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Effect of polyvinylpyrrolidone on the corrosion resistance of steel

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Abstract

The effect of polyvinylpyrrolidone (PVP) on the corrosion resistance of steel reinforced concrete was assessed by measuring the corrosion potential, linear polarization resistance and AC impedance during 60 days immersion in NaCl and NaCl + PVP solutions. Polarization resistance (R_p) values of PVP added reinforced concrete were much higher than those without PVP. The relationship between corrosion potential and linear polarization resistance was analysed. Results from corrosion potential measurements were well comparable with the linear polarization resistance data. AC impedance spectra revealed that the resistance of PVP mixed electrodes was also quite higher than the other electrodes. The mechanical properties of concrete were measured. It was observed that the compressive strength of concrete had increased approximately 44% in the specimens containing PVP.

Keywords: Reinforcing steel; Corrosion; Polyvinylpyrrolidone; Electrochemical measurements

1. Introduction

Reinforced concrete is one of the most widely used construction materials. Corrosion occurs with loss of the alkalinity in concrete in the form of carbonates by diffusion of CO_2 or the penetration of aggressive ion (such as chloride) to the reinforcing steel [1–5]. Reinforcement corrosion damages concrete because of the internal stresses created by the conversion of metallic iron to iron oxide. The oxidized iron occupies up to metal, creating great deal of internal stress on the concrete. This stress creates high tensile strength, resulting in cracking and spaling of concrete [6,7]. Various methods have been devised to protect corrosion of reinforcing steel; these contain variation of concrete formulation, cathodic protection, addition of inhibitors, surface treatment of rebars (e.g. epoxy coating), and so on. Organic inhibitors offer protection by forming a protective film or provide a physical barrier to the ingress of aggressive agents or by chemically stabilizing the steel.

Organic corrosion inhibitors, a combination of amines and oxygen in a water medium, have been developed as an alternative approach for protecting steel reinforcement. Several polymers have been used as inhibitors, with their function to adsorb on the surface of metal thus protecting it against the corrosive environment [8]. In addition, organic and polymer based inhibitor may be considered to decrease the chloride diffusion through the capillary channels in the concrete.

The main purpose of this work was to study the effectiveness of polyvinylpyrrolidone (PVP) in providing corrosion protection to reinforcing steel in 0.1 M NaCl solution. The effect of the inhibitor on the compressive strength of concrete was also determined. The corrosion resistance was evaluated by measuring corrosion potentials, resistance to linear polarisation and AC impedance spectroscopy.

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2. Experimental

Cylindrical reinforced concrete specimens 40 mm in diameter and 70 mm high were used. Copper wire cables were connected to each steel bar for electrochemical measurements. Fig. 1 shows the specimen geometry. The composition of the concrete is given in Table 1. Saturated dry surface density of aggregate is 2.59 g cm^{-3} and two other aggregate were used having sizes of 0.5–4 mm and 4–8 mm. External solution and mixing water compositions are shown in Table 2. Water/cement (w/c) ratio was 0.5. Mild steel rods were 10 mm in diameter. 50 mm long steel rebars used for reinforcement has the chemical composition of 0.13% C, 0.65% Mn, 0.030% S, 0.013% P and 0.017% Si and the rest Fe. Each bar was mechanically polished and prepared as test electrode, which had 17.27 cm^2 the contact area. The electrode was removed from the mold 24 h after placement. After curing, measurements were taken in the external solution.

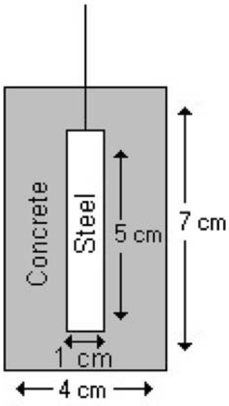

Fig. 1. Schematic representation of the test specimen.

