

Power generation based on the $\text{Ca}(\text{OH})_2/\text{CaO}$ thermochemical storage system – Experimental investigation of discharge operation modes in lab scale and corresponding conceptual process design



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HIGHLIGHTS

- Experimental investigation of thermal discharging in a lab scale reactor.
- Operation of storage system at 4–470 kPa and temperatures of 280–600 °C.
- Demonstration of operation modes at boundary conditions to drive a Rankine cycle.
- Analysis of power generation with CaO and water and assessment of storage efficiency.

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ABSTRACT

Thermochemical storage systems offer in theory promising advantages for a wide range of applications. In particular the reversible reaction of calcium hydroxide to calcium oxide and water vapour is intensively discussed as an alternative storage solution for concentrated solar power plants. The material is cheap, environmentally friendly and discharge temperatures of the reaction of 600 °C and above fit to the operating range of today's power plants. However, experimental data on the operation of the system in lab scale and at load conditions comparable to the real application is rarely reported.

Therefore the thermal discharge of the reaction system at vapour pressures between 4 and 470 kPa and temperatures between 280 and 600 °C is experimentally investigated in this study. In particular the influence of the cooling load at various vapour pressures on the achievable discharge temperatures is analysed. The presented data complements the experimental characterisation of the reaction system in the complete temperature and pressure range which is relevant for real process applications. Based on this knowledge the applicability of the storage for various processes can now be assessed more accurate. By means of the experimental results a first integration option of the thermochemical system in a CSP plant is proposed in this work and thermodynamically analysed. The analysis revealed that, when the required steam production during discharge is thermally integrated into the Rankine steam cycle, a high storage efficiency of up to 87% can be reached compared to only 60% in the reference case.

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1. Introduction

Concentrating solar power (CSP) plants can produce electricity completely renewable and free of carbon dioxide emissions. Since this technology converts solar irradiation into thermal energy in the first step a combination with large scale thermal energy storage system allows the decoupling of the availability of solar energy from the electricity production.

Until today, the parabolic through technology is the most advanced, with the greatest number of commercial plants in operation [1]. However the central receiver tower technology with molten salt as heat transfer fluid is gaining importance because they operate at higher maximum temperatures of currently 565 °C and the molten salt can directly be stored in large tanks with minimal losses [2,3]. Large molten salt tower plants like the Gemasolar (20 MWe and 15 h storage) in Spain or the Crescent Dunes plant (110 MWe and 10 h storage) in the US have been recently set into operation and more plants based on this technology are currently under development.

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Nomenclature

CSP	concentrated solar power	V	valve
cp	specific heat capacity	ϑ	temperature measurement point, thermocouple
EV	evaporator	X_{tot}	conversion
EX	extraction point	%w	weight percentage
F	filling level	d_{50}	median diameter of the particle size distribution
HEX	heat exchanger	$\dot{V}$	volume flow
HTF	heat transfer fluid	$\dot{Q}$	thermal power output
LP	low pressure	$\dot{n}$	molar rate of reaction
PH	preheater	$\dot{m}$	mass flow rate
P	electrical power output	η	efficiency
p	pressure	ΔH	enthalpy change
TCS	thermochemical system	$M_{\text{H}_2\text{O}}$	molar mass
T	temperature		

The direct two tank molten salt system is the state of the art storage system for today's CSP plants. Nevertheless in a typical configuration the salt itself accounts for around 50% of the cost of the storage system [4]. In order to reduce the costs researchers investigate alternative thermal storage solutions [5]. In the thermocline concept for example the expensive salt is partly replaced with inexpensive filler materials and only one storage tank is used [6]. Besides these approaches for cost reduction in sensible storage systems also latent [7–9] and thermochemical systems are gaining importance. Recently published review articles give a comprehensive overview of high temperature thermal storage technologies, their state of development and potential applications [10–14].

Among the thermal energy storage methods thermochemical systems offer in theory a very promising potential [15,16]. Some of the reaction systems have high energy densities, the storage principal itself is free of losses and especially the temperature at which the heat is released can be adjusted in a certain range [17,18]. A recent survey of thermochemical storage technologies and their level of maturity is given by Pardo et al. [19] and Prieto et al. [20].

