

Review

Recent Advances in Thermochemical Energy Storage via Solid–Gas Reversible Reactions at High Temperature

Laurie André¹ and Stéphane Abanades^{2,*}

- ¹ Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR 6302, CNRS, Univ. Bourgogne Franche-Comté, 9, Avenue Alain Savary, 21000 Dijon, France; Laurie.Andre@u-bourgogne.fr
- ² Processes, Materials and Solar Energy Laboratory, PROMES-CNRS, 7 Rue du Four Solaire, 66120 Font-Romeu, France
- * Correspondence: stephane.abanades@promes.cnrs.fr; Tel.: +33-(0)4-68-30-77-30

Received: 12 October 2020; Accepted: 6 November 2020; Published: 10 November 2020



Abstract: 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. Research is on-going on efficient and economically attractive TCES systems at high temperatures with long-term durability and performance stability. Indeed, the cycling stability with reduced or no loss in capacity over many cycles of heat charge and discharge of the material is pursued. The main thermochemical systems currently investigated are encompassing metal oxide redox pairs (MO_x/MO_{x-1}), non-stoichiometric perovskites $(ABO_3/ABO_{3-\delta})$, alkaline earth metal carbonates and hydroxides $(MCO_3/MO, M(OH)_2/MO$ with M = Ca, Sr, Ba). The metal oxides/perovskites can operate in open loop with air as the heat transfer fluid, while carbonates and hydroxides generally require closed loop operation with storage of the fluid (H_2O or CO_2). Alternative sources of natural components are also attracting interest, such as abundant and low-cost ore minerals or recycling waste. For example, limestone and dolomite are being studied to provide for one of the most promising systems, CaCO₃/CaO. Systems based on hydroxides are also progressing, although most of the recent works focused on Ca(OH)₂/CaO. Mixed metal oxides and perovskites are also largely developed and attractive materials, thanks to the possible tuning of both their operating temperature and energy storage capacity. The shape of the material and its stabilization are critical to adapt the material for their integration in reactors, such as packed bed and fluidized bed reactors, and assure a smooth transition for commercial use and development. The recent advances in TCES systems since 2016 are reviewed, and their integration in solar processes for continuous operation is particularly emphasized.

Keywords: thermochemical energy storage; solid-gas reaction; redox systems; carbonate; hydroxide; perovskite; concentrated solar power

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, H₂O and CO₂ 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.

The TCES integration within a solar power plant implies the utilization of a heat transfer fluid (HTF) (Figure 2). During on-sun hours, the HTF flows inside the solar receiver and is used to store heat in the TCES system (heat charge, endothermal). The TCES system can be combined with or integrated into the solar receiver (direct storage) or separated (indirect storage). The exiting HTF is then used to run the turbine of the power block. During off-sun hours, the HTF directly flows through the TCES system for heat recovery (discharge step, exothermal) in order to increase its temperature and provide heat to the downstream process, thereby enabling continuous operation.



Figure 2. Flow diagram and operating principle of thermochemical energy storage system integrated with solar thermal power plant for continuous power production.

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].

This study reviews the most advanced and potentially attractive TCES systems currently under development (including hydroxides, carbonates, metals oxides redox pairs, perovskites) with emphasis on their characteristics for practical implementation, and on their suitability for potential application and integration in solar processes for continuous operation. A comprehensive screening of TCES systems based on solid–gas reversible reactions for high temperature solar thermal energy storage was published by the authors in 2016 [8]. Since this date, much effort has been provided in this research field to investigate thermochemical systems for concentrated solar energy applications. Special attention is paid in this work to the active research developed in the most recent years by focusing on the latest advances in the field.

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

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

2. TCES Systems Based on Hydroxides

 $Ca(OH)_2/CaO$ has been demonstrated to date to be the most interesting studied thermochemical energy storage system based on metal hydroxides and has prompted tests in lab-scale reactors and thermogravimetry analysis (TGA) (Equation (1), Figure 3) [3,7,9–13]. 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 H₂O, and the presence of H₂O would accelerate the agglomeration of CaO particles [14].



$$\begin{aligned} \operatorname{CaO}_{(s)} + \operatorname{H_2O}_{(g)} \rightleftharpoons \operatorname{Ca}(\operatorname{OH})_{2(s)} \\ (\Delta \mathrm{H}^\circ = -109.2 \text{ kJ/mol}) \end{aligned} \tag{1}$$

Figure 3. 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 CaCO₃ to CaO at 850 °C under pure Ar.

The rehydration step is slower than the dehydration step [15], 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 [16]. 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 μ m) was investigated [17]. 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) [18]. The pellets of composite material were tested in a lab-scale packed bed reactor and were shown to enhance the heat transfer through the reaction bed. The inert honeycomb 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/Na₂CaSiO₄ composite was synthesized using sodium silicate to bind CaO/Ca(OH)₂ fine particles for fluidized or fixed beds [19]. 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 a continuous flow over time. To this end, calcium hydroxide was modified with nanostructured flow agents such as nanostructured silicon and/or aluminum oxide [20]. 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_2O_3 nanostructured particles [21]. 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_2O_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 [22] 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 KNO₃ addition to Ca(OH)₂, which reduced the dehydration reaction duration and decreased the dehydration temperature of the system due to a nitrate-hydroxide interaction as KNO₃ melts during the dehydration step [23]. The influence of the amount of added KNO₃ 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 KNO₃ 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 KNO₃ addition to Ca(OH)₂/CaO was conducted [24]. The optimum amount of KNO₃ 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 KNO₃-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% KNO₃ 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 KNO₃ 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 [25]. 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 [26]. 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 [27]. 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 [28]. However, the material suffers from slow and incomplete rehydration, as stated by Müller et al. (2019) [29]. 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 LiNO₃ with 1, 3, 6 and 10 wt% added [30]. The dehydration temperature of the LiNO₃-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 LiNO₃, 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 LiNO₃ doping, but the composite material presented lower released heat from the reaction. The mixture LiNO₃/Mg(OH)₂ was also studied explicitly for TCES at a lower temperature of Mg-based system (76 °C difference) [31,32].

3. TCES Systems Based on Carbonates

Metal carbonates present the advantage of being cheap and largely available materials. Several of them have demonstrated attractive performances for TCES application, such as CaO/CaCO₃, SrO/SrCO₃ or BaO/BaCO₃ [33]. Calcium-Looping (CaL) technology in particular, coupled with CSP, is being thoroughly studied for adaptation to TCES power plant (Equation (2)) [3,12,34–38]. This reversible cycle requires operating temperatures between 850 and 950 °C.

$$\begin{aligned} \operatorname{CaO}_{(\mathrm{s})} + \operatorname{CO}_{2(\mathrm{g})} &\rightleftharpoons \operatorname{CaCO}_{3(\mathrm{s})} \\ (\Delta \mathrm{H}^{\circ} = -178.2 \text{ kJ/mol}) \end{aligned} \tag{2}$$

However, due to sintering, the material gradually loses its porosity and facility for the reactive gas to access the active sites within the material [39,40]. To address this issue, the addition of an inert material for structure stabilization and sintering inhibition is a proven approach (Figure 4). For example, CaO/SiO₂ composites were synthesized using rice husk as support [41]. The composites containing 70 and 90% CaO retained the morphology of rice husk and showed enhanced conversion, as compared to limestone, and decreased pore-plugging effect. Pure CaO and nano silica doped systems (molar ratio 1:1) were compared, and a shift in reaction temperature was observed [42]. The pure material performed better between 750 and 925 °C, while for the silica-doped samples the decarbonation happened at lower temperatures, between 700 and 800 °C. Al₂O₃ has been demonstrated to efficiently stabilize CaO/CaCO₃ [43]. Thanks to using a space-confined chemical vapor deposition (CVD) method, Han et al. [43] presented a new way to synthesize a Al₂O₃ (5 mol%)-CaO composite which demonstrated high stability over 50 calcination/carbonation cycles as compared to samples using SiO_2 or TiO_2 as inert additives. The space-confined CVD method allowed CaO crystalline grains to be coated with inert oxide nanoparticles, as high contribution to thermal stability of the composite material. Further work was carried out by the same team on CaO-based materials, using the same method, and resulted in the synthesis of dense CaO grains using calcium formate as precursor, with Al₂O₃ deposited on the surface [44]. The resultant composite, optimized with 10 mol% Al, presented high volumetric energy storage density (2.07 GJ/m³) after 20 cycles. The properties of the Al₂O₃-doped CaO system were compared to CeO2-doped CaO and to a novel Al2O3/CeO2 co-doping [45]. The Al2O3/CeO2 co-doped CaO-based material was synthesized via a wet-mixing method and comprised a mixture of CaO, Ca₁₂Al₁₄O₃₃ and CeO₂. Co-doping of CaO using 5 wt% of Al₂O₃ and 5 wt% of CeO₂ gave the best results in terms of energy storage capacity, and the material proved to retain a good stability over 30 cycles with 7% conversion rate loss. The Al_2O_3/CeO_2 co-doping of CaO/CaCO₃ then also showed the benefit of enhancing the carbonation reactivity of the material, attributed to the presence of Ce³⁺ ions on its surface. ZrO₂ was also considered as a stabilizing agent and compared to Al₂O₃ [46]. CaCO₃ doped, via ball-milling, with ZrO₂ (40 wt%) or Al₂O₃ (20 wt%) both presented excellent cyclic stability. The CaCO₃-Al₂O₃ system managed to retain more than 80% of its cyclic stability over the course of 500 calcination/carbonation cycles. SiO₂ also proved to be an interesting dopant to stabilize CaCO₃ as it improved the system's energy storage capacity, enhanced the calcination kinetics and stabilized CaCO₃ over TCES cycles [47]. The stabilization of CaO/CaCO₃ was also attempted via the synthesis of composites composed of CaCO₃ nanoparticles and antioxidative graphite nanosheets [48]. Graphite nanosheets impregnated in H₃BO₃ showed higher antioxidant property. The porous structure of the composite helped to enhance CO_2 transportation within the material and to obtain a higher thermal conductivity. With only a 3 wt% graphite nanosheet, the composite was capable of cycling for 50 cycles under CO_2 and of maintaining a high heat storage capacity (1333 kJ/kg_{composite}), while pure CaCO₃ was deactivated after 50 cycles and the released heat decreased (down to 452 kJ/kg_{CaCO₃}). The stabilization of CaO was also studied through the use of sodium sulphate covering the surface of CaO particles at high temperatures. The molten salt was used to form a performant screen on the surface of reactive particles to prevent sintering during TCES cycles [49]. Another approach to hinder the agglomeration of CaO powder was proposed by Raganati et al. (2020) [50] who presented a

sound-assisted fluidization method of the reactive powder bed. Fine natural limestone ($<50 \mu$ m) was used in a lab-scale fluidized bed reactor and the effect of sound-assisted fluidization on the carbonation conversion of the material was studied for TCES using CSP conditions. The acoustic perturbations applied to the fine limestone particles proved to hinder the agglomeration of the particles and enhanced the carbonation performances of the material. The fluidization quality was enhanced together with a better solid–gas contact. In addition, the acoustic perturbation decreased the deactivation rate.



