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INFLUENCE OF THE GAS HYDRATES AND CONCENTRATION OF CORROSIVE COMPONENTS ON THE NATURE AND RATE OF CORROSION PROCESSES ON PIPELINES

Andrii Hrytsanchuk

*Ivano-Frankivsk National Technical University of Oil and Gas,
Ivano-Frankivsk, Ukraine*

Summary. *According to the results of corrosion-mechanical tests for the first time the regularities of mutual action of mechanical stresses, concentration of chlorides and hydrate formation on the rate and localization of corrosion processes were established. The coefficients of influence of hydration formation for general and local corrosion were calculated, which make up 1,13 and 1,32, respectively, which confirms the hypothesis about the intensification of local corrosion as a result of hydrate formation.*

Key words: *pipeline, gas hydrate, intrinsic corrosion, corrosion-mechanical tests.*

Statement of the problem. At the time, when the oil and gas industries are being developed, the problem of the protection of the environment must be solved as soil, water, air being the factors of technological process themselves are subjected to the disadvantageous transformation. That is why the decrease or elimination of the disadvantageous outcomes can guarantee ecological or economic safety.

It is impossible to overestimate the importance of gas for the economy of Ukraine. The portion of gas in the consumption structure of the primary power carriers (45%) is about in two times higher that average in Europe and in the world. Today the gas industry in Ukraine is the leading industry of the fuel-energy complex and the gas transporting system is its pivot, solving two the most important tasks: providing the industrial and private consumers and population by the natural gas, increasing of the remained reserves output (the extraction being over 85% of the main deposits). These deposits are great reserves and provide the main gas output in Ukraine, the new gas deposits being discovered now.

The process of the fuel transportation faces many problems, one of which being the pipeline cross-section covering by the gas-hydrate formations, which contributes to the financial expenditures and the decrease of gas output. The obstruction of the industrial gas pipelines by the gas hydrates during the autumn-winter period is always accompanied by the favorable thermodynamic environmental conditions, high pressure and low temperature of transporting.

Analysis of the available results of investigations. One of the less investigated is the corrosion caused by the gas hydrates. The formed hydrates can obstruct the pipelines, under-water transporting pipes. In the case of the gas blow-out during drilling the standpipe in the antiblow-out preventer and in the pipe-connection sleeve. It will cause partial or total obstruction of the pipeline inner side. If it is not eliminated immediately, it will cause the increase of pressure inside the pipe and can contribute to the accident. As the result different economic and environmental problems can arise and sufficient risks for the service staff and equipment safety.

The gas hydrates can initiate the development of different types corrosion in the internal part of the natural gas pipelines caused by the physical, chemical and electrochemical processes

revealed at the stage of the hydrates formation. The sizes of hydrates and the period of their contact with the pipe surface were determined [1, 2]. The acidic gases (H_2S, CO_2 and Cl^-), contained by the hydrate are the cause of the corrosion. Water is the corrosion agent as well. At every stage of the hydrate processes the interaction and reaction take place between the hydrate components and the pipe inner wall initiating the corrosion development.

At different stages of creation the solution is transformed from its liquid state into the semi-solid hydrate, and, at last, into the solid hydrate. During every of these stages the constant and continuous interaction between the hydrate phase and the pipe wall can cause cavitation, erosion, spot corrosion and corrosion cracking [3].

At the first stage of its formation hydrate is in the semi-solid state, the hydrate corks having liquid inside the cavity. They are easily ruined while striking the rigid surface, that is, the pipe wall, causing the development of the cavitation corrosion.

Then hydrates are gradually transformed from the semi-solid state into the solid one. Under the high rate these lumps bomb the inner surface of the pipe wall causing the erosion.

Thus, the hydrate lumps are gradually accumulated creating large-size corks, which contributes to greater expenditures for the gas transporting along the pipe wall surface. This motion inducts the relative motion between the pipe wall and the hydrate cork and facilitates the development of large-scale erosion corrosion. The gases CO_2 or H_2S from the gas composition, as well as the Cl ions sometimes and acidic acid (CH_3COOH) from water always react with the available water formed during the hydrate formation. It results in the formation of the acidic solutions being further decomposed into separate products of the corrosion electrolysis, which actively react with the internal surface of the pipe during the hydrates solidification or melting (when hydrates are eliminated) [4, 5]. Eventually, the corrosion processes are more active under the effect of these components being under the electro-chemical reactions up till the initiation of the electro-chemical and electrolytic corrosion.

The natural gas hydrates can form accumulations (up till the formation of the gas hydrate deposits in the waterless valley depths and under the sea bottom), which are promising for the industry although being scattered. New type of the scattered gas hydrates in the area of the eternally frozen rocks – relic gas hydrates being reserved due to the self-conservation effect – the effect of the slow decomposition (up till the total stop) of the methane hydrates and the other gases at the temperatures, which are lower than -2°C under the decrease of the hydrate formation pressure, which is lower than the three-phase balance system gas-ice-hydrate and the covering by the surface ice film (coating), which prevents or dramatically decreases the rate of its further decomposition. As the result the gas hydrate sample is the metal-stable state for a long time (from the Greek μετα – the prefix meaning the intermediate state, change, transformation, limited stable). In some cases the natural gas hydrates are treated as the efficient complex factor causing the technological difficulties while drilling and operation of the oil and gas wells, constructing of the floating platforms, etc. Some natural disasters and so-called mysterious phenomena are explained by the "gas hydration" (e.g. the Bermudas triangle, underwater landslips and covings, etc.) [3].

