

Effect of Molar Ratio and Resin Modification on the Protection Properties of Zinc-rich Alkali Silicate Primer

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Abstract

The influence of increasing the SiO₂/K₂O molar ratio on the electrochemical action of a waterborne potassium silicate zinc-rich coating was investigated by means of electrochemical impedance spectroscopy (EIS) and corrosion potential (E_{corr}) measurements. The EIS results showed that increasing the SiO₂/K₂O molar ratio in the range of 3.135 to 5 by the addition of nano-SiO₂ to the resins improved the resistance of coatings; however, higher molar ratios showed an adverse effect. Moreover, the alkali silicate binder of the sample with a SiO₂/K₂O molar ratio of 5 was improved by adding 5, 10, and 15 wt.% of acrylic resin and acrylic/styrene copolymer to potassium silicate resin. These formulated coatings were sprayed over carbon steel plates and the adhesion and morphology of these primers were evaluated by pull-off, cross cut, and scanning electron microscopy tests. Electrochemical measurements showed that the sample with a SiO₂/K₂O molar ratio of 5 had better corrosion properties than the other samples. Adhesion and SEM tests also showed that B1 and C2 with respectively 5 and 10% acrylic derivatives had less holes, cracks, and better adhesive properties.

Keywords: Zn-rich Coating, Molar Ratio, EIS, Adhesion, SEM

1. Introduction

Zinc-rich coatings are very useful for corrosion protection of steel structures (Chua et al., 1978; Gergely et al., 2011; Hammouda et al., 2011; Morizane et al., 2011; Canosa et al., 2012; Kakaei et al., 2012; Gervasi et al., 1994). Because of zero volatile organic compound (VOC) contents of waterborne inorganic zinc-rich coatings they are entirely environmental friendly and have been used very much. Because of porous nature of these coatings, electrolyte can penetrate through the coating to the steel/coating interface. At first, the cathodic protection of steel substrate is done for a short time by zinc particles scarification. Then, by formation of zinc corrosion products, the barrier protection of steel substrate begins gradually. Subsequently, because of the accumulation of zinc corrosion products, which have poor electrical conductivity, the cathodic protection is reduced and the electrical contact between zinc particles themselves or zinc particles and the steel substrate is lost (Morizane et al., 2011; Canosa et al., 2012; Kakaei et al., 2012; Gervasi et al., 1994).

A standard zinc silicate ratio (3.75:1 SiO₂:K₂O) must be post-cured by heat or acid wash, otherwise it has a long-term self-curing process. In 1970, NASA raised the ratio from 3.75:1 to 5.3:1. This high-ratio self-cure zinc silicate cured very fast by losing water vapor and had excellent properties.

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Nowadays, the waterborne inorganic paints use the high $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio potassium silicate aqueous as the binder (Pedram et al., 1978).

For giving good electrical conduction between the zinc particles and between the zinc particles and the steel substrate, the pigment volume concentration (PVC) of Zn pigment in the zinc-rich coatings should be more than the critical PVC (CPVC) (Gervasi et al., 1994; Shreepathia et al., 2010; Abreu et al., 1996). If the PVC to CPVC ratio is greater than one, there is not enough resin to wet the zinc particles and substrate; therefore. It results in poor mechanical properties of the coating such as adhesion, flexibility, cohesion, abrasion resistance, etc. Also, dispersion of the zinc particles in these high PVC coatings uniformly is difficult (Canosa et al., 2012; Knudsen et al., 2005; O'Donoghue et al., 2005).

Alkali silicate salts and colloidal nanosilica, which can also contain an organic resin or latex, have been used as aqueous inorganic coating modifiers. In this subject, a number of patent applications have been filed (Kemp et al., 1966; Davies et al., 2012; Beers et al., 1975; Neel et al., 1969). Adding small amounts of organic resins to inorganic zinc coatings decreases the surface tension of the vehicle and increases the wettability of the pigment by vehicle. Alkali silicate binder modification also improves the dispersion of the zinc pigments in the coating, cohesion of the film, adhesion of the coating to the substrate, and corrosion resistance of the coating (Zhang et al., 2012).

The aim of this work is to study the effect of increasing $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio. The corrosion resistance properties of these coatings were examined by electrochemical impedance spectroscopy (EIS) and open-circuit potential during immersion in artificial seawater.

Also, waterborne inorganic potassium silicate binder modification by adding small amounts of organic acrylic-based resins was studied. Finally, the dispersion of the zinc pigments in the coating and the adhesion to the substrate were examined by scanning electron microscopy, pull-off, and cross cut tests.

2. Experimental

2.1. Materials and formulations

Commercial potassium silicate aqueous solutions with 3.13:1 silica/alkali molar ratio were provided by Iran silicate industries. To increase the silica/alkali molar ratio from 3.13:1 to 5.5:1, a 30% (wt./wt.) nanosilica colloidal solution with 10-20 nm particle size (produced by Sharif Nano Pigment Company) was used. These binders were represented by A1, A2, A3, A4, A5, and A6 with a respective $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio of 3.135 (without nano- SiO_2), 3.5, 4, 4.5, 5, and 5.5, and were produced by admixing the nanosilica colloidal solution into the potassium silicate resin slowly. The formulated compositions of the coatings are tabulated in Table 1 and the calculation of the coatings is given at the end of this section.

