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# Latent heat thermal energy storage of a binary mixture—flow and heat transfer characteristics in a horizontal cylinder

N. HIMENO, K. HIJIKATA and A. SEKIKAWA
Department of Physical Engineering, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152, Japan

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**Abstract**—The characteristics of melting and solidification of a binary mixture of $p$-$C_6H_4Cl_2$ and $p$-$C_6H_4Br_2$ were experimentally investigated in a horizontal cylindrical capsule. Since segregation occurs in the solidification and density stratification occurs in the melting, non-uniform concentration profiles were formed in both solid and liquid phases. These non-uniform density profiles generated several horizontal cells by free convection in the melting process, while only a few large vortices were generated for pure $p$-$C_6H_4Cl_2$. As a result of this difference of free convective motion, heat transfer performance of a binary mixture becomes smaller compared with that of pure material.

## 1. INTRODUCTION

RECENTLY, many studies on thermal energy storage have been carried out, accompanying the development of efficient energy utilization technology, such as energy conversions from geothermal energy, solar energy and exhaust factory heat. Among various ways of thermal energy storage, latent heat thermal energy storage is the most attractive due to a high density of heat storage. There have been many reports on the latent heat thermal energy storage. Kamimoto *et al.* [1] investigated the heat-storage material having large latent heat of fusion and stable physical properties. In refs. [2–6], heat transfer characteristics in a heat-storage vessel or a capsule were investigated. In order to decrease the available energy loss caused by heat storage or release. Saitoh and Hirose [7] proposed the combination of two-heat-storage materials having different melting temperatures along the flow direction. However, advanced studies on this subject have not yet been carried out.

If several kinds of heat-storage materials having different melting points can be used, the available energy loss becomes smaller and the stored energy can be released at a temperature close to that of the high-temperature heat source. Therefore, in a high performance heat storage, we need a material which possesses the desired melting temperature. The authors suggested that such a material might be obtained by mixing two miscible materials having different melting points [8]. The melting temperature could be changed by changing the mixing ratio of two materials. However, in accordance with the heat release from such a mixed material, the component having the higher melting point solidifies first and the concentration of the other component increases, that is, segregation occurs. Therefore, the performance and the heat transfer process of the latent heat thermal energy storage of the binary mixture of miscible materials should be different from that of a pure material. As a result of the segregation, the following effects should be considered. First, the melting or solidification temperature would be varied as melting or solidification progresses, since the mixing ratio is not uniform in the material. Secondly, when the densities of both components differ greatly, characteristics of free convective motion due to the temperature difference should differ from that of a pure material. In order to clarify these effects on the heat transfer performance, we performed an experiment on one-dimensional melting and solidification, and clarified the fundamental heat transfer characteristics of a binary mixture of heat storage materials. Since in practical situations, the phase change does not occur one-dimensionally, a horizontal cylinder was used as a typical two-dimensional capsule in this paper.

## 2. EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic diagram of the experimental apparatus is shown in Fig. 1. A cylindrical capsule of 55 mm o.d. was set in a reservoir of dimensions 250 × 120 × 340 mm. Silicon oil flowed upward in the reservoir for heating or cooling the capsule. Its temperature was adjusted by a heater or a cooler in the circulating loop. Mesh was installed at both the upper and lower parts in the reservoir to obtain uniform flow. In order to obtain a sharp temperature change in the reservoir at the start of the phase-change experiment, the silicon oil was previously circulated in a bypass loop. The phenomena of melting and solidification were observed through windows at both ends of the cylinder.

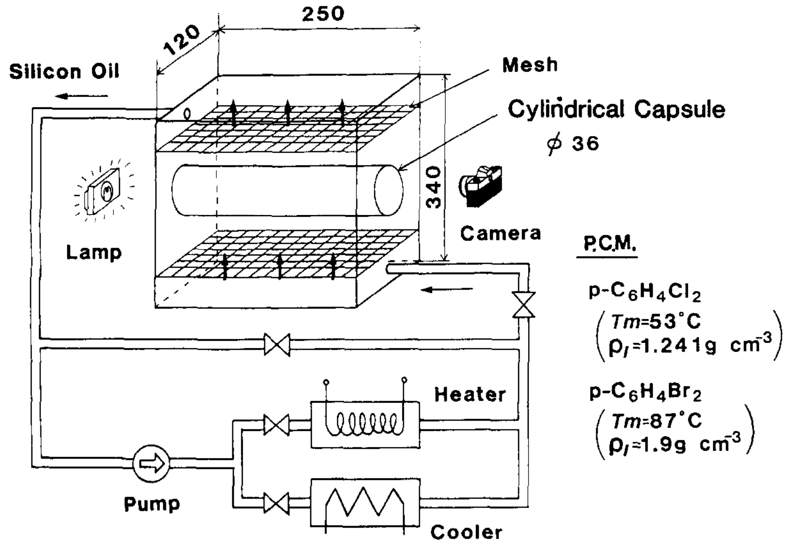


FIG. 1. Schematic diagram of experimental apparatus.

