

Investigation of the corrosiveness of moisture condensation conditions at gas production facilities in the presence of CO₂

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Abstract

Internal corrosion and corrosion protection measures represent a pressing challenge that hydrocarbon production facilities are faced with. The presence of CO₂ and condensation water in the produced gas, as well as a number of other factors stimulate intensive propagation of carbon dioxide corrosion and local defects on steel. Corrosion tests were carried out under moisture condensation conditions, when a temperature gradient arises and the gas is rapidly cooled to determine the local corrosion limit rates. Tests studied the influence of various factors on corrosion processes under moisture condensation conditions in the presence of CO₂: humidity and acidity of the environment, alcohol footprint, temperature, steel grade and the weld availability. The temperature gradient that occurs between the medium and the steel surface and leads to moisture condensation has a strong impact on intensification of the localized corrosion. The strong growth of local defects can be caused by the presence of CH₃COOH in the medium, which acidifies the moisture film, facilitates corrosion, and dissolves the forming layers of corrosion products (iron carbonate) on the steel surface. Due to heterogeneity of the surface in the weld area, the growth of local defects here is more active during moisture condensation, as compare to parent pipe. The paper investigates corrosion impact factors under condensation of water and alcohol solutions present in media and used as a hydrate inhibitor in gas production. It is shown that gas humidity and alcohol concentration are decisive for the development of this type of corrosion under CO₂ conditions. The rate of corrosion depends on the amount and composition of the liquid condensing on the metal surface. The rate of local carbon dioxide corrosion in such environments can reach several mm/year.

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Introduction

During hydrocarbon production, increased attention is paid to the problems of ensuring safety and durability at infrastructure facilities made of steel [1, 2]. One of the main problems is the risk of internal corrosion development due to the presence of hazardous H₂S and CO₂ in the produced fluids accompanied by additional corrosive factors (presence of water, elevated temperatures, *etc.*). Many operating gas production facilities are characterized by

increased amounts of CO₂ [3, 4]. A high degree of corrosion defects localization is the main hazard of carbon dioxide corrosion (CDC) [5–7].

Gas production facilities that differ from oil fields by corrosive conditions demonstrate several main corrosion formation zones [8, 9]:

- the lower part of the pipe (when moisture accumulates or bottom-of-line corrosion (BOL));
- the top of the pipe (in case of moisture condensation or top-of-line corrosion (TOL));
- places of moisture accumulation (cracks, gaps, stagnant zones, level difference *etc.*).

Basically, corrosion in the aqueous phase (BOL corrosion) is the main focus of corrosion studies, including those performed at hydrocarbon production facilities [10, 11]. TOL cases accompanied by formation of condensation water during gas production have been limitedly studied in relation to the Russian gas fields. Our analysis showed that TOL corrosion was mainly investigated in the works of the foreign authors [7, 12–14].

In this study, we focused on the TOL corrosion, which is specific for and occurs at gas production facilities. Corrosion factors for the TOL tests were selected for the operating conditions of the Russian gas fields.

TOL corrosion initiate and development conditions as follows: high moisture content of the produced formation gas, creation of thermobaric conditions for water separation from the gaseous medium and its condensation on the inner surface of the upper part of the pipe.

Experimental

Experiments described in [15] for the atmospheric moisture condensation conditions were taken as a basis, when planning and carrying out CDC tests in a gaseous environment. Glass desiccators with a volume of up to 8 dm³ served as corrosion cells. Glass tubes were placed inside (for cooling) to let, a cooler (cold water) pass (to reduce the temperature to 10°C). To create saturated water vapor a liquid (distilled water separately or together with alcohol) was placed in a desiccator. The inlet and outlet of the cooler and gaseous CO₂ and/or N₂ were installed in the test cell. Gases separately or their mixture after premixing at a certain ratio were fed through a tube to the bottom of the desiccator across a liquid layer to accelerate saturation with liquid vapor. Steel samples were placed on cooling tubes to form a moisture film by condensation. An air thermostat was used to carry out the tests at higher than ambient temperatures. Thus, CDC tests were carried out under moisture condensation conditions at normal (20–25°C) and elevated (50°C) temperatures [16].

Various carbon and low alloy steel samples (09Mn2Si, X65), and steel, which is applied in the production of pipe tubing (J55LT) were used in tests. The temperature difference between the air environment (20–25°C) and the artificially cooled steel surface (10°C) reached up to 10–15°C.

The authors have carried out tests under moisture condensation conditions in the presence of CO₂. After the tests, corrosion rate (K) was registered and measured. The rate of general corrosion was determined by the weight loss of the sample ($K_{\text{gen.}}$).

Local corrosion was determined by the depth of corrosion damage:

- average ($K_{loc.av.}$) – by averaging all local defects;
- maximum ($K_{loc.max.}$) – for the deepest local defect.

