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PETRYNA DMYTRO
Ivano-Frankivsk National Technical University University of Oil and Gas
https://orcid.org/0000-0003-0663-746X
e-mail: pepperiko@ukr.net

CORROSION RATE COMPARISON OF LOW-CARBON PIPES STEEL IN VARIOUS AGGRESSIVE ENVIRONMENTS

Low-carbon steel is the main material for the production of main oil and gas pipelines. Currently, X70, X80 type steels are used in world practice, however pipelines that have been in operation for more than 45 years were made of 17Г1С (X50, X52) steels. Steels of the new generation X100 and X120 have improved strength indicators and therefore they are increasingly used for the manufacture of high-pressure pipelines and marine pipelines. Corrosion of the internal and external parts of pipes is the main factor in failure of pipelines. Aggressive environments and places of their action will cause different types of corrosion. During the operation of low-carbon pipe steels, their corrosion rate was investigated under different operational parameters and environments. The main results of many researchers do not always coincide with each other, and therefore the comparison of corrosion rates for pipe steels of different generations is relevant today. The influence of aggressive environments on the corrosion rate of low-carbon steels of different generations was studied, with possible consideration of similar operating parameters and types of these environments. Different electrochemical parameters for all generations of steels are compared. The most sensitive parameters of corrosion resistance, which respond to the difference in environments and pipe materials, have been determined. It was found that a more aggressive environment and extreme operating characteristics for different steels give a clearer difference in determining the rate of corrosion. It was established that for a more aggressive environment, the difference in the rate of corrosion for different steels becomes more significant. The best indicators of corrosion resistance in various aggressive environments were shown by X70 and X80 steels, while X80 steel is the leader in corrosion resistance in many studies. Steel 17G1C, as expected, showed the worst indicators. Steels of the new generation X100 and X120 showed a worse level of corrosion rate than steel X80, but the best strength indicators are the main factor in their selection as pipeline materials that work in critical conditions.

Key words: pipe steels, corrosion of metals, gas and oil pipelines, electrochemical parameters, corrosion rate, corrosion permeability.

ПЕТРИНА ДМИТРО
Ivano-Frankivsk National Technical University University of Oil and Gas

ПОРІВНЯННЯ ШВИДКОСТІ КОРОЗІЇ НИЗЬКОВУГЛЕЦЕВИХ ТРУБНИХ СТАЛЕЙ У РІЗНИХ АГРЕСИВНИХ СЕРЕДОВИЩАХ

Низьковуглецеві сталі є основним матеріалом для виробництва магістральних нафто- і газопроводів. В даний час у світовій практиці використовуються сталі типу X70, X80, проте трубопроводи, які експлуатуються більше 45 років виготовлялися зі сталей 17Г1С (X50, X52). Сталі нового покоління X100 та X120 мають покращені показники міцності і тому їх все частіше застосовують для виготовлення трубопроводів високого тиску, та морських трубопроводів. Корозія внутрішньої і зовнішньої частин труб є основним фактором виходу з ладу трубопроводів. Агресивні середовища та місця їх дії будуть спричиняти різні типи корозії. На протязі експлуатації низьковуглецевих трубних сталей досліджувалася їх швидкість корозії при різних експлуатаційних параметрах та середовищах. Основні результати багатьох дослідників не завжди співпадають між собою і тому проведення порівняння швидкості корозії для трубних сталей різних поколінь є актуальним на сьогоднішній час. Досліджено вплив агресивних середовищ на швидкість корозії низьковуглецевих сталей різних поколінь з можливим врахуванням подібних експлуатаційних параметрів та видів цих середовищ. Порівняно різні електрохімічні показники для всіх поколінь сталей. Визначені найбільш чутливі параметри корозійної стійкості, які реагують на різницю середовищ та матеріалів труб. Виявлено, що більш агресивне середовище та екстремальні експлуатаційні характеристики для різних сталей дають більш чітку відмінність у визначенні швидкості корозії. Встановлено, що для більш агресивного середовища різниця в швидкості корозії для різних сталей стає більш істотною. Найкращі показники корозійної стійкості в різних агресивних середовищах показали сталі X70 та X80, при цьому сталь X80 є лідером по корозійній тривкості у багатьох дослідженнях. Сталь 17Г1С очікувано показала найгірші показники. Сталі нового покоління X100 та X120 показали гірший рівень швидкості корозії ніж сталь X80, проте найкращі показники міцності є основним чинником їх вибору в якості матеріалів трубопроводів, які працюють в критичних умовах.

