



Semipermeable encapsulation of calcium hydroxide for thermochemical heat storage solutions



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ABSTRACT

Thermochemical heat storage concepts offer a promising contribution to an efficient, economic and sustainable future energy supply. One of the most considered reaction systems for Concentrated Solar Power (CSP) applications is the system $\text{CaO}/\text{Ca}(\text{OH})_2$. In contrast to the cost efficiency and good availability of this material, its poor powder properties advise to complex and therefore costly reactor solutions. Thus, this work presents an approach for the design of the storage material as an adaption to its utilization in moving bed reactors. Options for particle size stabilization are discussed and criteria for the selection of encapsulation materials are derived. In order to prevent agglomeration of the cohesive storage material powder during thermochemical cycling by stabilization of the particle size in the micrometre-range, a method for a novel encapsulation of pre-granulated $\text{Ca}(\text{OH})_2$ with a ceramic shell is developed. To ensure the required transport of steam through the shell material, a semipermeable ceramic material is investigated. Basic physical material properties of the encapsulated storage material are determined and compared to the granulated $\text{Ca}(\text{OH})_2$ and to the ceramic as reference materials. By investigation of the porosity and the microstructure of the encapsulated storage material, it is shown that by the encapsulation process a porous and throughout closed shell around the storage material is formed. Thermochemical cyclability over ten reaction cycles is proven by thermal analysis. The elemental phase composition is examined qualitatively and quantitatively before and after thermochemical cycling, giving the storage material content and information about possible side products. As expected, a loss in storage capacity of the storage material is not observed. Considering the overall sample mass, the specific storage capacity is lowered correlative to the amount of inert ceramic capsule material. By measurements of the crushing strength (CS) it is shown, that upon ceramic encapsulation, the mechanical stability before and after thermochemical cycling is significantly increased.

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1. Introduction

The utilization of alternative energy sources and the increase of efficiency of conventional energy sources gains in importance as energy prices increase, conventional resources as mineral oil and coal run short and the climate change got into collective awareness.

A fundamental issue concerning the efficiency of alternative energy sources is the discontinuous power generation. In order to enhance the efficiency of alternative energy sources, load peaks in power generation have to be retained (André et al., 2016). The potential of CSP was calculated based on NASA data for the annual direct normal sun irradiation on various regions on the earth and

could reach a global technical potential of 3,000,000 TW h/year (Trieb, 2009).

Yet, the most developed for thermal energy storage are sensible and latent technologies. Sensible storage systems store heat by a temperature change of the storage material. Beside temperature, the storage density depends on the mass and the specific heat capacity of the storage medium. In case of latent storage systems, heat is stored by a phase change of the medium and the storage density depends beside the mass of the medium on the specific latent heat of the phase change, which is either a transition from solid to liquid or solid to solid phase (Miró et al., 2016; Li and Zheng, 2016; Abedin, 2011). In comparison to sensible and latent heat storage, thermochemical storage is based on the enthalpy of reversible chemical reactions, offering possibilities of low losses and long term, even seasonal storage, with comparatively high energy densities in the range of 400 kW h/m^3 (370 kW h/t)

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(Schaube et al., 2012; Lefebvre and Tezel, 2017; Cot-Gores et al., 2012; Michel et al., 2012; Haider and Werner, 2013). However, among all three thermal storage technologies, thermochemical energy storage is yet the less developed (Prieto et al., 2016).

Due to its ratio of raw material costs (~ 100 EUR/t) to energy density (~ 450 kW h/m³), the reaction system CaO/Ca(OH)₂ is one of the most considered for thermochemical energy storage among metal oxide reaction systems in the high temperature range since its first citations by Wentworth in 1976 and Ervin in 1977 (Schaube et al., 2012; Cot-Gores et al., 2012; Fujimoto et al., 2002; Ervin, 1977; Azpiazu et al., 2003; Pardo et al., 2014; Aydin et al., 2015; Wentworth and Chen, 1976).



$$\Delta H_R = -104.4 \text{ kJ/mol} \quad (\text{Schaube et al., 2012})$$

$$T_{eq} = 505 \text{ }^\circ\text{C at } p_{\text{H}_2\text{O}} = 1 \text{ bar} \quad (\text{Schaube et al., 2012})$$

Using the example of CaO/Ca(OH)₂, the working principle of thermochemical reaction systems can be divided into charging and discharging processes. The first process corresponds to the thermal decomposition of calcium hydroxide into calcium oxide and steam as reaction products. During the latter process, CaO and water are recombined under formation of Ca(OH)₂ under the release of heat equal to the reaction enthalpy (Eq. (1)).

