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Scientificpaper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.5937/zasmat2303340S

Zastita Materijala 64 (3)
340 - 350 (2023)

Influence of an emulsion coating on the corrosion resistance of hull plates made of mild steel in natural sea water

ABSTRACT

The corrosion resistance of mild steel, used to make hull plates in ship technology, in sea water before paint coating [Nippon paint SUMO XTRA durable exterior emulsion coating (emulsion coating)] 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 decrease. 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. The corrosion inhibition efficiency was greater than 99%. The hull plates made of mild steel may be coated with durable exterior emulsion coating (emulsion coating). This will control the corrosion of the hull plates in the sea water. There will be increase in the life time of the hull plates.

Keywords: *emulsion coating, corrosion resistance, hull plates, mild steel, natural sea water, electrochemical studies.*

1. INTRODUCTION

Seawater is a complex mixture of 96.5 percent water, 2.5 percent salts, and smaller amounts of other substances, including dissolved inorganic and organic materials, particulates, and a few atmospheric gases. Seawater constitutes a rich source of various commercially important chemical elements. Sea water can be used in cooling water systems, provided suitable corrosion inhibitors are used along with sea water. Mild steel can be used to make hull plates of the ships. The hull plates are always in contact with sea water which contains corrosive ions such as sodium chloride. Hence the hull plates of the ships undergo corrosion. To prevent corrosion several corrosion inhibitors and coatings have been used. Several research works have been carried out in this field.

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Paper received: 12. 05. 2023.
Paper accepted: 16. 06. 2023.
Paper is available on the website: www.idk.org.rs/journal

Role of different microorganisms on the mechanical characteristics, self-healing efficiency, and corrosion protection of concrete under different curing conditions has been reported by Osman et al. A comparison between the action of introducing two Bacillus species, and D. salina alga on the compressive and flexural strengths, corrosion rate, and self-healing ability of concrete has been explored. Internal application of either bacteria displayed efficient crack healing more than the external one, especially when prisms were cured in sea water. The bacterial and algal activity engaged the rebar's passive layer protection and corrosion inhibition, besides the other target properties improvement [1]. Zhu et al. have reported the efficiency of Gemini surfactant containing semi-rigid spacer as microbial corrosion inhibitor for carbon steel in simulated seawater. Quantum chemical calculation and molecular dynamics simulation were used to study the structure–activity relationship [2]. Anticorrosive and microbial inhibition performance of a coating loaded with

Andrographis paniculata on stainless steel in seawater have been investigated by Kamaruzzaman et al. With the trend for green technology, the study focused on utilizing a forgotten herb to produce an eco-friendly coating [3]. One-step electrochemical deposition leading to superhydrophobic matrix for inhibiting abiotic and microbiologically influenced corrosion of Cu in seawater environment has been reported by Li et al. Superhydrophobic matrix exhibits excellent corrosion resistance in harsh sulfate reducing bacteria (SRB) suspension, demonstrating a prominent role to combat microbiologically influenced corrosion in seawater environment [4]. Cerium sulfate preparation from egyptian monazite's rare earth cake for its application as corrosion inhibitor of aluminum alloy AA6061 in two solutions namely 1.0M disodium hydrogen orthophosphate and 3.5% sodium chloride (simulation of sea water) has been reported by Abdellah et al.[5]. Katona et al. have reported on the quantitative assessment of environmental phenomena on maximum pit size predictions in marine environments. It has been noted that dehydration reactions coupled with precipitation in the cathode will have the largest effect on predicted pit size, and cause the most significant inhibition of corrosion damage [6]. Microbial influenced corrosion of processing industry by re-circulating waste water and its control measures have been reported by Kokilaramani et al. Instead of chemical inhibitors, green inhibitors (natural products like plant leaves, flowers, stem, buds, roots and sea algae) are developed and used in industries [7].

