EKOLOŠKI PRIHVATLJIVI INHIBITORI KOROZIJE UGLJIČNOG ČELIKA U SLANIM UVJETIMA

ENVIRONMENTALLY FRIENDLY INHIBITORS OF CARBON STEEL CORROSION IN CHLORIDE ENVIRONMENTS

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Sažetak

U ovom radu istraživan je utjecaj inhibitora cerij (III) klorida heptahidrata (CC) i natrij glukonata (SG) na koroziju ugljičnih čelika C45 (1531) i DIN RSt 37-2 (0361) u slanim uvjetima koristeći metodu Tafel-ove polarizacije, EIS metodu i mjerenje gubitka mase. Istraživanja su provedena u morskoj vodi i 3.5 %-tnoj otopini NaCl. Raspon koncentracija CC bio je od 0.04 do 10 mmol/L, a SG od 1 do 4.5 mmol/L. Radi usporedbe provedeni su i eksperimenti s dodatkom komercijalnog inhibitora korozije. Dobiveni rezultati pokazuju da se primjenom CC i SG u slanim uvjetima može ostvariti značajna inhibicija korozije, pri čemu dolazi do sinergijskog djelovanja ova dva inhibitora. Inhibitor SG prvenstveno djeluje kao anodni inhibitor, dok CC pokazuje inhibiciju i anodne i katodne reakcije pa je inhibicija korozije uz dodatak oba inhibitora anodnog tipa.

Abstract

In this research the effect of cerium (III) chloride heptahydrate (CC) and sodium gluconate (SG) on the corrosion inhibition of carbon steels C45 (1531) and DIN RSt 37-2 (0361) in chloride environments has been evaluated using Tafel polarization technique, EIS method and weight loss measurements. Experiments were performed in seawater and 3.5 % NaCl solution. The concentration of CC varied from 0.04 to 10 mmol/L and SG from 1 to 4.5 mmol/L. In order to compare accomplished efficiencies experiments with commercial inhibitors were also performed. The results show that substantial corrosion inhibition using CC and SG in chloride environments can be obtained in synergistic manner. SG acts predominately as anodic inhibitor whereas CC acts as mixed type inhibitor. Thus, using both inhibitors overall inhibition is anodic inhibition.

Ključne riječi: ugljični čelik, inhibitori korozije, glukonati, cerij klorid, slani uvjeti

Keywords: carbon steel, corrosion inhibitors, gluconates, cerium chloride, chloride environments

1. INTRODUCTION

Seawater and brines are increasingly used in industrial practice (cooling water systems, desalination plants, sea water injection, fire fighting, ballast, pressure testing of pipelines) [1]. Because of its complexity and variability, seawater is not easily simulated in the laboratory for corrosion testing purposes. A 3.5 % NaCl solution is used frequently for this purpose and is known to be more aggressive toward carbon steel than natural seawaters [2, 3]. Although the corrosiveness of the natural seawater depends on many variable factors, the main cause of the corrosiveness of both natural seawater and 3.5 % NaCl solution are chlorides. Chloride ions have autocatalytic effect on pitting corrosion and therefore facilitate initiation and propagation of pits which have lower pH and are higher in chlorides [4].

Due to low cost and ease of fabrication carbon and low-alloy steels are, despite pronounced tendency towards corrosion, the most widely used materials for marine environments regarding both structural components and pressure-retaining applications [5]. In saline conditions carbon steels are susceptible to general, localized and galvanic corrosion. They protection is accomplished using protective coatings, corrosion inhibitors, galvanic protection or combination.

Since environmental regulations are becoming more and more stringent regarding disposal and emission of toxic substances, application of chemical substances for corrosion inhibition is turning “green” too. The major improvement is in the area of eliminating toxic compounds such as chromates, dichromates and nitrites [6]. In spite of their toxicity, chromates are still used in the manufacture and maintenance of aircraft. The health problems associated with the use of chromates and the increased costs associated with their safe use and disposal, has led to efforts in finding suitable alternate inhibitors [7].

Environmentally friendly or more precisely environmentally acceptable inhibitors are those inhibitors which, in applied concentrations, do not disturb ecological balance (stable balance in the numbers of each species in an ecosystem) or take negative impact on human health. They can be divided on *ad hoc* basis in three groups: inorganic substances such as rare-earth metal (REM) salts, borates, silicates, molybdates; organic compounds such as thioglycollates, phosphonates, sulfonates, carboxylic acids and their salts (amino acids, fatty acids, gluconates), vitamins, pigments, antibiotic or antifungal drugs (e.g. imidazole compounds), alkaloids (nicotine, caffeine); and true “green” inhibitors such as various herbal extracts (water, alcohol or acid extracts). Extracts of natural plants are environmentally friendly, non-toxic, less expensive and easily biodegradable. However, this biodegradability limits the storage and long-term usage of plant extracts [8]. Another drawback is that they are complex mixtures of variety of compounds with uncertain exact composition and therefore it is not easy to predict their inhibitory action. Therefore, they are still rarely commercially applied in spite their ever growing popularity in numerous scientific researches.

