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Corrosion of Steel in Blended Concretes Containing OPC, PFA, GGBS and SF

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The chloride threshold level (CTL) in mixed concrete containing, ordinary Portland cement (OPC), pulverized fuel ash (PFA) ground granulated blast furnace slag (GGBS), and silica fume (SF) is important for study on corrosion of reinforced concrete structures. The CTL is defined as a critical content of chloride at the steel depth of the steel which causes the breakdown of the passive film. The criterion of the CTL represented by total chloride content has been used due to convenience and practicality. In order to demonstrate a relationship between the CTL by total chloride content and the CTL by free chloride content, corrosion test and chloride binding capacity test were carried out. In corrosion test, Mortar specimens were cast using OPC, PFA, GGBS and SF, chlorides were admixed ranging 0.0, 0.2, 0.4, 0.8, 1.0, 1.5, 2.0, 2.5 and 3.0% by weight of binder. All specimens were cured 28 days, and then the corrosion rate was measured by the Tafel's extrapolation method. In chloride binding capacity, paste specimens were casting using OPC, PFA, GGBS and SF, chlorides were admixed ranging 0.1, 0.2, 0.3, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0% by weight of binders. At 28days, solution mixed with the powder of ground specimens was used to measure binding capacity. All specimens of both experiments were wrapped in polythene film to avoid leaching out of chloride and hydroxyl ions. As a result, the CTL by total chloride content ranged from 0.36-1.44% by weight of binders and the CTL by free chloride content ranged from 0.14-0.96%. Accordingly, the difference was ranging, from 0.22 to 0.48% by weight of binder. The order of difference for binder is OPC > 10% SF > 30% PFA > 60% GGBS.

Keywords : *reinforced concrete structures; chloride threshold level; free chloride; bound chloride; corrosion rate*

1. Introduction

The steel corrosion is a major factor of deterioration in reinforced concrete structures. In general concrete protects steel from corrosion because of a high alkalinity of the pore solution. The alkalinity of pore solution passivates the steel embedded concrete by thin inert layer of the oxide layer (passive film: γ-$Fe_2O_3 \cdot H_2O$) on surface of steel.[1] Chloride ions weaken the passive film, thus local steel corrosion was initiated. The importance of chloride ions has led to chloride threshold level (CTL). It is defined as chloride content at the depth of the steel to initiate the corrosion of steel[2] and the CTL has been used for criterion of deterioration of concrete structures. Thus, it is important to analyze and quantify the CTL. Those chlorides penetrate into concrete and then some chloride ions move freely in concrete pores structure (i.e. free chlorides) although the other are trapped/removed in the concrete pore solution (i.e. bond chlorides). It is noted that total chloride ions can be divided by free chloride ions and bound chloride ions. On the whole, total chloride expressed by weight of binder has been the best representation of CTL because of its convenience in determining the concentration in concrete and thus chloride profile. Although free chlorides in concrete are in fact risky for steel corrosion, total chloride concentration is considered in assessing the onset of corrosion and the CTL. It has been argued that the effect of chloride binding on the CTL. In respect of chloride binding, the CTL is decreased due to the bound chloride content. From the literature review, CTL expressed by free chloride is increased according to increase of the total chloride contents.[3] Bound chloride also has been regarded as being negligible to corrosion risk.[4] In contrast, Oh et al. found relationship of CTL using both free chloride and bound chloride.[5] Moreover, corrosion rate of steel was measured throughout the half cell potential test. However, the method has some risks to measure the corrosion rate incorrectly because of the uncertainty (i.e. humidity, carbo-

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nation and chloride content). On the other hand, Haussman performed the corrosion test only use a chloride-dissolved solution.[6] However, it is unacceptable to use of CTL because of ignoring an inhibition effect of hydrations.

