Superduty steel / Стали особого назначения

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Problems of selection of corrosion-resistant steels and alloys in oil and gas industry for operating conditions

A. S. Fedorov, **V. S. Karasev, E. L. Alekseeva, A. A. Al'khimenko, N. O. Shaposhnikov**

Peter the Great St. Petersburg Polytechnic University (29 Politekhnicheskaya Str., St. Petersburg 195251, Russian Federation)

fedorov_as@spbstu.ru

Abstract. Corrosion-resistant steels and alloys have a number of unique properties. This allows them to be used in various industries. Despite their name, they are to some extent subject to various types of corrosion and corrosion-mechanical damage. This article discusses cases of corrosion damage of products made of corrosion-resistant steels and alloys in the oil and gas industry. The reasons of material failure can be incorrect exploitation of material, low-quality material of products, and incorrect selection of material for operating conditions. For each group of failure causes the examples from open sources and from the practice of the team of authors of this work are considered. The paper substantiates the importance of preliminary laboratory studies of corrosion-resistant materials and their testing with simulation of environmental factors. It is necessary for reasonable choice under specific operating conditions. It is shown that in practice the reasonable choice of corrosion-resistant materials is not always given due attention, so the seemingly economically favorable solutions may turn out to be incorrect. The main focus is made on the practical side of the issue in order to avoid such problems in the future. The relevance of the work is confirmed by the recent acute problem of substitution of foreign steel grades.

Keywords: corrosion-resistant steels and alloys, reasonable selection, causes of failure, operating conditions, incorrect operation, laboratory tests, physical simulation

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Проблемы подбора коррозионностойких сталей и сплавов в нефтегазовой отрасли под условия эксплуатации

А. С. Федоров, **В. С. Карасев, Е. Л. Алексеева, А. А. Альхименко, Н. О. Шапошников**

Санкт-Петербургский политехнический университет Петра Великого (Россия, 195251, Санкт-Петербург, ул. Политехническая, 29)

fedorov_as@spbstu.ru

Аннотация. Коррозионностойкие стали и сплавы обладают рядом уникальных свойств, позволяющих использовать их в различных отраслях промышленности. Однако, несмотря на свое название, они в той или иной мере подвержены различным видам коррозионных и коррозионно-механических повреждений. В данной работе рассматриваются случаи коррозионного разрушения изделий из коррозионностойких сталей и сплавов в нефтегазовой отрасли. Установлено, что причинами разрушения могут стать как некорректная эксплуатация и некачественный материал изделий, так и некорректный подбор материала под условия эксплуатации. Для каждой группы причин отказа рассмотрены примеры из открытых источников и из практики коллектива авторов работы. Обоснована важность проведения предварительных лабораторных исследований коррозионностойких материалов и их испытаний с воспроизведением факторов среды для обоснованного выбора под конкретные условия эксплуатации. Показано, что на практике обоснованному выбору коррозионностойких материалов не всегда уделяется должное внимание, поэтому кажущиеся на первый взгляд экономически выгодными решения могут оказаться некорректными. Основной фокус сделан на практической стороне вопроса для того, чтобы в будущем избежать подобных проблем. Актуальность работы подтверждается остро стоящей в последнее время проблемой замещения зарубежных марок сталей.

Ключевые слова: коррозионностойкие стали и сплавы, обоснованный выбор, причины разрушений, условия эксплуатации, некорректная эксплуатация, лабораторные испытания, физическое моделирование

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Introduction

Corrosion-resistant materials play a significant role in various industrial sectors [1 – 4]. Possessing enhanced corrosion resistance combined with the required mechanical properties [5 – 7], corrosion-resistant materials are used in aggressive environments where longevity without loss of operational characteristics is essential [8; 9]. Historically, the high cost of corrosion-resistant materials limited their use. However, over time, the understanding of the advantages of corrosion-resistant materials has led to their increasingly widespread use, particularly through the optimization of composition and properties for application in specific environments in critical components and structures [10 – 12]. At present, corrosion-resistant steels and alloys are used for more critical, expensive, and complex equipment where the potential risks, costs, or benefits outweigh the material's cost.

