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Latent storage for low temperature applications

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Abstract

The Scottish company Sunamp Ltd produces latent thermal storage batteries in which heat or cold is stored using phase change materials (PCM). Sunamp manufactures a variety of batteries with storage temperatures from -5°C to 120°C. Sunamp together with the Lucerne University of Applied Sciences and Arts, have set themselves the goal of developing a latent storage system for cold storage at temperatures between -30°C and -5°C. For low temperature applications in this temperature range there is currently no product available on the market which uses latent storage. The most common way currently used for thermal cold storage at low temperatures, is sensible storage with water-glycol mixtures. The aim of this bachelor thesis is to find PCM which are suitable for use in a low-temperature latent storage.

At first a market analysis was carried out to find out at which temperatures a latent storage could be needed. Afterwards, materials were researched, and candidates were selected. At last the thermal properties of the selected materials were determined in various measurements and experiments.

In the market analysis it was investigated what temperatures are used in the food industry. It was found that temperatures between -30°C to -18°C are used for the transport, the storage and the retail of frozen food. Within this temperature range materials were researched with suitable phase change temperatures. The properties such as phase change enthalpy and toxicity of the found materials were compared, and the most suitable materials were selected for experimental analysis. The eight selected PCM candidates included three eutectic salt water solutions and five are organic compounds of different classes of materials. The selected eutectic water-salt solutions are aluminum nitrate solution ($Al(NO_3)_3$), Magnesium chloride solution ($MgCl_2$), and sodium chloride solution (NaCl). The selected organic materials include 1,3-Dibromopropane, 1-Heptanol, n-Decane, Propionic acid and Nonaldehyde. DSC measurements, T-History experiments, and material compatibility experiments were performed with the selected materials. With the DSC measurements the phase change temperature, the melting enthalpy and the specific heat capacity were measured. With the help of the T-History experiment the subcooling could be determined and crystallization could be observed. With the material compatibility experiments, it was possible to determine how the materials behave in combination with copper, steel and aluminum. In addition, a setup was developed and constructed for future cycle stability measurements.

It was shown that the eutectic salt water mixtures have the best thermophysical properties such as enthalpy of fusion and specific heat, however they exhibit a poor compatibility with metals. The organic materials have good thermophysical properties. The organics have good compatibilities with aluminum. The compatibility with copper and steel depends on the material.

Zusammenfassung

Die schottische Firma Sunamp Ltd verkauft und produziert thermische Wärmespeicher-Batterien in denen Wärme oder Kälte mit Phasenwechselmaterialien (PCM) gespeichert wird. Sunamp stellt verschiedene Batterien mit Speichertemperaturen von -5°C bis 120°C her. Sunamp zusammen mit der Hochschule Luzern haben sich das Ziel gesetzt einen Latent-speicher für Kältespeicherung im Temperaturbereich von -30°C bis -5°C zu entwickeln. Für Tieftemperaturanwendungen in diesem Temperaturbereich gibt es noch kein Produkt auf dem Markt, welches latente Speicherung verwendet. Zur Kältespeicherung im Tieftemperatur-bereich wird momentan hauptsächlich sensible Kältespeicherung mit Wasser-Glykol Mischungen eingesetzt. Ziel dieser Bachelor-Thesis ist es PCM zu finden welche für die Anwendung in einem Tieftemperatur Latentspeicher geeignet sind.

Als erstes wurde eine Marktanalyse durchgeführt um herauszufinden bei welchen Temperaturen ein Latentspeicher Anwendung finden könnte. Danach wurden Materialien recherchiert und geeignete Kandidaten wurden ausgewählt. Als letztes wurden die thermischen Eigenschaften der ausgewählten Materialien in verschiedenen Experimenten untersucht.

In der Marktanalyse wurden die Temperaturen in der Lebensmittelindustrie untersucht. Es konnte herausgefunden werden, dass für den Transport, die Lagerung und den Verkauf von tiefgekühlten Lebensmitteln Temperaturen im Bereich von -30°C bis -18°C verwendet werden. Von den Materialien die für diesen Temperaturbereich gefunden wurden, wurden acht ausgewählt die ungiftig sind, günstig sind und eine hohe Phasenwechselenthalpie aufweisen. Von den gewählten Materialien sind drei eutektische Salzwasser-Lösungen und fünf sind organische Verbindungen. Die ausgewählten eutektischen Salzwasser-Lösungen sind Aluminiumnitratlösung (Al(NO3)3), Magnesiumchloridlösung (MgCl2) und Natrium-chloridlösung (NaCl). Die ausgewählten organischen Materialien sind 1,3-Dibrompropan, 1-Heptanol, n-Decan, Propionsäure und Nonaldehyd. Mit den gewählten Materialien wurden DSC-Messungen, T-History Experimente und Materialverträglichkeits-Experimente durch-geführt. Durch DSC Messungen wurde die Phasenwechseltemperatur, die Schmelzenthalpie und die spezifische Wärmekapazität gemessen. Mithilfe des T-History-Experiments konnte das Subcooling bestimmt werden und die Kristallisation beobachtet werden. Mit den Material-verträglichkeits-Experimenten, konnte bestimmt werden wie die Materialien sich in Kombination mit Kupfer Stahl und Aluminium verhalten. Zusätzlich wurde ein Prüfstand für zukünftige Zyklenstabilitätsmessungen ausgelegt und aufgebaut.

Es zeigte sich, dass die eutektischen Salzwasser-Lösungen die besten thermophysikalischen Eigenschaften wie Phasenwechselenthalpie und spezifische Wärmekapizität aufweisen. Die Verträglichkeit der Salzwasser-Lösungen mit Metallen ist mangelhaft. Die organischen Verbindungen besitzen gute thermophysikalische Eigenschaften. Die Verträglichkeit mit Aluminium ist gut. Bei Kupfer und Stahl ist die Verträglichkeit von dem Material abhängig.

Table of content

Appendices

1   Introduction

Low temperature refrigeration is widely employed in the food and pharmaceutical industries. Applications with temperatures far below 0°C are of daily use the production, processing, transport and storage of foods or pharmaceutical products. The most common way of thermal cold storage at temperatures lower than 0°C is the application of sensible storage with liquid water-glycol mixtures in stratified storage tanks.

The Scotland-based company Sunamp Ltd is a producer of latent thermal storage batteries. Those batteries use phase change materials (PCM) to store heat and cold at temperatures ranging from -5°C up to 120°C. Sunamp aims to develop a low temperature thermal storage battery with PCM where cold can be stored at temperatures between -30°C and -5°C. The important advantage of heat storage with PCM in contrast to sensible heat storage with water-glycol is a larger heat storage capacity in relation to volume. Currently there is no product available on the market comparable.

This bachelor thesis was carried out within the scope of the eurostars-project STOREF. In this project Sunamp Ltd together with the Lucerne University of Applied Sciences and Arts want to develop and validate a latent thermal cold storage for refrigeration processes in the temperature range of -30°C to -5°C. The goal of STOREF is to get as close as possible to a commercial product.

The goal of this bachelor thesis was to find materials that are suitable for the use as PCM in a cold storage battery. At first was finding temperatures at which a cold storage battery could be needed on the market. The second step was to find and select PCM candidate materials. The third step was to analyze if the selected materials have desirable characteristics for the use as PCM. The fourth and last step was to check if the characteristics of the selected materials stay the same over several charging and discharging cycles.

A market analysis was carried out in order to determine the temperatures used in the food industry for the range between -30 and -5. As a consequence to the market analysis, Sunamp defined two final temperature ranges. Preliminary PCM candidates have been selected after a literature research, acceptable materials have their phase change temperature within the defined range, Among the selected materials, the most promising were select as candidates. The found materials were then compared and the most suitable were selected as PCM candidates. Experiments were carried out to determine the properties of the candidate materials. Those experiments include DSC measurements, T-History measurements and material compatibility tests. To determine if the materials stay stable over several cycles, a cycle stability test setup was built for future cycle stability tests.
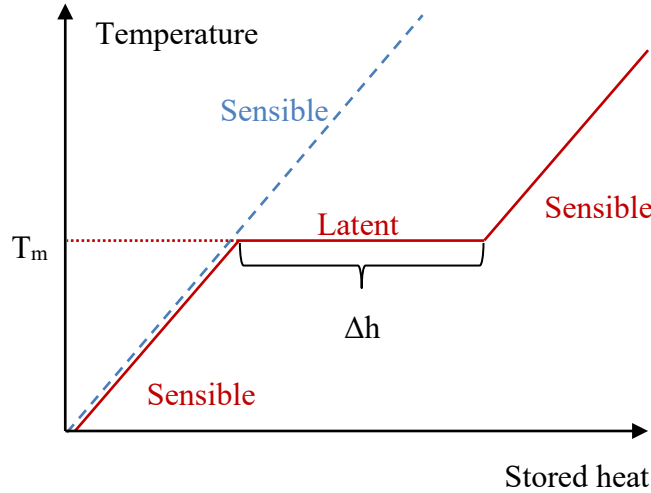
2 State of the art

Figure 1: Comparison of sensible and latent heat storage. The dashed line represents sensible heat storage and the solid line latent heat storage[1].

2.1 Latent heat storage with PCM

There are two ways to store heat using physical processes in the field of thermal energy storage (TES); sensible storage and latent storage. With sensible storage, the temperature of the storage medium increases proportionally to the heat input (Figure 1: dashed line). The storage capacity is determined by the specific heat of the storage medium and the temperature difference. With latent heat storage, the storage medium undergoes a phase change due to the heat input. The phase change of a material is the change of the aggregate state. Storage mediums used for latent heat storage are called phase change material (PCM). In most cases the solid-liquid phase change of the PCM is used. During the solid-liquid phase change the storage medium can take up or give off heat while the temperature stays the same (Figure 1: horizontal solid line). The temperature where the phase change takes place is material-specific and is called phase change temperature T_m. The charging (Figure 2, cooling) of a latent cold storage takes place as follows: The liquid PCM gives off heat and cools down until it reaches the phase change temperature. Until that point it only gave off sensible heat. Then it starts to solidify and gives off heat with a constant temperature until the solidification is complete. After solidification it cools down again while giving off heat until it reaches the desired temperature. At this point it gave off sensible heat in liquid and solid form, and latent heat. The discharging of the PCM happens the other way around (Figure 2, heating). Melting and solidification may occur at different temperatures. The difference between those temperatures is called hysteresis. The heat stored within the phase change is called latent heat or Enthalpy of fusion Δh. The stored heat with latent heat storage can be determined by the addition of the sensible heat in the solid phase, the enthalpy of fusion, and the sensible heat of the liquid phase. The advantages of latent thermal storage in contrast to sensible storage are a higher storage capacity and a lower temperature difference. [1] [2] [3]
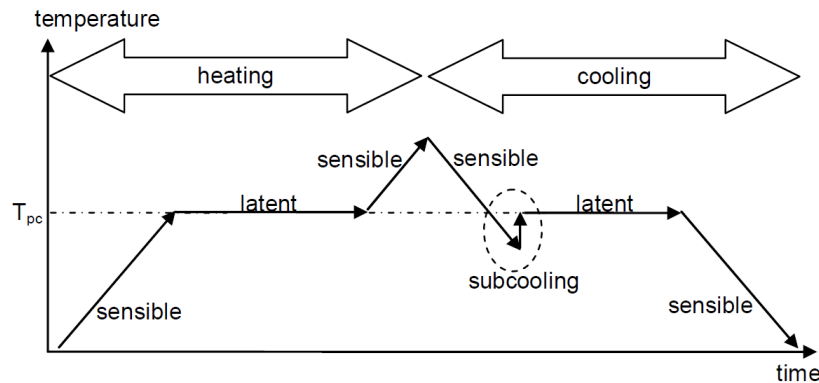
2.2   Common problems of PCM

Figure 2 shows a heating and cooling cycle of a PCM with subcooling[1].

2.2.1   Subcooling

A PCM exhibits subcooling, also called supercooling, if it remains liquid during the cooling process below the phase change temperature (Figure 2) [1]. This effect is caused by a lack of crystal nuclei or low crystal growth. If crystallization does not take place, the PCM only stores sensible heat. The probability of crystallization increases with lower temperatures. The degree of subcooling is dependent on several factors such as impurities, temperature gradient and pressure gradient[4]. Subcooling can occur in materials of all classes of materials. Possible solutions to reduce subcooling include using material-specific nucleation agents, keeping a small amount of PCM always solid with a local cooling device (cold finger), or using a nucleation trigger device which solidifies a small amount of PCM through pressure[5].

2.2.2   Phase separation

If a material consists of one pure component, it will have the same composition as liquid and as solid. In this case the material has congruent melting and solidification. If a material used as PCM consists of two or more components, it is possible that it will divide into two or more phases during the solidification process. If those phases have different densities, then the phases with higher density will sink to the bottom and the ones with a lower density will rise to the top. This phenomenon is called phase separation or decomposition. Phase separation can occur in salt hydrates organic solutions and water-salt solutions. To prevent the phase separation, it is possible to thicken the PCM. If the separation already occurred, it can be rectified by mixing the PCM in the liquid state through agitation. [1]

2.3   Requirements for an ideal PCM

Any material which undergoes a solid-liquid phase change can be called a PCM. If the material is to be used as a latent heat storage it should meet certain physical, technical and economic requirements as listed in Table 1. What importance assigned to each requirement depends on the application of the PCM. [1]

Category	Requirement
Physical requirements	Suitable phase change temperature
	Large enthalpy of fusion per unit volume
	Reproducible phase change / Cycling stability
	Little subcooling
	High specific heat
	High thermal conductivity
Technical requirements	Low vapor pressure
	Small volume change
	Chemical stability
	Compatibility with other materials
	Safety constrains like Toxicity and Flammability
Economic requirements:	Low Price
	Availability

Table 1: Requirements for a material to be used as PCM. [1]

2.4   Classes of materials

There are several classes of materials which are typical for the use as PCM. Classes of inorganic materials include eutectic water-salt solutions, salt hydrates, salts and Eutectic metals [1] [6]. Classes of organic materials include paraffines, fatty acids, sugar alcohols, polyethylene glycols and esters [1]. The classes of materials that feature PCM with a phase change temperature within the temperature range of -30°C and -5°C are eutectic water-salt solutions, paraffines, polyethylene glycols and fatty acids[2]. After the definition of the final temperature range as mentioned in 3.2, polyethylene glycols were not considered further.

