Applied Thermal Engineering 133 (2018) 261–268

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

Thermal cycling stability of thermochemical energy storage system $Ca(OH)_2/CaO$

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HIGHLIGHTS

- A TCS experimental setup was built to investigate temperature and mole fraction change details of the $Ca(OH)_2/CaO$ system.
- Mass and heat transfer performance and cyclic reversibility of the $Ca(OH)_2/CaO$ system are analyzed.
- Existing problems and its corresponding solution to improve cycle life of the system are concluded and raised.

ARTICLE INFO

Keywords:
Thermochemical energy storage
$Ca(OH)_2$
Dehydration process
Hydration process
Cycling stability

ABSTRACT

Thermochemical energy storage (TCS) stores and releases heat through a reversible chemical reaction. And since thermochemical material (TCM) is the most important part of an energy storage system, its properties directly affect the entire system. On account of a variety of advantages such as low cost, broad availability and suitable temperature range, thermochemical method based on reversible decomposition reaction has become a famous research. In this study, a TCS experimental setup was built to investigate thermal cycling stability of the $Ca(OH)_2/CaO$ system. Through successive 20 dehydration-hydration cycles, amount of stored thermal capacity and cyclic reversibility of the $Ca(OH)_2/CaO$ system are analyzed. After research and analysis, existing problems of the $Ca(OH)_2/CaO$ energy storage system including agglomeration and sintering, poor thermal conductivity, unevenness of heat release rate are concluded and raised. After an explanation of superior performance and existing problems occurred during the dehydration and hydration process, this research lays the foundation of applying the $Ca(OH)_2/CaO$ system to practical.

1. Introduction

Thermochemical energy storage (TCS) is a significant technology which could alleviate negative effect caused by fossil energy. And it promotes the development of a cleaner and more efficient energy system. TCS is mainly applied in three aspects. Firstly, it could provide a time delay between energy production and consumption. Secondly, it could be utilized to provide thermal inertial and thermal protection (including temperature control). Thirdly, it could guarantee the energy security. According to differences of heat storage theory, thermal energy storage methods are generally classified as sensible heat storage, latent heat storage and thermochemical heat storage [1,2]. Sensible heat storage technology is mature, but its energy storage density is low and the temperature fluctuation range is large relative to typical TCS [3]. At present, high-temperature phase change energy storage is widely studied and frequently applied. However, wide application of phase change energy storage still exists lots of difficulties to be solved [4]. Moreover, phase change energy storage is unable to conserve heat completely. The heat loss is large. And the higher the temperature is, the greater the loss will be. Due to mismatch and inhomogeneity between energy supply and demand caused by time and location, energy efficiency is usually low. TCS provides a new approach to improve energy efficiency and equipment availability. It uses its special energy conversion conception (thermal energy - chemical energy - thermal energy) to solve the problem. Therefore, in comparison with traditional methods, common TCM has large energy storage density, high output temperature, almost no heat loss and ability of long-term preservation at ambient temperature [5]. As early as 1988, Solar Energy Research Center (SERC) [6] had pointed out that TCS was a very potential high-temperature heat storage method. Under support of the National Energy Administration, American Pacific Northwest National Laboratory (PNNL) starts the research on the $Ca(OH)_2/CaO + H_2O$ energy storage

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https://doi.org/10.1016/j.applthermaleng.2018.01.059
Received 14 March 2017; Received in revised form 10 December 2017; Accepted 16 January 2018
Available online 20 February 2018

Nomenclature

Abbreviations

AR	analytically pure
PNNL	Pacific Northwest National Laboratory
SERC	Solar Energy Research Center
TCM	thermochemical material
TCS	thermochemical energy storage

Latin symbols

d	diameter
H_r	molar reaction enthalpy
M	mass
P	pressure
P_{H_2O}	water vapor pressure
q_d	thermal storage capacity per unit mass of the reactant
q_h	gross heat output per unit mass of the reactant
T	temperature
t	time
n	reaction bed mass
w_h	average thermal output rate
x	reacted fraction

Subscripts

d	dehydration
h	hydration
hy	Calcium hydroxide
ini	initial
ox	Calcium oxide

Greek symbols

Δ	difference

system. Hence, TCS as a new thermal energy storage form, has attracted more and more attention [7].

In general, the first step of constructing a TCS system is choosing suitable chemical reaction and studying its chemical properties. Ideal TCM needs to have the following characteristics [8]: appropriate reaction temperature and high reaction heat; good reversibility and no obvious side reactions; reaction rate of both sides; easy separation and stable storage of products; non-toxic, non-corrosive, non-flammable; little volume change; cheap and easy availability.

