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| RESEARCH ARTICLE

Solidification Enhancement of Thermal Energy Storage Systems Using CuO–Ethylene Glycol Nano-Enhanced Phase Change Materials: A Comprehensive Review

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| ABSTRACT
Latent heat thermal energy storage (LHTES) with phase change materials (PCMs) has high energy density and near-isothermal operation; however, the low thermal conductivity of PCM is a big challenge. This review article explores the nano-enhanced phase change materials (NePCMs) with copper oxide–ethylene glycol (CuO–EG) and copper oxide–water–ethylene glycol (CuO–water–EG) and evaluates their use to enhance the solidification process in cold thermal energy storage (TES) systems. The review critically synthesizes pertinent literature on the preparation routes, dispersion stability, thermophysical properties, heat transfer mechanisms, TES configurations, hybrid strategies, numerical modeling, applications, and challenges. The results presented in the reviewed works demonstrate that CuO addition can enhance the thermal conductivity by 5–35% and decrease the solidification time by 5–25% when low to moderate CuO loading, which is usually 1–3 wt.%, is used, providing a balance of heat transfer enhancement and storage performance. But a high level of CuO concentration can lead to high viscosity, agglomeration, and settling, and low latent heat of capacity. However, for a scalable, reliable, and efficient cold TES operation and application in real systems, optimized formulation, long-term cyclic validation, and application-specific TES design are required.

| KEYWORDS

Copper oxide nanoparticles; ethylene glycol; nano-enhanced phase change material; solidification; cold thermal energy storage; latent heat thermal energy storage.

| ARTICLE INFORMATION

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1. Introduction

With the growing importance of renewable energy resources like solar and wind power, and their intermittent and weather-dependent availability, the mismatch between energy supply and energy demand has been a constant challenge because of the time changing requirements for energy in buildings, industry and transportation for heating and cooling [Tofani, 2021]. TES solves this mismatch by storing energy that cannot be used immediately when it is available and using it when it is needed, thus increasing the efficiency, reliability and flexibility of HVAC, refrigeration, solar thermal and district cooling systems [Teggar, 2022]. Latent heat thermal energy storage is one of the most promising TES technologies as it is capable of storing or extracting significant amount of energy over a very limited temperature difference at the transition of a suitable material. Now that demand for cooling is growing at a global level, and renewable electricity is becoming more volatile, compact, efficient TES systems are becoming more and more important for sustainable energy systems, and efforts are being made to research materials and configurations that can provide fast and reliable charging and discharging.

A major advantage of LHTES systems is their high energy density compared to sensible heat storage systems and their near isothermal operating behavior, which makes control of the temperature so much easier, with heat being stored or retrieved primarily in the form of latent heat mainly from melting (charging) or solidification (discharging) of the PCM [Nandi, 2025]. But conventional PCMs have a number of widely recognized limitations when it comes to their real-world performance. The inherent thermal conductivity of most organic and inorganic PCMs is low, which causes heat transfer between the PCM and the heat transfer fluid (HTF) to be slow and causes the charging/discharging times to be longer [Shah, 2018], [Williams, 2021]. Furthermore, the ability of many PCMs to remain subcooled when cooling below the equilibrium freezing temperature (ETFT) and to undergo phase segregation in salt hydrate systems, and volume change at the phase transition which complicates container design are obstacles [Yadav, 2024]. These constraints all contribute to a decrease in the round-trip efficiency and responsiveness of PCM-based TES and have fueled much research into methods for increasing the thermal conductivity of PCMs, such as dissolving nanoparticles in the PCM or its base fluid.

While a substantial body of literature has examined melting (charging) behavior of PCMs and NePCMs, the solidification (discharging) process is equally, if not more, critical for the practical operation of TES systems because it governs how quickly and reliably stored thermal energy can be released to meet an instantaneous cooling or heating demand [Afsharpanah, 2022]. Slow or incomplete solidification directly leads to a reduction in cooling capacity, the recovery time between discharge cycles and oversized storage volumes in applications like cold TES in building air conditioning systems, refrigerated transport and district cooling. The solidification process is also inherently more conduction dominated than the melting process, as the solidification layer will increasingly isolate the liquid PCM from the heat transfer surface and reduce the effect of the natural convection flow, especially during the discharging process [Eisapour, 2022]. However, systematic studies on the enhancement of solidification are still much less numerous than those on melting, so there is a clear need for a systematic review on this topic.

Copper oxide (CuO) is among several nanoparticles that are being explored for use in PCM enhancement, with relatively high thermal conductivity, easy availability, low cost in comparison with other nanomaterials such as those based on noble-metals or carbon-based, and it has been shown to serve as a nucleation aid that can reduce subcooling and increase solidification speed [Srinivasan, 2024]. Ethylene glycol (EG) and water-ethylene glycol (water-EG) mixtures are commonly used in low-temperature (LT) and cold TES applications as base fluids or PCM media, due to the ability of EG to lower the freezing point of water, to provide a wider operating temperature range below 0 degC, and to have experience as heat transfer fluids in HVAC, refrigeration, and automotive cooling systems [Hosseinzadeh, 2023], [Kazem, 2022]. By pairing CuO nanoparticles with EG or water-EG, then, a practical path towards thermal conductivity enhancement and nucleation and operating temperature in the cold range applicable to cold TES can be pursued, while continuing to leverage a large body of work on CuO-water-EG nanofluids for heat transfer applications [Kotkar, 2025].

There are several broad reviews which cover various categories of nanoparticles, different types of base PCMs, enhancement techniques for heat transfer and the applications of TES using nano-enhanced PCMs, respectively [Mirahmad, 2025], [Khlissa, 2023], [Sathishkumar, 2024]. But, a systematic, detailed review which specifically summarizes the solidification characteristics of CuO–ethylene glycol/water–EG NePCs for cold thermal energy storage is not available [Mohammadpour, 2022]. Hence, the aims of this review are to critically examine the preparation, stability, thermophysical properties, heat transfer mechanisms, TES configurations, hybrid enhancement strategies and numerical modelling approaches related to the solidification of CuO–EG/water–EG NePCs. For this synthesis, the review is structured around a conceptual framework to link the material system, research motivation, PCM limitations, enhancement routes, and coverage of the review as shown in Fig. 1.

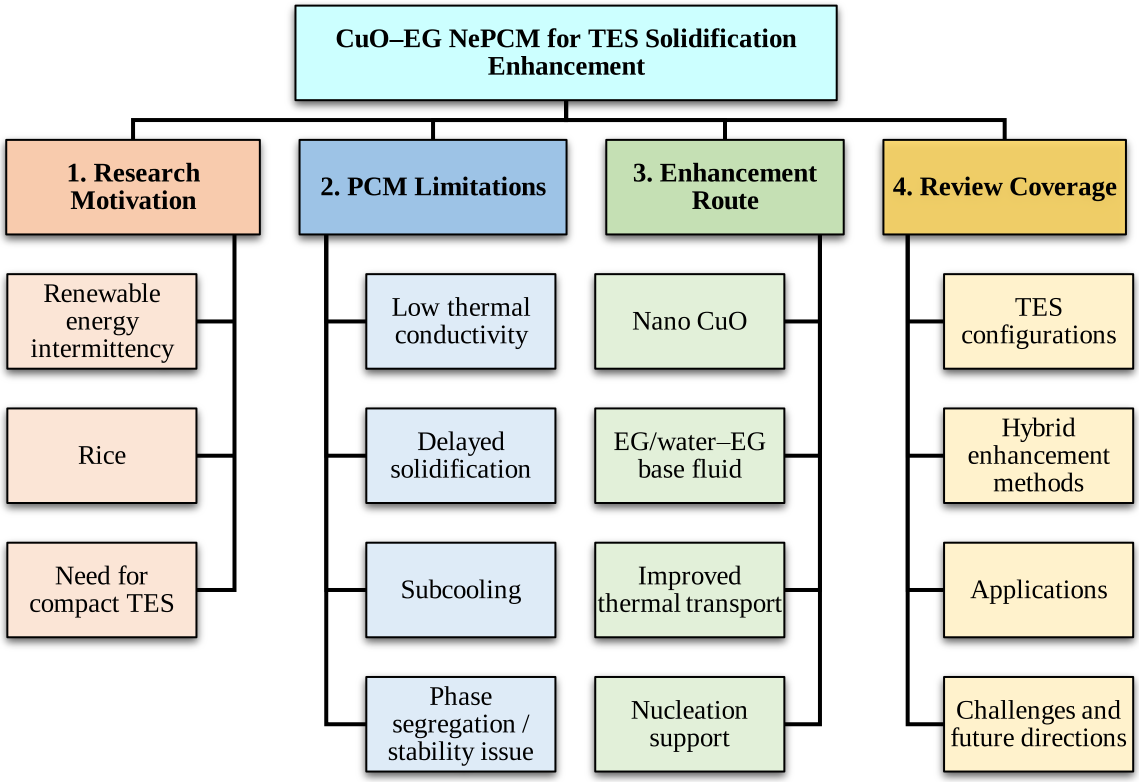

Fig. 1. Conceptual framework

The figure provides a summary of the logical structure of this review, presenting the central theme of CuO–EG NePCM-based TES solidification enhancement and four major aspects, which include research motivation, limitations of conventional PCMs, enhancement routes, and review coverage. The intermittent nature of renewable energy, increased cooling/heating loads, and compact TES drive the development of CuO–EG NePCMs, whereas traditional PCM challenges like low thermal conductivity, delayed solidification, subcooling, and phase segregation/stability are solved by adding CuO nanoparticles, using EG/water–EG base fluids, optimizing thermal transport and nucleation support. Based on this framework, the main contributions of this review are: (i) this paper has attempted to consolidate the scattered studies on the CuO–EG/water–EG NePCM used for TES applications focused on solidification process; (ii) the effects of different alternatives of CuO concentration, EG/water ratio, TES geometry, and hybrid enhancement techniques on solidification performance were compared; and (iii) key challenges and future research directions of developing stable, efficient, and scalable CuO–EG-based cold TES systems were identified.

