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Study of Corrosion and Mechanical Resistance of Structural Pipe Steels of Long-term Operation in Hydrogen Sulfur Containing Environments

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Abstract. Analysis of literature sources, as well as practical data indicate that the existing scientific, technical and technological developments to ensure reliable corrosion-mechanical resistance and durability of oil and gas pipelines and other shell metal structures of critical use and subordinate to the State Service for Mining Supervision and Industrial Safety of Ukraine largely find contradictions and uncertainty; there are no quantitatively substantiated recommendations for practical application in order to ensure corrosion and mechanical resistance of pipelines operating in technologically aggressive environments under alternating temperature and barometric conditions and loads; there is a need for a systematic study of the causes, conditions and mechanisms of corrosion and mechanical damage of long-term equipment, which will significantly increase the operational reliability of industrial equipment. Experimental studies have established the causes and substantiated the mechanisms of metal softening with increasing service life (from 0 to 25 years) that leads to its degradation, especially during long-term operation in corrosive environments. A method for forecasting the residual working (accident-free) life of pipeline metal structures has been developed, which makes it possible to purposefully regulate their operational condition. This allows the timely use of technical, design and technological measures to improve the performance of such structures. Numerous and diverse results of experimental tests of metal samples for various purposes have been obtained, which provide an opportunity to create a base for comparative analysis of steels in many parameters of crack resistance, which will become a reliable basis for scientific and practical substantiation of the equivalent replacement of some steel grades with other grades, taking into account technological loads, corrosive environments and others.

Introduction

Development and operation of oil and gas fields of Ukraine with complex engineering and geological conditions cause special requirements for the quality of pipes, welding, installation and insulation works in the construction of oil and gas pipelines, which are complex technical systems [1]. The destruction of such structures usually leads to significant economic and environmental consequences, as a result of which the operation of oil and gas pipelines is associated with danger to service personnel and environment and has its problems. Analysis of literature data [1-3] and the results of our own long-term observations shows that the main problems of industrial safety and reliability of pipeline structures are associated with their long service life.

According to the existing normative documentation [4-6] at the stage of designing industrial oil pipelines and manufacturing pipes, the estimated assessment of metal resistance to brittle fracture taking into account local crack resistance of metal under the influence of hydrogen sulfide degradation of its structural components is not provided. Only the level of ductility of the metal in the initial state is normalized by the relative value of impact strength [7]. The use of only one parameter of impact strength as the main characteristic of crack resistance of tubular steels does not guarantee trouble-free operation of pipelines. Moreover, in the process of operation in chemically aggressive environments with the simultaneous action of alternating loads on the walls of the pipes appear defects, cracks develop, metal weakens and screams as a result of fatigue and deformation aging. Due to the lack of reliable criteria for estimating the residual life of industrial pipelines, it is not possible to accurately predict their reliability and decide on further use. Therefore, this paper presents the results of many years of experimental research, which can be used as a basis for a new approach to solving an important and complex problem: prolongation of trouble-free, long-term operation of pipeline and generally shell structures, which includes sensitive to changes in the structure in local areas of the metal in the process of corrosion-hydrogen degradation during long-term operation.

Much attention is paid to the study of the influence of various factors on the criteria of crack resistance, which characterize the resistance of the metal to brittle fracture, and also adequately reflect a specific type of hydrogen sulfide corrosion – sulfide stress corrosion cracking (SSCC).

It is known that the problems of crack resistance and embrittlement of metals, which are exploited in corrosion media with hydrogen sulfide impurities in the fields of oil and gas fields, were dealt with as domestic [8-10] (A.G. Gumerov, K.M. Yamaleiev, O.I. Radkevych, G.N. Nykyforchyn, A.B. Vainman, R.V. Paliy, V.V. Panasiuk, O.M. Romanov, etc.), and foreign [11] (M. Galis, C. Ortiz, S. Serna, B. Campillo, M.R. Trucbon, J.I. Croler, etc.) scientists.

