

Review

Advances in Solid–Gas Reaction-Based Thermochemical Energy Storage Systems

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Abstract

Thermochemical energy storage (TCES) has emerged as one of the pivotal technologies for enhancing the stability and efficiency of energy systems, owing to its advantages including high energy storage density, low heat loss and long-term energy storage capability. Among various TCES technologies, solid–gas reaction-based TCES exhibits tremendous potential in medium- and high-temperature applications. This paper first overviews the research progress of solid–gas reaction-based TCES technologies. Focusing on four major TCES material systems, namely hydroxides, carbonates, metal oxides and metal hydrides, it discusses their energy storage mechanisms, material modification strategies, and reaction kinetics, as well as approaches to improve thermal conductivity and cycling stability. Subsequently, reactor types (including fixed bed, moving bed and fluidized bed reactors) applicable to different materials and the latest research progress of diverse reaction systems are elaborated in detail, and the optimal designs of heat transfer performance for the four reaction materials in corresponding reactors are clarified. Based on the comparative analysis, the $\text{Ca}(\text{OH})_2/\text{CaO}$ system is identified as the most promising material system for engineering deployment, owing to its moderate operating temperature, low material cost, and validated pilot-scale performance. The intrinsic complementarity between material modification strategies and reactor heat transfer enhancement is also elucidated, providing a theoretical foundation for scalable implementation.

Keywords: thermochemical energy storage; solid–gas reaction; energy storage material; reactors with diverse beds; optimal design



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1. Introduction

The continuous growth of global energy demand and environmental challenges posed by fossil fuels are driving the transformation of the energy structure toward renewable energies represented by solar and wind power [1,2]. Nevertheless, the inherent intermittency and instability of such energy sources urgently require efficient and reliable energy storage technologies to balance energy supply and demand and improve the stability of energy systems [3,4]. Among various energy storage technologies, thermal energy storage has attracted considerable attention owing to its capability to realize the collaborative integration of power and thermal systems [5]. It can be classified into three categories: sensible heat storage (SHS), latent heat storage (LHS) and thermochemical energy storage (TCES). SHS utilizes the temperature rise of the medium to store heat, but it has a low

volumetric energy storage density (approximately 180 MJ/m³) and a short storage period due to easy heat loss. LHS utilizes latent heat during phase change to store heat, with a moderate volumetric energy density (around 360 MJ/m³). However, its storage period is also not long because heat is likewise prone to loss. TCES stores and releases heat based on reversible chemical reactions or adsorption/desorption processes [6,7]. Featuring a high energy storage density (up to 1800 MJ/m³), a wide operating temperature range (310–780 °C), and the ability to achieve long-term storage with nearly zero heat loss, TCES demonstrates enormous potential in medium- and high-temperature applications such as concentrated solar power and industrial waste heat recovery [8].

Benefiting from the separable reaction products that can be stored at ambient temperature, TCES can theoretically realize long-term energy storage and long-distance energy transportation [9]. According to the reactant states, TCES systems are classified into solid–gas, gas–gas and liquid–gas. Among them, medium- and high-temperature solid–gas reaction TCES, involving the decomposition and synthesis of hydroxides, carbonates, metal oxides and metal hydrides, has become a current research hotspot owing to its controllable reactions, easily separable products and high energy storage density [10]. Nevertheless, low-temperature TCES has also attracted increasing attention in recent years, particularly in building heating/cooling and seasonal heat storage applications. Typical low-temperature working pairs include salt hydrates (e.g., SrBr₂·6H₂O, MgSO₄·7H₂O) [11] and metal halide–ammonia complexes (e.g., MnCl₂·NH₃, CaCl₂·NH₃) [12], with operating temperatures as low as 0–120 °C. Although these systems offer high energy density and long-term storage capability, they still face challenges such as mechanical instability, deliquescence, agglomeration, and chemical instability [13]. The present review focuses on medium- and high-temperature (typically above 300 °C) solid–gas TCES systems, and does not provide a detailed discussion on low-temperature TCES.

The energy storage performance of solid–gas reaction TCES is not only determined by material properties, but is also closely related to reactor design. Reactor types of solid–gas reaction TCES directly affect heat and mass transfer efficiency and overall system performance [14,15], including fixed bed reactor, moving bed reactor and fluidized bed reactor. Currently, review articles in the field of thermochemical energy storage tend to focus separately on either the modification of single material systems or the heat transfer characteristics of specific reactor types, lacking a cross-cutting analysis that systematically integrates material-level optimization with reactor-level thermal management. To fill this gap, this review uniquely incorporates the four major material systems (hydroxides, carbonates, metal oxides, and metal hydrides) and the three primary reactor configurations (fixed bed, moving bed, and fluidized bed) into a unified analytical framework. The literature selection and review framework of this paper are as follows. This paper first elucidates the modification strategies for four material systems—hydroxides, carbonates, metal oxides, and metal hydrides—aimed at improving thermal conductivity, reaction kinetics, and cyclic stability. Subsequently, it introduces their applications and optimal designs in various reactors, such as fixed bed reactor, moving bed reactor, and fluidized bed reactor systems, thereby systematically integrating material modification with reactor optimization. This work thus provides a theoretical basis and technical guidance for the future development and application of key solid–gas TCES.

2. A Review of Materials for Solid–Gas Reaction Material-Based TCES

According to the characteristics including reaction temperature, reversibility, material stability, toxicity and corrosiveness, solid–gas reaction-based TCES materials are mainly divided into carbonates, hydroxides, metal hydrides and metal oxides [16], and their main parameters are listed in Table 1 [10,17]. It is worth noting that the thermodynamic

parameters of the TCES materials listed in the tables of this section—specifically Tables 1, 2, 4, 7, and 10—were all obtained under standard atmospheric pressure. The mechanisms, advantages and disadvantages of different material systems are illustrated in Figure 1 [18].

Table 1. Main parameters of various solid–gas TCES materials.

Reactant Materials for TCES	Typical Chemical Reaction	Gravimetric Energy Density/(kJ/kg)	Reaction Temperature/°C	Reaction Enthalpy/(kJ/mol)
Hydroxides	$\text{Ca(OH)}_2 + \Delta H \leftrightarrow \text{CaO} + \text{H}_2\text{O}$	409.4–1352.0	70–1005	47.8–100.2
Carbonates	$\text{CaCO}_3 + \Delta H \leftrightarrow \text{CaO} + \text{CO}_2$	314.0–1656.8	120–1555	68.3–202.3
Metal Oxides	$2\text{Co}_3\text{O}_4 + \Delta H \leftrightarrow 6\text{CoO} + \text{O}_2$	123.0–982.1	105–1710	21.4–249.3
Metal Hydrides	$\text{MgH}_2 + \Delta H \leftrightarrow \text{Mg} + \text{H}_2$	865.0–2814.0	253–1400	64.6–186.0

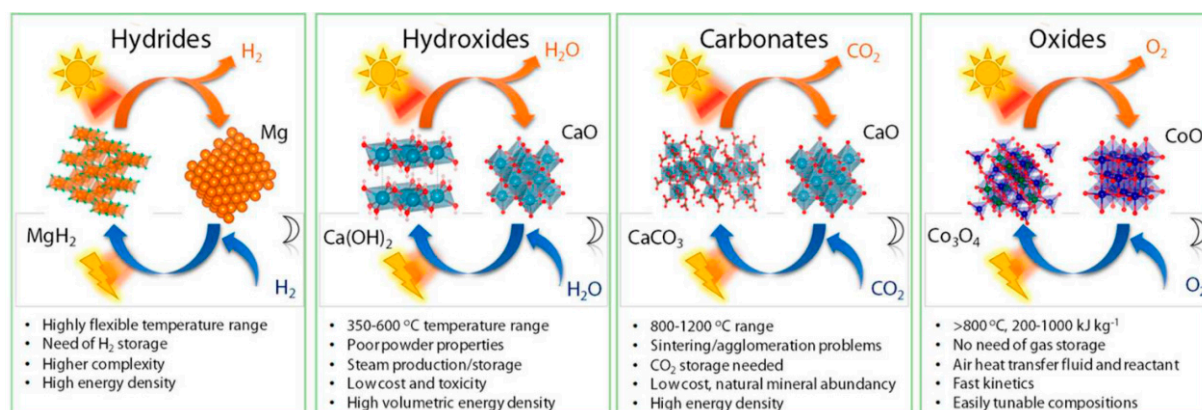
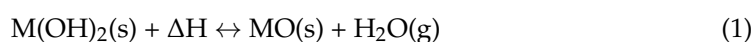


Figure 1. Comparison of mechanisms, advantages and disadvantages of different material systems [18]. Reproduced with permission from A.J. Carrillo, J. González-Aguilar, M. Romero et al., *Chemical Reviews*; published by ACS, 2019 [18].

2.1. Hydroxides

The hydroxide reaction-based TCES is shown in Equation (1). The theoretical decomposition temperatures and thermodynamic parameters of various hydroxides are listed in Table 2 [17]. It can be seen from the gravimetric energy density and reaction enthalpy in the table that the $\text{Ca(OH)}_2/\text{CaO}$ and $\text{Mg(OH)}_2/\text{MgO}$ reaction systems exhibit prominent energy storage potential [19]. Among them, the Mg(OH)_2 -based system features low energy storage cost but sluggish hydration kinetics. To accelerate the hydration process, Tian et al. [20] fabricated $\text{Fe/LiNO}_3/\text{TiN}$ modified MgO composites via a wet mixing method, which increased the MgO hydration conversion rate by 6.3 times within 30 min and reduced the hydration energy barrier by 62.76%. Nevertheless, its reaction rate decreases with rising temperature. Accordingly, Wu et al. [21] constructed NC- MgO - LiCl ternary composites through calcination, achieving a remarkable improvement in both dehydration and hydration rates. Yang et al. [22] prepared Mg(OH)_2 /expanded graphite (EG) composites by wet ball milling, shortening the dehydration and hydration reaction time by 19.7% and 39.5%, respectively. Poor hydration reaction kinetics hinders heat release and restricts the application of the $\text{Mg(OH)}_2/\text{MgO}$ system in TCES [8]. In contrast, the $\text{Ca(OH)}_2/\text{CaO}$ system has attracted extensive attention in TCES owing to its high energy storage density, wide reaction temperature range, excellent reversibility and environmental friendliness [10,23].



Dai et al. [16] investigated the cyclic dehydration/hydration process of Ca(OH)_2 , and found that the material suffers from low thermal conductivity, uneven heat release rate, material sintering and agglomeration, as well as poor cycling stability. These issues can be alleviated to a certain extent through strategies such as doping, construction of special

structures, and surface coating. The specific modification strategies and their corresponding results are summarized in Table 3.

Table 2. Thermodynamic parameters of hydroxides.

Hydroxides	Gravimetric Energy Density/(kJ/kg)	Turning Temperature/°C	Reaction Enthalpy/(kJ/mol)
Ca(OH) ₂ /CaO	1352.0	515	100.2
Mg(OH) ₂ /MgO	1333.0	265	77.7
Be(OH) ₂ /BeO	1191.0	70	51.3
Mn(OH) ₂ /MnO	754.0	190	67.1
Sr(OH) ₂ /SrO	728.3	755	88.6
Ba(OH) ₂ /BaO	545.5	1005	93.5
Ni(OH) ₂ /NiO	516.0	70	47.8
Zn(OH) ₂ /ZnO	498.9	55	49.6
Cd(OH) ₂ /CdO	409.4	125	60.0

Table 3. Modification strategies for Ca(OH)₂/CaO-based TCES.