In this study, the aim of this paper is study corrosion resistance of the blended concrete by providing the relationship of CTL, expressed by between the total chloride contents and the free chloride contents. Chloride binding capacity test and corrosion test were carried out using four different binders; ordinary Portland cement (OPC), 30% pulverized fuel ash (PFA), ground granulated blast furnace slag (GGBS), and 10% silica fume (SF), respectively, considering 10 levels of chloride concentration, ranging from 0.0% to 3.0%. Thus, for the chloride binding capacity test, only free chloride contents were extracted using Langmuir isotherm. From corrosion test, Tafel's extrapolation technique (electrochemical polarization) and polarization resistance method were conducted to measure the corrosion rate. Finally, the CTL represented by total chloride ions and free chloride ions were discussed.

2. Experiments

2.1 Corrosion test

Mortar specimens were used for corrosion test. As binders for mortar specimens, ordinary Portland cement (OPC), pulverized fuel ash (PFA), ground granulated blast furnace slag (GGBS), and 10% silica fume (SF) were used. The oxide compositions of these binders are given in Table 1. Replacement ratio of OPC: PFA: GGBS: SF was 1: 0.3: 0.6: 0.1 in weight of cement. Also, 10 levels of chloride concentration were 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5 and 3.0% by weight of binders.

After ends of steel (diameter: 10.0 mm, height: 90.0 mm) were coated by rich paste and rubber, they were kept in vacuum desiccators until the casting mortar specimens. At casting mortar specimens for corrosion test a steel bar was centrally located in a cylinder plastic mould (diameter: 50.0 mm, height: 90.0 mm) using a plastic bridge. Thus the uncoated part of steel (height: 60.0 mm) located in mortar was shined by acetone to remove the mill-scale on the surface of the steel. After demoulding, the specimens were wrapped in polythene film and cured at experimental environment for 28 days due to prevent leaching out of chlorides in specimens.

In order to measure corrosion rate of steel embedded in mortar, specimens were immersed in 0.5 M NaCl solution for 24 hrs before measuring for stabilizing the specimens. During immersing, the top of specimens were kept open to the air to supply oxygen for cathodic reaction.

An experimental set-up to measure the corrosion rate is given in Fig 1. Calomel electrode and carbon bar were used for the reference and counter electrodes. Range of the corrosion potential was between +25 mV and -25 mV, and then applied a low scan rate of 0.1 mV/sec. The corrosion rate was derived by extrapolating Tafel's curve, which determine the cathodic and anodic slops as given in the Eq.(1). The calculation of the corrosion rate is graphically given in Fig. 2 with Tafel's extrapolation technique applied.

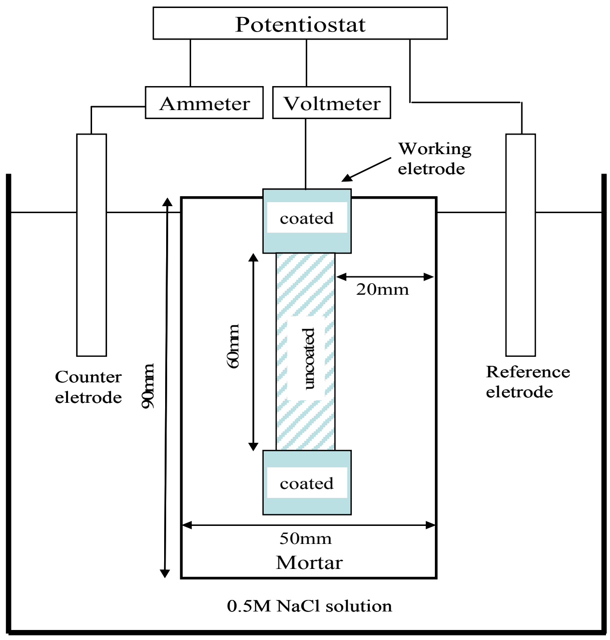

Fig. 1. Experimetal set-up for corrosion test

Table 1. Oxide composition of binders

Binder	SiO_2 (%)	Al_2O_3(%)	Fe_2O_3(%)	CaO(%)	MgO(%)	SO_3(%)	K_2O(%)	Na_2O(%)
OPC	22.10	5.00	3.00	63.80	1.60	2.00	0.64	0.35
PFA	52.00	25.37	9.84	6.79	1.63	0.72	0.48	0.19
GGBS	37.50	9.01	1.21	35.75	6.04	2.42	0.37	0.31
SF	95.00	0.23	0.07	0.31	0.04	0.17	0.56	0.15

