

MODELLING OF FREEZING AND THAWING PROCESSES IN BUILDING MATERIALS

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ABSTRACT

This paper presents a mathematical model for simultaneous heat and moisture transfer under freezing-thawing in porous material. Even below zero degree centigrade, unfrozen liquid water exist which play important roll in the process. Moisture (chemical) potential of unfrozen liquid water is unique function of local temperature during freezing. The model takes account for existence of unfrozen liquid water. Simple example of simulation for freezing processes are shown..

INTRODUCTION

In the field of building thermal engineering, prediction of transient moisture behavior in buildings and their elements are required for thermal and hygric design of building as well as thermal behavior. During these two or three decades, the governing equations of transient heat and moisture transfer have been developed [1-5]. But they covered only for non-freezing regime above 0 degree centigrade.

Temperature in building elements is frequently decrease below 0°C during winter. Recently, need increases concerning evaluation of durability of building materials to freezing, prevention of ice formation in building materials and evaluation of freeze damage on building elements as well as prediction of thermal behavior below 0°C. In this paper, a mathematical model for heat and moisture transfer in porous materials under freezing condition below 0°C are derived which is valid also in non freezing regime. Mathematical model of freezing process in porous media had been presented during 1950's by Luikov[1], treated as coupled heat and mass transfer problem. His equations, however, is not closed or were not taking account existence of unfrozen water and temperature depression of freezing depending on liquid water content. In soil science, Haran[6], Guymon and Luthin[7] and Taylor and Luthin[8] presented models for partially frozen soil as a coupled heat and moisture transfer problem. Those has wide applicability. In the field of material science, Bazant etal.[9] presented the mathematical model for freeze-thaw durability of concrete as a

coupled heat and moisture transfer problems. But due to complexity of equilibrium relation of unfrozen water, they did not clearly show closed form of the equations.

In this paper, considering wide variation of moisture content in building elements and importance of complex boundary condition, a mathematical model for freezing/thawing regime is presented, using water chemical potential as a moisture potential. This potential is common with in non-freezing regime. To close the governing equations, equilibrium relation of moisture (unfrozen water) below 0°C are discussed. Unfrozen liquid water content is uniquely determined by local temperature if solid water (ice) exists or, in the other word, if moisture (chemical) potential is equal to critical moisture (chemical) potential which is uniquely determined by local temperature. On the other hand, when (chemical) moisture potential is lower than the critical (chemical) moisture potential, freezing does not occur even below 0°C. Under those non-freezing condition, governing equations are same as those above 0°C. To understand those relations, it is important to introduce concept of equilibrium relation between unfrozen liquid water and chemical potential of moisture (gas, liquid and solid phase of water) and temperature. In this paper we show and discuss those relation. And we present estimation of those relation. Introducing relations mentioned above, governing equations derived from mass and energy balance are closed and we can solve particular problems.

Applying this model presented in this paper, freezing/thawing processes are numerically analyzed, as a numerical example. Numerical procedure are discuss.

MATHEMATICAL MODEL

During freezing, moisture in porous media exists in three phases, solid, liquid and gas. Governing equations are obtained by conservation of mass of each phase of moisture and energy. Derived equations are based on the following assumptions:

- (1) Each phase of moisture in the porous media is in local equilibrium with each other.

(2) Total pressure of gas phase (moist air) in the porous media is assumed to be kept constant. Bulk flow of dry air is not existed, i.e. mass average velocity of dry air is zero.

(3) The porous media are non deformable. It is assumed that stresses in the porous media are kept constant and uniform.

(4) All values are single valued; i.e. hysteresis is not present.

(5) There is no dissolved salts or dissolved salt is immovable and is in equilibrium locally with salts in solid skeleton.

With the assumption of local equilibrium of moisture, there is no difference of water chemical potential between phases. Mass conservation of each phase of moisture in porous media are as follows.

