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TG AND DSC INVESTIGATION OF $CaCl_2.6H_2O$, A PHASE CHANGE MATERIAL FOR ENERGY STORAGE

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ABSTRACT

A number of $CaCl_2.6H_2O$ samples with various amounts of NaCl, KCl, $SrCl_2$ and $BaSO_4$ have been prepared and studied by TG and DSC. There are two effects of inorganic salts on the dehydration curves of $CaCl_2.6H_2O$. The appropriate amount of additive can improve the stability of intermediate hydrate and change the stoichiometry of the dehydration process.

INTRODUCTION

$CaCl_2.6H_2O$ was suggested as appropriate heat storage material about 1950 |1|. It melts at about 30°C with a heat of fusion of 170 J/g. Phase change materials (PCM) to be used in reversible storage systems should have suitable temperature of phase transition and congruent melting/solidification. There are two disadvantages of $CaCl_2.6H_2O$ when used as PCM, supercooling and semicongruent melting |2|. Both effects lower the thermal capacity of the storage system. When liquid $CaCl_2.6H_2O$ is cooled at equilibrium, α-$CaCl_2.4H_2O$ can begin to precipitate at 32°C |3,4|. There were several attempts to modify $CaCl_2.6H_2O$ in order to improve its heat storage performances.

Lane |5| modified the phase equilibrium with dissolved additives, rendering solid tetrahydrate metastable. Carlsson and coworkers |6| made $CaCl_2.6H_2O$ congruent melting by adding $SrCl_2.6H_2O$ or $Ca(OH)_2$. The effect of $SrCl_2.6H_2O$ was also studied by other authors, however with some contradicting results |7,8|. The application of $SrCl_2.6H_2O$ together with thickening agents showed good performances for heat storage |9,10|. The influence of NaCl

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or KCl on the growth of $CaCl_2.6H_2O$ crystals was shown to be remarkable for NaCl and not clear for KCl |11|. NaCl and NaF were found to have excellent nucleating ability for $CaCl_2.6H_2O$ |12|. The addition of $CaBr_2.6H_2O$ has no practical advantage, however $CaBr_2.6H_2O$ without $CaCl_2.6H_2O$ seems to be useful as PCM at 33°C |13|. The addition of KCl to $CaCl_2.6H_2O$ reduces the tendency to form the undesired phase $CaCl_2.4H_2O$, but even 8 w.% KCl is not sufficient to prevent totally the formation of the tetrahydrate. These samples did not show any suppresion of supercooling |14|. The limited application of KCl |13,14| was also proved by infrared spectroscopic characteristics of undercooled molten $CaCl_2.6H_2O$ |15|. Lane reported |14| that $CaCl_2.4H_2O$ can be totally prevented from crystallizing if KCl was used in combination with NaCl, $SrCl_2$ or several Ba-salts.

The properties of molten $CaCl_2.6H_2O$ are obviously altered when other inorganic salts are added. In solutions rich in $CaCl_2$ the solubility of KCl increases at 30°C and at higher temperatures. It was supposed that complex ions are present in the solutions |16,17|. In the solid phase however a double salt of composition $CaCl_2.KCl$ was found. Its lowest formation temperature is 37.80°C. The invariant equilibria of the binary $CaCl_2$-H_2O system $CaCl_2.6H_2O+\alpha CaCl_2.4H_2O$ at 29.8°C and $\alpha CaCl_2.4H_2O+CaCl_2.2H_2O$ at 45.3°C change on addition of KCl to $CaCl_2.6H_2O+\alpha CaCl_2.4H_2O+KCl$ at 27.00°C and $\alpha CaCl_2.4H_2O+CaCl_2.KCl+CaCl_2.2H_2O$ at 43.40°C. The melting behaviour of $CaCl_2.6H_2O$ has also been studied using infrared spectroscopy |11|. The two librations of water molecule, rocking and wagging, are very sensitive to the surroundings of the water molecule as they depend on the hydrogen bond strength. NaCl-doped, liquid sample has the same position of water libration absorption peak (540 cm^{-1}) as the undoped one. In KCl-doped liquid sample, the libration peak shifted to 720 cm^{-1} indicating stronger hydrogen bonding.

