Int. J. Electrochem. Sci., 11 **(2016)** 10238 – 10245, doi: 10.20964/2016.12.36

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Corrosion Investigation of Reinforced Concrete Under Qinghai Salt Lake Environment By EIS

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Received: 6 September 2016 / *Accepted:* 4 October 2016 / *Published:* 10 November 2016

In this work, we studied the corrosion behavior of the reinforcing steel in salt lake water with various immersion time by the measurement of electrochemical impedance spectroscopy (EIS). We found that the polarization resistance and capacitive loop decreased when increasing the immersion time. Moreover, the corrosion process was also influenced by the temperature of the salt lake water. The generation, growth and break of the passivation film on the embedded steel was investigated according to the dependence of the temperature and immersion time.

Keywords: Concrete; Corrosion; Electrochemical impedance spectroscopy; Salt lake

1. INTRODUCTION

Corrosion assessment of concrete structures is of great significance for the safety evaluation of concrete-constructions. The corrosion of embedded reinforcing steel generally causes the damage to concrete. What's more, the chloride infiltration leads by raining, automobile exhaust and specific environment will consequently trigger the process of corrosion [1, 2]. For the sake of evaluating the impact of chloride infiltration, various techniques such as multiple electrode method [3, 4], modulated confinement approach [5, 6] as well as galvanostatic pulse technique [7-12] have developed as the measurement of corrosion potential. However, few studies have concentrated in arid and high salinity environment with the feature of severe Cl^- contamination and low relative humidity (<50% RH) with lowest to 30% RH. Widely distributed on earth and mostly located in semi-arid or arid area, the salt lake zone can typically represent the arid and high salinity environment.

Since salt lakes are rich in mineral resources (such as lithium, which is of great importance for the development of Li battery, 70% of the total world reserves are contained in the salt lake), many countries including China have increasingly concerned about the exploitation and utilization of salt lakes. Different from those of desert and marine climate [13], extreme dryness and high salinity stands the key features of the salt lake environment. Therefore, the concrete that exposed in salt lake environment were affected by special corrosion behaviours [14-16]. According to the preliminary survey of corrosion in West China, carbon steels exposed in arid and high salinity environment corrode much more slowly than that exposed in other typical climate areas. In contrast, the corrosion rate of stainless steels and aluminium exposed in arid and high salinity environment was even higher than that exposed in marine and acid rain environment, which could be obviously attributed to the high deposit of salt.

At the same time, the water in salt lakes (e.g., Chaerhan Salt Lake) is rich in magnesium ions, which is not the same as that of the seawater (e.g., Dead Sea). Nevertheless, there are rare researches about the effect of other cations including Mg^{2+} rather than Na^+ on the corrosion of reinforced concrete. Moreover, some laboratory researches in controlled environments even comes into inconsistent results of the effect of different cations [17, 18]. Blücher et al. studied the aluminium corrosion under the environment of 95% RH with NaCl and $MgCl_2$ salts. It was found that similar corrosion rates were obtained by studied salts with unobservable magnesium-contained corrosion products in the condition of existed carbon dioxide [17]. As shown by the laboratory-accelerated corrosion experiments of aluminium with various soluble salts under cyclic wet-dry conditions, $MgCl_2$ had a greater impact on the corrosion of aluminium than NaCl [18] owing to its lower deliquescence relative humidity (DRH) which could extend the wetness time.

Thereafter, the corrosiveness for common concrete in the salt lake environment has attracted great attention. Electrochemical impedance spectroscopy (EIS) is a promising technique to measure corrosion potential [19-30]. In the specific method, potentials at various frequencies were applied to the embedded reinforcing steel and the measured value of electrical impedance was then used for the evaluation of the corrosion potential of reinforcing steel in concrete [31-35]. In this work, an exposure test of concrete in diluted water from Qinghai salt lake has been carried out.

2. EXPERIMENTAL

In this work, R235 reinforcing steel was employed as the specimen. The compositions of R235 in mass percent were described as below: P<0.045; S<0.05; Si: 0.12–0.30; C: 0.14–0.22; Mn: 0.30–0.65; Fe: the rest. First, the steel was cut into disks with an area of Ø11.3mm × 3 mm, and then was sealed by the epoxy with the exception of the working surface with an area of 1.00 cm^2. Subsequently, the specimen was ground to the grade of 1200 by the SiC paper and cleaned with acetone and alcohol in ultrasonic for 5 min respectively, in prior to the measurements. The content of the salt lake water in Qinghai was illustrated in Table 1. All the samples were immediately dipped into the simulated salt lake water in large plastic containers after being formed and stabilized.