Table 1
Specification of the formulated coatings with different $\text{SiO}_2/\text{K}_2\text{O}$ molar ratios.

Type of coating	Zinc dust (%)	Binder (resin+nano- SiO_2) (%)	$\text{SiO}_2/\text{K}_2\text{O}$ ratio
A1	90	10	3.135 (without nano- SiO_2)
A2	90	10	3.5
A3	90	10	4
A4	90	10	4.5
A5	90	10	5
A6	90	10	5.5

The potassium silicate resin (A5) was modified by admixing various quantity of acrylic/styrene copolymer and acrylic emulsion. General properties of the acrylic and acrylic/styrene resins which were produced by Simab Resin Company (Iran) are given in Table 2.

Table 2
General properties of acrylic and acrylic/styrene resins used.

Resin	Color	Crosslinking type	Emulsifying system	Solids (%)	pH	T_g (°C)	Viscosity (cP)	MFFT (°C)
Acrylic	Milky white Liquid	Self-crosslink	Nonionic	45±1	2-3	-14	1000	<0
Acrylic styrene	Milky Liquid	Self-crosslink	Anionic	47±1	6-8	-2	3000	0

The binder solution modified with 5, 10, and 20% acrylic/styrene copolymer were respectively represented by B1, B2, and B3, while those modified with acrylic emulsion were indicated by C1, C2, and C3 for 5, 10, and 20% of the emulsion respectively. The specified coatings compositions are given in Table 3. Fine zinc dust with an average particle diameter of 4 μm was used in the zinc-rich coatings. Zinc dust was mixed with the resins to produce unmodified and modified zinc-rich coatings. For adequate electrical connection between zinc particles and steel substrate the weight percentage of zinc dust was 90%.

Table 3
Specification of the binder modified by acrylic derivatives coatings.

Coating code	Zinc dust content (%)	Binder content (%)	Used modifier organic resin	Organic resin/total resin
A5	90	10	-	-
B1	90	10	Acrylic/Styrene	5%
B2	90	10	Acrylic/Styrene	10%
B3	90	10	Acrylic/Styrene	20%
C1	90	10	Acrylic	5%
C2	90	10	Acrylic	10%
C3	90	10	Acrylic	20%

Step 1:

At first, the silica/alkali molar ratio of the resin was calculated by considering a resin silica/alkali weight ratio of 2:1.

$$K_{MW}=39.09 \quad \text{SiO}_2 = 28.08 + 2(15.99) = 60.083 \text{ gr}$$

$$O_{MW}=15.99 \quad \text{K}_2\text{O} = 2(39.09) + 15.99 = 94.195 \text{ gr}$$

$$Si_{MW}=28.08$$

K ₂ O:	1 mole	94.195 gr		SiO ₂ :	1 mole	60.083 gr
	Y mole	1 gr			X mole	2 gr

$$\text{Molar ratio: } X/Y = 0.033287/0.010616 = 3.135$$

Step 2:

Next, the calculations for obtaining a special silica/alkali molar ratio such as 5:1 by adding a certain amount of a 30% (wt./wt.) colloidal acidic solution of nanosilica to the potassium silicate with a silica/alkali molar ratio of 3.13:1 were carried out.

It is assumed that 30 gr potassium silicate with a silica/alkali molar ratio of 3.13:1 is available. By considering the (40% (wt./wt.)) potassium silicate, there is 12 gr solid content in 30 gr potassium silicate including 8 gr SiO₂ and 4 gr K₂O.

$$\frac{\text{mole of nano SiO}_2 + \text{mole of SiO}_2}{\text{mole of K}_2\text{O}} = \text{specific molar ratio of SiO}_2/\text{K}_2\text{O}$$

$$\frac{\text{mole of nano SiO}_2 + 0.1331491}{0.0424650} = 5 \rightarrow \text{mole of nano SiO}_2 = 0.0791759$$

SiO ₂ :	1 mole	60.083 gr
	0.0791759 mole	gram of nano-SiO ₂ solid content

Thus, the gram of nano-SiO₂ solid content is equal to 4.7571256.

$$30\% \text{ (wt./wt.) colloidal solution of nanosilica} \rightarrow 30\% \quad 4.7571256 \text{ gr} \quad \rightarrow \text{colloidal solution} =$$

$$100\% \text{ colloidal solution gr} \quad 15.8570853$$

Similarly, the amount of the colloidal solution of nanosilica needed to obtain different silica/alkali molar ratios was calculated.

