Pooviah Shanthy[1], Karunaivel Kavipriya[2], Arockiasamy Santhiya Brintha[1,3], Ganesan Priyanka[1], Krishnasamy Vigneswari[1], Veerapandian Velkannan[4], Gurmeet Singh[5], Abdulhameed Al-Hashem[6], Anitha Nilavan[7], Susai Rajendran[7,8], Caslav Lacnjevac[9]*

[1]PG Department of Chemistry, Sri Meenakshi Government Arts College for Women (Autonomous), Madurai, India, [2]Department of Chemistry, PSNA College of Engineering and Technology, Dindigul, India, [3]Department of Chemistry, Sacred Heart College of Arts and Science, Dindigul, India, [4]Department of Chemistry, Thiagarajar College of Engineering, Thiruparankundram, Madurai, Tamil Nadu, India, [5]Vice Chancellor, Pondicherry University, Puducherry, India, [6]Petroleum Research Centre, Kuwait Institute for Scientific Research, Kuwait, [7]Department of Chemistry, Corrosion Research Centre , St. Antony's College of Arts and Sciences for Women, Dindigul-624005(Mother Teresa Women's University,Kodaikanal, India), [8]Adjunct Professor, Centre for Nanoscience and Technology, Pondicherry University, Puducherry, India, [9]Faculty of Agriculture, University of Belgrade, Serbia.

Scientific paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.5937/zasmat2204447S

Zastita Materijala 63 (4)
447 - 453 (2022)

Influence of thiourea on the corrosion resistance of mild steel immersed in simulated concrete pore solution

ABSTRACT

The corrosion resistance of mild steel in simulated concrete pore solution (SCPS) in the absence and presence of thiourea has been investigated by polarization study and AC impedance spectra. Polarisation study reveals that thiourea system functions as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. When mild steel is used as rebar, thiourea may be mixed with concrete. Thus the mild steel will be protected from corrosion. The protective film consists of iron-thiourea complex formed on metal surface. In the presence of thiourea the linear polarisation resistance increases, corrosion current decreases, charge transfer resistance (R_t) increases, impedance increases, phase angle increases and double layer capacitance (C_{dl}) value decreases. This formulation may find application in concrete technology.

Keywords: *thiourea, corrosion resistance, mild steel, simulated concrete pore solution, electrochemical studies*

1. INTRODUCTION

In concrete structures mild steel rebars are used. To increase the life time of the rebars many inhibitors have been used. Multiscale modeling of steel corrosion in concrete based on micropore connectivity has been investigated by Ohno et al. [1]. Ming et al. have studied the Effects of stray current and silicate ions on electrochemical behavior of a high-strength prestressing steel in simulated concrete pore solutions [2]. Behera et al. have studied Corrosion behavior of bent plain reinforcing bars used in concrete [3]. Study of the effectiveness of realkalisation treatment on reinforcement repassivation by using simulated concrete pore solution has been reported by Carvalho et al. [4].

Nanostructured Poly(methyl Methacrylate)-Silica Coatings for Corrosion Protection of Reinforcing Steel is recommended by Uvida et al. [5]. Jin et al. have analysed the Comprehensive properties of passive film formed in simulated pore solution of alkali-activated concrete [6]. Sajid et al. have reported the use of Soy-protein and corn-derived polyol based coatings for corrosion mitigation in reinforced concrete [7]. Liu et al. have investigated the Corrosion Behavior of Steel Subjected to Different Corrosive Ions in Simulated Concrete Pore Solution [8]. Passivation and depassivation properties of Cr–Mo alloyed corrosion-resistant steel in simulated concrete pore solution have been reported by Jin et al.[9]. Naderi et al. have reported the use of licorice plant extract for controlling corrosion of steel rebar in chloride-polluted concrete pore solution [10].

In the present study, the influence of thiourea [11,12] on the corrosion resistance of mild steel immersed in simulated concrete pore solution has

*Corresponding author: Santhiya Brintha
E-mai: susairajendran@gmail.com
Paper received: 10. 05. 2022.
Paper accepted: 28. 05. 2022.
Paper is available on the website: www.idk.org.rs/journal

been evaluated by electrochemical studies, such as polarization study and AC impedance spectra.

