1. Introduction

Out of all the industries that run using the energy, building sector alone utilises approximately 40 % of the world’s energy. Hence, the conservation of energy, and utilization of alternative energy sources and systems must satisfy a major portion of the cooling/heating that is needed for the buildings. This present study shows the improved thermophysical properties of the NFPCM are extremely useful to run the cool thermal energy storage (CTES) system and the solidification behaviour of aqua based NFPCM enclosed in a spherical container.

The CTES technique, finely described as ‘accumulating cool energy for future use so that we can bridge the time interval between the energy availability and energy use’ Chearlathan et al.1 experimentally showed the CTES plays a vital role in central air-conditioning in the large buildings. Marimon et al.2 done the experimental study on refrigeration in supermarkets. Nasser Mostafavinia et al.3 showed that the thermal energy can be stored in the three ways of sensible heat (SH), latent heat and thermochemical reactions low temperature heat exchangers. Sun et al.4 investigated the effect of NFPCM in high powered electronic cooling applications and Deepak sharma et al.6 different industrial process cooling applications where the cooling necessity is highly irregular. The CTES system with the PCMs is better in lots of applications compared to SH storage, due to its huge storage capability within a tiny phase conversion temperature range [Py et al.7, Kumaresan et al.8 and Lee et al.9]. The available literature was reviewed related to CTES on the PCM selection and heat transfer improvement and the thermophysical properties of usually used secondary refrigerant. The researchers tried to improve the thermophysical properties of the PCM for enhancing the thermal performance of CTES system by different methods.

It is clear that concept of thermal energy systems that the integration of the CTES system will be very useful to reduce maximum energy demand by storing the energy during off period time and releasing the stored...
energy during peak period. However, the low thermal conductivity of the PCMs reduces the heat transfer rate during the charging and discharging process that appreciably reduce the thermal performance of the CTES system. In addition, the sub cooling behaviour of the PCM demands for the lower evaporator temperature which in turn results with the higher energy consumption. The above two major problems will be overcome by the current interesting developments in the field of nanotechnology [Hong et al.10, Hwang et al.11 and Hwang et al.12]. Recent researchers are focusing much attention to produce nano sort of PCMs called as nanofluid PCM (NFPCM) by suspending nanoparticles in the base PCM. It is observed from the literatures the use of NFPCM appreciably enhanced the rate of heat transfer due to the thermal conductivity raise. Limited works have been reported by the researchers with aqua as the base PCM for the CTES applications. The solidification behaviour of the NFPCM with aqua as the base PCM and graphene as the nanomaterial have not been investigated. Considering the pressing need to enhance the thermal performance of CTES system suitable for space cooling and high thermal transport properties of graphene, the specific motive of present work is to examine the heat transfer behaviour of NFPCM with aqua as the base PCM and GNP as the nanomaterial.

2. Preparation of NEPCM

2.1 Selection of base PCM and Nanomaterial

Considering the operating temperature of the chiller (-12°C to -9°C), water is selected as the base PCM due to its high latent heat, easy availability and high solid to liquid thermal conductivity and the thermophysical properties are listed in Table 1.

Commonly used nanoparticles for the preparation of nanofluids are metallic materials, such as copper, gold, silver and aluminium etc., and metal oxides such as copper oxide, iron oxide, titanium oxide, and alumina etc., and carbon based such as carbon nanotubes (CNT) and graphene. Higher thermal conductivity (k = 4800 to 5300 W/m K), lower density and large scale production of graphene with minimum environmental impact are the major factors for selecting graphene for present work as shown in Table 2. The graphene was procured from Cheap Tubes USA and its specifications are provided by the manufacturer and the TEM image of the graphene nanoplatelets as shown in Figure 1 and size of the graphene is found to be 8 nm thicknesses.

