◉ 研究論文

SOLIDIFICATION OF AQUEOUS BINARY SOLUTIONS SATURATED PACKED BED FROM ABOVE

J. Choi and B.C. Kim*

다공성물질이 충전된 수용성 혼합용액의 동결거동에 관한 실험 연구

최 주 열*·김 병 철

Abstract

다공성 물질이 충전된 밀폐용기 내에서 수용성 이원혼합용액($H_2O + NaCl$)이 수평한 상부 전열면으로 부터 동결될 때 혼합용액의 초기농도, 액체의 과열 및 다공성물질의 입자직경 크기가 온도와 농도분포에 미치는 영향을 실험하였으며 동결이 진행됨에 따라 이동하는 고액상 혼합영역의 계면위치를 측정하였다. 다공성물질은 평균직경이 2.85mm, 6mm인 구형의 유리 구슬을 이용하였다. 수용성 혼합용액의 초기농도는 공융농도도 이하로 하였으며 상부 전열면 은 공융온도 이하로, 하부전열면은 액상선온도 이상으로 유지하여 동결 실험한 결과 상부 전 열면으로 부터 고체영역, 고액상혼합영역, 액체영역으로 구분되었다. 액체의 초기농도가 5% 인 경우 과냉현상이 관찰되었으나 10%, 15%인 경우 액체온도는 액상선 온도보다 더 높았 다. 용액의 초기농도를 감소시킬 수록 고체와 고액상혼합영역의 범위는 증대되었으며 고액상 혼합영역과 고체영역의 계면은 더욱 강해진 자연대류에 의하여 2차원성이 증가된 형상을 보 였다. 용액의 자연대류는 다공성물질의 직경이 클 수록 증대되었으며 계면에서의 재용해현상 은 관찰되지 않았다.

NOMENCLATURE

C : concentration of solute, wt%
C_i : initial concentration of solute, wt%
D_a : Darcy number, K/H^2
d : mean bead diameter, mm
K : permeability, $d^2\phi^3/175(1-\phi)^2$, m²

H : hight of cavity, mm
L : width of cavity, mm
Ra* : modified Rayleigh number, $g\beta(T_h - T_{eq})KH/\nu\alpha$
T : temperature, ℃
t : time, s
z : vertical space cordinate measured from

* 정회원, 공학박사, 목포해양전문대학

the bottom, mm

η : dimensionless distance, z/H

θ : dimensionless temperature

ξ : dimensionless distance, x/L

ϕ : porosity

Subscripts

c : refers to cold surface

eq: refers to equilibrium corresponding to the initial salt concentration

h : refers to hot surface

i : refers to initial

INTRODUCTION

Solidification of multicomponent system saturating a solid permeable matrix is of considerable geophysical and technogical interest. Examples of such processes include of soil which occurs beneath roads, airstrips, burried utility lines and seasonal ice in cold climates. Long term freezing can occur beneath chilled pipelines, cryogenic storage tanks and year-round surface. In addition, artificial freezing of ground as a construction technique for supporting poor soils has been used in practice for some time. Metallurgical applications include solidification of ingots and castings and purification of materials. Other technological applications include freezing of mixtures and alloys saturating permeable matrix, manufacture of composite materials, production and preservation of biological materials etc. Reference is made to a recent review for applications[1], and an extensive literature source on problems of phase change heat transfer in porous medium. The complexity of heat and mass transfer during freezing of saturated porous matrix is mainly due to the conditions prevailing at the moving interface and the system undergoing solidification. The process is futher complicated by the structure (dendrite, columar, etc.) of the frozen/freezing liquid in the mushy region. Fluid motion is clearly possible in this two phase region. The presence of natural convection was studied during freezing of $NaNo_3$ solution from upper boundary[2]. During the freezing process of isopropanol and Na_2SO_4 from above[3,4,5], the thickness of the growing mushy layer, the disequilibrium at the mushy-liquid interface, an the compositional strativication within the solid were investigated both experimentally and theoretically. The effects of orientation, configuration, and temperature of a cold surface during the solidification of pure water and amonium chloride solution from below was studied experimentally[6,7]. Freezing of aqueous saline solution saturated packed bed in a rectangular cell were studied[8,9], and found that heat properties did not affect significantly in the mushy region.

