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Inhibition of corrosion of SS 18/8 alloy in sea water by Thiourea-Zn²⁺ system

ABSTRACT

The corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor named Thiourea-Zn²⁺ has been evaluated. Weight loss method, polarization study and AC impedance spectra have been employed to evaluate the corrosion resistance of SS 18/8 alloy in natural sea water, in presence of an inhibitor named Thiourea-Zn²⁺ system. Weight loss method reveals that Thiourea-Zn²⁺ system offers a maximum corrosion inhibition efficiency of 95% in controlling corrosion of SS 18/8 alloy in natural sea water. Synergism parameters are found to be greater than 1, confirming the synergistic effect existing between Thiourea-Zn²⁺. Adsorption of inhibitor molecules on the metal surface obey Langmuir adsorption isotherm. Polarisation study reveals that the inhibitors named Thiourea-Zn²⁺ system functions as mixed type of inhibitor. AC impedance spectra confirm the formation of a protective film on the metal surface. This formulation of Thiourea-Zn²⁺ may be used in cooling water systems where SS 18/8 alloy pipelines are used to carry sea water which is used as coolant. Also, Thiourea-Zn²⁺ 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.

Keywords: sea water corrosion, SS 18/8 alloy pipelines, SS 18/8 alloy hull plates, Thiourea-Zn²⁺ system, Langmuir adsorption isotherm

1. INTRODUCTION

Sea water is available in plenty. It can be used in cooling water systems. However, the aggressive ions present in sea water may corrode the pipelines made of mild steel and other materials. Several research works have been undertaken in this line. Many inhibitors have used to prevent the corrosion of metals. Shen et al. have investigated pitting corrosion inhibition effect on aluminum alloy in seawater by biomineralized film. It was noted that the bacteria promoted the formation of the CaMg (CO₃)₂ film, which blocked seawater from the alloy and consequently, inhibited pitting corrosion [1]. A barrier to inhibit bioadhesion and microbiologically induced corrosion has been studied by Ouyang et al. [2].

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The study revealed that by decreasing bio adhesion, the corrosion current density of Cu covered by liquid infused surface (LIS) in sulfate-reducing bacteria (SRB) medium has drastically decreased, suggesting the promising role for microbiologically induced corrosion (MIC) inhibition application [2]. Xu et al. have undertaken a study on steel rebar corrosion in artificial reef concrete with sulphoaluminate cement[3]. The study revealed that a 2% dosage of corrosion inhibitor can significantly decrease the steel rebar corrosion in new artificial reef concrete (NARC) to a corrosion degree of ordinary artificial reef concrete (ARC). The feasibility of using marine sand and seawater in **sulphoaluminate cement** (SAC)-based ARC is verified[3]. Soluble extracellular polymeric substances (s-EPS) secreted by *Bacillus cereus* (B. cereus) were studied as a novel, dual bio-functional corrosion and scale inhibiting material, in artificial seawater by Li et al.[4]. It has been suggested that B. cereus s-EPS may offer a green, sustainable, and economic strategy for anti-corrosion and anti-scale application in industry [4]. Elbasuney et al. have reported on the facile

synthesis of colloidal ZrO_2 nanoparticles with consistent product quality using continuous hydrothermal synthesis [5]. Colloidal ZrO_2 nanoparticles have been used for corrosion protection of AA2024.

A hydrothermal processing that offers effective fabrication of novel stable colloidal corrosion inhibitor where extensive surface area and reactivity were accomplished [5]. Erosion corrosion inhibition of 6061 aluminum alloy in artificial sea water in a jet impingement rig was studied using eco-friendly green inhibitor glucose amine sulfate by Lavanya et al. [6]. Potentiodynamic and electrochemical impedance techniques were employed for corrosion and inhibition studies. Surface morphology studies clearly demonstrated the efficacy of glucose amine sulfate in controlling the erosion corrosion of 6061 aluminum alloy [6].

Noorbakhsh Nezhad et al. have investigated the synergistic effect of two corrosion control strategies named, application of an inhibitor and enhancing the surface superhydrophobicity, for protection of electrodeposited nickel in saline solutions. For this purpose, 4-Mercaptopyridine (C_5H_5NS) was added to the synthetic sea water solution and its corrosion inhibition efficiency was evaluated on electrodeposited smooth bright nickel layer and nickel films with hierarchical micro/nano structure. Stearic acid was used to tune the wetting properties of nickel films, from hydrophilic to superhydrophobic. Contact angle measurement, scanning electron microscopy, and Fourier-transform infrared spectroscopy were utilized in the characterization of deposited nickel layers. Potentiodynamic polarization and electrochemical impedance spectroscopy were employed to assess the corrosion inhibition performance of inhibitor on different nickel films [7]. In the Arctic marine conditions, the problems of reliability and safety of marine corrosion protection systems are relevant. Reliability can be enhanced by corrosion inhibitors. For the equipment not subject to painting, safe technologies for preservation of water-based compounds are substantiated by bioassay methods. When carrying out painting work carried out by crew members at sea, a simplified chemical surface preparation was proposed with the phosphating compound with anode inhibitors. To increase the safety of work, hexavalent chromium compounds were removed [8]. Liu has reported on the corrosion inhibition performance of composite inhibitors for carbon steel in simulated seawater. It was observed that the concentration of tungstate inhibitor was too high, but the inhibition rate was very low when tungstate and molybdate are combined. When sodium citrate and molybdate were combined and tungstate was added, the corrosion inhibition rate of the composite inhibitor

increased obviously, but increased first and then decreased, indicating that there was an optimum ratio between sodium tungstate and sodium citrate, which made the inhibitor have a good synergistic effect [9]. Duduna et al. have compared various adsorption isotherm models for allium cepa as corrosion inhibitor on austenitic stainless steel in sea water. The corrosion inhibition study was carried out using weight loss method at room temperature. The values of inhibition efficiency increased with increasing concentration of the allium cepa extract. The values of the Gibbs free energy of adsorption obtained were negative indicating a spontaneous adsorption process. The mechanism of adsorption for the study was physisorption. The sorption data of the extract obeyed Langmuir, Freundlich, Temkin, El-Awady and Adejo Ekwenchi isotherm of which Langmuir Isotherm gave the best model fit [10].