Figure 4. Thermogravimetry (TG) analysis of SrCO₃/SrO and BaCO₃/BaO showing cycling stability improvement of carbonates via the addition of MgO as inert additive [33]. (**a**) SrCO₃/SrO (a. commercial SrCO₃, b. commercial SrCO₃ with 20 wt% MgO, c. SrCO₃ synthesized with 20 wt% MgO, d. commercial SrCO₃ with 32 wt% MgO), and (**b**) BaCO₃/BaO (a. commercial BaCO₃ with 44 wt% MgO, b. synthesized BaCO₃ with 30 wt% MgO, c. 30 wt% MgO presenting low porosity, d. 30 wt% MgO presenting high porosity).

The solar absorption efficiency of the reactive material itself was recently questioned. An innovative approach using the CaO/CaCO₃ system proposed to use dark calcium carbonate particles, instead of the naturally white material, by doping the material with Cu, Fe, Co or Cr via a sol-gel method [51,52]. The energy storage density of the material was significantly increased by the binary doping using Cu and Mn, reaching 1952 kJ/kg, while the energy storage density of pure CaO/CaCO₃ is around 1061 kJ/kg. A variation in the solar absorptance of the material was noted depending on the doping metal. For example, when doped with Cu only, the CaCO₃ particles had a higher solar absorptance

An impact on the cycling stability of the material was also observed, as it was enhanced via Mn and Al doping, but reduced with the addition of Cr. The solar absorption capacity of CaCO₃ was also addressed via the doping of the system with Mn-Fe oxides [53]. Porous CaCO₃ was synthesized using calcium gluconate (Ca(C₆H₁₁O₇)₂), and it was doped with Mn-Fe using two different methods—wet grinding using MnFe₂O₄ powder with ethanol, and adding Fe³⁺ (Fe(NO₃)₃) and Mn²⁺ (Mn(NO₃)₂) to Ca(C₆H₁₁O₇)₂ in solution to produce Ca-Mn-Fe oxides (Ca:Mn:Fe mole ratio: 100:2:4, 100:4:8 and 100:6:12). The best results were obtained with the mixed oxide containing Ca:Mn:Fe = 100:6:12 mole ratio, which demonstrated a solar absorptance of 90.15% against 11.23% for pure CaCO₃. This material also retained above 93% of its heat release capacity over 60 cycles, with over 1438 kJ/kg energy storage density. A similar study also recently reported the synthesis of Ca₂FeMnO₅/CaCO₃ to improve the direct solar energy absorption of the material [54]. The material presented excellent cycling stability and high energy density (2.51 MJ/kg after 20 cycles) and improved the optical absorption up to seven times higher than pure CaCO₃.

Cheaper sources of calcium carbonate are being researched along with ways to improve their efficiency, in order to recycle waste and provide a cheap source of material for TCES based on calcium looping (CaL). For example, limestone was used for the development of new models of fluidized bed reactors for TCES application at high temperatures, reaching a maximum stable temperature state at 1175 °C [55]. Other natural CaCO₃ minerals were also evaluated for TCES such as chalk and marble [56]. The various materials possess similar composition but present different cycling stability in CaL-CSP conditions, which is attributed to differences in particle size and microstructure. However, pure CaCO₃/CaO material suffers from pore-plugging and the addition of an inert material has proved to help reduce the sintering effect. As an example, the cycling stability of CaO derived from limestone and from pure CaCO₃ both suffers from pore-plugging mechanism, but the reaction of CaO derived from dolomite is not limited by this mechanism due to the presence of inert MgO which helps with the diffusion of CO₂ into the material [57]. The durability of CaO pellets synthesized from CaO powder with MgO added and from the mixture of limestone and dolomite were compared. Porous CaO powder stabilized with MgO was synthesized, using citric acid as sacrificial template, starting from a solution of calcium and magnesium nitrates [58]. The porous CaO powder showed optimum stability over 20 cycles of calcination/carbonation with 10 mol% of MgO added, greatly enhancing the resistance of the material to sintering. The other synthesis approach using dry mixing of citric acid with limestone-dolomite mixtures was used to make MgO-stabilized CaO porous pellets. The pellets demonstrated negligible capacity losses over the course of 20 cycles as compared to pure CaO powder. However, the pellets made from the limestone-dolomite mixture presented a slightly lower initial thermal energy released than MgO-stabilized CaO powder made from the nitrates reagents, and this difference was attributed to the sintering of impurities present in the limestone-dolomite mixtures. Well-dispersed MgO nanoparticle coating CaO/CaCO₃ grains were obtained using calcium and magnesium acetate as precursors [59]. The obtained porous material presented an enhanced resistance to pore-plugging and sintering, together with long-term effective conversion after 30 calcination/carbonation cycles. Samples originating from mined dolomite were also studied, and they demonstrated good qualities as energy storage materials, because they contain impurities, such as quartz, which prevents the grain agglomeration during the calcination/carbonation cycles [60]. The mined samples also had a high porosity which favors gas transport within the material. In this study, the dolomite samples, commercial with and without impurities and mined dolomite, were mixed with molten salt, NaCl:MgCl₂ mixture, which was considered to serve as catalyst. The studied mixtures of dolomite and molten salt could sustain over 10 cycles at around 50% capacity between 450 and 550 °C without further loss in capacity. A different cheap and renewable option presented recently is the use of biomineralized CaCO₃ from waste [61]. Eggshell and snailshell from food waste were investigated as potential precursors for CaL applications. The study revealed that the results obtained on the multicyclic conversion of the biomineralized CaCO₃ were comparable to the results reported for limestone, with the precision that biomineralized $CaCO_3$ required a lower temperature than limestone to reach full calcination. Again, in comparison to limestone, the shells presented better carbonation performances and faster decarbonation. Another waste material, carbide slag, was studied and compared to limestone [62]. The measured optimum carbonation temperature range for energy storage using carbide slag carbonated under 1.3 MPa was 800-850 °C, against slightly higher temperature for limestone, 850–900 °C. Under these operating conditions, the carbonation conversion of carbide slag was slower than that of limestone. However, the carbonated carbide slag showed higher cyclic stability than limestone, under high pressure. Oil shale ash was also proposed to be repurposed for TCES, as their main components are calcium, magnesium and silica, but it presented little potential for TCES [63]. The disposal of fly ash, a hazardous material resulting from solid waste incineration and containing CaO, was considered for its use in TCES application [64]. The analysis of the material revealed the presence of different heavy metals, and fly ash particles would agglomerate and be subjected to sintering when heated to 1150 °C. The fly ash particles could store energy, and one of the samples could release the stored energy (240 kJ/kg) (when compared to two other fly ash samples, it contained a higher amount of SiO₂, but less Na₂O and Cl⁻). Another work aimed to investigate the physical and chemical characterization of six fly ash samples obtained from different municipal solid waste incinerators, namely grate furnaces, rotary kiln and fluidized bed reactor, to determine their potential for CO₂ storage and TCES [65]. Other materials such as a calcium-rich steel and blast furnace slags, treated with acetic acid, were considered and compared to limestone [66]. The various studied CaO-based samples featured a complex elemental composition including Si, Al, Fe, Mg, Mn and Cr. The study revealed the attractiveness of calcium and calcium magnesium acetates. However, the presence of Si was reported to enhance the mesoporosity of the sample after calcination, and to promote pore plugging. Moreover, the presence of Al was also reported to hinder the performance of the blast furnace slag samples due to leading to the formation of calcium aluminates.

