

EFFECT OF CHLORIDE IONS SOURCE ON CORROSION OF REINFORCED NORMAL AND HIGH PERFORMANCE CONCRETE

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ABSTRACT. The aim of this paper is to investigate the influence of chloride ions source on corrosion of steel embedded in different types of concrete. The experimental part consisted of: chloride content analysis, rapid chloride permeability test (RCPT), and linear polarization resistance (LPR). Sodium chloride was dissolved in the mixing water and added to concrete to achieve an internal chloride content of 0.8 % by weight of cement. External exposure was provided by curing the concrete specimens in 4.5 % of NaCl solution. The chloride analysis results indicated that the ratio between (Cl_{free}/Cl_{total}) for high performance concrete was always less by about 76% to 82% than that of normal concrete. Exposure to external chloride increases both total and free chloride inside the concrete specimens irrespective of concrete type. Internal chloride had increased the electrical conductivity at 28-day age of the concrete by about 45% and 40% for normal and high performance concrete respectively. The corrosion current density was found to have a positive relationship with Cl_{free} of concrete. That may be due to the influence of chloride ions on the destruction of the passive film around the steel which cause corrosion to take place and proceed. Higher measured corrosion rates are also observed in the early stage which may be related to the change of anode and cathode areas with age.

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1. INTRODUCTION

The corrosion of metals, especially steel, in concrete has always received increasing attention because of its widespread occurrence in certain types of structures and the high cost of repairs. The corrosion of steel reinforcement was first observed in marine structures and chemical manufacturing plants. More recently, numerous reports of its occurrence in bridge decks, parking structures, and other structures exposed to chlorides have made the problem particularly prominent (ACI 222R-01).

Corrosion due to chloride attack is one of the major worldwide deterioration problems for reinforced concrete structures. The high alkaline environment of good quality concrete forms a passive film on the surface of

embedded steel which normally prevents the steel from further corrosion. However, under chloride attack, the passive film is disrupted or destroyed, and the steel spontaneously corrodes. The volume of rust products is about four to six times larger than that of iron, this volume increase induces internal tensile stresses in the cover concrete, and when these stresses exceed the tensile strength of the concrete, the concrete cover is damaged by cracking, delaminating and spalling. A reinforced-concrete member may suffer structural damage due to loss of bond between steel and concrete and loss of rebar cross-sectional area (Liu- 1996).

Chloride ion originates from different sources (i.e. external and internal). Using deicing salts and exposure to seawater are examples for external attack of chloride ions. The chloride ion diffuses into the hardened con-

crete to contact the steel and initiate the corrosion process. This diffusion process is a bit uneven because of the variability of the way in which the chloride is introduced on the surface and also the variability of the concrete properties.

Chloride ions in mixing water or in aggregate, higher than the allowable chloride levels, are the causes for internal attack. Chloride salts, such as: CaCl_2 , was added to some concrete mixes as an accelerator of the Portland cement setting. This accelerated set is desired in cold weather and used in building construction during winter.

2. MECHANISM OF CHLORIDE IONS TRANSPORT

Diffusion, hydrostatic pressure, and capillary absorption are the means by which chloride ions can penetrate concrete. The most familiar method is diffusion, the movement of chloride ions under a concentration gradient. For this to occur the concrete must have a continuous capillary pores and there must be a chloride ion concentration gradient. It is rare for a significant hydraulic head to be exerted on the structure, and the effect of absorption is typically limited to small concrete cover. In the bulk of the concrete, the pores remain saturated and chloride ion movement is controlled by concentration gradients, (Hooton et al. - 1997). Diffusion of chlorides through the pore solution of wet concrete occurs more slowly, typical diffusion rates for fully saturated cement paste are in the order of $10^{-8} \text{ cm}^2/\text{s}$ ($15.5 \times 10^{-10} \text{ in}^2/\text{s}$), (Ngala et al.-1995).

While it has been determined that chloride ions act as catalysts for the loss of the protection offered by the passive film, the exact mechanisms of this process are not well understood. However, attack on the passive film by chloride ions is generally accepted to be a localized phenomenon. This form of attack causes micro galvanic cells to form on the reinforcing steel. In regions where the depassivation has occurred, iron will be lost by oxidation (these regions act as anodes). The areas that remain protected by the passive film will become sites of oxygen reduction (i.e. cathodic).

