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MULTI-PHASE MOISTURE TRANSFER IN POROUS MEDIA SUBJECTED TO TEMPERATURE GRADIENT*

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Abstract—To describe the history of moisture migration in porous media, the dependence on the relevant material characteristics must be considered. A diffusion theory with a linear or nonlinear coefficient of diffusivity is not adequate for the description of the behavior of mass transfer in a porous medium. Transfers of mass of all phases and the transfer of heat must be considered simultaneously. Based upon the principle of non-equilibrium irreversible thermodynamics, the macroscopic laws of conservation, and the liquid–vapor equilibrium of a porous system, a set of basic equations for simultaneous mass and heat transfer is developed. The developed theory is applied to the investigation of moisture migration in a light-weight concrete wall subjected to a temperature gradient. The result reveals that in addition to diffusion, both the capillary and the evaporation–condensation mechanisms, which are strongly affected by the topology of a porous system, are important in the drying process.

NOMENCLATURE

M,	averaged mass for mixture;
M_i,	molecular weight of the *i*th-component $[\mathrm{kg\,mol^{-1}}]$;
$\mathbf{X}_i$,	body force acting on the *i*th-component $[\mathrm{kg\,m\,s^{-2}\cdot mol^{-1}}]$;
V,	molar volume of the mixture $[\mathrm{m^3\,mol^{-1}}]$;
P,	total macroscopic pressure $[\mathrm{kg\,m^{-1}\,s^{-2}}]$;
a_{ij},	phenomenological coefficients;
k_i,	thermal conductivity of the *i*th-component $[\mathrm{kg\,m\,s^{-3}\,K^{-1}}]$;
k,	effective thermal conductivity tensor $[\mathrm{kg\,m\,s^{-3}\,K^{-1}}]$;
$\hat{k}$,	unit normal vector perpendicular to the earth surface;
D,	diffusivity of gas $[\mathrm{m^2\,s^{-1}}]$;
D_T,	thermal diffusivity $[\mathrm{kg\,m^{-1}\,s^{-1}}]$;
$\mathbf{v}_g$,	microscopic local velocity of gas $[\mathrm{m\,s^{-1}}]$;
p_i,	microscopic local pressure of the *i*th-component $[\mathrm{kg\,m^{-1}\,s^{-2}}]$;
p_v^0,	equilibrium vapor pressure of bulk water $[\mathrm{kg\,m^{-1}\,s^{-2}}]$;
h_i,	specific enthalpy of the *i*th-component $[\mathrm{m^2\,s^{-2}}]$;
$\mathbf{v}$,	mass average velocity $[\mathrm{m\,s^{-1}}]$;
c,	empirical parameter;
r,	hydraulic porous radius or characteristic length of a porous medium $[\mathrm{m}]$;
m,	volumetric moisture content per unit volume of the porous body $[\mathrm{m^3\,m^{-3}}]$;
$\mathbf{n}_i$,	the vector of absolute mass flux for the *i*th-component $[\mathrm{kg\,m^{-2}\,s^{-1}}]$;
n,	topological parameter of the porous medium [dimensionless];
$\mathbf{v}$,	the bulk velocity vector $[\mathrm{m\,s^{-1}}]$;
$\mathbf{v}_i$,	the absolute velocity vector of the *i*th-component $[\mathrm{kg\,m^{-2}\,s^{-1}}]$;
$\bar{O}_p$,	expression in coefficients [dimensionless];
$\bar{O}_p$,	expression in coefficients $[\mathrm{m\,s^2\,kg^{-1}}]$;
$\bar{O}_T$,	expression in coefficients $[\mathrm{K^{-1}}]$;
$\mathbf{q}_i,\mathbf{q}$,	heat flux of the *i*th-component $[\mathrm{kg\,s^{-3}}]$;
T,	absolute temperature $[\mathrm{K}]$;
$\mathbf{J}_i$,	mass flux of the *i*th-component relative to the mixture average velocity $[\mathrm{kg\,m^{-2}\,s^{-1}}]$;
R,	gas constant $[\mathrm{m\,s^2\,kg^{-1}}]$;
$\bar{W}_p$,	expression in coefficients $[\mathrm{m\,s^2\,kg^{-1}}]$;
$\bar{W}_T$,	expression in coefficients $[\mathrm{K^{-1}}]$;
$\bar{Y}$,	expression in coefficients [dimensionless].

Greek symbols

ε,	porosity of the porous system $[\mathrm{m^3\,m^{-3}}]$;
$\varepsilon_i(t)$,	volume fraction of the *i*th-component $[\mathrm{m^3\,m^{-3}}]$;
ϕ,	mole fraction of water vapor of the gaseous component [mol/mol];
δ,	mass concentration per unit volume of the porous system $[\mathrm{kg\,m^{-3}}]$;
$\delta_i(t)$,	mass concentration of the *i*th-component per unit volume of the porous system $[\mathrm{kg\,m^{-3}}]$;
ρ_i,	density of the *i*th-component $[\mathrm{kg\,m^{-3}}]$;
Γ_i,	the mass rate of source of *i*th-component; the mass rate of evaporation per unit volume of the porous system $[\mathrm{kg\,m^{-3}\,s^{-1}}]$ (without subscript);
μ_i,	chemical potential for the *i*th-component $[\mathrm{kg\,m^2\,s^{-2}\,mol^{-1}}]$;
γ,	dimensionless parameter defined in equation (2.2.14);
η_i^*,	bulk viscosity of the *i*th-component $[\mathrm{kg\,m^{-1}\,s^{-1}}]$;
κ_i,κ,	permeability of the *i*th-component and mixture through the porous system, respectively $[\mathrm{m^2}]$;

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η_i,	shear viscosity of the ith-component $[\mathrm{kg\,m^{-1}\,s^{-1}}]$;
Ψ,	rate of heat generation $[\mathrm{kg\,m^{-1}\,s^{-3}}]$;
Φ,	gravitational potential;
$\tilde{\tau}$,	viscous stress tensor $[\mathrm{kg\,s^{-2}\,m^{-1}}]$;
λ,	latent heat of vaporization from the bulk liquid $[\mathrm{m^2\,s^{-1}}]$;
$\tilde{\sigma}$,	stress tensor $[\mathrm{kg\,m^{-1}\,s^{-2}}]$;
σ,	surface tension of gas–liquid interface $[\mathrm{kg\,s^{-2}}]$;
σ_0,	surface tension at the reference temperature $[\mathrm{kg\,s^{-2}}]$;
σ_s,	Stefan–Boltzman constant $[\mathrm{kg\,s^{-3}\,K^{-4}}]$;
β,	empirical constant $[\mathrm{kg\,s^{-2}\,K^{-1}}]$;
θ,	moisture content;
ζ,	relative permeability $= \kappa_g/\kappa_g^0$;
α,	mass transfer coefficient $[\mathrm{mol\,m^{-2}\,s^{-1}}]$.

Subscripts

i,	ith-component of the mixture;
s,	of solid;
l,	of liquid;
g,	of gaseous mixture;
gv,	of vapor in a gaseous mixture;
ga,	of air in a gaseous mixture;
w,	of water.

1. INTRODUCTION

TO DESCRIBE the history of moisture migration in porous media, the dependence on the relevant material characteristics (the topology of the solid matrix, interface phenomena among solid, liquid, gaseous vapor and air, and liquid–vapor equilibria) must be considered. The phenomena relevant for moisture, pressure, and temperature distribution are coupled. A diffusion theory with a linear or a nonlinear coefficient of diffusivity is not adequate for the description of the behavior of mass transfer in a porous medium. Transfers of mass of all phases and the transfer of heat must be considered simultaneously. During the funicular stage (liquid saturated stage), diffusion seems to be the mechanism of moisture transport. However, in the pendular stage (unsaturated liquid flow stage), experience shows that diffusion, capillary and evaporation–condensation are the governing mechanisms in the mass transfer process. Experimental evidences prove that the pore size distribution of a porous medium is the important parameter affecting moisture transfer in the porous system in such a state. Theoretical analysis also confirms such a result [1]. Therefore, a general mathematical model for multi-phase moisture transfer in porous media must be constructed by using the principle of non-equilibrium irreversible flows of heat and mass. With the linear phenomenological equations and the laws of conservation in macroscopic sense [2], a set of differential equations for simultaneous heat and moisture transfer in porous media is developed. The set of differential equations is well-posed. With the given boundary and initial conditions, the differential equations can be solved readily by a digital computer. In this paper, the developed theory is applied to the investigation of moisture migration in a light-weight concrete wall of 0.1 m thickness, subjected to a temperature gradient. The result reveals the distinction of different stages: constant rate, funicular state and pendular state. It shows that temperature gradient plays an important role in a drying process. This fact finds a significant application in engineering.

