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CORROSION INHIBITION OF CARBON STEEL IN SALINE SOLUTIONS BY GLUCONATE, ZINC SULPHATE AND CLAY ELUATE

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Original scientific paper

The effect of gluconate, zinc sulphate and green clay eluate on the corrosion inhibition of carbon steel (EN S235 JRG) in 0,5 % and 3,5 % sodium chloride solution has been evaluated in this work using Tafel polarization technique. Substantial general corrosion inhibition using sodium gluconate solely can be obtained with moderate concentrations. In this case, corrosion inhibition is predominately obtained by anodic mechanism and is limited to general corrosion, whereas carbon steel becomes liable to localised pitting corrosion. However, when sodium gluconate is combined with zinc sulphate and/or green clay eluate in adequate concentrations both general and localized corrosion are diminished which indicates good synergy between applied inhibitors.

Keywords: *carbon steel, corrosion inhibition, gluconate, green clay, saline solution*

Inhibicija korozije ugljičnog čelika u slanim otopinama pomoću glukonata, cink sulfata i eluata gline

Izvorni znanstveni članak

U ovom je radu procijenjen utjecaj glukonata, cink sulfata i eluata zelene gline na inhibiciju korozije ugljičnog čelika (EN S235 JRG) u 0,5 % i 3,5 % otopini natrij klorida pomoću metode Tafelove polarizacije. Primjenom umjerenih koncentracija natrij glukonata postignuta je značajna inhibicija opće korozije. U tom je slučaju inhibicija uglavnom ostvarena anodnim mehanizmom inhibicije opće korozije, uz pojavu lokalne "pitting" korozije ugljičnog čelika. Međutim, u slučaju kada je natrij glukonat pomiješan s cinkovim sulfatom i/ili eluatom zelene gline u odgovarajućim koncentracijama, dolazi do smanjenja i opće i lokalne korozije što ukazuje na dobro sinergijsko djelovanje između uporabljenih inhibitora.

Ključne riječi: *inhibicija korozije, glukonat, otopina natrij klorida, ugljični čelik, zelena glina*

1 Introduction

Gluconic acid and its salts are known to be efficient scaling and corrosion inhibitors in cooling water systems [1 ÷ 6]. They are environmentally suitable non-toxic compounds having also useful applications in medicine. Gluconates are recommended in mixture with water soluble polymeric dispersant, organophosphonate and silicate or other efficient inhibitors [7, 8]. 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, 3, 9 ÷ 19]. A successful inhibition of carbon steel was obtained in the seawater or solutions containing different chloride concentrations by gluconate [9, 18 ÷ 22]. Since carbon and low-alloy steels are the most widely used materials in the marine environment, for both structural components and pressure-retaining applications [23], these results are of considerable practical application. Moreover, seawater and different brines are increasingly used in industrial practice (cooling water systems, desalination plants, injection water) due to both economic and ecological grounds. 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 [18, 24]. 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 [25]. Zinc ions are frequently used as cathodic inorganic corrosion inhibitor, predominately as sulphate salt. Although zinc sulphate is inhibitor with modest efficiency, it is mixed with other inhibitors to obtain significant synergistic action [14, 26 ÷ 29]. The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired. Associated phases in clay may include materials that do not impart plasticity and organic matter [30]. Clays have been used in architecture, agriculture, water treatment, biotechnology, nanotechnology, oil, food, cosmetics, pharmaceutical, paint, paper, ceramics, plastics and rubber industries [31-33].

To the authors best knowledge green clay or its components have not been yet employed as corrosion inhibitor. The aim of this research was to evaluate the capability of sodium gluconate, zinc sulfate and green clay eluate as corrosion inhibitors for carbon steel in 3,5 % NaCl solution, to optimize their concentrations in inhibitor mixtures and to determine possible synergetic effect among these inhibitors.

