Experimental studies on cycling stable characteristics of inorganic phase change material CaCl₂·6H₂O-MgCl₂·6H₂O modified with SrCl₂·6H₂O and CMC

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Abstract. By means of mass ratio method, binary eutectic hydrated salts inorganic phase change thermal energy storage system CaCl₂·6H₂O-20wt% MgCl₂·6H₂O was prepared, and through adding nucleating agent 1wt% SrCl₂·6H₂O and thickening agent 0.5wt% carboxy methyl cellulose (CMC), inoganic phase change material (PCM) modified was obtained. With recording cooling-melting curves simultaneously, this PCM was frozen and melted for 100 cycles under programmable temperature control. After per 10 cycles, the PCM was charaterized by differential scanning calorimeter (DSC), X-ray diffraction (XRD) and density meter, then analysing variation characteristics of phase change temperature, supercooling degree, superheat degree, latent heat, crystal structure and density with the increase of cycle index. The results showed that the average values of average phase change temperature for cooling and heating process were 25.70℃ and 27.39℃ respectively with small changes. The average values of average supercooling and superheat degree were 0.59℃ and 0.49℃ respectively, and the maximum value was 1.10℃. The average value and standard deviation of latent heat of fusion were 120.62 J/g and 1.90 J/g respectively. Non-molten white solid sediments resulted from phase separation were tachyhydrite (CaMg₂Cl₆·12H₂O), which was characterized by XRD. Measuring density of the PCM after per 10 cycles, and the results suggested that the total mass of tachyhydrite was limited. In summary, such modified inoganic PCM CaCl₂·6H₂O-20wt% MgCl₂·6H₂O-1wt% SrCl₂·6H₂O-0.5wt% CMC could stay excellent circulation stability within 100 cycles, and providing reference value in practical use.

1. Introduction

In recent years, with the rapid development of economy, energy shortage and environmental issues become more and more serious. Thus, it is absolutely urgent to improve energy utilization efficiency and protect environment. Energy storage techniques are hopeful to solve these problems and make the thermal energy sources match the demands [1-2]. As the core of energy storage technology, phase change materials(PCMs) can effectively store or release a great amount of latent heat during the

process of phase change. In addition, PCMs have already attracted enormous attention to investigators owing to their high energy storage density, isothermal operating process and quite small temperature variation [3-4]. PCMs are divided into organic PCMs, inorganic PCMs and eutectic PCMs according to inherent properties of the materials [5]. Even though the investigation about the characteristics of organic PCMs is relatively mature [6-9], high cost, low thermal conductivity and in flammability become the vital factors which restrain extensively practical applications. Inorganic hydrated salts, as the behalf of inorganic PCMs, have become a hot area of research due to their low cost, easy availability, non-flammability and high energy storage density. Common inorganic hydrated salts include $CaCl_2 \cdot 6H_2O$ [10-13], $Na_2SO_4 \cdot 10H_2O$ [14-17] and $CH_3COONa \cdot 3H_2O$ [18-21]. Because inorganic hydrated salts have poor nucleation property and are easy to melt incongruently, the current research work focuses on solving supecooling and phase separation. To solve these two main problems, the general measures taken are adding nucleating agents and adding thickeners.

$CaCl_2 \cdot 6H_2O$ is a representative inorganic hydrated salt PCM with melting point of 29.92℃ and relatively high latent heat of fusion. It can be used for thermal energy storage because of non-toxicity, wide availability and non-flammability. However, $CaCl_2 \cdot 6H_2O$ displays relatively large degree of supercooling. Lane et al. [22] reported that $SrCl_2 \cdot 6H_2O$ could be used as a nucleating agent in $CaCl_2 \cdot 6H_2O$ phase change thermal storage system. Supercooling could be effectively suppressed. Bilen et al. [23] added 3wt% KNO_3 to $CaCl_2 \cdot 6H_2O$ phase change system as a nucleating agent to prevent supercooling, which obviously improved systematic performance. Li et al. [24] prepared $CaCl_2 \cdot 6H_2O/SrCl_2 \cdot 6H_2O/EGO$ composite phase change system. By adding 1.0wt% EGO, the supercooling degree was controlled within 1℃. Moreover, the composite PCMs showed excellent thermal cycling stability. Tyaji et al. [25] studied the supercooling behavior of $CaCl_2 \cdot 6H_2O$ and the effect of pH value, which suggested that the supercooling degree of the PCM could be decreased or removed by adjusting the pH value. Tyaji et al. [26] carried out 1000 cycles of melting-cooling process to study the thermal cycling stability of $CaCl_2 \cdot 6H_2O$, and the results showed the phase change temperature and latent heat changed little.