Effective anticorrosive performance of benzo-imidazo-pyrimidine-g-graphene oxide composite coating for copper in natural and artificial sea water has been reported by Pareek et al. [8]. The adsorption of coating material was confirmed by FE-SEM, XPS, Raman spectroscopy, FTIR, and UV–vis studies.Evaluation of bio corrosion-resistant and antifouling properties of gold metallosurfactant monolayer on galvanised steel in simulated sea media inoculated with halophiles has been reported by Mehta et al.[9].Inhibition of corrosion of SS 18/8 alloy is sea water by thiourea-Zn^{2+} system has been reported by Praveena et al. [10]. Thiourea-Zn^{2+} coating can be given on SS 18/8 alloy to protect it from corrosion by sea water when SS 18/8 alloy is used as hull plates in ship industry.Corrosion resistance of mild steel (Hull plate) in sea water in the presence of a coating of an oil extract of plant materials has been reported by Dorothy et al.[11]. It has been suggested that this oil coating containing extracts of plant material may be coated on hull plates made of mild steel to protect them from severe corrosion due to the aggressive ions present in sea water.The present work is undertaken to investigate the corrosion resistance of hull plates made of mild steel immersed in natural sea water in the absence and presence of a paint coating namely, Nippon paint SUMO XTRA Durable exterior emulsion , by electrochemical studies such as polarization study and AC impedance spectra.

2. EXPERIMENTAL

Electrochemical studies

The corrosion resistance of mild steel (used to make hull plates in ship technology) in sea water has been measured by electrochemical 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. 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 = ba and cathodic = bc) and Linear polarisation resistance (LPR) were calculated. The scan rate (V/S) was 0.01. Hold time at (Efcs) was zero and quit times (s) was two.

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 impedence 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 Nyguist 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 shipping 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

Sea water

The corrosion resistance of mild steel in sea water was investigated, before paintt coating and after paint coating. The composition of sea water used in this study is given in Table 2. Sea water 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 sea water used in this study

Tabela 2. Sastav morske vode korišćene 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

Influence of a paint, namely Nippon paint SUMO XTRA Durable exterior emulsion , on the corrosion resistance of hull plate made of mild steel in sea water has been investigated by electro-chemical methods such as polarization study and AC impedance spectra [12-26].

Analysis of Results of Polarisation study

The Polarization curves of mild steel in sea water the absence and presence of paint coating are shown in Figures 1 and 2. The corrosion parameters are given in Table 3.

