An experimental study on the stability and reliability of the thermal properties of barium hydroxide octahydrate as a phase change material

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Abstract

Hydrated salts are attractive materials for use in thermal energy storage. However, the supercooling and phase segregation limit their practical applications. This article exploits the possibility of barium hydroxide octahydrate as a PCM and reports the experimental results of its thermal stability and reliability. The material has a very large volumetric storage density of about 620J/cc. The results show that barium hydroxide octahydrate does not exhibit any supercooling and phase segregation after more than 500 thermal cycles. No obvious changes in the melting temperatures and the fusion heat of barium hydroxide octahydrate were observed with increasing number of thermal cycles. Therefore the material may be an important phase change material for thermal energy storage.

Keywords: Thermal energy storage; PCMs; thermal reliability; hydrated salts; barium hydroxide octahydrate; DSC

1. Introduction

Latent heat thermal energy storage is a particularly attractive technique, and there have been increasing interests in using this essential technique for thermal applications such as heating, hot water, air conditioning and so on. It provides higher energy storage density and has the capacity to store heat as latent heat of fusion at a constant temperature corresponding to the phase transition temperature of phase change materials (PCMs). For example, in the case of water, 80 times as much energy is required to melt 1 kg of ice as to raise the temperature of 1 kg of water by 1℃. This means that much smaller weight and volume of materials are needed to store a certain amount of energy.

In 1983 Abhat [1] gave a useful classification of substances used for thermal energy storage (TES). Relatively few solid-solid PCMs have been identified that have heats of fusion and transition temperatures suitable for thermal storage applications. Solid-liquid PCMs are useful because they store a relatively large quantity of heat over a narrow temperature range, without a corresponding large volume change. Liquid-gas PCMs usually have very high latent heats, but they are not usually considered for practical applications due to the large volume change during phase transition. Table.1 [2] shows a comparison between the sensible heat storage in a rock bed

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and water tank and the latent heat storage using organic and inorganic compounds. The advantages of the latent heat storage over the sensible heat storage are clear in view of volume and mass of the storage unit necessary for storing a certain amount of heat. It is also clear from Table.1 that inorganic compounds (for example, hydrated salts) have higher volumetric thermal storage density than those of most organic compounds due to higher latent heat and density.

Table.1. Comparison of various heat storage media (stored energy=10^6kJ/300kWh;ΔT=15K)

	Heat Storage Material			
	Sensible heat storage		Phase Change Materials	
Property	Rock	Water	Organic	Inorganic
Latent heat of fusion (kJ/kg)			190	230
Specific heat (kJ/kg)	1.0	4.2	2.0	2.0
Density (kg/m^3)	2240	1000	800	1600
Storage mass for storing 10^6kJ (kg)	67000	16000	5300	4350
Storage volume for storing 10^6kJ (m^3)	30	16	6.6	2.7

The selection of the heat storage material as phase change material (PCM) in the latent heat thermal energy storage method plays an important role in view of thermal efficiency, economic feasibility and utility life of the system. So, many studies have focused on the development of new PCMs and improvement of their thermal properties for TES in respect of different climate conditions. Hydrated salts are attractive materials for the use in thermal energy storage. However, the problems of supercooling and phase segregation have limited their applications. There are several studies on the thermal stability of hydrated salts after many heating－cooling cycles. Wada et al. [3] investigated the decreasing heat storage capacity of CH3COONa·3H2O during thermal cycling and performed calorimetric measurements on three kinds of samples. They studied the effect of the addition of a thickening agent to the sample on the latent heat storage capacity of the sample, and they reported that the addition of the thickening agent considerably improves the latent heat capacity after 500 thermal cycles. Ting et al. [4] conducted accelerated cycle tests of N2SO4·nH2O as PCM. They performed 1000 melt/freeze cycles to study the effect of thermal cycling on the container tube but did not analyze the effect on the thermo-physical properties of the PCM. Porosino [5] tested the thermal performance reliability of some salt hydrates with melting points between 15 and 32℃ after repeated 5650 thermal cycles by measuring the latent heat of fusion and melting temperature.

In the light of the literature survey mentioned above, a comprehensive knowledge of the thermal reliability of the PCMs as functions of repeated heating－cooling cycles is essential for the assurance of the long term performance and economic feasibility of a latent heat storage system. In this regard, this study aims at determining the change in the melting temperatures and the latent heats of fusion of barium hydrate octahydrate with thermal cycling increasing.

