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Binding of externally supplied chlorides in micro silica concrete under field exposure conditions

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ABSTRACT

Chloride binding has remarkable influence on the chloride penetration and hence, on the time to corrosion initiation in reinforced concrete structures. Previous studies have mainly looked at the chloride binding from internal sources in laboratory, which is not representative of practical situations. The current work focuses on the chloride binding characteristics of concrete samples exposed to an external source of chlorides from the sea water at Persian Gulf region. Some of the important parameters including w/c ratio, silica fume replacement and effect of chloride concentration on chloride binding were investigated in order to provide insight into the distribution of free and bound chloride ions after a long-term exposure.

The results of the current study suggest that the chloride binding capacity increases with increasing the w/c ratio and chloride concentration but decreases by using silica fume. A general equation was also developed correlating the total and bound chloride in order to obtain more accurate service life prediction.

1. Introduction

The corrosion of steel reinforcement initiated by the chloride ion attack to the passive layer of steel is the dominant cause of deterioration of reinforced concrete structures in marine environment [1]. The corrosion damage in these concrete infrastructures is often observed by rust-staining of the surface and cracking and spalling of the concrete cover due to the formation of expansive corrosion products [2]. Corrosion can also lead to the decrease in the reinforcing steel cross-section that, in turn, results in the loss of serviceability often much earlier than the designed service life of the structure [3]. A significant cost for the repair and other associated issues is annually imposed specially in hot weather areas such as Persian Gulf region. A challenge for civil engineers is to find preventive solutions, and to be able to estimate the service life of concrete infrastructure.

Chloride ions can be present in concrete from different sources such as aggregate contamination, use of chloride bearing water or chloride bearing admixtures. However, most commonly chlorides ingress into concrete from the external environment, for example, through de-icing salt or sea water [4–6]. It is known that the chlorides either added during mixing or later penetrated into concrete, can be bound to the hydrated cement products in concrete by physisorption and chemisorptions [7]. In the context of chloride-induced corrosion, the service life of concrete structures is divided into two periods according to Tutti's model: the first is generally related to the time required to reach to a critical chloride concentration at the steel bar surface (t_{init}), and the second is the time for corrosion propagation when the structure has been damaged by corrosion beyond acceptable limits (t_{prop}). The former is regarded as the service life in some models [8,9], while the latter has been considered as the service life of a structure in other models [10].

Chloride binding has an important effect on chloride penetration and hence, on the time to corrosion initiation. Chloride binding process removes some part of the chloride ions from the diffusion path and only the free chlorides are likely to ingress further toward the rebar, and hence the time to achieve a threshold level of chloride ions at the steel surface is increased. Additionally, the formation of Friedel's salt modifies the pore structure of the cement paste by decreasing the porosity which results in a decrease of the rate of chloride penetration [11]. Therefore chloride binding has significant implications in the study of the service life of concrete structures.

A complete set of field experiments were conducted in order to investigate the effect of different parameters on chloride diffusion and binding isotherm. These experiments were carried out as the main part of a national project on the durability of concrete in Iran [6,10,12–15]. Concrete specimens of 20 mix designs were prepared

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and exposed to marine conditions in Persian Gulf environment. Sampling was performed at various ages up to 60 months and analyzed for chloride diffusion coefficient and binding characteristics.

2. Parameters affecting the chloride binding

Several parameters are known to affect the binding capacity, including: cement composition specially the C_3A and C_4AF contents, chloride concentration, water to cementing material ratio (w/cm), curing condition, pH (hydroxyl concentration), temperature, carbonation, sulfate ions, cation associated with chlorides, and supplementary cementing materials [1,11,15].

It is known that C_3A component of Portland cement plays a major role in the binding of chloride ions. The chloride ions are consumed in the chemical reactions with C_3A to produce calcium chloroaluminate hydrate ($C_3A{\cdot}CaCl_2{\cdot}10H_2O$) commonly known as Friedel's salt [1]. The increase in C_3A content of the Portland cement, therefore, results in an increase of binding capacity. Usually OPC has a considerably higher binding capacity than sulfate resisting Portland cement (SRPC) due to the relatively low C_3A content in the latter [15]. It has also been suggested that a similar reaction between C_4AF and chlorides results in the formation of an equivalent product to Friedel's salt, known as calcium chloroferrite ($C_3F{\cdot}CaCl_2{\cdot}10H_2O$) [1]. Adsorption of chloride ion to the C–S–H surfaces as physical binding is another mechanism by which chloride ions are bound. Ramachandran [16] distinguished three types of interaction between chlorides and C–S–H: chlorides can either be present in a chemisorbed layer on the hydrated calcium silicates, penetrate into the C–S–H interlayer spaces, or be intimately bound in the C–S–H lattice.

Chloride concentration is also one of the important factors affecting the chloride binding. Several studies have confirmed that a higher concentration of external chloride results in a relatively higher level of chloride binding [17–19]. Moreover, by increasing w/c ratio, chloride binding increases and by increasing OH^- concentration chloride binding decreases [1]. Tritthart [20] immersed cement pastes in chloride solutions having variable pH values, and found that chloride binding increased with decreasing the pH value. Other researchers [21,22] also found that the hydroxyl concentration in the external environment has a significant influence on the chloride binding. The general tendency is that the higher the hydroxyl concentration in the pore solution, the lower the amount of bound chloride. As pointed out by Tritthart [20], a competition exists between hydroxyl and chloride ion for adsorption sites on hydrated cement surface. On the other hand, Roberts [23] suggested that an increase in the pH of the pore solution increases the solubility of Friedel's salt, thereby; releasing chloride to the pore solution and reducing the amount of chemically bound chloride. Curing has an important effect for samples with internal chloride and by increasing curing time chloride binding increases [15].

