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INVESTIGATION OF LATENT HEAT THERMAL ENERGY STORAGE MATERIALS
V. THERMOANALYTICAL EVALUATION OF BINARY EUTECTIC MIXTURES AND COMPOUNDS OF NaOH WITH $NaNO_3$ OR $NaNO_2$ *

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ABSTRACT

Differential scanning calorimetry was applied to the evaluation of binary eutectic mixtures and compounds of NaOH with $NaNO_3$ or $NaNO_2$ as latent heat thermal energy storage materials. There are two compounds and three eutectic mixtures consisting of NaOH and $NaNO_3$ and one compound and two eutectic mixtures consisting of NaOH and $NaNO_2$. The heats of fusion of all compounds and mixtures were more than 200 J g^{-1}. The thermal behaviour of these materials was observed, and some compounds and mixtures show a great tendency to supercool. The specific heat capacity was also measured. Because the eutectic mixture 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH is the most promising material for use in a nuclear power plant, this mixture made from industrial products was examined further. After 1000 cycles of melting and crystallization in bench-scale equipment the material shows little change.

INTRODUCTION

In a previous series of papers [1–4], screening and thermoanalytical evaluations of latent heat thermal energy storage materials, whose operating temperatures cover a range from 130 to 230 °C, were reported. Prototype and bench-scale equipments using the materials thus selected were made and tested, and excellent performance characteristics of latent heat thermal energy storage were demonstrated and described in our previous papers [5–9]; the unique characteristics are large energy density, high thermal efficiency and heat release at a constant temperature.

In this paper we report the thermoanalytical evaluation of compounds and eutectic mixtures of NaOH with $NaNO_2$ or $NaNO_3$; these are only

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candidate materials chosen in the temperature range 230–300 °C by our previous comprehensive screening from viewpoints of energy density and economy [10,11]. Because of this melting temperature range, these materials are very suitable for the application of thermal energy storage in a nuclear power plant. In this scheme, the thermal output from a nuclear reactor is introduced into the storage unit at night when the electricity consumption decreases remarkably. In daytime, when the electricity consumption increases drastically, the heat released from the storage unit is used for electricity generation. The latent heat thermal energy storage is very suitable for this purpose because of its large energy storage density even for such a small temperature swing or a small difference in the temperature between output and input.

EXPERIMENTAL

Apparatus

The apparatus, sample container and method of differential scanning calorimetry (DSC) for measurements of the latent heat and the heat capacity are the same as those described in our previous papers [4,12].

Materials

The chemical reagents NaOH, $NaNO_2$ and $NaNO_3$ of guaranteed grade purchased from Showa Chemicals Co. Ltd. were used without further purification. Because industrial products are supposed to be used in a practical thermal energy storage unit, NaOH obtained as an industrial product from the mercury electrode process, asbestos separator process and ion exchange membrane process, all supplied by Nippon Soda Co., were also examined, and their compositions are shown in Table 1. Industrially produced $NaNO_3$ (99% purity), purchased from Mitsubishi Chemical Industries, was also used.

TABLE 1

Composition of NaOH from various sources

Source	NaOH (wt.%)	Na_2CO_3 (wt.%)	NaCl (wt.%)
Mercury electrode process	99.33	0.49	0.03
Asbestos separator process	97.08	0.66	1.76
Ion exchange membrane process	99.6	0.17	0.06

RESULTS AND DISCUSSION

The NaOH and $NaNO_3$ system

As shown in a reported phase diagram of the system [13,14], there are two compounds, $NaNO_3 \cdot NaOH$ and $NaNO_3 \cdot 2NaOH$. Therefore, three eutectic mixtures also exist in the system, and their compositions are reported to be 72 mol.% $NaNO_3$–28 mol.% NaOH, 41 mol.% $NaNO_3$–59 mol.% NaOH and 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH respectively. To observe their thermal behaviour, DSC was applied to these materials and heating and cooling DSC curves were obtained. Typical examples are reproduced in Figs. 1 and 2. As seen in these figures, the compound shows a relatively great supercooling tendency, while the difference between the melting temperature and the crystallization temperature of the mixture is not so large. Because the supercooling tendency is undesirable for thermal energy storage, the crystallization temperature is listed in Table 2 together with the melting temperature.

