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## CORROSION DEGRADATION OF STEEL OF LONG-TERM OPERATED GAS PIPELINE ELBOW WITH LARGE-SCALE DELAMINATION

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The electrochemical corrosion behaviour of the low-carbon steel of the long-term operated gas pipeline elbow with extensive hydrogen-induced delamination was investigated in 0.3% (wt.) NaCl and 8.55 mM NaHCO<sub>3</sub> aqueous solutions. The degradation of the corrosion resistance of the pipe elbow steel in both investigated corrosive environments was revealed. The pipe elbow steel (both the compressed and the tensioned sections) was characterized by lower corrosion resistance than the metal of the straight pipe section. It was shown that the corrosion resistance degradation of the pipe elbow steel correlated with the degradation of its mechanical properties. It was established that the corrosion resistance characteristics of the degraded material (corrosion current density and polarization resistance) could be informative of its state changes caused by long-term operation and could be used for diagnostics of mechanical properties degradation of the hydrogen-affected steels.

**Keywords:** *pipeline steel, pipe elbow, degradation, macrodefect, electrochemical characteristics.* 

Today delaminations in pipeline steels, being caused by both manufacturing process and operational factors, are a well known problem. They are formed by relatively weaker texture planes which are aligned parallel to the rolling direction. Their formation is influenced by the presence of carbide and inclusions particles, seams, inclusion alignment in the rolling plane, intergranular fracture, texture, banding, segregation bands, and anisotropic plastic deformation [1, 2]. In oil and gas pipelines absorbed hydrogen, being generated by internal or external corrosion, can penetrate into the steel [3, 4]. Accumulation of hydrogen at imperfections, due to recombination of atomic hydrogen to the molecular state, generates tremendous pressure and leads to macrodefect formation, e.g. delamination, hydrogen cracks or blisters [5, 6]. Such macrodefects can eventually cause the pipeline failures [7].

There is a wide range of available sources of hydrogen in both manufacturing and service environments. The specific long-term service of oil and gas pipelines promotes the pipeline steel hydrogenation as a result of hydrogen evolution on metal surface under corrosion processes in the external and/or internal environmental conditions [4, 8, 9]. So, the risk of hydrogen-caused macrodelamination in corrosive environments with high hydrogenating ability, especially in the presence of hydrogen sulphide, is very high. It should also be noted that no external stress is usually required to induce this damage. Such macrodefects in oil and gas pipelines are often revealed as a pipe wall thinning by using ultrasonic testing [10].

Recently an extensive delamination in the pipe elbow body revealed in the long-term operated lateral pipeline of the gas transmission pipelines system was investigated, and

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degradation of the metal close to the macrodefect was revealed [11]. A strong decrease in plasticity of the pipe elbow steel was observed. The electrochemical approach to diagnostics of mechanical properties degradation of structural materials by non-destructive methods has been recently proposed [12–14], based on the correlation between electrochemical and mechanical properties changes of the material due to its long-term service. Thus, the focus of this study is to investigate electrochemical corrosion behaviour of steel of the long-term operated gas pipeline elbow with a macrodefect to obtain information on its state changes.

**Objects, materials and methods.** The object of the present study was a pipe elbow made of low carbon 0.20 C pipeline steel. The pipe elbow, being a part of above-ground lateral pipeline of the gas transmission pipelines system and located behind the compressor station, was operated for 40 years. It was removed from the lateral pipeline after non-destructive testing by ultrasound thickness meter revealing a macrodefect in the pipe body [11]. The dimensions of the pipe elbow were the following: outer diameter D = 219 mm and wall thickness t = 18 mm. The 90° elbow was made by cold bending without any further heat treatment. The maximum working pressure was 5.5 MPa and the working temperature of the pipe elbow steel was up to 80°C.