2. Fundamentals of PCM-Based TES and PCM Selection

2.1 Thermal Energy Storage Systems

Thermal energy storage technologies can be broadly categorized into three different types depending on how thermal energy is stored: sensible heat thermal energy storage (SHS), LHTES, and thermochemical thermal energy storage (TCS) [Tofani, 2021]. SHS stores energy in the form of heat by either heating or cooling a medium, like water, rock, concrete or molten salt. Easy to implement, inexpensive, commercially available but typically needs high storage volume and does not deliver a smooth temperature change on charging and discharging operation [Said, 2024]. LHTES, on the other hand, stores and releases latent heat in a narrow temperature range via the solid–liquid or solid–solid phase transition of a PCM. This results in higher energy density and near isothermal operation which is beneficial for cold TES, HVAC, refrigeration, solar thermal storage and building thermal regulation [Nandi, 2025]. But its performance is restricted by the poor thermal conductivity of most of the PCMs and the other problems like subcooling, phase segregation and volume change [Teggar, 2022], [Williams, 2021]. The energy can be stored in TCS by reversible chemical reactions or sorption processes; it can have a high theoretical energy density and a low long-term heat loss, but it requires a complicated reactor design, materials which can be used in the reaction process, and control of heat and mass transfer. Table 1 offers a comparative overview of the three types of education systems, SHS, LHTES and TCS. In general, LHTES have a good trade-off between compactness, temperature stability and practical use; thus, this review will concentrate on CuO–EG/water–EG nano-enhanced PCMs as a potentially viable method to enhance solidification performance in cold TES systems.

Table 1: Comparison of SHS, LHTES, and TCS systems

TES type	Storage mechanism	Advantages	Limitations	Suitable applications
SHS	Temperature change of a storage medium	Simple, low cost, mature, wide material choice	Large temperature swing, lower energy density, large storage volume	Hot/cold water tanks, rock-bed and packed-bed storage, district heating buffers
LHTES	Solid-liquid phase transition of a PCM at near-constant temperature	High energy density, near-isothermal output, compact footprint	Low thermal conductivity of most PCMs, subcooling, possible phase segregation	Cold TES, HVAC, solar thermal buffering, building envelope integration
TCS	Reversible chemical reaction or sorption	Highest theoretical energy density, low long-term storage losses	High system complexity, high cost, limited commercial maturity	High-temperature CSP, seasonal storage, industrial waste-heat recovery

2.2 Classification of Phase Change Materials

Based on the different phases that exist at the melting and solidification temperatures, TES PCMs can be broadly divided into three categories: organic PCMs, inorganic PCMs, and eutectic mixtures, as illustrated in Fig. 2 [Shah, 2018]. Organic PCMs (such as paraffins, fatty acids, and polyalcohol's) are chemically stable, non-corrosive, and have a small subcooling, but in most cases have a low thermal conductivity and can be flammable (for paraffins). The inorganic PCMs mostly consist of salt hydrates and metallics and generally have increased latent heat and thermal conductivity compared to the organic PCMs and are also non-flammable, but many salt hydrates experience subcooling and phase segregation with repeated cycles, and metallic PCMs are good conductors but dense and expensive [Yadav, 2024]. Eutectic PCMs are combinations of two or more of the following: organic, inorganic and/or organic–organic or inorganic–inorganic systems that melt and freeze at a specified temperature. This makes it possible to tailor the operating temperature range of a TES system to an application, such as cold storage, HVAC, refrigeration, building cooling or solar thermal storage [Nandi, 2025], [Williams, 2021].

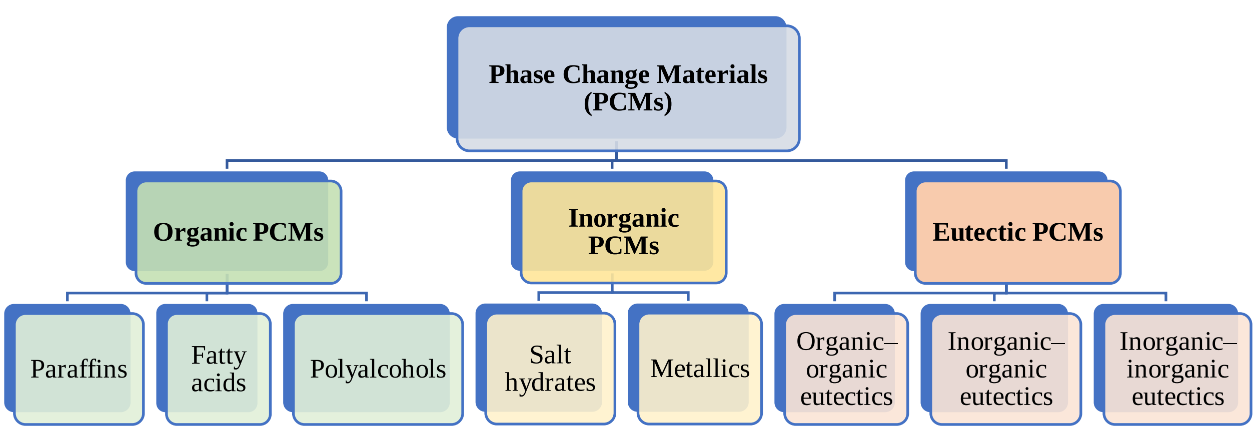

Fig. 2. Classification of PCMs for thermal energy storage

The figure categorizes the PCMs as Organic, Inorganic and Eutectic, that is, paraffins, fatty acids and polyalcohol's, salt hydrates and metallic PCMs and organic–organic, inorganic–organic and inorganic–inorganic mixtures, respectively. The classification is significant because the thermal behavior, operating suitability and limitations differ for each group of PCMs. PCMs are also categorized as high-, medium-, and low-temperature PCMs, depending on their operating temperature, which is generally below 120 °C, 120–300 °C, and above 300 °C, respectively [Said, 2024]. For cold TES, HVAC, refrigeration and building cooling, the low-temperature PCM is most relevant, as they can work within the temperature range desired to be cooled, and the EG/water–EG system can also provide sub-zero operation due to the effect of freezing-point depression [Hosseinzadeh, 2023], [Kazem, 2022]. Many of the low temperature PCMs still have shortcomings such as slow solidification due to low thermal conductivity, subcooling, and stability limitations [Sathishkumar, 2024], [Rashid, 2023]. Thus, this classification is used as a basis for the material selection of the development of CuO–EG/water–EG NePCMs, in which the objectives are low-temperature operation, better heat transfer, faster solidification, and good long-term stability.

2.3 PCM Selection Criteria for Solidification Studies

There are several interrelated criteria to consider when choosing a suitable PCM or formulating a suitable NePCM for solidification TES studies [Williams, 2021]. A high latent heat of fusion per unit mass or volume is required to be able to obtain a high energy storage density; the melting/freezing temperature should be as close as possible to the temperature range of the intended application, to ensure predictable charging and discharging [Altuntas, 2025]. The total discharge time is also a function of the thermal conductivity, which must be adequate as well. The importance of low level of subcooling cannot be overemphasized, especially in solidification studies where higher level of subcooling can mask the actual advantage of using nanoparticles and can adversely affect the nucleation process [Singh, 2023]. Moreover, thermal cycling stability, low volume change, chemical compatibility and low corrosion tendency are required for long-term TES reliability. In addition to the above, for NePCMs, these criteria should be considered in conjunction with the factors of nanoparticles distribution stability, tendency to agglomerate, viscosity change, and compatibility with container/heat exchanger material [Upadhyay, 2024], [Barthwal, 2021]. The main selection criteria are summarized in Table 2.

Table 2: The selection criteria for the studies of solidification of PCM/NePCM

Ref.	Criterion	Solidification relevance	Measuring method
[Adera, 2025]	Latent heat capacity	High latent heat is required for the good cold energy storage density, at the same time, excessive loading of nanoparticles is not desirable to decrease the latent heat.	DSC
[Williams, 2021]	Thermal conductivity	Higher conductivity accelerates solidification-front movement and reduces discharge time	Transient hot-wire / thermal property analyzer
[Radebe, 2024]	Freezing temperature and subcooling	A suitable freezing range and low subcooling ensure predictable solidification onset and completion	DSC / T-history / cooling curve
[Razzaq, 2025]	Dynamic viscosity	Excessive viscosity suppresses convection and increases pumping power in active TES systems	Rheometer
[Zhang, 2024]	Dispersion stability and compatibility	Stable dispersion to prevent agglomeration, sedimentation and long-term performance degradation	Zeta potential, DLS, SEM/TEM, FTIR

In general, these criteria indicate that an appropriate PCM for the development of CuO–EG NePCM should have not only a high storage capacity but also should have the following characteristics: high rate of solidification, low subcooling, stability of the dispersion of nanoparticles, and compatibility with TES components.

