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Investigation of T-history Method Application for Sub-zero Phase Change Material Thermal Properties

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Abstract: The T-history method, first proposed by Zhang & Jiang, is a simple method used to determine the latent heat, specific heat, thermal conductivity, melting point, and degree of supercooling of a phase-change material (PCM). The method is based on the measurement of the temperature of the material over time. It assumes that the PCM sample and the reference material exchange thermal energy with the environment in a similar manner, because it is based on the lumped capacitance method, and the temperature distribution inside the sample is uniform. There are multiple advantages that the T history method has over conventional methods; however, the T history method also has some downfalls, which have been improved over the years by different authors. This study experimentally investigates the reliability of this technique for PCM with a phase change temperature below 0 ° C. The technique is used to first determine the properties of denoised water with a phase change temperature of 0 ° C, using ethylene glycol with a mixture ratio of 50/50 as reference material. Second, by determining the properties of KCl with a concentration of 19.5% salt to water for a phase change temperature of -10 ° C. Two analytical approaches were used, one by immersing the samples in antifreeze during the charging process and the other by exposing the samples to ambient air during the discharging phase. The experimental results were further validated using the known literature to determine the latent heat of KCl. This study found that the latent heat of KCl measured using the technique has a 6.2% difference from the known results determined by the DSC. This study recommends the use of the T history method when designing latent heat thermal energy storage systems (LHTESS), because the sample size is an important characteristic for accurate thermophysical properties during the design process.

Keywords - T-history method, latent heat, specific capacity, eutectic salt/water solution, lumped capacitance method.

NOMENCLATURE

Ac	heat transfer area	[m ²]
Bi	Biot number	
B _{air}	beta	[1/K]
cp	specific heat capacity	[J/kg °C]
d	internal diameter of the tube	[m]
D	outer diameter of tube	[m]
Gr	Grashof number	

H _m	heat of fusion	[kJ/kg K]
h	heat transfer coefficient	[W/m ² K]
K	thermal conductivity of air	[W/mK]
L	length of the tube	[m]
m	mass	[kg]
T	temperature	[°C]
t	time	[s]
T _{film}	film temperature	[K]
v _{air}	kinematic viscosity of air	[m ² /s]

Superscript

'	reference material
0	initial state
a	atmosphere
f	final state
i	inflection point
l	liquid
m	melting point
p	phase change material
r	reference material
s	solid
t	tube
w	water
∞	surrounding temperature

I. INTRODUCTION

The T-history method is part of the Thermal Analysis Group (TA), which includes differential scanning calorimetry (DSC), differential thermometry (DTA), and thermogravimetric analysis (TGA). The T-history method is relatively inexpensive, able to measure large samples, and has more thermophysical properties than the DSC, DTA, and TGA. The T-history method is a simple method used to determine the latent heat, specific heat, and thermal conductivity of a phase change material (PCM). This method was proposed by Zhang & Jiang [1] to determine the thermophysical properties of PCM samples simultaneously. These thermophysical properties also include

the melting point of a PCM and the degree of supercooling that corresponds to the properties mentioned above.

The method is based on measuring the temperature of a material over time. It assumes that the PCM sample and the reference material exchange thermal energy with the environment in a similar manner. During the cooling process, both the PCM sample and the reference material temperature were evaluated with time and recorded against the ambient temperature. The method requires that during the cooling process the reference material remain in the same state (usually liquid) and must be a substance with well-known thermophysical properties [2].

Table I compares these popular methods for determining the thermophysical properties of PCM. When a latent heat thermal energy storage system (LHTESS) is designed, the sample size is an important characteristic for accurate thermophysical properties. Small samples result in a decrease in the response time of the system [3]. In Table I the T-history method is the most suitable measurement technique to be used in this case, as it is relatively economical, able to measure large samples, and has more thermophysical properties. There are multiple

advantages that the T history method has over conventional methods; however, the T history method also has some downfalls, which have been improved over the years by different authors. Sole *et al.* [3] published a review article summarising the previous improvements made to the T history method.

Zhang & Jiang [1], only focused on the charging phase for phase change materials with a phase change temperature above 0 ° C. For phase change materials with a sub-zero phase change temperature, a new method derived from the original work of Zhang was proposed by [4]. Therefore, this study was aimed at using the original work by Zhang for both the charging and discharging phases at subzero temperatures to determine the specific heat, the latent heat, and the thermal conductivity. Ethylene glycol was used as a reference material. Deionised water was used as the first phase-change material to calibrate the experimental setup and improve its accuracy. The same experimental setup was then used on potassium chloride and saltwater solution for both the charging and discharging phase.

