CHAPTER 12
THERMAL ENERGY STORAGE TECHNOLOGIES

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Abstract

Thermal storage technologies have the potential to provide large capacity, long-duration storage to enable high penetrations of intermittent renewable energy, flexible energy generation for conventional baseload sources, and seasonal energy needs. Thermal storage options include sensible, latent, and thermochemical technologies. Sensible thermal storage includes storing heat in liquids such as molten salts and in solids such as concrete blocks, rocks, or sand-like particles. Latent heat storage involves storing heat in a phase-change material that utilizes the large latent heat of phase change during melting of a solid to a liquid. Thermochemical storage converts heat into chemical bonds, which is reversible and beneficial for long-term storage applications. Current research in each of the thermal storage technologies is described, along with remaining challenges and future opportunities.

Key Terms

Thermal storage, sensible storage, latent storage, thermochemical storage, long-duration storage

1. Introduction

Increasing penetrations of intermittent renewable energy sources (e.g., photovoltaics [PV] and wind energy) have increased the need for energy storage technologies to accommodate daily periods of overgeneration and peak loads. These diurnal energy-storage requirements are categorized in this chapter as short-duration and span periods from seconds to hours with capacities ranging from kilowatts to gigawatts. Previous studies have suggested that the decreasing costs of batteries and associated technologies may enable battery systems to meet the short-duration needs of the grid with high penetrations of intermittent renewable energy systems [1, 2]. However, recent studies have shown that long-duration energy storage (days to months) will be needed to accommodate 100% renewable (or carbon-free) energy generation [3]. In addition, long-duration energy storage will be needed to increase the security and resilience of the electrical grid in the face of increasing natural disasters and intentional threats.

1.1. Thermal Storage Applications

Figure 1 shows a chart of current energy storage technologies as a function of discharge times and power capacity for short-duration energy storage [4]. Within the range of short-duration energy storage capacities, applications include reserve and response services (1–100 kW), transmission and distribution support grid (100 kW–10 MW), and bulk power management (10 MW–1 GW). Although thermal storage technology is included in the chart as cryogenic energy storage, hot thermal storage using sensible, latent, or thermochemical methods [5, 6] is not shown. Commercial concentrating solar power (CSP) using sensible heat storage has demonstrated the ability to provide on the order of 100 MW of power capacity over 10 hours (~1 GWh) for both grid support and bulk power management.

Thermal storage technologies are also being considered for nuclear power plants to increase the flexibility of these traditionally baseload systems [6]. At times of low or negative electricity prices,

heat (or electricity) generated by the nuclear reactor would be sent to thermal storage. At times of high electricity prices, the heat from the reactor and thermal storage would be used to produce maximum electricity output (Figure 2). New Generation IV nuclear reactors deliver higher temperatures to the power cycle relative to water-cooled reactors, which is beneficial for thermal storage because at higher temperatures, less storage material is required to deliver a desired amount of thermal power. In addition, the higher temperatures enable more efficient thermal-to-electric power conversion. Adding thermal energy storage to geothermal power plants to increase flexibility and dispatchability has also been considered [7].
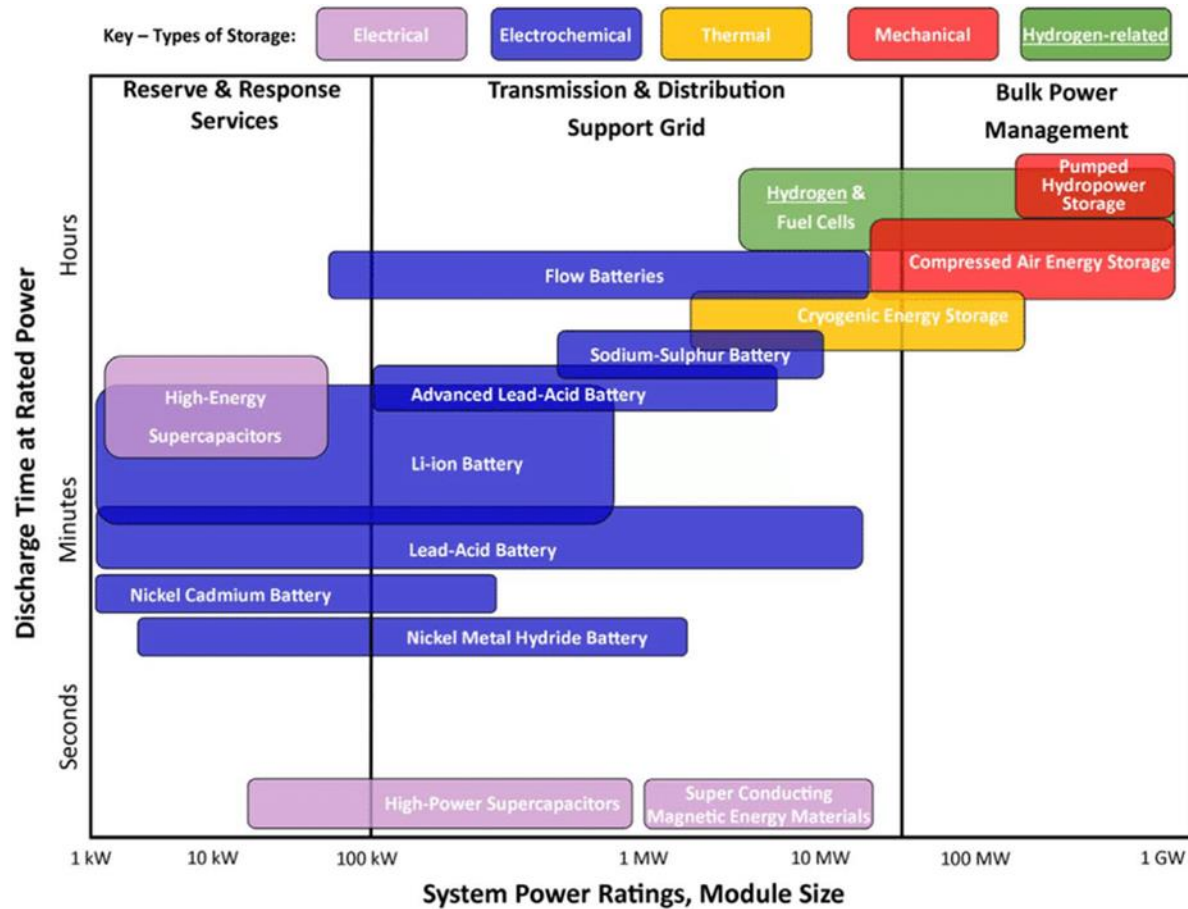
Figure 1. Discharge time and capacity of various energy storage technologies [4]. Hot thermal storage technologies are not shown but can provide hundreds of megawatts for many hours
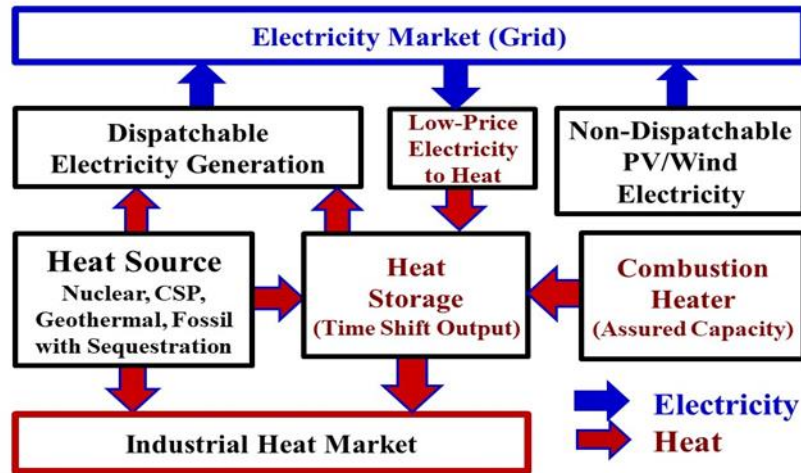
Figure 2. Diagram illustrating how thermal storage can increase the flexibility of traditional baseload power plants that rely on thermal energy [6].

