Corrosion of pipe steels 20 and 17G1S-U in ground electrolytes with a hydrogen indicator close to neutral

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ABSTRACT

Purpose: of this paper is to analyse the mechanism of near-neutral pH corrosion of main gas pipelines. The stages of main gas pipelines in model environments that meet the soil conditions of Ukraine have been studied.

Design/methodology/approach: The corrosion rate of steel specimens from steels 17G1S-U and 20 and the influence of borate buffers on their protective properties were evaluated. The influence of corrosion time on changes in pH of model media is shown. Morphological features of surface damages of pipe steels are established. The defect analysis of specimens from steels 17G1S-U and 20 by electron scanning microscopy is carried out.

Findings: The effect of borate buffers on the protective properties of the steel grades studied was revealed, and changes in the pH of the model media during corrosion processes were described. The main regularities in corrosion, as well as the surface morphology of damaged specimens, were studied by scanning electron microscopy.

Research limitations/implications: Detailed investigation of localised corrosion phenomena induced by inclusions that are present in steels 17G1S-U and 20 is extremely critical. In particular, there is still ambiguity as to whether the localised corrosion initiation induced by non-metallic inclusions is an electrochemical process or a chemical process.

Practical implications: The research findings will be used when testing specimens from pipe steels under cyclic loading in the model media studied, as well as for predicting the residual life of gas pipelines with corrosion defects. Their generalization will make it possible to develop the effective methods of ground diagnostics and prediction of SCC of main pipelines.

Originality/value: It was found that the corrosion rate is determined by internal (nature and properties of the metal) and external (properties of the aggressive medium and the corrosion process conditions) factors. The protective effect for steel 17G1S in medium NS_4 + borate buffer (1: 1) was 61.5%. Steel 20 had the greatest protective effect in medium NS_4 + borate buffer (1: 3), which was 87.05%.

RESEARCH PAPER

PROPERTIES

1. Introduction

Gas mains of Ukraine have been in service for 30-50 years. During operation, they are exposed to the influence of aggressive media both from outside (inflow of groundwater in case of damage to the protective coating of the pipe) and inside (corrosive effect of gas condensate) [1]. The influence of static (transported gas pressure) and cyclic (temperature fluctuations) stresses causes degradation of the pipe steel [1-3].

This is most typical of pipeline sections with damaged insulation, when their walls come into contact with electrolytic solutions. This affects the material corrosion, leading to the occurrence of micro-corrosive pairs [5,6]. In case of underground pipelines, this causes changes in the anodic and cathodic polarization characteristics of the steel. The world experience with gas mains testifies to a growing number of accidents due to stress corrosion cracking (SCC) [7,8].

The processes of corrosion, deterioration of the protective properties of the passive film, pitting corrosion and corrosion cracking are interrelated, therefore, they require careful, comprehensive study [9-13].

To date, there is no unambiguous description of the regularities in the corrosion-mechanical behaviour of pipe steels, taking into account an increase or decrease in the SCC intensity. Even though intergranular cracking of pipe steels in alkaline media has long been known [3-8,14], new SCC types may occur on the outer pipe wall during the long-term operation of gas mains. They are characterized by a transcrystalline mechanism of crack propagation and are observed mainly in soils with a pH close to neutral [14]. The main danger of intergranular corrosion is the selective destruction of grain boundaries, therefore, it cannot always

be determined visually. This leads to a practically un-controlled structural and mechanical degradation, a decrease in strength properties, and a depletion of plasticity. To understand the SCC mechanism of pipe steels, it is necessary to systematize the regularities of their behaviour in soil electrolytes of various chemical compositions, which have not been sufficiently studied to date. Their generalization will make it possible to develop the effective methods of ground diagnostics and SCC prediction for main pipelines.

The purpose of this research is to establish the regularities in corrosion damage of pipe steels 20 and 17G1S-U in model soil electrolytes with a pH value close to neutral.

2. Materials and methods

The object of research were specimens from pipe steels 20 and 17G1S-U in the initial state, measuring 10x30x1 mm. Specimens were cut with a water-cooled disc cutter to avoid microstructure changes in the machining zone. The specimens were not polished, since the surface of the main gas pipeline contains micro-roughness. The chemical composition of the investigated steels is presented in Table 1.

