
RESEARCH NOTE

STUDY OF PITTING CORROSION INHIBITION OF MILD STEEL BY NITRITE IN CONCRETE PORE SOLUTION BY POLARIZATION AND ZERO RESISTANCE AMMETERY (ZRA) TECHNIQUES

M.H. Moayed*, Z. Abbaspour and M.H. Sadegian

Department of Materials and Metallurgical Engineering, Ferdowsi University of Mashhad
P.O. Box 91775-1111, Mashhad, Iran
mhmoayed@um.ac.ir - mhmsadegian@yahoo.com

*Corresponding Author

(Received: December 24, 2007 – Accepted in Revised Form: July 2, 2009)

Abstract A research on the corrosion inhibition of mild steel pitting corrosion in concrete pore solution by sodium nitrite was carried out by employing potentiodynamic, potentiostatic polarization and zero resistance ammeter (ZRA) techniques. Passivity breakdown potential was decreased from the transpassive potential of 700 mV at the absence of chloride to a value of -50 mV when just 0.01M NaCl was added to the test solution and further a decrease to -350 mV was recorded when the concentration of chloride was increased to 0.5M. Addition of NaNO₂ into the saturated Ca(OH)₂ solution containing 0.5 M NaCl considerably shifted the pitting potential towards noble values. Similar results of inhibitive effect of nitrite were obtained from couple potential and current measurement between two nominal identical electrodes through ZRA establishment. In the test solution containing NaNO₂, continuous increasing of the corrosion potential towards noble values and simultaneous decrease in couple current density towards zero proved the stability and improvement of the passive film. Whereas, continuous decrease in couple potential accompanied with sharp increase in couple current density with a stable value of 3μA/cm² at the absence of NaNO₂ demonstrated the occurrence of pitting corrosion.

Keywords Concrete Pore Solution, Zero Resistance Ammeter (ZRA), Pitting Corrosion, Sodium Nitrite

چکیده بررسی جلوگیری از خوردگی حفره‌ای فولاد ساده کربنی در محلول حفره بتن با استفاده از روش های پلاریزاسیون با پتانسیل متغیر، پلاریزاسیون با پتانسیل ثابت و آمپر متر با مقاومت صفر انجام شد. اضافه کردن محلول ۰/۰۱ مولار نمک طعام به محلول حفره بتن، پتانسیل تخریب رویینگی فولاد را از ۷۰۰ میلی ولت فرارویینگی به ۵۰- میلی ولت کاهش داد و افزایش غلظت نمک طعام به ۰/۵ مولار منجر به کاهش آن به ۳۵۰- میلی ولت شد. اضافه کردن نیتريت سدیم به محلول اشباع حفره بتن حاوی ۰/۵ مولار نمک طعام باعث تغییر قابل توجه در پتانسیل حفره دار شدن به سمت مقادیر نوبلتر شد. نتایج مشابهی از تاثیر یون نیتريت در اندازه گیری پتانسیل و شدت جریان اتصال دو الکتروود هم نام با روش (ZRA) بدست آمد. در محلول حاوی یون نیتريت، افزایش مداوم پتانسیل خوردگی به سمت مقادیر نوبلتر و کاهش همزمان شدت جریان اتصال به سمت صفر بیانگر پایداری و بهبود فیلم رویین بود. از طرفی ثبت کاهش پتانسیل خوردگی و افزایش شدید شدت جریان اتصال در محلول عاری از یون نیتريت وقوع خوردگی حفره‌ای را نشان داد.

1. INTRODUCTION

Concrete is a hardened mixture of cement, aggregate and water. The reactions between cement and water (hydration) take place slowly because important properties such as strength and

permeability change continuously. If there is no interaction with the environment, the reaction will improve with time, the concrete will be stronger and denser (less permeable) and therefore protect reinforcement. The first important factor when it comes to corrosion prevention of rebar is the pH

and chemistry of the concrete, or rather the pH of the pore solution in the concrete at the steel surface. The composition of the pore solution depends on the reaction between the cement and the mixing water. During the first hours of cement hydration, an alkaline solution with the pH of 12-13 is created mainly due to the formation of supersaturated calcium hydroxide and partly sodium and potassium hydroxide. This alkaline solution is called concrete pore solution which is in direct contact with embedded steel rebar in concrete [1].

Corrosion of reinforcing steel bars embedded in concrete frequently results from localized corrosion of the concrete mainly pitting corrosion in the high alkaline condition. Passivity breakdown as a result of localized corrosion occurs when a critical chloride concentration, which depends on the potential [2,3] is reached on the reinforcing bar surface. Using statistical interpretation of pitting potential, Li, et al [4] found that in artificial concrete pore solution with pH of 13.6, the critical chloride concentration is 0.4-0.6 M while in saturate $\text{Ca}(\text{OH})_2$ the chloride threshold is somewhat between 0.01 and 0.04 M. According to Bertolini et al, [5] the critical chloride content for pitting corrosion of carbon steel is between 0.028 and 0.17 M at pH of 12.6 and increases to 0.28 M in a NaOH solution at pH of 13.9. Another work conducted by Gouda [6] revealed that addition of sodium chloride up to 0.007 M does not affect the passivity of steel in a saturated $\text{Ca}(\text{OH})_2$ solution.

Nitrites (calcium or sodium salt) are anodic inhibitors [7,8] and they compete with chloride ions for the ferrous ions to form a film of ferric oxide (Fe_2O_3) on surface [9,10]. Passivation of steel surface as a result of ferric oxide or hydroxy-ferroxide ($\gamma\text{-FeOOH}$) formation on the surface inhibits steel from localized corrosion. However, full protection depends greatly on the concentration of aggressive anions such as the chloride ion, and severe pitting corrosion may occur when insufficient quantity of inhibitor is used compared to the level of chloride ion in the concrete [11].

