THERMAL ENERGY STORAGE MATERIALS — A DSC STUDY *

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ABSTRACT

A DSC investigation of a thermal energy storage, first-order phase change system has been carried out. The material is a borax—common salt modified sodium sulfate decahydrate system, distributed throughout a fumed silica supporting matrix. The qualitative features of the thermal behavior of the material can be explained in terms of the phase diagram of the sodium sulfate—water peritectic system, modified by the presence of a low-temperature eutectic. Fusion and recrystallization enthalpies have been measured as a function of cycle number. The thermal conversion efficiency of the system is high. Combining these data with specific heat measurements, the calculated storage capacity is in good agreement with published engineering information.

INTRODUCTION

Thermal energy storage is assuming an ever-increasing role in the energy debate as an efficient potential means of utilizing solar energy. TES materials are chosen on the basis of their ability to accumulate heat, which task they accomplish by two means. Firstly, by means of a temperature increase, and secondly, by undergoing a first-order phase change, namely fusion. On cooling, the reversible heat is released. In order to assess the storage capability and thermal efficiency of a potential material cycled through a temperature interval encompassing the phase transition, the specific heat—temperature functions of the two phases, as well as the fusion and recrystallization enthalpies, should be known.

A number of searches have been made for possible TES materials. Lane et al. [1] have presented their literature survey and DTA evaluation of potential candidates. Lammers [2] has discussed the physico-chemical and heat transfer aspects of the operation of these material systems. Potential phase change candidate materials should be cheap, chemically inert, have a large specific heat and enthalpy of fusion, and should melt congruently at a temperature not too far removed from ambient.

Inorganic salt hydrates have long been considered potential materials. A

number of studies have been made regarding the thermochemistry of this class of materials [3—5,7]. Belton and Ajami [3] have discussed single hydrates, while Kauffman and Gruntfest [4] list possible binary and ternary eutectics. Sodium sulfate decahydrate was first studied by Telkès [6]. Unfortunately, it melts incongruently [3,7] at 305.6 K (32.4°C), producing anhydrous sodium sulfate and a saturated aqueous solution of this salt. The denser solid sinks, resulting in stratification. The saturated solution exhibits excessive supercooling. Recently, Biswas [8] has shown that the amount of anhydrous salt produced on melting the solid stratified system increases on continual thermal cycling. These occurrences result in performance degradation on repeated cycling, and a reduction in thermal capacity. He suggested that these problems may be obviated by selecting as TES material a composition slightly to the water-rich side of the invariant point in the sodium sulfate—water phase diagram. Earlier, Telkès [6] had shown that the problems could be minimized by adding to the system a small amount, nominally 3%, of borax, which acts as a nucleating agent for the recrystallization of the saturated solution of sodium sulfate. The same amount of finely divided silica is often included in the mix. This matrix further aids and stabilizes the solidification of the melt. In order to lower the effective melting range of the system, a small quantity of one or more alkali metal and ammonium halides are often added. Such a mixture, containing 8% sodium chloride, is commercially available [9] (Cabot Corporation, Boston, Mass.), and has been used in two independent long-term engineering studies [9,10].

Since DSC is an ideal tool for the study of the operational behavior of such TES materials, a thermoanalytical investigation of this commerical, so-called "chemical core", material has been carried out. The main purpose of this study was to demonstrate the efficacy of the DSC technique, and to compare resulting thermal capacity information with that obtained from large-scale engineering data.

EXPERIMENTAL

All measurements were made with the Mettler TA2000B heat flow DSC system. Specific heat, enthalpy and temperature information were obtained from data monitored and analyzed in the following manner. Using the Mettler CT data transfer system, amplified DSC analog data were digitized and recorded on tape at selected intervals for off-line computer analysis, using appropriate FORTRAN programs. For very slow heating and cooling rate experiments over relatively large temperature intervals, the data was digitized and transferred, using the Mettler TA2000Z system, to a Hewlett—Packard 9815A programmable calculator for on-line analysis [11].

Using the individual system components, five TES material mixes were prepared by direct weighing; solids first, water last. The container was immediately closed, held at ca. 34°C for 30 min, and then the mix was allowed to cool with occasional stirring. In this manner, homogeneous mixes were obtained, as evidenced by the reproducible, characteristic DSC behavior on thermal cycling. The TES "chemical core" material comprises 38% sodium