2. EXPERIMENTAL

Preparation of Simulated Concrete Pore Solution (SCPS)

Generally, simulated concrete pore solution consisted mainly of saturated $Ca(OH)_2$, KOH, NaOH with the pH 13.5. But in our present study, a saturated solution of calcium hydroxide alone is used as SCP solution.

Inhibitor

200 ppm of thiourea is used as corrosion inhibitor.

Electrochemical studies

The corrosion resistance of mild steel 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 = b_a andcathodic = b_c) 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 impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated from Nyquist plots and Bode plots

3. RESULTS AND DISCUSSION

Analysis of polarisation curves

Polarisation study has been used to detect the formation of protective film on the metal surface. When a protective film formed on the metal surface, the linear polarisation resistance (LPR) increases and the corrosion current (I_{corr}) decreases [13-27]. The potentiodynamic polarisation curves of mild steel immersed in various test solutions are shown in Figures 1 and 2.

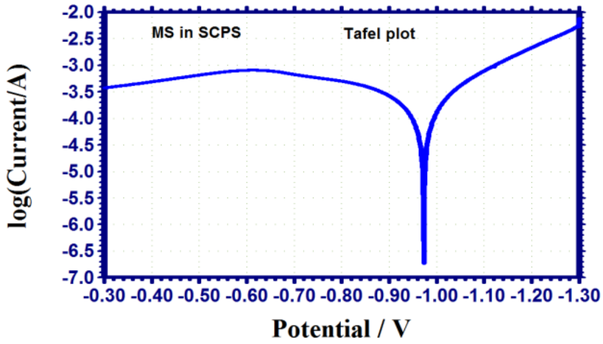

Figure 1. Potentiodynamic polarisation curve of mild steel immersed in SCPS

Slika 1. Potenciodinamička polarizaciona kriva mekog čelika uronjenog u SCPS

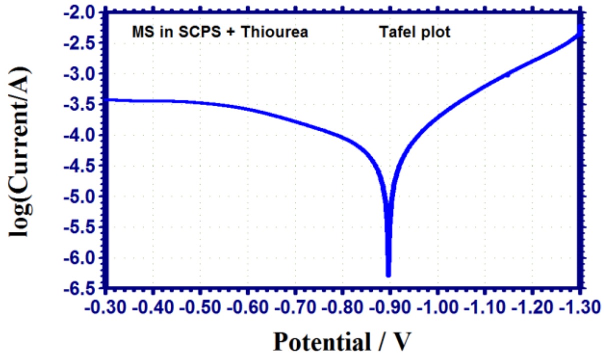

Figure 2. Potentiodynamic polarisation curve of mild steel immersed in SCPS + thiourea.

Slika 2. Potenciodinamička polarizaciona kriva mekog čelika uronjenog u SCPS + tiourea

The corrosion parameters namely, corrosion potential (E_{corr}), Tafel slopes (b_c= cathodic; b_a= anodic) linear polarisation resistance (LPR) and the corrosion current (I_{corr}) are given in Table1. They are compared in Figure 3.

Table 1. Corrosion Parametres of mild steel immersed in various test solutions containing SCPS obtained by polarisation study

Tabela 1. Parametri korozije mekog čelika uronjenog u različite test rastvore koji sadrže SCPS dobijeni polarizacionom studijom

System	E_{corr}, mV/SCE	b_c, mV/decade	b_a, mV/decade	LPR, Ohmcm^2	I_{corr}, A/cm^2
SCPS	-973	165	248	226	1.901x10^{-4}
SCPS + Thiourea 200 ppm	-897	148	261	778	0.5262x10^{-4}