The reason for the shoulder on the DSC cooling curve of Fig. 1 is not clear, but it may be caused by the low thermal conductivity of the sample container which is made of polytetrafluoroethylene. It may also be caused by the tendency of the melt of the sample to form droplets on the bottom of the sample container owing to its low wettability. The extrapolated onset temperature of the shoulder is reported as the crystallization temperature in Table 2.

The heat capacity and heat of fusion are both very important characteristics of thermal energy storage materials. DSC was applied to the measure-

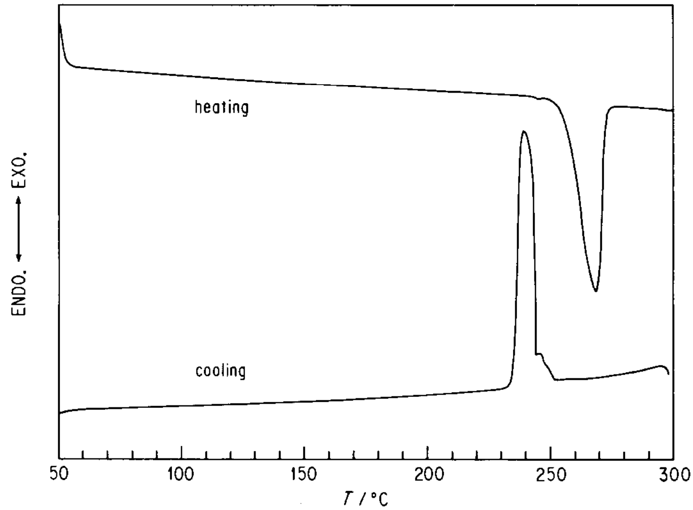

Fig. 1. DSC curves of 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH eutectic mixture.

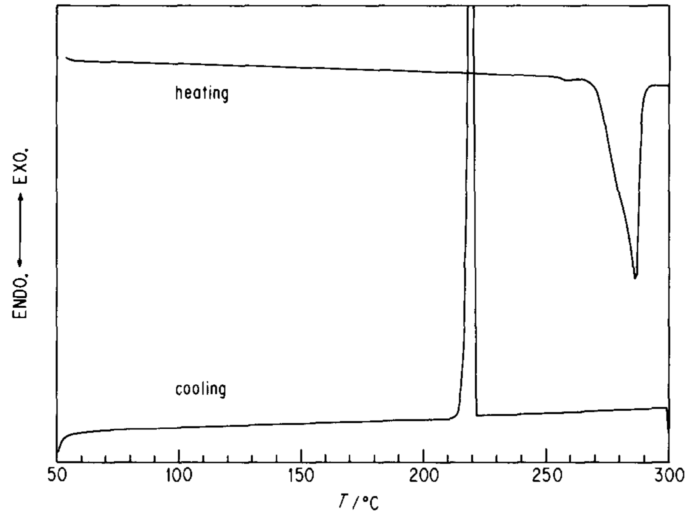

Fig. 2. DSC curves of $NaNO_3 \cdot 2NaOH$ compound.

ment of these thermophysical properties. The measured heats of fusion are listed in Table 2, and the measured heat capacities are shown in Figs. 3–7 and tabulated in Tables 3 and 4. In the tables, the heat capacities in the solid state are tabulated at 5 °C intervals, while average values are listed for the liquid state, because the temperature dependence in the liquid state is small.

As seen in Fig. 3 for the equimolar compound, a sharp little peak exists at 154 °C, and similar small peaks are also seen at the same temperature in Figs. 5 and 6. Therefore, this peak is assigned to a transition of the equimolar compound, although this is not apparent in the phase diagram [13,14]. The heat of transition is estimated to be 2.3 J g^{-1}. The peaks were clearly recognized because of the large magnification of the ordinate.