Application Methods	Key Findings	Reference
Doping with 9% expanded graphite (EG)	The thermal conductivity reaches $2.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is approximately 3 times that of the pure material.	[24]
Doping with 15 wt% hexagonal boron nitride(HBN)	Significantly improves the thermal conductivity of Ca(OH) ₂ .	[25]
Synthesis of Co-doped CaO nanomaterials via MOF-derived method	The porous structure facilitates heat and mass transfer.	[26]
Incorporation of SiO ₂ particles (via reactive molecular dynamics simulation)	Result: It can suppress sintering and agglomeration behavior and enhance structural stability. Mechanism: It increases the activation energy of the diffusion process and strengthens the van der Waals forces between atoms.	[27,28]
Doping with cellulose and TiO ₂	The energy storage density of the composite reaches 1827.7 kJ/kg after 20 cycles; CaTiO ₃ particles improve the structural stability and anti-sintering performance of the composite.	[29]
Doping with sodium carboxymethyl cellulose (CMC) and vermiculite	It maintains excellent structural integrity after multiple dehydration/hydration cycles. The volumetric energy density of the granular composite is increased by approximately 124%. The heat storage rate of the composite is higher than that of the pristine material.	[30]
Composite with Si-SiC ceramic foam to form a porous honeycomb structure	The thermal discharge power density reaches 0.71–0.97 kW/L; volume variation is reduced by 80%; no agglomeration occurs after 15 cycles.	[31,32]
Hydrothermal synthesis of hollow CaO microspheres with porous shell structure	The average energy storage density reaches 1755 kJ/kg after 30 cycles; volume expansion is reduced from 250% to 32%, which effectively suppresses agglomeration. The reaction kinetics is twice that of pure CaO.	[33]
Doping with sodium silicate	Inhibits complete hydration of CaO grains and improves cyclic stability.	[34]
SiO ₂ coating on CaO particles	After 10 cycles, the increase in average particle size decreases from 33% to 11%; the expansion rate and attrition rate are reduced by 45.4% and 48.5%, respectively; the volumetric energy density is improved by 33.2%.	[35]
Nano-Al ₂ O ₃ .coated Ca(OH) ₂	The conversion rate remains at approximately 88% during cycles, which significantly improves structural integrity and mechanical stability.	[36]
Two types of composite pellets: shelled (M-CaO-SD) and shell-free (M-CaO)	Both composite pellets exhibit the characteristics of suppressing volume expansion and enhancing reactivity.	[37]

In addition, regarding optimization studies on reducing the dehydration temperature (normally around 500 °C) of the Ca(OH)₂/CaO reaction system to cut energy consumption, Wang et al. [38] reported that adding 10 wt% KNO₃ reduces the dehydration temperature of Ca(OH)₂ by approximately 70 °C, accelerates the reaction, and causes no loss in energy

storage density. Yan and Zhao [39] found that Li doping reduces the dehydration energy barrier from 0.40 eV to 0.11 eV, promotes the cleavage of OH bonds and shortens the dehydration duration. Huang et al. [40] demonstrated that doping with rare earth ions (Sc, Y, La, Gd, Lu) lowers the initial decomposition temperature by 50 °C. Among them, Sc or Y doping increases the dehydration rate by more than 3 times at 320 °C and improves cycling stability. Subsequently, Huang and Wang et al. [41] found that Li/La or Li/Ti dual-doped crystal structures significantly reduced the energy barrier of the Ca(OH)_2 dehydration process. The energy barrier value was 0.59 eV for the undoped crystal, and decreased to 0.09 eV and 0.20 eV after doping with Li/La or Li/Ti, respectively. Moreover, the sample co-doped with Li/La elements (at a molar percentage of only 5%) exhibited a reduction in onset dehydration temperature of approximately 40 °C. Bian et al. [42] revealed that Mn and Ce doping enhances the adsorption energy of CaO toward H_2O . Specifically, Mn doping reduces the hydration energy barrier by 84.3%, which significantly improves hydration reactivity and conversion ratio.

2.2. Carbonates

The carbonate reaction-based TCES is shown in Equation (2). It generally operates at temperatures above 800 °C with an energy storage density of approximately 3027.6 kJ/kg. Featuring low operating pressure, non-toxicity, non-corrosiveness, abundant reserves and low cost, carbonates have become one of the most popular TCES materials [43]. Among carbonates, CaCO_3 , PbCO_3 , BaCO_3 , SrCO_3 and MgCO_3 are commonly investigated energy storage materials [44], and their thermodynamic parameters are listed in Table 4 [17]. Among them, CaCO_3 is regarded as the most promising energy storage material [43].

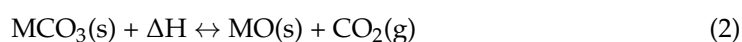


Table 4. Thermodynamic parameters of different carbonates.

Carbonate	Gravimetric Energy Density/(kJ/kg)	Turning Temperature/°C	Reaction Enthalpy/(kJ/mol)
CaCO_3	1656.8	885	165.8
SrCO_3	1370.7	1220	202.3
PbCO_3	314.0	310	83.9
BaCO_3	836.6	1555	165.1
MgCO_3	1174.0	300	99.0

Numerous studies have indicated that the CaCO_3/CaO system suffers from critical issues including sintering, agglomeration and degraded cyclic stability after multiple cycles. During sintering, the porosity on the CaO surface decreases, increasing the difficulty for CO_2 to access active sites inside the material [45], which results in reduced energy storage efficiency. Doping with inert materials can retard the sintering phenomenon, and the doping effects vary with different inert materials and their proportions. Additionally, doping with metal compounds can enhance the cyclic stability of the material, and different doping methods and types also lead to different results. The specific doping materials and the corresponding final results are shown in Table 5. Meanwhile, to further suppress sintering and agglomeration of CaCO_3/CaO , alternative sources of calcium carbonate materials are being investigated, with key findings listed in Table 6.

Table 5. Doping strategies for CaCO₃/CaO-based TCES.

Application Methods	Main Findings	Reference
Synthesis of CaO/SiO ₂ composite from rice husk	The 70%CaO/30%SiO ₂ sample exhibits higher effective conversion after 50 cycles than the 90%CaO/10%SiO ₂ sample.	[46]
Doping with 2.5 mol% TiO ₂	Enhancing the anti-sintering property and cyclic stability of CaCO ₃ ; reducing the reaction activation energy and initial decarbonation temperature.	[47]
Co-doping CaO with Al ₂ O ₃ /CeO ₂	The optimal energy storage performance is achieved at 5 wt% Al ₂ O ₃ and 5 wt% CeO ₂ doping. Ce ³⁺ generates oxygen vacancies on the surface, increases adsorbed oxygen content, and promotes the carbonation reaction of CaO.	[48]
Doping nano-CaO with Li ₂ SO ₄	The optimal doping content is 3–5 wt%. The conversion rate reaches 51% after 11 cycles (27.3% for pure nano-CaO). Li ₂ SO ₄ increases the surface pore ratio and pore size of the material.	[49]
Preparation of MgO-doped CaO via coprecipitation method	The 10% MgO sample exhibits excellent CO ₂ absorption capacity during 30 cycles.	[50]
Co-doping Ca-based honeycomb material with MgO/ZnO	The optimal energy storage performance is achieved when the mass ratio of CaO:MgO:ZnO is 100:10:3. ZnO enhances the supporting effect of MgO on CaO.	[51]
Preparation of Porous MgO and nano-CaO Powder by Secondary Calcination	This method can effectively resist pore blockage, suppress sintering, and achieve a high long-term conversion rate.	[52]
Synthesis of Mn/Fe co-doped CaO composites via sol–gel method	It inhibits sintering and agglomeration, and improves cyclic stability.	[53]

Table 6. Main findings of different alternative materials.

Alternative Materials	Main Findings	Reference
Chalk and marble	They show significant differences in cyclic activity compared with limestone, along with differences in particle size and microstructure.	[54]
Dolomite	It contains inert MgO grains and can maintain gas diffusion channels. It exhibits high cyclic conversion rate regardless of particle size, and avoids common deactivation caused by pore blockage.	[55]
Eggshell and snail shell	They require lower calcination temperature, which helps reduce energy consumption.	[56]
Scallop shells	The sample containing 5 wt% Cr/Mn achieved an energy storage density of 2968 kJ/kg and reached a relative decomposition conversion of 0.9 within 9.8 min. After 100 heat storage–release cycles, the energy storage density remained at 2298 kJ/kg, with a retention rate of 78%.	[57]
Estonian oil shale ash	The results indicate its limited application potential in TCES.	[58]

SrCO₃ features a high reaction temperature and high energy density (205 kJ/mol), yet it also suffers from sintering issues. Its cyclic stability can be improved via doping strategies. From the perspective of reaction mechanism, Zhang et al. [59] found that H₂ can significantly promote the decomposition of SrCO₃. At 900 °C, the decomposition rate is 10 times that under N₂ atmosphere, and SrO exhibits a self-catalytic effect. Williamson et al. [60] reported that the SrTiO₃-doped composite retains 80% capacity after 55 cycles, while the lower-cost SrZrO₃ doping only reserves 11% capacity after 53 cycles. Amghar et al. [61] investigated SrCO₃ composites modified with ZrO₂, SiO₂ and MgO. Among them, the 10% SrSi sample achieves the optimal cyclic stability, with volumetric energy density maintained at 1.70–2.10 GJ/m³ after 20 cycles.

In addition, although MgCO_3 is abundant in reserves, non-toxic and low-cost, it suffers from poor reverse reaction kinetics. The conversion ratio from pure MgO to MgCO_3 is less than 2%, which severely restricts its heat release performance [62,63]. Xu and Zhao [64] optimized reaction kinetics by regulating the physical morphology of MgO . They found that SD-cotton- MgO with mesoporous structure achieves a carbonation conversion rate of 76.98% and a thermal energy storage density of 1385.7 kJ/kg at 400 °C. André et al. [65] reported that BaCO_3 encounters melting problems during calcination, and the addition of MgO fails to improve its cyclic stability. The PbCO_3/PbO system has rarely been investigated due to poor reaction reversibility and material toxicity [7].

2.3. Metal Oxides

The metal oxide reaction-based TCES systems are shown in Equation (3) [66]. The volumetric density and reaction temperatures of metal oxides are illustrated in Figure 2. Among them, Cr_5O_{12} , Li_2O_2 and MgO_2 exhibit sluggish redox reactions at low temperatures, making it difficult to release heat effectively. Rh_2O_3 , PtO_2 and UO_2 suffer from excessively high cost. Lead and vanadium oxides tend to form various intermediate compounds, rendering controlled heat release unachievable. Antimony oxides possess complex conversion pathways, and their feasibility remains to be verified [67]. The reduction of MnO_2 to Mn_2O_3 is irreversible under atmospheric pressure. Meanwhile, the reduction temperature of Mn_3O_4 to MnO reaches 1700 °C, which hinders its direct application [68]. Considering the favorable reaction temperature, high energy storage density, excellent kinetics and cost advantages, BaO_2/BaO , $\text{Co}_3\text{O}_4/\text{CoO}$, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$, $\text{CuO}/\text{Cu}_2\text{O}$ and $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ are the most promising redox pairs [69]. Their thermodynamic parameters related to energy storage are listed in Table 7 [17].

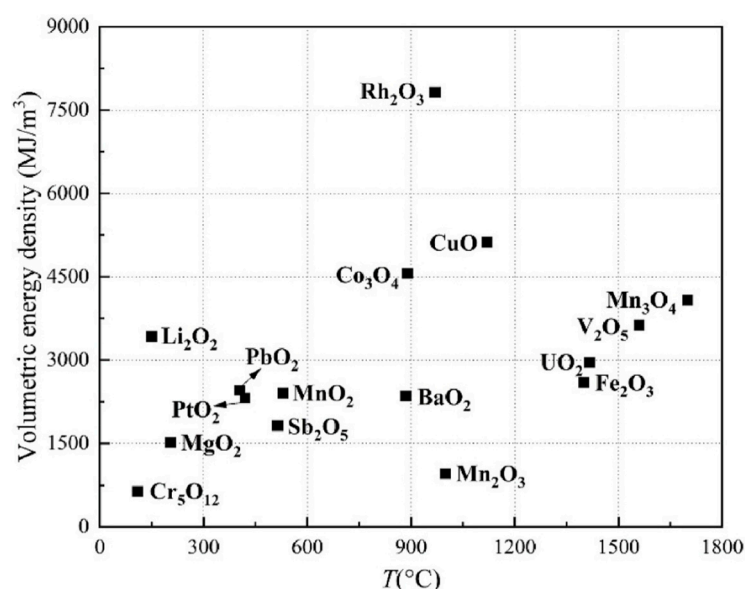


Figure 2. Volumetric density and reaction temperature of various metal oxides [67]. Reproduced with permission from X. Han, L. Wang, H. Ling et al., *Renewable and Sustainable Energy Reviews*; published by ELSEVIER, 2022 [67].

Wang et al. [70] investigated the $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ system using synchronous thermal analysis and various microstructural characterization techniques. The results show that Mn_3O_4 reversibly converts to Mn_2O_3 with a conversion efficiency of up to 100% over five cycles, and the activation energy for the reduction reaction of Mn_2O_3 is 249.87 kJ/mol.

But pure Mn_2O_3 is prone to sintering, which restricts oxygen diffusion and hinders re-oxidation [71]. Studies have shown that sintering can be suppressed via doping strategies to facilitate re-oxidation. The effects of different doping types and contents on the thermal energy storage properties of $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ are listed in Table 8.

Table 7. Thermodynamic parameters of metal oxides.

