Model for Predicting the Depassivation Time of Reinforcing Steel in Fly Ash Concrete

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Abstract

This paper presents a model for predicting the starting point of the depassivation of steel bars embedded in the cement-fly ash concrete. The model consists of a chloride binding capacity model, an ion exchange model and a depassivation criterion. The chloride binding capacity model is computed based on the fixed chloride factor of binder (cement + fly ash) and bound chloride per unit weight of inert materials. The ion exchange model is adopted to explain the rate of exchange between chloride and hydroxide ions during the penetration of external chloride ion. The depassivation criterion model is used to determine the threshold concentration of chloride, which will induce depassivation of the steel in the concrete. The threshold concentration of chloride ion is assumed to be dependent on the hydroxyl ion concentration in the pore solution. By incorporating the mentioned models and criterion into the computer program for simulating chloride movement, jointly developed by the second author with other researchers, the starting point of the depassivation of steel in fly ash concrete is simulated. It was found that the starting point of the depassivation will be longer than the cement-only concrete when fly ash ratio is higher, however, shorter when fly ash ratio is too large. For small fly ash replacement ratio, fly ash with smaller CaO content results in longer depassivation time. On the other hand, for concrete with large fly ash replacement ratio, fly ash with larger CaO content leads to longer depassivation time.

1. Introduction

Concrete protects reinforcing steel with its alkalinity. The high alkaline environment in concrete passivates the steel and protects it from corrosion until the passivity of the reinforcing steel in the concrete is damaged. Chloride ions are considered to be the main factor, which damages the passivity of the reinforcement. Chlorides in concrete are present in two major forms. One is the free chloride, which can travel by diffusion process according to its concentration gradient in the pore solution of the concrete. Another is the bound chloride or fixed chloride, which is bound by chemical adsorption and physical adsorption. Free chloride ions are presented in the pore solution of concrete together with other negative and positive ions and a balance of negative and positive charge is maintained during the diffusion. During the penetration of chloride ion, the hydroxyl ion is one of the main negative ion to be exchanged by the chloride ion, causing the pH of the concrete to reduce. Thus, depassivation of the embedded steel will occur. When the embedded steel loses passivity and if oxygen and moisture are also available for the corrosion reaction, the corrosion of the reinforcing steel will start.

Maruya, Tangtermsirikul and Matsuoka proposed a model for simulating the movement of chloride in hardened concrete [1,2]. However, their model did not consider the effect of chemical composition of the fly ash, content of the fly ash in the binders and the effect of chloride physically bound by non-reactive particles like aggregates and limestone powder. Furthermore, the proposed model still did not include the prediction of the time of depassivation of the reinforcing steel. Thus, this paper aims to propose the model for predicting the time of depassivation of the reinforcement by including the model of chloride binding capacity of cement-fly ash system, the model of ion exchange and the criteria of depassivation of the steel.

2. Computational Program for Simulating Chloride Ion Movement in Hardened Concrete

The program for simulating chloride movement in hardened concrete was developed by Maruya, Tangtermsirikul and Matsuoka. [1,2]. Total chloride in concrete is considered to be composed of fixed and free chlorides. Free chloride is the only chloride, which is movable according to its concentration gradient. The proposed program includes the equilibrium between fixed and free chlorides, the effect of carbonation, change of water content in concrete due to drying and wetting, concept of chloride condensation due to cyclic wetting and drying with salt water and chloride condensation at the surface layer. The analytical process is illustrated in Fig.1. Here, only a brief description of the analytical process will be explained. The amount of free chloride is essential since it is the only chloride, which induces the depassivation of the embedded steel. Thus, the amount of free chloride is quantified from the equilibrium between fixed and free chloride. The fixed chloride factor (α_{fixed}) is used to be a factor for determining the equilibrium between fixed and free chloride and computing the amount of free chloride. In the carbonation environment, with the ingress of carbonation, the equilibrium between fixed and free chloride changes because Friedel' s chloride and adsorbed chloride can be released from the fixed chloride into free chloride. This causes the concentration of free chloride in the carbonated area to be higher than that in the non-carbonated one. So, the effect of carbonation on the amount free chloride is considered in term of degree of carbonation (β_c), which is used to obtain the free and fixed chloride content after carbonation.