Arya et al. [15] studied the chloride binding behavior of cement paste with 15% silica fume by exposing the cement paste to 0.56 M NaCl solution, and found that the partial replacement of cement with silica fume decreased chloride binding, which was also confirmed by other studies in the case of external chloride [1,23]. It has been suggested that three changes may occur by partial replacement of cement with silica fume: (1) an increase of the content of C–S–H having lower C/S ratio; (2) a reduction in pH value and (3) a dilution effect of C_3A [11]. The increase in C–S–H by using silica fume may be in favor of binding and physical binding improved, but, the lower C/S ratio in silica fume samples may also have a negative impact on binding [11,24]. Page and Vennesland [25] utilized differential thermal analysis and thermogravimetry and found that the amount of Friedel's salt decreases with increasing the silica fume content. Lambert et al. [26] and Page and Vennesland [27] in another research investigated the influence of micro silica additions on the capacity of Portland cement to bind chloride ions, introduced as sodium chloride dissolved in the mix water. They concluded that the proportion of bound chloride present in pastes with w/b ratio of 0.5, containing total chloride ion additions equivalent to 1.0% by mass of (cement + silica fume) decreased as the proportion of micro silica was increased. This was attributed to a decrease of pH from 13.9 in control sample to 11.5 when 30% of the cement was replaced by micro silica.

3. Methods of chloride extraction

Chloride ions as penetrate into concrete can be bound to the hydrated cement products in the form of Fridel's salt or sorbed to C–S–H. Since only "free" chloride ions in the pore solution can move, chloride binding can affect the resistance of concrete to chloride ingress by delaying the penetration process and must to be measured for estimation of service life of concrete structures. Most laboratories working on the durability of concrete are equipped to determine the total chloride content in a sample using current standard methods [28,29]. The free chloride content, however, can be determined through several methods which has certain practical difficulties. [30]. Arya and Newman [31] assessed four methods of determining the free chloride content including: extraction and analysis of pore fluid, leaching techniques, quantitative X-ray diffraction analysis and empirical relationships. Loser et al. [32] defined the chloride content determined with diluted nitric acid as the total chloride whereas the water-soluble chloride content is defined as the free chloride content. Among these methods, a relatively reliable method is to extract and analyze the pore fluid which is accurate but requires special equipment not always available and cannot be easily applied on the existing structures.

Some investigators suggested that the leaching techniques overestimates free chloride content, because in this way only a small amount of free chloride remains in pore solution of concrete and most of chloride ion leached from pore solution by different leaching techniques. [31,33]. According to Arya and Newman [31] a good agreement exists between the chloride content values obtained through pore solution extraction and the results from the leaching technique. However, the leaching technique offered a more practical method of determining the free chloride content. Loser et al. [32] and Round-Robin tests [29] show that the free chloride content can be determined reasonably rigorously if the contact time between water and crushed concrete sample lasts a short time. The pore solution is always considered to be at equilibrium with the solids in the cement paste. This assumption may be valid, when the chloride ions penetrate slowly, just in the case of diffusion alone. Mohammed and Hamada [34] suggested that the prediction of a relationship between the total and free chloride contents in concrete requires long-term exposure experiments under marine environment where chlorides are allowed to diffuse into concrete naturally. The present study considers the total chloride to be the acid-soluble chloride in concrete according to ASTM C1152 and free chloride refers to the water-soluble chloride in concrete extracted by water according to ASTM C1218.

It should be noted that, in field studies, chloride ions may penetrate into concrete through different mechanisms. The diffusion is, however, the dominating mechanism in the case of saturated concrete such as concrete submerged in seawater. In the present research concrete samples were placed in the tidal zone. Therefore, in order to analyze the results under pure diffusion, the first outer layer of concrete (about 10 mm) which refers to convection zone [35,36] was not considered in the calculations. Below the "convection zone" in the cover region, the concrete remains moist and chlorides penetrate further by diffusion regardless of the external moisture conditions.

4. Experimental program

4.1. Materials

The cementitious materials used in this study were Portland cement (PC) equivalent to ASTM Type II, silica fume (SF) obtained from Azna ferro-silicon alloy manufacture. The aggregates used were crushed limestone from Metosak plant and were graded according to ASTM C33. Polycarboxylate ether polymer superplasticizer and lignosulphonate plasticizer were used for the mixes in order to achieve a comparable workability in the fresh concrete for different mix designs.

4.2. Mixture proportions

Four separate series of concrete mixes were developed at the water to cementitious ratios of 0.35, 0.40, 0.45 and 0.50. All series included four SF mixes with 5%, 7.5%, 10% and 12.5% replacement of cement by silica fume. All series were proportioned to have the same total cementitious materials content of approximately 400 kg/m (cement + silica fume) which is typical of those used in the marine concrete structures in Iran. The details of the concrete mixture proportions are given in Table 1.

4.3. Specimen preparation, casting and curing

The concrete mixtures were prepared in the laboratory. The freshly mixed concrete was tested for air content according to ASTM C231; slump according to ASTM C143 and unit weight in accordance with ASTM C138. Properties of fresh concrete are summarized in Table 2. Concrete prisms measuring 150 × 150 × 600 mm in dimension were cast in steel mold and compacted on a vibrating table. The molds were covered with the burlap kept moist for 24 h after casting. The specimens were removed from the molds and were cured in water saturated with calcium hydroxide at 21 °C for 28 days. After the curing period, the specimens were sealed on four sides using epoxy polyurethane coating. This was conducted in order to ensure that one dimensional diffusion occurs during the exposure of the specimens to chlorides. The specimens were moved to a research site in the city

Table 2
Properties of mixture samples.

