

Developments in calcium/chemical looping and metal oxide redox cycles for high-temperature thermochemical energy storage: A review

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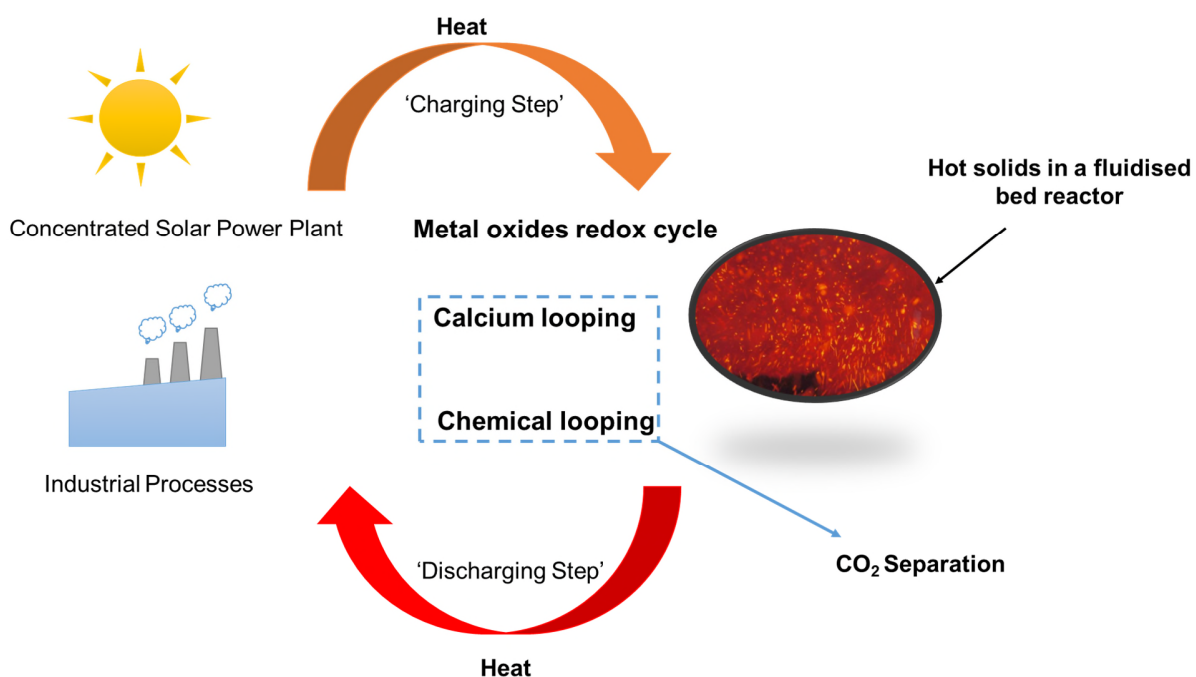
Abstract

Energy storage is one of the most critical factors for maximising the availability of renewable energy systems whilst delivering firm capacity on an as-and-when required basis, thus improving the balance of grid energy. Chemical and calcium looping are two technologies which are promising from both the point of view of minimising greenhouse gas emissions and because of their suitability for integrating with energy storage. A particularly promising route is to combine these technologies with solar heating, thus minimising the use of fossil fuels during the materials regeneration steps. For chemical looping, the development of mixed oxide carrier systems remains the highest impact research and development goal, and for calcium looping, minimising the decay in CO₂ carrying capacity with natural sorbents appears to be the most economical option. In particular, sorbent stabilisers such as those based on Mg are particularly promising. In both cases, energy can be stored thermally as hot solids or chemically as unreacted materials, but there is a need to build suitable pilot plant demonstration units if the technology is to advance.

Highlights

- Calcium and chemical looping can potentially be deployed at commercial scale within the next two decades.
- Both technologies have the potential for energy storage, either by means of sensible heat stored in solids or as chemical energy.
- A critical requirement for such development is construction and testing of suitable pilot and demonstration plants.
- Both technologies can be combined with solar power to offer particularly attractive systems with thermochemical energy storage.

Graphical abstract



Keywords

Calcium looping, chemical looping, metal oxide, thermochemical energy storage, carbon capture and storage

1. Introduction

Currently, renewables are making increasing strides worldwide contributing to the total capacity delivered by power generators, to the point where many question the need for decarbonisation of fossil-fuelled firm capacity by carbon capture and storage (CCS) [1,2]. However, fossil fuels are still the dominant source of energy for the utility and industrial sectors, and for transportation, and due to their widespread availability and low cost there are overwhelming pressures to use them [3]; the term dangerous abundance has been used to describe fossil fuels [4]. Alternative options, such as a massive transformation to 100% nuclear or renewable systems, have been advocated [5], but seem unlikely to be able to overcome political and economic challenges, while battery storage is unlikely to make a significant difference to the utility sector in the next few decades [6]. There is also an increasing recognition that many new technologies cannot be brought to market in a sufficient time-scale to meet the current challenge of rising CO₂ levels, and that delaying development in the hope that ground-breaking new technologies will emerge is problematic; indeed, such hopes have been critiqued as waiting for unicorn technologies [7].

In light of this, CCS remains essential if fossil fuels are to continue to be used while meeting climate change goals. Moreover, CCS offers the possibility of making even deeper cuts into anthropogenic CO₂ emissions if it is combined with bioenergy and carbon capture and storage (BECCS) [8]. Other options of keeping firm capacity in place include operating at peak load continuously, by producing a by-product, so that thermal plants can operate at maximum efficiency, with the production of a saleable product, thus avoiding inefficient part-load conditions [9]. Alternatively, operating at extremely high pressures to achieve enhanced performance characteristics [10], or finding methods to replace fossil fuels with hydrogen remain potential options for increasing the cost competitiveness of CCS technologies [11]. Nonetheless, questions that must be asked are, first, are these technologies technically feasible at commercial scale, to which the likely answer is yes, and second, can they be brought to market at scale at an acceptable cost within the next two or three decades, and here, there is much greater doubt.

Failing this, possible options like using CO₂ can be considered, but face the apparently insuperable challenge that anthropogenic CO₂ production vastly exceeds any likely sink in terms of a chemical product, while enhanced oil recovery (EOR) options simply produce a net increase of “new” fossil fuel carbon into the environment [12]. Power generation decarbonisation efforts also include the deployment of renewables at an ever-increasing share of total capacity. Yet nations cannot decarbonise power or energy generation via renewables alone due to the intermittency factor and the overcapacity required if it is to be ignored. Thus, energy storage will be needed in some form that is affordable, scalable, responsive, and doesn’t impact on the environment in its production or use [13]. It is within these contexts that energy storage becomes more attractive, allowing larger power generation plants to operate under near-peak conditions 100% of the time, thus increasing efficiency and cost-effectiveness of operation, and facilitating the deployment of renewables in greater amounts. Some of the newer CCS technologies such as calcium looping (CaL) and chemical looping combustion (CLC) [14,15] appear to be compatible with solutions involving energy storage and, moreover, involve no major engineering developments, which would slow their development during the period in which CO₂ levels are likely to significantly exceed current climate change targets [16].

1.1. Calcium looping technology

CaL is shown schematically in Fig. 1, and offers a more efficient option for post-combustion CO₂ separation than the existing amine scrubbing technology due to its lower efficiency penalties and costs [17]. This lime-based looping process is applicable both for new plants and retrofitting [18]. Here, flue gas from a combustor or gasifier is fed to the carbonator (operating in a temperature range of 550-700 °C), where it reacts with calcium oxide to form calcium carbonate (forward direction of Rx. 1). The CaCO₃/CaO mixture

is then transported to the calciner (operating in a temperature range of 850-950 °C) and heated to regenerate the calcium oxide and release the captured CO₂ (reverse direction of Rx. 1).



The heat required for calcination is commonly provided by oxy-fuel combustion, thus producing a highly-concentrated CO₂ stream ready for transportation and sequestration, while the regenerated calcium oxide is recycled back into the carbonator in a loop. Because the fuel needed for supplying sufficient heat for calcination is only a fraction of the total fuel requirements, the required oxygen is typically about 1/3 of the oxygen required for an oxy-fuel combustion process. CaO derived from limestone/dolomite has the further advantage that it is naturally available at numerous geographical sites worldwide, and the spent material from the process can be used in a variety of industrial processes including cement manufacture [19].

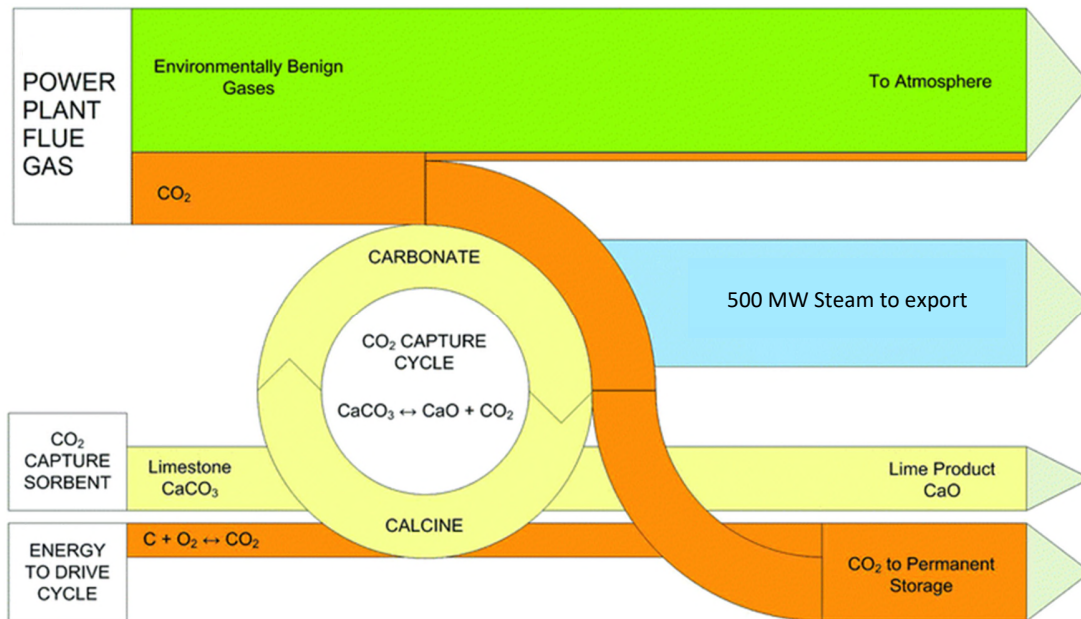
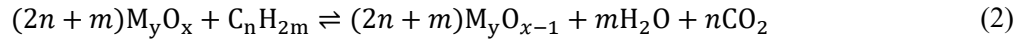


Figure 1. The Calcium Looping process [15].