2 Experimental

All experiments were performed using carbon steel specimen EN S235 JRG of the following composition: C 0,17 %, P 0,05 %, S 0,05 %, N 0,007 % (working electrode with a 1 cm^2 area). Before measurements the specimen was polished with emery paper (400, 600, 1000 and finally 2000 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 °C). pH values of investigated media were measured using pH meter Mettler Toledo, SevenMulti. 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 Potenciostat/Galvanostat EG&G PAR, Model 273 A using software SoftCorr III. 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 $mV \cdot s^{-1}$) 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 from the corrosion potential (E_{corr}) with a polarization rate 0,1666 $mV \cdot s^{-1}$. From Tafel polarization curves the following corrosion parameters were calculated: the corrosion current density (j_{corr}) and corrosion rate (v_{corr}). The inhibition efficiency (Z) was calculated using equation (1). Experiments were performed on 2 different media: 0,5 % and 3,5 % NaCl solution (demineralized water with addition of NaCl). The results were compared to unprotected steel.

$$Z = \frac{(j_{ni} - j_{inh})}{j_{ni}} \times 100, \tag{1}$$

Z − inhibition efficiency (%)
j_{ni} − corrosion current density of uninhibited experiment ($\mu A \cdot cm^{-2}$)
j_{inh} − corrosion current density of inhibited experiment ($\mu A \cdot cm^{-2}$).

For electrolyte (medium) preparation sodium gluconate (SG) and zinc gluconate (ZG) salts were used as corrosion inhibitors (p.a. Alfa Aesar), along with zinc sulfate heptahydrate (ZS, p.a. Sigma-Aldrich) and green clay manufactured by Argital with chemical composition described elsewhere [34]. Green clay eluate (CE) was prepared by mixing 100 g of green clay with demineralized water up to volume of 1 L and stored at 4 °C for 5 days. Afterwards, green clay was removed by centrifugation for 15 minutes at 4000 min^{-1}. Supernatant was diluted with demineralized water to 1 g/L dry matter and was used for media preparation. SG and ZG were selected as organic inhibitors, ZS as inorganic and CE as predominately inorganic inhibitor, but contained also low concentrations of decomposed organic matter. Kern ABS 220-4 balance was used for weighting. After electrochemical measurements, the surface of the steel specimen was observed using stereomicroscope Leica MZ6.

3 Results and discussion

3.1 The effect of ZG and CE addition on corrosion inhibition in 0,5% NaCl

The effect of ZG and CE addition on protective properties of carbon steel in 0,5 % NaCl was evaluated using 0,2 g/L ZG and 1 g/L CE. In order to evaluate inhibitor performance an experiment without inhibitor addition was also performed. Tafel polarization curves for the above mentioned concentrations are presented in Fig. 1.

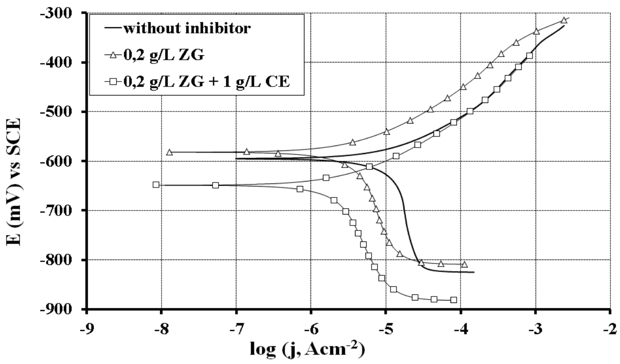
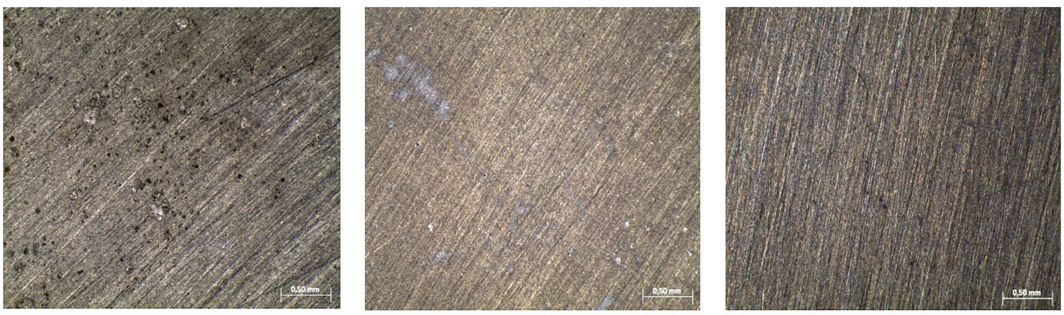


