論文 Coupled Moisture Transport, Structure Formation and Hydration in Cementitious Materials

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ABSTRACT : To study the early age development of young concrete, multi-component hydration heat model of cement and multi component model of moisture transport are coupled with pore structure development model in a FEM program. The pore structure development model embodies the idea of through-solution mechanism of structure formation for arbitrary *W/C* ratio. Through the analysis, the effect of different curing conditions on the strength gain, moisture loss and pore structure development of various specimens is investigated.

KEYWORDS : Durability, Cementitious materials, Moisture transport, Pore structure, Hydration

1. INTRODUCTION

Various physical and chemical deterioration mechanisms of concrete are linked to the heat and moisture transport process, which in turn are dependent on the early age developments and micro-pore characteristics of concrete. This study attempts to analytically study the inter-relationship of hydration, moisture transport and pore-structure development processes using fundamental physical material models. Physical processes related to the moisture transport are formulated at the micro-pore scale and integrated over a representative elementary volume to give macro scale mass transport behavior. Hydration process is based on a multi-component hydration heat model of powder materials. A hydration degree based pore structure development model is dynamically coupled to the transport-hydration models. Predicted computational pore structures are used as a basis for moisture transport computations. As a result, development of pore structure along with moisture content and temperature can be dynamically traced with the increase of degree of hydration for any arbitrary initial and boundary condition. This methodology serves as a basis for the quantitative evaluation of parameters relevant for the durability of structural concrete.

2. PORE STRUCTURE DEVELOPMENT

The powder material in concrete mix is idealized as consisting of spherical particles of same radius. After the contact with water, these particles start to *dissolve* and reaction products get precipitated. Figure 1 shows a schematic representation of various phases present at any arbitrary stage of hydration. The precipitation on the outer surface of particles and in the pore solution phase leads to the formation of outer products whereas so called inner products are formed inside the original particle boundary[1]. Thus powder particles can be considered as expanding concentric spheres. Throughout the process of structure formation, inner product porosity and properties are assumed to be constant and almost identical to the CSH gel. The voids formed between the solidified mass of outer product and inter

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particle space is taken as capillary porosity. The solidified CSH gel mass accounts for the gel and interlayer porosity. Characteristic porosity of the CSH solids ϕ_{ch} is assumed to be constant throughout the progress of hydration. In this study a value of 0.28 is assumed which includes both interlayer as well as micro-gel porosity. Undertaking these assumptions, weight W_s and volume V_s of gel solids can be computed, provided average degree of hydration α and the amount of chemically combined water β per unit weight of powder material is known. These two parameters are obtained from the multi-component hydration heat model described later. As reported by past researchers, a layer structure for hardened gel solids is assumed with interlayer spacing of one water molecule[2]. Overall volume balance thus gives interlayer(ϕ_l), gel(ϕ_g) and capillary(ϕ_c) porosity. These parameters are computed as,

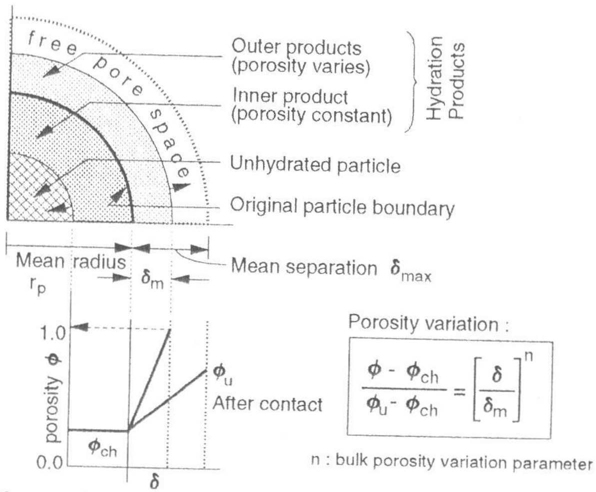

Figure 1 : Hydration of a single cement particle.

