

Enhanced mass balance Tafel slope model for computer based FEM computation of corrosion rate of steel reinforced concrete coupled with CO₂ transport

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Abstract. This research paper aims at computer based modeling of carbonation induced corrosion under extreme conditions and its experimental verification by incorporating enhanced electrochemical and mass balance equations based on thermo-hygro physics with strong coupling of mass transport and equilibrium in micro-pore structure of carbonated concrete for which the previous research data is limited. In this paper the carbonation induced electrochemical corrosion model is developed and coupled with carbon dioxide transport computational model by the use of a concrete durability computer based model DuCOM developed by our research group at concrete laboratory in the University of Tokyo and its reliability is checked in the light of experiment results of carbonation induced corrosion mass loss obtained in this research. The comparison of model analysis and experiment results shows a fair agreement. The carbonation induced corrosion model computation reasonably predicts the quantitative behavior of corrosion rate for normal air dry relative humidity conditions. The computational model developed also shows fair qualitative corrosion rate simulation and analysis for various *pH* levels and coupled environmental actions of chloride and carbonation. Detailed verification of the model for the quantitative carbonation induced corrosion rate computation under varying relative conditions, different *pH* levels and combined effects of carbonation and chloride attack remain as scope for future research.

Keywords: carbonation; corrosion rate; reinforced concrete; mass transport; computational modeling; computer applications in concrete.

1. Introduction

Carbonation induced corrosion of reinforced concrete is typically defined as the chemical reaction between atmospheric carbon dioxide, of which normal indoor concentration is approximately 370 ppmv and outdoor of 700 ppmv, and the product of hydration, mainly calcium hydroxide reducing the *pH* of concrete and destroying the passive layer on steel rebars which gives start to corrosion. In the past, several researchers have investigated the phenomenon of carbonation and its effect on corrosion of reinforced concrete structures. Several studies have evaluated the carbonation process and associated corrosion rates using physical modeling approach at micro level (P.F Marques and costa 2009, Seung and Won 2009, David *et al.* 2009, Anna *et al.* 2005, Alexander *et al.* 2002, Saetta *et al.* 1995, Saetta *et al.* 1993, Sakei *et al.* 1991, Papadakis *et al.* 1991). In these studies, diffusion processes in concrete (moisture, carbon dioxide, and so on), carbonation induced corrosion

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modeling, and a linear or a non-linear diffusion equation is solved in the analysis. Pakawat (2004) showed that carbonation causes conversion of fixed chloride to free chloride and proposed an empirical model for this phenomenon. Law and Cairns (2003) investigated that carbonation induced corrosion is much less in magnitude than chloride induced corrosion. There are several more researchers who studied modeling of carbonation process and associated corrosion in concrete (Luca *et al.* 2009, Aperador *et al.* 2009, Valcarce and Yazquez 2009, Marlova *et al.* 2009, Farina and Duffo 2007, Kubo *et al.* 2007, Hamada 1999, Claisse *et al.* 1999, Matsumoto *et al.* 1998, Uomoto and Takada 1993, Tanano and Masuda 1991) etc. In this research mass balance electrochemical numerical modeling based on thermo-hygro physics with strong coupling of mass transport and equilibrium in micro-pore structure of carbonated concrete for which the previous data is limited has been carried out in order to scientifically clarify various aspects of carbonation induced corrosion in reinforced concrete.

2. Computational modeling

2.1 Mass balance law

Initially, the model has been adopted from the previous research (Ishida and Maekawa 2000). In general, when dealing with mass, energy and momentum flows in a control volume, the starting point is to build appropriate balance equations. In other words, the summation of rate of mass efflux from a control volume, the rate of mass flow into the control volume, and the rate of accumulation of mass within the control volume should be zero. In this section, the mass balance conditions for