The Hull of the ship is always in contact with sea water. So the hull material undergoes corrosion rapidly, since sea water contains about 3.5 % of sodium chloride. Chloride is the most dangerous culprit in the field of corrosion. The Hull of the ship may be constructed with stainless steel such as SS 18/8. The present study is undertaken to evaluate the corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor named Thiourea. Weight loss method, polarization study and AC impedance spectra will be employed to evaluate the corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor named Thiourea.

2. EXPERIMENTAL PROCEDURE

Corrosion resistance of SS 18/8 alloy in sea water in the absence and presence of inhibitor system [Thiourea (TU)- Zn^{2+}] has been investigated.

18/8 Grade Stainless Steel

This refers to the 300 series of Stainless Steel with a Chromium and Nickel content in percentages. That means that an 18/8 grade fastener has 18% Chromium and 8% Nickel content. 18/8 type stainless steel has better resistance to corrosion than the 400 series. It can be hardened only by cold working, and it is not magnetic.

Pros and Cons of 18/8 Grade Stainless Steel

18/8 grade stainless steel is celebrated for its superior corrosion resistance. However, it is known to show signs of corrosion when exposed to chlorides, such as salt. Therefore, it is not the ideal stainless steel to use for marine applications. On the up side, 18/8 grade stainless steel properties include the fact that it can be bent and moulded without it having an effect on its overall strength

and durability. This type of stainless steel is also not only extremely budget-friendly, but it also requires little to no maintenance. 18/8 stainless steel yield strength is also impressive.

Application of 18/8 Grade Stainless Steel

18/8 grade stainless steel is utilized within a number of different industries, including the wastewater treatment, restaurant and catering, medical, and transportation industries. It is not suitable for marine applications.

Thiourea

Thiourea (Figure 1) is an organosulfur compound with the formula $SC(NH_2)_2$. It is structurally similar to urea, except that the oxygen atom is replaced by a sulfur atom, but the properties of urea and Thiourea differ significantly.

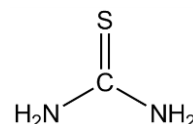


Figure 1. Structure of a Thiourea

Slika 1. Struktura tiouree

Structure and bonding

Thiourea is a planar molecule. The C=S bond distance is 1.71 Å. The C-N distances average 1.33 Å. The weakening of the C-S bond by C-N pi-bonding is indicated by the short C=S bond in thiobenzophenone, which is 1.63 Å.

Sea water

The composition of sea water used in this study is given in Table 1. Sea water was collected in Bay of Bengal, located at Kanampadi, East Coast Road, Chennai, India.

Table 1. Composition of Sea water (All the values, except pH, are in ppm)

Tabela 1. Sastav morske vode (Sve vrednosti, osim pH, su u ppm)

Physical Examination	Acceptable Limit	Permissible limit	Sample Value
1. Colour	-	-	Colourless & Clear
2. Odour	Unobjectionable		Unobjectionable
3. Turbidity NT Units	1	5	0.2
4. Total Dissolved Solids mg/l	500	2000	29400
5. Electrical Conductivity micro mho/cm	-	-	42000
Chemical Examination	Acceptable Limit	Permissible limit	Sample Value
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
Chemical Examination	Acceptable Limit	Permissible limit	Sample Value
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

Preparation of inhibitor solutions

Thiourea solution

1 g of Thiourea was dissolved in distilled water and made upto 100 ml. 1ml of this solution when diluted to 100 ml gives 100 ppm of Thiourea.

Zinc sulphate solution ($ZnSO_4 \cdot 7H_2O$)

1.1g of this salt was dissolved in water and made upto 250ml. 1ml of this solution diluted to 100ml gives 10 ppm of Zn^{2+} .

Weight loss method

Weights of the three polished SS 18/8 alloy specimens were measured before and after immersion in various test solutions. The inhibition efficiencies were calculated from the relation

$$IE = [(CR_1 - CR_2) / CR_1] 100 \%$$

where CR_1 is corrosion rate in the absence of inhibitor and CR_2 is the corrosion rate in the presence of inhibitor.

Electrochemical studies

In the present work corrosion resistance of SS 18/8 alloy specimens immersed in various test solutions were measured by Polarization study and AC impedance spectra.

Polarization study

Polarization studies were carried out in a CHI Electrochemical work station model 660A. It was provided with automatic iR compensation facility. A three electrode cell assembly was used (Figure 2).

The working electrode was SS 18/8 alloy. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = ba and cathodic = bc and LPR (linear polarisation resistance) value. The scan rate (V/S) was 0.01. Hold time at (E_{fcs}) was zero and quiet time (s) was 2.

