⊙ 研究論文

EFFECT OF INITIAL SALT CONCENTRATION ON THE FREEZING OF BINARY MIXTURE SATURATED PACKED BED

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이원혼합용액의 초기농도가 동결에 미치는 영향에 관한 실험연구

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Key words : Concentratin, freeging, supercooling, remelting, aqueous binary mixture

Abstract

Freezing of an aqueous sodium chloride solution (Nacl – H20) saturating a packed bed with initial salt concentrations of 5, 10, 15% by weight is investigated experimentally in a rectangular cavity. The system was cooled from the top, bottom and a vertical side wall. For the freezing experiments from below, there was little effect of the initial salt concentration throughout the freezing process, and the global freezing rate was not affected by the initial salt concentration. For the freezing from above, the size of the mush region decreased and the mush/liquid interface became flatter as the initial liquid concentration is decreased. For the freezing from vertical side wall, reheating of the mixture was intensified with an increase in the initial salt concentration. For Ci= 5%, supercooling was observed only at the early times of freezing process, but for Ci= 15% small supercooling was observed throughout the freezing process.

NOMENCLATURES

C = Concentration of solute, wt%
Da = Darcy number, K/H^2
H = Hight of cavity, mm
K = Permeability, m^2
L = Width of cavity, mm
Ra* = Modified Rayleigh number, $g\beta(T_h - T_c)KH/\nu\alpha$
T = Temperature, ℃
t = time, s
x = horizontal space cordinate, mm
z = vertical space cordinate, mm
θ = dimensionless temperature, $(T - T_c)/(T_h - T_c)$

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η=dimensionless distance, z/H

ξ=dimensionless distance, x/H

φ=porosity

SUBSCRIPTS

c=cold surface

eq=equilibrium corresponding to the initial salt concentration

eut=eutectic

h=hot surface

i=initial

1. INTRODUCTION

Freezing of an aqueous binary system saturating a permeable solid matrix is of considerable geophysical and technological interest. Applications are relevant to seasonal freezing of soil, artificial freezing of ground as a construction technique for supporting poor soils, insulation of underground buildings and latent heat-effusion thermal energy storage in porous medium. Phenomena occurring during the freezing of an aqueous binary system are similar to those found in the solidification of metal alloys. Metallurgical applications include the solidification of castings and ingots.

The salt redistribution process occurring during the freezing of a NaCl solution was examined using fixed microconductance probes in the test cell, and the factors responsible for controlling salt rejection were analyzed [1]. They found that the redistribution process of the solute rejected from the solid/liquid interface is controlled by the concentration of the liquid phase at the interface and the thermal driving force imposed on the system.

Solidification of NaCl-H_2O solutions were studied in a vertical cavity [2]. In the study, a Mach-Zehnder interferometer was utilized to monitor the liquid phase concentration in the layer which developed ahead of the advancing solid-liquid region. Solidification experiments with ammonium chloride-water solutions inside a rectangular enclosure were performed to study the fluid motion in a liquid region [3] and confirmed that the solidification process was significantly affected by the double-diffusive convection in the liquid zone.

Despite the abundance of experimental evidence of freezing of an aqueous binary system, very little systematic work has been performed to establish the effect of liquid concentration on the temperature field, supercooling of the liquid, remelting at the mush/liquid interface and the effect of orientation of the test cell.

This paper reports on the effect of initial salt concentration on the temperature distribution for an aqueous binary system saturated porous medium was cooled from below, above and a vertical side wall. The supercooling of the liquid, the remelting of the mushy-liquid interface and the mushy-liquid interface position variations with the salt concentrations of 5, 10 and 15wt% are documented. The main objective of the work is to obtain fundamental understanding of the heat and mass transfer processes and experimental data which could later be used to validate theoretical solidification models.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

Transient freezing experiments were performed with a saline solution in a rectangular test cell with inner dimensions of 149.2 mm in height and 73 mm in depth [4]. Spherical soda-lime glass beads having average diameters of 6.0 mm($K=35.0 \times 10-9\ m^2$, $\varphi=0.396$) constituted the porous medium. The system is cooled from below, above and a vertical side wall. The hot and cold surfaces were multi-pass heat exchangers made from copper plates. The other walls of the test cell were made of acrylic plate.

