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Experimental study on optimized composition of mixed carbonate for phase change thermal storage in solar thermal power plant

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Abstract 36 kinds of mixed carbonate molten salts were prepared by mixing potassium carbonate, lithium carbonate, sodium carbonate in accordance with different proportions. The data of melting point and latent heat are measured by the analysis of DSC curves of 36 kinds of salts, which show that the majority of ternary carbonate's melting points are close at around 400 °C. 24 kinds of eutectic molten salts were selected among 36 kinds of molten salts. With high latent heat, ternary carbonate salt has the potential to be employed for phase change thermal storage. The costs for phase change thermal storage of 24 kinds of carbonate salts are calculated. Finally, 13 kinds of ternary carbonate salts with lower cost for phase change thermal storage are recommended, where there are 6 kinds of mixed carbonates have the considerably larger latent heat of melting.

Keywords Mixed carbonate salts · Differential scanning calorimetry · Latent heat · Heat storage

Introduction

From the outer space looks our livable world, the Earth, rather fragile. In the Earth's history, this layer contains self-reliant entity of mankind, which is becoming to exceedingly wear away its friendly surrounding by plentiful utilization of raw materials, over-burning fossils, abundant traffic and generation of superfluous wastes, which in fact destroys the living conditions on planet [1]. So we urgently need an energy revolution, changing the world's energy mix to a majority of non-polluting sources. CSP (Concentrating Solar Power) system is a large-scale, commercially available way to make electricity, which does not contribute to climate change and the source will never run out. CSP systems with storage can provide consistent power and thus are attractive relative to intermittent power sources, e.g., solar photovoltaics and wind. According to the Global CSP Outlook 2009 [2], under an advanced industry development scenario with high levels of energy efficiency, CSP could meet up to 7% of the world's projected power needs in 2030 and a full quarter by 2050.

The appropriate storage medium is a key technological issue for the future success of CSP technologies. Table 1 [3] displays the common heat storage mediums in Solar Thermal Power. The system of application of sand–stone–mineral oil is complex and inefficient. The requirement for internal exchange tube is relatively high in the system of concrete used for heat storage medium. The disadvantage of heat conducting oil is that its pressure is very high under high temperature, for example, which is higher than 1 MPa at 400 °C. In addition, heat conducting oil easily leads to fires and its cost is considerably high. Although, liquid metal, with higher using temperate, large density and high heat conductivity, has good performance of endothermic and exothermic, but its heat capacity is small, temperature fluctuate visibly during large heat load and it is easy to combust and blast in contact with air. While, molten salt with a lot of advantages such as low cost, wide range of use temperature, large heat capacity, low viscosity, low vapor pressure, and good chemical stability, has become an extremely potential medium for storage in CSP plants.

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Table 1 Common heat storage mediums in solar thermal power

Storage medium	Temperature range		Average density	Average heat transfer coefficient	Average thermal storage capacity	Cost
	Low/°C	High/°C	kg/m^3	W/m K	kJ/kg K	$/kg
Sand–stone–mineral oil	200	300	1700	1.0	1.30	0.15
Concrete	200	400	2200	1.5	0.85	0.05
Heat conducting oil	200	350	900	0.11	2.3	3.0
Nitrate salt	265	565	1870	0.52	1.6	0.5
Liquid sodium	270	530	850	71.0	1.3	2.0

Molten salts have been used in large scale in the experimental or commercial solar thermal power plants. For example, 1400 and 30000 t mixed nitrate salts had been used in the CSP plants of Solar Two [4] and Andasol 1 [5], respectively.

Utilizing the latent heat of melting to make power is a possible kind of storage energy manner, especially for distributed solar thermal power. The melting point of mixed nitrate used in the current stations is about at range of 150–200 °C, which can not meet the requirement of high storage temperature. However, mixed carbonate, with high melting point and larger latent heat of melting, is a promising kind of high temperature phase change materials. Basic thermo physical properties of nitrate salts mixture at different temperature, such as specific heat, thermal conductivity, density, dynamic viscosity and so on, have been tested and analysis by some researchers [6, 7]. However, by far, no experimental data of thermal physical properties with mixed carbonate salts may be found in open literature.

