Int. J. Electrochem. Sci., 11 **(2016)** 4658 – 4666, doi: 10.20964/2016.06.56

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Steel Corrosion Behavior Measurement Based on Electrochemical Approach

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Received: 6 March 2016 / *Accepted:* 4 April 2016 / *Published:* 4 May 2016

Concrete is an important material commonly used in the building. The exposure of the reinforced concrete in different environment could cause different rate of corrosion. Chloride ions and carbon dioxide are two major substances could accelerate the corrosion rate. In this contribution, we used the electrochemical methods for evaluating the corrosion rate of the two different types of concrete in the presence of chloride ions and carbon dioxide environment. Polarization resistance, polarization curves intersection and electrochemical impedance spectroscopy were applied for detail analysis. The results showed the corrosion rate of both concrete was similarly when exposed to carbon dioxide while the binder played an important role when the environment contained chloride ions.

Keywords: Cement; Corrosion; Concrete; Electrochemistry; Polarization resistance; Electrochemical impedance spectroscopy

1. INTRODUCTION

Concrete corrosion has generated much concern with regard to safety issue. The desired service life time of the reinforced concrete should be longer than the environment condition corrosion could damage its structure [1-3]. As is known to all that the steel bar corrosion is the major problem of the reinforced concrete which high affect its durability [4-6]. Chloride ions and carbon dioxide are two aggressive substances could accelerate this corrosion process [7, 8]. Moreover, more than 80% carbon dioxide emissions in the building industry are caused by the cement production [9, 10]. Usually, the corrosion process of the reinforced concrete is called “camouflaged” phenomenon, which the beginning of the corrosion should no sign at all [11-15]. The notice of corrosion sign commonly indicated the corrosion process has begun very long time and the corrosion was already spread.

Therefore, the determination of reinforced concrete corrosion is very important for construction safety [16-21].

Different methods have been developed for determination and analysis of corrosion in reinforced concrete [22, 23]. Among them, the electrochemical approach was found more reliable, fast and do not need to cause serious damage of building structure [24-33]. Moreover, the electrochemical approach can be applied for both laboratory and field analysis. For example, electrochemical impedance spectroscopy is a useful approach for determination of the behaviour of the steel embedded within the concrete, which provides important information about the corrosion process. In this contribution, the reinforced concrete sample was exposed in the chloride ion and carbon dioxide rich environment. The corrosion behaviour of the embedded steel was tested. Three different corrosion rate measurement methods, electrochemical impedance spectroscopy, polarization resistance and polarization curve intersection were applied for analysis.

2. EXPERIMENTS

2.1. Reinforced concrete sample preparation

The reinforced concrete sample was prepared using general use cement and slag cement. Table 1 shows the chemical compositions of both cement. Cement, coarse aggregate, water, water reducer (Fabplast 50) were used for concrete preparation. The general use cement and slag cement prepared concrete were denoted as GU-C and SL-C, respectively. The steel rebars (diameter 8 mm) was embedded in into the concrete. Table 2 shows the chemical compositions of the steel rebars.

Table 1. Chemical compositions of the general use cement and slag cement (all values are in wt/%).

Name	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Alkali	Free lime	Loss on ignition
General use cement	60.22	19.51	5.08	3.55	4.36	2.44	0.51	0.89	1.42	2.02
Slag cement	25.88	49.65	9.66	0.65	0.74	11.12	0.52	0.15	0.08	1.55

Table 2. Chemical compositions of steel rebar (all values are in wt/%).

C	Si	Mn	Cr	Mo	Ni	Cu	P	S
0.35	0.05	0.36	0.65	0.14	0.02	0.12	0.02	0.08

2.2. Chloride ion and carbon dioxide exposure environment

For chloride ion exposure experiment, the sample was partially immersed into a 2M NaCl solution. For carbon dioxide exposure experiment, the sample was placed at a closed desiccator with connection of a pressurized carbon dioxide tank. Carbon dioxide was continued to apply into the desiccator to keep the high concentration of carbon dioxide. For chloride ion and carbon dioxide both exposure, the sample was treated with NaCl for one week followed with one week carbon dioxide treatment.