Metal Oxides	Gravimetric Energy Storage Density/(kJ/kg)	Turning Temperature/ $^{\circ}\text{C}$	Reaction Enthalpy/(kJ/mol)
$\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$	850.6	1700	194.6
$\text{CuO}/\text{Cu}_2\text{O}$	810.2	1115	64.4
$\text{Co}_3\text{O}_4/\text{CoO}$	816.1	935	196.5
$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$	485.6	1360	232.6
BaO_2/BaO	432.6	880	73.3

Table 8. Summary of research on sintering inhibition of manganese oxides.

Method	Result	Reference
Doping silicon	Reduction conversion rates reach 96.18% and 94.71% at doping contents of 3% and 5%, respectively. Si^{4+} introduces lattice defects and promotes oxidation reactions.	[71]
Doping TiO_2	Optimal performance is achieved at a TiO_2 particle size of 25 nm and a doping ratio of 0.05. Mn_2TiO_4 increases the initial oxidation temperature and energy storage density.	[72]
Bismuth-type $(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{O}_3$ honeycomb material	It forms a core-shell structure $\text{MnFe}_2\text{O}_4@\text{Mn}_{2.7}\text{Fe}_{0.3}\text{O}_4$, promotes oxygen adsorption and dissociation, and retains 85% capacity after 100 cycles.	[73]
Doping 5%Cr	Cyclic stability is improved, while the oxidation rate is significantly reduced.	[74]

$\text{CuO}/\text{Cu}_2\text{O}$ features high energy density and abundant reserves, yet it suffers from incomplete oxidation from Cu_2O to CuO as well as sintering and melting issues [66]. To address these problems, sintering inhibitors, MgO and Al_2O_3 doping, and surface coating modification can be adopted for mitigation. The detailed results are summarized in Table 9.

Table 9. Summary of research on sintering inhibition of copper oxides.

Method	Result	Reference
Yttria-stabilized zirconia (YSZ) as sintering inhibitor	High reversibility and conversion rate are maintained after 100 cycles. The gravimetric energy storage density of 50–60 wt% CuO -YSZ reaches 470–615 kJ/kg.	[75]
Cu-Ce oxides prepared via impregnation pyrolysis method	Capacity retention exceeds 97% after 600 cycles, and the energy release efficiency remains 99.4% after 2 years of storage in air.	[76]
Doping with low-cost MgO and Al_2O_3	The reaction rate and re-oxidation rate reach 97% and 96.3% after 250 cycles, respectively.	[77]
15 wt% MgCr_2O_4	The reaction rate increased by 3.7 times; the re-oxidation degree was optimized from 46% to 99.9%; the energy storage density and heat release energy density reached -818.23 kJ/kg and 812.90 kJ/kg, respectively; after 600 cycles, the reduction and oxidation reaction degrees remained at 99% and 98.77%, respectively.	[78]
15 wt% NiAl_2O_4	The reaction rate is increased by 4.2 times; the re-oxidation degree is optimized from 46% to 99.9%; the energy storage and heat release densities reach -772.726 kJ/kg and 764.655 kJ/kg, respectively; after 1000 cycles, the reduction and oxidation reaction degrees remain at 99.9% and 98%, respectively.	[79]
$\text{Cu}_2\text{MgO}_3/\text{Mg}_{0.78}\text{Cu}_{0.22}\text{O}$ composite	The re-oxidation degree is increased from 46% to 99%, and the energy release rate is increased by 3.5 times. It remains 99.9% reduction and 97.1% oxidation activity after 3000 cycles.	[80]

$\text{Co}_3\text{O}_4/\text{CoO}$ possesses a high energy density (844 kJ/kg) and excellent reversibility [81], yet it suffers from thermal hysteresis and sintering issues [82]. Han et al. [81] performed Al and Cr doping on Co_3O_4 . Both elements can reduce the thermal hysteresis range, and 10% Al doping exhibits the optimal effect, decreasing the thermal hysteresis range to 4.02 °C. Meanwhile, sintering is suppressed, and the average conversion rate reaches 77.75% after 15 cycles. Wu et al. [83] investigated Co_3O_4 composites co-doped with LiCoO_2 and CuO . The thermal hysteresis range is reduced to approximately 5 °C; the practical energy storage density reaches 81.6% of the theoretical value (higher than 64.1% for the pure sample), and the conversion rate remains above 88% after 32 cycles. Liu et al. [84] synthesized Co_3O_4 with various morphologies and found that the cubic structure achieves the best comprehensive performance. The re-oxidation rate stabilizes at 180 $\mu\text{mol}/\text{min}/\text{g}$ after 30 cycles with nearly intact morphology, whereas the commercial sample undergoes severe sintering after only 5 cycles. The thermal hysteresis value of cubic Co_3O_4 is 10.1 °C, which is 59% lower than that of the commercial sample (24.7 °C), resulting in significantly lower energy loss.

$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ features abundant reserves, low cost and moderate energy storage density (about 485 kJ/kg) [17], but it has a high reduction temperature (1400 °C) and poor reversibility [85]. Notably, Zhou et al. [86] found iron-based minerals containing small amounts of aluminosilicate impurities in coal fly ash. The results show that their energy storage density ranges from 297.79 to 342.00 kJ/mol, with a peak value higher than commercial Fe_2O_3 . The iron-based minerals possess a relatively dense pore structure, leading to slow oxidation reaction kinetics. Economic evaluation indicates that applying such materials to concentrated solar power plants is expected to reduce coal consumption by 139.4 tons per day, demonstrating great application potential for large-scale TCES.

The BaO_2/BaO reaction system exhibits a reduction temperature of approximately 800 °C, an oxidation temperature of 600–700 °C, and an energy storage density ranging from 390 kJ/kg to 526 kJ/kg [8]. Nevertheless, it suffers from poor cyclic stability [87], as the formation of ash stratification prevents further oxidation of BaO . Lei et al. [88] prepared MgO -doped BaO_2 -based energy storage materials via a precipitation method. The results reveal that the cyclic stability and redox activity of the material are significantly improved with increasing MgO doping content, whereas the energy storage density decreases. The BaO_2 composite containing 15 wt% MgO displays the optimal cyclic stability, with a mass change rate of 6.62% and an energy storage density of approximately 338 kJ/kg.

2.4. Metal Hydrides

According to the requirements of energy storage density, operating temperature and pressure, and reaction kinetics, the main metal hydride material-based TCES systems include MgH_2 , CaH_2 , NaH , TiH_2 , etc. [89]. The reaction equations are shown in Equation (4), and the corresponding thermodynamic parameters are listed in Table 10 [10]. Among them, MgH_2 and CaH_2 exhibit outstanding energy storage performance. Nevertheless, CaH_2 suffers from volatility, corrosivity, sluggish reactivity, hydrogen dissolution in metallic calcium and other issues [90]. Griffond et al. [91] investigated the effects of silicon or Ca_xSi_y compounds on the energy storage performance of CaH_2 at different molar ratios. Experimental results indicate that the optimal reaction condition is achieved at a $\text{CaH}_2:\text{CaSi}$ molar ratio of 2:3 and a hydrogen pressure of 1 bar, with a decomposition temperature of 747 ± 33 °C. Doping calcium halides (CaCl_2 , CaBr_2 and CaI_2) into CaH_2 can reduce its thermal stability [92], enabling it to operate under a hydrogen pressure of 1–10 bar at approximately 600–800 °C. In addition, when the operating temperature of CaH_2 exceeds 1100 °C, the cost of vessel materials becomes extremely high. Meanwhile, CaH_2 is readily oxidized to CaO , which shortens its service life and hinders its practical application [93].

Moreover, other drawbacks of MgH_2 require further attention [19], including sluggish reaction kinetics [94], poor cyclic stability caused by its low melting point (650°C) [95], and low thermal conductivity [96].

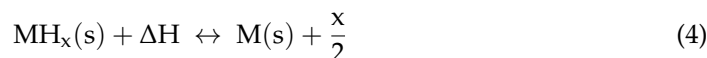


Table 10. Thermodynamic parameters of metal hydrides.

Metal Hydride	Gravimetric Energy Storage Density/(kJ/kg)	Reaction Temperature/ $^\circ\text{C}$	Reaction Enthalpy/(kJ/mol)
MgH_2	2160.0	300~480	75
NaH	2072.0	500~650	117
CaH_2	3857.0	1100~1400	186
TiH_2	890.0	650~750	170

A small amount of efficient catalyst introduced can significantly improve the hydrogen absorption and desorption reaction rates of hydrides [97]. The effects of adding different types and contents of catalysts on the reaction process of metal hydrides are shown in Table 11.

Table 11. Summary of catalysts for enhancing MgH_2 reaction kinetics.

Method	Result	Reference
Nitrogen-doped carbon-coated Ni/MnO (Ni/MnO@NC) nanospheres	A 10 wt% addition reduces the initial dehydrogenation temperature of MgH_2 to 498.2 K and decreases the dehydrogenation activation energy to 97.68 kJ/mol ; at 300°C , $6.36\text{ wt\% H}_2$ is released within 5 min, $5.77\text{ wt\% H}_2$ is absorbed within 1 min at 150°C , and $2.92\text{ wt\% H}_2$ is absorbed within 30 min at 50°C ; after 30 cycles, the hydrogen storage capacity remains at 97.3% .	[98]
CaTiO_3	A 15 wt% addition reduces the initial desorption temperature to 188°C ; $4.6\text{ wt\% H}_2$ is absorbed at 150°C (only $0.7\text{ wt\%}$ for the pure sample), and $5.7\text{ wt\% H}_2$ is absorbed within 2.5 min at 300°C ; the activation energy is decreased to 77.3 kJ/mol (136.6 kJ/mol for the pure sample).	[99]
High-Entropy Alloy TiVCrFeNi	An addition of 5 wt% reduces the dehydrogenation activation energy to 71.49 kJ/mol (a decrease of 42.4%); the initial desorption temperature is reduced to 182°C (a decrease of 80°C).	[100]
Nano NiFe/CoFe	An addition of 5 wt% enables the absorption of $5.96\text{ wt\% H}_2$ within 60 s at 350°C , and the desorption of $5.95\text{ wt\% H}_2$ within 10 min, with an average desorption rate 15 times that of the pure sample; an addition of 10 wt% can absorb $4.88\text{ wt\% H}_2$ at 150°C ; the desorption peak temperature is reduced to 281.01°C , which is 162.60°C lower than that of the pure sample.	[101]
Three-Dimensional Honeycomb Fe/N-MXene	The initial dehydrogenation temperature of MgH_2 is reduced to 198°C ; the dehydrogenation and hydrogen absorption activation energies are decreased by 68.1 kJ/mol and 50.9 kJ/mol , respectively; $5.14\text{ wt\% H}_2$ can be absorbed within 20 min at 100°C .	[102]
Nickel-based metal–organic framework coated with carbon (NiMOF@C)	The 5 wt% NiMOF@C- MgH_2 sample achieved a maximum hydrogen uptake of $6.47\text{ wt\%}$ and absorbed $6.03\text{ wt\%}$ of H_2 within 10 min. After 20 cycles, it retained 97.8% of its absorption capacity and 97.4% of its desorption capacity. The desorption activation energy was significantly reduced to 91.03 kJ/mol , compared with 181.4 kJ/mol for pure MgH_2 .	[103]

Doping modification and composite synthesis can alleviate the poor cyclic stability of MgH_2 arising from its low melting point. Among these strategies, Mg-Nb nanocomposites

exhibit the highest capacity retention rate, and the detailed results of other methods are listed in Table 12.

Table 12. Enhancement of the cyclic stability of MgH_2 .

Method	Result	Reference
Doping $\text{Co}_2\text{V}_2\text{O}_7$	After 15 cycles, the hydrogen capacity of the 10 wt% composite material remains 6.1 wt%, with a capacity retention rate of 92.4%.	[104]
Preparation of Mg-Nb Nanocomposites	When the ratio of Mg:Nb is 10:1, the capacity retention rate reaches as high as 99.98% after 100 cycles.	[105]
Synthesis of $\text{TiO}_2\text{-ZnTiO}_3$ Composite Materials Containing carbon nanotubes (CNTs)	After 20 cycles, the capacity retention rate of $\text{MgH}_2 + 10 \text{ wt}\% \text{TiO}_2\text{-ZnTiO}_3\text{@CNTs}$ is 97%, which is higher than 92% of the system without CNTs.	[106]
Ni-MoS ₂ modified MgH_2	The initial dehydrogenation temperature is reduced to 198 °C; the dehydrogenation activation energy is decreased from 151 kJ/mol to 85 kJ/mol; 6.1 wt% H_2 is released within 10 min at 300 °C; the dehydrogenation capacity remains 6.1 wt% even after the 50th cycle.	[107]

The thermal conductivity of MgH_2 can be improved by adding high-thermal-conductivity materials. Chaise et al. [108] compounded and compacted MgH_2 with expanded natural graphite (ENG). After adding ENG, the thermal conductivity increases linearly with the content of ENG. At 10 wt% ENG content, the radial thermal conductivity is 10 times higher than that of the compacted disk without ENG, and 30 times higher than that of the uncompacted powder. Popilevsky et al. [109] prepared Mg-2 wt% multi-walled carbon nanotube composites, whose thermal conductivity is 20% higher than that of pure magnesium; during the synthesis process, the carbon nanotubes are transformed into 20–30 nm nanoparticle chains, and the hydride phase preferentially grows along them. The residual magnesium phase forms an interpenetrating network, which is conducive to long-range heat transport.