In this experiment, $p$-dichlorobenzene ($p$-$C_6H_4Cl_2$; melting point, 53°C; latent heat of fusion, 124.2 kJ $kg^{-1}$) and $p$-dibromobenzene ($p$-$C_6H_4Br_2$; melting point, 87°C; latent heat of fusion, 87.3 kJ $kg^{-1}$) were used as heat-storage materials because of their miscibility with each other and the transparence of the mixed liquid. They are chemically stable and their physical properties including the equilibrium diagram of the mixture are well known, though their latent heats of fusion are not so large. When we compare the densities of both components in the liquid phase, the density of $p$-$C_6H_4Br_2$ (1.9 g $cm^{-3}$), having the higher melting point, is larger than $p$-$C_6H_4Cl_2$ (1.2 g $cm^{-3}$). The experiments were performed for pure $p$-$C_6H_4Cl_2$ as a reference and for binary mixtures of 30 and 80% by weight of $p$-$C_6H_4Br_2$. The fundamental heat transfer characteristics of these phase-change materials were already clarified in the one-dimensional situation [8].

The cylindrical capsule consisted of two concentric tubes, as shown in Fig. 2. The space between the two tubes was filled with resin and the heat flux was calculated from the temperature difference between them. The outer tube had a 55 mm o.d. and was 3 mm thick; the inner cylinder had a 40 mm o.d. and was 2 mm thick. They were made of copper to establish a constant wall-temperature condition. The surface temperature was measured by Cu–Co thermocouples at eight points along the circumferential direction of the inner tube. The surface temperature was constant within 0.1°C. A piston cylinder was installed at one end of the cylindrical capsule to absorb the volume change of the heat-storage material during the melting or solidification. The piston was heated by an electrical heater so that movement was possible during the solidification process. The other end of the cylinder was made of glass to enable observations during the phase-change process. The temperature profile in the cylinder capsule was measured by Cu–Co thermocouples located at 2 mm intervals in both the horizontal and vertical directions. A stainless steel wire 0.2 mm in diameter was set along the cylinder axis so that the solid phase could not drop in the melting process.

## 3. RESULTS AND DISCUSSION

A binary mixture of heat-storage materials should have a different heat transfer characteristic from that of a pure material, since a non-uniform concentration profile is formed by segregation in the solidification process. In order to make clear the difference of heat transfer performances between a pure material and a binary mixture of materials, the variation of the temperature profile with time at 5 min intervals in the horizontal and vertical planes including the axis of the cylindrical capsule were measured using $p$-$C_6H_4Cl_2$ and a binary mixture of 70% $p$-$C_6H_4Cl_2$ and 30% $p$-$C_6H_4Br_2$.

For the solidification profile, results are shown in Figs. 3 and 4, where $r$ is a distance from the axis. The temperature profile on the left-hand side of the axis in the horizontal plane is omitted because of the symmetry of the profile. For the pure material, until the wall temperature decreases to the melting point, a uniform temperature profile is obtained in the heat-storage material due to free convection, which can be detected by visual observation, as shown in Fig. 3. When the wall temperature reaches the melting point of the pure material, the liquid phase begins to solidify at that temperature. Therefore, the temperature in the liquid core region is constant and equal to the solidification temperature, while a conduction-type temperature profile appears in the solid phase near the wall. Changes of the temperature profiles in one measuring interval are small due to the release of the latent heat of fusion at the interface between the liquid and solid. After the solidification has finished, the

