THERMOANALYTICAL INVESTIGATION OF SOME ALKALINE EARTH HYDROXIDE HYDRATES ON APPLICATION AS LATENT HEAT STORAGE MATERIALS

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Owing to their high specific melting enthalpy and the range of the melting temperatures the alkaline-earth hydroxide hydrates $Ba(OH)_2 \cdot 8H_2O$ and $Sr(OH)_2 \cdot 8H_2O$ are promising latent heat storage materials.

The investigations of the melting and solidification behaviour of $Sr(OH)_2 \cdot 8H_2O$ and its mixtures with $Ba(OH)_2 \cdot 8H_2O$, which had been performed by means of DTA and DSC methods in the closed system with a constant gross composition lead to statements on the melting temperature and specific melting enthalpy *vs.* concentration. Theoretical storage densities of 532 MJ/m^3 are obtained for the mixture of $Ba(OH)_2 \cdot 8H_2O$ and $Sr(OH)_2 \cdot 8H_2O$ (80/20) and a value of 655 MJ/m^3 can be achieved for $Sr(OH)_2 \cdot 8H_2O$. The kinetics of rehydration to the octahydrates has a great influence on the storage temperature and storage density.

Keywords: alkaline earth hydroxide hydrate, heat storage materials

Introduction

Utilization of the melting enthalpy of selected salt hydrates for storage of low-temperature heat in the temperature range of 0°–120°C has already been the subject of many investigations [1]. Recently the development of heat storage units for motorcars has become a particularly interesting fact. Subject of this research is the utilization of the engine waste heat for the charge of a heat storage unit and its discharge in the starting phase for a rapid heating of the engine and wind screen of the motorcar. This results in a reduction of the emission of pollutants and engine wear and an improvement in convenience.

If the cooling water of the engine is used as a heat carrier medium, a range of about 70°–75°C is envisaged as working temperature of the heat storage unit. Among the known salt hydrates the alkaline-earth hydroxide hydrates

$Ba(OH)_2 \cdot 8H_2O$ and $Sr(OH)_2 \cdot 8H_2O$ are of special interest to this range. Appropriate investigations of $Ba(OH)_2 \cdot 8H_2O$ have been the subject of many papers [2–9]. Except for table values with respect to the melting temperature of 88°C and the melting enthalpy of 352 J/g [10] there are no data for the thermochemical behaviour of $Sr(OH)_2 \cdot 8H_2O$ (pure) and in the mixture with $Ba(OH)_2 \cdot 8H_2O$ concerning a relevance as latent heat storage materials.

Experimental

$Ba(OH)_2 \cdot 8H_2O$ and $Sr(OH)_2 \cdot 8H_2O$ have been twice-recrystallized from water in a CO_2-free atmosphere and the water content was determined according to the decomposition of samples to water-free products at 200°C.

DTA investigations were performed with sample weights of 30–50 mg by means of a thermoanalyzer (SETARAM SA, France) with the low-temperature equipment (cryostat, crucible holder suspension with platinel thermocouples) in closed glass ampoules in the 600 μl platinum crucibles. The chosen heating and cooling rates were 2 deg/min.

Mixtures of the salt hydrates were melted in closed ampoules, homogenized by shaking, quenched in ice and tempered at room temperature for about 24 hours.

Calibration of the apparatus under the special measuring conditions was performed by means of ice, acetamide and indium. The uncertainty of the measured melting enthalpies is ±3%.

X-ray investigations of the different samples were carried out at 20°C and elevated temperatures by means of the Philips PW 1050/70 X-ray diffractometer and graphite monochromator coupled with a HTK P-10 high-temperature accessory.

Results and discussion

On first heating of $Sr(OH)_2 \cdot 8H_2O$ the highly endothermic transition of the octahydrate to monohydrate and melt is observed at 85.4°C (Fig. 1). Values of 340–350 J/g are found for the specific melting enthalpy due to small deviations from the stoichiometric water content of the samples. In contrast to $Ba(OH)_2 \cdot 8H_2O$ where thinner melts with a low content of solid phase of $Ba(OH)_2 \cdot 3H_2O$ are encountered, pasty melts in the case of $Sr(OH)_2 \cdot 8H_2O$ are formed as a result of the high incongruence of the system. During cooling of the melts two exothermic processes are always observed. The first peak is located at about 62°–64°C, the second one at −11°C. The first peak may be due to the tran-

sition to $Sr(OH)_2 \cdot 8H_2O$ and the second process is attributed to the eutectic solid-ification in the $Sr(OH)_2-H_2O$ system. The two processes proceed with a considerable subcooling. Melting of the ice being formed at the eutectic temperature is observed on reheating of the sample at $-0.1°$ up to $-0.2°C$. According to data on solubility [11] the eutectic line can be observed at $-0.1°C$.

