Realistic models for degree of hydration and moisture distribution in concrete at early age

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ABSTRACT: Hydration is the major factor for the growth of the material properties. The time is not an exact parameter to control the chemical and physical processes, but the degree of hydration. Therefore, it is necessary that all material parameters and the development of microstructure should be formulated in terms of degree of hydration. The purpose of the present study is to propose and to integrate numerous material laws, e.g. a reasonable model for the degree of hydration and also the models for other important material properties including thermal and moisture properties, in finite element program. The 3D finite element procedure is formulated to evaluate degree of hydration, temperature and moisture distributions in hardening concrete. The mathematical formulation of degree of hydration is based on the combination of three rate functions of reaction. All moisture parameters were considered to be age-dependent. Prediction of a moisture sink due to the hydration process, i.e. self-desiccation, is related to autogenous shrinkage, which may cause early-age cracking in high strength and high performance concrete. The realistic models and the finite element program described in this study are strongly necessary for a realistic thermal and shrinkage stress analyses of concrete structures at early ages.

1 INTRODUCTION

At early ages the main part of the development of material properties takes place due to chemical reactions of cementitious materials. The degree of reaction is affected by curing condition, e.g. temperature and moisture conditions, as well as curing time. Concerning early-age concrete, only the temperature effect has been generally considered to control the reaction process as a curing condition. However, moisture condition in concrete plays an important role in chemical reactions of cement (Powers 1947, Parrott 1986, Jonasson 1994, Norling Mjörnell 1994).

For a precise definition of material properties in hardening concrete, chemical reaction and development of microstructure can be modeled by means of the degree of hydration. The degree of hydration may be obtained from the consequence of temperature and moisture distributions. It is reasonable to determine the material properties such as thermal, moisture and mechanical properties under these conditions.

Moisture plays a significant role for concrete, not only in the hydration process but also in physical and chemical processes in various deterioration phenomena, such as frost damage, early shrinkage and shrinkage cracking as well as movement of ions and gases (Nilsson 1996). Bazant (1993) pointed out that for concrete structures exposed to the environment there is no hope of obtaining realistic stresses, and thus of predicting cracking, without solving the associated problems of moisture and heat transport.

Material properties, such as fixation and transport of moisture are fairly well known for mature concrete, and material data and models for calculating moisture conditions in hardening concrete, e.g. age-dependent transport coefficient and sorption isotherm, have also been studied.

Related to durability and serviceability of concrete structures, autogenous shrinkage due to self-desiccation is an important issue. In the prediction of the moisture conditions in concrete, the effect of self-desiccation - it is a very important property of high-strength concrete (HSC) and of high-performance concrete (HPC) – will be considered in this paper.

A framework has been established for formulation of mathematical models for analysis with finite element method. During the analysis, the temperature development and moisture distribution are determined simultaneously by solving two nonlinear diffusion equations as well as the field of degree of hydration. After degree of hydration, temperature and moisture distributions are determined in this study, the stresses induced by thermal and hygral

gradients are then determined using temperature and moisture distributions.

2 MODELING THE DEGREE OF HYDRATION

2.1 Definition of degree of hydration

When cement becomes hydrated the water is chemically bound. Either the amount of chemically bound water or the degree of heat liberation can be estimated from various test data.

$$\alpha = \frac{Q}{\max Q} = \frac{W_n}{\max W_n} \quad (1)$$

where Q = amount of heat liberated; and W_n = amount of nonevaporable water. The rate of reaction of binders in a paste depends on the composition of the paste, in particular W/C and type and fineness of cement, as well as on the temperature and moisture conditions in the material.

2.2 Mathematical model for the degree of reaction of cement

The effect of temperature on the rate of reaction has been extensively investigated during last five decades. When early age concrete is dealt with, only temperature rate factor has been generally considered to control the reaction process. This approximate approach assumes that the maximum heat of hydration is obtained from adiabatic tests at the moment when all particles of cement have reacted. Recently many researchers have considered the effect of water distribution on the rate of reaction in terms of internal relative humidity. However, those show considerable differences when compared to each other. The water shortage and water distribution influence the degree of hydration. The rate factor for water shortage is associated with the effect of W/C ratio on the progress of hydration. The rate factor for water distribution is associated with the effect of free capillary water distribution in the pore system.

