



Electrochemical Behavior of Reinforcement Steel in Simulate Concrete Pore Solution with and without Chloride Ions

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ABSTRACT

Reinforcement steel working electrode was used in electrochemical tests (EIS and PDP) after 0 h and 24 h immersion in SCP solutions (saturated $\text{Ca}(\text{OH})_2$) maintained at 30°C with and without various $[\text{Cl}^-]$. EIS data obtained both at 0 h and 24 h immersion revealed that at $0.01 \text{ M} < [\text{Cl}^-] < 0.10 \text{ M}$, steel resists corrosion more than the Cl^- free solution, while at $[\text{Cl}^-] \geq 0.10 \text{ M}$ steel corrosion rate increases appreciably. PDP data showed that at (i) $[\text{Cl}^-] < 0.05 \text{ M}$ for 0 h immersion and (ii) $[\text{Cl}^-] < 0.25 \text{ M}$ for 24 h immersion, steel resists pitting corrosion even if it was polarized to the oxygen evolution potential, indicating film formation of corrosion products on the steel surface which becomes more denser with increasing immersion time. Accordingly, the CTL and the corresponding ratio ($[\text{OH}^-]/[\text{Cl}^-]$) of steel in SCP solution varied with the immersion period as well as with the techniques used.

Keywords: Corrosion, Steel, Concrete, Pore solution, Chloride ions, Potentiodynamic, Impedance

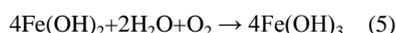
INTRODUCTION

Steel-reinforced concrete is considered the most important material used extensively in the construction due to its economical and durable properties [1,2]. Reinforcing steel bars (rebar) embedded in the concrete not only to give the structure with best possible strength but also to create a protective surroundings for the rebar. As a result of the high alkalinity environment of concrete and low diffusion rate of both oxygen and water from atmosphere to the concrete pores, the rebar will be protected by a stable passive film and hence insignificant level of corrosion rate is maintained [3-5]. The corrosion rate of rebar becomes significant when some environmental factors cause deterioration of the cover concrete and enhance the diffusivity of aggressive species [6]. Carbon dioxide (CO_2) and chloride ions (Cl^-) are of the major aggressive species responsible for the corrosion problems of reinforcement steel in concrete structures. The ingress of CO_2 will reduce the pore solution alkalinity and eventually passivity breakdown and corrosion of rebar take place. While, the Cl^- ions either present initially or by diffusion from outside environment play an important role for the most damage in concrete structures by the so called chloride-induced corrosion [6,7]. The main characteristic of chloride-induced corrosion is as follows [6]: (i) Separation between the anodic and cathodic areas is occurred, and corrosion rate is significant and localized. (ii) Once the localized (pitting) corrosion is initiated, it is far more difficult to remedy than carbonation.

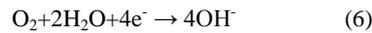
For corrosion to be initiated, the passive film must be penetrated by the Cl^- ions and excite the surface of the steel to form an anode as follows [8]:



The activated (i.e., depassivated) area becomes an anode, while the passivated surface becomes a cathode. At the anode of the cell, the reaction is described by:



In contrast, the cathodic reaction is given by:



According to Equation 2, Cl^- ion is regenerated so that the rust (Eqn. 5) contains no chloride, although the iron chloride is formed as the intermediate stages (Eqn. 1). So, Cl^- ions are not consumed in the process but facilitate to break down the passive film of oxide on the steel and permit the corrosion process to proceed rapidly.

The field of chloride-induced reinforcement steel corrosion has been covered extensively by various investigations either in concrete or in Simulated Concrete Pore (SCP) [7,9-12]. Generally, the existence of critical chloride concentration called Chloride Threshold Level (CTL) which result in a serious corrosion rate is clear cut. However, no unified conclusion about the value of CTL was stated. This may be due to the variance in experimental conditions and methods used to predict corrosion rates.

