

Synergistic Inhibition of Carbon Steel Corrosion by Inhibitor-Blends in Chloride - Containing Simulated Cooling Water

Abdul Shaban^{1,†}, Ilona Felhosi¹, and Gyongyi Vastag²

¹*Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, 1117, Budapest, Magyar tudósok körútja 2, Hungary*

²*University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia*

(Received March 17, 2017; Revised April 26, 2017; Accepted April 27, 2017)

The objective of this work was to develop efficient synergistic inhibitor combinations comprising sodium nitrite (NaNO_2) and an inhibitor-blend code named (SN-50), keeping in view of their application in industrial cooling water systems. The electrochemical characteristics of the carbon steel working electrode in simulated cooling water (SCW), without and with the addition of different combinations of the inhibitors, were investigated using electrochemical impedance spectroscopy (EIS), open circuit potential (OCP). The electrode surface changes were followed by visual characterization methods. It was demonstrated in this study that all the combinations of the inhibitors exhibited synergistic benefit and higher inhibition efficiencies than did either of the individual inhibitors. The addition of SN-50 inhibitor to the SCW shifted the OCP to more anodic values and increased the polarization resistance (R_p) values of carbon steel at all applied concentrations. The higher the applied sodium nitrite concentration (in the protection concentration range), the higher the obtained R_p values and the inhibition efficiency improved by increasing the inhibitor concentration.

Keywords: inhibition, sodium nitrite, polarization resistance, carbon steel, anodic inhibition

1. Introduction

Metals and alloys applications increase with technologic and economic development in many industries. The corrosion of metals or their alloys is a deteriorating electrochemical process that takes place at the surface of a metal substrate, when it is exposed to water, oxygen, and other corrosive elements [1]. There are several ways to protect metals and their alloys from the corrosion damage. The most common defensive approach against corrosion damage is to apply inhibitor. Corrosion inhibitors are chemical substances or combination of substances that, when present in the environment, prevent or reduce the corrosion rate significantly [2]. Several research publications dealt with investigating different chemicals as potentially environmentally friendly corrosion inhibitors and the development of the effective blends as synergistic corrosion inhibitors [3-7].

Passivating inhibitors are the most efficient inhibitors used in cooling water systems [2,8]. Passivators, which appreciably shift the potential of a metal to a more noble

value by forming a protective oxide film on the metal anodic sites, are widely used because of its high effectiveness, on steels and their alloys, compared to other types of inhibitors [9]. However, in general, passivating inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, passivators must be applied with caution.

Nitrite is one of the most commonly used anodic inhibitors, shifting the open circuit potential (OCP) to more noble values and reducing the corrosion current [2,4,5,8,9]. Sodium nitrite (NaNO_2) is classified as an anodic inhibitor and requires a critical concentration for the protection of steels [10-12]. At low concentrations, the nitrite may create imperfect passivity and subsequently the corrosion will be increased. The chloride concentration is equally important since when the chloride/nitrite ratio is high, the passivity effect is lost [11]. Nitrites should not be used in open systems as they would oxidize to nitrates in the presence of oxygen. Even though they are the most effective and widely used inhibitors, sodium nitrites have economical high cost disadvantage. One more factor that should be taken in consideration is the presence of chloride and sulfate ions, which can damage the protective film

[†] Corresponding author: shaban.abdul@ttk.mta.hu

Table 1 Composition of the simulated cooling water (SCW)

Chemical added	Weight (mg)	Ions	Concentration (ppm)
NaCl	524	Cl ⁻	318
CaSO ₂ ·2H ₂ O	503	Ca ²⁺	117
MgSO ₄ ·H ₂ O	322	Mg ²⁺	56

Table 2 Composition of the carbon steel working electrode

Element	C	P	S	N	Fe
Weight (%)	0.17	0.045	0.045	0.009	Balance

thus additives must be blended with the inhibitor components to prevent such deterioration of the inhibitive film [13,14].

Extensive studies had been undertaken in order to find other additives with which to synergize so allowing lower levels of nitrates to be effectively used [15,16]. Synergism, which implies applying multicomponent inhibitor mixtures, can play a big role in developing more efficient, less toxic chemicals and at lower concentrations blend as corrosion inhibitors with optimal anticorrosion effect.

The inhibitor, Corin SN-50, was originally developed, by the chemical research center of the Hungarian Academy of Sciences, for cooling liquids of automobiles, which besides softening water prevents the corrosion of all metallic parts of the radiator. It has synergistic compositions of organic and inorganic compounds containing nitrogen, phosphorous, and sulphur but no chromates.

