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Thermal Storage and Thermodynamic Characteristics of Phase Change Materials Slurries

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Abstract This study was aimed at developing a low cost cold storage system for agricultural products. Three kinds of slurries: K_1, K_2, and K_3 slurries were developed using phase change materials (PCMs) such as tetradecane, octadecane, and sodium polyacrylate to maintain the desired temperature ranges. The slurries were manufactured by *in-situ* polymerization. Tetradecane and octadecane were capsulated in a core with melamine at the surface. The thermodynamic characteristics of the slurries were measured and analyzed. The latent heats of the K_1, K_2, and K_3 slurries at the melting points were 206.41, 186.88, and 147.91 kJ/kg, respectively. A transportable cold storage container was built to investigate the performance of the slurries as thermal storage media. The temperatures at the insides of the container could be maintained in the ranges of 0-5, 5-10, and 10-15^{o}C for more than 23, 27, and 60 hr with the K_1, K_2, and K_3 slurries, respectively.

Keywords: latent heat, phase change material (PCM), slurry, thermal storage

Introduction

Conventional cooling systems have long pipe lines to convey heat transfer fluid between heat exchangers. Thermal energy is transferred by the sensible heat of the fluid. Although sensible heat storage by means of water is simple and technically well developed, the efficiency of these systems is relatively low. Latent heat storage using phase change material (PCM) has advantages of high thermal storage capacity and heat retrieval at constant temperature during the phase change (1,2).

PCMs have been used for various thermal energy applications as a heat transfer and thermal storage medium (3). PCM particles suspended in a fluid provide additional thermal capacity from latent heat associated with the solid-liquid phase change. Because PCM particles can stick together to form large lumps, clogging often occurs in pipes, resulting in a failure to circulate the slurry in cooling systems. Several researches have shown that microencapsulated phase change materials (MPCMs) have no effect on their melting temperatures or latent heats.

Yamagishi *et al.* (4) studied the hydrodynamic and heat transfer characteristics of slurries containing MPCMs as a heat transfer fluid. Slurries consisting of octadecane ($C_{18}H_{38}$) contained in 2-10 μm diameter microcapsules and pure water were used. Felsing and Jessen (5) and Patterson and Felsing (6) studied heat capacities of gaseous mono- and di-methylamines and heats of solution of gaseous di- and tri-methylamine. They reported that MPCM slurries with larger latent heats, higher phase change rates, and no supercooling demonstrated promising heat transfer performance. Lee *et al.* (7) designed and tested a cooling system using MPCM slurries to investigate the performance of the MPCM as a thermal storage medium. The MPCM slurries were manufactured by *in-situ* polymerization. The surface of the MPCM was composed of melamine while tetradecane ($C_{14}H_{30}$) was in the center of the MPCM. The discharge times of the 10 and 20 wt% MPCM slurries were up to 105 and 285 min longer, respectively, than a water cooling system.

In Korea, small amounts of various kinds of agricultural products are delivered from farmers to consumers every day by vehicle. Optimal temperature control is important to maintain the freshness of the agricultural products during transportation (8). The desired temperatures depend on the varieties and packing conditions of the agricultural products. Low cost and energy efficient cooling systems are needed to maintain the quality of agricultural products for distribution. Cooling systems using the latent heat of PCMs are particularly attractive with respect to thermal storage capacity and cost, and can be utilized to transport the agricultural products.

This study was carried out to develop a low cost cold storage system for agricultural products. Three kinds of slurries using MPCMs were developed, and their thermodynamic characteristics were analyzed. A transportable cold storage system using packs of MPCM slurries was designed and the performances of the MPCM slurries as thermal storage media were investigated.

Materials and Methods

Phase change materials Three kinds of slurries: K_1, K_2, and K_3 slurries were developed using MPCMs such as tetradecane ($C_{14}H_{30}$), octadecane ($C_{18}H_{38}$), and sodium polyacrylate (0.15 wt%) to maintain different temperature ranges of the cold storage system (9,10). The K_1, K_2, and K_3 slurries were designed to maintain the desired temperature ranges of 0-5, 5-10, and 10-15^{o}C, respectively. The K_1 slurry consisted of 2 components: 5% tetradecane and 95%

