

Reactor Cycling of Granulated $\text{Ca}(\text{OH})_2$ Encapsulated with Chemically Modified Semipermeable Shell Materials

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One major scientific challenge is a shift of the energy generation and utilization towards sustainability and efficiency. Therefore, thermochemical heat storage concepts offer a promising contribution as for example by integration in Concentrated Solar Power (CSP) applications. The reaction system $\text{Ca}(\text{OH})_2/\text{CaO}$ is seen as a superior candidate but its poor powder properties yet hinder a technical implementation. The authors have recently proven, that these obstacles can be overcome by a persistent particle size stabilization of the pre-granulated storage material. Within the present study, the mechanical capsule material properties are improved by admixing of additives to the powdery precursor. By thermochemical conversion in a laboratory reactor, the cyclability and the suitability for moved reaction beds of the storage material is proven. The investigations are complemented by attrition tests on the most promising sample material and an encapsulated reference material. It is shown that the chemically enhanced encapsulation is a suitable approach to retain good flow properties and reduce attrition significantly. An encapsulated sample with an enhanced shell material composition containing 5%(w/w) of diatomaceous earth and 1%(w/w) of flux agent is found to be of superior stability over ten thermochemical cycles. A comparative macroscopic evaluation of the sample material after tenfold thermochemical cycling emphasizes the potential of this approach.

Introduction

The total available capacity of concentrated solar power (CSP) installations has increased significantly in the past decade, multiplying from 0.5 GW in 2008 to around 5.5 GW in 2018 [1,2]. In order to obtain further deployment of CSP installations, the use of large-scale heat storage systems is essential [3]. To overcome limitations due to temporal intermittency in energy generation and balance volatility in energy supply, either a backup system (fossil fuel, biomass) or an energy storage system is needed. With an added deployment of 0.5 GW in 2018, Concentrated Solar Power (CSP) growth is seen mostly in emerging economies especially in Morocco and South Africa [2]. Investment costs remain high, hence further deployment needs a better remuneration of storage capacity [4]. The development of an efficient and cost-effective storage system is crucial for the next step of prospective and profitable CSP technologies.

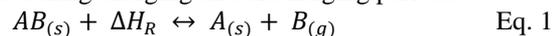
Suitable energy storage technologies for CSP applications include basically thermal energy storages (TES), which are seen in general as one key component to increase the efficiency of energy generation from renewables [5].

TES can be separated into three basic principles:

1. Sensible – Simple heating of the storage medium
2. Latent – Utilizing the enthalpy of a phase transitions

3. Thermochemical – Utilizing the reaction enthalpy reversible chemical reactions

Besides several other advantages, thermochemical energy storage offers storage capacities up to five times higher than latent or sensible storages. However, this group of storages is the yet the least developed technology [6]. While sensible or latent storage solutions store heat isothermally and thus have to be insulated elaborately to extend storage periods, thermochemical energy storages (TCS) utilize reversible chemical reactions. Yet, reversible gas – solid reactions are the most considered in this field (Eq. 1). Therefore, these systems provide the advantageous possibility to separate the charged, decomposed solids phase from the gaseous reactant during storage periods. Hence, energy dissipation is limited to sensible losses of the reactants during charging and discharging periods.



To release the stored reaction enthalpy ΔH_R in form of heat and to reform the initial, discharged solid phase AB, the charged solid phase A and the gaseous reactant B are being recombined. As known, the system specific equilibrium temperature can be influenced by adjusting the partial pressure of the gaseous reactant. This effect can be utilized to expand the application of the technology from storage to heat transformation. Out of several reversible gas-solid reactions suitable for utilization as

thermochemical energy storages [6-9], the hydration/dehydration of $\text{CaO}/\text{Ca}(\text{OH})_2$ has emerged as a suitable candidate for use in CSP applications, since the specific equilibrium temperature of the reversible reaction is similar to the temperature level of the steam cycle and the material features several crucial advantages. It combines high cost efficiency, environmental sustainability with cycling stability [10,11], fast reaction rates and a high reaction enthalpy of 104 kJ/mol [11-13]. Since the 1970s the strong exothermic reaction of quicklime (CaO) and water, which is added as a gaseous reactant to form calcium hydroxide ($\text{Ca}(\text{OH})_2$) is subjected to research [14-15] with regard to an implementation in several TES applications.

Within the context of thermochemical energy storages, fixed and moving bed reactors are discussed as possible reactor systems for future technical implementations in literature [16-18]. In fixed bed reactors, the storage material bulk is thermochemically cycled without internal movement and remains in the reactor, which also serves as a silo. Without material movement or mixing within the reactor and due to the fact that a gas flow through a fine bulk layer results in a high pressure drop [19], heat and mass transfer are highly limited in this setup. However, due to their relative simplicity, fixed bed reactors are still a good choice for lab-scale testing of respective storage materials. The thermochemical heat storage in a rotary tube reactor is critically evaluated by the authors due to high parasitic losses of the system, increased effort in ensuring gas tightness at transitions between rotating and stationary parts as well as due to the challenges in avoiding high sensible heat losses across the outer walls of the rotating reactor. All of these factors increase the complexity of a thermochemical storage reactor considerably and, according to the authors, cannot be compensated by the variety of positive properties mentioned. While in literature proof of concepts are oftentimes limited to fixed bed reactors, the present work pursues the approach to achieve the separation of capacity and power output by moving the material through a reactor, thereby increasing the level of technological readiness (Fig. 1). The potential of the high storage density of the reaction system cannot be exploited by a fixed bed since the scale up of the power output of a fixed bed reactor system is tied directly to an increase of the specific investment costs of the reactor. Moving reaction beds, especially fluidized beds, are known for enhanced heat transfer properties and offer the general advantage that reacted material can be carried out during the process to be stored elsewhere. While separate storage of the reactants in inert atmosphere ensures a loss-free storage of the charged CaO phase, the continuously fed reactor allows an efficient process and reaction control unattached to the storage capacity. Thus, substantial cost savings for the storage system can be obtained with an individually adapted dimensioning of the reactor depending on the application [37].