Eutectic water-salt solutions

The addition of salt reduces the melting temperature of water. Therefore, all water-salt solutions have melting points lower than 0°C. Since water-salt solutions consist of two or more components, phase separation can occur. To prevent phase separation only water-salt solutions

with a eutectic composition are used as PCM. A eutectic composition is a mixture of two or more components where the solidification takes place simultaneously at a minimal freezing point. Since the solution freezes as one phase, no phase separation can take place. Eutectic water-salt solutions show a good storage density in respect to volume, a similar specific heat as water, and a low vapor pressure. Like water they can exhibit subcooling and can show a volume expansion of 5 to 10% during solidification. Water-salt solutions can have a corrosive effect on metals. [1]

Paraffins

Paraffines is the technical term used for alkanes. Alkanes are organic compounds with the formula C_nH_{n+2} [6]. They are hydrocarbons which consist of CH_2 chains with a CH_3 group at each end. Melting temperatures of paraffins can range from far below zero to over 100°C. The longer hydrocarbon chain, the higher the melting temperature. Paraffins show a good storage density in respect to mass but have low densities. They show little to no subcooling and have low vapor pressures. The thermal conductivity of paraffins is comparatively low. They can show a volume increase of around 10% upon melting. Paraffins do not react with most common materials and show a very good compatibility with metals[1]. Paraffins with a chain length of n < 14 have melting points lower than 0°C[7].

Fatty acids

Fatty acids are organic compounds characterized with the formula $CH_3(CH_2)_nCOOH$. A fatty acid is a carboxylic acid with an alkane radical. The difference to an alkane is the carboxylic (-COOH) group at one end of the chain. As with alkanes, the melting temperature of fatty acids increases with the length of the chain. Fatty acids have a low thermal conductivity and show little to no subcooling [1]. Due to the carboxylic group, fatty acids exhibit acid behavior and can be corrosive towards metal. The degree of acidity is dependent on the length of the chain. The shorter the chain the stronger the acidity[8]. Fatty acids with n < 8 are labelled as corrosive (GHS code 05). Fatty Acids with n < 6 have a melting point lower than 0°C[7].

3 Methods

3.1 Market analysis

A market analysis was carried out to get an overview of the temperatures at what a cold storage battery could be used.

Step one was to investigate how the market is structured. Step two was to find out in what parts of the market temperatures in the range of -30°C to -5°C might be used. Step three was to take a closer look into the regulation and structure market segments as defined in step two. Step four was to find specific examples of temperatures used in these market segments.

The market defined by Sunamp was the food industry. The aim was to get a qualitative overview of the temperatures used in the defined market. A quantitative assessment of the market and the investigated segments was not conducted. The following sources were used; research papers, patent applications, web presence of companies in the market, government regulations, industry unions and news articles.

3.2 PCM selection

The goal of the PCM selection is to find candidate materials for the possible use as PCM at low temperatures. After viewing the results of the market analysis, Sunamp chose to define two temperature ranges. The first temperature range is from -30°C to -25°C and the second temperature range is from -22°C to -18°C. The selection criteria according to which the candidate materials were chosen are listed in Table 2.

Fixed criteria	
Phase change temperature:	The phase change temperature must be in one of the temperature ranges.
Safety:	The material must not exhibit any acute toxicity of categories 1 2 or 3 (GHS code 06).
Soft criteria	
Enthalpy of fusion:	The enthalpy of fusion per unit volume should be as high as possible.
Vapor pressure:	The material should not exhibit a high vapor pressure.
Availability & cost:	The material should be available on the market in large quantities and at low cost.

Table 2: List of fixed and soft selection criteria and their description.

Two different kind of possible PCM have been explored: PCM candidates and commercial PCM products. The PCM candidates include materials known for their use as PCM from literature and materials which are not known to have been used as PCM. Commercial PCM products are commercially available PCM.

The process of finding and selecting materials was conducted in three main steps. Step one was to find as many materials as possible with the phase change temperature in one of the temperature ranges. Step two was to find data on the properties and the preselection of the materials found in step one. The investigated properties were the enthalpy of fusion and the density to assess the requirement of phase change enthalpy per unit volume, GHS hazard classification to assess the safety requirement, vapor pressure, and wholesale availability. During the preselection any materials which did not meet the safety requirement or no sufficient data on the properties could be found were not considered further. In step three the soft criteria of the preselected materials were compared, and the final selection was made. If a material had a comparatively high enthalpy of fusion, low vapor pressure and low wholesale cost, it was considered for further analysis. The final selection was made in consultation with the supervisors.

3.3   PCM analysis

In this part several experiments were conducted to assess the applicability of the selected materials for the use as PCM. On the one hand, experiments were carried out to confirm their properties as described in literature, which include phase change temperature and enthalpy of fusion. On the other hand, experiments were carried out to assess other physical and technical requirements for the use as PCM, which include specific heat, subcooling, and compatibility with materials.

The single compound materials were procured as chemical reagents with purities of at least 98%. For the eutectic solutions the salt was obtained, and the solutions were prepared in the laboratory with deionized water.

3.3.1   Measurements with DSC

DSC stands for dynamic scanning calorimetry. A DSC meter measures the absorbed or emitted heat of a sample while it is being heated or cooled. Sample preparation and measurement are done as follows: 8 to 10 mg of sample are placed into the bottom of an aluminum crucible. The crucible is then closed with a lid and the two parts are fixed and sealed through cold welding. The closed crucible is then placed onto the sensor plate. The sensor plate is inside the furnace of the DSC meter and it has two sensor surfaces (Figure 3, left). The sample crucible is placed on the left sensor. On the right sensor is an empty reference crucible. During the measurement the inside of the furnace is heated or cooled at a defined rate and the heat flow of the sample and the reference crucible is recorded. To calculate the sample heat flow, the heat flow of the reference crucible is subtracted from the heat flow of the sample crucible. [1] [9]

DSC measurement was used to determine the melting temperature, the enthalpy of fusion and the specific heat. The DSC meter used for analysis was a Mettler Toledo DSC823^e. The lowest temperature this DSC meter can reach is -50°C.
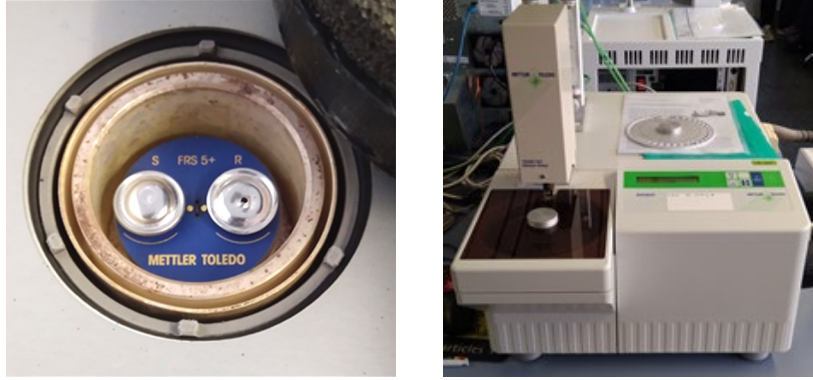
Figure 3 shows on the left side the furnace of the DSC meter with the sensor plate inside and the sample (S) and reference (R) crucible. On the right is the used DSC823^e.

Enthalpy of fusion measurement

For this measurement, the DSC performs two cycles of heating and cooling. Each cycle consists of a heating slope and a cooling slope. Between the slopes the temperature is maintained for several minutes. The first cycle is performed at a higher speed and the second cycle at a lower speed. The first cycle is made to condition the sample. The recorded data of the heating slope and cooling slope of the second cycle is then used for the calculation of the enthalpy of fusion. The curve output by the device is the heat flow [in mW] as a function of temperature. The melting or solidification of the sample produces a peak on the curve. The enthalpy of fusion [in j/g] is then calculated through integration of the peak area and division through the sample weight. The onset temperature of the peak is used as the value for the melting temperature.

There were two different methods used for this measurement. Both methods used speeds of 5 K/min for the first cycle and 1 K/min for the second cycle. The first method had temperature slopes from -40°C to -10°C and the pause between slopes was 5 minutes. The second method had temperature slopes from -50°C to -10°C and the pause between slopes was 10 minutes.

Measurement of specific heat capacity

The comparison with sapphire was used to determine the specific heat. This way is called the "sapphire method" and it is the most accurate way to measure the specific heat capacity. For this the DSC measures the samples and the sapphire standard with the same method. The method consists of a single temperature slope. Before and after the slope are isothermal segments, where the start and the end temperature of the slope are maintained for at least 5 minutes. The specific heat for every measurement point can then be calculated by comparing the heat flows of the sample and the sapphire standard (formula 3-1). [9]

$$c_p = \frac{\dot{Q} * m_{sapp}}{\dot{Q}_{sapp} * m} * c_{p,sapp} \tag{3-1}$$

The method used for the measurements had a temperature slope from -50°C to -0°C with a speed of 2 K/min and isothermal segments at the beginning and the end of the slope with durations of 10 minutes.

3.3.2   T-history experiment

It was planned to record the T-history of the materials with the help of an EasyMax workstation. Since the available EasyMax workstation could not to reach suitably low temperatures, a substitute experiment was created. The T-history (temperature history) of a sample is the change in temperature as a function of time. To record the T-history, the sample is cooled until it is completely solidified and reheated until it is completely melted. During the whole process the temperature of the sample is recorded. [1]

The T-history experiment was used for the measurement of the hysteresis and the degree of subcooling. With the substitute experiment it was also possible to observe the crystallization.
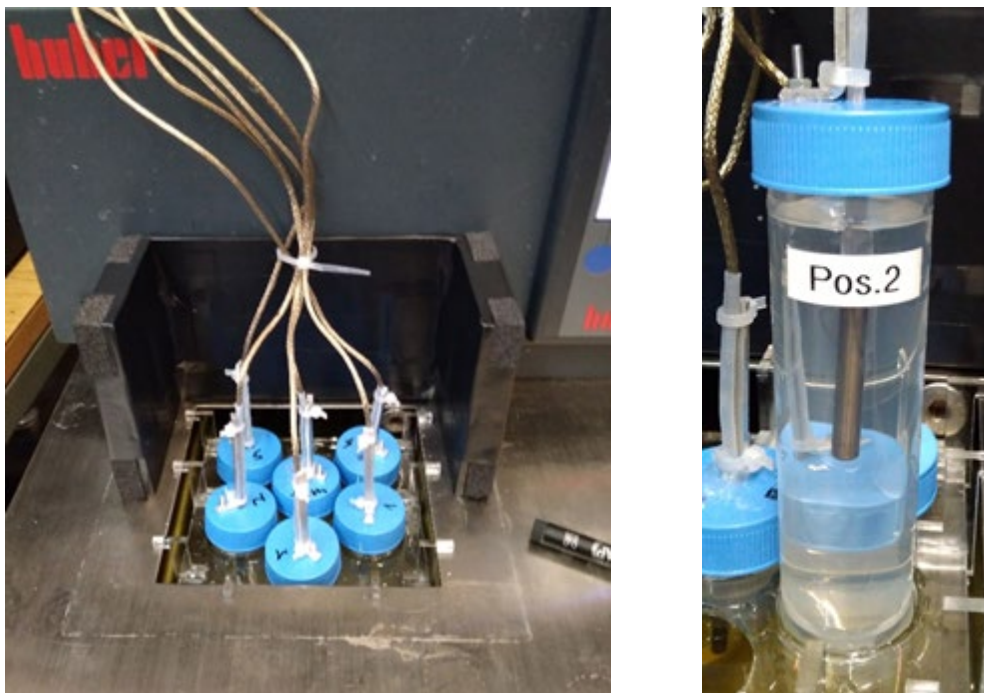
Experimental setup

Figure 4: Experimental setup of the T-History experiment. On the left picture the sample-rack inside the bath of the thermostat with sample test tubes is shown. On the right picture a single test tube filled with sample and outfitted with a temperature sensor is shown.

For the measurement of the T-history, approximately 40 ml of sample were filled into a polypropylene test tube (Figure 4, right). The tube was then closed with a lid which was equipped with a temperature sensor. The sensor was attached so that the tip of the sensor is positioned in the middle of the sample. The opening through which the sensor was mounted on the lid was sealed with silicone sealant. A Huber CC 505 thermostat was used for temperature control. The samples were placed into the internal bath of the thermostat (Figure 4, left). For this the thermostat was outfitted with a purpose-built sample rack and insulated top cover (Picture A 1 and Picture A 2). The sample rack fits up to six samples. The tubes were placed in the rack so that the fluid level of the samples is below the level of the bath. The heat transfer medium used in the thermostat bath was a mixture of 60% Antifrogen N with water. The setting point of this mixture is at approximately -43°C. The thermostat was tested with this fluid at -40°C for 4 hours. To ensure that the test tubes did not move due to the circulation of the bath, iron weights were put on top of the lids.

Polypropylene has a glass-transition around 0°C and can get brittle at lower temperatures [10]. Since water-salt solutions can exhibit a volume expansion at temperatures lower than 0°C, damage to the test tubes may occur. Therefore, the rigidity of test tubes was tested by filling one of them with water and cool it down to -30°C. Water exhibits a similar expansion upon solidification as water-salt solutions. Hence, if the test tube is not damaged by solidification of water the, a damage by the solidification of water-salt solutions is unlikely. After three times of freezing at -30°C, the test tube stayed intact (Picture A 3).

The sensors used for the temperature measurement were PT-100 sensors. The sensors were calibrated at 0°C and -40°C. The 0°C point was set using an ice bath and the -40°C point was set using the bath of the thermostat. The temperature data was collected using a National Instruments (NI) rack and were processed with the program NI Signal Express.