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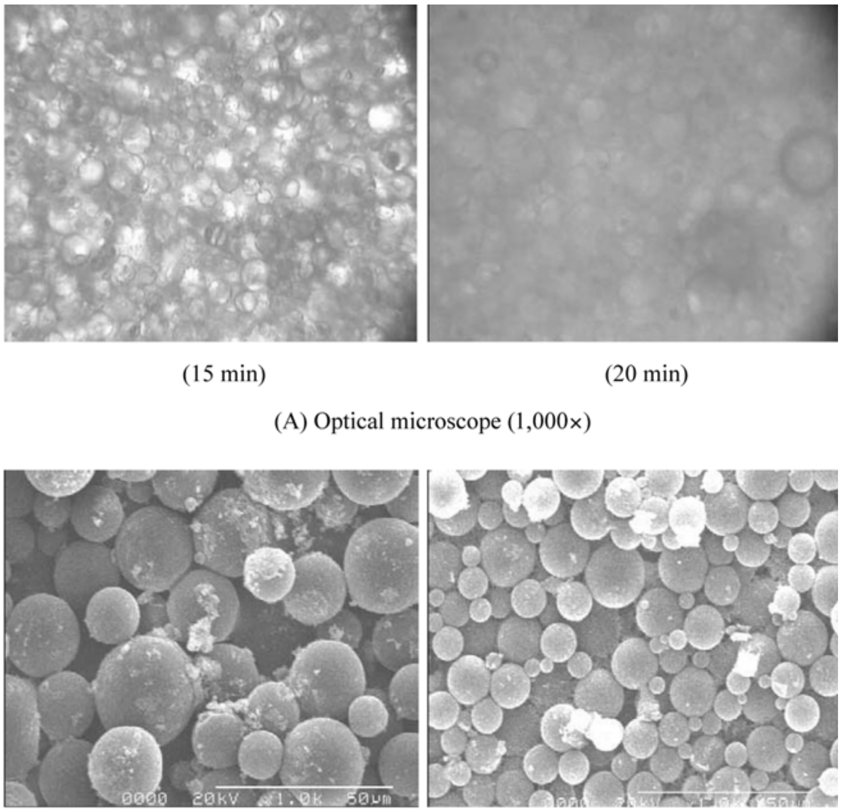

(15 min) (20 min)

(A) Optical microscope (1,000×)

(15 min) (20 min)

(B) Scanning electron microscope

Fig. 1. Surface change of K_2 slurry with 15 and 20 min of homogenization.

sodium polyacrylate (0.15 wt%). The K_2 slurry consisted of 3 components: 94% tetradecane, 4% octadecane, and 2% sodium polyacrylate (0.15 wt%). The K_3 slurry consisted of 64% tetradecane, 34% octadecane, and 2% sodium polyacrylate (0.15 wt%).

The K_1, K_2, and K_3 slurries were manufactured by *in-situ* polymerization as described by Lee *et al.* (7) and Kwon *et al.* (11). Tetradecane and octadecane were capsulated in a core with melamine at the surface. Stealy meth acrylate (SMA) was used as an emulsifier. Sodium polyacrylate was added in the capsules as the nucleating agent to reduce the supercooling phenomena of tetradecane and octadecane. The concentration of the MPCM particles in the slurries was 25 wt%.

The capsule shape and the degree of aggregation of the MPCMs were observed with an optical microscope (Mw 200 Bi, Samsung SDI, Yongin, Gyeonggi, Korea). The surface of the MPCMs was analyzed by a scanning electron microscope (SEM, S-2380N; Hitachi, Ibaraki, Japan). The degree of aggregation changes of the K_2 slurry with 15 and 20 min of homogenization are shown in Fig. 1. The diameters and specific gravities of the MPCM particles were in the range of 5-15 μm and 0.87-0.91, respectively. The thermal characteristics of the K_1, K_2, and K_3 slurries were analyzed by a differential scanning calorimeter (Unix DSC 7; PerkinElmer, Waltham, MA, USA) (12). The latent heats of the MPCM slurries at freezing and melting temperatures were analyzed initially and after 400 thermal cycles, where 1 cycle included both melting and solidification processes. The degree of supercooling can be defined as the difference between the melting and solidification temperatures (13). The supercooling phenomena were analyzed by measuring the thermal energies of the MPCM slurries.