First demonstration of the effectiveness of rare-earth metals as corrosion inhibitors was described in a 1984 patent of Goldie and McCaroll [9]. Since then, rare earth compounds have successfully been used as corrosion inhibitors on different metals and alloys [10–16]. Their advantage is effectiveness, low toxicity [17, 18] and economic competitiveness [19].

Gluconic acid and its salts are environmentally suitable non-toxic compounds having also useful applications in medicine. For example, calcium gluconate is used as a health strengthening substance as well as for the treatment of calcium deficiency. Zinc gluconate is used for common cold treatment and for better wound healing. The efficiency and the mechanism of the corrosion inhibition by gluconates, either as single compound or in a mixture, have been described in a number of recent studies [2, 20-27]. A successful inhibition of carbon steel was obtained in the seawater or solutions containing different chloride concentrations by gluconate [1, 2, 22, 27-30].

The efficiency of gluconate inhibition depends on inhibitor concentration, pH value and chemical composition of investigated solution, the nature of cations introduced in the solution as gluconate or already present in water and the state of the metal surface [24, 31]. In previous researches the anodic inhibition mechanism of mild steel corrosion using sodium gluconate has been shown [2, 32]. The influence of bivalent ions (Ca^{2+} and Zn^{2+}) on the decrease of the cathodic reaction rate was recognized in solutions of their gluconate salts [33]. Gluconates are part of the successful commercial corrosion inhibitors and are recommended in mixture with water soluble polymeric dispersant, organophosphonate and silicate [34].

The aim of this research was to evaluate the capability of cerium chloride and sodium gluconate as corrosion inhibitors for carbon steel in chloride environments, to optimize their concentrations in inhibitor mixtures and to determine possible synergetic effect among these inhibitors.

2. EXPERIMENTAL PROCEDURES

The electrochemical experiments were performed using carbon steel specimens C45 (1531) and DIN RSt 37-2 (0361) of following composition: C45 (C 0.45%, P 0.03 %, S 0.03%, Si 0.22%, Cr 0.06%, Mn 0.57%, Cu 0.07%); RSt 37-2 (C 0.17%, P 0.05%, S 0.05%, N 0.007%). Working electrode area was 1 cm^2. Before measurements the specimen was polished with emery paper (400, 600, 800 and 1200 grade) degreased with ethanol and rinsed with demineralized water. Afterwards the working electrode was immersed in electrochemical cell containing 600 ml of investigated medium. All experiments were performed at ambient temperature (22 ±2 ^{o}C). The electrochemical cell was equipped with graphite auxiliary electrode and a reference saturated calomel electrode which was connected to the working electrode over Luggin capillary. Electrochemical measurements were performed on Potentiostat/Galvanostat EG&G PAR, Model 273 A using software SoftCorr III. The open circuit potential (OCP) was measured as a function of time in order to understand the corrosion behaviour of the sample in the electrolyte. A soon as the sample was immersed into the electrolyte, the initial potential of the sample was noted and monitored as a function of time until the sample attained a constant potential E_{corr} (typically 30–60 min). Afterwards, linear polarization method was applied (from –20 mV to +20 mV, polarization rate 0.166 mVs^{-1}) in order to calculate the value of polarization resistance (R_P). Finally, the method of quasi potentiostatic polarization or the Tafel extrapolation method was carried out recording polarization curves in the range ± 250 mV from the corrosion potential (E_{corr}) with a polarization rate 0.1666 mVs^{-1}. From Tafel polarization curves following corrosion parameters were calculated: the corrosion current density (j_{corr}) and corrosion rate (v_{corr}). The inhibition efficiency (E) was calculated using equation (1).

$$E = \frac{v_{ni} - v_{inh}}{v_{ni}} \times 100; \% \qquad (1)$$

E – inhibition efficiency (%)
v_{ni} - corrosion rate of uninhibited experiment (mmy^{-1})
v_{inh} - corrosion rate of inhibited experiment (mmy^{-1})

Experiments were performed on natural sea water and 3.5% NaCl solution (demineralized water with addition of NaCl). Seven different CC concentrations were investigated on natural seawater and compared to unprotected steel. The results are presented in Table 1.

