An Experimental Study of Dynamic Solid-Liquid Phase Equilibrium in a Porous Medium*

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An experimental study has verified the dynamic equation of state derived from a thermodynamic model representing simultaneous heat and mass transfer from the liquid supply front to the solid-liquid interface in a liquid saturated porous medium. Measurement of pore liquid pressure at the solid-liquid interface fixed on the top surface of an Ohya-tuff specimen (the porous medium) enabled us to experimentally verify the relationship between temperature, pore liquid pressure and solid pressure at the interface, and liquid supply pressure. This experimental method was established by re-verifying the so-called Clausius-Clapeyron equation (GCCE), the static equation for a porous medium without liquid flow. This study also clarified the relationship between the dynamic equation of state and the GCCE on the pore liquid pressure-liquid supply pressure plane.

Key Words: Equation of State, Heat and Mass Transfer, Porous Medium, Solidification, Freezing, Frost Heave, Segregation

1. Introduction

When a porous medium saturated with liquid, for example water saturated clay, is freezing, the liquid migrates to the frozen part of the porous medium and freezes. This process causes expansion of the frozen part of the porous medium, and is known as the frost expansion phenomenon. This phenomenon is interesting from the thermal engineering point of view, because it is expected to be applied in future in the area of cryogenic heat accumulation systems.

Furthermore, frost heave, which occurs when soil freezes, causes deformation of in-ground and surface piping in cold regions. This phenomenon is also observed when ground is artificially frozen, for example, LNG in-ground storage tanks without heat barriers, which cause surrounding soil to freeze. In such

cases of low-temperature structures, the influence of this phenomenon needs to be predicted. Many experimental and theoretical studies have been carried out to derive a prediction method. Among them, Taber⁽¹⁾ confirmed experimentally that benzene or nitrobenzene in a porous medium causes the frost expansion. His findings imply that knowledge regarding frost heave is also valid for general frost expansion phenomena. That is, a liquid-saturated porous medium can be represented by a water-saturated soil when we study the frost expansion phenomenon. This enables us to easily compare the study results with published experimental data. Therefore, in this paper, we describe an experimental investigation on the dynamic solid-liquid phase equilibrium observed in the process of freezing liquid-saturated porous media, by using a soil saturated with water.

1.1 Frost heave phenomena and ice lenses

The most notable point of the frost heave phenomenon is the behavior of the pore water. The water saturating the soil (pore water) which does not move at room temperature migrates from the unfrozen soil to the frozen soil when the soil freezes. To clarify the basic character of frost heave, let us consider a

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simplified model comprising a cylinder of soil with a heat-insulated side-wall, a cooling source at the top and a heating source at the bottom. The soil is thus cooled one-dimensionally from the top down. The model is set such that the freezing front (temperature about 0°C) is in the soil and is parallel to the top and bottom faces. Above the freezing front, i.e., in a frozen soil, most of the pore water is frozen. However, in the frozen soil, water exists in the form of an unfrozen water film on the surface of the soil particles. This film can stay unfrozen due to depression of the freezing point caused by the physical and chemical effects of the soil particles⁽²⁾. It is known that the unfrozen water film is not frozen even at -30°C ⁽³⁾. This unfrozen water film enables water to migrate through the frozen soil.

As the freezing front moves downward, multiple horizontal layers of crystallized pure ice, called ice lenses, are generated in the frozen soil. These ice lenses, which do not contain soil particles, are observed as a striped pattern like a bar code. The frost expansion rate (frost heave rate) of the frozen soil as a whole is almost equal to the thickness increasing rate of the ice lens nearest the freezing front. It is 1.09 times the volume flux of water supplied from the bottom face of the soil cylinder (water supply front)⁽⁴⁾. It is noted that 1.09 is the specific volume ratio of ice to water. Thus, the frost expansion mechanism is understood to be as follows. The water, which travels through the unfrozen water film and reaches the bottom surface of the ice lens, comes out of the unfrozen water film. It then freezes to form part of the ice lens. This occurs because the water, which remains unfrozen in the water film due to the depression of freezing point, changes its state to that of sub-cooled water at the same temperature outside the water film, and is then ready to freeze. The bottom surface of the ice lens where ice and water co-exist is the end front terminating the water migration. It is also the front of changing solid-liquid phase where the latent heat of freezing is generated. Thus, this front is important since it plays the role of an inner boundary of the model used for the analysis of frost heave. Hereafter the front of the changing solid-liquid phase at the ice lens is called as the "ice lens forming front".

The main purpose of this study was to experimentally verify the equation of state which is valid at the ice lens forming front under the condition where the water migration and its accompanying phase change take place in steady state. In this paper, the condition in which water migration and heat transfer co-exist in steady state is referred to as the "dynamic state".

