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# Safety of Technogenic and Natural Systems

Technosphere Safety

Machine Building

Chemical Technologies, Materials Sciences, Metallurgy





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of the Editorial Office: 1, Gagarin Sq. Rostov-on-Don, 344003, Russian Federation

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 E-mail:
 vestnik@donstu.ru

 Телефон:
 +7 (863) 2–738–372

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#### **Contents**

#### TECHNOSPHERE SAFETY

	Assessment and Prediction of the Environmental Performance of Multi-Component Cements Using	
	Statistical Analysis	. 87
	Elena E. Smirnova	
	Assessment of the Potential Risk of Poisonous Plants in Rostov-on-Don	. 102
	Mikhail M. Sereda	
	Natural Sorbent Based on Zeolite-Containing Rocks of Tatarsko-Shatrashan Deposit for Treatment	
	of Surface and Waste Water from Organic Pollutants	. 112
	Alina V. Taneeva, Yuliya V. Snigireva, Radik N. Khizbullin, Darya A. Shlykova, Vyacheslav F. Novikov	
	Methodological Principle for Personnel Safety Assessment Based on Likelihood of Negative Events	121
	Anatoly I. Fomin, Dmitrii A. Besperstov, Anatoly A. Trubitsyn, Nelya V. Trubitsyna, Ekaterina A. Popova,	
	Valeriya A. Petrova	
	Green Roofs in Infill Development to Improve the Environmental Safety of Urban Areas	136
	Svetlana E. Manzhilevskaya, Aleksandr I. Evtushenko, Dmitrii R. Mailyan	
ΜA	CHINE BUILDING	
	Probability Grid Method for Fisher-Tippett Law	146
	Anatoly A. Kotesov	
	Methodology for Determining the Classification Group of Jib Cranes of Foreign Companies	
	when Assessing Their Technical Condition during Current Sanctions	158
	Dmitry N. Simonov, Roman V. Khvan, Elvira A. Panfilova, Leonid A. Ternovskoi	
СН	EMICAL TECHNOLOGIES, MATERIALS SCIENCES, METALLURGY	
	Influence of Pre-Carburization on the Structure and Properties of Chromium Coatings on Steels Formed	
	by Diffusion Alloying in Liquid Metal Media Solutions	170
	Lev I. Svistun. Eduard E. Bobylyov, Aslan D. Nirov, Ivan D. Storozhenko, Roman A. Popov	0

#### Содержание

#### ТЕХНОСФЕРНАЯ БЕЗОПАСНОСТЬ

	Оценка и прогноз экологической эффективности многокомпонентных цементов на основе статистического анализа	87
	Е.Э. Смирнова	
	Оценка потенциальной опасности ядовитых растений г. Ростова-на-Дону	102
	Природный сорбент на основе цеолитсодержащих пород Татарско-Шатрашанского	
	месторождения для очистки поверхностных и сточных вод от органических загрязнителей	112
	Методологический принцип оценки обеспечения безопасности персонала на основе	121
	вероятности возникновения негативных событий	121
	Применение зеленых крыш в точечном строительстве для повышения экологической безопасности городских территорий	136
MAl	ШИНОСТРОЕНИЕ	
	Метод вероятностной сетки для закона Фишера – Типпета	146
	Методика определения группы классификации стреловых кранов зарубежных фирм при оценке их технического состояния в период действующих санкций	158
ХИМ	мические технологии, науки о материалах, металлургия	
	Влияние предварительной цементации на структуру и свойства диффузионных покрытий на основе хрома на сталях, полученных в среде легкоплавких жидкометаллических растворов	170

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Original Empirical Research

#### Assessment and Prediction of the Environmental Performance of Multi-Component Cements Using Statistical Analysis

Elena E. Smirnova



St. Petersburg State Chemical and Pharmaceutical University, St. Petersburg, Russian Federation ⊠ esmirnovae@yandex.ru



#### **Abstract**

Introduction. The cement industry, a cornerstone of the construction sector, generates significant CO<sub>2</sub> emissions (5–8% of global totals). Amid growing demands for sustainable development and green construction, the development of multi-component cements (MCCs) with clinker partially replaced by active mineral additives (slag, phosphogypsum) is critical for reducing environmental impact while enhancing properties such as sulfate resistance, strength, and deformation control. The core problem lies in the lack of systematic statistical approaches to optimize MCC compositions, which hinders achieving a balance between environmental sustainability and performance characteristics. Many studies on MCCs focus on strength and sulfate resistance, but rarely employ statistical methods for comprehensive composition optimization. Other works highlight the environmental benefits of MCCs, yet fail to propose systematic approaches for property prediction. The research gap stems from insufficient correlation analyses of the relationships between chemical composition and MCCs properties, as well as limited investigation into the impact of impurities (e.g., MgO, alkali oxides) on sulfate resistance, which restricts the development of versatile formulations. This study aims to develop statistical approaches for optimizing MCC compositions to enhance sulfate resistance, control self-stress and linear expansion, and reduce carbon footprint, thereby addressing the identified research gap. To achieve this, the following tasks are defined: conduct correlation analysis of the relationships between MCC chemical composition (SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, etc.) and performance characteristics (sulfate resistance, self-stress, linear expansion) based on experimental data; evaluate the environmental efficiency of replacing clinker with active mineral additives (blast-furnace slag, phosphogypsum, calcium hydrogarnets) through carbon footprint calculations; identify key chemical components with the greatest influence on sulfate resistance and deformation properties, and provide optimization recommendations; investigate the impact of impurities in active additives (e.g., MgO, alkali oxides) on sulfate resistance and propose mitigation strategies; develop an adapted MCC component matrix to predict cement properties and ensure compliance with sustainable construction requirements. These objectives and tasks aim to bridge the scientific knowledge gap by integrating statistical methods into MCC development, enabling the creation of environmentally safe, high-performance building materials that meet modern standards.

Materials and Methods. The research is derived from the statistical assessment of experimental data presented in patent RU2079458C1 (authors Andreev V.V., Smirnova E.E.). Data on 8 formulations of multi-component cements were analyzed, including Portland cement clinker (Pikalevo), blast-furnace slags (Cherepovets, Magnitogorsk), electrothermosulfate slag (SPTI), calcium hydrogarnets (GGK-1, GGK-2), and phosphogypsum (Kingisepp). Relationships between the chemical makeup of constituents (SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, etc.) and their performance characteristics (self-stress, linear expansion, and sulfate resistance), determined according to standard methods (GOST 310.1-76, GOST 310.4-81, TU 21-26-13-90), were examined. Correlation evaluation was used as the main method. Visualization of correlation matrices was carried out using heatmaps (Seaborn library in Python). Additionally, calculations of the economic and environmental efficiency of partially replacing clinker with the specified active admixtures were performed.

Results. The findings of the statistical review confirmed the significant impact of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and other elements on the performance attributes of cements. It was determined that the calculated replacement of 30% of clinker with SCMs allows for a mitigation of the carbon footprint by 25–40%. It was revealed that enhancing the SiO<sub>2</sub> content in the cement formulation improves the sulfate resistance of the cement paste, and literature data suggest that thermal activation of slags boosts compressive strength by 12–15%, improving the degree of hydration of constituents and forming a denser cement matrix. Economic assessment demonstrated that clinker substitution with active supplements can decrease cement production costs by 10–15%.

Discussion and Conclusion. Correlation assessment substantiated the pivotal role of SiO<sub>2</sub> in bolstering the sulfate resistance of the cementitious material. It was found that the silicate blast-furnace admixture used (slag A) can diminish sulfate resistance, which is presumably explained by the presence of impurities such as MgO and alkali oxides. Evaluation of the basicity coefficient (B =  $(CaO + MgO + Al_2O_3) / SiO_2$ ) revealed that when B < 1, hydration processes deteriorate, resulting in the formation of weak gel structures necessitating compensation with pozzolanic supplements. Statistical calculations highlighted a strong positive correlation (r = 0.89) between sulfate resistance and linear expansion, validating the potential for regulating these features through the precise makeup of cement mixtures. Furthermore, calculations indicated that lowering the C<sub>3</sub>A content in clinker below 8% significantly enhances cement durability in aggressive environments. The developed statistical techniques can be used for refining formulations to create environmentally sustainable binders with improved performance characteristics. The need for further investigation to verify the models on a wider range of materials and under industrial conditions is acknowledged.

**Keywords:** correlation analysis, multi-component cements, statistical analysis, sulfate resistance, carbon footprint, environmental sustainability

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Оригинальное эмпирическое исследование

### Оценка и прогноз экологической эффективности многокомпонентных цементов на основе статистического анализа

#### Е.Э. Смирнова

Санкт-Петербургский государственный химико-фармацевтический университет, г. Санкт-Петербург, Российская Федерация  $\bowtie$  esmirnovae@yandex.ru

#### Аннотация

Введение. Цементная промышленность, обеспечивая строительный сектор, генерирует значительные выбросы СО2 (5-8 % от глобальных). В условиях устойчивого развития и зеленого строительства актуальна разработка многокомпонентных цементов (МКЦ) с заменой клинкера активными добавками (шлаки, фосфогипс) для снижения экологической нагрузки и улучшения свойств (сульфатостойкость, прочность, контроль деформаций). Проблема заключается в отсутствии систематических статистических подходов к оптимизации составов МКЦ, что затрудняет определение баланса между экологичностью и эксплуатационными характеристиками. Многие исследования МКЦ фокусируются на прочности и сульфатостойкости, но редко используются статистические методы для комплексной оптимизации состава. В некоторых исследованиях подчеркиваются экологические преимущества МКЦ, но не предлагаются системные подходы к прогнозированию их свойств. Таким образом, можно говорить о недостатке корреляционного анализа взаимосвязей между химическим составом и свойствами МКЦ, а также о недостаточно изученном влиянии примесей (MgO, щелочи) на сульфатостойкость, что ограничивает составление универсальных рецептур. Целью данного исследования является разработка статистических подходов к оптимизации состава МКЦ для повышения их сульфатостойкости, контроля самонапряжения и линейного расширения, а также снижения углеродного следа, что позволит заполнить выявленный пробел в научном знании. Для достижения поставленной цели необходимо провести корреляционный анализ взаимосвязей между химическим составом МКЦ (содержание  $SiO_2$ , CaO,  $Al_2O_3$ ,  $Fe_2O_3$ ,  $SO_3$  и др.) и их эксплуатационными характеристиками (сульфатостойкость, самонапряжение, линейное расширение) на основе экспериментальных данных, оценить экологическую эффективность замены клинкера активными минеральными добавками (доменные шлаки, фосфогипс, гидрогранаты кальция) с использованием расчетов углеродного следа, выявить ключевые химические компоненты, оказывающие наибольшее влияние на сульфатостойкость и деформационные свойства и разработать рекомендации по их оптимизации, исследовать влияние примесей в активных добавках (например, MgO, щелочные оксиды) на сульфатостойкость и предложить пути их минимизации, разработать адаптированную матрицу компонентов МКЦ, позволяющую прогнозировать свойства цементов и обеспечивать их соответствие требованиям устойчивого строительства. Достижение цели исследования позволит заполнить пробел в научном знании путем интеграции статистических методов в процесс разработки МКЦ, что даст возможность создавать экологически безопасные и высокопроизводительные строительные материалы, отвечающие современным требованиям.

Материалы и методы. Исследование основано на статистическом анализе экспериментальных данных, представленных в патенте RU 2079458 C1 (авторы — Андреев В.В., Смирнова Е.Э.). Анализировались данные по восьми составам МКЦ, включающим портландцементный клинкер (Пикалево), доменные шлаки (Череповец, Магнитогорск), электротермосульфатный шлак (СПТИ), гидрогранаты кальция (ГГК-1, ГГК-2) и фосфогипс (Кингисепп). Рассматривались взаимосвязи между химическим составом компонентов (SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> и др.) и эксплуатационными характеристиками (самонапряжение, линейное расширение, сульфатостойкость), определенными согласно стандартным методикам (ГОСТ 310.1–76, ГОСТ 310.4–81, ТУ 21–26–13–90). В качестве основного метода использовался корреляционный анализ. Визуализация корреляционных матриц осуществлялась с помощью тепловых карт (библиотека Seaborn в Python). Дополнительно проведены расчеты экономической и экологической эффективности замены части клинкера указанными активными добавками.

**Результаты** исследования. Результаты статистического анализа подтвердили значительное влияние содержания  $SiO_2$ ,  $Al_2O_3$  и других компонентов на эксплуатационные характеристики цементов. Установлено, что расчетная замена клинкера на 30 % активными добавками позволяет снизить углеродный след на 25–40 %. Установлено, что оптимизация содержания  $SiO_2$  в составе цемента увеличивает сульфатостойкость цементного камня, а данные уже имеющихся научных изысканий указывают на то, что термоактивация шлаков усиливает их прочность на 12–15 %, повышая степень гидратации компонентов и формируя более плотную цементную матрицу. Экономический анализ показал, что замена клинкера позволяет снизить стоимость производства цементов на 10–15 %.

Обсуждение и заключение. Корреляционный анализ подтвердил ключевую роль  $SiO_2$  в обеспечении сульфатостойкости цемента. Обнаружено, что использованная силикатная доменная добавка (шлак A) может снижать сульфатостойкость, что предположительно объясняется наличием примесей, таких как MgO и щелочные оксиды. Анализ коэффициента основности (B = (CaO + MgO + Al<sub>2</sub>O<sub>3</sub>) / SiO<sub>2</sub>) показал, что при B < 1 происходит ухудшение гидратации и образование слабых гелевых структур, требующих компенсации пуццолановыми добавками. Статистические расчеты продемонстрировали высокую положительную корреляцию между сульфатостойкостью и линейным расширением (r = 0,89), подтверждая возможность регулирования этих свойств через состав цементных смесей. Расчеты также показали, что снижение содержания  $C_3A$  в клинкере ниже 8 % способствует повышению долговечности цементов в агрессивных средах. Разработанные статистические подходы могут быть использованы для оптимизации рецептур с целью создания экологически устойчивых цементов с улучшенными эксплуатационными характеристиками. Признается необходимость дальнейших исследований для верификации моделей на более широком спектре материалов и в промышленных условиях.

**Ключевые слова:** корреляционный анализ, многокомпонентные цементы, статистический анализ, сульфатостойкость, углеродный след, экологическая безопасность

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**Introduction.** MCCs play a key role in the modern construction industry due to their environmental and operational advantages. They can reduce the carbon footprint and improve the durability of structures, which makes their research extremely relevant in the context of increasing demands for sustainable construction. A review of recent publications shows considerable attention to the chemical composition of MCCs and their properties. In the works of A. Rashad (2023),

the influence of steel fibers and calcium oxide on the properties of cements, including strength and resistance to aggressive media, is considered [1]. Geopolymers, being a promising alternative to cement due to their environmental friendliness and good compressive strength, have a significant disadvantage — brittleness, which results in low bending and tensile strength. To eliminate this, steel fibers of various shapes are introduced into the geopolymer matrix. In geopolymers based on slag or mixed binders, the introduction of fibers often leads to a decrease in water absorption and permeability, which is an important factor in increasing the durability of the material [2]. Studies by M. Rahman & M. Bassuoni (2014) [3], and M. Sakr & M. Bassuoni (2020) [4] emphasize the importance of preventing sulfate corrosion by optimizing cement composition. It also highlights the importance of reducing C<sub>3</sub>A content to increase the resistance of concrete to aggressive environments (Sivkov, 2015) [5]. M. Thomas et al. (2008) focus on delayed ettringite formation as a factor affecting durability [6]. I.P. Pavlova (2016) notes that plasticizing additives significantly affect strength characteristics and deformations of expanding cement systems. The choice of a plasticizer with the appropriate chemical structure significantly improves the characteristics of cement systems, contributing to their adaptation to the specific requirements of construction [7]. The work of T. Markiv et al. (2020) confirms the importance of studying the composition of cements in order to achieve optimal characteristics [8]. L. Srikakulam & V. Khed (2020) model the design of an engineering cement composite (ECC) with the addition of various mineral additives and fibers [9]. The article by Yum et al. (2020) evaluates the effect of calcium formate (CF) on strength development and microstructure of the CaO-activated crushed granular blast furnace slag (GGBFS) system [10]. Sanytsky et al. (2020) show that the introduction of nanomodifiers leads to significant improvements in cement properties [11].

L.D. Shakhova and D.E. Kucherov (2008) consider the practice of using MCCs in Germany. With the transition of cement industry to standardized production, it becomes necessary to choose cement based on its material and mineralogical compositions. Composite and multicomponent cements, including active additives and inert fillers, are of limited use in Russia. However, their use reduces the proportion of clinker and helps reduce CO<sub>2</sub> emissions, as well as increases the strength and durability of concrete. The article also discusses the regulatory requirements and potential of new cements in various fields of construction [12].

M.N. Chomaeva (2019) analyzes the impact of cement industry on the environment and emphasizes the need to develop new types of cements with improved environmental performance. Problems with generation of toxic gases such as dioxins and cyanides require strict control over the composition of raw materials and the process temperature to prevent their formation and protect public health. The introduction of integrated technologies for dechromatization and waste disposal in the cement industry significantly reduces the level of heavy metals and other harmful impurities, which is an important step towards environmentally friendly production [13]. O.N. Khokhryakov's dissertation (2022) is devoted to the introduction of highly dispersed binders and the use of industrial waste in cement production to create new building materials that meet the requirements of modern construction. To improve the properties of cements, the author suggests using polycarboxylate superplasticizers, which increase fluidity and reduce water consumption, which makes it possible to achieve higher strength and durability of concrete structures [14]. Scientists emphasize that carbonate cements with low water consumption represent a promising and environmentally friendly alternative to traditional cements in Russia. They contribute to reducing carbon emissions and increasing the sustainability of building materials. Due to their ability to reduce water consumption and improve the plasticity of concrete mixtures, carbonate cements provide not only economic but also environmental efficiency, which meets the requirements of sustainable development [15]. In modern research on the mechanics of composites, special attention is paid to increasing the initial strength of cement materials through mechanical activation. The most noticeable results are achieved when activating a binary mixture of cement and sand, which significantly increases strength characteristics in the early stages of hardening [16]. The use of finely dispersed additives and superplasticizers allows achieving significant results in increasing the strength and durability of powder-activated concretes [17].

