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Short Communication

Effect of Kaolin Addition on Electrochemical Corrosion Resistance of Duplex 2205 Stainless Steel Embedded in Concrete Exposed in Marine Environment

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As steel reinforced concrete is exposed to marine environments, chloride ions penetrate the concrete structures and lead to corrosion of the reinforced bars, which causes serious destruction of the bridge structures. In order to decrease the cost of repairs and the durability of reinforced bars, use of admixtures in concrete structures has attracted the attention of engineers and researchers around the world. In this work, the effect of Kaolin admixtures as partial replacement of ordinary Portland cement on the corrosion resistance of duplex 2205 stainless steel rebar were considered by open circuit potential, electrochemical impedance spectroscopy and polarization analysis after immersion to the marine environment. The electrochemical results indicated that the specimen with 8 kg/m^3 Kaolin had higher corrosion resistance and potential than all the others. The surface morphologies of the samples revealed that corrosion products on the surface of DS steel rebar were reduced by addition of Kaolin. The results show that the Kaolin as additives enhance the durability of the concrete and prevent corrosive ions from reaching the surface of metal rebars, which may be an alternative material for development of the construction industry.

Keywords: Kaolin admixture; Ordinary Portland cement; Electrochemical corrosion resistance; Duplex stainless steel seinforced concrete

1. INTRODUCTION

With the development of modern technology and society, reinforced concrete as a method to construct structures have been used extensively in China [1, 2]. When reinforced concrete is exposed to the marine environments, chloride (Cl^-) ions penetrate the concrete structures and cause in the reinforced bar corrosion, thus resulting serious destruction to the bridge structures [3]. Several problems produced by the reinforced bar corrosion have been reported worldwide [4]. Furthermore, Maintenance and repair of concrete structures associated with corrosion have cost many billions of USD annually [5, 6].

In order to decrease the cost of repairs, the durability of reinforced bars, especially those exposed to marine media, has been well-known as an effective tool to ensure the concrete service life, which has attracted the attention of engineers and researchers around the world [7-9].

Many researchers have used admixtures into concrete structures to develop their delay and durability in the corrosion. Typical admixtures are silica fume, calcium nitrite, blast furnace slag, fly ash, hydroxyalkylamines, and sodium monofluorophosphate [10-12]. The logic behind using these materials is simple. They form a denser concrete, decrease its permeability, limit ion flow, and enhance electrical resistance and slow corrosion current. Many researchers have revealed that supplementary cementitious materials (SCMs) reduce chloride penetration and porosity [13, 14]. Incorporating SCMs into a concrete mix decreases the capillary pores of concrete and reduces its penetrating properties. As a result, it becomes more difficult to achieve a surface of steel reinforcement for chloride-contaminated water [15].

Numerous studies have been conducted to expand reinforced concrete by different types of admixtures, which has improved its chemical resistance and mechanical properties [16, 17]. These properties are main variables that can contribute to the application of concrete in the construction sector. Moreover, Kaolin admixture is an important approach that can be assumed to reduce physical and mechanical restrictions of reinforced concrete and advance a wide range of their applications [18].

Although Kaolin has been confirmed able to improve the electrical resistivity and decrease the permeability and specific surface area, the effect of Kaolin admixture on the corrosion behavior of steel reinforced concrete had not been reported previously. Thus, in this research, we have investigated the concentration effect of Kaolin admixture on corrosion resistance of duplex 2205 stainless steel rebars.

2. MATERIALS AND METHODS

Table 1. Chemical composition of OPC

Parameters (%)	OPC	Kaolin
SiO_2	20.92	39.11
Al_2O_3	5.75	31.04
Fe_2O_3	3.12	1.2
CaO	61.53	0.38
MgO	2.14	0.24
K_2O	0.60	0.24
Na_2O	0.37	0.18
SO_3	2.31	-
TiO_2	-	1.38
LOI	3.26	26.20

Concrete samples were produced by replacement of ordinary Portland cement (OPC) by different concentrations of Kaolin. The kaolin was purchased from Beihai Hepu Jinhai Kaolin Company, China.

