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## Thermal conductivity enhancement of sodium acetate trihydrate by adding graphite powder and the effect on stability of supercooling

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### Abstract

Sodium acetate trihydrate and graphite powder mixtures have been evaluated to investigate the influence of the graphite powder on the stability of supercooling. A sodium acetate and water mixture mixed with graphite powder was successfully supercooled at ambient indoor temperatures for five months. The graphite powder was stabilized using carboxymethyl cellulose and successfully tested in heating and supercooling cycles with no loss of performance. Thermal conductivity enhancing properties of graphite powder was shown in samples.

Since the experiments were conducted in small scale, at 200 g per sample, large scale experiments are required to validate graphite as a thermo conductivity enhancing agent, suitable for use in seasonal heat storage applications utilizing SAT.

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### 1. Introduction

One of the fundamental challenges in using solar heat energy for any application is that it is an intermittent energy source. When using a solar domestic hot water system, SDHW system, or a solar combisystem, a heat storage is needed since supply and demand oftentimes are not in sync. For SDHW systems a water storage tank is often used

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as a short term store, so that solar heat can be used at a later time when there is no energy available from the sun. But the energy from the sun varies both over the course of a day but also with the seasons if the system is located some distance from the earth's equator. For a solar combisystem with both DHW supply and space heating some form of long term heat storage is necessary for the system to have a high solar fraction.[1]

There are several types of seasonal heat storage technologies available, as sorption heat storage and chemical heat storage but the focus of this paper is on latent heat storage in a solid to liquid phase change material. This technology utilizes the phenomenon that when materials change phases, this being from solid to liquid or from liquid to gas, it requires a large amount of energy to break the intermolecular bonds. This energy can be recovered as heat once the material is either condensed in to liquid or solidified. In this kind of energy storage there is the potential for zero loss of energy over time and this decoupling of energy loss and time means that a seasonal heat store for a one family house becomes a practical possibility.[2]

For different applications there are differently suited phase change materials (PCM) which melt or evaporate at a specific temperature. Water used in DHW applications should not have a tap temperature above 60 °C due to the risk of scalding of the user. To prevent calcite precipitation, if the water contains this, and unnecessary heat loss from the hot water tank the storage temperature of water should not be sustained above 55 °C, although periodic cycling to higher temperatures to inhibit bacteria growth is advised.[3]

In light of these temperature restraints a PCM with a melting temperature about 50 to 60 °C should be used to supply DHW. One such material is the salt hydrate Sodium Acetate Trihydrate (SAT). This material has several properties which makes it suited for use in DWH and heating systems:

- It has a latent energy content at 265 J/g.[4]
- It has a melting point of 58 °C.[4]
- It is nontoxic.
- It is inexpensive.
- It is available in large industrial quantities.
- It has the ability to supercool.

This last attribute is of special importance when it comes to seasonal heat storage applications. Supercooling enables the SAT to retain the latent energy of melting the salt crystals at 58 °C even when it is cooled to ambient temperature. In this liquid supercooled state the energy can theoretically be stored indifferently without loss.

One of the common problems with PCM's is their poor thermal conductivity. This means that their ability to charge and discharge heat leads to lower overall system performance than could have been obtained. There have been tested many compounds in the literature to improve the thermal conductivity of PCM's.[5][6] One of the most promising compounds is graphite. This carbon compound has many characteristics which makes it ideal as a thermal conductivity enhancer.

- It has a comparatively high thermal conductivity 25-500 W/mK.
- It is non-metallic which means that there is no galvanic corrosion risk.
- It is nontoxic.
- It is inexpensive.
- It is available in large industrial quantities.

In most applications where SAT has been used with any additives the supercooling effect has been sought avoided. This means that the subject of stable supercooling of SAT combined with graphite has not been investigated, and since this supercooling is a central principle of the seasonal heat storage it is essential. It is this subject which this paper will evaluate through a thorough investigation.

## 2. Investigations

In the following sections several test methods have been used to investigate the phenomenon surrounding the interaction of SAT and graphite. A special interest has been given to the subject of supercooling. In the first part of the investigation the subject of supercooling pure SAT and the prerequisites for this are examined.