2. ANALYSIS OF MASS AND ENERGY TRANSFER IN POROUS MEDIA

During drying of a saturated porous system, a large amount of moisture evaporates from the boundary surface of the porous system to the environment at a rate which is equal to, or slightly lower than, the rate of evaporation from a bulk flat water surface under identical environmental conditions. The rate of evaporation is almost constant. If the latent heat of vaporization is supplied solely by molecular transport, the surface temperature of the porous medium is near the wet-bulb temperature of the ambient atmosphere. This period of drying is called "constant rate period".

When the moisture content continuously drops, the mechanism of the removal of vapor from the boundary surface is still predominant. The drying rate gradually decreases, because the fraction of the surface which is saturated becomes smaller, as dry spots slowly appear and grow in the boundary surface. Inside the porous medium, the liquid phase of moisture filling the pore space remains continuous. This stage of drying is termed "funicular saturation stage". As the drying continues, the drying rate is controlled by internal moisture diffusion, capillary action, and evaporation–condensation mechanisms [3]. The drying rate becomes relatively insensitive to the velocity and relative humidity of ambient air and decreases significantly. The surface of the drying front, from which the evaporation occurs, may retreat from the boundary surface inward to the inside of the porous system. The drying period is termed "pendular saturation stage". The duration of this stage depends strongly on the topology of the porous system.

In this analysis, transports of a liquid and its vapor, mixing with chemically inert air, in a rigid porous system are considered. The moisture content, temperature, and pressure distribution in the porous medium are of interest. These functions can be determined by the application of the principle of nonequilibrium thermodynamics and of the macroscopic conservation laws of mass, momentum, and energy. The macroscopic continuum approach is adopted in this analysis; the actual multi-phase porous medium is replaced by an ideal continuum which is a structureless substance. To any point of which we can assign kinematic and dynamic variables and the state parameters that are continuous functions of the spatial

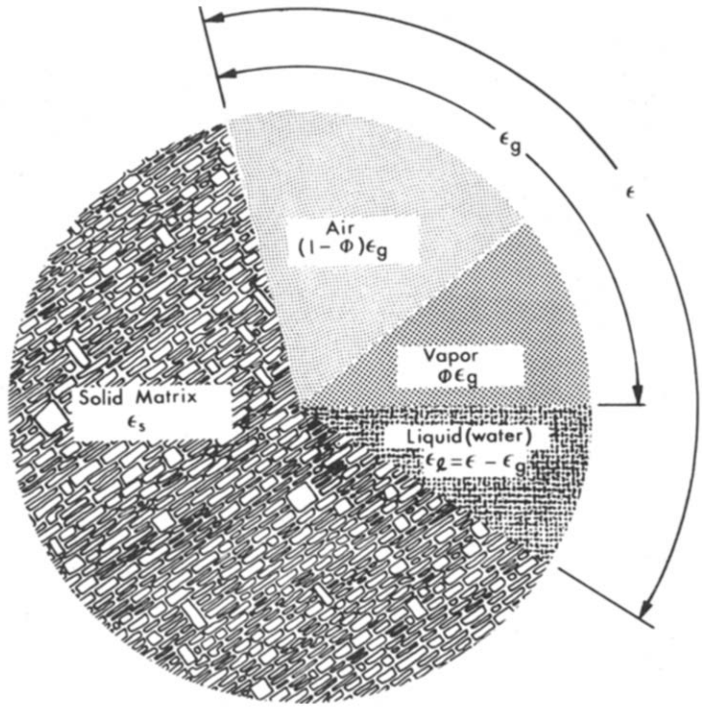

FIG. 1. A volumetric element of porous media.

Table 1. Constituents of the porous system

Components		Volume fraction $cm^3\,cm^{-3}$	Mass concentration $g\,cm^{-3}$
Solid		$\varepsilon_s = 1-\varepsilon$	$\delta_s = \rho_s\varepsilon_s = \rho_s(1-\varepsilon)$
Liquid (water)		$\varepsilon_l = \varepsilon-\varepsilon_g$	$\delta_l = \rho_l\varepsilon_l = \rho_l(\varepsilon-\varepsilon_g)$
	(vapor)	$\phi\varepsilon_g$	
gas		ε_g	$\delta_g = \rho_g\varepsilon_g = \rho_v(\phi\varepsilon_g)+\rho_a(1-\phi)\varepsilon_g$
	(air)	$(1-\phi)\varepsilon_g$	
Total		$\varepsilon_s+\varepsilon_l+\varepsilon_g = 1$	$\delta_s+\delta_l+\delta_{ga}+\delta_{gv} = \delta$

coordinates and time. Thus, the following assumptions are made:

1. The multi-phase porous system is in thermodynamic equilibrium locally;
2. The solid matrix is rigid, and is fixed in an inertial frame;
3. The liquid component is incompressible;
4. The vapor, air, and their mixture are ideal gases; and
5. The moisture content in the vapor phase is negligible in comparison with the moisture content in the liquid phase.

A logical consequence of the first assumption is that the local variables such as mass concentrations, temperature, pressure, enthalpy, and others can be specified at any point in the porous medium. For convenience, the volume fraction and the mass concentration for various components are summarized in Table 1. Also the relations of volume fractions of a unit volumetric element of porous media are shown in Fig. 1.

A. Macroscopic laws of conservation

(a) *The macroscopic conservation law of mass for each component.*

$$\delta_s = \text{constant}, \tag{2.1}$$

$$\frac{\partial \delta_l}{\partial t} + \nabla\cdot\mathbf{n}_l = \Gamma_l, \tag{2.2}$$

$$\frac{\partial \delta_{gv}}{\partial t} + \nabla\cdot\mathbf{n}_{gv} = \Gamma_{gv}, \tag{2.3}$$

$$\frac{\partial \delta_{ga}}{\partial t} + \nabla\cdot\mathbf{n}_{ga} = 0, \tag{2.4}$$

and

$$\Gamma_l + \Gamma_{gv} = 0, \tag{2.5}$$

where δ_i denotes the mass concentration for the ith-component, $\mathbf{n}_i$ the absolute mass flux of ith-component, t is time parameter, and Γ_i is the source for ith-component.

In equation (2.1) we have assumed that the mass concentration of a solid is constant. This assumption is not true when the chemical reactions and the mechanical swellings of solids are included.

(b) *The conservation of linear momentum.* In a conventional drying process, the characteristic time for drying is generally large and is of the order of days and months, and the transfers of heat and mass are rather slow. Thus, it is reasonable to treat the process of flows as quasi-steady. In such cases, the conservation of linear momentum equation can be replaced by the Darcy equation [4]:

$$\mathbf{v} = -\frac{\tilde{\kappa}}{\eta\varepsilon}\nabla\cdot(P+\Phi), \tag{2.6}$$

where $\tilde{\kappa}$ denotes the permeability tensor. For an isotropic porous system, $\tilde{\kappa} = \kappa\delta_{ij}$; η is the viscosity of the fluid, ε the porosity of the solid matrix, P the total pressure, and Φ denotes the gravitational potential.

Darcy's equation was originally considered to be the equation of motion for a fluid moving through an isotropic and homogeneous porous medium. It has been extended and applied to gaseous flows in a porous media [4, 5] for cases where the inertia term in the equation of motion is negligible.

The convective velocity of a fluid flow is defined as the mass average velocity as follows:

$$\mathbf{v} = \left(\sum_{i=1}^{N}\delta_i\mathbf{v}_i\right)\bigg/\delta = \left(\sum_{i=1}^{N}\mathbf{n}_i\right)\bigg/\delta, \tag{2.7}$$

where the mass average velocity $\mathbf{v}$ is called barycentric velocity of the mixture, and δ the density of the mixture, defined as

$$\delta = \sum_{i=1}^{N}\delta_i.$$

Microscopically, there exists in each open system a collection of N different components of molecules. The molecules of the ith-component participating in a gross motion move with an absolute velocity $\mathbf{v}_i$. A relative mass flux for ith-component, $\mathbf{J}_i$, is thus defined as [6]:

$$\mathbf{J}_i = \delta_i(\mathbf{v}_i-\mathbf{v}) = \mathbf{n}_i-\delta_i\mathbf{v}, \tag{2.8}$$

where the barycentric velocity $\mathbf{v}$ is a measure of the absolute macroscopic velocity of the mixture, and $(\mathbf{v}_i-\mathbf{v})$ is a means of the diffusion velocity for the ith-component with respect to the barycentric velocity $\mathbf{v}$.

