

Investigation of corrosion inhibitors with demulsifiers in their composition

E. Podgorbunskikh,^{ID}* T. Skripkina,^{ID} L. Semikhina^{ID}
and R. Abdrashitova^{ID}

Laboratory of geological and hydrogeological support for the development of hydrocarbon fields, Industrial University of Tyumen, 625000 Tyumen, Russian Federation

*E-mail: podgorbunskikh@bk.ru

Abstract

The paper examines the potential utilization of corrosion inhibitors reagents with a complex effect (Complex Effect Reagents, CER), containing chemical compounds that are not only typical for corrosion inhibitors but also possess demulsifying properties, as corrosion inhibitors for carbon steel. The work examines the inhibitory properties of three samples obtained by mixing a commercially produced sample with phosphorus and amine compounds, and non-ionic surface active agents. CERs were prepared with the addition of modifiers in the form of potassium salt of phosphoric acid (CER-1); ethoxylated phenolic resins and block copolymers of diethanolamine (CER-2); and block copolymers of diethanolamine (CER-3). The inhibition efficacy of carbon steel was demonstrated through the weight loss and potentiodynamic polarization methods, microscopic analysis of corrosion morphology (SEM, TEM), XRD, EDS, and FTIR. The most effective is the complex effect reagent mixed with phenolic resins and block copolymers of diethanolamine, which is confirmed by weight loss and potentiodynamic polarization experiments. According to the data of potentiodynamic polarization method, the inhibition efficiency of the CER with the addition of modifiers in the form of potassium salt of phosphoric acid (CER-1) has only 52%. The CER based on ethoxylated phenolic resins and diethanolamine block copolymers (CER-2) has an inhibition efficiency of 68%. The CER-3 based on block copolymers of diethanolamine (CER-3) has an inhibition efficiency of 55%.

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Keywords: carbon steel, corrosion, corrosion inhibitors, demulsifiers, potentiodynamic polarization, TEM.

1. Introduction

Despite the advancement of alternative energy sources, oil and natural gas remain the primary sources of energy throughout the world. One common technique for oil recovery is waterflooding, which involves injecting water into the well to maintain or augment reservoir pressure. This process may lead to corrosion of pipelines and equipment [1–3], as well as the formation of oil-water emulsions [3]. The issue of oil water cut that arises as a result of water injection into the reservoir at most oil fields may be solved by introducing demulsifiers [4, 5].

Carbon steel (CS) equipment is extensively utilized in the oil and gas industry due to its superior performance attributes [6]. Nonetheless, the corrosion resistance of carbon steel in corrosive aqueous environments is comparatively limited, necessitating the utilization of corrosion inhibitors to enhance equipment longevity [7]. The most common forms of corrosion are carbon dioxide (CO₂) and hydrogen sulfide (H₂S) corrosion, as well as corrosion caused by dissolved oxygen in produced water-cut oil [8]. Inhibitors utilized in the oil industry must satisfy a diverse range of criteria, including possessing a significant protective effect at minimal concentrations, exhibiting minimal adverse effects on the technological processes of oil collection, preparation, transportation, and processing, and possessing a moderate toxic profile. Several known organic inhibitors contain heteroatoms (N, O, P, S), π -electrons, as well as aromatic rings and double or triple bonds. Nonetheless, the data pertaining to the corrosion protection of steel equipment in solutions that are closer to the conditions of formation water is insufficient [9].

There are few studies in the literature that evaluate the effect of the joint use of demulsifiers and corrosion inhibitors on the technological process of oil production and treatment in the fields. It is demonstrated in references [10, 11] that corrosion inhibitors can both reduce and increase the effect of demulsifiers. It is assumed that demulsifiers will reduce the effectiveness of corrosion inhibitors due to their ability to remove the adsorption films of corrosion inhibitors from the surface of the equipment. Previously, it was demonstrated that the simultaneous action of demulsifiers and corrosion inhibitors in a real oil field in Russia can be observed as a complete suppression of the technological action of both demulsifiers and corrosion inhibitors [12].

The use of complex action reagents (CER), which combine the properties of demulsifiers and corrosion inhibitors, will help to avoid suppression of the technological action of individual components. However, the development of CERs has only recently begun, and in most cases, such reagents have a reduced efficiency compared to individual demulsifiers or corrosion inhibitors [13].

The possibility of obtaining CER through the optimal composition of a mixture of demulsifiers and corrosion inhibitors is illustrated in reference [14]. Furthermore, the CER obtained this way acquired a higher technological efficiency compared to the initial reagents as corrosion inhibitors and demulsifiers, which demonstrates the possibility of developing highly effective CER, as well as the prospect of such reagents. According to [14], CER was prepared from two off-the-shelf multicomponent commercial forms of demulsifier and corrosion inhibitor based on imported reagents. The aim of this study is to develop CER with the properties of corrosion inhibitors and demulsifiers based on phosphoric acid salts, ethoxylated phenolic resins and diethanolamine block copolymers, and to investigate their principle of action and protective corrosion properties.

2. Materials and Methods

2.1. Preparation of complex effect reagents

The selection of reagents for the manufacture of CERs with corrosion inhibitor properties was based on a review [11] in which possible compositions of corrosion inhibitors for various aggressive aqueous media were given. A critical analysis of [11] led to the conclusion that, regardless of the water composition, phosphorus and amine compounds, as well as various non-ionogenic surface active agents (surfactants) should be introduced into the corrosion inhibitor composition. In Figure 1, the chemical structures of phosphoric acid, ethoxylated phenolic resins, and diethanolamine are shown.

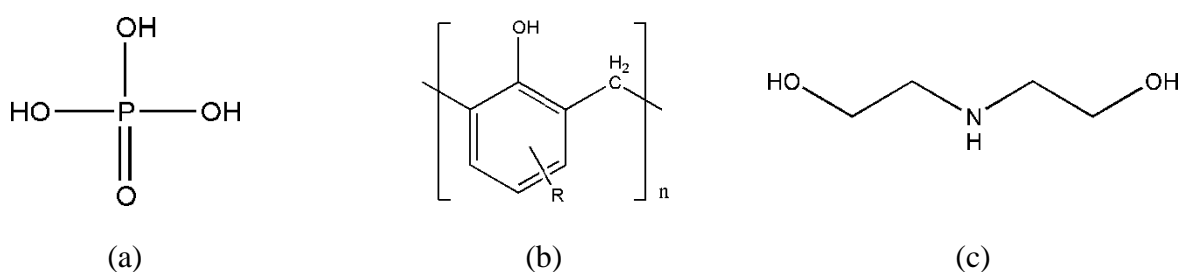


Figure 1. Structures of phosphoric acid (a), ethoxylated phenolic resins (b), and diethanolamine (c).

The complex reagents included potassium salt of phosphoric acid (PJSC Khimprom, Novocheboksarsk Russia) as a phosphorus compound, and “Lapramol 6504” (LLC R&D company “Macromer”, Vladimir, Russia) as an amine compound. The advantage of “Lapramol 6504” is that it also has fairly good demulsifying ability (Table 1). And ethoxylated resins (Resin Alkoxylyte) with high demulsifying ability were introduced into CER as nonionic surfactants.

Table 1. Comparison of the demulsifying efficiency of reagents used in the composition of commercial corrosion inhibitors (LLC R&D company “Macromer”, Vladimir, Russia), by the volume of water (V_{water} , %) released from the artificial 50% highly stable water-oil emulsion 1 and 2 hours after their introduction (temperature $T=50^{\circ}\text{C}$, demulsifier dose 60 g/t oil).