Measurement

Three experiments with different temperatures were conducted with this setup. In the first experiment the samples were cooled down to -30°C, in the second to -35°C and in the third to -40°C. After cooling down the temperature was held for two hours. Then they were heated up to 0°C and held at this temperature for two hours. Each experiment was conducted in two parts. In part one the cycles were conducted to only record the T-history. In part two the samples were taken out of the bath every ten minutes to observe how the solidification and melting process takes place.

3.3.3 Material compatibility tests

Figure 5 shows examples of the performed material compatibility tests at day 1. From left to right: copper, steel, stainless steel, aluminum in n-Decane.

Tests with three different metals were performed to qualitatively assess the material compatibility of the materials. Chosen for the tests were metals used by Sunamp for the construction of heat exchangers; copper, steel and aluminum. For the test, 2 milliliters of sample material were filled into a glass test tube. Then an approximately 0.5 cm² piece of 1 mm thick metal sheet was put into the test tube. The test tubes were sealed with Parafilm M to prevent the intrusion of foreign materials. The samples were stored at room temperature (~22°C) for five weeks (Aluminum: four weeks). The condition of the materials and the metals were visually assessed within the first three days every 24 hours. After that the condition was assessed in intervals of one week. Additional tests with stainless steel were carried out with PCM materials that caused a corrosion of steel after 24h. The photographs were all taken with a Xiaomi A4 13 MP camera and are displayed unchanged.

4   Results

4.1   Market analysis

The food industry encompasses all processes from agricultural production in the fields to the retail of the finished food products in the supermarket. It also includes provided services related to food production such as marketing, research, financial services and the manufacturing of farm equipment, agrichemicals and seeds. [12]

The chain of food production can be split in three parts; The agricultural food production, industrial food processing, and distribution [13]. The foods can be divided into three categories; Non-refrigerated foods (handled at room temperature), refrigerated foods (handled at temperatures between 0°C and room temperature), and frozen foods (handled at temperatures below 0°C) [14]. Since only frozen foods fit the defined temperature range, the production and distribution of frozen foods was further investigated.

4.1.1   Industrial food production

Industrial food production uses the foods produced in agriculture and turns them into semi-finished or finished food products. For this several physical, biological, or chemical manufacturing processes are applied [15]. Most of them take place at temperatures higher than 0°C. The processes found to use temperatures below 0°C include flash freezing, freeze drying, and ice cream production.

Flash freezing

Flash freezing is the primary method used to produce frozen foods. The difference between flash freezing and "slow" freezing is the growth of the water crystals. If foods are frozen, the water in the cells expands upon freezing and can damage the cell membranes. If they are frozen fast enough, the water in the cells solidifies in small crystals and the cells membranes are left undamaged. [16]

There are three different methods of flash freezing. The cryogenic method uses liquid nitrogen (-196°C) or dry ice (-56°C). The cold air method uses air with temperatures of -50°C to -35°C to freeze the food [16]. The third method freezes the foods through conduction with temperatures of -40°C [17].

Freeze drying

Freeze drying is a process where food can be dried without heating. The food is chilled to temperatures of -80°C to -60°C. Then the pressure is reduced until the water inside the food sublimates. [18]

Ice cream production

Ice cream production is not a single process, but a chain of processes. The following processes are performed at temperatures lower than 0°C: freezing, forming, and hardening [19]. During the freezing process the ice cream is frozen and mixed with air at temperatures between -15°C and -4°C [20]. At temperatures of -6°C to -5°C the frozen ice cream can be molded into the desired shape. Before packaging, the ice cream is hardened at temperatures of -40°C to -30°C [19].

4.1.2 Distribution of frozen foods

The distribution of frozen foods is conducted using the cold chain principle. If goods are distributed through an uninterrupted cold chain, it implies that at all stations from production to retail the goods were held in a temperature-controlled environment.

The investigated regulations for the distribution of frozen foods in Europe were the EU regulation 89/108/EWG and the Swiss regulation EDI 817.024.1. The investigated American regulations were from the Food Safety Inspection Service of the US Department of Agriculture (USDA) and the "Code of recommended practices" of the Frozen Food Roundtable. Also investigated was the international regulation "Codex Alimentarius" from the United Nations Food and Agriculture Organization.

Transport

The most common ways frozen foods are transported is by road, ship, and airfreight. On the road the frozen foods are transported in temperature-controlled freight trucks with diesel or battery powered refrigeration units. For transport by ship, the frozen goods are in most cases held in a refrigerated (reefer) container. Otherwise they are held in specialized reefer ships [21]. Each reefer container has its own refrigeration unit which can be powered from the internal diesel generator or it can be powered externally using electricity.

No specific temperature values could be found for the transport of frozen foods. Most investigated transport companies showed their offered temperature ranges for refrigerated transport. The lowest offered temperatures of refrigerated trucks were between -20°C and -25°C. The lowest offered temperatures of seaborne reefer logistics were between -25°C and -40°C. (Table A 2, Table A 3)

The regulations concerning the transport of frozen foods are listed in Table 3.

Institution and name	Description	Source
European Union: 89/108/EWG	Transport at -18°C or lower, with a rise to -15°C allowed for short periods.	[22]
Switzerland: EDI 817.024.1	The transported goods must always have a core temperature of -18°C with a maximal temperature of -15°C allowed on the surface layers.	[14]
United States: USDA & FFR Code	Transport at -18°C (0°F) or lower. Frozen foods delivered with a temperature higher than -12°C should be rejected.	[14] [23]
United Nations FAO: Codex Alimentarius	Transport at -18°C with a rise to -12°C allowed for short periods.	[14]

Table 3: Regulations concerning the temperatures during the transport of frozen foods.

Warehouse Storage

The investigated regulations regarding the storage of frozen foods all prescribe that frozen foods must be stored at temperatures of -18°C or lower [14] [22] [23]. The applied temperatures in the investigated cold storage warehouses were in all cases lower than legally required. According to the World Food Logistics Organization the shelf life of frozen foods like meat, fish, or precooked lean foods can be increased when stored at temperatures lower than -18°C (Table A 5) [24]. A study done at the Swiss Department of Economic Activity concluded that temperatures of -25°C or lower should be recommended for the warehouse storage frozen food [14].

Cold storage warehouses in Switzerland, Europe, and the US were investigated. The temperatures used in these warehouses were between -35°C to -18°C. The most commonly found temperatures were -26°C and -25°C. (Table A 1)

Retail

The investigated regulations regarding the handling of frozen foods in retail all prescribe that the temperatures of the frozen foods displayed in stores should be at -18°C or lower. The regulations differ on the allowed temperatures frozen foods may reach during the restocking or defrosting of the supermarket freezers. The Swiss [14] and the EU [22] regulations allow rises to -15°C. The Codex Alimentarius [14] allows a rise to -12°C and additionally requires all freezers used in supermarkets to be equipped with an always visible thermometer. [23]

To investigate the temperatures used in retail, several local supermarkets were visited. All freezers in all supermarkets featured a thermometer. The displayed temperatures were between -20°C and -18°C. (Table A 4)
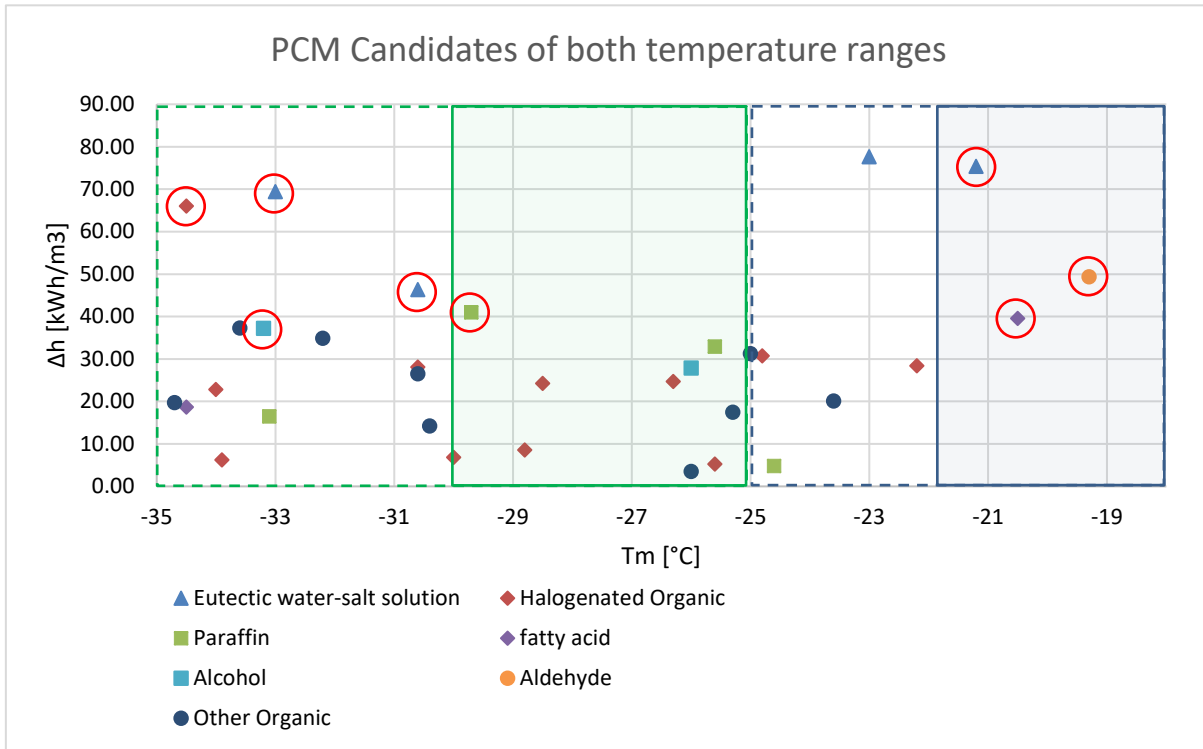
4.2 PCM Selection

Figure 6: Comparison of melting temperatures and enthalpies of fusion of the PCM candidates. The temperature ranges are marked green for range one and blue for range two. The chosen candidates are circled red.

To search for PCM candidate materials, the defined temperature ranges mentioned in section 3.2 were extended downwards. For the first temperature range, materials were sought with a melting temperature between -35°C and -25°C. For the second temperature range, materials were sought with a melting temperature between -25°C and -18°C. About 100 materials could be found for those temperature ranges of which materials 80 met the safety requirement. For 35 of the remaining candidate materials, values for the enthalpy of fusion could be found in literature. The classes of materials represented among those materials include organics such as halogenated aromatic and aliphatic compounds, paraffines, fatty acids, alcohols, aldehydes, and aromatics. Also included are inorganic materials which are mainly Eutectic water-salt solutions. A comparison of PCM candidates in respect of melting temperatures and enthalpies of fusion per unit volume is shown in Figure 6. The original temperature ranges are bordered in Figure 6 with solid lines, and the extended ranges with dashed lines. Green lines are for the first temperature range and blue lines for the second temperature range. The eight materials selected for analysis are circled red in Figure 6 and their names and properties are listed in Table 4.

In the same temperature ranges 24 available commercial PCM products could be found. Since it proved to be difficult to obtain samples of those products, Sunamp decided that they should not be further investigated. A comparison of the enthalpies of the commercial PCM products with the possible PCM materials is presented in Picture A 4.

4.2.1 Selected PCM candidates

N°	Name (solutions: [%w/w])	T_m [°C]	Δh [J/g]	Δh [kWh/m³]	Hazards (GHS)
1	1,3-Dibromopropane	-34.5	120	66	F ; Xi ; N
2	1-Heptanol	-33.2	156	37	Xi
3	$MgCl_2$-water-Solution (21.01%)	-33	206	69	-
4	$Al(NO_3)_3$-water-Solution (30.5%)	-30.6	130	46	O ; Xi
5	n-Decane	-29.7	202	41	F ; Xn
6	NaCl-water-Solution (22.4%)	-21.2	222	72	-
7	NaCl-water-Solution (23.3%)	-21.2	233	75	-
8	Propionic Acid	-20.5	144	40	F ; C ; Xn
9	Nonaldehyde	-19.5	214	49	Xi

Table 4: Overview of the selected PCM candidate materials with the literature values for phase change temperature, enthalpy of fusion per unit mass and unit volume, and Hazard initial. The hazard initials listed for the water-salt solutions are the ones of the salt. (Table A 7). [2] [7] [25] [26]

Of the eight chosen materials listed in Table 4, $MgCl_2$-water-solution, $Al(NO_3)_3$-water-Solution, n-Decane, NaCl-water-Solution and Propionic acid are known PCM from literature. 1.3-Dibromopropane, 1-Heptanol and Nonaldehyde are materials not known to be used as PCM. In the further course of this thesis, the selected PCM materials are frequently denoted by the numbers mentioned in Table 4.

Known PCM materials

The solutions of *Magnesium chloride* ($MgCl_2$), *Aluminum nitrate* ($Al(NO_3)_3$) and *sodium chloride* (NaCl) with the weight percentages listed in Table 4, are eutectic water-salt solutions. The properties of eutectic water-salt solutions are explained in section 2.4.The literature about which ratio constitutes a eutectic composition is unclear. As an example, for eutectic $MgCl_2$-water-solutions five different values of weight percent were found in literature (Table A 8). The values for eutectic compositions as listed in [2] were used to prepare the solutions. For sodium chloride there were two compositions listed in [2]. Since sodium chloride is cheap and abundant, it was decided to prepare both compositions. Magnesium chloride and sodium chloride were procured as anhydrous salt. Aluminum nitrate was procured as nonahydrate ($Al(NO_3)_3 \times 9H_2O$).

n-Decane is a paraffine with n = 10. The formula is $C_{10}H_{12}$. N-Decane is a petroleum product and is a constituent of gasoline and kerosene. The use of paraffines as PCM is very common. The properties of paraffines are explained in section 2.4.

Propionic Acid is a fatty acid with n = 2 and has the formula $CH_3(CH_2)_2COOH$. The properties of fatty acids are explained in section 2.4.

