ABSTRACT

A diffusion theory with a linear or a nonlinear coefficient of diffusivity is insufficient for the characterization of the drying behavior of hydrated concrete slabs. A general mathematical model, based on nonequilibrium, irreversible flows of heat and mass, yields a set of nonlinear partial differential equations of parabolic type. Implicit finite difference calculations for a concrete slab yield moisture, temperature, and pressure histories as well as global average drying rates. Graphs show that during the pendular state of dessication, diffusion, capillary, and evaporation-condensation processes are the governing mechanisms in drying.
1. Introduction

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 in the mathematical description of moisture transfer in a concrete slab. A diffusion theory alone, with either linear [1] or nonlinear diffusivity [2], is inadequate for the description of mass transfer in porous media. Transfers of mass and heat, which occur in stages, must be considered simultaneously. During the funicular or liquid saturated stage, diffusion seems to be the mechanism of moisture transport. Experiments show that in the pendular or unsaturated liquid flow stage, diffusion, capillary, and evaporation-condensation actions govern the mass transfer process [3]. They also indicate that the pore size distribution in a porous medium strongly affects moisture transfer in this state [4]. The results obtained by Huang et al., agree with the experimental observations [5,6]. A well-posed system of partial differential equations for multi-phase moisture transfer in porous media has been constructed using principles of non-equilibrium, irreversible flows of heat and mass; linear phenomenological equations; and the laws of conservation in a macroscopic sense [7,8]. In this paper, this theory is used to investigate moisture migration in a light-weight concrete wall subjected to temperature gradients. The set of three nonlinear partial differential equations which govern heat and mass transport in concrete are solved numerically using an implicit finite difference scheme. The results show distinct behaviors during the constant rate, funicular, and pendular states. In all states, temperature gradients play important roles in drying.

2. The Effects of Porosity on Diffusion and Convection in Solids

The mechanisms of moisture movement in porous media are dominated by its physical and chemical structure. Layers of water molecules next to the surface of small enough pores are bound by van der Waals forces which limit their mobility to surface diffusion. In somewhat larger pores, liquid water beyond the adsorbed surface film, although more mobile, is still constrained by surface tensions in capillary-like structures. Here, mobility is mostly by convection. In the gaseous phase, air and vapor mixtures can be transported by both molecular diffusion and convection on a macroscopic scale.

It is apparent that neither single phase diffusion nor capillary flow theory are adequate for modelling heat and mass transfer in porous media, although they may be used with some success for coarse, granular soils. The surface energy of the pore space, which is ignored in both of these theories, significantly affects the movement of moisture [9].

Hardened cement paste, as described by Powers and Brownyard [10], contains gel pores in the shapes of fibers, rolled foils, tubes, or plane sheets, of average diameter 18 \( \text{A} \), having enormous specific surfaces, perhaps of the order of \( 2 \times 10^{5} \text{m}^2/\text{Kg dry weight} \); and capillary pores of diameter greater than 200 \( \text{A} \) scattered throughout the cement gel. The size and distribution of pores are major characteristics of the structure of cement pastes, as discussed by Wittman [11].

3. Equilibria Sorption

The movements of moisture in porous media are controlled by diffusion and adsorption in the liquid phase, and by molecular diffusion and convection on a macroscopic scale in the gaseous phase. The water vapor concentration in the mixture can be determined from the equilibrium sorption relation. In turn, the equilibrium sorption relation depends on the
characteristics of the porous system, such as the porosity, the specific surface of the solid matrix, and the distribution of pore sizes. Vol'kovich et al., [4] have proposed that the equilibrium sorption relation could be expressed as a functional relation between the moisture content \( \theta \) and the "equivalent pore diameter" \( r \).

\[
\theta = \theta(r) \tag{1}
\]

where the moisture content can be approximated as

\[
\theta(r) = \frac{m(r)}{c} = 1 - \frac{\epsilon_g(r)}{\epsilon} \tag{2}
\]

because the water content in the gaseous phase is negligible in comparison with that in the liquid phase. In Eq. (2), \( \epsilon \) denotes the porosity of the porous system, \( \epsilon_g \) the volume fraction of the gaseous phase, and \( m \) the volumetric moisture content.

From the Kelvin equation, \( r \) is expressible as a function of temperature and the relative vapor pressure as

\[
r = \frac{2\sigma M_w}{\rho_w R} \cdot \frac{1}{\ln(P_v/P_v^0)} \tag{3}
\]

where \( \sigma \) denotes the surface tension, \( M_w \) the molecular weight of water, \( \rho_w \) density of water, and \( R \) the gas constant.