2.2.1 Basic rate of reaction formulas for the degree of hydration

The following expression has been used to describe the degree of reaction of cement, α (Byfors 1980):

$$\alpha = \exp\left(-\lambda_1 \left(\ln(1+\frac{t_{eq}}{t_1})\right)^{-\kappa_1}\right) \quad (2)$$

where t_{eq} = equivalent maturity age; and λ_1, t_1, κ_1 and λ_2, t_2, κ_2 = fitting parameters.

The equivalent maturity time for cement t_{eq} in Equation (2) is defined as

$$t_{eq} = \int_0^t \beta_T \ \beta_{W/C} \ \beta_w \ dt \quad (3)$$

The rate factor β_T, $\beta_{W/C}$, and β_w takes into account the curing temperature, water shortage and water distribution, respectively. Reference conditions for Equations (2) and (3) are hypothetical in the sense assumed that curing condition is fully saturated during the entire hydration process, and all cement particles will react at a given W/C.

2.2.2 The Influence of temperature on the rate of reaction

The Arrhenius-type rate equation is widely used in describing the temperature effect on the maturity growth of concrete:

$$\beta_T = \exp\left(\frac{E}{R}\left(\frac{1}{293} - \frac{1}{T+273}\right)\right) \quad (4)$$

where E/R is activation temperature (K) and 20°C is chosen as reference temperature. Jonasson (1994) reports the temperature dependency of the activation temperature:

$$\frac{E}{R} = \theta_{ref}\left(\frac{30}{T+10}\right)^{\kappa_3} \quad (5)$$

The parameters θ_{ref} and κ_3 are material constants, which can be obtained from experimental adaptations, typical values being 5400K and 0.54, respectively (Byfors 1980, Jonasson 1994, Hedlund 1996).

2.2.3 The Influence of water to cement ratio on the rate of reaction

The theoretical minimum W/C required to bring cement to its ultimate degree of reaction is about 0.40. As reaction of hydration proceeds, the pore system lacks of water. Even though there is enough water and space available, all cement will not react. Before the ultimate degree of reaction is reached, the rate of reaction will have substantially decreased. The reason is that the dense cement gel formed around the cement grains obstructs the transport of water into the anhydrous cement grains.

The ultimate degree of reaction, α_{max}, is determined by Mill's formula and the rate factor, $\beta_{W/C}$, can be expressed as:

$$\beta_{W/C} = \left(\frac{\alpha_{max} - \alpha}{\alpha_{max}}\right)^r$$

where $\alpha_{max} = \frac{1.031 \cdot W/C}{0.194 + W/C}$ \quad (6)

2.2.4 The Influence of water distributions on the rate of reaction

During the hydration process the capillary pores become gradually empty until a thermodynamic equilibrium is reached. This state of equilibrium de-

pends on the relative humidity in the pore system, the pore size distribution and the pore size.

The pore system consists of chemically bound water, physically bound water and free capillary water. In order to determine the free capillary water, pore size distribution is needed. In modeling the pore size distribution, the HYMOSTRUC (Breugel 1991), a simplified approach based on Mercury intrusion, is used in this paper.

Physically absorption layer does not contribute to progress of hydration and only free capillary water is available for further hydration. The relationship between the thickness of the adsorption layer and the relative humidity in the pore system has been investigated by several researchers (Setzer 1976, Badmann et al. 1981).

The rate factor β_w for water distribution is defined as:

$$\beta_w = \frac{A_{wal}(\alpha)}{A_{tot}(\alpha)} \tag{7}$$

where A_{tot} and A_{wal} are the total pore wall area and the wall area of the pores which are completely filled at a degree of hydration α, respectively.

2.3 Verification of model for degree of hydration

A general model for the reaction of cement has been established. Figure 1 shows the predicted and measured degree of hydration as a function of W/C. Test data is obtained from thermogravimetric analysis of nonevaporable water (Atlassi 1995). The prediction model is in good agreement with test results. The reaction of cement is greatly affected by W/C.