One reaction system suggested for CSP applications is the reversible reaction of calcium hydroxide to calcium oxide and water vapour. First of all, the material is very cheap and abundantly available in industrial scale. Combined with the high enthalpy of reaction the material offers in principle a very cheap storage capacity. Secondly the theoretical temperature range of the reaction between 300 °C and up to 600 °C fits to the operating range of the plant. Thirdly, the gaseous reactant, water vapour, can safely be handled and stored volume efficient as liquid water.

Despite these advantages the technology development is still in an early research state. The majority of the works focus on investigations with small sample masses in thermogravimetric apparatus. Cycle stability has first been proven by Rosemary for 1171 cycles [21]. Kinetic equations for the de- and rehydration have been derived by several authors [22–24] and the development of simulation models is still ongoing [25,26]. Other groups focus on the modification of the material in order to enhance the reaction rate [27], adapt the reaction temperatures [28], or to encapsulate the storage material in a permeable shell [29]. These investigations on the material level are important to improve the fundamental understanding of the reaction system. But for the development of a thermochemical storage systems additional experimental research in larger reactors and under process relevant boundary conditions is essential.

In lab and pilot scale set-ups two different type of reactor concepts are currently realized. One is the so called directly heated concept where the heat transfer fluid is in direct contact with the reacting particles. Pardo et al. carried out the reaction in a fluidized

bed for 1.9 kg of material composed of 30 %w $\text{Ca}(\text{OH})_2$ and 70 %w inert easy to fluidize particles [30]. Criado et al. presented a theoretical study on a fluidized bed concept for large CSP plants [31] while recently the group proofed the concept experimentally in a newly constructed lab scale set up [32].

The second concept is the so called indirectly heated reactor where the heat transfer fluid is physically separated from the storage material and the thermal energy is transferred via a heat exchanging surface. Experimental data on the operation of indirectly heated reactors is rather scarce. Ogura et al. firstly presented a reactor where heat from the exothermal reaction was transferred to an air flow at ambient temperature [33] and Yan et al. performed the exothermal reaction at different vapour pressures but the reactor did not allow the recovery of the released heat [34]. Even though these investigations are helpful to understand the reaction in larger scale, the experiments do not sufficiently represent the required operation modes of an indirectly heated storage system in the real application. In case of thermal energy storage both the endo- and exothermal reaction will be thermally driven by the heat transfer fluid and the reaction system has to be operated in a pressure and temperature range which depends on the boundary conditions of the process only.

Fig. 1 shows the theoretical equilibrium line of the reaction calculated by values from Barin [35] as well as the upper and lower

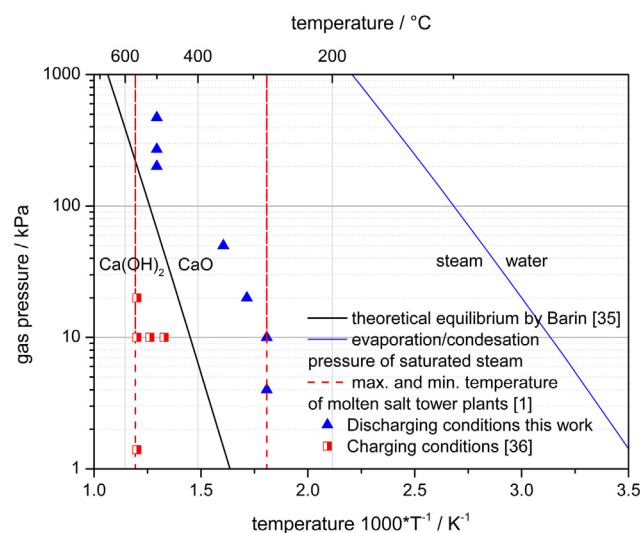


Fig. 1. Equilibrium line of the reaction system $\text{Ca}(\text{OH})_2/\text{CaO}$ and operating temperature range of molten salt; experimental conditions of the presented experiments in this work.

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