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Molten salt composition and composites for improved latent heat thermal energy storage

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Abstract: The growing concern over nonrenewable fuel sources, coupled with the continued increase in global energy demand has incentivised research into numerous new and pre-existing renewable energy sources. Concentrated solar thermal (CST) takes advantage of the high heat capacity of molten salts to provide an alternative solar solution to photovoltaic cells that allows reduced downtime through heat storage for use during suboptimal conditions. This meta-study examines the effectiveness of various eutectic Molten Salt compositions and materials as thermo-physical augmenters, with a focus on improved thermal conductivity when composited with molten salts as a method of enhancing the efficiency of concentrated solar thermal storage technology. The study is based on literature retrieved from scientific databases to investigate information available about enhancing LHTES technology. Research into carbon composites such as Expanded Graphite (EG) exhibits promising results revealing thermal conductivity increases as high as 40% in eutectic salt materials, however, inconsistencies in measurements and materials used reveal a need for a greater analysis. Although molten salt thermal storage systems are not optimal in their current state, an indication was found that composite storage mediums could potentially solidify their spot as a viable renewable energy source.

Keywords: Molten Salt; Composite; Concentrated Solar Power; Latent Heat Thermal Energy Storage

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1. Introduction

Continuous and focused research into enhancing the efficiency of renewable energy systems is paramount due to the negative effects of non-renewable energy production on the environment. A significant aspect of renewable energy systems which plays a pivotal role in the future of renewable energy is thermal heat storage [1].

This meta-study focuses on Latent Heat Thermal Energy Storage (LHTES) utilising molten salt as the fluid used to collect, store and exchange heat to the commonly used Rankine cycle in CSP technology [2, 3]. Molten salt is known as an LHTES due to it being a Phase change material (PCM) meaning it has a high heat of fusion. This property allows the Molten Salt the ability to release and store large amounts of energy when the material transforms from a solid to liquid or the reverse process [1]. LHTES systems moreover achieve notably higher storage densities in comparison to other known methods such as sensible heat storage [4].

Previously, indirect storage systems utilising synthetic oil which incur many performance drawbacks were used in CSP technology as the heat transfer fluid. These drawbacks are due to the energy lost while transferring between collector and storage. Thus molten salt is utilised due to substantially greater physical properties, improvements in Rankine cycle efficiency and minimising collector area needed per MW, while simultaneously being low cost and contain the ability to be operating as both heat transfer fluid and the thermal storage medium [3]. Additionally, molten salt is favoured due to its high potential working temperature $\approx$ 500°c, low vapour pressure and corrosivity to avoid damage within the storage system, high heat capacity and superior thermal and physical properties over precious materials such as oil for higher energy storage and transfer [2].

Though molten salt shows great promise for the future of LHTES, currently utilised compositions including the popular "Solar Salt" used in California's 10MWe solar tower central receiver project and the indirect TES system at the Andosol Solar Power Station in Spain composed of 60wt%$NaNO_3$ and 40wt%KNO_3 are not yet thermodynamically efficient enough to solve the problem of renewable energy storage [2]. A primary reason for this being the salts moderately low thermal conductivity at the optimum hot salt temperature of concentrated solar plants 565°C, which is (0.470±0.3) W/mK for $NaNO_3$ and (0.334±0.4) $W/\mathrm{m}K$ for KNO_3 extrapolated from available data [5-7].

Employing alternate eutectic salt material composition and composite materials, however, could be the answer. The efficiency of the molten salt LHTES is characterised by a range of thermo-physical properties most importantly thermal stability, heat capacity, thermal conductivity and melting point, these properties directly effecting heat storage capacity and transfer rates [8]. Standard solar salts exhibit low thermal conductivity, therefore altering the material's thermo-physical properties to increase this, may prove to be very beneficial for various commercial applications including CSP technology [9]. Utilising composite materials such as a $NaNO_3$-KNO_3-EG (Expanded Graphite) mixture has shown an increase in thermal conductivity compared to the pure nitrate by about 10-20% and 30-40% for a 5wt% and 10% addition of EG respectively [10]. Moreover, the utilization of nanoparticles has been widely researched due to their known beneficial properties as a result of an abundance of surface area, allowing optimal conductive ability. When dispersed within a fluid considerable enhancements in thermal conductivity are documented [11]. This measures how well heat is conducted and propagated throughout the system. This property plays a sizeable role in efficiency; directly effecting heat exchange rates during charge and discharge process and melting point. Thus, techniques to alter this property could yield very beneficial results [9, 12, 13].