### 2.1. Supercooling of SAT

Sodium Acetate Trihydrate,  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , is an inorganic salt hydrate which has been the subject of many scientific investigations with regards to its use as a heat energy storage PCM.[7] Sodium acetate is a natural acid present in most fruit and has the European food additive number E262.[8] Being the only hydrate containing sodium acetate which is stable, SAT contains 60,28 wt% sodium acetate and 39,72 wt% water. It has a relatively high latent heat of fusion compared to other PCM's, it is available in industrial volumes and relatively inexpensive. In many other applications the supercooling properties of the SAT is seen as a disadvantage, but in the case of seasonal heat storage this phenomenon is of great importance. It is precisely this ability to be supercooled to ambient temperatures which enables the SAT to store energy indefinitely.

SAT has a melting point of 58 °C but at this temperature the sodium acetate is not fully soluble in the corresponding water coming from the SAT. One observation done in this research work is that if the SAT is only melted and not further heated it is very unlikely to stably supercool because of nucleation crystals. As it can be seen from Fig. 1 the sodium acetate is first fully soluble at temperatures above 83 °C. This means that the SAT should be heated to more than 83 °C to facilitate stable supercooling.

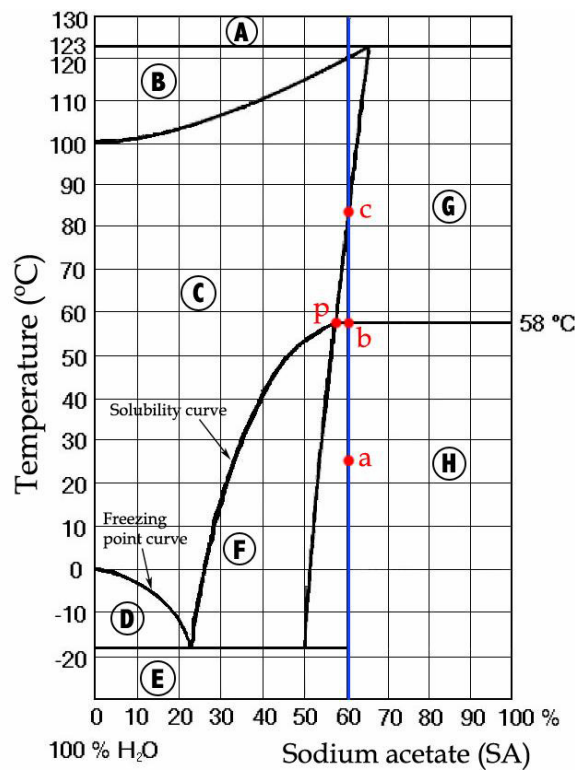


Fig. 1 Phase diagram of sodium acetate and water. A: Vapor, B: Anhydrous sodium acetate and water vapor, C: Liquid sodium acetate solution, D: Sodium acetate in liquid state and water in solid state, E: Water in solid state and sodium acetate trihydrate, F: Solid sodium acetate trihydrate with excess liquid water (not supercooled), G: Liquid sodium acetate trihydrate and water (when supercooled), H: Anhydrous sodium acetate in liquid, brine type of phase, H: Solid sodium acetate trihydrate and solid anhydrous sodium acetate (not supercooled), H: Liquid sodium acetate trihydrate with precipitate of anhydrous sodium acetate (when supercooled).[9]

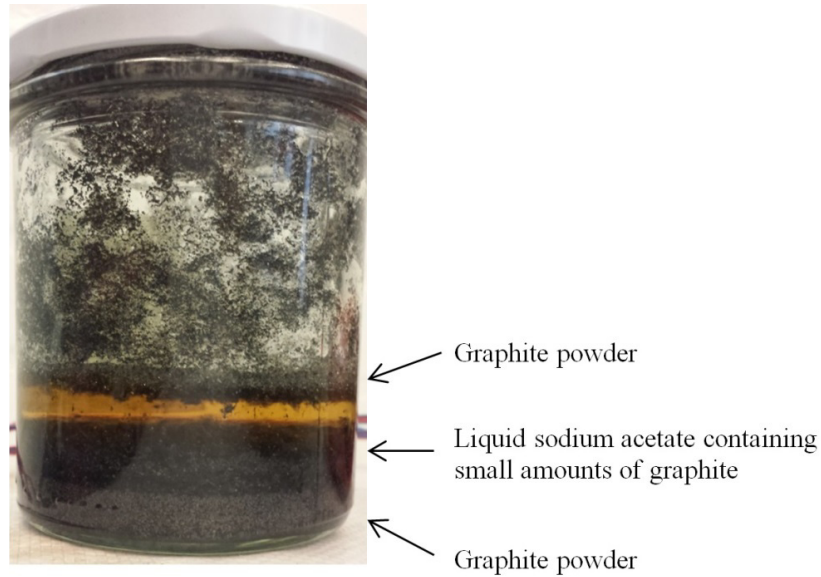


Fig. 2 Sample containing a sodium acetate and water mixture with added graphite powder supercooled for five months.