Six thermocouples were placed along the surface of both heat exchangers to check the uniformity of the temperature along their faces. A booster pump was installed to increase the coolant flow rate through the cold wall on the discharge side of the constant temperature bath. In the freezing experiments from below and above wall, fifteen thermocouples were placed at equal intervals between $\eta=0.07$ and $\eta=0.93$. For the freezing experiments from a vertical side wall, fifteen thermocouples were placed at the same position $\xi=0.07$, 0.26, 0.44, 0.62 and 0.81 and $\eta=0.11$, 0.5 and 0.89 on the center line of the test cell. All thermocouples (type T) were calibrated with an accuracy of ± 0.1℃. The surface temperatures of the heat exchangers and the temperature distribution in the test cell were recorded by an HP3497 data acquisition system at predetermined time intervals(150 seconds).

Ethyl-alcohol (100%) was circulated through the heat exchangers from constant temperature baths (NESLAB ULT-80DD and HAAKE A82).

Distilled and deionized water was mixed with requisite amounts of research grade NACl to obtain the desired salt concentrations, and the solution was carefully siphoned into the test cell to eliminate introducing of air bubbles. Through appropriate valve settings, the cold and hot walls could be maintained at either the same temperature to achieve the thermal equilibrium in the test cell before initiating an experiments or imposing a different temperature to start the experiment.

During the freezing process few drops of solution were extracted by hypodermic needles to measure the salt concentration in the liquid and the mushy regions using the Kernco hand refrectometer.

3. RESULTS AND DISCUSSION

Nine experiments with initial salt concentration of 5, 10 and 15% and different cold and hot wall temperatures were conducted and are listed in Table 1. The orientation of the cold wall was varied and the experiments are designated as follows: below(Exps. B-1 through B-3), above (Exps.A-1 through A-3), and vertical side wall(Exps.S-1 through S-3). Sodium chloride solution (Nacl+H_2O) is an aqueous binary solution with an eutectic temperature of -21.12 ℃ and eutectic composition of 23.31% by weight(Fig. 1). All experiments were on the hypoeutectic composition side, the cold wall temperature was lower than the eutectic point, and the hot wall temperature was higher than the liquidus temperature. Under these experimental conditions three distinct regions - solid, mushy and liquid region - come into existence during the freezing process. As a hypoeutectic saline solution freezes, the solute is rejected from the solid-liquid interface to the liquid and is redistributed both by diffusion and convection from the mush region to the melt. As a result, the salt concentration in the liquid increases from the initial salt concentra-

Table 1. Summary of the experimental conditions

Exp.	Ci(%)	Teq(℃)	Tc(℃)	Th=Ti(℃)	Ra*
A-1	5	-3.0	-39.4	9.4	848
A-2	10	-6.5	-39.4	9.4	1287
A-3	15	-10.7	-39.4	9.4	1392
B-1	5	-3.0	-39.4	4.0	479
B-2	10	-6.5	-39.4	4.0	844
B-3	15	-10.7	-39.4	9.9	1426
S-1	5	-3.0	-39.4	14.0	1163
S-2	10	-6.5	-39.4	13.9	1641
S-3	15	-10.7	-39.4	13.8	1694

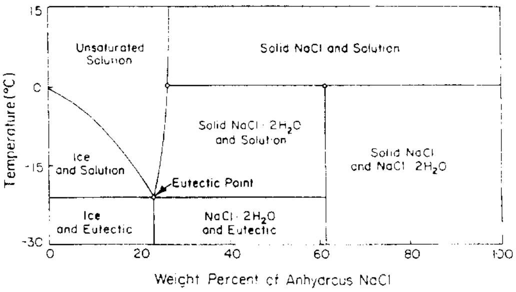

fig. 1 Equilibrium phase diagram for sodium chloride solution

tion as freezing progresses.

Figure 2 shows the typical dimensionless temperature distribution θ as a function of dimensionless position η for experiment A - 2. In the experiment, the eutectic point is at θ= 0.375, and the liquidus temperature is at θ= 0.746. The temperature distributions in the solid and mushy regions are practically linear. These figure show that at η= 0.74 there is vigorous natural convection and that there is little change in temperature 3 hours after the freezing process was initiated. The effect of the initial salt concentration on the freezing rate can be examined by comparing the temperature distributions at t= 1, 5 and 9 hours after the freezing process was initiated.