Typical TCS systems include thermal decomposition of inorganic hydroxides; SO_3, CS_2; ammonium salt, metal hydrides; decomposition of NH_3, carbonation, sulfate, oxide and peroxide; hydrogenation of organic, dehydrogenation reaction and so on [9]. Among them, $Ca(OH)_2$ has a variety of advantages, TCS method based on the reversible decomposition reaction of $Ca(OH)_2$ has aroused wide attention and research [10,11].

Schaube et al. [12,13] had a research on cycling stability of the $Ca(OH)_2/CaO$ system. An experiment about de- and rehydration of 60 g $Ca(OH)_2$ in a reactor shows no apparent performance degradation after 25 cycles. In another experiment, 10 mg $Ca(OH)_2$ were tabbed into an Al_2O_3 crucible, when cycles were increased to 100, the materials still shows no obvious performance degradation. $Ca(OH)_2/CaO + H_2O$ has a series of advantages, such as rapid and efficient reaction kinetics [14,15], high reaction enthalpy (104.4 kJ/mol) [16] and adjustable temperature range (410–600 °C) [17]. All of these characteristics make it a very promising material for concentrated solar power plants [18,19]. Chemical equilibrium equation of the $Ca(OH)_2/CaO$ system is shown below.

$$Ca(OH)_2(s) + \Delta H_r \leftrightharpoons CaO(s) + H_2O(g) \quad \Delta H_r = 104.4\,\text{kJ mol}^{-1} \tag{1}$$

Fig. 1 shows energy variation process. It can be seen that, under atmospheric pressure, 148.6 kJ energy needs to be provided for a mole of reactants decomposing into CaO and vapor. Suppose CaO saved in solid form and vapor in liquid form at 25 °C, then a total of 85 kJ energy would be released in sensible and latent heat. The rest of 63.6 kJ would truly be stored in the form of chemical energy, which is equal to 42.8% of total input energy.

Application of the $Ca(OH)_2/CaO$ system to heat pump has also aroused wide study. And the research involve heat and mass transfer enhancement of heat pump system [22], application of heat pump system to heat storage [23], heating/cooling efficiency [24], application to heat storage [25], and thermal regeneration [26].

Since TCM is one of the most important parts of the whole heat storage system, their cost, durability, energy density and dynamics performance are important affecting factors. In this paper, three aspects of the $Ca(OH)_2/CaO$ system based on its dehydration/hydration process have been studied. Firstly, temperature in the reactor, conversion of reactants, and influence of different dehydration temperature to reactivity. Secondly, gross heat input changes and gross heat output of the reaction bed. Thirdly, thermal cycling stability of the reactants. Solutions based on problems appearing in the experiment were proposed.

2. Experimental investigation

2.1. Reagent and instruments

Reagent: $Ca(OH)_2$, analytically pure (AR), purity ≥ 95%, average particle size $d_{50} = 5\,\mu m$, true density = 2200 kg/m^3, produced by Tianjin Damao Chemical Reagent Co., Ltd.

Instrument: electronic scale (BL-3000, 0.1–2000 ± 0.1 g, Ruian LeQi Trade Co., Ltd.), electrical heating filament (5 kW, Yancheng High Electric Equipment Co., Ltd.), k-type thermocouple (TM-902C, 0–900 ± 1 °C, Shenzhen Xinbo Hengye Technology Co., Ltd.).

2.2. Experimental apparatus

Experimental apparatus is composed of electronic scale, electrical heating filament, reactor, pressure gage, k-type thermocouple, water storage tank and cooling pipe, as shown in Fig. 2. Reactor 7 is a stainless steel cylinder with an inner diameter around 52 mm, a thickness about 1 mm, and a height about 70 mm. it's connected with water storage tank 11 by stop valve 6. Electronic scale could measure quality change caused by vapor release/storage. Reactor filled with $Ca(OH)_2$ is located in the center of reaction chamber 3. Temperature of the reactor is controlled by electrical heating filament 4. And pressure gage 5 measures inner pressure of the reaction chamber 3. Water Storage tank 11 could produce water vapor for the hydration process via the interior

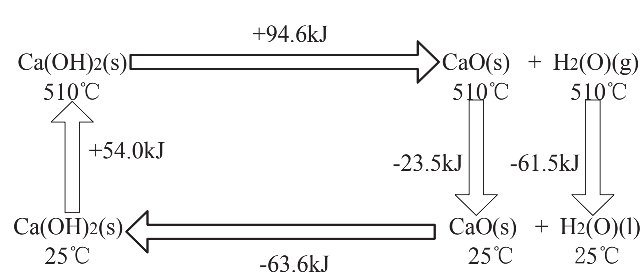

Fig. 1. Energy storage/release process in a $Ca(OH)_2/CaO$ system [20,21].