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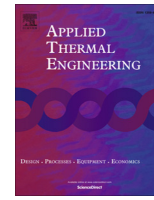

Research Paper

Porosity and density measurements of sodium acetate trihydrate for thermal energy storage

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HIGHLIGHTS

- Density of liquid and solid sodium acetate trihydrate (SAT) was measured.
- Density of supercooled SAT with extra water was measured.
- Solidified SAT contained cavities.
- Cavity fraction in solid SAT depended on solidification.
- The density of SAT was lower after solidified with a high degree of supercooling.

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ABSTRACT

Sodium acetate trihydrate (SAT) can be used as phase change material in latent heat storage with or without utilizing supercooling. The change of density from liquid to solid state leads to formation of cavities inside the bulk SAT during solidification. Samples of SAT which had solidified from supercooled state at ambient temperature and samples which had solidified with a minimal degree supercooled were investigated. The temperature dependent densities of liquid and the two types of solid SAT were measured with a density meter and a thermomechanical analyzer. The cavities formed inside samples of solid SAT, which had solidified after a high or minimal degree of supercooling, were investigated by X-ray scanning and computer tomography. The apparent density of solid SAT depended on whether it solidified from a supercooled state or not. A sample which solidified from a supercooled liquid contained 15% cavities and had a density of 1.26 g/cm^3 at 25 °C. SAT which had solidified with minimal supercooling contained 9% cavities and had a density of 1.34 g/cm^3 at 25 °C. The apparent densities of the solid SAT samples were significant lower than the value of solid SAT reported in literature of 1.45 g/cm^3. The density of liquid and supercooled SAT with extra water was also determined at different temperatures.

1. Introduction

Thermal energy storage is needed to match the varying supply of renewable energy sources such as solar energy with the more predictable demand for heating of buildings. A lot of research focuses on phase change materials (PCM) because they allow for denser heat storage compared to a sensible heat storage with e.g. water as the storage medium. The ability of the PCM to remain at the melting point for an extended period during charge and discharge while absorbing or releasing thermal energy allows for favorable operating conditions for some applications. Especially in some applications where the melting temperature of the PCM fits the supply and demand temperatures.

Sodium acetate trihydrate (SAT) was identified as a heat storage material with high potential [1–8]. SAT has a relatively high melting enthalpy or latent heat of fusion compared to other PCMs and a

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melting point of approximately 58 °C. In addition, the thermal conductivity of salt hydrates is generally higher than e.g. paraffins [9]. These characteristics fit well with space heating requirements and domestic hot water preparation [10]. This temperature level is also easily reached by simple solar thermal collectors and potentially by heat pumps. Stability of the SAT composite in repeated thermal cycles needs to be confirmed with boundaries representing the intended application.

1.1. Supercooling

The material SAT itself has the ability to supercool far below its melting point. In most applications, the supercooling has been seen as a problem. This has been avoided by adding nucleation agents to the SAT mixture to start solidification with minimal supercooling during discharge [2,11,12]. Several researchers look into developing PCM composites of SAT with thickening agents and nucleation agents for improving the PCMs performance in systems where supercooling is suppressed [13–15]. On the other hand, actively utilizing the supercooling gives the possibility to store energy over long periods without thermal loss in part of the storage period. This is done by having the melted SAT remain in supercooled state in the storage period at ambient temperature so that the latent heat of fusion can be stored long term [4,8].

1.2. Material properties

SAT, with the chemical notation $NaCH_3COO{\cdot}3H_2O$, consists of 60.3% sodium acetate and 39.7% water. SAT is considered an incongruently melting salt hydrate, which suffers from phase separation. The problem of phase separation has been sought solved by adding thickeners or extra water to the SAT [7,8,16–20]. The key properties, which determine the capacity of a PCM heat storage, are the specific heat capacity in solid and liquid phase, latent heat and the density of the PCM. These thermophysical properties are important to know when designing and sizing a storage. Ma et al. did a study on SAT for seasonal heat storage which include listing thermo-physical properties of SAT and aqueous solution of sodium acetate [21].

