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Short Communication

Corrosion Behavior of ASTM A615 Steel Rebars Embedded in Concrete with Ceramic Waste Dustas a Partial Replacement of Portland Cement

Xiaojuan Lv

Institute of civil engineering, Huanghuai University, Zhumadian, Henan 463000, china E-mail:<u>xiaojuanlv2000@sina.com</u> and <u>20070905@huanghuai.edu.cn</u>

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In the present investigation, the effect of ceramic waste dust (CWD) as a partial replacement of Portland cement (PC) on the corrosion behavior of ASTM A615 steel rebarwere evaluated byelectrochemical impedance spectroscopy (EIS), open circuit potential (OCP) andwater absorption tests after exposure to the marine environment. All samples with CWDs show a decrease in water absorption with increasing exposure time compared to the PC concrete. The samples with 15% CWD revealed the highest compressive strength during theentire exposure time in3.5 wt% NaCl solution. The OCP value of the reinforced concrete samples with 15 wt% CWDs stayed in the low or uncertain corrosion area for much longer. The surface morphologies of carbon steel rebarsindicated that the amount of pitting corrosion on the steel bar embedded in 15 wt% CWD concrete sample was significantly lower than that of the others. The electrochemical results showed that the higher content of CWDs up to 15 wt% in PC has significantly improved the concrete structure as well as reduced corrosion rate.

Keywords: Ceramic waste dust; Partial replacement of Portland cement; Corrosion resistance; Carbon steel rebar; Electrochemical technique

1. INTRODUCTION

The corrosion of steel reinforced concrete reduces the durability of concrete structures [1].Corrosion happens irregardless of the intrinsic capability of concrete for protection of steel rebar [2].Corrosion is caused bythepenetrationof aggressive ions or the loss ofconcrete alkalinity [3]. Techniques of corrosion control contain cathodic protection, the use of a partial replacement in the concrete cement and surface treatments of the steel rebars[4]. The use of admixtures are individually attractive because they arerelatively and simply low cost [5, 6]. The quality of concrete structure can be improved by the addition of different mineral admixtures such as fly Ash, metakaolin, Silica Fume, Palm Oil Fuel Ash andRice Husk Ash [7-10]. Mineral additives affect the hardened features of

concrete. By combining these admixtures, the amount of cement is decreased which reduce environmentalimpact and increases the concrete quality [11]. Disposal problems may also be reduced because these additives are part of industrial products.Many studies have been done to expand concrete reinforced by different kind of waste dusts, which had led to the improvement of its mechanical properties and chemical resistance [12, 13]. A partial replacement of Portland cement (PC) with ceramic waste dust (CWD) prepares a substantial modification in physical and chemical properties, making them appropriate for the construction of concrete [14].

Although waste dusts have been shown to enhance the electrical resistivity and reduce the specific surface area and permeability, the effect of partial replacement of CWDs in PC on the electrochemical corrosion behavior of steel rebarshadnot been previously reported. Thus, this work aims to evaluate the influence of CWDs on the corrosion behavior of carbon steel rebars. The content of CWDs ranged from 0 wt% to 20 wt% by total mass of Portland cement. Electrochemical impedance spectroscopy, open circuit potential and water absorption tests as well as field emission scanning electron microscopy analysis were applied to characterize the samples.

2. MATERIALS AND METHODS

Portland cement (PC) was utilized as the main binder for the preparation of concrete samples. The ceramic waste dust (CWD) was a waste material generated by the production of hollow bricks which was used as the partial replacement of PC in the mixed binders. The chemical composition of PC and CWD are indicated in Table 1.

	PC (wt%)	CWD (wt%)
SiO ₂	21.35	54.74
Al ₂ O ₃	4.64	14.26
Fe ₂ O ₃	3.12	4.98
CaO	64.65	11.34
MgO	2.14	3.53
K ₂ O	0.63	3.13
Na ₂ O	0.28	1.28
SO ₃	2.96	2.78
LOI	0.88	0.00

Table 1. Chemical properties of PC and CWD

All mortars were produced by the same ratio of sand tocement (3:1). CWD was used for 0 wt%, 5 wt%, 10 wt%, 15 wt% and 20 wt% replacement of PC. The exact composition of the concrete mixtures designed is given in Table 2. In this work, the grade M20 was used with the nominal mixture according to IS 456-2000. The water to cement ratio was 0.47.Compressive strength experiment was done on 20 cm cubic samples at 1, 4 and 12 weeks.

Mixture	0 wt%	5 wt%	10 wt%	15 wt%	20 wt%
Water	235	235	235	235	235
Cement	500	475	450	425	400
Sand	1500	1500	1500	1500	1500
CWD	0	25	50	75	100

Table 2. Concrete mixture proportions (kg/m³)

ASTM A615 steel rebar is most commonly used in low-stress applications and less-demanding which offers economic choices. Table 2 reveals its chemical composition which utilized as rebar in this work.

