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Observation of Freezing Phenomena in Saturated Mixture

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Abstract

Several saturated mixtures, such as methyl orange solution, agar, glass beads, bentonite, and sand, were frozen downward using a specially designed freezing apparatus to grasp the characteristics of freezing phenomena. Exclusion of solute with advancing freezing front was observed in the methyl orange solution, while not in the column of agar. It was found from comparison of the temperature profelies which were measured in each freezing sample that macroscopic water convection did not occur during freezing in the columns of agar, clay, and sand while it occurred in the methyl orange solution.

Key words: Freezing phenomena · Exclusion of solution · Temperature profiles

I. Introduction

Soil freezing induces upward movement of water from unfrozen to frozen regions in soils[1–3]; subsequently the soil expansion called frost heaving takes place.[4–7] To prevent disasters by the frost heaving, such as destruction of paved roads, breakdown of buildings, heaving of railways, and severance of plant roots, the transport of water and heat during soil freezing has been studied extensively in cold regions.[4–6]

From the viewpoint of chemical pollution of the environment, the problem of chemicals used to prevent frost heaving has recently been pointed out.[7] For example, de-icing salt[8], used in winter to reduce the frost heaving of paved roads, often flows into a river and causes water pollution. Also, when the frozen soil thaws in fields, the melt water, enriched with nutrients which are concentrated during freezing in winter, runs into rivers and lakes. In order to solve such problems, it is important to know movement of solute in soils subject to freezing.

Freezing is a phenomenon in which liquid phase changes into soild phase with decreasing temperature. During the freezing of saline soil, not only the transport of heat and water but also exclusion of solute occurs.[9–11] The observations of the heat transfer and the exclusion of solute during freezing are helpful to analyze the transport phenomena of soil water, heat and solute in freezing soils. In this study saturated mixtures, such as methyl orange solution, agar, glass beads, bentonite, and sand, were frozen dowanward on temperature condition that the upper end was at −10°C and the lower end was at 5°C. Temperature profiles and solute exclusion during freezing are described for each freezing sample in the paper.

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II. Experimental Method

1. *Apparatus*

A schematic diagram of experimental apparatus is shown in Fig. 1. Samples were frozen downward. A tube for a sample was a Plexiglas cylinder, 80 mm inside diameter, 250 mm long and 4 mm thick. The upper and lower ends of the tube were covered with Aluminum plates and attached to water jackets. Theremocouples (E: chromel-constantan of 0.1 mm diameter) were fixed in the center of a sample to measure temperature by an AD converter and a computer. To keep the position of the thermocouples from the shift due to freezing expansion, they were fixed at the depth of 0, 0.5, 1.0, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20 and 25 cm in a rod, 250 mm long and 2.5 mm square. The column had a drain in the lower part of the samples in order to keep water table level at the upper end and to prevent expansion pressure by freezing.

