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## CORROSION TESTING OF SA 387 GR. 91 STEEL ISPITIVANJE OTPORNOSTI PREMA KOROZIJI ČELIKA SA 387 GR. 91

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### Keywords

- steels
- corrosion
- electrochemical techniques
- structural life

### Abstract

*Corrosion behaviour of steel Sa 387 Gr. 91 is tested in solutions containing chloride and sulphate anions. These solutions simulate the conditions of marine and industrial atmosphere. The tests are carried out in a slightly acidic and moderately acidic environment. It is shown that the steel corrodes uniformly without pitting or other forms of local dissolution. Corrosion current density is determined by three independent electrochemical techniques (linear polarization resistance, electrochemical impedance spectroscopy and linear sweep voltammetry). Values of corrosion rate are calculated based on values of corrosion current density. Values of corrosion rate obtained by different electrochemical techniques are in a very good agreement. An estimation of the working life of a pressure vessel made of steel Sa 387 Gr. 91 is given from the standpoint of general (uniform) corrosion.*

### INTRODUCTION

Sa 387 Gr. 91 steel belongs to a class of structural Cr-Mo steels /1/. This steel has been widely used for manufacturing pressure vessels. Pressure vessels are often exposed to atmospheric corrosion, so it is necessary to determine the corrosion resistance of the above steel according to this type of corrosion. General atmospheric corrosion is manifested as a uniform dissolution which results in a gradual decrease of the steel thickness. In the initial period, the atmospheric corrosion occurs more quickly than later. Over time, layers of corrosion products are formed on the steel surface. These layers of corrosion product have a protective character to some extent. The formation of corrosion product layers ends after several years, so that the corrosion rate becomes approximately constant, /2/.

The quantitative indicator of general (uniform) corrosion is the corrosion rate  $v_{corr}$ . Its value can be determined in different ways: on the basis of mass loss of steel specimens after exposure in different natural environments (long-term tests) or in laboratory chambers, /3/. The value of corrosion

### Ključne reči

- čelici
- korozija
- elektrohemijske tehnike
- radni vek konstrukcije

### Izvod

*Ispitano je koroziono ponašanje čelika Sa 387 Gr. 91 u rastvorima koji sadrže hloridne i sulfatne anjone. Ovi rastvori simuliraju uslove morske, odnosno, industrijske atmosfere. Ispitivanja su izvršena u blago kiseloj i umereno kiseloj sredini. Pokazano je da se u datim uslovima površina čelika ravnomerno rastvara, bez pojave pitinga ili drugih oblika lokalnog rastvaranja. Gustina struje korozije određena je pomoću tri nezavisne elektrohemijske tehnike (linearna polarizaciona otpornost, elektrohemijaska impedansna spektroskopija i voltametrijia sa linearnom promenom potencijala). Na osnovu vrednosti gustine struje korozije, izračunate su odgovarajuće vrednosti brzine korozije. Vrednosti brzine korozije dobijene primenom različitih elektrohemijaskih tehnika pokazuju veoma dobro slaganje. Na osnovu brzine korozije data je procena radnog veka konstrukcije od navedenog čelika sa stanovišta opšte ravnomerne korozije.*

rate can be determined in a short time by electrochemical techniques. As a result of electrochemical measurements, the corrosion current density  $j_{corr}$  is obtained, which can be expressed as the corrosion rate  $v_{corr}$  /4-6/.

Corrosion rate of steel Sa 387 Gr. 91 in slightly acidic and moderately acidic solutions is determined in this work, using several modern electrochemical techniques. The aim is to predict a reduction of the steel wall thickness after some period of exploitation, based on the obtained results of the electrochemical corrosion measurements.

### EXPERIMENTAL

#### Material

Chemical composition of tested steel is given in Table 1.

Table 1. Chemical composition of steel Sa 387 Gr. 91.

Element	C	Cr	Mo	Mn	Si	V
Mass. %	0.08	8.00	0.85	0.30	0.20	0.18

### Linear polarization resistance technique (LPR)

This technique is used to determine the polarization resistance  $R_p$  of the tested steel in the corrosion environment (test solutions). The value of  $R_p$  is inversely proportional to corrosion current density  $j_{corr}$  and to corrosion rate  $v_{corr}$ , /7/. The steel sample is polarized in a narrow potential range ( $E = \pm 10$  mV) with respect to corrosion potential  $E_{corr}$ , starting from the cathodic to the anodic region, and the corresponding current  $j$  is recorded. The potential sweep rate is  $0.166$  mVs<sup>-1</sup>. The value of  $R_p$  is determined as the slope of the experimental  $E$ - $j$  curve, at the corrosion potential  $E_{corr}$ . Corrosion current density  $j_{corr}$  is calculated using the experimentally determined value of  $R_p$ .