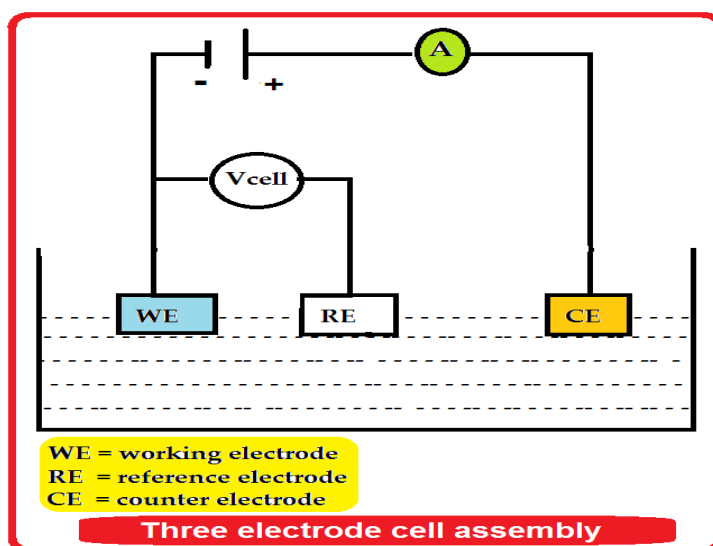


Figure 2. Three electrode cell assembly

Slika 2. Sklop ćelije sa tri electrode

AC Impedance spectra

The same instrument and set-up used for polarization study was used to record AC impedance spectra also. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initial $E(v) = 0$, high frequency ($Hz = 1 \times 10^5$), low frequency ($Hz = 1$), amplitude (V) = 0.005 and quiet time (s) = 2. From Nyquist plot the values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

Langmuir adsorption isotherm

There are various types of adsorption isotherms such as Langmuir, Freundlich and Temkin. In the case of Langmuir adsorption

isotherm a plot of C vs C/θ gives a straight line. Where C is concentration of the inhibitor and θ is surface coverage which is equal to $\% IE/100$.

3. RESULTS AND DISCUSSION

The present study is undertaken to evaluate the corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor named Thiourea. Weight loss method, polarization study and AC impedance spectra have been employed to evaluate the corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor named Thiourea. The experimental data collected are presented and discussed scientifically in this section under the following headings and useful conclusions are derived from the interpretation of the experimental data.

Analysis of results of weight loss method

Corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor Thiourea (TU) + Zn²⁺ has been evaluated by weight loss method. The results are given in Tables 2 and 3.

Table 2. Inhibition of corrosion of SS 18/8 immersed in sea water, Inhibitor system: Thiourea (TU) + Zn²⁺, Immersion period: 1 day

Tabela 2. Inhibicija korozije SS 18/8 uronjenog u morsku vodu, Sistem inhibitora: Thiourea (TU) + Zn²⁺, Period potapanja: 1 dan

Thiourea (ppm)	Zn ²⁺ (ppm)	Corrosion rate (mdd)	Inhibition Efficiency (%)	Surface coverage (θ)
0	0	15.25	-	
50	0	12.05	21	0.21
60	0	11.29	26	0.26
70	0	10.52	31	0.31
80	0	9.76	36	0.36
90	0	8.99	41	0.41
100	0	8.24	46	0.46

Table 3. Inhibition of corrosion of SS 18/8 immersed in sea water, Inhibitor system: Thiourea (TU) + Zn²⁺, Immersion period: 1 day

Tabela 3. Inhibicija korozije SS 18/8 uronjenog u morsku vodu, Sistem inhibitora: Thiourea (TU) + Zn²⁺, Period potapanja: 1 dan

Thiourea (ppm)	Zn ²⁺ (ppm)	Corrosion rate (mdd)	Inhibition Efficiency (%)	Surface coverage (θ)
0	0	15.25	-	
50	50	4.58	70	0.70
60	50	3.66	76	0.76
70	50	3.20	79	0.79
80	50	2.44	84	0.84
90	50	1.68	89	0.89
100	50	0.76	95	0.95
0	50	12.96	15	0.15

It is observed from the Tables 2 and 3 that Thiourea (TU) has some inhibition efficiency (IE). As the concentration of TU increases, Surface coverage (θ) increases, corrosion rate (CR, mdd)

decreases and inhibition efficiency (IE,%) increases (Figure 3).

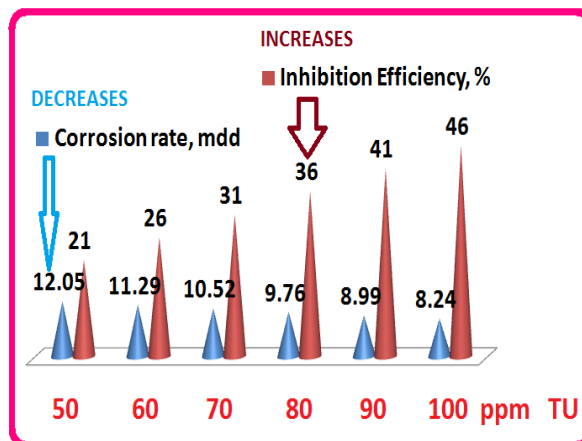


Figure 3. Correlation among concentration of Thiourea (TU), Corrosion Rate (CR, mdd) and Inhibition Efficiency (IE, %)

Slika 3. Korelacija između koncentracije Thiourea (TU), brzine korozije (CR, mdd) i efikasnosti inhibicije (IE,%)

Influence of addition of Zn²⁺ on the inhibition efficiency (IE, %) of Thiourea (TU)

Influence of addition of Zn²⁺ on the inhibition efficiency (IE, %) of Thiourea (TU) is given in Table 3. It is observed that in presence of 50 ppm of Zn²⁺, the inhibition efficiency (IE, %) of Thiourea (TU) increases tremendously. A synergistic effect exists between Thiourea and Zn²⁺. A mixture of inhibitors shows better inhibition efficiency (IE, %) than that of individual members (Scheme A).

Synergistic Effect

"A mixture of inhibitors shows better inhibition efficiency (IE, %) than that of individual members"

Scheme A. Synergistic effect

Šema A. Sinergijski efekat

For example, 50 ppm of Zn²⁺ has 15% inhibition efficiency. 100 ppm of Thiourea (TU) has 46% inhibition efficiency. But their combination has 95% inhibition efficiency. This confirms the synergistic effect existing between Thiourea and Zn²⁺ (Figure 4).