Chemical compositions of the OPC and Kaolin used are revealed in Table 1. The OPC was blended with sand, gravel and water (1.5: 3: 1: 0.5) to produce concrete samples. In this research, Kaolin with concentrations of 0.0, 1.0, 2.0, 4.0 and 8.0 kg/m^3 were replaced in OPC. The concrete mixtures are summarized in Table 2.

Table 2. The details of the concrete mixtures

Samples	OPC (kg/m^3)	Kaolin (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Water (kg/m^3)	W/C
0 kg/m^3 K	300	0	600	200	150	0.5
1 kg/m^3 K	299	1	600	200	150	0.5
2 kg/m^3 K	298	2	600	200	150	0.5
4 kg/m^3 K	296	4	600	200	150	0.5
8 kg/m^3 K	292	8	600	200	150	0.5

The chemical compositions of duplex 2205 stainless (DS) steel rebar was C (0.03 wt%), Mn(1.2 wt%), Si(0.9 wt%), Cr(22.05 wt%), Ni(5.2 wt%), N(0.01 wt%) and MO(3.5 wt%). DS steel rebars were washed by acetone solution and deionized water and then dried at room temperature. DS steel reinforcement with 7 cm length and 1 cm diameter was transferred in the cylinder with diameter of 3 cm.

The corrosion rate of steel rebar was measured by determining the mass loss of rebars [19].

$$Corrosion\ rate = \frac{87.6 \times W}{D \times A \times T} \tag{1}$$

where, W and D are the weight loss (g) and density of the used material, respectively. A and T are the area of the sample (cm^2) and the time duration (h), respectively.

A three-electrode electrochemical method, including the DS steel rebar, a standard copper/copper sulfate and a graphite electrode were utilized as the working, reference and counter electrodes, respectively. The open-circuit potential (OCP) of the different specimens were periodically recorded by an ideal voltmeter with input resistance of 10 MΩ. All studies were performed in the 3.5% wt% NaCl solution as a simulated marine environment after 8-weeks immersion time. Electrochemical impedance spectroscopy (EIS) was done in a scanning range of 0.01Hz to 0.1MHz. The potentiodynamic polarization analysis was performed at 1 mV/s scanning rate. Scanning electron microscope (SEM) was used to consider the surface morphologies of samples.

3. RESULTS AND DISCUSSION

One of the known methods for evaluating steel corrosion in concrete specimens is the OCP technique. The potential difference between reinforcing steel bars into concrete specimens and a Cu/Cu sulphate electrode (reference electrode) was measured consistent with ASTM C-876. Figure 1a indicates the OCP result for eight weeks. With increasing Kaolin content to 8.0kg/m^3, the potential values were significantly shifted toward more positive. Figure 1b shows the corrosion rate of DS steel reinforced concretes with various Kaolin concentration. The concrete prepared with Kaolin admixtures revealed a lower corrosion rate than the specimens without Kaolin after one week exposure to marine environment. The sample with 8.0 kg/m^3 Kaolin has the minimum corrosion rate which can be associated with the chemical and physical features of Kaolin admixtures that delayed the early corrosion process and reduced the permeability, volumetric contraction and expansion. Moreover, it also revealed the ability of Kaolin admixtures to decrease the formation and diffusion of cracks.

