

# PROPERTIES OF INORGANIC PCM

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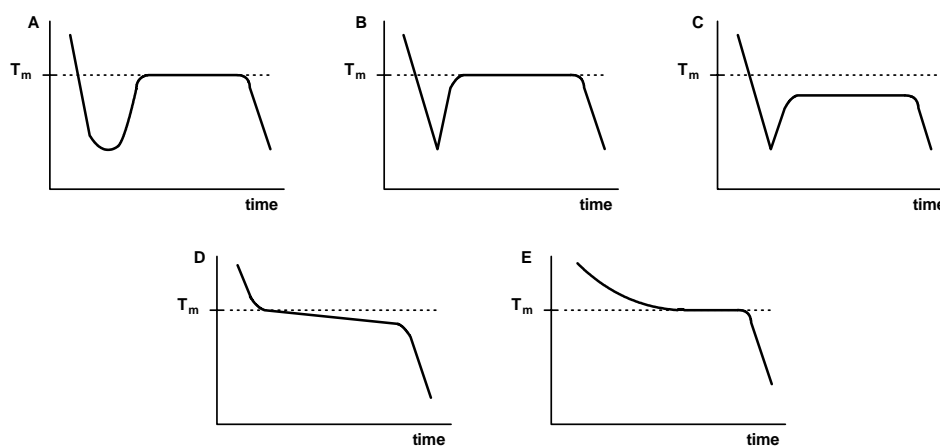
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## ABSTRACT

Properties of inorganic PCM are described, which are suitable for solar thermal energy storage.

## 1 INTRODUCTION

Phase changes of materials are a perspective way of thermal energy storage. Such materials are called PCM. Big latent heat, good thermal conductivity and inflammability are the main advantages of inorganic materials. But they cause corrosion and suffer from loss of  $H_2O$ . Incongruent melting and supercooling are the biggest problem with their exploitation. During melting and freezing there are precipitations of other phases which do not take part in next process of charging and discharging. Impurities can have a strong influence on the curves. In this article we will be interested in properties of  $CaCl_2 \cdot 6H_2O$  and its modification.