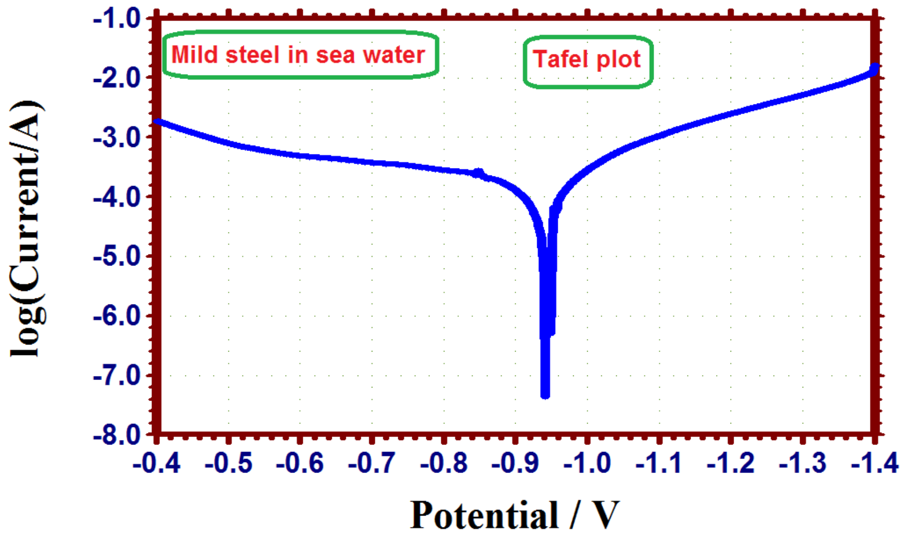

Figure 1. Polarisation curve of mild steel in sea water

Slika 1. Kriva polarizacije mekog čelika u morskoj vodi

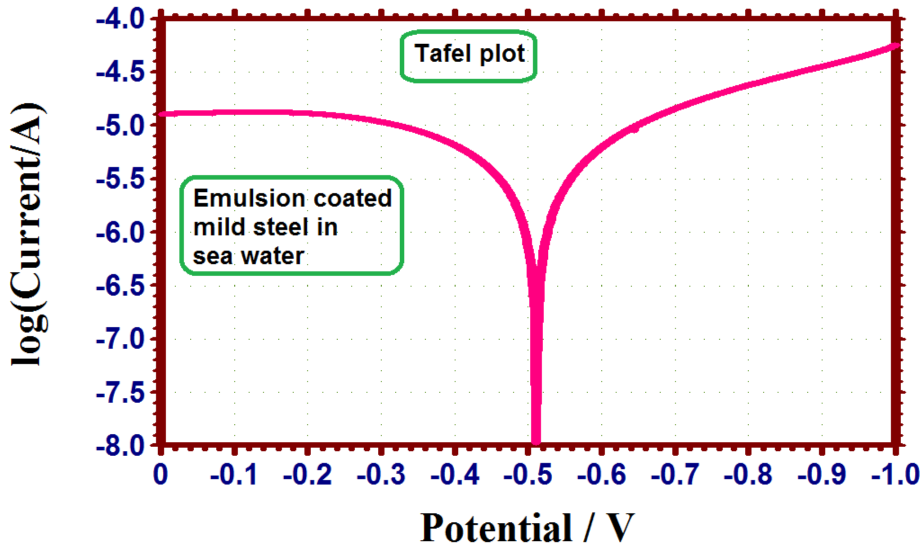

Figure 2. Polarisation curve of emulsion coated mild steel in sea water

Slika 2. Kriva polarizacije mekog čelika obloženog emulzijom u morskoj vodi

Table 3. Corrosion Parameters of mild steel immersed in sea water before and after durable exterior emulsion coating (emulsion coating) obtained by polarisation study

Tabela 3. Parametri korozije mekog čelika uronjenog u morsku vodu pre i poslei zdržljivog spoljašnjeg emulzionog premaza (emulzionog premaza) dobijenog proučavanjem polarizacije

System	E_{corr}, mV vsSCE	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 x10^{-4}
emulsion coated mild steel	-511	187	225	15028	2.957 x10^{-6}

According to the principles of polarization study, "when a protective film is formed, corrosion resistance increases, LPR increases and corrosion current decreases" (Figure 3).

Based on the principles of polarization study, it is inferred from Table 1 that in the presence of durable exterior emulsion coating (emulsion coating) corrosion resistance of the hull plate made of mild steel in sea water increases. This is due to the fact that in the presence of paint coating, there in increase in LPR value and decrease in corrosion current. The inhibition efficiency is 97.17%. It is also inferred that the paint coating controls the anodic reaction of metal dissolution predominantly. This is revealed by the fact in the presence of paint coating corrosion potential shifts from -941 mV vs SCE to -511mV vs SCE (anodic shift).

Implication

The hull plates made of mild steel may be coated with Nippon paint SUMO XTRA Durable exterior emulsion. This will control the corrosion of the hull plates in the sea water. 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.

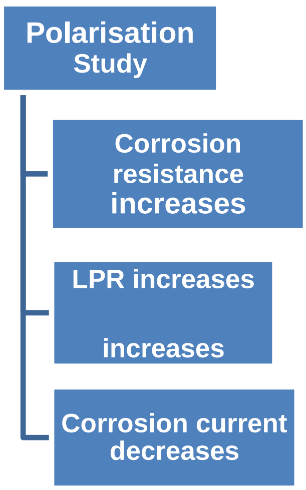

Figure 3. Correlation among corrosion parameters of polarization study
Slika 3. Korelacija između korozijskih parametara studije polarizacije

According to the principles of AC impedance spectra ,"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 4).

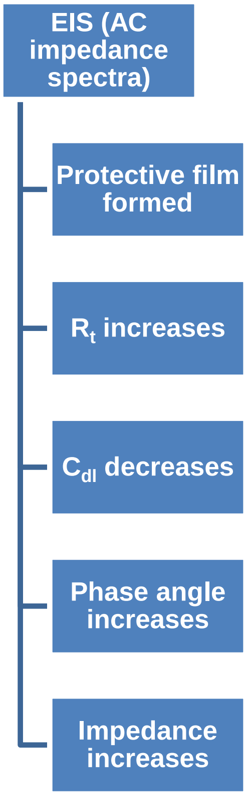

Figure 4. Correlation among corrosion parameters of AC impedance spectra

Slika 4. Korelacija između parametara korozije spektra impedanse naizmenične struje