The aim of our studies to develop and investigate new nitrite based inhibitor blends against iron corrosion in SCW containing high chloride concentration. The investigation will blend the inhibitor SN-50 with NaNO₂ in order to see the effect of the blend. Electrochemical methods, both open circuit potential and EIS methods are applied in this study. Polarization resistance (R_p) values were registered by the EIS system over longer time.

2. Experimental Methods

2.1. Electrolytes

The composition of the applied SCW is prepared by adding the chemicals in Table 1, to 1 L of distilled water.

The inhibitor, SN-50, is a blend of the sodium form of several compounds, such as nitrites and silicates etc. The product density was 1.2 g/cm³ at 20°C, pH of ≈ 12,

and was available at 25% concentration. In this study: 500, 1000 and 1500 ppm product concentrations have been investigated, which corresponds to 125, 250 and 375 ppm of inhibitor concentration. The inhibition of nitrite on steel corrosion is investigated in different concentrations of nitrite anion: 300, 450, and 600 ppm (equal to 450, 675, and 900 ppm NaNO₂).

2.2. OCP and EIS measurements

The protective effect of different inhibitor compositions was followed by measuring the OCP and the EIS spectra in time. Electrochemical experiments were performed using a standard three-electrode cell of 500 cm³ volume at room temperature. The working electrode (WE) was CS embedded into epoxy resin, the counter electrode (CE) was platinum net, and reference electrode (RE) was a saturated calomel electrode (SCE). All measured potentials are related to this reference electrode. The WE had the composition of (A38, according to MSZ-500-1989), as shown in Table 2.

The WE electrode was wet-polished with SiC papers (grit sizes of 800 and 1200), rinsed with acetone and double distilled water, then immersed in the electrolyte solution. Measurements were performed at room temperature according to the procedure described in ASTM G5-14 standard [17].

EIS measurements were carried out using Solartron Electrochemical Interface ECI-1286 and a frequency response analyzer FRA-1250, controlled by CorrWare and ZPlot software packages. The applied frequency range (time necessary to measure the impedance spectra) was previously optimized according to the change of OCP in time. The frequency range of 30 kHz to 10 mHz was applied. Polarization resistance values (R_p) from impedance spectra were registered in time with batch mode in order to monitor the change of inhibitor effect in time for 3 days:

- Open circuit potential was measured during the first hour of immersion, and the first impedance spectrum was measured after it.
- The second impedance spectrum was recorded after 2 hours of immersion.
- Further, 90 min waiting time was applied between measurements of impedance spectra.

The quantitative analysis of the experimental impedance data was performed by the non-linear least square minimization method using a theoretical transfer function. The inhibition efficiency was calculated using the following relationship:

Table 3 Summary of total inhibitor concentrations and nitrite contents applied in the studies

Diluted Corin SN-50 product (25%)	Inhibitor concentration (ppm)	NaNO ₂ concentration (ppm)
500 ppm	125	12.6
1000 ppm	250	25.2
1500 ppm	375	37.8
2000 ppm	500	50.4

Table 4 Total inhibitor concentrations and nitrite contents of the investigated inhibitor mixtures

Name	Inhibitor mixture		Total inhibitor concentration (ppm)	Total NaNO ₂ concentration (ppm)
	Corin SN-50 (25%)	NaNO ₂		
A	500 ppm	150 ppm	275	162.6
B	500 ppm	300 ppm	425	312.6
C	500 ppm	450 ppm	575	462.6
D	1000 ppm	150 ppm	400	175.2

$$\eta (\%) = \frac{R_p - R_0}{R_p} \times 100 \tag{1}$$

where R_p and R_0 are the polarization resistance of CS in the presence and absence of the inhibitor, respectively.

2.3. Applied concentrations of sodium nitrates, SN-50 and their blends

In the first part of this study, the inhibition of nitrite on carbon steel corrosion was investigated in different concentrations of nitrite anion: $C_1 = 300$ ppm, $C_2 = 450$ ppm and $C_3 = 600$ ppm, which corresponds to equivalent NaNO₂ concentrations of 450, 675 and 900 ppm, respectively.

In the second part of this study, the effects of 500, 1000, 1500, (and 2000) ppm product concentrations (which corresponds to 125, 250, 375, and 500 ppm inhibitor concentration) as shown in Table 3 have been investigated.

In the third part, the inhibitor efficiency of the newly formulated inhibitor blend for steel corrosion is investigated. Four different blends (A, B, C, and D) were tested, as shown in Table 4. The inhibitor mixture contains NaNO₂ in high concentration due to the anodic nature of SN-50.