Table 1. Thermophysical properties of water

| Property                                  | Value            |
|-------------------------------------------|------------------|
| Liquid thermal conductivity at 20°C       | 0.598 W m⁻¹K⁻¹  |
| Solid k                                   | 2.2 W m⁻¹K⁻¹    |
| Solid density                             | 920 kg m⁻³       |
| Liquid density at 4°C                     | 1,000 kg m⁻³     |
| Melting/freezing temperature              | 0 °C             |
| Latent heat of melting                    | 334 kJ kg⁻¹      |
| Specific heat water                       | 4.187 kJ kg⁻¹K⁻¹|
| Specific heat ice                         | 2.108 kJ kg⁻¹K⁻¹|

Table 2. Nanomaterial specification

| Material specification                  | Graphene nanoplatelets |
|-----------------------------------------|------------------------|
| Grade                                   | Grade 3 (industrial)   |
| Surface area                            | 600 – 750 m²/g (4 to 5 layers) |
| Thickness                               | 8nm                    |
| Particle diameters                      | <2 microns             |

2.2 Preparation of NEPCM

The NEPCM preparation is of vital importance when using it as a working fluid in any thermal system. The term NEPCM would not be a simple blend of the nanoparticles and a base fluid. The correct mixing and stability of the nanoparticles are required, in order to prepare stable NEPCM. Two-step approaches are used to prepare the NFPCM and the following methodology is used to prepare the NEPCM. The surfactant (0.5wt. %)
is mixed with known volume of DI water (200ml) and the blend is stirred for 15mins using a magnetic stirrer. The graphene is then dispersed in the above mixture and the solution is stirred for 30mins. The solution is then placed in an ultrasonicator and the dispersion of graphene in the solution is achieved through continuous ultrasonication for a period of 180 min. Using two step methods, around nine samples were prepared by using three different surfactants such as triton, sodium dodecyl sulphate (SDS) and gum Arabic. It has been notified that there was no deposition of GNPs even after three months of preparation in the case of NEPCM using SDS as the surfactant and the prepared samples as shown in Figure 2.

After ensuring no visual sedimentation, the size of the dispersed graphene platelets in water was measured using the scanning electron microscopy (SEM) as shown in Figure 3 (a-c). It is observed that the graphene platelets are having around 120nm thickness and 2-3 micro meter diameter as shown in Figure 3 (a-c).

Figure 2. Photographic view of prepared samples using SDS.

Figure 3. ISEM images of the dispersed graphene nanoplatelets in water (a) 0.2 wt.% (b) 0.4 wt.% (c) 0.6 wt.%.  

3. Measurement of Density and Thermal Conductivity

The density of both the aqua and NEPCM are measured at atmospheric temperature by weighing a liquid sample in a standard volumetric flask (Class A) of 25 ml and 50 ml, using a high accuracy electronic balance (± 0.002 g) with airlock container. The procedure is repeated five times in order to achieve good accuracy. The relation used to calculate density is,

\[ \rho_{nf} = \frac{m_t - m_f}{V_{nf}} \]  

(1)

Where, \(m_t\), \(m_f\) are the mass of the flask with the NFPCM and the empty flask respectively, and \(V_{nf}\) is the
NFPCM volume taken in the flask and the data collected regarding density measurements are tabulated (Table 3).

The difference in the thermal transport properties of the PCMs with respect to temperature is an energetic factor for TES applications, when the NFPCMs are exposed to varying temperatures during the freezing and melting processes. The thermal conductivity is measured using KD2 Pro thermal analyser. The accuracy of this measurement is ±5%. The NFPCM was packed in the small spherical capsule and the probe was immersed at the centre of the spherical capsule.

**4. Experimental Setup for the Solidification Test**

In order to assess the role of graphene it is proposed to study the solidification characteristic of NEPCM using the experimental facility as shown in Figure 4. This experimental setup contain a stainless steel tank of volume 0.01m$^3$, packed with a blend of 60% water and 40% ethylene glycol (EG) by volume and the remaining components were fitted to keep the constant temperature.

For the experiments with water based NEPCMs, one spherical capsule prepared using low-density polyethylene (LDPE) with diameter of 140 mm and this capsule is kept in the constant temperature liquid bath. Three RTD’s are located in various radial locations of the spherical capsule to observe the temperature deviation of the PCM at different radial locations. All the RTDs are joined to a data logger (Agilent 34970A). The experimentations were performed with Deionized water and DI water with GNP at the surrounding bath temperature of -9ºC and -12ºC.

The temperature is continuously observed by one RTD sensor and another temperature control valve. The ball is fixed in the centre of the constant temperature bath.