Despite significant advances in the study of MCCs, the problem of increasing their environmental sustainability while maintaining operational characteristics remains unresolved. One of the key tasks is to develop an adapted component matrix that would optimize the composition of cements for various operating conditions [18].

The relevance of the study is confirmed by modern requirements for reducing the carbon footprint in the construction industry and the need for environmentally friendly building materials [19]. In addition, international standards and programs require new approaches to the assessment and optimization of cement properties. According to S. Yang et al. (2023), the development of the construction industry in recent decades has been driven by increasing demands for optimal and efficient use of raw materials and energy resources. The need to follow a low-carbon development strategy is emphasized, which leads to an urgent need to increase the production of cements and concretes with reduced content of energy-intensive clinker and, as a result, to reduce CO<sub>2</sub> emissions during their production. The article mentions specific initiatives such as the EU strategy for reducing greenhouse gas emissions and the Green Deal Program aimed at achieving climate neutrality by 2050, which indicates the global scale of the

problem [20]. According to other authors, progress in construction and stricter requirements for safety and reliability of structures stimulate the development of new, highly efficient materials with increased strength and durability. At the same time, the importance of reducing the carbon footprint and improving the environmental safety of building materials is emphasized. It is noted that traditionally, a material such as ECC (engineered cementitious composite) is characterized by an increased cement content compared to conventional concrete, which not only causes technical problems (increased heat generation, shrinkage), but also negatively affects the cost and environmental impact of the material. As a solution to this problem, Sydor N., Marushchak U., Braichenko S., Rusyn B. propose partial replacement of Portland cement with industrial waste — fly ash [21]. The results of this study are of practical importance for manufacturers of building materials, as they allow us to develop new formulations of cements that enhance their stability and durability. They also contribute to solving global environmental problems related to reducing CO<sub>2</sub> emissions. The aim of this work is to study the effect of MCCs on environmental performance and performance characteristics, as well as to develop approaches to optimizing their composition.

Materials and Methods. The objectives of the article were based on the analysis of current problems in the field of MCCs, including the need to reduce their carbon footprint, increase their durability and resistance to aggressive environments. Literature analysis made it possible to determine the current state of research, identify key problems and formulate aims of research.

The work used an integrated approach to determine the relationship between the chemical composition of cement components (SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> etc.) and its performance characteristics (self-tension, linear expansion, sulfate resistance). The analysis was performed using the Pandas library and visualized using Seaborn heatmaps in Python. Python-based software was used for data analysis, which made it possible to efficiently process and visualize the results. Cement samples were obtained from a variety of sources, including Portland cement, blast furnace slag, and phosphogypsum, which provided a wide range of characteristics [22]. The data from the patent on the MCCs composition became the basis for a correlation analysis in order to assess the environmental effectiveness of cements and their predictive characteristics (Table 1).

Table 1 Chemical composition of components for cement mixtures (% by weight)

Component	$SiO_2$	CaO	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub> FeO	MgO	Na <sub>2</sub> O/ Na <sub>2</sub> O <sub>3</sub>	$K_2O$	S/ <sup>c</sup> OS	$TiO_2$	$P_2O_5$	MnO	$H_2O$	пшп	Others
1. Portland cement clinker (Pikalevo)	22.15	64.21	4.54	3.36	1.25	0.66	0.60	0.23	0.32	_	_	_	2.08	_
2. Blast furnace slag (Cherepovets, A)	38.90	39.60	8.90	0.54	10.54	_	ı	0.59	-	_	0.29	-	ı	_
3. Blast furnace slag (Magnitogorsk, B)	37.48	40.87	11.00	0.25	7.67	_	1	0.93	0.51	_	0.21	_	-	-
4. Electrothermal sulfate slag (SPTI)	41.25	46.83	2.63	2.61	2.47	_	1	0.35	-	0.25	-	-	1	1.16
5. Calcium hydrogarnet (GGK-1, Pikalevo))	0.1 1.58	37.72 38.31	24.60 24.91	0.16	0.70	5.75 5.84	-	_	_	_	_	_	24.96 29.49	_
6. Calcium hydrogamet (GGK-2, SPTI))	0.12 2.10	45.46 46.39	29.12 29.72	0.19	0.85	6.78 6.92	1	-	-	-	-	_	15.52 15.81	_
7. Quartz sand (Volsk)	98.55	0.58	0.64	0.13	_	_	I	I	I	_	l	_	I	0.10
8. Phosphogypsum (Kingisepp)	0.50	32.50	0.60	0.20	_	_	ı	44.30	ı	1.60	_	19.40	ı	_

In order to correctly interpret the results of statistical analysis and evaluate their representativeness and applicability, it was necessary to consider the methodology for obtaining the initial experimental data on which this analysis was based. These data were obtained during the work on patent RU 2079458 C1 and included the following stages of sample preparation and testing. The components were ground to a fineness of 10 of the residue on a 008 sieve, and then mixed in a laboratory mixer. As a result, eight MCC formulations were obtained and tested. Data on performance characteristics (self-tension, linear expansion, and sulfate resistance coefficient) was collected through standard laboratory tests of samples made from these eight compounds. Clearly identified components were used for their preparation: Portland cement clinker from the Pikalevsky association "Glinozem", blast-furnace granular slags from Cherepovets and Magnitogorsk Metallurgical Plants, electrothermal sulfate slag from the SPTI (TU), two types of calcium hydrogarnet (GGK-1 from the Pikalevsky association "Glinozem" and GGK-2 from the SPTI (TU), quartz sand from the Volsky deposit and phosphogypsum from the Kingisepp association "Phosphorite". Standard cement tests were performed in accordance with GOST 310.1.76<sup>1</sup>, GOST 310.4.81<sup>2</sup> (extended in 2003), self-stress was determined according to TU 21–26–13–90 (in rings)<sup>3</sup>.

**Results.** Correlation analysis. The aim was to identify the relationships between the chemical composition of cement components and their properties, including self-stress, linear expansion, and sulfate resistance.

We used the code and got the correlation matrix (Fig. 1):

```
import pandas as pd
import seaborn as sns
import matplotlib.pyplot as plt
# Data on the composition and properties of cement:
data = {
  "SiO2 clinker": [22.15] * 8,
  "SiO2_slag_domen_A": [38.9, 0, 38.9, 38.9, 38.9, 38.9, 38.9, 38.9],
  "SiO2 slag domen_B": [0, 37.48, 0, 0, 0, 0, 0, 0],
  "SiO2 шлак ЭТС": [0, 0, 0, 0, 0, 0, 0, 41.25],
  "SiO2 ggk1": [0.84] * 8, # Average (0.1 + 1.58) / 2
  "SiO2 ggk2": [1.11] * 8, # Average (0.12 + 2.1) / 2
  "SiO2 sand": [98.55] * 8,
  "SiO2 phosphogypsum": [0, 0.5, 0, 0, 0, 0, 0, 0],
  "Al2O3 clinker ": [4.54] * 8,
  "Al2O3_slag_domen_A": [8.9] * 8,
  "Al2O3 slag domen B": [0, 11.0, 0, 0, 0, 0, 0, 0],
  "Al2O3 slag ETS": [0, 0, 0, 0, 0, 0, 0, 2.63],
  "Fe2O3 clinker ": [3.36] * 8,
  "Fe2O3 slag domen A": [0.54] * 8,
  "Fe2O3 slag domen B": [0, 0.25, 0, 0, 0, 0, 0, 0],
  "Fe2O3 slag ETS": [0, 0, 0, 0, 0, 0, 0, 2.61],
  "Sulfate gypsum": [2.5, 0, 0, 0, 0, 0, 0, 0],
  "Sulfate phosphogypsum": [0, 2.0, 4.0, 3.0, 3.0, 3.0, 0, 5.0],
  "Silicate slag_domen_A": [40, 0, 40, 35, 40, 40, 40, 0],
  "GGK 1": [0.0, 3.75, 6.0, 3.0, 7.5, 0.0, 10.0, 5.0],
  "GGK 2": [0.0, 3.75, 3.0, 2.0, 0.0, 7.5, 5.0, 10.0],
  "Clinker": [57.5, 69.5, 47.0, 57.0, 49.5, 49.5, 40.0, 40.0],
  "Expansion": [0.95, 1.40, 1.94, 1.89, 1.99, 1.90, 1.95, 1.50],
  "Tensile Strength": [0.0, 2.50, 4.61, 4.0, 3.79, 0.26, 3.60, 0.70],
  "Sulfate Resistance": [1.01, 1.70, 1.62, 1.77, 0.96, 1.50, 1.60, 1.78]
}
```

<sup>&</sup>lt;sup>1</sup> GOST 310.1.76. Cements. Test Methods. General. (In Russ.) URL: <a href="https://internet-law.ru/gosts/gost/34404/?ysclid=m9hv0dql9976146066">https://internet-law.ru/gosts/gost/34404/?ysclid=m9hv0dql9976146066</a> (accessed: 13.01.2025).

<sup>&</sup>lt;sup>2</sup> GOST 310.4–81. Cements. Methods of Bending and Compression Strength Determination. (In Russ.) URL: <a href="https://internet-law.ru/gosts/gost/13713/">https://internet-law.ru/gosts/gost/13713/</a> (accessed: 13.01.2025).

<sup>&</sup>lt;sup>3</sup> TU 21–26–13–90. Self-Stressing Cements. Unupdated Version. (In Russ.) URL: <a href="https://nd.gostinfo.ru/document/3203787.aspx">https://nd.gostinfo.ru/document/3203787.aspx</a> (accessed: 13.01.2025). Current GOST R 56727–2015. Self-Stressing Cements. Specifications. (In Russ.) URL: <a href="https://files.stroyinf.ru/Data2/1/4293758/4293758145.pdf">https://files.stroyinf.ru/Data2/1/4293758/4293758145.pdf</a> (accessed: 13.01.2025).

```
# Creating a DataFrame and calculating the correlation
     df = pd.DataFrame(data)
     corr_matrix = df.corr()
     # Visualization of the heatmap
     plt.figure(figsize=(12, 10))
     sns.heatmap(corr matrix, annot=True, fmt=".2f", cmap="coolwarm", cbar kws={"label": "Correlation"})
     plt.title("Correlation of cement components and properties")
     plt.tight layout()
     plt.show()
                                                                                               a)
                                                                                                                                                                                             1.00
         SiO2 clinker -
  SiO2_slag_domen_A -
                                                                                                                                        0.08 0.02
                                                                                                                                                         0.31 -0.01 -0.26
                                                                                                                                                         -0.31 0.01 0.26
                                          -0.14
                                                                                         -0.14
                                                                                                                -0.14 -0.14 -0.11
                                                                                                                                        -0.08 -0.02
  SiO2 slag domen B -
                                                                                                                                                                                            0.75
                                                                                                                                                    -0.46 -0.21 -0.38 0.36
     SiO2 шлак ЭТС -
                              0.14 -0.14
                                                                                                                                        0.07
           SiO2_ggk1 -
           SiO2_ggk2 -
                                                                                                                                                                                            - 0.50
           SiO2 sand -
                                                                                    1.00 -0.14
                                                                                                                                    0.65 -0.08 -0.02
                                                                                                                                                         -0.31 0.01 0.26
 SiO2 phosphogypsum -
                                         -0.14
        Al2O3 clinker -
 Al2O3_slag_domen_A -
                                                                                                                                                                                            0.25
                                                                                                                                                        -0.31 0.01 0.26
                                                                                                                 -0.14 -0.14 -0.11
                                                                                                                                       -0.08 -0.02
 Al2O3_slag_domen_B -
                                                                                                                                                    -0.46 -0.21 -0.38 0.36
      Al2O3 slag ETS -
        Fe2O3 clinker -
                                                                                                                                                                                            - 0.00
Fe2O3_slag_domen_A -
                                                                                                                -0.14 -0.14 -0.11 -0.6
                                                                                                                                       -0.08 -0.02 0.75 -0.31 0.01 0.26
 Fe2O3_slag_domen_B -
                                         -0.14
                                                                                                                                       0.07 0.70 -0.46 -0.21 -0.38 0.36
                              0.14 -0.14 1.00
      Fe2O3 slag ETS -
                                                                                                                                  0.24 -0.51 -0.45 0.26 -0.80 -0.53
       Sulfate_gypsum -
                              0.14 -0.14 -0.14
                                                                 -0.14
                                                                                   -0.14 -0.14
                                                                                                           -0.14 -0.14 1.00
                              0.11 -0.11
                                                                                                                                  -0.37 -0.00 0.46 -0.24 0.35 0.11 0.40
Sulfate_phosphogypsum -
                                                                 -0.11
                                                                                   -0.11
                                                                                                                     0.24 -0.37 1.00 0.02 -0.51 -0.25 0.38 0.25 -0.51
Silicate slag domen A -
                                                                                                                                                                                             -0.50
                                                                                                           -0.08 0.07 -0.51 -0.00 0.02 1.00 0.00 -0.51 0.54
              GGK_1 -
                              0.08 -0.08 0.07
                                                                 -0.08
                                                                                   -0.08 0.07
                              0.02 -0.02 0.70
                                                                 -0.02
                                                                                   -0.02
                                                                                                                     -0.45 0.46 -0.51 0.00 1.00 -0.47 0.11 -0.39
              GGK 2 -
                                                                                    .75 -0.46
                                                                                                                -0.46 0.26 -0.24 -0.25 -0.51 -0.47 1.00 -0.45 -0.05 -0.08
               Clinker -
                                         -0.46
                                                                                                                                                                                             -0.75
                                                                                                           -0.31 -0.21
                                                                                                                            0.35 0.38
                                                                                                                                             0.11 -0.45
            Expansion -
                              0.31 -0.31 -0.21
                                                                  -0.31
                                                                                   -0.31 -0.21
                              -0.01 0.01 -0.38
                                                                  0.01
                                                                                   0.01 -0.38
                                                                                                           0.01 -0.38 -0.53 0.11 0.25 0.69 -0.39 -0.05
      Tensile_Strength -
                                                                  0.26
                                                                                   0.26 0.36
                                                                                                                       -0.60 0.40 -0.51 0.11
                                                                                                                                                                                              -1.00
                                                                                   Al2O3_slag_domen_B -
                              SiO2_slag_domen_A
                                                            SiO2_sand
                                                                              VI2O3_slag_domen_A -
                                                                                          ETS
                                                                                                     Fe2O3_slag_domen_A
                                                                                                           Fe2O3_slag_domen_B
                                                                                                                 ETS
                                                                                                                                              GGK 2
                                                                                                                                                    Clinker
                                     SiO2_slag_domen_B
                                                      SiO2_ggk2
                                                SiO2_ggk1
                                                                  SiO2_phosphogypsum
                                                                                                                                   slag_domen_A
                                                                                                                                                           Expansion
                                          шлак_ЭТС
                                                                                                                       Sulfate_gypsum
                                                                                                                                                                      Sulfate Resistance
                                                                        Al2O3_clinker
                                                                                               Fe2O3_clinker
                                                                                                                             phosphogypsum
                                                                                                                 slag
                                                                                          Al203_slag
                        SiO2
                                                                                                                 Fe2O3
                                           SiO2
                                                                                               b)
```

Fig. 1. Correlation matrix of chemical composition and properties of cement:

a — code (components: chemical compounds — SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> from various sources

(clinker, blast furnace slag A and B, ETS slag, sand, phosphogypsum, GGK1, GGK2), additives: Sulfate\_gypsum,

Sulfate\_phosphogypsum, Silicate\_slag\_domen\_A, GGK\_1, GGK\_2, Clinker, properties:

Expansion, Tensile Strength, Sulfate Resistance;

b — heatmap (red (>0): positive correlation (an increase in one variable is associated with an increase in the other), blue (<0): negative correlation, white ( $\approx$ 0): no correlation. Some columns (for example, SiO<sub>2</sub>\_clinker, SiO<sub>2</sub>\_clinker) have constant values, which leads to zero correlation with other variables (NaN in the matrix is displayed as 0 or empty cells)

The correlation heatmap provides visual representation of strength and direction of linear relationships between various cement components (silicon oxides, aluminum oxides, iron oxides, calcium oxides, sulfates, and hydrogranates) and its properties (tensile strength, expansion, and sulfate resistance). The analysis of the map makes it possible to identify significant factors affecting the quality and behavior of the cement. Values close to +1.00 and -1.00 show a strong correlation. The map shows a negative correlation between SiO<sub>2</sub>\_slag\_domen\_A and SiO<sub>2</sub>\_slag\_domen\_B,

which is expected, since both components are blast furnace slag with a high SiO<sub>2</sub> content, and if the amount of one increases, the other decreases in order to maintain the total mass and chemical balance. In slag production, it is important to maintain an optimal ratio of oxides to achieve the desired properties. Slag stoichiometry should take into account a certain ratio of SiO<sub>2</sub> and CaO to achieve good strength and sulfate resistance. When using different types of ore or melting temperatures, the SiO<sub>2</sub> content has different variations. Less strong positive correlations are observed between different oxides within the same type of slag.

