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Influence of a paint coating on the corrosion of hull plates made of mild steel in natural seawater

ABSTRACT

The corrosion resistance of mild steel (used to make hull plates in ship technology) in seawater before paint coating (Nippon paint, weatherbond advance) and after paint coating has been measured by electrochemical studies such as Polarisation study and AC impedance spectra. It is observed that after paint coating, the corrosion resistance of mild steel hull plates increases. Polarization study reveals that after paint coating, the linear polarization resistance increases and corrosion current decreases. AC impedance spectra reveal that in the presence of paint coating charge transfer resistance value increases, impedance value increases, phase angle increases and double layer capacitance value decreases.

Keywords: paint coating, corrosion inhibition, hull plates, mild steel, natural seawater, electrochemical studies

1. INTRODUCTION

Evaluation of leaf and bark extracts of *Acacia tortilis* as corrosion inhibitors for mild steel in seawater has been reported by Ali et al. Polarisation study reveals that the extracts act as mixed type inhibitors. AC impedance spectra confirm the formation of a protective layer on the metal surface. The adsorption of the inhibitors on the steel surface follow Langmuir adsorption isotherm model [1]. Ahmad et al. have reported synthesis, identification, theoretical and experimental studies for carbon steel corrosion inhibition in seawater for new urea and thiourea derivatives linkage to 5-Nitro Isatin Moiety. Isatin derivative is chosen as the best inhibitor by polarization study [2]. Influence of inhibitors on reinforced bar corrosion of coral aggregate seawater concrete has been investigated by Da et al.

The effect of inhibitors on corrosion behavior of reinforced bar in coral aggregate seawater concrete (CASC) in artificial seawater was studied by means of linear polarization resistance method (LPR) and electrochemical impedance spectroscopy (EIS). Two inhibitors, calcium nitrite rust inhibitor (CN) and amino-alcohol rust inhibitor (AA) are used. The effect of inhibitors on corrosion behavior of reinforced bar in coral aggregate seawater concrete (CASC) in artificial seawater was studied by means of linear polarization resistance method (LPR) and electrochemical impedance spectroscopy (EIS) [3]. Managing corrosion in desalination plants has been discussed by Schorr et al. To protect the desalination plant (DP) materials, industrial paints, polymeric coatings and rubber linings compatible with the DP fluids are applied. Cathodic protection with sacrificial anodic metals or impressed direct electrical current and corrosion inhibitors are supplied [4]. Corrosion studies of zinc coated steel parts in seawater have been made by Karthikeyan and Jeeva [5]. The corrosion inhibition of zinc coated steel sheets immersed in 3.5% NaCl with sulfisoxazole (SSZ) has been reported by weight

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loss, potentiodynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation studies and quantum mechanical studies.

Polarization studies confirmed that the inhibition mode follows a mixed type. The adsorption of the compounds onto the zinc coated steel surface obeyed Langmuir adsorption isotherm [5]. The corrosion inhibition of zinc coated steel sheets immersed in 3.5% NaCl with sulfisoxazole (SSZ) has been reported by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation studies and quantum mechanical studies. Polarization studies confirmed that the inhibition mode follows a mixed type. Duduna et al. have compared various adsorption isotherm models for allium cepa as corrosion inhibitor on austenitic stainless steel in seawater. The sorption data of the allium cepa extract obeyed Langmuir, Freundlich, Temkin, El-Awady and Adejo Ekwenchi isotherm of which Langmuir Isotherm gave the best model fit [6]. In marine conditions, especially in the Arctic, the problems of reliability and safety of marine corrosion protection systems are relevant. Reliability can be enhanced by corrosion inhibitors. Phosphating compound with anode inhibitors have been used by Plaskeeva and Trusov [7]. Colloidal ZrO_2 nanoparticles have been used for corrosion protection of AA2024 in synthetic seawater by Elbasuney et al. Inhibition efficiency of 93.6% was achieved. It was noted that ZrO_2 could act as cathodic inhibitor by suppressing the dealloying of the intermetallic particles [8]. Shen et al. have made a Study of pitting corrosion inhibition effect on aluminum alloy in seawater by biomineralized film. The electrochemical results showed that the radius of the impedance arc of the alloy immersed in seawater with bacteria increased gradually with time. The bacteria promoted the formation of the $CaMg(CO_3)_2$ film, which blocked seawater from the alloy and consequently, inhibited pitting corrosion [9]. Xu et al. have investigated steel rebar corrosion in artificial reef concrete with sulphoaluminate cement. It has been observed that 2% dosage of corrosion inhibitor can significantly decrease the steel rebar corrosion in a new artificial reef concrete (NARC) to a similar corrosion degree of ordinary artificial reef concrete (ARC) [10]. The present work is undertaken to investigate the influence of a paint coating, namely, "Nippon paint, weatherbond advance" on the corrosion of hull plates made of mild steel in natural seawater, by electrochemical studies such as Polarisation study and AC impedance spectra.