1.2. Chemical looping technology

Chemical Looping Combustion (CLC), also referred to as metal oxide redox cycles in the energy storage field, using CuO to oxidise methane, was first suggested by Lewis, Gilliland and Reed in a paper published in 1949 [20]. Subsequently, these workers proposed the use of this approach for the production of a pure CO₂ stream from a hydrocarbon gas [21]. Later, the idea of using a metal oxide to combust a gaseous hydrocarbon was again proposed as a method of achieving “controlled combustion” by Richter and Knoche [22]. At its heart, chemical looping is the concept that a metal oxide may reversibly take oxygen from the

air and then oxidise a hydrocarbon via a series of reactions, summarised by Rx. 2. Thus, upon combustion, a stream of easily separable CO₂ and H₂O is produced, suitable for eventual CO₂ sequestration.



Chemical looping operates in a similar manner to CaL with two interconnected fluidised beds operating at high temperatures (>600 °C), with one reactor acting as the fuel reactor, and the other as the air reactor. In the air reactor the metal oxide particles are oxidised in the presence of air (Rx. 3), and are then reduced in the ‘fuel reactor’ by reaction with a hydrocarbon fuel; these processes occur as a continuous loop by cycling the solid material.



Reduction of the oxidised metal may also release some of its oxygen into the gaseous phase, which is designated as the chemical looping oxygen uncoupled (CLOU) process. For solid fuels, this is faster than depending on an inherently slow gasification step followed by the internal and external mass transfer of syngas to the surface of the metal oxides [23]. Since the early days of CLC research there has been an explosion of research into new oxygen carriers, supports and different CLC configurations, as well as efforts to use CLC directly with solid fuels [24,25].

Metal oxide thermochemical redox cycles apply a theory similar to that of CLC, and can convert solar energy to chemical energy via a reduction of metal oxides and release the energy through the oxidation of metal oxide [26].

1.3. Thermochemical energy storage

Energy storage is critical in all future energy mixes, due to the intermittency of renewable energy supply, and the characteristic ‘duck curve’ of energy markets with high renewable energy penetration. The only alternative to a low-energy storage, high-renewable energy grid is an over-capacity of renewable generation to ensure demand is met [27]. Most nations are not endowed with large quantities of hydropower resources or plentiful clean energy such as geothermal and are, thus, reliant on mixing power generators with energy storage. Excluding hydropower reservoirs, that are often not possible due to geographical constraints, large-scale energy storage for seasonal, daily peak shifting and grid balancing is currently only available in the form of natural gas/hydrogen gas turbines, compressed air energy storage, thermal cycling of materials and, more recently, batteries [28–30]. A comparison of energy storage technologies is illustrated in **Table 1**.

Compared to other energy storage technologies, TCES is a less mature technology and inherently has an additional set of complexity that affects its operation and design. However, it exhibits a great potential for high-temperature energy storage and has the advantages of a high energy storage density (on average, 15 times greater than that of Sensible Energy Storage and 6 times than that of Latent Energy Storage)[29],

long storage duration, high operation flexibility and a moderate initial capital cost. It is also worth noting that the energy density of some of the thermochemical energy storage technologies, such as calcium looping and metal oxides redox cycles, are varied in terms of the process conditions and physio-chemical properties of materials. For instance, the energy density of CaL-CSP temperatures can vary widely from literature. It is reported their energy density is around of 800-1000 kWh/m³ calculated from the reaction enthalpy, while it would be decreased to 250-555 kWh/m³ by considering gas and solids vessels and reaction conditions [31].

Table 1. A comparison of energy storage technologies [29,32]

Parameter	Energy Storage Technologies					
	Pumped hydro power	Compressed air	Batteries	Sensible energy storage	Latent energy storage	Thermochemical energy storage
Energy form	Mechanical	Mechanical	Electrochemical	Thermal	Thermal	Thermochemical
Efficiency (%)	65-80	60-79	70-95	50-90	75-90	80-99
Initial capital cost (USD/kW)	500-4600	500-1500	300-3500	3400-4500	6000-15000	1000-3000
Energy density (kWh/m ³)	0.5-1.5	3-6	15-600	25	100	500
Storage capacity (MW)	100-5000	5-3000	0-40	0.1-300	0.1-300	0.1-300
Technology readiness level (TRL)	9	9	5-9	9	9	3-4

Concentrated Solar Power (CSP) is a technology reliant on focussing solar energy to a central location (heliostat tower) by means of a large array of heliostat mirrors, where the energy is utilised to heat up a working heat transfer medium or the thermal cycling material itself, using the energy collected to run a steam cycle or stored for a later time when energy is in higher demand, or during the night. Thermal energy storage (TES) can be further divided into sensible energy storage, latent energy storage, and

thermochemical energy storage (TCES). These options are regarded as promising technologies that can ensure the continuous operation of CSP plants [29]. A brief comparison among thermochemical energy storage and other thermal energy technologies is illustrated in Figure 2. In general, thermochemical energy storage that consists of a charge step in the endothermic reactor and a discharge step in the exothermic reactor to release the stored heat is currently at the laboratory scale, but its high energy density and operation flexibility have recently attracted vast interest.

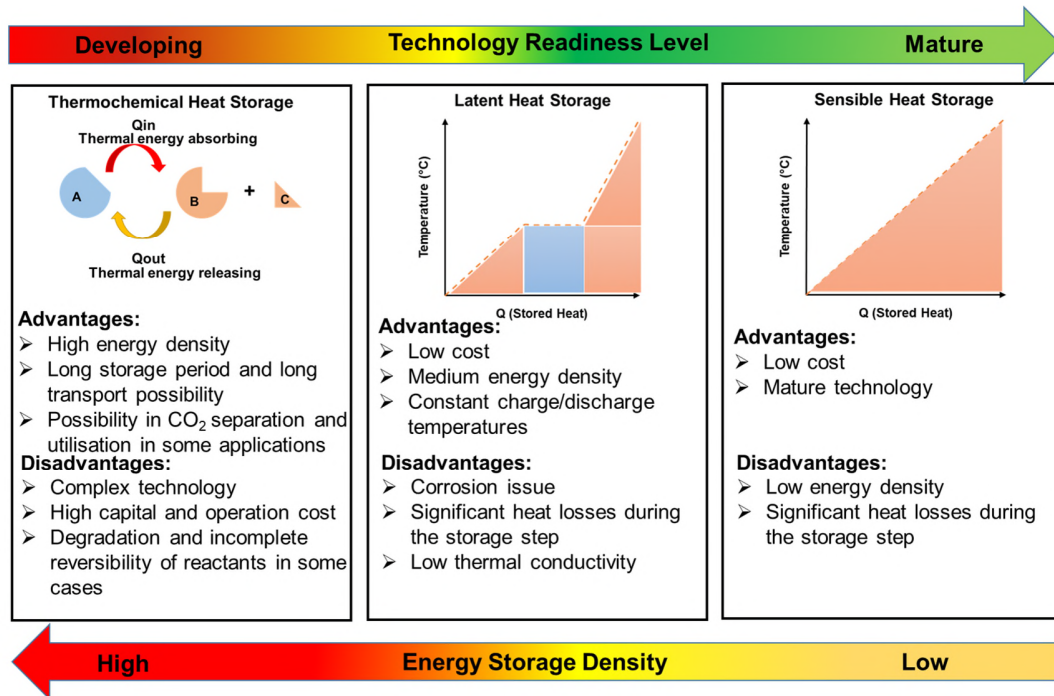


Figure 2. A brief summary and comparison of thermal energy storage technologies.

The integration of CaL, CLC and a metal oxide redox cycle with CSP or other energy sources for energy storage is a form of ‘thermal cycling of materials’—high-temperature gas-solid thermochemical energy storage systems, although the production of hydrogen, or oxygen is also possible from these processes [9,33].

Molten salts are the primary material used for energy storage thermal cycling at present, and store thermal energy as sensible heat with a relatively high energy density, near 0.8 GJ/m³ [34,35]. Nevertheless, the use of molten salts suffers serious limitations that reduce the competitiveness of CSP with energy storage, vs. coal power plants. Thus, one problem is that of a low “upper working temperature” for salts due to their decomposition above ~600 °C [36,37], minimising the potential for high thermal and electrical efficiencies in comparison to fossil fuel-fired power plants. Another issue is the high solidification point of such molten salts (120–220 °C) [38], which makes it necessary to keep the salts at temperatures above these values, which in turn may require additional fossil fuel use, especially overnight [39]. Additionally, molten

salts are often corrosive [40,41], requiring the installation of expensive materials for transport and storage. CaL, CLC and the metal oxide redox cycles, by contrast, offer the potential to overcome these issues and increase the efficiency of the overall energy storage and power generation processes. The materials used in CaL, CLC and metal oxide redox cycles have a higher operating temperature range leading to greater potential exergy, do not have solidification issues, and can be stored in relatively simple vessels.

1.4. Scope of this review

The aims of this review are as follows:

- To provide an overview of calcium/chemical looping and metal redox systems for high-temperature thermochemical energy storage.
- To identify the potential profits of applying calcium/chemical looping and metal redox systems for thermochemical energy storage.
- To identify and illustrate the concept and process design of calcium/chemical looping and metal redox systems for thermochemical energy storage.
- To review and identify suitable thermochemical storage materials for calcium/chemical looping and metal redox systems.
- To identify the future development of calcium/chemical looping and metal redox systems for thermochemical energy storage.

2. Gas-solid looping systems for high-temperature thermochemical energy storage

2.1. Classification of gas-solid looping systems

Gas-solid looping systems, which can be classified into metal hydrides, carbonates, hydroxides and metal oxides, are the most commonly used systems in TCES [42–44]. Figure 3 briefly compares the reaction mechanisms, advantages and disadvantages of different gas-solid looping systems for TCES.

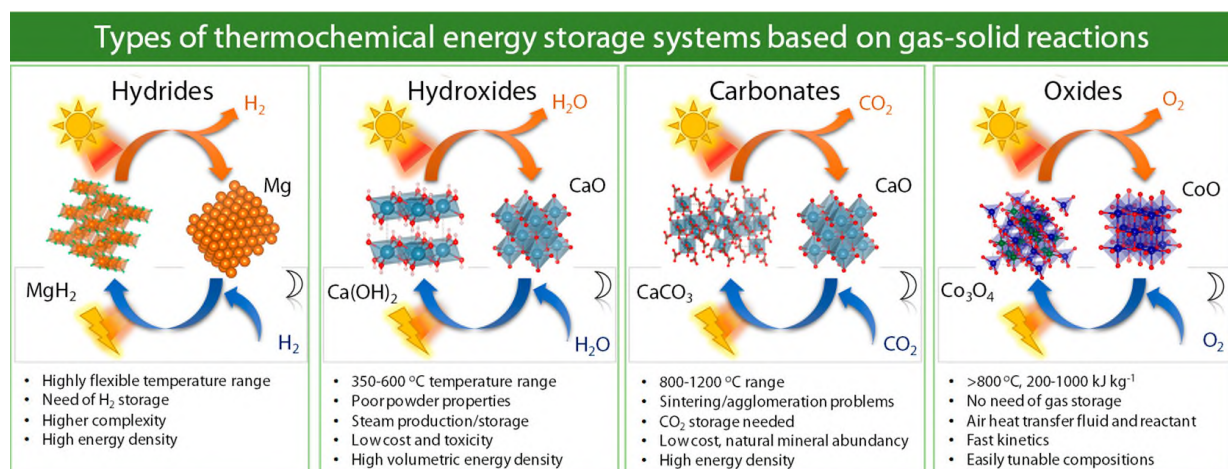


Figure 3. Summary and comparison of different gas-solid systems for thermochemical energy storage [42].