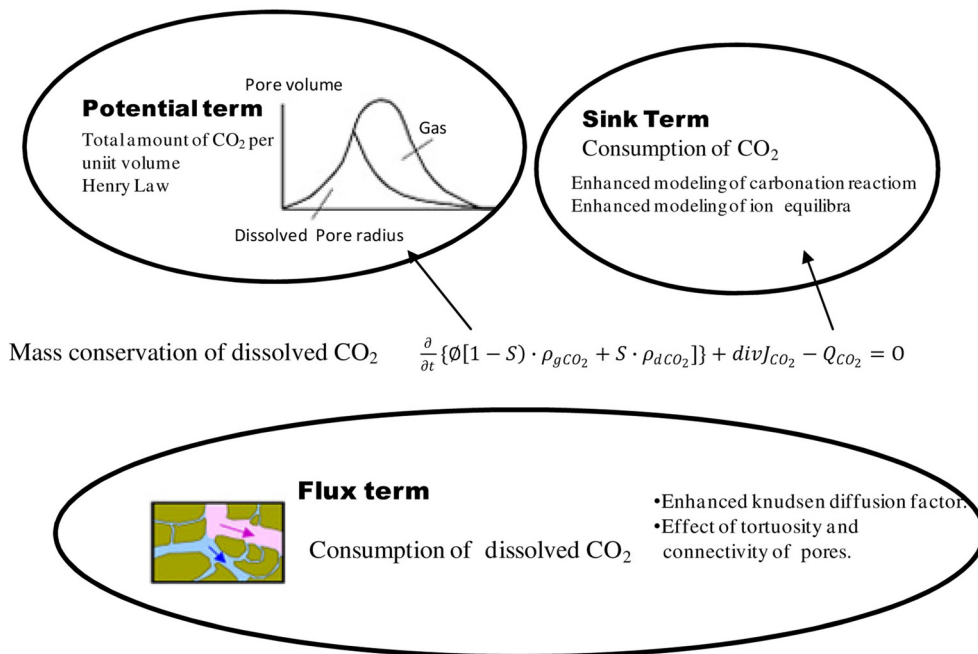


Fig. 1 Governing computational equation and constituting models

carbon dioxide in a porous medium are formulated. Two phases of carbon dioxide existing in concrete are considered; gaseous carbon dioxide and carbon dioxide dissolved in pore water. By solving the mass balance equation under given initial and boundary conditions, the non-steady state conduction of carbon dioxide is quantified. The mass balance equation for a porous medium can be expressed as Eq. (1).

$$\frac{\partial}{\partial t} \{ \phi[(1-S) \cdot \tilde{n}_{gCO_2} + S \cdot \tilde{n}_{dCO_2}] \} + \text{div} J_{CO_2} - Q_{CO_2} = 0 \quad (1)$$

Where, ϕ is porosity of the porous media, S is degree of saturation of the porous media (there are no units for porosity and saturation as they are ratios varying from 0-100%), $\tilde{n}_d$ is density of dissolved CO_2 in pore water (kg/m^3), $\tilde{n}_{gCO_2}$ is density of gaseous CO_2 (kg/m^3), J_{CO_2} is total flux of dissolved and gaseous CO_2 (kg/m^2s), and a sink term Q_{CO_2} , which represents the rate of CO_2 consumption due to corrosion (kg/m^3s). The above equation gives the concentrations of gaseous and dissolved carbon dioxide with time and space. The Fig. 1 below elaborates the flow of above governing equation.

2.2 Equilibrium conditions for gaseous and dissolved carbon dioxide

The local equilibrium between gaseous and dissolved carbon dioxide is represented here by Henry's law (Welty 1969), which states the relationship between gas solubility in pore water and the partial gas pressure. In this research, it is assumed that the system will instantaneously reach local equilibrium between the two phases as Eq. (2).

$$P_{CO_2} = H_{CO_2} \cdot \rho_d \quad (2)$$

Where P_{CO_2} : equilibrium partial pressure of carbon dioxide in the gas phase, ρ_d : mole fraction of gaseous CO_2 [mol of CO_2 /total mol of solution], and H_{CO_2} : Henry's constant for carbon dioxide ($= 4.06 \times 10^9$ [Pa/mol fraction] at 25 degrees Celsius). For one cubic meter of dilute solution, the moles of water in the solution n_{H_2O} will be approximately 5.56×10^4 [mol/ m^3]; accordingly the concentration of dissolved carbon dioxide per cubic meter of solution ρ_d [kg/m^3] can be expressed as Eq. (3).

$$\rho_d = P_{CO_2} / H_{CO_2} \cdot n_{H_2O} \cdot M_{CO_2} = P_{CO_2} / H_{CO_2} \quad (3)$$

Where, M_{CO_2} is the molecular mass of carbon dioxide ($= 0.044$ [kg/mol]). The complete perfect-gas equation is then

$$P_{CO_2} = \rho_g \frac{RT}{M_{CO_2}} \quad (4)$$

Where, ρ_g : concentration of gaseous carbon dioxide [kg/m^3], R : gas constant [J/mol.K], and T : temperature [K]. From above Eqs. the equilibrium relationship between gas and dissolved CO_2 can be expressed as

$$\rho_g = \frac{M_{CO_2}}{RT} \cdot H_{CO_2} \cdot \rho_d = K_{CO_2} \cdot \rho_d \quad (5)$$

After dissolving into solution, carbon dioxide reacts with calcium ions, and so the concentration of dissolved CO_2 can fluctuate from the above equilibrium condition. Strictly speaking, therefore,

the equilibrium condition cannot be formulated by Henry's law alone; it is also necessary to determine the amount of dissolved CO₂ based on the rate of chemical reactions, which represents kinetic fluctuations dependent on the distribution of CO₂ concentration. However, it seems difficult to take into account such kinetic fluctuations as it is, and in fact, it is expected that the rate of CO₂ gas dissolution will be faster when the partial pressure of CO₂ gas becomes large. For these reasons, in the model it is assumed that the amount of dissolved CO₂ can be approximately described by Henry's law (Sakei *et al.* 1991, Papadakis *et al.* 1991).