Analysis of the literature shows that the existing domestic and foreign methods of calculating the strength of pipelines and tanks, as a rule, provide for independent processes of corrosion, fatigue and creep, although in practice these processes take place simultaneously in different combinations. In addition, the analysis of existing methods of non-destructive testing of damage and degradation of metal shows their low efficiency in assessing the life of industrial equipment. Thus, the inherent shortcomings of the methods in assessing the performance of structures and their residual life show that currently important are the calculation methods using the criteria of crack resistance, sensitive to changes in the structure of the metal during long operation, especially in corrosion-active technological environments at alternating dynamic loadings. In addition, in today's difficult for the oil and gas industry, when the renewal of physically and morally obsolete fixed assets due to financial difficulties is limited, it is important to maintain and extend the life of industrial equipment, including pipelines, by increasing the maintenance cycle. Therefore, the development and use in the regulatory documentation of modern criteria for crack resistance, taking into account the hydrogen sulfide degradation of the metal will more accurately predict the residual life of long-life tubular steel.

It should be noted that most authors [12] studied steels that were not in operation at all, or a long period of time, and therefore it is difficult to predict the behaviour of steels in the process of long service life ($\geq$ 10-30 years) in an aggressive working environment containing hydrogen sulfide, oxides, various solutions of acids and alkalis. There is no information in the literature on the detailed study of the mechanisms of fragility and destruction of petroleum and gas metals using high-precision laboratory equipment and modern foreign methods (for example, the Specification of the International Corrosion Association – NACE).

In general, the analysis of literature sources, as well as practical data show that the existing scientific, technical and technological developments to ensure reliable corrosion and mechanical resistance and durability of oil and gas pipelines and other shell metal structures of responsible purpose and subordinate SNIP of Ukraine are largely contradictions and uncertainties. There are no quantitatively substantiated recommendations for practical application in order to ensure corrosion and mechanical resistance of pipelines operating in technologically aggressive environments under alternating temperature and barometric conditions and loads; there is a need for a systematic study of the causes, conditions and mechanisms of corrosion and mechanical damage to long-term equipment, which will significantly increase the operational reliability of industrial equipment. Thus, the results of this work are relevant for both oil and gas and several related industries (eg, metallurgy, chemical, mining), and also have significant scientific and practical significance and value.

The purpose of the work is laboratory-experimental studies of corrosion-mechanical properties of structural steels of long operation in chemically aggressive technological environments of the oil and gas industry.

The main tasks of the research:

– the choice of methods and criteria for assessing the corrosion and mechanical properties and crack resistance of structural steels grades 10, 20, 20K, 09G2S, 17G1S, VSt3sp long-term operation (from 0 to 25 years);

– research of corrosion-mechanical properties of metal of long operation in corrosion-aggressive environments with use of criteria of modern mechanics of destruction.

– comparative analysis of long-life pipe steels based on the results of experimental studies.

– development of recommendations for increasing the corrosion and mechanical crack resistance of long-term metal structures and extending their trouble-free service life in chemically aggressive environments of industrial production.

Methods

Corrosion curves of long-term fatigue of samples of pipelines with different service life (from 0 to 25 years) were performed in the model corrosion environment NACE according to the method detailed in [13]. In the course of the experiments, the corrosion-mechanical fatigue (long-term strength) of the metal was investigated on samples cut from different grades of tubular steels, which were used for a long time in corrosive environments. The samples were tested in NACE model medium, which was a 5% NaCl solution containing 0.5% CH_3COOH with additional H_2S saturation; pH = 3; $t = 20 \pm 2$°C. Samples were tested on a weight-type installation USMR-6 under an axially symmetrical load $\sigma_{0.2}^{min}$ (5 samples were used in each experiment).

When choosing research methods, the authors proceeded from the technical conditions that establish the following requirements for corrosion and mechanical resistance: for SSCC time to the destruction of research samples should not be less than 480 hours at $P = 0.8\ \sigma_{0.2}^{min}$, where $\sigma_{0.2}^{min}$ – the minimum allowable value of the yield strength [14]. Cylindrical samples with a diameter of 6.4 mm (working part with a length of 25.4 mm) were tested.

