THE EFFECT OF SOIL ENVIRONMENT ON THE CORROSION OF PIPELINE

Jana Cervová[1)*], *Mária Hagarová*[1)]
[1)] *Technical University of Košice, Faculty of Metallurgy, Košice, Slovakia*

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[*]Corresponding author: *e-mail: jana.cervova@tuke.sk*, *Tel.:+421 55 602 2539, Department of Materials Science, Faculty of Metallurgy, Technical University of Košice, Letná 9, 042 00 Košice, Slovakia*

Abstract

The aim of this work was to investigate the effect of soil environment on steel pipeline corrosion. The corrosion of the gas pipeline DN 500 after 48-year operation was studied by electrochemical methods. The samples of the pipeline were tested in soil electrolyte for 6 hours. Corrosion resistance of the steel samples was evaluated by open circuit potential and potentiodynamic polarization resistance measurements. Corrosion rate i_{corr} of studied steel was determined using a potentiodynamic polarization method. Corrosion behavior of surface without and with corrosion products was compared. The corrosion rate i_{corr} of the sample with corrosion layer reached the lower value compared to the sample without corrosion layer.

Keywords: steel pipeline, corrosion, soil

1 Introduction

Underground metal structures also called pipelines represent highly integrated distribution network that transport natural gas and crude oil over long distances in the world. The most commonly used material in gas industry is carbon steel due to low cost, mechanical properties and easy availability [1-2]. These pipelines are exposed to different environmental aggressive conditions (soil, underground water, seawater) which can cause the corrosion attack. Corrosion is the electrochemical process that involves the flow of electrical currents on a micro or macro scale. For corroding steel, anodic and cathodic reactions produce the electrochemical cell. The anodic, Equation 1, and cathodic electrochemical reaction, Equation 2, must occur simultaneously. The corrosion process takes place in neutral environment according to Equation 3 and 4; in environment with higher concentration of oxygen according to Equation 5 and with lower concentration of oxygen according to Equation 6 [3-6].

$$\boldsymbol{Fe \rightarrow Fe^{2+} + 2e^-} \tag{1}$$

$$\boldsymbol{H_2O + ½\, O_2 + 2e^- = 2OH^-} \tag{2}$$

$$Fe + 2\,H_2O \rightarrow (FeOH)^+_{ad} + H^+ + 2e^- \tag{3}$$

$$(FeOH)^+_{ad} + H_2O \rightarrow Fe(OH)_{2\,ad} + H^+ \tag{4}$$

$$2\,Fe(OH)_2 + H_2O + ½\,O_2 \rightarrow 2\,Fe(OH)_3 \rightarrow 2\,FeOOH + 2\,H_2O \tag{5}$$

$$3\,Fe(OH)_2 \rightarrow Fe_3O_4 + 2H^+ + 2\,H_2O + 2\,e^- \tag{6}$$

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Pipelines corrosion belongs to the most significant problems in the gas industry, which are caused by several factors such as: types of soil, moisture content in soil, pH, soil resistivity, aeration degree, redox potential, oxidation-redox potential, bacterial activity and concentration of chlorides, sulphates, HCO_3^- and oxygen [7-9]. The presence of sulphates and chlorides in the soil is considered as corrosive environment for steel pipelines. If chloride and sulphate concentration in soil is below 100 mg.L^{-1} and 200 mg.L^{-1} respectively, the soil environment is evaluated as slightly aggressive. On the other hand, sulphate concentration higher than 200 mg.L^{-1} presents a significant corrosion risk for natural gas pipelines. The microbiological induced corrosion of the pipelines widely occurs in soil environment, too. The same types of bacterial strains are able to damage both outer and inner surface of the pipe and to form corrosion products, which may be observed as deposits. The largest group of microorganisms that are responsible for the corrosion degradation of pipelines are among the sulphate - reducing bacteria [10-14]. The corrosion resistance of steel pipelines can be divided into four classes. This classification is given in Table 1 [14].