The technology of corrosion rate measurements has been advanced for lab or field studies in order to give accurate and timely corrosion measurements. Electrochemical techniques have been used widely to study fundamental phenomenological corrosion reactions of steel in concrete or SCP solutions [7,10-12]. The general methods being used include electrical resistance, Potentiodynamic Polarization (PDP), Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS). In The present study the influence of Cl^- ions concentration, $[\text{Cl}^-]$, on the corrosion behavior of reinforcement steel in SCP solutions for 0 h (once immersion) and 24 h immersion at 30°C was investigated by applying PDP and EIS measurements. The upper limit of CTL was determined based on the electrochemical parameters such as polarization resistance (R_p), pitting potential (E_{pit}) and corrosion current density (I_{corr}).

EXPERIMENTAL

Saturated calcium hydroxide ($\text{Ca}(\text{OH})_2$) was used in this work to simulate concrete pore solutions with pH value of 12.6. A set of SCP solutions containing various chloride levels in the range from 0.01 to 1.00 M were used to simulate chloride contamination. All solutions were prepared using analytical reagent chemicals and deionized water.

The material of working electrode was commercial reinforcement steel rebar which had the following composition by percent weight: C: 0.280; Si: 0.220; Mn: 0.730; P: 0.015; S: 0.006; N: 0.007; Fe: balance. The steel was cut into cylindrical rod of 5 cm in length and 1 cm in diameter. The steel rod was preserved with epoxy resin except the working surface of 0.785 cm^2 which exposed to the tested solutions. Before each experiment, the working electrode was polished with different grades of emery paper up to 1200, washed with deionized water and degreased with ethanol and finally dried with stream of air.

EIS and PDP tests were performed in an electrochemical cell of three electrodes using ACM instrument version 5 (Gill AC serial no. 1649). The steel working electrode, which was explained in the previous paragraph. A Coiled platinum wire (0.2 mm diameter) was used as an auxiliary electrode. The reference electrode was Ag/AgCl , KCl_{sat} . All measurements were done after 0 h and 24 h immersion in stagnant SCP solutions with and without various $[\text{Cl}^-]$ and at 30°C. The EIS spectra were collected over the frequency range from 30 kHz to 0.1 Hz using 30 mV sinusoidal perturbation. The PDP curves were recorded in the potential range from -1000 to 800 mV with a scan rate of 2.5 $\text{mV}\cdot\text{s}^{-1}$. The impedance spectra were fitted to appropriate equivalent circuit using ZsimDemo 3.20, while the polarization curves were analyzed by using ACM instrument software version 5.

RESULTS AND DISCUSSION

EIS measurements

Figures 1 and 2, show the initial and final frequency response of reinforcement steel electrode after immersion directly (0 h) in SCP solution with and without different $[\text{Cl}^-]$ where they represented in the form of Nyquist and Bode, respectively. The shape of the experimental curves (Figure 1) reflected the typical response of reinforcement steel in the SCP solutions in the presence of chlorides [13].

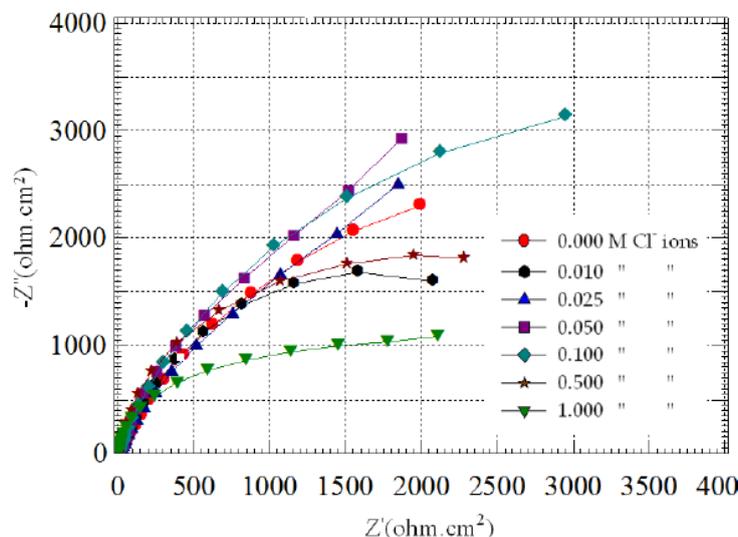


Figure 1: Nyquist plots for reinforcement steel in SCP solutions with and without different concentrations of Cl^- ions at 0 h immersion