All the electrochemical tests were performed at room temperature, where a three electrode system was utilized. Here, the reinforcing steel was employed as the working electrode, while the saturated calomel electrode (SCE)and the Pt foil acted as the reference electrode and the counter electrode respectively. The EIS and LPR measurements were conducted continuously every 1 h when the open circuit potential became steady by The Autolab PGSTA30 (ECO Chemie B.V., The Netherlands) with FRA module. Noted that the EIS test was performed under the frequency domain of 10^5 Hz to 10^{-2}Hz with a sinusoidal potential perturbation of 10 mV. A fitting simulation of the FRA software was used to analyze the EIS data. According to the Stem-Geary relationship, the current density of corrosion was obtained by the LPR measurement, which was conducted in the potential range of E_{corr} ± 15 mV when the scan rate was 0.1 mV/s.

Table 1. The content of the salt lake water in Qinghai (wt.%, pH 5.0).

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-
Content	0.12	0.06	1.58	0.45	35.51

3. RESULT AND DISCUSSION

The EIS data of the reinforcing steel samples dipped in the salt lake water for various time was illustrated in Figure 1A. It was observed in Nyquist plots that the diameter of the capacitive loop kept at around 120 kΩ cm^2 when the immersion time was below 5 days. However, the capacitive loop decreased rapidly when the immersion time reached up to 10 days. In Figure 1B, it was obvious that the phase angle reduced and divided into two peaks when the immersion time increased to 10 days.

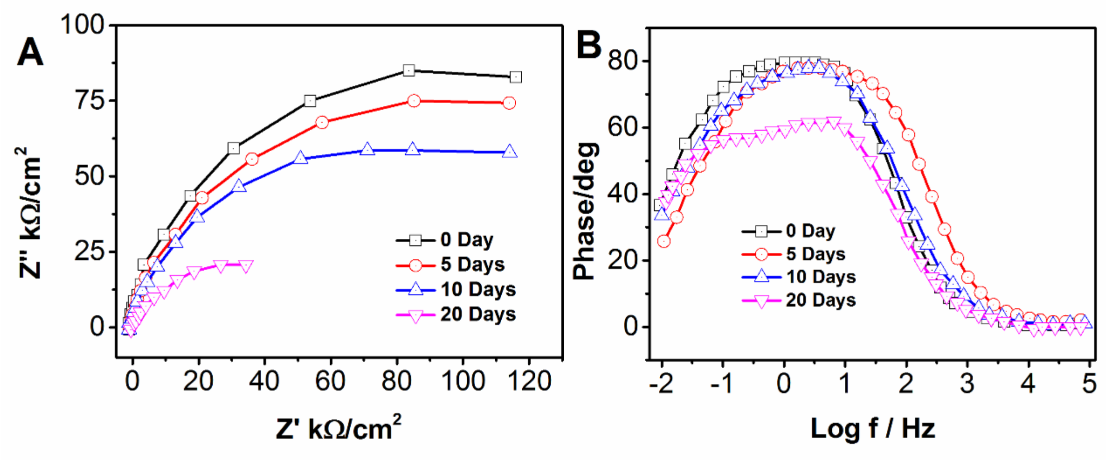

Figure 1. The variations of the Nyquist plots (A) and the plots of the phase angle (B) of the reinforcing steel in salt lake water under various immersion time.

Table 2 showed the fitting results of the EIS measurement of the reinforcing steel. It was obvious that the resistance of the solution decreased to 32.1 kΩ cm^2 from 76.8 kΩ cm^2, which was ascribed to the solution of which the conductivity became higher when longer immersion was employed. The decrease of n_f indicated that the passive film became increasingly inhomogeneous or defective due to the penetration of the chloride ions.

Table 2. The fitting results of EIS of the reinforcing steel in salt lake water under various immersion time.

Immersion time	R_s (Ωcm^2)	R_f (Ωcm^2)	R_{ct} (Ωcm^2)
0 Day	76.8	135	94.7
5 Days	71.4	120	91.6
10 Days	54.9	78	54.1
20 Days	32.1	0.124	2.89