The specimens (working electrodes) of three different sections of the pipe elbow were studied, including tensioned and compressed sections of the pipe elbow and a straight pipe section. The working electrodes were made in the form of bars  $1.5 \times 1$  cm and a length of 2.5 cm, with all surfaces polished. Before testing all surfaces of the working electrodes were coated by a special waterproof dielectric isolation, except of the small area  $\sim 0.35$  cm<sup>2</sup> for electrochemical studies. The electrochemical behaviour of the specimens was analysed on the basis of the electrochemical tests performed by potentiodynamic method using potentiostat IPC-Pro controlled with a computer. The electrolytes were 0.3% (wt.) NaCl and 8.55 mM NaHCO<sub>3</sub> aqueous solutions used without any pre-treatment. All electrochemical tests were carried out using a standard temperature-controlled electrochemical cell with a typical three-electrode system consisting of the working electrode, Ag/AgCl (saturated KCl) reference electrode and Pt auxiliary electrode. Tests were conducted at room temperature. Potentiodynamic polarization curves were performed by sweeping the potential at a sweep rate of  $1.0 \text{ mV} \cdot \text{s}^{-1}$ . The basic electrochemical characteristics of steels (corrosion potential  $E_{corr}$ , corrosion current density  $i_{corr}$ , Tafel constants of anodic and cathode reactions  $b_a$ ,  $b_c$ ) were determined by the graph-analytic method. Polarization resistance  $R_p$  was calculated using the Stern-Geary equation:

$$\frac{\Delta E}{\Delta i} = R_p = \frac{K}{i_{\text{corr}}}$$
, where the constant  $K = \frac{b_a \cdot b_c}{2.3 \cdot (b_a + b_c)}$ 

The characteristics of the tensioned and compressed sections of the pipe elbow were compared between themselves and with properties of the straight pipe material.

Test results and discussion. The polarization curves obtained for the low-carbon steel of the straight pipe section of the elbow as well as of its tensioned and compressed sections in 0.3% (wt.) NaCl and 8.55 mM NaHCO<sub>3</sub> aqueous solutions are shown in the Figure. The corrosion potential ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ) values calculated using the Tafel extrapolation method are given in the Table.

There is no passive region observed in the potentiodynamic polarization curves (see the Figure) for any of the investigated materials in any of the studied media, only active dissolution is observed. At studied potentials, cathodic and anodic polarization curves for the straight pipe metal and the deformed steel of the pipe elbow (of the compressed and tensioned sections) were nearly identical, with slight increases in current densities for the deformed steel. Diffusion of depolariser (oxygen) was a limiting stage of the corrosion process, as it was indicated by the region of the diffusion limiting current on the cathodic polarization curves shown in the Figure.



Potentiodynamic polarization curves of the low-carbon 0.20 C steel of different sections of the pipe elbow in 0.3% (wt.) NaCl (*a*) and 8.55 mM NaHCO<sub>3</sub> (*b*) aqueous solutions: I – straight pipe section; 2 – compressed; 3 – tensioned sections of the pipe elbow, respectively.

For all studied materials the values of Tafel constant of anodic reactions  $b_a$  were about 0.046 and 0.057 V in 0.3% (wt.) NaCl and 8.55 mM NaHCO<sub>3</sub> solutions, respectively.

Analysing the results obtained by electrochemical testing of the pipe elbow steel from different sections (see the Table) it can be seen that the steel of the tensioned section was characterized by slightly lower corrosion resistance than the steel of the compressed section. Thus, corrosion current densities of the materials, obtained from different sections of the pipe elbow, which were loaded in compression or in tension during long-term service, slightly differed.

Section of the pipe elbow	$E_{\rm corr},{ m V}$	$i_{\rm corr},\mu{\rm A/cm}^2$	$R_p$ , k $\Omega \cdot \mathrm{cm}^2$
0.3% (wt.) NaCl solution			
Straight	-0.658	3.37	4.14
Compressed	-0.663	3.81	3.66
Tensioned	-0.667	3.96	3.53
8.55 mM NaHCO <sub>3</sub> solution			
Straight	-0.686	2.84	5.56
Compressed	-0.690	3.36	4.70
Tensioned	-0.695	3.48	4.54

Electrochemical characteristics of the low-carbon 0.20 C steel of different sections of the pipe elbow in different corrosive environments

The lower corrosion resistance of the pipe elbow steel (both the compressed and the tensioned sections) in comparison with the metal of the straight pipe section was revealed in both investigated corrosive environments. Thus, the values of polarization resistance of the straight pipe steel were the highest: 4.14 and 5.56 k $\Omega$ ·cm<sup>2</sup> in 0.3% (wt.) NaCl and 8.55 mM NaHCO<sub>3</sub> solutions, respectively (see the Table). The steel of the straight pipe was characterized by the most positive value of corrosion potential  $E_{corr}$ , and the pipeline steel of the tensioned section of the elbow – by the most negative value among the studied steels in corrosive environments. The obtained results showed the degradation of corrosion resistance of the pipe elbow steel.

