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Stability Testing of a Phase Change Material for Refrigeration Applications

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Abstract

PCM failure, in particular separation, can be reduced with the use of encapsulation, thickeners and, in this case, mixing. It is the scope of this work to demonstrate that mixing can maintain stability and prevent the breakdown of the thermophysical properties of the PCM. The paper provides details on a special purpose-built test rig for testing the stability of PCMs. Furthermore, a PCM with freezing point of -6°C was tested using the rig. Samples of PCM where taken periodically from the cycling rig and analysed using a Pseudo T-history method and a Differential Scanning Calorimeter. After 100 cycles, no degradation in latent heat was observed.

1.   Introduction

Phase change materials, or PCMs as they are commonly referred to, are any material which has the ability to change phase from a liquid to a solid to store thermal energy. A PCM's suitability as a thermal storage medium depends primarily on the application of the stored energy. Selection of a PCM generally commences with establishing a freezing/melting temperature suitable for the application and then narrowing down the potential candidates by favouring the one with the highest inherent latent heat of fusion. Theoretically, the choice can be made and the energy storage can be sized and energy savings calculated. However, the nature of repeatedly freezing and melting a PCM can lead to a change of its thermophysical properties and render it useless as a thermal storage medium in a very short period of time. Changes in properties can range from a shift in melting/freezing point to a reduction of latent storage capacity, primarily caused by the separation of the PCM outside of its original eutectic composition into different phases (Liu et al. 2016; Brancato et al. 2017; Solé et al. 2014). Hence it is essential to test the properties of a PCM as a thermal storage medium under similar conditions as to its intended application.

Stability testing generally includes repeatedly subjecting a small sample of PCM to temperatures above and below its melting point whilst logging its temperature profile during consecutive phase changes. This test is commonly performed using a Differential Scanning Calorimeter (DSC) with a sample size of between 5 and 100mg. A measure of stability can be

gained from a comparison of progressive temperature versus heat flow profiles and noting any changes after each cycle or at the end of a large number of cycles. Larger samples of about 50 to 200g (Figure 1 left and centre), are also commonly used for testing stability. In this case, temperature versus time profiles are analysed for changes. Deviations in the profile could be changes to the time it takes the sample to undergo a phase change or the progressive change in slope of the phase change profile. Another measure could be via visual inspection after phase change, noting any separation of the PCM components. This is not possible to do with a DSC test (Figure 1 right).

Figure 1. 80mL sample of PCM subjected to cycling tests (left and centre) and 2500mL of -6PCM failure due to separation (right).

T-history is another method that could be used to test for stability (Marin et al., 2003). This method utilizes larger samples than the DSC but generally smaller than temperature versus time profiles due to the necessity to maintain the Biot Number, $Bi < 0.1$. The T-history method setup is experimentally similar to the temperature versus time profiling of samples but with the addition of a reference sample (Figure 2 left) along with significant data manipulation and analysis.

Figure 2. Pseudo T-history setup with the sample, reference and ambient temperature measurements shown on the left, the constant room temperature enclosure centred and the constant temperature freezer with controllers shown on the right.

Research has been conducted into the potential of mixing to maintain stability and prevent separation of the PCM. However, this work was done over a small number of cycles and mixing was done manually (Tay et al., 2013).

This paper describes a representative large scale PCM cycling rig, applying mixing to demonstrate PCM stability. Measurements using DSC and a Pseudo T-history method are taken regularly to identify the variation of the latent heat over the testing period.

2. Method

Small scale stability testing of PCM cycling is generally not representative of the field application. The short comings of laboratory cyclic stability testing is the dis-similar nature of the cycling regime compared with the field application. In order to overcome this, a representative sample is taken from a specifically designed system representative of the field application, known as the PCM Stability Test Rig (Figure 3), then tested independently from the rig (RAL, 2018). The testing of samples taken from the PCM Stability Test Rig is analogous to taking samples from the field unit. The sample was tested on the DSC and in a Pseudo T-history set up. The sample was tested for changes in latent heat of fusion, comparison of temperature/time profiles and any other changes visually.

Figure 3. PCM Stability Test Rig (left), visual inspection of the PCM (right).

