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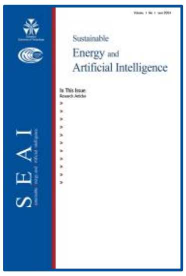

Molten Salt Nanofluids for High-Temperature Thermal Energy Storage: Advances, Mechanisms, and Challenges

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Abstract

The transition to clean energy demands advanced thermal energy storage (TES) solutions, especially for high-temperature applications like concentrated solar power (CSP) and industrial processes. Molten salt nanofluids-formed by dispersing nanoparticles in molten salts-offer a promising pathway to enhance thermal properties while maintaining high thermal stability and cost-effectiveness. This review summarizes the recent progress in the development, properties, preparation, and potential applications of these materials. Key focus areas include enhancements in specific heat capacity and thermal conductivity, which are critical for efficient heat storage and transfer. Notably, experimental studies report up to 100% increases in specific heat—defying classical predictions-possibly due to interfacial nanolayers, ionic rearrangement, or secondary nanostructures. Thermal conductivity improvements vary depending on nanoparticle type, morphology, and dispersion quality. The review also covers common base salts (nitrates, carbonates, chlorides) and a wide range of nanoparticle additives. Preparation methods such as ultrasonication and in-situ synthesis are discussed, along with challenges related to nanoparticle agglomeration, sedimentation, and long-term stability. Viscosity, corrosion behavior, and thermal cycling stability are also examined, as they critically affect system efficiency, pumping power, and material compatibility. Molten salt nanofluids hold strong potential for CSP, geothermal energy, enhanced oil recovery, and next-generation nuclear systems. However, commercialization is hindered by uncertainties in scalability, lifecycle impacts, and regulatory readiness. The review highlights the need for standardized methodologies, cross-disciplinary collaboration, and integrated performance-sustainability assessments to advance these materials toward practical deployment.

Keywords**:** Advanced thermal fluids, Nanostructured energy materials, Solar thermal systems, Heat capacity, Energy storage.

1. Introduction

The pursuit of more efficient and sustainable energy storage solutions stands at the forefront of contemporary energy research. Among the numerous alternatives explored, the development and deployment of nanofluids-base fluids infused with nano-scaled solid particles-has emerged as a particularly promising way for advancing heat transfer and storage technologies [1]. Over the last two decades, research into nanofluids has experienced remarkable growth, with scientists initially focusing on conventional water-based nanofluids to enhance thermal conductivity and later shifting attention to more innovative classes that operate under higher temperature regimes, suitable for concentrated solar power and other large-scale industrial applications [2]. Molten salt nanofluids, which comprise a base of inorganic molten salts doped with nanoparticles, have been assumed as a transformative solution for high-temperature thermal energy storage. They are uniquely positioned in the intersection between the stability of traditional molten salts, their cost-effectiveness, and the extraordinary thermal properties imparted by well-dispersed nanoparticles. Their direct application in concentrated solar power (CSP) and potentially geothermal energy storage, among others, marks them as critical focal points in the transition towards more resilient renewable energy infrastructures. This review sets out to provide a comprehensive explanation of the state of molten salt nanofluid research. It systematically addresses the types of nanofluids based on their melting points, preparation methods, thermophysical and rheological properties-including specific heat, latent heat, viscosity, and thermal conductivity-as well as the crucial issues of stability, corrosivity, synthesis scalability, limitations, and application prospects in the energy sector [3]. The work explores into the underlying mechanisms driving anomalous enhancements in specific heat capacity, an area of some controversy in the literature, and contextualizes the discussion within the operational frameworks of CSP plants and beyond [4].

2. Historical Background and the Emergence of Nanofluids

The foundation for using nanofluids-base fluids containing nanoparticles-as advanced heat transfer and thermal storage media was back to the mid-1990s through the pioneering work of Choi and Eastman. Their influential research demonstrated that adding just a small volume fraction (for example, 5%) of copper oxide nanoparticles to water could produce a dramatic increase, up to 60%, in the fluid's thermal conductivity. This remarkable finding fundamentally challenged prior conceptions about the limits of fluid-based heat transfer and initiated substantial interest across the scientific community [5]. Following these breakthrough results, the research landscape quickly diversified. Scientists expanded their exploration to a variety of nanoparticle types-including carbon-based, metallic, and ceramic species-coupled with different base fluids such as water and ethylene glycol. Each new combination presented an opportunity to optimize thermal properties, explore interactions at the nanoscale, and discover tailored solutions for specific applications. Despite substantial laboratory progress, the widespread use of conventional water-based or glycol-based nanofluids was ultimately limited by their thermal stability: these fluids would boil or decompose at relatively moderate temperatures, making them unsuitable for applications requiring operation well above 150°C, such as concentrated solar power (CSP), high-temperature industrial processes, and other advanced energy systems. To overcome these limitations, attention naturally shifted toward fluids capable of withstanding much higher temperatures. This technological evolution led to the emergence of molten salt nanofluids, where inorganic salts serve as the high-temperature base fluid, and nanoparticles are introduced to further enhance thermophysical properties. These new systems benefited from several critical advantages: high thermal stability (often up to and exceeding 600°C), non-flammability, cost effectiveness, and the potential for customization through the choice of salt composition and nanoparticle type. Such features made them especially attractive for CSP plants and later for possible applications in geothermal energy storage and high-temperature heat exchangers. Research into molten salt nanofluids thus built on foundational nanofluid science, extending its research into industrial high-temperature environments. The field has since expanded to probe not only enhancement of thermal conductivity but also anomalous improvements in specific heat capacity, the mechanisms underlying these effects, and the challenges associated with stability, corrosion, preparation scalability, and integration into real-world energy infrastructure [6].

3. Transition to Molten Salt Nanofluids for High-Temperature Applications

The increasing adoption of concentrated solar power (CSP) plants presented a demand for advanced heat transfer fluids capable of stable operation above 300°C-temperatures where traditional nanofluids lose efficacy [7]. Initial alternatives such as thermal oils, while offering some improvement, still suffered from thermal degradation and high costs at temperatures exceeding about 400°C. Molten salts emerged as compelling base fluids due to their high thermal stability, non-flammability, cost-effectiveness, and capacity for operation across extended temperature ranges up to and beyond 600°C. Their relatively low cost and robustness compared to both organic fluids and exotic ionic liquids made them attractive for both sensible and latent heat storage in CSP settings [8]. Yet, their application at industrial scale remained constrained by inherently low thermal conductivity and, in some case, significant viscosity, factors that diminished heat transfer efficiency and increased the need for high-power pumps. To overcome these limitations, researchers began incorporating nanoscale particles into molten salts, yielding the eponymous molten salt nanofluids. The trailblazing work by Shin and Banerjee exemplified this movement: they synthesized a nanofluid with Li_2CO_3-K_2CO_3 (62:38 molar ratio) as the base salt and silica nanoparticles as the additive [9]. Remarkably, just 1% wt. of nanoparticles resulted in a doubling of the specific heat relative to the pure salt. Pointing to both improved energy storage density and potential cost savings, the total investment cost for thermal storage tanks could be reduced by 50%. Despite these advances, the thermophysical property enhancements have proven to be non-uniform across different studies. Variations in base salt composition, nanoparticle type and morphology, preparation and dispersion methods, and measurement techniques have led to inconsistent-and occasionally contradictory-reports regarding the magnitude and even the direction of specific heat change. This remains a salient point of debate and active investigation in contemporary research [10].