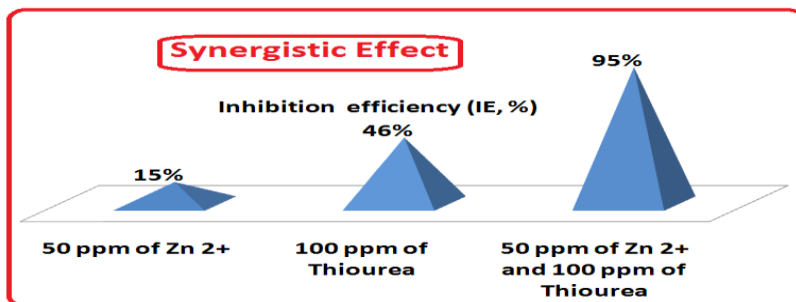


Figure 4. Synergistic effect existing between Thiourea and Zn²⁺

Slika 4. Sinergijski efekat koji postoji između Thiouree i Zn²⁺

Corrosion rate, inhibition efficiency and surface coverage

When surface coverage increases, corrosion rate decreases and inhibition efficiency increases (Figures 5 and 6).

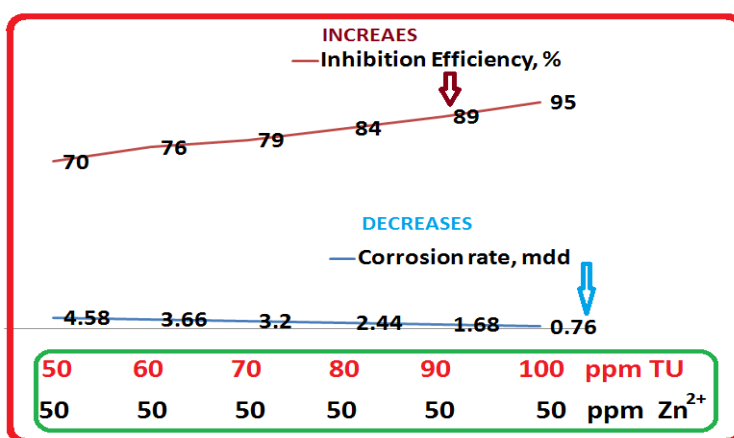


Figure 5. Inhibition efficiency and corrosion rate existing between Thiourea and Zn²⁺

Slika 5. Efikasnost inhibicije i brzina korozije koja postoji između Thiouree i Zn²⁺

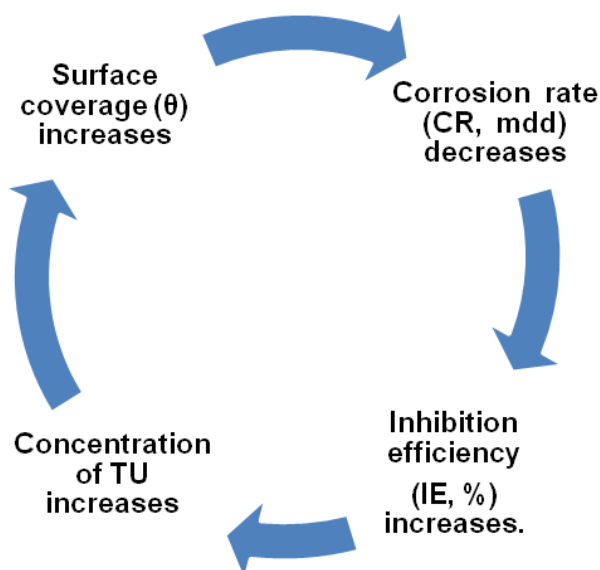


Figure 6. Correlation among Concentration of Thiourea (TU), Corrosion Rate (CR, mdd) and Inhibition Efficiency (IE, %)

Slika 6. Korelacija između koncentracije Thiourea (TU), brzine korozije (CR, mdd) i efikasnosti inhibicije (IE, %)

Synergism parameters

When two substances are used as corrosion inhibitors, synergistic effect is noticed between them. That is, "A mixture of inhibitors shows better inhibition efficiency (IE, %) than that of individual members". To confirm this Synergism parameters (S_i) are calculated using the relation

$$S_i = (1 - \theta_{1+2}) / (1 - \theta'_{1+2})$$

where

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \times \theta_2)$$

θ_1 = surface coverage by inhibitor 1

θ_2 = surface coverage by inhibitor 2

θ'_{1+2} = Combined surface coverage by inhibitors 1 and 2.

If there is synergistic effect, the Synergism parameter (S_i) will be greater than 1. The Synergism parameters (S_i) calculated for various combinations of [Thiourea] and [Zn^{2+}] given in Table 4.

It is observed that the Synergism parameters (S_i) are greater than 1, indicating, synergistic effect existing between Thiourea and Zn^{2+} . The mechanism of synergistic effect can be explained as follows.

Mechanism of synergistic effect

- When Thiourea (TU) and Zn^{2+} are mixed in the solution, TU- Zn^{2+} complex is formed in solution.
- When mild steel is immersed in this solution (containing sea water), Fe^{2+} is released on the anodic sites of the metal surface.
- TU - Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.
- On the metal surface, Fe^{2+} - TU complex is formed on the anodic sites of the metal surface. Zn^{2+} is released.
- The released Zn^{2+} combines with OH^- formed on the cathodic sites of the metal surface to precipitate as insoluble $Zn(OH)_2$
- $Zn^{2+} + 2 OH^- \rightarrow Zn(OH)_2$
- Thus the anodic reaction of metal dissolution ($Fe \rightarrow Fe^{2+} + 2e^-$) is controlled by the formation of Fe^{2+} - TU complex on the anodic sites of the metal surface.
- The cathodic reaction of formation of OH^- ($4e^- + 2H_2O + O_2 \rightarrow 4OH^-$) is controlled by the formation of insoluble $Zn(OH)_2$ on the cathodic sites of the metal surface as precipitate.
- Thus anodic reaction and cathodic reaction in a corrosion process in a neutral (alkaline) medium is controlled.
- This accounts for the synergistic effect and higher inhibition efficiency (IE, %) offered by the Thiourea (TU) - Zn^{2+} system.