Despite metal hydrides having the highest energy storage density and the potential for hydrogen storage, the slow reaction kinetics, low dissociation temperatures, and the need of hydrogen storage have limited their application [45]. In addition, some systems suffer due to the nature of the reactants, for instance, a PbCO_3 -based carbonate system is prohibited due to toxicity considerations [29].

Hydroxides-based (Mg or Ca) systems are promising for low- (35-350°C) and medium- (350-600°C) temperature thermochemical energy storage [42,44]. Ervin first investigated solar heat storage using the dehydration/hydration reactions of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ in 1977 [46]. Since then a vast number of studies have been conducted in this area based on improving the performance of materials, modelling of the process and improving reactor configurations [42,44]. Recently, there have been remarkable improvements in attrition resistant of Ca-based materials by using sodium silicate to combine with fine $\text{CaO}/\text{Ca}(\text{OH})_2$ particles, which can reduce the decay in TCES over hundreds of cycles [47]. In addition to such developments, conceptual process design and experimental investigation of the process of $\text{CaO}/\text{Ca}(\text{OH})_2$ for thermochemical energy storage applications have been conducted, which will be useful to scale up this technology and accelerate the application of hydroxides-based systems for TCES [48–50].

In this work, we focus on high-temperature gas-solid looping systems that include calcium/chemical looping and metal oxides redox cycle systems for TCES, and here the ‘high-temperature’ means an operation temperature over 600°C; for such systems high energy storage densities and high-temperature gas-solid systems will play a vital role in future development of CSP technology.

2.2. Calcium looping with thermochemical energy storage

2.2.1. Process concept

The idea of applying the CaL process in concentrated solar power (CSP) plants for TCES dates back to the 1970-80s [51]. CaL-CSP integration has received renewed interest due to several potential advantages for TCES in CSP, including: i) high working temperature ($\sim 850^\circ\text{C}$ under high CO_2 partial pressure) [52], which allows employing high-efficiency steam cycles, thus overcoming the low temperature limits ($\sim 600^\circ\text{C}$) of molten salts; ii) high energy density due to the reaction enthalpy ($\sim 3.2 \text{ GJ/m}^3$) [53,54] and inherently high thermal conductivity ($\sim 1.5 \text{ W m}^{-1}\text{K}^{-1}$ at 500°C) [55], which is around three times higher than that of molten salts; iii) the reactants and products can be stored at ambient temperature without the problem of solidification [56]; iv) such technology uses well-documented processes which are already applied in the cement and lime industry [19,57]; and v) take advantage of the low price ($\sim 10 \text{ \$/t}$), wide availability and non-toxicity of natural Ca-based minerals (limestone or dolomite) that can be used as the CaO precursor [9,17]. Notably, energy density values for CaL-CSP vary widely since they are not only determined by the reaction enthalpy but also dependent on the physio-chemical properties of CaO/CaCO_3

and the relevant CaL-CSP conditions (size of the vessels, packing density of solids, CO₂ pressure, CO₂ temperature and CaO conversion)..

Fundamentally, the integrated CaL-CSP system comprises a solar calciner, carbonator, reservoirs for CaO, CaCO₃, and CO₂ storage, and power generation unit, as shown in the flow diagram of Figure 4 [58]. The energy needed for the CaCO₃ endothermic decomposition is supplied by direct solar radiation in the calciner, serving to store the excess heat as chemical energy. The CO₂ (separated from the superheated steam by condensation), and the CaO solids both have their sensible heat extracted by heat exchangers before being stored independently at ambient temperature. Moreover, the CO₂ gas stream is compressed under supercritical conditions by means of intercooling compression. Storage conditions and residence times are flexible and can be adapted to meet energy demand. When required, CaO solids (from the reservoir) and compressed CO₂ are recirculated into a carbonator reactor where the heat of the carbonation reaction is released. The excess of CO₂ exiting the carbonator at high temperature/pressure serves as heat carrier to produce electric power through a turbine. Carbonation may be performed at significantly high temperature (~850 °C) under high CO₂ concentration to maximise the thermoelectric efficiency.

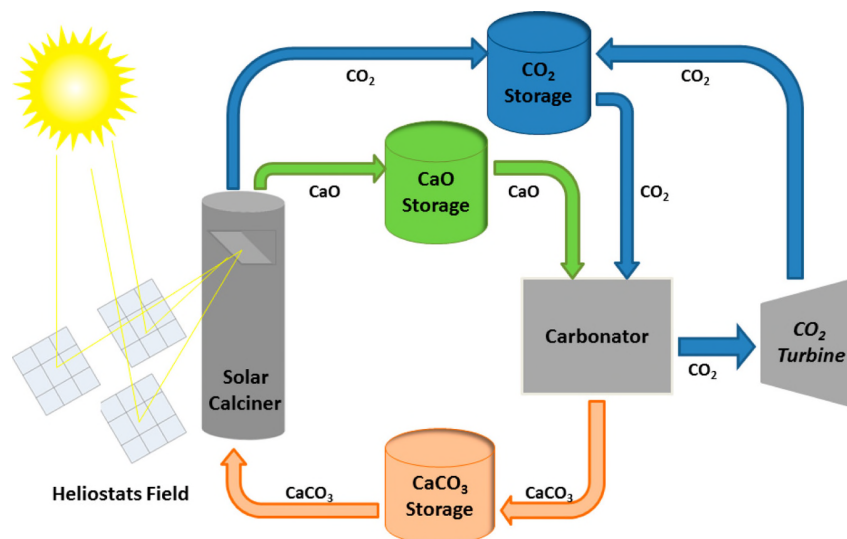


Figure 4. Flow diagram of the calcium-looping thermochemical energy storage system for concentrated solar power plants [58].

Various schemes have been proposed to integrate the CaL process and CSP. Tregambi et al. [59] developed a configuration in which CaCO₃ calcination is assisted by CSP to reduce the energy penalty related to CO₂ capture. Zhai et al. [60] examined several schemes whereby CSP is used to recover energy in the CO₂ capture system. Edwards et al. [61] analysed a CaL-CSP integration in which the heat derived from the carbonation reactor served to generate power through a CO₂/air open cycle. Muñoz-Anton et al. [62] studied the integration of a CO₂ Brayton cycle in a CSP power plant without storage to obtain a higher

cycle efficiency. Chacartegui et al. [53] explored a CO₂ closed loop for the CaL cycle and power production with a relatively high efficiency. Alovio et al. [63] used the pinch-analysis methodology to optimise the CaL-CSP integration of a CO₂ Brayton cycle. Ortiz et al. [64] compared several possible integration schemes in which power production was carried out directly or indirectly. Overall, a global thermal-to-electric efficiency of above 45% was predicted using a closed CO₂ Brayton power cycle [64] without considering the efficiency of the solar receiver as calciner, which is a critical component that remain to be developed. Furthermore, heat exchanger is another critical component, which needs to be optimised to achieve high efficiencies owing to the potential high temperature differences between the calciner, the storage vessels and the carbonator. Ortiz et al. [31] reported that the global plant efficiencies could be increased when adding a gas-solid heat exchangers on both the charging and discharging sides. Chen et al. [65] demonstrated that the important role of sensible heat in the CSP-CaL system. The maximum storage efficiencies are increased to 61.59% when the sensible heat is totally used. Additionally, solids conveying, gas separation and storage system are still required to be specifically designed to fulfill scaling-up of CaL-CSP system.

However, currently the net efficiency of CSP with CaL thermochemical energy storage system from process modelling is from 38% to 46% [64,66], which is slightly lower than that of the commercial CSP with molten salts (40% to 49%) [67]. The auxiliary energy consumption of CO₂ compressors account for the major energy penalty of CSP-CaL processes, around 10-14% reduction of the energy efficiency [64,66,68].

2.2.2. Process conditions

The CaL conditions in the CaL-CSP integrated process should be optimised to achieve maximum overall efficiency, which may involve high-temperature carbonation (>850 °C) under high CO₂ partial pressure (approaching 100 vol.%) and low-temperature calcination (<800 °C) under low CO₂ partial pressures. These conditions are remarkably different from those corresponding to CaL as a CO₂ capture process where carbonation is performed at a relatively lower temperature (~650 °C) under low CO₂ partial pressure (~15 vol.%) and calcination occurs under high CO₂ concentration (>85 vol.%) at high temperature (930-950 °C) [52]. Extensive studies [15,69,70], indicate that under CaL-CO₂ capture conditions, CaO particles/grains are severely sintered, causing CaO carbonation activity to experience a marked deactivation in just a few carbonation/calcination cycles. Here, the multicycle activity of the CaO under specific of CaL-CSP conditions is radically different from that in CaL-CO₂ capture conditions.

Using thermogravimetric analysis (TGA), Benitez-Guerrero et al. [71] compared the carbonation kinetics of limestone-derived CaO under CaL-CSP conditions with those under CaL-CO₂ capture conditions. As shown in Figure 5, for the first carbonation cycle, the type of CaL conditions plays a critical

role in the kinetics of the carbonation stage. It is well documented that carbonation proceeds through an initial fast reaction-controlled phase occurring on the surface of CaO, followed by a relatively slow diffusion-controlled phase characterised by the diffusion of CO₂ through the CaCO₃ product layer covering the CaO core [66]. The fast reaction-controlled phase is mainly responsible for CO₂ uptake under CaL-CSP conditions, which highlights the importance of using high CO₂ concentrations (100 vol.%) and carbonation temperatures (850 °C) to improve the reaction kinetics (Figure 5a). Here, the fast reaction phase is considerably reduced under CaL-CO₂ capture conditions (Figure 5b), due to the lower CO₂ partial pressure (15 vol.%) and lower carbonation temperature (650 °C) [71]. To increase the CO₂ uptake in CaL-CO₂ capture, the solids residence time in the carbonator may need to be increased to above 5 min because of the dominant role of the slow diffusion-controlled carbonation phase (Figure 5b). However, for the CaL-CSP system this strategy would have limited benefit as there is negligible contribution from the slow diffusion-controlled carbonation phase under CaL-CSP conditions (Figure 5a).

