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Management Systems in Production Engineering

2020, Volume 28, Issue 3, pp. 141-147

Date of submission of the article to the Editor: 01/2020
Date of acceptance of the article by the Editor: 06/2020

DOI 10.2478/mspe-2020-0021

INFLUENCE OF HYDRATE FORMATION AND CONCENTRATION OF SALTS ON THE CORROSION OF STEEL 20 PIPELINES

Lubomyr POBEREZHNY, Ihor CHUDYK, Andrii HRYTSANCHUK, Oleg MANDRYK, Tetyana KALYN, Halyna HRYTSULIAK, Yaroslav YAKYMECHKO
Ivano-Frankivsk National Technical University of Oil and Gas

Abstract:
One of the ways to increase natural gas production is to conserve and/or intensify existing wells with their subsequent development. They are characterized by a high content of highly mineralized water, which leads to an increased risk of hydrate formation and internal corrosion. The issue of the formation of gas hydrates in industrial pipelines, which is a major problem for the exploitation of industrial gas pipelines, requires considerable attention to be made to exclude emergency situations. The main task of the study – to determine the effect of hydrates on the corrosion of the pipeline in order to prevent emergencies. A technique for studying the effect of hydration on the corrosion of pipelines has been developed. The combined analysis of the corrosion behavior of pipe material in aggressive media of chloride type was done. According to the results of corrosion-mechanical tests, regularities of joint action of mechanical stresses, concentration of chlorides and hydrate formation on the speed and localization of corrosion processes are established.

Key words: *chloride media, formation water, internal hydrate corrosion, hydrate formation*

INTRODUCTION

Concurrent with the development of the oil and gas industry, environmental issues also have to be addressed. Since soil, water, and air are the direct factors of the technological process, undergo an adverse transformation, only reducing or eliminating the negative effects guarantees environmental and economic security. Blocking gas hydrates of industrial gas pipelines in autumn and winter is always accompanied by favorable thermodynamic environmental conditions, high pressure, and low transport temperature [5, 7, 8, 14].

Hydrates can initiate certain types of internal corrosion of gas pipelines. This problem is many-sided because of the physical and chemical processes that depend on the size of the hydrate formed, the stage and period of its contact with the pipeline, resulting in the destruction of protective films on the surface. Acid gases, in particular H_2S, CO_2, which are components in the formation of gas hydrates, as well as Cl – ions, when interacting with water, contribute to accelerating the internal corrosion of gas pipelines. At each stage of the hydrate formation process, there is a chemical interaction between the hydrate components and the pipeline metal, which initiates the onset of internal corrosion, which will subsequently lead to a gradual degradation of the material and deterioration of the pipe integrity. The gas pipeline will start to leak and this can cause a full-blown gap. This prospect can cause economic, environmental and political consequences, and will lead to the replacement of pipes along the entire length of the pipeline and additional production costs [5, 8]. Therefore, the urgent task is to analyze the causes of emergencies as a result of the formation of gas hydrates, in particular pipe corrosion, and to establish patterns of influence of gas hydrates on the physical and mechanical characteristics of the pipeline material. This will allow for the development of science-based engineering solutions to overcome the problems of the gas industry associated with gas hydrate formations.

LITERATURE REVIEW

One of the poorly studied is the corrosion of gas hydrates. Formed hydrates can clog pipelines, underwater transportation lines, and in the case of gas ejection during drilling, hydrates can be formed in the wellhead in the blowout preventer and on the fitting line. This will cause partial or complete blockage of the inside of the gas pipeline, and if not removed quickly, it will lead to an increase in pressure inside the pipe and a possible accident. This may result in various economic and environmental problems and serious risks to the safety of personnel and equipment. development of corrosion [5, 9, 15].