sulfate (8.56 mole%), 48% water (85.2 mole%), 3% borax (0.25 mole%), 8% sodium chloride (4.38 mole%) and 3% fumed silica (1.6 mole%). The other mixes prepared were the chemical core without borax, the chemical core without sodium chloride, the chemical core without both borax and sodium chloride, and sodium sulfate decahydrate alone. In all mixes, the relative proportions of the components were as in the chemical core. All DSC experimental samples were enclosed in hermetically sealed, disposable, aluminum crucibles. No weight losses were encountered following any thermal experiment. In recording analog heat flow data, exotherms and endotherms are characterized by excursions above and below the dynamic baseline, respectively. All temperature marks, superimposed on the DSC curves, indicate the programmed furnace temperature in °C. A sample mass of ca. 26 mg was chosen for the majority of the work. This quantity was selected for two reasons. Firstly, it is difficult to weigh less than this amount of the chemical core rapidly at room temperature, due to its deliquescent state. Secondly, 26 mg is about the maximum quantity of sodium sulfate decahydrate crystals which can be contained in the 40 μl hermetically sealed crucibles.

RESULTS AND DISCUSSION

Figure 1A shows the DSC data characterizing the behavior of initially melted sodium sulfate decahydrate, cycled at ±1°C min^{-1} from 40°C through −50°C through 50°C. The saturated aqueous solution of sodium sulfate supercools to ca. 7°C before reycrystallizing. Figure 1C shows the characteristic water—ice crystallization exotherm, and ice—water fusion endotherm in the same crucible environment. There is noticeable supercooling (12—15°C) prior to nucleation. The sharp 0°C endotherm is indicative of the high purity of the conductivity water used. A dynamic analysis of four such melt endotherms yielded >99.98 mole% purity with ΔH_f = 5.936 (σ = 0.058) kJ mole^{-1}, which is in excellent agreement with the accepted value of 6.007 kJ mole^{-1} [12]. In the case of the sodium sulfate—water system, a small amount of free water remains on cooling, due to the slow peritectic solidification of the saturated aqueous solution. This is evidenced by the extremely small exotherm at ca. −17°C, and the 0°C endotherm seen in Fig. 1A. On cycling, the sodium sulfate decahydrate exotherm and endotherm diminish, and the water exotherm and endotherm increase in size until, after about five cycles, the characteristic reproducible behavior, shown in Fig. 1B, is obtained. This behavior is in agreement with that expected on the basis of the compositional changes in this stratified system, discussed by Telkès [6] and Biswas [8]. Nine dynamic heating experiments were performed on freshly prepared sodium sulfate decahydrate samples, covering the range 5—27 mg, in order to attempt to measure the enthalpy and temperature of fusion. Since the process is actually a peritectic decomposition, the results, although reasonably consistent, differ from quoted values, i.e. 71.1 (σ = 2.2) kJ mole^{-1} at 34.4°C compared with 80.9 kJ mole^{-1} at 32.4°C [8].

First cycle DSC curves at ±1°C min^{-1} are shown in Fig. 2, characterizing
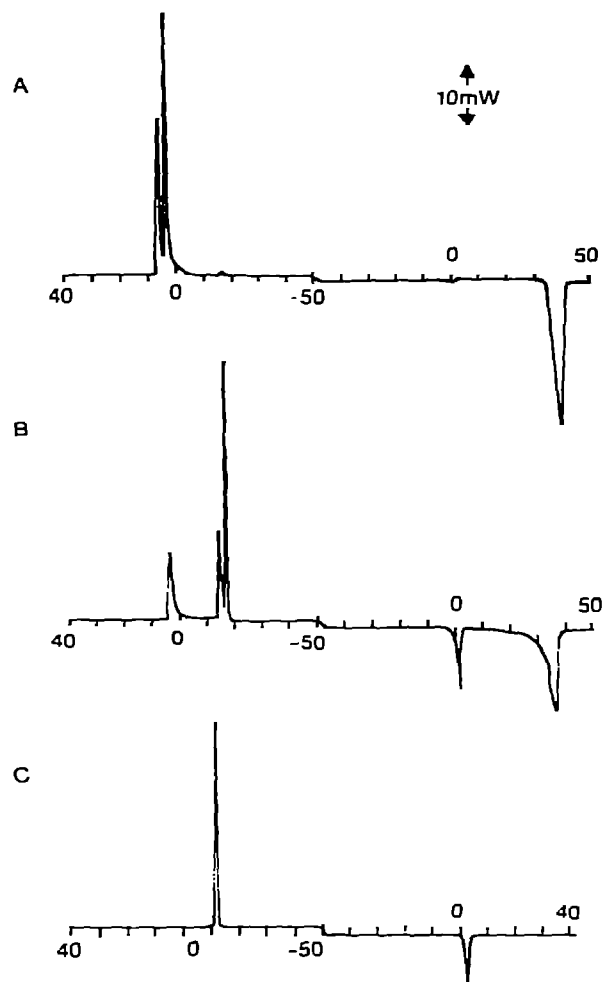
Fig. 1. A, cycle 1, B, cycle 5, sodium sulfate decahydrate, 26.5 mg; C, water, 2.791 mg. Scan rate: ±1°C min⁻¹.