Clinker and oxides of Si, Al, Fe in blast furnace slags and phosphogypsum (r = 0.75). A positive correlation indicates their interaction in the cement structure. Various minerals such as  $C_3S$  (tricalcium silicate),  $C_2S$  (calcium disilicate),  $C_3A$  (tricalcium aluminate) and  $C_4AF$  (tetracalcium aluminoferrite) are formed during the firing of clinker raw materials (usually at temperatures around  $1400-1500^{\circ}C$ .). These minerals have different mechanical and chemical properties, and their formation depends on the content of  $SiO_2$ ,  $Al_2O_3$ , and FeO. Oxides contribute to the formation of stronger structural units in clinker, which is reflected in a positive correlation [23].

The GGK components (hydraulic additives) and Expansion, Tensile\_Strength, Sulfate Resistance (r = 0.54 – 0.69). A moderate correlation indicates their statistical relationship. Changes in the clinker content directly alter the properties of the GGK components. This is important to control hydration and improve the early strength of the cement. The clinker content affects volume change of hydraulic additives. For example, certain minerals in clinker cause hydration, which leads to an increase in volume, which is associated with the formation of new phases or with changes in the structure of the material. The high content of clinker improves mechanical properties such as tensile strength due to the formation of durable minerals such as C<sub>3</sub>S and C<sub>2</sub>S, which provide good adhesion and strength in the hydrated state. Sulfate resistance depends on the ratio of oxides in clinker and the presence of certain phases such as C<sub>4</sub>A<sub>3</sub>S. An increase in the content of clinker rich in aluminates increases the resistance to sulfates, which is important for the long-term operation of concrete in aggressive conditions. Nevertheless, in cements containing active mineral additives, high sulfate resistance is ensured by a reduced content of C<sub>3</sub>A in clinker. Thus, in the standards of Great Britain, Germany and China, the content of C<sub>3</sub>A in high-sulfate-resistant cement is allowed equal to 3.5, 3.0 and 5.0, respectively. Optimizing the SiO<sub>2</sub> content will help regulate the mechanical properties and prevent microcracks. An excessive increase in the proportion of SiO<sub>2</sub> in clinker leads to deterioration in the sulfate resistance of cement [5].

A significant part of positive correlations is observed between the components associated with the same type of slag. The positive correlation between calcium oxide in blast furnace slag and sulfate resistance indicates sulfate resistance. Inclusion of CaO (3–5%) as an activator in the matrix reduces water absorption, overall porosity, increases wetting/drying, and acid resistance. CaO has a significant impact on compressive strength at an early age, compared to later age. The correlation between sulfates and sulfate resistance is expected to be weakly positive [1].

Tensile\_Strength and Expansion (r = 0.67) suggests that the use of blast furnace slag contributes to the controlled expansion of cement.

Sulfate\_phosphogypsum and Sulfate Resistance (r = 0.40). Phosphogypsum has a positive effect on sulfate resistance, confirming the importance of an alternative and environmentally friendly material capable of effectively suppressing linear deformations of cement mortars.

Silicate blast furnace additive (Silicate\_slag\_domen\_A) and Sulfate Resistance (r = -0.51). The negative correlation contradicts the expected effect. Although the above slag composition looks typical, some components or impurities significantly reduce the resistance to sulfate corrosion. For example, the increased content of free magnesium oxide (MgO) or alkalis (Na<sub>2</sub>O, K<sub>2</sub>O) reduces the resistance to sulfates. Sulfate medium can cause the formation of thaumasite in the initial stages of the silicate-containing phase or delayed ettringite formation, which "explodes" concrete from the inside [3].

Clinker and Sulfate Resistance (r = -0.08). An increase in the proportion of clinker leads to a decrease in the ability to withstand sulfate attacks. The reason for this is low chemical resistance of clinker in a sulphate environment, which makes it necessary to replace it with alternative additives. Clinker, especially if it contains a high level of tricalcium aluminate ( $C_3A$ ), is less resistant to sulfate attacks. In this regard, it is advisable to use slag additives to improve sulfate resistance.

Clinker and Expansion (r = -0.45) indicate that clinker reduces the ability of cement to expand in a controlled manner, impairing mechanical stability. The high content of clinker leads to uncontrollable volume changes in concrete. Clinker minerals can affect hydration and the formation of hydrated phases. As a result, internal stress causes cracking [6].

 $Fe_2O_3$  of blast furnace slag A and Expansion (r = -0.31). An increase in the  $Fe_2O_3$  content reduces linear expansion due to the formation of more stable phases less susceptible to volume changes, which is useful for preventing cracking under aggressive conditions.

Thus, correlation analysis shows that minimizing clinker, replacing traditional additives with alternative materials (slags, phosphogypsum, etc.) and controlling the content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and sulfate components are key strategies for improving the environmental safety of cement. This not only reduces the carbon footprint during production, but also increases the durability and sustainability of building materials, which is consistent with the principles of green construction.

Transition to an adapted matrix. The development of cement with predictable and improved characteristics requires a transition to an adapted matrix. It is necessary to accurately assess the key factors affecting the properties of cement and the needs for optimizing the composition in order to achieve the target characteristics. The requirement for sulphate resistance of cement, which must be at least 9 units for use in aggressive environments, is extremely relevant. This indicator, as can be seen from the analysis, has a strong correlation with the content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and sulfate components, which emphasizes their priority importance in simplifying the matrix.

Another important consideration is the optimization of linear expansion. The data show that an increase in the  $SiO_2$  content of blast furnace slag and sand contributes to controlled expansion, which is critically important for preventing cracking in structures. The components that directly affect this indicator should be identified as the key ones. The transition to a simplified matrix will allow us to focus on the most important factors and develop a more accurate and practical model for predicting cement properties.

The updated code is provided below. After that, we obtain the correlation matrix (Fig. 2):

```
import pandas as pd
import seaborn as sns
import matplotlib.pyplot as plt
# Data (adapted to the patent)
data = {
  "CaO": [38.31, 45.46, 40.87, 39.6],
  "SiO2": [22.15, 37.48, 38.9, 41.25],
  "Al2O3": [4.54, 11.0, 8.9, 2.63],
  "Sulphate Component": [2.5, 4.0, 3.5, 5.0],
  "Sulfate Resistance": [8.5, 9.1, 8.9, 9.5],
  "Tensile Strength": [7.2, 7.5, 7.3, 7.8],
  "Linear Expansion": [0.15, 0.75, 1.25, 1.85]}
df = pd.DataFrame(data)
# Correlation matrix
corr matrix = df.corr()
# Visualization
sns.heatmap(corr matrix, annot=True, cmap="coolwarm")
plt.title("Correlation matrix of chemical composition and properties of cement")
plt.show()
```

a)

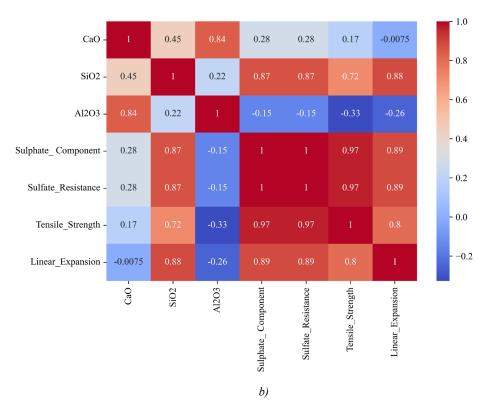


Fig. 2. Updated correlation matrix of chemical composition and properties of cement:

a — code (components: chemical compounds — CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, additive: Sulphate\_Component, properties: Sulfate\_Resistance, Tensile\_Strength, Linear\_Expansion);
 b — heatmap (high correlation between CaO and Sulfate resistance indicates the effect of calcium on the resistance of cement to sulfates. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have a weak correlation with each other if their content varies independently. Linear\_Expansion and Tensile\_Strength correlate with Sulphate\_Component, reflecting the effect of additives on deformation properties)

#### Matrix analysis and conclusions:

- It is found that sulfate resistance of cements has a weakly positive correlation with the CaO content (r = 0.28). To increase it, you need to focus on other components (for example, SiO<sub>2</sub> or Self Tension) that show a stronger effect;
- Strong positive correlation between SiO<sub>2</sub> content and sulfate resistance (0.87) indicates the need to optimize the proportion of SiO<sub>2</sub> to increase environmental sustainability;
- Self-tension level strongly correlates with sulfate resistance (0.97), which confirms its importance for this property. Self-tension helps the material to cope with the chemical stresses caused by sulfates;
- Correlation (1.0) means that the Sulfate\_Component (for example,  $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O)$  and sulfate resistance change together;
- High positive correlation (0.89) between sulfate resistance and linear expansion in expanding MCCs is explained by the complex interaction of components, including additives, slags and hydrogarnets, which can simultaneously affect both properties, as well as controlled expansion in the early stages of hydration, potentially increasing sulfate resistance within certain limits [7].
- An increase in the silicon oxide content leads to an increase in linear expansion and vice versa (0.88). This indicates that SiO<sub>2</sub> is the main component for controlling cement expansion [24]. Typically, the mass fraction of SiO<sub>2</sub> in Portland cement is at least 25%<sup>4</sup>. To increase the sulfate resistance of cement, it is recommended to reduce the content of tricalcium aluminate (C<sub>3</sub>A) to no more than 8%<sup>5</sup>. Forecast: an adjustment of the SiO<sub>2</sub> fraction by 10% will provide an increase in sulfate resistance by 8.7%, including the composition optimization (the introduction of a more active sulfate component phosphogypsum or fluorogypsum).

<sup>&</sup>lt;sup>4</sup> GOST 31108–2020 Common Cements. Specifications. (In Russ.) URL: <a href="https://internet-law.ru/gosts/gost/73873/?ysclid=m9iwx3cpwg983001164">https://internet-law.ru/gosts/gost/73873/?ysclid=m9iwx3cpwg983001164</a> (accessed: 13.01.2025).

<sup>&</sup>lt;sup>5</sup> Yezhov VB. *Technology of Concrete, Building Products and Structures*. Manual. Yekaterinburg: Ural Federal University named after the first President of Russia B.N. Yeltsin; 2014. 206 p. (In Russ.) URL: <a href="https://study.urfu.ru/Aid/Publication/12435/1/Ejov\_2.pdf">https://study.urfu.ru/Aid/Publication/12435/1/Ejov\_2.pdf</a> (accessed: 13.01.2025).

**Discussion and Conclusion.** Regarding the representativeness and applicability of the conclusions. It is beyond argument that, the direct quantitative transfer of the results to all possible real production conditions requires caution. However, the use of standardized test methods and components from well-known industrial sources provides a certain basis for assessing the identified dependencies. Eight tested formulations represent variations of multicomponent systems that allow us to identify statistical trends.

When it comes to the applicability of conclusions beyond a specific context, qualitative and quantitative aspects should be distinguished. The conclusions about the key role of SiO<sub>2</sub> in providing sulfate resistance, the effect of C<sub>3</sub>A content, the positive correlation between sulfate resistance and linear expansion, as well as the environmental and economic effects of replacing clinker with active additives are generally consistent with general scientific concepts and the results of other studies cited in the article [1, 3, 5, 12]. These qualitative patterns are likely to have broader applicability. However, specific quantitative correlations and forecasts (for example, an increase in sulfate resistance by 1% SiO<sub>2</sub>) are strictly applicable to this studied system and require additional verification and adaptation to other types of cements, raw materials from other regions or other production conditions.

Regarding the limitations of the scale of application and the variability of slags, we can agree that the article does not sufficiently address the issues of scaling results to industrial conditions and the impact of differences in technological processes at different plants. However, the study focuses on analyzing laboratory-level data. It is recognized that the effectiveness of additives, in particular blast furnace slags (and their thermal activation, which is mentioned later in the discussion), can vary depending on their chemical composition, the presence of impurities (MgO, alkalis) and production conditions, which differ in different regions. The observed negative correlation for one type of slag may be related to these factors. Therefore, the applicability of the developed approaches on an industrial scale requires further research and adaptation, taking into account the specifics of a particular production and the raw materials used.

An unexpected negative correlation (r = -0.51) between silicate blast furnace additive (slag A, Cherepovets) and sulfate resistance has been identified and recognized above. As explanations, hypotheses are put forward about the influence of impurities in this particular slag, such as MgO or alkaline oxides, or about the possible formation of harmful phases such as thaumasite or delayed ettringite in the presence of sulfates. This phenomenon requires further, more in-depth research to clarify the exact mechanisms underlying it, which goes beyond the scope of the conducted correlation analysis.

Taking into account the limitations of the laboratory scale, the variability of raw materials and the need for further research on some points, it can be argued that the analysis nevertheless revealed statistically significant trends. The results of the correlation analysis showed complex relationships between the composition of MCCs and their properties. The importance of reducing the proportion of clinker to increase sulfate resistance and control linear expansion has been confirmed. Studies by A.S. Brykov (2014) [23] and A.M. Rashad (2023) [1] demonstrate that reducing the proportion of clinker by 30% and replacing it with activated additives (e.g. slags and phosphogypsum) leads to a 25–40% reduction in CO<sub>2</sub> emissions. However, the optimal use of slag in concrete mixtures should be monitored. It makes up about 40% of the total binder content [25]. According to J. He et al. (2023), the production of AAS (alkali-activated slag) cement can reduce CO<sub>2</sub> emissions by up to 78.1%, compared with conventional Portland cement, contributing to a reduction in environmental impact [26]. In the framework of this study, this is confirmed by calculations. The equation of environmental efficiency:

$$E = \frac{C_{base} - C_{mod}}{C_{base}} \cdot 100\%, \tag{1}$$

where  $C_{base}$  — content of clinker in the basic composition (65%);  $C_{mod}$  — content of clinker in the modified composition (35%).

If the proportion of clinker is replaced by 30%, the reduction in CO<sub>2</sub> emissions will be:

$$E = \frac{65 - 35}{65} \cdot 100 \% = 42.6\%,$$

This indicator is consistent with data from the scientific literature and highlights the contribution of this study to environmentally friendly technologies.

Replacing clinker with additives reduces the cost of cement by introducing production waste, which corresponds to the conclusions of economic efficiency. The economic contribution can be calculated using the formula:

$$S = C_{clinker} \cdot P_{clinker} - C_{additive} \cdot P_{additive}, \tag{2}$$

where C — volume of the component; P — unit cost.

For example, patent RU 2342337 C1 states that when adding 10% of the mineral additive by weight of clinker, the cost of cement decreases by about 8–10%, and when adding 20% — by 13–15% [27].

A strong correlation is found between the  $SiO_2$  content and sulfate resistance (r = 0.87), which opens up opportunities for optimizing the cement composition by regulating the proportion of silica. The indicator coincides with the data of S.V. Bastrygina and R.V. Konokhov (2022). According to their model, an increase in the proportion of  $SiO_2$  in the amount of 0.5–2.0 wt. % increases the strength of concrete by 15–40% [28]. The article by N.E. Dzhabbarova and U.F. Gasanova also claims that the addition of silica to cement in an amount of 10% increases the compressive and bending strength (by 50 and 16%, respectively), in an amount of 20% — leads to a maximum increase in strength (72 and 18%) [29]. In our study, the calculations show that to achieve the required sulfate resistance (at least 9 units) at an initial value of 8.5, it will take:

$$\Delta C_{\text{SiO2}} = \frac{T - S_{base}}{K},\tag{3}$$

where T = 9T = 9 (target sulfate resistance);  $S_{base} = 8.5$  (initial resistance); K = 0.5 (average increase in resistance by 1% SiO<sub>2</sub>). Let us find the value of sulfate resistance:

$$\Delta C_{\text{SiO2}} = \frac{9 - 8.5}{0.5} = 1\%,$$

This calculation is generally consistent with the literature data and highlights the role of  $SiO_2$  in the development of cements for aggressive environments.

Similarly, M.M. Rahman et al. (2014) emphasizes the importance of optimizing the  $SiO_2$  content to increase the durability of cements [3]. Our study also confirmed a strong positive correlation (r = 0.87) between  $SiO_2$  and sulfate resistance.

The correlation analysis results show significant correlations between the component composition of MCCs and their properties. In particular, a study by M. Thomas et al. (2021) notes that the use of thermal activation of slags leads to an improvement in strength characteristics [6]. This coincides with the data obtained, where thermally activated slags showed an increase in strength by 12–15%, compared with non-activated ones [1]. Thermal activation increases the reactivity of components. According to literature data, thermal activation increases the degree of hydration of slags, which leads to the formation of a stronger cement matrix [25]. Let us make a calculation based on the composition and correlation analysis. To assess the effect of thermal activation on strength, we use the strength gain formula:

$$\Delta \sigma = \sigma_{\text{active}} - \sigma_{\text{inactive}}, \tag{4}$$

where  $\sigma_{active}$  — strength of cement with thermally-activated slags;  $\sigma_{inactive}$  — strength of cement with inactive slags.

According to the correlation analysis results, formula (3) takes the form:

$$\sigma_{\text{active}} = 1.15 \cdot \sigma_{\text{inactive}}$$
 (increased by 15%). (5)

Thus, if the base strength of cement ( $\sigma_{\text{inactive}}$ ) is, for example, 30 MPa, then the change will be as follows:

$$\Delta \sigma = 1.15 \cdot 30 - 30 = 4.5 \text{ MPa}.$$

This corresponds to the literature data and confirms the correlation presented in the study. Optimal activation of additives, for example, blast furnace slag, leads to an increase in strength by 12–15%, which is consistent with the specified coefficient.

A study by A.M. Rashad (2023) shows that the addition of CaO to the cement matrix increases strength in the early stages of hardening, but reduces resistance to sulfate attacks [1]. Our data confirm this: the correlation between CaO and sulfate resistance is only r = 0.28. At the same time, the use of additives rich in aluminates leads to improved resistance in aggressive environments.