Reagent	V_{water} (%) through	
	1 hour	2 hours
Block copolymer	42	54
Lapramol 6504	31	52
Resin Alkoxylyte 1	31	57
Resin Alkoxylyte 2	52	92

The work examined the inhibitory properties of three samples obtained by mixing a commercially produced sample under the brand name “Reapon K” (LLC R&D company “Macromer”, Russia) with phosphorus and amine compounds, and non-ionogenic surface active agents (surfactants). CERs were prepared with the addition of modifiers in the form of potassium salt of phosphoric acid (CER-1); ethoxylated phenolic resins and block copolymers of diethanolamine (“Lapramol 6504”) (CER-2); and block copolymers of diethanolamine (“Lapramol 6504”) (CER-3). From these reagents, three liquid 50% commercial forms of CER samples (CER-1; CER-2; and CER-3) were prepared in an alcohol solvent, the compositions of which were optimized by the dielectric method using a patented procedure [15, 16].

2.2. Specimens and solutions

In this study, carbon steel (CS) coupons were utilized as metal substrates. The chemical composition of CS is shown in Table 2.

Table 2. Chemical composition of carbon steel used in the work.

Element	C	Si	Mn	S	P	Ni	Cr	Cu	As	Fe
wt.%	0.17–0.24	0.17–0.37	0.35–0.65	<0.04	<0.035	<0.3	<0.25	<0.3	<0.08	Balance

CS from the steel pipe is cut into coupons with dimensions of 10×10×4 mm for weight loss measurements. In order to conduct electrochemical experiments, specifically potentiodynamic polarization measurements, the non-working area of the steel sample was sealed with epoxy resin, while the working surface was subjected to mechanical grinding and polishing. The coupons were meticulously ground using silicon carbide (SiC) grit sandpaper up to 1200 grit, followed by washing with acetone and drying at room temperature. A sample of CS was used as a working electrode. The area that was exposed in these samples was 3.6 cm².

The corrosion rate of steel samples was studied using aqueous solutions of complex reagents (CER-1; CER-2; and CER-3) at a concentration of 10–25 mL/L, typical for oil fields. Most of the experiments were conducted in the presence of atmospheric oxygen on a model of the formation water, which was simulated by 2.0 wt.% NaCl solution.

Additionally, the suitability of the fabricated CERs for use in a reservoir pressure maintenance system was investigated. These experiments were conducted at a temperature of 35°C in an appropriate corrosive aqueous environment containing 15 mg/L hydrogen sulfide, 10 mg/L carbon dioxide (oxygen is not present), and the ionic composition of water presented in Table 3. The electrolyte solution was pre-blown with nitrogen before the test in order to remove dissolved oxygen. The deaeration time at a nitrogen flow rate of 70 L/hour was 10 minutes. The corrosion rate of metal samples was assessed in a turbulent mode when stirring the aqueous medium at a speed of 500 rpm.

Table 3. Ionic composition of model water.

Ion content, mg/L									
SO ₄ ²⁻	PO ₄ ³⁻	HCO ₃ ⁻	Cl ⁻	Si ²⁺	Ca ²⁺	Na ⁺	K ⁺	Mg ²⁺	Ba ²⁺
1939.2	<0.5	280.6	18176.0	12.0	621.2	10143.0	1033.6	0.12	

The reagents used in this study were as follows: sodium hydroxide (SIGMA-Aldrich), and acetone (CAS 67-64-1, EKOS-1 JSC, Moscow, Russia).

2.3. Weight loss measurements

The effect of treatment with CER-1–3 on the corrosion rate of carbon steel in a 2.0 wt.% NaCl solution in the presence of air oxygen was investigated using the static mass loss method. The coupons were weighed using an analytical electronic digital scales FA2104A (LLC Pushchino Laboratories Company, Pushchino, Russia) before being immersed in a container with 100 ml of a 2.0 wt.% NaCl solution. Solutions were fixed for up to 12 days. The determination of the weight loss of the electrodes following a duration of 12 days of experimentation drying was made by determining the variance in the weight of the electrodes. The coupons were thoroughly cleaned and washed with distilled water, degreased with acetone and weighed with an electronic balance. Each experiment was conducted on three occasions, and the average values were subsequently calculated.

The corrosion rates (*CR*) of carbon steel and the inhibition efficiency (*IE*) of corrosion inhibitors were calculated using the following formulas [17]:

$$CR = \frac{\Delta W \cdot 87600}{S \cdot t \cdot \rho} \quad (1)$$

$$IE\% = \frac{CR^0 - CR}{CR^0} \cdot 100\% \quad (2)$$

where, ΔW (g) is the mass difference of the carbon steel samples before and after the experiment; S (cm²) is the surface area of the carbon steel samples for the experiment; t (h) is the immersion time of the samples; ρ (g/cm³) is the density of the carbon steel samples used in the experiment; CR and CR^0 (mm/y) are the corrosion rates of the carbon steel samples in the solution with the corrosion inhibitors and in the blank solution, respectively.

2.4. Potentiodynamic polarization (PDP) measurements

The corrosion resistance tests for CS samples were carried out in 2.0 wt.% NaCl solution in a three-electrode cell connected to a VoltaLab 50 potentiostat (Radiometer Analytical, Villeurbanne, France) at room temperature.

Potentiodynamic polarization measurements were carried out at electrode potentials from –800 to 200 mV with respect to open circuit potential (OCP) at a scan rate of 1 mV/s.

All measured potentials were recalculated relative to a standard hydrogen electrode. Corrosion potential and current density were calculated using Tafel extrapolation.

The corrosion protection efficiency (*IE*) and corrosion rate (*CR*) were calculated by the following equation [18, 19]:

$$IE\% = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \cdot 100\% , \quad (3)$$

$$CR = \frac{3270 \cdot M \cdot i_{\text{corr}}}{\rho \cdot Z} \quad (4)$$

where i_{corr}^0 and i_{corr} present the corrosion current densities without and with inhibitor, respectively, 3270 (rel. units) – constant, M (g/mol) – atomic mass of metal, ρ (g/cm³) – density of corroding metal, Z = number of electrons transferred per metal atom ($Z=2$).

2.5. Fourier transform infrared spectroscopy (FTIR)

The determination of functional groups on the metal surface was carried out by employing the Cary-630 Agilent Fourier transform IR spectrophotometer (Agilent Technologies, Santa Clara, CA, United States). The analysis was conducted by scanning the sample through a wave number range of 400 to 4000 cm⁻¹.

2.6. Microstructure and composition of surface morphology

The microstructure and composition of carbon steel samples were examined using scanning electron microscopy (SEM) on a S-3400N electron microscope (Hitachi, Tokyo, Japan) at an accelerating voltage of 15 kV. Additionally, energy-dispersive X-ray spectroscopy (EDS) was conducted on the coupons using an attachment for energy dispersive spectroscopy (EDS) system NORAN (Thermo Fisher Scientific Inc., Waltham, MA, USA).

2.7. X-Ray diffraction analysis (XRD)

The X-ray diffraction analysis (XRD) of steel samples was performed using a D8 Advance diffractometer (Bruker, Karlsruhe, Germany) using monochromatic Cu-K α radiation in the Bragg-Brentano geometry. Analysis was performed from a wide range of angles between 10 and 120 degrees.