Sponsored by Ministry of Sciences & Technology and National Natural Science Foundation of China, scientific research of thermal fluid science with molten salts has been conducted since 2003 at the Key Laboratory of Enhanced Heat Transfer and Energy Conservation of Ministry of Education in Beijing University of Technology [8, 9]. Investigations were made for the preparation of molten salts mixture and determination of thermal physical properties. This article is mainly on thermal physics properties of 36 kinds of ternary carbonates. It is hoped that the research project can provide useful information both in academic and technological aspects.

Fig. 1 STA-409PC

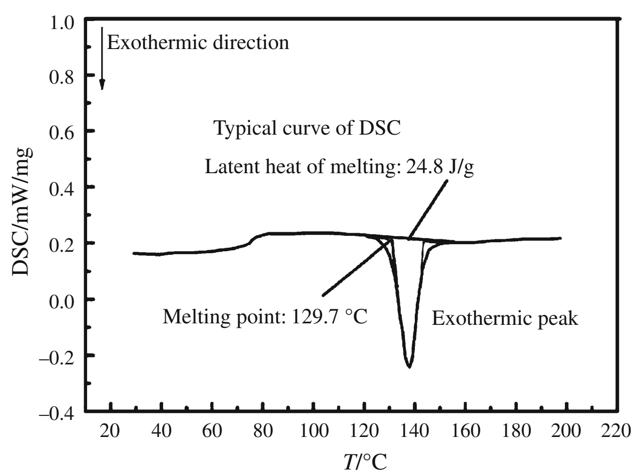

Fig. 2 Typical DSC curve

Experiment system and verification

Experiment instrument

In this paper, Differential Scanning Calorimetry instrument STA-409PC (shown in Fig. 1), produced by German NETZSCH Company, was used to measure molten salt's melting point and latent heat. We used the balance with precision high up to 0.1 mg to prepare mixed molten salts.

The principle of measurement

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the

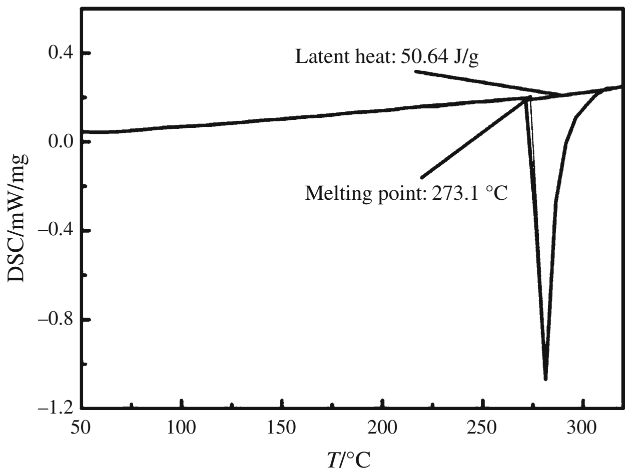

Fig. 3 DSC curve of Bi presented with Al_2O_3-pan

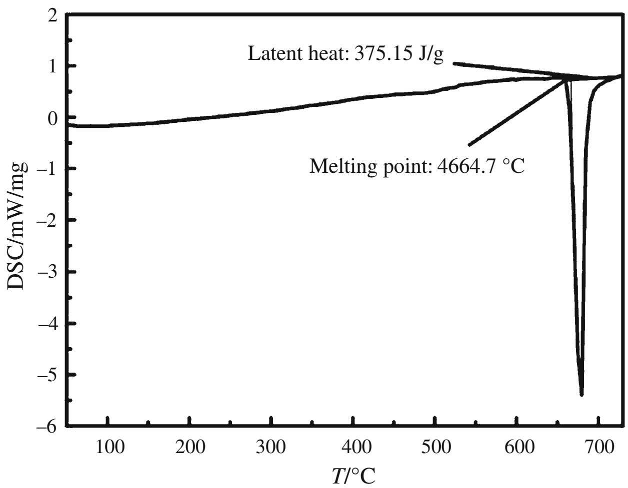

Fig. 4 DSC curve of Al presented with Al_2O_3-pan

experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The result of a DSC experiment is a curve of heat flux versus temperature or versus time. A typical DSC curve may be plotted as Fig. 2. Melting point and latent heat can be obtained from the DSC curves.

