Investigation of Corrosion Resistance and Surface roughness of Carbon Steel Treated with Zinc Phosphate Coating in saline water

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ABSTRACT

Carbon steel is widely used in industrial applications due to its mechanical properties and high availability. In order to improve its corrosion resistance and promote better adhesion between metal surfaces and subsequent treatments, zinc phosphate conversion coating is commonly used for surface pretreatment in various industries.

In this study, two zinc phosphating solutions were prepared and carbon steel samples were treated with these solutions at a temperature of 90 °C. The solutions contained nitric acid, zinc oxide, phosphoric acid, and sodium carbonate. Nickel carbonate was added to the solution to create different zinc phosphate layers on the surface of the carbon steel samples.

The research focused on evaluating the corrosion resistance and surface roughness of the samples before and after exposure to corrosive media . Potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy techniques (EIS) were used for evaluation. Additionally, the surface properties, specifically surface roughness, were assessed using scanning electron microscopy (SEM) after exposure to seawater with 3.5% sodium chloride NaCl

The SEM analysis revealed the impact of the corrosive solutions on the zinc phosphate coating layer. In the presence of 3.5% NaCl solution, the coating dissolved, exposing the carbon steel surface and leading to localized corrosion with pits. This resulted in a rough surface with deposited pitting corrosion products. Furthermore, incorporating nickel carbonate in the treatment of carbon steel significantly improved its corrosion resistance.

In summary, this study demonstrated that the addition of nickel carbonate effectively enhanced the corrosion resistance of carbon steel samples treated with zinc phosphate coating. The evaluation was performed using potentiodynamic polarization, electrochemical impedance spectroscopy, and surface roughness analysis. These findings contribute to the understanding of surface pretreatment methods for improving the performance and durability of carbon steel in various industrial applications.

Keywords: carbon steel corrosion, pitting corrosion , surface roughness, phosphate coating ,

1. INTRODUCTION

Corrosion poses a significant challenge to industries today, with costs comparable to those of natural disasters such as floods, tornadoes, and earthquakes [1]. Considering the effects of corrosion on the lifespan of equipment is crucial in industrial designs. Failure to do so can result in catastrophic losses amounting to billions of dollars [2]. Corrosion occurs due to chemical or electrochemical reactions between a metal and its environment, which can have adverse effects on the properties of the metal [3]. There are two main reasons why corrosion is of utmost importance: economics and safety [4]. Direct losses include the cost of replacing corroded structures, while indirect losses involve efficiency loss, product contamination, environmental pollution, and work shutdown. Hence, economic factors serve as significant motivators for corrosion research [5].

Corrosion inhibitors play a crucial role in reducing the corrosion rate and protecting metals and alloys from deterioration. They create a protective barrier that isolates the metal from its environment [6-8].

Corrosion inhibitors are considered the first line of defences against corrosion [9]. These inhibitors can be classified based on their chemical nature, such as organic or inorganic coatings [10]

Phosphate conversion coating, which is known as phosphating, is a chemical process that involves depositing a layer of insoluble metal phosphates onto the surface of a metal substrate. Typically, this process includes immersing the metal part in a solution containing phosphate ions that react with the metal surface to form an insoluble layer of metal phosphate [11]. This layer provides corrosion protection resistance and enhances the adhesion of subsequently applied coatings, such as paint or powder coatings [12]. Phosphate conversion coatings are commonly used in industries such as automotive, aerospace, and military to enhance the durability and performance of metal parts[13] . Phosphating can be easily applied to various metals like steel [14], aluminium [15], galvanized steel [16], and magnesium. [17]

The corrosion resistance of phosphate coatings depends on various factors, including the coating thickness, surface roughness, and the composition of the surrounding environment. In aqueous media, corrosion can occur due to the presence of dissolved oxygen, chloride ions, and other corrosive agents. However, phosphate coatings can act as a barrier to prevent the diffusion of these agents into the metal substrate, thereby reducing the corrosion rate [18-19].

Surface roughness is an important factor that affects the adhesion and performance of coatings [20]. In the case of phosphate coatings, surface roughness can influence the coating thickness, uniformity, as well as the surface texture and topography [21]. Moreover, the surface roughness of the substrate can impact the adhesion of the coating, as a rough surface provides more mechanical interlocking sites for the coating to adhere to [22].

The present study is an attempt to evaluate the corrosion resistance and surface properties of carbon steel coated with phosphate in saline water is crucial for understanding the performance and durability of coated materials in practical applications. By comprehending the factors that influence the corrosion resistance and surface roughness of phosphate coatings, researchers can develop new coating formulations and optimization techniques to enhance the performance of coated materials in corrosive environments.

2. EXPERIMENTAL PROCEDURES

2.1. Material

The samples used in this study are Carbon steel plates with the following dimension (2mm*10mm*10mm) .The chemical composition of the studied Carbon steel samples shown in the table 1.

Table 1. chemical composition of Carbon steel sample

Element	**Fe**	**Mo**	**Cu**	**Mn**	**Cr**	**Si**	**C**	**other**
Weight%	**98.5042**	**0.2480**	**0.0332**	**0.5751**	**0.0237**	**0.2465**	**0.3535**	

2.2. Sampling configuration

2.2.1 The Samples were a braded in sequence on (220 , 400 , 600 , 1000) grades, Then the samples was drilled in to (1.5mm) diameter hole for the structural solution as well as the base of electrochemical cell.

