

THE CARBONATION OF CONCRETE AND THE MECHANISM OF MOISTURE, HEAT AND CARBON DIOXIDE FLOW THROUGH POROUS MATERIALS

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ABSTRACT

The governing equations of moisture, heat and carbon dioxide flows through concrete within the framework of a distributed parameter model are described. The coupling terms and the non-linearity of the problem are taken into account and a numerical procedure based on the finite element method is developed to solve the set of equations. The influence of relative humidity and temperature is investigated and typical results are presented. Comparisons with experimental tests are also carried out and one example is presented in detail in order to show the reliability and the effectiveness of the proposed numerical model.

Introduction

The durability of plain and reinforced concrete structures has recently received much attention. Several experimental studies [e.g. 1 to 5] as well as theoretical models [e.g. 6 to 9] to analyze the different mechanism of material deterioration have been developed.

The study of the durability of concrete structures needs a multidisciplinary approach based on the physics and chemistry of materials. In particular the durability depends both on the ability of concrete to resist the penetration of aggressive substances from the environment, and on its ability to protect embedded steel reinforcement. The transport of aggressive species may follow different mechanisms, depending on the pore structure of the concrete, the exposure conditions and the characteristics of the diffusing substances. The penetration of carbon dioxide or oxygen, as well as of many other gaseous substances, may occur only if the pores of concrete are almost dry, while the diffusion of chloride or sulphate ions takes place only in water. Therefore all these mechanisms should be studied together with the evolution of moisture content inside the concrete.

One of the processes which takes place in the pores of concrete and which may limit the service life of reinforced concrete structures is the carbonation of material, i.e. the chemical process denoting the reaction of calcium hydroxide with carbon dioxide resulting in the formation of calcium carbonate and water [1, 11, 12]. The main consequence of carbonation is the drop of the pH of the pore solution of concrete from the standard values between 12.5 and 13.5, to a value of about 8.3 in the fully carbonated zones, so that the passive layer that usually covers and protects the reinforcing steel against corrosion becomes no longer stable [8, 10].

Actually the real mechanism of carbonation is complex and involves different steps that are mutually interdependent, hence making necessary a careful review of the experimental results listed in literature [see 13,14]. The numerical models presented in literature [e.g. 6] have proved to be powerful tools, allowing to treat these complex interactive processes in a quantitative way. Obviously, the parameters used in the simulation must be linked with concrete characteristics and with exposure conditions by means of suitable, and always necessary, experimental studies.

The carbonation rate is essentially controlled physically by the carbon dioxide diffusion process and chemically by the reserve of calcium hydroxide of the concrete. Therefore an effective numerical model to simulate the whole phenomenon should consider the interaction between many processes, namely the CO₂ diffusion, the moisture and heat transfer, the mechanism of CaCO₃ formation and the availability of Ca(OH)₂ in pore solution due to its transport by water movement.

Since the carbonation of concrete is only "one piece in the jigsaw puzzle" [17], it should be studied in context with other processes, such as chloride penetration, sulphate attack, crack formation, freezing of pore solution, oxygen diffusion and water sorptivity, that under normal and/or extreme climatic conditions may affect the durability of the structure. In particular carbonation is usually associated with volume changes, which can cause microcracking and cracking, which in turn can change the effective permeability. Therefore carbonation probably causes changes in permeability and diffusivity directly. All these phenomena would affect the diffusion equations and should be taken into account in the development of this research.

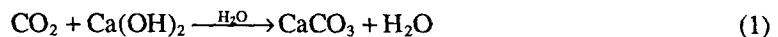
One possible way to ensure durability of the structure could be to specify and assess directly the required quality of concrete, namely its resistance to chemical and physical attacks which are at the origin of damage.

In this study the fundamental relationships describing the carbonation of concrete at variable temperature are presented with reference to internal and external influences. The governing partial differential equations are developed on the basis of the works of Wittmann et al. [6, 18 to 20], and are solved numerically to calculate the depth of carbonation as function of time. As suggested by Wittmann, material parameters are included in the analytical description so allowing to represent the influence of concrete characteristics on the chemical-physical processes. In particular, since the diffusion of carbon dioxide into concrete depends on the moisture content in the pores and on the temperature, as well as on carbon dioxide atmospheric concentration, the equation of CO₂ diffusion is coupled with the differential equations governing the heat and mass flow in the drying process of the material [21 to 27]. This mass flow is expressed in terms of pore humidity, taking also into account the non-linearity typical of these phenomena.