Figure 2A illustrated the capacitances of the double layer (C_{dl}), which was calculated based on the data shown in Table 2. It indicated that the capacitances increased with the immersion time and raised remarkably when the immersion time increased to 10 days. Nevertheless, the typical value of C_{dl} decreased to the range of 10 to 40 μF/cm^2. The relationship between capacitance C_{dl} and the content of the chloride could also be clarified by the equation described below:

$$C_{dl} = \xi_0 \xi A / d$$

Here, the dielectric constants of the medium, the dielectric constants of the vacuum, the surface area of the electrode and the thickness of the double layer or the passive film were represented with ε, ε_o, A and d, respectively. In the case of the concrete in salt lake water, the capacitance increased by two causes. First, the passive layer became thinner and exhibited breakdown, which induced the decrease of d. Second, the porosity of the electrode surface became more prominent, which was attributed to the pitting corrosion which was caused by the chloride. On the other side, the capacitance became higher when the pitting corrosion became more serious. The remarkably high capacitance could be ascribed to the rough surface of the specimen induced by the increasing pitting corrosion. It demonstrated that EIS was effective to evaluate the pitting corrosion of the reinforcing steel in salt lake water induced by chloride based on the variation of the capacitance. This behavior has been reported in Wang et al [36]. They studied the corrosion behaviors of typical high-strength aluminum alloy LC4 was studied by atmospheric exposure test, combining the experimental techniques including mass loss,morphological check of samples and analysis of corrosion products.

Moreover, Figure 2B illustrated the changes of R_f and R_{ct} with the immersion time. It was obvious that the R_f and R_{ct} decreased with the immersion time. This indicated that the passivation coating on the surface of the steel was a complete protecting layer, while the chloride content was below the threshold value. However, the passive film became unstable and exhibited local breakdown when the immersion time increased. Meanwhile, the pitting pores took place in some positions of the steel surface. Consequently, Rf decreased to tens of Ω/cm^2 from hundreds of kΩ/cm^2 when the immersion time increased.

Moreover, in Figure 1B, obvious changes of peak number and magnitude were observed in the phase angle when the immersion time increased. Generally, the number of the time constants were represented with the number of the peaks of the phase angle. Besides, the time constants, which were depended on their relevant value, might overlap with each other. For instance, R_f and Y_f was almost the same as R_{ct} and Y_{dl} of the steel in the salt lake water when less immersion time was used. Thus, the constant of the relaxation time of the passivation film might be close to the constant of the electrochemical reaction time, which were hard to be differentiated as only a broad peak of phase angle could clearly be observed in the plots of phase angle. However, R_f was significantly smaller than R_{ct} when increasing the immersion time to 10 days, as the passivation film on the surface of the sample de-passivated. Consequently, the constant of the relaxation time of the passivation film was differentiated from the time constant of the electrochemical reaction, where an additional peak appeared obviously. The passive film became unstable when extending the immersion time continuously to 20 days. Besides, only the corresponding relaxation time constant was obvious to be observed. In comparison with the Nyquist plots, it was demonstrated that more information in relevant with the time constant of the reinforcing steel in salt lake water was obtained with the Bode plots. Therefore, Bode plots analysis is essential for the concrete corrosion status investigation [37].

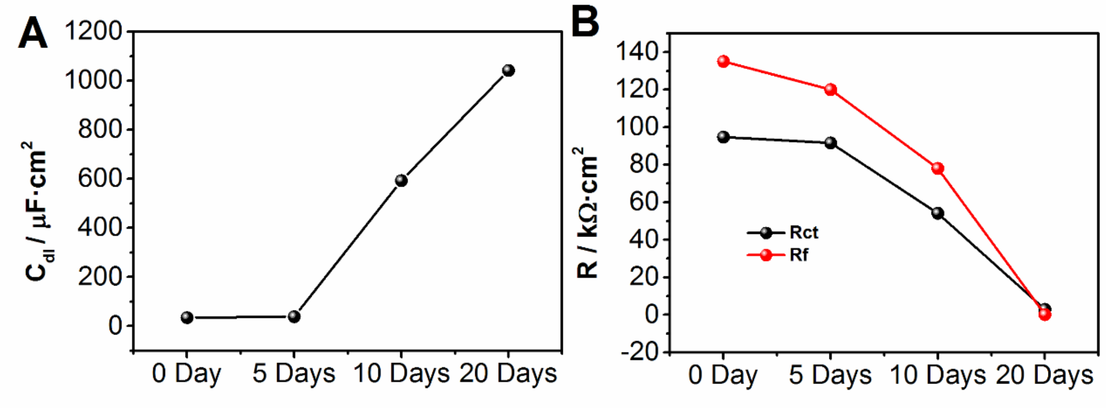

Figure 2. The variations of the capacitance (A) and resistance (B) of the reinforcing steel in salt lake water with the immersion time.