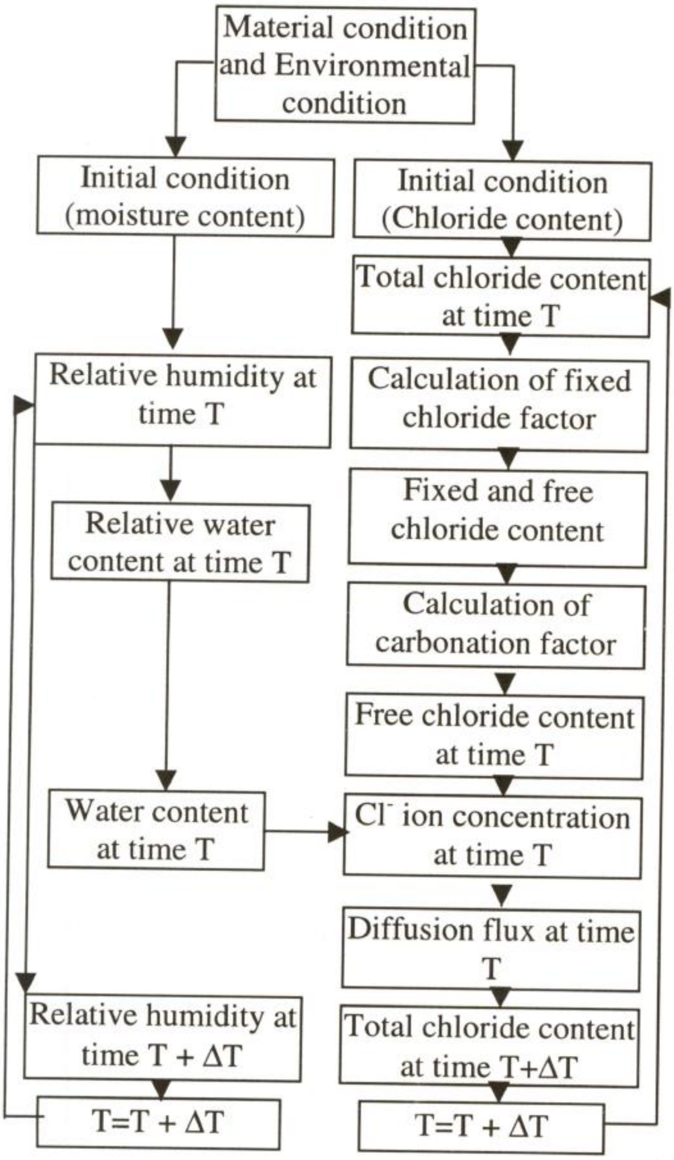

Fig.1 Flow chart of calculating procedure

In the proposed model, the amount of water in concrete pores is an important factor controlling the degree of carbonation, and is required in the calculation of free chloride concentration in the concrete pore. So, it is necessary to incorporate the model for simulating water movement due to drying into the analytical program. Water in hardened concrete is considered to move through the pore structure according to the vapor pressure gradient. The rate of water vapor transfer is assumed to obey Fick's law of diffusion.

Therefore, the water content can be computed from the relative humidity in the concrete element. When the water content in concrete is known the free chloride concentration is calculated. Free chloride ion moves according to its concentration gradient and the process of movement was assumed to be Fick's diffusion theory.

The diffusion coefficient of the exposed surface layer of the concrete is assumed to be larger than that of the bulk of concrete because chloride ions have to move along the pore within the concrete at the same time, they can move in all directions at the boundary. Maruya, Tangtermsirikul and Matsuoka [2] found that the chloride ion concentration near the surface layer could be higher than the concentration of the surrounding solution. This behavior can be explained by the combined effect of surface condensation due to ion absorption and diffusion theory. Chloride condensation at the surface layer can be expressed as in the following equation.

$$F_c' = F_c + S_c \qquad (1)$$

where F'_c is the total flux of chloride ions entering the concrete at the surface and is the sum of the fluxes due to diffusion and ion adsorption (mol/cm^2/day), F_c is the flux of chloride ions due to diffusion only (mol/cm^2/day), and S_c is the flux of chloride ion due to ion adsorption only (mol/cm^2/day).

Cyclic wetting and drying simulates the conditions of a splash zone or a tidal zone in an actual environment. In the drying period, water evaporates from the exposed surface of the concrete into the environment, causing a reduction in the relative water content in the concrete near the exposed surface. In the wetting period, salt water enters the dried concrete from the environment, saturating or closely saturating the concrete within a relatively short time period. Therefore, when the wetting and drying process is continued for long period, chloride concentration near the concrete surface increases considerably. The phenomenon was included in simulating the condition of wetting and drying with salt water.