1.2. Technology Overview

The remainder of this chapter provides a summary of thermal storage technologies, which can include sensible, latent, and thermochemical systems. Sensible storage relies on a temperature difference within the storage medium to enable useful work to be performed, such as using hot molten salt to heat water and generate steam to spin a turbine for electricity production. Latent storage involves storing heat in a phase-change material that utilizes the large latent heat of phase change, for example, during isothermal melting of a solid to a liquid, which requires heat, and subsequent freezing of the liquid to a solid, which releases heat, isothermally. Thermochemical energy storage (TCES) reversibly converts heat into chemical bonds using a reactive storage medium. When the energy is needed, a reverse reaction combines the reactants, releasing energy. Table 1 summarizes the different thermal storage technologies and key attributes.

Table 1. Summary of thermal storage technologies

	Sensible Heat Storage [5, 8-12]	Latent Heat Storage [5, 9, 10, 12, 13]	Thermochemical Storage [9, 11, 13]
Storage mechanism	Energy stored as temperature difference in solid (e.g., concrete, rock, sand) or liquid media (molten salt)	Energy stored using phase change materials (e.g., salts, metals, organics)	Energy stored in chemical bonds
Energy Density	• ~200 – 500 kJ/kg (for ~200 – 400 °C temperature differential)	• ~100 – 200 kJ/kg for nitrate salts; ~200 – 500 kJ/kg for metals; ~1000 kJ/kg for fluoride salts	• ~300 – 6,000 kJ/kg

	Sensible Heat Storage [5, 8-12]	Latent Heat Storage [5, 9, 10, 12, 13]	Thermochemical Storage [9, 11, 13]
Advantages	• Demonstrated large energy capacity (~GWh) • Inexpensive media • Solid media does not freeze and can achieve >1000°C	• Good for isothermal or low ⌷T applications • Can provide large energy density with combined sensible and latent heat storage	• Large energy densities • Small heat losses • Potential for long-term storage • Compact storage system • Oxide TCES Stable at high temperatures (> 1000°C)
Challenges	• Requires insulation to mitigate heat losses • Lower energy density requires larger volumes • Molten salts freeze at ~200 °C.	• Potential for corrosion • For larger ⌷T, may need cascaded systems (adds costs and complexity) • Low maturity	• Higher complexity • Low maturity • Higher capital costs • May require storage of gaseous products
Maturity	High	Low	Low
Cost	• ~$1/kg for molten salts and ceramic particles • ~$0.1/kg for rock and sands • ~$1/MJ – $10/MJ (system capital cost)	• ~$4/kg – $300/kg • ~$10/MJ – $100/MJ (system capital cost)	• ~$10/MJ – $100/MJ (system capital cost)

2. State of Current Technology

2.1. Sensible heat storage

Sensible heat storage consists of heating a material to increase its internal energy. The resulting temperature difference, together with thermophysical properties (density, specific heat) and volume of storage material, determine its energy capacity (J or kWh):

$$E_{sensible} = \rho V \int_{T_C}^{T_H} c_p(T) dT \qquad (1)$$

Desirable features of sensible storage materials include large densities, ρ (kg/m^3), large specific heats, c_P (J/kg-K), and large temperature differences between the hot and cold states, $T_H - T_C$ (K). Key advantages include a low cost of sensible storage materials, high maturity level, and large energy capacities. Table 2 provides a summary of thermophysical properties of various sensible solid and liquid storage media.

Table 2. Thermophysical properties of sensible storage media (adapted from [5]). Calculation of volumetric and gravimetric storage densities assume a temperature differential of 350°C.

Storage Medium	Specific Heat (kJ/kg-K)	Density (kg/m³)	Temperature Range (°C) Cold	Hot	Gravimetric Storage Density (kJ/kg)	Volumetric Storage Density (MJ/m³)
Solids						
Concrete	0.9	2200	200	400	315	693
Sintered bauxite particles	1.1	2000	400	1000	385	770
NaCl	0.9	2160	200	500	315	680
Cast iron	0.6	7200	200	400	210	1512
Cast steel	0.6	7800	200	700	210	1638
Silica fire bricks	1	1820	200	700	350	637
Magnesia fire bricks	1.2	3000	200	1200	420	1260
Graphite	1.9	1700	500	850	665	1131
Aluminum oxide	1.3	4000	200	700	455	1820
Slag	0.84	2700	200	700	294	794
Liquids						
Nitrate salts (ex. KNO_3-0.46$NaNO_3$)	1.6	1815	300	600	560	1016
Therminol VP-1 ®	2.5	750	300	400	875	656
Silicone oil	2.1	900	300	400	735	662
Carbonate salts	1.8	2100	450	850	630	1323
Caloria HT-43 ®	2.8	690	150	316	980	676
Sodium liquid metal	1.3	960	316	700	455	437
Na-0.79K metal eutectic	1.1	900	300	700	385	347
Hydroxide salts (ex. NaOH)	2.1	1700	350	1100	735	1250
Silicon	0.71	2300	1900	2400	250	575

