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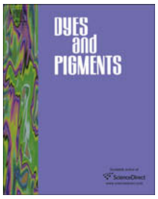

The inhibitive performance of polyphosphate-based anticorrosion pigments using electrochemical techniques

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ABSTRACT

Electrochemical impedance spectroscopy and linear polarization revealed the superiority of zinc aluminum polyphosphate compared to strontium aluminum polyphosphate. Film formation on the surface of steel samples was confirmed for both pigments through surface analysis. However, scanning electron microscopy and energy dispersive X-ray analysis showed that the composition and morphology of the precipitated layers were different for the two types of pigments.

1. Introduction

Applying organic coatings is considered as the approach most commonly employed to combat the corrosion of steel structures. To enhance protective performance of organic coatings especially when they undergo damage, anticorrosion pigments should be taken into consideration. Utilizing anticorrosion pigments is so crucial that there has been continued investigation in order to find the most effective compounds. Chromates, as one of the most efficient classes of anticorrosion pigments, have been extensively used for a long time. In fact, they belong to the group of inhibitors exhibiting excellent corrosion inhibitive performance. However, the same properties making these compounds superior corrosion inhibitors also make them dangerous. By virtue of increasing concerns for environmental protection and potential health hazard associated with chromates, their use is being restricted. The corrosion inhibition properties of numerous compounds have been examined through the years in the hope of providing effective chromate replacements [1–8]. So far, the classical alternative, zinc phosphate, has been widely used. However, a chasm between zinc phosphate and chromate pigments concerning the inhibitive performance makes physical and/or chemical modifications to zinc phosphate necessary. In this sense, anionic constituent as well as cationic part could be taken into account [2,9–11]. Polyphosphates composed of chains in which each phosphorus atom is linked to its neighbors through two oxygen atoms can be used as a substitute for simple phosphate anion. Thanks to higher phosphate content and also high chelate building potential with multivalent metal cations [12,13], the polyphosphates appear to exhibit better inhibitive performance compared to orthophosphates [14]. Moreover, it has been found that polyphosphates have sufficient water solubility to provide corrosion inhibition [9,10,15]. Their inhibition mechanism has been described by migration of the positively charged complexes, formed in the presence of metallic cations, to the cathode leading to a protective film precipitated on the surface through a process of electrodeposition [12,16–18]. In case of the cationic part, combination of various polyvalent metals has been suggested [11].

Since corrosion is an electrochemical process, evaluation of anticorrosion behavior of various systems using electrochemical techniques could provide valuable data. Electrochemical impedance spectroscopy (EIS) as a powerful non-destructive test is capable of obtaining significant quantitative and qualitative data. This technique is widely used to study effective parameters in association with corrosion process as well as different approaches for protecting metallic structures against corrosion [19–22]. Taking advantage of EIS, inhibitive performance of anticorrosion pigments could be studied [5,23,24]. In order to interpret impedance spectra, the data should be modeled by the proper equivalent circuits. As suggested elsewhere, employing EIS along with other

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Table 1
Composition of steel panels

Elements	Fe	C	Si	Mn	P	S	Cr	Mo	Co	Cu	Nb
wt %	97.7	0.19	0.415	1.39	<0.0050	<0.0050	0.026	0.018	0.0559	0.0429	0.0481

Table 2
Technical data for employed pigments

Pigment	Trade Mark	Zinc (%)	Phosphorus (%)		Aluminum (%)	Strontium (%)	Loss on ignition 600 °C (%)	Density (g/cm^3)	Average particle size (μm)
			As P_2O_5	As PO_4					
Zinc orthophosphate hydrate	Zinc phosphate ZP 10	50.5–52	–	47–49	–	–	8.5–13	3.7	2–3.5
Zinc aluminum polyphosphate	HEUCOPHOS ZAPP	28–31	46–49	–	11–13	–	8–12	3.1	2–3.5
Strontium aluminum polyphosphate	HEUCOPHOS SAPP	–	43.5–48	–	10.5–13.5	23.5–30	9.5–15	2.9	2–3.5

electrochemical tests may lead to more reliable interpretation and taking out much more information [25].