The mentioned concepts and models were assembled to construct a computational program for simulating the chloride movement in hardened concrete as shown in the flow chart. However, the effect of chemical composition of the fly ash, content of the fly ash in the binders and the effect of chloride binding by non-reactive materials such as aggregates were not considered in their computational program. Furthermore, the mechanisms of ion exchange due to chloride penetration and criteria for depassivation of reinforcement were not included either. Therefore, the program cannot be used to predict the time of depassivation of reinforcement in cement-fly ash concrete. In this paper, the effect of chemical composition and amount of fly ash in the binder on chloride binding capacity and the binding capacity of inert materials will be included quantitatively. In addition, the mechanisms of ion exchange due to chloride penetration and criteria for depassivation of reinforcement will be adopted in this paper for predicting the time of depassivation of reinforcement.

3. Chloride Binding Capacity of Cement-Fly Ash Concrete

The fixed chloride factor was used as an index for defining the chloride binding capacity of cementitious materials [1,2]. Whereas, the fixed chloride content per unit weight of non-reactive materials was defined as the chloride binding capacity of the non-reactive materials [3]. Considering these factors, the amount of fixed chloride, which includes Friedel's chloride and adsorbed chloride in solid phase, can be computed from

$$C_{fixed} = \alpha_{fixed}(binders) \times \frac{C_{tot}}{100} \times B + \sum_{i=1}^{n} \phi_{fixed,i} \times W_i \qquad (2)$$

where α_{fixed}(binder) is the fixed chloride factor of cementitttious binders. $\phi_{fixed,i}$ is the fixed chloride content per unit weight of non-reactive materials i. C_{tot} is the total chloride content (wt% of binder). C_{fixed} is the fixed chloride content in 1 m^3 of concrete (kg/m^3). B is the weight of total binder. W_i is the weight of non-reactive material i in 1 m^3 of concrete (kg/m^3).

Chloride binding capacity of reactive materials

The pozzolanic reaction factor was used for determining the effect of pozzolanic reaction on the chloride binding capacity of the cement-fly ash system. By assuming that the chloride binding capacity of the cement-fly ash binder will be r times of the chloride binding capacity of the cement only binder [3]. Thus, the fixed chloride factor of binders can be calculated by the following relationship.

$$\alpha_{fixed}(binder) = r \times \alpha_{fixed}(cement) \quad (3)$$

where α_{fixed}(cement) is the fixed chloride factor of cement and r is the pozzolanic reaction factor.

The relationship between the pozzolanic reaction factor and the glass to lime ratio is shown in Fig.2 and can be expressed as follows.

$$r = 1 \qquad for\ C_{tot} \le 0.1$$

$$r = 1 + A \times \left(23.6 \times C_{tot}^{0.006} - 23.4\right) \times sin\left[\frac{\pi}{0.8} \times \left(\left(\frac{SiO_2}{CaO}\right)_{c+f} - \left(\frac{SiO_2}{CaO}\right)_c\right)\right] \qquad for\ 0.3 \le C_{tot} \le 2.4$$

$$r = 1 + A \times \left(0.31 - 0.018 \times C_{tot}^{1.638}\right) \times sin\left[\frac{\pi}{0.8} \times \left(\left(\frac{SiO_2}{CaO}\right)_{c+f} - \left(\frac{SiO_2}{CaO}\right)_c\right)\right] \qquad for\ 2.4 \le C_{tot}$$

$$A = 1\ for \left(\frac{SiO_2}{CaO}\right)_{c+f} \le 1.1\ and\ A = 10\ for \left(\frac{SiO_2}{CaO}\right)_{c+f} > 1.1$$

$$\left(\frac{SiO_2}{CaO}\right) = \frac{R \times (SiO_2)_f + (1-R) \times (SiO_2)_c}{R \times (CaO)_f + (1-R) \times (CaO)_c} \qquad (4)$$

where $(SiO_2/CaO)_{c+f}$ is the SiO_2 to CaO ratio of cement-fly ash system, $(SiO_2/CaO)_c$ is the SiO_2 to CaO ratio of cement, R is the replacement ratio by weight of fly ash in total binder, f/(c+f), $(SiO_2)_f$ and $(CaO)_f$ are the SiO_2 content and the CaO content in fly ash(%), respectively., $(SiO_2)_c$ and $(CaO)_c$ are the SiO_2 content and the CaO content in cement(%), respectively.

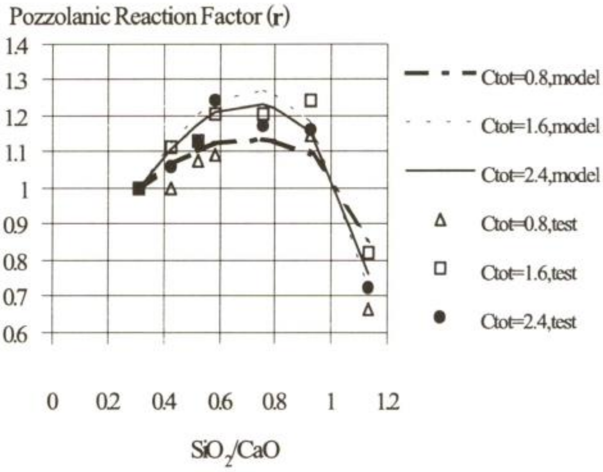

Fig.2 The relationship between the pozzolanic reaction factor and the SiO_2 to CaO ratio

Chloride binding capacity of non-reactive materials

It was assumed that chloride binding capacity of inert materials is independent on the cement, and fixed chloride content per unit weight of non-reactive materials (ϕ_{fixed}) is the function of specific surface area of the material and is not time-dependent [3].

