



Investigations of nano coated calcium hydroxide cycled in a thermochemical heat storage



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ABSTRACT

Thermochemical heat storage systems are a promising new technology for concentrated solar power plants and can contribute to improve the efficiency of industrial processes Neveu et al. (2013) [21]. However, for example for the reaction system calcium oxide/calcium hydroxide (CaO/Ca(OH)₂), the good availability at low cost is accompanied by poor powder properties that demand complex reactor solutions. During thermochemical cycling agglomeration effects occur and originate inhomogeneity resulting in permanent changes of bed characteristics especially related to the heat and mass transport. One approach in order to stabilize the material is to coat the reacting material with nanoparticles in order to minimize attractive forces leading to less agglomeration. But, high temperatures, change of volume and surface configuration, permeance for reaction gas, side reactions and mechanical stresses within the storage represent challenges for nanoparticles. Therefore, in this work, Aerosil® as additive for thermochemical storage is investigated during cycling in an indirect operating pilot-scale thermochemical reactor with regard to side reactions, stability on the surface and various coating configurations. It is shown that the reaction bed properties can be highly improved depending on the modality of the insertion process whereas occurring side reactions lead to a stabilization of the surface structure at the expense of a capacity loss of the thermochemical reactor.

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1. Introduction

Increasing energy prices and the shortage of resources demand an increasing share of alternative energy sources as well as a more reasonable utilization of the available energy. Thermal energy storage can contribute on the one hand to reach higher efficiencies in industrial processes and on the other hand to enable base load capability for regenerative energy production, e.g. in concentrated solar power (CSP) plants [21]. Besides sensible and latent heat storage, thermochemical storage possesses great potential with regard to energy density which is up to 400 kWh/m³ (370 kWh/t) and long-term storage behaviour [1]. A further advantage is the possibility to transform heat in order to utilize available temperature, pressure or concentration differences and allows for higher discharging temperatures as required temperatures for the charging process. An appropriate high-temperature reaction system working in a temperature range from 400 to 600 °C is the CaO/Ca(OH)₂ system [22]:



The decomposition of fine-grained Ca(OH)₂ to its educts, fine-grained CaO and water vapour, under the impact of heat is termed charging process. Afterwards the two educts are stored separately. The reverse exothermic reaction step is called discharging process, where CaO and gaseous H₂O get in contact thereby releasing thermal energy. For a partial pressure of 1 bar the equilibrium temperature corresponds to 505 °C [2]. In an indirect operational mode, the heat of reaction has to be transported through the powder bed to heat exchanger surfaces that are in contact with a heat transfer fluid (HTF). So, on the one hand the thermal conductivity, dependent on the bulk density, through the reaction material plays an important role. But on the other hand the bulk density of the material cannot exceed a certain limit since the reaction gas has to reach every region in the reactor sufficiently. In order to ensure both, a homogeneous distribution of the single particles within the reaction bed is required. But, agglomeration effects within the fine-grained bulk material lead to a continuous growing of the particles during the cycling of the material [3]. These agglomeration lumps affect both the heat as well as the mass transfer through the bulk material [4]. Since in this case, material properties are not constant

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and can hardly be estimated, the modelling and the development of thermochemical heat storage is all but impossible if a homogeneous distribution of the particles is not given.

In order to solve this problem two main approaches are known in literature [5]. One is to artificially increase the size of particles by pelletizing or structuring the material in order to prevent further agglomeration processes. However, due to volume changes of the single particles during the reaction, these structures break during intensive cycling which leads to smaller particles, again with a comparable agglomeration tendency [6]. So far, larger particles of $\text{Ca}(\text{OH})_2$ have not been cycle stable. Another approach is to increase the surface roughness of the particles in order to decrease the Van-der-Waals forces [7]. In bulk industries several flow agents are known in order to improve the powder flowability mainly for better handling properties [8,9]. However, for thermochemical heat storage, the additives have to keep their reducing effect during intensive cycling. So, they have to resist temperatures up to 600 °C and their impact should still be efficient – even after size or rather shape changes of the host particles during the chemical reaction. Furthermore, the chemical reaction should take place in the presence of these additives and in anticipation of a large-scale application they should be offered at a low price.

For this purpose, silicium dioxide (SiO_2) nanoparticles, brand name Aerosil[®], by Evonik Industries are applied. They are commonly used in food and drug industries as flow agents. The substantial difference for the coating process performed in this work is the inorganic character and the fissured irregular shape of $\text{Ca}(\text{OH})_2$ particles. So, whereas amounts up to 1 w% are sufficient in bulk industries, a generally higher addition is necessary for a sufficient decrease of Van-der-Waals forces.