4. Classification and Types of Molten Salt Nanofluids

The diagram of Fig. 1 illustrates the main concerns closely related with the synthesis and characterization of the molten salt nanofluids, together with their performance evaluation in flow boiling applications. Molten salt nanofluids can be categorized according to the melting point of the primary salt(s) employed. This choice is dictated not only by the application requirements (thermal stability, storage temperatures, and cost) but also by compatibility with nanoparticle additives and the practicality of synthesis.

4-1. Low Melting Point Salts (70–200°C)

Low melting point salts, such as Hitec and Hitec XL, find application primarily where avoiding freezing in the circuits is paramount [11]. These salts facilitate improved energy storage and reduction in tank size. However, their upper thermal stability remains limited (by the decomposition of nitrites or nitrates), translating to restricted operational lifespans and increased viscosity, particularly if calcium nitrate is present [12].

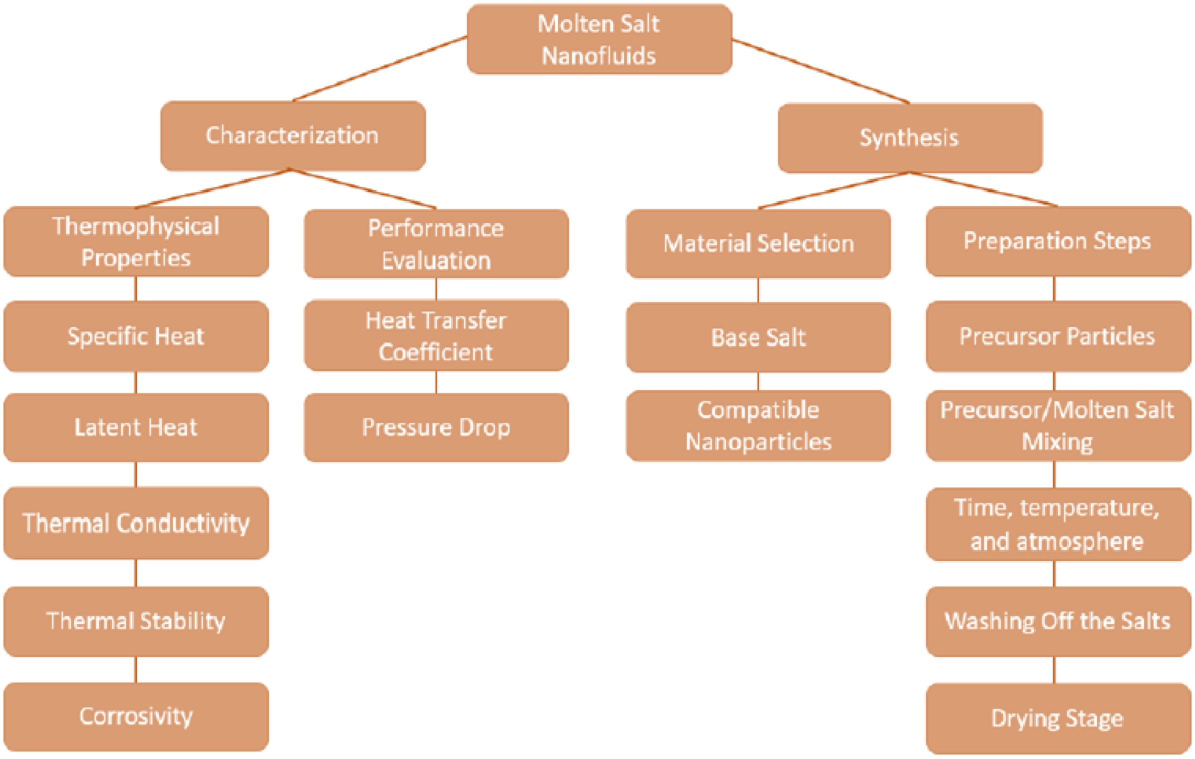

Fig. 1. Characterization and synthesis issues of the molten salt nanofluids

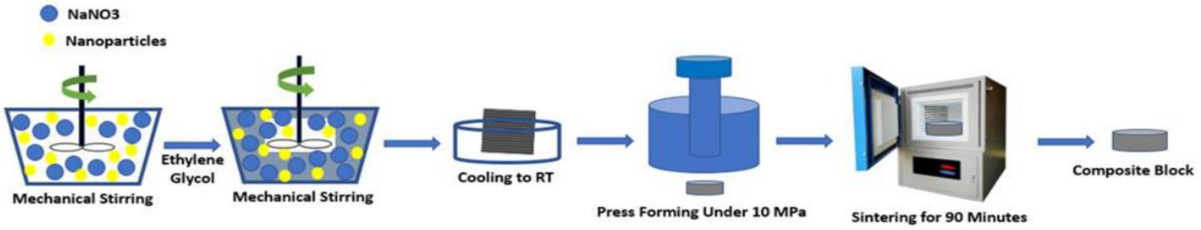

Fig. 2. Schematic diagram of the mechanical dispersion method for preparing a composite phase change material

4-2. Medium Melting Point Salts (200–350°C)

The most prominent example of a medium melting point salt is "solar salt" (a binary nitrate mixture, typically $NaNO_3$-KNO_3, 50:50). This variety strikes a balance between reasonable melting point, relatively low corrosion, and high operational temperatures (up to about 565°C) suitable for classic CSP implementation. Their chemical safety and modest corrosivity compared to chloride or fluoride salts favor their industrial-scale utilization [13].

4-3. High Melting Point Salts (>350°C)

Chloride, carbonate, and fluoride molten salts are explored for applications that require very high temperature operation-including advanced nuclear power reactors, high-temperature fuel cells, and next-generation CSP [14]. Though these salts boast high thermal stability and excellent heat transfer characteristics, their drawbacks include high corrosivity (especially for chlorides), high material costs (notably for lithium and zinc salts), and complex compatibility requirements for piping and containment materials. Mixing and matching multiple base salts to yield a ternary or quaternary composition allows researchers to "tune" the melting point and other properties, often seeking eutectic formulas for lower melting temperatures and improved energy density [15].

5. Preparation Methods

One of the most critical facets underlying the ultimate performance and reliability of molten salt nanofluids is the choice and rigor of the preparation method. The dispersion of nanoparticles must be both homogeneous and stable, otherwise agglomeration and sedimentation will occur over time, degrading property enhancements and compromising system longevity.