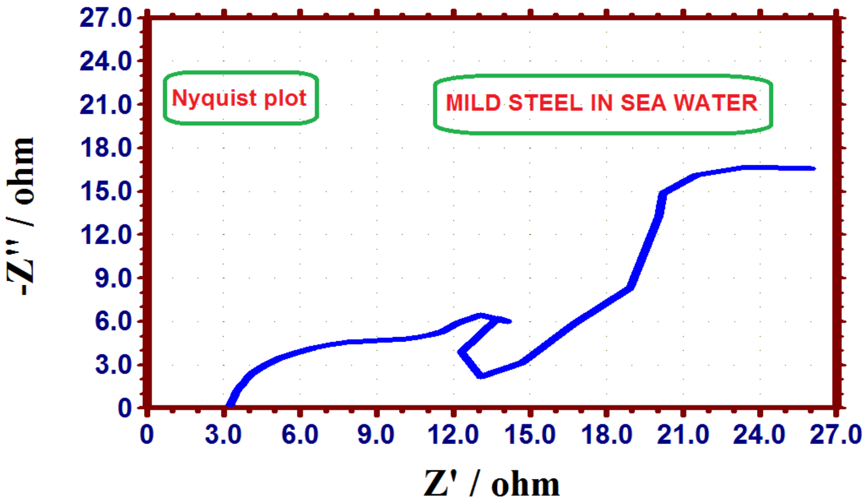

Figure 5. Nyquist plot of mild steel in sea water

Slika 5. Nyquist-ova kriva mekog čelika u morskoj vodi

The AC impedance spectra of mild steel in sea water the absence and presence of paint coating are shown in Figures 5-10.The Nyquist plots are shown in Figures 5 and 8. The Bode plots are shown in Figures 6 and 9 . The interactive 3D plots-log frequency are shown in Figures 7 and 10. The corrosion parameters are given in Table 4.