the thermal behavior of the chemical core (A) compared with first cycle data for sodium sulfate decahydrate (B) and water (C). As can be seen, there is a marked reduction in the extent to which the TES material supercools, there is no free water, but a characteristic low-temperature eutectic exists; this also exhibits marked supercooling (ca. 7—10°C) prior to freezing and melts at ca. —20°C. The presence of the eutectic noticeably lowers the melting range of the sodium sulfate decahydrate. Figure 3 shows that the eutectic results only from the presence of sodium chloride in the TES material. This is the sixth cycle data of comparable quantities of the chemical core with (A) and without (B) common salt, when thermally cycled at 1°C min⁻¹ from 50 to —50°C. The "free water" and eutectic crystallization and fusion processes are clearly seen. The necessity for the addition of a nucleating agent is effectively demonstrated in Fig. 4, where the sixth cycle data for the chemical core without sodium chloride (A) and borax (B) are compared. The sodium chloride in no way assists in the reproducible solidification of the sodium
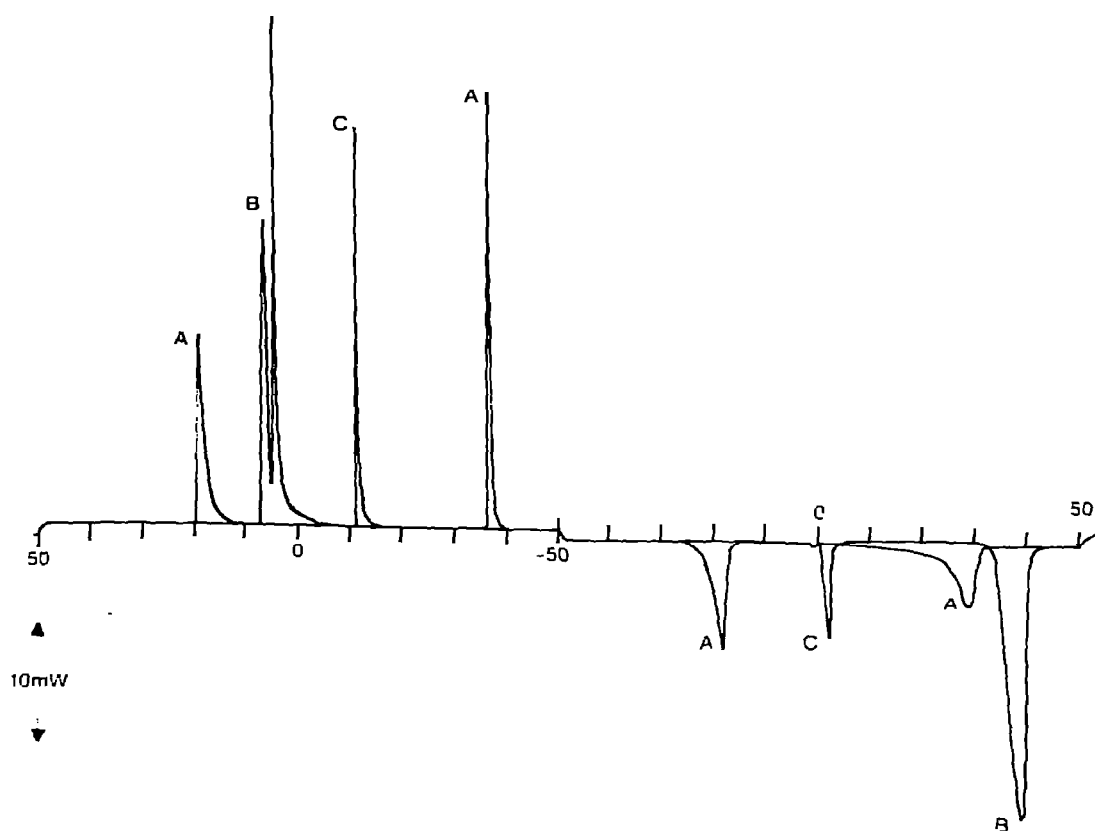
Fig. 2. A, chemical core, 25.4 mg; B, sodium sulfate decahydrate, 26.62 mg; C, water, 2.791 mg. Cycle 1, scan rate: $\pm 1°C$ min^{-1}.

sulfate decahydrate. The relatively large breadth of the two low intensity B exotherms is indicative of the slow peritectic solidification. The fact that two separate exotherms are observed in this temperature region supports the view of Telkès regarding the build-up of stratified layers on cycling in the absence of a nucleating agent.