2.2. Application of the coatings

The SAE 1010 steel with dimensions of 15×7×0.2 cm was used as a substrate. The metal surface was sandblasted according to SA 2-1/2 (SIS Standard 05 59 00/1967) before applying the coating. The coating was immediately applied over blasted steel panels by air spray equipment. The thickness of the produced zinc-rich coatings was 70±5 μm for EIS tests of A series and 50±5 μm for B and C series. The coated plates were putted in the laboratory atmosphere for one week to make sure of full curing of the resins.

2.3. Laboratory tests

The electrochemical impedance spectroscopy (EIS) measurement was performed utilizing Autolab PGSTAT 302N potentiostat/galvanostat (Autolab, Italy) in a 3.5 wt.% NaCl solution at room temperature. In addition, the corrosion potential (E_{corr}) measurements were carried out for the verification of cathodic protection duration. Two clear polyvinyl chloride cylindrical tubes were connected to each coated steel plate (to check repeatability). The exposed surface area of the working electrode was 2 cm². Frequency response analyzer software, FRA2, (Eco Chemie B.V., Netherlands) was used to carry out EIS measurements. All of the measurements were done at open circuit potential at sinusoidal voltage amplitude of 10 mV over a frequency range of 10 mHz to 100 kHz at various immersion times. The electrochemical measurements were performed in a three-electrode cell with saturated Ag/AgCl reference electrode and platinum rod counter electrode.

The scanning electron microscope (SEM) studies were done by a SEM model VEGA3 XM (TESCAN, Czech Republic). A scanning electron micrograph was taken of the zinc-rich coating plates before salt exposure and the surface structure of these coatings were studied at a magnification of x3.00 k.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

The Nyquist impedance diagrams for the coatings at different immersion times in 3.5 wt.% NaCl solutions are presented in Figures 1-6.

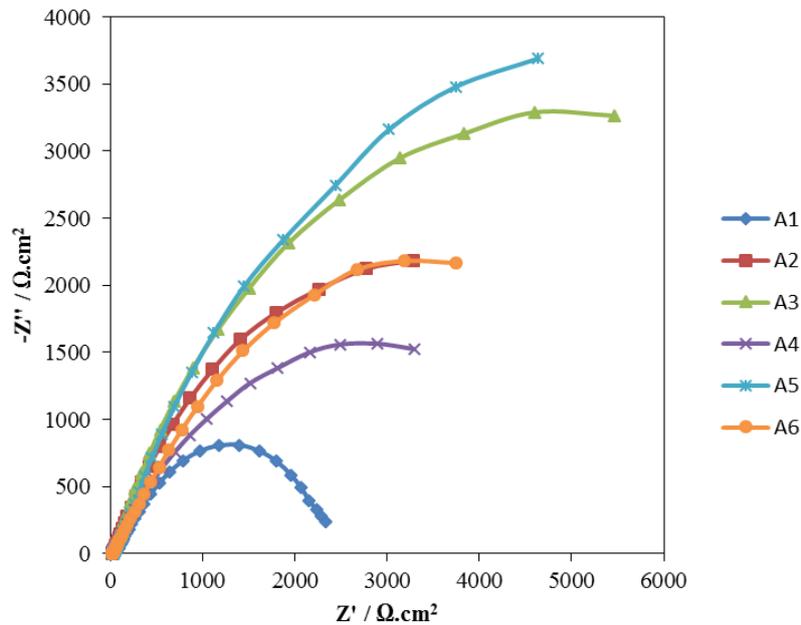


Figure 1

The Nyquist impedance diagrams of the samples with different $\text{SiO}_2/\text{K}_2\text{O}$ molar ratios (A series) after 30-minute exposure to the saline solution.