Commercial CSP plants that employ sensible thermal storage with over 1 GWh of storage have been deployed worldwide. For comparison, Figure 3 shows the total number of large-scale battery demonstration facilities in the United States at the end of 2017 along with two CSP plants. Each CSP plant provides more energy storage capacity than all ~100 PV demonstration facilities combined.
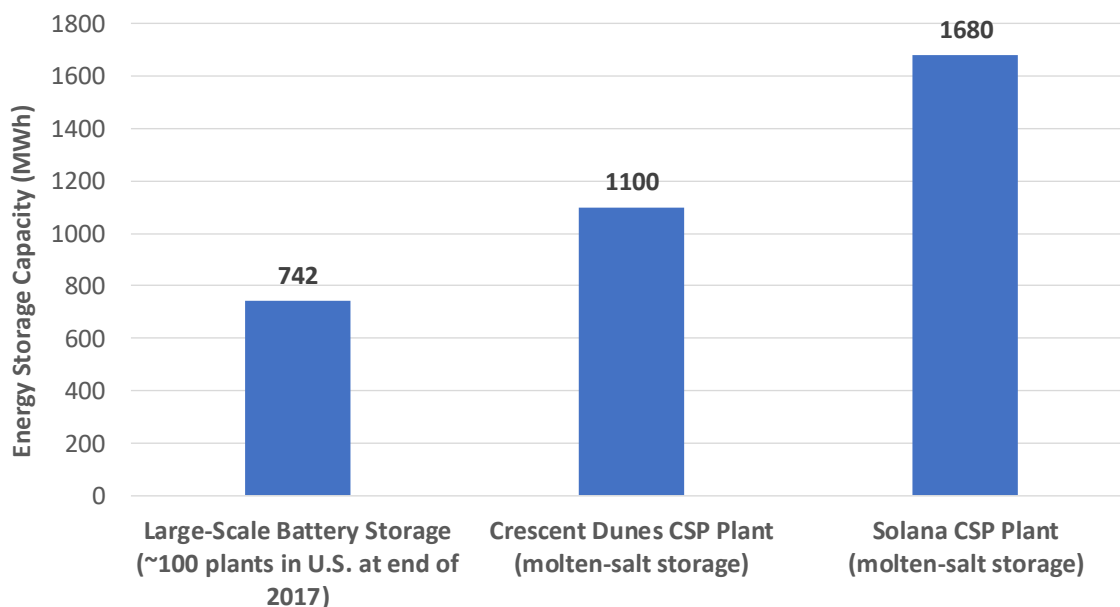
Figure 3. Comparison of energy storage capacity for battery and CSP plants. Battery data from U.S. Energy Information Administration [14].

2.1.1. Current Implementation

Current implementation of high-temperature sensible heat storage for electricity production uses liquids (e.g., molten salts) and solids (concrete, rocks).

2.1.1.1. Liquid

Molten nitrate salt (60% $NaNO_3$, 40% KNO_3) is being used in commercial CSP plants around the world to provide gigawatt-hours of thermal energy storage. It has a low vapor pressure, so it is not pressurized at typical storage temperatures up to ~600°C, and it can be pumped from one location to another.

Figure 4 shows a photograph and schematic of the 110 MW Crescent Dunes CSP plant with 1.1 GWh of thermal storage using molten nitrate salt. Molten salt is heated in a receiver on top of a tower by concentrated sunlight from a field of heliostats. The hot molten salt (~565°C) flows to a hot storage tank (right tank in Figure 4). When needed, molten salt is pumped from the hot storage tank to a heat exchanger where it heats water and generates steam to spin a turbine/generator for electricity. The cooled molten salt (~300°C) is pumped to a cold storage tank (left tank in Figure 4) and back to the receiver to be heated when the sun is shining. CSP plants can operate with large capacity factors (70–80%) and provide dispatchable energy.
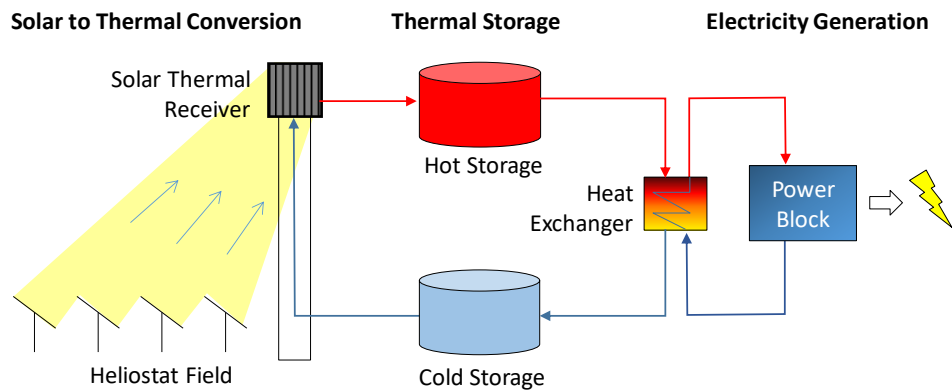
Figure 4. Top: 110 MW Crescent Dunes CSP plant with 1.1 GWh of thermal storage using molten nitrate salt [15]. Bottom: Schematic of sensible two-tank thermal storage system in a CSP plant.

2.1.1.2. Solid

Solid thermal storage has been used in several commercial and demonstration facilities. In 2011, Graphite Energy developed a 3 MW_e CSP plant in Lake Cargelligo in New South Wales, Australia, that used graphite blocks in the receivers on top of multiple towers. The graphite blocks in the receiver, irradiated by concentrated sunlight, served as both the storage system and boiler to generate steam for power production.

EnergyNest, based in Norway, developed a concrete-based thermal energy storage system that consists of an array of modular pipes filled with concrete and steel tubes. The tubes carry heat-transfer fluid that can heat the concrete when charging and extract heat from the concrete when discharging to power a turbine/generator or provide process heating. The system can charge/discharge in ~30 minutes and the stored energy can last for several days with less than 2% heat loss per 24 hours for large-scale systems.

Siemens Gamesa in Germany has developed a 130 MWh$_t$ Electric Thermal Energy Storage (ETES) system comprises rocks stored in a building. Air is resistively heated using electricity (when price is low) and passed directly through the bed of rocks. The rocks are heated to ~600°C, and, when needed, air is passed through the hot rocks to heat steam for a Rankine power cycle. The 130 MWh$_t$ demonstration plant became operational in 2019, and the company is planning a design for a 30 MW commercial pilot plant.

2.1.2. Challenges

The relatively low energy density of sensible-heat storage materials requires large volumes of material for large-capacity energy storage, which increases the overall storage cost. In addition, some power cycles that employ recuperation to increase the thermal-to-electric efficiency require relatively low temperature differentials between the hot and cold states of the storage material. For example, the supercritical CO_2 recompression Brayton cycle requires a temperature increase of only ~200°C in the primary heat exchanger [16]. As a result, the required mass inventory of storage material must increase to deliver the same amount of energy for a lower temperature differential, which increases costs. The target capital cost for the U.S. Department of Energy (DOE) CSP program is $15/kWh for the entire thermal storage system.

