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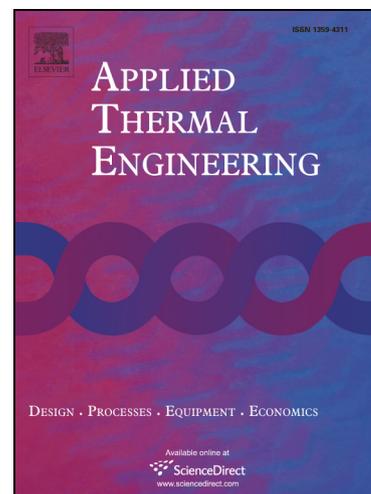
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# Experimental investigations on phase separation for different heights of sodium acetate water mixtures under different conditions

Weiqiang Kong<sup>\*</sup>, Mark Dannemand, Jakob Berg Johansen, Jianhua Fan and Simon Furbo

<sup>a</sup> *Department of Civil Engineering, Technical University of Denmark, Brovej, DK-2880 Kgs. Lyngby, Denmark*

*\*Corresponding author: Weiqiang Kong*

## Abstract

Phase separation is a key problem when using sodium acetate trihydrate (SAT) as phase change heat storage material. The formation of phase separation is highly correlated to the composition of SAT based heat storage material, the material height, operation method and environmental condition. This study focus on the phase separation investigation by means of measuring exact water proportions in different layers of SAT samples. The SAT samples were made with or without different amount of excess water or thickening agents at different heights. Then the samples were tested in supercooled state under different environmental conditions such as short or long term supercooling periods, standing still or shaking from time to time during supercooling, repeated heating and activating and low ambient temperature. The solidification of supercooled samples was activated from top or bottom in order to verify the influence of activation methods. The water proportions in different layers of SAT samples were measured and summarized for comparison. It can be concluded from the experiments that suitable amount of excess water or thickening agents and proper shaking are beneficial to reduce or avoid phase separation. On the other hand, SAT without any additives, repeated heating and activating and low ambient temperature are favourable to forming phase separation for supercooled SAT materials.

**Key words:** sodium acetate trihydrate; phase separation; water proportion; phase change material; heat storage

## 1 Introduction

### 1.1 Background

Heat storage [1,2] has become a hot research issue and a key point in renewable energy systems since it is a promising way of solving the mismatch of heat demand and intermittent renewable energy supply. Heat storage can be widely used in different application areas, such as domestic hot water and space heating [3], building integration[4,5], industry process heat [6] and so on.

For decades, Phase Change Materials (PCMs) were investigated as promising heat storage materials due to its high energy density by using of the latent heat of fusion [7]. For some long term or seasonal heat storage application, PCM can be applied without heat loss by using its stable supercooling ability [8]. Dannemand [9] reported a cylindrical heat storage unit utilizing stable supercooling of sodium acetate trihydrate composites. It was tested in a laboratory with charging and discharging cycles and validated that the principle of utilizing stable supercooling for partly loss-free heat storage can work. A European Union funded project COMTES [10] demonstrated a solar combi system with compact long term PCM heat storage [11]. The flat plate “sandwich” shape heat storage unit also employed sodium acetate trihydrate as the PCM[12,13]. The principle of utilizing long term supercooling for seasonal heat storage was validated[14,15].

### ***1.2 Sodium acetate trihydrate and phase separation problem***

Sodium acetate trihydrate (SAT) is a potential PCM candidate widely used in domestic temperature range, short term heat storage and seasonal heat storage applications. SAT, according to its chemical molecular,  $\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , consisting of 39.7% (wt.%) water and 60.3% (wt.%) sodium acetate. It has the ability of stable supercooling under ambient temperature for long time [16] and has relatively high heat of fusion 264 kJ/kg at the melting temperature of 58 °C [7]. The solidification of supercooled SAT can be easily induced by different kinds of methods [17] and then the latent heat of fusion will be released. It was investigated that the solid SAT needs to be heated to 83 °C then a stable supercooling can be achieved [18]. Therefore, the sensible heat is also available to use in short term. Besides that, SAT has many other advantages in practical applications such as it is cheap, safe and non-toxic and it has no corrosion with steel.

