

THERMAL ENERGY STORAGE USING CALCIUM CHLORIDE HEXAHYDRATE

by

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The solid-liquid phase change material named as PCM-Ca with 49.1% in mass water, 49.7% calcium chloride, and 1.2% strontium chloride was discovered and outlined in this paper. Differential scanning calorimetry, simultaneous thermal analyzer, thermal conductivity analyzer, temperature recorder, and digital vibrating-tube densimeter were used to characterize the thermal properties of PCM-Ca. The results indicated that PCM-Ca has the phase change temperature at 28.7 °C, the latent heats in the process of fusing and crystallizing are 193.4 and 193.0 kJ/kg, the thermal conductivity is 1.2801 W/mK at the melting point, and the density is $1.48 \cdot 10^3$ kg/m³ at room temperature. Thirty times repeated thermal cycling tests show excellent thermal stability in terms of latent heat and nucleation temperature, and the maximum deviations of the latent heat and the phase change temperature of PCM-Ca are 0.2% and 2.7%, respectively.

Key words: *phase change materials, supercooling, calcium chloride hexahydrate*

Introduction

Phase change materials (PCM) utilize latent heat to store or release thermal energy and the temperature can stay nearly constant during the process of phase change, which can be effectively solved the imbalance of energy supply and demand in time and space. On the basis of this feature, PCM can be widely applied in solar energy utilization, heat exchanger, building energy-saving, textiles, electric peak-shaving and so on [1-6].

According to the phase change behavior, PCM can be generally made up of four categories: solid-solid PCM, solid-liquid PCM, solid-gas PCM, and liquid-gas PCM [7, 8]. According to the listed sequence order, the value of latent heat of PCM is become bigger and bigger, but the latter two PCM are never adopted because of the very large volume variations with the occurrence of the gas phase. Compared with solid-solid PCM, solid-liquid PCM are most widely application because of its suitable phase change temperature, large latent heat, and relatively small volume. In addition, there are also some special PCM whose phase change properties are laid between solid-solid PCM and solid-liquid PCM, which were being named form-stable or shape-stabilized PCM and composed of working substances and supporting materials [9, 10].

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Water is commonly regarded as the most suitable material for thermal energy storage for it is low-cost and high heat capacity. An alternate means for thermal energy storage is to use the latent heat of a reaction. The purpose of this paper is to describe a method for obtaining the advantages of the calcium chloride (CaCl_2) and H_2O reaction while eliminate the solid-state diffusion problem. The weight percent of CaCl_2 in PCM-Ca was optimized and discussed, and the thermal characteristics of PCM-Ca were measured by differential scanning calorimeter, simultaneous thermal analyzer, thermal conductivity analyzer, temperature recorder, and digital vibrating-tube densimeter, respectively. In addition, a thirty-run-cycling test was also conducted to investigate the thermal stability of PCM-Ca.

Experimental

Materials

The chemicals used were of analytical reagent: CaCl_2 , (96% in mass) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 98% in mass) were obtained from the Tianjin Guangfu Fine Chemical Research Institute, strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, 99.5% in mass) and barium carbonate (BaCO_3 , 99% in mass) were purchased from the Tianjin Fuchen Chemical Reagents Factory, borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 99.5% in mass) was purchased from the Tianjin Yingda rare Chemical Reagents Factory, and barium fluoride (BaF_2 , 98% in mass) was purchased from the Tianjin Beifang Medical Chemical Reagents Factory. Doubly deionized water (DDW) with conductivity less than $1 \cdot 10^{-4} \text{ Sm}^{-1}$ and pH 6.60 at room temperature (25 °C) was used in this study.