3. Advances in Solid–Gas Reaction-Based TCES with Different Materials and Reactors

The solid–gas reactor-based TCES systems are mainly divided into three types: fixed bed, moving bed and fluidized bed [15]. We compared the three types of reactors from multiple aspects, as presented in Table 13 [110–112].

Table 13. Multi-aspect comparison of the three solid–gas TCES reactors.

Reaction Types	Fixed Bed	Moving Bed	Fluidized Bed
Particle size (mm)	0~30	0.5~5	0.5~6
Operating temperature (K)	600~2100	~800~	1000~1600
Heat transfer rate	Low	Medium to high	High
Advantages	Simple structure, low cost, little particle wear, and easy operation.	The heat and mass transfer efficiency is superior to that of the fixed bed; the particle residence time is controllable.	High heat and mass transfer; continuous operation.
Disadvantages	Insufficient heat and mass transfer; high pressure drop; risks of volume expansion and contraction.	High pressure drop under high speed of gas or solid; particle wear exists.	Severe particle wear and entrainment; high energy consumption; severe equipment wear.
Applicable scenarios	Slow reaction speed, small scale, expensive or easily worn materials.	Large-scale and continuous energy conversion is required.	Fast reaction speed and high requirements for heat and mass transfer.

3.1. TCES with Hydroxide in Different Reactors

3.1.1. TCES with Hydroxide in Fixed Bed Reactor

Schaube et al. [113] found through comparison that indirect fixed bed reactor TCES is limited by the low thermal conductivity of materials, so direct fixed bed reactor TCES

is more advantageous. Yan and Zhao et al. [114] investigated direct fixed bed reactor (Figure 3a) TCES and demonstrated that a higher outlet dehydration temperature (T_{out}) results in a faster heat storage rate. When T_{out} is 510 °C and 540 °C, the heat storage efficiencies reach 47% and 65% within 300 min, respectively. Increasing steam pressure significantly intensifies the exothermic reaction, and the reaction extents are 31.7%, 60.9% and 72.8% at 0.18 MPa, 0.24 MPa and 0.32 MPa, respectively. Schmidt et al. [115] developed a 20 kg scale indirect fixed bed reactor (Figure 3b). Under dehydration at 450 °C and rehydration at 550 °C, the reversible conversion efficiency remains at 77% after 10 cycles, with a peak power of 7.5 kWth. Jashari et al. [116] conducted cyclic tests on $\text{Ca}(\text{OH})_2$ powder samples and granule samples in a fixed bed reactor. The results showed that the granule samples with a diameter of 2–4 mm exhibited good durability over 15 cycles, with their conversion rate remaining largely stable. In contrast, the powder samples showed significantly lower conversion rates under the same number of cycles, along with more pronounced fluctuations, which were mainly attributed to agglomeration effects. Ranjha and Oztekin et al. [117] conducted simulations on a three-dimensional rectangular fixed bed TCES system with fine $\text{Ca}(\text{OH})_2/\text{CaO}$ particles. The results show that low porosity improves energy storage density but reduces reaction rate; owing to low thermal conductivity, the bed width should be controlled to shorten heat transfer paths, and a comprehensive trade-off between the two factors is required. To enhance the heat transfer performance of fixed bed reactors, structures such as Y-shaped fins, annular channels, tube bundles and porous baffles can be embedded in reactors, and the research results of specific optimized structures are summarized in Table 14.

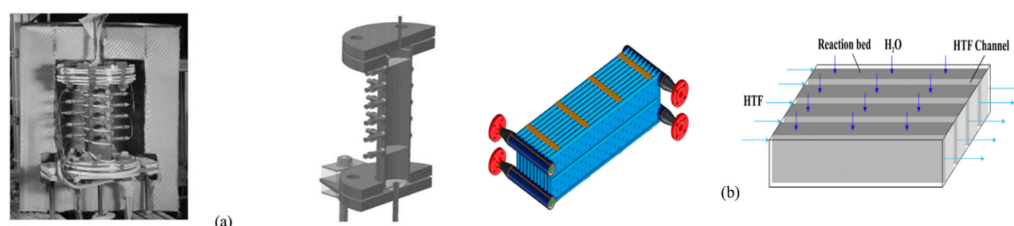


Figure 3. Fixed bed reactor: (a) direct; (b) indirect [113]. Reproduced with permission from F. Schaubé, A. Wörner, R. Tamme, *Journal of Solar Energy Engineering*; published by ASME, 2011 [113].

Table 14. Summary of research on optimization of fixed bed TCES reaction devices. Reproduced with permission from [118–121]. For detailed copyright information, please refer to Appendix A.

Structure	Results	Illustration	Reference
Y-shaped fins	When L_2 is 18.75 mm and α is 150°, the heat storage time of the Y-shaped fin reactor is shortened by 45.59% compared with that of the reactor without fins, which is better than 43.14% of the rectangular fins.		[118]
Integrated annular heat exchange channel	Compared with the double-pipe reactor, the average heat storage power is increased by 2.24 times, the temperature non-uniformity coefficient is reduced by about 80%, and the heat storage density only decreases by 0.7%; under the optimal operating conditions, the average heat storage power can reach 555.78 W, and the heat storage density is 0.813 GJ/m ³ .		[119]

Table 14. Cont.

Structure	Results	Illustration	Reference
Embed heating tube bundles	The optimal porosity is about 0.65, and the optimal heating tube radius is about 14 mm; the smaller the reactor height, the larger the reactor radius and heating tube radius, the higher the energy storage rate; when the height is 300 mm, the radius is 162.46 mm, and the heating tube radius is 30.92 mm, the maximum energy storage rate reaches 1.04 kW.		[120]
Porous baffles	The pressure drop is reduced by 64%, the heat storage time is shortened by 29.14%, the heat release time is reduced by 35.45%, and the outlet can maintain a long-term high-temperature output; the inlet flow rate of the direct heat transfer fluid has the greatest impact on the heat storage/release process, while the indirect flow rate has the least impact; the thermal conductivity and permeability of the porous baffle have a relatively small impact, and the air distribution chamber has a significant impact.		[121]

3.1.2. TCES with Hydroxide in Moving Bed Reactor

Moving bed reactors have the advantages of low pressure drop and high heat and mass transfer efficiency. Schmidt et al. [122] designed a 10 kW tube bundle counter-current moving bed reactor to achieve efficient heat transfer of $\text{Ca}(\text{OH})_2$, as shown in Figure 4. Cosquillo Mejia et al. [123] adopted a moving bed reaction system to test ceramic-encapsulated and Al_2O_3 -coated $\text{Ca}(\text{OH})_2$ particles, and verified the stable operation of encapsulated particles in large-scale reactors, as shown in Figure 5. Subsequently, Cosquillo Mejia et al. [124] developed a directly heated moving bed reactor. The results show that both $\text{Ca}(\text{OH})_2$ and Al_2O_3 nano-coated particles achieve complete conversion without thermal performance degradation. Direct gas–solid contact can effectively inhibit particle agglomeration. In particular, the coated particles form a reinforced structure due to new phases generated on the surface, which significantly improves mechanical stability while maintaining energy storage density.

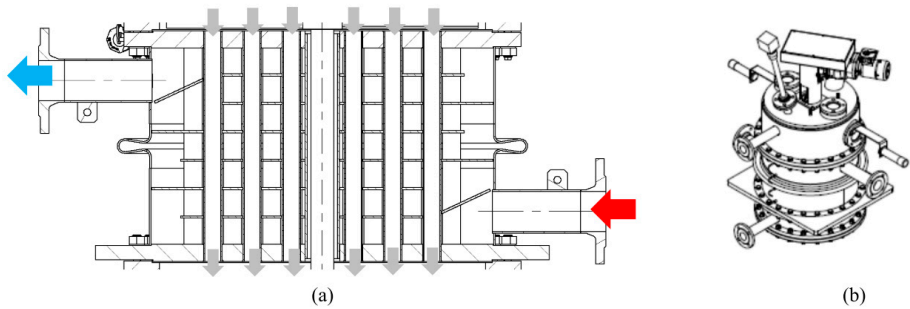


Figure 4. (a) Heat exchanger for moving particles and air; (b) moving bed reactor [122]. Reproduced with permission from M. Schmidt, M. Gollsch, F. Giger et al., Cape Town, South Africa; published by AIP Publishing, 2016 [122].

3.1.3. TCES with Hydroxide in Fluidized Bed Reactor

Fluidized bed reactors have shown great potential in the research of $\text{CaO}/\text{Ca}(\text{OH})_2$ TCES. Pardo et al. [125] found that mixing 30% $\text{Ca}(\text{OH})_2$ powder with 70% Al_2O_3 -B achieves no by-product formation after 50 cycles, with an average energy storage density of 60 kW·h/m³. After separation, the energy storage density of recovered $\text{Ca}(\text{OH})_2$ material reaches 156 kW·h/m³. Criado et al. [126] pointed out that the hydration reaction

is controlled by the slow kinetics of CaO, and considerable emulsion-bubble mass transfer resistance exists during the dehydration process. Bian et al. [127] demonstrated that a fluidized bed reactor can significantly suppress CaO agglomeration, with an optimal fluidization number of 4. Increasing steam concentration is beneficial to heat release but deteriorates fluidization performance. The carrier gas type has a remarkable influence: the hydration conversion rate exceeds 95% after 20 cycles under N₂ atmosphere, while the conversion rate drops sharply in air due to CaCO₃ formation caused by CO₂. With continuous cycling, CaO particles tend to become porous and grow in particle size. In addition, Yan et al. [128] investigated MgO/Mg(OH)₂ TCES and reported that reducing inner diameter or increasing material loading raises bed temperature during heat storage. During heat release, higher material loading promotes bed temperature rise, whereas larger reactor inner diameter or higher inlet gas velocity tends to reduce bed temperature. The slow hydration kinetics of MgO remains the primary factor restricting heat release performance. An optimal curve that makes the actual reaction temperature approach the boundary surface temperature can reduce sensible heat loss and improve thermochemical conversion efficiency.

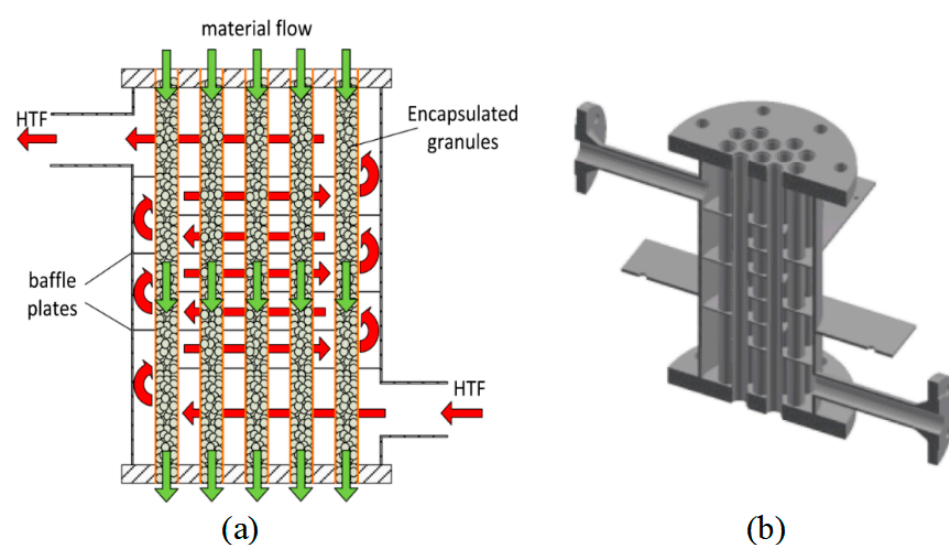


Figure 5. (a): Schematic diagram of the heat transfer fluid flow (red arrows) on the shell side and the storage material inside the reactor tube (green arrows); (b) three-dimensional image of the tube bundle reactor [123]. Reproduced with permission from A. Cosquillo Mejia, S. Afflerbach, M. Linder et al.; *Applied Thermal Engineering*; published by ELSEVIER, 2020 [123].