2. EXPERIMENTAL WORK

Electrochemical studies

The corrosion resistance of mild steel (used to make hull plates in ship technology) in seawater has been measured by electro chemical studies such as Polarisation study and AC impedance spectra.

Polarisation study

A CHI electrochemical work station with impedance model 660A was used for this purpose. A three-electrode cell assembly electrode was used in the present study (Figure1). Mild steel was used as working electrode; saturated calomel electrode was used as reference electrode and Platinum electrode was used as counter electrode. From the Polarisation study corrosion parameters such as corrosion potential (E_{corr}) corrosion current (I_{corr}) and Tafel slope values (anodic = b_a and cathodic = b_c) and Linear polarisation resistance (LPR) were calculated. The scan rate (V/S) was 0.01. Hold time at (E_{fcs}) was zero and quit times (s) was two.

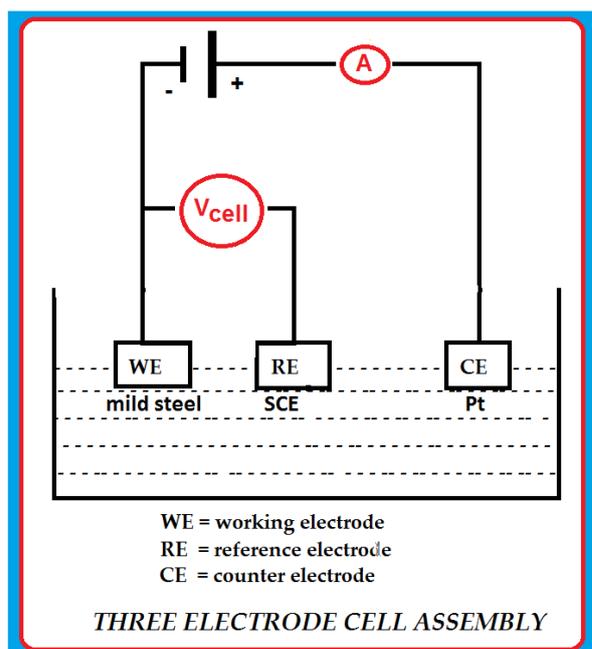


Figure 1. Circuit diagram of three-electrode cell assembly

Slika 1. Šema sklopa ćelije sa tri elektrode

AC impedance spectra

AC impedance spectral studies were carried out on a CHI – Electrochemical workstation with impedance, Model 660A. A three – electrode cell assembly was used. The working electrode was mild steel, A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode.

The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}), impedance value and phase angle were calculated from Nyquist plots and Bode plots.

Composition of mild steel

The composition of mild steel used in this study is given in Table1. This mild steel is used as hull plates in shipbuilding industry.