However, it was found that phase separation/segregation is the main problem of using SAT as the heat storage material because part of the latent heat of fusion will dissipate to environment when phase separation was forming. Phase separation is the phenomenon that the water content of supercooled SAT is lower than 39.7% which means the trihydrate structure of SAT collapsed. It was caused by the solubility of sodium acetate in water 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 [19]. Therefore the anhydrous salt will settle down to the bottom of the container as sediment due to its higher density. Phase separation will start from the bottom part of a SAT volume and the situation could be even worse that the middle part could also suffer from phase separation.

It was experimentally verified that phase separation will cause severe energy loss during the SAT supercooling period [20]. In theory, the heat content of SAT at 20 °C was 230 kJ/kg. However, 162 kJ/kg heat was released after 14 days supercooling due to visible phase separation in SAT samples. Nearly 30% of the latent heat of SAT was lost. The phase separation problem was even worse when the heat content of SAT was measured after supercooled for a long term period up to 100 days. Only 99 kJ/kg latent heat was released which means 57% of the latent heat was lost. Therefore it is important to avoid phase separation problem for SAT as a heat storage material.

## **2 Theory**

### ***2.1 Methods of avoiding phase separation***

Possible methods of reducing or avoiding phase separation for incongruent melting materials were summarized in general in [1]: Mechanical stirring, rotating storage devices, adding the thickening agents [21–23] to hold the suspension of unsolved salt, adding excess water to solve the sodium acetate salt completely and using chemical ways to make the materials congruent and so on. Kong et al.[20] investigated the phase separation problem of SAT from the heat content point of view. Samples of SAT, SAT with excess water, SAT with thickening agent and SAT with other polymer additives were made and the heat content of the above mentioned samples were measured. It was found that samples of SAT 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.

### ***2.2 Key factor***

According to the mechanism of forming phase separation and the valid methods of reducing or avoiding phase separation mentioned in the existing research literature, it can be concluded that the key fact is the water content in certain positions, especially at the bottom of containers, plays the most important role regarding to the phase separation problem. As long as the water content of SAT in

anywhere in its container can keep at least 39.7% weight of the total material, it will not suffer from phase separation. Therefore in the contrary, if the water content of SAT is measured less than 39.7%, phase separation would definitely existing in that location. Besides, it needs to be noted that phase separation phenomenon is not always visible where solid structure can be seen obviously. Supercooled SAT material with transparent appearance can also have phase separation.

### **2.3 Experiment design**

According to the above analysis, it can be concluded that phase separation is directly related to the water content distribution in supercooled SAT materials. Many factors will influence the water content distribution in connecting to the phase separation problem such as the SAT sample height, the amount of excess water, with or without additives, supercooling condition and testing environment and so on. However, there is no detailed investigation on phase separation from the water proportion point of view and no evaluation on the different influential factors. This study focus on the investigations of different influential factors of the phase separation of supercooled SAT by means of measuring the exact water proportions at different layers of SAT samples.

The following controlled influential factors for SAT samples or testing environment were investigated:

1. 4 cm, 5 cm and 8 cm heights of SAT samples
2. 40%, 42%, 45% and 46% water content of sodium acetate water mixtures
3. SAT samples with thickening agents CMC and Xanthan Gum
4. Top or bottom activation methods
5. Short term and long term supercooling periods
6. Shaking SAT samples from time to time or standing still SAT samples during supercooling
7. Repeated heating and activating SAT samples
8. Low ambient temperature during supercooling of SAT samples

### 3 Experiments

The main method is to measure the water content at the different layers of SAT samples which were prepared at different heights with different compositions and undergone with different test conditions. The detailed method of sample preparation, experimental procedure, activation method and test conditions were described in the following subsections.

#### 3.1 Sample preparation

The SAT (analytical degree, purity>99%) used in this study was produced by Shijiazhuang Haosheng Chemical Co. Ltd in China.

Thickening agents were provided by the company of CP Kelco - Carboxymethyl Cellulose (CMC) under the product name CEKOL® 30000 and Xanthan Gum (X-Gum) under the product name Keltrol® Advance Performance.

The water added in SAT samples was distilled water.

The samples were prepared in two kinds of VWR Polypropylene (PP) bottles under the production NR. 215-5683 and 215-5684 which is shown in Figure 1. The material density at 20 °C is 0.89-0.91 g/cm<sup>3</sup> and can be heated up to 121 °C. The smaller bottle has a capacity of 250 ml with the height of 119 mm and the diameter of 63 mm. The bigger bottle has a capacity of 500 ml with the height of 152 mm and the diameter of 78 mm. The smaller bottle is used to prepare the SAT samples in supercooled state with the heights of 4 cm and 5 cm and three even layers will be cut after solidification of SAT samples. The larger bottle is used for the 8 cm SAT samples and four even layers will be cut. See Figure 2.

