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Ageing stability of sodium acetate trihydrate with and without additives for seasonal heat storage

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Abstract

Sodium acetate trihydrate is a promising phase change material used for seasonal heat storage because it can supercool in a stable way down to ambient temperature. One challenge of this material is that it might suffer from phase separation resulting in a low utilization of the heat of fusion. Adding extra water or thickening additive has been suggested as an effective way to reduce the phase separation problem and thereby maximize the heat content of the sodium acetate trihydrate. Investigations of phase separation and heat content of supercooled sodium acetate trihydrate with and without extra water and additives were carried out under different test conditions. It was found that sodium acetate water mixtures with water contents lower than or equal to 42% would suffer from phase separation for the height of heat storage up to 8 cm. The heat content of sodium acetate trihydrate will be decreased by adding extra water. Sodium acetate trihydrate with Carboxy-Methyl Cellulose and Xanthan Gum as additives are promising heat storage materials with high heat contents and ageing stability.

Keywords: *sodium acetate trihydrate, phase change material, ageing stability, phase separation*

1. Introduction

Sodium acetate trihydrate ($\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$), consisting of 60.3% (weight %) sodium acetate and 39.7% (weight %) water, is a promising Phase Change Material (PCM) used for seasonal heat storage because of its relative high heat of fusion at the melting point of 58°C and its long term stable supercooling ability (Furbo et al., 2010). Sodium acetate trihydrate or its water mixture is long time stable and no ageing effects are known. Experiments have shown that the salt water mixture can be stable supercooled for years. Fig. 1 shows supercooled sodium acetate water mixture samples which have been in supercooled state for approximately 3 years at indoor temperature. Even impurities such as rusty iron immersed in the supercooled sodium acetate water mixture has not influenced the stability of the supercooling, see the right sample of Fig. 1.



Fig. 1: Long term supercooled sodium acetate trihydrate water mixture samples

In practical applications sodium acetate trihydrate might suffer from phase separation especially in the supercooled state. This is the phenomenon where anhydrous salt settles to the bottom due to its higher density compared to the density of saturated sodium acetate water solution. The heat released from the crystallization of the supercooled sodium acetate trihydrate with phase separation will be lower compared to the heat released from supercooled sodium acetate trihydrate without phase separation. Adding extra water (Furbo and Svendsen, 1977) or thickening agent (Cabeza et al., 2003) has been suggested as effective ways to reduce the phase separation and to maximize the heat content of the sodium acetate trihydrate.

This paper investigates phase separation for different heights of long term supercooled sodium acetate water mixtures by measuring the water contents in different layers, the heat content of different sodium acetate water mixtures after short and long periods with supercooling and the heat content of sodium acetate trihydrate with thickening agents CMC and X-Gum by cycle and long term tests. The test results show that sodium acetate trihydrate with CMC and with X-Gum as additives is promising heat storage materials with high heat contents and long term stability.

2. Phase separation investigations for different heights of long term supercooled sodium acetate water mixtures

The test method is described as follows:

Step 1: Prepare samples of sodium acetate water mixtures with 40%, 42%, 45%, and 46% (weight %) water with the same height in the plastic bottles shown in Fig. 2.

Step 2: Heat the samples in the oven to a temperature between 80 °C and 85 °C until the salt water mixture is fully melted.

Step 3: Take the samples out from the oven. Let them cool down to indoor ambient temperature and let them stay in a supercooled state for the desired duration.

Step 4: Initialize the crystallization of the samples, so that the salt water mixtures solidifies. The samples are left to cool down to the ambient temperature.

Step 5: Cut each sample evenly into 3 or 4 horizontal layers and put into glass bowl as shown in Fig. 3. Measure the mass of the empty glass bowls and the glass bowls with salt water mixtures before heating.

Step 6: Put the glass bowls with salt water mixtures into an oven with the temperature above 100 °C and measure the mass when all water is evaporated.

Step 7: The water percentages of each layer of the samples are determined based on the mass measurements.



Fig. 2: Plastic bottles with sodium acetate water mixtures



Fig. 3: Empty glass bowls

Experiments were carried out with 4 cm, 5 cm and 8 cm heights of the liquid sodium acetate water mixtures.

