Preparation and Experimental Study of Three Element Mixed Molten Salt

Quanying Yan, Chenyu Wang*, Zhang Jing, Chao Liu, Qingzhu Fan
Beijing Municipality Key Lab of Heating, Gas Supply, Ventilating and Air Conditioning Engineering, Beijing University of civil Engineering and Architecture, Beijing, 100044, China
*Email: wangchenyuc@163.com

Abstract: 36 kinds of mixed salts made of KCl, Na₂CO₃ and K₂CO₃ were prepared in this paper. The melting point and solidification point of the sample were studied by DSC, and the stability of the selected samples is also tested. The experimental results show that the smaller component of KCl, the smaller melting point of molten salt. The melting point of the samples which melted together was 570 -580°C, and the freezing point is mainly between 550 and 570 C. The test ratio of the samples were selected from experiments was 2: 3: 5 (KCl: Na₂CO₃: K₂CO₃). The sample has a low melting point at 568.9°C and a low freezing point at 545.3°C, which can effectively avoid the blockage of piping system. The research results in this paper will provide reference and basis for the application of ternary mixed molten salt in solar energy field.

1. Introduction
Solar thermal power generation technology can make good use of solar energy. Heat transfer and heat storage technology is the core of solar thermal power generation technology. It is very important to choose suitable heat storage materials. Molten salt has the advantages of high operating temperature, low viscosity, high specific heat capacity and low cost, and is often used as the preferred thermal storage material. When chloride or carbonate is mixed separately, the phase transition temperature and latent heat are lower. When mixed with two salts of chloride and carbonate, phase transition temperature and phase transition can be prepared. The heat storage material with relatively high latent heat is more suitable for application in solar heat storage technology.

Guo Chauxiu The large number of experimental data obtained the melting point, thermal conductivity, volume expansion coefficient and latent heat value [1] of the nitrate mixed molten salt. Peng Qiang et al. used a static melting method to prepare ternary mixed nitrate and added 7% of it to it. Additives make the mixed molten salt more stable in high temperature environments [2]. Hu Baohua et al. prepared a mixed chloride salt of anhydrous calcium chloride and sodium chloride with a melting point of 497.6°C, a latent heat of phase change of 86.85 J/g, and a maximum operable temperature of 800°C [3]. Sun Liping used 36 kinds of chloride salts of potassium chloride, magnesium chloride and sodium chloride as raw materials to prepare 36 kinds of mixed chloride salts with different ratios. When the mass ratio of the three substances was 1:2:7 The mixed chloride salt can reach 400°C due to the melting point and has the lowest heat storage cost [4]. He Wanyu prepared 36 kinds of ternary mixed chloride salts composed of NaCl, KCl and LiCl. Through analysis, it is concluded that the sample of sodium chloride-potassium chloride-lithium chloride (10%-50%-40%) has lower melting point and higher latent heat of phase change, which can reduce the cost of the system and improve the system. Economic[5]. Zhang Yuping's people mixed carbonate, potassium carbonate and lithium carbonate according to the ratio of the substance to 30.6:26.8:42.5 to prepare
carbonate. After mixing, the melting point of the molten salt was reduced to 393°C [6]. Liao Min et al. prepared a mixed molten salt of sodium carbonate and potassium carbonate with a mass ratio of 1:1 by static melting method. When the content of sodium chloride reached 22.81% (mass fraction), a modified molten salt was obtained. The latent heat of phase change is twice that of the binary carbonate molten salt, and the melting point is reduced by 133°C [7] than the binary carbonate molten salt. Wang Lijuan prepared 36 kinds of ternary mixed carbonates composed of Na₂CO₃, Li₂CO₃ and K₂CO₃, which gave the highest cost-effective ternary mixture. Carbonate ratio [8]. Ren N et al. formulated 36 mixed carbonates. Most ternary carbonates have a melting point of 400°C. 13 lower cost ternary carbonates are recommended for phase change accumulators [9]. Peng Q et al. are working on the thermal stability [10] of molten salts composed of sodium nitrate, sodium nitrite, potassium nitrate and the addition of certain additives. In this paper, the heat storage properties of mixtures of different kinds of molten salts are studied, aiming to find phase change materials suitable for solar energy storage.

