

Degradation of the internal well equipment steel under continuous service in the corrosive and aggressive environments

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Abstract

Purpose is to analyze steel degradation of the internal well equipment during its continuous service while contacting directly the corrosive environments.

Methods. A range of research concerning the damaged metal tubes of the internal equipment for oil and gas wells, in particular regarding continuous service tubing, comprised both standard and specific studies involving different variations of X-ray spectral analysis with the use of scanning electron microscope JSM-35CF (JEOL Company, Japan) and SEM-515 with microanalyzer Link by Philips Company. The studied samples have been made of tubing in the period of the unauthorized and emergency well shutdowns; life of the wells is 0 up to 15 years. To analyze both structure and chemical composition of metal inclusive of such gases as oxygen and hydrogen, chippings were produced mechanically from various parts of tube walls.

Findings. X-ray structural studies have made it possible to obtain data confirming cementite decay (Fe_3C) in the tube metal during continuous operation of the internal well equipment. X-ray structural analysis methods have helped identify the parameters of crystal lattice of a matrix; and a level of elastic distortions of the lattice (i.e. microstresses of the distortions) has been evaluated as well as carbon distribution within ferrite and cementite. The abovementioned offered the possibility to describe both reason and mechanism of the reduced resistance to corrosion in the context of internal well equipment.

Originality. New regularities under cementite decay in tube metal have been identified in addition to changes in the parameters of a crystal lattice; microstresses of the lattice distortions; and carbon distribution within ferrite and cementite. The aforesaid helps explain in a new way both reason and mechanism of the reduced resistance to corrosion in the context of internal well structures operating continuously in aggressive environments. The basic sources and mechanisms of tube steel degradation, resulting from the metal hydrogenation and oxidation, have been defined which becomes the foundation to develop scientifically the substantiated measures mitigating the negative impact on the condition of the internal well facilities operating continuously in the chemically aggressive environments.

Practical implications. Degrading hydrogen effect on the crystal lattice of metal has been proved. The effect creates conditions under which tube structures of oil and gas wells experience their failure.

Keywords: corrosion, steel, failure, degradation, well

1. Introduction

As practices of well operation within Poltava Region oil and gas fields show, the most intensive tubing (T) corrosion is observed within the certain intervals of wells. In this context, the corrosion is of local nature since it concentrates within the areas where water condensate is accumulated in addition to stress emergence and flow turbulence. Seal rings are the first ones starting corrode among the well armature. Corrosion grooves are formed inside the rings; later, the grooves widen turning into through holes.

Tubing corrosion has a form of pits and longitudinal grooves. More active T-failure takes place within the union joints. Inside the tubes (i.e. within its lower edge, wrapped in

coupling), corrosion chamfers originate widening towards a flow and turning into corrosion pits. The process is stipulated by gas swirl and condensate water accumulation favouring active corrosion within the union joints.

Scientific sources [1]-[4] and practical data confirm the idea that the available scientific and technical as well as technological developments providing reliable corrosion-mechanical stability and longevity of the internal well equipment in the oil and gas industry have significant contradictions and uncertainties. The matter is that there are no quantitatively substantiated recommendations concerning practical ways and techniques to improve corrosion-mechanical stability of the facilities operating in the aggressive environments under alternating temperature and baric

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conditions as well as their putting into operation at oil and gas enterprises. It became necessary to study systematically the reasons, conditions, and mechanisms of corrosion damage of continuously working equipment and features of processes of hydrogen sulfide metal degradation resulting in failure of internal well structures [2].

To select and implement either innovative or enhanced techniques and materials favouring the improvement of corrosion-mechanical stability of metal tube structures, operating continuously in the aggressive environments, one should know thoroughly the corrosion process mechanisms along with factors and conditions under which metal degradation takes place.

Velocity and distribution of internal T corrosion depend upon the water-gas-oil mixture structure and motion mode; composition and characteristics of the produced oil, formation water, and oil gas; their temporal changes; content of corrosive agents (i.e. CO₂, O₂, low-molecular acids etc.); availability of abrasive components within the liquid flow; possible salt and paraffin deposition and implementation of measures to eliminate them; pressure and temperature changes along a well bore; well operating procedure; stress level of tube metal; mechanical wear under friction; specific activities (i.e. use of chemical, acid reagents) to intensify production and restrict water inflow as well as leakage of the threaded connections, and manufacturing defects of tubes and connectors etc [5]-[7].

Tube corrosion is influenced heavily by hydrogen and sulfur availability in the process medium. It has been identified by [3] that the samples where hydrogen content is 10 ml/100 g and more experience fragile corrosion with numerous cracks in the fractured zone. Metal hydration plays a special negative role in the functional reliability of oil and gas pipelines operating in the chemically aggressive environments under alternating loads [4]. Consequently, the problem of corrosion and corrosion-mechanical failure of tube structures of oil wells is topical; moreover, it is of great practical importance.