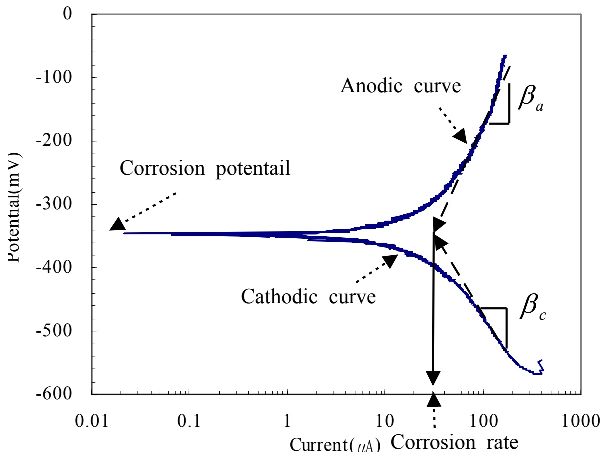

Fig. 2. Tafel's extrapolation technique

$$I_{corr} = \frac{\beta_a \beta_c}{2.3R_P(\beta_a + \beta_c)} \tag{1}$$

Where, I_{corr} = corrosion rate (mA, A)
β_a = anodic curve slop (Constant)
β_c = cathodic curve slop (Constant)
R_P = polarization resistance (Ωm^2)

2.2 Chloride binding capacity test

Specimens for chloride binding test were cast in a cylinder mould (Diameter: 55.0 mm, height: 50.0 mm). Mix proportion of paste cement: water was 1.00: 0.4 in weight. Nine levels of chloride concentration (0.1, 0.2, 0.3, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0% by weight of binders) were added. As binders, ordinary Portalnd cement (OPC), 30% pulverished fuel ash (PFA), ground granulated blast furnace slag (GGBS), and 10% silica fume (SF) were used to examine the chloride binding capacity. The oxide composition of binders is given in Table 1. To minimize segregation, the specimens were rotated 6 rpm for 24 hrs. After demoulding, the specimens were wrapped in polythene film and cured at experimental environment for 28 days to prevent leaching out of chlorides in cast.

At 28 days, the specimen was crushed to obtain powder and then sieved into the 300 μm fineness sieve. Then the sample collected from sieve was stirred in distilled water at 50 ℃ for 5 minutes to extract free chloride. The solution containing the powder was filtered by filtering papers, the filtered solution was used to measure the concentration of chloride ion, determined by potentiometric titration against silver nitrate.

3. Results and discussion

3.1 Chloride binding test

In order of binding capacity of binders, ordinary Portland cement (OPC), pulverished fuel ash (PFA), ground granulate blast furnace slag (GGBS) and silica fume (SF), is 30% PFA > 60% GGBS > OPC > 10% SF given Fig. 3. Blended mortars containing SF have a reduced binding capacity and the blended mortars containing PFA and GGBS have an increased binding capacity. Fig. 4 shows relationship of contents between total chloride and free chloride according to the binders. Once chloride capacity of each binder is calculated, the relationship is also derived using the Eq.(2) of Langmuir isotherm. Table 2 gives the constants of Langmuir isotherm and standard deviation. Using the equation, concentration of total chloride is converted into concentration of free chloride.