The Objective of the paper is to determine the regularities of the mutual effect of the corrosion environment, mechanical stresses and the hydrate formation on the corrosion of the industrial pipelines.

Statement of the task. According to the results of the corrode surfaces of the samples, held in the gas hydrate, the mechanism of its effect on the pipelines material corrosion was determined. The hydrate itself does not cause the corrosion, it only intensifies and localizes the effect of the reservoir water corrosive components (Fig. 1). At the first stage (the stage of the hydrate formation) the metal surface near it keeps covering with the passive films of the corrosion products, while this process stops on the metal surface under the hydrate.

Besides, as the result of the hydrate crystals formation from the moisture absorbed by the corrosion products, the partial damage of the passive film occurs, as the volume of the formed crystals is in $2 - 3$ time greater than that of water volume. After the hydrate dissociation (stage 2 the potentials difference is created between the described metal areas, which causes the appearance of the corrosion microgalvanic elements, which accelerate the metal solution in the less passive area (ig. 1,b). Further, when the thermobaric conditions favorable for the hydrate formation are created, it will be the most efficient in the area of the created corrosion action, as the latter is the crystallization center. With the every next cycle of the gas hydrate "formation-decomposition" the depth of the corrosion defect increases. Thus, the mechanism of the mutual effect of the corrosion environment and the gas hydrates deals with the intensification and localisation of the corrosion processes.
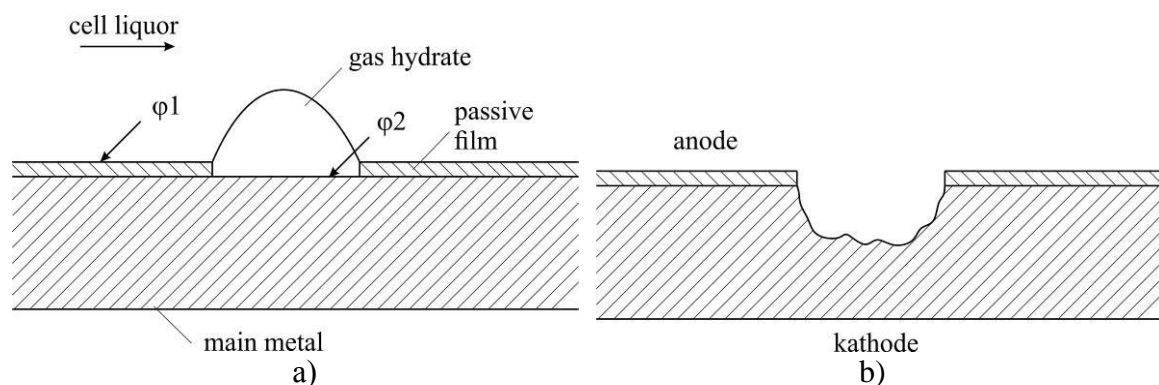

Figure 1. The mutual effect of gas hydrate and reservoir water on the metal pipeline at the first (a) and second (b) stages

As the corrosion mechanism in the chloride environments is mutual for both intrinsic corrosion and ground corrosion, the earlier obtained data on the ground corrosion [6, 8] were used to describe more thoroughly the process and to determine correctly the general regularities of the chloride-ions effect.

The results of investigations. The investigations of corrosion in the model environments (ME), which are similar to the ground with the chloride type of salinity (Table 1) have testified [Fig. 2, 5] sufficient increase of the general corrosion rate, when the concentration of the chloride-ions during the transformation from ME1 to ME2 is greater, and a little less during the transition from ME2 to ME3 [6, 8].

Similar nature of the effect is noticed for the both investigated steels.

Table 1. Chemical composition of solutions for the corrosion tests

№ ME	Concentration of NaCl, mol/l	Corrosion type
1	0,01	Ground corrosion
2	0,05	
3	0,1	
4	0,5	Intrinsic corrosion
5	1,5	
6	2,5	
7	3,75	
8	5	

Having analyzed together Fig. 1, Fig. 3, and Fig. 6 and compared the rates of general and local corrosions, we can state sufficient intensification of the local corrosion processes, here this being greater, when the chloride-ions concentration is greater too.
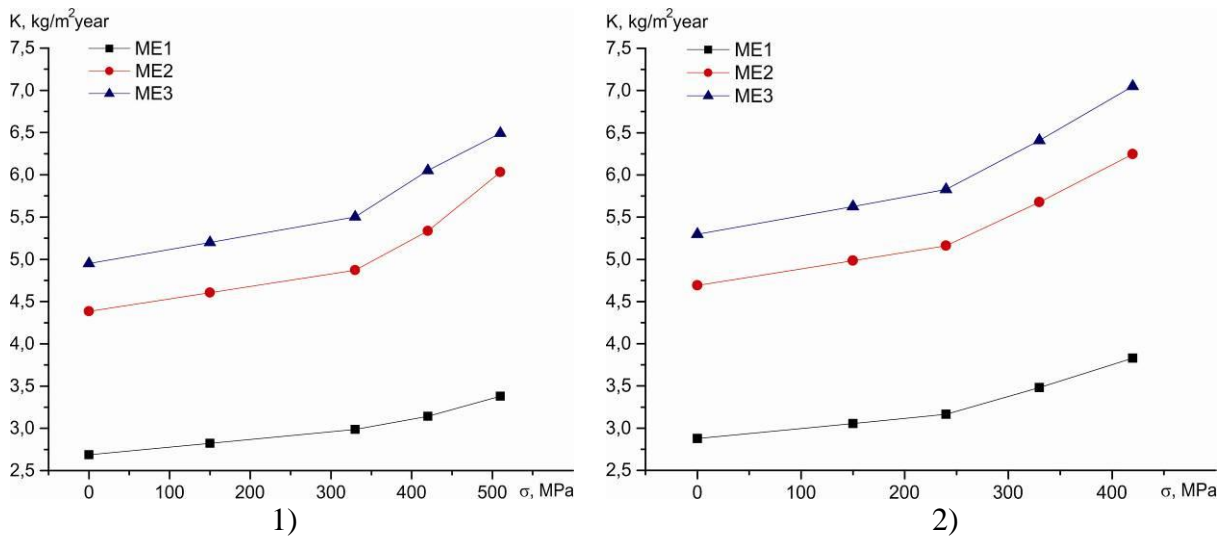

