Recommendations for Increasing the Durability of Oilfield Pipes Working in aggressive CO_2-Containing Environment

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Abstract. The present paper aims to give recommendations for improving the durability of seamless oilfield pipes used in CO_2-containing environments. It also focuses on the problem of selecting steel grades needed for their production. We analysed the regulatory and technical documentation currently used by oil companies, namely the technical requirements for the quality of pipe products. It has been found that the reviewed normative documents make requirements for the resistance of steel to hydrogen induced cracking (HIC) and stress corrosion cracking (SSC), referring to the relevant standard test methods. All these normative documents lack information on methods for assessing resistance in CO_2-containing environments. Furthermore, the paper analyses—literature data on corrosion mechanisms and on the influence of alloying elements present in steel on corrosion attack rate. The research has shown that in order to solve the issue of low durability of oilfield pipes, it is to properly choose the material used for pipe manufacturing. Of a particular interest is a complex steel alloying, including synergistic effect, which may allow replacing expensive alloying elements, reduce the cost of steel and, improve its mechanical and corrosive properties. This type of material will increase the durability of seamless oilfield pipes that operate in aggressive CO_2-containing environments.

Keywords: Oilfield pipes · Material selection · Corrosion resistance

1 Introduction

The majority of oil fields in Russia (Western Siberia, Eastern Siberia, Volga Region, Ural and others) are characterised by high corrosiveness of the produced oilfield environment. The high aggressivity of the environments is related to the increased concentration of CO_2, H_2S and chlorides. Consequently, it is of great importance to study the problem of development and selection of materials for manufacturing pipes that possess sufficient corrosion resistance. It should be noted that, generally, the use of stainless steels is not economically justified due to the great length of pipelines. Therefore, low-alloy steels are frequently used in oilfield pipes manufacturing.

In order to develop recommendations that will help to increase the durability of oilfield pipes, the following analyses were carried out:

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- Analysis of normative and technical documentation for the presence material requirements of oilfield pipes operating in aggressive environments.
- Analysis of literature data on corrosion mechanisms and on the influence of alloying elements present in steel on corrosion attack rate.

2 Analysis of Normative and Technical Documentation Currently Used by Oil Companies

Requirements for seamless oil and gas pipes are formulated both by consumers—oil companies and manufacturers—and pipe mills. We analysed technical requirements of two major domestic oil companies—PJSC Gazprom Neft [1] and PJSC Rosneft Oil Company [2], as well as the technical specifications of the two largest manufacturers of seamless pipes: PJSC TMK [3] and PJSC ChelPipe Group [4]. The international standard for oil and gas pipes API Spec 5L [5] was considered for comparison.

The regulatory documents of oil companies contain not only requirements for pipes, but also a ranking of oilfield environments according to their corrosiveness. Oil company documents specify several levels of pipe requirements:

- general-purpose pipes;
- cold-resistant pipes;
- pipes resistant to stress corrosion cracking in hydrogen sulphide-containing environments;
- pipes with enhanced resistance to stress corrosion cracking in environments containing CO_2; these pipes are generally resistant to stress corrosion cracking in hydrogen sulphide-containing environments.

A wide range of chemical compositions of steel used in the production of general-purpose and cold-resistant pipes is currently accessible to manufacturers. With a rational choice of composition, mechanical properties and impact strength can be obtained relatively easily by volume heat treatment of pipes.

During the analysis of the regulatory documentation, it has been established that:

1. PJSC Gazprom Neft's document does not clearly indicate what groups of pipes should be used in the highlighted groups of corrosive environments. The scope of use of hydrogen sulphide resistant pipes can be determined by referring to ISO 15156 [6] or the guidelines (Table 1). The scope of use of CO_2 corrosion resistant pipes is not defined by the standard.
2. PJSC Rosneft Oil Company's regulatory document provides a classification of operating environments according to the degree of aggressive impact on pipes depending on the concentration of H_2S and CO_2, O_2 and salinity of the produced water (Table 2). As in the case of PJSC Gazprom Neft's document, the given classification differs from that of the international standard ISO 15156.
   Depending on oxygen, water and salinity content of the environment, an additional division is introduced for the environments containing $P_{H_2}S < 300\,\text{Pa}$ and $P_{CO_2} <$

Table 1 Data on the ranking of transported environment based on the content of aggressive components