Composition	w/b ratio	Air content (%)	Comp. strength (MPa)	
			7-day	28-day
PC*	0.35	2.8	51.5	53.2
PC	0.40	2.9	50.0	41.4
PC	0.45	3.1	36.3	44.9
PC	0.50	2.7	25.9	33.9
PC + 5%SF**	0.35	3.5	49.8	66.8
PC + 5%SF	0.40	3.0	47.4	69.8
PC + 5%SF	0.45	2.6	38.3	57.9
PC + 5%SF	0.50	3.6	37.3	50.4
PC + 7.5%SF	0.35	3.6	50.6	74.8
PC + 7.5%SF	0.40	3.0	44.0	65.3
PC + 7.5%SF	0.45	2.6	37.8	59.6
PC + 7.5%SF	0.50	1.6	34.4	53.9
PC + 10%SF	0.35	3.1	57.9	79.6
PC + 10%SF	0.40	2.9	47.3	71.7
PC + 10%SF	0.45	2.1	35.4	55.0
PC + 10%SF	0.50	2.5	27.7	44.2
PC + 12.5%SF	0.35	3.0	51.6	64.6
PC + 12.5%SF	0.40	3.1	43.2	66.9
PC + 12.5%SF	0.45	2.6	37.9	65.9
PC + 12.5%SF	0.50	2.4	24.7	49.1

* Control mix.
** Silica fume.

Table 3
Chemical analysis of Persian Gulf water.

Ion	Content (ppm)
Ca^{++}	480
Mg^{+}	1600
Na^{+}	12,600
K^{+}	470
SO_4^{-}	3300
Cl^{-}	23,400

Table 1
Details of the concrete mixtures.

w/b	SF (%)	Binder	(kg/m^3)	Fine aggregates (kg/m^3)	Coarse aggregates (kg/m^3)	Superplasticizer (kg/m^3)
		Cement	SF			
0.35	0	400	–	936	973	7.2
0.35	5	380	20	931	968	–
0.35	7.5	370	30	931	968	6.0
0.35	10	360	40	906	968	6.4
0.35	12.5	350	50	929	964	4.8
0.40	0	400	–	836	1022	2.2
0.40	5	380	20	833	1018	3.6
0.40	7.5	370	30	832	1017	3.2
0.40	10	360	40	830	1014	3.6
0.40	12.5	350	50	829	1012	3.8
0.45	0	400	–	815	997	2.4*
0.45	5	380	20	810	990	1.2
0.45	7.5	370	30	808	998	2.0
0.45	10	360	40	807	985	1.8
0.45	12.5	350	50	806	986	2.0
0.50	0	400	–	778	956	1.2
0.50	5	380	20	793	991	0.8
0.50	7.5	370	30	784	959	1.2
0.50	10	360	40	820	1020	1.8
0.50	12.5	350	50	782	955	2.0

* In this mix Lignosulphonate plasticizer was used instead of polycarboxylate ether polymer superplasticizer.

of Bandar-Abbas located on the north shore of the Persian Gulf, and subjected to tidal zone exposure condition. Chemical analysis of sea water is shown in Table 3.

4.4. Sampling and testing

The current work presents the long-term results obtained by sampling after 5 years of exposure. A 100 mm width section was cut from end of the prism specimens. The cut surface of the remaining part was coated and the specimen was moved back to the exposure condition for future sampling. Additional details can be found elsewhere [12]. The 150 × 150 × 100 mm slices were taken to the laboratory for the determination of the chloride content. A nominal 45 mm diameter core was taken from each slice for chloride concentration profiles. Each core was ground in eight increments at regular intervals from the exposed surface to the depth of chloride penetration. The depth intervals for powder grinding were determined according to chloride penetration depth so that a minimum of 8 points span the range from 1 mm below the exposed surface to a depth with a chloride-ion content equal to, or slightly greater than, the initial chloride-ion content. The first 1 mm powder was not included in calculations as it might be affected by actions such as washout. The fine particles from each ground layer were collected and analyzed separately for acid-soluble chloride according to ASTM C1152 and ASTM C114, part 19 and water-soluble chloride according to ASTM C1218. It is noted that the water-soluble chloride concentration is defined here as the free chloride and acid-soluble chloride concentration as the total chloride. Also the ratio of bound/total chloride was defined as the chloride binding capacity.

5. Results

5.1. Effect of w/c ratio on chloride binding

It has been reported that the water to cement ratio has some influence on the binding isotherms of pastes, but has little influence on the isotherms of the mortars, and the binding capacity of the pastes is apparently higher than that of the mortars [7]. Arya et al. suggested that the free chloride content increases with increasing w/c ratio, the bound chloride remains approximately constant and, therefore, the percentage of binding decreases with increasing w/c ratio [15].

Fig. 1 presents the results for the effect of the w/c ratio on the bound chloride content of the control mixture (Portland cement concrete). It is observed that the 0.35 w/c ratio samples clearly tend to bind lower chloride than the 0.50 w/c ratio mixtures. The amount of bound chloride in mixtures with 0.40 and 0.45 water/cement ratios are similar to each other and both series of curves remain very close together. The authors believe that as previously discussed by Arya et al. [15], in this state by increasing water/binder ratio, the amount of bound chloride increases and this is probably due to the greater porosity and permeability of the higher w/c ratio paste allowing greater access of chloride ions to the cement particles. This trend repeated for mixtures including different percent of silica fume for two different total chloride concentration of 0.50% and 0.10% by mass of concrete (Fig. 2). The results in Fig. 2 clearly confirm that by increasing the water/binder ratio, the amount of bound chloride increases noticeably but for mixtures with 0.40 and 0.45 water/binder ratio does not change very much and the total amount of bound chlorides in these cases appear to be independent of the water/binder ratio. Also by using silica fume not only bound chloride content decreases for all the mixtures, but also the slope of the curve is initially high until about 5% silica fume and then decreases by increasing the silica fume replacement. When total chloride is low (Fig. 2b) the results agree well with the trend in those in Fig. 2a.

