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Cyclic voltammetry study of reinforcement steel behavior in simulated carbonated concrete pore solution in presence of chloride and sulfate ions

A. Missour, M. Zertoubi, D. Benmessaoud Left, M. Azzi

Laboratoire Interface Matériaux Environnement(LIME), Faculté des Sciences Ain Chock, Université Hassan II Casablanca, B.P 5366 Maârif Casablanca Morocco.

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missourlime@gmail.com

1. Introduction

Abstract

The corrosion behavior of steel in simulated carbonate concrete pore solution has been studied by using cyclic voltammetric technique. The effect of temperature and the presence of several concentrations of aggressive ions have been investigated. The results show complex dependency between temperature and the corrosion behavior of steel. In carbonate solution without Cl⁻ rising temperature has a negative effect, while in the presence of Cl⁻ has a positive effect. Adding sulfates does not influence the corrosion resistance in carbonate with and without chlorides.

Steel in concrete is normally protected by the alkaline solution contained in the interstitial pore solution of the hydrated cement paste (with pH values higher than 13), which promotes passivation by the formation of a thin protective oxide film on the surface of the steel [1]. However, the passive film can be destroyed by carbonation of concrete or by the presence of chloride ions [1-2].

Chloride contamination of concrete is a frequent cause of corrosion of reinforcing steel [1]. Once the chloride content at the steel surface has reached a certain threshold value, the corrosion pitting will occur. In literature, this value is normally referred to as critical chloride content or chloride threshold value [3]. Pitting corrosion is defined as a localized dissolution of metals that occurs due to the breakdown of the protective passive film [4]. Pitting corrosion is characterized by pitting potential, E_{pit} the pitting potential can be defined, in a potentiostatic polarization curve, as the potential below which the metal surface remains passive and above which pitting corrosion starts to grow on the metal surface [5]. The pitting potential depends on many factors like pH, temperature and the presence or the absence of an inhibitor [1].

Carbonation of concrete is another mean of corrosion of steel reinforcement. The carbonation is the result of the reaction of carbon dioxide in the atmosphere with the hydroxide in the concrete [1]. During this reaction, carbonation of concrete reduces the initially high pH value of the pore solution phase to a level at which the passive film can break down [6]. Meanwhile, previous works have showed that bicarbonate and carbonate ions are beneficial for inhibition of corrosion. Yong Teck Tan et al [7] showed that bicarbonate/carbonate ions have an inhibitive effect on pitting corrosion. This inhibitive effectiveness was found to be around one order of magnitude lower relative to hydroxide, but can be dominant when the hydroxide concentration is much lower than the bicarbonate/carbonate concentration.

Only a few studies were carried out concerning the effect of temperature on the corrosion behavior of steel [8-10]. However, temperature is a key factor in chemical reactions kinetics, including corrosion. Samin Sharifi-Asl et al [8] reported that in alkaline solution (Saturated calcium hydroxide) and for all chloride concentrations, an increase in temperature from 25°C to 85°C results in a decrease in localized corrosion resistance.

The rapid cyclic voltammetric method is fast, reproducible, and provides information on the corrosiveness of the pore solution environment surrounding the embedded metal [11]. In addition to these benefits, it is worth noting

that a using high scan rate does not permit the achievement of equilibrium condition on the electrode surface, which means that only reaction transients will be evidenced by this technique, therefore crevice risk will be almost negligible [12].

In this paper, the effect of temperature and aggressive ions on the corrosion behavior of steel in a medium rich with bicarbonate/carbonate content was evaluated using cyclic voltammetric technique.

2. Material and Methods

2.1. Sample and solution preparation

The FeE500 reinforcement steel with the chemical composition shown in table 1 was used as working electrode according to a geometric shape adaptable to the rotating disk electrode, leaving a surface area of 0.158 cm². The exposed area was mechanically polished with 400, 800, 1200 and 1500 grades of abrasive papers, rinsed abundantly with distilled water and degreased with acetone before each electrochemical experiment.

