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THE INVESTIGATION OF NACE SOLUTION COMPOSITION AND TESTING CONDITION INFLUENCE ON 20 STEEL CORROSION RATE AND ITS ELECTROCHEMICAL CHARACTERISTICS

Zvenomyra Slobodyan; Lyudmila Mahlatiuk; Roma Kupovych

Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Lviv, Ukraine

Summary. *The influence of the NACE composition solutions (NACE-1: 3% NaCl + 0.25% CH₃COOH; NACE-2: 5% NaCl + 0.5% CH₃COOH) on the corrosion rate and the electrochemical characteristics of 20 steel is investigated. It is determined that in the acidic NACE-1 and NACE-2 weakly environments, the test time (2 ... 72) hours increase leads to a significant reduction of 20 steel corrosion rate. This dependence is typical for neutral and weakly acidic environments in which corrosion products are deposited on the metal surface in the form of barrier film.*

The difference between 20 steel corrosion rates in both NACE solutions in static and dynamic conditions is most noticeable in 24 hours. The corrosion rate in the flowing environment after 72 hours increases 7-12 times, which is caused by the acceleration of the oxygen transport to the metal surface and the barrier film blurring.

The role of dissolved oxygen, as a depolarizer, is confirmed by polarization studies and gravimetric tests after oxygen removing. So, after nitrogen lancing of NACE solutions (complete removal of O₂ is fixed polarographically), the steel corrosion rate was reduced by 11%.

The differences between the corrosion and electrochemical characteristics of 20 steel in NACE-1 and NACE-2 (i_{cor} , i_d , E_{cor} , b_c ma b_a) are determined the lower solubility of O₂ in solutions with a NaCl concentration greater than 3%.

Key words: *corrosion rate, corrosion deep indicator, NACE environment, compromise corrosion potential, corrosion current, limiting diffusion current, Tafel constants.*

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Statement of the problem. Investigation of the protective properties of corrosion inhibitors for oil and gas equipment in laboratory conditions is carried out in standardized test NACE solutions, which may slightly differ in concentration and composition of components. These solutions may additionally contain dissolved gases H₂S, CO₂, O₂ [1], which, changing the pH of the solution, significantly affect its corrosion activity. This also affect the protective properties of corrosion inhibitors.

Analysis of the available investigation results. According to one of the methods [2], the composition of the components of the NACE solution is as follows: 3% NaCl + 0,25% CH₃COOH (NACE-1), while the American standard [3] suggests slightly higher concentrations of components: 5% NaCl + 0,5% CH₃COOH (NACE-2).

Comparison of the inhibitors effectiveness carried out by independent laboratories in various standardized solutions is also complicated by various test conditions, such as, exposure time, temperature and mixing of the solution. There are also some differences in the conditions for removing oxygen and saturation with carbon dioxide of these solutions. As a result, the obtained values for corrosion rates can differ significantly, resulting in significant complication of the comparative evaluation of the steels corrosion resistance and the inhibitors effectiveness.

It is also important to understand the peculiarities of the electrochemical behaviour of steel in these weakly acid solutions.

The objective of the paper is to investigate the influence of the NACE solution composition with various concentrations, without hydrogen sulphide saturation (NACE-1 and

NACE-2), and the conditions of corrosion rate tests and the electrochemical characteristics of steel 20.

Materials and methods of investigation. The corrosion activity of NACE solutions was investigated by gravimetric and electrochemical methods. For gravimetric investigations, samples made of 20 steel in the delivery state, made in the form of disks ($d = 20$ mm, $h = 1,5$ mm) were used. The surface of the samples was grinded to roughness not more than $R_a = 0,63$ μm . The sample for electrochemical investigations was cylindrical, with the working surface area $0,0254$ cm^2 made of 20 steel and pressed into fluoroplast-4.

The samples were washed in acetone and alcohol, dried and kept in a desiccator for 2 h. Prepared samples were weighed on the analytical grade with an accuracy $\pm 0,0002$ g and keep up in a desiccator for no more than 24 hours.

Solutions for research were prepared on distilled water without saturation of H_2S using reagents of qualification hc. Solution NACE-1: 3% $\text{NaCl} + 0,25\%$ CH_3COOH ; solution NACE-2: 5% $\text{NaCl} + 0,5\%$ CH_3COOH The removal of oxygen from solutions was carried out by blowing nitrogen. The completeness of the removal of oxygen was confirmed by the absence of oxygen half-wave [4] in the polarograms.