Four samples of sodium acetate water mixture of each height were made: 40% water & 60% sodium acetate, 42% water & 58% sodium acetate, 45% water & 65% sodium acetate and 46% water & 54% sodium acetate. All 12 samples was left unmoved in supercooled state for approximately 130 days and then activated by dropping seed crystals in the plastic bottle. The photos of supercooled samples of different heights before activation are shown in Figs. 4-6.



Fig. 4: 4 cm salt water mixtures after 126 days supercooling, 46%, 45%, 42%, 40% water samples from left to right



Fig. 5: 5 cm salt water mixtures after 129 days supercooling, 46%, 45%, 42%, 40% water samples from left to right



Fig. 6: 8 cm salt water mixtures after 131 days supercooling, 46%, 45%, 42%, 40% water samples from left to right

From Fig. 4 to Fig. 6 it can be seen that all the 40% and 42% salt water mixtures had visible solid segregations, while the 45% and 46% salt water mixtures remained clear and transparent after 120 days in supercooled state. The segregated salt in the 40% and 42% salt water mixtures was “soft” and “loose”. Both the 40% and 42% salt water mixtures had a clear solution layer on the top.

Table 1 to Table 3 show the water contents distribution in the layers of each sample indicated by “Top”, “Middle” and “Bottom”. The four layers used in the 8 cm samples are referred as “Top”, “Upper Middle”, “Lower Middle” and “Bottom”. The accuracy of measured mass is 0.1 g. It is assumed that if the water content in a layer is lower than the 39.7% of the trihydrate composition then phase separation is occurring. The water percentages which were lower than 39.7% are shown with red color indicating phase separation. The last row is used for checking the total water content of samples after cutting and heating by summing up evaporated water and salt water mixture of all layers.

Tab. 1 Water content distribution in 4 cm high salt water mixture samples after 126 days supercooling

4 cm samples	40% water sample (%)	42% water sample (%)	45% water sample (%)	46% water sample (%)
Top	44.7	43.5	45.4	45.8
Middle	38.6	42.1	45.3	46.0
Bottom	37.3	42.0	45.6	45.9
Water Recheck	40.2	42.5	45.4	45.9

Tab. 2 Water content distribution in 5 cm high salt water mixture samples after 129 days supercooling

5 cm samples	40% water sample (%)	42% water sample (%)	45% water sample (%)	46% water sample (%)
Top	43.9	45.0	45.4	46.4
Middle	39.4	44.9	45.6	46.4
Bottom	38.0	39.5	45.2	46.6
Water Recheck	40.0	42.4	45.4	46.5

Tab. 3 Water content distribution in 8 cm high salt water mixture samples after 131 days supercooling

8 cm samples	40% water sample (%)	42% water sample (%)	45% water sample (%)	46% water sample (%)
Top	44.7	44.9	45.9	46.5
Upper Middle	40.2	43.5	45.8	46.5
Lower Middle	38.6	40.1	45.5	46.2
Bottom	37.0	39.7	44.3	46.0
Water Recheck	39.9	42.0	45.2	46.3

From Table 1 to 3 it can be seen that the 40% water content salt water mixtures of 4 cm, 5 cm and 8 cm height all suffered from phase separation because the water content of the bottom layer was lower than 39.7% after 120 days in supercooled state which means sodium acetate trihydrate cannot be used as a stable heat storage material for container height higher than or equal to 4 cm.

All the 42% water content salt water mixtures had water contents in the lower parts of the samples of minimum 40%. The smaller the height of the salt water mixture is, the lower the difference between the water content from the bottom to the top of the sample will be. The results indicates that sodium acetate water mixtures consisting of 42% water and 58% sodium acetate won't suffer from phase separation problems as long as the salt water mixture height is lower than 8 cm. However, conclusions on the long term stability of 42% mixtures must also include considerations of the heat content stability, see section 3.

All the 45% and 46% water content samples have relatively even water content in each layer and don't suffer from phase separation.

It can be concluded from the experiments that too low water content and a too high sample height will cause phase separation problems for long term supercooled sodium acetate water mixtures.

