An investigation of low-temperature phase-change materials for short-term energy storage in greenhouses

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McMullin, M. and Ben-Abdallah, N. 1988. **An investigation of low-temperature phase-change materials for short-term energy storage in greenhouses**. Can. Agric. Eng. **30**: 65–68. Several materials have been investigated to determine their suitability for use as phase-change energy storage media at low temperatures. The most feasible proved to be calcium chloride hexahydrate, and further tests were carried out on this substance to determine the effect of adding extra water on the melting point and latent heat of fusion of the mixture. The results show the melting point is lowered and the heat of fusion increased as the level of excess water increases. Benefits and limitations of "excess water" mixture are presented and discussed.

Plusieurs hydrates à changement de phase ont été étudiés dans le but d'établir leur application en stockage d'énergie demandant une température de transition liquide-solide relativement basse. On a trouvé que l'hydrate le plus prometteur était le chlorure de calcium hexahydraté (CCH). Des tests ont été effectués sur le materiau afin de déterminer la diminution du rapport CCH/H_2O (excès d'eau) sur la temperature de transition, ainsi que sur la chaleur latente de fusion du mélange. Les résultats des tests ont démontré qu'un mélange de CCH contenant 10 pour cent d'excès d'eau entraine une meilleure stabilité du produit, une baisse de la température de transition et une augmentation de la chaleur latente de fusion. Enfin, les avantages et les inconvénients d'un mélange dilué de CCH sont présentés et discutés.

INTRODUCTION

Thermal storage systems which are compact and provide an efficient means of storing and recovering the energy upon demand are extremely important to most solar energy applications. Recently, phase-change materials (PCM) have come under more intensive investigation due to the advantages they have over sensible heat storage media. The smaller storage space required when PCMs are used is particularly important. Also, the fact that heat is stored and recovered under isothermal conditions leads to advantages such as lower heat loss and better efficiency in solar heating systems. However, because the heat transfer is isothermal, the PCM to be used in a given situation must be carefully chosen to ensure its melting point is suitable for the operating conditions, which for building heating requirements is in the range of 20–30°C.

The objective of this study was to obtain a suitable phase-change material for storage of thermal energy in the 22–27°C range, which would be useful in situations such as excess heat recovery in greenhouses.

Nishina and Takakura (1984) studied the use of inorganic PCMs in an attempt to use the available solar energy in greenhouses more efficiently. Their principle choice was sodium sulfate decahydrate (Glauber's salt), with additives which lower the melting point to approximately 20°C.

Kern and Aldrich (1979) investigated the use of calcium chloride hexahydrate with a melting point of 29°C. In their study, approximately 60–80% of the heat stored was recovered. However, due to the high transition temperature of the salt hydrate, temperatures in the crop zone of the greenhouse often rose to 30° or 33°C, which is higher than desirable for many crops.

Gawron and Schroder (1977) and Telkes (1974) examined the properties of various salt hydrates which might be used as storage media. By matching the salt crystallization temperature with the required temperature of heat storage, they were able to present a number of system compositions which cover a wide range of temperature level applications. Lane (1980) examined over 20 000 compounds or mixtures for possible use as storage media. More than 200 compositions were chosen as most promising and about half of these were selected for more detailed investigation. A list of 25 recommended substances with melting points ranging from 8 to 117°C was then established. Of these, however, only three melt at near-ambient temperature, all of which have a relatively low heat storage capacity.

A further search of the literature limited the choice of low-melting-point PCMs to: (i) lead acetate decahydrate, (ii) sodium sulfate decahydrate, (iii) calcium chloride hexahydrate, and (iv) a mixture consisting of 40% by weight of calcium chloride, 10% magnesium nitrate and 50% water. It should be noted that, while sodium sulfate decahydrate and calcium chloride hexahydrate do not normally melt at temperatures in the required range, they can be made to do so by the addition of excess water. These four substances qualified so far as melting point and cost were concerned. Therefore, it was decided to conduct experiments to check for supercooling or incongruent melting, both of which, if they could not be controlled would effectively eliminate any potential PCM from further consideration.

The problems posed by supercooling could be solved satisfactorily by adding suitable nucleation agents; however, those due to incongruent melting are more difficult to solve. Incongruent melting gives rise to an irreversible phase separation during cycling (i.e., repeated melting and crystallization) particularly for nonagitated systems.

During the melting process, phase separation will lead to at least three zones that are stratified one above the other in order of density. At the bottom there is a solid layer formed by salt precipitation from the solution. Above this there is an active salt hydrate zone. At the top there is a dilute solution of the salt hydrate. During the next freezing process, additional salt may precipitate from the solution which means an accumulation of the solid material upon repeated cycling.

