Influence of Composition of Soil Electrolyte Model Environments on Corrosion Rate of Tube Steel

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ABSTRACT

A study on the influence of the composition of the model media of the soil electrolyte (NS1–NS2) on the corrosion rate of tubular steels 17G1S and 13G1S-U in a long-term experiment. The phase composition and structure of corrosion products were determined by X-ray analysis. using an X-ray diffractometer Shimadzu XRD-7000. It was found that, regardless of the steel grade, the composition of corrosion products in the environment of NS1 will be mainly characterized by the presence of lepidocrocite, and in the environment of NS2 – goethite. The corroding samples in both media will have a small amount of magnetite. During the exposure (609 days) of steel samples in the studied model media, the rate of corrosion processes depends on the component composition of the model media, steel grade and pH. The obtained results are important for predicting the behavior of underground pipelines in soils of different corrosive activity.

Keywords: tubular steel, model media, corrosion rate, soil electrolyte.

INTRODUCTION

Underground pipelines are cost-effective structures, the service life of which is mainly determined by their corrosion resistance. Corrosion of underground metal structures leads to significant material damage. According to statistics, about 4% of the world's metal corrodes annually due to soil corrosion. Thus, according to American experts in 2015, the annual losses of the American oil and gas industry from corrosion of equipment, and especially pipelines, amounted to – 13.4 billion dollars [Andreyuk 1980; Blahnik, 1985]. The metal of long-operated tubular steels in the underground environment is subject to corrosive destruction under the influence of soil electrolyte, the association of soil microorganisms [Polutrenko, 2018; Kryzhanivsky, 2019; Krivenko, 2005; Lopushniak, 2021].

This is especially true for pipelines operated in areas where the insulation of the pipeline is broken in the conditions of contact with electrolytic solutions. In such areas, the development of corrosion of the pipeline increases, which leads to unpredictable failures in its operation. The reasons for pipeline failures are covered in the works of domestic and foreign scientists [Krivenko, 2005; Kutukov, 2004; Mironyuk, 2001, Serednitsky, 2004; Lopushniak, 2022]. Unforeseen failures of pipelines due to corrosion lead to significant economic losses and severe environmental consequences, often accompanied by fires and explosions, pollution of water bodies, soil and air basin (Fig. 1).

The processes of metal corrosion in the underground environment are characterized by a special complexity due to the peculiar course of electrochemical processes in the capillary-porous medium. Usually, the processes in underground conditions are dynamic. Underground structures are exposed to a huge number of constantly changing factors that determine the intensity of metal corrosion. The most significant factors determining the corrosion activity of soils are

Figure. 1. The result of unforeseen failures of pipelines due to corrosion

their structure and particle size distribution, humidity, mineralogical composition of the soil electrolyte, the concentration of hydrogen ions, redox potential, electrical resistance of the soil.

In view of this, the problem of protecting underground pipelines from corrosion has been and remains relevant, as their destruction is associated with disruption of energy supply to consumers, causing great material damage and environmental damage to the environment. To solve this problem, scientists are actively conducting research to determine the corrosion rate of tubular steels of different strength classes (X52, X60, X70) in solutions [Andreykiv, 2012; Gredil, 2017; Han P, 2015], which simulate the soil environment. Since the underground pipelines are operated in the soil electrolyte, which is heterogeneous in mineralization, it was considered appropriate to conduct research to establish the patterns of corrosive behavior of tubular steels in soil electrolytes of different mineralogical composition.

The aim of the work is to evaluate the influence of the mineralogical composition of model environments, such as imitations of soil electrolyte, on the corrosion rate of tubular steels in a long-term experiment.

MATERIALS AND METHODS

The object of the study were samples of pipe steel 17G1S and 13G1S-U in the size of 10×50×1.0 mm. During the research, the conditions close to the operating conditions of the main pipelines on the territory of Ukraine were modeled. 2 compositions of model media of soil electrolyte NS1 and NS2 were prepared according to

European standards of composition, mm: 1,999 KCl, 5.999 $NaHCO_3$, 1.082 $CaCl_2$ $2H_2O$, 0.430 $MgSO_4$ $7H_2O$ and 1.905 KCl, 12.868 $NaHCO_3$, 0.497 $PSOHO_3$, 7.80 and 8.87 (293K). The hydrogen index of the media (pH) was determined using glass and silver chloride reference electrodes on a pH meter brand MI-1500.

At the end of the research, metal samples were subjected to mechanical and chemical treatment to remove corrosion products from their surface. The corrosion rate of metal samples was determined by the gravimetric corrosion rate

$$K_{gr} = m - m_0/S\,\tau \ (\text{mg/dm}^2\text{day}) \qquad (1)$$

where: m – final mass of the sample, mg;
m_0 – mass of the sample before corrosion, mg;
S – surface area of the sample, dm^2;
τ – exposure time, day.

The structure of corrosion products were analyzed by X-ray analysis using Shimadzu XRD-7000 X-ray diffractometer (CuKα radiation was used in 20 scanning from 10° to 60°, 2° per minute in 0.02° increments). (Match! / FullProf software).