2.1. PCM Stability Test Rig

Commercial thermal storage systems are proposed to be 26kL large with a height of up to 3m. The height of the PCM storage tank raised questions to its effect on the chosen PCM with regard to its separation stability. Having the ability to cycle the PCM under geometrically and functionally similar conditions to the field application within the laboratory will provide confidence of its stability in the field. The PCM Stability Test Rig stands over three metres tall. It is of similar height to the commercial system's PCM storage tank. The Test Rig also incorporates the Dynamic Melt loop as presented by Gasia et al., 2017.

The total volume of PCM able to be tested in this rig is 30 litres. Its transparent polycarbonate cylindrical tank provides the ability to perform visual inspections of the PCM while undergoing phase change (Figure 3 right). This is a valuable tool in exploring possible modes of PCM instability. Accurate temperature and flow sensing facilitates the characterisation of the PCM under investigation. Temperature/time profiles are measured and compared with subsequent profiles. The rig consists of a programmable chiller delivering a heat transfer fluid (HTF) through a U-tube heat exchanger submerged in the tank. The chiller and associated pipework is capable of delivering a temperature range of -29ºC to +88ºC to the heat exchanger. A PCM mixing pump is also fitted. This pump maintains a uniform PCM mixture and enables a representative temperature measurement within the medium (Gasia et al. 2017).

The results of the first PCM tested with this rig are presented in this paper. The PCM has a melting point of -6°C and has undergone one hundred consecutive cycles of freezing and melting. Each cycle consisting of freezing with the HTF in the heat exchanger set at -12°C for 8 hours and melting with the HTF in the heat exchanger set at 4°C for 8 hours. Each cycle is completed when approximately 75% of the PCM has frozen and the PCM has completely melted. Increasing the freeze time or decreasing the melt time may lead to a rupture of the polycarbonate tube due to the expansion of the solid PCM.

With an overlaid plot of the temperature versus time data at 25 cycle sampling intervals, any changes to the characteristics would be easily be observed.

2.2. *Pseudo T-history*

The temperature verses time profile is obtained by physically shifting the sample, fitted with a temperature probe, from a higher constant temperature environment to lower constant temperature environment and vice versa. A temperature verses time profile would reveal a progressive change in stability between each sample. Repeating this process on the same sample, without mixing, would provide an example of separation failure.

With a PCM sample, of approximately 150ml, taken every 25 cycles, including the initial and the last, gives five samples requiring testing. This is a relatively small number of samples, and together, all samples could be tested for differences simultaneously, removing uncertainties in test setup conditions. Ongoing field sampling of the PCM would prove difficult to compare with previous samples simultaneously using this technique. The accumulation of samples over the coming years of service of the field unit would require a standardized approach for the comparison of samples and their results. The T-history method provides a means to compare each individual PCM sample taken along with a reference material of known properties. It is then possible to calculate the latent heat of fusion of that individual sample.

In this study, as DSC testing would be performed in any case, the absolute value of latent heat of fusion is not required from the T-history method. This led to the justification of modifying the T-history method to suit the needs of this study, namely, to investigate change between samples. Forgoing the requirement of $Bi < 0.1$ removes the restriction of sample container dimensions and thus providing a numerical value to an existing qualitative experiment. Although values of latent heat of fusion are determined using this "Pseudo T-history" method, they can only be used to compare one sample to the next under similar test conditions. These values are not universal and cannot be taken out of context. These values for the first cycle of each sample taken are presented in Table 1.

2.3. DSC

The DSC has the ability to cycle the same sample indefinitely but the results for the -6PCM displays signs of failure on the second cycle. This failure is not an indication of the prospective failure in the field but simply a failure in the chosen test method. The DSC is unable to cycle the sample in a manner that is representative of the commercial setup. Thus, the PCM samples were taken at 25 cycle intervals from the PCM Stability Test Rig and then tested on the PerkinElmer DSC8000 to measure its latent heat. Analysis of the samples was performed with a heating rate of 10K/min and was repeated three times. The results are presented in Table 1.

3. Results

PCM failure by separation is of prime concern for -6PCM. Figure 4 shows the effect of separation over six consecutive cycles of a single 100.0g sample using the Pseudo T-history setup. The recorded temperature/time profiles show a reduction in the phase change time with each cycle demonstrating degradation of the PCM.