In addition, pipe samples were examined at elevated loads and σ_{tssc}^{480} threshold sulfide stress cracking levels were determined on the basis of tests equal to 480 h, which is important for predictive estimation of material life. So, when pipe steel of a certain grade does not satisfy the conditions [15], then its resistance SSCC was investigated according to the standard [16] and the threshold stresses were determined σ_{ssc}, to be able to compare the quality of steels of different brands and plants that produce pipes. Test conditions according to this standard are as follows: test duration 720 h in 5% solution NaCl+CH_3COOH, in saturated with hydrogen sulfide(H_2S); pH-3; $t = 20 \pm 2$°C. The parameters σ_{tssc}^{480} and σ_{ssc} were determined from the dependences $\sigma_i - \ell g\tau$ (σ_i is initial load; τ is time to unloading, h), at which the samples are not destroyed on the accepted test base. It should be noted that the ratio $\sigma_{tssc}/\sigma_{0.2}$ (σ_m) is not a standardized, but at the same time a generally accepted criterion for the suitability of steel for operation in an environment containing hydrogen sulfide. When this ratio exceeds 0.8, the material is considered usable.

In fracture mechanics of metal structures, the critical stress intensity parameter is widely used to assess the toughness of a metal, which characterizes the metal's resistance to opening and crack propagation. The threshold (critical) value is designated when tested in corrosive environments by the value K_{ssc}, MPa·m$^{1/2}$. Fatigue cracks in the samples were grown using a hydropulsator CDMP-10 (Germany) at a load frequency of 10-15 Hz and a cycle asymmetry coefficient $r = 0.1$-0.2. Tests to determine the parameter Ki were performed on the installation of UME-10 according to the standard method described in [17], both in air and in a corrosive solution with H_2S (NASE method). Research materials – tubular steels, the characteristics of which are given in Table 1 and 2.

Table 1. Steel grades and their purpose

Steel grade	Purpose	Heat treatment
10; 20; 20K; 09G2S; 17G1S; VST3sp	Metal structures of machine-building, oil and gas, metallurgical, chemical, agrarian, municipal and other industries	Normalization

Table 2. Chemical composition of steels

Steel grade	Content of elements, %							
	C	Si	Mn	P	S	Cr	Ni	Cu
10	0.12	0.30	0.55	0.035	0.035	0.15	0.10	0.10
20	0.20	0.30	0.55	0.035	0.035	0.15	0.10	0.10
29K	0.22	0.35	0.65	0.3	0.03	0.12	0.12	0.10
09G2S	1.12	0.37	1.80	0.025	0.025	0.08	0.05	-
17G1S	0.19	0.60	1.21	0.03	0.03	-	0.30	0.30
VSt3sp	0.12	0.27	0.40	0.04	0.04	-	-	-

In Table 3, the grain size of steel is determined according to GOST 5639-69 or FSME112-74, and the carbon equivalent by the formula: C_{equiv} = C + Mn/6 + (Cr + Mo + V)/5 + (Cu + Ni)/15.

Table 3. Mechanical characteristics of steels

Steel grade	Mechanical characteristics				C_{equiv}, %	Grain size of steel
	σ_v, MPa	σ_t, MPa	ψ, %	δ, %		
10	360	220	52	24	0.32	7-8
20	485	287	56	27	0.33	7-8
20K	310	310	55	21	0.36	7-8
09G2S	497	289	46	23	0.441	≥ 7-8
17G1S	515	362	43	24	0.430	≥ 7-8
VSt3sp	360	210	42	25	0.34	≥ 6-7

Results and Discussion

The results of experimental studies of tubular steels samples with different service life are shown in Fig. 1-3.