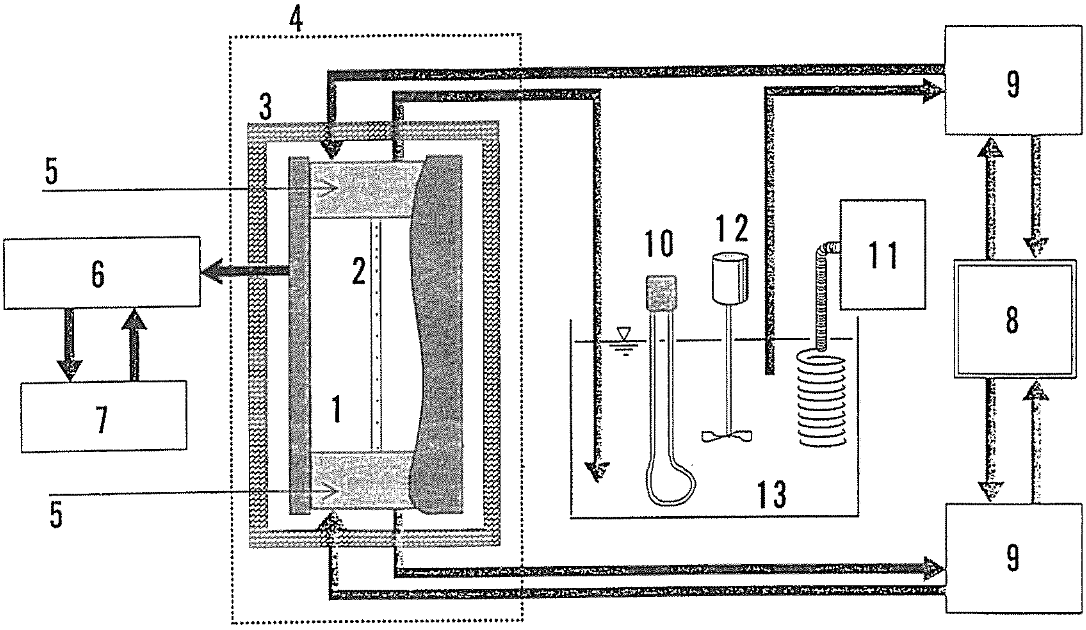

Fig. 1 Schematic diagram of experimental apparatus.
1. Sample 2. Thermocouples 3. Insulator box 4. Refrigerator 5. Water jacket 6. AD converter 7. Computer 8. Heat exchange 9. Pump 10. Heater 11. Cooler 12. Stirrer 13. Coolant

The sample, insulated with two sheets of cotton and 5 cm thick stylofoam, was in an insulation box to keep one dimensional heat flow. By circulating ethyl alcohol solution of which temperature was controlled by a cooler and a heater, the temperatures of the upper and lower water jackets were kept at −10°C and 5°C, respectively.

2. *Materials*

Materials used in the experiment were saturated mixtures: methyl orange solution, agar, glass beads, bentonite, and sand. The methyl orange solution was a mixture of pure water and proper methyl orange powder. The agar sample was a gel which was cooled in a tube after boiling with methyl orange solution. The bentonite sample was a paste of 748% water content, which was made of dried bentonite powder (Kunimine Koukakougyou, Kunigel-V1) and pure water. The glass beads (#80) sample was a pile which was saturated upward with methyl orange solution after being packed in a tube. The sand, Toyoura sand, was a pile which was saturated upward with pure water after being packed at the bulk density of 1.57 g/cm^3.

III. Results and Discussion

1. *Observation of freezing*

A sample was initially in a refrigerator of 5°C for 24 hours, and frozen for 24 hours at the upper and lower temperatures of −10 and 5°C, respectively. The characteristic of each sample was compared.

Photo. 1 and Photo. 2 show observations of freezing phenomena in the methyl orange solution and the agar, respectively. Frozen regions in the methyl orange solution were limpid because solute was excluded downward during freezing. On the other hand, frozen regions in the agar did not discolor. This result shows that the agar holds solute in the network.

As well as the methyl orange solution, the color of frozen regions in the glass beads sample turned white as shown in Photo. 3. However, when the frozen part of the sample thawed, the white color turned orange again as shown in Photo. 4. This means that the color of frozen glass beads turned white not because solute was excluded from frozen regions to unfrozen regions but because solute was remained in the freezing void and only its optical property changed by freezing.

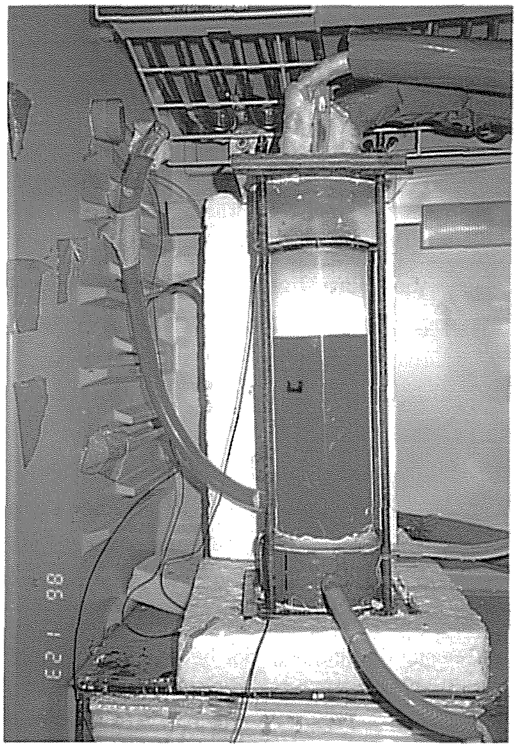

Photo. 1 Frozen methyl orange solution.

Photo. 2 Frozen agar.

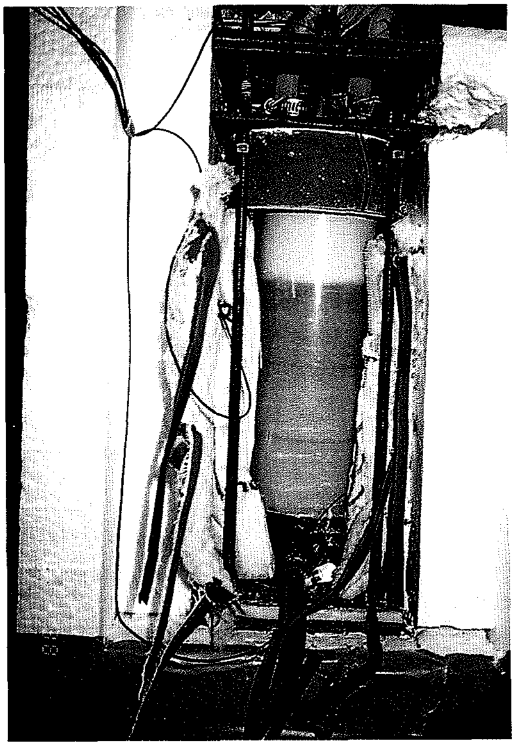

Photo. 3 Frozen glass beads containing methyl orange solution.

