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Study On Anti-Blocking Agent of Calcium Chloride Hexahydrate Phase Change Materials

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Abstract

Anti-blocking agent was studied against the agglomeration phenomenon of Calcium chloride hexahydrate Phase Change Materials. Uniform design software was used to prepare anti-blocking agent. Regression equation and full permutation optimization were established to check and predict the experiment data. Synergistic effect between each variables was investigated and the results showed that there were different degrees of synergistic effect during their value range, which could definitely influence the crystallization of $CaCl_2$ $6H_2O$ phase change materials. It could be gained from the experiment that The optimum formula in mass fraction can be described as 1.85% Sodium dodecyl benzene sulfonate, 2.39% SHMP, 1.77% Sodium polyacrylate, and 1.27% Cetyl trimethyl ammonium bromide, 0.55% EDTA-2Na. The phase change materials possessed excellent stabilities and had no agglomeration phenomena when this anti-blocking agent was added into the system.

Keywords: Cacl₂ 6H₂O; Phase Change Materials; Uniform Design; Optimization; Agglomeration

1 INTRODUCTION

It's a very active academic frontiers in the field of material science and energy use by using phase change latent heat of phase change materials(PCM) for energy storage and utilization in recent years, because it can be beneficial to the development of energy efficient and environmentally friendly phase change composite material. Due to the heat storage properties of phase change materials, it can absorb heat when environment temperature rise, and can give off heat energy when the temperature decrease. By this way, phase change materials have been widely used in many fields.

Among all sorts of phase change materials, the inorganic salt hydrate proved to be a material with the largest latent heat when the temperature was below 150 ℃[1]. $CaCl_2$ $6H_2O$ has excellent solidifying characteristics, meanwhile its melting characteristics are also equally good. So calcium chloride hex hydrate is a potential PCM and can be used in low temperature thermal energy storages [2]. $CaCl_2$ $6H_2O$ has many advantages compared to other compound, high thermal conductivity, good chemical stability, non-toxic, low cost, easy to get, all these properties make it a promising materials[3]. In order to study the changes in latent heat of fusion and melting temperature of calcium chloride hex hydrate ($CaCl_2$ $6H_2O$) inorganic salt as a latent heat storage material, VV detected the effect of thermal cycling and the reliability by using differential scanning calorimeter (DSC), and found that $CaCl_2$ $6H_2O$ could be for heating and cooling process in building applications [4].

However, corrosion, phase separation, lack of thermal stability, undercooling, and agglomeration phenomenon are some of the problems encountered while using inorganics as PCM [5]. Which extremely limit the application of PCM, especially the agglomeration phenomenon. Most inorganic hydrated salt would appear agglomeration phenomenon after they were repeatly heated and cooled. These phenomenon can not only significantly reduce the capacity of heat storage, but also cut down the service life of phase change materials [6]. The main measures to solve supercooling is adding anti-blocking agent to phase change materials. The method to prevent separation is adding thickening agent and suspending agent. Owning to its special structural characteristics, the surfactant could significantly reduce the surface of solution and change the contact angle between the solid and liquid when they were added. A small amount of surfactant could effectively prevent caking phenomenon.

Uniform design is a commonly used software, it can select corresponding table in accordance with the number of independent ariables in experiment and proposed experiment times. These variables distributes well in a multidimensional space, thus we can gain the most amount of information form the least experiment times [7]. In this paper, we analysed the selected anticaking materials by means of uniform design method, and then carried on experiment according to the results, finally we got the optimum formula on the basis of crystallization conditions. The obtained phase change materials through this way had no agglomeration phenomenon when this anti-blocking agent was introduced into the system.

2 EXPERIMENTS

2.1 Experimental Materials

The used reagents are listed in table 1.