The author prepared inorganic PCM $CaCl_2 \cdot 6H_2O$ by mass ratio method, and its crystal structure was characterized successfully by XRD. By adding 20wt% $MgCl_2 \cdot 6H_2O$, 1wt% $SrCl_2 \cdot 6H_2O$ and 0.5wt% CMC, the phase change temperature could be decreased and the supecooling degree was reduced to 0.57℃ [27]. However, in practical application, the thermal cycling stability of PCMs is crucial. It is necessary to analyze the variations of phase change temperature, latent heat and supercooling degree with the increase of cycle index. At present, few published literatures are concerning the investigations of cycling stability. In cycling experiments of PCMs, side reactions or by-products may produce, which will minish thermal energy storage density and shorten service life of PCMs. To evaluate degree of attenuation of PCMs, 100 cycling experiments can be carried out and the variations of phase change temperature, latent heat, and supercooling degree will be analyzed [28].

In this study, binary eutectic hydrated salts phase change thermal energy storage system $CaCl_2 \cdot 6H_2O$-20wt% $MgCl_2 \cdot 6H_2O$-1wt% $SrCl_2 \cdot 6H_2O$-0.5wt% CMC was prepared. The modified inorganic PCM froze and melted for 100 cycles under programmable temperature control, recording cooling-melting curves at the same time. The samples obtained after every 10 cycles were characterized by DSC, XRD and density meter. According to the results, the variations of phase change characteritics, latent heat, crystal structure, and density with the increase of cycle index were analyzed.

2. Experimental works

2.1. Materials

Anhydrous calcium chloride ($CaCl_2$, analytical reagent grade, purity≥96.0%), Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, analytical reagent grade, purity≥98.0%) and strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$, analytical reagent grade, purity≥99.0%) were offered by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Carboxy methyl cellulose (CMC, chemical pure grade,

with high viscosity of 800-1200 mpa·s) was provided by Yuanye Biotechnology Co., Ltd (Shanghai, China). All chemicals were used as received without further purification.

2.2. Preparation of modified inorganic PCM CaCl2·6H2O

The farinose $CaCl_2$ and deionized water were taken in terms of mass ratio as 1.027:1, and 20wt% $MgCl_2·6H_2O$, 1wt% $SrCl_2·6H_2O$ and 0.5wt% CMC were obtained simultaneously. After adding $MgCl_2·6H_2O$ into deionized water, $CaCl_2$ was added to the solution with stirring and releasing heat. Finally, $SrCl_2·6H_2O$ and CMC were added. The obtained solution was stirred for a while with a magnetic stirrer (90-4, Shanghai zhenrong scientific instrument Co., Ltd, China). A little solution was kept as sample before cycling, which was marked as Cycle0. Then, the other solution was transferred to a water jacketed glass vessel connected with a cooling bath thermostat (CC-K6 with Pilot ONE, Huber, Germany). After freezing completely under 18℃, water bath temperature rose to 30, 40 or 35 ℃. Freezing-melting processes were observed, and cooling-melting curves were recorded. Programmable temperature control was set for 100 cycles, and a freezing-melting process was regarded as 1 cycle. An example for programmable temperature control is shown in Table 1. Apparatus of cycling experiments is given in Figure 1.

Table 1. An example for programmable temperature control of cycling experiments

Order	Temperature setting/℃	Time/min	Mode	Stable mode
1	35.00	2.0	Inside	Time
2	18.00	2.0	Inside	Temperature
3	18.00	200.0	Inside	Time
4	35.00	2.0	Inside	Temperature
5	35.00	120.0	Inside	Time

computer   cooling bath thermostat   water jacketed glass vessel
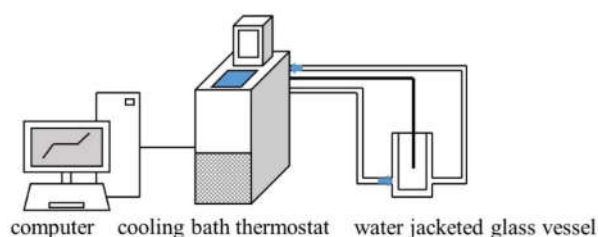
Figure 1. Apparatus of cycling experiments

2.3. Characterization

2.3.1. Differential scanning calorimetry(DSC), To analyse variation of latent heat of fusion of the PCM with the increase of cycle index, the DSC melting curves of supernatant liquid obtained after per 10 cycles and sample Cycle0 were measured with DSC (DSC 1, Mettler Toledo, Switzerland). 10 samples were marked as Cycle10-1, Cycle20-1 , Cycle90-1, Cycle100-1 successively. All samples were measured under a nitrogen flow of 50 ml/min at a heating rate of 10℃/min.