Comparison of the results obtained by electrochemical and mechanical (see [11]) tests of the steel of the three studied sections of the pipe elbow (the compressed, the tensioned and the straight pipe elbow sections) showed good correlation between its electrochemical (corrosion current density and polarization resistance) and mechanical (reduction in area) properties. Thus, the intensive degradation of the steel of the pipe elbow with a macrodefect was revealed by mechanical testing [11]. At the same time the degradation of the pipe elbow steel was higher than that of the straight pipe steel regardless of the tensioned or compressed section. However, the steel of the tensioned section of the pipe elbow was characterized by the most intensive damage. Nevertheless, the steel of the tensioned section of the pipe elbow was characterized by the lowest plasticity (reduction in area  $\psi_R = 30.0$ ) and the steel of the straight pipe section - by the highest one ( $\psi_R = 38.7$ ). With reference to the obtained results it was established that the degradation of the pipe elbow steel caused by its long-term service resulted in the weakening of cohesion of the lengthened non-metallic inclusions with the matrix, being facilitated by the influence of hydrogen. Moreover, high temperature (up to 80°C) of the steel of the pipe elbow caused by its locating behind the compressor station intensified hydrogen diffusion through the steel and, in turn, contributed to the degradation of the metal. It can be assumed that in-service degradation of the pipe elbow steel is accompanied by intense internal damage caused by mutual action of the working stress and hydrogen. Therefore, it can be concluded that the electrochemical properties of the pipe elbow steel, such as corrosion current density icorr and polarization resistance  $R_p$ , being sensitive to changes in the state of degraded steel and correlated with its mechanical properties, could be informative of changes caused by the longterm operation.

## CONCLUSIONS

The results presented here, describing the electrochemical corrosion behaviour of the low-carbon 0.20 C steel of three different sections (the compressed, the tensioned and the straight sections) cut from the pipe elbow of above-ground lateral pipeline of the gas transmission pipelines system tested in 0.3% (wt.) NaCl and 8.55 mM NaHCO<sub>3</sub> aqueous solutions, revealed the degradation of corrosion resistance of the pipe elbow steel:

- the corrosion resistance of the steel of the tensioned section was slightly lower than corrosion resistance of the steel of the compressed section;

- the corrosion resistance of the pipe elbow steel (both the compressed and the tensioned sections) was lower than of the straight pipe section metal.

The degradation of corrosion resistance of the pipe elbow steel correlated with the degradation of its mechanical properties. Thus, the corrosion resistance characteristics of the degraded material, such as corrosion current density and polarization resistance, could be informative of its state changes caused by the long-term operation.

*РЕЗЮМЕ*. Досліджено корозійно-електрохімічну поведінку у водних розчинах 0,3% NaCl та 8,55 mM NaHCO<sub>3</sub> маловуглецевої сталі тривало експлуатованого гину газопроводу з общирним воднем ініційованим розшаруванням. Виявлено деградацію корозійної тривкості сталі гину труби в обох досліджених корозивних середовищах. Сталь гину труби (як стиснутої, так і розтягнутої ділянок) характеризувалась нижчим опором корозії, ніж метал прямої ділянки труби. Показано, що деградація корозійної тривкості сталі гину труби корелює з деградацією її механічних властивостей. Встановлено, що характеристики корозійної тривкості деградованого матеріалу (густина струму корозії та поляризаційний опір) можуть бути інформативними параметрами змін його стану, спричинених тривалою експлуатацію, і їх можна використовувати для діагностування деградації механічних властивостей сталей, пошкоджених воднем.