Ключові слова: трубні сталі, корозія металів, газонафтопроводи, електрохімічні показники, швидкість корозії, корозійна проникність.

Introduction

Steel main pipelines are the main and cheapest method of transporting gas and oil over considerable distances. About 60% of pipeline failures are associated with corrosion of pipe materials. Both internal and external corrosion of pipes are distinguished. In this comparison, we will consider internal corrosion, which will fundamentally affect the performance of pipeline transport and which is difficult to detect by non-destructive control methods, and partly external corrosion, which will occur due to damage to the external protection of pipes. The main factors that affect the intensity of corrosion are the temperature of the environment, the working pressure of the gas, the concentration of hydrogen sulfide and low molecular weight carboxylic acids in the water condensate of the gas, the exposure time, the static or dynamic state of the corrosive environment [1-11]. The rate of corrosion will also depend on the place of contact with an aggressive environment (top-bottom). The duration of operation will also have a significant effect on the corrosion resistance of pipeline materials.

Analysis of recent sources

The corrosion process will contribute to the formation of a sulfide film on the surface of the pipe metal and, thus, will serve as a kind of protection against further corrosion penetration and destruction of the pipe wall [1]. Different generations of pipe steels and different operating conditions of pipelines will affect the speed of this process. The chemical composition of the steel will be the main factor that will affect the composition and speed of the sulfide film and the further course of this process [1].

The use of new generation steels poses new challenges to pipeline corrosion researchers. Such studies are conducted under different conditions and corrosion factors, which does not make it possible to draw unambiguous conclusions and systematize the results. Comparison of the corrosion rate for steels of different generations requires the analysis of previous studies and the formation of a single method for further studies.

As materials for comparison, we will consider pipe steels of three generations. First of all, these are low-carbon steels of the 17Г1С type (X50, X52 according to the АРИ classification), which are the main material of pipelines on the territory of Ukraine, the second generation are X60, X70 and X80 steels, which have proven themselves well as the main material of pipelines in the whole world and showed good characteristics of corrosion resistance under different modes of operation [4-6] . High-strength low-carbon steels X100 and X120 were intended for pipelines that are operated at high pressure and show a fairly high level of corrosion speed, however, with longer exposure in an aqueous solution, a homogeneous sulfide layer forms on the surface of such materials, which will protect the main material from further exposure to a corrosive environment [7, 8, 10, 11]. The main need for such steels is to reduce the cost by reducing the thickness of the pipe wall due to increasing the strength of pipelines when transporting hydrocarbons over long distances.

The main purpose of this study is the possibility of comparing the corrosion rate of different types of pipe steels of different generations and identifying the difference in this process. Determine the most sensitive indicators characterizing corrosion resistance and give recommendations for further comparative studies.

Main studies

The chemical composition of steels and the manufacturing technology are one of the main factors affecting the mechanical characteristics of pipe steels and their corrosion resistance. Let's consider the main chemical composition of the studied steels and, to compare the main components, present them in Table 1.