Among metal carbonates, strontium carbonate is also a very attractive material and is also considered for implementation in solar power plants (Equation (3)) [67,68]. A recent kinetic study focused on the investigation of the degree of the reaction, reaction rate constant, activation energy and diffusion coefficient of carbon dioxide through a series of experiments conducted between 800 and 1000 °C and under a CO₂ concentration of 5–40 vol% [69]. The stability of the material over several cycles was improved by the addition of inert materials such as MgO (Figure 4). The stability of the $SrCO_3/SrO$ system was also enhanced through the addition of Al_2O_3 (34 to 50 wt%), inhibiting the sintering of the material as well as enhancing the flow of particles, and it was studied in a lab-scale fluidized bed reactor [70]. The optimal amount of 34 wt% of Al₂O₃ to SrCO₃ was determined to limit the sintering. The dispersion of SrO particles before carbonation using polymorphic spacers such as $CaSO_4$ and $Sr_3(PO_4)_2$ was used in order to answer the issue of sintering in the $SrO/SrCO_3$ system [67]. When using $Sr_3(PO_4)_2$ contents between 25 and 50 wt% the system could go through multiple TCES cycles (10 to 30) with a stable energy storage density around 500 kJ/kg. While both calcium sulfate and strontium phosphate seemed to hinder sintering, strontium phosphate proved to be superior to calcium sulfate, showing higher gravimetric energy density at similar weight percentage added. The addition of MgO to SrCO₃/SrO proved to greatly enhance the cycling stability performances [33]. MgO was used to stabilize SrO-based materials using different synthesis methods: co-precipitation, sol-gel, wet-mixing and dry-mixing [71]. The wet-mixing method, using strontium acetate hemilydrate and porous magnesium oxide as precursors, produced the sample showing the highest performances between 1000 and 1100 °C. From this method, the sample containing 40 wt% SrO exhibited a high cycling stability (100 cycles), at 1000 °C with a gravimetric energy density of 0.81 MJ/kg.

$$SrO_{(s)} + CO_{2(g)} \rightleftharpoons SrCO_{3(s)}$$

$$(\Delta H^{\circ} = -241.5 \text{ kJ/mol})$$
(3)

A new concept of composite material based on $BaO/BaCO_3$ was recently introduced for application in TCES (Equations (4) and (5)) [72]. The study focused on the destabilization of $BaCO_3$ (which is

thermally stable up to high temperatures, 1150–1400 °C), for using this system at lower temperatures (700–1000 °C). The material was synthesized from a BaCO₃-BaSiO₃ mixture and could be reduced at a temperature 350 °C lower than pure BaCO₃ while retaining about 60% of the energy storage capacity. Furthermore, the material benefited from the addition of a catalytic amount of CaCO₃ which improved the reaction kinetics through the formation of Ba_{2-x}Ca_xSiO₄ intermediate compounds. Indeed, this improvement was attributed to the formation of Ba_{2-x}Ca_xSiO₄ facilitating Ba²⁺ and O²⁻ mobility through induced crystal defects. Due to the part of inactive material, the conversion rate of BaCO₃-BaSiO₃ mixture with CaCO₃ was about 60%, which closely relates to the expected amount of active material.

$$BaO_{(s)} + CO_{2(g)} \rightleftharpoons BaCO_{3(s)}$$

$$(\Delta H^{\circ} = -272.5 \text{ kJ/mol})$$
(4)

$$BaCO_{3(s)} + BaSiO_{3(s)} \rightleftharpoons Ba_2SiO_{4(s)} + CO_{2(g)}$$

$$(\Delta H_{850 \,^{\circ}C} = 126.9 \text{ kJ/mol})$$
(5)

Application of lithium silicate for TCES at high temperatures was proposed by Takasu et al. [73]. The carbonation/decarbonation of the system (Equation (6)) was tested in TGA under various CO_2 pressures and presented a gravimetric energy density of 780 kJ/kg at around 400–700 °C, under 100% CO_2 , with good durability over the course of 5 cycles.

$$Li_4SiO_{4(s)} + CO_{2(g)} \rightleftharpoons Li_2CO_{3(s)} + Li_2SiO_{3(s)} + \Delta H_r$$

$$(\Delta H_r = -94 \text{ kJ/mol})$$
(6)

The carbonation of transition metals was also considered to provide new materials for TCES at temperatures below 500 °C [74]. The carbonation of CoO, MnO, PbO and ZnO was studied, to obtain CoCO₃, MnCO₃, PbCO₃ and ZnCO₃, respectively, under high CO₂ pressure (8–50 bar), along with the effect of moisture and temperature (25–500 °C). Among these, only ZnCO₃ could not be obtained. At temperatures between 50 and 500 °C, in the presence of moisture under 8 bar CO₂, the corresponding ternary oxides of CoO and MnO were obtained. In the same conditions, PbO reacted to give both PbCO₃.PbO and PbCO₃.2PbO, and the latter was successfully cycled by varying the pressure between 8 and 2 bar. The carbonation of MnO and PbO was also observed in a reactor, under 50 bar in the presence of water.

4. TCES systems Based on Metal Oxides

Metal oxide based TCES systems are especially attractive as they permit working with an open cycle, using air (Equation (7), Figure 5). For this reason, the study of metal oxide systems in similar conditions with control of oxygen partial pressure (pO_2) is important. As a common trend, it can be observed that the reduction temperature decreases together with lower partial pressure of the reactive gas (O_2). The variation of the temperature as a function of pO_2 was illustrated using a Van't Hoff diagram for several metal oxide pairs (Figure 6).

$$MO_{red(s)} + O_{2(g)} \rightleftharpoons MO_{ox(s)} + \Delta H_r$$
 (7)

The potential of CuO/Cu₂O, Co₃O₄/CoO, Mn₂O₃/Mn₃O₄ and Pb₃O₄/PbO was investigated under isotherms while varying pO₂ between 0.5 and 0.8 bar [75]. The copper and cobalt oxides showed good reversibility, but manganese oxide showed a beginning of sintering and lead oxide was eliminated as it showed no potential under these operating conditions. The Cu₂O/CuO system is also interesting as it possesses high reaction enthalpy and reacts at high temperatures [76]. This system was studied between 800 and 930 °C and focused on the effect of partial pressure variation on the reaction kinetics with pO₂ = 0.1, 0.2, 0.5 and 1.0 bar. The Avrami-Erofeev's two-dimensional nucleation model (A2) was determined as the best fitting conversion model and gave an activation energy of 233 kJ/mol, with a frequency factor of 5×10^9 1/s. The potential of liquid multivalent metal oxides was tested in

liquid chemical looping thermal energy storage (LCL-TES) [77]. The free Gibbs energy of PbO/Pb, MnO₂/Mn and BaO₂/Ba, were determined using the Ellingham diagram, and these oxides were eliminated for TES application as their ΔG° were found to be positive. Conversely, the negative ΔG° of PbO₂/PbO, PbO₂/Pb₃O₄, Pb₃O₄/PbO, CuO/Cu₂O and Sb₂O₅/Sb₂O₃ validated them as potential candidates. CuO/Cu₂O presented the highest total enthalpy of 404.67 kJ/mol, but formation of the molten phase occurred at very high temperatures (~1200 °C), and the corrosiveness of the system when molten would make the implementation difficult. Pb oxides were noted as easier to implement since lead's melting temperature is below 1000 °C even though the associated total reaction enthalpy is lower (250.09 kJ/mol) and toxicity may be a barrier. The integration of CuO/Cu₂O to TCES processes was considered, and the reaction kinetics and stability of the material was studied in a fixed-bed reactor [78]. Kinetic models were derived for the charging and discharging steps using isokinetic and isothermal measurement. The cycling of Fe_2O_3/Fe_3O_4 was studied using pressure-swing by performing the reduction under vacuum and the re-oxidation using compressed air stream [79]. The study of BaO₂/BaO revealed its capacity to undergo several redox cycles without deactivation (Equation (8)), using a thermal pre-treatment at high temperatures to enhance the oxidation conversion of the material [80]. Since the high temperature pre-treatment eliminated impurities in the sample, it is speculated that a high purity of BaO₂ would show better redox performances.

$$2BaO_{(s)} + O_{2(g)} \rightleftharpoons 2BaO_{2(s)}$$

$$(\Delta H^{\circ} = -86.3 \text{ kJ/mol BaO})$$
(8)

Moreover, it was demonstrated that mixed metal oxides (e.g., Mn-Fe-O) can exhibit higher reaction enthalpy and cycling durability than the related pure metal oxide (Mn_2O_3) [81–83]. Other parameters can be tuned via metal oxide doping, such as the reaction kinetics and the gap in temperature between the charging and discharging steps of the system, and the cost of the energy storage material must also be taken into account for future system implementation [8,84–88]. In addition, for specific systems, such as Co-Fe-O, a linear correlation between the variation of the oxygen mass loss/gain and the reaction enthalpy was observed (Figure 5) [84]. Several mixed oxide systems were reported for their high potential for TCES by several studies, such as cobalt oxide/iron oxide, copper oxide/cobalt oxide, copper oxide/manganese oxide and manganese oxide/iron oxide [82,84–86].



Figure 5. Principle of open loop operation with metal oxides and correlation between enthalpy and oxygen mass exchange in mixed metal oxides.



Figure 6. Transition temperature variation (1/T) as a function of pO₂ for a selection of metal oxides represented through Van't Hoff diagram.

Mn₂O₃/Mn₃O₄ is a largely studied redox system for TCES application (MnO₂ was eliminated because of no reversibility [8]), due to the relatively high gravimetric energy storage density of the material and its availability, low toxicity and cost. However, the stability of this system decreases greatly over several oxidation/reduction cycles due to sintering and to the formation of the hausmannite phase which decreases the reversibility [84]. The doping of Mn_2O_3 with silicon oxides is a recently investigated option to answer the reversibility issues of manganese oxide-based TCES systems. The reactivity and stability of Mn/Si particles were studied in a packed-bed reactor using 2 to 10 wt% added silica, with an interest for Si-doping potential to help spontaneous O₂ release and increase the stability of the material over several reduction/oxidation cycles [89]. In both TGA and packed-bed reactor, the sample composed of 6 wt% SiO₂ and 94 wt% Mn₃O₄ presented the highest amount of oxygen release. In addition, MnSiO₃ particles demonstrated a good physical stability under air at high temperatures. The effect of Si^{4+} doping to Mn_2O_3 on the reactivity and stability of the Mn_2O_3/Mn_3O_4 system was also studied, over 40 reduction/oxidation cycles [90]. The re-oxidation of Mn_3O_4 was improved with the introduction of Si cations, especially for a sample synthesized via a sol-gel method using 1 mol% Si-doping. The segregation of Si⁴⁺ on Mn₂O₃ grain surfaces was observed and proved to help control and reduce the diffusivity at the grain boundaries. A method based on a combination of drop calorimetry and acid-solution calorimetry was used to measure the total enthalpy and standard enthalpy of materials forming at high temperatures, Mn-Mg oxides, involving tin (II) chloride as a reducing agent to increase their dissolution rate [91,92]. With this method, the chemical energy storage found for Mn-Mg-O systems (1000–1500 $^{\circ}$ C, pO₂ = 0.2 atm) with different molar ratios of Mn/Mg (2/1, 1/1, and 2/3) was 565.3 ± 54.8, 586.3 ± 55.0 and 590.9 ± 62.5 kJ/kg, respectively. The volumetric energy density of the 1/1 composition under $pO_2 = 0.2$ atm was measured at 1813 ± 175 MJ/m³ during the reduction [93]. The study concludes that the manganese ratio should not be raised above 2/1. The study also investigated further doping of the manganese-magnesium oxide system with cobalt, iron, zinc or nickel oxides, which did not improve the reactivity, energy density nor stability of the system. Among the investigated metal doping for the enhancement of manganese oxide cycling performances, the addition of iron was demonstrated to yield especially good results. A study focusing on the mixed oxide $(Mn_{0.7}Fe_{0.3})_2O_3$ investigated the improvement of the particle stability via the