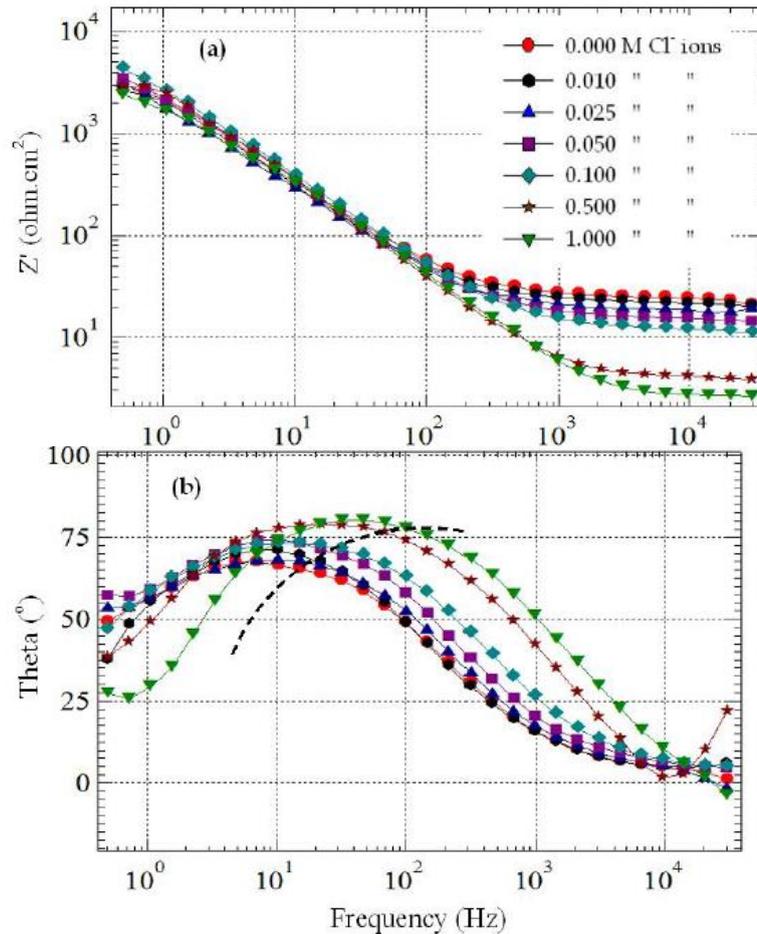


Figure 2: Bode plots for reinforcement steel in SCP solutions with and without different concentrations of Cl⁻ ions at 0 h immersion

Figure 2 illustrates that at low frequencies, the real impedance is corresponding to the polarization resistance (R_p) plus the solution resistance (R_s). While, at high frequencies, the real impedance is just equal to R_s . As was observed the impedance at both limits depends on $[Cl^-]$. On the other hand, as was shown by the broken line in Figure 2b, the position of the maximum phase angle shifts towards higher frequencies with increasing $[Cl^-]$, indicating resistive behavior associated with less protective film on the electrode surface. The deviations of phase angle from 90° (Figure 2b) and of the slope in the impedance modulus plot from -1 (Figure 2a) expressed that the system did not behave like an ideal capacitor [14,15]. Similar EIS spectra (not included) were obtained for reinforcement steel electrode at 24 h immersion in SCP solutions with and without different $[Cl^-]$.

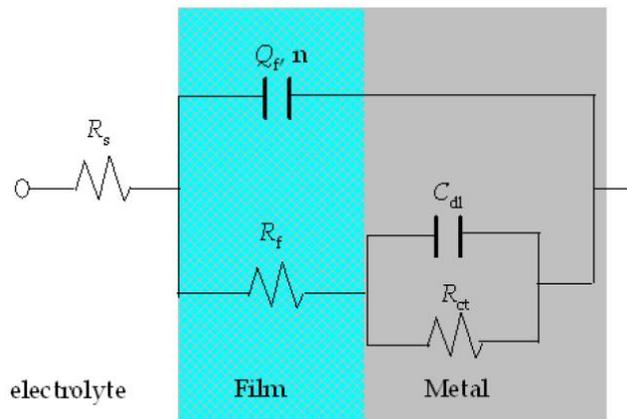


Figure 3: Equivalent circuit of reinforcement steel corrosion in SCP solutions with and without different concentrations of Cl⁻ ions