Reliability and profitability of oil and gas producing enterprises depend upon sustainable selection of the materials while equipping and servicing of the internal well facilities among which tubing (T) and deep pump rods (DPRs) are the basic components. Correct selection of tube steel grades as well as their dimensions provides economical efficiency of hydrocarbon production with minimum expenses for the unauthorized and emergency well shutdowns due to corrosion-mechanical damages [8].

Oil and gas production is the basic operation schedule at oil and gas enterprises. For the purpose, pump-compression tubes, deep pump rods, and pump units are used in wells. Increase in oil mixture temperature up to 60-80°C as well as pressure rise up to 40-60 MPa results in the reduced mechanical strength of steel tube, rod structures, and power equipment (i.e. pump cases). Hence, it is required to increase wall thickness of the parts, for instance, T and DPRs. High temperature and pressure of the heated oil-gas mixture increases significantly danger of internal (i.e. steam-gas-water) corrosion of tube structures. Among other things, it concerns well casing (WC), T, and cases of pump units [2]-[9]. Consequently, the problems, connected with the analysis of reasons and factors causing corrosion damage of certain parts of the internal well facilities, need further research to solve the issues of engineering reliability and accident-free operation improvement for power well facilities. In addition, it is important for oil and gas industry to study sources and mechanisms of

corrosion damage of internal well tubing as well as other machinery while oil and gas well equipping and servicing.

Technological media of oil and gas industrial production with their complex aggregate of chemical elements and compounds stipulate the development of complex electrochemical processes at the surface of tube metal structures due to continuous operation. Then, the processes favour corrosion and, hence, damage of working units, tubes, and cases of pump units. Even elementary sulfur fragments initiate actively corrosion at the surface of well equipment tubes after various depositions were removed with the help of chemical solutions and other chemically active reagents (for instance, calcium sulfate etc.). On all occasions, corrosion in the acid environments follows acid carbon mechanism. The corrosion is influenced directly by such chemically active components of technological medium as oxygen, hydrogen, and sulfur. Hence, analysis of their simultaneous complex effect on acid carbon metal corrosion is important and topical for the oil and gas industry as well as for the processing industry since it will help develop advantageous techniques to counteract corrosion-mechanical damages and failure of technological facilities of oil and gas enterprises.

Reliability of the internal well equipment depends heavily upon the corrosion-mechanical characteristics of tube steel for T and DPRs. Nevertheless, the available scientific-technical and technological developments aimed at the improvement of operational reliability and longevity of tube structures are controversial and undeterminable from the viewpoint of researchers and producing people due to lack of a clear idea of sources and factors causing failure and destruction of the internal well equipment as well as due to lack of scientifically substantiated practical recommendations concerning optimal selection of tube steel grades operating in the chemically aggressive environments under alternating temperature and baric conditions of oil and gas production enterprises [4]-[10]. In turn, the abovementioned prevents from the development of efficient organizational and technical measures avoiding both failure and emergency damage of well tube structures which may result in drastic technological, and economic and environmental consequences. In this connection, the need has arisen to study wall corrosion of the internal well facilities which will become the basis for the development of technological and operational measures improving corrosion-mechanical resistance of tube steel grades to be applied in the oil and gas industry.

In such a way, the abovementioned data confirm topicality of the corrosion problem in the context of metal used for internal well facilities if oxygen-hydrogen medium is available. Analysis of its features should involve future research.

The research is to develop new, still not understood mechanisms of sulfur and especially hydrogen influence on the corrosion-hydrogen degradation processes contributing to damages with further failure of tube structures operating continuously in the chemically aggressive technological environments of oil enterprises; the aforesaid may be used in practice to improve service characteristics of metal applied for internal well equipment.

2. The research methods

In addition to the standard research efforts, the system for the damaged metal analysis also involved following specific techniques: different variations of X-ray spectral analysis

with the use of scanning electron microscope JSM-35CF (JEOL Company, Japan) and SEM-515 with microanalyzer Link by Philips Company.

Moreover, hydrogen, sulfur, and oxygen content within the metal was identified by means of local laser microprobe mass spectrometry and a technique of metal sample melting in the carrying gas flow using a device by Leco Company. Depending upon the formulated problem, the analysis locality varied from 3 up to 50 μm .

Non-metallic inclusions were studied using a television microscope Quantimet-120 by Metals Research Company (the Great Britain) and PEM JSM-35CF.

A microanalyzer JSM-35 was applied for fractographic analysis of sample fracture; composition of the non-metallic inclusions was studied with the help of an energy dispersive spectrometer Link-860 (Link Company, the Great Britain).

Corrosion velocity was measured using a gravimetric method reducing the sample mass after corrosion tests with 10^{-4} g weighing accuracy; then, recalculation in terms of mm/year took place. The testing term was 144 hours 24 hours each. Corrosion products were removed during 15-hour keeping the samples in 10% citric acid solution at 60°C. After that, the samples were treated by acetone and water, dried, and weighted.

Chemical composition of the metal was identified by means of the standard methods as well as by energy dispersive analysis (an energy dispersive adapter Link and a scanning electron microscope JSM-35 were applied).