At different stages of formation, the liquid is transformed from a liquid state into a semi-solid hydrate, finally into a solid hydrate [16, 25]. During each of these steps, constant and continuous interaction between the hydrate phase and the pipe wall can cause cavitation, erosion,

spot corrosion, corrosion cracking [11, 12, 15]. In the first stage of formation of the gas hydrate is a semi-solid state, the hydration plugs have a liquid inside the cavities. They are easily destroyed by impact on a hard surface, that is, the pipe wall, thus causing cavitation corrosion [5, 17]. Over time, the hydrates gradually transition from semi-solid to solid. When moving at high speed, these lumps bombard the inner surface of the pipe wall, causing erosion. In the same way, the lumps of hydrate accumulate over time and form larger pipes, which in turn requires more gas transportation along the pipe wall surface [9, 23]. This movement induces relative movement between the pipe wall and the hydration plug and activates the development of large-scale erosion corrosion [5, 6, 14].

Studies [15, 17] have shown an increase in the level of localization of corrosion processes, but no explanation for this phenomenon has been provided. In general, most of the results reported in the literature describe hydrate formation during offshore gas [4, 23, 25] and gas transportation by offshore or onshore pipelines [9, 16, 20].

Mathematical models of corrosion effects of gas hydrates [1, 2, 3, 6, 21, 22, 24] do not take into account the effect on the metal or passive films of the hydrate itself, but only the pH of the medium or the concentration of CO_2 in the gas. Also, the effect of mechanical stresses and hydrate formation on internal corrosion has not been sufficiently studied. Therefore, the purpose of this study is to investigate the combined effect of salt concentration in reservoir waters, the level of mechanical stresses, and hydration formation on the corrosion of flow lines.

METHODOLOGY OF RESEARCH

The object of study was selected pipelines made of low carbon steel St20 (Table 1).

Table 1

Chemical composition of St20 steel, %

C	Si	Mn	P	S	Cr	Cu	Ni	As
0.17-0.24	0.17-0.37	0.35-0.65	<0.04	<0.04	<0.25	<0.25	<0.25	<0.08

The operation of the installation for the synthesis of gas hydrates on the surface of samples of models of pipeline material [11, 19] (Fig. 1).

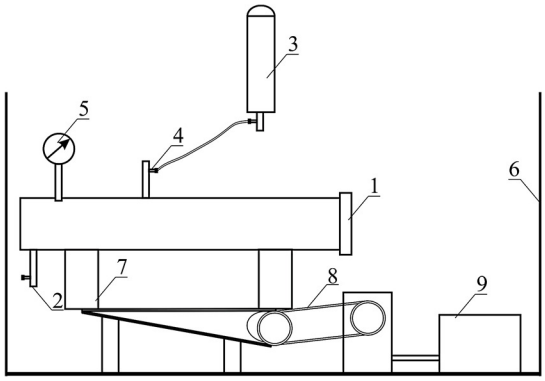


Fig. 1 General scheme of the installation for synthesis of gas hydrates: 1 - research reactor, 2 - discharge pipe, 3 - gas cylinder, 4 - inlet pipe, 5 - manometer, 6 - refrigerator, 7 - support, 8 - belt transmission, 9 - electric motor

According to the developed method:

- In the first stage, a detailed analysis of the interaction of the system "material – construction – loads and impacts" is carried out;
- On the second – model samples are made from the material of certain sections of the pipeline or separately taken pipes, in order to effectively use the theory of structural similarity;
- On the third – the schemes of loading and test modes are selected with the purpose of achievement on the samples-models, with the pre-determined configuration, imitation of work of the investigated material in the design;
- The fourth stage is the synthesis of gas hydrates (Fig. 1).

There are several schemes of formation of gas hydrates:

I. Scheme without mechanical vibrations of the reactor:

The sample is fixed in the holes of the rings made of plexiglas, the location of the samples is shown in Fig. 2.