2. Preparation of Ternary Mixed Molten Salt

2.1 Experimental Materials and Equipments

The phase change materials used in the experiment included analytical pure potassium chloride (melting point 770°C, phase change heat 359.6 J / g), sodium carbonate (melting point 851°C, phase change heat 290 J / g), potassium carbonate (melting point 891°C, phase heat up 235J/g).

The experimental equipment includes: Differential Scanning Calorimeter (DSC), vacuum drying oven, beaker, aluminum crucible, porcelain crucible, tweezers, dryer, muffle furnace, tray, mortar, and electronic heaven. The DSC instrument is the 200PC model of the German NETZSCH company.

2.2 Sample Preparation

| NO. | KCl | Na₂CO₃ | K₂CO₃ | NO. | KCl | Na₂CO₃ | K₂CO₃ |
|-----|-----|--------|-------|-----|-----|--------|-------|
| 1   | 10% | 10%    | 80%   | 19  | 30% | 40%    | 30%   |
| 2   | 10% | 20%    | 70%   | 20  | 30% | 50%    | 20%   |
| 3   | 10% | 30%    | 60%   | 21  | 30% | 60%    | 10%   |
| 4   | 10% | 40%    | 50%   | 22  | 40% | 10%    | 50%   |
| 5   | 10% | 50%    | 40%   | 23  | 40% | 20%    | 40%   |
| 6   | 10% | 60%    | 30%   | 24  | 40% | 30%    | 30%   |
| 7   | 10% | 70%    | 20%   | 25  | 40% | 40%    | 20%   |
| 8   | 10% | 80%    | 10%   | 26  | 40% | 50%    | 10%   |
| 9   | 20% | 10%    | 70%   | 27  | 50% | 10%    | 40%   |
| 10  | 20% | 20%    | 60%   | 28  | 50% | 20%    | 30%   |
| 11  | 20% | 30%    | 50%   | 29  | 50% | 30%    | 20%   |
| 12  | 20% | 40%    | 40%   | 30  | 50% | 40%    | 10%   |
| 13  | 20% | 50%    | 30%   | 31  | 60% | 10%    | 30%   |
| 14  | 20% | 60%    | 20%   | 32  | 60% | 20%    | 20%   |
| 15  | 20% | 70%    | 10%   | 33  | 60% | 30%    | 10%   |
| 16  | 30% | 10%    | 60%   | 34  | 70% | 10%    | 20%   |
| 17  | 30% | 20%    | 50%   | 35  | 70% | 20%    | 10%   |
| 18  | 30% | 30%    | 40%   | 36  | 80% | 10%    | 10%   |

The mixed phase change material was prepared according to the mass ratio set in Table 1. The potassium chloride, sodium carbonate and potassium carbonate salts were placed in a vacuum drying oven for more than 24 hours before the preparation of the sample, and the temperature of the drying
oven was set to 120°C. The mixed molten salt was placed in a muffle furnace for heating, and the temperature of the muffle furnace was set to 600°C and the heating time was 3 h. It was taken out after melting and then solidified in the air. The solidified mixed molten salt was ground in a mortar, and the ground powder was weighed to a sample of 7 mg to 15 mg with an electronic balance, and placed in a DSC instrument for measurement.

3. Experimental Results and Analysis

3.1 Determination of Melting Point of Ternary Mixed Molten Salt Sample

The melting points of the 36 mixed molten salts tested by the DSC instrument are shown in Table 2.

| KCl:Na2CO3:K2CO3 | Melting point (°C) | Freezing point (°C) |
|------------------|-------------------|--------------------|
| 1:2:7            | 579.2             | 560.1              |
| 1:5:4            | 576.5             | 554.3              |
| 1:6:3            | 580.8             | 559.2              |
| 1:8:1            | —                 | —                  |
| 2:1:7            | —                 | —                  |
| 2:2:6            | —                 | —                  |
| 2:3:5            | 568.9             | 545.0              |
| 2:4:4            | 571.2             | 552.3              |
| 2:5:3            | 578.3             | 550.2              |
| 2:6:2            | 582.9             | 561.6              |
| 2:7:1            | —                 | —                  |
| 3:1:6            | 580.8             | 571.0              |
| 3:2:5            | —                 | —                  |
| 3:3:4            | 581.6             | 551.9              |