For the domestic metallurgical industry, the issue of producing import-substituting grades of corrosion-resistant steels and alloys is currently pressing. Russia accounts for 0.4 % of global corrosion-resistant steel production, with the volume of products produced satisfying no more than 25 % of the total domestic consumption of steel in various industries [13 – 15]. In 2021, 120,000 tonnes of corrosion-resistant steel were produced in Russia, while 463,000 tonnes were imported from abroad. Moreover, domestic equivalents do not always meet the end user's requirements for physical, mechanical, and corrosion properties.

A significant problem is that the domestic regulatory and technical documentation (RTD), containing requirements for the production technology and quality assessment of corrosion-resistant steels and alloys, is either outdated with minimal product requirements or entirely absent.

The relevance of this study lies in the emergence of numerous requests for import substitution, selection, and comparative evaluation of the properties of stainless steels and alloys for the implementation of domestic products, equipment, and technologies. Additionally, it draws on data from open sources and the many years of experience in failure analysis by the Scientific and Technological Complex "New Technologies and materials" at Peter the Great St. Petersburg Polytechnic University.

It is also important to note that discussions on the topic of failures and, moreover, their open analysis is a very contentious issue, as it leads to the search for culprits and punishment. However, in this work, the authors focused on the scientific or practical side of the issue to avoid similar problems in the future.

Review of failures

Conducting laboratory tests and research is an integral part of the justified selection of materials for specified operating conditions or their range [16 – 18]. In laboratory conditions, it is possible to carry out both standard tests according to existing methodologies (GOST, ASTM, ISO, DIN, etc.) and research work simulating aggressive environments close to real objects.

As numerous examples from open sources and the authors' extensive practice show, the choice of a particular material depending on operating conditions can often be incorrect [19 – 22]. Additionally, factors such as installation conditions, technological impacts [23 – 25], interactions with other materials [26 – 28], changes in operating conditions, and metallurgical quality [29 – 31] may not be taken into account. All these factors lead to failures and serious economic and environmental consequences.

Tables 1 – 3 provide an overview of failures of various products made from corrosion-resistant materials in the oil and gas industry and show the causes of these failures. Analysis of the sources revealed that cases of failures can be grouped into three categories: incorrect operation of the material, low-quality material of the products, and incorrect selection of material for the operating conditions. Among the cases of incorrect operation, those where the condition of the material was compromised during installation on-site – such as during welding work in the construction of structures made from corrosion-resistant steels – were also included.

Let us examine in detail the most interesting cases of damage and the methods for resolving the problems from each category.

Incorrect operation of the material. Consider an example from open sources. The authors of [21] analyzed the causes of corrosion damage in the rectification column of a cellulose acetate production plant, made from duplex

Table 1. **Overview of damage to corrosion-resistant materials. Incorrect exploitation of material**

Таблица 1. **Обзор разрушений коррозионностойких материалов. Некорректная эксплуатация материала**

No.	Material	Product	Failure/Causes	Source
1	UNS S32760 0.025 % C – 25 % Cr – 7.5 % Ni – 3.8 % Mo – 0.25 % N – – 0.57 % Cu – 0.5 % W	Welded oil transportation pipe	The pipe failed after one month of operation due to pitting in the heat-affected zone (HAZ) caused by the formation of σ-phase in an amount of 8 vol. % during the pre-welding heating process.	[20]
2	UNS S31803 0.016 % C – 22.4 % Cr – – 5.8 % Ni – 3.1 % Mo – – 0.17 % N – 0.55 % Si	Rectification column	The material exhibited a high rate of general corrosion after just a few months of use. The column operated in an oxygen-free environment with an excess of sulphuric acid in the liquid, which prevented the formation of a stable passive film on the steel surface.	[21]
3	UNS S32750 0.020 % C – 24.2 % Cr – – 8.7 % Ni – 3.8 % Mo – – 0.22 % N – 0.5 % Si – – 0.1 % Cu – 0.38 % Mn	Welded high-pressure vessel	Stress corrosion cracking (SCC) occurred in the heat-affected zone (HAZ). During welding, σ-phase formed in the HAZ in an amount of 2 vol. %. The operational environment was saturated with chlorides (~220 ppm), and the operating temperature was 110 °C. Crevice corrosion contributed to the propagation of SCC along the ferrite-austenite boundaries.	[22]