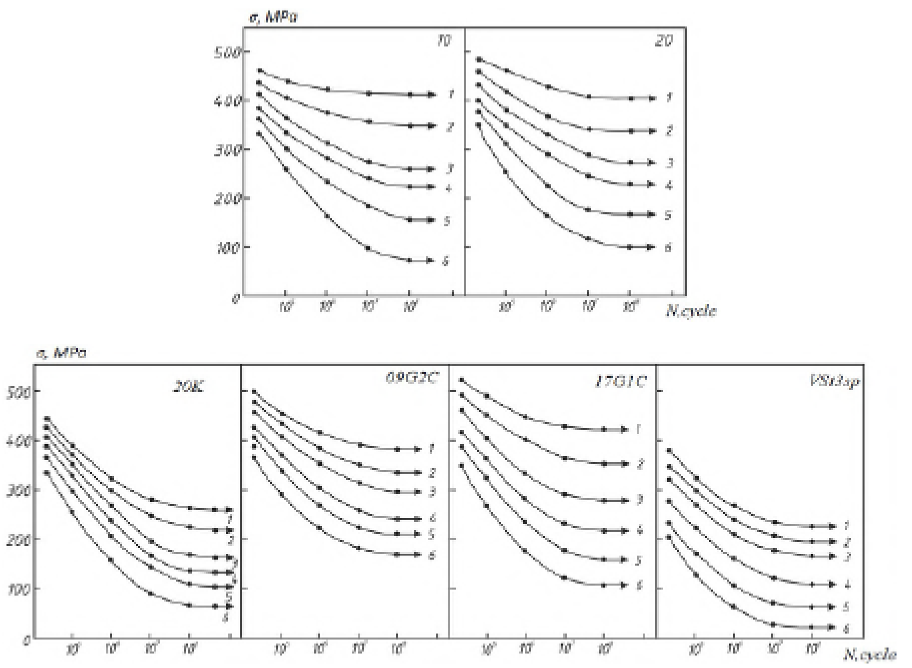

Fig. 1. Curves of corrosion long fatigue of pipelines samples with various terms of operation: 1 – 0 years; 2 – 5 years; 3 – 10 years; 4 – 15 years; 5 – 20 years; 6 – 25 years. Model corrosion environment NACE

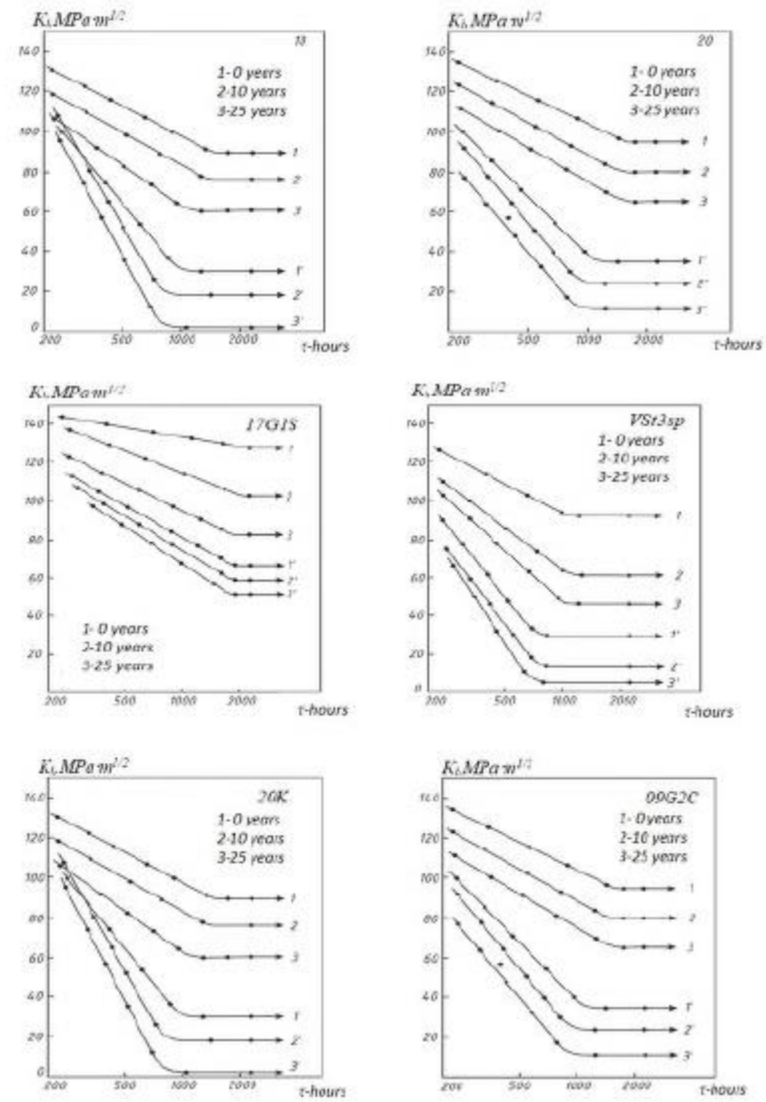

Fig. 2. Dependence of K_i is τ for steels with different service life when tested in air (1; 2; 3) and in NACE solution (1'; 2'; 3') threshold voltages and ratio

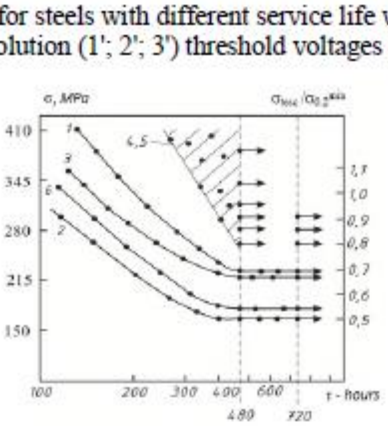

Fig. 3. Susceptibility to hydrogen sulfide cracking of unused steels of grades: 1 - 10; 2 - 20; 3 - 20K; 4 - 09G2S; 5 - 17G1S; 6 – VSt3sp.

