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Screening of thermochemical systems based on solid-gas reversible reactions for high temperature solar thermal energy storage

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ABSTRACT

A viable way to manage the inherently intermittent availability of solar energy in concentrated solar power plants is to store solar energy during on-sun hours to be able to use it later during off-sun hours, enabling on-demand electricity delivery. Thermochemical heat storage systems present some noteworthy advantages when compared with latent and sensible heat storage, namely (i) high energy storage density because the storage capacity by unit of mass or volume corresponding to the reaction enthalpy is generally high, (ii) heat storage at room temperature and long term energy storage because the products can be cooled and stored at room temperature without energy losses as heat can be stored indefinitely in chemical bonds, (iii) facility of transport because solid materials can be transferred over long distances, (iv) constant restitution temperature providing constant heat source because exothermic reactions are carried out at sufficiently high temperatures to generate electricity in constant conditions and therefore to produce a constant power. This paper presents an overview of the different potential thermochemical systems based on reversible solid-gas reactions operating at high temperatures and a screening of suitable materials that are interesting candidates in the 400–1200 °C range for thermochemical heat storage in concentrated solar power systems. The most promising materials belonging to the metal oxides, hydroxides, and carbonates solid-gas systems are selected for experimental validation and further investigations.

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1. Introduction

Most of the world energy sources come from fossil fuels. However, the use of fossil fuels in combustion processes produces greenhouse gases such as carbon dioxide in quantities that cannot be consumed or balanced naturally. In addition, the natural reserves of fossil fuels are gradually being depleted. Consequently, it has become necessary to search for new renewable pathways to produce energy. To address this matter, several options have been exploited, such as hydraulic energy, wind energy, waste-to-energy, solar energy and many others. Concentrated solar power (CSP) associated to thermal energy storage (TES) can be used as an environmentally friendly way to produce electricity. This paper focuses on thermochemical solid-gas systems applied to solar energy conversion and storage, and thus far, many systems have been studied in order to fulfill nowadays requirements for sustainable production [1–5]. In fact, solar energy represents an abundant renewable source of energy and technologies using solar light and/or heat, for example solar thermal energy or photovoltaics, have been developed. Moreover, a more efficient way to use solar energy is to store some of this energy to use it during off-sun hours and then be able to keep a constant production for industrial processes. Thermal energy storage is a key feature of CSP plants to match the intermittent energy source supply with the variable electricity demand, improving energy generation dispatchability. Three main routes have been explored in this optic and they are latent heat storage, sensible heat storage and thermochemical heat storage. Latent heat storage and sensible heat storage are thermophysical processes. Latent heat storage systems make use of phase change materials and mainly focus on a solid to liquid phase transition partly due to the additional difficulty of storing gas when working with liquid to gas phase change. Sensible heat storage generally relies on molten nitrate salts as heat storage media but also as heat transfer fluids in CSP applications with direct storage systems. If an indirect storage system is used, the energy is transferred from the heat transfer fluid to the storage medium through a heat exchanger. Sensible heat storage is being developed commercially, in contrast to latent and thermochemical heat storage. Though, one drawback of sensible heat storage is its requirement for high quantities of storage media, which can become costly when adapted to large scale systems. Thermochemical heat storage has shown specific advantages over the two other paths [4,6,7] (Table 1) and has been scarcely investigated for the past fifty years. For example, it shall be possible to reach higher energy storage densities and longer storage duration with the thermochemical approach. The main current challenge consists in developing thermochemical cycles with high conversion rate, rapid reaction kinetics and materials performance stability upon cycling. This review paper presents a screening of potential candidates for thermochemical energy storage using thermochemical cycles based on reversible solid-gas reactions.

2. Thermochemical heat storage systems

The concept of thermochemical cycles was first postulated in 1966 by Funk and Reinstorm [8], and can be used for thermochemical heat storage applications. Thermochemical heat storage systems present the advantages, over latent and sensible heat storage, to achieve higher energy storage densities thanks to high enthalpies of reaction, to show suitability for large-scale application, and to enable long storage duration and long-range transport at ambient temperature [9]. By the means of materials storage in solid state at room temperature, the transportation of the materials in which the energy is stored as chemical bonds is facilitated. Furthermore, the exothermic reactions release heat at a constant restitution temperature and allow a consistency in the generation of electricity through industrial processes which, combined with the storage of solar energy, may provide a constant power production.

Heat is released at a constant temperature during reversible chemical reaction, which provides a constant heat source. A thermochemical cycle can thus be selected to match the required turbine operating temperature. Thermochemical cycles find applications in diverse fields such as the production of renewable fuels through water-splitting or CO_2-splitting reactions to generate hydrogen or syngas [10] and thermal energy storage when the exploitation of the heat effects of the reactions for the storage of solar heat is favored over the production of chemical fuels. Thermochemical cycles are qualified as such because of the reagents being recycled. Such a cycle makes use of the heat produced in a solar receiver during on-sun operation to power an endothermic chemical reaction that should be completely reversible, thereby enabling the complete recovery of the thermal energy via the reverse reaction taking place during off-sun operation (Fig. 1).

During the heat charge, a compound $A_{(s)}$ is heated up using CSP and decomposes into the products $B_{(s)}$ and $C_{(g)}$ through an endothermic reaction (Fig. 2). The $B_{(s)}$ product stores the thermal energy converted into chemical energy as chemical bonds. $B_{(s)}$ can be isolated from the gas $C_{(g)}$ in order to be stored indefinitely as a stable solid material with minimal environmental effect. It can be advantageously cooled and stored at room temperature, which simplifies the

Table 1
Comparison of TES types [4,6].

Storage type	*Sensible*	*Latent*	*Thermochemical*
Gravimetric energy density (kWh kg^{-1} of material)	~0.02–0.03 kWh kg^{-1} of material	~0.05–0.1 kWh kg^{-1} of material	~0.5–1 kWh kg^{-1} of reactant
Maturity	Industrial scale	Pilot scale	Laboratory scale
Storage Period	Limited (thermal losses)	Limited (thermal losses)	Theoretically unlimited
Transport	Small distance	Small distance	Distance theoretically unlimited
Technology	Simple	Medium	Complex
Disadvantage	Significant heat loss over time (depending on the level of insulation). Large volume needed	Significant heat loss over time (depending on the level of insulation). Corrosivity of the material. Low heat conductivity	High capital cost. Technically complex