The present paper reports are an experimental investigation concerned with freezing of a packed bed of glass spheres saturated by a water-NaCl mixture and cooled through the top wall. The paper examines the effects of initial mixture concentration, superheat and paticle diameter on temperature and concentration distributions, and documents the position of the mush-liquid regions of the solidifying system as a function of time. The main objective of the work is to obtain fundamental understanding of the heat and mass transfer processes during solification and experimental data which could later be used to validate theoretical solidification models.

EXPERIMETAL APPARATUS AND PROCEDURE

Freezing experiments wers performed in a squrare cross-section test cell with inner dimensions of 149.2mm in height and 73mm in depth. Figure 1 shows schematically the experimental apparatus. The front, back and side wall of the test cell were made of acrylic plate. The horizontal bottom and top surface were made of acrylic plate. The horizontal bottom and top surface were copper plates of multi-pass heat exchangers and served as hot and cold walls. All acrylic walls were insulated with 50mm thick Styrofoam to achieve the adiabatic conditions. Ethyl-alcohol (100%) was circulated through the heat exchangers from constant temperature baths. Sperical soda - lime glass beads having average diameters 2.85mm and 6mm constituted the porous medium. Distilled and deionized water was mixed with requiste amounts of research grade NaCl to obtain the desired salt

concentrations. Heat exchangers were connected through a valve system to two constant temperature baths (NESLAB ULT-80DD and HAAKE A82). The temperature of the hot bottom wall was maintained throughout the experiment at the same value as the initial liquid temperature. A booster pump was installed to increase the coolant flow rate through the cold wall on the discharge side of the constant temperature bath. Six thermocouples were placed along the surface of both heat exchangers to achieve the uniformity of the temperature along their faces, and fifteen thermocouples were placed at the equal intervals between $\eta = 0.07$ and $\eta = 0.93$ on the vertical center line of the test cell. All copper-constantan thermocouples (type T) were caliblated with an accuracy of $\pm 0.1°C$. The wall temperatures of the heat exchangers and the temperature distribution in the test cell were recorded by an HP3497 data logger system at predetermined time intervals (150 second). During the freezing process, few drops
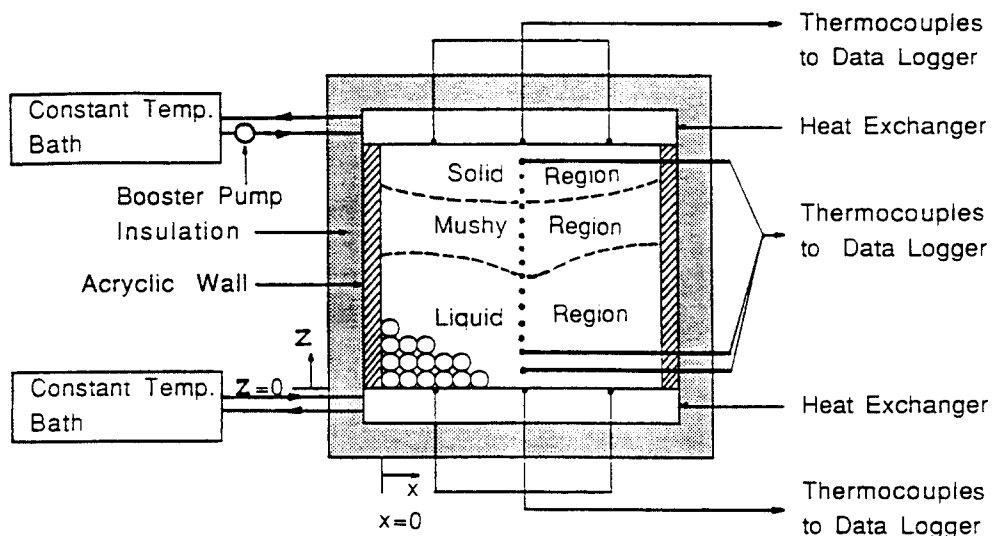

Fig. 1   Schematic diagram of the test cell.

of solution were extracted by hypodermic needles to measure the concentration of the liquid and the mushy regions using the Kernco Hand Refrectometer. Experiments for temperature measurement, flow visualization and concentration measurement were conducted seperately to avoid heat gains or losses from the ambient and the disturbance of the flow and temperature fields.