Since the temperature region in which the TES material is employed in practice is that encompassing the crystallization and fusion processes of the modified sodium sulfate—water system, long-term cycling experiments were performed only in this range. The measured heats of fusion and recrystallization decrease gradually on cycling, reaching a steady value after about the 12th cycle. Figure 5 shows the characteristic DSC data for cycle 12 of 26.93 mg of the chemical core at $\pm 1°C$ min^{-1}. In the first cycle, the measured enthalpy and temperature of fusion were 83.1 J g^{-1} and 28.6°C, respectively. The thermal efficiency, $\Delta H_{recryst}/\Delta H_f$, is 96.4%. At cycle 12, ΔH_f = 77.2 J g^{-1} at T_f = 28.4°C, with a 95.5% efficiency. For cycles 13 and 14, ΔH_f = 73.6 J g^{-1} at T_f = 28.7°C, with the same thermal efficiency (95.7%). Figure 6 shows similar data obtained at a much slower scanning rate. This is the 11th cycle data for 26.50 mg of the chemical core cycled at 0.1°C min^{-1} from 40 to 15°C. The material crystallizes at 22.5°C, the same temperature found at the 1°C min^{-1} scanning rate. Comparable heats of recrystallization
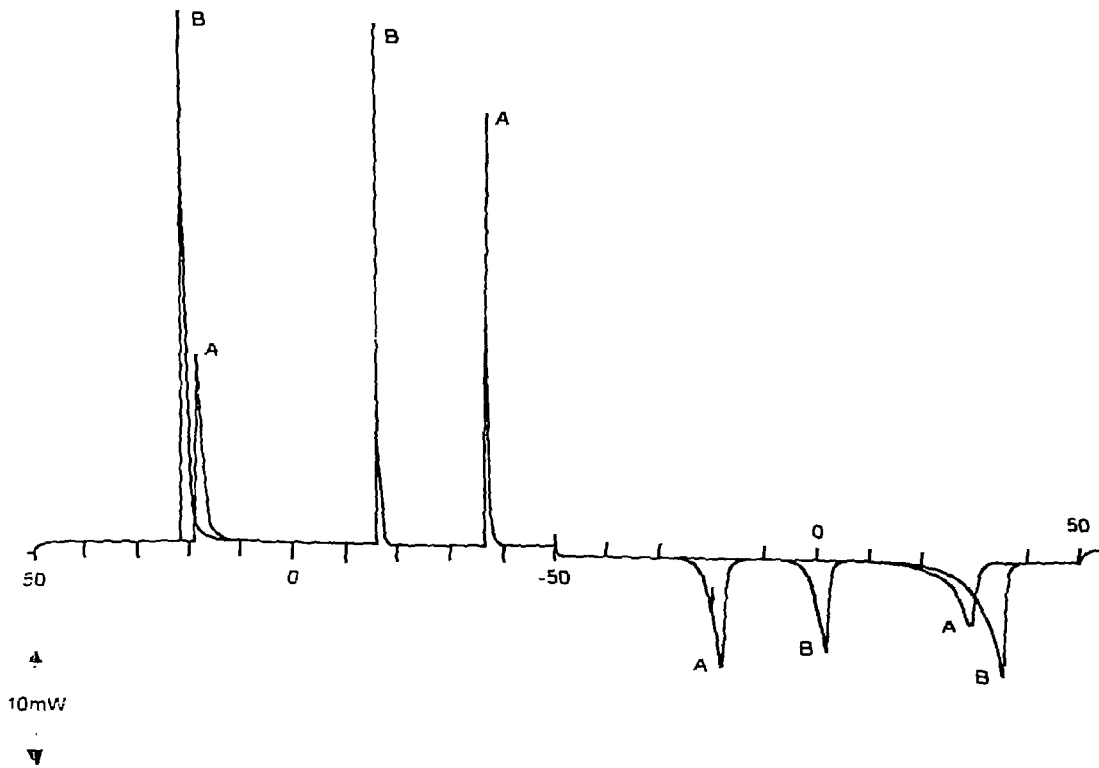
Fig. 3. A, chemical core, 25.4 mg; B, chemical core without sodium chloride, 26.7 mg. Cycle 6, scan rate: ±1°C min⁻¹.
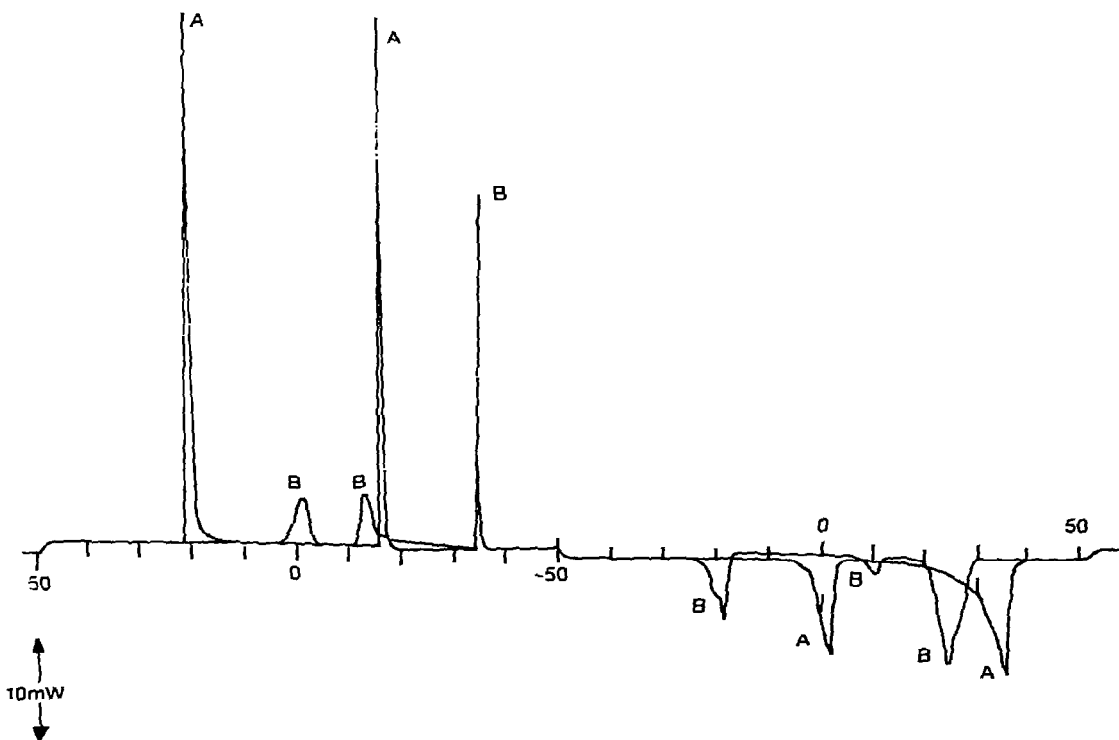