Nonstandard eutectic salt mixtures such as (K, $NaNO_2$, Cl, NO_3) have been tested to exhibit a melting point of 140°C where low melting point is an optimal characteristic to prevent freezing within the system, thermal stability was measured at 500°C and also 550°C for a short time which is also more favourable than the properties of standard "solar salt" [2]. To put these enhancements into perspective, an increase in Rankine cycle efficiency of the power block steam turbine from just 37.6% - 40% would create a reduction in levelised energy cost by 2cent/kWh [2].

Various attempts to develop materials with close to optimal thermal conductivity for use in an array of thermal energy storage systems have been undertaken in the past. CONTEST & WESPE are two research programs that utilised ceramic or concrete media reinforced by stainless steel to increase thermal conductivity. However, storage capacity proved too low, furthermore charge and discharge temperatures triggered structural degradation and complications regarding thermal regulation [14]. Another project pursuing enhanced latent heat storage through PCM's is the DISTOR project, which attempted to discover a PCM with low cost, high storage capacity, stability and thermal conductivity at a range at 8W/mK. This is in comparison to the current $\approx$1W/mK of solar salt, as well as low environmental impact and high availability although they have yet to be successful [14]. This meta-study attempts to reveal and make a clear comparison between current technological developments to display the current state and progress of Molten Salt latent heat thermal energy storage technology.

This meta-study does not take into consideration political, social, ecological and legal factors behind the research conducted on molten salt LHETS. It is limited however to the thermodynamics associated with molten salt with slight consideration taken into the economics of applying these systems due to monetary implications playing a deciding factor in the future of this technology.

2. Methods

This meta-study was conducted utilising research published in databases such as Science direct (Elsevier), Medline (OVID), PubMed Central (PCM) and the Beilstein Journal of Nanotechnology. The Articles and Journals used for reference regarding new developments in the thermodynamic processes of Molten salt thermal energy storage systems were restricted to the last ten years for the relevance of data, background information and definitions, however, utilise a variety of sources.

This meta-study attempts to identify the most optimal thermo-physical characteristics of Molten Salt material for use in CSP technology through material composition. This technology has only begun to substantially develop commercially in the last ten years, thus this restriction aids in maintaining a quality in the information presented due to most serious and up to date research being conducted during this time. Background information and details on the current state of commercial CSP technology was gathered from the National Renewable Energy Laboratory (NREL) and the Deutsche Zentrum für Luft- und Raumfahrt (DLR) institute of solar research [15, 16].

Political, social, ecological and legal factors were not taken into consideration in this Meta study, limiting research to the thermodynamics of molten salts and composites with slight consideration taken into the economics of this technology. This meta-study's scope is comprised of an investigation into thermo-physical properties including thermal conductivity, heat capacity, melting point, operating temperature, energy density of known materials and composites for molten salt LHTES technology, as well as issues regarding their implementation, and potential advancements in this technology.

3. Results and Discussion

3.1 Inconsistencies in thermo-physical property calculation methods.

Many different practical, theoretical and numerical methods for calculating the thermo-physical properties of molten salt and its constituents, as well as potential composites and their mixture exists. This is clear in the research conducted in this field as there is very little consistency between the methods used to derive these values. Variations constantly occur in the results of the same properties of materials which in theory should be almost identical taking into consider the variations in the purity of the materials used [3, 7, 9, 14]. Bauera [8] and his team found a ±7% and ±15% variation in data for heat capacity, and thermal diffusivity and conductivity of solar salt respectively compared to previously calculated values revealing inconsistency with tested results. For example, the maximum thermal stability in the aforementioned study was discovered to be significantly lower than that of the solar two project in Albuquerque [17]. For real-world applicability of this research, experiments must attempt to be consistent to avoid complications such as under or oversized molten salt storage systems which can be caused by poor heat capacity values. The DLR Institute of Solar Research is conducting continuous research in this field to combat these issues [16]. Although inconsistencies exist, these values must still be taken into consideration despite the comparison between research papers being imperfect, this may, however, harm the validity of the information presented in these paper, potentially impairing the development and progression of this technology.