Results and Discussion

Laboratory tests in the gas environment have been carried out earlier [17, 18], including those performed for CO₂. But in the vapor phase above the aqueous (water-hydrocarbon) environment where the test samples were located, due to the absence of a moisture film, corrosion was low, especially for CO₂ environments (even under periodic shaking and contacting with a liquid medium under laboratory conditions). The samples were predominantly in a dry atmosphere, and corrosion did not develop. The rate of general corrosion in the vapor phase above the liquid was low and did not exceed 0.1 mm/year:

- in autoclave tests ($P(\text{CO}_2) = 5\text{--}10$ MPa) it totaled 0.001–0.011 mm/year (without contact with the aqueous phase) [18];
- in autoclave tests 0.026 mm/year (without contact with the aqueous phase) and 0.065 mm/year (with periodic contact with the aqueous phase) [17].

Steel St20 test data show that the rate of the general corrosion of the samples located above the CO₂ aqueous medium is 0.01 mm/year: no local defects [9]. In the absence of a direct contact with the aqueous phase, corrosion is low-significantly below 0.1 mm/year. Similar data were obtained in [19] for carbon steel in a CO₂ atmosphere over an aqueous electrolyte, where the rate of general corrosion was not higher than 0.02 mm/year, even with periodic wetting of the samples by shaking the test cell.

It is known [14] that TOL corrosion in the presence of CO₂ requires a large amount of condensation moisture. This refers exactly to a permanent moisture film that appears on the steel surface.

It is a TOL corrosion typical of the gas fields that highlights the difference in corrosion conditions between gas and oil facilities [6]. When wet raw gas comes from the well and is transported through a pipeline, water vapor from the gas phase condenses on the inner surface of the pipe due to the temperature gradient between the wet gas flow and the environment, which leads to TOL corrosion. Evaluation studies show that the Russian and foreign fields can experience moisture condensation even in the well, when gas rises from the formation the TOL corrosion [6, 9, 20].

Globally, carbon and low-alloy steels are frequently used in the construction of pipelines, and do not contain sufficient amount of chromium that can increase corrosion resistance [21]. Such steels are not resistant to CDC and are subject to TOL corrosion, which leads to destruction of pipelines. It is reported in [22] that the TOL corrosion rate of X65 steel can reach up to 3 mm/year and is accompanied by a significant localization of the corrosion destruction process.

As was confirmed in [23], the corrosion rate depends on the humidity conditions of the vapor environment. The presence of MgCl₂ reduces the water vapor content above the

solution, thereby lowering the relative humidity, which, in turn, reduces the amount of water condensation falling out, and can even prevent its precipitation. As an example, we considered the dependences for saturated and semi-saturated MgCl_2 (Figure 1). To create conditions for difference levels of moisture formation, we took: distilled water (100% relative humidity), a saturated solution of MgCl_2 diluted 2 times with water (~66% relative humidity), and a saturated solution of MgCl_2 (~33% relative humidity). At 100% relative humidity (line 1): cooling of saturated water vapor from the experiment temperature (t_{env}) 23°C to the refrigerator temperature (t_{cold}) 12°C (line 1') provides of ~10 g/m³ in the water vapor content, which gives the amount of moisture condensate required for the volume of the desiccator and the area of the cold elements. With a similar temperature drop (line 2') for a relative humidity of 66% (line 2, for semi-saturated MgCl_2), moisture condensate does not form as the temperature decreases to about 16°C, because the dew point (100% relative humidity) is not reached. Further cooling gives an amount of condensate proportional to the difference in water vapor content above line 1 (a segment in the area exceeding 100% relative humidity), *i.e.* approximately proportional to the drop in water vapor content by 3 g/m³. For saturated MgCl_2 (line 3), 33% relative humidity, such temperature change (line 3') is not capable to bring the system into the condensation range (the system does not reach 100% relative humidity) given the conditions of our experiment.

