[1148]　A Study of the Moisture Transport Process in Concrete as a Composite Material

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1. INTRODUCTION

It is a well known fact that most of the deterioration mechanisms, both physical as well as chemical are closely coupled with the moisture transport process in concrete. In this study an attempt has been made to rationally consider the physics of moisture transport in concrete. Basic phenomenons relevant to moisture transport are formulated at the pore or micro scale which are integrated over a representative elementary volume to give macro scale mass transport behavior in a homogenous porous media. Since concrete is a composite porous material consisting of various components such as aggregates, matrix as well as interfaces and macro-defects, the concept of multiple porosity is adopted to correctly define the moisture history of concrete in space and time domains. Interaction between various components is considered at macro scale. For practical considerations the formulation is kept simple enough which can be directly used in a regular FEM code.

Ingress of moisture into the pores of concrete is a thermodynamic process, driven by the overall potential (pressure and temperature) gradients. Temperature effects are neglected in this study. Thus progress of moisture can be viewed as adsorption, condensation process. The same phenomenons also define the *moisture capacity* or retention characteristics of the porous media. At the macro scale concrete can be subdivided into three components. Namely, matrix made of cement paste, aggregates and interfaces between aggregate and the matrix. Role and significance of these components in the moisture transport process has already been discussed in the past by the authors[5]. If the constitutive relations of moisture interaction between these components are known, the overall mass transport process can be predicted.

2. MOISTURE CAPACITY OF THE POROUS MEDIA

Of the total water present in concrete pores, some fraction of it can be termed as *fixed*, which is under the influence of strong surface forces and which perhaps does not moves under the application of pore pressure potential gradients. Since surface forces can be neglected for pores having radii greater than 5 to 10 nm, it appears that most of this fixed water is retained in the conventional gel and interlayer region having pore radii less than 5 nm. In this study water present in the cement paste matrix is divided into two parts, (I) water present in the interlayer region, (II) water present in the matrix porosity region measurable by mercury intrusion. To account for the interlayer water modified

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Feldman and Sereda model of cement paste micro-structure is adopted[1]. Water retained after D-drying[1] is taken as the water present in interlayer zone. Relationship of pore fraction of interlayer water V_I with total volumetric porosity ϕ for varying degrees of hydration of OPC concrete is shown in Fig.1[8]. Hysteresis in the moisture isotherms at lower humidity is partly explained due to the nature of entry and exit of interlayer water. Primarily, bulk of the de-saturation in V_I during drying occurs at relative humidity below 10% whereas, re-saturation of V_I zone during wetting

Figure 1 : V_I vs. porosity for OPC mortar.

occurs gradually till 60% RH[1]. Hysteresis due to other reasons such as ink-bottle effect, entrapment of air-bubbles etc. is not considered. Amount of water disposed in concrete microstructure as condensed and adsorbed phases can be obtained by integrating the degree of saturation S_r of individual pores over the known porosity distribution dV/dr as given by the following modified BET equation[2]:
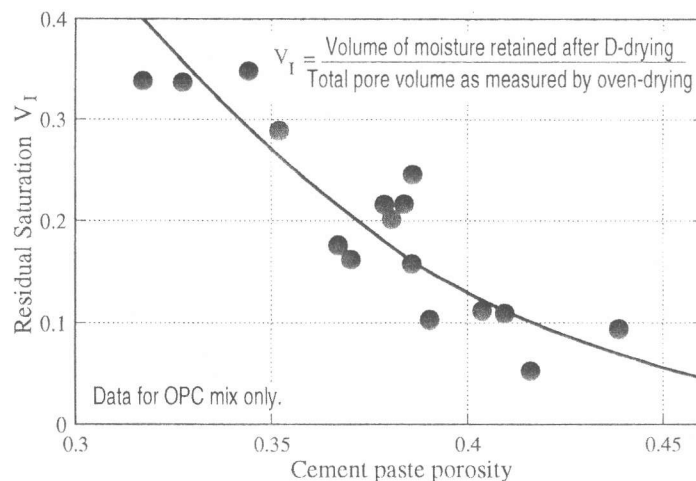
$$V_{II} = (1-V_I)\int_{r_{min}}^{\infty} S_r dV \qquad t_a = \frac{t_w h C}{(1-h/h_m)(1-h/h_m + Ch)} \tag{1}$$
$$S_r = 1-(1-t_a/r)^2 \qquad h_m = \exp\left(-\gamma M/\rho RT\,(r-t_a)\right)$$

