TCES Systems Based on Hydroxides

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The exploitation of solar energy, an unlimited and renewable energy resource, is of prime interest to support the replacement of fossil fuels by renewable energy alternatives. Solar energy can be used via concentrated solar power (CSP) combined with thermochemical energy storage (TCES) for the conversion and storage of concentrated solar energy via reversible solid–gas reactions, thus enabling round the clock operation and continuous production. This entry is about High-temperature thermochemical energy storage using the enthalpy of reversible reactions.

thermochemical energy storage | solid-gas reaction | hydroxide | concentrated solar power | reversible reactions

1. Introduction

The enthalpy of solid-gas chemical reactions stored in chemical materials can be used to generate heat when necessary via endothermal/exothermal reversible reactions. The stored and released heat can be used for example to run power cycles or more generally in industrial processes operating at high temperatures and thus requiring high amounts of energy that are usually provided by fossil fuel combustion. Thus, thermochemical energy storage (TCES) has potential to lower fossil fuel consumption and related greenhouse gas emissions [1]. A high potential also exists in the combination of TCES systems with renewable energy systems. Thermal energy storage is indeed particularly suitable for being combined with concentrated solar energy that relies on an intermittent resource, with the aim to operate the process continuously (day and night as well as stable operation during fluctuating solar energy input) (Figure 1). Indeed, solar energy is variable and can fluctuate a lot in nature due to clouds and weather conditions, thus requiring a storage system for smooth and stable operation under fluctuating solar irradiation conditions. TCES is thus attractive since continuous operation allows a strong increase in the capacity factor of the solar plant, while it can further contribute to eliminating transient effects due to start-up/shutdown periods and unstable/variable solar conditions. The possible envisioned applications are pertaining to electricity production by concentrated solar power (CSP) plants or more generally high temperature chemical processes requiring an external energy input as the process heat supply (e.g., cement and concrete production, minerals calcination, metallurgical processes, fuel production processes or chemical industrial processes). Most industrial energy-intensive processes require a high temperature heat source generally provided by fossil fuel burning. In such high temperature processes, the required high temperature heat for running power cycles or driving endothermal reactions can be generated with solar concentrating systems (parabolic dish, trough, linear Fresnel systems or solar tower receivers with heliostat field). This is the case of CSP plants for electricity generation and solar thermochemical processes for fuels (syngas production via reforming, gasification of carbonaceous feedstocks, H_2O and CO_2 splitting via thermochemical cycles, etc.) or chemical commodity production (cement, metals, etc.). Thus, the interest in TCES integration in such processes for continuous operation is constantly growing. Another possible application is the utilization of TCES for the recovery and storage of waste heat of various energy and industrial processes at different temperature levels in order to increase process efficiencies or to produce additional extra heat/electricity.