RESULTS AND DISCUSSION

Nine experiments were conducted and are listed in Table 1. Sodium chloride solution is an aqueous binary system with an eutectic point at-21.12℃ and eutectic composition of 23.31% by weight salt. In the study reported in this paper, all experiments were on the hypoeutectic composition side, and cold wall temperature was lower than the eutectic point, and hot wall temperature was higher than the liquidus temperature. When alloy saturated with porous medium is frozen from above, freezing occurs in the pores of the solid matrix and it is such that three distinct regions come into existence. In the solid region adjacent to the cold top wall, the pores of the matrix were occupied by the frozen solid and appeared white and easily distinguishable from the mush region. When freezing takes place in the mush or mixed region, solid and liquid coexist at various temperatures depending on the concentration of the binary alloy system. The liquid region adjacent to the hot bottom wall is simply a part of the porous medium saturated with the saline solution that has not yet been solidified.

Figure 2 shows the temperature distributions as a function of time for experiment 4, and illustrates that there is natural convection in the vicinity of the hot
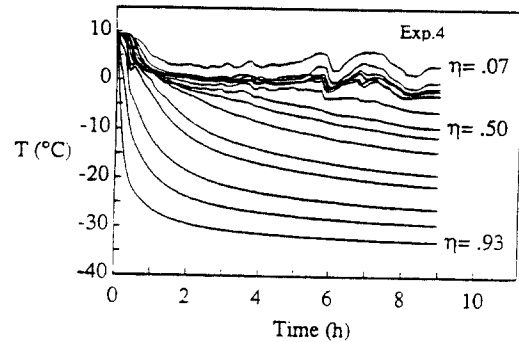

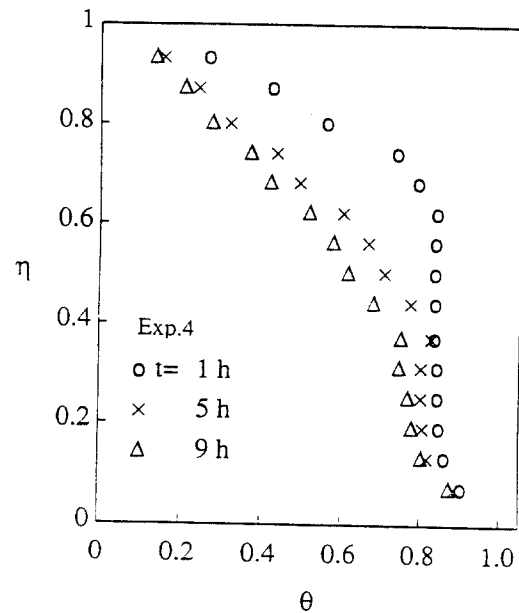**Fig. 2**   Temperature vs. time history for experiment 4.

Fig. 3   Temperature distribution of the center line of the test cell for experiment 4.

wall. A typical dimensionless temperature distribution θ as a function of dimensionless position η for experiment 4 is shown in Fig. 3. The temperature distributions in the solid and mushy regions are practically linear. In this figure, the eutectic point is at $\theta = 0.375$ and the liquidus temperature is at $\theta = 0.746$. The temperature data reveal that at early time(t = 1hr) during the freezing process natural convection is much more vigorous than during

later times(t = 9h). This is owing to the fact that the solutal buoyancy force opposes the thermal buoyancy force and the former increases relatively to the latter as salt is rejected into the melt and the salt concentration increases with time.

Figure 4 compares the temperature variation with time for 2.85mm(Da = 2.28 × 10^{-7}) and 6mm(Da = 15.7 × 10^{-7}) bead diameters at the vertical center line of locations η = 0.87, 0.68 and 0.50. In this figure, the solid line represents the data for experiment 2(d = 2.85mm) and the dashed line is for experiment 4(d = 6mm). There was little effect of the bead diameter in the vicinity of cold top wall(η = 0.87). But, at positions η = 0.68 and 0.50, the effect of the bead diameter is clearly discernible, and temperatures for d = 2.85mm are lower than for d = 6mm. At early times of the freezing process, the temperature distribution for d = 6mm is lower than for d = 2.85mm, because of more vigorous natural convection in the vicinity of η = 0.5.