The melting point is determined by the cross point between a line extended from the baseline at lower temperature side and a tangent line drawn at the maxim inclination point on the lower temperature side of a fusion peak.

The latent heat of melting is proportional to the area of melting peak and is calculated by the software automatically.

Accuracy verification of STA

In this article, the standard samples of Bi and Al are used to make calibration of DSC instrument. Because the standard samples are all metal, so the Al_2O_3-pan not Al-pan or PtRh-pan is used to make calibration in order to avoid occurring chemical reaction. Figures 3 and 4 are the DSC curves of a particular measurement of Bi and Al presented with Al_2O_3-pan. Tables 2 and 3 display the error analysis of three measurements for every sample. The three relative errors of melting point of Bi are 0.63, 0.66, and 0.77%, while, the ones of Al are 0.67, 0.68, and 0.55%, respectively. In addition, the three relative errors of latent heat of Bi are 4.99, 2.96, and 4.67%, while, the ones of Al are 5.26, 5.50, and 4.42%, respectively. Because thermal conductivity of Al_2O_3-pan is not better than Al-pan and PtRh-pan, so the measured melting point is a little higher than real melting point and the measured latent heat is a little less than real one. However, the accuracy and precision of the DSC instrument are relatively high and can meet the test requirement.

Because the test samples are molten salt not metal, so the industry $LiNO_3$ is used to make calibration of the DSC instrument besides. Figure 5 shows two DSC curves of industrial grade $LiNO_3$ by using Al-pan and Pt–Rh-pan, respectively. Good agreements between the two DSC curves are seen from Fig 3. Table 4 shows the measured value, literature value [10] and deviations between them. It is found that deviation of melting point of $LiNO_3$ between measured value and literature's value is less than 2% from the Table 4.

Table 2 Error analysis of melting point of Bi and Al

Test number	Sample							
	Bi				Al			
	Real melting point/°C	Measured value/°C	Absolute error/°C	Relative error/%	Real melting point/°C	Measured value/°C	Absolute error/°C	Relative error/%
1	271.4	273.1	1.7	0.63	660.3	664.7	4.4	0.67
2	271.4	273.2	1.8	0.66	660.3	664.8	4.5	0.68
3	271.4	273.5	2.1	0.77	660.3	663.9	3.6	0.55

Table 3 Error analysis of latent heat of Bi and Al

Test number	Sample							
	Bi				Al			
	Real latent heat/J/g	Measured value/J/g	Absolute error/J/g	Relative error/%	Real latent heat/J/g	Measured value/g^{-1}	Absolute error/J/g	Relative error/%
1	53.3	50.64	2.66	4.99	397	376.12	20.88	5.26
2	53.3	51.72	1.58	2.96	397	375.15	21.85	5.50
3	53.3	50.79	2.49	4.71	397	379.44	17.56	4.42

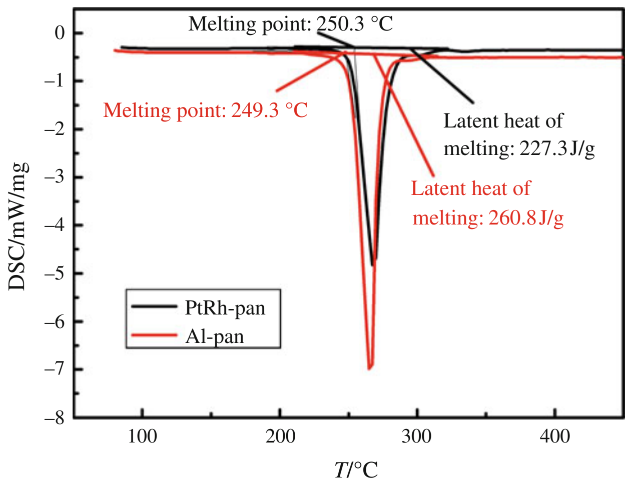

Fig. 5 DSC curves of $LiNO_3$ presented with Al-pan and Pt–Rh-pan

Table 4 The melting point of $LiNO_3$ presented with Al-pan and Pt–Rh-pan

Pan type	Measured value/°C	Literature value/°C	Error/%
Al	249.3	253	1.5
Pt–Rh (adding Al_2O_3 gasket)	250	253	1.2