Table 2. **Overview of damage to corrosion-resistant materials. Low-quality material**

Таблица 2. **Обзор разрушений коррозионностойких материалов. Некачественный материал изделий**

No.	Material	Product	Failure/Causes	Source
1	UNS S32900 0.040 % C – 25 % Cr – 4 % Ni – – 1.5 % Mo – 0.5 % Si – 0.5 % Mn	Stem of a double-disc shut-off valve	The stem of a double-disc shut-off valve failed after 30 years of operation in an environment containing hydrogen sulphide (pH = 4, operating temperature 128 °C) due to sulphide stress corrosion cracking (SSCC). The SSCC crack predominantly propagated in the ferrite and along the ferrite-austenite boundary due to the presence of the σ-phase. Although the stem operated for 30 years, it could have lasted longer with properly conducted heat treatment.	[23]
2	UNS S32304 0.020 % C – 23.7 % Cr – – 4.2 % Ni – 0.3 % Mo – – 0.09 % N – 0.67 % Si – – 0.31 % Cu – 1.4 % Mn	Welded flexible pipe	The pipe experienced intergranular corrosion, leading to cracks in the welds. The cause of this was an excess of ferrite (~70 %) in the weld and the additional presence of unfavorable chromium nitrides at the ferrite-austenite boundaries. The excessive ferrite content resulted from the low linear energy values used during the welding process.	[24]

Table 2 (continutation). **Overview of damage to corrosion-resistant materials. Low-quality material**

Таблица 2 (продолжение). **Обзор разрушений коррозионностойких материалов. Некачественный материал изделий**

No.	Material	Product	Failure/Causes	Source
3	AISI 304 0.052 % C – 17.1 % Cr – 8.1 % Ni – 0.1 % Mo – 0.36 % Si – 1.02 % Mn	Convective pipe for geothermal water	Improper heat treatment before putting the pipe into operation led to sensitisation, which increases susceptibility to intergranular cracking. Residual stresses arising during production also contributed to the failure process. The presence of chlorides in the working environment caused SCC cracks to appear. In the initial stage, SCC cracks propagated along the austenite grain boundaries, then they transformed into a coexisting mode of intergranular and transgranular cracking. The authors attribute the pipe failure to the synergistic effect of sensitisation, the presence of chlorides, and residual stresses.	[25]
4	14Cr17N2 0.135 % C – 16.8 % Cr – – 1.66 % Ni – 0.51 % Si – – 0.58 % Mn	Flange of shut-off valve	The flange exhibited structural heterogeneity and a high content of chromium carbides along the grain boundaries. In addition to isolated pitting and localized corrosion damage, intergranular failure of the metal surface was observed. The poor metallurgical quality of the flange was exacerbated by active corrosion processes in an aggressive environment containing chlorides. As a result, the steel from this production is unsuitable for operation in seawater conditions.	STC "New Technologies and materials"
5	AISI 904L 0.011 % C – 20.7 % Cr – – 23.2 % Ni – 4.2 % Mo – – 0.32 % Si – 1.46 % Cu – – 1.16 % Mn	Steel plate	In this case, the cause of intergranular corrosion was the presence of excess phases located along the boundaries of the austenite grains in the base metal and in the interdendritic spaces of the weld joint, as well as micropores that served as concentrators for the propagation of intergranular corrosion cracks.	STC "New Technologies and materials"
6	EN 1.4469 (GX2CrNiMoN26-7-4) 0.020 % C – 27.3 % Cr – – 7.5 % Ni –4 % Mo – 0.67 % Si – 0.55 % Cu – 0.59 % Mn – – 0.2 % N – 0.05 % Ti	Cast components of centrifugal pumps	The main reason for the reduced resistance to crevice corrosion was the presence of grain boundary σ-phase precipitates (6.7 vol. %), which deplete the solid solution of alloying elements responsible for corrosion resistance, such as chromium and molybdenum.	STC "New Technologies and materials"
7	07Cr16Ni6 0.040 % C – 15.2 % Cr – 6.6 % Ni – 0.64 % Si – 0.16 % Cu – 0.49 % Mn	First stage impeller of the rotor	The cause of the failure was the presence of structural heterogeneity and the precipitation of carbides at the phase boundaries. These factors led to the failure of the impeller through the mechanism of stress corrosion cracking (SCC).	STC "New Technologies and materials"

