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INFLUENCE OF ADDITIVE NaCl ON THE PHASE-CHANGE HEAT TRANSFER AND STORAGE CAPACITY OF $NaNO_3$–KNO_3 MIXTURE

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ABSTRACT

Efficient absorption and storage of heat is indispensable to achieve continuous utilization of low-grade energies. Molten salts are deemed as one of the most suitable materials for high-temperature heat storage. In this paper eutectic $NaNO_3$–KNO_3 mixed salts were prepared as base material, and NaCl was used as additives to lower the salt mixtures' melting temperatures and consequently to extend their use temperature ranges. Major thermal properties of the mixtures are characterized using Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimetry (DSC). Here we find that the smelting temperatures of the salt mixtures are approximately 10℃ lower than that of the pure solar salt. The addition of a limited amount of NaCl causes no significant deterioration to the latent heats. The decomposition temperatures basically decrease with the amount of NaCl added at identical weight losses. In the temperature interval 280–380℃ the specific heat capacities decrease gradually with the temperature. It reveals that the NaCl additive plays a positive role in improving the thermal properties of the $NaNO_3$–KNO_3 mixtures for phase-change heat transfer and storage.

Keywords: thermal energy storage; latent heat; phase-change heat transfer; $NaNO_3$–KNO_3 mixture; NaCl additive

1. INTRODUCTION

With the rapid development of modern industry and the steady increase of residential spending, shortage and pollution of fossil fuels are becoming one of the most formidable global issues in our society. This situation has long urged us to exploit clean and renewable energy sources. Among the alternatives, efficient utilization of solar radiation is regarded as a prospective approach in many parts of the world, owing to its excellent versatility in applications [1–3]. Recent studies on solar energy utilization are focused on the thermal power generation and the thermal hydrogen chemical reaction [4]. However, the large-scale thermal utilization of solar energy is possible only if the problem of intermittent and unsteady supply is solved with acceptable capital and running costs.

Heat storage is proved to be an effective method to provide continuous energy supply for a solar thermal utilization system, especially for a solar thermal power plant to match the electrical output for peak and off-peak demands [5,6]. One prospective technique for storing thermal energy is the application of phase change materials (PCMs) [7–10]. These materials can promote the performance of solar heat absorption and storage systems to a large extent. Inorganic molten salts, a major kind of PCMs, have wide use temperature range, high heat conductivity, low viscosity, low cost, and good compatibility with metal materials and pipes [11]. They are regarded as the most mature media for heat transfer and storage with phase change in practical applications [12,13]. Further investigations found that two sorts of nitrate molten salt mixtures, solar salt (60% $NaNO_3$ – 40% KNO_3) and HITEC (7% $NaNO_3$ – 53% KNO_3 – 40% $NaNO_2$), are particularly suitable for concentrating solar power. For example, the solar salt with 220℃ melting temperature and 600℃ maximum service temperature was adopted in Solar Two generation [5], which demonstrated its feasibility, reliability and good economy as a heat transfer and storage medium [14,15]. Successful applications of inorganic molten salts in parabolic trough solar power plants as heat transfer fluid were also reported [16–18].

Lowering the melting temperature of an inorganic molten salt mixture would improve its performance efficiency by expanding use temperature range, as well as providing operational convenience and quality security [19]. For this purpose, we use eutectic solar salt as base material, and add a limited amount of NaCl into it to decrease its melting temperature. Thus a new kind of modified salt mixture is prepared in this study. Major thermal properties of these salt mixtures are measured with Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimetry (DSC) to characterize their performance as phase-change heat transfer and storage media.

2. EXPERIMENTAL

Inorganic salts ($NaNO_3$, KNO_3, NaCl) produced by Guangdong Xilong Fine Chemicals Co., Ltd. were used as the experimental materials to prepare the molten salt mixtures. The parameters of these salts are shown in Tab. 1.

After the pure salts were dried and ground thoroughly, eleven groups of salt mixtures were prepared according to the contents listed in Tab.2. Each salt mixture was heated to melting in an electric furnace at constant power, and then was

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maintained for 2–3 h to produce homogeneous liquidus mixture. After naturally cooled to room temperature, the mixture was crushed and sealed in cool and dry place for test. Thermal properties, such as the melting temperature, phase-change latent heat, can be tested by Simultaneous DSC-TGA Instrument SDT Q600 (TA Instruments.US). Alumina crucibles were used. The tested amount of molten salts was 10–20 mg, and the temperature range was 50–700℃ with a heating rate of 20℃ per minute.

Tab.1 The relevant parameters of the salts used.

Salts	Melting temperature (℃)	Relative molecular mass	Purity (%)
$NaNO_3$	307	84.99	≥99.0
KNO_3	334	101.10	≥99.0
NaCl	801	58.44	≥99.5

Tab.2 The contents of the salt mixtures studied.