2. Experiments

2.1 Materials

The barium hydroxide octahydrate with analytical purity was obtained from the Beijing Yili

Chemistry Company. It's molecular formula is $Ba(OH)_2 \cdot 8H_2O$ and molecular weight is 315.5. Solid barium hydroxide octahydrate is white crystal and is classified in Monoclinic crystal system. It has large mass density of $2.18 \times 10^3 kg/m^3$. It's melting point is 78℃. The solubility of barium hydroxide octahydrate in water changes largely with temperature changing, for instance, the solubility is 5.6g/100ml in 16 ℃ water and is 94.7g/100ml in 78℃ water. The solution of barium hydroxide octahydrate shows alkalescence. Anhydrous barium hydroxide when exposed to the air trends to react with carbon dioxide to form barium carbonate. So the container filled with barium hydroxide octahydrate must be well sealed. Barium salt with solubility has certain toxicity, which does harm to person's skin and heart. Barium carbonate with very little solubility in water can act with stomach acid to form barium chloride. The reasons of these damages to body are possibly that Ba^{2+} is liable to replace Ca^{2+} and Mg^{2+} in person's body. [6] Taking in the amount of 0.2 – 0.5g barium chloride will lead to poisoning and 0.8 – 0.9g is the death dosage for human beings. If the swallow had happened, the emergency treatments should be done, for example taking quickly magnesium sulplate and sodium sulphate, cleaning gizzard, bowel lavage and promoting emesis. [7]

2.2 Accelerated test process and DSC analysis

To determine the effects of a large number of accelerated thermal cycles on the phase change temperature and the latent heat of fusion of the barium hydroxide octahydrate, the cylindrical capsules were used. The capsules, made of stainless steel with a lid, were airtight but contained a certain amount of air. The inner diameter and height of the capsules were 25 and 180 mm, respectively. The sealed capsules were filled with the barium hydroxide octahydrate and then set into a thermostatic chamber with a temperature controller. The temperature of the thermostatic water bath is about 93℃. The PCMs were heated beyond their melting temperature to about 85℃, then they were put into another thermostatic chamber whose temperature of water bath is about 63 ℃ to freeze. When PCMs' temperature decreased to about 65℃, they were set into about 93℃ water bath again. A thermal cycle was conducted as a heating (melting) and a cooling (solidifying) process. The experiment equipment is showed as Fig.1.

There were four barium hydroxide octahydrate samples sealed in the capsules that were used to perform 160, 230, 330, 500 thermal cycles, respectively. Data acquisition registered the curves of temperature change of PCMs through thermocouples. The temperature curves would show clearly whether PCMs had supercooling and how many degrees the supercooling degrees were.

The differential scanning calorimetry (DSC) was used to evaluate the melting temperature and the latent heat storage capacity of the uncycled and cycled barium hydroxide octahydrate. For this aim, a DSC200PC instrument from the NETZSCH Company was used. All DSC samples with the mass of 4.500-10.00mg were encapsulated in high-pressure crucible of chrome nickel steel with gold-plated surface. The heating rate for all runs was 2K/min. The N_2 (≥99.999% pure) was used purge gas with 20ml/min constant flow rate and protective gas with 60ml/min constant flow rate. The melting temperature of barium hydroxide octahydrate corresponds to the Onset temperature. The latent heat of fusion of barium hydroxide octahydrate was calculated as the area under the peak by numerical integration.