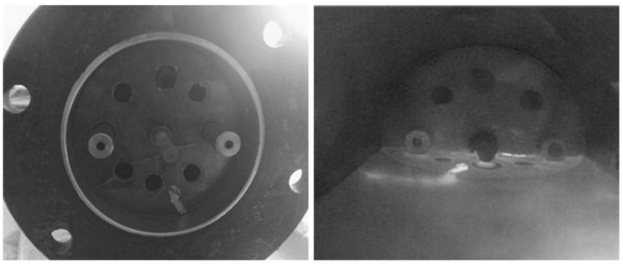


Fig. 2 Location of model samples

II. Scheme with the action of mechanical vibrations of the reactor:

This scheme is similar to scheme 1 only after the formation of hydrate on the sample surface (Fig. 3) additionally included a generator of mechanical vibrations of the reactor.

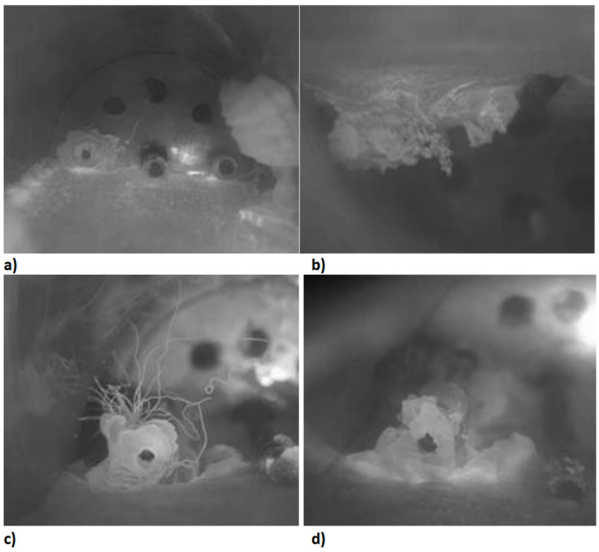


Fig. 3 Artificial gas hydrate on the surface of the sample model in the gas part (a, c, d) and in the liquid (b)

This method of testing allows a better assessment of the impact of hydrate in the presence of a large number of bottom water in conditions of significant turbulence gas-flow.

For this scheme envisages the establishment of the samples in random order in the frame, because after the lumps of hydrate and the inclusion of a generator of mechanical vibrations, the action to all samples model will be across the plane of the frame.

The process of laying the samples in the rector for the synthesis of gas hydrates is carried out in the following sequence:

- disconnect end of reactor 1, which provides access to the middle of the reactor;
- close the drain valve 2;
- in the reactor through its side face with the flanges, filled with fresh water in a volume of 1 l;
- lowered into the reactor the studied samples are mounted on a frame that prevents their twisting during the research;
- closing the end of the reactor a metal ring with a hole, between which is placed the Plexiglas thickness of 3 cm to observe the formation of crystals of gas hydrate;
- using the gas compressor 3 is injected through the valve 4 gas – methane, before the establishment of the system pressure level 45 ATM, as indicated by the pressure gauge 5;
- refrigeration unit 6 is the temperature of 2.5 °C;
- the reactor is mounted on supports 7 in the middle of the cooling unit;
- for schema 2, you must enable the motor 9, which through a belt drive 8 will cause the reactor to oscillatory movement;
- samples of pipeline material maintained in the reactor for a certain exposure time.
- A few selected schemes sample installation models in the reactor relative to the liquid level (Fig. 4).

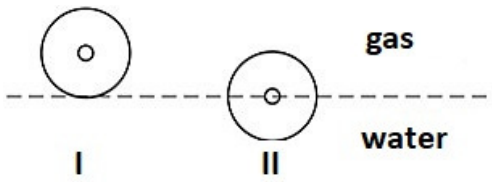


Fig. 4 Sampling schemes: sample above water level (I), middle of sample at gas-water phase separation (II)

The gravimetric method was used to estimate the corrosion rate. It is used in two variants: to determine the increase in the mass of the sample as a result of the formation of corrosion roducts on its surface and to determine the loss of mass after removal of corrosion products. The second option is more common due to its versatility.

According to the results of chemical analysis of reservoir waters, model media for corrosion tests were selected (Table 2).