addition of either 20 wt% TiO₂, ZrO₂ or CeO₂ [94]. All the tested additives permitted an improvement against the manganese oxide particle agglomeration. However, the addition of TiO₂ showed to have a negative effect on the chemical reactivity of the oxide, while the addition of ZrO₂ brought the best enhancement towards increasing the attrition resistance of the particles. The effect of the addition of Al_2O_3 , Fe_2O_3 and ZrO_2 to manganese oxide spray-dried particles on their energy storage capacity, flowability and physical and chemical stability was studied [95]. The samples mixed with zirconia and alumina allowed the individual particles to better retain their structure; however, the sample containing iron performed better during redox cycles. A reaction enthalpy of 175.7 kJ/kg was measured for the mixture with Mn_2O_3 and 67 wt% Fe₂O₃ prepared by intensive mixing, which then performed better than the spray-dried sample with similar composition (contaminated with sodium). The formation of a spinel $MnFe_2O_4$ was obtained through the reduction of a mixture of 2:1 Fe_2O_3 : Mn_2O_3 . The reaction of re-oxidation was described through two reaction mechanisms, starting with a diffusion-controlled reaction mechanism with no phase change, and followed by a nucleation-growth reaction mechanism, with activation energies of 192 and 181 kJ/mol for each reaction, respectively. A similar mixed oxide with Fe/Mn (2:1) was studied in a packed-bed reactor using small particles (0.5–1.0 mm) of iron-manganese oxide [96]. This work also presents a model comparing heat transfer, mass transfer and the thermochemical reaction with experimental data. Tests in a lab-scale tube reactor, between 800 and 1040 °C in air, were conducted on a previously validated Fe/Mn 1/3 granular mixture which showed no degradation over the course of 17 cycles [97,98]. The experiment demonstrated the presence of characteristic temperature profiles along the bed height, which were shown to be dependent on the thermodynamic properties and kinetic behavior of the redox reaction. The tuning of the reaction temperatures of oxides is very important to optimize the system energy storage since the gap in temperature between both charge and discharge steps can be reduced. Co-doping, using Fe and Cu, on manganese oxide was used to reduce this gap in temperature [83]. Indeed, the incorporation of Fe to the system was used to increase oxidation temperature, and Cu addition was used to reduce the reduction temperature. The gap in temperature was decreased from 225 °C for pure manganese oxide, to 81 °C for a composition with 20 mol% Fe and 5 mol% Cu. However, the addition of Cu induced a decrease in the reduction rate and a gradual decrease in the oxidation rate, which was attributed to the formation of segregated mixed Mn–Cu spinel.

Cobalt oxide based TCES systems have demonstrated the best performances among pure metal oxides, with high enthalpy and excellent cycling stability (Figure 7a), and are attracting attention for pilot scale tests [99]. However, this still leaves room for improvement and attempts to reduce the material cost and toxicity via the synthesis of mixed oxides [81,85–87,100]. In addition, the temperature gap between the reduction and oxidation step could be reduced with the same approach (Figure 7b). Storage material made from inert honeycomb supports (cordierite) and coated with cobalt oxide was studied at pilot-scale [99]. A large amount of redox material (88 kg) was cycled for 22 charging/discharging cycles with absence of degradation. The Co-Mn-O system demonstrated good reversibility for low amounts of manganese, and an increase in temperature compared to the pure oxides [81]. The reaction temperature of various Co-Mn mixed oxides, $Co_{3-x}Mn_xO_4$ ($0 \le x \le 3$), was investigated between 850 and 1700 °C [101,102]. The measured reaction temperatures for Co_{2.5}Mn_{0.5}O₄, Co₂MnO₄, Co_{1.5}Mn_{1.5}O₄, CoMn₂O₄ and Co_{0.5}Mn_{2.5}O₄ were (red-ox) 980–910, 1129–1050, 1230–1162, 1320–1260 and 1428–1410°C, respectively. The phase transition from the cubic-to-tetragonal phase within 1.2 < x < 1.9 was thoroughly examined. The mixed oxides presented higher enthalpies than the respective pure oxides, with the $Co_{1.5}Mn_{1.5}O_4$ sample showing the highest enthalpy (1264 kJ/kg). The mixed oxides have higher reduction temperatures than pure Co_3O_4 , reaching up to 1428 °C for $Co_{0.5}Mn_{2.5}O_4$.



Figure 7. (a) Redox activity of Co_3O_4/CoO foam made from commercial Co_3O_4 , (b) variation of the temperature gap between the reduction and oxidation step of Co_3O_4/CoO depending on the doping composition.

5. TCES Systems Based on Perovskites

Perovskites have also been considered as an innovative option for TCES application. Taking advantage of oxygen vacancies in perovskites structures and their oxygen ion conducting properties, ABO₃ perovskites can be used to store energy via O₂ exchange (Equation (9)). Some perovskites offer the interesting ability to store and release oxygen in a continuous way following the variation in temperature [103] (Figure 8). Different perovskites with Fe, Co or Mn on the B site were studied, and Co-based perovskites showed the highest O₂ exchange capacity together with high reaction enthalpies [103]. The enhancement of O₂ exchange capacity in these systems was achieved with the presence of Ba on the A site (BaCoO₃, BaFeO₃ and Ba_{0.5}Sr_{0.5}CoO₃), as compared to the presence of Sr. However, only BaCoO₃ could be re-oxidized completely under 20% O₂ atmosphere.

$$ABO_{3-\delta} \rightleftharpoons ABO_{3-\delta-\Delta\delta} + 1/2 \,\Delta\delta O_2 \tag{9}$$

The Ba_ySr_{1-y}CoO_{3-δ} system was also studied, along with La_xSr_{1-x} (Mn, Fe, Co)O_{3-δ}, by Gokon et al. [104]. The study concluded on the suitability of Ba_{0.3}Sr_{0.7}CoO_{3-δ} and Ba_{0.7}Sr_{0.3}CoO_{3-δ} for TCES above 600 °C in air stream. It was noted that no direct correlation was observed between the oxygen storage capacity and the tendency of the heat storage capacity for these systems. For comparison, it is mentioned that the charging/discharging capacity of Ba_{0.3}Sr_{0.7}CoO_{3-δ} is higher than that of Fe-doped manganese oxides, which have been shown to be a promising system for TCES. The La_xSr_{1-x}(Mn, Fe, Co)O_{3-δ} system was studied further with focus on the La_xSr_{1-x}Co_yMn_{1-y}O_{3-δ} (LSCM) and La_xSr_{1-x}Co_yFe_{1-y}O_{3-δ} (LSCF) series [105,106]. TGA and structural investigation revealed that the systems with low La content presented the highest redox activity, with an optimum reached for x = 0.3, while the perovskites adopted a cubic structure, or tetragonal structure for LSCM. Higher La content led to a higher distortion in the perovskite structure, related to a decrease in redox activity. Among all the systems studied, the LSCM3791 composition presented the highest gravimetric energy density (250 kJ/kg-ABO₃). Very recently, dual-phase La_{0.65}Sr_{0.35}MnO_{3-x}CeO₂ composites (with x = 0, 5, 10, 20, 50, and 100%) were investigated for oxygen exchange and CO₂ splitting, via thermochemical redox reactions, for the purpose of fuel production [107]. This work demonstrated the enhancement in

oxygen exchange obtained for the La_{0.65}Sr_{0.35}MnO₃ type perovskite material using the addition of ceria. The composite material presented higher oxygen release and high CO₂ conversion for solar-to-fuel production. Another Co-based perovskite, YBaCo₄O_{7+ δ}, was recently investigated for its suitability for thermochemical cycles and solar thermochemical fuel production, although at medium temperature (275–400 °C) [108]. The material, studied with TGA and within a small-scale vacuum test, presented low kinetics at low pO₂ level. Along with the influence of pO₂, the temperature and the particle size also showed an impact on the oxygen uptake capacity and kinetics of YBaCo₄O_{7+ δ}.



Figure 8. Thermogravimetry (TG) analysis of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite during redox cycles showing a continuous release and intake of oxygen under a dynamic heating program in 20% O₂/Ar.