3.2. TCES with Carbonate in Different Reactors

3.2.1. TCES with Carbonate in Fixed Bed Reactor

Researchers have carried out extensive research on the heat storage performance of CaCO₃/CaO in fixed bed reactors. Tian et al. [129] experimentally found that, after calcination in nitrogen at 850 °C for 8 h, the decomposition conversion rate of CaCO₃ reaches 63.8%; after carbonation in carbon dioxide at 750 °C for 4 h, the conversion rate is 67.2%. High calcination temperature and a porosity of 0.6–0.7 are the key factors to improve heat storage efficiency and energy release, while carbonation temperature and thermal conductivity have relatively weak effects. Khosa et al. [130] developed a high-temperature and high-pressure fixed bed reactor. The results show that the energy storage efficiency increases with rising temperature, reaching 0.85% at 750 °C and 43% at 950 °C, respectively. Doping with SiO₂ and ZnO can increase interparticle pores, promote CO₂ release and enhance heat transfer. In the carbonation reaction, the reaction rate and reaction extent (19%) under a pure 100% CO₂ atmosphere are significantly superior to those under a 75%

CO₂ atmosphere (3.2%). To address the sintering issue during CaCO₃ decomposition, Yue et al. [131] investigated the CaCO₃/CaO reaction system in a vacuum fixed bed reactor. It is found that, when the relative pressure difference $(P_{eq}-P^{*}CO_2)/P_{eq} > 0.98$, the inhibitory effect of CO₂ partial pressure on decomposition can be eliminated. In addition, Zhang et al. [132] designed topology-optimized fin structures based on K₂CO₃, as shown in Figure 6. The results indicate that its heat transfer performance is superior to that of finless, circular fin and rectangular fin reactors, which can accelerate the reaction rate and shorten the reaction time. Increasing the number of fins improves heat transfer capacity at the initial stage, but excessive fins cause excessive cooling and reduce the reaction rate instead. Water vapor partial pressure has little impact on reaction time and conversion rate, and the topology-optimized fins exhibit excellent heat transfer performance under various partial pressures.

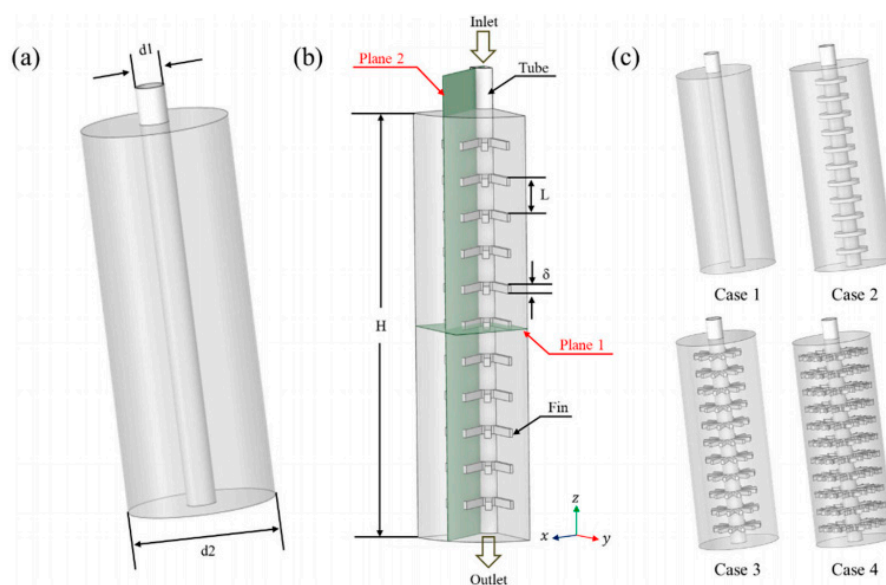


Figure 6. (a) Schematic diagram of the fixed bed reactor structure; (b) quarter cross-sectional view of the reactor; (c) schematic diagrams of different fin structures [132]. Reproduced with permission from Y. Zhang, D. Liu, J. Ma et al., *Journal of Energy Storage*; published by ELSEVIER, 2025 [132].

3.2.2. TCES with Carbonate in Fluidized Bed Reactor

Esence et al. [133] designed a shallow cross-flow fluidized bed reactor with four serially connected chambers, as shown in Figure 7. The study indicates that dolomite particles can only achieve partial decomposition, converting into MgO, CaCO₃, and CO₂, with a conversion rate of 100% but a thermal efficiency of only 6%. Tregambi and Padula et al. [134] designed a batch fluidized bed experimental reactor based on the “autothermal” principle, as illustrated in Figure 8. This reactor integrates a fountain-type particle absorber and a double-tube heat exchanger, and using CaCO₃ calcination/carbonation as the model, the average energy storage density of the system reaches approximately 1.0 GJ/m³ after 12 cycles. Tregambi and Di Lauro et al. [135] investigated the reaction performance of mixed bed materials (silica sand and lime) in a fluidized bed reactor, as shown in Figure 9. The results demonstrate that the average carbonation degree in the direct irradiation fluidized bed reactor decreases from 61% in the first cycle to 4% in the 20th cycle, with an average value of approximately 14% over 20 cycles. The main reason for performance degradation is that the mechanical interaction between silica sand and lime leads to a significant reduction in the total porosity and active porosity of the adsorbent. Li et al. [136] simulated the wear and breakage behavior of CaCO₃/CaO particles in a fluidized bed reactor using CFD. The results show that particle wear is concentrated in the upper-middle part of the bed, reaching

a peak (accounting for 28.68%) within 15–20 s, which increases radiant heat transfer by 10% and conductive heat transfer by nearly double. Breakage mainly occurs in the core area; wear reduces the bed porosity and deteriorates fluidization stability.

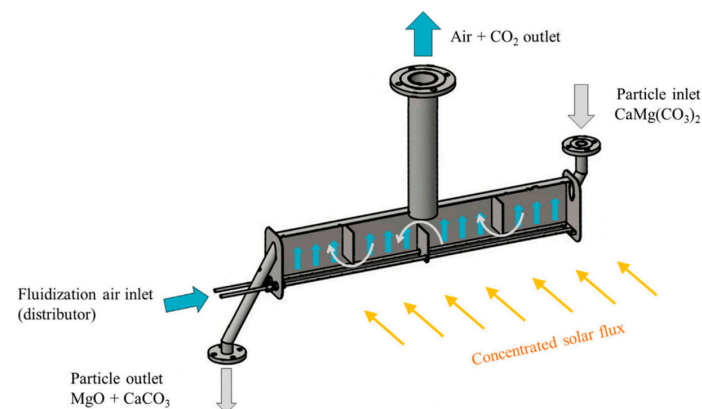


Figure 7. Cross-sectional view of the reactor–receiver and schematic diagram of the principle of particles and gas flow [133]. Reproduced with permission from Y. Zhang, D. Liu, J. Ma et al., *Solar Energy*; published by ELSEVIER, 2020 [133].

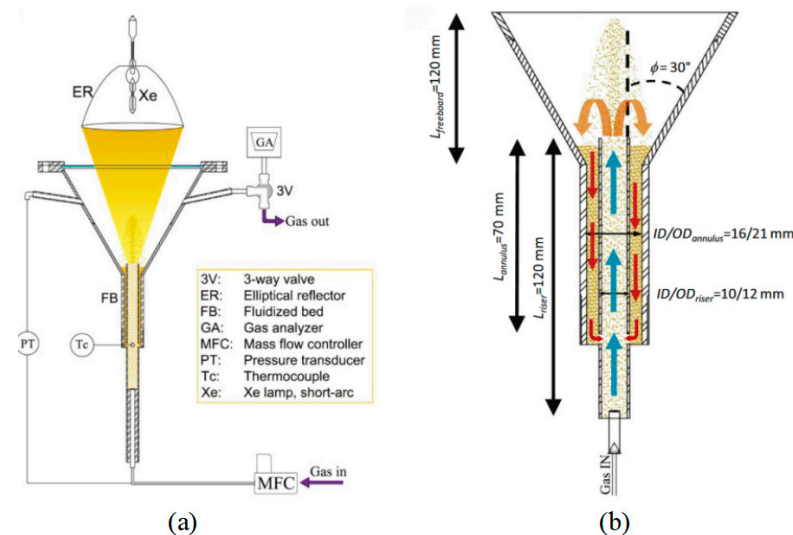


Figure 8. (a) Schematic diagram of the experimental setup and auxiliary equipment; (b) close-up view of the local part of the fluidized bed reactor [134]. Reproduced with permission from C. Tregambi, S. Padula, M. Galbusieri et al., *Solar Energy*; published by ELSEVIER, 2020 [134].

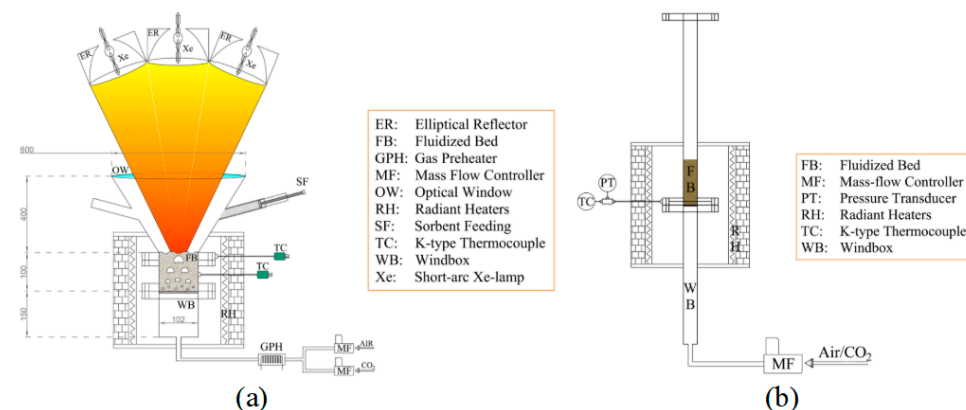


Figure 9. (a) Direct irradiation fluidized bed reactor; (b) electrically heated fluidized bed reactor [135]. Reproduced with permission from C. Tregambi, F. Di Lauro, S. Pascual et al., *Chemical Engineering Journal*; published by ELSEVIER, 2023 [135].

3.2.3. TCES with Carbonate in Moving Bed Reactor

Xu et al. [137] developed an external-heat moving bed reactor with a built-in central gas flow channel, as shown in Figure 10, which is used for the calcination of small-particle-size carbonates (such as 0–6 mm magnesite) to co-produce lightly calcined oxides and high-concentration CO_2 . This design effectively solves the problem of easy blockage caused by vertical air flow in the fine-particle moving bed layer by guiding the generated gas to flow transversely into the channel. The results show that, when magnesite is continuously processed at a rate of $8.3 \text{ kg}\cdot\text{h}^{-1}$, the decomposition rate reaches 97.5–98.0%, the purity of the obtained CO_2 is about 99%, and the proportion of fine powder with a particle size of 0–1 mm is 54–59%. The structure of this reactor has universality, providing theoretical guidance for the optimization of the thermal decomposition co-production process of various carbonates in moving beds in the future.

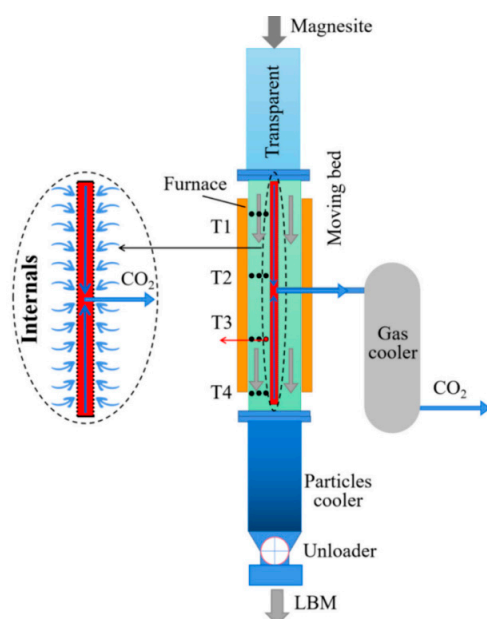


Figure 10. Schematic diagram of a pilot-scale external-heated moving bed equipped with a central gas flow channel [137]. Reproduced with permission from Z. Xu, X. Huang, Y. Yan et al., *Powder Technology*; published by ELSEVIER, 2024 [137].