Subcooling of about $22°C$ in the case of the small samples of 40–50 mg can also be observed with great samples of about 10 g.
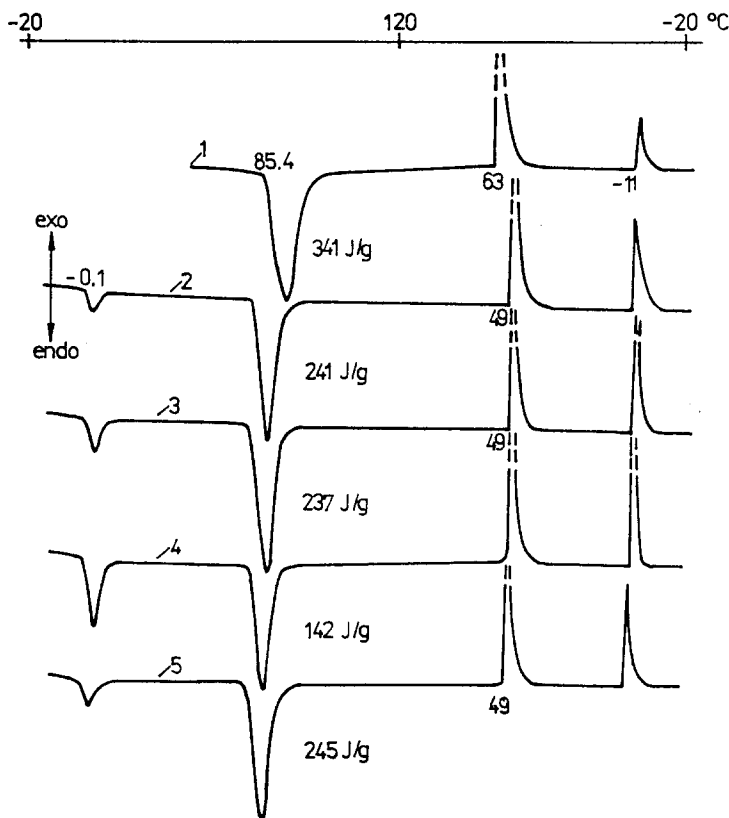

Fig. 1 DTA/DSC cycles of $Sr(OH)_2 \cdot 8H_2O$; q=2 deg/min; m=41.98 mg; DTA=250 μV; 1- first run; 2,3- run after 16 h tempering; 4- reheating without tempering; 5- reheating after 64 h tempering at room temperature

On cyclic heating and cooling of the samples the same thermal effects are measured (Fig. 1, curves 2–5). However, rehydration to $Sr(OH)_2 \cdot 8H_2O$ is not finished completely. This can be seen by the melting peak elevation of ice at $-0.1°C$. Therefore, there is a decrease in melting enthalpy at $85.4°C$. However, samples which have been tempered at room temperature show a clearly visible