1.2 Dynamic state

Frost heave is usually observed in the unsteady

state. The process is too complicated to be rigorously described by an equation of state for the ice lens forming front, since the conditions change from hour to hour in the unsteady state. However, understanding the process at the ice lens forming front is indispensable to understand the frost heave phenomenon. Thus, an attempt is required to simplify it to find out its core principle. Specifically, the simplest cases of the frost heave phenomenon are studied where both water migration and heat transfer occur simultaneously in the steady state, in other words, the dynamic state. In the dynamic state, pore water migrating from the freezing front to the ice lens forming front does not freeze. Therefore, the frost heave phenomenon can be simply represented as the ice lens growth phenomenon.

If the pore water pressure at the ice lens forming front is known, the unfrozen water flow rate in the frozen soil can be determined. The unfrozen water flow rate in the frozen soil is proportional to the water pressure gradient in the frozen soil^{(5),(6)}, which is the same as for unfrozen soil. Therefore, the water flow rate, which is proportional to the frost heave rate, is determined by substituting the pressure difference between the pore water pressure at the ice lens forming front and the pressure at the water supply front (water supply pressure) into Darcy's law. Furthermore, if the temperature at the ice lens forming front is known, the heat flux into it can be quantified. This is obtained by substituting into Fourier's heat transfer law the temperature difference between the temperature at the ice lens forming front and that at the freezing front. It is noted that the latent heat due to freezing at the ice lens forming front is proportional to the mass flux of the water migrating to it. Thus, the pore water pressure P_{wi} and temperature θ_i are interrelated according to the equation of state for phase equilibrium at this front.

1.3 Theories and equation of state in published papers

A characteristic point in the soil-particles-water-ice system is that the ice pressure P_{ii} at the ice lens forming front is equal to the overburden pressure P_{oi} (the pressure imposed from the top to the ice lens) as external force. Furthermore, P_{ii} is supported by the sum of the pore water pressure P_{wi} at the bottom of the ice lens and the bearing pressure of the soil particles. Thus, $P_{ii} \neq P_{wi}$. In the water-ice system, $P_{ii} = P_{wi}$. Then, the well known Clausius-Clapeyron equation (differential equation form)⁽⁷⁾ becomes valid at the ice lens forming front in the water-ice system. Being similar to the derivation of Clausius-Clapeyron equation, the equation of state for the soil-particles-water-ice system is derived by starting with the

condition that the Gibbs' free energies of ice and water are equal, and then utilizing the condition that $P_{ii} \neq P_{wi}$. The differential equation is thus formulated. Finally, this differential equation is integrated from the reference state, yielding the following Eq. (1).

$$P_{wi}v_w - P_{ii}v_i - \frac{L_w}{T_o}\theta_i = 0 \quad (1)$$

Here, we assume that the specific volume of both ice and water phases and the latent heat of freezing are constant and the temperature change from the reference state is small.

In 1943, Edlefsen and Anderson⁽⁸⁾ clarified the physical meaning of Eq. (1) using a static thermodynamic model. They named this equation the "Generalized Clausius-Clapeyron Equation (GCCE)". Thereafter, the experiments⁽⁹⁾⁻⁽¹¹⁾ showed that GCCE (1) was valid where water migration did not take place under static conditions. It is thus obvious that GCCE (1) is the equation of state for the soil-particles-water-ice system when ice lens exist but no water migration takes place under static conditions.

However, typical methods for analyzing frost heave have employed the GCCE (1)⁽¹²⁾⁻⁽¹⁴⁾, assuming that frost heave accompanying water migration can be approximated by the static equation of state, GCCE (1). Thus, these methods have inherently poor accuracy when predicting the volume of frost expansion. To accurately predict this volume by using the theory proposed by Gilpin⁽¹⁴⁾, it is reported that correction needs to be applied for the physical properties of individual soils and then individual frost heave tests are necessary for each such soil⁽¹⁵⁾. It is not good practice to compensate the theoretical inconsistency by correcting the physical properties. However, this was done because insufficient investigation has been made from the thermodynamics point of view on frost heave for about 50 years since Edlefsen and Anderson⁽⁸⁾ made the investigation. Thus, it is currently necessary to carry out a study on the equation of state for phase equilibrium when water migration takes place.

1.4 Dynamic equation of state

The dynamic equation of state can be applied to the ice lens forming front where both water migration and heat transfer occur under steady state conditions. Before investigating the dynamic equation of state, the physical meaning of GCCE (1) has to be interpreted based on the assumption that the static condition can be regarded as an extreme case of the dynamic condition where the water migration volume is close to zero. The mechanical energy consumed by water migration under the static condition in this sense is very close to zero. The other work done in the static condition is the displacement work for the

phase change. The third term of the left hand side of GCCE (1) represents the total energy emanating when sub-cooled water changes to the ice phase, and the absolute value of the sum of the first and second terms of the left hand side represents the displacement work necessary for the phase change. Thus GCCE (1) implies that the total energy produced due to the phase change is all consumed in the displacement work for the phase change.