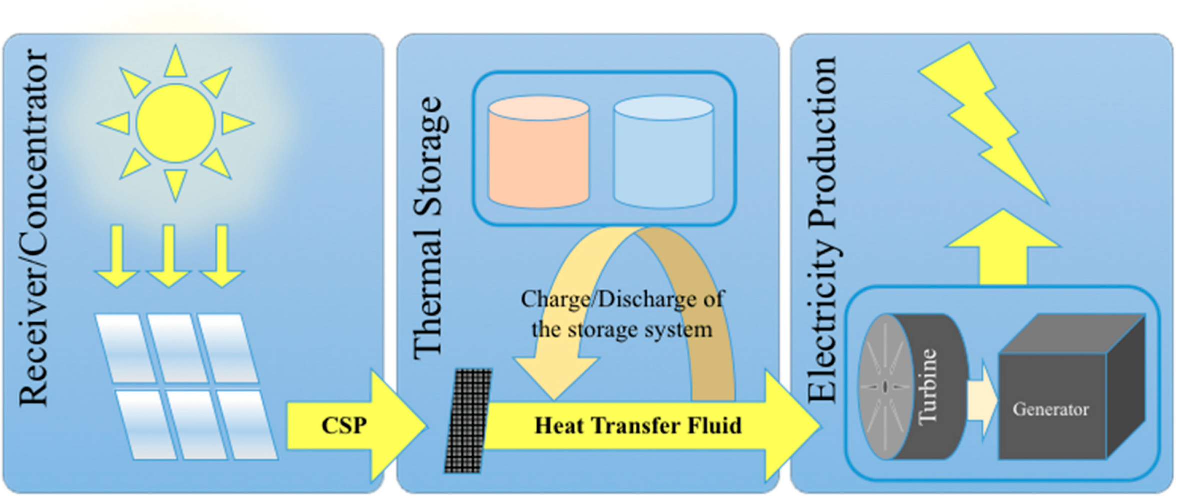

Figure 1. Scheme of the solar power plant main components integrating buffer thermal energy storage system.

In contrast to other energy storage systems including sensible and/or latent energy storage, thermochemical storage offers the possibility of high energy densities in the form of chemical bonds as well as long-term storage and long-range transport in the form of stable and safe materials (Table 1). In addition, the operating conditions can be tuned in a wide range of temperatures and pressures depending on the used TCES system and involved chemical reactions, thus offering the possibility of being combined with various processes. In contrast to sensible or latent heat storage systems that have been developed and optimized, and are even commercially available and applied at large scale, thermochemical energy storage is a new research area in which many aspects are still unknown and are still to be discovered [2]. Research advances are thus needed for potential industrial implementation, while also taking into account the energy consumption by auxiliary equipment and feedstock cost that impact the system capital cost [3]. The main fields in which strong efforts are necessary to develop practical TCES systems and bridge the gap from fundamental research to application are the discovery of cost effective, abundant and affordable chemical materials with high energy densities, cycle stability and fast kinetics for heat storage and release [1]. Furthermore, additional research and technological developments are needed in the optimal design of heat storage-chemical reactor systems for maximum heat transfer between the storage medium and the high temperature solar process, and the complete system integration in large scale plants (optimization of heat and mass flows, dynamic simulation during transient events and fluctuating solar conditions, techno-economics, etc.) [4][5].

Table 1. Comparison of the main options for thermal energy storage using concentrated solar power (CSP), adapted with permission from [6][7], Elsevier, 2020.

Storage Type	**Sensible Heat Storage (SHS)**	**Latent Heat Storage (LHT)**	**Thermochemical Energy Storage (TCES)**
Gravimetric energy density	~0.02–0.03 kWh/kg	~0.05–0.1 kWh/kg	~0.5–1 kWh/kg
Volumetric energy density	~50 kWh/m^3	~100 kWh/m^3	~500 kWh/m^3
Storage temperature	Charging step temperature	Charging step temperature	Room temperature
Technology development	Industrial scale	Pilot scale	Laboratory and pilot scale
Energy storage period	Limited (Thermal loss)	Limited (Thermal loss)	Theoretically unlimited
Theoretical energy transport	Very short distance	Very short distance	Very long distance (>100 km)
Technology complexity	Simple	Medium	Complex
Drawbacks	Important thermal losses over time Large quantity of storage material required	Important thermal losses over time Corrosive materials Low heat conductivity	Expensive investment cost Complex technique

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2. TCES Systems Based on Hydroxides

$Ca(OH)_2/CaO$ has been demonstrated to date to be the most interesting studied high-temperature energy storage system based on metal hydroxides and has been prompted tests in lab-scale reactors and thermogravimetry analysis (TGA) (Equation (1), Figure 2) [3][7][8][9][10][11][12]. However, the enhancement of material stability is required to reduce the sintering effect. $Ca(OH)_2$ particles were shown to agglomerate faster than CaO particles in the presence of H_2O, and the presence of H_2O would accelerate the agglomeration of CaO particles [13].