5-1. Two-Step Method [16]

This is currently the prevailing approach in laboratory settings. In essence, nanoparticles (often purchased as commercially produced nanopowders) are combined with the base salt through several sequential operations:

- **Weighing and mixing:** Accurate preparation of salt and nanoparticle ratios.
- **Dissolution in water:** The mixture is dissolved in water to facilitate uniform nanoparticle distribution [17].
- **Ultrasonic stabilization:** Sonication is used to break up clusters (arising from Van der Waals interactions) and achieve a stable, well-dispersed mixture. The duration and intensity of sonication are critical-too little leads to insufficient dispersion; too much can promote agglomeration [8].
- **Dehydration and drying:** Evaporation of water, typically on hot plates or in ovens, produces the final dry nanofluid. The drying process must be controlled to avoid boiling (which promotes clustering and loss of specific heat enhancement), and various heating rates and durations have been reported [18].

5-2. Mechanical Dispersion

As shown in Fig. 2, an alternative is to disperse nanoparticles directly in the molten (or dry) base salt using mechanical means-such as high-shear mixing, ball milling, or compounding. This method is suitable for potentially larger batches and avoids water usage [19]. However, it can lead to heterogeneous dispersions or even contamination if the milling media degrade. Variants also include pre-dispersing nanoparticles in a volatile solvent (e.g., acetone) followed by injection into the molten salt [20].

5-3. In-Situ Production

A "one-step" method, in-situ production involves synthesizing nanoparticles directly within the molten salt matrix, either by physical (e.g., vapor condensation, arc spray, laser ablation) or chemical means (e.g., precipitation, thermal decomposition of precursors) [21]. While this approach can mitigate issues of initial agglomeration and potentially yield uniform, functionally-graded nanoparticle dispersions, it introduces new complexity: controlling nanoparticle size, shape, and composition can be difficult, and remaining synthesis reagents can inadvertently alter nanofluid properties. Still, in-situ routes are considered promising for future large-scale, cost-effective production [22]. A comparative summary reveals that each method carries trade-offs between ease of implementation, scalability, risk of agglomeration, and reproducibility of desired properties [23].

6. Thermophysical Properties

6-1. Thermal Conductivity and Diffusivity

Thermal conductivity is a core thermophysical property that determines a material's intrinsic ability to transfer heat [24,25]. In the context of thermal energy storage and heat transfer fluids, materials with higher thermal conductivity facilitate more efficient heat movement, directly enhancing the performance of storage media and heat exchange systems. For molten salt nanofluids, the central goal is to overcome the inherent limitation of traditional molten salts, which tend to have relatively low thermal conductivity-thus restricting their utility in high-performance energy applications [26]. Although the corrosive nature and high melting points of molten salts complicate thermal characterization, experimental and simulation-based research has provided valuable insights into how nanoparticles affect these thermophysical properties. Many studies on molten salt nanofluids report significant enhancements in thermal conductivity, often observing increases of more than 20% compared to pure salt mixtures [27]. Such improvements have been particularly pronounced with the incorporation of metal oxide nanoparticles, carbon nanotubes, or expanded graphite, whose high intrinsic conductivities and large surface areas modify the base fluid's heat conduction behavior [28]**.** Yet, the magnitude and even the direction of these changes vary significantly depending on several interacting variables:

- **Nanoparticle concentration:** There is typically an optimal loading level. If nanoparticle content is too low, enhancement is minimal; but if it's too high, agglomeration can occur, leading to diminishing or even negative returns on conductivity.
- **Particle size and morphology:** Smaller nanoparticles offer higher surface area-to-volume ratios, which can intensify nanostructure interactions, but also make the system more prone to aggregation.
- **Temperature and phase state:** The relative thermal conductivity can change depending on whether the salt is in a solid or a molten phase, with Brownian motion effects and phase state transitions further modulating heat transfer.
- **Brownian motion:** At higher temperatures, increased kinetic activity (Brownian motion) can promote "micro convection," thus further altering effective heat transfer rates [29].

Not all nanofluid formulations display improved conductivity. Some experiments have reported no substantive change or even observed a reduction in thermal conductivity upon nanoparticle addition. One explanation for these negative outcomes involves interfacial thermal resistance (often called "Kapitza resistance") [30]- a phenomenon in which a thermal barrier forms at the interface between the molten salt matrix and the nanoparticles. This barrier can counteract the potential conductivity gains introduced by the highly conductive nanoparticles themselves [31]. Furthermore, the existence of a non-uniform interfacial region (possibly a nanolayer of structured salt around the particle) can add to thermal resistance. These complex interface effects are dealt with molecular dynamic simulations, which show that heat transfer enhancement arises not only due to the conductivity of the nanoparticles, but also involves:

- Local structural rearrangements in the salt near the nanoparticle,
- Ion migration and clustering effects,
- Alterations in the phonon (lattice vibration) transport due to atomic-scale mismatches [32].

6-2. Specific Heat Capacity

Specific heat, the amount of energy required to raise the temperature of a unit mass by one degree, is arguably the most critical property for a substance used in thermal energy storage. The principal aim of deploying nanofluids as storage media is often to maximize this figure, thus raising the energy density and efficiency of the system [33]. Many studies report substantial enhancements in specific heat when nanoparticles are dispersed (often 20%–100%), which goes against the conventional expectation from simple mixture rules-where the overall specific heat should be a weighted average of the constituents. Since nanoparticles (metals, oxides, etc.) usually have much lower specific heats than molten salts, one would expect a decrease in the specific heat of mixture. This anomalous enhancement has been the subject of much recent investigation. For better understanding, several mechanisms have been proposed in Fig. 3:

- **Compressed liquid layer:** The compressed liquid layer at the nanoparticle–molten salt interface is widely recognized as a key contributor to the enhancement of specific heat in molten salt nanofluids. This layer consists of highly ordered, dense fluid molecules [34] that form due to the strong interfacial interactions between the molten salt and nanoparticle surfaces. Experimental work by Tiznobaik and Shin [35] demonstrated that the presence of such a layer can lead to specific heat enhancements of up to 25%, an effect that disappeared when surface modifiers (e.g., hydroxides) disrupted the layer's formation. The formation and effectiveness of the compressed layer are influenced by several factors, including nanoparticle size, morphology, and dispersion quality. Smaller nanoparticles with high surface area promote more extensive interfacial regions and, consequently, thicker compressed layers. Conversely, agglomeration reduces the total surface area and diminishes the heat capacity enhancement. Molecular dynamics simulations revealed that the structural and thermodynamic properties of this layer are also dependent on salt composition. Specifically, potassium ions tend to accumulate near carbon-based nanoparticles, enhancing the layer's density and associated energy storage capability. The increased order and potential energy of the compressed layer molecules require more energy to activate thermal motion, thereby increasing the nanofluid's specific heat. Although theoretical predictions often underestimate this effect, experimental studies confirm its significance, particularly in systems using alumina nanoparticles with sizes between 10 and 50nm.
- **Secondary nanostructures:** The formation of secondary nanostructures in molten salt nanofluids significantly contributes to enhancing their specific heat capacity. These structures arise from the preferential surface adsorption of molten salt species onto dispersed nanoparticles, initiating the nucleation and growth of dendritic, long-range nanostructures. These formations, often fractal-like and extending from 100 nm to several microns, originate from a semi-solid phase with crystalline characteristics similar to the nanoparticle surfaces. Tiznobaik et al. [36] observed that the incorporation of silica, alumina, and magnesia nanoparticles in molten salts led to comparable specific heat increases of 27%, 33%, and 22%, respectively, despite differences in nanoparticle material. This outcome suggests that the enhancement is more related to the presence of dendritic secondary structures than the nanoparticle composition itself. The largest structures were noted in magnesia-based nanofluids, which corresponded with the lowest surface area and the smallest improvement in heat capacity. This highlights the inverse relationship between structure size and surface area. The volume fraction of these nanostructures often exceeds that of the nanoparticles, suggesting a long-range ionic influence triggered by the nanoparticle–salt interactions. Furthermore, surface charge accumulation due to ion adsorption promotes electrostatic forces that facilitate the alignment and extension of ordered molecular layers, potentially interconnecting nanoparticles in foam-like networks.

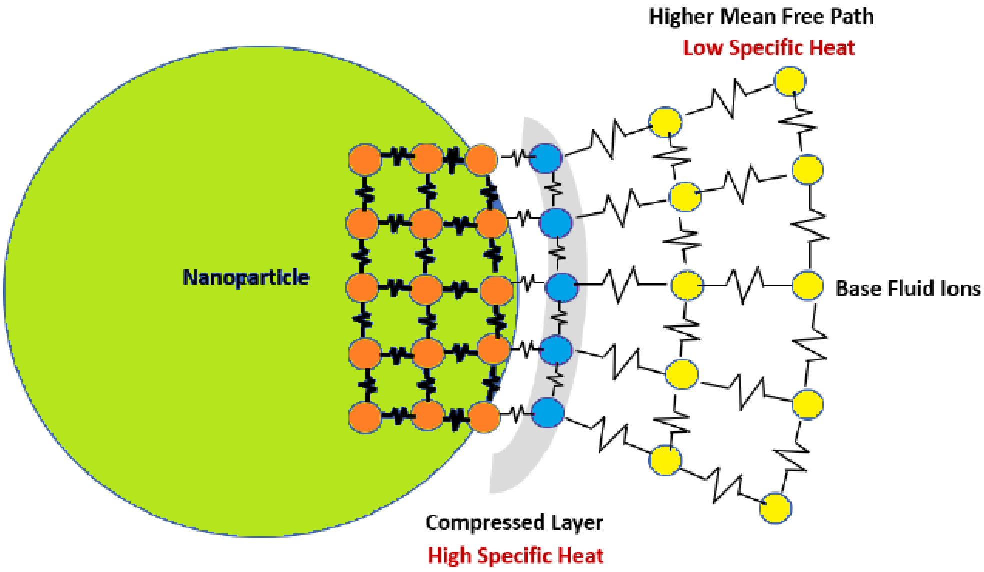

Fig. 3. Compressed layer formation and involved ions in a molten salt nanofluid

- **Interfacial thermal resistance (Kapitza resistance):** The interfacial thermal resistance, also known as Kapitza resistance, plays a fundamental role in the thermal behavior of molten salt nanofluids, particularly affecting their specific heat capacity. This resistance arises at the boundary between nanoparticles and the surrounding salt molecules, where a mismatch in vibrational properties (phonons) hinders efficient heat transfer. Instead of impeding performance, this thermal bottleneck contributes positively by enhancing the nanofluid's heat storage capability. The interface essentially acts as a region of energy accumulation, delaying heat conduction and thereby increasing specific heat. The influence of interfacial resistance depends heavily on nanoparticle characteristics such as concentration, size, shape, and dispersion quality. For instance, multi-walled carbon nanotubes (MWCNTs) show a pronounced dependence on dispersion state. At low concentrations, they enhance heat storage through improved salt-nanotube interactions. However, at higher loadings or in poorly dispersed systems, nanotube–nanotube interactions dominate, reducing interfacial area with the salt and degrading specific heat enhancement. Gold nanoparticles, with their spherical geometry and chemical stability, exhibit superior phonon scattering and greater interfacial thermal resistance [37], resulting in more pronounced specific heat gains. Furthermore, smaller nanoparticles are advantageous as they couple more effectively with low-frequency vibrational modes, maximizing interfacial resistance benefits. Ultimately, effective tuning of the nanoparticle-salt interface, through size optimization and proper dispersion techniques, is key to maximizing thermal storage performance in molten salt nanofluids.
- **Ion exchange capacity:** Mondragón et al. [38] investigated the interaction between functionalized nanoparticles and nitrate molten salts, focusing on the influence of ionic exchange capacity on the specific heat of molten salt nanofluids. Their study demonstrated that nanoparticles dispersed in nitrate molten salts undergo ionic exchange with nitrate ions, specifically involving H^+ ion exchange facilitated by functional groups on the nanoparticle surface. Infrared analysis confirmed the adsorption of nitrate ions onto the nanoparticles, indicating a modification of the nanoparticle surface chemistry during synthesis. The research showed that when the ionic exchange capacity was low, due to insufficient nanoparticle functionalization, the enhancement in specific heat was minimal. Conversely, exceeding a certain threshold of ionic exchange capacity resulted in a significant increase in specific heat, attributed to the contribution of the functionalized nanoparticles. For instance, non-protonated silica nanoparticles with low ionic exchange capacity produced only a 1.3% improvement in specific heat, whereas protonated nanoparticles achieved an enhancement of 10.1%. Furthermore, the study highlighted the complex role of nanoparticle concentration. Increasing concentration led to agglomeration, which enlarged particle size and reduced the effective surface area available for ion exchange, ultimately lowering both ionic exchange capacity and specific heat enhancement. Thus, an optimal balance between nanoparticle loading and functionalization degree is necessary to maximize thermal performance. The authors also emphasized that factors such as salt composition, nanoparticle morphology, and operating temperature influence ionic exchange capacity and should be carefully optimized. This work confirms that ionic exchange-driven functionalization of nanoparticles is a key mechanism for improving the thermal properties of molten salt nanofluids, with implications for thermal energy storage applications.
- **Cloud Nuclei:** This posits that salt ions condense in layers around nanoparticles due to competing van der Waals and electrostatic interactions, creating cloud "cores" or nuclei that alter both specific heat and, in some cases, thermal conductivity or phase change properties [39]. The formation, growth, and ultimate dissolution of these cores upon heating or agitation are key to observed property variations [40]. Cloud nuclei hypothesis is used to explain the anomalous enhancements in specific heat capacity observed in molten salt nanofluids. As depicted schematically in Fig. 4, this mechanism involves the spontaneous formation of fractal-like secondary nanostructures around the primary nanoparticles suspended in the molten salt. These cloud nuclei are hypothesized to emerge due to strong electrostatic interactions between the ions in the salt and the nanoparticle surfaces, particularly under thermal cycling or high-temperature conditions. This localized restructuring of the fluid matrix leads to the development of ordered ionic domains at the nanoparticle interface, which increases the system's heat storage capacity beyond classical expectations. The formation of such nanodomains is thermodynamically favorable within specific concentration and temperature windows, suggesting that the enhancement in specific heat is not merely a function of nanoparticle inclusion but