Considering the potential solutions for the design of a reactor for thermochemical energy storage mentioned above, it becomes apparent, that future research has to

pursue strategies to enhance the flow properties of the reaction system. This concerns the solids flow in a moving bed reactor as well as the fluid flow of the gaseous reactant through the reaction bed in different reactor designs. The reason for this necessary adaptation is the small particle size of the powdery bulk material. Combined with mechanistic features of the de- and rehydration of the system $\text{Ca}(\text{OH})_2/\text{CaO}$ this leads to a reduction of the primary particle size well below the value of 20 μm [36], further promoting a cohesive behavior of the reactant [20].

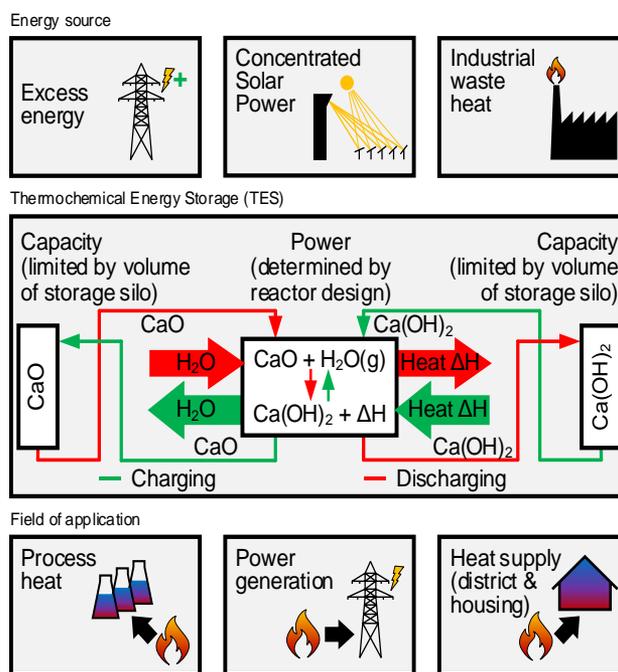


Fig. 1. Scheme of the separation of storage power and capacity using the example of the reaction system $\text{CaO} / \text{Ca}(\text{OH})_2$ and embedding of the TES in the energy supply infrastructure.

Table 1 points out the main advantages and disadvantages of exemplary reactor designs considered in literature. A particle size of below 20 μm represents a crucial benchmark in the context of fluidized beds as Geldart highlights in his basic work on gas fluidization [27]. Regardless of the density difference between the solids and fluid phase, a bulk with a mean particle size below the limit of 20 μm is practically not fluidizable due to the cohesive interactions of the particles. As pointed out above, repeated reversible reactions do not affect the particle size significantly. While agglomeration of primary particles may lead to the formation of secondary particles with a particle size above 20 μm , mechanical forces resulting from expansion and contraction of the material during thermochemical cycling as well as attrition due to the movement of the material during charging or discharging, e.g. in a fluidized bed, cause the disassembling of the agglomerates. The key problem in attaining technical maturity is thus the conversion of the powdery raw material into a usable form for technical application.

Table 1. Qualitative comparison of exemplary reactor designs on how they meet the required criteria for a suitable thermochemical energy storage system (The pursued approach is highlighted and further reading is indicated).

Reactor design \ Criteria	Fixed bed	Moving bed	Rotary kiln	Fluidized bed
Direct heat exchange	[19]			[21]
Indirect heat exchange	[17, 22 - 23]			
Energy dissipation				
Storage density				[13]
Potential scale up				
Control & distribution of residence time			[24]	
Material strain / attrition				[10, 25]
Required material modifications	[19]	[6, 26]		[6, 27, 28]

Legend:

bad	below average	average	good	excellent
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In **Table 2** the advantages and disadvantages of different strategies to enhance the material properties in order to obtain a technically implementable material are comparatively enlisted.

Table 2. Qualitative comparison of different approaches to enhance material properties of a thermochemical energy storage material and how they meet fundamental requirements for a technically implementable thermochemical energy storage system (The pursued approach is highlighted and further reading is indicated).