increase as a result of rehydration. Compared with the pure components, mixtures of $Sr(OH)_2 \cdot 8H_2O$ and $Ba(OH)_2 \cdot 8H_2O$ show a different thermal behaviour depending on the concentration.
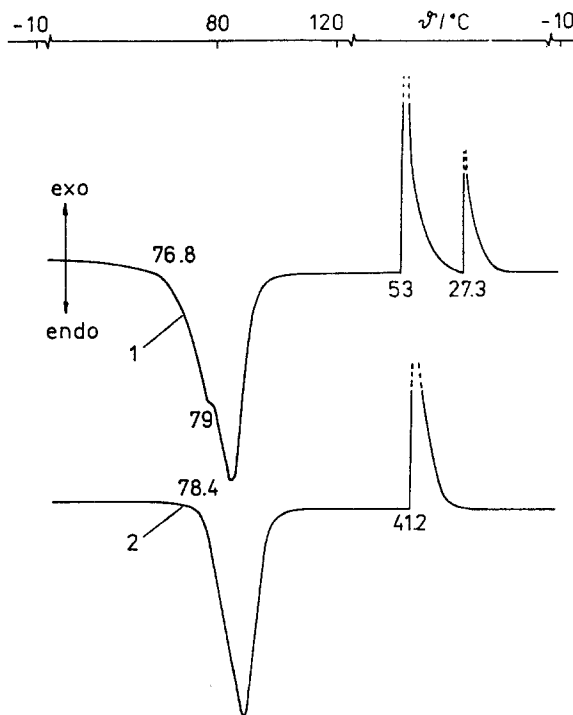
Fig. 2 DTA cycles of $Ba(OH)_2 \cdot 8H_2O$ – $Sr(OH)_2 \cdot 8H_2O$ mixtures; 1- $Ba(OH)_2 \cdot 8H_2O$ –
$Sr(OH)_2 \cdot 8H_2O$ (80/20 mol%); 2- $Ba(OH)_2 \cdot 8H_2O$ – $Sr(OH)_2 \cdot 8H_2O$ (20/80 mol%)

In the region rich in $Ba(OH)_2 \cdot 8H_2O$ up to about 50 mol% two overlapping melting effects are always observed (Fig. 2, curve 1). Compared with the pure salt hydrates, the melting temperatures of the mixtures are lowered (Fig. 3). Solidification also proceeds in multiple stages. The two single components are found in the X-ray pattern of the solid phase. In contrast to this, in the region rich in $Sr(OH)_2 \cdot 8H_2O$ the interferences of this compound can exclusively be found [12]. The thermal behaviour shown in Fig. 2, curve 2, also indicates the existence of a mixed crystal with the lattice of $Sr(OH)_2 \cdot 8H_2O$. In each case only a widened melting and solidification effect becomes apparent.

The range of the melting temperature and the specific melting enthalpy are of decisive importance to an estimation for the use as latent heat storage material in the course of a greater number of melting and solidification cycles.
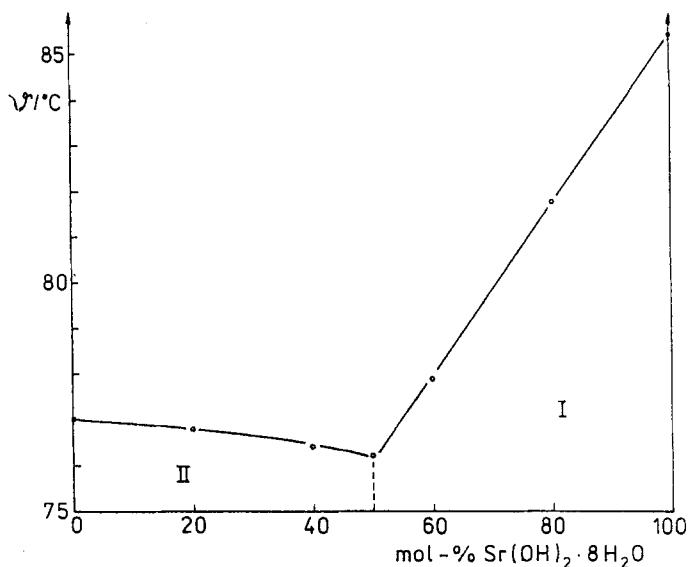
Fig. 3 Onset temperatures depend on the gross composition of $Ba(OH)_2 \cdot 8H_2O$ – $Sr(OH)_2 \cdot 8H_2O$ mixtures during first heating run; I- mixed crystal; II- separated compounds
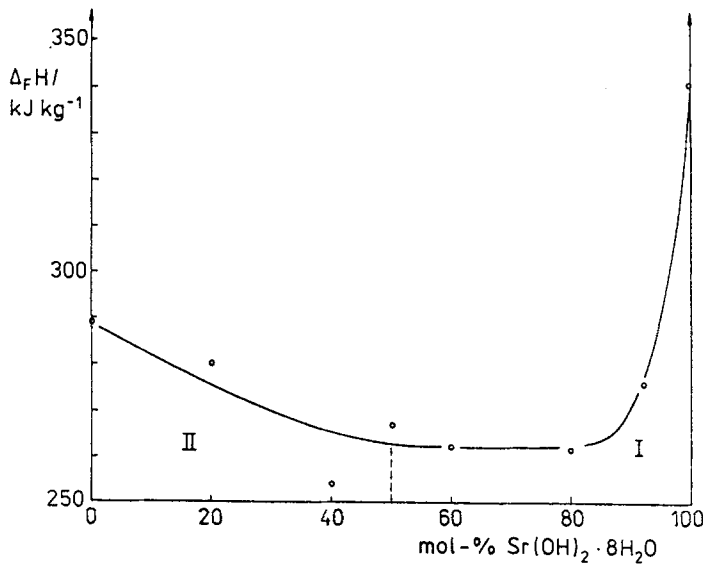
Fig. 4 Specific melting enthalpy of $Ba(OH)_2 \cdot 8H_2O$ – $Sr(OH)_2 \cdot 8H_2O$ mixtures (first heating run); I- mixed crystal; II- separated compounds