Table 1 Classification of corrosion resistance [14]

Corrosion rate (mm/year)	**Corrosion resistance**
< 0,05	excellent
0,05 - 0,1	good
0,1 – 0,5	middle
> 0,5	bad

Outer surface corrosion of pipelines causes more than 80 per cent of corrosion failure in distribution pipelines. Therefore, there is a need of external pipeline surface protection. The corrosion control can have a major impact on economics, safety and environmental protection of natural gas pipeline operation [10, 15-16].

Passive protection is a set of preventive measurements against outer surface corrosion. The aim of passive protection is the prevention the metal structure against to electrochemical corrosion and to support active protection. The 3-layer polyethylene, polyethylene (3 LPE), fusion bonded epoxy (FBE), polyethylene (PE), polyurethane (PUR), bitumen coatings are the most commonly used passive protection system of the pipelines. However, the passive protection is frequently used in combination with active protection. There are two ways to obtain electrochemical controlled current flow: using sacrificial anode system or impressed current cathodic protection system [17-20].

As mentioned above the corrosion process of the experimental steel pipeline has the electrochemical character. For this reason it was important to determine the electrochemical characteristic of the process using the Tafel and Stern methods.

The measurements of polarization resistance R_p based on Stern-Geary equation represent slope of the linear current δj and potential δE dependence at the zero current and lower potential than 20 mV. The current density, which is proportional to the inverse R_p, provides instantaneous electrode corrosion rate i_{corr}, using Stern-Geary **Equations 7 – 10** [21-23]:

$$\mathrm{R_p} = \frac{\delta E}{\delta j} \tag{7}$$

$$\frac{\delta E}{\delta j} = \frac{B}{i_{corr}} \tag{8}$$

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$$B = \frac{\beta_a \times \beta_c}{2.303\,(\beta_a + \beta_c)} \tag{9}$$

$$i_{corr} = \frac{\beta_a \times \beta_c}{2.303\,(\beta_a + \beta_c)} \times \frac{\delta j}{\delta E} \tag{10}$$

where: B (mV) – the Stern and Geary coefficient
R_p ($\Omega.cm^2$) – the polarization resistance
$ß_a$ (V/decade) – the anodic Tafel slope
$ß_c$ (V/decade) – the cathodic Tafel slope
$\delta j/\delta E$ (Ωcm^2) – slope of the polarization curve; so called R_p

Linear polarization resistance is known as derived an equation relating the slope of linear region to the corrosion rate and Tafel plot. The cathodic ($ß_c$) and anodic ($ß_a$) branch of Tafel are intersected at the point which determines the corrosion potential E_{corr} and corrosion density i_{corr} of samples in a given electrolyte. This theory explains the corrosion reactions on the basis of cathodic and anodic partial reactions that are occurring at the interface electrode of metal and electrolyte [21].

2 Experimental material and methods

The investigated material in these experiments was steel EN 10028/2-92 after 48-year operation. Both the surface samples after grinding (surface without corrosion products) and the surface samples with corrosion layer were tested. The thickness of corrosion products was 53.09 μm. The chemical composition of the steel pipeline is given in **Table 2**. The structure of the steel is documented in **Fig. 1**. The experimental samples sizes of 20 x 15 x 10 mm were impressed in the soil electrolyte, which presented corrosion environment, for 6 hours. Macroscopic analysis of the samples surface after corrosion tests was carried out using the macroscope LeicaWild M3Z.

Table 2 Chemical composition of EN 10028/2-92 steel used in corrosion tests, (wt %)

Material	**C**	**Mn**	**Si**	**P**	**S**	**Fe**
EN 10028/2-92	0.18	1.05	0.26	0.02	0.02	98.47

The corrosion behaviour of the pipeline steel was determined in soil electrolyte by measuring of basic corrosion characteristics. The soil electrolyte was prepared in the ratio of 2:1, what basically means distilled water (volume) and soil (weight). Corrosion potential E_{SCE} was established against that of the saturated calomel electrode (SCE) during exposure of samples in soil electrolyte, employing the digital voltmeter type of 5 ½ Digit Multimeter Agilent 34405 A. The characteristics of soil environment for corrosion tests are given in **Table 3**.