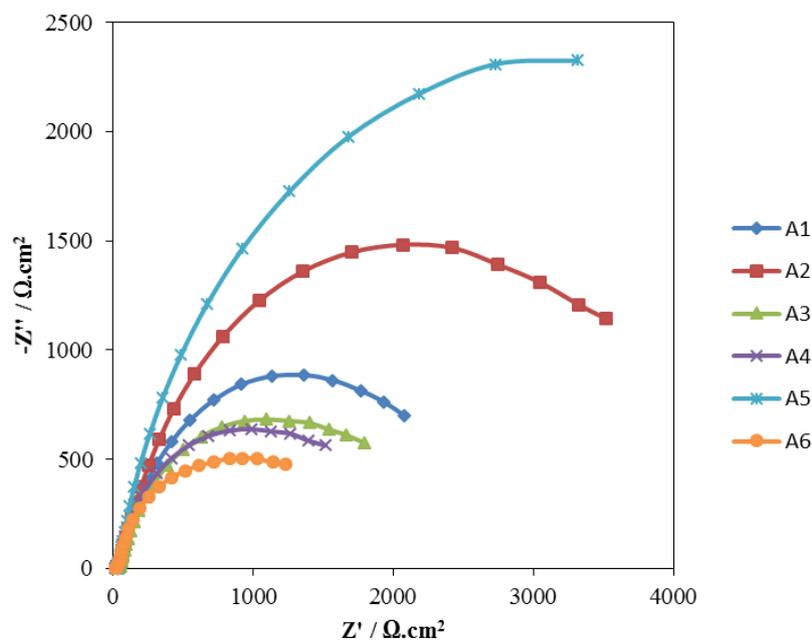
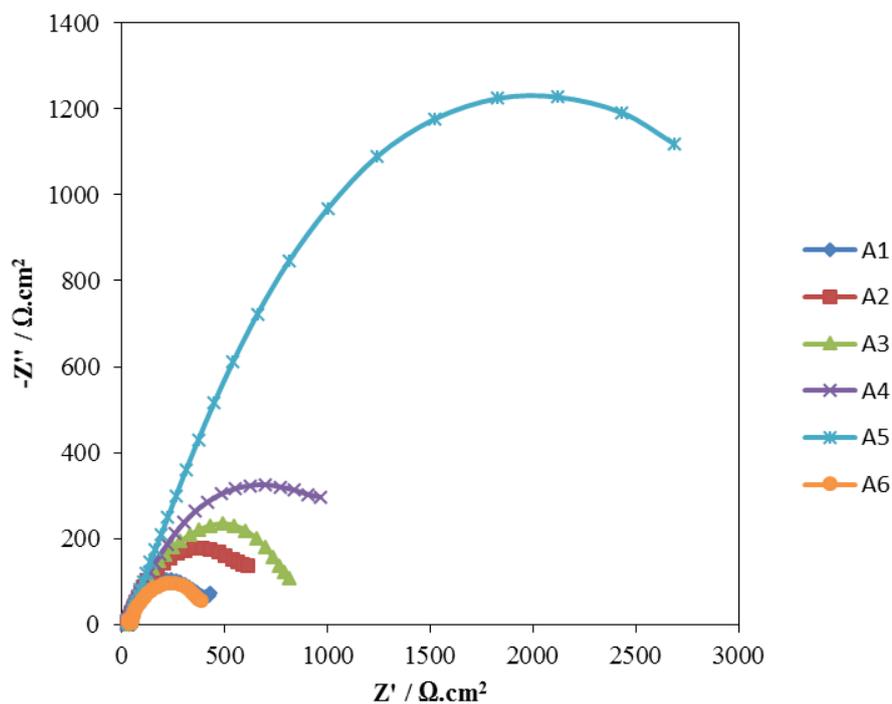
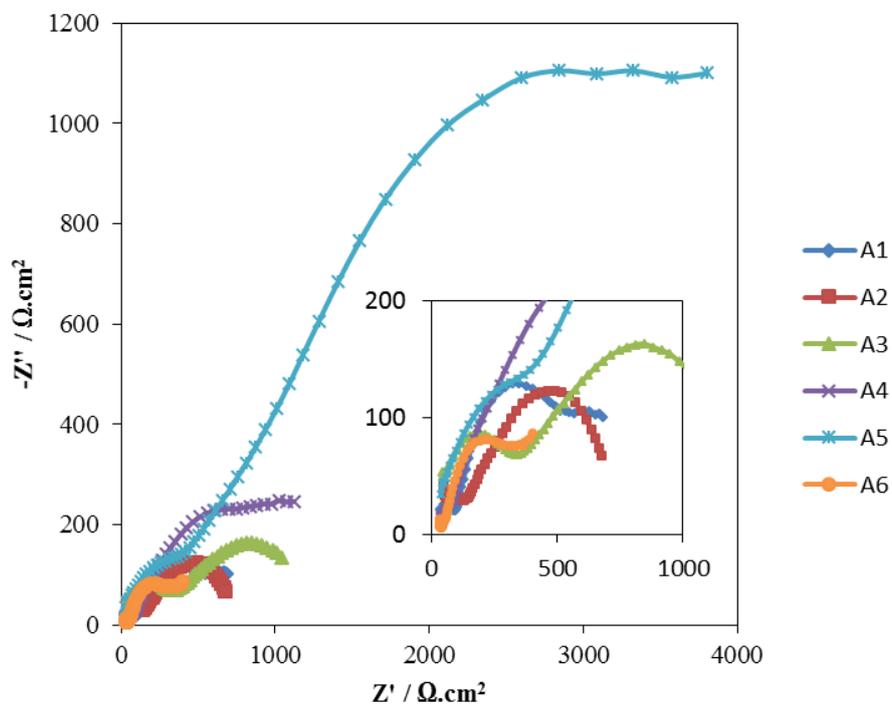


Figure 2

The Nyquist impedance diagrams of the samples with different $\text{SiO}_2/\text{K}_2\text{O}$ molar ratios (A series) after 1-day exposure to the saline solution.

**Figure 3**

The Nyquist impedance diagrams of the samples with different SiO₂/K₂O molar ratios (A series) after 9-day exposure to the saline solution.

**Figure 4**

The Nyquist impedance diagrams of the samples with different SiO₂/K₂O molar ratios (A series) after 28-day exposure to the saline solution.