To initiate reinforcement corrosion it is necessary for the chloride to penetrate into the concrete from outside and to exceed the critical corrosion-inducing limit at the reinforcement in the reinforced concrete. The process of growing concentration of chloride ions until a corrosion-initiating limit is reached depends on the amount of chloride available from the external surroundings and on the concrete technology parameters, which affect the chloride transport and the chloride

diffusion as well as the chloride binding. The critical factor in chloride-induced corrosion is ultimately the concentration of chloride ions which are free, and therefore actively corrosive, in the concrete pore solution which causes depassivation of the steel surface.

3. RESEARCH SIGNIFICANCE

Chloride ions can be either contained in concrete basic materials and/or penetrate later into the concrete from outside environment. It is necessary for these ions to exceed the critical corrosion-inducing limit inside reinforced concrete to initiate reinforcement corrosion. This process depends on the amount of chloride available and on permeability of concrete. Using supplementary cementitious materials, like Metakaolin, would reduce permeability and provide an additional alumina source to combine with free chloride, keeping in mind that only free chlorides are participating in corrosion process.

4. MATERIALS, MIXES, AND TESTING PROCEDURES

Type I, ordinary Portland cement (ASTM C150-02a) was used throughout this work. Its fineness (Blaine) was $243 \text{ m}^2/\text{kg}$ ($1186 \text{ ft}^2/\text{lb}$) and C_3A content was 11.4 %. Natural sand, with 2.2 fineness modulus and 0.03 % total chloride content, was the fine aggregate. The coarse aggregate was crushed gravel with 19 mm (0.75 in) maximum size and 0.036 % total chloride content. Metakaolin with 8 % replacement by weight of cement was incorporated in producing high performance concrete in addition to Sikament NN which was used as high-range water reducer (ASTM C494-99a, Type F) with a dosage of 2.3 % by weight of cement. The Metakaolin was with $1100 \text{ m}^2/\text{kg}$ ($5370 \text{ ft}^2/\text{lb}$) fineness (Blaine) and has 107 % strength activity index (ASTM C311-02, Type N). Sodium chloride salt had been used as a source for internal chloride ions. It was dissolved in the mixing water and added to concrete to achieve a chloride content of 0.8 percent by weight of cement. Meanwhile, external exposure was provided by curing the concrete specimens with 4.5 % of NaCl solution. For more details see Abdul-Kareem (2007).

Two mixtures were designed in this study. The first was proportioned according to ACI 211.1-91 (2004). It represented the normal concrete reference mix with minimum 28-day compressive strength of 35 MPa (5075 psi) and slump $125 \pm 5 \text{ mm}$ ($5 \pm 0.2 \text{ in}$). The mix

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proportions by weight were (1: 1.77: 3.1: 0.45). The second mixture was high performance concrete with minimum 28-day compressive strength of 60 MPa (8700 psi), slump 125± 5mm (5 ± 0.2 in) and mix

proportions by weight were (1: 1.23: 2.16: 0.30). The mix proportions were selected according to ACI 211.4R-98 (2004). The details of mixes used throughout this study are given in Table 1.

Table 1

Details of concrete mixes

Mix	Cement kg/m ³ (lb/ft ³)	M kg/m ³ (lb/ft ³)	Fine Agg. kg/m ³ (lb/ft ³)	Coarse Agg. kg/m ³ (lb/ft ³)	Water, kg/m ³ (lb/ft ³)	HRWR percent by wt. of cement	W/CM Ratio by weight	Added NaCl, kg/m ³ (lb/ft ³)	Curing solution
A ₁	330 (5287)	-	584 (9356)	1020 (16340)	149 (2387)	0.9	0.45	-	Tap water
A ₂						0.9	0.45		NaCl
A ₃						0.9	0.45	3.4 (55)	Tap water
A ₄						0.9	0.45		NaCl
B ₁	437 (7001)	38 (609)	584 (9356)	1020 (16340)	143 (2291)	2.3	0.30	-	Tap water
B ₂						2.3	0.30		NaCl
B ₃						2.3	0.30	4.6 (74)	Tap water
B ₄						2.3	0.30		NaCl

Chloride Content Tests

Two test methods, water soluble (ASTM C 1218-99) and acid soluble (ASTM C 1152-97) chloride content, were performed at the ages of one-day and 270-day for all specimens in different exposure conditions.

