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THERMAL PROPERTIES OF A HEAT STORAGE DEVICE CONTAINING SODIUM ACETATE TRIHYDRATE

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Abstract

A heat storage device containing sodium acetate trihydrate and excess water without seeding crystals has been examined. The proper arrangement of heating tubes inside the container assured a thermoconvective flow during the heating cycle to mix the separated phases (sodium acetate trihydrate and saturated solution) formed in exhausted state.

Keywords: heat storage, phase change, sodium acetate.

Introduction

The energy problems of our days have brought about a revival in a number of new research fields. This phenomenon is well illustrated by the example of phase change materials. The first paper on the subject was published by M. TELKES [1] as early as 1949, however, there were hardly any researchers to deal with phase change materials until 1972–73. The oil crisis produced an upward trend, and the number of publications, and especially of patents began to increase remarkably. The appeal of phase change materials lies in the fact that their use may bridge the time lag between availability and utilization of energy, thus making the use of solar energy more economical, and by storing electrical energy in the form of thermal energy in periods outside the peaks, the load of electrical power stations may be made uniform.

Phase Change Materials

In spite of the fact that most substances can undergo solid to liquid phase transition, the number of materials that can be used in practice is limited. The rules of selection of phase change materials for practical use were summarised by H.G. Lorsch [2]. It is very difficult to select a material which meets all the known thermodynamic, kinetic, chemical and economical criteria. There are, however, a number of materials which, to some extent, fulfil the requirements mentioned above.

The most crucial characteristics of heat storage materials is their tendency of supercooling and incongruent melting. These are characteristic mainly of materials whose phase transition takes place at low temperature ($t < 100$ °C), e.g. of inorganic salt hydrates.

Organic substances, e.g. paraffins, stearic acid, polyethylene glycols usually pose no serious physicochemical problems when used as heat storage materials (there is usually no supercooling or incongruent melting), however, the high price, inflammability, low thermal conductivity of the solid substance may cause serious difficulties during use.

Of low temperature phase change materials salt hydrates are the most popular: $Na_2SO_4 \cdot 10H_2O$, $CaCl_2 \cdot 6H_2O$, $Na_2HPO_4 \cdot 12H_2O$, $CH_3COONa \cdot 3H_2O$. Some physical data of a few heat storage substances are summarized in *Table 1* [3-4].

Table 1

Some physical data of some phase change materials applicable as heat storage substances

Material	m.p.	H_f	Density (kg/dm^3)		Specific heat (kJ/kgK)		Therm. Cond. (W/mK)	
	°C	(kJ/kg)	solid	liquid	solid	liquid	solid	liquid
$MgCl_2 \cdot 6H_2O$	116	165	1.50	–	1.72	2.82	0.69	0.57
$Ba(OH)_2 \cdot 8H_2O$	78	267	2.18	2.06	1.17	–	1.25	0.65
Stearic acid	70	203	0.94	0.95	1.67	2.35	0.3	0.2
$CH_3COONa \cdot 3H_2O$	58	226	1.45	1.28	2.79	–	–	–
Paraffin	55	189	0.9	0.77	1.55	2.1	0.3–0.2	0.16
$Na_2S_2O_3 \cdot 5H_2O$	48	201	1.73	1.67	1.46	2.4–3.05	0.6	–
$Na_2HPO_4 \cdot 12H_2O$	35	281	1.52	1.44	1.9–1.5	1.7–3.2	0.51	0.47
$Na_2SO_4 \cdot 10H_2O$	32	254	1.48	1.41	1.9–1.7	3.31	0.5	0.3
$CaCl_2 \cdot 6H_2O$	29	171	1.62	1.5	1.45	1.47	0.6–1.08	0.3–0.55

Sodium Acetate Trihydrate Based Heat Storage Systems

Sodium acetate trihydrate has recently attracted attention as a useful heat storage material because of its large latent heat of fusion (252 kJ/kg) at moderate temperature (melting point: 58 °C) [5-7].

The promising material has two very unpleasant properties: the salt melts incongruently forming anhydrous sodium acetate, and the molten phase can supercool heavily. The details of the phase diagram of $CH_3COONa-H_2O$ are shown in *Fig. 1.* Melting is of a peritectic character. However, fusion is not accompanied by phase separation because, for sufficiently rapid melting, sodium acetate trihydrate becomes a homogeneous phase. The peritectic character is manifested mainly by the liquid–solid change of state. In the cooling of the melt corresponding to $CH_3COONa \cdot 3H_2O$, a phase is first attained where anhydrous CH_3COONa is the stable phase. On further decreasing the temperature, CH_3COONa should be converted below the peritectic temperature into the stable trihydrate. In practice, this equilibrium state cannot be attained and thus the behaviour of heat storage packings based on the phase transformation of sodium acetate trihydrate can be interpreted only by studying non-equilibrium processes.