2.3.2. X-Ray diffraction(XRD), Non-molten white solid sediments were observed at the bottom of water jacketed glass vessel during cycling experiments. In order to figure out the crystal structure of the sediments, the bottom samples taken after per 10 cycles were characterized by XRD. 10 samples were marked as Cycle10-2, Cycle20-2, Cycle90-2, Cycle100-2 respectively. Powder XRD was

conducted at an automated D8 focus X-ray diffractometer (Bruker, Germany) with a Cu Kα radiation source (λ= 1.5418 Å) under a voltage of 40 kV and a current of 40 mA. The samples were scanned in the range of diffraction angle 2 theta from 5.0° to 90.0073°, at a scan speed of 0.2°/s at room temperature.

2.3.3. Density measurement, In order to briefly analyze the variation of mass of the sediments with the increase of cycle index, the densities of samples Cycle0, Cycle10-1, Cycle20-1, Cycle90-1, Cycle100-1 were measured with density meter under 25℃ (DMA 5000 M, Anton Paar, Austria).
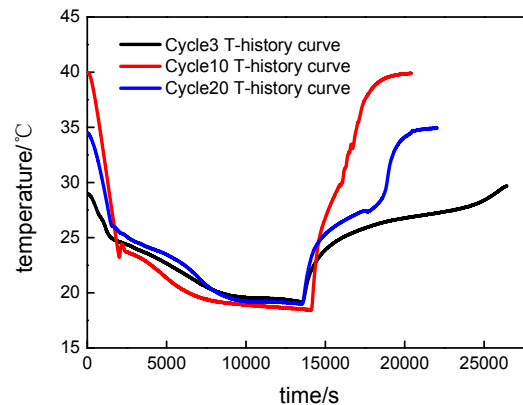
3. Results and discussion

3.1. Cooling-melting curves

Table 2 is about comparison of phase change characteristics for 3 different cycling experiments. From Table 2, both initial temperature of the modified inorganic PCM for cooling process and heating bath temperature for heating process are 30℃ for Cycle1-3. Correspondingly, for Cycle4-10 being 40℃ and for Cycle11-20 being 35℃. What's more, the average time for the PCM melting completely to heating bath temperature is 195 min in Cycle1-3, 113 min in Cycle4-10 and 121 min in Cycle11-20. The more time PCM takes, the slower efficiency of thermal energy storage. Besides, the average supercooling degree is 0.47℃ and 0.02℃ for Cycle4-10 and Cycle11-20 respectively. Therefore, heating bath temperature keeps at 35℃ for subsequent cycling experiments, and cooling bath temperature stays at 18℃. The average time for the PCM freezing completely to cooling bath temperature 18℃ is 213 min, 234 min and 223 min for Cycle1-3, Cycle4-10 and Cycle11-20 respectively, which means initial temperature of the PCM may have little impact on cooling bath time under the same cooling bath temperature. However, under the same initial temperature of the PCM, heating bath temperature has obvious influence on heating bath time. The reasons for above two conclusions need further investigation. Cooling-melting curves of Cycle3, Cycle10 and Cycle20 are shown in Figure 2.

Table 2. Comparison of phase change characteristics of 3 different cycling experiments

Cycle	Cooling process				Heating process		
	Initial temperature /℃	Cooling bath temperature /℃	Average cooling bath time /min	Average supercooling degree/℃	Initial temperature /℃	Heating bath temperature/℃	Average heating bath time/min
1-3	30	18	213	0	18	30	195
4-10	40	18	234	0.47	18	40	113
11-20	35	18	223	0.02	18	35	121