Fig. 4. A, chemical core without sodium chloride, 26.7 mg; B, chemical core without borax, 26.92 mg. Cycle 6, scan rate: ±1°C min⁻¹.

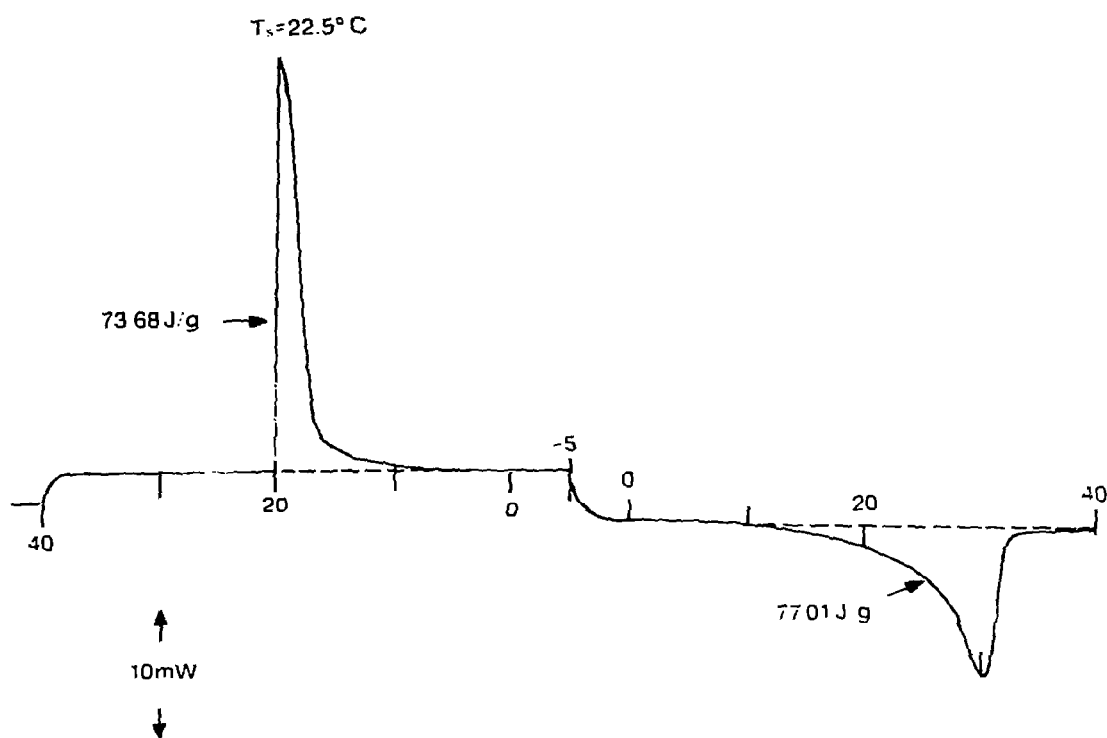Fig. 5. Chemical core, 26.93 mg. Cycle 12, scan rate: ±1°C min⁻¹.