2.2.2 The specimens underwent a series of cleaning steps. First, they were washed with tap water, then with distilled water, then subjected to alkaline etching using a Sodium Hydroxide solution with a concentration of 5wt % , then etching by 10% concertation HCl solution , the specimens were rinsed again with distilled water.

2.2.3 Phosphate coating samples

The Zinc Phosphate layer to cover the surface of Carbon steel specimen was performed by Phosphate acid , Zinc oxide , Nitric oxide and Sodium carbonates shown in Table 2 .

The surface of the sample were prepared by immersing them for (10 min) in an alkaline degreasing solution (solution temperature 80 C°) , after which they were immersed for (5min) in acid picking solution (at room temperature) .Thus the samples were immersed in the Phosphate bath solution for (10min) at temperature (90) ± 2C° .

At the end of Phosphate process , the samples were dried in distilled water at (90-95) C° then dry by hot air .

Table 2 the Zinc Phosphate bath Carbon steel samples

composition	**ST1**	**ST2**
H_3PO_4	**400 ml**	**400 ml**
ZnO	**160 g**	**160 g**
HNO_3	**142 ml**	**142 ml**
$NaPO_4$	**3 g**	**3 g**
$NiCO_3$	**------**	**3 g**

Where :

ST1 steel phosphating without nickel carbonate.

ST2 steel phosphating with nickel carbonate.

ST steel without coating .

2.3. Experimental Sets

2.3.1. Electrochemical polarization (Tafel) :

The corrosion current density (icorr) is a kinetic parameter which represents the rate of corrosion under specified equilibrium condition. The rate of corrosion (CR mm/y) in a given environment is directly proportional with its corrosion current density (icorr) as follows.

CR (mm/y) =3.27× Icorr. e/ρ Where:

CR: Corrosion rate (mm/y)

Icorr : Corrosion current density μA/cm^2.

e : Equivalent weight (atomic weight / valance).

ρ: Density of metal g/cm^3.[24]

and the efficiency calculated by formula:

PE% = ((CR0 – CR) / CR0) x 100) [25].

Figures 1,2 and 3. illustrate that the corrosion rates for ST, ST1 and ST2 .The results demonstrate that depositing a phosphate layer on steel surface can improve its corrosion resistance , phosphate coatings create an insoluble crystalline layer that reacts chemically with the surface to provide a protection layer.

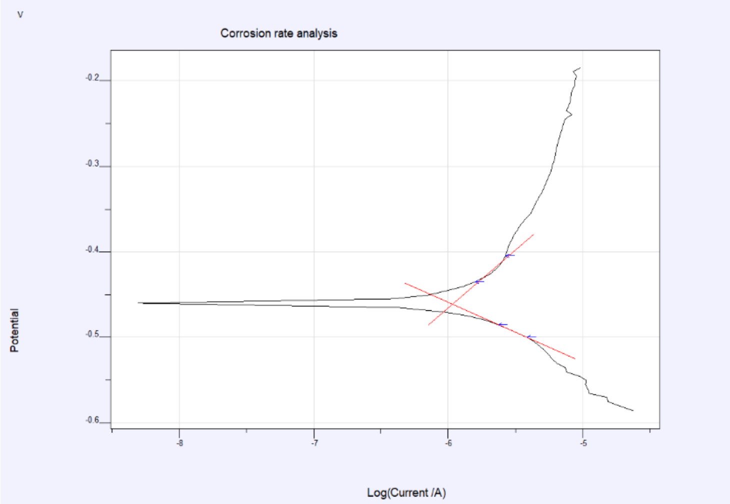


Fig 1. polarization curves of ST in 3.5% NaCl solution

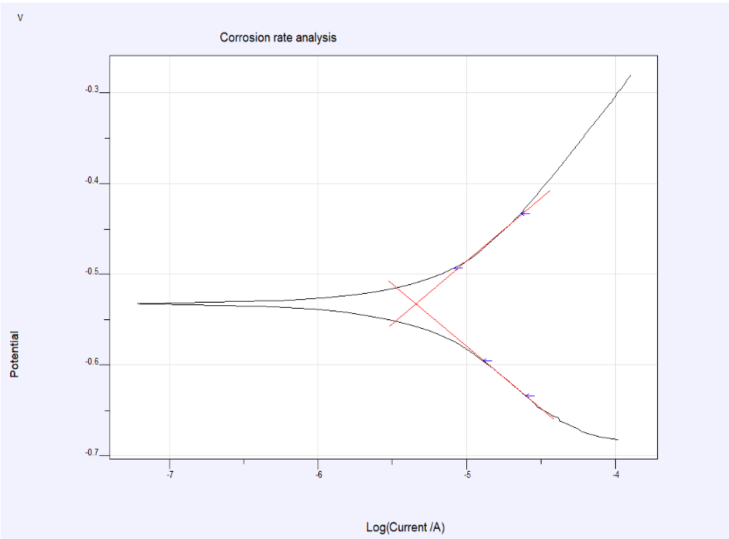


Fig 2. polarization curves of ST1in 3.5% NaCl solution.