(c) *The macroscopic conservation of energy equation.*

$$\delta\frac{\mathrm{D}h}{\mathrm{D}t} = -\nabla\cdot\mathbf{q}+\frac{\mathrm{D}P}{\mathrm{D}t}-\nabla\mathbf{v}:\tilde{\tau}+\psi, \tag{2.9}$$

where h is the macroscopic enthalpy per unit mass, $\mathbf{q}$ is the apparent heat flux, $\tilde{\tau}$ is the viscous stress tensor, and ψ represents the source of heat rate.

Equations (2.1)–(2.6) and (2.9) constitute the transport equations of moisture transfer in a porous medium under the aforementioned restrictions.

B. Two modes of mass and heat transfer

(a) *Molecular diffusion in gaseous phase.* In the gaseous phase, molecular mass and heat transfer occur simultaneously. For a binary system (vapor and air), the following conjugated fluxes and forces are considered, [2, 6, 7]:

Flux	Forces
$\mathbf{q}_g$	$-\frac{1}{T}(\nabla T)$
$\mathbf{J}_v$	$-\frac{1}{M_l}(\nabla_T\mu_v-\mathbf{X})$
$\mathbf{J}_a$	$-\frac{1}{M_a}(\nabla_T\mu_a-\mathbf{X}_a)$,

where $\mathbf{q}_g$ denotes the gaseous heat flux, T is the absolute temperature, $\mathbf{J}_i$, μ_i and M_i are the relative mass flux, the chemical potential, and the molecular mass of ith-component, respectively; ∇_T is the nabla operator with the constant temperature; and $\mathbf{X}_i$ the body force of ith-component. By the definition (2.8), the relative mass fluxes for vapor and air are:

$$\mathbf{J}_v = \delta_{gv}(\mathbf{v}_{gv}-\mathbf{v}_g), \tag{2.10}$$

and

$$\mathbf{J}_a = \delta_{ga}(\mathbf{v}_{ga}-\mathbf{v}_g), \tag{2.11}$$

respectively, where the mass average velocity of the gas mixture is defined by:

$$\mathbf{v}_g = [\delta_{gv}v_{gv}+\delta_{ga}v_{ga}]/(\delta_{gv}+\delta_{ga}). \tag{2.12}$$

Summation of equations (2.10) and (2.11) yields

$$\mathbf{J}_v+\mathbf{J}_a = 0. \tag{2.13}$$

Using the linear law of irreversible thermodynamics and the Onsager reciprocal relations [2], we obtain the phenomenological equations:

$$-\mathbf{q}_g = \varepsilon_g\left\{\frac{a_{11}}{T}\nabla T+a_{12}A\right\}, \tag{2.14}$$

and

$$-\mathbf{J}_v = \mathbf{J}_a = \varepsilon_g\left\{\frac{a_{12}}{T}\nabla T+a_{22}A\right\}, \tag{2.15}$$

where

$$A = \left[\frac{1}{M_l}(\nabla_T\mu_v-\mathbf{X}_v)-\frac{1}{M_a}(\nabla_T\mu_a-\mathbf{X}_a)\right],$$

and $a_{ij}(i,j = 1,2)$ are the phenomenological coefficients.

At a constant temperature, the Gibbs–Duhem–Margules equation gives

$$\phi\nabla_T\mu_v+(1-\phi)\nabla_T\mu_a-V\nabla P = 0.$$

The expression A can be re-written as:

$$A = \frac{1}{M_a(1-\phi)}\left\{\frac{M}{M_l}(\nabla_T\mu_v-\mathbf{X}_v)-V\nabla P+\mathbf{X}\right\}, \tag{2.16}$$

where

$$M = M_l\phi+M_a(1-\phi),$$
$$\mathbf{X} = \mathbf{X}_v\phi+\mathbf{X}_a(1-\phi),$$

and where V is the molar volume of the mixture.

With assumption (4), the chemical potential for vapor can be expressed as

$$\mu_v(\phi, T, P) = \text{const} + RT \ln(\phi P), \tag{2.17}$$

and, with the densities of the gas components given by

$$\rho_v = \frac{M_l P}{RT}, \quad \rho_a = \frac{M_a P}{RT}$$

and

$$\rho_g = \frac{P}{RT}[M_l \phi + M_a(1-\phi)].$$

In turn, equation (2.16) can be rewritten as:

$$A = \frac{M}{M_a(1-\phi)}\left\{\frac{RT}{M_l\phi}\nabla\phi + \left(\frac{V_v}{M_l} - \frac{V}{M}\right)\nabla P - \left(\frac{\mathbf{X}_v}{M_l} - \frac{\mathbf{X}}{M}\right)\right\}. \tag{2.18}$$

It can be shown from the kinetic theory of dilute gases [8] that the phenomenological coefficients may be expressed as

$$a_{11} = Tk_g,$$

$$a_{22} = \rho_g\phi(1-\phi)D\left(\frac{M_l}{M}\right)^2\left(\frac{M_a}{M}\right)^2\frac{M}{RT},$$

and

$$a_{12} = D_T, \tag{2.19}$$

where k_g is the thermal conductivity, D the diffusivity, and D_T thermal diffusivity of the gaseous mixture.

Substitution of equations (2.19) and (2.18) into equations (2.14) and (2.15) yields:

$$-\mathbf{q}_g = \varepsilon_g k_g \nabla T + \frac{\rho_g \varepsilon_g \gamma^D}{M(1-\phi)}\left\{\frac{RT}{\phi}\nabla\phi + \left(\frac{V_v}{M_l} - \frac{V}{M}\right) \times M_l \nabla P - M_l\left(\frac{\mathbf{X}_v}{M_l} - \frac{\mathbf{X}}{M}\right)\right\}, \tag{2.20}$$

and

$$-\mathbf{J}_v = \mathbf{J}_a = \rho_g \varepsilon_g D \frac{M_l M_a}{M^2}\nabla\phi + \rho_g \varepsilon_g D \frac{M_l M_a}{M^2 T} \times \left\{\gamma \nabla T - \frac{M_l \phi}{R}\left(\frac{V_v}{M_l} - \frac{V}{M}\right)\nabla P - \frac{M_l \phi}{R}\left(\frac{\mathbf{X}_v}{M_l} - \frac{\mathbf{X}}{M}\right)\right\}, \tag{2.21}$$

where γ is a nondimensional parameter defined as:

$$\gamma = \left(\frac{M}{M_l}\right)\left(\frac{M}{M_a}\right)\frac{D_T}{\rho_g D}.$$

If gravitation is the only body force acting on the gaseous subsystem, $\mathbf{X}_v/M_l = \mathbf{X}/M = -g\hat{k}$. In fact, the term inside the braces of equation (2.20) represents the Dufour effect, and the term in equation (2.21) is the Soret effect. In natural drying processes, both the Defour and Soret effects may be neglected [6]. Thus, the molecular fluxes in the gaseous phase may be simplified to:

$$\mathbf{q}_g = -\varepsilon_g k_g \nabla T, \tag{2.22}$$

and

$$\mathbf{J}_v = -\mathbf{J}_a = -\rho_g \varepsilon_g D \frac{M_l M_a}{M^2}\nabla\phi. \tag{2.23}$$

(b) *Convective mass transfer*. To determine the liquid and gas barycentric velocities, the macroscopic conservation law of linear momentum for the liquid and gaseous phase should be used. In a drying process, the process of flow is reasonable to be treated as quasi-steady, and the linear momentum equations for liquid and for gaseous mixture thus yield [4]:

$$\mathbf{v}_l = -\frac{\kappa_l}{\eta_w \varepsilon_l}\nabla(P + \Phi), \tag{2.24}$$

and

$$\mathbf{v}_g = -\frac{\kappa_g}{\eta_g \varepsilon_g}\nabla P. \tag{2.25}$$

In gaseous convective flow, the influence of the gravitational force is negligible in comparison with that of the pressure gradient.