The temperature/time profiles as measured on the PCM Stability Test Rig are shown in Figure 5. There are five profiles superimposed, each at 25 cycles apart. No change in the temperature/time profile can be observed indicating PCM stability.
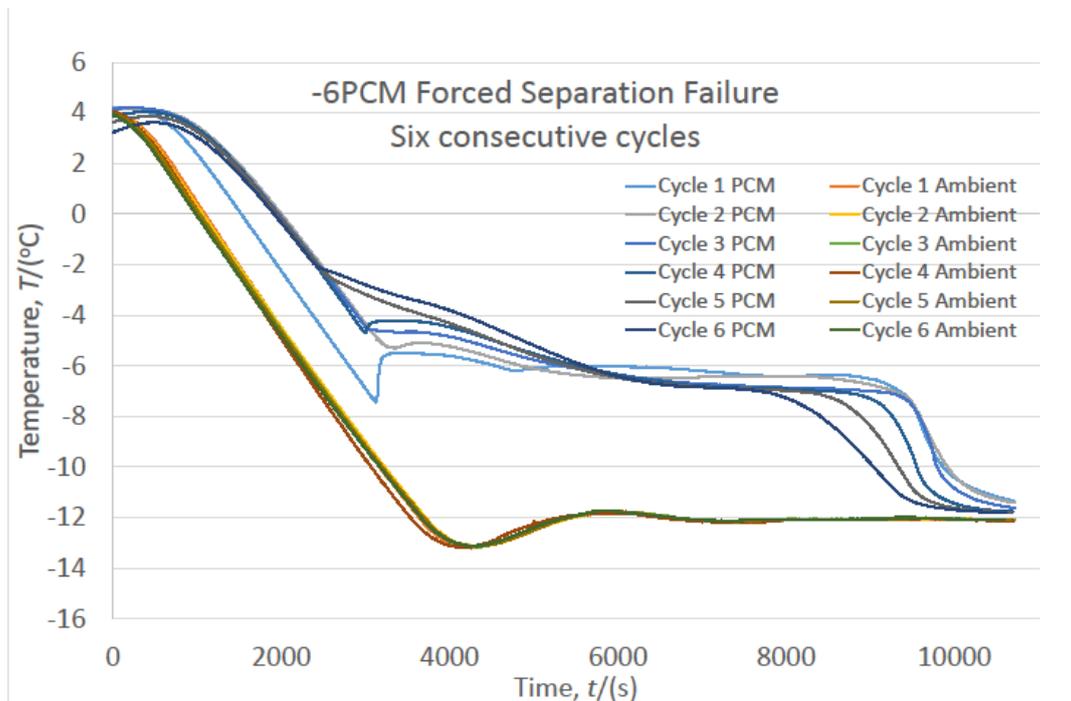

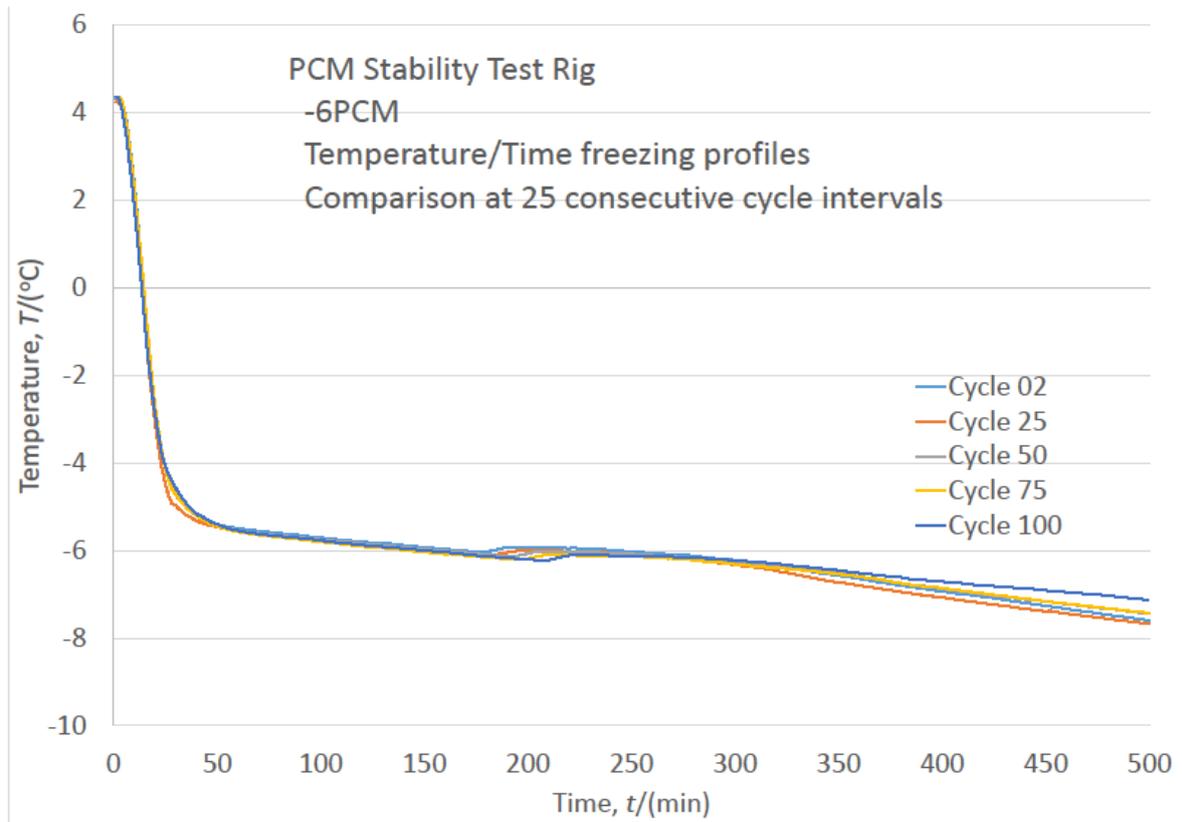**Figure 4. Temperature/Time profile of -6PCM experiencing separation failure**