Corrosion study of steel in concrete from media standpoint is divided into two main categories. Many of researchers used concrete pore solution for their study and the others investigate embedded steel in concrete. Various electrochemical techniques have been used for detection of steel corrosion embedded in concrete or immersed in pore

solution. Because of their simplicity, measurements of open-circuit potential (OCP) are more frequently used in the field. However, open-circuit potential measurement does not provide any information about the actual kinetics of corrosion process, and in certain cases interpretation of the results can be difficult [12]. Measuring concrete ohmic resistivity [13], linear polarization resistance of embedded steel [14], polarization by galvanostatic pulse [12], electrochemical impedance spectroscopy [9] and electrochemical noise [15] are also widely employed for corrosion evaluation of steel in concrete. The aim of present study is to make a correlation between more commonly used potentiodynamic technique with measuring couple current density and potential of two identical steel electrodes (without imposing any polarization from external device) through a ZRA setup.

2. EXPERIMENTAL PROCEDURE

Type st37 mild steel was used for present study. In order to avoid crevice corrosion occurrence as a result of specimen mounting in resin, a rode of 0.6 cm diameter and 7 cm length, with one rounded end was used for all polarization measurements. The other (non-rounded) end of the specimen was connected to the connection wire (copper wire) through a screw. Prior to each experiment, the specimens were polished with silicon carbide paper (600 grit), washed with de-ionized water and dried with air and about 5 cm² of the specimens were immersed for measurements. For ZRA measurement two nominal identical electrodes specimen; each with an area of 0.5 cm² were mounted in a single mould. Similar preparation procedures as those used to specimens of polarization measurements employed for them. In all polarization measurements a three electrode set up including working, reference and counter electrodes were used. For reference and counter electrodes, saturated calomel reference electrode (Azar Electrode Co.) and platinum wire with a surface of 2 cm² as counter electrode were selected.

Analytical grade $\text{Ca}(\text{OH})_2$, NaCl and NaNO_2 , and de-ionized water, were used throughout this work. Saturated $\text{Ca}(\text{OH})_2$ was prepared by dissolving appropriate amount of $\text{Ca}(\text{OH})_2$ salt in

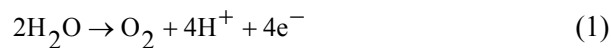
de-ionized water by stirring the solution and then allowing precipitation of Ca(OH)₂. The solution above the precipitated salt (supernatant) was used for all studies on saturated Ca(OH)₂ test solution throughout this investigation. The pH of saturated Ca(OH)₂ solution was measured by calibrated laboratory pH meter. A pH of 12.7 was read in each measurement. For test solutions containing NaCl and NaNO₂ salts, appropriate amount of their salts were added to the saturated Ca(OH)₂ solution. For each experiment a fresh test solution was used.

Throughout this work an ACM (ACM Instrument) potentiostat in conjunction with a sweep generator was used to control and sweep applied potential. Three electrochemical techniques including potentiodynamic pitting potential measurement, potentiostatic anodic polarization and also couple current and potential measurements of two nominal identical electrodes in open circuit condition were used. The potentiodynamic pitting potential measurement method involves the anodic potentiodynamic polarization of the working electrode with a sweeping rate of 1 mV/s in a test solution open to air. Before running the polarization tests, the working electrode was held at the corrosion potential for 5 minutes. Repetitive potentiodynamic experiments were carried out and then from the polarization curves, the pitting potential was determined from the anodic current density associated with 100 $\mu\text{A}/\text{cm}^2$ [16]. Current density and potential of the two identical couple electrodes was continuously recorded through a high input resistance electrometer in ZRA set up of potentiostat. All mentioned potential in this investigation is presented with respect to SCE electrode. After each potentiodynamic polarization test leading to pitting corrosion, the specimen was examined visually and microscopically for evidence of pitting corrosion initiation and propagation. For SEM examination, the samples were gently rinsed and then were subjected to ultrasonic treatment in acetone to remove the lacy pit cover.

3. RESULTS AND DISCUSSIONS

Calcium hydroxide owns a very low solubility in water and its hydration in saturated condition creates a solution with a pH in the range of 12 to 13. Mild steel in basic aqueous solution in the

absence of any aggressive anions such as Cl⁻ shows passivity. Passive film forms on many reactive metals. If the passive films show semi conductive properties, as Fe, Cr, Ni, and Cu, they will grow up only to a few nanometers in thickness to the potential required for oxygen evolution. Other metals such as Al, Nb, Ta, Ti, Zr and Hf form an insulating oxide film that may grow up to more than 100 V without oxygen evolution with thickness reaching to several tens of nanometers. Anodic polarization of used specimen in this work is illustrated in Figure 1. The specimen shows a passivation behavior with a passive current density of 6 $\mu\text{A}/\text{cm}^2$ that subsequently follows by anodic current density at 700 mV due to the oxygen evolution according to the following electrochemical reaction:



Considering a pH of 12.7 for saturated Ca(OH)₂ test solution and comparing the reversible potential of above reaction with the transpassive potential of Figure 1 reveals a reasonable high overpotential for water oxidation on the steel passive film in saturated Ca(OH)₂ solution. The anodic behavior of specimen has been strongly affected in the presence of chloride ions in the test solution. The anodic polarization curves show a passive range, where the passive current density for lower chloride concentration is about $6 \times 10^{-3} \text{ A}/\text{cm}^2$ and increases as the chloride concentration increases to 0.1 and 0.5M (Figure 1). Passivity breakdown as a result of pit formation occurs upon the presence of chloride ions in the solution. Pitting corrosion occurs when the applied potential in a potentiodynamic test and free corrosion potential in naturally immersed specimen exceeds a critical value called pitting electrochemical potential (E_{pit}). The pitting electrochemical potential showed a chloride concentration dependency and the corrosion potential also shifted toward lower values while increasing the chloride concentration. In order to examine pit shape and feature, SEM investigation of the polarized working electrode beyond the pitting electrochemical potential was carried out. The shape of the most pits were irregular and the pit surrounding area was covered by the passive film mainly iron hydroxide. Figure 2 illustrates the morphology of a single pit after