2.3 Carbon dioxide transport

Transport of CO₂ is considered for both dissolved and gaseous oxygen phases. The CO₂ gas can move through unsaturated pores, whereas dissolved CO₂ is transported within pore liquid water. In the model, it is assumed that all pores have a cylindrical shape. In the model, molecular diffusion and Knudsen diffusion are considered, whereas the contribution of surface diffusion is ignored, since surface diffusion takes places when molecules which have been adsorbed are transported along the pore wall, and normally it plays a minor role in diffusion within concrete materials under typical environmental conditions (Maekawa *et al.* 1999, Kunii 1980, Kobayashi 1986). The conditions transiting to Knudsen diffusion are expressed by the following equation using Knudsen number N_k as

$$N_k = \frac{l_m}{2r_e} > 1.0 \quad (6)$$

Where, l_m : the mean free path length of a molecule of gas, and r_e : the actual pore radius, which means the radius of a pore minus the thickness of the adsorbed layer of water obtained by B.E.T. theory (Maekawa *et al.* 1999). Considering molecular diffusion and Knudsen diffusion, the one dimensional gaseous flux through a single pore of radius r can be expressed as

$$J_g^r = -\frac{D_o^g}{1 + \left(\frac{l_m}{2r_e}\right)} > \frac{\partial \rho_g}{\partial x} \quad (7)$$

Where, D_o^g [m²/s] is the diffusivity of CO₂ in a free atmosphere ($=1.34 \times 10^{-5}$) (Welty 1969). Similarly, the flux of dissolved oxygen can be obtained as

$$J_d^r = -D_0^d \frac{\partial \tilde{n}_d}{\partial x} \quad (8)$$

Where, D_0^d [m²/s] is the diffusivity of dissolved CO₂ in pore water ($=1.0 \times 10^{-9}$) (Welty 1969).

The total flux within porous bodies can be obtained by integrating above Eqs. over the entire porosity distribution. By integrating the gaseous and dissolved fluxes of CO₂, respectively, the entire flux of carbon dioxide is formulated as

$$J_{CO_2} = -\left(\frac{\phi D_0^d}{\Omega} \int_0^{r_c} dV \frac{\partial \rho_d}{\partial x} + \frac{\phi D_0^g}{\Omega} \int_{r_c}^{\infty} \frac{dV}{1 + N_k} \frac{\partial \rho_g}{\partial x} \right) \quad (9)$$

Where, V is the pore volume, and $\Omega = (\pi/2)^2$ accounts for the average tortuosity of a single pore as a fictitious pipe for mass transfer. The latter parameter considers the tortuosity of a hardened cement paste matrix, which is uniformly and randomly connected in a 3-D system (Maekawa *et al.* 1999).

The first term of the right-hand side in the above equation denotes the diffusive component of dissolved carbon dioxide in the pore liquid, whereas the second term represents the component of gaseous diffusion. The substitution of porosity saturation S for the integrals in the above equation in order to generalize the expression for an arbitrary moisture history gives

$$J_{CO_2} = -(D_{gO_2} \nabla P_d + D_{gO_2} \nabla P_g) = -(D_g K_{CO_2} + D_{gCO_2}) \nabla P_d$$

$$D_{gCO_2} = \frac{\phi D_0^g}{\Omega} \frac{(1-S)}{1 + l_m / (2r_m - r_t)}, \quad D_{gCO_2} = \frac{\phi S D_0^d}{\Omega} \quad (10)$$

Where, D_{gCO_2} : diffusion coefficient of gaseous CO_2 in a porous medium [m^2/s], and D_{dCO_2} : diffusion coefficient of dissolved CO_2 in a porous medium [m^2/s]. In the above equation, the integral of the Knudsen number is simplified so that it can be easily put into practical computational use; r_m is the average radius of unsaturated pores, and t_m is the thickness of the adsorbed water layer in the pore whose radius is r_m .

It has to be noted that the above formulations do not include the complete effects of the connectivity of pores on diffusivity. That is to say, considering one-dimensional transport of gaseous phases, all unsaturated pores, which are route for gas movement, are assumed to be connected with perfect continuity (Fig. 2, left). In actual pore structures that have complicated connectivity, however, the movement of gas will be blocked by saturated pores containing liquid water (Fig. 2, right). Here, as the saturation of pores decreases, the open pore space gains higher connectivity so that total diffusivity increases nonlinearly. One potential model for this phenomenon would be based on percolation theory (Cusack 1987); however, we adopt the following model for the sake of simplicity.

Consider a finite field that consists of segments small enough to have continuity of pores, as shown in Fig. 2, right. In the cross section of each unit, the ratio of gas transportation paths will be $(1-S)$. Assuming that the probability of unsaturated pores being connected to each other would be proportional to the ratio of the volume in a cross section, the overall flux can be expressed as in Eq. (11),

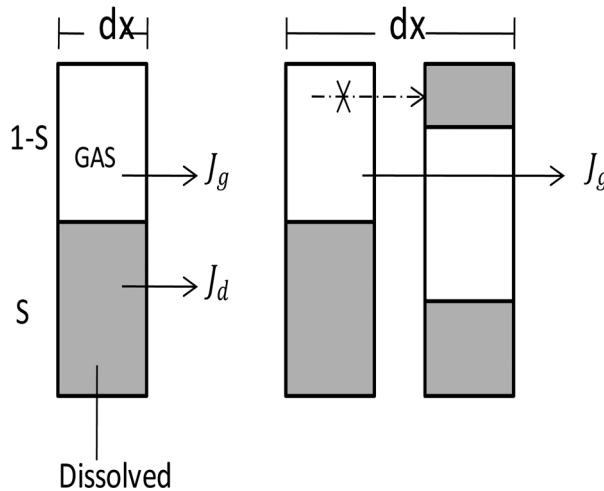


Fig. 2 Effect of connectivity of pores on CO_2 transport model

$$D_{gCO_2} = \frac{\phi D_0^g}{\Omega} \frac{(1-S)}{1+l_m/2(r_m-r_i)}, D_{gCO_2} = \frac{\phi S^n D_0^d}{\Omega} \quad (11)$$

where, n is a parameter representing the connectivity of the pore structure, and might vary with the geometrical characteristics of the pores. However, at this stage, it is difficult to take account of the exact connectivity situation. In this study, through sensitivity analysis, n is tentatively assumed to be 6.0, which is the most appropriate value for expressing the reduction of CO_2 diffusivity with the decrease of relative humidity (Papadakis *et al.* 1991).