3 MOISTURE DISTRIBUTION AND DUFFUION PARAMETERS IN HARDENING CONCRETE

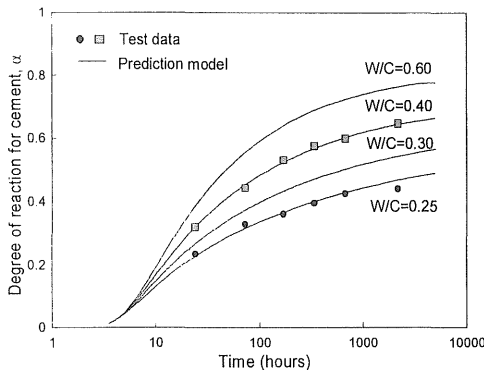Moisture diffusion is very important for the long-term performance of cementitious materials. The

Figure 1. Calculated and measured degree of hydration versus time for different *W/C*.

moisture diffusion can be described by diffusion equations and solved by various numerical methods, provided that the coefficients are known. The major difficulty in establishing reliable diffusion parameters is that diffusion of moisture inside cementitious materials is basically controlled by the microstructure of the material, and especially by the pore size distribution. The microstructure is changing with age as well as with relative humidity in the pores. However, only few models proposed in the literature have taken enough parameters (Hedenblad 1993, Norling Mjörnell 1997) into consideration.

3.1 Governing equation of moisture diffusion

In this study, the state variable is used in terms of pore relative humidity, φ, because the use of φ appears to be more practical, e. g. it is convenient to impose the initial and boundary conditions and relative humidity is mainly real value determined in experiments.

$$\frac{\partial \varphi}{\partial t} = (c\rho)_w^{-1} \nabla \cdot \left(D_\varphi \nabla \varphi\right) + \frac{\partial \varphi_s}{\partial t} \tag{8}$$

where $(c\rho)_w^{-1} = \partial \varphi / \partial w_e$ = reciprocal of moisture capacity, i.e. slope of desorption isotherm (m³/kg); D_φ = moisture transport coefficient when the corresponding potential is the moisture content (kg/m·s); and φ_s = humidity drop due to self-desiccation.

3.2 Moisture transport coefficient

The diffusion coefficient is strongly dependent on the moisture content in the pore system. Bazant and Najjar (1972) expressed the moisture transport coefficient as a function of the relative humidity, φ. Diffusion coefficient includes a constant moisture capacity, it is inadequate in hardening concrete. In the model proposed by Xi et al. (1994a, b), the coefficients α, β, and γ are strongly affected by W/C and the effect of curing time on the coefficients could be considered negligible. It seems that the proposed formulae for α, β, and γ are limited to high values of W/C because it is calibrated by test data with W/C above 0.5.

$$D_\varphi = \alpha + \beta \cdot (1 - 2^{-10 \cdot \gamma \cdot (\varphi-1)}) \tag{9}$$

where D_φ = diffusivity; α, β, γ = coefficients to be calibrated from test data; and φ = relative humidity.

Hedenblad (1997) proposed the following expression for the moisture transport coefficient:

$$D_\varphi = D_{\varphi=60\%} + (D_{\varphi=100\%} - D_{\varphi=60\%})\left(\frac{\varphi-0.6}{0.4}\right)^k \tag{10}$$

where $D_{\varphi=60\%}$ = moisture transport coefficient at $\varphi=60\%$; $D_{\varphi=100\%}$ = moisture transport coefficient at

$\varphi = 100\%$: and k = constant which mainly depends on $H^{\cdot} / C^{\cdot}$.

$$D_{\varphi=60\%} = a + b \cdot P_{cap} \qquad (11a)$$

$$D_{\varphi=100\%} = c + d \cdot P_{cap}^{2} \qquad (11b)$$

Transport coefficient (Equation (10)) is adopted in the finite element formulation and it is more advantageous than others as the hardening concrete and substantial self-desiccation of HSC and HPC are dealt with in this study.

3.3 Mathematical modelling of desorption isotherms

The best-known isotherm model is the famous BET model (1938), derived from statistical thermodynamics of adsorption. But contrary to early assumptions, the range of validity to the BET equation for cement and concrete does not cover the practical range of relative humidity. A number of attempts have been made to modify the BET equation in order to obtain better agreement with experimental isotherm data in the multi-layer region.