The relationship between the fixed chloride content per unit weight of non-reactive materials (ϕ_{fixed}) and the specific surface area of the material (S) (cm^2/g) is shown in Fig.3 and can be expressed as follows.

$$\phi_{fixed} \;=\; 6\times 10^{-5}(S)^{0.5474} \qquad (5)$$

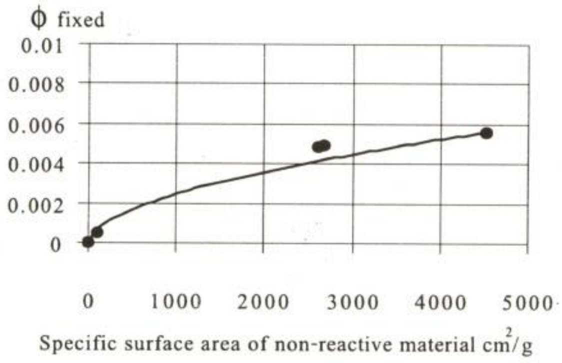

Fig.3 Relationship between ϕ_{fixed} and specific surface area of non-reactive materials (cm^2/g)

4. Mechanism of Ion Exchange due to Chloride Penetration

It is suggested that a reasonably accurate estimation of the experimentally determined hydroxyl concentration may be obtained from charge balance consideration after diffusion of all the other ions besides hydroxyl. Therefore, it is assumed in this paper that when the external chloride ions penetrate into the concrete, chloride ions are presented in the pore solution of concrete together with other negative and positive ions and a balance of negative and positive ions is maintained by only exchanging hydroxyl ions with chloride ions. However, by extracting the results of some intensive studies [4,5], the relationship in Fig.4 could be obtained. Fig.4 shows that for the low concentration of the chloride ion, only hydroxyl ion is exchanged and ratio of hydroxyl ion exchanged with chloride ion is one to one. In contrast, when chloride ion concentration becomes higher, not only hydroxyl ion but also other negative ions in the pore solution are also exchanged. This causes the lower ratio of hydroxyl ion exchange with chloride ion when chloride ion concentration becomes high. In this paper, the ratio of hydroxyl ion exchanged with chloride ion is considered to be the function of the ratio between chloride ion concentration to hydroxyl ion concentration. The ratio of hydroxyl ion exchange can be expressed by the following equation.

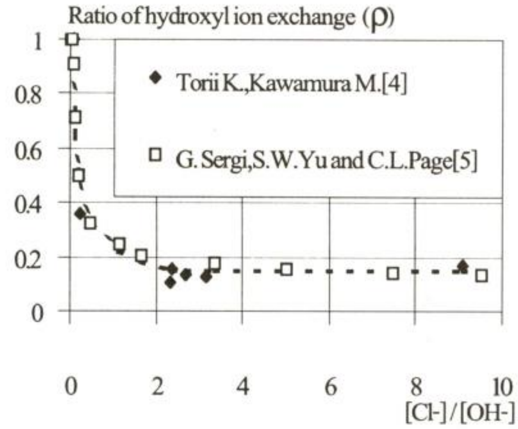

Fig.4 Relationship between the ratio of hydroxyl ion exchange and the chloride ion to hydroxyl ion ratio

$$\rho = 1.0 \qquad for 0.08 \leq \frac{[Cl^-]}{[OH^-]}$$

$$\rho = 0.235\times\left[\frac{[Cl^-]}{[OH^-]}\right]^{-0.473} \qquad for 0.08 \leq \frac{[Cl^-]}{[OH^-]} \leq 2.0$$

$$\rho = 0.15 \qquad for 2.0 \leq \frac{[Cl^-]}{[OH^-]} \qquad (6)$$

where ρ is the ratio of hydroxyl ion exchange, [Cl$^-$]is the chloride ion concentration (mol/l) and [OH$^-$]is the hydroxyl concentration (mol/l). The results in Fig.4 and Eq.6 are used as the mechanisms of ion exchange in this study.