Figure 5. Temperature/Time profile taken directly from the PCM Stability Test Rig.

The calculation of latent heat of fusion is performed with the Pseudo T-history and the PerkinElmer DSC. These values are compared in Table 1 for each of the 25 cycles when samples were collected.

Table 1. Values of latent heat of fusion as determine by the Pseudo T-history and DSC test methods.

Latent heat of fusion	Pseudo T-History	DSC (run 1)	DSC (run 2)	DSC (run 3)	DSC (average)
Cycle #	$L_{Ps\ T\text{-History}}$/(kJ/kg)	L_{DSC}/(kJ/kg)	L_{DSC}/(kJ/kg)	L_{DSC}/(kJ/kg)	L_{DSC}/(kJ/kg)
0	281	256	256	255	256
25	302	257	253	248	253
50	289	262	261	263	262
75	299	261	263	264	263
100	293	260	258	260	259
	292±11				259±6

4.   Discussion

The PCM failure by separation as forced in the laboratory using the Pseudo T-history setup graphically shows its diminishing useful properties in Figure 4. In particular, the trend is an increasing temperature range for phase change and a shortening of phase change time. A visual inspection of the sample used in this test also shows that separation is occurring with the accumulation of solid granules at the base of the vial. This test sets a benchmark for separation failure and its corresponding temperature/time profile should it occur in the PCM Stability Test Rig.

The superimposed 25 cycle interval temperature/time profiles presented in Figure 5 of the -6PCM tested in the PCM Stability Test Rig show little to no change between each interval. When compared with the profiles of the forced separation, there is no indication of separation occurring.

The samples taken from the PCM Stability Test Rig at 25 cycle intervals were tested in the Pseudo T-history setup for changes in latent heat of fusion and for validation of this setup to measure changes when compared to DSC measurements. The maximum variation from the mean of each sample tested is within 5%. This show little to no change in latent heat of fusion throughout the cycling regime of the PCM Stability Test Rig.

The samples taken from the PCM Stability Test Rig at 25 cycle intervals were also tested in the PerkinElmer DSC for absolute values of latent heat of fusion. The average value of latent heat of fusion for the -6PCM for all sampled cycles is 259±6 kJ/kg, i.e., each sample tested is within 3% of each other. This also shows that there is no discernable difference between each sampled cycle. The DSC results also contributes to the validation process of the Pseudo T-history setup to measure changes in latent heat of fusion.

5.   Conclusions

The stability of -6PCM as tested in the PCM Stability Test Rig, with mixing, for 100 cycles is excellent. There are no signs of failure due to separation as can be induced in static laboratory cycling. No other signs of instability have been observed or measured. The -6PCM is suitable, from a stability perspective, for the proposed field application of the Thermal Energy Storage System.

6.   Recommendations

Incorporation of a mixing pump is not without cost to the efficiency of the system. Future testing will be to limit the operation of the pump to strategic periods of the charging/discharging cycle. The flow rate of the mixing loop will also be investigated in an attempt to reduce pump size and improve efficiency.

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