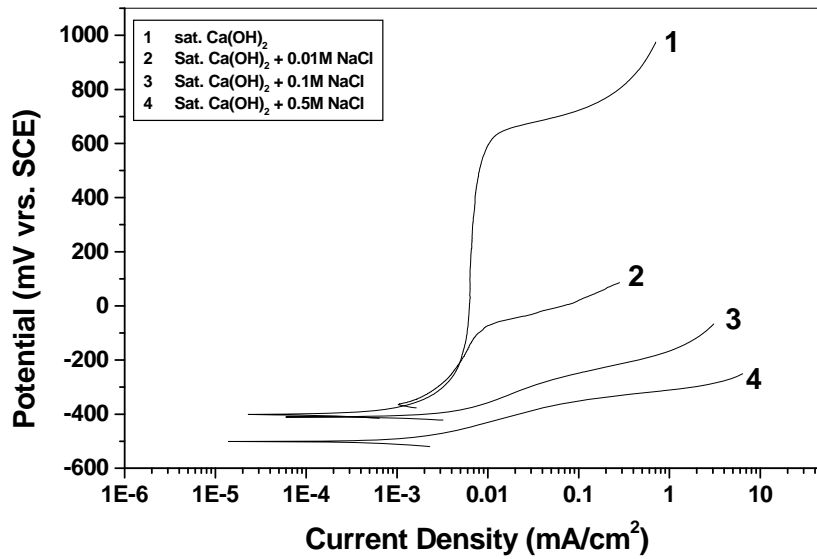


Figure 1. Polarization curves for mild steel in saturated Ca(OH)_2 and saturated Ca(OH)_2 solution containing 0.01, 0.1 and 0.5M NaCl at ambient temperature with a potential scan rate of 1mV/s.

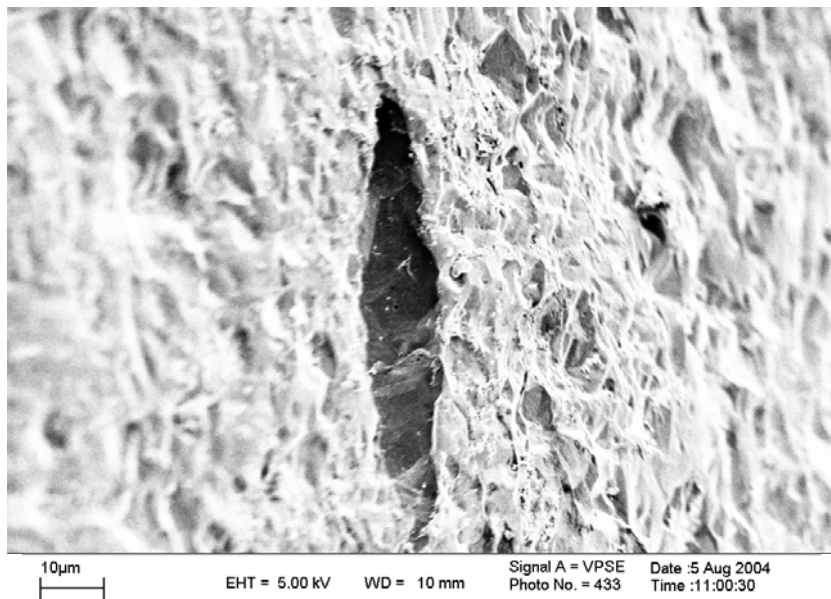


Figure 2. Scanning electron micrograph of a crevice-like pit on the mild steel surface after potentiodynamic polarization in saturated Ca(OH)_2 solution containing 0.5M NaCl.

polarization above to the pitting electrochemical potential. The pit appears as a groove-like cavity. The dependency of pitting potential on chloride concentration has been reported in several investigations and in general a logarithmic

relationship according to the following equation is proposed [17,18].

$$E_{\text{pit}} = a - b \log [\text{Cl}^-] \quad (2)$$

Similar relationship was found in this research (Figure 3) with values of -445 and -235 mV for (a) and (b) parameters, respectively. The value of pitting potential depends on chloride ion concentration in the solution. The lowest pitting potential was recorded for solution of $\text{Ca}(\text{OH})_2$ +

0.5M NaCl with a value of 380 mV.

In order to prove that the anodic behavior which occurs at 700 mV is due to oxygen evolution, applied potential was back scanned (scanned in reverse direction) when the anodic current density reached to $300 \mu\text{A}/\text{cm}^2$. Figure 4 illustrates back

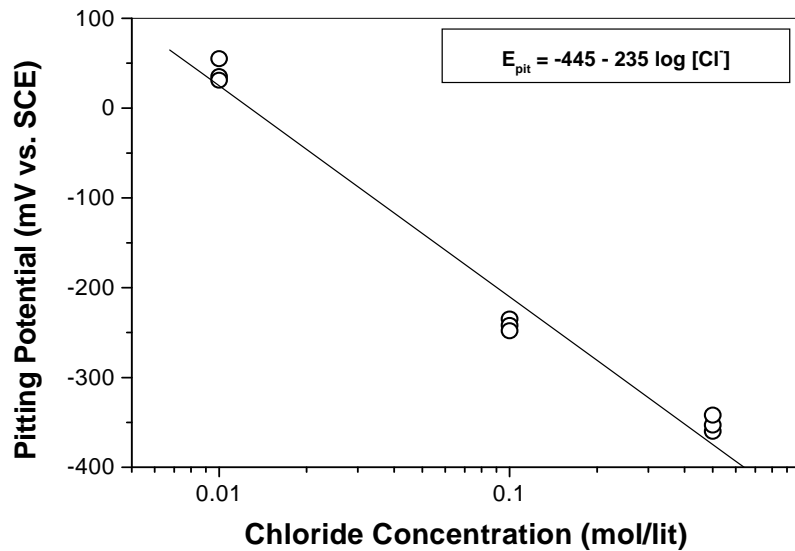


Figure 3. Logarithmic relationship between mild steel pitting potential and chloride concentration obtained from potentiodynamic polarization data.

