ANALYTICAL THEORY ON COUPLED HEAT AND WATER TRANSFER THROUGH POROUS MATERIALS

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ABSTRACT

New thermodynamic energy "water potential" based on the chemical potential of a component of mixture gases is defined as the driving force of gaseous phase water flux. Adhesive power, which is a kind of stress called "capillary attraction" and a part of the water potential, is proved as the driving force of liquid phase water flux. Then numerical model of coupled heat and water transfer using the water potential is introduced and influences of stress such as gravity and stationary pressure on water flux are clarified from the viewpoint of thermodynamics. The way to estimate diffusivities of gaseous and liquid phase water through porous materials is also proposed. Furthermore accuracy of the numerical model is shown through a comparison between calculation and experiment on behavior of water content in a porous material.

INTRODUCTION

Existing analytical theories on coupled heat and water transfer through porous materials are using physical amounts as the driving force of water flux. The physical amounts, such as vapour pressure, water content, relative humidity, temperature and so on seem to be certainly one of the driving forces but it is unthinkable that they are perfectly correct as the driving force from the viewpoint of thermodynamics. Then new driving forces of gaseous and liquid phase water flux are defined by the thermodynamic energy and the numerical model on coupled heat and water transfer is proposed.

DRIVING FORCE OF WATER FLUX

Driving force of gaseous phase water flux (Definition of the water potential)

Chemical potential is defined as Gibbs free energy per mole and used as an index of a mass equilibrium state in the thermodynamic equilibrium system. The thermodynamic system changes toward the lower condition of chemical potential in the mass non-equilibrium state (Mass transfer merely occurs in case of no chemical change). By applying the chemical potential to moisture diffusion, new thermodynamic function "water potential" can be introduced as an index of moisture equilibrium state [1]. So the water potential signifies the thermodynamic energy and the driving force of moisture flux (gaseous phase water flux).

If the component gas i occupies all the volume independently, the following Gibbs free energy is obtained.

$$G_i = n_i h_{o,i} - n_i T s_{o,i} + n_i \int_{T_o}^{T} c_{p,i} dT - n_i T \int_{T_o}^{T} \frac{c_{p,i}}{T} dT + n_i RT \ln \frac{p_i}{p_o} \tag{1}$$

In which c_p, h, n, p, R, s and T are specific heat, enthalpy, mole number, pressure, gaseous constant, entropy and temperature, respectively. Then the chemical potential of the component gas i of mixture gases is defined as Eq.(2) by dividing n_i into Eq.(1) and substituting the molar fraction $c_i = p_i/p$.

$$\mu_i(p,T) = h_{o,i} - T s_{o,i} + \int_{T_o}^{T} c_{p,i} dT - T \int_{T_o}^{T} \frac{c_{p,i}}{T} dT + RT \ln \frac{p}{p_o} + RT \ln c_i \tag{2}$$

Water in air can be supposed to be a single ingredient system in which gaseous and liquid phase water coexist because components of air are much the same anywhere except moisture quantity and they are not affected by phase change of water. For this reason, the driving force of moisture flux is expressed by the chemical potential of water in the isothermal and equal pressure field. It is established by the Onsager's reciprocal theory that the chemical potential of water is also the driving force of moisture flux even in the thermodynamic non-equilibrium system (the non-isothermal field) [2]. Then if $c_{p,w}$ is regarded as a constant and p is replaced by p_s, the chemical potential of water is defined as follows.

$$\mu_w(p,T) = \mu_w^o(T) + \mu(p) \tag{3}$$

$$\mu_w^o(T) = h_{o,w} - Ts_{o,w} + c_{p,w}(T - T_o) - Tc_{p,w}\ln\frac{T}{T_o} + R_vT\ln\frac{p_s}{p_o} \tag{4}$$

$$\mu(p) = R_vT\ln\frac{p_w}{p_s} \tag{5}$$

In which T_o and p_o are the standard temperature and pressure. p_w and p_s are the vapor pressure and the saturated vapor pressure of the humid air. The water potential is defined as the value per unit weight by applying the reduced values per unit weight as $c_{p,w}$ and R_v (specific heat [J/(kg K)], R_v=8.31441[J/(mol K)] /18.016×10³[kg/mol] =461.50[J/(kg K)]). Furthermore, by providing 0°C (=273.15K) as the standard temperature T_o and 1atm (=1.01325×10⁵Pa) as the standard pressure p_o, and introducing Eq.(6) as the standard enthalpy h_o and entropy s_o, Eq.(4) is rewritten to Eq.(7).