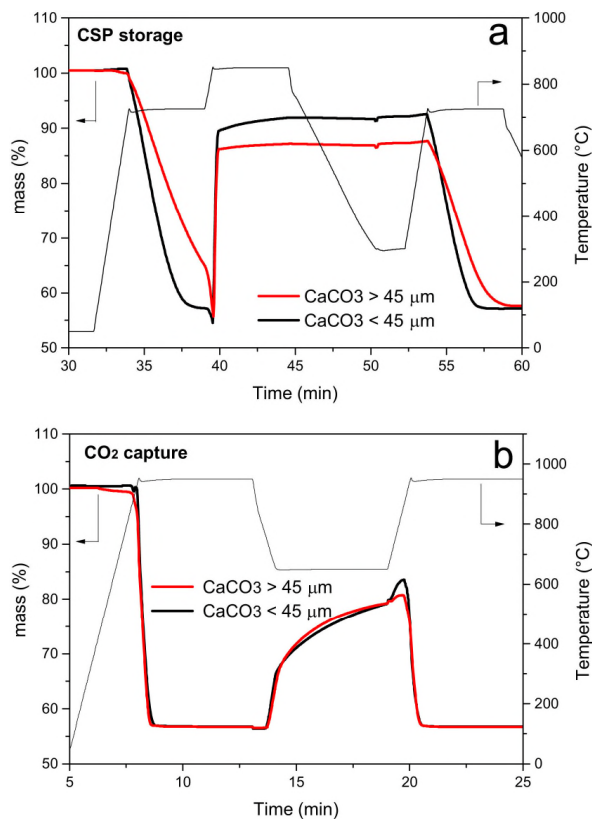


Figure 5. Time evolution of temperature and sample weight for the first carbonation cycle of CaCO₃ using different particle sizes, under (a) CaL-CSP and (b) CaL-CO₂ capture conditions [71].

The role of residence time on the carbonation kinetics under CaL-CSP conditions during carbonation/calcination cycles has been further explored by using different residence times (1, 5 and 10 min). For the first cycle (Figure 6a), carbonation in the slow diffusion-controlled phase is insignificant at

all three residence times. Nevertheless, by the 21st cycle (Figure 6b), using the shortest residence time (1 min) noticeably reduces the CO₂ uptake of regenerated CaO during the fast reaction-controlled phase [72]. Interestingly, prolonging the residence time beyond 5 minutes does not appear to offer significant benefits; therefore, the optimised residence time in practice may be of the order of ~5 minutes.

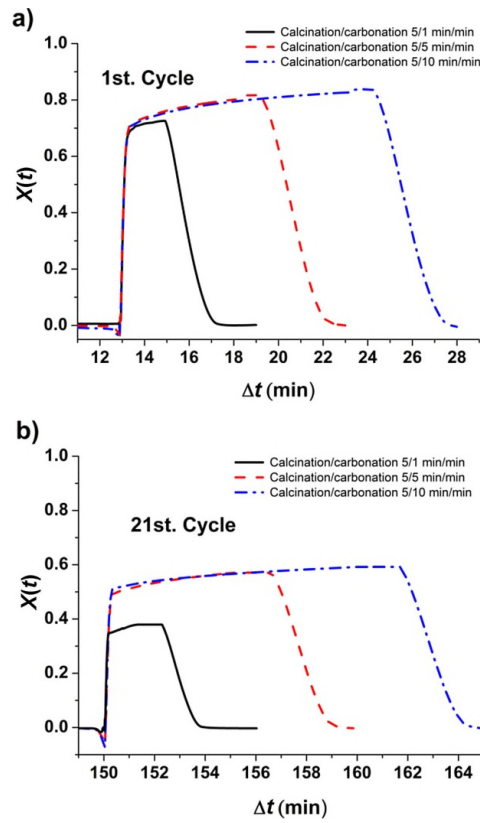


Figure 6. Time evolution of CaO conversion during the (a) first and (b) 21st cycle for carbonation/calcination tests carried out under CaL–CSP conditions [72].

In addition to reducing the time for the carbonation reaction in the CSP–CaL integration, a further issue to consider to ensure efficiently storing solar energy is that the calcination reaction needs to be close to completion as rapidly as possible and at the lowest possible temperature. From an economic point of view, reducing the calcination temperature and decreasing the reaction time enable the application of large low-cost volumetric receivers composed of cheap metal alloys [72]. Consequently, gases with high thermal

conductivity including He or superheated steam (SHS) have been suggested and explored to improve calcination at low temperatures [72].

Sarrion et al. [72] examined the effect of calcination atmosphere (pure N₂ or He) on the decomposition of limestone under the relevant CaL–CSP conditions. As shown in Figure 7, compared to N₂, calcination takes place at a relatively faster rate under He, due to the notably higher thermal conductivity of He, thereby, generating a higher diffusivity for the released CO₂. Here, calcination could be accomplished under He at temperatures as low as 725 °C in less than 2 min. Valverde et al. [73], using an *in situ* x-ray powder diffraction (XRD) analyser, confirmed that the presence of He, even at a considerably low concentration, significantly promoted the calcination process of limestone at high CO₂ partial pressures. Furthermore, the structure and reactivity of the produced CaO was unchanged, suggesting that the mechanical strength of CaO particles was not reduced.

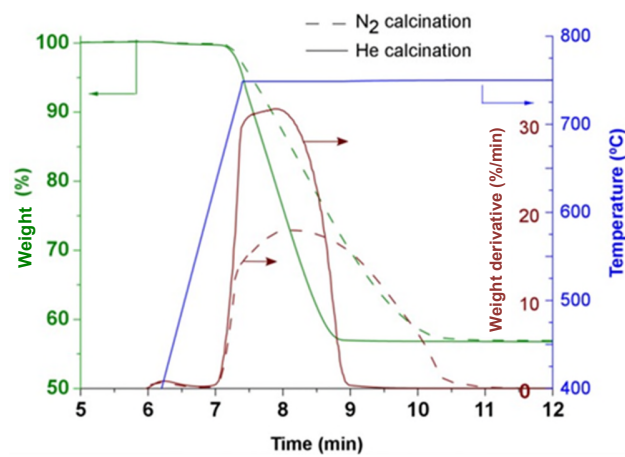


Figure 7. The time evolution of weight, weight derivative, and temperature during the decomposition of limestone under either a pure N₂ or He atmosphere [72].

The noted benefit of using He allows significantly decreasing the calcination temperature and speeding up the calcination rate. As a consequence, the energy penalty for CSP–CaL integration is considerably mitigated. Moreover, He can be easily separated from the CO₂/He mixture by commercial membranes. In the CaL–CSP integration the effluent gas stream from the calciner must be cleared of particles before sending it to the membrane for He/CO₂ separation. Therefore, a cyclone separator should be used to remove the particulates from the gas mixture. Although He presents a high cost and has limited availability, this gas could be used in a low total volume and in a closed loop for CSP–CaL integration. Further techno-economic analysis needs to be carried out to determine the effect of possible He consumption and membrane separation ineffectiveness and overall plant performance. It is possible that the reduction in cost by lowering the temperature of the calciner is offset by additional He/CO₂ separation.

Similarly to He addition, previous work [74,75] has shown that the addition of SHS in the calcination at high concentrations results in a noticeable increase of the reaction rate. However, a side effect of this SHS addition is that the mechanical strength of CaO formed is severely reduced, leading to further particle attrition and mass loss. This undesirable effect may pose a serious problem for the practical application of steam in circulating fluidised beds (CFBs) during the CaL-CSP process, since fine particles (around 10 μm) generated due to fracturing are difficult to recover with commercial cyclones. Fortunately, recent *in situ* XRD results based on the time evolution of the weight change and crystallite size of the sorbent material, have demonstrated that the presence of SHS at small concentrations still results in remarkably improved calcination reaction rates while the mechanical strength of the CaO formed is not significantly reduced [76].

Another issue is the cyclic activity of the CaO during carbonation/calcination cycles under CaL-CSP conditions. For both CaL-CO₂ capture and CaL-CSP systems, CaO conversion decreases with repeated cycling, so that deactivation of CaO would still present a major issue for CaL-CSP. In contrast to the case of CaL-CO₂ capture, however, deactivation is greatly mitigated for CaL-CSP as indicated by higher residual values of CaO conversion (X_r) and a lower deactivation rate constant. Scanning electron microscopy (SEM) analysis further confirms that the mild calcination conditions (low temperature (725 °C) and low CO₂ concentration) protect the regenerated CaO from severe sintering, thereby maintaining a large CaO surface area suitable for the subsequent carbonation phases. Importantly, higher residual conversion is achieved for the optimised residence time described above (5 min), which may allow the use of CFBs which offer highly effective heat/mass transfer. When compared with CaO derived from limestone, dolomite-derived CaO exhibits even higher residual conversion under CaL-CSP conditions, which may be caused by the inert MgO grains, segregating the CaO grains, preventing them from aggregation and sintering, as suggested by SEM images [72]. Sarrión et al. [77] proposed a novel integration scheme in which carbonation is conducted in pure CO₂ (CaL-CSP-CO₂) at high temperatures (950 °C), while calcination occurs in pure He atmosphere (CaL-CSP-He). Interestingly, dolomite displayed similar, stable cyclic activity under the two CaL-CSP conditions, potentially indicating that the material has a greater influence on performance than the gas composition. A pure CaL-CSP-CO₂ process avoids using selective membranes to separate He from CO₂ even though requiring more solar receptors to generate the energy required for the higher-temperature calcination. These results demonstrate the crucial role of calcination/carbonation conditions on the cyclic performance of CaO derived from natural minerals.

In addition to carbonation/calcination atmospheres and operating temperatures, another relevant issue is carbonation pressure, since process simulations have shown that the thermoelectric efficiency can be promoted with an increased carbonator pressure [53]. The increase in the pressure of the carbonator not only enhances the conversion rate and decrease the residence time, but also increase the temperature of

carbonator, which can improve the power cycle efficiency [68]. While, the pressurised calciner is not favourable under CaL-TCES conditions due to increasing in calcination temperature and sorbent sintering [78].

A feasible strategy to further reduce capital cost and technical complexity is using just one reactor both as calciner and carbonator, as both stages can be performed in one-day cycles. Using a thermobalance, Sarrion et al. [79] examined the multicycle performance of limestone- and dolomite-derived CaO at different carbonator pressures for CaL-CSP, as shown in Figure 8. The multicycle CaO conversions are noticeably hindered when the reaction pressure is increased to 3 bar. CaO sintering is significantly enhanced with an increase of pressure, preventing CO₂ uptake by the regenerated CaO in subsequent cycles. On the other hand, such an adverse effect is mitigated when using dolomite-derived CaO due to the presence of inert MgO grains, which serves to reduce CaO sintering, depressing the loss of CaO reactivity and facilitating calcination. However, increased reactor pressure increases the successive MgO–CaO segregation, during the carbonation stage and demands temperatures well beyond the CaCO₃ Tamman temperature, leading to a rapid loss of the improved performance of dolomite.