Images of the electrodes were made in order to visualize the corrosion and inhibition effects.

3. Results and Discussion

At first, the inhibition effect of NaNO₂, which is the main component of inhibitor blend, is discussed.

3.1. Inhibition effect of NaNO₂ on CS corrosion

Since nitrite is an anodic inhibitor, a great care must be taken to select the applied inhibitor concentration (protective concentration (C_p)). At concentrations lower than the critical concentration (C_c), acceleration of corrosion takes place; hence the term “dangerous inhibitor” is used. The reason of the acceleration of corrosion is that at concentrations lower than C_p , the surface is only partially covered with inhibitor, and the electrode potential is shifted strongly to more anodic direction, so the corrosion rate at the uncovered areas is increasing significantly. At concentrations higher than C_p , nitrite anions inhibit corrosion effectively.

In the literature data, it was estimated that $C_{\text{nitrite}} = 240$ ppm is the minimum nitrite concentration required to protect steel in the simulated model solution.

The change of OCP of CS during the 3 days of immersion time (measured before each impedance spectra) is shown in Fig. 1. The change of OCP of CS, in inhibited and uninhibited solutions, is good indication of the inhibition effect of the applied inhibitors. Usually, by applying anodic inhibitors the higher the shift of OCP to anodic direction, the higher the inhibition efficiency may be estimated. But in case of mixed type inhibitors, this relationship between OCP and inhibitor efficiency is not applicable due to mixed behavior of anodic or cathodic shifts.

The OCP of CS increased from active to pre-passive potential range in the first hour of immersion time, in presence of NaNO₂ inhibitor in all investigated concentration, as shown in Fig. 1. This is due to the formation

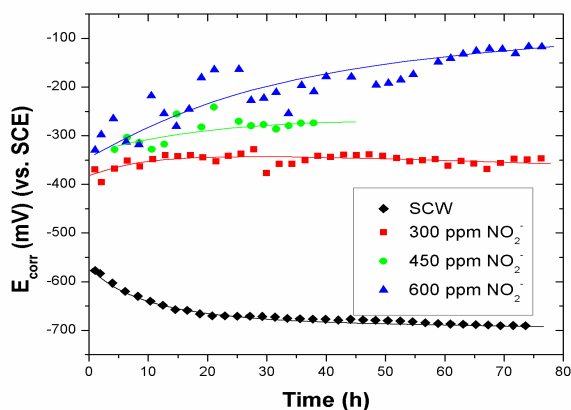


Fig. 1 Change of OCP of CS in SCW with and without NaNO_2 inhibitor during 72 hrs of immersion.

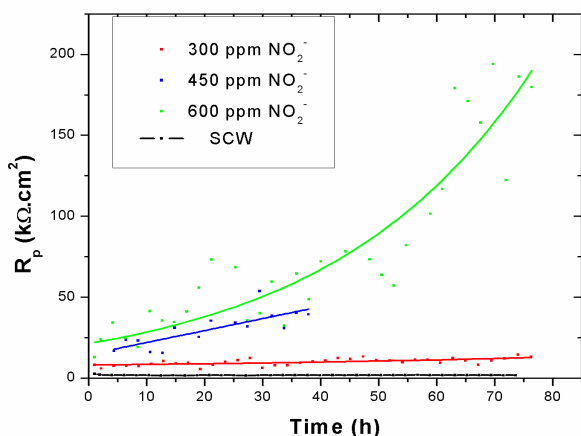


Fig. 2 R_p values of CS in SCW with and without NaNO_2 inhibitor during 72 hrs of immersion.

of a protective layer on steel preceding the immersion of the electrode into the solution. Fig. 1 shows further increase of OCP is taking place in time during the 3 days

immersion period. Applying a concentration of 600 ppm nitrite, the potential reaching the value of -120 mV (vs. SCE) is an indication that passivation took place at the steel surface.

The change of R_p value of CS in time in uninhibited SCW and with the addition of NaNO_2 inhibitor during three days of immersion is plotted in Fig. 2. The polarization resistance of CS in uninhibited model water reached a constant value of $1.8 \text{ k}\Omega\cdot\text{cm}^2$ after 5 hours of immersion, which is generally obtained in near neutral solutions for steel corrosion, independent of the composition of supporting electrolyte and exact composition of CS, and determined mostly by the diffusion controlled oxygen reduction. The stable OCP, near to 680 mV (Fig. 1) indicates that the steel is in active metal dissolution state.