Where V_{II} : volume fraction of moisture in II porosity zone, r_{min} : 3.5 nm, h : relative humidity, h_m : relative humidity required to completely fill the pore, t_w : thickness of one layer of water molecule = 0.38 nm, t_a : thickness of the adsorbed layer [m], r : radius of the pore [m], C : a material constant for cementitious material = 15, γ : surface tension of water [N/m], ρ : liquid water density [kg/m³], M : molecular mass of water [kg/mol], R : universal gas constant [J/mol.K], T : absolute temperature [K]. Thus, at any given relative humidity total saturation as a sum of the contributions of water in regions (I) and (II) can be obtained. It is therefore possible to compute moisture capacity for any relative humidity, defined as the slope of the isotherm at constant temperature.

3. MOISTURE TRANSPORT PROCESS

Concrete pores in region II are idealized as cylindrical shaped. Any kind of liquid movement occurring on the surface of pore walls during adsorbed phase is neglected. Pores of successively larger radii would be filled with increasing humidity. During bulk flow of liquid, it is hypothesized that some narrow **necks** exist between continuously connected larger pores which offer maximum resistance to the flow. Therefore, overall bulk liquid flow properties are governed mainly by these necks. The radii of these necks at any arbitrary saturation would be less than the largest filled pore. In other words, the neck radius can be termed as the *critical radius* of the porous media for a particular saturation. With above stated assumptions and using random pore model, the authors propose overall flux q_l of moisture in the liquid phase for a continuous pore distribution as, [7],

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[1] D-drying here refers to drying of a initially fully saturated $4\times4\times16$ cm³ sized mortar specimen in a vacuum desiccator at room temperature, until constant weight was achieved.

$$q_l = -\left(\frac{\rho \phi^2 (1-V_l)^2 V_{ll} \int_{r_m}^{r_{kc}} (r-t_a)^2 dV}{8\,\mu_a\,\Omega \int_{r_m}^{r_k} dV} \right) \frac{dP_l}{dx} = -K_l \frac{dP_l}{dx} \tag{2}$$

where, ϕ : total volumetric porosity, r_m : minimum capillary radius = 2.5nm (IUPAC classification), r_k : radius of the largest filled pore for a given relative humidity, r_{kc} : critical capillary pore radius for a particular saturation, $\Omega = (\pi/2)^4$ for a 3-D pore network which is uniformly randomly connected, P_l : pore water pressure which is related to relative humidity by Kelvin's equation [Pa], dV : differential pore volume, such that $\int_0^\infty dV=1$, μ_a : actual viscosity of water in the porous media $= \mu_i\, exp(\Delta G^*/RT)$ where μ_i : viscosity of water under ideal conditions, ΔG^* : extra Gibbs free energy for the activation of flow. It has to be commented at this point that ΔG^* appears to be dependent on the moisture history. It probably reaches a maximum value of the order of 8.0 *Kjoules/mol* under prolonged saturated condition of the specimen. Moreover, ΔG^* is generally observed to decrease with an increase in the matrix porosity. Thus liquid conductivity K_l is in fact a history dependent parameter. In the numerical simulation a combination of pore distributions $V=1-(1+ar^n)^{-1}$ is adopted to best fit the experimental pore distribution. Critical neck radius r_{kc} is determined from the inflection point of V vs. r^{-1} curves for a particular saturation. Flux of vapor phase is governed by the Fick's first law of diffusion. However, factors such as complicated pore network, reduction of pore volume through which vapor movement can take place with increasing saturation, Knudsen diffusion etc. reduce the apparent diffusivity of vapor. To account for the complicated pore network, a random pore model as in the previous case is adopted. Thus, flux of moisture q_v in the vapor phase can be expressed as

$$q_v = -\frac{\rho_v \phi^2 D_a}{\Omega} \left(\int_{rk}^\infty \left(1 + 0.5f/(r-t_a) \right)^{-1} dV \right) \frac{dh}{dx} = -D_v \frac{dh}{dx} \tag{3}$$