NaCl (%)	$NaNO_3$ (%)	KNO_3 (%)
1	59.4	39.6
2	58.8	39.2
3	58.2	38.8
4	57.6	38.4
5	57.0	38.0
6	56.4	37.6
7	55.8	37.2
8	55.2	36.8
9	54.6	36.4
10	54.0	36.0

3. RESULTS AND DISCUSSION

Fig.1 and Fig.2 give the TG and DSC curves of the eutectic $NaNO_3$–KNO_3 mixtures with 1% and 5% NaCl additive, respectively. These two TG curves are quite similar in shape, and both begin to descend markedly from about 600℃. The higher the temperature, the more rapidly the weight loss decreases. However, there is a distinct difference between the DSC curves: Fig.2 (b) has a small wave trough at 150–200℃ before melting. The reason may be that the salt mixture melted incongruently when the NaCl additive was up to 5%. Moreover, melting temperatures and latent heats of the salt mixtures are extracted from the DSC curves.

Fig.3 shows the melting temperatures of the salt mixtures with NaCl additive amount from 1% to 10%, and also the melting temperature of the pure eutectic solar salt is provided as reference. It is clear that the melting temperatures of the salt mixtures with NaCl additive all decreased considerably. They are around 209℃, lower than that of the pure Solar Salt (about 220℃). The lowest melting temperature is 209.14℃, achieved at the case with 9% NaCl additive. When the molten salt mixture is employed in a solar thermal energy storage system, lower melting temperature will be helpful to avoid clotting in pipes, reduce heat loss and cut down insulation cost.

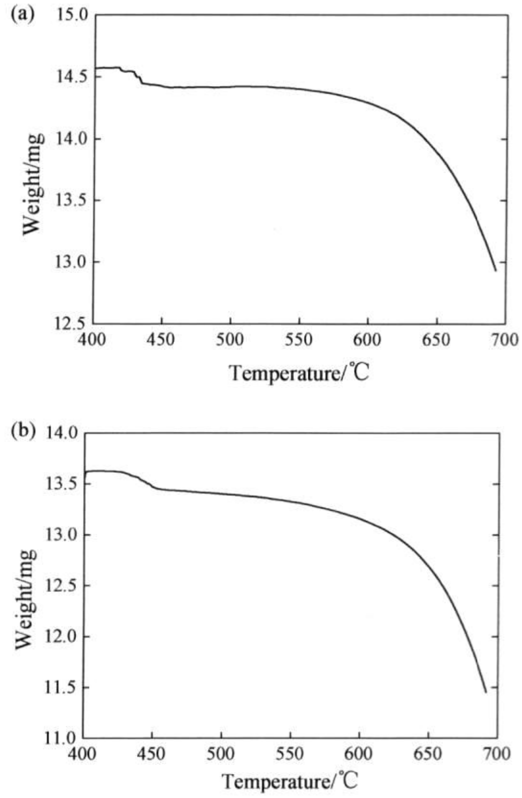

Fig.1 TG curves of the salt mixtures: (a) with 1% NaCl additive; (b) with 5% NaCl additive.

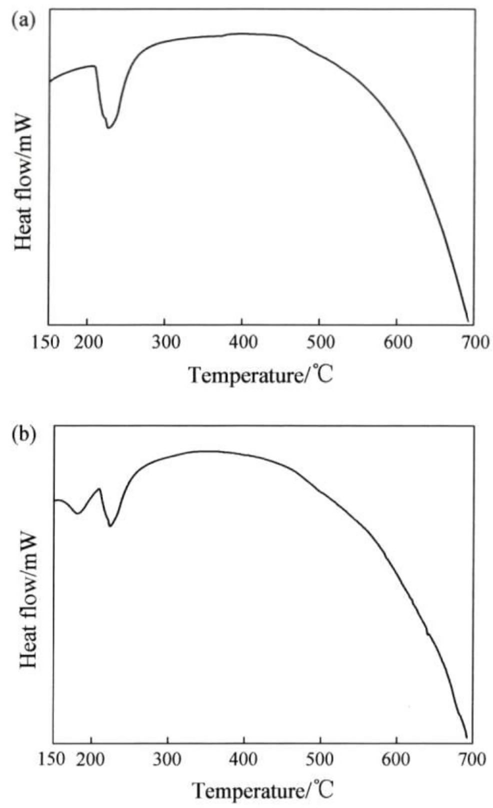

Fig.2 DSC curves of the salt mixtures: (a) with 1% NaCl additive; (b) with 5% NaCl additive.