Uncharted PCM materials

Halogenated organics are organic compounds with at least one halogen (F, Cl, Br, I) in their structure. *1,3-Dibromopropane* is a halogenated alkane with two brome atoms in its structure and the formula $C_3H_6Br_2$. It is used in the industry as a reagent for chemical syntheses [27]. Examples of familiar halogenated organics are chlorofluorocarbons or polyvinylchloride (PVC) [8]. They are not known for the use as PCM. Many halogenated organics researched for the PCM selection are categorized as flammable, irritating, health hazard, and environmental hazard.

Alcohols are organic compounds which feature at least one -OH group. *1-Heptanol* is an alkane alcohol with a chain length of seven and one -OH group at the end. It has the formula $C_7H_{15}OH$. 1-Heptanol is often used as ingredient for fragrances [28]. The use of poly-alcohols like sugar alcohols [6] as PCM is very common and examples for the use of single alcohols as PCM are known[1]. A familiar example of a single alcohol is Ethanol (drinking alcohol). Common single alkane alcohols have melting temperatures in the range of -96°C (Methanol) to 90°C (Triacontanol) [7].
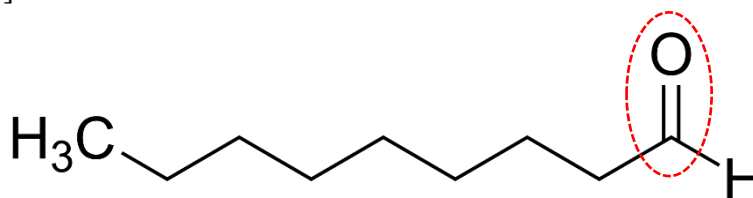
Figure 7 shows the structure formula of Nonaldehyde. The carbonyl group is circled in red. [29]

Aldehydes are organic materials with a carbonyl (-CO-) group (Figure 7) at one end. *Nonaldehyde*, also called Nonanal, is an alkane aldehyde with a chain length of nine (Figure 7). It has the formula $C_8H_{17}COH$. Nonaldehyde is applied as a component of fragrances [30] and can be used as attractant for insects [31]. Examples of familiar aldehydes are Formaldehyde and Vanillin. Aldehydes are not known for the use as PCM. Common alkane aldehydes have melting temperatures in the range of -120°C (Ethanal) to 12°C (Dodecanal) [7].

4.3 PCM Analysis

PCM N°	DSC Analysis			Material compatibility				T-History
	Δh/Tₘ	c_{p,l}	c_{p,s}	Cu	C-St	St-St	Al	
1	F	X	F	X	X	-	X	F
2	X	X	X	X	X	-	X	F
3	X	X	F	X	X	X	X	-
4	F	X	F	X	X	-	X	-
5	X	X	X	X	X	-	X	X
6	X	X	X	X	X	X	X	X
7	X	X	X	X	X	X	X	X
8	X	X	X	X	X	X	X	X
9	X	X	X	X	X	-	X	X

Table 5: Overview of the experiments that were conducted. Explanation: "X" experiment successful, "F" experiment not successful, "-" no experiment conducted.

The in section 4.2 selected materials were analyzed using methods in described section 3.3. The majority of experiments were carried out with all materials, most of them being successful. An overview of what experiments were done and if they were successful is shown in Table 5.

4.3.1 DSC Measurements

PCM	T_m		Δh		$c_{p, liquid}$		$c_{p, solid}$
	[°C]		[J/g]		[J/(g*K)]		[J/(g*K)]
	Literature	DSC	Literature	DSC	Literature	DSC	DSC
1	*-34.5*	-	*120*	-	-	1.20	-
2	*-33.2*	-33.4	*157*	170	*2.05*	2.56	1.27
3	*-33.0*	-31.4	*206*	187	-	2.61	-
4	*-30.6*	-	*130*	-	-	3.45	2.40
5	*-29.7*	-28.7	*202*	200	*2.08*	2.61	2.76
6	*-21.2*	-21.3	*222*	246	-	3.91	2.53
7	*-21.2*	-21.2	*233*	237	-	3.90	2.41
8	*-20.5*	-21.8	*144*	147	*1.96*	2.71	2.47
9	*-19.5*	-20.7	*214*	191	-	1.93	1.76

Table 6: Comparison of the DSC measurement results with literature values.

The results of the DSC measurements are listed in Table 6. It was mentioned section 3.3.1 that the recommended sample amount for liquids is 8 to 10 mg. The heat flow of the sample is measured through the floor of the crucible. In order to obtain valid measurement point results, the whole floor of the crucible should be covered with sample. To achieve this, larger amounts of some samples had to be used. According to Mettler Toledo, the crucible may be filled with a maximum of three fourth of the volume.

Enthalpy of fusion measurement

The first run of measurements was carried out using method one (Section 3.3.1). None of samples except Nonaldehyde crystallized and no peak could be detected. When measuring all samples with method two (Section 3.3.1), all measurements were successful except for 1.3-Dibromopropane and aluminum nitrate. Those samples did not solidify at -50°C, which is the lowest temperature the used DSC could reach. Since possibility of solidification also increases with a larger sample amount [1], the measurements of 1,3-Dibromopropane and aluminum nitrate were repeated with the maximum allowed sample amount. Those measurements yielded inconclusive results.

Specific heat measurement
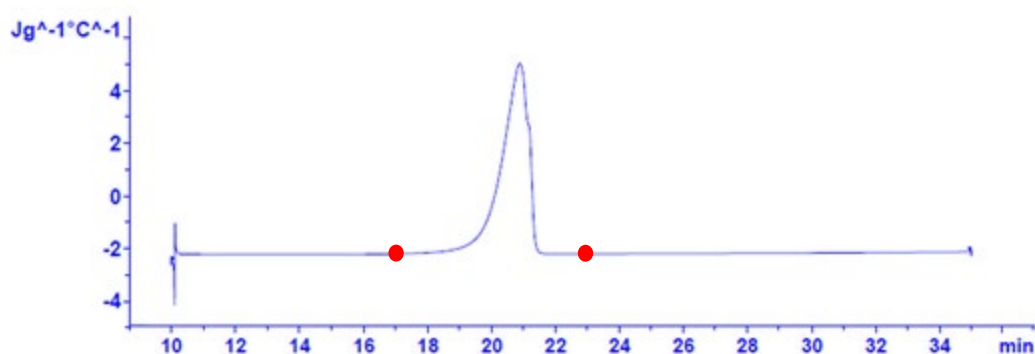
Figure 8: Specific heat capacity curve of the measurement of n-Decane. Point chosen for solid c_p-value: 17 min (-35°C). Point chosen for liquid c_p-value: 23 min (-26°C).

As mentioned in section 3.3.1, the specific heat capacity measurement using the sapphire method produces a c_p-value for every measurement point. The melting of the sample during the c_p measurement results in a peak on the result curve (Figure 8). The results in the temperature range of the melting peak are not usable as c_p-values. The c_p-values in the vicinity of the peak may be influenced by the onset and offset bow of the peak. For the evaluation of the solid c_p and liquid c_p-values, points on the c_p curve with sufficient distance from the peak were chosen (Figure 8, red dots).

4.3.2   T-history Experiments

The measurements with -30°C and -35°C could be carried out without complications. When using the thermostat with temperatures lower than -35°C, the thermostat stopped either before reaching the set temperature or less than 30 minutes upon reaching the set temperature. Several measures as described in the instruction manual or recommended by the manufacturer have been applied to no effect. After two cycles of the second experiment the thermostat showed the same behavior before reaching -35°C. For this reason, no further cycles were made with -30°C and -35°C. The third experiment was carried out using the cycle stability test setup described in section 5.1.

Experiment 1: -30°C

The PCM materials measured in this experiment were both NaCl compositions (22.4% on position 1, 23.3% on position 2), Propionic acid (position 3), and Nonaldehyde (position 4). Propionic acid did not crystallize in this experiment and was measured again in experiment two. The temperature curves in Figure 9 are taken from the first run without assessing the crystallization of the materials.
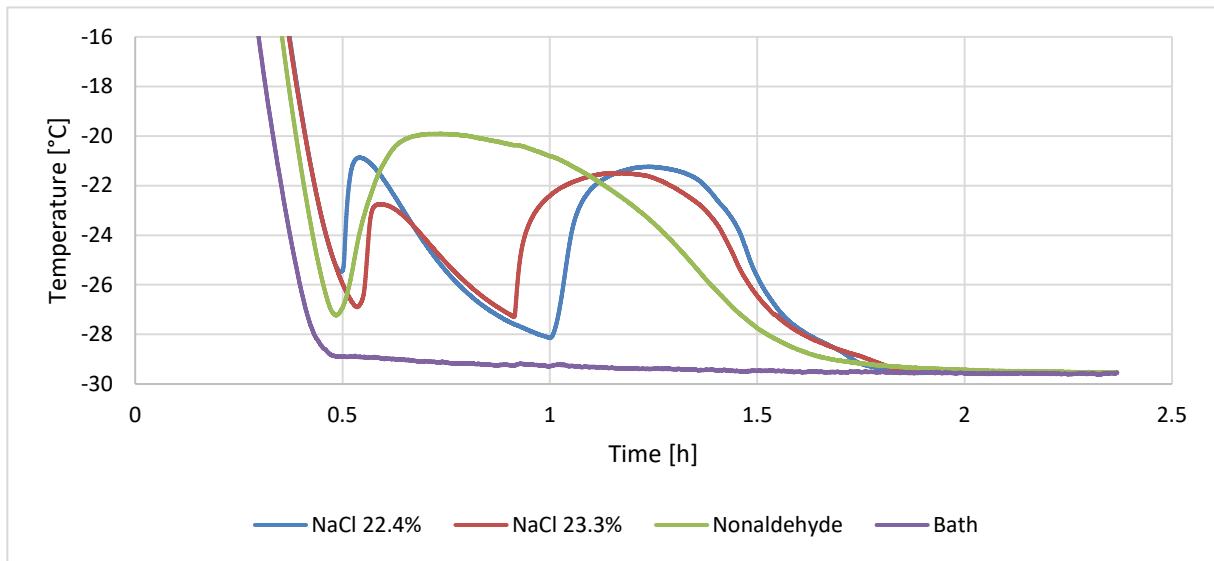
Figure 9: Aligned temperature curves of the samples and the bath during T-history experiment 1

The green line in Figure 9 represents the temperature curve of Nonaldehyde. The curve shows that Nonaldehyde solidifies in one phase and that it exhibits subcooling. The degree of subcooling and the phase change temperature are listed in Table 7. The crystallization of Nonaldehyde begins at multiple places on the interior surface of the test tube. After 10 minutes a crystal layer covers the whole interior surface (Picture A 9). From that point on, this solidified layer on the interior wall of the test tube grows further inward until the whole sample is completely solidified. The melting of Nonaldehyde starts on the interior surface of the test tube and progresses inward. At the same time, it starts to melt at the top and the melting progresses downward (Picture A 10).
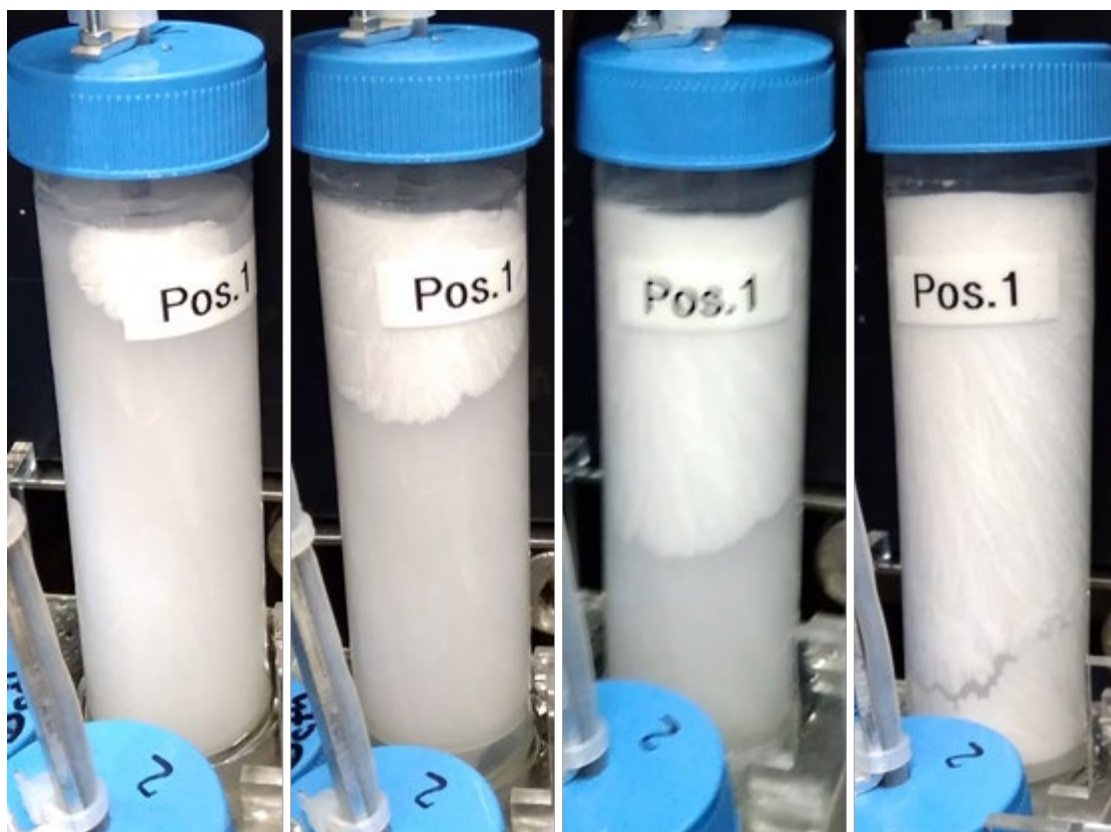
Figure 10 shows the crystallization process of 22.4% NaCl solution. The pictures from left to right were made within time intervals of 10 minutes. 10 minutes before the picture onthe left was made, the sample was completely liquid.