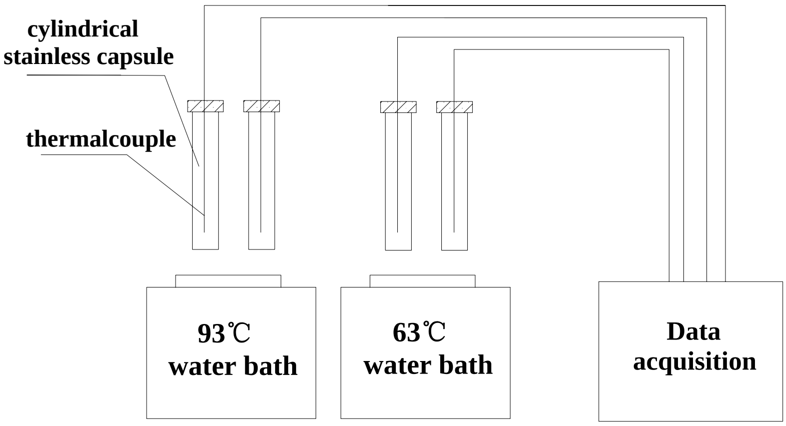

Fig.1. The experiment equipment to subject to thermal cycles

3. Experimental results and discussion

The curves of temperature change of PCMs registered by Data acquisition are showed in Fig.2 and 3. From these curves, it can be seen that barium hydroxide octahydrate has not supercooling which is most of hydrate salts own character. Zhang Yinping [8] had also pointed out barium hydroxide octahydrate had not supercooling. In addition in this study, the glass test tubes filled with barium hydroxide octahydrate were used to observe the melting and solidifying behavior. Barium hydroxide octahydrate had not phase segregation in solidifying and was just like liquid water after melting. But glass test tubes were liable to breaking during many thermal cycles.

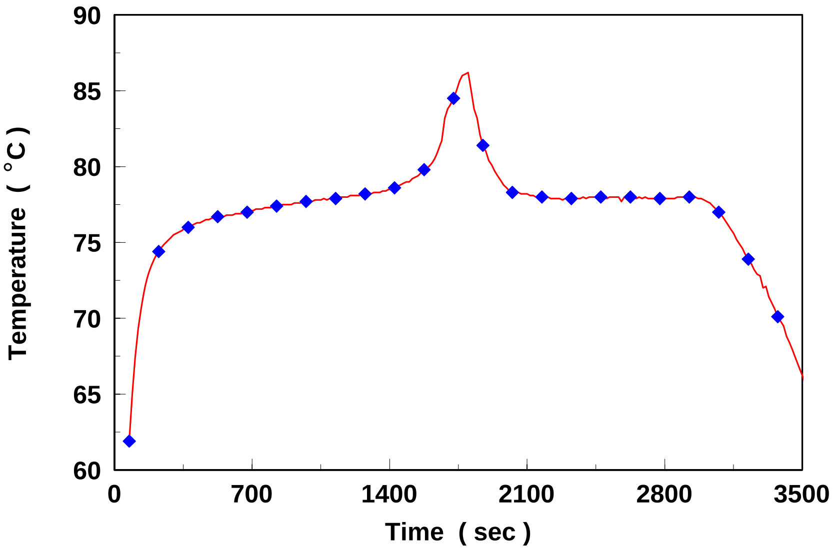

Fig.2. Supercooling curve of fresh (uncycled) barium hydroxide octahydrate

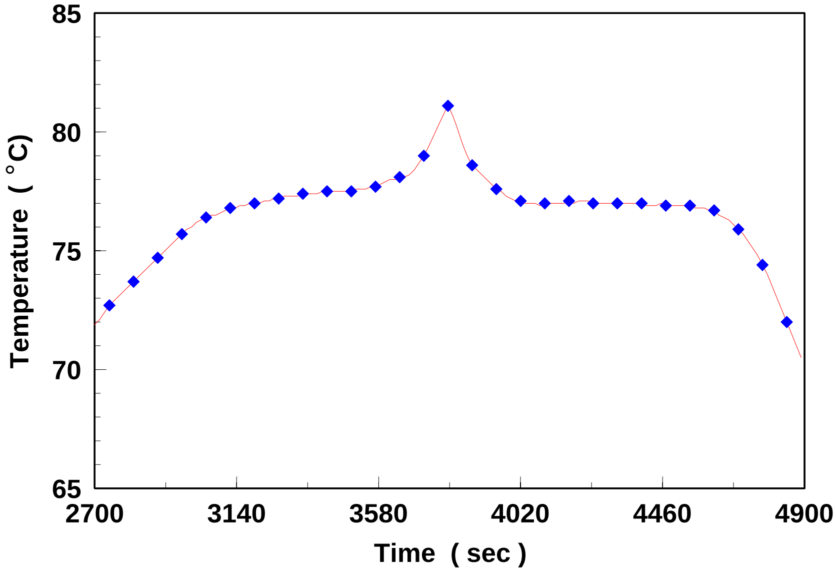

Fig.3. Supercooling curve of barium hydroxide octahydrate after 500 test cycles

The melting temperatures and latent heat of PCMs were measured by DSC instrument after 0, 160, 230, 330, 500 accelerated test cycles and are given in Table.2. The DSC curves after the 0th,