Figure 2. Dependence of the rate of general corrosion in chloride electrolytes:
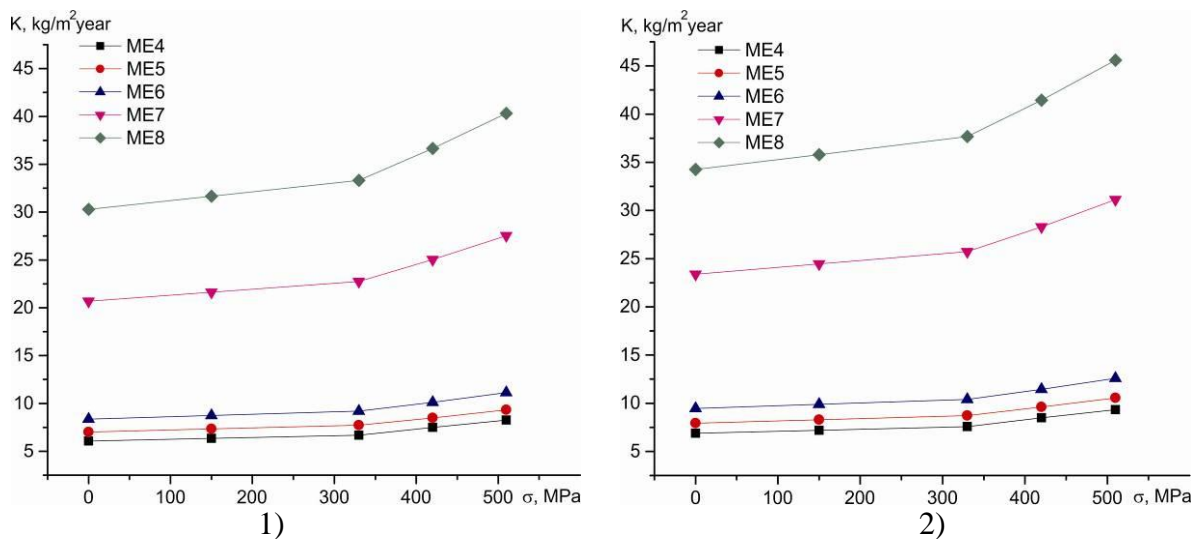17GS (1) and St20 (2) (ground corrosion)

Figure 3. Dependence of the rate of general corrosion in chloride electrolytes (in-tube corrosion):
control sample (1) and sample held in gas hydrate (2) for 17GS steel

When the chloride-ions concentration increases, the mechanical factor action grows as-well, as in the case of both the general corrosion degradation and the local corrosion. Under the intrinsic corrosion in the highly-mineralized reservoir water (Fig. 3, 4, 6, 7) the dramatic growth of the corrosion rate is noticed during the transition from ME6 to ME7.

Such corrosion behavior, from our point of view, is caused by the accelerated fracture of the passive films by the chloride-ions, when some critical concentration is being approached.

The increase of general and local corrosion rates for the samples held in the gas hydrate in comparison with the control samples is noticed (Fig. 3, 4, 6, 7). Basing on the obtained results the coefficient of the gas hydrate effect on the corrosion was calculated, which equals 1,13 for the general corrosion and 1,32 for the local corrosion.
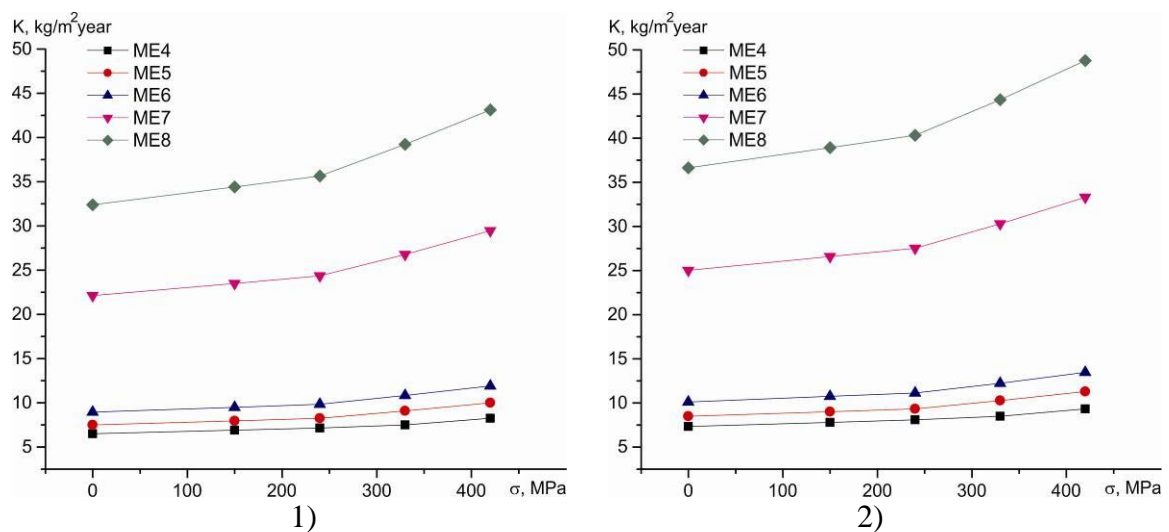
Figure 4. Dependence of the rate of general corrosion in chloride electrolytes (in-tube corrosion): control sample (1) and sample held in gas hydrate (2) for steel 20