Thus, a functional relation among moisture content \( \theta \), temperature \( T \), and the relative vapor pressure \( (P_v/P_v^0) \) is established. It should be noted that the variable \( r \) in Eq. (3) should be interpreted as a characteristic length of pore space. Also, the analysis assumes that practically all portions of the pore space with pore size larger than that given by the Kelvin Eq. (3) are accessible to the gaseous phase.

Fig. 1 shows an experimental curve of sorption equilibrium, \( m = m(r) \), for a light-weight concrete [12]. Because only the drying processes will be considered, the curves for desorption equilibrium are presented. From Eqs. (1), (2) and (3), the relation between the effective porosity \( \epsilon_g \) and the water content is found to be

\[
\epsilon_g = \epsilon [1 - \theta(r(\phi,P,T))] = \epsilon - m(\phi,P,T) \tag{4}
\]

4. Basic Equations for Heat and Mass Transfer in Cement Paste

The basic equations for heat and mass transfer, assuming local thermal and chemical equilibrium exists in the porous system and that the gaseous vapor phase is the major factor in mass transfer, derived from laws of conservation of mass, momentum, energy, and the kinetic theory of ideal gases, for one-dimensional mass and heat transfer in a slab of thickness \( L \), are [5]:

\[
A_1 \frac{\partial \phi}{\partial t} + B_1 \frac{\partial P}{\partial t} + C_1 \frac{\partial T}{\partial t} = D_1 \frac{\partial^2 \phi}{\partial x^2} + E_1 \frac{\partial^2 P}{\partial x^2} + F_1 \frac{\partial^2 T}{\partial x^2} + G_1 \left( \frac{\partial P}{\partial x} \right)^2 + H_1 \left( \frac{\partial T}{\partial x} \right)^2 + I_1 \left( \frac{\partial T}{\partial x} \right) \tag{5}
\]

where the coefficients \( A_1, \ldots, L_1 \) are functions of the dependent variables \( \phi, P, T \), and \( \epsilon_g \).

They are defined as follows:

\[
A_1 = \tilde{V} (\partial \epsilon_g / \partial \phi) + \epsilon_g \cdot A_2 = (1-\phi)(\partial \epsilon_g / \partial \phi) - \epsilon_g \cdot B_1 = \tilde{V} (\partial \epsilon_g / \partial P) + \epsilon_g (\partial \phi / P) \cdot B_2 = (1-\phi) \tilde{G} \cdot C_1 = \tilde{V} (\partial \epsilon_g / \partial T) - \epsilon_g (\partial \phi / T) \cdot C_2 = (1-\phi) \tilde{G}_T \cdot D_1 = \epsilon_g \rho (M_a / M) \cdot D_2 = -D \tilde{G}_g (M_w / M) \n\]

---

H 1/6
\[
\begin{align*}
E_1 &= \zeta \left( \kappa \rho \right), \quad E_2 = \zeta (1-\epsilon) \left( \kappa \rho \right), \quad F_1 = 0, \quad F_2 = 0, \quad C_1 = -D_\phi \left( \frac{M_g}{M} \right), \quad C_2 = D_\phi \left( \frac{M_g}{M} \right), \\
H_1 &= \phi \left( \frac{\kappa \rho}{\kappa \rho} \right), \quad H_2 = (1-\epsilon) \bar{H} \left( \frac{\kappa \rho}{\kappa \rho} \right), \quad I_1 = 0, \quad I_2 = 0, \\
I_1' &= -D_\phi \left( \frac{M_g}{M} \right) + \left( \kappa \rho \right) \left( \frac{\kappa \rho}{\kappa \rho} \right), \quad I_2' = (1-\epsilon) \frac{\kappa \rho}{\kappa \rho}, \quad \gamma_1 = \frac{\kappa \rho}{\kappa \rho}, \quad \gamma_2 = \frac{\kappa \rho}{\kappa \rho}, \quad \gamma_3 = \frac{\kappa \rho}{\kappa \rho}, \quad \gamma_4 = \frac{\kappa \rho}{\kappa \rho}, \quad \gamma_5 = \frac{\kappa \rho}{\kappa \rho}, \quad \gamma_6 = \frac{\kappa \rho}{\kappa \rho}, \\
\end{align*}
\]