$$h_{o,w} - T_os_{o,w} = 6.44243\times10^5 \tag{6}$$

$$\mu_w^o(T) = 6.44243\times10^5 + c_{p,w}(T - 273.15) - Tc_{p,w}\ln\frac{T}{273.15} + R_vT\ln\frac{p_s}{1.01325\times10^5} \tag{7}$$

Eq.(3), (5), (7) show the established expressions of the water potential defined as the driving force of moisture flux. As Eq.(3) shows, the water potential is composed by saturated water potential μ_w^o and unsaturated water potential μ.

Driving force of liquid phase water flux
The water potential of void air in porous materials becomes the same as that of surrounding air in the moisture equilibrium state. Then capillary tubes of porous materials adsorb and desorb water to keep moisture equilibrium with void air. In this condition the water potential of the void air and capillary water become the same because adhesive power, which is a kind of stress called "capillary attraction", is at work to capillary tubes even if the surface of capillary water is saturated. In other words, the water potential of capillary water can be expressed by the sum of saturated water potential μ_w^o and adhesive power μ_s, and μ_s is equal to unsaturated water potential μ of void air. Incidentally, $\mu = \mu_s$ is represented by Kelvin's equation as Eq.(8).

$$\mu = R_vT\ln\left(\frac{p_w}{p_s}\right) = -\frac{2\gamma}{r_c\rho_{lw}}\cos\theta \tag{8}$$

In which r_c is capillary radius, γ and ρ_{lw} are surface tension and specific weight of liquid phase water, and θ is angle between capillary surface and meniscus of capillary water. Therefore the relation between μ and water content is obtained from distribution of capillary radius measured by gas adsorption method and so on and water capacity $\partial\phi/\partial\mu$ which is defined in the next paragraph can be estimated. That is to say, μ is the thermodynamics energy, which indicates the state of water content, and expresses driving force of liquid phase water flux through porous materials.

NUMERICAL MODEL OF COUPLED HEAT AND WATER TRANSFER

Water balance

Equilibrium equation of moisture transfer in porous material is obtained from law of conservation of mass.

$$\frac{\partial W}{\partial t} + \nabla J_w = 0 \tag{9}$$

J_w is the amount of water flux per unit area and W is weight of water content per unit volume of material. If it is assumed that internal pressure of material is kept constant and stresses such as gravitation work nothing to material, and then if the water potential μ_w and unsaturated water potential μ are used as the driving forces of gaseous and liquid phase water flux j_{gw} and j_{lw}, J_w is expressed by Eq.(10)

$$J_w = j_{gw} + j_{lw} = -\lambda_g' \nabla \mu_w - \lambda_l' \nabla \mu \tag{10}$$

λ_g' and λ_l' are gaseous and liquid phase water conductivity for μ_w and μ gradient. λ_g' can be regarded as a constant value in the hygroscopic range without liquid phase water flux. W is obtained by summing gaseous and liquid phase water content (by summing both quantities of moisture in voids and adsorbed water in capillary).

$$W = \rho_{gw} \psi + \rho_{lw} \phi \tag{11}$$

ψ and ϕ are ratio of voids and water content per unit volume of porous material. ρ_{gw} and ρ_{lw} are absolute humidity per unit volume of air and specific weight of liquid phase water. By substituting Eq.(10), (11), Eq.(9) is changed to Eq.(12).

$$\frac{\partial \rho_{gw} \psi}{\partial t} + \frac{\partial \rho_{lw} \phi}{\partial t} = \nabla \lambda_g' \nabla \mu_w + \nabla \lambda_l' \nabla \mu \tag{12}$$

The left hand second term of Eq.(12) becomes to the following equation by assuming ϕ as a function of μ_w and using Eq.(3).

$$\frac{\partial \rho_{lw} \phi}{\partial t} = \rho_{lw} \left(\frac{\partial \phi}{\partial \mu_w^o} \frac{\partial \mu_w^o}{\partial t} + \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial t} \right) \tag{13}$$