Table1. Composition of mild steel

Tabela 1. Sastav mekog čelika

Name	Average %	Abs. Std.Dev	Ref. Std.Dev	1	2
C	0.101	0.0014	1.4	0.102	0.1
Si	0.055	0.0021	3.89	0.053	0.056
Mn	1.629	0.0057	0.35	1.633	1.625
P	0.0087	0.0003	3.25	0.0085	0.0089
S	0.0028	0.0003	10.1	0.0026	0.003
Cr	0.036	0.0014	3.93	0.037	0.035
Mo	0.0086	0.00007	0.83	0.0086	0.0085
Ni	0.033	0.0007	2.18	0.033	0.32
Cu	0.0063	0.00007	1.13	0.0062	0.0063
Al	0.044	0.0014	3.21	0.043	0.045
As	0.0011	0	0	0.0011	0.011
B	0.0027	0.0005	18.68	<0.00010	<0.00010
Bi	<0.00010	0.00002	84.85	<0.0025	0.003
Ce	0.0032	0.0013	42.65	0.0041	0.0022
Co	0.011	0	0	0.011	0.011
Mg	0.0003	0	0	0.0003	0.0003
Nb	0.03	0.0007	2.4	0.029	0.03
Pb	0.0081	0.0013	15.71	0.0072	0.009
Sb	0.004	0.0004	8.95	0.0037	0.0042
Sn	0.0034	0	0	0.0034	0.0034
Ta	0.03	0.0071	23.57	0.025	0.035
La	0.0071	0	0	0.0071	0.0071
Ti	0.0035	0	0	0.0035	0.0035
V	0.138	0.0014	1.02	0.137	0.139
W	0.071	0.0078	11.03	0.076	0.065
Zn	0.0024	0	0	0.0024	0.0024
Zr	0.0051	0.0002	0.2	0.0052	0.0049
Se	<0.0005	0.0001	4.42	<0.0005	<0.0005
N	0.0093	0.00007	0.76	0.0092	0.0093
Ca	0.0014	0.0001	10.1	0.0013	0.0015
Te	0.0026	0.0025	97.91	<0.0010	0.0044
Fe	97.74	0	0	97.74	97.74

Seawater

The corrosion resistance of mild steel in seawater was investigated, before paint coating and after paint coating. The composition of

seawater used in this study is given in Table 2. Seawater was collected in Bay of Bengal, located at Kanathur, East Coast Road, Chennai, India (near AMET University, Kanathur, East Coast Road, Chennai, India).

Table 2. Composition of seawater used in this study

Tabela 2. Sastav morske vode korišćen u ovoj studiji

S. No.	Physical Examination	Acceptable Limit	Permissible limit	Sample Value
1	Colour	–	–	Unobjectionable
2	Odour	Unobjectionable		Unobjectionable
3	Turbidity NT Units	1	5	0.2
4	Total Dissolved Solids mg/1	500	2000	29400
5	Electrical Conductivity micro mho/cm	–	–	42000
6	pH	6.5–8.5	6.5–8.5	7.46
7	pH Alkalinity as CaCO ₃	–	0	0
8	Total Alkalinity as CaCO ₃	200	600	140
9	Total Hardness as CaCO ₃	200	600	4000
10	Calcium as Ca	75	200	1200
11	Manganese as Mn	30	100	240
12	Iron as Fe	0.1	1	0
13	Magnesium as Mg	0.1	0.3	NT
14	Free Ammonia as NH ₃	0.5	0.5	0.48
15	Nitrite as NO ₂	0.5	0.5	0.104
16	Nitrate as NO ₃	45	45	25
17	Chloride as Cl	250	1000	15000
18	Fluoride as F	1	1.5	1.8
19	Sulphate as SO ₄	200	400	1170
20	Phosphate as PO ₄	0.5	0.5	1.47
21	Tids Test 4hrs as O ₂	–	–	NT

3. RESULTS AND DISCUSSION

The influence of a paint, namely Nippon paint, weatherbond advance, on the corrosion resistance of hull plate made of mild steel in seawater has been investigated by electrochemical methods such as polarization study and AC impedance spectra [11-26].

Analysis of Results of Polarisation study

The Polarization curves of mild steel in seawater with the absence and presence of paint coating are shown in Figures 2 and 3. The corrosion parameters are given in Table 3.