Additionally, experiments with selected concentrations of CC and three SG concentrations were performed on natural seawater and the results are given in Table 2. For electrolyte (media) preparation cerium (III) chloride heptahydrate (p.a. Acros) and sodium gluconate were used (p.a. Alfa Aesar). Synergism parameter (Si) was calculated using the relation:

$$\mathrm{Si} = \frac{1-\bar{\ }_{1+2}}{1-\bar{\ }'_{1+2}} \qquad (2)$$

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \times \theta_2), \qquad (3)$$

$\theta = E/100$; θ_1=surface coverage of inhibitor 1, θ_2 = surface coverage of inhibitor 2, θ'_{1+2} = combined surface coverage in presence of inhibitors 1 and 2. When a synergistic effect exists between two inhibitors, the synergism parameter will be greater than 1.
Electrochemical impedance spectroscopy was performed at E_{corr} in the frequency range 100 kHz – 10 mHz with a 10 mV rms amplitude using a PAR 263A potentiostat / galvanostat and frequency response detector PAR 1025.

Weight loss method
Pre-weighted carbon steel specimens (7×3.5×1) in duplicate were immersed in 200 mL of the solutions (seawater or 3.5% NaCl) containing various concentrations of the inhibitor for 10 days. After the removal of corrosion products the specimens were weighted. The corrosion rate (v) was then calculated using the equation:

$$v = 87.6 \times (W / DAT)\ [\mathrm{mmy}^{-1}] \qquad (4)$$

where:

W = weight loss in milligrams
D = metal density in gcm^{-3}
A = area of sample in cm^2
T = time of exposure of the metal sample in hours
The inhibition efficiency (E) was calculated using equation (1).

For weighting of CC, SG and specimens a Kern ABS 220-4 balance was used. After electrochemical measurements, the surface of the steel specimen was observed and photographed using stereomicroscope LeicaMZ6 (low amplification).

3. RESULTS AND DISCUSSION

The effect of cerium chloride addition on corrosion inhibition in seawater

The effect of cerium chloride addition on protective properties of carbon steel C45 in seawater was evaluated using cerium chloride heptahydrate in various concentrations. In order to evaluate inhibitor performance an experiment without inhibitor addition was also performed. Concentration range of cerium chloride varied from 0.04 to 10 mmolL^{-1}. Tafel polarization curves for characteristic experiments are presented in Figure 1. The values of corrosion parameters evaluated from electrochemical studies (E_{corr}, v_{corr}, j_{corr}, E) are given in Table 1. Lower cerium chloride concentrations (less than 0.4 mmolL^{-1}) have tendency to shift E_{corr} value in the negative direction negligibly when compared to uninhibited curve, achieving minor reduction of the corrosion rate. Higher cerium chloride concentrations (up to 2 mmolL^{-1}) mainly showed tendency to shift E_{corr} value in the positive direction and achieved considerable corrosion rate reduction (Table 1). Concentration with highest corrosion resistance was 2 mM. Higher concentration showed diminished corrosion rate reduction (Table 1, Figure 1). Cerium chloride acts predominately as mixed inhibitor in natural seawater which is in good agreement with previous researches [6]. Giving the fact that surface of the carbon steel specimens after electrochemical research (Figure 2) is still not well protected exhibiting general corrosion occurrence, it can be concluded that employed inhibitor is not sufficient for effective corrosion inhibition in seawater. Therefore, sequential experiments were performed by mixing selected concentrations (0.4, 1 and 2 mmolL^{-1}) of CC with various concentrations of SG.

Table 1. Corrosion parameters of carbon steel C45 in seawater- cerium chloride addition

CC mmolL^{-1}	**E_{corr}**	**v_{corr}**	**j_{corr}**	**E**
	mV	**mmy^{-1}**	**µAcm^{-2}**	**%**
0	-660.6	0.2803	23.98	0
0.04	-684	0.229	19.63	18.14
0.1	-683	0.2352	20.12	16.1
0.2	-679.3	0.2331	19.94	16.85
0.4	-687	0.1045	8.942	62.71
1	-637	0.0835	7.138	70.23
2	-621.5	0.0487	3.496	**85.42**
10	-560	0.112	10.87	54.67