$$\phi_l = \frac{t_w\ s_l\ \rho_s}{2} \qquad \phi_c = 1 - V_s - (1-\alpha)\frac{W_p}{\rho_p}$$
$$\phi_g = \phi_{ch} V_s - \phi_l \qquad V_s = \frac{\alpha W_p}{1-\phi_{ch}}\left(\frac{1}{\rho_p} + \frac{\beta}{\rho_w}\right) \tag{1}$$

where t_w : Interlayer thickness, s_l : specific surface area of interlayer, W_p : Weight of the powder materials per unit volume, ρ_p : specific density of the powder material, ρ_w : pore water density, ρ_s : dry density of gel = $(1+\beta)(1-\phi_{ch})/(\rho^{-1}+\beta\rho_w^{-1})$. The outer product thickness δ_m is computed by assuming a bulk porosity variation which increases from the characteristic porosity of solid mass ϕ_{ch} at the particle surface to unity or ϕ_u at the external boundary of outer product. Surface areas of capillary(S_c) and gel pores(S_g) per unit volume of matrix are obtained as

$$S_c = \frac{3\delta_m\left[A\delta_m^2 + B\delta_m + C\right]}{l_g(1-\phi_{ch})(r_p+\delta_{max})^3} \qquad S_g = W_s s_g \tag{2}$$

where, l_s : average volume to surface ratio of solid crystals, r_p : Mean powder particle radius, δ_{max} : R - r_p, where R denotes equivalent radius of particle cell, s_g : specific surface area of gel mass, A : $\{n(1-\phi_{ch})+3(1-\phi_u)\}/\{3(n+3)\}$, B : $\{n(1-\phi_{ch})+2(1-\phi_u)\}r_p/(n+2)$, C : $\{n(1-\phi_{ch})+(1-\phi_u)\}r_p^2/(n+1)$. It is implicitly assumed that the inner mass tends to grow with constant properties throughout the hydration process whereas, representative solid gel of constant and uniform properties gets precipitated in the outer pore solution phase. With the maturity of hydrating matrix capillary voids are filled with the hydration products leading to a more uniform microstructural properties in the outer and inner products. It has to be noted that after outward growing particles make contact, porosity ϕ_u would decrease from unity. In the computational model a bi-modal *R-R* porosity distribution is assumed signifying capillary and gel pores. Thus total porosity function $\phi(r)$ is obtained as

$$\phi(r) = \phi_l + \phi_g\left\{1-\exp(-B_g r)\right\} + \phi_c\left\{1-\exp(-B_c r)\right\} \qquad r\ :\ \text{pore radius} \tag{3}$$

Distribution parameters B_c and B_g can be easily obtained from the computed porosity and surface area values for the capillary and micro-gel region.

3. MOISTURE TRANSPORT FORMULATION

Ingress of moisture into the pores of concrete is a thermodynamic process, driven by the pressure and temperature potential gradients. In this study, total water present in matrix pores is subdivided into interlayer, adsorbed and condensed water. Interlayer water is probably the water which is under the influence of strong surface forces and which perhaps does not moves under the application of pore pressure potential gradients. Absorption-desorption characteristics of the interlayer water is modelled based on Feldman and Sereda interlayer model[2]. Amount of water disposed in the remaining microstructure as condensed and adsorbed phases is obtained by integrating the degree of saturation of individual pores as computed by modified BET theory[3] over computed porosity distribution. During the early age hydration, substantial amount of moisture is consumed in the hydration process as chemically combined water. Thus, overall moisture balance can be obtained as

$$\rho\left(\sum \phi_i \frac{\partial S_i}{\partial P}\right)\frac{\partial P}{\partial t} - div\left(K(P,T,PD)\,\nabla P\right) + \rho\sum S_i\frac{\partial \phi_i}{\partial t} - W_p\frac{\partial \beta}{\partial t} = 0 \qquad (4)$$

where, ϕ_i : porosity of each component(interlayer, gel and capillary), S_i : degree of saturation of each component, P : equivalent liquid pore pressure, ρ : density of pore water. Moisture conductivity K is obtained from the flux models proposed by the authors[4], using the computed R-R distribution function. Overall moisture capacity is obtained from the summation of moisture capacity for each component of pore water. The rate of moisture consumption $W_p.d\beta/dt$ is dependent on the rate of hydration α, which is in turn dependent on the available free water (taken as capillary condensed water in this model). This inter-dependency makes the early age hydration problem dynamically coupled.