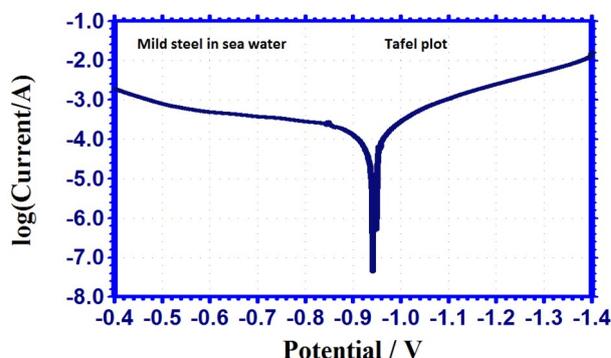


Figure 2. Polarisation curve of mild steel in seawater

Slika 2. Polarizaciona kriva mekog čelika u morskoj vodi

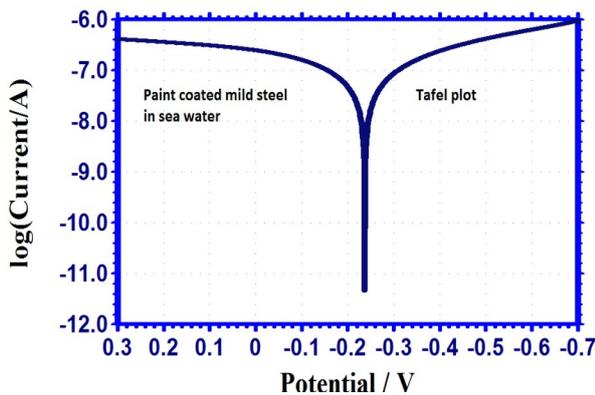


Figure 3. Polarisation curve of paint coated mild steel in seawater

Slika 3. Kriva polarizacije mekog čelika premazanog bojom u morskoj vodi

Table3 . Corrosion Parameters of mild steel immersed in seawater, before and after paint coating (Nippon paint, weatherbond advance) obtained by polarisation study

Tabela 3. Parametri korozije mekog čelika uronjenog u morsku vodu, pre i posle premaza boje (Nippon boja, vremenska veza unapred) dobijeni proučavanjem polarizacije

System	E_{corr} , mV vs SCE	b_c , mV/decade	b_a , mV/decade	LPR, Ohm cm^2	I_{corr} , A/ cm^2
mild steel	-941	153	324	425	1.062×10^{-4}
paint coated mild steel	-237	191	220	770339	5.765×10^{-8}

According to the principles of polarization study, “when corrosion resistance increases, LPR increases and corrosion current decreases” (Figure 4).

Based on the principles of polarization study, it is inferred from Table 1 that in the presence of paint coating corrosion resistance of the hull plate made of mild steel in seawater increases. This is due to the fact that in the presence of paint coating, there is increase in LPR value and decrease in corrosion current. The inhibition efficiency is 99.94%. It is also inferred that the paint coating controls the anodic reaction of metal dissolution predominantly. This is revealed by the fact where the presence of paint coating corrosion potential shifts from -941 mV vs SCE to -237mV vs SCE (anodic shift).

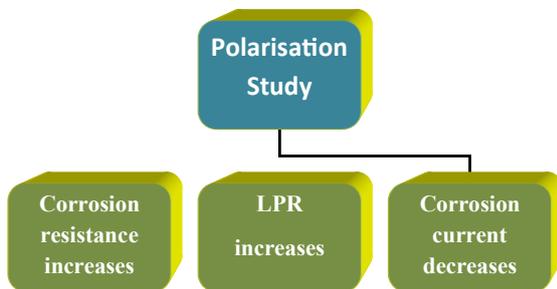


Figure 4. Correlation among corrosion parameters of polarization study

Slika 4. Korelacija između korozionih parametara proučavanja polarizacije

Implication

The hull plates made of mild steel may be coated with Nippon paint, weatherbond advance. This will control the corrosion of the hull plates in the seawater. There will be increase in the life time of the hull plates.

Analysis of AC Impedance spectra

AC impedance spectra (also known as EIS) have been used to detect the formation of the film on the metal surface. According to the principles of AC impedance spectra (also known as EIS), “when a protective film is formed, charge transfer

resistance (R_t) increases, double layer capacitance (C_{dl}) decreases, phase angle increases and impedance value increases” (Figure 5).



Figure 5. Correlation among corrosion parameters of AC impedance spectra

Slika 5. Korelacija između korozionih parametara spektra impedance naizmenične struje

The AC impedance spectra of mild steel in seawater the absence and presence of paint

coating are shown in Figures 6-11. The Nyquist plots are shown in Figures 6 and 9. The Bode plots are shown in Figures 7 and 10. The interactive 3D plots-log frequencies are shown in Figures 8 and 11. The corrosion parameters are given in Table 4.