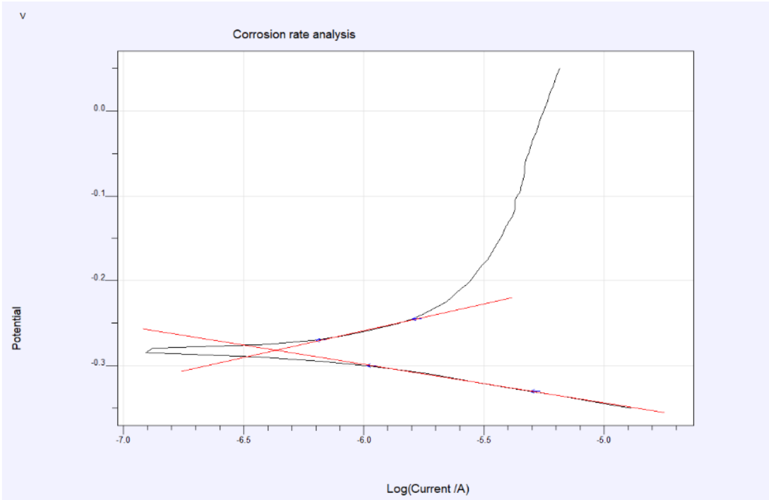


Fig 3. polarization curves of ST2 in 3.5% NaCl solution.

Table 3. show that zinc phosphate coating reduces the corrosion current density (icorr) of ST1 and ST2 coatings. These results indicate that zinc phosphate coating greatly enhances corrosion resistance, with 76.24% for ST1 and 90.44 % for ST2 in a 3.5% NaCl solution, the zinc phosphate coating effectively isolates the metal surface in a corrosive NaCl environment.

Table 3. parameters for ST, ST1 and ST2 in 3.5% NaCl solution.

sample	T (k)	$-E_{corr}$ (mV)	I_{corr}	B_c (mV/dec)	B_a (mV/dec)	C.R (mm/y)	R_P(Ω/cm^2)	PE%
ST	**300**	**532**	**0.01858**	**137**	**138**	**0.05267**	**6589**	
ST1	**300**	**461**	**0.001077**	**71**	**135**	**0.01251**	**18690**	**76.24 %**
ST2	**300**	**282**	**0.000433**	**45**	**63**	**0.00503**	**26470**	**90.44 %**

These measurements were performed to investigate the effected of zinc phosphate coatings ST2, on corrosion resistance in a 3.5% NaCl solution, as compared to uncoated sample ST and ST1.

The corrosion current of the samples decreased as shown in the table and the corrosion rates for ST, ST1 and ST2 were **0.05267** mm/y , **0.01251** mm/y and **0.00503** mm/y respectively .These results indicate that zinc phosphate coating, especially ST2, greatly enhances corrosion resistance, with **76.24%** protection efficiency for ST1 and **90.44 %** for ST2 in a 3.5% NaCl solution, the zinc phosphate coating effectively isolates the metal surface in a corrosive NaCl environment.

2.3.2. **Electrochemical Impedance in aqueous media**

Electrochemical impedance spectroscopy (EIS) used to study the corrosion behaviour of steel in 3.5 % NaCl solution.

Fig 4 to 6. the result were as following in 3.5%NaCl solution immersion along 15 minute for two sample ST, ST1 and ST2 as follows