Table 3. **Overview of damage to corrosion-resistant materials. Incorrect selection of material for operating conditions**

Таблица 3. **Обзор разрушений коррозионностойких материалов. Некорректный подбор материала под условия эксплуатации**

No.	Material	Product	Failure/Causes	Source
1	42CrMN (AISI 4130) 0.30 % C – 1 % Cr – 0.2 % Mo – – 0.25 % Si – 0.5 % Mn	Key	The occurrence of contact corrosion at the point of contact between the key and the valve stem led to the failure, resulting in the release of the pumped fluid into the environment.	[26]
	22Cr (DSS) 0.03 % C – 22.5 % Cr – 5.5 % Ni – – 3 % Mo – 1 % Mn	Valve stem		
2	AISI 410 0.07 % C – 13 % Cr – 0.5 % Ni – – 0.3 % Mo – 0.2 % Si – 0.5 % Mn	Steam turbine blades	The predominant mechanism is fatigue failure caused by changing operating conditions of the blades in the incoming steam. The presence of corrosion pits and intergranular cracks contributed to the activation of corrosion fatigue. Cyclic loading at high temperatures led to the rapid growth and propagation of cracks.	[27]
3	Super 13Cr 0.03 % C – 13 % Cr – 6 % Ni – – 1.7 % Mo – 0.3 % Si – 0.1 % Cu – – 0.7 % Mn – 0.09 % N	Pipeline of Resak A-6 Well in Malaysia	Intergranular cracks were found on all fracture surfaces of the extracted components. The presence of oxygen, CO_2, and H_2S in the $CaCl_2$ salt solution was the most likely cause of the failure. Laboratory test results showed that this steel is susceptible to SCC in the operational environment at the reservoir water temperature of the well.	[28]
4	12Cr18Ni9 (AISI 304) 0.05 % C – 18.1 % Cr – 8.1 % Ni – – 0.05 % Mo – 0.5 % Si – – 0.05 % Cu – 1.22 % Mn	Heat exchanger elements of the low-temperature natural gas separation unit	According to the approved project documentation, the material for the heat exchanger unit should have been 12Cr18Ni10T (AISI 321). However, the research revealed a substitution of this steel grade with 12Cr18Ni9 (AISI 304). The primary cause of the failure was a violation of the project documentation requirements regarding the unsanctioned change of the steel grade. This led to the incorrect selection of the welding mode, which caused the activation of the metal in the heat-affected zone of the non-stabilized titanium steel, resulting in through pitting under the influence of the corrosive environment.	STC "New Technologies and materials"
5	05Х16Н4Д2Б 0.020 % C – 13 % Cr – 4 % Ni – – 0.18 % Si – 2.1 % Cu – – 0.32 % Mn	Pump shaft	The hardness of this material did not match the quality certificate and did not meet the requirements of the NACE MR0175 standard. During laboratory tests for SCC resistance, failure occurred in all cases within the first day of testing.	STC "New Technologies and materials"

steel UNS S31803. The process fluid was an aqueous solution of 80 % acetic acid, which was separated by rectification. Due to the incomplete neutralisation of sulphuric acid in the process fluid used as a catalyst for ester hydrolysis, the column operated in a reducing environment, preventing the formation of a stable passive film on the metal surface.

To solve this problem, the authors proposed modifying the composition of the process fluid. By adding hydrogen peroxide under laboratory conditions, they created oxidizing conditions that promoted the formation of a stable passive film. Based on the results of laboratory studies, hydrogen peroxide was continuously added to the operating column. This approach proved successful in stopping corrosion processes until the next scheduled maintenance shutdown.