The presence of sodium nitrite in all investigated concentration increased the R_p of steel in the chloride containing SCW (Fig. 2). The higher the applied nitrite concentration (in the C_p range), the higher the polarization resistance obtained. It is worth mentioning that by increasing the inhibitor concentration resulted in significant non-linear increase of polarization resistance (Table 5).

The average values of polarization resistance for 300, 450 and 600 ppm nitrite anion are 11, 36 and $150 \text{ k}\Omega\cdot\text{cm}^2$, respectively, and the inhibition efficiency values are higher than 80% in all cases.

Comparing the pictures of CS surfaces after 3 days of corrosion test, it can be stated that the blemished area decreased due to the addition of nitrite inhibitor, but the surface was not protected completely (Fig. 3).

3.2. Inhibition effect of Corin SN-50 on CS corrosion

In this part of the study SN-50 product concentrations of 500, 1000, 1500, and 2000 ppm, which corresponds

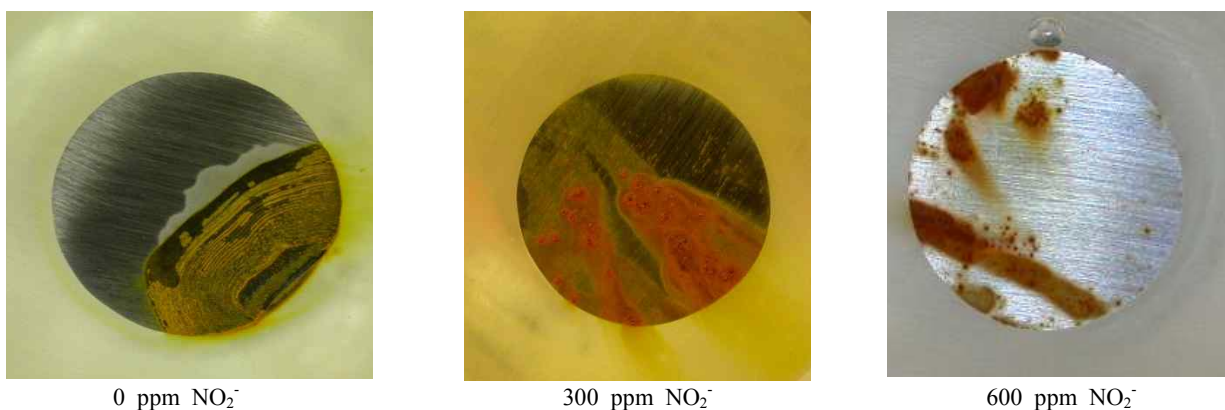


Fig. 3 Surface of CS electrodes after 3 days of immersion in SCW in the presence of nitrate anions.

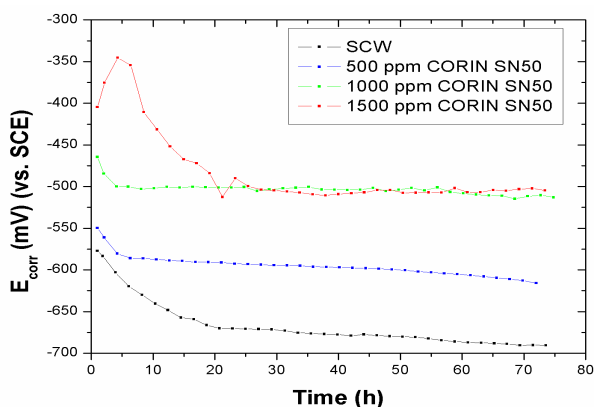


Fig. 4 Change of OCP of CS in SCW with and without Corin SN-50 during 3 days of immersion.

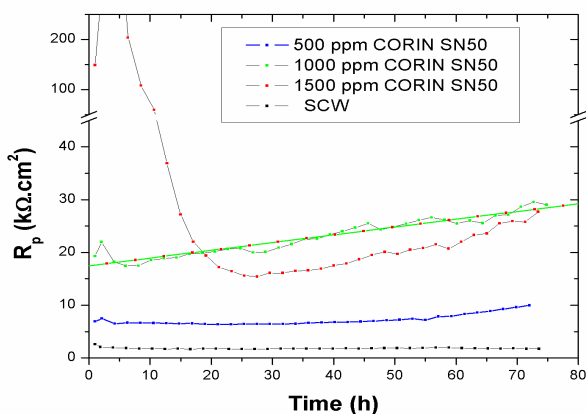


Fig. 5 Change of R_p of CS in SCW with Corin SN-50 during 3 days of immersion.