In which $\partial \phi / \partial \mu_w^o$ can be omitted ($\partial \phi / \partial \mu_w^o \equiv 0$), then ϕ is obtained as a function of μ. So equilibrium equation of moisture transfer is expressed by Eq.(14).

$$\frac{\partial \rho_{gw} \psi}{\partial t} + \rho_{lw} \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial t} = \nabla \lambda_g' \nabla \mu_w + \nabla \lambda_l' \nabla \mu \tag{14}$$

Furthermore $\partial \rho_{gw} \psi / \partial t$ can be also neglected in general materials because ρ_{gw} is far less than ρ_{lw} and ψ is very small, then Eq.(14) is rearranged to Eq.(15).

$$\rho_{lw} \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial t} = \nabla \lambda_g' \nabla \mu_w + \nabla \lambda_l' \nabla \mu = \nabla \lambda_g' \nabla \mu_w^o + \nabla \lambda_g' \nabla \mu + \nabla \lambda_l' \nabla \mu \tag{15}$$

Thermal balance

Equilibrium equation of heat transfer in porous material is obtained from heat flux q per unit area and enthalpy H per unit volume.

$$\frac{\partial H}{\partial t} + \nabla q = 0 \tag{16}$$

Eq.(16) is changed to the following equation.

$$\frac{\partial C \rho T}{\partial t} + \left(c_{gw} j_{gw} + c_{lw} j_{lw} \right) \nabla T = \nabla \lambda \nabla T + r \cdot r_{gl} \tag{17}$$

C and ρ are specific heat and specific weight of material containing water. c_{gw} and c_{lw} are specific heat of gaseous and liquid phase water. λ is thermal conductivity. r is heat of

adsorption (= latent heat from gaseous to liquid phase water). r_{gl} is amount of phase change per unit volume of material and expressed by Eq.(18).

$$r_{gl} = \nabla \lambda'_g \nabla \mu_w - \frac{\partial \rho_{gw} \psi}{\partial t} \tag{18}$$

Therefor equilibrium equation of heat transfer is rewritten as Eq.(19)

$$\frac{\partial C\rho T}{\partial t} + \left(c_{gw} j_{gw} + c_{lw} j_{lw}\right)\nabla T = \nabla \lambda \nabla T + r\left(\nabla \lambda'_g \nabla \mu_w - \frac{\partial \rho_{gw} \psi}{\partial t}\right) \tag{19}$$

$c_{gw} j_{gw} \nabla T$ and $\partial \rho_{gw} \psi / \partial t$ can be neglected because of few j_{gw} and by reason of mentioned above, and then Eq.(19) is rearranged to Eq.(20)

$$\frac{\partial C\rho T}{\partial t} + c_{lw} j_{lw} \nabla T = \nabla \lambda \nabla T + r\nabla \lambda'_g \nabla \mu_w \tag{20}$$

Boundary condition
Boundary conditions are expressed as follows.

$$-\lambda'_g \frac{\partial \mu_w}{\partial n_s} = \alpha'\left(\mu_{w,a} - \mu_{w,s}\right) \tag{21}$$

$$-\lambda \frac{\partial T}{\partial n_s} - r \cdot \lambda'_g \frac{\partial \mu_w}{\partial n_s} = \alpha_c\left(T_a - T_s\right) + r \cdot \alpha'\left(\mu_{w,a} - \mu_{w,s}\right) + q_s \tag{22}$$

In which n_s is normal line vector directed inward on a boundary surface, q_s is quantity of radiant heat, α_c is convective heat transfer coefficient and α' is convective moisture transfer coefficient for the water potential gradient. $\mu_{w,a}$, $\mu_{w,s}$, T_a and T_s are the water potential and temperature of the outside air and surface, respectively.

