be smoothed or balanced.

Solar thermal power is one renewable technology currently in active development. Parabolic troughs and solar towers, or central receiver systems, are the two systems that have proven themselves as technologically and economically feasible. Due to the degree of concentration of solar energy achieved in solar tower systems these typically operate at higher temperatures and efficiencies than parabolic trough systems. Several solar thermal power plants have reached demonstration plant stage (Geyer and Blanco, 1997; Lasich et al., 2009; Wang et al., 2010; Alexopoulos and Hoffschmidt, 2010).

A solar thermal power plant comprises a method of reflecting and concentrating solar radiation onto a solar receiver where energy is stored in a heat transfer medium. This medium is then transported to a power conversion unit such as a turbine. Solar plants do not produce carbon dioxide, or other combustion gases and particulates.

* Corresponding author.
E-mail address: s.edwards@irl.cri.nz (S.E.B. Edwards).

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However they only collect solar power during daylight hours. In addition to issues with power balancing, direct link solar power plants also require specialist turbines with quick start-up times (Larsen, 2010). Solar power plants commissioned so far have also tended to have quite low efficiency. This is in part due to the utilization of steam turbines at comparatively low temperatures.

A buffer energy storage between the solar receiver and the turbine would decouple these two units and the plant could be operated as a base load or variable demand load power plant. By averaging power over a 24 h period, the size and cost of the comparatively expensive turbine unit could be minimised and the need for frequent ramping of the turbine could be eliminated. Such technology could also allow for more feasible use of solar power for micro-grid power plant applications.

Table 1 contains a comparison of different heat storage methods. The storage volumes required for both sensible and latent heat methods are still large, and as both methods also involve progressive loss of energy over time they are not suitable for long term storage.

Thermochemical heat methods, or chemical storage, involve reversible chemical reactions. Thermochemical systems generally require higher temperatures to initiate storage of energy, but conversely provide higher temperatures on the release of that energy. They also have the highest energy density. Thermochemical methods involve quite stable energy storage media and are suitable for longer term storage of energy (weeks or months).

In this work, a novel CSP power plant concept is proposed which uses calcium looping for heat transport and storage. A simplified heat and mass balance model was developed to provide a first order estimate of the potential performance of such a plant and to determine critical parameters for its operation.

1.1. Calcium looping CSP plant concept

Fig. 1 shows the application of the calcium looping cycle to solar power plants. Solar heat is supplied to the calciner

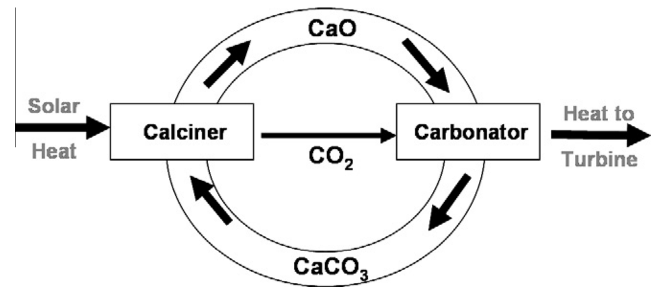

Fig. 1. The calcium looping cycle applied to solar power thermal transport and storage.

and used to heat and decompose particulate $CaCO_3$ (limestone/calcium carbonate) into CaO (lime) and CO_2 (carbon dioxide). In the carbonator, CaO and CO_2 recombine to form $CaCO_3$, and as a result release the heat of carbonation

$$CaO + CO_2 \leftrightarrow CaCO_3 \quad \Delta H_{(20^\circ C)} = -178.4 MJ/kmol \tag{1}$$

Given that the carbonation can be performed at high temperatures (600–900 °C, depending on the CO_2 pressure) it is possible and advantageous to use a gas turbine to produce electricity. In the concept proposed in this work, the heat of carbonation is transferred to an air flow which powers a Brayton Cycle to produce electricity as required. Fig. 2 shows a schematic of a calcium looping CSP plant. The plant contains two reactor units that operate independently. The solar calciner uses concentrated solar energy to start the calcium looping by heating the $CaCO_3$ and providing the energy required to split it into CaO and CO_2. The carbonator recombines the CaO and CO_2 releasing heat into the carrying air to transfer it to the gas turbine. In between these two units are storage vessels for $CaCO_3$, CaO and CO_2. These vessels can be sized to provide buffer storage so that the solar calciner can consume $CaCO_3$ and produce CaO and CO_2 during daylight hours, but the carbonator/turbine can run 24 h a day with varying load as required.

Table 1
Comparison of high temperature heat storage materials.

Thermal energy storage methods	Operating temp (°C)	Energy density (MJ/m^3)	Ref.
Sensible heat			
Silicone oil	300–400 °C	189	Gil et al. (2010)
Nitrite salts	250–450 °C	548	
Nitrate salts	265–565 °C	898	
Carbonate salts	450–850 °C	1512	
Liquid sodium	270–530 °C	287	
Latent heat – high temp molten salts	Phase change temp		
Sodium nitrite $NaNO_2$	270 °C	373	Tamme et al. (2008)
Sodium nitrate $NaNO_3$	307 °C	389	Gil et al. (2010)
Potassium nitrate KNO_3	333 °C	561	Pincemin et al. (2008)
Sodium carbonate Na_2CO_3	854 °C	701	Hoshi et al. (2005)
Thermochemical			
Iron carbonate $FeCO_3 - FeO + CO_2$	180 °C	2600	N'Tsoukpoe et al. (2009)
Calcium hydroxide, $Ca(OH)_2$–$CaO + H_2O$	500 °C	3000	Gil et al. (2010)
Calcium carbonate, $CaCO_3$–$CaO + CO_2$	800–900 °C	4400	Gil et al. (2010)