An unexpected result was the negative effect of the silicate blast furnace additive on sulfate resistance. This requires further investigation and may be due to the presence of impurities in the slag or the specifics of its interaction with other

cement components. The work of M.R. Sakr and M.T. Bassuoni (2021) discusses impurities (MgO, K<sub>2</sub>O) in slags, which can reduce the stability of cements [4]. This is consistent with the assumption of a possible influence of slag composition in our study. The effect of C<sub>3</sub>A content on sulfate resistance also requires additional research, as there are conflicting data in the literature and standards from different countries.

The correlation between self-tension and sulfate resistance (r = 0.97) highlights the importance of the material's internal resistance to aggressive media. The result complements the known data presented in the article by I.P. Pavlova and K.Yu. Belomesova (2021), in which self-tension is associated with increased strength and durability [30].

The relationship of linear expansion with the  $SiO_2$  content (r = 0.88) confirms that silica plays a key role in controlling the volume changes of cement. However, the MCC composition shows different behavior when using hydrogranates, which is due to their different crystal structure. This opens up new perspectives for studying the interactions between the components and the possibilities of optimizing the composition to achieve the required characteristics.

Thus, the results of the study fill in the gaps in knowledge about the effect of the composition of MCCs on their properties and provide mathematically sound recommendations for improving environmental and economic efficiency.

Statistical processing of experimental data confirmed the significant effect of MCCs composition on their operational characteristics, including sulfate resistance, linear expansion and self-tension. The correlation analysis carried out in the framework of the study revealed a strong relationship between the SiO<sub>2</sub> content and sulfate resistance, as well as between self-tension and sulfate resistance, which is important for the development of environmentally effective formulations. An increase in the proportion of SiO<sub>2</sub> by 1% provides an increase in sulfate resistance by 0.5 units, which is consistent with calculations and data from literary sources and confirms the key role of SiO<sub>2</sub> in managing cement properties.

Statistical evaluation shows that reducing the proportion of clinker and replacing it with alternative materials such as slags and phosphogypsum improves the environmental performance of the MCC by reducing CO<sub>2</sub> emissions and reducing cost. Calculations based on the experimental data confirmed a 46.2% reduction in CO<sub>2</sub> emissions when replacing a part of the clinker, which corresponds to the sustainable development goals. The economic effect of replacing clinker with additives is expressed in reducing the cost of cement production by 10–15% due to the use of waste. This result is consistent with the data from the literature and highlights the environmental importance of using industrial wastea.

The analysis carried out by the author confirmed the significant influence of the MCCs chemical composition on their operational characteristics. It was found that reducing the clinker content by 30% and replacing it with activated additives such as blast furnace slags and phosphogypsum could reduce the carbon footprint by 25–40%.

The use of thermal activation of slags has shown an increase in the strength characteristics of cements by 12–15%. This is due to the improved reactivity of the activated components, which contributes to the formation of a more dense and durable cement matrix. Further research is needed to clarify the optimal temperatures and conditions of thermal activation.

The effect of hydrogarnets on the properties of cements revealed their complex behavior due to their crystalline structure. It has been established that changes in the content of hydrogarnets affect linear expansion and self-tension, which opens up prospects for the creation of materials with specified characteristics. This area requires additional research for an in-depth study of the mechanisms of interaction of the components.

The results obtained during statistical processing, in particular the negative correlation between silicate blast furnace additive and sulfate resistance, indicate the need for further research. A more detailed statistical analysis of the influence of impurities in the slag, the content of C<sub>3</sub>A and other factors on the sulfate resistance and properties of MCCs is required to develop optimal environmentally friendly formulations.

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#### About the Author:

**Elena E. Smirnova**, Cand. Sci. (Eng.), Associate Professor of the Department of Industrial Ecology, Saint Petersburg State Chemical and Pharmaceutical University (14, Professora Popova St., lit. A, St. Petersburg, 197376, Russian Federation), <u>SPIN-code</u>, <u>ORCID</u>, <u>esmirnovae@yandex.ru</u>

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#### Об авторе:

**Елена Эдуардовна Смирнова,** кандидат технических наук, доцент кафедры промышленной экологии Санкт-Петербургского государственного химико-фармацевтического университета (197376, Российская Федерация, г. Санкт-Петербург, ул. Профессора Попова, 14, литер A), <u>SPIN-код</u>, <u>ORCID</u>, <u>esmirnovae@yandex.ru</u>

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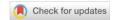
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#### Assessment of the Potential Risk of Poisonous Plants in Rostov-on-Don

Mikhail M. Sereda

Don State Technical University, Rostov-on-Don, Russian Federation ⊠ seredam@yandex.ru



#### **Abstract**

Introduction. The flora of most urban areas has received scant attention regarding toxicity, resulting in the potential for humans and animals to encounter poisonous plants. Furthermore, there is an influx of new potentially hazardous species into populated areas. It is evident that there are two primary mechanisms through which their propagation occurs. The first of these is natural population increase. The second is the introduction of ornamental species in landscape projects. The presence of poisonous plants in urban areas is frequently identified solely on the basis of symptoms including poisoning, dermal and eye burns. Children are the most vulnerable in this regard. The situation in Russia has been examined using the example of several urban ecosystems; however, the distribution of toxic flora in Rostov-on-Don remains unstudied. The aim of this research is to evaluate the potential hazard posed by poisonous plants in Rostov-on-Don.

*Materials and Methods.* The research focused on species of poisonous vascular plants growing within the city limits of Rostov-on-Don. The data was collected during fieldwork in 2023–2024 using the route method. Information on the presence of poisonous plants on the territory of the city in 2007–2022 was also taken into account. The names of the plant species are given according to the Plant List database. The toxicity class was determined according to the A. Filmer scale.

Results. In the urban context of Rostov-on-Don, a total of 66 species of poisonous plants were identified (8% of the city's total floral biodiversity). They belonged to diverse hazard categories according to their potential impact on human and animal health. A thorough analysis of taxonomic structure of the toxic flora revealed the most prominent orders: Ranunculales (14 species) and Solanales (6 species). The potentially lethal plants within the city limits included Hyoscyamus niger, Conium maculatum, Aristolochia clematitis, Convallaria majalis, Ricinus communis, and others (21 species). The ecological and cenotic analysis demonstrated that almost one third of the detected toxic plant species (30%) were associated with ruderal habitats, i.e. roadsides and abandoned areas. The majority of species (41%) were found to be associated with artificial phytocenoses that were created for ornamentation. Of particular concern were plants bearing poisonous fruits of high ornamental value. This group comprised 14 species, including Parthenocissus sp., Phytolacca americana, and Wisteria sinensis. A biomorphological analysis of the toxic flora revealed the predominance of perennial and annual grasses (66%). Shrubbery, conversely, exhibited a lower level of diversity (16%), yet demonstrated a more extensive geographical distribution.

**Discussion and Conclusions.** This is the first study to assess the potential threat posed by poisonous plants in urban ecosystems within the southern Russian region. The identification of toxic plant species, their role in the urban landscape and ways of their further development will help to minimize poisoning by poisonous plants. Uncontrollably spreading ruderal toxic plants, among which particularly dangerous species have been found, require special attention. During landscaping and green construction, the toxicity of each specimen should be taken into account.

**Keywords:** toxic flora of Rostov-on-Don, toxic plants in cities, classes of plant toxicity, ruderal toxic plants, introduction of ornamental toxic plants

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Оригинальное эмпирическое исследование

#### Оценка потенциальной опасности ядовитых растений города Ростова-на-Дону

М.М. Середа

Донской государственный технический университет, г. Ростов-на-Дону, Российская Федерация  $\boxtimes$  seredam@yandex.ru

#### Аннотация

**Введение.** Флора большинства городов слабо изучена с точки зрения токсичности, при том что люди и животные рискуют столкнуться с ядовитыми растениями. К тому же на территории населенных пунктов проникают новые потенциально опасные виды. Известны два основных пути их распространения. Первый — естественное увеличение популяции. Второй — внедрение декоративных видов в ландшафтных проектах. Ядовитые растения в городе часто выявляются только при отравлениях, ожогах кожи или глаз. Наиболее уязвимы в этом плане дети. Ситуация в России рассматривалась на примере нескольких городских экосистем, однако проблема распространения токсикофлоры в Ростове-на-Дону не изучалась. Поэтому цель представленной научной работы — оценка потенциальной опасности, которую представляют ядовитые растения в Ростове-на-Дону.

*Материалы и методы.* Исследовались ядовитые сосудистые растения, произрастающие в черте Ростова-на-Дону. Данные собирались в ходе полевых работ в 2023–2024 годах маршрутным методом. Также учитывались сведения о ядовитых растениях, обнаруженных в городе с 2007 по 2022 год. Названия видов растений приводятся в соответствии с базой данных Plant List<sup>1</sup>. Класс токсичности определялся по шкале А. Филмера.

Результаты исследования. В Ростове-на-Дону обнаружено 66 видов ядовитых растений (8 % от общего числа видов флоры города). Они относятся к различным классам опасности по степени воздействия на человека и животных. Анализ таксономической структуры токсикофлоры выявил наиболее крупные группы — лютикоцветные (14 видов) и пасленоцветные (6 видов). Потенциально смертельно опасны Hyoscyamus niger, Conium maculatum, Aristolochia clematitis, Convallaria majalis, Ricinus communis и другие (всего 21 вид). Эколого-ценотический анализ показал, что 30 % видов токсических растений связаны с рудеральными местообитаниями — обочинами дорог и заброшенными территориями. 41 % видов ассоциированы с искусственными фитоценозами декоративного назначения. Особенно опасны декоративно ценные растения с ядовитыми плодами: Parthenocissus sp., Phytolacca americana, Wisteria sinensis и др. (всего 14 видов). Биоморфологический анализ токсикофлоры выявил преобладание трав (66 %). Кустарники менее разнообразны (16 %), но широко распространены.

Обсуждение и заключение. Впервые оценена доля и потенциальная опасность ядовитых растений в экосистеме Ростова-на-Дону. Выявление токсических видов растений, их роли в ландшафте и путей распространения поможет минимизировать риски отравления ядовитыми растениями. Требуют особого внимания бесконтрольно распространяющиеся рудеральные токсические растения, среди которых обнаружены особо опасные виды. При ландшафтных работах и зеленом строительстве следует учитывать токсичность каждого экземпляра.

**Ключевые слова:** токсикофлора Ростова-на-Дону, токсические растения в городах, классы токсичности растений, рудеральные токсические растения, внедрение декоративных токсических растений.

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**Introduction**. Poisonous plants in urban environments pose a threat to humans and animals. Incidents of poisoning by weeds, wild plants, as well as those used in landscape design have been reported. In Germany, for example, between 2001 and 2010, approximately 13,000 incidents were recorded, with children accounting for 85% of victims [1]. According to the American Association of Poison Control Centers, from 2000 to 2008, plants were responsible for 3.4% of all poisonings in the United States, and children under the age of six accounted for almost 70% of cases [2]. The analysis of various Poison Control Centers in Australia, Germany [3], Morocco [4], New Zealand [5], Thailand [6], and the United Kingdom found that plant exposure was the cause of 1.8–8% of all referrals [7]. In most cases, significant intoxication was not recorded, but there were reports of severe and life-threatening poisoning. The risk of poisoning in urban areas remains high. A study of the urban flora in Hong Kong revealed 26 species of poisonous plants, which were

<sup>&</sup>lt;sup>1</sup> World Flora Online, WFO. URL: <a href="https://wfoplantlist.org/">https://wfoplantlist.org/</a> (accessed: 11.02.2025).

associated with 65 cases of poisoning ranging in severity from 2003 to 2017 [8]. The flora in Novi Sad (Serbia) included 22 species of poisonous plants, and the authors [9] noted their dangerous proximity to children's institutions.

Poisonous plants are those that, when touched or ingested, can cause harm or even death. They also include plants that may cause a toxic or fatal reaction [10].

Poisonous plants are related to allergenic plants, which have been previously studied in Rostov-on-Don [11]. While allergenic plants can cause allergies, poisonous ones can be much more dangerous.

According to statistics, more than 15,000 cases of poisoning from poisonous plants are reported annually in Russia. Typically, plant toxins affect the body through the digestive system, eyes, and skin. Of these cases, 80% involve children under the age of six [12].

The analysis of literary sources has revealed a lack of knowledge about the distribution and species composition of poisonous plants in cities of the Russian Federation. The most comprehensive information is available for Saratov. The authors [13] mention 46 species of poisonous plants from 29 families found within the city. Poisonous flora of Voronezh, Buinaksk, and Makhachkala has also been studied insufficiently and separately [14].

Poisonous plants in Rostov-on-Don have not been studied specifically. There is little information available about the Lower Don region [15].

The aim of the presented work was to assess the potential threat posed by poisonous plants growing in Rostov-on-Don.

**Materials and Methods**. The species of poisonous vascular plants in Rostov-on-Don were studied. The primary data was collected by the route method during field work in 2023–2024.

The toxicity class of plants was determined in accordance with the modified classification proposed by A. Filmer [16].

- A strong toxic effect, may cause serious illness or death;
- B minor toxic effect, vomiting or diarrhea occurs if the plant is swallowed;
- C effect is caused by oxalate crystals (irritation of the mouth, tongue and throat, can lead to swelling of the throat, difficulty breathing, burning pain and upset stomach);
  - D juice or thorns can cause skin rash or irritation.

Rostov-on-Don has a temperate continental climate with mild winters and hot, dry summers. According to long-term weather observations, the average air temperature is +11.0°C. January is the coldest month with an average temperature of -2.0°C, and July is the warmest month with an average of +23.4°C. The annual average precipitation in Rostov-on-Don is 618 millimeters. The surrounding vegetation is mainly steppe [17].

**Results**. As a result of research in Rostov-on-Don, 66 species of poisonous vascular plants belonging to 23 orders of flowering plants have been identified. According to D.V. Vakhnenko [18], the entire flora of the Rostov urban agglomeration consisted of 848 species. Thus, the share of registered toxic flora species was about 8% of the total number of species of the Rostov flora.

The order Ranunculales was found to be the largest, with 14 toxic plant species (21%). The order Solanaceae included 6 species (9%). The Asparagales order was in third place (5 species, 8%). The remaining 20 orders were relatively small and included from 1 to 4 species.

According to Ya.M. Golovanov [19], 67 species of poisonous plants were found in the flora of the city of Meleuz (Bashkortostan), which was close to the Rostov number.

For comparison, the flora of poisonous plants in Saratov was 30% smaller than in Rostov. It had 46 species [13]. Obviously, the greater diversity was due to the Rostov climate, which was more favorable for plants such as *Hedera helix, Toxicodendron radicans, Wisteria sinensis*, etc. They were often used in landscape design.

The studied toxic flora included various families, some of which were not typical for this region (Phytolaccaceae, Anacardiaceae, Hydrangeaceae). Most of the poisonous plants belonged to the Ranunculaceae and Solanaceae families, which was expected, as representatives of these families were generally toxic to varying degrees. Most of the poisonous plants in Rostov-on-Don were represented by 1–2 species. The intraspecific diversity of the toxic flora was very heterogeneous, since cultural forms also belonged to poisonous ones. Ornamental crops such as *Hosta, Hydrangea*, and *Paeonia* had a significant number of varieties, but all of them contained certain toxic substances.

Table 1 provides a complete list of poisonous plants found in Rostov-on-Don.