It is worth noting that the mathematical analysis of diffusion phenomena and chemical reactions is similar to the corrosion problem of steel in concrete and the freeze-thaw problem [28 to 30]

Basic Hypotheses and Model Description

The carbon dioxide diffuses from the atmosphere into the capillary pores of concrete and combines with water forming carbonic acid which then reacts with the alkali hydroxide, sodium, potassium and calcium, forming carbonates. Since the concentration of calcium hydroxide in normal concrete is usually higher than the concentration of the other hydration products, the reaction of CO₂ with Ca(OH)₂ predominates, and the carbonation process can be simply described by the following chemical reaction:



Actually this equation represents only the final result of several steps through which the true reaction occurs. Further simplification is to consider the reaction (1) irreversible and instantaneous, so that the calcium carbonate immediately precipitates once the two reactants coexist in solution. If the pores are filled with water, the penetration of carbon dioxide is hindered because of the low rate of diffusion of CO₂ in water, while if the pores are completely dry the reaction of carbon dioxide with water molecules is absent (in practice this is the case of oven-dried concrete).

In both cases carbonation would be very largely ruled out because of the absence of necessary conditions. Actually the case of pores only partly filled with water is normally the condition of the concrete surface, and the carbonation can proceed only to the depth at which the concrete pores have partially dried out.

According to Bažant [21 to 25], the formulation of drying coupled with heat transfer is developed in terms of relative humidity rather than water content and the diffusivities of water and carbon dioxide are assumed to be strongly dependent on pore humidity, temperature and also on the degree of hydration of concrete. Note that the use of evaporable water content, w_e , as basic variable actually involves certain errors [22], since Fick's law in terms of w_e cannot be applied to obtain the differential equation governing the drying phenomenon when hydration proceeds. This is because the porosity becomes non-uniform in time and equal values of evaporable water content do not correspond to equal value of pore humidity in the same points.

Rate of carbonation

The amount of calcium carbonate [CaCO_3] that forms in a unit of time depends on the degree of carbonation (i.e. the availability of calcium hydroxide [$\text{Ca}(\text{OH})_2$]), the temperature T , the carbon dioxide concentration [CO_2], and the relative humidity h into the pore structure of concrete. Assuming that reaction (1) is of the first order with respect to CO_2 and $\text{Ca}(\text{OH})_2$ concentrations, its rate v can be written as

$$v = \frac{\partial[\text{CaCO}_3]}{\partial t} = f(h, T) \times [\text{Ca}(\text{OH})_2] \times [\text{CO}_2]$$

and the function $f(h, T)$, can be expressed as follows:

$$f(h, T) = f_1(h) \times \alpha_1 \times k$$

in which $k = A \cdot e^{-E_0/RT}$ represents the Arrhenius equation for thermally activated processes, α_1 is a material parameter, and $f_1(h)$ takes into account the moisture influence on carbonation. Therefore the carbonation rate can be written in the following way, very similar to that proposed by Wittmann [6,7]:

$$\frac{\partial c}{\partial t} = v = \alpha_1 \times f_1(h) \times f_2(g) \times f_3(c) \times f_4(T) \quad (2)$$

In this equation $f_3(c)$ describes the influence of the degree of carbonation c , and varies between 0 and 1 according to the following relationship:

$$f_3(c) = 1 - \left(\frac{c}{c_{\max}} \right)^m \quad (3)$$

in which c_{\max} is the maximum amount of calcium carbonate and m is usually taken equal to 1.

Also the function $f_2(g)$ ranges between 0, in the zones where carbon dioxide has not yet penetrated, and 1, where carbon dioxide concentration is equal to its maximum g_{\max} . The following linear relationship can be assumed:

$$f_2(g) = \frac{g}{g_{\max}} \quad (4)$$

The function $f_1(h)$ is introduced to take into account that reaction (1) may occur only in presence of water. For almost dry concrete ($h \leq 0.5$) this function is equal to zero, hence stopping the progress of carbonation:

$$f_i(h) = \begin{cases} 0 & 0 \leq h \leq 0.5 \\ \frac{5}{2}(h - 0.5) & 0.5 \leq h \leq 0.9 \\ 1 & 0.9 \leq h \leq 1 \end{cases} \quad (5)$$

The fourth function $f_4(T) = A \cdot e^{-E_0/RT}$ is the above mentioned Arrhenius equation, in which E_0 is the activation energy of the carbonation process, R is the constant of gas and T is the absolute temperature.

Finally the material parameter α_1 , depending on the concrete characteristics, takes into account that the carbonation reaction occurs in an open system, i.e. the concrete, and this fact may modify the rate of reaction deducible from simple chemical considerations.