Rapid Chloride Permeability (RCP) Test

The rapid chloride permeability test (RCPT), as described in ASTM C 1202-97, was performed on three replicate cylindrical specimens with diameter of 102 mm (4 in) and height of 51 mm (2 in) at ages 28, 60, 90, 180 and 300 days. This test was carried out only for mixes A₁, A₃, B₁, and B₃.

Linear Polarization Resistance Measurement (LPR) Test

Linear polarization resistance measurement is a well-established method for determining corrosion rate by using electrolytic test cells (ASTM G 59-97). This test was performed on 40 reinforced concrete standard cylinders with diameter of 152 mm (6 in) and height of 305 mm (12 in). The experimental program had extended to 300 days age.

The technique involves measuring the change in the open-circuit potential of the electrolytic cell when an external current is applied to the cell. For a small perturbation about the open-circuit potential, there is a linear relationship between the change in applied current per unit area of electrode Δi and the change in the measured voltage ΔE . The ratio of ΔE to Δi is called the polarization resistance R_p . The corrosion rate, expressed

as the corrosion current density, is inversely related to the polarization resistance, as showed in eq. (1).

$$I_{corr} = B/R_p \quad (1)$$

where: I_{corr} is the corrosion current density in $\mu A/cm^2$ ($1 \mu A/cm^2 = 6.45 \mu A/in^2$); B – a constant in Volt; R_p – the polarization resistance in Ω/cm^2 ($1 \Omega/cm^2 = 6.45 \Omega/in^2$).

The constant B is a characteristic of the polarization curves, and a value of 26 mV is commonly used for steel that is actively corroded in concrete.

5. RESULTS AND DISCUSSION

Chloride Content Analysis

Table 2 shows both total chloride and free chloride content at ages 1 day and 270 days for concrete specimens with different curing solutions. It was observed that final chloride content (total or free) for concrete specimens immersed in tap water does not show major difference from the initial value and that could be attributed to the weak effect of tap water on wash-out chloride ions from concrete especially for specimens with initial chloride content 0.8 % by weight of cement (mixes A₃ and B₃). This observation was in agreement with the results that obtained by Hooton and Honga (2000). Meanwhile for the specimens immersed in NaCl solution (external chloride source) the results show that both total and free chloride content for all specimens increases at different rates depending on the type of concrete and initial chloride content. The chloride analysis results indicated that the ratio between

(Cl_{free}/Cl_{total}) for high performance concrete mixes was always less by about 76% to 82% than that of normal concrete. Moreover, it was found that exposure to the

external chloride increases both total and free chloride inside the concrete specimens irrespective of concrete type.

Table 2

Total and free chloride content analysis for different concrete mixes

Mixes	Added NaCl, kg/m ³ (lb/ft ³)	Curing Solution	% Cl _{total} by weight of cement		% Cl _{free} by weight of cement		Cl _{free} /Cl _{total}	
			1-day	270-day	1-day	270-day	1-day	270-day
A ₁	0	Tap water	0.27	0.26	0.13	0.12	0.48	0.46
A ₂		NaCl	0.27	0.78	0.13	0.6	0.48	0.76
A ₃	3.4 (55)	Tap water	0.82	0.84	0.64	0.66	0.78	0.79
A ₄		NaCl	0.82	1.14	0.65	0.94	0.79	0.82
B ₁	0	Tap water	0.2	0.2	0.022	0.021	0.11	0.11
B ₂		NaCl	0.2	0.38	0.022	0.052	0.11	0.14
B ₃	4.6 (74)	Tap water	0.83	0.83	0.12	0.12	0.14	0.14
B ₄		NaCl	0.83	0.85	0.12	0.13	0.14	0.15

Table 3

The total charge passing through concrete specimens.

Mixes	% Cl- by wt. of cement	Metakaolin by wt. of cement %	Total charge (coulomb) at age:				
			28 day	60 day	90 day	180 day	300 day
A ₁	0	0	1340	1044	837	541	223
A ₃	0.8	0	2460	2032	1680	781	317
B ₁	0	8	632	433	279	122	37
B ₃	0.8	8	1070	781	654	475	127

According to the chemical analysis, it could be concluded that the percentages of the total and free chloride are dependent on certain characteristics of concrete. These characteristics could be classified into two groups according to their effect:

1) Permeability related characteristics: using low water to cementitious materials ratio, high-range water reducer and Metakaolin have direct effects on the permeability of the concrete and tend to enhance the resistance to chloride transport through the pore structures of concrete. In particular, the effect of Metakaolin on porosity is attributed to the products of the pozzolan-lime reaction, which has higher molecular weight silicate chains than those of the C-S-H phase of hydrated Portland cements. Comparing Cl_{total} at 270-day of mix A₂ to that of mix B₂ shows that high performance concrete is more resistant to chloride ions ingress than normal concrete especially when keeping in mind that these mixes is exposed to external source only.

