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Chloride Binding Capacity in Fly Ash Concrete

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Abstract

This paper is aimed to propose a model for deriving chloride binding capacity or amount of fixed chloride in cement-fly ash concrete. The model for fixed chloride is useful for computing free chloride concentration in the pore solution of hardened concrete. Free chloride is the type of chloride, which can travel in the concrete and is vulnerable to the reinforcing steel. In this study, the chloride was considered to be bound by the cement-fly ash paste system and other inert materials such as aggregates. Chloride binding capacity of binders is reasonably considered to depend on both the chloride binding capacity of hydration and pozzolanic reaction products. Chloride binding capacity of the binders was then assumed to vary with the cement content and the pozzolanic reaction factor of fly ash. Tests were conducted to find equations for chloride binding capacity of cement-fly ash paste and it was proposed that the SiO_2/CaO ratio of the total binder was useful as a pozzolanic reaction factor for deriving the chloride binding capacity of the cement-fly ash system. For both tested types of fly ashes, increase the content of fly ash in the cement-fly ash system increased the binding capacity until the amount of fly ash was too large (SiO_2/CaO ratio was larger than 0.8), then the binding capacity reduced. The equations for determining chloride binding capacity of cement-fly ash binders were proposed. The equations will be utilized in the mathematical model for simulating chloride movement and steel corrosion in hardened concrete.

1. Introduction

Among various exposure conditions that concrete and reinforced concrete structures may be subjected to during their service life, corrosion of steel reinforcement is one of the major causes of deterioration leading to shortened service life of reinforced concrete structures. Chloride induced corrosion is the most seriously known type of corrosion.

With years of researches and studies into the fly ash and the behavior of fly ash concrete, it has been confirmed that fly ash can be used to improve many performances of the concrete [1,2,3]. Many researches reported the benefit of fly ash to reduce chloride penetration into the concrete. Also, various mathematical models had been developed to simulate chloride movement in concrete [1]. As only the free chloride in the pore solution is able to travel in the concrete, it is necessary to determine the chloride binding capacity of the concrete. Various studies had been conducted to determine the chloride binding capacity of binding materials. However, it was considered in this study that all particles, reactive or inert, in the concrete can bind chloride.

Maruya, Tangtermsirikul and Matsuoka proposed a mathematical model to simulate chloride movement in hardened concrete under various environments [1]. They introduced a constitutive model for chloride binding capacity of different types of binder including cement only, binary binders such as cement-fly ash, cement-slag and trinary binder like cement-fly ash-slag. However, the effect of difference in chemical composition of the pozzolans and content of the pozzolans in the binders were not considered. The effect of chloride binding by aggregates was not considered either. In this paper, the effect of chemical composition and amount of fly ash in the binder on chloride binding capacity and also the binding capacity of inert materials like aggregates will be quantificatively formulated.

2. Theoretical Background

Generally, with respect to the individual corrosion phenomena as well as for the transport processes, two types of chloride in concrete must be distinguished. These are the free chloride ions dissolved in the concrete pore solution, and chloride ions that are combined in or bound to different reaction products of the cementitious materials.

It is known that the chloride binding capacity depends on chemical composition of cement, especially the content of C_3A and the type and content of blending compounds such as fly ash [2,3], because they affect both the fixed chloride ions by chemical absorption and physical absorption. Blending Portland cement with fly ash, lowers the content of C_3A, which is the most important compound for chemical binding of chloride ion to form Friedel's salt, $3CaO.Al_2O_3.CaCl_2.10H_2O$, in contrast, increases the formation of CSH and CSH like phases, which bind chlorides by physical absorption due to surface forces.[2]

2.1. Quantification of Fixed and Free Chlorides

The quantification of fixed chloride in concrete is achieved from the concept that chloride is bound by the chemical adsorption of cementitious powders (reactive materials) and the physical adsorption of non-reactive materials (inert material) such as aggregate and limestone powder. In this study, the fixed chloride factor, which is the weight ratio of fixed chloride content to total chloride content, was used as an index for defining the chloride binding capacity of cementitious materials. Whereas, the fixed chloride content per unit weight of non-reactive materials was defined as the chloride binding capacity of the non-reactive materials. Considering these factors, the following equation was proposed to determine the amount of fixed chloride in the cement-fly ash concrete, which includes Friedel's chloride and adsorbed chloride in solid phase.