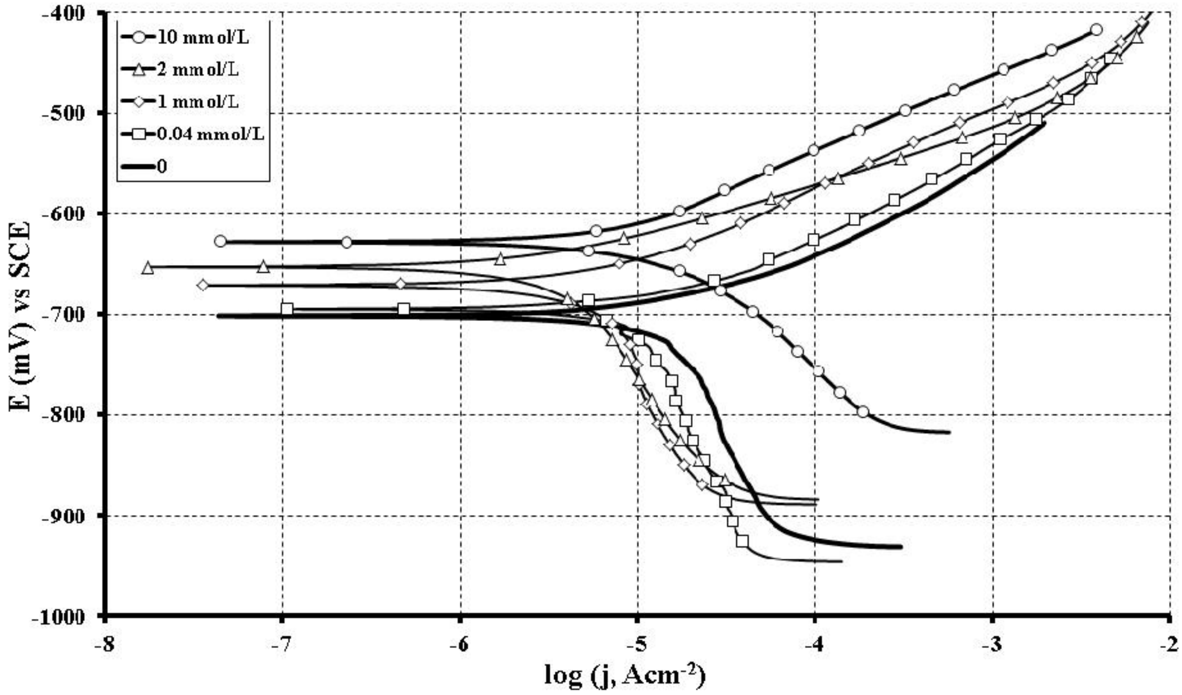
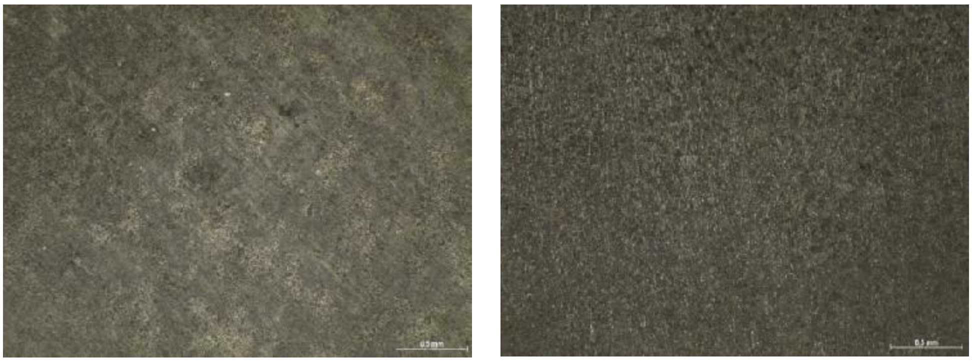


Figure 1. Tafel polarization curves of carbon steel C45 in seawater -cerium chloride addition



a) Without inhibitor **b) 2 mmolL^{-1} (85.42 %)**

Figure 2. Surface of the carbon steel specimens after electrochemical measurements in seawater (CC adition)

The effect of CC and SG addition on corrosion inhibition in seawater

In order to determine possible synergistic effect on corrosion inhibition, CC was supplemented with SG in two component system (Table 2). Tafel polarization curves for the characteristic experiments are presented in Figure 3 along with comparison to commercial inhibitor at recommended concentration.

All of the inhibitor combinations showed substantial corrosion rate reduction compared to uninhibited medium. Moreover, all inhibitor combinations had tendency to shift E_{corr} value in the positive direction when compared to uninhibited curve, thereby acting as anodic inhibitors which was also confirmed by Tafel polarisation curves (Table 2, Figure 3). Consequently, with the increase of inhibitor concentration, corrosion rate decreased significantly.

Accordingly, experiments with 1 mmolL^{-1}, which was lowest concentration of SG, showed pronounced corrosion inhibition only at higher concentrations of CC (at 2 mmolL^{-1} corrosion inhibition was 89.18 %). Experiments with 2.25 mmolL^{-1} of SG showed even more expressed corrosion inhibition at high CC content, as well as experiments with 4.5 mmolL^{-1} of SG. Therefore, experiments with highest CC addition showed improved corrosion inhibition properties, with efficiency that reached around 90% at lowest SG addition, or higher than 90% at higher SG additions. Also experiment with highest SG addition and 1 mmolL^{-1} CC showed excellent corrosion resistance (93.05 %). The best accomplished result was with both CC and SG at highest levels and that experiment reached 94.98 % inhibition. Those experiments were selected for additional weight loss measurements, along with the best experiment without SG addition (Table 1) and control experiment. When compared to commercial inhibitor applied at recommended concentration (0.75 %) the best combination of CC and SG showed somewhat lower corrosion inhibition. Therefore, it could further be optimised through even higher inhibitor content addition, or by mixing with other inhibitor that would act in synergistic manner. Moreover, commercial inhibitor is significantly different regarding mechanism of corrosion protection when compared to SG and CC system since it acts more as cathodic inhibitor, considering the fact that Tafel curve has a tendency to move towards the negative potential values when compared to uninhibited curve (Figure 3).