**Figure 4.** Schematic diagram of the experimental setup.

**5. Result and Discussions**

**5.1 Density of the NEPCM**

Table 3 shows that there is no much variation in the densities of the four different samples. It has been noticed that the density of the NEPCM increased with respect to concentration of the graphene. It has also been absorbed from the table 3 that the density of water increased to a maximum of 1.16% related to that of deionized water in addition with 0.6 wt. % of GNPs.

**5.2 Measurement of Thermal Conductivity**

The thermal conductivity of water based NFPCM was recorded in various surrounding bath temperatures using KD2 Pro thermal analyser [Lee et al., Li et al. and Sari et al.]. The experimental data has been compared with ASHRAE standards 1997 as shown in Figure 5. It is

| Table 3. Density of the NEPCM |
|-------------------------------|
| **Flask volume = 25 ml** |
| Samples | Compositions | m$_f$ (kg) | m$_t$ (kg) | ρ(kg m$^{-3}$) | % of increase in density |
| Sample 1 | Base PCM | 0.05280 | 0.02803 | 991.0 | - |
| Sample 2 | NFPCM with 0.2 wt. % graphene | 0.05288 | 0.02803 | 994.0 | 0.302 |
| Sample 3 | NFPCM with 0.4 wt. % graphene | 0.05300 | 0.02803 | 999.1 | 0.817 |
| Sample 4 | NFPCM with 0.6 wt. % graphene | 0.05306 | 0.02803 | 1002.3 | 1.140 |
| **Flask volume = 50 ml** |
| Sample 1 | Base PCM | 0.092440 | 0.042855 | 991.7 | - |
| Sample 2 | NFPCM with 0.2 wt. % graphene | 0.092558 | 0.042855 | 994.06 | 0.308 |
| Sample 3 | NFPCM with 0.4 wt. % graphene | 0.092842 | 0.042855 | 999.74 | 0.881 |
| Sample 4 | NFPCM with 0.6 wt. % graphene | 0.092983 | 0.042855 | 1002.5 | 1.160 |
noticed that the thermal conductivity enhancement of 9.5% achieved with addition of 0.6 wt. % of graphene nanoplatelets in DI water. The thermal conductivity of the NFPCMs increased linearly for increasing surrounding bath temperature.

![Figure 5. Thermal conductivity of NFPCMs compared with ASHRAE standards.](image1)

**Figure 5.** Thermal conductivity of NFPCMs compared with ASHRAE standards.

### 5.3 Transient Temperature Variation of NFPCMs during Solidification Test

#### 5.3.1 Transient Temperature Variation of NFPCM at $T_{\text{surr}} = -9^\circ\text{C}$

The effects of bath temperature and GNPs concentration on the freezing behaviour of water are explained in this section. Figure 6 shows the impermanent temperature variation of nanofluids in a spherical capsule for different radial positions. It is observed that the centre portion of the capsule takes more time to solidify as shown in Figure 6. Figure 7 shows the variation in temperature with different concentrations of GNPs at bath temperature of -9 °C. Deionized water and nanofluid PCM with 0.6 wt. % graphene experienced a lower subcooling degree of -6 °C and -3.4 °C respectively as shown in Figure 7. Additionally, the investigational results exhibited a valuable reduction in the freezing time of nanofluid PCMs compared to that of the pure PCM. The extreme reduction in the solidification time of 24 % obtained for

![Figure 6. Transient temperature variation of the Deionized water at various positions ($T_{\text{surr}} = -12^\circ\text{C}$).](image2)

**Figure 6.** Transient temperature variation of the Deionized water at various positions ($T_{\text{surr}} = -12^\circ\text{C}$).

![Figure 7. Temperature variation of the NFPCM at $T_{\text{surr}} = -9^\circ\text{C}$.](image3)

**Figure 7.** Temperature variation of the NFPCM at $T_{\text{surr}} = -9^\circ\text{C}$.

#### 5.3.2 Transient Temperature Variation of NFPCM at $T_{\text{surr}} = -12^\circ\text{C}$

Figure 8 shows the impermanent temperature variation of NFPCM, when the temperature of the bath fluid is maintained at -12°C. Deionized water and nanofluid PCM with 0.6 wt. % graphene experienced a lower subcooling degree of -7 °C and -2.8 °C respectively as shown in Figure 8. Additionally, the investigational results exhibited a valuable reduction in the freezing time of nanofluid PCMs compared to that of the pure PCM. The extreme reduction in the solidification time of 24 % obtained for
NFPCM containing 0.6 wt. % of GNP. this is due to high conductive nano-layers with the higher specific surface area in the NFPCM.