Table 3 Characteristics of soil electrolyte

Steel	**pH**	**T (°C)**	**EC (μS)**
without protection	8.5	21.7	136
with corrosion layer	8.4	22.1	234
EC - electrical conductivity			

Corrosion potential E_{corr} and corrosion rate i_{corr} were determined on the basis of the relationship: corrosion current density – corrosion potential, by means of potentiodynamic polarization.

During the measurement, the specimens were gradually polarized by direct current from an external source in an interval from - 900 to + 900 mV at the change of potential rate 5 mV.s^{-1}. Linear polarization was measured using the Voltalab P6P 201. During the measuring the three -electrode setup composed of tested specimen, reference saturated calomel electrode (SCE) and auxiliary Pt electrode was used. The results of corrosion potential E_{corr}, current density j_{corr} and polarization resistance R_p measurement were evaluated using software Voltmaster 4. The corrosion rate was evaluated from the polarisation curves by Tafel extrapolation. Polarization resistance R_p was measured in the area of corrosion potential 20 mV [23]. Corrosion tests were performed by immersing the steel samples in the prepared corrosion electrolyte at room temperature for 6 hours. The corrosion rate of the steel samples immersed in the experimental electrolyte was determined according to the Equation 11 [24]:

$$CR = ((j_{corr} \times M) / (\rho_{Fe} \times Z)) \times 3270 \qquad (11)$$

where: CR (mm.year^{-1}) – the corrosion rate
j_{corr} (A/cm^2) – the corrosion current density
M (g/mol) – the atomic weight of the metal
ρ_{Fe} (g/cm^3) – the density of the metal
z (-) – number of electrons of the dissolving metals

3 Results and discussion

Microstructure of the experimental material, shown in **Fig. 1**, is ferrite - pearlite with areas of line ordering grains. The surface state of steel samples (surface without protection and with corrosion layer) before exposure and after 6 hours exposure in the soil is documented in **Figs. 2 - Fig. 5**. On the surface without protection it can be seen the signs of corrosion attack after exposure in the soil electrolyte. The appearance of surface with corrosion products did not change significantly.

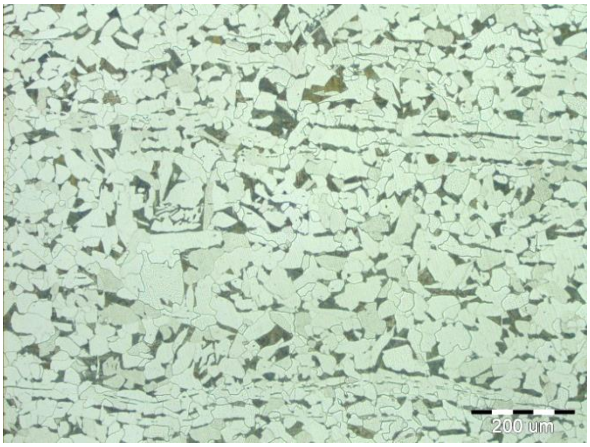

Fig. 1 Polyhedral ferrite – pearlite structure with areas of line ordering grains, etch. 2 % Nital

Time dependence E_{corr} is shown in **Fig. 6**. On the steel surface without corrosion products the corrosion potential decreased from the initial value -499 mV to -685 mV after 60 minute exposure in the soil. This decrease was caused by anodic dissolution of the steel (according to

Equation 1) and by the formation corrosion layer on the sample surface. Steady corrosion state on the sample surface was achieved after 60 min of the corrosion test, Fig. 7, when protective effect of formed corrosion layer was demonstrated. Time course of the potential E_{corr} of corrosion products on the sample surface was steady at the value of 26 mV.