From mass balance of gas phase of moisture

$$\frac{\partial \rho_s \Phi_g}{\partial t} = \nabla(\lambda'_{\mu g}(\nabla\mu - F)) + \nabla\lambda'_{Tg}\nabla T - J_{gl} - J_{gi} \quad (1)$$

From mass balance of liquid phase of moisture

$$\frac{\partial \rho_l \Phi_l}{\partial t} = \nabla(\lambda'_{\mu l}(\nabla\mu - F)) + \nabla\lambda'_{Tl}\nabla T + J_{gl} - J_{li} \quad (2)$$

From mass balance of solid phase of moisture

$$\frac{\partial \rho_i \Phi_i}{\partial t} = \nabla(\lambda'_{\mu i}(\nabla\mu - F)) + \nabla\lambda'_{Ti}\nabla T + J_{gi} + J_{li} \quad (3)$$

In solid phase, solid moisture is immovable, i.e. $\lambda'_{\mu i} = \lambda'_{Ti} \approx 0$, then equation (3) reduce to

$$\frac{\partial \rho_i \Phi_i}{\partial t} = J_{gi} + J_{li}. \quad (4)$$

Sum of equations (1),(2) and (4) yields total moisture balance equation

Total mass balance equation of moisture is

$$\frac{\partial \rho_l \Phi_l}{\partial t} = \nabla(\lambda'_{\mu}(\nabla\mu - F)) + \nabla\lambda'_{T}\nabla T - \frac{\partial \rho_s \Phi_g}{\partial t} - \frac{\partial \rho_i \Phi_i}{\partial t} \quad (5)$$

where

$$\lambda'_{\mu} = \lambda'_{\mu l} + \lambda'_{\mu g} \quad \text{and} \quad \lambda'_{T} = \lambda'_{Tl} + \lambda'_{Tg}$$

Values of moisture conductivity of vapor phase is not generally small, compared with moisture conductivity of liquid phase. Densities of ice and liquid water, are assumed to be kept constant. Moisture accumulation in vapor phase, shown by the third term in right-hand side of equation (5), is usually negligibly small as compared with that in liquid phase.

Energy balance equation is as follows

$$\left(\frac{\partial(\rho_s \Phi_s H_s + \rho_l \Phi_l H_l)}{\partial t} \right) + \left(\frac{\partial(\rho_g \Phi_g H_g + \rho_a \Phi_a H_a)}{\partial t} \right) + \frac{\partial \rho_i \Phi_i H_i}{\partial t} = \nabla\lambda\nabla T - \nabla(H_g J_g) - \nabla(H_l J_l) \quad (6)$$

Moisture flux J_l and J_g are obtained from constitutive relations (simultaneous diffusion equations of heat and moisture)

$$\begin{aligned} J_l &= -\lambda'_{\mu l}(\nabla\mu - F) - \lambda'_{Tl}\nabla T \\ J_g &= -\lambda'_{\mu g}(\nabla\mu - F) - \lambda'_{Tg}\nabla T \end{aligned} \quad (7)$$

Substituting mass balance equations (1), (2) and (4) into energy balance equation (6), energy equation (6) is reduced to

$$\begin{aligned} c\rho \frac{\partial T}{\partial t} + H_{gl} \frac{\partial \rho_s \Phi_g}{\partial t} + J_g C_g \nabla T + J_l C_l \nabla T \\ = \nabla\lambda\nabla T + H_{gl}[\nabla(\lambda'_{\mu g}(\nabla\mu - F) + \lambda'_{Tg}\nabla T)] + H_{li} \frac{\partial \rho_i \Phi_i}{\partial t} \end{aligned} \quad (8)$$

where

$$c\rho = c_s \rho_s \Phi_s + c_l \rho_l \Phi_l + c_g \rho_g \Phi_g + c_a \rho_a \Phi_a + c_i \rho_i \Phi_i \quad (9)$$

The second and third term of left-hand side in equation(8) is small compared with other term. Neglecting those two terms, equation (8) is reduced to

$$\begin{aligned} c\rho \frac{\partial T}{\partial t} + J_l C_l \nabla T \\ = \nabla\lambda\nabla T + H_{gl}[\nabla(\lambda'_{\mu g}(\nabla\mu - F) + \lambda'_{Tg}\nabla T)] + H_{li} \frac{\partial \rho_i \Phi_i}{\partial t} \end{aligned} \quad (10)$$

Governing equations of simultaneous heat and moisture transfer are equation (5) and (10). They can be applicable to freezing regime ($\phi_i > 0$) as well as nonfreezing regime ($\phi_i = 0$). In the equations above, unknown dependent variables are T, μ and ϕ_i because ϕ_l is function of μ , T from equilibrium relation $\phi_l = f(\mu, T)$. Then, in non-freezing regime,

unknown variables are T and μ , because $\phi_i = 0$. Then equation (5) and (10) is closed in nonfreezing regime. In freezing regime, in addition to equilibrium relation $\phi_i = f(\mu, T)$ in freezing regime, one more relation must be introduced to close the equation. Introduced such relation, unknown dependent variables are ϕ_i and T (or μ) in freezing regime. Those two relations in freezing regime are introduced and discussed in the following Sections.