6. Conclusion

The solidification behaviour of water based NFPCM was examined experimentally with different temperatures and the observations are listed below,

- The density measurement reviewed that the increasing density is not appreciable is compared to that of other metal/metal oxide nanomaterials.
- The maximum thermal conductivity enhancement of 9.5% achieved for 0.6wt. % GNP in DI water. This is due to larger surface area for heat transfer.
- The presence of GNP decreases the subcooling appreciably and the reduction in solidification time was achieved 18 % and 24 % of NFPCM with 0.6 wt. % for the bath temperature of -9 °C and -12 °C respectively.

Decreasing the energy consumption in building sector will helps to overcome the energy demand. The energy efficient CTES will be achieved by improving the thermophysical properties of PCM.

7. References

1. Cheralathan M, Velraj R, Renganarayanan S. Performance analysis on industrial refrigeration system integrated with encapsulated PCM based cool thermal energy storage system. Int J Energ Res. 2007; 31(14):1398–413.
2. Marimon MA, Arias J, Lundqvist P, Bruno JC, Coronas A. Integration of trigeneration in an indirect cascade refrigeration system in supermarkets. Energ Buildings. 2011; 43:1427–34.
3. Mostafavinia N, Eghvay S et al. Numerical Analysis of Melting of Nano-Enhanced Phase Change Material (NEPCM) in a Cavity with Different Positions of Two Heat Source-Sink Pairs. Indian Journal of Science and Technology. 2015; (8):49–6.
4. Sun X, Zhang Q, Medina MA, Liu Y, Liao S et al. A study on the use of phase change materials in combination with a natural cold source for space cooling in telecommunications base stations in China. Appl Energy. 2014; 117:95–103.
5. Sehar T, Murugaiyan V et al. Solidification and Stabilization of Chromium Bearing Waste. Indian Journal of Science and Technology. 2016; 9(20).
6. Sharma D, Pandey KM. Numerical Investigation of Heat Transfer Characteristics in Triangular Channel in Light Water Nuclear Reactor by using CuO-Water based Nanofluids. Indian Journal of Science and Technology. 2016; 9(16).
7. Py X, Olives R, Mauarin S. Paraffin/porous graphite matrix composite as a high and constant power thermal storage material. International Journal of Heat and Mass Transfer. 2001; 44(14):2727‒37.
8. Kumaresan V, Chandrasekaran P, Nanda M. Role of PCM based nanofluids for energy efficient cool thermal storage system. International Journal of Refrigeration. 2013; 36.
9. Lee S, Choi SUS. Application of metallic nanoparticle suspensions in advanced cooling systems. International Mechanical Engineering Congress and Exposition, Atlanta, USA. 1996.
10. Hong K, Hong TK, Yang HS. Thermal conductivity of Fe nanofluids depending on the cluster size of nanoparticles. Applied Physics Letters. 2006; 88(3):31901.
11. Hwang Y, Lee JK, Jung YM, Cheong SI, Lee CG, Ku BC, Jang SP. Stability and thermal conductivity characteristics of nanofluids. Thermochimica Acta. 2007; 455(1-2):70–4.
12. Hwang Y, Park HS, Lee JK, Jung WH. Thermal conductivity and lubrication characteristics of nanofluids. Current Applied Physics. 2006; 6S1(1):e67–e71.
13. Lee S, Choi SUS, Li S, Eastman JA. Measuring thermal conductivity of fluids containing oxide nanoparticles. Journal of Heat Transfer. 1999; 121(2):280–9.
14. Li CH, Peterson GP. Experimental investigation of temperature and volume fraction variations on the effective thermal conductivity of nanoparticle suspensions (nanofluids). Journal of Applied Physics. 2006; 99(8):084314.

15. Sari A, Karaipkli A. Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material. Applied Thermal Engineering. 2007; 27(8-9):1271–7.

16. Kreith F. American Society of Heating, Refrigerating and Air-conditioning Engineers, ASHRAE Handbook: Fundamentals, Atlanta, GA, 1999.