The blue and red line in Figure 9 represent the two compositions of NaCl. The blue is the 22.4%-solution and the red line the 23.3%-solution. Those temperature curves show that both compositions show subcooling, and that both do not freeze in one phase. The temperature curves of the two compositions behave similarly. They have two freezing phases with different temperatures and both phases show subcooling. The degree of subcooling and the phase change temperature for both phases are listed in Table 7. The observed crystallization processes are also indicating two phases of solidification. The crystallization of the 22.4% NaCl-solution takes place as follows in Figure 10: Within a 10-minute interval the liquid sample crystalizes as a lightly translucent white solid. At the top of the crystallized solution is a spot white opaque crystal. Over time this spot grows until it covers the whole visible surface of the sample. During a test run of the experiment, the observation was made that those white spots are not superficial. They appear to be clusters of opaque white solid which melt slower than the lightly transparent solid (Picture A 11). The crystallization process of the 23.3% NaCl-solution is similar, except that the white spots start to appear at several places instead of starting from one point. After the first cycle, solid crystals could be seen at the bottom of the 23.3% NaCl-solution (Picture A 12).

During the second cycle of experiment one, the test tubes of both NaCl-solutions cracked after two hours at -30°C. The test tubes of Nonaldehyde and Propionic acid remained intact.

PCM	T_m (Lit.) [°C]	T_m 1 [°C]	Subcooling [K]	T_m 2 [°C]	Subcooling [K]
Nonaldehyde	-19.5	-20.0*	6.0	-	-
NaCl 22.4%	-21.2	-21.2*	4.7	-21.6*	7.0
NaCl 23.3%	-21.2	-22.7*	4.2	-21.5*	5.8

*Table 7: Melting temperature and subcooling values of experiment 1. *Section 6*

Experiment 2: -35°C

The PCM materials measured in this experiment were n-Decane, 1-Heptanol, and Propionic acid. 1-Heptanol did not solidify in this experiment and was measured again in experiment three. The temperature curves in Figure 11 the results of the second run of experiment 2 while assessing the crystallization. There was a problem with the recording of the temperature curves of the first run, thus the temperatures of the second run were used to assess the subcooling. the temperature curves may show sudden abrupt changes due to the frequent moving of the samples.
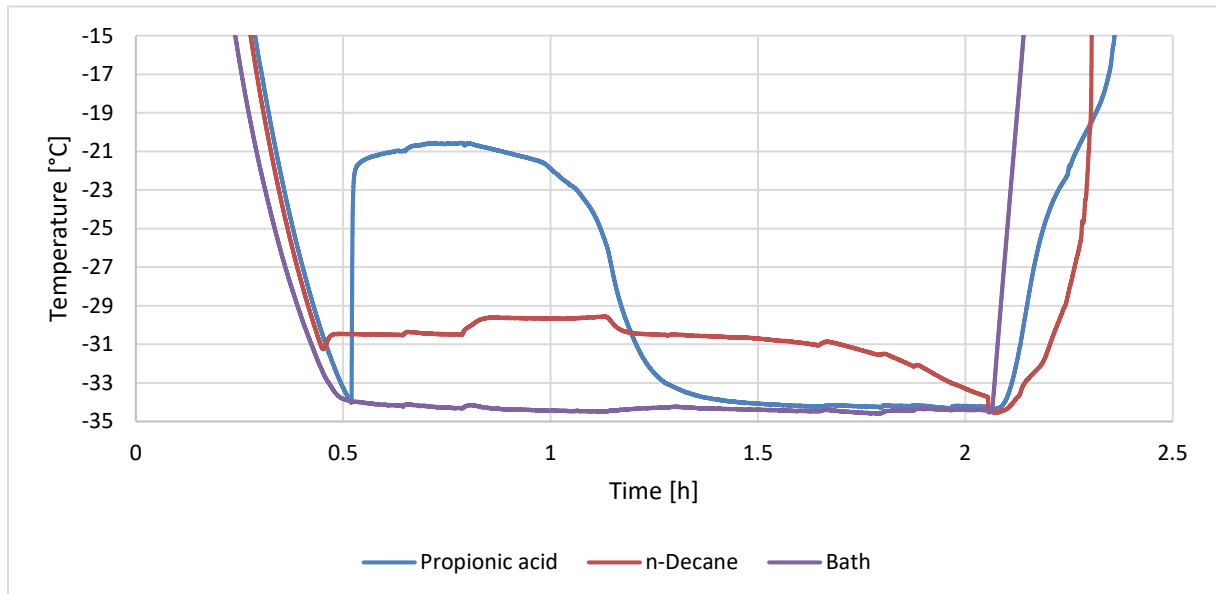
Figure 11: Aligned temperature curves of the samples and the bath during T-history experiment 2.

The blue line in Figure 11 represents the temperature curve of Propionic acid. The curve shows that Propionic acid crystallizes in one phase and has comparatively large subcooling. Propionic acid crystallizes as a white lightly translucent solid. The red line represents the temperature curve of n-Decane. The curve shows that n-Decane has comparatively little subcooling. Crystallization and Melting of n-Decane and Propionic acid follow the same pattern as Nonaldehyde. The values for subcooling and melting temperature are listed in Table 8.

PCM	T_m (Lit.)	T_m	Subcooling
	[°C]	[°C]	[K]
Propionic acid	-20.5	-20.7*	11.7
N-Decane	-29.7	-29.7*	0.7

*Table 8: Melting temperature and subcooling values of experiment 2. *Section 6*

Experiment 3: -40°C

Experiment 3 was performed with 1-Heptanol and 1.3-Dibromopropane. This experiment was not carried out using the setup described in section 3.3.2 following the problems reported at the beginning of this section. None of the samples did crystallize in this experiment. After two hours at -40°C, an attempt was made to trigger solidification trough swirling and tapping on the test tube. After another hour at -40°C with no solidification, the experiment was aborted.

4.3.3 Material compatibility Tests

The pictures showed in this part were made after 5 weeks (Aluminum: 4 weeks) at room temperature.

PCM	Copper	Steel	St-Steel	Aluminum
1,3-Dibromopropane	+	-	N/A	+
1-Heptanol	+	+	N/A	+
$MgCl_2$-water-Solution	-	-	N/A	-*
$Al(NO_3)_3$-water-Solution	-	-	+	-
n-Decane	+	+	N/A	+
NaCl-water-Solution	-	-	+	-*
Propionic Acid	-	-	+	+
Nonaldehyde	-	+	N/A	+

*Table 9: Overview of the results of all material compatibility tests. *Section 6*

A combination of PCM and metal is labeled with a good compatibility (+) when no change of the PCM or the metal took place. If a change of the PCM or metal could be observed the compatibility is labelled as bad (-). No combination of PCM and metals showed an immediate reaction, like the formation of bubbles or a discoloration of the metal.

Combinations with stainless steel.

The combinations of PCM with stainless steel did not show alteration of either metal or liquid after five weeks.
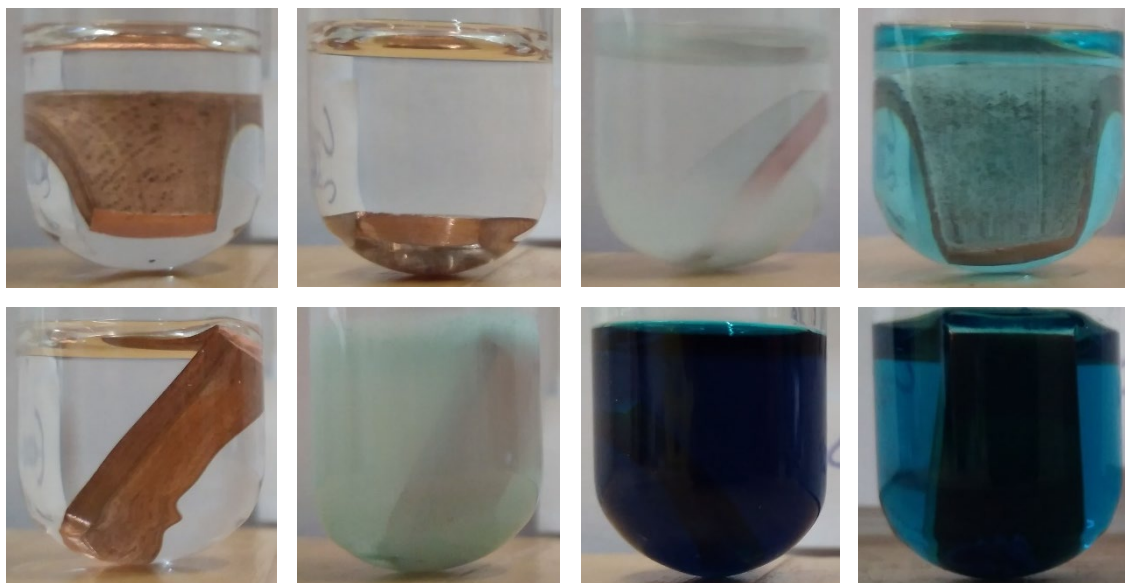
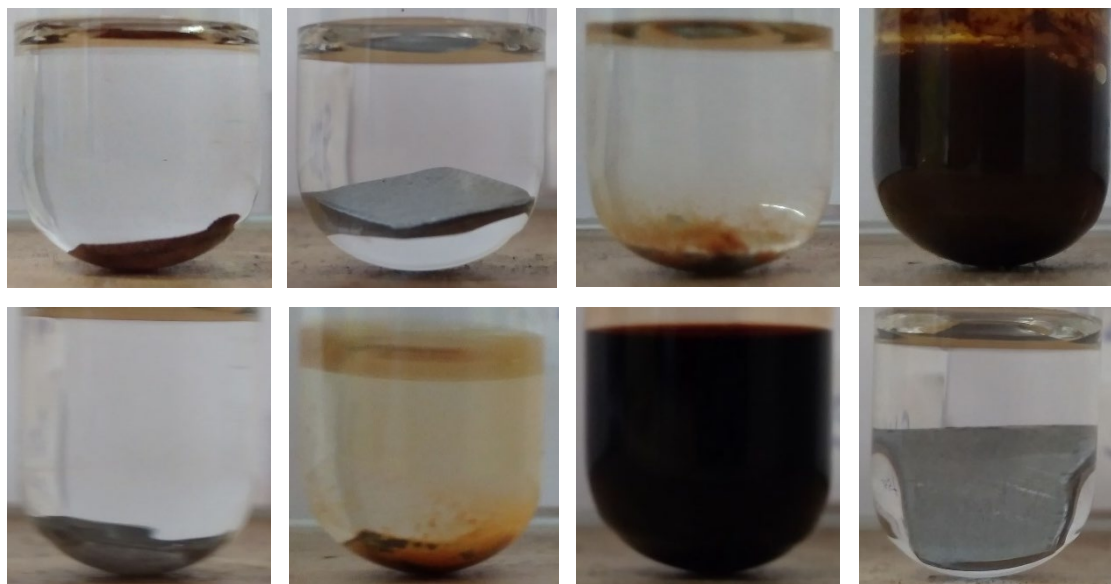*Figure 12: combinations of the PCM with copper. Top row from left to right: 1,3-Dibromopropane, 1-Heptanol, MgCl₂-solution, Al(NO₃)₃-solution. Bottom row: Decane, NaCl-solution, Propionic acid, Nonaldehyde.*

Combinations with Copper

The combinations of the PCM with copper after five weeks are shown in Figure 12. The combinations with 1,3-Dibromopropane, Heptanol and Decane did not show any visible change after 5 weeks. The combinations with $MgCl_2$ and NaCl-solution started to get cloudy after one week. The cloudiness grew stronger with every week. After two weeks, the NaCl-solution started to turn blue and one week later the $MgCl_2$-solution also started to turn blue. The combinations with Propionic acid and Nonaldehyde started to turn blue after 24 hours, and the Aluminum chloride solution started to turn blue after one week. The blue discoloration of the combinations with NaCl-solution, Propionic acid and Nonaldehyde increased in intensity every week. The discoloration of the combination with aluminum nitrate increases until week two and stayed the same since.
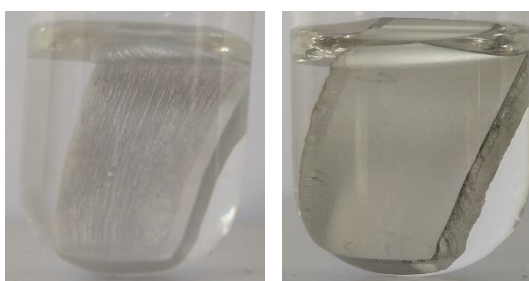
Figure 13: Left picture: Aluminum in combination with aluminum nitrate solution. Right picture: Aluminum in n-Decane

Combinations with Aluminum.

The aluminum metal piece inside the aluminum nitrate solution started to show grooves on the surface after four weeks (Figure 13, left. The combination with n-Decane on the right for comparison). The combinations with NaCl- and MgCl₂-solution show a white precipitation after four weeks. All other combination of PCM with aluminum showed no alteration of either metal or liquid after four weeks.

Figure 14: combinations of the PCM with steel. Top row from left to right: 1,3-Dibromopropane, 1-Heptanol, MgCl₂-solution, Al(NO₃)₃-solution. Bottom row: Decane, NaCl-solution, Propionic acid, Nonaldehyde.

Combinations with Steel

The combinations of the PCM with steel after 5 weeks are shown in Figure 14. The combinations of 1-Heptanol, n-Decane, and Nonaldehyde with steel did not show any change after five weeks. The combination with aluminum nitrate solution showed the strongest reaction. After 24h the liquid turned orange-brown and cloudy. The steel plate inside was completely dissolved after 48h. Propionic acid in combination with steel turned a translucent light orange liquid after 24h. The discoloration increased in intensity over time and after three weeks, the steel plate inside was no longer visible. The steel plate inside the NaCl-solution started to show a bright orange flash rust after 24h. This flash rust separates from the metal when the sample is moved and settles down as bright orange precipitation. The amount of rust increases over time. The sample with MgCl₂-solution started to show the same kind of rust after two weeks. In the sample with 1,3-Dibromopropane, the steel plate started to show spots of orange brown rust forming on the surface after 48h. The number of spots increased until the whole surface was covered with rust after one week. The rust does not come off when shaking the sample, and the steel plate did not show any further change.