$$CaO_{(s)} + H_2O_{(g)} \rightleftarrows Ca(OH)_{2(s)} \quad (\Delta H^\circ = -109.2\ kJ/mol) \qquad (1)$$

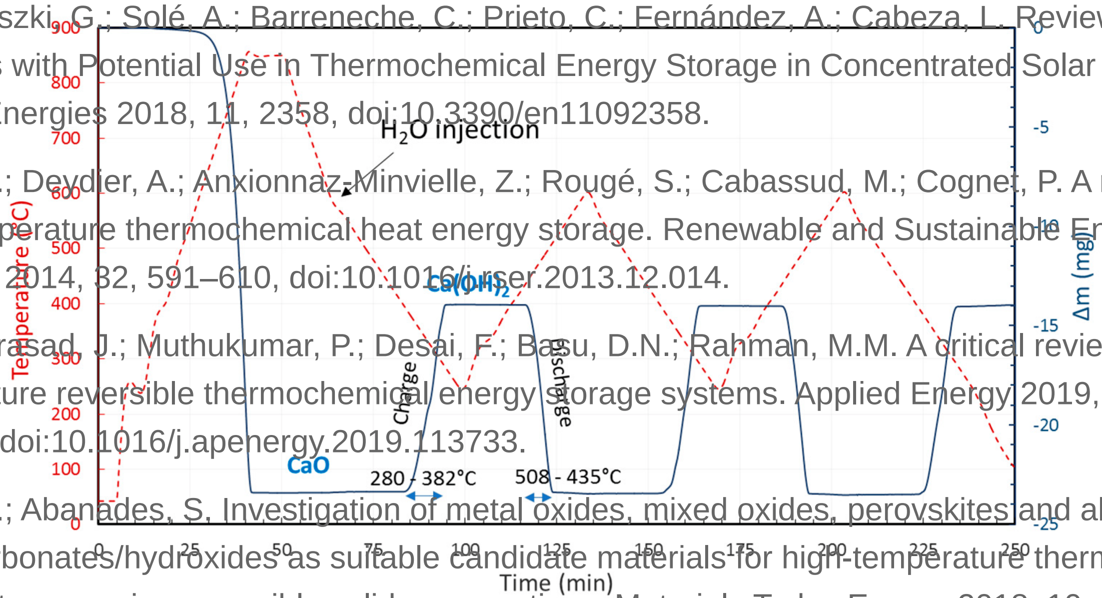

Figure 2. TGA of $CaO/Ca(OH)_2$ showing excellent reversibility during charge/discharge cycles under 21 mol% $H_2O_{(g)}$. CaO was first obtained from calcination of commercial $CaCO_3$ to CaO at 850 °C under N_2/Ar.

The rehydration step is slower than the dehydration step [14], and the hydration of CaO agglomerated lump proved to be more difficult than that of fresh particles, which hindered the cycling stability of the material. Due to particle agglomeration, $CaO/Ca(OH)_2$ powder bed and pellets used in packed bed reactors suffer from a loss in reactivity and a change in bulk volume. Powdered $Ca(OH)_2/CaO$ was recently evaluated under reactor conditions [15]. During the hydration/dehydration cycles, the temperature was uneven between the middle of the packed bed and the outside. During the first part of the heating, the outside of the packed bed remained at a higher temperature than the middle for at least one hour (70 min). Afterwards, the opposite was observed, with the outer part of the packed bed being at a lower temperature than the center. Under experimental conditions, the highest temperature reached was 475 °C. In fact, the study underlines the unevenness of the heat release rate and the poor thermal conductivity as main issues. To address the improvement of heat transfer through $CaO/Ca(OH)_2$ in a packed bed reactor, a composite material using silicon carbide/silicon (SiC/Si) foam to support $CaO/Ca(OH)_2$ in its pores (400 μm) was investigated [16]. Over ten cycles, the composite material retained a high reactivity and good stability of the bulk volume during dehydration/hydration reactions. A study was recently accomplished on $CaO/Ca(OH)_2$ supported on ceramic honeycomb composed of silicon carbide and silicon (SiC-Si) [17]. The pellets of composite material were