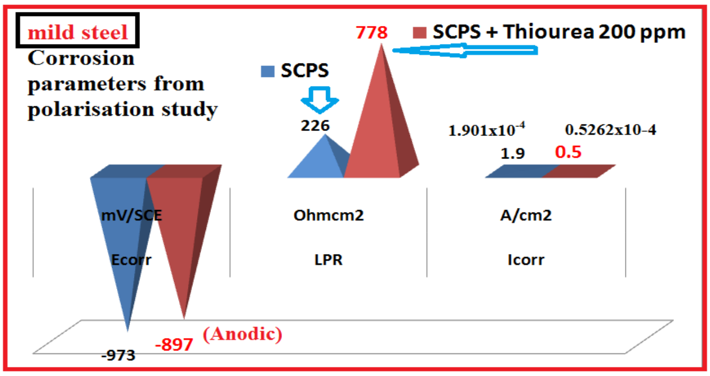

Figure 3. Comparison of corrosion parameters from polarization study

Slika 3. Poređenje parametara korozije iz studije polarizacije

Influence of thiourea on the corrosion résistance of mild steel immersed in SCPS

The formulation consisting of 200 ppm of thiourea shifts the corrosion potential to from -973 to -897 mV vs SCE. The corrosion potential is shifted to anodic side. This indicates that the anodic reaction is controlled predominantly. The LPR value increases from 226 to 778 ohmcm^2, and the corrosion current decreases from 1.901x10^{-4} to 0.5262x10^{-4} A/cm^2. In the presence of inhibitor, LPR value increases and corrosion current decreases (Figure 3). These results suggest that a protective film is formed on the metal surface and probably the protective film consists of Fe^{2+}-inhibitor complex apart from $CaCO_3$ and CaO.

AC impedance spectra

AC impedance spectra have been used to detect the formation of the film formed on the metal surface. If the protective film is formed, the charge transfer resistance (R_t) increases, impedance increases, phase angle increases and double layer capacitance (C_{dl}) value decreases. The AC Impedance spectra of mild steel immersed in various solutions are shown in Figures 4-9. The corrosion parameters are compared in Figure 10.