In order to obtain more insight into the general corrosion behavior of reinforcement steel under the studies conditions, an equivalent circuit shown in Figure 3 was successfully used to interpret the EIS data for reinforcement steel in SCP solutions after 0 h and 24 h immersion with and without Cl^- ions which in good agreement with literature [7,11,16]. In this circuit, two separated time constants in series with the solution resistance (R_s) were observed. The low-frequency time constant ($R_{ct}C_{dl}$) reflects the charge transfer process of steel electrode, and the high-frequency time constant (R_fQ_f) is associated with the redox reactions (Fe^{2+}/Fe^{3+}) of the inert film [7,16]. Where R_f , R_{ct} and C_{dl} represent respectively the film resistance, the charge transfer resistance and the double layer capacitance.

Once a non-ideal frequency response is in attendance may be due to surface roughness and in homogeneities of working electrode, it is normally accepted to apply distributed circuit elements in an equivalent circuit. In the present work, a constant phase element (CPE expressed as Q_f) was used to replace the film capacitance. The values determined for R_f oscillate a lot, probably because the difficulties of analyze spectra with so overlapped time constants [17]. However, the R_p values ($R_p=R_f+R_{ct}$) were successfully used for the prediction of CTL using EIS measurements.

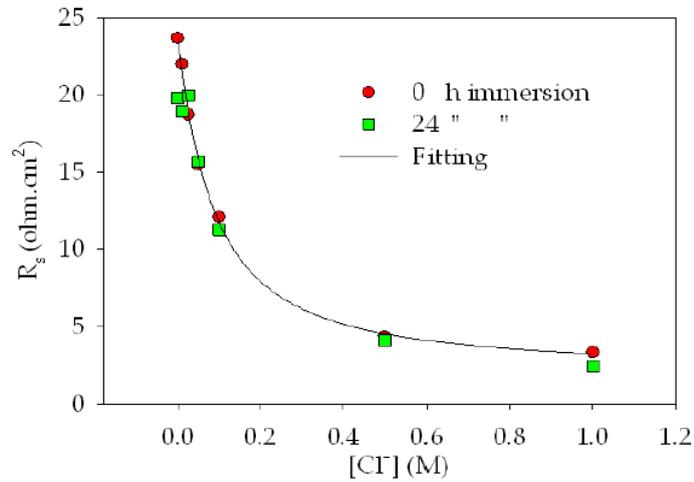


Figure 4: Variation of R_s with Cl^- ions concentration

Figure 4, shows that R_s decreased exponentially with increasing $[Cl^-]$ may be due to conductivity enhancement by Cl^- ions addition which indirectly proportional to the solution resistance. Similar findings were obtained in previous studies [18-20]. Moreover, Sahoo and Balasubramaniam [21] reported that R_s for saturated $Ca(OH)_2$ solution free of Cl^- ions was about 25 ohm.cm² which in good agreement with that recorded in the present study. Anyway, R_s values do not vary appreciably with the immersion period in the studied range of $[Cl^-]$, possibly indicative that Cl^- ions do not consume with time.

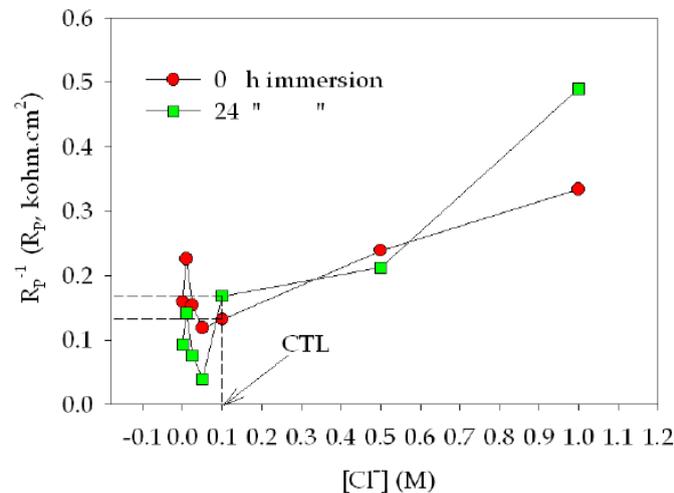


Figure 5: The effect of Cl^- ions concentration on the value of R_p^{-1} for reinforcement steel in SCP solution