3.3. TCES with Metal Oxide in Different Reactors

3.3.1. TCES with Metal Oxide in Fixed Bed Reactor

Researchers have systematically investigated the TCES performance of metal oxides in fixed bed reactors. Wang et al. [138] experimentally and numerically studied the reduction process of iron–manganese oxides. The results show that the temperature distribution in the reaction zone is uniform. At 927°C , the apparent absorptivity of the cavity is 0.8, the reaction tube absorbs approximately 40% of the incident radiative power, and the peak instantaneous solar-to-chemical energy efficiency reaches 9.3%. The corresponding instantaneous efficiency for converting radiant energy into particle sensible heat and chemical energy is 25.6%. In addition, Wokon et al. [139] investigated the heat storage and release performance of manganese–iron oxides using air as the heat transfer fluid and oxygen as the carrier gas, as shown in Figure 11a. The results indicate that variations in oxygen concentration affect the heat capacity flow rate of the heat transfer fluid, and the heating and cooling rates exert a significant influence on the reaction process. Redox reactions can stably regulate the bed temperature. No performance degradation is observed for the material after 17 cycles, whereas sintering induces microstructural changes and reduced mechanical strength of particles.

Deutsch et al. [140] compared the performance of CuO/Cu₂O in a simultaneous thermal analyzer (STA) and a fixed bed reactor. The results show that the oxidation rate decreases with increasing temperature in the STA, whereas this phenomenon does not occur in the fixed bed reactor. STA measurements reveal excellent cyclic stability of the system over 20 cycles. Nevertheless, severe sintering occurs in the fixed bed reactor, leading to a substantial reduction in reaction extent. To address the structural stability issues induced by sintering, Ma et al. [141] designed a high-thermal-conductivity porous fixed bed reactor, as shown in Figure 11b. At an inlet temperature of 1000 °C, the peak heat storage power is increased by 33.59 W and the reaction time is shortened by 90%. The optimal thermal efficiency is achieved in the temperature range of 640–960 °C. Pressure gradient can enhance heat transfer but requires structural reinforcement. High porosity (0.8–0.9) facilitates oxygen release, with a peak thermal power of 61.95 W, which is suitable for solar thermal energy storage. Low porosity (0.5–0.7) improves thermal conduction but prolongs reaction time, making it applicable for industrial waste heat recovery.

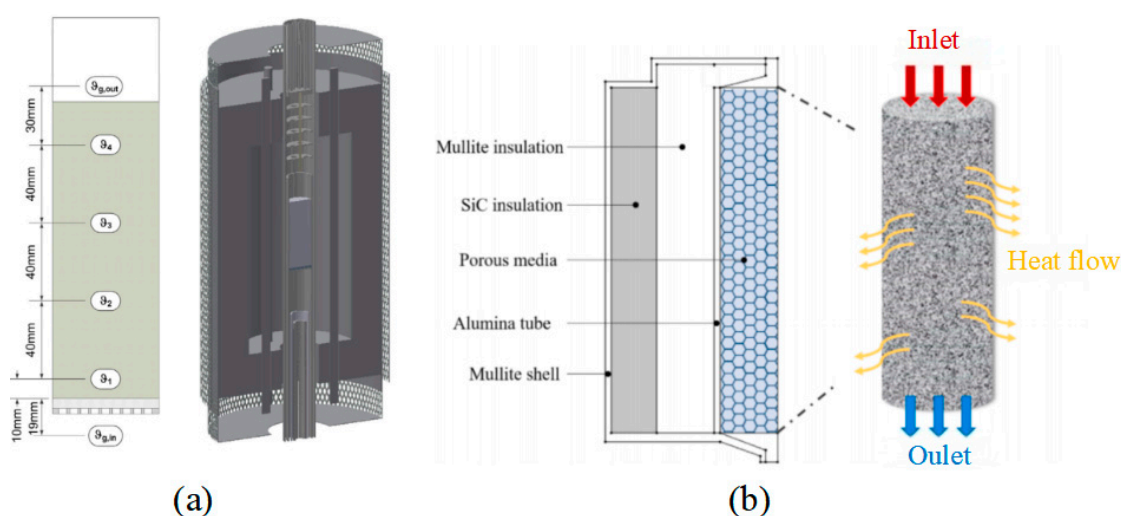


Figure 11. (a) Reactor geometry [139]; (b) schematic diagram of the reactor structure [141]. Reproduced with permission from M. Wokon, A. Kohzer, M. Linder, *Solar Energy*; published by ELSEVIER, 2017 [139]. Reproduced with permission from D. Ma, S. Zhang, B. Geng et al., *Applied Thermal Engineering*; published by ELSEVIER, 2025 [141].

3.3.2. TCES with Metal Oxide in Moving Bed Reactor

Preisner and Bürger et al. [142] performed numerical simulations on a counter-current moving bed reactor of manganese–iron oxides to investigate the coupled utilization of thermochemical energy and sensible heat. The results show that, when the gas flow rate is below the critical value, an approximately isothermal distribution forms along the bed height. When the material is cooled from 1050 °C to 300 °C during oxidation, the maximum energy density reaches 933 kJ/kg. Reaction kinetics is the key factor affecting energy density and thermal power, and the two exhibit opposite variation trends. Complete conversion can be achieved at low particle flow rates (0.001 kg/s), whereas excessively high particle flow rates result in strong cooling effects and a sharp drop in conversion rate. Preisner and Linder [143] developed a kilowatt-scale counter-current moving bed heat exchanger, with thermal insulation designs adopted for both the reduction section and oxidation section. Experimental results indicate that a thermal power of 2 kW can be transferred to the gas flow under steady state. The particle reduction ratio and oxidation ratio reach 77.1% and 80.2%, respectively, and indirect heat exchange can further improve the oxidation ratio. Good material stability is verified by 60 thermogravimetric cycles. Nevertheless, particle

fluidity deteriorates at high temperatures. Its mechanism needs further investigation to realize continuous operation.

Schrader et al. [144] integrated the $\text{Co}_3\text{O}_4/\text{CoO}$ redox cycle into an air Brayton cycle, and designed a horizontal vacuum solar reactor equipped with inclined ramps and quartz windows, which realizes direct irradiation of particle materials. Parametric studies show that the optimal operating conditions are a cavity depth of 125 mm, a particle inlet temperature of 700 K, and a concentration ratio of 3900. Under these conditions, the average outlet conversion rate is 0.91, the average outlet temperature is 1112 °C and the absorption efficiency is 0.76. Huang et al. [145] designed a counter-current moving bed reactor with high reducibility and heat recovery performance for the thermochemical reduction of magnesium–manganese oxides. A uniform flow model and a plug flow model were established, achieving a chemical energy storage efficiency of approximately 95% and an energy storage efficiency of about 30%, which verifies the feasibility of the design.

3.4. TCES with Metal Hydride in Fixed Bed Reactor

3.4.1. TCES with Metal Hydride in Tubular Fixed Bed Reactors

1. Tubular fixed bed reactors with different shapes

In metal hydride TCES systems, fixed bed reactors dominate the market share (>90%) owing to their simple structure, excellent airtightness, and easy integration with heat exchange systems. Fixed bed metal hydride reactors are classified into three categories according to geometric configurations: tubular, disk-type and tank-type (chamber-type), as illustrated in Figure 12 [146]. Most tubular reactors adopt circular tubes, while elliptical tubes are more advantageous owing to their compact structure and low hydraulic loss [147]. In addition, single-tube structures are commonly used in small-scale studies, whereas bundle structures arranged in parallel, square or hexagonal patterns are adopted in large-scale studies [148]. Disk-type reactors employ flat bed layers (length-to-diameter ratio $\ll 1$), which feature large heat transfer area and fast reaction kinetics in thin beds. Nevertheless, they suffer from limited single-disk capacity and difficult capacity expansion. By contrast, the annular-disk design (Figure 12b) realizes adjustable modular capacity expansion and rapid reaction through radial mass transfer channels and simultaneous heat exchange on the outer surface [149]. Tank-type reactors consist of large cylindrical or cubic chambers with the largest hydrogen storage capacity. Heat exchange is achieved by embedded components, including spiral coils [150], heat pipes [151], conventional tube bundles [152] and microchannel technology [153]. Among these types, tubular reactors have become the mainstream choice due to excellent airtightness, high pressure resistance, favorable heat and mass transfer performance, and modular unit design for easy capacity expansion [146]. Their structural optimization will be emphatically discussed in the following sections.

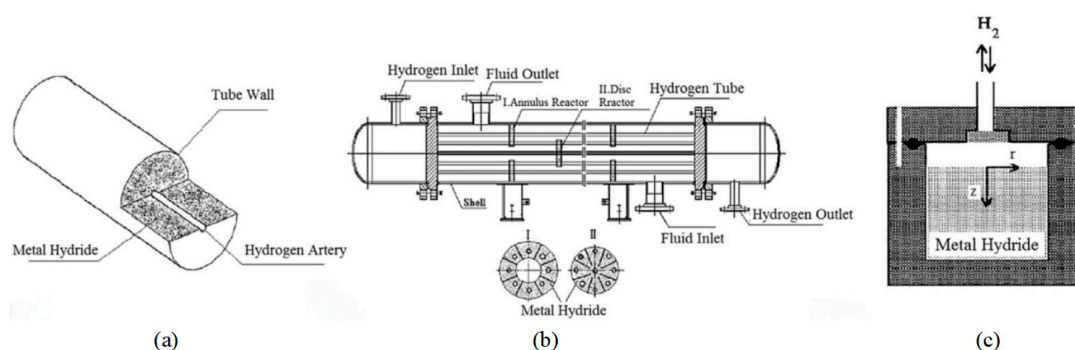


Figure 12. Schematic diagrams of reactors with different geometric configurations: (a) tubular reactor; (b) annular-disk reactor; (c) tank-type reactor [146]. Reproduced with permission from Shafiee, S., McCay, M.H., *International Journal of Hydrogen Energy*; published by ELSEVIER, 2016 [146].

The geometric shape of a reactor directly affects its internal surface area, pressure distribution, and hydrogen absorption/desorption rate. It is necessary to maximize the internal surface area to enhance heat dissipation [154]. Cylindrical reactors (Figure 13a) achieve uniform distribution of pressure, stress, heat transfer and mass transfer due to symmetry. They are suitable for high-pressure environments and can be easily matched with heat exchangers [155]; spherical reactors (Figure 13b) have the smallest surface-area-to-volume ratio and high design difficulty, yet they provide the largest available space for the bed layer [156]; prismatic reactors (Figure 13c) feature high space utilization but are unsuitable for high-pressure systems [157]. Nam et al. [157] found that prismatic reactors with a rectangular base exhibit faster cooling and hydrogen absorption rates owing to their high external-surface-area-to-volume ratio. Mellouli et al. [156] compared metal hydride hydrogen storage systems with phase change materials. A spherical reactor requires 625 s to reach 80% hydrogen storage capacity, while a cylindrical reactor takes 800 s. Nevertheless, cylindrical reactors are superior in uniform stress distribution, heat and mass transfer regulation, and heat exchanger compatibility [155], remaining the most widely adopted type.

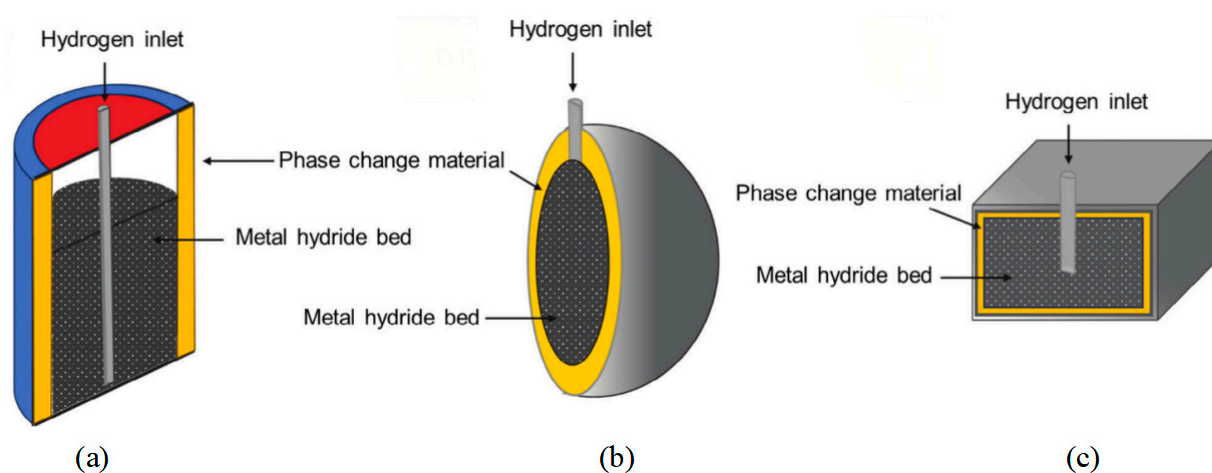


Figure 13. Configurations of metal hydride reactors: (a) cylindrical; (b) spherical; (c) prismatic [154]. Reproduced with permission from W. Liu, J.A. Tupe, K. Aguey-Zinsou, *Particle & Particle Systems Characterization*; published by WILEY, 2025 [154].

