Anti - caking KAl $(SO_4)_2{\cdot}12H_2O$ - $MgSO_4{\cdot}7H_2O$ Composite for Thermal Storage Material by Addition of Al_2O_3 Powder

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Abstract. Alumina powder is added as anti- caking agent to prevent the agglomeration of phase transition thermal storage composite KAl $(SO_4)_2$ $\cdot 12H_2O$ - $MgSO_4$ $7H_2O$ with the ratio of 2:8, heating and cooling cycle test is conducted to characterize its cyclic properties. The results show that the mixed salt system with alumina anti- caking agent is with good thermal storage property. The exothermic enthalpy of phase transition is still kept at 188.5J / g after 200 cycles, super-cooling of average 2°C, stable exothermic phase transition temperature of average 47 °C and longer duration of exothermic platform of average 7.2 min. It is demonstrated that the alumina powder is active in preventing the mixed salt thermal storage material from agglomeration.

1. Introduction

Caking is a common phenomenon for material from a loose state to dense one [1]. Most inorganic salt product behaves this caking phenomenon [2], this feature changes their original property and causes inconvenience sometimes.

In the study of cyclic properties of hydrated inorganic salt phase change materials, it found that some thermal storage materials also produce agglomeration after several thermal cycles, thus affecting the material's heat storage performance. In order to improve this feature, anti- caking agents are often added to the material to prevent the hydrated inorganic salt from agglomerating.

Currently, the common mechanism for crystal agglomeration is the crystalline bridging theory and capillary adsorption theory proposed by Gamondes in 1977 [3]. The agglomeration theory suggests that the agglomeration of the crystal occurs after the surface is dissolved and re-crystallized; the small crystal grains fuse into clusters afterword. Therefore, the inert anti- caking agent is inserted into the crystal particles so as to form a barrier and prevent formation of the crystal bridge during the dissolution and re-crystallization. Thus the agglomeration is easily broken. Arno A. C. Bode et al studied the effect of anti- caking agent on sodium chloride [4], Stefan Baueregger et al analyzed the effect of inert powder kaolin on latex polymer film forming [5].

Phase change material could lose its ability of thermal storage due to the formation of caking. On the other hand, when the inert anti- caking agent is added to inorganic salt, it will hinder the crystallization process, and thus affecting its heat storage performance as well. Therefore, suitable

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inert anti- caking agent and its amount should be selected appropriately, so as to optimize the PCM thermal storage properties.

$KAl(SO_4)_2 \cdot 12H_2O$-$MgSO_4 \cdot 7H_2O$ mixed hydrated inorganic salt system is a group of thermal storage material with advantages of high energy density, cheap and easily to conduct preparation. As to the mass ratio of $KAl(SO_4)_2 \cdot 12H_2O$ to $MgSO_4 \cdot 7H_2O$ being 2 to 8, it has the characteristics of high latent heat of phase change, good thermal conductivity, low degree of super-cooling (about 1 ℃), and no segregation [6]. The phase change temperature of the material is stable at about 48 ℃ after several cycles of cooling and heating, which is a good hydrated salt phase change heat storage material suitable for low temperature solar air - drying system. However, this material suffers from agglomerate when circulated to about 20 times, and the dense agglomeration increases gradually with the cyclic number.

The aim of the present paper is to prevent the material with the mass ratio of $KAl(SO_4)_2 \cdot 12H_2O$ to $MgSO_4 \cdot 7H_2O$ being 2 to 8 from agglomeration, alumina powder is added as an anti- caking agent to perform the work.

2. Preparation and basic test

2.1. Experimental material

The main chemicals are: $KAl(SO_4)_2 \cdot 12H_2O$, Zhengzhou Paiey Chemical Reagent, Zhengzhou, purity of 99.5%; $MgSO_4 \cdot 7H_2O$, Tianli Chemical Reagent Co. Ltd., Tianjin, purity of 99%; Al_2O_3 powder, Xi'an Chemical Reagent, Xi'an, purity of 99.5%.

2.2. Laboratory equipment

The experimental equipments include: HCT-1 differential scanning calorimetry balance, DZF-6030 vacuum oven; DF-101S constant temperature heater with magnetic stirrer; a thermometer (apuhua TM-902C, -50 ℃ ~ 1300 ℃, accuracy 0.1 ℃); JJ124BC electronic balance (Max = 120g, Min = 20d, d = 0.1mg).