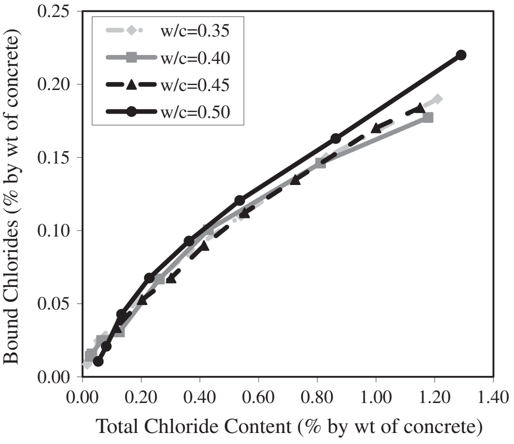

Fig. 1. Chloride binding isotherms of control mixtures with different w/c ratio.

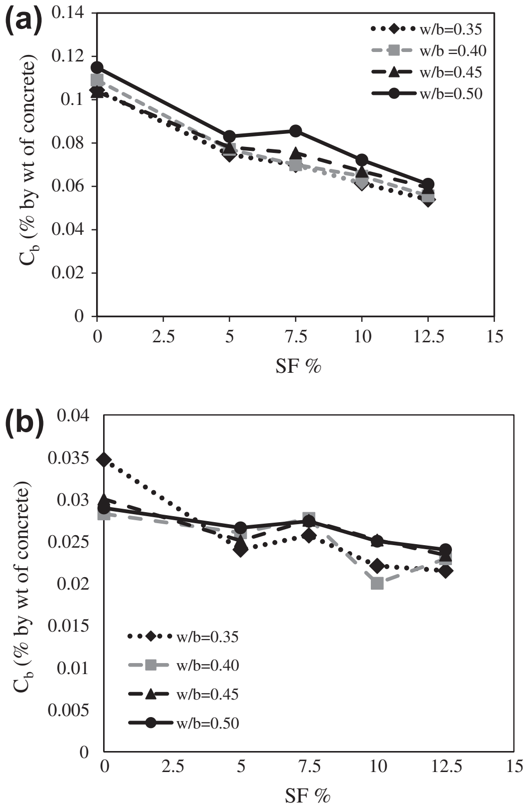

Fig. 2. Chloride binding isotherms of mixtures with different water/binder ratio and silica fume replacement (a) $C_t = 0.50$ and (b) $C_t = 0.10$ (wt% of concrete).

5.2. Chloride concentration

Chloride concentration is one of the main factors affecting the chloride binding. Several studies have confirmed that a higher concentration of external chloride results in a higher chloride concentration in the pore solution, and consequently a higher level of chloride binding [32,37–39]. The amount of bound chlorides for different total chloride concentration (0.70–0.05% by weight of concrete) versus four water/binder ratio is presented in Fig. 3. For all mixes the amount of bound chlorides markedly increases when the pore solution has higher chloride concentration. It is of interest

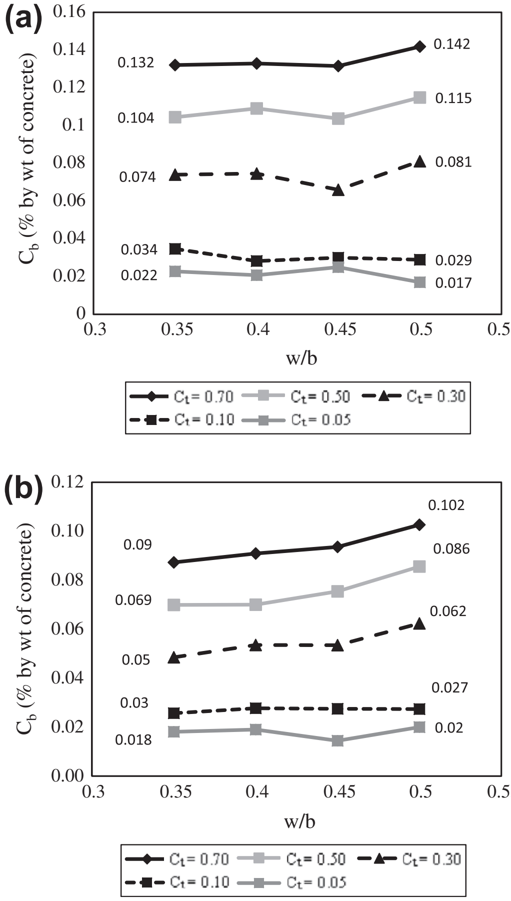

Fig. 3. Effect of Chloride concentration on chloride binding for (a) control mixture and (b) 7.5% silica fume replacement.

to notice that the bound chloride content of the control mixture at lower chloride concentration (<0.1 wt% of concrete) is similar to concrete samples containing silica fume. This may suggest that at low chloride concentrations the OPC substitution with silica fume does not generally improve the chloride binding capacity. As it can be observed in Fig. 3, these results agree with previous part, i.e. by increasing water/binder ratio bound chloride content increases unsensible. The influence of the water/binder ratio is particularly marked in the (1) high water/binder ratio range and (2) high chloride concentration. For instance, for control mixture in total chloride concentration of 0.70% (by weight of concrete) by increasing water/cement ratio from 0.35 to 0.50, the amount of bound chloride enhances 8% and for 0.10% and 0.05% chloride concentration, the amount of bound chloride is almost constant. For 7.5% silica fume mixture the amount of bound chlorides is much higher for the 0.7% chloride concentration than 0.10% and 0.05% (by weight of concrete). The minor difference noted between the amount of bound chloride of mixture including 0.40 and 0.45 water/binder ratio is insignificant with respect to the experimental precision. Accordingly, it should be emphasized that the amount of bound chlorides affected by high water/binder ratio and high chloride concentration.