For technical implementations of the storage material in reactor systems, beside the intrinsic material characteristics, its bulk properties play a major role for the transport of heat and mass during thermochemical cycling. Concerning the transport of heat through fixed reaction beds, one drawback is the low thermal conductivity of the powdery storage material of around 0.11 W/(m K), as measured by the authors for a Ca(OH)₂ powder bulk of 1 kg using a Heat Flow Meter (Netzsch, HFM 436 Lambda). Upon compaction of the powder, the thermal conductivity can be increased up to 0.5 W/(m K), while at the same time mass transport through the powder in the reaction bed is reduced due to a strong pressure drop. But since a homogeneous flow of steam as reaction gas is required, compaction of the powder must not exceed a certain limit. Additionally, the formation of agglomeration lumps during thermal cycling leads to a formation of channels within the reaction bed, causing an inhomogeneous flow of the reaction gas (Schaube et al., 2013). In contrast, fluidized reaction beds offer the advantage of enhanced heat transfer. Yet, the cohesiveness of the powder counteracts an implementation in such reactor types (Geldart, 1973). A modification of the material seems to be promising in order to enhance its flowability and to stabilize its particle size, maintaining constant material properties over a multitude of reaction cycles. Thereby, suitable modifications could ensure a homogeneous particle distribution by prevention of agglomeration effects, as required for fixed reaction beds, or stabilize particles as a whole either for moving or fluidized reaction beds. Requirements for the mechanical stability of modified storage materials have to be defined considering mechanical stress in a respective reactor type. While in fluidized reaction beds beside impacts of individual particles also strong abrasive forces emerge, thermochemical cycling in moving reaction beds is comparatively gentle to the material.

Up to now, only a few approaches for particle stabilization of thermochemical storage materials are described in literature. In order to avoid losses in storage density, the most obvious option for particle size stabilization is a shaping of the pure storage material in form of granules or pellets of appropriate size. But due to the significant changes in molar density and molar volume going along with the thermochemical cycling of Ca(OH)₂, shaped particles

decompose quickly upon repeated de- and rehydration (thermochemical cycling) (Eq. (1)).

Fuji et al. developed a kinetic model for the decomposition of Ca(OH)₂ pellets and validated their theoretical approach with experimental measurements and a description of the breakage of pure and Cu-, Zn- and Al-doped pellets of the storage material (Fujii et al., 1994). Thereby, it was observed that Al-doped pellets retain their shape for one reaction cycle. Pure and doped pellets decomposed after repeated cycling, resulting in a fine grained powder with a strong agglomeration tendency. Similar results upon aluminium doping of calcium oxide based materials were recently reported by Sakellariou et al. (2015). These approaches are summarized in Fig. 1 as shaping of the storage material.

For a reduction of van der Waals forces between individual particles in a powder, the application of flow enhancing agents is described (Zhou et al., 2011; Mullarney et al., 2011). In order to stabilize individual particles within a fine grained powder of Ca(OH)₂, the effect of admixture of flow enhancing nanostructured SiO₂ by a dry mixing process has been investigated (Roßkopf et al., 2014, 2015). It was shown, that before thermochemical cycling the flowability of the overall powder is significantly increased. Agglomeration of this material during thermochemical cycling within a fixed reaction bed is slightly reduced compared to the pure storage material. This effect was ascribed to the formation of a partial coating of the micro-scaled storage material particles ($d_{50} \approx 10 \mu\text{m}$) with calico-chondrodite side product. However, the storage density was significantly reduced due to the formation of a calcium silicate phase as side product. The calcium silicate phase formed under hydrothermal conditions at temperatures above 500 °C (Buckle and Taylor, 1958) is inert towards dehydration under the applied temperature and steam pressure during thermochemical cycling (Roßkopf et al., 2015). It was stated, that the coating effect is not dependent on the size of particles (all Geldart class C powders), but on their chemical composition and on milling parameters as milling speed and duration (He and Schoenung, 2002). These approaches are regarded in this work to correspond to a micro-encapsulation of powder particles (Fig. 1).

Besides a coating of the fine grained storage material with nanostructured additives, composite materials are described where powder particles are precipitated in or mixed with a matrix as carrier material. One approach is presented by Shkatulov et al., where Mg(OH)₂ as storage material is precipitated in expanded vermiculite (Shkatulov et al., 2012). But since the work from Shkatulov was focused on the lowering of the storage materials decomposition temperature, the mechanical cycling stability of the material was not investigated. Other investigations are reported for the bulk modification of salt hydrates for thermochemical energy storage where beside agglomeration effects also melting and deliquescence of the storage material under operating conditions are limiting factors for the bulk performance. Therein, the impregnation of porous carbon and vermiculite with storage material is described and improved de- and rehydration behaviour as well as improved heat conductivity of the overall material was

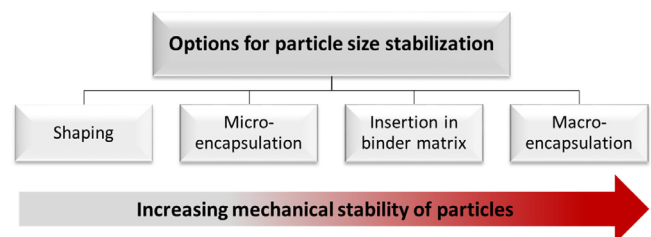


Fig. 1. Options for particle size stabilization of materials for thermochemical energy storage ordered by mechanical stability.

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