Here, an inconsistency arises when GCCE (1) is utilized in the above-mentioned methods⁽¹²⁾⁻⁽¹⁴⁾ for the frost heave analysis to determine the pore water pressure at the ice lens forming front when water migration occurs. The inconsistency is that water migration can be continuous, regardless of the influence of mechanical energy (available energy).

To remove this inconsistency and to establish a method, which predicts frost heave accurately, the thermodynamic investigation should be carried out. Firstly, the very small volume containing the ice lens forming front is defined as the system to be investigated, which is an open system in the isothermal process. Accordingly, the work that the system performs upon the surroundings is equal to the decrement of the Gibbs' free energy⁽¹⁶⁾. Two kinds of work are done by the system during frost heave in the steady state. They are the displacement work necessary for the phase change and the work necessary for water suction. As induced from the physical meaning of GCCE (1), the displacement work for the phase change is obviously included in the equation for the definition of the Gibbs' free energy. Thus, this external work must be the work done in water suction. Therefore, the difference between the Gibbs' free energies of water and ice $g_{wi} - g_{ii}$ is equal to the work done in water suction $(P_{ws} - P_{wi})v_w$. From this relationship, an equation of state for the steady flow process, i.e., the dynamic equation of state, is derived as shown in Eq. (2).

$$P_{wi}v_w - P_{ii}v_i - \frac{L_w}{T_o}\theta_i = (P_{ws} - P_{wi})v_w \quad (2)$$

The physical meaning of this equation can be explained as follows. The mechanical energy generated by the solid-liquid phase change described on the left side of the Eq. (2) is equal to the dissipation of mechanical energy due to the accompanying water migration described on the right side. This equation is consistent even when the process shifts from the dynamic condition to the static condition, because it agrees with GCCE (1) under the static condition of $P_{wi} = P_{ws}$. The above investigation results show that the dynamic equation of state (2) is extremely important, since it describes the framework of the frost heave theory. However, no quantitative

verification of this equation has been possible, because the pore water pressure P_{wi} at the ice lens forming front has not been measured up to the present.

1.5 Experimental verification-specific purpose of this study

Miyata and Akagawa⁽¹⁷⁾ have developed a unfrozen pore water pressure gauge to measure the pressure of unfrozen water at the ice lens forming front in order to verify the dynamic equation of state (2). They have also developed a special experimental apparatus for fixing the position of the ice lens forming front. This was necessary because the position of the unfrozen pore water pressure gauge is fixed. The accuracy of the unfrozen pore water pressure gauge was confirmed by the experiment for re-verification of the static equation of state, GCCE (1), under the condition of no water migration. It is noted that GCCE (1) has already been verified both theoretically⁽⁸⁾ and experimentally⁽⁹⁾⁻⁽¹¹⁾. As a result, it is proved that the newly developed unfrozen pore water pressure gauge is practical and reliable for measuring the relative value to any reference value, although the absolute value cannot be accurately measured because of the apparatus' own bias error, as described later.

This paper attempts to verify experimentally the dynamic equation of state (2). This verification will be based on the comparison between the relative values converted from the measured pore water pressure during water migration in the steady state and the dynamic equation of state (2) expressed by relative values. Section 3 introduces an experiment apparatus. Section 4 compares the experiment results with the theoretical ones. Section 5 shows that the verified results based on the relative values have generality.

2. Notations

- L_w : latent heat of freezing of water [MJ/kg]
- P_1 : heaving pressure [MPa]
- P_3 : confining pressure [MPa]
- P_b : boiling pressure [MPa]
- P_{ii} : ice pressure at the ice lens forming front [MPa]
- P_{oi} : overburden pressure [MPa]
- P_{wi} : unfrozen pore water pressure at the ice lens forming front [MPa]
- P_{wi0} : reference value of P_{wi} [MPa]
- P_{wL} : lower limit of pore water pressure [MPa]
- P_{wLi} : lower limit of pore water pressure at the ice lens forming front [MPa]
- P_{ws} : water supply pressure [MPa]
- T_0 : reference temperature [K]
- v_i : specific volume of ice [m^3/kg]

- v_w : specific volume of water [m^3/kg]
- x_m : pressure term of GCCE [MPa]
- x_{m0} : reference value of pressure term of GCCE [MPa]
- y_m : temperature term of GCCE [MPa]
- y_{m0} : reference value of pressure term of GCCE [MPa]
- ΔP_{ii} : relative ice pressure of the ice lens forming front [MPa]
- ΔP_{wi} : relative unfrozen water pressure of the ice lens forming front [MPa]
- ΔP_{ws} : relative water supply pressure [MPa]
- $\Delta \theta_i$: relative temperature of the ice lens forming front [$^{\circ}\text{C}$]
- ε : residual [MPa]
- ε_0 : reference value of residual [MPa]
- θ : temperature [$^{\circ}\text{C}$]
- θ_c : cooling temperature [$^{\circ}\text{C}$]
- θ_h : heating temperature [$^{\circ}\text{C}$]
- θ_i : temperature of the ice lens forming front [$^{\circ}\text{C}$]
- σ_t : tensile strength [MPa]