Before the investigation was started and after it was completed, the pH of the solutions was measured with the pH-meter I-160M. After exposure of the samples in the corrosive environment and elimination of corrosion products, the visual evaluation of the nature of corrosion damages was made. After that, the samples were again washed in acetone and weighed. The calculation of the corrosion rate K_m ($\text{g}/(\text{cm}^2 \cdot \text{h})$) under static and dynamic conditions (rotary speed of the mixer 800 cycl/min) [5] was carried out according to the formula

$$K_m = \frac{\Delta m}{S \cdot \tau}, \quad (1)$$

where Δm – is the change of the sample weight after exposure in a corrosive environment and elimination of corrosion products, g; S – is the sample area, cm^2 ; τ – is the time of its exposure, h.

The obtained values were scaled on the deep corrosion index Π (mm/year):

$$\Pi = \frac{K_m \cdot k}{\gamma} \cdot 10^{-1}, \quad (2)$$

where k – is the scale factor equal to 8,76 h/ year; γ – is the metal density (for steel 7,86 g/cm^3).

Electrochemical investigations were carried out by the IP-Pro potentiostat with software according to the three-electrode scheme. The cylindrical sample of 20 steel, pressed into fluoroplastics with a working surface area of $0,0254$ cm^2 was used as the working electrode. Comparison electrode – silver chloride saturated, auxiliary – platinum. Before each measurement, the sample was grinded on the grinding paper No. 0, degreased with acetone and dried. After the sample immersion into the investigated solution, the potential was recorded for at least 0,5 h, taking potential at the exposure and as compromise potential of corrosion E_{corr} . The density of the corrosion current i_{cor} , of Tafel constants of cathode b_c and anode b_a reactions were determined by the graph-analytical method from the linea sections of the polarization curves [6].

Results and discussions. The gravimetric investigations showed that the corrosion activity of both NACE solutions under static conditions were slightly different in the entire time range (2...72 h) and with the increase of the time of the sample exposure in the corrosive environment decreased (Fig. 1). This is due to the fact that in neutral and weak acid medium, a chemisorptional or phase protective film formed by corrosion products in the neutral and weak

acid medium, which, by preventing the access of oxygen as a depolarizer, directly to the metal surface, played the screening role.

The influence of oxygen on the rate of corrosion of 20 steel in weak acid NACE solutions (pH = 4) is confirmed by tests under dynamic conditions. Thus, compared to static conditions, the rate of corrosion during mixing significantly increases in both NACE solutions (Fig. 1, Table 1). After being tested for 2 h the coefficient of the corrosion rate change increases in 2...2,2 times, and after 72 h it reaches 7...12 times. The lower rates of corrosion in NACE-2 solution with the higher concentration of NaCl under dynamic conditions are caused by lower solubility of O₂ in it (the maximum solubility of oxygen is observed in 3% NaCl).

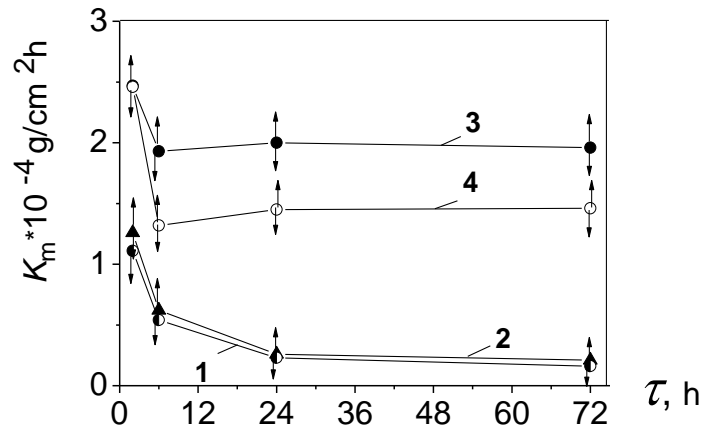


Figure 1. Dependence of 20 steel corrosion rate on time exposition in solutions: 1 – NACE-1; 2 – NACE-2 (under static conditions); 3 – NACE-1; 4 – NACE-2 (under dynamic conditions)