From data in Table 2. synergism parameter (Si) was calculated for the best experiment. The value of Si was 1.65, which indicates that significant synergistic behaviour between CC and SG exists in terms of corrosion inhibition. Electrochemical impedance spectroscopy was performed for carbon steel C45 immersed in seawater: without inhibitor, with CC (2 mmolL^{-1}) and with CC and SG addition (2 and 4.5 mmolL^{-1}, respectively).

Table 2. Corrosion parameters of carbon steel C45 in seawater**-** cerium chloride and sodium gluconate addition

SG mmolL^{-1}	**CC mmolL^{-1}**	E_{corr}	v_{corr}	j_{corr}	E
		mV	**mmy^{-1}**	**µAcm^{-2}**	**%**
0	0	-660.6	0.2803	23.98	0
1	0	-597	0.1852	15.84	34
1	0.4	-601.7	0.1063	9.089	62.1
1	1	-587	0.0917	7.843	67.3
1	2	-603.6	0.0303	2.595	**89.18**
2.25	0	-555	0.1545	13.21	44.9
2.25	0.4	-548.7	0.105	8.97	62.59
2.25	1	-562.7	0.0572	4.89	79.6
2.25	2	-572.6	0.018	1.54	**93.58**
4.5	0	-542.7	0.159	13.59	43.33
4.5	0.4	-540	0.0526	4.497	81.25
4.5	1	-585	0.0195	1.666	**93.05**
4.5	2	-598.5	0.0141	1.203	**94.98**
VpCI 645 (0.75 %)		-675	0.0084	0.715	**97.02**

Si (4.5/2)=**1.65**

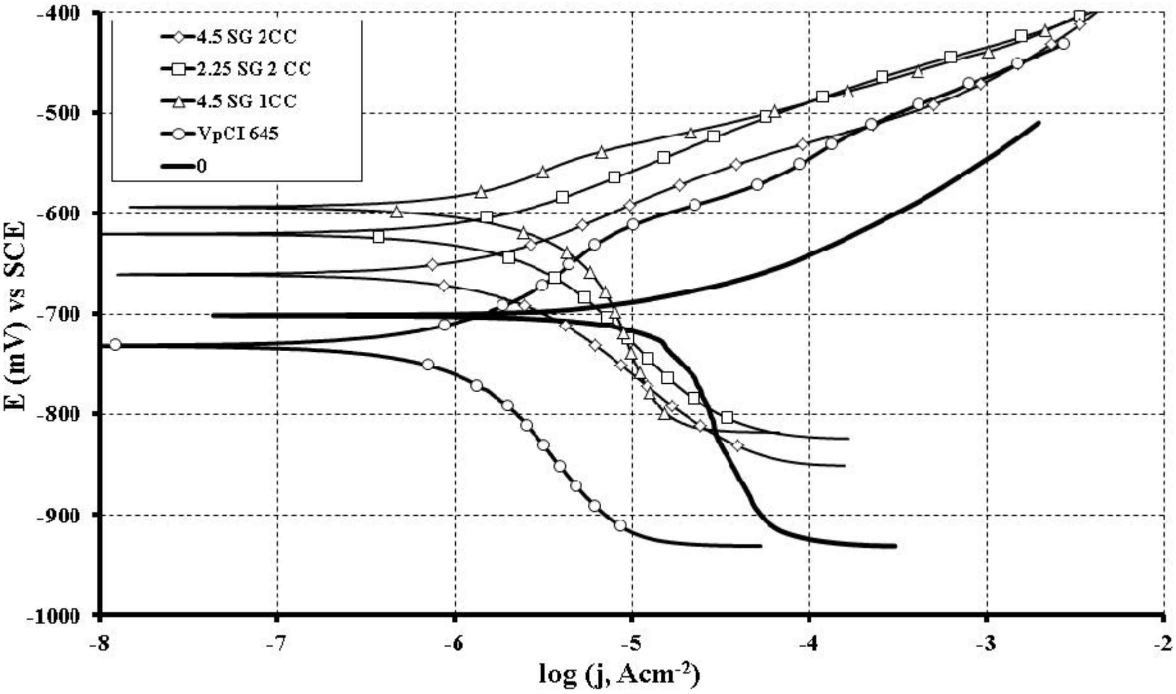


Figure 3. Tafel polarization curves of carbon steel C45 in seawater -cerium chloride and sodium gluconate addition (comparison to commercial corrosion inhibitor)