### Electrochemical impedance spectroscopy (EIS)

The value of  $R_p$  is also determined using EIS technique, /8/. The alternating potential of small amplitude ( $\pm 10$  mV) is imposed to the working electrode (tested steel) in the test solutions. The applied frequencies  $f$  are from 0.01 Hz to 100 000 Hz. The value of  $R_p$  is determined on the basis of electrochemical impedance at very high and very low frequencies. Corrosion current density and corrosion rate are then calculated using the experimental value of  $R_p$ . Corrosion current density  $j_{corr}$  is calculated using the Stern-Geary equation:

$$j_{corr} = B/R_p \quad (1)$$

where:  $B$  is a constant that depends on values of Tafel slopes.

The value of the constant  $B$  for tested steel in solutions with different pH is 17 mV (pH2.3), 20 mV (pH3.3) and 25 mV (pH6.3), respectively, /9/. According to Eq.(1), the corrosion current density  $j_{corr}$  is:

$$\begin{aligned} j_{corr} &= 17 \text{ mV}/R_p, \\ j_{corr} &= 20 \text{ mV}/R_p, \\ j_{corr} &= 25 \text{ mV}/R_p. \end{aligned} \quad (2)$$

Corrosion rate  $v_{corr}$  (mm·yr<sup>-1</sup>) is calculated using the Faraday law, based on corrosion current density  $j_{corr}$  ( $\mu\text{A}\cdot\text{cm}^{-2}$ ), in accordance with ASTM G102, /5/:

$$v_{corr} = 0.01166 \cdot j_{corr} \quad (3)$$

### Linear sweep voltammetry (LSV)

This technique is used to obtain Tafel polarisation diagrams, /6/. The steel is polarized in the potential range  $E = \pm 0.200$  V relative to  $E_{corr}$  and the corresponding current density  $j$  is recorded. The applied potential sweep rate is  $1$  mVs<sup>-1</sup>. Corrosion current density  $j_{corr}$  is directly determined from the obtained Tafel diagrams by extrapolation of linear parts of anodic and cathodic polarization curves to the corrosion potential  $E_{corr}$ .

Electrochemical tests are carried out using the potentiostat/galvanostat Bio-Logic SP-200, in solutions of different pH value, containing sulphate and chloride anions ( $0.25 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.25 \text{ mol}\cdot\text{dm}^{-3} \text{ NaCl}$ ).  $\text{H}_2\text{SO}_4$  is added to the test solutions to achieve the desired pH value (pH2.3, pH3.3, and pH6.3). The tests are performed at room temperature, in the presence of atmospheric oxygen.

The tests are carried out in an electrochemical cell with a saturated calomel electrode (SCE) as a reference electrode

and a Pt mesh as an auxiliary electrode. The working electrode is the sample of the tested steel. Before the test, the sample is ground with progressively finer grinding paper with SiC (up to 600 grit), washed with ethanol and air-dried. Before the beginning of polarization measurements, the sample is held for a time at open circuit potential, to establish a stable corrosion potential  $E_{corr}$ .