5 Cycle stability experiment

To determine if the PCM candidates fulfill the requirement of a reproducible phase change, cycle stability tests will be made. A cycle consists of the complete solidifying and melting of the PCM. For a cycle stability test, the PCM-samples are filled into closed containers and put into a temperature-controlled environment. The temperature of the environment is then lowered to a temperature where all PCM-samples are able to solidify. The temperature is held until all samples reached complete solidification. Then the temperature is raised back to the starting temperature and held until all samples completely melted. The number of cycles is dependent on the application.
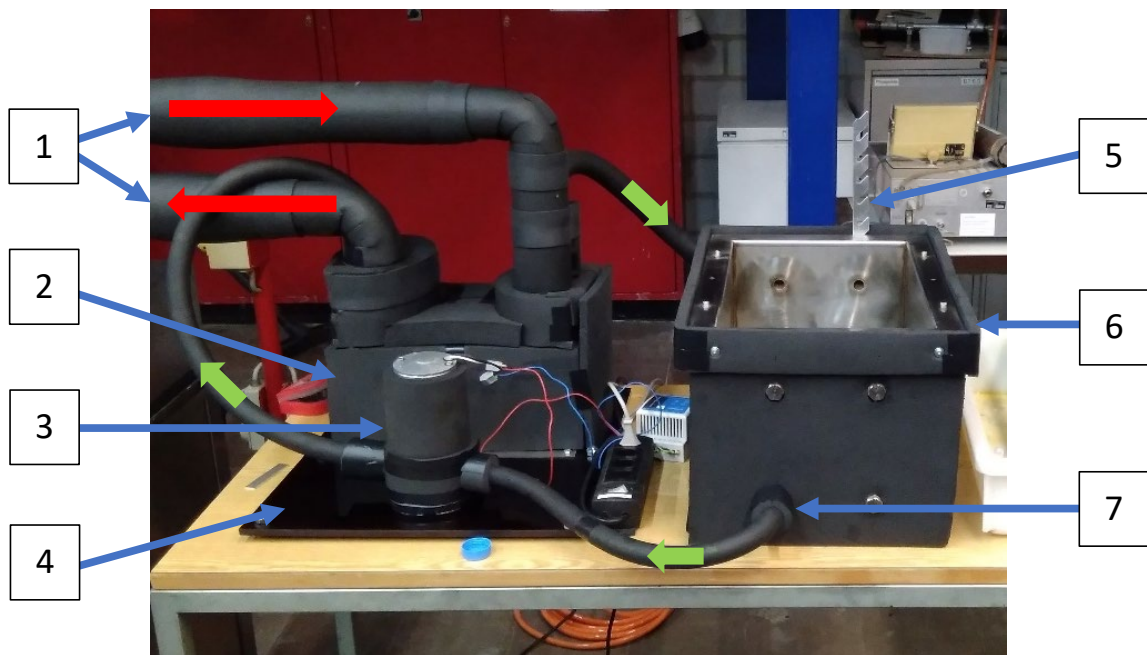
Figure 15: Cycle stability test setup.

5.1 Design and construction of the setup

The cycle stability test setup built in this bachelor thesis is shown in Figure 15 and the parts are described in this paragraph. The main components of this setup are a thermostat, an insulated box (6), and a Heat exchanger (2). The purpose of this setup is to create a temperature-controlled environment inside the insulated stainless-steel box where the samples can be cycled. The setup consists of two circuits of heat transfer liquid. The first circuit (Figure 15, red arrows) is connected to the thermostat (1, Picture A 13) and the heat exchanger. In this circuit the heat transfer medium is circulated by the internal pump of the thermostat. The insulated box is filled to a third with thermal oil. During the cycle tests, the bottles with PCM sample are immersed in the thermal oil. The second circuit (Figure 15, green arrows) circulates the thermal oil from the box. The oil goes out the front of the box (7), goes through the heat exchanger and goes back into the box at the backside. The thermal oil in this circuit is circulated by a gear pump (3). The tubes and hoses which connect the heat exchanger with the thermostat are made of stainless steel. To prevent the heat exchanger from tipping over when not connected to the thermostat, the heat exchanger was mounted onto a wooden plate (4).
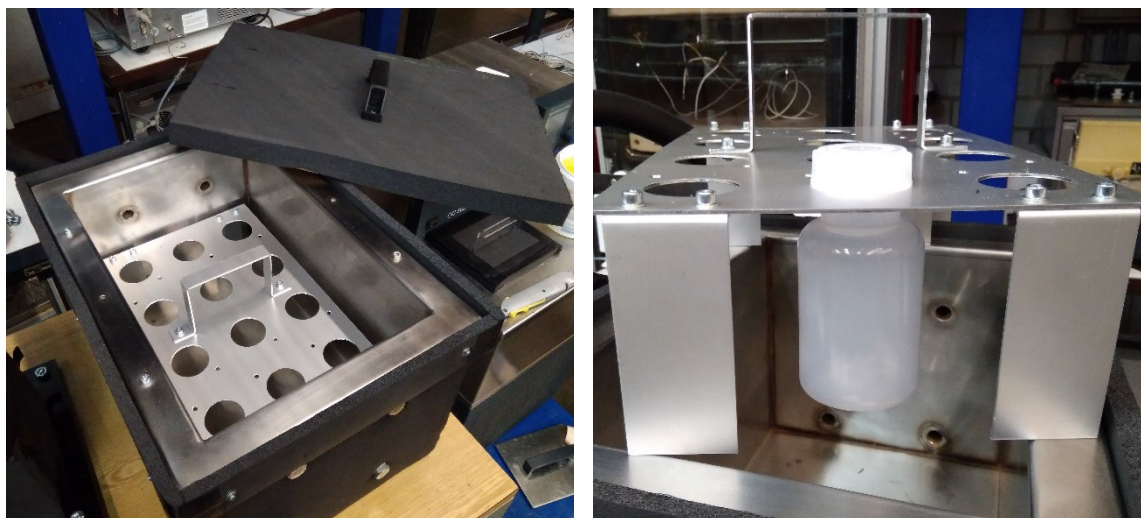
Figure 16: On the left: The insulated box with sample rack and lid. On the right: LDPE-bottle mounted on the sample rack.

For cycling, the PCM are filled into plastic bottles. The bottles with PCM are fixed onto a custom-built sample rack made of aluminum (Figure 16). The holes in the sample rack were made with a diameter larger than the lid of the bottles and smaller than the neck of the bottles. To attach the bottles to the rack, the lid of the bottle is removed, the neck of the bottle put through the hole in the rack and then the lid is reattached onto the bottle. Through that, the bottles are hanging from the lid inside the rack (Figure 16, on the right). The rack can fit up to twelve bottles with PCM sample. The lids of the bottles are all equipped with a temperature sensor to measure the temperature of the PCM during the cycling. The rack can also be equipped with temperature sensors at several places to measure temperature of the bath. The rack with the attached sample bottles can then be placed into the insulated box. Inside the box the bottles are then immersed in the thermal oil. The cords of the temperature sensors mounted on the bottles and the rack can be fixed on an aluminum plate on the backside of the box (Figure 15, number 5). Before starting the test, the box is closed with a custom-built insulated wooden lid. The heads of the screws in the top frame of the box (Figure 16, on the left) correspond with holes on the bottom of the lid and keep the lid from moving when put on top of the box.

The setup was designed for cycling the samples between 0°C and -40°C. The cooling power needed for cycling the samples at -40°C was estimated to be between 240W (ADX10) and 330W (Antifrogen N, 60%). The thermostat used for the setup is a Huber Unistat 510. It is capable to cool down to -50°C and has a cooling power of 900 W at -40°C [32].The thermal oil used in the thermostat and the in first circuit is a silicon oil applicable for temperatures down to -120°C. The heat exchanger used to connect the two circuits is a SWEP B12MT plate heat exchanger with 60 stainless steel plates. The thermal oil used in the second circuit is Therminol ADX10. ADX10 is an aromatic organic thermal oil, has the setting point at -85°C and has an application range of -45°C to 250°C [33]. The pump used to circulate circuit one is a Viscomat DC 60/1 gear pump. It has a flow rate of ~3.3 l/min and can pump liquids with viscosities up to 2000 cSt (mm^2/s)[34]. The comparably high viscosity of ADX10 at low temperatures is the reason for the application range being limited to -45°C. Since the kinetic viscosity of ADX10 at -50°C is 867 mm^2/s and the gear pump is capable of pumping fluids wit up to 2000 mm^2/s, the pump and oil should be able to function at -50°C [33]. The plastic bottles for holding the samples are 250ml LDPE bottles. LDPE has a glass transition lower than -50°C and therefore the bottles stay flexible at -40°C [35].

The setup was tested with two cycles down to -40°C and one cycle down to -45°C. The temperature difference between the set temperature of the thermostat and the temperature in the box was between 2 and 2.5 K. The pump was functional at both temperatures. The flow rate of the pump decreased the lower the temperature. One LDPE bottle was inside the box during the test cycles. The bottle showed no visible change after the cycles. At -40°C the rigidity of the bottle was tested through compressing it by hand. The bottle was still flexible and did not break.

5.2   Measurement

The purpose of cycle stability tests is to determine if the phase change of the PCM differs after solidifying and melting a defined number of times. During the whole process the temperature of the samples will be measured. Through comparison of the temperature curves, it can be determined if the phase change shows a difference before and after cycles. The way in which PCMs might change during cycle stability tests are chemical degradation and phase separation. Chemical degradation can happen at high temperatures, through radiation or contamination with foreign substances [1]. Chemical degradation may cause a discoloration of the PCM. Since the samples are cycled at temperatures lower than room temperature, are in closed containers and no radiation source is close to the setup, chemical degradation is not expected to happen. The effect of phase separation, as mentioned section 2.2.2, can happen in two component materials and results in a differing material composition on top and bottom of the sample. In the case of water salt solutions, the sample has different densities and percentages of salt on top and bottom when phase separation occurred. Phase separation can result in precipitation of solid salt because the composition on the bottom may reach the saturation point of the solution.

To determine the degree of phase separation, right after cycling, small amounts of sample are taken from the top and from the bottom of the cycled PCM. The extraction of the samples must be conducted without stirring the PCM in the process. The composition of those samples can then be determined through density measurement or TGA-Analysis.

When no visible change to the PCM, no phase separation and no change in the temperature curve took place, the PCM can be considered cycle-stable.

6 Discussion of results

Since the cold storage battery should feature a higher thermal storage capacity than existing variants of cold storage, the enthalpy of fusion per unit volume was decided to be the most important criteria in the selection of the PCM candidate materials. As shown in Figure 6, only few materials with a high enthalpy of fusion could be found for the temperature range of -30 to -25°C. The range of -22 to -18°C, did not feature a large choice of materials, yet most of those materials had a comparably high enthalpy of fusion. Due to the lack of candidates in the range of -30°C to -25°C, the selection criteria in regards of the temperature had to be loosened, consequently materials with lower phase change temperatures were also considered as PCM.

The $MgCl_2$-solution prepared in the lab, started to show a white precipitation after two weeks. The solution was prepared again in a different bottle and all measurements except for the material compatibility was repeated. The precipitation also appeared in the second solution (Picture A 7). An oversaturation is of the solution not likely, because the saturation point of $MgCl_2$ in water is at room temperature is over 30% [37]. Since the used $MgCl_2$-salt was not newly obtained for this project, it is likely that the cause for the precipitation lies in the salt.

The DSC measurements confirmed that the phase change temperature and the enthalpy of fusion most of the procured PCM do not deviate significantly from the literature values. For those PCM which showed a larger deviation, the measurement was repeated. The literature for c_p-values is scarce and available values (1-Heptanol, n-Decane and Propionic acid) tend to be significantly lower than the c_p-values measured with DSC (Table 6).

The experimental setup created to record the T-history of the PCM candidates could be used to determine the subcooling and the temperature curves for the freezing of the samples. Since the thermostat can utilize more power at 0°C than at -30 to -40°C, the melting of the samples happened much faster and no clear melting temperature could be derived from the temperature curve. Therefore, the conducted experiment was not conclusive for determining the hysteresis of the PCM candidates. The temperature sensors were calibrated several times and gave plausible values for temperatures over 0°C. However, the recorded temperatures showed increasing divergences at lower temperatures. The divergence between all six sensors at 22°C and 0°C was 0.6K. At -40°C however, the divergence was over 7K. The temperature curves in Figure 9 and Figure 11 were aligned to the bath temperature. The raw temperature curves are shown in Picture A 8. The T_m-values marked with an asterisk (*) in Table 7 and Table 8 are from the aligned curves and can therefore not be considered as accurate. A manual calibration was attempted by recording the temperatures of each sensor by hand at the calibration points of 0°C and -40°C and calculate the calibrated value afterwards. However, it could be established that the values measured with the same sensor in different measurement cycles are not congruent. Therefore, a manual calibration was not possible. The subcooling in Table 7 and Table 8 was calculated using the raw data of the experiments.

The test tubes were not acquired specifically for this experiment. Since it was known that polypropylene may get brittle at temperatures lower than 0°C, it was expected that damage to the test tubes can happen due to the volume expansion of eutectic water-salt solutions upon melting as mentioned in section 2.4. Hence, the rigidity of the test tubes was tested with tap water at -30°C as mentioned in section 3.3.2. Since the vials were damaged during the NaCl-measurements, damage to the vials was likely to occur with all water-salt solutions and therefore no T-History measurements were made with the magnesium chloride and aluminum nitrate solutions.

The crystallization and melting of the organic PCM observed in the T-History experiment, happened as expected: Freezing from the outside in and melting from the top down.

The measurement of the T-History of the NaCl-solutions showed that both solutions do not solidify in one phase, based on the temperature curve and the observed crystallization process. Therefore, the assumption can be made that both analyzed solutions are not eutectic solutions. The crystals found at the bottom of the test tube with 23.3% NaCl-solution might be an indication for phase separation taking place after one cycle. Since phase separation of water-salt-solutions results in a higher concentrated solution at the bottom of the PCM, and the percentage of 23.3% is close to the saturation point at room temperature (26.3%, Picture A 5), found crystals are likely to be solid NaCl.