Boundary conditions are equations (11) and (12), identical with that of non-freezing circumstance.

$$-\lambda'_{\mu} \left(\frac{\partial \mu}{\partial n} - F_n \right) - \lambda'_{T} \frac{\partial T}{\partial n} = \alpha'_{\mu} (\mu_0 - \mu) + \alpha'_{T} (T_0 - T) + m \quad (11)$$

$$-\lambda \frac{\partial T}{\partial n} - H_{gl} \left(\lambda'_{\mu} \mu_g \left(\frac{\partial \mu}{\partial n} - F_n \right) + \lambda'_{Tg} \frac{\partial T}{\partial n} \right) = \alpha'_{\mu} H_{gl} (\mu_0 - \mu) + (\alpha + \alpha'_{T} H_{gl}) (T_0 - T) + q_s \quad (12)$$

FREEZING POINT DEPRESSION

During freezing, it is assumed that local equilibrium between water vapor, non-freezing water and solid ice exists. With this, it is assumed that total pressure in gas phase, i.e. moist air, is kept constant in the porous media, and pressure exerted on moisture in solid phase (ice) is assumed to be kept constant.[10]

$$\begin{aligned} \mu_g &= \mu_l = \mu_i \equiv \mu \\ d\mu_g &= d\mu_l = d\mu_i \equiv d\mu_a \\ dP_i &= 0 \end{aligned}$$

Applying this assumption to Gibbs-Duhem equation, a following equation is obtained

$$v_l dP_l - s_l dT = -s_i dT \quad (13)$$

where T is absolute temperature(K). Using definition of chemical potential, $\mu = H - Ts$, equation (13) is reduced to

$$dP_l = \frac{H_{il}}{v_l} \frac{dT}{T} \quad (14)$$

Assuming that H_{il} and $v_l P_l$ are constant and using relation

$$\mu_l = v_l P_l \quad (15)$$

relation between temperature depression of freezing point and moisture (chemical) potential is obtained.

$$\mu = H_{il} \ln \frac{T}{T_0} \quad (16)$$

where $T_0 = 273.16$ K ($=0^\circ\text{C}$). Equation (14) is equivalent to Clausius-Clayton equation between liquid and solid phase. Equation(16) means that moisture (chemical) potential μ of unfrozen liquid is uniquely determined by local temperature T when $\phi_i > 0$ or existence of equilibrium between three phases of water. That is moisture (chemical) potential μ is not unknown variable in governing equations (5) and (10).

Introducing this relation, under the condition $\phi_i > 0$, a unknown (dependent) variables in governing equations (5) and (10) are solid water (ice) content ϕ_i and temperature T (or μ). And the governing equations (5) and (10) are closed. Of equilibrium relation between ϕ_i and μ (or T) we discuss in the following.

With same assumption with relation (14), saturation partial vapor pressure in equilibrium with solid water (ice) and unfrozen liquid water are obtained, as well known.

When moisture (chemical) potential of liquid water in a capillary, which depends strongly on capillary radius and is almost independent on other thermodynamic state variables, is lower than the value calculated with equation (16) at local temperature T below 0°C , liquid water in the capillary is not freezes. On the contrary, if water chemical potential of liquid water in capillary is higher than the value given by equation (16), liquid water in the capillary freezes. These knowledge suggest that equilibrium relation of unfrozen liquid moisture below 0°C keep same as equilibrium relation above 0°C .