The ratio of hydroxyl ion exchange is used to obtain the hydroxyl ion concentration in pore solution after the penetration of chloride ion as shown in Eq.7 and Eq.8

$$\Delta OH^-(t) = \rho \times \Delta Cl^-(t) \quad (7)$$

$$OH^-(t+\Delta t) = OH^-(t) - \Delta OH^-(t) \quad (8)$$

where $\Delta OH^-(t)$ is the exchanged ion of hydroxyl at time t (mol), $\Delta Cl^-(t)$ is the penetrated chloride at time t (mol), $OH^-(t+\Delta t)$ is the amount of hydroxyl at time $t+\Delta t$ (mol) and $OH^-(t)$ is the amount of hydroxyl at time t (mol).

5. Criteria for Depassivation of Reinforcement

The corrosive action of chlorides on steel reinforcement consists of the local depassivation of the steel surface causing pitting corrosion. Depassivation of the steel surface requires a chloride concentration exceeding a threshold value, which is referred to as the critical chloride concentration. It was popularly assumed that the critical chloride ion concentration, which induces depassivation, is dependent on the alkalinity of pore solution in concrete. However, it is known that the critical chloride concentration is not a constant value for any type of concrete or exposure condition but depends on many parameters. In this paper, the results in Fig.5, which was extracted from the study of C.L.Page and Vennesland [6], is used to identify the criteria of depassivation. Fig.5 shows that if the hydroxyl ion concentration in pore solution is higher, the critical chloride ion concentration causing depassivation is also higher. Thus, in this paper, the relationship between the critical chloride ion concentration and the hydroxyl ion concentration around the steel location is proposed in the term of numerical equation as expressed in Eq.9

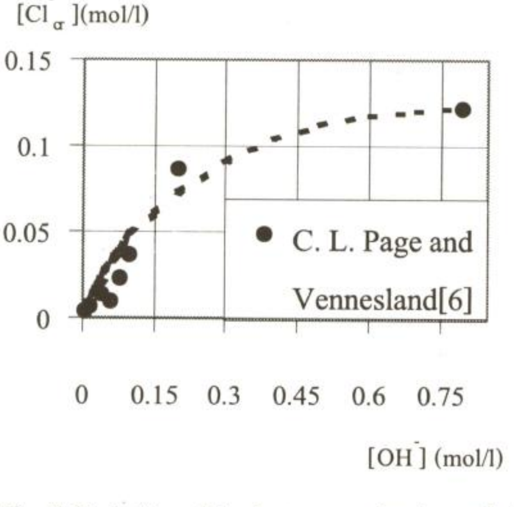

Fig.5 Relationship between hydroxyl ion concentration and critical chloride ion concentration

$$[Cl_{cr}^-] = 8.0 \times [OH^-] - 7.87 \times [OH^-]^{1.02} \quad (9)$$

where $[Cl^-_{cr}]$ is the critical chloride ion concentration (mol/l) and $[OH^-]$ is the hydroxyl ion concentration (mol/l)

The chloride binding capacity model, mechanism of ion exchange and criteria for depassivation were incorporated into the original computerized program to construct the program for predicting the starting time of the depassivation of reinforcing steel in fly ash concrete as shown in Fig.6.

6. Verification and Simulation Results

Verification of the chloride ion movement simulation

The chemical composition of cement and fly ashes used in the computational model for verification is shown in Table 1. Mix proportions of the mortars and concrete tested by Maruya, Tangtermsirikul and Matsuoka [1] are shown in Table 2. Examples of verification results of the movement of chloride ion in cement-fly ash mortar, presented by comparing the test results [1] with the computational results. Fig.7 and Fig.8 show the test and analytical results of the mortar calculated under the condition in which the mortar is submerged in salt water having 3% of sodium chloride (equivalent to 1.82% of chloride). Fig.9 and Fig.10 show the test and analytical results of the concrete calculated under the cyclic wetting and drying condition by using the 3% NaCl solution (7-day wetting and 7-day drying as 1 cycle).