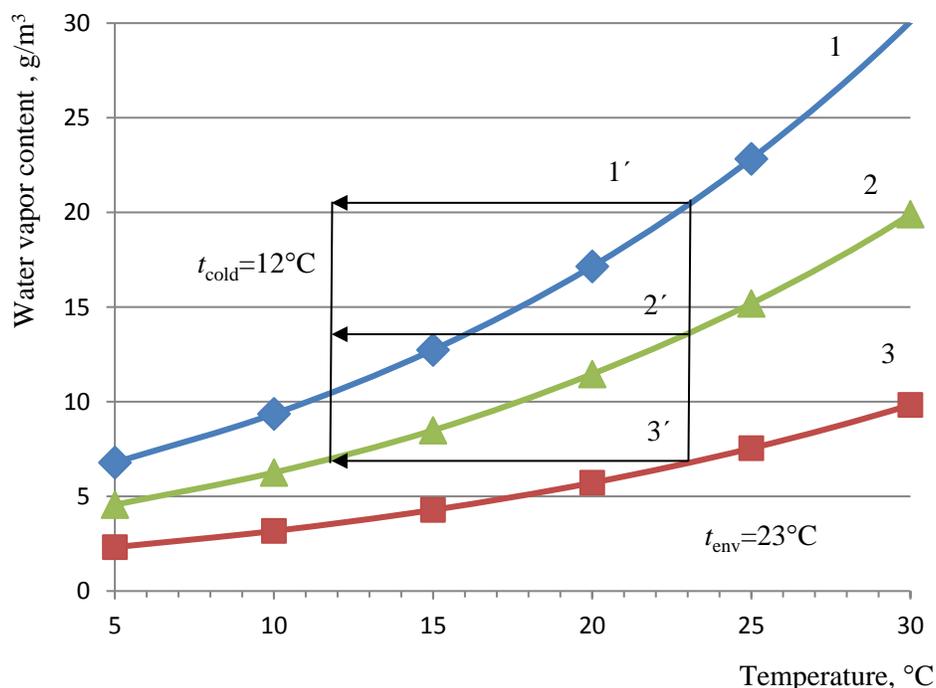


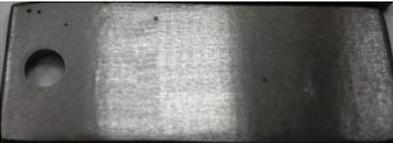
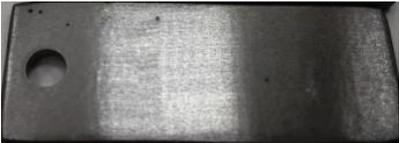
Figure 1. The water vapor content above: 1 – distilled water (100% relative humidity), 2 – saturated MgCl_2 solution diluted 2 times with water (~66% relative humidity), and 3 – saturated MgCl_2 solution (~33% relative humidity) according to [23].

Tables 1 and 2 show the results of evaluating the corrosion rate depending on the humidity conditions of the vapor environment. It can be seen that 33% humidity (saturated with MgCl₂) with no moisture condensation occurred during the temperature drop, provides a low general corrosion rate (0.0012 mm/year), and no local corrosion. This is confirmed by the external view of samples after testing (Table 2): corrosion products are not formed, the surface of the steel sample remains unchanged. However, if there is a possibility of a slight difference in the content of water vapor (3 g/m³) under 66% humidity (semi-saturated MgCl₂) the steel surface changes its appearance upon reaction with corrosive reagents (water and CO₂). But the amount of moisture is insignificant, and there is also no development of dangerous local damages: the general corrosion rate (0.0070 mm/year) remains at a low level (Table 1).

Table 1. St20 steel corrosion rate after testing under moisture condensation in the presence of CO₂ according to [23].

Relative conditions humidity, %	Corrosion rate, mm/year		
	<i>K</i> _{gen.}	<i>K</i> _{loc.av.}	<i>K</i> _{loc.max.}
100	0.014	0.400	0.6
66	0.0070	No corrosion	No corrosion
33	0.0012	No corrosion	No corrosion

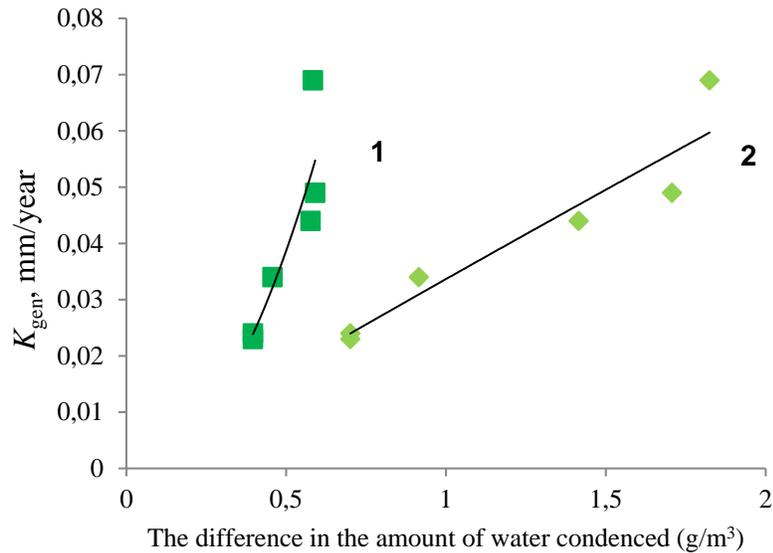
Table 2. External view of steel samples after testing under moisture condensation conditions and in the presence of CO₂ according to [23].