Modification \ Criteria	Un-modified	Pelletization	Flow enhancing additives	Semi-perm. encapsulation
Thermal stability				
Chemical inertness / side products				
Mech. stability		[18, 26, 29, 30]		
Heat transfer	[31]		in fluidized bed	
Mass transfer of gaseous reactant	[31]	[30]		
Handling of solids phase	[27]	[18]	[13, 33]	
Storage density			[13]	

Legend:

bad	below average	average	good	excellent
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The unmodified material offers several advantages that emphasize the basic suitability of the material for thermochemical energy storage e.g. thermal stability, cycling stability and a high storage density. However, in addition to the flow properties, the low mechanical stability of secondary particles as well as the poor thermal conductivity are adverse. Considering the resulting negative effects on heat and mass transfer, it can be stated that the kinetics proven by Schaube *et al.* [12] in laboratory scale cannot be transferred to a packed bulk. As an alternative to constructive degrees of freedom directly in the reactor, the heat and mass transfer can be improved by chemical adaption of the thermochemical storage material ([9] referring to [32]). Pelletizing or granulating the raw material is a conceivable strategy that has already been subject to research. However, for thermochemical energy storage this method alone is not suitable, since the chemical reaction is accompanied by a rapid change of volume. After a few reaction cycles this causes a breakage of the pellets or granules, leading back to small particle sizes, e.g. to a highly cohesive powder [26]. The current state of research is that in all approaches contemplated, the use of external additives is considered to be beneficial for increasing the mechanical stability of pellets or granules [29], and is being investigated in order to improve the overall material properties. However, a relatively simple approach to facilitate the fluidization of the storage material by adding easy-to-fluidize Al₂O₃ particles [13] shows, that the influence on the material properties by additives is accompanied by a significant reduction of the storage density of around 70%. Recent literature also indicates limitations of the positive effects due to the addition of nanostructured flow agents [33]. Another negative effect accompanying the usage of additives is the possible unintended formation of side products under the conditions applied during thermochemical cycling. Especially in case of large contact area between the storage material and the additive, the formation of thermochemically inert side products can consume the storage material to a significant extent. For example the approach reported by Roßkopf *et al.* [31] of stabilizing the particle size of powdery Ca(OH)₂/CaO (d₅₀~10 µm) by coating with nanostructured SiO₂ leads to a pronounced formation of inert side products after only ten thermochemical cycles. And thus a large part of the materials storage capacity is lost without retaining the positive effect of avoiding agglomeration.

A novel approach is the persistent stabilization of the pre-granulated storage material in the millimetre range by encapsulation with a semipermeable ceramic material. The shell material provides an open porosity which facilitates the transport of the gaseous reaction partner during charging and discharging while, due to the small pore sizes in the µm- to nm-range the storage material particles are kept inside. Since a persistent particle size during

thermochemical cycling is mandatory for use in a moving bed reactor, this specific modification is intended to combine properties of advanced mechanical durability with improved flow properties. Previous results from the successful proof of principle [34] are promising so that research on further optimization of the shell material seems reasonable and is, beside the investigation of cyclability in reactor scale as well as attrition resistance, focused in the present work.

Experimental

Materials

A commercial, pre-granulated $\text{Ca}(\text{OH})_2$ (Sorbacal H90, Rheinkalk GmbH) was used as raw material for the reactive particle core. The starting template consists of grains with diameters between 1 mm and 4 mm. The main component for the shell is a commercial powdery dry ceramic precursor (FT-E, Sibelco Deutschland GmbH). As adhesion promoting agent between the storage material core and the ceramic precursor, high-viscosity paraffin oil (Ph. Eur., Car Roth GmbH) was used.

For optimization of the shell's properties during cycling, e.g. its mechanical stability as well as its porosity, additives were admixed to the ceramic precursor. Material optimization is generally possible with regard to different parameters. While in principle the improvement of the thermal conductivity is also conceivable through the addition of substances offering high thermal conduction. In this work additives are utilized with the aim of optimizing the mass transfer by tuning the porosity of the shell as well as its mechanical stability by enhancing the formation of a denser microstructure of the amorphous glass phase contained in the ceramic shell after sintering. These both parameters are seen as the most critical features for reaching the next stage of technological maturity (see [34]). However, both properties are mutual competitors. On one hand, the mechanical stability of the particles must be sufficient to withstand abrasion forces, inter-particle impacts as well as impacts between the particles and the reactor walls as well as the significant change in molar volume accompanying the charging and discharging reactions of the contained storage material. On the other hand, mass transfer of the gaseous reactant must be ensured to enable thermochemical cyclability. For this reason and since a mutual influence of the selected additives is expected, each two additives were combined in different concentrations within a design of experiments (DoE), to find an optimum in mechanical stability and semipermeability. The following sections lists the selected additives and briefly explains their expected, favourable influence on the shell materials properties.

Flux agent (F)

An essential factor for the durability of the encapsulated granules is the formation of the glass phase on the outer surface of the shell during the sintering process. In order to densify the microstructure of the glass phase at constant

sintering time and hence to minimize the risk of cracking, the effect of a flux agents is investigated. In the present work, Na_2CO_3 (purity $\geq 99\%$, Carl Roth GmbH) is added to the shell material precursor of respective samples.

Activated carbon (C)

Since a densified glass matrix may decrease to pore size as well as the overall porosity, activated carbon (Carl Roth GmbH) was admixed to respective samples. During sintering, these particles are oxidized, thereby forming pores in the microstructure of the shell.