Molten salts freeze at >200°C, which requires expensive trace heating to maintain all components at temperatures well above the freezing point. If the salt freezes, flow can be blocked, and thawing must occur before operation can begin. Stress within the large storage tanks has also caused issues at CSP plants. Thermal gradients at the base of the tank can create thermomechanical stresses that damage the tank structure. Appropriate consideration of thermomechanical stresses is critical to the design of large-scale thermal storage tanks.

2.1.3. Opportunities

A number of institutions have been pursuing small, sand-like particle-based thermal storage for CSP plants and stand-alone thermal energy storage systems. Unlike the previous solid-based thermal storage systems, rather than passing air or a heat-transfer fluid through the storage media, the particles are heated directly and conveyed through a heat exchanger to heat the working fluid [8]. The particles are lifted to the top of the receiver where they are irradiated and heated by concentrated sunlight. The hot particles flow into an insulated storage tank where they can be held for hours or days. When needed, the particles are released through a particle heat exchanger to heat a working fluid that spins a turbine/generator for electricity production (Figure 5).
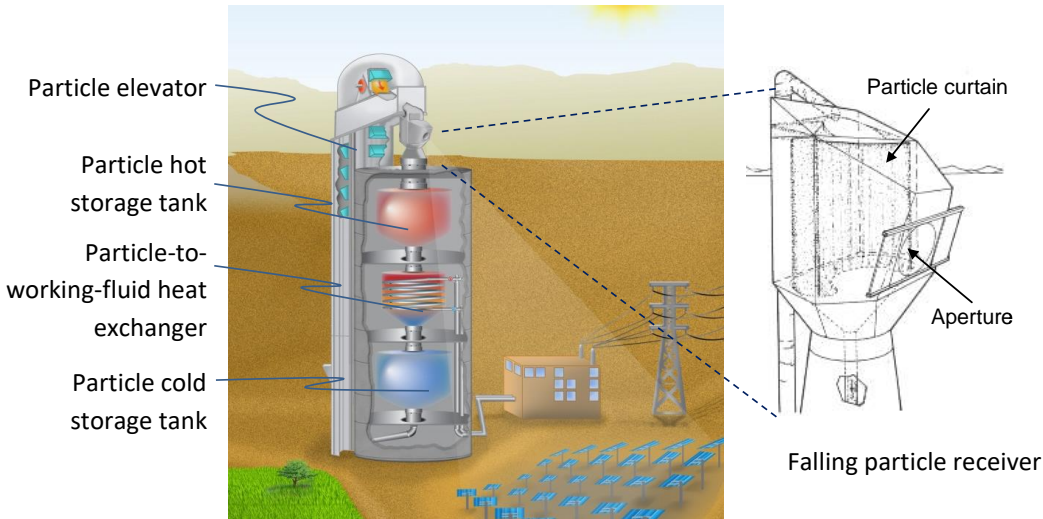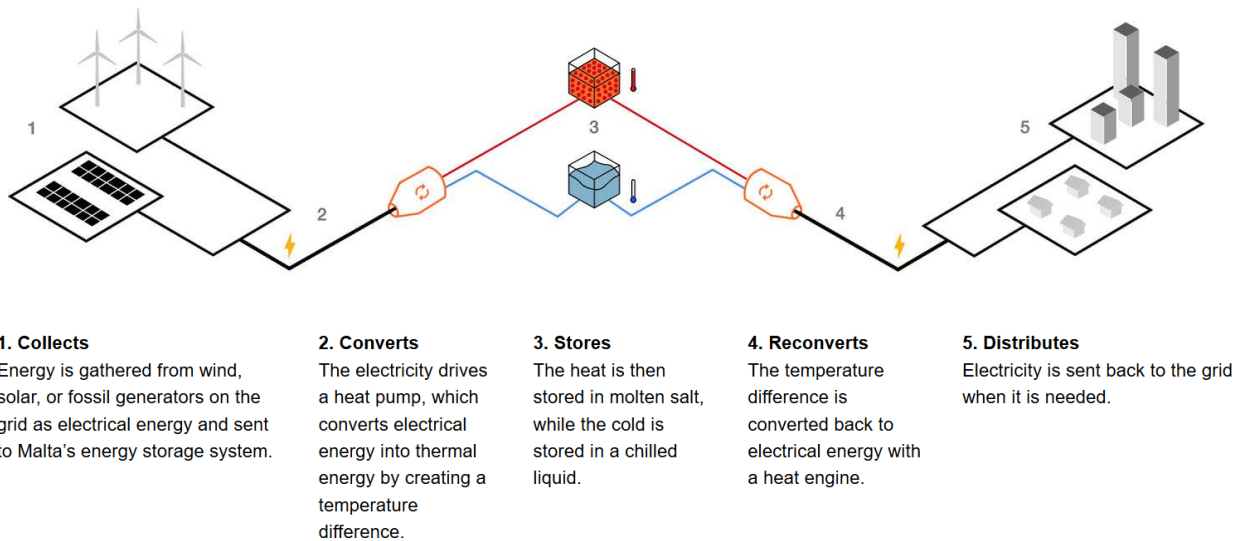
Figure 5. Illustration of a high-temperature falling particle receiver with tower-integrated storage and heat-exchanger for dispatchable electricity production [17]

Like the other solid-based thermal storage technologies, inexpensive particle storage can accommodate increasing penetrations of renewables by allowing heat to be stored when electricity demand is low, and then using that stored heat to produce electricity when demand and prices are higher. This time-shifting of energy production and use can increase the flexibility of traditional baseload power plants, including nuclear and geothermal.

Solid storage media has the advantage of being inert, inexpensive, non-corrosive, and easy to handle. In addition, many solid materials exhibit a much wider operating temperature range than molten salts. Rock, sand, and sintered bauxite have all been utilized in thermal storage systems and can operate in sub-freezing to >1000°C temperatures. Large volumes of bulk solid material can also provide self-insulation from the cooler ambient environment. As the volume of the bulk storage tank increases, the ratio of its surface area to volume decreases, which reduces heat loss. So, large storage tanks or containment systems yield both performance benefits and economies of scale.

Pumped thermal energy storage uses electricity in a heat pump to transfers heat from a cold reservoir to a hot reservoir similar to a refrigerator. When electricity is needed, the heat pump is reversed to allow the heat from the hot reservoir to drive a heat engine and spin a turbine/generator. The large potential temperature differences between the hot and cold reservoirs can enable highly efficient power cycles. Malta, a spinoff from Google X, is designing a pumped-thermal energy storage system (Figure 6).

