Experimental results of a 10 kW high temperature thermochemical storage reactor based on calcium hydroxide

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HIGHLIGHTS

- Multifunctional test bench and indirect operated reactor developed and in operation.
- Proof of principal for a 10 kW, 20 kg calcium hydroxide thermochemical storage reactor.
- Several charge and discharge cycles were performed at adjustable storage temperatures.

ARTICLE INFO

ABSTRACT

One promising possibility to store thermal energy is by means of reversible gas solid reactions. In this context, the endothermal dehydration of calcium hydroxide ($Ca(OH)_2$) to calcium oxide (CaO) is a well known, cycle stable reaction able to store heat at temperatures above 410 °C and pressures above 0.1 bar. Additionally, the storage material itself is a widely available low cost raw material which allows for low cost thermal energy storage capacities. Therefore, a multifunctional test bench for thermochemical storage reactors has been developed and set into operation. Simultaneously an indirect operated reactor for ~20 kg $Ca(OH)_2$ was designed, manufactured and integrated into the test bench. Within this work the charge and discharge characteristics of the reactor concerning possible limitations due to heat and mass transfer were studied experimentally. Thereby, the possibility to store and release the heat of reaction at an adjustable temperature level was demonstrated in a technical relevant scale. The storage material remained stable and showed no degradation effects after ten cycles.

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1. Introduction

Efficient thermal energy storage systems for high temperatures at reasonable costs are essential for the economic success of concentrated solar power and increase efficiency through the recovery of waste heat in industrial processes. An overview on the wide variety of thermal storage methods and possible applications is given by Dincer et al. [1]. The thermochemical storage of heat using gas—solid reactions offers several advantages compared to conventional sensible and latent heat storage methods: storage densities are higher, thermal losses are minimal and heat can be transformed within a certain temperature range through the variation of the partial pressure of the gaseous reactant. Additionally,

application of different reaction systems with adjustable equilibrium temperatures offers the possibility to adapt the storage temperatures to the respective process needs.

So far, salt hydrates have been characterized as suitable candidates for heat storage in the temperature range between 20 and 200 °C [1—3] while several metal hydroxide systems are considered to cover a temperature range between 250 and 600 °C [4,5]. However, especially regarding the high temperature applications, available literature deals in general with thermal analysis measurements [7—9] of a few gram sample or investigations in small scale laboratory reactors with a maximum of 400 g of storage material [10—14]. The behavior of a 20 kg reaction bed in an indirect operated reactor is still unclear and therefore experimentally investigated in this work.

Due to the good availability at low cost and its favorable temperature range, previous work at DLR focused on the reversible dissociation reaction of $Ca(OH)_2$:

$$Ca(OH)_2(s) + \Delta H_{reaction} \leftrightarrow CaO(s) + H_2O(g) \qquad (1)$$
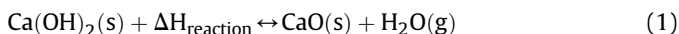
Complete reversibility, cycling stability and sufficiently fast reaction kinetics of the system have been demonstrated in thermal gravimetric analysis studies [8]. No degradation effects have been observed after 100 performed cycles. Consequently, the material can be considered as long term stable, if side reactions during handling or storage of larger bulks can be avoided. Furthermore, the high reaction enthalpy of about 100 kJ/mol and the adjustable temperature range between 410 °C and 520 °C make the system a promising candidate e.g. for application in concentrated solar power plants [6].

However, besides the thermochemical characterization of the storage material, efficient and upscalable reactor concepts need to be developed. In a directly operated reactor the heat transfer fluid (HTF) flows through the reaction bed offering good heat transfer but high pressure drop. In order to avoid high pressure drop, the HTF can be physically separated from the storage material by an integrated heat exchanger. Disadvantageous with this indirectly operated reactor concept is that heat transfer into the reaction bed is poor, due to the generally low thermal conductivity of the storage material bulk of 0.1 W/mK.

Schaube et al. demonstrated the feasibility of the directly operated reactor concept in laboratory scale [11]. However, because of the high pressure drop of the powder bed an upscaling of this concept is considered uneconomical. Therefore an indirectly operated reactor was designed and manufactured. Simultaneously a multifunctional test bench capable to investigate different thermochemical reactors was build and set in operation at DLR [15].

In order to investigate the reaction material in larger scale, this study focuses on hydration and dehydration cycles of this indirectly operated reactor in pilot scale (20 kg of CaO). The reached temperatures of the HTF and the bed are measured for both cycle directions and the amount of stored and released heat is balanced. The coherency between the applied steam partial pressure and the temperatures reached in the reaction bed is shown experimentally and corresponds to the theoretically calculated values. In principle, a peak power mode, where the maximum thermal load was observed and a nominal power mode, where a smaller load was supplied for an extended time, were realized for the discharge of the storage reactor.