There are two main SAT sample categories. First is SAT with and without excess water at a certain height. Second is SAT with the thickening agents of CMC or Xanthan Gum at a certain height. The height of a SAT sample was measured in its supercooled state.

SAT contains approximately 40% (precisely 39.7%) water. Therefore the 40% water content SAT sample described in this study represents pure SAT sample without extra water. The exact mass composition of SAT and extra water were calculated for 42%, 45% and 46% water content SAT samples. In order to prepare a certain height of a supercooled SAT sample, the inner size of plastic bottles was carefully measured. Therefore the 4 cm, 5 cm and 8 cm height and 40%, 42%, 45%, 46% water content SAT samples can be made based on the calculation of SAT mass, water mass and plastic bottle size. The

calculated mass of SAT and extra water needed for the 4 cm, 5 cm and 8 cm samples were listed in Table 1.

SAT samples with thickening agent were prepared by mixing SAT and CMC or Xanthan Gum. Since the proportion of the thickening agent was small (maximum 1%), only the mass of SAT and the size of plastic bottles were measured and calculated for a certain sample height. The solid SAT and thickening agents powder were shaken up and down for the purpose of fully mixing before melting.

Unless the shaking operation was noted, all the samples were standing still during supercooling period.



Figure 1. VWR PP bottles

Table 1 Calculated mass of SAT and extra water for a certain height of supercooled sample

Water content	SAT (g)	Extra water (g)	Total weight (g)
4 cm sample			
40%	153	0	153
42%	146	5.8	151.8
45%	136	13.1	149.1
46%	133	15.5	148.5
5 cm sample			
40%	191	0	191
42%	182	7.2	189.2
45%	170	16.3	186.4
46%	167	19.5	186.5
8 cm sample			

40%	405	0	405
42%	385	15.3	400.3
45%	360	34.7	394.7
46%	352	41.1	393.1

### **3.2 Experimental procedure**

Step 1: Prepare SAT samples in solid state. For example the sodium acetate water mixtures with 40%, 42%, 45%, and 46% (wt. %) water at the same height in the plastic bottles.

Step 2: Heat the prepared samples in an oven to a temperature between 80 °C and 85 °C until the samples were fully melted.

Step 3: Take the samples out from the oven. Let them cool down to indoor ambient temperature and let them stay in supercooled state under different test conditions.

Step 4: Activate the samples, so that the supercooled SAT samples solidified. The samples were left to cool down to the indoor ambient temperature again.

Step 5: Cut each sample evenly into 3 or 4 horizontal layers which is shown in Figure 2. Put each layer of the SAT sample into glass jars shown in Figure 3. The glass jars is big enough to hold the salt water mixtures. Weight the empty glass jars and the glass jars with salt water mixtures before heating.

Step 6: Put the glass jars with the cut samples into an oven with the temperature above 100 °C until all water was evaporated which is shown in Figure 4. The heating time for evaporating all water out usually cost more than 24 hours. The glass jars were weighted for many times during heating time until the weights unchanged. In this way the complete evaporation of water can be guaranteed.

Step 7: Weight the glass jars with salt inside again. The water proportion of each layer of the samples can be calculated based on the mass measurements.