3. Ethylene Glycol and CuO Nanoparticles for NePCM Formulation

3.1 Ethylene Glycol as Base Fluid/PCM Medium

Ethylene glycol (EG) is a base fluid that can be mixed with water to significantly lower the freezing point of the mixture and is used in TES systems for low-temperature and cold applications which requires stable operation below 0 °C [Hosseinzadeh, 2023], [Jaberi, 2024]. Water–EG mixtures are used already in various HVAC systems, refrigeration systems, automotive cooling systems and as antifreeze in thermal loop systems, and their thermophysical properties, such as density, specific heat, thermal conductivity or viscosity change significantly with the EG/water ratio and temperature of operation [Zahan, 2022], [Minh, 2025]. The higher the EG content, the lower the freezing temperature and the larger the usable low-temperature range, but the viscosity will also rise and the specific heat and thermal conductivity will fall from that of pure water [Maselugbo, 2023]. Thus, the EG/water ratio is an important parameter to consider for the CuO–EG/water–EG NePCM system as a too large fraction of EG may improve the antifreeze properties, but also lower the heat transfer efficiency and the pumping power [Kazem, 2022]. The representative thermophysical properties of EG/water–EG mixtures are summarized in Table 3, and the freezing-point depression–heat transfer performance trade-off is demonstrated.

Table 3: Representative thermophysical properties of the EG/water–EG mixtures display the compromise between the freezing-point depression and the heat transfer potential

Ref.	EG/water ratio	Freezing point and density, ρ	Heat transfer properties, C_p, k, μ	Suitable application
[28]	0:100, pure water	0 °C; ρ = 998 kg/m^3	C_p = 4180 J/kg·K; k = 0.60 W/m·K; μ = 1.0 mPa·s	Baseline reference fluid
[29]	20:80	−8 °C; ρ = 1028 kg/m^3	C_p = 3900 J/kg·K; k = 0.50 W/m·K; μ = 1.8 mPa·s	Mild antifreeze, HVAC loops
[10]	40:60	−23 °C; ρ = 1054 kg/m^3	C_p = 3500 J/kg·K; k = 0.43 W/m·K; μ = 3.0 mPa·s	Cold TES, refrigeration
[11]	50:50	−33 °C; ρ = 1065 kg/m^3	C_p = 3300 J/kg·K; k = 0.39 W/m·K; μ = 4.0 mPa·s	Sub-zero cold TES
[30]	60:40	−48 °C; ρ = 1075 kg/m^3	C_p = 3100 J/kg·K; k = 0.36 W/m·K; μ = 5.5 mPa·s	Very low-temperature coolant
[28]	100:0, pure EG	−13 °C; ρ = 1113 kg/m^3	C_p = 2400 J/kg·K; k = 0.25 W/m·K; μ = 16.0 mPa·s	Pure EG reference fluid

It is observed that the pure water has the highest heat transfer performance due to high specific heat capacity (C_p), high thermal conductivity (k) and low dynamic viscosity (μ), however, due to its freezing point around 0 °C, it cannot be directly used in cold TES. As the EG fraction increases, the freezing point drops and the freezing point depression (antifreeze property) increases, but the C_p and k decrease and the μ increases. In this case, ρ is the density, C_p is the specific heat capacity, k is the thermal conductivity and μ is the dynamic viscosity. Thus, the intermediate EG/water mixtures especially in the range of 40-50:50 EG/water are the most convenient range to operate the CuO–EG/water–EG NePCM system at a low temperature while maintaining the desired heat transfer performance.

3.2 Thermophysical Properties of CuO Nanoparticles

Among the most frequently studied metal oxide additives for enhancement of thermal conductivity of the base fluids and PCM's are copper oxide (CuO) nanoparticles. They are attractive for formulation of NePCM because of their relatively high thermal conductivity, good chemical stability, wide availability and lower cost than noble-metal or carbon-based nanomaterials [Zhang, 2024]. In the study of the NePCM and other nanofluids, CuO nanoparticles are frequently reported to have an average size of approximately 20–60 nm and are mostly spherical or near-spherical in shape [Razzaq, 2025]. The loading levels reported depend on the material system. The concentrations of nanoparticles in CuO-based NePCM formulations are typically reported in the range of 0.1–3 wt.% [Zhang, 2024] while in broader studies of NePCMs, the concentration of nanoparticles is reported to be up to 5 vol.% [Adera, 2023]. In the case of hybrid systems, GNP–CuO nanofluid PCMs have been reported 0.05–0.3 wt.% [Singh, 2020].

The CuO loading values in water/EG-based nanofluids are reported to be in the range of 0.05–1.0 wt. % [Liu, 2022]. CuO is particularly interesting for EG/water–EG systems due to its ability to enhance heat transfer properties in glycol-based fluids without compromising its low-temperature thermal application.

Among the materials, CuO offers a practical compromise of thermal enhancement, cost and dispersion feasibility compared to Al_2O_3, TiO_2, ZnO, graphene nanoplatelets and carbon nanotubes. In spite of their higher intrinsic thermal conductivity, graphene nanoplatelets and CNTs exhibit a high agglomeration tendency, are difficult to disperse and have a higher processing cost, which might restrict the use of this material in TES on a large scale [Razzaq, 2025], [Babar, 2025]. However, CuO is capable of achieving moderate thermal conductivity enhancement, which is relatively simpler to prepare, particularly if the stirring, ultrasonication, surfactant choice, and pH control are optimized for CuO [Kotkar, 2025], [Srinivasan, 2025]. In addition, CuO has also been studied in order to use it with Cu and graphene-like materials in hybrid nanofluid or hybrid NePCM system to increase the effective thermal conductivity and heat transfer performance [Srinivasan, 2024], [Girhe, 2023].

The thermophysical effect of CuO addition is not only limited to the improvement of the thermal conductivity. CuO nanoparticles can also act as heterogeneous nuclei for freezing and hence the subcooling and hence solidification reliability can be improved in the PCM based TES systems [Soudagar, 2026]. However, there are a number of penalties associated with the increase in CuO concentration. If too many nanoparticles are loaded into the NePCM, the effective latent heat capacity of the NePCM can be decreased due to the absence of the phase-change process in CuO [Pandya, 2023]. A higher CuO content can also cause the viscosity to be higher, the grain to clump together or settle, and the dispersion stability to become poor or poor over time, particularly after repeated thermal cycling [Estellé, 2017], [Szabó, 2025]. Hence, the amount of loading of CuO should not be maximized, but optimized. For the development of CuO–EG/water–EG NePCM, the formulation with the prominent properties to improve thermal conductivity, low subcooling, viscosity, latent heat retention, dispersion stability, and long-term compatibility with TES components should be considered [Zhang, 2024], [Rahman, 2025].

3.3 Preparation of CuO-EG NePCM

The preparation of CuO–EG/ water–EG NePCMs can be performed by one-step process or two-step process. The two-step method is more popular due to the ease of dispersing commercially available CuO nano powders directly into EG or water-EG base fluids by mechanical mixing and ultrasonication [Agrawal, 2022], [Xiong, 2020]. In this method, first a known quantity of CuO nanoparticles is added to the prepared EG/water–EG based fluid. It may include the use of a suitable surfactant, e.g., CTAB or SDBS, and pH adjustment to improve the dispersion stability, preventing agglomeration [Mehta, 2023]. The suspension is then mixed with the assistance of magnetic stirring and processed again with bath or probe ultrasonication to disperse the particles in clusters and maximize uniformity. Once prepared, the NePCM is analyzed for stability, typically by visual sedimentation, zeta potential or UV–Vis analysis, and then thermophysical and structural characterization is carried out by methods such as SEM, TEM, XRD, DSC, TGA, FTIR and DLS [Xian, 2020], [Kahraman, 2022]. The synthesis method of CuO–EG NePCM is summarized in Fig. 3. The typical two-step preparation procedure is shown in the figure, which includes weighing CuO nanoparticles and preparation of EG/water–EG base fluid, followed by addition of the surfactant, control of pH, magnetic stirring, ultrasonication, stability testing, characterization of properties, and finally, the evaluation of the TES performance. This sequence is crucial as the dispersion quality directly influences the thermal conductivity, viscosity, stability and solidification performance.

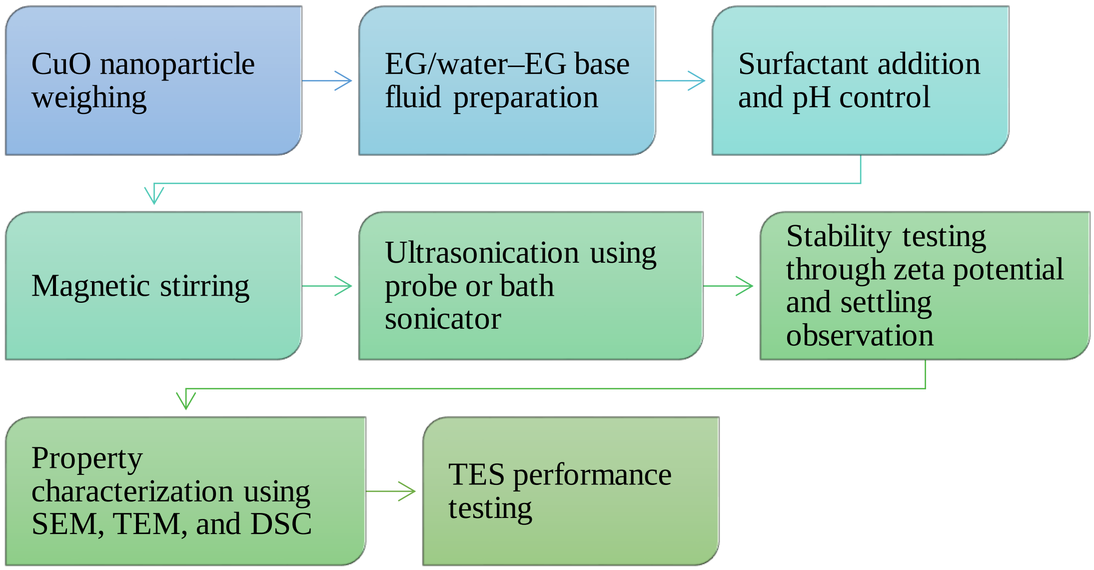

Fig. 3. Preparation of CuO-ethylene glycol NePCM

3.4 Stability and Characterization Methods

The stability of the CuO-EG/water-EG NePCs against time will be a key factor in their practical utility as the effect on the enhancement of the thermal conductivity and the rheological properties of the fluid will continually degrade due to sedimentation and agglomeration of the nanoparticles [Sahooli, 2012]. Suspension stability is often determined by visual sedimentation observation over days to weeks, zeta potential determination (where values above ~30 mV are considered good electrostatic stability) and UV-Vi's spectroscopy to check for changes in absorbance of the suspension with time [Nugroho, 2025]. Usually, the microstructural and compositional characterizations are carried out by scanning and transmission electron microscopy (SEM/TEM) to gain information on particle size, shape and state of agglomeration, X-ray diffraction (XRD) to confirm the crystal structure and phase purity of the nano particles, and Fourier-transform infrared spectroscopy (FTIR) to verify the presence of any attached surfactant or chemical interaction [Srinivasan, 2025], [Inkson, 2016]. The method of thermal characterization uses DSC to determine the melting/freezing temperatures and latent heat, TGA to determine the thermal decomposition behaviour, thermal conductivity analyzers for determination of k, and rheometers for viscosity as a function of shear rate and temperature [Kotkar, 2025]. The preparation and evaluation methods reported for CuO based NePCM and related nanofluid systems are summarized in Table 4 and the main findings, dispersion route, stability testing and characterization methods are emphasized.