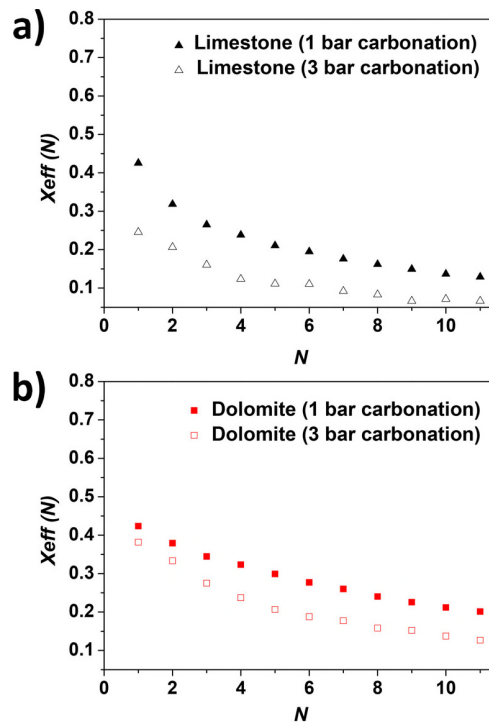


Figure 8. Multicycle effective conversion data for (a) natural limestone and (b) dolomite, as a function of the number of carbonation/calcination cycles, under atmospheric and high-pressure carbonation [79].

For CaL-CSP system, materials, heat exchangers, vessels, reactors, and conveying systems have been well investigated due to their applications in cement industry and carbon capture process. It is therefore significant to pay more attention to the energetic and economic penalties of CO₂ storage process and the

design of solar calciner. In general, cooled CO₂ from the calciner is compressed to a minimum pressure of 75 bar to be stored under supercritical conditions, at ambient temperature, to reduce the size of the CO₂ storage volumes [64]. It can also be stored as adsorbed gas or in the form of carbonate [151]. Recently, Meroueh et al. [152] evaluated the subsystem of a 800 MWh_{th} CaL-TCES. They compared the performance of CaL based on SrCO₃ for TCES with two different options for CO₂ storage, and found that CO₂ stored in the form of carbonates was more economic (153±64 \$kWh⁻¹ and 48±18 \$kWh⁻¹ for CO₂ stored as a gas and via an ad/absorbent, respectively). It was also noted in this work that it CaL-TCES should be able to meet the target of 15 \$kWh_{th}⁻¹ set by the U.S. DOE, although more work is required to accurately calculate the costs storage tanks, compressors, and other externalities of the system. Nevertheless, most of current process modelling and optimisation work of CaL-TCES system [31,63,64,153] is focused on gas compression for CO₂ storage for CaL-TCES systems, which has so far been found to be unsuitable to reach the cost target of \$15 kWh_{th}⁻¹ set by the U.S. DOE [152]. In addition, the source and quality of CO₂ should be also investigated. It is common that pure CO₂ stream has been used in the lab-scale experiments. But with the development of CCS, the supply of CO₂ to CaL-CSP process may contain some impurities such as SO_x and NO_x, which should be considered, and a pre-treatment unit might be required.

The process conditions can have significant impacts on the performance of CaL sorbents, thus it influences the energy density of CaL – TCES systems. The theoretical energy density of CaL-TCES based on limestone is between of 3-4 GJ/m³, but limestone is estimated to actually have an energy density in the range of 0.9-2.4 GJ/m³ by taking into account the gas and solids silos and/or conversion of carbonation [31]. The optimal CaL conditions for TCES in CSP occurs at high-temperature carbonation (>850 °C) under high CO₂ partial pressures (approaching 100 vol.%) and low-temperature calcination (<800 °C) under low CO₂ partial pressures. The carbonation rate is increased with the carbonator temperature until it reaches the maximum rate, where any further increase adversely affects the rate as the temperature approaches the thermodynamic equilibrium [68]. An increase in pressure of carbonator will shorten the residence time and has been shown to improve the power cycle efficiency. Furthermore, altering the calcination atmosphere to helium or a low concentrations of superheated steam has the benefit of lowering the calcination temperature and speeding up the calcination rate. Despite these benefits, a thorough economic analysis needs to be undertaken to evaluate the additional cost and complexity when applied to a large-scale system.

2.2.3. Physio-chemical properties of sorbents

Particle size is a critical physical property for the CaL-CSP process in CFBs where particle-gas separation is primarily conducted with cyclones. For cyclone separators the collection efficiency, particle trajectories, and residence times are all critically dependent on the particle size and gas flow rate. The cyclic activity for CaL-CSP and CaL-CO₂ capture using various-sized natural limestone minerals was compared [71], and it was found that for CaL-CSP conditions, the multicycle conversion was notably reduced for limestone and marble when their particles were larger than 45 μm . Conversely, there was no clear effect of particle size on the multicycle performance of two natural mineral-derived CaO under CaL-CO₂ capture conditions.

The type of carbonate mineral is also important for cyclic stability under CaL-CSP conditions. In addition to limestone, other naturally-occurring carbonate minerals (chalk, marble and dolomite) have been explored [80]. Although such materials have a similar chemical composition of primarily calcium carbonate, limestone, chalk and marble have rather different cyclic activity, which may be caused by varied particle sizes and differences in their microstructure. However, pore plugging is still a controlling mechanism on their cyclic carbonation performance. By contrast, dolomite exhibits a high cyclic activity regardless of particle size, which can be attributed to the presence of inert MgO grains supporting the porous CaO structure and allowing the diffusion of CO₂ [80]. It seems that pore plugging poses less of an effect on repeated carbonations for CaL-CSP. Here, the rapid calcination can be completed at lower temperature for dolomite compared to limestone due to its weaker crystalline structure [80]. Consequently, dolomite could be considered as a more suitable alternative for the integrated CaL-CSP.

Besides these naturally-occurring carbonate minerals, one promising type of Ca-based industrial waste material is steel slag. According to the EU's Waste Framework Directive, the generation of slag in the European Union was approximately 21.8 Mt in 2010, of which around 24% was disposed of in landfills [81]. Furthermore, this abundant, cheap, and nontoxic material also exhibits highly desirable heat-transfer characteristics such as a high thermal conductivity (1.4 WK⁻¹m⁻¹) and excellent thermal stability [82], which make this potential energy storage material cost competitive. More importantly, multicycle calcination/carbonation results have demonstrated that CaO derived from a simple acetic acid pre-treatment of steel slag attains a high and stable cyclic performance, making steel slag a promising choice for the integrated CaL-CSP [83].

Another type of Ca-based industrial waste, blast furnace slag, was also examined as potential material for CaL-CSP [84]. The prepared blast furnace slag retains high and stable multicycle activity when treated with acid and filtration (raw furnace slag requires an acid pre-treatment step to obtain calcium acetate and then CaO upon calcination). During the acid pre-treatment, an intermediate filtration has also been used to

remove silica. Morphological and pore characterisation further showed that the presence of nanosilica enhanced the preservation of mesopores (2-50 nm), which greatly reduced the multicycle activity, since smaller pores tend to become plugged more easily. On the other hand, the existence of aluminium compounds in the blast furnace slags would hinder the multicycle conversions, because the irreversible generation of calcium aluminates upon calcination will draw active CaO for carbonation [84].

Most of the natural/industrial Ca-based materials described above suffered successive degradation during repeated carbonation/calcination cycles of CaL-CSP; however, five stabilising compounds have been recently tested, which appear to minimise this deactivation, namely: SiO₂, Al₂O₃, ZrO₂, MgO, and graphite. Whilst these stabilising compounds improve the cyclic activity of the sorbent materials, it is important to consider the techno-economics of such stabilisation additions. In this regard, silica is a promising candidate, since it is low in cost and widely available; in particular, nanosized silica is potentially an excellent choice as it can be produced from rice husk [85]. Chen et al. [86] studied the thermodynamics, kinetics and cycling stability of nanosilica/CaO physical mixtures, showing that the addition of nanosilica had a slightly negative effect on heat storage capacity, whereas the magnitude of the released heat was enhanced. Here, 20% enhancement of the specific heat capacity was also obtained when doping with SiO₂ due to the higher thermal conductivity of SiO₂ than that of CaCO₃. Thus, the sensible heat in CaL-CSP system may be enhanced by doping limestone with higher thermal conductivity of metallic oxide. Valverde et al. [58,87] examined the addition effect of nanosilica on the multicycle performance of limestone under CaL-CSP conditions. The presence of nanosilica generates impaired CaO activity as particle size becomes large, whereas CaO pore size is reduced. SEM analysis further supports that pore plugging rather than CaO grain sintering acts as the main barrier to multicycle performance.

To avoid this undesirable effect of pore plugging, the same group further tailored nanosilica/CaO composites through a low-cost biotemplate method [87]. In this procedure, a calcium nitrate solution was used to fill the pores of the biotemplate nanosilica support and subsequent thermal treatment produced a nanosilica/CaO composite, exhibiting significantly enhanced cyclic activity compared to natural limestone for CaL-CSP. The porous textures and deep cavities of the composite facilitate the diffusion of CO₂ inside the porous CaO skeletons during carbonation, thus reducing pore plugging.

Several Ca/Al composites have been explored for CaL-CSP by various researchers, including the work by Sakellariou et al. [88] who examined the calcination/carbonation performance of Al-stabilised CaO using calcium and aluminium nitrates with different Ca/Al molar ratios through the modified Pechini route. Obermeier et al. [89] also prepared different types of Al-modified CaO from Ca-citrate and Al-nitrate, and tested their cyclic activity upon introducing a steam hydration stage at different temperatures. Their results suggested that neither an increase in temperature nor the addition of steam had a sizeable effect on the CaO

activity. Recently, a simple and cost-effective method to synthesise Al-based compounds was developed by physically mixing and milling nanoalumina/limestone mixtures [90]. The results showed that a calcium aluminate with ratio $\text{Ca}/\text{Al} < 1$ ($\text{Ca}_4\text{Al}_6\text{O}_{13}$) was generated in the thermal cycling of CaL-CSP, which served to preserve the CaO microstructure and reduce pore plugging (Figure 9). A crystalline phase of $\text{Ca}_3\text{Al}_2\text{O}_6$ was produced ($\text{Ca}/\text{Al} > 1$) under CaL- CO_2 capture thermal cycling conditions, probably as a result of the higher calcination temperature, leading to a greater availability of CaO.