The viscosities of the slurries were measured by a viscometer (DV-II; Brookfield, Middleboro, MA, USA) at 3 different temperature levels: 0, 5, and 20°C for the K_1 slurry, 0, 10, and 20°C for the K_2 slurry, and 0, 15, and 20°C for the K_3 slurry. A 300 cm^3 sample was taken at each temperature and rotated at an angular velocity of 100 rpm for 30 sec. The viscosity measurements using a spindle that is used to measure low viscosity were repeated 3 times to obtain average values. The weights of the slurry samples were measured at 20°C, and the average values were used to determine the densities of the slurries.

Experimental apparatus and method A transportable cold storage container, 700 (W)×800 (D)×1,450 mm (H), was built to investigate the performance of the MPCM slurries as thermal storage media. The transportable cold storage container with a thermal capacity of 0.7 RT (1 RT =13.89 MJ) was designed to maintain temperatures in the range of −10-15°C for more than 12 hr when the ambient temperature was 35°C. The experimental container included a cold storage module at the bottom, a blower for air circulation at the top, an air mix duct, and a cooling air

Table 1. Thermodynamic characteristics of microencapsulated phase change materials (MPCMs) slurries

MPCM slurry[1)]	Phase change temperature (°C)		Latent heat (kJ/kg)		Degree of supercooling (°C)	Number of components
	Freezing point	Melting point	Freezing point	Melting point		
K_1	-3.5	6.3	215.80	206.41	3.4	2
K_2	-2.6	6.3	189.16	186.88	3.5	3
K_3	-2.0	5.6	137.84	147.91	2.5	3

[1)] K_1, slurry consisted of 5% tetradecane and 95% sodium polyacrylate (0.15 wt%); K_2, slurry consisted of 94% tetradecane, 4% octadecane, and 2% sodium polyacrylate (0.15 wt%); and K_3, slurry consisted of 64% tetradecane, 34% octadecane, and 2% sodium polyacrylate (0.15 wt%).

duct (14). The produced K_1, K_2, and K_3 slurries were filled in 700 mL polyethylene (PE) packs and sealed. A total of 22 PE packs were used as thermal storage media in the cold storage module.

Tests were conducted to analyze the temperature changes at the insides of the experimental container and the discharge times of the MPCM slurries. The PE packs filled with K_1, K_2, and K_3 slurries were used to maintain the temperature of the container at 3, 8, and 13°C, respectively. The PE packs filled with slurries were left in a constant temperature bath at 20°C to remove the latent heats of the MPCMs. The PE packs were put in the cold storage module and cooled at −10°C until the temperatures of the slurries reached 0°C for the K_1 slurry, −3°C for the K_2 slurry, and −5°C for the K_3 slurry. The temperatures were measured at the insides (left, right, middle, and bottom positions) of the container and slurry filled PE packs every 30 sec. T-type thermocouples with diameters of 0.3 mm and a multi-junction data acquisition device (2625A; Fluke, Everett, WA, USA) were used for the temperature measurements.

Results and Discussion

Thermodynamic characteristics of K_1, K_2, and K_3 slurries The thermal energy analysis showed that all slurries had more than 2 heat absorption peaks, due to the differences of the materials at the inner and outer parts of the capsules. The freezing and melting point temperatures were found to be −3.5 and 6.3°C for the K_1 slurry, −2.2 and 6.3°C for the K_2 slurry, and −2.0 and 5.6°C for the K_3 slurry, respectively. As shown in Table 1, the latent heats of the K_1, K_2, and K_3 slurries at the freezing points were 215.80, 189.16, and 137.84 kJ/kg, and the latent heats at the melting points were 206.41, 186.88, and 147.91 kJ/kg, respectively. The latent heats of tetradecane and octadecane at the melting points are 229.8 and 243.7 kJ/kg, respectively (15). The 25 wt% K_1, K_2, and K_3 slurries were developed to maintain the desired temperature ranges of 0-5, 5-10, and 10-15°C, respectively. The results show that the latent heats of the slurries decreased as the desired temperature ranges increased due to the different MPCMs mixing ratios. The degrees of supercooling of the K_1, K_2, and K_3 slurries were 3.43, 3.52, and 2.53°C, respectively. The degree of supercooling of tetradecane (30 wt%) was found to be 6.16°C.