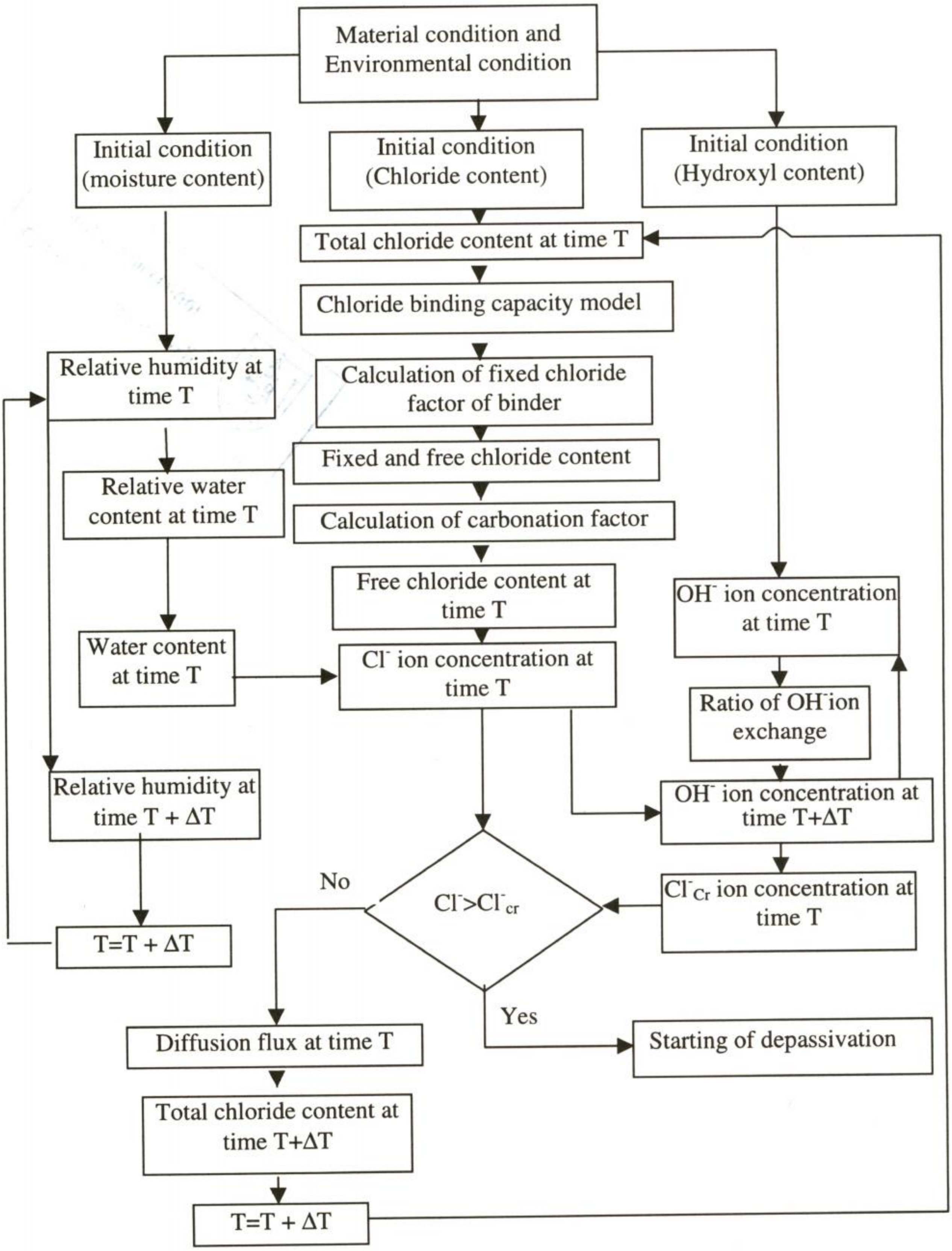

Fig.6 Flow chart of calculating procedure

Table 1 Chemical composition of the tested cement and fly ash [1]

Binder type	Chemical composition (% by weight)							
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
Cement	64.0	21.6	5.4	2.6	1.8	2.0	0.38	0.55
Fly ash	8.69	51.4	24.7	5.69	2.0	0.49	1.61	1.22

Table 2 Mix proportion of the tested mortar and concrete [1]

Mix type	W/b (%)	Component (kg/m^3)				
		Cement (C)	Fly Ash (FA)	Water (W)	Gravel (G)	Sand (S)
Mortar	50	431	108	269	-	1332
Concrete	50	175	-	350	956	866