Study of corrosion behavior of the bare metal immersed in inhibitor compounds extracts is the concept employed in this work in order to have a better understanding of performance of polyphosphate-based anticorrosion pigments. Taking advantage of electrochemical tests, i.e. linear polarization and electrochemical impedance spectroscopy, as well as surface analysis, the effect of

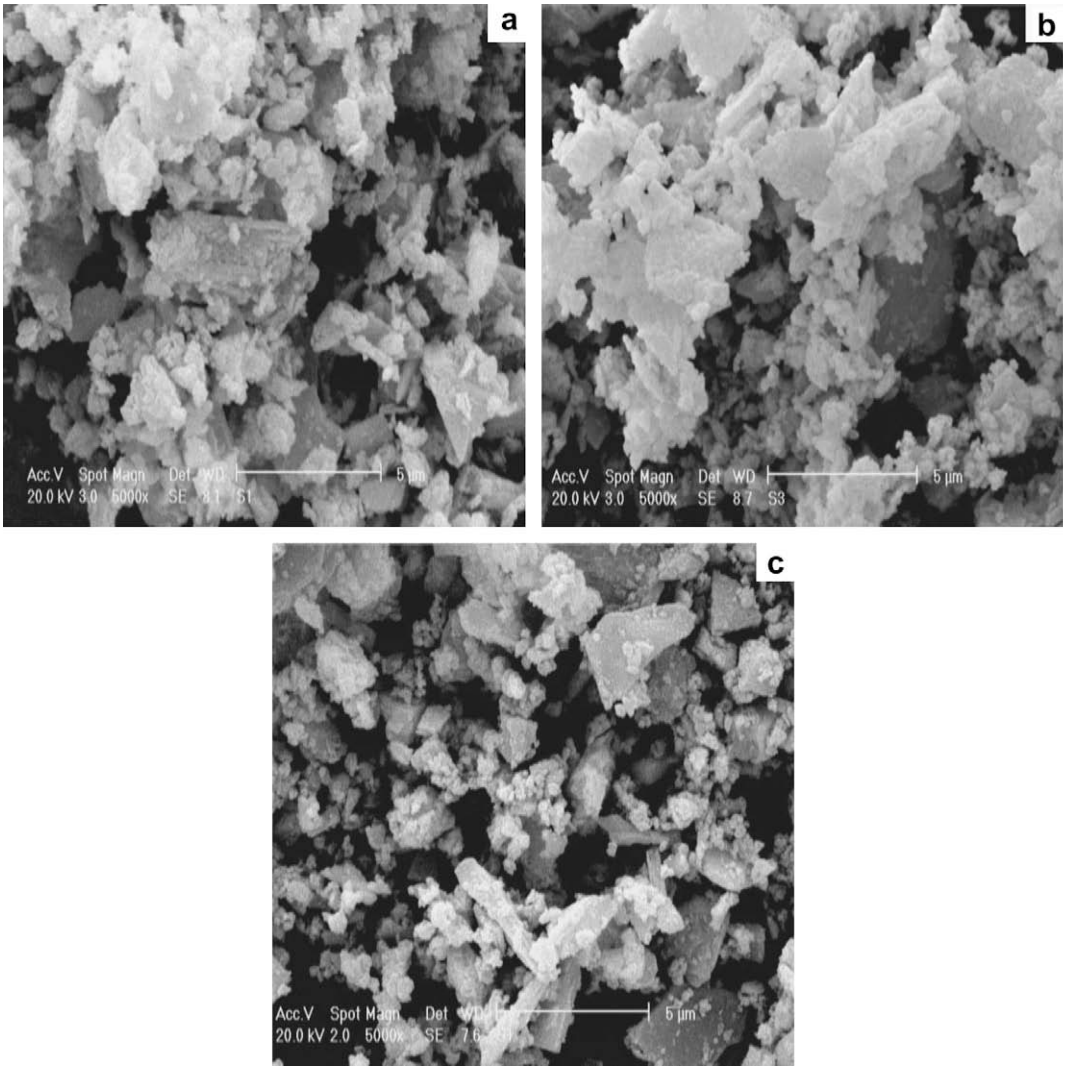

Fig. 1. SEM images for (a) SAPP powder, (b) ZAPP powder and (c) ZP powder.

