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LATENT HEAT STORES AND PHASE CHANGE MATERIALS - AN EXTENSIVE AREA FOR THERMAL ANALYSIS, CALORIMETRY AND CHEMICAL THERMODYNAMICS

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ABSTRACT

Standard thermoanalytical techniques such as TG, DTA and DSC are used in search of suitable Phase Change Materials (PCMs) for high-capacity latent heat storage.

We investigated eutectic mixtures of the ternary system $NaOH-NaOH\cdot H_2O-KOH\cdot H_2O$ (ref.1) and found them excellent storage media in the low-temperature range 46-62°C with storage capacities between 482 and 526J/cm^3. Reinvestigation of the proposed (ref.2) reversible reaction $Ba(OH)_2\cdot 8H_2O + 2KNO_3 \rightleftharpoons 2KOH + Ba(NO_3)_2 + 8H_2O$ (65°C;ΔH=445J/cm^3) revealed the system not to react in the sense of a double conversion; generally, reciprocal salt pairs seem to be less suited for thermal energy storage.

The main problems of static latent heat stores are prevented by a new dynamic concept (ref.3): the system works with an auxiliary PCM (liquid⇌vapour) ensuring optimized conditions of heat transfer and homogenization of the storage material.

INTRODUCTION

First order phase changes connected with significant changes in enthalpy are of particular interest in the field of latent heat storage. Table 1 gives a common survey of homogeneous and heterogeneous systems which in principle may be suited for thermal energy storage.

TABLE 1

Phase change systems for thermal energy storage (s=solid, l=liquid, v=vapour)

SYSTEM / PHASE COMPOSITION	NOTATION (EXAMPLE)	
$s \rightleftharpoons l$	Fusion, congruent	
$s(1) + s(2) + \dots s(n) \rightleftharpoons l$	eutectic	(binary, multinary)
$s(1) \rightleftharpoons s(2) + l$	Fusion, incongruent	
$s(1) \rightleftharpoons s(2) + v$	Thermal Decomposition	
$s \rightleftharpoons l + v$		(Gas-Hydrates)
$s\cdot v \rightleftharpoons s + v$		(Zeolite/Water)
$l \rightleftharpoons s + v$	Evaporation	
$l(1) \rightleftharpoons l(2) + v$	Heterogeneous Evaporation	(Ammonia/Water)

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Compounds with congruent melting behaviour as well as eutectic mixtures are ideal PCMs for latent heat storage, because they work at constant temperatures and do not tend to phase separations (incongruent fusion, see Table 1) even under static conditions. A number of PCMs (mainly inorganic salts, salt hydrates and respective eutectic mixtures) are already tested and were shown (ref.4) to have suitable storage properties; occurrence of the undesired effects of supercooling is mainly reduced by heterogeneous seeding of the storage materials.

Systems which produce two-phase equilibria at higher temperatures, especially those containing a vapour phase (see Table 1), can be used for long-time heat storage by escaping the vapour and condensing it into a separate vessel; back-reaction is attained by anew evaporation of the condensed liquid and contact of the vapour with the second phase. The system Calciumchloride-Water represents one example of a feasible long-time heat store (ref.5).

In this paper we report on our thermoanalytical investigations in low-temperature PCMs for latent heat storage based upon eutectic mixtures of the ternary system $NaOH$-$NaOH \cdot H_2O$-$KOH \cdot H_2O$ (ref.1) and upon a proposed reciprocal salt pair reaction (ref.2). Furthermore we describe a new dynamic concept of latent heat storage (ref.3) which ensures optimized conditions of heat exchange and homogenization of the storage medium and prevents the undesired effects of supercooling.

THE TERNARY SYSTEM $NaOH$ - $NaOH \cdot H_2O$ - $KOH \cdot H_2O$

The pure components $NaOH$, $NaOH \cdot H_2O$ and $KOH \cdot H_2O$ melt congruently (320°C, 65°C and 147°C) with enthalpies of fusion $328 J/cm^3$, $446 J/cm^3$ and $629 J/cm^3$. As we were interested in PCMs with storage temperatures below 65°C we investigated the binary systems $NaOH$-$NaOH \cdot H_2O$ (reinvestigation; see ref.6), $NaOH \cdot H_2O$-$KOH \cdot H_2O$ and the ternary system $NaOH$-$NaOH \cdot H_2O$-$KOH \cdot H_2O$ in order to find out compositions, temperatures and phase change enthalpies of the respective eutectics. Phase equilibria were derived from DTA-measurements in closed tubes during heating (3°C/min) and with sample amounts in the range of 1-2g. Enthalpies of fusion were determined using a Mettler DSC 20 with heating- and cooling-cycles under dynamic and static (just above/below the eutectic temperatures) conditions as well. The results are summarized in Table 2. Storage capacities of the eutectic mixtures may be compared with PCMs which are already used in this temperature range, such as $Na_2S_2O_3 \cdot 5H_2O$ ($T=48^0C$;$\Delta H=334 J/cm^3$) and $NaCH_3COO \cdot 3H_2O$ ($T=58^0C$; $\Delta H=328 J/cm^3$). Both, the thiosulfate and the acetate, melt incongruently and there is need of heterogeneous seeding to avoid strong supercooling; supercooling of the eutectic mixtures given in Table 2 is not more than 1-2°C, even without seeding. The high storage capacities of the eutectic mixtures containing solid $NaOH$ cannot be explained by exclusive consideration of the enthalpies of fusion of the pure components, which