Kousksou et al. did a review article on applications and challenges of energy storage and touched on latent heat storage [6]. They mention that despite the fact that PCMs are extensively researched, their thermophysical properties are lacking in the literature. Kenisarin and Mahkamov summaries the material properties of different salt hydrates including SAT in a review article [9]. They indicate that the values of the thermophysical properties of SAT measured by different researchers have significant variations. Typical values in the literature for densities of SAT are 1.45 g/cm^3 for solid phase and 1.28 g/cm^3 for the liquid phase with no dependence on temperature or thermal expansion coefficients provided [22]. Noting that the density of the solid SAT of 1.45 g/cm^3 is for a SAT crystal formed with a cooling rate low enough to have the crystallization process occur slowly and form a dense crystal. Only Inaba et al. present results of temperature dependent densities of solid and liquid SAT [23]. In that study, the presented equation giving the density of liquid SAT as a function of the temperature does however not match with the diagram shown in the article. The same faulty expression is listed by Kenisarin and Mahkamov [9].

The effective density of SAT, may in the case, where it has solidified from supercooled state be very much like the density of the liquid SAT because it will solidify rapidly without time to contract to a dense mass. Therefore, a volume of cavities representing the difference in liquid and solid density may be enclosed in the solidified SAT.

1.3. Limitations

One of the limitations of using PCMs as heat storage material is a low heat transfer to and from the PCM (especially in solid state). The heat transfer is affected by the heat exchanger design and the properties of the PCM. The thermal conductivity governs the heat transfer when the PCM is in solid phase. In liquid state convection and thermal conduction governs the heat transfer. As most other PCMs, SAT has a relatively low thermal conductivity. The values in the literature for thermal conductivity of solid SAT varies between 0.4 and 0.7 W/(m·K) [9].

Dannemand et al. reported that the crystal structure of SAT which had solidified from a supercooled state was different from SAT which had solidified with minimal supercooling [19]. They state that the SAT solidified from a supercooled state did not contract uniformly and cavities were formed in the PCM during the fast solidification and crystallization. They showed that the measured thermal conductivity was lower in a sample which had solidified from supercooled state (0.3–0.6 W/(m·K)) compared to a sample which had solidified with minimal supercooling (0.7 W/(m·K)).

1.4. Heat storage applications

Various PCMs have been applied in heat storage development. Khan et al. did a review on ways to enhance the performance of PCMs in heat storages [24]. Dheep and Sreekumar did a review on the influence of nanoparticles on properties of different PCMs [25]. Sharif et al. describes ways to integrate PCM into domestic hot water storage systems (DHW) and concludes that PCM thermal energy storage is expected to lower cost and the volumes of heating and DHW systems [26]. Xu et al. did a review article on seasonal heat storage for solar heating system and mention SAT with supercooling as one of the technologies [27]. Zhou and Han did a numerical simulation of supercooled SAT in heat storage application [28]. Aydin et al. concluded that latent heat storage can improve the performance of solar heating systems and are especially useful during autumn and spring in the Istanbul climate [29]. Fazilati and Alemrajabi investigated adding PCM to a water tank for the solar heating system and find that the PCM improves its performance [30]. Sharma et al. also did an extensive review on thermal storage applications with PCM and state that the high storage density and isothermal storage process makes PCMs effective storage materials [7]. Cabeza et al. did a review on PCMs in building applications and presents different ways of applying the materials [22]. They present an overview of a range of PCMs, list important characteristics of PCMs, which has to be considered when designing an application. They also show different ways of encapsulating PCMs. Also a group of researchers in the International Energy Agency Solar Heating and Cooling program have in Task 32 and Task 42 investigated material properties and applications with PCMs including SAT [31,32].

When applying SAT or any other PCM in a heat storage it must be considered how the material will act in bulk quantities. It may be that the dimensions of the storage, operating temperature, repeated cycling etc. may cause the PCM to act differently compared to investigations made on small samples. Also, whether the storage is intended to operate with supercooling or not must be considered as it affects the thermal conductivity of the solid SAT.

In a heat storage design, the change of density between solid and liquid states and the associated volume change has to be accommodated for in some way. In experimental investigations Dannemand et al. solved the expansion and contraction of SAT inside prototype heat storage units by integrating an expansion tank in the storage design [16,17]. This allowed for operating the