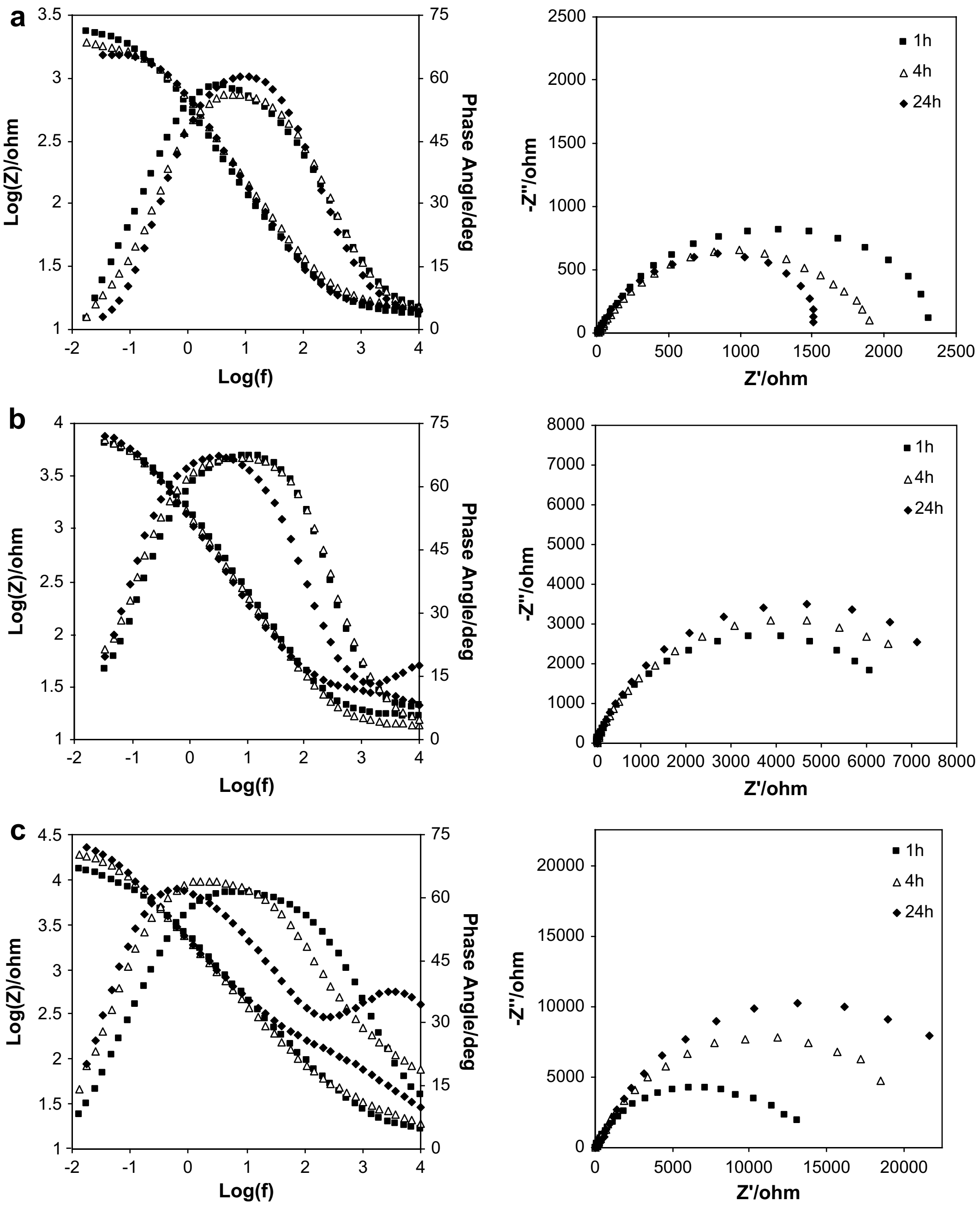

Fig. 2. Nyquist and Bode diagrams for carbon steel after 1, 4 and 24 h of immersion in 3.5% NaCl solution containing (a) ZP extract, (b) SAPP extract and (c) ZAPP extract.

different cations incorporated into the composition of the modified anticorrosion pigments is evaluated.

2. Experimental

Table 1 shows the composition of steel panels used for different tests. Polished steel specimens, with dimensions of 3 cm × 3 cm × 0.7 cm, were degreased by acetone. In order to seal the edges and back sides of the steel panels, they were covered by a mixture of beeswax and colophony resin, leaving the apparent geometrical area of 1 cm^2 unmasked.