2.8. Transmission electron spectroscopy (TEM)

The fine structure of corrosion products was studied using high-resolution transmission electron microscopy (HR-TEM) on a JEM-2100 microscope (Jeol, Japan) using a dual tilt beryllium holder (Jeol, Japan). The chemical composition of the local regions was measured using an 80 TLE X-Max detector (Oxford, UK) using an EDS.

3. Results and Discussion

3.1. Weight loss measurement

The gravimetric technique is the most straightforward and preferred corrosion analysis technique utilized to evaluate the inhibitory effect of inhibitors. It has gained widespread acceptance due to its lack of intricate instruments. In this particular technique, the mass loss of CS samples following corrosion and inhibition processes was measured, and the resulting values were utilized to estimate significant parameters such as corrosion rate and inhibition efficiency (Table 4). The primary constituent of CER-1 is the potassium salt of phosphoric acid, which impairs the capacity to form a protective layer on the surface of carbon steel. As can be observed, the minimal protective effect is attributed to CER-1, composition with a specific anticorrosive effect included only the salt of phosphoric acid. All other constituents are non-ionogenic surfactants possessing demulsifying capabilities. CER-2 and CER-3 are inhibitors that incorporate chemical compounds that possess demulsifying properties, enabling them to simultaneously break oil-water emulsions that are formed during oil production. The incorporation of an amine compound (“Lapramol 6402”) into the composition of CER-2 and CER-3 significantly enhanced the efficacy of these reagents as corrosion inhibitors. In contrast to CER-1, the CER-2–3 exhibit superior performance. The inhibition efficiency (*IE*) increases to 60% in the presence of demulsifiers, and the CER-2 exhibits the highest efficiency (64.0%). The CER-2 comprises ethoxylated phenolic resins and a block copolymer based on diethanolamine, which enhances the adsorption capacity not only on the metal surface but also at the oil-water and oil-water emulsion interface. The CER-3 differs from the CER-2 through the incorporation only of a block copolymer based on diethanolamine, resulting in a significant enhancement of demulsifying capability, albeit with a slight decrease in protective ability (Table 4).

Table 4. Corrosion rate and corrosion inhibition efficiency of CER 1–3 in 2 wt.% NaCl solution measured by weight loss method.

Inhibitors	C_{inh} , mL/L	CR, mm/y	IE, %
Blank	–	0.511	–
CER-1	10.0	0.229	55.2
CER-2	10.0	0.184	64.0
CER-3	10.0	0.193	62.2

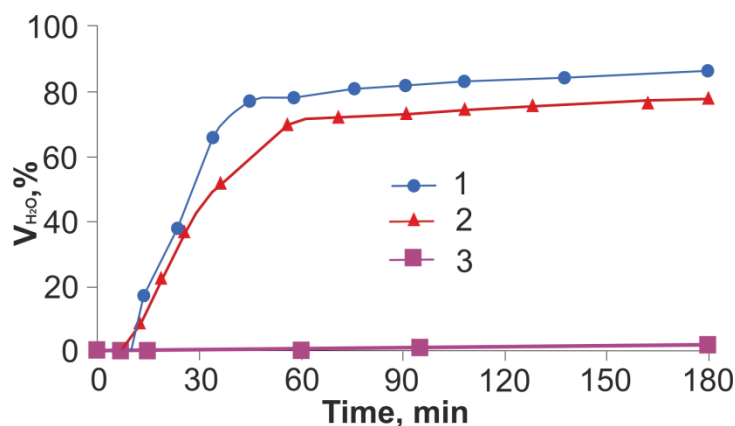
A more significant difference in the effect of manufactured reagents as corrosion inhibitors was shown in the experiment, in which the corrosion of CS samples was evaluated in a corrosive aqueous medium containing hydrogen sulfide (15 mg/L) and carbon dioxide (10 mg/L) (no oxygen), and when it was stirred in turbulent mode (stirring speed 500 rpm). The protective effect of CER-1 in this experiment was only 20%, which is very low, and the concentration dependence of the protective effect of CER-2 is shown in Table 5.

Table 5. Corrosion rate and corrosion inhibition efficiency sample solution CER-2 with 15–25 mg/L concentration in water (composition of water presented in Table 3) measured by weight loss method.

Inhibitors	C_{inh} , mL/L	CR, mm/y	IE, %
CER 2	0	0.259	–
	15	0.095	63.3
	20	0.073	71.8
	25	0.054	79.2

As can be seen, the protective effect of CER-2 increases with increasing dosage in water, and at the studied maximum dosage in water (25 mL/L), the protective effect is not satisfactory. It is obvious that the reason is the excessively high solubility of CER-2 in water, which requires higher dosages in order to form a continuous adsorption layer in its solutions. The protective effect of CER-3 was lower than for CER-2 and was 75.4% at a concentration of 25 mL/L. Our future plans are to identify the composition of a more optimal additive for CER-2, which could provide a 91% protective effect of CER already at its dose in water not more than 10–15 mL/L. This corresponds to the protective effect of the best corrosion inhibitors.

Figure 2 illustrates that the demulsifying efficacy of CER-2 is only marginally inferior to that of Separol WF-41 (BASF, Germany), a demulsifier that has been extensively compared across various demulsifiers developed in Russia for a considerable period of time.

**Figure 2.** Dynamics of water release from 50% artificial oil-water emulsion without a demulsifier (3) and after introduction of 40 g/t Separol WF-41 demulsifier (1) and CER-2 (2).

The reagents CER-1–3 studied in this work have a complex action, which is determined by the presence of demulsifiers in their composition. Hence, the utilization of CER enables a significant reduction in the expenses associated with oilfield reagents at oil fields, resulting in a significant reduction of almost tenfold. Furthermore, the incorporation of components manufactured in Russia in CER compositions, specifically LLC SPE “Macromer” (Vladimir,

Russia), not only mitigates the incompatibility of diverse reagents, but also, with the appropriate selection, can enhance their mutual reinforcement.

3.2. Potentiodynamic polarization measurements

The degradation of carbon steel in a 2.0 wt.% NaCl solution in the presence and absence of corrosion inhibitors was studied using potentiodynamic polarization. Tafel polarization curves are presented in Figure 3. Table 6 summarizes the parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion rate (CR), and percentage efficiency (IE). i_{corr} was used to calculate the corrosion rate (CR) and inhibition efficiency (IE) by utilizing equations (3) and (4), respectively.