2.3. Characteristics of thermal properties of $MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ components

The experimental procedure for DTA and step-cooling curve tests are described as those in [6].

As to step-cooling curve, temperature data is recorded every 10s for once; step cooling curve is drawn after the cooling temperature tests. While for DTA test, the temperature ranges from room temperature to 150 ℃ with heating rate of 1 ℃ / min.

While the DTA curve and the step cooling curve of $KAl(SO_4)_2 \cdot 12H_2O$ are shown in [6]. The DTA curve shows a single endothermic peak at 75.7 ℃, which exhibits a large latent heat of 882.58kJ/kg.

The step cooling curve of $KAl(SO_4)_2 \cdot 12H_2O$ represents that the crystallization of the molten of $KAl(SO_4)_2 \cdot 12H_2O$ begins at 63.0 ℃ followed by a temperature rising to 73.4 ℃, which is because of the releasing of latent heat as well, and implies a relative bigger super-cooling of 10.4 ℃.

The experimental DTA curve and step cooling curve for $MgSO_4 \cdot 7H_2O$ are shown in [7] respectively.

From DTA curve of $MgSO_4 \cdot 7H_2O$, it can be seen that $MgSO_4 \cdot 7H_2O$ exhibits three endothermic peaks during heating process at 46.1 ℃, 81.4 ℃ and 106.4 ℃, respectively. The total phase change latent heat is 811.97kJ/kg, which is phase change material with high latent heat.

The step cooling curve of $MgSO_4 \cdot 7H_2O$ shows that the molten $MgSO_4 \cdot 7H_2O$ begins to crystallize at 51.8 ℃ followed by a temperature rising to 60.4 ℃, which is owing to the releasing of latent heat, and indicates a super-cooling of 8.6 ℃.

3. Preparation of anti - caking phase change heat storage composite material and its property test

3.1. Preparation of anti - caking phase change heat storage composite material

The preparation process is as follows,

(1) The milled KAl $(SO_4)_2 \cdot 12H_2O$ and $MgSO_4 \cdot 7H_2O$ powders are mixed and poured into a ϕ20×50ml plastic test tube, the mass ratio is 2:8. The total amount is 10g; then, the milled anti-caking agent Al_2O_3 of 0.1 g is poured into the test tube as well.

(2) The test tube is placed in the thermostat heating magnetic stirrer with a constant temperature heater, and kept half an hour after the material fully melting;

(3) The test tube is removed from the thermostat heating magnetic stirrer and stood at room temperature, the temperature data is recorded every 10s, and then a step cooling curve could be drawn after the tests.

3.2. Step cooling curve analysis of anti - caking composite materials

Shown in figure 1 is the initial step - cooling curve of the composite, while figure 2 is the step - cooling curve of the composite suffering 70th, 100th, 150th, 200th cyclic heating-cooling tests. The shapes of the step - cooling curves of the composite are different from those of their components, says, $MgSO_4 \cdot 7H_2O$ and KAl $(SO_4)_2 \cdot 12H_2O$, but a little bit like that of $MgSO_4 \cdot 7H_2O$ because more $MgSO_4 \cdot 7H_2O$ is contained in the composite. The tested solidifying temperature T_c, the duration of exothermic platform t_p and super-cooling T_{sc} from Figures 1 and 2 are listed in Table 1.

As can be seen from table 1, the solidifying temperature T_c, the duration of exothermic platform t_p and super-cooling T_{sc} of this anti- caking composite keep almost unchanged during cyclic heating-cooling process.