2.1. Pigment extract preparation

The commercial grade anticorrosion pigments selected for this study were of three types, namely, zinc phosphate, zinc aluminum polyphosphate and strontium aluminum polyphosphate known under the trade marks ZP, ZAPP and SAPP, respectively. Some of technical data for the pigments published by supplier (Heubach Ltd.) are summarized in Table 2. SEM images for pigment powders are depicted in Fig. 1. In order to prepare extracts, 2 g of each pigment was stirred in 1 l 3.5% w/w NaCl aqueous solution for 24 h then filtered. Solubility (g/l) obtained for ZP, ZAPP and SAPP was 0.15, 0.28 and 0.41, respectively.

2.2. Electrochemical tests

The electrochemical cell with a three-electrode configuration including Ag/AgCl reference electrode (RE), steel panels as the working electrode (WE) and platinum counter electrode (CE) was used to run the tests. Each test was conducted using three replicate panels to ensure repeatability.

The impedance measurements were carried out using a sine wave of 10 mV amplitude peak to peak at the open circuit potential, E_{corr}. The frequency range was from 10 kHz down to 10 mHz. The working, counter and reference electrodes were connected to the terminals of an Autolab instrument model PGSTAT12. Data analysis was made using FRA software.

Likewise, a PGSTAT12 was employed to obtain polarization curves at scan rate of 1 mV/s. GPES software was used to analyze data.

The tests were conducted as a function of immersion time, namely after 1, 4 and 24 h, to indicate how electrochemical parameters varied depending upon the immersion period.

2.3. Surface analysis

The morphology of the film formed on the surface and the composition of the deposition were studied after 24 h by scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX).

3. Results and discussion

3.1. EIS measurements

Fig. 2 displays Nyquist and Bode plots of specimens after immersion in 3.5% NaCl solution containing ZP, SAPP and ZAPP extracts for 1, 4 and 24 h. Considering the plots with one relaxation time for ZP, the relevant spectra could be modeled by the equivalent circuit shown in Fig. 3a where R_s represents solution resistance, R_{ct} charge transfer resistance and C_{dl} double layer capacitance. In the case of ZAPP and SAPP, diagrams revealed quite different behavior. The circuit depicted in Fig. 3a is used to simulate spectra obtained after 1 and 4 h of immersion due to appearance of one relaxation time. However, two relaxation processes were distinguished after 24 h, especially from the Bode diagrams. To model the mentioned behavior, the circuit displayed in Fig. 3b, where R_f and C_f represent parameters concerning the film possibly formed on the surface was employed.

From Fig. 4 showing charge transfer resistance values of the samples in the test solutions, it is evident that the steel samples exposed to modified pigment extracts yielded higher charge transfer resistance values compared to ZP. One can detect two distinct patterns for R_{ct} parameters. The first associated with ZP declined steadily as time progresses whereas a reverse trend could be identified in terms of ZAPP. A similar trend was observed for samples that came into contact with aqueous extract of SAPP but the order of magnitude of results was lower in comparison with ZAPP.

Basically, it is important to note that the polyphosphate-based anticorrosion pigments' performance revealed the success of the zinc phosphate modification. Zinc phosphate inhibitive properties compared to ZAPP and SAPP characterized by increased solubility and also higher phosphate content were negligible. These parameters facilitate a much more inhibiting species to be released into solution, increasing the opportunity for the exposed surface to be inhibited. In other words, by taking an anticorrosion

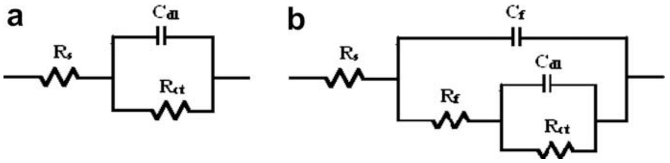

Fig. 3. Equivalent circuit to model behavior of steel samples exposed to (a) ZP extract (for all immersion periods) as well as ZAPP and SAPP extracts (after 1 and 4 h of immersion) and (b) ZAPP and SAPP extracts after 24 h of immersion, where R_s represents solution resistance, R_{ct}, the charge transfer resistance, C_{dl}, the double layer capacitance, R_f, the precipitated layer resistance and C_f, the precipitated layer capacitance.