Relative humidity, %	With corrosion products	After removing of corrosion products
100		
66		
33		

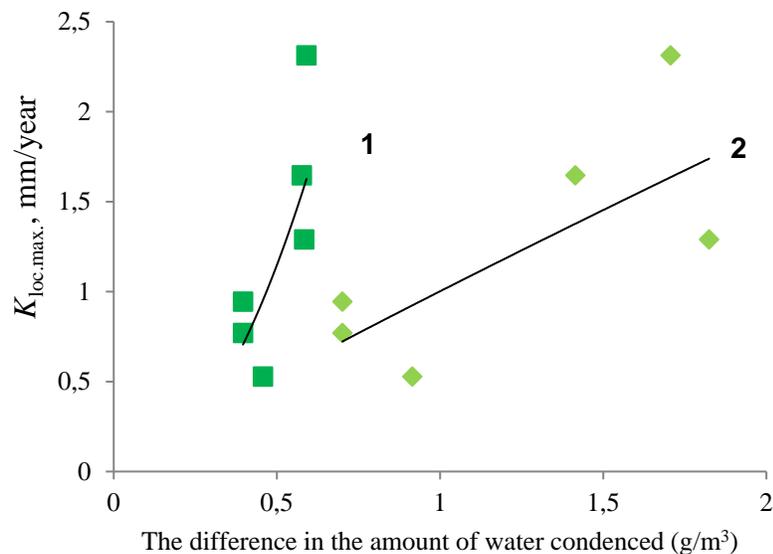
Localization of CDC corrosive processes occurs only at 100% humidity. Multiple pitting defects are visible on the steel sample after removal of corrosion products (Table 2). Calculations show (Table 1) that at a sufficiently low general corrosion rate of

0.014 mm/year, the rates of local average and maximum corrosion reach 0.4 and 0.6 mm/year respectively.

A decrease in temperature and the associated change in the amount of moisture in the air also affects the formation and development of TOL corrosion [24–27].



(A)



(B)

Figure 2. Dependence of the general (A) and maximum local (B) corrosion rates of carbon and low-alloy steels on the difference in the amount of water condensed on the steel surface relative to the test temperature (1) and to the temperature of the “cooler” (2) in the presence of CO₂ and under moisture condensation conditions according to [28].

The results of TOL tests on different types of steel (09Mn2Si, J55LT) showed [16] that the rate of local corrosion ($K_{loc.av.} = 0.42–1.43$ mm/year; $K_{loc.max.} = 0.54–1.95$ mm/year) was

higher at a greater temperature difference between the air environment and the steel sample surface, which may be associated with a large amount of moisture precipitation. General corrosion rate remains low (below 0.1 mm/year). Additional test data for different steels provided in [16] are shown in Figure 2. As can be seen, the rates of the general and maximum local corrosion in the tested carbon and low-alloy steels (St20, 09G2S, J55LT) depend on the amount of moisture condensed on the steel surface. The water content in the Figure 2 is given relative to the test temperature and to the temperature of the "cooler" (glass tubes through which cold water is transported), where steel samples are located and cooled.

Table 3. Corrosion rates under moisture condensation conditions and CO₂ partial pressure (0.1 MPa).

Steel type / Corrosion environment / Conditions	$K_{gen.}$, mm/year	$K_{loc.av.}$, mm/year	View of steel samples after test
Stainless steel 12X18H10T	0.0001	No local corrosion	
Carbon steels / water	0.02	0.8	
Carbon steels / water / elevated temperature	0.2	1.9	
Carbon steels / water- alcohol solution (WAS)	0.05	0.8	
Carbon steels / WAS / elevated temperature	0.09	1.7	
Carbon steels / water / weld	0.08	1.6	

The temperature can accelerate moisture condensation (Table 3). According to the results of X65 TOL tests carbon steel at 20–25 and 50°C, increase in the rate of moisture condensation caused by a larger temperature gradient (at a higher initial temperature of metal samples) is the main factor in the corrosion process: the local corrosion rate increases from 0.8 to 1.9 mm/year (Table 3) [16]. As the temperature rises, the determining factor in the

acceleration of TOL corrosion is the increase in the amount of condensation moisture, although an additional influence of the temperature factor is also possible [29].

TOL corrosion at foreign gas fields with high CO₂ content [30–32] causes the development of local defects at a rate of 0.95–1.9 mm/year. The analysis highlights that the rates of the local TOL corrosion (up to several mm/year) obtained during simulation tests of carbon and low-alloy steels (Table 3) are similar to pitting corrosion recorded during the operation of gas production facilities.

TOL corrosion tests and corrosion resistance analysis [33] underscored that local defects can develop on carbon and low-alloy steels in the operating conditions of production facilities in the presence of CO₂ and moisture condensation. Alloys with a high chromium content for example stainless steel can be more resistant in such harsh conditions. According to the test data, stainless steel 12X18H10T (18% Cr) was resistant and did not change after the TOL corrosion tests (Table 3). Such corrosion-resistant steels can be effective and resistant to CDC due to the formation of protective chromate films on the steel [34].

A water-alcohol solution (WAS) was taken as the test liquid, because methanol is used as an inhibitor of hydrate formation at gas facilities [35, 36]. Transmitted WAS can have different concentrations depending on the alcohol content and the amount of water (condensation or reservoir) and can vary across the field infrastructure. 10% water solution of isopropanol was used in test. Deep local damage is observed on steel 20: local corrosion rate is 0.8 and 1.7 mm/year at 20–25 and 50°C, respectively (Table 3). The general corrosion rate of the same steel samples remains low (0.061 mm/year). Figure 3 shows that temperature accelerates corrosion not only in water, but also in WAS.

