

Thermal Cycle Testing of a few Selected Inorganic Salts as Latent Heat Storage Materials for High-Temperature Thermal Storage

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Abstract - Thermal cycling test was conducted for 50 cycles to determine the suitability of some commercial-grade phase change materials (PCMs) for solar thermal latent heat storage in terms of melting temperature, latent heat of fusion, and thermal stability. Four samples comprising of three single inorganic salts (NaNO_3 and KNO_3), one binary (KNO_3/KCl), and one ternary ($\text{MgCl}_2/\text{NaCl}/\text{KCl}$) eutectic were studied. It was discovered that all the samples have melting temperatures near the manufacturer's quoted temperatures. However, the latent heat varies significantly for some and perfectly for sodium nitrate (NaNO_3) and nearly for potassium nitrate (KNO_3). In terms of stability, the Thermogravimetric analysis (TGA) test conducted indicates that all the tested PCMs are stable and after undergoing so many thermal cycles.

Keywords — Thermal cycle, PCM, Eutectics, Energy storage, solar power plant.

I. INTRODUCTION

Storage of thermal energy is one of the key processes towards the effective utilization of thermal energy. Latent heat storage using phase change materials (PCMs) presents an attractive option for low, medium, and even high-temperature applications. In choosing a PCM for any application, characteristics such as availability, stability, cost, life span, conductivity, latent heat capacity, density, and low negative environmental impacts are usually taken into consideration. A number of studies/reviews have been conducted on thermal energy storage materials and systems [1-6]. Zhou et al. and Sami [7-8] had reviewed the phase change materials application as thermal storage materials in buildings. They explained that the indoor temperature fluctuations could be regulated to reflect the thermal comfort of occupants with the help of phase change materials. Few researchers [9-13] have investigated the thermal performance of low-temperature latent heat storage material. After repeated cycles, the potential use of these materials has been reported and also analyzed the disparities in melting /freezing temperatures and latent heat of fusion using micro and macro testing. In any case, there should not be large variations with an increasing number of thermal cycles as that will distort the performance of the PCM. Organic and inorganic PCMs were studied by Zalba

et al. [14], and they explained that whereas organic PCMs have lower corrosion rates and better thermal and chemical stability, they are characterized by very low latent heat and thermal conductivity values. Inorganic PCMs, on the other hand, have higher latent heat values but pose serious corrosion issues to the container materials and also possess weak thermal stability. Energy storage capacity is the product of density and latent heat derived from PCM during the phase transition process. PCMs such as NaNO_3 , KNO_3 , NaOH , KOH , and NaCl-KCl (58:42 % wt.) are reported potential candidates for latent heat storage in concentrated solar power (CSP) systems because their melting temperature ranges from 220 °C to 400 °C, which corresponds with the Rankine cycle operation temperature [15]. However, their thermal cycle tests could not be found in the literature. Other PCMs that performs at higher temperature up to above 600 °C includes some fluorides, few chlorides and also few carbonates.

According to Hoshi et al. [16], the melting point of single PCMs tends to appreciate in the order of nitrates, chlorides, carbonates, and fluorides. As for the eutectics of such salts, the melting temperature, subcooling (if any), solidification temperature, latent heat, and almost all other properties depends on the properties of the individual components as well as their percentage quantity in the eutectic mixture. Liu et al. [17] had performed experimental research on some PCMs comprising of carbonate and chloride salts. As for the chlorides, they noticed very low subcooling in contrast with the carbonates that have higher degrees of subcooling. This manifests itself in the freezing or solidification process, where lower temperatures were noticed in comparison with the melting temperature [18]. So, in this case, chlorides can be more applicable in heat storage, especially for high-temperature applications as compared to carbonate-based salts. This is because, as the temperature increases, so the subcooling becomes more severe, and that will make the heat recovery too difficult and eventually rendered the PCM unsuitable for usage.

In a real sense, the target is to have a PCM that will meet the required thermophysical standard in terms of melting temperature, latent heat, thermal stability over many thermal cycles without undergoing any considerable change in these characteristics [19]. Though a lot of literature can be found on studies of latent heat storage



materials, however, right feasibility studies on the thermal behavior after repeating heating/cooling cycles are missing. Therefore, in this paper, accelerated thermal cycle tests were conducted for on 4 inorganic materials viz. (i) sodium nitrate (ii) potassium nitrate and eutectics of (iii) potassium nitrate & potassium chloride and (iv) sodium chloride, sodium chloride & potassium chloride to check their potential candidacy as phase change materials.

II. EXPERIMENTAL DESIGN

Throughout the lifetime of any thermal storage system, it is believed that it will undergo at least a cycle per day and 30 cycles per month. A simple laboratory experimental setup was designed to study the thermal cycle behavior of the identified materials. Identified commercial-grade inorganic materials to be used as PCMs were procured from local markets, which were easily available at low cost and with a relatively accepted level of purity level ranging between 94 – 98%. The samples were kept in closed stainless steel vessels, and accelerated thermal cycles were conducted for the samples using an electrical heating system with a mechanism of temperature control using similar procedures as reported by [11-12]. The temperature readings of the material during the heating process were recorded at a time interval of five minutes till the material melts completely. The experiments were conducted for 50 cycles of each material. After 1st, 30th, and 50th cycles, a small part of the sample is taken and preserved, and all such preserved samples were subjected to a differential scanning calorimetry (DSC) test in order to confirm the changes in both the melting temperature and the latent heat value. Furthermore, thermogravimetric analysis (TGA) was also conducted to determine the stability of the material as to whether it undergoes degradation in the form of mass loss after several thermal cycles or not. Perkin-

Elmer Differential Scanning Calorimetry (DSC) and Thermogravimetry Analyzer (TGA) were used for thermal analysis with a heating rate of 10 °C /minute.