It is well-known that the permeability of porous media depends strongly on the moisture content of the porous system. When a simultaneous flow of two or more immiscible fluids in a porous medium is considered, the flow rate of one of the fluids at a point of the porous system is reduced, since part of the pore space in the vicinity of that point is occupied by another fluid. Thus, the concept of relative permeability should be employed [4]. Permeabilities κ_l and κ_g for the liquid and gaseous flows in an isotropic porous medium are generally expressed as fractions of the single-phase permeabilities, κ_l^0 and κ_g^0 respectively. The ratios κ_l/κ_l^0 and κ_g/κ_g^0 are defined as relative permeabilities, and denoted by ζ_l and ζ_g, respectively. For a particular porous system, ζ_l and ζ_g are obtained directly from experiments. Thus, the equations of motion for the liquid and gaseous phases are:

$$\mathbf{v}_l = -\frac{\zeta_l \kappa_l^0}{\eta_l \varepsilon_l}\nabla(P + \Phi), \tag{2.26}$$

and

$$\mathbf{v}_g = -\frac{\zeta_g \kappa_g^0}{\eta_g \varepsilon_g}\nabla P. \tag{2.27}$$

At the transition from the funicular to the pendular saturation stages, an unsaturated flow begins in the porous medium. The liquid phase in the medium is in general discontinuous. Determination of a local value of total pressure P becomes complicated because of the presence of the capillary and adsorption forces.

In pendular saturation stage, there exist a great number of isolated liquid islands in the porous system. The liquid film transfer on the surface of pores is hindered by the adsorptive force field of solid matrices. The vapor movement is thus the major mechanism of mass and energy transfer for this stage [9].

3. DIFFERENTIAL EQUATIONS FOR DRYING PROCESSES

There exists a general agreement that the durations of constant-rate and funicular saturation stages are very often only a small fraction of the total drying time. The moisture migration in coarse granular solids is the only exceptional case. Nevertheless, in the following, the basic differential equations for the funicular and pendular saturation stages will be discussed separately.

A. Differential equations for mass transfer in funicular stage

At the beginning of a drying process, the pore spaces in the porous medium are saturated with liquid which forms a continuous fluid phase within the matrix. Even if the pore space initially is saturated with liquid, a finite value of the capillary pressure must exist and must exceed a critical value before air can intrude into the element of the pore space [10]. As the drying proceeds, a certain pressure must be built up to displace the liquid fluid. Such a pressure may be expressed as a function of hydrostatic and capillary pressures. In the funicular saturation state, we can assume that the gaseous and solid phases are stationary, i.e.,

$$\mathbf{v}_g = \mathbf{v}_s = 0, \tag{3.1}$$

and thus, the equations of continuity (2.2)–(2.4) yield

$$\frac{\partial}{\partial t}(\varepsilon_l) + \nabla\cdot(\varepsilon_l \mathbf{v}_l) = -(\Gamma_{gl}/\rho_l) \tag{3.2}$$

and

$$\frac{\partial}{\partial t}(\rho_g \varepsilon_g) = \Gamma_{gl}. \tag{3.3}$$

The pressure P exerted on the liquid phase is a function of the liquid volume fraction ε_l, and temperature T [11, 12]. Thus, the gradient of P is expressible as:

$$\nabla P = D_\varepsilon \nabla \varepsilon_l + D_T \nabla T, \tag{3.4}$$

where D_ε and D_T are the coefficients of diffusivity which represent the partial differentials $(\partial P/\partial \varepsilon_l)_T$ and $(\partial P/\partial T)_{\varepsilon_l}$, respectively.

Substitution of equation (3.4) into equation (2.24) yields:

$$\mathbf{v}_l = -\frac{\zeta_l \kappa_l^0}{\eta_l \varepsilon_l}\left[D_\varepsilon \nabla \varepsilon_l + D_T \nabla T - \rho_l \hat{k}\right]. \tag{3.5}$$

We substitute this result into equation (3.2) to obtain

$$\frac{\partial \varepsilon_l}{\partial t} - \nabla\cdot\left\{\frac{\zeta_l \kappa_l^0}{\eta_l}\left(D_\varepsilon \nabla \varepsilon_l + D_T \nabla T\right)\right\} + \nabla\cdot\left\{\frac{\zeta_l \kappa_l^0}{\eta_l}\rho_l \hat{k}\right\} + \frac{\Gamma_{gl}}{\rho_l} = 0. \tag{3.6}$$

Combination of equations (3.3) and (3.6) yields:

$$\frac{\partial}{\partial t}(\rho_l \varepsilon_l + \rho_g \varepsilon_g) + \nabla\cdot\left\{\frac{\rho_l \zeta_l \kappa_l^0}{\eta_l}(D_\varepsilon \nabla \varepsilon_l + D_T \nabla T)\right\} + \nabla\cdot\left\{\frac{\rho_l^2 \zeta_l \kappa_l^0}{\eta_l}\hat{k}\right\} = 0. \tag{3.7}$$

Many investigators [13, 14] have shown that moisture transfer under temperature gradients is negligibly small both in very wet and very dry porous media. Thus the term associated with the temperature gradient can be dropped for $\rho_g \varepsilon_g \ll \rho_l \varepsilon_l$, and equation (3.7) then becomes

$$\frac{\partial \varepsilon_l}{\partial t} + \nabla\cdot\left\{\frac{\zeta_l \kappa_l^0}{\eta_l}(D_\varepsilon \nabla \varepsilon_l + \rho_l \hat{k})\right\} = 0. \tag{3.8}$$

This equation governs the mass transfer in the funicular saturation stage, and is analogous to the transport equation called "Darcy's equation for unsaturated flow" in the soil science proposed by Buckingham [15].

B. Equations for mass and heat transfer in the pendular stage

The mechanisms of moisture transfer in the transient period (from the funicular to the pendular saturation stage) are much more complex than that for the cases with liquid or gaseous continuity. Fortunately, the transient period occurs during only a small fraction of the total drying time. Therefore, we may assume that once the continuity of the liquid phase in a porous system breaks down, the bulk vapor transfer takes place immediately.

As the liquid phase is discontinuous, several mechanisms for moisture transfer (such as capillarity, evaporation–condensation) are involved in the pendular stage of drying. The transport equations derived in the preceding section are no longer applicable; their solutions could not fit the experimental data [16]. To explain this discrepancy, many investigators have proposed an evaporation–condensation theory which includes the effects of temperature gradient on the movement of moisture in porous systems [11, 12]. Based on the principles of continuum mechanics and thermodynamics, Luikov [17] derived a set of linear mass and heat transport equations. Closed form solutions were obtained for several simple drying cases. Unfortunately, the effect of phase change is not considered, and the dependence of the transfer coefficients (constant coefficients) on the temperature, concentration, and pressure gradients is neglected. Assuming that all moisture transfer took place in the gaseous phase only, Harmathy [18] investigated moisture and heat transfer in porous media.

In this section, Harmathy's model [18] is employed and extended. Since the capillary and the evaporation–condensation mechanism play a primary role in the transport equations for the pendular stage, the major driving forces in the porous system are the gradients of mass concentration, temperature, and pressure [17]. Inside the porous system, there exist liquid islands through which the vapor flux is transported by the vapor-pressure gradient across the air-filled pores. The flux through the liquid islands adjusts itself to carry on the vapor moisture flow. Moleculars of condensed liquid are adsorbed by the interior surface of solid matrix, to form the thin films covering the surface. Both liquid islands and films possess rather small mobility in comparison with the vapor fluxes. Therefore, both the solid matrix and particles of liquid film are assumed stationary in this stage, i.e.,

$$\mathbf{v}_l = \mathbf{v}_s = 0. \qquad (3.9)$$

Consequently, the equations of continuity for mass (2.2) through (2.5), become

$$\frac{\partial \delta_l}{\partial t} = -\Gamma, \qquad (3.10)$$

$$\frac{\partial \delta_{gv}}{\partial t} + \nabla \cdot [\mathbf{J}_{gv} + \delta_{gv}\mathbf{v}_g] = \Gamma, \qquad (3.11)$$

$$\frac{\partial \delta_{ga}}{\partial t} + \nabla \cdot [\mathbf{J}_{ga} + \delta_{ga}\mathbf{v}_g] = 0, \qquad (3.12)$$

and

$$\Gamma_{gv} = -\Gamma_l = \Gamma. \qquad (3.13)$$

Since natural drying is a slow process which takes place at atmospheric pressure, the liquid phase of moisture is considered to be incompressible, and the gaseous phase is taken to be ideal. Thus,

$$\rho_l \simeq \rho_w, \quad \rho_v = \frac{M_w P}{RT}, \quad \rho_a = \frac{M_a P}{RT},$$

