Scientia Iranica, Vol. 4, No. 4, pp 201–205
© Sharif University of Technology, January 1998

SCIENTIA
IRANICA

Research Note

The Effect of Chloride Ion Concentration on the Corrosion of Concrete

M. Pakshir* and **S. Esmaili**[1]

In many cases, chemical analysis of corroded reinforced concrete has shown the existence of chloride ion in concrete. This ion may be present in concrete due to use of contaminated aggregates or chloride-containing admixtures, or penetration from external sources such as seawater (specially in the gulf area) or a marine environment. The aim of this work is to investigate the influence of different cations and chloride ion on the corrosion of reinforced concrete which has been carried out in two ways. In the first method, different concentrations of calcium and sodium chlorides were mixed with water. During casting, the specimens and their corrosion activities were observed through natural and accelerated processes. In the second method, similar concrete specimens were exposed to solutions of different chloride concentrations and again their corrosion activities were observed.

INTRODUCTION

The phenomenon of steel corrosion in concrete has been studied extensively since 1960. Various investigations prior to 1960 identified the basic correlation between chloride ions and the corrosion of steel in concrete [1,2]. The nature of the interaction, however, was not clearly understood. Most research in the 1960's concentrated on the corrosion of mild steel reinforcement used in bridges. The corrosion potential of prestressed steel was also recognized and researchers eventually realized that the principles governing chloride-induced corrosion of mild steel in concrete apply to prestressed steel as well [3,4].

It is generally believed that due to the high alkalinity of concrete environments (pH $\approx$ 12.5), a protective layer is formed on the surface of the steel which provides adequate corrosion resistance. However, small amounts of Cl^- will destroy this inhibitive property of a concrete surface. Reinforced concrete construction exposed to high Cl^- environments, such as marine structures and bridge decks, undergoes premature deterioration and failure [5–8].

MECHANISM

Chloride is probably responsible for most of the economic loss due to steel corrosion in concrete structures. Therefore, determining the mechanism of steel corrosion in concrete due to chloride is necessary since it could lead to inhibition methods of such destruction.

As proposed by Uhlig [9], chloride ion present in the environment can act as a catalyst for the oxidation of iron through formation of the $FeCl_3^-$ complex which is unstable and can be drawn into the solution where it reacts with available hydroxide ions to form $Fe(OH)_2$. This results the release of Cl^- ions back into the solution and consumption of hydroxyl ions, as shown in the following reactions:

$$2Fe + 6Cl^- \leftrightarrow 2FeCl_3^- + 4e^- \qquad (1)$$

followed by :

$$FeCl_3^- + 2OH^- \leftrightarrow Fe(OH)_2 + 3Cl^- \qquad (2)$$

The electrons released in the oxidation (Equation 1) flow through the steel to the cathode surface. Consequently, concentration of chloride ions increases and pH at the points of corrosion initiation decreases, probably accounting for the process of pitting corrosion. The lowered pH at these sites contributes to the continual breakdown of the passive oxide film [10].

Therefore, decrease in the ferrous ion concentration, due to its reaction with chloride, leads to a

---

* *Corresponding author, School of Engineering, Department of Material Science and Engineering, Shiraz University, Shiraz, I.R. Iran.*

[1] *School of Engineering, Department of Material Science and Engineering, Shiraz University, Shiraz, I.R. Iran.*

change in half-cell potential, which can be measured by the procedures of ASTM C 876–87 [11]. Thus, lower half-cell potential does not indicate that "more rust is present" but, actually, demonstrates dynamically that a corrosion mechanism is almost certainly in operation. This is the reason that, according to [11], the half-cell measurements being more negative than −0.35 volts vs Cu/CuSO$_4$ electrode demonstrates 90 percent certainty of possible corrosion.

EXPERIMENTAL PROCEDURE

Reinforced Concrete Test Specimens

The experimental investigation included three groups of specimens:

Group A : Ordinary concretes.

Group B : Concretes with premixed sodium chloride (0.1%, 0.5%, 1% and 2% NaCl was added to the mixing water).