3. Heat content measurements of supercooled sodium acetate samples

3.1. Experimental method and test facilities

A simple heat loss method was used to determine the heat content of different supercooled sodium acetate trihydrate samples with and without additives. This was done by recording the temperature history after starting the crystallization of the supercooled samples at ambient temperature. The crystallizations were started by dropping crystals into the samples, which were placed in a glass jars. After crystallization the samples cooled down to ambient temperature again inside a well-insulated box. When the heat loss coefficient of the glass jar in the well-insulated box is determined the heat released from the samples cooling down can be calculated by Eq. (1).

$$E = \int_{t_b}^{t_e} UA(t) \cdot [T_s(t) - T_a(t)] \cdot dt / m \quad (\text{eq.1})$$

Where E (kJ/kg) is the measured heat content, T_s (°C) and T_a (°C) are the sample and ambient temperature. t_b (s) and t_e (s) are the begin and end time during the heat release process. m (kg) is the sample mass. UA (W/K) is the heat loss coefficient of the glass jar in the well-insulated box determined by testing the cooling process of hot water in the same glass jars with the same height as sodium acetate samples. The UA can be calculated by Eq. (2).

$$UA = \frac{mC}{t_e - t_b} \ln \frac{T_e - T_a}{T_b - T_a} \quad (\text{eq.2})$$

Where mC (J/K) is the total heat capacity including water, glass jars and lid. T_b (°C) and T_e (°C) are the start and end sample temperature during the period from t_b to t_e .

The samples were all prepared in glass jars as shown in Fig. 7(c) with the height of 5 cm. Three thermocouples pasted outside were used to estimate the average sample temperature, see Fig. 7(b). One thermocouple was fixed outside of the box for recording the ambient temperature, see Fig. 7(a).

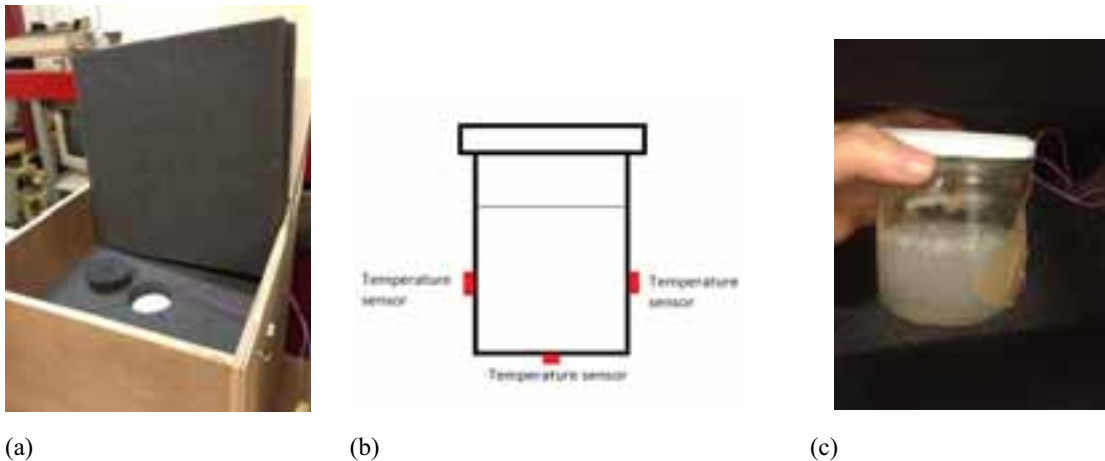


Fig. 7: (a) The well insulated box (b) Temperature locations (c) Glass jar

3.2. Heat content measurement of sodium acetate water mixtures with different supercooled duration

Samples of sodium acetate water mixtures with 40%, 42%, 45% and 46% water content with a sample height

of 5 cm were prepared in glass jars. Three glass jars of each sodium acetate water mixture, in total 12 glass jars were prepared. The sodium acetate water mixtures were tested with different durations of the supercooled period: short supercooled period less than 14 days, 41 days and 100 days. The tests with the short period of less than 14 days were repeated several times and the average results are given. The results are shown in Table 4 and plotted in Fig. 8 (D2.4, 2015).

It can be seen that for the short term supercooled duration tests the 42% mixture had the highest heat content. If the water content was decreased to lower values than 42% or increased to higher values than 42%, the heat content will decrease. By increasing the supercooled duration to 41 days, the heat content was only reduced for the 42% mixture. By increasing the supercooled duration to 100 days, the heat content of both the 40% and 42% mixtures were significant lower compared to the shorter supercooled duration, while the heat content of the 45% and 46% mixtures were not decreased. The reduced heat contents are marked with red color.