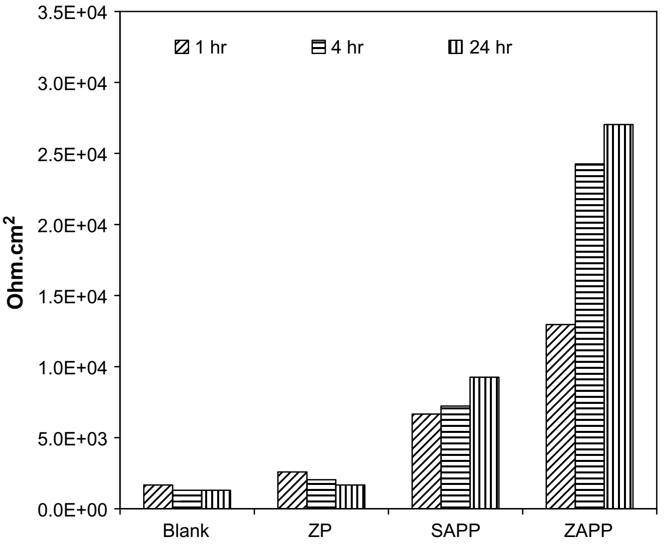

Fig. 4. Charge transfer resistance (R_{ct}) evolution in the presence of ZAPP and SAPP.

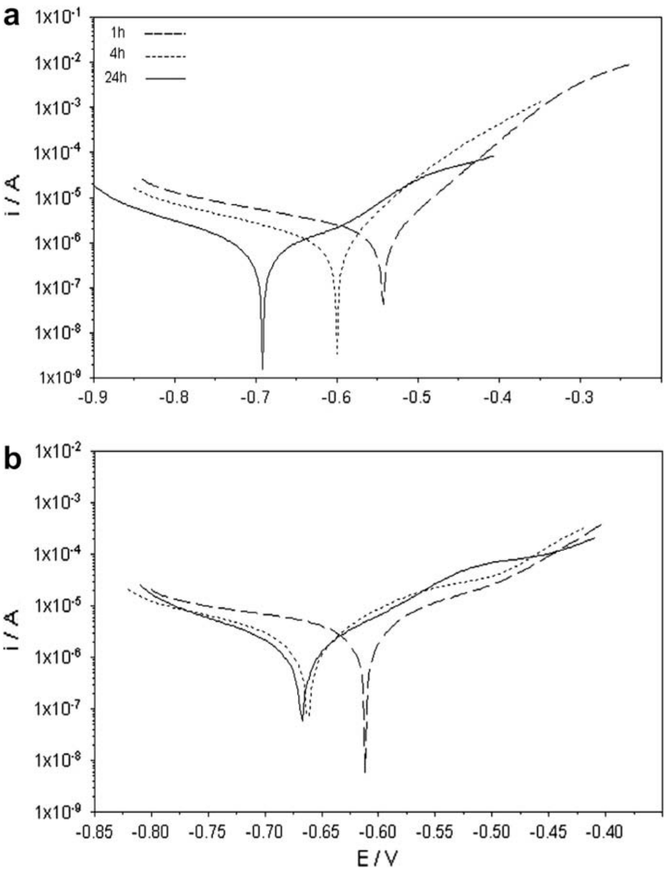

Fig. 5. Polarization curves of steel samples after 1, 4 and 24 h immersion in 3.5% NaCl solution containing (a) ZAPP extract and (b) SAPP extract.

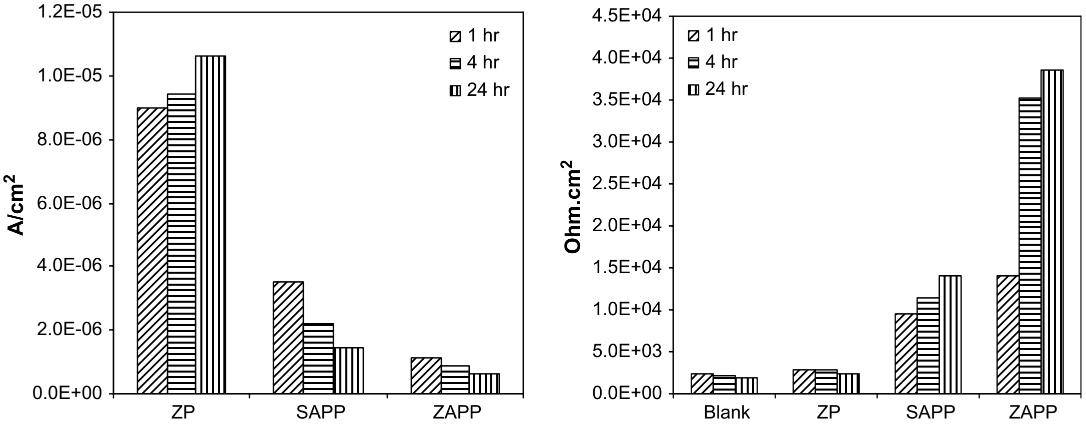

Fig. 6. Influence of ZAPP, SAPP and ZP presence on polarization resistance (right) and corrosion current density (left).