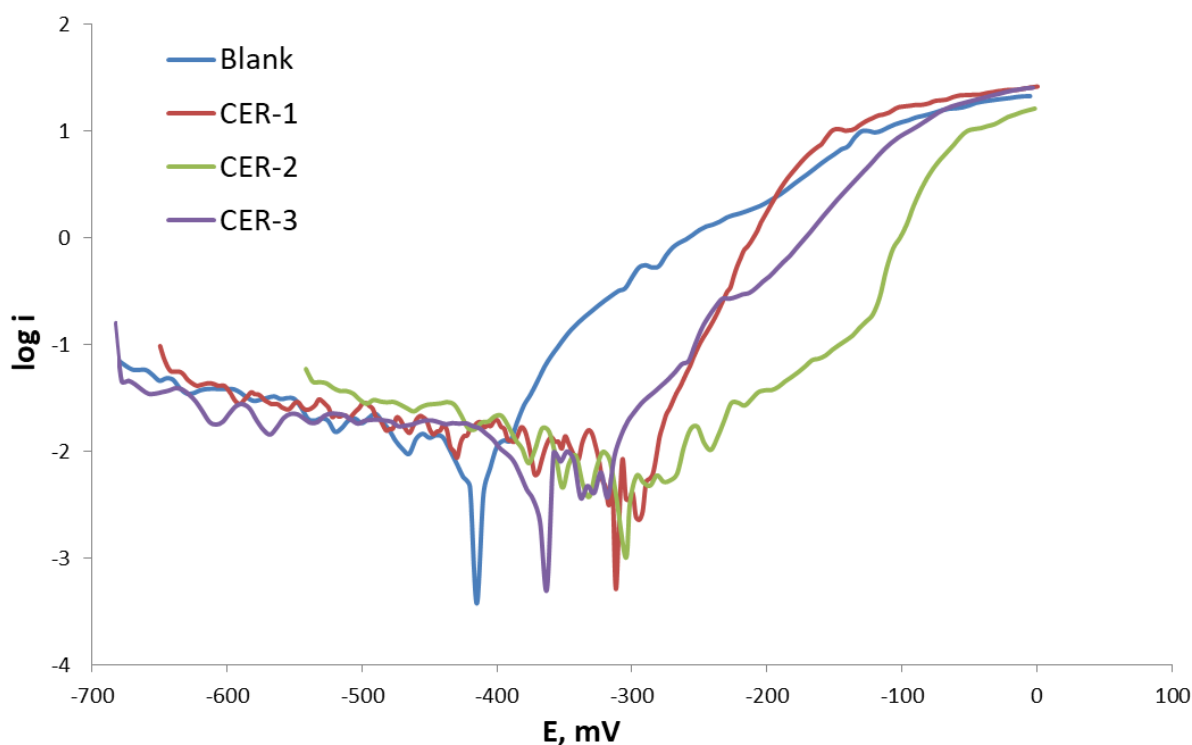


Figure 3. Polarization curves in 2.0 wt.% NaCl solution in the absence and in the presence of CER-1–3 (C_{inh} 10 mL/L).

The decrease in i_{corr} value for all three inhibitors shows that the addition of inhibitor inhibits the corrosion attack.

As depicted in Figure 3, the corrosion potential of the system exhibited a positive shift subsequent to the addition of CER-1–3. In contrast to the control sample (Blank), the cathodic slope of solutions containing CER-1–3 exhibits no discernible variations. According to [20, 21], the displacement in E_{corr} is greater than ± 85 mV relating to the corrosion potential of the blank, the inhibitor may be considered to be cathodic or anodic type. This implies that CER-1 and CER-2 are a kind of anodic inhibitor [22, 23]. The corrosion inhibitor may be classified as mixed type if the change in E_{corr} is less than ± 85 mV. For CER-3, the E_{corr} offset is ± 70 mV, which indicates that it is a mixed type inhibitor.

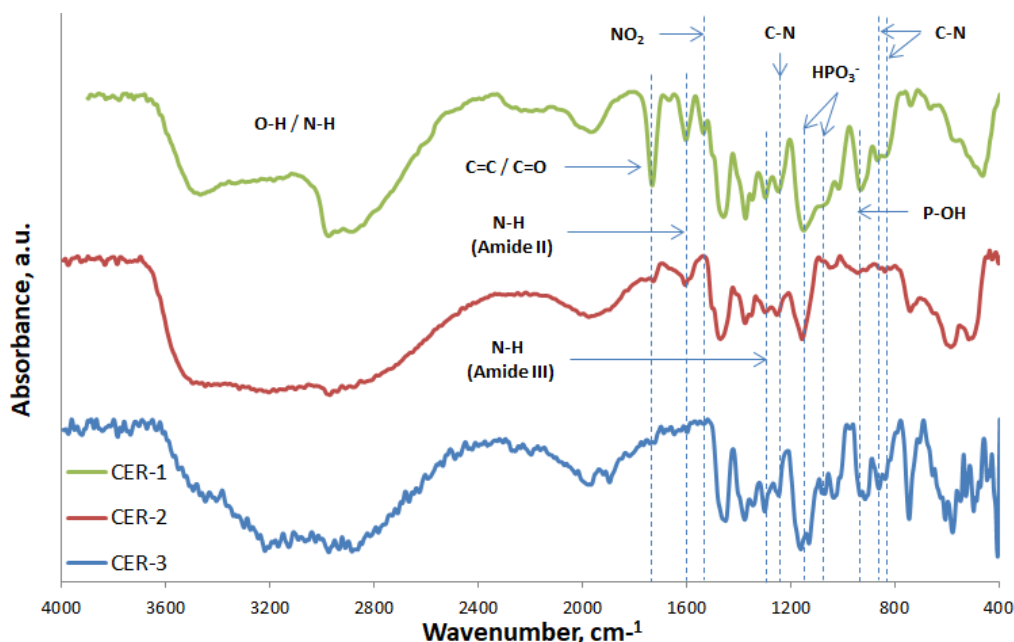
Table 6. Corrosion potential and corrosion current density of carbon steel in 2.0 wt.% NaCl solution in the absence and presence of CER-1–3.

Inhibitors	C_{inh} , mL/L	E_{corr} , mV	i_{corr} , $\mu\text{A}/\text{cm}^2$	CR, mm/y	IE, %
Blank	–	–430	10.0	0.1165	–
CER-1	10.0	–312	4.8	0.0559	52.05
CER-2	10.0	–304	3.2	0.0373	68.11
CER-3	10.0	–360	4.5	0.0524	55.09

The incorporation of demulsifiers-inhibitors with anti-corrosion effect CER-1–3 significantly reduces the corrosion current. With the addition of CER-2, the corrosion current reaches a minimum, which corresponds to an inhibition efficiency of 68%. The conclusion is consistent with the findings of the weight loss experiment.

3.3. Fourier transform infrared spectroscopy

Furthermore, the presence of corrosion protection was confirmed by FTIR spectra of the surface of carbon steel immersed in 2.0 wt.% NaCl for 12 days. The main components of the presented CER-1–3 are phosphoric acid, phenolic resins and diethylamine. The primary constituents, namely heteroatoms, are accountable for the formation of a film on the metal surface. The FTIR spectra are presented in Figure 4. The IR spectra were normalized to the spectrum of the control sample. The control sample (carbon steel coupons in 2.0 wt.% NaCl solution without reagents, Blank) does not have streaks that are not related to the structure of the steel coupon.

**Figure 4.** FTIR spectra of carbon steel treated with CER-1–3 (C_{inh} 10 mL/L) after immersion in a solution of 2.0 wt.% NaCl.

FTIR spectra of the prepared coupons show a broad peak at 3417–3406 cm^{-1} , which corresponds to N–H and O–H stretching vibrations. These bands are attributed to asymmetric and symmetric C–H stretching vibrations at 2935, 2858, and 1452 cm^{-1} . The bands located at approximately 1724 cm^{-1} are attributed to the stretching vibration bands of C=C or C=O, which correspond to the stretching vibration modes of carbonyl groups. Additionally, a second vibration occurs at 1026 cm^{-1} , which is attributed to a single bond (C–O). Bending bands of C–H in $-\text{CH}_2$ and $-\text{CH}_3$ are located at 1454 and 1369 cm^{-1} respectively. The bands located around 1290 cm^{-1} are attributed to the bending vibrations of N–H groups (amide III). The bands located at 1242–1253 cm^{-1} are characterized by C–N stretching vibrations in arylamines.