EQUILIBRIUM RELATION OF NON-FREEZING WATER

Applying calorimetric method, equilibrium relationships between unfrozen liquid water content and temperature are measured in freezing regime ($T < 0^\circ\text{C}$), using measurement device schematically shown in figure 1 [11]. Converting temperature T into moisture (chemical) potential μ by applying equation(16), measured values are compared with equilibrium moisture content of liquid phase (sorption isotherm) above 0°C which are measured by the tensiometer method and the pressure membrane method. Of LEDA clay, results of measurement are

shown in figure 2. In figure 2, measured values under freezing condition co-existed with solid (ice) and liquid water are shown by circle \bigcirc indicated by calorimetric method. Measured values under $T > 0^\circ\text{C}$ are shown by \square and \blacksquare indicated by pressure membrane method and tensiometer method. Figure 2 shows that measured values under freezing condition \bigcirc agree well with measured values \square and \blacksquare under $T > 0^\circ\text{C}$. Those results indicate that equilibrium relations of non-freezing liquid water are equal to those under non-freezing regime. Of course, under condition $T < 0$ without solid water, equilibrium relations between liquid water content and moisture (chemical) potential coincide with each other, except for little effect of temperature.

From results mentioned above, it is concluded that moisture (chemical) potential in porous media depends only on its temperature in freezing zone. And equilibrium relation below 0°C is same as that above 0°C .

Using results of thermodynamic equilibrium relations, obtained above, governing equations (5) and (10) with boundary conditions (11) and (12) are closed, both in freezing regime and non-freezing regime below 0°C , as same as in $T > 0^\circ\text{C}$. Unknown variables in two governing equations (5) and (10) are solid water (ice) content ϕ_i and temperature T (or μ) when $\phi_i > 0$. When $\phi_i = 0$, unknown variables are μ and T . This indicate that unknown variables change from moisture potential μ to solid water (ice) content ϕ_i when value of μ agree with value of critical moisture (chemical) potential given by equation (16). Then problem solved is looked as moving boundary problem.

NUMERICAL EXAMPLE

~~FREEZING AND THAWING PROSESS~~

COMPUTATIONAL CONDITIONS

A two layer building wall, as shown in figure 3, is numerically analyzed by finite difference method [12]. Materials of the wall are clay (10cm thickness) and glass wool (2.5cm thickness). At a outer surface of the wall contacted with outdoor air, thin film of moisture barrier is laid on it. So, at the surface, no moisture flow is assumed through the film. The building wall is laid between outdoor air and indoor air.

Boundary conditions are as follows. Outdoor air

temperature $T_0(t)$ is set as
 $T_0(t) = -2.5 + 2.5 \cos(2 \pi t/24)$

where t is time (hour)

Indoor temperature is set at $18.0[^\circ\text{C}]$ and the relative

humidity is 40% (corresponding to $\mu = -123,160$ J/kg).

Initial conditions of the numerical simulation are set as follows. The outdoor surface temperature is 0°C and $\mu = -200$ [J/kg] (liquid water content of 3.0% and no solid water content), respectively. The indoor surface temperature and moisture (chemical) potential are 18.0°C and $\mu = -170$ [J/kg] (liquid water content of 3.2%), respectively.

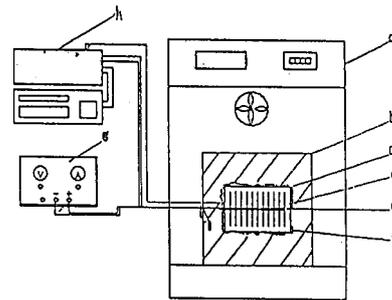


Figure 1 Schematic diagram of apparatus
a. Air bath d. Specimen g. Voltage stabilizer
b. Insulated box e. Heater h. Recorder
c. Container box f. THERmocouple

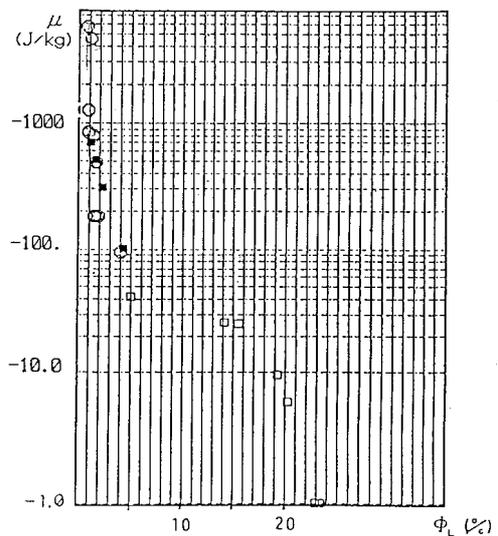


Figure 2 Equilibrium relation of liquid water content

- \blacksquare Tensiometer method ($T > 0^\circ\text{C}$)
- \square Pressure membrane method ($T > 0^\circ\text{C}$)
- \bigcirc Calorimetric method ($\Phi_i > 0$)