Low-quality material of the products. Consider a case from the authors' practice involving intergranular corrosion, using AISI 904L steel plate as an example. Before putting the material into operation, acceptance tests for resistance to intergranular corrosion (IGC) were required. The tests were conducted according to GOST 6032 – 2017 using the weight loss method in a boiling aqueous solution of ferric sulfate ($Fe_2(SO_4)_3 \cdot 9H_2O$) and sulphuric acid (H_2SO_4) in a flask with a reflux condenser. The duration of exposure in the boiling solution was 48 h. Upon completion of the tests, samples were bent at a 90° angle to assess the cracking of the base metal and the welded joint. Figs. 1, *a* and *b* show intergranular cracks in the base metal and the weld metal.

In this case, the cause of intergranular corrosion was the presence of excess phases located along the boundaries of the austenitic grains of the base metal and in the interdendritic spaces of the welded joint, as well as micro-voids that served as stress concentrators for the propagation of IGC cracks. Thus, laboratory tests established that the material of this production is prone to IGC. Introducing this plate into operation poses a high risk of subsequent cracking.

Incorrect selection of material for operating conditions. Consider the failure of heat exchanger elements in a low-temperature natural gas separation unit due to through pitting corrosion in the weld area, based on the authors' practice (see Fig. 2). According to the approved project documentation, the material for this unit should have been steel 12Cr18Ni10T (AISI 321) with a titanium content of 0.4 to 1.0 wt. %. However, investigations revealed a substitution of the steel grade with 12Cr18Ni9 (AISI 304). In terms of pitting corrosion resistance, 12Cr18Ni10T and 12Cr18Ni9 steels are similar in their corrosion properties [32; 33]. However, in the case of welding non-stabilized steels, the corrosion resistance of the weld and the heat-affected zone can be significantly lower than that of the base metal [34].