Figure 1 Tafel polarization curves of carbon steel in 0,5% NaCl solution

Table 1 Corrosion parameters of carbon steel in 0,5 % NaCl solution

Composition		E_{corr}	v_{corr}	j_{corr}	R_P	Z
Inhibitors	$g \cdot L^{-1}$	mV	$mm \cdot y^{-1}$	$\mu A \cdot cm^{-2}$	kΩ	%
Without inhibitor		−572	0,21	17,99	1,8	0
ZG	0,2	−555	0,057	4,88	4,04	72,9
ZG+CE	0,2+1	−633	0,032	2,72	4,63	84,9



Without inhibitor | 0,2 g/L ZG | 0,2 g/L ZG +1 g/L CE

Figure 2 Surface of the carbon steel specimens after electrochemical measurements in 0,5 % NaCl solution

The values of corrosion parameters evaluated from electrochemical studies (E_{corr}, v_{corr}, j_{corr}, R_P, Z) are given in Tab. 1. Low ZG concentration without CE addition have tendency to shift E_{corr} value in the positive direction when compared to uninhibited curve, achieving considerable reduction (72,9 %) of the corrosion rate. ZG acts predominately as an anodic inhibitor in this water type. Giving the fact that surface of the carbon steel specimens after electrochemical research (0,2 g/L ZG) is still not well protected (Fig. 2), exhibiting local corrosion initiation sites as well as general corrosion occurrence, it can be concluded that employed concentration is not sufficient for effective corrosion inhibition. When 0,2 g/L ZG were combined with 1 g/L CE Tafel curve (Fig. 1) has a tendency to move towards the negative potential values, thereby indicating that employed inhibitor mixture acts predominately as cathodic inhibitor in this water type. Also, corrosion inhibition was more effective reaching 84,9 % (Tab. 1) and the surface of the carbon steel specimens after electrochemical research (Fig. 2) was mainly clean without distinct signs of local or general corrosion. R_P values were consistent with corrosion rate measurements. Although this mixture could further be optimized for inhibition in 0,5 % NaCl solution, hereafter the employed corrosive solution was 3,5 % NaCl solution as more suitable model solution for marine environment research in submerged condition. Also, ZG was replaced with SG and ZS in order to individually examine the effects of gluconate and zinc ions on corrosion behaviour.

3.2 The effect of SG, ZS and CE addition on corrosion inhibition in 3,5 % NaCl- one inhibitor

In order to separately evaluate corrosion inhibition efficiency SG, ZS and CE were examined in system with one inhibitor in concentrations presented in Tab. 2. Tafel polarization curves are presented in Fig. 3. All three inhibitors had tendency to shift E_{corr} value in the positive direction when compared to uninhibited curve. SG and ZS alone achieved modest reduction of the corrosion rate, whereas CE triggered substantial increase of the corrosion rate (57,4 %) therefore acted as corrosion activator. The surface of the carbon steel specimen after electrochemical research (Fig. 4) without inhibitor displayed substantial general corrosion formation as well as carbon steel specimen protected with 1 g/L ZS (medium 3). The surface of specimen immerged in medium 1 (1,5 g/L SG) after the research was largely covered with pitting corrosion areas whereas specimen in solution with 4 g/L SG (solution 2) had just a few pits at the same time displaying best general (65,35 %) and localized corrosion resistance among analyzed samples in this experimental set.

