

# Migration of chloride ion in the pore solution of reinforced Concrete steel bar

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**Abstract :** Usually, the reinforced concrete structure exposed in deicing salts, surrounding of salt sprays and in the peripherals of sea water from which these chloride ions slowly penetrate into the concrete, mostly through the pores in the hydrated cement solution. These chloride ions will eventually reach the steel and then accumulate to beyond a certain concentration level, at which the protective film is destroyed and the steel begins to corrode, when oxygen and moisture are present in the steel-concrete interface. For understanding reinforced steel corrosion in concrete, it is necessary to get out the parameters affect the corrosion phenomena and simultaneously examine the chemical reactions involved. In concrete, the presence of abundant amount of calcium hydroxide and relatively small amounts of alkali elements, such as sodium and potassium, gives concrete a very high alkalinity-with pH of 12 to 13.5. It is widely accepted that, at the early age of the concrete, this high alkalinity results in the transformation of a surface layer of the embedded steel to a tightly adhering film, that is comprised of an inner dense spinel phase in epitaxial orientation to the steel substrate and an outer layer of ferric hydroxide. As long as this film is not disturbed, it will keep the steel passive and protected from further corrosion. The role and effect of the chloride ion in reinforced steel corrosion is evaluated from the viewpoint of developing the concept that would lead to a general explanation. The experimental observations relating to such factors as the oxygen effect, concentration of Cl<sup>-</sup>, cation, temperature, and pH dependence are reviewed. Some of the observations on the relative corrosion effects of various ions are described. These experimental factors are discussed in terms of oxide film formation theory and adsorption mechanisms. It is concluded that the anion effects can best be interpreted in terms of the complexes that are formed between Fe and the anion. In many acid solutions, halide compounds are stable enough to form the pit or cavity on the steel surface leads to catalytic corrosion.

**Key words:** (Pit formation, reinforced steel corrosion, Sodium chloride salt)

## 1. Introduction

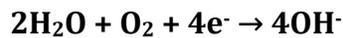
Corrosion of reinforcing steel is the leading cause of deterioration in concrete structures. Usually, the embedded steel in the concrete structure corrodes in presence of aggressive surroundings since it is not a naturally occurring material. The production steps that transform iron ore into steel add energy to the metal since iron ore is smelted and refined to produce steel. Steel like most metals except gold and platinum is thermodynamically unstable under normal atmospheric conditions

that release energy and trying to revert back to its natural state such as iron oxides and the whole process is called corrosion [1-4]. The steel corrodes under aggressive environmental condition such as in presence of chloride ions and carbon dioxide resulting in formation of rust over the steel surface and occupies a greater volume than the steel. This expands and creates stresses in and around the concrete that can eventually causes cracking on the surface, delamination, and ultimately spallation from the surface. For occurrence of corrosion there must be an alloy in which two locations on a single alloy system acts as an anode and cathode, an electrolyte and a metallic connection between them. In reinforced concrete, the rebar may have many separate areas at different energy levels acts as anode and cathode. Concrete acts as the electrolyte, and the metallic connection is provided by wire ties, or the rebar itself.

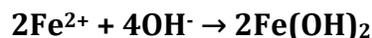
Corrosion is an electrochemical process involving the flow of charges (electrons and ions). At active sites on the bar called anodes in which iron atoms lose electrons and move into the surrounding concrete as ferrous ions ( $\text{Fe}^{n+}$ ). This process is called a half-cell oxidation reaction, or the anodic reaction, and is represented as:



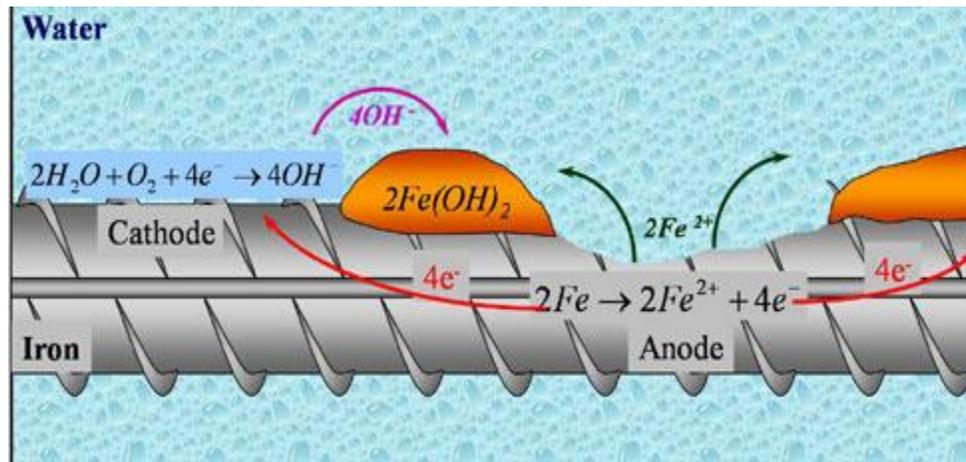
The electrons remain in the bar and flow to sites called cathodes, where they combine with water and oxygen present in the concrete. The reaction occur at the cathode is called a reduction reaction. A common reduction reaction can be expressed as below



To maintain electrical neutrality, the ferrous ions migrate through the concrete pore solution to these cathodic sites where they combine to form iron hydroxides called as rust. The reaction can be expressed as



This initial precipitated hydroxide tends to react further with oxygen to form higher oxides. The increases in volume as the reaction products react further with dissolved oxygen leads to internal stress within the concrete that may be sufficient to cause cracking and spalling in the concrete cover [5-7].

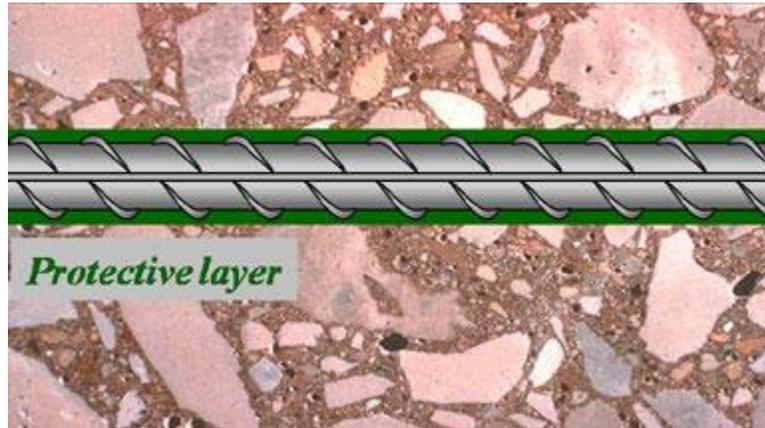


**Fig.1:** Pictograph indicates anodic and cathodic reaction on embedded steel structure

Corrosion of embedded steel alloys in concrete can be greatly reduced by placing crack-free concrete with low permeability and sufficient concrete cover. Low-permeability concrete can be attained by decreasing the water to cement (w/c) ratio in the concrete. Another way to reduce corrosion reaction by providing minimum concrete covers that will help protect the embedded steel from corrosive environments. This concrete can increase the resistivity and thus reducing the corrosion reaction even after it initiates. Additional measures to mitigate corrosion of steel reinforcement in concrete include the use of coating of reinforcement and use corrosion inhibiting admixtures [8-13].

### 1.1. Concrete and the Passive Layer

The natural tendency of steel is to undergo corrosion reactions resulted in formation of hydroxides over the steel surface that creates the alkaline environment of concrete and the pH of the solution rises ranging from 12-13.5. At this high pH range provides to protect the steel from further corrosion reaction since a thin oxide layer forms on the steel surface and prevents iron atoms from dissolving. If this oxide layer is compact and dense over the surface it reduces the corrosion rate to an insignificant level. This also indicating that the formed passive film on the surface does not actually stop corrosion. In many literatures reported that for steel in concrete, the passive corrosion rate is typically 0.1 μm per year and without the passive film, the steel can corrode at rates at least 1,000 times higher[14,15].