2) Chloride ions liberation related characteristics: the effect of using high cement content is related to the percentage of the C₃A in the cement, which has a significant effect on the reaction with chloride ions and forming (Friedel's salt) (3CaO·Al₂O₃·CaCl₂·10H₂O),

which is insoluble (Kurtis and Monteiro-1999). The later reaction causes the lowering of free chloride content. In addition to that, using Metakaolin is another governing factor. It provides an additional alumina source to combine with free chloride and form insoluble salt and, consequently, reduces the activity of chloride ions. Table 2 shows the ratio of (Cl_{free}/Cl_{total}) for all mixes and it is very clear that high performance mixes had always the lower ratios.

Rapid Chloride Permeability Test (RCPT)

Table 3 and Fig. 1 clarify the effect of age and type of concrete on the total charge that passes through. The results show a significant difference between total charge passing through high performance concrete and that passing through normal concrete. There was a decrease by about 53% at age 28 days and 83% at 300 days in total charge passed through mix B₁ relative to mix A₁. Meanwhile, this decrease was about 57% at age 28 days and 60% at 300 days in total charge passed through mix B₃ relative to mix A₃. These differences refer to the difference in the electrical conductivity of concrete which is related to many factors such as: mix proportions, use of supplementary cementing materials, chemical admixtures etc.

These factors had very significant effects on the concentration of conductive ions in the pore solution (Shi-2004).

According to the present work, it could be concluded that the addition of chloride to the mixes (for both normal and high performance concrete) increases the electrical conductivity of concrete but with different rates. This increase could be due to the fact that the existence of chloride ions would enhance the ability of the electrolyte to transmit the charge and electrons (Liu 1996). Therefore, even for high performance concrete, which has relatively low permeability, internal chloride could increase the corrosion process rate through increasing the electrical conductivity of concrete.

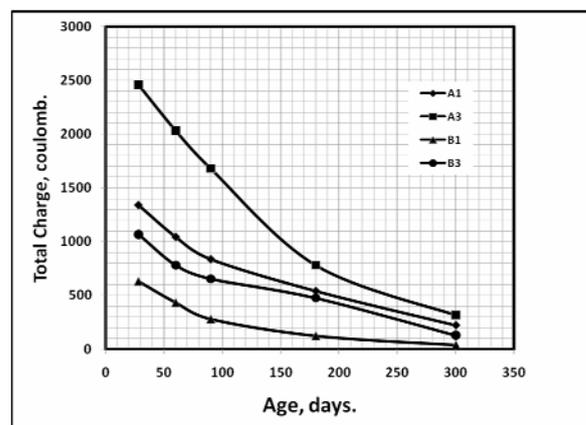


Fig. 1. The total charge passing through different concrete specimens with time.

Table 4

LPR test results at age 270 days and the relationship with Cl_{free} of concrete.

Mixes	% of added Cl by wt. of cement	Type of exposure solution	R_p , Polarization resistance, Ω/cm^2 (Ω/in^2)	I_{corr} , Corrosion current density, $\mu A/cm^2$ ($\mu A/in^2$)	% Cl_{free} by weight of cement
A1	0	Tap water	1584.2 (10218.1)	0.016 (0.103)	0.12
A2		NaCl	959.25 (6187.2)	0.0674 (0.435)	0.6
A3	0.8	Tap water	494.75 (3191.1)	0.088 (0.568)	0.66
A4		NaCl	305.2 (1967.2)	0.129 (0.832)	0.94
B1	0	Tap water	5951.7 (38388.5)	0.014 (0.0903)	0.021
B2		NaCl	5505 (35507.2)	0.032 (0.206)	0.051
B3	0.8	Tap water	1981.2 (12778.7)	0.021 (0.135)	0.12
B4		NaCl	1275 (8223.7)	0.053 (0.342)	0.13

Linear Polarization Resistance (LRP)

The chloride ions have a significant effect on reducing the polarization resistance (which is inversely proportional to corrosion current density I_{corr}) values for specimens by destroying of the passive film on the steel surface. According to Table 4, the present results show that this effect depends on the concrete type (normal or high performance concrete) and chloride source (internal or external sources). High performance concrete mixes ($B_1 - B_4$) showed always higher polarization resistance (or lower corrosion current density I_{corr}) than mixes ($A_1 - A_4$). The electrical conductivity of concrete is the main cause of this behavior.