2.4 Enhanced electrochemical model for simulation of carbonation induced corrosion rate

Initially, the model has been adopted from the previous research (Hussain and Ishida 2007). In this paper the model has been enhanced and coupled with the CO_2 transport model to calculate the carbonation induced corrosion rate and corrosion potential by taking into account the variation in pH value of concrete caused by carbonation reaction and transport as discussed in the previous sections. Nernst equation (Nernst 1889) describes the potential of electrochemical cell as a function of concentrations of ions taking part in the reaction. The enhancement proceeds in the following six steps.

2.4.1 pH

The pH of a solution is a measure of the molar concentration of hydrogen ions in the solution and as such is a measure of the acidity or basicity of the solution.

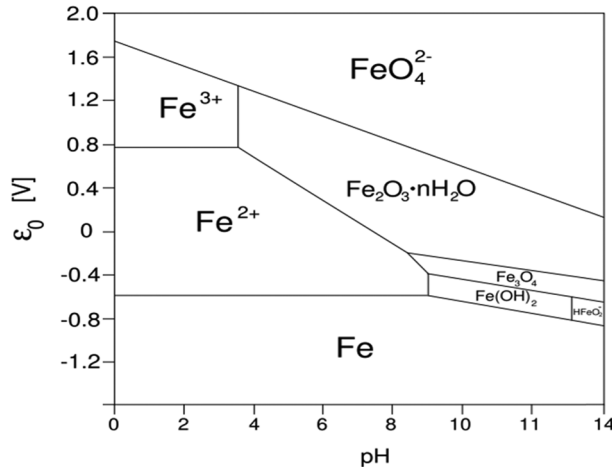
$$pH = -\log_{10}[H^+] \quad (12)$$

2.4.2 Corrosion potential model

The measurement of the pH of a sample can be done by obtaining the cell potential of that sample in reference to a standard hydrogen electrode, as in the accepted procedure for measuring standard electrode potentials. This procedure would give a value of zero for a 1 Molar solution of H^+ ions, so that defines the zero of the pH scale. The cell potential for any other value of H^+ concentration can be obtained with the use of the Nernst equation. For a solution at $25^\circ C$ this gives

$$E_{cell} = -0.0592 \log_{10}[H^+] \quad (13)$$

For this expression, a base change from the natural log to the base 10 logarithm was made in the Nernst equation. For constant temperature expression ' RT/F ' has a constant value. In most cases, the activity of hydrogen ions in solution can be approximated by the Molar concentration of hydrogen ions ($[H^+]$) in a solution. To simplify calculations it is often combined with conversion factor between natural logarithm (denoted here by $\ln$) and decimal logarithm (denoted here by $\log$) to form value of '0.0591' (for $25^\circ C$). Here in this model the value has been rounded off to '0.06' for simplicity. To be precise one should not use concentrations, but thermodynamic activities of the ions present in the solution. When applied to the full cell formed from half cells present on inside and outside of the corrosion cell (Haber and Klemensiewicz 1908, Wang and Copeland 1973), Nernst equation takes form as shown in Eq. (14). It is a known fact that any cell potential is a function of concentration of species. Therefore when the concentration of hydrogen ion varies which is actually the variation of pH , the cell potential also varies accordingly as shown by Eq. (14) below.

Fig. 3 Pourbaix diagram relation between pH and potential state

$$E_{02} = E_{02}^{\ominus} + (RT/(z_{02}F)) \ln(P_{02}/P^{\ominus}) - 0.06pH \quad (14)$$

Where, pH : power of hydrogen ion concentration (12.3 for non-carbonated concrete in the model), E_{02} : standard cell potential of O_2 , cath. (V, SHE), $E_{02}^{\ominus}$: standard cell potential of O_2 at 25°C (= 0.40V), z_{02} : the number of charge of O_2 (=2), $P^{\ominus}$: atmospheric pressure, T : surrounding temperature in Kelvin scale.

2.4.3 Pourbaix diagram

In general, the relation between potential and pH value is given by Pourbaix diagram (Marcel Pourbaix 1963). Based on thermodynamic conditions, the state of passivity is evaluated by the Pourbaix diagram, where steel corrodes, areas where protective oxides form, an area of immunity to corrosion depending on pH and the potential of steel reinforcement (Fig. 3). Usually, the Pourbaix diagrams can be used for different types of functions. One is the predominance area diagram, in which the dominant aqueous species will be given as a function of pH and E , where pH means $-\log a(H^+)$ and E is the corresponding variable for electrical potential. Resulting area of each aqueous species can be expressed in terms of convex polygons.

2.4.4 Thermodynamics

In the enhanced carbonation induced corrosion model, through the use of thermodynamic theory (the Nernst equation, Nernst 1889), so-called Pourbaix diagrams are constructed. These diagrams show the thermodynamic stability of species as a function of potential and pH . Although many basic assumptions must be considered in their derivation, such diagrams can provide valuable information in the modeling of carbonation induced corrosion phenomena.