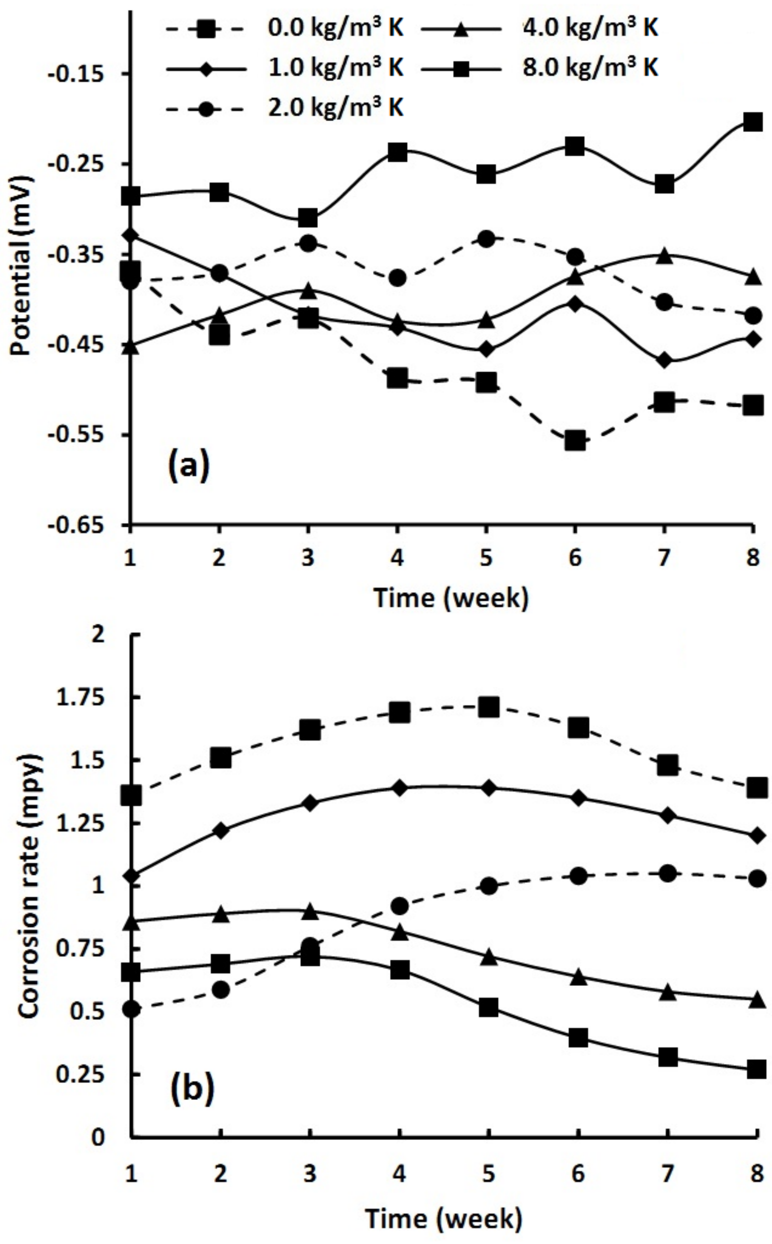

Figure 1. (a) Open-circuit potential and (b) Corrosion rate of reinforced concrete specimens with different Kaolin contents immersed in 3.5wt% NaCl environment

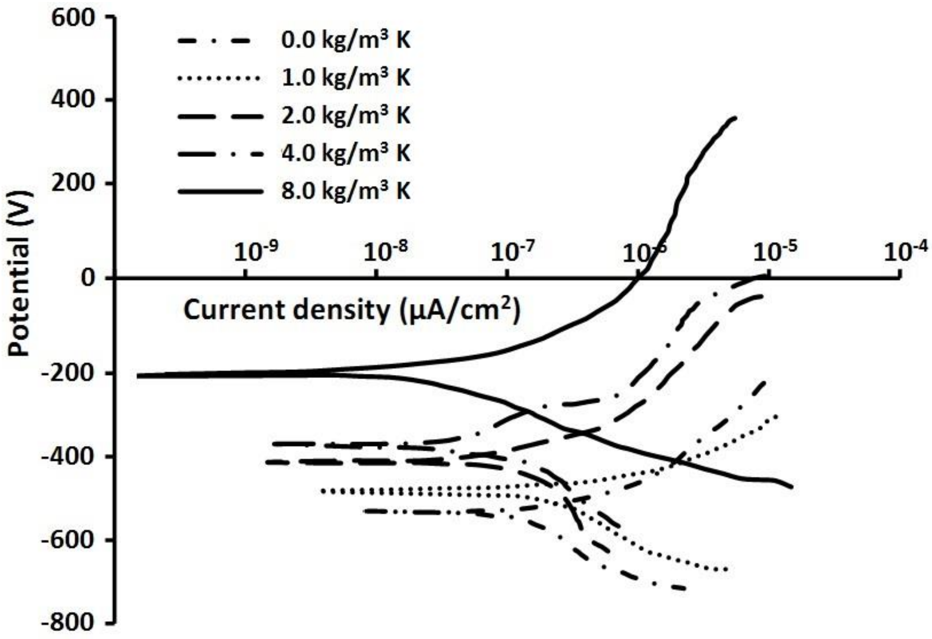

Figure 2. Polarization curves of DS steel reinforced concrete specimens with different concentrations of Kaolin immersed to 3.5 wt% NaCl environment for 8 weeks