Table 4: CuO based NePCM nanofluid systems

Ref.	Material system	Preparation details	characterization methods	Key observation
[12]	Water/EG-based CuO nanofluid	0.05–1.0 wt% CuO; CTAB surfactant; magnetic stirring and bath sonication	Visual settling, zeta potential, SEM, XRD, DLS, thermal conductivity analyzer	CTAB improved dispersion stability and supported thermal property enhancement
[11]	CuO water–EG nanofluid for PV/T system	0.1–1 wt% CuO; stirring and sonication; surfactant not clearly reported	Visual settling, TEM, thermal conductivity measurement	CuO water–EG nanofluid improved heat transfer performance in PV/T loop
[35]	Water-based single/hybrid nanofluid PCM	0.1–0.5 wt% nanoparticles; surfactant comparison; stirring and sonication	Zeta potential, visual settling, UV–Vis, FTIR, DSC	Surfactant selection strongly affected stability and phase-change behavior
[46]	CuO@polystyrene-encapsulated octadecanol	CuO incorporated into hierarchical porous foam shell; encapsulation approach	SEM, FTIR, DSC, TGA, thermal cycling	Encapsulation improved shape stability and reduced PCM leakage
[9]	GNP–CuO/water hybrid nanofluid PCM	0.05–0.3 wt% hybrid loading; functionalized GNP–CuO; stirring and sonication	Zeta potential, sedimentation test, SEM, TEM, DSC, thermal conductivity analyzer	Hybrid GNP–CuO improved thermal conductivity and solidification behavior

As can be seen in Table, the majority of the CuO based systems use a two-step procedure of dispersion, stirring and ultrasonication of the nanoparticles, and stability is typically tested by observing sedimentation, zeta potential, UV–vis or DLS analyses. The comparison also shows that the choice of surfactant, the sonication conditions, and the encapsulation strategy are critical for ensuring dispersion stability and enhancing long-term TES performance.

4. Thermophysical Properties and Solidification Mechanisms of CuO–EG NePCM

4.1 Thermophysical Property Modification by CuO Addition

The addition of CuO nanoparticles to ethylene glycol (EG), water–EG mixtures or media based on PCM changes several important thermophysical properties, which directly affect the charging/discharging process of TES systems. Thermal conductivity is the most significant property among these properties since the intrinsic thermal conductivity of most of the PCMs is among the key reasons for slow heat transfer in solidification [Harikrishnan, 2013], [Shafiq, 2025]. Compared to standard organic PCMs and water–EG base fluids, CuO nanoparticles possess higher thermal conductivity, which means that when added to the storage medium, they can provide additional conductive pathways within the storage medium. This allows more heat to be transferred away from the PCM as the PCM is discharged, and the solidification front to travel faster from the cooled surface to the inner liquid region [Suraparaju, 2026].

The actual improvement in the reported thermal conductivity for CuO-based nanofluids and NePCMs depends on the concentration of nanoparticles, particle size, dispersion quality, the use of a surfactant, the base-fluid composition, and the temperature of the measurement and has ranges from a small increase for very low nanoparticle loading to about 15–30% for moderate concentrations [Alrowaili, 2022], [Tiwari, 2023], [Lu, 2025]. However, the thermal conductivity enhancement may be even higher for hybrid formulations consisting of a mixture of CuO with other highly conductive additives such as Cu, graphene nanoplatelets, or carbon nanotubes, as this may be capable of creating even better conductive networks in the base medium [Srinivasan, 2024], [Zou, 2018]. This improvement is particularly valuable in solidification, as the solidifying layer will gradually increase thermal resistance and decrease the rate of heat transfer away from the liquid during solidification, as compared to melting.

The CuO addition, however, brings also some thermophysical drawbacks. The CuO nanoparticles do not melt or freeze in the working temperature range of the TES system, so they do not affect the latent heat storage. Instead, they take up a part of the mass and volume of the PCM or base-fluid. Thus, the higher the CuO concentration, the lower the latent heat of fusion per unit mass of the NePCM [Zhang, 2024], [Jaliliantabar, 2022], [Aly, 2022]. The specific heat capacity also tends to decrease due to the low specific heat capacity of CuO as compared to water–EG mixtures and many organic PCMs. This implies that while the material may have a higher amount of heat transfer, the overall heat storage capability could be reduced in the case of high concentration of nanoparticles [Kandasamy, 2018].

The other important effect is the increase in dynamic viscosity. The effect of the internal flow resistance of the fluid is stronger with increasing concentrations of the CuO nanoparticles and decreasing operating temperatures [Zahan, 2022], [Sarkar, 2023]. Increase in viscosity can reduce the natural convection in liquid state of the remaining liquid during the phase change process and may also require more pumping power in the active TES or nanofluid circulation system. Thus, the maximum thermal conductivity is not the proper criterion to choose the best CuO–EG NePCM formulation [Said, 2023]. Rather, it should be designed to be thermally conductive, latent heat holding, high specific heat, low viscosity, subcooling reducing and long-term dispersion stable. Table 5 summarizes the important thermophysical property changes reported for the CuO–EG/CuO-based NePCM and related nanofluid systems.

Table 5: Thermophysical properties changes and solidification related effects of NePCM systems containing CuO–EG/CuO

Ref.	Material system	CuO/nanoparticle loading	Main property change	Key implication for TES
[62]	GNP–CuO/water hybrid PCM	0.05–0.3 wt% hybrid loading	k increased by about 12–22%; C_p and latent heat slightly decreased; subcooling reduced	Hybrid GNP–CuO improved solidification rate while maintaining acceptable storage performance
[36]	Hybrid CuO–Cu/water nanofluid	0.1–1 vol%	k increased by about 10–25%; viscosity increased moderately	CuO–Cu hybrid nanofluid improved solar TES heat transfer response
[30]	EG/propylene glycol with conductive nano-additives	0.05–0.5 wt%	k increased significantly, with moderate viscosity increase	EG-based nanofluids can improve heat transfer, but viscosity must be controlled
[63]	PEG with Al_2O_3/CuO hybrid nanoparticles	0.5–2 wt%	k increased, while latent heat and C_p decreased	Hybrid oxide nanoparticles improved thermal response but reduced storage capacity
[64]	General NePCM formulation	0.5–3 wt%	k increased by about 10–30%; viscosity increased; latent heat decreased	Optimum loading was required to balance heat transfer gain and storage loss
[43]	Review synthesis of NePCM systems	0.05–5 wt%	Property changes depended strongly on loading and dispersion stability	Agglomeration and high loading can limit long-term performance

The comparison shows that the addition of CuO will generally enhance the thermal conductivity, and perhaps decrease the subcooling; however, high loading of nanoparticles will cause a decrease in latent heat, specific heat capacity, increase in viscosity, and agglomeration. A is thermal conductivity and C is specific heat capacity here. In conclusion, concentrations of CuO within the low to moderate range are more appropriate for TES use as they offer some heat transfer enhancement while maintaining acceptable storage capacity and fluidity.

4.2 Heat Transfer Mechanisms During Solidification

The main mechanism of solidification in PCM-based TES systems is the removal of heat from the liquid PCM to the already solidified layer to the cooled boundary. When the PCM starts to solidify, the temperature in the vicinity of the cold wall or heat exchanger surface first reduces in the sensible heat domain and then begins to decrease in the freezing domain. After the formation of a thin solid layer, this thin layer becomes a thermal barrier between the cooling surface and the rest of the liquid PCM [Afsharpanah, 2022]. With continued solidification, the thickness of this solid region will build up, and the heat will have to pass through a longer solid path. This slows down the rate of solidification after initial solidification. For this reason, solidification is typically more conduction dominated than melting where natural convection in the liquid PCM can have a stronger effect on the heat transfer [Eisapour, 2022], [Karagöz, 2025].

The conduction-limited process is improved using CuO nanoparticles by providing an increase in the effective thermal conductivity of the PCM or EG/water–EG medium. The particles act as high conductivity inclusions in the base material and provide an increase in the thermal pathways both in the liquid and solidifying states [Bondareva, 2024]. This permits heat extraction to be more effective from the growing solid layer and may decrease overall solidification time. In cold TES, the discharge of the medium would have to be replenished rapidly after it is discharged, so it can again provide cooling on the next cycle; this is especially true in the case of cold TES.