$$Y = \frac{aX}{1 + bX} \tag{2}$$

Where, Y = Free chloride content
X = Total chloride content

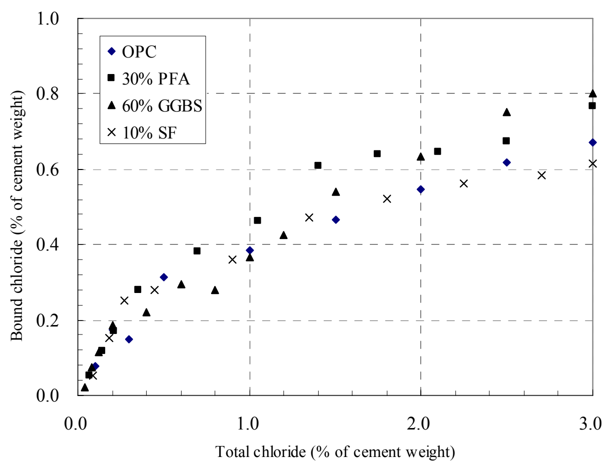

Fig. 3. Bound chloride after 28 days for each binder

Table 2. Langmuir isotherm between total chloride and free chloride

binder	Langmuir isotherm		R^2
	a	b	
OPC	0.498	-0.116	0.997
30% PFA	0.577	-0.089	0.998
60% GGBS	0.568	-0.076	0.998
10% SF	0.560	-0.103	0.998

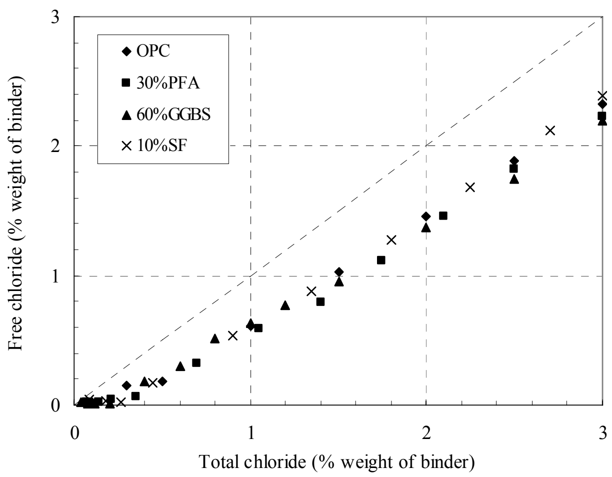

Fig. 4. Relation between free chloride and total chloride

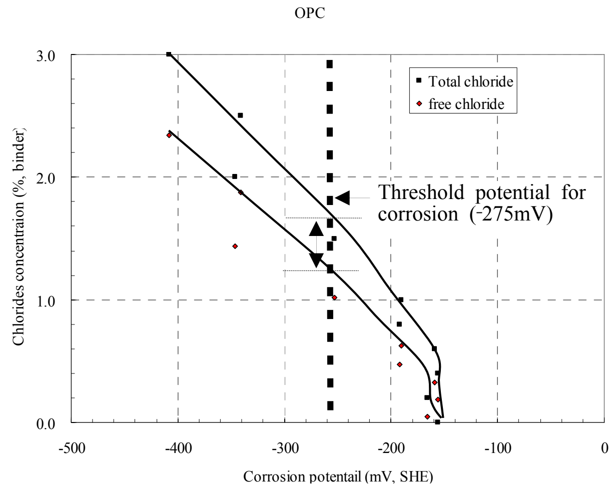

Fig. 5. Corrosion potential with chloride concentration in OPC mortar

3.2 Corrosion potential

In this study, the corrosion rate of steel embedded concrete was measured using the Tafel's extrapolation technique and then calculated the corrosion potential. Fig. 5 shows the corrosion potential for different levels of chloride in OPC mortar specimens. Difference for expressing by two types of chloride (total chloride and bound chloride) initiation is about 0.4% chloride concentration. Moreover, the difference is decreasing with increase of corrosion potential. It is shown that low corrosion potential, below -275 mV, means high generation of corrosion as well as bigger difference of chloride contents between free and bound chlorides.

3.3 Corrosion rate

The corrosion rate of steel embedded in mortar with the concentration of chloride ions is given in Fig. 6. The corrosion rate was increased by an increase in chlorides even before the onset of corrosion. Also the development of the corrosion rate is much influenced by binder. In the state of passivation, for OPC and 10% SF mortars, the corrosion rate was even lower than for 30% PFA and 60% GGBS, which were lowered even after the corrosion initiation. It is an important finding in assessing the rate of corrosion propagation, as a parameter for a judgment to determine the time to repair the concrete structure subjected to steel corrosion. This result shows the pozzolanic materials may not enhance values of the CTL, but may delay of the rate of corrosion propagation.