RESULTS AND DISCUSSION

At the end of long-term tests (609 days) the surface of steel samples was evenly covered with corrosion products of different colors from yellow to brown-brown and up to black. Corrosion products were easily separated from the metal when the samples were treated with concentrated hydrochloric acid. Processing of the taken radiographs of corrosion products of 13G1S-U steel showed the presence of several basic iron

oxides – with the structure of lepidocrocite – γ-FeOOH and goethite – α-FeOOH. In the 13G1S-U sample exhibited in the NS1 medium, lepidocrocite is predominant, in contrast to the 13G1S-U sample in the NS2 medium, in which goethite is mainly present. Magnetite - Fe_3O_4 - is found in small amounts in metal samples aged in NS1 and NS2 media. The presence of hematite - α-Fe_2O_3 in the sample 13G1S-U in NS1 is also clearly expressed (Figure 2).

Radiographs of corrosion products of 17G1S steel samples in the studied media, shown in Figure 3, showed the presence of magnetite in both samples. Sample 17G1S in NS1 medium consists mainly of lepidocrocite, and sample 17G1S in NS2 medium consists of goethite. Sample 17G1S in NS2 medium is also characterized by the expansion of peaks, which may indicate extremely small particle sizes and amorphization of the material. Radiographs of corrosion products of 17G1S steel samples in the studied media, shown in Figure 3, showed the presence of magnetite in both samples. Sample 17G1S in NS1 medium consists mainly of lepidocrocite, and sample 17G1S in NS2 medium consists of goethite. Sample 17G1S in NS2 medium is also characterized by the expansion of peaks, which may indicate extremely small particle sizes and amorphization of the material.
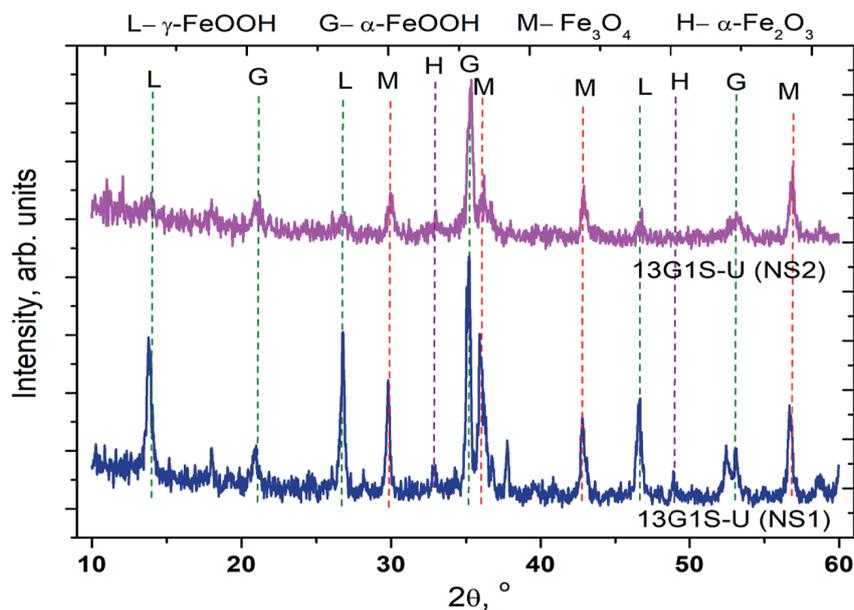
Figure 2. Radiographs of corrosion products of ST. 13G1S-U steel samples in NS1 and NS2 media
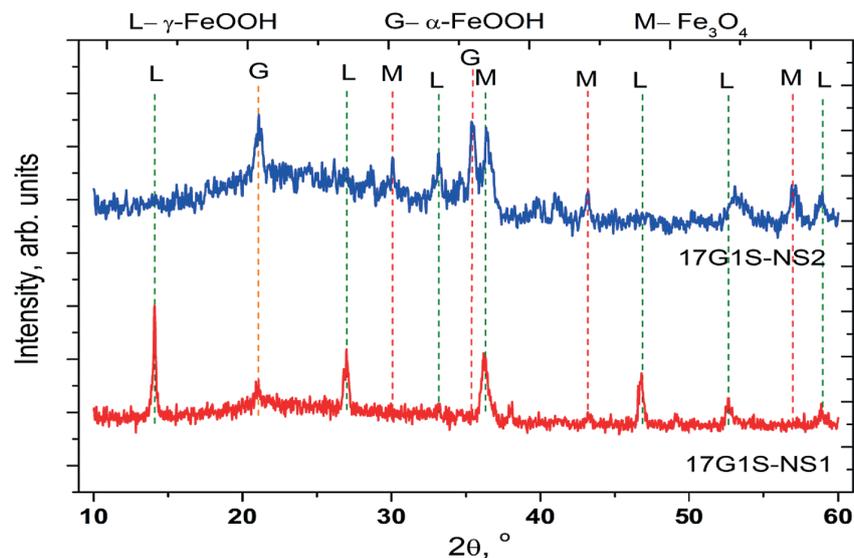
Figure 3. Radiographs of corrosion products of 17G1S steel samples in NS1 and NS2 media

