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# Investigation on performance of multi-salt composite sorbents for multilevel sorption thermal energy storage

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## HIGHLIGHTS

- Novel multi-salt composite sorbents are developed and investigated.
- Sorption hysteresis can be alleviated and even eliminated by multi-salt composite sorbent.
- The highest energy storage density of reaction heat is about and 1949 kJ/kg.
- Multilevel STES technology reveals the great potential for utilization of variable heat source.

## ARTICLE INFO

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## ABSTRACT

Novel bi-salt and tri-salt composite sorbents are developed, and expanded natural graphite treated with sulfuric acid (ENG-TSA) is integrated as the matrix with different mass ratios for heat transfer intensification. Tri-salt composite sorbent is mainly composed of Manganese chloride ($MnCl_2$), Calcium chloride ($CaCl_2$) and Ammonium chloride ($NH_4Cl$) whereas bi-salt composite sorbent comprises Calcium chloride ($CaCl_2$) and Ammonium chloride ($NH_4Cl$). Sorption characteristics under non-equilibrium condition are investigated and compared with that under equilibrium condition. Results show that the sorption hysteresis can be alleviated by bi-salt composite sorbent and even eliminated by tri-salt composite sorbent. Based on testing results, multilevel sorption thermal energy storage (STES) is analyzed, which can greatly enhance the versatility and working reliability. It is also worth noting that the highest energy storage density of reaction heat is 1802 kJ/kg and 1949 kJ/kg for tri-salt and bi-salt composite sorbents, respectively. Performance of bi-salt composite sorbent is relatively close to the theoretical data, which indicates three main stages. Comparably, performance of tri-salt composite sorbent shows continuous variation with the increment of reaction temperature. The promising multilevel STES reveals the great potential for energy utilization of variable heat source such as solar power when compared with conventional heat storage methods.



## 1. Introduction

Utilization of low grade heat is one of the main options to overcome the developing constraints with ever rising energy demands [1]. It is extensively acknowledged that thermal energy storage (TES) has played the leading role in efficient utilization of renewable energy such as solar energy, geothermal and industrial waste heat [2]. TES technology is able to overcome the disadvantages of time discrepancy, distance discrepancy and instability of renewable energy by adjusting mismatch between energy supply and demand [3]. Generally speaking, TES can be divided into three aspects, i.e. sensible heat storage by using concrete and pebbles, etc., latent heat storage by means of phase change materials (PCM) and thermochemical energy storage [4].

The aim of advanced TES system technologies is to seek for the high energy storage density which will result in the storage system more compact. Under this scenario, various researchers have made great efforts to investigate the efficient approaches for TES [5]. Sorption process, characterized as one common thermochemical process, has been extensively studied for refrigeration and heat pump system [6]. Likewise, sorption working process has been investigated for the possibility to be applied for TES in recent decades [7]. Since low grade heat is able to be stored in form of chemical bonds with thermochemical sorption process, the higher

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**Nomenclature**

| | |
|---|---|
| $A$ | the effective area of ammonia in the evaporator/condenser ($m^2$) |
| Bi-salt | two kinds of sorbents |
| $c$ | specific heat (J/(g K)) |
| $g$ | gravity acceleration ($m/s^2$) |
| HTS | high temperature salts |
| LTS | low temperature salts |
| MTS | middle temperature salts |
| $m$ | mass (kg) |
| $P$ | pressure (Pa) |
| PCM | phase change materials |
| $Q$ | Heat (J) |
| $R$ | gas constant (J/(mol K)) |
| STES | sorption thermal energy storage |
| Tri-salt | three kinds of sorbents |
| $T$ | temperature (K) |
| TES | thermal energy storage |
| $V$ | volume of liquid ammonia ($m^3$) |
| $x$ | sorption quantities (mol/mol) |

*Greek letters*

| | |
|---|---|
| $\Delta H$ | enthalpy difference (kJ/mol) |
| $\Delta S$ | entropy difference (J/K) |
| $v'(T_e)$ | specific volume of saturated liquid ammonia ($m^3$/kg) |

*Subscripts*

| | |
|---|---|
| c | cross section |
| de | desorption |
| eg | ENG-TSA |
| eq | equilibrium |
| h | heat |
| ideal | ideal condition |
| in | input |
| m | metal |
| $NH_3$ | ammonia |
| out | output |
| R | reaction |
| s | sorbent |
| s,s | stainless steel |
| salt | chloride |

energy density can be obtained in comparison with conventional sensible heat and latent heat storage. Theoretically, owing to the monovariant characteristic of equilibrium performance, sorption thermal energy storage (STES) has good adaptability to one stable heat source temperature [8]. Furthermore, based on a wide range of chemical sorbents [9], STES has the capacity of different working modes such as direct energy supply, energy upgrade, and combined cooling and heating supply, which could meet different needs of end users [10].

