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Experimental investigations on heat content of supercooled sodium acetate trihydrate by a simple heat loss method

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ABSTRACT

Sodium acetate trihydrate is a phase change material that can be used for long term heat storage in solar heating systems because of its relatively high heat of fusion, a melting temperature of 58 °C and its ability to supercool stable. In practical applications sodium acetate trihydrate tend to suffer from phase separation which is the phenomenon where anhydrous salt settles to the bottom over time. This happens especially in supercooled state. The heat released from the crystallization of supercooled sodium acetate trihydrate with phase separation will be lower than the heat released from sodium acetate trihydrate without phase separation. Possible ways of avoiding or reducing the problem of phase separation were investigated. A wide variety of composites of sodium acetate trihydrate with additives including extra water, thickening agents, solid and liquid polymers have been experimentally investigated by a simple heat loss method. The aim was to find compositions of maximum heat released from the crystallization of supercooled sodium acetate trihydrate samples at ambient temperature. It was found that samples of sodium acetate trihydrate with 0.5–2% (wt.%) Carboxy-Methyl Cellulose, 0.3–0.5 % (wt.%) Xanthan Gum or 1–2% (wt.%) of some solid or liquid polymers as additives had significantly higher heat contents compared to samples of sodium acetate trihydrate suffering from phase separation.

1. Introduction

Solar energy along with other renewable energy sources can play an important role in clean energy utilization in modern society. However, solar energy has the characteristic of being intermittent on a daily basis and has an uneven seasonal distribution. Heat storage is one possible and effective way of solving the mismatch between heat demand and solar energy supply. Solar energy systems combined with long term heat storage are being widely studied in many projects. For example in the four EU funded projects (van Helden, 2013) (SAM.SSA, MERITS, SOTHERCO, COMTES), and in IEA SHC Task 42 and IEA ECES Annex 29. Phase change materials (PCMs) are considered as promising heat storage materials due to their latent heat of fusion which can possibly increase storage density compared to sensible heat storages. In some PCMs the latent heat of fusion can be preserved without heat loss for a long term storage period via the principle of stable supercooling (Kousksou et al., 2014; Xu et al., 2013; Zalba et al., 2003)

1.1. Sodium acetate trihydrate as heat storage material

Sodium acetate trihydrate (SAT), $NaCH_3COO{\cdot}3H_2O$, consisting of 60.3% (wt.%) sodium acetate and 39.7% (wt.%) water, has the ability to supercool stable to ambient temperatures and has relatively high latent heat of fusion of 264 kJ/kg at the melting temperature of 58 °C (Zalba et al., 2003). Once the solidification of the supercooled SAT is activated the latent heat of fusion from the phase change will be released. This energy can be used for space heating and domestic hot water preparation. The ways of activating the solidification are easy and flexible such as cooling a part of the SAT to its maximum degree of supercooling by either evaporating liquid CO_2 (Furbo et al., 2012) or by a Peltier element cooling or by mechanically introducing a seed crystal. Therefore SAT is a promising phase change material which can be used for long term heat storage.

Fig. 1(a) shows one sample of supercooled sodium acetate water mixtures which have been in supercooled state for more than 2 years at indoor temperatures. Even impurities such as rusty iron immersed in the supercooled sodium acetate water mixture did not influence the stability of the supercooling, as can be seen in Fig. 1(b).

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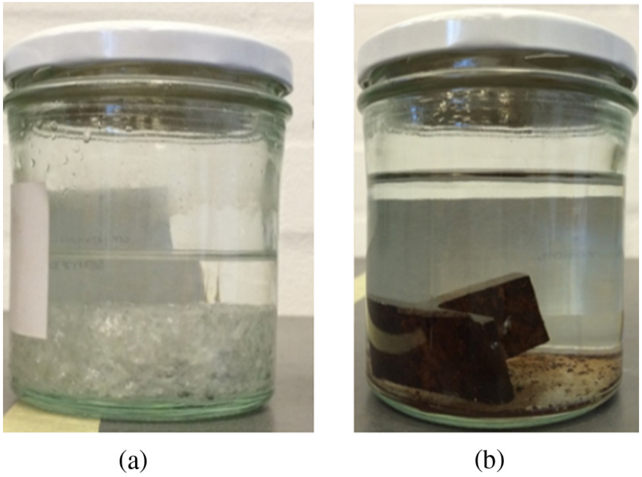

Fig. 1. Long term supercooled samples of (a) SAT with extra water, (b) SAT with extra water and immersed steel.