Table 1

Chemical composition of the studied steels

Steel	C	P	S	Si	Mn	Cu	Al	Ni	Mo	Nb	Ti
17Г1С	0,2	0,01	0,04	0,4	1,3	0,1	0,04	0,15	-	-	-
X70	0,06	0,08	0,01	0,25	1,65	0,2	0,026	0,18	0,1	0,04	-
X80	0,04	0,06	0,002	0,22	1,88	0,23	0,04	0,26	0,29	0,1	-
X100	0,065	0,002	0,04	0,95	1,69	0,2	0,046	0,03	0,27	0,055	0,01
X120	0,049	0,002	0,04	0,101	1,96	0,2	0,04	0,03	0,32	0,012	0,07

As can be seen from Table 1, steel 17Г1С has the highest percentage of carbon, steels X70 and X80 have an increased percentage of manganese, which will significantly increase strength indicators. The main difference between these steels is the sheet rolling technology. For steels of the newer generation, modern high-temperature rolling is used with the addition of an alloying element of niobium, which will create a structure of acicular ferrite. Such a manufacturing process will contribute to obtaining better mechanical characteristics, and a low percentage of carbon will improve the weldability of such steels. Since the composition of the pipe material is one of the key points that will affect the rate of corrosion processes, it is necessary to focus on their differences.

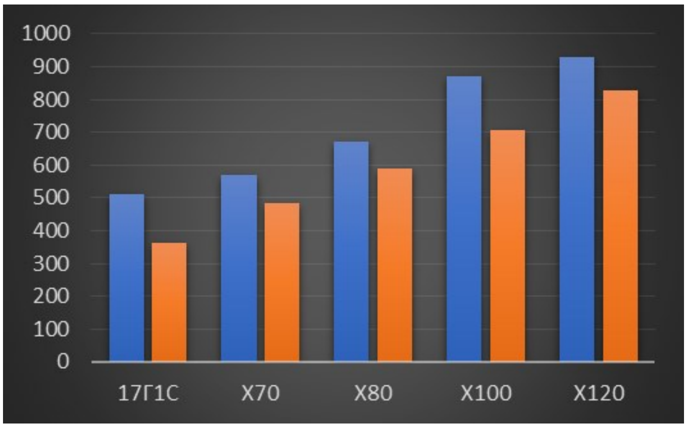

Fig. 1. Strength characteristics of pipe steels

The technological process of rolling sheets of X100 and X120 steels allows obtaining a stronger bainite structure [10, 11] . At the same time, X100 steel gets an upper bainite structure, and the improved rolling technology for X120 steel and the introduction of titanium as an alloying element allows us to get a lower bainite structure, which is close in structure to martensite. For such a steel, the strength characteristics will increase with an increase in the percentage of carbon. The main strength characteristics of the studied steels are presented in Figure 1.

Our studies [1, 2] show that the use of electrochemical indicators has prospects for technical diagnosis of the state of materials of long-term operational structures. The number of electrochemical indicators that can potentially be used for this purpose may include corrosion potential E_{cor}, Tafel coefficients в_aand в_c, current at a certain anodic potential and corrosion current j_{aand} j_{cor}, accordingly, polarization resistance R_p.

Among all the electrochemical characteristics of pipe steels, the highest sensitivity to all the above-mentioned factors that will affect the level of corrosion in a model solution of water condensate is shown by polarization resistance R_p and corrosion potential E_{cor} [1].

To compare the corrosion indicators, it is difficult to comply with the conditions for the coincidence of all the operational factors listed above. Therefore, to begin with, we will consider the influence of the critical temperature on the polarization resistance. For comparison, the data for steels were taken, which were studied, if possible, under the same conditions of concentration of hydrogen sulfide as the main factor of corrosion. The corrosion rate increased most intensively at temperatures from 40 °C to 70 °C and reached a maximum at 60-70 °C [1-9].

Comparison of the corrosion rate was carried out with the possible selection of the same characteristics of environments that will affect the corrosion rate. We used a 3% NaCl solution with different levels of hydrogen sulfide saturation from 0 to 20 mg/m 3 , an aqueous emulsion of oil transportation products (H_2S concentration of 7 mg/m^3), and a soil solution with a hydrogen sulfide concentration of 7 to 20 mg/m^3 . The research temperature was taken in the range from 300K to 340K, the pressure in the pipes p=0.1MPa. Saturation with hydrogen sulfide was controlled using controllers followed by measurement of electrochemical parameters and pH level .