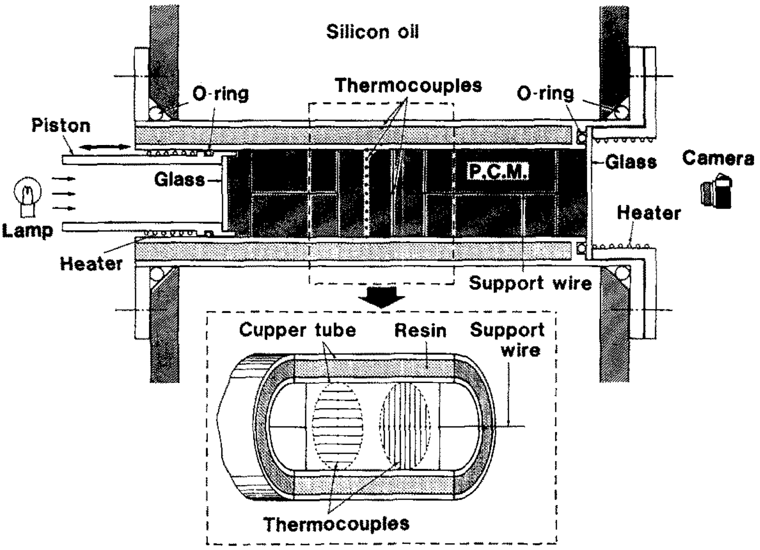


FIG. 2. Schematic diagram of heat storage cylindrical capsule.

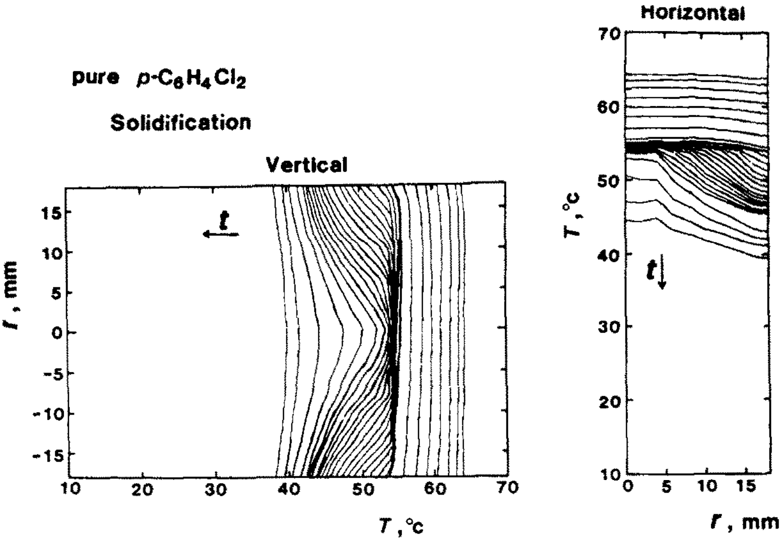


FIG. 3. Temperature profile during solidification for pure $p$-$C_6H_4Cl_2$.

temperature profile is determined by simple unsteady heat conduction without heat release. Since the wall temperature was almost constant along the circumferential direction, this solidification process is considered axisymmetrical.

In the case of the binary mixture, the solidification temperature spatially varies in the heat-storage material as shown in Fig. 4. It becomes higher in the downward direction of the vertical plane and in the outside direction of the horizontal plane. As high solidification temperature means large $p$-$C_6H_4Br_2$ content, the variation of solidification temperature in the horizontal direction is caused by segregation, that is, the separation of the mixed materials. Namely, the higher melting-temperature component solidifies first and the concentration of the lower melting-temperature component increases in the liquid. The vertical temperature profile shows larger variation of solidification temperature compared with that in the horizontal plane. The melting temperature becomes high in the lower part of the capsule. This is caused by the nonuniformity of the $p$-$C_6H_4Br_2$ concentration in the liquid at the initial stage of solidification. It is higher in the lower part of the capsule.

When the cylindrical capsule was filled with heat-storage materials, these materials were uniformly premixed. Even if the solidification temperature was uniform throughout the capsule, the concentration profile became nonuniform in the solid phase after the occurrence of solidification. Therefore, when a solid mixture having such a concentration profile is melted, $p$-$C_6H_4Br_2$, which melts first, will gather in the bottom part of the capsule because the density of $p$-$C_6H_4Br_2$ in liquid is higher than that of $p$-$C_6H_4Cl_2$. Thus the density stratification appears in the capsule. In the experiments, it was observed that the shape of the