1. Collects

Energy is gathered from wind, solar, or fossil generators on the grid as electrical energy and sent to Malta's energy storage system.

2. Converts

The electricity drives a heat pump, which converts electrical energy into thermal energy by creating a temperature difference.

3. Stores

The heat is then stored in molten salt, while the cold is stored in a chilled liquid.

4. Reconverts

The temperature difference is converted back to electrical energy with a heat engine.

5. Distributes

Electricity is sent back to the grid when it is needed.

Figure 6. Malta's pumped thermal energy storage concept [Malta, 2020 #13799]

MIT is investigating another storage technology that would use cheap or excess electricity to sensibly heat molten silicon to ultra-high temperatures in large, insulated graphite tanks. The molten silicon would be held at "cold" temperatures of ~1900°C (above its melting point of 1414°C) and heated with electrical heating elements to nearly 2400°C, where it is stored in a second "hot" tank. When electricity is needed, the molten silicon is pumped from the hot tank through tubes that emit thermal radiation to multijunction photovoltaic cells that generate electricity. The cooled molten silicon is then collected in the cold storage tank.

2.2. Latent heat storage

Latent heat storage systems use the latent heat of phase change to store energy. Latent heat of fusion is the energy required to change the state of substance from a solid to a liquid, and latent heat of evaporation is the energy required to change the state of substance from a liquid to a gas. Salts and metals can be melted, and the combined sensible and latent heat can be used to store the added thermal energy. Table 3 summarizes the thermophysical property values of different latent-heat storage materials. The latent heat of reaction (kJ/kg) shown in the second column would be added to the sensible heat capacity in Eq. (1) to determine the total heat capacity of latent heat storage materials being heated from one state to another. In most cases, the materials are solid/liquid phase change materials that are stored as liquids that can subsequently release energy when converted back to a solid state. Some liquid/gas substances (nitrogen and oxygen) are also shown because cryogenic "liquid air" storage has also been demonstrated for grid energy storage applications.

Table 3. Thermophysical properties of phase-change storage materials at standard conditions, unless otherwise noted (adapted from [5])

Storage Medium	Specific Heat (kJ/kg-K)	Latent or Reaction Heat (kJ/kg)	Density (kg/m³)	Melting Point (°C)	Boiling Point (°C)	Gravimetric Storage Density (kJ/kg)	Volumetric Storage Density (MJ/m³)
Liquid/Solid Phase Change Materials							
Aluminum	1.2	397	2380	660	-	397	945
Aluminum alloys (ex. Al-0.13Si)	1.5	515	2250	579	-	515	1159
Copper alloys (ex. Cu-0.29Si)	-	196	7090	803	-	196	1390
Carbonate salts (ex. Li$_2$CO$_3$)	-	607	2200	726	-	607	1335
Nitrate salts (ex. KNO$_3$-0.46NaNO$_3$)	1.5	100	1950	222	-	100	195
Bromide salts (ex. KBr)	0.53	215	2400	730	-	215	516
Chloride salts (ex. NaCl)	1.1	481	2170	801	-	481	1044
Fluoride salts (ex. LiF)	2.4	1044	2200	842	-	1044	2297
Lithium hydride	8.04	2582	790	683	-	2582	2040
Hydroxide salts (ex. NaOH)	1.47	160	2070	320	-	160	331
Silicon	0.71	1800	2300	1414	-	1800	4140
Liquid/Gas Phase Change Materials							
Nitrogen	1.04	199	809 (liquid)	-	-196	199	161
Oxygen	0.92	213	1140 (liquid)	-	-183	213	243

2.2.1. Current Implementation

Phase change materials (PCMs) have been encapsulated in spheres to form packed beds of encapsulated PCMs [9]. Heat-transfer fluid can be passed through the packed-bed of spheres to charge or discharge energy to/from the encapsulated PCMs. The phase change occurs at nearly isothermal conditions, so this method is useful for applications where the heat addition needs to occur at a specific temperature. At larger temperature ranges, cascaded PCM systems can be designed, but with additional complexity and cost. To date, encapsulated PCM systems have been tested and demonstrated at small scales. Commercial systems have not been demonstrated.

Molten silicon systems have been developed to exploit the large heat of phase change when melting/solidifying silicon (~1800 kJ/kg). The Australian company, 1414 Degrees, has designed thermal energy storage systems ranging from 10–200 MWh, and they began operating a prototype facility in 2019. The systems melt silicon at ~1400°C and recoup the latent energy during solidification to power combined cycles.

On the opposite end of the temperature scale, Highview Power has demonstrated cryogenic energy storage using "liquid air" at demonstration facilities with 2.5 kWh (300 kW peak power) and 15 MWh (5 MW peak power) of energy storage. The system operates by using electricity to cool air from ambient temperatures to -195°C using the Claude Cycle. The liquified air is stored at atmospheric pressure in large vacuum-insulated tanks. The volume occupied by the liquid air is ~1,000 times less than that of air at ambient conditions. When electricity is needed, the liquid air is pumped at high pressures through a heat exchanger that exposes the liquid air to ambient temperatures (or waste heat from an industrial heat source). The liquid air vaporizes, causing sudden expansion, which spins and turbine/generator for electricity production. The heat

exchanger can consist of a gravel bed that serves as a cold store of low-temperature material after giving up its energy to vaporize the liquid air. The low-temperature material can then be used to help cool the air during the next refrigeration cycle.

2.2.2. Challenges

Challenges with PCMs include relatively high costs and narrow operating temperature ranges. Using PCMs to provide energy to a heat engine will typically require a cascaded system with multiple PCMs with different melting points. The use of molten silicon at high temperatures provides challenges with materials containment and heat loss. Phase-change systems must still be well insulated to prevent heat loss and subsequent phase change.

2.2.3. Opportunities

1414 Degrees appears to have successfully developed a prototype molten-silicon system that exploits very high latent heats of fusion. Other systems and materials that can exploit high latent heats of fusion at low costs may provide alternative thermal storage capabilities.