4. MULTI-COMPONENT HYDRATION MODEL

Hydration process is simulated using multi-component model for hydration heat of cement[5]. Specified chemical components of clinker minerals are treated as the characteristic parameter and influence of variable moisture content and powder material proportions in the mix is taken into consideration. Total heat generation rate H per unit volume is idealized as

$$H = C\overline{H}$$
$$\overline{H} = \sum p_i\overline{H}_i \qquad (5)$$

where C is the cement content per unit volume of concrete, $\overline{H}$ is the specific heat rate of cement, $\overline{H}_i$ is the specific heat generation rate of individual clinker component, p_i : corresponding mass ratio in the cement. $\overline{H}_i$ is computed using Arrhenius's law as

$$\overline{H}_i = \overline{H}_{i,T_o}\exp\left[-\frac{E_i}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right] \qquad (6)$$

where E_i is the activation energy of i-th component hydration, R is gas constant and $\overline{H}_{i,To}$ is the referential heat rate of i-th component when temperature is T_o. The referential heat rate of each reaction embodies the probability of molecular collision with which hydration proceeds. In the model it is taken as a function of the amounts of free water, the thickness of the cluster made by already hydrated products and unhydrated chemical compound. Primary coupling of hydration process with moisture transport occurs due to the referential heat generation rate variable $\overline{H}_{i,To}$ of each mineral component. The referential heat generation rate is dependent on the amounts of *free* water ω_{free}, the thickness of the cluster η_i made by already hydrated product and unhydrated chemical compound, and on the total accumulated heat $\overline{Q}_i$ of each clinker component. Expressed in a functional form

$$\overline{H}_{i,T_o} = \overline{H}_{i,T_o}\left(\omega_{free},\eta_i,\overline{Q}_i\right) \qquad (7)$$

The amount of free water ω_{free} in above model is in fact the total condensed water in developing micro-structure. The total amount of water consumed per unit volume of concrete βW_p due to the chemical reactions with clinker components is incrementaly computed at any point of hydration from the usual set of stoichiometric equations of hydration[5].

5. VERIFICATIONS

Early age development involves a simultaneous occurrence of all the three processes described in sections 2,3 and 4. Under moisture sealed curing conditions, most of the hydration process occurs within 2 days after casting. Also a rapid increase of strength gain accompanied by particle to particle contact occurs after few hours of casting. To simulate and verify such processes, a FEM code was written using an explicit coupled scheme of solution to obtain solutions of temperature, pore pressure and other material properties in 3-D space and time domain. Three different case studies were conducted. First case involves the quantitative study of effect of different curing conditions on the strength development. Incremental average compressive strength df_c' [MPa] as a function of incremental degree of hydration $d\alpha_i$ of major clinker mineral component was computed as[6]

$$df_c' = 25 w_{C_3S} d\alpha_{C_3S} + 40 w_{C_2S} d\alpha_{C_2S} + 27 w_{SG} d\alpha_{SG} + 40 w_{FL} d\alpha_{FL} \qquad (8)$$

where, w_i : ratio of weight of *i-th* clinker mineral in the powder to mix water. The major clinker mineral components considered for strength evaluation were Tricalcium silicate (C_3S), Dicalcium silicate (C_2S), Slag (SG) and Flyash (FL). The experimental data[7] was obtained for different curing conditions and various mix proportions as shown in Table I.

Table I : Mix proportions and curing conditions for curing-strength gain experiment[7].

Case	W/C	Air	Mix Unit Weight kg/m^3						
	(%)	(%)	W	C	MC	L18	Slag	Sand	G
MS	33.5	3.5	172	--	513	28	--	828	827
S6	55.8	3.5	172	--	308	17	200	828	827
OP	55.0	4.5	165	300	--	--	--	927	924

Case	Curing Condition
SL	Sealed curing
16	Form stripped at 16 hrs
2D	Form stripped at 2 days
WT	Submerged in water

Note

W : Water; **C** : Ordinary Portland Cement; **MC** : Medium Heat Cement; **L18** : Lime; **G** : Gravel