III. RESULTS AND DISCUSSION

A. Sodium Nitrate (NaNO_3) Salt

Sodium nitrate with a density of 2.26 g/cm³ is one of the PCMs been reported for thermal storage in various applications, especially at high temperatures. A thermal cycling test was conducted in order to determine its suitability for application in solar thermal power plants as a PCM for the storage system. In the thermal cycling test, which was done for 50-cycles, the melting temperature profiles were recorded and are shown in Figures 1 for the 1st and 50th cycles. The melting point varied between 303 °C – 308 °C (Figure 1). The DSC results were obtained for the 1st, 30th, and 50th cycles and are tabulated for these respective cycles in table 1. The results show an agreement with the thermal cycling test conducted and reported in literature till the 50th cycle [20]. A representative DSC is the graph for the 50th cycle is given in figure 2. A small peach can be seen in the DSC figure 2, which may be due to nitrite impurity available in the commercial-grade sodium nitrate, as reported by Thomas et al. [21]. As can be seen from figure 2 and table 1, the DSC result for the 1st cycle indicates a melting temperature of 305.9 °C with a corresponding latent heat of 175.9 J/g, while the result for the 50th Cycle also indicates melting temperature of 306.1 °C and $\Delta H = 177.2$ J/g. These results are in agreement with what was reported by Michels and Roberts [22] as melting temperature of 306 °C and $\Delta H = 172$ J/g and Tamme [23] with melting temperature of 306 °C and $\Delta H = 175$ J/g. However, they have not mentioned the number of cycles.

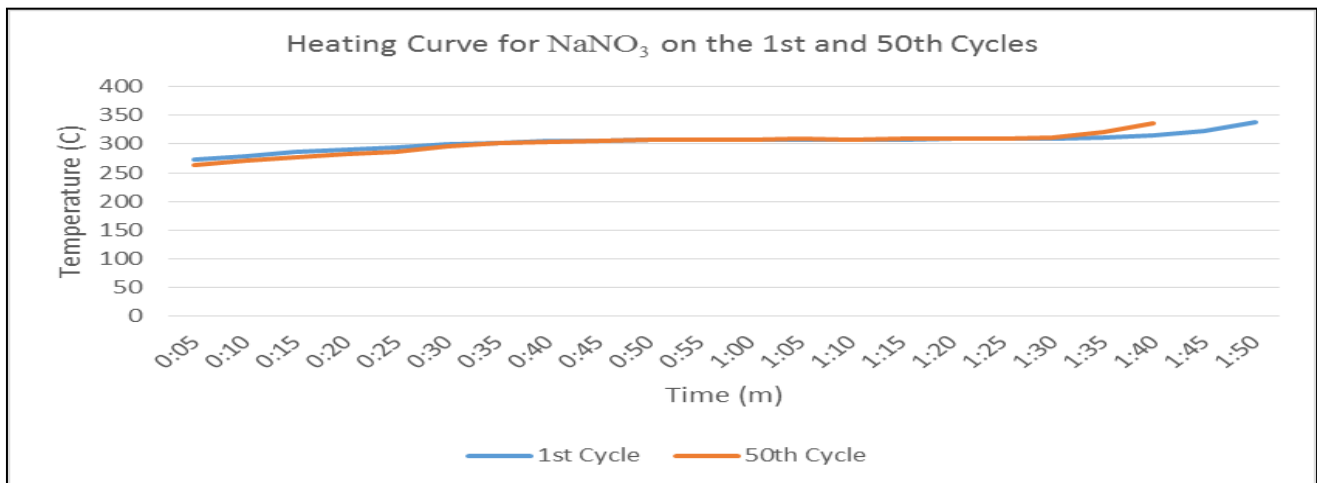


Figure 1: Heating Curves for the 1st and 50th Cycles of NaNO_3 salt

Table 1: DSC results for the various cycles of the NaNO_3

Thermal cycle Number	Melting Temperature (°C)	Latent Heat of Fusion (J/g)
1 st	305.9	175.9
30 th	305.8	168.4
50 th	306.1	177.2