Group C : Concretes with premixed calcium chloride (0.1%, 0.5%, 1% and 2% CaCl$_2$ was added to the mixing water).

All the specimens were cured for 7 days and had a cover thickness of 3 cm. Ordinary Portland cement was used with a w/c ratio of 0.56. Table 1 shows the characteristics of each specimen.

Corrosion Measurement

The corrosion investigation was divided into two phases of activity.

Phase 1 (Natural Process)

Specimens of Group A were partially submerged into four different solutions of 0.1%, 0.5%, 1% and 2% NaCl.

Specimens of Groups B and C were partially submerged into sea water for a three-month period. In this phase, the half-cell potential of the steel was compared with a saturated copper-sulfate electrode and measured periodically according to ASTM C 876–87 [11].

Phase 2 (Accelerated Process)

In the second phase, specimens of Groups B and C were submerged into sea water. The reaction was accelerated by introducing current from a DC rectifier of a constant voltage (3 volts) and the current in the embedded rebars was measured periodically.

RESULTS

The corrosion of reinforcement in concrete is expressed in terms of potential and current of the embedded rebars as a function of time.

Figure 1 shows the result of submerging ordinary concretes in different sodium chloride solutions, i.e., 0.1, 0.5, 1 and 2% NaCl solutions.

Figure 2a shows the effect of premixed CaCl$_2$ on the corrosion behavior of reinforced concrete by natural process, whilst Figure 2b exhibits the same effect through accelerated process.

Figures 3a and 3b demonstrate the result of natural and accelerated tests performed on samples with NaCl, respectively.

DISCUSSION

Rise in the concentration of sodium chloride increases susceptibility to corrosion which is shown in Figure 1. The specimen submerged into a 2% NaCl solution was corroded after 8 days; 10 and 22 days were observed respectively for 1% and 0.2% NaCl solutions. The specimen in 0.1% NaCl solution showed maximum resistance and corroded after 60 days of exposure. Diffusion of chloride ions from the solution to the embedded bar becomes more difficult by increasing the NaCl concentration, therefore, the curves belonging to

Table 1. Characteristics of reinforced concrete specimens.

GROUP A

No.	Immersion Solution
1	0.1% NaCl
2	0.5% NaCl
3	1% NaCl
4	2% NaCl

GROUP B

No.	Percent of Premixed NaCl	Test Method
5	0.1%	NP**
6	0.1%	AP***
7	0.5%	NP
8	0.5%	AP
9	1%	NP
10	1%	AP
11	2%	NP
12	2%	AP

GROUP C

No.	Percent of Premixed CaCl$_2$	Test Method
13	0.1%	NP
14	0.1%	AP
15	0.5%	NP
16	0.5%	AP
17	1%	NP
18	1%	AP
19	2%	NP
20	2%	AP