TABLE 2

Eutectics ($T<65^0C$) of the ternary system $NaOH-NaOH\cdot H_2O-KOH\cdot H_2O$

SYSTEM : EUTECTIC COMPOSITION	T|^0C|	ΔH|J/cm^3|
$NaOH\cdot H_2O-KOH\cdot H_2O$:		
$NaOH\cdot H_2O$ 77.5mole-% + $KOH\cdot H_2O$ 22.5mole-%	48	482
$NaOH-NaOH\cdot H_2O$:		
NaOH 51.5mole-% + H_2O 48.5mole-%	62	526
$NaOH-NaOH\cdot H_2O-KOH\cdot H_2O$:		
NaOH 43mole-% + KOH 9mole-% + H_2O 48mole-%	46	510

in the case of NaOH is only $328J/cm^3$. In this connection it is important to note that solid NaOH shows a phase-transformation $\alpha\rightleftharpoons\beta$ at 300^0C with $\Delta H=383J/cm^3$; the significant increase of the storage capacities of the eutectic mixtures may therefore be contributed by a large heat of fusion of low-temperature α-NaOH.

RECIPROCAL SALT PAIRS

The double conversion of reciprocal salt pairs, especially reaction (1), has been proposed (ref.2) for low-temperature latent heat storage.

$$Ba(OH)_2\cdot 8H_2O + 2KNO_3 \rightleftharpoons Ba(NO_3)_2 + 2KOH + 8H_2O \qquad (1)$$

Our thermoanalytical redetermination of the reaction temperature (65^0C) and enthalpy change ($438J/cm^3$) is in accordance with (ref.2). However, the X-ray investigations (Guinier-Simon-technique) revealed the system not to react in the sense of a double conversion (1), but as a simple process of melting (2).

$$Ba(OH)_2\cdot 8H_2O + 2KNO_3 \rightleftharpoons Ba(OH)_2\cdot H_2O + (2KNO_3) + \text{liquid } (7H_2O) \qquad (2)$$

Pure $Ba(OH)_2\cdot 8H_2O$ melts incongruently at 78^0C with $\Delta H=658J/cm^3$. The stoichiometric mixture (2) contains 61% of the octahydrate which in this way already contributes $402J/cm^3$ to the observed storage capacity of $438J/cm^3$; the remaining difference may be balanced by partial solution of KNO_3 which is also indicated by decrease of the intensities of the KNO_3-reflections. Lowering of the reaction temperature form 78^0C (pure octahydrate) to 65^0C is caused by the multi-component mixture. Improvement of the storage capacity of the mixture by varying the amounts of KNO_3 has not yet been investigated.

Generally, double conversions of reciprocal salt pairs (hydrates) do not react quantitatively at a constant temperature (invariant point with five-phase equilibrium), but show an interval of transformation (ref.7). Hence, reciprocal salt pairs are less suited for thermal energy storage.

DYNAMIC LATENT HEAT STORAGE BY USE OF AN AUXILIARY PCM

Storage media working in the condensed state in principle are connected with a number of specific problems which mainly arise from the effects of soopercooling, phase separation, heterogeneous crystallization, bulk solidification and bad thermal conductivity. Prevention of these effects by current techniques such as selective nucleation, incapsulation, mechanical movement, addition of inert materials with high thermal conductivity and one-phase contact fluids, respectively, is not yet really satisfying. A new dynamic concept working with an auxiliary PCM (ref.3) seems to be successful; Figure 1 gives a schematic representation of the system.

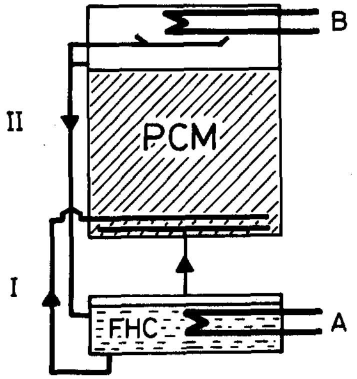

Fig.1. Schematic representation of a dynamic system for latent heat storage using an auxiliary PCM (Fluorinated Hydrocarbon, FHC, with phase change liquid ⇌ vapour) which is in direct contact, immiscible with an inert to the storage medium.

Heat transfer to the solid PCM (congruent fusion) is realized by evaporation of the FHC at A and condensation in contact with the PCM; T(evaporation FHC) ≥ T (fusion PCM). Loading of the store is finished after the PCM is completely molten; the layer of liquid FHC at the top of the liquid PCM is continuously drawn off via II. The stored thermal energy is then set free by pumping liquid FHC (T(evaporation FHC) <T(fusion PCM)) into the liquid PCM via I: immediately the FHC starts to boil, is evaporated out of the PCM, condensated at the external heat exchanger B and led back to A via II. Evaporation of the FHC out of the PCM causes its (local)crystallization and the complete system is continuously mixed by strong boiling phenomena of the FHC. After the cycle is finished the PCM is present as a porous solid and a new loading process can be started without any problems. Regulation of the system is realized by pressure-control.

REFERENCES

1 R. Kniep, DE-P 3431978 (1984)
2 F. Reiter and R. Rota, Solar Energy, 32 (1984) 499-503
3 M. Laumen, DE-P 3236319 (1982)
4 J. Schröder and K. Gawron, Energy Research, 5 (1981) 103-109
5 D. Brodalla, D. Hollenberg and R. Kniep, Proceedings of the 1978 International Solar Forum, Vol. 2, 405-414
6 S. U. Pickering, J. Chem. Soc., 63 (1893) 890-909
7 A. Findlay, Phasenlehre, Verlag Joh. Ambros. Barth, 1925