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# Power cycles integration in concentrated solar power plants with energy storage based on calcium looping

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## ABSTRACT

Efficient, low-cost and environmentally friendly storage of thermal energy stands as a main challenge for large scale deployment of solar energy. This work explores the integration into concentrated solar power plants of the calcium looping process based upon the reversible carbonation/calcination of calcium oxide for thermochemical energy storage. An efficient concentrated solar power–calcium looping integration would allow storing energy in the long term by calcination of calcium carbonate thus overcoming the hurdle of variable power generation from solar. After calcination, the stored products of the reaction (calcium oxide and carbon dioxide) are brought together in a carbonator reactor whereby the high temperature exothermic reaction releases the stored energy for efficient power production when needed. This work analyses several power cycle configurations with the main goal of optimizing the performance of the overall system integration. Possible integration schemes are proposed in which power production is carried out directly (using a closed carbon dioxide Brayton power cycle) or indirectly (by means of a steam reheat Rankine cycle or a supercritical carbon dioxide Brayton cycle). The results obtained show that the highest plant efficiencies (up to 45–46%) are achievable using a closed carbon dioxide Brayton power cycle.

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## 1. Introduction

The commercial expansion of renewable energy technologies is an urgent need to limit global warming to “well below” 2.0 °C (by 2100) and pursue 1.5 °C above pre-industrial levels as was agreed at Paris COP21 Conference [1]. In particular, Concentrated Solar Power (CSP) should play a leading role within the new energy landscape as it lends itself to potentially cheap storage of energy in the form of heat [2]. Thus, efficient and affordable thermal energy storage systems must be developed in order to decouple production and demand [3], which would allow a deep penetration of solar energy power generation into the grid.

In recent years a large number of potential thermal storage technologies for medium to high temperature CSP systems have been proposed [4] based upon three main concepts: (i) sensible Thermal Energy Storage (TES), such as direct steam storage [5] or molten salt systems [6]; (ii) latent heat storage using Phase Change Materials (PCMs), on which Zalba et al. [7] published a comprehensive review of materials and applications; and (iii) Thermochemi-

cal Energy Storage (TCES). Regarding TCES, a large number of potential systems [8], experimental research under practical conditions [9] and TCES reactor designs [10] can be found in the recent literature. Essentially, TCES consists of using the heat obtained from an external source, such as CSP, to drive an endothermic reaction. When energy is needed, the separately stored by-products of the reaction are brought together at the necessary conditions for the reverse exothermic reaction to occur, which releases the previously used heat for power production. The main advantages of TCES as compared to TES and PCMs are the considerably high energy density attainable, which is well above the energy density of molten salts currently used in commercial plants ( $\sim 0.5 \text{ GJ/m}^3$ ) [11], and the possibility of storing energy in the long term [8]. An extended review on long-term solar heat storage can be found in Ref. [12]. Moreover, in addition to the chemically stored heat, sensible heat stored in the reaction by-products is also usable.

The focus of the present manuscript is on TCES in CSP tower plants. In order to achieve an efficient and cost-effective thermochemical storage process, a proper selection of the reversible reaction is a crucial issue. Among the possibilities explored for TCES in CSP tower plants at large scale, one of the most promising systems is the Calcium Looping (CaL) process, which relies on the

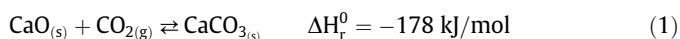
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## Notation