Diatomaceous earth (D)

Another option to support the implementation of porous structures into the outer glass phase is the addition of diatomaceous earth (Kieselgur, Carl Roth GmbH). It seems also reasonable to assume that the admixture of this tube structured SiO_2 improves the mechanical stability by enhancing the coalescence of the shell material in the course of the sintering process.

Sample declaration

In the present work, sample names are abbreviated with according to the type and concentration of the respective two additives. A prior number provides the first additive concentration in $\%(\text{w}/\text{w})$ followed by a letter determining the type of the first additive. A second number provides the next additive concentration in $\%(\text{w}/\text{w})$ followed by a letter determining the type of the second additive (F: Flux agent, C: Activated carbon; D: Diatomaceous earth).

Encapsulation and sintering process

The encapsulation process started with weighing of the raw materials into separate vessels with a ratio of 5:3:6 of the pre-granulated $\text{Ca}(\text{OH})_2$ to adhesion promoting agent to ceramic precursor. In case of the actual work, the raw material for encapsulation was previously admixed with a concentration of each two additives in concentrations of 3 $\%(\text{w}/\text{w})$, 5 $\%(\text{w}/\text{w})$ and 10 $\%(\text{w}/\text{w})$. Therefore, respective compounds were filled in a mixer (Type R02E, Eirich) and homogenized for four minutes in counter current rotation with a speed of 150 rpm.

In order to prevent a large amount of shell precursor material sticking at the mixing vessel walls, residues on the walls were removed and returned to the mixture repeatedly during homogenization.

To achieve comparable results for all prepared samples, the encapsulation process was standardized. The process is initiated with the addition of 500 g of the pre-granulated storage material into the mixer, running in co-current flow at 240 rpm. Subsequently, the adhesion promoting agent is admixed under constant mixing in co-current flow. Afterwards, according to the ratio mentioned above, a defined amount of ceramic precursor was added, which immediately covered the storage materials surface. Finally, a small amount of paraffin oil is added in order to prevent agglomeration of the encapsulated particles upon removal.

Finally, the samples were sintered in a ceramic furnace (Nabertherm, N°60/HR) to obtain the desired mechanical stability of the shell material. The sintering step included a four-hour isothermal segment after the two-stage heating up to 120°C (1.7 K/min) and 650°C (2.9 K/min) before heating to an upper process temperature of 1150°C (8.3 K/min), which again is held isothermally for one hour. Afterwards, the samples were cooled to room temperature with a rate of 9.5 K/min and stored in an evacuated desiccator over P₂O₅ to avoid hydration or carbonation of the now charged storage material core.

Sample selection

Before thermochemical cycling, a preselection of promising samples was made according to test results of the mechanical stability measured by a force gauge (SOLAR ENERGY 2020, Review), the absolute values of crushing strength measured for these samples is listed in the supporting material.

Laboratory reactor

The utilized laboratory scale reactor is designed as an electrically heated tube reactor, which can be operated up to a temperature of 950°C. The volume of the sample material tested therein is limited to 100 ml. Before initiating thermochemical cycling, the samples is placed between to layers of thermally inert mineral filter wool, which is held in its position by stainless steel wool. This setup fixes the sample material during the experiment, when a gas flow passes the bulk from bottom to top. Thereby, discharging of fines is reduced to a minimum. The atmosphere required for discharging (inert atmosphere, N₂) or charging (mixture of water vapor (H₂O_(g)) and N₂) is adjusted by mass flow controllers interposed between the reactor and the gas supply and water vapor generator. A partial stream of the gas discharged from the reactor is fed to a gas analyser via heated pipes. During each experiment, temperatures and pressures were measured and recorded on different positions in the reaction bed, as well as the mass flows and gas concentrations. All recorded values were utilized for comparative evaluation of the samples. A schematic figure of the described reactor is included in the supporting information of this article.

Thermochemical cycling

A volume of each 15 ml of those samples was filled inside the reactor. The flow through the reactor was set to 50 standard litres per hour, leading to an excess pressure in a range between 10 and 25 mbar. Since each sample of the encapsulated storage material is charged, e.g. converted to CaO, during the sintering step, reactor cycling could have been started with a first hydration step. But since the material is highly reactive towards H₂O and CO₂ contained in ambient air, it cannot be excluded that Ca(OH)₂ or CaCO₃ have formed during sample preparation. Hence, the material was first subjected to an initial heating above the decarbonation temperature to 925°C. During this initial step, the CO₂ concentration was constantly recorded to

detect the progress of the decarbonation reaction. The temperature was held until the CO₂ concentration signal dropped to zero, indicating a completion of the reaction. Afterwards, the reactor unit was passively cooled in nitrogen atmosphere to the upper process temperature applied during thermochemical cycling of 550°C. As this temperature was reached, the mixture of N₂ / H₂O(g) with a water vapor partial pressure of 500 mbar was injected while the system continued to passively cool down to the lower process temperature of 350°C. Depending on the intensity of the chemical reaction and thus the heat released by the storage material, the lower process temperature is reached after roughly 50 minutes. The temperature control of the reactor prevents further cooling below 350°C. To separate the hydration from the dehydration processes, the reactor was inerted with a five-minute nitrogen rinse. In order to avoid instationary effects in water vapor supply, the steam generator continued operating in the dehydration phase and was just switched to bypass mode. After inertization, the dehydration phase was initiated by heating to the upper process temperature in pure N₂ atmosphere. For this phase of the cycle, a period of 30 minutes was defined for all experiments.

