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TG AND DSC INVESTIGATION OF $CaCl_2 \cdot 6H_2O$ PCM MATERIAL

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ABSTRACT

Samples of calcium chloride hexahydrate containing varying amounts of KCl in combination with $SrCl_2$, $BaSO_4$ and NaCl have been prepared and studied by thermogravimetric and differential scanning calorimetric methods. The additives improve the stability of the intermediate hydrate and change the stoichiometry of the dehydration process.

INTRODUCTION

Calcium chloride hexahydrate is a promising material for the storage of solar heat because it has a high heat of fusion and a melting point of 29.8 °C. Two effects lower the thermal capacity of the material: semi-congruent melting and supercooling. Both of these effects can now be overcome by the addition of various inorganic salts.

Carlsson et al. [1] have studied the influence of $SrCl_2 \cdot 6H_2O$ in the $CaCl_2 + H_2O$ system. They suggest that the addition of isomorphous $SrCl_2 \cdot 6H_2O$ increases the solubility of the tetrahydrate and suppresses tetrahydrate formation on repeated melting and crystallization. However, potassium chloride and sodium chloride have an opposite influence on the solubilities.

Lane [2] has patented a congruent melting mixture of hydrated $CaCl_2$. Samples of $CaCl_2 \cdot 4H_2O$ can be completely prevented from crystallizing if KCl is added in combination with NaCl and various barium and strontium salts.

Kimura and Kai [3] have reported that the addition of about 1 wt.% NaCl or NaF has an excellent nucleating effect on $CaCl_2 \cdot 6H_2O$ when the mole ratio of water ($CaCl_2 : H_2O = 1 : 6.11$) is less than that of peritectic composition ($CaCl_2 : H_2O = 1 : 6.14$).

We have reported recently on the preparation of a number of samples containing $CaCl_2 \cdot 6H_2O$ as the main component and one of the inorganic salts, e.g. sodium chloride, potassium chloride, barium sulphate or strontium

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chloride [4]. We studied the thermal dehydration of these mixtures and found that an appropriate amount of additive can improve the stability of the intermediate hydrate during thermal dehydration, and also change the stoichiometry of the dehydration process. These effects were most clearly observed on the addition of KCl to $CaCl_2 \cdot 6H_2O$.

It has also been found [2] that the addition of KCl to $CaCl_2 \cdot 6H_2O$ reduces the formation of crystal forms other than $CaCl_2 \cdot 6H_2O$, but does not suppress problematic supercooling of $CaCl_2 \cdot 6H_2O$. Adding nucleating agents such as $Ba(OH)_2$, BaO, $BaCO_3$, $BaCl_2$ $BaSO_4$, $SrCl_2$ and $Sr(OH)_2$, or adding NaCl (the reason behind the effect of this additive is not known) to the hydrated $CaCl_2$ + KCl system reduces the supercooling of this system on repeated melting and crystallization.

The present work reports on a study of the thermal dehydration of a number of systems containing $CaCl_2$ and a hydrated mixture of KCl with varying amounts of NaCl, $BaSO_4$ and $SrCl_2$.

EXPERIMENTAL

Samples were prepared from $CaCl_2 \cdot 2H_2O$ (Zorka), $BaSO_4$ (Carlo Erba), NaCl (Kemika) and KCl (Merck).

Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves were recorded using a Mettler thermoanalyser (TA2000C). Experimental conditions: TG and DSC sample holder, flat platinum crucible 7 mm in diameter; sample masses, 36–50 mg; heating rate, 5 K min^{-1}; reference material for DSC, inert alumina; atmosphere, dry air with a flow rate 30 ml min^{-1}.

RESULTS AND DISCUSSION

The curves shown in Figs. 1, 2 and 3 refer to mixtures of $CaCl_2 + H_2O$ with KCl in combination with $SrCl_2$, $BaSO_4$ and NaCl. In each, the effect of adding KCl can be seen. An intermediate phase is detected on the TG and DSC curves. However, the stability of this phase depends not only on the amount of KCl added, but also on the nucleating agent. An improved separation of the dehydration steps can be obtained [4] if the amount of KCl is at least 5%. For samples containing less than 5% KCl the two phases are less well resolved. In materials containing $SrCl_2$, $BaSO_4$ or NaCl in addition to KCl, the separation of the two phases is not always the same (Table 1). When 0.5% $SrCl_2$ is added as a nucleating agent an intermediate phase is detected on the TG and DSC curves for Samples A and B (10 and 5.1% KCl, respectively) in the temperature range 110–142°C (Fig. 1). The first and second dehydration steps overlap between 1.7 and 1.9 mol of water loss. For