Analysis methods

The heat of fusion and melting point of PCM-Ca were determined using a differential scanning calorimeter – DSC (200F3, Netzsch Instrument Inc., Germany; Labsys, Setaram Co. Ltd., France) with the scanning rate of 1 °C per minute, under the nitrogen atmosphere from 0 to 50 °C. The exothermic curves were determined using the temperature recorder (Shanghai Yadu Electronic Technology Co. Ltd, VX2103R/C2/U/TP1, China) in the biochemistry incubator (Shanghai Yiheng Scientific Instruments Co. Ltd, LRH-150, China) with the constant temperature of 5 °C. Thermal conductivity was metered by thermal conductivity analyzer (DRE-2B, Xiangtan Instrument Co. Ltd., China) with the uncertainty within $\pm 3\%$ in mass. In addition, the density was measured by using a digital vibrating-tube densimeter (DMA 4500, Anton Paar Co. Ltd., Austria) with an uncertainty of less than $\pm 0.01 \text{ mg/cm}^3$.

Preparation

The Ca-based solution was prepared with CaCl_2 and DDW with the mass ratio of 50.7 : 49.3. The CaCl_2 and DDW were weighted and adequately diversified in a closed container until dissolved completely. Then strontium chloride hexahydrate was added into the calcium-based solution under stirring and the solution was heated until it was melted completely at 80 °C in a water bath (K20-cc-NR, Huber Co. Ltd, Germany). After that, the sample cooled down to room temperature and the target product was obtained.

Thermal cycle test

In this work, thermal cycle test was used to evaluate thermal stability of PCM-Ca, and the test was performed consecutively up to thirty times of thermal cycling by using a biochemistry incubator as the heating and cooling facility. Schematic diagram of thermal cycle test apparatus was shown in fig. 1. Twenty gram samples were weighted and placed in a test

tube (20 mm diameter and 300 mm high), and the thermocouple of temperature recorder was inserted into the center of the test tube, after then they were put in a constant temperature of 5 °C biochemistry incubator for solidification. When the exothermic process ended, the temperature of the biochemistry incubator was set-up to 35 °C and the endothermic process was beginning. While the endothermic process ended, the temperature of the biochemistry incubator was set up to 5 °C again to lead the next exothermic process.

Results and discussion

Composition of PCM-Ca

Salt-water system phase diagram of the binary system ($\text{CaCl}_2 + \text{H}_2\text{O}$) at different temperatures is presented in fig. 2 [11]. It can be seen that curve AB is the solubility curve of ice, and curve BCDEF are the solubility curves of CaCl_2 hydrated salts including $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ which was precipitated at different stages with an increasing in the concentration of CaCl_2 . When the composition of CaCl_2 is more than 50.68% in mass, there is a phenomenon of conversion solution with the increasing of temperature, that is to say, once the composition of CaCl_2 is over 50.68% in mass, generated salts are all of unstable hydrated salts. Herein, we choose the composition of CaCl_2 at 50.68% as the main research object (named calcium-based solution), in such case the solid-state diffusion problem can be eliminated as a reaction. In other words, the calcium-based solution as the main research object was prepared with the mole ratio of CaCl_2 and DDW by 1 : 6, and the precipitated hydrated salt was only $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Reduction of the supercooling degree of PCM-Ca

Supercooling is a serious problem associated with almost all inorganic PCM [12]. In order to solve the problem of supercooling, researchers use many ingenious methods to reach a reasonable rate of nucleation. At present the most frequently-used method is adding a suitable nucleating agent which provides the nucleon for crystal formation [13, 14]. The calcium-based solution as a PCM was found to undergo serious supercooling degree up to 15.5 °C below the phase change temperature. According to nucleating agent screening principle of the scope of lattice parameter within 15% in mass [15], borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), barium fluoride (BaF_2), barium carbonate (BaCO_3), and strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) were chosen to act as the candidate nucleating agent of the calcium-base solution, and the results show that $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was the most effective nucleating agent for the calcium-base solution.