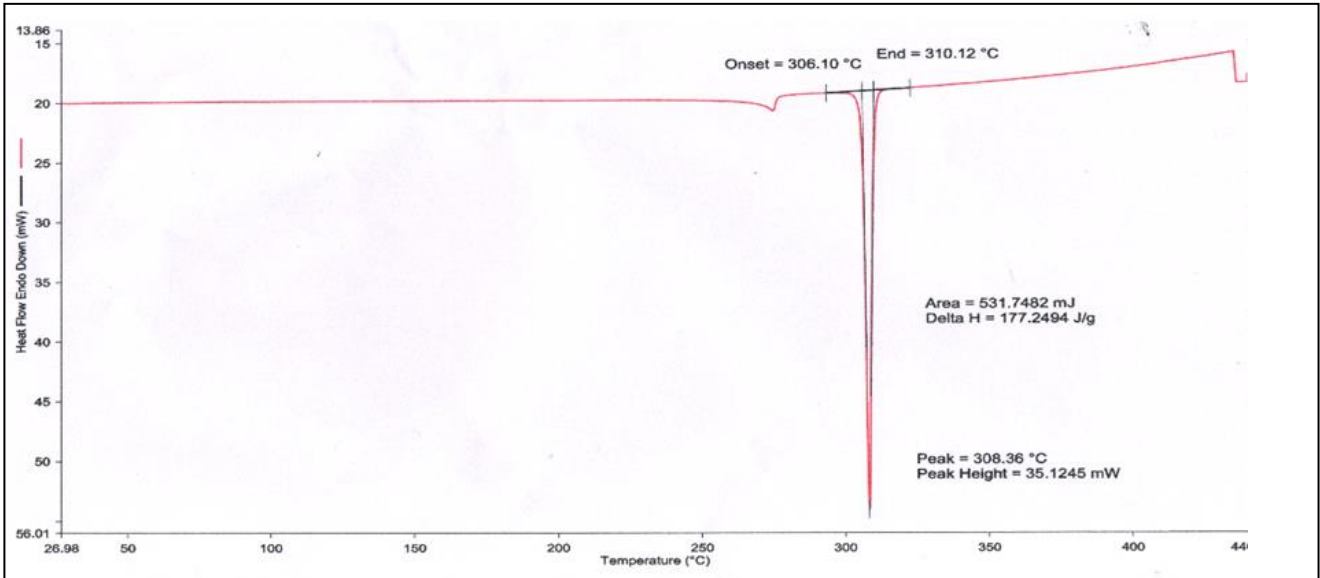


Figure 2: DSC graphs of latent heat of fusion and melting temperature of NaNO₃ for 50th Cycle

The TGA analysis indicates that the sample PCM is very stable as it only experiences a negligible change in its weight which is 0.74 %. This may not be unconnected with the fact that there is little change in density with increasing temperature, as no loss of matter was noticed

during the experiment in terms of fumes or color change. It also did not show any change in texture up to the 50th cycle. This shows that the PCM is thermally stable and can be used for a fairly long time.

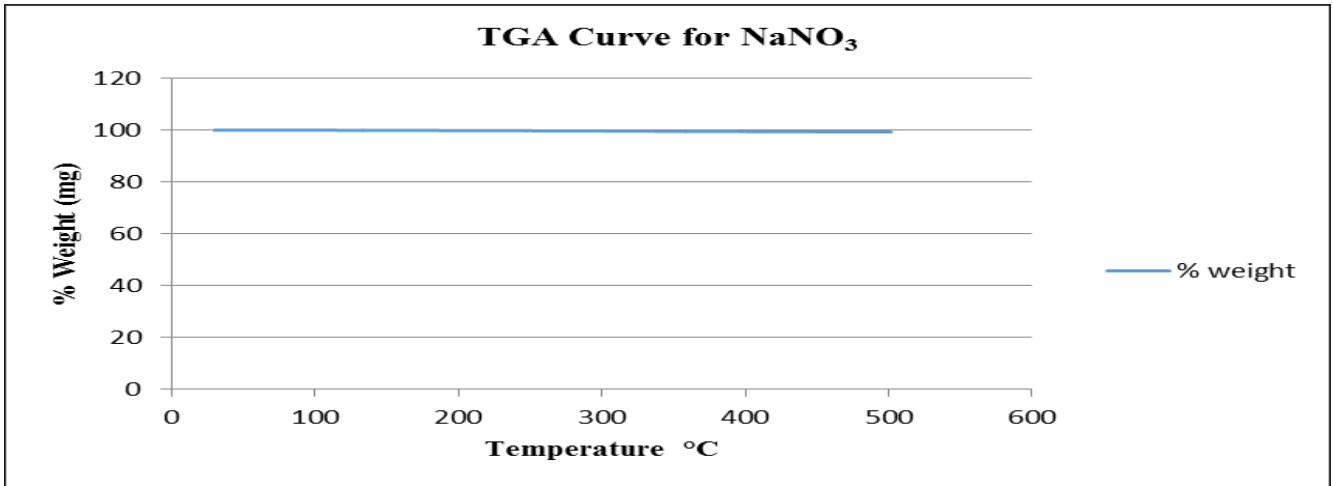


Figure 3: TGA curve for the NaNO₃ single salt for the 50th-Cycle

B. Potassium Nitrate (KNO₃) Salt

Potassium nitrate (KNO₃) with a density of 2.11 g/cm³ as a single salt was also thermally tested for 50 cycles. The thermal cycles indicate a melting temperature range of 322 °C – 338 °C over the thermal cycles. This can be seen from the heating curves of the 1st and 50th cycles in figure 4; however, very good repeatability can be seen from this figure for both the cycles. DSC result indicates a melting point of 328 °C – 329 °C with a corresponding latent heat of 92.04 J/g for the 1st cycle and 94.9 J/g for the 50th cycle. The results are tabulated in table 2, and a DSC representative graph is shown in figure 5. Similar values have been reported in kinds of literature by Deng et al. [24]

even though it was not mentioned whether such samples of the salt were from commercial or industrial grade since purity is significant in determining both the melting temperature and the latent heat of fusion. After 50 cycles, the melting temperature as well as the latent heat of fusion both remains stable within the above-quoted values. This signifies that the commercial-grade salt obtained from the local market is good enough to be used as storage material in thermal power plants and other similar applications. Other applications that may require higher temperatures can also utilize this material since its melting temperature is a bit wider in range and not fixed to a single value or a very short range.