Table 1
Composition of the concrete

	Mass (kg)	Density (kg/dm^3)	Volume(dm^3)
Water	180.00	1.00	180.00
Cement	360.00	2.96	120.96
Aggregate	1731.10	2.59	668.38
Air	–	–	30.00

Table 2
External solution and mixing water environments

Specimens	External solution	Mixing solution
A	0.1 M NaCl	Distilled water
B	0.1 M NaCl	Distilled water + 100 ppm PVP
C	0.1 M NaCl + 100 ppm PVP	Distilled water
A′	0.1 M NaCl	0.1 M NaCl
B′	0.1 M NaCl	0.1 M NaCl + 100 ppm PVP
C′	0.1 M NaCl + 100 ppm PVP	0.1 M NaCl

All specimens were immersed in 0.1 M NaCl solution for conducting the electrochemical tests. Electrochemical measurements were performed using a three-electrode system. The electrode consisted of a reinforced concrete specimen as working electrode. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference, respectively. An EG&G Model 360 potentiostat, was used for electrochemical measurements. Additionally, a computer program, wisidaq was used for applying the potential scan (scan rate was 1 mV/sec) and analysing the resistance to polarization. The variations of corrosion potentials (E_{cor}) with time were recorded with respect to a saturated calomel reference electrode at room temperature. Initially these measurements were taken every day, until equilibrium conditions were established. Impedance measurements were carried out with applied sinusoidal potential waves of 5 mV amplitudes around corrosion potential, with frequencies ranging from 10^5 Hz to 10^{-1} Hz. The measurements were carried out on the 1, 2, 7, 28 and 60th day of the curing period. In the compressive experiments, cubic shaped concrete specimens (15 cm × 15 cm × 15 cm) were used. The compressive strength of these specimens, in MPa (σ) was measured after curing for 28 days in external solution (0.1 M NaCl or 0.1 M NaCl + 100 ppm PVP) by using Tonitecnic compressive testing machine. All experiments were done three times and reproducible results have been obtained.

3. Results and discussions

The effects of PVP addition on the corrosion potentials of rebar in the concrete were monitored and results are shown in Fig. 2(a) and (b). E_{cor} for the specimens in all media were almost indistinguishable and varied from −0.140 V to −0.590 V (vs SCE) during 60 days with only small variation (Fig. 2(a)). The control specimen (Specimen A) generally shows the most negative potentials and the specimen with PVP (Specimen B) shows most positive potentials among the specimens (Fig. 2(a)). The values of specimen A′ shows small variation and implies that the curves of E_{cor} of rebar was more negative potential than specimen B′ and specimen C′ (Fig. 2(b)). The specimen containing PVP (B′) shows the most positive corrosion potential in chloride solution. On the average, the E_{cor} of the rebar in specimen B was 0.200 V, more positive than that of rebar in all specimens (Fig. 2). The more negative potentials indicate greater corrosion tendency for the rebar in concrete. The E_{cor} of the rebar in specimen A′ was 0.150 V, more negative than that the rebar in specimen B′ (Fig. 2(b)). In the literature, it is reported that probability of

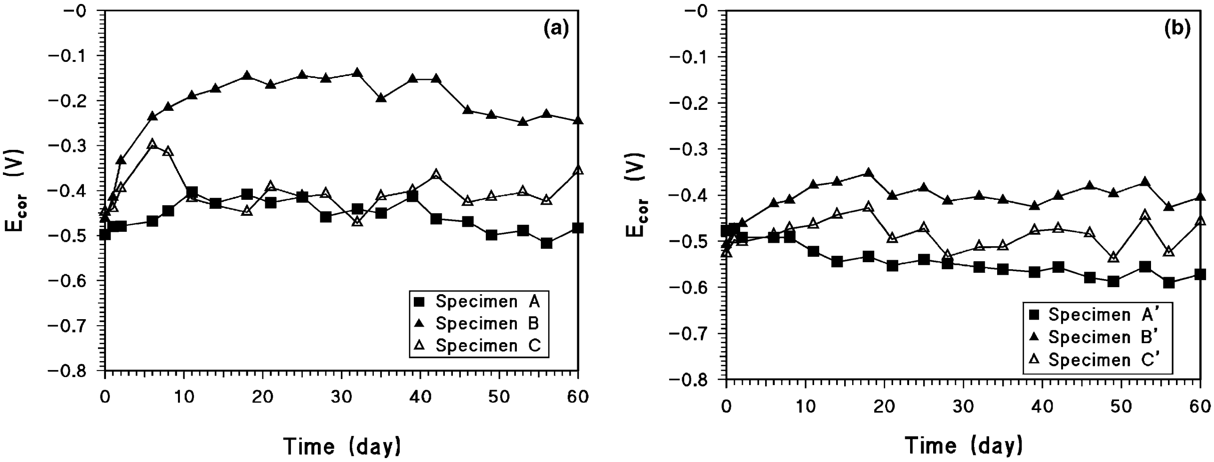

Fig. 2. The variation of corrosion potentials with time.