Table 4. Corrosion parameters of mild steel immersed in seawater, before and after paint coating (Nippon paint, weatherbond advance) obtained by AC impedance spectra

Tabela 4. Parametri korozije mekog čelika uronjenog u morsku vodu, pre i posle nanošenja boje (Nippon boja, vremenska veza unapred) dobijeni spektrom AC impedanse

System	R_t , Ohm cm^2	C_{dl} , F/ cm^2	Impedance, Log(Z/ohm)	Phase angle $^\circ$
mild steel	23	2.217×10^{-7}	1.499	33.83
paint coated mild steel	487080	1.047×10^{-11}	5.655	63.87

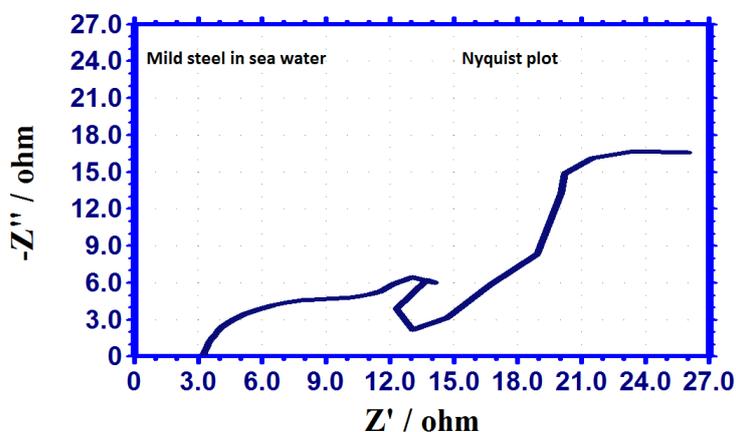


Figure 6. Nyquist plot of mild steel in seawater

Slika 6. Nyquist-ova kriva za meki čelik u morskoj vodi

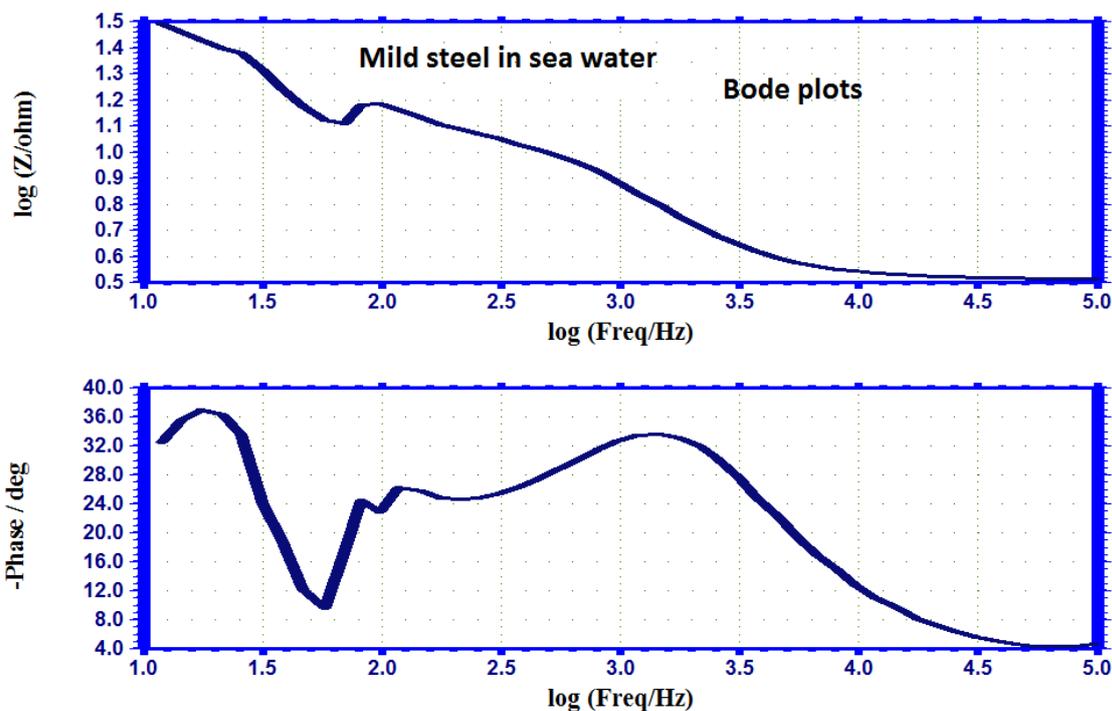


Figure 7. Bode plot of mild steel in seawater

Slika 7. Bode-ove krive za meki čelik u morskoj vodi

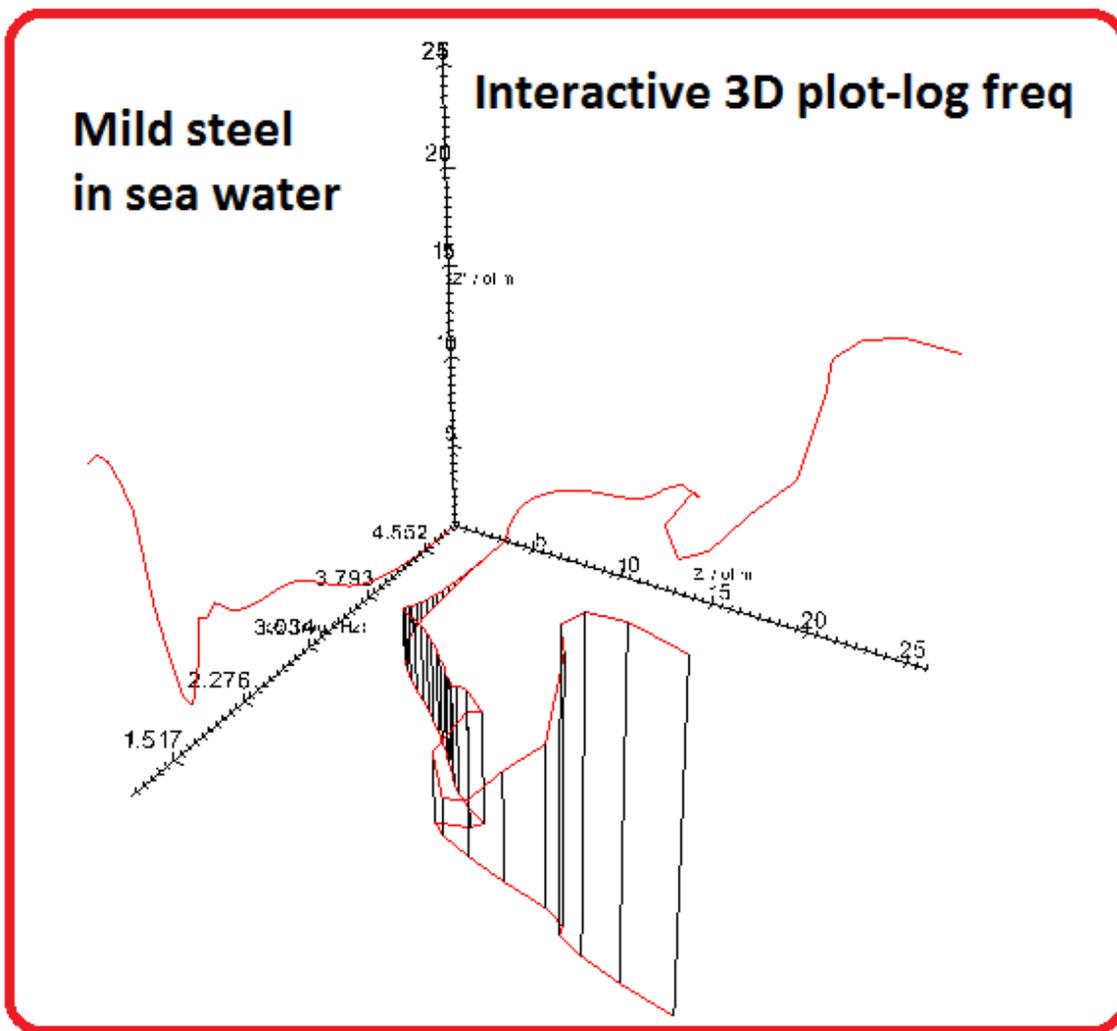


Figure 8. Interactive 3 D-log freq plot of mild steel in seawater

Slika 8. Interaktivni 3 D-log freq dijagram mekog čelika u morskoj vodi

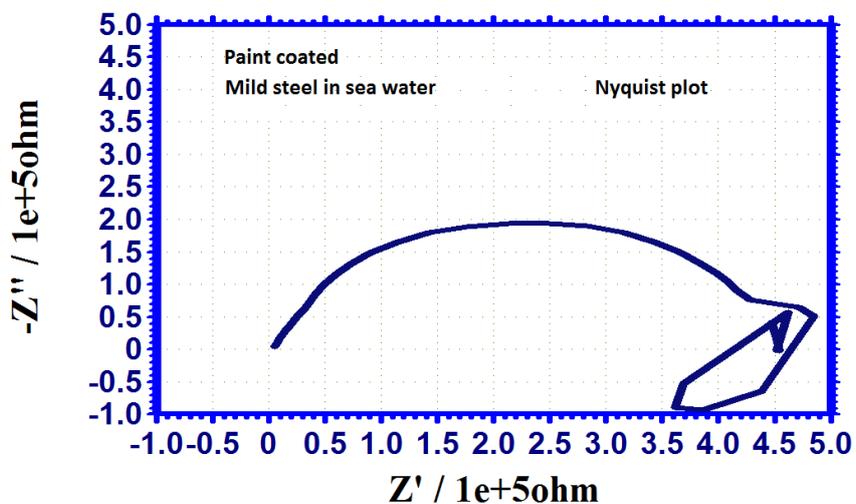