3. Apparatus and Experimental Method

3.1 Apparatus

Figure 1 is a conceptual illustration of the test apparatus, which can be characterized as having the following features. The ice lens forming front can be fixed at a specified position and the unfrozen pore water pressure can be measured at that position. To realize these features, Ohya-tuff was employed for the specimen. Ohya-tuff is a porous medium the same as the soil. Accordingly, it has permeability even after it

Fig. 1 Conceptual illustration of test apparatus

is frozen. This is due to the presence of an unfrozen water film caused by the depression of freezing point of water. However, it is more difficult to generate an ice lens in Ohya-tuff than in a soil because Ohya-tuff has a tensile strength, as explained in section 3.2. Therefore, it is easy to fix the ice lens forming front at a specified position.

The specimen is placed in a pressure cell whose structure is basically the same as that of a triaxial compression apparatus for a soil test. Water is supplied through a tube with a valve connected to the bottom of the pressure cell. The valve is open during the open type test which allows water migration. It is closed for the closed type test which does not allow water migration.

The pressure cell contains the testing elements from the bottom to the top as follows: (1) a lower pedestal, (2) a highly permeable porous plate to enable uniform water supply, (3) Ohya-tuff as a porous medium specimen 60 mm in diameter by 20 mm high, (4) a 60 mm high brass cylinder as a non-permeable and highly heat-conductive spacer and (5) an upper pedestal. The cooler and heater are provided at the upper and lower pedestals, respectively. Heat from the cooler and heater is transferred to the Ohya-tuff specimen via a heat medium in the pedestals. This freezes the upper part of the Ohya-tuff specimen. The side of the cylinder from the upper to the lower pedestals including the Ohya-tuff and brass spacer is covered by a rubber membrane. This membrane protects the water migration in the Ohya-tuff from disturbance by air invasion into the specimen. Water is supplied to the bottom of the porous plate through a tube via a valve.

By pressurizing the inside of the pressure cell, the Ohya-tuff specimen is subjected to the confining pressure P_3 in the axial direction and the radial direction. A rod is provided at the top of the upper pedestal penetrating the pressure cell. This rod is used for measuring the frost heave displacement, and for loading the overburden in the axial direction or for constraining the frost heave displacement.

This test apparatus fixes the location of the ice lens forming front at the top face of the Ohya-tuff specimen, as described later. The unfrozen pore water pressure P_{wi} at the ice lens forming front is measured by a newly developed unfrozen pore water pressure gauge (referred to in section 3.3). This new pressure gauge is installed in a cylindrical space with an inside diameter of 10 mm. This space is formed at the center of the specimen along its axis. The opening face of the new pressure gauge is located so that it aligns with the surface of the Ohya-tuff specimen.

The test apparatus uses platinum resistance ther-

mometers (accuracy $\pm 0.01^\circ\text{C}$). These thermometers are located on the top surface of the brass spacer and the top and bottom surfaces of the Ohya-tuff specimen to measure the cooling temperature θ_c , the temperature of the ice lens forming front θ_i and the heating temperature θ_h , respectively. Wire strain gauge type pressure gauges are employed to measure the water supply pressure and the confining pressure P_3 . A displacement gauge (accuracy $\pm 0.075\%$) is used to measure the axial direction displacement.

3.2 Location fixing of the ice lens forming front

Ohya-tuff is a mechanically strong porous medium having a tensile strength σ_t of 1.4 MPa and a specific surface of $17.2\text{ m}^2/\text{g}$. The ice lens have to overcome the mechanical resistance of the porous media when they expand inside it. Thus, the ice lens is generated at the point of least mechanical resistance. If an artificial fracture is made in the Ohya-tuff, the ice lens will grow first at this fracture. When such a fracture is provided, the Ohya-tuff having a lower temperature above the fracture simply plays the role of a heat transfer medium. In the test apparatus, the brass spacer is regarded as a replacement for the lower-temperature Ohya-tuff above the fracture, conditioned to minimize the disturbance. With this setup, the ice lens forming front can be made stationary at the bottom surface of the fracture, i.e., at the top surface of the Ohya-tuff.