Table 5 Summary of polarization resistance and inhibitor efficiency values of investigated inhibitor mixtures applied in our studies

Inhibitor mixture	R_p ($k\Omega.cm^2$)	Efficiency (η) _{average} 48-72 h (%)
Blank solution	1.8	-
300 ppm NO_2^-	11	83.6
450 ppm NO_2^-	36	95.0*
600 ppm NO_2^-	150	98.8
500 ppm Corin SN-50	8.5	78.8
1000 ppm Corin SN-50	27	93.3
1500 ppm Corin SN-50	24	92.5
2000 ppm Corin SN-50	22	92.0
Inhibitor composition A	23	92.2
Inhibitor composition B	2900	> 99.9
Inhibitor composition C	3400	> 99.9
Inhibitor composition D	5100	> 99.9

* Average between 24 h - 48 h.

to 125, 250, 375, and 500 ppm active inhibitor concentration, have been investigated (Table 3).

The change of OCP of steel in time in SCW, containing Corin SN-50 inhibitor, during the 3 days of corrosion test is plotted in Fig. 4.

The OCP shifts to anodic direction due to the effect of inhibitor addition to the SCW. The OCP is stable after 20 h of immersion in each case (Fig. 4), at -680 mV (active state) in uninhibited solution, and at slightly higher potentials in inhibited solutions near to -600 mV (500 ppm Corin SN-50, which is equal to 125 ppm inhibitor content) and -500 mV (1000 and 1500 ppm Corin SN-50, which is equal to 250 and 375 ppm inhibitor content). This indicated that the corrosion inhibition is under mixed control, with slightly more pronounced anodic effect.

The change of polarization resistance of steel in time during 3 days of immersion in uninhibited SCW and with the presence of Corin SN-50 inhibitor is plotted in Fig. 5.

The addition of inhibitor in all applied concentration increased the polarization resistance of steel (Fig. 5). The average value of polarization resistance between 48 h and 72 h immersion is $8.5 k\Omega.cm^2$, in case of applying 500 ppm SN-50 (125 ppm inhibitor), which means 79% inhibition efficiency compared to the uninhibited solution. Improvement in inhibition effect was obtained with increasing the inhibitor concentrations: the polarization resistance is $27 k\Omega.cm^2$ applying 1000 ppm SN-50 product (250 ppm inhibitor), and $24 k\Omega.cm^2$ applying 1500 ppm SN-50 product (375 ppm inhibitor).

An interesting, unusual difference has been observed comparing the changes of inhibition effect in solution containing 1000 and 1500 ppm product (250 ppm and 275 ppm inhibitor) concentration in time in the first 20 h of immersion. Applying higher, 1500 ppm concentration (375 ppm inhibitor), the inhibitor tend to passivate steel for shorter time (few hours), the OCP is increasing continuously up to -340 mV (Fig. 4), and the polarization resistance is increasing up to $200 k\Omega.cm^2$ (Fig. 5). The passivation process was not completed, and after 6 hrs of immersion decrease in both OCP and polarization resistance is taking place, relating to the so-called breakdown of passive film in the presence of chloride ions in the solution. After 20 hrs of immersion, the polarization resistance is $24 k\Omega.cm^2$, which is actually the same as the polarization resistance in the presence of 1000 ppm Corin product (250 ppm inhibitor). In this time period (20-72 h) the inhibitor protects steel with classical mixed type corrosion inhibition, with inhibition efficiency of 92-93%.

In order to better understand the phenomena described above, the inhibition effect of inhibitor in higher concen-

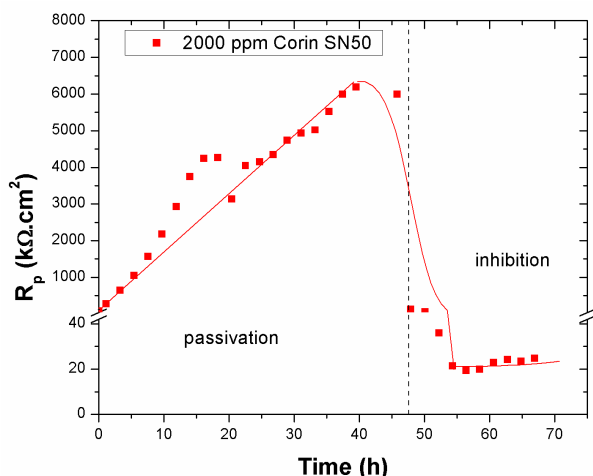


Fig. 6 Change of R_p of CS in SCW with 2000 ppm Corin SN-50 during 72 hrs of immersion.