2. Tubular fixed bed reactors with different configurations

To further improve the heat transfer performance of metal hydride tubular reactor TCES systems, adding fins is one of the most widely adopted methods. Fins are classified into longitudinal fins and transverse fins, as shown in Figure 14. Meanwhile, fins can also be divided into internal fins and external fins. Internal fins are used to enhance heat transfer within the reaction bed, whereas external fins are generally adopted to strengthen heat exchange between the reactor and the external environment [158]. The heat transfer performance of the reaction bed is affected by the structure, quantity and dimensions of different fins, among which the fin number has the most significant influence. An increase in fin number can remarkably accelerate the hydrogen absorption rate. Detailed structures and research results of internal and external fins are presented in Table 15 and Table 16, respectively.

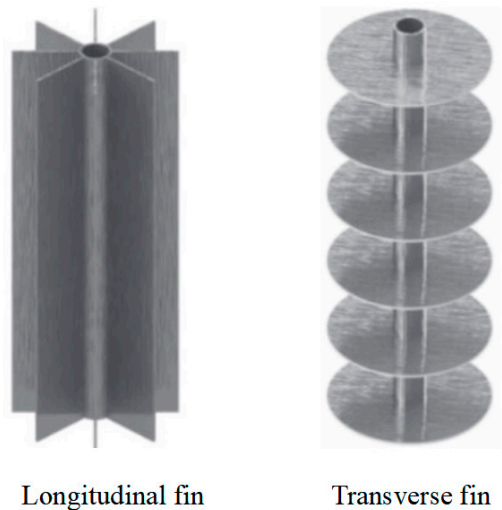
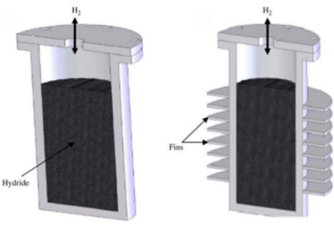
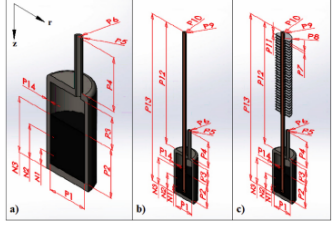
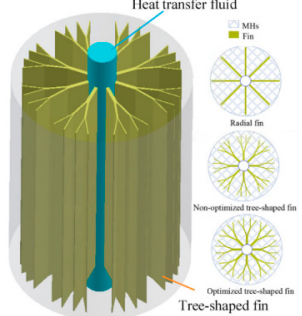
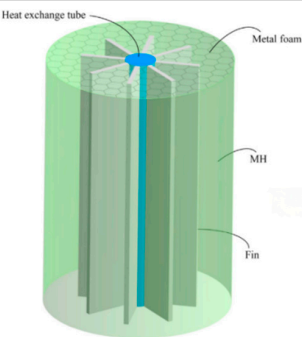
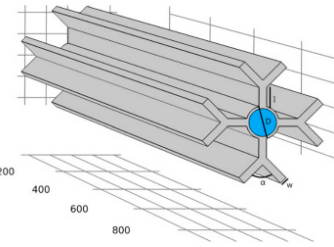


Figure 14. Fin types [158]. Reproduced with permission from J. W. Su, X. Y. Tang, X. S. Bai et al., *International Journal of Hydrogen Energy*; published by ELSEVIER, 2025 [158].

Table 15. Optimization research on internal fins of metal hydride tubular reactors. Reproduced with permission from [159–163]. For detailed copyright information, please refer to Appendix A.

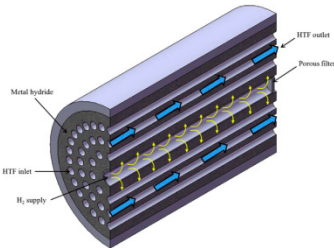
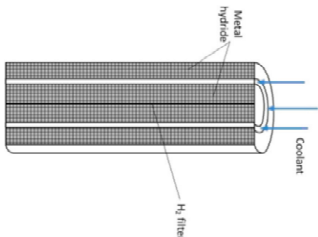
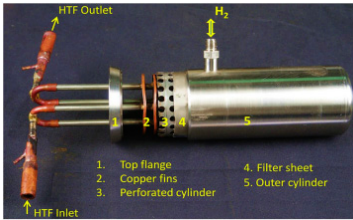
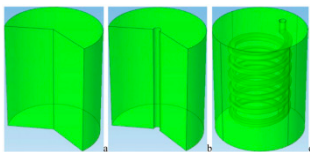
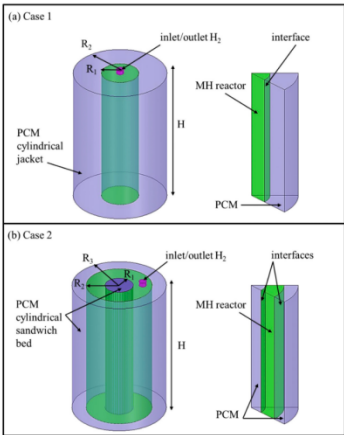
Structure	Results	Illustration	Reference
Internal fins	An increase in the radius, thickness and number of transverse fins can all reduce thermal resistance, among which the fin number exerts the most significant effect. The average bed temperature decreases with rising fin radius.		[159]
	When the number of fins increases from 4 to 13, the time required to absorb 12 g of hydrogen is shortened from 1180 s to 610 s. As the heat exchange tube diameter increases from 3.4 mm to 5.4 mm, the hydrogen charging time is reduced from 725 s to 515 s.		[160]
	When six longitudinal fins with a thickness of 0.1 cm are in full contact with the inner wall, the hydrogen charging rate is improved by 41% within 720 s.		[161]
Internal fins	The structure with 19 fins and 6 heat exchange tubes exhibits the optimal performance, requiring only 290 s and 375 s to reach 80% and 90% saturation, respectively.		[162]
	Corrugated fins (5 mm height, 2 mm length, 13 pieces) reduce the hydrogen absorption time to 80% saturation by 32% compared with conventional circular fins.		[163]

Table 16. Optimization research on external fins of metal hydride tubular reactors. Reproduced with permission from [164–168]. For detailed copyright information, please refer to Appendix A.

Structure	Results	Illustration	Reference
Independent addition of external fins	The effect of independently adding external fins is limited, with the hydrogen storage time shortened by only 10%.		[164]
Heat pipe reactor with external fins	The finned heat pipe reactor can absorb 1.8 g of hydrogen within 500 s, which is superior to the ordinary heat pipe (1000 s) and the reactor without a heat pipe (1500 s); the hydrogen charging time is reduced by 75% and 60%, respectively.		[165]
Tree-shaped fins	The time to reach 90% hydrogen storage is 1249 s, which is 7% shorter than that of the unoptimized tree-shaped fins and 20.7% shorter than that of the radial fins.		[166]
Fin-metal foam composite structure	The hydrogen storage time is 6.9% shorter than that of the metal foam reactor and 38% shorter than that of the pure fin reactor.		[167]
Bifurcated longitudinal fin cooling tube	The number of cooling tubes (53.41%), fin length (30.90%), number of fins (10.87%) and cooling tube diameter (3.05%) have significant effects, while other factors have no significant impact.		[168]

In metal hydride tubular reactors, the heat transfer performance can also be improved by embedding various heat exchange structures inside the reactor, such as straight cooling tubes, annular tubes, U-shaped tubes, spiral tubes and phase change material interlayers. Detailed structures and research results of different heat exchangers are presented in Table 17.

Table 17. Summary of research on embedded heat exchangers in metal hydride tubular reactors. Reproduced with permission from [169–173]. For detailed copyright information, please refer to Appendix A.

Structure	Results	Illustration	Reference
Straight cooling tubes	The time for 60 straight cooling tubes to reach the maximum hydrogen storage capacity is 19 min.		[169]
Annular tube heat exchanger	The time to reach 99% hydrogen storage capacity is shortened by nearly 60%.		[170]
U-shaped cooling tube with perforated annular copper fins	Using 1 kg of LaNi ₅ alloy, a hydrogen storage capacity of 1.2 wt% is achieved within 490 s under certain conditions.		[171]
Comparative study	The reactors without heat exchangers, with straight-tube heat exchangers, and with spiral-tube heat exchangers take 1531 s, 1012 s, and 419 s respectively to reach 90% hydrogen storage capacity, and the efficiency of the spiral-tube type is significantly better.		[172]
Phase change material interlayer bed structure	Compared with the traditional wrapped type, the hydrogenation and dehydrogenation times are shortened by 81.5% and 73%, respectively, which significantly improves the heat transfer rate.		[173]

3.4.2. Optimization of Thermal Conductivity for TCES with Metal Hydride in Fixed Bed Reactors

1. Incorporating thermally conductive materials

To address the problems of high thermal resistance and limited reaction kinetics caused by the low thermal conductivity ($0.1\text{--}1\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) of the fixed bed in metal hydride tubu-

lar reactors, the incorporation of high thermal conductive composite materials is the main enhancement method [158]. Due to its porous structure and high porosity, metal foam has little impact on the mass hydrogen storage density of the bed [148]. Commonly used foam metals include aluminum, nickel, zinc, titanium, copper, etc. Among them, aluminum foam is the optimal choice due to its high thermal conductivity and low thermal mass [174], which can increase the thermal conductivity of the bed to $8\text{--}10\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [175]. Laurencelle and Goyette et al. [176] have shown that the addition of aluminum foam increases the effective thermal conductivity from $0.15\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $10\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Similarly, Mellouli et al. [177] found that aluminum foam can shorten the time to reach 90% hydrogen storage capacity by about 60%, but it is necessary to add concentric heat exchange tubes to give full play to its effect. However, metal foam also has shortcomings such as high contact thermal resistance, difficulty in powder densification, reduced hydrogen storage capacity when its proportion is too high, and high cost [175].

Expanded natural graphite (ENG) is easier to operate and has higher thermal conductivity, with an addition amount generally ranging from 0 to 30 wt% [178]. The thermal conductivity, porosity and permeability of the bed can be controlled by adjusting the size of ENG [179]. Shim et al. [180] studied MgH_2 added with ENG and found that hydrogen pressure, ENG flake size and content jointly affect the thermal conductivity, reaching $9.3\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 1 bar H_2 and 20 wt% ENG; the thermal conductivity increases continuously as the pressure rises to 20 bar, and then the growth rate slows down; the thermal conductivity reaches a peak when the ENG size increases to $200\text{ }\mu\text{m}$, and then decreases. Pohlmann et al. [181] adjusted the ENG content to make the radial thermal conductivity of hydrogen alloy particles reach up to $63\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The effective thermal conductivity of the ENG composite material is higher than that of aluminum foam, but the hydrogen adsorption rate is slightly lower; when the mass ratio of ENG is greater than 20% and the porosity is about 70%, its comprehensive performance can be better than that of the aluminum foam system [182].

2. Compressed metal hydride powder

There are pores in the metal hydride powder bed reactor, which will significantly weaken its actual thermal conductivity. If the powder is mechanically compacted, the porosity of the bed can be reduced and the bulk density can be increased, which not only improves the heat transfer effect but also increases the hydrogen storage capacity per unit volume [183]. At the same time, the compaction treatment can also improve the safety and stability of the powder when exposed to air or water environments. This technology has become a conventional method for the densification treatment of loose metal hydride powder bed reactors [184]. For example, in the study by Dehouche et al. [185], the thermal conductivity of compacted $\text{LaNi}_{4.8}\text{Sn}_{0.2}$, $\text{LaNi}_{4.9}\text{Sn}_{0.1}$ and $\text{MmNi}_{4.7}\text{Al}_{0.3}$ was compared with that before compaction, and the effective thermal conductivity increased from $0.1\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $1.7\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Humphries et al. [186] compacted MgH_2 powder under the conditions of argon atmosphere, 370 MPa pressure and room temperature, and its thermal conductivity could reach $2.08\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

4. Comprehensive Discussion and Conclusion

4.1. Comprehensive Discussion and Critical Comparison

The preceding sections have systematically reviewed the current state of research of four solid–gas reaction-based TCES material systems (hydroxides, carbonates, metal oxides, and metal hydrides) and three reactor types (fixed bed, moving bed, and fluidized bed). Each material and reactor configuration has its own merits and demerits. This section provides a cross-cutting comparison, discusses material–reactor matching principles, and summarizes key technical bottlenecks with corresponding mitigation strategies.