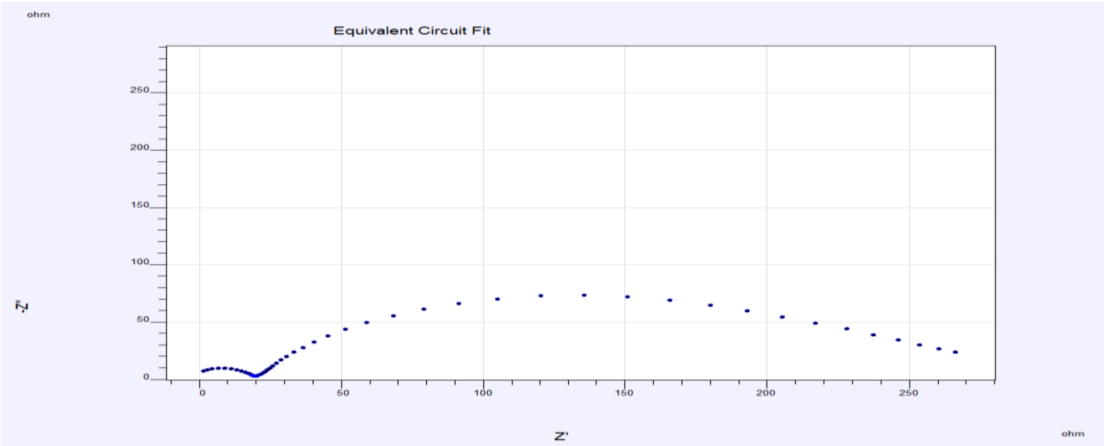


Fig 4. Nyquist of ST in NaCl solution

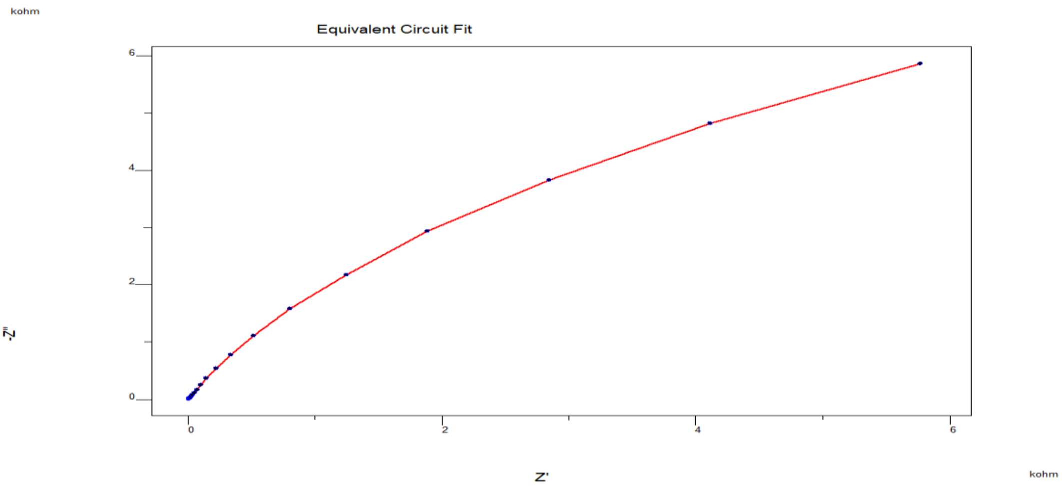


Fig 5. Nyquist of ST1 in NaCl solution

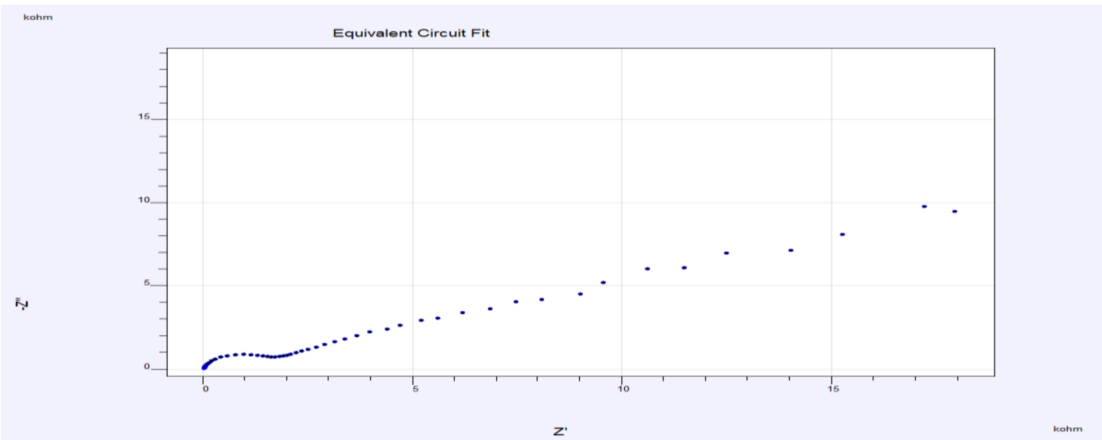


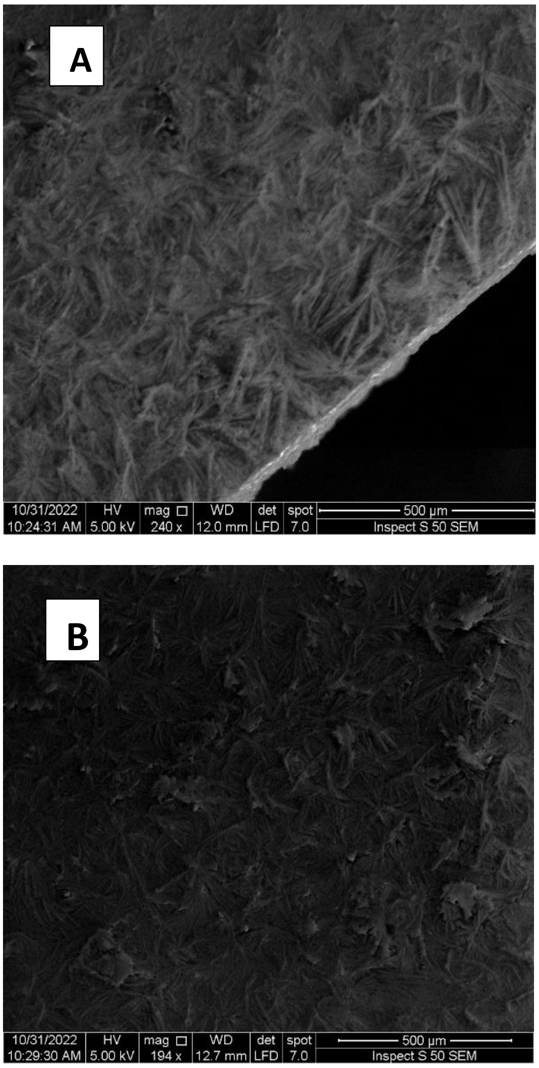
Fig 6. Nyquist of ST2 in NaCl solution

In the Nyquist plots obtained from the EIS measurements, it is evident that ST2 exhibits superior corrosion resistance compared to ST and ST1 in a NaCl solution. This is indicated by the fact that ST2 shows a higher impedance value than another samples .

2.4. surface properties effected by corrosive solution.

The surface roughness and morphology of carbon steel coatings treated with zinc phosphate were investigated specifically for ST2, as it demonstrated higher corrosion resistance compared to ST1 when immersed in a corrosive solution. The surface analysis was conducted using various techniques, including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM).

Scanning microscopy analysis fig 7. revealed that the protective coating on the steel surface was compact, well crystallized, and provided complete coverage. The coating layer appeared homogeneous, with a uniform grey colour. The coating demonstrated a large surface area, indicating effective overlapping at the microscopic level. This resulted in a layer composed of numerous small needle-shaped crystals.