The Ca-Mn-based perovskite system has also attracted strong attention for TCES, for example with the doped calcium manganite $CaB_xMn_{1-x}O_{3-\delta}$ (with x = 0.2 and B = Al or Ti) [109]. This class of perovskite offers the highest reaction enthalpy (390 kJ/kg) among perovskites systems studied for this application. When compared to $La_{0.3}Sr_{0.7}Co_{0.9}Mn_{0.1}O_{3-\delta}$, the materials require a higher reduction temperature and then present a higher reaction enthalpy for the reduction step. In addition, $CaB_xMn_{1-x}O_{3-\delta}$ possesses a reduced molecular weight (35% less), reducing the cost of potential implementation as the storage capacity is increased per mass of material, and reaction enthalpy extraction can be carried out at up to $1250 \, ^{\circ}\text{C}$ (pO₂ = 0.001 atm). Systems such as $Ca_{1-x}Sr_xMnO_{3-\delta}$ have also demonstrated interesting properties while being studied for TCES [110–112]. Similar variations were observed among different compositions for Sr-doped CaMnO_{3- δ} materials—e.g., $Ca_{0.9}Sr_{0.1}MnO_{3-\delta}$ —such as an improved conversion efficiency (solar-to-electric) with higher reduction temperature and higher pO_2 , during the reduction and with no reduction in the specific energy storage capacity [111]. A thorough screening of A-site doped $Ca_{1-x}Sr_xMnO_{3-\delta}$ and B-site doped $CaMe_vMn_{1-v}O_{3-\delta}$ (with Me = Cr, Ti, and Fe and $y \le 0.1$) was conducted. The study investigated the oxygen non-stoichiometry (δ) of the various systems according to temperature and pO₂ [113]. The compositions $Ca_{1-x}Sr_xMnO_{3-\delta}$ (x = 0.05 and 0.10) and $CaCr_yMn_{1-y}O_{3-\delta}$ (y = 0.05 and 0.10) were selected for further characterization. Among them, the Sr-doped $Ca_{1-x}Sr_xMnO_{3-\delta}$ compositions exhibited the highest specific energy storage capacity with a thermodynamic limit of ≈700 kJ·kg⁻¹ (900 °C, pO₂ = 10^{-4} bar). The CaCr_{0.1}Mn_{0.9}O_{3- δ} composition also showed good potential for TCES, with close performances to CaMnO_{3- δ} in terms of oxidation temperature, mass-change and reaction enthalpy, and in addition, the B-site chromium doping raised cycling durability of the perovskite material [114]. Recently, $CaMnO_{3-\delta}$ and $CaCr_{0.1}Mn_{0.9}O_{3-\delta}$ were identified as the most promising compositions out of different Ca-Mn-based perovskites studied for oxygen atmosphere control in solar thermochemical processes [115]. Aluminum-doped calcium manganite $CaAl_{0.2}Mn_{0.8}O_{3-\delta}$ particles

were synthesized and tested in a 5 kW_{th} scale (seven-lamp high-flux solar simulator) reactor under vacuum for TCES via reversible point defect reactions [116,117]. The material was introduced to the reactor in the form of particle flow using temperatures up to 900 °C to avoid particle agglomeration. The performances of the reactor were assessed for particle flow varying between 230 and 300 g/min, reactor inclination angle from 31° to 35° and radiative heat flux of 4.3 to 5.2 kW_{th}. The study of the Cu-doped perovskite system SrFeO_{3- δ}, SrFe_{1-x}Cu_xO_{3- δ}, demonstrated that with x = 0.05 both Cu and Fe are reduced, while for x = 0.15, the reduction occurs with a change in Fe oxidation state [118]. The re-oxidation of the material is fast around 150 °C, and the system is considered for oxygen storage application.

6. Conclusions

The most developed TCES systems were reviewed as this energy storage approach offers interesting prospects in view of future integration in solar processes for the aim of continuous round-the-clock operation. The relevant solar processes for high temperature energy storage application are the power production via thermodynamic cycles in CSP plants, but also the thermochemical processes requiring high temperature process heat to drive endothermal reactions (such as industrial processes for cement or iron/steel production, as well as chemical and fuel production processes). The main benefits of thermochemical energy storage over the other commonly-used and more developed storage systems (sensible or latent) are the possible long-term storage in the form of stable chemical materials, the high energy storage densities accessible and the heat storage at high temperatures in a wide range (from 400 to above 1000 °C). The main targeted benefits offered by TCES are the possible 24/7 operation and continuous production under fluctuating and intermittent solar irradiation conditions. This review shows that research is currently active in the fields of hydroxides and carbonates (mainly Ca-based), but also metal oxides and perovskites that allow operating in open loop under air as both the heat transfer fluid and the gaseous reactant (oxygen) during the heat charge/discharge steps. Strong research efforts and strategies are deployed to optimize the materials reactivity/stability over multiple cycles and avoid any loss in performance. Alternative materials are also being searched, such as abundant and low-cost ore minerals, residues from industrial wastes or side products for their potential use as TCES material. The materials' shaping and integration in reactor systems for heat storage and release are also another area of interest that requires the design and optimization of suitable reactor and heat exchanger concepts. Further investigations in the area of TCES should also focus on the kinetic investigations of the charge/discharge steps for practical implementation of TCES systems. Finally, systems analysis (heat and mass flow optimization, dynamic simulation for investigating impact of transient effects, energy/exergy performance analysis), process flowsheets and techno-economic analysis of the integrated system are also necessary to demonstrate the beneficial impacts of thermochemical energy storage on increasing the capacity factor of the solar plant thanks to continuous operation and on enhancing the viability of the whole solar process.

Author Contributions: Conceptualization, L.A. and S.A.; methodology, L.A. and S.A.; investigation, L.A. and S.A.; writing—original draft preparation, L.A. and S.A.; writing—review and editing, L.A. and S.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Yan, Y.; Wang, K.; Clough, P.T.; Anthony, E.J. Developments in calcium/chemical looping and metal oxide redox cycles for high-temperature thermochemical energy storage: A review. *Fuel Process. Technol.* 2020, 199, 106280. [CrossRef]
- Chen, X.; Zhang, Z.; Qi, C.; Ling, X.; Peng, H. State of the art on the high-temperature thermochemical energy storage systems. *Energy Convers. Manag.* 2018, 177, 792–815. [CrossRef]

- Bayon, A.; Bader, R.; Jafarian, M.; Fedunik-Hofman, L.; Sun, Y.; Hinkley, J.; Miller, S.; Lipiński, W. Techno-economic assessment of solid–gas thermochemical energy storage systems for solar thermal power applications. *Energy* 2018, 149, 473–484. [CrossRef]
- 4. Pan, Z.H.; Zhao, C.Y. Gas–solid thermochemical heat storage reactors for high-temperature applications. *Energy* **2017**, *130*, 155–173. [CrossRef]
- Zsembinszki, G.; Solé, A.; Barreneche, C.; Prieto, C.; Fernández, A.; Cabeza, L. Review of Reactors with Potential Use in Thermochemical Energy Storage in Concentrated Solar Power Plants. *Energies* 2018, 11, 2358. [CrossRef]
- 6. Pardo, P.; Deydier, A.; Anxionnaz-Minvielle, Z.; Rougé, S.; Cabassud, M.; Cognet, P. A review on high temperature thermochemical heat energy storage. *Renew. Sustain. Energy Rev.* 2014, 32, 591–610. [CrossRef]
- 7. Sunku Prasad, J.; Muthukumar, P.; Desai, F.; Basu, D.N.; Rahman, M.M. A critical review of high-temperature reversible thermochemical energy storage systems. *Appl. Energy* **2019**, 254, 113733. [CrossRef]
- André, L.; Abanades, S.; Flamant, G. Screening of thermochemical systems based on solid-gas reversible reactions for high temperature solar thermal energy storage. *Renew. Sustain. Energy Rev.* 2016, 64, 703–715. [CrossRef]
- 9. André, L.; Abanades, S. Investigation of metal oxides, mixed oxides, perovskites and alkaline earth carbonates/hydroxides as suitable candidate materials for high-temperature thermochemical energy storage using reversible solid-gas reactions. *Mater. Today Energy* **2018**, *10*, 48–61. [CrossRef]
- Schmidt, M.; Gutierrez, A.; Linder, M. Thermochemical energy storage with CaO/Ca(OH)₂—Experimental investigation of the thermal capability at low vapor pressures in a lab scale reactor. *Appl. Energy* 2017, *188*, 672–681. [CrossRef]
- Rougé, S.; Criado, Y.A.; Soriano, O.; Abanades, J.C. Continuous CaO/Ca(OH)₂ Fluidized Bed Reactor for Energy Storage: First Experimental Results and Reactor Model Validation. *Ind. Eng. Chem. Res.* 2017, 56, 844–852. [CrossRef]
- 12. Yuan, Y.; Li, Y.; Zhao, J. Development on Thermochemical Energy Storage Based on CaO-Based Materials: A Review. *Sustainability* **2018**, *10*, 2660. [CrossRef]
- 13. Funayama, S.; Takasu, H.; Zamengo, M.; Kariya, J.; Kim, S.T.; Kato, Y. Performance of thermochemical energy storage of a packed bed of calcium hydroxide pellets. *Energy Storage* **2019**, *1*, e40. [CrossRef]
- Xu, M.; Huai, X.; Cai, J. Agglomeration Behavior of Calcium Hydroxide/Calcium Oxide as Thermochemical Heat Storage Material: A Reactive Molecular Dynamics Study. J. Phys. Chem. C 2017, 121, 3025–3033. [CrossRef]
- Criado, Y.A.; Huille, A.; Rougé, S.; Abanades, J.C. Experimental investigation and model validation of a CaO/Ca(OH)₂ fluidized bed reactor for thermochemical energy storage applications. *Chem. Eng. J.* 2017, 313, 1194–1205. [CrossRef]
- 16. Dai, L.; Long, X.-F.; Lou, B.; Wu, J. Thermal cycling stability of thermochemical energy storage system Ca(OH)₂/CaO. *Appl. Therm. Eng.* **2018**, *133*, 261–268. [CrossRef]
- 17. Funayama, S.; Takasu, H.; Zamengo, M.; Kariya, J.; Kim, S.T.; Kato, Y. Composite material for high-temperature thermochemical energy storage using calcium hydroxide and ceramic foam. *Energy Storage* **2019**, *1*, e53. [CrossRef]
- Funayama, S.; Takasu, H.; Kim, S.T.; Kato, Y. Thermochemical storage performance of a packed bed of calcium hydroxide composite with a silicon-based ceramic honeycomb support. *Energy* 2020, 201, 117673. [CrossRef]
- 19. Criado, Y.A.; Alonso, M.; Abanades, J.C. Enhancement of a CaO/Ca(OH)₂ based material for thermochemical energy storage. *Sol. Energy* **2016**, *135*, 800–809. [CrossRef]
- Gollsch, M.; Afflerbach, S.; Angadi, B.V.; Linder, M. Investigation of calcium hydroxide powder for thermochemical storage modified with nanostructured flow agents. *Sol. Energy* 2020, 201, 810–818. [CrossRef]
- Cosquillo Mejia, A.; Afflerbach, S.; Linder, M.; Schmidt, M. Experimental analysis of encapsulated CaO/Ca(OH)₂ granules as thermochemical storage in a novel moving bed reactor. *Appl. Therm. Eng.* 2020, 169, 114961. [CrossRef]
- 22. Xia, B.Q.; Zhao, C.Y.; Yan, J.; Khosa, A.A. Development of granular thermochemical heat storage composite based on calcium oxide. *Renew. Energy* **2020**, *147*, 969–978. [CrossRef]