2. Experimental setup

2.1. Reactor concept

For the experiments in this work an indirectly operated reactor based on a plate heat exchanger concept (see Fig. 1) was
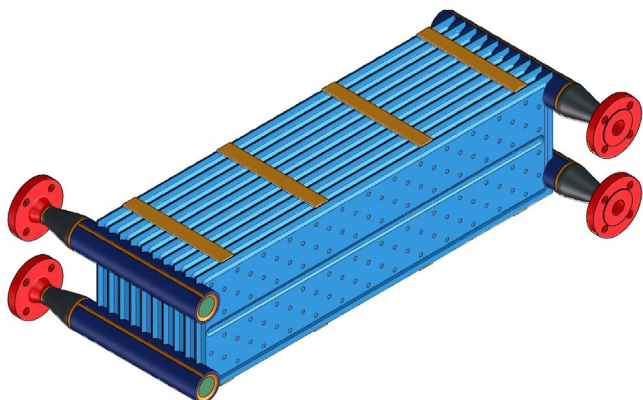

Fig. 1. Schematic of the indirectly operated reactor [16].

Table 1
Specifications of the reactor.

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Material (reactor and thermoshelves):	1.4404 − X2CrNiMo 17-12-2
Metal weight:	145 kg
Reaction bed dimensions:	45 l (~25 kg Ca(OH)$_2$)
	20 × 200 × 850 mm (10 channels)
Max. permissible temperature:	600 °C
Max. permissible pressure:	Reaction gas side: 0.1–2.5 bar
	HTF side: 0–5.0 bar
Thermoshelves:	1.5 × 250 × 850 mm (10 shelves)
	4.25 m^2 total heat transfer area
Power:	$P_{Nominal}$ = 5 kW$_{th}$
	P_{max} = 10 kW$_{th}$
HTF mass flow:	$\dot{m}$ = 0.00283–0.0531 kg/s
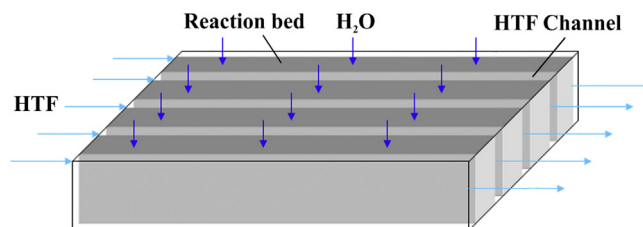
Fig. 2. Schematic of the cross flow design of the pilot reactor [15].

manufactured and integrated into the test bench. Characteristic numbers of weight, volume and permissible temperatures are given in Table 1. All parts of the reactor are made from a high temperature alloy (see Table 1). Based on prior operating experience with a laboratory reactor [11], we do not expect corrosion problems.

On the right side the HTF, in this case air, enters the reactor at the two flange connections. The HTF flows through ten spot-welded thermoshelves which distribute the flow uniformly over the reactor height (Fig. 1). Between the thermoshelves the storage material is placed in the 20 mm wide channels (Fig. 2). Along the length of the reactor the HTF takes up or releases heat to or from the powder bed and leaves the reactor at the opposite site.

The water vapor enters or leaves the reaction chamber through an inlet pipe placed in the center of the cover plate. A 30 mm gap between the inlet and the surface of the bulk ensures uniform distribution of the reaction gas. This cross-flow arrangement between the HTF and the reaction gas allows for sufficient heat exchange area along the length of the reactor while the reaction gas only has to overcome a short distance through the reaction bed to the bottom of the reactor (Fig. 2). Thus, the pressure drop over the reaction bed is minimal and a uniform equilibrium temperature over the entire bed volume can be expected.

To observe the reaction front and to identify possible limitations due to heat and mass transfer of the gaseous reactant 21 thermocouples (type K, class 1, 2 mm) are installed inside the reaction bed. Fig. 3 shows the position of the thermocouples in the reactor. 13 thermocouples ($T_1 - T_{13}$) are installed in the central channel along the direction of flow in various depths. Additionally, one thermocouple is installed in each of the 8 parallel channels ($T_{14} - T_{21}$).

2.2. Material sample

For the experiments in this study, calcium hydroxide by HeidelbergCement Group is used. It is a commercial product, called "lime hydrate ip500", which is mainly applied in building industry for the mortar production but also in food and paper industries. It is produced by slaking calcium oxide with water.