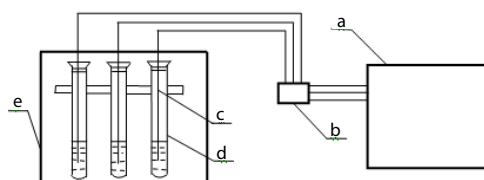


Figure 1. Schematic diagram of thermal cycle test apparatus; (a) – computer processor, (b) – temperature recorder, (c) – thermocouple, (d) – test tube, and (e) – biochemistry incubators

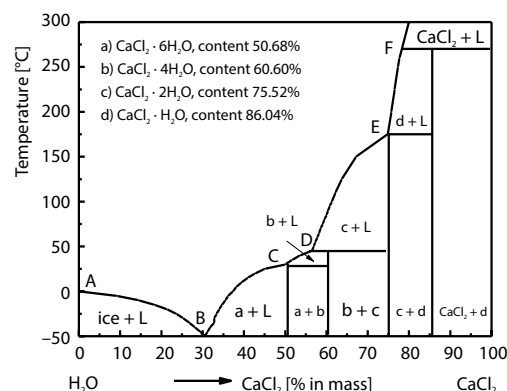


Figure 2. Phase diagram of the binary system ($\text{CaCl}_2 + \text{H}_2\text{O}$) at different temperatures

Influence of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ concentration on the supercooling degree of the calcium-base solution was also investigated, and the results was illustrated in fig. 3. Supercooling degrees of the calcium-base solution after adding 0.0%, 0.5%, 1.0%, 2.0%, and 3.0% in mass $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ were 15.5 °C, 2.9 °C, 1.8 °C, 0.4 °C, and 1.7 °C, respectively. With the increasing concentration of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, supercooling degree of the calcium-base solution was decreased sharply, but once the mass percent of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was more than 2% in mass, supercooling degree was increased instead. Therefore, 2% in mass $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was selected as the nucleating agent. Hence, the composite PCM named as PCM-Ca was a mixture solution with the mass ratio of DDW: CaCl_2 : SrCl_2 = 49.1 : 49.7 : 1.2. In addition, cooling curve of PCM-Ca under the condition of room temperature was also measured and presented in fig. 4. It can be seen from fig. 4 that the degree of supercooling in the cooling process of PCM-Ca is 1.2 °C, the phase change temperature is 28.8 °C and the exothermic lasting time is more than 90 minutes. In other word, the latent heat of PCM-Ca was large for thermal energy storage.

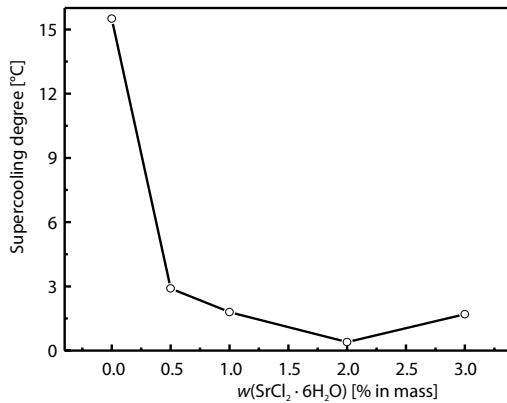


Figure 3. Effect of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ concentration on the supercooling degree of PCM-Ca

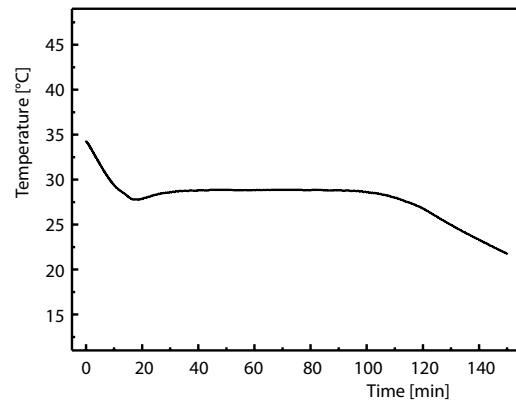


Figure 4. Cooling curve of PCM-Ca

The DSC analysis

Figure 5 presents DSC curve of PCM-Ca in the process of heating and cooling. It can be seen that the melting and crystallizing temperature of PCM-Ca are 28.8 °C and 27.9 °C, the latent heat of phase change in fusing and crystallizing process are 193.4 kJ/kg and 193.0 kJ/kg, respectively. Almost all of the total absorbed thermal energy in the process of melting was released in the process of crystallizing. From the DSC thermal analysis results, it can be suggested that the phase change temperature and the latent heat of fusion of PCM-Ca make it potential material for thermal energy storage.