Table 1

Corrosion rate K_m (g/(cm²·h)) and corrosion deep indicator Π (mm/year) of 20 steel in NACE solution under different time exposition (τ , h) at $t = 20^\circ\text{C}$

| Medium | Static conditions | | | Dynamic conditions | | |
|--------|-------------------|------------------|-------|--------------------|-------|----------|
| | τ | $K_m \cdot 10^4$ | Π | $K_m \cdot 10^4$ | Π | κ |
| NACE-1 | 2 | 1,11 | 1,23 | 2,47 | 2,75 | 2,2 |
| | 6 | 0,54 | 0,60 | 1,93 | 2,15 | 3,6 |
| | 24 | 0,23 | 0,26 | 2,00 | 2,22 | 8,7 |
| | 72 | 0,16 | 0,18 | 1,96 | 2,18 | 12,2 |
| NACE-2 | 2 | 1,26 | 1,4 | 2,46 | 2,74 | 1,9 |
| | 6 | 0,62 | 0,69 | 1,32 | 1,47 | 2,1 |
| | 24 | 0,26 | 0,29 | 1,45 | 1,61 | 5,6 |
| | 72 | 0,21 | 0,23 | 1,46 | 1,62 | 6,9 |

κ – is the coefficient of the corrosion rate growth while transferring to dynamic conditions, times.

The removal of oxygen from NACE solutions by blowing nitrogen for 20 min (O₂ absence is confirmed polarographically) results in the decrease of 20 steel corrosion rate by 11,5% (Table 2), which is in accordance with the literature data.

It is known that dissolved oxygen can act not only as the depolarizer according to the reaction:



but also, interacting with protons on the metal surface



shift the equilibrium of the dissociation reaction of the weak acetic acid towards the production of ions H^+

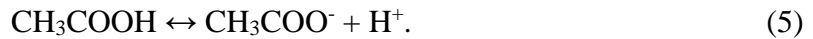


Table 2

Corrosion rate K_m (g/(cm²·h)) of 20 steel in NACE solution (under dynamic conditions, nitrogen blowing $\tau = 72$ h)

| Medium | Blowing | $K_m \cdot 10^4$ | $\alpha, \%$ |
|--------|----------------|------------------|--------------|
| NACE-1 | – | 1,96 | – |
| NACE-1 | N ₂ | 1,73 | 11,7 |
| NACE-2 | – | 1,46 | – |
| NACE-2 | N ₂ | 1,28 | 11,6 |

Therefore, the cathode reaction is mixed (Fig. 2).

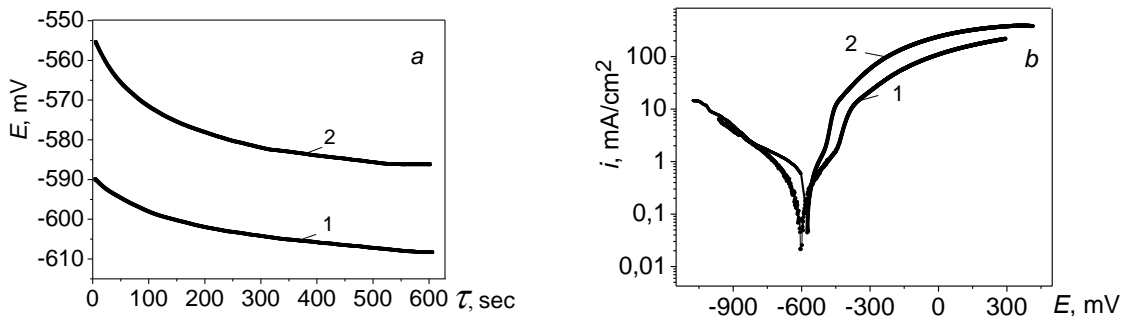


Figure 2. Kinetics of the compromise corrosion potential (a) and polarization curves (b) on the 20 steel in solutions: 1 – NACE–1, 2 – NACE–2

Electrochemical investigations also showed some differences in the properties of NACE–1 and NACE–2 solutions concerning 20 steel. Area of the boundary diffusion current (640...700) mV on 20 steel is more clearly expressed in NACE–2. The boundary diffusion current is 0,7 mA/cm² and 1,0 mA/cm², relatively, in NACE–2 and NACE–1. The next area of the cathode curve caused by the hydrogen depolarization, has more rapid motion in NACE–2, indicating the dominance of hydrogen depolarization. The compromise corrosion potential of NACE–1 is shifted by 22 mV towards more negative values compared to the corresponding potential in NACE–2.