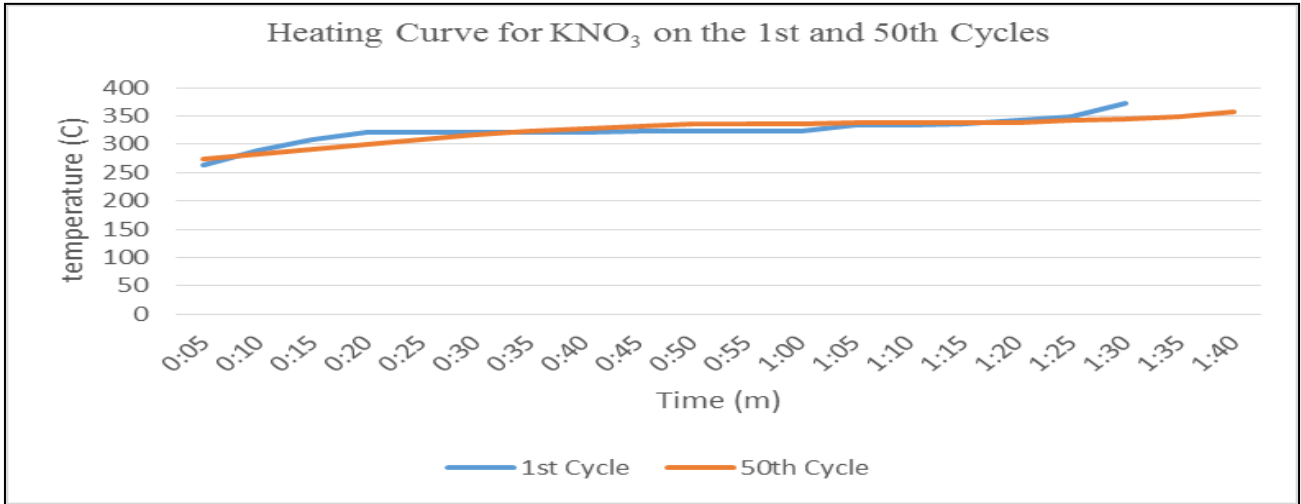


Figure 4: Heating Curves for 1st and 50th Cycles of KNO₃

Table 2: DSC results for the various cycles of the KNO₃

Thermal Cycle Number	Melting Temperature (°C)	Latent Heat of Fusion (J/g)
1 st	329.0	92.4
30 th	328.6	91.0
50 th	328.2	94.9

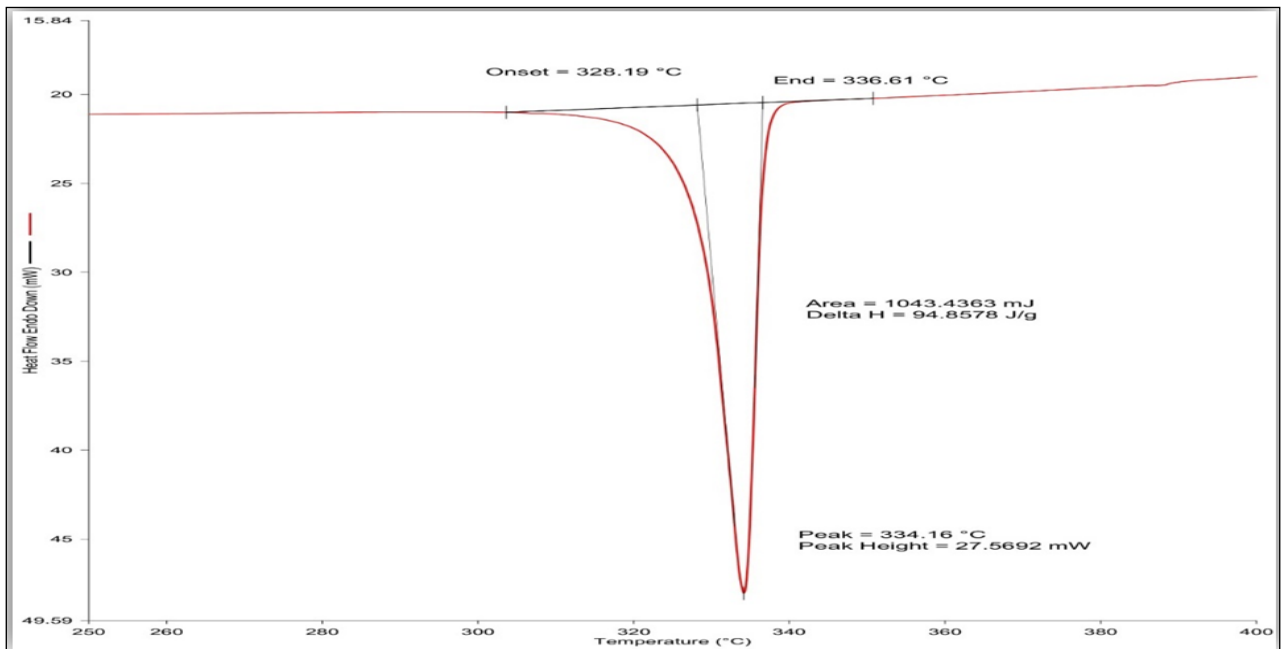


Figure 5: DSC Curve of KNO₃ for the 50th Cycle

Thermo-gravimetric analysis (TGA) of the 50th cycle of the sample PCM indicates that the decrease in mass is only 0.42% which is quite negligible. This shows that this PCM is thermally stable within the above-stated temperature range and can withstand repeated cycles usually associated with solar thermal storage systems and therefore suitable

for high-temperature applications. The melting temperature and the corresponding latent heat have both remained stable, and this is a pointer that the mass may most likely remain stable since repeated thermal cycles within this temperature range had shown stable properties.