Incongruent melting decreases the overall heat-storage capacity since phase separation results in the top and bottom layers providing only sensible heat to the total quantity of heat of an energy-storage system. Control of phase separation could be accomplished by adding suitable thickening agents.

APPARATUS

The apparatus for the phase transition temperature measurement consists of a hot bath (40°C) and a cold bath (18°C), both of which have stirrers and constant temperature controllers. A copper/constantan thermocouple attached to a Fisher Recordall/ series 5000 chart recorder was used to monitor the PCM temperature. Apparatus for measurement of heat of fusion consists of a standard calorimeter with an interior container in which the PCM is placed, a 1-L capacity insulated outer chamber and a thermometer of 0.01°C accuracy for temperature measurement.

PROCEDURE

A sample of 100 g of each material to be studied was placed in the cold bath and allowed to freeze, with the temperature being continually recorded by the chart recorder. The sample was remelted, heated to 35°C and placed in the inner flask of the calorimeter. The flask was then submerged in 200 g of water at 10°C in the calorimeter and allowed to freeze. After freezing of the PCM, the temperature rise of the water was noted in order to calculate the PCM's latent heat of fusion. The sample was then cycled again (melting and freezing) to recheck the freezing point. The entire process of freezing point measurement and latent heat of fusion determination was carried out twenty times on each sample.

RESULTS AND DISCUSSION

The procedure showed that all four substances were subject to both supercooling and incongruent melting. Typical cooling curves for the substances studied are included.

Figure 1 shows the cooling of lead acetate during the first cycle. Lead acetate was very difficult to dissolve and crystallized out of solution rapidly as the temperature was lowered, causing the solution to cool far below its normal phase transition point (29.7°C) without freezing.

Figure 2 shows the cooling curve of the $CaCl_2$-$MgNO_3$-H_2O mixture during the first and tenth cycles. The effect of incongruency has become quite significant already, lowering the freezing point from 25.2 to 12°C.

Figure 3 shows the sodium sulfate decahydrate has undergone a similar breakdown. Its freezing point decreased from 32 to 21°C after 10 cycles.

However, since incongruency is the more serious flaw, attempts were first made to eliminate this flaw in each of the four materials. Stirring slightly decreased the incongruency of sodium sulfate decahydrate and calcium chloride hexahydrate but had no effect on the other two. Indeed, the lead acetate decahydrate would not even remain in solution when agitated vigorously and heated to 40°C. It was therefore removed from further consideration. The $CaCl_2$-$MgNO_3$-H_2O mixture showed very severely incongruent behavior. A search for useful additives was made. However, this type of effort is as much art as science and in many instances futile.

The incongruency of sodium sulfate decahydrate, according to the literature (Telkes 1952, 1974; Marks 1980; Lane 1980; Nishina and Takakura 1984), has never been completely eliminated. The possible solution discussed by Telkes and Marks

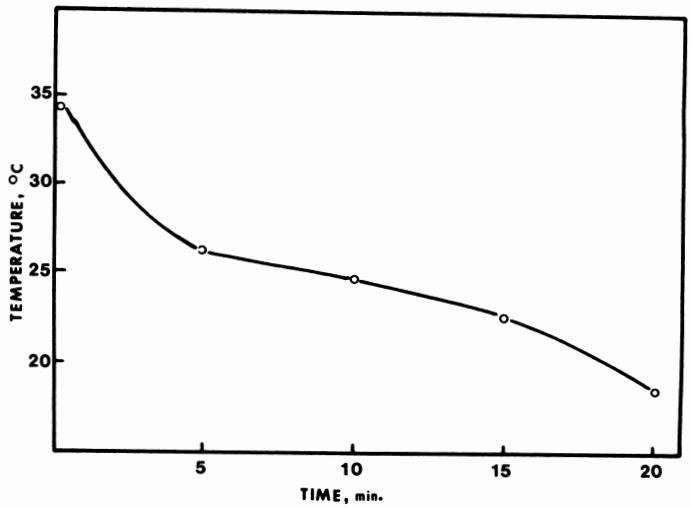

Figure 1. Cooling curve of lead acetate decahydrate $Pb(C_2H_3O_2)_2 \cdot 10H_2O$.