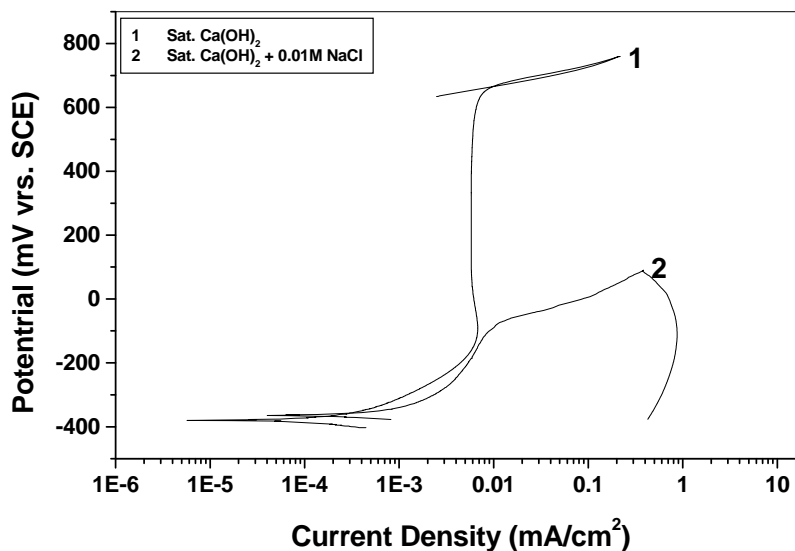


Figure 4. Polarization curve accompanied with potential backscanning for mild steel in saturated $\text{Ca}(\text{OH})_2$ and saturated $\text{Ca}(\text{OH})_2$ + 0.01M NaCl test solutions at ambient temperature with a potential scan rate of 1mV/s.

scanning of applied potential when oxygen evolution occurs. Since electrochemical reaction of oxygen evolution occurs throughout the surface it acts such an active electrochemical reaction, so the current density of forward and reverse state should be associated to similar potential. Similar back scanning of applied potential was carried out at the anodic current density of $300 \mu\text{A}/\text{cm}^2$ in saturated solution of $\text{Ca}(\text{OH})_2 + 0.01 \text{ M NaCl}$. Since the reversed current dose not coincident with the forward current, the measured current increasing at -80 mV is related to the pitting electrochemical corrosion.

In order to find out whether the measured anodic current density prior to pitting corrosion was the result of passivity, a series of potentiostatic polarization tests were carried out at an anodic potential of 50 mV in saturated $\text{Ca}(\text{OH})_2$ and saturated $\text{Ca}(\text{OH})_2$ containing 0.5M NaCl . Figure 5 shows comparison of the result of potentiostatic tests at applied 50 mV in both solutions. A gradual

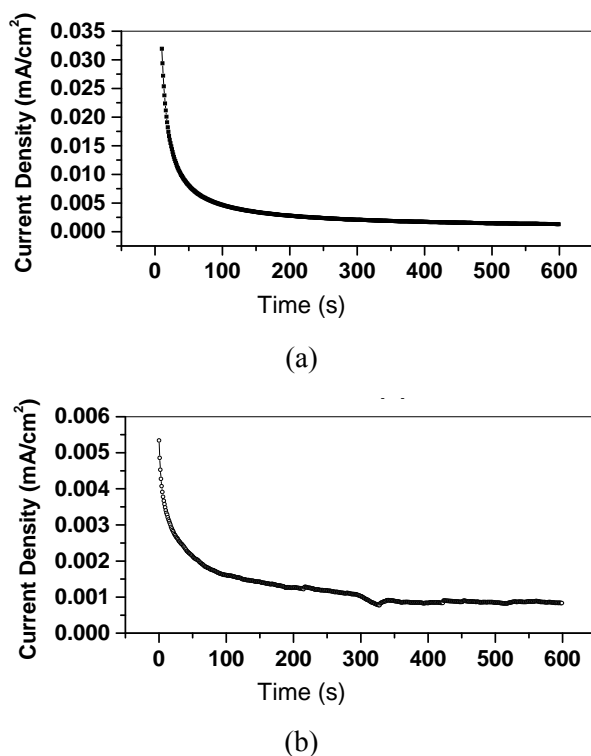


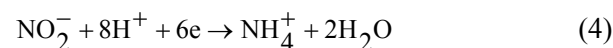
Figure 5. Current density-time relationship of anodic potentiostatic polarization tests at applied potential of 50 mV in saturated $\text{Ca}(\text{OH})_2$ (a) and saturated $\text{Ca}(\text{OH})_2 + 0.5\text{M NaCl}$ (b) test solutions at ambient temperature.

decreasing trend in the anodic current density with time is observed in both solutions; however the solution containing Cl^- shows a higher passive current density. This is attributed to the effect of chloride adsorption on metal surface that hinders the establishment of passivity. The results for $\text{Ca}(\text{OH})_2 + 0.5\text{M NaCl}$ solution prove that the specimen has shown passive behavior prior to pitting corrosion.