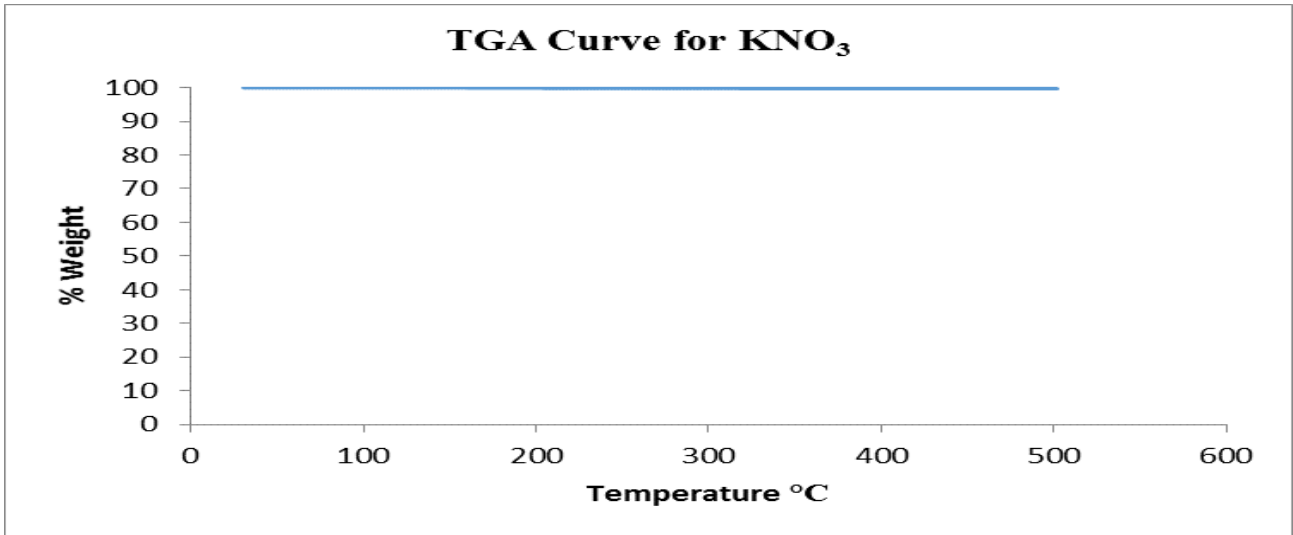


Figure 6: TGA curve for the KNO₃ for 50th Cycle

C. Potassium Nitrate-Potassium Chloride (KNO₃/KCl) Eutectic Composition

A binary eutectic of potassium nitrate and potassium chloride was formed with a ratio of 90:10 by weight, respectively. The eutectic was subjected to a thermal cycling test for 50 cycles, and the result shows a stable melting temperature of between 321 °C – 326 °C throughout the 50 cycles. The heating profile with time for the 1st and 50th cycles is depicted in Figure 6. In all the cycles, the eutectic melted congruently, with no phase separation of the composite compounds observed. In general, the eutectic remains stable in all the temperatures from room temperature to 440 °C. Such stability was also reported by Bauer et al. [25-26] and Cordaro et al. [27]. When the samples were tested through DSC, it was observed that melting temperature ranges between 308.4

°C to 308.5 °C between 1st and 50th cycles. A representative DSC curve for the 50th cycle of the eutectic is shown in figure 7. From this figure, it has been observed that part of latent heat was also absorbed prior to the complete melting of the eutectic. For the binary salt, two endothermic peak points were obtained, and the possibility of the final peak corresponds to the solid-state phase transition associated with KNO₃ eutectoid and the second peak point corresponds to the melting temperature. Similar DSC results were also reported by Benes et al. [28]. The DSC results obtained are tabulated in table 3. The difference between heating profile temperature and DSC temperature may be due to the number of materials. The recorded latent heat of fusion is very low, of the order of 18-24 J/g. Therefore, the developed eutectic candidacy is poor.

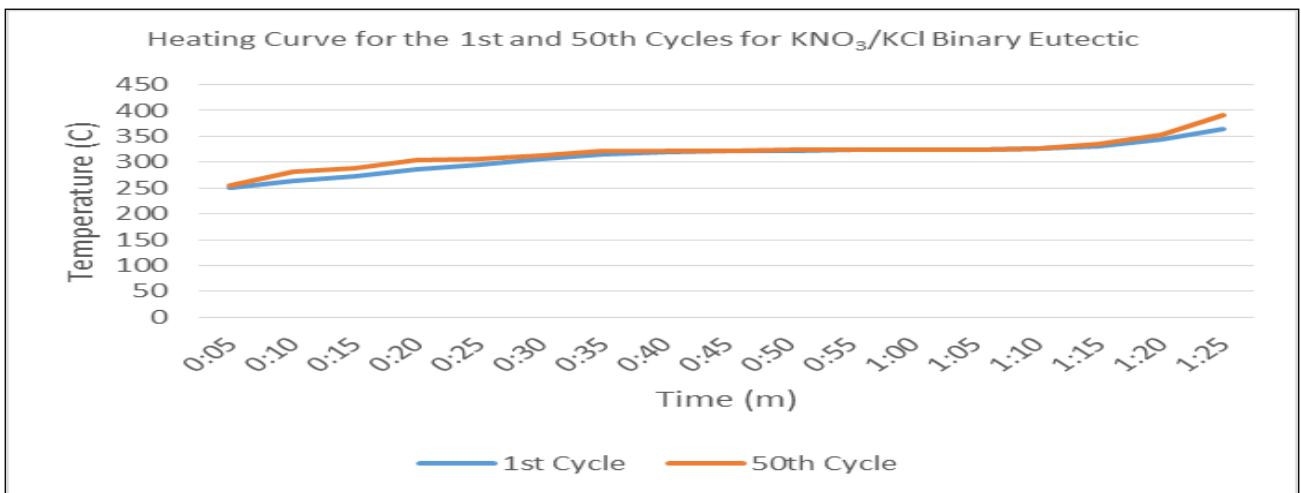


Figure 6: Heating curve profile for the 1st and 50th Cycles of KNO₃/KCl binary eutectic

Table 3: DSC results for the various cycles of the KNO₃/KCl binary eutectic composition

Thermal cycle Number	Melting Temperature (°C)	Latent Heat of Fusion (J/g)
1 st	308.4	17.8
30 th	308.5	24.6
50 th	308.2	23.9