Once an ice lens segregates inside the Ohya-tuff specimen, the flow of the unfrozen water stops at the location of the segregation. Thus, under such conditions, it is impossible to measure the pore water pressure at the ice lens forming front by the unfrozen pore water pressure gauge whose opening is located at the top surface of the Ohya-tuff specimen. The conditions under which the ice lens does not segregate in the Ohya-tuff specimen are as follows. The ice pressure P_{ii} of the ice lens is lower than the confined pressure in the axial direction, namely the sum of overburden pressure $P_{0i}(=P_3)$ and tensile strength σ_t . By letting the local temperature of the Ohya-tuff be θ_i and by substituting $P_{ii} \leq P_{0i} + \sigma_t$ into GCCE (1), the condition of a temperature which does not cause segregation of the ice lens is given as:

$$\theta_i \geq -\frac{v_i T_o}{L_w} \sigma_t - \frac{v_w T_o}{L_w} \left[\frac{v_i}{v_w} P_{0i} - P_{wi} \right] \quad (3)$$

It is noted that the second term on the right hand side of Eq.(3) is always positive because of the following reason. In this test including the case of water migration, the conditions are that $P_{ws} \geq P_{wi}$ and $P_{0i} \geq P_{ws}$. Then, if P_{wi} is replaced by P_{0i} in the second term of the right hand side of Eq.(3), this term is positive, since $v_i/v_w > 1$. Thus, even if this term is neglected, the ice lens will not segregate in the Ohya-tuff

specimen as long as the temperature θ_i is set higher than the first term of the right hand side. By substituting 1.4 MPa as the tensile strength of the Ohya-tuff into Eq. (3), the first term of the right hand side becomes -1.2°C . Thus, if the temperature of the specimen is maintained higher than this value, the ice lens forming front can be made stationary at the upper part of the Ohya-tuff specimen.

3.3 Measurement of unfrozen pore water pressure

The unfrozen pore water pressure gauge consists of a vessel made of polyvinyl chloride having an opening in the top only. An Ohya-tuff cylinder 8 mm in diameter and 20 mm long is inserted into the opening like a plug. The vessel is then filled with water. The pore water pressure at the ice lens forming front in contact with the opening is transmitted via an unfrozen water film to the pressure gauge and measured. The pressure gauge is located in the lower part of the vessel. It is a semi-conductor strain gauge type water pressure gauge (accuracy $\pm 0.05\%$).

3.4 Experiment method

To prepare for the experiment, the air in the Ohya-tuff is completely displaced by carbon dioxide, which is easily soluble in water. This prevents bubble formation in the specimen, which disturbs the water migration. Since it is an open type experiment, water is supplied by opening the valve of the tube connected to the lower part of the pressure cell. The air pressure P_3 inside the pressure cell and the water supply pressure P_{ws} are set as specified test conditions, and maintained constant throughout the test.

The test progresses according to the following procedures and produces several sets of results. (1) The cooler and heater temperatures are set as specified test conditions. (2) The change in pore water pressure at the ice lens forming front is monitored. After the pore water pressure at the ice lens forming front reaches a steady state, or dynamic (steady state) water migration is observed, the pressures and temperatures and so on are measured. (3) The above step (2) is repeated by changing the cooling temperature.

4. Results of Open Type Test

4.1 Test conditions

The left columns of Table 1 show the conditions of the open type tests. It is noted that all the presented gauge pressures are given relative to atmospheric pressure. In Test No. 01, the varying four temperatures θ_i of the ice lens forming front were measured. In Test Nos. 02, 03 and 04, the temperature was changed three times, four times and twice, respectively. Thus, there were a total of 13 temperature

Table 1 Open type test conditions and results

No.	Conditions					Measured	
	Temp. ($^\circ\text{C}$)		Pres. (kPa)			Temp. ($^\circ\text{C}$)	Pres. (kPa)
	θ_c	θ_h	P_{ws}	P_1	P_3	θ_i	P_{wi}
O1	-0.36	2.39	487	13	534	-0.23	373
	-0.48					-0.35	335
	-0.53					-0.39	285
	-0.66					-0.52	209
O2	-0.53	3.95	491	13	513	-0.34	487
	-0.68					-0.48	444
	-0.85					-0.65	245
O3	-0.67	3.93	488	13	511	-0.47	468
	-0.81					-0.60	377
	-0.83					-0.63	357
	-0.90					-0.68	296
O4	-0.80	3.88	490	13	514	-0.60	161
	-0.99					-0.78	45

changes.

4.2 Results

The right column of Table 1 shows the test results. Because they are similar to the closed type tests, the measured results may contain bias error. To cancel bias error, the results were evaluated as the difference between the measured values and reference values.

Firstly, let us derive the dynamic equation of state in terms of the relative value. The dynamic equation of state (2) is first transformed to Eq. (4).

$$\frac{1}{2} \frac{v_i}{v_w} P_{ii} - P_{wi} + \frac{1}{2} P_{ws} = -\frac{1}{2} \frac{L_w}{v_w T_0} \theta_i \quad (4)$$

Then, the measured values (x_m , y_m) are defined in Eqs. (5) and (6).

$$y_m = \frac{1}{2} \frac{v_i}{v_w} P_{ii} - P_{wi} + \frac{1}{2} P_{ws} \quad (5)$$

$$x_m = -\frac{1}{2} \frac{L_w}{v_w T_0} \theta_i \quad (6)$$

When ε denotes the residual contained in the measured value due to the measurement error, the measured values (x_m , y_m) satisfy the following relationship.