The polarization curves of DS steel reinforced concrete specimens with different concentrations of Kaolin immersed to 3.5 wt% NaCl environment for 8 weeks are indicated in Fig. 2 to assess the effect of Kaolin content on corrosion resistance of DS steel reinforced concrete. The values of corrosion potential (E_{corr}) and the corrosion current density (I_{corr}) are shown in table 3 which are attained from the polarization plots in Fig. 2. The concrete sample without Kaolin admixture had the minimum E_{corr} compared to the other reinforced concrete samples which was very prone to corrosion. The steel rebar covered by concrete sample with 1.0 kg/m^3 of Kaolin was into the passive-state and had lower corrosion than concrete sample without Kaolin. As shown in Fig. 2, increasing Kaolin concentration leads to a major increase in E_{corr}. Therefore, the E_{corr} had shifted toward more positive values. Moreover, I_{corr} shifted to the left side which revealed that there was lower I_{corr} on the steel rebar surface [20]. The corrosion level may be well-defined in four levels specified by Durar Network Specification [21, 22]. However, the I_{corr} of steel rebar covered by concrete sample with 8.0 kg/m^3 Kaolin in 3.5wt% NaCl solution was lower compared to the other specimens (Table 3). Hence, except the 0.0kg/m^3 Kaolin sample, all DS steel rebars stayed in the passive-state during the electrochemical process which indicated their excellent corrosion resistance for DS steel rebar in 3.5wt% NaCl solution [23].

Table 3. I_{corr} and E_{corr} of the DS steel reinforced concrete

Admixtures	I_{corr} (μA/cm^2)	E_{corr} (mV)
0.0 kg/m^3 Kaolin	0.128	-548
1.0 kg/m^3 Kaolin	0.094	-506
2.0 kg/m^3 Kaolin	0.058	-429
4.0 kg/m^3 Kaolin	0.046	-384
8.0 kg/m^3 Kaolin	0.025	-238

The concrete permeability is directly associated with the increase in Kaolin content which leads to denser concrete production [24, 25]. Therefore, due to the entrance of few chloride ions into the concrete samples, the I_{corr} was less and the E_{corr} was more positive. Corrosion of DS steel rebar in concrete samples with 8.0 kg/m^3 Kaolin was strongly decreased after 8 weeks exposed to marine environments which were more resistant to corrosion compared with other specimens. It can be related to the concentration of Kaolin which had a direct impact on the performance of DS steel reinforced concrete.

Table 4 shows comparison of corrosion behavior of steel rebar embedded in various admixtures reported in previous studies. The results indicate that the corrosion behavior of DS steel embedded in concrete containing kaolin admixture were comparable with other admixtures obtained from the literature.

Table 4. Comparison of corrosion behavior of various steel rebars reported in previous studies

Admixture	**Environment**	**Corrosion potential (mV)**	**Corrosion current density (μAcm^{-2})**	**Ref.**
Lime stone	3.5 wt% NaCl	-164	0.054	[26]
Silicon fume and Fly ash	3.5 wt% NaCl	- 237	0.013	[27]
Fly ash	Alkaline solutions	-174	0.028	[28]
Metakaolin	5 wt% NaCl	-165	2.3	[29]
Kaolin	3.5 wt% NaCl	-238	0.025	This work

The EIS analysis of DS steel rebars were investigated after two months immersed to 3.5 wt% NaCl environment. The Nyquist diagrams for the steel reinforced concrete specimens with different content of Kaolin admixture are indicated in Fig. 3. All the mixtures show two capacitive properties. The high frequency loop belongs to the concrete specimen which covers the DS steel bar. The low frequency loop belongs to the surface of steel. Therefore, the equivalent circuit is indicated inset of Fig. 3. This circuit have a parallel resistance (R_c) and capacitance (C_c) of the concrete in high frequencies in an across series with parallel charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) of DS steel surface at low frequencies [30]. The solution resistance (R_s) value was related to the resistance to electrolyte solution that was negligible compared with the resistance of other parameters. As indicated in Fig. 3, the response of the steel surface was greater than that of concrete, thus sample corrosion properties are expected to be controlled by the steel surface elements.