$c_{p,i}$	specific heat (kJ/(kmol K))	$T$	temperature (K)
$dT_{\min,HE}$	minimum temperature approach (°C)	$T_{carb}$	carbonator temperature (K)
$F_i$	molar flow rate of component $i$ (kmol/s)	$T_{in,CO_2}$	CO <sub>2</sub> temperature at carbonator inlet (°C)
$F_{CaCO_3}$	molar flow rate of CaCO <sub>3</sub>	$T_{in,CaO}$	CaO temperature at carbonator inlet (°C)
$F_{CaCO_3,carb}$	molar flow rate of CaCO <sub>3</sub> (carbonator side)	$T_{reheat}$	reheat temperature (Rankine cycle) (°C)
$F_{CaCO_3,clc}$	molar flow rate of CaCO <sub>3</sub> (calciner side)	$T_{vv}$	live steam temperature (°C)
$F_{CaO,carb}$	molar flow rate of CaO (carbonator side)	$W_{comp,1}$	compressor 1 power, sCO <sub>2</sub> (MW)
$F_{CaO,clc}$	molar flow rate of regenerated sorbent	$W_{comp,2}$	compressor 2 power, sCO <sub>2</sub> (MW)
$F_{CaO,unr,carb}$	molar flow rate of unreacted CaO (carbonator side)	$W_{turb}$	turbine power, sCO <sub>2</sub> (MW)
$F_{CaO,unr,clc}$	molar flow rate of unreacted CaO (calciner side)	$\dot{W}$	mechanical power (kW)
$F_{CO_2,clc,out}$	molar flow rate of CO <sub>2</sub> at calciner outlet	$X$	CaO conversion
$F_{R,carb}$	recirculating molar flow rate (carbonator side)	$X_{slp}$	split factor, sCO <sub>2</sub>
$F_{R,clc}$	recirculating molar flow rate (calciner side)	$\eta_c$	isentropic compressor efficiency
$h_i$	enthalpy (kJ/kmol)	$\eta_t$	isentropic turbine efficiency
HXA	solid-solid heat exchanger	$\eta_{integration}$	global integration performance
HXB	gas-solid heat exchanger	$\eta_{storage}$	storage performance
HXE	gas-solid heat exchanger	$\eta_{cycle}$	power cycle performance
HXF	gas-solid heat exchanger	$\eta_{cc}$	combined cycle performance
HXI	gas-solid heat exchanger	$\phi_{cycle}$	power cycle practicability
HXG	gas-solid heat exchanger	$\Delta t_{sun}$	average daytime period
$\dot{m}_{CO_2,carb}$	CO <sub>2</sub> mass flow rate through carbonator	$\Delta H_R(T_{react})$	heat of reaction at the reactor temperature
$\dot{m}_{solids}$	solids mass flow rate (kg/s)	$\xi$	extent of reaction per unit time
$P_{carb}$	absolute carbonator pressure (bar)	$\Phi$	heat flux
$Q_{input}$	thermal power input (MW)	$\Phi_{carbonation}$	available heat of carbonation
$P_{eq}$	CO <sub>2</sub> partial pressure at equilibrium (bar)	$\varepsilon_{rec}$	recuperator efficiency (%)
$PR$	pressure ratio	$\Delta P_{R,hot}$	pressure drop recuperator- hot side (%)
$P_{drop}$	pressure drops in CO <sub>2</sub> circuit, bar	$\Delta P_{R,cold}$	pressure drop recuperator- coldside (%)
$P_{vv}$	live steam pressure (bar)	$\Delta P_{R,HE}$	pressure drop heat exchanger- sCO <sub>2</sub> (%)
$y_{CO_2,carb,in}$	inlet molar fraction of CO <sub>2</sub> in the carbonator		
$P_{out,turb}$	outlet turbine pressure (bar)		
$y_{eq}$	equilibrium fraction of CO <sub>2</sub> in the carbonator		

carbonation-calcination reaction of calcium oxide (CaO) (Eq. (1)) [13]. The use of several CaO precursors for TCES in CSP plants has been analysed in [14].



Generally, the CaL process would begin with the decomposition of calcium carbonate (CaCO<sub>3</sub>) particulate solids in a calcination reactor (calciner) yielding CaO and CO<sub>2</sub> as by-products. A high energy input is necessary to rise the solids stream temperature up to the value required for the reaction to occur at a sufficiently fast rate and to carry out the endothermic calcination reaction [15]. Thus, the optimum calcination temperature is essentially determined by the composition of the gas in the calcination environment [16]. Once the sensible heat from the calciner outlet streams (CaO and CO<sub>2</sub> streams) is recovered, these products are separately stored. Storage conditions and time are flexible and could be accommodated to energy demand and environmental circumstances. When needed, the CaO and CO<sub>2</sub> products are circulated into a carbonator reactor, where energy is recovered from the carbonation reaction.

A great benefit of the CaL process is the low price (~10 \$/ton), wide availability and harmlessness towards the environment of natural limestone or dolomite to be used as CaO precursor [17]. However, a usually claimed drawback of the CaL process is the marked deactivation of CaO derived from these natural minerals with the number of carbonation/calcination cycles. CaO deactivation is indeed particularly relevant when the CaL process is used for CO<sub>2</sub> capture [18] under conditions that necessary involve regeneration of CaO by high temperature (around 950 °C) calcination at high CO<sub>2</sub> partial pressure and carbonation at low CO<sub>2</sub> partial

pressure (~0.15 bar). Nevertheless, CaL conditions to achieve a high global efficiency for TCES and electricity generation in CSP plants can be radically different to those corresponding to its application for CO<sub>2</sub> capture [19]. In the CSP-CaL integration, carbonation would be carried out under high CO<sub>2</sub> partial pressure and high temperature (around or above 850 °C) whereas calcination could be ideally performed at relatively low temperature (~700 °C) under a gas easily separable from CO<sub>2</sub> such as Helium [16] or superheated steam [20]. Under these conditions, CaO derived from natural limestone or dolomite may exhibit a high value of the residual conversion [19].

In addition to enhancing solar energy storage capacity, advanced high efficiency CSP-TEs-power cycle integrations should be developed exploiting energy storage conditions to achieve a significant improvement of CSP plant performance. Integration of power cycles in commercial CSP tower plants with thermal storage in the form of sensible heat using molten salts is limited by a maximum temperature achievable around 550–600 °C. This limitation is mainly imposed by the degradation of molten salts at higher temperatures [21]. In recent years, molten alkali carbonates salts (MACs) have been investigated for energy storage. According to Frangini et al. [22], temperature stability of additives limits the applicability of oxidizing MAC salts at temperatures below 650 °C. On the other hand, thermal radiation losses at the open focal point [23] adds a further temperature limitation in currently CSP plants. This implies that most of the commercial CSP tower plants currently under operation are based in Rankine cycle process [24]. Peak solar to electricity conversion efficiencies in these commercial CSP tower plants are around 25–30%, with an annual solar-to-electricity conversion efficiency lower than 20% [25]. In

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