Figure 9. Nyquist plot of paint coated mild steel in seawater

Slika 9. Nyquist-ova kriva mekog čelika premazanog bojom u morskoj vodi

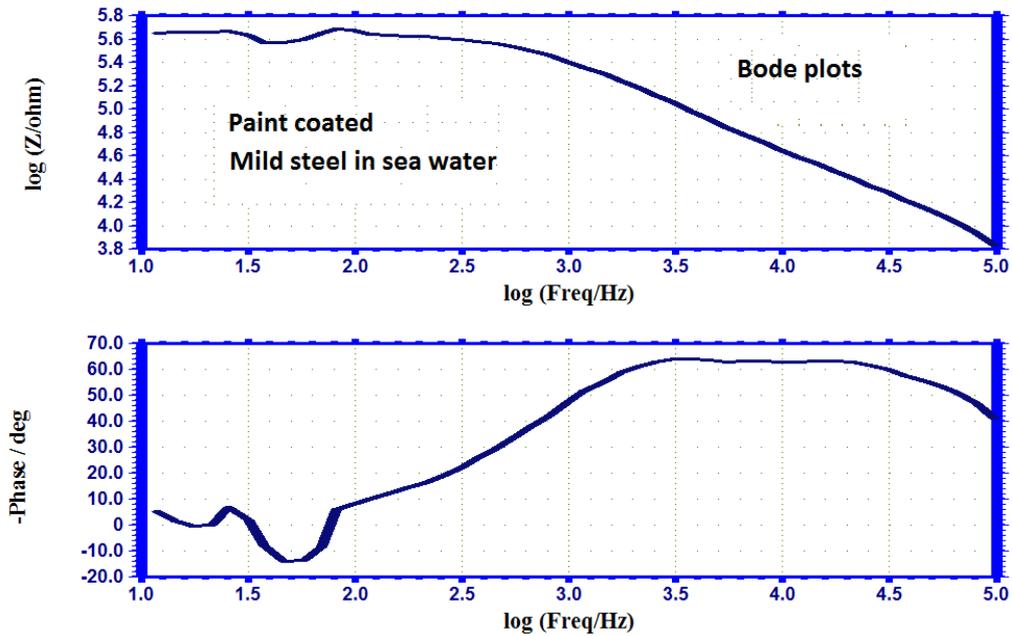


Figure 10. Bode plot of paint coated mild steel in seawater

Slika 10. Bode-ova kriva za meki čelik premazan bojom u morskoj vodi

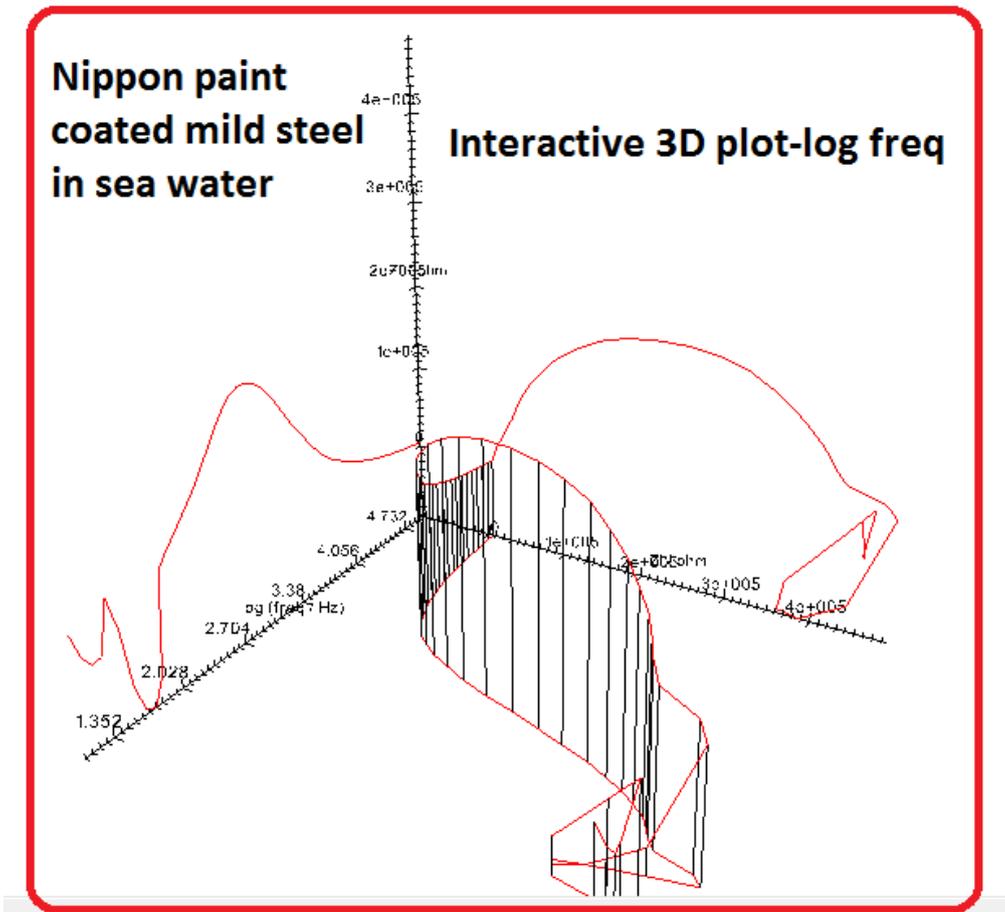


Figure 11. Interactive 3D-log freq plot of paint coated mild steel in seawater

Slika 11. Interaktivni 3 D-log freq dijagram mekog čelika premazanog bojom u morskoj vodi

Based on the principles of the AC impedance spectra, it is inferred from Table 4 that in the presence of paint coating corrosion resistance of the hull plate made of mild steel in seawater increases. This is due to the fact that in the presence of paint coating, charge transfer resistance (R_t) increases, double layer capacitance (C_{dl}) decreases, phase angle increases and impedance value increases. The corrosion inhibition efficiency is 99.99%.

Implication