The combined analysis of the corrosion behavior of the pipes material in the chloride-type aggressive environments demonstrates similar regularities of the mutual effect of the corrosive environment and the mechanical factors on the corrosion processes rate. For the both analyzed cases of corrosion the intensification of the mechanical factor is noticed, when the chlorides concentration increases. In the ME1, ME4 and ME5 insufficient changes in the process dynamics are seen during the transition from the elastic into elastic-plastic area. In the ME2, ME3, ME7 and ME8 these changes are more sufficient (Fig. 5 – 7).
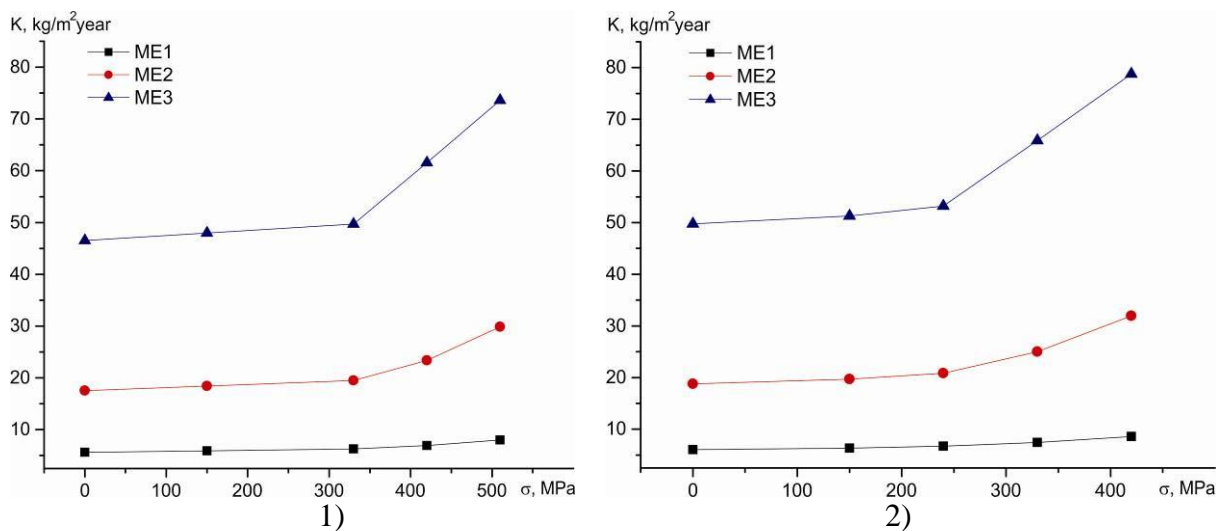

Figure 5. Dependence of the rate of local corrosion in chloride electrolytes: 17GS (1) and St20 (2) (ground corrosion)

Under the local corrosion, when the level of mechanical stresses is increased, sufficient intensification of the corrosion processes is noticed, especially in the area of the elastic-plastic strain (the range $1,35\,\sigma_{0,2}^{*} - 1,65\,\sigma_{0,2}^{*}$ – for the steel 17GS, and $1,45\,\sigma_{0,2}^{*} - 1,8\,\sigma_{0,2}^{*}$ – for steel 20).
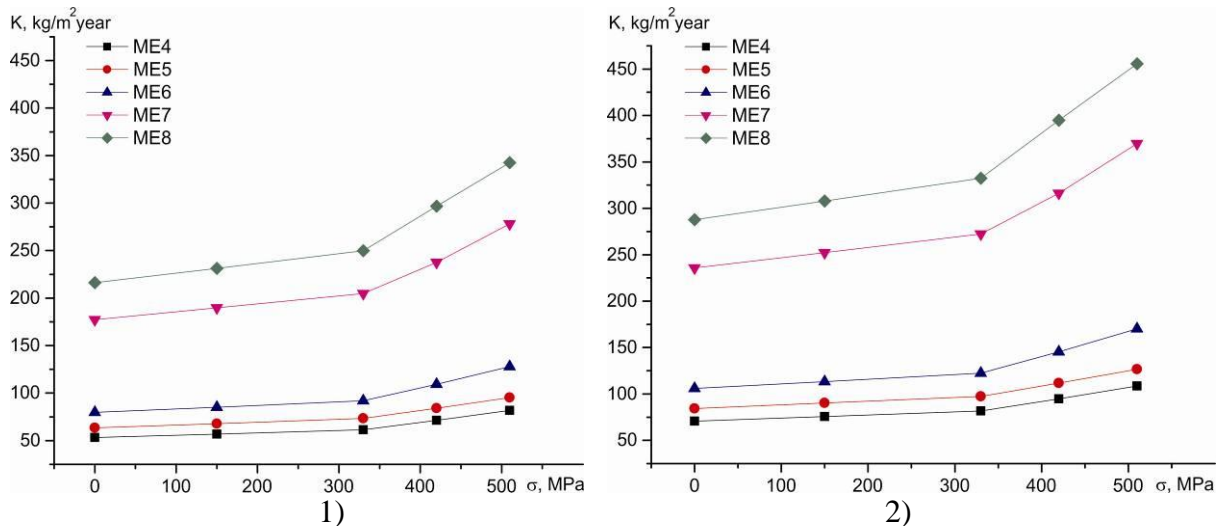
Figure 6. Dependence of the rate of local corrosion in chloride electrolytes (in-tube corrosion): control sample (1) and sample held in gas hydrate (2) for 17GS steel