Table 2

Chemical composition of solutions for corrosion testing

№ model environment	The concentration of NaCl, mol/l	Type of corrosion
1	0.01	Low salt concentration (soil corrosion)
2	0.05	
3	0.1	
4	0.5	High salt concentration (internal corrosion)
5	1.5	
6	2.5	
7	3.75	
8	5	

The corrosion rate is determined by the formula:

$$V_{\text{BM}} = \frac{n \cdot (m_1 - m_0)}{S \cdot t} \quad (1)$$

where:

m_0 – is the initial mass of the sample, g;

m_1 – is the mass of the sample with corrosion products, g;

S – sample area, m^2;

t – is the time of the experiment, hours;

n – is the coefficient that depends on the composition of the corrosion products.

RESULTS

According to the results of the study of the corroded surfaces of the samples maintained in the gas hydrate, the mechanism of its influence on the corrosion of the pipeline material is established. By itself, the hydrate of corrosion does not cause, but only intensifies and localizes the influence of corrosive components of formation waters (Fig. 5).

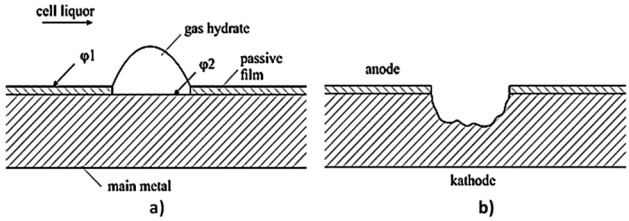


Fig. 5 Combined effect of gas hydrate and formation water on pipeline metal in the first (a) and second (b) stages

In the first stage (the formation stage of the hydrate), the metal surface around it continues to be covered by passive films of corrosion products, while on the metal surface under the hydrate such process stops [12].

In addition, as a result of the formation of hydrate crystals due to the moisture absorbed by the corrosion products, the passive film is partially destroyed, since the volume of the formed crystals is 2-3 times greater than the volume of water. After dissociation of the hydrate (stage 2), a potential difference is formed between the described sections of the metal, which causes the formation of corrosive micro-galvanic elements that accelerate the dissolution of the metal in the less passive zone (Fig. 5b).

In the future, in the case of thermobaric conditions favorable for hydration, it will take place most actively in the area of the formed corrosion lesion, since the latter plays the role of the center of crystallization. With each cycle of gas hydrate formation/decay, the depth of the corrosion defect increases. Thus, the mechanism of the joint influence of corrosive medium and gas hydrates is to intensify and localize corrosion processes. As the mechanism of corrosion in chloride, media is common for both inner pipe and soil corrosion, the previously obtained data for soil corrosion were used in addition to the results obtained in the work for soil corrosion, in addition to the results obtained in the work [10, 13, 18].

Studies of corrosion in model environments (ME) corresponding to soils with chloride-type salinization (Table 1) showed (Fig. 6) a significant increase in the rate of general corrosion with increasing concentrations of chloride ions during the transition from 0.01 M NaCl to 0.05 M NaCl, and slightly less during the transition from 0.05 M NaCl to 0.1 M NaCl. A similar pattern of influence can be traced to both steels under study. Having analyzed together Fig. 6-8, and comparing the rates of general and local corrosion, we can see a sharp intensification of local corrosion processes, and it increases with increasing concentration of chloride ions.