TABLE 2

Melting temperatures (T_m), crystallization temperatures (T_c) and heats of fusion (ΔH)

Composition (mol.%)	T_m (°C)	T_c (°C)	ΔH (J g^{-1})
$NaNO_3 \cdot NaOH$	271	213	265
$NaNO_3 \cdot 2NaOH$	270	218	295
72% $NaNO_3$–28% NaOH	247	213	237
41% $NaNO_3$–59%NaOH	266	221	278
18.5% $NaNO_3$–81.5% NaOH	257	254	292
$NaNO_2 \cdot NaOH$	265	228	313
80% $NaNO_2$–20% NaOH	232	232	252
27% $NaNO_2$–73% NaOH	237	227	294

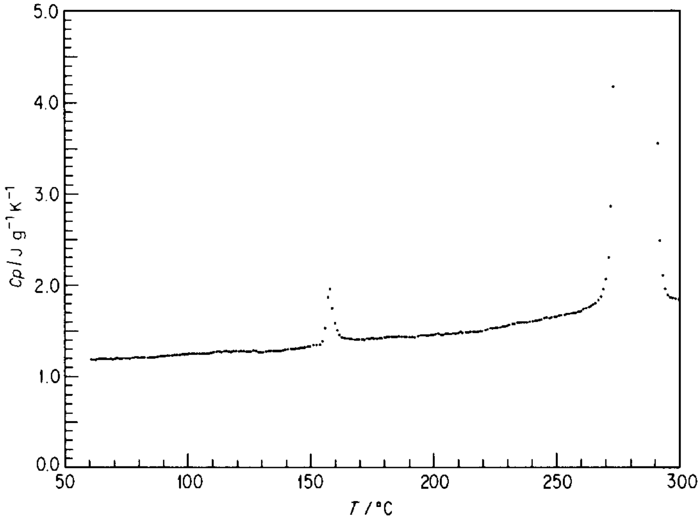

Fig. 3. Heat capacity of $NaNO_3 \cdot NaOH$ equimolar compound.

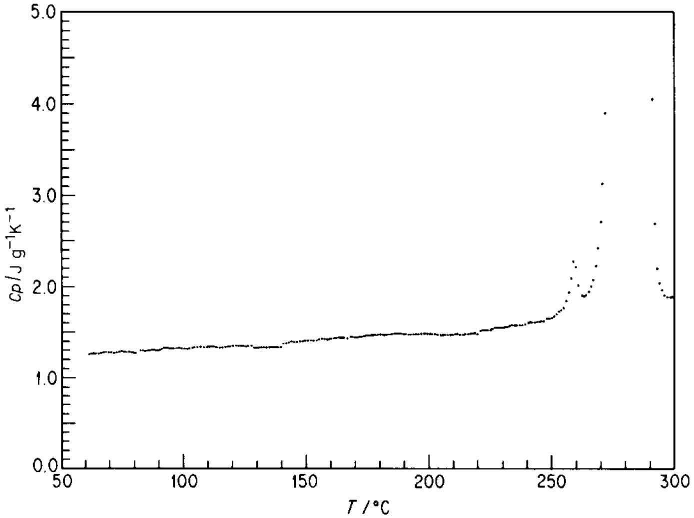

Fig. 4. Heat capacity of $NaNO_3 \cdot 2NaOH$ compound.

A small peak at about 255 °C in Fig. 4 seems to be caused by a small difference between the composition of the sample and that of the compound $NaNO_3 \cdot 2NaOH$.