In addition to the direct conduction enhancement, there are several secondary mechanisms that can contribute to CuO-assisted solidification. In the liquid state ahead of the solidification front, Brownian motion of nanoparticles can cause some microscale convective effects, which can induce a small enhancement in the energy transport at the microscale. This effect is, however, reduced when the liquid fraction gets reduced and the PCM solidifies [Sheikholeslami, 2018], [Alsabery, 2022]. It is therefore more appropriate to consider Brownian motion in the early stage of solidification when it is convection dominated than in the later conduction dominated stage. Light clustering of nanoparticles may also form conductive chains similar to those of percolation, so that heat can flow through the PCM efficiently, rather than the classical models based on the assumption of completely isolated spherical particles [Daviran, 2017].

CuO nanoparticles can be also used as heterogeneous nucleation centres. During freezing, the formation of stable solid crystals requires nucleation. When nucleation is delayed, the PCM might subcool that is, cool below its equilibrium freezing point before solidification. Solid crystals can lower their nucleation energy barrier by providing surfaces on which they will nucleate, which is the effect of the CuO particles [Srinivasan, 2024]. This can lessen the subcooling and improve the freezing rate. But this is highly contingent on the dispersion quality. The uniformly distributed nucleation sites offered by well-dispersed CuO particles would lead to uniformly distributed freezing points and consistent solidification behavior, while the non-uniform freezing points and behavior would result from agglomerated particles.

Excessive agglomeration is one of the main negative mechanisms in CuO–EG NePCMs. The formation of large aggregates of nanoparticles can lead to sedimentation under gravitational forces, decrease the effective number of nanoparticles in the suspension, and lead to local variations in thermal properties [Razzaq, 2025]. This will decrease the stability of the NePCM and will gradually weaken the initial thermal conductivity enhancement when repeated cycles are performed. Thus, the mechanisms of heat transfer for CuO–EG NePCM can only be beneficial if the dispersion of the nanoparticles is appropriately achieved by the proper choice of concentration, type of surfactant, stirring, and ultrasonication. These positive and negative mechanisms are summarized as shown in the schematic diagram in Fig 4.

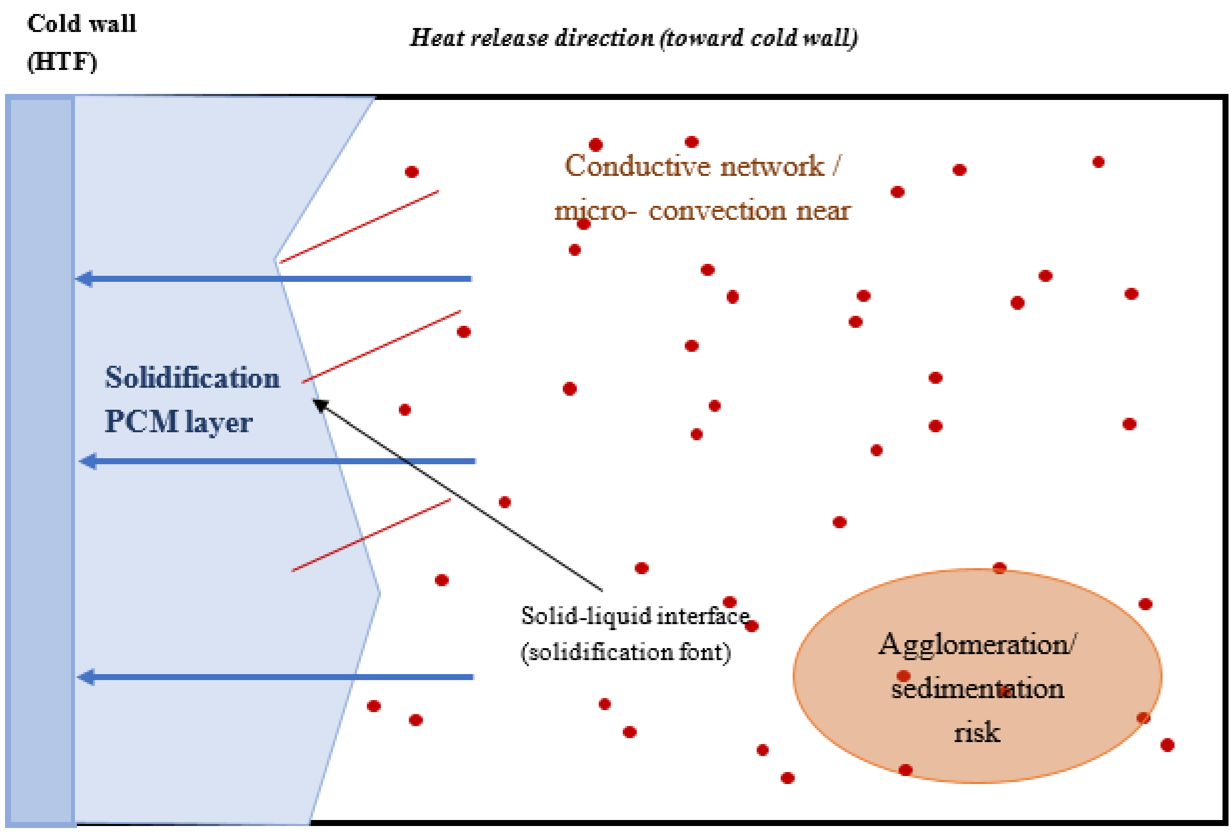

Fig. 4. During solidification, the heat transfer mechanisms of CuO–EG NePCM

The figure illustrates the role of CuO nanoparticles in improving solidification, such as by increasing the thermal conductivity, supporting micro-convection in the liquid phase with the aid of Brownian motion, providing heterogeneous nucleation support, and possibly forming a conductive network in the liquid phase. It also reveals unwanted phenomena of high loading of nanoparticles such as agglomeration, sedimentation, viscosity increase and latent heat dilution.

4.3 Concentration Effect, Particle-Size Effect, and Property Correlations

The nanoparticles concentration plays a significant role in the performance of CuO–EG NePCM. As the concentration of CuO was increased, the thermal conductivity increased, however not in a linear manner. In general, their effects on conductivity were small at low concentrations (typically less than 1 wt%), while the effects on viscosity and latent heat were also small, but negative. The effects on conductivity were relatively small at low concentrations (typically less than 1 wt%), while the effects on viscosity and latent heat were relatively small and negative [Adera, 2025], [Nandi, 2025]. This range is beneficial if the ultimate heat transfer enhancement is of lesser concern than long-term stability and minimal property penalty. Many studies have found the best overall balance between the conductivity enhancement and the acceptable thermophysical penalties in the range of moderate concentrations, typically between 1 and 3 wt% [Nandi, 2022]. Within this range, the CuO nanoparticles could significantly increase the solidification front velocity for useful rates of solidification without excessive viscosity and latent heat.

The overall benefit may reduce at high levels, usually greater than approximately 3-5 wt%. Despite a nominal increase in the thermal conductivity, the NePCM may experience increased viscosity, increased agglomeration tendency, sedimentation, and decreased latent heat capacity [Nižetić, 2020]. These effects can cancel out the benefits of increased conductivity. Thus, the best concentration of CuO loading is not the highest possible content, but rather it is the concentration that leads to an increase in the solidification rate that outweighs the decrease in storage density and flow rate. This optimum will depend on the type of PCM/EG/water ratio, TES geometry, cooling BC, particle size and preparation quality [Emara, 2025].

Another salient point is the particle size. Smaller CuO nanoparticles are likely to have a greater surface area per unit mass and may be able to provide a greater number of nucleation sites, thus enhancing conductivity, and minimizing subcooling. Smaller particles, however, also possess higher surface energy and are more susceptible to agglomeration particularly when there is no appropriate surfactant or insufficient ultrasonication. Particles larger than this will be more stable, but likely to offer less thermal enhancement per unit mass. Hence, the size of CuO particles should not be considered as an independent variable alone, but should always be taken along with the concentrations and dispersion technique [Millavithanachchi, 2025], [Akarken, 2024].

Analytical and numerical models require thermophysical property correlations of the CuO–EG NePCs. The effective density is usually estimated using a "Volume Fraction Based" mixture rule, and effective specific heat is obtained using either mass- or volume-based heat-capacity models [Ghalambaz, 2019]. The Maxwell model and the modified effective-medium correlations are used to predict thermal conductivity. However, these models do not account for clustering or for interfacial layering or particle-network formation and hence might underestimate, or overestimate, the true conductivity [Bondareva, 2024], [Kiradjiev, 2019]. The viscosity of a nanofluid is then often approximated by the Brinkman model or by empirical correlations based on the measured data from the nanofluid, while latent heat is calculated by applying a mixture rule, which considers the inactive CuO fraction that does not participate in phase change [Klazly, 2025].

The correlations are useful for numerical simulation of solidification particularly in enthalpy-based and CFD models, as they give the effective properties for the governing equations. The accuracy of their results is, however, dependent on the reliability of the experimental input data. Experiments validating the property data for CuO–EG/ water–EG NePCMs are still limited, especially at sub-zero temperatures and multiple thermal cycles. Hence, future modelling studies should be based on the measured rather than idealized mixture rules for the thermal conductivity, viscosity, latent heat, freezing temperature and stability, whenever possible. It is essential to make reliable predictions of solidification time, heat release rate and longtime TES performance.

5. CuO NePCM Solidification Performance

5.1 Solidification Performance Indicators and CuO Concentration Effect

The solidification performance of CuO–EG/water–EG NePCM is mainly evaluated using total solidification time, solid or liquid fraction evolution, heat release rate, temperature distribution, and solidification-front movement. Amidst these indicators, total solidification time is most direct one as it reflects the cooling condition and how fast the TES unit can solidify the liquid [Sathishkumar, 2022]. Another significant factor to consider is the heat release rate, which refers to how well the TES can provide the stored cooling or thermal energy during discharge, particularly when the demand fluctuates over time [Reddy, 2025]. From a numerical point of view, dimensionless parameters like Nusselt number, Stefan number, Fourier number, and Rayleigh number are often used to compare the results of different geometries, scales and operating conditions [Hyun, 2026].