Table 4. Synergism parameters

Tabela 4. Parametri sinergizma

TU, ppm	θ_1	θ'_{1+2}	θ_2	θ_{1+2}	S_i
50	0.21	0.70	0.15	0.3285	2.24
60	0.26	0.76	0.15	0.3710	2.62
70	0.31	0.79	0.15	0.4135	2.79
80	0.36	0.84	0.15	0.4560	3.4
90	0.41	0.89	0.15	0.4985	4.56
100	0.46	0.95	0.15	0.5410	9.18

Langmuir adsorption isotherm

The formation of protective film on the metal surface is due to adsorption of inhibitor molecules on the metal surface. This adsorption obeys various adsorption isotherm processes such as Langmuir and Freundlich. In Langmuir adsorption isotherm, a straight line is obtained when a "C vs C/ θ " is made. Here, C is the concentration of the inhibitor and θ is surface coverage.

In the present study, Langmuir adsorption isotherms were plotted for Thiourea system and Thiourea (TU) - Zn^{2+} system.

Thiourea system

The data needed for the isotherm are given in Tables 5 and 6. The plot of "C vs C/ θ " gives a straight line with R^2 value of 0.949. Thus it is inferred that the adsorption Thiourea on the metal surface obeys Langmuir adsorption isotherm (Figure 7).

Table 5. Data for Langmuir adsorption isotherm

Tabela 5. Podaci za Langmuirovu adsorpcionu izotermu

C, ppm	IE, %	Surface coverage, θ	C/ θ
50	21	0.21	238.09
60	26	0.26	230.77
70	31	0.31	225.81
80	36	0.36	222.22
90	41	0.41	219.51
100	46	0.46	217.39

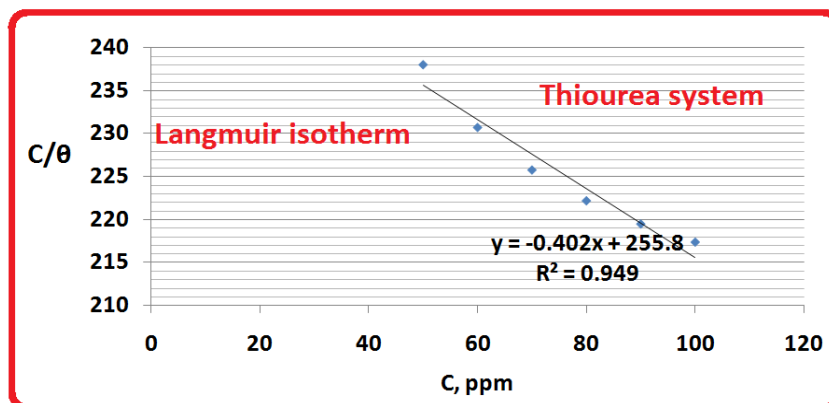


Figure 7. Langmuir adsorption isotherm for Thiourea (TU) system
 Slika 7. Langmuirova adsorpciona izoterma za sistem Thiourea (TU)

Table 6. Data for Langmuir adsorption isotherm C, ppm vs C/θ

Tabela 6. Podaci za Langmuirovu adsorpcionu izoterma: C, ppm u odnosu na C / θ

C, ppm	C/θ
50	238.09
60	230.77
70	225.81
80	222.22
90	219.51
100	217.39

Thiourea (TU) - Zn²⁺ system

The data needed for the isotherm are given in Tables 7 and 8. The plot of “C Vs. C/ θ” gives a straight line with R² value of 0.983. Thus it is inferred that the adsorption of Thiourea, in presence of Zn²⁺, on the metal surface obeys Langmuir adsorption isotherm.

Table 7. Data for Langmuir adsorption isotherm for Thiourea (TU) - Zn²⁺ system

Tabela 7. Podaci za Langmuirovu adsorpcionu izoterma za sistem Thiourea (TU) - Zn²⁺

C, ppm	IE, %	Surface coverage, θ	C/θ
50	70	0.70	71.43
60	76	0.76	78.95
70	79	0.79	88.61
80	84	0.84	95.24
90	89	0.89	101.12
100	95	0.95	105.26

Table 8. Data for Langmuir adsorption isotherm for Thiourea (TU)-Zn²⁺ system (C,ppm vs C/θ)

Tabela 8. Podaci za Langmuirovu adsorpcionu izoterma za sistem Thiourea (TU) - Zn²⁺ (C, ppm vs C/θ)

C, ppm	C/θ
50	71.43
60	78.95
70	88.61
80	95.24
90	101.12
100	105.26

Electrochemical studies

Electrochemical studies such as polarization study and AC impedance spectra have been used in corrosion inhibition studies [11-24].

Analysis of Polarisation curves

Corrosion parameters derived from polarisation study, named corrosion potential (E_{corr}, Tafel slope (b_c, b_a), Linear Polarisation Resistance (LPR) values and Corrosion Current (I_{corr}) values are given in Table 9.

The polarisation curves of SS 18/8 alloy immersed in sea water (SW) in the absence and presence of inhibitor system are shown in Figure 9.