The efficient growth of the general and the local corrosion rate is registered (Fig. 2 – 7), although in the case ME1 the growth of the local corrosion rate is insufficient, which results from the relatively small localization of the corrosion processes.
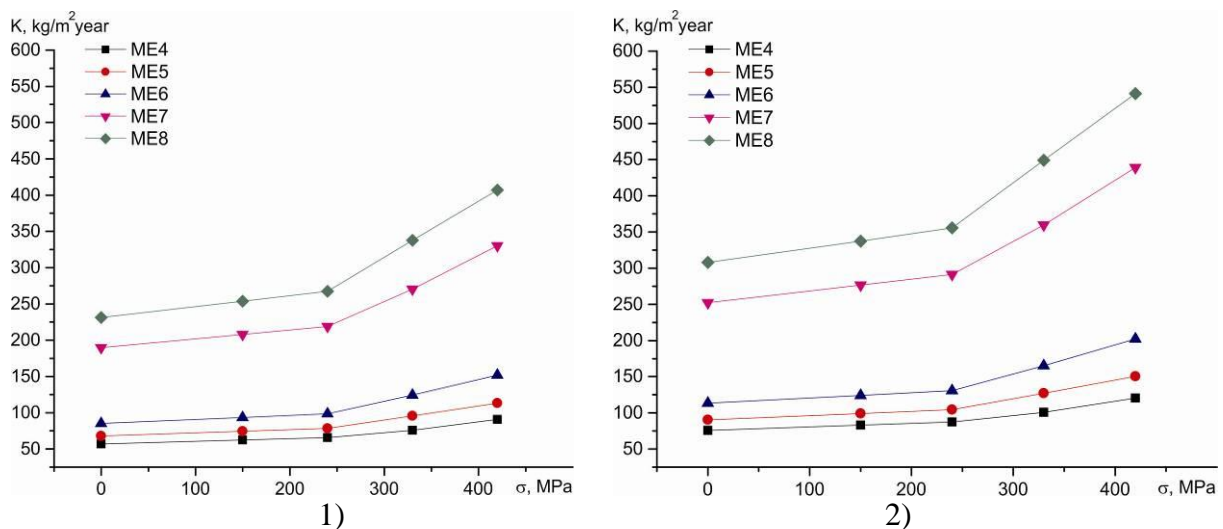

Figure 7. Dependence of the rate of local corrosion in chloride electrolytes (in-tube corrosion): control sample (1) and sample held in gas hydrate (2) for steel 20

The values of the local corrosion rate in the modeled reservoir water (Fig. 3, 4 and Fig. 6, 7) are of special attention. As well as in the case of the uniform corrosion more intensive action of the mechanical factor is registered during the transition from the elastic to the elastic-plastic strain.

But for the local corrosion the increased role of the mechanical factor is more efficient. From our point view, it is caused by the formation of the local galvanic elements and the fact, that the process of the metal solution in the area of tension is easier as the result of smaller interaction between the atoms, because of the increase of distance between the lattice points. During the local corrosion damage development, the mechanical factor importance is greater, which is caused by the stresses concentration in the bottom of the corrosion pits and pots. Thus, more favorable conditions for their growth in depth, but not in width, are created. Another

sufficient factor is the ability of the chloride-ions to damage the passive films. As the result of it the sufficient increase of both local and uniform corrosion rates is noticed during the transition from ME6 to ME7 and ME8 (Fig. 3, 4, 6, 7).

To estimate correctly the operation risks, operation life and the residual operation life of the safety operation, the rate of the pipeline wall thickness during the pipeline operation is of the paramount importance in order to prevent in time the possible accidents (Fig. 8 – Fig. 13). Regularities, similar to the corresponding dependences of the sufficient losses, are noticed.