TABLE 1. EXPERIMENTAL REAGENTS

Name of agents	Manufacturer	Reagent grade
Sodium dodecyl benzene sulfonate	Tianjin fu chen chemical reagents factory	Chemically pure
SHMP	Beijing chemical factory	Analytically pure
Sodium polyacrylate	Commercially available	Industrial grade
Cetyl trimethyl ammonium bromide	Tianjin fu chen chemical reagents factory	Analytically pure
EDTA-2Na	Tianjin fu chen chemical reagents factory	Analytically pure

2.2 Experimental Instrument

HWS24 Electric-heated thermal static water bath from Shanghai yiheng scientific instrument limited company; JJ-1 motor stirrer from gongyi yuhua instrument limited company; DC-1006 Low-temperature thermostat bath from Shanghai hengping scientific instrument limited company; TA1004 Electronic analytical balance.

2.3 Experimental Process

A certain amount of $CaCl_2 \cdot 6H_2O$ was put into a beaker, then they were heated in constant temperature water at 50℃. After $CaCl_2 \cdot 6H_2O$ was melt, the selected materials were added in mixing situation. When the reaction reacted completely, put all these materials into a plastic bag, then it was cooled in a low-temperature thermostat bath. We would give a evaluation to each bag according to their crystallization conditions. Each experiment was 100g in convenience.

3 EXPERIMENTS RESULTS AND DISCUSSION

3.1The Formula Design of Phase Change Materials

Uniform design software was used to calculate the following variables: Sodium dodecyl benzene sulfonate, SHMP, CMC, Sodium polyacrylate, Cetyl trimethyl ammonium bromide, EDTA-2Na. The value ranges of each variables were listed on table 2.

TABLE 2. THE QUANTITY RANGE OF EACH SUBSTANCES

Independent variables	**Code name**	**Lower limit**	**Upper limit**
Sodium dodecyl benzene sulfonate	X_1	0	2
SHMP	X_2	0.5	3
Sodium polyacrylate	X_3	1	2
Cetyl trimethyl ammonium bromide	X_4	0	2
EDTA-2Na	X_5	0	3

The designed results and experimental results are listed on table 3.The evaluation grades represent crystallization effect, which is good or bad. The lowest grade 1 suggests that the crystallization effect is the worst, and the highest grade 10 suggests that the crystallization effect is the best, which had no agglomeration phenomenon.

TABLE 3. THE RESULTS OF UNIFORM DESIGN FOR ANTI-BLOCKING AGENT

Group	X_1	X_2	X_3	X_4	X_5
1	0.571	1.571	1.571	1.429	3.000
2	1.286	2.821	1.071	0.714	2.786
3	2.000	1.214	1.714	0	2.571
4	0.429	2.464	1.214	1.571	2.357
5	1.143	0.857	1.857	0.857	2.143
6	1.857	2.107	1.357	0.143	1.929
7	0.286	0.500	2.000	1.714	1.714
8	1.000	1.750	1.500	1.000	1.500
9	1.714	3.000	1.000	0.286	1.286
10	0.143	1.393	1.643	1.857	1.071
11	0.857	2.643	1.143	1.143	0.857
12	1.571	1.036	1.786	0.429	0.643
13	0	2.286	1.286	2.000	0.429
14	0.714	0.679	1.929	1.286	0.214
15	1.429	1.929	1.429	0.571	0

3.2 The Establish Repression Function

The Evaluation grades were gained based on the conditions of phenomenon such as supercooling, caking and phase separation so as to process the experimental data and results. In this repression function, the selected materials was independent variables meanwhile the evaluation grades were dependent variable. The function is shown as follows.

$$\begin{aligned} Y = &-1.71*10^7 - 1.29*X_1*X_4 - 1.87*X_4*X_5 + 1.57*10^6*X_1*X_2 \\ &+3.16*10^3*X_5 - 2.77*X_5^2 - 2.04*10^4*X_2*X_3 - 4.51*10^3*X_2^2 \\ &-2.28*10^4*X_3^2 + 1.57*10^6*X_2*X_4 + 7.82*10^6*X_3 \end{aligned} \quad (1)$$

The repression function means the corresponding values of dependent variable when the independent variable changes.