### 2.2. Long term supercooling of SAT and graphite

To evaluate the effects on the stability of supercooling of SAT when graphite powder is added several experiments were undertaken. One such experiment was looking at SAT mixed with graphite and the long term supercooling stability. To reduce the effects of SAT phase separation extra water was added so the final water content of the sodium acetate and water mixture was 46 wt% water. Samples were heated to 95 °C and then cooled to ambient temperature. Periodically mechanical agitation of the sample was made to evaluate the stability of the supercooling. As can be seen by Fig. 2 there was no change in the sample during the five months experiment with supercooling. The composition of the samples can be seen in table 1. At the present time the samples have not shown any signs of spontaneous solidification. Graphite powder as well as expanded graphite powder was examined to determine the effect on supercooling.

Table 1 The composition of the samples which has been supercooled for five months.

Water [wt%]	Sodium Acetate [wt%]	Graphite [wt%]	Compound	Grain size [ $\mu\text{m}$ ]
43.7	51.3	5	Powder	<50
41.4	48.6	10	Powder	<50
43.7	51.3	5	Expanded	100
41.4	48.6	10	Expanded	100

### 2.3. SAT and graphite thermal conductivity

As has been described in the literature, there is ample evidence to support the claim that graphite can work as a thermal conductivity agent, [6][10]. In this experiment 1 wt% graphite powder was mixed with a sodium acetate and water mixture containing 45% water and put in a mold of 30 x 30 x 3 cm (width x depth x height). After solidification a thermal conductivity test was conducted using an *Isomet heat transfer analyzer model 2104*. An

identical reference sample containing sodium acetate and water mixture and 1wt% CMC was made. The thermal conductivity was measured five different places on the two samples and an average thermal conductivity was ascertained at 25 °C. This test showed an average difference in thermal conductivity of 39.3 % from 0.433 W/mK to 0.603 W/mK with an accuracy of 10%, from the sample containing CMC to the sample containing graphite powder. A similar test was done using SAT, 0.5wt% xanthan gum and 5wt% graphite powder. Here the thermal conductivity was measured to be 0.746 W/mK, even though the sample had water content lower than the other two samples. This result is comparable with results found in other studies where the results shows the potential of graphite to enhance the thermal conductivity by several hundred percent.[6]

#### 2.4. SAT, graphite and additives in cycle test

Since the aim of this paper is to describe SAT in the context of seasonal heat storage application, and aspect of this is that the mixture should be able to withstand many heating, cooling and solidification cycles. In order for the SAT to be used in this application the thermal performance cannot decrease significantly without affecting the overall system performance. As has been the experience during this investigation and also reported by several studies in the literature SAT suffers from severe phase separation when subjected to heating and cooling cycles.[11] As has also been shown with the long term supercooling test in this report the density difference between the graphite particles and the SAT prevents a homogeneous mixture without stabilizing additives.

In the literature many compounds have been tested to reduce or eliminate phase separation of PCM's, and CMC has been shown to both eliminate phase separation and improve the heat energy content.[12] In the experiments conducted as a part of this investigation CMC has also outperformed Xanthan gum (X-gum), another gelation agent, in all tests with regard to temperature of sample after activation. One thing which makes CMC and SAT such a good match is that CMC gets a very low viscosity at around 80 °C and this reduces the need for strong mixing since osmosis will contribute to the mixing of the compounds. Since SAT needs to be heated to higher temperatures to insure stable supercooling this means that a homogeneous mixing of the compounds is assured. Like SAT and graphite CMC is also nontoxic (European food additive number E466), inexpensive and available in industrial quantities, as it is used for many applications like in the production of ice cream and toothpaste.