Table 1 Poisonous plants growing in Rostov-on-Don

Name	Order	Biotope <sup>1</sup>	Localization <sup>2</sup>	LF <sup>3</sup>	Class	Toxicity Substance
Hosta sp.	Asparagales	Fg	Everywhere	P B, D		Saponin
Adonis aestivalis	Ranunculales	Rh	Everywhere	A	A	Cardiac glycosides
Alstroemeria aurea	Liliales	Fg	Everywhere	P B, D		Glycoside
Ambrosia artemisiifolia	Asterales	Rh	Everywhere, seeds	A	В	Allergenic proteins
Amorpha fruticosa	Fabales	Ud	Seeds	S	В	Glycoside amorphin
Anemonoides sylvestris	Ranunculales	Fg	Aerial parts of plants	P	A	Anemonin
Aquilegia vulgaris	Ranunculales	Fg	Everywhere	P	A	Cyanide
Aristolochia clematitis	Piperales	Rh	Everywhere	P	A	Alkaloid aristolokhin
Bryonia alba	Cucurbitales	Rh, Ud	Everywhere, especially fruits	P	A, B	Bryonin glycoside
Buxus sempervirens	Buxales	Ud, Ra	Everywhere	S	B, D	Alkaloids
Cannabis sativa	Rosales	Rh	Everywhere	A	В	Cannabinoids
Catharanthus roseus	Gentianales	Fg	Everywhere	A	В	Alkaloids
Chelidonium majus	Ranunculales	Rh	Everywhere, especially roots	P	B, D	Alkaloids
Clematis sp.	Ranunculales	Ra	Everywhere	L	D	Alkaloid clematin, anemonol
Colchicum autumnale	Liliales	Fg	Bulbs	P	B, D	Colchicine alkaloids
Coleus scutellarioides	Lamiales	Fg	Everywhere	P	B, D	Diterpene coleonol
Conium maculatum	Apiales	Rh	Everywhere	В	A	Alkaloid coniine, conhydrin, pseudoconhydrin
Consolida regalis	Ranunculales	Rh	Everywhere, especially seeds	A	A	Triterpene alkaloids
Convallaria majalis	Asparagales	Fg, Ud	Everywhere	P	A	Saponin convallin and cardiac glycosides (convallamarin, convallatoxin, etc.)
Convolvulus arvensis	Solanales	Rh	Everywhere	A	В	Alkaloids: convolvin, convolamine
Delphinium ajacis	Ranunculales	Rh, Fg	Everywhere, especially seeds	A	A	Triterpene alkaloids
Cynoglossum officinale	Boraginales	Rh	Everywhere	P	A	Glycoside cynoglossin
Datura stramonium	Solanales	Fg	Everywhere	A	A	Alkaloid atropine, hyoscyamine scopolamine
Delphinium elatum	Ranunculales	Fg	Aerial parts of plants	P	A	Triterpene alkaloids
Digitalis purpurea	Lamiales	Fg	Everywhere	P	A	Cardiac glycosides
Echium vulgare	Boraginales	Rh	Everywhere	P	B, D	Glycoside cynoglossin, consolidin
Ranunculus ficaria	Ranunculales	Fg, Rh	Everywhere	P	A	Protoanemonin, prussic acid
Glaucium corniculatum	Ranunculales	Rh	Everywhere	A	В	Alkaloid protopine
Hedera helix	Apiales	Ra	Everywhere	L	B, D	Saponin gederin
Heliotropium arborescens	Boraginales	Fg	Aerial parts of plants	P	A	Glycoside cynoglossin
Hemerocallis fulva	Asparagales	Fg	Everywhere	P	В	Glycoalkaloid
Hyacinthus orientalis	Asparagales	Fg	Bulbs	P	B, D	Oxalates
Hydrangea macrophylla	Cornales	Fg	Everywhere	P	В	Cyanogenic glycosides

Hyoscyamus niger	Solanales	Rh	Everywhere	P	A	Alkaloid atropine, hyoscyamine, scopolamine
Іротоеа ригригеа	Solanales	Fg	Seeds	A	В	Ergine alkaloid
Juniperus virginiana	Pinales	Ud, Ra	Aerial parts of plants, seeds	S	B, D	Alcohol sabinol
Juniperus foetidissima	Pinales	Ud, Ra	Aerial parts of plants, seeds	S	B, D	Alcohol sabinol
Lactuca serriola	Asterales	Rh	Everywhere, in senile period	A	В	Lacturaria resin
Lactuca tatarica	Asterales	Rh	Everywhere	P	В	Coumarin
Ligustrum vulgare	Lamiales	Ud, Ra	Aerial parts of plants, fruits	S	В	Ligustrin glycoside
Lonicera caprifolium	Dipsacales	Ud, Ra	Fruits	S	B, D	Xylostein glycoside
Maclura pomifera	Rosales	Ra	Fruits	T	C, D	Glycosides
Narcissus poeticus	Asparagales	Fg	Everywhere	P	В	Alkaloid lycorin
Paeonia lactiflora	Saxifragales	Fg	Everywhere	P	В	Glycoside salicin, alkaloids
Papaver rhoeas	Ranunculales	Fg	Everywhere	A	A	Alkaloids
Papaver somniferum	Ranunculales	Rh	Everywhere	A	A	Alkaloids
Parthenocissus quinquefolia	Vitales	Ra	Fruits	L	В	Oxalic acid
Parthenocissus tricuspidata	Vitales	Ra, Ud	Fruits	L	В	Oxalic acid
Pelargonium zonale	Geraniales	Fg	Everywhere	P	B, D	Alcohol geraniol, linaliol
Phytolacca americana	Caryophyllales	Ra	Everywhere, especially fruits	S	В	Glycoprotein, saponin, phytolaccotoxin alkaloid
Ranunculus repens	Ranunculales	Fg	Everywhere	P	A	Protoanemonin, prussic acid
Ranunculus sceleratus	Ranunculales	Fg	Everywhere	P	A	Protoanemonin, prussic acid
Rhus typhina	Sapindales	Ra, Ud	Aerial parts of plants	T	D	Urushiol
Ricinus communis	Malpighiáles	Fg	Everywhere, especially fruits	A	A	Ricin, ricinine
Ruta graveolens	Sapindales	Fg	Aerial parts of plants	S	B, D	Alkaloids
Sambucus nigra	Dipsacales	Ra, Ud	Everywhere, especially unripe fruits	S	В	Glycoside d-amygdalin
Sedum sp	Saxifragales	Fg	Everywhere	P	B, D	Alkaloid sedamine
Jacobaea vulgaris	Asterales	Rh	Everywhere	Дв	В	Alkaloid yakonin
Solanum dulcamara	Solanales	Rh	Everywhere	P	В	Alkaloid solanine
Solanum nigrum	Solanales	Rh	Unripe fruits	P	В	Alkaloid solanine
Styphnolobium japonicum	Fabales	Ra, Ud	Fruits	В	В	Alkaloid cytisine
Symphoricarpos albus	Dipsacales	Ra, Ud	Fruits	S	В	Alkaloid chelidonin
Toxicodendron radicans	Sapindales	Ra	Aerial parts of plants	L	D	Urushiol
Vinca minor	Gentianales	Fg	Everywhere	P	В	Alkaloids
Wisteria sinensis	Fabales	Ra	Seeds, fruits	S	B, D	Glycoside vistarin
Aesculus hippocastanum	Sapindales	Ra, Ud	Fruits	Т	В	Glycosides, saponins

 $<sup>^1</sup>Fg$  — communities of herbaceous ornamental plants; Rh — ruderal communities; Ud — urban dendrocenoses; Ra — communities of residential area.

 $<sup>^2</sup>$  Part of the plant in which hazardous substances are concentrated.

 $<sup>^3</sup>LF$  — life forms of plants. T — trees, S — shrubs, L — lianas, P — perennials, A — annuals.

Rostov-on-Don ecological and cenotic analysis of the flora of poisonous plants shows the relationship of some species with certain types of habitats and cenoses (Fig. 1).

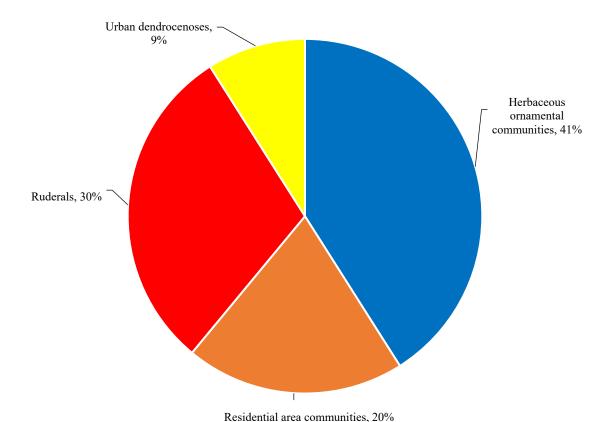


Fig. 1. Distribution of species of poisonous plants by Rostov-on-Don biotopes

Most poisonous plants were found in flower beds and parterres, that is, in communities of ornamental herbaceous plants (Flower garden) — 27 species (41% of the total number of species). Twenty species (30%) were associated with Ruderal cenoses. Thirteen species (20%) were found in the Residential areas. The least number of species was included in urban dendrocenoses — 6 species (9%).

The resulting distribution was quite natural, considering that artificial communities of flower beds and parterres included a diverse range of plants. However, planning elements of landscape design and green construction did not take into account the risks of poisoning by poisonous ornamental plants. For example, representatives of the buttercup family from the genera *Anemone* and *Aquilegia* contain alkaloids and glycosides that are dangerous to life and health, yet they are very popular among flower growers.

Many poisonous plants belonged to the group of ruderals. They grew in littered, unkempt territories, on roadsides, wastelands, etc. Ruderal poisonous plants were characterized by high rates of reproduction, quickly capturing new habitats, that is, they were powerful and uncontrolled sources of toxic substances. The group included such deadly species as poison hemlock (*Conium maculatum*), black henbane (*Hyasciamus niger*), European birthwort (*Aristolochia clemetitis*), and others.

Poisonous plants of residential areas were, as a rule, single specimens or group plantings in the private sector or elements of phytodesign on the territory of residential complexes. With an unqualified selection of the species, only decorative characteristics of the planting material were considered. However, such plants were quite dangerous, even in small numbers.

In recent decades, the American pokeweed (*Phytolacca americana*) has become widespread in southern Russia, including Rostov-on-Don. Pokeweed is native to North America, but the species is widespread on the Eurasian continent. The decorative qualities of pokeweed have caused it to be cultivated in different countries, and as a result, local ecosystems have suffered from another invasive species. Pokeweed has negatively affected the biocenoses of South Korea [20] and Italy [21]. It spreads due to its unpretentiousness, ability to grow rapidly and reproduce by producing large numbers of seeds. All parts of pokeweed, including attractive berries, contain saponins and alkaloids [22], which can cause serious poisoning when ingested by humans and animals.

Biomorphological analysis of the toxic flora of Rostov-on-Don revealed the predominance of perennial grasses. These included 30 plant species (45% of the total number of studied species). 14 species (21%) of poisonous plants were annual. Shrubs and trees came in third place with 15 species (23%). Lianas and biennials were also found among

the poisonous plants, the proportion of which did not exceed the total number of species. The resulting distribution was expected and reflected the proportion of life forms in the flora of the Rostov-on-Don agglomeration, where perennial grasses also predominated, and shrubs and trees were represented in smaller numbers [18]. It is worth noting that the largest number of poisonous plants belonged specifically to families with a predominance of herbaceous forms (Ranunculaceae, Solanaceae). A similar distribution of biomorphs was observed in the toxic flora of Saratov, where perennial grasses and shrubs also played a significant role [13].

Toxicity classes reflect the degree of danger of a particular species to humans and animals (Fig. 2).

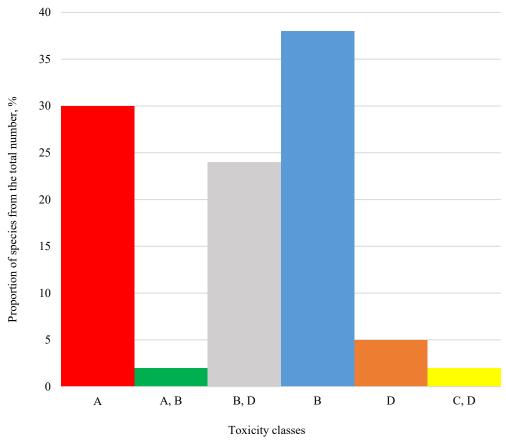


Fig. 2. Distribution of species of poisonous plants in Rostov-on-Don by toxicity classes

Some types combined the properties of two classes. As an example, *Hedera helix* and Hedera colchica ivies were climbing, evergreen vines that were increasingly used in private gardening (Fig. 3). The juice of these plants could cause burns and skin irritation (Class D), and when ingested, ivy caused gastrointestinal disorders (Class B).



Fig. 3. Colchian ivy (Hedera colchica) in the residential area of Rostov-on-Don

Most of the identified poisonous plant species did not have a significant toxic effect, although their use could lead to gastrointestinal discomfort. There were 42 such species, accounting for 64% of all identified species. Of these, 16 caused irritation or skin damage, and were therefore classified as Class D. Plants with the most severe toxic effect

from Class A included 21 species (32%). Only one species from Class C was identified (*Maclura pomifera*). The use of these plants threatened calcium oxalate poisoning with edema of the upper gastrointestinal tract and respiratory organs. *Maclura pomifera* was rare, but was found in private landscaping. It was chosen because of the interesting shape of its fruits.

Let us focus on ragweed (*Ambrosia artemisiifolia*) separately. Its allergenic activity in Rostov-on-Don was previously discussed [11]. Some authors pointed to toxic substances in all parts of ragweed, which could lead to negative consequences for the body [23].

Some species, often found in ruderal habitats, had an unconfirmed hazard status, i.e. there was no consensus on their toxicity. These were, for example, Schleicher fumitory (*Fumaria schleicheri*), chickweed (*Stellaria media*), and roadside pepperweed (*Lepidium ruderale*) [19].

The toxicity of plants in all identified cases was due to the presence of alkaloids — 28 species (42% of the total number of species), glycosides — 17 species (26%), saponins — 5 species (7%) and other toxic compounds.

Accessible and attractive plants with noticeable, bright fruits are dangerous (especially for children). In Rostov-on-Don, 14 such species were found (21% of the total number of species). They belonged to the toxicity class B, as a rule, they did not give an acute toxic effect, but they could cause moderate poisoning. Examples included *Parthenocissus sp.* [24] and *Symphoricarpos albus* [25].

**Discussion and Conclusion.** It is necessary to educate the population of Rostov-on-Don about the possible dangers of plants used for landscaping.

The scientific research described in this article revealed the presence of poisonous plants throughout the city. A significant proportion of these plants were found to be associated with ruderal habitats, where they grow freely and are easily accessible to humans and animals. Additionally, the diversity of toxic flora in urban environments is increasing due to the introduction of ornamental grasses and shrubs that contain dangerous compounds. These findings should be taken into consideration in landscape design projects to ensure the safety of both humans and wildlife.

The study of poisonous flora for the cities of southern Russia has been conducted for the first time. It is planned to study the quantitative characteristics of urban plant communities with toxic species. The data collected will be used to develop recommendations for landscaping and landscape design.

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#### About the Author:

**Mikhail M. Sereda,** Cand. Sci. (Biol.), Associate Professor, Head of the Department of Botany and Bioresources, Faculty of Bioengineering and Veterinary Medicine, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344003, Russian Federation), <u>SPIN-code</u>, <u>ORCID</u>, <u>Scopus</u>, <u>seredam@yandex.ru</u>

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#### Об авторе:

**Михаил Михайлович Середа**, кандидат биологических наук, доцент, заведующий кафедрой ботаники и биоресурсов факультета биоинженерии и ветеринарной медицины Донского государственного технического университета (344003, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), <u>SPIN-код</u>, <u>ORCID</u>, <u>Scopus</u>, <u>seredam@yandex.ru</u>

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**Natural Sorbent Based on Zeolite-Containing Rocks** of Tatarsko-Shatrashan Deposit for Treatment of Surface and Waste Water from Organic Pollutants

Alina V. Taneeva , Yuliya V. Snigireva, Radik N. Khizbullin, Darya A. Shlykova<sup>D</sup>, Vyacheslav F. Novikov<sup>D</sup>

Kazan State Power Engineering University, Kazan, Russian Federation





#### **Abstract**

Introduction. The modern industrial and environmental challenges require the identification of optimal sorbents for water purification from organic contaminants. Sorbents like activated carbon and silicon dioxide have been widely used, but the problem of selecting the optimal sorbent that can adequately purify water remains relevant. There is information in the scientific literature about potential use of sorbents from natural zeolite-containing minerals for this purpose. However, this approach is not well developed; the materials are poorly studied and, as a result, are rarely used to solve environmental problems. This work aims to fill this gap by studying the sorption properties of a natural sorbent based on zeolite-containing rocks of the Tatarsko-Shatrashan deposit.

Materials and Methods. The method of ascending liquid column chromatography became the basis for this study. The sorption material was loaded into a chromatographic column with a length of 120 mm and an inner diameter of 3 mm. The model organic substances in the vial moved along the length of the sorption layer. Trichloroethane, ethyl acetate, methyl ethyl ketone, dichloroethane, and trichloroethylene were used as model compounds. We summarized the significant data in tables and visually represented it in graphs.

Results. The technological characteristics of natural sorbents obtained on the basis of zeolite-containing rocks of the Tatarsko-Shatrashan deposit have been experimentally investigated. The absolute retention time of the studied sorbates, as well as their sorption capacity in relation to zeolite-containing rocks of the Tatarsko-Shatrashansky deposit, were determined. The dependence of the retention time of model organic substances on the length of the sorption layer, which was determined by the physical-chemical nature of the sorbate under study, has been established. From the same point of view (as components of the dependence), the boiling points of model organic substances, dipole moments, refractive indices, and densities were considered. The experimental data were statistically processed, and the absolute and relative errors of a single measurement were determined. All sorbates considered in the framework of this scientific work showed significant or high sorption capacity. The recorded minimum was 34% (methyl ethyl ketone); the maximum was 72% (ethyl acetate). At the same time, ethyl acetate had an extremely short retention time in a 10-centimeter sorption layer (26 min). The longest retention time was for methyl ethyl ketone (314 min). Its sorption capacity was minimal (34%).

Discussion and Conclusion. The prospects of the studied material for the purification of surface and waste water from major pollutants in the natural environment have been experimentally proven. It has been determined that zeolite-containing rocks from the Tatarsko-Shatrashan deposit can adsorb 34-72% of organic compounds that pollute water. They can be used in technological processes for the purification of natural and wastewater from major environmental pollutants.

Keywords: zeolite-containing rocks, model organic substances, sorption capacity, liquid chromatography, water purification from organic pollutants

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Оригинальное теоретическое исследование

#### Природный сорбент на основе цеолитсодержащих пород Татарско-Шатрашанского месторождения для очистки поверхностных и сточных вод от органических загрязнителей

#### Аннотация

Введение. Современная производственная и экологическая повестка ставит задачу выявления оптимальных сорбентов для очистки воды от органических загрязняющих веществ. Широкое практическое применение получили такие сорбенты, как активированный уголь, диоксид кремния и др. Однако сохраняет актуальность проблема поиска оптимального по селективности сорбента. Он должен приемлемо или хорошо очищать воду от главных органических загрязнителей. В научной литературе есть сведения о перспективах использования в рассматриваемых целях сорбентов из природных цеолитсодержащих минералов. Однако такой подход недостаточно проработан, материалы малоизучены и, как следствие, редко используются для решения экологических проблем. Представленная научная работа призвана восполнить этот пробел. Ее цель — исследование сорбционных характеристик природного сорбента на основе цеолитсодержащих пород Татарско-Шатрашанского месторождения.