Microhardness was determined using a device of FISCHER SCOPE H100C model involving a mechanism of the diamond pyramid indentation under light load and a microhardness analyzer. Image Expert TM Program was applied to process the experimental results.

X-ray spectroscopy and a mass spectral method helped study a structure of oxide layers of corrosion damages. It has been identified that while contacting the active environment, carbon steel (for instance, of grade 40), which structure has ∞ – Fe crystal lattice, forms an oxide layer where crystalline lattice mainly consists of FeO. If steel alloy is meant (for instance, 36Г2С and 20H2M) with γ – Fe structure and γ – 3.64 Å lattice spacing, then a layer consists of FeO – Fe₃O₄ and CaO · 2FeO spinel. In such a way, anions play a small part in the epitaxial (i.e. transitional) layer shaping; i.e. availability of compounds in the form of carbonate is not the essential conditions of an oxide layer building at the corroded metal surface. Oxide crust adheres to the metal surface if only interlayer appears between them; the interlayer structure resembles either ∞ – Fe or γ – Fe structure, i.e. it favours epitaxial oxide-metal interlocking.

The X-ray structural analysis methods have helped identify the parameters of crystalline lattice of α matrix; simultaneously, a level of elastic lattice deformation (i.e. bend microstresses σ) has been evaluated as well as carbon distribution within ferrite and cementite of steel for internal well equipment being T and WC. Samples of well casing and tubing taken during the unauthorized and emergency well shutdowns (life of the wells was 0 up to 15 years) were the research subjects.

Table 1 demonstrates characteristics, mechanical properties, and chemical composition of the tubes. To study both structure and chemical composition of the metal, inclusive of gases being oxygen and hydrogen, metal chips were obtained mechanically from different areas of the tube walls.

The X-ray structural studies have made it possible to obtain data confirming cementite (Fe₃C) decay within the tube metal during long-term operation of the internal well equipment of oil fields (Table 2).

Table 1. Characteristics, chemical composition, and mechanical properties of tubes for the internal well equipment (i.e. T and WC)

Steel grade	Tube type	Content of alloying elements, %					Breaking stress σ_b , MPa	Yield stress σ_{02} , MPa	Hydration [H], %
		C	Si	Mn	S	P			
D*	WC	0.44	0.27	0.82	0.039	0.040	>650	>380	0.0037
E**		0.39	0.26	1.01	0.022	0.024	>699	>562	0.0039
K***	T	0.45	0.21	0.95	0.020	0.022	>687	>491	0.0030
L****		0.42	0.24	1.20	0.021	0.023	>800	>650	0.0046

Note: WC is well casing; T is tubing.

*Indicators of steel grade D are as follows: breaking stress σ_b being no less than 655 MPa; yield stress σ_{02} being 379-552 MPa; and relative elongation being $\delta = 14.3\%$.

**Indicators of steel grade E are as follows: breaking stress σ_b being no less than 688 MPa; yield stress σ_{02} being 552-758 MPa; and relative elongation being $\delta = 13.0\%$.

***Indicators of steel grade K are as follows: breaking stress σ_b being no less than 687 MPa; yield stress σ_{02} being 490-552 MPa; and relative elongation being $\delta = 12\%$.

****Indicators of steel grade L are as follows: breaking stress σ_b being no less than 758 MPa; yield stress σ_{02} being 655-862 MPa; and relative elongation being $\delta = 12.3\%$.

Table 2. Cementite (Fe₃C) amount decayed in the metal of well tubes T and WC

Steel grade	Lifetime, years	Fe ₃ C, %	Steel grade	Lifetime, years	Fe ₃ C, %
K	T		D	WC	
	0.0	100		0	100
	0.5	7-9		0.5	5-7
	1.5	12-14		2.5	11-13
	3.0	15-16		5.0	14-17
	5.0	16-18		7.5	19-23
L	8.0	19-23	12.0	26-30	
	0.0	100	0.0	100	
	0.5	5-7	1.5	6-8	
	2.5	9-11	5.0	10-12	
	7.0	16-18	10.0	18-21	
	10.0	22-26	15.0	25-30	

Figure 1 shows a chart of sample cuts from T and WC tubes; in this regard, samples from different producing oil wells were analyzed varying in their corrosive activity.

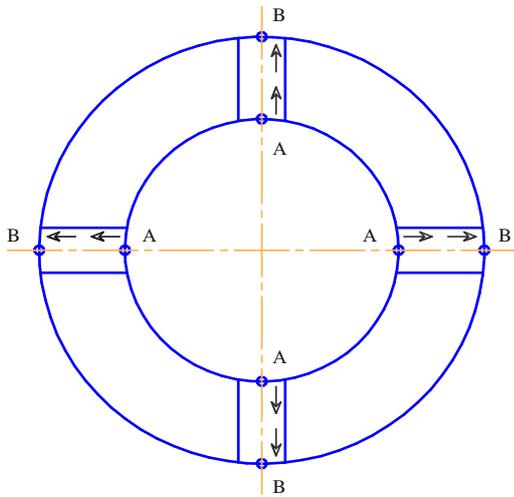


Figure 1. A chart of sample cuts to be analyzed and scanning directions of T and WC tube samples

For the samples, the internal well equipment metal in the process of the unauthorized and emergency well shutdowns have been used. Namely, the studies applied T tube made of 36Г2С steel grade belonging to K strength group (heating – hardening + treatment); deep pump rods (DPRs) made of 20H2M steel grade (heating – normalization + treatment); well casing (WC) made of P-110 steel grade belonging to D strength group; cases of electric-centrifugal pump facilities (ECPFs) made of 35 steel grade; and well pump rod facilities (WRPFs) made of 30Г steel grade.