Photo. 4 Thawing the frozen glass beads containing methyl orange solution.

In the frozen saturated bentonite, ice wedges were observed downward as shown in Photo. 5; ice and clay particles were separated in the freezing clay and that ice segregation grew downward. This observation suggests that the freezing front (the boundary between frozen and unfrozen regions) was not plane. After thawing the frozen saturated bentonite returned to its original gel. Some investigators$^{12-14)}$ have observed by X-ray diffraction that the clay gels after freezing and thawing retained the arrangement of particles. As well as their observations, the bentonite used in the experiment also seems to have retained the arrangement of particles.

In the frozen agar sample, on the other hand, the ice wedges were not visually observed as shown in Photo. 2. Instead, vertical wrinkles were observed in the frozen regions after thawing as shown in Photo. 6. Nakagaki et al.$^{15)}$ have described that while the gelatin gels after freezing and thawing retain the arrangement the frozen agar gels lose water and become wrinkles after thawing, and referred the difference in the behavior between the gelatin and the agar gels to the amount of bonding water in the gels. The observation of the frozen agar agrees with their description, and according to them the bentonite will belong to the group of the gelatin. However, it is necessary to investigate the difference in the freezing-thawing behavior between the bentonite and the agar in details with respect to unfrozen water (bonding water).

Photo. 5 Frozen bentonite.

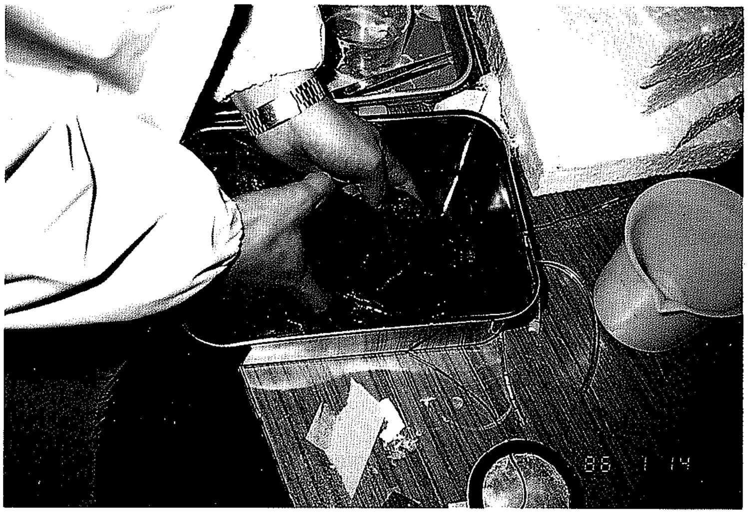

Photo. 6 Thawing the frozen agar.

2. *Temperature Profiles in freezing Samples*

Fig. 2 shows temperature profiles in the freezing methyl orange solution. The temperature profiles were spatially divided into three parts: upper, middle, and lower parts. The temperature of the middle part was constant at 4°C. This temperature profile is related to Benard convection and can be explained in terms of gravity and water density which is dependent on temperature.[16] In general, the density of liquid water is maximum at 4°C; it decreases at temperature below 4°C with decreasing temperature and decreases at temperature over 4°C with increasing temperature. Consequently, when the upper end of the solution having the initial temperature of 5°C is cooled, the upper water has the highest density at 4°C, thus falling down by gravity. When the whole solution except near the bottom reaches 4°C, freezing occurs from the top. As a result, the temperature profiles in the solution should be divided into three parts. This is related to three kinds of heat transfer in freezing solution: conduction in the part below 4°C, convection in the part at 4°C, and convection and conduction in the part at the temperature from 4 to 5°C.