Figure 2 shows a comparison of predicted and experimental compressive strength values at 7 and 28 days for various curing conditions. The second case is the prediction of weight loss with time for specimens of different mix proportions and cured for different periods. After a stipulated period of curing the specimens were put in a vacuum desiccator and weight measurements were taken with time[8]. Computed results show reasonable agreement not only in terms of the rate of weight loss, but also in terms of the absolute amount of weight loss (Figure 3). The third case of study is the qualitative comparison of effect of early drying on micro-structure formation. Specimens of 0.265 *W/C* ratio were exposed to 1-D drying in 40%RH and 20°C after one day moisture sealed curing. After several days of drying, microstructure were measured, at 1 cm interval from the exposed surface. Experimental data showed that hydration almost immediately stops near the surface after exposure while inner parts continue to hydrate. Microstructure formed in the surface zone is markedly different compared to the inner zones. Numerical simulation using the same initial and boundary condition shows a similar trend and proves the extremely strong coupling of hydration and moisture transport process in the early age of hydration (Figure 4).

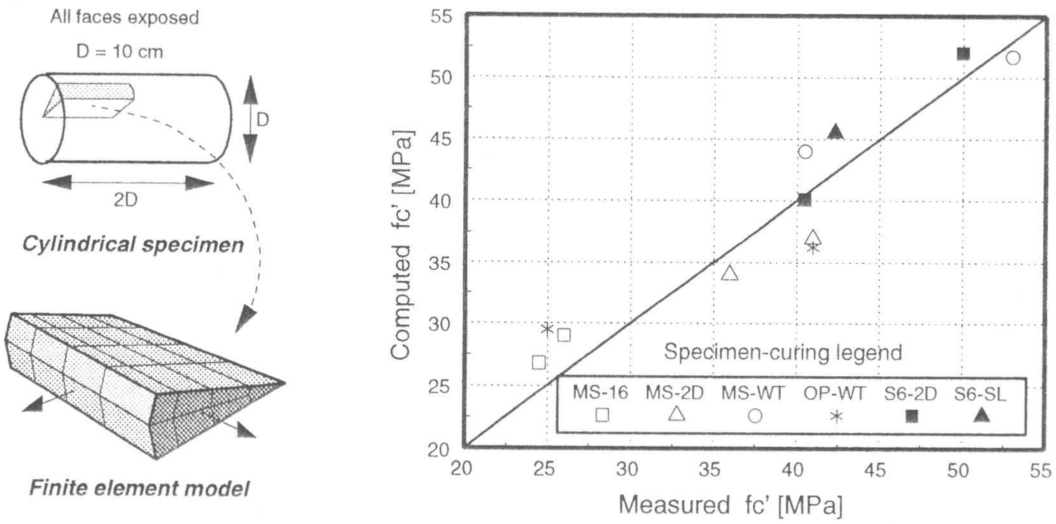