Water diffusion and heat transfer in non-saturated concrete

Since the diffusion of water through concrete is a very slow phenomenon, the different phases of water in the single pore can be considered in thermodynamic equilibrium at any time. Therefore the desorption/sorption isotherms govern the relationships between the relative humidity h and the water content w ($dh = k dw$).

If, as usual, the slope k of the desorption isotherm at room temperature is approximately taken as constant in a wide range of relative humidity (i.e. $0.15 \leq h \leq 0.95$), it may be combined with the permeability of concrete c , yielding the diffusivity $C = k c$. In this hypothesis, the equation governing the drying of concrete can be written [21, 22]:

$$\frac{\partial h}{\partial t} = \text{div} (C \text{ grad } h) + \frac{\partial h_s}{\partial t} + K \frac{\partial T}{\partial t} \quad (6)$$

where h is the relative humidity, T is the variable, but almost uniform, temperature, K is the hygrothermic coefficient given by:

$$K(h) = \left(\frac{\partial h}{\partial T} \right)_{w, t_e} = 0.0135 \times h \times \frac{(1-h)}{(1.25-h)} \quad (7)$$

and h_s (i.e. the self-desiccation) is an empirical function that represents the gradual decrease of pore humidity from the initial value of 1.00 (initially wet specimen) to about 0.96 - 0.98 after long conservation and in sealed conditions (i.e. without external drying).

The diffusivity, or diffusion coefficient, $C = k c$ of concrete depends on h and T , according to the following relationship [22, 24]:

$$C(h, T) = C_1(t_e, T) \left[\alpha_0 + \frac{1 - \alpha_0}{1 + \left(\frac{1-h}{1-h_c} \right)^n} \right] \quad (8)$$

where α_0 , n and h_c are constant parameters representing respectively the ratio $\min C / \max C$, ranging between 0.025 to 0.10; the spread of the drop in the diffusivity C , variable between $n=6$ to $n=16$ and, finally, the humidity at which the diffusivity C drops half-way between its maximum and minimum values ($h_c = 0.75$). A suitable expression for C_1 , that stands for the diffusivity at humidity $h = 1$, is the semi-empirical formula, proposed by Bažant [23, 24]:

$$C_1(T, t_e) = C_0 \left[0.3 + \sqrt{\frac{13}{t_e}} \right] \frac{T}{T_0} \exp \left(\frac{Q}{RT_0} - \frac{Q}{RT} \right) \quad (9)$$

In this equation Q is the activation energy of the diffusion process, R is the gas constant

(usually $Q/R = 4700$ K), T_0 is the chosen reference temperature (in Kelvin, normally 296 K), C_0 is the diffusivity for $T = T_0$, after 28 days, and t_e is the equivalent hydration period, defined by:

$$t_e = \int_0^1 \beta_T \beta_h dt \quad (10)$$

with

$$\beta_T = \exp\left[\frac{U_h}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad (11)$$

$$\beta_h = [1 + (\alpha - \alpha h)^4]^{-1}$$

in which U_h is the activation energy of hydration and the ratio U_h/R can be expressed by the empirical relation $U_h/R = 4600 [30 / (T-263)]^{0.39}$. The value of parameter α is obtained by test data and it is roughly about 5.

In order to take into account the water liberated during the reaction (1), the differential equation (6) must be replaced by the following one:

$$\frac{\partial h}{\partial t} = \text{div}(C \text{ grad } h) + \frac{\partial h_s}{\partial t} + K \frac{\partial T}{\partial t} + \frac{\partial h_c}{\partial t} \quad (12)$$

where:

- $\frac{\partial h_c}{\partial t} = \alpha_2 \frac{\partial c}{\partial t}$ is the change of the relative humidity due to carbonation in a unit of time;
- α_2 is a nondimensional parameter that varies between 0 and 1, according to the concrete characteristics, like the parameter introduced by Wittmann in the equation governing the moisture diffusion in terms of moisture content w [6]. This coefficient accounts for the possible interaction between the water liberated during carbonation and the concrete components;
- $\partial c / \partial t$ is the rate of carbonation, given by equation (2).

The use of pore humidity, h , as basic variable allows us to neglect the self-dessication term $\partial h_s / \partial t$ in the equation (6), since for usual water/cement ratios the drop in h due to this process is rather small ($h_s > 0.95$). On the contrary, in the equation governing drying phenomena written in terms of evaporable water content [22], the rate of loss in free water due to hydration reaction ($\partial w_w / \partial t$) must be included.