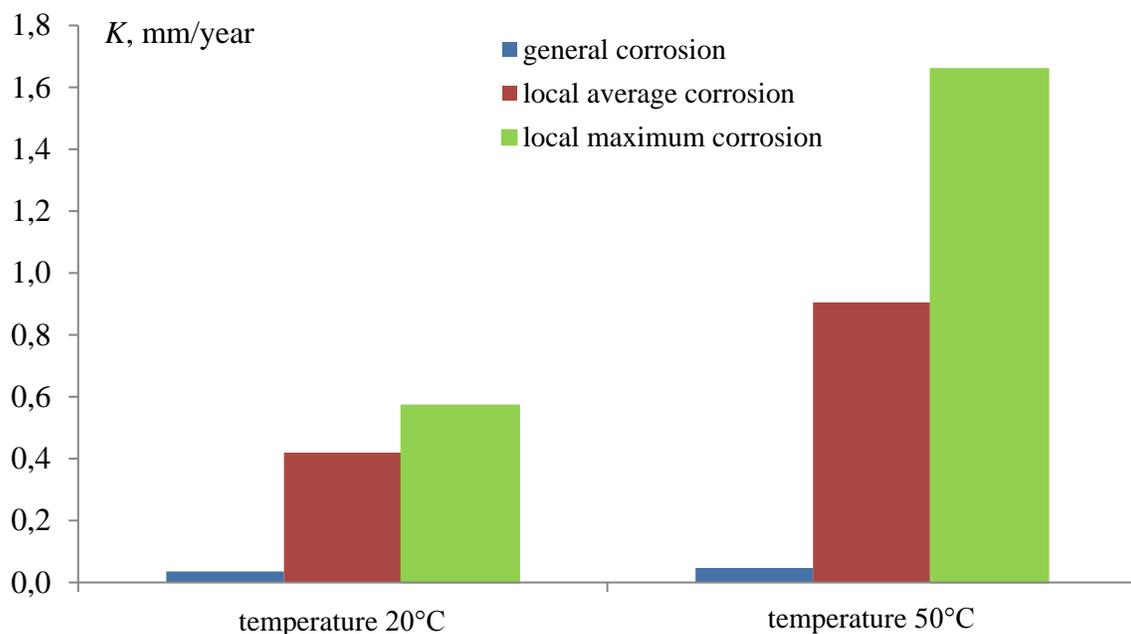


Figure 3. View of steel St20 samples after testing under moisture condensation conditions (water:isopropanol = 90:10) in the presence of CO₂.

The test results in WAS (10% isopropanol) are identical to a purely aqueous solution: local defects are formed (Table 3). During processing of the produced gas, the concentration of alcohol in WAS can increase and after its regeneration can reach up to 85–90%. Such technological transformations are accompanied by WAS heating/cooling and its condensation. Therefore, TOL corrosion tests were carried out for X65 carbon steel in the presence of CO₂ in a range of different concentrations of WAS (Figure 4). It can be seen that TOL corrosion rate grows in the presence of CO₂ upon condensation of WAS (up to 75% isopropanol). But starting from 75–80% concentration, isopropanol begins to suppress the CDC in the film of condensed liquid and there is a downward trend.

In contrast to water test conditions (BOL corrosion), when the addition of alcohol can directly (to some extent) reduce the destruction of steel (due to the replacement of corrosive water by alcohol) under liquid condensation conditions (TOL corrosion), the composition of the medium condensed on a steel surface plays a decisive role. It may differ in the concentration of alcohol from the original evaporated WAS. In the same way, the composition of the condensation layer (with an increase in the alcohol content) will also affect the CDC.

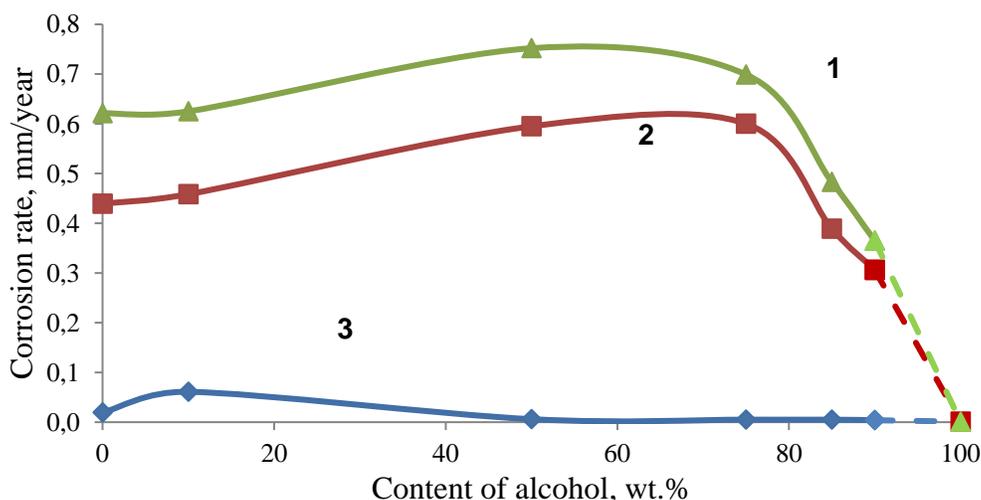


Figure 4. Dependence of steel 20 corrosion rates on the concentration (wt.%) of the evaporated WAS: 1 – $K_{loc.max.}$; 2 – $K_{loc.av.}$; 3 – $K_{gen.}$ [37].