In which
\[
\begin{align*}
\bar{C}_1 &= \left( \kappa \rho / \kappa \rho \right), \quad \bar{C}_2 = \left( \kappa \rho / \kappa \rho \right), \quad \bar{C}_3 = \left( \kappa \rho / \kappa \rho \right), \quad \bar{C}_4 = \left( \kappa \rho / \kappa \rho \right), \quad \bar{C}_5 = \left( \kappa \rho / \kappa \rho \right), \quad \bar{C}_6 = \left( \kappa \rho / \kappa \rho \right), \quad \bar{C}_7 = \left( \kappa \rho / \kappa \rho \right), \\
\theta_1 &= \left( \kappa \rho / \kappa \rho \right), \quad \theta_2 = \left( \kappa \rho / \kappa \rho \right), \quad \theta_3 = \left( \kappa \rho / \kappa \rho \right), \quad \theta_4 = \left( \kappa \rho / \kappa \rho \right), \quad \theta_5 = \left( \kappa \rho / \kappa \rho \right), \quad \theta_6 = \left( \kappa \rho / \kappa \rho \right), \quad \theta_7 = \left( \kappa \rho / \kappa \rho \right), \\
\end{align*}
\]

The three basic Eqs. (5) contain four variables \(\phi(x,t), P(x,t), T(x,t),\) and \(\epsilon_g\). Eqs. (5) should be incorporated with Eq. (4) to form a complete set of governing differential equations.

The boundary conditions on the surfaces of the slab are (x = 0 for x = 0; \(x = 1\) for x = L)

\[
\begin{align*}
\frac{\partial \phi}{\partial x} &= 0 \quad (x = 0), \quad P(x,0) = 0 \quad (x = 0), \quad \frac{\partial T}{\partial x} &= -\frac{h}{L} (T - T_0) \quad (x = 0), \quad P = P_0 \quad (x = L), \\
\end{align*}
\]

where \(\alpha\) denotes the mass transfer coefficient, \(D\) the diffusion coefficient, \(h\) the heat transfer coefficient, and \(k\) thermal conductivity. \(\phi_{out}, T_{out}, P_{out}\), respectively, are the mole fractions of water vapor, temperature, and pressure of the surrounding of the porous system.

For a slab surrounded by air at atmospheric pressure and temperatures between 0°C and 60°C, the transfer coefficients may be expressed by

\[
\begin{align*}
\alpha &= \alpha_p + 1.63 \times 10^{-5} \left( \frac{T_m - T}{T_m} \right) \quad \text{(7)}, \quad h = 2.75 \times 10^8 \quad \text{(8)} \quad w = \left( \frac{T_e - T_i}{T_e - T_i} \right)^{1/2}, \\
\end{align*}
\]

where \(\alpha_p\) denotes the mass transfer coefficient due to forced convection, \(B\) is a characteristic length of the slab, \(\sigma_s\) the Stefan-Boltzmann constant, \(T_{el}\) the temperature of the enclosure of the system, and \(n\) the topological constant of the porous system. \(k_g, k_l, k_s, k_l\) and \(k_s\) are the conductivities for gas, liquid, and solid matrix respectively; \(\epsilon, \epsilon_g, \epsilon_l, \epsilon_s\) are the porosity of the porous system, the volume fraction for gas, and the volume fraction for liquid, respectively.

The initial conditions used here are given by

\[
\begin{align*}
\phi(x,0) &= \phi_0 , \quad P(x,0) = P_{atm}, \quad T(x,0) = T_0. \\
\end{align*}
\]

Eqs. (4,5,...,10) form a nonlinear initial-boundary value problem for the simultaneous mass and heat transfer in a concrete slab.

5. Numerical Calculation and Conclusions

The given equations are replaced by a set of algebraic, finite difference, backward-in-time equations relating \(\phi, P,\) and \(T\) to discrete points in the \(x,t\) space. For stable numerical solutions, the space and time differences must be chosen so that \(\Delta t / (Ax)^2 \leq \frac{C}{2}\), where \(C\)
is a parameter determined by ratios of the coefficients \( A_1, \ldots, K_1 \). As \( C \) varies with time, the increment \( \Delta t \) must be adjusted continually in order to provide both economy and stability of calculations.