The material compatibility tests clearly show what combinations of PCM and metal causes a corrosion of the metal, a change of the PCM or both. The assessment of the material compatibility was not graduated into different levels. The only labels given were good or bad compatibility. This was decided, because the use of the PCM in latent storage batteries is a long-term application and any change shown within five weeks could increase over time. Since the sodium chloride solutions only have a small difference in weight percentage, the assumption was made that the material compatibility will not differ significantly between the two compositions, therefore the tests were only carried out with the 22.4% NaCl-solution. The compatibilities of NaCl-solution and-$MgCl_2$ solution were marked with an asterisk (*) in Table 9 because the changes of those combinations were only detectable at the last assessment and were not severe enough to mark them as clearly incompatible. They both showed a white precipitation but no visible change on the metal. Since corrosion on aluminum through oxygen and chlorine are white salts [7], and aluminum ions have no distinctive color, it is unclear if the precipitation is caused by the metal or the PCM. Those combinations should be tested over a longer period to make a clear assessment.

7   Conclusion

Several materials could be found which are non-toxic, have a high phase change enthalpy per unit volume and are available at low cost could be found in both temperature ranges. Some of those materials have likely never been considered as for use PCM. the phase change temperature, melting enthalpy, heat capacity, subcooling and material compatibility with metals could successfully be determined analytically or experimentally for most of these materials. There was only a single cause why some measurements could not be conducted successfully this was due to the temperatures being not low enough.

1,3-Dibromopropane is the organic compound which has with the highest value for enthalpy of fusion per unit volume according to 66 kWh/m^3 literature. this value could, however, not be confirmed with DSC measurement since the sample did not solidify at -50°C. In the T-History analysis it did not solidify either, therefore one can conclude that it shows subcooling of at least 5 K. Furthermore, the c_p-value of 1.2 J/(g×K) was the lowest measured throughout all analyzed PCM. 1,3-Dibromopropane exhibits a good material compatibility with copper and aluminum and a bad compatibility with steel.

The DSC measurement of *1-Heptanol* revealed a higher value for enthalpy of fusion than the literature value, 170 J/g compared to 156 J/g found in literature. 1-Heptanol shows a large difference between the liquid and solid specific heat capacity. The solid c_p-value is less than 50% of the liquid value. It shows a good compatibility with all metals. It did not solidify in the T-History experiment at -40°C and exhibits therefore subcooling of at least 7K.

Since both prepared Magnesium chloride solutions started to show precipitation after two weeks, all values determined of this PCM must be considered with caution.

The enthalpy of fusion measurement of the *Aluminum nitrate* solution was not successful, since the DSC sample did not solidify at -50°C. It showed a bad material compatibility with copper, steel and aluminum and a good compatibility with stainless steel.

All measurements with *n-Decane* were successful. The enthalpy of fusion and phase change temperature determined experimentally were very similar the literature value. It showed subcooling of less than 1K and had a good material compatibility with all metals.

The *Sodium chloride* solutions show higher values for enthalpy of fusion compared to the literature values. The 22.4% NaCl-solution has a significantly higher value with, 246 J/g compared to 222 J/g. Both compositions exhibit a two-phase solidification and are therefore likely not eutectic. Sodium chloride solutions are the analyzed PCM having the highest enthalpy of fusion per unit volume, with experimental values between 77 to 80 kWh/m^3. They show a subcooling of 4K to 7K. Sodium chloride solution is incompatible with copper, and steel. The compatibility with stainless steel is good and the compatibility with aluminum is unclear.

All measurements with *Propionic acid* were successful. The divergence of the phase change temperature and enthalpy of fusion values from the literature values is small. With 12K, it shows a rather large subcooling. It is compatible with stainless steel and aluminum and incompatible with copper and steel.

The enthalpy of fusion value Nonaldehyde measured with DSC is with 14% significantly smaller than the literature value. Nonaldehyde has rather small c_p-values of 1.9 J/(g×K) and 1.7 J/(g×K) and a moderate subcooling of 6K. It is compatible with steel and aluminum, and incompatible with copper.

7.1   Comparison of the PCM

The experimentally determined values of the PCM within each temperature range are compared and for each temperature range the PCM with the best thermophysical properties and a PCM with the best all-around properties are designated.

Temperature range 1: -30°C to -25°C (-35°C to -25°C)

The PCM with the best thermophysical properties is $MgCl_2$ with a Δh of 63 kWh/m^3 and a c_p of 3.0 J/(g×K). It has, however, a poor compatibility with all tested metals. The PCM compatible with all tested metals are 1-Heptanol and n-Decane. Since n-Decane has lower subcooling, higher Δh and higher c_p than 1-Heptanol, it is the PCM with the best all-around properties for this temperature range. The other two PCM were not compared since the enthalpy of fusion could not be determined.

Temperature range 2: -22°C to -18°C

The PCM with the best thermophysical properties is 22.4%-NaCl-solution with a Δh of 80kWh/m^3 and a c_p of 3.9 J/(g×K). It has, however, a poor compatibility with metals and seems to be a non-eutectic solution. The 23.3%-NaCl-solution has also good thermophysical properties but seems to be non-eutectic as well. When comparing the two organic PCM, Nonaldehyde has a lower subcooling, higher Δh and is only incompatible with copper. Since Propionic acid only has a higher c_p-value, Nonaldehyde is the with the best all-around properties for this temperature range.

7.2   Outlook

The results obtained in this bachelor thesis and the constructed cycle stability test setup will be used in the further continuation of the project STOREF. Further Experiments and analyses with the PCM researched in this Bachelor thesis and additional PCM will be carried out. The further experiments will include cycle stability tests and measurements on a close to scale prototype of the cold storage battery. The analysis of further properties might include the determination of thermal conductivity and the determination of liquid and solid densities.

8   Directory of symbols

Formula Symbols

T_m	°C	Phase change temperature
Δh	J/g	Enthalpy of fusion
m	kg	mass
c_p	J/kg K	specific heat capacity
$\dot{Q}$	W	Heat flow

Indices

sapp	sapphire
s	solid
l	liquid
S	sample
R	reference

Abbreviations

TES	Thermal Energy Storage
PCM	Phase Change Material
NI	National instruments
St	Steel
St-St	Stainless steel

9   List of references

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10 Picture Directory

11 Table Directory

A1   T-History Setup

Picture A 1: Sample Rack for T-History experiment

Picture A 2: Insulated lid for T-history experiment
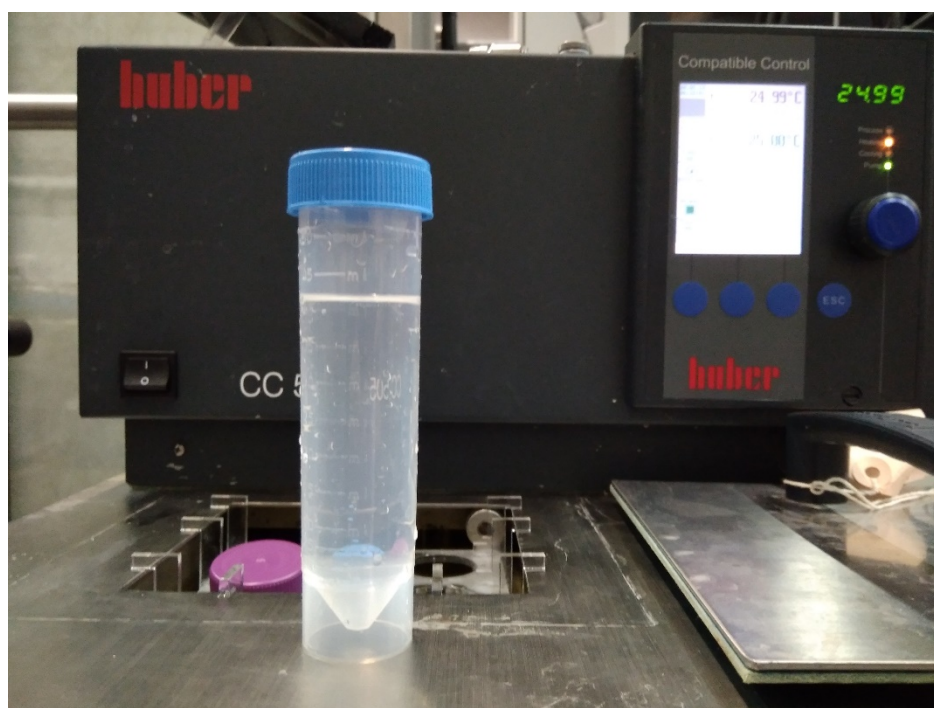
Picture A 3: Intact PP test tube after rigidity test

A2 Market analysis data

The sources are listed in Table A 6

Company / Warehouse	Nation	Temperature	Source
Kühlhaus Neuhof	CH	-28°C ; Flash frozen goods: -38°C	1
Häfliger Logistik	CH	-20 to -25°C	2
Migros Neuendorf	CH	-26°C	3
Blättler	CH	-25°C	4
Frigosuisse	CH	-26°C	5
Migros Generally	CH	-26°C	7
US Cold Storage	US	-18°C to -29°C	22
Interstate Chicago	US	Down to -23°C	28
TKC Bocholt	DE	-22°C and lower	23
TKC Dortmund	DE	-25°C	23
TKC Münster	DE	-22°C to -28°C	23
Frillemena	FR	-20°C and -35°C	24
C froid	FR	-20°C to -25°C	27
Pacaro	IT	-25°C	25
Sodele	IT	-25°C	26

Table A 1: Temperatures in cold storage warehouses

Company	Nation	Temperatures	Source
Blättler	CH	-20°C	4
Sebeto	IT	Down to -25°C	29
PSI-Spedition	DE	Down to -20°C	30
Cool Cargo	UK	-17°C to -20°C	31

Table A 2: Offered temperature ranges in refrigerated trucks

Company	Nation	Temperatures	Source
Cooltainer	CH	Down to -25°C	9
CMA CGM	FR	Down to -35°C	10
Hapag-Lloyd	DE	Down to -40	11
Maersk	DK	Down to -30 / -35°C / (-60°C)	12

Table A 3: Offered temperature ranges in reefer containers

Supermarket	Freezer Temperature
Coop Kriens	-20°C, -23°C for seafood
Coop Sempach	-20°C
Denner Sursee	-19°C
Migros Sursee	-20°C,
Migros Neuenkirch	-20°C
Spar Neuenkirch	-19°C
Aldi Luzern	-18°C

Table A 4: Temperatures found in supermarket freezers

Storage Temp.		Practical Storage Life, in Months						
°F	°C	Raw and pre-cooked lean meat	Raw and pre-cooked fat meat	Lean fish	Pre-cooked foods without gravy	Fat fish without any special treatment	Fruits and berries	Vegetables
23	- 5	2-12	1 - 5	1- 3	2- 6	1- 2	1- 5*	1- 4
14	-10	5-21	6-17	2- 6	3- 9	1- 3	3- 17	3- 10
5	-15	10-37	10-27	4-12	5-15	2- 5	17-70	8-20
-4	-20	16-70	13-40	6-20	8-28	3- 8	Over 70	21-70
-13	-25	30-70 +	20-60	11-40	15-47	4-12	--	---
-22	-30	53-70 +	30-70 +	---	27-70 +	6-18	---	---

Table A 5: Storage life of frozen foods acording to WFLO [24]

1	https://www.gilgen.com/home/news-kuehlhaus-neuhof-ag.html
2	https://www.haefliger-sursee.ch/index.php?id=511
3	http://www.soba-inter.com/unternehmen/unternehmen/aktuelles/fugenabdichtung-migros-tiefkuehllager/
4	http://www.blaettler-littau.ch/dienstleistungen/kuehllogistik
5	http://www.frigosuisse.ch/index.cfm?dolphin=38da85f7-1143-cd1e-33a8-d6acd337e565
6	https://www.foodaktuell.ch/vollautomatisch-und-tiefgekuehlt/
7	https://www.mvn.ch/index.asp?inc=logistik/prozess.asp#Lagerung
9	https://search.proquest.com/docview/1503701842/fulltext/45F06C7412734038PQ/1?accountid=15920
10	https://www.cma-cgm.com/products-services/reefer/containers-fleet
11	https://www.hapag-lloyd.com/content/dam/website/downloads/press_and_media/publications/18083_Reefer_Broschure_Keep_cool_We_Care_update_Web.pdf
12	https://www.maersk.com/solutions/shipping/refrigerated-cargo
13	https://www.youtube.com/watch?v=BAzqj9LoAew
15	http://www.cold.org.gr/library/downloads/Docs/FrozenFoodsHandling.pdf
16	https://www.uoguelph.ca/foodscience/book-page/ice-cream-manufacture
22	http://www.uscold.com/services/warehouse-services/
23	http://www.tkc-net.de/
24	http://frillemena.com/en/company.html
25	https://www.pacaro.it/
26	https://www.magazzinisodele.com/en-gb/servizi
27	http://cfroid.com/stockage/
28	https://www.tippmanngroup.com/interstate-warehousing-chicago-joliet-illinois/
29	https://www.sebetotrasporti.it/en/services/refrigerated-semitrailers.html
30	https://www.psi-spedition.de/thermo-transporte/
31	https://www.coolcargo.co.uk/frozen-food-shipping