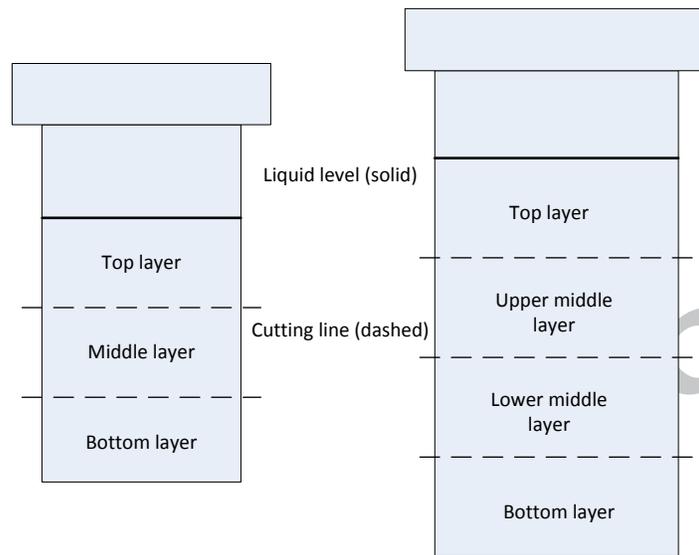


Figure 2. Diagram of cutting layers for the two kinds of PP bottles



Figure 3. Empty glass jars



Figure 4. Glass jars with SAT material inside oven during heating

### 3.3 Activation method

There are many activation methods to trigger the solidification process of supercooled SAT in practical applications. In this study solid SAT crystal was used to induce the solidification of supercooled SAT samples in plastic bottles either from the top or from the bottom. The top activation method is simple. Twist off the lid of plastic bottle and drop a tiny amount of SAT crystals from top into the bottle. Then the solidification will be activated right away. The bottom activation method can be carried out by using a needle shown in Figure 5. The needle is first dipped into solid SAT and some crystals will adhere to the needle. Then push the needle into plastic bottle from the bottom. The adhered SAT crystals will induce the solidification of supercooled SAT samples from the bottom. The plastic bottle needs to be kept vertical during bottom activation to avoid tilted top level.



Figure 5. Bottom activation by needling method

### 3.4 Test conditions

Four test conditions for SAT samples were designed according to the relevance of forming phase separation. They are SAT samples standing still or shake from time to time during its supercooled period, repeated heating and activating cycles and low ambient temperature during supercooling.

Shaking the bottles of supercooled SAT samples by hand is safe for keeping supercooling and solidification of SAT samples was never happened. The frequency of shaking is twice a day and lasting around 30 seconds.

A heating and activating cycle is the process from step 2 to step 4 described in section 2.2 after SAT sample was prepared. The aim of the repeated heating and activating process is to investigate the relevance of the severity of phase separation with the increasing cycle times.

Low ambient temperature environment was created by a fridge which can keep the temperature around 5 °C. The prepared SAT samples were then put into the fridge standing still in supercooled state.

## 4 Results and discussion

All the experiments were carried out at the laboratory of Department of Civil Engineering, Technical University of Denmark. The results were classified and summarized into four scenarios.

### ***4.1 Scenario 1: Short term and long term supercooled period, top activation***

In this scenario, 40%, 42%, 45% and 46% water content salt water mixtures were made with the heights of 4 cm, 5 cm and 8 cm in two sets. One set of the samples stayed in short term supercooled state for 18 - 19 days before activation. The other set of the samples stayed in long term supercooled state for around 130 days before activation. Then the solidification of the samples was activated from the top of the bottles. The photos of the 8 cm samples of short term and long term supercooled state before activation were chosen as an example shown in Figure 6 and Figure 7.

From Figure 6, it can be seen that the 40% and 42% salt water mixtures after short term supercooling had visible solid structure. The 45% and 46% salt water mixtures remained transparent in their supercooled state except from the fact that some unclear solid grid structure appeared at the bottom. The 40% salt water mixture had no clear solution layer on the top while the 42% salt water mixture had a very thin solution layer on the top. There were some small bubbles on the wall in the 45% and 46% salt water mixtures.

The photos of the 4 cm and 5 cm samples before activation were also taken. For simplicity, only 8 cm samples were shown as Figure 6 and Figure 7. The 4 cm and 5 cm samples had similar appearance with the 8 cm samples. The only one difference is that the solid structure of the 8 cm 40% and 42% salt water mixtures was “hard” and “compact” compared to that of the 4 cm and 5 cm samples which was “soft” and “loose” when the bottles were pressed by hand. It can be explained that the 8 cm salt water mixture has higher height and longer diameter than the 4 cm or 5 cm salt water mixture which will cause higher pressure to form more compact bottom layer. But the real water content at the bottom may not consist with the samples height and tactile feedback. It needs to be tested by the following experiments.

From Figure 7, it can be seen that the 40% and 42% salt water mixtures also had visible solid structure while the 45% and 46% salt water mixtures still remained transparent after long term supercooling period. The 40% and 42% salt water mixture had clear solution layer on the top. The 45% and 46% salt water mixtures had bubbles on the wall.