**Fig. 1:** *Freezing curves with supercooling*

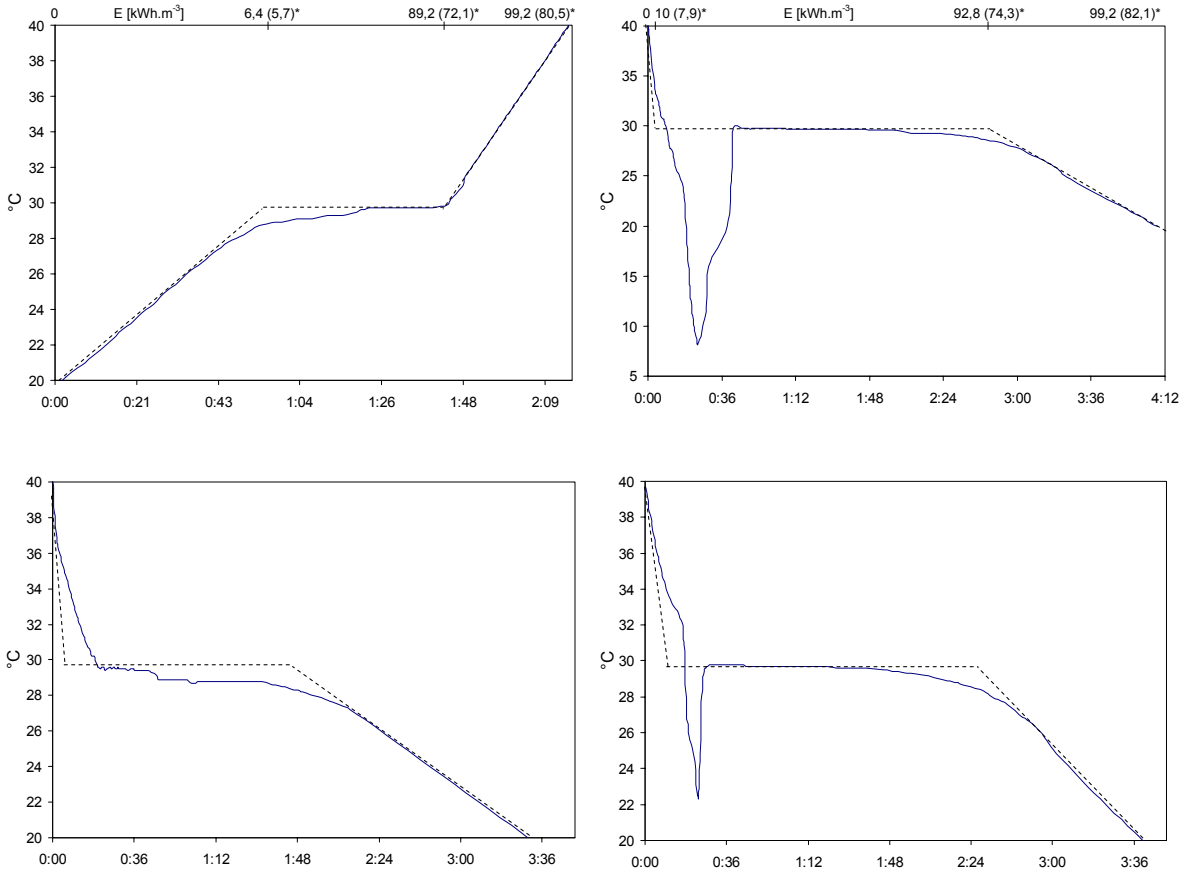
Curves A, B, C indicate that PCM supercools before solidification. A, B show that only the liquid supercools due to poor nucleation. The curve C shows supercooling in both liquid and solid due to poor rate of crystal growth. The PCM of curve D begins to solidify at  $T_m$

indicating no nucleation problems. However, the liquid and solid supercool during freezing, which could be due to a very high rate of heat removal. The temperature takes a long time to drop to  $T_m$  in case of curve E implying low thermal diffusivity in the liquid.

## 2 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

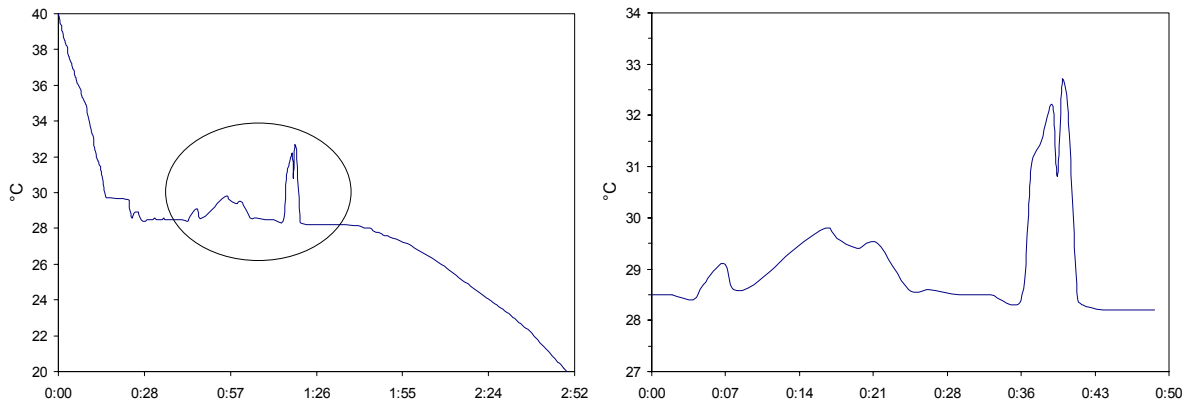
According to measuring the values of thermal conductivity in solid, liquid and latent heat are about 10-30% less than values from literatures. There are more possible reasons. First, quality of materials depends on producer (on purity of PCM). Inaccuracy of calorimetric measuring is another reason. This fact is crucial. For next work it is necessary to respect tabular values or carry out new very exact measuring.