1.2. Limitations of the material

Phase separation/segregation is a key problem of using SAT for heat storage. It causes the heat content of the supercooled SAT to decrease over time (Kimura and Kai, 1985). It is caused by the fact that SAT is an incongruently melting salt hydrate. An incongruently melting salt hydrate consists of an anhydrous salt with corresponding crystal water. The solubility of the anhydrous salt in water, which is given in (Furbo and Svendsen, 1977) is not high enough at the melting point of 58 °C to dissolve all the anhydrous salt in the corresponding crystal water of the trihydrate composition. Therefore the molten salt hydrate at a temperature just above the melting point consists of a saturated salt solution and some anhydrous salt undissolved in the water (Kimura and Kai, 1985). When nothing is done to prevent it, the anhydrous salt settles to the bottom of the container as sediment due to its higher density, which can be seen in Fig. 1(a). In supercooled state below the melting point, even less anhydrous salt will be dissolved and the problem increases. This can be realized by observing the phase diagram for the sodium acetate - water system (Araki et al., 1995). When the crystallization of a sample is initiated, the anhydrous salt at the bottom is unable to bind with the water in the top of the container. Therefore only a part of the anhydrous salt is active during phase change. The solidified salt hydrate with phase separation consists of three parts: At the bottom the solid salt hydrate crystals with additional anhydrous salt, in the middle a layer of salt hydrate crystals, and at the top the salt hydrate crystals with some additional water in which some salt dissolves in. The amount of sediment increases with repeated cycles, and the heat storage capacity will therefore decrease with each melting/crystallization cycle. Therefore phase separation has to be avoided.

1.3. Solutions

Different possible ways of avoiding or reducing phase separation were investigated in previous studies. For example, the problem does not occur for the incongruently melting Glauber's salt, $Na_2SO_4{\cdot}10H_2O$, if the height of the container is smaller than 0.9 cm according to Kauffman and Pan (1972). Glauber's salt has a much larger difference between the salt solubility at the melting point and the content of anhydrous salt in the salt hydrate compared to the difference between the salt solubility at the melting point and the content of anhydrous salt in SAT. Therefore it could be possible that a low material height can avoid phase separation. Adding extra water is suggested a way to avoid phase separation and was studied by Furbo and Svendsen (1977). The stored energy in SAT with extra water has however shown to decrease after a number of cycles in tests with prototype heat storage units with a PCM heights of 5 cm (Dannemand et al., 2015b; Dannemand and Furbo, 2014). Phase separation can also be reduced by adding thickening agents which were widely investigated in the literature. Hu et al. (2011) presented the mixture of SAT with 4% Carboxy-Methyl Cellulose (CMC) as thickening agent and 5% AIN nanoparticles as nucleating agent which had a high latent heat and avoids the supercooling. Similarly, Garay Ramirez et al. (2013) used 0.5% AgNPs to reduce the supercooling and mixing silica gel with CMC to avoid phase separation and yielded an increment in the stability of the phase change behaviour. Nearly 95% of the latent heat of SAT was recovered in this study. In a study by Cabeza et al. (2003), bentonite, starch and cellulose were investigated for the thickening effect on SAT and they found an enthalpy decrease between 20% and 35% depending on the type and amount of thickening agents used. In a study by Ryu et al. (1992), a super-absorbent polymer (SAP) made from acrylic acid copolymer and CMC-Na was investigated as thickening agent to avoid phase separation, together with K_2SO_4 as the nucleating agents. The combination of SAT with 1% SAP, 2% CMC-Na and 2% K_2SO_4 was used in a study by Choi et al. of heat storage systems (Choi et al., 1996).

Studies (Cabeza et al., 2003; Choi et al., 1996; Garay Ramirez et al., 2013; Haillot et al., 2012, 2011; Hu et al., 2011; Ryu et al., 1992) focused on short term heat storage in which supercooling of the storage materials has to be avoided. Therefore nucleating agents, which reduce the degree of supercooling, were used in those studies. For seasonal heat storage using the principle of stable supercooling, nucleating agents should be avoided and therefore the total mass of the PCM material is reduced. That's one of the advantages of utilizing long term supercooling.

Suggested ways of reducing phase separation can be summarized in the following ways:

- Low height of material
- Adding extra water
- Adding thickening agent

1.4. Measurement techniques

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods (Höhne et al., 2003) are conventional method for determining the latent heat of fusion and the specific heat of PCMs. However, DTA and DSC measurement facilities are complicated and expensive and the tested samples are usually very small (1–10 mg), which does not represent the bulk PCMs in actual storages (Zalba et al., 2003). Yinping et al. (1999) proposed the T-history method, as a simple alternative to the DTA and DSC methods, to determine the melting point, heat of fusion, specific heat and thermal conductivity of the bulk PCMs with additives in a sealed tube. The T-history method was then widely recognized and used in studies. Further modification and improvement for the T-history method were proposed by researchers in order to remove unstable phase change, enhance the measurement accuracy and enlarge the range of applications (Hong et al., 2004, 2003; Peck et al., 2006).

In this study, possible additives for reducing phase separation including extra water, thickening agents, solid and liquid polymers were investigated. Adding extra water will allow for more anhydrous salt to dissolve. Thickening agents can increase the viscosity of the solution and suspend the anhydrous salt in the container so that it does not settle to the bottom of the container. Solid or liquid additives can work in such a way that the salt solubility is increased so much that phase separation is avoided.