Figure 6. 8 cm salt water mixtures after 19 days supercooling



Figure 7. 8 cm salt water mixtures after 131 days supercooling

The water proportions at different layers in all the samples in this scenario were summarized in Table 2. The water proportion marked as bold number represent phase separation occurred in this layer since the water content was lower than 39.7%. The supercooling time of each set of samples was illustrated in parentheses.

**Table 2 Water proportions in different layers – Short and long term supercooling and top activation**

Water content of sample	Layer (supercooling days)	4 cm (19 days)	5 cm (18 days)	8 cm (19 days)	4 cm (126 days)	5 cm (129 days)	8 cm (131 days)
40%	Top	43.5	43.7	40.9	44.7	43.9	44.7
	Middle	<b>38.5</b>	42.3	39.9	<b>38.6</b>	<b>39.4</b>	40.2
				40.0			<b>38.6</b>
Bottom	<b>39.0</b>	<b>34.7</b>	<b>39.6</b>	<b>37.3</b>	<b>38.0</b>	<b>37.0</b>	
42%	Top	42.0	42.4	42.7	43.5	45.0	44.9
	Middle	42.4	41.8	42.4	42.1	44.9	43.5
				42.2			40.1
Bottom	41.6	42.0	42.2	42.0	<b>39.5</b>	<b>39.7</b>	
45%	Top	46.0	45.6	47.1	45.4	45.4	45.9
	Middle	46.2	45.7	46.7	45.3	45.6	45.8
				45.4			45.5
Bottom	43.9	45.2	41.9	45.6	45.2	44.3	
46%	Top	47.1	46.5	48.6	45.8	46.4	46.5
	Middle	46.9	46.4	47.9	46.0	46.4	46.5
				46.2			46.2
Bottom	45.5	46.4	42.6	45.9	46.6	46.0	

From Table 2 it can be seen that all the 40% samples suffered from phase separation problem both in short and long term supercooling conditions. The long term samples had severer phase separation problem than short term samples because the middle layer water proportion of the 5cm and 8 cm samples of long term supercooling were lower than 39.7% while the middle layer water proportion of the short term samples of 5 cm and 8 cm were above 39.7%.

The 42% samples only suffered from phase separation problem in long term supercooling condition in the bottom layer for the 5 cm and 8 cm samples. But it can still be concluded from other samples' results that 42% sample tends to suffer from phase separation in long supercooling period and higher material height than 5 cm.

There was no phase separation formed in the 45% and 46% samples. They had relatively even water distribution compared to the 40% and 42% samples. It also can be seen from the comparison that the 45% and 46% samples in long term supercooling had more even water distribution compared to the samples in short term supercooling which indicates that for high water content SAT samples the long supercooling period is in favour of forming even water distribution.

#### 4.2 Scenario 2: Short term supercooled period and bottom activation

In this scenario, one set of the 40%, 42%, 45% and 46% water content salt water mixtures with the heights of 4 cm, 5 cm and 8 cm were prepared and stayed in short term supercooled period for around 20 days. Then the solidifications were activated at the bottom of the bottles by the needle method described in section 3.3.

The photo of the 8 cm samples in supercooling state before activation was shown in Figure 8. They were almost the same as the samples' appearance in Figure 6. The only difference is that the 42% salt water mixture in Figure 6 had a very thin transparent layer on the top while the layer cannot be seen in the 42% salt water mixture in Figure 8. This could be caused by the slightly different conditions between the two scenarios in preparing samples or during supercooling period.



Figure 8. 8 cm salt water mixtures after 21 days supercooling

The results of the water proportions at different layers of all samples were shown in Table 2. It can be seen from the table that only the 40% samples were suffered from phase separation problem. The result was the same as the top activation samples in Table 2. However, compared to the same height samples activated from top, the samples activated from bottom had relatively higher water proportion

in the bottom layer and lower water proportion in the top layer. It seems that activation from bottom has the effect that “sucking” more water from top to the lower part of the sample during activation process.