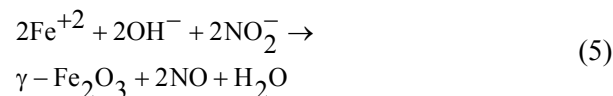
The anodic polarization curves of steel in saturated $\text{Ca}(\text{OH})_2 + 0.5\text{M NaCl}$ with and without various concentrations of $0.01, 0.1$ and 0.5M nitrite is illustrated in Figure 6. Addition of nitrite to the solution causes a shift on corrosion potential about 100 mV toward positive values and also a decrease on passive current density. The important role of nitrite is evident on the sharp increase of pitting potential up to 500 mV and widening passivity range for solution containing $0.5\text{M Na}_2\text{NO}_2$. Figure 7 shows the dependency of pitting electrochemical potential (E_{pit}) on logarithmic concentration of NO_2^- similar to the following equation that was proposed by other researchers [19,20].

$$E_{\text{pit}} = a + b \log[\text{NO}_2^-] \quad (3)$$

The results of potentiodynamic polarization revealed values of -280 and 240 mV for (a) and (b) parameters, respectively. It is clear that addition of NO_2^- ion inhibits pitting corrosion. The inhibition effect of NO_2^- ions increases with increasing of the NO_2^- concentration. It is probable that the role of NO_2^- in the inhibition of pitting corrosion is due to its fast reduction to NH_4^+ during the steel dissolution reaction inside the pit cavity according to the following electrochemical reaction:



Consuming H^+ increases the pH of occlusion on the surface and facilitates passivation [19]. Another widely accepted mechanism for inhibiting the effect of nitrite ions is based on passive film formation according to the following reaction [9,10]:



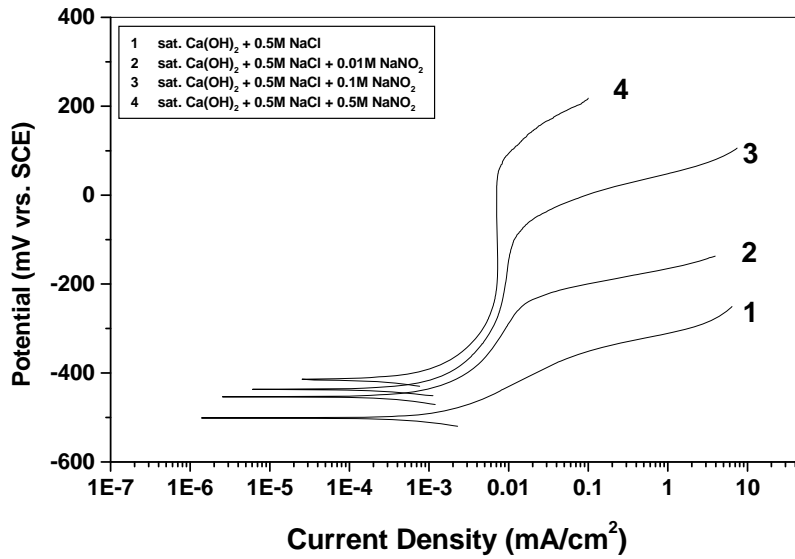


Figure 6. Polarization curves for mild steel in saturated $\text{Ca(OH)}_2 + 0.5\text{M NaCl}$ solution containing 0.01, 0.1 and 0.5M NaNO_2 at ambient temperature with a potential scan rate of 1mV/s.

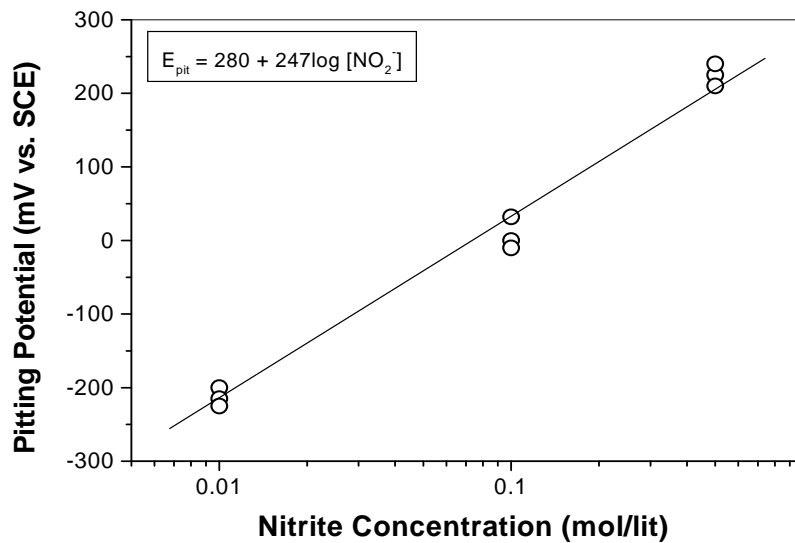
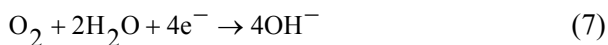
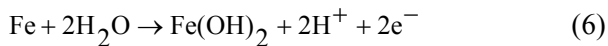


Figure 7. Linear relationship between pitting potential and nitrite concentration obtained from potentiodynamic polarization data.

Formation of $\gamma\text{-Fe}_2\text{O}_3$ film leads to the passivity of the surface. Moreover, NO_2^- ions can be adsorbed on the surface oxide film and dislodge Cl^- ions from the sites, through it preferentially penetrate into the passive film and thereby enhance the pitting corrosion resistance [19].

Application of ZRA technique for evaluation of localized corrosion of stainless steels has been investigated by some researchers [21,22]. ZRA technique was employed to investigate the initiation potential for pitting corrosion of mild steel in saturate Ca(OH)_2 containing aggressive

anions of chloride in the absence and presence of inhibitive anions of nitrite. Figure 8 shows the variation of potential with respect to time in different environments and it can be distinguished that in saturated Ca(OH)₂ solution after a sharp increase of potential, about 40 mV, the potential is flattened for 300 s and then gradually increases about 80 mV at the end of the experiment. Similar trend for potential variation of the steel in solution containing aggressive anion of chloride and inhibitive anion of nitrite can be observed. Due to the oxidizing power of the solution as a result of nitrite presence, the potential increases sharply from -440 to -330 mV for the first 2000 s of the experiment and then gradually increases to -300 mV at the end of experiment. Figure 9 shows the variation of couple electrodes current density with respect to time. Associated current density of steel in saturated Ca(OH)₂ solution and also saturated Ca(OH)₂ solution containing 0.5M NaCl and NaNO₂ shows passivity behavior with a feature of current density decreasing gradually with time. The state of passivity for steel in every environment is attributed to the interception of the sum of anodic and cathodic currents according to mixed potential theory. The main anodic and cathodic currents are proposed by formation of iron hydroxide and oxygen reduction reactions according to the following electrochemical reactions:



When two nominal identical electrodes are in passive state with the identical ability for formation of passive film, since both electrodes are at the same corrosion potential, there is no driving force to generate net current. The resulting measured current by ZRA should show the feature of fluctuation around zero. Any dissimilarity on the surface of electrode due to the presence of surface inclusion, which their interface with the metallic matrix acts as sites for current leakage, causes a net current. If this net current has a trend of passive current it implies that both electrodes are in the passive state with a delay of ability to form passive film. In fact the current feature of couple electrodes in solutions of saturated Ca(OH)₂ and

Ca(OH)₂ containing 0.5M NaCl and 0.5M NaNO₂ shows a passive behavior (Figure 9).

Considering the formation of iron hydroxide passive layer as the anodic current (I_{pass}) and oxygen reduction reaction as the cathodic current ($I_{\text{O}_2/4\text{OH}^-}$) which is illustrated in Figure 10a, the resultant current measured by ZRA (I_{couple}) is defined as follow:

$$I_{\text{couple}} = \left(\sum I_{\text{anodic}} \right)_2 - \left(\sum I_{\text{cathodic}} \right)_2 = \left(\sum I_{\text{cathodic}} \right)_1 - \left(\sum I_{\text{anodic}} \right)_1 \quad (8)$$

$$I_{\text{couple}} = \left(I_{\text{pass}} \right)_2 - \left(I_{\text{O}_2/4\text{OH}^-} \right)_2 = \left(I_{\text{O}_2/4\text{OH}^-} \right)_1 - \left(I_{\text{pass}} \right)_1 \quad (9)$$

where number 1 and 2 represent the situation of electrodes in a couple electrodes illustrated in Figure 10. When the net current flows from electrode 2 towards 1, it mean that the electrode 2 plays as the anode of the cell whereas the electrode 1 as the cathode. According to the measured current density, which is the result of I_{couple} divided to the electrode surface area (A), for solution of saturated Ca(OH)₂ (Figure 9), the state of both electrodes in role of anode and cathode remains unchanged during one hour of measurement. While, for solution containing chloride and nitrite the role of electrodes in anode and cathode point of view is changed after 1500 s of measurement followed by situation that both electrodes remain at the same potential where no net current density is measured between 5000 to 8000 s of measurement. Finally, a negligible net current density flows between two electrodes in the remaining period of measurement (Figure 9).

A different variation of couple potential and current density between identical steel electrodes was measured in saturated Ca(OH)₂ containing 0.5M NaCl. The characteristic of current and potential variation are similar to previous mentioned solutions for the first 300 s of the experiment and in this period a sharp increasing of potential and decreasing associated with current density reveals establishment of passivity on both electrodes.

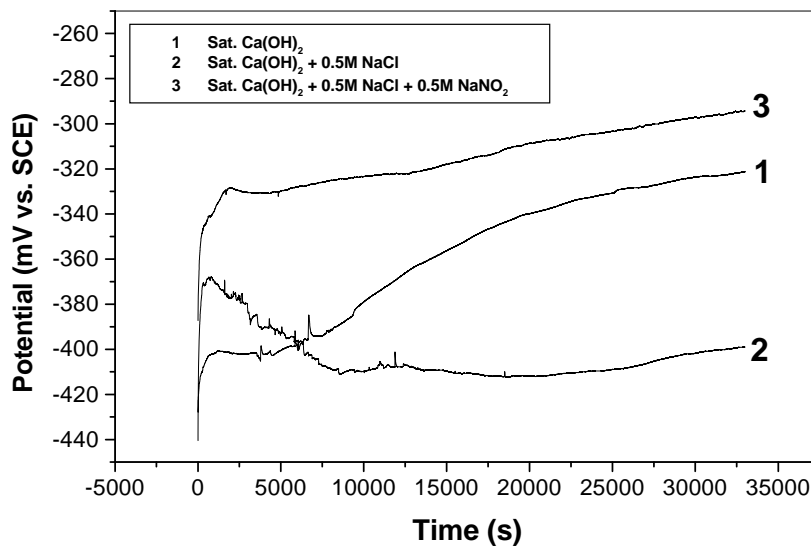


Figure 8. Variation of corrosion potential with immersion time of coupled nominal identical electrodes of mild steel in various test solution.

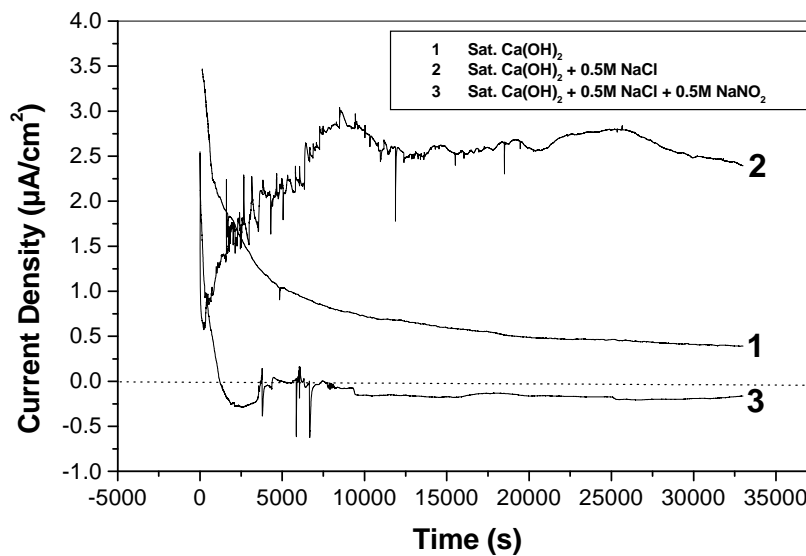
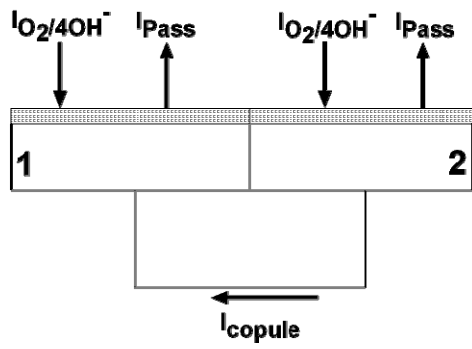


Figure 9. Variation of couple current density with immersion time of coupled nominal identical electrodes of mild steel in various test solution.