**Fig.2:** Pictograph indicates passivation on embedded steel

Reinforcing steel does not corrode in the majority of concrete structures due to concrete’s inherent protection. However, if the passive formed layer destroyed by any means then corrosion reaction may occur in faster way. Usually, the destruction of the passive layer occurs when the alkalinity of the concrete is reduced and it is only possible when the concentration of chloride ions in concrete is increased to a certain level.

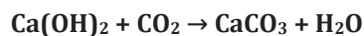
### 1.2. The Role of Chloride Ions

Exposure of reinforced concrete to chloride ions is the primary cause of premature corrosion of steel reinforcement. Chloride ions dissolved in water can permeate through concrete and thus reach to the steel that initiate cracks on the surface. Chloride ions from chloride containing admixtures present in the concrete pore solution can also ingress through the pores and thus cause corrosion in the embedded steel. The usual sources of chloride ions are in the deicing salts and seawater or in the concrete pores itself which induce into reinforced concrete and can cause steel corrosion. In presence of oxygen and moisture the rate of reaction may become faster and thus results in higher corrosion rate. No other contaminant is documented as extensively in the literature as a cause of corrosion of metals in concrete than chloride ions. The mechanism by which chlorides promote corrosion is not entirely understood, but the most popular theory is that chloride ions penetrate the protective oxide film effortlessly than do other ions, leaving the steel vulnerable to corrosion. The risk and extent of corrosion increases as the chloride content in the concrete increases. When the chloride content at the surface of the steel exceeds a certain limit called the threshold value, corrosion can occur certainly. In presence of water and oxygen the reaction rate becomes faster and the surface becomes to spallation. Many literatures showed that a threshold limit of 0.20 percent total acid-soluble chloride by weight of cement could induce corrosion of reinforcing steel in many concrete structures such as bridges, dams etc. Also it is observed that some acid-soluble chlorides may be bound within aggregates and unavailable to promote corrosion. However, water-soluble chlorides promote corrosion without difficulty. The conversion factor from acid-soluble to water-soluble chlorides ranges from 0.35 to 0.90 depending on the constituents and history of the concrete. Arbitrarily, 0.75 was chosen, resulting in a water-soluble chloride limit of 0.15 percent by weight of cement [16,17]. Although

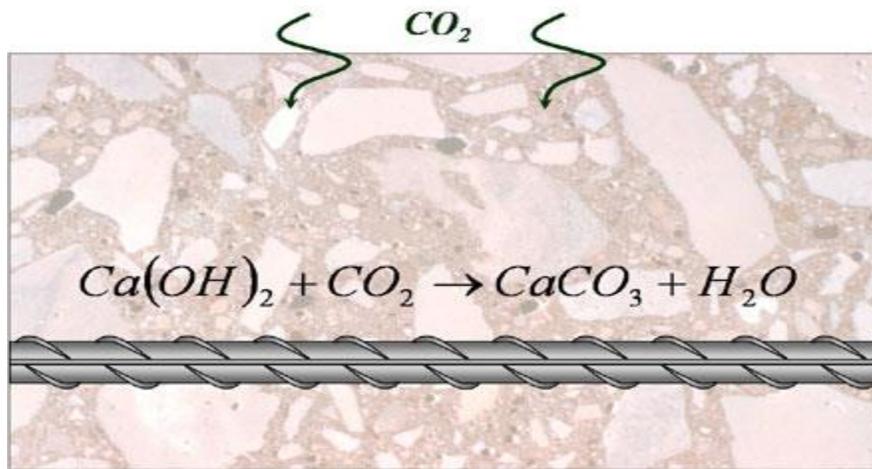
chlorides are directly responsible for the initiation of corrosion, they appear to play only an indirect role in the rate of corrosion after initiation. The primary rate-controlling factors are the availability of oxygen, the electrical resistivity and relative humidity of the concrete, and the pH and temperature [18-20].