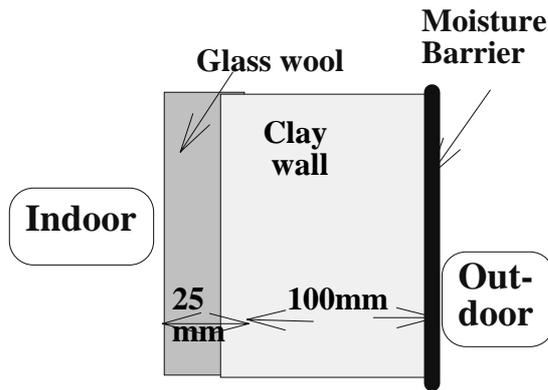


Figure 3 System analyzed

Linear temperature and moisture (chemical) potential distribution are assumed between the two surfaces. The heat transfer coefficient and coefficient of water vapor transfer at the inner wall surface are set at $9.3 \text{ [W/m}^2 \text{ K]}$ and $0.0044 \text{ [kg/m}^2 \text{ s (kg/kg}^{\circ}\text{)]}$, respectively. The physical properties of clay in reference [12] is used. All of the properties strongly depend on dependent variables, μ and T as well known. While thermal resistance of the glass wool layer is set at $0.905 \text{ [m}^2 \text{ K/W]}$, the thermal capacity and resistance to water vapor flow is ignored.

METHOD OF NUMERICAL CALCULATION

The governing equations (5) and (10) with boundary conditions (11) and (12) are solved by an explicit finite difference method. Outline of the computation is as follows[12].

- (1) Initial conditions of temperature and moisture (chemical) potential are given
- (2) Calculate diffusion coefficients, using state variables μ and T .
- (3) Calculate moisture and heat fluxes.
- (4) If the mesh point is saturated, moisture influxes is set zero.
- (5) Calculate the temperature and moisture (chemical) potential at the next time step in a non-freezing regime.
- (6) In the case of a freezing regime, instead of step 5, perform a iterative calculation of the temperature, moisture (chemical) potential and solid water (ice) content at the next time step.
- (7) Go back to step 2

Mesh size is set as 4mm on clay layer, which is 1/25 of thickness of clay layer..

RESULTS OF SIMULATION AND DISCUSSION

(1) Distribution of ice and liquid water content

Figure 4 shows the ice content distribution on the 5th day. The ice content has a peak value around 50mm from the outer surface, however maximum value of ice content occur at the outer surface. This partly because the effect of initial temperature fade away and the temperature near there drops, and partly because water inflow from the room side increases due to the increase in overall moisture content. As a whole, the ice content is gradually increase compared with preceding days. This tendency becomes evident on the 10th day, and the ice content at a point 48mm from outer surface increases up to 3.8%. However, the ice content at the outer surface becomes highest over 7%.. At the outer surface freezing and thawing occur faster than in the other places, due to the fluctuation of the outdoor temperature.

As shown in figure 5, the ice content distribution on the 30th day indicates that the ice content at the outer surface reaches saturation (the value of 37.5% corresponds to the saturation). Figure 6 for total moisture distribution shows that saturation occurs on the outer surface. As shown in figure 7, the increase of maximum ice content on the outer surface decreases from 29th to 30th day because saturation reaches there. In figure 8, the liquid water content distributions are shown. Due to the freezing and thawing, the liquid water content at the outer surface fluctuate between 2% (freezing) and 12%(thawing).

Furthermore, the frozen zone shrinks toward the outer surface (Figure 4 and 5) which could be attributed to an increase in heat release due to the freezing which occurs over time. That is, the total amount of moisture accumulated in the wall increases with time, which means by an increase in the total amount of ice and melted moisture. The heat release caused by the freezing makes the potential zone for freezing closer to the cold side and narrower with time. This, along with the increase of the total amount of moisture, causes the total moisture to increase rapidly to the point of saturation.