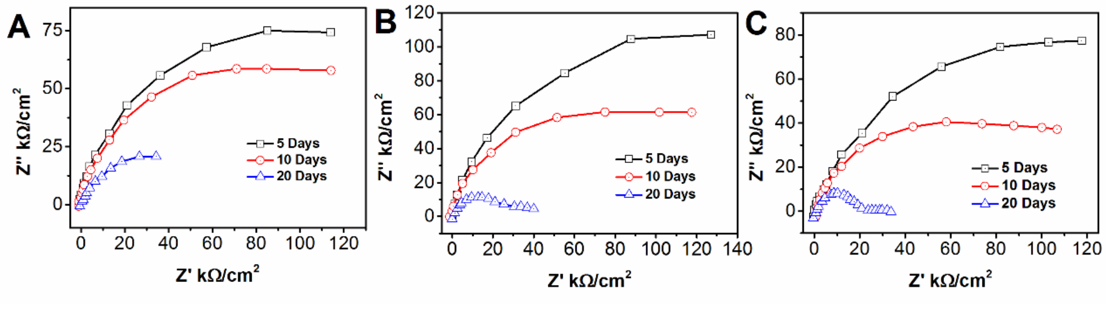

Figure 3. The variations of Nyquist plots of the reinforcing steel in salt lake water at (A) 20 °C, (B) 30 °C and (C) 40 °C.

The EIS measurements of the samples were conducted continuously during the beginning of the 20-day immersion to investigate the effect of the temperature on the erosion performance of the rebar in salt lake water. As shown in Figure 3, it was obvious that the diameter of the Nyquist plots grew with the increasing temperature when the immersion time was below 10 days. Meanwhile, the phase angle varied upward, where the peak of phase angle also became broad. Moreover, this tendency kept until the immersion time exceeded 10 days, whereas slight decreases were observed in the phase angel peak and the diameter of the capacitive loop. It can be ascribed to the continues corrosion progress [38].

As shown in Figure 4, the values of R_f and R_{ct} was fitted to illustrate the influence of the temperature on the erosion performance of the reinforcing steel in salt lake water. The R_f and R_{cf}, which were above 10 kΩ/cm^2, increased with temperature when low temperature was employed. This indicated that the passive film grew and thickened. However, the R_f and R_{cf} would not increase with the temperature when increasing the immersion time to 10 days, because of the de-passivation of the passive film. Especially when the immersion time reached up to 20 days, R_f and R_{cf} decreased dramatically and became below 10 kΩ/cm^2 despite of the different temperatures.

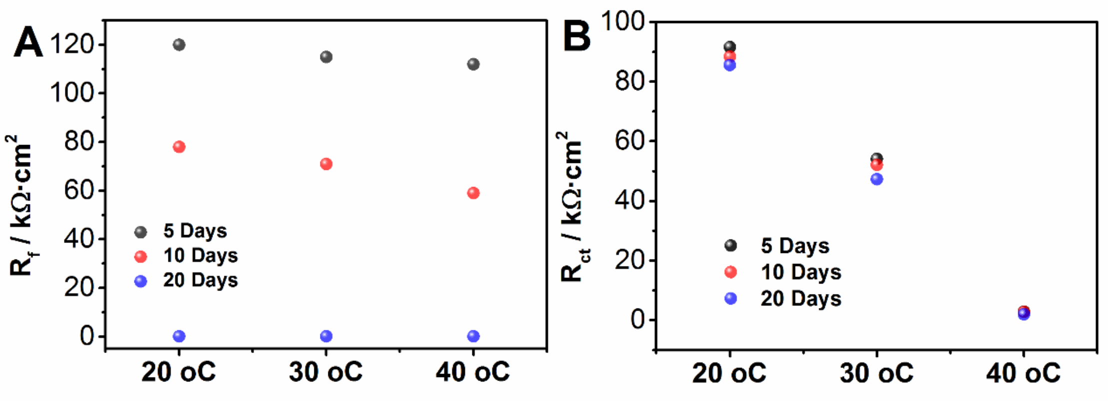

Figure 4. The changes of (A) R_f and (B) R_{ct} of the reinforcing steel in salt lake water under various temperatures during 20 days immersion.

4. CONCLUSION

In conclusion, we reported that the EIS is an effective instrument to study the corrosion caused by the salt lake water. In general, the high capacitance suggested that the corrosion resulted in that the roughness of the surface of the sample increased. The decrease of the resistance of $R_f$and R_{ct}, particularly below 10 kΩ/cm^2, indicated that the passivation coating of the reinforcing steel was unstable. Besides, the local breakdown would take place when longer immersion time was employed. In addition, it was demonstrated that the peaks of phase angle increased and broadened by the growth of the passive film when the enhancement of the corrosion process decreased.

ACKNOWLEDGEMENTS
This work was funded by The Research on Green High-Performance Recycled Concrete in Qinghai - Tibet Plateaus (2013-G-209).

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