and the density for the gaseous mixture is

$$\rho_g = \frac{PM}{RT} = \frac{P}{RT}[M_w \phi + M_a(1-\phi)]. \qquad (3.14)$$

Equation (3.10) shows that the only local rate of change of liquid is caused by the phase change of liquid to vapor. With the aid of Table 1, equations (2.22), (2.23) and (2.25), the equations of continuity for vapor and air (3.11 and 3.12) yield the two second-order nonlinear partial differential equations:

$$\begin{aligned} A_1\dot{\phi} + B_1\dot{P} + C_1\dot{T} &= D_1\nabla^2\phi + E_1\nabla^2 P + G_1(\nabla\phi)^2 \\ &\quad + H_1(\nabla P)^2 + J_1(\nabla\phi\cdot\nabla P) + K_1(\nabla\phi\cdot\nabla T) \\ &\quad + L_1(\nabla P\cdot\nabla T) \qquad (3.15) \end{aligned}$$

and

$$\begin{aligned} A_2\dot{\phi} + B_2\dot{P} + C_2\dot{T} &= D_2\nabla^2\phi + E_2\nabla^2 P + G_2(\nabla\phi)^2 \\ &\quad + H_2(\nabla P)^2 + J_2(\nabla\phi\cdot\nabla P) + K_2(\nabla\phi\cdot\nabla T) \\ &\quad + L_2(\nabla P\cdot\nabla T), \qquad (3.16) \end{aligned}$$

respectively, where $\dot{\phi}$ denotes the partial derivatives of ϕ with respect to time, and where the coefficients $A_i, \ldots, L_i$ are functions of dependent variables ϕ, P, T and the volume fraction ε_g. They are defined as follows:

$A_1 = \bar{Y}(\partial\varepsilon_g/\partial\phi) + \varepsilon_g,$ $\quad A_2 = (1-\phi)(\partial\varepsilon_g/\partial\phi) - \varepsilon_g,$

$B_1 = \bar{Y}(\partial\varepsilon_g/\partial P) + \varepsilon_g(\phi/P),$ $\quad B_2 = (1-\phi)\bar{O}_p,$

$C_1 = \bar{Y}(\partial\varepsilon_g/\partial T) - \varepsilon_g(\phi/T),$ $\quad C_2 = -(1-\phi)\bar{O}_T,$

$D_1 = D\varepsilon_g(M_a/M),$ $\quad D_2 = -D\varepsilon_g(M_w/M),$

$E_1 = \zeta\phi(\kappa_g^0/\eta_g),$ $\quad E_2 = \zeta(1-\phi)(\kappa_g^0/\eta_g),$

$F_1 = 0,$ $\quad F_2 = 0,$

$G_1 = -D\bar{O}_\phi(M_a/M),$ $\quad G_2 = D\bar{O}_\phi(M_w/M),$

$H_1 = \phi\bar{W}_p(\kappa_g^0/\eta_g),$ $\quad H_2 = (1-\phi)\bar{W}_p(\kappa_g^0/\eta_g),$

$I_1 = 0,$ $\quad I_2 = 0,$

$J_1 = D\bar{O}_p(M_a/M) + (\kappa_g^0/\eta_g)[\phi(\partial\zeta/\partial\varepsilon_g) \cdot (\partial\varepsilon_g/\partial\phi) + \zeta],$ $\quad J_2 = -D\bar{O}_p(M_w/M) + (\kappa_g^0/\eta_g)[(1-\phi)(\partial\zeta/\partial\varepsilon_g \cdot (\partial\varepsilon_g/\partial\phi) - \zeta],$

$K_1 = -D\bar{O}_T(M_a/M),$ $\quad K_2 = D\bar{O}_T(M_w/M),$

$L_1 = -\phi\bar{w}_T(\kappa_g^0/\eta_g),$ $\quad L_2 = -(1-\phi)\bar{w}_T(\kappa_g^0/\eta_g),$

in which

$$\begin{aligned} \bar{O}_\phi &= \varepsilon_g[(M_w - M_a)/M] - (\partial\varepsilon_g/\partial\phi), \\ \bar{O}_p &= (\varepsilon_g/P) + (\partial\varepsilon_g/\partial P), \\ \bar{O}_T &= (\varepsilon_g/T) - (\partial\varepsilon_g/\partial T), \\ \bar{Y} &= \phi - (\rho_w RT/M_w P), \\ \bar{W}_p &= (\zeta/P) + (\partial\zeta/\partial\varepsilon_g)(\partial\varepsilon_g/\partial P), \end{aligned}$$

and

$$\bar{W}_T = (\zeta/T) - (\partial\zeta/\partial\varepsilon_g)(\partial\varepsilon_g/\partial T).$$

A general form of the law of conservation of energy is given in equation (2.9). Nevertheless, a rather explicit form of the energy equation for a porous system which consists of solid, liquid, vapor and air, can be written as follows [6]:

$$\begin{aligned} &\frac{\partial}{\partial t}(\delta_{gv}h_v + \delta_{ga}h_a + \delta_l h_l + \delta_s h_s) + \nabla \cdot (\mathbf{n}_{gv}h_v + \mathbf{n}_{ga}h_a) \\ &\qquad = -\nabla\cdot\mathbf{q} + \frac{\mathrm{D}P}{\mathrm{D}t} - \nabla\mathbf{v} : \tilde{\tau} + \Psi, \qquad (3.17) \end{aligned}$$

where the mass average velocity $\mathbf{v}$ is defined by

$$\mathbf{v} = (\delta_{gv}\mathbf{v}_{gv} + \delta_{ga}\mathbf{v}_{ga} + \delta_l\mathbf{v}_l + \delta_s\mathbf{v}_s)/\delta. \qquad (3.18)$$

With the aid of equation (3.9) we can show that the mass average velocity of the porous system $\mathbf{v}$ is a negligible fraction of the mass average velocity of gaseous mixture, $\mathbf{v}_g$. Thus the term $(\mathbf{v}\cdot\nabla P)$ may be omitted. The viscous dissipation, $(\nabla\mathbf{v} : \tilde{\tau})$, is positive (from the second law of thermodynamics) and represents an irreversible degradation of mechanical to thermal energy. In general, it is negligible in considering the drying processes. Furthermore, the heat source term, Ψ, including effects of emission and absorption of radiant energy, may also be neglected. Thus, the energy equation (3.17) becomes:

$$\begin{aligned} &\left(\delta_{gv}\frac{\partial h_v}{\partial t} + \delta_{ga}\frac{\partial h_a}{\partial t} + \delta_l\frac{\partial h_l}{\partial t} + \delta_s\frac{\partial h_s}{\partial t}\right) \\ &\qquad + (\mathbf{n}_{gv}\cdot\nabla h_v + \mathbf{n}_{ga}\cdot\nabla h_a) \\ &\qquad\qquad + \frac{\partial \delta_l}{\partial t}Q + \nabla\cdot\mathbf{q} - \frac{\partial P}{\partial t} = 0, \qquad (3.19) \end{aligned}$$

where

$$Q = h_v - h_l. \qquad (3.20)$$

Several thermodynamic relations are needed to relate the total thermal energy to the dependent variables ϕ, P, and T. First, with the vapor behaving as an ideal gas, the Clausius–Clapeyron equation gives the equilibrium vapor pressure P_v^0 in terms of the latent heat λ of free bulk water surface as

$$P_v^0 = \frac{1}{c}\exp[-\lambda(M_w/RT)], \tag{3.21}$$

where c denotes a constant of integration. Using Kelvin's equation, the vapor pressure P_v in a capillary porous system with the hydraulic radius r can be expressed as

$$\ln(P_v/P_v^0) = -(2\sigma/\rho_w r)\cdot(M_w/RT), \tag{3.22}$$

where σ denotes the surface tension in the gas–liquid interface. The surface tension is a function of temperature. For a small variation of temperature, the surface tension may be expressed as a linear function of absolute temperature as

$$\sigma = \sigma_0 - \beta T, \tag{3.23}$$

where σ_0 and β are empirical constants. Substitution of equation (3.21) into equation (3.22) yields the expression for the vapor pressure in the porous system:

$$P_v = \frac{1}{c}\exp\left[-\frac{M_w}{RT}\left(\lambda + \frac{2\sigma}{\rho_w r}\right)\right]. \tag{3.24}$$

Note that the vapor pressure in the pores is made up of two parts: (1) the first part is the pressure that exists when the gas–liquid interface is flat, and (2) the second is the pressure caused by the effect of curvature of the menisci. Thus, the total latent heat of evaporation in a porous system is:

$$Q = \lambda + \frac{2\sigma}{\rho_w r}. \tag{3.25}$$

In general, Q is a weak function of the gaseous volume fraction ε_g. For simplicity, we will assume that the Q is independent of ε_g.