The NaOH and $NaNO_2$ system

According to the phase diagram [13], one equimolar compound and two eutectic mixtures, i.e. 27 mol.% $NaNO_2$–73 mol.% NaOH and 80 mol.%

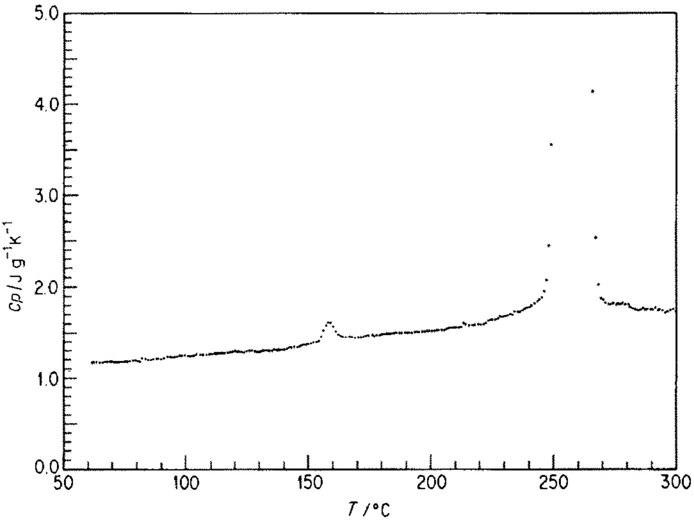

Fig. 5. Heat capacity of 72 mol.% $NaNO_3$–28 mol.% NaOH eutectic mixture.

$NaNO_2$–20 mol.% NaOH are formed in the system. In the same way as for the above system, the melting and crystallization temperatures are listed in Table 2 together with the heats of fusion, and their heat capacities, greatly magnified, are shown in Figs. 8–10. A small peak at about 160 °C seen in Fig. 9 can be assigned to a reported transition of $NaNO_2$ [13] and its peak temperature is 166 °C. A small peak in Fig. 8 was revealed by the large magnification and its temperature is in accordance with those of both the

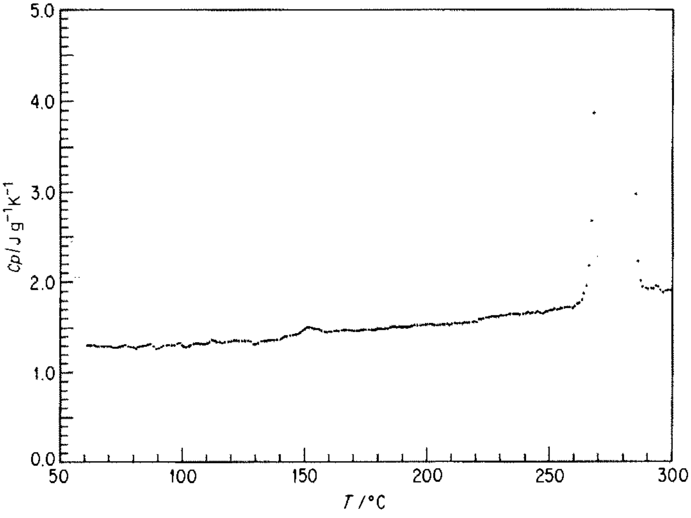

Fig. 6. Heat capacity of 41 mol.% $NaNO_3$–59 mol.% NaOH eutectic mixture.

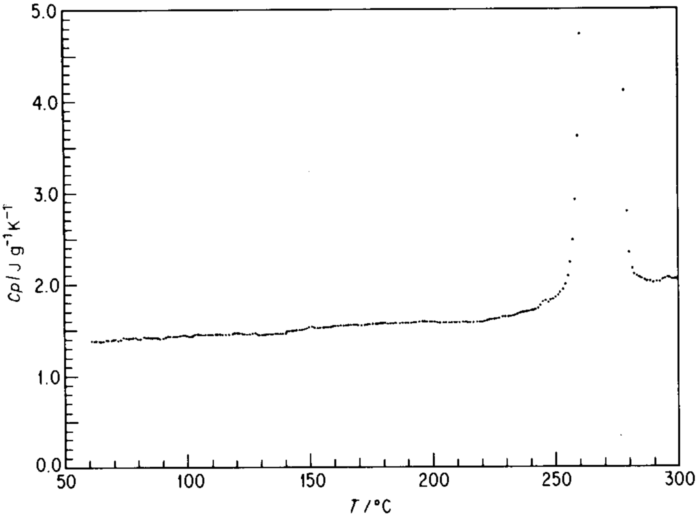

Fig. 7. Heat capacity of 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH eutectic mixture.

eutectic mixtures. Therefore, the peak is attributed to the fusion of either of the eutectic mixtures owing to the small difference between the sample composition and the equimolar composition.