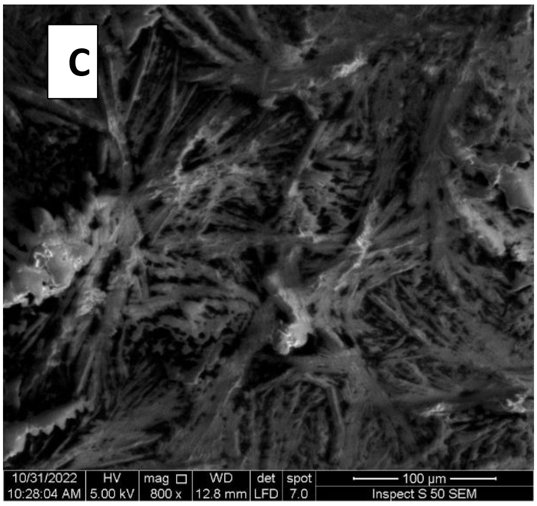


Fig 7. a , b and c SEM images for the ST2 before immersion in NaCl solution.

The energy dispersive spectroscopy (EDS) spectra of the phosphate layer are also presented in table **4** the EDS analysis on the phosphate show that the layer contain mainly iron , zinc and phosphate , the high peak of iron is mainly due to the metallic substrate. the EDS analysis of the zinc phosphate coating layer on carbon steel shows the presence of zinc, phosphorous, oxygen, and possibly carbon and iron from the underlying steel substrate , the EDS spectrum show distinct peaks for each element, with the intensity of each peak indicating the relative concentration of the element.

Table 4 . The EDS of ST2 sample before immersion.

Element	weight	Atomic%	Error %
O	32.61	58.62	1.71
P	16.57	17.60	0.01
Zn	44.18	21.43	0.32
Fe	6.64	2.35	2.23

Fig **8 to 10** illustrate AFM analysis information about the surface roughness and topography of the zinc phosphate coating before immersion in corrosion media

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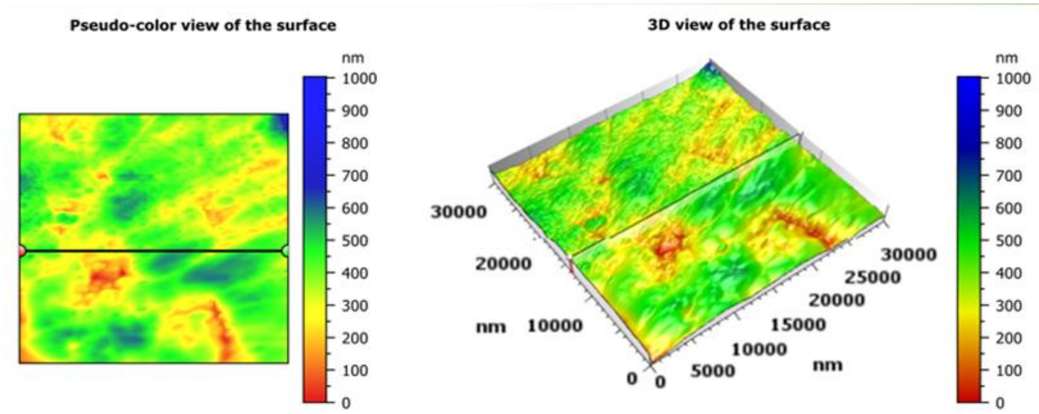
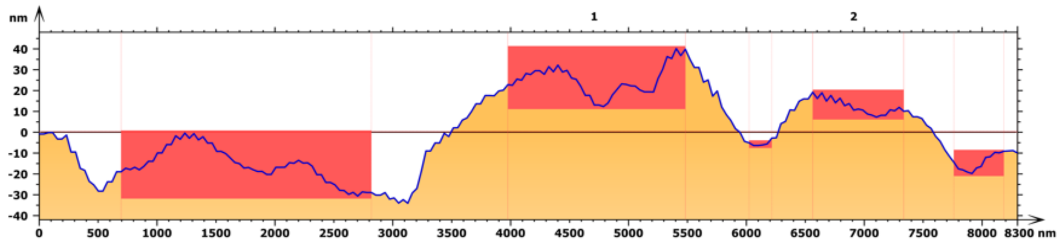


ISO 21920 - Roughness (S-L)				
S-filter (λs): None				
F: [Workflow] Leveled (LS-line)				
L-filter (λc): Gaussian, 0.0295 mm, Ends not cut				
Evaluation length: All λc (1)				
Height parameters				
Rq	80.60	nm		*Root mean square height*
Rsk	1.033			*Skewness*
Rku	10.91			*Kurtosis*
Rt	746.5	nm		*Total height*
Rpt	125.4	nm	*Max of values on: All λc (1)*	*Maximum hill height*
Rp	125.4	nm	*Average of values on: All λc (1)*	*Mean hill height*
Rvt	184.8	nm	*Max of values on: All λc (1)*	*Maximum dale depth*
Rv	184.8	nm	*Average of values on: All λc (1)*	*Mean dale depth*
Rzx	310.3	nm	*Max of values on: All λc (1)*	*Maximum height*
Rz	310.3	nm	*Average of values on: All λc (1)*	*Mean height*
Ra	62.27	nm		*Arithmetic mean absolute height*

Fig 8 . AFM of ST2 before immersion in NaCl solution



Parameters	Unit	Mean	Min	Max	Step 1	Step 2
Width	nm	1139	772.1	1506	1506	772.1
Maximum height	nm	29.69	19.24	40.15	40.15	19.24
Mean height	**nm**	**18.61**	12.50	24.71	24.71	12.50

Fig 9. profile surface roughness of ST2 before immersion in NaCl solution.