The differential equation that describes the heat diffusion coupled with the drying process in concrete can be written in the usual way as follows [26]:

$$\rho C_q \frac{\partial T}{\partial t} = \text{div}(b \text{ grad } T) + \frac{\partial Q_h}{\partial t} \quad (13)$$

where ρ and C_q represent respectively the mass density and the isobaric heat capacity of the concrete, Q_h is the outflow of heat per unit volume of solid, b is the heat conductivity. Similarly to the case of moisture diffusion, equation (13) must be modified to take into account the heat developed during carbonation, and it can be rewritten as:

$$\rho C_q \frac{\partial T}{\partial t} = \text{div}(b \text{ grad } T) + \frac{\partial Q_h}{\partial t} + \frac{\partial T_c}{\partial t} \quad (14)$$

where:

- $\frac{\partial T_c}{\partial t} = \alpha_3 \frac{\partial c}{\partial t}$ represents the change of the temperature due to carbonation in a unit of time;
- α_3 is a nondimensional parameter, like α_2 in equations (12), that varies between 0 and 1, according to the concrete characteristics.

Carbon dioxide diffusion process

The process of CO₂ diffusion into porous materials, such as concrete, can be described by means of the usual diffusion equation, resulting from Fick's first and second laws:

$$\frac{\partial g}{\partial t} = \text{div}[D_g \text{grad}(g)] \quad (15)$$

where D_g stands for the diffusivity of carbon dioxide, that depends on temperature and relative humidity content of concrete. In order to take into account the loss of carbon dioxide taking place during reaction (1), the differential equation (15) must be replaced by the following one:

$$\frac{\partial g}{\partial t} = \text{div}[D_g \text{grad}(g)] - \frac{\partial g_c}{\partial t} \quad (16)$$

where:

- $\frac{\partial g_c}{\partial t} = \alpha_4 \frac{\partial c}{\partial t}$ represents the change of CO₂ concentration due to carbonation in a unit of time;
- α_4 is a nondimensional parameter, like α_2 used in equation (12), that varies between 0 and 1, according to the concrete characteristics. This parameter is the same as that introduced by Wittmann, [6].

Numerical Examples

Due to the complexity resulting from the non-linearities and the coupling of the differential equations (2), (12), (14) and (16), analytical solutions are very difficult to obtain and a numerical approach should be preferred [e.g. 31]. For the mathematical expression of the diffusion equations and chemical reactions we can observe that it is similar to the mathematical formulation of the corrosion problem of steel in concrete and of the freeze-thaw problem [28 to 30]

In this study, the standard finite element method is applied both in time and in space. After space discretization using a Galerkin procedure, we obtain the following system of coupled ordinary differential equation in time:

$$\begin{aligned} \mathbf{Q} \mathbf{h} + \mathbf{I} \frac{d\mathbf{h}}{dt} - \mathbf{TH} \frac{dT}{dt} - \mathbf{CH} \frac{dc}{dt} - \frac{\partial \mathbf{HG}}{\partial t} &= \mathbf{0} \\ \mathbf{L} \mathbf{g} + \mathbf{I} \frac{d\mathbf{g}}{dt} + \mathbf{CG} \frac{dc}{dt} &= \mathbf{0} \\ \mathbf{I} \frac{dc}{dt} + \mathbf{Sc} - \mathbf{CJ} &= \mathbf{0} \\ \mathbf{TRT} + \mathbf{TS} \frac{dT}{dt} - \mathbf{CT} \frac{dc}{dt} - \frac{\partial \mathbf{TG}}{\partial t} &= \mathbf{0} \end{aligned} \quad (17)$$

where \mathbf{h} , \mathbf{c} , \mathbf{g} and \mathbf{T} are respectively the discrete relative humidity, the discrete carbonate concentration, the discrete relative carbon dioxide concentration and the discrete temperature vectors; \mathbf{Q} , \mathbf{I} , \mathbf{TH} , \mathbf{HG} , \mathbf{TR} , \mathbf{TS} , \mathbf{TG} are the usual matrices of the discretized mass and heat transfer equations [27]; \mathbf{CH} , \mathbf{CG} and \mathbf{CT} are the matrices representing respectively the coupling between the carbonation process and the humidity diffusion phenomenon, the carbon dioxide diffusion phenomenon and the heat transfer; \mathbf{L} is the carbon dioxide diffusion matrix; \mathbf{S} and \mathbf{CJ} are the matrices that represent the influence of relative humidity and temperature at the previous time-step on the carbonation process. For the detailed expression of the matrices, see References 27 and 33.

The system (17) can be written in the following more concise form:

$$B\dot{x} + Cx = F \tag{18}$$

where the meaning of the terms of equation (18) follows immediately from equation (17). This system (18) after time discretization (i.e. one-step algorithm), becomes:

$$[B + C\alpha\Delta t]x_{n+1} = [B - C(1 - \alpha)\Delta t]x_n + F_{n+\alpha}\Delta t \tag{19}$$

with the usual meaning of the symbols [32]. The algebraic non-linear equation (19) is solved by means of a direct approach. The necessary convergence analysis has been made by imposing the limitation of the total error. In particular the stability conditions, the convergence conditions and the compatibility conditions have been carried out [33, 34].