2.4.5 Corrosion rate model

As shown in Fig. 4(a) decreasing trend of pH shifts the cathodic line diagonally towards the upward-rightward position. Thus, moving the point of intersection between cathode and anode lines towards the more corrosion current side. This answers the electro-chemical reason for the increase in corrosion rate due to decrease in pH caused by carbonation of concrete surrounding the steel rebar.

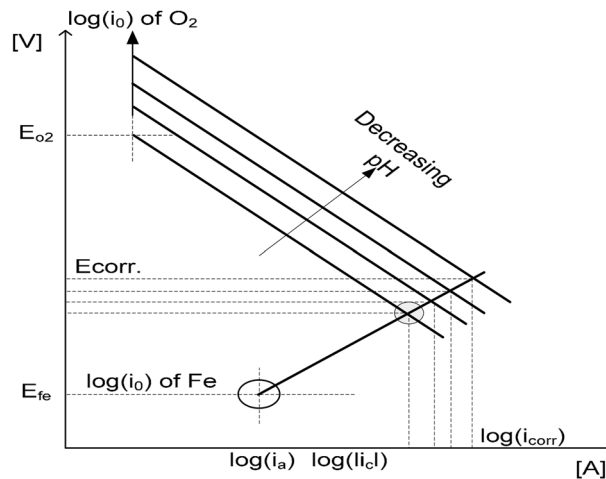


Fig. 4 Modeling of carbonation induced corrosion (relation between pH and oxidation cell potential)

2.4.6 Limitations of enhanced carbonation induced corrosion model

Limited information on corrosion kinetics is provided by this enhanced model. The model is derived for specific temperature and pressure conditions. The model works for selected concentrations of ionic species. The model considers pure substances only and additional computations must be made if other species are involved. In areas where the model shows oxides to be thermodynamically stable, these oxides are not necessarily of a protective (passivating) nature.

2.5 FEM mass balance computer based model of concrete (DuCOM)

All the formulations developed above are implemented into the finite-element computational program DuCOM. The overall computational scheme is shown in Fig. 5. The constituent material models are based on microphysical phenomena such as hydration, moisture transport, and the formation of pore-structure, and they take into account the inter-relationships between these in a natural way. A detailed discussion on DuCOM regarding the material models and system dynamics for describing their interactions can be found in published papers (Maekawa *et al.* 1999, Maekawa *et al.* 2003).

3. Computational simulation

3.1 Data for numerical analysis

Standard values were used as basic input data in numerical model analysis. The basic concrete composition assumed for numerical analysis input consists of 370 kg/m³ of OPC as per JIS R5210 specifications with W/C = 0.45. The chloride content in the analysis was varied from 0%-8% free chloride by mass of binder. The aggregates were assumed to be natural river sand passed through JIS A1102 sieve No. 4 (4.75-mm openings) used as fine aggregate and crushed limestone with a maximum size of 20 mm was taken as coarse aggregate for all concrete mixes as input data in model analysis.

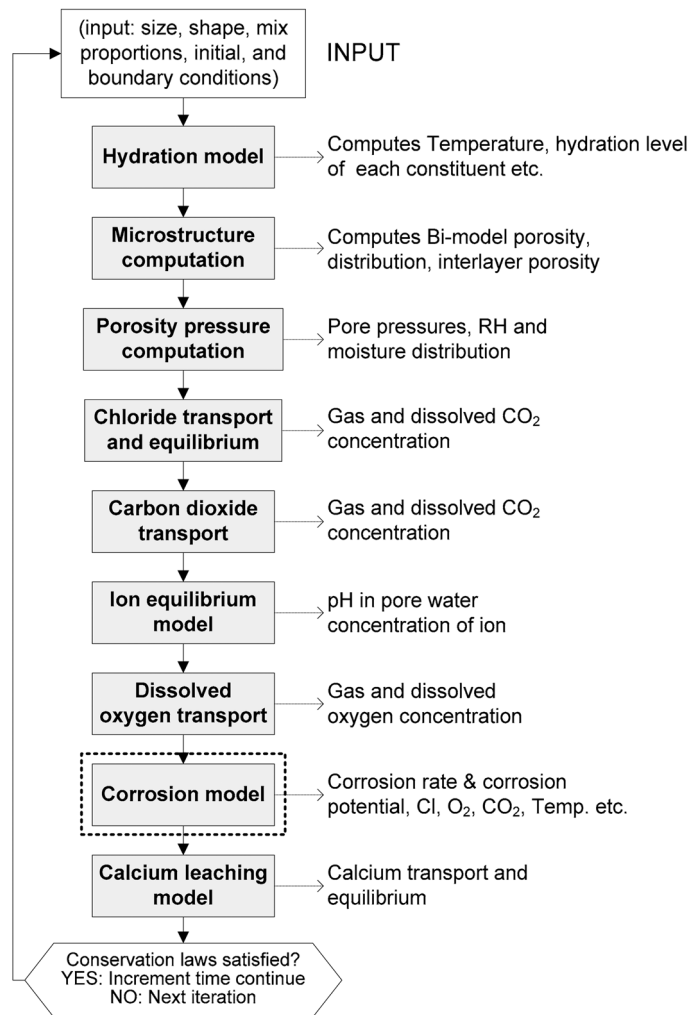


Fig. 5 Computational framework of DuCOM (Durability Concrete Model)

3.2 Modelling of environmental exposure conditions

The most severe environmental conditions for maximum carbonation rate were modelled consisting of accelerated 10% carbon dioxide concentration in the environment, 30°C temperature and 55% Relative humidity (R.H).