The equilibrium compositions of the mixtures have a lower melting enthalpy compared with the pure compounds (Fig. 4).

A particularly drastic drop can be observed in the region of the mixed crystal.

On cyclization with ±2 deg/min between 20° and 120°C the melting temperature is lowered to about 70°C. At the same time there is a further drop in the specific melting enthalpy to about 210 kJ/kg (Fig. 5).
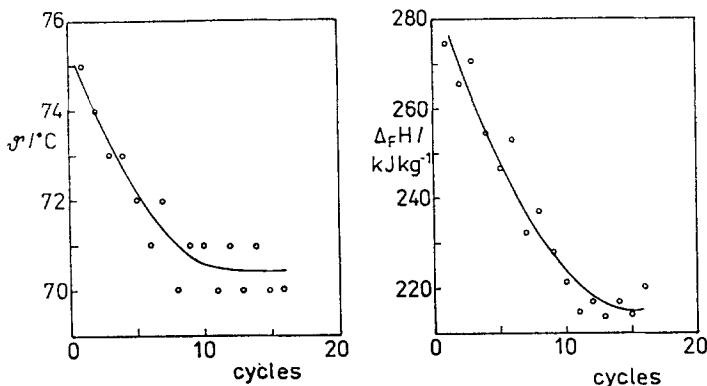

Fig. 5 Melting temperatures and enthalpies vs. number of cycles of the Ba(OH)$_2$·8H$_2$O – Sr(OH)$_2$·8H$_2$O mixture (80/20 mol%)

The use of mixtures of Sr(OH)$_2$·8H$_2$O and Ba(OH)$_2$·8H$_2$O in latent heat storage units decisively depends on the conditions of application. For the use in motorcars the found melting temperature of about 70°C is in accordance with the set target. The kinetics of rehydration to Sr(OH)$_2$·8H$_2$O determines the potential heat transfer power and the storage density. In theory, with the density of 1900 kg/m^3 storage densities of 532 MJ/m^3 are obtained for the mixture of Sr(OH)$_2$·8H$_2$O and Ba(OH)$_2$·8H$_2$O (20/80). Storage densities of 655 MJ/m^3 are found for pure Sr(OH)$_2$·8H$_2$O.

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Zusammenfassung — Entsprechend ihrer hohen spezifischen Schmelzenthalpie und dem Bereich der Schmelztemperaturen sind die Hydrate der Alkalierdmetallhydroxide $Ba(OH)_2 \cdot 8H_2O$ und $Sr(OH)_2 \cdot 8H_2O$ potentielle Umwandlungswärme-Speichersubstanzen.

Die mittels DTA- und DSC-Methoden durchgeführten Untersuchungen des Schmelz- und Erstarrungsverhaltens von $Sr(OH)_2 \cdot 8H_2O$ und seinen Gemischen mit $Ba(OH)_2 \cdot 8H_2O$ in einem geschlossenen System und mit einer konstanten Makrozusammensetzung führen zu Feststellungen über die Schmelztemperatur und die spezifische Schmelzwärme in Abhängigkeit von der Konzentration. Eine theoretische Speicherdichte von 532 MJ/m^3 konnte für das Gemische aus 80% $Ba(OH)_2 \cdot 8H_2O$ und 20% $Sr(OH)_2 \cdot 8H_2O$ und ein Wert von 655 MJ/m^3 für $Sr(OH)_2 \cdot 8H_2O$ ermittelt werden. Die Kinetik der Rehydratation zu den Oktahydraten besitzt einen großen Einfluß auf die Speichertemperatur und die Speicherdichte.