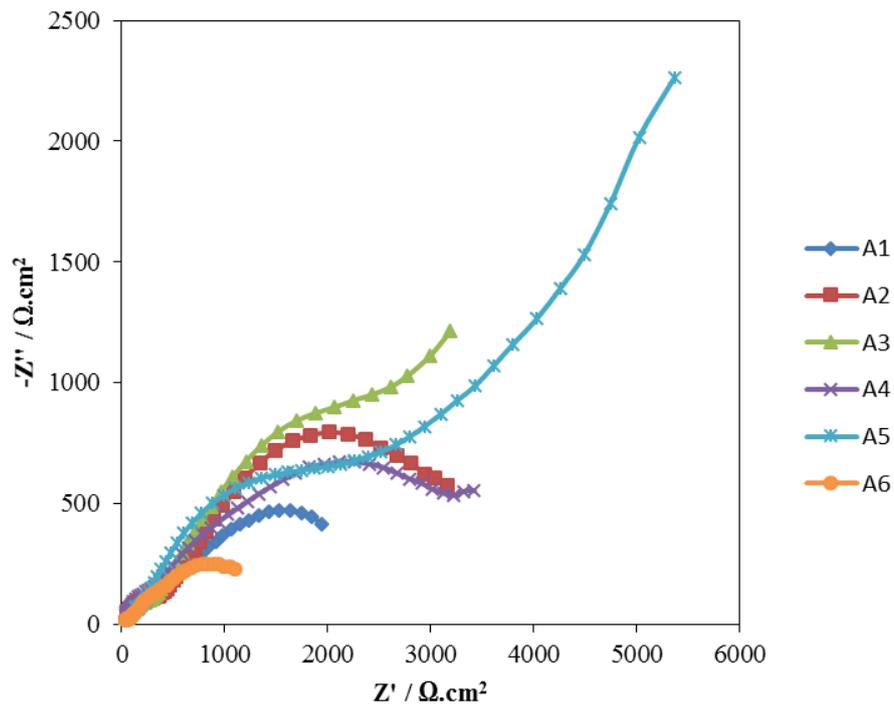


Figure 5
The Nyquist impedance diagrams of the samples with different SiO₂/K₂O molar ratios (A series) after 72-day exposure to the saline solution.

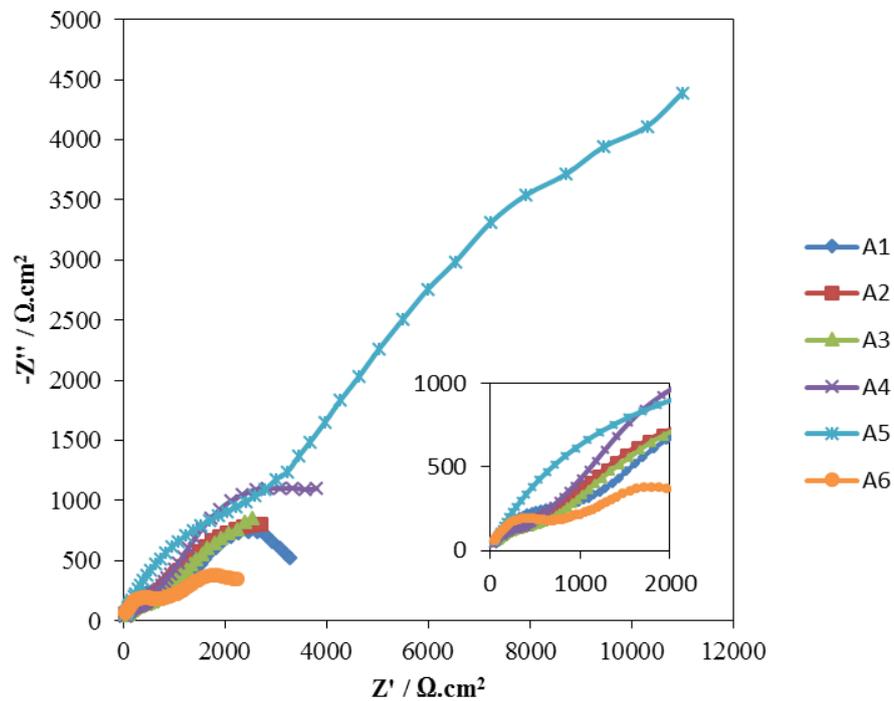


Figure 6
The Nyquist impedance diagrams of the samples with different SiO₂/K₂O molar ratios (A series) after 120-day exposure to the saline solution.