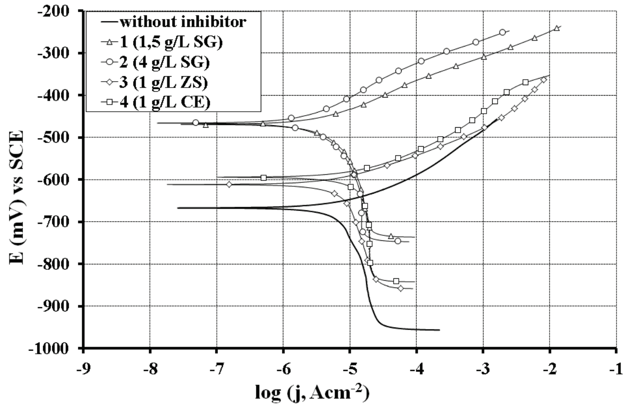


Figure 3 Tafel polarization curves of carbon steel in 3,5 % NaCl solution - one inhibitor

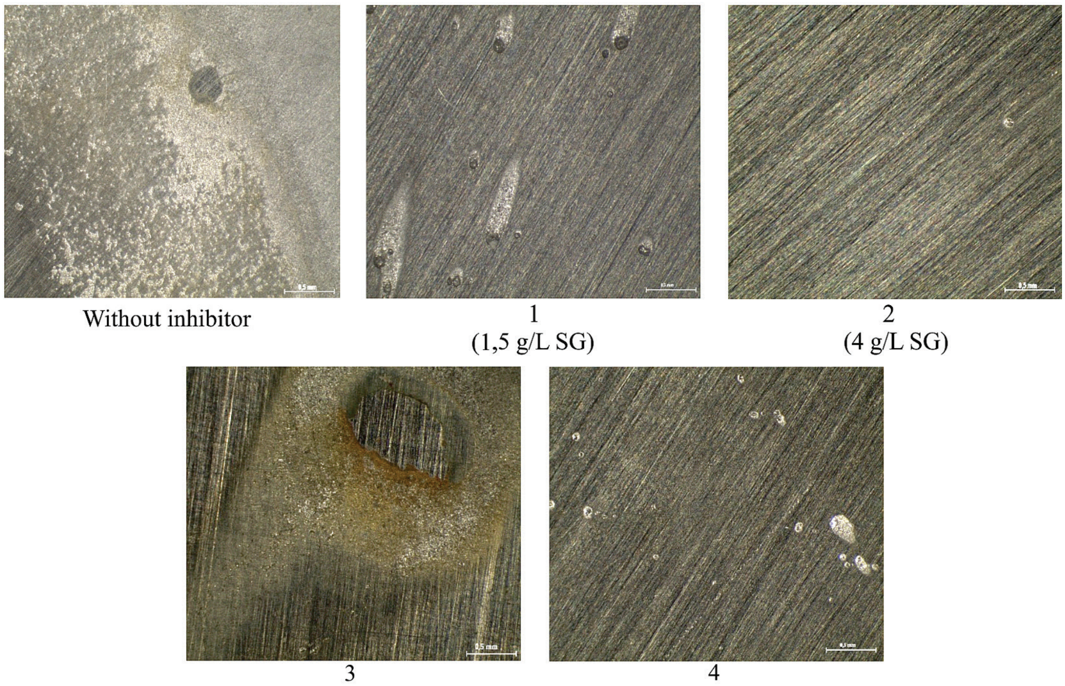


Figure 4 Surface of the carbon steel specimens after electrochemical measurements in 3,5 % NaCl solution - one inhibitor

Table 2 Corrosion parameters of carbon steel in 3,5 % NaCl solution-one inhibitor

Medium No.	Composition Inhibitors	g·L^{-1}	E_{corr} mV	v_{corr} mm·y^{-1}	j_{corr} μA·cm^{-2}	R_P kΩ	pH	Z %
-	Without inhibitor		−705	0,15	12,87	1,9	5,08	0
1	SG	1,5	−487	0,064	5,48	4,79	5,43	57,4
2	SG	4	−490	0,052	4,46	5,47	5,55	65,35
3	ZS	1	−600	0,101	8,68	2,24	5,15	32,56
4	CE	1	−584	0,237	20,26	1,61	7,75	−57,4

The surface of the sample protected by CE was largely covered with pits and, as already stated before, demonstrated poor resistance to both localized and general corrosion. CE changed pH value of the solution from slightly acidic to near neutral values. All measured R_p values were consistent with corrosion rate measurements. All three inhibitors were further evaluated as two and three component mixtures.