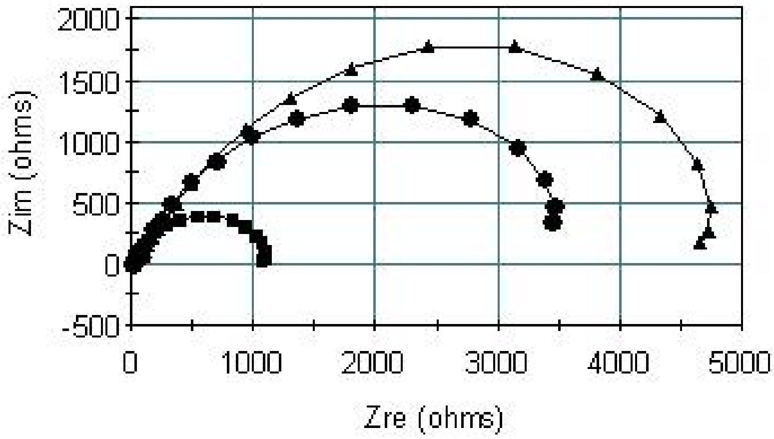
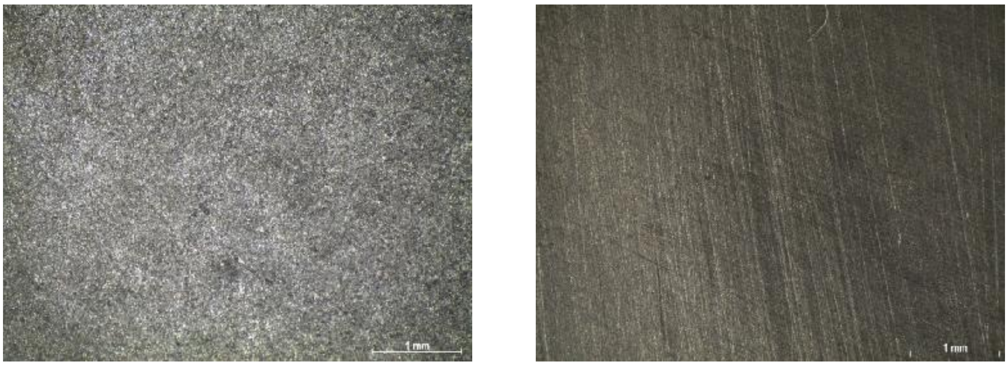


Figure 4. Nyquist plots for carbon steel C45 in seawater (-■- 0; -●- 2 mmolL^{-1} CC;
-▲- 2 mmolL^{-1} CC + 4.5 mmolL^{-1} SG)

It is clearly shown in Figure 4 that addition of CC results in increased impedance values compared to uninhibited semi-circle. The widest semi-circle was obtained by mixing both inhibitors at highest concentrations. Therefore, the results of EIS confirmed previous results of this work.