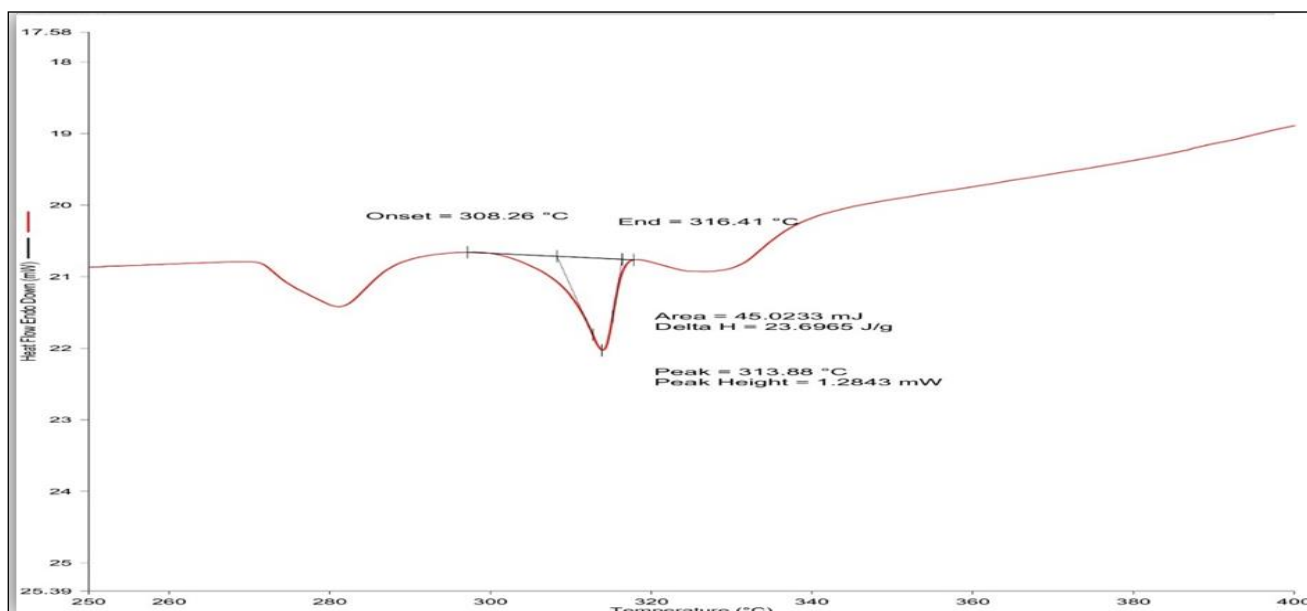


Figure 7: DSC curve of latent heat and melting temperature of KNO₃/KCl binary eutectic composition for the 50th Cycle

However, thermo-gravimetric analysis (TGA) indicates that the eutectic is highly stable, and no loss of mass is observed during heating. The sample tested indicates a loss of 1.09% of the original mass. This is negligible, and the trend may likely stop after few more cycles since KNO₃ is hygroscopic in nature and may have likely absorbed

moisture earlier before undergoing thermal cycling, which will make the moisture evaporate looking at the fact that the trend occurs at around 100 °C which is the boiling point of water. TGA profile of mass versus temperature of 50th cycle is given in figure 8.

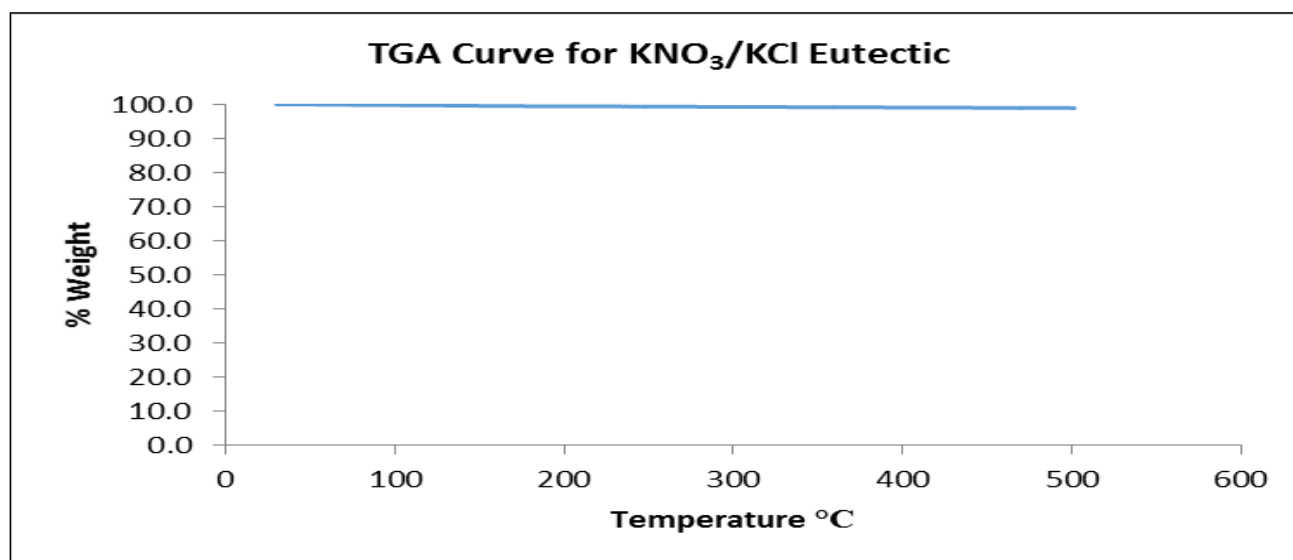


Figure 8: TGA curve for the KNO₃/KCl eutectic composition for the 50th-Cycle

D. Magnesium Chloride-Sodium Chloride-Potassium Chloride (MgCl₂/NaCl/KCl) Ternary Eutectic

A ternary eutectic salt was formed by using three chlorides, namely magnesium chloride, sodium chloride, and potassium chloride, in the ratio 50:30:20 by weight, respectively. In the melting cycles, the temperature profile of the macro size sample was nearly constant between 393-396 °C for 1st and 50th cycles, which fairly can represent