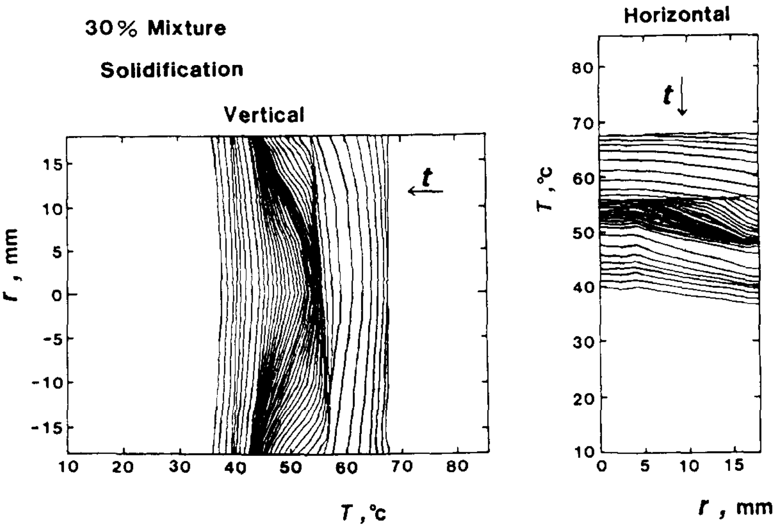


FIG. 4. Temperature profile during solidification for binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$.

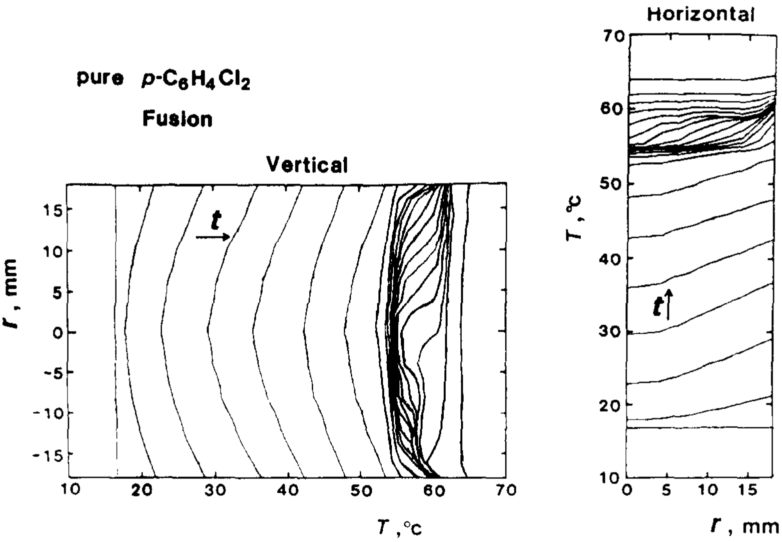


FIG. 5. Temperature profile during melting for pure $p$-$C_6H_4Cl_2$.

interface between the solid and liquid phases in the first experiment differed from those after several cycles of melting and solidification. In Fig. 4, the reproducible result after five cycles is shown. The temperature profile in the liquid phase is not flat but has a gradient in the core, which is the main difference from the result using pure material shown in Fig. 3. This means that free convection is weak in the liquid due to the density stratification, where the flow is stable, and the solidification occurs more slowly.

In the melting process, the variations of the temperature profiles with time in the vertical and horizontal planes are shown in Figs. 5 and 6 for pure $p$-$C_6H_4Cl_2$ and a binary mixture of 70% $p$-$C_6H_4Cl_2$ and 30% $p$-$C_6H_4Br_2$, respectively. For pure $p$-$C_6H_4Cl_2$, as shown in Fig. 5, the temperature profile above the melting temperature is flat due to the free convection. As can be seen from the temperature profile in the vertical plane, the melting rate is faster in the upper region than in the lower one. In the lower part of the liquid, the temperature profile is S-shaped, which means that the thermal boundary layers are formed both in the vicinity of the wall and below the melting front. On the other hand, in the upper part, the thermal boundary layer can only be seen in the vicinity of the melting front. The temperature profile near the upper wall is flat. Therefore, the temperature difference between the bulk of the liquid and the melting front in the upper part is twice as large as that in the lower part, which causes the higher heat transfer performance at the upper melting front. Thus, in the melting of the pure material, the melting in the upper part of the capsule is important from the heat transfer viewpoint.