- 23. Shkatulov, A.; Aristov, Y. Calcium hydroxide doped by KNO₃ as a promising candidate for thermochemical storage of solar heat. *RSC Adv.* **2017**, *7*, 42929–42939. [CrossRef]
- 24. Wang, T.; Zhao, C.Y.; Yan, J. Investigation on the Ca(OH)₂/CaO thermochemical energy storage system with potassium nitrate addition. *Sol. Energy Mater. Sol. Cells* **2020**, *215*, 110646. [CrossRef]
- 25. Yan, J.; Zhao, C.Y. Experimental study of CaO/Ca(OH)₂ in a fixed-bed reactor for thermochemical heat storage. *Appl. Energy* **2016**, 175, 277–284. [CrossRef]
- Huang, C.; Xu, M.; Huai, X. Experimental investigation on thermodynamic and kinetic of calcium hydroxide dehydration with hexagonal boron nitride doping for thermochemical energy storage. *Chem. Eng. Sci.* 2019, 206, 518–526. [CrossRef]
- 27. Huang, C.; Xu, M.; Huai, X. Synthesis and performances evaluation of the spindle-shaped calcium hydroxide nanomaterials for thermochemical energy storage. *J. Nanopart. Res.* **2019**, *21*, 262. [CrossRef]
- Flegkas, S.; Birkelbach, F.; Winter, F.; Groenewold, H.; Werner, A. Profitability Analysis and Capital Cost Estimation of a Thermochemical Energy Storage System Utilizing Fluidized Bed Reactors and the Reaction System MgO/Mg(OH)₂. *Energies* 2019, *12*, 4788. [CrossRef]
- 29. Müller, D.; Knoll, C.; Gravogl, G.; Artner, W.; Welch, J.M.; Eitenberger, E.; Friedbacher, G.; Schreiner, M.; Harasek, M.; Hradil, K.; et al. Tuning the performance of MgO for thermochemical energy storage by dehydration—From fundamentals to phase impurities. *Appl. Energy* **2019**, *253*, 113562. [CrossRef]
- 30. Li, S.; Liu, J.; Tan, T.; Nie, J.; Zhang, H. Optimization of LiNO₃–Mg(OH)₂ composites as thermo-chemical energy storage materials. *J. Environ. Manag.* **2020**, *262*, 110258. [CrossRef]
- 31. Shkatulov, A.I.; Aristov, Y. Thermochemical Energy Storage using LiNO₃-Doped Mg(OH)₂: A Dehydration Study. *Energy Technol.* **2018**, *6*, 1844–1851. [CrossRef]
- 32. Shkatulov, A.; Takasu, H.; Kato, Y.; Aristov, Y. Thermochemical energy storage by LiNO₃-doped Mg(OH)₂: Rehydration study. *J. Energy Storage* **2019**, *22*, 302–310. [CrossRef]
- André, L.; Abanades, S. Evaluation and performances comparison of calcium, strontium and barium carbonates during calcination/carbonation reactions for solar thermochemical energy storage. *J. Energy Storage* 2017, 13, 193–205. [CrossRef]
- 34. Abanades, S.; André, L. Design and demonstration of a high temperature solar-heated rotary tube reactor for continuous particles calcination. *Appl. Energy* **2018**, *212*, 1310–1320. [CrossRef]
- 35. Ortiz, C.; Romano, M.C.; Valverde, J.M.; Binotti, M.; Chacartegui, R. Process integration of Calcium-Looping thermochemical energy storage system in concentrating solar power plants. *Energy* **2018**, *155*, 535–551. [CrossRef]
- Ortiz, C.; Valverde, J.M.; Chacartegui, R.; Perez-Maqueda, L.A.; Giménez, P. The Calcium-Looping (CaCO₃/CaO) process for thermochemical energy storage in Concentrating Solar Power plants. *Renew. Sustain. Energy Rev.* 2019, 113, 109252. [CrossRef]
- 37. Astolfi, M.; De Lena, E.; Romano, M.C. Improved flexibility and economics of Calcium Looping power plants by thermochemical energy storage. *Int. J. Greenh. Gas Control* **2019**, *83*, 140–155. [CrossRef]
- 38. Cannone, S.F.; Stendardo, S.; Lanzini, A. Solar-Powered Rankine Cycle Assisted by an Innovative Calcium Looping Process as an Energy Storage System. *Ind. Eng. Chem. Res.* **2020**, *59*, 6977–6993. [CrossRef]
- Durán-Martín, J.D.; Sánchez Jimenez, P.E.; Valverde, J.M.; Perejón, A.; Arcenegui-Troya, J.; García Triñanes, P.; Pérez Maqueda, L.A. Role of particle size on the multicycle calcium looping activity of limestone for thermochemical energy storage. *J. Adv. Res.* 2020, 22, 67–76. [CrossRef]
- 40. Fedunik-Hofman, L.; Bayon, A.; Donne, S.W. Kinetics of Solid-Gas Reactions and Their Application to Carbonate Looping Systems. *Energies* **2019**, *12*, 2981. [CrossRef]
- 41. Benitez-Guerrero, M.; Valverde, J.M.; Perejon, A.; Sanchez-Jimenez, P.E.; Perez-Maqueda, L.A. Low-cost Ca-based composites synthesized by biotemplate method for thermochemical energy storage of concentrated solar power. *Appl. Energy* **2018**, *210*, 108–116. [CrossRef]
- 42. Khosa, A.A.; Zhao, C.Y. Heat storage and release performance analysis of CaCO₃/CaO thermal energy storage system after doping nano silica. *Sol. Energy* **2019**, *188*, 619–630. [CrossRef]
- 43. Han, R.; Gao, J.; Wei, S.; Su, Y.; Su, C.; Li, J.; Liu, Q.; Qin, Y. High-performance CaO-based composites synthesized using a space-confined chemical vapor deposition strategy for thermochemical energy storage. *Sol. Energy Mater. Sol. Cells* **2020**, *206*, 110346. [CrossRef]