is rooted in emergent mesoscale phenomena. This interpretation aligns with earlier insights [6,41], offering a framework to design high-performance thermal energy storage media through controlled nanostructure formation.

- **Salt composition ratio:** The composition ratio of molten salt nanofluids significantly impacts their specific heat capacity, with synthesis methods playing a crucial role in these compositional changes. Sang et al. (2) synthesized a K_2CO_3-Li_2CO_3-Na_2CO_3 carbonate salt (4:4:2 mass ratio) with 1%wt. silica nanoparticles using various evaporation temperatures. Their study revealed that the ternary carbonate's composition altered during evaporation in an electrothermal drier, influenced by water solubility and heating mode. Evaporating at 180°C increased the nanofluid's specific heat by 79.9% to 113.7% between 500°C and 540°C, partly due to altered Li_2CO_3 mass fraction. Evaporation temperature influenced nanostructure formation, and different heating procedures (e.g., hot plate vs. electrothermal drier) also strongly altered salt composition. Jo and Banerjee [43] investigated the impact of Li_2CO_3-K_2CO_3 carbonate salt composition on specific heat by adding 1%wt. multi-walled carbon nanotubes to mixtures. They found that a 62:38 molar ratio of Li_2CO_3-K_2CO_3 minimized specific heat. Conversely, a 1%wt. silica nanoparticle molten salt showed augmented specific heat near its eutectic composition. Nanofluids with very high or low Li_2CO_3 fractions exhibited minimal specific heat increases, or even decreases. These studies conclude that molten salt nanofluid composition ratio affects specific heat enhancement, with heating modes during synthesis determining compositional changes. Different compositions can lead to varied nano-scaled structures, directly influencing final specific heat capacity.
- **Size and shape of nanoparticles:** Numerous studies explore the impact of nanoparticle size and shape on molten salt nanofluid specific heat, yielding inconsistent findings. Tiznobaik and Shin [35] observed up to a 25% specific heat increase in silicon dioxide nanofluids (5-60nm diameter) compared to pure molten salt. Conversely, Jung and Banerjee [44] found that increasing carbon nanotube dimensions reduced specific heat in Li_2CO_3-K_2CO_3 nanofluids, with negligible enhancement above 20nm due to reduced specific surface area. Thoms [45] reported that 10nm alumina nanoparticles decreased specific heat in $LiNO_3$-based nanofluids, while 200nm particles showed negligible increment, attributing this to the reduced interfacial area of larger particles. In contrast, Dudda and Shin [46] found specific heat increases with larger silica nanoparticles (5-60nm), with 60nm particles yielding a 28% increase versus 10% for 5nm, suggesting larger nanoparticles promoted more effective nanostructures. They attributed smaller nanoparticle underperformance to dispersion issues and agglomeration. Riazi et al. [47] demonstrated specific heat dependence on nanoparticle morphology, with spherical, smaller silica nanoparticles (19-92nm) yielding a maximum 17.6% increase. Agglomeration significantly negated specific heat enhancement. Overall, while most studies report specific heat improvement with nanoparticle addition, conflicting results persist regarding optimal size and morphology, highlighting the need for more experimental research and comprehensive correlations beyond operating temperature [17,48].

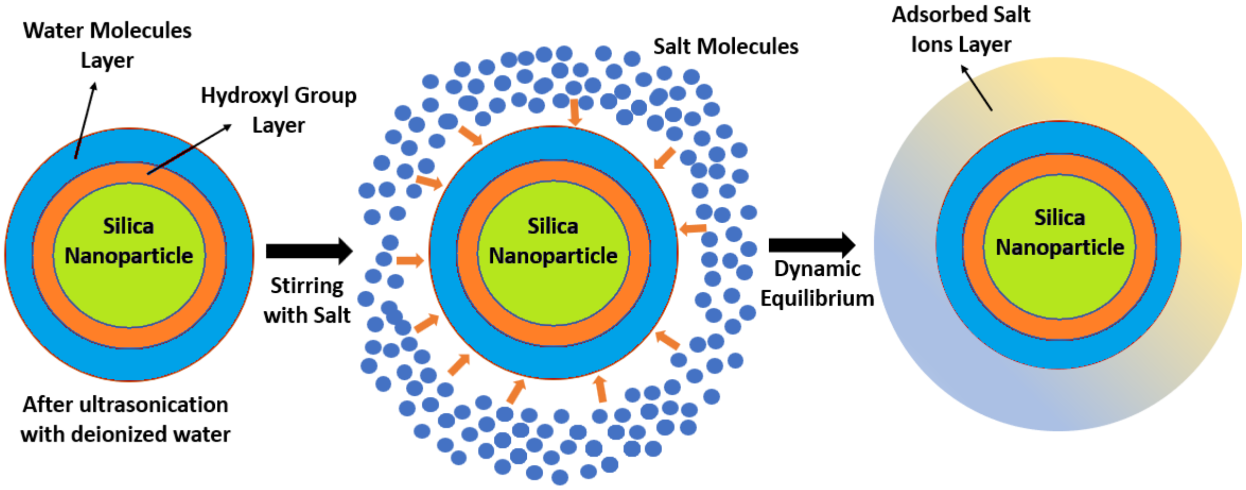

Fig. 4. Schematic representation of the formation mechanism of the three-layered cloud nuclei surrounding the added silica nanoparticles. Adapted from [42]

6-3. Latent Heat

Latent heat refers to the amount of energy absorbed or released by a material during a phase change-typically between solid and liquid phases-without a change in temperature. In thermal energy storage (TES) systems, materials that exploit latent heat are known as phase change materials (PCMs). The use of PCMs allows the system to store large quantities of thermal energy at nearly constant temperatures, which is beneficial for both energy storage density and thermal management [49].

6-3-1. Molten Salt Nanofluids and Phase Change

For molten salt nanofluids, incorporating nanoparticles into traditional molten salts offers a unique approach to enhance both sensible heat (energy stored as temperature rises) and latent heat (energy stored during phase transition). While most early research focused heavily on improving sensible heat capacities, recent interest has grown regarding the effects of nanoparticles on the latent heat behavior of molten salts.