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tested in a lab-scale packed bed reactor, and was shown to enhance the heat transfer through the reaction bed. The alteration of the support did not form any side product during the tests; however, cracks and deformations appeared over the course of ten cycles. This approach is promising for the dispersion and shaping of packed beds using hydroxides for TCES. A CaO/Ca(OH)$_2$/Na$_2$CaSiO$_4$ composite was synthesized using sodium silicate to bind CaO/Ca(OH)$_2$ fine particles for fluidized or fixed beds [18]. This work noted the effect of the anisotropic expansion of Ca(OH)$_2$ being the cause of the reduction in the crushing strength of the pellets.

The adaptation/integration of powdered material systems to CSP irradiated reactors such as fluidized bed is necessary for an effective exploitation of the TCES system in continuous flow. To this end, calcium hydroxide was mixed with nanostructured flow agents such as nanostructured silicon and aluminum oxide [19]. The study focused on the modification of calcium hydroxide powder using nanostructured agents, in order to enhance the flowability of the material in dynamic energy storage systems. However, the mixtures all presented lower flowability than pure Ca(OH)$_2$/CaO powder, as the agglomeration of the pure particles led to bigger particles with better flowability. In addition, the samples from the mixture generated side products such as calcium silicate and aluminate phases which contributed to the reduction in the total heat release measured for the material. With this conclusion, it is recommended to rather improve the stability of moderately bigger particles of pure material rather than mix them with additives as a means to enhance the flowability of the material. As the low thermal conductivity and cohesiveness of powder bulk material are ill-suited for moving bed reactors, studies usually aim for granular materials for such application. To answer this issue, a recent study investigated the effect of the encapsulation of CaO granules in ceramic and of Ca(OH)$_2$ granules coated with Al$_2$O$_3$ nanostructured particles [20]. Both encapsulated materials could retain their shape after six hydration/dehydration cycles, but the ceramic shell of CaO was sometimes cracked or lost. On the one hand, the reaction performances of Ca(OH)$_2$ encapsulated in Al$_2$O$_3$ proved to be similar to that of unmodified Ca(OH)$_2$ granules, but the expansion of the material during the hydration step tended to clog the reactor tubes. On the other hand, CaO granules encapsulated in ceramic flowed freely through the reactor, but their reaction performances were reduced and they could not reach full conversion. As a maneuver to answer industrial requirements—e.g., for a moving bed reactor with appropriate material size and stability, a composite based on calcium oxide was synthesized for TCES application, using the CaO/Ca(OH)$_2$ system [21] mixed with carboxymethyl cellulose sodium (CMC) and vermiculite. When compared to the performances of pure Ca(OH)$_2$ tablets, the composite tablets better retained their structural integrity over several hydration/dehydration cycles. Within the material, vermiculite provided enough space for the CaO/Ca(OH)$_2$ reaction, with an average pore diameter between 11 and 16 nm depending on the synthesis conditions for the composite material. In addition, the backbone structure of the composite possessed abundant micropores and mesopores for the gas transport during the cycles. Furthermore, the decomposition temperature of Ca(OH)$_2$ within the composite material was reduced, which is attributed to the generation of activated carbon during the carbonization of CMC. Finally, the gravimetric storage density of the granular composite material was reduced (71% of the value obtained for pure Ca(OH)$_2$), while the volumetric storage density was higher than that of Ca(OH)$_2$ powder.