- 44. Han, R.; Gao, J.; Wei, S.; Sun, F.; Liu, Q.; Qin, Y. Development of dense Ca-based, Al-stabilized composites with high volumetric energy density for thermochemical energy storage of concentrated solar power. *Energy Convers. Manag.* **2020**, *221*, 113201. [CrossRef]
- 45. Sun, H.; Li, Y.; Yan, X.; Zhao, J.; Wang, Z. Thermochemical energy storage performance of Al₂O₃/CeO₂ co-doped CaO-based material under high carbonation pressure. *Appl. Energy* **2020**, *263*, 114650. [CrossRef]
- 46. Møller, K.T.; Ibrahim, A.; Buckley, C.E.; Paskevicius, M. Inexpensive thermochemical energy storage utilising additive enhanced limestone. *J. Mater. Chem. A* **2020**, *8*, 9646–9653. [CrossRef]
- 47. Chen, X.; Jin, X.; Liu, Z.; Ling, X.; Wang, Y. Experimental investigation on the CaO/CaCO₃ thermochemical energy storage with SiO₂ doping. *Energy* **2018**, *155*, 128–138. [CrossRef]
- Han, R.; Gao, J.; Wei, S.; Su, Y.; Sun, F.; Zhao, G.; Qin, Y. Strongly coupled calcium carbonate/antioxidative graphite nanosheets composites with high cycling stability for thermochemical energy storage. *Appl. Energy* 2018, 231, 412–422. [CrossRef]
- 49. Chen, Q.; Zhang, Y.; Ding, Y. Wettability of molten sodium sulfate salt on nanoscale calcium oxide surface in high-temperature thermochemical energy storage. *Appl. Surf. Sci.* **2020**, *505*, 144550. [CrossRef]
- 50. Raganati, F.; Chirone, R.; Ammendola, P. Calcium-looping for thermochemical energy storage in concentrating solar power applications: Evaluation of the effect of acoustic perturbation on the fluidized bed carbonation. *Chem. Eng. J.* **2020**, *392*, 123658. [CrossRef]
- 51. Da, Y.; Xuan, Y.; Teng, L.; Zhang, K.; Liu, X.; Ding, Y. Calcium-based composites for direct solar-thermal conversion and thermochemical energy storage. *Chem. Eng. J.* **2020**, *382*, 122815. [CrossRef]
- 52. Zheng, H.; Song, C.; Bao, C.; Liu, X.; Xuan, Y.; Li, Y.; Ding, Y. Dark calcium carbonate particles for simultaneous full-spectrum solar thermal conversion and large-capacity thermochemical energy storage. *Sol. Energy Mater. Sol. Cells* **2020**, *207*, 110364. [CrossRef]
- 53. Teng, L.; Xuan, Y.; Da, Y.; Liu, X.; Ding, Y. Modified Ca-Looping materials for directly capturing solar energy and high-temperature storage. *Energy Storage Mater.* **2020**, *25*, 836–845. [CrossRef]
- 54. Yang, L.; Huang, Z.; Huang, G. Fe- and Mn-Doped Ca-Based Materials for Thermochemical Energy Storage Systems. *Energy Fuels* **2020**, *34*, 11479–11488. [CrossRef]
- 55. Tregambi, C.; Padula, S.; Galbusieri, M.; Coppola, G.; Montagnaro, F.; Salatino, P.; Troiano, M.; Solimene, R. Directly irradiated fluidized bed reactor for thermochemical energy storage and solar fuels production. *Powder Technol.* 2020, 366, 460–469. [CrossRef]
- Benitez-Guerrero, M.; Valverde, J.M.; Sanchez-Jimenez, P.E.; Perejon, A.; Perez-Maqueda, L.A. Multicycle activity of natural CaCO₃ minerals for thermochemical energy storage in Concentrated Solar Power plants. *Sol. Energy* 2017, 153, 188–199. [CrossRef]
- Benitez-Guerrero, M.; Sarrion, B.; Perejon, A.; Sanchez-Jimenez, P.E.; Perez-Maqueda, L.A.; Manuel Valverde, J. Large-scale high-temperature solar energy storage using natural minerals. *Sol. Energy Mater. Sol. Cells* 2017, 168, 14–21. [CrossRef]
- Wang, K.; Gu, F.; Clough, P.T.; Zhao, P.; Anthony, E.J. Porous MgO-stabilized CaO-based powders/pellets via a citric acid-based carbon template for thermochemical energy storage in concentrated solar power plants. *Chem. Eng. J.* 2020, 390, 124163. [CrossRef]
- 59. Sánchez Jiménez, P.E.; Perejón, A.; Benítez Guerrero, M.; Valverde, J.M.; Ortiz, C.; Pérez Maqueda, L.A. High-performance and low-cost macroporous calcium oxide based materials for thermochemical energy storage in concentrated solar power plants. *Appl. Energy* **2019**, *235*, 543–552. [CrossRef]
- Humphries, T.D.; Møller, K.T.; Rickard, W.D.A.; Sofianos, M.V.; Liu, S.; Buckley, C.E.; Paskevicius, M. Dolomite: A low cost thermochemical energy storage material. *J. Mater. Chem. A* 2019, 7, 1206–1215. [CrossRef]
- Arcenegui-Troya, J.; Sánchez-Jiménez, P.E.; Perejón, A.; Valverde, J.M.; Chacartegui, R.; Pérez-Maqueda, L.A. Calcium-Looping Performance of Biomineralized CaCO₃ for CO₂ Capture and Thermochemical Energy Storage. *Ind. Eng. Chem. Res.* 2020, *59*, 12924–12933. [CrossRef]
- Sun, H.; Li, Y.; Bian, Z.; Yan, X.; Wang, Z.; Liu, W. Thermochemical energy storage performances of Ca-based natural and waste materials under high pressure during CaO/CaCO₃ cycles. *Energy Convers. Manag.* 2019, 197, 111885. [CrossRef]
- 63. Maaten, B.; Konist, A.; Siirde, A. Potential of solid residues from power plants as thermochemical energy storage materials. *J. Anal. Calorim.* **2020**. [CrossRef]

- 64. Setoodeh Jahromy, S.; Jordan, C.; Azam, M.; Werner, A.; Harasek, M.; Winter, F. Fly Ash from Municipal Solid Waste Incineration as a Potential Thermochemical Energy Storage Material. *Energy Fuels* **2019**, *33*, 5810–5819. [CrossRef]
- 65. Setoodeh Jahromy, S.; Azam, M.; Huber, F.; Jordan, C.; Wesenauer, F.; Huber, C.; Naghdi, S.; Schwendtner, K.; Neuwirth, E.; Laminger, T.; et al. Comparing Fly Ash Samples from Different Types of Incinerators for Their Potential as Storage Materials for Thermochemical Energy and CO₂. *Materials* **2019**, *12*, 3358. [CrossRef]
- 66. Valverde, J.M.; Miranda-Pizarro, J.; Perejón, A.; Sánchez-Jiménez, P.E.; Pérez-Maqueda, L.A. Calcium-Looping performance of steel and blast furnace slags for thermochemical energy storage in concentrated solar power plants. *J. CO2 Util.* **2017**, *22*, 143–154. [CrossRef]
- 67. Bagherisereshki, E.; Tran, J.; Lei, F.; AuYeung, N. Investigation into SrO/SrCO₃ for high temperature thermochemical energy storage. *Sol. Energy* **2018**, *160*, 85–93. [CrossRef]
- Meroueh, L.; Yenduru, K.; Dasgupta, A.; Jiang, D.; AuYeung, N. Energy storage based on SrCO₃ and Sorbents—A probabilistic analysis towards realizing solar thermochemical power plants. *Renew. Energy* 2019, 133, 770–786. [CrossRef]
- Zare Ghorbaei, S.; Ale Ebrahim, H. Carbonation reaction of strontium oxide for thermochemical energy storage and CO₂ removal applications: Kinetic study and reactor performance prediction. *Appl. Energy* 2020, 277, 115604. [CrossRef]
- 70. Ammendola, P.; Raganati, F.; Miccio, F.; Murri, A.N.; Landi, E. Insights into utilization of strontium carbonate for thermochemical energy storage. *Renew. Energy* **2020**, *157*, 769–781. [CrossRef]
- 71. Gigantino, M.; Kiwic, D.; Steinfeld, A. Thermochemical energy storage via isothermal carbonation-calcination cycles of MgO-stabilized SrO in the range of 1000–1100 °C. *Sol. Energy* **2019**, *188*, 720–729. [CrossRef]
- 72. Møller, K.T.; Williamson, K.; Buckley, C.E.; Paskevicius, M. Thermochemical energy storage properties of a barium based reactive carbonate composite. *J. Mater. Chem. A* **2020**, *8*, 10935–10942. [CrossRef]
- 73. Takasu, H.; Ryu, J.; Kato, Y. Application of lithium orthosilicate for high-temperature thermochemical energy storage. *Appl. Energy* **2017**, *193*, 74–83. [CrossRef]
- 74. Gravogl, G.; Knoll, C.; Artner, W.; Welch, J.M.; Eitenberger, E.; Friedbacher, G.; Harasek, M.; Hradil, K.; Werner, A.; Weinberger, P.; et al. Pressure effects on the carbonation of MeO (Me = Co, Mn, Pb, Zn) for thermochemical energy storage. *Appl. Energy* **2019**, *252*, 113451. [CrossRef]
- 75. Silakhori, M.; Jafarian, M.; Arjomandi, M.; Nathan, G.J. Thermogravimetric analysis of Cu, Mn, Co, and Pb oxides for thermochemical energy storage. *J. Energy Storage* **2019**, *23*, 138–147. [CrossRef]
- 76. Setoodeh Jahromy, S.; Birkelbach, F.; Jordan, C.; Huber, C.; Harasek, M.; Werner, A.; Winter, F. Impact of Partial Pressure, Conversion, and Temperature on the Oxidation Reaction Kinetics of Cu₂O to CuO in Thermochemical Energy Storage. *Energies* 2019, 12, 508. [CrossRef]
- 77. Silakhori, M.; Jafarian, M.; Arjomandi, M.; Nathan, G.J. Comparing the thermodynamic potential of alternative liquid metal oxides for the storage of solar thermal energy. *Sol. Energy* **2017**, *157*, 251–258. [CrossRef]
- 78. Deutsch, M.; Horvath, F.; Knoll, C.; Lager, D.; Gierl-Mayer, C.; Weinberger, P.; Winter, F. High-Temperature Energy Storage: Kinetic Investigations of the CuO/Cu₂O Reaction Cycle. *Energy Fuels* 2017, *31*, 2324–2334. [CrossRef]
- 79. Bush, H.E.; Loutzenhiser, P.G. Solar electricity via an Air Brayton cycle with an integrated two-step thermochemical cycle for heat storage based on Fe₂O₃/Fe₃O₄ redox reactions: Thermodynamic and kinetic analyses. *Sol. Energy* **2018**, *174*, 617–627. [CrossRef]
- 80. Carrillo, A.J.; Sastre, D.; Serrano, D.P.; Pizarro, P.; Coronado, J.M. Revisiting the BaO₂/BaO redox cycle for solar thermochemical energy storage. *Phys. Chem. Chem. Phys.* **2016**, *18*, 8039–8048. [CrossRef]
- André, L.; Abanades, S.; Cassayre, L. Experimental Investigation of Co–Cu, Mn–Co, and Mn–Cu Redox Materials Applied to Solar Thermochemical Energy Storage. ACS Appl. Energy Mater. 2018, 1, 3385–3395.
 [CrossRef]
- 82. Block, T.; Schmücker, M. Metal oxides for thermochemical energy storage: A comparison of several metal oxide systems. *Sol. Energy* **2016**, *126*, 195–207. [CrossRef]
- 83. Carrillo, A.J.; Serrano, D.P.; Pizarro, P.; Coronado, J.M. Manganese oxide-based thermochemical energy storage: Modulating temperatures of redox cycles by Fe–Cu co-doping. *J. Energy Storage* **2016**, *5*, 169–176. [CrossRef]