Nonetheless, with a variety of forms, energy sometimes varies with the time and place randomly. Solar energy is one good example of variable heat source [11]. It is quite difficult to store the heat with variable temperature through one certain kind of material within a large temperature slide. To deal with that, various researchers have investigated the cascaded energy storage materials as far as PCM technology is concerned. Peiró et al. [12] evaluated the advantages of using the multiple PCM instead of the single PCM configuration in TES systems. Results demonstrated an average enhancement of 19.36% could be obtained for multiple PCM in comparison with the single PCM configuration on the heat transfer fluid (HTF) temperature difference. Xu and Zhao [13,14] investigated both steady and unsteady cascaded thermal storage system with multiple PCMs of different phase-change temperatures. It was indicated that the optimization of cascaded PCM enjoyed the higher exergy efficiency of heat utilization. Compared with multiple PCM technology, concept of the cascading STES just starts, which take the advantages of relatively less heat loss and higher efficiency. Li et al. [15] proposed a novel cascaded solar thermal battery on basis of the solid-gas thermochemical sorption materials. Results revealed that heat storage density was higher than 1200 kJ/kg through the novel energy storage method. However, the limited selections of reaction working pairs will restrict the further application of this cascading STES technology. It is noted that equilibrium reaction lines of the different sorbents are often used to analyze the performance of STES. The equilibrium sorption process is regarded as monovariant characteristic, which varies with temperature or pressure. Comparably, real sorption process is the non-equilibrium process, and it will cause the inaccuracy and limitation if performance of STES is analyzed based on the equilibrium condition. Researches have verified that the sorption hysteresis occurs on the non-equilibrium condition [16]. Non-equilibrium hysteresis phenomena would cause sorption process into a bivariate process, which require both temperature and pressure to determine the reaction process [17,18]. Moreover, for multilevel STES, different kinds of sorbents will be mixed together to realize the low grade heat utilization with a large temperature range. Therefore, it is not suitable to analyze the performance of multilevel STES by the equilibrium reaction line of each sorbent because the mixture of several sorbents probably lead to some novel characteristics, which will either improve or hinder its application.

There is less report about the multilevel STES technology which is regard as potential solution to the problem of solar power storage and utilization. In this paper, multi-salt composite sorbent is developed, and desorption and sorption process are both investigated to analyze the sorption hysteresis phenomenon. Expanded natural graphite treated with sulfuric acid (ENG-TSA) is chosen as the matrix of sorbent, which has proved to enhance the heat and mass transfer performance [19]. On basis of the testing results, multilevel STES is developed and further analyzed to enhance the versatility and working reliability by widening the working temperature scope.

## 2. Material characterization

### 2.1. Development of multi-salt composite sorbents

For multi-salt composite sorbent, $MnCl_2$, $CaCl_2$, $NH_4Cl$ are selected from high temperature salts (HTS), middle temperature salts (MTS), and low temperature salts (LTS). The thermochemical reaction process of these salts with ammonia can be referred to the Eqs. (1)–(5). To the simplified the description of thermochemical reaction process of different sorbents, phrases of $MnCl_2$ 6/2, $CaCl_2$ 8/4, $CaCl_2$ 4/2 and $NH_4Cl$ 3/0 are used in the paper. For example, $MnCl_2$ 6/2 represents the process in which $MnCl_2$ ammoniate reacts with ammonia from 2 mol to 6 mol. Details of multi-salt composite sorbents in developing process can be referred to the Ref. [20]. First, ENG-TSA is dried in the oven with controlled temperature of 120 °C. The different chlorides of $MnCl_2$, $CaCl_2$