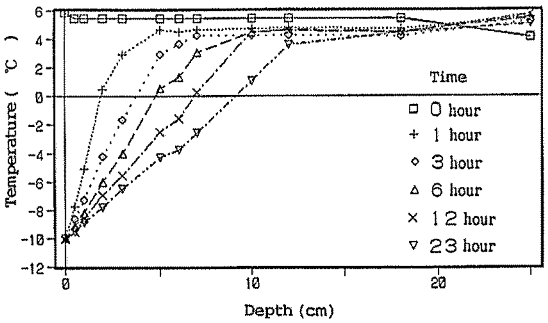

Fig. 2 Temperature profiles during freezing methyl orange. Initial temperature: 5°C, Boundary temperatures: −10, 5°C

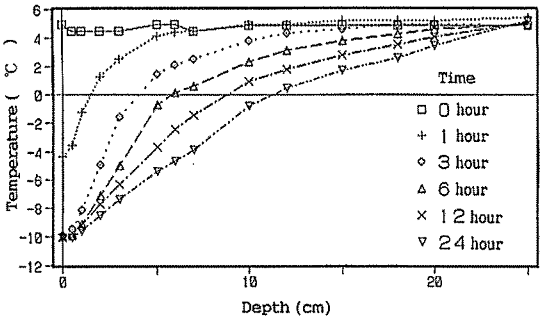

Fig. 3 Temperature profiles during freezing agar. Initial temperature: 5°C, Boundary temperatures: −10, 5°C

Fig. 3 shows temperature profiles in the freezing agar. The temperature profiles in the agar did not have such a 4°C part as appeared in the freezing methyl orange solution. Instead, the temperature decreased downward continuously. This resut suggests that macroscopic convection did not occur in the freezing agar. After 20 hours, the temperature gradients of frozen and unfrozen regions became constant and were about 1.0 and 0.33°C/cm, respectively. This is attributed to the difference in thermal conductivities between frozen and unfrozen agar.

From the observation of ice wedges in the frozen bentonite, the freezing front is assumed not to be plane. Therefore, latent heat of fusion per unit volume and thermal properties, heat capacity and thermal conductivity, will be spatially different in the frozen fringe. Then the thermal properties are expected to have some effects on temperature profiles. In the profile at 12 hours in Fig. 4, the temperature gradients around 9 cm appears to decrease slightly. However, we cannot assert that this is attributed to the effect of the thermal properties in the frozen fringe.

Fig. 5 shows temperature profiles in the freezing sand. The profiles did not have constant temperature regions and were analogous to the temperature profiles of the agar rather than of the methyl orange solution. This result suggests that less convection occurs macroscopically in the freezing saturated sand. Considering the macroscopic convection was not observed in the bentonite, the convection during freezing will be negligiblely small in a general saturated soil which is composed of several sized particles from clay to sand. Hence, the effect of convection can be ignored sufficiently in freezing unsaturated soils of which hydraulic conductivity is lower than saturated soils.

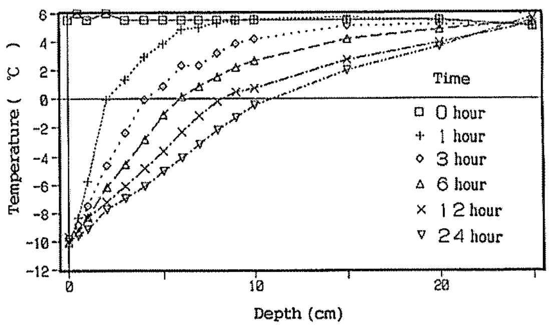

Fig. 4 Temeprature profiles during freezing bentonite gel. Initial temperature: 5°C, Boundary temperatures: −10, 5°C

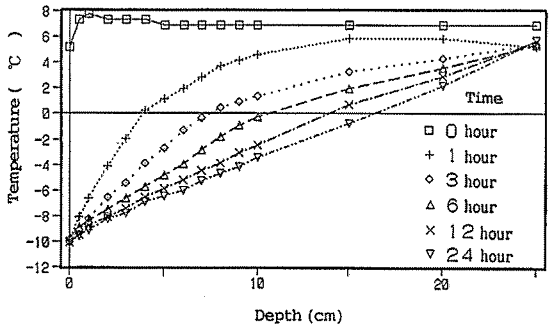

Fig. 5 Temperature profiles during freezing saturated sand. Initial temperature: 5°C, Boundary temperatures: −10, 5°C

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飽和混合物の凍結現象の観察

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凍結現象の特徴を把握するために，メチルオレンジ溶液および水分飽和状態の寒天，ガラスビーズ，ベントナイト，砂の各試料を，試作した凍結実験装置で下向きに凍結させた。メチルオレンジ溶液では凍結前線の進行に伴い溶質の排除が観察されたが，寒天試料では溶質の排除が見られなかった。各凍結試料に対する温度分布を比較することにより，寒天，粘土および砂では凍結過程で巨視的な水分の対流が起きないが，メチルオレンジ溶液では対流が生じていることがわかった。