On the other hand, for the binary mixture of 30% by weight $p$-$C_6H_4Br_2$, the motion caused by the free

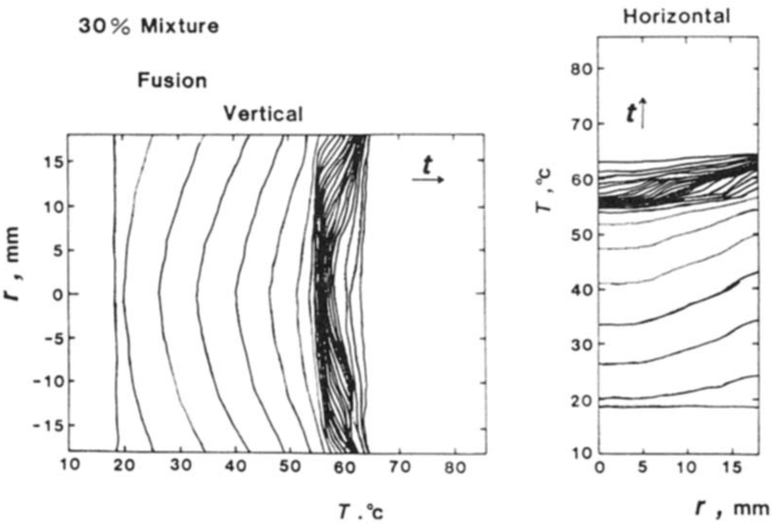
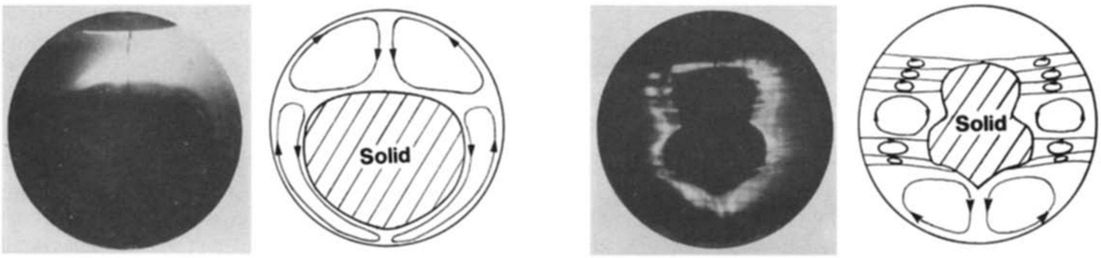


FIG. 6. Temperature profile during melting for binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$.



pure $p$-$C_6H_4Cl_2$ 30% Mixture

FIG. 7. Photographs of the melting process (left: pure $p$-$C_6H_4Cl_2$; right: binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$).

convection can be easily recognized from the S-shaped temperature profiles in the lower part, as shown in Fig. 6, but a flat temperature profile cannot be detected in the upper part. Rather only a conduction-type temperature profile can be seen. In addition, the melting rate is slower in the upper part compared with that in the lower part.

These results were confirmed by visual observations. Figure 7 shows photographs of the melting process in pure $p$-$C_6H_4Cl_2$ and in a binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$. At the center of the cylindrical capsule, the solid phase remains in both cases, but their shapes are quite different. In the liquid phase, the free convection creates the upward flow along the wall due to heating and the downward flow along the melting front. This free convective motion was observed from the trace of the floating fine solid fragment of the heat-storage material the size of which is less than 1 mm. For the pure material, four large vortices were observed as shown in Fig. 7(a). In the upper vortices, the flows heated by the wall move upwards, impinge upon each other, move downwards and then impinge directly upon the upper solid surface without cooling. As a result, heat is directly transmitted to the solid in the upper region, and the melting occurs more quickly. On the other hand, in the lower vortices, the upward heated flow impinges upon both sides of the solid core and descends along the solid–liquid interface. Therefore, heat was not so well transmitted to the solid in the bottom part and the melting rate was slow. As shown in Fig. 7, heat is well transferred to the solid in the upper part because the thermal boundary layer does not exist near the upper wall, but in the lower part, the thermal boundary layer exists in the vicinity of both the walls and the melting front. Therefore, melting does not occur axisymmetrically.

For the binary mixture of melting materials, it was observed that several small vortices were generated and that small cells separated by horizontal layers appeared, as shown in Fig. 7(b). This is because of the density stratification due to the concentration gradient. The density is higher in the lower direction in the concentration profile described above. As a result of the density stratification, the free convective motion is restricted to the small cells. The density changes due to the temperature and the concentration gradients interfere with each other. As the interfaces between adjoining layers were able to be observed clearly, it was confirmed that there exists a sharp density change between two adjoining layers, brought about by the difference of refraction indices.