In the freezing experiments from below (Exps. B - 1 and B - 3), as shown in Fig.3, there was little effect of the initial salt concentration on the temperature distribution, and the temperatures for Ci= 15% are lower than those for Ci= 5% throughout the freezing process. The differences in temperature are small, however, in the freezing experiments from above (Exps. A - 1 and A - 2). The effect of the initial salt

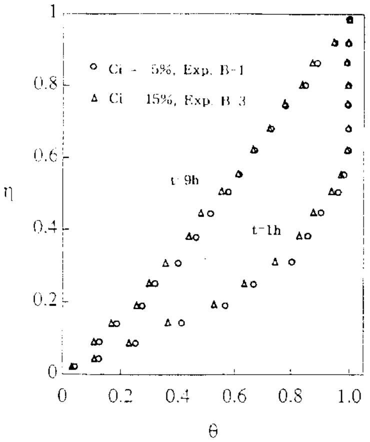

fig. 3 Effect of initial salt concentration on temperature distributions between Exp.B - 1 (Ci=5%) and Exp.B - 3 (Ci=15%)

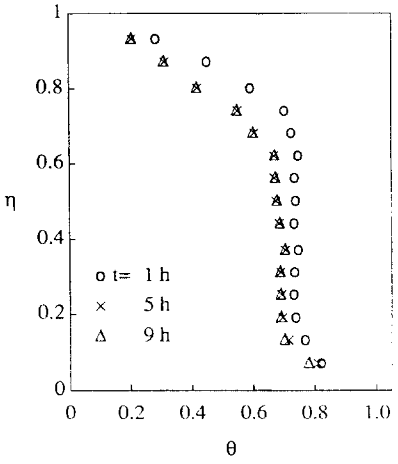

fig. 2 Temperature distribution at the vertical center line of the test cell at t=1, 5, 9h for Exp. A - 2.

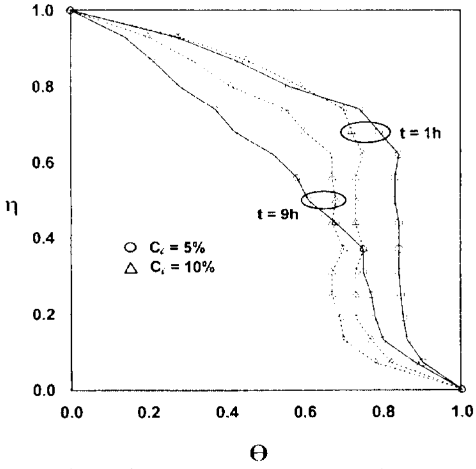

fig. 4 Effect of initial salt concentration on temperature distributions between Exp.A - 1 (Ci=5%) and Exp.A - 2 (Ci=10%)

concentration was small in the vicinity of cold top wall at the early times of the freezing process (t=1 h) (refer to Fig.4). However, as the freezing progressed the temperature difference between the Ci= 5 and 10% initial salt concentrations increased. The temperature for Ci= 5% in the immediate vicinity of the cold top wall was lower than that for Ci= 10%. At locations away from the cold top wall, the temperatures for Ci= 5% are inverted, and the temperature becomes higher than these for Ci= 10%. This is caused by the increased superheat and vigorous natural convection during the freezing of saline solution.

In order to measure the concentration in the mushy and liquid regions during the freezing process, few drops of saline solution were extracted by the hypodermic needles, and measured concentration variation by Kernco hand refretometer. For the freezing experiments from above, the hypodermic needles were placed on the vertical center line at η= 0.19, 0.80 and 0.87. As shown in Fig.5 (measured at η= 0.87), the concentration in the mushy region increases rapidly at the early times of the freezing process, but the increases levels off as the, eutectic composition is approached. The same phenomena was observed as for the freezing experiments from below and the vertical side wall.