The most promising materials and their practical application

From a comparison of the melting temperatures, heats of fusion and supercooling tendencies of the materials, we concluded that the most prom-

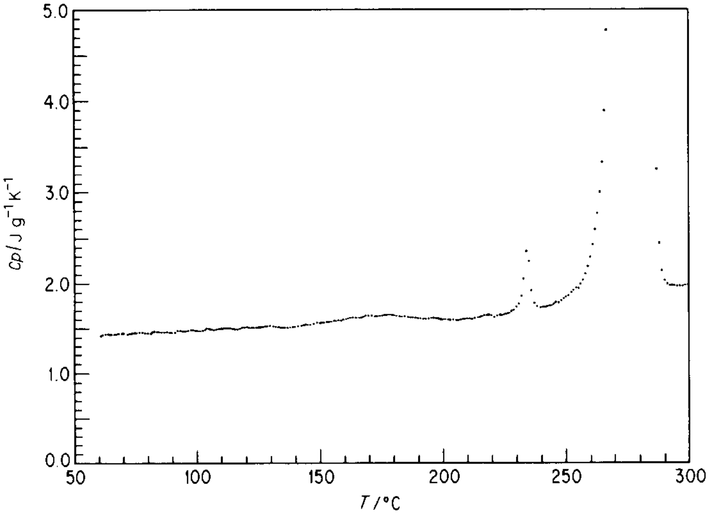

Fig. 8. Heat capacity of $NaNO_2 \cdot NaOH$ equimolar compound.

TABLE 3

Heat capacities in solid state

T (°C)	C_p (J g^{-1} K^{-1})							
	$NaNO_3$–NaOH			$NaNO_3$ ·NaOH	$NaNO_3$ ·2NaOH	$NaNO_2$–NaOH		$NaNO_2$ ·NaOH
	18.5–81.5	41–59	72–28			27–73	80–20	
60	1.39	1.27	1.15	1.18	1.26	1.45	1.34	1.41
65	1.40	1.28	1.16	1.19	1.27	1.46	1.34	1.42
70	1.40	1.28	1.17	1.20	1.28	1.47	1.35	1.43
75	1.40	1.28	1.19	1.20	1.28	1.48	1.36	1.44
80	1.40	1.29	1.20	1.21	1.29	1.48	1.37	1.45
85	1.41	1.29	1.21	1.22	1.30	1.49	1.38	1.46
90	1.41	1.30	1.22	1.23	1.30	1.50	1.40	1.47
95	1.42	1.31	1.23	1.23	1.31	1.51	1.42	1.47
100	1.42	1.31	1.24	1.24	1.32	1.51	1.44	1.48
105	1.43	1.32	1.25	1.25	1.33	1.52	1.47	1.49
110	1.43	1.33	1.26	1.26	1.33	1.53	1.49	1.50
115	1.44	1.34	1.27	1.26	1.34	1.54	1.52	1.51
120	1.45	1.35	1.28	1.27	1.35	1.54	1.55	1.51
125	1.46	1.36	1.29	1.28	1.36	1.55	1.58	1.52
130	1.46	1.37	1.30	1.29	1.36	1.56	1.61	1.53
135	1.47	1.38	1.31	1.29	1.37	1.56	1.64	1.54
140	1.48	1.39	1.32	1.30	1.38	1.57	1.68	1.54
145	1.49	1.40	1.33	1.31	1.39	1.58		1.55
150	1.50	1.41	1.33	1.32	1.40	1.58		1.56
155	1.51	Tr [a]	1.34	Tr	1.41	1.59	Tr	1.56
160	1.52	1.43	Tr		1.42	1.60		1.57
165	1.53	1.44	1.47	1.42	1.42	1.60		1.57
170	1.54	1.46	1.47	1.42	1.43	1.61		1.58
175	1.55	1.47	1.47	1.42	1.44	1.62		1.59
180	1.56	1.48	1.48	1.42	1.45	1.62	1.80	1.59
185	1.57	1.49	1.48	1.42	1.46	1.63	1.78	1.60
190	1.58	1.51	1.49	1.43	1.47	1.64	1.77	1.60
195	1.59	1.52	1.51	1.44	1.48	1.64	1.76	1.61
200	1.60	1.53	1.52	1.45	1.49	1.65	1.77	1.61
205	1.61	1.55	1.54	1.46	1.50	1.66	1.78	1.62
210	1.62	1.56	1.56	1.48	1.51	1.66	1.79	1.62
215	1.63	1.58	1.59	1.50	1.52	1.67	1.82	1.63
220	1.64	1.59	1.61	1.52	1.53	1.68	1.85	1.63
225	1.66	1.61	1.64	1.54	1.54		1.88	
230	1.67	1.62	1.67	1.56	1.55	M [b]	1.92	M
235	1.68	1.64		1.58	1.56			
240	1.69	1.65	M	1.61	1.57		M	
245	1.70	1.67		1.63				
250	1.72	1.68		1.66	M			
255		1.70		1.69				
260	M	1.71		1.72				