where ρ_v : water vapor density [kg/m^3], D_a : vapor diffusivity in free atmosphere [m^2/s], f : mean free path length of water vapor molecule [m], D_v : vapor mass diffusivity in porous medium [kg/m.s]. Integral in above expression sums up the effect of Knudsen diffusion over the whole pore distribution. Absorption and desorption isotherms as well as transport coefficients calculated for a typical combination of pore structures using above expressions are shown in Fig. 2.
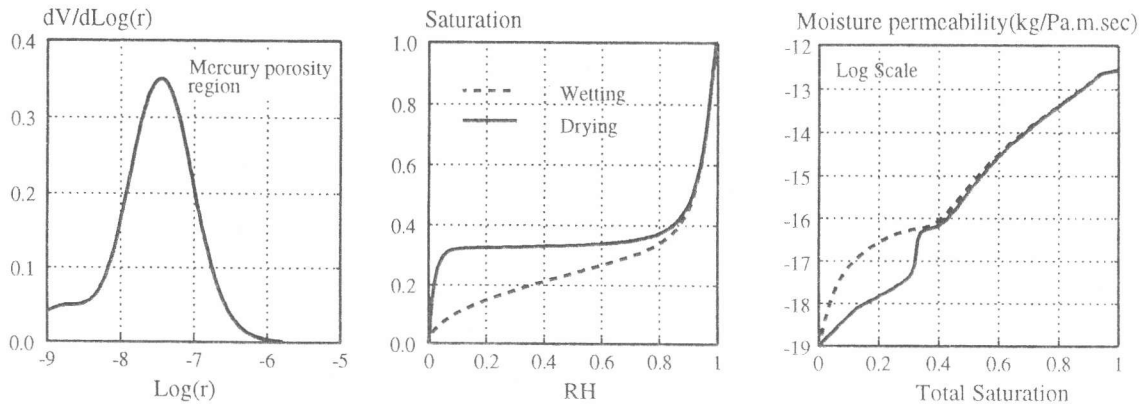

Figure. 2. Isotherms and diffusion coefficients computed for typical pore distributions.

Mass of vapor present in the pores can be neglected compared to the mass of liquid water. With this assumption, using (2) and (3) and Kelvin's equation, total moisture balance is obtained as

$$\partial\theta/\partial t = -div\,q = div \left[\left\{ \left(\frac{\rho RT}{M\,h} K_l + D_v \right) \frac{\partial h}{\partial\theta} \right\} \nabla\theta \right] \tag{4}$$

where θ : moisture content per unit volume of the porous media [kg/m^3], q : total moisture flux combining the contributions of vapor and liquid water [kg/m^2.s]. It has to be noted that hydration is
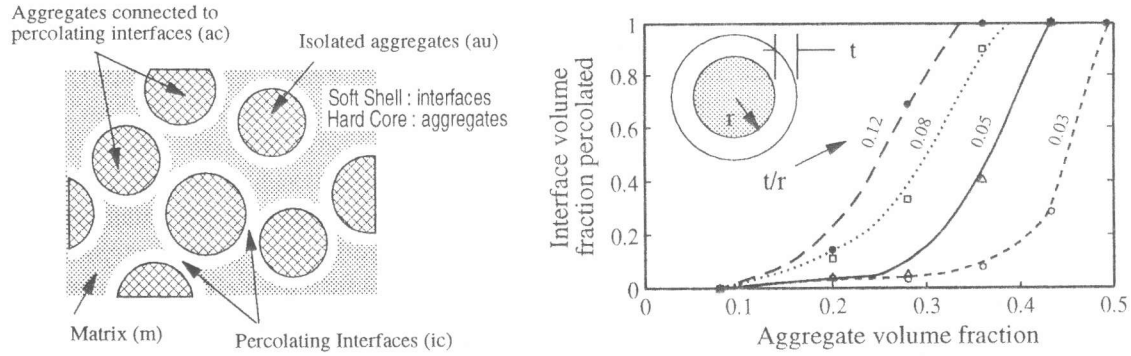
Figure 3 : (a) Schematics of Soft Shell Hard Core model (b) Effect of interface thickness and aggregate content on interface fraction percolation.

assumed to be complete and self-desiccation terms are neglected. As a composite or multi-porosity system concrete consists of aggregates and corresponding interfacial zones. Rate of moisture transfer in these components is quite different from each other, under which conditions usual equilibrium assumption as used in (4) is invalid and therefore treatment of each component distinctly is imperative.