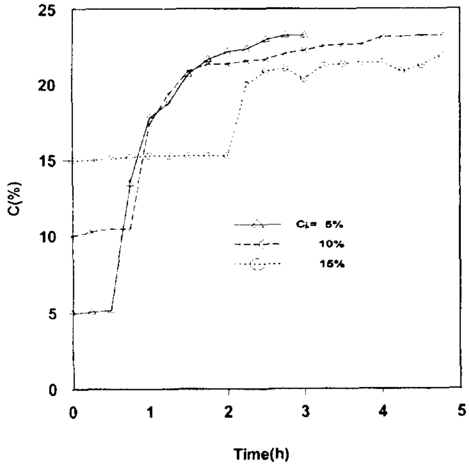

fig. 5 Concentration variation with time during the freezing from above at η= 0.87

During these freezing experiments it took longer to reach the eutectic point from the initial salt concentration as the initial salt concentration is increased. This indicates that the freezing rate is increased with a decrease in the initial salt concentration. For the freezing experiments from below, there is no change in the concentration at the upper part of the liquid region (η= 0.80). This illustrates that the thermal and solutal fields are very stable and convection currents are absent in the system.

In the freezing experiments from above, the concentration variations observed in the liquid were relatively small at the position of η= 0.19. This is due to active thermal and solutal convection in the porous medium during the freezing process. In the freezing experiments from the left vertical side wall, three experiments with Ci= 5,10 and 15% by weight salt were performed. In the lower part of the liquid region (η = 0.13 and ξ= 0.74), the liquid concentration increased to 6.8, 12.8 and 18.9%, respectively, by weight salt 4 hours after the freezing was initiated. However, in the upper part of the liquid region(η=0.87 and ξ=0.74) the concentration variation is less than 0.2% by weight salt. This means that a stratified and stagnant layer developed in the bottom part of the liquid region, and this layer is separated from the remaining bulk liquid (where natural convection is present) by a thin interface. This enriched solute may lead to constitutional supercooling in the melt during the freezing process.

Figure 6 illustrates the effect of initial salt concentration on the location of the mush/liquid interface at t= 9 h for the freezing experi-

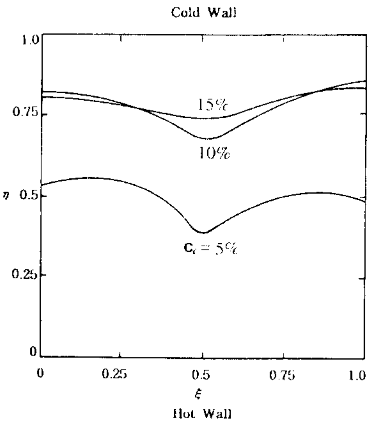

fig. 6 Effect of initial salt concentration for Experiments A-1, A-2 and A-3 on the mush/liquid interface position at t= 9 h

ments from above. The figure reveals that the extent of the mushy region is decreased, and the interface becomes flatter as the initial liquid concentration is increased.

In the freezing experiments from below, the locations of the mush/liquid interface was not affected by the initial salt concentration but was influenced by the cold and hot wall temperatures. Figure 7 shows the locations of mush/liquid interface for the freezing experiments from a vertical side wall at t= 2 and 8 hours after the process was initiated. In the figure the dashed-line, dashed-dot-line and solid line represent the positions of the mush/liquid interface for Ci= 5% (Exp.S-1), 10% (Exp.S-2), 15% (Exp.S-3) by weight salt, respectively. The global freezing rate(i.e., average frozen layer thickness) decreased, and the ridges formed moved downward with an increasing the initial salt concentration. This is owing to the fact that natural convection was more vigorous, and the thickness of the solutally stratified layer decreased with a decrease in the initial salt concentration. The solutally stratified layer which developed in the lower part of the liquid region was thicker near the hot wall than at the mush/liquid interface. In the freezing experiments from below and above, remelting was not observed at the solid/mush and/or mush/liquid interfaces. But, in the freezing experiments from the vertical side wall, remelting was observed only at the mush/liquid interface for the experiments with Ci= 10 and 15% by weight salt, but not for Ci= 5%. This remelting occured in the lower part of the test cell where the local freezing rate was maximum at the end of the freezing process.