The results of the heat content investigations are in line with the findings of phase separation investigations in section 2. The 40% and 42% salt water mixtures with 5 cm heights suffered from phase separation problems for long term heat storage periods. Adding more extra water is an effective way to solve the phase separation problem but the heat content will be decreased.

Tab. 4 Heat content of the 40%, 42%, 45% and 46% water salt mixtures

Water content of salt water mixture	Heat content (kJ/kg)		
	Short term average	Long term (41 days)	long term (100 days)
40%	162	162	99
42%	194	162	165
45%	165	163	172
46%	159	156	150

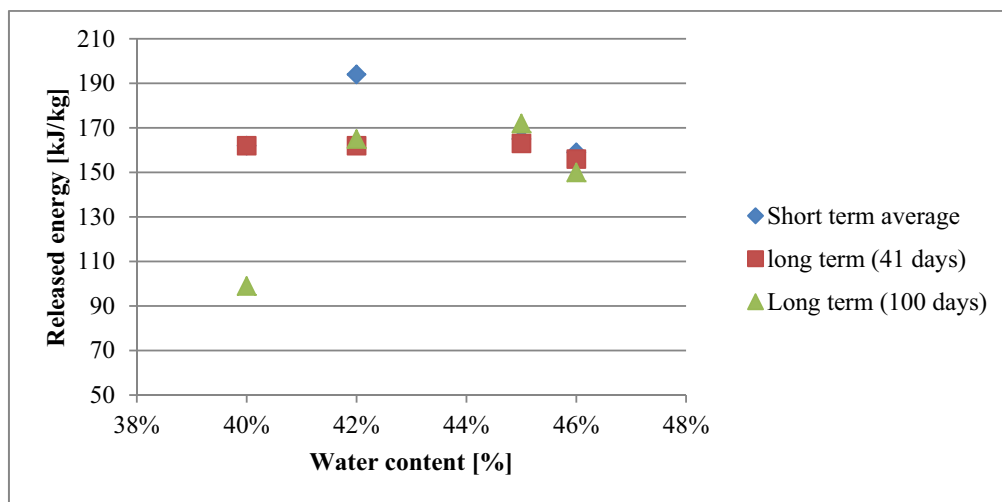


Fig. 8: Heat content of the 40%, 42%, 45% and 46% water salt mixtures

3.3 Heat content measurement of sodium acetate trihydrate with thickening additives

Carboxymethyl Cellulose (CMC) and Xanthan Gum (X-Gum) are thickening agents widely used in the food industry. The thickening effect can increase the viscosity of the liquid sodium acetate trihydrate and suspend the anhydrous salt in the container so that phase separation is reduced.

In small scale experiments, previous studies (Kong et al., 2015) showed that the heat content of sodium acetate trihydrate with 0.5% to 2% CMC or 0.3% to 0.5% X-Gum was increased typically 30% compared to pure sodium acetate trihydrate suffering from phase separation in short supercooled periods, see Fig. 9. The

green line and the purple line are the average heat contents of the 40% and 42% water content salt water mixtures. The blue and red pillars represent the results of the heat contents of sodium acetate trihydrate with different quantities of X-Gum and CMC.