corrosion would be greater than 95% if the observed corrosion potential is more negative than −0.270 V [9–11]. Hence, while the addition of PVP to concrete greatly reduced the corrosion probability, whereas addition of PVP with chloride could not be more effective on corrosion resistance of rebar in concrete. In the case the shifting the corrosion potential-time curve to the positive direction was not observed as the case of addition of PVP without chloride (specimen B). It could be seen that the specimens containing more chloride ions were more corrosive than the specimens without chloride just as expected. This is due to their greater pore size causing chloride ion diffusion in concrete matrix easily and activating the passive film on the reinforced steel's surface.

Fig. 3 shows the variation of the polarization resistance versus the exposure time (day) for the steel-reinforced concrete. From the curves, it can be seen that the measured polarization resistance increases with time. Polarization resistance values versus exposure time graphs of the specimens varied between 9 kΩ cm^2 and 98 kΩ cm^2 in all media during the 60 days period. The R_p values of specimen A–C show that PVP had not influenced greatly on corrosion resistance during 30 days, than the polarization resistance values of specimen containing PVP in mixing solution were higher than that of control specimen especially after the 30th day (Fig. 3(a)). The polarization resistance value for specimen A′ was smaller than the values of specimen B′ and indicates higher values than the values of specimen C′ in Fig. 3(b). Polarization resistance technique is used to determined corrosion rates of steel in concrete. R_p is directly related with the corrosion rate. As the R_p increases, corrosion rate decreases. The decreasing resistance with time must have been caused by anodic dissolution of the embedded steel surface [12]. Thus, while the R_p values of specimen A were lower than specimen B, probably due to the consequence an impregnated mortar, which reduces the chloride ingress from the external solution. R_p values obtained for specimen B′ indicated that corrosion resistance of rebar is higher than specimen A′ (Fig. 3(b)). Correlations between corrosion potential and polarization resistance are plotted

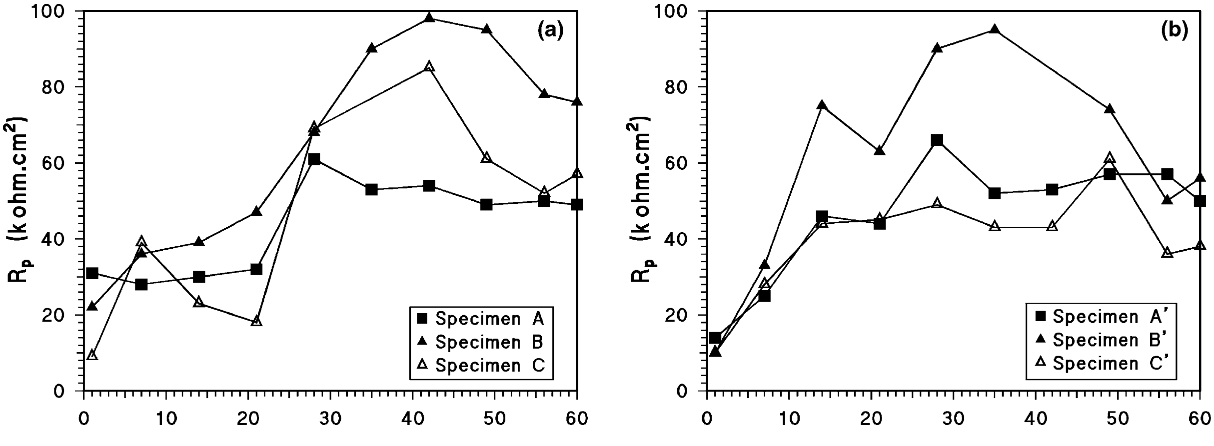

Fig. 3. The variation of polarization resistance (R_p) with time.