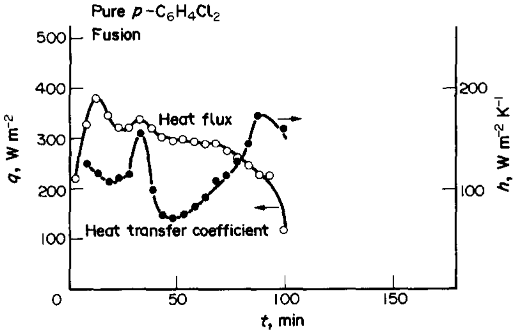


FIG. 8. Heat transfer coefficient during melting for pure $p$-$C_6H_4Cl_2$.

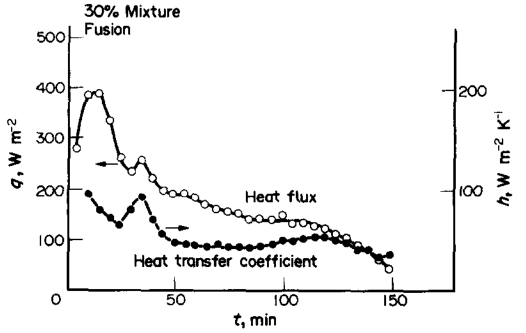


FIG. 9. Heat transfer coefficient during melting for binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$.

The separation into small horizontal layers of free convection resulted in the weak free convective motion in the upper layers. Consequently, the heat transfer performance worsened and the melting rate slowed in the upper part. The above results are consistent with the temperature profiles shown in Fig. 4. In latent heat thermal energy storage using a binary mixture, this flow characteristic as well as the variation of the melting temperature by segregation are important factors.

For discussing the heat transfer performance qualitatively, variations of the heat flux $q$ and the heat transfer coefficient $h$ with time during the melting process for pure $p$-$C_6H_4Cl_2$ and a binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$ are shown in Figs. 8 and 9, respectively. The characteristic temperature difference for calculating the heat transfer coefficient was the difference between the average temperature of the heat-storage material and the wall temperature. As shown in Figs. 8 and 9, the heat flux peaks after about 15 min in both cases. Since the heat capacity of the test vessel was so small, 15 min was needed to increase the temperature of the heat-transmitting oil (silicon) up to a set point. Thus, the apparent heat transfer coefficient was increased during this unsteady period. After the temperature of the silicon oil reached the set point, the heat flux decreased with time, since heat was only transferred by conduction in the solid phase of the heat-storage material. When the solid phase begun to melt, both the heat flux and the heat transfer coefficient peaked after 30 min in the case of pure $p$-$C_6H_4Cl_2$. Just after the occurrence of melting, the temperature of the melting front was kept constant and the location of the melting front was very near to the wall. Therefore, the temperature gradient became large at the wall, which brought about these maximum values. As the melting progressed, the free convective motion became strong because of an expansion of the liquid-phase region. Since the temperature difference between the wall and the melting front was almost constant, the decrease of the heat flux with time was very slow. On the other hand, the heat transfer coefficient increased remarkably with time, since the temperature difference between the heat-storage material and the wall decreased more rapidly than the heat flux.

For the binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$, as shown in Fig. 9, the heat flux and the heat transfer coefficient have the same peaks with those for the pure material. However, both peaks are lower and the time for establishing complete melting is longer compared with those for the pure material. This is because the free convective motion is weaker in the case of the binary mixture, as described above.

The flow and heat transfer characteristics for the binary mixture of 30% $p$-$C_6H_4Br_2$ and 70% $p$-$C_6H_4Cl_2$ have been clarified by comparing them with those for pure $p$-$C_6H_4Cl_2$. Now, the results of melting and solidification processes of 80% $p$-$C_6H_4Br_2$ and 20% $p$-$C_6H_4Cl_2$ will be discussed in order to clarify the effect of concentration of $p$-$C_6H_4Cl_2$, because the concentration has a large effect on heat transfer characteristics. The variation of the temperature profile in melting and solidification at 5 min intervals are shown in Figs. 10 and 11, respectively. In the melting process, several small cells were observed to separate into horizontal layers, as in the case of the binary mixture of 30% $p$-$C_6H_4Br_2$. From the results in the vertical plane, it is seen that free convection is predominant only in the lower part of the capsule, as distinguished by a flat temperature profile. However, in the upper part, the effect of free convection is very weak and heat conduction is important because of high-density stratification. In this mixture, we cannot detect a definite melting temperature in the horizontal plane, but the temperature profile in the vertical plane suggests a large variation of melting temperatures in the cross section. The reason for the problems with regard to the horizontal plane is that dendrites were formed in the solidification process. In the growth of dendrites, as the segregation occurs perpendicularly to the dendrite surface, large local variations of concentration in the horizontal plane are generated, even in a very small area. This is why we cannot detect a definite melting temperature in the horizontal plane.