$$y_m = x_m + \varepsilon \quad (7)$$

An arbitrary reference point (x_{m0} , y_{m0}) can be chosen from the sets of measured values in every run of tests. When ε denotes the residual contained in the reference point due to measurement error, the relationship can be expressed by Eq. (8).

$$y_{m0} = x_{m0} + \varepsilon_0 \quad (8)$$

It is noted that the bias errors of the individual measured values such as P_{ii} , P_{wi} and θ_i could be

regarded as constant. The dispersion of such errors due to accidental error could be regarded as negligible. Therefore, $|(\varepsilon - \varepsilon_0)/(x_m - x_{m0})| \ll 1$ is valid. Equation (9) is derived by taking the difference between Eqs. (7) and (8).

$$y_m - y_{m0} = x_m - x_{m0} \quad (9)$$

The differences between individual measured values and the individual reference values for the water supply pressure, the ice pressure of the ice lens and the pressure and temperature of the unfrozen pore water are denoted as ΔP_{ws} , ΔP_{ii} , ΔP_{wi} and $\Delta \theta_i$, respectively. This yields the following equations.

$$y_m - y_{m0} = \frac{1}{2} \frac{v_i}{v_w} \Delta P_{ii} - \Delta P_{wi} + \frac{1}{2} \Delta P_{ws} \quad (10)$$

$$x_m - x_{m0} = -\frac{1}{2} \frac{L_w}{v_w T_0} \Delta \theta_i \quad (11)$$

Substituting Eqs.(10) and (11) into Eq.(9), yields the dynamic equation of state (12) in terms of the relative value in the same form as Eq.(4).

$$\frac{1}{2} \frac{v_i}{v_w} \Delta P_{ii} - \Delta P_{wi} + \frac{1}{2} \Delta P_{ws} = -\frac{1}{2} \frac{L_w}{v_w T_0} \Delta \theta_i \quad (12)$$

It should be noted that $\Delta P_{ws}=0$ and $\Delta P_{ii}=0$, since the water supply pressure P_{ws} and the ice pressure P_{ii} were maintained constant throughout the series of tests.

Subsequently, let us compare the test results with values yielded by Eq.(12). The measured values are shown in the right columns of Table 1. Table 2 shows the regression lines of the results of the open type tests in terms of (x_m, y_m) defined by Eqs. (5) and (6). For each test, we can arbitrarily choose the reference point which is used for calculating the relative values. Here, let us choose the x -intercept of the regression line of a test for its reference. In other words, we shift measured values (x_m, y_m) of the test parallel with the x -axis so that its regression line crosses the origin point. This makes $\varepsilon_0=0$, that is, the bias error becomes zero. The relative values thus obtained are shown in Fig. 2. The 99% confidence interval with respect to the gradient of each regression line is shown in Table 3. The solid line of Fig. 2 expresses the dynamic equation of state (12).

In all the tests except for Test No. 04, which has only two measured points, the theoretical gradient 0.5 of Eq.(12) is included in the 99% confidence interval. Thus, the dynamic equation of state (12) is experimentally verified.

5. Discussions

5.1 Derivation of the dynamic equation of state from the test results

A counter argument may be raised to the above results, since the tests verify Eq.(12) using the relative values. Thus, a possible comment is that the tests

Table 2 Regression lines

	O1	O2	O3	O4
Coefficient	0.479	0.668	0.627	0.543
Y-Intercept	15	-268	-310	-73
Coef. of M. Cor.	0.974	0.959	0.981	1.00

Note: M. Cor. = Multiple Correlation

Table 3 99 % confidence interval

	O1	O2	O3	O4	All
Coefficient	0.479	0.668	0.627	0.543	0.535
Conf. Interval					
Upper Limit	0.386	-0.17	0.468	0.543	0.475
Lower Limit	0.572	1.508	0.785	0.543	0.596

Fig. 2 Open type test results

verify only the coefficient 0.5 on the right hand side of the original dynamic equation of state (4), but does not necessarily verify Eq.(4) itself. This section shows that the dynamic equation of state (4) can be derived by using the results for verification of Eq.(12).

The reference values for Eq.(12) can be chosen arbitrarily as long as they satisfy this equation. Furthermore, GCCE (1) is included in the dynamic equation of state (4), since the condition that water migration does not occur is the special case of water migration. Thus, GCCE (1) is transformed to Eq. (13). The reference values for Eq.(12) are chosen so that they satisfy Eq.(13).

$$\frac{v_i}{v_w} P_{ii} - P_{wi0} = -\frac{L_w}{v_w T_0} \theta_{i0} \quad (13)$$

where θ_{i0} is a reference value of temperature. The reference value of pore water pressure P_{wi0} is equal to the water supply pressure P_{ws} , from the static condition (no water migration) of GCCE.

Based on these reference values, each variable of Eq.(12) is expressed as below.

$$\Delta P_{wi} = P_{wi} - P_{wi0} \quad (14)$$

$$\Delta \theta_i = \theta_i - \theta_{i0} \quad (15)$$

Equation (4) is derived by substituting Eqs.(13) through (15), $\Delta P_{ws}=0$, $\Delta P_{ii}=0$ and $P_{wi0}=P_{ws}$ into Eq.(12) and transforming it.