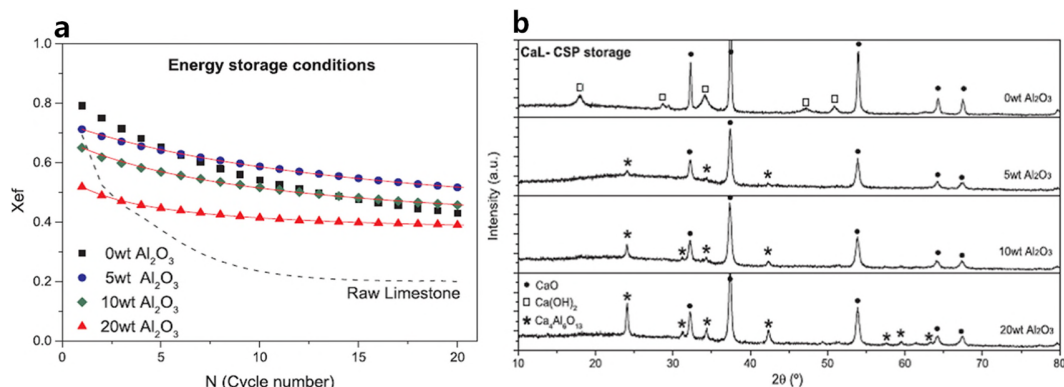


Figure 9. (a) Multicycle activity of milled limestone and $\text{Al}_2\text{O}_3/\text{CaCO}_3$ mixtures with different Al_2O_3 amounts and (b) X-ray diffractograms of milled limestone and composites after the 20th CaL cycle under energy storage conditions [90].

Besides SiO_2 and Al_2O_3 , ZrO_2 has also been investigated as a support material for Ca-based sorbents under CaL-CSP conditions [77,91]. A $\text{ZrO}_2/\text{CaCO}_3$ sample with a small mass percentage of inert solids (5 wt.% ZrO_2) indicates an improved performance for both carbonation under absolute pressure of 1 and 3 bar [79]. Microscopic analysis suggested that segregation of the inert ZrO_2 is less marked in $\text{ZrO}_2/\text{CaCO}_3$ composite than the case of dolomite, thus explaining its better performance [91]. However, the deactivation occurs at a similar rate with the repeated cycles for both materials, seemingly ruling it out as a particularly promising material for CaL-CSP.

Sánchez Jiménez et al. [92] prepared porous $\text{CaCO}_3\text{-MgO}$ composites using acetic acid-treated dolomite for TCES. The presence of pore volume and inert MgO stabilisers synergistically reduced sintering of CaO, leading to a high and stable conversion (0.7 mol/mol) and improved the overall CaL-CSP energy storage efficiency (Figure 10a). This simple and cost-effective preparation appears to have potential for use at the industrial scale.

Han et al. [93] developed a one-pot method to produce tailored novel $\text{CaCO}_3/\text{graphite}$ nanosheets composites for thermochemical energy storage applications. H_3BO_3 impregnation was used to prevent the antioxidant activity of graphite nanosheets in CO_2 atmosphere at high temperature. When coated with only

3 wt% of graphite, the composite showed a highly efficient and stabilised carrying capacity for heat energy storage due to reduced sintering and aggregation (Figure 10b).

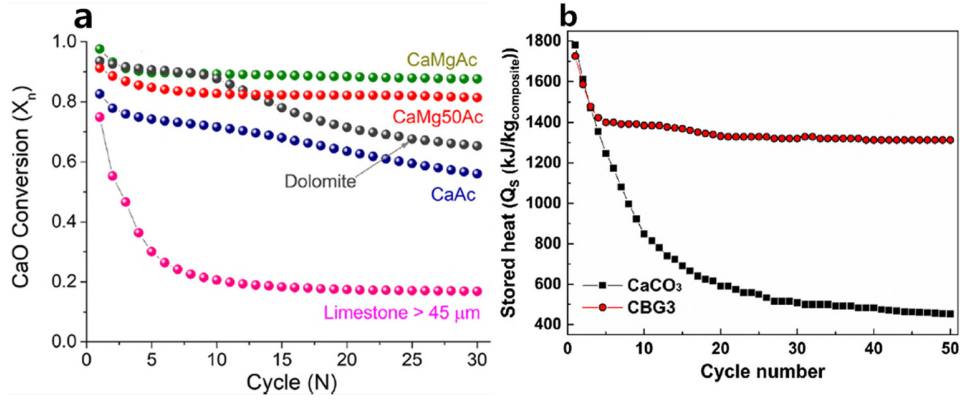


Figure 10. (a) Multicycle CaO conversion of different sorbents under energy storage conditions and (b) the long-term cyclic stored heat performance of pure CaCO₃ and CaCO₃/graphite [93].

2.3. Chemical-looping combustion and metal oxides redox cycles for thermochemical energy storage

CLC technology has been regarded as one of the lower-energy-penalty carbon capture technologies for power generation and fuel upgrading and has already reached a technology readiness level (TRL) of 6 [15,94]. The largest scale of chemical looping combustion for power generation is now validated at 1 to 3 MW_{th} prototype scale [95,96]. The idea of applying high-temperature metal oxide redox systems for energy storage was first proposed by Wentworth and Chen in 1976 [97]. However, there were no serious investigations in this area in the following two decades, mainly because of the relatively low cost of fossil fuels [29]. In recent years, high-temperature metal oxide redox systems for TCES have received significantly more attention due to their potential for high energy storage density, high operating temperature and reduced environmental impacts, although the status of the metal oxide redox system for TCES is currently still at the laboratory scale [29]. However, a 300-kW_{th} central receiver test facility based on metal oxides was built at the King Saud University in Saudi Arabia [98,99].

2.3.1. Process concept of metal oxides redox cycle

The general reaction form of metal oxide redox systems is described as follows:



In the reduction step, the energy required for reduction, which can come from any high-temperature thermal processes or CSP, is absorbed and stored through the endothermic reduction reaction of the metal

oxides [100]. In the following oxidation step, the reduced metal oxides are oxidised back to the original oxides and the stored energy can be released.

With over 40 years of research in the metal oxide redox system for TCES, a number of benefits have been identified [29,32,100–102]:

- Higher operating temperatures (350 to 1200 °C) provide higher efficiency for CSP plants.
- Higher energy storage density compared to sensible energy storage, latent energy storage systems.
- Air acts as both the heat transfer medium and reactant and there are no requirements for compressing, separating and storing the gas.
- Heat is released at a stable temperature and can provide constant heat source.
- Simple system operation with no catalysts required in the metal oxide redox cycle.
- Low hazard posed on environment, health and safety.

2.3.2. Process concept of chemical looping combustion for thermochemical energy storage

Theoretically, the use of redox reactions by means of solid oxygen carriers to oxidise the fuel can also serve as a TES system, as shown in Figure 11. More specifically, the endothermic fuel oxidation reaction in the fuel reactor can potentially store solar energy or energy from other sources as forms of chemical energy or sensible heat through the oxygen carriers or its inert material together with CO₂ separation [103,104].

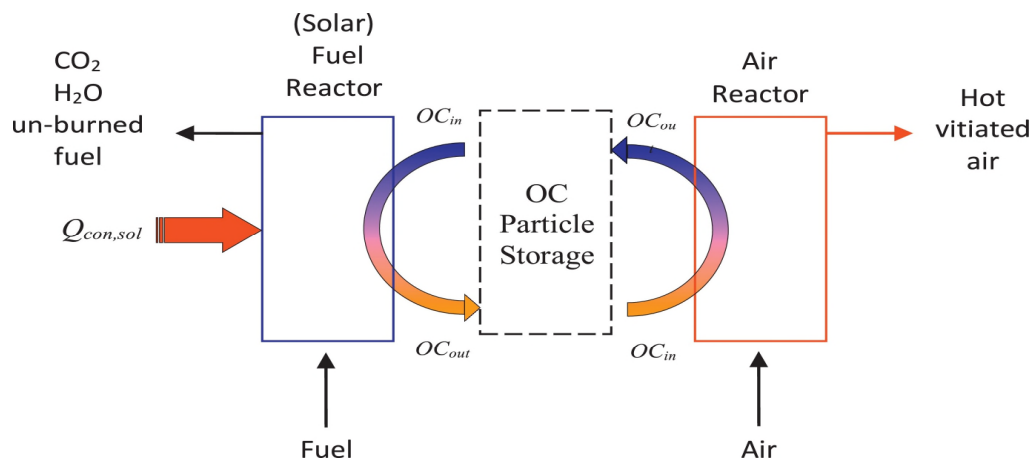


Figure 11. Schematic diagram of a hybrid solar chemical looping combustion process for thermochemical energy storage [104]. Here, OC refers to the oxygen carrier materials.

Recently, some researchers [103,105,106] have proposed the concept and simulated the process integration of the CSP plant with CLC to overcome the drawback of solar energy intermittency and also decrease the cost of the solar TES system with CO₂ mitigation. The potential advantages of a hybrid solar CLC process for thermochemical energy storage are as follows [103–105,107]:

- High energy density due to the combination of thermochemical and sensible heat storage.
- No decrease in exergy efficiency compared to the equivalent conventional CLC technology.
- Simultaneous CO₂ capture and thermochemical energy storage.
- Flexible operation; the process can be operated in the conventional CLC mode during times of insufficient solar radiation.
- Reduced cost of CLC technology with CO₂ capture with sharing of infrastructure.

Jafarian *et al.* [105] proposed the concept of hybrid solar CLC processes for TES with the use of oxygen carriers as a storage medium (Figure 12 shows a conceptual design). The cavity-type reactor configuration has been reported as being the most suitable solar receiver to utilise concentrated solar radiation effectively [108]. The cavity-fuel reactor first receives concentrated solar radiation from the heliostat field and provides the energy for an endothermic reaction such as that provided by the Ni/NiO system. Compared with the normal CLC plant, three oxygen particle storage tanks, storing the thermochemical and sensible energy, are added between the fuel reactor and air reactor in order to provide a constant mass flow rate of evenly heated oxygen carriers to the air reactor, thus smoothing out the impacts of solar radiation variations over a day [105]. The heat can be released through convection/radiation and the exothermic oxidation reaction of the oxygen carriers in the air reactor. CO₂ produced from the combustion of fuel with the oxygen carriers in the fuel reactor, can be easily separated from the simultaneously produced steam, thus facilitating CO₂ capture and storage.

