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Experimental investigations on prototype heat storage units utilizing stable supercooling of sodium acetate trihydrate mixtures

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HIGHLIGHTS

- Heat storage based on stable supercooling of sodium acetate trihydrate is demonstrated.
- Thermal energy is stored partly loss free for two months.
- Heat exchange capacity rate and discharge power are evaluated.
- Energy contents of storage units with two different PCM mixtures are determined.
- Supercooling and thermal cycling stability are evaluated.

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ABSTRACT

Laboratory tests of two heat storage units based on the principle of stable supercooling of sodium acetate trihydrate (SAT) mixtures were carried out. One unit was filled with 199.5 kg of SAT with 9% extra water to avoid phase separation of the incongruently melting salt hydrate. The other unit was filled with 220 kg SAT mixture thickened with 1% carboxymethyl cellulose. The heat exchange capacity rate during the charging of the unit with the extra water was significantly higher than for the unit with the thickening agent due to the different levels of convection. The SAT mixtures in the units were stable and supercooled at indoor ambient temperatures for up to two months, after which the units were discharged. The energy discharged after solidification of the supercooled SAT and water mixture was 194 kJ/kg in the first test cycle, dropping to 179 kJ/kg after 20 test cycles. The energy discharged from the unit with SAT and the thickening agent after solidification was stable at 205 kJ/kg over 6 test cycles.

1. Introduction

Heating of buildings and domestic hot water represent a large part of society's energy demand. Heating demands are especially high in winter. Solar energy is available all year round in most regions on earth, but it is limited in high-latitude regions in winter. It is more abundant in summer, when it can easily be harvested as low-grade thermal energy using solar collectors.

Thermal energy storage integrated in energy systems can help to optimize the use of energy resources by peak-shaving and making it possible to implement more renewable energy sources in our energy infrastructure [1]. This can lead to a reduction in greenhouse gas emissions from our thermal energy use and a reduction in environmental pollutants. Implementing more thermal energy storage may lead to more sustainable energy systems and may help to reduce climate change.

1.1. State of the art

Short-term storage of solar thermal energy for space heating and domestic hot water is typically done in small water stores, where continuous heat loss limits the storage period. With very large water stores, it is possible to store enough thermal energy to heat a single-family house during a winter. Alternatively, a form of thermal energy storage without continuous heat losses would allow for a more compact storage, where thermal energy could be stored from summer to winter in a seasonal heat storage. Large water stores for centralized systems are based on a relativity mature technology. Bauer et al. reported on various types of seasonal sensible heat stores for central solar heating plants in Germany [2], and Novo et al. did a review seasonal heat storage in large water tanks and pits for centralized heating systems [3]. In

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both cases, the authors find the use of large sensible heat storage units feasible in centralized heating systems. On the smaller scale of individual buildings, Colclough and McGrath made a life cycle analysis of a low-energy single-family house with a solar combi system with a 23 m^3 water seasonal thermal energy storage [4]. They found that implementing seasonal heat storage in the combi system would reduce the carbon emissions and life cycle energy consumption of the system in the long term. Persson and Westermark looked at the financial aspect of seasonal thermal energy stores for individual houses and found that more competitive investment and annual costs could be offered if they were applied to passive houses [5]. Xu et al. did a review on available technologies for seasonal heat storage and reported that sensible heat storage technology has been implemented in many large-scale plants [6]. Their review also covered latent heat and chemical stores, which are still at the stage of material investigations and lab-scale experiments. Pinel et al. reviewed methods for seasonal storage of solar heat in residential applications, mainly focusing on sensible heat stores [7]. Their paper also mentions chemical and latent thermal energy storage principles. These technologies could be used to store thermal energy over longer periods in more compact systems, but they need further development. Yan et al. have reviewed promising candidate reactions for chemical heat storage [8], and Aydin et al. have reviewed thermochemical heat storage systems, including comparison with other storage methods. Both reviews conclude that the chemical storage principle is a promising technology, but needs further development before it can reach the market. Zondag et al. reported on the development of a small-scale prototype thermochemical heat storage system [9], and Mette et al. presented a solar thermal combi system with a thermochemical energy storage for long-term heat storage [10]. Both these reports demonstrate the storage principles, although they need more research.