No.	Classification of operating environments based on the degree of aggressive impact	Partial pressure H_2S, [Pa]	Partial pressure CO_2, [Pa]	Additional requirements
1	With a high content of hydrogen sulphide	$PH_2S > 350$*	$Pco_2 \geq 200{,}000$**	With oxygen content over 0.3 [mg/l]
2	With a low content of hydrogen sulphide	$PH_2S < 350$*	$Pco_2 \geq 200{,}000$**	With oxygen content under 0.3 [mg/l]

*Requirements for the material used in pipes operated in environments with increased concentration of H_2S are specified in GOST R 53678-2009 [6]
**There is no normative documentation stipulating the material requirements for pipes operated in environments with elevated concentrations of CO_2

50,000 Pa. For environments of class 0.A, steel pipes with impact strength requirement and no corrosion resistance requirement are recommended. For Class 0.B environments, local corrosion resistance of steel is regulated. It should be noted that the term "local corrosion" is not defined in the standard, and it is proposed to perform tests in iron chloride solution according to GOST 9.912 [7]. The GOST describes a testing of stainless steels, while Rosneft's document covers only low-alloy and carbon steels. The usefulness of GOST 9.912 for testings of low-alloy steels is not clear.

For environments with a high content of corrosive gases, the use of pipes with a specified resistance to stress corrosion cracking is prescribed. For such steels, testings complying with the internationally recognised standards for oil pipes, NACE TM0177 [8] and TM0284 [9] are recommended.

3. The international standard ISO 15156 can be used for evaluating the oilfield environments' potential of inducing stress corrosion cracking and selecting an appropriate grade of pipe steel. There are no standard methods for selecting pipe materials that are resistant to other types of corrosion typical of oilfield environments, such as pitting corrosion in environments containing CO_2 and H_2S, microbiological corrosion, corrosion-erosion wear and others.
4. The above normative documents set out requirements for the resistance of steels to HIC and SSC cracking by, referring to the relevant standard test methods. None of the normative documents provide information on methods of evaluating resistance to CO_2-containing environments. There is no indication of the acceptable values for general local corrosion.
5. All of the given normative documents do not specify requirements for environments containing corrosive bacteria (SRM, TB, IOB, HOB). They may exacerbate corrosiveness of the transported environment by enhancing local degradation. Technical

Table 2 Classification of operating environments based on the content of aggressive components

No.	Classification of operating environments based on the degree of aggressive impact	Partial pressure H_2S, [Pa]	Partial pressure CO_2, [Pa]	Operating environment designation
1	None	$P_{H2S} < 300$	$P_{CO_2} < 50{,}000$	0.A Water environments: salinity <5 [g/l]; water–oil environments: O_2 content <0.1 [mg/l];
2				0.B Water environments: salinity >5 [g/l]; water–oil environments: O_2 content >0.1 [mg/l]
3	Low	$P_{H2S} < 300$	$P_{CO_2} \geq 50{,}000$	1
4	Low	$300 \leq P_{H2S} < 10{,}000$	$P_{CO_2} < 50{,}000$	1
5	Medium	$300 \leq P_{H2S} < 10{,}000$	$P_{CO_2} \geq 50{,}000$	2
6	Medium	$10{,}000 \leq P_{H2S} < 1{,}000{,}000$	$P_{CO_2} < 50{,}000$	2
7	High	$10{,}000 \leq P_{H2S} < 1{,}000{,}000$	$P_{CO_2} \geq 50{,}000$	3
8	High	$P_{H2S} \geq 1{,}000{,}000$	$P_{CO_2} \geq 50{,}000$	3

and normative documentation should stipulate the method of analysis of the transported environment not only for planktonic forms of bacteria, but also for attached bacteria, as well as to evaluate the amount of bacteria and index of their biochemical activity.

6. The preliminary analysis of oil companies' standards shows that hydrogen sulphide—resistant pipes are frequently used by both PJSC Rosneft Oil Company and PJSC Gazprom Neft. Such pipes of strength class K52 can be manufactured with proper selection of chemical composition and heat treatment conditions for pipes.
7. Steels alloyed with 0.5–1% chrome are used for making pipes with enhanced resistance to carbonic corrosion. Such pipes are described only in PJSC Gazprom Neft's documentation. PJSC Rosneft Oil Company restricts the use of chrome containing steels.