The samples in glass jars with metal lids were heated in an oven for at least 12 hours to a temperature above 85 °C. Then the samples were placed at room temperature and the cooling of the samples was monitored. After the samples had cooled, the temperature of the samples was monitored for several days. The samples were then solidified by dropping single crystals of SAT on top of the mixtures. The subsequent heating of the samples was monitored until the samples reached ambient temperature again and the samples were placed in the oven for reheating. As it can be seen from Fig. 3 that repeated supercooling of the samples is possible.

Table 2 The composition of samples containing two types of gelation agents.

Number	SAT [g]	Graphite [g]	%wt	Additive [g]
1	205.05	10.25	5	4.10 X-gum
2	205.01	10.25	5	4.10 CMC

The composition of the samples can be seen in Table 2. The composition is the result of a large amount of experiments considering both the amount of graphite necessary to sufficiently enhance the thermal conductivity to be used in practical applications and the amount of gelation agent necessary to eliminate phase separation over a large number of heating and cooling cycles.

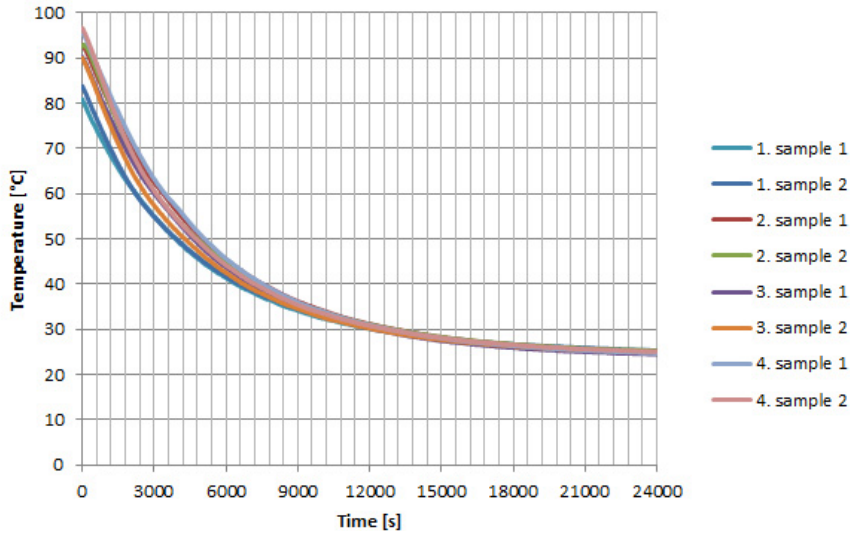


Fig. 3 Temperatures for samples containing SAT, graphite and gelation additives during 4 supercooling periods.

After the samples supercool they are activated by introducing single grains of SAT to the surface of the samples. The solidification happens in the course of a few seconds and the heat is then dissipated to the surroundings in approximately five hours, as can be seen on Fig. 4.

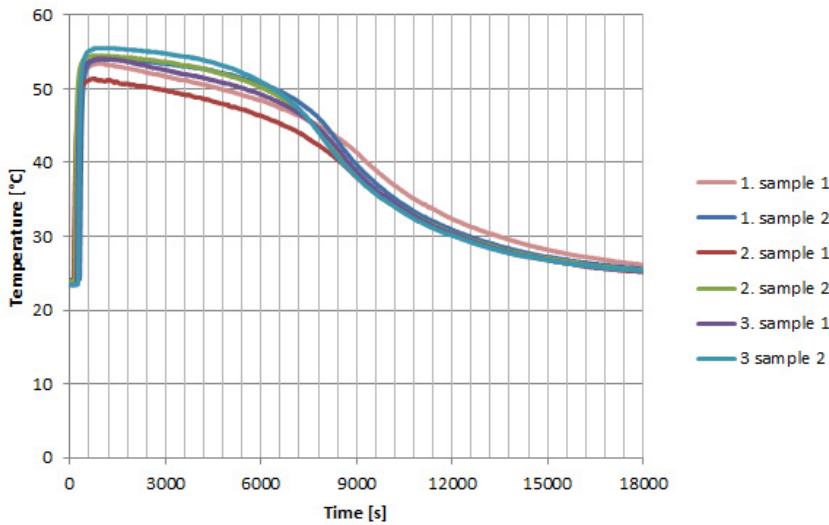


Fig. 4 Activation of samples and dissipation of heat energy after 3 supercooling periods.