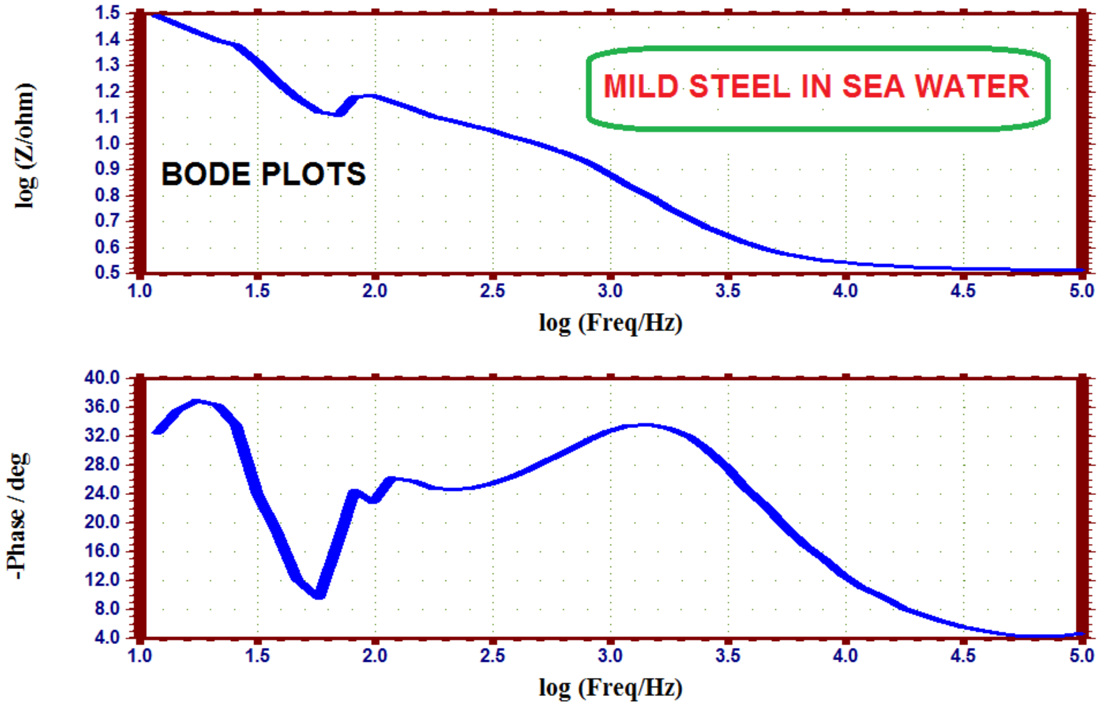

Figure 6. Bode plots of mild steel in sea water

Slika 6. Bode-ova kriva mekog čelika u morskoj vodi

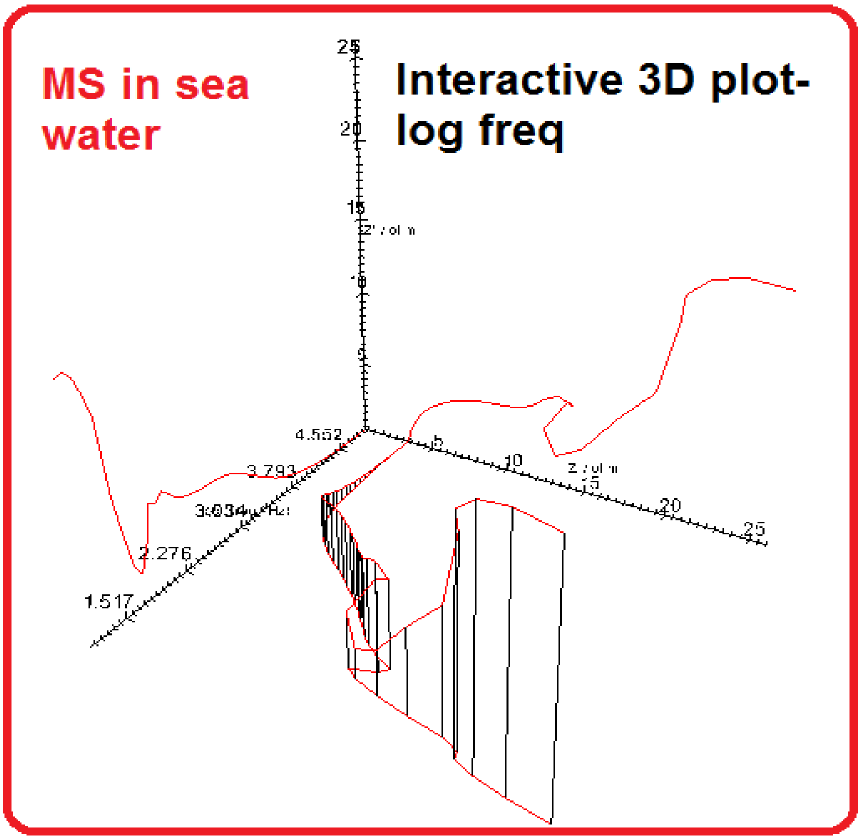

Figure 7. Interactive 3 D-log freq plot of mild steel in sea water

Slika 7. Interaktivni 3 D-log frek dijagram mekog čelika u morskoj vodi

Table 4. Corrosion parameters of mild steel immersed in sea water, before and after durable exterior emulsion coating (emulsion coating) obtained by AC impedance spectra

Tabela 4. Parametri korozije mekog čelika uronjenog u morsku vodu, pre i posle izdržljivog spoljašnjeg emulzionog premaza (emulzionog premaza) dobijenog spektrom impedanse naizmenične struje

System	R_t,Ohmcm^2	C_{dl}, F/cm^2	Impedance,Log(Z/ohm)	Phase angle°
mild steel	23	2210 x10-^{10}	1.5	34
emulsion coated mild steel	6974	7.313x10-^{10}	3.9	39