The enhancement of the reaction properties of the Ca(OH)$_2$/CaO system was studied via KNO$_3$ addition to Ca(OH)$_2$, which reduced the dehydration reaction duration and decreased the dehydration temperature of the

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system due to a nitrate-hydroxide interaction, as KNO_3 melts during the dehydration step [22]. The influence of the amount of added KNO_3 on the reaction temperature was then investigated and showed that the minimum dehydration onset temperature (459 °C, instead of 494 °C for pure $Ca(OH)_2$) was reached with 5 wt% of KNO_3 added, with the material losing only 7% of its energy storage capacity, down to 1280 kJ/kg. Additional information on the system is available, as a kinetic study of the effect of KNO_3 addition to $Ca(OH)_2/CaO$ was conducted [23]. The optimum amount of KNO_3 was determined to be around 10 wt% to reduce the charging temperature to 428.49 °C and accelerate the reaction with little loss in energy storage density. The cycling stability of the mixture was tested under air and under nitrogen atmosphere. The KNO_3-doped calcium hydroxide fared poorly under air, due to the presence of CO_2 and carbonation of the sample, but results revealed a good cycling stability under nitrogen atmosphere. SEM observations showed that within the $Ca(OH)_2$/10 wt% KNO_3 mixture, the once dehydrated material changes to a flower-like structure when rehydrated. When dehydrated again, the flower-like structure shrinks back into a blocky structure. This modification of the material morphology is attributed to the addition of KNO_3 and contributes to enhancing the mass transfer during the storage cycles. Another example of reaction enhancement via doping is the improvement of reduction kinetics of $Ca(OH)_2$ via Li doping [24]. The enhancement of the $Ca(OH)_2/CaO$ system was also approached via a modification of the structure of the material, for example with the synthesis of hexagonal boron nitride (HBN)-doped calcium hydroxide composite [25]. The material was tested in TGA/DSC (thermogravimetry analysis/differential scanning calorimetry) and showed better cycling stability than pure calcium hydroxide, showing 67% rehydration after ten dehydration/hydration cycles, with an optimum amount of HBN added at 15 wt%, and the dehydration kinetics were also enhanced. In addition, the composite material exhibited higher thermal conductivity and reaction enthalpy as compared to pure calcium hydroxide. Another studied approach to modify the properties of the system is the modification of the structure of the pure material. $Ca(OH)_2$ nanomaterials with spindle and hexagonal structure were synthesized by a deposition-precipitation method and compared to commercial nanoparticles [26]. The spindle-shaped $Ca(OH)_2$ demonstrated the highest specific surface area in BET and the energy storage density among the tested nanomaterials. In addition, the dehydration/hydration kinetics were improved with the spindle-shaped material and it presented the best cycling stability over ten cycles, as it retained a conversion rate above 70%.

$Mg(OH)_2/MgO$ is another potential system for TCES which is currently getting attention. $Mg(OH)_2$ was considered at reactor scale, and an economical study was conducted [27]. However, the material suffers from slow and incomplete rehydration, as stated by Müller et al. (2019) [28]. The authors recently studied the rehydration mechanism of MgO and of natural magnesite in order to assess the effect of impurities on the reaction. The enhancement of the TCES system consisting of $MgO/Mg(OH)_2$ was studied via the addition of $LiNO_3$ with 1, 3, 6 and 10 wt% added [29]. The dehydration temperature of the $LiNO_3$-$Mg(OH)_2$ composites was lower, from 289 down to 269 °C for 1 wt% and 10 wt% doping, respectively, than that of pure $Mg(OH)_2$ which was measured at 325 °C. The dehydration temperature of the $LiNO_3$-$Mg(OH)_2$ composite may then be tuned via the addition of an adequate amount of $LiNO_3$, and the composite materials could sustain more than ten dehydration/rehydration cycles without losing thermal efficiency. In addition, the calculated dehydration rate constant was higher with $LiNO_3$ doping, but the composite material presented lower released heat from the reaction. The mixture $LiNO_3/Mg(OH)_2$ was also

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studied explicitly for TCES at a lower temperature (<300 °C) since the addition of $LiNO_3$ to $Mg(OH)_2$ decreases the dehydration temperature of Mg-based system (76 °C difference) [30][31].