Using only CuO as an enhancement method, the freezing time for the NePCM is usually shorter than that for the base PCM as CuO enhances the effective thermal conductivity of the storage medium and also offers additional heterogeneous nucleation sites during the freezing process [Said, 2024]. The reported reductions in solidification time for CuO-based NePCMs are generally in the range of 5–25% (for different nanoparticle concentrations, particle sizes, dispersion quality, PCM/base-fluid composition, TES geometry and cooling boundary conditions) [Harikrishnan, 2012]. This improvement is not direct, but concentration dependent. The conductivity gain is small but generally constant at low levels of CuO, typically in the range of 1-3 wt. % at moderate level, and is generally adequate to meet the requirement for a relatively fast freezing rate, acceptable viscosity, and minimal latent heat loss. When concentrations increase, the increased conductivity may be counterbalanced by agglomeration, sedimentation, viscosity increase, and latent heat dilution [Qahiti, 2023] and may result in a decrease in the net performance improvement. The representative behaviour with concentration is shown schematically in Fig. 5 in which the concentration increases from 0 wt.% CuO to 0.25 wt.% CuO; the concentration increases from 0.25 wt.% CuO to 0.5 wt.% CuO; the concentration increases from 0.5 wt.% CuO to 1 wt.% CuO; the concentration increases from 1 wt.% CuO to 2–2.5 wt% CuO; the concentration increases from 2–2.5 wt.% CuO to nearly 24%. Thereafter, a slight decrease in improvement is observed from 20% to 15% at 4 wt. % and 5 wt. % respectively, showing that it is not always the highest loading of nanoparticles that leads to the maximum improvement.

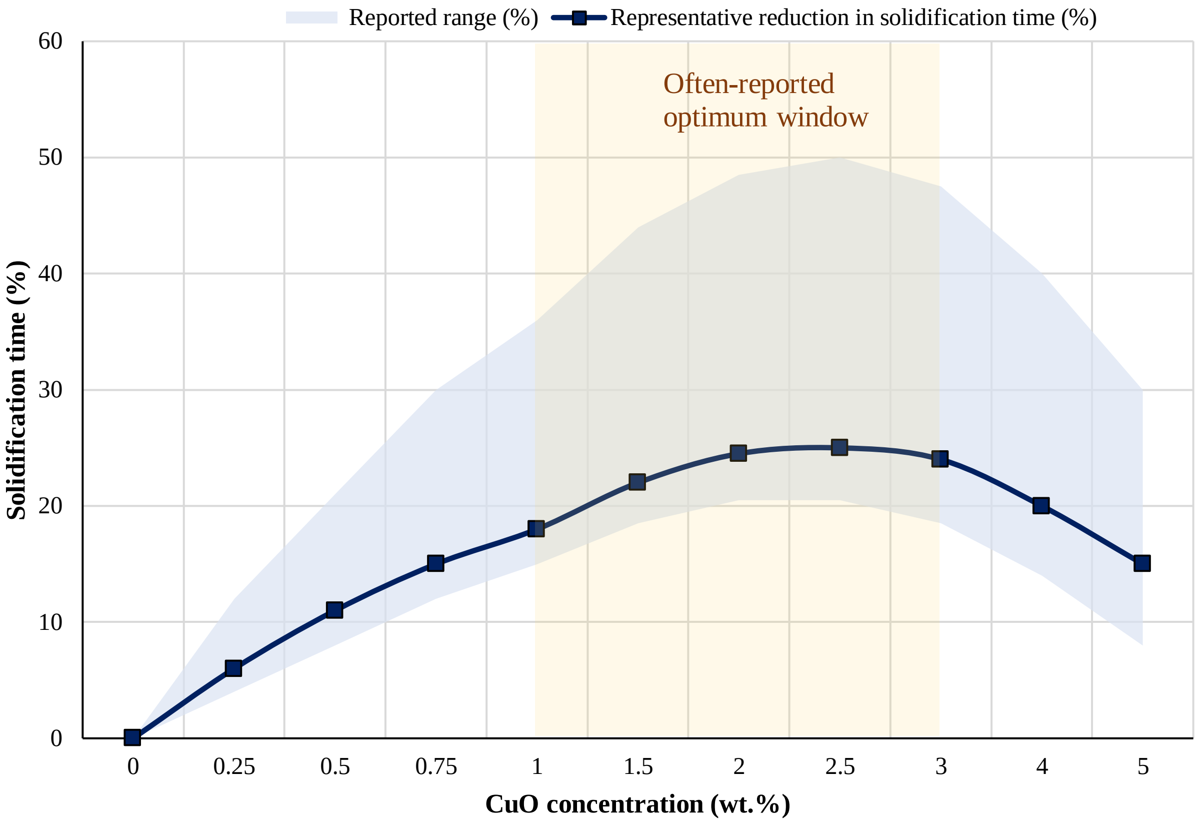

Fig. 5. The effect of CuO concentration on a reduction in the solidification time

5.2 TES Configurations for CuO–EG NePCM Solidification

The TES geometry is critical for the performance of CuO–EG/HTF–EG/NePCM, as it determines the heat transfer surface area, conduction path length, HTF–PCM contact pattern, and shape of the solidification front. Mostly cylindrical and shell and tube type configurations are studied for clear observation of radial solidification from the cooled tube or wall to the liquid PCM core [Afsharpanah, 2022]. The layer of growth in this type of system gradually raises the thermal resistance, and CuO nanoparticles enhance the heat conduction in this layer [Eisapour, 2022]. Inlet temperature of HTF, HTF flow rate, tube arrangement and boundary condition are also the factors that affect the solidification rate [Afsharpanah, 2022].

Spherical capsule and encapsulated TES systems are of great value for cold TES and packed-bed storage, due to their high surface area to volume ratio. Smaller capsules generally solidify faster since more of the PCM stays in closer contact with the capsule shell, and the addition of CuO can enhance the thermal response and decrease the subcooling [Cofré-Toledo, 2024]. The capsules' diameter, however, as well as the thermal resistance of capsule shells and the confinement of nucleation behavior, can play a significant influence on the final performance [Naharros-Molinero, 2024], [Sundaram, 2022]. The coil, serpentine, triplex-tube, and finned heat exchanger configurations present a higher area for heat exchange and shorter conduction path [Lee, 2023] and are compact systems. For these systems, the dominant improvement is generally the geometry, and CuO can give local conductivity enhancement as well [Saeed, 2022]. There are some typical TES designs for NePCM solidification, as indicated in Fig. 6.

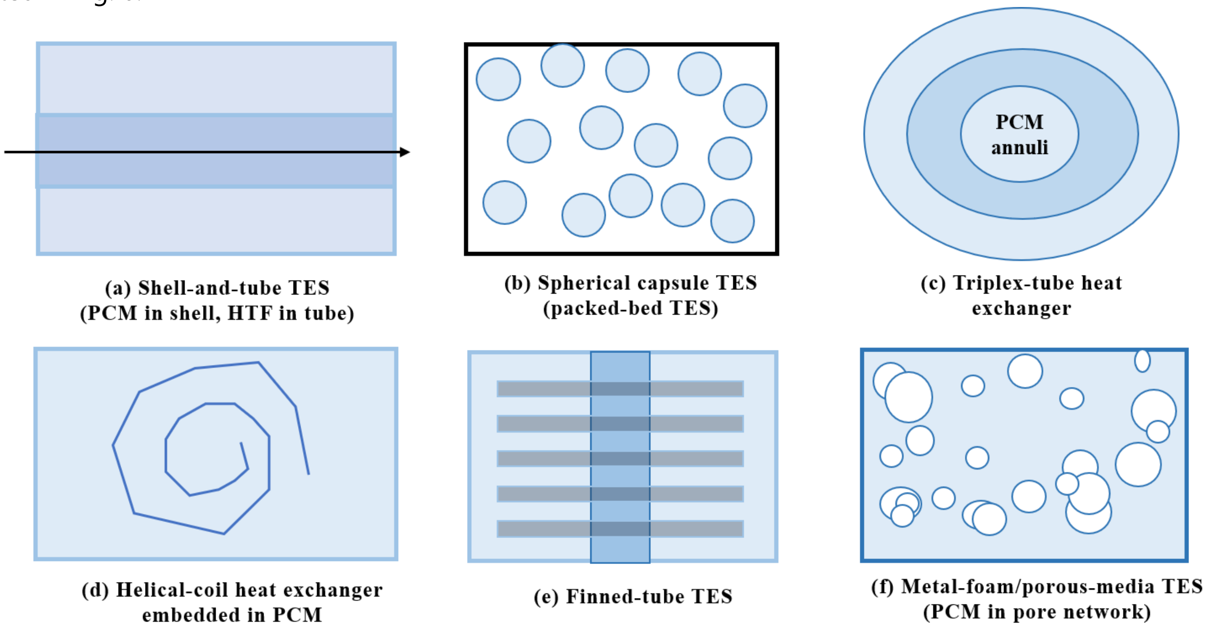

Fig. 6. Typical TES setups for NePCM solidification

The figure shows examples of typical TES designs employed in order to enhance heat transfer and solidification behavior in NePCM-based TES, such as shell-and-tube, packed-bed spherical capsule, annular PCM heat exchangers with a triple-tube, helical-coil heat exchangers filled inside with PCM, fin-enhanced tube, and metal-foam or porous-media enclosures. Because these geometries result in higher heat transfer area, reduce the conduction path, enhance temperature distribution and shorten solidification time of the storage medium, they are generally employed. Shell-and-tube and triplex-tube systems are simple and practical solutions for heat-exchanger arrangement providing good heat transfer between the heat transfer fluid and the PCM; encapsulated systems and packed-bed systems increase the surface-area-to-volume ratio, and improve the uniformity of charging/discharging [Hekmat, 2025]. Two types of geometries have been proposed coil-like and fin-enhanced that increase the heat transfer area and decrease the thermal resistance that will cause the solidification front to move faster. Metal-foam and porous-media systems are other conductive network systems that are installed within the PCM domain and extensively documented as promising structural enhancement techniques to improve the solidification and, overall, the TES thermal response [Shafi, 2025]. In general, TES geometry has a significant effect on solidification time, thermal uniformity and the extent to which the conductivity enhancement of CuO-based NePCM in practical storage systems can be effectively used.

