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Optimal concentration of alumina nanoparticles in molten Hitec salt to maximize its specific heat capacity

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ABSTRACT

The investigation experimentally studies the optimal concentration of alumina nanoparticles in doped molten Hitec that maximizes its specific heat capacity. A simplified model of the interfacial area is developed to explain the optimal concentration. The specific heat capacities of pure Hitec and nano-Hitec fluid are measured using a differential scanning calorimeter (DSC), and the microstructures following solidification are observed using a scanning electron microscope (SEM). A novel sampling apparatus and process for preparing molten Hitec nanofluids were developed to prevent the precipitation of nanoparticles. An optimal concentration of 0.063 wt.% is identified as yielding the greatest enhancement of specific heat capacity of 19.9%. At a concentration of 2 wt.%, the detrimental effect of the dopant nanoparticles on the specific heat capacity is evident at all temperatures. The negative effect is more significant than that predicted by the thermal equilibrium model. The SEM images following the solidification of samples and the developed model reveal the uniform dispersion of nanoparticles with negligible agglomeration at concentrations of under 0.016 wt.%. The agglomeration becomes significant and the particle clusters seem to be inter-connected at high concentrations. Moreover, the optimal concentration is approximately the concentration at which the contributions of isolated particles and clusters of sizes from 0.2 to 0.6 μm in the interfacial area to the specific heat capacity are equal.

1. Introduction

Like photovoltaic systems, concentrating solar power systems (CSP) effectively supply renewable energy to help reduce global carbon dioxide emissions. For example, the DESERTEC solar thermal power project, associated with a group of 12 companies in Africa and Europe, aims to meet as much as 15% of European electricity demand by 2050 using amount of renewable solar energy from the desert in North Africa [1]. A solar thermal power plant requires effective energy storage and so the working fluid critically affects its performance. High-temperature molten salt typically has a high heat capacity and is effective as a working fluid for CSP systems [2,3]. Kearney et al. [4] noted that molten salt can increase electrical efficiency and reduce the levelized cost of electricity. However, the high freezing point of molten salt may result in its solidification on a cloudy day or at night.

Some studies of the fluid flow and heat transfer of molten salts have been published. Kungi et al. [5] revealed that the molten salt exhibits poor heat transfer performance resulting in which cause non-uniform heating and laminarization phenomena. Wu et al. [6] experimentally investigated heat transfer characteristics of molten salt ($LiNO_3$) in a circular tube, and compared them with well-known empirical results. They found that the correlations of Sieder-Tate, Petukhov and Hausen agree closely with their experimental data for Prandtl numbers from 0.7 to 59.9. Wu et al. [7] determined the heat transfer coefficient for the turbulent and transition flows of molten Hitec salt (53% KNO_3 – 40%$NaNO_2$ – 7%$NaNO_3$, mol.%) in a circular tube. The correlation of Hausen and Gnielinski agreed closely well with their data on transition flow and the correlation of Sieder-Tate agreed excellently with their data on turbulent flow.

Molten salt normally exhibits with low thermal conductivity, and effectively improving its thermal properties is of great interest. Several studies [8–10] utilized alternative heat transfer salt, i.e., Hitec, experimentally to simulate lithium-beryllium fluoride salt (FLiBe) in a molten salt flow loop, and developed a packed-bed channel to enhance the heat transfer performance of Hitec flow. Their experimental results demonstrated that adding stainless steel spheres effectively enhanced heat transfer performance but also clear obviously increased the pressure drop in a circular tube. Yang et al. [11] experimentally demonstrated that the Nusselt

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Nomenclature

A_t	total interfacial area, m^2
C	concentration, wt.%
C_p	specific heat capacity, kJ/kg K
d_c	diameter of cluster, m
d_p	diameter of nanoparticle, m
N_c	number of clusters
N_p	number of isolated particles
$N_{p,count}$	number of isolated particles determined from SEM image
N_t	total number of nanoparticles
$m_{p,t}$	total weight of particles, kg
$m_{p,i}$	weight of single nanoparticle, kg
m_{salt}	weight of Hitec eutectic, kg

Greek symbols

ρ	density, kg/m^3
φ	volume of isolated particles as fraction of total solid volume

Subscripts

f	base fluid
max	maximum
nf	nanofluid
p	nanoparticle

numbers of Hitec that flows in a spiral surface on the tube of such a tube are on average three times those of Hitec in smooth tubes.