In summary, Eq.(12), as verified in the current tests, is valid for arbitrary reference values. As described in the Introduction, GCCE (1) has already been verified experimentally and theoretically to be valid under the condition without water migration. It has also been verified theoretically in Section 1.4 that GCCE (1) is the same as the dynamic equation of state (4) as P_{ws} asymptotically approaches P_{wi} . Thus, the values obtained using GCCE (1) are usable for the reference values of Eq.(12). The dynamic equation of state (4) is obtained by substituting the obtained reference values into Eq.(12). It is thus shown that the experimental verification of Eq.(12) using the relative values is equivalent to the verification of the dynamic equation of state (4), i.e., Eq.(2).

5.2 Measurement error of unfrozen pore water pressure gauge

In this section the measurement error of the unfrozen pore water pressure gauge is first clarified, and then it is shown by using experimental data that GCCE (1) is included in the dynamic equation of state (2).

Table 4⁽¹⁷⁾ shows the results of the closed type tests aimed at confirming the effectiveness of the verification method for the dynamic equation of state. In the closed type test, the pore water pressure P_{wi} at the ice lens forming front is equal to the water supply pressure P_{ws} . Equation (1) is transformed to Eq.(16) to evaluate the measurement error of the unfrozen pore water pressure gauge.

$$P_{ws} - P_{wi} = -\frac{L_w}{v_w T_0} \theta_i - \frac{v_i}{v_w} P_{ii} + P_{ws} \quad (16)$$

Errors by gauges can be evaluated from this equation. That is, the errors of the unfrozen pore water pressure gauge and the temperature gauge can be evaluated from the values of the left and right hand sides, respectively. Figure 3 shows the results obtained by substituting the measured values shown in Table 4 into the equation. From Fig. 3, it is found that the measurement errors in the pore water pressure P_{wi} consist of bias errors and accidental errors in Test Nos. C1 through C3. The bias errors vary from test to test. The accidental errors overlaying the bias errors are much smaller (maximum ± 35 kPa) than the bias errors. The findings regarding the temperature at the ice lens forming front θ_i are given below.

Table 4 Closed type test results

No	Conditions			Measured Values			
	Temp. (°C)		Pres. (kPa)	Temp. (°C)	Pres. (kPa)		
	θ_c	θ_h	P_3	θ_i	P_{ws}	P_{wi}	P_{ii}
C1	-0.38	2.35	532	-0.12	454	161	7
	-0.60			-0.31	398	45	130
	-0.73			-0.43	389	28	254
	-0.90			-0.57	350	18	348
C2	-0.40	2.27	527	-0.13	505	405	94
	-0.61			-0.31	419	268	146
	-0.81			-0.51	393	252	304
	-0.99			-0.68	358	231	410
C3	-0.36	2.25	522	-0.08	490	490	18
	-0.47			-0.17	489	448	101
	-0.50			-0.19	487	453	120
	-0.65			-0.33	467	398	240
	-0.70			-0.34	463	402	274
	-0.83			-0.49	437	377	377
							878

Note: $P_{ii}=P_I+P_3$

Fig. 3 Errors in closed type tests

Except for Test No. C2, the measurement errors consist of bias errors and similar levels (maximum ± 35 kPa in pressure equivalence) of accidental errors overlaying them. In Test No. C2, the error range is as large as ± 80 kPa, which is much larger than in the other tests. This is considered a special case, where the temperature gauge moved upwards after it was trapped in the ice lens. Here we do not touch on the causes of the bias errors because they have already been discussed in detail in Ref.(17). The accidental errors of the unfrozen pore water pressure gauge are less than or equal to 10% of the highly reliable measured water supply pressures. The error of the temperature gauge becomes less than or equal to 5% if it

is expressed by the pressure-equivalent value which is converted by using the first term of the right hand side of Eq.(16). This result indicates that the validity evaluation for the equation of state (2) can be made by canceling the bias errors as shown in Section 4.2.

The authors have also shown in Ref.(17) that the results of the close type tests agree well GCCE (1). Now let us convert the results of the close type tests to the relative values corresponding to both sides of Eq.(12) using the method described in Section 4.2. In this conversion, relative values of the water supply pressures of Eq.(12) are set to become $\Delta P_{ws} = \Delta P_{wi}$, because in the closed type test where water migration does not take place, water supply pressure P_{ws} is the same as the pore water pressure P_{wi} , as stated earlier. The converted results are shown in Fig. 4 where they are overlaid on the results of the open type tests shown in Fig. 2. It is found that both are on the same single straight line. As a result, it has been experimentally confirmed that the GCCE (1) agrees with the extreme case of the dynamic equation of state (2), where water migration does not take place.