Table 3. Chemical composition (%) of ASTM A615 steel rebar

C%	Mn%	Si%	S%	P%	Cu%	Cr%	Ni%	Mo%	V%
0.29	0.83	0.33	0.005	0.008	0.03	0.01	0.02	0.01	0.002

The steel rebars were cleaned by SiC sandpaper and then washed by deionized water and ethanol.Theheight andradius of the prepared concrete cylinder were 15 cm and 5 cm, respectively. The reinforced concrete specimens were posited in a chamber at 25 °C temperature to accelerate the corrosion procedure of the steel rebar.

The electrochemical impedance spectroscopy (EIS) was applied to evaluate the corrosion behavior of samples. The steel rebar, standard copper/copper sulfate (Cu/CuSO4) and graphite electrodes were used as a working, reference and counter electrodes, respectively.

The corrosion potential was determined for the samples consistent with the ASTM C876-15 standards. The steel reinforced concrete specimens were subjected to 3.5 wt% NaCl environment. EIS measurements were done in the frequency range of 0.1 mHz to 100 kHz at open-circuit potential with 10 mV amplitude of the AC perturbation. Water absorption was calculated according to ASTM C642. The samples were immersed in 3.5 wt% NaCl solution for 1, 4 and 12 weeks. The morphologies of the specimens were studied by FEI/Nova NanoSEM 450 scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Compressive strength of the reinforced concrete mixtures with CWD as partial replacement of PC after 1, 4 and 12 weeks of exposure to a 3.5 wt% NaCl solution are indicated in Figure 1. All the samples show a decrease in compressive strength with increasing exposure time. The samples with 15% CWD revealed the highest compressive strength throughout theentire exposure time in3.5 wt% NaCl solution. It can be associated to the enhanced bonding capability of CWD particles andmicro-filler act, which led to the improvement of concrete microstructure. Furthermore, the samples with 20 wt% CWD exhibited the lowest strength after being exposed o 3.5 wt% NaCl solution which means

that an extreme amounts of CWD as a partial replacement of PC reduces the compressive strength [15]. It can be related to the weak microstructure of concrete samples with higher CWD replacements [16].



Figure 1. Compressive strength of the reinforced concrete mixtures with CWD as partial replacement of PC after 1, 4 and 12 weeks of exposure to a 3.5 wt% NaCl solution



Figure 2. Water absorption of reinforced concrete mixtures with CWD as a partial replacement of PC after 1, 4 and 12 weeks of exposure to a 3.5 wt% NaCl solution

The water absorption of reinforced concrete mixtures with CWD as a partial replacement of PC after 1, 4 and 12 weeks of exposure to a 3.5 wt% NaCl solution are indicated in Figure 2.As shown, all the samples with CWD show a decrease in water absorption with increasing exposure time compared to the PC concrete. Thismeans that CWD admixture in concrete samples can reduce the water

absorption of concrete after being exposed to salty environment. Therefore, the water absorption of the samples decreases as the concentration of CWD increases. Furthermore, it may be concluded that CWD admixtures in concrete had no considerable effect on water absorption in comparison with other properties.

Although the presence of water in the early stages of corrosion is essential, adsorption and permeability of concrete sample do not play a major role in the corrosion behavior of reinforced concrete which was in agreement with previous studies [17]. In fact, it is more important to investigate the chloride and oxygen diffusions for anodic and cathodic reactions, respectively.

Figure 3 reveals the difference of open circuit potential (OCP) values of carbon steel bars reinforcement in concrete samples after 12 weeks of immersion in 3.5 wt% NaCl solution. The lines in Figure 3 separate the various zones of potential corrosion risk. As shown,three regions can be differentiated when risk of corrosion is considered according to ASTM C876-91 [18]. Based on this, OCP values below -350 mV indicate the possibility of strong corrosion.



Figure 3. Open circuit potential of carbon steel bars in concrete samples after 12 weeks of immersion in 3.5 wt% NaCl solution

The value of OCP increased during the curing process because of the increase of pH around the steel rebar. Moreover, the exposure of the samples to the chloride solution reduced theOCP values. It can be attributed to the aggressive anions and the passive film formed on the surface of steel rebar [19]. In NaCl solution, chloride ion (Cl⁻) is the main aggressive anions. Cl⁻ activates the surface of steel rebar and degrade the hydroxide passive film formed on the steel rebar in alkaline environment [20]. For this purpose, chloride ions must penetrate into the reinforced concrete structure and transfer to the surface of the steel rebar, resulting in more corrosion. The addition of CWD to the concrete mixture can have positive effects through filling the concrete structurepores and hence, it can prevent the chloride penetration into the concrete pores [21]. As shown in figure 3, the OCP value of reinforced concrete samples without CWD admixture falls quickly into the corrosion zone, while concrete samples with 15 wt% CWD stays in the low or uncertain corrosion area for much longer.