The validation of the numerical model presented in this paper has been made by using several experimental data, both taken from literature and from new experimental tests. For the sake of brevity, in the following only one comparison test is presented to show good agreement between numerical and experimental data. Some numerical examples are presented to show the influence of variable temperature and relative external humidity on the carbonation phenomena.

The material parameters $\alpha_1, \alpha_2, \alpha_3$ and α_4 introduced in the differential equations (2), (12), (14) and (16) and also the values of the diffusivities of carbon dioxide and water, must be evaluated by fitting experimental data. In particular the influence of water/cement ratio, concrete composition, initial degree of hydration and curing time conditions have to be taken into account. Moreover the changes in permeability and diffusivity due to the microcracking and cracking phenomena directly due to the carbonation process, have to be also evaluated and included in the numerical model.

At this stage of the research, some values of these parameters $\alpha_1, \alpha_2, \alpha_3$ and α_4 and diffusivities of carbon dioxide and water are taken from literature and others are calibrated by available test data.

Comparison test

Figure 1 shows the comparison between experimental data obtained by Ho and Lewis [15], and the numerical results obtained from the solution of the set of equations (2), (12), (14) and (16). The different types of concrete, characterized by different 28-days strength level (i. e. 25 MPa, 30 MPa and 38 MPa), are taken into account in the numerical model by means of different values for the diffusivities of carbon dioxide and water. Also the parameter α_1 is

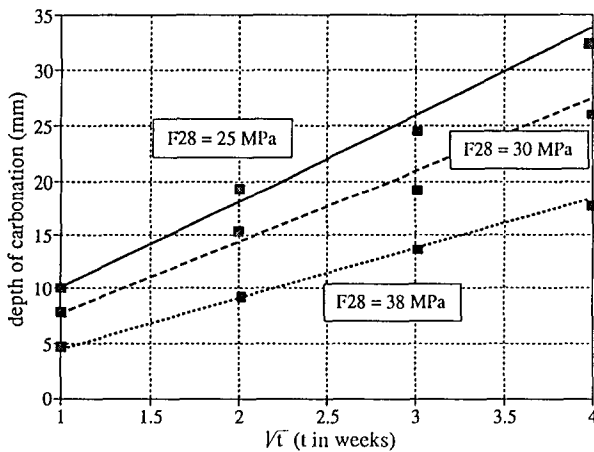


FIG. 1

Carbonation depth-exposure time relationships as influenced by the 28-days strength levels. Comparison between numerical and experimental results (dots) [15]

supposed to vary (the lower value is used for the concrete with 28-days strength level equal to 38 MPa), while α_4 , α_3 and α_2 are kept constant for all the concretes.

It is worth emphasizing that the values of the parameters α_1 , α_2 , α_3 and α_4 have been estimated in the preliminary phase of testing of the numerical model, by using both experimental data and the values given in literature. In this example, the different values of α_1 assumed for different strength level, depend on the different rate of reaction observed in the experimental tests. On the contrary the parameters α_4 , α_3 and α_2 can be assumed constant with the strength level, as shown both by the experimental tests and by the data available in literature.

Note that the agreement is good, and that the short term tests of reference [15] follow the classical square root relationship between depth of carbonation and time.

Variable temperature and relative external humidity influences

Figure 2 depicts the influence of variable external temperature (i.e. 1 °C, 20 °C and 90 °C) on the depth of carbonation. Figure 3 deals with the case of variable humidity (i.e. Relative Humidity RH = 40%, 60% and 80%) and shows the trend of carbonate (Figure 3a), carbon dioxide (Figure 3b) and pore humidity content (Figure 3c) after 250, 500, 750 and 1000 days, for a concrete made with Ordinary Portland Cement, with a water/cement ratio equal to 0.50 and initial relative humidity equal to 0.98. All the relationships shown in figures 2 and 3 have been obtained by using the numerical model presented in this paper.

Conclusions and Discussion

The need to design durable concrete structures in chemically aggressive environments leads to ever more sophisticated modelling of deterioration phenomena. In these models it is essential to consider coupling and non-linearities of all the processes involved in the damage mechanism.

Since concrete is a porous material, the penetration of aggressive species, such as carbon dioxide or chloride ions, is basically determined by the pore structure of the material and by the level of pore waterfilling. Therefore the coupling between drying phenomena of concrete and carbon dioxide diffusion process must be considered, together with the influence of temperature, to make the simulation close to the experimental reality.