The analysis of ariance in this experiment was shown on table 4. We can see from table 4 that when fiducially limit α is 0.17, statistical alue F is larger than F(10, 4), which could indicate that the repression function is significant. Besides, the multiple correlation coefficient is 0.935152392, from which we can say that the repression function can demonstrate well the relation between dependent variable and seven independent variables, that is to say, the relation between evaluation grade and seven selected materials.

TABLE 4. ANALYSIS OF VARIANCES

Source of variance	Sum of squares	Degree of freedom	Mean sum of square	Significance
Regression	100.07	10	10.00	when fiducially limit α is 0.17
Residual	14.38	4	3.60	statistical alue F =2.78
Total	114.4	14		F(10, 4)=76

Note: the multiple correlation coefficient is 0.935152392

The comparison diagram between regression equation and specimen is present on figure1. The abscissa represents the sample number and the ordinate represents the value of dependent ariable Y. The sample values are expressed by circle and fitted values are expressed by red dot. The smaller the vertical distance between sample values and fitted values, the closer between experimental values and fitted values, which indicates that the fitting precision is pretty good.

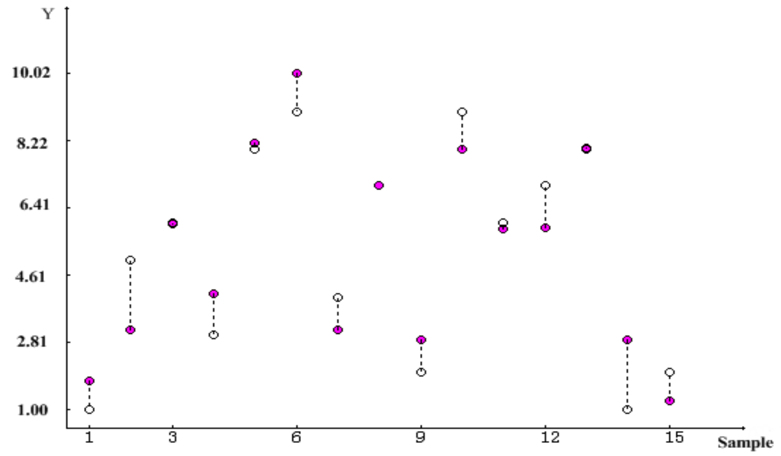

FIG 1. THE COMPARISON DIAGRAM BETWEEN REGRESSION EQUATION AND SPECIMEN

2.3 The Influence of Relationship between Each Variable on Crystallization

The uniform design isogram is used to investigate the interrelationship of seven independent variables. The isogram is a profile of multi-dimensional space, from the profile we can get the changes of dependent variables when two independent variables vary on condition that other ariables are constant. Also we can see whether two independent bariables have interaction. The interrelationship of variables will be change when the selected profile of multi-dimensional space once the initial condition alters.

The influence of synergistic effect of five independent variables on crystallization effect of phase change materials are presented from figure 2 to figure 4.The larger of numerical value, the better of crystallization effect of phase change materials. The numerical value which pink line represents is the largest, and the numerical value which blue line represents is the smallest.

From figure 2, it can be seen that the synergistic effect is significant between independent variables X_1 and X_3. The crystallization condition of phase change materials will be better when X1 is added from 1.17 to 2.0g and X_3 from 1.7 to 2.0g. The of borax can promote the crystallization of $CaCl_2$ $6H_2O$. The surfactant could significantly reduce the surface of solution and change the contact angle between the sold and liquid when they are added, hence can prevent gather phenomenon in crystallization.

From figure 3, it can be seen that X_2 and X_3 have linear relation which is negative correlation. The crystallization condition of phase change materials will be better when X_2 is added from 2.15 to 3g and X_3 from 1.7 to 2.0g. The add of SHMP changed the crystallization progress due to it's special structure property, thus could prevent the agglomeration phenomenon.

From figure 4, it can be seen that X_3 and X_4 have linear relation which is negative correlation. The crystallization condition of phase change materials will be better when X_3 is added from 1.7 to 2g as well as X_4 is added from 1.17 to 2g.