3.3 The effect of SG, ZS and CE addition on corrosion inhibition in 3,5 % NaCl- two inhibitors mixture

In order to determine possible synergistic effect on corrosion inhibition SG was supplemented with ZS or CE in two component system (Tab. 3). Tafel polarization curves for the above mentioned concentrations are presented in Fig. 5.

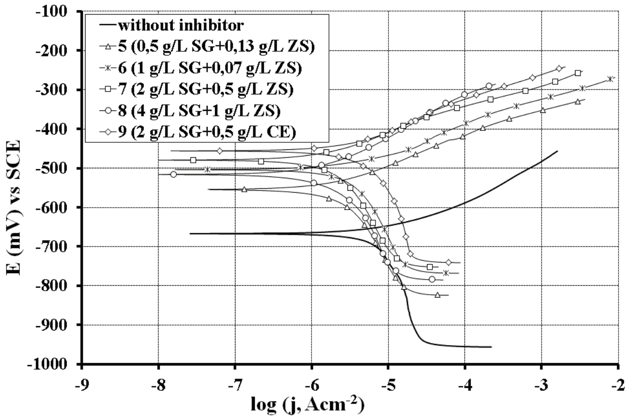
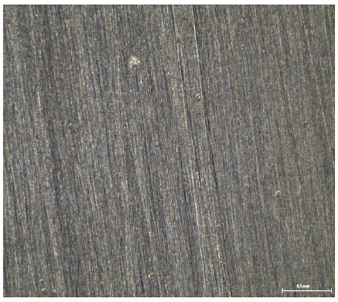


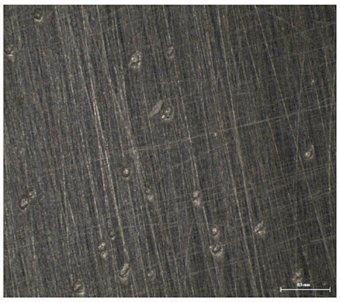
Figure 5 Tafel polarization curves of carbon steel in 3,5 % NaCl solution- two inhibitors mixture

Table 3 Corrosion parameters of carbon steel in 3,5 % NaCl solution- two inhibitors mixture

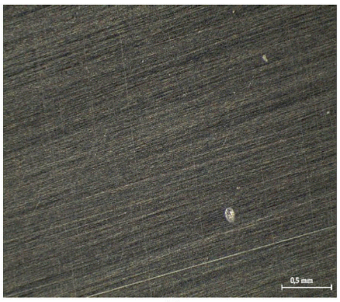
Medium	Composition		E_{corr}	v_{corr}	j_{corr}	R_P	pH	Z
No.	Inhibitors	$g \cdot L^{-1}$	mV	$mm \cdot y^{-1}$	$\mu A \cdot cm^{-2}$	kΩ		%
5	SG+ZS	0,5+0,13	−556	0,037	3,17	6,66	5,57	75,37
6	SG+ZS	1+0,07	−515	0,038	3,27	5,69	5,77	74,6
7	SG+ZS	2+0,5	−499	0,021	1,823	9,54	5,51	85,84
8	SG+ZS	4+1	−529	0,022	1,868	9,61	5,58	85,5
9	SG+CE	2+0,5	−489	0,047	4,029	5,64	6,32	68,7