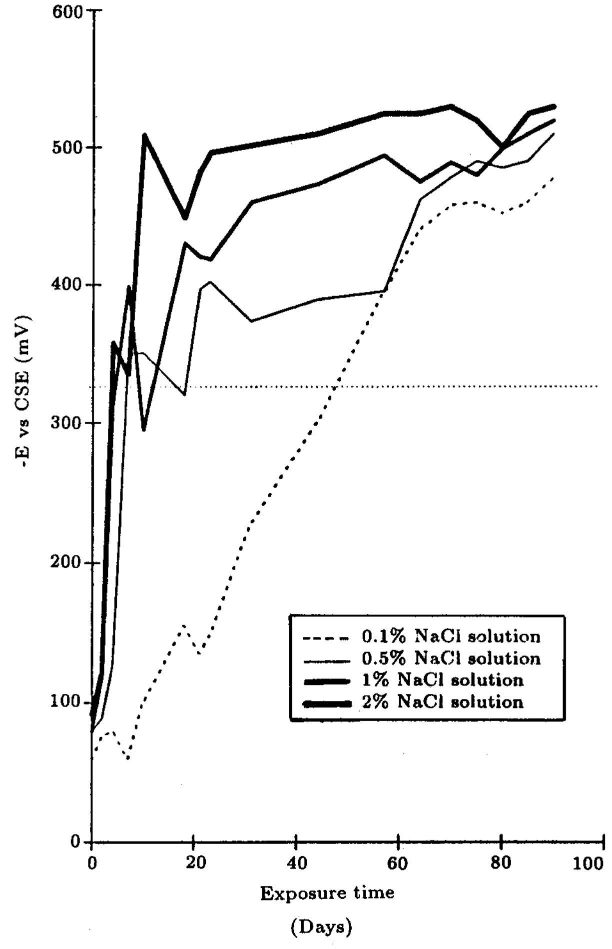
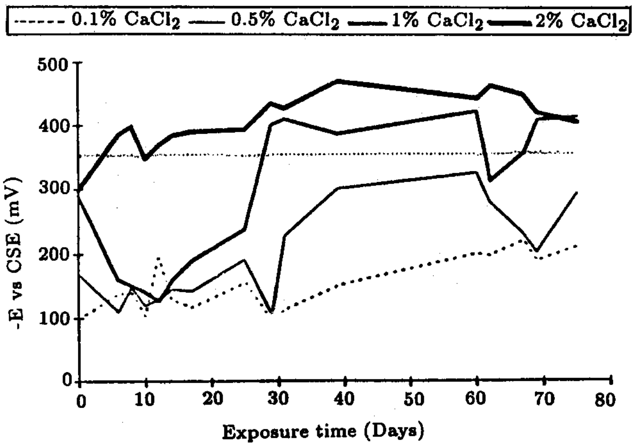
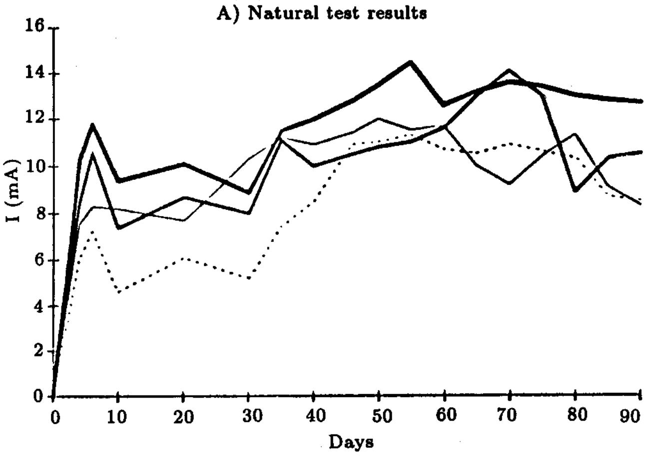


Figure 1. The effect of chloride concentration on the corrosion behavior of reinforced concrete (dashed line shows the onset of corrosion).



A) Natural test results



B) Accelerated test results

Figure 2. The effect of premixed $CaCl_2$ on the corrosion behavior of reinforced concrete(dashed line shows the onset of corrosion).

1% and 2% NaCl solutions appear adjacent to each other.

The chloride ion acts as an essential part of the corrosion cell in one of the following two ways. It either lowers the pH of the concrete pore water in contact with the steel which, consequently, dissolves the passive oxide film on the steel surface, or attacks the passive film directly by penetrating through the film surface to react with metallic ion and transports it into the electrolyte. As stated earlier, the resulting iron chloride complex ion then combines with hydroxyl ions to form $Fe(OH)_2$ in solution and lowers the pH. This, in turn, thins out the oxide film and allows easier penetration of chloride ions, permitting corrosion to continue in the newly initiated pit.