3 Analysis of Literature Data on the Influence of Alloying Elements on CO_2 Corrosion Resistance of Steel

Carbon dioxide corrosion is a complex process affected by a large number of parameters:

- Properties of the transported environment: chemical composition, temperature, flow velocity;
- Physical and metallurgical properties of steel: chemical composition, heat treatment, microstructure, mechanical properties and others.

The characteristic feature of CO_2 corrosion is the local nature of the damage. It is difficult to predict the rate of growth of corrosion pits, as well as their place of formation.

It should be noted that the majority of Western Siberian, Eastern Siberian, Volga and other fields are characterised by the presence of high concentration of CO_2 in the transported environment. The problem of oilfield equipment failure due to carbon dioxide corrosion is urgent and requires developing measures to prevent it.

Numerous publications investigate the mechanism of carbon dioxide corrosion. The majority of publications focus on the influence of the characteristics of the environment and do not provide data on the influence of the chemical elements present in steel composition on its resistance to CO_2 corrosion [10, 11].

In order to tackle the problem of carbon dioxide corrosion, it is necessary to have reliable information about the mechanism of corrosion and the influence of the alloying elements present in steel on corrosion attack rate. We examined publications that relate, depending on experimental conditions, chemical composition of steels and their structure to the CO_2 corrosion rate. The complexity of comparative analysis is due to the fact that the authors determine the corrosion rate by different methods.

Despite the use of different techniques for evaluating the corrosion rate of metal given in articles [12–20], the same pattern in the behaviour of steel in the presence or absence of certain alloying elements is observed.

Steels with a content of about 1.5% of manganese (without chromium) showed a high corrosion rate which indicates low corrosion resistance of manganese alloys in an aggressive environment.

The articles indicate that the strongest effect is caused by alloying with chromium. When the concentration of this element increases, the corrosion rate decreases significantly. This fact is confirmed by the results of laboratory experiments in all reviewed articles.

The effect of molybdenum and copper on corrosion resistance is ambiguous. However, this fact requires further investigation as the experiment was conducted on steels with a higher manganese content.

The main parameters affecting the rate of carbonic acid corrosion are the following:

1. Test temperature;
2. pH and chemical composition of the test environment;
3. Steel chemical composition;
4. Steel microstructure and its heat treatment;

These papers show that no definite answer can be given as to the effect of alloying elements, heat treatment and microstructure on the corrosion resistance of steel. The results are ambiguous and require further research. In order to select the optimal chemical composition of steel and the percentage of alloying elements, it is necessary to study the physical and chemical processes taking place on the boundary between metal and environment, as well as the influence of the above parameters (temperature, pH, chemical composition, microstructure and heat treatment).

The complex alloying of steel is of interest. It includes a synergistic effect that can replace expensive alloying elements, reduce the cost of steel and increase mechanical and corrosion properties. The choice of heat treatment must take into account that if the elements necessary to make the steel resistant to CO_2 corrosion are in a bound state (carbides, nitrides), the effect of corrosion resistance will be reduced.

4 Conclusion

1. The main operating normative documents of manufacturers (PJSC Gazprom Neft and PJSC Rosneft Oil Company) and their technical requirements for the quality of pipe products were reviewed and analysed. The classification of corrosive properties of oilfield environments formulated in the above documents does not comply with the generally accepted international practice; therefore, it raises doubt about its adequacy. The standards impose only very general requirements on pipes designed for transportation of environments containing H_2S and CO_2; the level of properties regulated by the oil company documentation is lower (for PJSC Rosneft Oil Company document) or significantly lower (for PJSC Gazprom Neft document) than standard requirements of the international document API Spec 5L, PSL-2, Appendix H.
2. Oil companies use low-alloy pipe steel which is suitable for transportation of CO_2-containing environments and has an increased resistance to pitting corrosion. It is possible to increase steel resistance to carbon dioxide corrosion by the use of economical alloying with 0.50–1.0% chrome and other elements (V, Cu, Si, Mo and others). The development of the chemical composition of such steel and the technology of its heat treatment should be considered as a promising task. The solution of this problem is made more difficult by the following factors:

   - Absence of a generally accepted methodology for assessing the carbon dioxide corrosion resistance of steel
   - The restriction of chromium content in steel to no more than 0.5% adopted in PJSC Rosneft Oil Company's normative documentation and API Spec 5L.

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