2.3. Thermochemical storage

Thermochemical energy storage (TCES) is a promising storage technology, especially at high temperatures (> 700°C), as it allows for the storage of heat through chemical reactions, for example, the breaking/reforming of bonds. A conceptual illustration of TCES is shown in Figure 7.
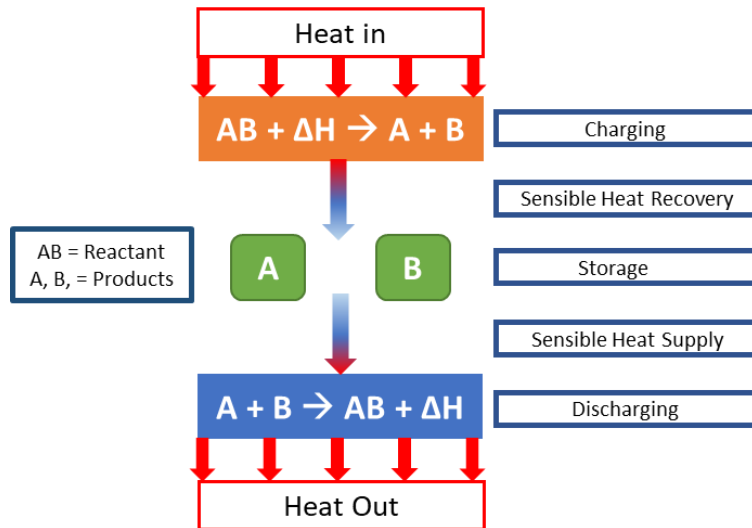
Figure 7. Schematic of steps involved in TCES: charging, storage, and discharging [18]

The thermochemical storage reaction, in its most basic form, can be written as

$$AB + \Delta H_{rxn} \leftrightarrow A + B \tag{2}$$

In this equation, Reactant AB is dissociated into Products A + B via the application of heat (heat of reaction shown in Table 3) in an endothermic reaction. The individual products can be stored separately for an indefinite amount of time. In times of thermal demand, A + B recombine in an exothermic reaction, releasing heat (the reaction proceeds to the left).

The TCES process compared to other thermal storage technologies is summarized in Table 1. The potential benefits of TCES include (1) enabling more efficient high-temperature power cycles (sCO₂ or air Brayton) that are inaccessible using current molten salt technologies, (2) potential higher-density and long-term storage, and (3) higher exergy. In addition, certain TCES processes (e.g., redox-active oxides) are also amenable to generating hydrogen via water-splitting. The hydrogen can then be used on-site to run a fuel cell for back-up generation. For TCES to be a practical storage technology, the materials must have a large reaction enthalpy and fast reaction kinetics, high thermal conductivity, good cyclic stability without the formation of unwanted phases or side reactions. They should also consist of abundant and economically inexpensive elements [19-22].

2.3.1. Implementation

A variety of potential TCES processes exist, though no TCES material has been implemented on an industrial scale. TCES can be applicable over a wide range of temperatures and conditions. Heat source, the type of power cycle, operating temperature, and receiver configuration all influence the selection of a candidate TCES material. Table 4 lists the most promising TCES reactions by type, reaction temperatures, enthalpies, and gravimetric storage energies. The operating temperatures and storage densities are representative values, but can differ depending on operating conditions, such as pressure, as well as the morphology of the solid species. The solid species can be particles, monoliths, or supported on inert or reactive scaffolds to avoid sintering or deactivation of the material [23].

Table 4. Candidate materials systems for thermochemical energy storage

Storage Medium	Reaction Enthalpy (kJ/mol)	Temperature Range (°C)	Gravimetric Storage Density (kJ/kg)	Volumetric Storage Density (MJ/m³)
Carbonates				
$CaCO_3(s)+\Delta H \leftrightarrow CO_2(g) + CaO(s)+CO_2(g)$	178	850-1273	1764	2491
$SrCO_3(s)+\Delta H \leftrightarrow SrO(s) + CO_2(g)$	234	900-1200	300-1000	1200-1500
$BaCO_3(s)+\Delta H \leftrightarrow BaO(s) + CO_2(g)$	273	~1290		
Hydroxides				
$Ca(OH)_2(s)+\Delta H \leftrightarrow CaO(s)+ H_2O(g)$	104	400600	1406	1640
$Mg(OH)_2(s)+\Delta H \leftrightarrow MgO(s)+ H_2O(g)$	81	350-	1340	1396
Hydrides				
$MgH_2(s)+\Delta H \leftrightarrow Mg(s)+H_2(g)$	75	300-480	2880	2088
$Mg_2FeH_6(s)+\Delta H \leftrightarrow 2Mg(s)+Fe(s)+H_2(g)$	74	300-500	2106 (theo.), 1921 (expt)	5768 (theo) 2344(expt)
$Mg_2NiH_4(s)+\Delta H \leftrightarrow Mg_2Ni(s)+2H_2(g)$	77	300-500	1160	3142
$NaMg_2H3(s)+\Delta H \leftrightarrow NaH(s)+Mg(s)+H_2(g)$	87	430-585	1721	~1721
$NaMgH_2F(s)+\Delta H \leftrightarrow NaF(s)+Mg(s)+H_2(g)$	97	510-605	1416	1968
$CaH2(s)+\Delta H \leftrightarrow Ca(s)+H2(g)$	186	1000-1400	3587	7374

Storage Medium	Reaction Enthalpy (kJ/mol)	Temperature Range (°C)	Gravimetric Storage Density (kJ/kg)	Volumetric Storage Density (MJ/m³)
Ammonia				
$NH_3(g) \leftrightarrow \frac{1}{2} N_2(g) + 3/2\ H_2(g)$	67	400-700	3924	2682
Redox Active Oxides [*]				-
$2Co_3O_4 (s) + \Delta H \leftrightarrow 6CoO(s) + O_2(g)$	205	900	844	-
$2BaO_2(s) + \Delta H \leftrightarrow 6BaO(s) + O_2(g)$	79	693-780	474	-
$6Mn_2O_3(s) + \Delta H \leftrightarrow 4Mn_3O_4(s) + O_2(g)$	32	1000	204	-
$4CuO(s) + \Delta H \leftrightarrow 2Cu_2O(s) + O_2(g)$	64	1030	-	-
$Ca_{0.95}Sr_{0.05}MnO_3(s) + \Delta H \leftrightarrow Ca_{0.95}Sr_{0.05}MnO_{2.7}(s) + 0.15\ O_2(g)$	-	1000	555	-
$CaAl_{0.02}Mn_{0.8}O_3 (s) \leftrightarrow CaAl_{0.02}Mn_{0.8}O_{2.68} (s) + 0.16\ O_2(g)$	368	200-1250	390	-
$La_{0.3}Sr_{0.7}Co_{0.9}Mn_{0.1}O_3(s) + \Delta H \leftrightarrow La_{0.3}Sr_{0.7}Co_{0.9}Mn_{0.1}O_{2.54}(s) + 0.23\ O_2(g)$	350	200-1250	250	-

*Storage values for redox materials do not take into account the sensible heat storage contributions of these oxide materials.

Table 5 lists the pros and cons of each type of cycle as well as its technology status.