Table 1: Chemical composition (wt%) of reinforcement steel (FeE500).												
С	Р	S	N_2	Mn	Cr	Ni	Cu	Sn	Mo	V	Si	Fe
0.22	0.05	0.05	0.012	0.80	0.3	0.3	0.5	0.05	0.05	0.08	0.3	Balance

The testing solution was composed of (K₂CO₃ (0.125M), KHCO₃ (0.25M), Na₂CO₃ (0.025M) and NaHCO₃ (0.05M)), which simulates the carbonated concrete pore solution (CCPS). The value of pH was (\approx 9). The solution was prepared using grade chemical reagents and distilled water. Chloride was added to the simulated pore solutions at concentrations of up to 1.0 M to simulate marine exposures. These solution compositions and Cl⁻ concentrations were selected considering that at 100+ years. Cl⁻ concentrations at the concrete cover depth may begin to approach or exceed that present at the surface of the concrete, and the concrete may show a reduction in pH due to carbonation through the cover depth [13].

2.2. Electrochemical measurements

Electrochemical measurements, including open circuit potential and cyclic voltammetry, were performed in a three-electrode cell. The reinforcement steel (FeE500) was used as working electrode, platinum as counter electrode and a saturated Ag/AgCl as reference electrode. The open circuit potential curves were recorded for one hour in the absence and presence of different concentrations of chloride and sulfate ions. All experiments were thermo-stated at different temperatures (20°C, 30°C and 40°C). Cyclic voltammetry was performed at scan rate 50 mV/s by a forward scan from a cathodic potential 1.2 V/Ag/AgCl to an anodic potential 0.6 V/Ag/AgCl and a backward scan with the same limits. Electrochemical experiments were performed with a potentiostat/galvanostat model voltalab 40 PGZ 301 (Radiometer Analytical), monitored by voltamaster 4 software. The rotation rate of the working electrode is adjusted at 1000 rpm. Each experiment was repeated three times to confirm reproducibility of the results. Values are mean of \pm standard deviation of three experiments.

2.3. Surface analysis

The surface morphology of the reinforcement steel was examined by a metallurgical microscope (OLYMPUS BX60F5).

3. Results and discussion

3.1. Carbonated solution: Effect of temperature

Figure 1 represents the forward scan of cyclic voltammograms curves of carbon steel in simulated carbonated concrete at different temperatures. For the forward scan and at a temperature of 20°C, two anodic peaks were identified: the first peak at low potential was associated with the formation of ferrous hydroxide and ferrous carbonate simultaneously, and the second one at high potential is related to the transformation of ferrous carbonate to iron oxides [7, 14, 15].

In order to evaluate the effect of the solution temperature on the behavior of steel in carbonated medium, we rose the temperature to 40°C, which led to an increase in dissolution rate (peaks I and II), the same result was reported in previous work [14]. There are a few hypotheses that may explain the effect of temperature on the behavior of steel in aerated and carbonated medium. Bruno et al [16] suggested that the increase of corrosion rate in peak I is due to the oxidation of carbonate ferrous into oxy-hydroxide: this reaction will generate a local acidification according to the equilibrium (1):

$$2H_2O + FeCO_{3(aq)}$$
 \clubsuit $FeOOH + e^- + HCO_3^- + 2H^+$ $eq(1)$



Figure 1: Forward scan Curves of steel in simulated carbonated concrete at different temperatures.