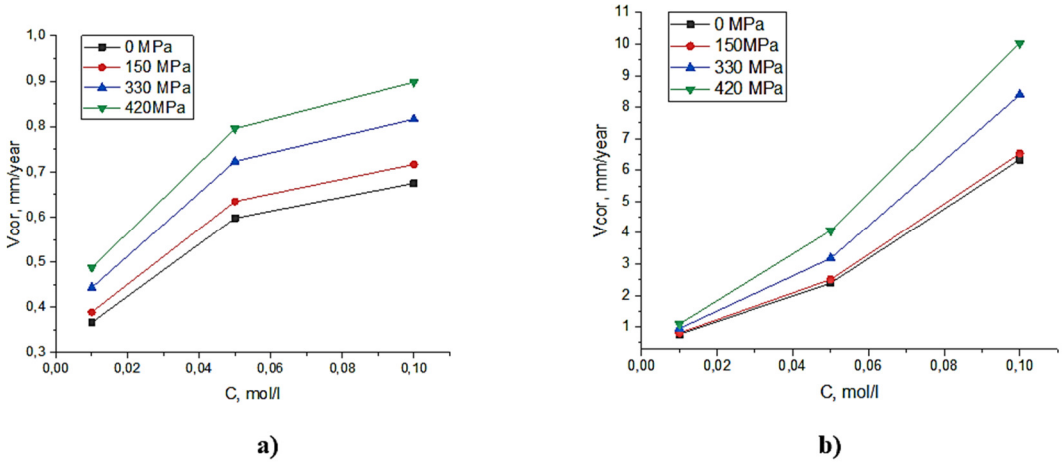


Fig. 6 Dependence of pipe wall thinning rate in chloride electrolytes: a – general corrosion b – local corrosion

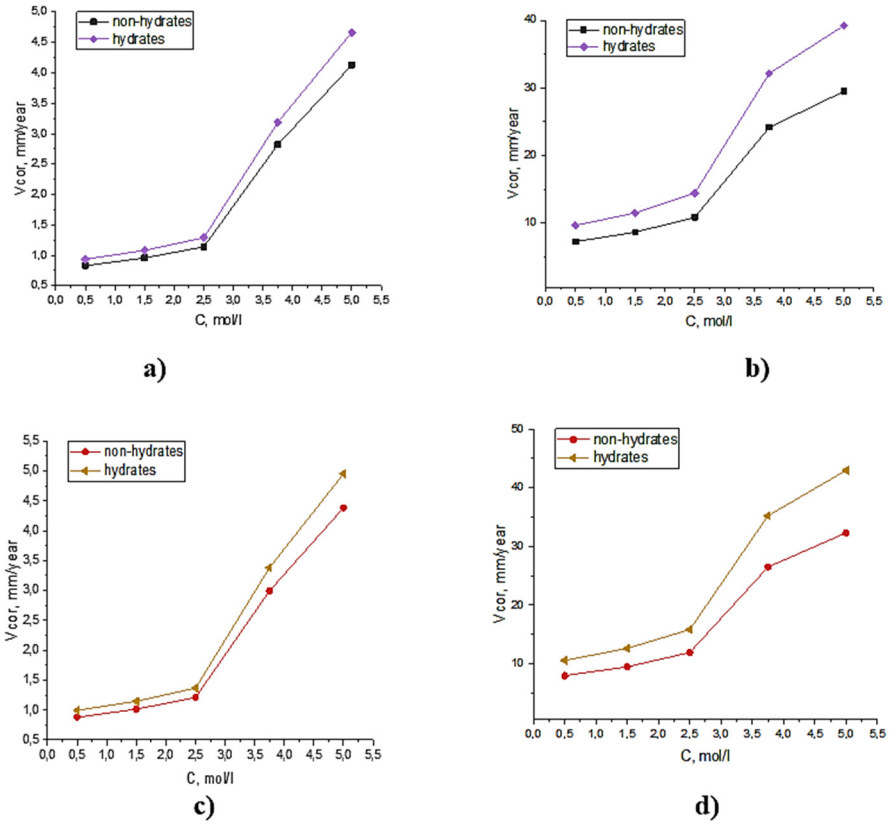


Fig. 7 Ifluenvce of chloride concentration on pipe wall thinning for mechanical stress level below yield limit 0 MPa general corrosion (a) local corrosion (b) 150MPa general corrosion (c) local corrosion (d)