Table 5. Advantages and drawbacks of TCES materials (adapted from [16])

Material	Advantages	Drawbacks	Technology Status
Carbonates	• Cheap, abundant, and non-toxic • High energy density • High operating temperatures (up to 1700 K) suitable for high-temperature power generation	• Less reversibility • Low cyclic stability (10–20 cycles) • Sintering	Lab-scale (fixed or fluidized-bed reactors) and pilot-scale (CaL technology for CO_2 capture)
Hydroxides	• Low material cost • Abundant • Non-toxic	• Agglomeration of material • Side reactions with CO_2	Lab-scale and pilot-scale
Metal Hydrides	• High energy density • High reversibility • A lot of experimental feedback on H_2-storage and heat pump applications	• Poor reaction kinetics • Hydrogen embrittlement • Sintering • Higher material cost	Pilot-scale

Material	Advantages	Drawbacks	Technology Status
Oxides	• High reaction enthalpy (205 kJ/mol) • Wide operating temperature (400–1473 K) • Low operating pressure (0–10 bar) • No catalyst • No side reaction (BaO/BaO_2) • High reversibility (500 cycles (Co_3O_4/CoO; 1000 cycles $Ca_xSr_{1-x}AlO_3$) • Can take advantage of sensible heat to increase storage density	• Toxicity of some products ($Co_3O_4/$ • CoO) • Cost of products • Heat transfer • Sintering • Low maturity level	Lab-scale
Ammonia Synthesis/ Dissociation	• Easy to control • No side reactions • Vast industrial experience (Haber-Bosch)	• Toxic • High cost of containment • Lower volumetric energy density • Higher operating pressures	Pilot-scale
Sulfur-Based Cycles	• Cheap and commercially available • Stable storage • Energy density of 9 MJ/kg • Sulfur is a cost-effective material (< 200 €/t) • Vast industrial experience	• Corrosive • Toxic • Highly protective containment is required	Lab-scale

Although a variety of potential TCES processes exist, no TCES system has yet been implemented on an industrial scale. Several bench-scale and pilot-scale demonstrations have been reported, several of which are described later in this chapter. A number of recent reviews also provide comprehensive explanations of these processes [13, 18, 23-25]. One of the most-developed TCES systems is the ammonia-based reaction, which has been studied for over 40 years, most notably at Australian National University (ANU). Figure 8 shows a schematic for a proposed storage system [26]. Ammonia (NH_3) is dissociated on-sun into H_2 and N_2 gases which can be stored indefinitely in a pressurized vessel. When heat is required, the gases are reacted to re-synthesize NH_3 in an exothermic process similar to the industrial Haber-Bosch process. In 1999, ANU tested a 10 kW_t closed-loop solar ammonia TCES system over the course of 5 hours, demonstrating solar dissociation and re-synthesis of NH_3 with storage and heat recovery [27]. In 2018, Chen et al. proposed and evaluated—using parametric modeling—an NH_3 TCES system utilizing supercritical steam as a heat transfer fluid [28].

In another conceptual design, Schmidt et al have performed multiple lab-scale tests on the calcium hydroxide [Ca(OH)$_2$] system demonstrating dehydration and rehydration (450°C and 550°C, respectively) of 20 kg of Ca(OH)$_2$. They attained a maximum thermal power of 7.5 kW$_{th}$ with an air outlet temperature of 450°C for 35 minutes [29]. In ensuing experiments, they showed that the outlet temperature could be increased to 600°C if the system was operated at 450 kPa. Based on these results, they proposed and thermodynamically analyzed a concept for integration into a CSP plant for up to 15 hours of storage, shown in Figure 9.
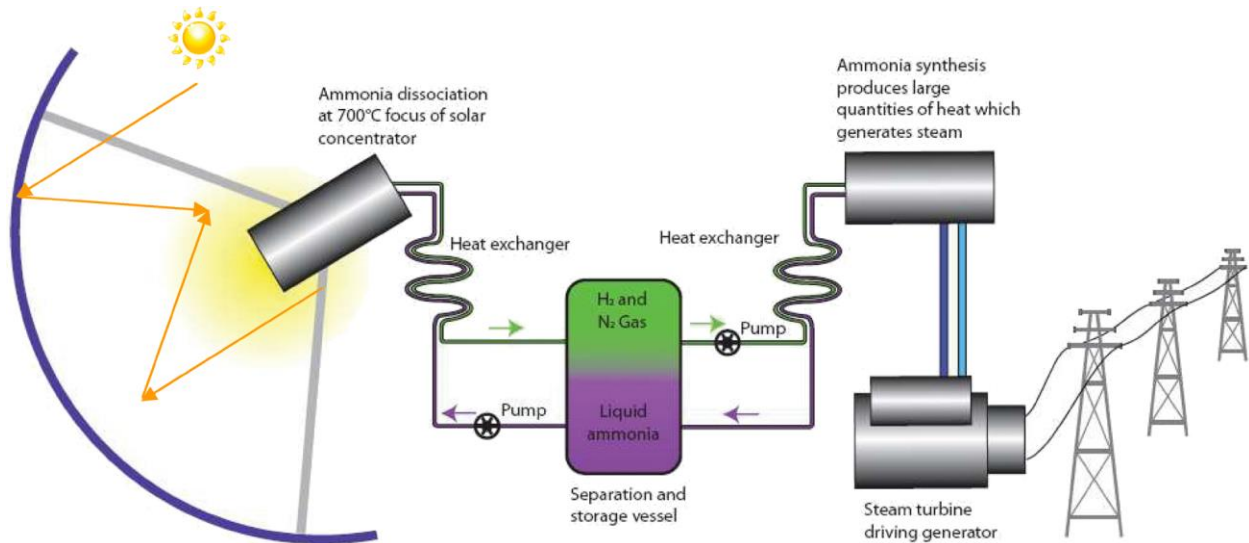