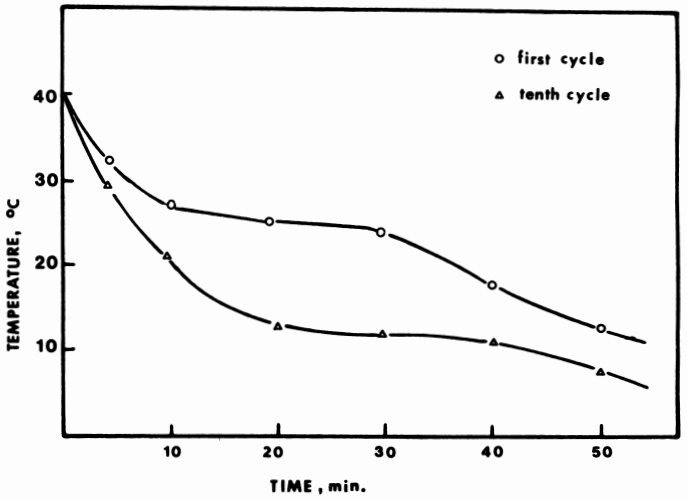

Figure 2. Cooling curves of mixture 40% $CaCl_2$, 10% $MgNO_3$, 50% H_2O by weight.

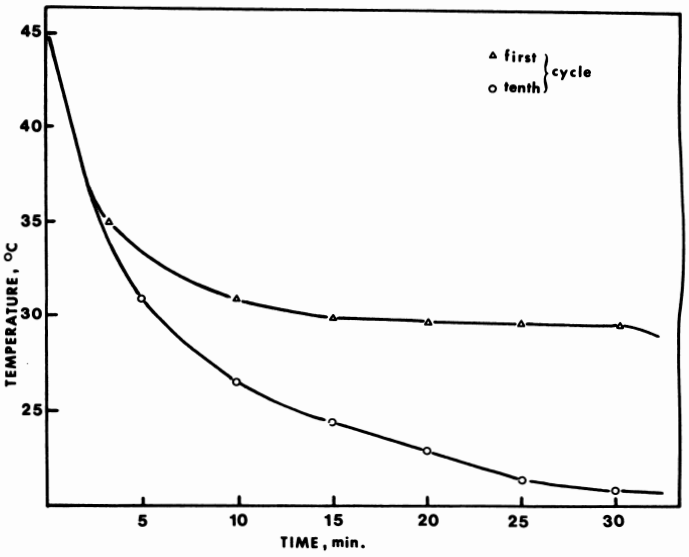

Figure 3. Cooling curves of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) with 1.0% by weight borax added.

only delays the effects of incongruent melting, it does not eliminate them. It was therefore decided to concentrate further efforts on studying calcium chloride hexahydrate with various levels of excess water added to adjust the phase transition point.

The supercooling and incongruency of $CaCl_2$-$6H_2O$ were eliminated by the addition of 0.01% by weight barium hydroxide and 2% strontium chloride, as suggested by Carlsson et al. (1979). Typical cooling curves after 10 cycles are presented in Fig. 4 for the mixture with and without the additives.

Barium hydroxide acts as a seed crystal around which the crystallization of the calcium chloride hexahydrate can begin. Because of its presence, supercooling is eliminated. Strontium chloride has the effect of altering the phase diagram of the calcium chloride/water system so that, on cooling, the precipitation of tetrahydrate crystals does not occur. As can be seen, the additives allow the solution to melt correctly at the proper transition temperature of 29.6°C. Because of their importance, these additives were included in all samples tested.

The effect of excess water on the crystallization temperature is presented in Fig. 5. As expected, the freezing point decreased as the level of excess water increased. The phase transition points correspond quite closely with those given in the phase diagram presented by Carlsson et al. (1979). The slight variations were probably due to the 2% strontium chloride added in the present study. Theoretically, the freezing point could be made as low as required by simply increasing the amount of excess water. However, at levels of excess water greater than approximately 10%, stratification tends to increase significantly. That is, the solution tends to separate into two regions: a calcium chloride hexahydrate region with a relatively pure water region above it. This would necessitate adequate stirring to keep the solution homogeneous and the freezing point constant during repeated cycling.

Over the concentration range studied, the latent heat of fusion of the mixture increased from 168 J g^{-1} for pure $CaCl_2$•$6H_2O$ to 195 J g^{-1} for a solution having 12.5% by weight added water (Fig. 6). This is to be expected since the solution composition is moving closer to that of pure water, which has a latent heat of fusion of 335 J g^{-1}.

No signs of incongruency were observed during the procedure. This was due, at least in part, to the addition of strontium chloride. However, when the excess water is greater than approximately 2% by weight, the mixture enters the region of the phase diagram where tetrahydrate formation should not occur, thereby theoretically eliminating incongruency without the need for additives.