Because the moisture capacity is defined as the derivative of the desorption isotherm, a mathematical sorption isotherm is needed for numerical analysis of moisture diffusion problems. A semi-empirical formula for the age-dependent desorption isotherm, based on gel and capillary isotherm, will be used in this paper. The empirical expression for desorption isotherm was originally formulated by Hedberg and is modified to take into consideration the effect of degree of reaction on the shape of the isotherm.

$$\frac{W_c(\varphi, \alpha_c)}{C} = \frac{W_{gel}(\varphi, \alpha_c)}{C} + \frac{W_{cap}(\varphi, \alpha_c)}{C}$$
$$= \gamma_{gel} \frac{W_{gel}}{C} + \gamma_{cap} \frac{W_{cap}}{C} \qquad (12)$$

where γ_{gel} and γ_{cap} = gel and capillary filling factor, respectively ($0 \leq \gamma_{gel}, \gamma_{cap} \leq 1$);

3.4 Computational model of moisture capacity

Moisture capacity can be derived from the equilibrium sorption isotherm with respect to relative humidity, φ. In hardening concrete, the slope of the sorption isotherm cannot be assumed to be constant within the practical humidity range. This slope is varying significantly in the entire humidity range.

3.5 Computational model for the prediction of self-desiccation

The moisture sink term in Equation (8) means self-desiccation due to hydration. Self-desiccation appears in cement matrix with low water cement ratio, $W / C < 0.5$ (Neville 1995), since a major part of mixing water is bound by the cement. The percentual reduction in humidity is very small (from 100% to 95%) for usual W / C. But the moisture conditions of concrete with low W / C depend on self-desiccation to a large extent; especially in HSC and HPC, the humidity drop is greater and therefore the transport coefficient is smaller than in ordinary concrete. The humidity drop in concrete due to hydration is calculated from the inverse of the theoretical desorption isotherm (Norling Mjörnell 1994).

4 FINITE ELEMENT PROCEDURE FOR NONLINEAR DIFFUSION PROBLEMS

4.1 Structure of developed program

To solve the nonlinear transient thermal and hygral problems realistic numerical method is needed. Finite element analysis procedures are used to solve nonlinear diffusion equations for temperature and humidity fields in this paper. The progress of hydration, i.e. maturity development, is mainly governed by two diffusion processes. The analysis of temperature and moisture distribution has been done to predict the field of degree of hydration (Cha 1999). It is assumed that temperature and humidity fields are fully uncoupled and only the degree of hydration is coupled with two state variables. Figure 2 shows the flow of calculation procedure for the fields of temperature, moisture and degree of hydration.

4.2 Governing equation and boundary conditions of the diffusion problem

The diffusion analysis is formulated for determination of the temperature distribution and moisture diffusion. Heat balance is expressed with the transient Fourier equation, for heat conduction with internal
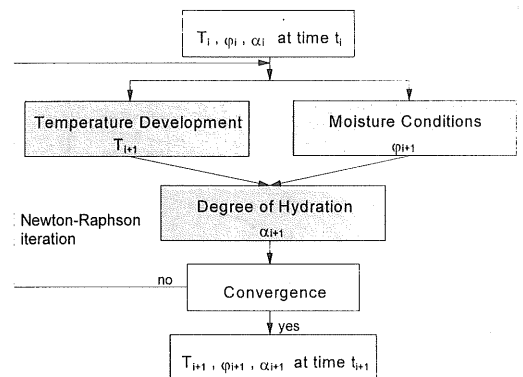

Figure 2. Determination of the fields of temperature, moisture and degree of hydration.

sources (internal sink in the moisture field)

$$c\rho \frac{\partial T}{\partial t} = k\, \nabla^2 T + q \qquad (13)$$

where ρ = density; c = specific heat capacity; k = constitutive matrix, a diagonal matrix containing k_x, k_y and k_z; $\nabla^2 = \nabla \cdot \nabla$; and q = internal rate of energy production by hydration.