The study of the effect of temperature on the intensity of corrosion damage of the gas pipeline material was carried out in an environment that was a mixture of natural gas with hydrogen sulfide concentration of 20 mg /m^3 . Initially, the working pressure was constant and was 0.1 MPa. The results of the comparison are presented on the diagrams below (figure 2, figure 3).

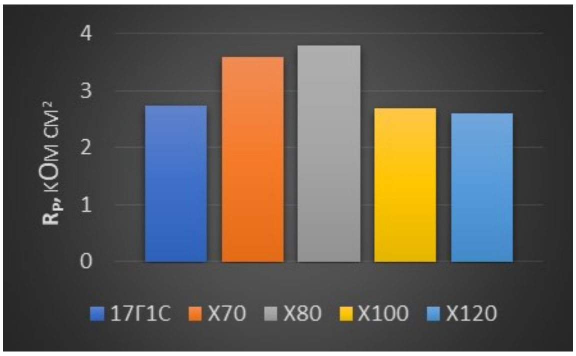

Fig. 2. Comparison of polarization resistance R_p for different pipe steels

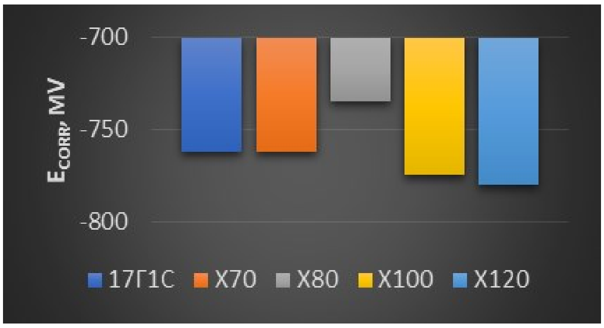

Fig. 3. Comparison of corrosion potential E_{cor} for different pipe steels

Comparing the effect of hydrogen sulfide saturation in a 3% NaCl environment among many posts, it should be said that under such conditions, the formation of a sulfide protective film takes place the fastest at the maximum concentration of H_2S , while the rate of further corrosion decreases sharply. Aqueous emulsion of oil transportation products and soil solution with different concentrations of hydrogen sulfide showed a slower corrosion process, however, the formation of a protective film was also unstable, which means that at a certain speed of movement of substances, not such a stable coating and protection is possible. It should be noted that when oil is transported for a long time, a paraffin layer forms on the surface of the pipes, which will help protect the surface and change the type of corrosion (bacterial).

Therefore, it should be noted that any comparative studies of the corrosion rate in different environments for different steels must be carried out under the most critical operating factors that could give excellent results. Under such conditions, the influence of additional factors, namely the period of operation, the influence of watering, the influence of another bacterial environment or carboxylic acids would be insignificant, and the anti-corrosion characteristics would be more pronounced for the comparison of different steels. Also, these comparative studies must be conducted under as similar conditions as possible, because the synergistic effect of additional factors can be critical in changing the type of corrosion and its speed.

The rate of corrosion is not a constant value throughout the year, because changes in temperature and operating parameters, instability of the structure of the hydrogen sulfide solution will affect the speed of this process. In this work, indicators were compared with fairly similar input parameters. This study is an attempt to summarize own results and data of other authors and draw initial conclusions and make recommendations for further research. Therefore, the results of comparing the corrosion rate for different pipe steels in different corrosive environments are presented in fig. 4.