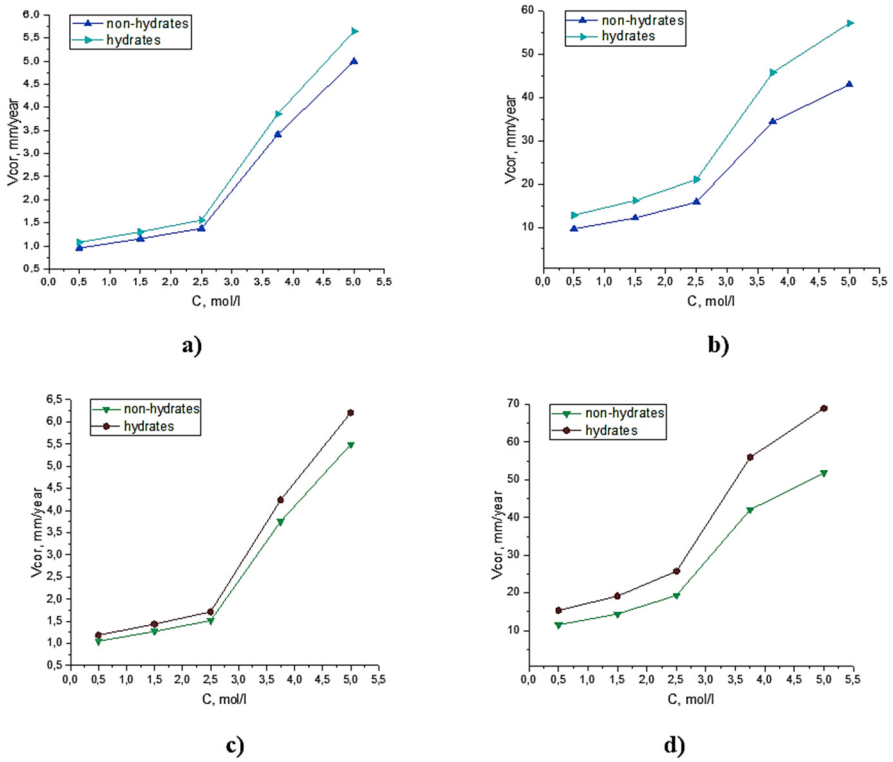


Fig. 8 Ifluenvce of chloride concentration on pipe wall thinning for mechanical stress level above yield limit 330 MPa general corrosion (a) local corrosion (b); 420 MPa general corrosion (c) local corrosion (d)

As the chloride ion concentration increases, the effect of the mechanical factor also increases significantly both in the case of general corrosion degradation and for local corrosion. There is a sharp increase in the corrosion rate during the transition from 2.5 M NaCl to 3.75 M NaCl for the iner pipe corrosion in highly mineralized reservoir waters (Fig. 7, 8).

Such corrosion behavior, in our opinion, is caused by rapid destruction of the passive film of chloride ions when a certain critical concentration.

The observed increase in corrosion rate for the samples aged in the gas hydrate in comparison with the control (Fig 6, 7), from the obtained results we calculated the coefficient of influence of gas hydrate to corrosion, for which general corrosion is of 1.13 and for the local corrosion is 1.32.

DISCUSSION

The combined analysis of the corrosion behavior of the material of the pipes in aggressive environments chloride type shows similar patterns of joint effects of environment and mechanical factors on the rate of corrosion processes. Active growth velocities of general and local corrosion (Fig. 6-8), although in the case of 0.01 M NaCl the growth of the local corrosion rate is negligible, due to the relatively small localized corrosion processes.

For the correct assessment of operational risk, resource and residual resource of safe operation is extremely important to know the speed of the wall thinning of the pipeline during the operation process for the timely prevention of possible emergency situations (Fig. 6, 7, 8). Observed similar to the corresponding dependences in the mass loss patterns.

I can say that for the case of low salt concentration (soil corrosion), provided the insulation be damaged and the lack or improper quality of active corrosion protection, the annual rate thinning in the area of operational loads can reach up to 0.45-0.55 mm/year (Fig. 6a), and with the localization process in the case of 0.1 M NaCl to exceed 6 mm/year (Fig. 6b), which indicates a significant risk of depressurization of pipelines, especially those that have operated more than 15...25 years outdated and short-lived anti-corrosive bitumen coating.