The electrochemical theory postulated that the corrosion rate is inversely proportional to the polarization resistance [21]. So, the effect of $[Cl^-]$ on the corrosion rate of reinforcement steel in SCP solutions after 0 h and 24 h immersion can be clarified by plotting R_s^{-1} vs. $[Cl^-]$ as shown in Figure 5. The results showed that the corrosion rate of reinforcement steel increases somewhat with the first level of Cl^- ions addition (0.01M), then it tends to decrease until reaches minimum value at 0.05 M of Cl^- ions after which it obviously increases with increasing Cl^- ions concentration in the studied range. If the passive film destroyed, corrosion can begin. In general, chloride ions are described as a specific and unique destroyer [22]. But cannot deny the inhibitive action of chloride ions. According to the work of Angappan *et al.* [23] the thickness of the passive film on 304 stainless steel in alkaline solution was increased with low chloride additions. This behaviour was attributed to the dehydration of the oxide thin layer leading to the accumulation of excess OH^- ions at the oxide/electrolyte interface. Based on the obtained results from Figure 5, 0.1 M of Cl^- ions can be suggested as the upper limit of CTL, because steel corrosion rate starts to increase continuously after this level [24]. Taking into consideration that the pH of the studied SCP solution is about 12.6 and does not change significantly by the addition of NaCl, the $[Cl^-]/[OH^-]$ ratio at the CTL is approximately 2.5 which is higher than that ($[Cl^-]/[OH^-]=0.6$) proposed by Haussman [24]. Unfortunately, the chloride threshold values reported in the literature exhibit a broad scatter and have been estimated using a variety of different experimental approaches, therefore making comparison of results uncertain [25].

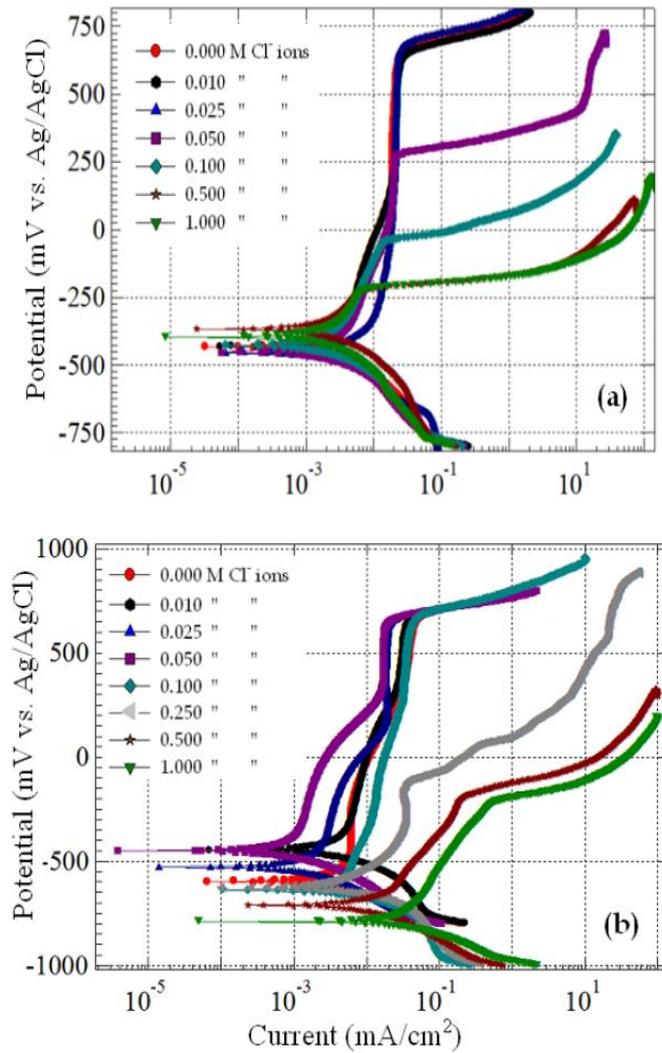


Figure 6: Potentiodynamic polarization curves for reinforcement steel in SCP solution without and with different concentrations of chloride ion at (a) 0 h and (b) 24 h immersion