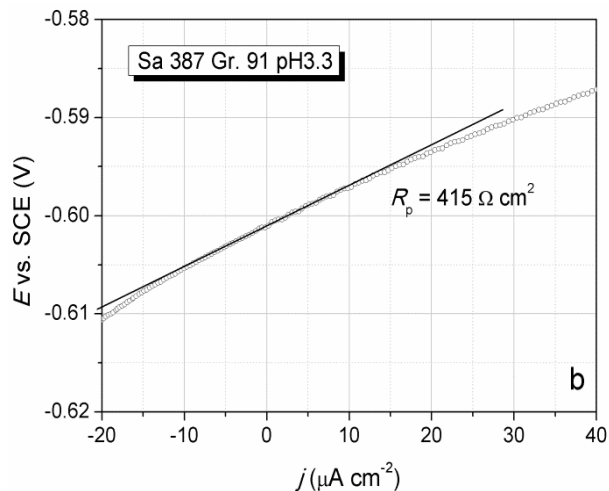
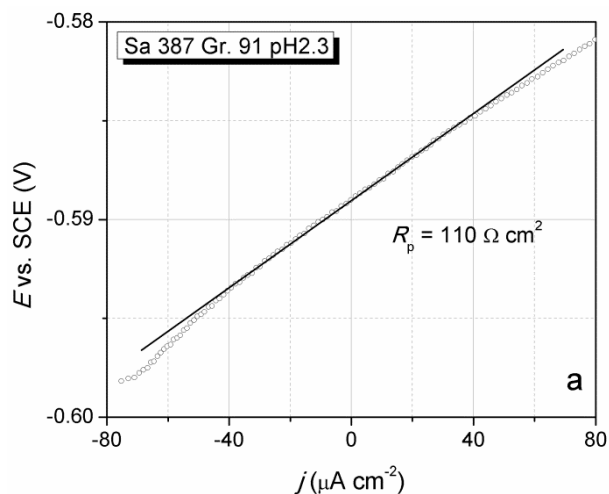
## RESULTS AND DISCUSSION

### Linear polarization resistance technique

Polarisation  $E$ - $j$  diagrams obtained by LPR technique in solutions with different pH values are shown in Fig. 1a-c. The summary diagram is shown in Fig. 1d.

The slope of the polarisation curve ( $\Delta E/\Delta j$ ) at corrosion potential  $E_{corr}$  corresponds to the value of polarization resistance  $R_p$ . The value of  $R_p = 110 \Omega\cdot\text{cm}^2$  in the test solution with pH2.3 (Fig. 1a). A significantly higher  $R_p$  value is obtained in the solution with pH3.3 ( $R_p = 415 \Omega\cdot\text{cm}^2$ , Fig. 1b). The highest value of  $R_p$  ( $82\,000 \Omega\cdot\text{cm}^2$ ) is obtained in the solution with pH6.3 (Fig. 1c), as expected. The obtained results are given in Table 2.

Corrosion current density  $j_{corr}$  is calculated based on the experimental values of  $R_p$  according to Eq.(2). Corrosion current density is directly proportional to corrosion rate  $v_{corr}$ . The corrosion rate is calculated using Eq.(3), and the obtained results are given in Table 3.



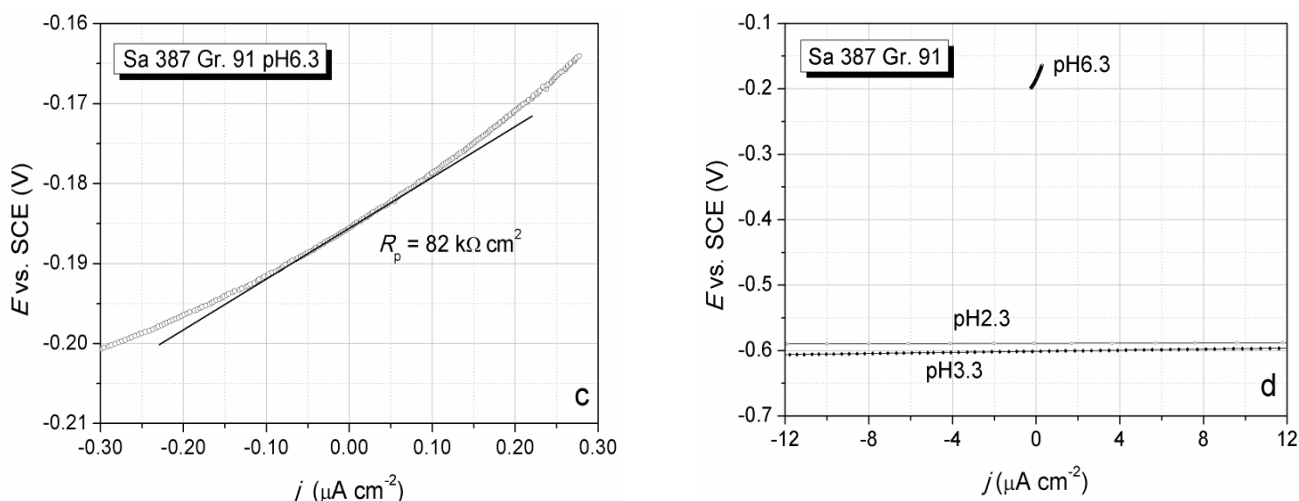


Figure 1. LPR diagrams: a) pH2.3, b) pH3.3, c) pH6.3 and d) summary diagram.