(2) Temperature Distribution

Figure 9 shows the temperature distribution on the 1st, 3rd, 5th and 10th days. From this figure, it is found that the temperature distribution rizes day by day. This seems due to the same reason that the frozen zone got narrow

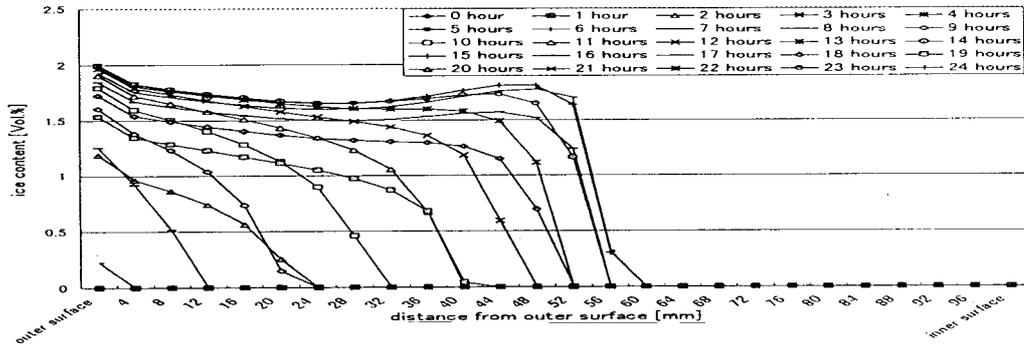


Figure 4 Ice content distribution (5th days)

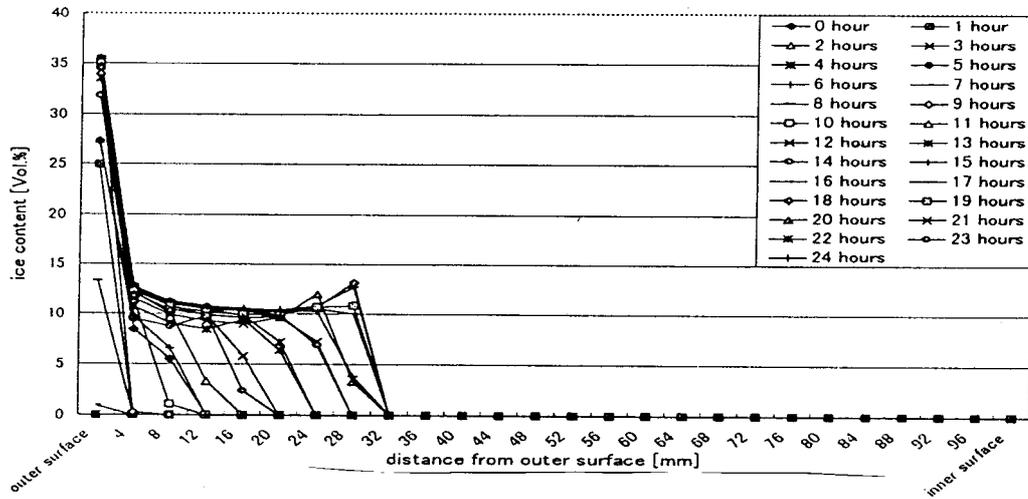


Figure 5 Ice content distribution (30th day)