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

where α_{fixed}(binder) is the fixed chloride factor of 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).

2.2. Chloride binding capacity of reactive materials

In the cement-fly ash system, the powders can bind chloride by the chemical reaction of C_3A in the cement and the physical absorption of CSH gel, which is produced from the hydration reaction of C_3S, C_2S in the cement and the pozzolanic reaction of fly ash. For the reaction of fly ash, the supply of water and $Ca(OH)_2$ must be enough for the reaction of the fly ash. The $Ca(OH)_2$ produced by the reaction of cement with water are essential for the reaction of the fly ash to produce CSH gel. If there is an insufficient supply of $Ca(OH)_2$ in liquid state, the reaction of fly ash is decreased and the quantity of bound chloride is also decreased. In the proposed model for material parameter of cement-fly ash system, 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. Thus, the fixed chloride factor of binders with any type of fly ash and any replacement percentage can be calculated by the following relationship.

$$\alpha_{fixed}(binder) = r \times \alpha_{fixed}(cement) \quad (2)$$

where α_{fixed}(binder) is the fixed chloride factor of binders, α_{fixed}(cement) is the fixed chloride factor of cement and r is the pozzolanic reaction factor indicating the effect of pozzolanic reaction of fly ash on chloride binding capacity of the cement-fly ash binder.

The fixed chloride factor of cement was obtained from previous study [1]. The equation of fixed chloride factor of cement was

$$\begin{aligned}
&for\ C_{tot} \leq 0.15 \\
&\alpha_{fixed}(cement) = 1 \\
&for\ 0.15 \leq C_{tot} \leq 1.0 \\
&\alpha_{fixed}(cement) = -0.060 \times C_{tot}^{6} + 0.637 \times C_{tot}^{5} \\
&\quad -2.688 \times C_{tot}^{4} + 5.762 \times C_{tot}^{3} \\
&\quad -6.608 \times C_{tot}^{2} + 3.861 \times C_{tot} \\
&\quad -0.375 \\
&for\ 1.0 \leq C_{tot} \leq 2.8 \\
&\alpha_{fixed}(cement) = -0.001 \times C_{tot}^{6} + 0.018 \times C_{tot}^{5} \\
&\quad -0.104 \times C_{tot}^{4} + 0.327 \times C_{tot}^{3} \\
&\quad -0.595 \times C_{tot}^{2} + 0.572 \times C_{tot} \\
&\quad +0.315 \\
&for\ 2.8 \leq C_{tot} \\
&\alpha_{fixed}(cement) = 0.009 \times C_{tot} + 0.474 \qquad (3)
\end{aligned}$$

shown in Eq.(3)

It is, therefore, necessary to determine r to be able to quantify the fixed chloride content of cement-fly ash system.

2.3. Chloride Binding Capacity of Non-Reactive Materials

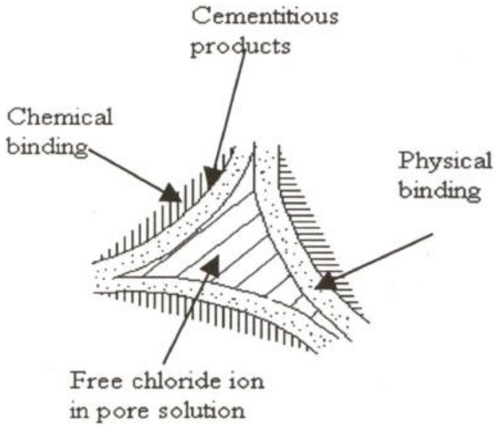

Fig.1 3-Forms of chlorides in concrete

Since concrete also includes inert materials such as, sand, limestone powder and coarse aggregate, etc. These materials can adsorb chloride ion by the surface force. Fig 1 illustrates 3 forms of chlorides in the concrete, e.g., chemically bonded, physically bonded and free chloride ions. It is reasonably considered from Fig 1 that the amount of physically bonded chloride depends on the surface area of the solid particle. So, for fine particles, the chloride binding capacity is considered to relate to the specific surface area.