### 2.5. SAT and graphite in low temperature test

Samples in glass jars with metal lids containing 180 g of SAT were heated to 89 °C for 24 hours and then placed in a freezer with a temperature of -35 °C. One sample type with SAT and 1% graphite powder and one only with SAT. This was to investigate if SAT and graphite spontaneously solidified at another temperature than pure SAT. The SAT and graphite mixture had an activation temperature of -12.7 °C which is only 1.7 K higher than pure SAT. The experiment was repeated several times and an example of the cooldown curve can be seen on Fig. 5.

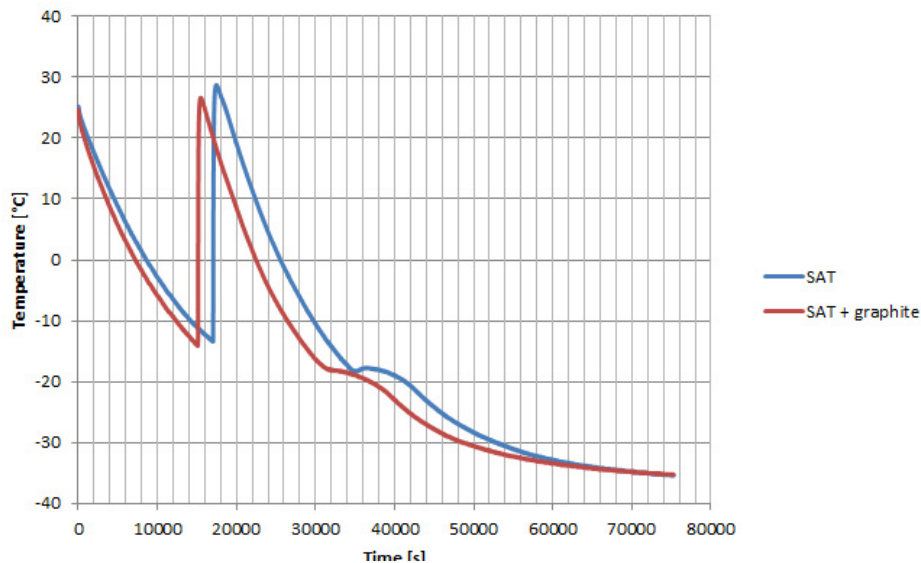


Fig. 5 The cool down curves for SAT samples containing additives.

### 3. Discussion

The aim of this investigation is to elucidate the relationship between SAT and graphite with a special interest in supercooling. Since supercooling is essential when utilizing SAT in seasonal heat storage applications it is paramount that this ability is not compromised when additives are added.

It has been shown by the data presented in this paper that SAT can stably supercool with additives. There has however only been presented results from small scale experiments conducted at 1000<sup>th</sup> of the scale of a practical SAT seasonal heat storage module. The typical sample size was no larger than 200 g of SAT and module sizes are expected to be in the 200 kg range. There has in other scientific studies been reported problems when changing from small scale ideal conditions to real life size modules.[13]

Problems with phase separation was also found between the graphite additive and the SAT. This was resolved by adding CMC to the mixture. Since the heat storage modules in a practical system would be heated to nearly 100 °C for several months the CMC would be under considerable thermal stress. Under previous experiments this heating caused the CMC to become darkened and this can be seen as a sign of the degradation of the CMC under such conditions.

#### 4. Conclusions

In this paper results of a number of small scale tests have been presented. The topic of the investigation has been to investigate SAT and the effects graphite powder has on the ability of the SAT to supercool. Graphite can be used as a very potent thermal conductivity enhancing agent. It has been shown that a sodium acetate and water mixture can stably supercool for at least five months and showing no signs of spontaneous solidification, when 5 wt% graphite powder was added. Several cycle experiments were conducted to show the continued ability of the SAT to stably supercool with graphite powder added. Freezing test was conducted and a minute rising in the spontaneous solidification temperature was detected. This temperature of -12.7 °C is however below the expected operating temperature of a seasonal heat storage system, and does not exclude graphite as an additive.

To combat phase separation CMC was used and showed a stabilizing effect. The thermal conductivity test conducted showed a 39 % increase in the thermal conductivity of the samples containing 1 wt% graphite.

Further tests should be made to evaluate the scaling of the results to full scale applications.

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