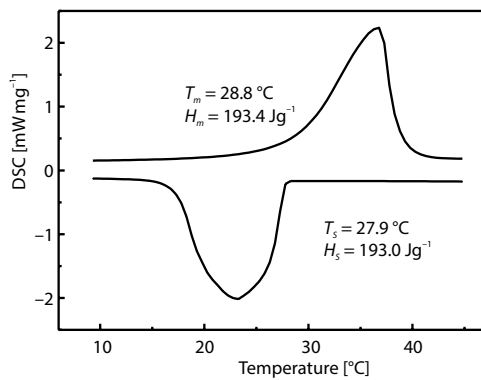


Figure 5. The DSC curve of PCM-Ca

Thermal conductivity and density analysis

One of the key measure gauge for the rates of heat storage and release in the process of fusing and crystallizing is thermal conductivity, λ . A low thermal conductivity not only reduced the rate of

endothermic and exothermic but also restricted its applications. To increase thermal conductivity, some additives such as Fe_3O_4 nanoparticles can be added [16]. In this study, thermal conductivity of PCM-Ca was measured by a thermal conductivity analyzer, and thermal conductivities of PCM-Ca from 15 °C to 40 °C were shown in fig. 6. Thermal conductivity of PCM-Ca in the solid-state was slowly increasing from 0.7453 W/mK at 15 °C to 0.9327 W/mK at 28 °C and in the liquid state is approximate to 0.6311 W/mK, but the thermal conductivity is significantly increases to 1.3637 W/mK in the phase change process. That is to say, PCM-Ca with a high thermal conductivity is suitable to be used as a PCM.

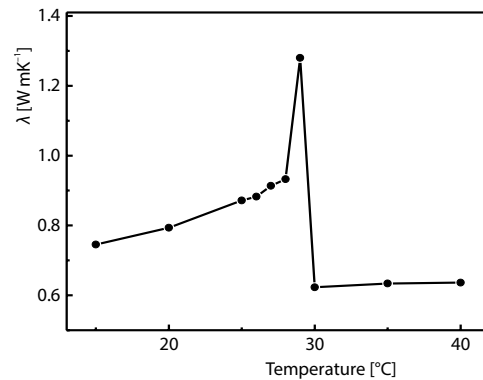


Figure 6. Thermal conductivity of PCM-Ca at different temperatures

During the process of experiment, empirical observation of the volume change of PCM-Ca from solid to liquid is very small. Hence, the density of PCM-Ca was measured only at room temperature with the value of $1.48 \cdot 10^3 \text{ kg/m}^3$. In other word, the heat of fusion of PCM-Ca is $2.86 \cdot 10^5 \text{ kJ/m}^3$, which was large latent heat as a PCM for thermal energy storage.

Thermal stability of PCM-Ca

In this work, thermal stability of PCM-Ca was monitored through thermal cycle test. Depending on the experimental data, repeatability properties tests of PCM-Ca and comparison of DSC curves of PCM-Ca before and after 30 times recycle-used are presented in figs. 7 and 8. From figs. 7 and 8, it can be seen that PCM-Ca has a good thermal stability, *i. e.* the highest and lowest temperatures are 28.6 °C and 27.0 °C, and the supercooling degrees are within the range of 0~1.5 °C. Before recycle-used, absorbed heat, energy released, melting, and crystallizing temperature of PCM-Ca are 193.4 kJ/kg, 193.0 kJ/kg, 28.8 °C, and 27.9 °C, respectively. While after 30 times recycle-used, absorbed heat, energy released, melting, and crystallizing temperature of PCM-Ca are 193.1 kJ/kg, 192.1 kJ/kg, 28.2 °C, and 28.0 °C, respectively. Within thirty times repeated melting and crystallizing cycles, the maximum deviations of melting temperature and latent heat of PCM-Ca are 2.7% and 0.2%, respectively.