It must be noted, that for the case of the ground corrosion (ME1 – ME3), when the isolation is injured or when the anticorrosion protection is not available or its quality is not good enough, the annual value of the thickness in the area of the operation loadings can be 0,45 – 0,55 mm (Fig. 8). But when the process localizations is taken into account in the case ME3 it can exceed 6mm/per year (Fig. 10), which testifies the great danger of the pipelines seal failure, especially those, which have been operating for more than 15…25 years and are out-of-date having poor operation-life bituminous anticorrosion coating.
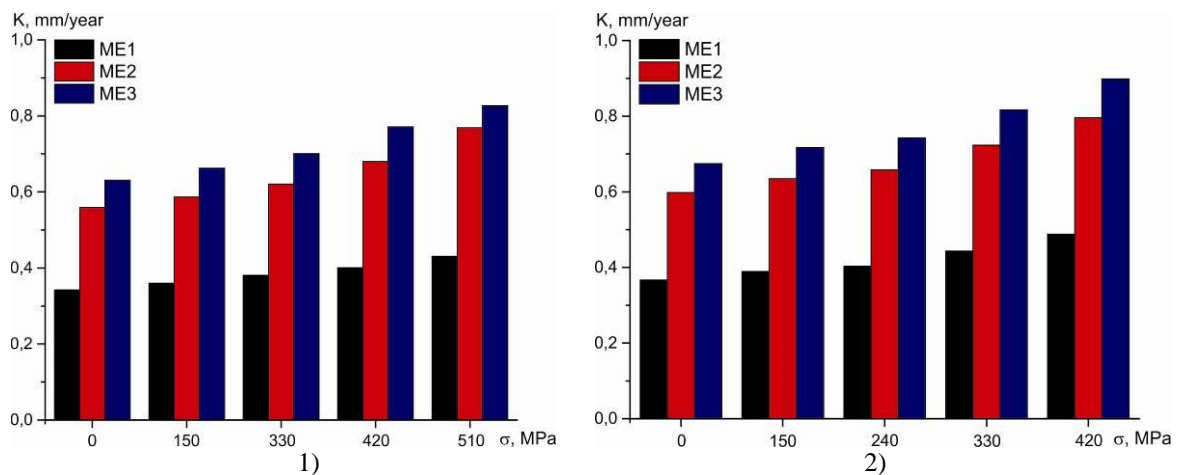

Figure 8. Dependence of pipe wall thickness under uniform corrosion in chloride electrolytes of corrosion (ground corrosion): 17GS (1) and steel 20 (2)
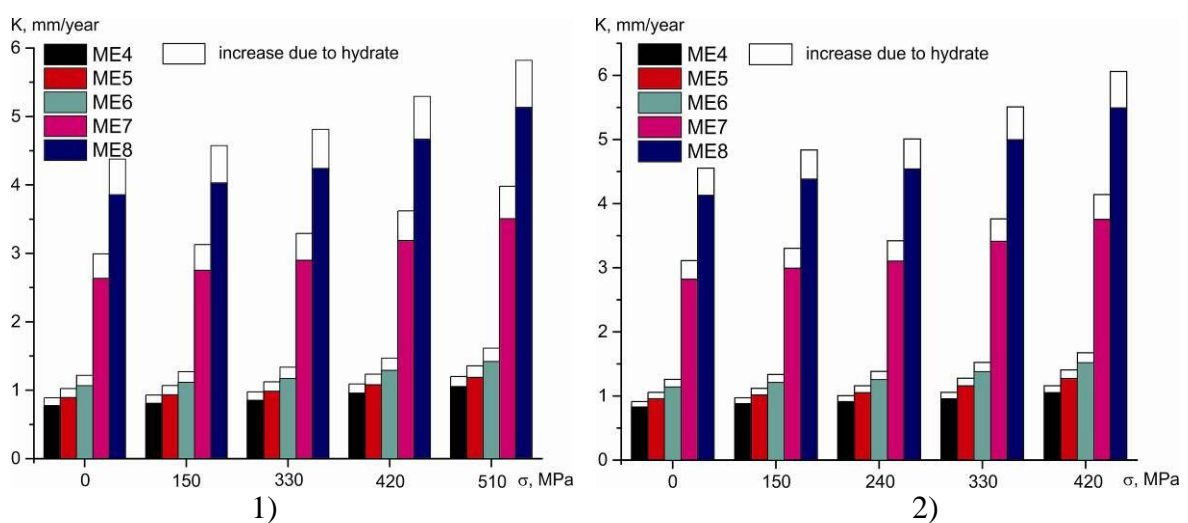

Figure 9. Effect of gas hydrates on the rate of the pipeline wall thickness for 17GS (1) steel and steel 20 (2)

The analysis of the ground water along the pipelining is of special importance to estimate in time the corrosion degradation risks of the pipelines steel to prevent and predict the seal failure or other more difficult failures or accidents [9].

The increased risks of accidents, caused by the corrosion-mechanical processes, will be evident foremost for the other industrial pipelines being in operation without effective anticorrosion protective.