With the definition $P_v = P\phi$, solving equations (3.21) and (3.22) for r yields:

$$r = -(2\sigma M_w)/\{\rho_w R[T\ln(a\phi P) + (\lambda M_w)/R]\}. \tag{3.26}$$

Substitution of equation (3.26) into equation (3.25) gives the useful expression:

$$Q = \lambda - \frac{R}{M_w}\left[T\ln(a\phi P) + \frac{\lambda M_w}{R}\right]. \tag{3.27}$$

Next, we should consider the enthalpy of multicomponent mixtures in terms of dependent variables ϕ, P and T, hence,

$$\mathrm{d}h = \frac{\partial h}{\partial \phi}\mathrm{d}\phi + \frac{\partial h}{\partial P}\mathrm{d}P + \frac{\partial h}{\partial T}\mathrm{d}T. \tag{3.28}$$

Using Maxwell's reciprocity relations, equation (3.28) can be rewritten as:

$$\mathrm{d}h = \frac{\partial h}{\partial \phi}\mathrm{d}\phi + \left[\frac{1}{\rho} - T\left\{\partial\left(\frac{1}{\rho}\right)\Big/\partial T\right\}\right]_{\phi,P}\mathrm{d}P + C_p\,\mathrm{d}T. \tag{3.29}$$

The $(\partial h/\partial \phi)$ term is generally negligible in comparison with $(C_p\mathrm{d}T)$ in drying processes. Under the assumptions (3) and (4), the change of enthalpy for each constituent in the porous system is

(1) Solid $\quad \mathrm{d}h_s = \dfrac{1}{\rho_s}\mathrm{d}P + (C_p)_s\mathrm{d}T,$

(2) Liquid $\quad \mathrm{d}h_l = \dfrac{1}{\rho_l}\mathrm{d}P + (C_p)_w\mathrm{d}T,$

(3) Gaseous vapor $\quad \mathrm{d}h_v = (C_p)_v\mathrm{d}T,$

and

(4) air $\quad \mathrm{d}h_a = (C_p)_a\mathrm{d}T. \qquad (3.30)$

The multicomponent energy flux $\mathbf{q}$ is a macroscopic average of conductive energy fluxes for gaseous mixture, solids and liquids. Since the mass average velocity $\mathbf{v}$ for the porous system is relatively small, the multicomponent energy flux and force follow Fourier's law

$$\mathbf{q} = -k\nabla T, \tag{3.31}$$

where k is the locally averaged thermal conductivity of the porous system and is a function of the moisture content, topology of pores, and the thermal conductivities of the solid, liquid and gaseous components. Although a considerable effort was devoted to find explicit functions for k, unfortunately, no analytical expression for a multicomponent real porous system was found [19]. A useful empirical formula for an isotropic and homogeneous porous medium, proposed by Kingery [20],

$$k = [(k_g)^n\varepsilon_g + (k_l)^n(\varepsilon - \varepsilon_g) + (k_s)^n(1-\varepsilon)]^{1/n}, \tag{3.32}$$

will be used, where k_i is the thermal conductivity of the ith-component; n is the topological parameter of the porous system (which should be determined experimentally).

After some algebraic manipulation, the total energy equation (3.19) can be expressed as

$$\begin{aligned} A_3\dot{\phi} + B_3\dot{P} + C_3\dot{T} &= F_3\nabla^2 T \\ &\quad + I_3(\nabla T)^2 + K_3\nabla\phi\cdot\nabla T + L_3\nabla P\cdot\nabla T, \end{aligned} \tag{3.33}$$

where the coefficients $A_3, \ldots, L_3$ are functions of ϕ, P, T and ε_g. They are:

$$\begin{aligned}
&A_3 = \rho_w Q(\partial\varepsilon_g/\partial\phi), \quad B_3 = \rho_w Q(\partial\varepsilon_g/\partial P) - \varepsilon_g, \\
&C_3 = \rho_w Q(\partial\varepsilon_g/\partial T) \\
&\qquad + [(\varepsilon-\varepsilon_g)\rho_w(C_p)_w + \rho_s(1-\varepsilon)(C_p)_s] \\
&\qquad + \varepsilon_g P[\phi M_w(C_p)_v + (1-\phi)M_a(C_p)_a]/RT, \\
&D_3 = 0, \quad E_3 = 0, \quad G_3 = 0, \quad H_3 = 0, \\
&F_3 = k, \quad I_3 = (\partial k/\partial\varepsilon_g)(\partial\varepsilon_g/\partial T), \quad J_3 = 0, \\
&K_3 = (\partial k/\partial\varepsilon_g)(\partial\varepsilon_g/\partial\phi) \\
&\qquad - DM_aM_w\varepsilon_g P[(C_p)_a - (C_p)_v]/RTM,
\end{aligned}$$

and

$$\begin{aligned}
&L_3 = (\partial k/\partial\varepsilon_g)(\partial\varepsilon_g/\partial P) \\
&\qquad + (\kappa_g^0\zeta P)[M_w(C_p)_v\phi + M_a(C_p)_a(1-\phi)]/RT.
\end{aligned}$$

As we examine these coefficients of equations (3.15, 3.16, and 3.33) closely, we realize that the coefficients are functions of four independent variables (ϕ, P, T, and ε_g), while only three basic equations are derived. A fourth equation, which describes the relation between the four variables, is needed.

The existence of local equilibrium at any point of the porous system is assumed. The partial vapor pressure at any point of the system can be determined from a sorption relation,

$$m = m(P_v, T),$$

which characterizes the porous system (pore size distribution) and must be determined experimentally. The equilibrium vapor pressure can be approximated by Kelvin's equation, provided that the "r" in Kelvin's equation is interpreted as a characteristic length of pores.

Nerpin [21] and Vol'fkovich [22] proposed that a liquid–vapor equilibrium in a porous system can be expressed as a functional relation between the moisture content and the hydraulic radius of the porous system, as

$$m = m(r),$$

where m is the volumetric moisture content per unit volume of the porous body. Such an extension is purely empirical, and the validity of the extension should be verified by experiment [22].

With the definition of r from Kelvin's equation (3.22), equation (3.33) gives the dependence of m upon the variables T and P_v:

$$m = m(r) = m(P_v, T) = m(\phi, P, T), \quad (3.34)$$

and provides the required equation.

Various experimental techniques, such as the

Table 2. Values of the constants used in the equations (light weight concrete)

Type of const.	Symbol	Value	Unit
Physic. const.	R	8.3149×10^{-14}	$kg\,m^2\,s^{-2}\,K^{-1}\,mol^{-1}$
	σ_s	5.670×10^{-8}	$kg\,s^{-3}\,K^{-4}$
	$(C_p)_a$	1.0063×10^3	$m^{-2}\,s^{-2}\,K^{-2}$
	$(C_p)_s$	0.879×10^3	$m^2\,s^{-2}\,K^{-2}$
	$(C_p)_v$	1.8646×10^3	$m^{-2}\,s^{-2}\,K^{-2}$
	$(C_p)_w$	4.1793×10^3	$m^2\,s^{-2}\,K^{-2}$
	D	0.256×10^{-4}	$m^2\,s^{-1}$
	e	0.8	
Physical properties	k_g	0.02613	$kg\,m\,s^{-3} \cdot K^{-1}$
	k_s	1.4422	$kg\,m\,s^{-3}\,K^{-1}$
	k_w	0.616	$kg\,m\,s^{-3}\,K^{-1}$
	M_a	28.952×10^{-3}	$kg\,mol^{-1}$
	M_w	18.016×10^{-3}	$kg\,mol^{-1}$
	ε	0.3	$m^3\,m^{-3}$
	η_g	1.83×10^{-5}	$kg\,m^{-1}\,s^{-1}$
	K_g^0	2.50×10^{-14}	m^2
	λ	2.4418×10^6	$m^2\,s^{-2}$
	ρ_s	2.6×10^3	$kg\,m^{-3}$
	ρ_w	0.99707×10^3	$kg\,m^{-3}$
Geom. const.	L	0.10	m
	B	2.00	m
Empirical const.	a	1.209658×10^{-11}	$m\,s^2\,kg^{-1}$
	b	5080	K
	n	0.25	
	β	0.167×10^{-3}	$kg\,s^{-2}\,K^{-1}$
	v	1.0	
	σ_0	121.2×10^{-3}	$kg\,s^{-2}$
Initial conditions	P_{atm}	1.01325×10^5	$kg\,m^{-1}\,s^{-2}$
	m_{ini}	0.096	$m^3\,m^{-3}$
	T_{ini}	294.8	K
Boundary conditions	ϕ_0	$\phi_{00} = 0.013400$	mol/mol
		$\phi_{01} = 0.003548$	mol/mol
	T_{0i}	$T_{00} = 302.99$	K
		$T_{01} = 294.0$	K
	T_{ei}	$T_{e0} = 304.0$	K
		$T_{e1} = 293.0$	K
	α_F	0.0	$mol\,m^{-2}\,s^{-1}$