The DSC measurement results of the K_1, K_2, and K_3 slurries are shown in Fig. 2. The latent heats of the slurries at freezing and melting points were analyzed after 400 thermal cycles. The freezing and the melting point temperatures were −2.93 and 5.23°C for the K_1 slurry, −3.23 and 5.49°C for the K_2 slurry, and −2.43 and 4.90°C for the K_3 slurry, respectively. The latent heats at the melting and the freezing points were 137.50 and 135.60 kJ/kg for the K_1 slurry, 132.97 and 131.95 kJ/kg for the K_2 slurry, and 111.52 and 108.88 kJ/kg for the K_3 slurry, respectively, after 400 cycles. It was found that the phase change temperatures changed by less than 1.5. However, the latent heats of the slurries decreased as the number of thermal cycles increased. The latent heats of the K_1, K_2, and K_3 slurries at the melting points were decreased by 36.6, 29.6, and 16.2%, respectively, after 400 cycles. This indicates that the PE packs of the slurries may not be usable as thermal storage media after 400 cycles. A method to preserve the latent heats of the slurries over extended thermal cycles will be required for long term use.

The average viscosities of the K_1 slurry were 9.86, 7.70, and 7.23 cp at 1.66, 6.03, and 20.8°C, respectively. As shown in Table 2, the viscosities of the K_2 slurry were 44.06, 34.36, and 28.76 cp at 0.83, 9.93, and 21.3°C, and the viscosities of the K_3 slurry were 47.80, 30.36, and 29.76 cp at 0.16, 15.13, and 20.4°C, respectively. The viscosity of sodium polyacrylate is much higher than the viscosities of tetradecane, octadecane, and water. The viscosities of the K_1, K_2, and K_3 slurries were 7, 28, and 29 times greater, respectively, than that of water at 20°C due to the addition of sodium polyacrylate. The results showed that the viscosities of the slurries decreased as the temperature increased. The densities of the K_1, K_2, and K_3 slurries at 20°C were 0.99, 0.95, and 0.93 g/cm^3, respectively. The density of sodium polyacrylate is greater than the densities of tetradecane and octadecane. The density of the K_1 slurry was greater than the densities of the K_2 and K_3 slurries, because the K_1 slurry included more sodium polyacrylate than the other slurries. The viscosities and the densities of the slurries were affected by the mixing ratios of the phase change materials.

Performance of K_1, K_2, and K_3 slurries A transportable cold storage container was built and used to investigate the performance of the K_1, K_2, and K_3 slurries as thermal storage media. The slurries, filled in the PE packs, were cooled at −10°C to store thermal energy and the latent heats of the slurries were then used to maintain the temperatures of the experimental container. Temperatures were measured at the insides of the container and in the slurries in the PE packs until the temperatures increased above the desired temperatures.

The temperature changes at the insides of the experimental container with the K_1 slurry are shown in Fig. 3. The K_1 slurry was designed to keep the temperature of the container at 3°C, and used to maintain the temperatures at 0-5°C. The