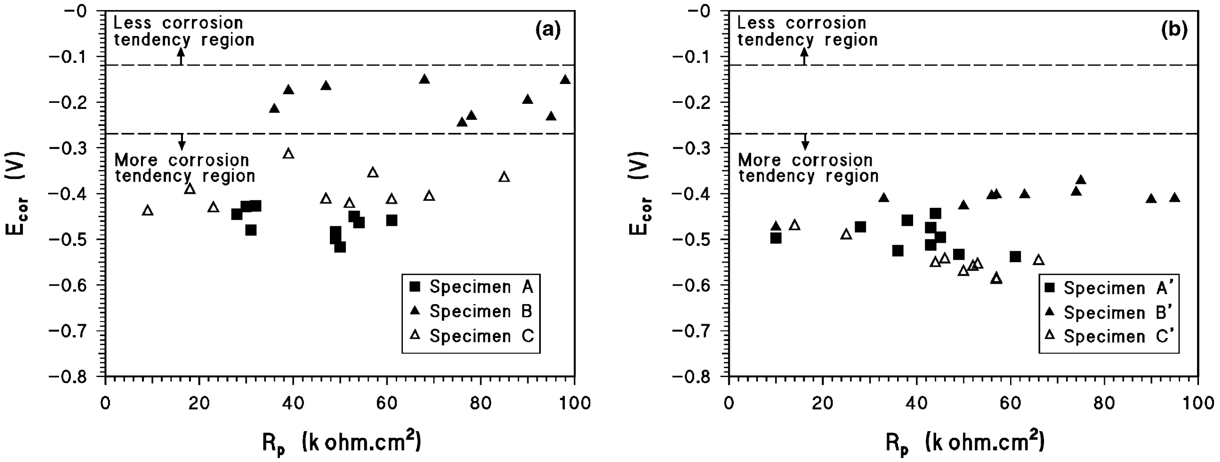

Fig. 4. Plot of the corrosion potential (E_{cor}) versus polarization resistance (R_{p}) for the specimens.

in Fig. 4. It can be seen that the specimen containing PVP in mixing solution (Specimen B), there is a less tendency to corrode than specimen A and C and that the corrosion activity is considered uncertain as is shown Fig. 4(a). In concrete containing chloride (Specimen A′–C′), there is a tendency for specimens to have greater probability of corrosion. However, specimen B shows fewer tendencies for corrosion among all the specimens (Fig. 4(a) and (b)). The corrosion potential provide qualitative and probably indicate reinforcement corrosion. Quantitative and reliable information on reinforcement corrosion can be obtained by measuring the resistance or corrosion current density. Linear polarization resistance increases with additive, this increament indicates the decrease of corrosion rate. However, apart from the concrete without chloride, the variation of the corrosion potentials indicates that the corrosion probability is still high (Fig. 4).

Fig. 5(a)–(e) show the typical AC impedance behaviour observed up to 60 days exposure in specimens A–C′. As shown in Fig. 5(a), (Specimen A) the diagram exhibits semicircular change representing $R_{\mathrm{s}} + R_{\mathrm{ct}}$ until the real impedance value reaches 36 Ω (21.93 kHz) during the first day in Table 3. In this table, the frequency values at the beginning of Warburg region are also given. This region that is known as semicircle, can attain only one section because the surface structure is not disturbed at the applied maximum frequency. The solution resistance (R_{s}) can be obtained by extrapolating the semicircle curve to the real impedance axis (Z'/Ω). The region of the real impedance and the imaginary impedance, which increases continuously, is known as Warburg impedance. This resistance is due to coating, accumulating on the surface and concrete, causes shielding effect or resistance effect for the metal corrosion [13–17]. Charge transfer resistance is the rate determining resistance at the reinforcing steel corrosion. While $R_{\mathrm{s}} + R_{\mathrm{ct}}$ value for specimen A, made of steel embedded in concrete coating containing only distilled water as mixing solution and 0.1 M NaCl as external solution, was 36 Ω, this value has increased to 45 Ω and 80 Ω for specimen B and C respectively during the first day. The resistance of the specimen A′ containing 0.1 M NaCl as mixing solution, was 38 Ω, when 0.1 M NaCl solution was used, increased to 50 Ω and 80 Ω at specimen B′ and C′ respectively. This indicates that specimen A′ had already suffered from severe damage on its passive layer and the addition of PVP to the concrete, formed a protective layer on the steel and concrete surface. However, when waiting period of the electrodes (Specimen A–C′) was increased in the external solution, the resistance values have also increased. These resistance increment come from the diffuse layer effect and diffusion resistance (R_{d}) addition to the $R_{\mathrm{s}} + R_{\mathrm{ct}}$ then, $R_{\mathrm{s}} + R_{\mathrm{ct}} + R_{\mathrm{d}}$ values waiting to 60 days for specimen B has increased from 45 Ω to 210 Ω and from 80 Ω to 620 Ω for specimen C. Reinforced concrete containing chloride and PVP in mixing and external solutions showed similar increment in resistances (50–230 Ω and 80–620 Ω) for specimen B′ and C′, respectively. It is worth mentioning here that in all media, Warburg impedance region showed similar changes. As it is seen from the Bode plots, all the diagrams show only one time constant at high frequency and in Warburg region. R_{ct} and C_{dl} that shows resistance and capacitance and also R_{con}, concrete resistance, C_{con}, concrete capacitance, C_{dl}, diffuse layer capacitance are given within the equivalent circuit in Fig. 6.