Table.2 The change of characteristics with thermal cycles increasing

No.of test cycles	**Melting temperature (℃)**	**Latent heat of fusion (kJ/kg)**	**Volumetric storage density (J/cc)**
0	78	288.6	629.15
160	77.9	286.1	623.70
230	77.7	285.1	621.52
330	77.6	284.6	620.43
500	77.6	285.6	622.61

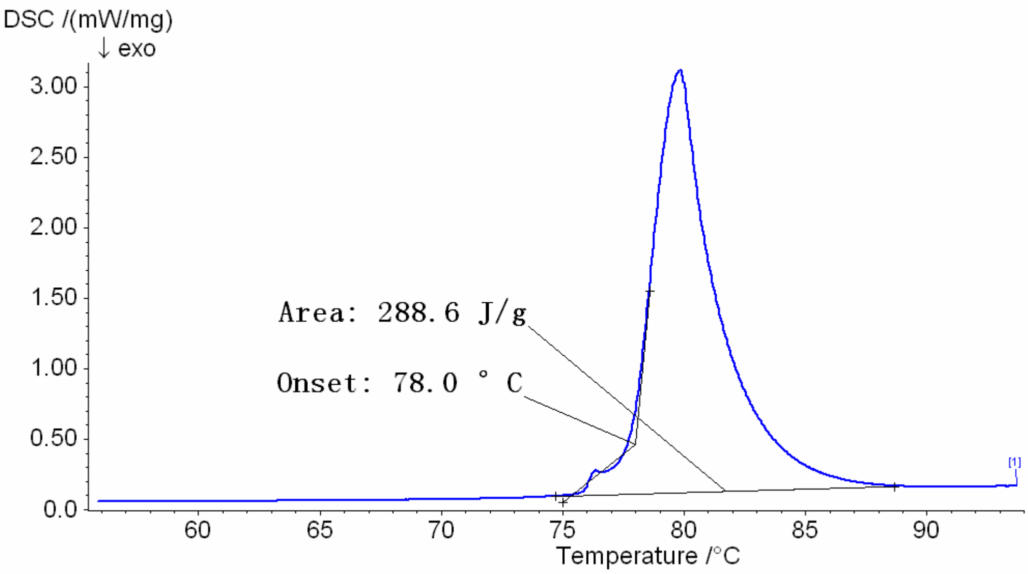

Fig.4. DSC curve of fresh (uncycled) barium hydroxide octahydrate

230th and 500th test cycles of barium hydroxide octahydrate are showed in Figs.4 to 6. From