2.3. Corrosion rate measurement

The corrosion state of the steel bar was measured by the corrosion rate. In this study, three different electrochemical based methods were applied for corrosion rate measurement including linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and Tafel extrapolation (ITE). The corrosion rate can be estimated based on corrosion current using following equation : corrosion rate (mm/y) = $[(A\times I_{corr})/(n\times F\times \rho)]\times 87600$, where A is atomic weight; I_{corr} is the corrosion current; n is the electron transfer during the electrochemical reaction; F is Faraday constant; ρ is the density of the metal.

AUTOLAB potentiostat/galvanostat was used for Tafel extrapolation measurement. A stainless steel mesh was used as a counter electrode. An Ag/AgCl electrode was applied as a reference electrode. The working electrode was connected to the steel bar and the E_{corr} value was collected. The anodic and cathodic slopes were deduced by the intensity-voltage values. The scanning potential and rate were set as 0.15 V and 0.001 V/s, respectively.

Scanning potentiostat 362 from EG&G Instruments was used for linear polarization resistance measurement. A stainless steel mesh was used as a counter electrode. An Ag/AgCl electrode was applied as a reference electrode. The scanning potential range and rate were set as [E_{corr}-10 mV, E_{corr}+10mV] and 0.5 mV/s, respectively. Due to the low perturbation effect of the linear polarization resistance measurement. The whole experiment was carried out in a Faraday cage.

AUTOLAB, potentiostat/galvanostat with frequency response analysis module was applied for electrochemical impedance spectroscopy measurement. The frequency measurement range was set as 1 mHz to 1 MHz. Figure 1 shows the equivalent circuit used for the electrochemical impedance spectra fitting, where R_s is the resistance of the electrolyte; C_{dc} is the double layer capacitance; R_p is the charge transfer resistance; C_0 and R_0 are the capacitance and resistance associated to redox processes in the oxide layer, respectively.

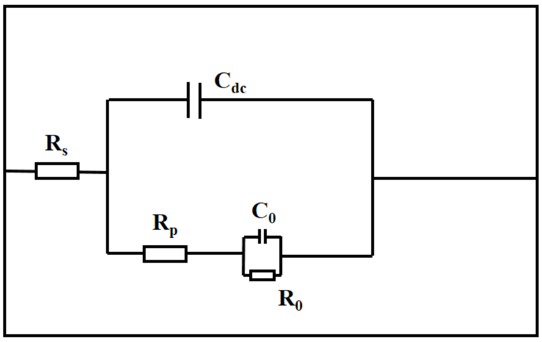

Figure 1. Equivalent circuit used for the electrochemical impedance spectra fitting

3. RESULTS AND DISCUSSION

Figure 2A and B shows the variation in E_{corr} of two concrete samples using linear polarization resistance and Tafel extrapolation methods as function of exposure time in 2 M NaCl solution. The value presented in the figure is the average value of three identical measurements. 90% chance of corrosion will lead the E_{corr} below -270 mV. As observed in the Figure 2, there is a considerable difference in E_{corr} value between the GU-C and SL-C. Two types of concrete showed a similar decreasing trend of E_{corr} during the first 50 days measurements. After 150 days measurements, the E_{corr} of GU-C and SL-C approached stable with -590 mV and -510 mV, respectively. It can be stated that the simultaneous presence of moisture, oxygen and chloride ions at the interface of steel and concrete can destroy the passive film at different sites of rebar. Therefore, active corrosion is followed and E_{corr} gradually decreases. The decrease in corrosion potential value is an indication of the gradual penetration of electrolyte through the existing pinholes in surface. Although both techniques measurements had a slightly different result, similar trends were observed and confirmed the corrosion process.