5.3 Relationship between dynamic equation of state and GCCE

Subsequently, the inter-relationship between the dynamic equation of state (2) and GCCE (1) is clarified. Equation (2) can be transformed as follows:

$$P_{ws} = 2P_{wi} - \frac{v_i}{v_w} P_{ii} - \frac{L_w}{v_w T_0} \theta_i \quad (17)$$

The second and the third terms of the right hand side of Eq.(17) are the functions of the ice lens forming front temperature θ_i only. Here, we introduce a new concept: the lower limit of pore water pressure P_{wLi} . P_{wLi} is the minimum value which the pore water

pressure can take under certain given conditions. Therefore, if the volume of water migration approaches the limit of zero, i.e., $(P_{ws} - P_{wi}) \geq 0$, P_{wi} converges to the lower limit of pore water pressure P_{wLi} specified in Eq.(18).

$$P_{wLi} = \frac{v_i}{v_w} P_{ii} + \frac{L_w}{v_w T_0} \theta_i \quad (18)$$

Using P_{wLi} , Eq.(17) becomes Eq.(19).

$$P_{ws} = 2P_{wi} - P_{wLi} \quad (19)$$

Equation (19) is displayed in the P_{wi} - P_{ws} plane as a group of straight lines (DES as shown in Fig. 5) with a gradient of two and a y-intercept of $-P_{wLi}$, if expressed by the parameter P_{wLi} . The range within which this straight line can have a physical meaning is confined by several conditions. One is that the water can migrate from the unfrozen soil to the ice lens, i.e., $P_{ws} \geq P_{wi}$. Another is that the pore water pressure cannot heave the ice lens, i.e., $P_{wi} \leq P_{ii}$. The last is that the water is saturated. That is, if the pressure where water starts rapidly vaporizing is P_b (boiling pressure), the conditions are that $P_{ws} > P_b$ and $P_{wi} > P_b$. In the range having a physical meaning, all the above conditions need to be simultaneously satisfied. This range is shown by the shaded area of Fig. 5.

Since GCCE (1) is a static equation of state which is valid for no water migration, it becomes the following straight line in the P_{wi} - P_{ws} plane.

$$P_{ws} = P_{wi} \quad (20)$$

This agrees with the limit of the valid range $P_{ws} \geq P_{wi}$ for Eq.(19). Thus, GCCE (1) becomes a limiting case of the dynamic equation of state. Furthermore, in the water-ice system where soil particles are not present, there is no supporting pressure of the soil particles, as discussed in the Introduction. Thus, in this case $P_{wi} = P_{ii}$. Therefore, the equation of state for

Fig. 4 Open and closed type test results

Fig. 5 Dynamic equation of state and GCCE

such a system, i.e., the Clausius-Clapeyron Equation (CCE), is valid in the limiting case where $P_{wi}=P_{ii}$ in the GCCE (1).

Finally, Fig. 5 clarifies an erroneous point of the theories⁽¹²⁾⁻⁽¹⁴⁾ which use GCCE (1) in estimating the pore water pressure P_{wi} at the ice lens forming front. Point A in the P_{wi} - P_{ws} plane is the state with the water supply pressure P_{ws} and the lower limit of pore water pressure P_{wLi} , specified by Eq.(18), which is a function of the pore water pressure P_{wi} , ice pressure P_{ii} and temperature θ_i . The intercept of Eq.(19) crossing point A and Eq.(20) is point B, whose coordinates are (P_{wLi}, P_{wLi}) . Point C is the intercept of Eq.(20) and the straight line which is parallel to the P_{wi} axis and passes Point A, and its coordinates are (P_{ws}, P_{ws}) . Point D is the intercept of the straight line drawn from point B perpendicular to the extension of the straight line CA. The coordinates of Point D are (P_{wLi}, P_{ms}) . Since the pressure loss due to water migration from the water supply front to the ice lens forming front is $P_{ws}-P_{wi}$, it is graphically presented as line segment CA. However, with the above theories of analyzing frost heave using GCCE (1), the above pressure loss becomes $P_{ws}-P_{wLi}$, since the pore water pressure is made P_{wLi} regardless of the water supply pressure P_{ws} . Thus, the pressure loss becomes the line segment CD in the figure. As a result, the pressure difference between the water supply pressure and the ice lens forming front is estimated as double that by the dynamic equation of state (2), if the theories using GCCE (1) are applied. Therefore, the theories give a rate of water migration double that given by the dynamic equation of state.

6. Conclusions

Results of a series of open type tests using an unfrozen pore water pressure gauge have experimentally verified the validity of the dynamic equation of state. That is, it has been verified that the dynamic equation of state at the solid-liquid phase changing front can be applied to the case where liquid migrates in a liquid saturated porous medium.

Based on the above, the inter-relationship between the dynamic equation of state (2) and GCCE (1) has been clarified (Fig. 5). It has also been clarified that the error became 100% where the dynamic equation of state is not used but GCCE (1) is used for the frost heave analysis.

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