and fusion were obtained with a thermal efficiency of 96.9%. One pertinent experimental fact should be noted: even though, as indicated in Fig. 6, the melt process appears to be complete at a programmed furnace temperature of 29°C, the subsequent sharp recrystallization exotherm is not produced unless the sample had been previously heated to at least ca. 33°C at the slow rate of 0.1°C min⁻¹. The reason for this occurrence would appear to be asso-

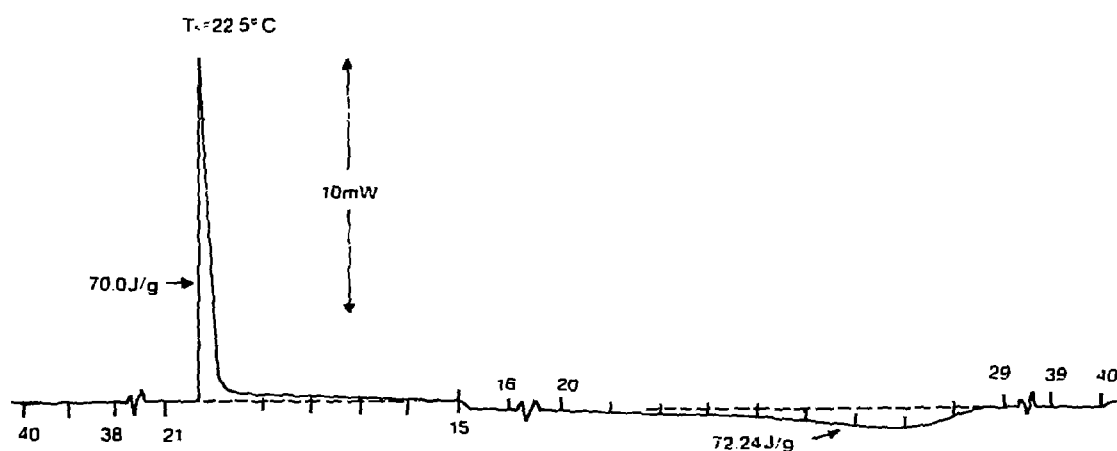
Fig. 6. Chemical core, 26.5 mg. Cycle 11, scan rate: ±0.1°C min⁻¹.

ciated in some way with the incongruency of the sodium sulfate decahydrate fusion. Since the $1°C$ min^{-1} scan rate DSC data yielded enthalpic and sample temperature information as precise and accurate as that obtained at $0.1°C$ min^{-1} (see above, the measured ice fusion enthalpy), it was considered un-necessary to perform any further work at the lower scan rate.