TABLE I
COMPARISON OF FOUR THERMAL ANALYSIS METHODS [1]

	Thermogravimetric analysis (TGA)	Differential Thermal Analysis (DTA)	Differential scanning calorimetry (DSC)	T-history
Sample size (mg)	10–150	10–150	1–50	15,000
Measurement time (min)	100	100	100	40
Maintenance	++	++	++	+
Equipment price	++	++	++	+
Phenomenon	<ul style="list-style-type: none"> • Thermal stability • Decomposition • Sublimination • Evaporation • Dehydration 	<ul style="list-style-type: none"> • Decomposition • Glass Transition • Melting 	<ul style="list-style-type: none"> • Melting • Glass Transition • Degree of subcooling • Reaction (curing / polymerisation) 	<ul style="list-style-type: none"> • Melting • Visual phase change • Degree of subcooling
Thermophysical Properties	% sample mass loss f(T,t)	$-\Delta T_m(T,t)$ Hm (T, t)	Cp (T, t) Hm (T, t) Tm	Cp (T, t) Hm (T,t) Tm k

II. METHODOLOGY

A. Description of the Method

For this study, three solutions were used: ethylene glycol with a 50/50 mixture ratio as the reference material, deionised water as the first PCM, and a potassium chloride saltwater solution with a concentration ratio of 19.4% as the second PCM. The experimental setup proposed in this study was a reference from [2]

- The PVC test tubes had a length of 220 mm; an internal diameter of 9 mm; and a thickness of 0.2mm. PVC test tubes were used after observing that glass test tubes had previously shattered under conditions of -26 ° C.
- For the charging phase, as shown in Fig. , the samples were immersed in an antifreeze solution, in a chest freezer

operating at -30 ° C. Type K thermocouples were initially used and connected to a GL820 Graphtec data logger. Temperature fluctuations in the container were observed as a result of uneven temperature distribution. The containers were then fitted with Pt100 temperature probes to measure the uniform temperature in the container and increase the accuracy of the results.

- For the discharge phase, the samples were placed in ambient air until the temperatures of the solutions reached the same temperature as those of the surrounding air. The schematic diagram also follows the same procedure as in Fig. .

TABLE II
 PROPERTIES

	Ethylene glycol [3]	Water [4]	KCl [5]	PVC tube [4]	Mercury [4]
Mixture ratio (%)	50/50	100	19.5/80.5		
Phase change temperature (°C)	-36.8	0	-10.7		
Density (kg/m ³)	1103	999.7	1980	1470	13545.84
Specific heat (J/kg °C)	3470	4217 (liquid) 2100 (solid)	3.25 (liquid) 2.108 (solid)	840(solid)	
Latent heat (kJ/kg)		330	253.18		
Thermal conductivity (W/m K)		0.561 (liquid) 2.16 (solid)			

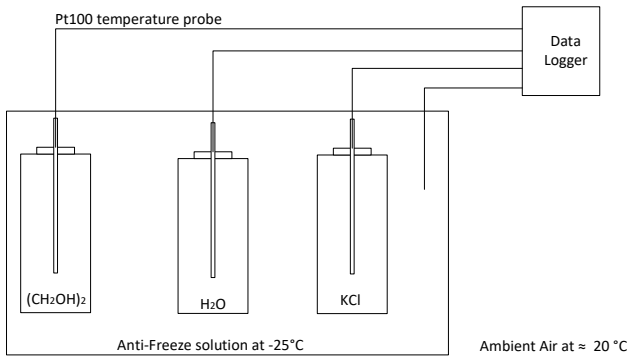


Fig. 1 Experimental Setup for the Charging/Discharging Phase

B. Evaluation

This study determined the Biot number to ensure that the test tubes meet the lumped system in front of the ambient air because the test tubes were changed from glass to PVC. Because of the lack of thermal properties for ethylene glycol, the Biot number could only be determined during the discharging phase. During the discharge phase, from the film temperature between the surface temperature of the tube at -25°C and 20°C , the thermal conductivity, Prandtl number, beta and kinematic viscosity of air were determined. The Grashof number expressed in Equation 1 was used to determine whether the Nusselt number of the vertical cylinder can be used as a vertical plate.

$$\text{Gr}_L = \frac{g \cdot \beta \cdot (T_s - T_{\infty}) \cdot L_c^3}{\nu^2} \quad (1)$$

and

$$D \geq 35L / \text{Gr}_L^{\frac{1}{4}} \quad (2)$$

It was found that the diameter of the tube was extremely small compared to the ratio expressed in equation 2, so the Nusselt number for the vertical plate could not be used; the option chosen was to assume that the tubes had to be placed horizontally. Sparrow & Gregg [6], were able to determine the formula for the Nusselt number of the vertical cylinder. However, the test tube was prepared under the assumption that they were placed horizontally.

The Rayleigh number, the Nusselt number, and the convective heat transfer coefficient were determined as suggested in [4]. The Biot number was determined using the volume of the cylinder and the surface area. The thermal conductivity of solid water was used. The final Biot number value was $0.0102 < 0.1$, therefore, the experiments satisfied the lumped capacitance method.