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[a] Tr, transition region. [b] M, melting region.

TABLE 4

Heat capacities (average) in liquid state

Composition (mol.%)	T (°C)	C_p (J g^{-1} K^{-1})
18.5% $NaNO_3$–81.5% NaOH	284–300	2.05
41% $NaNO_3$–59% NaOH	290–300	1.92
72% $NaNO_3$–28% NaOH	271–300	1.77
$NaNO_3 \cdot NaOH$	295–300	1.86
$NaNO_3 \cdot 2NaOH$	295–300	1.93
27% $NaNO_2$–73% NaOH	261–300	2.07
80% $NaNO_2$–20% NaOH	255–300	1.80
$NaNO_2 \cdot NaOH$	291–300	1.96

ising material for application in a nuclear power plant is the eutectic mixture 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH; its melting temperature is a little lower than the output temperature of a pressurized water reactor and a boiling water reactor, and the heat of fusion is fairly large; its small supercooling tendency was also taken into account. For the same reasons, the second most promising material is the eutectic mixture 27 mol.% $NaNO_2$–73 mol.% NaOH.

In the practical application of the above materials [15], industrial products will be used; for instance, about 60 kt of the material would be used for storage of about 4.2 GWh thermal energy which corresponds to 1.2 GWh storage capacity or to a rated output of 200 MW of electrical energy. In our

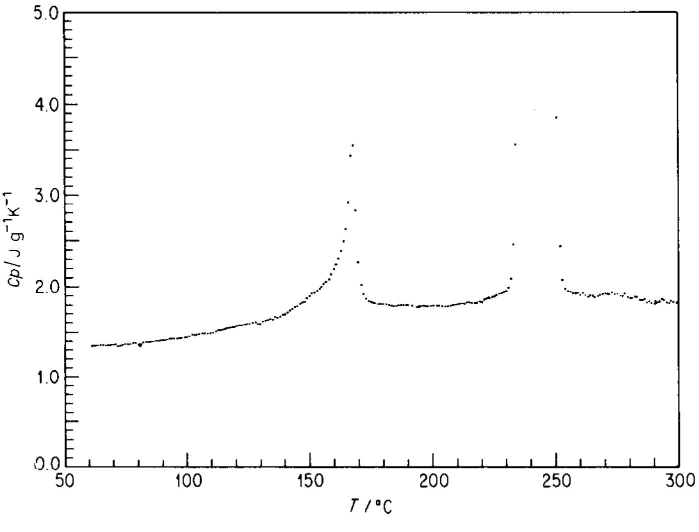

Fig. 9. Heat capacity of 80 mol.% $NaNO_2$–20 mol.% NaOH eutectic mixture.