The boundary conditions may be described in three different ways, i.e. essential, natural and convective boundary.

$$T = T_p \text{ on } A_p, \qquad (14a)$$

$$q^c = h_c (T - T_c) \text{ on } A_c, \qquad (14b)$$

$$q^f = \mathbf{q}^T \mathbf{n} = f \text{ on } A_f \qquad (14c)$$

where T_p = prescribed temperature on boundary A_p; q^c = heat convection normal to the boundary A_c; h_c = convection coefficient, depends on the environmental conditions and the surface texture of the structure; T_c = environmental temperature; q^f = prescribed heat flux on boundary A_f; $\mathbf{q}$ = heat flux; and $\mathbf{n}$ = a unit vector pointing out of the structural body.

4.3 Finite element formulation

In this study, a three dimensional eight-node solid element is adopted. After spatial discretization, then the resulting finite element equations are:

$$\mathbf{K}\,\mathbf{T} + \mathbf{C}\,\dot{\mathbf{T}} = \mathbf{R} \qquad (15)$$

$$\mathbf{K} = \int_V \mathbf{B}^T \mathbf{k}\, \mathbf{B}\; dV + \int_{A_c} h_c \mathbf{N}^T \mathbf{N}\; dA \qquad (16)$$

$$\mathbf{C} = \int_V \mathbf{N}^T c\rho\, \mathbf{N}\; dV \qquad (17)$$

$$\mathbf{R} = -\int_{A_f} \mathbf{N}^T f\; dA + \int_{A_c} \mathbf{N}^T h_c T_e\; dA + \int_V \mathbf{N}^T q\; dV \quad (18)$$

where $\mathbf{K}$ = conductivity matrix; $\mathbf{C}$ = capacity matrix; $\mathbf{R}$ = load vector. This equilibrium equation is ready for time approximation.

4.4 Time approximation scheme

The differential equation (15) should be integrated with respect to time to obtain the transient response. Diffusion problems with strong nonlinearities, such as those with moisture diffusion, Arrhenius-type heat sources require iterative techniques and Newton's method, i.e. second-order iteration schemes may be used. In this study, generalized Crank-Nicolson method (Zienkiewicz & Taylor 1989) is adapted for the solution of the temperature field as a function of time and this consists of the following approximation:

$$[\mathbf{C}(\mathbf{T}^a) + \theta\Delta t \mathbf{K}(\mathbf{T}^a)]\mathbf{T}_{n+1}$$
$$= \Delta t[\theta \mathbf{R}_{n+1} + (1-\theta)\mathbf{R}_n] + [\mathbf{C}(\mathbf{T}^a) - (1-\theta)\mathbf{K}(\mathbf{T}^a)]\mathbf{T}_n \qquad (19)$$

where Δt = time step; θ = parameter that determines where in the time interval, t_n to $t_{n+1} = t_n + \Delta t$; when $\theta = 0.5$, it is trapezoidal scheme and unconditionally stable.

4.5 Modelling of heat development and moisture sink

4.5.1 Rate of heat evolution
Computational reasons require the transformation of the adiabatic process to a maturity-equivalent isothermal process. Therefore the rate of heat evolution is:

$$q(t) = \max Q \frac{\partial \alpha}{\partial t} = \max Q \frac{\partial \alpha}{\partial t_{eq}} \frac{\partial t_{eq}}{\partial t} \qquad (20)$$

$$\text{where} \quad \frac{\partial \alpha}{\partial t_{eq}} = \alpha \frac{\lambda_1 \kappa_1}{t_1 + t_{eq}} \left(\ln\left(1 + \frac{t_{eq}}{t_1} \right) \right)^{-\kappa_1 - 1}, \qquad (21a)$$

$$\frac{\partial t_{eq}}{\partial t} = \beta_T\, \beta_{W/C}\, \beta_w \qquad (21b)$$

4.5.2 Rate of self-desiccation
In this study, governing equation (Equation (8)) is used to solve the nonlinear moisture transport problem. The analytic formula of self-desiccation rate is needed in order to solve Equation (8). From the definition of degree of hydration, the rate of heat evolution is proportional to the rate of degree of hydration. This proportionality, however, is not applicable to the rate of self-desiccation. Thus prediction formula of self-desiccation and its rate is proposed through Equations (22) to (24). This formula is obtained by normalization of self-desiccation and degree of hydration.