This tendency is observed for WAS in a wide range of alcohol concentrations in water (in an evaporated liquid). For TOL corrosion, the composition of the liquid condensed on the steel surface is important, as corrosion processes take place exactly there. When the concentration of alcohol in the WAS condensed on steel reaches high values, the local corrosion rate begins to decrease.

Our TOL tests have shown that X65 steel, like other steels (Steel 20, 09Mn2Si, J55LT) is not resistant to local CDC (Table 3). Pipeline weld seams can be exposed to greater corrosion destruction and instability to CDC [8]. These areas affected by thermal impact will

have heterogeneity with respect to the parent pipe surface, and therefore may be subject to increased corrosion hazard in the case of CDC.

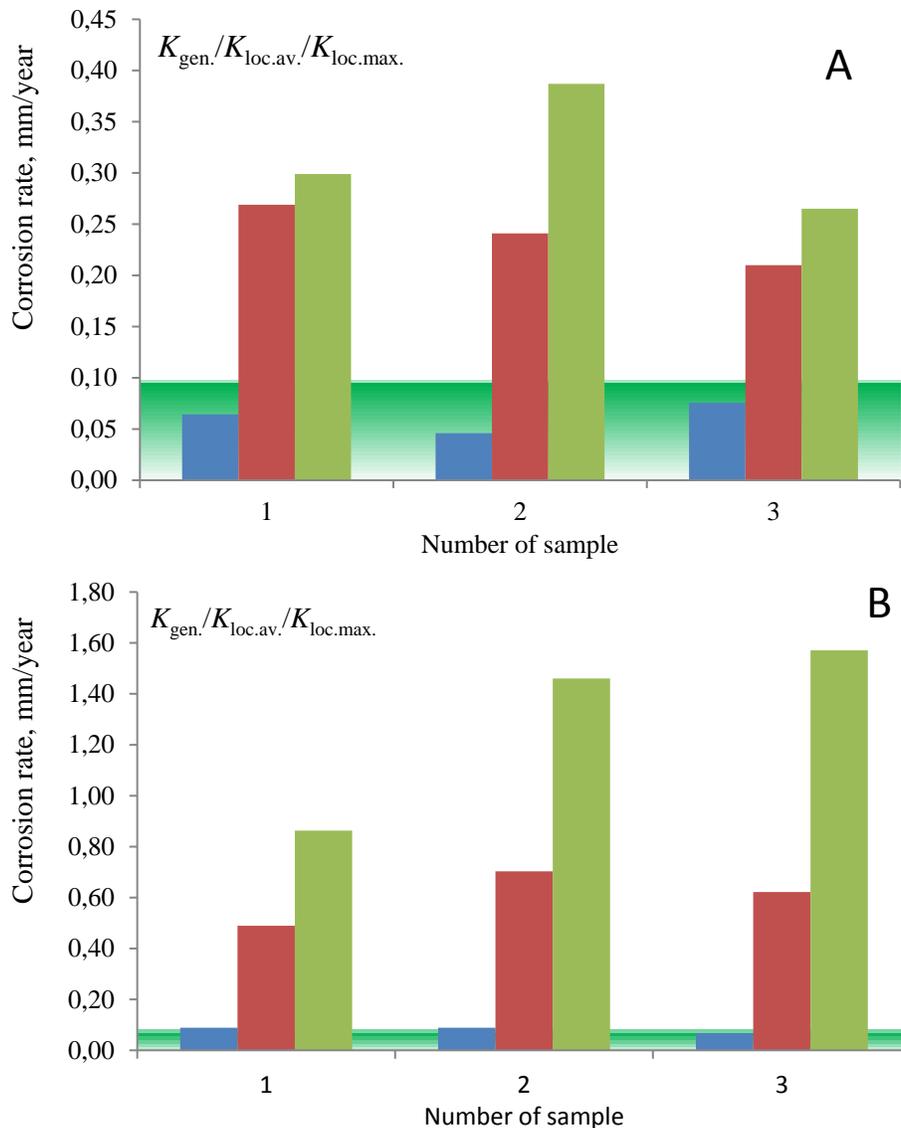


Figure 5. Comparison of steel corrosion rates: $K_{gen.}/K_{loc.av.}/K_{loc.max.}$: A – parent pipe; B – weld seam [28].