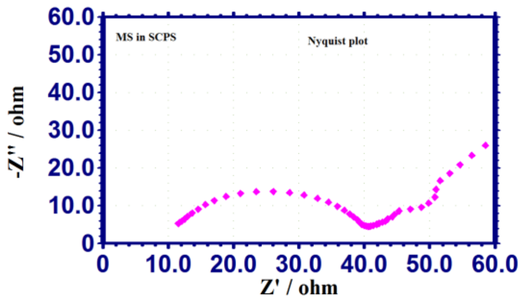

Figure 4. Nyquist plot of mild steel immersed in SCPS

Slika 4. Nyquist-ova kriva mekog čelika uronjen u SCPS

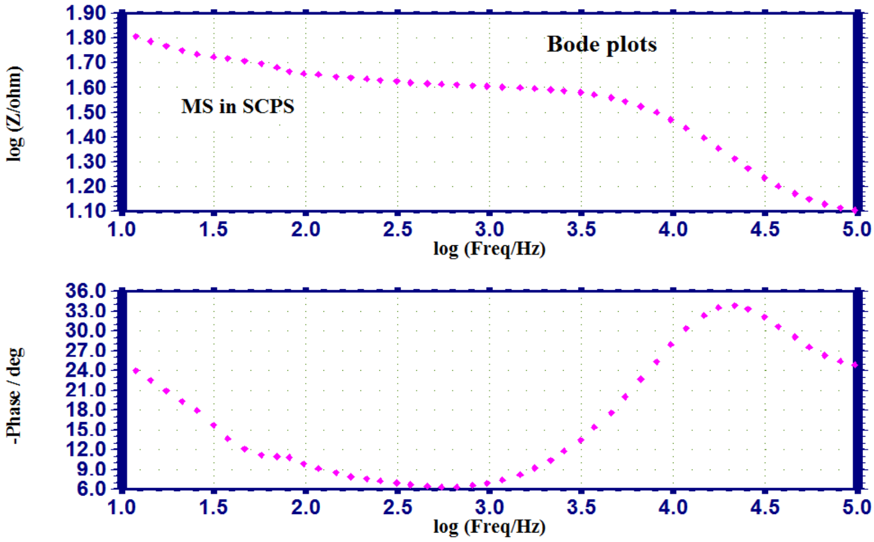

Figure 5. Bode plots of mild steel immersed in SCPS

Slika 5. Bode-ova kriva mekog čelika uronjenog u SCPS

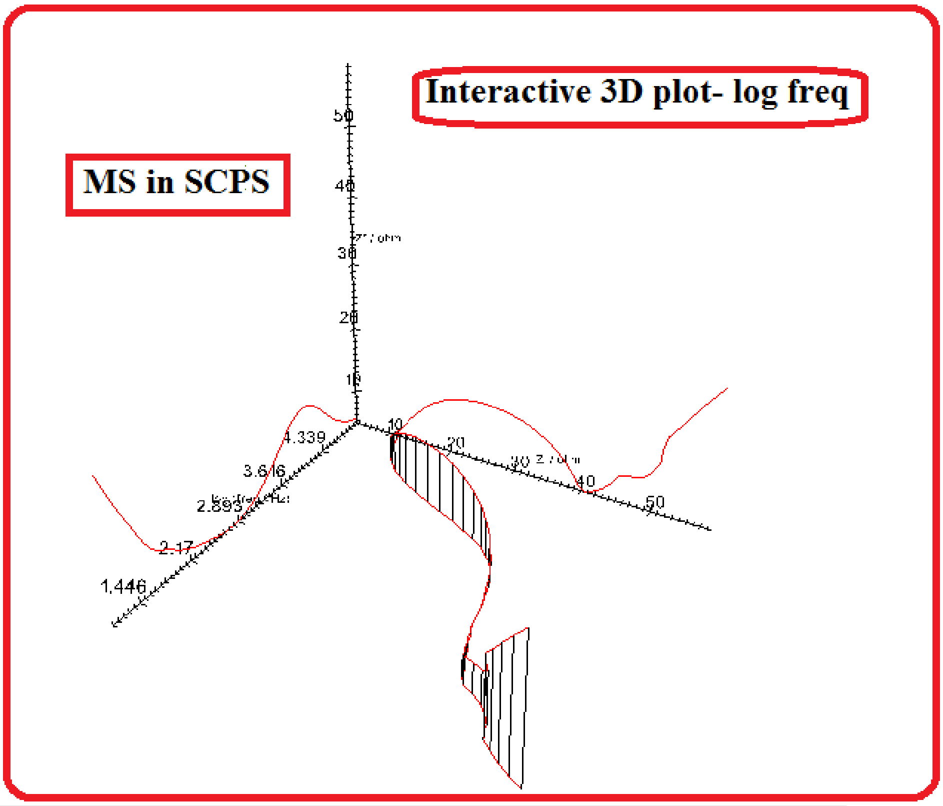

Figure 6. Interactive 3D plot for mild steel immersed in SCPS

Slika 6. Interaktivna 3D grafika za meki čelik uronjenog u SCPS

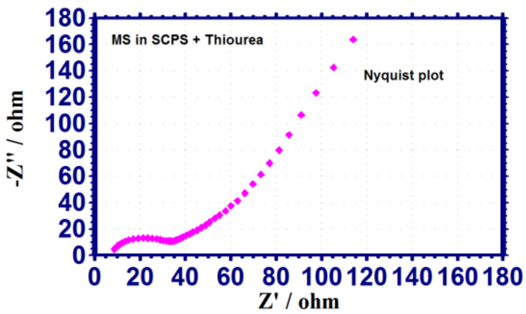

Figure 7. Nyquist plot of mild steel immersed in SCPS+ Thiourea

Slika 7. Nyquist-ova kriva mekog čelika uronjenog u SCPS + tiourea

The AC Impedance parameters, namely charge transfer resistance (R_t), impedance, phase angle and double layer capacitance (C_{dl}) are given in Table 2. It is observed from the Table 2 that when mild steel is immersed in simulated concrete pore (SCPS) solution, the charge transfer resistance (R_t) increases, impedance increases, phase angle increases and double layer capacitance (C_{dl}) value decreases (Figure 10). These results suggest that a protective film is formed on the metal surface and probably the protective film consists of Fe^{2+}-inhibitor complex apart from $CaCO_3$ and CaO.