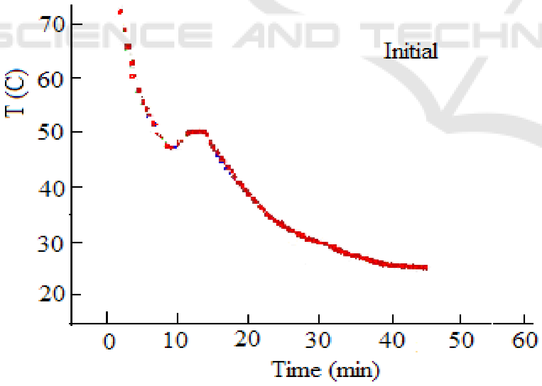

Figure 1.step cooling curve of the composite

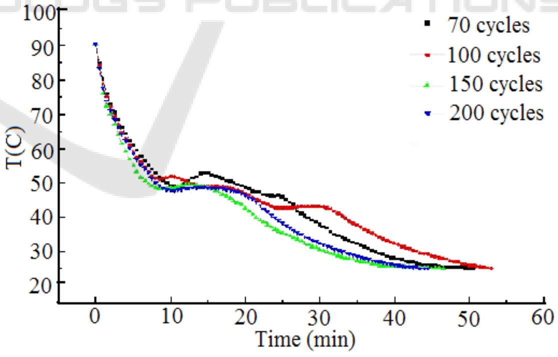

Figure 2.step cooling curve vs cyclic number

Table 1.the solidifying temperature T_c, platform t_p and super-cooling T_{sc}

No. of cycling	initial	70	100	150	200
T_c(℃)	46	48	43	48	49
t_p (min)	6	10	7	7	8
T_{sc}(℃)	4	4	0.4	1	0.8

3.3. DTA Analysis of $MgSO_4 \cdot 7H_2O$ - $KAl(SO_4)_2 \cdot 12H_2O$ anti - caking composite

Take about 10mg anti - caking composite samples of $KAl(SO_4)_2 \cdot 12H_2O$ - $MgSO_4 \cdot 7H_2O$ to conduct their DTA test, the temperature ranges from room temperature to 150 ℃ with heating rate of 1 ℃ /min.

Figure 3 shows the DTA curves of the anti- caking composite after 70 and 100 heating – cooling circles.

While figure 4 shows the DTA curves of the anti- caking composite after 150 and 200 heating – cooling circles. Table 2 shows the thermal properties of this material by DTA test after some cycles.

The shapes of the DTA curves of the composite are different from those of their components, says, $MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$, maybe some metamorphosis is concerned.

Compared Figures 3 and 4 as well as table 2, it can be seen that the thermal properties of this anti - caking composite keep stable, which implies that the interaction of the various components make the composite stable.

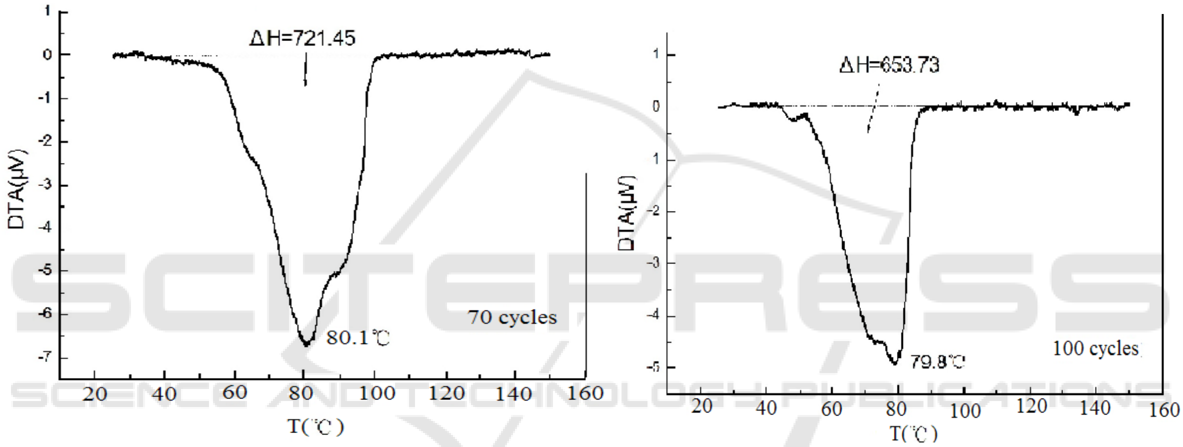

Figure 3.DTA curves of the anti - caking composite after 70 and 100 heating – cooling cycles