During the study, physicochemical environments were simulated that are close to in-service conditions of gas mains on the territory of Ukraine. To this end, tests were carried out in media with a pH close to neutral, in particular, a model soil electrolyte (NS_4 according to the European composition standards, mM: 1.64 KCl, 5.75 $NaHCO_3$, 1.23 $CaCl_2$, 0.74 $MgSO_4$); the pH of the initial medium NS_4 was 7.83. Borate buffers were used to simulate soil electrolytes with a pH close to neutral.

Specimens from steel 17G1SU were kept in media 1 and 11: 1 – medium NS_4, 11 – medium NS_4 + borate buffer (1: 1);

Table 1.
Chemical composition of the investigated pipe steels 20 and 17G1S-U

Steel	Chemical composition, %										
	C	Si	Mn	Ni	S	P	Cr	V	N	Cu	As
20	0.17-0.24	0.17-0.37	0.35-0.65	≤0.25	≤0.035	≤0.035	≤0.25	-	-	-	-
17G1S-U	0.15-0.2	0.4-0.6	1.15-1.55	≤ 0.3	≤ 0.035	≤ 0.03	≤ 0.3	≤ 0.12	≤ 0.012	≤ 0.3	≤ 0.08

Specimens from steel 20 were kept in media 2 and 21: 2 – medium NS4, 21 – medium NS4 + borate buffer (1: 3).

Four compositions of ground electrolyte of different chemical composition with initial pH values of 7.83; 6.93; 7.83; 6.69 were used. The hydrogen indicator of the medium (pH) was determined using glass and silver chloride reference electrodes on a MI-1500 pH meter and monitored during the experiment. At the end of the research, metal specimens were mechanically and chemically cleaned to remove corrosion products from their surface [15]. The corrosion rate of metal specimens was determined by the gravimetric corrosion rate indicator (K_{gr}):

The corrosion rate K_{gr}, (mg/(dm^2·days), was determined by gravimetric method:

$$K_{gr} = \frac{m_0 - m_f}{S \times \tau},$$ (1)

where m_f is the final mass of the specimen, mg; m_0 is the specimen mass before corrosion, mg; S is the surface area of the specimen, dm^2; τ is the exposure time, days.

3. Results and discussion

3.1. Experimental results and discussion

After the tests, the specimen surface was covered with a uniform layer of corrosion products of reddish-brown colour, which turned black in local areas. The product layer had a loosened appearance and was characterized by a non-uniform adhesion to the metal surface; a part of it settled to the bottom of the model media, Figure 1.
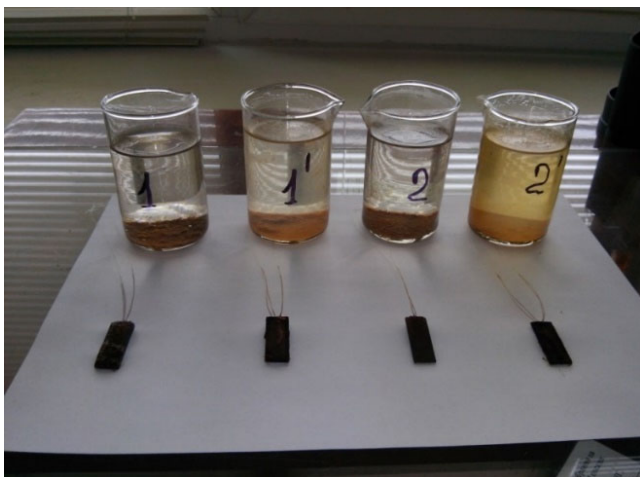

Fig. 1. Photos of specimens from steels 20 and 17G1S-U, and model media after testing

Specimens from steel 17G1S-U after testing in NS4 medium were covered with a thick layer of reddish-brown corrosion products, which could be easily removed by applying mechanical stress. The specimen surface has acquired a black colour under this layer. When a specimen with corrosion products was dowsed in the concentrated hydrochloric acid, a violent evolution of gas was observed, the solution acquired a yellow-orange colour due to the formation of soluble ferric chloride. After a complete removal of corrosion products, corrosion spots and small pitting were found on the specimen surface (Fig. 2 – specimen 1).