The mean height of surface **18.61 nm** before immersion in corrosive solution .

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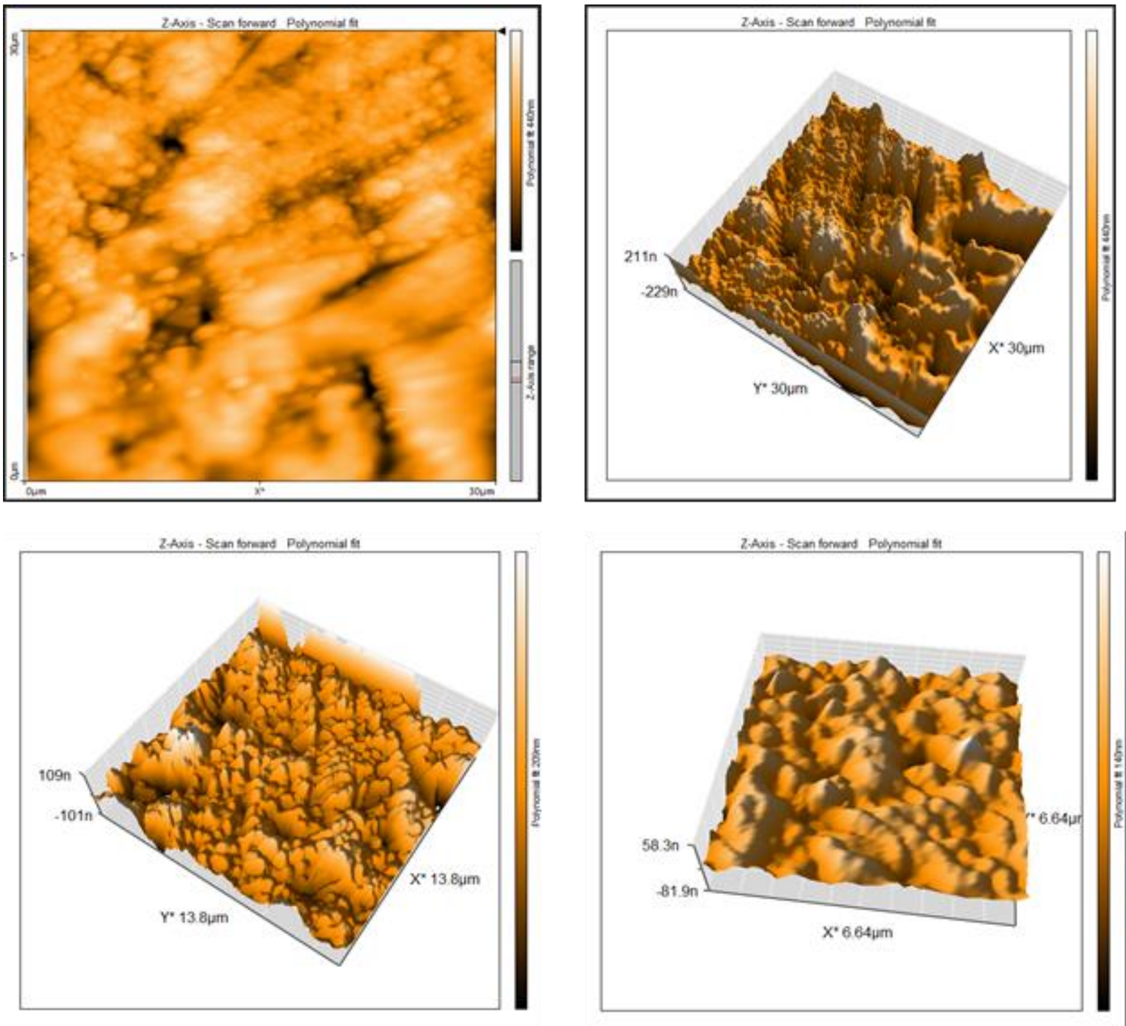

Fig 10. 2D and 3D topography of ST2 before immersion.

The **fig 8 and 9** surface roughness analysis root mean square value (62.27) nm. The fig 10 obtained for the zinc phosphate ST2 sample , the bath caused structural refinement of the crystal and also helped to achieve maximum surface coverage .

4.3.2. Surface roughness effected in NaCl corrosive solution

The surface roughness and morphology of carbon steel coatings by zinc phosphate after immersion effected by corrosive solutions as following :

The SEM analysis evaluated the surface morphology of the coating layer after exposure to 3.5% NaCl. The surface appear rougher and more irregular than before exposure, and the coating layer may be thinner due to reaction.

small pitting corrosion products was deposited on the surface of the sample and a structure gives the crust a small porosity as a pitting corrosion at some area position, the coating provided a good protection layer in corrosive media as shown in **fig11** .