At the macro scale, concrete can be schematically visualized as in Fig. 3a. where aggregates are modelled as hard spheres and interfaces as a soft shell. Usually the interfacial zones are discontinuous for low aggregate contents. As aggregate volume fraction G is increased, interfaces tend to percolate over a finite domain of concrete. Beyond a critical aggregate volume fraction G_{crit} dependent on the size distribution of aggregates and interfacial characteristics, interfaces form a completely connected network over infinite length. Clearly, from the durability point of view aggregate contents higher than G_{crit} are undesirable. It is therefore important to predict G_{crit} as well as the overall transport characteristics for a known aggregate content and volume fraction. A computer simulation code was written to obtain the percolation characteristics of a composite material (Fig. 3a.) in 3D. Hard cores are not allowed to overlap whereas overlapping of the soft shell is permissible. Input to this continuum computer model are aggregate grading and interface thickness dependent on radius. Aggregates from larger to smaller radii are randomly parked in a unit volume of concrete or mortar. On completion information about all possible clusters (soft shells overlapping) is obtained. Number of completely spanning clusters if any and the volume as well as the surface area of interfaces contained in these clusters is also computed. Periodic boundary conditions are adopted to avoid any artificial effect arising due to finite size. The computer model can be used as a tool of inverse analysis to compute relation of interfacial zone thickness to aggregate radii. Fig. 3b. shows the effect of interfacial zone thickness and aggregate volume fraction (same radii aggregates) to the fraction of interfaces percolated which is the ratio of percolated interface volume to the total interface volume.

4. INTER COMPONENT MOISTURE TRANSFER

A continuum approach is adopted in defining the local mass transfer. Main driving mechanism for local mass transfer in an isothermal case is taken as the difference of liquid potential between participating components. This result can be obtained if it is assumed that the potential gradient in local mass transfer zone is linear. Thus an expression for local mass transfer can be obtained as

$$r_{12} = q_{12} A_{12} = -\left(2 A_{12} / \sum_{i=1}^{2} (\delta_i / K_i) \right) (P_2 - P_1) = R_{12}(P_2 - P_1) \tag{5}$$

where r_{12} : rate of moisture transfer from component 1 to 2 per unit volume of concrete [kg/m^3.s], q_{12} : total moisture flux from component 1 to 2 [kg/m^2.s], A_{12} : effective area of contact between

interacting pair per unit volume of concrete [m^2/m^3], δ_i : thickness or length scale of *ith* component, K_i : effective moisture conductivity of *ith* component, P_1, P_2 : pressure potential of 1*st* and 2*nd* component, R_{12} : local moisture transport coefficient between components 1 and 2 [kg/m^3.Pa.s]. Since, moisture conductivity K is a nonlinear function of pressure potential P, the intercomponent moisture transfer model is non-linear in nature. Various parameters as appearing in above equation can be obtained from the soft shell, hard core computer model described earlier.

5. MULTI-POROSITY MOISTURE TRANSFER

For a general case as shown in Fig. 3a, various components for which mass balance needs to be obtained are (i) Hardened matrix (ii) Percolating interfaces (iii) Aggregates connected to percolating backbone of interfaces and (iv) Isolated aggregates. Last two components need to be considered when a substantial fraction of total porosity is contained in aggregates. Interfaces need not be considered if the aggregate volume fraction is less than G_{crit}. Notation used to identify these four components are *m*, *ic*, *ac* and *au* respectively. Overall equations of moisture transport can be therefore obtained as

$$\partial\theta_m/\partial t = -div D_m \nabla\theta_m + \alpha R_{m.ic}(P_{ic}-P_m) + (1-\alpha)R_{m.au}(P_{au}-P_m)$$
$$\partial\theta_{ic}/\partial t = -div D_{ic} \nabla\theta_{ic} + \alpha R_{m.ic}(P_m-P_{ic}) + \alpha R_{ic.ac}(P_{ac}-P_{ic})$$
$$\partial\theta_{ac}/\partial t = \alpha R_{ic.ac}(P_{ic}-P_{ac})$$
$$\partial\theta_{au}/\partial t = (1-\alpha)R_{m.au}(P_m-P_{au})$$

(6)

Where, $R_{i,j}$ terms denote the local moisture transfer coefficients of pairs i and j (Eqn. 5), α : the volume fraction of percolating interfaces [m^3/m^3], D_m, D_{ic} : total macroscopic diffusivity of matrix and interface components respectively [m^2/sec]. It can be noticed that equations degenerate to lesser unknowns when either $\alpha = 1$ or $\alpha = 0$.