The Nyquist diagrams show one semicircle in short exposure times and the loop come to be smaller with increasing exposure time. Figures 1-3 correspond to the model shown in Figure 7a. After 28 days of immersion, the Nyquist plots show two capacitive loops related to two capacitive time constants; Figures 4-6 correspond to the model shown in Figure 7b. In Figure 7, R_s shows the NaCl solution resistance; the constant phase element (CPE_c) is related to the double layer capacity of the solution/coating interface responded at high frequency. CPE was applied rather than the “ideal” capacitance taking into consideration heterogeneous, roughness of the surface, and porous nature of the zinc-rich coatings. R_c represents the charge transfer resistance processes occurring within the pores of the coating; R_{ct} and CPE_{dl} show the resistance and the capacitance of substrate/coating interface in the range of low frequencies respectively. The first loop in the high frequency range is related to the coating properties and the second loop at lower frequencies represents the corrosion process, i.e. zinc dissolution process, (see Figures 4-6). The impedance reduction for the first few days is due to zinc particle activation, while the subsequent increase is due to a decrease in the active surface area caused by zinc depletion and zinc corrosion product accumulation in the pores of the coatings. Spectra depression is also ascribed to the porous nature of the coatings (Gervasi et al., 1994; Selvaraj et al., 1997). The EIS data were fitted using Zview and Zsim software packages.

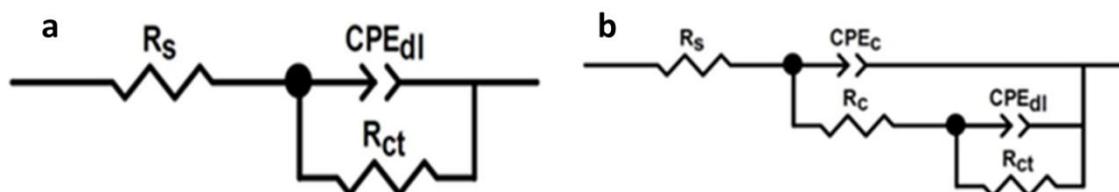


Figure 7

Equivalent circuits used for interpret impedance spectra of the samples with different $\text{SiO}_2/\text{K}_2\text{O}$ molar ratios (A series) at various immersion times: (a) short immersion times and (b) long immersion times.

Table 4 lists the EIS extracted parameters for A series. The results show that the charge transfer resistance of A5 (molar ratio of 5 $\text{SiO}_2:\text{K}_2\text{O}$) is higher than the others during immersion time and it shows better corrosion resistance than the others.

These results show that increasing the $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio in the range of 3.135 to 5 by the addition of nano- SiO_2 to the resins improves the corrosion resistance of the coatings; however, higher molar ratios decrease the corrosion resistance of the coatings indicating that $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio of the potassium silicate solution promotes the formation of more anticorrosive silicate coatings. The R_{ct} value of A5 is remarkably higher than the other samples, which may be attributed to the formation of a most compact interface layer in the silicate solution with $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio of 5. Moreover, the dissolution of zinc of A5 is suppressed and it shows the best corrosion performance.

3.2. Corrosion potential (E_{corr}) measurements

In order to study the electrochemical activity of the coatings and comparing the cathodic protection duration of samples, E_{corr} measurements were carried out. Figure 8 shows the variation in corrosion potentials during immersion time for different formulated samples exposed to saline solution. Variation of E_{corr} values related to the ratio of zinc to steel (active areas) (Abreu et al., 1996). According to the commonly accepted criterion for providing cathodic protection, E_{corr} value should remain below the -0.735 V (Ag/AgCl) equivalent to -0.780 V (SCE) (Feliu et al., 2001).

Table 4
Parameters obtained from the fittings of EIS spectra of A series.

Immersion time (days)	Coatings	R_s	R_{ct}	CPE_{dl-Q}	CPE_{dl-n}	R_c	CPE_c-C	CPE_c-n
1	A1	52.74	2846	0.00033652	0.61412			
	A2	25.52	8229	0.00073256	0.68551			
	A3	29.2	10959	0.00042122	0.71741			
	A4	26.19	5909	0.00054951	0.63017			
	A5	32.81	21246	0.00056231	0.65185			
	A6	24.76	11124	0.00059556	0.60316			
9	A1	27.57	179.4	0.0011917	0.66787			
	A2	28.05	697.7	0.0012531	0.60917			
	A3	26.64	847.8	0.00074	0.64635			
	A4	28.41	1237	0.001143	0.61325			
	A5	35.71	4942	0.00069996	0.62917			
	A6	37.81	394.2	0.0013587	0.57285			
28	A1	21.46	57.52	5.137E-7	0.8874	624.4	0.0004679	0.5161
	A2	22.6	92.94	1.212E-6	0.6943	829.1	0.001026	0.3505
	A3	23.7	301.1	6.906E-6	0.5792	1147	0.001008	0.3432
	A4	22.3	66.19	2.991E-5	0.4842	1420	0.0005916	0.4104
	A5	24.1	516.3	2.567E-5	0.4978	6104	0.000343	0.459
	A6	18.23	35.01	1.107E-7	0.8604	430.8	0.001203	0.4683
120	A1	26.3	1176	3.19E-5	0.4728	2963	0.0003782	0.5408
	A2	25.7	533.9	2.6E-5	0.4857	5263	0.0003737	0.3832
	A3	24.9	560.3	3.772E-5	0.4548	7150	0.0006613	0.3548
	A4	26.8	522.9	2.54E-5	0.5011	6011	0.0003427	0.4633
	A5	35.2	3085	1.877E-5	0.5211	2.198E4	0.0001647	0.4777
	A6	22.6	638.7	5.739E-6	0.587	2808	0.0005253	0.3267