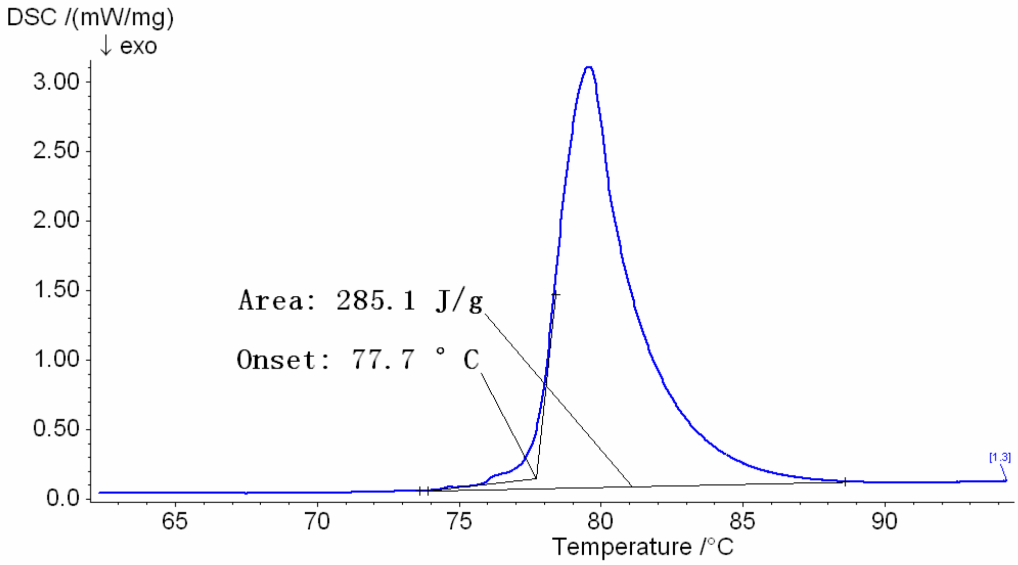

Fig.5. DSC curve of barium hydroxide octahydrate subjected to 220 thermal cycles

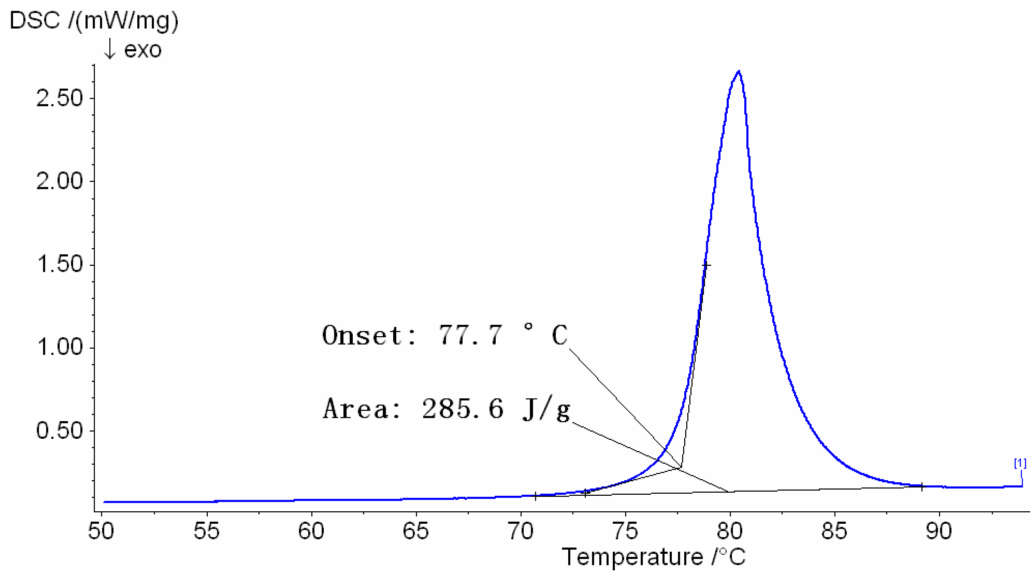

Fig.6.DSC curve of barium hydroxide octahydrate subjected to 500 thermal cycles

Table.2, it can be seen that the melting temperatures decreased with increasing number of thermal cycles, however, no major change in the melting temperatures of barium hydroxide octahydrate was noticed. After 160, 230, 330, 500 test cycles, the changes in the latent heats of fusion were –0.87%, —1.21%, –1.39%, –1.04%, respectively. It can be observed from these values that barium hydroxide octahydrate's latent heat of fusion decreased after thermal cycles, but the change rate was basically invariable as thermal test cycles increasing. The phase change behavior of barium hydroxide octahydrate may be due to its impurities. The literature [9] pointed out that the melting temperature and latent heat of mixture were less than that of any component of it. The impurities and barium hydroxide octahydrate formed mixture of which melting temperature and latent heat of fusion were both less than that of any component in the mixture. So barium hydroxide octahydrate has good thermal reliability in view of the latent heat of fusion and melting temperature after 500 test cycles.

4. Conclusions

It can be concluded from the experimental results that no obvious changes in the melting temperatures and the latent heat of fusion for barium hydroxide octahydrate was found with increasing number of thermal cycles. It has not still supercooling and phase segregation which were most hydrate salts' characteristics after 160, 230, 330, 500 thermal cycles. So barium hydroxide octahydrate has good thermal reliability in view of the latent heat of fusion and melting temperature after 500 thermal cycles. In addition, it has large volumetric storage density about 620J/cc. But barium hydroxide octahydrate has toxicity. If the material is well sealed and a effective measures are set up to prevent its toxicity, then barium hydroxide octahydrate should be a very good PCM for thermal energy storage applications.

Acknowledgements

This work is supported by the Key Project No. G2000026306 of The National Fundamental Research and Development Program, The Ministry of Science and Technology of The People's Republic of China, The National Key Technologies R & D Program Project No. 2003BA808A19-7, Chinese National Natural Science Foundation Project No. 50276001 and Beijing Natural Science Foundation Project No. 3032007.

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