The bands located at 1060 and 1153 cm^{-1} corresponded to HPO_3^- , and the band with a wavenumber of 921 cm^{-1} (stretching vibrations of P–OH of HPO_3^- was considered as a characteristic band of the P–O–M (metal) bond [24]), appeared on the coupon treated with CER-1 with the highest content of potassium salt of phosphoric acid. Asymmetric vibrations of $-\text{NO}_2$ groups at 1535 cm^{-1} were present only for the sample treated with CER-1.

The band of bending vibrations of N–H (amide II) at 1600 cm^{-1} is observed in samples treated with CER-1 and CER-2.

The samples treated with CER-1 and CER-3 exhibited stretching vibrations of the C–N bond in $-\text{NO}_2$ at 920–830 cm^{-1} .

The band located at 1720–1728 cm^{-1} , which corresponds to the stretching vibrations of C=O bonds of carbonyl groups in the sample treated with CER-2 and CER-3, either disappears or transforms into a shoulder.

The results obtained indicate the formation of films on the surface of carbon steel coupons corresponding to the composition of complex action reagents.

3.4. Microstructure and composition of surface morphology

Surface microstructure changes were investigated using SEM and EDS measurements, as shown in Figure 5a–d and Table 7. To confirm the protective effect of complex corrosion inhibitors with demulsifying action, the surface morphology of carbon steel immersed for 12 days in a solution simulating reservoir conditions of formation water (2 wt.% NaCl) at 25°C was analyzed. The results of the SEM analysis indicate that the prepolished smooth surface of CS with polishing marks exhibits degradation in the presence of a corrosive NaCl solution. The aggressive action of the corrosive electrolyte causes increased pitting on the CS surface, which leads to greater weight loss and high corrosion rates (Figure 5a). Figure 5b–d depicts the surface of steel that has been treated with CER-1, CER-2, and CER-3 respectively. A dense protective film has been observed. All surfaces were protected from corrosion. Nonetheless, the surface of CS that has been treated with a complex CER-2 containing amino groups exhibits a significantly denser protective surface layer, thereby delivering enhanced protection.

After immersion in a blank electrolyte solution containing CER-1–3, an EDS analysis was performed to determine the composition of particles formed on the surface of carbon steel, as depicted in Table 7. The surface of the carbon steel coupon was subjected to a corrosive solution, as depicted in Figure 5a. This demonstrates the presence of Fe and C, as the primary constituents of the alloy. And additionally, it reveals the presence of Cl, Na, O, and trace amounts of P. This indicates that the corrosion of carbon steel is caused by the formation of iron oxide film on the surface of the metal. The presence of Cl indicates the presence of chloride salts that have been generated during the corrosion process. EDS-analysis of the CS surface exposed to CER-1–3 shows a decrease in the Fe content on the CS surface. It can be seen that the protective layer that is formed upon the addition of intricate complex effect reagents shields the steel surface from the corrosive effects of an aggressive environment.

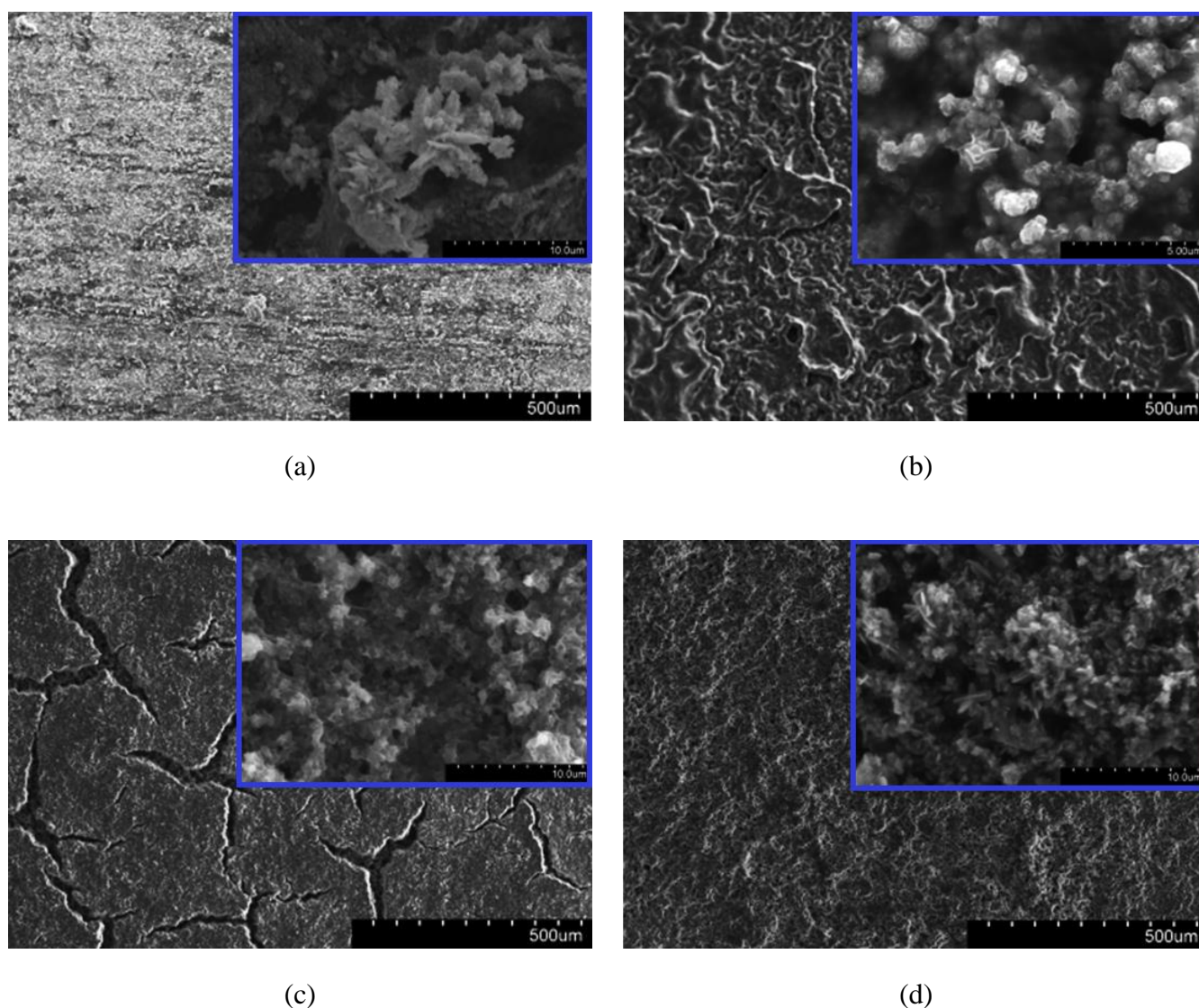


Figure 5. SEM micrographs of the blank CS (a) and the CS treated by CER-1 (b); CER-2 (c); CER-3 (d) in the 2.0 wt.% NaCl solution at 25°C (C_{inh} 10 mL/L).

The primary component of CER-1 is the potassium salt of phosphoric acid, which reduces the ability to form a protective film on the surface of carbon steel. CER-2 and CER-3 are dominated by the content of block copolymers of diethanolamine and a block copolymer based on ethylene oxide and propylene, respectively, which increases the adsorption capacity on the surface of carbon steel.