Table 2. Corrosion Parameters of mild steel immersed in various test solutions containing SCPS obtained by AC Impedance spectra

Tabela 2. Parametri korozije mekog čelika uronjenog u različite test rastvore koji sadrže SCPS dobijeni spektrom naizmenične impedanse

System	R_t Ohmcm^2	C_{dl} F/cm^2	Impedance Log(Z/ohm)	Phase angle°
SCPS	48.1	1.060 x10^{-7}	1.817	34.34
SCPS + Thiourea 200 ppm	108.6	0.4696 x10^{-7}	2.328	38.83

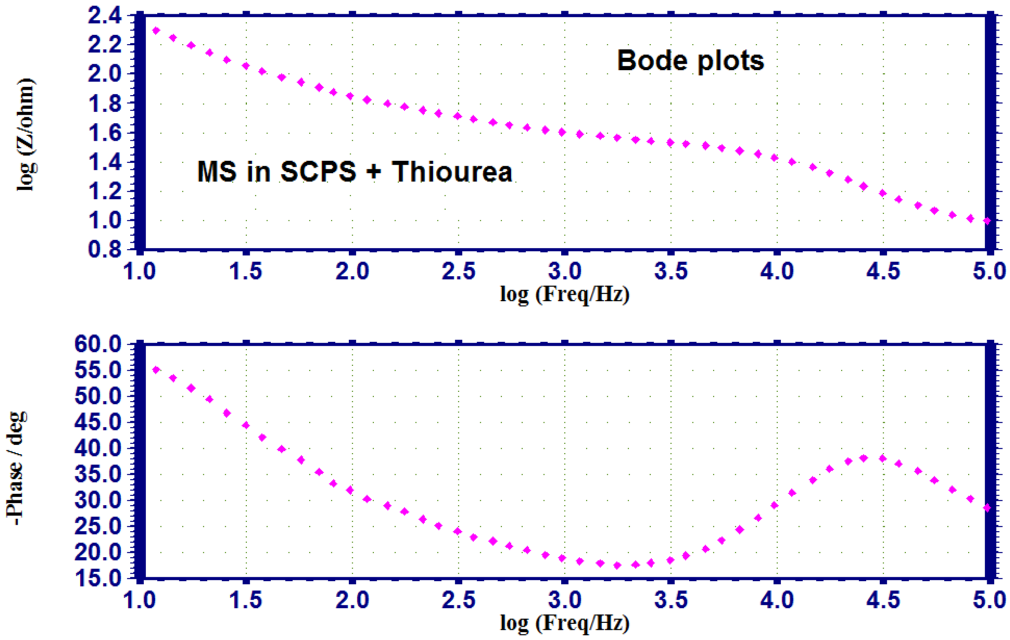

Figure 8. Bode plots of mild steel immersed in SCPS+ Thiourea

Slika 8. Bode-ova kriva mekog čelika uronjenog u SCPS + tiourea

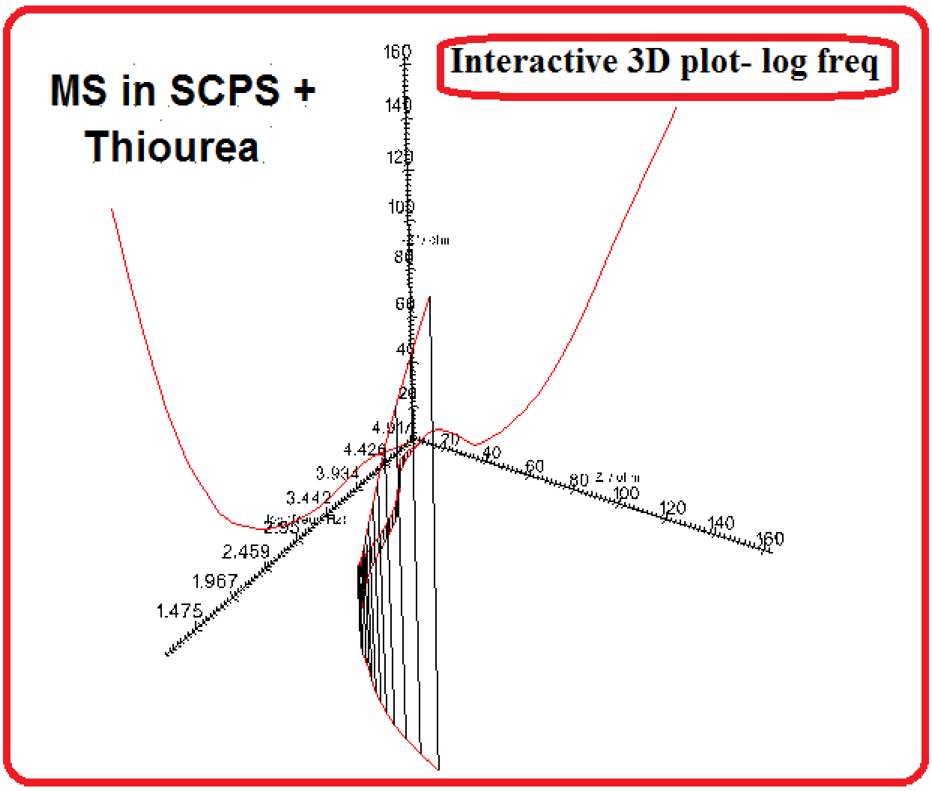

Figure 9. Interactive 3D plot of mild steel immersed in SCPS+ Thiourea

Slika 9. Interaktivna 3D grafika za meki čelik uronjenog u SCPS + tiourea

Implication

When mild steel is used as rebar, thiourea may be mixed with concrete. Thus the mild steel will be protected from corrosion.

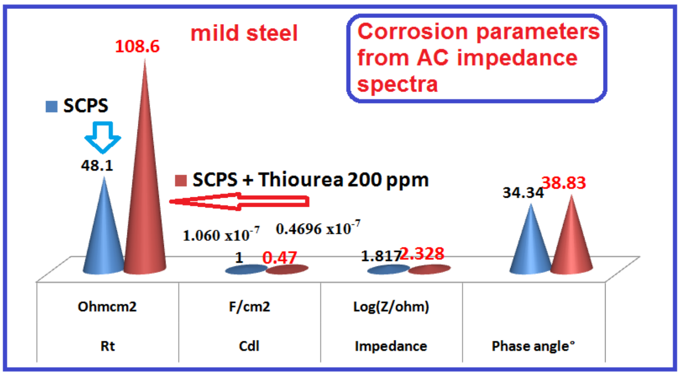

Figure 10. Comparison of corrosion parameters from AC impedance spectra

Slika 10. Poređenje parametara korozije iz spektra impedanse naizmenične struje

4. CONCLUSIONS

The corrosion resistance of mild steel in SCPS in the absence and presence of thiourea has been investigated by polarization study and AC impedance spectra.

The present study leads to the following conclusions

- Polarisation study reveals that thiourea system functions as anodic inhibitor.
- AC impedance spectra reveal that a protective film is formed on the metal surface.
- When mild steel is used as rebar, thiourea may be mixed with concrete.
- Thus the mild steel will be protected from corrosion.
- This formulation may find application in concrete technology.

5. REFERENCES

[1] M.Ohno, P.Limtong, T.Ishida (2022) Multiscale modeling of steel corrosion in concrete based on micropore connectivity, Journal of Building Engineering, 47, 103855.

[2] J.Ming, X.Zhou, H.Zuo, L.Jiang, Y.Zou, J.Shi (2022) Effects of stray current and silicate ions on electrochemical behavior of a high-strength prestressing steel in simulated concrete pore solutions, Corrosion Science, 197, 110083.

[3] P.K.Behera, S.Misra, K.Mondal (2022) Corrosion behavior of bent plain reinforcing bars used in concrete, Materials and Structures/Materiaux et Constructions, 55(2), 37-45.