C. Identification of PCM Properties

Peck *et al.* [7] improved the precision of the mathematical model by introducing the inflection point as the boundary between the phase change and the solid period. This release

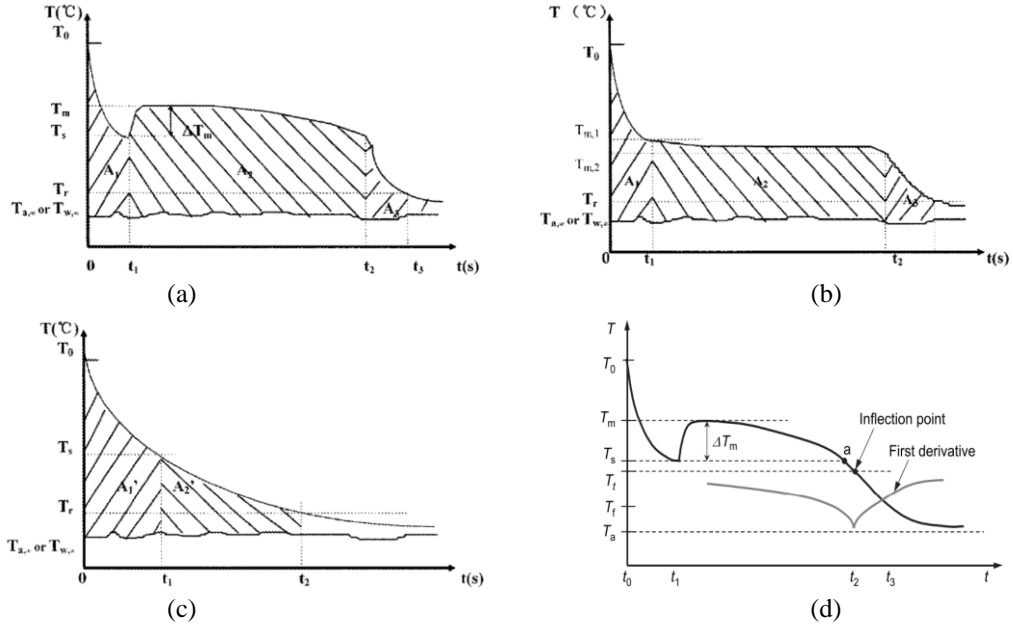


Fig. 2 Typical T history curves during the charging phase (a) PCM curve with supercooling, (b) PCM curve without supercooling, (c) reference material curve [8], (d) with inflection point using the first derivative [7].

The point is determined at the end of the phase change period where the first derivative becomes minimum, as displayed in

Fig. (d). PCM. Zhang *et al.* [9] Improved the T history by using the first and second derivatives of the step cooling curve to determine the phase change interval of the PCM. The authors further determined the latent heat and thermal conductivity of the PCM by mathematical derivation. The equations used for the specific heat of solid and liquid and the latent heat during the charging phase are Equations 3, 4 and 5. Since the discharging phase is the inverse of the charging phase, the equations used were still shown in equations 6, 7 and 8 with the corrected subscripts.

$$c_{p,s} = \frac{m_r \cdot c_{p,r} + m_{t,r} \cdot c_{p,t} \cdot \frac{A_3}{A_2} - \frac{m_{t,p}}{m_p} c_{p,t}}{m_p} \quad (3)$$

$$c_{p,l} = \frac{m_r \cdot c_{p,r} + m_{t,r} \cdot c_{p,t} \cdot \frac{A_1}{A_1'} - \frac{m_{t,p}}{m_p} c_{p,t}}{m_p} \quad (4)$$

$$H_m = \frac{m_r \cdot c_{p,r} + m_{t,r} \cdot c_{p,t} \cdot \frac{A_2}{A_1'} (T_0 - T_s) - \left(\frac{m_{t,p}}{m_p} \cdot c_{p,t} (T_{m,1} - T_{m,2}) \right)}{m_p} \quad (5)$$

and

$$c_{p,s} = \frac{m_r \cdot c_{p,r} + m_{t,r} \cdot c_{p,t} \cdot \frac{A_1}{A_1'} - \frac{m_{t,p}}{m_p} c_{p,t}}{m_p} \quad (6)$$

$$c_{p,l} = \frac{m_r \cdot c_{p,r} + m_{t,r} \cdot c_{p,t} \cdot \frac{A_3}{A_2'} - \frac{m_{t,p}}{m_p} c_{p,t}}{m_p} \quad (7)$$

$$H_m = \frac{m_r \cdot c_{p,r} + m_{t,r} \cdot c_{p,t} \cdot \frac{A_2}{A_2'} (T_0 - T_{m,1}) - \left(\frac{m_{t,p}}{m_p} \cdot c_{p,t} (T_{m,1} - T_{m,2}) \right)}{m_p} \quad (8)$$