Depending on the stress values and for the certain model environment the growth of the general corrosion rate caused by the gas hydrate for the steel 17GS is from 0,1 till 0,67 mm/year, for the steel 20 – from 0,11 till 0,72 mm per/year (Fig. 9).
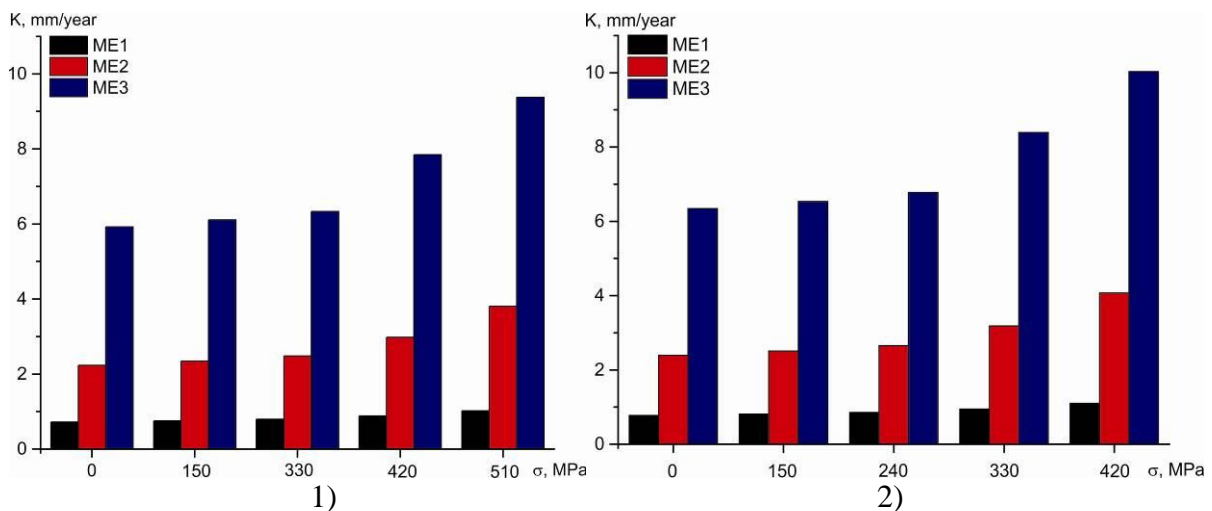

Figure 10. Dependence of the wall thickness taking into account the of localization in chloride electrolytes (ground corrosion): 17GS (1) and steel 20 (2)
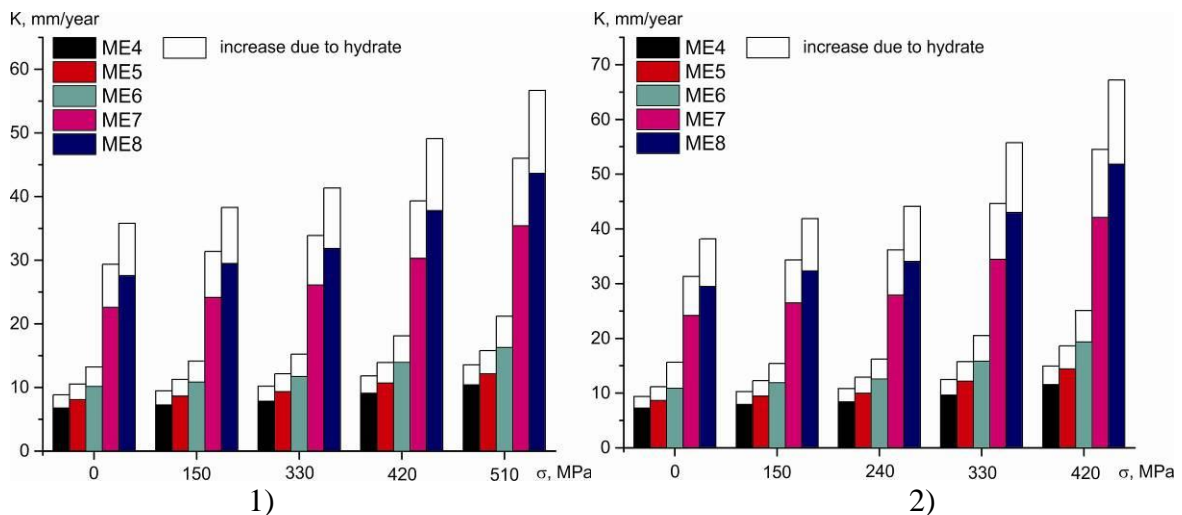

Figure 11. Effect of the gas hydrates on the pipeline wall thickness taking into account the localisation for steel 17GC (1) and steel 20 (2)

For the corrosion in the reservoir water the characteristic feature is the jump of the corrosion rates during the transition from ME6 to ME7 and ME8. This dramatic change of values makes one think about the regularities change of the corrosion processes development.

For the corrosion, when the localization is taken into account depending on the stresses values and for the corresponding model environment, the growth caused by the gas hydrate for

steel 17GC is from 6,8 till 14,4 mm/per year, for the steel 20 – from 7,3 till 17,1 mm/per year (Fug. 11).

In order to verify this hypothesis the dependence of the corrosion rate (without taking into account the localization) on the chlorides concentration in the operation environment, was plotted. For different kinds of steel, the law-alloyed steel 17GC and the carbon steel 20 in particular, single-type nature of the rate value change of the control samples mass loss, is being noticed (Fig. 12).

The analysis of the corrosion rate dependence on the chloride-ions concentration (Fig. 12) makes possible to specify two concentration intervals. At the first one the intensive rate growth is noticed with the further fading. At the second – the corrosion processes are intensified and the rate, in fact, increases linearly. Such behavior of the pipeline steel testifies the presented hypothesis on the change of the mechanism of the corrosion processes procedure [10].
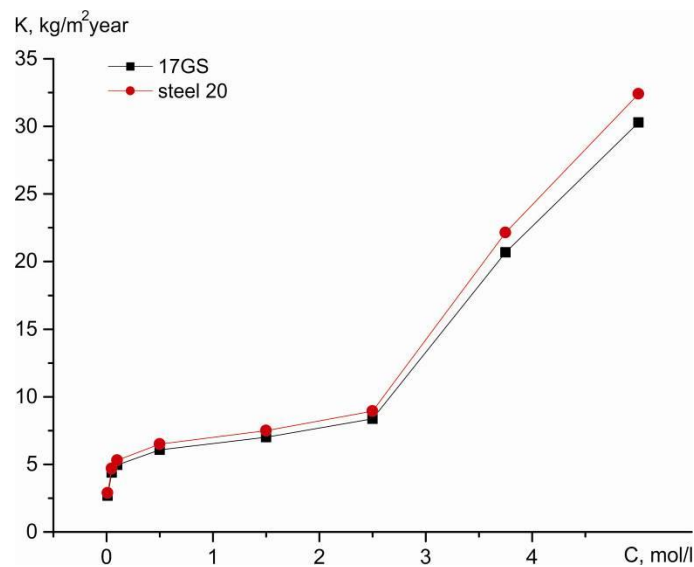