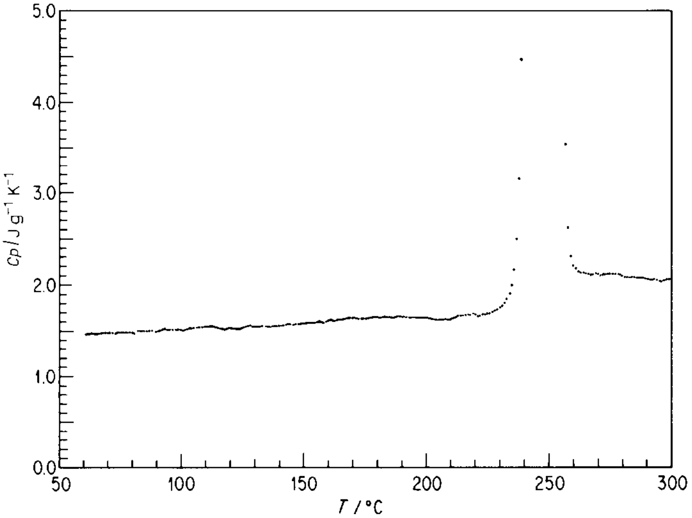

Fig. 10. Heat capacity of 27 mol.% $NaNO_2$–73 mol.% NaOH eutectic mixture.

country, production of NaOH by the mercury electrode process is prohibited because of its potential environmental pollution. NaOH is now produced by the asbestos separator process, while facilities for the ion exchange membrane process are beginning to be operated. As seen in Table 1, the industrially produced NaOH contains NaCl as an impurity and it may have some influence on the thermal characteristics of the storage material.

To observe the effect of this impurity, the following five samples were examined by DSC: A, 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH made from the reagents; B, 18.8 mol.% $NaNO_3$–80.0 mol.% NaOH–1.2 mol.% NaCl made from the reagents; C, 18.3 mol.% $NaNO_3$–78.1 mol.% NaOH–3.6 mol.% NaCl made from the reagents; D, 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH made from the industrial products of the asbestos separator process; E, 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH made from the industrial products of the ion exchange membrane process.

Samples D and E contain a few percent of NaCl and the composition of sample B is the same as that of sample D. The composition of sample C is the same as the composition of the ternary eutectic mixture of NaCl, $NaNO_3$ and NaOH reported by Kruglov and Basova [16]. We have also used the material made from the industrial products of the asbestos separator process in bench-scale equipment [15], and sample F was taken from the equipment before the test. After 1000 cycles of charging and discharging of the equipment (the time that the material was kept above its melting temperature is, on average, over 3000 h), sample G was taken from the centre of the equipment and sample G_b was taken from the bottom of the equipment. The composition of sample F is the same as that of samples D and B.

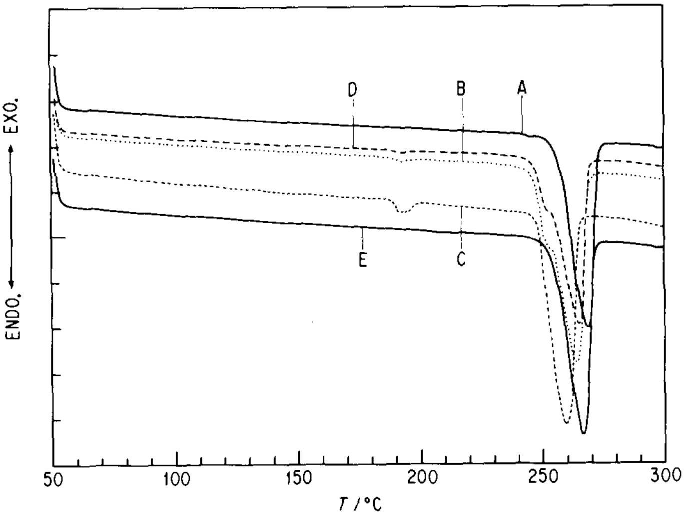

Fig. 11. DSC heating curves of 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH eutectic mixture from various sources.