Non-Equilibrium Processes in the Heat Storage System $CH_3COONa \cdot 3H_2O$

The melting cycle of sodium acetate trihydrate is free of problems according to experiments carried out to date. However, during crystallisation greater difficulties have to be tackled. In the heat storage substance $CH_3COONa \cdot 3H_2O$, the quality of anhydrous CH_3COONa increases substantially by the third or fourth heat storage cycle if crystallisation proceeds at an environmental temperature of 18–20 °C.

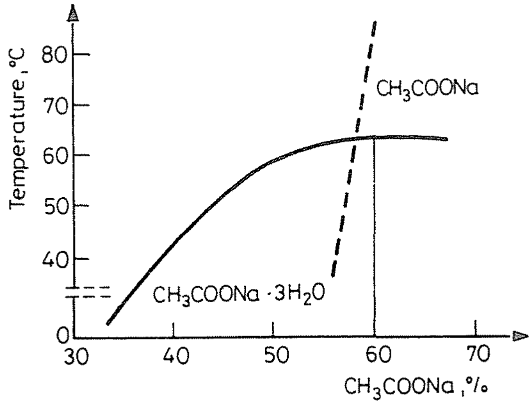

Fig. 1. Section of the phase diagram of the system $CH_3COONa-H_2O$

If no mixing is applied the quantity of the anhydrous CH_3COONa continuously increases with increasing cycle number. On termination of the cycle (corresponding to minimum heat content) three phases are present:

1. Solid anhydrous CH_3COONa at the bottom.
2. Solid sodium acetate trihydrate, separated from the sodium acetate solution, which became richer in water because of the separation of the salt hydrate, with lower water content.
3. Upper aqueous sodium acetate solution in a quantity depending on the end temperature of the discharge section.

At the beginning of the new heat storage cycle, $CH_3COONa \cdot 3H_2O$, melting on top of the anhydrous CH_3COONa during the melting process, does not mix satisfactorily with the supernatant sodium acetate solution of lower density. Therefore, in the crystallisation (i.e. discharge stage) section further anhydrous sodium acetate separates from this phase. This process is continued until the composition of the molten $CH_3COONa \cdot 3H_2O$ phase equals the peritectic composition as a result of mass transfer processes with the upper aqueous phase, caused by diffusion and forced flow. This process is accompanied by a considerable decrease in heat storage capacity [8–11].

Supercooling also represents a serious problem in the application of sodium acetate trihydrate. During nucleation, the free energy of water must increase, as the water molecules rearrange themselves into the surroundings of the solid hydrate, because the free energy of water in crystalline state is higher than that in the supercooled melt. The difference in the free energies may be considered as a rough measure of the barrier to nucleation [12].

No isomorphous nucleation agent is known for the salt. A heterogeneous nucleation agent may often help eliminating supercooling [13-14]. The use of partial melting (some solid sodium acetate trihydrate must remain in solid phase at the end of the heating cycle, 'cold finger') may be an aid to render the system reversible.

Consequently, two problems connected with the behaviour of this hydrate, phase segregation and supercooling must be solved before it can be used as a latent heat storage material.

Experimental

In order to eliminate phase segregation, two methods have been applied. In the well-known excess water method, the water content of the liquid heat storage material has been increased, and a specially designed container has been applied [15]. The container geometry and the proper heat input arrangement permitted any concentration inhomogeneity in the molten phase during the heat charging cycles (*Fig. 2*) to be avoided.