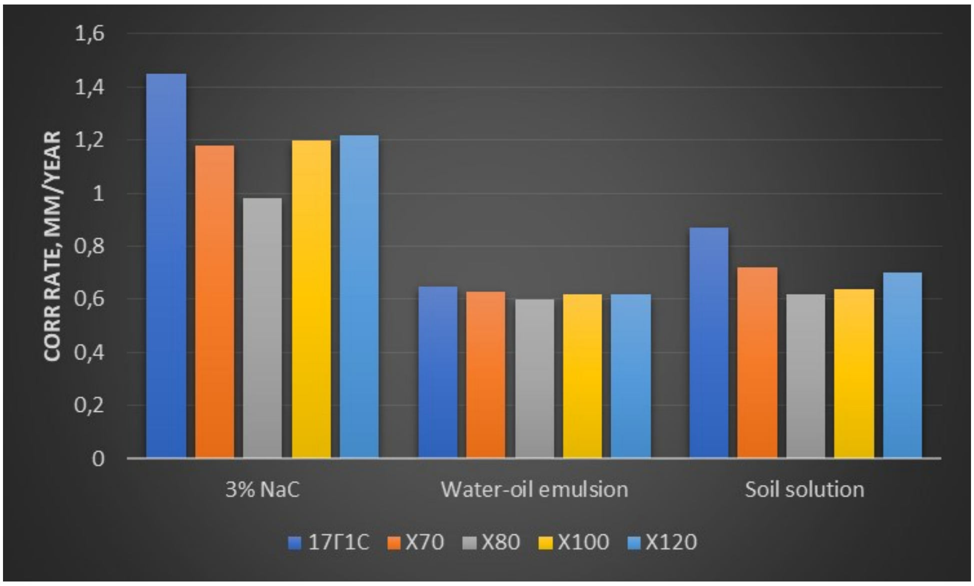

Fig. 4. Corrosion rate of various pipe steels in various aggressive environments

Steel 17Г1С showed the worst corrosion rate indicators among other pipe steels under similar operating conditions. Outdated rolling technology, variations in the chemical composition of different samples and the highest level of carbon are the main factors of such results. However, it should be said that this difference is not critical and, under moderate operating factors, it shows the same results as modern steels under more aggressive operating conditions. This steel is the main steel of pipelines built 50 or more years ago and there is a large amount of stock pipe used to repair emergency areas, so its use is a cheaper alternative to modern steels. For pipelines that have been in operation for more than 40 years, it is necessary to take into account the level of hydrogen degradation, which will significantly worsen the corrosion resistance of these steels.

The updated rolling technological process and improved chemical composition for X70 and X80 steels make it possible to obtain better mechanical indicators. These steels are the main materials of most oil and gas pipelines that have been built in the last 30 years around the world and have shown good operational performance and behavior under critical conditions. In our comparative study, X70 and X80 steels showed the best results in corrosion resistance. X80 steel is the leader in all investigated indicators.

Steels of the new generation X100 and X120 are increasingly used for the construction of oil and gas pipelines that work under high pressure and as marine pipelines. Also, pipes made of these steels are used for major repairs of pipelines made of other types of steel. Improved mechanical characteristics due to the updated technological process of rolling and changed chemical composition allow to reduce the thickness of the pipe wall and, thereby, to save on material capacity. Since the corresponding steels began to be used not so long ago, there are few experimental data on their corrosion resistance and quite often they are contradictory. However, most researchers claim that the corresponding steels have worse corrosion rates than X70 and X80 steels.

The production of large-diameter pipes, as the most economically expedient method of transporting hydrocarbons, is constantly being improved and changed to ensure the main mechanical characteristics of the material, such as strength, weldability, corrosion resistance. Along with new materials, there is a large number of pipelines made of pipe steels of an older generation. As the mechanical characteristics and chemical composition of steels change, the susceptibility of the material to corrosive destruction changes, which must be investigated and controlled.

Conclusion

X70 and X80 steels showed the best indicators of corrosion resistance among other steels of different generations, and the best results were expected to be shown by X80 steel. The worst indicators of the corrosion rate of steels of type 17Г1С (X50, X52) are caused by the increased carbon content and the outdated technological process of rolling and possible hydrogen degradation. New generation X100 and X120 steels show worse corrosion resistance compared to X80 steel. However, the improved mechanical characteristics are the basis of the fact that these steels will be a further priority for the production of oil and gas pipelines. More critical operating conditions and the presence of a more aggressive working environment reveal more sensitive steels to corrosion. A critical difference in one or another factor can lead to discrepancies in the results of research on the corrosion rate. For further comparative studies, it is necessary to focus on similar operating conditions and, if possible, to study the influence of some individual factor.

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