PDP measurements

Figures 6a and 6b depict the anodic and cathodic polarization curves for reinforcement steel immersed in SCP solutions with and without different $[Cl^-]$ for 0 h and 24 h immersion, respectively. It can be seen that the steel has a passive area that ongoing straight away after the Tafel area and sustained until E_{pit} was reached at which abrupt current increase is observed. E_{pit} is a measure for the metal resistance of pitting (localized) corrosion. Since it is interpreted as the potential above which nucleated pits can propagate to attain stable growth so it is more distinctive of pit growth processes rather than passivity breakdown [25]. It was found that in solutions without and with (i) $[Cl^-] < 0.05$ M (Figure 6a) and (ii) $[Cl^-] < 0.25$ M (Figure 6b), a rapid increase in current density was obtained at potentials of average value about 650 mV vs. Ag/AgCl, $KCl_{sat.}$. The increase in current density at -600 mV vs. SCE was probable due to the oxygen evolution process, as estimated from the H_2O electrochemical stability diagram [26]. For the PDP experiments, sometimes pitting either did not occur or occurred only after the oxygen evolution potential was overcome. In point of the fact that the corrosion potential never go over the oxygen evolution potential in systems containing no more than dissolved oxygen as the strongest oxidizing agent, chloride concentrations for which E_{pit} observed in the same range of that for oxygen evolution were not taken into consideration when deciding the CTL required for pitting [27]. The electrochemical parameters such as β_a , β_c , E_{corr} , E_{pit} and I_{corr} were estimated and expressed in relation with $[Cl^-]$ or $\log [Cl^-]$ as shown in Figure 7(a-d), respectively. The obtained results based on the immersion time would be interpreted as below.

For 0 h immersion

β_a values were higher than the corresponding values of β_c (Figure 7a), indicating anodic control due to the oxide film on the steel surface that formed normally in such high alkaline solutions. Obviously, β_a value decreased with increasing $[Cl^-]$. This change can be considered as being due to the catalytic participation of Cl^- ions in film dissolution mechanism [8].

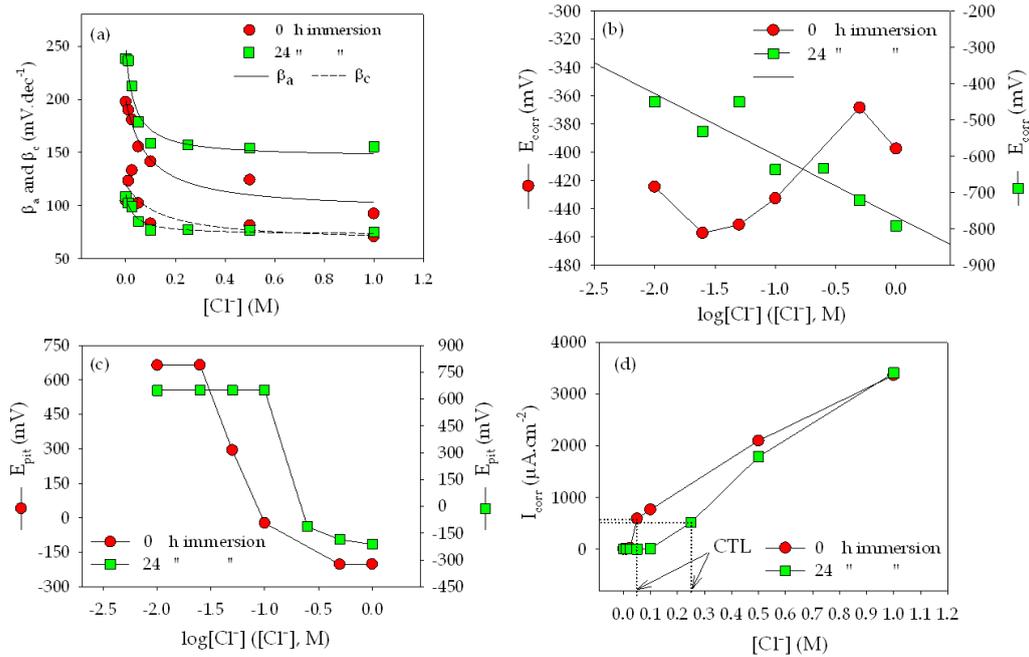


Figure 7: The effect of Cl^- ions concentration on the PDP parameters: (a) β_a and β_c (b) E_{corr} , (c) E_{pit} and (d) I_{corr} for reinforcement steel in SCP solution