Based on the data of X-ray analysis of corrosion products of tubular steels 17G1S and 13G1S-U, it can be stated that, regardless of steel grade, the composition of corrosion products in NS1 will be mainly characterized by the presence of lepidocrocite and NS2 – goethite. In this case, the corroding samples in both media will have a small amount of magnetite. The presence of established crystalline forms in the corrosion products, consistent with the scheme of their formation. As the concentration of Fe^{2+} in the solution increases, iron (II) hydroxide is formed: by reaction 2, which in the presence of dissolved oxygen easily turns into iron (III) hydroxide by reaction 3:

$$Fe^{2+} + H_2O + 2OH^- \rightarrow Fe(OH)_2\downarrow \qquad (2)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3\downarrow \qquad (3)$$
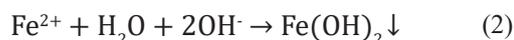
Comparing the solubility of iron (II) hydroxide $P_{Fe(OH)2} = 1.51\ 10^{-4}$ g/l at 20 °C with the product of the solubility of iron (III) hydroxide $DR_{Fe(OH)3} = 6.5\ 10^{-47}$ it becomes clear that the solubility iron (III) hydroxide is much less soluble in iron (II) hydroxide. This indicates that when Fe^{2+} ions come into contact with oxygen, $Fe(OH)_2$ cannot be formed earlier than $Fe(OH)_3$. The iron (III) hydroxide that precipitates can be of different shades of red and brown. According to the data of [Strizhevsky, 1968], after coagulation of colloidal particles and complete dehydration of $Fe(OH)_3$ precipitate, crystalline compounds α-Fe_2O_3, γ-Fe_2O_3 and FeOOH were detected. Iron (III) hydroxide in the precipitate can be converted to iron (III) oxyhydroxide by equation 4:

$$2Fe(OH)_3 \rightarrow 2FeOOH + H_2O \qquad (4)$$
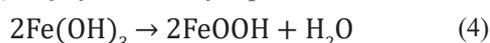
Iron (III) oxyhydroxide FeOOH can be found in four crystalline forms: α-FeOOH – yellow goethite, β-FeOOH orange acageneite, γ-FeOOH brown lepidocrocite and δ-FeOOH – untitled. The presence of α-FeOOH and γ-FeOOH in corrosion products was confirmed by a series of studies conducted by us. It should be noted that long-term corrosion in the aqueous medium produces magnetite – Fe_3O_4 black or brown-black color according to equation 5:

$$Fe(OH)_2 + 2FeOOH \rightarrow Fe_3O_4 + 2H_2O \qquad (5)$$
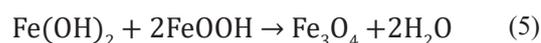
We found that during the exposure of steel samples in the studied model environments, the rate of corrosive processes depends on the total mineralization of the model environments, steel grade and pH (Table 1).

From the above data it is seen that the steel 13G1S-U in the studied environment corrodes more intensely compared to steel 17G1S. Thus, in the NS1 environment the corrosion rate is higher by 8.8%, and in the NS2 environment – by 26.3%. The fact that 17G1C and 13G1S-U steels corrode more slowly in NS2 is probably due to the fact that the formed corrosion products adhere more tightly to the metal surface and thus block the access of oxygen to the metal, which reduces the corrosion rate.

The results of research showed that in the process of long-term contact of steel samples in simulations of soil electrolyte of different mineralization, there was some shift in the pH of the medium at the end of exposure to the alkaline region. For steel 17G1S in the environment of NS1 the pH increased by 12.9%, in NS2 – by 8.7%. Under comparative conditions for steel 13G1S-U in NS1 there was an increase in pH by 10.5%, and in NS2 – 9.6%. This indicates that in real operating conditions of underground pipelines, soils with pH> 8,5 are considered potentially corrosive to carbon steel.

Thus, on the basis of the conducted researches the results which are important for forecasting of behavior of underground pipelines in soils of various corrosive activity are received.

CONCLUSIONS

A study on the influence of the composition of the model media of the soil electrolyte (NS1–NS2) on the corrosion rate of tubular steels 17G1S and 13G1S-U in a long-term experiment. The phase composition and structure of corrosion products by X-ray analysis are determined. using an X-ray

Table 1. Influence of composition of model media and pH on corrosion rate of steel samples

Steel brand	Environment	pH start	pH finish	K g.mg/dm^2 day
17G1S	NS1	7.80	8.81	20.53
	NS2	8.87	9.64	12.59
13G1S-U	NS1	7.80	8.62	22.33
	NS2	8.87	9.72	15.91

diffractometer Shimadzu XRD-7000. It was found that, regardless of the steel grade, the composition of corrosion products in the environment of NS1 will be mainly characterized by the presence of lepidocrocite, and in the environment of NS2 - goethite. In this case, the corroding samples in both media will have a small amount of magnetite. During the exposure (609 days) of steel samples in the studied model environments, the rate of corrosive processes depends on the total mineralization of the model environments, steel grade and pH. The obtained results are important for predicting the behavior of underground pipelines in soils of different corrosive activity.

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