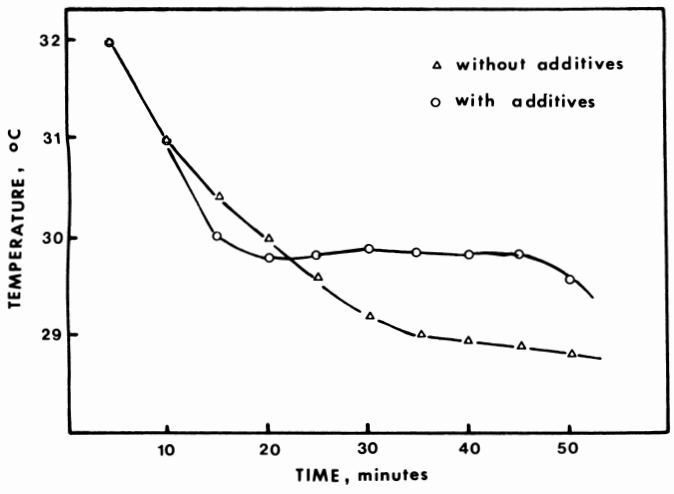

Figure 4. Effect of additives (strontium chloride, barium hydroxide) in eliminating incongruency of $CaCl_2$•$6H_2O$.

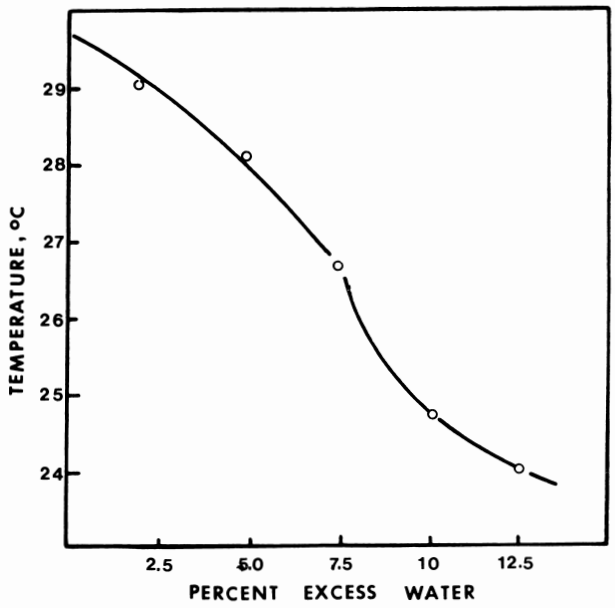

Figure 5. Effect of excess water on the freezing point of calcium chloride hexahydrate.

SUMMARY

Of the four PCMs tested, the most promising proved to be calcium chloride hexahydrate with added water. The results of experiments conducted on mixtures containing various levels of excess water showed that a mixture of 90% $CaCl_2$•$6H_2O$ and 10% water has a freezing point of approximately 25°C, which makes it quite a feasible candidate for heat storage in applications where the melting point of pure $CaCl_2$•$6H_2O$ is too high. The melting point may be lowered even further by the addition

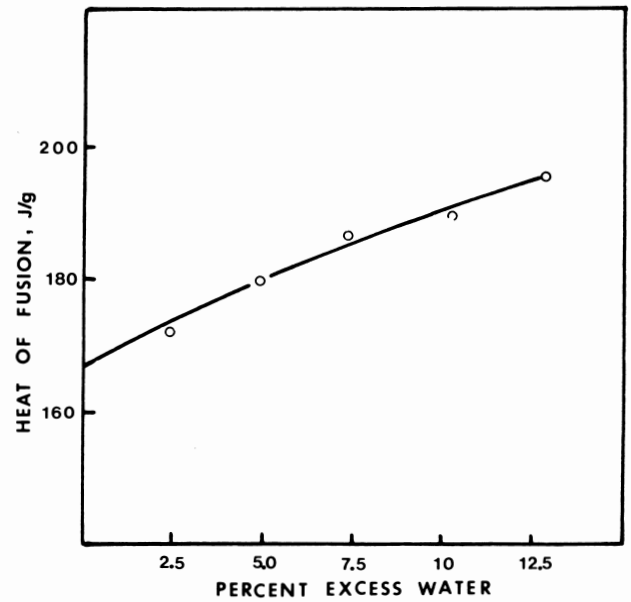

Figure 6. Effect of excess water on the latent heat of fusion of calcium chloride hexahydrate.

of more water, but adequate mixing then becomes more of a problem.

In addition to the advantage of a lower freezing point, the increased latent heat of fusion is also of importance as it would allow for greater heat storage. These advantages make excess water mixtures attractive as low temperature storage media, and a viable alternative to pure calcium chloride hexahydrate.

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