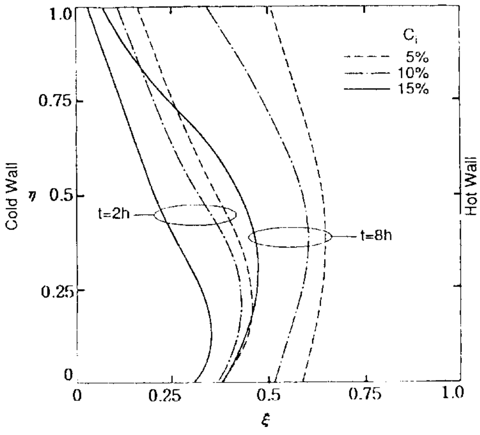

fig. 7 Location of mushy-liquid interface for Ci= 5% (Exp.S-1), 10% (Exp.S-2) and 15% (Exp.S-3) at t=2 and 8 h

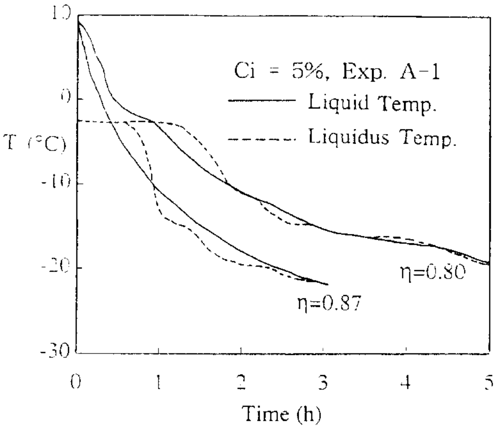

fig. 8 Dependence of the liquid and liquidus temperatures on time for freezing from above with Ci=5% (Exp. A-1)

Figure 8 illustrates the relation between the liquid and liquidus temperatures during freezing from above. In this figure the solid line represents liquid temperature measured by the thermocouples, and the dashed line denotes liquidus temperature corresponding to the measured concentration of saline solution during the freezing process. In the freezing experiments from below, supercooling was observed throughout the freezing process at the vicinity of the cold bottom wall ($\eta=0.25$) because the thermal diffusivity of the salt solution is two orders of magnitude greater than the mass diffusivity. At the position of $\eta=0.31$ and $\xi=0.5$, very small supercooling was observed at early times of the process. After that, liquidus temperature was lead to lower than the liquid temperature. The same phenomena was observed for experiments with Ci= 10 and 15% by weight salt.

In the freezing experiments from above[4], the hypodermic needles were located at the position of $\xi=0.5$ and $\eta=0.80$ and 0.87. For Ci= 5%, at the early times of the freezing process, relatively small supercooling was observed. But, as the freezing continued, the liquid temperature became higher than the liquidus temperature. For Ci= 15%, supercooling of the alloy was not observed, and the liquid temperature was higher than the liquidus temperature throughout the freezing process. The supercooling is caused by much smaller mass transfer rate than the heat transfer rate and the fact that convection in the mush region is affected by vigorous natural convection. In the freezing experiments from the vertical side wall (Ci= 5%), supercooling was observed only at the early times of the process. As the freezing continued, the liquid temperature became higher than the liquidus temperature. But, for Ci= 15% by weight small supercooling was observed throughout the freezing process.

4. CONCLUSIONS

A number of freezing experiments have been performed to investigate the effect of the initial liquid concentration on heat and mass transfer during freezing of an aqueous sodium chloride solutions saturating a porous medium from below, above and a vertical side wall.

For the freezing experiments from below, there was little effect of initial salt concentration throughout the freezing process, and the freezing rate was not affected by the initial salt concentration.

For the freezing experiments from above, the size of the mushy region was decreased, and the mush/liquid interface became flatter as the initial liquid concentration was increased. For Ci= 5%, at the early times of the freezing progress, relatively small supercooling was observed. But as the freezing continued the liquid temperature became higher than the liquidus temperature. For Ci= 15% supercooling of the alloy was not observed, and the liquid temperature was higher than the liquidus temperature throughout the freezing process. The mush region was affected by natural convection motion.

For the freezing experiments from a vertical side wall, reheating of the mixture was intensified with an increase in the initial salt concentration. This gave rise to remelting at the mush/liquid interface. The global freezing rate decreased, and the ridges moved downward with an increase in the initial salt concentration.

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