### 1.3. Carbonation

Carbonation occurs when carbon dioxide from the air penetrates into the concrete and reacts with hydroxides such as calcium hydroxide to form carbonates. In the reaction with calcium hydroxide calcium carbonate is formed:



This reaction reduces the pH of the pore solution to as low as 10.5-8.5 at which level the passive film on the steel is not stable. Carbonation is generally a slow process. In high-quality concrete, it has been estimated that carbonation will proceed at a rate up to 0.04 inches per year. The amount of carbonation is significantly increased in concrete with a high water-to-cement ratio, low cement content, short curing period, low strength, and highly permeable or porous paste. The process of carbonation is mainly dependent on the relative humidity present in the concrete. In many literatures showed that the highest rates of carbonation occur when the relative humidity is maintained between 50 to 75 percent. Below 25 percent relative humidity, the degree of carbonation that takes place is considered insignificant. Above 75 percent relative humidity, moisture in the pores restricts CO<sub>2</sub> penetration. Thus it is found that the carbonation-induced corrosion often occurs at the areas of building porticos that are exposed to rainfall, shaded from sunlight, and low concrete cover over the reinforcing steel. This process also lowers the amount of chloride ions needed to promote corrosion in concrete embedded steel. In new concrete with a pH of 12 to 13, about 7,000 to 8,000 ppm of chlorides is required to start corrosion in embedded steel[21,22]. If, however, the pH is lowered to a range of 10 to 11, the chloride threshold for corrosion is significantly lower at or below 100 parts per million. Like chloride ions carbonation also destroys the passive film that formed on the steel surface of the reinforcement, but does not influence the rate of corrosion in greater extent for example, in concrete with w/c ratio of 0.45 and concrete cover 25 mm, it will require more than 100 years for carbonation to reach the concrete immediately surrounding the steel [23-25].



**Fig.3:** Pictograph representing process of carbonation



**Fig.4:** Macrograph of exposed building façade due to carbonation

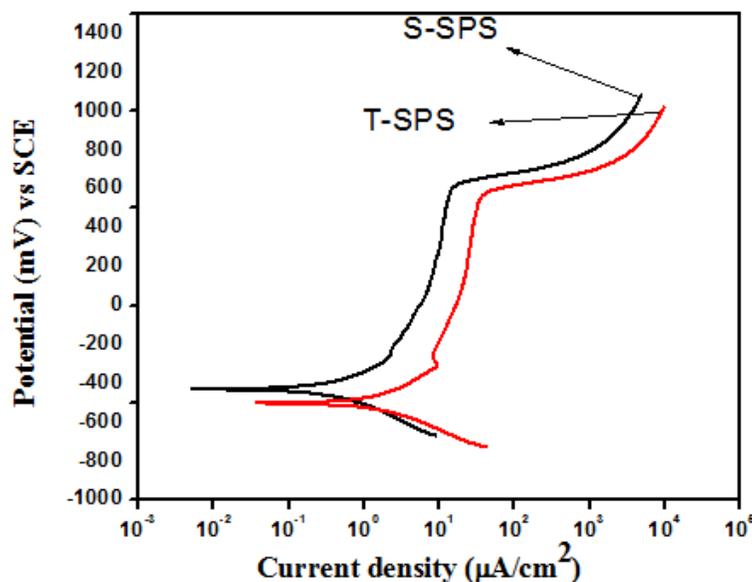
## 2. Experimental procedure:

In the present study two numbers of steel samples were made in the size of 20 mm dia and 10 mm length for the electrochemical test such as potentiodynamic test in a simulated solution called as concrete pore solution. Later on 3.5% of sodium chloride was added in the solution to know the performance of these steel samples in aggressive situations. Before exposure into the solution the open cross sectional area of both the steel specimens were polished on metallurgical polishing machine starting from 80 to 1000 grit emery papers and finally on alumina paste of the size of 1  $\mu$ m. The chemical compositions of the specimens were observed using optical emission spectroscopy technique and the results indicated in