After completion of each ten thermochemical cycles, the shutdown was initiated by a hydration of the respective sample material. Therefore, temperature and atmosphere were maintained for another hour before passive cooling in N₂ / H₂O mixture in order to promote the formation of the discharged Ca(OH)₂ phase for further sample evaluation. Before the condensation temperature at the given water vapor concentration was reached, it was bypassed at the end of the cooling period, before the material was removed from the reactor.

Device for attrition test

The mechanical stress profile for a thermochemical storage material in a moving bed reactor cannot be assessed solely by the application of a punctual mechanical load, as measured by a force gauge. For this reason, the effects of mechanical stress in form of a long-term abrasive load applied on the particles were simulated. For this purpose, the most advantageous sample 5D1F and a less advantageous sample 1D1F identified by thermochemical cycling were selected. To characterize its mechanical durability, a test rig with rotating test chambers was used (for figure see supporting material). The design of this test chamber is based on an industrial standard procedure for determining the mechanical durability of pellets of solid secondary fuels (see DIN CEN/TS 15639:2010). Since there is no standardized investigation scenario for the evaluation of the abrasion resistance of particle size stabilized thermochemical storage materials, the test procedure was derived from the above-mentioned standard. The study is of particular interest for comparison, as an attrition test performed by Sakellariou *et al.* [35], using a jet cup actually designed for measuring attrition resistance of oxygen carrier particles for chemical looping combustion, was limited to the investigation of non-

rehydrated particles due to a restricted amount of rehydrated sample material.

For testing, an amount of 500 g sample material with a particle size > 2.0 mm was filled into the chamber and subjected to rotation at 50 rpm for ten minutes. The baffle plate integrated in the chamber ensures thorough load on the tested particles. The tests were carried out at ambient temperature. Upon removing, each sample was passed through a screening machine. The selected sieve inserts have screening gaps of 1.4 mm to 1.0 mm, respectively. The sieve retention at the 1.4 mm screen is labelled as intact encapsulated material, whereas the 1.0 mm screen retains fragments of the tested particles and therefore is declared as disintegrated. The test amount passing through the 1.0 mm sieve is declared as the fine content of the material sample.

Results and discussion

Thermochemical cycling

From the results obtained from thermochemical cycling of the unmodified, pre-granulated reference material, it has been found that it shows no significant changes in its temperature profile and water vapor concentration during de- and rehydration over the course of ten reaction cycles. For this reason, and for a better compatibility of the reference to the encapsulated sample materials, the measured temperature and H₂O concentration of the reference has been averaged over ten cycles to give reference curves, depicting the temperature profile and H₂O concentration. The progression of both values is shown in Fig. 2.

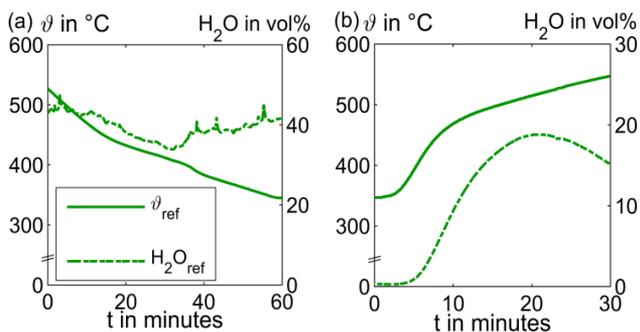


Fig. 2. Profile of the reactor temperature (solid line) and H₂O concentration (dashed line) measured for the reference sample Sorbacal H (averaged over ten cycles) during Rehydration (a) and Dehydration (b).

The thermochemical cycle can be divided into two processes, the rehydration (a) and the dehydration of the sample (b), separated by inertization periods. During rehydration of the material, the exothermic chemical reaction slows down the reactor's temperature drop below the equilibrium temperature of the reaction system. This leads to a deviation from the typical progress of a cooling curve according to Newton's law of cooling over the course of the sixty-minute process. The endothermic release of water vapor at the onset of dehydration above 450°C leads

to a temporarily inhibited heating during the thirty-minute dehydration process.

Fig. 3 shows the temperature profile and the progression of H₂O concentration measured by the gas analyser for the investigated samples 5D1F, 3C3D, 1D1F, 3C1F.