pigment into consideration as a reservoir, solubility can play the role of a discharge valve making the inhibitor species kinetically available [1]. Concerning charge transfer resistance values of modified pigments, the upward trend is a reflection of the fact that corrosion inhibition characteristics were enhanced as time elapsed. Consequently, resistance values within exposure as well as spectra appearance after 24 h comprised two relaxation times could be attributed to the possibility of developing a precipitate on the surface of the steel samples immersed in the solutions containing ZAPP and SAPP extracts. Therefore, access of the aggressive species to the steel surface could be restricted. In addition, from a visual point of view, no signs of corrosion were observed in the presence of ZAPP and SAPP extracts, whereas some corrosion spots were clearly seen on the surface of samples exposed to ZP extract.

Comparing the performance of the two modified pigments, EIS data showed that the presence of zinc in conjunction with polyphosphate provided inhibitive properties greater than those obtained in the absence of Zn ion. One should not forget that zinc ions alone can make a major contribution to corrosion inhibition. Furthermore, the presence of zinc markedly accelerates the establishment of a protective film and also film repair [12].

3.2. Polarization measurements

Fig. 5 compares the polarization test results for the samples dipped into ZAPP and SAPP extracts. Polarization curves illustrate the significant effect of ZAPP and SAPP addition on cathodic branches. As can be seen from the plots, both extracts cathodically polarize the steel samples during the exposure time. However, polarization in the presence of ZAPP is more noticeable. In general, formation of a deposit on cathodic areas could be responsible for cathodic polarization. The graphs in Fig. 6 show the corrosion kinetic parameters extracted from the curves in Fig. 5. From comparative data displayed in Fig. 6, it is evident that the results of polarization tests were consistent with those of impedance measurements in which the modified pigments show superior performance in comparison with zinc phosphate. In the presence of ZAPP and SAPP, current density exhibited a steady drop until the end of the experiments, while a reverse trend in respect of polarization resistance (R_p) was met. As a general rule, the rate of development of the protective film on the metal surfaces is influenced by the rate of supplying orthophosphate as well as polyphosphate to the metal surface. Since the rate of introducing the inhibitor to the metal surface under quiescent conditions is primarily dependent upon diffusion which is a slow process, formation of the barrier layer is slow in stagnant extracts [17]. This might lead to a continued decrease in corrosion current when the steel samples are exposed to modified pigment extracts.

Table 3
Corrosion inhibition efficiencies (IE) for polyphosphate-based anticorrosion pigment extracts

IE (%)	1 h	4 h	24 h
ZAPP	87.1	94.4	95.4
SAPP	75.5	80.3	86.6

Table 3 shows corrosion inhibition efficiencies (IE) for polyphosphate-based pigment extracts after 1, 4 and 24 h. From the polarization curves, inhibition efficiencies were calculated in accordance with the equation [$\mathrm{IE} = (R_p - R^0_p)/R_p$] where R_p and R^0_p are polarization resistance of steel samples immersed into 3.5% w/w NaCl aqueous solution with and without pigment extracts, respectively. According to the inhibition efficiencies, inclusion of zinc in the polyphosphate-based anticorrosion pigment composition results in an improved inhibitive action.

3.3. Surface analysis

Evidence provided by SEM confirmed the inferences made in Sections 3.1 and 3.2 relating to film formation. Based on the SEM results, the surfaces exposed to solutions containing ZAPP and SAPP extracts were covered by films with the morphologies presented in Fig. 7. Predominant presence of aluminum, phosphorous, zinc and strontium on the immersed surfaces was confirmed. The composition of the detected layers obtained by EDX was mainly [Fe (83%), Zn (10%), P (2.8%) and Al (0.5%)] and [Fe (92.7%), Sr (4.2%), P (2.68%) and Al (0.39%)] for ZAPP and SAPP, respectively. In contrast, no film was detected in case of ZP and scattered corrosion products were only observed on the surface.