DSC heating curves of these samples are reproduced in Figs. 11 and 12. For sample D, an additional peak is observed at about 190 °C and a shoulder is seen on the melting peak. The same curve was also obtained for sample B. For sample C, a distinct small peak is observed at 190 °C and a

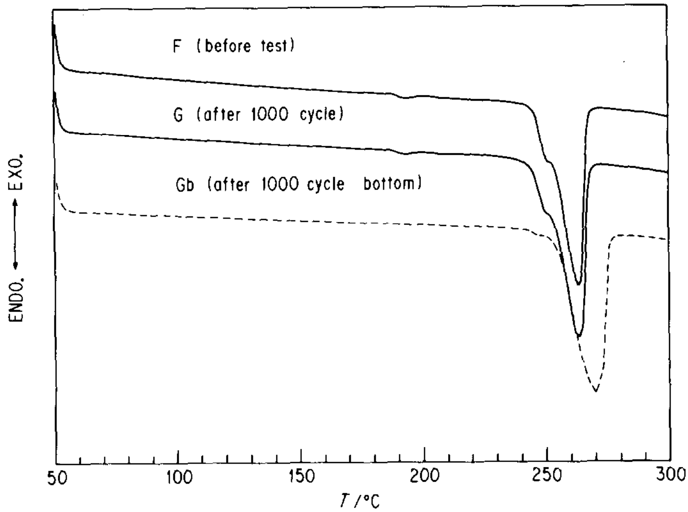

Fig. 12. DSC heating curves of 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH eutectic mixture before 1000 cycles of melting and crystallization in bench-scale thermal energy storage equipment.

TABLE 5

Melting temperature T_m (extrapolated onset temperature) and heat of fusion ΔH of the most promising material, 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH eutectic mixture, from various sources

Sample	T_m (°C)	ΔH ($J\ g^{-1}$)
A	257	292
B	247	271
C	248	253
D	245	276
E	253	282
F	Same as sample D	Same as sample D
G	243	270
G_b	254	278

single melting peak at 248 °C. By comparing these three curves, we conclude that the small peak at 190 °C and the shoulder are caused by the existence of the ternary eutectic mixture in samples B and D. As seen in Fig. 12, a similar DSC curve was also obtained for sample F, and the curve for sample G is essentially the same as that for sample F, though coloration was observed after long usage of sample G presumably owing to contamination from the steel component of the storage unit. For sample G_b, both the peak at about 190 °C and the shoulder on the melting peak became a little smaller than those of the original material. This fact is presumably caused by the unintended effect of zone refining due to the 1000 cycles of melting and crystallization, because the melting proceeds from the top to the bottom and the crystallization proceeds vice versa. DSC curves similar to that of sample G were also obtained for the samples taken from different parts of the equipment after the 1000 cycles. From the similarity among the DSC curves of these samples, we conclude that little change would occur in the practical usage of the material.

The melting temperatures and the heats of fusion estimated from heat capacity measurements [11] are listed in Table 5, where the extrapolated onset temperature is tabulated. The melting temperature and the heat of fusion of sample E are very close to those of sample A. Moreover, the small peak and the shoulder were not observed in the DSC curve of sample E (see Fig. 11). For these reasons, the material made from NaOH produced by the ion exchange membrane process is preferable to that produced by the asbestos separator process.

CONCLUSION

It is concluded from the above-mentioned experiments that the binary eutectic mixture 18.5 mol.% $NaNO_3$–81.5 mol.% NaOH is the most promising material in an operating temperature range 230–300 ° C, especially for thermal energy storage in a nuclear power plant, because it has a large heat of fusion and little supercooling tendency, while the melting temperature is very suitable for storing the thermal output from a nuclear reactor. For practical use, NaOH produced by the ion exchange membrane process is preferable to that produced by the asbestos separator process and the mercury electrode process because of the negligible effect of impurity and little environmental impact. Degradation of the material during its long-term usage can also be neglected because little change was observed after the 1000 cycle test in the bench-scale equipment.

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