Table 2. Summary results of electrochemical corrosion tests.

pH	$E_{corr}$ (mV)	$R_{p, LPR}$ ( $\Omega \text{ cm}^2$ )	$R_{p, EIS}$ ( $\Omega \text{ cm}^2$ )	$j_{corr, LSV}$ ( $\mu\text{A cm}^{-2}$ )
2.3	-590	110	100	150
3.3	-570	415	480	48
6.3	-180	82000	84000	0.50

Table 3. Calculated values of the corrosion rate.

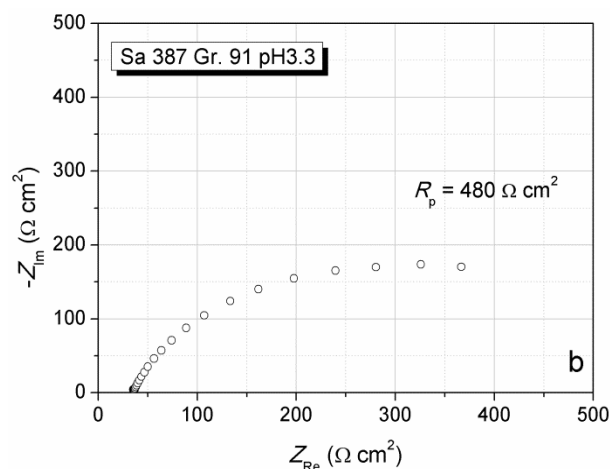
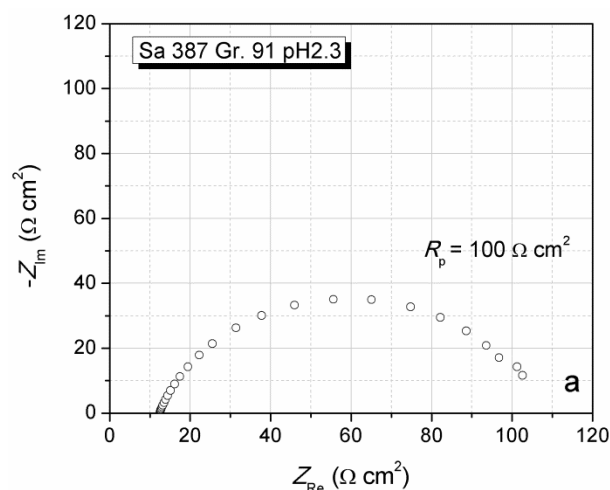
pH	$v_{corr}$ (mm yr <sup>-1</sup> )		
	LPR	EIS	LSV
2.3	1.81	1.98	1.75
3.3	0.56	0.49	0.56
6.3	0.0036	0.0035	0.0058

Electrochemical impedance spectroscopy (EIS)

Nyquist diagrams obtained in the test solutions with different pH value, using EIS technique, are shown in Fig. 2a-c. The summary diagram is presented in Fig. 2d. An enlarged part of the diagram in Fig. 2d, at low frequencies, is shown in the inset. Nyquist diagrams obtained in solutions with pH2.3 and pH3.3 can be clearly seen in the inset.

Nyquist diagram shows the real component of impedance ( $Z_{Re}$ ) and imaginary component of impedance ( $Z_{Im}$ ) in linear coordinates. It can be seen that the solution resistance is  $R_e = 10 \Omega \cdot \text{cm}^2$  (left side of the diagram in Fig. 2a). Total resistance is  $R_e + R_p = 110 \Omega \cdot \text{cm}^2$ , as can be seen on the right side of the diagram. Accordingly,  $R_p = 100 \Omega \cdot \text{cm}^2$  (for pH2.3).  $R_p = 480 \Omega \cdot \text{cm}^2$  (for pH3.3) and  $R_p = 84000 \Omega \cdot \text{cm}^2$  (for pH6.3). The values of corrosion current density  $j_{corr}$  are calculated using Eq.(2), while the values of corrosion rate  $v_{corr}$  are calculated using Eq.(3). The obtained results are shown in Table 3.