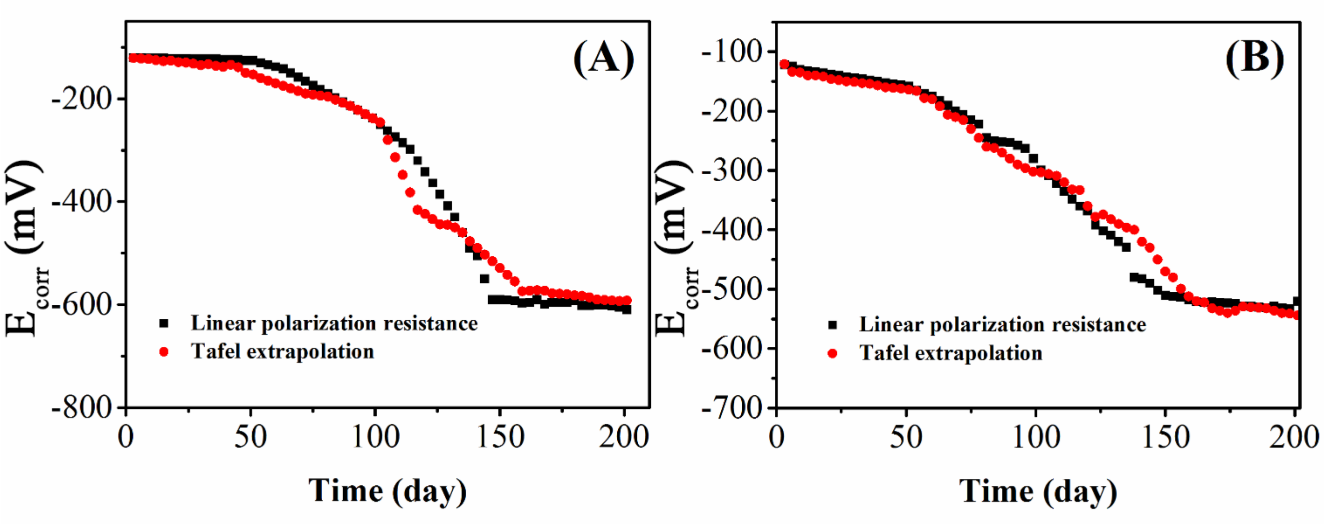

Figure 2. Evolution of E_{corr} of (A) GU-C and (B) SL-C using linear polarization resistance and Tafel extrapolation methods after samples exposed in 2 M NaCl solution with different time period..

Figure 3A and B displays the variation in E_{corr} of GU-C and SL-C under high concentration of carbon dioxide exposure using linear polarization resistance and Tafel extrapolation methods. A similar trend was observed in the experiments compared with the chloride ion exposure measurement. Both concrete samples showed a slow E_{corr} decreasing before 80 days followed by the rapidly decreasing process. However, the linear polarization resistance measurement results in this case showed a many larger difference compared with the chloride ion exposure experiment. It can be ascribed to the dry condition of the sample gave unstable measurements of linear polarization resistance. It was difficult to obtain a stable value of E_{corr}, needed previously to the potential scanning. In those cases it was almost impossible to obtain a reliable value of I_{corr}. Therefore, the linear polarization resistance is not reliable for measuring corrosion rate of the concrete exposure in carbon dioxide.