[4] M.R.Carvalho, G.R.Meira, P.R.R.Ferreira, M. Medeiros (2022) Study of the effectiveness of realkalisation treatment on reinforcement repassivation by using simulated concrete pore solution, Construction and Building Materials, 321, 126318.

[5] M.C.Uvida, A.Trentin, S.V.Harb, S.H.Pulcinelli, C.V.Santilli, P.Hammer (2022) Nanostructured Poly(methyl Methacrylate)-Silica Coatings for Corrosion Protection of Reinforcing Steel, ACS Applied Nano Materials, 5(2), 2603-2615.

[6] Z.Jin, X.Zhao, Y.Du, S.Yang, D.Wang, T.Zhao, Y.Bai (2022) Comprehensive properties of passive film formed in simulated pore solution of alkali-activated concrete, Construction and Building Materials, 319, 126142.

[7] H.U.Sajid, R.Kiran, D.S.Bajwa (2022) Soy-protein and corn-derived polyol based coatings for corrosion mitigation in reinforced concrete, Construction and Building Materials, 319, 126056.

[8] G.Liu, H.Zhu, Y.Zhang, L.Yang, C.Liu (2022) Corrosion Behavior of Steel Subjected to Different Corrosive Ions in Simulated Concrete Pore Solution, Kuei Suan Jen Hsueh Pao/Journal of the Chinese Ceramic Society, 50(2), 413-419.

[9] Z.Jin, C.Xiong, T.Zhao, Y.Yu, P.Wang (2022) Passivation and depassivation properties of Cr–Mo alloyed corrosion-resistant steel in simulated concrete pore solution, Cement and Concrete Composites, 126, 104375.

[10] R.Naderi, A.Bautista, F.Velasco, M.Soleimani, M.Pourfath (2022) Use of licorice plant extract for controlling corrosion of steel rebar in chloride-polluted concrete pore solution, Journal of Molecular Liquids, 346, 117856.

[11] https://www.google.com/search?q=thiourea&oq=&aqs=chrome.0.35i39i362l8.1637344j0j15&sourceid=chrome&ie=UTF-8

[12] https://en.wikipedia.org/wiki/Thiourea#:~:text=Thiourea%20(%2F%CB%8C%CE%B8a%C9%AA..,a%20reagent%20in%20organic%20synthesis.

[13] P.Shanthy, J.A.Thangakani, S.Karthika, S.Rajendran, J.Jeyasundari (2021) Corrosion inhibition by an aqueous extract of ervatamiadivaricata, International Journal of Corrosion and Scale Inhibition, 10(1), 331-348.

[14] S.J.H.M.Jessima, A.Berisha, S.S.Srikandan, S.Subhashini (2020) Preparation, characterization, and evaluation of corrosion inhibition efficiency of sodium lauryl sulfate modified chitosan for mild steel in the acid pickling process, Journal of Molecular Liquids, 320,114382.

[15] A.S.Fouda, G.Y.Elewady, A.EL-Askalany, K. Shalabi, (2010), Inhibition of aluminum corrosion in

hydrochloric acid media by three Schiff base compounds, Zast. Mater ., 51, 205-219.

[16] S.Rajendran, V.Sribharathy, A.Krishnaveni, J. Jeyasundari, J.Sathiyabama, T.S.Muthumegala, M. manivannan, (2011) Inhibition effect of self assembled films formed by adipic acid molecules on carbon steel surface, Zast. Mater., 52, 163-172.

[17] M.E.Belghiti, Y.E.Ouadi, S.Echihi, F.Bentiss, A.Dafali (2020) Anticorrosive properties of two 3,5-disubstituted-4-amino-1,2,4-triazole derivatives on copper in hydrochloric acid environment: Ac impedance, thermodynamic and computational investigations, Surfaces and Interfaces, 21, 100692.

[18] A.S.Prabha, K.Kavitha, H.B.Shrine, S.Rajendran (2020) Inhibition of corrosion of mild steel in simulated oil well water by an aqueous extract of Andrographis paniculata, Indian Journal of Chemical Technology, 27(6), 452-460.