*Материалы и методы*. Базовым для данного исследования стал метод восходящей жидкостной колоночной хроматографии. Сорбционный материал загружали в хроматографическую колонку длиной 120 мм и внутренним диаметром 3 мм. Модельные органические вещества в виале перемещались по длине сорбционного слоя. В качестве модельных соединений использовали трихлорэтан, этилацетат, метилэтилкетон, дихлорэтан и трихлорэтилен. Значимые данные обобщены в виде таблиц и графически визуализированы.

Результаты исследования. Экспериментально исследованы технологические характеристики природных сорбентов, полученных на основе цеолитсодержащих пород Татарско-Шатрашанского месторождения. Определены абсолютное время удерживания исследуемых сорбатов, а также их сорбционная емкость по отношению к цеолитсодержащим породам Татарско-Шатрашанского месторождения. Установлена зависимость времени удерживания модельных органических веществ от длины сорбционного слоя, которая определяется физико-кимической природой исследуемого сорбата. С этой же точки зрения (как составляющие зависимости) рассмотрены температуры кипения модельных органических веществ, дипольные моменты, показатели преломления и плотности. Экспериментальные данные статистически обработали, определили абсолютную и относительную погрешность единичного измерения. Все сорбаты, рассмотренные в рамках данной научной работы, показали значимую или высокую сорбционную емкость. Зафиксированный минимум — 34 % (метилэтилкетон), максимум — 72 % (этилацетат). При этом у этилацетата экстремально малое значение времени удерживания в 10-сантиметровом сорбционном слое (26 мин). Самое продолжительное время удерживания — у метилэтилкетона (314 мин). Его сорбционная емкость — минимальная (34 %).

**Обсуждение и заключение.** Экспериментально доказана перспективность исследуемого материала для очистки поверхностных и сточных вод от главных загрязнителей природной среды. Установлено, что цеолитсодержащие породы Татарско-Шатрашанского месторождения могут адсорбировать 34—72 % загрязняющих воду органических соединений. Их можно использовать в технологических процессах очистки природных и сточных вод от основных загрязнителей окружающей природной среды.

**Ключевые слова:** цеолитсодержащие породы, модельные органические вещества, сорбционная емкость, жидкостная хроматография, очистка воды от органических загрязняющих веществ

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Introduction. One of the conditions for environmental safety is the protection of water bodies from anthropogenic and natural pollution. A special case of this problem is the negative impact of organic compounds such as petroleum products, phenols, aromatic hydrocarbons, and organochlorine [1]. These pollutants spread relatively quickly in water over considerable distances and harm the environment even in neighboring regions, which can lead to irreversible changes in the ecosystem [2]. Phenol and its derivatives are especially dangerous for the environment and humans, as many of them are mutagens and teratogens capable of disrupting the endocrine system [3]. In addition, under certain conditions, the phenol molecule is transformed into compounds with a higher hazard class [4]. Biodegradation of phenol can accelerate in summer, when aerobic microorganisms intensively oxidize organic compounds [5]. The limiting stage of this process is the mass transfer of oxygen molecules from the gas phase to the aqueous phase [6]. In addition to phenols, other classes of organic compounds can be found in surface waters: aromatics and alkylaromatics, alkanes, carboxylic acids, hexachlorane, hexachlorobenzene, benz(a)pyrene, acetatanaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(k)fluoranthene, benzo(k)fluoranthene, benzo(k)fluoranthene, benzo(k)fluoranthene,

Source [8] provides information collected over 15 years on the contamination of organic compounds in the bottom sediments of the Belaya River. Analysis of the ecological status of surface waters in various regions of Russia [9] has revealed that in many cases, water resources do not meet the standards. As a rule, cities rely on surface water for their water supply. Water utilities treat and chlorinate this water [10], which can lead to the formation of organochloride compounds that pollute drinking water. These compounds can be removed through various methods, such as sorption, which uses activated carbon and synthetic zeolite materials to remove toxic impurities from water. Recent studies indicate that natural zeolite minerals have promising potential for this purpose due to their well-developed systems of macro- and micropores that effectively remove organic compounds from water [11]. A system of cavities and channels run through the three-dimensional alumino–silico–oxygen framework of natural zeolites. The huge inner surface and cavernous structure of zeolite-containing rocks ensures strength of adsorption processes, which is sufficient for efficient wastewater treatment by industrial enterprises from toxic impurities. However, natural zeolite rocks are not well studied, which hinders their widespread use in solving environmental problems [12].

The aim of this study is to experimentally investigate the technological properties of natural sorbents based on zeolite-containing rocks of the Tatarsko-Shatrashansky deposit.

**Materials and Methods.** A natural sorbent based on zeolite-containing rocks from the Tatarsko-Shatrashansky deposit has been studied (Table 1).

Chemical composition of the natural sorbent [12]

Table 1

Elements	% wt
Silicon dioxide SiO <sub>2</sub>	66.00
Titanium dioxide TiO <sub>2</sub>	0.35
Aluminum oxide Al <sub>2</sub> O <sub>3</sub>	6.19
Iron oxide Fe <sub>2</sub> O	2.65
Manganese oxide MnO	0.01
Calcium oxide CaO	17.00
Magnesium oxide MgO	1.45
Sodium oxide Na <sub>2</sub> O	0.16
Potassium oxide K <sub>2</sub> O	1.43
Phosphorus oxide P <sub>2</sub> O <sub>5</sub>	0.13

The natural elements under consideration are thermally stable and acid resistant. The total cation exchange capacity — 130.0 mg-eq / 100 g. Calcium plays a major role in the metabolic process. Table 2 provides the main characteristics of the material under study.

Characteristics of the natural sorbent under study

Indicators	Physical and mechanical properties					
Appearance	Granules of light gray or white color					
Porosity	37.25–55.72%					
Density	2.03–2.37 g/cm <sup>3</sup>					
Mechanical crushing strength	At 200 °C — 46 kg/cm², at 2500 °C — 59 kg/cm²					
Vibration wear	0.96%					
Bulk weight	0.4–1.2 g/cm <sup>3</sup>					
Volume weight	1.10 g/cm <sup>3</sup>					
Effective pore diameter	0.4 Nm (4A°)					
Thermal resistance	Higher than 450°C					
Solubility in water	Insoluble					

To prepare the sorbent, rocks containing zeolite from the Tatarsko-Shatrashansky deposit were mechanically activated. They were crushed in a ball mill; the fractions were separated, and then treated with a 1:1 solution of hydrochloric acid. Next, the resulting material was washed with water until a neutral reaction was achieved and subjected to heat treatment at 450–500°C for 5 hours. The sorbent obtained was placed in 150 mm long glass chromatographic columns with an inner diameter of 3 mm. Vials containing the model liquids under study, organic substances with various physical and chemical properties, were attached to the bottom of the columns. As the model organic substances passed through the sorption layer of the zeolite-containing rock, their movement up through the channels and pores was recorded. The time of passage was measured every 10 millimeters of the sorbent and kinetic curves were plotted for the dependence of the retention of model organic substances on the height of the sorption layer.

Sorption properties were determined by the formula:

$$A = \frac{m_2 - m_1}{m_1} \cdot 100\%,\tag{1}$$

where A — sorption capacity of the material under study, %;  $m_1$  — mass of the initial adsorbent;  $m_2$  — mass of the adsorbent saturated with an organic solvent.

For statistical processing of experimental data, the absolute and relative errors of a single measurement were determined with a confidence probability of 0.95. Table 3 provides the results for hexane sorption.

Table 3
Absolute and relative errors in the measurement of hexane on the tested sorbents

Measurement criteria	Error				
Weasurement Criteria	absolute, $\Delta$	relative, $\delta$ %			
5	7.16	13.64			
10	6.40	12.12			
20	5.29	11.96			
30	5.15	10.78			

Table 2

**Results.** Table 4 provides information on physical-chemical properties of model organic substances (sorbates).

### Characteristics of model sorbates\*

Model sorbates	Formula	$T_{\text{кип}}$	d	$n_{D}^{20}$	$t_{10}$	A	μ
Trichlorethane	CHCl <sub>3</sub>	74	1.453	1.4463	152	45	1.15
Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	77.1	0.900	1.3720	26	72	2.48
Methyl ethyl ketone	C <sub>4</sub> H <sub>8</sub> O	79.6	0.805	1.3800	314	34	2.84
Dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	83.5	1.253	1.4400	61	62	1.80
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	87.2	1.464	1.4800	88	56	0.85
Hexane	C <sub>6</sub> H <sub>14</sub>	68.0	0.660	1.416	59	46	0.05

where \*d — density, g/cm³; Ткип — boiling point, °C;  $n_D^{20}$  — refractive indices at 20°C;  $t_{10}$  — retention time of model organic substances in a 10-centimeter sorption layer, min; A — sorption capacity, %;  $\mu$  — dipole moment, D

As a result of the experiments (Table 4) the retention time of ethyl acetate was extremely low (26 min). Trichloroethane, which had a lower boiling point (74°C), was washed out of the column later than ethyl acetate with a boiling point of 77.1°C. Obviously, this could be explained by the higher molecular weight of trichloroethane (M = 119.4 g/mol) compared to ethyl acetate (M = 88.11 g/mol). In this case, the order in which the components exit was not determined by their boiling points. This dependence was more complicated. It took into account the chemical nature of the model organic substances used, as well as the possibility of their adsorption and desorption by the pores of the material under study. At the same time, despite the low retention time of ethyl acetate, its sorption capacity was relatively high (72%) compared to other organic substances studied. The sorption capacity of all the studied organic substances was quite high (34–72%), which made it possible to use these materials to purify water from organic compounds.

To evaluate the kinetic characteristics of the sorption process, dependencies were constructed linking the retention time of model sorbates and the height of the sorption layer in the ranges from 0 to 5 cm (Fig. 1) and from 5 to 10 cm (Fig. 2).

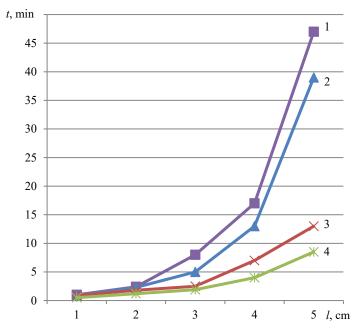


Fig. 1. The effect of retention of model sorbates on the nature of sorption processes (sorbent layer from 0 to 5 cm):

1 — methyl ethyl ketone; 2 — trichloroethane; 3 — trichloroethylene; 4 — dichloroethane

As it can be seen from Figure 1, the dependence had a parabolic character. Obviously, this was due to the fact that at the initial moment of time (up to 5 mm of the sorption layer) there was no equilibrium between the organic liquid and the solid. It was established after sorption, and an almost linear pattern was observed at a distance of more than 5 cm. The exception was methyl ethyl ketone, which had a sufficiently high value of the dipole moment ( $\mu = 2.84D$ )

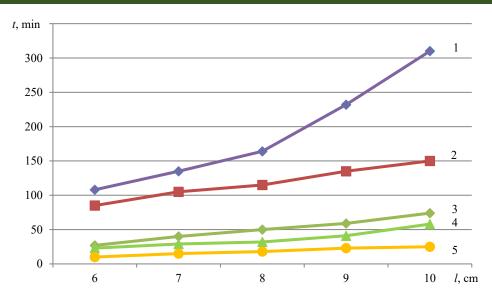


Fig. 2. Dependence of the retention time of model organic substances on the height of the sorption layer of zeolite-containing rock (from 5 to 10 cm): 1 — methyl ethyl ketone; 2 — trichloroethane; 3 — trichloroethylene; 4 — dichloroethane; 5 — ethyl acetate

It should be noted that for all the organochlorine compounds studied (trichloroethane, dichloroethane, trichloroethylene), the angles of inclination of straight lines were almost identical (Fig. 2). This indicated the additivity of the sorption process for organochlorine compounds.

An important parameter of an organic molecule is the dipole moment. It characterizes the asymmetry of charge distribution in an electrically neutral molecule, which makes it possible to form electric dipoles with the same charge values +g and -g. The dipole moment of a molecule is determined as a result of vector addition of the dipole moments of individual bonds. The dipole moments of organic compounds characterize the polar properties of a molecule, as well as determine the direction and strength of intermolecular electrostatic interactions and the sorption properties of porous materials.

Figure 3 shows the dependence of the retention time of model sorbates ( $t_{y\pi}$ ) on their boiling points ( $T_{KHII}$ , °C) and dipole moments ( $\mu$ , D).

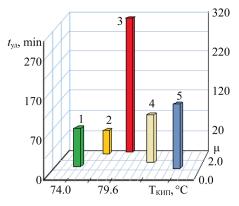


Fig. 3. Dependence of the retention time of model organic substances on their boiling points and dipole moments: 1 — trichloroethane; 2 — ethyl acetate; 3 — methyl ethyl ketone; 4 — dichloroethane; 5 — trichloroethylene

As it can be seen from Figure 3, the release time of ethyl acetate (2) and methyl ethyl ketone (3) differed significantly, although they had similar values of dipole moments and boiling points. Methyl ethyl ketone retained significantly longer ( $t_{yx} = 314$  min) than ethyl acetate ( $t_{yx} = 26$  min), dichloroethane ( $t_{yx} = 61$  min), trichloroethylene ( $t_{yx} = 88$  min), and trichloroethane ( $t_{yx} = 152$  min). Let us note that according to the Rorschneider classification in the sorbate—sorbent system, methyl ethyl ketone determines the dispersion interaction. Obviously, the Van der Waals forces play a leading role in this process, and the sorption time is more significant. This is also due to the fact that methyl ethyl ketone is characterized by a higher polarity (dipole moment —  $\mu = 2.84$ D), as well as a higher boiling point ( $T_{RHII} = 79.6$ °C).

The refractive index also determines the polarity of the model organic substances. It is related to molecular refraction, and is a measure of the electronic polarizability of the shell of a substance molecule.

Figure 4 shows the dependence of the retention time of the model sorbates on their boiling temperatures ( $T_{\text{KMII}}$ , °C) and refractive indices ( $n_D^{20}$ ).

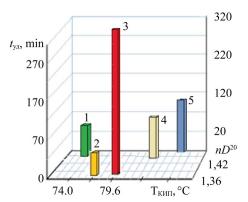


Fig. 4. Dependence of the retention time of model organic substances on their boiling points and refractive indices: 1 — trichloroethane; 2 — ethyl acetate; 3 — methyl ethyl ketone; 4 — dichloroethane; 5 — trichloroethylene

As it can be seen from Figure 4, ethyl acetate and methyl ethyl ketone were similar in two parameters:

- boiling points (77.1°C and 79.6°C respectively);
- refraction (1.37 and 1.38 respectively).

Methyl ethyl ketone is characterized by a higher retention time compared to other sorbates studied. Apparently, this is due to the higher energy of the orientational interaction of methyl ethyl ketone with the sorbent surface.

Figure 5 allows us to consider the density of sorbates in relation to retention time and boiling point.

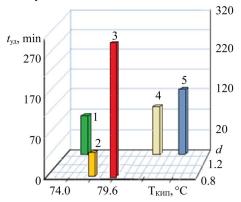


Fig. 5. Dependence of the retention time of model organic substances on their boiling points and density: 1 — trichloroethane; 2 — ethyl acetate; 3 — methyl ethyl ketone; 4 — dichloroethane; 5 — trichloroethylene

Thus, within the framework of this scientific work, it was found that the sorption capacity of the materials under consideration varied from 34% to 72%. Ethyl acetate ( $C_4H_8O_2$ ) had a particularly high rate (72%). Its other characteristics were: dipole moment — 2,48; retention time of model organic substances in a 10-centimeter sorption layer — 26 min; refractive index at 20°C — 1.3720; boiling point — 77.1°C; density — 0.9 g/cm³. Methyl ethyl ketone was similar to ethyl acetate in terms of boiling point, density, refraction, and dipole moment. However, among the sorbates considered, its sorption capacity was minimal (34%), and the retention time was the longest (314 min).

**Discussion and Conclusion.** The results of the study indicate that a high-quality sorbent can be produced using zeolite-containing rocks from the Tatarsko-Shatrashansky deposit. This material has the potential to purify water from major organic pollutants. It was found that, the best result in terms of sorption capacity was to remove ethyl acetate if necessary. The sorbent in question takes 72% of this substance from the water. The minimum is associated with methyl ethyl ketone. In this case, the lowest but acceptable sorption capacity (34%) is established.

Thus, the sorption properties of natural zeolites are considered to be good. The findings of this scientific study can be applied in technological processes for water purification from major contaminants.

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### About the Authors:

Alina V. Taneeva, Cand. Sci. (Chemistry), Associate Professor of the Department of Energy Supply of Enterprises, Construction of Buildings and Structures, Kazan State Power Engineering University (51, Krasnoselskaya St., Kazan, 420066, Russian Federation), SPIN-code, ORCID, ScopusID, alinataneeva@mail.ru

**Yuliya V. Snigireva,** Postgraduate Student of the Department of Energy Supply of Enterprises, Construction of Buildings and Structures, Kazan State Power Engineering University (51, Krasnoselskaya St., Kazan, 420066, Russian Federation), <a href="mailto:oRCID">ORCID</a>, <a href="mailto:sneg987@mail.ru">sneg987@mail.ru</a>

Radik N. Khizbullin, Cand.Sci. (Phys.-Math.), Associate Professor of the Electric Stations Named after V.K. Shibanov Department, Kazan State Power Engineering University (51, Krasnoselskaya St., Kazan, 420066, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:ORCID">ORCID</a>, <a href="mailto:rad-khizbullin@mail.ru">rad-khizbullin@mail.ru</a>

**Darya A. Shlykova,** Postgraduate Student of the Electric Stations Named after V.K. Shibanov Department, Kazan State Power Engineering University (51, Krasnoselskaya St., Kazan, 420066, Russian Federation), ORCID, zagrek90@inbox.ru

**Vyacheslav F. Novikov**, Dr. Sci. (Chemistry), Professor, Professor of the Department of Energy Supply of Enterprises, Construction of Buildings and Structures, Kazan State Power Engineering University (51, Krasnoselskaya St., Kazan, 420066, Russian Federation), SPIN-code, ORCID, npo\_aist@mail.ru

### Claimed Contributorship:

AV Taneev: methodology development, visualization.