3.3 Simulation results

The model was analyzed using the above mentioned data and simulation results were obtained for various pH values ranging from 14-7.0 as shown in Fig. 6. It can be seen that the model reasonably predicts the behaviour of carbonation induced corrosion qualitatively. The corrosion rate of un-carbonated concrete (assumed at pH 12.3) is lowest and the corrosion rate increases gradually with the fall in pH reaching the maximum corrosion rate at pH 7.0 where the pore

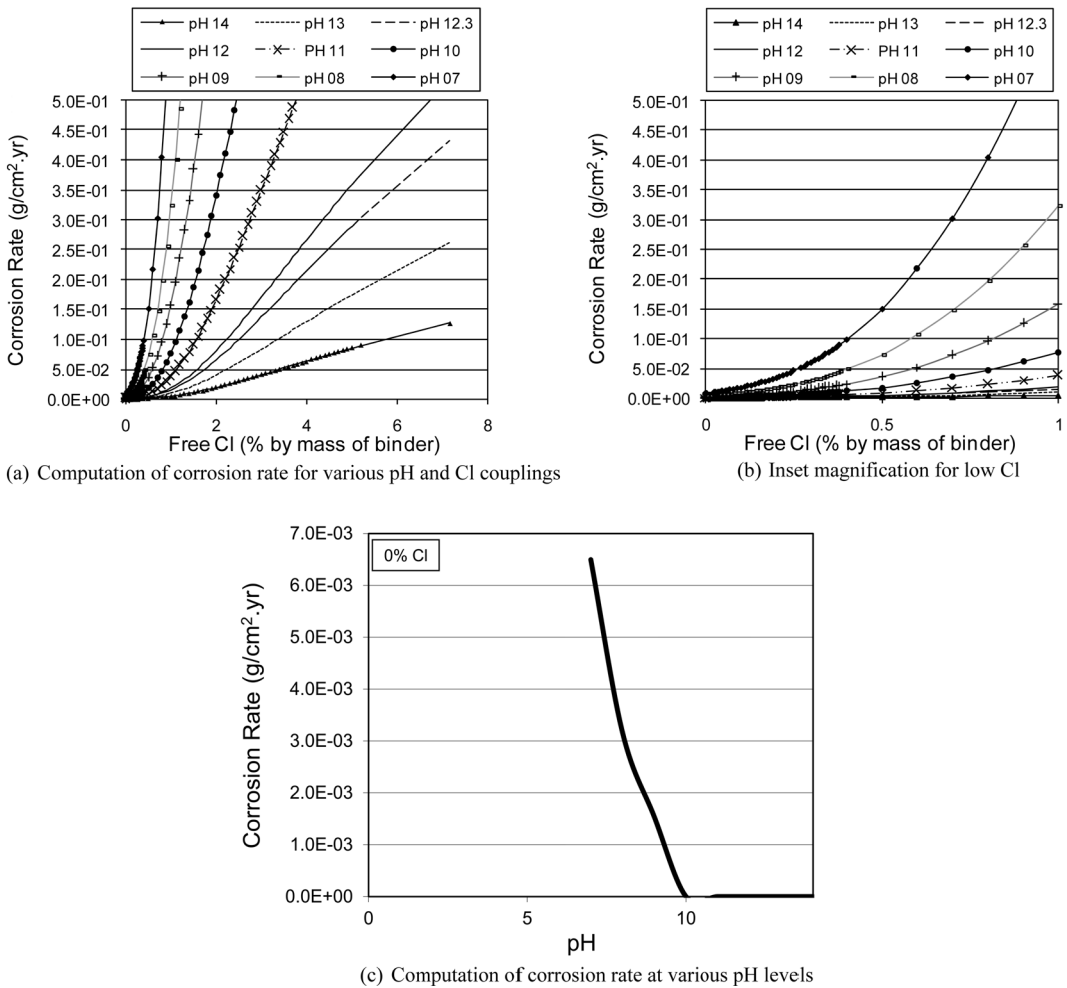


Fig. 6 (a)-(c) Analytical results of carbonation induced corrosion model

solution becomes acidic and highly susceptible to corrosion in nature. In general, the pH value of carbonated concrete is less than 9. Therefore, it can be said that the corrosion rates represented by the curves of pH 9.0 or less are under coupled attack of chloride and carbonation corrosion.

3.4 Need for experimental verification

One more aspect which can be seen from these simulations is that under the coupled effect of chloride and carbonation, the corrosion rate is very high. But, when the chloride concentration is zero or very low, the carbonation induced corrosion rate is very low. In order to check in reality if this fact is true that the corrosion rate due to carbonation only is low and to verify the enhanced model simulation, following experiments were conducted.

4. Experimentation

4.1 Aims

The aims of this experimentation are:

- Verification of enhanced carbonation induced corrosion model.
- Determination of extent of maximum corrosion rate in fully carbonated reinforced concrete.