An additional point is that the weld reinforcement can result in possible delay and accumulation of aqueous liquid before and after it. The results of TOL tests of X65 steel samples cut from the parent metal (“pipe body”, without a weld seam) and with a welded seam (in the middle of the specimen) are showed in Figure 5 and in Table 4. According to our research, the local corrosion rate measured by the depth of corrosion damage totals 0.265–0.387 mm/year during condensation and the creation of a thin film of moisture in the presence of CO₂ on the parent pipe samples. Under the same conditions, the growth rate of local damage in weld seam can reach up to 0.867–1.571 mm/year (Figure 5). In TOL

conditions, the CDC develops on a weld seam 3–4 times faster than on a parent pipe sample. Table 4 shows that after the tests, the appearance of the weld seam specimen differs in color, with local defects mainly in the welded zone.

Steel samples were tested under moisture condensation conditions to evaluate the impact of different CO₂ content (partial pressure): for CO₂ (0, 25, 50, 75 and 100%), the partial pressure totaled 0; 0.025; 0.05; 0.075 and 0.1 MPa CO₂ respectively. For such condensation conditions, corrosion defects were localized on the surface of metal samples as multiple pits (Table 5).

Table 4. General view of parent pipe and weld seam specimens after removal of corrosion products [28].

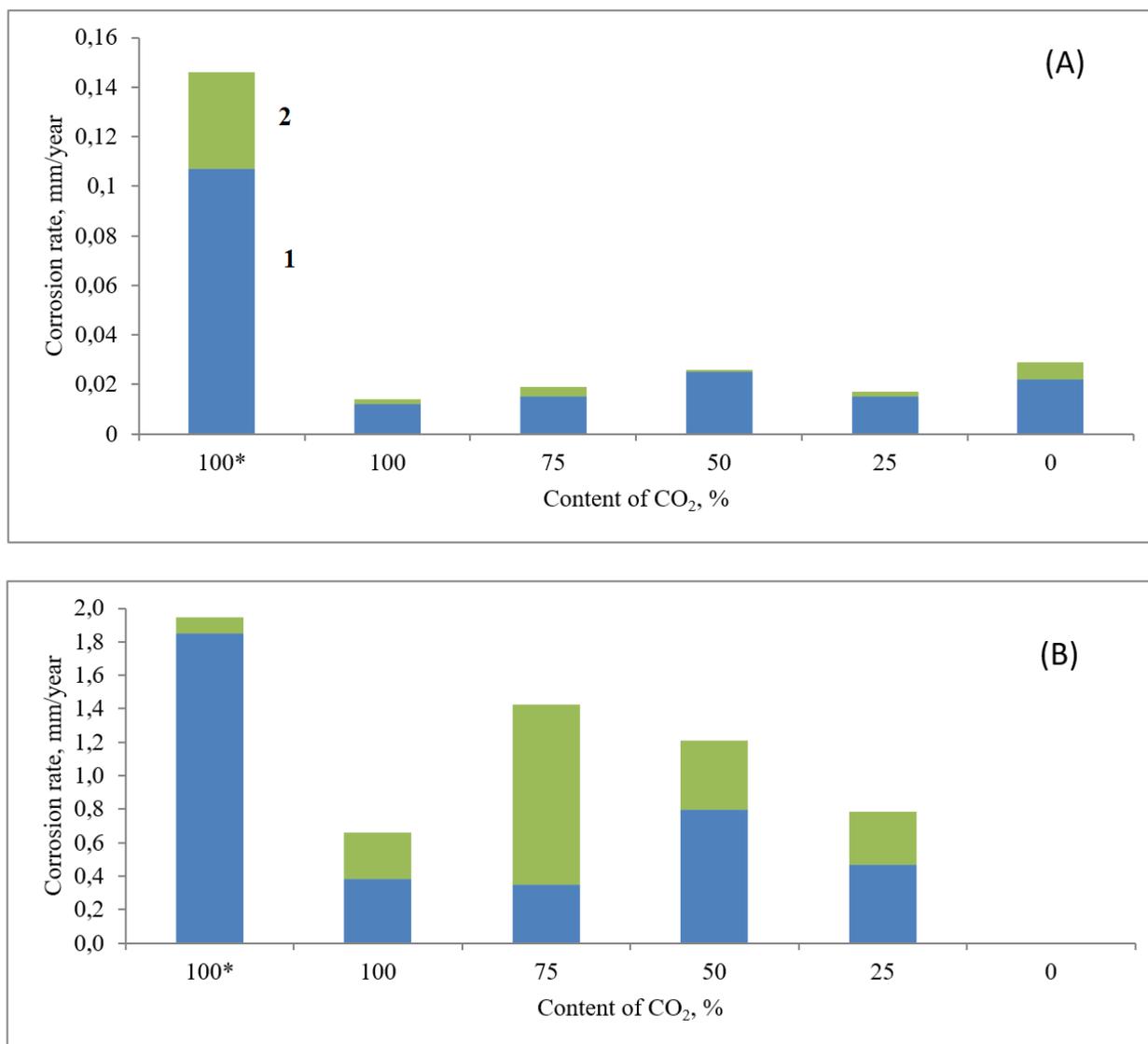
Number of the sample	General view	
	Parent pipe	Weld seam
1		
2		
3		

Figure 6 provides summary 09Mn2Si pipe steel test data for moisture condensation in the presence of CO₂.