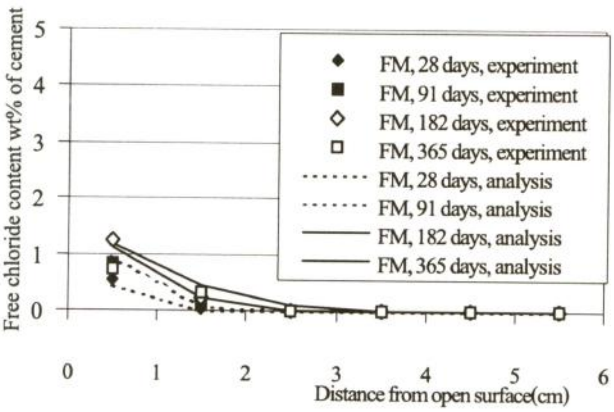

Fig.7 Distribution of Free chloride content in cement-fly ash mortar

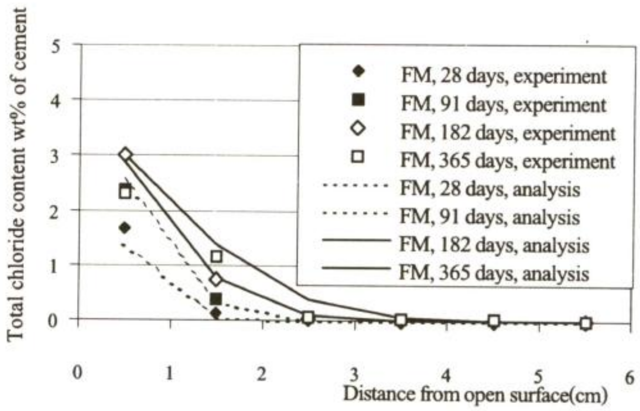

Fig.8 Distribution of Total chloride content in cement-fly ash mortar

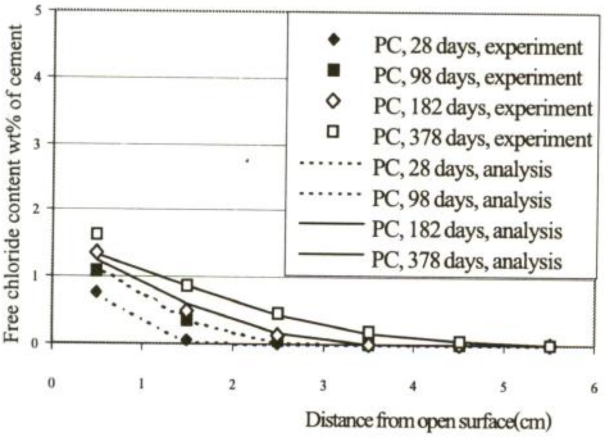

Fig.9 Distribution of free chloride content in cement concrete

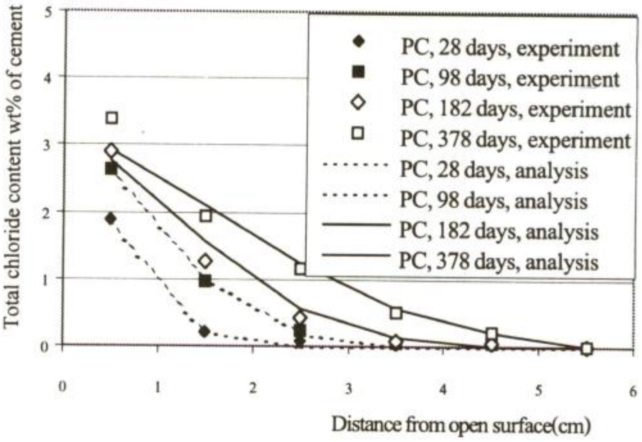

Fig.10 Distribution of total chloride content in cement concrete

Verification of the depassivation time of the reinforcement of conventional concrete

The model for predicting the depassivation time of the reinforcing steel is verified by comparing the computed results with Torii and Kawamura's test results on conventional concrete [4]. The chemical composition of cement and fly ashes is shown in Table 3. Mix proportion of concrete for verification is shown in Table 4.

Table 3 Chemical composition of the tested cement and fly ash [4]

Binder	Chemical composition (% by weight)							
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
Cement*	64.0	21.6	5.4	2.6	1.8	2.0	0.38	0.55
Fly ash	6.0	56.0	27.4	9.2	1.0	0.45	0.12	0.68

* assume the same chemical composition of cement as in Table 1

Table 4 Mix proportion of the tested concrete [4]

W/b (%)	Component (kg/m^3)				
	Cement (C)	Fly Ash (FA)	Water (W)	Gravel (G)	Sand (S)
55	210	90	165	1241	698

The simulated result is calculated under the cyclic wetting and drying condition by using the 3% NaCl solution in the simulation (7-day wetting and 7-day drying as 1 cycle). The depassivation time of reinforcing steel obtained from the simulation model is 2 years and 2 months while the depassivation time obtained from Torii and Kawamura's test is 2 years.

Table 5 Mix proportion of the concrete used in simulation

Mix	W/b (%)	f/b (%)	Component (kg/m^3)				
			W	C	FA	G	S
1	50	0	269	539	0	956	866
2	50	20	269	431	108	956	866
3	50	40	269	324	215	956	866
4	50	70	269	162	377	956	866

Simulation of the depassivation time of the reinforcement of fly ash concrete

The starting time of depassivation of the steel in fly ash concrete is simulated by using the mix proportions of concrete shown in Table 5. The chemical composition of various types of fly ash used in the simulation is shown in Table 6. The simulation results were calculated under the cyclic wetting and drying condition (7-day wetting and 7-day drying as 1 cycle) by using the 3% NaCl solution in the wetting period. For the effect of fly ash content, it was found that for all types of fly ash the starting time of depassivation will be longer than the cement-only concrete when fly ash ratio is higher. However, when fly ash ratio is too large, i.e. 70% from the simulation results, the steel in fly ash concrete will depassivate sooner than the concrete with cement only.