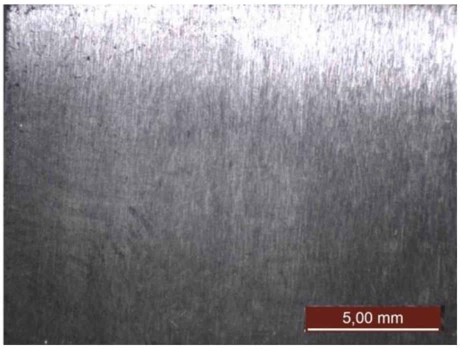

Fig. 2 Steel surface state without corrosion layer before exposure in the soil

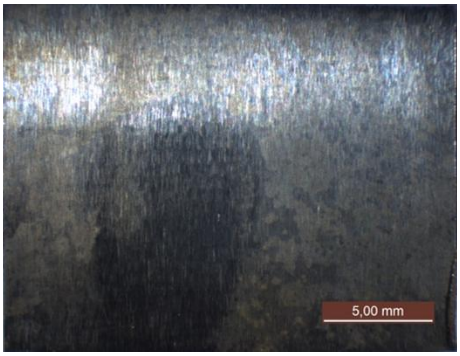

Fig. 3 Steel surface state without corrosion layer after 6 hours exposure in the soil

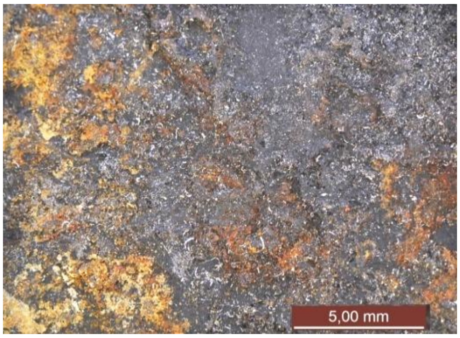

Fig. 4 Steel surface state with protection corrosion layer before exposure in the soil

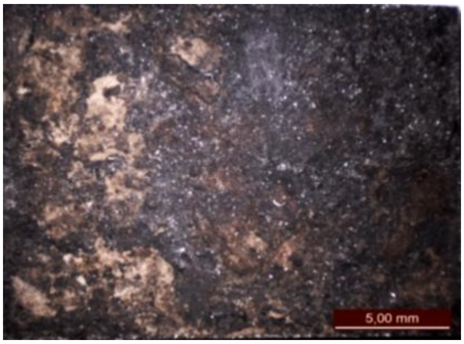

Fig. 5 Steel surface state with protection corrosion layer after 6 hours exposure in the soil

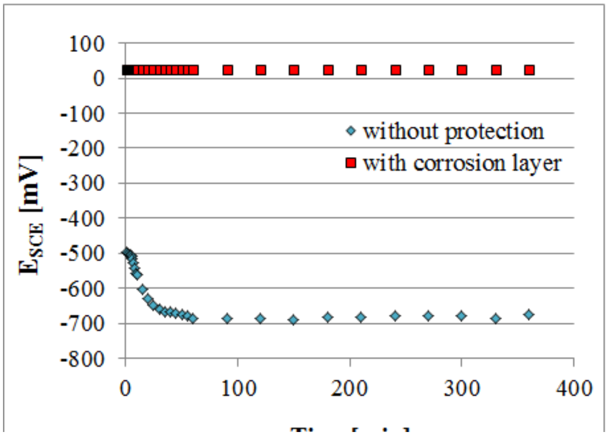

Fig. 6 Corrosion potential E_{corr} over time

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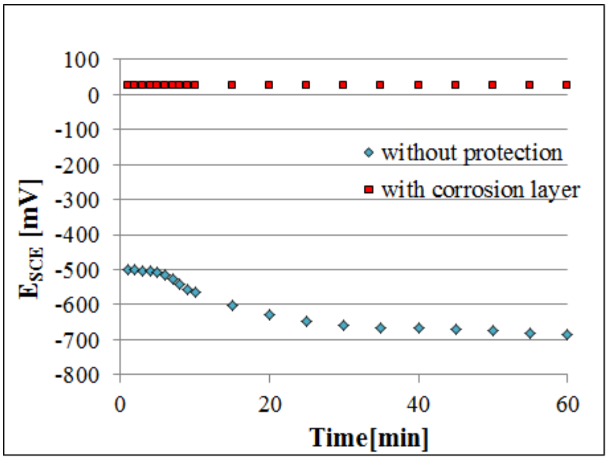