As shown in Table 2, the melting point of most of the samples was concentrated at 560°C ~ 580°C, and the freezing point was concentrated at 550°C ~ 570°C. There are also a small number of samples that do not have a fixed melting point and freezing point due to the incompatibility state, which cannot be measured with a DSC instrument. Another part is that in the muffle furnace at 600°C, these samples cannot be melted and cannot be measured, the ratio is: KCl: Na2CO3: K2CO3 = 1: 1:8, KCl: Na2CO3: K2CO3 = 1: 3: 6, KCl: Na2CO3: K2CO3 = 1: 4: 5, KCl: Na2CO3: K2CO3 = 1: 7: 2, KCl: Na2CO3: K2CO3 = 5: 1: 4, KCl: Na2CO3: K2CO3 = 6: 3: 1, KCl: Na2CO3: K2CO3 = 7: 1: 2, KCl: Na2CO3: K2CO3 = 7: 2: 1, KCl: Na2CO3: K2CO3 = 8: 1: 1. It is not difficult to find from the ratio of these infusible samples that there is always one component in each sample in a ratio of one.
3.2 Image Analysis of Samples

Figure 1. Mixed molten salt No.9 (KCl: Na₂CO₃: K₂CO₃ = 2: 1: 7) DSC curve

Figure 2. Mixed molten salt No.17 (KCl: Na₂CO₃: K₂CO₃ = 3: 2: 5) DSC curve

Figure 3. Mixed molten salt No.22 (KCl: Na₂CO₃: K₂CO₃ = 4: 1: 5) DSC curve

It can be seen from Fig.1 - Fig.3 that the mixed molten salt of No. 9, No. 17, No. 22 does not reach the
eutectic state, and the DSC curve of No. 9 molten salt is extremely irregular, so the melting point shown in the figure is not accurate. The molten salt of No. 17 and No. 22 have the same DSC curve, and both have two melting peaks, so they do not reach the eutectic state and have no determined melting point.

Figure 4. Mixed molten salt No.11 (KCl: Na₂CO₃: K₂CO₃ = 2: 3: 5) DSC curve

Figure 5. Mixed molten salt No.20 (KCl: Na₂CO₃: K₂CO₃ = 3: 5: 2) DSC curve

Figure 6. Mixed molten salt No.21 (KCl: Na₂CO₃: K₂CO₃ = 3: 5: 2) DSC curve
It can be seen from Fig.4- Fig.6 that the molten salt of No.11, No.20 and No.21 still has similar trend DSC curves, all of which have stable melting point and freezing point. Compared with the melting point of other samples in the table, No. 21 sample can be found. It has a lower melting point and a higher freezing point, so it is more in line with the characteristics of heat storage materials in solar thermal power generation technology, and is expected to be applied to solar thermal power generation technology.

4. Stability Experiment of Ternary Mixed Molten Salt

Table 3. Test results of No. 21 mixed molten salt (KCl: Na₂CO₃: K₂CO₃=3:5:2)

| Experimental order | Melting point (°C) | Freezing point (°C) |
|--------------------|--------------------|---------------------|
| 1                   | 568.9              | 545.3               |
| 2                   | 567.6              | 545.2               |
| 3                   | 567.8              | 545.2               |
| 4                   | 567.8              | 544.9               |
| 5                   | 567.8              | 545.1               |
| average value       | 567.9              | 545.0               |

The No.21 mixed molten salt (KCl: Na₂CO₃: K₂CO₃ = 3: 5: 2) was tested for five consecutive DSC curves, and the obtained figures were compared. It was found that the five times of pattern coincidence was extremely high, and both had the trend of Fig. 6, and the measured melting point and freezing point were extremely small, and the results of the five tests are shown in Table 3.