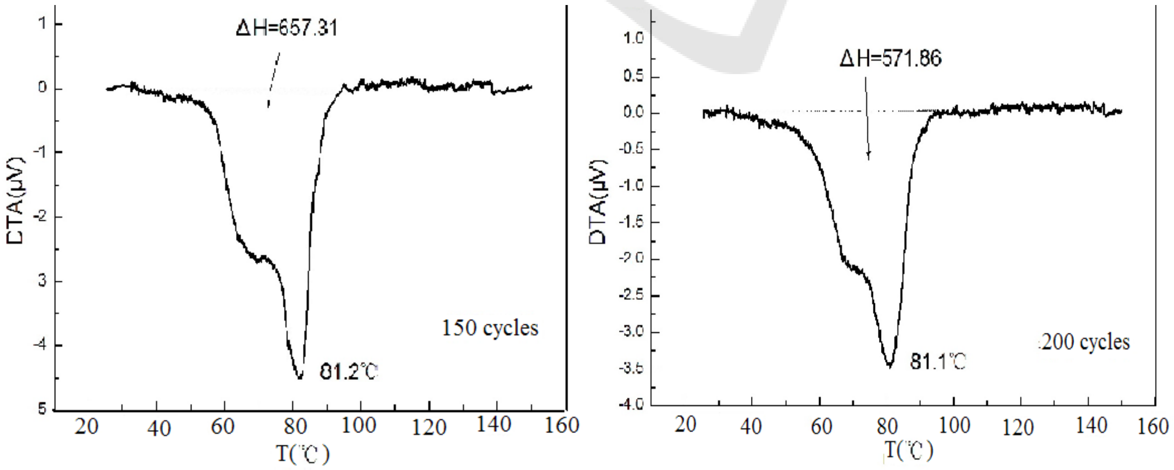

Figure 4.DTA curves of the anti - caking composite after 150 and 200 heating – cooling cycles

Table 2. Thermal properties of this material by DTA test after some cycles

No. of cycling	initial	70	100	150	200
ΔH (kJ/kg)	702.41	721.45	653.73	657.31	571.86
DTA peak (℃)	80.1	80.1	79.8	81.2	81.1

3.4. Heat release test of the anti - caking $MgSO_4 \cdot 7H_2O$ - $KAl(SO_4)_2 \cdot 12H_2O$ composite

Take about 3g composite samples of KAl $(SO_4)_2 \cdot 12H_2O$ - $MgSO_4 \cdot 7H_2O$ into a sealed tube to conduct their heat release test. The sealed tube is warmed to 80 degree and kept for 30min. Thereafter, the warmed sealed tube is put into an adiabatic vessel with 30 g water to measure the change of temperature, and then compute the heat release amount of the composite.

Table 3 shows the heat release amount of the composite material after some cycles.

Table 3.heat release amount of the composite material after some cycles

No. of cycling	initial	70	100	150	200
ΔW (kJ/kg)	204.1	211.6	205.2	194.7	188.5

Compared the data in table 2, it can be seen that the change of heat release amount of the composite material after 200 cycles is not so significant.

4. Conclusions

(1) The anti - caking agent Al_2O_3 is effective for KAl $(SO_4)_2 \cdot 12H_2O$ - $MgSO_4 \cdot 7H_2O$ composite.

(2) The solidifying temperature T_c, the duration of exothermic platform t_p and super-cooling T_{sc} of this anti - caking composite keep almost unchanged during cyclic heating-cooling process.

(3) The thermal properties of this anti - caking composite keep stable.

(4) The change of heat release amount of the anti - caking composite material after 200 circles is not so significant.

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References

[1] Liu B F 1993 Caking and Prevention of Inorganic Salt, *Shanxi Chem. Eng* **2** 20-22

[2] Yang Z L, Bao C G and Yan Z Y 1994 Effect of Surface Active Agent on Caking, *Yunnan Chem. Eng.* **3** 25-30

[3] Gamondes J P and Van't Hoff J B 1977 How to Prevent Fertilizer Caking *Nitorgen* 105 32

[4] Bode Arno A C, Melvin V, Martin J 2015 Influence of Anti- caking agents on the Caking of Sodium Chloride at the Powder and Two-crystal Scale *Powder Technology* **277** 262-267

[5] Stefan B A, Margarita P and Johann P *2014 Influence of Anti-Caking Agent Kaolin on Film Formation of Ethylene-vinylacetate and Carboxylated Styrene-butadiene latex polymers, Cement and Concrete Research* **58** 112-120

[6] Zheng M, Luo J W, Zhang Y H and Chen P 2017 Preparation and characterization of composite material $Na_2SO_4 \cdot 10H_2O$ - $KAl(SO_4)_2 \cdot 12H_2O$ for thermal storage, 1st International Conference on New Material and Chemical Industry (NMCI2016), *IOP Conf. Series: Materials Science and Engineering* **167** 012007 doi:10.1088/1757-

899X/167/1/012007.

[7] Zheng M, Luo J W, Zhang Y H and Long Y P 2016 Preparation and characterization of composite of $MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ thermal storage material, *Proceedings of the 6th International Conference on Mechatronics, Materials, Biotechnology and Environment (ICMMBE 2016)*, doi:10.2991/icmmbe-16.2016.55. 2016: 280-285