In the chart 2 there exhibited phase changes of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  during heating and cooling. Dashed lines would show theoretical behavior if melting and freezing were at constant temperature – case of pure crystalline substance. Impurity and methodology of measuring (probe always is only in small amount of hexahydrate) are the cause of variances. Other three charts show solidification. Two supercooling happened because of weak nucleation. Crystallization was initiated due to a solid particle of PCM, which we threw to the measured sample. Otherwise there would be no crystallization. Supercooling may be to the temperature of  $-30^\circ\text{C}$  at this salt. We can use plastics, mild steel or copper for enclosures of hexahydrate. Aluminum or stainless steel are not suitable.

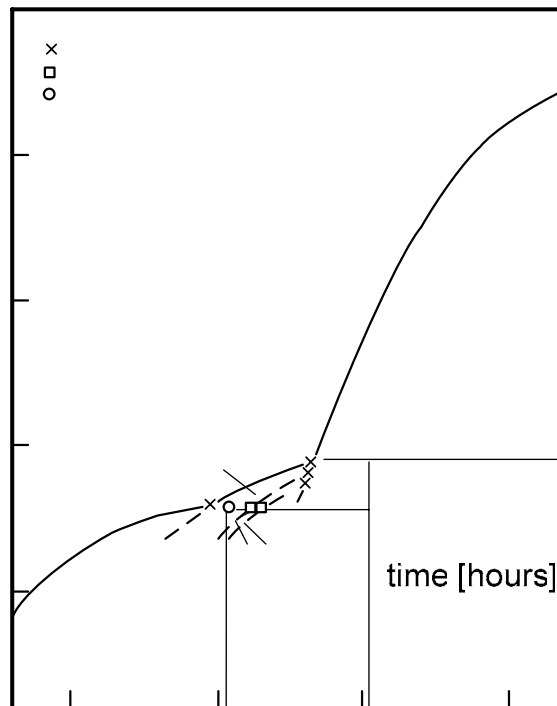


**Fig. 2:** Phase change of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

We can see temperature fluctuation above  $T_m$  during solidification (chart 3). We found an explanation in binary diagram (chart 4).



**Fig. 3:** Phase change of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  ( $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  crystallization)



**Fig. 4:** Binary diagram of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

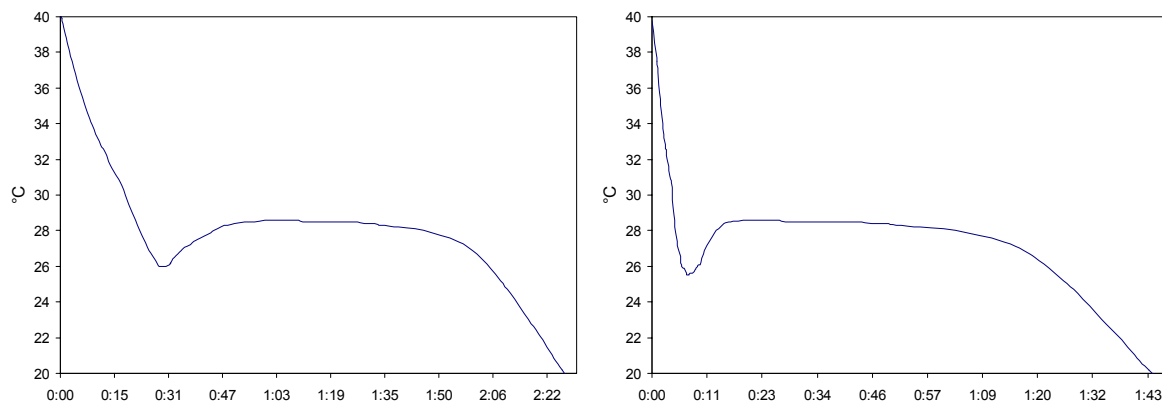
Figure 4 shows the binary phase diagram of calcium chloride and water. The hexahydrate contains 50,66 wt%  $\text{CaCl}_2$ , and the tetrahydrate 60,63 wt%. The melting point of the hexahydrate is 29,6 °C, and of the tetrahydrate 45,3 °C. The hexahydrate- $\alpha$ -tetrahydrate peritectic point is at 49,62 wt%  $\text{CaCl}_2$ -50,38 wt%  $\text{H}_2\text{O}$ , and 29,45 °C. In addition to the stable  $\alpha$  form, there are two monotropic polymorphs of the tetrahydrate salt,  $\beta$  and  $\gamma$ . The latter two are rarely encountered when dealing with the hexahydrate composition; however, the  $\alpha$  tetrahydrate is stable from its liquidus temperature, 32,78 °C down to the peritectic point,