tration has been also investigated. The time dependence of polarization resistance of steel during three days of immersion in the presence of 2000 ppm Corin SN-50 (500 ppm inhibitor content) is plotted in Fig. 6. The protection behavior of inhibitor can be clearly divided into two parts:

- At first, during 48 h of immersion, passivation of steel is taking place; the passive layer formation is continuous in time, resulting of thickening of passive oxide layer, thus increasing the polarization resistance. The time period of passive state is larger than that was observed in 1500 ppm containing solution.

In second, breakdown of passive state is taking place after 48 h of immersion, and the inhibitor efficiency in this range is 92% ($R_p=22 k\Omega \cdot cm^2$) which is same with the previously discussed cases (1000 ppm and 1500 ppm). The obtained 92-93% inhibition efficiency is characteristic for our inhibitor in large concentration range after longer immersion time.

Comparing the images of steel surface after 3 days of corrosion test (Fig. 7), it was found that the corroded area is decreased, but pitting type corrosion spots is visible.

For this reason, modification of inhibitor composition is necessary with increasing the concentration of $NaNO_2$, in order to eliminate the pitting attack completely.

3.3. Inhibitor effect of the newly formulated inhibitor blend for steel corrosion

In this chapter the inhibitor efficiency of our newly formulated inhibitor blend for steel corrosion is presented. The inhibitor mixture contains $NaNO_2$ in high concentration. Because of the anodic nature of the nitrite, addition of other inhibitor components is necessary. The inhibitor mixture contains both anodic and cathodic inhibitor components and the synergistic effect is optimized.

In the previous results section, it was presented, that the Corin SN-50 product is good corrosion inhibitor for steel, but does not protect steel completely from the localized pitting attack, when the cooling water contains chloride in high concentration.

In order to eliminate the pitting corrosion, the concentration of $NaNO_2$ was increased; Table 4 summarizes the concentrations of applied inhibitor mixtures.

The change of OCP of steel in time in inhibited SCW (containing A, B, C and D inhibitor compositions) during days of immersion is presented in Fig. 8. The OCP of steel shifted to more anodic direction in the first hour of immersion, which is due to the inhibitor addition effect. It indicates the buildup of protective inhibitor layer on the steel surface just after the immersion of the electrode into the inhibited solution. Further increase of OCP is taking place in time during 72 hrs, in case of applying inhibitor B, C and D (Fig. 8). The potential reaching the value of $-200 mV$ vs. SCE, indicating that the steel surface has been passivated. Lesser potential shift to anodic

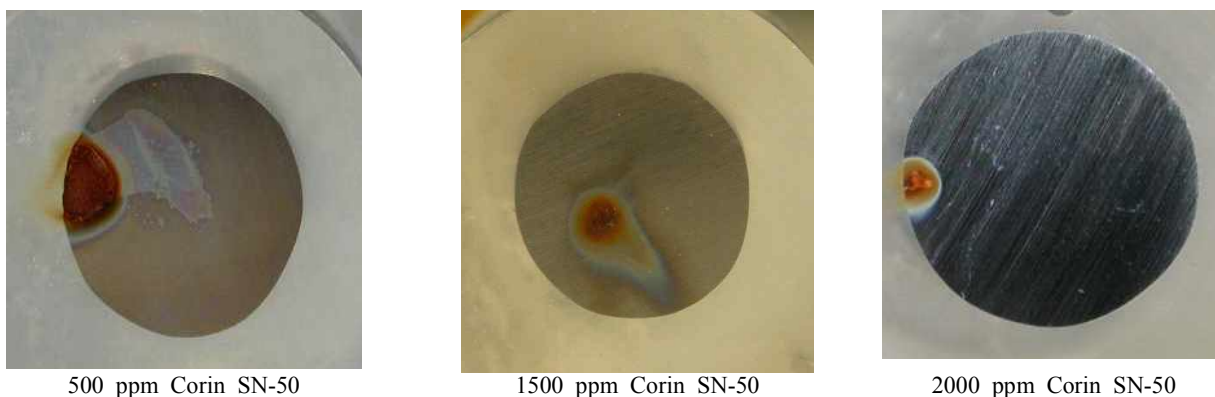


Fig. 7 Surface of steel electrodes after 72 hrs of immersion in SCW in the presence of Corin SN-50 inhibitor.