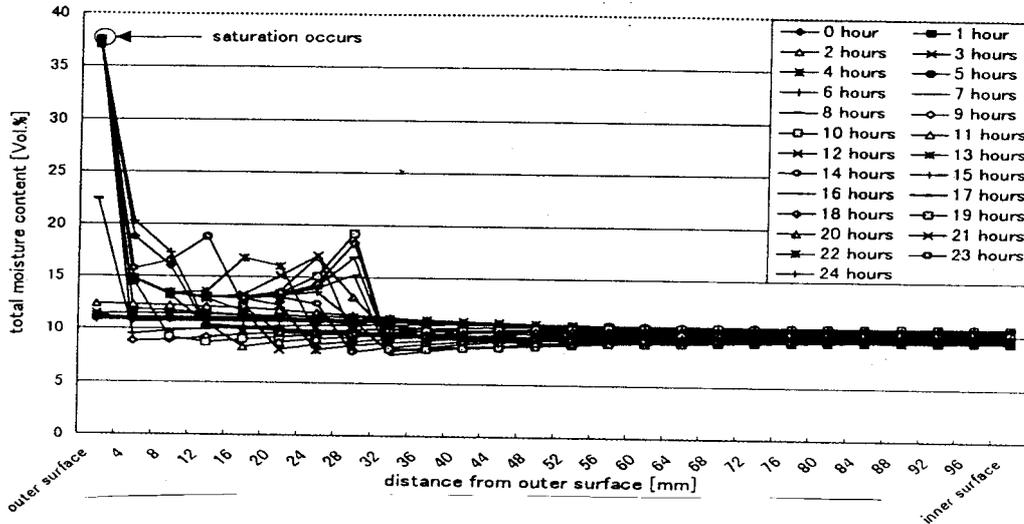


Figure 6 Distribution of Total moisture content (30th day)

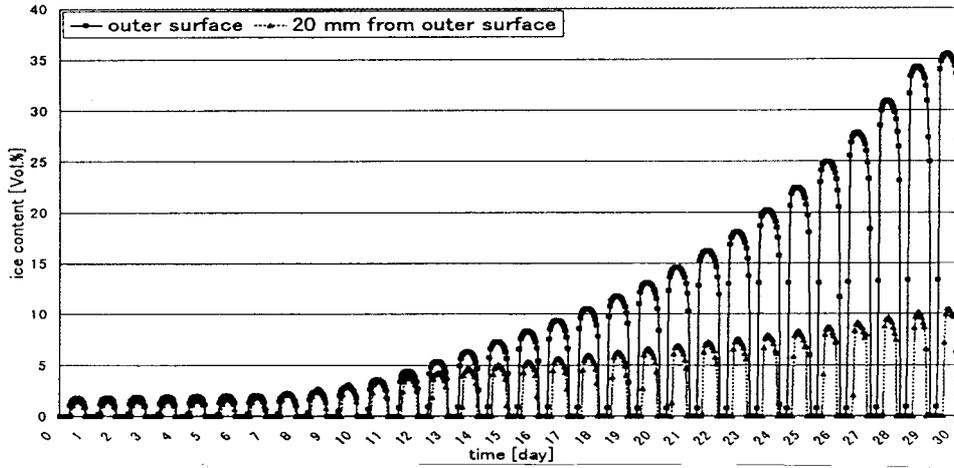


Figure 7 Ice content change for 30 days

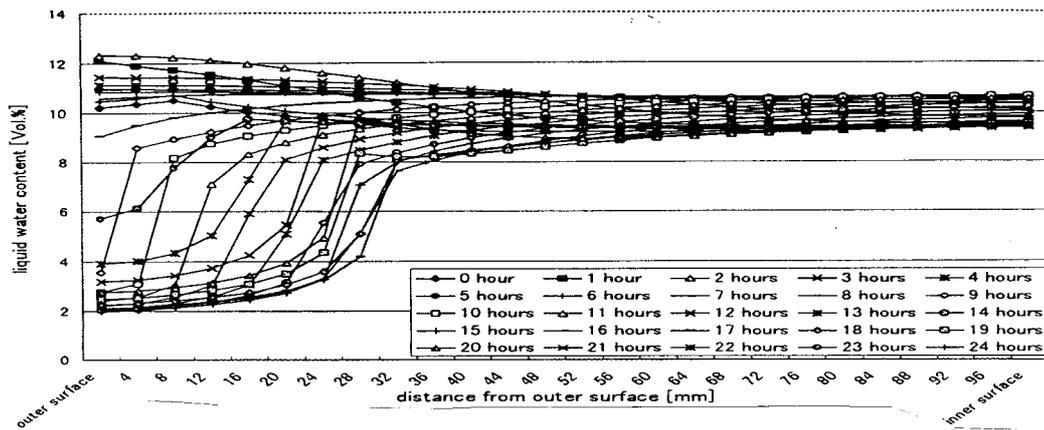


Figure 8 Liquid water content distribution (30th day)