5.3 Hybrid Enhancement Strategies and TES Design Comparison

The CuO nanoparticles alone offer moderate solidification enhancement, and when material-level enhancement is used in conjunction with geometry-based or structural enhancement, stronger solidification enhancement is typically achieved. Fins are one of the best methods as they increase the heat transfer surface area of the PCM and shorten the heat conduction path length [Sathishkumar, 2024], [Sathishkumar, 2020]. By using CuO–EG NePCM, macro-scale heat transfer pathways of fins and local thermal conductivity of the PCM are provided by CuO nanoparticles. These two effects are not mutually exclusive. The fins, however, not only decrease the active PCM volume for a given amount of product but also increase the manufacturing complexity, so the number, length, thickness and configuration of the fins should be optimized [Afsharpanah, 2020].

Another enhancement route that is multi-scale is metal foam and porous media. The conductive porous skeleton spreads the heat into the PCM domain while CuO nanoparticles enhance the heat transfer inside the pores filled with PCM. This could significantly speed up solidification but could also lower PCM volume fraction and increase the cost. Due to the high effective thermal conductivity, heat pipes can also be used to remove the heat from the PCM to an external heat sink at a high rate [Esapour, 2018]. There are few studies that have integrated cold-TES with CuO–EG NePCM however. Cascaded systems, encapsulation and slurry-based systems are also potential solutions as they can maintain good temperature differences, minimize leakage and enhance handling stability [Kahraman, 2022], [Gouga, 2026]. Table 6 shows a brief overview of the TES configurations and enhancement strategies discussed in the rest of the document.

Table 6: TES configuration and hybrid enhancement of NePCM solidification using CuO

Ref.	Configuration/enhancement	Working principle	Main benefit	Key limitation/design issue
[15]	CuO/GNP–CuO nanoparticles in PCM	Enhances nucleation and efficient conductivity	Reduces solidification time and subcooling	Excess loading may reduce stability and storage capacity
[27]	Cylindrical enclosure with NePCM–porous composite	Radial solidification with enhanced porous PCM	Accelerates solidification-front movement	Porous structure reduces active PCM volume
[8]	Double elliptical LHTES with NePCM	Wavy geometry shortens heat transfer path	Reduces solidification time	Requires geometry optimization
[85]	Encapsulated NePCM capsules	PCM freezes inside externally cooled capsule	Freezing/melting rate is controlled by capsule size	Shell resistance affects performance
[89]	Finned pear-shaped TES with NePCM	Fins increase heat transfer area	Provides strong heat transfer augmentation	Fin effect may dominate nanoparticle effect
[84]	Serpentine tube with extended surfaces	Improves HTF–PCM heat exchange	Enhances cold TES charging performance	Added geometry increases complexity
[94]	Metal foam with NePCM	Conductive skeleton distributes heat	Allows for multi-scale improvement	Foam reduces PCM fraction and raises cost
[46]	CuO-based encapsulated PCM	Encapsulation increases stability and reduces leakage.	Improves handling and cycling reliability	Shell may add thermal resistance

Table shows that the addition of CuO nanoparticle has a beneficial effect on solidification, with the optimized TES geometry, geometry of the fins, the porous media, and encapsulation providing the most beneficial effect. Thus, the design must consider the heat transfer gain, the volume of the active PCM, its stability, the cost, and the complexity of the fabrication process.

5.4 Numerical Modeling Approaches and Validation

Due to the difficulty of experimental observation of the internal temperature field, liquid fraction and moving solidification front of CuO–EG NePCM, numerical modeling is widely used to analyze the solidification process of NePCM. Most models are based on the conservation equations of mass, momentum and energy and latent heat release is represented either through an enthalpy formulation or a phase change source term [Irwan, 2019]. The energy equation uses effective NePCM properties: density, specific heat, thermal conductivity, viscosity and latent heat. Typically, these properties are computed based on mixture rules, Maxwell-type conductivity models, Brinkman-type viscosity models, or the measured thermophysical properties [Amudhalapalli, 2022].

The enthalpy-porosity method is the most widely used method for PCM and NePCM solidification since it can account for the solid–liquid phase change on a fixed computational grid without explicitly tracking the moving interface [Eisapour, 2022]. In this approach the liquid fraction in each computational cell is defined in the range 0 to 1, and Darcy-type momentum sink will reduce the velocity in the solid and mushy regions [Fadl, 2019]. ANSYS fluent is often utilized, and COMSOL multiphysics [Daneshazarian, 2023] as well as finite element methods (FEM), lattice

Boltzmann methods (LBM), and numerical experimental hybrid methods are also reported. Table 7 summarizes a sample of numerical methods and presents a review-style summary.

Table 7: Numerical modelling for solidification of CuO–EG/ CuO-based NePCM

Ref.	Geometry/system	Numerical method	Modeling and validation details	Key finding
[58]	Separated cavity with NePCM-filled wall	Finite volume CFD; enthalpy-based model	Navier–Stokes and energy equations; Maxwell/Brinkman properties; benchmark validation	NePCM characteristics had an impact on phase transition and natural convection
[99]	Encapsulated spherical capsules	Finite volume CFD; enthalpy-porosity	Maxwell-type k model, mixture rules, Darcy source term, and validation against previous data	Phase-change rate determined by capsule size and NePCM characteristics
[66]	Metal-foam-filled enclosure with NePCM	CFD in finite volume with foam-NePCM coupling	Foam porosity terms; effective properties;	NePCM-infused foam greatly improved heat transmission
[89]	Pear-shaped finned TES	Finite volume CFD; enthalpy-porosity	Mixture-rule properties; constant HTF temperature; grid/time-step tests	Fin geometry predominated, while NePCM provided further enhancement
[83]	Difficult discharging geometry	Transient finite volume CFD	Grid-independence check, mixture properties, and enthalpy-porosity model	Discharging time was greatly impacted by geometry and NePCM characteristics
[98]	General NePCM TES evaluation	Numerical–experimental hybrid	When accessible, an energy-balance model with measured inputs is validated experimentally	Novel NePCM showed measurable improvement over base PCM

It is shown that finite volume CFD with enthalpy-porosity treatment is a more dominant method than NePCM in modelling the solidification of a NePCM in practical TES due to its ability to model the transient phase change behaviour. The accuracy of the prediction, however, relies on correlations with the experimental results and effectiveness of the properties, grid independence, time-step independence, selection of boundary conditions, and experimental validation [Bondareva, 2024]. Further experimental measurements of sub-zero thermophysical properties and validation of the solidification datasets are still needed for CuO–EG/water–EG NePCM, to further enhance the reliability of the model. The typical numerical modeling process for the analysis of NePCM solidification is briefly summarized in Fig. 7.

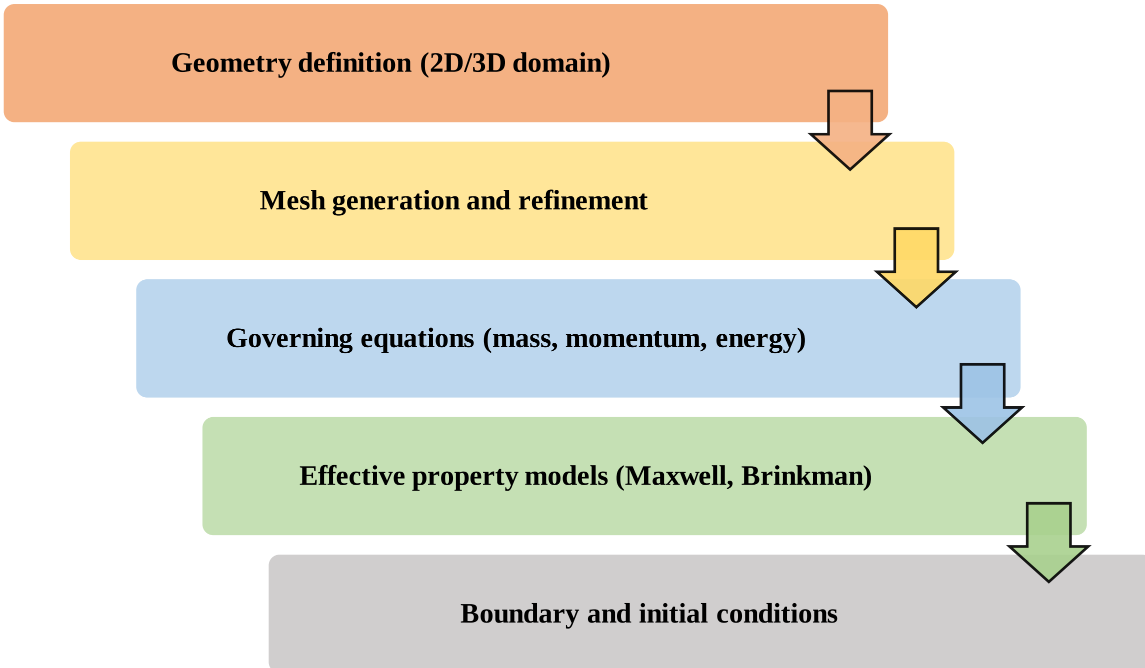

Fig. 7. Numerical modeling process

The figure shows the step-by-step numerical modeling process for NePCM solidification, which involves specifying the geometry, creating the model mesh, refining the mesh, defining the governing equations, determining effective properties, setting the boundary and initial conditions, numerically solving the equations, validation, and performance prediction.