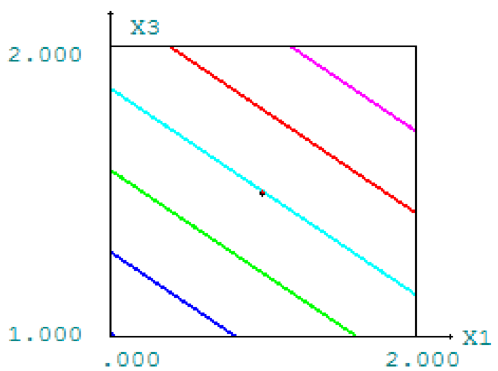

FIG 2. THE SYNERGISTIC EFFECT BETWEEN X_1 AND X_3

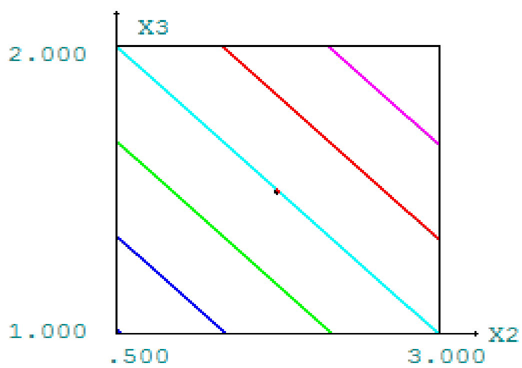

FIG 3. THE SYNERGISTIC EFFECT BETWEEN X_2 AND X_3

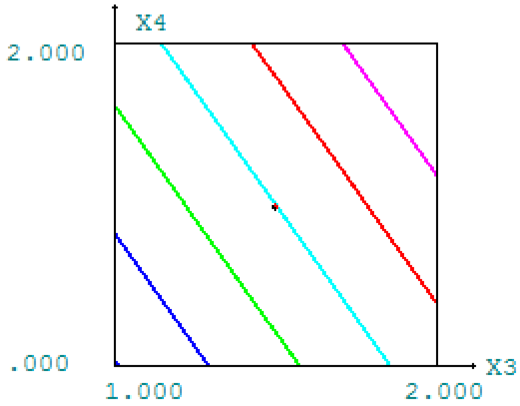

FIG 4. THE SYNERGISTIC EFFECT BETWEEN X_3 AND X_4

2.4 The Optimization and Checking Of Formula

Full permutation optimization was done according to the value range of five independent variables mentioned above. The optimal formula can be got on the basis of results from optimization procedure. We selected three data sets which had excellent predictability to check the experiment. The optimization data were listed on table 5.

TABLE 5. PREDICTION DATA

Group number	X_1/g	X_2/g	X_3/g	X_4/g	X_5/g
1	1.52	2.56	1.85	1.68	0.37
2	1.26	2.31	1.92	1.79	0.69
3	1.85	2.39	1.77	1.27	0.55

Experiments were carried out based on the data above. The crystallization and its stability were investigated after the samples were repeatedly heated and cooled. The results were listed on table 6.

TABLE 6. THE RESULTS OF STABILITY

Times of heating and cooling	1	2	3	4	5	6	7	8
1	9	8	8	6	6	7	8	6
2	8	8	5	5	6	7	6	6
3	10	10	9	9	9	10	9	9

From the experiment results we can draw a conclusion that both of group 1 and group 2 are short of stability after they were repeatedly heated and cooled. On the contrary, group 3 shows excellent stability and has no caking phenomenon.

4 CONCLUSION

In this article, we used uniform design software to investigate the selected five materials and established regression equation to check experimental data. Synergistic effect between each variables was investigated, and it proved that there were different degrees of synergistic effect during their alue range, which could definitely influence the crystallization of $CaCl_2$ $6H_2O$ phase change materials. The optimum formula in mass fraction can be described as 1.85% Sodium dodecyl benzene sulfonate, 2.39% SHMP, 1.77% Sodium polyacrylate, and 1.27% Cetyl trimethyl ammonium bromide, 0.55% EDTA-2Na. The phase change materials prepared by this formula possess excellent stability while crystalling and had no agglomeration phenomenon

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