Weight loss measurements

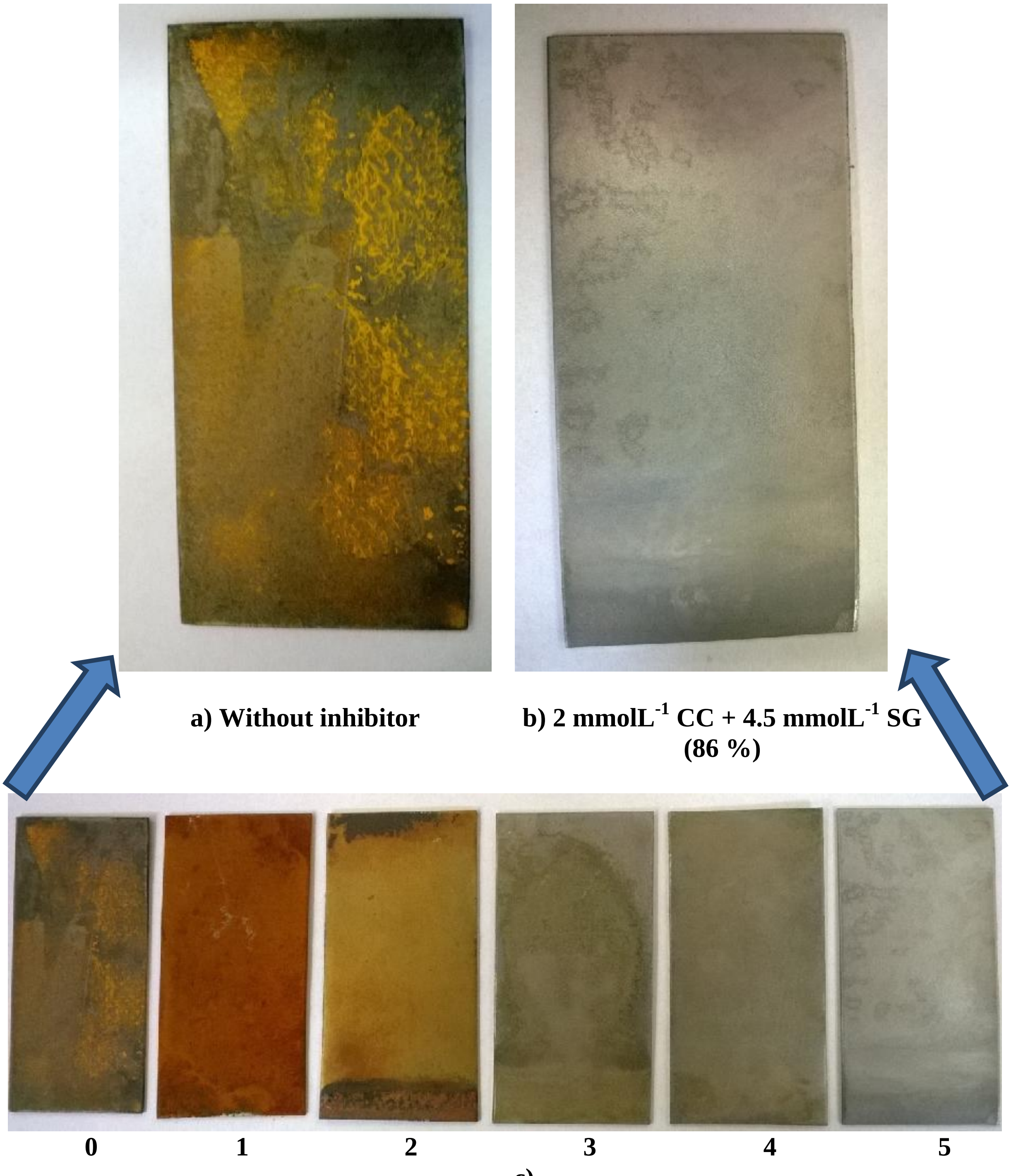
In order to further evaluate inhibitors effectiveness weight loss measurements were performed. First set of experiments was performed in seawater on carbon steel C45. Unprotected and protected surfaces of steel specimens after 10 days of seawater immersion are shown in Figure 5. Bulk corrosion product formation is visible on unprotected carbon steel specimen, whereas a protected specimen is homogenous and corrosion product free. The efficiency of corrosion inhibition calculated from weight loss was 91% which is in good agreement with efficiency from electrochemical measurements.



a) Without inhibitor **b) 2 mmolL^{-1} CC + 4.5 mmolL^{-1} SG (91 %)**

Figure 5. Surface of carbon steel specimens C45 after 10 days immersion in seawater

For additional weight loss measurements RSt 37-2 carbon steel specimens were immersed in 3.5% NaCl solution for 10 days. The surfaces of specimens after exposure are shown in Figure 6. The addition of inhibitors was as follows (from left to right; all values are expressed as mmolL^{-1}): **0**-without inhibitor; **1**-2 CC; **2**-2 CC + 1 SG; **3-** 1 CC +4.5 SG; **4-** 2 CC + 2.25 SG; **5-** 2 CC + 4.5 SG. It can be seen that samples 1 and 2 are not well protected exhibiting expressed corrosion product formation, while samples 3, 4 and 5 showed improved corrosion resistance. Among them sample 5 was best protected (86%) and photo of its surface was enlarged and compared to sample 0 (top of Figure 6).



a) Without inhibitor

b) 2 mmolL^{-1} CC + 4.5 mmolL^{-1} SG (86 %)

c)

Figure 6. Surface of RSt 37-2 carbon steel specimens after 10 days immersion in 3.5 % NaCl

4. CONCLUSIONS

For concluding remarks it can be stated that cerium chloride acts predominately as mixed inhibitor in natural seawater. Its optimal concentration for carbon steel C45 was 2 mmolL^{-1}. By supplementation with sodium gluconate inhibitory effect was further improved. The mixtures of cerium chloride and sodium gluconate acted predominately as anodic inhibitors. Optimal concentration determined in this work was 2 mmolL^{-1} of cerium chloride with 4.5 mmolL^{-1} of sodium gluconate. That combination reached efficiency of about 95%. Moreover, significant synergistic effect was determined for cerium chloride and sodium gluconate at applied concentrations. Inhibitory action of cerium chloride and sodium gluconate was also confirmed by electrochemical impedance spectroscopy and weight loss measurements.