In the A series, at first, the corrosion potential shifted anodically to positive values because of a reduction in Zn/Fe area ratio caused by wetting steel substrate with electrolyte penetration through the porous coating. Then, the corrosion potential decreased to reach values close to zinc corrosion potential in the solution. The active steel surface was entirely wetted; however, the zinc particles were activating due to reaction with the electrolyte so the Zn/Fe area ratio increased. The subsequent ennobling of potentials is attributed to the decrease in Zn/Fe area ratio caused by zinc corrosion and losing electrical contact between them. The sample with SiO₂:K₂O molar ratio of 5 has more steady and negative corrosion potential values than those measured for the other samples.

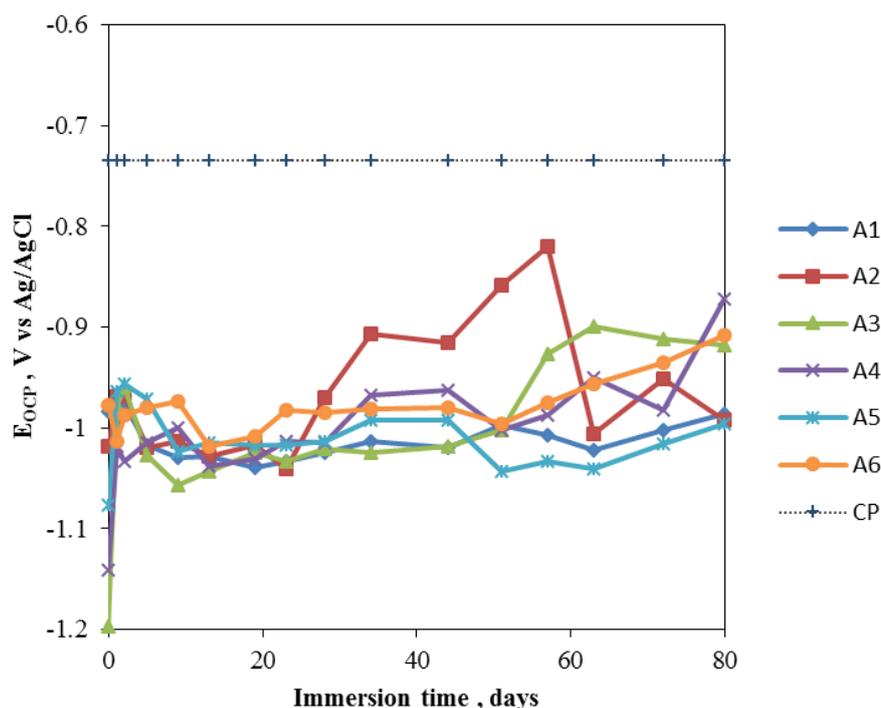


Figure 8

Variations of corrosion potential versus immersion time for samples with different $\text{SiO}_2/\text{K}_2\text{O}$ molar ratios (A series) during exposure to a 3.5 wt.% NaCl solution.

3.4. Adhesion measurement

The coating adhesion to the substrate was studied using the pull-off and cross cut testing methods by pull-off adhesion tester model 108 (Elcometer Corporation, UK) according to the ASTM D4541 type III and ASTM D 3359 respectively.

In the case of the pull-off adhesion test, before exposing the coated sample to corrosive environment, it was observed that all the coatings had such good adhesion to the substrate that the film did not detach from the substrate during increasing the applied force up to 18 MPa.

Table 5 tabulates the results of cross cut adhesion test; the B1 and C2 (modified) coatings have better adhesion to the substrate compared to the A5 (unmodified) coating. The modified potassium silicate vehicle contains acrylic derivatives that decrease the brittleness of the silicate coating and make adhesion better indirectly.

Table 5
Results of cross cut adhesion test.

Sample	B1	B2	B3	C1	C2	C3	A5
Grade	5B	4B	4B	3B	5B	4B	3B

3.5. SEM observation

To give an insight into the differentiation between the modified and unmodified vehicles (binders), scanning electron microscopy (SEM) was done. Figure 9 illustrates the SEM images of the samples. As can be seen, the zinc particles are compressed on the surface and there are a few cracks in the original coating surfaces. On the other hand, B1 and C2 have even fewer cracks and holes, which

proves the adhesion test results. These cracks are even more obvious in the unmodified coating and suppress corrosion resistance. This is due to the weak wetting characteristics of the resin and the inadequate dispersion of Zn pigments.