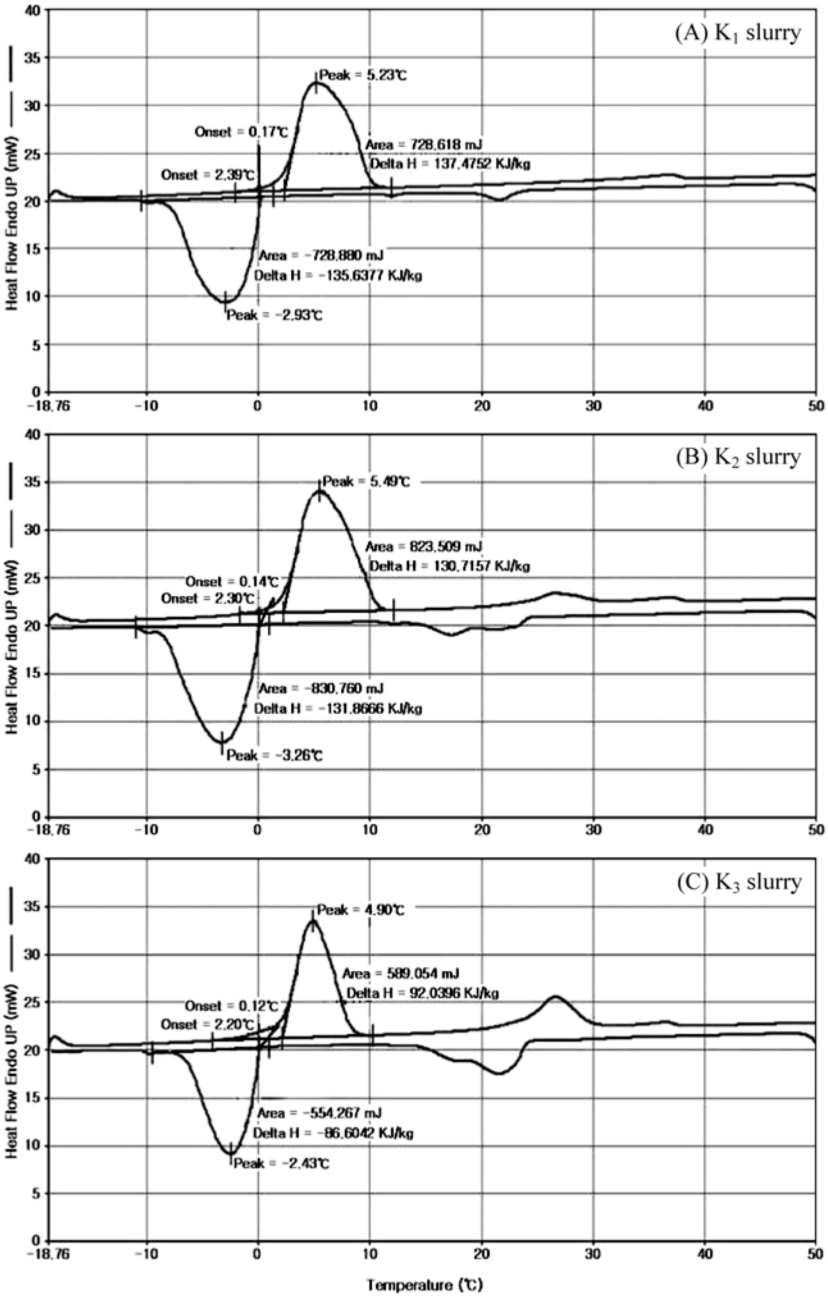

Fig. 2. Thermal characteristics of slurries after 400 thermal cycles.

ambient temperature was 22-24°C during this experiment. The K_1 slurry was cooled at −10°C until its temperature reached 0°C. It took 2.5 hr to cool the slurry and the temperature at the bottom position decreased to −2.5°C during this time. After the slurry cooling process, the temperature of the slurry was kept at 0°C for 23 hr and then increased rapidly. It was observed that the temperature of the slurry increased as the latent heat was discharged. The temperatures at the insides of the container were maintained at 3-4°C with small fluctuations before the temperature of the slurry increased. The temperatures were maintained in the range of 0-5°C for 23 hr at the left side and middle positions, and for 24 hr at the right side and bottom positions of the container. The results show that the temperatures of the container insides were maintained in the range of 0-5°C for more than 23 hr with the K_1 slurry.

The K_2 slurry was designed to keep the temperature of the container at 8°C, and used to maintain the temperatures at 5-10°C. The temperature changes at the insides of the experimental container with the K_2 slurry are shown in Fig. 4. During these experiments, the ambient temperature was 21-24°C. The K_2 slurry was cooled at −10°C until the temperature of the slurry reached −3°C. The cooling process took 3 hr, during which the temperature at the bottom position of the container decreased to −3°C. After cooling the slurry, the temperature of the slurry remained at −3°C for 19 hr, slowly increased until it reached 3°C, and then rapidly increased. The latent heat started to discharge after

Table 2. Viscosities of the K_1, K_2, and K_3 slurries at different temperatures

MPCM slurry	Temp. (°C)	Viscosity (cp)	Temp. (°C)	Viscosity (cp)	Temp. (°C)	Viscosity (cp)
K_1	1.6	9.86	6.0	7.70	20.8	7.23
K_2	0.8	44.0	9.9	34.3	21.3	28.7
K_3	0.1	47.8	15.1	30.3	20.4	29.7

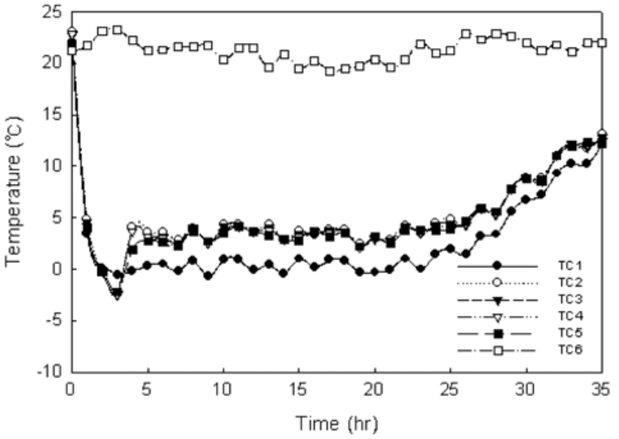

Fig. 3. Temperature changes of the cold storage system using the K_1 slurry for a desired temperature of 3°C. TC1, K_1 slurry in PE pack; TC2, left side of container; TC3, right side of container; TC4, middle of container; TC5, bottom of container; and TC6, ambient temperature.