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5. REFERENCES

[1] F. Ivušić, O. Lahodny-Šarc, I. Stojanović, Teh. vjesn. 21 (1), 107 (2013).
[2] F. Ivušić, O. Lahodny-Šarc, V. Alar, Materialwiss. Werkst. 44 (4), 319 (2013).
[3] Jones, D.A. Principles and Prevention of Corrosion. Prentice Hall, Upper Saddle River, (1996).
[4] Cramer S.D.; Covino B.S. ASM Handbook, Vol. 13A: Corrosion: Fundamentals, Testing, and Protection. ASM International, Materials Park, (2003).
[5] Francis, R.; Powell, C. Corrosion Performance of Metals for the Marine Environment: A Basic Guide. Maney Publishing, Leeds, (2012).
[6] M. Forsyth, K. Wilson, T. Behrsing, C. Forsyth, G. B. Deacon, A. Phanasgoankar, Corrosion, 58 (11), 953 (2002).
[7] V.S. Sastri, Green Corrosion Inhibitors: Theory and Practice. Wiley, New York, 2011.
[8] M. Sangeetha, S. Rajendran, T. S. Muthumegala, A. Krishnaveni, Zaštita materijala, 52 (1), 3 (2011).
[9] B.P.F. Goldie, J.J. McCaroll, Method of inhibitor corrosion in aqueous systems, Australian Patent AU-32947/84 (1984).
[10] M. Bethencourt, F.J. Botana, J.J. Calvino, M. Marcos, M.A. RodrI´guez-Chaco´n, Corros. Sci. 40, 1803 (1998).
[11] M.A. Arenas, M. Bethencourt, F.J. Botana, J. de Damborenea, M. Marcos, Corros. Sci. 43, 157 (2001).
[12] Y. Xingwen, C. Chunan, Y. Zhiming, Z. Derui, Y. Zhongda, Corros. Sci. 43, 1283 (2001).
[13] S. Virtanen, M.B. Ives, G.I. Sproule, P. Schmuki, M.J. Graham, Corros. Sci. 39, 1897 (1997).
[14] S.M. Powell, H.N. McMurray, D.A. Worsley, Corrosion, 55, 1040 (1999).
[15] C.B. Breslin, D.D. Macdonald, Electrochim. Acta, 44, 643 (1998).
[16] B. Hinton, Corrosion, 66, (2010).

[17] DHHS-NIOSH, Reg. of Toxic Effects of Chemical Substances, 86, DHHS-NIOSH Pub, 103, (1986).
[18] A.K. Mishra, R. Balasubramaniam, S. Tiwari, Anti-Corros. Method M, 54, 37 (2007).
[19] B. Claux, J. Serp, J. Fouletier, Electrochim. Acta, 56, 2771 (2011).
[20] R. Touir, M. Cenoui, M. El Bakri, M. Ebn Touhami, Corros. Sci, 50 (6), 1530 (2008).
[21] S. M. A. Shibli, V. A. Kumary, Anti-Corros. Method M, 51 (4), 277 (2004).
[22] L.Q. Zhu, D.D. Shan, B. Zhao, Material Science and Technology, 15 (5), 631 (2007).
[23] D.Q. Zhang, X. Jin, B. Xie, H. Goun Joo, L. X. Gao, K. Y. Lee, Surface and Interface Analysis, 44 (1), 78 (2012).
[24] O. Lahodny-Šarc, F. Kapor, R. Halle,. // Mater. Corros, 51 (3), 147 (2000).
[25] S. Rajendran, R. Maria Joany, B. V. Apparao, N. Palaniswamy, Transactions of the SAEST, 35 (3/4), 113 (2000).
[26] O. Lahodny-Šarc, F. Kapor, Materials Science Forum, 289-292 (2), 1205 (1998).
[27] S. Rajendran, B. V. Apparao, N. Palaniswamy, British Corrosion Journal, 33 (4), 315 (1998).
[28] O. Lahodny-Šarc, P. Orlović-Leko, Proceedings of the UK Corrosion and Eurocorr94 Conference, London, 120 (1994).
[29] O. Lahodny-Šarc, F. Kapor, R. Halle, Proceedings The European Corrosion Congress (Eurocorr99), Achen, 14 (1999).
[30] E.D. Mor, C. Wrubl, British Corrosion Journal, 11 (4), 199 (1976).
[31] O. Lahodny-Šarc presented at 8th Europ. Symp. Corr. Inhibitors, Ferrara, Italy, 421 (1995).
[32] O. Lahodny- Šarc, presented at 5th Europ. Symp. Corr. Inhibitors, Ferrara, Italy, 609 (1980).
[33] F. Ivušić, V. Alar, O. Šarc-Lahodny, I. Juraga, KORMAT 2012 / Stojanović, Ivan ; Alar, Vesna (ur.).Zagreb : Hrvatsko društvo za zaštitu materijala, 57 (2012).
[34] S.H. Shim, D. P. Bakalik, D. A. Johnson, B. Yang, F. F. Lu, US Patent 5589106, (1996).