It is observed from the Table 9 that when SS 18/8 Alloy is immersed in SW, the corrosion potential is -0.610V Vs SCE; the LPR value is 31825 ohm cm². The corrosion current value is 1.419 x 10⁻⁶A/cm². It is inferred from the table, that in presence of inhibitor, the corrosion potential is shifted from -0.610V to -0.582V vs SCE. This is a small shift. The shift is within 50 mV. It suggests that the inhibitor system (Thiourea -Zn²⁺) functions as mixed inhibitor system. That is the inhibitor

system controls both anodic reaction and cathodic reaction to an equal extent.

The LPR value increases (Figures 10 and 11) from 31825 ohmcm² to 50734 ohmcm². Correspondingly the corrosion current value decreases from 1.419 × 10⁻⁶ A/cm² to 8.835 × 10⁻⁷ A/cm².

These observations confirm that a protective film is formed on the metal surface. This controls the corrosion of metal. If a protective film is formed on the metal surface, LPR value increases and corrosion current decreases.

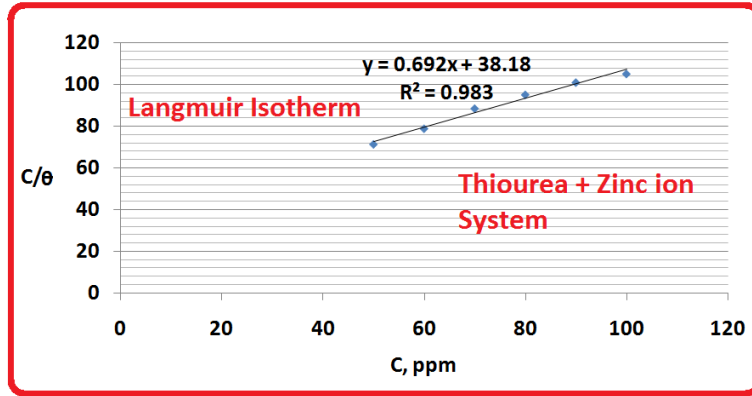


Figure 8. Langmuir adsorption isotherm for Thiourea (TU) - Zn²⁺ system
 Slika 8. Langmuirova adsorpciona izoterma za sistem Thiourea (TU) - Zn²⁺

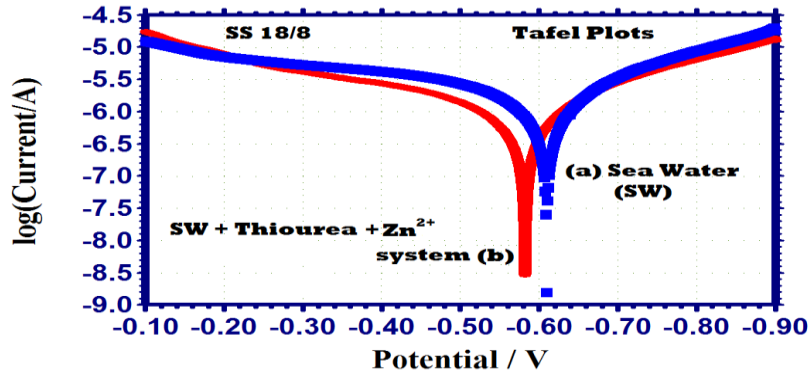


Figure 9. Tafel plots of various test solutions
 Slika 9. Tafelov prikaz različnih rešenja ispitivanja

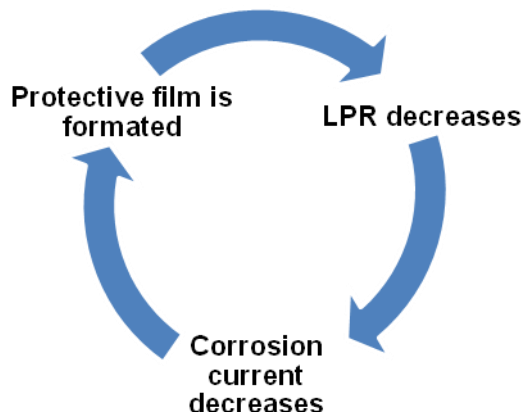


Figure10. Correlation among corrosion parameters
 Slika10. Korelacija među parametrima korozije

Table 9. Corrosion parameters of mild steel immersed in sea water in the absence and presence of inhibitor system [Thiourea (TU) –Zn²⁺] obtained by Polarization study

Tabela 9. Parametri korozije mekog čelika uronjenog u morsku vodu u odsustvu i prisustvu sistema inhibitora [Thiourea (TU) –Zn²⁺] dobijeni studijom polarizacije

System	E _{corr} V _{SCE}	b _c V/decade	b _a V/decade	LPR Ohmcm ²	I _{corr} A/cm ²
Sea water	-0.610	5.735	3.895	31825	1.419 × 10 ⁻⁶
Sea water+ TU(100ppm)+ Zn ²⁺ (50ppm)	-0.582	5.591	4.108	50734	8.835 × 10 ⁻⁷

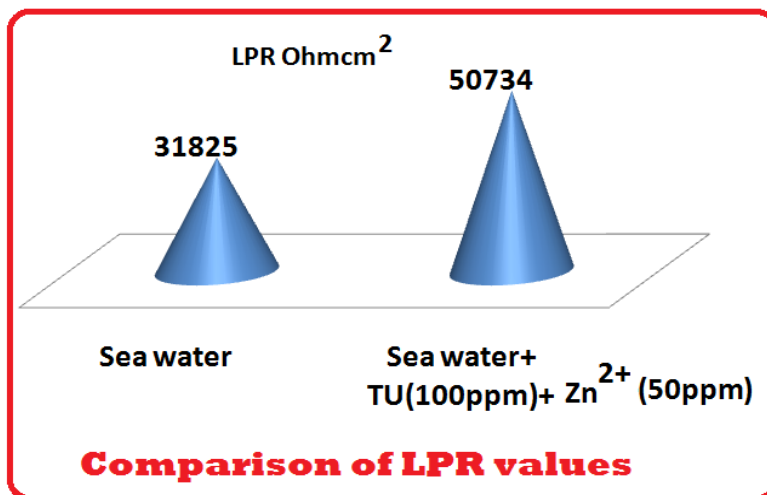


Figure 11. Comparison of LPR values between Thiourea and Zn²⁺

Slika 11. Poređenje vrednosti LPR između Thiouree i Zn²⁺

Analysis of AC impedance spectra

The protective film formed on the metal surface is confirmed by AC impedance spectra. If a protective film is formed on the metal surface, the charge transfer resistance (R_t) value increases; double layer capacitance value (C_{dl}) decreases and the impedance [log (Z/ohm)] value increases (Figures 12 and 13).