**Table 3 Water proportions in different layers – Short term supercooling and bottom activation**

Water content of sample	Layer	4 cm (21 days)	5cm (19 days)	8cm (21 days)
40%	Top	40.7	41.2	40.5
	Middle	<b>39.6</b>	<b>39.3</b>	39.8
				39.9
Bottom	39.9	<b>39.6</b>	<b>39.6</b>	
42%	Top	42.9	44.4	42.4
	Middle	42.0	42.0	42.0
				42.3
Bottom	42.2	41.3	42.2	
45%	Top	46.1	46.6	45.5
	Middle	45.5	46.0	45.3
				44.9
Bottom	43.7	43.5	45.0	
46%	Top	47.0	47.6	48.2
	Middle	46.3	46.5	47.6
				46.3
Bottom	45.5	43.5	43.6	

Since only the bottom activation samples were made for the tests in Table 3, there is no direct comparison for the samples between top activation method and bottom activation method at the same time. Therefore, further experiments of direct comparison on the effect of top and bottom activation methods were carried out for the 40% and 42% samples with the heights of 4 cm, 5 cm and 8 cm. All the samples were put standing still for 19 days supercooling before activation. All the samples for comparison were prepared and activated at the same time and stayed under the same environmental condition during supercooling. The results were listed in Table 4. It can be seen from the table that the 40% samples with the height of 5 cm and 8 cm suffered from phase separation problem while the 4 cm samples were on the edge of phase separation since the water proportions in the bottom and middle layers were just slightly higher than 39.7%. All the 42% samples did not suffer from phase separation problem.

When only the bottom layer water proportions were investigated for all the samples with top and bottom activation method, it can be found that only the 42% sample with 8 cm height had obvious higher water proportion by bottom activation than the samples by top activation, even though 0.4%

higher extra water was measured but it is still within error range. Therefore it can be concluded that the “sucking” effect caused by bottom activation method does not have dominating influence on the water distribution for water salt mixtures. The bottom or top activation method does not have obvious different impact on water distribution for SAT samples.

**Table 4 Water proportions in different layers – short term supercooling, top and bottom activation**

Sample height	Layer	40% salt water mixture		42% salt water mixture	
		Top activation	Bottom activation	Top activation	Bottom activation
4 cm	Top	40.8	40.9	44.0	43.3
	Middle	40.0	39.7	41.9	42.3
	Bottom	39.8	40.0	41.6	41.6
5 cm	Top	40.7	41.1	43.0	43.6
	Middle	40.1	39.8	42.3	42.2
	Bottom	<b>39.5</b>	<b>39.5</b>	42.2	41.7
8 cm	Top	42.9	42.5	42.8	42.9
	Upper Middle	<b>37.7</b>	<b>38.2</b>	41.9	41.8
	Lower middle	<b>39.0</b>	<b>39.4</b>	42.0	42.0
	Bottom	<b>38.7</b>	<b>38.9</b>	41.3	41.7

### 4.3 Scenario 3: SAT with thickening agent CMC or Xanthan Gum

Four SAT samples with the height of 5 cm were mixed with extra 0.5% and 1% Xanthan Gum and 0.1% and 0.2% CMC separately. They were put standing still in supercooled state for 19 days and then were activated from top. The photo of the samples before activation was shown in Figure 9. It shows that the samples with 0.5% and 1% Xanthan Gum had yellow jelly structure. The 1% Xanthan Gum sample had darker and harder solid structure compared to the 0.5% Xanthan Gum sample. The SAT samples with 0.1% and 0.2% CMC had transparent liquid phase without any jelly appearance.



**Figure 9. 5 cm salt water mixtures with additives after 19 days supercooling**

The water proportion results of the four samples were shown in Table 5. From the table it can be seen that all the samples were not suffered from phase separation which means that the thickening agents CMC and Xanthan Gum had the ability of “suspending” water in its layer. However, it still can be further concluded by comparison that the samples with CMC had more even water distribution than the samples with Xanthan Gum and the supercooled samples with CMC were in liquid phase and have higher flow ability. It is an advantage in practical application because liquid phase material is easier to be filled into container.

**Table 5 Water proportions in different layers – 5 cm SAT with thickening agent CMC and X-Gum**

Layer	SAT+0.1% CMC	SAT+0.2% CMC	SAT+0.5% X-Gum	SAT+1% X-Gum
Top	40.0	39.9	40.5	39.7
Middle	40.0	39.9	40.1	40.5
Bottom	40.2	39.9	40.5	40.5

Adding thickening agents was verified as an effective method of reducing or avoiding phase separation in lots of literature. According to the authors’ experimental experience, CMC and X-Gum were chosen to test in this small scale experiments. Long term test or cycle testing were carried out in other demonstration systems from the heat content point of view and it was found out that the CMC and X-Gum were still effective after long term supercooling period or cycle heating and cooling tests[9].