When using DSC as a tool for specific heat measurements, thermal scans are best carried out at high rates. It is important, therefore, to determine the maximum optimal scanning rate for this TES material system. In Fig. 7 is shown the DSC data for the chemical core cycled from 50 to $-60°C$ at a scanning rate of $5°C$ min^{-1}. The cooling leg exotherms are clearly separate. As can be seen, however, on heating the solidified material, the two melt endotherms are not sufficiently separated for accurate specific heat calcula-tions. These are based upon differential DSC measurements in temperature regions in which there is no contribution from first-order transitions. The values are calculated by measuring the DSC signal differential between the isothermal and dynamic baselines, as has been described previously [13]. Measurements were made using 54.4 mg of the chemical core. Since it is not possible to separate the contributions of the sample and the container in which it is hermetically sealed, dual measurements have to be made on it and on a weight-matched, empty, sealed crucible. In this case, the crucibles were matched to within 7 μg. Digital data were recorded at $0.5°C$ intervals while cooling from 50 to $-100°C$ at $5°C$ min^{-1}. Table 1 summarizes the specific heat—sample temperature relationships resulting from four sets of such dual
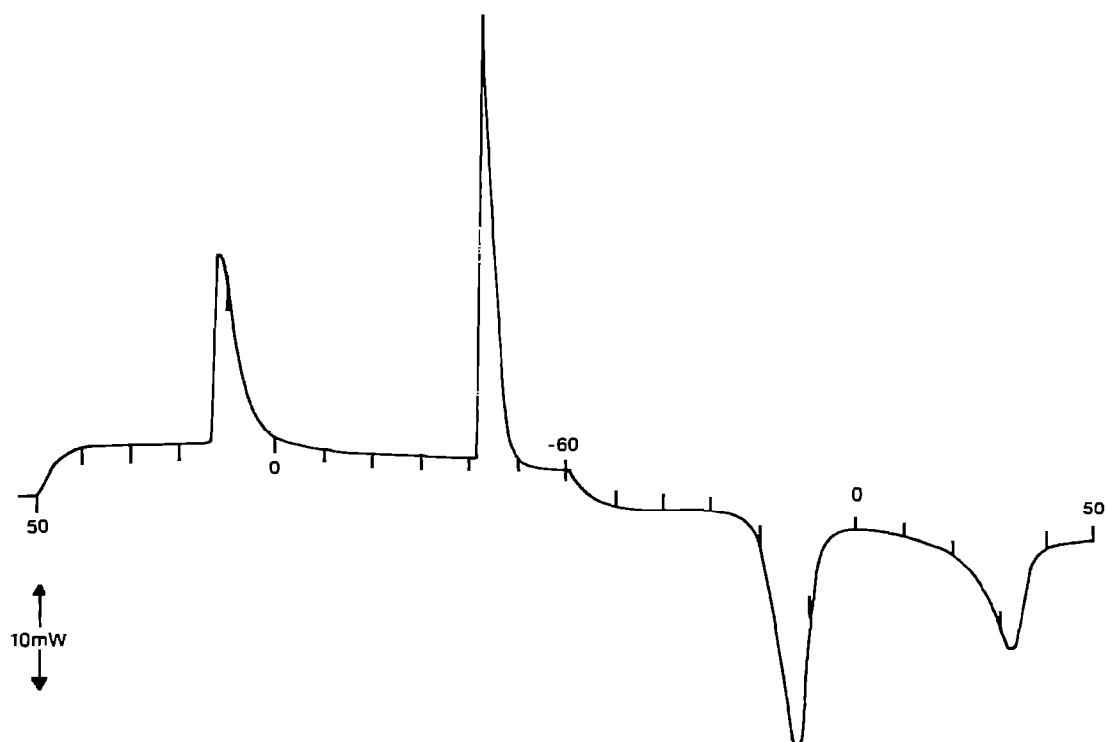

Fig. 7. Chemical core, 21.96 mg. Cycle 3, scan rate: $\pm5°C$ min^{-1}.

TABLE 1

Specific heat—temperature relationship (chemical core TES material)

Temp. (K)	Specific heat (C_p) (J g^{-1} K^{-1})	
	Mean	σ
201.4	1.241	0.029
208.9	1.248	0.029
211.4	1.259	0.029
213.9	1.273	0.028
216.4	1.292	0.030
244.5	2.120	0.033
247.0	2.135	0.032
249.5	2.151	0.034
252.0	2.170	0.034
254.6	2.202	0.035
292.3	2.703	0.033
294.8	2.683	0.032
297.3	2.674	0.031
299.7	2.659	0.033
302.2	2.646	0.033
304.7	2.623	0.033

measurements. These values conform to the following linear relationships with better than 97% correlation

$$T < 220 \text{ K} \qquad C_p = 0.189 + 5.08 \times 10^{-3}T \qquad (1a)$$

$$245 \text{ K} < T < 255 \text{ K} \qquad C_p = 0.183 + 7.91 \times 10^{-3}T \qquad (1b)$$

$$T > 292 \text{ K} \qquad C_p = 4.478 - 6.07 \times 10^{-3}T \qquad (1c)$$

Equation (1a) applies to the completely solid material below the eutectic recrystallization point, and will not be used in practical calculations of storage capacity. Equation (1c) applies to the completely molten material, which remains in this state down to the recrystallization point, T_r, namely 22.5°C. Because of supercooling, the TES material can be cooled below the recrystallization point to 19°C (292 K), but can solidify at any time when in this quasi-stable state.

The storage capacity, namely, the quantity of heat released per unit mass of TES material, when cooled from an upper temperature, T_2, to a lower limit, T_1, through the recrystallization point, T_r, is given by

$$Q = \int_{T_1}^{T_r} C_p(\text{solid}) \, dT + \Delta H_r + \int_{T_r}^{T_2} C_p(\text{liquid}) \, dT \qquad (2)$$

Below the recrystallization point, the solid chemical core contains liquid eutectic, and eqn. (1b) applies. Combining eqns. (1b) and (1c) with (2) one has

$$Q = \Delta H_r + [4.478T_2 - 3.04 \times 10^{-3}T_2^2 - 0.183T_1 - 3.96 \times 10^{-3}T_1^2 - 658.9] \qquad (3)$$