As can be seen from Table 3, for the sample No. 21, the melting point and the freezing point of the first test were both high, and the data measured in the last four times was slightly smaller, but the difference was small. Therefore, it can be inferred that when an infinite number of cycles are performed, the melting point and freezing point of the sample will gradually become the same. This indicates that after repeated DSC tests, the melting point and freezing point of the molten salt will become approximately constant, with good stability, which will greatly contribute to the safe operation of the system and can be developed into a solar phase change heat storage material.

5. Comparison between Ternary Mixed Molten Salts

Select KCl-Na₂CO₃-K₂CO₃ and Li₂CO₃-Na₂CO₃-K₂CO₃ Molten salt for comparison. Table 4 lists the melting points of the ternary mixed molten salt Li₂CO₃-Na₂CO₃-K₂CO₃ and the latent heat value, which are compared with Table 1.

From the comparison of Tables 1 and 4, it is easy to see that the melting point of Li₂CO₃-Na₂CO₃-K₂CO₃ mixed molten salt is generally lower than KCl-Na₂CO₃, the melting point of the former is mainly concentrated at about 580°C, and the melting point of the latter is mainly concentrated at about 400°C. It is possible that the melting point of KCl is higher than the melting point of Li₂CO₃, the melting point of the former is 770°C, and the melting point of the latter is 720°C. Since the solidification point of Li₂CO₃-Na₂CO₃-K₂CO₃ ternary mixed molten salt is mostly concentrated around 400°C, the freezing point of KCl-Na₂CO₃-K₂CO₃ mixture is concentrated at about 550 °C, so the latter is more suitable for high temperature phase change materials, the former is suitable for phase change materials with relatively low temperature.
Table 4. Melting point and latent heat value of ternary mixed molten salt (Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$)

| Li$_2$CO$_3$:Na$_2$CO$_3$:K$_2$CO$_3$ Melting point (°C) | Phase change latent heat (J/g) | KCl:Na$_2$CO$_3$:K$_2$CO$_3$ Melting point (°C) | Phase change latent heat (J/g) |
|--------------------------------------------------------|-------------------------------|----------------------------------|-------------------------------|
| 1:1:8 444.6 --- | --- | 3:4:3 397.0 | 250.2 |
| 1:2:7 428.5 --- | --- | 3:5:2 393.9 | --- |
| 1:3:6 428.2 --- | --- | 3:6:1 Uneutectic --- | --- |
| 1:4:5 408.8 --- | --- | 4:1:5 Uneutectic --- | --- |
| 1:5:4 403.1 93.96 | 4:2:4 399.6 | --- |
| 1:6:3 Unmelted --- | 4:3:3 401.6 | 257.4 |
| 1:7:2 Unmelted --- | 4:4:2 399.7 | 134.1 |
| 1:8:1 Unmelted --- | 4:5:1 394.4 | --- |
| 2:1:7 428.9 --- | 5:1:4 Uneutectic --- | --- |
| 2:2:6 424.6 --- | 5:2:3 398.4 | 157.4 |
| 2:3:5 403.1 --- | 5:3:2 396.8 | 120.6 |
| 2:4:4 Uneutectic --- | 5:4:1 Uneutectic --- | --- |
| 2:5:3 398.8 178.1 | 6:1:3 Uneutectic --- | --- |
| 2:6:2 Uneutectic --- | 6:2:2 402.4 | 173.3 |
| 2:7:1 Unmelted --- | 6:3:1 390.8 | --- |
| 3:1:6 Uneutectic --- | 7:1:2 400.9 | --- |
| 3:2:5 Uneutectic --- | 7:2:1 Unmelted --- | --- |
| 3:3:4 398.6 263.7 | 8:1:1 Unmelted --- | --- |

From the comparison of Tables 1 and 4, it is easy to see that the melting point of Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ mixed molten salt is generally lower than KCl-Na$_2$CO$_3$-K$_2$CO$_3$ is a melting point of a mixed molten salt. The melting point of the former is mainly concentrated at about 580°C, and the melting point of the latter is mainly concentrated at about 400°C. It is possible that the melting point of KCl is higher than the melting point of Li$_2$CO$_3$, the melting point of the former is 770°C, and the melting point of the latter is 720°C. Since the solidification point of Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ ternary mixed molten salt is mostly concentrated around 400°C, the freezing point of KCl-Na$_2$CO$_3$-K$_2$CO$_3$ mixture is concentrated at about 550 °C, so the latter is more suitable for high temperature phase change materials, the former is suitable for phase change materials with relatively low temperature.