6. APPLICATION OF MULTI-POROSITY MOISTURE TRANSPORT

As a case study, multi-porosity formulation was applied to study the influence of aggregate porosity on the drying shrinkage behavior. The drying shrinkage behavior was analyzed for 2-D case using capillary stress theory, initially proposed by Powers[4]. It has been shown recently that quite good predictions of shrinkage strains can be obtained from the capillary stress theory for an environmental relative humidity greater than 50%[6].
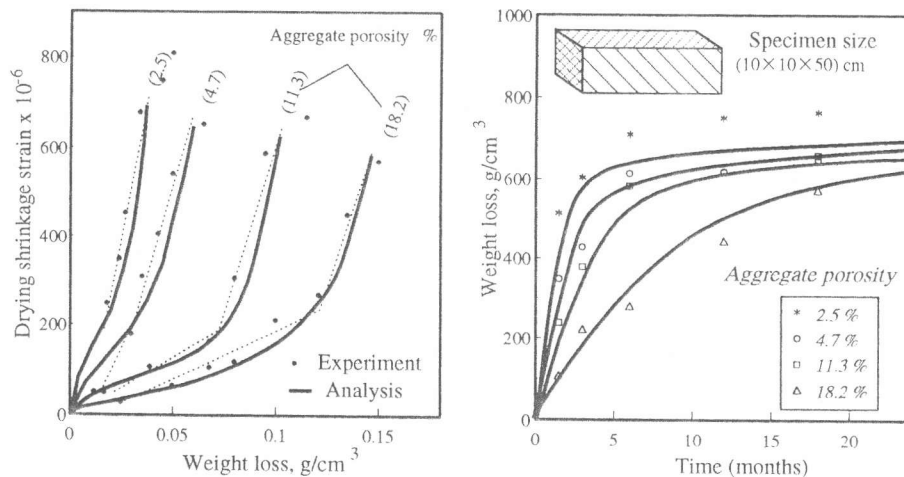
Figure 4 : Experimental and simulated weight loss with shrinkage and weight loss with time curves.

The data of systematic experiments of drying shrinkage conducted by Kokubu[3] were used to verify the multiporosity formulation. In the experiments measurements were done for weight loss as well as shrinkage strains varying over a span of several months. In the mix proportions, *W/C* ratio as

well as aggregate content (72% v/v) were kept same but aggregate porosity was varied from 2.5% to 18.2%. In the analysis as such all material properties were kept constant except the aggregate porosity.

From the Fig. 4, it is observed that predicted results are in reasonable agreement for all the cases, once material properties for a particular case is fixed. Also, it can be observed that as the aggregate porosity is increased, very little initial shrinkage occurs even for large weight loss. This is attributed to two reasons. First, some initial drying of larger voids takes place without resulting in any shrinkage. Second, moisture is transferred from aggregate pores to the cement paste pores which keeps it wet resulting in little shrinkage but large weight loss, wherein actual loss of moisture is occurring from aggregates. Moisture content of aggregates decreases till a point where the matrix and aggregate components are in thermodynamic equilibrium. Presence of interfaces further accelerates the loss from aggregates without resulting in any substantial shrinkage. During the later part of weight loss, moisture is mainly lost from the cement paste pores. Hence, resulting shrinkage weight loss behavior is *almost identical* for all the cases of different aggregate porosities. This trend is also confirmed by the experimental results.

7. CONCLUSIONS

Moisture transport and retention characteristics have a direct bearing with the overall microstructure of concrete. A substantial part of porosity is unmeasured using mercury intrusion or nitrogen adsorption methods. It is observed that retention characteristic is governed by the porosity lying in finer radii range whereas transport characteristic are primarily decided upon by larger pores. Moreover it appears that when exposed to moisture finer porosity zone exhibits a delayed response in terms of continuous decrease of liquid conductivity. From the macroscopic point of view this behavior can be attributed to an increase in the Gibbs free energy for the activation of flow.

As a composite, various transport characteristics of concrete can be obtained through computer simulation methods. Multi-porosity formulation can be a useful tool in understanding various aspects and phenomenons related to moisture transport process clearly. Effect of aggregate porosity on weight loss as well as drying shrinkage strains are successfully obtained with the present local mass transfer model. The multi-component concept of water transport is essential for unified theory of mass transport and related phenomenons of concrete.

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