Fig. 7 Corrosion potential E_{corr} over 60 min

The results of corrosion potential E_{corr}, polarization resistance R_p and corrosion current density j_k evaluated by the Tafel and Stern methods are shown in **Figs. 8** - **Fig**. 11. Presence of corrosion products on the steel surface increased its corrosion resistance; for these samples were measured less negative values of E_{corr}, lower corrosion rates i_{corr} and higher polarization resistance R_p in comparison with the samples without this layer. Barier effect of the corrosion layer had polarization resistance value of 41.08 kΩ.cm while the surface without corrosion products reached the value of 7.98 kΩ.cm. Corrosion rate of the sample with corrosion layer reached the value 1.36 µA.cm^{-2} what means about 72 % lower value compared to the surface without corrosion layer. It was also comfirmed by account of corrosion rate (CR) according to Equation 7. The measured values of corrosion characteristics according to Tafel and Stern and calculation of CR are presented in **Table 4**.

Table 4 Measured corrosion characteristics according to Tafel and Stern

Sample	**E_{corr} (mV)**	**I_{corr} (µA.cm^{-2})**	**Rp (kΩ.cm)**	**CR (mm.year^{-1})**
Without corrosion layer	-698.7	4.9778	7.98	0.0580
With corrosion layer	-590.9	1.3647	41.08	0.0159

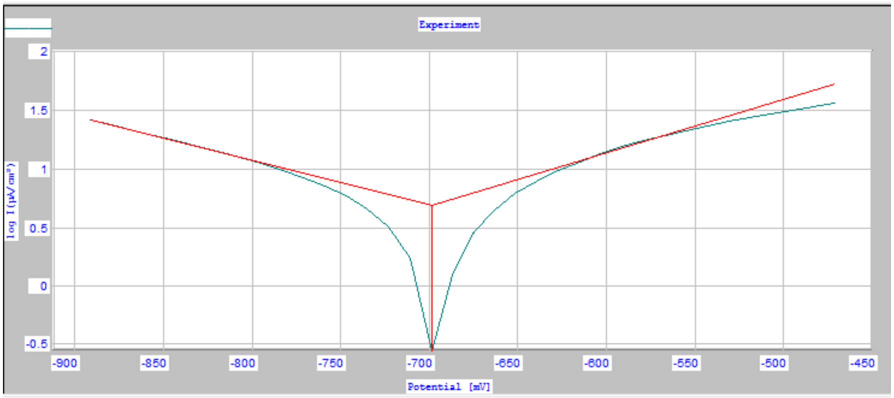

Fig. 8 Tafel plot of the sample without corrosion layer after 6 hours of exposure in the soil

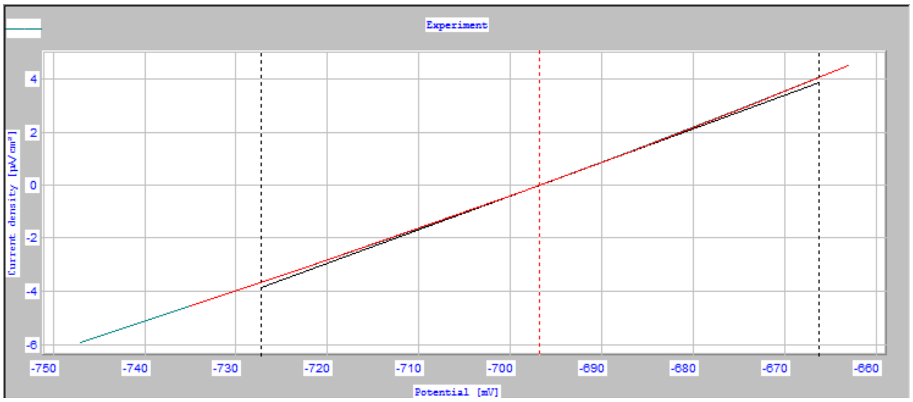

Fig. 9 Stern plot of the sample without corrosion layer after 6 hours of exposure in the soil