The areas under the curve for both the PCM and the reference material during the charging phase and the discharging phase are shown in Equations 9, 10 and 11.

$$A_1 = \int_{t_0}^{t_1} (T_p - T_r) dt, \quad A_1' = \int_{t_0}^{t_1} (T_p - T_r) dt \quad (9)$$

$$A_2 = \int_{t_1}^{t_2} (T_p - T_a) dt, \quad A_2' = \int_{t_1}^{t_2} (T_p - T_a) dt \quad (10)$$

$$A_3 = \int_{t_2}^{t_3} (T_p - T_a) dt, \quad (11)$$

$$k_s = \left[1 + \frac{c_p (T_m - T_{\infty,w})}{H_m} \right] / 4 \left(\frac{t_f (T_m - T_{\infty,w})}{\rho_p R^2 H_m} - \frac{1}{h_w R} \right) \quad (12)$$

The equation for the thermal conductivity is presented in Equation 12. Zhang & Jiang [8] proposed that the mass of the reference material in Equations 10, 11 and 12 should be replaced with the mass of mercury since mercury has a clear interface between the two faces (solid and liquid). Zhang & Jiang [8] further proposed that the term $-1/h_w R$ could be left out for most cases since it is relatively small to the term $t_f (T_m - T_{\infty,w}) / \rho_p R^2 H_m \gg 1/h_w R$.

III. RESULTS & DISCUSSION

D. Calibration with deionised water

From the experimental work, Fig. (a) shows the temperature-time curve results from the charging phase, and Fig. (b) shows the discharging phase. From Fig. (a) of the charging phase, the antifreeze solution maintained a constant temperature of -27°C . Both ethylene glycol and deionised water sample tubes were immersed at an initial temperature of 24.7°C in the antifreeze solution until the temperature of both solutions reached -25°C . In Fig. (b) of the discharging phase, the solutions were removed from the antifreeze solution and exposed to ambient air at 24°C . For both phases, the water

experienced a phase change temperature ranging from -5°C near 0°C .

The first derivatives proposed by [7] were used to mark the different regions of the temperature-time curve, the liquid region, the latent heat region, and the solid region. These

sections are shown in Fig. (a) for the deionised water and (b) for the ethylene glycol. From the original T history proposed by Zhang & Jiang [8], the temperatures of Fig. (a) were used to map out the regions in Fig. (b).

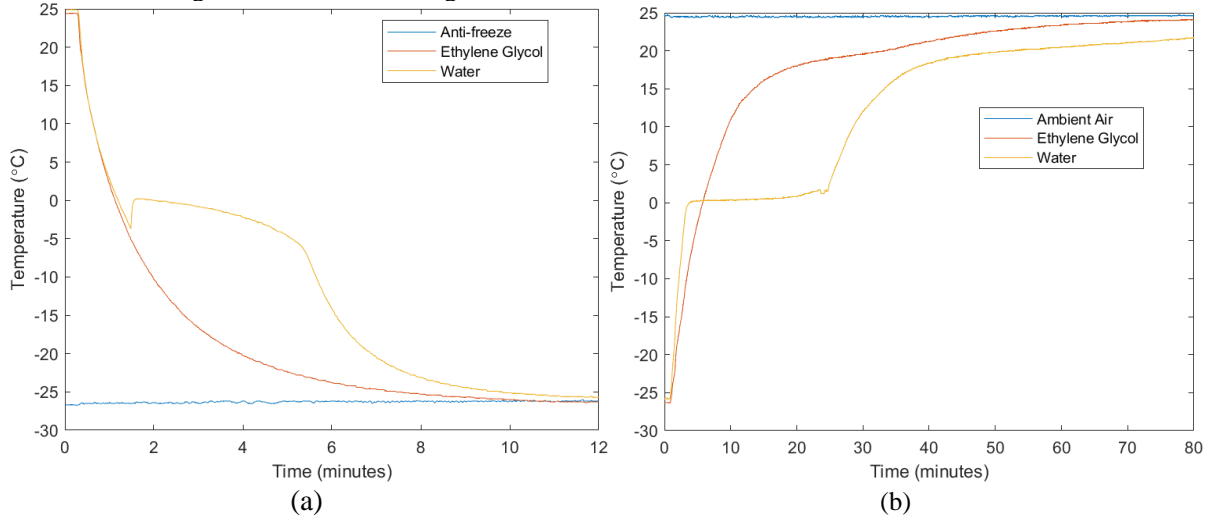


Fig. 3 Typical T history curve for water (a) charging phase and (b) discharging phase