3.2 Enhancements to thermo-physical properties of eutectic molten salt via metal foam composites

Metal foam is widely considered due to positive mechanical and thermo-physical properties, mainly low density and high thermal conductivity [9]. The foams furthermore won't increase material weight due to high open porosity, creating low bulk density, high strength, stiffness and particularly an increase in thermal conductivity due to the graphite skeleton. Eutectic Salt composed of (50wt% $NaNO_3$ and 50wt% KNO_3) demonstrating a melting temperature of 220°C was researched by Zhang and their team. Copper foam and nickel foam were used as different composites both demonstrating approximately 96% porosity. Heat storage tests at 240°C and 260°C were both conducted in this study and heat retrieval tests were conducted at cooling temps of 30°C-110°C, this is due to the difference in thermo-physical characteristics at different temperatures [14].

Table 1. *Thermo-physical properties and improvements of metal foams extracted from a study by Zhang [9].©*

Property/enhancement	**Copper Foam**	**Nickel Foam**
ε	96.54	97.48
ρ_s (kg/m^3)	8930	8900
k (W/m K)	398	91.4
C_{ps} (J/kg K)	386	444
Reduction in Heat storage rate when composited	21.6%	12.2%
Reduction in Heat retrieval rate when composited	28.8%	19.3%

In Table 1, the extracted data for both the Copper and Nickel exhibited improvements in the salts heat charge and discharge rates due to the enhanced thermal conductivity of the metal skeleton. However, it was stated that heat calculations could be impaired due to non-equilibrium temperatures between salt and metal foam at 6.8°C for copper and 4.4°C for Nickel. This, however, depicts considerable improvements in performance, output power and heat storage/retrieval rates of LHTESs when composited with Copper and Nickel foam. The Copper foam salt composite ultimately performed better than the Nickel due to higher thermal conductivity enhancement, although unfortunately, the drawback of this composite is its high corrosive property which will need to be addressed during the production of the storage system to avoid damage [9]. Alternate studies on Nickel foam composite combined with a Molten Salt which in its purest form displayed the same 220°C solid-liquid temperature, revealed a 25% reduction in charge time and a 23.3% reduction in discharge time which was stated to be directly correlated to an improvement in thermal conductivity. The composite furthermore did not significantly impair the heat capacity of the molten salt due to the high thermal conductivity and porosity of the Nickel, revealing its ability to magnify thermo-physical properties in Molten Salt with minimal repercussions [9].

3.3 Improvement in efficiency through nanofluid enhancement

As technology advances, light is constantly being shed on the remarkable properties of nanoparticles including their ability to enhance the thermal properties of heat transfer fluids when injected at even small doses [18]. Thus many research teams have attempted to enhance the heat capacity of thermal storage devices utilising an array of nanoparticles, varying in size and concentration.

Table 2. *Heat capacity enhancement via nanoparticles in various Molten Salt compositions compiled from numerous sources [19-30].©*

Salt	**Nanoparticle**	**Increase in Heat Capacity (Cp)**
62wt%Li_2CO_3 + 38wt%K_2CO_3	SiO_2 (10nm), 1% wt.	+19% to +24%
34wt%$BaCl_2$ + 13wt%NaCl + 40wt%$CaCl_2$ + 13wt%LiCl	SiO_2, 1% wt.	+14.5%
60wt%$NaNO_3$ +40wt%KNO_3	Al_2O_3 (13nm, 90nm), 0.9% to 4.6% wt.	-10% and 4.6%
62wt%Li2CO_3 + 38wt%K_2CO_3	SiO_2 (5 to 6nm), 1% wt.	+23% to +29%
62wt%Li2CO_3 + 38wt%K_2CO_3	SiO_2 (10nm), 1% wt.	+26%
62wt%Li2CO_3 + 38wt%K_2CO_3	SiO_2 (2 to 20nm), 1% wt.	+3%
60wt%Li2CO_3 + 40wt%K_2CO_3	SiO_2 (5 nm, 10 nm, 30 nm, 60 nm), 1% wt.	+10% (5nm) +13% (10nm), +21% (30nm), +28% (60nm)
60wt%$NaNO_3$ +40wt%KNO_3	SiO_2 (7nm), Al_2O_3 (13nm), TiO_2 (20nm), SiO_2 + Al_2O_3(2 to 200 nm), 0.5% to 1.5% wt.	+22.5% (SiO2 + Al_2O_3 (2 to 200 nm 1.0% wt.))
62wt%Li2CO_3 + 38wt%K_2CO_3	Graphite (50nm) + gum arabic	+100% (material 1), +33% (material 2)
62wt%Li2CO_3 + 38wt%K_2CO_3	Al_2O_3 (10nm), 1% wt.	+32%
7wt%$NaNO_3$+ 53wt%KNO_3 + 40wt%$NaNO_2$	Al_2O_3 (<50nm), 0.016% to 1% wt.	+19.9% (0.063% wt.)
60wt%$NaNO_3$ +40wt%KNO_3	SiO_2 (12nm), 0.5% to 2.0% wt.	+25% (1.0% wt.)