The surface of steel 17G1S-U in medium 11 (medium NS4 + borate buffer (1: 1)) was covered with a reddish-brown layer of corrosion products on one side, and with a black deposit on the other side, which could also be easily removed from the metal surface by applying mechanical stress. The specimen behaviour in the concentrated chloride acid was similar to that of series 1 specimens. After cleaning the surface from corrosion products, one corrosion pitting was found, while the other side of the specimen remained intact (Fig. 2 – specimen 1[1]).

Fig. 2. Photos of specimens from pipe steels and corrosion products after testing

Specimens of steel 20 examined in NS4 medium were covered with dark brown corrosion products that adhered tightly to the surface. When they were dissolved in the concentrated perchloric acid, a vigorous gas evolution was observed, the solution acquired a yellow-orange colour, indicating the corrosion processes similar to those in series 1 specimens. Two clearly defined boundaries of corrosion damage were observed on the metal surface (Fig. 2 – sample 2).

In medium 2^1 (NS$_4$ + borate buffer (1: 3)), a thin coating of corrosion products with a color gradient from dark brown to reddish-brown was formed on the specimens, which easily separated from the metal surface. After removal of the corrosion products, the specimen surface became dim, with no traces of corrosion observed (Fig. 2 - specimen 2^1).

3.2. Fractographic analysis of damaged specimen surfaces

Corrosion damage of steels 20 and 17G1S-U was analysed by scanning electron microscopy, as a result of which the following findings were obtained.

For steel 17G1S-U

1. The surface damaged by corrosion had a "loosened" appearance, with some areas etched to a greater extent. These zones represented micro-depressions on the specimen surface formed as a result of the corrosion process.

Corrosion was localized near the ridges of the initial relief formed during the machining of specimens, as evidenced by a large number of corrosion microdefects on its surfaces, Figures 3a, b.

1^1. The specimen surface had significant micro-corrosion damage. Localized corrosion defects with a size of 35-45 µm were found. The damage was represented by rounded pits, the edges of which were "blurred" or "smoothed out" due to corrosion. In general, the surface had a fairly developed relief with depressions and elevations, the boundaries of which had a low-sloped, smoothed out appearance, Figures 3c, d.