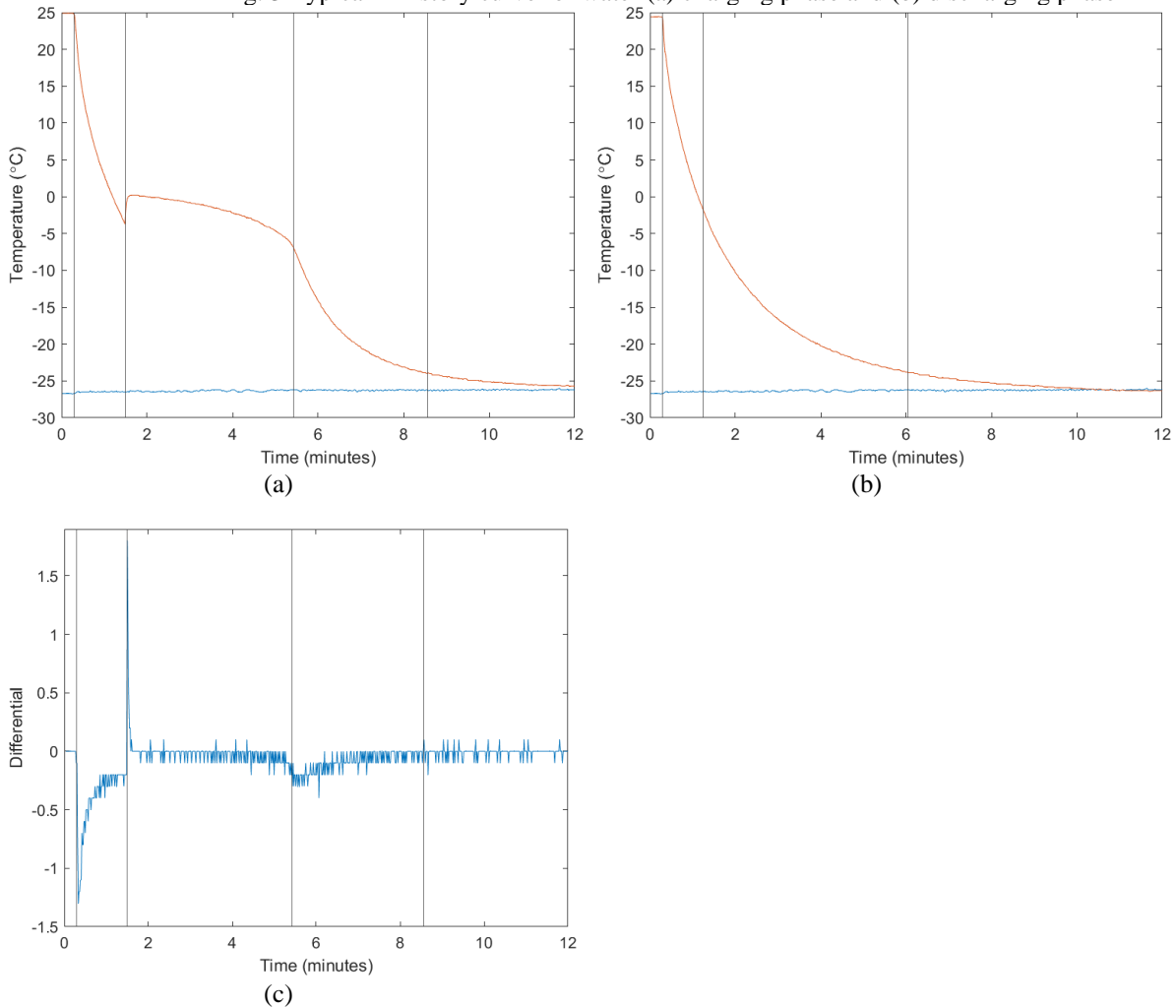


Fig. 4 Analysis of deionised water during charging phase (a) water, (b) ethylene glycol, and (c) first derivative for water.

The same process carried out during the charging phase was also carried out for the discharging phase in Fig. . From Fig. (a) the solid, latent heat and liquid regions were identified using the first derivative points in Fig. (c). unlike the charging phase, the first region during the discharging phase was the solid region ending with the liquid region; thus the analysis in

Fig. (b) and (c) had to be flipped around. The correct characters were used in equations 6, 7, and 8 for the solid, latent heat, and liquid regions.

The time for full solidification of the PCM was taken to be immediately after the latent heat region. the full solidification was time in Fig. (a) at 5.5 min, the results were tabulated in Table 3. Thus, the method proposed by Zhang & Jiang [8] was shown to be correct in suggesting that samples should be immersed in a liquid bath and not through air. However, it was slightly different for the discharging phase.

In Fig. (a) the full solidification time selected was 24.8 min. It was observed that the full solidification time after the latent heat region yielded a value close to the value of water in the known literature. The thermal conductivity of the samples immersed in antifreeze solution yielded unfavourable results. As a result of this uncertainty, it is recommended that further improvements be made to improve the accuracy of the proposed method.