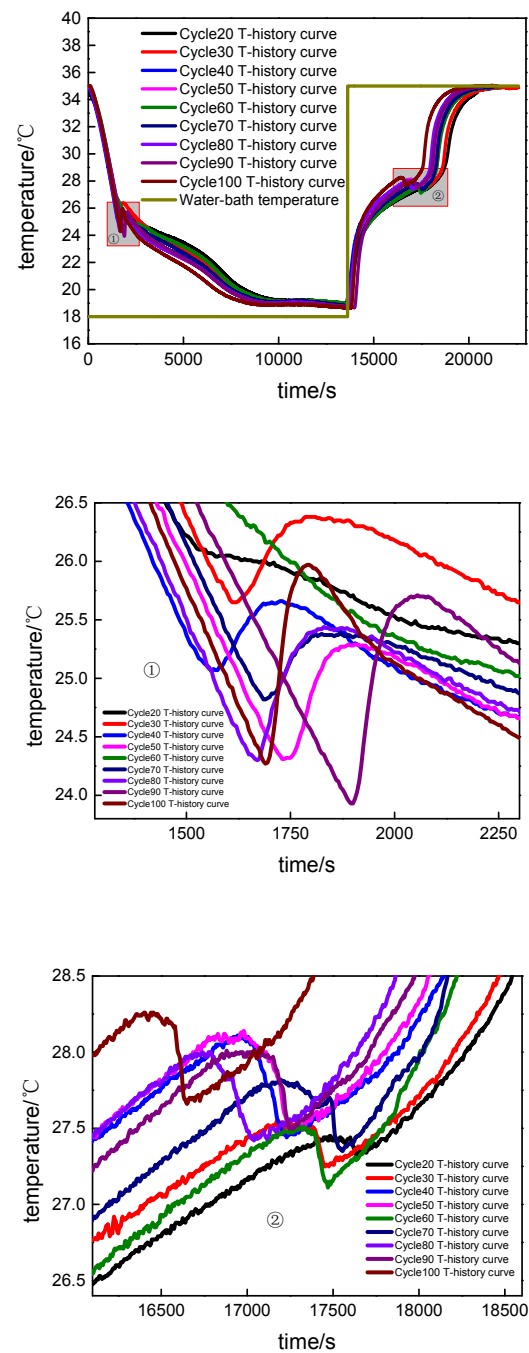**Figure 2.** Cooling-melting curves of Cycle3, Cycle10 and Cycle20

Table 3 and Table 4 list phase change characteristics for 9 groups of cycling experiments, each group including 10 cycles for freezing-melting process, thus 90 cycles in total. Figure 3 shows cooling-melting curves of final cycle for per group. Figure 4, Figure 5 and Figure 6 illustrate average phase change temperature, average supercooling and superheat degree and average cooling bath and heating bath time for 9 groups of cycling experiments respectively. As seen in Table 3 and Table 4, for 9 groups of cycling experiments, initial temperature of the modified inorganic PCM for cooling process and cooling bath temperature keep at 35℃ and 18℃ respectively, while initial temperature of the PCM for heating process and heating bath temperature stay at 18℃ and 35℃ respectively. In addition, the range of average cooling bath time is 223 min-231 min. The range of average phase change temperature for cooling process is 25.36℃-26.16℃. The range of average supercooling degree is 0.02℃-1.10℃. The range of average heating bath time is 121 min-128 min. The range of average phase change temperature for heating process is 27.17℃-27.61℃. The range of average superheat degree is 0.22℃-0.68℃. As shown in Figure 3, all cooling-melting curves can mostly overlap, which means cycling experiments can be reproduced and data can be trusted. Such modified inorganic PCM $CaCl_2 \cdot 6H_2O$-20wt% $MgCl_2 \cdot 6H_2O$-1wt% $SrCl_2 \cdot 6H_2O$-0.5wt% CMC has excellent circulation stability to some extent. The enlarged view for area① is common in cooling curves. However, the enlarged view for area② is rarely analyzed in published literatures, and it occurs in melting curves, showing that PCMs not only need to inhibit supercooling phenomenon to facilitate the release of latent heat promptly, but also focus on superheat phenomenon in melting process to avoid themal energy storage delaying. It can be seen from Figure 4 that the average phase change temperature for cooling and heating process has small changes. The average values are 25.70℃ and 27.39℃ respectively, with corresponding standard deviation 0.25℃ and 0.15℃. It proves that the phase change temperature for cooling or heating process of this PCM can basically maintain constant during cycling process. From Figure 5, average supercooling degree and superheat degree share the same variation trend with the increase of cycle index, namely, the value increasing at first, then decreasing and increasing again within 1.10℃. The average value and standard deviation of average supercooling degree are 0.59℃ and 0.34℃. Correspondingly, for average superheat degree, they are 0.49℃ and 0.17℃ respectively. The above results imply that the coexistence of nucleating agent $SrCl_2 \cdot 6H_2O$ and thickener CMC can suppress supercooling effectively, which promotes releasing phase change latent heat timely. Moreover, superheat phenomenon is primarily negligible. According to Figure 6, average cooling bath and heating bath time hardly change. The average values are 228 min and 126 min and the standard deviations are 2.39 min and 2.05 min. It is clear that this PCM can keep stable phase change process during circulations.