In 1902, Maxwell [12] proposed enhancing the thermal conductivity of fluids by dispersing solid particles with diameter of the order of millimeters or micrometer with high thermal conductivity. The experimental study of Hamilton and Crosser [13] confirmed this Maxwell's theoretical prediction, and determined that the geometry of particles considerably influenced their thermal conductivity. Choi and Eastman [14] were first to reveal the abnormal enhancement of the thermal conductivity of liquid by doping with nanometer scale particles and they called such a fluid that contained nanoparticles "nanofluids". Numerous investigations have reported similar thermal enhancements of nanofluids [15–18]. The mechanisms of enhancement of the effective thermal conductivity of nanofluids include the Brownian motion, aggregation, the shape effect of nanoparticles and layer of the solid–liquid interfaces [19–22]. The enhancement of thermal conductivity depends strongly on the size, shape, concentration and dispersion of nanoparticle, the fluid temperature and the surface area of the solid–liquid interface [23–27].

The literatures include some investigations of the specific heat capacity of nanofluids. Wang et al. [28] used mathematical models of statistical thermodynamics to examine the specific heat capacity of nanoparticles. They found that it increased as the size of the particles was reduced to the nanoscale. For example, the specific heat capacity of nanoscale CuO particles exceeds that of coarse particles above 225 K. The experimental results by Wang et al. [29] demonstrated that the specific heat of Al_2O_3 particles in nanoscale was increased around 15% in the temperature range 200 to 370 K, and especially at higher temperatures within that range. Snow et al. [30] shows that the specific heat capacity of 13 nm hematite (α-Fe_2O_3) was higher than that of bulk particles with temperature is increased. Nieto de Castro et al. [31] reported that the specific heat capacity of ionic fluid that was doped with multiwall carbon nanotubes was anomalously enhanced at temperatures between 60 and 90 °C. Nelson and Banerjee [32] observed that the dispersion of graphite nanoparticles (0.6 and 0.3 wt.%) in polyalphaolefin increased its specific heat capacity by approximately 50%. Conversely, several studies have reported doping with nanoparticles reduced its specific heat capacity. For example, Zhou and Ni [33] and O'Hanley et al. [34] found that the specific heat capacity of nanofluid falls as the concentration of nanoparticles increases between 20 and 55 °C. This finding is consistent with predictions based on the mixing theory based on the assumption of thermal equilibrium between particles and fluid. This thermal equilibrium model can be expressed as [35]:

$$Cp_{nf} = \frac{\phi(\rho_n Cp_n) + (1-\phi)(\rho_f Cp_f)}{\phi\rho_n + (1-\phi)\rho_f} \quad (1)$$

where Cp is the specific heat capacity, ϕ is the volume fraction of nanoparticles, and the subscripts nf, f, n, refer to the nanofluid, base fluid and nanoparticle, respectively. The studies of above mentioned literature reveal that particle size and operating temperature may be the significant factors affecting the specific heat capacity of nanofluid.

Bridges et al. [36] studied the specific heat capacity of the ionic liquid with that doped nanoparticles of Al_2O_3. Their results reveal that the specific heat capacity of ionic liquid with doped nanoparticles of Al_2O_3 is enhanced about 30%. Shin and Banerjee [37–41] and Tiznobaik and Shin [42] investigated the specific heat capacity of carbonate and alkali chloride salts with dispersed nanoparticles of SiO_2. They found that the specific heat of molten salt nanofluid was enhanced by 15–124% for concentrations from 1 to 1.5 wt.%, respectively. Shin and Banerjee proposed three mechanisms of this anomalous enhancement, including the size effect of nanoparticles and the high thermal resistance between solid–fluid interfaces and the semi-solid layer around the nanoparticles. Special needle-like structures and a percolation network in the salt eutectic have been observed in the scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images of solidified molten salts with nanoparticles [37,42], in which the needle-like structures may be formed by the effect of thermophoresis on the semi-solid layers. Jung et al. [43,44] developed a simple analytical model for the specific heat capacity of water-based nanofluid and alkaline metal carbonate salt eutectic mixture with dispersed nanoparticles with different geometries. The model proposed that the density, size and geometry of the nanoparticle and the compressed phase at the solid–liquid interface are significant factors for the enhancement of specific heat capacity of nanofluid. Dudda and Shin [45] showed that the dispersion of SiO_2 nanoparticle of size 5, 10, 30, 60 nm in binary nitrate eutectic increased its specific heat capacity by 8–24% in liquid state.

The present study investigates the optimal concentration of dopant nanoparticles that maximizes the specific heat capacity of molten salt (Hitec). Hitec (53%KNO_3 + 40%$NaNO_2$ + 7%$NaNO_3$, mol.%), a nitrate salt, is the base fluid that is used in this study, and the suspended nanoparticles are Al_2O_3. The nano-Hitec fluid in this study has no surfactant, allowing possible agglomeration and precipitation of nanoparticles. To solve these problems, an innovative sampling rig for preparing a high-temperature molten was developed. Uniform and reproducible molten salt nanofluids were made in a high-temperature sampling process. The specific