1.2. Phase change material heat storage

Stores that use the latent heat of fusion of a phase change material (PCM) have been suggested by many authors for improving performance compared to sensible heat stores. Nkwetta et al. carried out numerical investigations on incorporating PCM in water tanks and found that it could increase the energy stored [11]. López-Navarro et al. did experimental investigations on a storage tank with PCMs and made a full experimental characterisation of its performance [12]. Nkwetta and Haghighat [13] and Sharif et al. [14] have written reviews on thermal energy stores with PCMs. None of these authors report using the supercooling of a PCM for long-term heat storage. In fact, the supercooling of a PCM in a latent heat storage has usually been seen as an undesirable effect that needs be avoided by using various nucleation agents. This is because it prevents the heat of fusion from being released as desired during the discharge process when the melting point of the PCM is reached [15]. However, when a PCM is in a supercooled state in temperature equilibrium with the ambient, the melting enthalpy of the PCM is stored, but no continuous heat loss occurs, which makes long-term heat storage possible. Sandnes and Rekstad carried out laboratory investigations on the stored enthalpy in small samples of supercooled salt hydrates [16], but do not report investigations of constructed storage units. Dannemand et al. have previously reported a number of barriers and solutions for the reliable operation of a storage unit utilizing the principle of stable supercooling of sodium acetate trihydrate (SAT) mixtures and elucidated the theoretical storage potential with numerical calculations [17], but they did not investigate the actual measured performance of storage units. One of the problems they list is the phase separation of the SAT. In another article, Dannemand et al. investigated the performance of a prototype unit containing a SAT mixture with extra water. The extra water was added to solve the phase separation problem. They focused on cycling stability, discharge power and discharge temperatures [18], but they did not explore the heat exchange capacity rate. Another way of avoiding phase separation is to add a thickening agent to the SAT. This has been investigated by several authors in small sample sizes [19–22]. However, the performance of SAT mixtures with thickening agents actively being used for supercooling in large application-size heat storage units has not previously been reported.

1.3. Scope

This article reports on laboratory tests of two full-scale heat storage units for building heating purposes that use the principle of stable supercooling with two different PCM mixtures. The performance of a unit with a SAT mixture with extra water was compared with the performance a unit with a SAT mixture with carboxymethyl cellulose (CMC) – a thickening agent for avoiding phase separation. The experiments showed that the storage principle works in full-scale application-size units and that the unit with the SAT mixture with CMC as a thickening agent had the highest heat content. The heat exchange capacity rate of the heat storage prototypes, which is an important factor in system performance, was measured and compared. We also measured the energy released after the solidification of the supercooled PCMs, the discharge temperatures after solidification of the supercooled PCMs, and the cycling stability of the two units. The results verify the functionality of the storage concept in real application-size units and give an indication of the performance that can be expected from the first prototype storage units.

2. Experimental setup

The primary storage medium in the prototypes tested was sodium acetate trihydrate (SAT), which has a melting point of 58 °C and a latent heat of fusion of 264 kJ/kg [23]. It has been shown to supercool consistently down to temperatures well below 0 °C [24]. SAT is an incongruently melting salt hydrate and suffers from phase separation, especially over repeated heating and cooling cycles, where segregated anhydrous sodium acetate settles to the bottom of the PCM container and the water concentration in the upper part increases due to the density differences. When a PCM sample suffering from phase separation solidifies, not all possible trihydrate crystals will be formed because of the physical separation of water molecules in the upper part of the sample and segregated anhydrous sodium acetate in the lower part. This will reduce the effective latent heat of fusion of the bulk PCM and thereby also its storage capacity [25]. One solution that has been proposed is to add extra water to the salt hydrate so that the salt water mixture composition is always at a point where all salt is dissolved in the water when it is in supercooled liquid phase [26]. This requires soft mixing of the salt water mixture to avoid phase separation and reduces the energy density of the storage [27]. Another proposed solution for avoiding phase separation is to add a thickening agent to the PCM mixture. A suitable thickening agent will keep segregated anhydrous sodium acetate from settling to the bottom and keep the anhydrous salt suspended in the solution near the water it can recombine with at solidification.

2.1. PCM mixtures and material properties

A sodium acetate water mixture was prepared by melting the solid SAT in a closed barrel in a large oven for several days. To increase the water weight content from 39.7% of the SAT composi-