The impedance of carbon steel reinforced concretes were considered after 8 weeks exposureto 3.5 wt% NaCl solution. The Nyquist plots for the reinforced concrete samples with different value of CWD admixtures are shown in Figure 4. As indicated in Figure 4, all the mixtures reveal two capacitive properties. The low frequency loop of the plot is associated to the surface of metal. The high frequency loop from the Nyquist diagram is related to the concrete sample that covers the carbon steel rebar. Thus, the equivalent circuit model is shown in figure 5. This circuit includes a parallel capacitance (CPE_c) and resistance (R_c) for the covered concrete at high frequencies in across series with a parallel double-layer capacitance (CPE_{dl}) and charge-transfer resistance (Rct) of the steel surface in low frequencies [22]. Since the metal surface didnot act as a complete capacitorin electrochemical systems, therefore a constant phase element was introduced to model the double-layer.R_s is solution resistance[23]. The value of the R_s was associated to the resistivity of electrolyte solution, which was negligible in comparison with the resistivity of other elements[24]. As shown in Figure 4, the steel surface's response was larger than that oftheconcrete, therefore it was expected that the corrosion properties of the sample will be controlled by the steel surface elements.



Figure 4. Nyquist plots for reinforced concrete samples with different value of CWD admixtures



Figure 5. An equivalent circuit model used

In order toget the quantitative comparison of the EIS results, the data was fitted with the abovementioned equivalent circuit and analyzed by an EIS analyzer software which is shown in Table 4.It is observed that the Rct value of the samples increases with the increase of CWD admixture in the PC. Furthermore, the samples with 15 wt% CWD shows higher value of Rct compared to that of the others, which indicates that increasing the ratio of CWD to 15 wt% as a partial replacement of PC can enhance the corrosion behavior of reinforced concreates.

It can be related to the improvement of the concrete microstructure because of the micro-filler action and enhancement of bonding capability for the CWD particles which can reduce the air content, pore diameters and porosity and increase the internal surface area for the cement-matrix. As a result, the permeability of concrete-matrix is reduced. Polarization resistance, $R_P = R_{ct} + R_c$, was determined to consider the rate of chargetransfer in the interface layer [25]. As shown in Table 4, R_p values increase when the amount of CWDs as a partial replacement of PC increases, which decreases the surface alkalinity of carbon steel reinforced concrete and aid long-term corrosion resistance, as shown in previous studies [26, 27].

Table 4. EIS parameters from equivalent circuit for steel rebars in various concrete samples after 4 weeks immersed in 3.5 wt% NaCl solution

Admixture	$R_s (\Omega cm^2)$	$R_c (M\Omega \ cm^2)$	$CPE_c (\mu F \text{ cm}^{-2})$	R_{ct} (M Ω cm ²)	$CPE_{dl}(\mu F \text{ cm}^{-2})$
0 wt% CWD	72.4	0.41	3.1	0.68	4.2
5 wt% CWD	68.7	0.56	1.9	0.96	2.9
10 wt% CWD	75.6	0.89	1.3	1.36	2.1
15 wt% CWD	84.3	1.52	0.7	2.73	1.1
20 wt% CWD	77.5	1.05	0.9	1.85	1.8

Figure 6 shows the surface morphologies of the corrosion products on carbon steel rebars embedded in concrete sample with different CWD admixtures. As shown in FESEM images, the corroded areas found on the carbon steel rebars in 15 wt% CWD replaced cement were not severe and the amount of pitting corrosion on steel rebars was significantly lower than that of the others. Thus, based on these findings, an appropriate concrete mixture against corrosion should be provided with 15 wt% cement replacement.



Figure 6. FESEM images of corrosion products on carbon steel rebars embedded in concrete sample with different CWD admixtures(a) 0 wt% CWDs (b) 5 wt% CWDs (c) 15 wt% CWDs

4. CONCLUSIONS

In this work, the effect of CWDs as a partial replacement of PC on the corrosion behavior of ASTM A615 steel rebarwere evaluated by EIS, OCP and water absorption tests after exposureto the marine environment. All samples with CWDs showed a decrease in water absorption with increasing exposure time compared to the PC concrete. The samples with 15% CWD revealed the highest compressive strength throughout theentire exposure time in3.5 wt% NaCl solution. The OCP value of reinforced concrete samples with 15 wt% CWDs stayed the low or uncertain corrosion area for much longer. The surface morphologies of carbon steel rebarsindicated that the amount of pitting corrosion on steel bar embedded in 15 wt% CWD concrete sample was significantly lower than thatofthe othersamples. The electrochemical results showed that the higher content of CWDs up to 15 wt% in PC hadsignificantly improved the concrete structure as well as reduced the corrosion rate. It can be related to the improvement of concrete microstructure because of the micro-filler action and enhancement of bonding capability for the CWD particles which can reduce the air content, pore diameters and porosity and increase the internal surface area for the cement-matrix.

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