The dashed area in Fig. 4. is a steel with high corrosion resistance against SSCC.

Samples of all steels were found to have withstood a full cycle of tests, in particular, none of the five samples in each series collapsed within 480 hours. At the same time, the analysis of corrosion fatigue curves allowed us to draw the following conclusions: 1) steels of grades 10, 20, 20K and VSt3sp weakly resist long alternating loading, in particular after 10-15 years of operation the limit of long durability reaches tension (150-220 MPa), lower yield strength for these steels (230-260 MPa), and threshold (critical) values of stress σ_{tssc} are equal to 125-160 MPa.

At the same time, steels 09G2C and 17G1S meet the requirements of the NACE standard (Standard MR-01-75-96), in particular, the values of σ_{tssc} are equal to 250-262MPa. The results of calculating the ratio $\sigma_{tssc}/\sigma_m(\sigma_{0.2})$ for all grades of steels that were subjected to experimental studies are shown in Table 4.

Table 4 Threshold voltages and ratio $\sigma_{tssc}/\sigma_m(\sigma_{0.2})$ of steels

Grade of steel	Characteristics class	σ_{tssc}, MPa	$\sigma_{tssc}/\sigma_m(\sigma_{0.2})$
10	ferritic	150	0.68
20	ferritic	145	0.51
20K	ferritic	160	0.66
09G2S	pearlitic	250	0.86
17G1S	ferritic	262	0.89
VSt3sp	pearlitic	125	0.56

Analysis of the data in Table 4 shows that the ratio $\sigma_{tssc}/\sigma_m(\sigma_{0.2})$ is equal to 0.86 (steel 09G2S) and 0.89 (steel 17G1S), i.e. these two grades of steel meet the requirements of the technical conditions of NACE, and therefore can be recommended for use in the manufacture pipes that are designed for operation in chemically aggressive media containing hydrogen sulfide; 2) on the basis of the obtained experimental results the diagram of susceptibility to hydrogen sulfide cracking of not operated steels of grades is constructed: 10, 20, 20K, 09G2S, 17G1S, VSt3sp.

As the results of the dependence analysis show K_i-τ for steels with different service life when tested in air (1; 2; 3) and in NACE solution (1'; 2'; 3'), the hydrogen sulfide medium NACE more than 2.5-3.5 times reduces the fatigue limit of steel samples of grades 10, 20, 20K, VSt3sp and in 1.5-2 times for steels 09G2S i 17G1S. Thus, after 10 and 25 years of operation in a corrosive-aggressive environment NACE conditional fatigue limit for steel grade 09G1S is 82 and 95 $MPa{\cdot}m^{1/2}$, respectively, and for steel 17G1S – 87 and 105 $MPa{\cdot}m^{1/2}$. A similar trend is observed for steels of grades 10, 20, 20K and VSt3sp, in particular the value of the conditional threshold stress intensity coefficient K_{ssc} ($MPa{\cdot}m^{1/2}$) respectively equal to 23/80 (10 years), 5/65 (25 years); 30/85 (10 years), 10/75 (25 years); 35/80 (10 years), 22/70 (25 years); 15/62 (10 years), 5/50 (25 years). It should be noted that here in the denominator are the results of tests in the air and in the numerator - in a corrosive solution.

Comparison of the measured values of K_{ssc} for the studied steels with the results of [18] obtained for structural low-alloy steels with nickel and chromium-nickel steels of different classes, showed that without nickel steels of grades 08KMCA, 06X1, 09G2S and 17G1S are less sensitive to sulfide corrosion cracking (comparisons were made for similar in class and mechanical characteristics of nickel-containing steels). An example is hull sorbitol hardening steels, in particular steel 0XH5MF has $\sigma_{tssc} = 145$MPa, $\sigma_{tssc}/\sigma_{0.2} = 0.31$ and $K_{ssc} = 30\ MPa{\cdot}m^{1/2}$ (in solution without H_2S coefficient $K_{ssc} = 102\ MPa{\cdot}m^{1/2}$) – Fig. 3. A similar pattern is noted by other authors [19].