From these analyses, it is possible to conclude that the CS surface is highly corroded in the presence of an electrolyte simulating the composition of formation waters. The utilization of complex effect reagents significantly safeguards the substrate surface from further.

Table 7. Content of main elements on the surface of carbon steel in the absence and treated with CER-1–3 when immersed in a solution of 2.0 wt.% NaCl (C_{inh} 10 mL/L).

Inhibitors	Atomic ratio, %						
	C	N	O	Na	P	Cl	Fe
Blank	49.2	0.5	19.6	1.9	0.1	1.1	27.6
CER-1	68.5	2.0	24.5	1.5	0.1	1.2	2.2
CER-2	60.0	0.0	29.9	1.4	0.3	1.1	7.3
CER-3	59.1	0.0	31.2	1.4	0.1	1.4	6.8

3.5. X-ray diffraction analysis

The formation of a protective film was further studied by X-ray diffraction analysis. The X-ray patterns of corrosion products that are formed during exposure to an aggressive environment (formation water) on the surface of CS are depicted in Figure 6. The surface of the control sample (without reagents, Blank) is α -Fe with a cubic lattice and is covered with corrosion products – Fe_3O_4 (Figure 6).

The addition of CER-1 at a concentration of 10 mL/L does not cause significant changes in the phase composition of the CS coupon (α -Fe phase is observed). In Figure 6, reflections are observed indicating the formation of $FeO(OH)$, which is one of the intermediate compounds during the rusting of iron. The retention of carbon steel in a solution containing 2.0 wt.% NaCl for a duration of 12 days resulted in the accumulation of sodium chloride salt on the surface.

The application of CER-2 to the coupon did not result in significant modifications in the phase state of the sample (Figure 6). The presence of α -Fe, $FeO(OH)$, and Fe_3O_4 was observed. On the surface of the coupon treated with CER-3, similar to CER-1, deposits of NaCl, $FeO(OH)$, and Fe_3O_4 are formed.

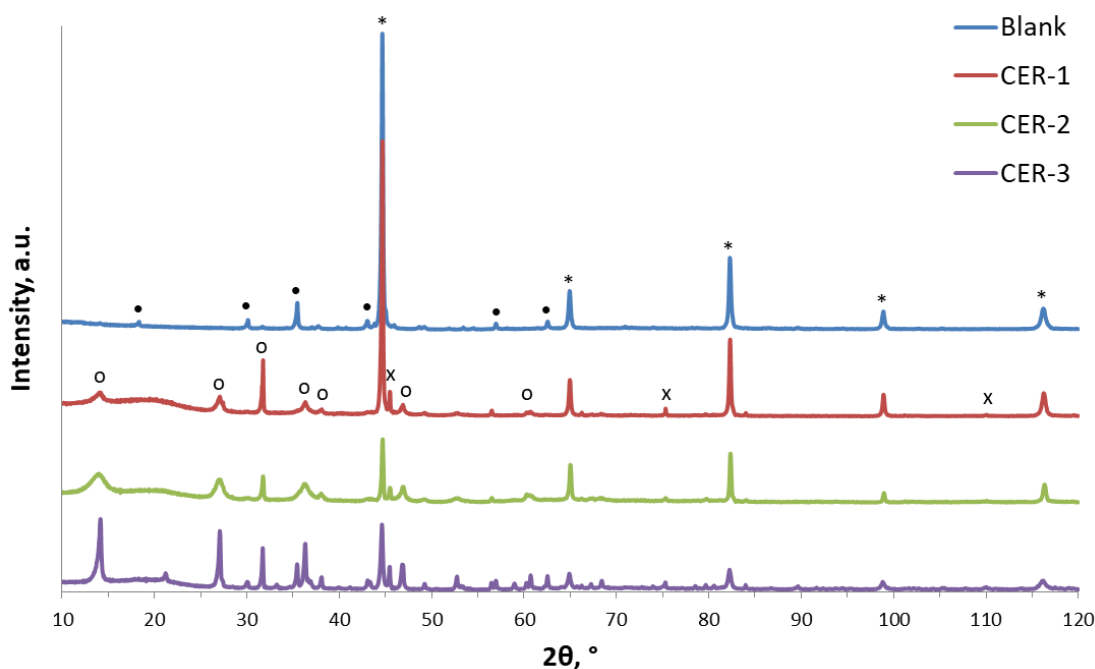


Figure 6. X-ray patterns of CS without complex effect reagents, and carbon CS treated with CER-1–3 in 2.0 wt.% NaCl solution at 25°C (C_{inh} 10 mL/L). * – α -Fe (COD 1100108); • – Fe_3O_4 (COD 9005812); o – $FeO(OH)$ (COD 1527237); x – NaCl (COD 9008678).

3.6. Transmission electron spectroscopy

A detailed study of corrosion deposits on the surface of the coupons after treatment with complex effect reagents was conducted using transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). The HR-TEM images depicting the investigated corrosion deposits are depicted in Figure 7.

EDS analysis indicated that Fe, O, Na, Cl were present on the surface of the coupon treated with CER-1, and there was also a peak of P (1.3%), indicating the presence of an inhibitory layer formed by the components of the inhibitor (Figure 7a).

After treatment with CER-2, Fe and O are observed on the surface of the coupon, predominantly forming the $FeO(OH)$ phase. This is confirmed by electron diffraction with a set of diffraction rings corresponding to this phase (Figure 7d). $FeO(OH)$ is exhibited in the form of large plate-shaped crystals. This dense phase has protective properties of the surface of CS from further exposure to the aqueous environment.

The results of the EDS analysis indicated that the surface of the coupon that was treated with CER-3 contained Fe, O, Na, and Cl, with a minimal amount of P, not exceeding 1% (Figure 7c). The corrosion layer predominantly comprises of Fe_3O_4 nanoparticles that are weakly bound. This layer is distinguished by a loose and porous structure (Figure 7e), in contrast to the dense $FeO(OH)$ layer, which facilitates the passage of Cl^- to the surface of CS.