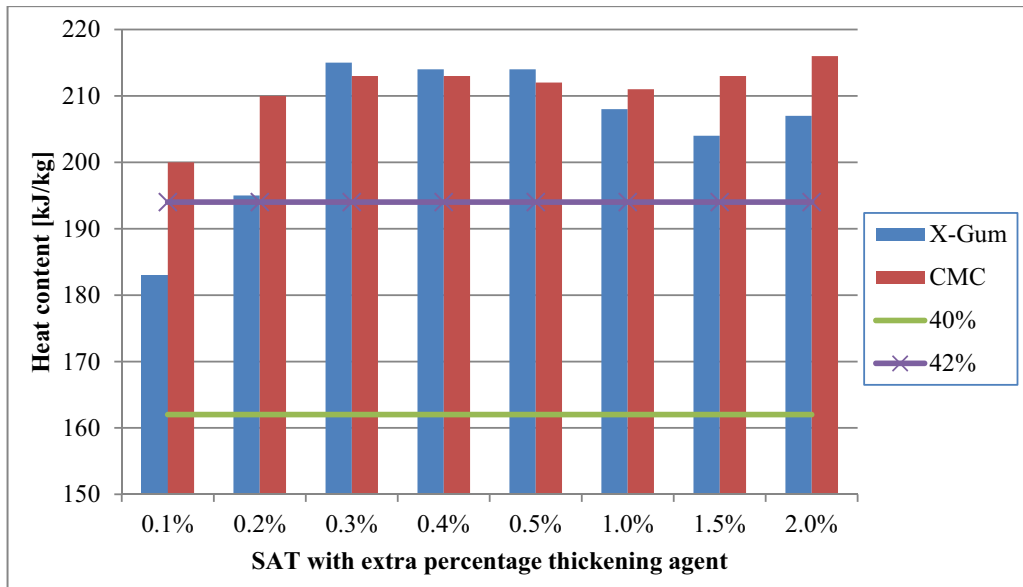


Fig. 9: Heat content of sodium acetate trihydrate with different quantities of thickening agents in short term supercooled period (Kong et al., 2015)

Ageing stability tests of sodium acetate trihydrate with extra water and with CMC were carried out through prototype modules which were designed for a demonstration seasonal heat storage system (Dannemand et al., 2015). The module was constructed by Nilan A/S as a flat plate shape. The chamber with the height of 5 cm containing PCM materials lies in the middle of module. An extension chamber is incorporated in one end at the top surface allowing for expansion of the PCMs when they are heated. An expansion bag or expansion vessel is connected to the extension chamber. Two heat exchangers with manifolds are attached on the top and bottom of the PCM chamber with the height of 4 mm. Parallel channels inside of the heat exchanger covered the entire area of the top and bottom surface of the PCM container aiming to guide a uniform flow distribution. Water is used as the heat transfer fluid running through the heat exchangers for transferring energy between PCM and test facility. The diagram and photo of the flat plate module can be seen in Figs. 10 and 11.



Fig. 10: Diagram of the prototype module (Dannemand et al., 2015)

Two flat plate modules with different PCM materials were tested. One module was filled with 199.5 kg of sodium acetate water mixture consisting of 44.8 % water and 55.2 % sodium acetate by weight. Repeating tests were carried out for 20 times with different flow rates, charge and discharge powers, temperatures settings and durations for a period of 8 month. The longest stable supercooled duration of the module at indoor ambient temperature was two months. Then it was activated manually and the latent energy was discharged. The energy discharged of the first test cycle was 194 kJ/kg and then it dropped to 179 kJ/kg in the later test cycles. That is a 7.5 % decrease of energy released after repeating test cycles.

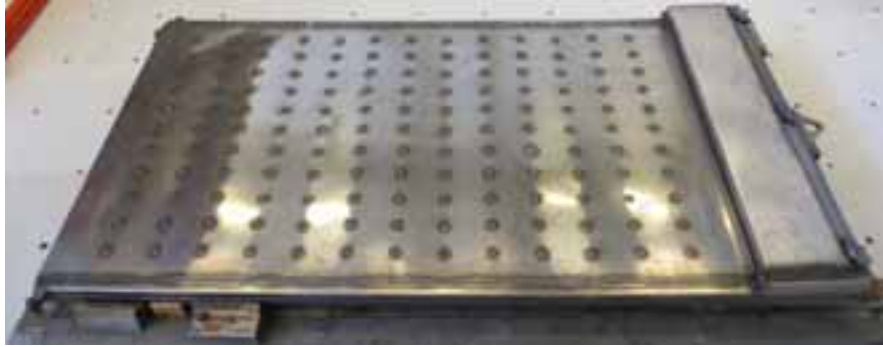


Fig. 11: Photo of the prototype module (Dannemand et al., 2015)

Another module was filled with sodium acetate trihydrate with 1% CMC, 2% graphite powder and 5 liter paraffin oil, totally 202 kg. The purpose of adding graphite and oil is to increase the heat exchange capacity rate. 10 repeating tests with similar flow rates, charge and discharge powers and temperatures settings were carried out over 2 month period. The energy discharged of the sodium acetate trihydrate with these additives was 200 kJ/kg in the first test cycle and kept stable around 201 kJ/kg in the following test cycles. The module reached stable supercooled at indoor ambient temperature for 8 days and then activated spontaneously. The energy discharged after 8 days was still 200 kJ/kg which illustrated that sodium acetate trihydrate with CMC as heat storage material had heat content stability after repeating tests and long term supercooling.