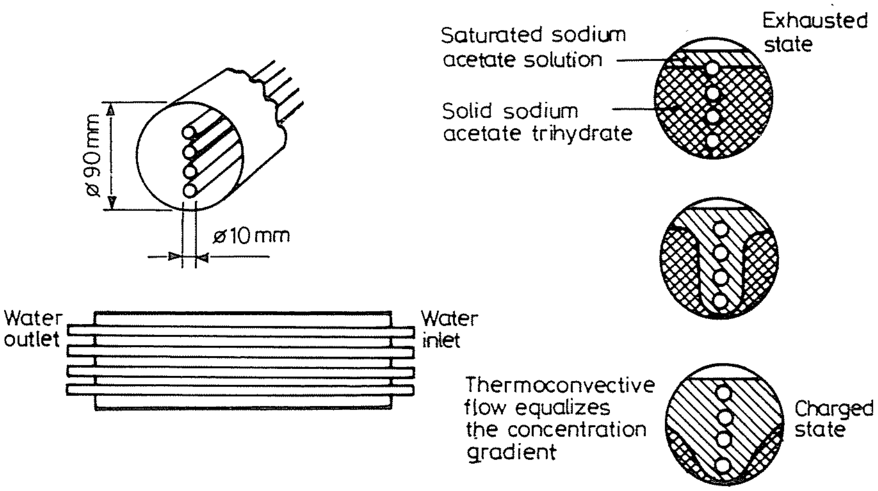

Fig. 2. Heat storage device containing sodium acetate trihydrate

A polypropylene tube containing sodium acetate trihydrate (technical grade) and excess water (0.3 mole of water /mole of trihydrate) was examined as heat storage device. Inside the tube small polypropylene tubes were inserted horizontally. The heat transfer medium was water. During the heat input the water temperature was 65 °C and during the cooling cycle it was 23 °C. The cycle time was one day and the stored heat was measured in the range 65 – 23 °C.

Results and Discussion

The specific stored heat versus cycle number is illustrated in *Fig. 3*.

In exhausted state two phases exist: a solid sodium acetate trihydrate (lower phase) and a saturated solution of sodium acetate trihydrate (upper phase). During heat input a liquid channel forms very quickly and the upward flowing melted sodium acetate starts mixing with the upper liquid phase. Further heat input widens the channel and the mixing proceeds. At the end of the heating cycle the concentration of the molten phase is smaller than the peritectic point and the trihydrate will solidify during the cooling cycle. The decrease in storage capacity is due to the imperfect mixing effect but a stable state at a lower heat storage level can be achieved.

The possibilities of nucleation of the molten phase have also been examined without addition of seeding crystals. A strict correlation was

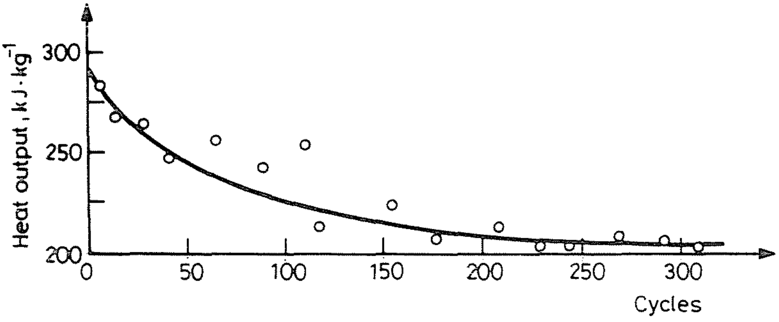

Fig. 3. Specific stored heat versus cycle number. Heat storage medium: sodium acetate trihydrate. Temperature range 65 °C–23 °C, cycle time 1 day

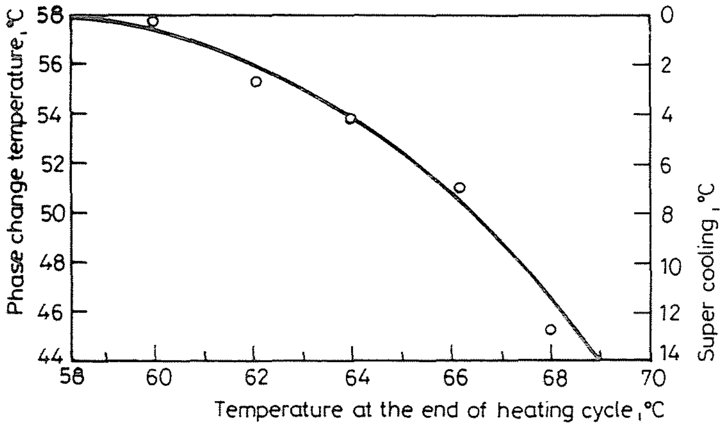

Fig. 4. Supercooling of heat storage material (sodium acetate trihydrate : water = 1 : 0.3 mole ratio) versus final temperature of the heating cycle

found between the supercooling and the maximum temperature at the end of molten phase in the range of 58 °C – 68 °C (*Fig. 4*).

More than 300 cycles proved that if the temperature of the molten phase does not rise above 65 °C, the degree of supercooling is not greater than 6 °C. The greater the temperature of the melt the smaller the remaining molecular order which helps the formation of nuclei.

Acknowledgement

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