*РЕЗЮМЕ*. Исследовано коррозионно-электрохимическое поведение в водных растворах 0,3% NaCl и 8,55 mM NaHCO<sub>3</sub> малоуглеродистой стали длительно эксплуатируемого колена газопровода с обширным водородом инициированным расслоением. Выявлено деградацию коррозионной стойкости стали колена трубы в обеих исследованных коррозионных средах. Сталь колена трубы (как сжатого, так и растянутого участков) характеризовалась более низким сопротивлением коррозии, чем металл прямого участка трубы. Показано, что деградация коррозионной стойкости стали колена трубы коррелирует с деградацией ее механических свойств. Установлено, что характеристики коррозионной стойкости деградированного материала (плотность тока коррозии и поляризационное сопротивление) могут быть информативными параметрами изменений его состояния, вызванных длительной эксплуатацией, и их можно использовать для диагностики деградации механических свойств сталей, поврежденных водородом.

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- Role of delamination and crystallography on anisotropy of Charpy toughness in API-X80 steel / M. S. Joo, D.-W. Suh, J. H. Bae, and H. K. D. H. Bhadeshia // Mater. Sci. Eng. A. - 2012. - 546. - P. 314-322.
- Mohtadi-Bonab M. A., Szpunar J. A., and Razavi-Tousi S. S. A comparative study of hydrogen induced cracking behavior in API 5L X60 and X70 pipeline steels // Engineering Failure Analysis. – 2013. – 33. – P. 163–175.
- Carneiro R. A., Ratnapuli R. C., and Lins V. F. C. The influence of chemical composition and microstructure of API linepipe steels on hydrogen induced cracking and sulfide stress corrosion cracking // Mater. Sci. Eng. A. – 2003. – 357. – P. 104–110.
- Influence of operation of Kh52 steel on corrosion processes in a model solution of gas condensate / O. T. Tsyrulnyk, Z. V. Slobodyan, O. I. Zvirko, M. I. Hredil, H. N. Nykyforchyn, and D. Gabetta // Materials Science. – 2008. – 44, № 5. – P. 619–629.
- Zapffe C. and Sims C. Hydrogen embrittlement, internal stress and defects in steel // TMS-AIME. – 1941. – 145. – P. 225–232.
- Herbsleb G., Poepperling R. K., and Schwenk W. Occurrence and Prevention of Hydrogen Induced Stepwise Cracking and Stress Corrosion Cracking of Low Alloy Pipeline Steels // Corrosion. – 1981. – 36, № 5. – P. 247–256.
- 7. *Polyakov V.N.* Catastrophes of large diameter pipelines: the role of hydrogen fields // Hydrogen Effects in Materials. Moran, Wyoming, USA, 1996. P. 991–1000.
- 8. *Hydrogen* degradation of steels in gas mains after long periods of operation / O. T. Tsyrul'nyk, H. M. Nykyforchyn, D. Yu. Petryna, M. I. Hredil, and I. M. Dzioba // Materials Science. 2007. **43**, № 5. P. 708–717.
- Nykyforchyn H. M. and Tsyrul'nyk O. T. Specific features of the in-service bulk degradation of structural steels under the action of corrosive media // Strength of Materials. – 2009. – 41, № 6. – P. 651–663.
- Mostert R. and Sharp W. Low temperature hydrogen damage assessment in the gas and refining industries // Proc. of the Middle East Nondestruct. Test. Conf. & Exhib. – Bahrain, Manama. – 2005. – 9 p.
- Diagnostics of hydrogen macrodelamination in the wall of a bent pipe in the system of gas mains / L. Ye. Kharchenko, O. Ye. Kunta, O. I. Zvirko, R. S. Savula, and Z. A. Duryahina // Materials Science. – 2016. – 51, № 4. – P. 530–537.
- Nykyforchyn H. M. and Tsyrul'nyk O. T. In-service degradation diagnostics of low-alloyed steels and aluminium alloys properties by electrochemical methods // Ultrasound. – 2009. – 64, № 1. – P. 46–49.
- Correlation between degradation of corrosion and mechanical properties of long-term operated oil and gas pipeline steels / H. Nykyforchyn, O. Tsyrulnyk, M. Hredil, and O. Zvirko // Zeszyty Naukowe. – Mechanika. Politechnika Opolska, 2011. – Z. 99. – S. 41–43.
- Kharchenko E. V., Polishchuk L. K., and Zvirko O. I. Estimation of the in-service degradation of steel shapes for the boom of a clamp-forming machine // Materials Science. 2014. 49, № 4. P. 501–507.