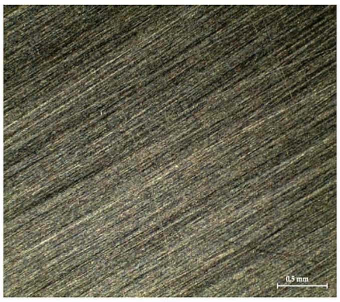
5
(0,5 g/L SG
+ 0,13 g/L ZS)



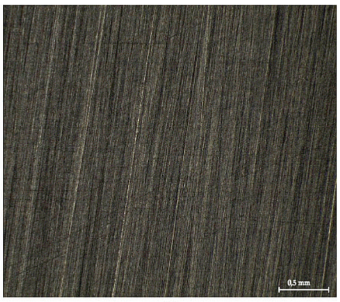
6
(1 g/L SG
+ 0,07 g/L ZS)



7
(2 g/L SG
+ 0,5 g/L ZS)



8
(4 g/L SG
+ 1 g/L ZS)



9
(2 g/L SG
+ 0,5 g/L CE)

Figure 6 Surface of the carbon steel specimens after electrochemical measurements in 3,5% NaCl solution- two inhibitors mixture

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. Medium with lowest applied inhibitor concentrations (medium 5) exhibited good general corrosion inhibition with few pits on the surface of the steel specimen after electrochemical measurement (Fig. 6). When doubling the SG content along with 50 % decrease of the ZS content (medium 6) corrosion rate and efficiency did not change significantly, but there were considerably more pits on the surface of the steel specimen after electrochemical measurement (Fig. 6), highlighting the effect of the ZS on the localized corrosion inhibition. Further increase of both inhibitor concentrations (medium 7) led to enhanced inhibition of general corrosion (85,84 %), while there were few pits visible on the specimen surface, similar to specimen from medium 5. Therefore, elevated concentrations of both inhibitors showed satisfactory general corrosion inhibition, but even so high levels of inhibitors were not sufficient for complete pitting corrosion inhibition. Therefore, medium 8 was prepared with double content of both SG and ZS and showed high degree of general and also local corrosion inhibition. Since this is a medium with high and thus impractical inhibitor concentration further experiments were performed in order to minimize inhibitor concentrations and to utilize synergistic effect of the applied inhibitors. Synergistic effect can be seen in the case of media 1, 5 and 6. Medium 6 (more concentrated) was inferior to medium 5 regarding particularly local corrosion and medium 1 (the most concentrated) was inferior to both medium 5 and 6. Also, when compared to previous experimental set, obvious synergistic behaviour is observable when considering media 2 and 4. In this case, the sum value of corrosion rates was significantly lower than corrosion rate from medium 8 (medium 8 was prepared as sum concentrations of media 2 and 4). Also, pitting corrosion was retarded only on steel specimen from medium 8. Optimization of the medium composition could also be done using convenient experimental design method, but in this case, there are two output values - corrosion rate (primarily describes general corrosion) and liability to pitting which is not so difficult to quantify but is difficult to correlate with general corrosion rate, optimal formulation was established step by step, empirically. For the same reasons the degree of synergy was not calculated. At last, medium 9 was prepared with 0,5 g/L CE addition and 2 g/L SG, similar to medium 7. That medium showed medium general corrosion inhibition, but also excellent resistance to pitting corrosion without visible signs of pit initiation, unlike medium 7 that was superior regarding general corrosion but displayed few pits on specimen surface. Therefore, in order to minimize both corrosion parameters all three inhibitors were mixed together for the further research. pH values of media 5 ÷ 8 were highly similar, just in medium 9, due to the CE addition, higher pH values were recorded presumably decreasing local corrosion inhibition.