The rebar present in reinforced concrete has a pore structure where the capillary channels are in contact with external medium. When these capillary channels approach the metal ends, electrical double layer forms thus allowing charge transfer in this layer. Charge transfer resistance and double layer capacitance at equivalent circuit are shown as R_{ct} and C_{dl} in Fig. 6. The outside concrete resistance (R_{con}) and the proposed capacitance

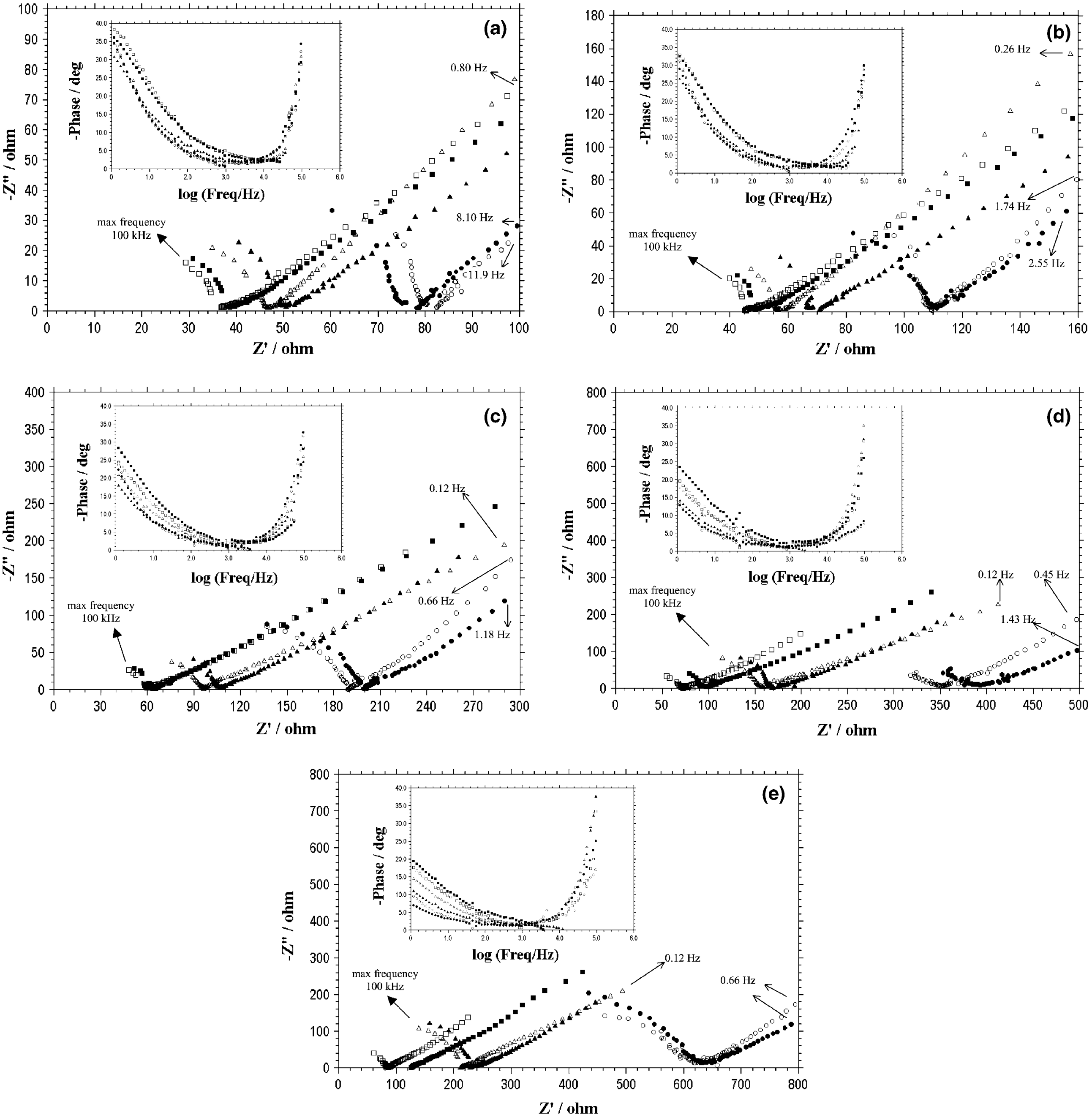

Fig. 5. Impedance spectra of reinforcing steel ((a) 1, (b) 2, (c) 7, (d) 28 and (e) 60 days. (□) Specimen A, (■) Specimen A′, (△) Specimen B, (▲) Specimen B′, (○) Specimen C, (●) Specimen *C*′). In all of the diagrams, the maximum frequency in 10^5 Hz. The minimum frequency values that correspond to Warburg region are given in Table 3. The minimum frequency values that belong to Warburg region are given within the diagrams.

for the concrete (C_{con}) were fixed onto the circuit. The outermost double layer formed within the capillary channels and the solution resistance (R_{s}) that arose between the outermost of the concrete and the potential point measurement is also shown in Fig. 6. According to the equivalent circuit; high frequency region of Nyquist diagram shows the charge transfer resistance and diffuse layer resistance. However, increasing imaginary impedance in the lower frequency region is also considered as Warburg impedance (Fig. 5). These impedances are evaluated as a total resistances produced from both the concrete and corrosion products.