As an example, heat and mass transfer were calculated for a light-weight concrete slab 0.1m thick, exposed to a temperature of 304\(^\circ\)K on side \( i=0 \), and 293\(^\circ\)K on side \( i=1 \), and to water vapor of 0.0134 mol/mol on side \( i=0 \), and 0.003548 mol/mol on side \( i=1 \), respectively. The boundary conditions for this problem are summarized in Table 1.

| TABLE 1. VALUES OF THE CONSTANTS USED IN THE EQUATIONS (Light-Weight Concrete) |
| --- | --- | --- | --- | --- | --- |
| Type of Const. | Symbol | Value | Unit | Type of Const. | Symbol | Value | Unit |
| Phys. Const. | \( R \) | \( 8.3149 \times 10^{-14} \) | Kg \( m^2/s^2 \) K mol \(^{-1} \) | | a | \( 1.209658 \times 10^{-11} \) | m \(^2\) s\(^{-2}\) Kg \(^{-1} \) |
| \( \sigma \) | \( 5.670 \times 10^{-8} \) | Kg/s\(^3\) m\(^4\) | | \( b \) | 5080 | K |
| \( (C_p)^a \) | \( 1.0063 \times 10^3 \) | Kg/m\(^3\) K\(^{-1} \) | | \( n \) | 0.25 | |
| \( (C_p)^s \) | \( 0.879 \times 10^3 \) | Kg/s\(^2\) K\(^{-1} \) | | \( \beta \) | \( 0.167 \times 10^{-3} \) | Kg/s\(^2\) K |
| \( (C_p)^v \) | \( 1.864 \times 10^3 \) | Kg/s\(^2\) K\(^{-1} \) | | \( v \) | 1.0 | |
| \( (C_p)^w \) | \( 4.1793 \times 10^3 \) | Kg/s\(^2\) K\(^{-1} \) | | \( \sigma_o \) | \( 121.2 \times 10^{-3} \) | Kg/s\(^2\) |
| D | \( 0.256 \times 10^{-4} \) | m/s | | \( P_{atm} \) | \( 1.01325 \times 10^5 \) | Kg/m s\(^2\) |
| e | 0.8 | | | \( m_{ini} \) | 0.096 | m\(^3\)/m\(^3\) |
| \( k_g \) | 0.02613 | Kg m/s\(^2\) K | | \( T_{ini} \) | 294.8 | K |
| \( k_s \) | 1.4422 | Kg m/s\(^2\) K | | | | |
| \( k_w \) | 0.616 | Kg m/s\(^3\) K | | \( \phi_{00} \) | \( \approx 0.013400 \) | mol/mol |
| \( M_g \) | \( 28.952 \times 10^{-3} \) | Kg/mol | | \( \phi_{01} \) | \( \approx 0.003548 \) | mol/mol |
| \( M_w \) | \( 18.016 \times 10^{-3} \) | Kg/mol | | | | |
| \( e \) | 0.3 | m\(^3\)/m\(^3\) | | \( T_0 \) | 302.99 | K |
| \( n_g \) | \( 1.83 \times 10^{-5} \) | Kg/m s | | \( T_1 \) | 294.0 | K |
| \( \kappa_g \) | \( 2.50 \times 10^{-14} \) | m\(^2\) | | \( T_{e0} \) | 304.0 = \( T_{00} \) | K |
| \( \lambda \) | \( 2.4418 \times 10^6 \) | m\(^2\)/s\(^2\) | | \( T_{e1} \) | 293.0 = \( T_{01} \) | K |
| \( \rho_s \) | \( 2.6 \times 10^3 \) | Kg/m\(^3\) | | \( \alpha_p \) | 0.0 | mol/m\(^2\) s |
| \( \rho_w \) | \( 0.99707 \times 10^3 \) | Kg/m\(^3\) | | | | |
| Geom. Const. | | | | | | |
| L | 0.10 | m | | | | |
| B | 2.00 | m | | | | |

Fig. 2 shows the average drying rate for the light-weight concrete slab subjected to a temperature gradient. The drying rate is high in the funicular saturation state (high moisture saturation). The moisture movement at this state is relatively independent of the properties of the concrete, and strongly dependent on the ambient temperature, velocity, and relative humidity of the surrounding air. As the pendular saturation state begins, the liquid threads in the pore space begin to break down, and true adsorption and capillary forces set in. Then, the internal characteristics of the porous system play the primary role in moisture migration. The histories of moisture, temperature, and pressure distribution
during the early pendular state is replotted in detail in Fig. 2. In this state, the moisture distribution curves are not convex. However, before and after this period, the moisture distribution curves appear to be smoothly convex curves which show that diffusion is the dominant mechanism. The histories of temperature and pressure distribution in the concrete slab (see Fig. 3) show transient phenomena. The temperature distribution in the system approaches thermal equilibrium rather slowly. Both temperature and pressure gradients play important roles in drying.

REFERENCES

Fig. 1. Liquid-Vapor Equilibrium Curve for a lightweight concrete

Fig. 2. Average Moisture Drying Rate