Table A 6: Internet sources of the market analysis

A3 PCM Selection
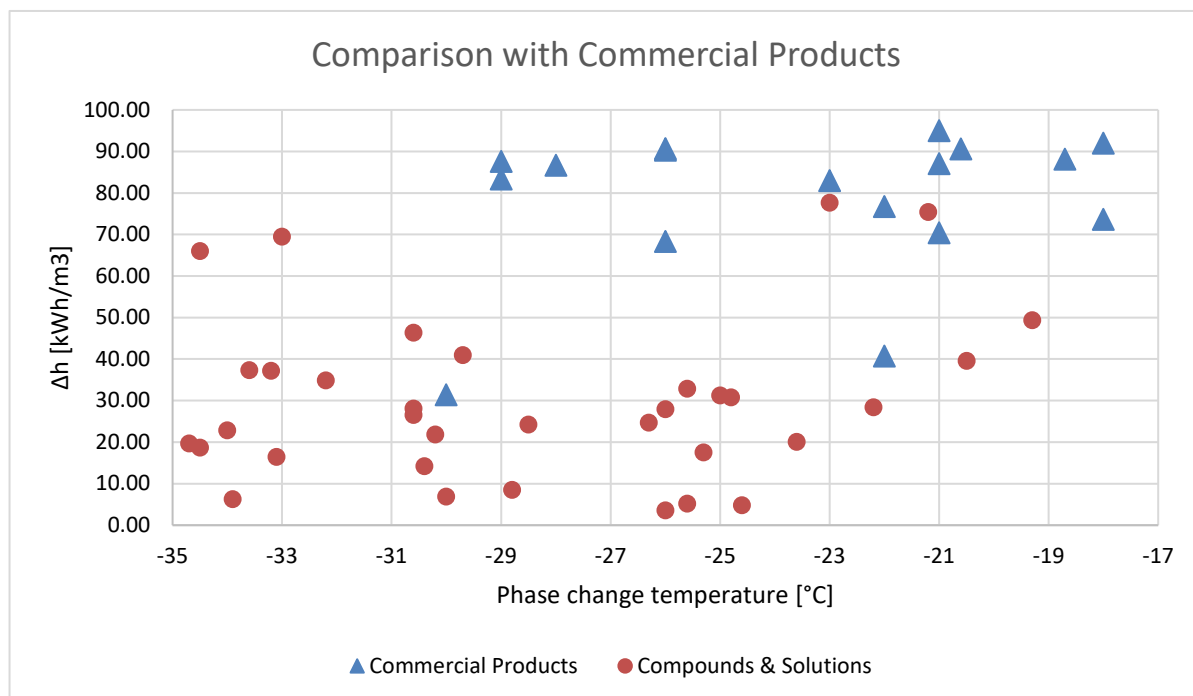
Picture A 4: Comparison of PCM candidates with commercial PCM products

A4 GHS hazard directory

Name	GHS Code	Old initial	Pictogram
Flammable	GHS02	**F**	
Oxidising	GHS03	**O**	
Corrosive	GHS05	**C**	
Toxic	GHS06	**T**	
Harmful	GHS07	**Xi**	
Health Hazard	GHS08	**Xn**	
Enviromental Hazard	GHS09	**N**	

Table A 7: Explanation of GHS initials

A5 Eutectic water-salt solutions

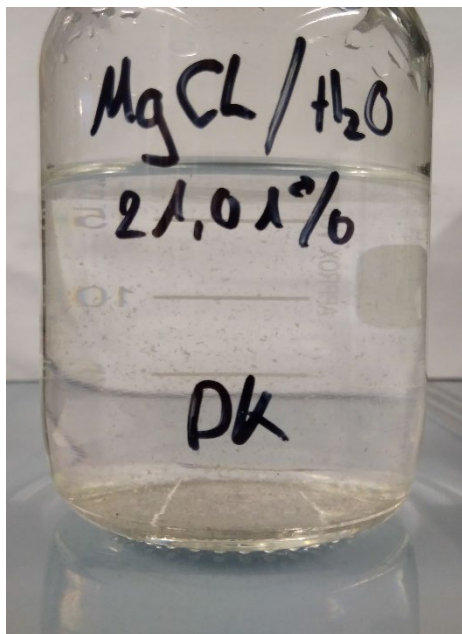| Salt	Melting temperature [°C]	Concentration [% w/w]	PC-Enthalpy [j/g]	Source
Al(NO3)3	-30.6	30.5	131	[2]
MgCl2	-33.5	21.01	-36.3 KJ/mol	[2]
	-33.6	20.6		[36]
	-33	22		[36]
	-33.2	21.6		[37]
NaBr	-29	40		[36]
	-28	40.3		[36]
NaCl	-21.2	22.4	222	[2]
	-21.2	23.3	233	[2]
	-21.1	23.4		[25]

Table A 8: Eutectic points of water-salt solutions
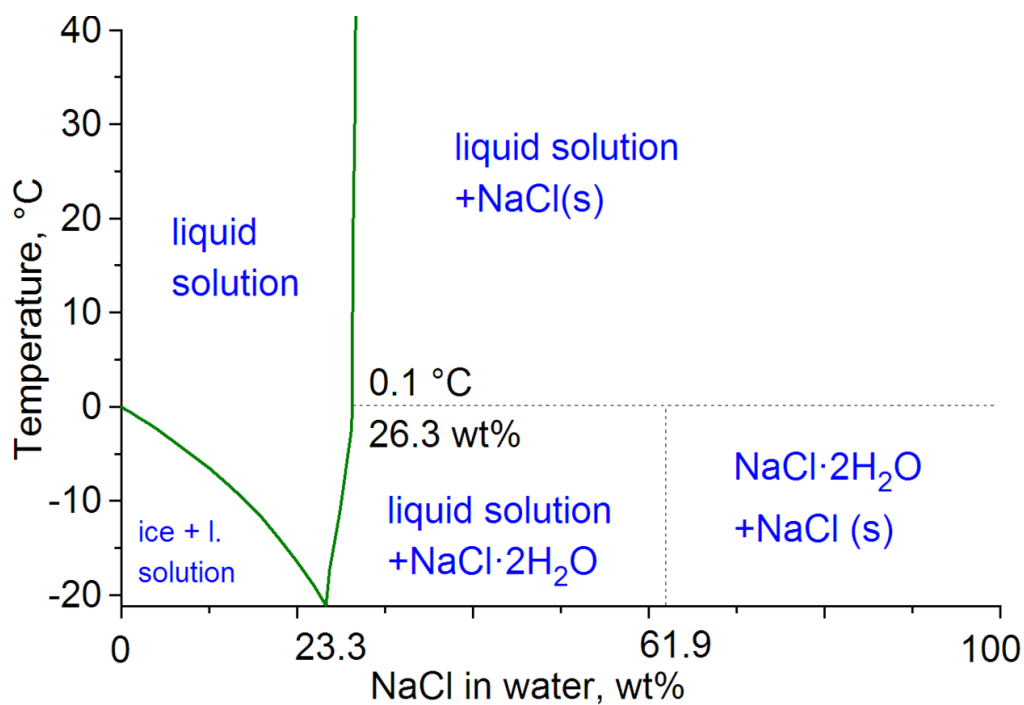
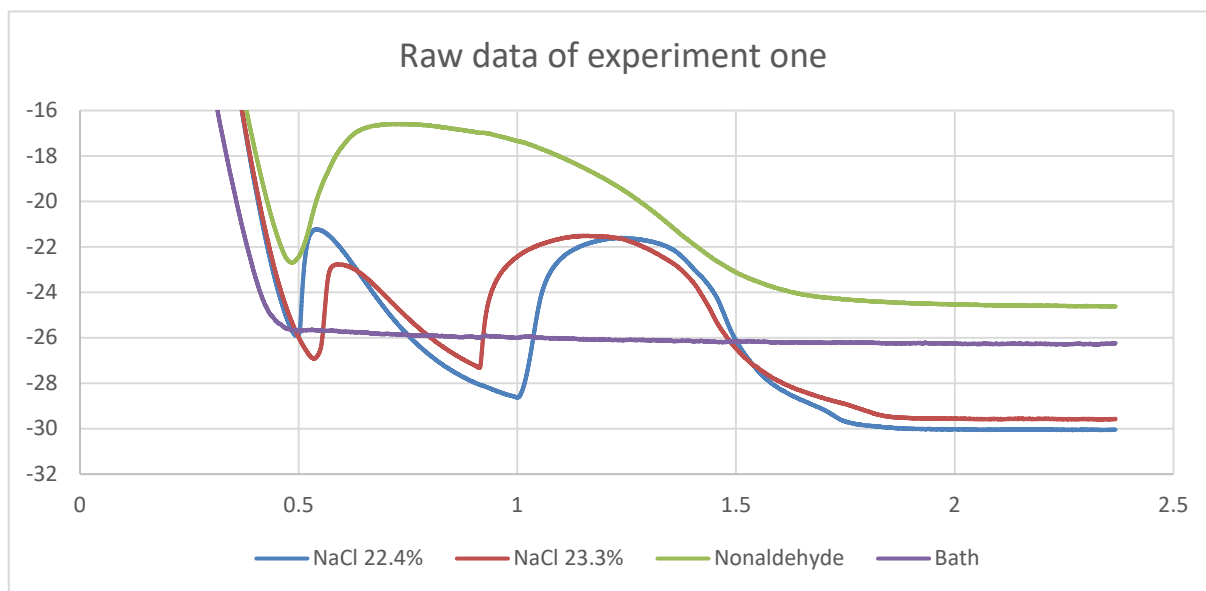*Picture A 5: Phase diagram of NaCl-water solution*
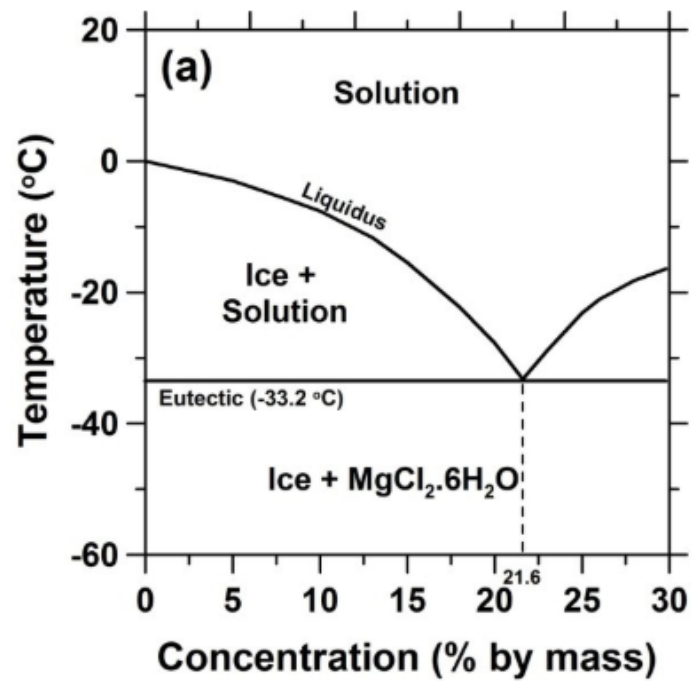
Picture A 6: Phase diagram of MgCl₂-water solution [37]
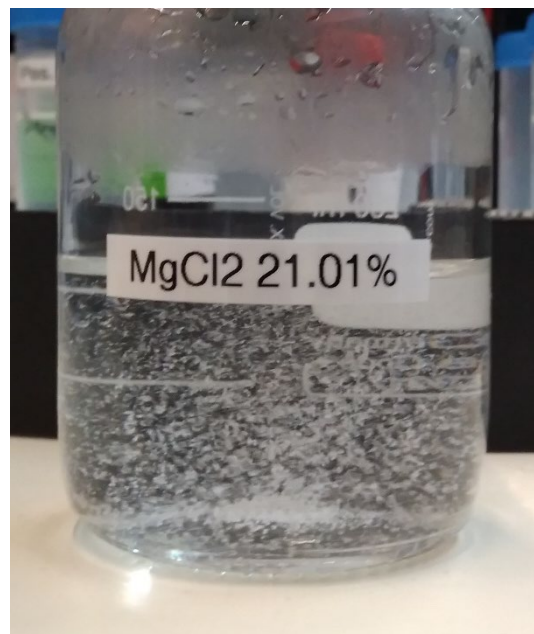
Picture A 7: First MgCl₂-solution on the left. Second MgCl₂-solution on the right.
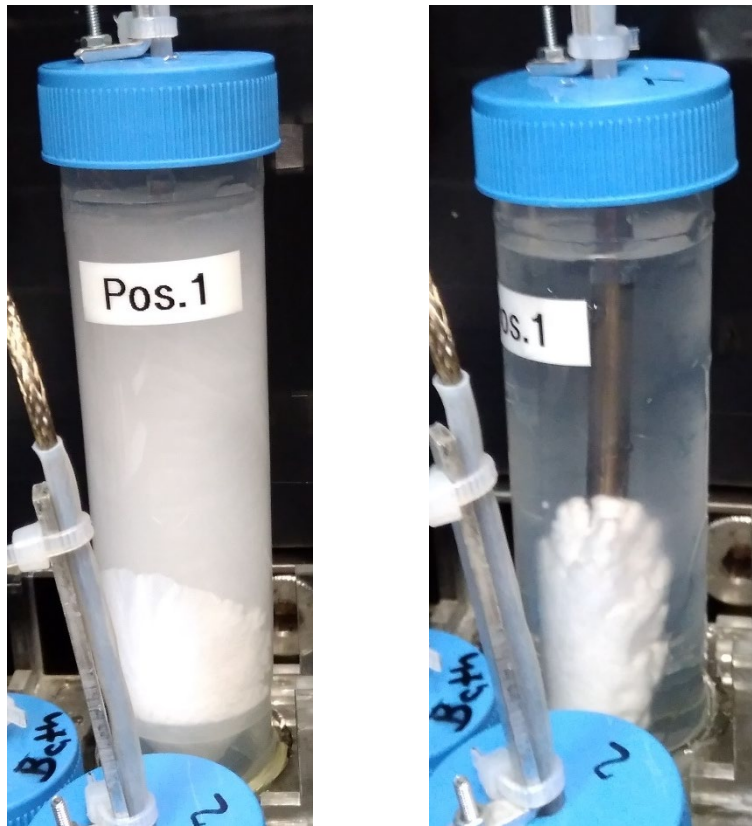
A6   T-History experiment

Picture A 8: Raw data temperature curves of experiment 1.

Picture A 9: Nonaldehyde freezing

Picture A 10: Nonaldehyde melting

Picture A 11: Opaque white solid during freezing process (left) and melting process (right) of 22.4% NaCl-solution

Picture A 12: Solid crystals at bottom of 23.3% NaCl-solution.

A7 Cycle stability Setup

Picture A 13: Thermostat for cycle stability setup.