論文 Analytical Study on Synergistic Effects of Carbonation and Chloride Ion Attack on Concrete

Mohamed BOULFIZA[*1], Koji SAKAI[*2], Nemkumar BANTHIA[*3], Hidenori YOSHIDA[*1]

ABSTRACT: The need to design durable concrete structures in chemically aggressive environments has led to increasingly sophisticated experiments and theoretical models of deterioration phenomena. In these models it is essential to consider coupling and non-linearities of all the processes involved in the damage mechanism. In this study, a numerical procedure has been developed to solve the coupled differential equations governing the moisture, heat, carbon dioxide flows, and chloride ion's ingress in concrete taking into account the major chemical and physical aspects of the carbonation process. The influences of variable temperature as well as variable relative humidity are taken into account.

KEYWORDS: Carbonation, chloride ingress, moisture movement, heat transfer, concrete.

1. INTRODUCTION

Realistic modeling of the transport and chemical reactions of major solutes in concrete structures requires consideration of water flow, heat transport and prediction of the dynamic changes in solutes' concentrations with space and time together with the chemical processes affecting them. The transport of aggressive substances 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. 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.

The carbonation rate is essentially controlled physically by the carbon dioxide diffusion process and chemically by the availability of calcium hydroxide in concrete. Therefore an effective numerical model to simulate the whole phenomenon should consider the interaction between many processes, namely the CO_2 diffusion, the moisture and heat transfer, the mechanism of $CaCO_3$ formation and the availability of $Ca(OH)_2$ in pore solution due to its transport by water movement.

In this study the fundamental models describing the carbonation of concrete at variable temperature are presented with reference to internal and external influences. The governing partial differential equations are developed and solved numerically to calculate the depth of carbonation together with its influence on chloride penetration as a function of time.


[*1] Department of Safety Systems Construction Eng. Kagawa University, Dr., Member of JCI
[*2] Department of Safety Systems Construction Eng. Kagawa University, Prof., Member of JCI
[*3] Department of Civil Engineering, University of British Columbia, Prof.

2. 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 CO_2 with $Ca(OH)_2$ predominates, and the carbonation process can be simply described by the following chemical reaction:

$$Ca(OH)_2 + CO_2 \xrightarrow{H_2O} CaCO_3 + H_2O \tag{1}$$
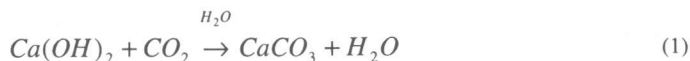
Actually this equation represents only the final result of several steps through which the true reaction occurs. Further simplification is to consider the reaction (1) irreversible and instantaneous, so that the calcium carbonate immediately precipitates once the two reactants coexist in solution. If 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 not occur because of the absence of necessary conditions. Actually the case of pores only partly filled with water is normally the condition of the surface concrete, and the carbonation can proceed only to the depth at which the concrete pores have partially dried out.

2.1 Rate of Carbonation [1]

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 [$Ca(OH)_2$]), 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 $Ca(OH)_2$ concentrations, its rate r can be written as

$$r = \frac{\partial[CaCo_3]}{\partial t} = \alpha_1 \, f_1(s) \, f_2(g) \, f_3(c) \, f_4(T) \tag{2}$$

In this equation, α_1 accounts for the fact that the carbonation reaction is taking place in an open system (substances can move with water), $f_1(s)$ describes the influence of moisture on carbonation and is given by

$$f_1(s) = \begin{cases} 0 & 0 \le s \le 0.5 \\ 5/2 \ (s - 0.5) & 0.5 \le s \le 0.9 \\ 1 & 0.9 \le s \le 1 \end{cases} \tag{3}$$

where s is saturation. Equation 3 assumes that carbonation can occur only in the presence of water, and that below 0.5 saturation, the reaction rate is essentially zero. This corresponds to the case of dry concrete under natural environmental conditions.