The hull plates made of mild steel may be coated with Nippon paint, weatherbond advance. This will control the corrosion of the hull plates in the seawater. It would lead to the increase in the lifetime of the hull plates.

4. CONCLUSIONS

The corrosion resistance of mild steel (used to make hull plates in shipbuilding technology) in seawater before paint coating (Nippon paint, weatherbond advance) and after paint coating has been measured by electrochemical studies such as Polarisation study and AC impedance spectra. It is observed that after paint coating, the corrosion resistance of mild steel hull plates increases. Polarization study reveals that after paint coating, the linear polarization resistance increases and corrosion current decreases. AC impedance spectra reveal that in the presence of paint coating charge transfer resistance value increases, impedance value increases, phase angle increases and double layer capacitance value decreases.

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IZVOD

UTICAJ PREMAZA NA KOROZIJU PLOČA TRUPA OD MEKOG ČELIKA U PRIRODNOJ MORSKOJ VODI

Otpornost na koroziju mekog čelika (koji se koristi za izradu ploča trupa u brodskoj industriji) u morskoj vodi pre nanošenja boje (Nippon boja, vremenska veza unapred) i posle premaza boje je merena elektrohemijским studijama kao što su studija polarizacije i spektri impedanse naizmenične struje. Primećeno je da se nakon nanošenja boje povećava otpornost na koroziju ploča trupa od mekog čelika. Studija polarizacije otkriva da nakon nanošenja boje, otpor linearne polarizacije raste a struja korozije opada. Spektri impedanse naizmenične struje otkrivaju da se u prisustvu bojenog premaza vrednost otpora prenosa naelektrisanja povećava, vrednost impedanse povećava, fazni ugao raste i vrednost dvoslojne kapacitivnosti opada.

Ključne reči: *premaz boje, inhibicija korozije, ploče trupa, meki čelik, prirodna morska voda, elektrohemijske studije*

Naučni rad

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