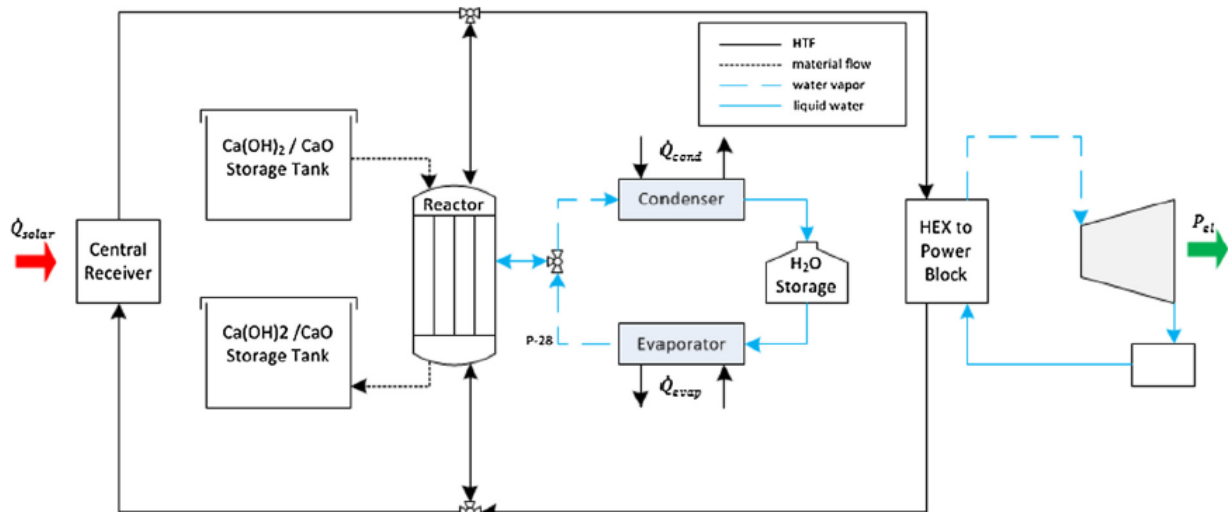**Figure 8. Ammonia dissociation and storage schematic [24]**

Figure 9. Conceptual process design of an indirectly heated Ca(OH)$_2$ thermochemical reactor in a CSP plant configuration [30]

Recently, there has been an increased interest in metal oxide TCES systems due to their capacity for high-temperature operation, energy density, ease of storage, and cyclability [23]. Tescari et al constructed and demonstrated a pilot scale TCES system utilizing cobalt oxide (Co_3O_4/CoO) as the TCES material, shown in Figure 10. Although the storage system was gas-powered and not solar-thermal-powered, it provided important data and proof-of-concept for this system. Twenty-two thermochemical charge/discharge cycles were carried out with no measurable performance degradation between cycles. The authors also showed that the TCES system almost doubled the storage capacity of the reactor compared to storage under the same conditions and volume using only sensible heat (47.0 kWh versus 25.3 kWh, respectively).

2.3.2. Challenges

While the concept of thermochemical energy storage holds promise, multiple challenges exist before the technology is ready for significant deployment. Specific challenges to the various types of storage systems are described in Table 5. Overarching issues include (1) development of novel solar receiver and reactor configurations that can be integrated into CSP designs, (2) low heat transfer efficiencies, (3) lack of large-scale testing and data, (4) material cyclability and lifetime, and (5) comprehensive technoeconomic analyses to determine cost, viability, and impacts. However, these challenges are not insurmountable, and ongoing research efforts can address the shortcomings.
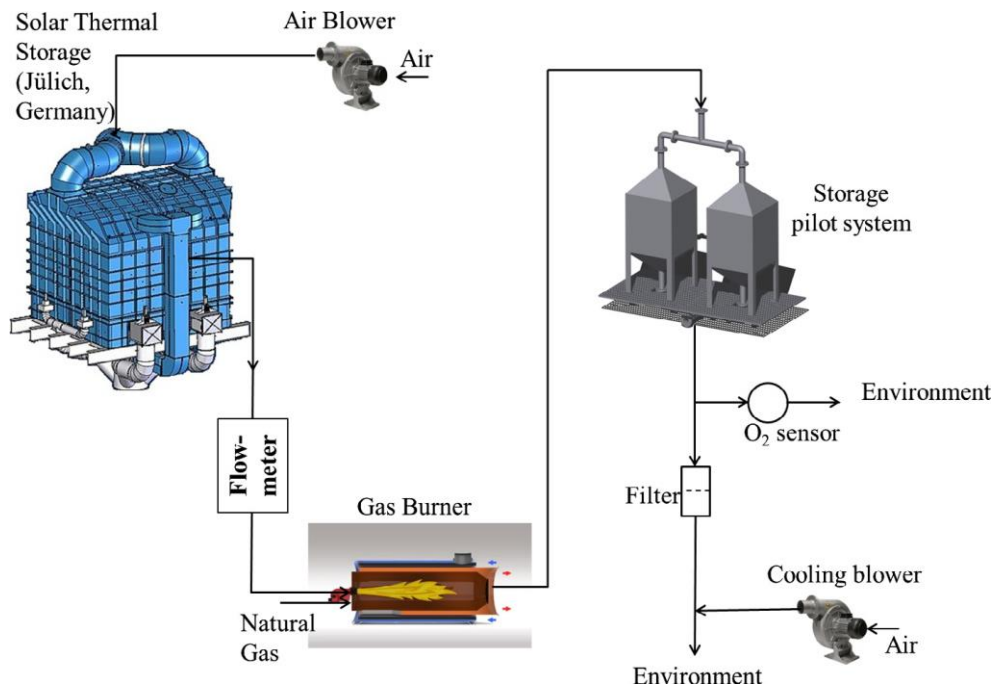

Figure 10. Schematic of the complete reactor system [31]

2.3.3. Opportunities

Thermochemical energy storage can potentially provide large-scale energy storage at costs lower than current electrochemical storage technologies. TCES materials can in theory store thermal energy indefinitely in the form of chemical bonds. This can allow for long-term, seasonable storage. In addition, some of the mixed-metal oxides are closely related to materials used in

thermochemical water spitting [32, 33] for the production of hydrogen, which can power fuel cells for power or transportation, thus representing another potential form of "energy storage." Some of the lower-temperature cycle materials can possibly be modified for thermal storage in hybrid photovoltaic/thermal systems.

3.   Summary

Thermal energy storage, which includes sensible, latent, and thermochemical energy storage technologies, is a viable alternative to batteries and pumped hydro for large-capacity, long-duration energy storage. Sensible energy storage technologies include the use of liquid molten salt stored at nearly 600°C in large insulated tanks, which can be dispatched when needed to heat a working fluid in a heat engine (steam Rankine cycle or Brayton cycle) to generate electricity. Sensible energy storage in solid media has also been demonstrated in large graphite blocks, concrete, rocks, and sand-like particles. The benefit of solid media is larger temperature ranges relative to molten nitrate salts (from below freezing to greater than 1000°C). Latent energy storage uses phase-change materials that change states from solid to liquid, providing additional energy storage capacity through the latent heat of fusion. Cryogenic energy storage employs a latent phase change from gas to liquid. Thermochemical energy storage uses reactive materials that use the heat of reaction to store energy in chemical bonds. The benefit of thermochemical storage is that the reactants can be stored for very long periods with minimal energy loss. When needed, the reaction can be reversed, releasing the heat of reaction. Phase-change materials and thermochemical storage materials are less mature than sensible heat-storage materials and are key areas for future research.

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