The effect of initial salt concentration on the freezing rate can be examined by comparing the temperature distributions for Exp.4 and Exp.5. Figure 5 shows the temperature distributions at the vertical
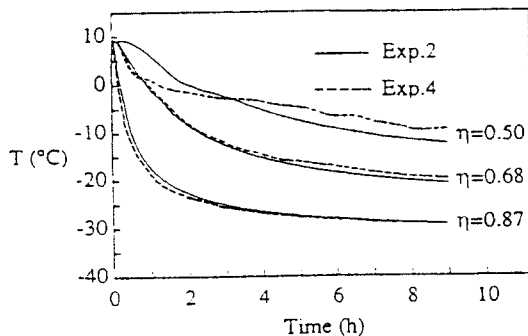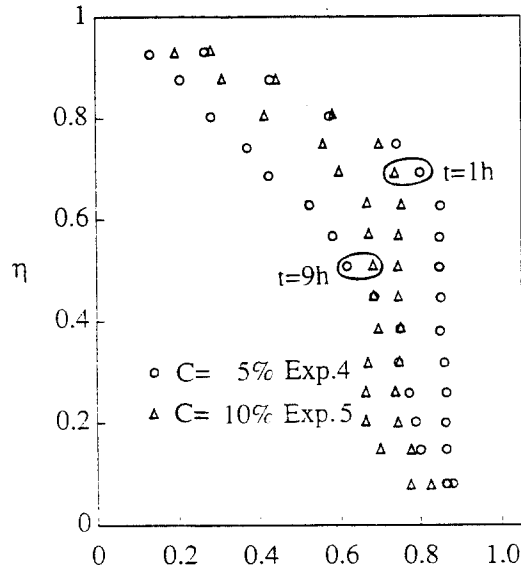

Fig. 5 Effect of initial salt concentration on the temperature distribution for experiments 4 and 5.

center line for C_i = 5%(Exp. 4) and C_i = 10% (Exp. 5) by weight at t = 1 and 9 hours after the freezing process was initiated. At early times of the freezing process(t = 1h), the effect of the initial salt concentration was small in the vicinity of cold top wall. As the freezing progressed, the temperature difference between the C_i = 5 and 10% initial salt concentrations increased. The temperature for C_i = 5% in the immediate vicinity of the cold top wall was lower than that for C_i = 10%. But, at locations away from the cold top wall, the temperatures for the C_i = 5% initial salt concentration are inverted. The temperatures become higher than that for C_i = 10% intial salt concentration. This is caused by the increased superheat and vigorous natural convection during the freezing of the saline solution.

Figure 6 illustrates the effect of superheat for the 6mm diameter beads during the freezing. The solid lines denote the data for
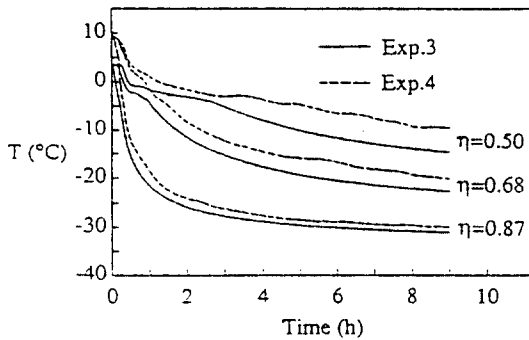

Fig. 4 Effect of bead diameter on the temperature vs. time history for experiments 2 and 4.

Fig. 6 Effect of superheat for 6mm diameter beads.

experiment 3 and the dashed lines represent the data for experiment 4 at $\eta = 0.5$, 0.68 and 0. 87, respectively. As shown in Figure 6, the effect of the superheat was small near the cold top wall. The effect of the superheat for the smaller diameter beads($d = 2.85$mm) was considerble smaller than that for the larger(6mm) diameter beads because of relatively small permeability. According to the Kozeny–Carman equation, the permeability, K, is proportional to the square of the particle diameter.

As a hypoeutectic saline solution freeze, the solution is rejected from the solid–liquid interface to the melt and is redistributed both by diffusion and convection from the mushy region to the liquid region. As a consequence, the salt concentration in the liquid increases from the initial salt concentration as freezing progresses and salt is rejected as more solution solidfies. In order to measure the concentration variation in the mushy and liquid regions during the freezing process of Nacl solution, three experiments(Exp.7 to 9) were conducted. Few drops of solution were extracted by the hypodermic needles located on the verticla center line at $\eta = 0.19$, 0.80, and 0.87. The concentration in the mushy increases rapidly at early times of the freezing process,