Figure 2 : Effect of curing condition on strength development

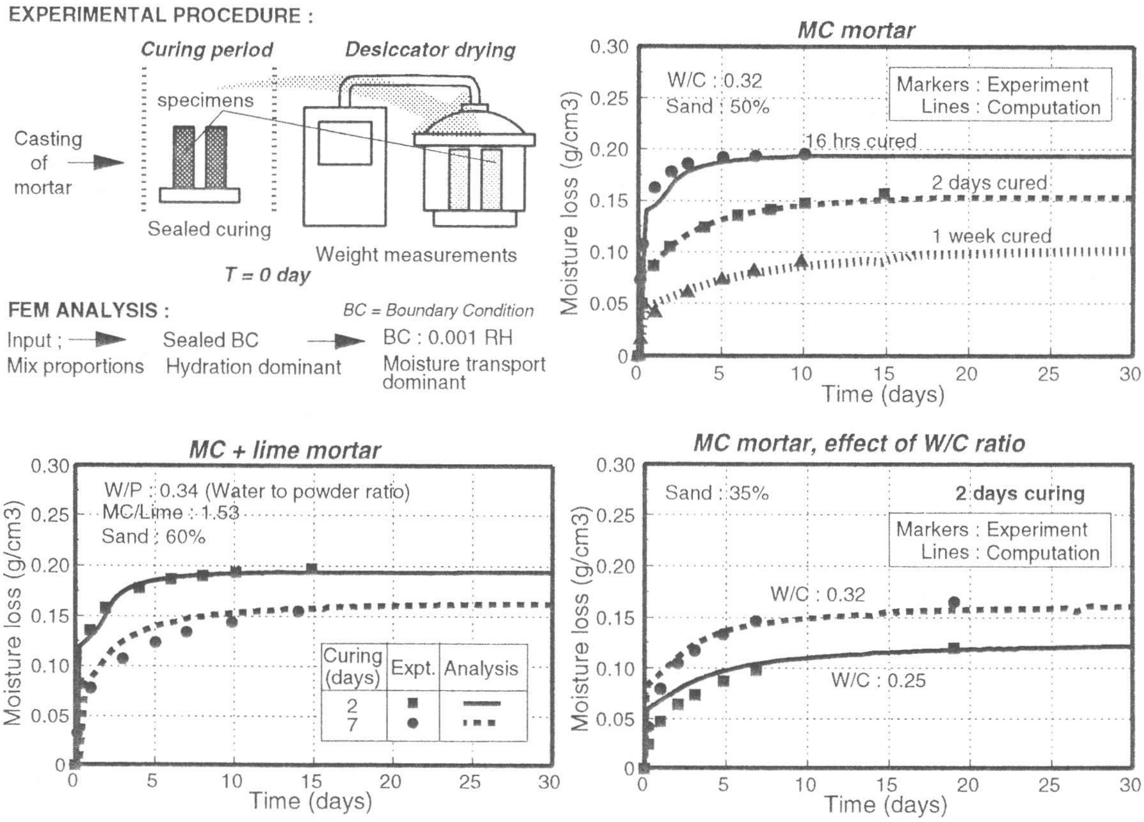

Figure 3 : Moisture loss behavior in desiccator for different curing periods.

6. CONCLUSIONS

Using simple physical models for the hydration, moisture transport and micro-structure development, early age development process and various parameters relevant for long term durability can be quantitatively obtained. A computational model has been developed by combining the pore-

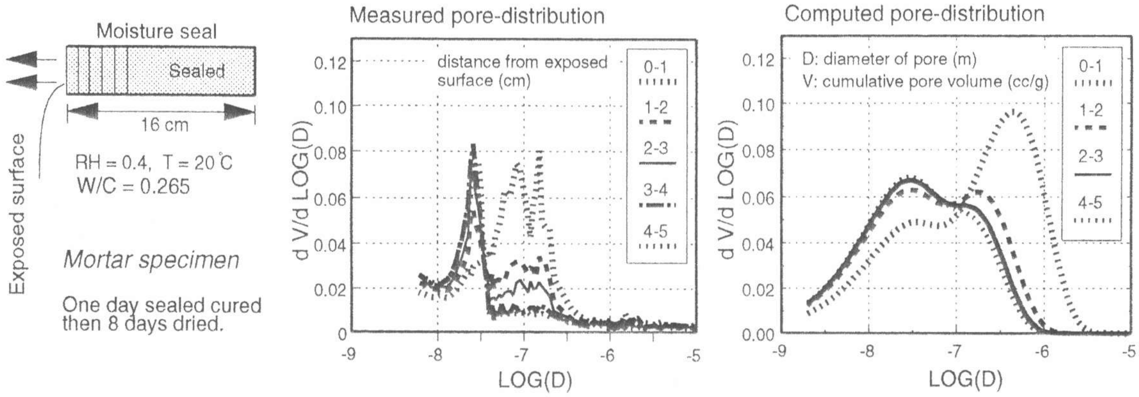

Figure 4 : Effect of early age drying on microstructure development.

structure development, hydration heat and moisture transport models. Contrary to the usual assumption of uniform properties in the outer products, an alternative model has been proposed for structure development which takes into consideration the non-uniform porosity variations in the outward growing powder particles during hydration. As such, this tool can be used to study the effect of curing conditions, mix-proportions etc. on early age development and related problems. Preliminary verifications of the overall model with regard to microstructure-strength development and moisture loss at early ages for different mix-proportions shows a reasonable agreement with the experimental data.

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