TABLE III
THERMAL CONDUCTIVITY RESULTS

	k solid	k liquid
T-history	2.5808	0.4976
Literature	2.16	0.561

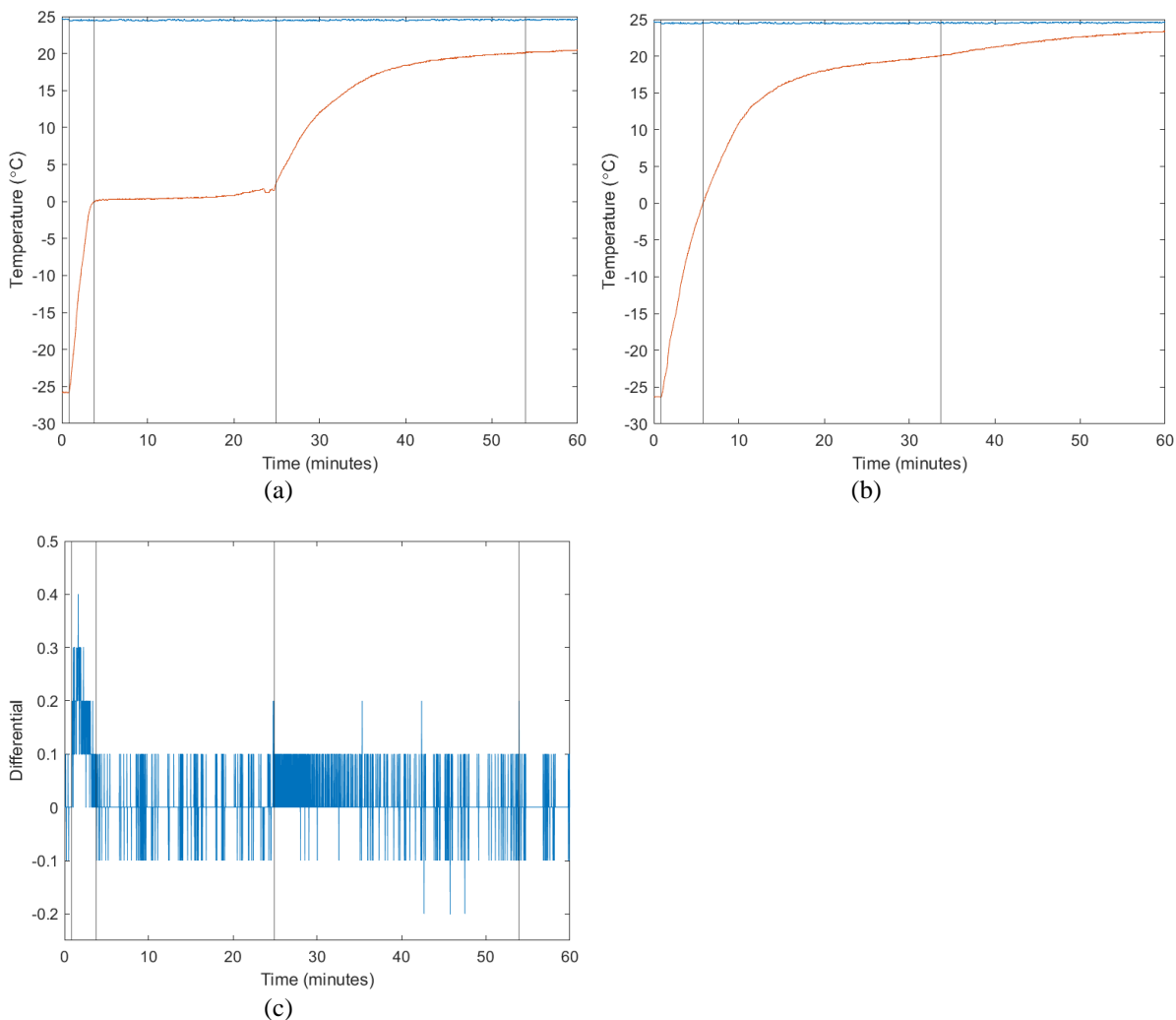


Fig. 5 Analysis of water during the discharging phase, (a) water, (b) ethylene glycol, and (c) first derivative for water.

E. Analysis of KCl

For the potassium chloride saltwater sample, the same experimental process was followed as for the deionised water. In Fig. (a) of the charging phase, both ethylene glycol and potassium chloride samples were immersed in antifreeze with a temperature of -25°C at an initial temperature of 25°C . The process continued until the temperature of the samples was equal to that of the antifreeze. It was observed from Fig. (a) that the potassium chloride sample had a sharp supercooling, then afterwards the temperature steadily declined until it reached the phase change temperature, which lasted over 5 minutes.