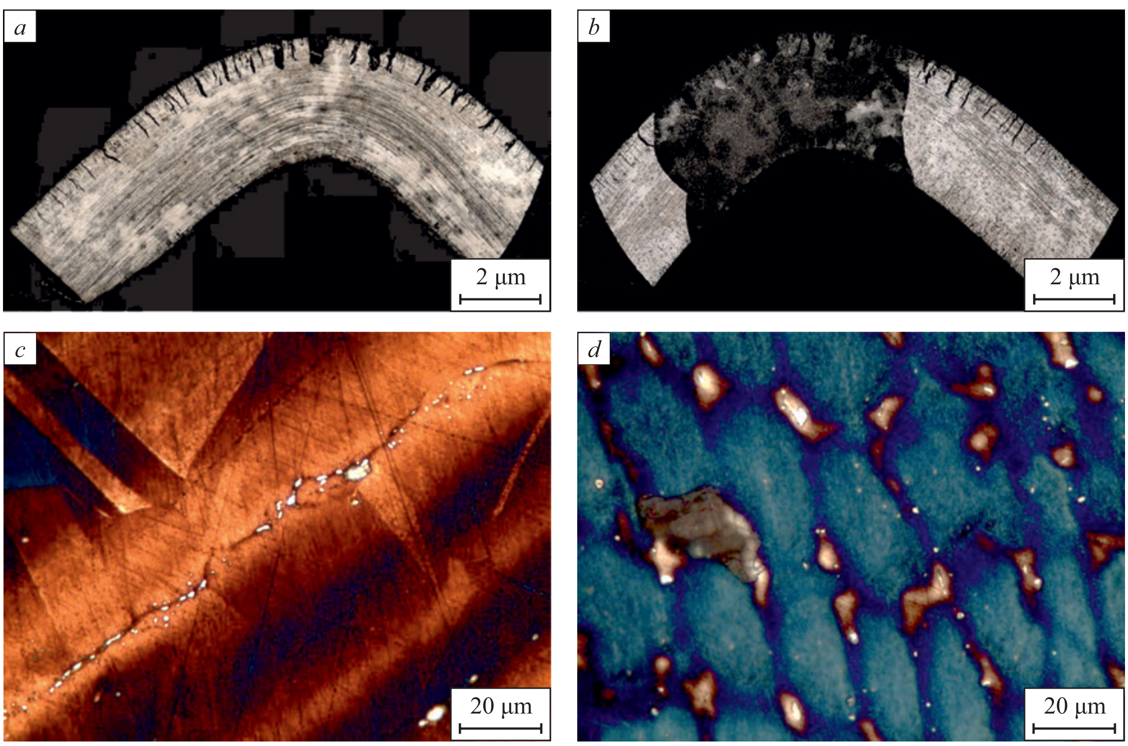


Fig. 1. Intergranular cracks in the base metal (*a*) and in the welded joint (*b*), and images of excess phases in the base metal (*c*) and in the welded joint (*d*)

Рис 1. Межкристаллитные трещины в основном металле (*a*) и в сварном соединении (*b*), а также изображения избыточных фаз в основном металле (*c*) и в сварном соединении (*d*)

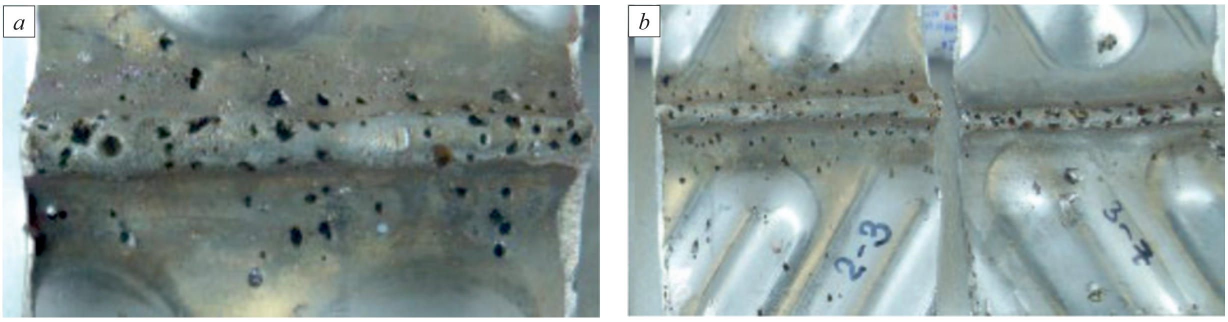


Fig. 2. Appearance of corrosion damage in the area of welded joint of heat-exchange elements of low-temperature natural gas separation unit

Рис. 2. Внешний вид коррозионных поражений в области сварного соединения теплообменных элементов аппарата низкотемпературной сепарации природного газа

The presence of titanium ensures the formation of favorable TiC carbides instead of undesirable $Cr_{23}C_6$ carbides, which reduce corrosion resistance.

Thus, the primary cause of the through defects in this case was the violation of the project documentation requirements regarding the unsanctioned change of the steel grade. This led to the incorrect selection of the welding mode, which caused activation of the metal in the heat-affected zone of the non-stabilized titanium steel, resulting in through pitting under the influence of the corrosive environment.

Results and discussion

The relatively small number of examined failures raises a broad spectrum of issues related to the production of high-quality corrosion-resistant steels and alloys, the selection of materials for operating conditions, the incompleteness of existing RTD, and the qualifications of specialists.

The issue of the quality of corrosion-resistant materials is extensive and requires the development and implementation of new RTD that describes quality requirements. This is a long-term and meticulous task; nevertheless, there are successful examples of such developments in domestic practice [35 – 38]. It is worth noting that currently, the only document in the oil and gas industry related to the selection and operation of corrosion-resistant steels is NACE MR0175, Part 3, which has not been harmonized with GOST. Moreover, this document only pertains to hydrogen sulphide-containing environments, while the evaluation of the possibility of using steels in CO_2-containing environments is becoming increasingly relevant [39].

Incorrect material selection is linked to the lack of selection methodologies and proper corrosion resistance assessment techniques. Material selection guidelines are usually developed within companies and are subject to internal policies. However, the relatively new Institute of Oil and Gas Technological Initiatives (“INTI”) can gradually address such issues. The testing methodologies being developed to assess the corrosion resistance of materials should consider the reproduction of aggressive operating conditions on the sites.