3.4 The effect of SG, ZS and CE addition on corrosion inhibition in 3,5 % NaCl- three inhibitors mixture

Three inhibitors mixtures were designed according to Tab. 4. Tafel polarization curves for the above mentioned concentrations are presented in Fig. 7. All of the inhibitor combinations showed substantial corrosion rate reduction compared to uninhibited medium. Corrosion rate reduction varied between 80 ÷ 90 %, except for medium 10, which contained the lowest concentrations of inhibitors. Similar to previous experimental set, all inhibitor combinations had tendency to shift E_{corr} value in the positive direction when compared to uninhibited curve, thus acting predominately as anodic inhibitors. Medium 10 which displayed highest corrosion rate also had shown less prominent tendency to shift E_{corr} value in the positive direction. Medium 10 exhibited moderate general corrosion inhibition (around 50 %), but showed quite good pitting resistance with no visible pits on the surface of the steel specimen after electrochemical measurement (Fig. 8). Media 15 and 16 which contained the highest inhibitor concentrations, both showed excellent pitting resistance with clean surface of steel specimen and also good efficiency of corrosion inhibition. Since medium 15 contained lower inhibitor content and was more efficient towards corrosion inhibition it is considered as more favourable.

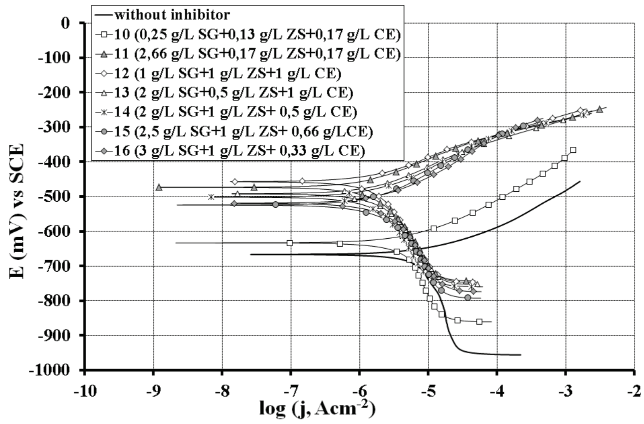


Figure 7 Tafel polarization curves of carbon steel in 3,5 % NaCl solution- three inhibitors mixture

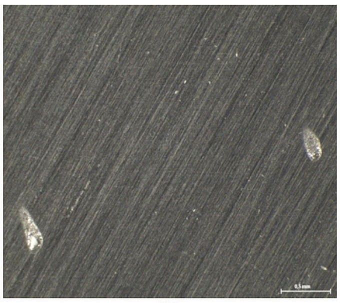
Table 4 Corrosion parameters of carbon steel in 3,5 % NaCl solution- three inhibitors

Medium No.	Composition		E_{corr}	v_{corr}	j_{corr}	R_P	pH	Z (efficiency)
	Inhibitor	$g \cdot L^{-1}$	mV	$mm \cdot y^{-1}$	$\mu A \cdot cm^{-2}$	kΩ		%
10	SG+ZS+CE	0,25+0,13+0,17	−608	0,073	6,22	3,39	5,74	51,67
11	SG+ZS+CE	2,66+0,17+0,17	−489	0,0146	1,24	8,6	5,86	90,37
12	SG+ZS+CE	1+1+1	−494	0,0226	1,93	9,83	7,11	85,00
13	SG+ZS+CE	2+0,5+1	−500	0,022	1,88	9,46	7,06	85,39
14	SG+ZS+CE	2+1+0,5	−507	0,0225	1,92	9,23	6,85	85,08
15	SG+ZS+CE	2,5+1+0,66	−540	0,0223	1,91	6,36	6,5	85,16
16	SG+ZS+CE	3+1+0,33	−520	0,031	2,65	6,57	5,96	79,41

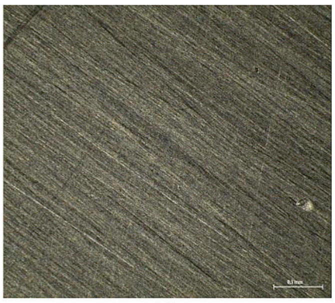
Medium 11, which had highest SG concentration and very low concentrations of ZS and CE was the best medium regarding corrosion rate inhibition, but showed poor pitting resistance (Fig. 8). Nevertheless, medium 12 which contained equal proportions of each inhibitor and was equally concentrated as medium 11, showed similar, although somewhat lower inhibition efficiency, but significantly better pitting resistance. Media 13 and 14 contained same aggregate inhibitor concentration, displayed highly similar corrosion rate inhibition, but medium 13 showed significantly better pitting resistance property. It is to be concluded that CE in the three component system with 2 g/L SG showed better inhibitive property when compared to ZS. However, straightforward conclusions are hard to be drawn since even just three components of inhibition mixture make complex system.