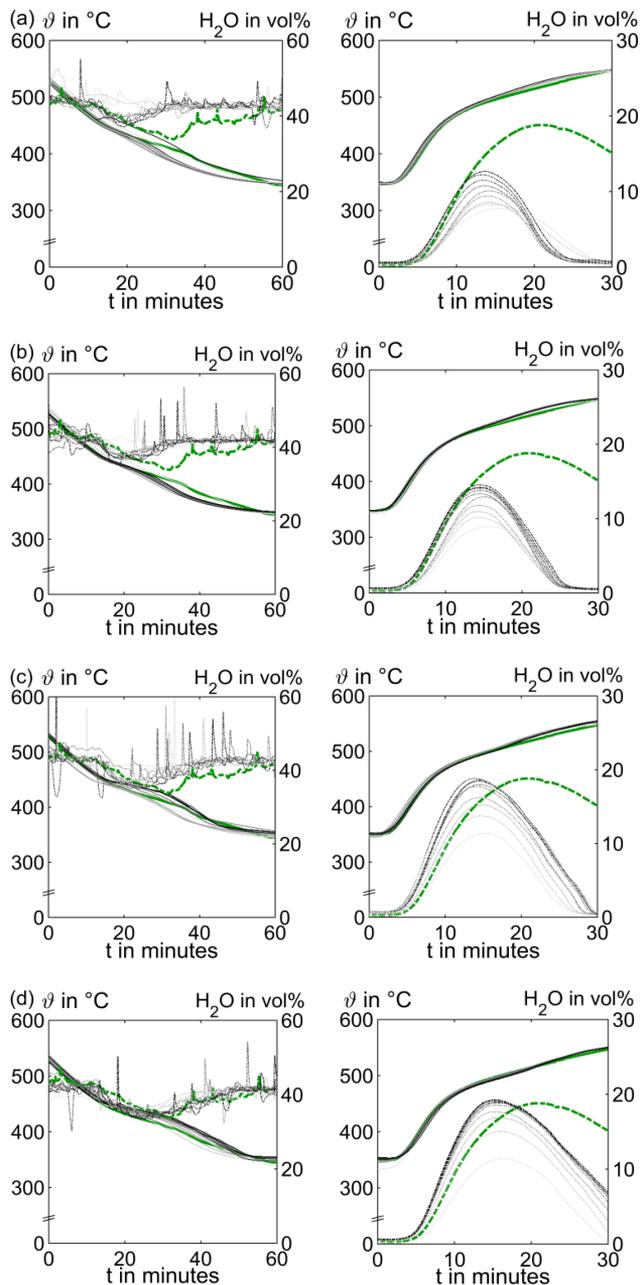


Fig. 3. Profile of the reactor temperature (solid line) and H₂O concentration (dashed line) measured for the enhanced samples 5D1F (a), 3C3D (b), 1D1F (c) and 3C1F (d) - coloring of the cycles according to cycle number from light to dark grey; the reference is contrasted in green.

The qualitative evaluation of the performance of the improved material samples is probed in comparison to the characteristic curves obtained for the reference sample (red graphs). Of particular interest is the release and intake of

water vapor by the reactive solid phase contained in encapsulated samples in relation to the reference but also by comparing individual reaction cycles per sample. For all samples, it can be seen that the water vapor release is limited during the first few cycles (shown in lighter gray) and the peak during dehydration becomes stronger as the number of thermochemical cycles increases. In principle, the observed release of water vapor proves that a chemical reaction of the encapsulated storage material occurs and that the capsule is thus exposed not only to thermal but also thermochemical stress as a result of the crystallization processes accompanying conversion of the material in the particle core.

In addition to the increase in peaking, a shift of the peaks towards faster hydration reactions can be observed in case of the samples 1D1F (c) and 3C1F (d). This suggests that the reaction starts at a higher rate, what can be interpreted as a sign that certain particle shells may have formed cracks or be disintegrated. Hence, mass transfer of the gaseous reactant can be facilitated faster, likewise providing an increased surface area of the storage material to the gaseous reaction partner, so that the reaction and the subsequent water vapor release is less inhibited. In addition, samples 5D1F (a) and 3C3D (b) deviate significantly from the temperature profile of the reference during rehydration. Specifically, the sample 3C1F shows a large correspondence with the respective curve of the non-encapsulated reference at both, the reactor temperature and the reaction-dependent water vapor absorption, whereas the samples 5D1F and 3C3D deviate more clearly from the reference.

The interpretation of the measured data above is confirmed by a macroscopic evaluation of the samples after removal from the reactor. **Fig. 4** exemplarily shows the appearance of the samples 5D1F and 1D1F, since those clearly highlight the differences. These samples were selected for comparison, since the course of dehydration of sample 3C3D is qualitatively comparable to 5D1F, whereas the water vapor release during dehydration of 3C1F corresponds qualitatively to 1D1F.

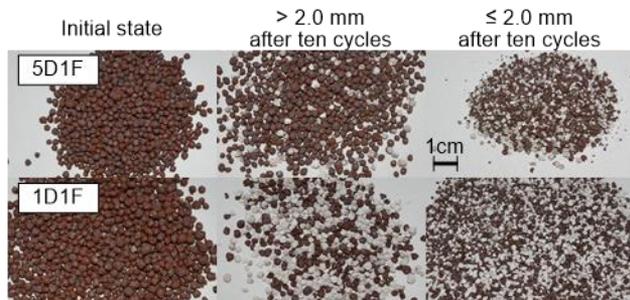


Fig. 4. Initial state of 5D1F and 1D1F and their state after ten thermochemical cycles divided into a fraction > 2.0 mm and a fraction of fragments and fines ≤ 2.0 mm.