5.3. Effect of silica fume

Chloride binding capacity is influenced by the content and type of the binder. Effect of silica fume replacement on chloride binding capacity is exhibited in Fig. 4. These results clearly show that the bound chloride concentration is influenced by both the use and replacement level of silica fume. Silica fume appears to have a significant influence on binding mechanisms as suggested in previous works [15,21]. In this regard the use of silica fume decreases the chloride binding capacity. It is also observed that the total amount of bound chlorides is clearly reduced for the samples containing silica fume. As it is shown in Fig. 4, the addition of 5% silica fume has markedly influenced the amount of bound chloride of all water/binder mixtures. According to Fig. 4a–d the amount of bound chlorides for all mixtures with different water/binder ratio are close to each other especially in low chloride concentration and by increasing chloride concentration, the curves far each other. In this respect the small influences of the water/cement ratio are consistent with the conclusions of previous part.

The chloride binding for 0.35 and 0.50 water/binder ratio mixtures are presented in Fig. 5. In these figures contour plot of bound to total chloride content (C_b/C_t) versus different silica fume replacement and different total chloride concentration is shown. The amount of bound chlorides appears to be predominantly influenced by the chloride concentration and silica fume. It has been established that the percentage of chloride binding increases as the depth from the surface increases regardless of water/binder ratio. It is suggested that in concrete surface chloride concentration is higher than in concrete depth, and according to part of (Section 5.2), bound chloride in concrete surface is higher than inner. As a result, although moving to inner layers of concrete, total and bound chloride concentrations both decreased, but finally C_b/C_t ratio increased because of larger reduction of C_t versus C_b.

It is noted that according to Fig. 5a, chloride binding contour has been divided in two parts: first part is for chloride concentration between 0.50% and 0.20% (by weight of concrete) and second part is for chloride concentration less than 0.20% by weight of concrete. In concrete samples including 5–12.5% silica fume replacement and chloride concentration higher than 0.2% (by weight of concrete), chloride binding measured 10–20%, While for chloride concentration less than 0.2% (by weight of concrete) chloride binding is limited to 20–40%. As previously mentioned, by reducing total chloride concentration, the amount of chloride binding (C_b/C_t) increases because of larger reduction of C_t versus C_b.

When water/binder ratio increases, similar to that is Fig. 5a, the amount of chloride binding is formed in two part. In this contour for chloride content higher than 0.25% by the weight of concrete, chloride binding measured 10–20% (Fig. 5b) whereas for chloride content less than 0.25%, chloride binding is limited to 20–30%. As previously mentioned by comparison between Fig. 5a and b, it has been expected that by increasing water/binder ratio chloride binding (C_b/C_t) decreases. In this regard results confirm as follows and by increasing water/binder ratio from 0.35 to 0.50, the amount of chloride binding reduced from 10–30% to 10–20% for first part and 20–40% to 20–30% for second part.

For control mixture with 0.35 w/c ratio the chloride binding measured about 20–30% for chloride content higher than 0.20% ($0.5\% < C_t < 0.2\%$) and 30–40% for chloride content less than 0.20% by weight of concrete. Whereas by increasing water/binder ratio, the chloride binging limited to 20–30% for whole of chloride concentration ($0.5\% < C_t < 0\%$ by wt of concrete).

5.4. pH of concrete

In addition to the chloride ions, the OH^- ion concentration in the pore solution is also known to play a significant role in the depassivation of steel. The pH of various concrete samples was measured by pH meter and is presented in Fig. 6 at various depths from the surface. These results clearly show that the hydroxyl ion concentration in the pore solution for all samples is relatively lower at surface layers of the concrete specimens. This is possibly due to the leaching of hydroxides in exposure to the external washing and drying under tidal conditions in sea water [1]. It is therefore suggested that the chloride binding isotherms, determined in the

