Study of the Influence of Cooling Rate on Water Supercooling

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Abstract – The aim is to study the effect of the cooling rate of a phase change material (PCM) on its crystallization temperature. The degree of supercooling is determined by combining a measurement of the temperature outside the sample with the result of a heat transfer model. Distilled water was chosen as the PCM. A volume of 3ml contained in tubes with an internal diameter of 10 mm was considered. The results show that varying the cooling rate from 1°C/min to 0.083°C/min has no significant effect on the degree of supercooling.

Nomenclature

LHTES	*Latent Heat Thermal Energy Storage*
NTC	*Negative Temperature Coefficient*
PCM	Phase Change Material
TES	Thermal Energy Storage
C_p	Specific heat capacity, $J.kg^{-1}.K^{-1}$
D	Diameter, m
h	Heat transfer coefficient, $W.m^{-2}.K^{-1}$
$\vec{g}$	gravitational acceleration vector
I	Identity Tensor
k	Thermal Conductivity, $W.m^{-1}.K^{-1}$
Pr	Prandtl Number
P	Pressure, , $N.m^{-2}$
Re	Reynolds Number
t	Time
T	Temperature, K
T_{ext}	External Temperature, K
$\vec{u}$	Velocity vector, $m.s^{-1}$
Q_{wall}	*Heat Flux,* $W.m^{-2}$
ρ	*Density,* $kg.m^{-3}$
μ	Dynamic Viscosity, $N.s.m^{-2}$

1. Introduction

Renewable energy has become inevitable for the world. In order to overcome inefficiencies and intermittent nature of the renewable energy sources, thermal energy storage (TES) can be crucial in the renewable energy systems [1]. Thermal energy storage can be either sensible heat storage, latent heat energy storage (LHTES) or thermo-chemical energy storage. LHTES has high energy storage capacity as compared to sensible heat storage and the possibility to store high quantities of energy within a low temperature range in the storage medium. The materials used in LHTES are called phase change materials (PCMs) [2]. PCMs can face several problems including supercooling. When PCMs undergo a liquid - solid phase change, they are expected to solidify at the solid-liquid equilibrium temperature. But, in some situations the temperature of the PCM decreases below this point without the PCM crystallization. The temperature difference between the solid-liquid equilibrium temperature and the crystallization temperature is called the supercooling degree [3]. This phenomenon is illustrated in Figure 1. The crystallization in the PCM will happen once the nucleation of a solid nuclei occurs.

The supercooling can be both advantageous and disadvantageous depending upon the application. There are two major disadvantages associated to this phenomenon [4]. First, the

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freezing temperature can be out of the system's operating range and second, extra energy consumption is necessary [5].

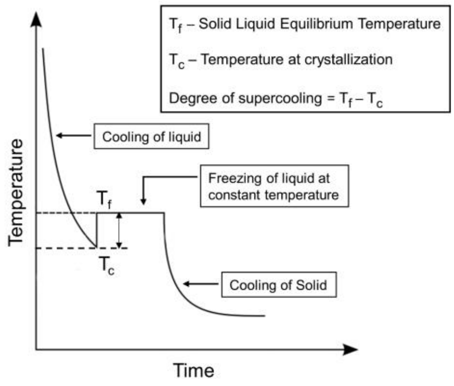

Figure. 1: *Evolution of the temperature inside a PCM for a cooling process.*

It is important to mitigate the supercooling for the applications when it is not desired. The factors affecting the supercooling have to be studied. The most significant ones are: (i) Volume, (ii) Surface roughness of the container, (iii) Thermal history, (iv) Purity of PCM, and (v) Cooling rate. On the scope of this study, we only focused on the impact of the cooling rate.