Thermal dehydration of $CaCl_2.6H_2O$ showed typical dependence on experimental conditions |19,20|. Dehydration in open crucibles in dry air gives an indication of the intermediate tetrahydrate formation. The reaction in self-generated atmosphere however, gives no intermediate tetrahydrate |20|, the first step observed being the dihydrate. In a further study on opened and closed samples the essential differences were again found |21|. DSC analysis in openned crucibles, made over several heating-cooling cycles, showed a stepwise decomposition of the samples. DSC measurements with hermetically closed pans gave single melting and crystallization peaks with practically constant phase change enthalpies. DSC curves, however, exhibited strong supercooling. The differences between the melting of $CaCl_2.6H_2O$ and the DSC peaks on cooling were up to 62 K. A limited applicability of DSC measurements was mentioned later on |9|, and an improved method for measuring the enthalpy of melting was designed |10|.

In spite of the mentioned limitations thermal analysis can give valuable information . The scope of our work was to find out the influence of additives on the thermal behaviour of PCM materials.

EXPERIMENTAL

Samples were prepared from $CaCl_2.2H_2O$ (Zorka, Šabac), $BaSO_4$ (Erba, Milano), NaCl (Kemika, Zagreb) and KCl (Merck).

TG and DSC curves were recorded using a Mettler thermoanalyser TA 2000C. Experimental conditions: TG-DSC sample holder, flat platinum crucibles 7mm in diameter; sample masses from 36 to 50 mg; heating rate $5kmin^{-1}$; reference material for DSC, inert alumina; atmosphere, dry air at 30 $mlmin^{-1}$ flow rate.

X-ray powder spectra were obtained with a Guinier-de Wolf camera using CuKα radiation.

RESULTS AND DISCUSSION

X-ray powder patterns of all materials show characteristic lines for $CaCl_2.6H_2O$. For samples with KCl and $BaSO_4$ the lines of added salts additionally appeared, proving that both materials are physical mixtures. NaCl also gives physical mixture with $CaCl_2.6H_2O$ |22|, but the intensity of NaCl lines are too weak to be seen. $SrCl_2.6H_2O$ forms a solid solution with $CaCl_2.6H_2O$ |22| as both salts are isostructural. Because of high concentration of $CaCl_2$ compared with that of $SrCl_2$, the unit cell of solid solution is practically that one of $CaCl_2.6H_2O$ as shown by X-ray powder pattern.

TG and DSC curves for these materials are shown in Figs.1-6 and some additional data in Table 1.

The melting point of $CaCl_2.6H_2O$ at about 30°C is very well resolved from the other DSC effects for all materials. TG curve of pure $CaCl_2.6H_2O$ corresponds well to the reported literature data |19,20|, indicating the possibility of $CaCl_2.4H_2O$ formation.

The addition of small amounts of NaCl changes the dehydration stoichiometry for the first intermediate step (Figs.1-2,Tab.1).

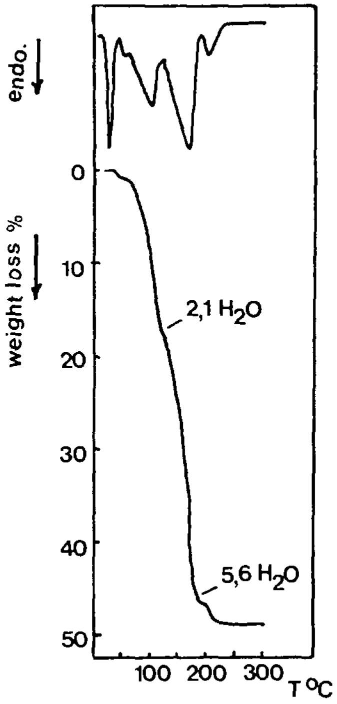

FIG.1. *.