According to Figure 6A, the K_{gen} is below 0.03 mm/year at room temperature under experimental conditions (20–25°C) for steels tested at all CO₂ contents (0–100%). But it increases 10 times, when the temperature drops to 15°C from a higher value (50°C), and the amount of precipitated moisture increases compared to the initial values of 20–25°C. General corrosion values exceed 0.1 mm/year with a larger temperature gradient.

A similar tendency is observed with a local corrosion, which grows 2–3 times with a temperature increase (from 20–25°C to 50°C). Figure 6B provides data on the maximum local corrosion calculated by the deepest pitting. In the absence of CO₂, local corrosion defects are not formed. With an increase in CO₂ content (from 25 to 75%), the rate of local corrosion also increases, which is significantly higher than 0.1 mm/year, and according to the

test results reaches 1.43 mm/year. Then it slightly decreases with a further increase to 100% CO₂.



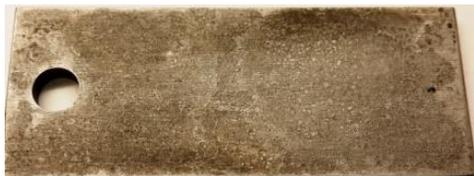
* test at elevated temperature 50°C corrosion.

Figure 6. The rate of corrosion measured on carbon steel samples in the presence of CO₂ under water condensation conditions, temperature 20°C: A – general corrosion; B – local corrosion. 1 – average value; 2 – difference between maximum and average values.

Perhaps this is due to the formation of corrosion products (iron carbonate): at 100% CO₂, the siderite, which forms more intensively and fills the pits on the steel surface at depth, prevents the deeper development of local defects. FeCO₃ precipitate in pitting can create difficulties in the supply of corrosive agents deep into the defect [38]. The appearance of specimens with local defects after testing shown in Table 5 confirms that at 75 and 100% CO₂ the number of defects is comparable, but the depth of the deepest ones is higher at 75%

(Figure 6B). When analyzing this case, the following should be noted: the value “1” in Figure 6 means the average K , and “2” – the difference between the maximum and average K values.

Table 5. Appearance of samples after tests with different CO₂ content at room temperature (20–25°C).

25% CO ₂	75% CO ₂
	
50% CO ₂	100% CO ₂
	
at elevated temperature (50°C) and 100% CO ₂	
	

Produced hydrocarbons may contain carboxylic acids, for example, CH₃COOH, which, due to their volatility, especially at high temperatures, will make the TOL condensed aqueous medium more acidic and intensify steel corrosion [39, 40]. TOL corrosion tests conducted under condensation of a liquid containing CH₃COOH and in the presence of CO₂ showed that there is an increase in the localization of defects on steel (Table 6). The general corrosion rate remains relatively low, while localized corrosion develops. The addition of CH₃COOH to the evaporated liquid provides 2–3 times increase in local defects in comparison with a non-acidic aqueous solution. A similar increase in TOL corrosion under CDC conditions and the presence of CH₃COOH was observed by foreign researchers [41, 42].

The resulting corrosion products (iron carbonates) can have a certain protective effect, which decreases under acidic conditions. The addition of CH₃COOH shifts the pH factor in the condensed moisture film to more acidic values, at which the formed corrosion products dissolve [43–45].

Table 6. The general and local corrosion rates measured on the same carbon steel samples St20 under moisture condensation conditions (distilled water) in the presence of 0.1 MPa CO₂, temperature 20°C [8].

Concentration of CH ₃ COOH, mg/L	$K_{gen.}$, mm/year	$K_{loc.av.}/K_{loc.max.}$, mm/year	View of steel samples after tests
0	0.02	0.32/0.384	
250	0.05	0.373/0.527	
1000	0.05	0.81/1.015	

Conclusions

TOL corrosion tests showed that the majority of carbon and low-alloy steels (Steel 20, 09Mn2Si, X65, *etc.*) can be exposed to local corrosion in the operating conditions of gas production facilities in the presence of CO₂ and moisture condensation. Alloys with a high chromium content are the most resistant in such a harsh environment. A larger temperature gradient of the medium and the steel surface leads to a greater condensation of moisture, and accordingly to an increase in local corrosion.

Tests indicate that initiation of TOL corrosion requires a high humidity level in the vapor environment sufficient for moisture condensation on the steel surface. The presence of CH₃COOH in the medium leads to an increase in the rate of TOL corrosion and the depth of local defects.

Weld seams and heat-affected zone are heterogeneous with respect to the parent pipe surface, and are more exposed to TOL corrosion. Local defects are mainly located on the weld seam and in the heat-affected zone of the steel specimen.

In a water-alcohol environment, the alcohol content of the condensate water on steel plays an important role in TOL corrosion tests, rather than the evaporated liquid. When the concentration of alcohol in water is 75–80% and higher, corrosion can slow down, and CDC in the film of liquid condensed can be suppressed.

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