The summary Bode modulus diagram, obtained by EIS technique for solutions with different pH, is presented in Fig. 3a. This diagram shows dependence of impedance modulus ( $Z_{Mod}$ ) on the applied frequency ( $f$ ), in logarithmic coordinates. An impedance plateau at low frequencies most usually corresponds to the value of  $R_p$ . Figure 3b shows the summary Bode phase diagram. This diagram shows the dependence of the impedance phase angle ( $\theta$ ) on the logarithm of frequency ( $f$ ). This diagram is used to determine the frequency range where corrosion reactions occur as well as for deeper insight in corrosion processes on the metal [8]. Figure 3b shows that the rate of electrochemical (corrosion) reaction increases at frequencies less than 10 Hz (pH2.3), or less than 1 Hz (pH3.3), and less than 0.01 Hz (pH6.3).



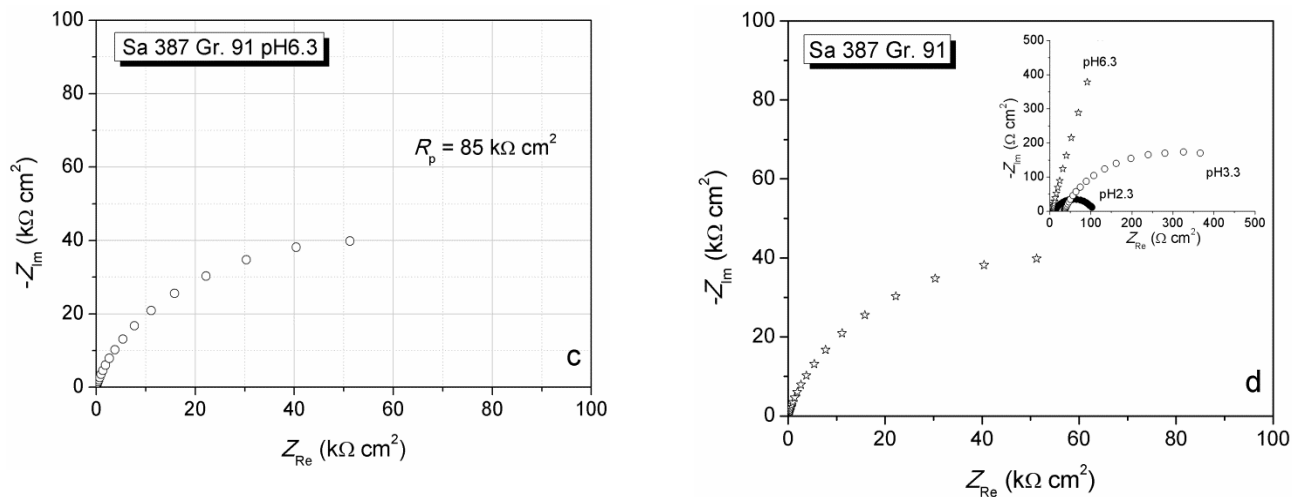


Figure 2. Nyquist diagrams: a) pH2.3, b) pH3.3, c) pH6.3 and d) summary diagram.

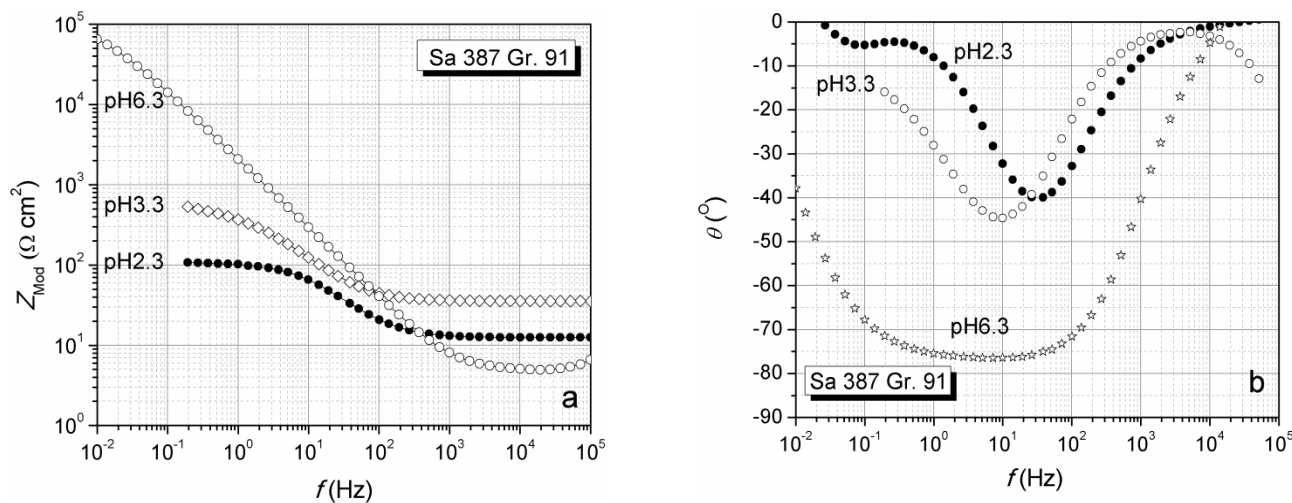


Figure 3. Summary EIS diagrams: a) Bode modulus diagrams; b) Bode phase diagrams.