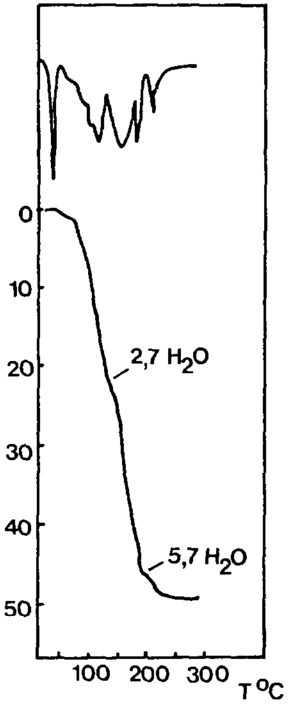

FIG.2 . 1,5 % NaCl .

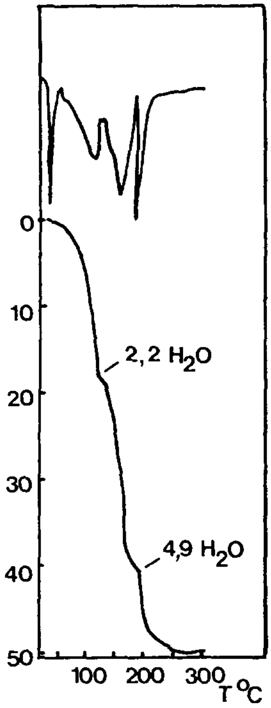

FIG.3 .1,5% $SrCl_2$.

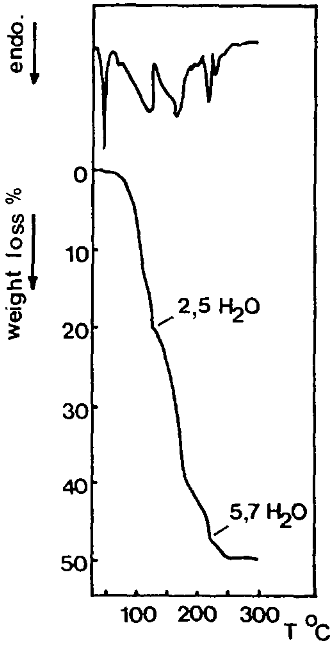

FIG.4 .10%$BaSO_4$.

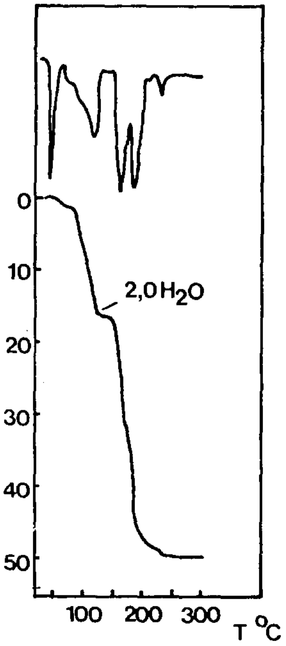

FIG. 5 . 10 % KCl .

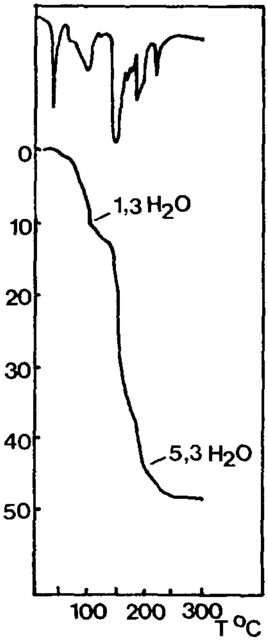

FIG.6 . 10% KCl
0,5%NaCl .