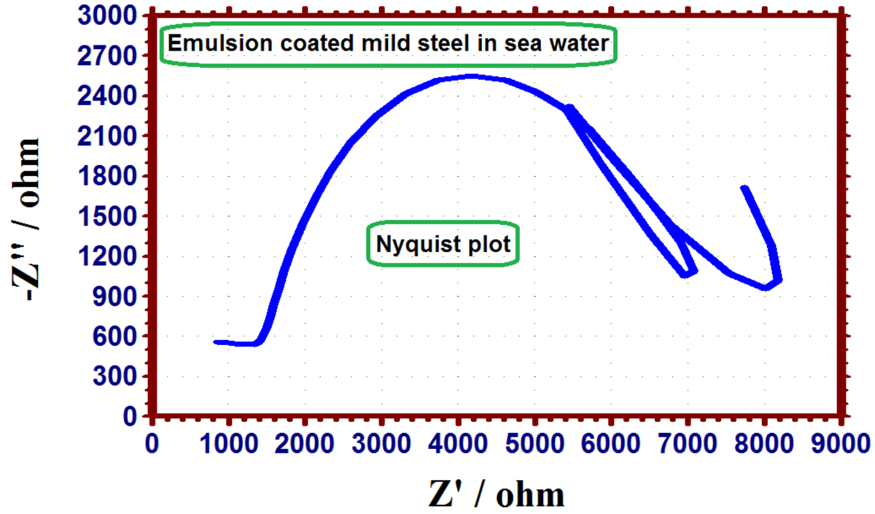

Figure 8. Nyquistplot ofemulsion coated mild steel in sea water

Slika 8. Nyquist-ova kriva mekog čelika obloženog emulzijom u morskoj vodi

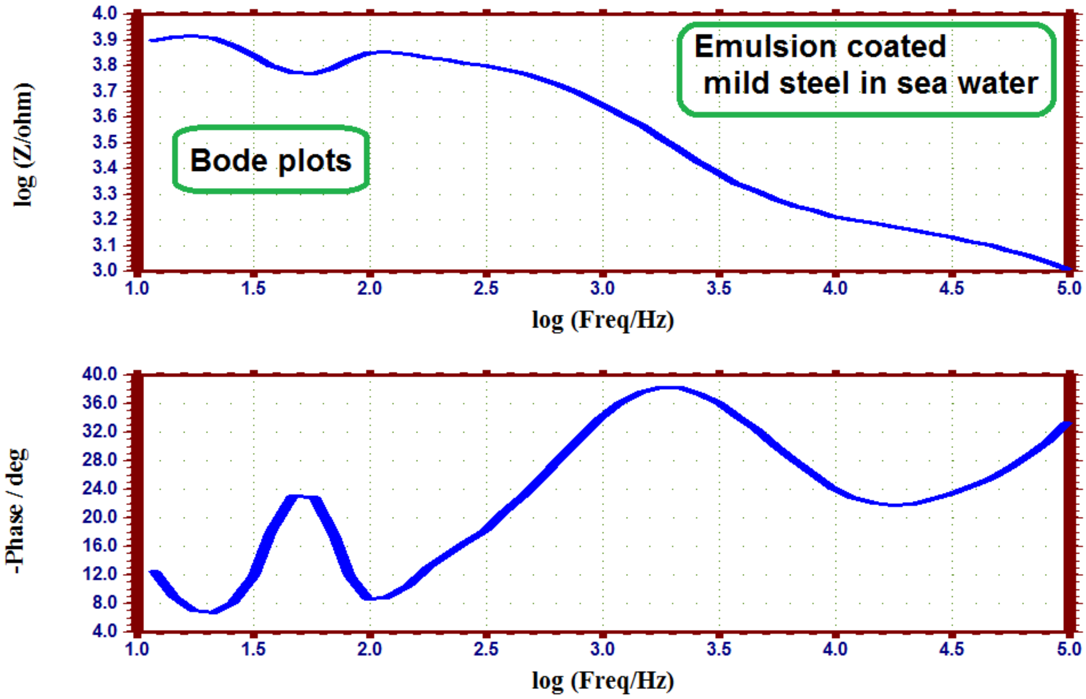

Figure 9. Bode plots ofemulsion coated mild steel in sea water

Slika 9. Bode-ova kriva mekog čelika obloženog emulzijom u morskoj vodi

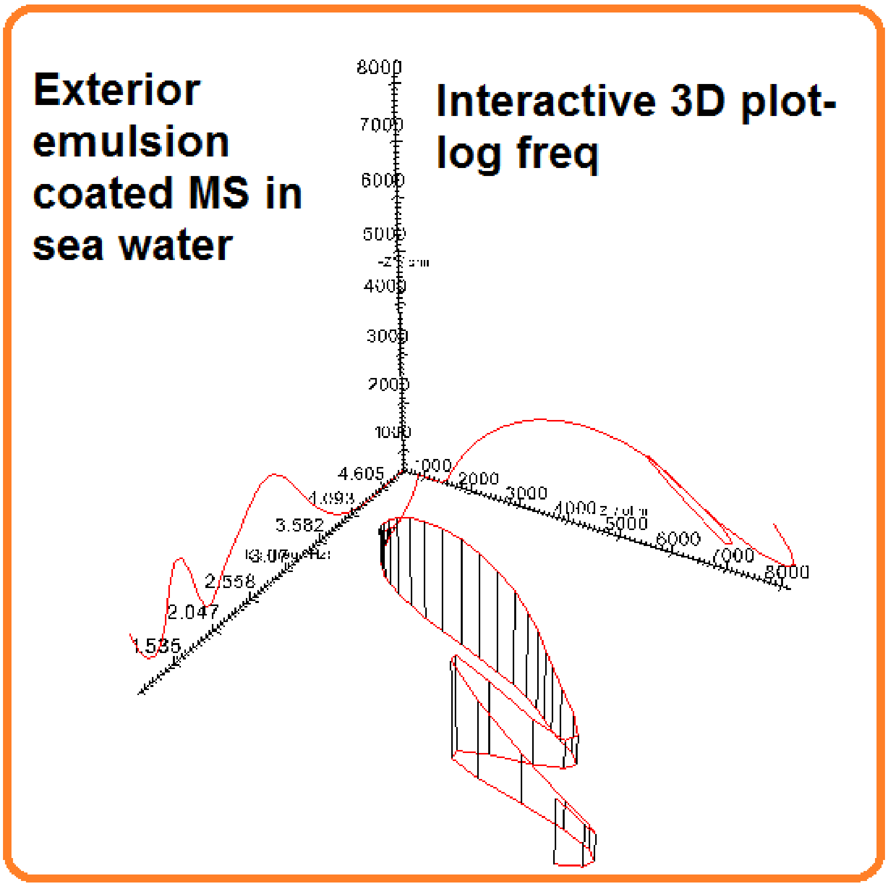

Figure 10. Interactive 3D-log freq plot ofemulsion coated mild steel in sea water

Slika 10. Interaktivni 3D-log dijagram frekvencija mekog čelika obloženog emulzijom 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 sea water increases. This is due to the fact that in the presence of paint coating [Nippon paint SUMO XTRA durable exterior emulsion coating (emulsion 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 99.67%.

Implication

The hull plates made of mild steel may be coated with durable exterior emulsion coating (emulsion coating). This will control the corrosion of the hull plates in the sea water. There will be increase in the life time of the hull plates.

4. CONCLUSIONS

