



# Thermochemical energy storage with CaO/Ca(OH)<sub>2</sub> – Experimental investigation of the thermal capability at low vapor pressures in a lab scale reactor



Matthias Schmidt<sup>a,\*</sup>, Andrea Gutierrez<sup>b</sup>, Marc Linder<sup>b</sup>

<sup>a</sup> German Aerospace Center – DLR e.V., Institute of Technical Thermodynamics, Linder Höhe, 51147 Köln, Germany

<sup>b</sup> German Aerospace Center – DLR e.V., Institute of Technical Thermodynamics, Pfaffenwaldring 38, 70569 Stuttgart, Germany

## HIGHLIGHTS

- Development of a novel indirectly heated reaction bed for thermochemical energy storage.
- Experimental demonstration of thermal charging and discharging at low vapor pressures (1.4–20 kPa).
- Experimental study of the reaction at various heating and cooling loads of the heat transfer fluid.
- Identification of operational limits under some technically relevant boundary conditions.

## ARTICLE INFO

### Article history:

Received 24 August 2016

Received in revised form 18 October 2016

Accepted 7 November 2016

Available online 21 December 2016

### Keywords:

Thermochemical energy storage

Calcium hydroxide

Calcium oxide

Operation modes

Low vapor pressures

Thermal charging and discharging

## ABSTRACT

The reversible reaction of calcium hydroxide (Ca(OH)<sub>2</sub>) to calcium oxide (CaO) and water vapor is well known in the context of thermochemical energy storage. Cheap material costs, a theoretically very high energy density and the potentially wide temperature range of the reaction imply that the storage system could be beneficial for many high temperature processes. For example the system could be applied to store and reutilize industrial waste heat or as an alternative storage solution in future concentrated solar power plants.

In this publication the reaction is experimentally investigated in an indirectly operated fixed bed reactor at different technically relevant but so far not investigated operating conditions. This in particular means the thermal charging and discharging of the storage at low water vapor pressures under different heating and cooling loads induced by a heat transfer fluid. The experiments revealed that the reaction gas handling not only affects the operating range of the storage but has also a significant influence on its thermal capability. Especially at low vapor pressures operational limits of the system have been identified and could be contributed to the effective reaction rate of the reaction material which is in the relevant operating range very sensitive to small changes of the local reaction conditions.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Thermochemical energy storage by means of the reversible gas solid reaction of calcium hydroxide (Ca(OH)<sub>2</sub>) to calcium oxide (CaO) and water vapor offers several advantages. Firstly, calcium hydroxide is a cheap industrial mass product abundantly available all over the world. Secondly, the enthalpy of reaction is high which leads to high possible energy storage densities. Thirdly, the charge and discharge temperature of the reaction can theoretically be

adapted in a wide range (approx. 300–650 °C). Thus the application of the system could potentially be beneficial for many high temperature processes such as the storage and reutilization of industrial waste heat [1] or as an alternative storage solution in future concentrated solar power plants [2–5].

The reaction system has been examined in many studies but the majority of the studies focus on the thermal analysis of small sample masses. Already in 1979 Rosemary and his colleagues demonstrated cycle stability of the reaction for 1171 cycles [6]. Until today different research groups derive kinetic equations from de- and rehydration experiments carried out in thermogravimetric devices [7–9]. Beyond that other groups focus on the modification

\* Corresponding author.

E-mail address: [Matthias.schmidt@dlr.de](mailto:Matthias.schmidt@dlr.de) (M. Schmidt).

### Nomenclature

HEX	heat exchanger	t	time
TGA	thermogravimetric analysis	$\vartheta$	temperature measurement point, thermocouple
P	pressure	$\dot{V}$	volume flow
T	temperature	$X_{\text{tot}}$	conversion
F	filling level	$d_{50}$	median diameter of the particle size distribution

of the material in order to adapt the reaction temperature [10], enhance the reaction rate [11], improve powder bed properties [12], or to achieve mechanically stable pellets [13]. Simulation models based on the kinetic equations and the theory of porous media have also been established [14,15].

Besides these investigations on the material level, reports on experiments with lab scale reactors are scarce. Schaubé et al. demonstrated the operation of a fixed bed reactor where the material is in direct contact with a gas mixture of air and water vapor [16]. Pardo et al. carried out the reaction in a fluidized bed reactor using a mixture of  $\text{Ca}(\text{OH})_2$  and 70 wt% inert easy to fluidize particles [17]. Yan et al. recently reported experiments with 400 g of material in a fixed bed set up. They analyzed the hydration reaction at different vapor pressures but the reactor concept did not allow the recovery of the released heat. Furthermore the dehydration reaction was driven by an electrical heating jacket [18].