4.2 Mix proportions

Trial concrete mixing was firstly conducted as per JCI (Japan Concrete Institute) mix design to achieve 50-80 mm of slump value and $3.5 \pm 1\%$ of air content. The concrete composition was kept identical to the data used in numerical simulation so that the experiment results can be compared with the model simulation (Table 1). It must be mentioned over here that no admixtures of any type were used in the concrete mix design to attain the original behaviour of pure concrete and to avoid the influence of any factor not taken into consideration during numerical modeling computations.

Table 1 Mix proportions

Specimens	W/C	OPC (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate (kg/m ³)
1,2	0.45	371	756	1031

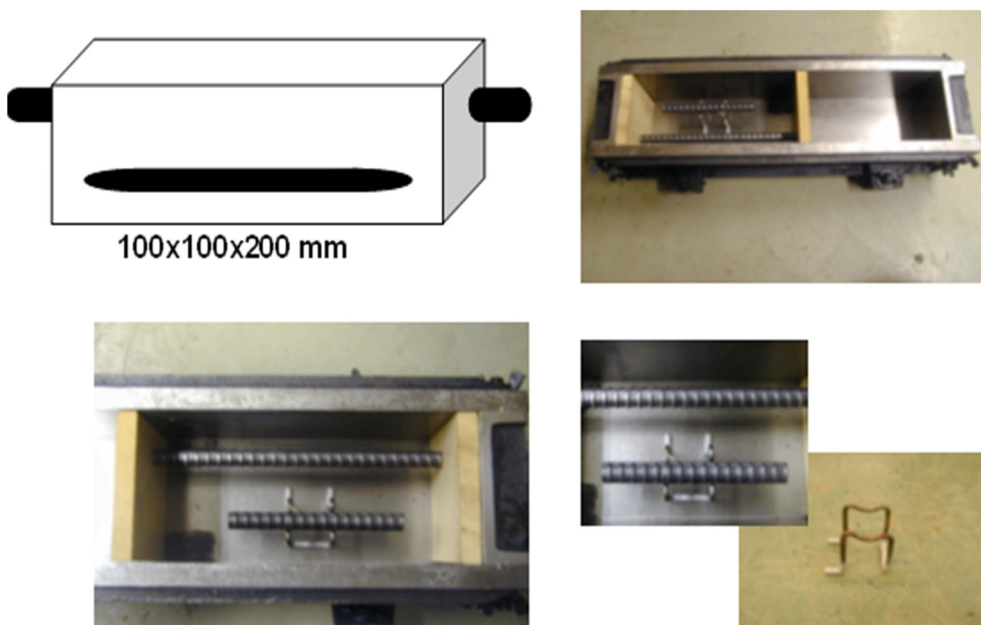


Fig. 7 Schematic and actual diagram of test specimen

4.3 Experiment scheme

RC specimens were carbonated in carbonation chamber controlled at 10% of carbon dioxide concentration, 30°C temperature and 55% R.H. Please note that actual concentrations of carbon dioxide are approximately 0.03% in an outdoor atmosphere and 0.07% in an indoor atmosphere. The specimens were cured for 28 days under sealed conditions and 20°C temperature before transferring to the carbonation chamber.

In this experiment prismatic specimens of $200 \times 100 \times 100$ mm (L $\times$ W $\times$ H) size were made in duplicate. Thin concrete cover of 13 mm was used to enable faster carbonation access from the surface of concrete to the rebar having same 13mm diameter. The specimens were sealed and cured for 28 days at 20°C temperature. Schematic and actual diagram of the prismatic concrete specimen is shown in the Fig. 7. The reinforced specimen has two 13 mm diameter steel bars, one emerging out from two sides for half cell potential measurements (which are submitted for publication elsewhere) and the other rebar completely embedded into the concrete for gravimetric mass loss determination.

Concrete was poured in four layers and each layer was compacted by standard tamping method. Since carbonation is a slow process, therefore, in this experimentation the specimens were carbonated by keeping them in a carbonation chamber set at accelerated carbonation conditions of 10% CO₂ concentration. The experimentation is accelerated by adoption of high level of carbon dioxide and low concrete cover. Therefore, conclusions drawn relate only to the experiment as described. After complete carbonation and completion of one year post-carbonation exposure duration, the specimens were split along the position of steel in concrete and steel bars completely embedded in concrete for gravimetric mass loss calculation were removed. Following the photographic documentation of bar condition, the specimens were subjected to aggressive cleaning in accordance with ASTM G1-03, method C.3.1 (2002) and weighed to the nearest 0.0001 gram immediately after drying using standard systematic step by step cleaning method.

5. Experiment results and discussions

The two identical specimens were broken and embedded steel bars were taken out for gravimetric corrosion mass loss determination. This mass loss was converted to corrosion rate by using Faraday's law (Ehl and Aaron 1954). The results are shown in Fig. 8. The average corrosion rate of the two specimens lies around 3.25×10^{-3} g/cm².yr which corresponds to $0.325 \mu\text{A}/\text{cm}^2$ of corrosion current. Compared to chloride induced corrosion in general this value is not very high and can be pronounced as a low rate of corrosion. However, it should be mentioned over here that in case of carbonation induced corrosion high relative humidity (RH) plays a decisive role. Due to the increased resistivity and reduced electrolytic conductivity of carbonated concrete, it needs high relative humidity to maintain high rates of corrosion. Since the specimen were exposed to 55% RH during carbonation and 60% RH after full carbonation until the end of experiment, the corrosion rates obtained by carbonation induced corrosion are in the low range. It is believed (Luca *et al.* 2000) that 80% RH is ideal for producing high corrosion rates due to carbonation. Therefore, in the future research carbonation induced corrosion rate should be calculated experimentally for high relative humidity conditions more than 80% RH.