Table 5 The latent heat of melting of $LiNO_3$ presented with Al-pan and Pt–Rh-pan

Pan type	Latent heat of melting/J/g	Correction coefficient	Corrected result/J/g	Literature value	Error/ %
Al	260.8	1	260.8	253	3.1
Pt–Rh (adding Al_2O_3 gasket)	227.3	1.2 (adding gasket)	272	253	7.5

Table 6 The relevant parameters of K_2CO_3,Li_2CO_3, and Na_2CO_3

Drug name	Melting point/°C	Boiling point (decomposition point)/°C	Content/ %
K_2CO_3	891	–	≥99.0
Li_2CO_3	618	1310	≥97.0
Na_2CO_3	851	–	≥99.8

Table 7 Ternary carbonate's mass ratio (K_2CO_3:Li_2CO_3:Na_2CO_3)

Serial number	K_2CO_3/%	Li_2CO_3/%	Na_2CO_3/%
01	10	10	80
02	10	20	70
03	10	30	60
04	10	40	50
05	10	50	40
06	10	60	30
07	10	70	20
08	10	80	10
09	20	10	70
10	20	20	60
11	20	30	50
12	20	40	40
13	20	50	30
14	20	60	20
15	20	70	10
16	30	10	60
17	30	20	50
18	30	30	40
19	30	40	30
20	30	50	20
21	30	60	10
22	40	10	50
23	40	20	40
24	40	30	30
25	40	40	20
26	40	50	10
27	50	10	40
28	50	20	30
29	50	30	20
30	50	40	10
31	60	10	30
32	60	20	20
33	60	30	10
34	70	10	20
35	70	20	10
36	80	10	10

The result of latent heat analyzing is shown in Table 5. The latent heats of melting of $LiNO_3$ presented with Al-pan and Pt–Rh-pan are 260.8 and 272 J/g, respectively, where there is 4.1% deviation between them. While compared to the literature value [11] 253 J/g, there are 3.1 and 7.4% deviations between them, respectively. According to investigation, the pan used in the literature is Al-pan. Thus, the deviation between the two measured values is only 3.1%. However, when using Pt–Rh-pan to measure the latent heat of melting of samples, in order to avoid adhesion of pan and bracket, adding gasket between them, which increases the thermal contact resistance and affects heat transfer performance and brings the higher deviation. In addition, the purity of sample and experimental environment are the main factors affecting the research result. However, all of the things do not affect the optimum selection of mixed molten salt.

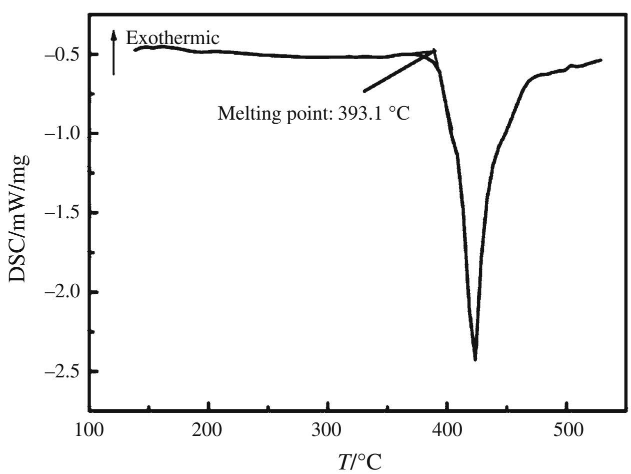

Fig. 6 Typical melting peak of ternary carbonate (mass ratio of 2:5:3)