At low frequency region (Warburg region), the influence of PVP was not seen and thus $R_{\mathrm{s}} + R_{\mathrm{ct}}$ which is mostly known as pore resistance must be changed with chemical adsorption effect. As it is well known, corrosion rate is inversely proportional with polarization resistance. However, polarization resistance measured by means of AC impedance includes solution (R_{s}) charge transfer (R_{ct}) diffuse layer resistances (R_{d}) as well

Table 3
Measured R_{ct}, R_s and frequency values determined from nyquist plots

Specimen	Time (day)	$R_{ct} + R_s(\Omega)$	Frequency (kHz)	Specimen	Time (day)	$R_{ct} + R_s(\Omega)$	Frequency (kHz)
A	1	36	21.93	A′	1	38	26.04
	2	46	36.76		2	50	36.76
	7	60	9.62		7	62	0.69
	28	74	0.96		28	95	0.96
	60	85	0.69		60	120	0.00012
B	1	45	1.23	B′	1	50	8.33
	2	60	0.54		2	70	0.83
	7	100	0.83		7	110	1.81
	28	150	1.51		28	170	2.19
	60	210	12.25		60	230	12.25
C	1	80	0.96	C′	1	80	0.83
	2	100	5.44		2	110	0.83
	7	190	3.21		7	200	3.21
	28	350	0.55		28	400	0.37
	60	620	0.83		60	620	1.17

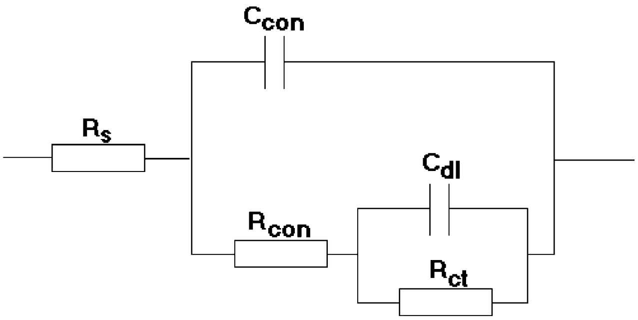

Fig. 6. Equivalent circuit for concrete (R_s solution resistance, R_{con} concrete resistance, R_{ct} charge transfer resistance, C_{con} concrete capacitance, C_{dl} diffuse layer capacitance).