In the solidification process as shown in Fig. 11, the region having a smaller temperature change during the same time interval corresponds to the liquid phase. In the vertical plane, a definite solidification temperature also cannot be observed, but the existence of variations of solidification temperature along the

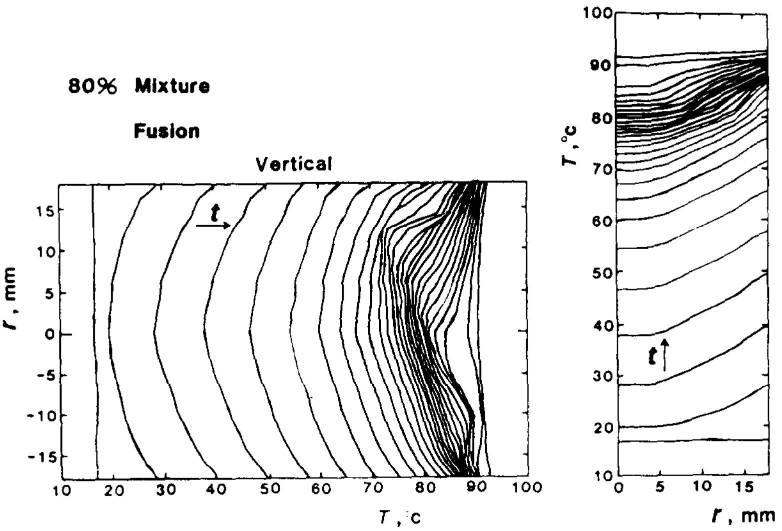


FIG. 10. Temperature profile during melting for binary mixture of 80% $p$-$C_6H_4Br_2$ and 20% $p$-$C_6H_4Cl_2$.

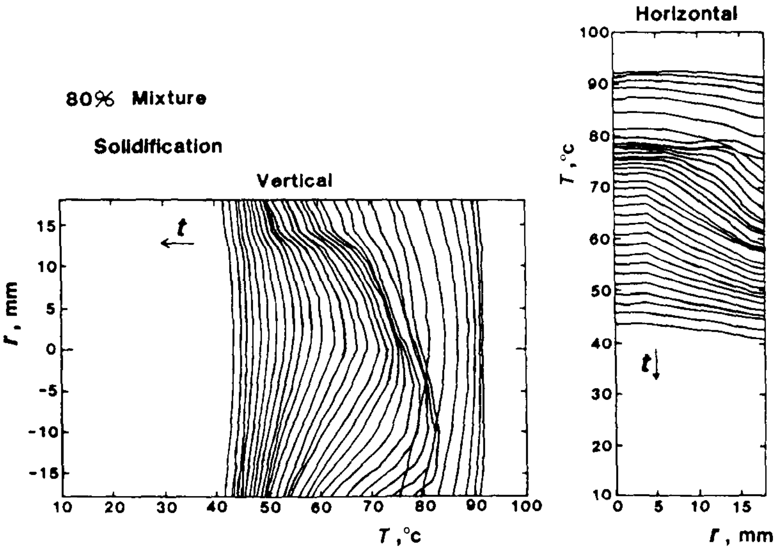


FIG. 11. Temperature profile during solidification for binary mixture of 80% $p$-$C_6H_4Br_2$ and 20% $p$-$C_6H_4Cl_2$.

vertical direction can be estimated. It is seen that the temperature profiles are convex in the liquid phase, which translates to weak free convective motion in the liquid phase caused by density stratification. The special feature in the solidification of a material having a high concentration of $p$-$C_6H_4Br_2$ is the existence of a supercooled state. In the lower part of the capsule, the sudden temperature rise was measured in the cooling process, as is clearly seen in Fig. 11. According to the decrease in wall temperature, the supercooled state occurred and the solid phase was suddenly generated as a dendrite when the degree of supercooling exceeded some value. After that, an equilibrium state was established. The rapid release of latent heat in the solidification of the supercooled liquid, created a sudden temperature rise. The rapid solidification from the supercooled liquid occurred only in the lower part of the capsule, and the generated interface between solid and liquid is thus not circular but planar and horizontal. In addition, the progress of the solidification was faster in the lower part of the capsule. These results indicate that the density stratification corresponding to variations of $p$-$C_6H_4Br_2$ concentration is the most important factor in the solidification process involving high concentrations of $p$-$C_6H_4Br_2$.

