



Thermal energy storage materials and systems for solar energy applications



Guruprasad Alva, Lingkun Liu, Xiang Huang, Guiyin Fang*

School of Physics, Nanjing University, Nanjing 210093, China

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ABSTRACT

Usage of renewable and clean solar energy is expanding at a rapid pace. Applications of thermal energy storage (TES) facility in solar energy field enable dispatchability in generation of electricity and home space heating requirements. It helps mitigate the intermittence issue with an energy source like solar energy. TES also helps in smoothing out fluctuations in energy demand during different time periods of the day. In this paper, a summary of various solar thermal energy storage materials and thermal energy storage systems that are currently in use is presented. The properties of solar thermal energy storage materials are discussed and analyzed. The dynamic performances of solar thermal energy storage systems in recent investigations are also presented and summarized.

1. Introduction

Solar energy applications are found in many aspects of our daily life, such as space heating of houses, hot water supply and cooking. One major drawback of solar energy is intermittence [1]. To mitigate this issue, need for energy storage system arises in most of the areas where solar energy is utilized. There are different types of energy storage solutions [2]. One of the most important fields for solar energy application is the electrical power generation. Here the best suited energy storage system depends on the type of technology adopted for electricity generation. For generating electrical power from solar energy, there is a choice between Photovoltaic (PV) and Concentrated Solar Power (CSP) options [3,4]. PV technology usually stores electrical energy as chemical energy in batteries [5], while CSP utilizes TES to store solar energy in thermal energy form. Many comparisons have been done between different energy storage technologies [2]. At a large scale, high temperature TES is found to be more suitable than battery technology with its higher load capacity and longer storage duration. There for CSP has a better dispatchability at large scale. But due to falling prices of the PV cells, there is an increased competition faced by CSP technology from PV technology [3]. There is a need for CSP to increase the performance in all aspects like cost, efficiency, reliability etc. Although the overall efficiency of the CSP depends on the performance of all components like collectors, receivers, thermal energy storage system, heat exchangers, turbines and generators etc., but the performance of the TES system is the most crucial factor. Therefore, progress in the efficiency of the TES technologies and reduction in cost of electricity generation are the need of the hour.

Currently there is a wide range of technologies used for the TES. The CSP plants operate TES systems at higher temperatures as it improves the efficiency of Rankine cycle of the plant. In other application areas, such as space heating in buildings, solar hot water supply and heat sinks of electronic systems like laptops etc, the lower temperature TES systems are involved. This review summarizes the current affairs of different technologies in the application fields and their performances.

2. The properties of solar thermal energy storage materials

Applications like house space heating require low temperature TES below 50 °C, while applications like electrical power generation require high temperature TES systems above 175 °C [2]. The performances of the TES systems depend on the properties of the thermal energy storage materials chosen. The thermophysical properties of thermal energy storage materials should be presented in the following aspects according to the given requirements of the application fields.

- Melting point: Phase change materials should have a melting point near the required operational temperature range of the TES system.
- Density: High density improves energy storage density which reduces the volume of the TES system.
- Latent heat of fusion: Phase change materials should have very high latent heat of fusion. High latent heat of fusion improves energy storage density of the system.
- Specific heat (C_p): Sensible heat storage materials should have high specific heat. High specific heat improves energy storage density of the system.

* Corresponding author.

E-mail address: gyfang@nju.edu.cn (G. Fang).

- **Thermal conductivity:** High thermal conductivity increases the thermal charging and discharging rate which is desired.
- **Super cooling:** For phase change materials, during the freezing process, super cooling should be minimal. Storage material should freeze completely at as close as possible to its freezing temperature.
- **Cost and availability:** Cheaper price of storage material reduces capital and operational costs. They should be abundantly available.
- **Thermal stability:** They should not decompose at high temperatures. This gives wider operating temperature range and higher energy storage capacity for the material. Material properties should be stable even after extended thermal cycles of heating and cooling.
- **Chemical stability:** High chemical stability of storage materials increases life of energy storage plant.
- **Volume change:** For phase change materials, change in volume during phase change process should be minimal. Material also should have low coefficient of thermal expansion. Big changes in volume increase the required size of the container. Large density difference between two phases also causes phase segregation issue.
- **Non-toxic:** They should not be harmful to health of operators and environment.
- **Non-corrosive:** Corrosive thermal energy storage materials bring down the energy storage plant life drastically due to corrosion of containers.
- **Flammability:** They should be non-flammable and non-explosive.
- **Congruent melting:** In case of salt hydrates, incongruent melting affects the reverse process as the salt settles down and the salt is unavailable during recombination process.
- **Vapor pressure:** They should have low vapor pressure in operational temperature range. High vapor pressure requires pressure withstanding containment at high temperatures. It also requires costly insulation.