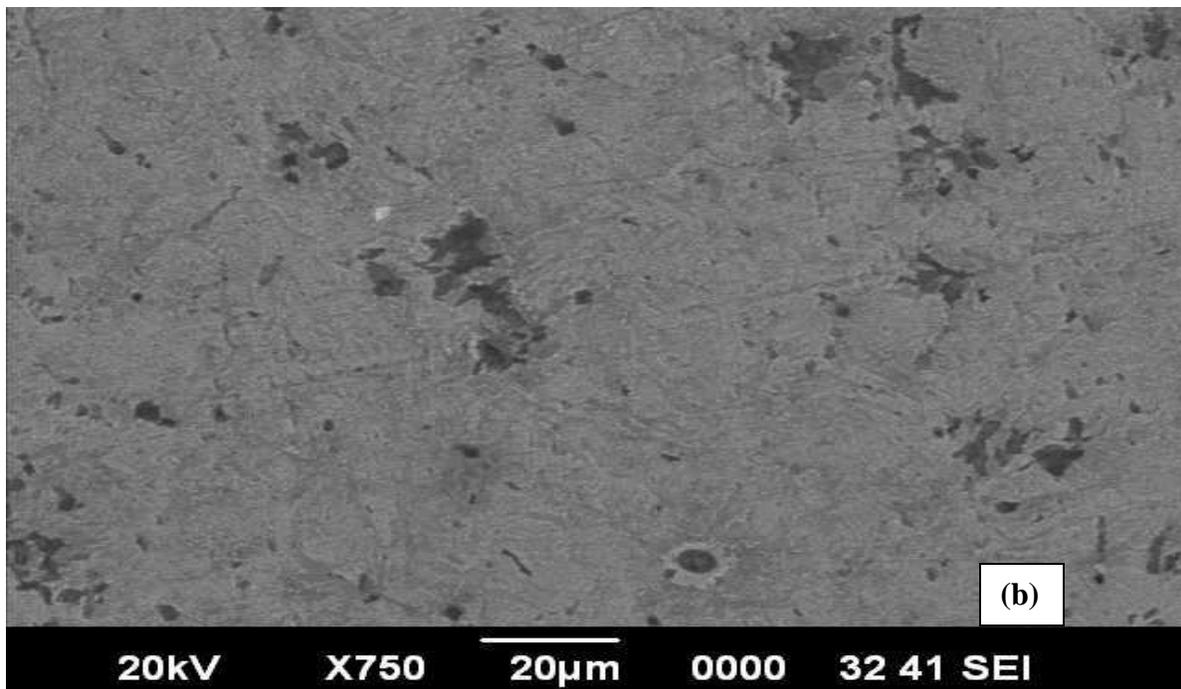
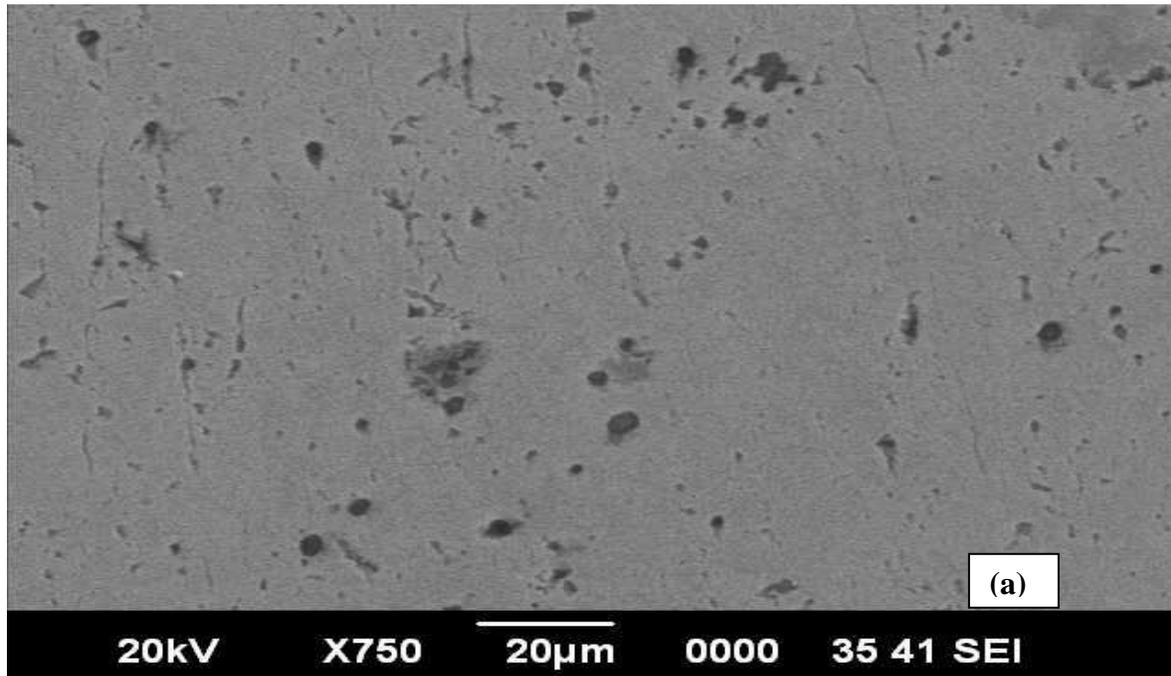
weight percentage as follows; for specimen S, C-0.26, Mn-0.79, Si-0.199, P-0.037, S-0.017, Cu-0.017, Ni-0.027, Cr-0.051 and for specimen T, of C-0.23, Mn-0.73, Si-0.179, P-0.016, S-0.023, Cu-0.003, Ni-0.048, Cr-0.010. The potentiodynamic test was performed since this method has become a well-established method of determining the instantaneous corrosion rate measurement of reinforcing steel in concrete. The technique is rapid and non-intrusive, requiring only localized damage to the concrete cover to enable an electrical connection to be made to the reinforcing steel. Due to the widespread corrosion of reinforcing steel in concrete structures there has been a concerted demand for the development of non-destructive techniques to enable accurate assessment of the condition of reinforced concrete structures. The corrosion rate monitoring in RCS has been developed to address this need. The technique is rapid and non-intrusive, requiring only a connection to the reinforcing steel. The data provides a valuable insight into the instantaneous corrosion rate of the steel reinforcement, giving more detailed information than a simple potential survey.