29,45 °C, a span of 3,33 °C. When liquid  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  is cooled at equilibrium, a  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  can begin to crystallize at 32,78 °C. When the peritectic is reached at 29,45 °C the tetrahydrate hydrates further to form hexahydrate, and the material freezes. The maximum amount of tetrahydrate which can be formed is 9,45 wt%, calculated by the lever rule. This process is reversed when solid  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  is heated at equilibrium. At 29,45 °C the peritectic reaction occurs, forming 9,45 % a  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and liquid of the peritectic composition. As the temperature increases further, the tetrahydrate melts, disappearing completely at 32,78 °C. Under actual freezing and melting conditions, the equilibrium processes described above may occur only partially, or not at all. Supercooling of the tetrahydrate may lead to initial crystallization of the hexahydrate at 29,6 °C, or lower if this phase also supercools.

It is possible to do modification by additives. From number of potential candidates  $\text{Ba}(\text{OH})_2$ ,  $\text{BaCO}_3$  and  $\text{Sr}(\text{OH})_2$  have been chosen. They seemed to be workable.

When we used  $\text{Ba}(\text{OH})_2$  and  $\text{Sr}(\text{OH})_2$  at 1 % part by weight there was no supercooling. We could increase stability of condition of equilibrium with addition of KCl (2 wt%) and NaCl. NaCl is weak soluble in  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , therefore part by weight is only about 0,5%. Disadvantage is that melting point decreases about 3 °C at 26-27 °C.

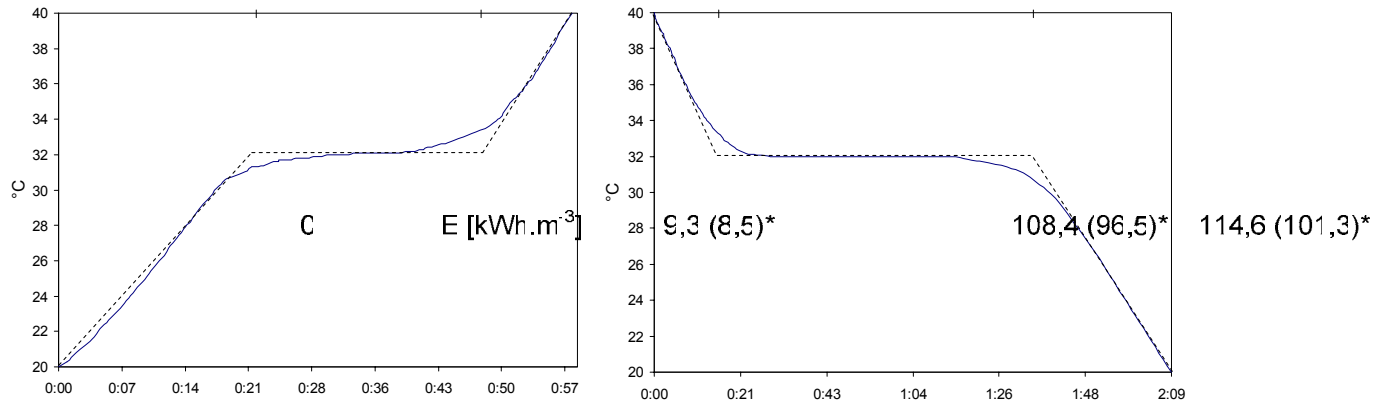
Due to availability on the market and price we chose for modification  $\text{BaCO}_3$ . We have got the best results for 1,2 wt%. In the figure 5 we can see that supercooling is 3-4 °C but then crystallization started and temperature increased at 28-29 °C. It is obvious that nucleation is slower in comparison with pure crystalline matter. Supercooling is not considered as an disadvantage. If we use  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in the heat accumulator we will be able to store energy at lower temperature (about 26 °C) and suppress heat losses. Next disadvantage of  $\text{BaCO}_3$  is that it carbonates because of atmospheric CO and  $\text{CO}_2$ . It means the loss of properties. In our case  $\text{BaCO}_3$  will be isolated from surrounding environment.