but the rate of increase levels off as the eutectic composition is approached. The variation of the concentration observed in the liquid was relatively small. This is caused by active thermal and solutal convection in the cavity during the freezing process. It takes longer to reach the eutectic point from the initial salt concentration as the initial salt concentration is increased. This implies that the freezing rate is increased with a decrease in the initial salt concentration. Figure 7 and 8 show the relation between the liquid and
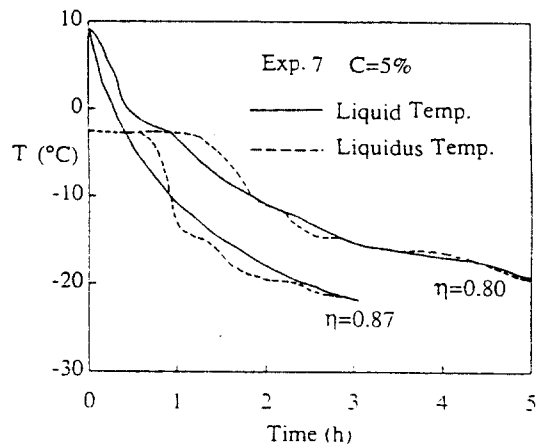

Fig. 7 Dependence of the liquid and liquidus temperatures on time for experiment 7.
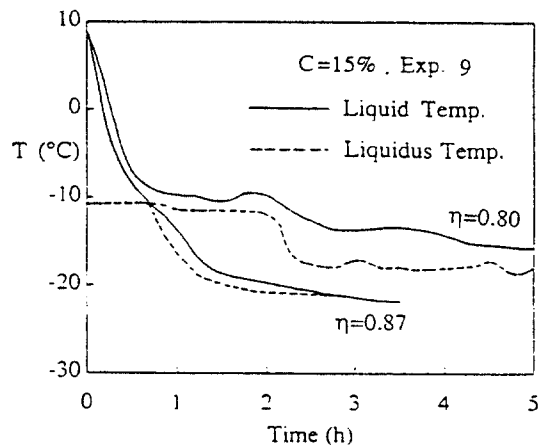

Fig. 8 Dependence of the liquid and liquidus temperatures on time for experiment 9.

liquidus temperatures during freezing of saline solutions at $C_i = 5\%$ and 15%, respectively. In these figure, the solid line represents the actual liquid temperature measured by the thermocouples and the dashed line denotes the liquidus temperature corresponding to the measured concentration of saline solution during the freezing process. The hypodermic needles were located on the vertical centerline at $\eta = 0.80$ and 0.87. In the case of $C_i = 5\%$, at the early times of the freezing process, relatively small supercooling was ovserved. But, as the freezing continued, the liquid temperature became higher than the liquidus temperature. For $C_i = 15\%$, supercooling of the alloy was not ovserved, and the liquid temperature was higher than the liquidus temperature throughout the freezing process. It appears that this is caused by the relatively lower mass transfer rate than the heat transfer rate, and the fact that concentration in the mushy region was affected by vigorous natural convection. These observed temperature differences indicate the strength of the remelting. In this study, there was only a very small increase in the temperature at the upper part of the mushy region. The magnitude of the temperature rise was too small to change the solid-mush and mush-liquid interfaces.

A flow visualization technique was based on the PH variation due to the electrolysis and consequent coloration of phenolphtalein in aqueous solution around a cathode[10]. At the early times of the freezing process, flow ascents from the outer side and descends to the inner side of the cavity. As the freezing progresses the circulation pattern changes gradually, and finally symmetrically shaned cells develop on either vertical side of the vertical plane passing through the center line

of the test cell. The dye generated during the experiment was incorporated into the surface of the mushy region where the local solid fraction is relatively small. This phenomena indicates that fluid penetrates the mushy region.

The mushy liquid interface evolutions during of the freezing was traced from the test cell side and are shown in Fig.9. Initially, a flat
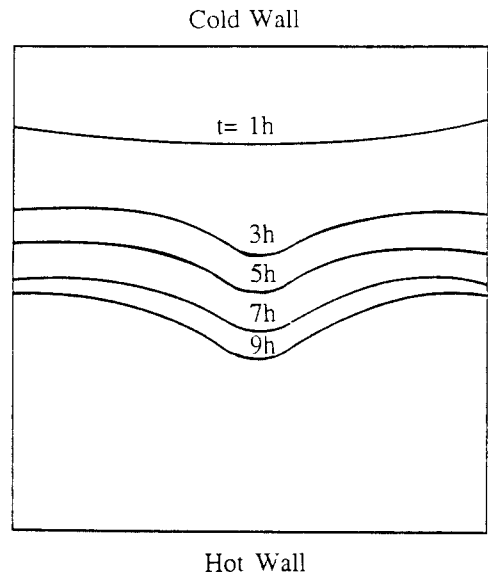
Cold Wall

Hot Wall

Fig. 9 Evolution of the mush-liquid interface with time for experment 2.