It was assumed in this study that chloride binding capacity of inert materials is independent of that of 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. For finer materials, such as limestone powder, specific surface area was tested by air permeability. However, for fine aggregate, the specific surface area of irregular aggregate can be estimated by multiplying the angularity factor ψ to the specific surface area of the assumed spherical aggregate [4].

3. Experiments

3.1. Chloride Binding Capacity of Reactive Materials

Mix details are shown in Table 1. The

Table 1 Mix proportion of the tested samples

Component					Test Age (days)	Total Cl % (by wt of binder)		
w/b	f/b	c (g)	f (g)	w (g)				
0.4	0	2091	0	836	90, 180	0.8	1.6	2.4
0.4	0.3FAA	1813	777	1036	90, 180	0.8	1.6	2.4
0.4	0.5FAA	1237	1237	989	90, 180	0.8	1.6	2.4
0.4	0.7FAA	710	1656	946	90, 180	0.8	1.6	2.4
0.4	0.3FAB	1813	777	1036	90, 180	0.8	1.6	2.4
0.4	0.5FAB	1237	1237	989	90, 180	0.8	1.6	2.4
0.4	0.7FAB	710	1656	946	90, 180	0.8	1.6	2.4

w : water, b : total binder(c+f), c : cement, f : fly ash.

Table 2 Chemical composition of the tested cement and fly ashes

Binder type	Chemical composition (% by weight)							
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
Cement	64.5	20.0	6.2	3.3	1.5	2.41	0.01	0.5
Fly ash A	15.2	40.1	22.8	11.7	3.5	2.09	0.91	2.4
Fly ash B	1.6	55.2	32.5	4.2	0.5	0.15	0.23	-

chemical composition of the cement and fly ashes, used in this study, are given in Table 2. Fly ash A is the fly ash collected from the Mae-Moh lignite power plant in Lampang province, north of Thailand. Fly ash B was collected from the coal power plant in Rayong province, in the eastern part of Thailand. The chloride ions were introduced into the mixture by dissolving appropriate quantities of NaCl in the mixing water. After thorough mixing, all specimens were cast in the cylinder mould with dimension $\phi 50\times 100$ mm and wrapped with plastic sheet in order to prevent water from evaporating from the specimens and to stabilize chemical composition in the specimens for curing.

At the test age, pore solution was expressed from four specimens with the same mix proportion using a pore solution apparatus in Fig 2. Each specimen was subjected to two loading cycles up to about 200 tons and the expressed pore solution, derived from the fluid drain at the base of the apparatus, was collected in a plastic syringe. Care was taken to avoid undue exposure of the solution to air and the samples obtained were stored in sealed plastic vials. The expressed solution was then diluted and analyzed for chloride ion concentration by titration with $AgNO_3$.

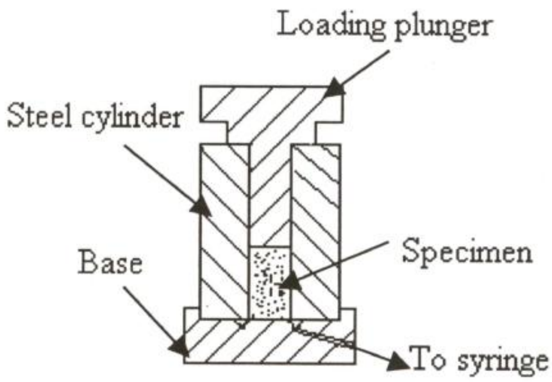

Fig 2 Pore solution apparatus

3.2. Chloride Binding Capacity of Non-Reactive Materials

For fine aggregate, the experiment was conducted by immersing 500g of river sand in the 2% NaCl solution and storing in the closed system condition, in order to prevent water from evaporating from the solution. After a period of 30 days, the solution was diluted and analyzed for chloride ion concentration. The chloride ion disappeared from the solution was considered to be bound by the sand. Then, the quantity of bound chloride was computed in the term of fixed chloride content per unit weight. For finer materials, three types of limestone powder (A, B, C), that have different specific surface area, were used in this study. They were obtained from the cement production plant in Saraburi province in the central part of Thailand. The specific surface area of the limestone powders is shown in Table 3. According to the assumption that the chloride binding capacity of inert materials is independent of the binding capacity of cement, the binding capacity of limestone powder was derived by subtracting the chloride binding capacity of the cement from that of the cement-limestone paste in the pore solution test. The mix proportions of the cement-limestone mixtures used in this test are shown in Table 4.