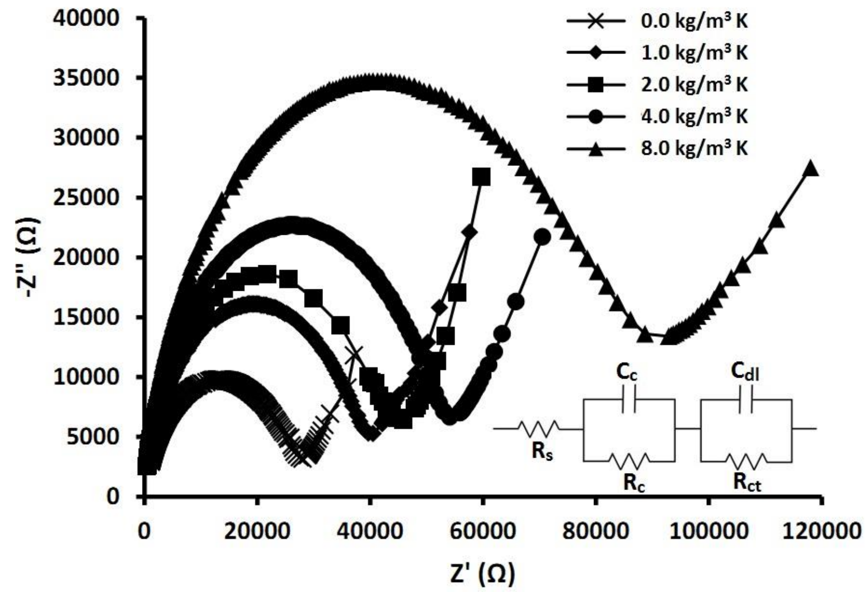

Figure 3. Nyquist diagrams for steel reinforced concrete specimens with different content of Kaolin admixtures after 8 weeks immersed to 3.5wt% NaCl solution. The inset shows an equivalent circuit model

It has been shown that R_{ct} value enhances by increasing Kaolin admixtures in the OPC. Moreover, the samples with 8.0 kg/m^3 Kaolin indicates higher value of R_{ct} in comparison with the others, which shows that increasing the Kaolin content as partial replacement of OPC can increase the corrosion resistance of DS steel reinforced concrete.

It may be associated with the advance of the concrete structure due to the filler action and improvement of bonding capability for Kaolin which can decrease the air content, porosity and pore diameters and enhance the internal surface of cement. Therefore, the permeability of concrete structures are decreased. Polarization resistance (R_p) was measured to study the rate of charge-transfer in the interface layer [31, 32]. The R_p values increase as the Kaolin content increases, which reduces the corrosion probability (Table 5). Hence, using Kaolin as partial replacement of OPC can improve surface alkalinity of the DS steel rebar and assist long-term corrosion protection, as indicated in previous studies [33, 34].

Table 5. EIS parameters of DS steel rebars in concrete specimens after 8 weeks immersed to 3.5wt% NaCl solution

Admixtures	R_s (Ω cm^2)	R_c (Ω cm^2)	C_c (μF cm^{-2})	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	R_p(Ω cm^2)
0.0 kg/m^3 Kaolin	77	17215	0.33	29823	0.46	47038
1.0 kg/m^3 Kaolin	69	27574	0.24	42371	0.31	69945
2.0 kg/m^3 Kaolin	72	31465	0.19	48667	0.27	80123
4.0 kg/m^3 Kaolin	81	39886	0.13	57239	0.22	97125
8.0 kg/m^3 Kaolin	75	58738	0.03	96718	0.08	155456