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:

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

The influence of the degree of carbonation c is accounted for through $f_3(c)$ which varies between 0 and 1 according to the following relationship

$$f_3(c) = 1 - \frac{c}{c_{max}} \tag{5}$$

in which c_{max} is the maximum amount of calcium carbonate. The fourth function $f_4(T)$ represents the Arrhenius equation for thermally activated processes, and is given by

$$f_4(T) = A \cdot e^{-E_0/RT} \tag{6}$$

where E_0 is the activation energy of the carbonation reaction, R is the gas constant and T is the absolute temperature.

3. MOISTURE MOVEMENT AND HEAT TRANSFER

Water movement in concrete is governed by the following partial differential equation in the case of a saturated or unsaturated flow

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i}\left[K\left(K_{ij}^A \frac{\partial h}{\partial x_j} + K_{iy}^A \right) \right] \tag{7}$$

where θ is the volumetric water content, h the pressure head, x_i $(i=1,2)$ are the spatial coordinates, t is time, K_{ij}^A are components of a dimensionless anisotropy tensor K^A, and K is the hydraulic conductivity (permeability).

Neglecting the effect of water vapor diffusion on transport, the transport of heat can be described by the following equation

$$C(\theta)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x_i}\left[\lambda_{ij}(\theta)\frac{\partial T}{\partial x_j} \right] - C_w q_i \frac{\partial T}{\partial x_i} \tag{8}$$

where T is the temperature, $\lambda_{ij}(\theta)$ is the coefficient of the apparent thermal conductivity of the material, $C(\theta)$ and C_w are the volumetric heat capacities of the concrete and the liquid phase, respectively. Volumetric heat capacity is defined as the product of the bulk density and gravimetric heat capacity. The first term on the right hand side of Eq. (8) represents the heat flow due to conduction and the second term the heat transported by the flowing water. The volumetric heat capacity can be expressed as

$$C(\theta) = C_n \theta_n + C_g \theta_g + C_w \theta \tag{9}$$

where θ is the volumetric fraction and subscripts n, g, w represent the solid, gas and liquid phases respectively.

4. CHLORIDES PENETRATION

The partial differential equation governing advective-diffusive chemical transport under transient water flow conditions in a partially saturated concrete is taken as

$$\frac{\partial(\theta c)}{\partial t} + \rho \frac{\partial \bar{c}}{\partial t} = \frac{\partial}{\partial x_i}\left[\theta D_{ij} \frac{\partial c}{\partial x_j} - q_i c \right] \tag{10}$$

where θ is the water content, c is the total concentration of free chlorides, $\bar{c}$ is the total concentration of bound chlorides, ρ is the bulk density of the medium, D_{ij} is the apparent diffusion coefficient tensor, and q_i is the volumetric flux. Partitioning between bound chlorides and free chlorides is governed by the chemical approach of ion exchange selectivity. The second term on the left side of Equation (10) is zero for components that do not undergo ion exchange.

5. CO₂ TRANSPORT

Gas transport in unsaturated concrete is a complex physical process that includes three general transport mechanisms: Knudsen diffusion, multicomponent molecular diffusion, and viscous flow. The equations that describe these transport mechanisms in a multicomponent gas mixture are fully coupled and generally highly nonlinear. In the models that have been proposed in previous studies, it has been considered that CO_2 transport occurs mainly by diffusion through the gaseous phase, or in more sophisticated models [2] both the gaseous and liquid phase have been taken into account while ignoring the transport by convection. We consider in this paper all phenomena of CO_2 transport by convection in water and diffusion in both water and the gas phase. Thus, CO_2 transport is governed by the following mass balance equation:

$$\frac{\partial C_T}{\partial t} = -\frac{\partial}{\partial x_i}\left(J_{dai} + J_{dwi} + J_{cwi} \right) + P \tag{11}$$