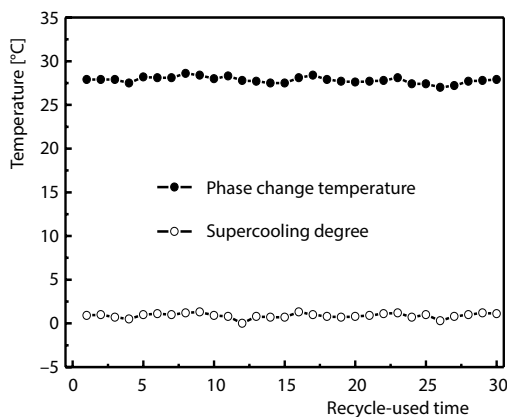


Figure 7. Repeatability properties tests for PCM-Ca

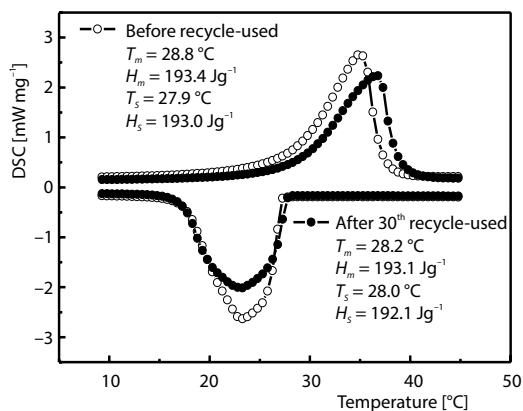


Figure 8. Comparison of DSC curve of PCM-Ca before and after 30 times recycle-used

Advantages of PCM-Ca

Industrial product of calcium CaCl_2 is one of abundant raw materials on the industrial chemical market and its price is less than 0.3 US\$ per kilogram. Hence, the price of PCM-Ca with the mass ratio of DDW: CaCl_2 : SrCl_2 = 49.1 : 49.7 : 1.2 will be cheaper. From a cost point of view, PCM-Ca as a PCM for thermal energy storage has the most appealing advantages.

So far as we know, CaCl_2 is one of non-toxic chemical materials, and the toxicity of strontium chloride hexahydrate is rather small. That is to say, the toxicity of CaCl_2 and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ are very low and they are almost harmless. In addition, PCM-Ca is nearly closed to neutral and has no flammability. From these facts, there is no legal problem with using the composite substances including CaCl_2 and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ as a PCM for thermal energy storage. Although the investigation of corrosion has not been conducted yet, empirical observation on the inner surface of the stainless steel thermocouple of temperature recorder used for determining cooling curve indicated that typical stainless steels are not damaged by these substances. In practice, it would be better for PCM-Ca to be encapsulated in a durable container. Hence, the authors think that the testing methods and procedures described above are useful and PCM-Ca can be as an ideal PCM for thermal energy storage.

Conclusion

A novel solid-liquid PCM named as PCM-Ca was prepared with the mass ratio of DDW : CaCl_2 : SrCl_2 = 49.1 : 49.7 : 1.2. The results show that phase change temperature of PCM-Ca was 28.7 °C, latent heats in the process of fusing and crystallizing are 193.4 kJ/kg and 193.0 kJ/kg, thermal conductivity is 1.2801 W/mK at phase change temperature, and the value of density is $1.48 \cdot 10^3 \text{ kg/m}^3$ under room temperature environment. Thirty times repeated thermal cycling tests show that PCM-Ca has a good thermal stability in terms of latent heat and nucleation temperature, and the maximum deviations of latent heat and melting temperature are 0.2% and 2.7%, respectively. In addition, low cost is also one of the advantages for PCM-Ca because there is no legal restriction with using PCM-Ca for thermal energy storage.

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