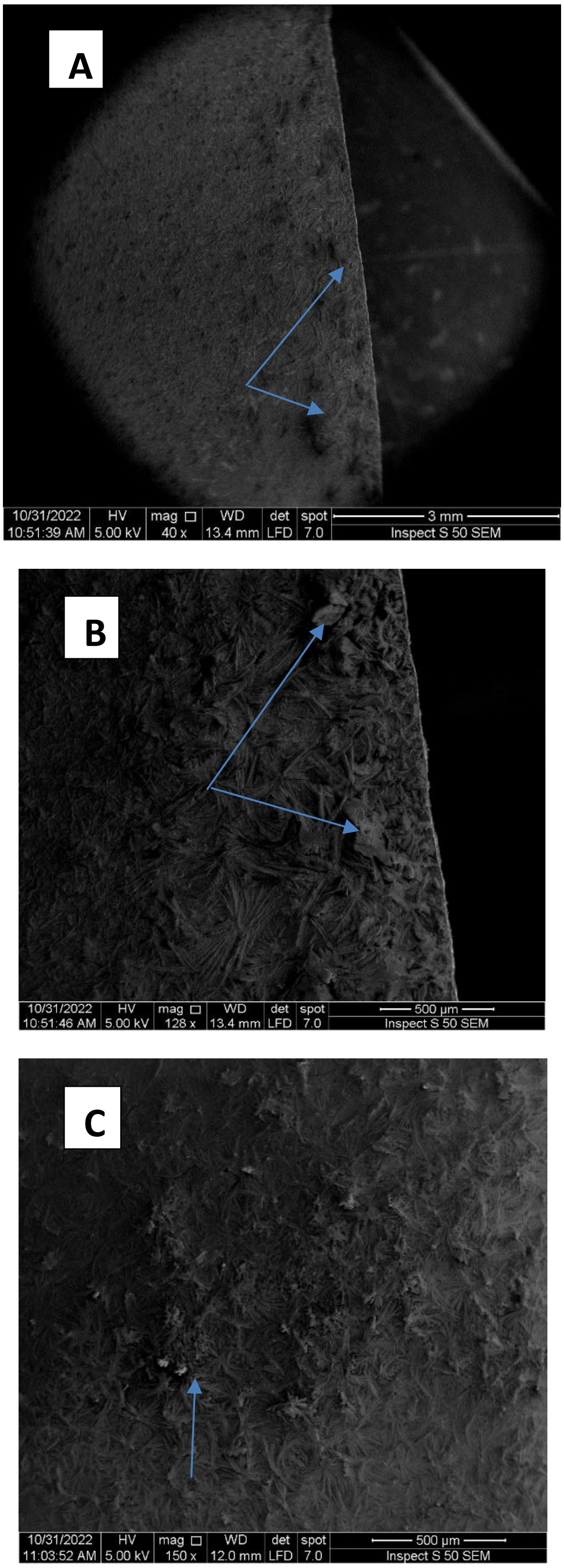

Fig 11 a ,b and c SEM images for the ST2 after immersion in NaCl solution.

Exposure to 3.5% NaCl can have a significant negative effect on the corrosion protection of zinc phosphate coating layer on carbon steel. The concentration of NaCl is a solution that can promote the initiation and propagation of corrosion on the surface of the coating layer. This is because NaCl can act

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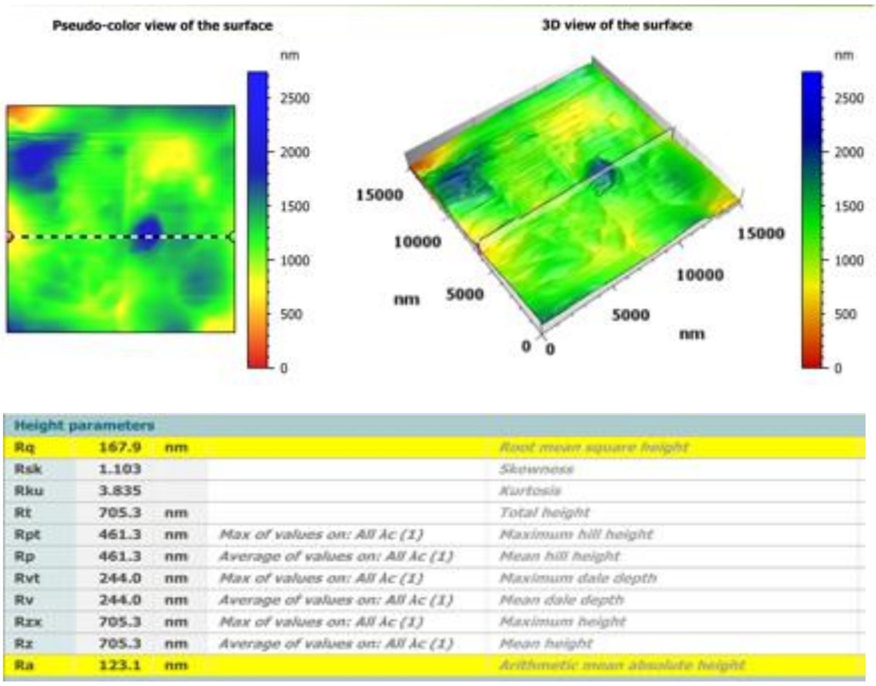
as an electrolyte and facilitate the flow of electrons, which can lead to the formation of localized corrosion.

the EDS analysis of the zinc phosphate coating layer on carbon steel table **5** show changes in the elemental composition of the layer, which reflected in the EDS spectrum.

Table 5 . EDS of ST2 After immersion in NaCl solution

Element	weight	Atomic%	Error%
O	21.11	45.26	0.23
P	12.44	14.72	0.00
Zn	31.15	18.19	0.02
Fe	35.30	21.83	3.07

The AFM analysis obtained information about the surface roughness of the zinc phosphate coating layer after exposure to the NaCl solution.