6-3-2. Experimental Observations

Experimental studies have demonstrated that adding nanoparticles to molten salts can produce both increases and decreases in latent heat, depending on several factors:

- In some nanofluid formulations, the latent heat of fusion (energy required to melt) has increased by up to 28.8%. This is particularly advantageous for TES because it leads to higher energy storage per unit mass during phase transitions [50].
- In other cases, the latent heat reduces with increasing nanoparticle content, or displays non-linear (parabolic or linear) relationships, indicating complex interactions between nanoparticles, salt components, and changing thermodynamic parameters [49,51].

6-3-3. Mechanisms Behind Latent Heat Modulation

Understanding and controlling the impact of nanoparticles on latent heat is critical for engineering molten salt nanofluid TES systems. Decisions about:

- Nanoparticle type (oxide, carbon nanotube, expanded graphite, etc.),
- Size and surface chemistry,
- Loading
- Preparation and dispersion method,

can all significantly influence the latent heat characteristics, and thus, the overall effectiveness and efficiency of the energy storage system [51]. The effect of nanoparticles on the latent heat of molten salts is attributed to several possible mechanisms [52]:

- **Entrapment at Interfaces:** Nanoparticles can trap salt molecules at their surface, creating interfacial layers that require more energy to melt than the bulk salt, thereby increasing apparent latent heat of fusion.
- **Altered Nucleation Dynamics:** The presence of nanoparticles changes how crystallization and melting begin and propagate through the material. Nanoparticles can act as nucleation sites, altering the microstructure and transition energetics.
- **Thermodynamic Interaction:** The energetic interaction between nanoparticles and molten salt ions can change the energy landscape of phase change, leading to shifts in both latent heat and phase transition temperatures.

These effects are not necessarily monotonic or universally beneficial. For example, if too many nanoparticles agglomerate, or if their presence overly restricts the mobility of salt ions, the latent heat performance may decline.

6-4. Viscosity

Maintaining low viscosity is critical for the practical use of molten salt nanofluids in thermal energy systems, as high viscosity leads to greater pressure drops and increased pumping power. While these nanofluids are primarily developed to enhance thermal properties, controlling their rheological behavior is equally essential. Current research on viscosity is limited, focusing mostly on the influence of nanoparticle concentration, type, temperature, and shear rate. Lasfargues et al. [53] demonstrated that adding 0.1wt% copper oxide nanoparticles to a 50:50 $NaNO_3$-KNO_3 mixture increased dynamic viscosity under temperatures from 250-450°C and shear rates of 100–1000s^{-1}. Both the base salt and nanofluid showed Newtonian behavior, but the nanofluid exhibited higher viscosity, likely due to surface vortices around the nanoparticles requiring additional energy to initiate flow. Jo and Banerjee [54] found that multi-walled carbon nanotubes (MWCNTs) added to Li_2CO_3-K_2CO_3 (62:38mol%) induced non-Newtonian shear-thinning behavior. A 5wt% addition led to a 130% increase in viscosity at

1000s^{-1}. The Krieger–Dougherty model accurately predicted this behavior, with nanoparticle clustering being the main contributor to the increase. Surfactant use (e.g., gallic acid) helped mitigate viscosity rise by up to 18%. Xiao et al. [55] examined 1–2wt% graphene in HITEC salt and alumina in solar salt across 200–500 °C and shear rates of 1–250s^{-1}. HITEC-graphene nanofluids showed complex, non-Newtonian trends with sharp viscosity increases at lower temperatures and higher concentrations (up to 987.3% at 350°C with 2wt% graphene). Solar salt–alumina nanofluids exhibited minimal viscosity changes (-9.2% to +68.1%), attributed to particle agglomeration and measurement uncertainty. Other studies reinforce that the viscosity response is highly sensitive to nanoparticle type, concentration, and morphology. For instance, silica-based nanofluids showed increases between 34% and 94.4% [56], while those with magnesium oxide remained nearly unchanged across various concentrations [32].

In summary, the practical utility of molten salt nanofluids as working fluids depends critically upon their viscosity: increases in viscosity can significantly hike pumping power requirements, raise operational costs, and cause mechanical stress in plant infrastructure [57]. Generally, the addition of nanoparticles does increase viscosity, though trends vary:

- Mild increases (within 10-30%) are usually manageable, especially if accompanied by strong performance gains in thermal storage [32,52].
- Greater increases (e.g., over 100%) have been observed with high loadings, large or aggregated nanoparticles, or with carbon nanotube additives [58,59].
- Surfactant usage, mechanical agitation, and optimized ultrasonication protocols can reduce viscosity by promoting better dispersion.

The rheological behavior of nanofluids can be Newtonian or non-Newtonian, depending on both concentration and the type of particles used. For instance, some fluids become “shear thinning,” which may be beneficial under turbulent flow conditions. Predictive models like the Krieger-Dougherty equation have been adapted to molten salt systems to account for aggregate formation [53].

6-5. Thermal Stability

Thermal stability is a key parameter in the application of molten salt nanofluids for thermal energy storage (TES), particularly in concentrated solar power (CSP) systems operating between 250°C and 400°C. However, the influence of nanoparticle incorporation on the thermal stability and decomposition kinetics of molten salts is still not fully understood. The literature presents conflicting results, with some studies reporting enhanced stability due to nanoparticles, others noting a decrease, and some observing negligible changes. Thermal stability in nitrate-based salts is closely linked to nitrate-to-nitrite conversion, which accelerates decomposition and enhances corrosion risks. Salim and Rahman [60] examined lithium-potassium carbonate mixtures with graphite nanoparticles at varying concentrations. Their findings revealed substantial mass loss below 100°C due to moisture retention by nanoparticles, which compromised thermal stability. However, higher nanoparticle concentrations reduced water uptake by forming a percolated network that blocked moisture penetration, ultimately improving high-temperature stability. Song et al. [61] investigated the thermal cycling behavior of $NaNO_3$-based salts with silica, titania, and graphite nanoparticles. Their study, involving 300 heating/cooling cycles to 400°C, showed initial mass loss mainly in the first 50 cycles, followed by stabilization. Specific heat and latent heat decreased only modestly (6–7%), indicating good long-term thermal performance. Overall, nanoparticle effects on thermal stability are highly dependent on material type, concentration, and thermal history. While some systems demonstrate improved resistance to decomposition and phase change degradation, others may suffer due to moisture absorption or chemical incompatibility. Comprehensive evaluation methods, including extended thermal cycling and decomposition monitoring, are essential for assessing nanofluid suitability in high-temperature TES applications.