For steel 20

2. An uneven (stained) surface corrosion was observed. Areas with etched grains alternated with "islands" of undamaged material. Despite the presence of such "islands", the corrosion between them generally developed fairly evenly, Figures 4a, b.
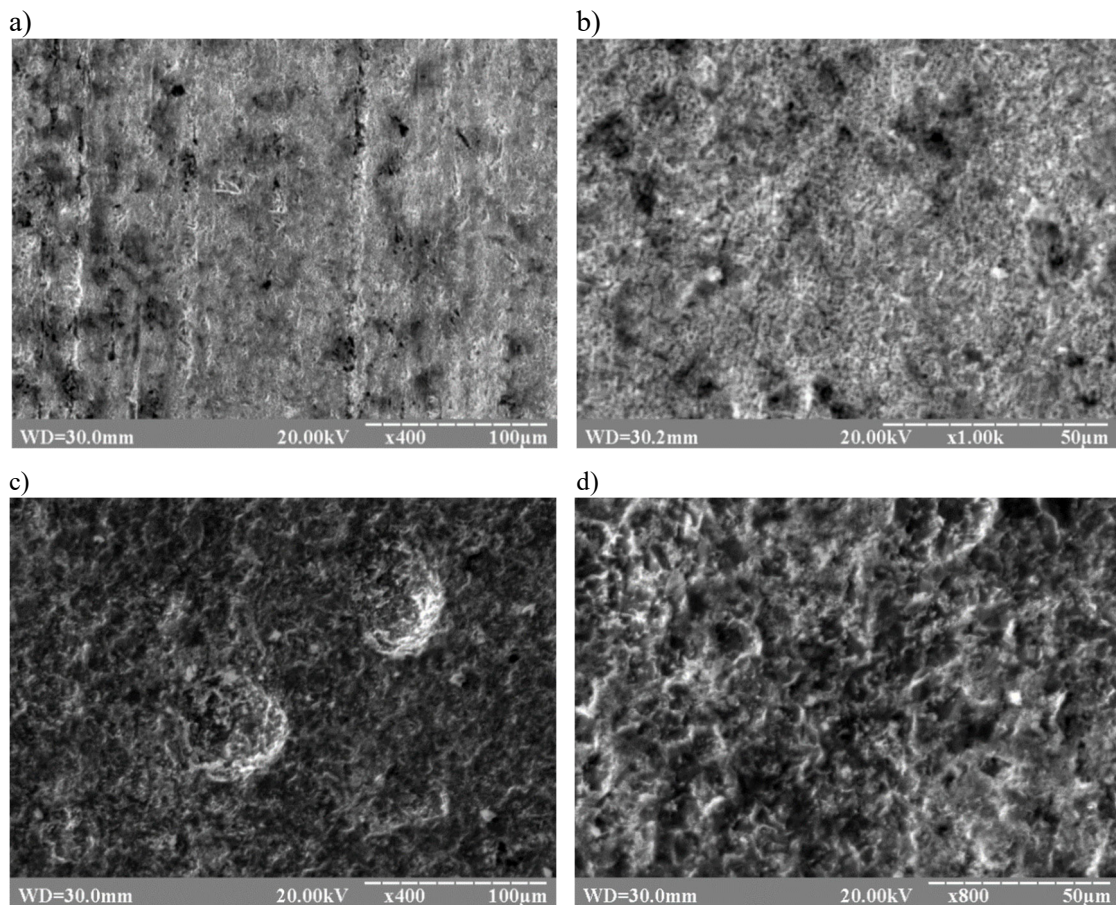

Fig. 3. Morphology of surface areas of specimens from steel 17G1S-U (a-d) and 20 (e-h) damaged under different test conditions: 1 – a,b; 1^1 – c,d

2^1. Corrosion damage was represented by rounded pits with "clear" edges, indicating a sufficiently large depth of defects. In general, the surface topography was well developed, and the areas damaged by corrosion alternated with the undamaged metal. Their boundaries were sufficiently smoothed, with no sharp gradients observed, Figures 4c,d.

3.3. Changes in pH

Changes in pH were studied during the exposure of steel specimens to various model media for 305 days. The dynamics of changes in the pH of the model media that occurred in the course of research are shown in Figures 5 and 6.

The research findings indicate that 104 days of exposure caused an increase in the pH of the test medium for steels of both grades studied. Similar patterns of an increase in pH indicate that the chemical composition of the steel has

practically no effect on this process. Subsequently, a slight monotonic increase in pH was observed, reaching a stationary level. In contrast to NS$_4$ medium, the borate buffer effect on changes in pH was more pronounced for both steels (Fig. 6). Within the first 90 days, an increase in pH by 5.92% was observed for steel 17G1S-U, while that for steel 20 was two times lower. Subsequently, the pH value remained practically unchanged for steel 17G1S-U (changes were observed within the error), and for steel 20 it slightly decreased.