It is particularly important to analyze groundwater along pipeline routes to assess in a timely manner the risks of corrosion degradation of the pipeline steel, to prevent and prevent depressurization or more severe failures and emergencies [10, 18].

The increased risks of emergency situations caused by corrosion-mechanical processes will be primarily for the discharge lines and other industrial pipelines operated without active anti-corrosion protection.

Depending on the stress level and the corresponding model environment, the increase in the general corrosion rate due to the action of the gas hydrate St20 from 0.11 to 0.72 mm/year (Fig. 7a, Fig. 8a).

In the case of corrosion in reservoir waters, the jump in corrosion rates during the transition from 2.5 M NaCl to 3.75 M NaCl and 5 M NaCl is even more evident. Such a dramatic change in indicators suggests a change in patterns of development of corrosion processes.

For corrosion, taking into account the localization, depending on the stress level and for the corresponding model environment, the increase due to the action of gas hydrate for steel 20 from 7.3 to 17.1 mm/year (Fig. 7b, Fig. 8b).

CONCLUSIONS

The technique of physical modeling of pipeline operation under conditions of joint long-term action of aggressive media with imitation of sharp acyclic overloads was developed, which first modeled hydration formation during operational modes. It has been established that the main corrosive component of the formation waters of the investigated fields are chlorides. 8 model media were selected for corrosion testing of industrial pipeline material. According to the experimental results, the regularities of the influence of the concentration of the corrosive components of the formation water on the corrosion rate of the pipe steel St20 were established. It is established that at a concentration of 2.5 mol/l the nature of the dependence changes from power to linear. The laws of joint influence of mechanical stresses, chloride concentration and hydration formation on the speed and localization of corrosion processes have been established. According to the results of the studies, the coefficient of influence of gas hydrates K_{hydr} was calculated. K_{hydr} = 1.13 for general corrosion and 1.32 for local corrosion.

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Lubomyr Poberezhny
ORCID ID: 0000-0001-6197-1060,
Ivano-Frankivsk National Technical University
of Oil and Gas
Institute of Tourism and Geosciences
Karpatska St., 15, 76019 Ivano-Frankivsk, Ukraine
e-mail: lubomyrpoberezhny@gmail.com

Ihor Chudyk
ORCID ID: 0000-0002-7402-6962
Ivano-Frankivsk National Technical University
of Oil and Gas
Karpatska St., 15, 76019 Ivano-Frankivsk, Ukraine
e-mail: chudoman@ukr.net

Andrii Hrytsanchuk
ORCID ID: 0000-0001-9894-0911
Ivano-Frankivsk National Technical University
of Oil and Gas
Institute of Petroleum Engineering
Karpatska St., 15, 76019 Ivano-Frankivsk, Ukraine
e-mail: andriihrytsanchuk@gmail.com

Oleg Mandryk
ORCID ID: 0000-0002-2689-7165
Ivano-Frankivsk National Technical University
of Oil and Gas
e-mail: mandryk68@gmail.com

Tetyana Kalyn
ORCID ID: 0000-0003-2343-3733
Ivano-Frankivsk National Technical University
of Oil and Gas
Institute of Tourism and Geosciences
Karpatska St., 15, 76019 Ivano-Frankivsk, Ukraine
e-mail: kalyntetyana68@gmail.com

Halyna Hrytsuliak
ORCID ID: 0000-0003-2463-4772
Ivano-Frankivsk National Technical University
of Oil and Gas
Institute of Tourism and Geosciences
Karpatska St., 15, 76019 Ivano-Frankivsk, Ukraine
e-mail: gritsulyaka@ukr.net

Yaroslav Yakymechko
ORCID ID: 0000-0002-4406-0094
Ivano-Frankivsk National Technical University
of Oil and Gas
Institute of Petroleum Engineering
Karpatska St., 15, 76019 Ivano-Frankivsk, Ukraine
e-mail: jarykjj@ukr.net