6-6. Corrosivity and Chemical Compatibility

The incorporation of nanoparticles into molten salts influences corrosion dynamics in complex ways [62]. Ideally, the right kind of nanoparticles can reduce corrosion by stabilizing oxidized passivation layers or by directly scavenging corrosive impurities. However, risks remain: improper dispersion, bubble formation, or choice of incompatible materials can exacerbate corrosion. Experimental evidence suggests that well-chosen and well-dispersed nanoparticles (such as silica or alumina) can reduce corrosion rates against carbon and stainless steels by 50% or more, particularly at high temperatures [63]. However, temperature and the presence of air bubbles can tip the balance toward increased corrosion, underscoring the need for careful formulation and process control. Physical and chemical adsorption of salt ions onto the nanoparticle surfaces can also establish local electric fields that suppress the oxidation of metals, acting as a kind of sacrificial "galvanic cell" for protection [64].

6-7. Agglomeration and Sedimentation: Threats to Long-Term Stability

One of the main challenges facing molten salt nanofluids in TES applications is ensuring long-term nanoparticle stability. At high operating temperatures, nanoparticles tend to agglomerate due to Brownian motion and interparticle interactions, eventually settling under gravity. This sedimentation depletes the active nanoparticle concentration in suspension, leading to degradation in specific heat capacity and thermal conductivity. Studies show that nanoparticle stability is influenced by both material properties and dispersion methods. For instance, Mondragón et al. [17] observed that a solar salt nanofluid with 0.5 wt.% silica nanoparticles exhibited significant sedimentation at 500°C, particularly in the upper layers of the sample, with a notable drop in specific heat. In contrast, alumina nanoparticles showed greater thermal stability under similar conditions. Lasfargues [65] compared dispersion techniques and found mechanical stirring to be most effective in preserving the thermophysical properties of copper oxide nanofluids, minimizing agglomeration. Similarly, Munoz-Sánchez et al. [66] demonstrated that higher surface area alumina nanoparticles improved initial dispersion but still showed rapid sedimentation within 30 minutes, eliminating specific heat gains. Navarrete et al. [67] used dynamic light scattering to assess stability in nanofluids with encapsulated aluminum/copper nanoparticles, which showed superior redispersion after several hours of static conditions, highlighting the importance of nanoparticle structure and composition. These findings underscore that achieving long-term colloidal stability in molten salt nanofluids requires careful selection of nanoparticle type and optimization of dispersion strategies. Further development of stabilization techniques, such as in-situ redispersion or nanoparticle surface modification, is essential for reliable TES operation at high temperatures.

7. Applications in Concentrated Solar Power and Beyond

The central industrial application for molten salt nanofluids is CSP technology [68]. CSP plants leverage solar energy focused onto a receiver, where a heat transfer fluid is used to transport and store the captured thermal energy [69]. A schematic diagram of concentrated solar power plant is shown in Fig. 5.

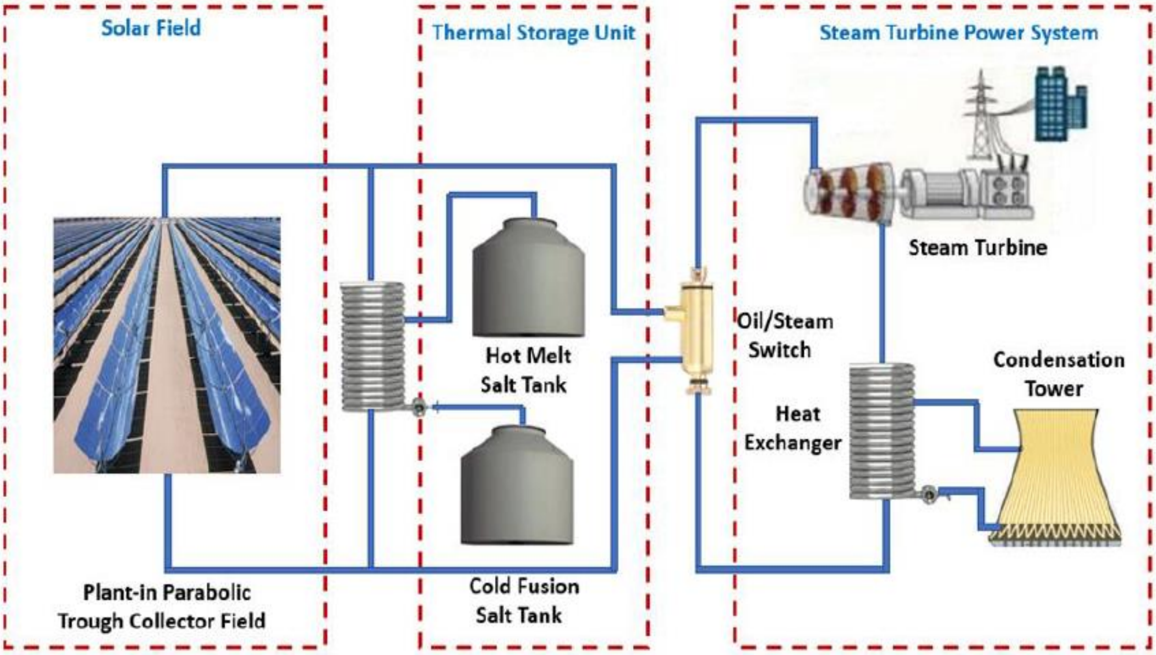

Fig. 5. Schematic representation of concentrated solar power plant

7-1. CSP Plant Architecture and Role of Nanofluids

The transition from fossil fuels to intermittent renewable energy sources like solar necessitates robust energy storage solutions to ensure consistent power generation. Concentrated Solar Power (CSP) plants commonly utilize a two-tank molten salt system for thermal energy storage (TES), where cold salt is heated by solar energy and stored. During periods of no sunlight, heat exchangers use this stored energy to maintain plant operation [69]. CSP plants convert solar energy into electricity using concentrators like mirrors and lenses focusing on a receiver, Fig. 5. Different configurations, such as parabolic trough, Fresnel collector, tower, and parabolic dish systems, operate at varying temperatures (e.g., line-focusing 0–400°C, point-focusing 290–560°C), dictating the choice of heat transfer fluids and TES materials (69,70). Critical thermophysical properties of the storage medium, including specific heat, thermal conductivity, thermal stability, and viscosity, directly influence plant efficiency. Molten salts, particularly solar salt (42mol% KNO_3 and 58mol% $NaNO_3$), are widely used in two-tank sensible energy storage designs. While nitrate salts decompose around 600°C, limiting current TES systems to 560°C, molten carbonate salts offer significant advantages. They exhibit superior thermophysical properties, including enhanced specific heat, improved thermal stability, reduced vapor pressure, and decreased corrosion, making them suitable for high-temperature TES applications above 600°C [41,71]. Their use could reduce investment costs by minimizing required TES material and tank dimensions, thereby lowering the levelized cost of electricity. Thermal energy storage can occur via three mechanisms [67]: sensible heat storage (temperature change without phase change), latent heat storage (phase change at constant temperature, e.g., using phase change materials like Li_2CO_3-Na_2CO_3 with high enthalpy [72,73]), and thermochemical energy storage (chemical bond breaking/forming). Sensible heat storage is most common in CSP. While conventional thermal oils are often used for heat transfer, their flammability and cost, compared to molten salts' superior thermal stability, non-flammability, and lower environmental impact, advocate for greater molten salt adoption. Key factors for TES material selection include volumetric storage capacity, thermal conductivity, stability, and economic viability. Molten salt mixtures like Hitec XL salt (melting at 140°C) and KNO_3-$LiNO_3$-$Ca(NO_3)_2$ (melting at 80°C) offer broad operating ranges [74,75]. Carbonate molten salts are particularly promising for high-temperature sensible heat storage (400–850°C) due to their higher service temperature range, cost-effectiveness over fluorides, and fewer corrosive concerns than chlorides [68,73,76]. Corrosion mitigation strategies, including salt purification and inhibiting nanoparticles, are also being explored [68,77].