Ageing stability tests of sodium acetate trihydrate with X-Gum were carried out with another kind of prototype module which was designed as a vertical cylindrical container made of stainless steel by H.M. Heizkörper GmbH & Co. KG (Dannemand and Furbo, 2014). The module with EPP insulation is shown in Fig. 12. A plastic tube is installed with one end connecting to the top of the module and with the other end connecting to an air filter. The design can keep the same pressure of inside and outside module by allowing air exchange through the tube and the air filter. There is a heat exchanger inside the cylindrical module which consist stainless steel pipes in a circular formation with thin aluminum fins attached and manifolds located on the top and the bottom. The module is connected to a heating and cooling test facility. Water is used as the heat transfer fluid passing through the heat exchanger from bottom to top.

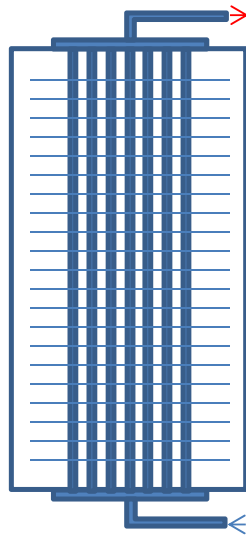


Fig. 12: Diagram and photo of cylinder module

The module contained sodium acetate trihydrate with 0.48% fine powder of Xanthan Gum (X-Gum-F) and 4.4% fine powder of graphite, totally 116.3 kg. The PCM material filled approximately 90% of the total

volume inside of the module. 20 repeating tests with similar charge and discharge flow rates, heating powers and temperature settings were carried out over four months. The module still had problems with stable supercooling possibly due to dust which caused spontaneous crystallization through the air filter and the tube into the top of the module. The longest supercooling period during these test cycles was 9 days. The energy discharged from the PCM was 205 kJ/kg at the first test cycle and stable at this level in the following test cycles.

Tab. 5 Summary of prototype module tests

PCM material	Prototype module	Heat content of the first test (kJ/kg)	Number of cycle tests	Heat content of last test (kJ/kg)	Longest supercooling duration (days)	Heat content after longest supercooled duration (kJ/kg)
44.8% water +55.2% sodium acetate	Flat plate	194	20	179	60	179
Sodium acetate trihydrate +1% CMC+2% graphite+5 liter paraffin oil	Flat plate	200	10	200	8	200
Sodium acetate trihydrate +0.48% X-Gum+4.4% graphite	Vertical cylinder	205	20	206	9	207

The prototype module test results are summarized in Table 5. It can be concluded from the laboratory prototype module tests that a sodium acetate water mixture with 44.8% water will suffer from phase separation and the energy released will decrease after repeating cycles and long term supercooled period. The sodium acetate trihydrate with CMC and X-Gum have high stability of released energy for repeating test cycles and are promising for stability for long term supercooling.

4. Conclusions

Phase separation is a key problem related to long term stability of seasonal heat storages based on stable supercooling of sodium acetate trihydrate with and without additives. Water content measurements in different layers of sodium acetate water mixtures after long term supercooled periods and heat contents measurements of sodium acetate trihydrate with additives in repeating and long term supercooled periods were investigated and presented in this paper. Based on the investigations it is concluded that:

Sodium acetate trihydrate and sodium acetate water mixtures with water contents lower than or equal to 42% will suffer from phase separation problems for the height of heat storage less than or equal to 8 cm. Sodium acetate water mixtures with water contents higher than 42% will not suffer from the phase separation if the heat storage height is lower than or equal to 8 cm. However, the heat content of the heat storage material will be decreased by adding extra water.

Sodium acetate trihydrate with the additive CMC and X-Gum are promising seasonal heat storage materials since they have high heat contents and ageing stabilities in repeating tests and long term supercooled durations.

5. References

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