Table 3. Comparison of phase change characteristics of 9 groups of cycling experiments for cooling process

| Group	Cycle	Cooling process				
		Initial temperature/℃	Cooling bath temperature/℃	Average cooling bath time/min	Average phase change temperature/℃	Average supercooling degree/℃
1	11-20	35	18	223	25.88	0.02
2	21-30	35	18	228	26.16	0.49
3	31-40	35	18	227	25.75	0.82
4	41-50	35	18	229	25.36	0.85
5	51-60	35	18	229	25.58	0.22
6	61-70	35	18	228	25.45	0.47
7	71-80	35	18	228	25.51	0.54
8	81-90	35	18	231	25.83	0.82
9	91-100	35	18	231	25.77	1.10
Average value		35	18	228	25.70	0.59
Standard deviation		0	0	2.39	0.25	0.34

Table 4. Comparison of phase change characteristics of 9 groups of cycling experiments for heating process

| Group	Cycle	Heating process				
		Initial temperature/℃	Heating bath temperature/℃	Average heating bath time/min	Average phase change temperature/℃	Average superheat degree/℃
1	11-20	18	35	121	27.29	0.22
2	21-30	18	35	126	27.24	0.23
3	31-40	18	35	127	27.51	0.59
4	41-50	18	35	127	27.48	0.68
5	51-60	18	35	128	27.17	0.40
6	61-70	18	35	127	27.28	0.51
7	71-80	18	35	127	27.49	0.55
8	81-90	18	35	127	27.42	0.59
9	91-100	18	35	126	27.61	0.62
Average value		18	35	126	27.39	0.49
Standard deviation		0	0	2.05	0.15	0.17

Figure 3. Cooling-melting curves of Cycle20, Cycle30, Cycle90, Cycle100
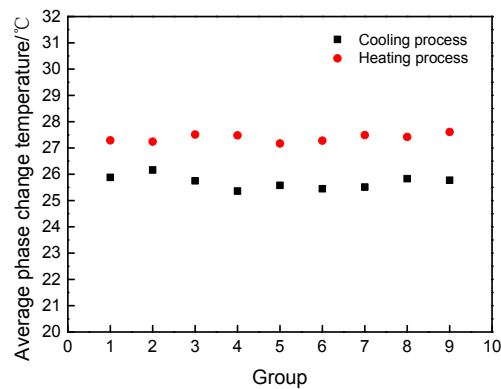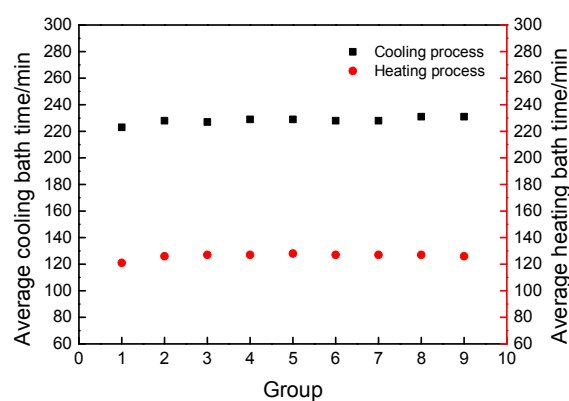
Figure 4. Average phase change temperature of 9 groups of cycling experiments
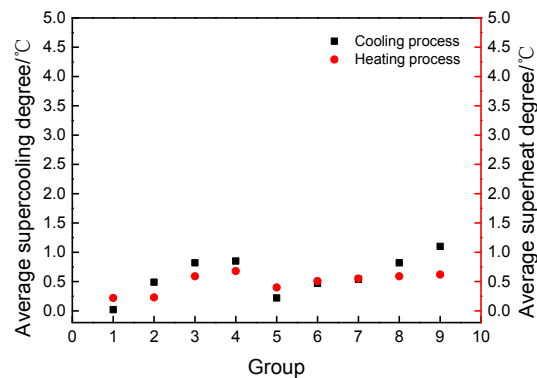
Figure 5. Average supercooling and superheat degree of 9 groups of cycling experiments


Figure 6. Average cooling bath and heating bath time of 9 groups of cycling experiments