7-2. Geothermal and Enhanced Oil Recovery

Molten salt nanofluids show significant promise in enhanced oil recovery (EOR) and geothermal heat extraction. Geothermal fluids, such as mineral oil, interact with underground surfaces, leading to mineral saturation, which presents a challenge in oil recovery from shale or hydrate-bearing sediments [78-81]. EOR's thermal recovery methods increase reservoir temperature to reduce crude oil viscosity and vaporize a fraction, facilitating recovery by decreasing the oil's mobility ratio. Techniques include steam flooding, in-situ combustion, electrical heating, and notably, nanofluid flooding. Molten salt nanofluids are highly suitable for nanofluid flooding due to their exceptional stability in harsh underground environments characterized by elevated temperatures, high shear stresses, pressures, and salinity. Further research is needed on using molten salt-based nanofluids, including those with silica or hybrid nanoparticles (e.g., iron oxide, alumina, silica), across different sediment types. Combining molten salt nanofluids with nano-scaled catalysts also presents a promising, innovative oil recovery approach that warrants extensive experimental assessment. Beyond EOR, molten salt nanofluids, acting as thermal storage media, hold potential for geothermal heat extraction and conversion from oil reservoirs via heat exchangers or pipes, although this application requires more experimental work and numerical simulations [82].

7-3. Life Cycle and Environmental Assessments

A comprehensive Life Cycle Assessment (LCA) was conducted to evaluate the environmental impacts of molten salt nanofluids compared to base salts in thermal energy storage systems. Following ISO 14040 guidelines and using the SimaPro and EcoInvent databases, the analysis considered the full system life cycle-including synthesis (via the explosive wire method), nanoparticle incorporation, operation in solar energy systems, and end-of-life disposal. The study focused on a $(Li, Na, K)_2CO_3$-based salt with alumina nanoparticles and benchmarked it against the base molten salt. A 30-year lifespan was assumed, with system inputs drawn from real-world CSP facilities such as GEMASOLAR [83], Andasol-1, and Solana [70]. The inclusion of alumina nanoparticles increased specific heat capacity by 12%, enabling a proportional reduction in both salt mass and storage tank volume. Moreover, corrosion rates were halved, significantly decreasing material usage in system construction. Environmental impacts-evaluated through the IMPACT 2002+ methodology-highlighted key concerns such as global warming potential, non-renewable energy use, ecotoxicity, and health risks. These were mainly tied to energy-intensive manufacturing and operational phases. Although chloride salts exhibited lower environmental footprints, their poor thermophysical performance and high corrosiveness made them less suitable than the nanofluid studied [84]. A critical finding was that increased viscosity, driven by nanoparticle addition, caused a 10% rise in environmental impact-partially negating gains from enhanced heat capacity and corrosion resistance. Thus, the viscosity increase should not exceed 20% to maintain net environmental benefits. Overall, the base salt synthesis and nanoparticle handling were dominant contributors to lifecycle impact. Careful control of viscosity and synthesis protocols is essential for optimizing the sustainability of molten salt nanofluid systems.

8. Limitations, Research Gaps, and Future Prospects

Despite notable advances, molten salt nanofluid technology faces a number of major challenges and unknowns:

- **Data scarcity and lack of standardization:** The field suffers from inconsistent reporting of nanoparticle morphology, preparation methods, and measurement protocols for key properties. Resulting difficulties in comparing results across studies have hampered the establishment of generalized, predictive models.
- **Scalability and reproducibility:** The leap from laboratory to industrial scale is complicated by energy-intensive procedures (e.g., ultrasonication, drying), inconsistent nanoparticle dispersion, and issues maintaining homogeneity in large volumes.
- **Mechanistic ambiguity:** The precise mechanisms underpinning specific heat and conductivity enhancement remain incompletely understood. Further numeric and molecular-level investigation is warranted, particularly concerning the nucleation, growth, and stability of secondary nanostructures and compressed layers.
- **Stability over time:** Long-term suspension stability remains a bottleneck. Research suggests blending vigorous mixing protocols (mechanical stirring, pumping) and surface functionalization for improved stability, but commercial solutions are yet to emerge.
- **Rheological challenges:** Excessive viscosity can defeat the purpose of improved thermophysical properties. New strategies for minimizing viscosity growth without sacrificing stability are an ongoing need.
- **Corrosion and material compatibility:** While some nanoparticle choices reduce corrosion, others can worsen it, particularly in the presence of bubbles, impurity ions, or poorly chosen salt compositions. In-depth studies of new salts, novel protective coatings, and advanced alloys are needed [85].
- **Economic and environmental analysis:** More thorough cost/benefit evaluations are necessary, balancing the capital expense (and potential toxicity) of nanoparticle production with operational gains. Life cycle assessment methodologies should be harmonized for consistent comparisons, especially vis-à-vis traditional solar salts or organic oils.

9. Conclusion

The field of molten salt nanofluids stands at an exciting juncture. Recent evidence demonstrates that, when successfully synthesized and stabilized, these fluids offer a substantial leap in the thermal energy storage and transfer capabilities of high-temperature power systems—especially concentrated solar power plants, industrial heat exchangers, and next-generation energy storage facilities. While progress toward industrial application is tangible, a set of unresolved scientific and engineering questions continue to shape the landscape. Notably, specific heat enhancement, while often spectacular, is neither universal nor entirely predictable, challenging researchers to deepen theoretical understanding through both molecular simulations and innovative laboratory methods. The synthesis method, nanoparticle choice and preparation, as well as system design parameters, must be approached holistically, considering not just short-term thermophysical gains but also long-term operational demands: stability, rheology, corrosion resistance, and environmental stewardship. The path forward involves standardizing measurement and preparation protocols, deepening mechanistic understanding, and continuously assessing life cycle impacts-ensuring that molten salt nanofluids become a reliable foundation for the future of sustainable, high-performance thermal energy storage.

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