4.1.1. Discussion of Four Material Systems

Exergy efficiency is an important system-level assessment metric; however, the current comparative analysis is constrained to the material level to ensure direct comparability across different reaction pairs. Therefore, exergy efficiency is not adopted as a fundamental indicator for material evaluation in this review. Instead, this section provides a comprehensive comparison of the four material systems across multiple key dimensions, including gravimetric energy density, operating temperature, cycling stability, and reaction kinetics, as summarized in Table 18 [5,9].

Table 18. Comprehensive comparison of four solid–gas TCES material systems.

Criteria	Hydroxides (Ca(OH) ₂ /CaO)	Carbonates (CaCO ₃ /CaO)	Metal Oxides (Mn ₂ O ₃ /Mn ₃ O ₄)	Metal Hydrides (MgH ₂ /Mg)
Gravimetric energy density (kJ/kg)	~1352	~1657	~851	~2160
Reaction temperature (°C)	~515~	~885~	~1700	300–480~
Material cost (USD/MJ)	0.120	0.047	4.992	608.07
Cycling durability	Composite with Si-SiC ceramic foam to form a porous honeycomb structure: no agglomeration occurs after 15 cycles	Doping nano-CaO with Li ₂ SO ₄ : the conversion rate reaches 51% after 11 cycles (27.3% for pure nano-CaO)	Bismuth-type (Mn _{0.8} Fe _{0.2}) ₂ O ₃ honeycomb material: it retains 85% capacity after 100 cycles	Preparation of Mg-Nb nanocomposites: the capacity retention rate reaches as high as 99.98% after 100 cycles
Reaction kinetics	Moderate (hydration limited)	Moderate (CO ₂ diffusion limited)	Moderate (oxygen diffusion limited)	Slow (hydrogen absorption and desorption)
Safety/toxicity	Non-toxic, non-corrosive	Non-toxic, non-corrosive	Low toxicity (CuO, Co ₃ O ₄)	Flammable H ₂
Technical bottlenecks	Low thermal conductivity; uneven heat release; material sintering and agglomeration; poor cycling stability	Sintering; agglomeration; degrading cyclic stability after multiple cycles	Incomplete oxidation; sintering; melting; thermal hysteresis	Sluggish reaction kinetics; poor cyclic stability; low thermal conductivity
Technology Readiness Level (TRL)	4–7			

1. Among the four systems, hydroxides (Ca(OH)₂/CaO) offer the best trade-off between energy density, operating temperature (well-suited for concentrated solar power and industrial waste heat), cost, and safety. The issues of sintering, agglomeration, and slow hydration kinetics can be effectively mitigated by incorporating SiO₂ particles or metal salts.
2. Carbonates (CaCO₃/CaO) have higher energy density but require temperatures above 800 °C. Severe sintering after a few cycles remains a critical barrier unless doping stabilizers (MgO, Al₂O₃) or natural minerals (dolomite) are used. Their advantage lies in the ability to co-produce high-purity CO₂, which may add value in certain industrial symbiosis scenarios.
3. Metal oxides (especially Co₃O₄/CoO and CuO/Cu₂O) exhibit excellent reversibility and tunable redox kinetics via doping, but they suffer from high material cost (cobalt), thermal hysteresis, and sintering. Their potential is in ultra-high-temperature applications integrated with air Brayton cycles, but significant work on structural stability and reactor engineering is required before pilot-scale demonstration.
4. Metal hydrides (MgH₂) possess the highest gravimetric energy density, yet their commercial viability is hampered by slow kinetics, low thermal conductivity, and low melting point (650 °C). While catalyst incorporation (e.g., Ni/MnO@NC, CaTiO₃) and high-conductivity matrices (ENG) greatly improve performance, system complexity and hydrogen safety concerns place them at a lower TRL. They are best suited for distributed hydrogen storage and medium-temperature heat release rather than large-scale centralized solar thermal storage.

4.1.2. Discussion of Material–Reactor Matching Principles

1. Fixed bed reactors are simple and suitable for slow-reacting, expensive, or easily worn materials. However, they suffer from poor heat transfer, requiring internal fins, annular channels, or metal foam inserts. They are the dominant choice for metal hydride TCES due to excellent sealing and high pressure capability. For $\text{Ca}(\text{OH})_2/\text{CaO}$, direct fixed bed operation outperforms indirect designs by avoiding thermal resistance through walls.
2. Moving bed reactors offer continuous operation, controlled particle residence time, and better heat/mass transfer than fixed bed reactors. They are particularly attractive for large-scale carbonate decomposition and for hydroxide systems with encapsulated or coated particles to suppress agglomeration. The main challenge is maintaining particle flowability at high temperatures, which requires careful selection of particle size and shape.
3. Fluidized bed reactors provide excellent heat and mass transfer, preventing localized hot spots and effectively inhibiting CaO sintering in hydroxide systems. However, they suffer from particle entrainment, severe attrition (especially for carbonates), and higher energy consumption.

Based on the above analysis, among the three reactor types, the moving bed reactor is considered the most promising configuration for large-scale industrial deployment, as it uniquely combines continuous operation, controllable particle residence time, and excellent heat and mass transfer performance. The fixed bed reactor, owing to its superior sealing and high-pressure resistance, remains the preferred choice for metal hydride systems; but its inherent heat transfer limitations render it less suitable for large-scale continuous operation. The fluidized bed reactor, despite its outstanding heat and mass transfer characteristics, is severely constrained by particle attrition and entrainment issues. Therefore, for current industrial applications, the moving bed configuration represents the optimal choice, while fluidized beds should only be considered after effective anti-attrition measures have been thoroughly validated.

4.1.3. Discussion of Technical Bottlenecks and Solutions

Table 19 summarizes the dominant challenges for each material system and the corresponding solutions at the material and reactor levels, as identified in this review.

Table 19. Technical bottlenecks and solutions.

Bottleneck	Affected Systems	Material-Level Solution	Reactor-Level Solution
Low thermal conductivity	Hydroxides, carbonates, metal oxides, metal hydrides	Doping with EG, metal foam, carbon nanotubes; ENG composites	Fins, annular channels, porous baffles; direct contact operation
Sintering/agglomeration	Hydroxides, carbonates, metal oxides	Doping with inert oxides (SiO_2 , MgO , TiO_2); surface coating; hollow microsphere design	Fluidized bed (continuously breaks agglomerates); moving bed with encapsulation
Slow reaction kinetics	Hydroxides (hydration), carbonates (carbonation), metal hydrides	Doping with rare earth ions, $\text{Ni}/\text{MnO}@\text{NC}$, TiVCrFeNi , etc.; Morphology control (mesoporous structures)	Increasing gas pressure; reducing particle size
Poor cyclic stability	Hydroxides, carbonates, metal oxides, metal hydrides	Doping with MgO , Al_2O_3 , $\text{Co}_2\text{V}_2\text{O}_7$, etc.; nanocomposite formation	High-thermal-conductivity porous fixed bed reactor

4.2. Conclusions

The solid–gas reaction-based TCES system has shown great potential in improving the stability and efficiency of energy systems in medium-to-high-temperature scenarios. Currently, review articles on solid–gas thermochemical energy storage tend to focus either on the modification of single material systems or on the heat transfer characteristics of specific reactor types, lacking a research direction that systematically links material modification with reactor heat transfer enhancement. This paper systematically reviews the research progress of solid–gas reaction-based TCES in terms of energy storage materials and reactors, combs the existing problems and challenges in material stability and reactor design, and provides theoretical reference and technical guidance for the development and application of key technologies of solid–gas reaction-based TCES in the future.

1. In terms of TCES materials, among hydroxide systems, the $\text{Ca(OH)}_2/\text{CaO}$ reaction system is the most promising due to its high energy storage density and low cost. By doping high-thermal-conductivity materials and structural stabilizers, its thermal conductivity and cycle stability can be effectively improved; doping Li and rare earth ions can significantly reduce the energy barrier of the dehydration reaction. Among carbonate systems, the CaCO_3/CaO reaction system is the most widely used, but it is prone to sintering and deactivation during cycling. This problem can be effectively alleviated by strategies such as adding inert carriers, doping metal compounds, and using natural minerals (dolomite). Among metal oxides, redox pairs such as BaO_2/BaO , $\text{Co}_3\text{O}_4/\text{CoO}$, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$, $\text{CuO}/\text{Cu}_2\text{O}$, and $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ are the most promising; through element doping, morphology control, and surface coating, sintering can be inhibited, and reversibility and cycle life can be improved. Among metal hydrides, MgH_2 has attracted much attention due to its high energy storage density, but its main bottlenecks are slow reaction kinetics, poor thermal conductivity, and insufficient cycle stability; the introduction of catalysts and high-thermal-conductivity media can significantly improve its performance. Among them, the $\text{Ca(OH)}_2/\text{CaO}$ system exhibits the most outstanding overall performance in the medium-temperature range (300–600 °C), while CaCO_3/CaO (limited by sintering) and $\text{Co}_3\text{O}_4/\text{CoO}$ and $\text{CuO}/\text{Cu}_2\text{O}$ (constrained by high cost and thermal hysteresis) are more promising candidates for high-temperature applications (>800 °C).
2. In terms of TCES reactors, for hydroxide TCES reactors, the fixed bed reactor enhances heat transfer through structural optimization such as fins and annular channels; the moving bed reactor is suitable for continuous operation, and its particle encapsulation can inhibit agglomeration; the fluidized bed reactor can effectively prevent CaO sintering, but the slow hydration kinetics remains a limiting factor. For carbonate TCES, in the fixed bed reactor, calcination temperature and porosity are key parameters; vacuum operation and topological fins can improve heat transfer; the moving bed reactor can realize efficient decomposition of small-particle-size carbonates and co-production of high-purity CO_2 ; particle wear is the main cause of performance degradation in the fluidized bed reactor. For metal oxide TCES reactors, the high-thermal-conductivity porous structure of the fixed bed can shorten the reaction time; the moving bed reactor can realize the synergistic utilization of sensible heat and chemical energy, but the particle fluidity at high temperatures needs to be improved. The mainstream of metal hydride TCES adopts fixed bed tubular reactors; through mechanical compaction, the addition of metal foam or expanded graphite, the optimization of fin structure and the integration of high-efficiency heat exchangers, the thermal conductivity of the bed and the hydrogen storage/release rate can be significantly improved. For industrial applications, the moving bed reactor holds the greatest potential for promotion in large-scale thermal energy storage scenarios, owing to its combined advantages of

continuous operation and excellent heat and mass transfer performance. The fixed bed reactor, due to its superior sealing capability, remains the preferred choice for metal hydride systems. The fluidized bed reactor requires cautious consideration in practical applications because of particle attrition issues.

3. The TCES technology based on solid–gas reactions still needs continuous breakthroughs in aspects such as the development of high-performance composite materials, the innovation of reactor in heat exchange structures, system integration, and engineering demonstration. On the engineering implementation front, pilot-scale moving bed or fluidized bed systems based on $\text{Ca}(\text{OH})_2/\text{CaO}$ are recommended for concentrated solar power plants or industrial waste heat recovery. In addition, further efforts are required to optimize thermal management and validate sealing technologies for MgH_2 -based composites in fixed bed reactors, aiming to provide critical technical support for distributed energy systems and hydrogen-based thermal energy storage, ultimately facilitating the development of a clean, stable, and sustainable energy system. Beyond the aforementioned systems that already possess a certain level of engineering feasibility, there remain several material–reactor combinations that urgently require in-depth investigation due to unresolved critical bottlenecks, including: CaCO_3/CaO in fluidized beds, where material failure is induced by attrition; MgH_2/Mg in moving or fluidized beds, where the low melting point of Mg leads to loss of flowability; and $\text{Co}_3\text{O}_4/\text{CoO}$ in moving beds, where high temperatures cause particle adhesion and stickiness. Furthermore, the introduction of machine learning and data-driven approaches holds promise for enabling the screening of advanced composite materials and the optimization of reactor operating parameters, although the application of such methods in solid–gas thermochemical energy storage systems still awaits robust experimental validation. Future engineering efforts should also prioritize techno-economic feasibility, system safety, environmental impact, and integration with concentrated solar power or industrial waste heat systems to enable successful commercial deployment.

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Abbreviations

The following abbreviations are used in this manuscript:

TCES Thermochemical energy storage
ENG Expanded natural graphite

Appendix A

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