For better optical differentiation, the samples have been divided into two fractions after removal from the reactor, so that a distinction can be made between intact particles and shell fragments. It is shown that the particles

of sample 5D1F are largely well preserved and have withstood thermochemical stress without extended macroscopic damage. Only in case of some particles, the capsule is disintegrated and chipped due to the mechanical stress. It can be assumed that in case of these particles, the explosive force of the expansion of the core material as a result of the rehydration reaction has exceeded the mechanical stability of the shell material. Most of these capsule fragments are found in the fraction ≤ 2.0 mm. In contrast, the shells of the sample 1D1F show significant damage on a macroscopic scale. A large number of particles has completely lost its shells. Also, half-cut shells are found among the larger fragments. In addition to the chipped ceramic capsules, some fragmented cores can be found in the fraction > 2.0 mm, which probably result from granules that have become unstable after losing their protective shell during thermochemical cycling. The representation of the state observed for the sample 1D1F can also be seen as an example for sample 3C1F, which shows an almost complete decay of the capsule over ten cycles as well.

These qualitative observations coincide with the conclusions derived from the increasing water vapor release during thermochemical cycling and are further substantiated by a gravimetric analysis of the samples before and after thermochemical cycling, shown in **Fig. 5**. Since the sample bulk volume was set to each 15 ml per sample in the reactor experiments, the deviations in the initial weight are to be explained by a general scattering due to the production process and the deviating additive components and proportions as well as a possible reaction of the reactive core material with H_2O and CO_2 of the ambient air. Deviations in the final weight are partly due to the fact that fines could have been lost during the removal. This is particularly important for the samples 1D1F and 3C1F. Since there is a high amount of fines, the final weight is correspondingly lower than the final weight of the other samples examined.

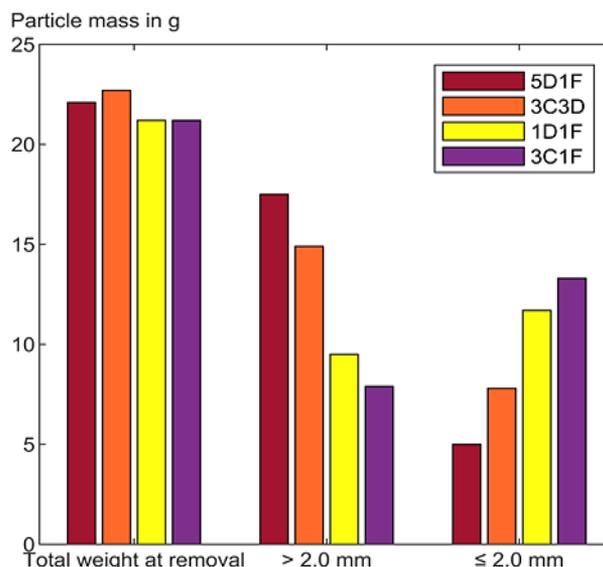


Fig. 5. Gravimetric comparison of the examined samples after thermochemical cycling.

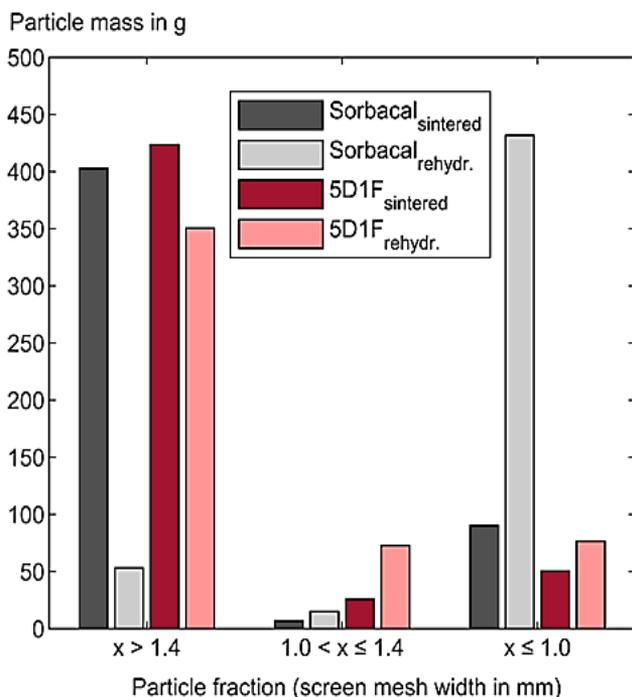


Fig. 5. Particle-size distribution after sintering (CaO phase) and rehydration (Ca(OH)₂ phase) for the reference sample Sorbocal H and the identified most suitable sample with an improved mechanical stability, identified by tenfold thermochemical cycling, containing 5 % (w/w) of diatomaceous earth (D) and 1 % (w/w) of flux agent (F). Particle-size fractions based upon DIN CEN TS 15639:2010 ([11] DIN, 2010).

Attrition resistance

As can be proven from the results of the attrition test, the encapsulated sample 5D1F has a significantly higher resistance towards the attrition load in bulk-scale as the non-capsulated reference sample (see **Fig. 6**). While the difference in particle mass for fraction $x > 1.4$ mm in sintered state is marginal due to the compact structure of the commercial reference, it becomes significant for the rehydrated samples as the microstructure of pure pre-granulated storage material is softened due to the expansion of the increase in molar volume accompanying recrystallization from CaO to Ca(OH)₂ during its reaction with water vapor. The granules disintegrate almost completely to a fine, cohesive powder during the applied friction load.