as Warburg region. Weak influence of PVP indicates that it is adsorbed physically. Thus, the effect of PVP should be in the form of increasing the diffuse layer resistance. Oxygen diffusion from the outer medium to the metal surface occurs through the capillary channels and pore in concrete. Since additives have blocked these capillary channels and pore, diffusion becomes more difficult and diffuse layer resistance increases [18]. The increase of the resistances in Nyquist diagrams, preventing the surface structure from deterioration and decreasing shift of Warburg region to low frequencies supports to the above observations. In chloride medium, since the capillary channels in the concrete have not blocked, it is easier for the additive (PVP) to pass through and reach the metal surface from the external solution (without PVP). When PVP is added to the mixing solution then PVP molecules cannot be mobile in chloride medium and this solution is not mobile, the effect will be much less than that in the external solution.

The polarization resistance measured with DC and AC techniques does not reflect directly corrosion rate, especially in the case of linear polarization resistance technique where the polarizing surface of the rebar in concrete brings about unappreciable results [13]. The measured resistance includes several resistances other than the charge transfer resistance. These increments indicate that PVP has also blocked the pores of the concrete and the diffusion of corrosive ions on the surface of rebar in concrete became more difficult. AC impedance results contain pore resistance and diffuse layer resistance and these values also comparatively with DC results. So, AC impedance results also supports above argument (Fig. 5(a)–(e)).

The compressive strength values of specimens cured for 28 days are given in Fig. 7. The value of blank (distilled water both mixing and external solution) was 19.4 MPa. The other values of the specimens for the environment A–C′ are varied between 20.8 and 27.9 MPa (Fig. 7). The weakest concrete is the one without additives. Compressive strength of the concrete containing distilled water as mixing and external solution was 19.4 MPa (Specimen 0), while the sample containing only distilled water as mixing and chloride as external solution was 20.8 MPa (specimen A). However the

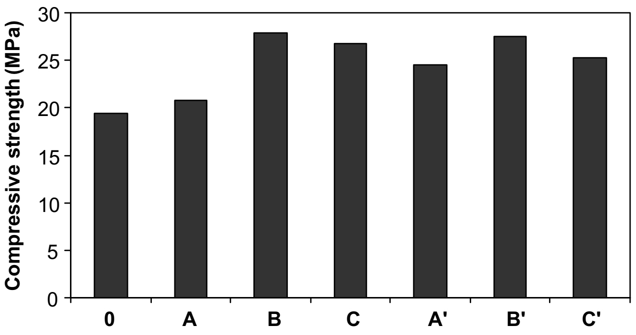

Fig. 7. 28’ day compressive strength values of the concrete specimens.

strongest concrete was the one containing distilled water with PVP as mixing solution and chloride as external solution (Specimen B). Chlorides diffuse to mortar will tend to react with the cement aluminates during the hydration of cement thus, allowing a quicker ingress of chlorides that comes from the environment once the concrete has hardened [18]. The results show that there was an increase of 26–44% in the strength of concrete by adding PVP.

4. Conclusion

The investigation was carried out to examine the effectiveness of polyvinylpyrrolidone in minimizing corrosion of steel embedded in concrete. PVP improved the corrosion resistance of concrete when added to mixing or external solution mainly due to the increase of the $R_s + R_{ct} + R_d$ resistance. When the specimen containing distilled water as mixing solution added PVP as mixing or external solution, increase the resistance of the same ratio. The corrosion of the rebar in chloride containing concrete was inactive even 0.1 M NaCl with PVP as external solution. Polarization resistance values indicated that adding PVP to mixing or external solution increased the values of R_p 30–50%. The addition of PVP to concrete greatly reduced the corrosion rate of steel in concrete samples prepared with distilled water. Compressive strength results show that there was an increase in the strength of concrete due to addition of PVP.

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