* $CaCl_2 \cdot 6H_2O$ without additives

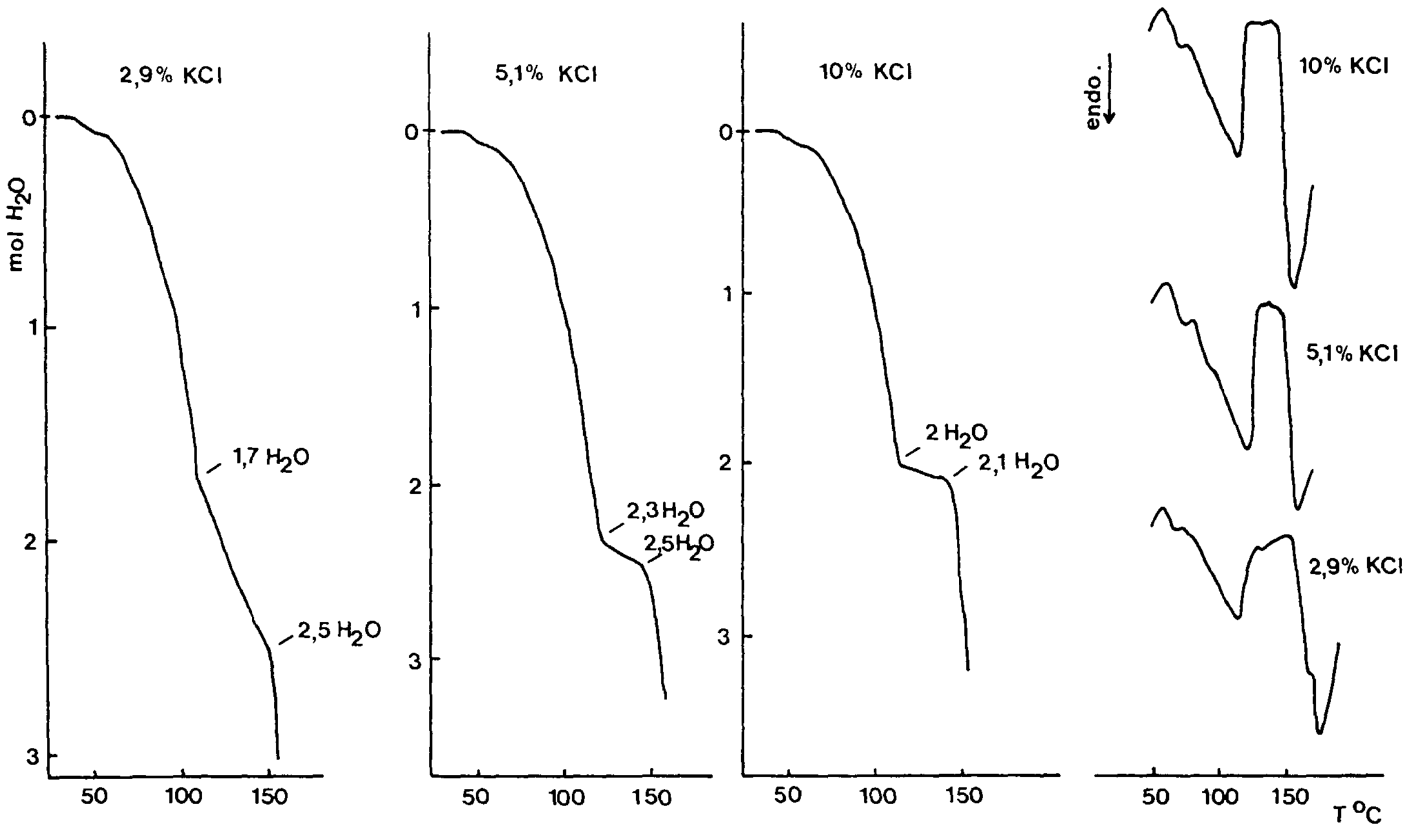

FIG. 7. TG and DSC curves of KCl doped $CaCl_2.6H_2O$.