All of these concepts have their special advantages and are worth investigating since at the current state of development an optimal reactor design is not available. However, some process applications require an indirectly heated concept. For example, if the heat transfer fluid of the process is liquid or a direct contact of the flue gas and the storage material could cause impurities. In both cases thermal energy has to be transferred via a heat exchanging surface that separates the reaction from the heat transfer fluid – a so called indirect concept. An additional advantage of this concept is that the reaction temperature can be adapted independently from the power output of the reactor. This in conclusion leads to more flexible operating modes and thus could extend process integration possibilities.

However for indirectly heated reactor concepts there is even less experimental data available. Ogura et al. were the first who demonstrated a concept where the heat released during the exothermic reaction was transferred via a heat exchanger to an air flow at ambient temperature [19]. The dehydration step though was still performed in a furnace. The first concept in which not only the discharging but also the charging step was driven by an indirect coupling of the reaction bed with a heat transfer fluid was presented from our group in a previous publication [20]. On one hand the reactor showed good performance especially for the discharge at reaction gas pressures of 100 kPa and higher. On the other hand the design of the reaction bed limited the operating range of the reactor. Particularly at low vapor pressures (e. g. 10 kPa) the performance during charging and discharging was significantly limited. We mainly contributed this limitation to the mass transfer of the reaction gas due to the low permeable reaction bed and its height of 200 mm.

Nevertheless, as soon as energy efficient process integration is considered, the operation of the storage system at low vapor pressures is of high technical relevance. There are two main reasons for that. Firstly, the dehydration at lower vapor pressures results in a lower reaction temperature. As a consequence we can use lower grade heat to charge the storage. Secondly, the hydration at lower vapor pressures requires only a reduced evaporation temperature. Therefore the enthalpy of evaporation can more likely be supplied by waste heat available from the process. On the other hand, operating the system at low

vapor pressures makes the reactor design more challenging and requires larger pipe diameters for the vapor connections. Thus it finally depends on the specific process if an operation at lower or higher pressure levels is more promising.

Fig. 1 shows the experimentally obtained equilibrium lines of the reaction system  $\text{Ca}(\text{OH})_2/\text{CaO}$  from Schaubé [8] and Samms [21] as well as the theoretical equilibrium line based on thermochemical values from Barin [22]. In addition reported onset temperatures, determined in thermogravimetric measurements from Schaubé [8] and Matsuda [23] are displayed as well as the results of equilibrium measurements performed by Halstead [24] in an appropriate test bench. It is obvious that within the important operating range for indirect concepts at low vapor pressure (marked as grey area), the results vary significantly. This may be on one side contributed to differences in the used material but on the other side also the measurement principle itself (e.g. dynamic or static) might have an influence.

In order to investigate the reaction for thermochemical storage under technically relevant operating conditions, we designed a novel reaction bed with minimized mass transfer limitations but a sufficient mass of reactive material to investigate thermal capabilities. With this reactor we performed several charging and discharging experiments at low vapor pressures and analyzed the influence of different heating and cooling loads induced by a heat transfer fluid. The operating conditions for the kg-scale experiments presented in this study are marked in Fig. 1 by the red triangles for the dehydration and the red squares for the hydration. For the analysis of the results, the experiments in lab-scale were complemented by thermogravimetric measurements in mg-scale with the same material.

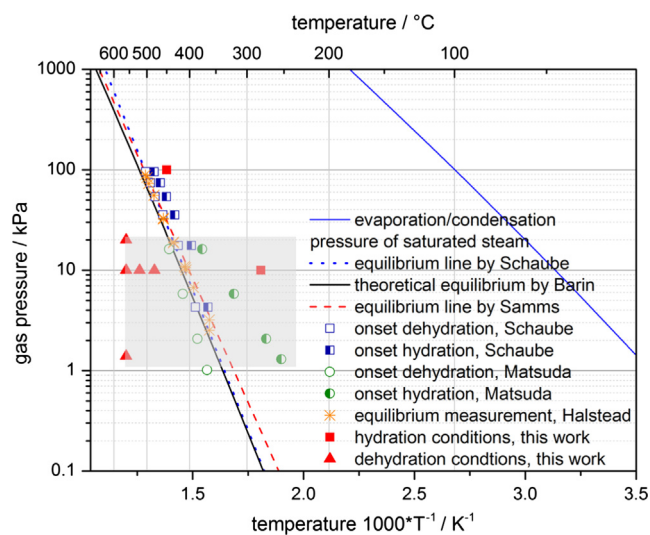


Fig. 1. Thermodynamic equilibrium lines for the  $\text{Ca}(\text{OH})_2/\text{CaO}$  reaction system and operating conditions of the performed experiments; evaporation/condensation pressure of saturated steam.

Download English Version:

<https://daneshyari.com/en/article/4911164>

Download Persian Version:

<https://daneshyari.com/article/4911164>

[Daneshyari.com](https://daneshyari.com)