YuV Snigireva: conducting research, manuscript drafting.

**RN Khizbullin:** conducting research, formal analysis.

**DA Shlykova:** validation of the results.

VF Novikov: concept development, academic advising, review and editing of the manuscript.

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### Об авторах:

**Алина Вячеславовна Танеева**, кандидат химических наук, доцент кафедры энергообеспечения предприятий, строительства зданий и сооружений Казанского государственного энергетического университета (420066, Российская Федерация, г. Казань, ул. Красносельская, 51), SPIN-код, ORCID, ScopusID, alinataneeva@mail.ru

**Юлия Вячеславовна Снигирева,** аспирант кафедры энергообеспечения предприятий, строительства зданий и сооружений Казанского государственного энергетического университета (420066, Российская Федерация, г. Казань, ул. Красносельская, 51), ORCID, sneg987@mail.ru

**Радик Накибович Хизбуллин,** кандидат физико-математических наук, доцент кафедры электрических станций им. В.К. Шибанова Казанского государственного энергетического университета (420066, Российская Федерация, г. Казань, ул. Красносельская, 51), <u>SPIN-код</u>, <u>ORCID</u>, <u>rad-khizbullin@mail.ru</u>

Дарья Андреевна Шлыкова, аспирант кафедры электрических станций им. В.К. Шибанова Казанского государственного энергетического университета (420066, Российская Федерация г. Казань, ул. Красносельская, 51), ORCID, zagrek90@inbox.ru

**Вячеслав Федорович Новиков,** доктор химических наук, профессор, профессор кафедры энергообеспечения предприятий, строительства зданий и сооружений Казанского государственного энергетического университета (420066, г. Казань, ул. Красносельская, 51), <u>SPIN-код</u>, <u>ORCID</u>, <u>npo aist@mail.ru</u>

### Заявленный вклад авторов:

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Ю.В. Снигирева: проведение исследования, написание черновика рукописи.

Р.Н. Хизбуллин: проведение исследования, формальный анализ.

Д.А. Шлыкова: валидация результатов.

В.Ф. Новиков: разработка концепции, научное руководство, рецензирование и редактирование рукописи.

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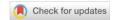
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# Technosphere Safety

## ТЕСНООSPHERE SAFETY ТЕХНОСФЕРНАЯ БЕЗОПАСНОСТЬ





Original Theoretical Research

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### Methodological Principle for Personnel Safety Assessment Based on Likelihood of Negative Events

Anatoly I. Fomin⊠¹, Dmitrii A. Besperstov², Anatoly A. Trubitsyn³, Nelya V. Trubitsyna³, Ekaterina A. Popova², Valeriya A. Petrova²

- <sup>1</sup> Vostochniy Research Institute for Mining Safety, Kemerovo, Russian Federation
- <sup>2</sup> Kemerovo State University, Kemerovo, Russian Federation
- <sup>3</sup> T.F. Gorbachev Kuzbass State Technical University, Kemerovo, Russian Federation



### **Abstract**

Introduction. Currently, for each area of human activity, there is a set of measures aimed at improving its safety from the effects of various negative factors that harm life and health. However, despite the existence and implementation of these measures, around 8,000 people still die from fires each year in the Russian Federation. Thus, the aim of the work is to improve the existing fire safety concept by defining a specific compliance condition for each specific type of assessment in this area. The basis for improving current methods and approaches to assessing the protection of facilities and population from fires is statistical analysis. This allows us to evaluate the likelihood of fire incidents and casualties based on the functional use of a facility, the causes of fires, and the social background of victims.

Materials and Methods. The research plan included both a theoretical and practical part. To solve the problem of the relationship between assessment forms and compliance conditions, we outlined the methodological principle of "one assessment form — one compliance condition". This principle was based on an analysis of the existing regulatory framework of the Russian Federation in the field of fire safety. In order to assess the effectiveness of a particular form of assessment for a particular facility, we proposed a probabilistic approach. This involved determining the risk of fire and deaths in the facility, given the implementation of the assessment form.

**Results.** As a result of the study, we determined the average probability of fires and fatalities for certain classes of functional hazards of objects. This allowed us to calculate the expected risk of death if one of the legal forms of fire safety assessment was applied. The proposed methodological approach was presented in the form of a draft, and the mathematical calculations were provided in the form of flowcharts and tables. These visual representations described the research and made it easier to understand. Both the proposed and existing methodological approaches were identified, highlighting their disadvantages and advantages. We proposed implementing and adding new forms and conditions to ensure the fire safety of facilities.

**Discussion and Conclusion.** The work will make it possible to develop methods for mathematically modeling hazardous working conditions for employees and to identify a catalogue of social and economic risks at industrial facilities. This is a necessary tool for professionals and owners to ensure industrial safety.

**Keywords:** assessment form, compliance conditions, safety provision, risk management, methodological principle, actual risks, expected risks, fire safety

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Оригинальное теоретическое исследование

### Методологический принцип оценки обеспечения безопасности персонала на основе вероятности возникновения негативных событий

А.И. Фомин¹ы, Д.А. Бесперстов², А.А. Трубицын³, Н.В. Трубицына³, Е.А. Попова², В.А. Петрова²

- <sup>1</sup> Научный центр ВостНИИ по промышленной и экологической безопасности в горной отрасли, г. Кемерово, Российская Федерация
- $^{2}$  Кемеровский государственный университет, г. Кемерово, Российская Федерация
- <sup>3</sup> Кузбасский государственный технический университет имени Т.Ф. Горбачёва,
- г. Кемерово, Российская Федерация
- ⊠ fomin-ai@kuzbasscot.ru

### Аннотация

Введение. В настоящее время для каждой сферы деятельности человека существует комплекс мероприятий, направленных на повышение его безопасности при воздействии различных негативных факторов, наносящих вред жизни и здоровью. Несмотря на наличие и соблюдение определенного перечня установленных мер, в Российской Федерации от пожаров тем не менее ежегодно гибнет около 8 000 человек. В связи с этим цель данной работы — усовершенствовать имеющуюся концепцию обеспечения пожарной безопасности. Для этого должны быть определены конкретные условия для улучшения существующих форм и методов оценки защищенности объектов и населения от пожаров. В их основу положен статистический анализ, позволяющий оценить вероятность возникновения пожаров и гибели людей на них, зависимость ее от функционального назначения объекта, причин возгораний и социального положения пострадавших.

**Материалы и методы.** План проведения исследования предусматривал теоретическую и практическую части. Так, для решения проблемы взаимосвязи формы оценок пожароопасности и условий соответствия их нормативно-правовой базе РФ в области пожарной безопасности изложен методологический принцип «одна форма оценки — одно условие соответствия». Данный принцип основан на анализе существующего законодательства Российской Федерации. Для того чтобы определить эффективность той или иной формы оценки конкретного объекта, предложен вероятностный подход, то есть определение риска возникновения пожаров и гибели людей на них при условии ее применения.

**Результаты** исследований. Была определена вероятность возникновения пожаров и смертельных случаев на них для отдельных классов функциональной опасности объектов, позволяющая рассчитать величину ожидаемого риска гибели людей при условии применения одной из определенных законодательством форм оценок пожарной безопасности. Предлагаемый методологический принцип изложен в виде проекта и математических расчётов, предоставленных на блок-схемах и в таблицах, наглядно описывающих проведение исследования, что облегчает их понимание. Определены как предлагаемые, так и существующие методологические принципы с изложением их недостатков и положительных аспектов. Предложены возможности реализации и дополнения форм и условий обеспечения пожаробезопасности объекта.

Обсуждение и заключение. Проведённое исследование позволит разработать методы математического моделирования опасных условий труда работников, а также определить перечень социальных и экономических рисков на производственных объектах, который должен стать необходимым инструментом для специалистов и собственников, обеспечивающих безопасность на производстве.

**Ключевые слова:** форма оценки, условия соответствия, обеспечение безопасности, управление рисками, методологический принцип, фактические риски, ожидаемые риски, пожарная безопасность

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**Introduction.** Currently, intensive work is underway in the Russian Federation and abroad to improve the safety of working and living conditions for citizens. In particular, safety of the population [1] is determined by fundamental legislative acts in our country [2]. However, despite this, the number of accidents, fires and man-made emergencies has not decreased. Major accidents, fires, and emergencies on a federal or interregional scale pose a particular danger to the public and enterprises.

Fire prevention work is carried out both in our country and abroad. For example, Portugal actively develops a strategy to prevent fires. A group of specialists analyzes the causes of fires for subsequent amendments to the country's legislative framework [3]. The catastrophic fires in the Brazilian forest in 2020 and 2021 have served as an impetus for developing measures to prevent future fires. New ways of prevention have been proposed, and successful fire management strategies have been created [4].

Based on the above, we can conclude that it is necessary to further update the existing measures to improve the safety of businesses and employees, as well as to develop new measures that take into account modern conditions and requirements. This is the aim of our research.

**Materials and Methods.** The analysis was based on the classical rule for calculating the risk (probability) of a negative situation [5]. The effectiveness of the fire safety assessment form for a particular facility depended on the expected risks of fire and casualties  $(R_{(cp.\phi)})$  [6]. In other words, for an object corresponding to a certain class of functional fire hazard, a negative situation was modeled — the occurrence of a fire, and then, using the classical sum law [7], the risk of death was determined [8], depending on the purpose of the object, the causes of fire, and the social status of victims  $(R_{(cp.\phi)})$ . Numerical values for the calculations were taken from statistical data on fires in the Russian Federation for 2022, which were freely available on the Internet on official resources. The calculations were performed using an engineering calculator with an extended set of functions that provided the required accuracy and support for complex mathematical operations.

**Results.** To develop measures necessary to ensure safety of the facility and its personnel, it is important to assess the current state of the company and determine the conditions under which both the company and its employees are protected from hazards associated with the production process.

According to fire safety standards [9], the forms of assessments, their positive and negative values [10], were defined, which are presented in Table 1 [11].

Table 1
Positive and negative values of the existing forms of assessing the compliance
of a facility with fire safety requirements

Assessment form	Positive aspects	Negative provisions
Federal State Fire Supervision, etc.	State-owned, financially independent form of assessment, the results of the proposed measures do not affect the monetary remuneration of the SFS inspector	Burden on enterprises and citizens in the form of administrative impact and separation from their main activities for participation in monitoring, supervising, and inspection activities

Positive and negative provisions of the existing compliance conditions are presented in Table 2.

Table 2 Conditions for compliance of objects, highlighting positive and negative aspects

Compli	Compliance conditions Positive aspects		Negative provisions
the requirements of the technical ions, taking into account	fire safety requirements	The standard of measures: formation of understanding by individuals and the organization of the general FS requirements; as a result of technical regulation, the division into mandatory and voluntary use	Limited development of organizations due to government frameworks (administrative barriers); government intervention in case of formal violations of requirements, without their actual impact on safety; modification, exclusion of requirements and their introduction confirms the inadequacy of mandatory measures once again (requirement for the sake of requirement)
When meeting the re regulations,	fire risk	It is possible to determine the safety of people by calculation, including in the presence of violations of fire safety requirements	Complex mathematical calculations; not all fire hazards and parameters of buildings and structures are taken into account.

In turn, the conditions for ensuring the safety of the facility are fulfilled when implementing the safety system outlined in the flowchart (Fig. 1)

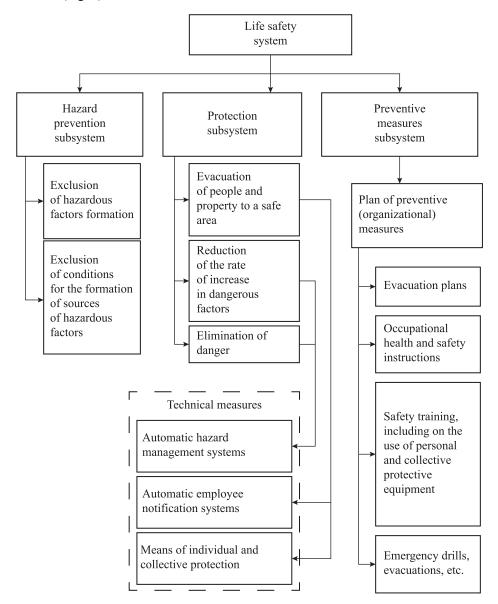


Fig. 1. Fire safety system of facilities

Taking into account positive and negative assessments of the safety of enterprises and their employees, Tables 3, 4, 5, and 6 present additional fire hazard assessments and measures to improve their implementation.

Table 3
Improving existing forms of safety assessments for enterprises and their employees

Form of assessment	Event improvement
Independent fire risk assessment (fire safety audit)	Legislative possibility of introducing rapid assessments and software for these purposes, the definition of requirements for persons engaged in IFRA
Federal State Fire Supervision	Preventive measures should not be the basis for initiating inspections.  The rights and duties of FSFS inspectors should be targeted, and the "other" innovation should be excluded

### Additional forms of object conformity assessment

Add	litional assessment forms	Reasons for the introduction of additional forms of assessments
Re	gional State Fire Safety	90% of fires and deaths occur in residential buildings, but there is no federal state
	Supervision	fire supervision in residential buildings.
D.	revention of violations	The form of assessment required by law is a preventive measure, along with the
F1	revention of violations	control, and supervision.

Table 5

### Improvement of the existing conditions of conformity of objects of protection

(	Com	plianc	e conditions	Improvement of conditions
eting the	ents of the	egulations,	fire safety requirements	Due to the "blind" fulfillment of requirements that do not always affect the fire hazard of the facility and do not involve financial costs on the part of organizations, their fulfillment is formal. It is necessary to expand the development of local requirements that are relevant to the protection object.
When me	requireme	technical rate taking into	fire risk	Introduction of various calculation methods at the legislative acts level, including those developed by individuals other than federal executive authorities (EMERCOM of Russia). Fire risks should be associated with other risks that can lead to a fire (arson, anti-terrorism, industrial safety)

Table 6 Additional conditions for fire safety at the facility

Additional compliance conditions	Grounds for the introduction of additional conditions
Act of the control (supervisory) FSFS event without violations	As an independent state form of assessment, it is the most objective condition for compliance. It does not require additional financial costs for businesses and individuals. It is possible to involve specialists, experts and expert organizations
Fire hazards after the evacuation of people	No need for environmental costs to meet fire safety requirements when evacuating people before the onset of fire hazards. People of enterprises have the right to risk and insure their property

Improvements and additions were based on the principles of ensuring and improving the safety of employees and property of the enterprise.

The analysis conducted allowed us to develop new methodological principles for assessing and ensuring the safety of an enterprise based on risk management.

A general existing principle for safety assessment and conditions is presented in Figure 2 in the form of a block diagram.

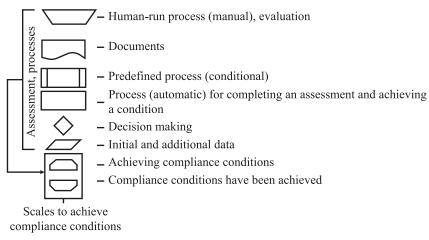


Fig. 2. The existing principle of fire safety assessment and conditions

The existing methodological principle of fire safety assessment and assurance is presented in the form of a general flowchart, since the norms provide for nine forms and five conditions that are not interrelated with each other, respectively (Fig. 3).

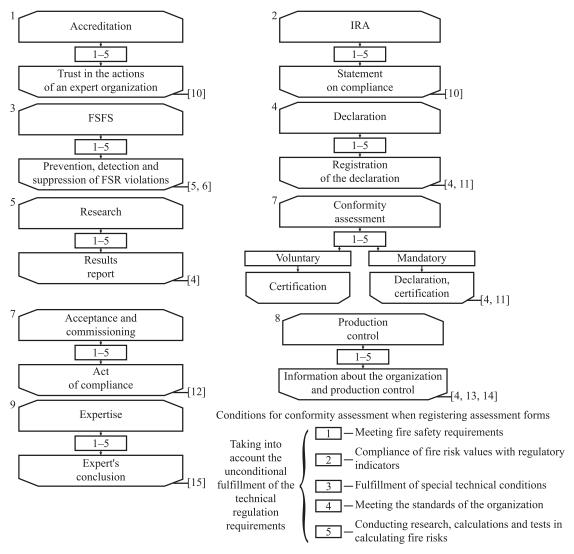


Fig. 3. The existing methodological principle of assessing and ensuring fire safety of facilities

Taking into account the above, the methodological principle "one form of assessment — one compliance condition" was proposed to solve the problem of the relationship between the form of assessments and the conditions of compliance (Table 7) [12].

One form of assessment — one compliance condition

Table 7

Form of assessment Compliance condition No. existing proposed existing proposed Compliance of equipment, 1 Accreditation premises, and employees Federal State Fire Meeting fire safety 2 requirements Supervision

This principle will ensure all safety conditions, taking into account the chosen necessary form of assessment. It also clearly shows which form is implemented under certain conditions. The chosen principle will not allow replacing assessments with ineffective forms to achieve the necessary compliance conditions.