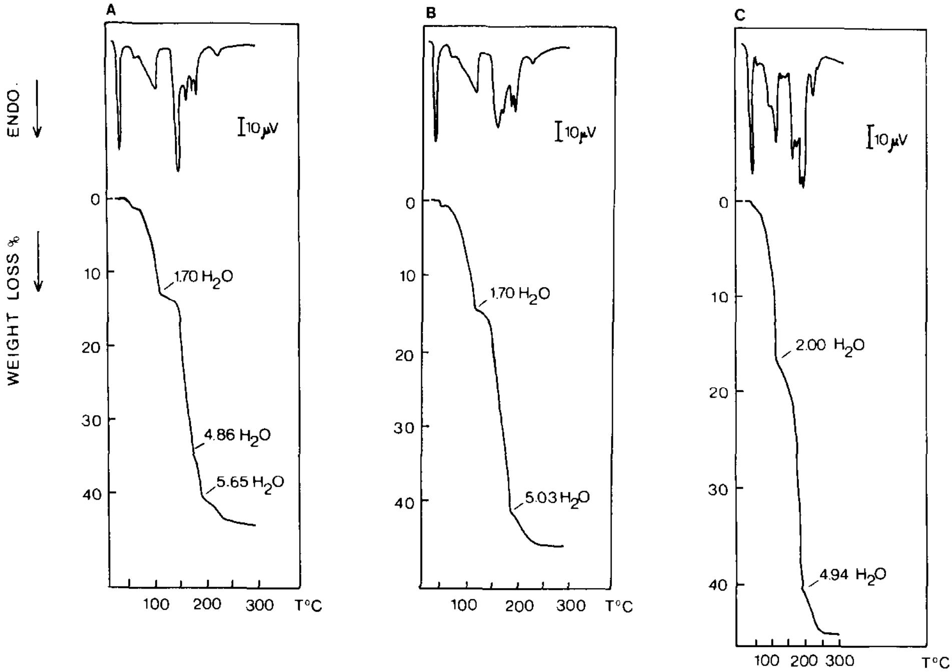

Fig. 1. TG and DSC curves of KCl + $SrCl_2$-doped $CaCl_2 \cdot 6H_2O$.

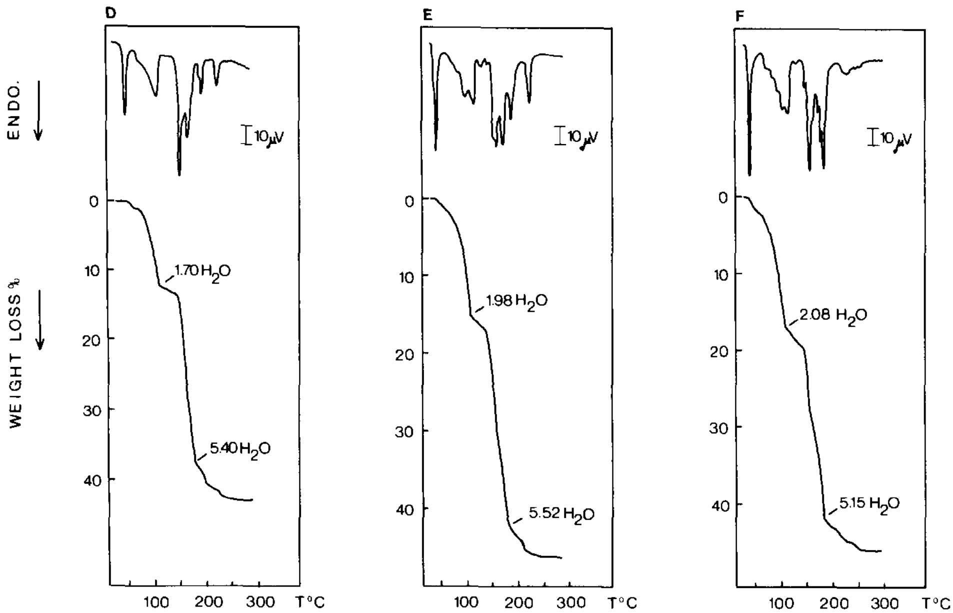

Fig. 2. TG and DSC curves of KCl + $BaSO_4$-doped $CaCl_2 \cdot 6H_2O$.