For the effect of types of fly ash, the simulation results show that for small fly ash replacement ratio (20%), fly ash with smaller CaO content results in longer depassivation time. On the other hand, for concrete with larger fly ash replacement ratio (40% and 70%), fly ash with larger CaO content leads to longer depassivation time. However, the differences are not very significant.

Table 6 Chemical composition of the cement and fly ashes used in the simulation

Chemical composition % by weight	Binder type			
	C	FA1	FA2	FA3
CaO	64.0	1.6	8.69	15
SiO_2	21.6	58.8	51.4	45.1
Al_2O_3	5.4	24.7	24.7	24.7
Fe_2O_3	2.6	5.69	5.69	5.69
MgO	1.8	2.0	2.0	2.0
SO_3	2.0	0.49	0.49	0.49
Na_2O	0.38	1.61	1.61	1.61
K_2O	0.55	1.22	1.22	1.22

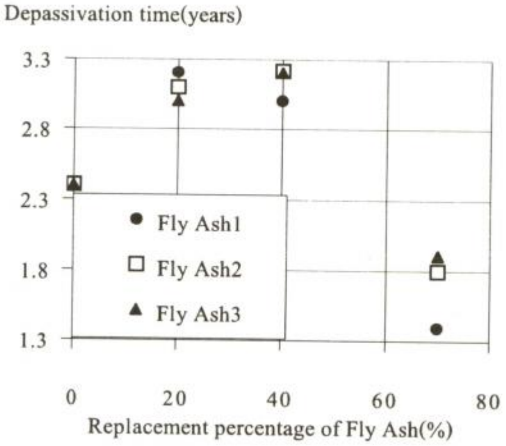

Fig.11 Depassivation time of various replacement percent of fly ash

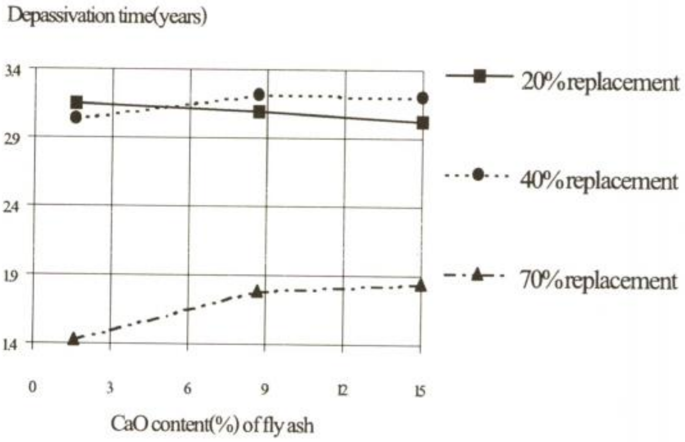

Fig.12 Depassivation time of various types of fly ash

7. Conclusion

The chloride binding model for cement-fly ash system, the model for deriving physically bound chloride in non-reactive materials, the concepts for ion exchange during chloride penetration and the criteria for depassivation were incorporated into the analytical program for chloride movement in hardened concrete for simulating the time of depassivation of steel in fly ash concrete. The results of simulation shows that the proposed model can satisfactorily simulate the movement of chloride in the tested cement-fly ash mortars and the time of depassivation of the reinforcing steel in the tested conventional concrete. For the effect of fly ash content, it was found that not too much fly ash replacement will increase the time of depassivation of the embedded steel in the fly ash concrete. In contrast, too much replacement of fly ash (70%), the depassivation of the steel will be occurred sooner than the concrete without fly ash. For the effect of fly ash type, the time of depassivation reduced with increasing CaO content if the concrete contained 20% of fly ash. However, the time of depassivation increased with the increasing of CaO content in fly ash when the fly ash replacements were 40% and 70%. The developed and modified program still can not be applied to predict the starting time of steel corrosion. For a more accurate prediction of the starting time of corrosion, the availability of the O_2 and the variation of permeability of concrete with types and content of fly ash must be considered in the program too.

References

[1] Maruya T., Tangtermsirikul S. and Matsuoka Y. (1992) "Simulation of Chloride Movement in Hardened Concrete", *Concrete Library of Japan Society of Civil Engineering*, No.20, pp.57-70