The results in Table. 2 show a consistent increase in heat capacity though the addition of the nanoparticles used with the exception of a 0.9% concentration of 13nm Al_2O_3, an increase in the size of the 77nm, however, revealed a positive increase, indicating a relationship between heat capacity improvement and particle size [30]. Andreu and her team's contribution claiming the last result displayed in Table. 2 revealed an optimum concentration for the 12nm SiO_2 nanoparticle at 1.0%wt, obtaining a 25% enhancement in heat capacity at 250°C-420°C. The aforementioned study furthermore confirmed; using TGA measurements at up to 750°C, the high temperature stability of the nanofluids, exhibiting strong characteristics for utilisation as LHTES enhancement. The largest increase in heat capacity, however, was induced by the 50nm Graphite, indicating Graphite as a powerful thermal conductivity enhancer.

Various methods of composite enhancement utilising carbon based materials exist, including conductive fins, oriented or random carbon fibers, metal dispersion, carbon nanofiber dispersion and expanded graphite (EG). Nonetheless, only EG displays drastic thermal conductivity augmentation, exhibiting an increase in the thermal conductivity of Paraffin from 0.24W/mK to 70W/mK [14]. Although these results are promising and indicate the potential of EG as a very beneficial composite, more studies need to be conducted to reinforce these effects on various nitrate compositions for CSP thermal energy storage. A study administered on a $NaNO_3$-KNO_3-EG (Expanded Graphite) mixture displayed an increase in thermal conductivity compared to the pure nitrate by about 10-20% and 30-40% for a 5wt% addition of Graphite and 10wt% addition respectively, this being quite a substantial improvement, revealing EG as a very suitable composite for thermo-physical enhancement [10]. X. Xiao Lists the constituent thermal conductivities as being 0.797 for the sodium nitrate, 0.691 for the Potassium nitrate and 160.211 for the graphite all values in W/mK calculated using the Maxwell-eucken Model. The melting temperature was also reduced by 5-18% for the 10%-EG concentration.

Pincemin conducted experiments at temperatures ranging from approximately 50°C to 200°C on a eutectic salt of NaNO3-KNO3 composited with four different types of industrial grade graphite seen in Table. 3 [14]. The thermal conductivity (k) of these new composited molten salts were recorded across this range to determine the thermal conductivity at a higher operational temperature and the difference between results at higher and lower temperatures. This range is recorded due to the dependence of thermal conductivity on temperature, meaning to achieve significant results tests must be conducted near operational temperature [14].

Table 3. *This table was assembled to compare the thermal conductivity at a high and low temperature and calculated percentage drop in thermal conductivity. The first value in the graphite name represents particle size in micrometers, the second value represents the concentration.©*

Composite Material	k at 50°C (W/m K)	k at 200°C (W/m K)	Drop in k (%)
SFG/75/5	≈3.9	≈2.8	≈28
NG/400/22	≈7.0	≈4.2	≈40
SFG/75/30	≈7.8	≈4.5	≈42
GFG/500/21	≈9.3	≈6.2	≈33

The variation in values from 50°C-200°C identified in Table. 3 are substantially large and must be taken into consideration for the design and estimated efficiency of the LHTES. The GFG/500/21 composite is revealed to augment the base salt to the highest thermal conductivity, with a relatively low drop with respect to temperature drop [14].

3.4 Alternative eutectic salt composition in LHTES

For pure eutectic molten salt composition, the focus shifts to energy storage density, melting point and heat capacity as thermal conductivity variations are almost negligible. The melting point and working temperature play a considerable role as salt solidification inside the system can create substantial issues [31]. Current contenders for thermal energy storage mediums are solar salt, HITEC, HITEC XL and Therminol VP-1 seen in the Table. 4.