Table 3 Specific surface area of limestone powder

Type	LSA	LSB	LSC
Specific surface area cm^2/g	4520	2620	2670

Table 4 Mixture proportion

Component					Test Age (days)	Total Cl (% by wt of binder)		
w/b	LS/b	c (g)	LS (g)	w (g)				
0.4	5%LSA	1900	100	800	90, 180	0.8	1.6	2.4
0.4	10%LSA	1800	200	800	90, 180	0.8	1.6	2.4
0.4	15%LSA	1700	300	800	90, 180	0.8	1.6	2.4
0.4	5%LSB	1900	100	800	90, 180	0.8	1.6	2.4
0.4	10%LSB	1800	200	800	90, 180	0.8	1.6	2.4
0.4	15%LSB	1700	300	800	90, 180	0.8	1.6	2.4
0.4	5%LSC	1900	100	800	90, 180	0.8	1.6	2.4
0.4	10%LSC	1800	200	800	90, 180	0.8	1.6	2.4
0.4	15%LSC	1700	300	800	90, 180	0.8	1.6	2.4

w : water, b : total binder(c+LS), c : cement, LS : limestone

4. Results and Discussions

4.1.Chloride Binding Capacity of Reactive Materials

It can be seen from Table 5 that for both types of the tested fly ash, the fixed chloride content of paste with larger fly ash content is larger, however the fixed chloride content reduces when fly ash content is too much increased. Also, the chloride binding capacity of the two fly ashes is not the same. It is assumed that the hydration and the pozzolanic

Table 5 Fixed Cl content to total Cl content ratio

Fly ash replacement percent	Fly ash type	Fixed Cl to total Cl ratio
30%	A	0.578
50%	A	0.603
70%	A	0.372
30%	B	0.545
50%	B	0.639
70%	B	0.598

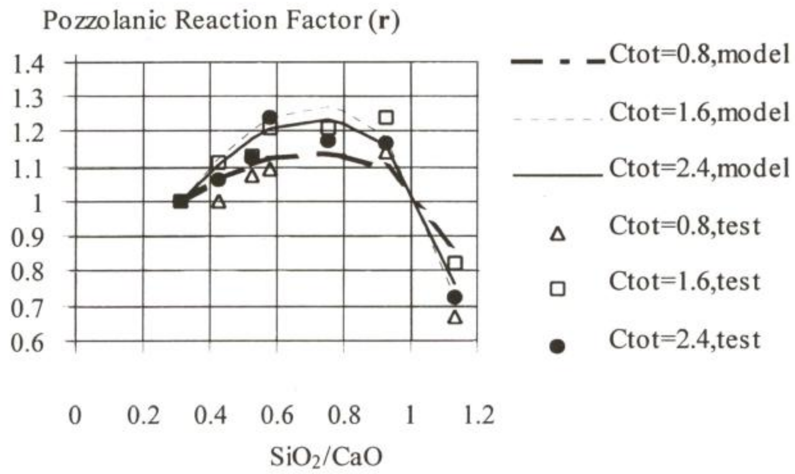

Fig.3 Relationship between the pozzolanic reaction factor and the SiO_2 to CaO ratio

reaction products are strongly dependent on the CaO and the SiO_2 content in cement-fly ash system. Therefore, it was proposed in this study that the SiO_2 to CaO ratio of the total binder would be used as a pozzolanic reaction factor for determining the chloride binding capacity of the cement-fly ash system. The relationship between the pozzolanic reaction factor and the SiO_2 to CaO ratio, obtained from the test result, was shown in Fig 3. By using the SiO_2 to CaO ratio as a parameter, the binding capacity of both fly ashes can be unified to a unique function as in Fig.3.