The AC impedance spectra of SS 18/8 alloy immersed in sea water (SW) in the absence and presence of inhibitor [Thiourea (TU)–Zn²⁺] are shown in Figure 14 (Nyquist plot), Figures 15 and 16 (Bode plots). The corrosion parameters, named R_t, C_{dl} and impedance values are given in Table 10. It is observed from the Table 10 that, when SS 18/8 Alloy is immersed in SW, the R_t value is 9736 Ohmcm². The C_{dl} value is 1.027x10⁻⁸F/cm². The impedance value is 4.084 Z/ohm. In the presence of inhibitor system, the R_t value increases (Figure 11) from 9736 ohmcm² to 11980 ohmcm². The C_{dl} value decreases from 1.027x10⁻⁸ F/cm² to 8.347x10⁻⁹ F/cm². The impedance value increases from 4.084to 4.153 Z/ohm.

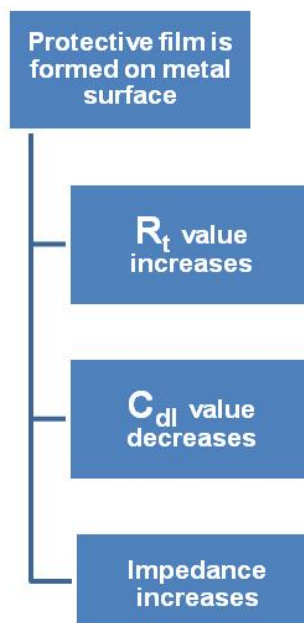


Figure12. Correlation among various AC impedance parameters

Slika12. Korelacija između različitih parametara impedance AC

Implication

SS 18/8 alloy samples were immersed in SW with inhibitor system [Thiourea (TU)–Zn²⁺] to evaluate corrosion inhibition efficiency of the inhibitor system. The inhibition efficiency increases with the increase in concentration of Thiourea. Inhibition efficiency up to 95% for SS 18/8 alloy was achieved. The results indicated that the corrosion rate decreases, as the concentration of TU inhibitor increases and simultaneously it enhances the inhibition efficiency of the samples.

This discovery may find application in cooling water systems where sea water is used as coolant and SS 18/8 alloy pipe lines are used. To prevent corrosion of mild steel pipelines carrying sea water, the inhibitor system [Thiourea (TU)–Zn²⁺] may be added, along with sea water. Further, when SS 18/8 alloy is used for making hull plates in shipping industry, a spray of Thiourea (TU)–Zn²⁺ coating on SS 18/8 alloy is recommended to prevent its corrosion when it comes in contact with sea water.

Table 10. Corrosion parameters of SS 18/8 alloy immersed in sea water in the absence and presence of inhibitor system [Thiourea (TU) –Zn²⁺] obtained by AC impedance spectra

Tabela 10. Parametri korozije legure SS 18/8 uronjene u morsku vodu u odsustvu i prisustvu sistema inhibitora [Thiourea (TU) –Zn²⁺] dobijeni spektrima AC impedanse

System	R _t Ohmcm ²	C _{dl} F/cm ²	Impedance Log (Z/Ohm)
Sea water	9736	1.027 × 10 ⁻⁸	4.084
Sea water+ TU (100 ppm)+ Zn ²⁺ (50 ppm)	11980	8.347 × 10 ⁻⁹	4.153

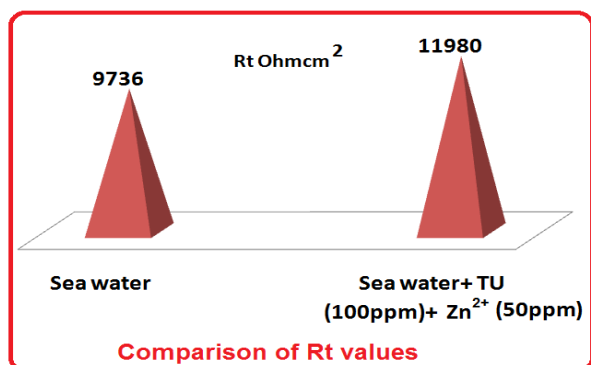


Figure 13. Comparison of Rt values
Slika 13. Poređenje vrednosti Rt

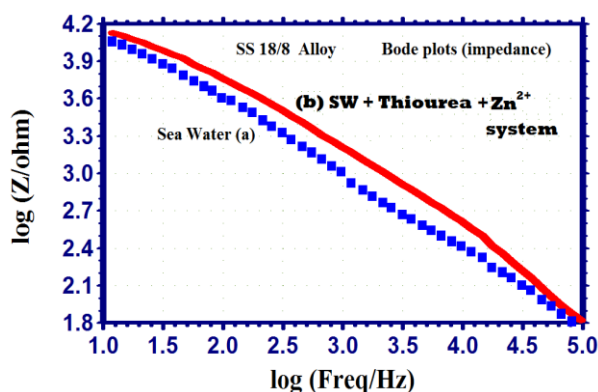


Figure 15. Bode plots (Impedance)
Slika 15. Bode krive (impedansa)