### 3. Results and Discussions:

The obtained results indicated that the corrosion resistance of steel-S is more in compared to steel-T in both the conditions. Both the steel corrodes in aggressive but the extent of rate of degradation is slower in both the specimens. This is due to the development in the steel that has been made by the addition of small amount of corrosion resistant alloying elements such as chromium, nickel and copper. In the steel-S the amount of these alloys are little bit more while in the case of other it slightly lower and thus results in lower resistance of degradation in aggressive conditions shown in Fig.5. The scanning electron micrographs of both the samples indicated the formation of pit on the surface. However, steel-T shown more depth of pit and thus results in more corrosion rate compared to steel -S shown in Fig.6.



**Fig.5:** Potentiodynamic test results of exposed sample in SPS with 3.5%NaCl



**Fig.6:** SEM results of exposed sample (a) Steel-S (b) Steel-T in SPS solution with 3.5%NaCl

#### 4. Conclusions

1. The major mechanisms for reinforced concrete corrosion are the intrusion of chloride ions into the concrete surroundings and atmospheric carbon dioxide ingress.
2. The corrosion and deterioration mechanisms are essentially different for both chloride attack and carbonation process.
3. The majority of reinforced concrete structures show excellent durability even after chlorination and carbonation processes and perform well over the time due to use of better quality of steel bar.
4. Adverse environments and poor selection of steel bar can lead to corrosion in the reinforcing steel in concrete.
5. Proper choice of materials, adequate cover to reinforcement, good quality concrete and attention to the environment during construction will enhance the durability of reinforced concrete structures.