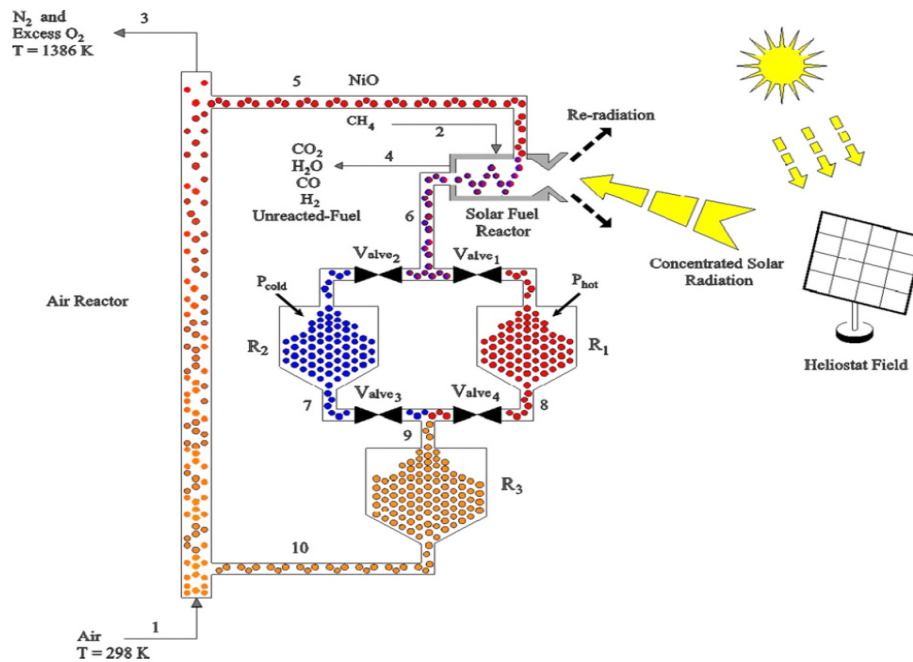


Figure 12. A conceptual design of hybrid solar chemical looping combustion energy storage system [105].

Subsequently, the same research group [103] developed a new conceptual design of the hybrid solar CLC system (Figure 13) with a higher amount (~60%) of solar energy reaching the fuel reactor (termed ‘solar share’) [105]. Solar Share defines the percentage amount of energy that is solar derived, i.e., a 50% solar share implies 50% of the total thermal input is from solar energy, the remainder coming from fossil fuel combustion. Solar shares for CLC-TCES can range from 0-100%, thereby highlighting the operational flexibility of the plant; however, when averaged over a whole year typical solar shares are ~60%, although this value is location- and environment-dependant [105]. Higher solar shares are beneficial in reaching higher operating temperatures, but this can lead to oxygen carrier degradation, whilst low solar shares means additional fuel needs to be used to sustain the reactions. The proposed system can be operated flexibly either in conventional CLC and solar CLC modes, depending on the solar radiation, and oxygen carrier particle feeding rate to the air reactor [103]. The results indicated that the proposed system could achieve continuous base-load power generation and that 95% of the input energy from CH₄ combustion and absorbed solar energy was stored in the oxygen carriers as sensible heat (46%) and chemical heat (54%) [103].

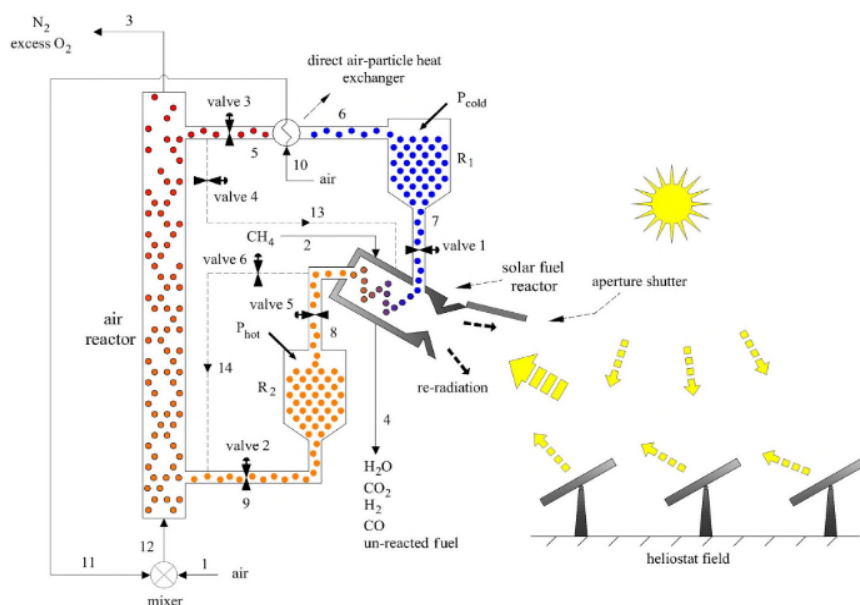


Figure 13 The proposed hybrid solar chemical looping combustion system with a high solar share [103].

2.3.3. Metal oxide materials

Metal oxides represent the critical element of the metal oxide redox cycle for thermochemical energy storage. The desired properties of the metal oxides for thermochemical energy storage are high operating temperature, high energy density, fast reaction kinetics, and ability to reversibly undergo many cycles with minimal degradation [29,100]. The metal oxides in the hybrid solar CLC system act as the oxygen carriers and solar TES materials simultaneously; thus, these metal oxide materials should have optimal performance in both CLC and TES processes.

Currently, the investigation of hybrid solar CLC system for TES is mainly focussed on utilisation of gaseous fuels such as CH_4 , CO and H_2 [109]. Solid and liquid fuels have not been reported in this area for thermochemical energy storage. There are several studies available to illustrate the concept and status of development in CLC and CLOU for combustion of solid fuels [25,110,111]. In theory, CLC and CLOU for combustion of solid fuels are feasible for solar hybrid CLC for TCES where the external thermal sources or solar energy can be stored by means of the endothermic reactions for gasification of char in CLC conditions or oxygen release from the oxygen carriers in CLOU conditions. To the best of our knowledge, no literature is currently available to evaluate the feasibility of CLC or CLOU for solid fuels in TCES. Additionally, another limitation is that CLC with solid and liquid fuels is more complex, and there are techno-economic uncertainties in developing suitable reactor designs, along with new fuel handling/processing treatment [109,111,112].

The development of the oxygen carriers in hybrid solar CLC systems for solar TES should broadly follow the same criteria and methods of the selection of metal oxides in CLC. It is worth noting that more

than 700 materials for CLC have been investigated in the laboratory, focussed on oxides of metals such as Ni, Cu, Fe, Mn, and Co as well as mixed and combined oxides [14]. Some of these materials have been tested in practical conditions in more than 20 CLC units, ranging in size from 0.3 kW – 3 MW [14]. The desired characteristics of the oxygen carriers for hybrid solar CLC for solar TES can be listed as follows [14,104,113]:

- High reactivity with fuel and oxygen, and ability to completely convert fuel to CO_2 and H_2O .
- Endothermic reaction in the fuel reactor is favourable. (The fuel reactor is where the concentrated solar energy is collected and used to drive the endothermic chemical reactions. A solar-CLC system would provide little benefit to an exothermic fuel reaction in the fuel reactor.)
- Fast reaction kinetics.
- Highly chemically reversible reactions and physical stability over large number of cycles.
- High oxygen carrying/transfer capacity.
- Low cost of material over the lifetime of the materials use.
- Low health, safety and environment risk from fines/toxicity.

Jafarian et al. investigated the energetic performance of various combinations of CH_4 , CO and H_2 with five different oxygen carriers (Co, Cu, Fe, Mn and Ni) together with inert materials, by thermal analysis using Aspen Plus software [109]. Their results indicate that only CoO/Co , NiO/Ni , and $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ can be used in the hybrid solar CLC-TES system with natural gas as the fuel, and that the utilisation of NiO/Ni as the oxygen carrier and TES material appears to offer the best performance in this system [109]. CO is not as favourable as the fuel in the proposed system due to its exothermic reaction with these oxygen carriers, and hydrogen can only be applied in the proposed system with $\text{Fe}_2\text{O}_3/\text{FeO}$ and FeO/Fe as the oxygen carriers [109]. To date, only pure metal oxides have been used to evaluate the process of hybrid solar CLC for solar TES, while the performance of combined mixed metal oxides still requires further investigation for this application. Although solar-fuel reactors appear to be feasible for chemical and solar energy storage [104], there is a lack of detailed investigation in this area to date.

Previous research of potential metal oxide materials for high-temperature TCES is focussed on the pure metal oxides such as $\text{Co}_3\text{O}_4/\text{CoO}$, BaO_2/BaO , $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$, $\text{CuO/Cu}_2\text{O}$ and $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ and also mixed metal oxides [29,101,102,114]. The key criteria for metal oxide materials for thermochemical energy storage are as follows [29,44,101]:

- Suitable reaction temperature (e.g., 400 – 1200 °C for CSP plants).
- High energy-storage density.
- Suitable thermodynamics and fast reaction kinetics.

- Complete reversibility of the reaction and cycling stability.
- Low cost and environmental/health risks.

Many techniques have been applied to study the performance of metal oxide redox systems for thermochemical energy storage. Thermogravimetric analysis is one of the most popular methods to determine the reaction temperature, reaction kinetics and redox reversibility [29,44] and the combination of TGA with differential scanning calorimetry (DSC) can measure the absorbed or released energy during the redox cycles [29].

$\text{Co}_3\text{O}_4/\text{CoO}$ is well recognised as a promising material choice for high-temperature TCES, as it offers high energy storage density (theoretically 844 kJ/kg) and excellent reversibility [29,44,101]. It has also been investigated in the solar-heated rotary kiln and powder-coated honeycomb reactor for TCES [115,116]. Neises et al. [115] proved that a solar-heated rotary kiln with cobalt oxide can be operated “on-sun” at 900 °C for thermal reduction and re-oxidation during “off-sun” conditions with high energy storage density (~400 kJ/kg) and good reversibility. Agrafiotis et al. [117,118] tested the chemical characteristics of pure cobalt oxide and Na, Ni, Mg and Cu cobaltates and showed that pure cobalt oxide could operate efficiently within the temperature range 800-1000 °C but no benefit in performance was observed for the mixed cobalt oxides [117]. However, the drawbacks is: a narrow temperature range (700-885 °C) for re-oxidation at atmospheric pressure, more expensive, and the fact that these are potentially carcinogenic materials, may limit applying cobalt oxide at commercial scale [44,119].

The barium-based oxide redox cycle for TCES was first investigated in the late 1970s [120]. These early results indicated that there was no degradation of the materials after 5 cycles and it achieved a maximum conversion of 93% for the oxidation [120]. Subsequently, Fahim and Ford [121] investigated the kinetics of the BaO_2/BaO cycle under two different ranges (450-580 °C and 650-850 °C), and observed poor reversibility under their experimental conditions. More recently, Carrillo et al. [122] revisited the BaO_2/BaO redox cycle for solar TCES in terms of thermodynamic calculations, characteristics of the redox cycles and kinetics analysis. They proposed that the BaO_2 -BaO redox couple was suitable for TCES due to the high energy density (390 kJ/kg), high reversibility over 30 cycles with stable reaction kinetics and ability to operate at more moderate temperatures [122]. In order to improve the performance of the pure barium oxide system, many types of metal oxides, such as $\text{NiO}/\text{TiO}_2/\text{Fe}_2\text{O}_3/\text{SnO}/\text{ZnO}$ have been investigated as the doping media for barium oxide. However, there was no clear improvement in its energy storage performance due to the high chemical stability of barium oxide [29,101].