3. Results and discussion

The experimental results are to develop new mechanisms of hydrogen influence on the corrosion-hydrogen degradation processes favouring damages with further failure of tube structures operating durably in the chemically aggressive technological environments of oil enterprises which may be implemented to improve service characteristics of metal used for the internal well equipment.

New regularities of hydrogen influence on the tube metal have been identified depending upon the increased life cycle which results inevitably in its weakening. Metallographic studies have proved cementite redistribution among structural components causing changes in perlite composition being the basic structural component of steel. Among other things, it makes cementite plate lose orientation in a perlite colony, fractionize, and becomes of a round shape. The processes provoke local metal cracking promoting shaping of microcavities which coagulation will result in crack formation with further seal failure of tube columns and their failure.

Figures 2-5 demonstrate the measurement results of hydrogen content as well as its distribution nature. It follows from the data in Figures 2-5 that in the process of continuous operation of the internal well equipment, severe metal hydration takes place resulting in its cracking as well as in the decreased plastic properties.

Figures 6-7 show the results of microhardness distribution along the DPR rod cut, experiencing continuous operation in oil wells and changes in plasticity as well as in hydrogen degree depending upon the service of the internal well equipment in oil fields.

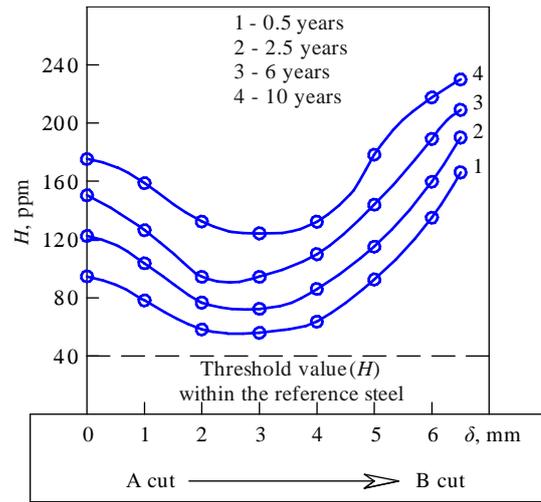


Figure 2. Nature of hydrogen distribution within the cut of T tube wall depending upon its continuous operation in oil wells

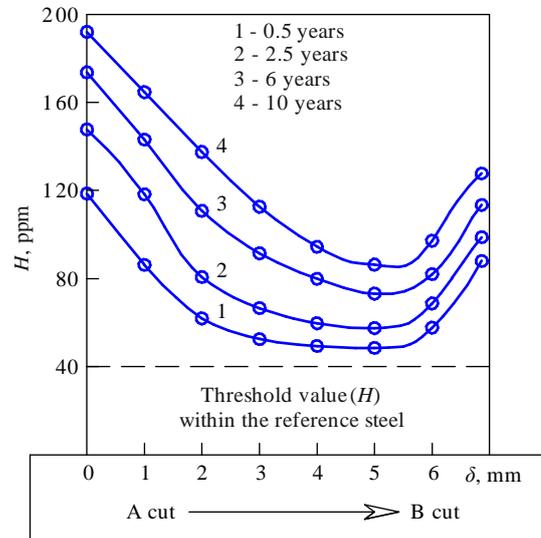


Figure 3. Nature of hydrogen distribution within the cut of WC tube wall depending upon its continuous operation in oil wells

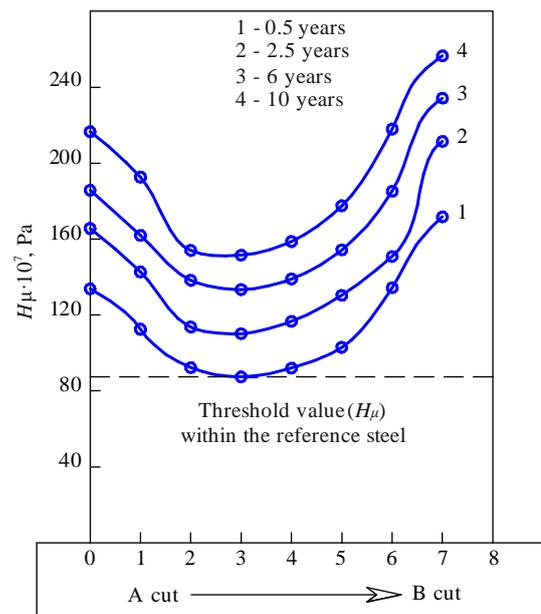


Figure 4. Nature of microhardness distribution within the cut of WC tube wall depending upon its continuous operation in oil wells