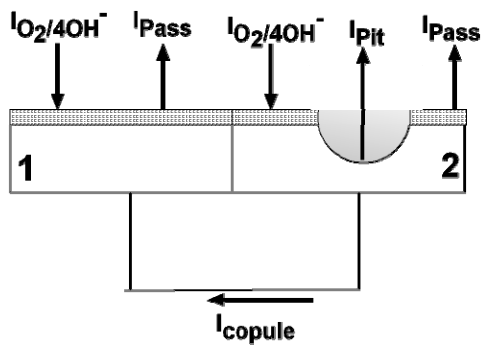
Pitting corrosion of specimen immersed naturally in solution containing chloride ions occurs when its corrosion potential exceeds the pitting potential.

It is visible that pitting corrosion occurs after immersion of couple electrodes for around 300 s at a

potential value of -370 mV. Pitting potential is a potential at which a decrease in potential and sharp and steady increase in current is observed (Figure 11). The pitting potential measured in potentiodynamic measurement (Figure 1) was very



(a)



(b)

Figure 10. Schematic presentation of couple identical electrodes; (a) corresponds to a condition when both electrodes are in passive state, (b) stands for a condition when one of the electrodes experiences pitting corrosion.

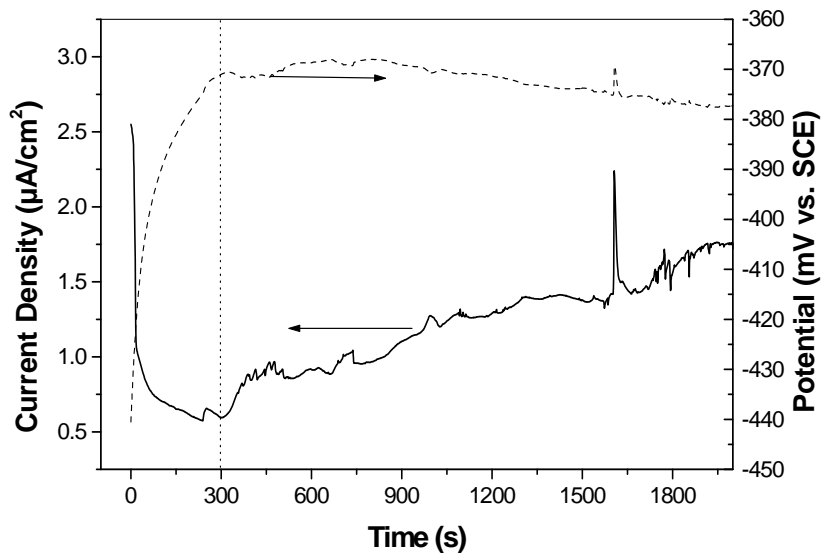


Figure 11. Variation of couple current density and potential with immersion time of nominal identical electrodes of mild steel in $\text{Ca(OH)}_2 + 0.5\text{M NaCl}$ solution.

comparable to pitting potential measured in couple electrode technique. In fact measuring net current of more than $2.5 \mu\text{A}/\text{cm}^2$ between two couple nominal identical electrodes is the result of net current difference between two connected electrodes. A net anodic current is generated in a specimen that pitting corrosion is occurred and identical net cathodic current is produced on the other electrode. The former electrode acts as the anode and the later as the cathode of the cell. Bearing in mind the additional anodic current (I_{pit}) as a result of pit formation in electrode 2 (Figure 10) and the existing anodic passive current (I_{pass}), the following formula can be demonstrated for the measured net current density after 300 s of immersion by ZRA:

$$I_{\text{couple}} = \left[\left(I_{\text{pass}} \right)_2 + \left(I_{\text{pit}} \right)_2 \right] - \left(I_{\text{O}_2/4\text{OH}^-} \right) = \left(I_{\text{O}_2/4\text{OH}^-} \right)_1 - \left(I_{\text{pass}} \right)_1 \quad (10)$$

$$i_{\text{couple}} = I_{\text{couple}} / A \quad (11)$$

Where A is the electrode surface area in cm^2 . Figure 10b illustrates schematic presentation of individual current and net resulting couple current that flows between two electrodes.

It should be finally mentioned that the galvanic currents measured by ZRA were all in the range of few μA . However, one should be aware that the values of current densities measured by ZRA are the average values on the whole sample surface and may underestimate the galvanic current sustainable due to the galvanic couple and are not the measure of local current generated by individual pit. In other words, the actual currents induced by pitting in microscopical level are much more than the values measured by ZRA for the same area as it has been reported elsewhere by employing local probe technique, SRET [23]. Therefore, although the galvanic current measured here by ZRA was not considerably high, but generating a sustainable and continuous current density of a few micro amperes from stable pits could cause a sever degradation in weld region.