It is well known the corrosion can initiate at 1-2 mA/m^2 with steel embedded in concrete.[7] This hypothesis gives a guideline to determine the CTL for chlorides in cast. In this study, the CTL was calculated by the development of the corrosion rate and given in Table 3 expressed by total chloride content and free chloride content. It was found that CTL by total chloride for OPC and 10% SF,

Table 3. Chloride threshold level

binder	Chloride threshold level (%, weight of binder)		
	total chloride content	free chloride content	difference range
OPC	1.28 - 1.44	0.89 - 0.96	0.39 - 0.48
30% PFA	0.36 - 0.45	0.14 - 0.21	0.22 - 0.24
60% GGBS	0.69 - 0.79	0.40 - 0.48	0.29 - 0.31
10% SF	1.30 - 1.40	0.89 - 0.94	0.41 - 0.46

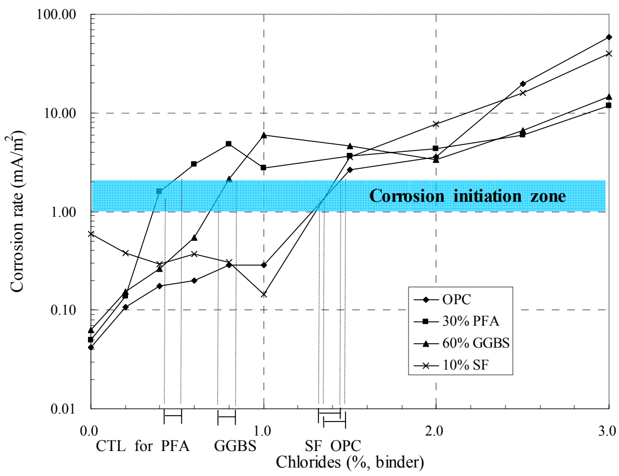

Fig. 6. Corrosion rate of steel in mortars with the concentration of total chloride

arranged 1.28-1.44% by weight of binder, but CTL of free chloride for OPC and 10% SF is decreasing until 0.89-0.96% by weight of binder. However, 30% PFA and 60% GGBS indicated much lower level of CTL both by total and free chloride. This may be attributed to different degrees of hydration in concrete. For PFA and GGBS, 28 days may not be sufficient for enough hydration, which usually take at least 60-90 days to reach the hydration level of OPC paste. However, the CTL obtained in this study is higher than the values that standards specified.

3.4 Polarization resistance

In this study, the polarization resistance of the steel embedded in mortar with the concentration of chlorides is given in Fig 7. It is shown that OPC mortars, irrespective

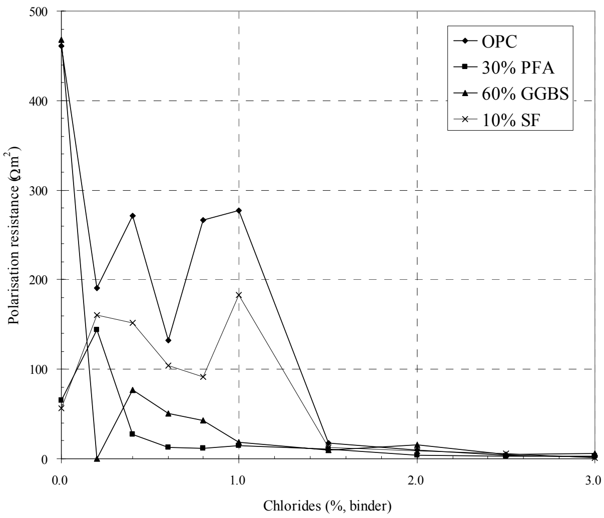

Fig. 7. Polarization resistance of the steel according to the concentration of chloride ions