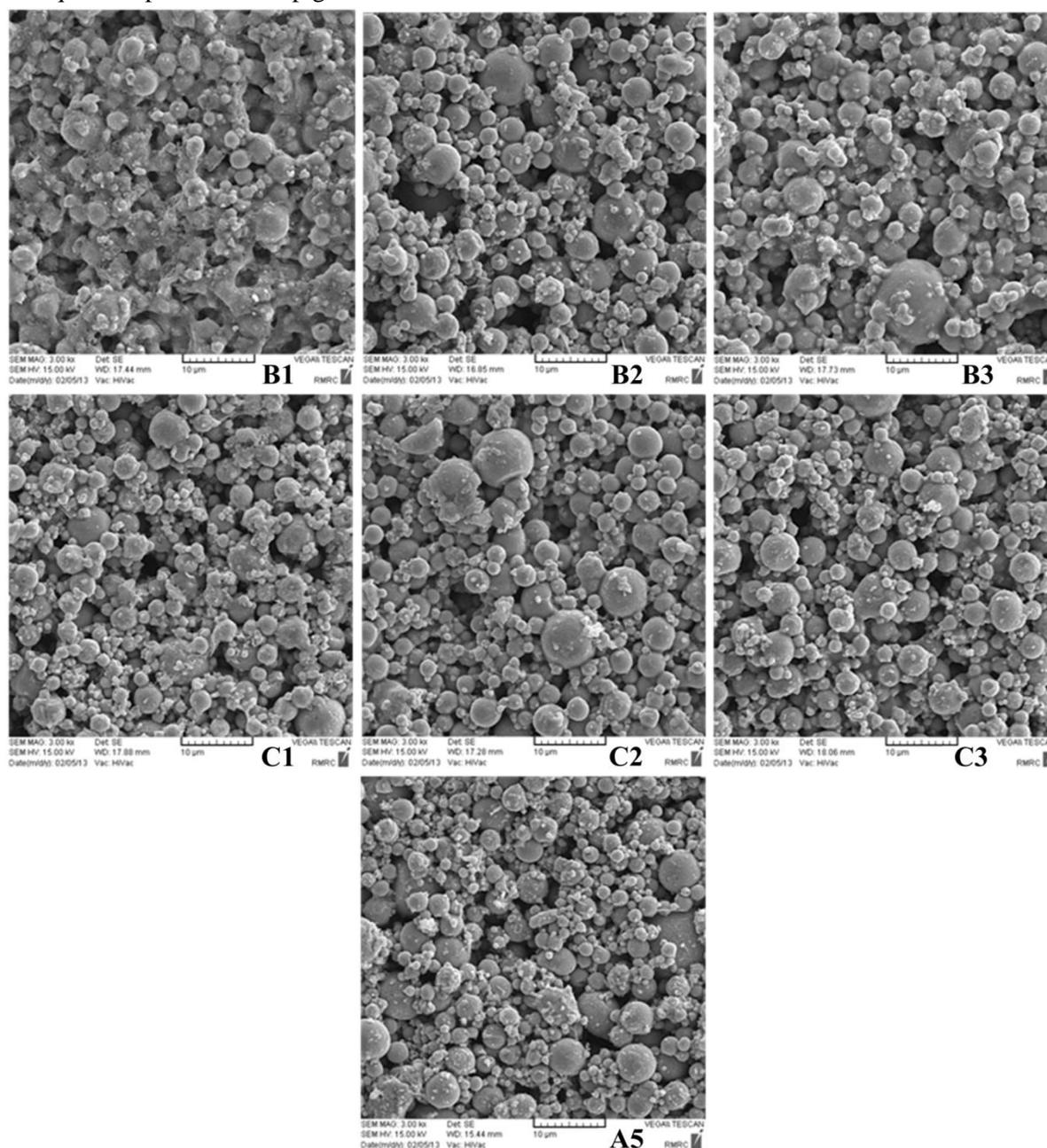


Figure 9
SEM images for the sample with a $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio of 5 (A5) and the samples modified by acrylic derivatives (B and C series) before exposure to a 3.5 wt.% NaCl solution.

5. Conclusions

The influence of the $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio of a potassium silicate solution on the electrochemical behavior of waterborne zinc-rich coatings was studied. Moreover, the addition of 5, 10, and 20 wt.% of acrylic and acrylic/styrene copolymers, as a binder modifier, to the formulation of these primers was evaluated. The motivation for performing this work was eliminating the weak wettability of

inorganic silicate binders. Electrochemical studies showed that increasing the SiO₂/K₂O molar ratio led to a better corrosion resistance due to the formation of a highly compact interface layer, increasing the shielding effect against the penetration of corrosives, and better cathodic protection.

The presence of water-based acrylic derivatives in the potassium silicate zinc-rich coating resulted in an improvement in the adhesion of the coating to the substrate and decreased the cracks and holes in the cured coatings.

Nomenclature

CPE	: Constant phase element
CPVC	: Critical pigment volume concentration
EIS	: Electrochemical impedance spectroscopy
PVC	: Pigment volume concentration
SEM	: Scanning electron microscopy
VOC	: Volatile organic compound

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