Davies and Burstein [17] proposed that at lower pH and low redox potential, the dissolution rate of steel depends on carbonate content. In such conditions, ferrous carbonated (FeCO₃) complex is predominant: $Fe^{2^+} + HCO_3^- \implies FeCO_3 + H^+ = eq(2)$

Both equilibrium (1) and (2) generate a local acidification which leads to accelerate the solubility of iron oxide. Previous work showed that the temperature influences the solubility of iron carbonate [18]. Raising temperature enhances the stability of FeCO₃ according to the equilibrium (3):

On the one hand, in a medium rich with carbonate content, and according to equilibrium (3), the increase of the temperature will generate a deficit of iron carbonate due to their precipitation. Thus, the equilibrium (3) will shift to the right in the sense of formation of more $FeCO_3$. As a result, the solubility of ferrous cations will increase. On the other hand, it is well known that the precipitation of $FeCO_3$ enhances the stability of the passive film and plays measure role in suppressing the underlying dissolution [15]. On the opposite, the increase of the solution temperature causes a high current density of the peaks I and II as well as a current density passivation.

After the first peak, a decrease in the density of the current was observed that may indicate the formation of a passive film. The density of the current recorded has a very high value and increases with the solution temperature, this result indicates that the formed film presents a high reactivity rather than efficiency to decrease the dissolution of metal, this is in good agreement with a recent work [15]. Previous studies reported that the density of oxygen vacancy increases with increasing the solution temperature, which can lead the film to be more inhomogeneous, and the film compaction character deteriorated. Accordingly, many transfer channels may be formed in the film and naturedly, the mobility of ions in the film should increase with increasing the solution temperature, and the protective effect of the passive film decreases [19]. The second peak corresponds to the transformation of iron carbonate to an iron oxide in the presence of oxygen, we notice that the current density increases with the solution temperature according to the equilibrium (4):

$$4FeCO_3 + O_2 + 4H_2O \qquad \checkmark \qquad 2Fe_2O_3 + 4HCO_3 + 4H^+ \qquad eq(4)$$

We notice that the current density increases with the solution temperature. Increase temperature revealed also that the first peak contains two peaks. A recent work that has been performed in carbonate solution showed that the formation kinetics of $Fe(OH)_2$ interferes with the formation kinetics of $FeCO_3$ [15]. Thus, increasing temperature may be leading to dissociate the formation kinetics of the two species.

3.2. Carbonated solution: Effect of temperature and chlorides

Figure 2 (a, b and c) represents the voltammetric curves of the steel in a carbonated solution in the presence of chloride ions, respectively, 1%, 3.5% and 5% of NaCl, at different temperatures. The forward scan reveals the existence of two peaks: the first one at a potential of -607 mV/Ag/AgCl may be attributed to the formation of a mixture of iron ferrous and iron carbonate, and the second one at -281 mV/Ag/AgCl may be due to the oxidation of iron carbonate to iron oxide [7]. When the anodic polarization of steel reaches a certain value of critical potential (pitting potential) the current increase abruptly, indicating the destruction of the passive layer.



Figure 2: Cyclic voltammetry curves of FeE500 steel in a carbonate solution in the presence of a) 1% NaCl – b) 3.5% NaCl – c) 5% NaCl; at different temperatures.

Raising the solution temperature until 40°C revealed a different behavior of steel in the presence of chloride ions. Figure 3 shows that the current density of the peaks I decrease with the solution temperature as well as the current density in passive domain. Previous studies reported that the presence of chlorides promotes a more oxidized passive layer [20].



Figure 3: Variation of the current pitting (peak I) with temperature for different concentrations of chloride ions.

The figure 4 shows that for a fixed concentration of chloride ions increasing solution temperature shifts the pitting potential to a more positive potential. Many investigations have been performed in carbonated solutions and in the presence of chloride ions. Yong Teck Tan [7] showed that Bicarbonate/carbonate ions have an inhibitive effect on pitting corrosion. This inhibitive effectiveness can be dominant when the hydroxide concentration is much lower than the bicarbonate/carbonate concentration. The presence of high levels of carbonate and bicarbonate has a beneficial effect on the chloride threshold and improves the resistance of carbon steel to localized corrosion.



Figure 4: Evolution of potential pitting with temperature at different concentrations of NaCl.