From the test result in Fig 3, the pozzolanic reaction factor increases with increase of the SiO_2 to CaO ratio due to the increase of pozzolanic reaction when SiO_2 content increases under the condition of sufficient $Ca(OH)_2$ paste environment. It can be noted that the pozzolanic reaction factor increases up to the SiO_2/CaO ratio about 0.8 whereas beyond 0.8, the binders is not capable of producing enough free lime ($Ca(OH_2)$) for pozzolanic reaction. For paste with cement only, the SiO_2/CaO ratio of the tested cement was 0.31. The pozzolanic reaction factor of the paste with cement only was set to be a reference value of 1.0 to be compatible to Eq (4). It means that, in the cement system, the chloride binding capacity does not depend on the pozzolanic reaction of fly ash but on the hydration reaction of cement only. From the best fit of test result, pozzolanic reaction factor can be computed by the following equations.

$$\textit{for } C_{tot} \le 0.3$$
$$r = 1$$

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

$$\textit{for } 2.4 < C_{tot}$$
$$r = 1 + A \times \left(0.31 - 0.018 \times C_{tot}^{1.638}\right) \times \sin\left[\frac{\pi}{0.8} \times \left(\left(\frac{SiO_2}{CaO}\right)_{c+f} - \left(\frac{SiO_2}{CaO}\right)_c\right)\right] \qquad (4)$$

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

$$A = 10 \textit{ for } 1.1 < \left(\frac{SiO_2}{CaO}\right)_{c+f}$$

$$\left(\frac{SiO_2}{CaO}\right) = \frac{R \times (SiO_2)_f + (1-R) \times (SiO_2)_c}{R \times (CaO)_f + (1-R) \times (CaO)_c} \qquad (5)$$

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 (%) and r is the pozzolanic reaction factor

4.2. Chloride Binding Capacity of Non-Reactive Materials

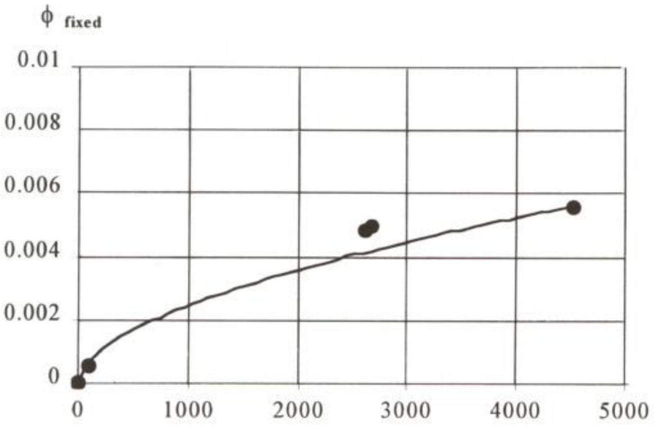

Fig.4 Relationship between ϕ_{fixed} and specific surface area of non-reactive materials (cm^2/g)

From the study of chloride binding capacity of non-reactive materials, 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 is shown in Fig 4 and can be expressed as follows.

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

From this relation, it can be found that if the specific surface area of non-reactive materials is higher, the amount of absorbed chloride per unit weight of the material is also higher.

For the coarse aggregate, it is reasonable to assume that the fixed chloride content per unit weight is very small when compared to those of sand and limestone powder. Therefore, it is proposed in this study that the fixed chloride content per unit weight of coarse aggregate may be neglected in the quantification of fixed chloride.

As in the above concept, these proposed relations are used to obtain the quantification of fixed chloride and free chloride as shown in Eq. (1) and Eq. (7).

$$C_{free} = \frac{C_{tot}}{100} \times B - C_{fixed} \quad (7)$$

where C_{free} is the free chloride content in 1 m^3 of concrete (kg/m^3).

5. Conclusion

For fly ashes both low and high percentages of CaO, increasing the content of the fly ash in the cement-fly ash system increased the binding capacity until the amount of fly ash was too large i.e. SiO_2/CaO ratio was larger than about 0.8, then the binding capacity reduced. For non-reactive materials, the fixed chloride content is higher when the specific surface area of the material is higher. The effect of fixed chloride content per unit weight of coarse aggregate may be neglected because it is very small when compared to those of sand and limestone powder.

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