INFLUENCE OF STRESS ON WATER FLUX

Gibbs free energy is expressed as the function of temperature, pressure and molar number n_i of each component i in an open system in which amount of components is changeable. So the change of Gibbs free energy caused by infinitesimal change of the open system is expressed by Eq.(23) in case that n_i is variable.

$$dG = -SdT + Vdp + \sum_{i=1}^{m} \mu_{c,i} dn_i \tag{23}$$

If a stress works to the system, Eq.(23) is rearranged as Eq.(24), (25) by estimating a work, except for density change, arisen from the energy increase of the system.

$$dG = -SdT + Vdp + d'W' \tag{24}$$

$$d'W' = \sum_{i=1}^{m} \mu_{c,i} dn_i + Xdy \tag{25}$$

In which X is the potential depending on the stress and Xdy is the amount of energy increase of system. y is extensive properties which is proportional to mass and related to molar number n_i as Eq.(26).

$$y = \sum_{i=1}^{m} n_i \bar{y}_i \tag{26}$$

If $\bar{y}_i$ is constant value, Eq.(25) is rewritten to (27), (28) and stress chemical potential is obtained as Eq.(28).

$$d'W' = \sum_{i=1}^{m} \tilde{\mu}_{c,i} dn_i \tag{27}$$

$$\tilde{\mu}_{c,i} = \mu_{c,i} + X\bar{y}_i \tag{28}$$

For example, if gravitation and stationary pressure are at work to the system, gz and p are supposed to be X and then gzM_i and $p\overline{V_i}$ are supposed to be $X\overline{y_i}$ because mass and volume of the system are established as y. g is acceleration of gravity, z is height from reference position, M_i is molecular weight and $\overline{V_i}$ is molecular volume. So the water potential including the effect of stress, which is called the stress water potential $\tilde{\mu}_w$, is defined by adding the stress potential on the water potential μ_w. The stress potential is obtained by dividing molecular weight of water into $X\overline{y_i}$ because the water potential is defined as the value per unit weight of water. Therefore the stress water potential which includes the effects of gravitation and stationary pressure is calculated by Eq.(29)

$$\tilde{\mu}_w = \mu_w + gz + p\overline{V}_w \qquad (29)$$

In which $\overline{V}_w$ is the volume per unit weight of water and $p\overline{V}_w$ is equal to R_vT. Even if there is no difference of p in each parts of the system, the stress potential R_vT should be estimated in case that T is different because $\overline{V}_w$ must be different.

When the stress acts on the void air, it also acts on the solid part that forms the void. So numerical model of coupled heat and water transfer including the influence of stress is expressed as follows by adding the stress potential F on both of driving forces of gaseous and liquid phase water μ_w and μ described by Eq.(3), (8). Then Eq.(30), (31) are introduced from Eq.(15), (20)

$$\rho_{lw}\frac{\partial\phi}{\partial\mu}\frac{\partial\mu}{\partial t} = \nabla\lambda'_g\nabla(\mu_w + F) + \nabla\lambda'_l\nabla(\mu + F)$$

$$= \nabla\lambda'_g\nabla\mu^o_w + \nabla\lambda'_g\nabla(\mu + F) + \nabla\lambda'_l\nabla(\mu + F) \qquad (30)$$

$$Cp\frac{\partial T}{\partial t} + (c_{lw}j_{lw})\nabla T = \nabla\lambda\nabla T + r\nabla\lambda'_g\nabla(\mu_w + F) \qquad (31)$$

DIFFUSIVITIES OF GASEOUS AND LIQUID PHASES WATER

One-dimensional water flux of steady state through porous material in isothermal field is expressed as Eq.(32) by using diffusivities of gaseous and liquid phase water for the water content and the water potential, D_w and λ'.

$$q_w = -D_w\frac{\partial\phi}{\partial x} = -D_w\frac{\partial\phi}{\partial\mu}\frac{\partial\mu}{\partial x} = -\lambda'\frac{\partial\mu}{\partial x} \qquad (32)$$

So λ' called "water conductivity" is obtained as the product of D_w by $\partial\phi/\partial\mu$ which can be measured easily by experiments. However both of D_w and λ' are the value for coexisted water flux of gaseous and liquid phases in high water content range. Then λ' can be separated as Eq.(33).

$$\lambda' = \lambda'_g + \lambda'_l \qquad (33)$$

λ'_g and λ'_l are the water conductivity of gaseous and liquid phases, respectively. λ'_g ($= \lambda'_{g,mw}$) in the hygroscopic range is a constant, while λ'_g ($= \lambda'_{g,hw}$) in the high water content range is approximated as Eq.(34) if the amount of moisture diffusion depends on only capillary space.

$$\lambda'_{g,hw} = \lambda'_{g,mw}\frac{\psi_{hw}}{\psi_{mw}} \qquad (34)$$

ψ_{hw} is the void rate of the high water content range and ψ_{mw} is the critical void rate of the hygroscopic range in which $\lambda'_{g,mw}$ is supposed to be constant and maximum ($\psi_{hw} \leq \psi_{mw}$). $\lambda'_{g,hw}$ can be also estimated experimentally from the relation between unsaturated water

potential μ (or water diffusivity D_w) and water content ϕ in the hygroscopic range.