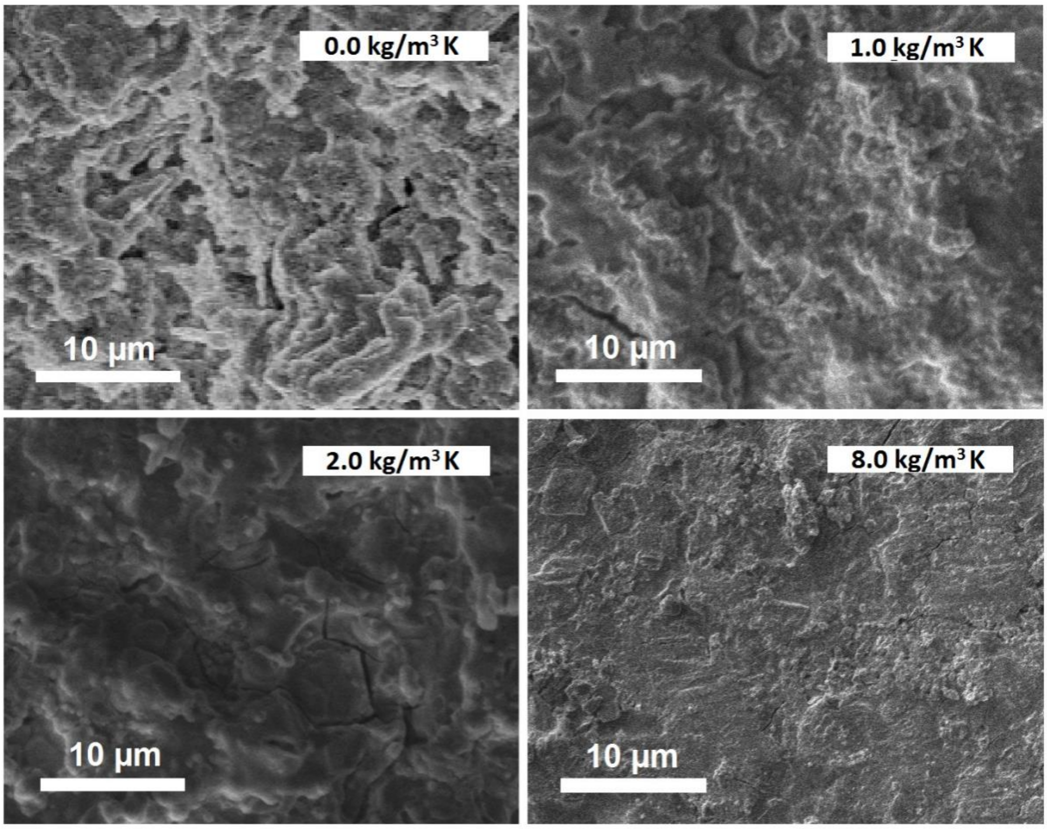

Figure 4. SEM images of steel rebars in different concrete samples after 8 weeks immersed to 3.5wt% NaCl environment

Figure 4 shows the surface morphologies of various concrete samples after eight weeks immersed in the marine environment. The surface of specimen with 8.0 kg/m^3 Kaolin content reveals low corrosion products and smallest pits, indicating the slight pitting corrosion shaped onto the surface of steel reinforced concrete, which is in agreement with the results obtained from electrochemical measurements. This could be related to the reduction of chloride ions and permeability of water in reinforced concrete samples. The large pores may be altered to smaller pores by addition of Kaolin, causing a change at the cement paste structure. These results indicated that Kaolin admixtures in OPC led to a reduction in corrosion rate and enhanced the corrosion protection of DS steel rebar due to the decrease of Cl^- ions and water permeability.

4. CONCLUSIONS

In this research, the effect of Kaolin concentration as partial replacement of OPC on the corrosion resistance of DS steel rebar was considered by OCP, EIS and polarization analysis after immersion to the marine environment. The electrochemical results indicated that the specimen with 8 kg/m^3 Kaolin had higher corrosion resistance and potential than all the others. The corrosion current density of steel rebar covered by concrete sample with 8.0 kg/m^3 Kaolin in 3.5wt% NaCl solution was lower compared to the other specimens. The SEM images of the samples revealed that corrosion products on the surface of steel rebar were reduced by addition of Kaolin. The results show that the Kaolin as additives enhance the durability of the concrete and prevent corrosive ions from reaching the surface of metal rebars, which may be an alternative material for development of the construction industry.

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