TABLE 1

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

Inorganic salt added	Total weight loss $\vert$mol $H_2O\vert$	Weight loss step one $\vert$mol $H_2O\vert$	Weight loss step two $\vert$mol $H_2O\vert$	DSC peak temperatures $\vert^oC\vert$						
	5.9	2.1	5.6	35	117	174	205			
0.5% NaCl	6.2	2.5	5.7	36	123	172	190	219		
1.0% NaCl	6.1	2.3	5.8	35	118	166	186	217		
1.5% NaCl	6.0	2.7	5.7	36	120	160	187	219		
2.9% KCl	5.8	1.7-2.5	5.3	35	113	188	192	226		
5.1% KCl	6.1	2.3-2.5	5.5	41	124	163	184	198	232	
10% KCl	6.1	2.0-2.1	—	41	115	161	184	230		
1.0% $BaSO_4$	5.7	2.6	—	39	134	179	196	202	235	
5.0% $BaSO_4$	5.8	2.2	5.5	40	120	167	196	217	236	
10% $BaSO_4$	6.0	2.5	5.7	39	120	161	186	196	217	228
0.2% $SrCl_2$	5.8	2.2	4.8	36	120	164	201			
0.5% $SrCl_2$	5.9	2.5	—	38	127	172	208			
1.5% $SrCl_2$	6.0	2.2	4.9	36	120	169	191			
0.5% NaCl 5.1% KCl	5.7	1.8	5.2	36	102	144	177	207		
0.5% NaCl 10% KCl	5.8	1.3	5.3	39	100	150	188	220		

The next stages with approximately 5.7 and 6 H_2O mols losses appeared for pure and NaCl doped materials. The latter ones have two sharp DSC peaks at the end of the reaction in contrast with the former with a single DSC effect. The first of both sharp peaks corresponds to the melting point of $CaCl_2.2H_2O$ |19|.

$SrCl_2$ (Fig.3) slightly increases the mass loss for the first step of the dehydration. In the next stage an intermediate with about $1H_2O$ seems to appear. The number of DSC effects, as well as their temperatures, are the same as for pure substance, but the last peak is much more pronounced.

The addition of $BaSO_4$ (Fig.4) produces an inflection point on TG with mass losses between 2.2 and 2.6 mols H_2O. The second part of the dehydration reaction is also different from those with other additives, which can be especially seen by comparing the DSC.

Application of KCl as an additive gives the dehydration curves shown in Figs.5 and 7. Here an intermediate phase has been detected on TG and DSC curves in the temperature range from 115 to 150°C, however the stability of this phase depends on the amount of KCl added. With 2.9% KCl there is an overlap of the first and the second dehydration step between 1.7 and 2.5 mols of H_2O loss. Finally for 10% KCl the separation of the two phases is much more improved with an overlap between 2.0 and 2.1 mols H_2O, for approximately the same temperature range.

The TG and DSC curves for materials with a combination of NaCl and KCl (Fig.6) show an improved separation of the dehydration steps if the amount of KCl was at least 5%.

For PCM performances especially the first part of the diagrams are interesting showing the formation of molten intermediate hydrates. Although the curves do not show equilibrium data, they reflect the relative stabilities of these intermediates. The addition of KCl improves the stability of molten $CaCl_2.4H_2O$, especially if at least 5% KCl is added. This is in accordance with infrared spectroscopic data |11|, mentioned before. The improved stability could also be explained by the proposed complex ions formation |16, 17|, but there is no direct experimental proof as yet. However, an increased stability of molten $CaCl_2.4H_2O$ may explain the experimental facts, namely that KCl suppresses the crystallization of $CaCl_2.4H_2O$ |2|. NaCl and $BaSO_4$ which also give physical mixtures with $CaCl_2.6H_2O$ do not stabilize $CaCl_2.4H_2O$ in the liquid state. The different behaviour of NaCl compared with KCl has been explained by weaker strength of hydrogen bonding |11|. Speaking of PCM, NaCl and $BaSO_4$ are nucleators, so the stabilization of intermediate, liquid $CaCl_2.4H_2O$ wouln't be logic, as it would suppress the crystallization. $SrCl_2.6H_2O$ forms solid solution with $CaCl_2.6H_2O$, however its role in PCM is the same as that of NaCl or $BaSO_4$. The similarity of all three additives is evident from the TG and DSC curves.

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