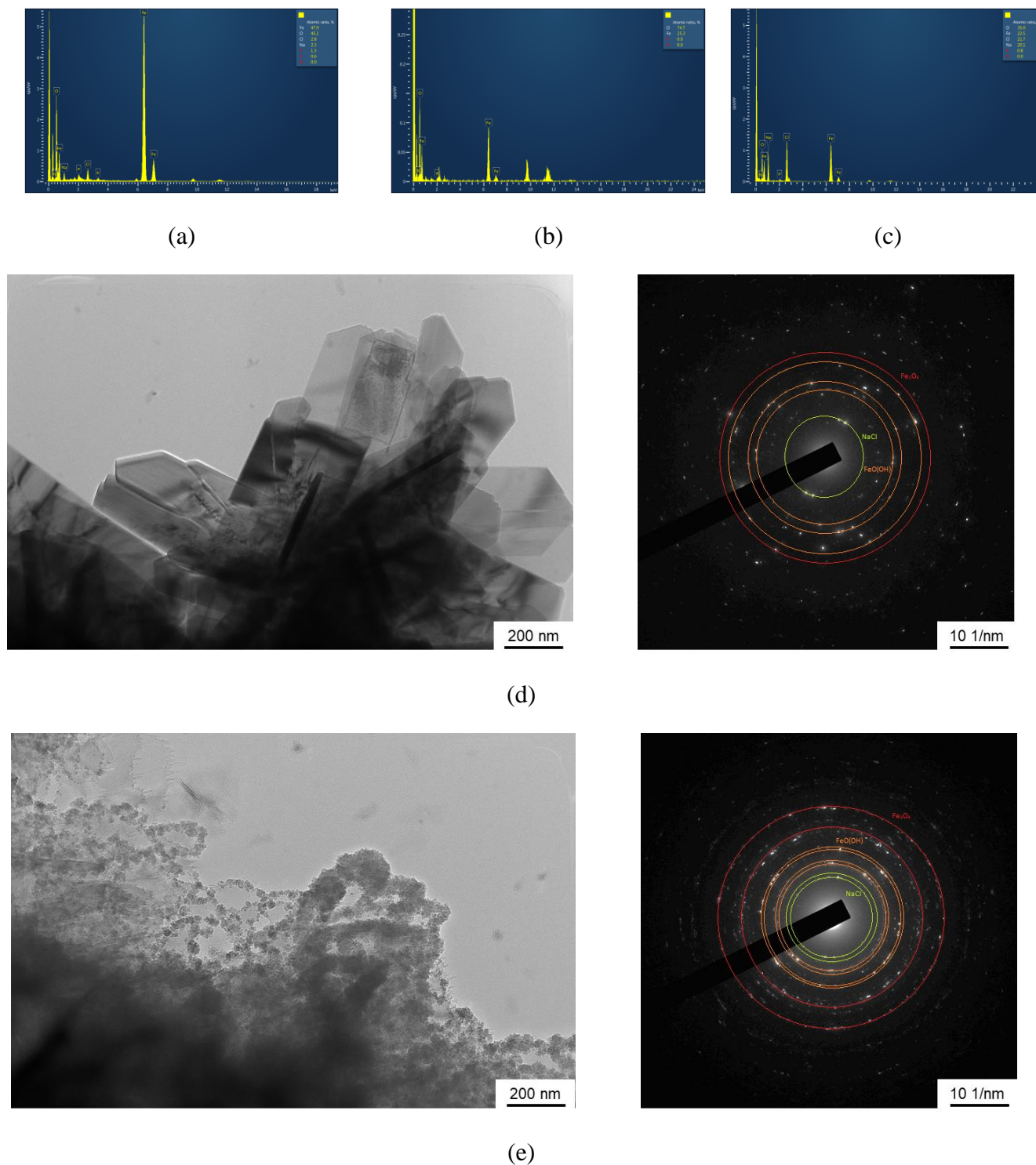


Figure 7. Studies of corrosion deposits after treatment of carbon steel coupons in 2.0 wt.% NaCl solution at 25°C (C_{inh} 10 mL/L): EDS spectra of corresponding samples (a–c); TEM image of the layer and electronogram of corrosion deposit products after treatment of coupon with CER-2 (d); TEM image of the layer and electronogram of corrosion deposit products after treatment of coupon with CER-3 (e).

4. Conclusion

At most oil fields, it is impossible to obtain marketable dehydrated oil without the use of demulsifiers. The use of corrosion inhibitors is required to reduce corrosion of oilfield equipment with water contained in oil. It is possible to reduce the consumption of inhibitors and demulsifiers by using reagents with a complex action.

Three reagents of different compositions based on components peculiar to corrosion inhibitors (phosphoric acid salt, amine compound), as well as demulsifiers (phenolic resins (Rezin Alkoxyate), block copolymers based on ethylene oxide and propylene oxide) were investigated. The bottle test method on CER-2 demonstrated that CERs had demulsifying properties. The efficacy of corrosion inhibition was substantiated through the application of the mass loss method.

The study examined the potential utilization of CER in conditions resembling the injection of formation water (2.0 wt.% NaCl) (in the presence of oxygen). The corrosion inhibitory properties of CER-1–3 were investigated through the weight loss method, Tafel polarization curve, microscopic analysis of corrosion morphology, X-ray diffraction analysis, and FTIR spectroscopy.

The data obtained indicates that CER-2 and CER-3 inhibit the corrosion of carbon steel in a solution containing 2.0 wt.% NaCl. It was shown that the complex effect reagents have a higher efficiency than the original one: CER-2 has an efficiency of 68%, and CER-3 has an efficiency of 55%, compared to an efficiency of 52% for CER-1. The most effective efficiency is demonstrated for CER-2, which has been mixed with phenolic resins. The conclusion is consistent with the findings of the weight loss experiment (2.0 wt.% NaCl solution in the presence of oxygen). By the potentiodynamic polarization method on the value of the shift of the corrosion potential E_{corr} of the metal it was concluded that CER-1 and CER-2 exhibit anodic type corrosion inhibitory properties, while CER-3 exhibits a mixed type inhibitory property.

The examination of the surface microstructure through the utilization of SEM and EDS measurements revealed that the pre-polished smooth surface of CS steel experiences corrosion in the presence of NaCl solution. When CERs is introduced, a protective film is formed on the steel surface, thereby safeguarding it from corrosion. This is substantiated by a noticeable decrease in the concentration of Fe ions on this surface compared to the blank experiment. The capability to form a protective film of CER-1–3 was also confirmed by FTIR spectra of the carbon steel surface, indicating that these reagents produce adsorption films on the steel surface.

The presence of CERs at a concentration of 10 mL/L in formation water (2.0 wt.% NaCl) leads to the formation of FeO(OH) on the surface of CS (intermediate compounds during the rusting of iron).

A detailed study of the corrosion deposits on the surface of steel samples after exposure to a 2.0 wt.% NaCl solution was conducted using TEM and EDS. The inhibitory layer on the steel surface in the presence of CER-1 is mainly determined by the phosphorus compound,

in the case of CER-2 by the formation of a dense phase on the surface in the form of large lamellar crystals of FeO(OH) with high protective properties, and in the case of CER-3 by the formation of weakly bound Fe₃O₄ nanoparticles with a loose and porous structure.

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References

1. A. Kadhim, N. Betti, H.A. Al-Bahrani, M.K.S. Al-Ghezi, T. Gaaz, A.H. Kadhum and A. Alamiery, A mini review on corrosion, inhibitors and mechanism types of mild steel inhibition in an acidic environment, *Int. J. Corros. Scale Inhib.*, 2021, **10**, no. 3, 861–884. doi: [10.17675/2305-6894-2021-10-3-2](https://doi.org/10.17675/2305-6894-2021-10-3-2)
2. P.B. Raja, M. Ismail, S. Ghoreishiamiri, J. Mirza, M.C. Ismail, S. Kakooei and A.A. Rahim, Reviews on Corrosion Inhibitors: A Short View, *Chem. Eng. Commun.*, 2016, **203**, no. 9, 1145–1156. doi: [10.1080/00986445.2016.1172485](https://doi.org/10.1080/00986445.2016.1172485)
3. M.M. Abdulredha, S.A. Hussain and L.C. Abdullah, Optimization of the demulsification of water in oil emulsion via non-ionic surfactant by the response surface method, *J. Pet. Sci. Eng.*, 2020, **184**, 106463. doi: [10.1016/j.petrol.2019.106463](https://doi.org/10.1016/j.petrol.2019.106463)
4. E. Yonguep, K.F. Kapiamba, K.J. Kabamba and M. Chowdhury, Formation, stabilization and chemical demulsification of crude oil-in-water emulsions: A review, *Pet. Res.*, 2022, **7**, no. 4, 459–472. doi: [10.1016/j.ptlrs.2022.01.007](https://doi.org/10.1016/j.ptlrs.2022.01.007)
5. R. Zolfaghari, A. Fakhru'l-Razi, L.C. Abdullah, S.S.E.H. Elnashaie and A. Pendashteh, Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry, *Sep. Purif. Technol.*, 2016, **170**, 377–407. doi: [10.1016/j.seppur.2016.06.026](https://doi.org/10.1016/j.seppur.2016.06.026)
6. K. Sotoodeh, Material selection and corrosion, in *Subsea Valves and Actuators for the Oil and Gas Industry*, ed. K. Sotoodeh, Gulf Professional Publishing, 2021, **12**, pp. 421–457. doi: [10.1016/B978-0-323-90605-0.00004-9](https://doi.org/10.1016/B978-0-323-90605-0.00004-9)
7. R. Yan, X. Gao, W. He, T. Chen and H. Ma, 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP)-Zn complex thin films for the corrosion protection of cold-rolled steel (CRS), *Corros. Sci.*, 2019, **157**, 116–125. doi: [10.1016/j.corsci.2019.05.033](https://doi.org/10.1016/j.corsci.2019.05.033)
8. Y. Ma, Y. Li and F. Wang, Corrosion of low carbon steel in atmospheric environments of different chloride content, *Corros. Sci.*, 2009, **51**, no. 5, 997–1006. doi: [10.1016/j.corsci.2009.02.009](https://doi.org/10.1016/j.corsci.2009.02.009)