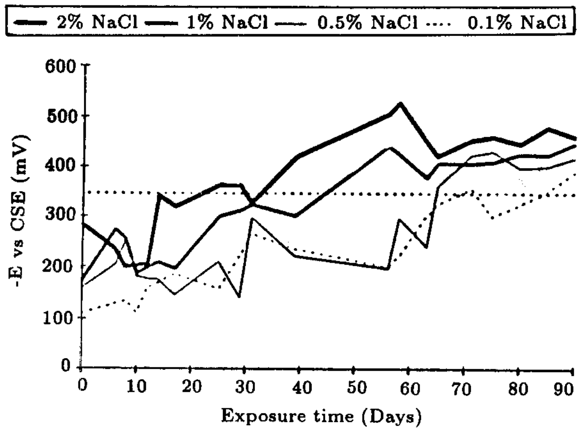
It has been shown by Fraczek [12] that, regardless of the method by which chloride ions initiate corrosion, a minimum threshold concentration is required in excess of the amount immobilized by reaction with tricalcium aluminate (C_3A), which is present in the Portland cement. This concentration may exist initially in the voids of the cement matrix in contact with steel surfaces. A commonly accepted value for the corrosion threshold is 0.2 percent total chloride ion by weight of cement [13,14].

The potential of steel reinforcement changes abruptly from passive to active when sufficient chloride ions come into contact with steel and cause corrosion (Figures 2a and 3a). As can be seen from Figure 2a, the time to reach the active potential of the steel bar is about 7 days for 2% premixed $CaCl_2$, 28 days for 1% and 38 days for 0.5%. The potential of the 0.1% premixed $CaCl_2$ specimen did not change to active value during the experiment.

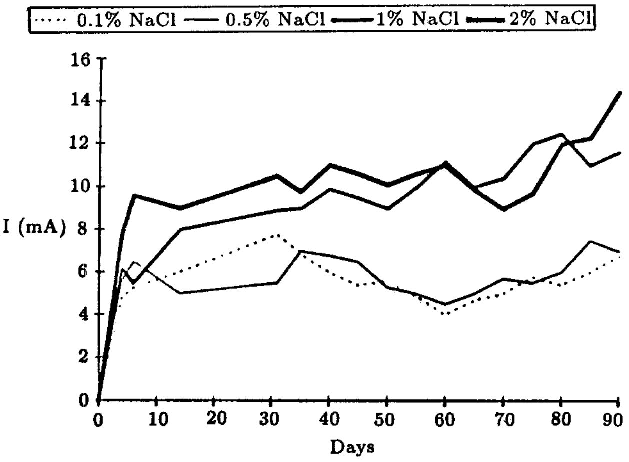
In the case of premixed NaCl specimens, the time taken to reach the active potential of a steel bar is 15 days for 2% , 25 days for 1% , 37 days for 0.5% and 67 days for 0.1% NaCl.

By comparing the results of the natural tests, it can be concluded that addition of 1% $CaCl_2$ and 2% NaCl to concrete is extremely dangerous, as far as corrosion of reinforcement is concerned, while specimens containing 0.1% and 0.2% $CaCl_2$ and NaCl appear to be more resistable during the period of the experiment.

Figures 2b and 3b show the normal trend of the current in steel with premixed $CaCl_2$ and NaCl for the



A) Natural test results



B) Accelerated test results

Figure 3. The effect of premixed NaCl on the corrosion behavior of reinforced concrete(dashed line shows the onset of corrosion).

accelerated process. As indicated in these two figures, rise in the premixed chloride concentration increases the corrosion current in the steel bar.

To investigate the effect of different binders, exposure conditions etc., there are obvious advantages in admixing chlorides into fresh concrete, since this allows more precise control of the total chloride concentration in the test specimen [15]. However, this test method appears to be limited for a number of reasons. Corrosion is initiated almost immediately after mixing and, as illustrated by Figures 2a and 3a, there is no opportunity for passive conditions to form prior to the chloride coming into contact with the steel, which is in accordance with previous works [16,17].

Since chlorides present in the mix constituents are strictly limited, some delay would normally be expected between construction and penetration of the full depth of cover by chloride. Admixing chloride may, therefore, not yield results that can be used to estimate the performance of different concretes in these situations. Moreover, binders are chemically very dynamic at these early stages and, therefore, have the potential to bind much higher quantities of chlorides than would be the case for mature systems [18]. However, there are many existing structures for which chlorides were introduced deliberately, in an attempt to understand corrosion in such cases admixing with calcium chloride may be more appropriate.