If the temperature limits, T_1 and T_2, are set at the values quoted in the engineering study [9], namely 65 and 73°F (291.5 K and 296 K), then using the DSC measured limiting value of $\Delta H_r = 70.7$ J g^{-1}, the heat released, $Q = 82$ J g^{-1}. This is in reasonable agreement with the quoted value, 85.2 J g^{-1} [9]. The actual heat flow into the chemical core as a function of its true temperature is shown in Fig. 8, in comparison with data for water and sodium sulfate decahydrate. The liquid fraction—sample temperature relations, listed in Table 2, were obtained from this dynamic scan data. Thus, in order to store the maximum possible heat in the chemical core, it should be raised to an upper limit, T_2, of 301.6 K (83°F). In this case, 93.7 J g^{-1} would be released on cooling to 291.5 K. It appears that in the large-scale thermal cycling study, the heat was accepted in an operating temperature range slightly lower than that predicted from dynamic scan DSC experiments. During the course of this investigation, a number of measurements of the fusion enthalpy of the chemical core were made by the isothermal step method [14]. From five such measurements, a mean value of the fusion enthalpy, $\Delta H_f = 69.5$ J g^{-1} was obtained. As can be seen from Table 2, the melting range under these equilibrium conditions is lower than that obtained under dynamic scan conditions. Although cycle times were not specified in the engineering study [9], it is probable that the data were obtained under conditions more nearly approaching equilibrium.

In conclusion, the DSC technique has proved very useful in the study of the qualitative and quantitative aspects of the operational behavior of a commercial TES system. The speed and simplicity of the method enabled a
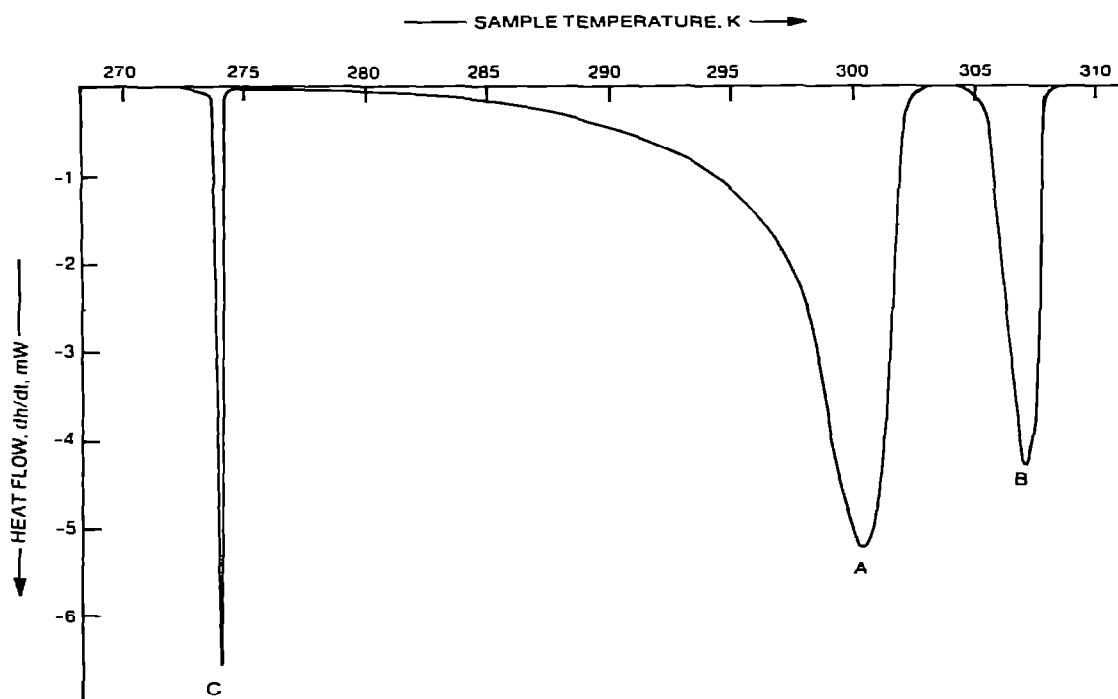

Fig. 8. Heat flow as a function of sample temperature A, for chemical core; B, sodium sulfate decahydrate; C, water.

TABLE 2

Liquid fraction—temperature functions (chemical core TES material)

Method	Temp. (K)	Liquid fraction (%)
Dynamic scan	290.7	21.5
	296.8	39.0
	298.6	51.2
	301.6	100.0
Isothermal step	290.7	18.4
	295.2	38.7
	296.2	47.0
	297.2	62.0
	298.2	78.4
	299.2	96.0

large amount of thermal data to be acquired in a short period of time. The enthalpic, temperature and conversion efficiency information is in excellent agreement with that resulting from a large-scale engineering study.

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