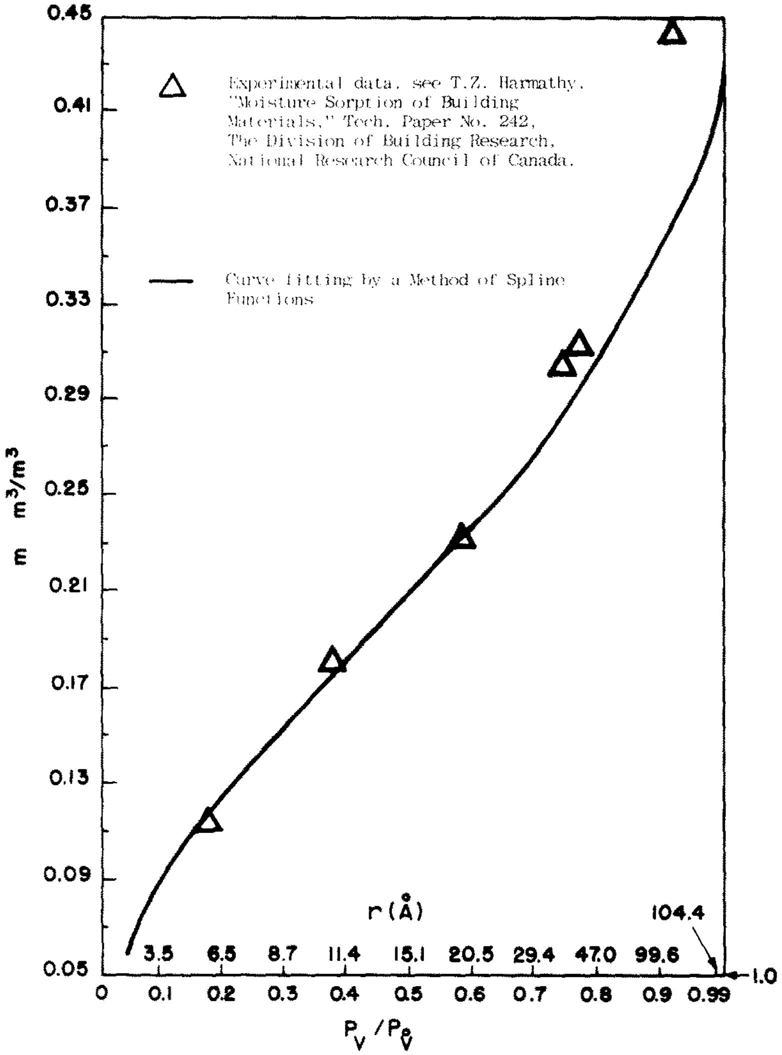

FIG. 2. Liquid vapor equilibrium curve for a light-weight concrete.

mercury-injection method, are commercially available for determining such a relationship (3.34).

From Fig. 1 we also note that

$$m = \varepsilon_l + \Delta(\phi\varepsilon_g),$$

where Δ denotes a very small positive value. Except for the bone-dry case, the following inequality usually holds (assumption No. 5):

$$\varepsilon_l \gg \Delta(\phi\varepsilon_g).$$

Consequently, the volumetric fraction of gas phase ε_g can be approximated by writing

$$\varepsilon_g = \varepsilon - m(\phi, P, T), \tag{3.35}$$

which provides the relationship between ε_g and ϕ.

Thus equations (3.15), (3.16), (3.33) and (3.35) form a complete workable set of nonlinear differential equations for unsaturated flow in porous media. The equations are similar to the equations derived by Harmathy [18].

4. APPLICATION OF THE TRANSPORT EQUATIONS

The solution of moisture migration in a thin concrete slab under natural drying conditions has been obtained by Huang *et al.* [1, 23]. In this paper, the moisture migration in an extended lightweight concrete wall of 0.1 m thickness subjected to a temperature gradient is studied.

For one-dimensional mass and heat transfer in a slab of thickness L, the equations (3.15), (3.16), (3.33) and (3.35) are given in the following form:

$$\begin{aligned} A_i\frac{\partial\phi}{\partial t} + B_i\frac{\partial P}{\partial t} + C_i\frac{\partial T}{\partial t} &= D_i\frac{\partial^2\phi}{\partial x^2} + E_i\frac{\partial^2 P}{\partial x^2} + F_i\frac{\partial^2 T}{\partial x^2} + G_i\left(\frac{\partial\phi}{\partial x}\right)^2 \\ &\quad + H_i\left(\frac{\partial P}{\partial x}\right)^2 + I_i\left(\frac{\partial T}{\partial x}\right)^2 + J_i\left(\frac{\partial\phi}{\partial x}\cdot\frac{\partial P}{\partial x}\right) \\ &\quad + K_i\left(\frac{\partial\phi}{\partial x}\cdot\frac{\partial T}{\partial x}\right) + L_i\left(\frac{\partial P}{\partial x}\cdot\frac{\partial T}{\partial x}\right) \end{aligned}$$

$$(i = 1,2,3), \tag{4.1}$$

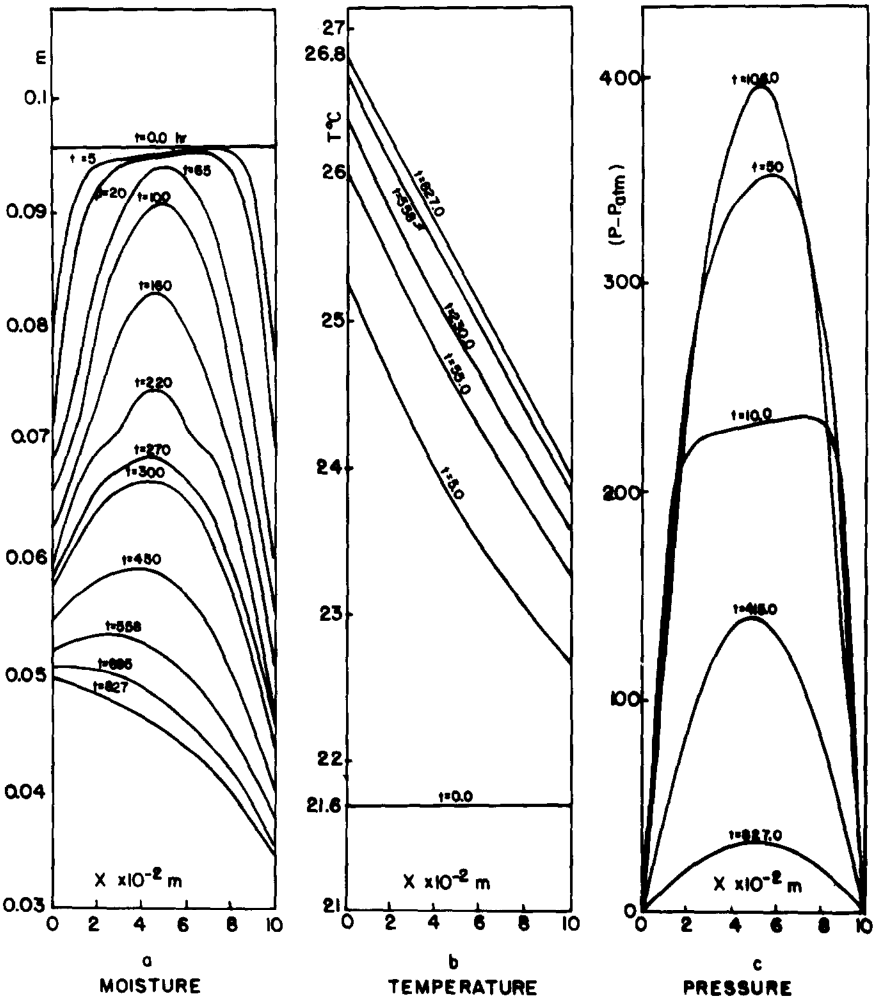

FIG. 3. Distribution of moisture (a), temperature (b) and pressure (c) in 10 cm light-weight concrete slab.

and

$$\varepsilon_g = \varepsilon\{1-\theta[r(\phi, P, T)]\}, \tag{4.2}$$

where the function, $\theta = m/\varepsilon$, denotes the moisture content. For future reference, equation (3.32) will be used to calculate the effective thermal conductivity of the porous walls.