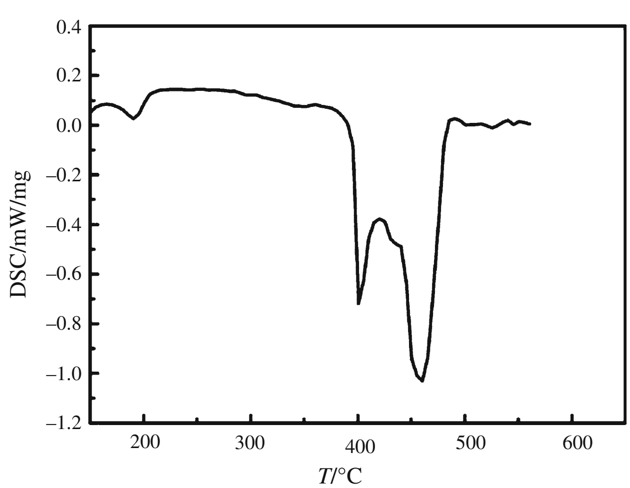

Fig. 7 Abnormal melting peaks of ternary carbonate (mass ratio of 1:3:6)

Molten salts preparation

Carbonate salts (K_2CO_3, Li_2CO_3, and Na_2CO_3) produced by Beijing Chemical Plant were used to prepare mixed carbonate salts, the parameters of these salts are shown in Table 6.

Through keeping one component ratio and varying the other two components at the step of 10%, 36 kinds of carbonate salts were prepared. The preparing procedure is

Table 8 Melting points and latent heat of 36 mixed carbonate salts

Serial number	Melting point/°C
01	–
02	459.5
03	–
04	–
05	–
06	422.0
07	438.0
08	461.4
09	395.6
10	395.8
11	395.8
12	392.1
13	393.1
14	410.7
15	430.0
16	396.0
17	397.0
19	407.8
20	416.4
21	396.0
22	396.6
23	396.8
24	397.9
25	402.7
26	427.3
27	395.4
28	396.7
29	396.7
30	399.4
31	396.0
32	397.1
33	398.6
34	396.4
35	398.0
36	438.6

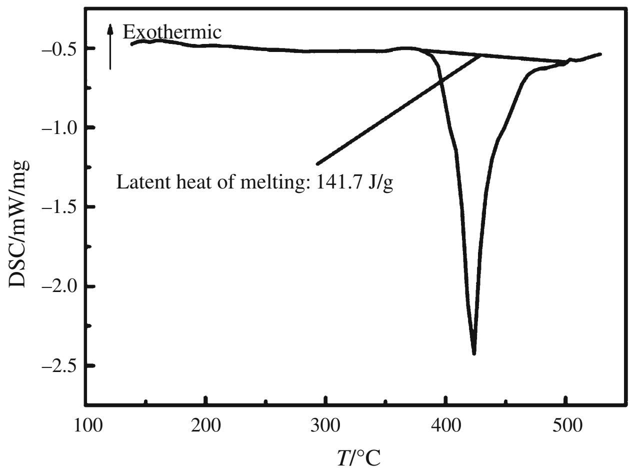

Fig. 8 Latent heat of melting of ternary carbonate (mass ratio of 2:5:3)

as follows: Firstly, the mass of every component of carbonate were calculated and weighed. Secondly, the salts were mixed and grind adequately. Detailed preparing proportion is showed in Table 7.

Results and discussion

Melting point of ternary carbonate

DSC curves of 36 kinds of mixed carbonate salts were obtained by heating every kind of mixed carbonates in Table 7 with fixed procedure of temperature. The DSC curves show that some carbonates' melting peak is typical as shows in Fig. 6, while some carbonates' melting peak is irregular, as shown in Fig. 7. In other words, those mixed carbonate salts with typical melting peak can form eutectic and those salts with irregular melting peak can not form eutectic. Through analyzing every DSC curve one by one, every carbonate's melting point in any mass ratio was obtained as shown in Table 8.