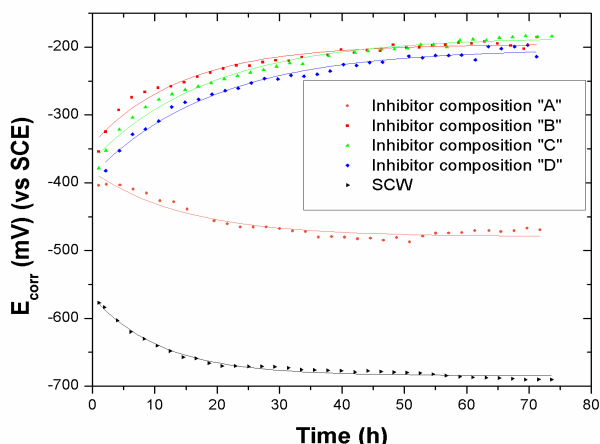


Fig. 8 Change of OCP of CS in SCW without and with (A, B, C and D Inh. Comp.) during 72 hrs of immersion.

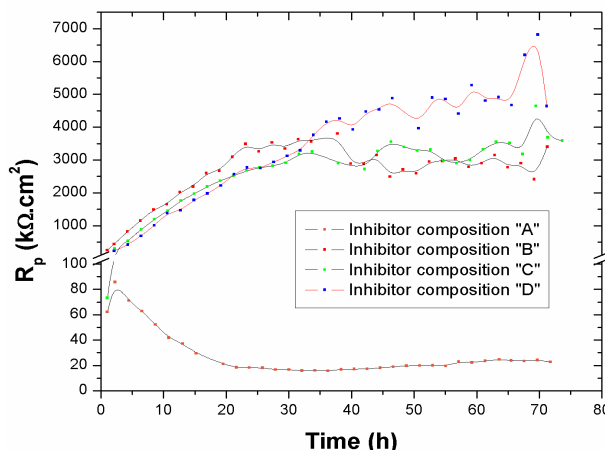


Fig. 9 Change of Rp of CS in SCW with (A, B, C, and D in Table 4) during 72 hrs of immersion.

direction was measured in case of inhibitor composition A (reaching the potential value of -470 mV vs. SCE), indicating lower protective effect against steel corrosion.

The change of polarization resistance of CS during 72 hrs of immersion in uninhibited SCW and with the presence of inhibitors is plotted in Fig. 9. Addition of inhibitor composition “A” increased the polarization resistance of steel in the SCW and reached the value of 23 kΩ.cm²,

(92% inhibitor efficiency) after 72 hrs of immersion period. This is similar to the inhibitory effect previously obtained in several cases (1000, 1500 and 2000 ppm Corin SN-50). This inhibitor mixture inhibits the steel, but some corrosion attacks are visible at the surface (Fig. 10).

Much larger improvement in inhibition effect has been obtained in case of “B”, “C” and “D” compositions. The polarization resistance values are 2000-6000 kΩ.cm² after