Chen and Lee [6] investigated the supercooling of water within horizontal cylinders. The cylinders had the length of 147mm, while they used 6 tubes of diameter, 32, 38, 47, 55, 62.4, and 124 mm. They varied cooling rates from 0.5 – 3.2°C/min. They defined the cooling rate as the ratio of the temperature difference between initial and crystallization temperature to time. Thermocouples were installed within the sample. The results showed that the smaller the cooling rate is, the greater the probability of nucleation is. Taylor et. al. [7] studied supercooling of a hydrated calcium chloride salt based commercial PCM, named PC25. The mass of the PCM sample was 9.1 ± 0.25 g. The temperature of the PCM was measured by placing NTC thermistors within the PCM. It was found that when the cooling rate was increased from 20 to 80 °C/min, the degree of supercooling increased from 9 to 22 °C. The cooling rate used by the authors was the slope ($\Delta T/\Delta t$) of the initial part of the curve before the onset of nucleation. Solomon et. al. [8] used PCM RT21. The experimental setup consisted of two concentric tubes. The outer tube was an acrylic tube, with a diameter of 140 mm, and the internal was a copper tube with a diameter of 75 mm. The heat transfer fluid (HTF) was flowing inside the copper tube while the PCM was placed in the annular space. The length of both cylinders was 280 mm. Several thermocouples were placed within the PCM at different locations They applied a cooling rate between 0.1 to 0.25 °C/min and they found that the supercooling increases when the cooling rate increases. Yoon et. al. [9] studied the impact of the cooling rate on distilled water in horizontal copper tubes with a diameter of 30mm. They varied the cooling rate from 1.2 to 18 °C/min. They evaluated the cooling rate from the average cooling rate at the inner wall of the copper tube from the start of cooling to the initiation of freezing. The thermocouples were installed at the inner surface of copper tube. They found for the high cooling rates (10 – 18 °C/min) a lower degree of supercooling (5 °C), while for the lower cooling rates, a higher degree of supercooling (7°C). Song et. al. [10] investigated the impact of the cooling rate on the degree of supercooling of decanoid acid. They took 11.82 mg of the sample and varied the cooling rate from 1 to 10 °C/min by using DSC. They found that there was no impact of cooling rate on the degree of supercooling. They also performed the same experiment on $MgCl_2\ 6H_2O$ and higher values of degree of supercooling were observed for higher cooling rates. S. C. MOSSOP [11] studied the impact of the cooling rate on the degree of supercooling of distilled water in capillary tube of 0.25 mm diameter. The thermocouples were installed within water samples. The author varied cooling rates from 0.05 to 5°C/min and subsequently, the difference between the degree of supercooling was less than 0.4°C, which is very insignificant.

In the literature review, no consensus has been found. Three different trends have been reported, which are, increasingly supercooling with cooling rates, decreasing supercooling with increasing cooling rates and no impact of varying cooling rates. Therefore, it is very important to investigate this impact.

The objective of this study is to find the impact of the cooling rate on distilled water. This research corresponds with one of the objectives of the PCM STORE project to have more knowledge about PCMs used in real systems and to develop thermal energy storage systems for cold storage. In order to predict the supercooling of real systems, the dependence of supercooling on various factors will be analysed at the laboratory scale. The final goal of our project is to use this laboratory scale data, which will be extrapolated with the help of statistical modelling. This article presents the results from the first part of this project, which is to analyse the laboratory scale dependence of the supercooling on various factors.

2. Materials and Methodology

2.1. Experimental Setup

Distilled water is used as PCM. Samples of water are taken in test tubes made of polypropylene. The inner diameter and thickness of the tubes are respectively 10mm and 1mm. Each tube is filled with a volume of water of 3ml. Two different configurations are made (Figure 2). The first configuration has one thermocouple outside the sample at the location of 1.5ml. The second configuration has two thermocouples, one inside, in the water and one outside on the outside wall, both at the location of 1.5ml. Wire type thermocouple probes are installed outside and are held close to the wall of the tube with the help of a zip-tie. Thermocouples with rigid probes are used when measuring the inside temperature. The rigids probes make sure that probes are exactly at the right position. All probes are of T type.

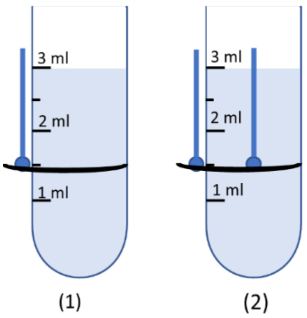

Figure 2: *Different configurations: (1) One thermocouple probe outside (2) Two probes, one inside and one outside*