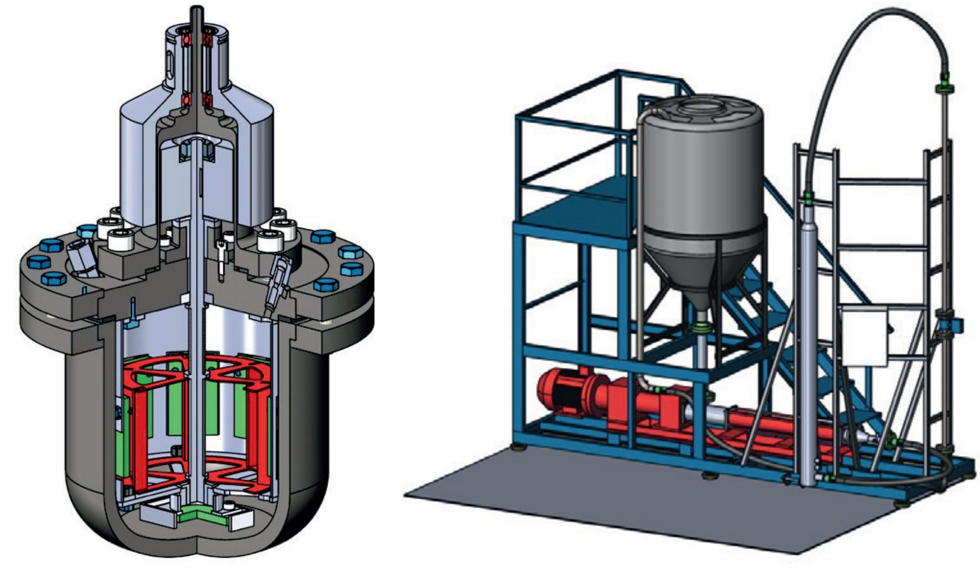
At the Scientific and Technological Complex “New Technologies and materials”, there is a substantial testing base of various stands and installations, allowing materials to be tested under conditions as close to operating conditions as possible, including flow parameters. The authors’ team designed and manufactured autoclave installations of various volumes (Fig. 3, *a*), allowing tests to be conducted at elevated pressure and temperature in both static and dynamic conditions [40]. Tests involving supercritical fluids are also conducted in autoclaves.

The aggressiveness of the environment can manifest not only through the presence of corrosion-active agents but also through abrasive particles leading to abrasive wear. The combined influence of these two factors can significantly exacerbate the material degradation process. Their combined effect can be simulated using closed “flow-loop” stands, which also consider thermobaric parameters and fluid flow impact (Fig. 3, *b*).

However, conducting tests where many environmental parameters are controlled requires a lot of time and resources. Therefore, databases are created using the results of numerous tests, considering parameters determined on the stand, which are then used in a mathematical model to develop a digital twin.

The review of issues related to the justified selection of corrosion-resistant steels and alloys in the oil and gas industry highlights important aspects related to their operation in aggressive environments.

In the oil and gas industry, materials face aggressive environments, high temperatures, cyclic loads, and mechanical stresses. In practice, justified selection of corrosion-resistant materials does not always receive adequate attention, so seemingly economically advantageous solutions can turn out to be incorrect. This can lead to serious problems and additional costs for replacement



a *b*

Fig. 3. Test facility for physical modelling with reproduction of aggressive operating conditions: dynamic autoclave with rotation (*a*); corrosion-erosion bench (*b*)

Рис. 3. Испытательная база для проведения физического моделирования с воспроизведением агрессивных условий эксплуатации: динамический автоклав с вращением (*a*); коррозионно-эрозионный стенд (*b*)

or major repairs. For successful application of corrosion-resistant materials, preliminary laboratory studies must be conducted to recreate environmental factors to confirm the material's quality and corrosion resistance under specific operating conditions. Effective solutions require close cooperation between engineers, scientists, researchers, and manufacturers.