According to Table 8, Nos. 1, 3–5 of ternary carbonates do not have the collective melting point. While the other 32 kinds of mixed salts have ones at the range of 390–460 °C. Melting points of different proportional molten salts are not the same, most of which are close at around 400 °C. The 32 kinds of carbonates with collective melting point are as the objects researched further.

Latent heat of melting of ternary carbonate

The latent heat of melting is proportional to the area of melting peak and is calculated by the software automatically, as illustrated in Fig. 8. Through analyzing the 32 DSC curves prepared one by one, their latent heats of melting are displayed in Table 9.

Table 9 Latent heat of 36 kinds selected mixed carbonate salts

Serial number	Melting peak/J/g K
02	56.72
06	103.0
07	75.92
08	53.99
09	68.05
10	–
11	–
12	172.2
13	141.7
14	101.8
15	72.20
16	72.42
17	125.1
18	161.9
19	197.4
20	140.2
21	82.6
22	58.55
23	124.6
24	166.4
25	183.8
26	145.9
27	–
28	124.8
29	174.0
30	–
31	–
32	123.4
33	–
34	–
35	–
36	62.98

According to Table 9, although some carbonates have the collective melting point, but their melting peaks are not regular. Among 32 kinds of mixed carbonates, there are 24 kinds of carbonates can form eutectic. However, these carbonates have considerably different latent heat of melting. For example, the latent heat of melting of No. 8 is only 53.99 J/(g K), while No. 19's is high to 197.4 J/(g K).

Table 10 Price List for three carbonate (industrial grade)

Name	K_2CO_3	Li_2CO_3	Na_2CO_3
Price/$/kg	1.38	7.67	0.20

Table 11 Cost of phase change heat storage for ternary carbonate

Serial number	K_2CO_3/%	Li_2CO_3/%	Na_2CO_3/%	Price/$/kg	Latent heat of melting value/kJ/kg	Cost/$/kWh
02	10	20	70	1.81	56.72	114.82
06	10	60	30	4.80	103.0	167.71
07	10	70	20	5.55	75.92	262.98
08	10	80	10	6.29	53.99	419.63
09	20	10	70	1.18	68.05	62.45
12	20	40	40	3.42	172.2	71.55
13	20	50	30	4.17	141.7	105.94
14	20	60	20	4.92	101.8	173.89
15	20	70	10	5.66	72.20	282.45
16	30	10	60	1.30	72.42	64.58
17	30	20	50	2.05	125.1	58.89
18	30	30	40	2.79	161.9	62.13
19	30	40	30	3.54	197.4	64.58
20	30	50	20	4.29	140.2	110.12
21	30	60	10	5.04	82.6	219.49
22	40	10	50	1.42	58.55	87.19
23	40	20	40	2.17	124.6	62.66
24	40	30	30	2.91	166.4	63.02
25	40	40	20	3.66	183.8	71.69
26	40	50	10	4.41	145.9	108.75
28	50	20	30	2.28	124.8	65.89
29	50	30	20	3.03	174.0	62.72
32	60	20	20	2.40	123.4	70.10
36	80	10	10	1.89	62.98	108.22

Optimum selection of the medium of phase change heat storage

Media cost per kWh thermal storage capacity is considered as the index of evaluating the mixed carbonate for heat storage. The prices of three carbonates were listed in Table 10.

The media cost per kg mixed carbonate can be calculated by:

$$PC = M_K \times PC_K + M_{Na} \times PC_{Na} + M_{Li} \times PC_{Li} \quad (1)$$

where, PC: the price of mixed carbonate, \$/kg; M_K, M_{Na}, M_{Li}: mass percentage of K_2CO_3, Na_2CO_3 and Li_2CO_3, respectively; and PC_K, PC_{Na}, and PC_{Li}: price of K_2CO_3, Na_2CO_3, and Li_2CO_3, respectively, \$/kg.

Mass latent heat of melting of mixed molten carbonate can be calculated by:

$$Q = \Delta h / 3600 \quad (2)$$

where, Q is the mass phase change heat storage capacity of mixed carbonate, kWh/kg and Δh is the mass latent heat of melting of mixed carbonate, kJ/kg.