Humidity drop due to self-desiccation is expressed as:

$$\frac{\varphi_s - 1}{\varphi_{s,\max} - 1} = \left(\frac{\alpha}{\alpha_{\max}} \right)^s \qquad (22)$$

where $\varphi_{s,\max}$ is the relative humidity due to self-desiccation at ultimate degree of hydration.

The rate of self-desiccation is calculated by differentiate in terms of time:

$$\frac{\partial \varphi_s}{\partial t} = \frac{\partial \varphi_s}{\partial \alpha} \frac{\partial \alpha}{\partial t} = \frac{\partial \varphi_s}{\partial \alpha} \frac{\partial \alpha}{\partial t_{eq}} \frac{\partial t_{eq}}{\partial t} \qquad (23)$$

where $\quad \dfrac{\partial \varphi_s}{\partial \alpha} = (\varphi_{s,\max} - 1) \cdot \dfrac{s}{\alpha_{\max}} \cdot \left(\dfrac{\alpha}{\alpha_{\max}} \right)^{s-1}$ (24)

The parameter s in the analytic formula is mainly dependent on W/C ratio and found to be about 3.0 to 6.0.

5 VERIFICATION OF MODEL FROM EXPERIMENTAL AND NUMERICAL ANALYSIS

5.1 *Adiabatic temperature rise*

Figure 3 shows the effect of type of cement on the adiabatic hydration curve as determined for concrete made with a Korean Portland cement of Type 1 and 4 (Ordinary Potland cement and low heat Portland cement), respectively. The hydration curves were obtained for concrete samples of which the mix proportion and initial temperature are given in the insert of Figure 3. Prediction curves are calculated by the developed nonlinear program. A good agreement was found between measured and theoretical hydration curve.
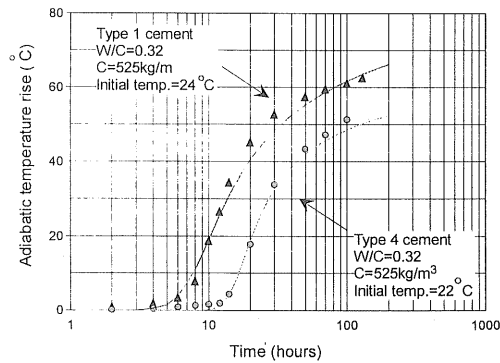

Figure 3. Predicted and measured adiabatic hydration curves.

5.2 *Comparison of prediction and measured data of self-desiccation*

Figure 4 shows the comparison of calculated and measured self-desiccation. The test data for Type 1 cement are taken from the literature (Atlassi 1991, Persson 1992, Mjörnell 1994, Hedlund 1996). Figure 4 indicates that the prediction correlates fairly well with test data.

5.3 *Comparisons between prediction and drying experiment*

Experimental results from Hedenblad (1993) are used for the verification of moisture prediction. The
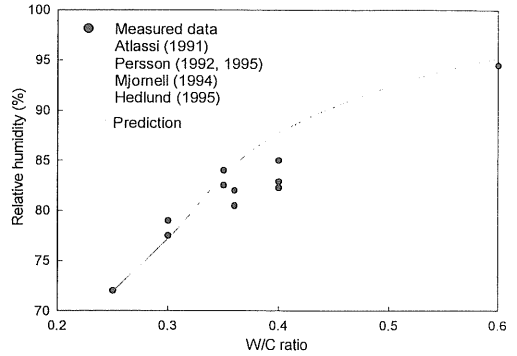

Figure 4. Predicted and measured self-desiccation.

experiment was performed for fully saturated mature concrete. The mature specimen with water to cement ratio of 0.6, is allowed to dry to about 60% (environmental humidity). Then it was immersed in water until it is fully saturated. Therefore, moisture sink due to progress of hydration can be ignored. The cross section of the test specimen is of 0.2×0.2 m and the specimen height, i.e. twice the drying path, is 0.063 m. Drying test is performed up to 185 days and internal relative humidity is measured at 7 points along the drying path. The desorption isotherm for the prediction of moisture condition is adopted from the verification of Nilsson's data (1980) for mature concrete. For mature concrete, the porosity is constant and thus the moisture conductivity depends merely on the relative humidity. Moisture permeability at high humidity is 3.4×10^{-7} kg/m s. Initial and boundary conditions are 98% and 60% respectively and convective coefficient is 2.1×10^{-9} m/s.