Latent heat is the ratio of the absorbed heat to the salt mixture's mass during the phase change process of DSC test. Fig.4 presents the latent heats of the salt mixtures studied as well as the pure solar salt. As seen in the figure, the latent heats of the salt mixtures fluctuate around that of the pure solar salt. The maximum latent heat is 193.9 J/g, appeared at 9% NaCl additive. However, the 5% NaCl addition have the smallest latent heat, even lower than the pure Solar Salt. The salt mixtures with 1% and 6% NaCl also have relatively high latent heat, which are 190.8 J/g and 185.5 J/g respectively. It demonstrates that adding appropriate amount of NaCl to solar salt does not cause marked deterioration of its latent heat; contrarily, the additive may increase the values of latent heats to some extent.

Decomposition temperature is a paramount parameter that can characterize the thermal stability of a salt mixture, and is normally correlated to the weight loss in thermogravimetric test. Fig.5 shows the decomposition temperatures of the salt mixtures with different NaCl additions, in terms of the weight loss from 1% to 5%. The results demonstrate that the amount of NaCl additive has a pronounced effect on the decomposition temperature. Generally, at an identical weight loss the increase of NaCl lowers the decomposition temperature, except for the case with 4% NaCl addition whose values are close to those of 1% NaCl addition. Moreover, the decomposition temperatures approach to each other at bigger weight loss (for instance, 5%), revealing a reduced influence of NaCl additive on the salt mixture's thermal stability.

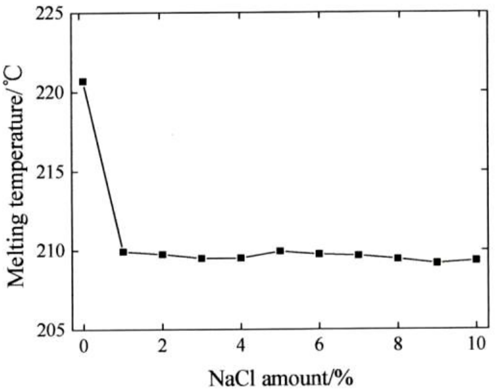

Fig.3 Melting temperatures of the salt mixtures with different amounts of NaCl.

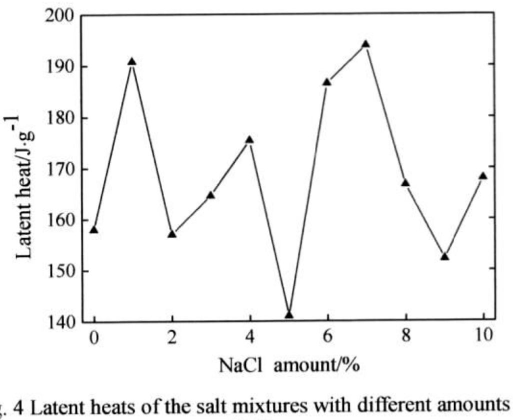

Fig. 4 Latent heats of the salt mixtures with different amounts of NaCl.

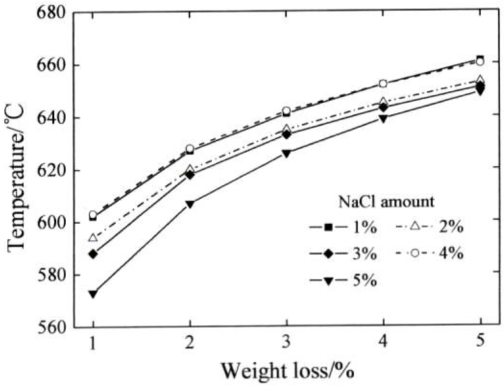

Fig.5 Decomposition temperatures versus weight losses for the salt mixtures with different amounts of NaCl additive.

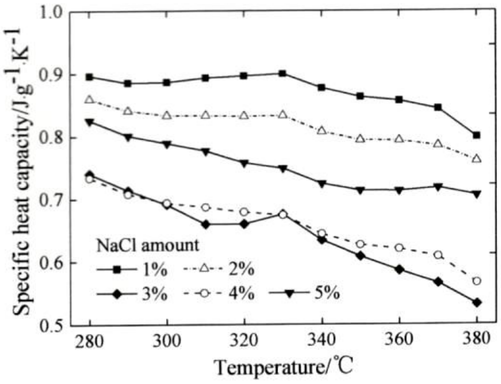

Fig.6 Specific heat capacities of the salt mixtures with different amounts of NaCl additive.

Specific heat capacity reflects the heat transfer and storage capacity of a salt mixture, which is a function of temperature and is also calculated from the DSC test. Fig. 6 gives the specific heat capacities of the salt mixtures with 1%–5% NaCl additive within 280–380℃. The reason for choosing this temperature interval is because the specific heat capacities of the salt mixtures begin to change since 280℃ during the melting process, and the use temperature of molten salt is normally below 380℃. From the figure, we find that in the above temperature interval the specific heat capacities of the salt mixtures minish with the temperature decrementally. The salt mixture with 1% NaCl additive has the biggest specific heat capacity, whereas the specific heat capacity of 3% NaCl additive is smaller than the other four groups at the same temperature.