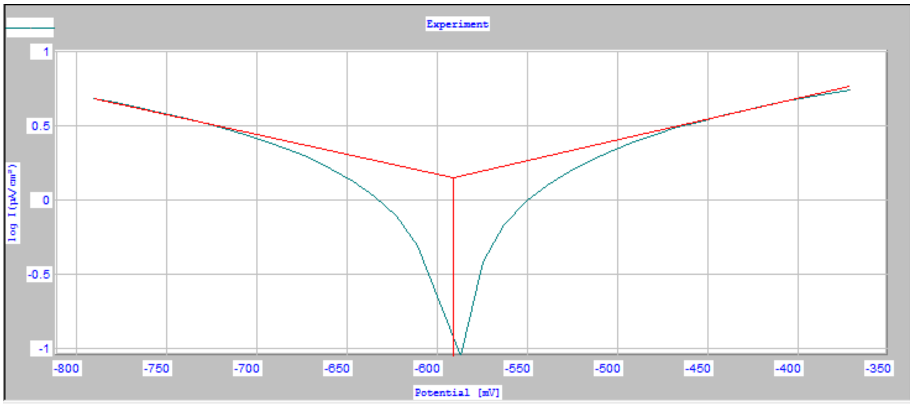

Fig. 10 Tafel plot of the sample with corrosion layer after 6 hours of exposure time in the soil

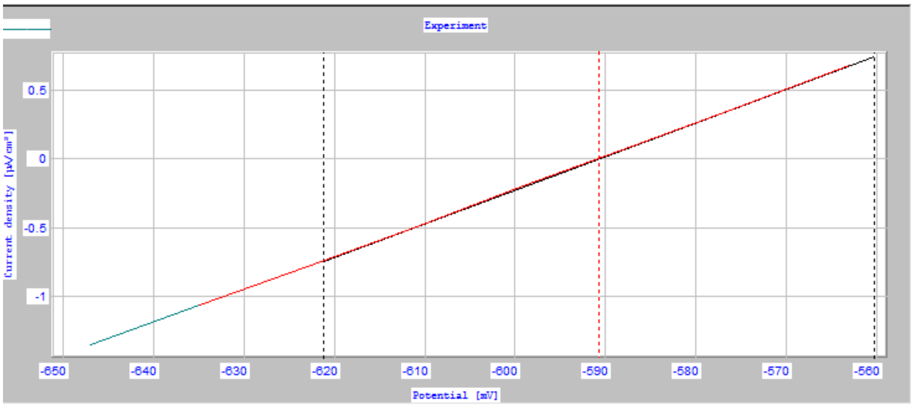

Fig. 11 Stern plot of the sample with corrosion layer after 6 hours of exposure in the soil

4 Conclusion

Corrosion degradation of the pipelines in the soil had electrochemical character. Therefore it is important to simulate the conditions of corrosion processes and to determine behaviour of steel materials with and without corrosion layers. Based on the corrosion tests of E_{corr} measurements and also basic corrosion characteristics E_{corr}, i_{corr} and R_p by Tafel and Stern it may be concluded:

- after only a short exposure time significant changes were observed on the samples without protection; whereas no visible changes were observed on the samples with corrosion products,
- the corrosion potential E_{corr} was stabilized at values which corresponded with formation of corrosion layer on the steel surface; the values of potential reached the value of – 698 mV. Corrosion potential E_{corr} of the samples with corrosion layer reached the value of + 26 mV,
- results according to Tafel and Stern confirmed that the corrosion layer provided the sufficient barrier against corrosion. Polarization resistance R_p of the sample with and without the corrosion layer had the value of 41.08 kΩ.cm and 7.98 kΩ.cm, respectively.

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