CONCLUSIONS

In general, other conditions being the same increasing chloride ion concentration results in an increase in the susceptibility of reinforcement corrosion in concrete.

No significant differences were observed between the two series(B and C) with respect to the quantity of chlorides causing corrosion.

The threshold chloride content that may be drawn from the results presented in this paper is 0.2% by weight of concrete.

The obtained results, both in normal and accelerated process, show that the corrosion of steel in concrete is more severe in the presence of calcium chloride than sodium chloride. This demonstrates that the cations, in addition to chloride ion, play an important role in the corrosion of reinforcement. In fact, chloride ion may combine with concrete compounds in different ways i.e., the differences in the corrosion behavior observed may be due to different permeability characteristics or the binding capacity of these salts with concrete compounds.

It may be concluded that the more aggressive behavior of calcium chloride is due to its chemical binding with Portland cement. The binding capacity of C_3A for sodium chloride is more than that of calcium chloride, therefore, more free chlorides are present in the latter concrete which results in a higher rate of corrosion in the case of premixed calcium chloride.

REFERENCES

1. Veits, R.I. "Use of a 2% solution of calcium chloride in prestressed concrete", *Stroitelnaya Promyshlenost*, **32** (9) (1955).
2. Evans, R.H. "Application of prestressed concrete to water supply and drainage", *Proc. Institute of Civil Engineering*, **4** (1955).
3. Haque, M.N. and Kayyali, O.A. "Aspects of chloride ion determination in concrete", *ACI Materials Journal* (Sept 1995).
4. ACI committee 222 "Corrosion of metals in concrete", *ACI Journal* (Jan 1985).
5. Hime, W. and Erlin, B. "Some chemical and physical aspects of phenomena associated with chloride induced corrosion", *ACI*, SP-102 (1987).
6. Johns, M.R., Dhir, R.K and McCarthy, M.J. "Quantifying chloride induced corrosion from half-cell potential", *Cem. and Concr. Res*, Col. **23** (1993).

7. Rasheeduzzafar, Al-musallam A., Hussain, S.E. and Al-Ghatani, A.S. "Factors affecting threshold chloride for reinforcement in concrete", *Cem. and Concr. Res.*, **25** (1995).
8. Weyers, R.E., Herald, S.E. and Feeney, M.A. "A field method for measuring the chloride content in concrete", *Cem. and Conc. Res.*, **23** (1993).
9. Fontana, M.G. and Green, N.D., *Corrosion Engineering*, McGraw-Hill, Inc. (1967).
10. Ritter, J.J. and Rodriguez, M.J. "Corrosion phenomena for iron covered with cellulose nitrate coating", *Corr., NACE*, **38**(4) (1982).
11. ANSI/ASTM C 876-87 publication (Philadelphia, PA: ASTM, 1977) in guides to practice series, Part 1 (London, UK: The Dept. Industry, n.d).
12. Fraczek, J. "A review of electrochemical principles as applied to corrosion of steel in concrete in grout environment", *ACI*, SP-102-2 (1987).
13. Hoar, T.P., Mears, R.B. and Rothwell, G.P., *Corrosion Science*, **5** (1965).
14. Hope, B.B. and IP, A.K. "Chloride corrosion threshold in concrete", *ACI Journal*, **84** (4) (1987).
15. Page, C.L. et al. "Investigations of reinforcement corrosion, electrochemical monitoring of steel in chloride contaminated concrete", *Material Structure*, **24** (1991).
16. Hansson, C.M. and Sornsen, B. "The threshold concentration of chloride in concrete for the initiation of reinforcement corrosion", ASTM, PA (1990).
17. Mehta, P.K. "Effect of cement composition on corrosion of reinforcing steel in concrete", ASTM, PA (1977).
18. Dhir, R.K. et al. "Physical characterization of UK PFA for use in concrete", *Mag. concrete Res.*, **39**(131) (1985).