5.5 Review Synthesis and Design Implications

Based on the reviewed literature, it is concluded that the CuO–EG NePCM is not just a conductivity-enhanced PCM but it should be considered as a material–system solution. Thermal conductivity, viscosity, subcooling and long-term stability depends on the concentration of CuO particles, particle size, ratio of EG to water, type of surfactant and sonication procedure at the material level. These material enhancements have a beneficial impact on faster solidification in the system level, depending on the geometry of the TES, temperature of the HTF, heat transfer area, capsule size, fin arrangement, foam porosity and boundary conditions [Reji, 2020].

In cases of simple shell-and-tube or cylindrical systems, the addition of CuO could give a visible improvement as a major resistance is the conduction by the increasing solid layer [Afsharpanah. 2022]. In systems that are already compact (such as those with fins or coils, serpentine tubes, or porous structures), CuO is typically a secondary and useful enhancement due to the reduced macroscopic thermal resistance caused by the compact geometry [Saeed, 2022]. The optimal design route is thus not simply loading maximum amount of CuO, but optimized concentrations of nanoparticles, the ratio of EG/ Water, stability of the dispersion, geometry of the TES and the enhancement strategy of nanoparticles/EG. Further research is needed on validated CuO–EG/water–EG solidification experiments, long-term thermal cycling, realistic cold-TES boundary conditions, and techno-economic analysis of combined NePCM–geometry systems [Mellah, 2025].

6. Applications, Challenges and Future Research Directions

The potential of the underlying enhancement mechanisms discussed in previous sections has been explored in a wide range of thermal energy storage applications of CuO-based nanofluids and NePCs, as shown below. Solar thermal systems: CuO-based hybrid nanofluids are employed either as a direct heat transfer fluid or in combination with phase change material (PCM)-based storage, for instance hybrid solar thermal energy storage (Solar TES) using carbon nanotube and CuO Nanofluids were found to be energy efficient working fluid for solar and TES applications [Mishra, 2025]. Another application area is photovoltaic-thermal (PVT) system and CuO water–ethylene glycol nanofluids have been experimentally applied to enhance the performance of PVT system, CuO nanofluid mixed with PCM has been applied to enhance the thermal response of PVT hybrid system [Kazem, 2022], [Tiwari, 2023]. Other CuO-based enhancement in solar-integrated storage systems, such as PCM/CuO nanofluid mixtures in PVTCs and latent heat TESs with serpentine absorbers, confirm the significance of CuO-based enhancement in solar-integrated storage systems [Tiwari, 2023]. It has been reported that in cold TES, when the PCM is enhanced with nanoparticles, it can enhance the cool thermal energy storage performance by controlling the subcooling behavior and reducing the solidification time [Sathishkumar, 2024]. Another relatively new area is building cooling and battery thermal management that can also be enhanced by the use of CuO based PCM composites to provide passive thermal regulation, heat absorption, and temperature control [Jagadeesh, 2025], [Thangapandian, 2022]. A summary of the major applications, limitations, and future research needs are summarized in the following Tabular Data 8.

Table 8: Applications and research needs of CuO–EG NePCM

Ref.	Application / issue	Current relevance or limitation	Future research need
[15]	Cold TES, HVAC, and refrigeration	EG enables low-temperature operation, while CuO can accelerate solidification and reduce subcooling	Optimize CuO concentration and EG/water ratio for sub-zero cold TES
[11]	Solar thermal and PVT systems	CuO-water–EG nanofluids improve thermal response and PVT performance	Evaluate pumping-power penalty and long-term stability in real solar loops
[103]	Battery thermal management	CuO/PCM systems can improve battery temperature regulation	Test durability, encapsulation, and safety under repeated cycles
[104]	Building cooling applications	CuO-based PCM composites can enhance passive thermal management	Assess cost, scale-up, and building-integrated performance
[14]	Agglomeration and sedimentation	Nanoparticle instability reduces effective conductivity enhancement over time	Develop stable surfactant, sonication, functionalization, or encapsulation methods
[25]	Viscosity and pumping-power penalty	Higher CuO loading increases viscosity and may reduce flow performance	Quantify pumping-power penalty against solidification-time reduction
[65]	Latent heat reduction	CuO is non-phase-changing, so excessive loading reduces storage density	Establish optimum loading based on heat transfer rate and storage capacity
[105]	Corrosion and material compatibility	CuO, surfactants, water–EG mixtures, and metallic containers may interact during long-term operation	Conduct corrosion, compatibility, and coating studies for TES hardware
[16]	Modeling and validation gap	Many studies rely on idealized property models rather than measured CuO–EG data	Generate validated experimental datasets for numerical model calibration
[17]	Scale-up and practical deployment	Laboratory-scale performance does not always translate directly to real TES systems	Perform pilot-scale tests, techno-economic analysis, and life-cycle assessment

As shown in Table 10, CuO–EG/water–EG NePCM shows great potential for cold TES, refrigeration, solar/PVT systems, building cooling, and battery thermal management, but it has to surmount both the material-level and system-level limitations for practical applications. Unstable CuO dispersion is one of the most important barriers that can lead to a decrease of effective thermal conductivity enhancement over time and to a decrease of the reliability of the long-term TES [Khlissa, 2023]. The addition of CuO can also lead to an increase in the viscosity, which can reduce convective heat transfer and increase the requirement for pumping power, particularly at high nanoparticle loading and low operating temperature [Razzaq, 2025]. Besides, CuO does not change phase, and hence, too high a concentration of CuO will decrease the latent heat capacity and hence the storage density of the

NePCM [Mirahmad, 2025]. The interaction of the CuO particles and surfactants, as well as the interaction of water and EG inside the metallic containers, can also be an important issue, as it relates to corrosion and compatibility, and can be crucial for long-term operation [Xu, 2022]. The foregoing limitations indicate that the optimization of CuO-EG NePCM must not be based solely on the value of thermal conductivity, but should be optimized with regard to the balance between the enhancement of thermal conductivity, latent heat storage, viscosity, dispersion stability, compatibility and cost.

To address this, future research should be conducted on an application-specific basis, instead of a blanket approach to CuO concentration. The discussion in Sections 4 and 5 reveals that the performance of CuO–EG/water–EG NePCM is sensitive to the coupled effect of the loading of nanoparticles, particle size, the ratio of EG/water, the viscosity of the NePCM, latent heat retention, the dispersion stability, the geometry of TES, and the cooling boundary condition. Hence the best loading amounts of CuO, the type of surfactant, the sonication time, and the composition of EG/Water should be optimized for each operating temperature range and TES configuration [Nandi, 2025]. Stability, cost and the loss in pumping-power penalties must be carefully considered for hybrid nanoparticle systems combining CuO with graphene, CNTs, or Cu to further enhance the thermal conductivity [Kahraman, 2022], [Lu, 2025]. The shape optimized nanoparticles and encapsulated CuO–PCM systems can lead to lesser agglomeration and cycling reliability. However, a number of key factors are required to bring CuO–EG/water–EG NePCMs from the lab to practical thermal energy storage deployment, including long-term thermal cycling, validated models, pilot-scale cold TES demonstrations, techno-economic analysis, and life-cycle assessment.

7. Conclusions

This review has examined the current state of knowledge on CuO–ethylene glycol/water–EG nano-enhanced phase change materials for solidification enhancement in thermal energy storage systems. The results from the discussion on formulation, thermophysical properties, heat transfer mechanisms, TES configurations, hybrid enhancement techniques and numerical modelling demonstrate that CuO–EG/water–EG NePCM is a promising solution to address low thermal conductivity of conventional TES systems based on PCM. The CuO/nanoparticles improve the thermal transport of the PCM, and the ethylene glycol/water – EG base fluids enable stable sub-zero and low temperature operation, making this material system more suitable for cold TES and HVAC and refrigeration applications.

There are several consistent findings from the reviewed studies. Addition of CuO nanoparticles to the base PCM/fluid results in an improvement of its effective thermal conductivity, which is reported in the range of 5–35%, depending on the concentration, particle size and quality of dispersion. This conductivity improvement can save 5-25% solidification time by itself for CuO-only formulations and even more when used in conjunction with geometric improvements like fins, foams, or favorable TES configurations. The nanoparticles of CuO can also act as heterogeneous nucleation sites and decrease the subcooling, which is highly dependent on the quality of the dispersion and the type of surfactant. These benefits have some important trade-offs, however: CuO loadings above the generally reported optimum level of approximately 1-3 wt. % can lead to increased viscosity, agglomeration and sedimentation, and decreased latent heat capacity due to the inert nature of CuO. This means that the net TES benefit could level off or even drop when concentration is high.

The best way to improve TES performance is through optimization, not depending on just one enhancement mechanism. This involves determining the optimal concentration and size of CuO in the specific PCM, EG/water ratio and TES geometry, ensuring stable dispersion with appropriate selection of surfactant, stirring, and sonication, and incorporating structural improvements (e.g., fins, metal foam, porous media, heat pipes). Further research is needed to focus on CuO–EG/water–EG solidification tests, long-term thermal cycling, pilot-scale demonstrations, cost and life-cycle analyses, and validated numerical models to be calibrated for the relevant concentration and temperature range. The practical applications of CuO–EG NePCM solidification enhancement methods may be further broadened with continued attention to bio-based and alternative PCMs.

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