The corrosion resistance of mild steel (used to make hull plates in ship technology) in sea water before paint coating [Nippon paint SUMO XTRA durable exterior emulsion coating (emulsion coating)] 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 decrease. 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 EMULZIONOG PREMAZA NA OTPORNOST 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 tehnologiji, u morskoj vodi pre nanošenja boje [Nippon boja SUMO KSTRA izdržljivi spoljašnji emulzioni premaz (emulzioni premaz)] i nakon nanošenja boje je izmerena elektrohemijskim studijama kao što je 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 se nakon nanošenja boje raste otpor linearne polarizacije i smanjuje struja korozije. Spektri impedanse naizmenične struje otkrivaju da se u prisustvu bojenog premaza vrednost otpora prenosa naelektrisanja povećava, vrednost impedanse povećava, fazni ugao raste i vrednost dvoslojnog kapacitivnosti opada. Efikasnost inhibicije korozije bila je veća od 99%. Ploče trupa od mekog čelika mogu biti premazane izdržljivim spoljašnjim emulzionim premazom (emulzioni premaz). Ovo će kontrolisati koroziju ploča trupa u morskoj vodi. Doći će do povećanja veka trajanja ploča trupa.

***Ključne reči**: emulzioni premaz, otpornost na koroziju, ploče trupa, meki čelik, prirodna morska voda, elektrohemijska ispitivanja.*

Naučni rad
Rad primljen: 12. 05. 2023.
Rad prihvaćen: 16.06.2023.
Rad je dostupan na sajtu:www.idk.org.rs/casopis