The predicted and measured distributions of relative humidity are shown Figure 5. Calculated humidity is in good agreement with measured data. This means that the proposed model and methodology are acceptable for determining the moisture conditions.
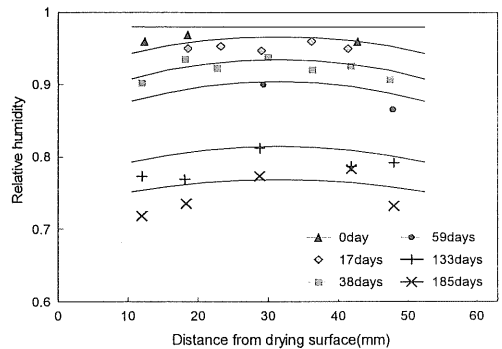

Figure 5. Calculated and measured distribution of relative humidity.

5.4 Numerical 3D Analysis of Drying

The geometry is 100mm cubic and moisture flow is in three directions. Material properties and boundary condition is identical with Section 5.3. As shown in Figure 6, geometry has three symmetric sections.

Figure 7 shows humidity changes from center to edge. In Figure 8, four points, from p1 to p4, means center point and points at which 1D, 2D and 3D
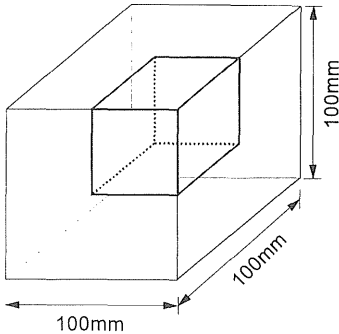

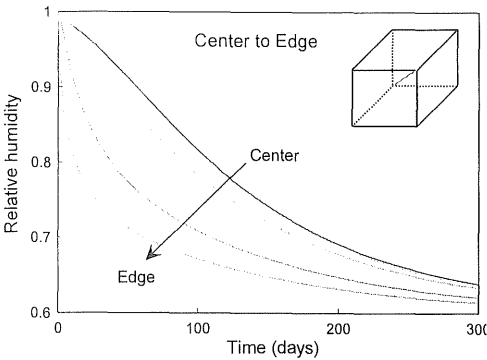Figure 6. Geometry of 3D moisture flow analysis
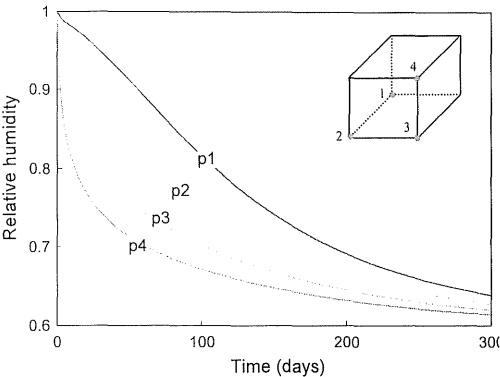

Figure 7. Humidity changes from center to edge

Figure 8. Humidity changes at single and multi-dimensional flow

moisture flow is dominant, respectively. As the p1 approaches the surface and multi-dimensional side, the humidity change is greater.

6 SUMMARY AND CONCLUSION

The present study is focused to integrate numerous material laws, e.g. a reasonable model for the degree of hydration and also the models for other important material properties including thermal and moisture properties, in a finite element program.

Hydration is the main reason for the growth of the material properties. Therefore the degree of hydration is a more accurate parameter to control the chemical and physical processes than the time. All material parameters were formulated in terms of degree of hydration. Mathematical formulation of degree of hydration is based on the combination of rate functions of cement reaction. The effect of moisture conditions as well as temperature on the rate of reaction was considered in the degree of hydration model. The progress of hydration is mainly governed by two nonlinear diffusion processes. It is assumed that temperature and humidity fields are fully uncoupled and only the degree of hydration is coupled with two state variables in diffusion analysis. Prediction of self-desiccation in high performance concrete was considered in this study.

The calculated temperature and humidity distributions show good agreement with measured data. This means that the proposed model and methodology are satisfactory for determining the temperature and moisture conditions in hardening concrete.

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