**Fig. 5:** Phase change of modification of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  at different speed of heat removal

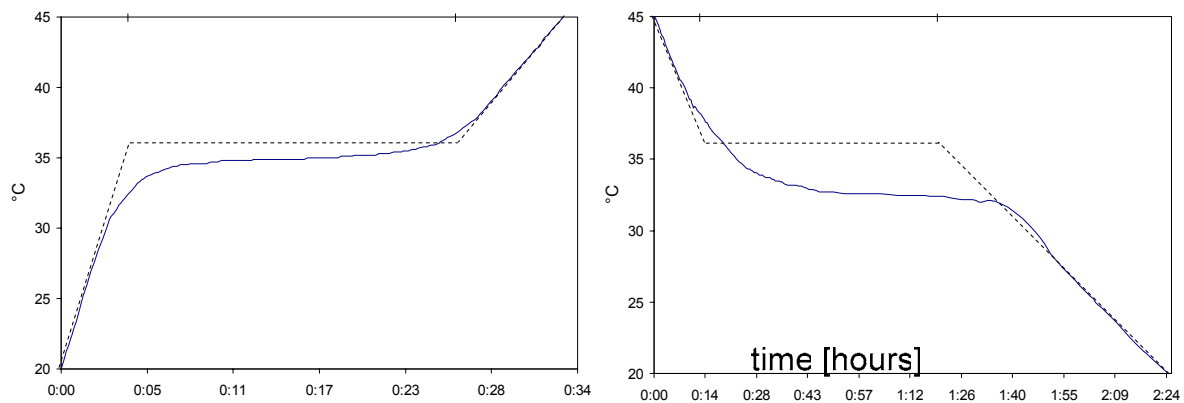
### 3 $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  has a big latent heat due to high content of water but it means lower density. There is precipitation of others phases, segregation and loss of hydroscopic water. Aluminum is unsuitable for enclosure. As the additives we can use for example  $\text{Sr}(\text{OH})_2$ .



**Fig. 6:** Phase change of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

Curves D, E (fig. 1) are characteristic for melting and freezing of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . This salt has a big latent heat due to high content of water again. As an addition we can use pieces of copper (100  $\mu\text{m}$ ). Enclosures requirements are the same like for  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .



**Fig. 7:** Phase change of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

#### 4 CONCLUSION

Unfortunately there is not enough room in the article to show all details and mathematical descriptions of phase change process. We showed practical results of measuring and suggest the modification of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  with using of  $\text{BaCO}_3$  (1,2 wt%). We will exploit this PCM in the heat accumulator in the laboratory in our department.

#### REFERENCES

- [1] Garg, H. P., Mullick, S. C., Bhargava, A. K.: Solar Thermal Energy Storage, Dordrecht (Holland): D. Reidel Publishing Company, 1985, ISBN 90-277-1930-6