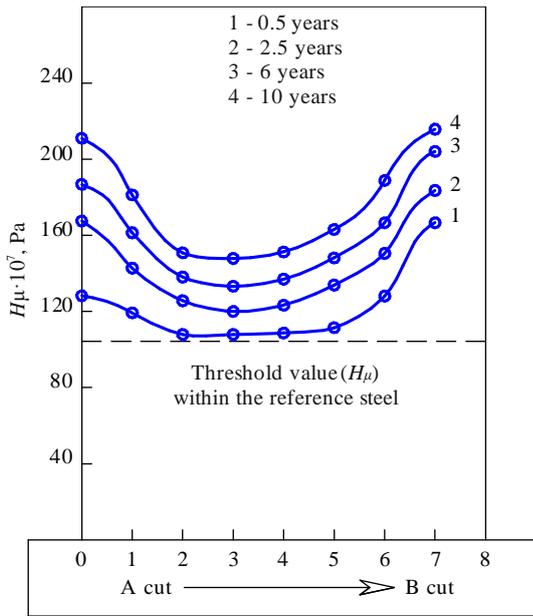


Figure 5. Nature of microhardness distribution within the cut of T tube wall depending upon its continuous operation in oil wells

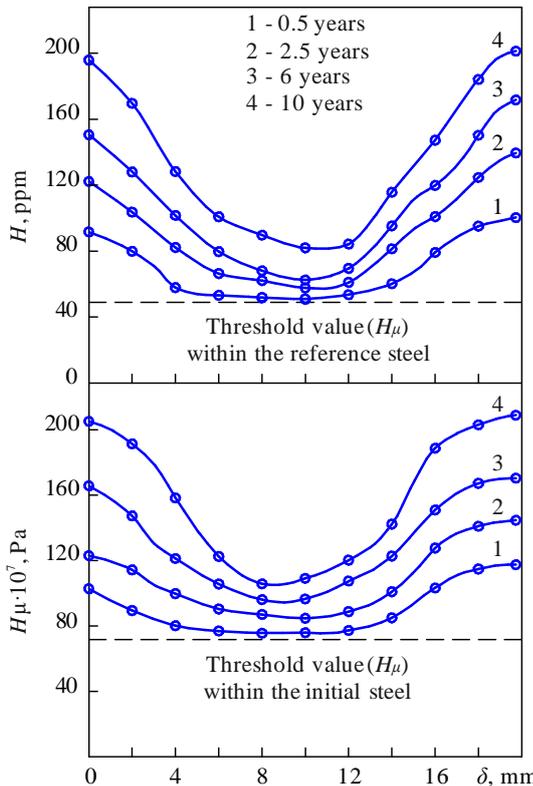


Figure 6. Nature of microhardness distribution within the cut of DPR rod depending upon its continuous operation in oil wells

As it follows from Figures 6-7, nature of changes in plasticity and in hydration degree depends upon service life and medium composition containing simultaneously hydrogen sulfide carbon dioxide (CO_2). The most active corrosion is shown in upper (near a wellhead) and lower (downhole) zones of producing wells. The fact can be explained by the most favourable conditions of a working environment attack on the T tube which multiply concentration is tens and hundreds of times higher than average corrosivity along walls. During operation, metal of well equipment tubes experiences cementite decay which keeps in step with the findings [11]-[15].

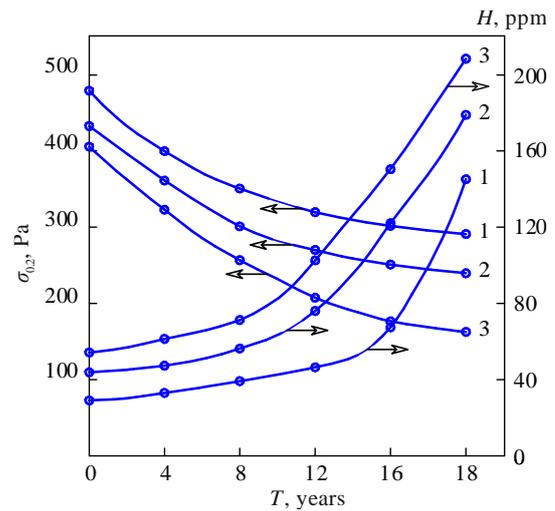


Figure 7. Graphs of changes in plasticity and in hydration degree depending upon the internal well operation in oil wells: 1 – tubing; 2 – well casing; 3 – deep pump rod

X-ray analysis has helped determine that increase in service life of underground well equipment decreases drastically cementite (Fe_3C) content in the metal. In this content, the greatest decrease of cementite share in tube steel of the well facilities takes place after 8-10-year operation (Fig. 8).