Figure 12. Dependence of the rate of general corrosion in chloride electrolytes on NaCl concentration

The mathematic description of the experiment results was performed and corresponding dependences for the first and second areas of the corrosion rate curve were obtained (Fig. 13).
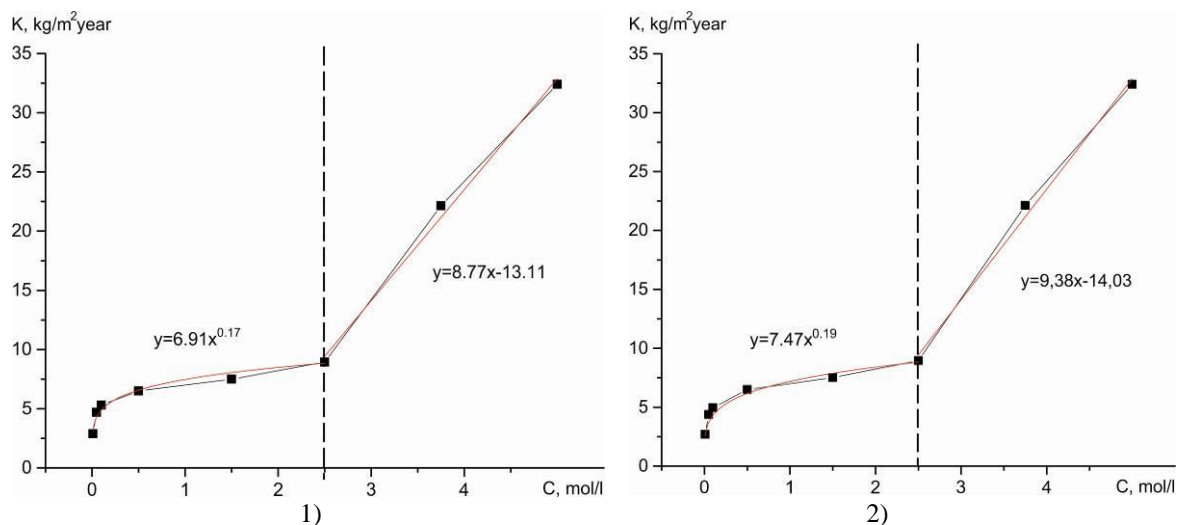

Figure 13. Mathematical description of the results of corrosion tests for the steel 17GS (1) and steel 20 (2)

For the mathematic description of the first area of the curve the power dependence of the $y=a \cdot x^b$ – type was proposed to be used, for the second area – the linear dependence $y=k \cdot x+b.$ Mathematic processing of data was carried out in the software package ORIGIN 2016. For the case of the control unloaded sample the equation will be obtained: for the steel 17GC – the first area, the second – $y=9.38 \cdot x-14.03$.

Conclusions. The regularities of the chlorides concentration effect on the corrosion rate of the pipe steels 17GC and steel 20 have been found and for the first time the dramatic growth of the corrosion rate have been recorded at the chloride concentration 2,5mol/lt, which, from our point view, is caused by the change of the corrosion mechanism, caused by the accelerated fracture of the passive films. The pipelines material corrosion in the aggressive operation environments has been investigated on the example of the ground electrolyte of the chloride type and the reservoir water. According to the results of the corrosion-mechanical tests the regularities of the mutual action of the mechanical stresses chlorides concentration and the hydrates formation on the rate and localization of the corrosion processes have been determined for the first time. The coefficients of the hydrate formation effect for the general and local corrosion, which equal 1,13 and 1,32 respectively, have been calculated, which verifies the hypothesis on the intensification of the local corrosion caused by the hydrate formation.

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ВПЛИВ ГАЗОВИХ ГІДРАТІВ І КОНЦЕНТРАЦІЇ КОРОЗІЙНИХ КОМПОНЕНТІВ НА ПРИРОДУ ТА ШВИДКІСТЬ КОРОЗІЙНИХ ПРОЦЕСІВ НА ТРУБОПРОВОДАХ

Андрій Грицанчук

Івано-Франківський національний технічний університет нафти і газу, Івано-Франківськ, Україна

Резюме. За результатами корозійно-механічних випробовувань вперше встановлено закономірності спільної дії механічних напружень, концентрації хлоридів і гідратоутворення на швидкість та локалізацію корозійних процесів. Розраховано коефіцієнти впливу гідратоутворення для загальної та локальної корозії, які становлять 1,13 і 1,32 відповідно, що підтверджує гіпотезу про інтенсифікацію локальної корозії внаслідок гідратоутворення.

Ключові слова: трубопровід, газовий гідрат, внутрішньотрубна корозія, корозійно-механічні випробовування.