Table 4. *Common heat transfer fluids used in commercial applications, VP-1 is a synthetic heat transfer fluid [31-34].©*

Salt	Composition	$T_{melting}$ (°C)	C_{heat} (J/g K)	e (MJ/m^3)	k (W/m K)
Solar Salt	$NaNO_3$ (60%) + KNO_3(40%)	220	1.5(280°C)	756	0.76(30°C)
HITEC	KNO_3(53%) + $NaNO_3$(7%) + $NaNO_2$ (40%)	142	1.57(182°C)	876	0.74(30°C)
HITEC XL	$Ca(NO_3)_2$(48%) + $NaNO_3$(7%) + KNO_3(45%)	133	1.44(300°C)	n/a	0.52 (300°C)
Therminol VP-1	$C_{12}H_{10}O$ (73.5%) + $C_{12}H_{10}$ (26.5%)	12	2.32(300°C)	n/a	0.15(30°C)

Improvements can always be made and a considerable amount of work is going into discovering a new more thermodynamically optimal eutectic salt composition for use in CSP technology to enhance efficiency.

Table 5. *Values extrapolated for thermodynamic properties of eutectic salt compositions [35]*

Salt	**Melting temp (°C)**	**Heat capacity at 600°C (J/g K)**	**Energy density (MJ/m^3)**
$LiNO_3$-$NaNO_3$-KNO_3	116	1.7	1162
$NaNO_3$- $NaNO_2$- KNO_3	123.8	1.68	1135
$LiNO_3$- $NaNO_3$- KNO_3-MgKN	98.6	1.55	1099
$LiNO_3$- $NaNO_3$- KNO_3-$NaNO_2$	98.6	1.66	1189
$LiNO_3$- $NaNO_3$- $NaNO_2$-KNO_3- KNO_2	95.7	1.7	1232
$LiNO_3$-$NaNO_3$-KNO_3-KNO_2	100	1.63	1174
$LiNO_3$-KNO_3-$NaNO_2$-KNO_2	108.1	1.67	1183
$LiNO_3$-KNO_3-$NaNO_2$-$Mg(NO_3)_2$	100.8	1.68	1192
$LiNO_3$-$NaNO_3$-KNO_3-$Mg(NO_3)_2$-MgK	103.6	1.7	1242

A correlation between composition and melting temperature, heat capacity and energy density can be seen in Table. 5. The $LiNO_3$- $NaNO_3$- $NaNO_2$-KNO_3- KNO_2 displayed the greatest improvement, decreasing melting temperature from standard solar salt by 104.3°C which would be very beneficial in an industrial CSP plant to avoid solidification within the system which can cause substantial damage. Heat capacity and Energy density were also measured to be higher than that of Solar Salt, which would increase heat storage and efficiency.

4. Conclusions

Previous studies on the thermos-physical properties of molten salt have shown strong inconsistencies and varying results, revealing a need for more accurate and definitive results for the development of the most optimal thermal energy storage systems.

The nanocomposites displayed great promise as thermo-physical augmenters in LHTES systems, producing a large increase in specific heat capacity in various molten salts and reducing costs in the production of CSP systems. For immediate application, the metal foams have sufficient research to begin the stages of implementation into LHTES technology to improve the thermos-physical properties outlined in the study. However, carbon materials such as EG and GFG/500/21 have shown the most promising composite enhancement properties due to its high thermal and electrical conductivity, low density, favourable thermo-chemical stability and compatibility with PCMs, thus further and more focused research into their effects in Molten Salt LHTES systems as composites could prove very beneficial to the industry[10, 14]. The exact characteristic of the nanoparticles ability to enhance these beneficial properties has yet to be identified. The discovery and manipulation of these properties would lead to the cost and power efficiency of these systems could be substantially increased.

These composite materials, however, will most likely have unexpected effects on the corrosiveness of the overall material which could compromise the whole operating system the molten salt works in, thus these effects must be tested and taken into consideration.

Alternate eutectic Molten Salt material may also lead to a more optimal LHTES system in the future, it has been shown that melting point, heat capacity, and energy density can be optimized depending on the composition of the material. Economically, however, the increase in efficiency will not benefit the overall progression of this technology if the cost of the material far outweighs the reduction in the cost of energy production. Thus, affordable materials must be considered if the technology wishes to continue to grow and be used commercially for wide-scale energy production. Otherwise, this Meta-Study has revealed that composite materials display much greater enhancements over that which would be achieved through changes in the base composition. Thus, as Solar Salt is already currently widely used, at this time the addition of composite material would enhance LHTES systems greater than changing the base material entirely. However, together these alterations could push large scale development of CSP technology over alternative energy producing methods.

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