the melting temperature of the sample and plotted in figure 9, i.e., no major changes were noticed. All the 3 samples of the eutectic of 1st, 30th and 50th cycles were tested for melting point and latent, and the results are shown in Table 4. The developed eutectic was very stable during these cycles. However, there were variations in the latent heat of fusion between 85.4 J/g to 100.8 J/g. A representative DSC measurement curve of the 50th cycle is given in figure 10.

Though the melting temperature confers with the literature [19], the latent heat of fusion was lesser than as reported by Garkushin et al. [29]. In the latent heat front, the initial (first cycle) analysis reveals a latent heat of 85.4 J/g, and subsequently, by the fiftieth (50th) thermal cycle, the latent heat of fusion is 100.8 J/g. So, while the melting temperature of the sample had remained averagely stable, there is appreciation in the magnitude of latent heat, which may possibly be linked to the fact that the sample becomes more pure and structured with more cycles as the individual PCMs that make up the eutectic becomes more

blended and release some of the impurities present in the sample. This can be deduced from the TGA curve, where the mass loss was visibly much in the beginning, and the sample only attended a stable state after some time. Within that time, many impurities most have been likely released together with the moisture, or the moisture itself must have tempered with the sample properties itself. However, such an increase is not expected to remain continuous as the sample may also start to worn out and loose its effectiveness with more thermal cycles.

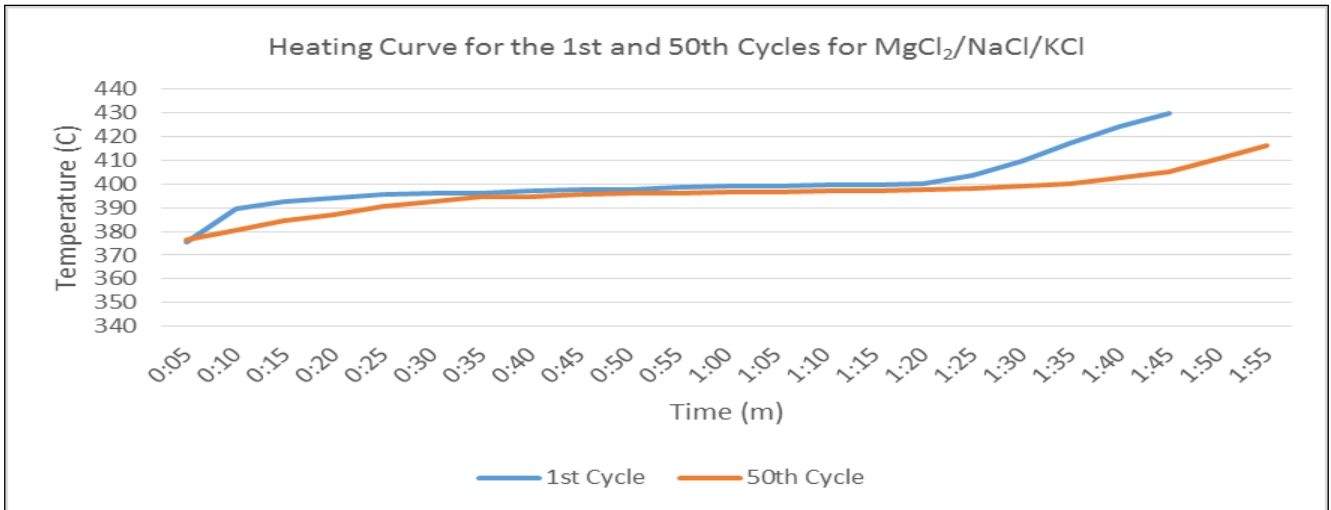


Figure 9: Heating Curve for the 1st and 50th Cycles of MgCl₂/NaCl/KCl eutectic

Table 4: DSC results for the various cycles of the MgCl₂/NaCl/KCl ternary eutectic

Thermal cycle Number	Melting Temperature (°C)	Latent Heat of Fusion (J/g)
1 st	401.9	85.4
30 th	401.1	90.3
50 th	401.2	100.8