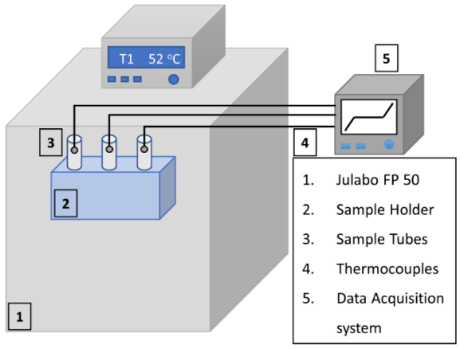

Figure 3: *Experimental setup*

It is well established that foreign surfaces may impact the supercooling of PCMs. Thermocouples probes placed in the PCMs can change the actual degree of supercooling of PCM. The degree of supercooling can decrease by placing thermocouple probe inside the sample. Therefore, the temperature of the sample is measured by placing probes outside the sample. Configuration 1 is used to measure the actual degree of supercooling, since there is no foreign object present inside the sample, but this measurement includes the thermal gradient across the tube wall. Therefore, with the help of a numerical model, the temperature inside the sample is estimated. Configuration 2 measures the temperature difference between the external wall of the tube and the center of the PCM and is used to validate the numerical model. This is summarized in Table. 1.

Table 1 *: Different Configurations of the PCM Samples*

Configuration	Location of Thermocouple	Purpose
1	Outside	To find actual supercooling
2	Inside and outside	To validate numerical model

Figure 3 shows the experimental setup. A refrigerated heating circulator (Julabo FP 50) including a bath is used to control the temperature of the heat transfer fluid (HTF) inside it. A sample test tube holder was immersed directly in the bath; the water sample tubes are placed in the tube holder. These tubes have thermocouples at different locations depending upon different configurations as given in table 1. Total 16 tubes are placed in tube holder for distilled water. Data acquisition system KEYSIGHT DAQ970A is used to record the temperature of the samples versus time. Accuracy of thermocouples is found to be ±0.1°C. In our work, the used HTF is an aqueous solution (50% water) of monoethylene glycol (Neutragel®)

2.2. Methodology

A temperature cycle was applied on the cooling bath containing the HTF and the rack with the distilled water samples. The temperature of the samples was recorded, and the degree of supercooling was measured by the difference between the temperature of crystallization and the solid-liquid equilibrium temperature (as explained in Figure. 1). There were 16 sample tubes in each experiment. The experiment was repeated 19 times to have a statistical average value of the degree of supercooling for each configuration at each cooling rate analysed. The schematic of applied cycle is shown in Figure 4. The cooling rate is also illustrated in Figure 4.

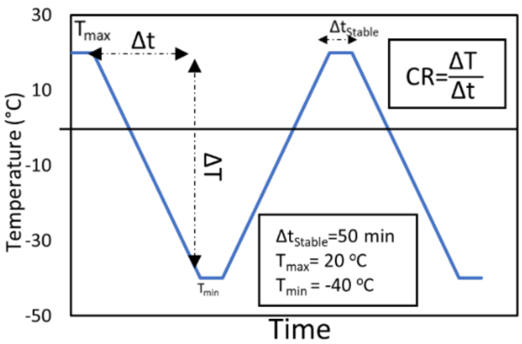

Figure 4*: Temperature cycle applied on the bath and explanation of the cooling rate.*

The error bounds for the experimental results are calculated by combining the accuracy of the thermocouple itself and the standard error of statistical data.

A numerical model was also used to calculate the temperature inside the tube in the case of configuration 1. For the case of numerical results, maximum validation error is also combined with the error.

2.3. Numerical Modelling

The goal of the simulation was to calculate the temperature inside the tube just before the beginning of the crystallization if the temperature of the bath is known experimentally. This is why it is not necessary to model the liquid-solid phase change. The geometry of the sample was constructed as 2D axis symmetric. The geometry is shown in Figure 5. The dimensions of the sample tube were the same as the tubes used in experiments.