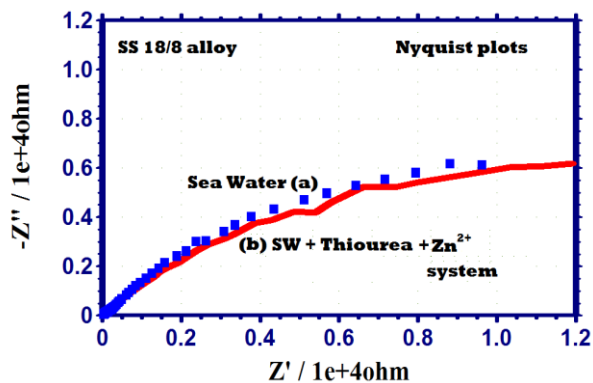


Figure 14. Nyquist plots
Slika 14. Nyquist krive

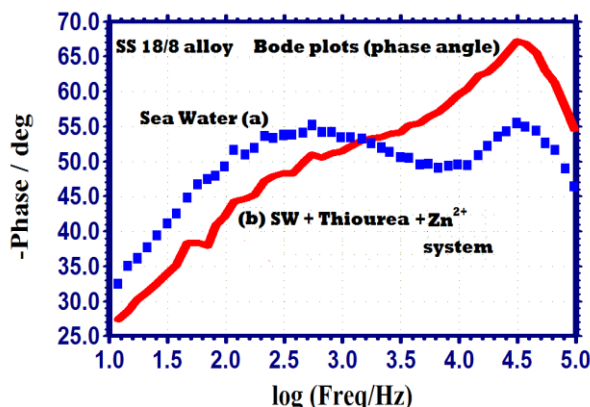


Figure 16. Bode plots (phase angle)
Slika 16. Bode krive (fazni ugao)

4. CONCLUSIONS

The present study has been undertaken to evaluate the corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor named Thiourea-Zn²⁺. Weight loss method, polarization study and AC impedance spectra have been employed to evaluate the corrosion resistance of SS 18/8 alloy in natural sea water, in presence of an inhibitor named Thiourea-Zn²⁺ system. The experimental data were collected and discussed scientifically.

Useful conclusions are derived from the interpretation of the experimental data:

1. Weight loss method reveals that Thiourea-Zn²⁺ system offers a maximum corrosion inhibition efficiency of 95% in controlling corrosion of SS 18/8 alloy in natural sea water,
2. Synergism parameters are found to be greater than 1, confirming the synergistic effect existing between Thiourea-Zn²⁺.
3. Langmuir adsorption isotherm: Adsorption of inhibitor molecules on the metal surface obey Langmuir adsorption isotherm.
4. Polarisation Study reveals that the inhibitors named Thiourea-Zn²⁺ system functions as mixed type of inhibitor.
5. AC impedance spectra confirm the formation of a protective film on the metal surface.
6. This formulation of Thiourea-Zn²⁺ may be used in cooling water systems where SS 18/8 alloy pipelines are used to carry sea water which is used as coolant.

Scope for further study

The present study has been undertaken to evaluate the corrosion resistance of SS 18/8 in natural sea water, in presence of an inhibitor named Thiourea-Zn²⁺. Weight loss method, polarization study and AC impedance spectra have been employed to evaluate the corrosion resistance of SS 18/8 alloy in natural sea water, in presence of an inhibitor named Thiourea-Zn²⁺ system. In future the following investigations can be carried out.

- Instead of SS 18/8 alloy, other alloys such as SS 316 alloy, mild steel etc can be used.
- Instead of sea water, ground water or rain water or well water can be used.
- Contact angle measurement can be made to know the hydrophobic nature of the protective film.
- The protective film can be analyzed by FTIR and AFM, SEM and EDAX.

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IZVOD

INHIBICIJA KOROZIJE LEGURE SS 18/8 U MORSKOJ VODI SISTEMOM THIOUREA-Zn²⁺

Procenjena je otpornost korozije SS 18/8 u prirodnoj morskoj vodi, u prisustvu inhibitora Thiourea-Zn²⁺. Za procenu otpornosti na koroziju legure SS 18/8 u prirodnoj morskoj vodi, u prisustvu inhibitora Thiourea-Zn²⁺ korišćeni su metod gubitka težine, studija polarizacije i spektri AC impedanse. Metoda gubitka težine otkriva da Thiourea-Zn²⁺ sistem nudi maksimalnu efikasnost inhibicije korozije od 95% u kontroli korozije legure SS 18/8 u prirodnoj morskoj vodi. Utvrđeno je da su parametri sinergizma veći od 1, što potvrđuje sinergijski efekat koji postoji između Thiourea-Zn²⁺. Adsorpcija molekula inhibitora na površini metala podleže Langmuir-ovoj adsorpcionoj izotermi. Studija polarizacije otkriva da inhibitori Thiourea-Zn²⁺ sistem funkcionišu kao mešani tip inhibitora. Spektri AC impedanse potvrđuju stvaranje zaštitnog filma na metalnoj površini. Ova formulacija Thiourea-Zn²⁺ može se koristiti u sistemima za hlađenje vodom gde se legirani cevovodi SS 18/8 koriste za transport morske vode, koja se koristi kao rashladna tečnost. Takođe, premaz Thiourea-Zn²⁺ može se naneti na leguru SS 18/8 da bi se zaštitio od korozije morskom vodom kada se legura SS 18/8 koristi kao ploče trupa u brodskoj industriji.

Ključne reči: korozija morske vode, legirani cevovodi SS 18/8, legurne ploče trupa SS 18/8, sistem Thiourea-Zn²⁺, izoterma Langmuir-ove adsorpcije.

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