The results are in accordance with the conclusions of Afflerbach *et al.* [34] that the mechanical stability and integrity of microstructure of the non-encapsulated, pre-granulated, commercial storage material is not persistent during thermochemical cycling. In particular, for the sintered state, however, it is also shown that the impact of punctually acting forces in the abrasion test stand usually do not lead to a breakage of the particles, so that intra-particle forces occurring during charging and discharging have a higher potential in causing damage than inter-particle collisions or those between particles and walls.

Conclusion & future prospective

Within the scope of the present work it is shown, that by suitable addition of the ceramic shell precursor, its mechanical properties as well as its durability during thermochemical cycling can be significantly enhanced while at the same time mass transfer of the gaseous reaction partner can be preserved by an open porous network and the bulk properties are optimized due to a persistent particle size.

In particular, the performance of the material sample 5D1F, containing 5 % (w/w) of diatomaceous earth (D) and 1 % (w/w) of flux agent (F), provides the confirmation that the chosen approach is expedient. Based on previous results and considerations, a standardized manufacturing procedure was developed to prepare the encapsulated material on a larger scale with a consistent quality. Based on previous results [36], four selected samples were subject to a semi-automated tenfold thermochemical cycling in a laboratory reactor utilizing a standardized procedure. The cyclability was shown in pilot scale obtaining results for chemical conversion consistent to the results of thermochemical cycling in a TA instrument in previous works [36]. While the focus of the present work was set on whether the material is suitable for a semi-automated reaction control with reproducible cycles, an expedient quantitative assessment of the conversion in the laboratory reactor is difficult due to the small amounts used. This is due to the fact that at the time of the investigations, although a scale up in the coating process has taken place, the subsequent sintering process has severely limited the production quantity per batch due to the agglomeration tendency of the individual particles. In future work, a higher process volume is possible using charge saggars and a higher filling volume of the reactor is to be strived for accordingly. After tenfold thermochemical cycling the encapsulated particles, samples 3C3D and 5D1F in particular, retain reasonable flowability compared to the unenhanced reference material.

In comparison to other strategies for stabilizing the particle size, the approach presented offers a significantly increased mechanical stability with low specific costs of the raw materials. The defined contact area between the capsule material and the reactive core at the boundary layer inside the shell limits the formation of side products under the hydrothermal conditions of multiple thermochemical cycling. Disadvantages are the relatively high proportion of capsule material and the brittle structure of the shell, which represents a weak point, particularly with regard to forces resulting from the expansion of the reactive core material.

The evaluation routine was firstly extended by an attrition test in the scale of 500 g in order to expand the investigation of the mechanical properties of the material. The examinations have clearly shown the potential of the chemically modified material, since the abrasion, especially in the rehydrated state, can be significantly reduced compared to the reference sample (70.1 % (w/w) > 2.0 mm

instead of 10.6 %). Non-encapsulated material, especially in the rehydrated $\text{Ca}(\text{OH})_2$ phase, cannot be moved without disintegration of the agglomerates. However, internal mechanical forces due to the expansion of the reactive core as a result of the chemical reaction continue to represent an enormous potential for damaging the capsules. The abrasion test usefully complements the investigations of the mechanical durability of individual particles with a force gauge and should also be used in future work to evaluate the long-term stability in thermochemical reactors with material movement. Since the experimental procedure has been derived from a standard for pellets of secondary fuel, adaptation to actual load characteristics in a moving bed reactor can be considered at this point. For this purpose, however, the load characteristics have to be determined in detail.

While this work provides valuable insights into the state of technological maturity, based on the knowledge gained, it is also clear how much potential is still to be exploited since a variety of parameters are left to be optimized in this promising approach. For example, the behavior of the material under harsher reaction conditions has to be investigated, as this leads to faster charging and discharging of the storage material. In the context of further material development, there is a variety of factors that impact the stability of the encapsulated particle. In addition to the identification of suitable material systems in relevant temperature ranges and the investigation of the reaction-related morphological changes in particle size and shape, future research focuses will also be on linking process conditions from different fields of application with the further development of the storage system. In lower temperature ranges e.g. the use of elastic polymers as a coating material is also conceivable insofar as material and heat transport can be ensured to a sufficient extent.

In conclusion, it should be emphasized that the implementation of thermochemical energy storages utilizing the reaction system $\text{CaO}/\text{Ca}(\text{OH})_2$ cannot be obtained solely by the conceptual and constructive design of reactors with moving reaction beds. Thus, the further optimization of the storage materials remains as an interdisciplinary subject of further, fundamental investigations in the field of process engineering and solid state chemistry.

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Conflicts of interest

There are no personal or financial conflicts to declare.

Keywords

Thermochemical energy storage, calcium hydroxide, core-shell particles, powder flowability, concentrated solar power, semipermeable encapsulation, porous ceramics.

Supporting information

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Graphical abstract

Manufacturing and testing procedure of a particle-size-stabilized energy storage material in reactor scale with subsequent evaluation of the materials performance during tenfold thermochemical cycling as well as a characterization of its mechanical properties.