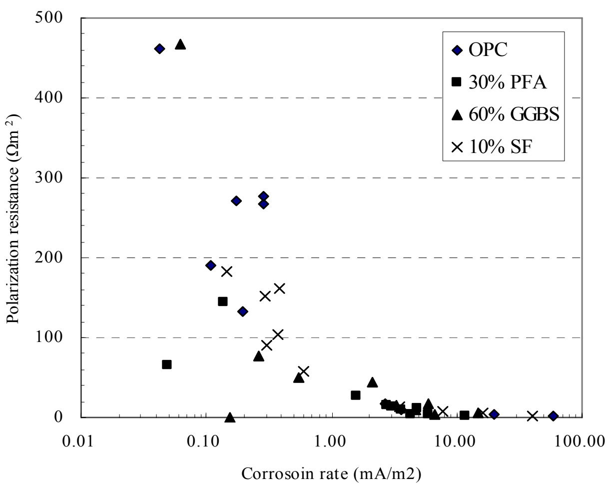

Fig. 8. Polarization resistance of corrosion rate

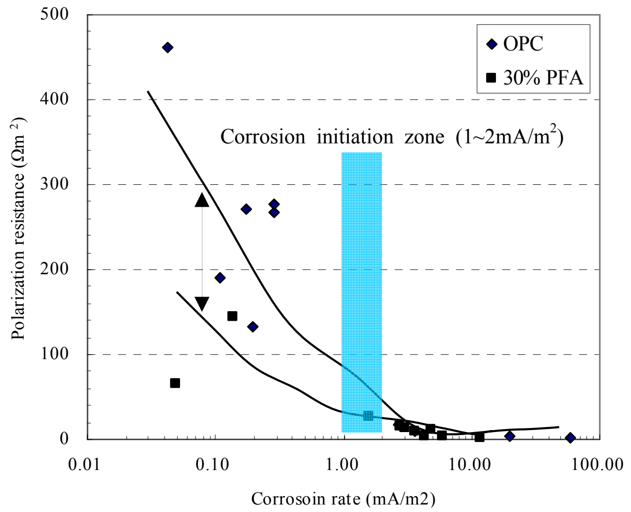

Fig. 9. Polarization resistance of the steel according to OPC mortar with the concentration of chloride ions

of the total chloride concentration, show high polarization resistance, followed by 10% SF, 30% PFA and 60% GGBS mortars. It means that OPC mortars provide more stable pore solution to the surface of the steel with high alkalinity, to enhance the passive film. However PFA and GGBS mortars show weaker passivation. The relationship between polarization resistance and the corrosion rate is given in Fig. 8. It is shown that low corrosion rate, below 1.0 mA/m^2, shows high polarization resistance. For OPC mortar and 30% PFA mortar, Fig. 9 shows the OPC mortar has higher polarization resistance than that of the 30% PFA mortar in low corrosion rate range.

4. Conclusions

This study investigated the relationship between the CTL expressed by total chloride and the CTL expressed by free chloride of OPC, 30% PFA, 60% GGBS and 10% SF mortars cast with chloride ions. The free chloride content was calculated from the contents of bound chloride and the value of corrosion initiation was determined using Tafel's extrapolation and then the relation between the corrosion potential and the polarization resistance was discussed. The conclusion is as follows:

1) Order of binding capacity for each binder is 30% PFA > 60% GGBS > OPC > 10% SF. Blended mortars containing SF show less binding capacity. However the blended mortars containing PFA and GGBS show more binding capacity

2) At 28days, the CTL expressed by total chloride content, of OPC, 30% PFA, 60% GGBS and 10% SF showed 1.28-1.44, 0.36-0.45, 0.69-0.79 and 1.30-1.40% by weight of binder.

3) the CTL expressed by free chloride, of OPC, 30% PFA, 60% GGBS and 10% SF showed 0.89-0.96, 0.14-0.21, 0.40-0.48 and 0.89-0.94 by weight of binder, when corrosion initiation is regarded as exceeding 1-2 mA/m^2.

4) Difference between the CTL ranges, expressed total chloride and free chloride was minimum and maximum 0.22%-0.48% by weight of binder. This difference for the CTL is more apparent at 60, 90 days.

5) The corrosion potential, threshold potential for corrosion, for OPC and 10% SF mortars were higher than for 30% PFA and 60% GGBS due to delayed hydration at early ages of PFA and GGBS.

6) The polarization resistances for OPC and 10% SF mortar were measured higher than those of 30% PFA and 60% GGBS due to high alkalinity of the pore solution.

Acknowledgments

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