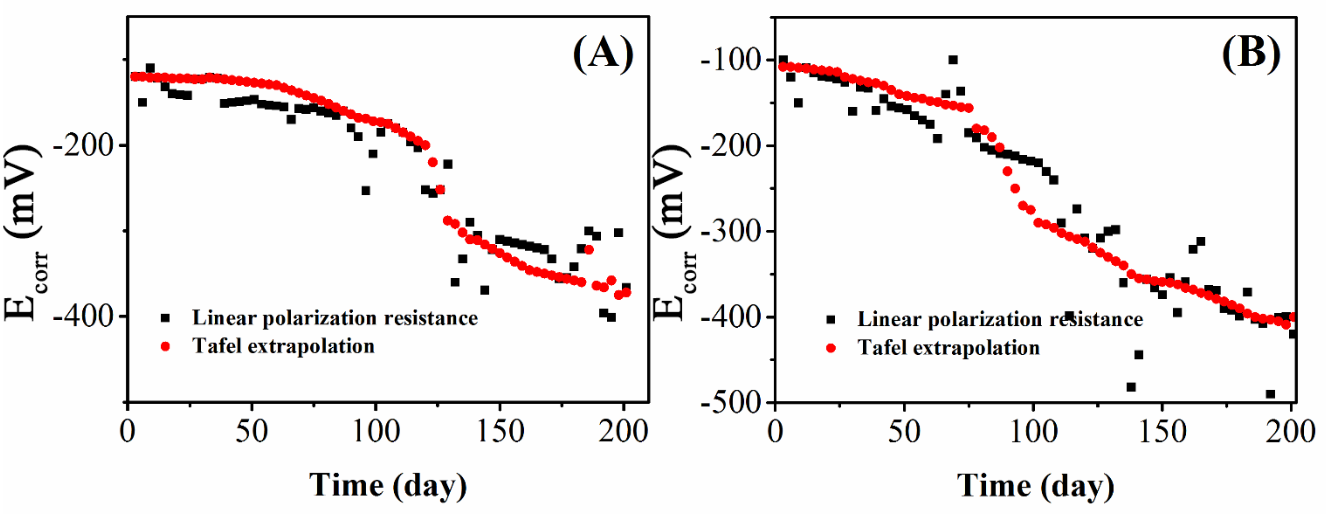

Figure 3. Evolution of E_{corr} of (A) GU-C and (B) SL-C using linear polarization resistance and Tafel extrapolation methods after samples exposed high concentration of carbon dioxide with different time period..

Figure 4 A-C shows the corrosion current of the GU-C and SL-C after exposed into carbon dioxide, chloride ion and chloride ion + carbon dioxide environments, respectively, using Tafel extrapolation method (representative Tafel polarization curves were shown in Figure 6). As can be seen in the figure, the corrosion rate of the GU-C and SL-C exposed into carbon dioxide showed a similar behavior with very low I_{corr}. In contrast, the I_{corr} of both samples showed a much higher value when the samples exposed in chloride ion environment. However, this value gradually decreasing after 100 days in SL-C sample, indicating the slower corrosion effect. It probably due to the refined pore structure of the SL-C provides better protection against corrosion. Another possible explanation is the corrosion happed in the SL-C was more localized compared with the GU-C. A moderate corrosion rates were observed in the both concrete samples in either exposed into carbon dioxide or chloride ion environments. The corrosion rates of the GU-C and SL-C after exposed into both aggressive agents were also investigated. As shown in Figure 4C, the corrosion rate of the both samples showed a similar process compared with the concrete exposed into the chloride ions, indicating the chloride ions dominated the corrosion process.

The values of corrosion potential of two types of concerts in three environmental conditions were also investigated using Tafel extrapolation method. As shown in Figure 5A, the corrosion potential of the GU-C and SL-C after exposed in high concentration of carbon dioxide were below than –0.2 V, suggesting the change of corrosion was very low. In contrast, the corrosion potential of the GU-C and SL-C after exposed in chloride ion environment were about –0.3 V, suggesting the chloride ion environment had much larger change for causing steel rebar corrosion [10, 34-37]. Moreover, the highest corrosion potential values of both GU-C and SL-C were obtained when their exposed into carbon dioxide + 1 M NaCl condition, indicating the combined action of the carbon dioxide and chloride ion could accelerate the corrosion process.