#### References

1. ACI Committee 222, Protection of Metals in Concrete Against Corrosion, ACI 222R-01, American Concrete Institute, Farmington Hills, Michigan, 2001, 41 pages.
2. PCA, Types and Causes of Concrete Deterioration, Portland Cement Association, Skokie, Illinois, 2002, 16 pages.
3. ACI Committee 318, Building Code Requirements for Structural Concrete, ACI 318-05, American Concrete Institute, Farmington Hills, Michigan, 2005, 443 pages.
4. Clear, K.C., and Hay, R.E., Time-to-Corrosion of Reinforcing Steel in Concrete Slabe, V.1: Effect of Mix Design and Construction Parameters, FHWA-RD-73-32, Federal Highway Administration, Washington, DC, April, 1973, 103 pages.
5. Clear K.C., Time-to-Corrosion of Reinforcing Steel in Concrete Slabs, Federal Highway Administration, PB 258 446, Vol. 3, April, 1976.
6. T. Nishimura, Rust formation and corrosion performance of Si and Al bearing ultrafine grained weathering steel, Corrosion. Sci. 50 (2008) 1306–1312.
7. M. Saremi, E. Mahallati, A study on chloride-induced depassivation of mild steel in simulated concrete pore solution, Cement and Concrete Research 32 (2002) 1915–1921
8. G.K. Glass, N.R. Buenfeld, The presentation of chloride threshold level for corrosion of steel in concrete, Corrosion. Sci. 39 (5) (1997) 1001– 101
9. J.P. Broomfield, Corrosion of Steel in Concrete, E & FN Spon, London, 1997
10. B.B. Hope, J.A. Page, A.K.C. Corrosion rates of steel in concrete, Cement. Concrete. Res. 16 (5) (1986) 771–781
11. B.B. Hope, A.K.C, Chloride corrosion threshold in concrete, ACI Mater. J. 84 (2) (1987) 306– 314
12. ACI 222R, Corr. of Metals in Concrete, American Concrete Institute, Detroit, 1989
13. H. Bohni, H. H. Uhlig, Environmental factors affecting the critical pitting potential of aluminium, J. Electrochemical. Soc. 116 (7) (1969) 906–910
14. G. Trabanelli, C. Monticelli T. V. Grassi and A. Frignani: Cement .Concrete. Res., 2005, 35, 1804.

15. M. C. Garcı Alonso, J. A. Gonza lez, J. Miranda, M. L. Escudero, M. J. Correia, M. Salta and A. Bennani: Cement. Concrete. Res., 2007, 37, 1562.
16. J. Fliss, D. Li, Y. T. Kho, H. W. K. Osseo-Asare and H. W. Pickering: Corrosion, 1992, 48, 706.
17. Duffo GS, Reinoso M, Ramos CP, Farina SB. Characterization of steel rebars embedded in a 70-year old concrete structure. Cement Concrete Res 2012; 42(1):111-7.
18. Lyon SB. Corrosion of carbon and low alloy steels. Shreir's Corrosion 2010; 3:1693-736.
19. Mohammed TU, Hamada H. Corrosion of steel bars in concrete with various steel surface conditions. ACI Mater J 2006; 103(4):233-42.
20. Pillai RG, Trejo D. Surface condition effects on critical chloride threshold of steel reinforcement. ACI Mater J 2005; 102(2):103-9.
21. Mohammed TU, Hamada H. Corrosion of steel bars in concrete with various steel surface conditions. ACI Mater J 2006; 103(4):233.
22. Ann KY, Ahn JH, Ryou JS. The importance of chloride content at the concrete surface in assessing the time to corrosion of steel in concrete structures. Construction & Build Mater 2009; 23:239-45.
23. Freire L, Carmezim MJ, Ferreira MGS, Montemor MF. The passive behavior of AISI 316 in alkaline media and the effect of pH: a combined electrochemical and analytical study. Electrochemical Acta 2010; 55:6174-81.
24. Duarte RG, Castela AS, Neves R, Freire L, Montemor MF. Corrosion behavior of stainless steel rebars embedded in concrete; and electrochemical impedance spectroscopy study. Electrochemical Acta 2014; 124:218-24.
25. Raja Rizwan Hussan, Abdulrahman Alhozaimy, Abdulaziz Al-Negheimish, D.D.N. Singh, Time-dependent variation of the electrochemical impedance for thermo-mechanically treated versus plain low alloy steel rebars in contact with simulated concrete pore solution, Construction and Building Materials 73 (2014) 283-288