Changes in pH during the experiment can be explained by the influence of the component composition of the model media. The composition of NS$_4$ medium contains salts, which shifts the pH to an alkaline region during hydrolysis, due to which metal corrosion occurs with oxygen depolarization. With an increase in the concentration of non-hydrolysed neutral salts (CaCl$_2$, KCl), the corrosion rate first increases and then decreases. An accelerated corrosion rate within a certain range of salt concentration may be associated with an increased electrical conductivity of the solution.
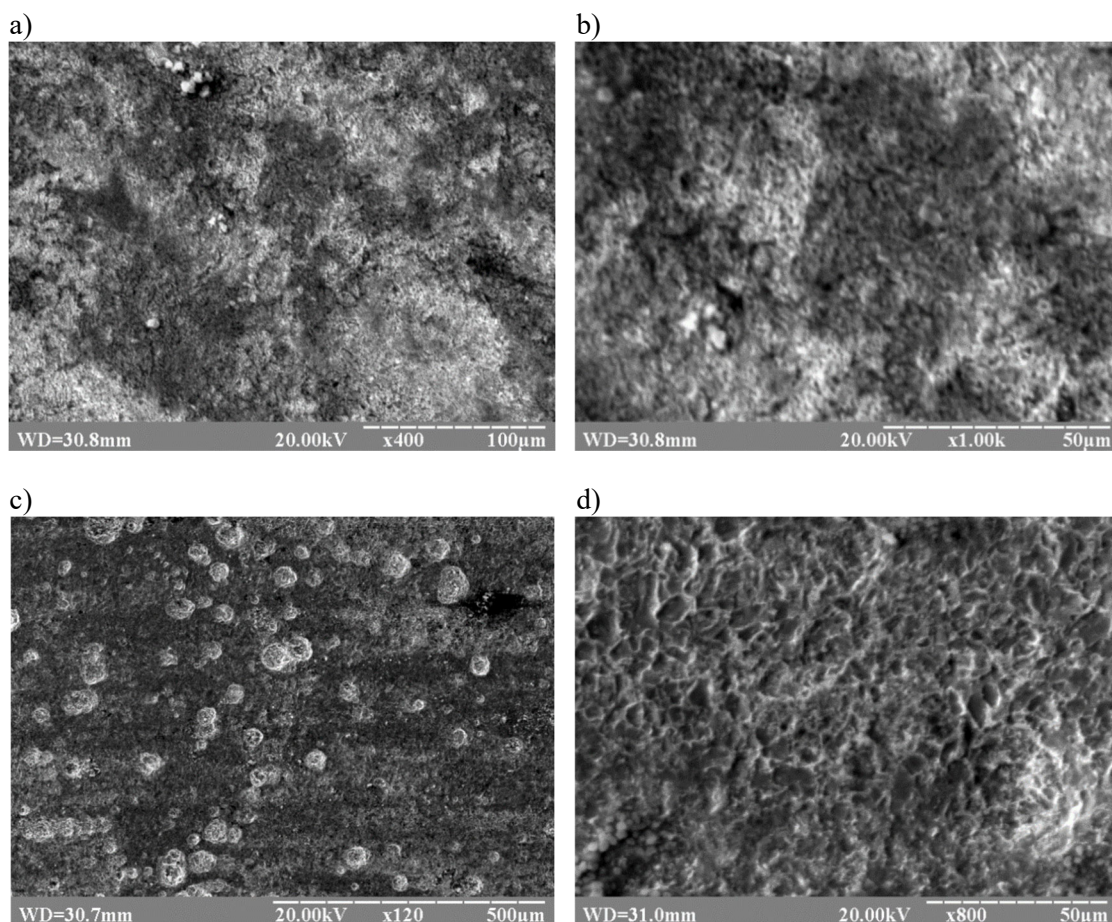