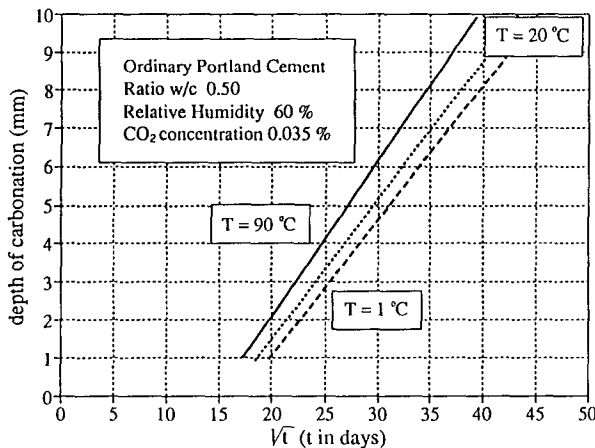


FIG. 2

Carbonation depth-exposure time relationships as influenced by variable temperature.
Numerical Solution

In this study a numerical procedure has been developed to solve the coupled differential equations governing the moisture, heat and carbon dioxide flows in concrete, taking into account all the chemical and physical aspects of the carbonation process. It is worth noting that carbonation may be important not only for the associated loss of alkalinity of concrete, but also for its interaction with the chloride effect on the corrosion of steel. Finally, even if carbonation of the surface of concrete structures cannot be avoided, the rate of carbonation progress can be kept

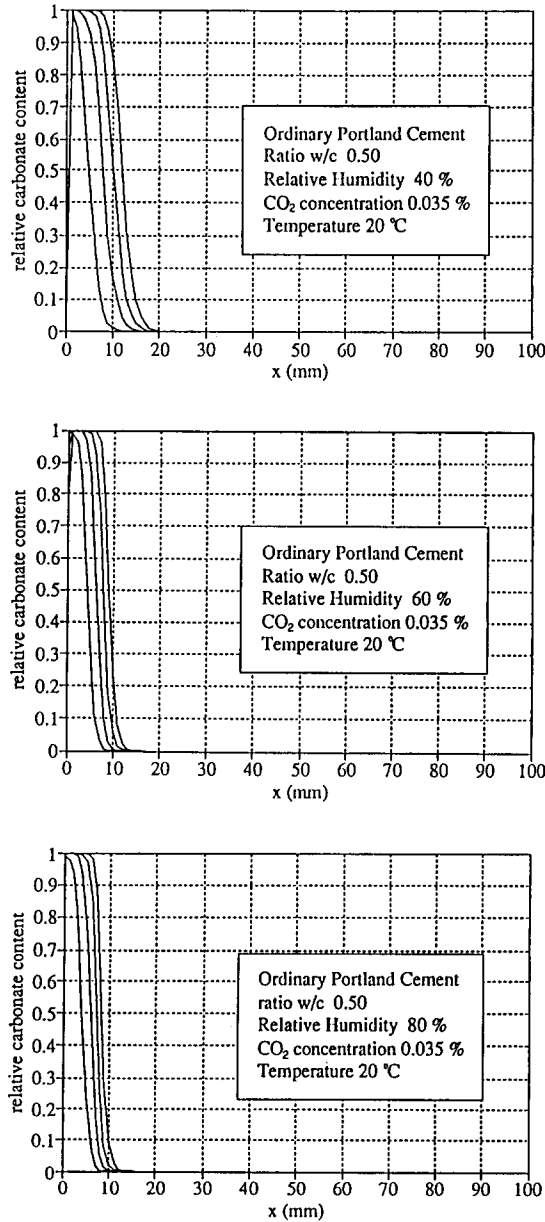


FIG. 3 a

Relative carbonate content after 250, 500, 750, 1000 days as influenced by variable external RH.
Numerical Solution

sufficiently low that the carbonation front does not reach the reinforcement during service life, and this should always be the aim and the scope of modern engineering.

