

PHYSICOCHEMICAL PROBLEMS CONNECTED WITH PHASE CHANGE MATERIALS

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Summary

The physicochemical problems and some results of the investigation of latent heat storage materials, first of all salt hydrates such as sodium sulphate decahydrate, calcium chloride hexahydrate disodium hydrogen phosphate dodecahydrate and sodium acetate trihydrate are briefly reviewed.

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 more uniform.

The work done with phase change materials during the past decade consisted mainly of fundamental research and pilot plant experiments, although buildings having heat storage system have been known for years [2, 3].

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 summarized by H. G. Lorsch [4].

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 [5–15].

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 ($t < 100^\circ\text{C}$), 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.

High-temperature heat storage systems [16–18] ($t > 100^\circ\text{C}$) do not meet all the requirements, either. Although supercooling or incongruent melting do not generally occur with these materials, except e.g. with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, due to the high price of the container material or the material itself (e.g. lithium fluoride) or comparative hazardousness (e.g. nitrates) their practical application requires consideration.

Of low-temperature phase change materials salt hydrates are the most popular: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$. Some physical data of a few heat storage substances are summarized in Table 1.

Table 1

Some physical data of some phase change materials applicable as heat storage substances [10, 12]

Material	m.p. ($^\circ\text{C}$)	H_f (kJ/kg)	Density (kJ/dm ³)		Specific heat (kJ/kg K)		Therm. cond. (W/m K)	
			solid	liquid	solid	liquid	solid	liquid
Stearic acid	70	203	0.94	0.95	1.67	2.35	0.3	0.2
Paraffin	55	189	0.9	0.77	1.55	2.1	0.3–0.2	0.16
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	29	171	1.62	1.5	1.45	1.47	0.6–1.08	0.3–0.55
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	32	254	1.48	1.41	1.9–1.7	3.31	0.5	0.3
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	35	281	1.52	1.44	1.9–1.5	1.7–3.2	0.51	0.47
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	48	201	1.73	1.67	1.46	2.4–3.05	0.6	–
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	78	267	2.18	2.06	1.17	–	1.25	0.65
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	116	165	1.50	–	1.72	2.82	0.69	0.57
$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$	58	226	1.45	1.28	2.79	–	–	–

Sodium sulphate decahydrate-based heat storage system

Sodium sulphate is one of the cheapest materials and by addition of other cheap materials e.g. NH_4Cl or NaCl , eutectics with different melting points can be obtained. Supercooling can be eliminated practically completely by addition of crystalline borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) [9].

Phase separation due to incongruent melting that is, the formation of solid dehydrated sodium sulphate crystals still remains a problem which has not yet been solved definitely in the case of static heat storage systems.

The heat storage capacity and reversibility of sodium sulphate based heat storage systems depend on the surface area available for the peritectic reaction. This surface area may reduce due to two reasons:

a) solid anhydrous sodium sulphate particles settle out and collect at the bottom of the container.

b) the volume of anhydrous sodium sulphate particles increases with increasing number of heating and cooling cycles, consequently their specific surface area decreases [20].

To prevent anhydrous sodium sulphate particles from settling out, the addition of suspension or thickening agents is recommended. Carboxymethyl cellulose, bentonite, fumed silica, polyacrylates, polyvinyl acetate are mostly used for this purpose. The phase transition heat of thickened heat storage systems reaches a value between 140 and 200 kJ/kg after a sufficiently long period of use.

Thickening, however, cannot be considered as an ultimate solution to the problem, as the gel structure sooner or later tends to degrade. This is especially true if the heat is released slowly and thus big crystals may be formed. After melting the defect in the gel structure in the place of the crystal will not completely disappear, as the high salt content of the melt markedly hinders gel swelling.

This phenomenon, however warns us that the extrapolation of the heat capacity values determined after several thousand cycles carried out in an accelerated experiment to the conditions of use is not fully justified.

The use of attapulgite thixotropic agent suggested by M. Telkes appears to be a much better solution to the problem. The bar-shaped units of attapulgite get tangled like stalks of straw in a straw-stack and the flexible skeleton thus formed ensures a uniform distribution of sodium sulphate crystals.

Attempts are made to control the size of anhydrous sodium sulphate crystals by addition of surfactants or solvents of high permittivity. However, so far no publication has appeared on the theoretical fundamentals of the effect of these additives. Contrasting with static heat storage systems, stored latent heat can be extracted almost completely if the heat storage material is stirred [21].

Calcium chloride hexahydrate-based heat storage systems

A great advantage of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ -based heat storage materials is that a good seeding agent is available: $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ [22, 23]. Even better results were achieved the author's laboratory using strontium hydroxide octahydrate, although the mechanism of crystallization is not yet understood, as the nucleation agent is not isomorphous with calcium chloride hexahydrate. A similar phenomenon was observed by Lane in the case of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, where reversible nucleation could be initiated by an insoluble oxide or hydroxide of the cation in the melt.

The greatest danger with calcium chloride hexahydrate-based systems is the appearance of a thermodynamically unstable, but apparently fairly stable $\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ phase.

Formation of the tetrahydrate may be prevented using the "extra water" principle suggested by S. Furbo [24]. This principle, which can be extended to other incongruently melting salt hydrates, is, that the melt should contain water in excess of the stoichiometric amount so that the mixture is more dilute than the peritectic composition. Even so, however, the reversibility of the system may cease to exist during repeated thermal cycling due to the settling of $\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$, if the mixing of phases is not ensured during melting [25].

Precipitation of $\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ can be prevented by adding $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Ca}(\text{OH})_2$ [26], but no unambiguous interpretation of the phenomenon has been offered yet [27].

Calcium chloride hexahydrate, is well suited to electrically heated floor-heating systems. There is a building with such a heating system that has been operating trouble-free for five years in Győr, Hungary [3].

Disodium hydrogenphosphate decahydrate based heat storage systems

It has the greatest heat storage capacity among salt hydrates, but melts incongruently and no isomorphous seed material is known. It is probably due to these facts that only few data of this substance have been published in literature.

Reversibility can be ensured, i.e. formation of the heptahydrate can be prevented by the principle of "extra water" [28, 29].

The material has been used successfully in direct contact heat exchangers, where $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ was dispersed in a hydrocarbon. No supercooling was observed [30].

Sodium acetate trihydrate based heat storage systems

This material is also melting incongruently, and no isomorphous seed material is known. Attempts have been made to overcome supercooling problems by using various additives, e.g. activated carbon [32].

Heterogeneous nucleation agents may often help eliminating supercooling, but, according to experience, mainly in cases where the temperature of the melt does not rise too high above the melting point. If no isomorphous crystals are available, the use of a "cold finger" may be an aid to render the system reversible.

Urea and formamide may be used to render the melting of sodium acetate trihydrate congruent. This way materials melting at 31.5 and 40.5°C, respectively, may be obtained with remarkable heat capacities (226 and 255 kJ/kg) [33, 34].

Promising experiments are in progress with embedding sodium acetate in polymer matrix [35].

Summing up it can be stated that a part of heat storage materials are ready for technological use, whereas further research is needed with the majority of such systems before they may be put to use.

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