Conclusions

A review of the causes of failures of products made from corrosion-resistant materials in the oil and gas industry has been conducted. It has been established that the causes of material failure can be incorrect operating conditions, poor-quality materials, and incorrect selection of materials for the operating conditions. Examples from open sources and the authors' practice have been considered for each group of failure causes. The importance of conducting preliminary laboratory studies of corrosion-resistant materials and their testing with the simulation of environmental factors for a justified choice under specific operating conditions has been substantiated. The approaches used by the authors' team for conducting physical modelling of environmental factors with the recreation of real conditions, including flow parameters, have been demonstrated.

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Information about the Authors / Сведения об авторах

***Aleksandr S. Fedorov**, Engineer of the Scientific and Technological Complex "New Technologies and Materials",* Peter the Great St. Petersburg Polytechnic University
ORCID: 0000-0003-2571-060X
E-mail: fedorov_as@spbstu.ru

***Vladimir S. Karasev**, Engineer of the Scientific and Educational Center "Severstal-Polytech",* Peter the Great St. Petersburg Polytechnic University
ORCID: 0009-0006-9622-7243
E-mail: karasev_vs@spbstu.ru

***Ekaterina L. Alekseeva**, Cand. Sci. (Eng.), Leading Engineer, Head of the Laboratory of the Scientific and Technological Complex "New Technologies and Materials",* Peter the Great St. Petersburg Polytechnic University
E-mail: alekseeva_el@spbstu.ru

***Aleksei A. Al'khimenko**, Director of the Scientific and Technological Complex "New Technologies and Materials",* Peter the Great St. Petersburg Polytechnic University
ORCID: 0000-0001-6701-1765
E-mail: a.alkhimenko@spbstu.ru

***Nikita O. Shaposhnikov**, Executive Director of the Scientific and Technological Complex "New Technologies and Materials",* Peter the Great St. Petersburg Polytechnic University
E-mail: shaposhnikovno@gmail.com

***Александр Сергеевич Федоров**, инженер Научно-технологического комплекса «Новые технологии и материалы»,* Санкт-Петербургский политехнический университет Петра Великого
ORCID: 0000-0003-2571-060X
E-mail: fedorov_as@spbstu.ru

***Владимир Сергеевич Карасев**, инженер Научно-образовательного центра «Северсталь-Политех»,* Санкт-Петербургский политехнический университет Петра Великого
ORCID: 0009-0006-9622-7243
E-mail: karasev_vs@spbstu.ru

***Екатерина Леонидовна Алексеева**, к.т.н., ведущий инженер, заведующий лабораторией Научно-технологического комплекса «Новые технологии и материалы»,* Санкт-Петербургский политехнический университет Петра Великого
E-mail: alekseeva_el@spbstu.ru

***Алексей Александрович Альхименко**, директор Научно-технологического комплекса «Новые технологии и материалы»,* Санкт-Петербургский политехнический университет Петра Великого
ORCID: 0000-0001-6701-1765
E-mail: a.alkhimenko@spbstu.ru

***Никита Олегович Шапошников**, исполнительный директор Научно-технологического комплекса «Новые технологии и материалы» центра НТИ,* Санкт-Петербургский политехнический университет Петра Великого
E-mail: shaposhnikovno@gmail.com

Contribution of the Authors

A. S. Fedorov – formation of the main research idea, development of the work methodology, analysis of research results.
V. S. Karasev – development of the work methodology, analysis of research results.
E. L. Alekseeva – formation of the main research idea, setting the tasks.
A. A. Al'khimenko – concept formation, scientific guidance.
N. O. Shaposhnikov – research plan development, scientific guidance.

Вклад авторов

А. С. Федоров – формирование основной идеи исследований, разработка методологии работы, анализ результатов исследований.
В. С. Карасев – разработка методологии работы, анализ результатов исследований.
Е. Л. Алексеева – формирование основной идеи исследований, постановка целей и задач работы.
А. А. Альхименко – формирование концепции, научное руководство.
Н. О. Шапошников – разработка плана исследований, научное руководство.

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