3.2. DSC

In general, DSC is divided into functional compensatory DSC and heat flux DSC according to various measurement method [15]. Test method adopted in this paper is heat flux DSC. Figure 7 shows DSC melting curves of supernatant liquid obtained after per 10 cycles and sample Cycle0. Table 5 lists
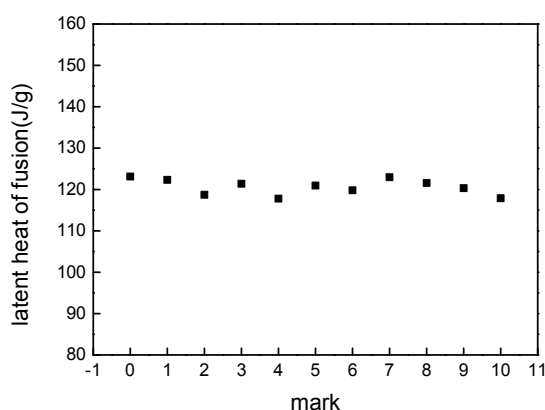
latent heat of fusion of total 11 samples. Figure 8 is corresponding variation diagram of latent heat of fusion. As seen in Figure 7, all DSC melting curves overlap partially, and all phase change melting peaks occur between 20℃-30℃, which is in accordance with intrinsic properties of the modified inorganic PCM. Furthermore, the value of heat flow decreases firstly then increases with the increment of the temperature. The range of measuring temperature is -20℃-80℃, and the range of heat flow is nearly -4 mW/mg-1 mW/mg. The latent heat of fusion of melting process was obtained from area integral, which formed from the curve and the horizontal baseline. According to Table 5, the range of latent heat of fusion is 117.88 J/g-123.13 J/g, and the average value and standard deviation are 120.62 J/g and 1.90 J/g respectively. The results indicate that in 100 cycles, latent heat of fusion of the PCM can keep relatively stable with the increase of cycle index. According to the author's published paper [27], the latent heat of fusion of pure $CaCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ is 223.54 J/g and 163.35 J/g respectively. Although the average latent heat of fusion (120.62 J/g) of the PCM is lower than that of $CaCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$, it is large enough to apply in real use. Figure 8 intuitively reflects the small change of latent heat of fusion. In a word, the DSC results demonstrate excellent cycling stability of the PCM again, which is helpful for it used in practical applications.
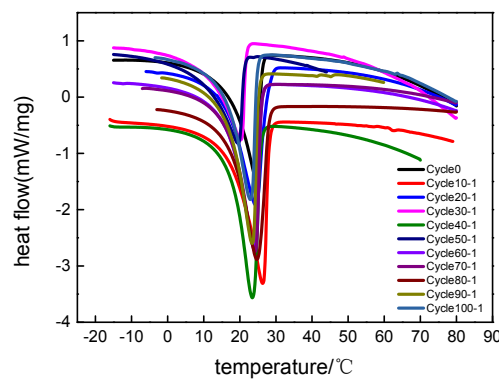
Figure 7. DSC melting curves of samples Cycle0, Cycle10-1, Cycle20-1, Cycle90-1, Cycle100-1

**Table 5.** Latent heat of fusion of samples Cycle0, Cycle10-1, Cycle20-1, Cycle90-1, Cycle100-1

| Mark	Sample	Latent heat of fusion/ (J/g)
0	Cycle0	123.13
1	Cycle10-1	122.32
2	Cycle20-1	118.72
3	Cycle30-1	121.40
4	Cycle40-1	117.79
5	Cycle50-1	120.94
6	Cycle60-1	119.79
7	Cycle70-1	122.95
8	Cycle80-1	121.58
9	Cycle90-1	120.32
10	Cycle100-1	117.88
Average value		120.62
Standard deviation		1.90

Figure 8. Latent heat of fusion of samples Cycle0, Cycle10-1, Cycle20-1, Cycle90-1, Cycle100-1