The solutions were then removed from the antifreeze for the discharging phase and exposed to ambient air at a temperature $<25^{\circ}\text{C}$, as illustrated in Fig. (b). The process was also carried

out until the temperature reached the ambient air temperature. From both Fig. (a) and (b), the phase change temperature of KCl was -13°C . After the discharging phase, small salt particles were observed at the bottom of the KCl sample, indicating that the samples experienced segregation.

In Fig. (a), the regions were also identified using the first derivative points. KCl showed a supercooling effect ranging from -21.3°C to -13°C and was analysed using Fig. (a).

In Fig. (b) the discharging phase, the solid, latent heat, and liquid region in Fig. (a) were identified using the first derivatives as in Fig. (a).

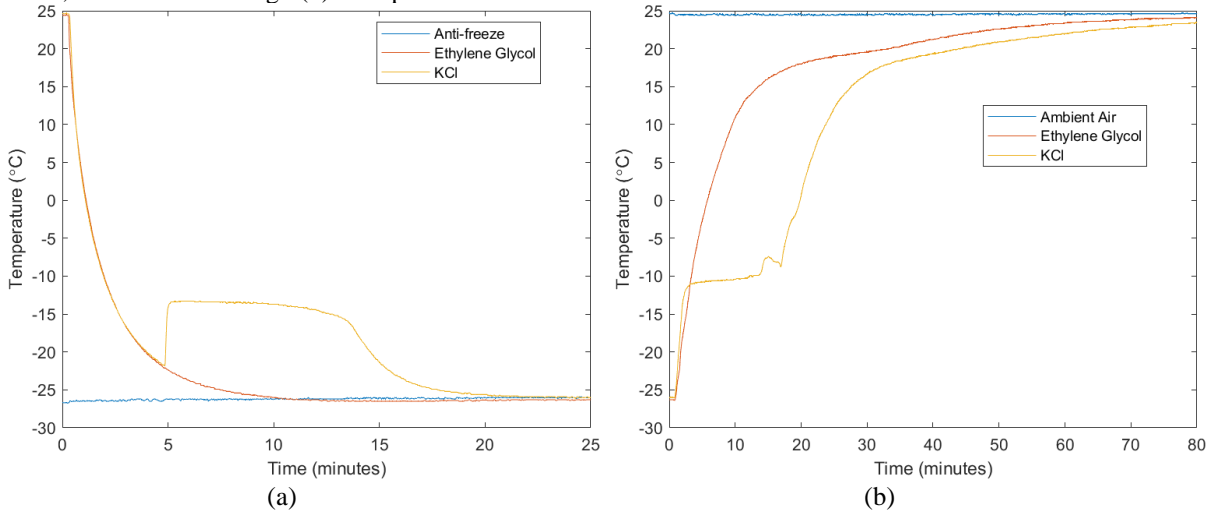


Fig. 6 Typical t history curve for potassium chloride (a) charging phase (b) discharging phase

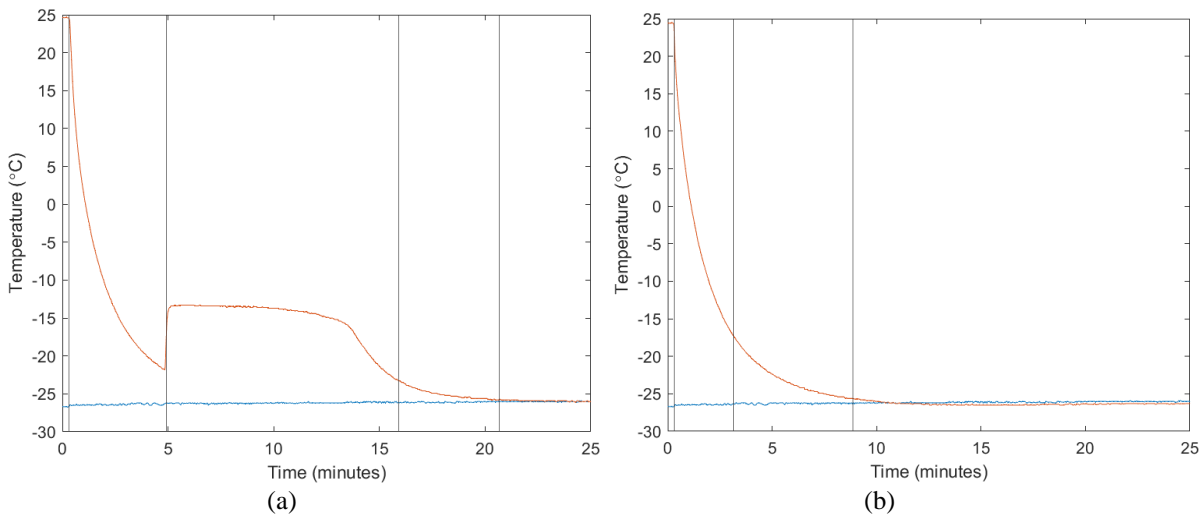


Fig. 7 Analysis of KCl during the charging phase (a) potassium chloride, (b) ethylene glycol