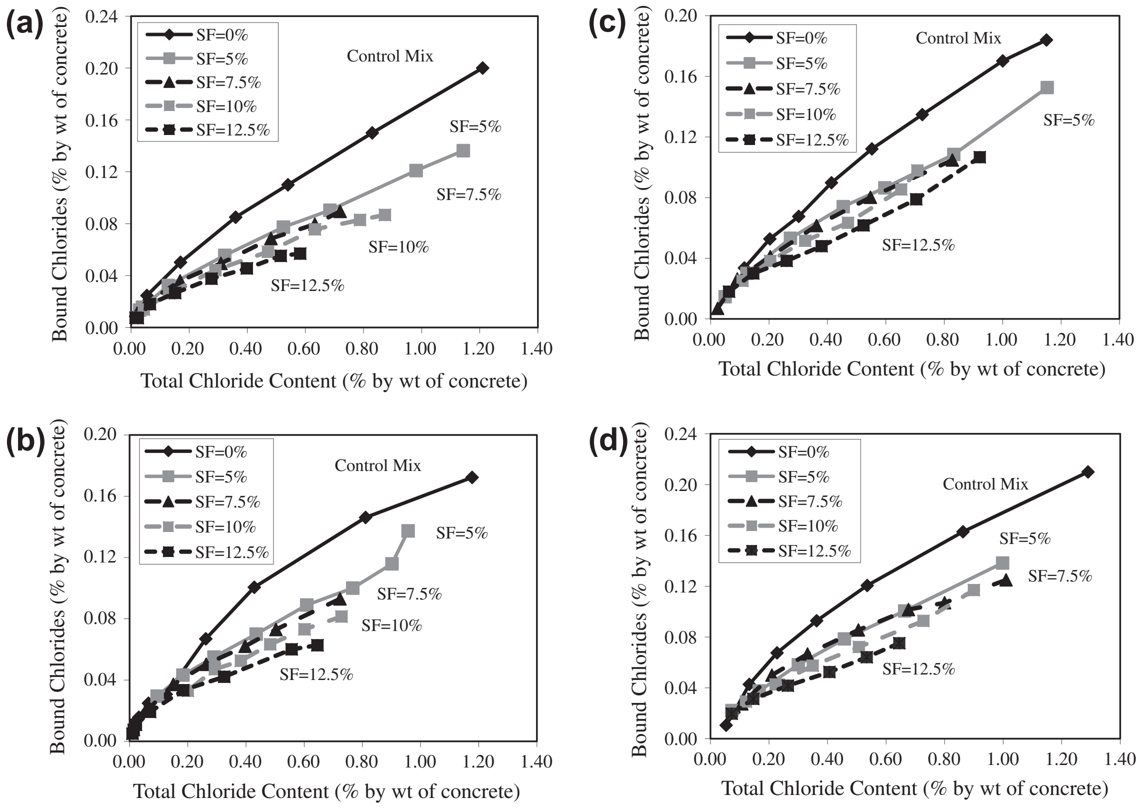

Fig. 4. Chloride binding isotherms of samples made of different silica fume replacement level after 5 years for (a) w/b = 0.35, (b) w/b = 0.40, (c) w/b = 0.45, and (d) w/b = 0.50.

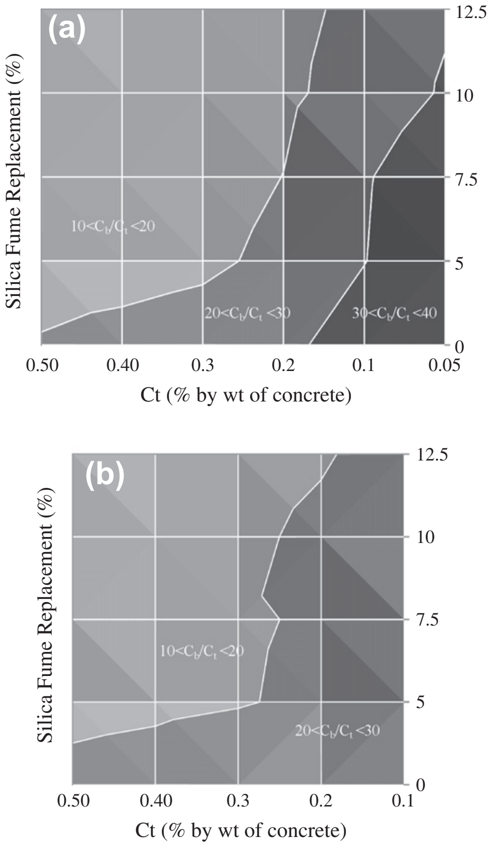

Fig. 5. Chloride binding for different Silica fume replacements for (a) w/b = 0.35 and (b) w/b = 0.50.

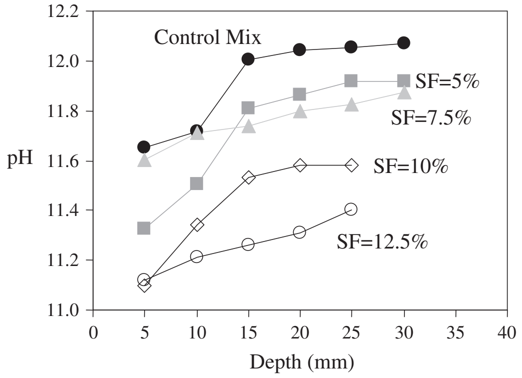

Fig. 6. Change of pH with depth for different silica fume replacement levels for w/b = 0.40.

laboratory at constant pH, are likely to result in errors when used in service life prediction models. As illustrated in Fig. 6, the OH^- ion concentration changes along the concrete depth and this counter diffusion of hydroxyl ions should be taken into consideration in service life prediction models, because of its implications on the chloride initiation time. In addition, when accounting for chloride binding in service life modeling, the variation of the pH across the depth of the concrete envelopes and its influence on chloride binding as well as the chloride threshold should be taken into account as well.

5.5. Chloride binding isotherms

Chloride binding describes the relationship between free and bound (or total) chlorides in concrete. The relationship between the free and total chloride in various samples are presented in

Fig. 7. According to these results a linear correlation is observed for all water/binder ratios and silica fume replacements. The linear isotherm can be described in the following form:

$$C_t = \alpha C_f + \beta \tag{1}$$

where α and β are constants. The α is indicative of the portion of chloride ions that are free or bound. This relationship was first proposed by Tuutti [39] and provided a good fit for his experimental data with chloride concentration lower than 20 g/l (0.56 M). Based on experimental work, some researchers suggested that this relationship is an oversimplification at high concentrations, and that it overestimates the chloride binding [1,38]. Nilsson [30] believes that Tuuti's equation for chloride isotherm underestimates chloride binding at low concentrations. Nevertheless, other researches showed that relationship is generally linear for the data obtained in situ [34,40].