The numerical model developed in this paper is only the first step of a more complete research [33], whose aim is to obtain a valuable method that includes the combined effects of carbonation, chlorides and sulphates attacks for calculating the real life expectancy of reinforced concrete

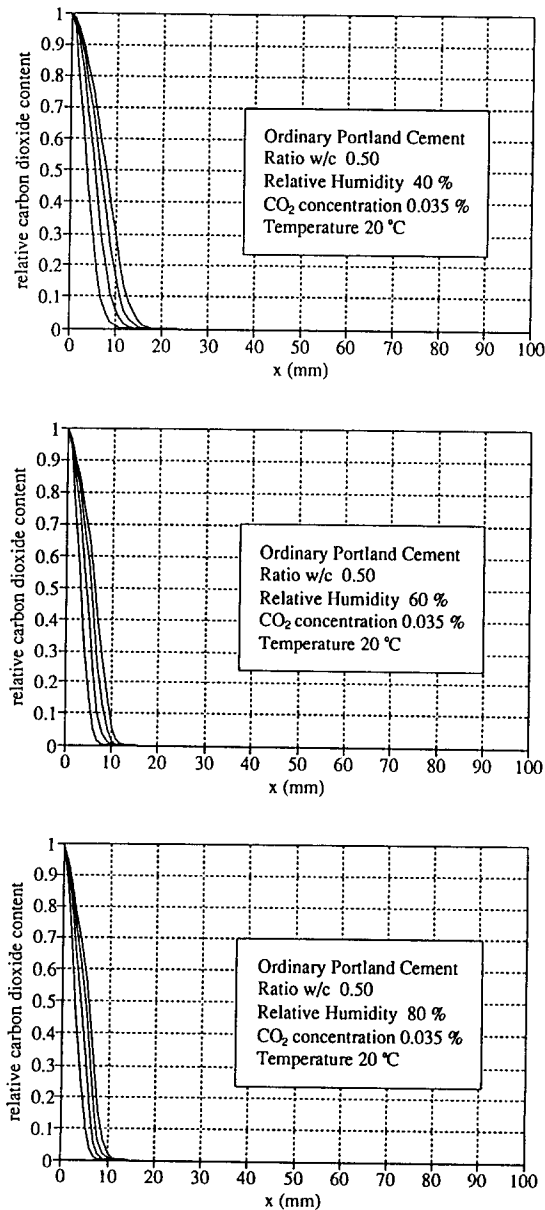


FIG. 3 b

Relative CO₂ content after 250, 500, 750, 1000 days as influenced by variable external RH.
Numerical Solution

components. At this first stage the prediction of durability of concrete can be made on the assumption that the material is only affected by carbonation. From the results of example 1 and from the results of the numerical tests carried out to validate the model [34, 35], we can assert that the results obtained with the presented model compare well with experimental data. The influence of variable temperature as well as variable relative humidity can be taken into account making hence possible the analysis of both the progress of carbonation and the associated durability conditions of reinforced concrete structures under almost arbitrary climatic conditions.

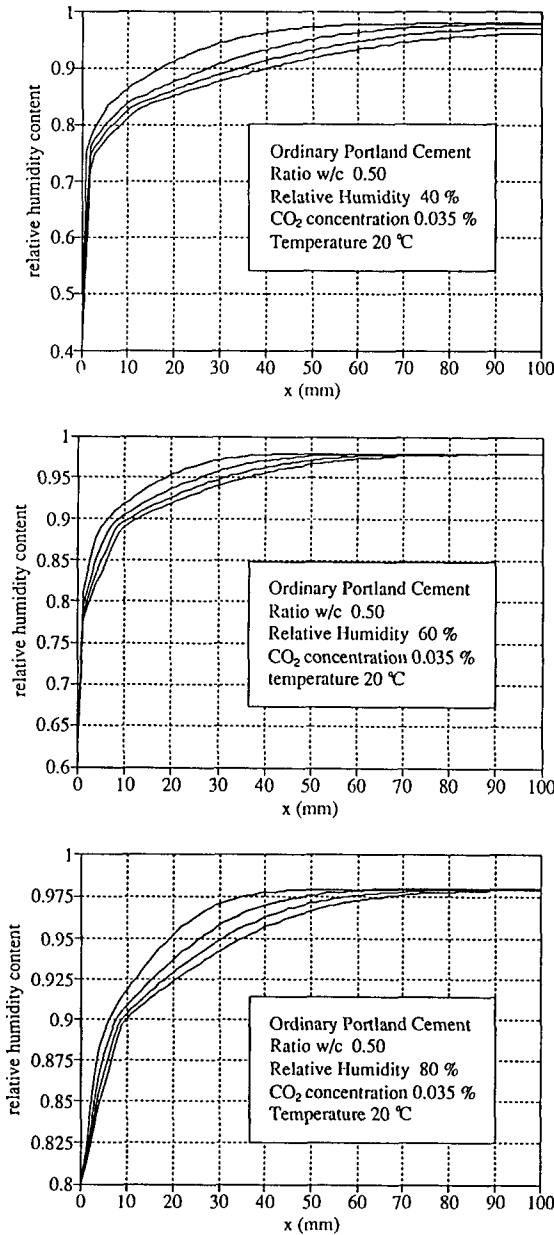


FIG. 3 c

Pore humidity content after 250, 500, 750, 1000 days as influenced by variable external RH.
Numerical Solution