3.3. XRD

Figure 9 shows melting state of the PCM after 3 cycles. Figure 10 and Figure 11 give XRD spectrums of non-molten white solid sediments after every 10 cycles. Phase separation in Figure 9 is quite obvious. Owing to the circulations were static, the sediments appeared at the bottom of glass vessel all the time. According to published literatures concerning inorganic PCMs [29-30], supercooling phenomenon and phase separation are the two essential factors which severely restrict wide application of inorganic PCMs. In particularly, phase separation may shorten service life of PCMs directly. The author's research previously focused on the investigation of supercooling characteristics of $CaCl_2 \cdot 6H_2O$ as a PCM [27]. Because nucleating agent $SrCl_2 \cdot 6H_2O$ and thickener CMC worked effectively, the average value of average supercooling degree for 9 groups of cycling experiments was only 0.59℃, which could be basically ignored. Nevertheless, distinct phase separation still emerged with static cycling experiments of freezing-melting process conducting. With the purpose of analyzing the crystal structure of the non-molten white solid sediments, these sediments were characterized by XRD under the same experimental condition. As shown in Figure 10 and Figure 11, the main peak positions of XRD spectrums for 10 samples are in accordance with that of tachyhydrite($CaMg_2Cl_6 \cdot 12H_2O$) as an inorganic hydrated salt, which demonstrates the structure of sediments is $CaMg_2Cl_6 \cdot 12H_2O$. Something can be deduced from literature [31] that calcic and magnesian solution formed after modified inorganic PCM $CaCl_2 \cdot 6H_2O$-20wt% $MgCl_2 \cdot 6H_2O$ melting will be crystallized with tachyhydrite with melting point over 40℃ under certain temperature. Although the structure of the PCM is supposed to be changed due to the emergence of tachyhydrite, the most important thing is that whether the PCM can be used to store energy with appropriate phase transition temperature for a long term or not. On the basis of results of 3.1 and 3.2 sections, the sediments have little influence on phase change temperature, supercooling and superheat degree, cooling bath and heating bath time and latent heat of fusion. Moreover, all cycling experiments were static. When observing experimental phenomena of cooling process, needle-like crystalline solid was firstly generated on the surface of sediments, which indicated that the sediments might work as nucleating agent and inhibit supercooling. However, in real application, dynamic circulation of PCMs may not only solve phase separation problem, but also suppress supercooling further.
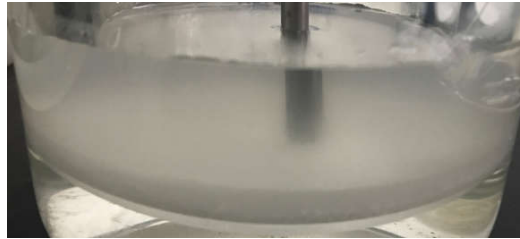
Figure 9. Melting state after 3 cycles.
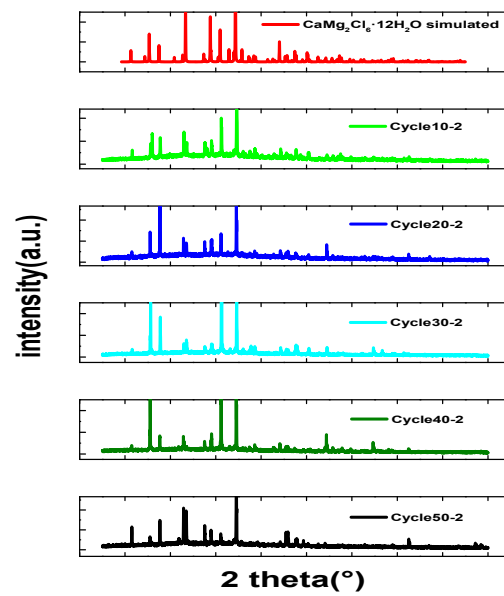
Figure 10. XRD spectrums of samples Cycle10-2, Cycle20-2, Cycle30-2, Cycle40-2 and Cycle50-2.
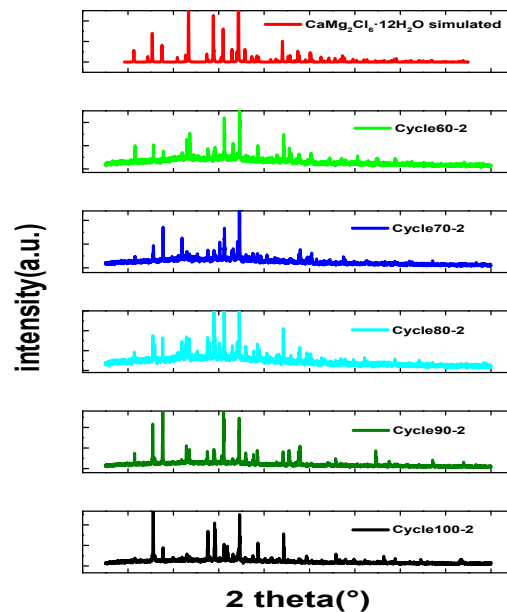
Figure 11. XRD spectrums of samples Cycle60-2, Cycle70-2, Cycle80-2, Cycle90-2 and Cycle100-2.