4. CONCLUSIONS

In this paper a new kind of modified solar slat mixtures are prepared by blending a limited amount of NaCl as additive to enhance the ability to transfer and store heat. Major thermal properties of these mixtures are characterized through TGA and DSC tests. It is found that the smelting temperatures of the salt mixtures are approximately 10℃ lower than that of the pure solar salt, and the NaCl additive does not cause significant deterioration to the latent heats. The decomposition temperatures of the salt mixtures basically decrease with the amount of NaCl added at identical weight losses, and approach to each other at bigger weight loss. In temperature interval 280–380℃ the specific heat capacities of the salt mixtures decrease with the temperature gradually. Thus we can conclude that the NaCl additive plays a positive role in improving the thermal properties of the salt mixtures, and is certain to have a good application prospect in the field of high-temperature heat storage.

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REFERENCES

1. A. Medjelled, A. Benchatti, et al, Experimental model for the study of heat transfer in unsaturated soil: Case of underground thermal storage, *International Journal of Heat and Technology*, vol. 26, pp. 95-102, 2008.
2. M. Thirugnanasambandam, S. Iniyan, et al, A review of solar thermal technologies, *Renewable and Sustainable Energy Reviews*, vol. 14, pp. 312-322,2010.
3. K. H. Solangi, M. R. Islam, et al. A review on global solar energy policy, *Renewable and Sustainable Energy Reviews*, vol.15, pp.2149-2163, 2011.
4. M. Conte, A. lacobazzi, et al, Hydrogen economy for a sustainable development: state-of-the-art and technological perspectives, *Journal of Power Sources,* vol. 100, pp. 171-187, 2001.
5. U. Herrmann and D. W. Kearney, Survey of thermal energy storage for parabolic trough power plants, *Journal of Solar Energy Engineering*, vol. 124, pp. 145-152, 2002.
6. H. Michels and R. Pitz-Paal, Cascaded latent heat storage for parabolic trough solar power plants, *Solar Energy*, vol. 81, pp. 829-837, 2007.
7. A. Hoshĭ, D. R. Mills, et al, Screening of high melting point phase change materials (PCM) in solar thermal concentrating technology based on CLFR, *Solar Energy*, vol. 79, pp. 332-339, 2005.
8. A. F. Regin, S. C. Solanki, et al, Heat transfer characteristics of thermal energy storage system using PCM capsules: A review, *Renewable and Sustainable Energy Reviews*, vol. 12, pp. 2438-2458, 2008.
9. C. Y. Zhao and Z. G. Wu, Thermal property characterization of a low melting-temperature ternary nitrate salt mixture for thermal energy storage systems, *Solar Energy Materials and Solar Cells*, vol. 95, pp. 3341-3346, 2011.
10. M. Faraji and H. El Qarnia, Numerical optimization of a thermal performance of a phase change material based heat sink, *International Journal of Heat and Technology*, vol. 26, pp. 17-24, 2008.
11. M. M. Kenisarin, High-temperature phase change materials for thermal energy storage, *Renewable and Sustainable Energy Reviews*, vol. 14, pp.955-970, 2010.
12. B. Zalba, J. M. Marin, et al, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, *Applied Thermal Engineering*, vol. 23, pp. 251-283, 2003.
13. A. F. Khadrawi and M. A. Al-Nimr, A simplistic way for cooling an intermittent operating internal combustion engine, *International Journal of Heat and Technology*, vol. 26, pp.175-178, 2008.
14. M. M. Farid, A. M. Khudhair,et al, A review on phase change energy storage: materials and applications, *Energy Conversion and Management*, vol.45, pp. 1597-1615, 2004.
15. U. Herrmann, B. Kelly, et al, Two-tank molten salt storage for parabolic trough solar power plants, *Energy*, vol. 29, pp. 883-893, 2004.
16. H. Price, E. Lüpfert, et al. Advances in parabolic trough solar power technology, *Journal of solar energy engineering*, vol. 124, pp. 109-125, 2002.
17. D. Kearney, U. Herrmann, et al, Assessment of a molten salt heat transfer fluid in a parabolic trough solar field, *ASME Journal of Solar Energy Engineering,* vol. 125, pp: 170-176, 2003.
18. D. Kearney, B. Kelly, et al, Engineering aspects of a molten salt heat transfer fluid in a trough solar field, *Energy*, vol. 29, pp. 861-870, 2004.
19. Q. Peng, J. Ding, et al, The preparation and properties of multi-component molten salts, *Applied Energy*, vol. 87, pp. 2812-2817, 2010.