The boundary conditions on the surfaces of the wall are ($i = 0$ for $x = 0$; $i = 1$ for $x = L$)

$$\frac{\partial \phi}{\partial x} = (-1)^i \alpha\left(\frac{RT}{PD}\right)(\phi - \phi_{0i}), \tag{4.3}$$

$$\frac{\partial T}{\partial x} = (-1)^i \frac{h}{k}(T - T_{0i}) \quad (\text{with } T = T_i), \tag{4.4}$$

and

$$P = P_{0i}. \tag{4.5}$$

where α denotes the mass transfer coefficient, D the diffusion coefficient, h the heat transfer coefficient, and k thermal conductivity. ϕ_{0i}, T_{0i}, and P_{0i} respectively are the mole fraction of water vapor, temperature, and pressure of the surroundings of the porous wall. For a wall surrounded by air at normal conditions (the air pressure is at atmospheric pressure and the temperature is between 0 and 80°C), the transfer coefficients may be expressed as [24]:

$$\alpha = \alpha_F + 1.63 \times 10^{-5}[(T_{0i} - T)/B]^{1/4} \tag{4.6}$$

$$h = 2.75 \times 10^8 \alpha + \sigma_s e(T_{ei}^4 - T^4)/(T_{ei} - T), \tag{4.7}$$

where α_F denotes the mass transfer coefficient due to forced convection. B is a characteristic length of the wall measured from the edge, σ_s the Stefan–Boltzman constant, T_{ei} the temperature of the enclosure of the system.

The initial conditions for the present study are given as follows:

$$\phi(x,0) = \phi_{ini},\ P(x,0) = P_{atm},\ T(x,0) = T_{ini}. \tag{4.8}$$

Therefore, equations (4.1–4.5 and 4.8) form a nonlinear boundary value problem for the simultaneous mass and heat transfer in a light-weight concrete wall.

5. NUMERICAL ANALYSIS AND CALCULATION

Obtaining an analytical solution for the nonlinear partial differential equations governing flows through porous media would not be possible. In this paper, an implicit finite difference scheme is employed for obtaining numerical results. The first step is to replace the differential equations by a set of algebraic finite backward-in-time equations, which give the relationships among the dependent variables ϕ, P, and T at neighboring points in an (x, t) space. The numerical solution of the simultaneous algebraic equations thus obtained yields the values of the dependent variables at the pre-assigned grid points throughout the domain investigated.

In the set of algebraic equations, there is one space increment Δx and one temporal increment Δt. The finer meshes for Δx and Δt will result in a smaller error. Yet, the magnitude of Δx and Δt cannot be chosen arbitrarily. It can be shown [25] that in order to have a stable solution of equation (4.1), one must properly choose Δx and Δt such that:

$$\Delta t/(\Delta x)^2 \leqslant \tfrac{1}{2}C,$$

where C is a parameter determined by the ratios of the coefficients $A_i, \ldots, K_i$. For the problem considered, the parameter C varies with time t because those coefficients also vary with time. In order to achieve a stable computation, a considerably smaller value of Δt must be used at the beginning stage of the computational simulation than at the advanced stages, due to errors associated with the initial guess of sorption equilibrium.

The physical parameters, boundary conditions, and initial conditions are summarized in Table 2. The liquid–vapor equilibrium curve for the light-weight concrete is shown in Fig. 2.

Numerical solutions for the histories of moisture, temperature, and pressure in the light-weight concrete wall are obtained by use of a digital computer, and shown in Fig. 3.

The result reveals that at high liquid saturation (funicular saturation) the moisture movement is relatively independent of the mechanical properties of the porous system and dependent on the parameters characterizing the surroundings, such as temperature, velocity and the relative humidity of the ambiance. When the liquid threads in the light-weight concrete begin to break down, and capillary action in the pore spaces sets in, the internal characteristics of the system play a primary role in moisture migration. The curve of moisture distribution is no longer convex. At the pendular saturation stage, liquid moisture has to be vaporized first in order to move from one location to another. The drying rate varies with time, and is different from one point to another throughout the thickness of the wall. The average drying rate in this stage is slower than that in the funicular stage. Obviously, the temperature and pressure gradients affect the moisture distributions, in particular, at the beginning of pendular stage. At low moisture, saturation, vapor flux is the only mechanism for moisture transfer in the system. The average drying rate at this stage becomes very slow because of the phenomenon of pure adsorption.

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TRANSFERT D'HUMIDITE DANS DES MILIEUX POREUX SOUMIS A UN GRADIENT DE TEMPERATURE

Résumé—Pour décrire l'histoire de la migration de l'humidité dans les milieux poreux, on considère la dépendance des caractéristiques matérielles agissantes. Une théorie de la diffusion avec une diffusivité linéaire ou non n'est pas correcte pour décrire le transfert massique. On doit considérer simultanément les transferts de masse de toutes les phases et le transfert de chaleur. A partir du principe de la thermodynamique hors d'équilibre, des lois macroscopiques de conservation et de l'équilibre liquide–vapeur d'un système poreux, on développe un système d'équations pour les transferts simultanés de chaleur et de masse. La théorie est appliquée à l'étude de la migration de l'humidité dans un mur de béton léger, soumis à un gradient de température. Les résultats montrent qu'en plus de la diffusion, les mécanismes de capillarité et d'évaporation–condensation qui sont fortement affectés par la topologie du système poreux, sont importants dans le séchage.

MEHRPHASIGER FEUCHTIGKEITSTRANSPORT IN PORÖSEN MEDIEN UNTER EINWIRKUNG EINES TEMPERATURGRADIENTEN

Zusammenfassung—Um die Geschichte der Feuchtigkeitausbreitung in porösen Medien zu beschreiben, muß die Abhängigkeit von den wesentlichen Materialeigenschaften in Betracht gezogen werden. Eine Diffusionstheorie mit linearem oder nichtlinearem Diffusionskoeffizienten ist nicht ausreichend für die Beschreibung des Stofftransportverhaltens in einem porösen Medium. Stofftransport aller Phasen und Wärmetransport müssen gleichzeitig berücksichtigt werden. Auf der Grundlage des Prinzips der irrevereiblen Nichtgleichgewichts-Thermodynamik sowie der makroskopischen Erhaltungssätze und des Dampf–Flüssigkeits-Gleichgewichts poröser Systeme wird ein Satz von Grundgleichungen für gleichzeitigen Stoff- und Wärmeübergang entwickelt. Die entwickelte Theorie wird bei der Untersuchung der Feuchtigkeitsausbreitung in einer Wand aus leichtbeton unter Einfluß eines Temperaturgradienten angewandt. Das Ergebnis zeigt, daß zusätzlich zur Diffusion sowohl der Kapillar—als auch der Verdampfungs-Kondensations—Mechanismus wesentlich sind, die beide stark von der Topologie eines porösen Systems abhängen.

МНОГОФАЗНЫЙ ПЕРЕНОС ВЛАГИ В ПОРИСТЫХ СРЕДАХ ПРИ НАЛИЧИИ ГРАДИЕНТА ТЕМПЕРАТУР

Аннотация — Рассмотрено влияние характеристик материала на процесс миграции влаги в пористых средах. Перенос массы в пористой среде нельзя адекватно описать с помощью диффузионного приближения с линейным или нелинейным коэффициентом диффузии. Данный процесс во всех его фазах должен рассматриваться одновременно с процессом переноса тепла. Для этого сформулирована система уравнений на основе принципов неравновесной термодинамики необратимых процессов, макроскопических законов сохранения и законов равновесия жидкость-пар для пористой системы. С помощью предложенного метода исследована миграция влаги в стенке из легкого бетона под действием градиента температур. Показано, что помимо диффузии большую роль в процессе сушки играют силы капиллярного взаимодействия, а также механизмы испарения и конденсации, которые сильно зависят от топологии пористой системы.