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References

1. RILEM, *International symposium on carbonation of concrete*, Cem. Concr. Ass., (1976).
2. RILEM, Seminar on the durability of concrete structure under normal outdoor exposure, 26th - 29th March, Hannover (1984).
3. Bakker F. M., Initiation period, in *Corrosion of Steel in Concrete*, ed. by P. Schiessl.
4. Kobayashi K., Uno Y., *Cem. Concr. Res.*, 20, p. 619, (1990).
5. CEB - RILEM, *Workshop Report*, ed. S. Rostam, Copenhagen, (1983).
6. Brieger L., Wittmann F.H., Numerical simulation of carbonation of concrete, *Material and Science Restoration*, Tech. Akad. Ess., Ostfildern, (1986).
7. Houst Y.F., Roelfstra P.E. and Wittmann F.H., Proc. *International Colloquium on Material Science and Restoration*, Ed. Lack & Chemie, Filderstadt, p. 181, (1983).
8. Rio A., *Convegno A.I.T.E.C.*, Padova (1987).
9. Brieger L., Roelfstra P.E., Wittmann F.H., *Symp. Cem. and Concr.*, CONFID, (1985).
10. Colleparidi M., Pratesi R., Moriconi G., Branca C., Simoncini S., *Aicap '89*, Napoli (1989).
11. Jungerman B., *Betonwerk + Fertigtell-Technik*, p. 358, 6, (1982).
12. Weber H., *Betonwerk + Fertigtell-Technik*, p. 508, Heft, 8/1983, (1983).
13. Parrott L.J., *Carbonation in reinforced concrete: a bibliography*, Cem. Concr. Ass., (1987).
14. Parrott L. J., *A review of carbonation in reinforced concrete*, Cem. Concr. Ass., (1987).
15. Ho D. W. S., Lewis R. K., *Cem. Concr. Res.*, vol. 17, p. 489, (1987).
16. Fattuhi N.I., *Cem. Concr. Res.*, vol. 18, p. 426, (1988).
17. Butler W.B., *Cem. Concr. Res.*, vol. 17, p. 1000, (1987).
18. Houst Y., Wittmann F.H., *IABSE Symposium*, p.139, Lisbon 1989.
19. Houst Y., Wittmann F.H., *IABSE Symposium*, p.255, Lisbon 1989.
20. Houst Y., Wittmann F.H., The diffusion of carbon dioxide and oxygen in areated concrete, *Material and Science Restoration*, Tech. Akad. Ess., Ostfildern, (1986).
21. Bažant Z.P., Najjar L.J., *Cem. Concr. Res.*, 1, p. 461, (1971).
22. Bažant Z.P., Najjar L.J., *Mat. and Struct.*, 5, p. 3, (1972).
23. Bažant Z.P., Mathematical Modeling of Creep and Shrinkage of Concrete, in *Creep and Shrinkage in Concrete Structures*, eds. Z.P. Bažant, F.H. Wittmann, p. 163, (1982).
24. Bažant Z.P., Materials model for structural analysis, in *Mathematical Modeling of Creep and Shrinkage of Concrete*, ed. Z. P. Bažant , p. 122, (1988).
25. Bažant Z.P., *Materials and Structures* (RILEM, Paris), 3, n° 13, p. 3, (1970).
26. Bažant Z.P., Thonguthai W., *J. Engng. Mech. Div.*, ASCE, 104, p. 1059, (1978).
27. Schrefler B.A., Simoni L., Majorana C.E., *Mat. and Struct.*, 22, p. 323, (1989).
28. Bažant Z.P., *J. Engng. Mech. Div.*, ASCE, 105, p. 1137, (1979).
29. Bažant Z.P., *J. Engng. Mech. Div.*, ASCE, 105, p. 1154, (1979). Disc 1980, p. 1194.
30. Bažant Z.P., Chern J.C., Rosenberg A.M., *J. of Amer. Ceram. Soc.*, 71 (9), p. 776, 1988.
31. Johnson C., *Numerical solution of partial differential equations by the finite element method*, Cambridge University Press, (1987).
32. Hughes T.J.R., *The Finite element method*, Prentice-Hall International, (1987).
33. Saetta A., *Ph.D. Thesis*, University of Padova, February (1992).
34. Schrefler B.A., Turska E., *Comp. Meth. in App. Mech. and Engng.*, in press.
35. Saetta A.V., Schrefler B.A., Vitaliani R.V., *Studi e Ricerche*, 13, p. 421, (1992).