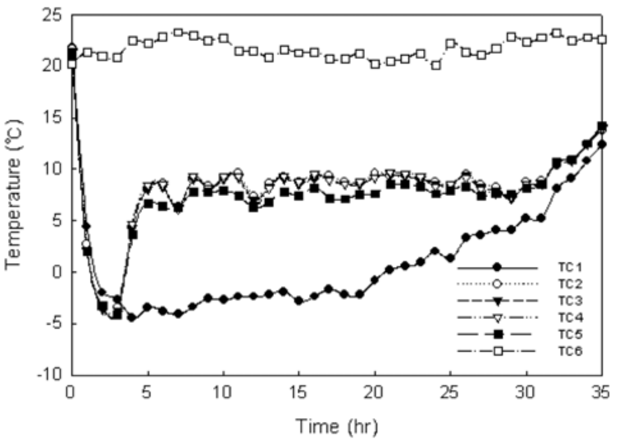

Fig. 4. Temperature changes of the cold storage system using the K_2 slurry for a desired temperature of 8°C. TC1, K_1 slurry in PE pack; TC2, left side of container; TC3, right side of container; TC4, middle of container; TC5, bottom of container; and TC6, ambient temperature.

the temperature of the slurry was maintained constantly at −3°C. The temperatures at the insides of the container were maintained at 7-8°C until the temperature of the slurry reached 3°C. The temperatures were maintained in the range of 5-10°C for 27 hr at the left side and bottom positions, and for 28 hr at the right side and middle positions of the container. The results show that the temperatures of the container insides were maintained in the range of 5-10°C for more than 21 hr with the K_2 slurry.

The temperature changes at the insides of the experimental container with the K_3 slurry are shown in Fig. 5. The K_3

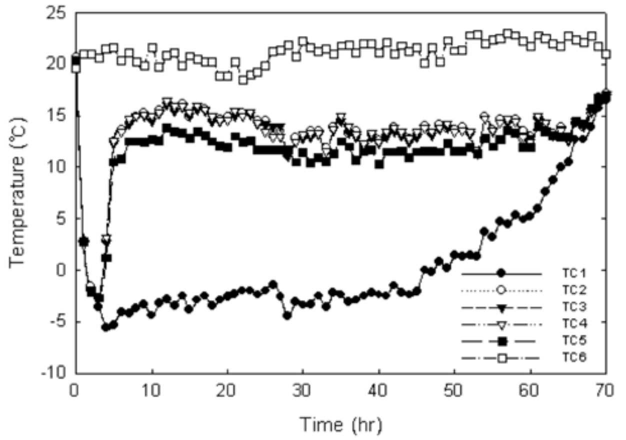

Fig. 5. Temperature changes of the cold storage system using the K_3 slurry for a desired temperature of 13°C. TC1, K_1 slurry in PE pack; TC2, left side of container; TC3, right side of container; TC4, middle of container; TC5, bottom of container; and TC6, ambient temperature.

slurry was designed to keep the temperature of the container at 13°C, and used to maintain the temperatures at 10-15°C. During this experiment, the ambient temperature was 19-23°C. The K_3 slurry was cooled at −10°C until the temperature of the slurry reached −5°C. The cooling process took 4 hr, during which the temperature at the bottom position of the container decreased to −6°C. After the cooling process of the slurry, the temperature of the slurry was kept at −3°C for 40 hr and then slowly increased. The temperature increase resulted from the discharging of the latent heat of the slurry. The temperatures at the insides of the container were maintained at 10-15°C until the temperature of the slurry reached 9°C. The temperatures were maintained in the range of 10-15°C for 60 hr at the left side and bottom positions, and for 61 hr at the right side and middle positions of the container. The temperature at the bottom was 2-3°C lower than that at the center position. The results show that the temperatures of the container insides were maintained in the range of 10-15°C for more than 60 hr with the K_3 slurry.

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