where J_{dai} describes the CO_2 flux caused by diffusion in the gas phase, J_{dwi} is the CO_2 flux caused by diffusion in water, and J_{cwi} the CO_2 flux caused by convection in water. The term C_T is the total volumetric concentration of CO_2, P is the CO_2 source/sink term. The individual terms can be defined as

$$J_{dai} = -\theta_a D_{ij}^a \frac{\partial C_a}{\partial x_j} \qquad J_{dwi} = -\theta_a D_{ij}^w \frac{\partial C_w}{\partial x_j} \qquad J_{cwi} = q_i C_w \tag{12}$$

where C_w and C_a are the volumetric concentrations of CO_2 in water and gas phase, respectively, D_{ij}^a is the effective diffusion coefficient tensor of CO_2 in the gas phase, D_{ij}^w is the effective diffusion coefficient tensor of CO_2 in the dissolved phase, q_i the pore water flux, and θ_a is the volumetric air content. The total CO_2 concentration, C_T, is defined as the sum of CO_2 in the gas and dissolved phases

$$C_T = C_a \theta_a + C_w \theta \tag{13}$$

The volumetric concentrations of CO_2 in the dissolved and gas phases are related by the following equation

$$C_w = K_c C_a \tag{14}$$

where K_c is the distribution constant which is strongly dependent on temperature. The term P, which accounts for the loss of carbon dioxide by chemical reaction, is given by

$$P = -\alpha_4 \frac{\partial[CO_2]}{\partial t} \tag{15}$$

with α_4 being a non-dimensional parameter that varies between 0 and 1, according to the concrete characteristics [1].

6. SYNERGETIC EFFECT OF CARBONATION AND CHLORIDE IONS INGRESS

The effect of carbonation on chloride ions' ingress is mainly related to the liberation of bound chlorides, leading to a higher penetration rate. The change of structure due to carbonation will first reduce the binding capacity of the solid phase in concrete leading to a higher amount of free chlorides in the pore solution. The total amount of free chlorides will then be migrated into the concrete by the chloride transport mechanisms of diffusion and advection. Bound chlorides are computed according to the solubility equilibrium of the Friedel's salt. In case of a drop in alkalinity due to carbonation, a certain amount of Friedel's salt is converted into free chloride ions according to the chemical approach of ion exchange selectivity. The total amount of chloride ions is the sum of bound chlorides and dissolved chloride ions. This approach has the advantage of addressing the issues of chloride binding under variable temperature and pH.

7. NUMERICAL SIMULATIONS

Due to the complexity resulting from the nonlinearities and the coupling of the differential equations presented earlier, it is practically impossible to obtain analytical solutions. Consequently, the finite element method has been adopted as the numerical tool for solving these equations. The material parameters introduced in the differential equations have been taken from the literature and/or calibrated with available test data [1,2]. The versatility of the proposed model is illustrated through the simulation of carbonation and chloride ions' ingress in concrete exposed to various environmental conditions, as can be seen in Figures 1, 2, 3 and 4. Figure 2 shows that $CaCO_3$ formation (normalized with respect to maximum $CaCO_3$ content corresponding to the maximum CO_2 concentration considered) is initially higher for the case of 60% RH, up to 500 days of exposure, and that this trend is no reversed at 1000 days. This behavior, that might seem strange at first sight, can be explained by noticing that CO_2 penetration is always faster at 40% RH, and due to a low RH, the conditions for carbonation are more favorable with 60% RH initially. However, as CO_2 penetrates deeper, more moisture becomes available and the trend is reversed at a certain time.