In literature, one application is discussed to a carbon dioxide (CO_2) capture process [10]. The nanoparticles are used to improve the fluidization behaviour of the $\text{Ca}(\text{OH})_2$ bulk material [11]. However, in the latter case, SiO_2 nanoparticle agglomerates are actually used as host particles. The $\text{Ca}(\text{OH})_2$ particles acting as guest particles are then attached to their surface. Therefore, an addition of up to 30 w% of Aerosil is required which is clearly too high for thermochemical heat storage applications since it affects both the storage density of the material as well as its cost [12]. Possible side reactions between $\text{Ca}(\text{OH})_2$ and SiO_2 to calcium silicates by pozzolanic reactions have been reported, however the initial positive effect on the mechanical properties of the powder is conserved during cycling [15]. Side reactions of less quantity of Aerosil and $\text{Ca}(\text{OH})_2$ were not observed in a previous study by the authors in a thermochemical reactor with direct flow-through concept at German Aerospace Center (DLR) [5].

2. Material and methods

2.1. Calcium hydroxide

Commercially available $\text{Ca}(\text{OH})_2$ has been used for the experiments presented in this work. The material is produced by the company “Heidelberger Kalk” and distributed as “ip 500 Weißkalkhydrat CL90-S”. The material properties as supplied by the manufacturer are summarized in Table 1:

Table 1
Material properties of $\text{Ca}(\text{OH})_2$.

True density	2240 kg/m ³
Purity	97%
Bulk density	470 kg/m ³
BET-surface	13 m ² /g
Mean diameter	50 μm
Heat capacity ($\text{Ca}(\text{OH})_2$)	1200–1600 J/kg

The unmodified material was filled into six channels of the reactor (compare Section 2.3). Whereas the 4 remaining channels have been filled with the material which was preliminary mixed with Aerosil[®] nanostructured particles as described in Section 2.2. The distribution of the different material compositions in the reactor channels is shown in Table 2.

In total 18.83 kg of material was filled into the reactor therefrom 0.45 kg Aerosil[®] 300 nanoparticles, furthermore abbreviated with A300, and 18.38 kg $\text{Ca}(\text{OH})_2$.

2.2. Aerosil

Aerosils (abbreviated A) are commonly used as flow agents in bulk industries. The hydrophilic version A300 was applied in this work. Their primary particle size is 7 nm and their density is similar to the one of $\text{Ca}(\text{OH})_2$. At a temperature of 1000 °C the loss on ignition is less than 2 w%.

In order to cover the particle surface of the $\text{Ca}(\text{OH})_2$, a dry mixing process was chosen. Thereby, an intensive mixer by Eirich breaks up the agglomerates of nanoparticles and coats the particle surfaces of $\text{Ca}(\text{OH})_2$ with the nanoparticles. The extend of coating can in principle be influenced by mixing time, intensity and the amount of added nanoparticles. The mixing time was fixed to 5 min each, whereas two different mixing intensities for an amount of 10 w% A300 are investigated: 500 U/min and 7200 U/min of the agitator. In general, a lower intensity of the mixing leads to larger nanoparticle agglomerates that are fixed to the surface of the $\text{Ca}(\text{OH})_2$ particles, whereas a high mixing intensity results in a well distributed nanoparticle layer on the surface of the $\text{Ca}(\text{OH})_2$ particles.

2.3. Test reactor

To investigate the bulk behaviour of the modified storage material an indirectly operated reactor available at the DLR test facility was used [13]. The reactor is based on a plate heat exchanger concept shown in Fig. 1.

The storage material is placed in ten 20 mm × 200 mm × 800 mm channels each separated by a heat exchanger plate (Fig. 1 left). The HTF (air) from the supply unit enters the reactor at the two flange connections and flows inside the heat exchanger plates taking up or delivering the heat of reaction. Then the HTF leaves the reactor at the opposite side. The reaction gas enters the reactor through the pipe placed in the centre of the cover (Fig. 1, right). At this pipe an additional tube bundle heat exchanger is connected. In this tube bundle heat exchanger the reaction gas can be condensed or evaporated at adjustable vapour pressures.

So, the test reactor allows for an operation of 10 identical channels in parallel. Since all channels are supplied with water vapour from the top, the experimental boundary conditions for the material samples are identical.

Table 2
Distribution of storage materials in the reactor channels.

Channel	Material	Mass (kg)
1	$\text{Ca}(\text{OH})_2$ + 10 w% Aerosil [®] 300 (mixed with high intensity)	1.26
2	$\text{Ca}(\text{OH})_2$ + 1 w% Aerosil [®] 300 (mixed with high intensity)	2.03
3	$\text{Ca}(\text{OH})_2$ + 10 w% Aerosil [®] 300 (mixed with low intensity)	1.16
5–10	Non modified $\text{Ca}(\text{OH})_2$ as specified in Table 1	12.58

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