Natural convection is considered inside the water:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathrm{u}) = 0 \tag{1}$$

$$\rho \frac{\partial \vec{\mathrm{u}}}{\partial t} + \rho(\vec{\mathrm{u}} \cdot \nabla)\vec{\mathrm{u}} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}] + \rho \vec{g} \tag{2}$$

$$\mathbf{K} = \mu\left(\nabla\vec{\mathrm{u}} + (\nabla\vec{\mathrm{u}})^{T}\right) \tag{3}$$

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \vec{u}.\nabla T = \nabla.(k \nabla T) \tag{4}$$

Conduction is considered in the tube wall:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla.(k \nabla T) \tag{5}$$

Heat exchange between the external tube wall and the heat transfer fluid is simulated by a convective boundary condition.

$$Q_{wall} = h(T_{ext} - T) \tag{6}$$

Where h is the heat transfer coefficient between the outer wall of the tube and HTF given by equation 7. This correlation is used when a cylinder is placed across a moving fluid [12]. The velocity of the HTF in the bath was found to be 0.0035 m/s.

$$h = \frac{k}{D}\left(0.3 + \frac{0.62\,\mathrm{Re}_D^{\frac{1}{2}}\,\mathrm{Pr}^{\frac{1}{3}}}{\left(1 + \left(\frac{0.4}{\mathrm{Pr}}\right)^{\frac{2}{3}}\right)^{\frac{1}{4}}}\left(1 + \left(\frac{\mathrm{Re}_D}{282000}\right)^{\frac{5}{8}}\right)^{\frac{4}{5}}\right) \tag{7}$$

Specific heat capacity, thermal conductivity, dynamic viscosity and density for the supercooling water was taken from data published in literature [13] , [14], [15]. While for the glycol-water (50% composition), properties were taken from [16]. Figure 5 shows the boundary conditions. The initial conditions are: $T = 20°\mathrm{C}$ and $\vec{u} = 0\ m\,\mathrm{s}^{-1}$.

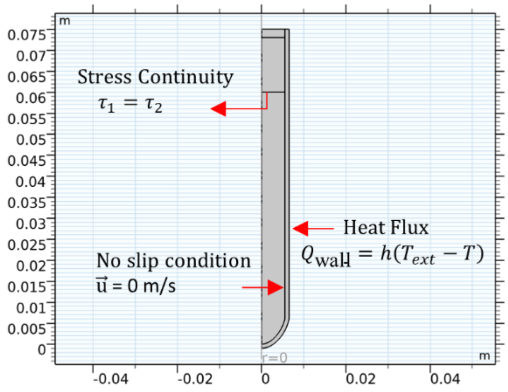

Figure 5: 2D axis symmetric geometry and boundary conditions

Simulations were performed by using COMSOL Multiphysics 6.1®.

2.3.1. Validation and Mesh Dependence

The experiments were performed with probes in the center of the sample and on the outer wall of the tube. These center probe results were compared with the numerical results obtained at the same position. The temperatures before the crystallization are used to validate the model, as the numerical model cannot predict the nucleation point. Figure 6 shows the evolution of the temperature versus time, both experimentally and numerically for one cooling rate. Figure 7 shows the difference between the experiment and the model for the temperature at the center of the PCM just before the crystallization. This difference is less than 3% for all the studied cooling rates. A mesh dependence was performed and when the domain elements were increased from 700 to 2400, there was no significant change in the results. The model is therefore validated and can be used to predict the temperatures inside the PCM.

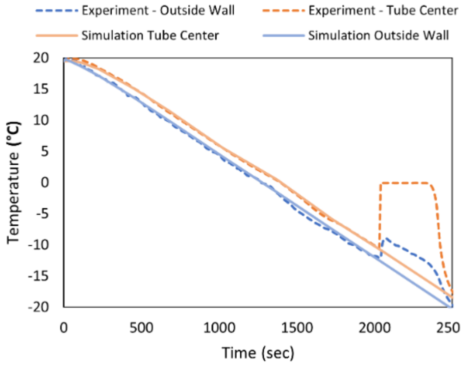

Figure 6: Experimental and numerical temperature evolutions at the outer wall and center

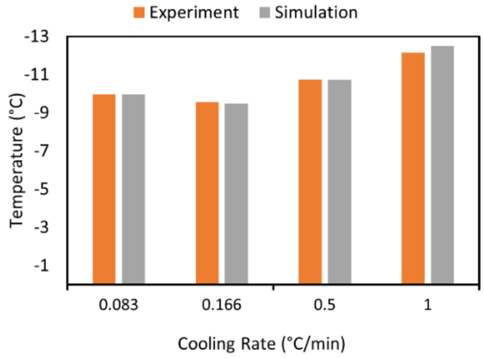

Figure 7: Temperature difference at the PCM center just before the crystallization between the numerical and experimental results for different cooling rates

3. Results and Discussion

3.1. Impact of Cooling Rate on the Degree of Supercooling

The degree of supercooling was measured by placing a thermocouple outside the tube containing the distilled water sample (configuration 1). The impact of the cooling rate on the degree of supercooling was investigated by varying the cooling rates. The studied cooling rates were 0.083, 0.16, 0.5 and 1 °C/min. The results are shown in Figure 8. There was no significant change in the degree of supercooling by varying cooling rates.