$\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ can achieve the reversible reaction for TCES within the temperature range 500 – 1050 °C [123]. However, some previous experimental investigation on $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ indicated that the Mn_2O_3 redox couple has poor kinetics, low energy density (202 kJ/kg) and poor reversibility [101,124]. However,

the incorporation of a second oxide (Fe_2O_3) boosted the oxidation kinetics and reversibility of the manganese oxide redox cycle [101,125,126]. Carrillo et al. showed that decreasing the particle size of $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ reduced the oxidation temperature and slowed down the reaction, and that materials degradation was determined by the particle size [125].

The copper oxide system is attractive for integration with CSP plants for TCES, especially in areas of emerging CSP markets with high solar resources, for instance, Mexico and northern Chile [127]. Several research groups reported kinetic investigations of the $\text{CuO}/\text{Cu}_2\text{O}$ redox cycle for high-temperature TCES. Chadda et al. [128] studied the cyclic reaction kinetics of $\text{CuO}/\text{Cu}_2\text{O}$ through a non-isothermal TGA method within the temperature range of 400-910 °C and found an insignificant loss in reactivity in 20 cycles. Later, Deutsch et al. investigated the kinetics and cycle stability of copper oxide by TGA and a fixed-bed reactor for the process of CSP-TCES [129]. It was found that the different supporting materials reduced the energy storage density of copper oxide and its kinetics [129]. Alonso et al. [130] suggested that copper oxide was a suitable candidate for TCES based on an experimental study on a rotary solar reactor and sintering of the materials was prevented. However, it is necessary to note that the melting point of Cu_2O is usually close to the operation temperature (1030-1134 °C). Several research groups reported that Mn-Cu-O, Co-Cu-O and Fe-Cu-O were attractive materials with benefits of low costs, suitable reaction temperatures and desirable energy storage density [126,131].

Limited work has been reported for applying pure iron oxide for TCES. This is mainly due to the higher operation temperature (~1300 °C) of the iron oxide system that offers challenges for a practical CSP plant, as well as the problem of poor reversibility of the iron oxide redox cycle [29,126]. Nevertheless, Fe-based mixed oxides, such as Cu-Fe-O, Mn-Fe-O and Co-Fe-O, are regarded as promising TCES materials owing to the relatively low costs, suitable temperature range and modest energy storage density [44,102,126].

Besides the above-proposed metal oxides for TCES, perovskite oxides are also considered to be applicable [119,132,133]. Babiniec et al. [132] investigated the materials of $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Mn}_{1-y}\text{O}_{3-\delta}$ (LSCM) and $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) families doped with Ba or K for TCES by TGA. The results indicated that LSCM has the largest reaction enthalpy (245 kJ/kg and good stability and reversibility over 100 cycles in the temperature range of 400-1050 °C in air [132]. However, the $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{M}_{1-y}\text{O}_{3-\delta}$ (M=Mn, Fe) perovskite materials use expensive and atomically heavy rare earth and transition metal cations, which will increase costs and decrease the mass-specific energy storage densities [119]. Previous studies on doped $\text{CaMnO}_{3-\delta}$ perovskite materials for CLC and TCES showed the potential benefits of the $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{M}_{1-y}\text{O}_{3-\delta}$ (M=Mn, Fe) perovskite materials because of their high reaction enthalpies relative to more traditional metal oxide materials [119,133,134].

2.4. Reactor designs for gas-solid looping systems

Only a limited number of research articles are available on the design of a solar CaL/CLC reactor system, as much of the work in this area has focussed on thermochemical storage material development and process modelling and optimisation. As noted in section 2.1.2, most of the experimental work on the CaL-CSP process has been conducted in a TGA, and the operation of CaL-CSP in practical conditions has large impacts on the performance of the sorbents. The most suitable reactors for gas-solid reactions are fluidised bed and rotary kiln that have been proposed to apply in the CLC and CaL-CSP process due to their high heat and mass transfer and ability to be applied at large scale [42,103,116,135–139].

Table 2 presents the features of different reactors for metal oxide TCES systems. The solar-driven fluidised bed reactor seems to be the optimal reactor for the hybrid solar chemical looping TCES systems due to its advantages on gas-solid reactions. There is a series of studies [140–144] available on simulation and experimental study of the performance of solar-driven fluidised bed reactor thermochemical processing and energy storage. Except for the reactors for the gas-solids reaction, heat exchangers or solar receivers should be evaluated to integrate with the gas-solid reactors. The classification of solar receivers can be divided into direct and indirect heating systems according to whether the solar radiation is absorbed by the reactants or the heat transfer fluid. There are also several studies available [108,141,145–147] which explore the design and configuration of solar receivers applicable to TCES systems.

It is important to note that the design and configuration of solar CLC systems for TCES are still at a low technology readiness level and will require significant research to develop optimal reactors for the integrated systems. One example of such a unit is the bench-scale single solar-driven fluidised bed reactor at Miyazaki, Japan, which consists of a solar receiver, compound parabolic concentrator (CPC), quartz window, fluidised bed reactor and air compressor. The first solar tests indicated that the proposed rig could achieve good fluidisation of the particles at bed temperatures of 960–1100 °C [144]. However, the system demands a complex mechanical design and control systems for the hybrid solar CLC systems for TCES. For this system, one must add dual fluidised bed reactors, cyclones, fuel supply system, solid oxides tanks and mass flow controllers/valves to the current single solar-driven fluidised bed reactor. In addition, the size and economic analysis for the design of such hybrid systems have still not been made.

Table 2. Comparison of different reactors for metal oxide thermochemical energy storage.

Type of reactor	Advantages	Disadvantages	Refs.
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Fixed/packed bed	Low cost Easy to build, operate and simulate	Insufficient heat and mass transfer High pressure drop Risk of bulk expansion, and shrinking Difficult to be applied in solar cavity-receiver	[29,101,148,149]
Moving bed	Direct gas-solid heat transfer Improved heat transfer coefficient Adjustable residence time of gas-solid reaction Less impacts of temperature difference than that of packed bed	High-pressure drop under high velocities of gases or solids Difficulties to integrate with solar reactors Non-uniform irradiance distributions on the particle flow	[29,149]
Gravity-driven	Low pressure drop No energy penalty for the flow of particles	Difficulties in controlling the distribution and residence time of particles Risk of fluid bypass and insufficient heat transfer	[149]
Rotary kiln	Increased particle mixing High chemical conversion due to good heat and mass transfer Minimises attrition Continuous operation Multipurpose reactors	Difficulties in scale-up of solar systems High energy penalty for parasitic equipment Higher maintenance costs of rotatory parts under high temperature	[115,138,150]
Fluidised bed	High heat and mass transfer Continuous operation Reduced risk of hot spots and thermal instability	Complex system and modelling Increase of energy penalty for gas fluidisation Erosion of internal components Attrition of materials over time	[49,103,137]

2.5. Comparisons of CaL, CLC and metal oxides redox systems for TCES

The concept and development of three high-temperature gas-solid looping systems have been discussed and demonstrated. Compared with other TES technologies, these technologies have the advantages of high energy storage density, high operational flexibility, and near-unlimited storage duration and transport distance. Comparing TCES CaL and CLC systems with metal oxides redox systems, the CaL and CLC

systems can be integrated with fossil fuel power plants not only for energy storage and power shaving, but also for capture of the CO₂ emissions from flue gases.

The differences between CaL and CLC for TCES are as follows:

- 1) The CaL-CSP system harnesses the carbonation and calcination of sorbents for thermochemical energy storage, while the CLC-CSP system utilises the redox reactions of metal oxides.
- 2) The CaL-CSP process requires an additional CO₂ storage tank and compressors for TCES if it is not integrated with a CO₂ production facility, such as a fossil fuel power plant.
- 3) The CLC for TCES has high operational flexibility as it can be operated without any solar input during the night.
- 4) The concept of CaL for TCES has been investigated at the laboratory scale, but the concept of CLC for TCES is only at the process modelling stage.

3. Future research potential

For CaL for TCES, the multicycle activity of sorbents has to date mostly been performed under unrealistic conditions (i.e., calcination in pure He or N₂) and most tests have been conducted for a limited number of cycles (~20 cycles), and only limited research has been conducted in fluidised bed carbonators for CaL-CSP conditions. Future testing should be carried out in fluidised bed carbonators under realistic conditions. Given the costs and manufacturing processes, it is of course preferable to use natural carbonate minerals and Ca-based industrial wastes, but where necessary, synthetic sorbents or adapted sorbents can be developed and there is some evidence that using Mg as a stabilising compound can produce real benefits. Furthermore, to date most sorbents have been tested as powders, but for fluidised bed carbonators these powders must be granulated, and efforts must be made to retain the enhanced pore microstructure of the sorbents upon granulation. An optimized design of the solar receiver/calciner is still a highly technical challenge. The CaL-CSP integration schemes based on heat exchangers should be further developed considering the temperature of the storage tanks and different levels of complexity. The solids conveying, gas separation and storage system should be specifically designed to achieve scalability, high thermal efficiency and long enough residence time for calcination.

Further studies are required on mixed metal oxides to investigate their kinetics, continuous operation tests under practical conditions, and pilot-scale tests of materials in fluidised bed reactors. The development of hybrid solar CLC for TCES is currently focussed on feasibility studies through process modelling. The results indicate that the hybrid system can theoretically achieve high exergy efficiency and energy storage density. The comprehensive techno-economic study of this technology at large scale is necessary. An

important caveat of any proposed hybrid solar CLC system for TCES is that it is more complex in design and operation than that of current chemical looping and redox systems, which may limit its application and development in the future without further drivers demanding a need for energy storage integration.

4. Conclusions

The present review explores the key past findings of applying CaL/CLC and metal oxides for high-temperature TCES. The concept, process conditions, materials and reactor development of CaL/CLC and metal oxides for high-temperature TCES have been evaluated and the key findings can be summarised as follows:

- 1) The CaL/CLC and metal oxide redox cycle processes are feasible to store solar energy in thermochemical form at high temperature, for diurnal usage, balancing out day-night solar availability.
- 2) The carbonation/calcination atmospheres, operating temperatures and pressures, types of solar collectors/reactors, particle size, and exact carbonate material used all influence the multicycle conversion and performance.
- 3) Solar-heated CLC has the potential to be utilised for CO₂ capture and, combined with intermediary material storage vessels, to then operate as a form of TCES.
- 4) Mixed metal oxides become attractive for TCES only if the synthesised materials can provide equal or better energy storage performance and lower lifetime costs than the stand-alone pure metal oxides.
- 5) Further research is required to explore high-performance and cost-effective thermochemical storage materials for CaL/CLC and metal oxide redox systems, and more pilot-scale testing on candidate materials is required under realistic CSP conditions.

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