The synergy between carbonation and chloride ions' ingress is depicted by Figure 5, where a concrete specimen is subjected to an atmosphere of 60% RH and temperature of 20 °C, containing 0.035 % of CO_2 together with a chloride concentration of 6.5 kg/m^3. It can be seen that the liberated chloride ions have pushed the peak of total chloride concentration inwards. The results have not been compared with experimental data due to a lack of quantitative data. However, the results seem to be reasonable qualitatively.
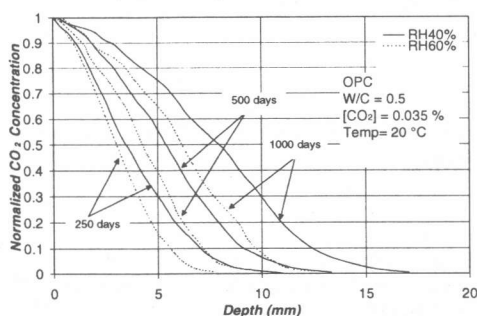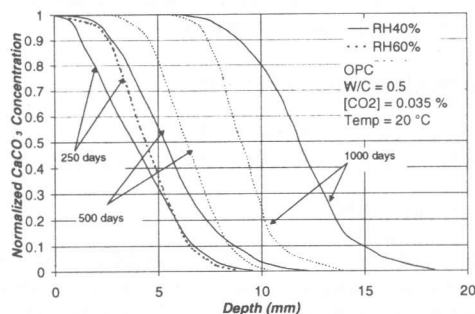

Figure 1. Effect of RH on CO2 diffusion
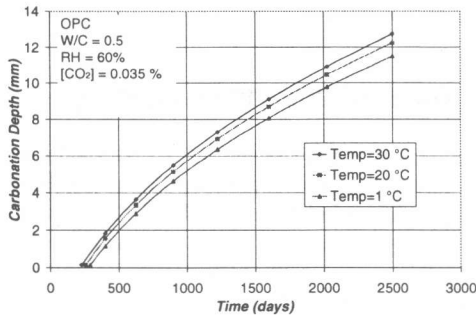
Figure 2. Effect of RH on CaCO3 formation
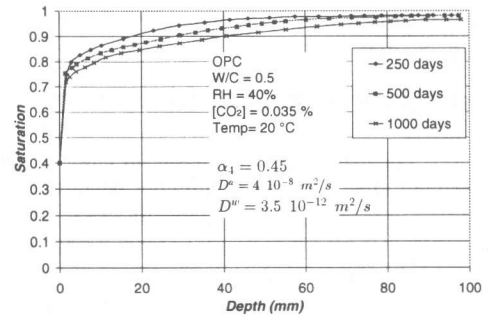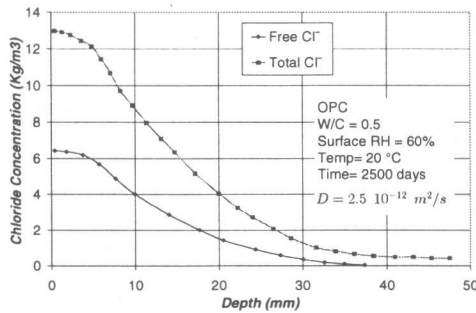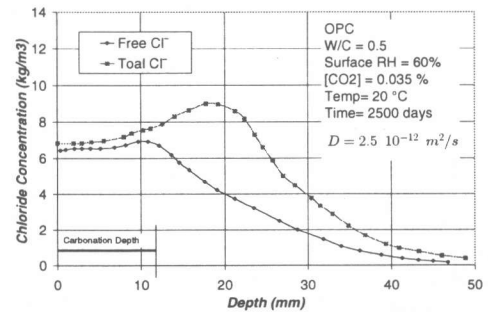
Figure 3. Effect of temperature on carbonation depth

Figure 4. Effect of surface RH on moisture distribution inside concrete

a) *without carbonation*

b) *with carbonation*

Figure 5. Chlorides penetration

8. CONCLUDING REMARKS

The following conclusions can be drawn:

1. An original approach has been proposed for predicting the synergetic effects between carbonation and chloride ions' ingress under variable temperature and pH.
2. The effects of atmospheric RH and temperature on CO_2 penetration, carbonation, and moisture distribution of concrete have been numerically assessed.
3. It has been shown that carbonation has a strong synergetic effect on chloride ions' ingress by liberating bound chlorides.

ACKNOWLEDGEMENTS

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