The media cost per kWh thermal storage capacity can be calculated by:

$$TC = \frac{PC}{Q} \quad (3)$$

where, TC is the media cost per kWh thermal storage capacity, \$/kWh.

According to Table 11, the serial number of carbonates with cost lower than 100\$/kWh are 9, 12, 16, 17, 18, 19, 22, 23, 24, 25, 28, 29, and 32, among which, Nos. 12, 18, 19, 24, 25, and 29 have the larger latent heat of melting. The factors of affecting cost of solar thermal power station are plentiful, cost of molten salt tank is the essential one of which. Obviously, at the same requirement of thermal storage, the larger latent heat of melting and density are, the less volume of tank becomes and the less material and occupied area needed, which will decreases the system cost greatly. It is necessary to consider every factor to seek the optimum ratio of ternary carbonate suitable for solar thermal storage during designing the power station.

Conclusions

According to analyzing upwards, we obtain some conclusions as follows:

(1) 32 kinds of ternary carbonates have collective melting points among the 36 kinds of ones, which are lower than melting point of any component in the mixtures. Molten salt with different mixed ratios have the different melting points at the range of 390–460 °C. While most of them are close around at 400 °C.
(2) Due to irregularity of melting peak, molten salts with collective melting point don't all have melting peak. That is some mixed salts cannot form eutectic. By calculating and analyzing the latent heat of melting and cost of phase change thermal storage, 13 kinds of carbonates with cost lower than 100$/kWh are selected, 6 kinds of which, with considerably larger latent heat of melting, may be as the optimum selection to be applied to solar thermal power.

In a word, several mixed carbonates in a fixing ratio can form eutectic well, whose latent heat of melting are higher than nitrate's used in solar power stations built. Thus, using mixed carbonates as the storage medium may improve the efficiency of solar thermal power. Of course, the study is far away from meeting the requirement of practical application, pending further research.

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References

1. Jaroslav S, Pavel H, Jirı JM. Thermal analysis scheme aimed at better understanding of the Earth's climate changes due to the alternating irradiation. J Therm Anal Calorim. 2010; 101: 567–575 http://www.greenpeace.org/international/en/publications/reports/concentrating-solar-power-2009/.
2. Wu Y, Zhang L, Ma C. High-temperature solar thermal power storage technology. Solar Energ, doi:CNKI:SUN:TYNZ.0.2007-03-010.
3. Bradshaw, Robert W, et al. Final Test and evaluation results from the solar two project. Sandia National Laboratories. doi: 10.2172/793226. http://www.srcf.ucam.org/cuens/img/Academic_Material/Gladen.pdf.
4. Alexis BZ. Solar power tower design basis document. Sandia National Laboratories. doi: 10.2172/786629.
5. Hoffman HW, Cohen SI. Fused salt heat transfer, part III: forced convection heat transfer in circular tubes containing the salt mixture $NaNO_2$-KNO_3- $NaNO_3$. Report No. ORNL-2433; 1960.
6. Wu Y, Liu B, Ma C, Guo H. Convective heat transfer in the laminar–turbulent transition region with molten salt in a circular tube. Exp Thermal Fluid Sci. 2009;33:1128–32.
7. Liu B, Wu Y, Ma C, Ye M, Guo H. Turbulent convective heat transfer with molten salt in a circular pipe. Intern Comm Heat Mass Trans. 2009;36:912–6.
8. Xie G. Theory and applications of molten salt. 1st ed. Beijing: Metallurgical Industry Press; 1998.
9. Xiong Y, Zhang L, Wu Y, Ma C. Experiment study on the thermal properties and stability of $lino_3$ in industrial level. J Eng Thermophys. 2008;7:1192–4.
10. Xie G. Theory and applications of molten salt. 1st ed. Beijing: Metallurgical Industry Press; 1998.
11. Xiong Y, Zhang L, Wu Y, Ma C. Experiment study on the thermal properties and stability of $LiNO_3$ in industrial level. J Eng Thermophys. 2008;7:1192–4.