Linear sweep voltammetry (LSV)

Tafel diagrams obtained by LSV technique in solutions with different pH value are shown in Fig. 4a-c. The summary Tafel diagram is presented in Fig. 4d.

Corrosion current density  $j_{corr}$  is determined at the intersection of anodic and cathodic Tafel lines (at corrosion potential  $E_{corr}$ ). For example,  $j_{corr} = 180 \mu A \cdot cm^{-2}$  (pH2.3), as can be seen in Fig. 4a. Corrosion rate  $v_{corr}$  is calculated based on the value of corrosion current density  $j_{corr}$  (Table 3).

Tables 2 and 3 summarize quantitative results of electrochemical tests. In addition to the values of  $R_p$ ,  $j_{corr}$  and  $v_{corr}$ , the values of corrosion potential  $E_{corr}$  are also listed. The  $E_{corr}$  is established on the steel surface before the beginning of electrochemical corrosion tests.  $E_{corr}$  is the thermodynamic indicator of metal susceptibility to corrosion in a given corrosion environment. The more positive is the value of  $E_{corr}$ , the less is the thermodynamic driving force for the corrosion process to occur, /3/.  $E_{corr}$  has the most positive value in the solution with pH6.3 and the most negative value in the solution with pH2.3 (Table 2).

It can be seen that values of corrosion rate obtained by various electrochemical techniques are in a very good agreement (Table 3).

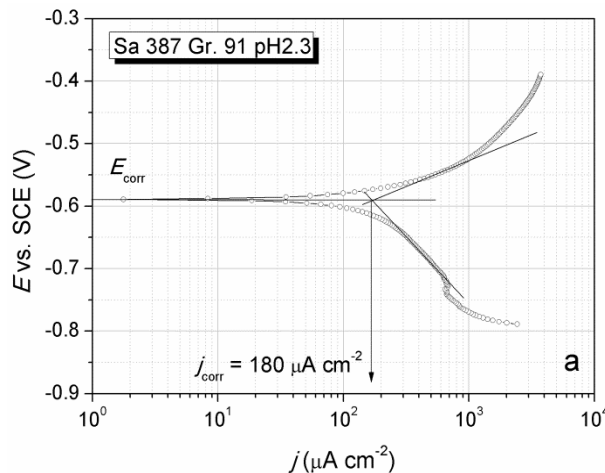


Figure 4. a)