The figure 5 shows the variation of the free potential in a carbonate medium in the presence of chloride ions, it is found that for a fixed concentration of chloride the temperature increase shifts the free corrosion potential to low values. Thus the rate of corrosion increases with the temperature of the solution. However, the voltacyclic curves show a totally different behavior, going from the temperature of 20 °Cto40 °C, a decrease in the oxidation rate is observed and the pit potential becomes more positive, so the results show that the behavior of metal depends on temperature, solution chemistry and the nature of the species formed on the surface of the steel.



Figure 5: Variation of the corrosion potential with temperature for different concentrations of chloride ions.

Figure 6 is optical micrographs of steel examples showing the pitting attack obtained after the cyclic voltammetry tests, it can be seen that the surface of the steel at 20°C is more damaged at 40°C.

3.3. Carbonated medium: Effect of temperature and sulfates ions

Figure 7 shows the forward scan of cyclic voltammetric curves of steel in simulated carbonated concrete with different concentrations of sulfate ions. The anodic region shows the presence of two peaks prior to a large passivation domain, no breakdown passivity have been recorded with increasing amount of sulfate ions. Previous work has been performed in a saturated hydroxide calcium solution: it revealed that the presence of sulfate ions leads to the formation of a sulfate film which is less protective than that the original iron oxide film [21]. Moreover, many investigations reported that sulfates present a more aggressive corrosion risk to steel than chlorides [22, 23]. The figure 7 shows that the presence of sulfates does not influence the behavior of steel in a medium rich with carbonate and bicarbonate ions, this fact may be due to the buffering effect of the solution. Figure 8 shows that the rate of corrosion decreases by increasing the temperature solution, this behavior may be due to the formation of FeCO₃ on the surface of the steel.

3.4. Carbonated medium: Effect of sulfates and chlorides

Recent works performed in saturated hydroxide solution, reported that corrosion rate of steel samples accelerates when both chlorides and sulfates are present in simulated concrete pore solution [22, 24].



Figure 6: Optical micrographs of steel after CV test in carbonated solution with 1% NaCl. a₁) and a₂) at temperature 20°C; and b₁) and b₂) at temperature 40°C.



Figure 7: Cyclic voltammetry curve traced in a carbonate solution in the presence of different concentration of sulfate.



Figure 8: Cyclic voltammetry curve traced in a carbonate solution in the presence of a) 1% Na₂SO₄ – b) 3.5% Na₂SO₄ – c) 5% Na₂SO₄ at different temperatures.

Figure 9 shows cyclic voltammetric curves of steel in simulated carbonated concrete in the presence of 3.5% NaCl and with different concentrations of sulfate ions. The result shows that increasing sulfate concentration has no influence neither on the current of the peak or the pitting potential. This result may be attributed to the

buffering effect of carbonate/bicarbonate solution. The figure 10 shows examples of the pitting attack after the cyclic voltammetry tests.



Figure 9: Cyclic voltammetry curve in a carbonate solution in the presence of a) $1\% \text{ Na}_2\text{SO}_4 - b) 3.5\% \text{ Na}_2\text{SO}_4 - c) 5\% \text{ Na}_2\text{SO}_4$ at different temperatures.



Figure 10: Optical micrographs of steel after CV test in carbonated solution with 3.5% NaCl and 3.5 Na₂SO₄ at temperature 20° C.

Conclusion

Through the present work, we highlighted the influence of the chloride and sulfate ions as well as the temperature effect on the behavior of reinforcement steel in carbonated concrete pore solution. The main conclusions that we can draw are:

- In a medium rich with bicarbonate/carbonate ions increasing the solution temperature leads to accelerate the dissolution of metal in lower as well as in more positive potential.
- The increase of temperature may be leading to dissociate the formation kinetics of the two species.
- In a medium rich with bicarbonate/carbonate and in the presence of chloride ions, temperature may be enhance the resistance of the metal against pitting corrosion and decelerate the dissolution of steel in lower potential.
- Adding sulfate ions to solution containing chloride ion or not does not influence the behavior of steel.

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