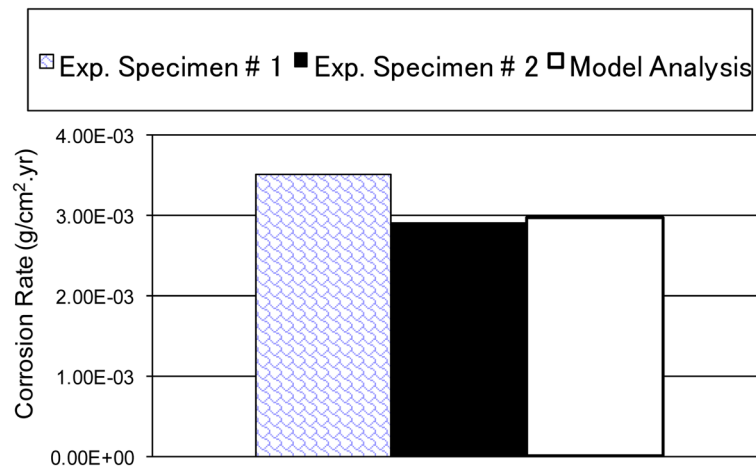


Fig. 8 Carbonation induced corrosion rates (model and experiment)

6. Verification of carbonation induced computational corrosion model of concrete

The comparison of carbonation induced corrosion model analysis and experiment results shows fair agreement as shown in Fig. 8. It should be noted over here that carbonation induced corrosion starts at pH levels below 9.0. In the comparison it is tentatively assumed that the pH of carbonated concrete is 8.0. It can also be seen that the model reasonably predicts the behaviour of carbonation induced corrosion at various pH levels and coupled chloride-carbonation effects qualitatively in general.

7. Conclusions

In this paper the carbonation induced electrochemical corrosion model is developed and coupled with carbon dioxide transport model. Influential parameters for the prediction of corrosion in fully carbonated reinforced concrete are numerically determined using the mass balance electrochemistry and verified by experimentation. For the purpose of enhancing the evaluation method for carbonation induced corrosion phenomenon, formulations are developed for the equilibrium of gaseous and dissolved carbon dioxide, their transport, ionic equilibriums, and the corrosion reaction electrochemistry. The main feature of this work is that the model is based on micro-physical phenomena coupled with electrochemistry based on Tafel's diagram, enabling the pH profile of pore water and degradation of steel reinforcement in carbonated concrete to be predicted for arbitrary conditions. This contrast with the conventional approach, where carbonation induced corrosion is generally evaluated using an empirical formula. The enhanced carbonation induced corrosion model roughly predicts the behaviour of corrosion for normal air dry relative humidity conditions quantitatively at carbonation level of pH 8.0. The model also shows fair qualitative simulation for various pH levels in general. The corrosion rate due to carbonation under air dry humidity condition (55%-60% R.H) is calculated as $0.325 \mu A/cm^2$ which is much lower than average chloride induced corrosion rate. Detailed verification of the model for quantitative carbonation induced corrosion rate under varying

relative humidity conditions, different *pH* levels and combined effects of carbonation and chloride remain as a scope for future research.

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CC

Notations

- ϕ = porosity of the porous media.
- S = degree of saturation of the porous media.
- ρ_d = density of dissolved CO_2 in pore water.
- $\rho_{g\text{CO}_2}$ = density of gaseous CO_2 (kg/m^3).
- J_{CO_2} = total flux of dissolved and gaseous CO_2 ($\text{kg/m}^2\text{s}$).
- Q_{CO_2} = sink term which represents the rate of CO_2 consumption due to corrosion ($\text{kg/m}^3\text{s}$).
- P_{CO_2} = equilibrium partial pressure CO_2 in the gas phase.
- $\rho'd$ = mole fraction of gaseous CO_2 [mol of CO_2 /total mol of solution].
- H_{CO_2} = Henry's constant for carbon dioxide
- ρ_d = the concentration of dissolved carbon dioxide per cubic meter of solution [kg/m^3].
- M_{CO_2} = the molecular mass of carbon dioxide.

Lm = the mean free path length of a molecule of gas.

r_e = the actual pore radius.

D_0^g = the diffusivity of CO_2 [m^2/s].

D_0^d = the diffusivity of dissolved CO_2 [m^2/s].

V = the pore volume.

Ω = $(\pi/2)^2$ accounts for the average tortuosity of a single pore as a fictitious pipe for mass transfer.

$D_{g\text{CO}_2}$ = diffusion coefficient of gaseous CO_2 in a porous medium [m^2/s].

E_{O_2} = standard cell potential of O_2 , cath. (V, SHE)

$E_{\text{O}_2}^\ominus$ = standard cell potential of O_2 at 25°C ($=0.40\text{V}$)

z_{O_2} = the number of charge of O_2 ($=2$)

$P^\ominus$ = atmospheric pressure.

pH = power of hydrogen ion concentration.