9. J. Porcayo-Calderon, M. Casales-Diaz, L.M. Rivera-Grau, D.M. Ortega-Toledo, J.A. Ascencio-Gutierrez and L. Martinez-Gomez, Effect of the Diesel, Inhibitor, and CO₂ Additions on the Corrosion Performance of 1018 Carbon Steel in 3% NaCl Solution, *J. Chem.*, 2014, **2014**, 940579. doi: [10.1155/2014/940579](https://doi.org/10.1155/2014/940579)
10. A.R. Farkhutdinova, N.I. Mukatdisov, A.A. Elpidinsky and A.A. Grechukhina, Study of the influence of corrosion inhibitors on the effectiveness of demulsifier reagents, *Bulletin of the Kazan Technological University*, 2012, **15**, no. 18, 85–87 (in Russian).
11. A.R. Farkhutdinova, N.I. Mukatdisov, A.A. Elpidinsky and A.A. Grechukhina, Composition of corrosion inhibitors for various environments, *Bulletin of the Kazan Technological University*, 2013, **16**, no. 14, 272–276 (in Russian).
12. L.P. Semikhina, E.N. Moskvina and I.V. Kolchevskaya, The phenomenon of synergy in mixtures of surfactants, *Bulletin of Tyumen State University. Ecology and Environmental management*, 2012, **5**, 85–91 (in Russian).
13. G. Cui, Q. Zhang, Z. Wang, T. Tang, Q. Zhao and Y. Liu, Synthesis of modified natural polysaccharides for demulsification and corrosion inhibition, *Colloids Surf. A Physicochem. Eng. Asp.*, 2022, **653**, 130045. doi: [10.1016/j.colsurfa.2022.130045](https://doi.org/10.1016/j.colsurfa.2022.130045)
14. L.P. Semikhina, E.N. Moskvina and O.V. Andreev, Development of the complex-action reagent based on technologically compatible demulsifier and corrosion inhibitor, *Neft' i gaz*, 2015, **6**, 69–74 (in Russian). doi: [10.31660/0445-0108-2015-6-69-74](https://doi.org/10.31660/0445-0108-2015-6-69-74)
15. L.P. Semikhina and D.V. Semikhin, *A method for identifying synergies in composite demulsifiers using low-frequency dielectric measurements*, RU Patent 2301253, 2007 (in Russian).
16. L.P. Semikhina, *A method for identifying the synergy effect in composite corrosion inhibitors using low-frequency dielectric measurements*, RU Patent 2416100, 2011 (in Russian).
17. A.A. Al-Amiery, A.B. Mohamad, A.A.H. Kadhum, L.M. Shaker, W.N.R.W. Isahak and M.S. Takriff, Experimental and theoretical study on the corrosion inhibition of mild steel by nonanedioic acid derivative in hydrochloric acid solution, *Sci. Rep.*, 2022, **12**, 4705. doi: [10.1038/s41598-022-08146-8](https://doi.org/10.1038/s41598-022-08146-8)
18. J. Hu, D. Zeng, Z. Zhang, T. Shi, G.-L. Song and X. Guo, 2-Hydroxy-4-methoxyacetophenone as an environment-friendly corrosion inhibitor for AZ91D magnesium alloy, *Corros. Sci.*, 2013, **74**, 35–43. doi: [10.1016/j.corsci.2013.04.005](https://doi.org/10.1016/j.corsci.2013.04.005)
19. P.P. Kumari, P. Shetty and S.A. Rao, Electrochemical measurements for the corrosion inhibition of mild steel in 1 M hydrochloric acid by using an aromatic hydrazide derivative, *Arab. J. Chem.*, 2017, **10**, no. 5, 653–663. doi: [10.1016/j.arabjc.2014.09.005](https://doi.org/10.1016/j.arabjc.2014.09.005)
20. T.K. Chaitra, K.N.S. Mohana and H.C. Tandon, Thermodynamic, electrochemical and quantum chemical evaluation of some triazole Schiff bases as mild steel corrosion inhibitors in acid media, *J. Mol. Liq.*, 2015, **211**, 1026–1038. doi: [10.1016/j.molliq.2015.08.031](https://doi.org/10.1016/j.molliq.2015.08.031)

-
21. M.D. Plotnikova, A.B. Shein, M.G. Scherban, A.N. Vasyanin and A.E. Rubtsov, Experimental and theoretical investigation of (*E*)-5-{[4-(dimethylamino)benzylidene]-amino}-1,3,4-thiadiazole-2(3*H*)-thione (DAT) as an acid corrosion inhibitor of mild steel, *Int. J. Corros. Scale Inhib.*, 2023, **12**, no. 4, 1365–1391. doi: [10.17675/2305-6894-2023-12-4-1](https://doi.org/10.17675/2305-6894-2023-12-4-1)
 22. N. Zulfareen, K. Kannan, T. Venugopal and S. Gnanavel, Synthesis, characterization and corrosion inhibition efficiency of N-(4-(Morpholinomethyl Carbamoyl Phenyl) Furan-2-Carboxamide for brass in HCl medium, *Arab. J. Chem.* 2016, **9**, no. 1, 121–135. doi: [10.1016/j.arabjc.2015.08.023](https://doi.org/10.1016/j.arabjc.2015.08.023)
 23. V. Saraswat, T.K. Sarkar and M. Yadav, Evaluation on corrosion mitigation capabilities of nitrogen doped carbon dots as corrosion inhibitors for mild steel in descaling solution, *Mater. Chem. Phys.*, 2024, **313**, 128678. doi: [10.1016/j.matchemphys.2023.128678](https://doi.org/10.1016/j.matchemphys.2023.128678)
 24. M.C. Zenobi, C.V. Luengo, M.J. Avena and E.H. Rueda, An ATR-FTIR study of different phosphonic acids in aqueous solution. *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2008, **70**, no. 2, 270–276. doi: [10.1016/j.saa.2007.07.043](https://doi.org/10.1016/j.saa.2007.07.043)