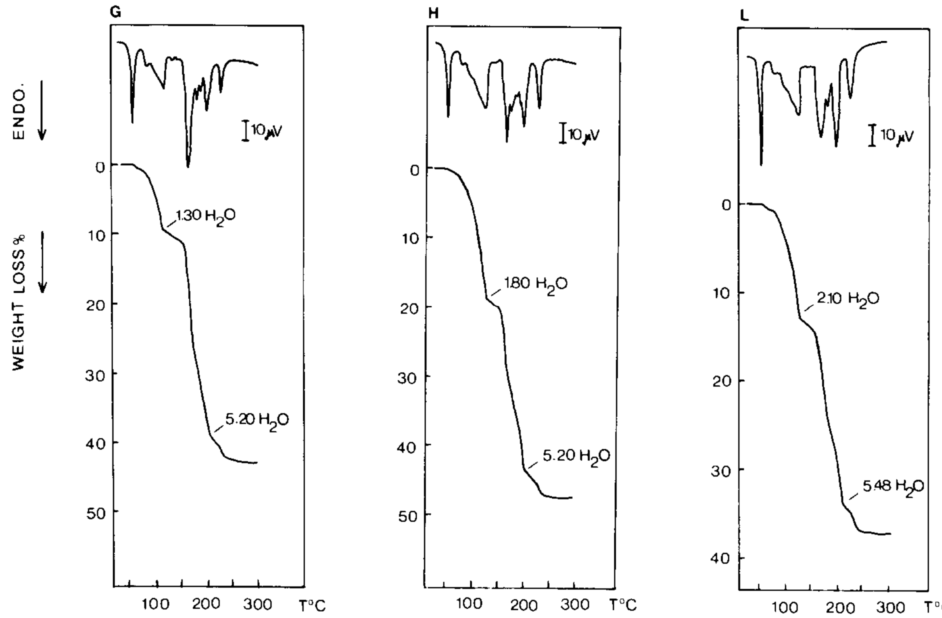

Fig. 3. TG and DSC curves of KCl + NaCl-doped $CaCl_2 \cdot 6H_2O$.

Sample C (2.9% KCl, 0.5% $SrCl_2$) the separation of the two phases is less clear. The overlap of the first and second intermediate steps is between 2 and 2.5 mol of water loss. For materials that contain only 2.9% KCl [4], the separation of the two steps is still less clear (1.7 to 2.5 mol of water loss). The further intermediate phases for all three materials are somewhat different. This could be due to varying amounts of water in the original materials. The intermediate phase with about 1 mol of water loss is not as well resolved as in the case when only $SrCl_2$ is added [4].

When a combination of KCl and $BaSO_4$ is added the separations of the intermediate phases are different to those described above (Fig. 2). However, the amount of KCl added also effects stoichiometry of the intermediate hydrate (see Table 1). Addition of 10% (Sample D) or 5.1% (Sample E) KCl does not have the same effect as occurs, for instance, with Samples A and B. The separation of the first and second intermediate steps is considerably improved by the addition of Sample D, but this is not the case with Samples E and F (Sample F: 2.9% KCl, 0.5% $BaSO_4$). The further intermediate phases are somewhat different, but the ends of the TG and DSC curves show closely similar dehydration processes for Samples D, E and F.

Addition of NaCl and KCl (Fig. 3, Table 1) produces the same effects as addition of NaCl or KCl separately [4]. The stoichiometry of the thermal dehydration depends not only on the amounts of the additives but also on the amount of water in the $CaCl_2 + H_2O$ mixture. A slight excess of water affects all three steps of the dehydration process. NaCl as well as $BaSO_4$ and

TABLE 1

TG and DSC data for the dehydration of $CaCl_2 \cdot 6H_2O$ phase change materials

Sample	Total weight loss (mol H_2O)	Weight loss		DSC peak temperatures (°C)						
		Step one (mol H_2O)	Step two (mol H_2O)							
(A) 10% KCl, 0.5% $SrCl_2$	6.13	1.70–1.90	4.86–5.65	34	109	150	160	180	227	
(B) 5.1% KCl, 0.5% $SrCl_2$	5.54	1.70–1.90	5.03	35	110	156	167	191	227	
(C) 2.0% KCl, 0.5% $SrCl_2$	5.49	2.00–2.49	4.94	38	113		163	190	227	
(D) 10% KCl, 0.5% $BaSO_4$	6.02	1.70–1.89	5.40	39	104	150	167	177	194	226
(E) 5.1% KCl, 0.5% $BaSO_4$	6.07	1.98–2.30	5.52	34	113	159	173	190	226	
(F) 2.9% KCl, 0.5% $BaSO_4$	5.66	2.08–2.41	5.15	34	122	157	178	186		
(G) 10% KCl, 0.5% NaCl	5.78	1.30–1.57	5.20	39	101	167	189	219		
(H) 5.1% KCl, 0.5% NaCl	5.66	1.80–1.97	5.20	36	112	144	177	207		
(I) 5.1% KCl, 0.5% NaCl	6.36	2.51–2.76	5.86	35	110	154	189	219		
(J) 5.4% KCl, 0.7% NaCl	6.18	2.11–2.37	5.60	36	109	152	187	217		
(K) 3.7% KCl, 0.6% NaCl	6.05	2.10–2.52	5.47	36	116	159	192	217		
(L) 3.8% KCl, 0.7% NaCl	6.04	2.10–2.43	5.48	36	111	159	190	218		
(M) 3.9% KCl, 0.7% NaCl	6.14	2.15–2.63	5.60	36	107	159	189	218		

$SrCl_2$ increases the separation of the first two intermediate phases in combination with KCl.

Thermal cycling experiments involving a great many cycles is the method usually used to determine the usefulness of PCM materials. Such experiments are currently underway in our laboratory, and thermal analysis before and during the cycling will be used to determine the correlation between thermal properties and heat storage performance.

REFERENCES

1 B. Carlsson, H. Stymne and G. Wettemark, Solar Energy, 23 (1979) 343.
2 A.G. Lane, European Patent 0063348 (1985).
3 H. Kimura and J. Kai, Solar Energy, 33 (1984) 557.
4 N. Bukovec, P. Bukovec and V. Arbanas, Proc. 9th ICTA, Jerusalem, 1988, in press.