Height parameters				
Rq	167.9	nm		Root mean square height
Rsk	1.103			Skewness
Rku	3.835			Kurtosis
Rt	705.3	nm		Total height
Rpt	461.3	nm	Max of values on: All Ac (1)	Maximum hill height
Rp	461.3	nm	Average of values on: All Ac (1)	Mean hill height
Rvt	244.0	nm	Max of values on: All Ac (1)	Maximum dale depth
Rv	244.0	nm	Average of values on: All Ac (1)	Mean dale depth
Rzx	705.3	nm	Max of values on: All Ac (1)	Maximum height
Rz	705.3	nm	Average of values on: All Ac (1)	Mean height
Ra	123.1	nm		Arithmetic mean absolute height

Fig 12. AFM of ST2 after immersion in NaCl solution

Fig **12** illustrates the surface roughness analysis and root mean square value is **(123.1) nm** this suggest a porosity obtained on zinc phosphate layer in NaCl solution and increase the surface roughness.

fig **13** illustrates the surface profile surface roughness of ST2 after immersion in NaCl , after immersing ST2 in NaCl, there is a noticeable change in the surface profile and roughness. The interaction between the protective layer and the corrosive environment has caused the dissolution of certain portions of the layer, creating possible porous areas that are prone to corrosion on the metal surface. Furthermore, this dissolution has led to an overall increase in surface roughness.

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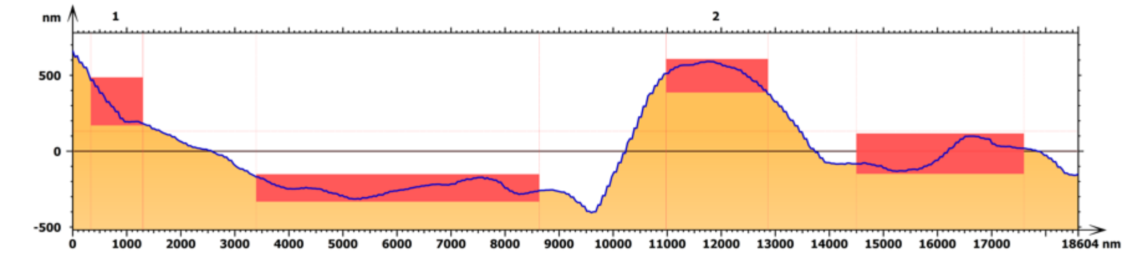

Parameters	Unit	Mean	Min	Max	Step 1	Step 2
Width	nm	1425	963.7	1886	963.7	1886
Maximum height	nm	529.7	469.0	590.4	469.0	590.4
Mean height	**nm**	**413.1**	288.9	537.3	288.9	537.3

Fig 13. profile surface roughness of ST2 after immersion in NaCl.

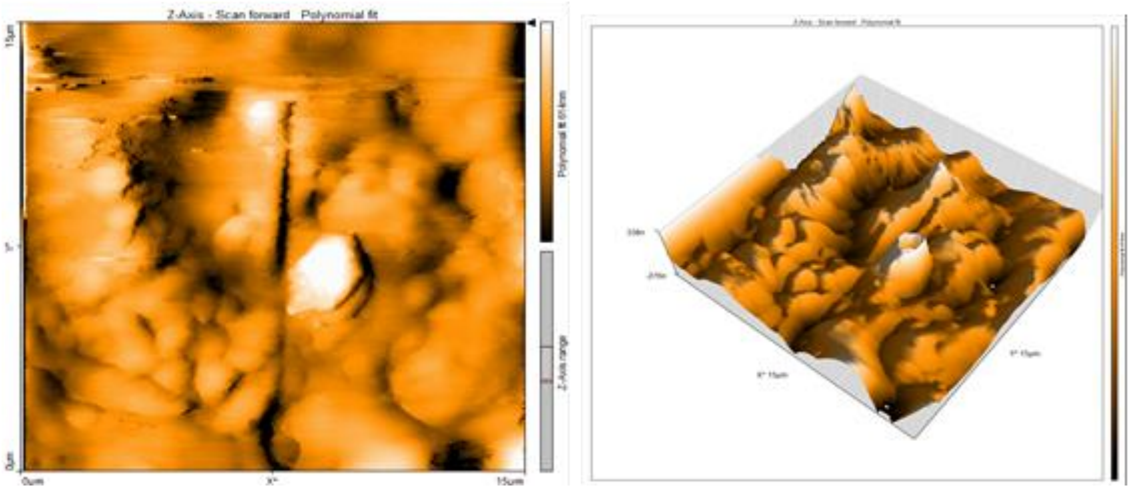

Fig 14 . 2D and 3D topography of ST2 after immersion in NaCl solution

The fig **14** 2D and 3D observation of increased surface roughness comparing with ST2 sample before immersion by using AFM after exposure to NaCl corrosive solution .

Conclusions

The standard zinc phosphating process using a phosphate bath without any additives demonstrated good corrosion resistance .

The incorporation of nickel carbonate (NiCO3) in the zinc phosphate treatment of carbon steel significantly improved its corrosion resistance compared to the standard phosphate treatment.

The zinc phosphate coating exhibited the highest effectiveness in enhancing corrosion resistance in a saline environment.

Exposure to corrosive media had an impact on surface roughness, with the highest roughness observed in seawater .

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