The temperature measured outside the sample does not represent the actual temperature of the PCM inside the sample. This is because of the temperature difference across the tube wall. In order to achieve the correct degree of supercooling, this temperature difference must be known, and subsequently removing it from the outside measured degree of supercooling.

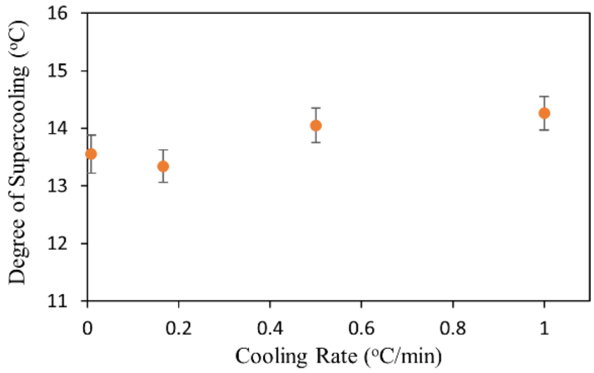

Figure 8: Impact of cooling rate on the degree of supercooling measured outside the sample.

3.2. Correcting Degree of Supercooling using Numerical Model

The actual supercooling can be estimated by knowing the temperature of the inner wall of the tube using the numerical model. This temperature is required rather than any other point in the sample because the nucleation occurs at the point of the lowest temperature inside the sample, which is at the interface of tube and PCM. Figure 9 shows that the temperature difference across the wall increases when the cooling rate increases. It confirms that supercooling measured by using the thermocouple probe outside the sample will not correspond to the actual nucleation temperature. Figure 10 shows the actual degree of supercooling estimated by knowing numerically the temperature difference across the wall. The degree of supercooling, when measured from outside of the sample (Figure 8), is higher than the actual degree of supercooling, because of the temperature difference across the tube wall. These results confirm the results found in section 3.1, that cooling rate does not influence the degree of supercooling in the studied range.

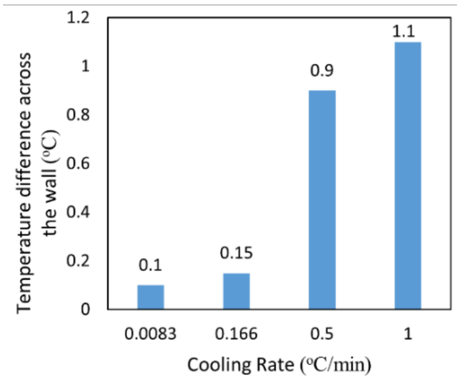

Figure 9: Temperature difference across the wall

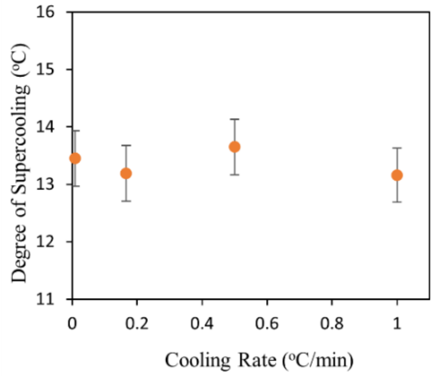

Figure 10: Degree of supercooling estimated at inner wall of tube

4. Conclusion

PCM Store, is a project to design thermal energy storage systems for cold storages. For this, it is necessary to know the dependence of supercooling on different parameters at the laboratory scale. Extrapolating this laboratory scale data will predict the supercooling of real systems. In this study, the dependence of supercooling on the cooling rate is investigated. The temperature is measured by placing a probe outside the sample because it will not impact the nucleation. Therefore, the temperature is initially measured outside the tube and further with the help of the simulation, the temperature inside the tube is estimated, which gives the actual degree of supercooling. It was observed that the studied cooling rate did not have a significant impact on the degree of supercooling of distilled water.

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