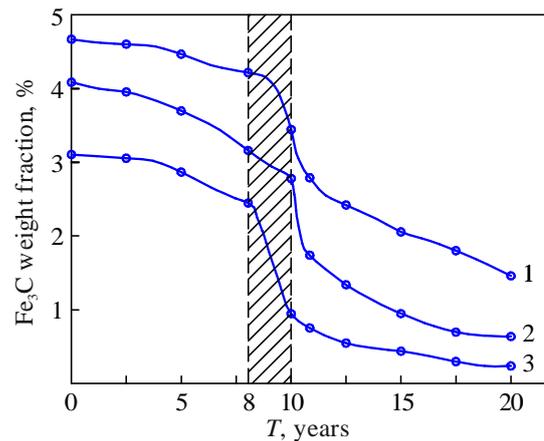


Figure 8. Change in cementite amount in steel depending upon service life of internal well equipment: 1 – tubing; 2 – well casing; 3 – deep pump rod

It is known that cementite decays easily if hydrogen atoms $\text{Fe}_3\text{C} + 2\text{H}_2 \leftrightarrow 3\text{Fe} + \text{CH}_4$ act on it. During the operation, active centres originate at the surface of tube metal or T, or at the surface of microcavities. Within the centres, dissociation of hydrogen molecules takes place as well as atomic hydrogen penetration into metal depth which results in microcrack origination within the metal causing at large degradation of steel underground structures.

In this regard, attention has been paid to the fact that simultaneously the steel structure experiences certain changes in the process of durable load; thus, perlite structure varies. Namely, cementite plates lose orientation within the perlite colony, decays, and take a round shape. Perlite areas take a shape being similar to the granular one.

As the authors of [16]-[20] papers mention, variable stresses in crystalline grains generate extra dislocations both in ferritic grains and in perlitic ones. Movable dislocations cut cementite plates removing simultaneously a part of carbon atoms. Fragmentation of perlite grains

varies morphology of cementite plates; as a result, certain share of cementite, which particles are less than critical value, dissolve. Some share experiences such fragmentation after which it stops having independent X-ray reflections. Moreover, the carbon atoms, liberated as a result of cementite decay, accumulate within the slip lines passing into a solid solution while concentrating within the boundaries of grains and microcracks to shape nuclei of new carbide parts. Generally, the processes give rise to local metal cracking of the internal well facilities. Under the favourable conditions (i.e. when alternative cyclic stresses are acting), micropores shape which coagulation results in crack formation.

As a rule, the processes cause local cracking of the underground well equipment metal contributing to the development of microcavities which coagulation propagate cracks initiating tube metal structure unsealing.

According to the data by chemical and microroentgenospectral analyses, it has become understood that the corrosion products (Fig. 9), formed within the environments with low content of calcium ions, are more compact; they adhere to metal tightly and protect metal surface against the contact with corrosive environment up to certain time.

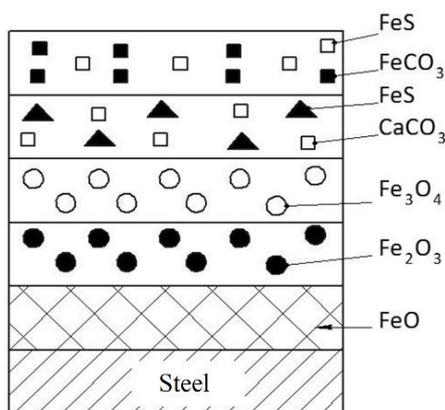


Figure 9. Diagrammatic structure of corrosion products at the surface of T tube

Scheme in Figure 9 explains that the corrosion products are composite being represented by alternating FeO, Fe₂O₃, Fe₃O₄, CaCO₃, and FeCO₃ phase layers as well as their compounds. In addition, the formation sequence of multilayer corrosion products is supported by thermodynamic calculations. According to Gibbs free energy value (ΔG_{298}^0 , kJ/mol), and reactions of -1929 (FeO); -1448 (Fe₂O₃); -1023 (Fe₃O₄); -496 (CaCO₃); -67 FeS; -33 (FeCO₃) phase formation, more negative values indicate higher metal reactivity as well as higher thermodynamic stability of the reaction products. As the analytical data show, oxide formation is more probable energetically than the formation of calcium of iron carbonates. From the energetic viewpoint, iron sulfide formation is possible. Loose carbonate layer within the corrosion products delaminate the latter from the metal surface; in such a way, pits (i.e. caverns) are shaped. Consequently, one of the promising tendencies to reduce corrosive activity of technological environment is calcium ion removal from tube space while using the specific chemical reagents [21].

It is known [22] that in the oxidation process of iron and its alloys, a surface oxide layer mainly consists of wustite (FeO) and magnetite (Fe₃O₄) which crystalline lattice finishes building α - Fe lattice. Since, such components as ions and anions are available in technological environments of oil wells favouring cubic latitude formation in the process of corrosion reactions (as a rule, they finish building FeO or Fe₃O₄ lattice) while promoting the interlayer development [23]. Periods of crystalline lattices of the basic compounds of corrosion products, expressed by angstroms, are as follows: α - Fe - 2.86; FeO - 4.30; Fe₃O₄ - 8.39; Fe₂O₃ - 8.52; and γ - Fe - 3.64.