VERIFICATION OF ANALYTICAL MODEL

Numerical model on coupled heat and water transfer as mentioned above is verified through the comparison with experiments. Water content distribution with temperature difference is examined for calcium silicate. Then Eq.(15), (20) and Eq.(30), (31) are solved by Crank-Nicolson method on the same condition at experiments and the calculated results are compared with the experimental one. Fig.1 shows the measuring instrument of water content distribution with temperature difference. Experimental materials (a piece of calcium silicate, 25x50x80mm) in it are thermal insulated and waterproofed. One side of them is heated up and the other side is cooled off at constant temperature. Outline symbols in Fig.2, 3 show the experimental results on the distribution of temperature and water content of materials after 21 days from the beginning. Water content, which is the mean value in each length of 20mm, becomes larger in the lower temperature side. Solid lines and black symbols in Fig.2, 3 show the calculated values by Eq.(30), (31) including the influence of stress with temperature difference, while broken lines show the calculated values by Eq.(15), (20) omitting the influence of stress. Distribution of temperature and water content calculated with stress perfectly agree with experimental one. However those without stress become larger in high temperature range and smaller in low temperature range than the real one.
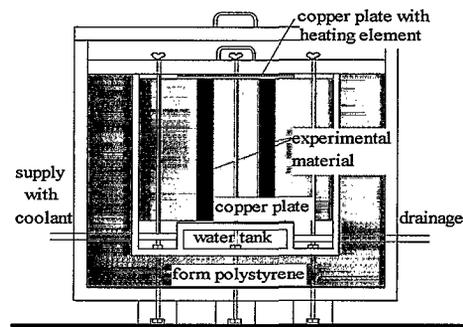

Fig.1 Measuring instrument of water content distribution with temperature gradient

CONCLUSION

New driving force of gaseous and liquid phase water flux is defined as "water potential" and "unsaturated water potential" on the basis of thermodynamic energy. The influence of stress such as gravity and stationary pressure on the water potential is also clarified as thermodynamic energy. So every driving force of water flux is introduced at the same energy unit. Then numerical model on coupled heat and water transfer is proposed and accuracy of the model is verified through the comparison with experiments.

REFERENCES

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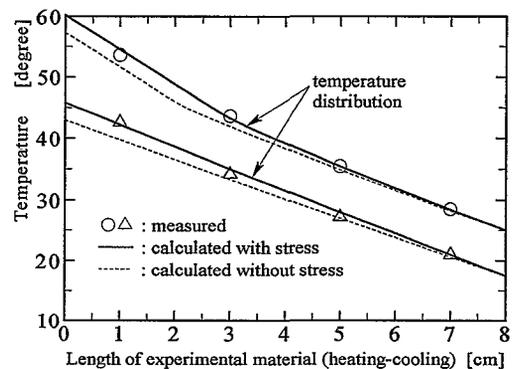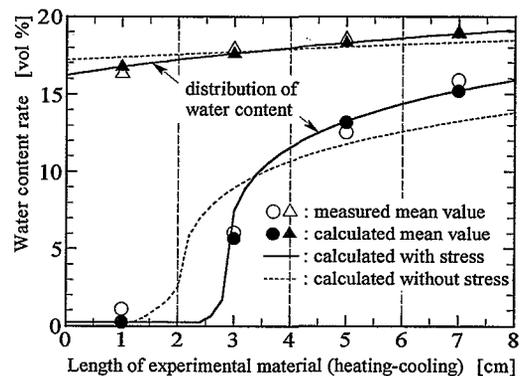2. A.Katchalsky and Peter F.Curran, "Nonequilibrium thermodynamics in biophysics", published by Misuzu Shobo, 1988

Fig.2 Distribution of temperature

Fig.3 Distribution of water content