## 4. CONCLUSIONS

The flow and heat transfer characteristics of a binary mixture of $p$-$C_6H_4Cl_2$ and $p$-$C_6H_4Br_2$ in a horizontal cylindrical capsule were investigated experimentally for understanding the heat transfer process in heat-storage material. The following conclusions were obtained.

(1) In the case of the heat-storage material consisting of a binary mixture of two miscible fluids, a non-uniform profile of the concentration is not only generated by the segregation in the solidification process but also by the density stratification in the melting process.

(2) In the melting in the horizontal cylindrical capsule, a few large vortices are generated by free convective motion in the liquid phase for the pure material. On the other hand, in the case of a binary mixture of materials having different densities, several small vortices are generated due to the density stratification, so that the free convective motion is quite different from that of a pure material.

(3) Heat transfer in the melting of a binary mixture worsens, compared with that in a pure material, since free convection in the upper region becomes weak as a result of the separation of the free convection layer into small horizontal cells.

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## STOCKAGE DE CHALEUR LATENTE DANS UN MELANGE BINAIRE ET CARACTERISTIQUES D'ECOULEMENT ET DE TRANSFERT THERMIQUE DANS UN CYLINDRE HORIZONTAL

**Résumé**—Les caractéristiques de fusion et de solidification d'un mélange binaire de $p$-$C_6H_4Cl_2$ et de $p$-$C_6H_4Br_2$ sont expérimentalement étudiées dans une capsule cylindrique horizontale. Puisque la ségrégation se fait dans la solidification et la stratification pendant la fusion, des profils de concentration apparaissent à la fois dans les phases solide et liquide. Ces profils provoquent plusieurs cellules horizontales par convection naturelle pendant la fusion, tandis que peu de grands tourbillons se forment pour le $p$-$C_6H_4Cl_2$ pur. En conséquence de cette différence de mouvement de convection naturelle, la performance du transfert thermique pour un mélange binaire est plus faible en comparaison avec le cas d'un matériau pur.

## LATENTWÄRMESPEICHERUNG IN EINEM ZWEISTOFFGEMISCH—STRÖMUNGS- UND WÄRMETRANSPORT-EIGENSCHAFTEN IN EINEM HORIZONTALEN ZYLINDER

**Zusammenfassung**—Das Verhalten beim Schmelzen und bei der Erstarrung eines Zweistoffgemisches aus $p$-$C_6H_4Cl_2$ und $p$-$C_6H_4Br_2$ wurde in einer horizontalen zylindrischen Kapsel untersucht. Da bei der Erstarrung Entmischungen und beim Schmelzen infolge von Dichteunterschieden Schichtungen auftreten, ergeben sich sowohl in der festen als auch in der flüssigen Phase Konzentrationsprofile. Diese Dichteprofile führen zu mehreren horizontalen Schichten mit natürlicher Konvektion beim Schmelzen, während bei reinem $p$-$C_6H_4Cl_2$ nur wenige große Strömungswalzen auftreten. Infolge dieser unterschiedlichen Arten der freien Konvektion ergibt sich eine Verringerung des Wärmetransports bei einem Zweistoffgemisch im Vergleich zu reinen Stoffen.

## АККУМУЛИРОВАНИЕ СКРЫТОЙ ТЕПЛОВОЙ ЭНЕРГИИ В БИНАРНОЙ СМЕСИ. ТЕЧЕНИЕ И ХАРАКТЕРИСТИКИ ТЕПЛОПЕРЕНОСА В ГОРИЗОНТАЛЬНОМ ЦИЛИНДРЕ

**Аннотация**—Экспериментально изучены характеристики плавления и затвердевания бинарной смеси $p - C_6H_4Cl_2$ и $p - C_6H_4Br_2$ в горизонтальной цилиндрической капсуле. Поскольку при затвердевании происходит разделение, а при плавлении—стратификация плотности, то как в твердой, так и в жидкой фазах образуются неоднородные концентрационные профили. Эти неоднородные профили концентрации генерируют несколько горизонтальных свободноконвективных ячеек в процессе плавления, в то время как в чистом $p - C_6H_4Cl_2$ возникает малое количество крупных вихрей. В результате этого различия в свободноконвективном движении теплоперенос в бинарной смеси слабее, чем в чистом материале.