[19] J.J.M.Praveena, J.A.Clara, S.Rajendran, A.J.Amalraj (2021) Inhibition of corrosion of mild steel in well water by an aqueous extract of soapnut (SapindusTrifoliatus), Zas. mater./Materials Protection, 62(4), 277-290.

[20] V.D.A.M.Jeslina, S.J.Kirubavathy, A.Al-Hashem, R.M.Joany, C.Lacnjevac (2021) Inhibition of corrosion of mild steel by an alcoholic extract of a seaweed Sargassummuticum, Zas. mater./Materials Protection, 62(4), 304-315.

[21] S.Y.Al-Nami, A.E.-A.S.Fouda (2020) Corrosion inhibition effect and adsorption activities of methanolic myrrh extract for cu in 2M HNO_3, International Journal of Electrochemical Science, 15(2), 1187-1205.

[22] S.S.Rajendran, T.S.Muthumegala, M. Pandiarajan, P.N.Devi, A.Krishnaveni, J.Jeyasundari, B.N.Samy, N.H.Beevi (2011) Corrosion resistance of SS316 L in simulated concrete pore solution in presence of trisodium citrate, Zast. Mater., 52, 85-89.

[23] N.Antony, H.B.Sherine, S.S.Rajendran (2010) Investigation of the inhibiting effect of nano film by sodium meta silicate- Zn2+ system on the corrosion of carbon steel in neutral chloride solution, Zast. Mater.,51, 11-18.

[24] S.Rajendran, V.Sribharathy, A.Krishnaveni, J.Jeyasundari, J.Sathiyabama, T.S. Muthumegala, M.Manivannan (2011) Inhibition effect of self assembled films formed by adipic acid molecules on carbon steel surface, Zast. Mater., 52, 163-172.

[25] A.Christy Catherine Mary, J.Jeyasundari, V.R. NazeeraBanu, S.Senthil Kumaran, A.Peter Pascal Regis (2020) Corrosion behavior of orthodontic wires in artificial saliva with presence of beverage (Book Chapter), Nanotechnology in the Beverage Industry: Fundamentals and Applications, 471-504.

[26] S.C.Joycee, A.S.Raja, A.S.Amalraj, S.Rajendran (2021) Inhibition of corrosion of mild steel pipeline carrying simulated oil well water by Allium sativum (Garlic) extract, International Journal of Corrosion and Scale Inhibition, 10(3), 943-960.

[27] R.Dorothy, T.Sasilatha, S.Rajendran (2021) Corrosion resistance of mild steel (Hull plate) in sea water in the presence of a coating of an oil extract of plant materials, International Journal of Corrosion and Scale Inhibition, 10(2), 676-699.

IZVOD

UTICAJ TIOUREE NA OTPORNOST NA KOROZIJU MEKOG ČELIKA URONJENOG U SIMULIRANI RASTVOR BETONSKIH PORA

Otpornost mekog čelika na koroziju u rastvoru simuliranih pora betona (SCPS) u odsustvu i prisustvu tiouree je ispitana polarizacionom studijom i spektrom impedanse naizmenične struje. Studija polarizacije otkriva da sistem tiouree funkcioniše kao anodni inhibitor. Spektri impedanse naizmenične struje otkrivaju da se na površini metala formira zaštitni film. Kada se kao armatura koristi meki čelik, tiourea se može mešati sa betonom. Tako će meki čelik biti zaštićen od korozije. Zaštitni film se sastoji od kompleksa gvožđe-tiourea formiranog na metalnoj površini. U prisustvu tiouree raste otpor linearne polarizacije, smanjuje se struja korozije, povećava otpor prenosa naelektrisanja (Rt), raste impedansa, povećava se fazni ugao i smanjuje se vrednost dvoslojnog kapacitivnosti (Cdl). Ova formulacija može naći primenu u tehnologiji betona.

***Ključne reči**: tiourea, otpornost na koroziju, meki čelik, simulirani rastvor betonskih pora, elektrohemijska ispitivanja*

Naučni rad

Rad primljen: 17. 05. 2022.

Rad prihvaćen: 28. 05. 2022.

Rad je dostupan na sajtu: www.idk.org.rs/casopis