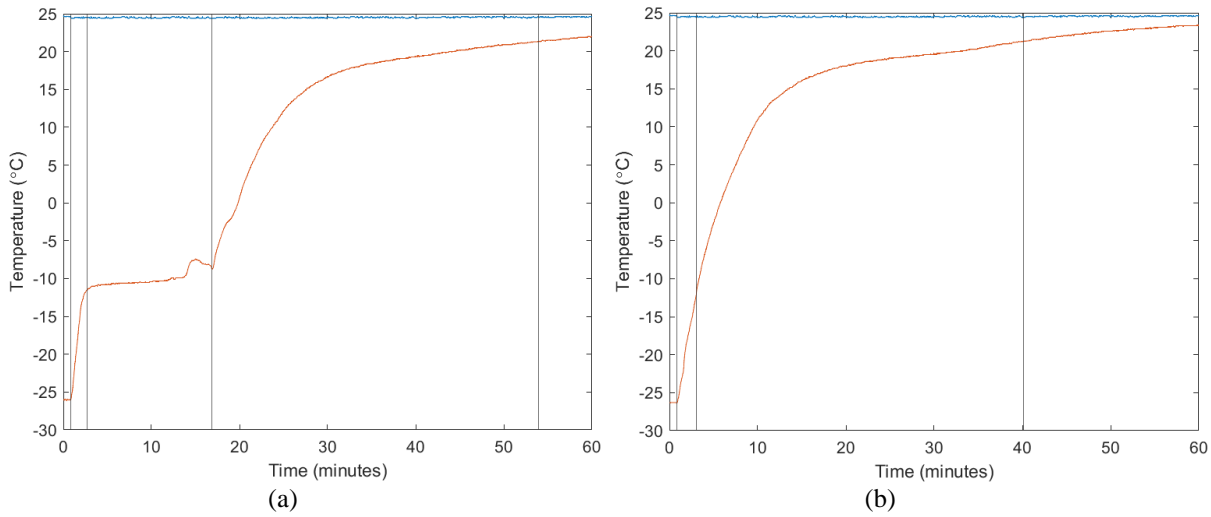


Fig. 8 Analysis of KCl during the discharging phase (a) potassium chloride, (b) ethylene glycol

The results are presented in Table 3. The calibration of the experimental setup was successful for both the charging and discharging processes. For the calibration of deionised water, the specific heat of solids (c_{ps}) differed by 16.6% during the charging phase and -4.7% during the discharging phase. The specific heat of the liquid (c_{pl}) differed by -8.27% during the charging phase and 8.6% during the discharge phase. Latent heat (H_m) differed by 5.3% during the charging phase and 13.7% during the discharge phase.

For potassium chloride, it was observed that the specific heat for solids (c_{ps}) and the specific heat for liquids (c_{pl}) for the charging phase were switched around. The specific heat for solids (c_{ps}) and the specific heat for liquids (c_{pl}) differed by -4.7% and -18.6% during the discharge phase. The latent heat (H_m) differed by -11.8% during the charging phase and 45.3% during the discharge phase.

TABLE IV
SUMMARY OF RESULTS

		C_p solid (kJ/kg °C)	C_p liquid (kJ/kg °C)	Latent heat (kJ/kg)
H₂O	T-history charging	1.7498	4.5658	312.63
	T-history discharge	2.1987	3.8541	284.77
	Literature	2.1	4.217	330
KCl	T-history charging	4.8491	2.4	153.240
	T-history discharge	1.1057	1.9381	138.280
	Literature	2.108	3.25	253

IV. CONCLUSIONS

The T-history method is relatively inexpensive, able to measure large samples, and has more thermophysical properties than the DSC, DTA, and TGA. The T-history method, first proposed by Zhang & Jiang is a simple method used to determine the latent heat, specific heat, and thermal conductivity of a PCM. This method is based on measuring the temperature of a material over time. It assumes that the PCM samples exchange thermal energy with the environment in a similar manner. The PCM samples used in this study were deionised water and a potassium chloride water solution. The reference material was ethylene glycol. During the charging and discharging process, both the PCM sample and the reference material temperature are evaluated over time and recorded. Peck *et al.* [7] improved the precision of the mathematical model by introducing the inflection point as the

boundary between the phase change and the solid period. This release point is determined at the end of the phase change period where the first derivative becomes minimum. The calibration of the experiments using deionised water proved to be successful, as the values of water in the known literature were obtained using this method and further properties of KCl were also obtained. The overall percentage difference between the experimental results and the known literature was approximately 10%. From this study, it is concluded that the method is reliable and accurate; however, high accuracy has to be applied when measuring the samples. It could be used for both the charging and discharging phases to determine the thermal physical properties of PCM with a phase change temperature below 0 °C.

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