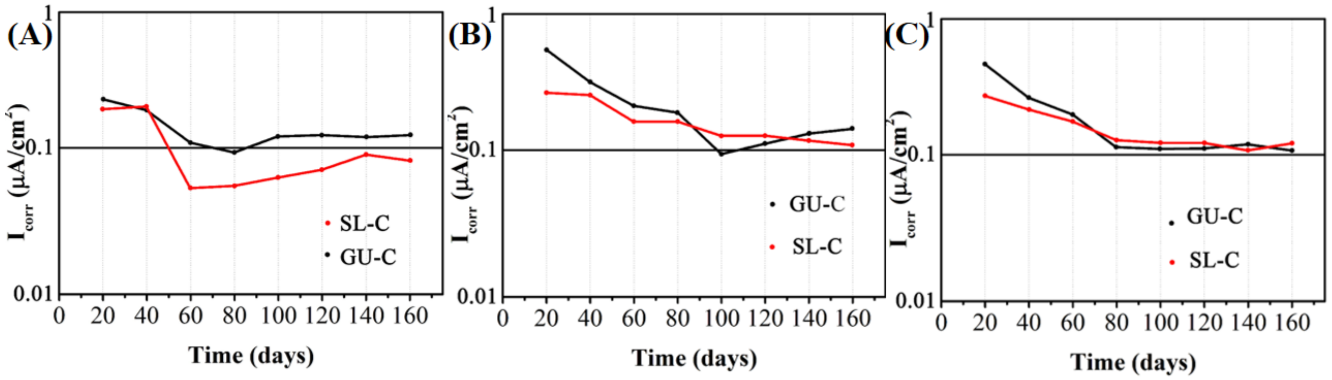

Figure 4. I_{corr} value of GU-C and SL-C when exposed to (A) carbon dioxide, (B) 1 M NaCl and (C) carbon dioxide + 1 M NaCl with different time period.

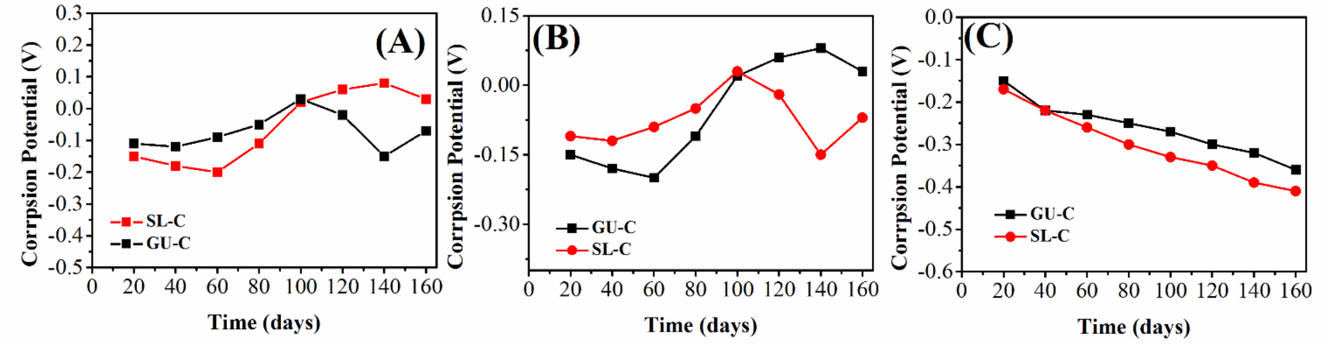

Figure 5. E_{corr} value of GU-C and SL-C when exposed to (A) carbon dioxide, (B) 1 M NaCl and (C) carbon dioxide + 1 M NaCl with different time period.

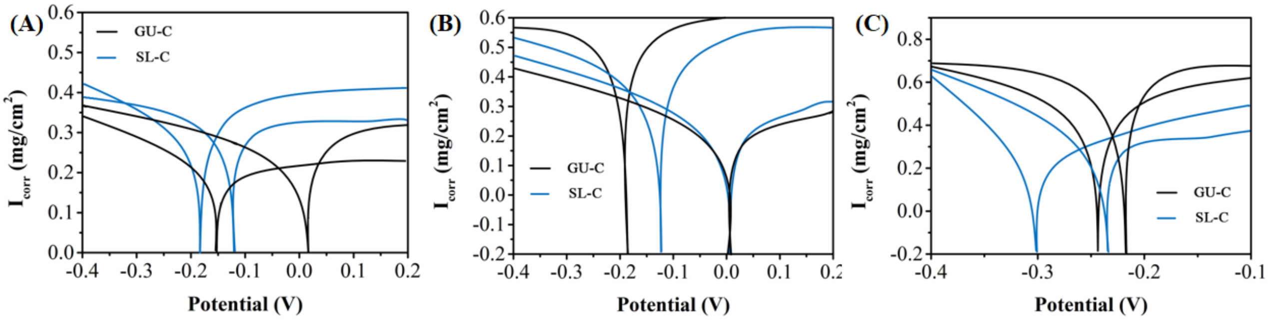

Figure 6. Tafel polarization curves of GU-C and SL-C exposed to (A) carbon dioxide, (B) 1 M NaCl and (C) carbon dioxide + 1 M NaCl with 40 and 120 days.