horizontal solid and mushy region was formed on the cold top wall. As the mushy region continues to grow, the mushy-liquid interface moves further at the center line of the cell because of thermal and solutal driven natural convection. The local freezing is increased at the vertical center line of the cavity and decreased at both side of the cavity. Figure 10 represents the locations of the mushy-liquid interface with concentration variation at t = 9h. The figure reveals that the size of the mushy region is decreased and the interface becomes flatter as the initial liquid
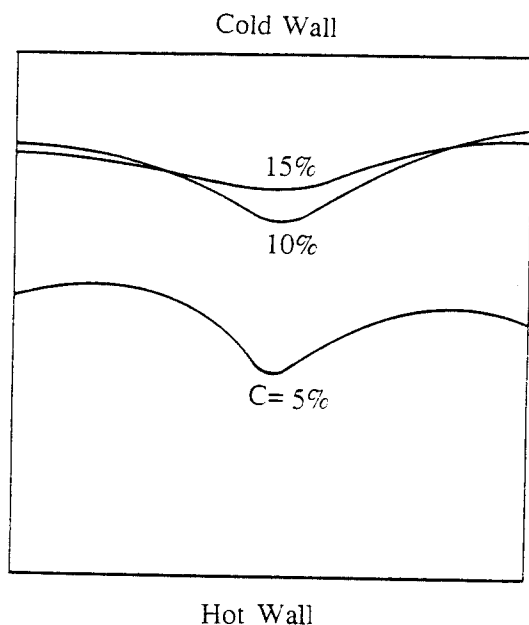
Cold Wall

Fig. 10   Effect of initial salt concentration on the
mush-liquid interface position at t=9h.

concentration is increased.

Freezing of a binary water-ammonium choride(H_2O-NH_4Cl)   solution saturating a packed bed of soda lime glass spheres was investigated experimentally by Cao and Poulikakos[11].   The bed was cooled through its top wall and heated at the bottom. They reported remelting phenomena at the solid-mushy and mushy-liquid interfaces caused by the thermal inertia and flow resistance of the packed bed. The remelting was more severe when the bottom wall was heated. To study the remelting at the solid-mush and/or mush-liquid interface during the freezing of aqueous saline solution saturating a porous medium, a number of freezing experiments were performed within the range of $T_c = -39.4$ to $-26.4°C$, $T_h = 3.5$ to $23°C$, $d = 2.85mm$ or $6mm$ and $C_i = 5$ to 15%. In the present experiments, remelting was not ovserved at both interfaces. In experiment at $T_c = -26.4°C$, $T_h = 23°C$, $C_i = 5\%$ and $d = 2.85mm$,

there was a small rise in temperature (about 0.5°C) at the upper part of the mushy region. However, during the experiments to observe the occurance of the remelting phenomena, the length of time that the window was removed was minimized to avoid heat gains from the ambient. As already mentioned, the experiments to measure temperature, visualize the flow structure and measure salt concentration were conducted separately to avoid heat gain from the ambient or disturbance of the flow in the test cell

CONCLUDING REMARKS

A number of freezing experiments have been concucted to investigate the effects of the bead diameter, liquid superheat, and initial liquid concentration on the heat transfer rate and the interface positions during freezing from above of aqueous sodium chloride solutions saturating a porous medium. There was a small effect on the bead diameter in the vicinity of the cold top wall, but away from the cold wall, the effect of the bead diameter was clearly discernible, and the temperatures for the 2.85mm diameter beads were lower than those for the 6mm diameter beads. The effect of superheat on the heat tranfer and the freezing rates was greater as the bead diameter and the cold top wall were increased. Near the cold top wall, the temperature for $C_i = 5\%$ was lower than that for $C_i = 10\%$, but away from the wall, the temperature vs. time variation for $C_i = 5\%$ initial salt concentration was inverted and became higher than that for $C_i = 10\%$.   This was due to increased superheat and more vigorous natural convection. Supercooling was oberved only at times of the freezing process for the experiment with $C_i = 5\%$,   and in the

experiments with $C_i = 10$ and 15%, the liquid temperature was found to be higher than the liquidus temperature throughout the entire freezing process. A decrease in the initial salt concentration increased the extent of the solid and mushy regions and the flat mush-liquid interface became more non-planar as natural convection in the melt intensified. There was a small temperature rise at the upper part of the mushy region, but remelting phenomena was not observed at both the solid-mush and mush-liquid interfaces.

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