Moreover, the complex composition of CE itself makes it even harder to predict inhibitive action of the particular inhibitor mixture. Nevertheless, in particular mixture all three components give significant contribution to the observed medium inhibition efficiency.

10
(0,25 g/L SG + 0,13 g/L ZS
+ 0,17 g/L CE)

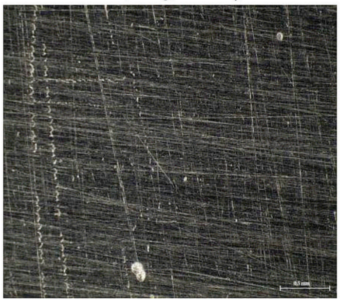


11
(2,66 g/L SG + 0,17 g/L ZS
+ 0,17 g/L CE)

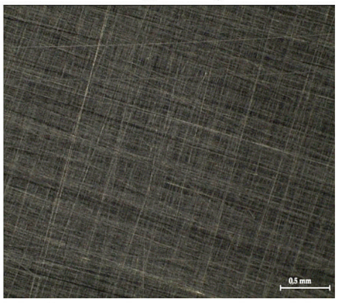


12
(1 g/L SG + 1 g/L ZS
+ 1 g/L CE)

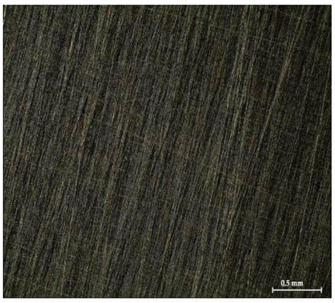
13
(2 g/L SG + 0,5 g/L ZS
+ 1 g/L CE)



14
(2 g/L SG + 1 g/L ZS
+ 0,5 g/L CE)



15
(2,5 g/L SG + 1 g/L ZS
+ 0,66 g/L CE)



16
(3 g/L SG + 1 g/L ZS
+ 0,33 g/L CE)

Figure 8 Surface of the carbon steel specimens after electrochemical measurements in 3,5 % NaCl solution- three inhibitors mixture

4 Conclusion

For the concluding remarks it can be stated that the benefits of using two and especially three inhibitors mixtures are evident in both 0,5 and 3,5 % NaCl solutions. In experiments with just one applied inhibitor all specimens showed expressed pitting or general corrosion. In experiments with two components inhibitor mixture pitting corrosion can be decreased if using moderately high inhibitor concentrations (medium 9). If high concentrated medium (medium 8) is used, both pitting and general corrosion are diminished. In experiments with three inhibitors mixture it is evident that even low concentrations of all three inhibitors (medium 10) could retard more harmful pitting corrosion. For the successful inhibition of both pitting and general corrosion more concentrated media are required (e.g. medium 15), but also less concentrated than in experiment with two inhibitors, denoting the importance of synergistic inhibitive effect among applied inhibitors. All three applied inhibitors are applicable for the protection of carbon steel in 3,5 % NaCl. Medium with best inhibitive properties towards both general and pitting corrosion is medium 15, containing 2,5 g/L SG, 1 g/L ZS and 0,66 g/L CE. For future research this medium could be employed for research in natural seawater. Different corrosive properties of seawater could lead to the modification of the proposed medium, probably to the decrease of the required inhibitor content. Other possibility for the decrease of inhibitor concentrations is further optimization by addition of low concentrations of other suitable and nontoxic inhibitors.

Acknoweledgements

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