Fig. 4. Morphology of surface areas of specimens from steel 17G1S-U (a-d) and 20 (e-h) damaged under different test conditions: 2 – a,b; 2^1 – c,d
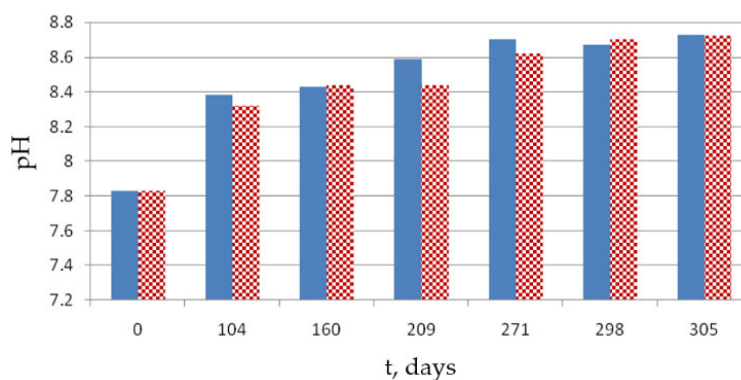
Fig. 5. Changes in pH of medium NS$_4$ during testing specimens from steels 20 (▨) and 17G1S-U (■)
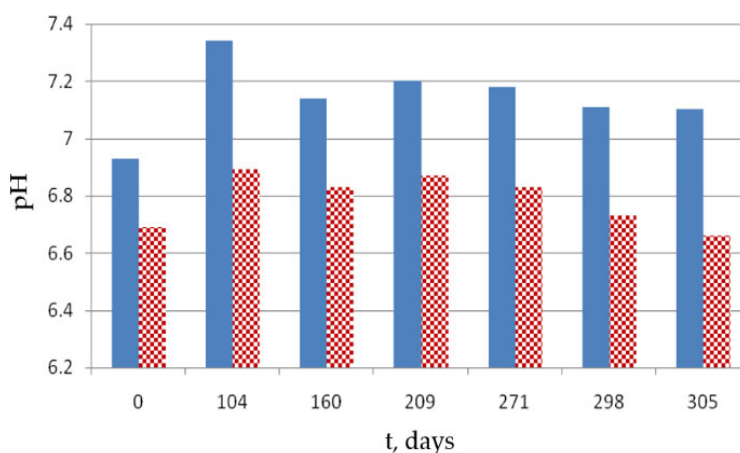

Fig. 6. Changes in pH of model media NS$_4$ + borate buffer (1: 1) and NS$_4$ + borate buffer (1: 3) during the experiment – steels 20 (▨) and 17G1S-U (■)

Table 2.
Regularities in corrosion of pipe steels 20 and 17G1S-U

Steel	Model media	K$_{gr}$, mg/dm^2 days
17G1S-U	NS$_4$	2.11
	NS$_4$ + borate buffer (1:1)	0.81
20	NS$_4$	1.93
	NS$_4$ + borate buffer (1:3)	0.25

With an increase in the concentration of Cl- ions, the anodic process is activated. When a borate buffer is added to NS$_4$ medium and the pH decreases to values close to neutral, the metal corrosion mechanism does not change, and further corrosion occurs with oxygen depolarization. It is noteworthy that a decreased concentration of salts and, accordingly, a decreased electrical conductivity of the solution also impede the anodic dissolution rate of the metal [16-18].

3.4. Corrosion rate

It should be emphasized that the loss of metal was different during the exposure of steel specimens to model media of different component composition, which indicates a different rate of corrosion processes (Tab. 2).

When analysing the research findings given in Table. 2, it should be noted that the corrosion processes kinetics is influenced by two factors: 1) the component composition of

the model media; 2) steel grade. The corrosion rate changes depending on the content of alloying additions in the steel. At the same time, the difference in the corrosion rates of the studied steel grades did not exceed 4.3% under comparable experimental conditions. The influence of the physico-chemical composition of the model media is much more pronounced. With an increase in the borate buffer content, the corrosion rate of steel 17G1S-U increases more than 3-fold (3.24) as compared to steel 20. These findings confirm that a decrease in the pH of the medium leads to an increase in the corrosion resistance of pipe steels. Thus, the protective effect for steel 17G1S in medium NS_4 + borate buffer (1: 1) was 61.5%. Steel 20 had the greatest protective effect in medium NS_4 + borate buffer (1: 3), which was 87.05%.

We have found that the corrosion rate is determined by internal (nature and properties of the metal) and external (aggressive medium properties and the corrosion process conditions) factors. In addition, one of the most important external factors is the concentration of hydrogen ions (medium acidity).

4. Conclusions

The corrosion rate of specimens from steels 20 and 17G1S-U in various model media, which simulate soil conditions of gas pipelines of Ukraine, was determined. The effect of borate buffers on the protective properties of the steel grades studied was revealed, and pH changes in the model media during corrosion were described.

The main regularities in corrosion, as well as the surface morphology of damaged specimens, were studied by scanning electron microscopy. The results obtained will be used when testing specimens from pipe steels under cyclic loading in the model media studied, as well as for predicting the residual life of gas pipelines with corrosion defects.

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