The results of studying the kinetics of local (point) corrosion damage of the pipe wall when tested in a corrosive environment (NACE method) are shown in Fig. 4. It is known that the rate of local corrosion of oil and gas pipelines is estimated by metal losses along the pipe wall thickness, which is expressed by the dependence $\Delta m = k{\cdot}\tau^{1/n}$, which in logarithmic coordinates is converted into a straight line, then the extrapolation of the straight line allows to predict the metal consumption of the pipe wall for a given time and determine the service life of the pipeline. The slope of the line to the abscissa $lg\tau$ determines the value of the coefficient n. Under the conditions of the experiment $n = 3$, i.e. the loss of mass of the metal is expressed by the law of the cubic root, which may indicate the control of the corrosion solution of the metal by the diffusion process in the layer of corrosion products. As shown by the analysis of the kinetic dependence of corrosion losses of metal of research samples cut from metal of different grades and purposes, in all test conditions there was a slowdown in corrosion damage over time, which can be expressed as a degree dependence $\Delta m = k \cdot \tau^{1/n}$, where Δm is loss of mass of the sample, g; τ is term of exposure, day; k is a constant. Fig. 4 shows the kinetic dependences of local corrosion damage of steel series pipe samples (six grades), which lead to the smallest and largest corrosion losses. This allows the timely application of technical and design measures to improve the trouble-free performance of structural steels of pipelines.

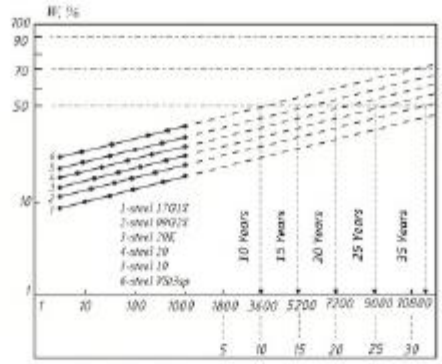

Fig. 4. Kinetics of pipe wall corrosion damage during the test in corrosion-aggressive environment (NACE methodology)

Metallographic studies of cross-sections of steels 10, 20, 20K and VSt3sp showed the formation of cracks along the texture of steels, caused by a hydrogen colony, and which emerge on the surface of the samples (Fig. 5a). Metallographic studies were carried out using a GSM-35 CF scanning electron microscope (Jeol, Japan). SSCC develops perpendicular to the direction of metal texture formation and to the load (Fig. 5b).

(a) (b) (c)

Fig. 5 VIR crack (a), SSC crack (b) and non-metallic inclusions (sulfides and oxy sulfides), which are the centers of crack formation (c) when testing steel samples. Notation: (a) – x540, (b) – x2000, (c) – x3000

It is believed [20] that the main cause of SSCC of tubular steels of the studied types, which are characterized by high viscosity-plastic properties and low hardness (HRC≤22), may be increased sulfur and phosphorus or local formation of needle structures of martensitic-bainite type.

It should be noted that our studies did not reveal the formation of needle structures in the studied metal samples. However, it was found that steels of grades 10, 20, 20K and VSt3sp contain too much sulfur (0.030-0.035%) and phosphorus (0.032-0.040%), which could lead to the formation of sulfide and other non-metallic inclusions, which are usually serve as a source of corrosion cracks (Fig. 5c). Regarding the causes and mechanisms of SSCC of individual steel grades, additional research is needed.

Conclusions

Experimental studies have established the causes and substantiated the mechanisms of hardening of the metal with increasing service life (from 0 to 25 years), which leads to its degradation, especially during long-term operation in corrosive environments.

A method for forecasting the residual working (accident-free) resource has been developed, which makes it possible to purposefully regulate their operational condition. This allows timely application of technical and design and technological measures to improve the efficiency of such structures (subordinate to the Technical Supervision of Ukraine).

Numerous and various results of experimental tests of metal samples for various purposes provide an opportunity to create a basis for comparative analysis of steels on many parameters of crack resistance, which will be a reliable basis for scientific and practical justification of equivalent replacement of some steel grades with others, taking into account technological modes, operating conditions power load systems, corrosive media, etc.

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