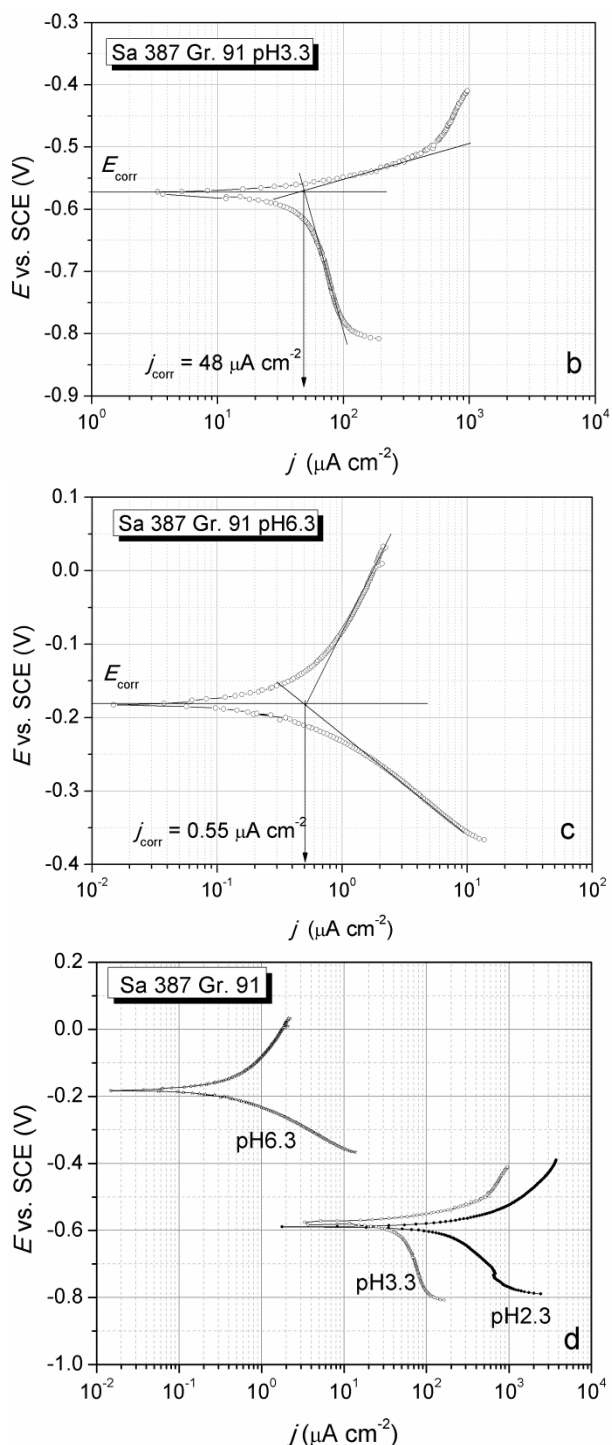


Figure 4. Tafel diagrams: a) pH2.3, b) pH3.3, c) pH6.3 and d) summary diagram.

The appearance of the steel surface after the LSV corrosion test is shown in Fig. 5.

The application of this technique involves high anodic polarizations, so that there is an intensive dissolution of the steel surface during the test. Dissolution of the steel surface is considerably less when using LPR or EIS technique.

Figure 5 shows that dissolution of the steel surface is uniform, without pitting or other forms of local dissolution, which means that corrosion on the surface of the tested steel is general (uniform) corrosion.

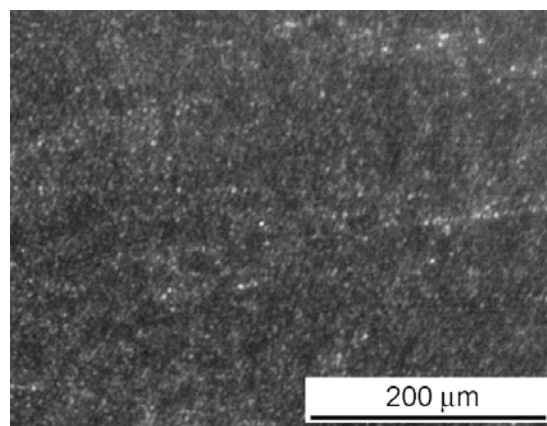


Figure 5. Surface appearance of Sa 387 Gr. 91 steel after LSV test.

Dependence of logarithmic values of polarization resistance  $R_p$  on the pH values is shown in Fig. 6a. The values of  $R_p$  are obtained by independent electrochemical techniques (LPR, EIS and LSV, Tables 2 and 3). It can be seen that dependence between  $R_p$  and log pH is linear. With increase in the solution pH value, the value of  $R_p$  rapidly increases. The dependence of logarithmic values of  $v_{corr}$  on pH values is shown in Fig. 6b. The value of corrosion rate  $v_{corr}$  sharply decreases with increase in solution pH value. The dependence  $\log v_{corr} - \text{pH}$  is also linear.