Thickening agents CMC and X-Gum are of course not perfect. They will increase the viscosity of the salt mixture and increase the difficulty of filling SAT into container or remove them out. On the other hand, the thickening agents cannot cooperate with extra water. There will have no extra water added to the SAT mixture. Therefore, it will have a risk of losing crystal water of SAT after repeated heating and cooling cycles and then phase separation problem could occur.

#### ***4.4 Scenario 4-6: Shaking, repeated heating and activating and low ambient temperature conditions***

Three sets of 40%, 42%, 45% and 46% salt water mixture with 5 cm height were made for three test conditions. The first set samples were tested under shaking condition during its supercooling period. After 34 days, the samples were still in supercooled state which was shown in Figure 10. Then they were activated from top. The appearance of the 40% and 42% samples in Figure 10 were different compared to the 40% and 42% samples in Figure 6 and Figure 8 without shaking. The solid structure in these two

samples was quite uneven due to the shaking effect. There was an obvious partly solid zone in the upper middle of the 40% sample and in the lower middle of the 42% sample. The 45% and 46% samples were transparent without any bubbles on the wall. They were still in the liquid phase but were turbid compared to the 45% and 46% samples without shaking.



**Figure 10. 5 cm salt water mixtures after 34 days supercooling with randomly shaking**

The second set samples were tested by 4 repeated heating and activating cycles. In the first cycle, the samples stayed for 10 days supercooling before activation while in the second cycle the supercooling period was 9 days and in the third cycle it was 10 days. In the fourth cycle, the samples stayed for 34 days supercooling before activation. The photo can be seen in Figure 11. Both the 40% and 42% samples had visible solid structure. There was a thin transparent layer on the top of the 40% sample while half of the 42% sample on the top was transparent solution. The 45% and 46% samples were transparent and there were small bubbles on the inside walls.

The third set samples were put into a fridge under ambient temperature of 5 °C in supercooled state for 30 days before activation. It is unfortunate that the photos were not saved before activation.



**Figure 11. 5 cm salt water mixtures after 3 times heating and activating and then 34 days supercooling**

The water proportion results of the three sets samples were summarized in Table 6. All the 40% samples were suffered from phase separation problem. The 40% sample under shaking and repeated heating and activating conditions only had the bottom layer while the 40% sample under low temperature condition had both the middle and bottom suffering from phase separation. The 42%, 45% and 46% samples did not suffer from phase separation problem.

Some difference can be found through the comparison of the 5 cm samples between Table 2 and Table 6. Firstly, the higher water proportion in the bottom layer of the 40% and 42% samples in Table 6 shows that the shaking action has the effect of “pushing” water down to lower part of the sample for the 40% and 42% samples while it has no influence for the 45% and 46% samples. The reason is that the shaking action has the “mixing” effect for the salt water mixture. The 42% salt water mixture will benefit from the shaking effect when it is in supercooled state. The 40% salt water mixture had higher water proportion at the bottom layer but it was still lower than 39.7%. The 45% and 46% sample will not benefit from the shaking effect because they have already had enough water at the lower part of the samples. Secondly, the repeated heating and activating treatment had an influencing effect for the 42% sample since the top and bottom layer water proportion had a big difference. Since the heating and activating cycles were carried out only four times, it is reasonable to deduce that the uneven water distribution would be worse after more heating and activating cycles. The last, all the samples were influenced by the low ambient temperature since the water distribution were not as even as the 5 cm samples in Table 2. It can be concluded that the low ambient temperature will increase the risk of suffering from phase separation for the SAT water mixture.

**Table 6 Water proportions in different layers – 5 cm samples under shaking, cycle heating and low ambient temperature conditions**

Condition	Water content of 5 cm sample	Top	Middle	Bottom
Shaking	40%	42.2	40.4	<b>37.6</b>
	42%	40.8	42.8	43.3
	45%	45.3	45.2	45.5
	46%	46.0	46.3	46.3
Repeated heating and activating	40%	42.1	40.0	<b>38.6</b>
	42%	44.9	41.7	40.2
	45%	45.5	45.1	45.2
	46%	46.5	46.1	46.0
Low ambient temperature	40%	41.1	<b>39.6</b>	<b>39.5</b>
	42%	44.8	42.0	40.2
	45%	45.9	46.0	43.8
	46%	47.0	46.7	45.2

#### **4.5 Uncertainty analysis**

The experiments were carried out carefully as best as we can. But errors were inevitable due to the systematic or environmental uncertainties.