The linearly fitted parameters of Eq. (1) for the relationship between the free and total chloride are given in Table 4 for various w/b ratios and silica fume contents. The decrease in the value of α as the water/binder ratio and high silica fume content decrease is in good agreement with the data presented in the previous sections, in which the low water/binder ratio and high silica fume replacement samples had lower bound chloride content.

In the present work, in order to develop a good and useful relationship between free and bound chloride as previously mentioned, the water/binder ratio parameter was not considered in the calculations because of negligible effect of water/binder ratio in comparison to the role of silica fume. To make a general relationship, not considering the effect of water/binder ratio, a non-linear regression analysis of the data has been performed in Figs. 8 and 9 and chloride binding capacity versus silica fume replacement level and parameter β versus silica fume replacement level for all mixtures are plotted. Accordingly, a linear equation is developed between total and bound chloride for various proportions of silica fume replacement.

Table 4
Relationship between free and total chloride.

SF (%)	w/b α				w/b β			
	0.35	0.40	0.45	0.50	0.35	0.40	0.45	0.50
0	1.164	1.166	1.172	1.177	0.024	0.023	0.025	0.024
5	1.125	1.132	1.136	1.132	0.023	0.023	0.022	0.006
7.5	1.113	1.117	1.115	1.112	0.021	0.020	0.019	0.007
10	1.101	1.101	1.105	1.102	0.017	0.020	0.019	0.019
12.5	1.087	1.099	1.107	1.101	0.018	0.015	0.015	0.017

$$C_b = AC_t + B \tag{2}$$

where

$$A = \frac{-0.58\mathrm{SF} + 0.164}{-0.58\mathrm{SF} + 1.164}$$

$$B = \frac{-0.06\mathrm{SF} + 0.0246}{-0.58\mathrm{SF} + 1.164}$$

C_t is the total chloride content (wt% of concrete), C_b the bound chloride content (wt% of concrete), and SF is the silica fume replacement amount (SF(%)/100).

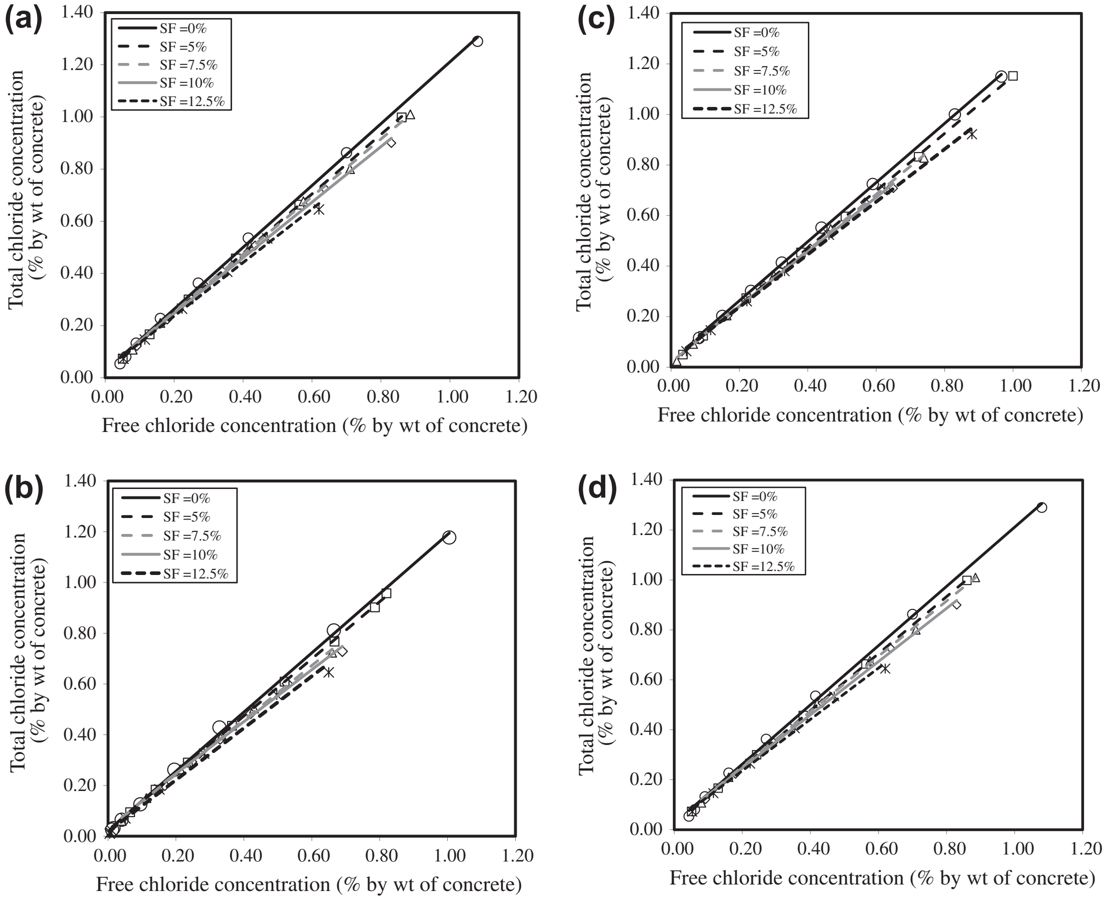

Fig. 7. Linear relationships between free and total chloride for different silica fume replacement levels: (a) w/b = 0.35, (b) w/b = 0.40, (c) w/b = 0.45, and (d) w/b = 0.50.