As the obtained data, shown in Table 3, confirm, an increase in service life of the internal well equipment results in the greater values of the volume-centered cubic crystalline lattice α , i.e. solid solution and increase in microstresses. In this context, some carbon share of the crushed cementite is removed to α matrix boundary. Possibly, another share remains within dislocations with further displacement to microcracks to shape new fine carbide particles. Relatively large carbide particles are formed within the grain boundaries between perlite and ferrite.

Table 3. Parameter values of crystalline α -Fe lattice of microstresses and carbon distribution within the steel used for WC and T internal well tubes

Steel grade	Service life, years	α , Å (angstrom)	σ , MPa	Carbon content, %	
				in ferrite	in steel
Tubing					
K	0.0	0.28665	110	0.020	0.45
	1.5	0.28668	186	0.028	0.442
	5.0	0.28670	215	0.035	0.430
	8.0	0.28675	243	0.040	0.423
L	0.0	0.28665	115	0.021	0.42
	2.5	0.28668	188	0.030	0.412
	7.0	0.28672	250	0.039	0.405
	10.0	0.28676	276	0.048	0.393
Well casing					
D	0.0	0.28665	74	0.020	0.44
	5.0	0.28667	164	0.030	0.438
	7.5	0.28670	215	0.042	0.429
	12.0	0.28674	288	0.056	0.421
E	0.0	0.28665	84	0.020	0.39
	5.0	0.28669	189	0.028	0.376
	10.0	0.28678	291	0.044	0.343
	15.0	0.28686	320	0.063	0.324

The experimental data (Table 3) have been applied to calculate through Formula (1) that during cementite decay, almost 10% of initial content of carbon atoms in ferrite pass into α solid solution:

$$\Delta C_{\alpha} = \Delta V_{\alpha} \cdot \frac{\alpha_{\alpha} - \alpha_{\alpha}^0}{39 \pm 4} \cdot 10^3 (\%), \quad (1)$$

where:

- ΔV_{α} – volume α -Fe share;
- α_{α} – current lattice parameter;
- $\alpha_{\alpha}^0 = 0.28668 \text{ \AA}$.

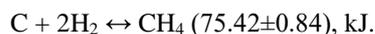
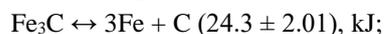
In the context of α -Fe, almost 35-40% of cementite carbon atoms (Table 4) pass into α solid solution during decay if service life of the internal well tube structures is from 7 to 15 years. It is believed that the cementite phase reduction results in the decreased strength metal characteristics [24].

Table 4. Values of volume cementite share in perlite, perlite, and cementite in steel used for the internal well tubes of T and WC

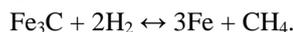
Steel grade	Service life, years	Content, %		
		perlite in steel, δ_p	cementite in perlite, δ_c	cementite in steel, δ_c
Tubing				
K	0	32.6	16.7	4.8
	1.5	28.6	16.0	4.5
	5	24.7	14.1	3.9
	8	22.0	13.8	3.7
L	0	31.5	15.9	4.9
	2.5	28.7	15.1	4.2
	7	24.8	13.6	3.9
	10	23.5	11.8	3.6
Well casing				
D	0	33.4	16.9	5.2
	5	30.1	15.8	4.7
	7.5	28.0	13.3	3.4
	12	26.7	11.4	2.9
L	0	30.7	15.5	4.6
	5	27.2	14.8	4.0
	10	23.3	12.2	3.6
	15	20.1	10.7	2.7

Durable operation of the internal well tubes (T and WC), results in cementite quantity decrease in the equipment; according to X-ray spectral analysis, it is almost 30-35%, and almost 20-25% according to the electron microscopic data.

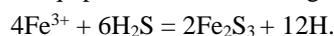
The abovementioned should involve the fact that cementite decays easily if hydrogen atoms interact with it:



Generally, the process is described through the reaction:



Atomic hydrogen releases readily with the sulphuretted hydrogen interaction; the latter gets differently into the formation fluid with the well equipment metal according to the reaction:



During deformation, active centres originate either at the surface of the internal well equipment or at the surface microcavities; within the centres, dissociation of hydrogen molecules takes place as well as atomic hydrogen penetration in the metal depth.

Tube steel experiences decarbonization during a long operational period favoured by simultaneous temperature and

barometric mode of the oil mixture pumping within the tube space of the well. Since carbon atom mobility within ferrite is poor under these conditions, the basic hydrogen reaction proceeds in a perlitic grain.

Table 5 shows diffusion coefficients of carbon and hydrogen atoms in α -Fe.