6. Conclusion
1. Of the 36 mixed molten salts, 9 of them were not meltable in a muffle furnace at 600°C because of a small content of only 10%.
2. There are 8 kinds of molten salt melting in the muffle furnace at 600°C, but these 8 kinds of molten salt do not have a stable peak, indicating that the substance does not reach the eutectic state, so there is no fixed melting point and freezing point, from the composition It can be seen that the same is due to the small content of a certain component, only 10% or 20%.
3. In all mixed molten salts where eutectic occurs, their melting points are probably concentrated at 570°C ~ 580°C; the freezing point is mainly concentrated at 550°C ~ 570°C.
4. Preferably, the sample No. 21 (potassium chloride: sodium carbonate: potassium carbonate = 2:3:5) is the best sample, which has a lower melting point of 568.9°C and a lower freezing point of 545.3°C, and has good stability. Effectively avoid the blockage problem of the pipeline system, improve the safety performance of the system, and meet the requirements of the heat transfer and heat storage medium in the solar thermal power generation technology.
7. Acknowledgments
The project was supported by Science and Technology Key Program of Beijing Municipal Education Commission (KZ201710016011) and National Energy Virtual Simulation Experimental Teaching Demonstration Center for Building Energy (Beijing University Of Civil Engineering And Architecture).

8. References
[1] Guo Chaxiu, Zhang Wujun, Xiong Huidong, et al. Numerical Simulation of Solidification Process of Eutectic Salt Cooling Ball[J]. HVAC, 2006, 36 (3): 17-21.
[2] Peng Qiang, Yang Xiaoxi, Ding Jing, et al. Experimental study and mechanism analysis of high temperature thermal stability of ternary nitrate molten salt [J]. CIESC Journal, 2013, 64 (5): 1507-1512.
[3] Hu Baohua, Ding Jing, Wei Xiaolan, et al. Thermal property test and thermal stability analysis of high temperature molten salt [J]. Inorganic Chemicals Industry, 2010, 42(1): 22-24.
[4] SUN Li-Ping, WU Yu-Ting, MA Chong-Fang. Experimental Study on the Optimization of Solar High Temperature Thermal Storage Molten Salt [J]. Journal of Solar Energy, 2008, 29(9): 1092-1095.
[5] He Wanyu. Experimental study on thermal properties and corrosivity of mixed chlorinated molten salt [D]. Beijing Jianzhu University, 2016.
[6] Zhang Yuping, Liu Zhenquan, Wang Xin, et al. Experimental Study on Cool Storage Characteristics of Low Temperature Phase Change Cool Storage Materials [J]. HVAC, 2005, 35(10): 114-117.
[7] Liao Min, Ding Jing, Wei Xiaolan, et al. Preparation and heat transfer and heat storage properties of high temperature carbonate molten salt [J]. Inorganic Salt Industry, 2008, 40(10): 15-17.
[8] Wang Lijuan. Experimental study on thermal properties and corrosion of high temperature mixed carbonate. Beijing Jianzhu University,2016.
[9] Ren N, Wu Y T, Wang T, et al. Experimental study on optimized composition of mixed carbonate for phase change thermal storage in solar thermal power plant [J]. Journal of Thermal Analysis & Calorimetry, 2011, 104(3): 1201-1208.
[10] Peng Q, Wei X, Ding J, et al. High-temperature thermal stability of molten salt materials [J]. International Journal of Energy Research, 2008, 32(12): 1164-1174.