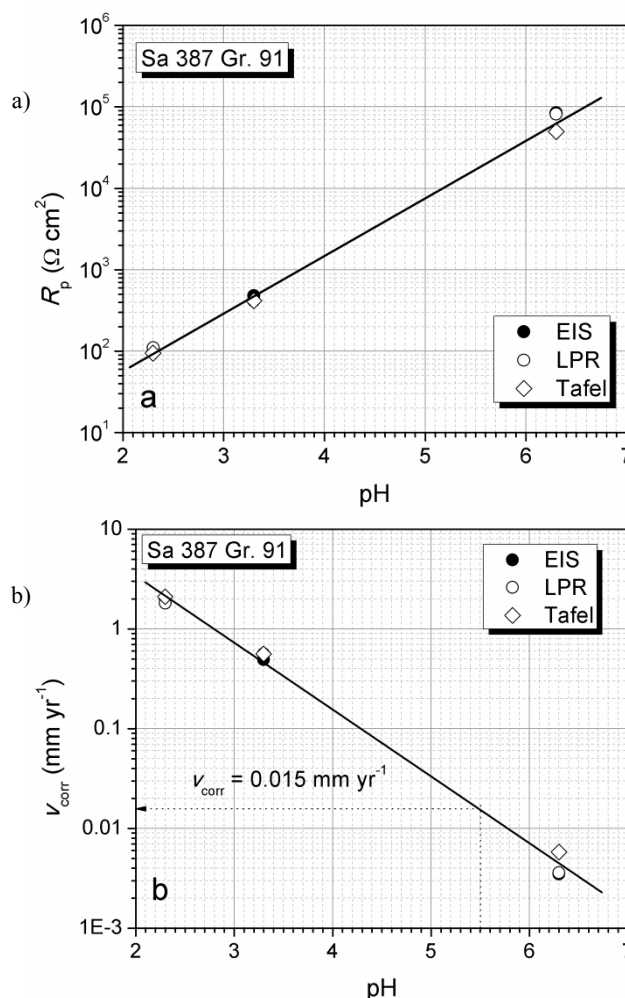


Figure 6. a)  $R_p$  dependence on pH and b)  $v_{corr}$  dependence on pH.

The service life of a pressure vessel made of Sa 387 Gr. 91 steel (used in the industrial atmosphere with a presence of significant amounts of chloride ions) can be estimated from the standpoint of general corrosion, using the diagram in Fig. 6b.

If it is assumed that the pH value of the corrosion environment is  $\sim$  pH5.5, the thickness of the steel wall will decrease gradually over time due to general corrosion (approximately 0.015 mm per year, Fig. 6b). This means that after 50 years of exploitation one can expect that the reduction in the wall thickness will be nearly 0.75 mm. In a neutral corrosion environment (pH7), the dissolution rate of the steel is less, and amounts to  $< 0.002 \text{ mm}\cdot\text{yr}^{-1}$ . According to the diagram in Fig. 6b, reduction in the thickness of the steel wall in this environment will be significantly less than in the corrosion environment with pH5.5. In addition, it should bear in mind that formation of corrosion products occurs on the steel surface in real operating conditions, over time. Corrosion products layers show protective character to some extent, which results in the decrease of corrosion rate over time. The presence of significant amounts of Cr and Mo in the Sa 387 Gr. 91 steel leads to the formation of more compact protective corrosion products.

## CONCLUSIONS

The corrosion behaviour of Sa 387 Gr. 91 steel is tested in solutions containing chloride and sulphate anions. Chemical composition of these solutions is very similar to the composition of marine and industrial atmosphere. Tests are carried out in slightly acidic and moderately acidic solutions (pH2.3, pH3.3 and pH6.3), in the presence of atmospheric oxygen. It is shown that the steel uniformly corrodes, without pitting or other forms of local dissolution. This means that general (uniform) corrosion occurs on the steel surface. Values of corrosion current density  $j_{corr}$  are determined using three independent electrochemical techniques. The corresponding values of corrosion rate  $v_{corr}$  are calculated based on  $j_{corr}$  values. It is shown that corrosion rate is the highest in the solution with lowest pH (pH2.3), while it is the lowest in the solution with the highest pH (pH6.3). The values of quantitative corrosion rate indicators ( $R_p$ ,  $j_{corr}$ ,  $v_{corr}$ ) obtained by different electrochemical techniques are in very good agreement.

The service life of pressure vessel made of Sa 387 Gr. 91 steel can be evaluated based on the obtained results, from the standpoint of the general (uniform) corrosion. In the solution with pH5.5, the thickness of steel wall gradually decreases over time with the rate of about 0.015 mm per year. This means that after 50 years of exploitation one can expect the reduction in the wall thickness of about 0.75 mm. In the corrosion environment with neutral pH (pH7) the corrosion rate of the steel is much lower, so that after 50 years of exploitation one can expect less reduction in the wall thickness. Also, layers of corrosion products are formed on the steel surface, in real conditions of exploitation. These layers show a protective character to some extent, due to the presence of significant amounts of Cr and Mo in Sa 387 Gr. 91 steel. Due to this, the corrosion rate

decreases with time. Thus, it can be expected that the value of real corrosion rate will be less than the calculated value.

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