The 20 steel corrosion current in NACE–2 is 2 times lower than in NACE–1, which is in accordance with the gravimetric results and further confirms the participation of oxygen in the corrosion process (Table 3).

The values of the Tafel constants b_c and b_a are higher in NACE–2 environment than in NACE–1, indicating the slow down of both cathode and anode reactions.

Table 3

Electrochemical characteristic of 20 steel in solutions NACE–1 and NACE–2

| Medium | Compromise corrosion potential $-E_{cor}$, mV | Current, $i_{cor} \cdot 10^5$, mA/cm ² | Boundary diffusion current, i_d , mA/cm ² | Tafel constants | |
|--------|--|--|--|-----------------|------------|
| | | | | b_c , mV | b_a , mV |
| NACE–1 | 608 | 4,0 | 1,0 | 53,0 | 80,0 |
| NACE–2 | 586 | 2,0 | 0,7 | 62,0 | 85,0 |

Conclusions. It is determined that in weak acid solutions NACE–1 and NACE–2 the increase in test time (2...72 h) caused significant reduction of 20 steel corrosion rate. Such dependence is typical for neutral and weak acid media where corrosion products are deposited in the form of barrier film on the metal surface. The difference between the rates of corrosion in NACE–1 and NACE–2 under static conditions is negligible, but becomes significant under dynamic conditions associated with the dominance of oxygen participation in the corrosion process. Polarization investigations prove the role of oxygen in general corrosion process. The cathode curves of 20 steel in NACE–1 and NACE–2 solutions have apparent area of the boundary diffusion current. The value of the corrosion currents and Tafel constants indicate the double role of oxygen: the depolarizer and the participant in the formation of protective oxide layer on the steel surface.

Further, it is planned to investigate the effectiveness of TIS-4 inhibitor in two-phase system "oil – NACE-2" under dynamic conditions.

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ДОСЛІДЖЕННЯ ВПЛИВУ СКЛАДУ РОЗЧИНУ NACE Й УМОВ ВИПРОБУВАНЬ НА ШВИДКІСТЬ КОРОЗІЇ ТА ЕЛЕКТРОХІМІЧНІ ХАРАКТЕРИСТИКИ СТАЛІ 20

Звеномира Слободян; Людмила Маглатюк; Рома Купович

*Фізико-механічний інститут ім. Г.В.Карпенка НАН України,
Львів, Україна*

Резюме. Досліджено вплив складу розчинів NACE (NACE-1: 3% NaCl + 0,25% CH₃COOH; NACE-2: 5% NaCl + 0,5% CH₃COOH) на швидкість корозії та електрохімічні характеристики сталі 20. Встановлено, що в слабкокислих середовищах NACE-1 та NACE-2 збільшення часу випробувань (2...72) hours призводить до суттєвого зниження швидкості корозії сталі 20. Така залежність характерна для нейтральних та слабкокислих середовищ, в яких продукти корозії осідають на поверхні металу у вигляді бар'єрної плівки.

Різниця між швидкостями корозії сталі 20 в обох розчинах NACE за статичних та динамічних умов найбільш помітна через 24 hours. Швидкість корозії в рухомому середовищі через 72 hours зростає у 7...12 разів, що пов'язано з прискоренням транспортування кисню до поверхні металу та розмиванням бар'єрної плівки.

Роль розчиненого кисню, як деполаризатора, підтверджено поляризаційними дослідженнями та гравіметричними випробуваннями при видаленні кисню. При продуванні розчинів NACE азотом (повне видалення O₂ зафіксовано полярографічно) швидкість корозії сталі знижується на 11%.

Відмінності корозійних та електрохімічних характеристик сталі 20 у NACE-1 та NACE-2 (i_{cor} , i_d , E_{cor} , b_c та b_d) пов'язані з меншою розчинністю O₂ у розчинах з концентрацією NaCl більшою, ніж 3%.

Ключові слова: швидкість корозії, глибинний показник корозії, середовище NACE, компромісний потенціал корозії, струм корозії, граничний дифузійний струм, константи Тафеля.

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