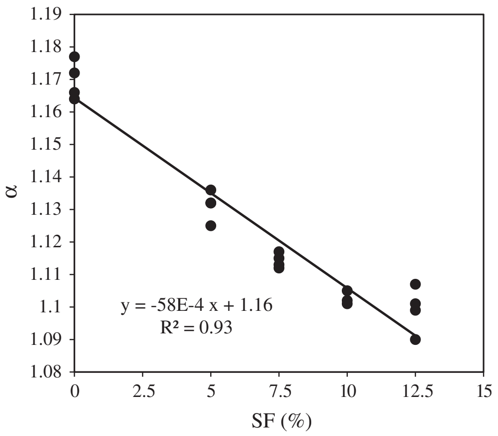

Fig. 8. α Coefficient defined in Eq. (1) versus silica fume replacement level.

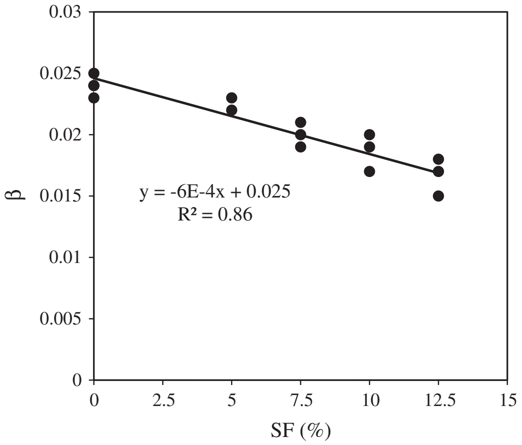

Fig. 9. β Coefficient defined in Eq. (1) versus silica fume replacement level.

6. Discussion

Chloride binding capacity was found to be decreased with increasing silica fume replacement levels and decreasing the chloride exposure concentration. Similar observations have been made by other researchers [15,21,37–39]. Partial replacement of OPC with silica fume results in a decrease in the chloride binding capacity of the cementitious material. Page and Vennesland [27] observed a similar trend and explained it in terms of the increase in solubility of calcium chloroaluminate due to a decrease in the alkalinity of the pore solution. As previously mentioned, it has been established that the mixture with the 0.50 water/cement ratio, exhibited higher binding capacities than those having the 0.35 water/cement ratio. The mixtures with silica fume addition exhibited a noticeable increase in binding capacity when the water/binder ratio was increased from 0.35 to 0.50. It is suggested that the higher hydration rate (in the mixes with w/c ratio of 0.50) both for the Portland cement and the pozzolanic action of silica fume results in the formation of a higher content of C–S–H phases. This, in turn, increases the physical chloride binding due to the relatively high surface area of the C–S–H. This observation is consistent with previously reported data [7,24]. Also the presence of silica fume has been suggested to reduce the Ca/Si ratio of the C–S–H [4]. It has been suggested that such a reduction may alter the surface characteristics of the C–S–H and reduce the number of adsorption sites [4].

The explanation related to the effect of silica fume replacement on the chloride binding is rather speculative at this stage. Additional chemical investigation is required in order to elucidate various aspects of the mechanisms related to the binding capacity of silica fume pastes. The authors believe that the increase in the content of C–S–H and reduction in pH by using silica fume, should supposedly increase the binding, and the negligible dilution of C_3A alone cannot possibly account for the reduction of binding. It has been suggested that the decrease in the C/S ratio of the C–S–H by using silica fume results in higher concentration of chloride in the pore water of silica fume sample and decreases the bound chloride content [24,41]. This may explain why, despite the increase in C–S–H, the overall effect would be a decrease in binding.

7. Concluding remarks

Chloride binding is a complicated process that is affected by many factors. Previous studies have mainly looked at the chloride binding from internal sources in laboratory, which is not representative of practical situations. The development of a relationship between the total and bound chloride contents in concrete requires long-term exposure experiments under marine environment where chlorides are allowed to diffuse into concrete naturally. The current work focused on the chloride binding characteristics of 20 concrete mixtures that were exposed to an external source of chlorides from seawater of the Persian Gulf for 60 months. The results of this work confirm that:

(1) By increasing the water/binder ratio, as in Figs. 1 and 2, the amount of bound chloride increases noticeably, but for mixtures with 0.40 and 0.45 water/binder ratios does not change very much. The total amount of bound chlorides in these cases appears to be independent of the water/binder ratio. Also by using silica fume, not only bound chloride content decreases for all the mixtures, but also the slope of the curve is initially high until about 5% silica fume and then decreases by increasing the silica fume replacement.
(2) The amount of bound chlorides appears to be predominantly influenced by the chloride concentration and silica fume replacement. In this regard, according to Fig. 3 for all mixtures, the amount of bound chlorides markedly increases when the pore solution has higher chloride concentration. It is notable that the bound chloride content of the control mixture at lower chloride concentration (<0.1% by wt of concrete) is similar to concrete samples containing silica fume. This may suggest that at low chloride concentrations the OPC substitution with silica fume does not generally improve the chloride binding capacity.
(3) It is observed that by using silica fume not only the total chloride content decreased, but also the amount of bound chloride is markedly decreased. As it is shown in Fig. 4, the addition of 5% silica fume has markedly influenced the amount of bound chloride of all water/binder mixtures.
(4) According to Fig. 5, the amount of bound chlorides appears to be predominantly influenced by the chloride concentration and silica fume. It has been established that the percentage of chloride binding increases as the depth from the surface increases regardless of water/binder ratio. As a result, although moving to inner layers of concrete, total and bound chloride concentrations both decreased, but finally C_b/C_t ratio increased because of larger reduction of C_t versus C_b.

The authors believe that, based on the results of several long-term experiments, the relationship between bound and total chloride for various types of mixtures in field condition and for total chloride concentration less than 1.2% mass of concrete ($C_t < 1.2\%$

by wt of concrete) is generally linear and could be described according to Eq. (2).

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