Table 5. Diffusion coefficients of carbon and hydrogen atoms in α -Fe

Temperature, °C	20	100
H	$1.5 \cdot 10^{-5}, \text{ cm}^2 \text{ s}$	$4.4 \cdot 10^{-5}, \text{ cm}^2 \text{ s}$
C	$2 \cdot 10^{-17}, \text{ cm}^2 \text{ s}$	$3.3 \cdot 10^{-14}, \text{ cm}^2 \text{ s}$

Initially, the reaction products, being methane and atomic hydrogen recombined into molecules, are accumulated in pores and microcavities within the boundary volumes of metal grains of the analyzed internal well tubes. Atoms of impurities and cavity are concentrated along the grain boundaries; as a result, the border-line grain areas are carbonized. Moreover, from the energetic viewpoint, grain boundaries are metastable [25]. In such cases, hydrogen pressure within the areas may achieve high values; hence, stresses, exceeding strength characteristics of the internal well tube metal, arise. Consequently, microcracks in metal originate causing generally seal failure as well as technological equipment destruction.

The results of the integrated and system experiments, complemented by the proposed solutions, may become the scientific basis to develop both organizational and technical and design-engineering measures preventing from hydration and cracking of tube structures aimed at durable operation in the corrosive environment in terms of simultaneous action of both internal and external alternating loads at the fields and oil enterprises.

4. Conclusions

The X-ray structural methods have helped identify accurately that corrosion of tubing and rods are followed by their active hydration, internal oxidation, and cracking almost up to intergranular decay of crystalline lattice. The process deepens obviously after the equipment operated durably in the corrosive environments of oil wells. It has been demonstrated simultaneously that during such a continuous service life, hydration of the internal well equipment results in significant degradation of plastic properties of metal factoring into its cracking as well as resistance to corrosion-mechanical failure.

The X-ray structural study has helped obtain the data supporting the idea of cementite decay in the metal of tubes used for internal well facilities during their continuous operation in the corrosion environments of oil fields.

The X-ray structural analysis has made it possible to identify the crystalline lattice parameters of α matrix; the elastic lattice bends (i.e. microstresses of bends) have been evaluated as well as carbon distribution in ferrite and cementite. The abovementioned enables to explain in a new way both reasons and mechanisms of resistance to corrosion in the context of internal well equipment.

It has been identified that deep rod failure by corrosive environment results from the complex and diverse processes of changes in a crystalline metal structure influenced heavily by the environment. A source of the corrosion fatigue failure is the metal hydration causing cracking and, consequently its destruction under the impact of alternating loads accelerated

by the corrosive environment. Further, under the effect of macrostresses, surface microfractures are developed into large discontinuities and cracks resulting in macrofractures.

Degrading hydrogen impact of crystalline metal structure has been shown creating conditions to damage tube structures of oil wells.

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Деградація сталей внутрішньо-свердловинного обладнання при тривалій експлуатації в корозійно-агресивних середовищах

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Мета. Дослідження деградації сталей внутрішньо-свердловинного обладнання тривалої експлуатації в умовах безпосереднього контакту з корозійно-активними середовищами.

Методика. Комплекс досліджень пошкоджених металевих труб внутрішньо-свердловинного обладнання нафтогазовидобувних свердловин, зокрема насосно-компресорних тривалою терміну експлуатації, включав, поряд зі стандартними, спеціальні види досліджень: різні варіанти рентгеноспектрального аналізу із використанням растрового електронного мікроскопа JSM-35CF (фірма “Джеол”, Японія) та SEM-515 з мікроаналізатором “Link” фірми “Philips”. Досліджувані зразки, виготовлені з насосно-компресорних труб у період несанкціонованих чи аварійних зупинок свердловин, термін експлуатації яких складав від 0 до

15 років. Для вивчення структури та хімічного складу металу, в тому числі газів – кисню й водню, механічним шляхом отримували стружку з різних ділянок стінки труб.

Результати. За допомогою рентгеноструктурних досліджень отримано дані, які свідчать про розпад цементиту (Fe_3C) в металі труб у процесі тривалої експлуатації внутрішньо-свердловинного обладнання. Методами рентгеноструктурного аналізу визначені параметри кристалічної решітки α -матриці, виконана оцінка рівня пружних викривлень решітки (мікронапруження викривлень), а також розподілу вуглецю в фериті й цементиті, що дало можливість, по-новому, пояснити причину і механізм зниження опору корозійному руйнуванню внутрішньо-свердловинного обладнання.

Наукова новизна. Встановлено нові закономірності при розпаді цементиту в металі труб, зміні параметра кристалічної α -решітки, мікронапруження викривлень решітки, а також розподілення вуглецю в фериті і цементиті, що надає можливість, по-новому, пояснити причину і механізм зниження опору корозійному руйнуванню внутрішньо-свердловинних конструкцій тривалої експлуатації в агресивних середовищах. Встановлені основні причини та механізми деградації трубних сталей, спричинених наводненням та окрихченням металу, що слугує підґрунтям для розробки науково обґрунтованих заходів зі зменшення цього негативно-го впливу на стан внутрішньо-свердловинного обладнання тривалого терміну експлуатації в хімічно-агресивних середовищах.

Практична значимість. Доведена деградуюча дія водню на кристалічну структуру металу, яка створює умови для руйнування трубних конструкцій нафтових і газових свердловин.

Ключові слова: корозія, сталь, руйнування, деградація, свердловина