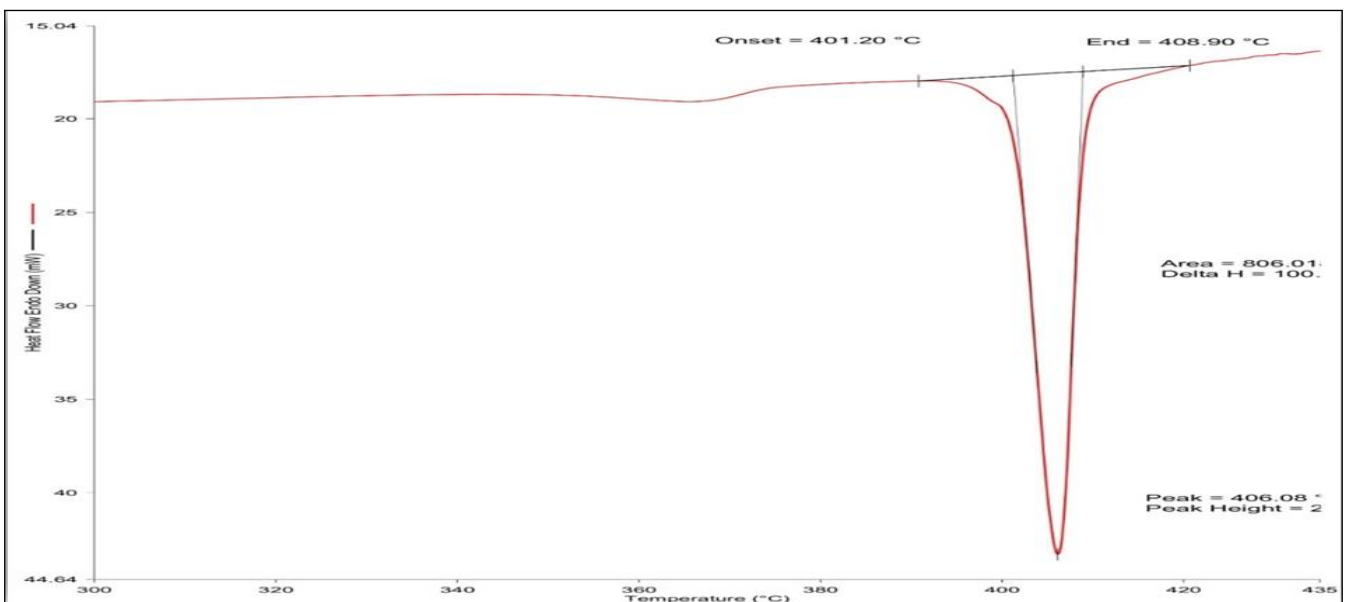


Figure 10: DSC curve of latent heat and melting temperature of MgCl₂/NaCl/KCl eutectic composition for the 50th Cycle

Thermo-gravimetric analysis was conducted for the 50th cycle to understand the profile of mass with heating and indicated that the eutectic first undergoes some stability then followed by a decrease in mass. The decrease continued till the total mass goes down to about 10.4 mg from the original mass, which is 13.321 mg. This represents a decrease of 21.9%. After this loss, the sample attains a fairly stable state, and the further loss of mass becomes so negligible. The loss is most likely due to the

loss of moisture which appears in the form of fumes during the experiment, and also, it can be seen that the weight loss starts occurring from the boiling temperature of water upwards to almost 200 °C. This is consistent with the fact that the water present in the sample is not pure. As such, its boiling point will definitely rise [30]. This is an indication that the eutectic is good and can be utilized as latent heat energy storage material. This behavior is indicated in figure 11.

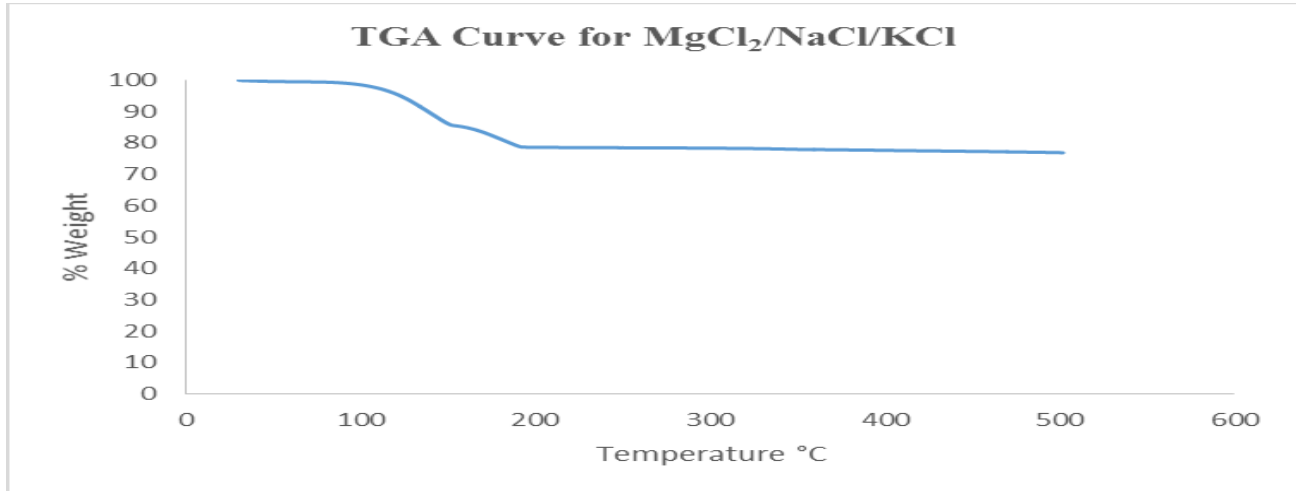


Figure 11: TGA curve for the MgCl₂/NaCl/KCl eutectic composition for the 50th-Cycle

IV. CONCLUSION

Commercial grade inorganic PCMs have been tested as single salts as well as binary and ternary eutectics. The melting temperature has been found to be within the range quoted by manufacturers, while the latent heat shows some more variations as compared with the previous kinds of literature. Specifically, sodium chloride was found to match the existing pieces of literature in both melting temperature and latent heat content, and while the rest of the three (3) samples comprising of potassium nitrate, potassium nitrate/potassium chloride binary eutectic, and magnesium chloride/sodium chloride/potassium chloride ternary eutectic have near match in terms of melting temperature with what was quoted by the manufacturers, the latent heat content is lower when compared with literature reports. However, as the purity may affect the performance of any commercial-grade PCM, testing and enhancement are important. This is because while they will be readily available in the market at affordable prices, the quality may not be guaranteed as such desired results may not be obtained if used directly without verification. Also, various enhancement procedures such as applications of fins, nanoparticles, and formation of eutectics at right weightage compositions instead of single salts will enhance the performance of PCMs in various dimensions.

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