- André, L.; Abanades, S.; Cassayre, L. Mixed Metal Oxide Systems Applied to Thermochemical Storage of Solar Energy: Benefits of Secondary Metal Addition in Co and Mn Oxides and Contribution of Thermodynamics. *Appl. Sci.* 2018, *8*, 2618. [CrossRef]
- Dizaji, H.B.; Hosseini, H. A review of material screening in pure and mixed-metal oxide thermochemical energy storage (TCES) systems for concentrated solar power (CSP) applications. *Renew. Sustain. Energy Rev.* 2018, 98, 9–26. [CrossRef]
- 86. Wu, S.; Zhou, C.; Doroodchi, E.; Nellore, R.; Moghtaderi, B. A review on high-temperature thermochemical energy storage based on metal oxides redox cycle. *Energy Convers. Manag.* **2018**, *168*, 421–453. [CrossRef]
- 87. Liu, J.; Baeyens, J.; Deng, Y.; Wang, X.; Zhang, H. High temperature Mn₂O₃/Mn₃O₄ and Co₃O₄/CoO systems for thermo-chemical energy storage. *J. Environ. Manag.* **2020**, *267*, 110582. [CrossRef] [PubMed]
- Müller, D.; Knoll, C.; Artner, W.; Harasek, M.; Gierl-Mayer, C.; Welch, J.M.; Werner, A.; Weinberger, P. Combining in-situ X-ray diffraction with thermogravimetry and differential scanning calorimetry—An investigation of Co₃O₄, MnO₂ and PbO₂ for thermochemical energy storage. *Sol. Energy* 2017, 153, 11–24. [CrossRef]
- 89. Yilmaz, D.; Darwish, E.; Leion, H. Investigation of the combined Mn-Si oxide system for thermochemical energy storage applications. *J. Energy Storage* 2020, *28*, 101180. [CrossRef]
- Bielsa, D.; Zaki, A.; Arias, P.L.; Faik, A. Improving the redox performance of Mn₂O₃/Mn₃O₄ pair by Si doping to be used as thermochemical energy storage for concentrated solar power plants. *Sol. Energy* 2020, 204, 144–154. [CrossRef]
- 91. King, K.; Randhir, K.; Klausner, J. Calorimetric method for determining the thermochemical energy storage capacities of redox metal oxides. *Thermochim. Acta* 2019, 673, 105–118. [CrossRef]
- Randhir, K.; King, K.; Rhodes, N.; Li, L.; Hahn, D.; Mei, R.; AuYeung, N.; Klausner, J. Magnesium-manganese oxides for high temperature thermochemical energy storage. J. Energy Storage 2019, 21, 599–610. [CrossRef]
- 93. King, K.; Randhir, K.; Petrasch, J.; Klausner, J. Enhancing thermochemical energy storage density of magnesium-manganese oxides. *Energy Storage* **2019**, *1*, e83. [CrossRef]
- 94. Preisner, N.C.; Block, T.; Linder, M.; Leion, H. Stabilizing Particles of Manganese-Iron Oxide with Additives for Thermochemical Energy Storage. *Energy Technol.* **2018**, *6*, 2154–2165. [CrossRef]
- Al-Shankiti, I.A.; Ehrhart, B.D.; Ward, B.J.; Bayon, A.; Wallace, M.A.; Bader, R.; Kreider, P.; Weimer, A.W. Particle design and oxidation kinetics of iron-manganese oxide redox materials for thermochemical energy storage. *Sol. Energy* 2019, *183*, 17–29. [CrossRef]
- Hamidi, M.; Wheeler, V.M.; Gao, X.; Pye, J.; Catchpole, K.; Weimer, A.W. Reduction of iron–manganese oxide particles in a lab-scale packed-bed reactor for thermochemical energy storage. *Chem. Eng. Sci.* 2020, 221, 115700. [CrossRef]
- 97. Wokon, M.; Kohzer, A.; Linder, M. Investigations on thermochemical energy storage based on technical grade manganese-iron oxide in a lab-scale packed bed reactor. *Sol. Energy* **2017**, *153*, 200–214. [CrossRef]
- Wokon, M.; Block, T.; Nicolai, S.; Linder, M.; Schmücker, M. Thermodynamic and kinetic investigation of a technical grade manganese-iron binary oxide for thermochemical energy storage. *Sol. Energy* 2017, 153, 471–485. [CrossRef]
- Tescari, S.; Singh, A.; Agrafiotis, C.; de Oliveira, L.; Breuer, S.; Schlögl-Knothe, B.; Roeb, M.; Sattler, C. Experimental evaluation of a pilot-scale thermochemical storage system for a concentrated solar power plant. *Appl. Energy* 2017, 189, 66–75. [CrossRef]
- 100. Zhou, X.; Mahmood, M.; Chen, J.; Yang, T.; Xiao, G.; Ferrari, M.L. Validated model of thermochemical energy storage based on cobalt oxides. *Appl. Therm. Eng.* **2019**, *159*, 113965. [CrossRef]
- Zaki, A.; Bielsa, D.; Faik, A. Development of a continuous solid solution with extended Red-Ox temperature range and unexpected high reaction enthalpies for thermochemical energy storage. *AIP Conf. Proc.* 2019, 2126, 210010. [CrossRef]
- 102. Zaki, A.; Carrasco, J.; Bielsa, D.; Faik, A. Tunable Redox Temperature of a Co_{3-x}Mn_xO₄ (0 ≤ x ≤ 3) Continuous Solid Solution for Thermochemical Energy Storage. ACS Appl. Mater. Interfaces 2020, 12, 7010–7020. [CrossRef] [PubMed]
- 103. Zhang, Z.; Andre, L.; Abanades, S. Experimental assessment of oxygen exchange capacity and thermochemical redox cycle behavior of Ba and Sr series perovskites for solar energy storage. *Sol. Energy* 2016, 134, 494–502. [CrossRef]

- 104. Gokon, N.; Yawata, T.; Bellan, S.; Kodama, T.; Cho, H.-S. Thermochemical behavior of perovskite oxides based on La_xSr_{1-x}(Mn, Fe, Co)O_{3-δ} and Ba_ySr_{1-y}CoO_{3-δ} redox system for thermochemical energy storage at high temperatures. *Energy* **2019**, *171*, 971–980. [CrossRef]
- 105. Babiniec, S.M.; Coker, E.N.; Miller, J.E.; Ambrosini, A. Investigation of $La_x Sr_{1-x} Co_y M_{1-y} O_{3-\delta}$ (M = Mn, Fe) perovskite materials as thermochemical energy storage media. *Sol. Energy* **2015**, *118*, 451–459. [CrossRef]
- 106. Babiniec, S.M.; Coker, E.N.; Ambrosini, A.; Miller, J.E. ABO₃ (A = La, Ba, Sr, K; B = Co, Mn, Fe) perovskites for thermochemical energy storage. *AIP Conf. Proc.* **2016**, 1734, 050006. [CrossRef]
- 107. Bork, A.H.; Carrillo, A.J.; Hood, Z.D.; Yildiz, B.; Rupp, J.L.M. Oxygen Exchange in Dual-Phase La_{0.65}Sr_{0.35}MnO₃–CeO₂ Composites for Solar Thermochemical Fuel Production. ACS Appl. Mater. Interfaces 2020, 12, 32622–32632. [CrossRef]
- 108. Xu, M.; Ermanoski, I.; Stechel, E.B.; Deng, S. Oxygen pumping characteristics of YBaCo₄O_{7+δ} for solar thermochemical cycles. *Chem. Eng. J.* **2020**, *389*, 124026. [CrossRef]
- 109. Babiniec, S.M.; Coker, E.N.; Miller, J.E.; Ambrosini, A. Doped calcium manganites for advanced high-temperature thermochemical energy storage. *Int. J. Energy Res.* **2016**, *40*, 280–284. [CrossRef]
- 110. Albrecht, K.J.; Jackson, G.S.; Braun, R.J. Thermodynamically consistent modeling of redox-stable perovskite oxides for thermochemical energy conversion and storage. *Appl. Energy* **2016**, *165*, 285–296. [CrossRef]
- Albrecht, K.J.; Jackson, G.S.; Braun, R.J. Evaluating thermodynamic performance limits of thermochemical energy storage subsystems using reactive perovskite oxide particles for concentrating solar power. *Sol. Energy* 2018, 167, 179–193. [CrossRef]
- Imponenti, L.; Albrecht, K.J.; Wands, J.W.; Sanders, M.D.; Jackson, G.S. Thermochemical energy storage in strontium-doped calcium manganites for concentrating solar power applications. *Sol. Energy* 2017, 151, 1–13. [CrossRef]
- 113. Imponenti, L.; Albrecht, K.J.; Kharait, R.; Sanders, M.D.; Jackson, G.S. Redox cycles with doped calcium manganites for thermochemical energy storage to 1000 °C. *Appl. Energy* **2018**, 230, 1–18. [CrossRef]
- 114. Lucio, B.; Romero, M.; González-Aguilar, J. Analysis of solid-state reaction in the performance of doped calcium manganites for thermal storage. *Solid State Ion.* **2019**, *338*, 47–57. [CrossRef]
- 115. Pein, M.; Agrafiotis, C.; Vieten, J.; Giasafaki, D.; Brendelberger, S.; Roeb, M.; Sattler, C. Redox thermochemistry of Ca-Mn-based perovskites for oxygen atmosphere control in solar-thermochemical processes. *Sol. Energy* 2020, 198, 612–622. [CrossRef]
- Schrader, A.J.; Schieber, G.L.; Ambrosini, A.; Loutzenhiser, P.G. Experimental demonstration of a 5 kWth granular-flow reactor for solar thermochemical energy storage with aluminum-doped calcium manganite particles. *Appl. Therm. Eng.* 2020, *173*, 115257. [CrossRef]
- 117. Schrader, A.J.; Bush, H.E.; Ranjan, D.; Loutzenhiser, P.G. Aluminum-doped calcium manganite particles for solar thermochemical energy storage: Reactor design, particle characterization, and heat and mass transfer modeling. *Int. J. Heat Mass Transf.* 2020, 152, 119461. [CrossRef]
- 118. Vieten, J.; Bulfin, B.; Starr, D.E.; Hariki, A.; de Groot, F.M.F.; Azarpira, A.; Zachäus, C.; Hävecker, M.; Skorupska, K.; Knoblauch, N.; et al. Redox Behavior of Solid Solutions in the SrFe_{1-x}Cu_xO_{3-δ} System for Application in Thermochemical Oxygen Storage and Air Separation. *Energy Technol.* 2019, *7*, 131–139. [CrossRef]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).