Electrochemical impedance spectroscopy (EIS) is a powerful, rapid and accurate non-destructive method for the evaluation of corrosion process. During EIS experiments, a small amplitude ac signal is applied to the system being studied. In this study, EIS was used for analyzing the corrosion process of the correct samples during the 3 months. Figure 6 A shows the Nyquist plots of GU-C and SL-C exposed into high concentration of carbon dioxide over 3 months. It can be seen that the Nyquist plots of two samples almost showed a constant performances over 3 months measurement, indicating the charge transfer resistance process of two samples showed constant ability [38, 39]. Therefore, the high concentration of carbon dioxide showed negligible effect towards concrete corrosion [40, 41]. Figure 7B shows the Nyquist plots of GU-C and SL-C exposed into chloride ion environment with different period. It can be seen that the both samples showed a two separate semicircles after 1 month measurement. The loop in high frequency and another straight line in moderate frequency respond to the indication of formation of porous corrosion products and the charge transfer resistance process occurring at metal/solution interface, respectively [42, 43]. Therefore, the chloride ion cannot penetrate enough into the concrete within short time. However, long time chloride ion environmental exposure could let sufficient concentration of chloride ions arrive at the metallic surface. A similar result was observed at the case of exposing concrete to the both carbon dioxide and chloride ions environments (Figure 7C).

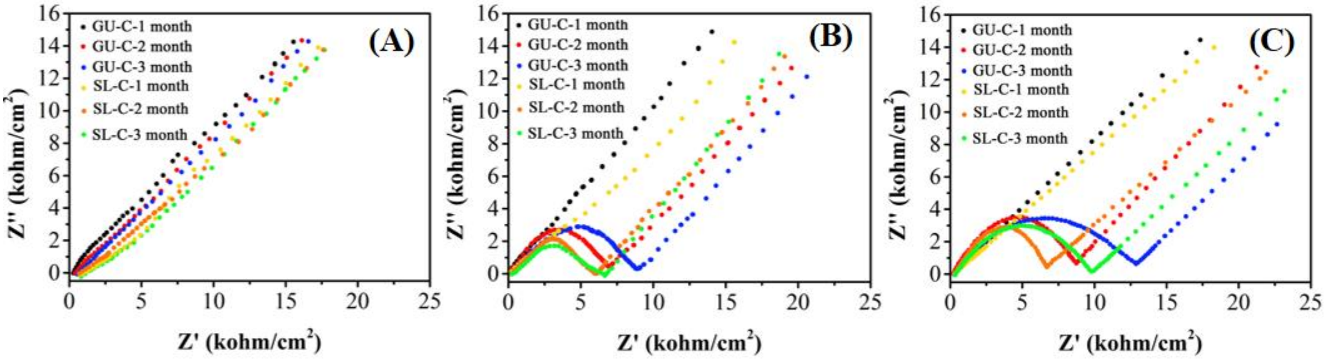

Figure 7. Nyquist plots of GU-C and SL-C when exposed to (A) carbon dioxide, (B) 1 M NaCl and (C) carbon dioxide + 1 M NaCl with different time period.

4. CONCLUSION

In summary, we used electrochemical impedance spectroscopy, polarization resistance and polarization curve intersection methods for two types of concrete corrosion measurements. Particularly, chloride ions and carbon dioxide were used as aggressive agents for corrosion behavior study. Study showed the carbon dioxide had no significant effect on the corrosion of the concrete. In contrast, the chloride ions showed a clear effect on the corrosion behavior of the concretes. Moreover, an accelerate corrosion behavior was observed when the concrete exposed in the both chloride ions and carbon dioxide environment.

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