4. Conclusion

The effect of different cations incorporated into the composition of polyphosphate-based anticorrosion pigments as different forms of the zinc phosphate modification was assessed through electrochemical tests as well as surface analysis. According to the results of EIS and polarization measurements, the modified pigments, i.e. ZAPP and SAPP, revealed greater inhibitive properties compared to conventional zinc phosphate. They appeared to act through

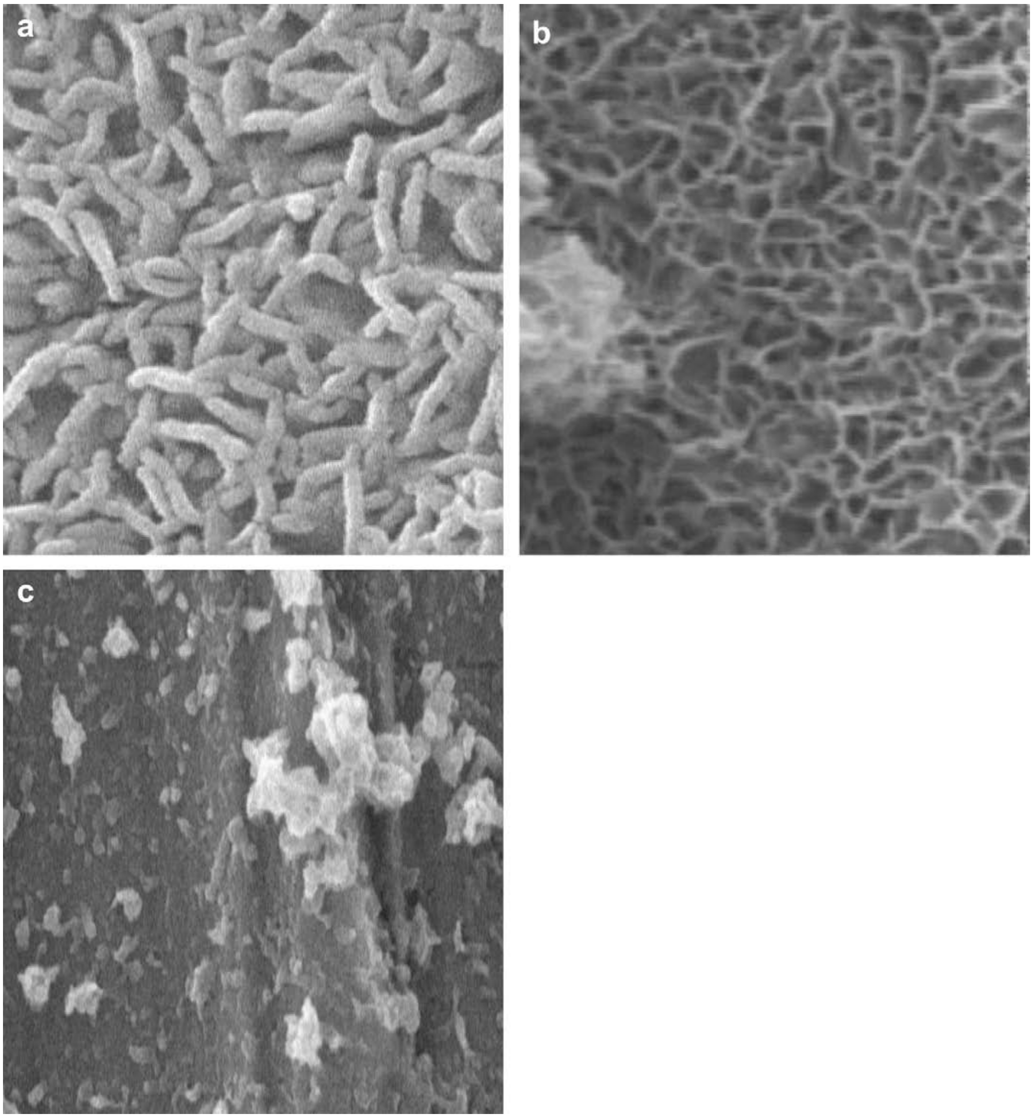

Fig. 7. Morphology of the surface of steel samples exposed to (a) ZAPP, (b) SAPP (Magn.15,000×) and (c) ZP (Magn.10,000×) detected by SEM after 24 h of immersion.

precipitation of a layer on the surface of the samples, supported by SEM/EDX results. Regarding results obtained for modified pigments, the zinc cation played a significant role in inhibitive characteristics, meaning ZAPP exhibited more effective anticorrosion performance.

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