4. CONCLUSION

- Pitting corrosion of mild steel in saturated $\text{Ca}(\text{OH})_2$ solution containing different concentration of NaCl depends on chloride concentration which decreases linearly with the logarithmic values of Cl^- concentration.
- Nitrite ions show an inhibition characteristic on pitting corrosion of mild steel in saturated $\text{Ca}(\text{OH})_2$ solution containing 0.5M NaCl. The pitting electrochemical potential value linearly increases toward more noble values with increasing the logarithmic values of nitrite concentration.
- A couple nominal identical electrode measurement technique shows a reliable method to evaluate pitting corrosion tendency of mild steel in saturated $\text{Ca}(\text{OH})_2$ solution containing 0.5M NaCl. Pitting potential measured by this technique is very close to the one measured by potentiodynamic measurement.

5. ACKNOWLEDGEMENTS

Authors would like to appreciate the financial support from Ferdowsi University of Mashhad provision of laboratory facilities during the period that this research was conducted

6. REFERENCES

1. Schiessl, P., "Corrosion of Steel in Concrete", Published by Chapman and Hall, New York, U.S.A., (1988).
2. Alonso, C., Andrade, C., Castello, M. and Castro, P., "Chloride Threshold Values to Depassivate Reinforcing Bars Embedded in a Standardized OPC Mortar", *Cem. Concr. Res.*, Vol. 30, (2000), 1047-1055.
3. Alonso, C., Castello, M. and Andrade, C., "Chloride Threshold Dependence of Pitting Potential of Reinforcements", *Electrochim. Acta*, Vol. 47, (2002), 3469-3532.
4. Li, L. and Sagues, A.A., "Effect of Chloride Concentration on Pitting and Repassivation Potentials of Reinforcing Steel in Alkaline Solutions", CORROSION/99, NACE, Houston, T.X., U.S.A., (1999).
5. Bertolini, L., Bolzoni, F., Pastore, T. and Pedeferra, P., "Stainless Steel Behavior in Concrete Pore Solution", *Br. Corros. J.*, Vol. 31, (1996), 218-223.

6. Gouda, V.K., "Corrosion and Corrosion Inhibition of Reinforcing Steel 1-Immersion in Alkaline Solution", *Br. Corros. J.*, Vol. 5, (1970), 198-204.
7. Dbouibi, L., Triki, E. and Raharinaivo, A. "Laboratory Experiments for Assessing the Effectiveness of Inhibitors Against Steel Corrosion in Concrete", *Proceeding of the Sixth International Symposium on Advances in Electrochemical Science and Technology*, Chennai, India, (1998).
8. Dbouibi, L., Triki, E., Salta, M., Rodriguez, P. and Raharinaivo, A., "Studies on Corrosion Inhibition of Steel Reinforcement by Phosphate and Nitrite", *Mater. Struct.*, Vol. 36, (2003), 530-539.
9. Andrade, C., Keddani, M., Novoa, X.R., Perez, M.C., Rangel, C.M. and Takenouti, H., "Electrochemical Behavior of Steel in Concrete: Influence of Environmental Factors and Cement Chemistry", *Electrochim Acta*, Vol. 46, (2001), 3905-3912.
10. Mammoliti, L., Hansson, C.M. and Hope, B.B., "Corrosion Inhibitors in Concrete. Part II: Effect on Chloride Threshold Values for Corrosion of Steel in Synthetic Pore Solutions", *Cem. Concr. Res.*, Vol. 29, (1999), 1583-1589.
11. ACI Committee 212, "Chemical Admixture for Concrete", *Concr. Inter.*, Vol. 44, (1999), 7.
12. Elsener, B., "Half-cell potential mapping to assess repair work on RC structures", *Const. Build. Mater.*, Vol. 15, (2001), 133-139.
13. Cigna, R., Andrade, C., Nuernberger, U., Polder, R., Weydert, R. and Siets, E., (Eds), COST 521 Action, "Corrosion of steel in reinforced concrete structure", Final Report, European Communities, Luxembourg, (2003).
14. Broomfield, J., Davies, K. and Hladky, K., "The use of Permanent Corrosion Monitoring in New and Existing Reinforced Concrete Structures", *Cem. Concr. Res.*, Vol. 24, (2002), 27-34.
15. Legat, A. and Zevnik, C., "The Electrochemical Noise of Mild and Stainless Steel in Various Water Solutions", *Corr. Sci.*, Vol. 35, (1993), 1661-1666.
16. Abd El Meguid, E.A. and Abd El Lattif, A.A., "Electrochemical and SEM Study on Type 254 SMO Stainless Steel in Chloride Solution", *Corr. Sci.*, Vol. 46, (2004), 2431-2444.
17. Azzeri, N., Mancina, F. and Tamba, A., "Electrochemical Prediction of Corrosion Behaviour of Stainless Steels in Chloride-Containing Water", *Corr. Sci.*, Vol. 22, (1982), 675-687.
18. Alvarez, M.G. and Galvele, J.R., "The Mechanism of Pitting of High Purity Iron in NaCl Solutions", *Corr. Sci.*, Vol. 24, (1984), 27-48.
19. Refaey, S.A.M., Abd El Rehim, S.S., Taha, F., Saleh, M.B. and Ahmed, R.A., "Inhibition of Chloride Localized Corrosion of Mild Steel by PO_4^{3-} , CrO_4^{2-} , MoO_4^{2-} , and NO_2^- Anions", *App. Surf. Sci.*, Vol. 158, (2000), 190-196.
20. Abd El Rehim, S.S., Hassan, H.H. and Amin, M.A., "Chronoamperometric studies of Pitting Corrosion of Al and (Al-Si) Alloys by Halide ions in Neutral Sulphate Solutions", *Corr. Sci.*, Vol. 46, (2004), 1921-1938.
21. Laycock, N.J., Stewart, J. and Newman, R.C., "The Initiation of Crevice Corrosion in Stainless Steel", *Corr. Sci.*, Vol. 39, (1997), 1791-1809.
22. Richter, S., Thorarinsdottir, R.I. and Jonsdottir, F., "On-line Corrosion Monitoring in Geothermal District Heating Systems", *Corr. Sci.*, Vol. 49, (2007), 1907-1917.