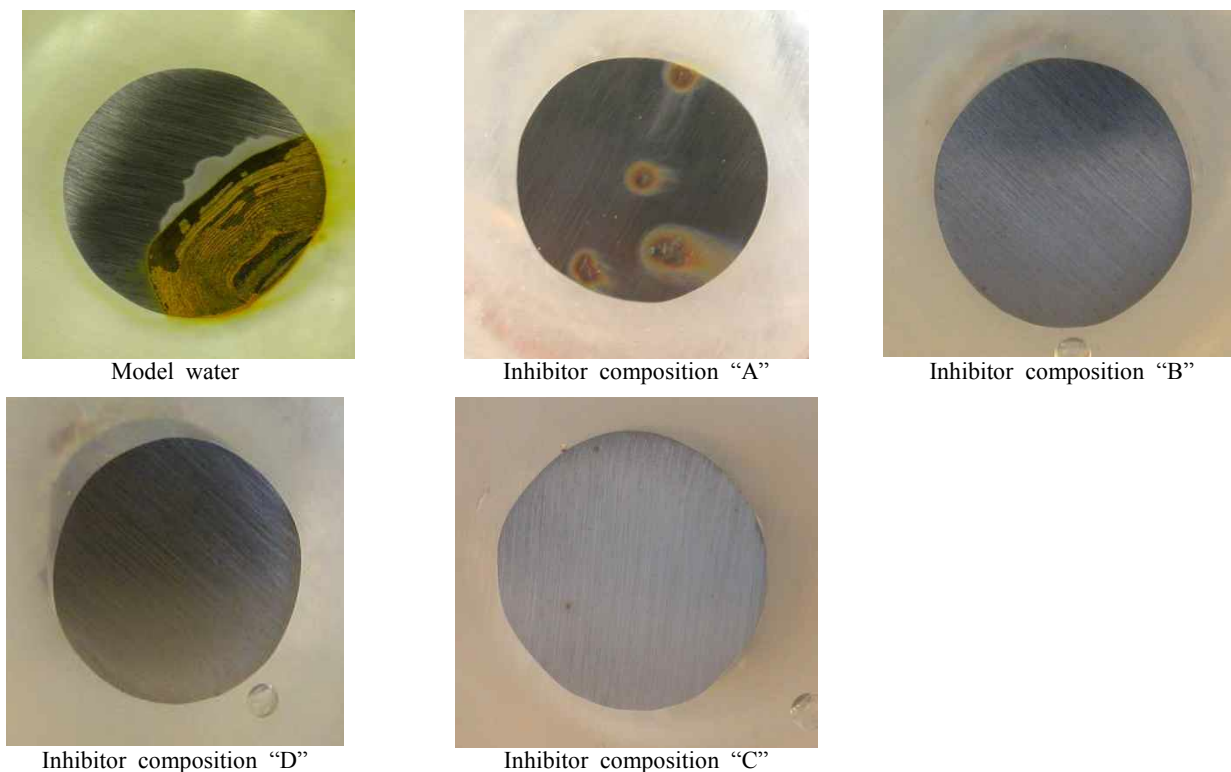


Fig. 10 Surface of steel electrodes after 72 hrs of immersion in SCW in the presence of (A, B, C, and D) inhibitor compositions.

3 days of immersion, indicating that the passive layer formation is complete, and no breakdown of passive layer was obtained during the whole corrosion test. Comparing the pictures, obtained after 72 hrs of corrosion tests, no corrosion attack is visible at the steel surface (Fig. 10). The corrosion protection of steel with these new product compositions is excellent.

These new inhibitor blends provided good protection, in spite of its low nitrite concentration. This is due to the synergistic effect between nitrite ions and other components of inhibitor mixture.

Synergism is one of the most important phenomena in corrosion inhibition processes and serves as a basis for all modern corrosion inhibition formulations [13]. The amount of chemicals applied can be decreased, and the application of environmentally acceptable but less effective compounds can be realized in this way. When the joint effect is better than expected by simple addition, it is suggested that the inhibitors have a synergistic effects on each other.

Synergism is a nonlinear effect resulting in non-additive efficiencies of inhibitor components [14]. Often, this effect can't be easily explained, but it is likely that at least for some mixtures the mechanism of inhibition by synergistic mixtures differs from the mechanisms of the individual inhibitors.

3.4. Solubility and stability tests for concentrated inhibitor products

Commercial inhibitor blends must be prepared in as high concentration as possible, in order to reduce the prices of transportation and storage before application. For this reason inhibitor products must be soluble and stable in high concentrations. We have prepared the inhibitor products in 25 m/m%. The solubility of inhibitor formulations "B", "C" and "D" in this concentration proved to be satisfied. Concentrated solutions must be stable in changing temperature conditions (winter/summer, day/night) during storage, or shaking during transportation or handling etc. For this reason the stability of solutions was tested for longer time applying cooling/warming up cycles and stirring. Inhibitor formulations of "B" and "D" in 25% concentration proved to be stable for long time, thus we can conclude that these inhibitor mixtures has potential application in high chloride-containing cooling water system after testing the inhibition efficiency in real operation conditions.

4. Conclusions

The synergetic effect by blending sodium nitrites with the inhibitor SN-50 was studied in SCW containing high chloride concentration.

The presence of sodium nitrites alone in the solution shifted the OCP to more anodic with inhibition efficiency of up to 98%, while the addition of SN-50 inhibitor produced an efficiency of 93%. Blends of the SN-50 inhibitor and sodium nitrites produced improved inhibition effectiveness where the efficiency reached 99.9%, which is the result of the completion of the formation of passive layer without any breakdown.

The formulated nitrate-Sn 50 compositions (A, B, C, and D) produced good protection against CS corrosion in SCW, in spite of their low nitrite concentration. This is due to the synergistic effect between nitrite ions and other components of SN-50 inhibitor mixture.

Visualizing the obtained images after 72 hrs of immersion tests, it is clear that no corrosion attack is visible at the Cs surface.

Acknowledgments

This work was supported by CRC-PCR projects.

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