Moreover the internal chloride has greater effect on reducing the polarization resistance than the chloride from external source. The ratio of polarization resistance values for (A_3/A_2) and (B_3/B_2) were 52% and 36% respectively. This aggressive effect may be due to high initial amount of chloride ions which cause the initiation of a corrosion cell at locations of steel bars having voids/gaps at the steel-concrete interface immediately

after casting concrete, and formation of deeper corrosion pits due to the deterioration effects of the chloride ions on the passive film around the steel surface as indicated by Mohammed et al. (2004). In contrast to that, the effect of external chloride depends on the diffusion rate of chloride through concrete and on the concentration of the chloride that causes the breakdown of the passivity of steel (Brown-1999).

Relationship between the Corrosion Current Density I_{corr} and Free Chloride Content of Concrete

A relationship between the percentage of free chloride content and corrosion current density I_{corr} at age of 270 days was observed and that is shown in Fig. 2. From this relationship, it was found that the corrosion rate increases with the increase of free chloride content in concrete. That may be due to the influence of chloride ions on destroying the passive film around the steel bar and let corrosion occurs. The higher measured corrosion rates were observed to take place in the early stage and that may be related to the change of anode and cathode areas with age.

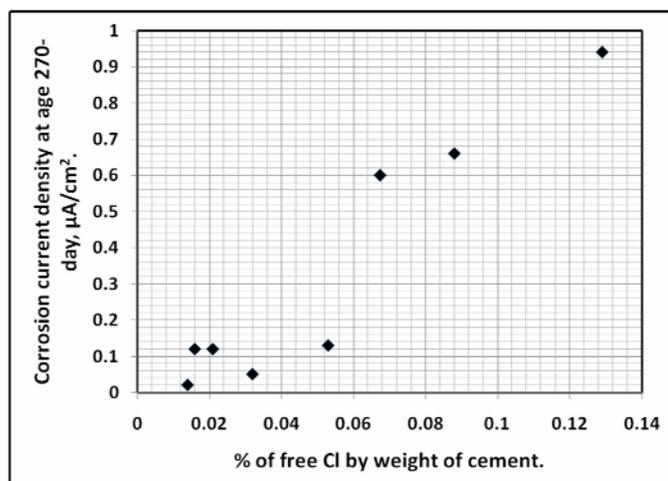


Fig. 2. Relationship between free chloride of concrete and corrosion current density (I_{corr}).

These results are in agreement with the ACI 222R-01 (2004) which showed that the corrosion increases as the chloride ions concentration increases until the maximum is reached. Moreover, Liu (1996) found that, when the amount of the added chloride exceeded 0.4% by weight of cement ($1.42 \text{ kg}/\text{m}^3$), the measured corrosion rate increases significantly with the increase of added chloride.

5. CONCLUSIONS

The following are the main conclusions that were extracted from the present work:

1) Exposure to the external chloride increases both total and free chloride inside the concrete specimens. The results indicate that the ratio between ($\text{Cl}_{\text{free}}/\text{Cl}_{\text{total}}$) for high performance concrete mixes is always less by about 76% to 82% than that of normal concrete mixes. This could be caused by using high cement content and Metakaolin. The later provides an additional alumina source to combine with free chloride and form insoluble salt that reduces the activity of chloride ions.

2) The addition of chloride to the mixes (for both normal and high performance concrete) increases the electrical conductivity of concrete but with different rates. This increase could be due to the fact that the existence of chloride ions would enhance the ability of the electrolyte to transmit the charge and electrons.

3) The internal chloride has greater effect on reducing the polarization resistance than the chloride from external source. This higher aggressive effect may be due to high initial amount of chloride ions which cause

the initiation of a corrosion cell at locations of steel bars having voids/gaps at the steel-concrete interface immediately after casting concrete.

4) The corrosion rate increases with the increase of free chloride content in concrete. That may be due to the influence of chloride ions on destroying the passive film around the steel bar and let corrosion occurs. The higher measured corrosion rates were observed to take place in the early stage and that may be related to the change of anode and cathode areas with age.

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