3.4. Density measurement

Table 6 lists density and specific gravity of supernatant liquid obtained after per 10 cycles and sample Cycle0. Figure 12 is the corresponding variation diagram of density and specific gravity with circulations proceeding. According to Table 6, the range of density under 25℃ is 1.45820 g/cm³-1.49463 g/cm³. As for specific gravity, the range is 1.46252 g/cm³-1.49906 g/cm³. With the help of Figure 12, the density of the modified inorganic PCM before cycling decreases sharply from 1.49463 g/cm³ to 1.48555g/cm³ after 10 cycles and further reduces to 1.45820g/cm³ after 30 cycles, which means the total mass of the sediments may be the largest after 30 cycles. However, the density of the PCM changes gently in subsequent cycling experiments. Specific gravity has the same changing trend. It implies that the density of the PCM declines suddenly due to the crystallization of tachyhydrite during prior cycling experiments. However, the density changes relatively little in later circulations, which shows that the total mass of tachyhydrite does not keep raising all the time with the increase of cycle index. It can be considered that the total mass of crystallized tachyhydrite is limited, which contributes to the maintenance of circulation stability for the modified inorganic PCM.
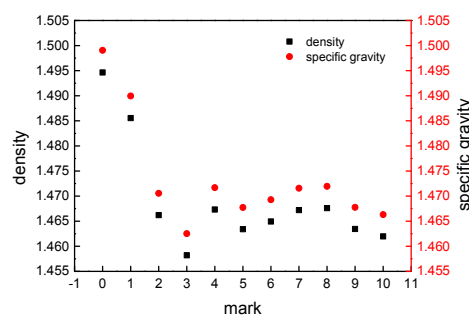
Figure 12. Density and specific gravity of samples Cycle0, Cycle10-1, Cycle20-1, Cycle90-1, Cycle100-1.

Table 6. Density and specific gravity of samples Cycle0, Cycle10-1, Cycle20-1, Cycle90-1, Cycle100-1.

Mark	Sample	Density/(g/cm^3) (25℃)	Specific gravity
0	Cycle0	1.49463	1.49906
1	Cycle10-1	1.48555	1.48996
2	Cycle20-1	1.46621	1.47056
3	Cycle30-1	1.45820	1.46252
4	Cycle40-1	1.46733	1.47169
5	Cycle50-1	1.46340	1.46774
6	Cycle60-1	1.46494	1.46928
7	Cycle70-1	1.46721	1.47157
8	Cycle80-1	1.46760	1.47195
9	Cycle90-1	1.46344	1.46777
10	Cycle100-1	1.46197	1.46631

4. Conclusion

Binary eutectic hydrated salts inorganic phase change thermal energy storage system $CaCl_2 \cdot 6H_2O$-20wt% $MgCl_2 \cdot 6H_2O$-1wt% $SrCl_2 \cdot 6H_2O$-0.5wt% CMC was prepared by mass ratio method. The PCM froze and melted for 100 cycles under programmable temperature control. The cooling bath temperature kept at 18℃. By analyzing cooling-melting curves under 3 different heating bath temperature, it was found that the average supercooling degree under heating bath temperature 35℃ was lower than that under 40℃, and the average heating bath time under 35℃ was shorter than that under 30℃. As a result, 35℃ was chosen to be the heating bath temperature for later cycling experiments.

a) Cycling experiments Cycle11-100 were divided into 9 groups, marked as Group1, Group2, …, Group8 and Group 9 respectively. By analyzing cooling-melting curves of each group, phase change characteristics for cooling and heating process were attained. The results show that no matter cooling or heating process, the average phase change temperature changes little, and the average values are 25.70℃ and 27.39℃ repectively. The average values of average supercooling and superheat degree are 0.59℃ and 0.49℃, with maximum of 1.10℃. That is to say the supercooling of the PCM is prevented with the addition of nucleating agent $SrCl_2 \cdot 6H_2O$ and thickener CMC, and the superheating situation can be neglected. Average cooling bath and heating bath time basically keep unchanged, and the average values are 228 min and 126 min. According to above analysis, the modified PCM can stay relatively stable within 100 cycles.

b) To investigate variation of thermal energy storage capacity of the PCM with the increase of cycling index, DSC melting curves of 11 samples were measured. The range of latent heat of fusion is 117.88 J/g-123.13 J/g. The average value and standard deviation are 120.62 J/g and 1.90 J/g respectively, which means that the PCM can relatively stable store and release heat in 100 cycles and it is vitally important to real applications.

c) Obvious phase separation occurred after 3 cycles. Via analyzing the crystal structure of the samples obtained after per 10 cycles with XRD, the sediments were recognized as tachyhydrite($CaMg_2Cl_6 \cdot 12H_2O$). It means that the calcic and magnesian solution formed after the PCM melting can crystallize tachyhydrite under certain temperature, which results in phase separation. According to results of 3.1 and 3.2 sections, it can be concluded that the appearance of tachyhydrite has little influence on phase change temperature, supercooling degree and latent heat of fusion, which is helpful for stability of the PCM.

d) The density of the samples obtained after per 10 cycles and Cycle0 was measured under 25℃. The results show that the density of the PCM decreases sharply after 30 cycles, which indicates that tachyhydrite crystallizes. However, the change of density becomes small in subsequent circulations,

which implies the total mass of tachyhydrite sustains relatively constant and the chemical compositions of the PCM basically do not transform in later cycling experiments.

Acknowledgements

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