2.1. Sensible heat thermal energy storage materials

Sensible heat thermal energy storage materials store heat energy in their specific heat capacity (C_p). The thermal energy stored by sensible heat can be expressed as $Q = m \cdot C_p \cdot \Delta T$, where m is the mass (kg), C_p is the specific heat capacity ($\text{kJ kg}^{-1} \text{K}^{-1}$) and ΔT is the raise in temperature during charging process. During the heat energy absorption process, there is no phase change happening and materials experience a raise in temperature. The amount of heat stored is proportional to the density, volume, specific heat and variation of temperature of the storage material. Some of the most common sensible heat storage materials are listed below.

2.1.1. Liquid storage medium

Advantage of a liquid storage medium is that it can be circulated easily and so can transport heat if required. Such a system where storage medium is circulated is called active system. Also due to density difference caused by heating of liquid, the buoyancy helps in creating a thermal gradient across the storage which is desirable [6]. Hot fluid moves up, and cold fluid moves down separating them. Some sensible heat storage liquids are as follows:

2.1.1.1. Water. Water is one of the best storage media for low temperature applications. Its operating temperature range is between 25–90 °C [7]. Its advantages are high specific heat, non-toxicity, cheap cost and easy availability. But it has few drawbacks like high vapor pressure and corrosiveness. Water is best used for house space heating and hot water supply type of applications. Salty water in solar ponds is used for collecting large amount of solar thermal energy at low temperatures (50–95 °C). Heat gets at the dense layer at the bottom of the pond due to dissolved salt which hinders natural convection. Salts like NaCl and MgCl_2 are used here. Water storage tanks are made from a wide variety of materials, like steel, aluminum, reinforced concrete and fiber glass. The tanks are insulated with glass wool,

mineral wool or polyurethane. The sizes of the tanks used vary from a few hundred liters to a few thousand cubic meters. Large water tanks require the development of technologies capable of guaranteeing water tightness, to minimize heat losses caused by steam diffusion through the walls and to optimize stratification within the tank, in order to preserve the thermal performance and life time of the solar heating plant. Water can also be used for large scale seasonal heat energy storage purposes in underground aquifers where water could be found mixed with sand gravel. Such a system will be very cost effective as we can avoid expensive water tank construction [8].

2.1.1.2. Mineral oil. Mineral oil is used as a heat transfer fluid (HTF) in CSP plants. It collects the heat at the receiver and then transports the heat to boiler where steam is generated for driving the turbine. The same can be also used to store thermal energy in a highly insulated storage tanks during the night. When the HTF also becomes energy storage material, it's a direct system. It eliminates need for heat exchanger reducing the cost. Mineral oil has a lower vapor pressure than water and is capable of operating at high temperatures in liquid form up to 400 °C. Also unlike molten salts, mineral oil does not freeze during the night in pipes which creates the need for antifreeze system. But mineral oil is costly compared to molten salts and recently few molten salt mixtures with low melting point have been discovered replacing mineral oil as energy storage material. Recent trend in CSP is to use indirect systems where mineral oil acts as HTF and molten salt mixtures act as sensible heat storage materials.

2.1.1.3. Molten salts. Molten salts are currently the most used thermal energy storage materials in CSP plants. They are cheap (especially the nitrates). Their density is high compared to other liquid storage medium, giving them high energy storage density. Molten salts have a lower vapor pressure than water and are capable of operating at high temperatures in liquid form up to 400 °C. This allows operation of the plant at high temperatures which improves the efficiency of Rankine cycle. It is desirable to have a lower melting point for molten salts, and close to ambient temperature so that they remain liquid during operation and need for antifreeze is minimal during the night when solar energy is not available. But pure molten salts usually have melting points above 200 °C which is a disadvantage. However, today the practice is to use salt composites (more salt mixtures) which brings down the melting point below 100 °C and yet have a high maximum temperature above 500 °C [9]. They can also act as HTF but it's safer to have antifreeze system to deal with any freezing risk. Otherwise mineral oil will be used as HTF. One of the drawbacks of molten salts is that they are oxidizing agents and very corrosive and to contain them at high temperatures is problematic. Also their thermal conductivity is low and has volume change around 6% during melting process.

2.1.1.4. Liquid metals and alloys. Pure metals and alloys having low melting points but above 300 °C also have potential as sensible heat storage media. They have a high thermal conductivity and high maximum operating temperature. Their vapor pressure is minimal. But they have drawback like high cost. Also they may require oxygen and oxide free environment in order to reduce corrosion [7].

2.1.2. Solid storage medium

Solid storage materials have low cost and easily available everywhere. They have no vapor pressure issue. There for the operating pressure is close to ambient pressure and so no need of pressure containing vessels and no leak issues. Since they cannot be circulated

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