Figure 7b showed no definite trend for E_{corr} value with $[Cl^-]$. This result was expected as the PDP curves were recorded in the early stage of immersion at which steady state potentials are not reached yet. At $[Cl^-] \geq 0.05$, I_{corr} value increases dramatically (Figure 7d) and E_{pit} drops to active potentials ($E_{pit} \leq 294.7$ mV vs. Ag/AgCl, KCl_{sat}) (Figure 7c), indicating pit development and the transition to active dissolution [28]. The CTL of steel can be suggested to be 0.05 M and the corresponding ratio $[Cl^-]/[OH^-]$ is about 1.26. This ratio is lower than that obtained using EIS measurements ($[Cl^-]/[OH^-]=2.5$) under the same conditions, possibly due to that EIS method was assigned as a non-destructive [29] and moreover, measurements were done directly when the steel becomes in contact with the tested solutions, where film breakdown does not occur immediately but takes some time [30].

For 24 h immersion

β_a and β_c values gave the same trend as in the case of 0 h immersion (Figure 7a) with noticing that β_a values were higher than the corresponding β_c values recorded at 0 immersion. In the studied range of $[Cl^-]$ may be attributed to that the corrosion products becomes more denser on the steel surface with increasing immersion time [31] leading to increase the anodic over potential of film dissolution. Figure 7-b showed active shift for E_{corr} to cathodic potentials with increasing $[Cl^-]$. This observation is in good consistency with previous studies [11,32,33]. Results showed that E_{pit} values are stabilized around oxygen evolution potential (Figure 7b) while I_{corr} values do not change appreciably (Figure 7c) over a wide range of $[Cl^-]$ from 0.01 to 0.1 M. This behaviour indicated that increasing immersion time for 24 h working to improve the pitting corrosion resistance. Eyu et al. [31] reported that both passivation and pitting potentials for steel in bicarbonate solutions containing chloride ions were increased with increasing immersion time. At $[Cl^-] \geq 0.25$ M, a sudden shift for E_{pit} values towards cathodic potentials was observed which normally associated with abrupt increase in the I_{corr} values, suggesting that the CTL of steel would be 0.25 M with ratio $[Cl^-]/[OH^-]$ is about 6.28. Figure 7c obviously showed that at $[Cl^-] < 1$ M, I_{corr} values is lesser than those recorded at 0 immersion, once again extended immersion time improves the steel corrosion resistance and this behavior is not the case with highest level of $[Cl^-]$. It was reported [33] that, steel current density increased with time in higher chloride containing solutions, and decreased rapidly and afterwards remained unchanged in all other solutions of low chloride concentrations.

CONCLUSION

The following points give the most important results obtained from this investigation:

- ❖ The resistance of SCP solution (R_s) decreased with increasing $[Cl^-]$ which attributed to the increase of solution conductivity with the addition of Cl^- ions.
- ❖ Both 0 h and 24 h immersion recorded a decrease in R_p^{-1} (i.e., corrosion rate) values with $[Cl^-]$ in the range from 0.01 M to 0.05 M, while a continuous increase was observed with $[Cl^-] \geq 0.10$ M.
- ❖ E_{corr} value shifted to more active potentials with $[Cl^-]$ and this behavior is more pronounced in the case of 24 h immersion.
- ❖ At $[Cl^-] < 1.00$ M, 24 h immersion condition showed less values for I_{corr} as compared with 0 h immersion, indicating that the corrosion products becomes more denser on the steel surface with increasing immersion time which increase the energy barrier for metal dissolution.
- ❖ R_p , E_{pit} and I_{corr} are good indicative parameters for the CTL of steel in SCP solutions contaminated with Cl^- ions.
- ❖ The results revealed that the value of CTL varied with immersion period and the technique used. The obtained CTL from EIS and PDP measurements are respectively (i) 0.1 M (for both 0 h and 24 h immersion) and (ii) 0.05 and 0.25 M (at zero and 24 h immersion, respectively).

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