Firstly, the uncertainty comes from the scale. The Sartorius I8100P electronic precision scale was used for all the measurements, see Figure 12. The standard deviation is less than  $\pm 0.01$  g. Since the materials used in the experiments were all heavier than hundred grams, it is believed that the precision of the scale is accurate enough.



**Figure 12. Sartorius I8100P electronic precision scale**

Secondly, the biggest uncertainty is assumed from the cutting process of the solidified samples. The height of each layer of solidified samples were carefully measured and noted before cutting. Then each layer was cut by a saw. In the process of sawing, it was impossible to cut samples strictly evenly. The error from the sawing process may influence the water content in the layer.

Then, during the water evaporation process in the oven, the temperature was over 100 °C. It can be seen that the SAT was expanded after heating. It might be that some SAT was carried out by the boiling water which is a source of uncertainty.

Finally, since the whole experiments last long time, the SAT material may also have slight difference in water content in different tests because SAT has hygroscopic property. The SAT material was well preserved as much as we can. But this factor cannot be easily neglected. Other inevitable uncertainty comes from environmental influence such as slight unintentional vibration during supercooling or the vibration from moving samples by hand and so on.

It can be seen that the water contents measured from the same layer of one test may differ from other tests even though the samples have the same composition and the same test conditions. The deviation comes from the above uncertainty analysis. However, all the tests show consistently results for the phase separation problem and concrete conclusion can be summarized. Therefore, the mentioned uncertainty is acceptable in this aspect.

## 5 Conclusions

Sodium acetate trihydrate (SAT) is a promising phase change heat storage material which can provide relatively high latent energy (264 kJ/Kg) with proper temperature range (up to 58 °C) for domestic hot water and space heating utilization. SAT has also stable supercooling ability therefore the long term stored latent energy has the potential to be used in seasonal heat storage applications. However, it was verified from the experiments that pure SAT in supercooled state will suffer from phase separation problem which means the water content in supercooled SAT is lower than its crystal water percentage (39.7%). Phase separation problem is the main risk of using SAT as heat storage material since it will dramatically decrease the stored latent heat. This study focus on experimental investigations on phase separation by means of measuring water proportions at different layers of SAT samples with different heights and under different test conditions.

The 42% water content SAT samples did not suffer from phase separation problem in short term supercooling period. But long term supercooling period and higher sample height are the positive influencing factors for the formation of phase separation in the material bottom part. The 45% and 46% water content SAT samples did not suffer from any phase separation problem in all test conditions. Therefore, it can be concluded that enough extra water is an effect way of reducing or avoiding phase separation and the 42% water content SAT is the lower limit for SAT water mixture.

The pure SAT with the thickening agents CMC or Xanthan Gum gave even water distribution in all the samples indicating that phase separation can be avoided by adding thickening agents. But SAT samples with CMC had more fluent fluid texture than SAT samples with Xanthan Gum.

The SAT samples activated by bottom activation method had slightly higher water proportions than the samples activated by top activation method but the tendency was not strong enough to conclude the bottom activation as an influencing factor of reducing phase separation problem.

Proper shaking is beneficial to even water distribution for all samples.

Repeated heating and activating condition has obvious influence on 42% SAT samples in which the top layer had higher water proportion and the bottom layer had lower water proportion. It can be reasonably deduced that the more heating and activating cycles will accelerate the formation of phase separation. The low ambient temperature is in favour of forming uneven water distribution/phase separation for all the SAT samples. Samples' height is not an important factor of forming phase separation.

In one word, adding suitable extra water (42% water content as least), adding thickening agents and proper shaking are beneficial methods to reduce or avoid phase separation while pure SAT without any additives, more heating and activating cycles and low ambient temperature are favourable to forming phase separation for supercooled SAT materials. The selection of proper composition of SAT with additives and appropriate operating conditions are important for using SAT as a long term heat storage material.

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## Highlights:

- SAT samples of different heights with or without extra water, thickening agents were tested in supercooled status at different designed conditions
- Water proportions at different layers of SAT samples were measured
- Phase separation problem was investigated from the water proportion point of view by experiments

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