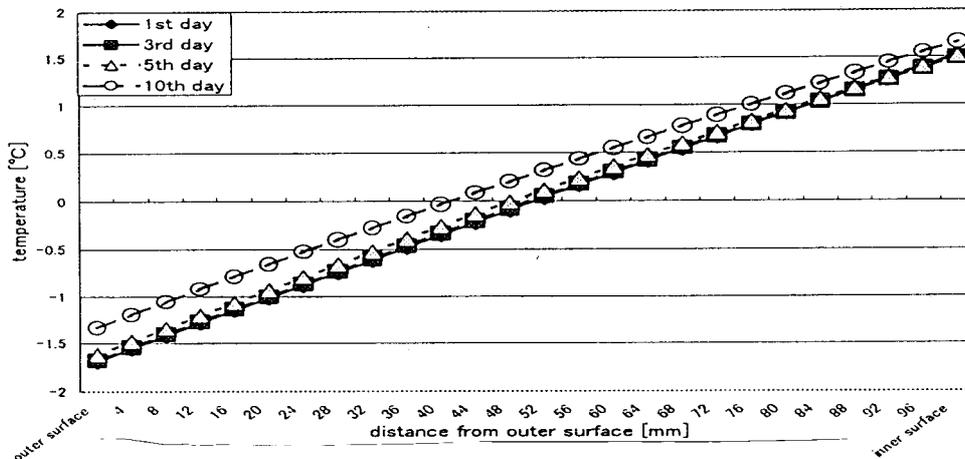


Figure 9 Temperature distribution each days (after 12hours)

CONCLUSIONS

1. Governing equations are derived for simultaneous heat and moisture transfer which can be applied to freezing and thawing processes. Closing of the equations is discussed.
2. For closing the governing equations, equilibrium relations of the liquid water content and moisture (chemical) potential under freezing regime are presented and discussed how to measure or how to estimate. Along with, the freezing point depression is shown as a function of moisture (chemical) potential.
3. As an example of simulation, freezing and thawing process in the building wall, thermally insulated by glass wool on inner side of the wall and layered by moisture barrier at outer surface, is numerically analyzed using the governing equations derived. Daily cyclic variations of outdoor temperature are applied to the building wall analyzed, while the indoor air temperature and moisture (chemical) potential is kept constant. The governing equations are numerically analyzed by explicit finite difference method. In numerical calculations iteration is required at freezing zone. Results of calculations show that the total amount of the ice and melted water increases with time and frozen area is confined into narrow region closer to the outer surface. This is because the increased amount of frozen water causes an average temperature increase in the wall as a whole.

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NOMENCLATURE

- c = specific heat [J/kg K]
 F = gravity potential [J/kg]
 H_j = enthalpy of j th phase [J/kg]
 $H_{1j} = H_1 - H_j$
 J_{1j} = moisture flow rate of phase change from i th phase to j th phase [$\text{kg}/\text{m}^2\text{s}$]
 S = entropy [J/kg K]
 T = temperature [K]
 α = heat transfer coefficient [$\text{W}/\text{m}^2\text{K}$]
 α'_μ = vapor transfer coefficient related to water chemical potential difference [$\text{kg}/\text{m}^2\text{s}(\text{J}/\text{kg})$]
 α'_T = vapor transfer coefficient related to temperature difference [$\text{kg}/\text{m}^2\text{s K}$]
 λ = thermal conductivity of moist porous material [$\text{W}/\text{m K}$]
 $\lambda'_{\mu g}$ = moisture conductivity in gas phase related to moisture chemical potential gradient [$\text{kg}/\text{m s J}/\text{kg}$]
 λ'_{Tg} = moisture conductivity in gas phase related to temperature gradient [$\text{kg}/\text{m s K}$]
 $\lambda'_{\mu l}$ = moisture conductivity in liquid phase related to moisture chemical potential gradient [$\text{kg}/\text{m s J}/\text{kg}$]
 λ'_{Tl} = moisture conductivity in liquid phase related to temperature gradient [$\text{kg}/\text{m s K}$]
 λ'_{Ti} = moisture conductivity in solid phase related to temperature gradient [$\text{kg}/\text{m s K}$]
 μ = moisture chemical potential referred to free water ($= RT \ln h$) [J/kg]
 ρ = density [kg/m^3]
 Φ_j = volume fraction of j th phase (=moisture content of j th phase) [m^3/m^3]

SUFFIX

- g = moisture in gas phase
 l = moisture in liquid phase
 i = moisture in solid phase