Ensuring the safety of employees and enterprises according to the proposed principle is presented in the form of a flowchart, which provides methodological support (Fig. 4).

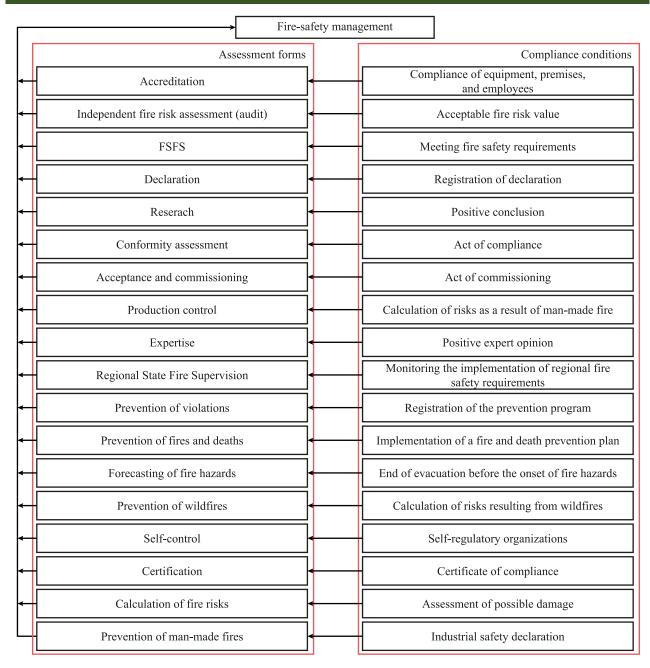


Fig. 4. Methodological support of fire safety for people based on the principle of "one form — one condition"

Thus, fire safety is ensured through the implementation of the attached forms and conditions. Figure 5 illustrates the implementation of the methodology in a flowchart.

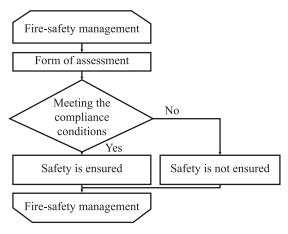


Fig. 5. The proposed methodological principle for ensuring fire safety of people

For the practical implementation of the proposed methodological principle, it was necessary to analyze the actual risks of negative situations. The existing principles of ensuring fire safety are presented in the form of a flowchart in Figure 6.

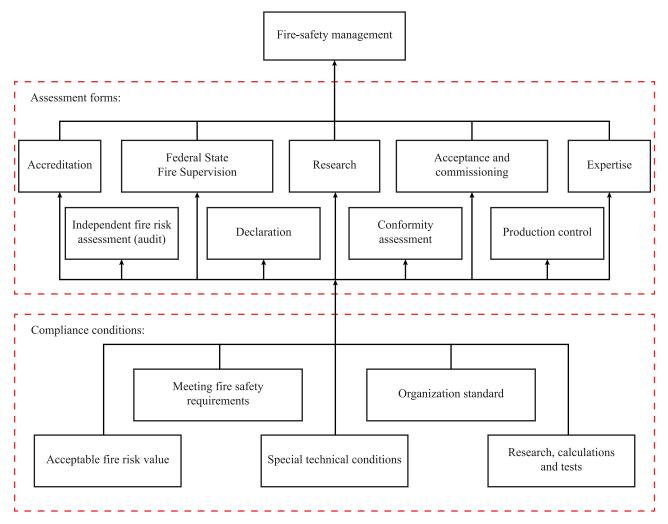


Fig. 6. The existing principle of ensuring fire safety based on regulatory forms of assessments and compliance conditions

It follows from this principle that all compliance conditions can be investigated for any form of assessment. Considering statistical indicators on fires, the probabilistic criteria for actual risks are provided in Table 8.

Table 8
Distribution of the probability of fires and deaths of people at facilities located on the territory
of the Russian Federation, 2022

Object number	Object name	Functional fire hazard class	Number of objects, units.(N <sub>0</sub> )	Number of fires in 2022, units (N <sub>II</sub> )	Probability of a fire at the facility (R <sub>n</sub> )	Number of people killed $(N_r)$	Probability of death in fires	of death from
1	Industrial buildings	F 5.1	173,544	2,349	1.35·10 <sup>-2</sup>	46	1.96·10 <sup>-2</sup>	2.7·10 <sup>-4</sup>
2	Warehouse buildings and structures	F 5.2	100,147	744	7. 4·10 <sup>-3</sup>	10	1.34·10-2	9.99·10 <sup>-5</sup>

In this table, fire probability at the facility is determined by the formula [13]:

$$R_{\Pi} = \frac{N_{\Pi}}{N_{\Omega}}.\tag{1}$$

The probability of death from fires at facilities is determined by the formula:

$$R_{\rm ro} = \frac{N_{\rm n}}{N_{\rm o}}.\tag{2}$$

The probability of death from fires:

$$R_{\rm rn} = \frac{N_{\rm n}}{N_{\rm o}},\tag{3}$$

where  $N_{\rm n}$  — number of fires, pcs;  $N_{\rm o}$  — number of objects, pcs.

Data on the risk of death from fires is presented in Table 9.

Table 9
The probability of death in the Russian Federation in 2022, depending on the causes

Name of the cause of death:	Number of deaths in 2022, people	$R_{\rm np.r}$
Poisoning by toxic combustion products	2,828	1.9·10-5
Unknown causes	1,519	1.04·10 <sup>-5</sup>
Exposure to high temperature	1,343	9.2·10-6

The probability of death of people depending on the causes ( $R_{\text{пр.г.}}$ ), that is, from exposure to primary and secondary fire hazards [14], is determined by the formula:

$$R_{\rm np.r} = \frac{N_{\rm np.r}}{N_{\rm \tiny Hac.P\Phi}},\tag{4}$$

where  $N_{\text{пр.r}}$  — number of people killed, depending on the causes, people;  $N_{\text{нас.P}\Phi}$  — number of people killed, depending on the causes, people.

Table 10 provides the data on the probability of death of the population of the Russian Federation in terms of their social status.

Table 10
The probability of death among people in the Russian Federation in 2022, based on their social status.

Social status of people who died in fires, including	Number of people who died in 2022 in the Russian Federation, people	R <sub>соцп</sub>
workers in blue-collar jobs	710	4.8·10 <sup>-6</sup>
engineering and technical workers	19	1.3·10-7
heads of organizations (enterprises)	7	4.8·10-8

The probability of death from fires in terms of people social status is determined by the formula:

$$R_{\text{пр.r}} = \frac{N_{\text{соц.п}}}{N_{\text{нас.Р}\Phi}},\tag{5}$$

where  $N_{\text{COIL},II}$  — number of people who died in the Russian Federation in 2022, according to their social status, people.

Next, we will combine the indicators of calculated risks by distributing the objects of fire according to the causes and social status of the victims. For convenience, we will use a symbol to represent the objects: 1, 2, 3...

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The related data is provided in Table 11.

Table 11
The related information on the objects where fires occurred, including those involving the death of people,
the causes of death and the social status of the victims

	Symbols of the object
Cause of death	where people died due to
	social status
Poisoning by toxic combustion	1. 2. 4. 6. 7. 8. 10. 11. 12.
products	13
Unknown causes	10. 12. 13

Social status of the deceased	Symbols of the object where people died depending on their social status
Workers in blue-collar jobs	1.2.3
Engineering and technical workers	1. 2. 7. 8

Then, using the formula below, we determine the overall probability of death of people, depending on their social status and causes:

$$R_{\rm cp.o} = \frac{R_{\rm II} + R_{\rm ro} + \sum_{N} \frac{R_{\rm IIp.F}}{N} + \sum_{N} \frac{R_{\rm cou.II}}{N}}{4},$$
 (6)

where N — number of probabilities of negative events related to fires.

The calculated information is presented in Table 12.

Table 12
Summarized information of the probability of occurrence of negative events
related to fires and deaths in Russia in 2022

Ordinal number of the object	Object name	Functional fire hazard class	<i>R</i> п.о.	$R_{\text{r.o.}}$	$R_{ m np.r.}$	$R_{ ext{ iny COU,II}}$ .	$R_{ m cp.o.}$
1	Production facility	F5.1	0.0135	0.00027	0.000019 0.0000092 0.0000046 0.0000042 0.00000023 0.000000096 0.000000048 0.000000027	0.0000046 0.00000013 0.00000048 0.0000043	0.0034443
					R <sub>cp.o.</sub> minimum		0.00014066 0.02527716

This table shows the minimum and maximum values of average probabilities. This data can be used by stakeholders and services to take preventive measures, up to the coordination of government policy, to prevent fires and deaths.

Next, we proceed to determining the expected risks, depending on the forms of assessments and conditions for compliance with fire safety regulations at the facilities. The implementation of fire safety measures at facilities of different functional fire hazard classes [15] involves various forms and conditions, including additional ones, as shown in Figure 7.

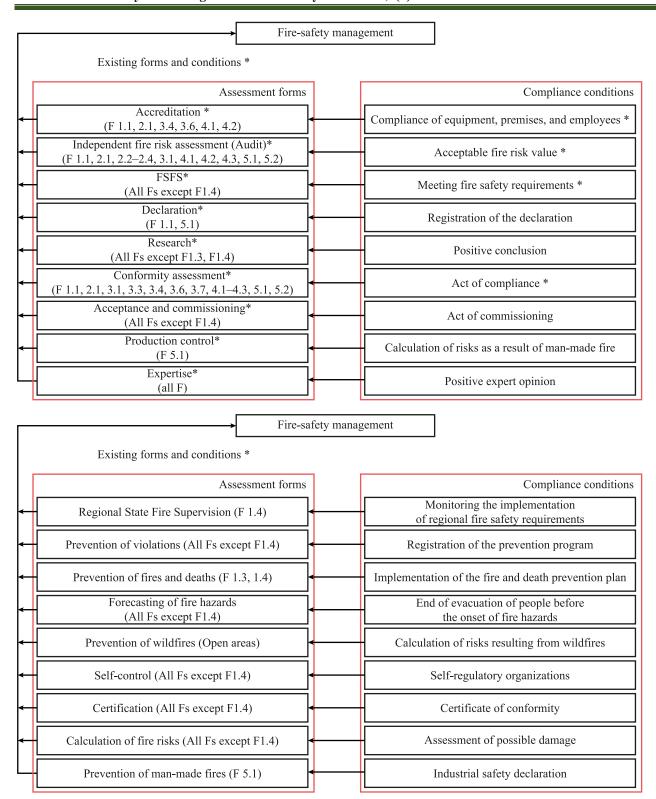


Fig. 7. Assessment forms and compliance conditions for ensuring fire safety at facilities, considering the functional purpose of the facilities

The expected risks for facilities by functional purpose  $(R_{cp,\phi})$  are determined by the formula:

$$R_{\text{cp,}\Phi} = \sum_{N} \frac{R_{\text{cp,o}}}{N} = \frac{\sum_{N} \frac{R_{\text{n}} + R_{\text{ro}} + \sum_{N} R_{\text{np,r}}}{N} + \sum_{N} \frac{R_{\text{r,coil,n}}}{N}}{4N} = \frac{\sum_{N} \frac{N_{\text{n}} + N_{\text{r}}}{N_{\text{o}}} + \sum_{N} \frac{N_{\text{np,r}}}{N}}{N} + \sum_{N} \frac{N_{\text{coil,n}}}{N}}{4N} \cdot (8)$$

The calculated values are summarized in Table 13.

Table 13
The values of the probability of expected risks in implementing the proposed methodological approach for assessing and ensuring human fire safety

Assessment form number	Assessment form name	Functional fire hazard class of the object			$R_{\text{cp.o.}}$ of the corresponding functional fire hazard class			$R_{ m cp. ar{\phi}.}$	
1	Accreditation	F1.1	F2.1	F3.4	0.0023	0.0019	0.00104071	0.001956785	
1	Accreditation	F3.6	F4.1	F4.2	0.0019	0.0023	0.0023	0.001930783	
		F1.1	F1.2	F1.3	0.0023	0.00509277	0.02527716		
		F2.1	F2.2	F2.3	0.0019	0.0019	0.0019		
2	Federal State	F2.4	F3.1	F3.2	0.0019	0.00126179	0.00404658	0.001074004	
2	Fire Supervision	F3.3	F3.4	F3.5	0.00404658	0.00104071	0.00303928	0.001974004	
	Supervision	F3.6	F3.7	F4.1	0.0019	0.0019	0.0023		
			F4.3	F5.1	0.0023	0.00139993	0.0034443		
	F5.2	F5.3		0.00187666	0.00332425				
					R	<sub>ср.ф.</sub> minimum v	alue	0.00014066	
					R	<sub>ср.ф.</sub> maximum v	alue	0.5	

The table shows the minimum and maximum values of the probability of negative events. The above-mentioned methodological principle of fire safety assessment is presented in the form of an algorithm in Figure 8.

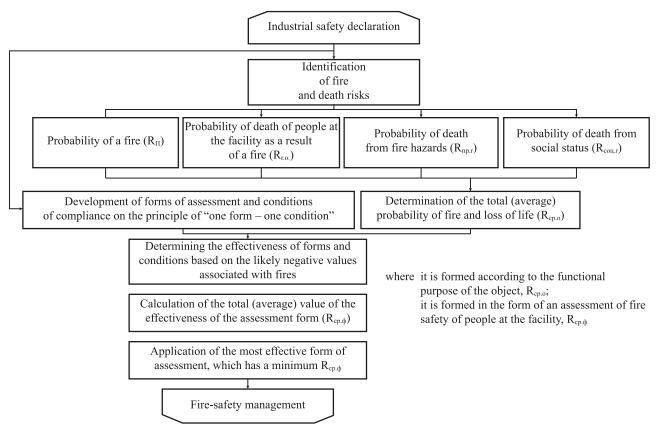


Fig. 8. Draft methodological principle for assessing and ensuring the fire safety of people

The proposed methodological principle for assessing the safety of people in fires improves the current procedure established by the legislation of the Russian Federation. This principle is based on actual values of risk of adverse events, which allows interested parties to take necessary preventive measures in advance.

**Discussion and Conclusion.** Updating the existing principles for assessing the safety of facilities, their employees, and the public based on regulatory documents and those proposed through risk management of potential negative situations allows interested individuals and legal entities to choose the most appropriate forms and conditions for implementation. Mathematical calculations presented in the study allow us to justify the benefits of proposed measures. Applying the principle of predictable risks supports the impossibility of achieving unconditional safety for an enterprise and its employees due to a significant number of unpredictable negative situations resulting from natural and human-made causes.

The practical significance of this research lies in the fact that the methodological approach proposed by the authors is based on mathematical calculations. By taking into account the potential risks, it is possible to develop preventative measures to avoid and minimize negative consequences associated with emergencies, accidents, workplace injuries, and fires.

The results of the work are especially relevant for owners of businesses and other infrastructure facilities. Their primary concern is ensuring the safety of their employees and the general public. Owners will be able to choose an appropriate form of assessment, not only based on the functional classification of the fire risk of the facility, but also considering the minimal risk of death if certain conditions are met. This will allow them to redistribute financial resources within the organization to meet specific fire safety requirements based on the chosen form of assessment.

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### About the Authors:

Anatoly I. Fomin, Dr. Sci. (Eng.), Professor of the Department of Aerology, Occupational Safety and Nature, T.F. Gorbachev Kuzbass State Technical University, Senior Researcher at Vostochniy Research Institute for Mining Safety (28, Vesennyaya St., Kemerovo, 650000, Russian Federation), SPIN-code, ScopusID, fomin-ai@kuzbasscot.ru

Anatoly A. Trubitsyn, Dr. Sci. (Eng.), Professor of the Department of Aerology, Occupational Safety and Nature, T.F. Gorbachev Kuzbass State Technical University (28, Vesennyaya St., Kemerovo, 650000, Russian Federation), SPIN-code, ScopusID, atrubitsyn@rambler.ru

**Nelya V. Trubitsyna,** Dr. Sci. (Eng.), Associate Professor of the Department of Aerology, Occupational Safety and Nature, T.F. Gorbachev Kuzbass State Technical University (28, Vesennyaya St., Kemerovo, 650000, Russian Federation), SPIN-code, ScopusID, ntrubitsyna@rambler.ru

**Dmitrii A. Besperstov,** Cand. Sci. (Eng.), Associate Professor of the Department of Technosphere Safety, Kemerovo State University (47, Stroiteley Ave., Kemerovo, 650056, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:gpnbesperstov@yandex.ru">gpnbesperstov@yandex.ru</a>

**Ekaterina A. Popova,** Associate Professor of the Department of Technosphere Safety, Kemerovo State University (47, Stroiteley Ave., Kemerovo, 650056, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:popovakatalpa@gmail.com">popovakatalpa@gmail.com</a>

Valeriya A. Petrova, Sudent of the Department of Technosphere Safety, Kemerovo State University (47, Stroiteley Ave., Kemerovo, 650056, Russian Federation), ORCID, valera petrova@inbox.ru

### Claimed Contributorship:

AI Fomin: supervision, leadership and mentoring in the process of planning and conducting research.

AA Trubitsyn: creation and preparation of the manuscript, visualization of the research results and data obtained.

**NE Trubitsyna:** the use of statistical, mathematical, and computational methods for analyzing or synthesizing the research data.

**DA Besperstov:** implementation of the research process, including data collection.

**EA Popova:** development of the research methodology.

VA Petrova: creation and preparation of the manuscript, writing a draft, including its translation into a foreign language.

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All the authors have read and approved the final manuscript.

### Об авторах:

**Анатолий Иосифович Фомин,** доктор технических наук, профессор кафедры аэрологии, охраны труда и природы Кузбасского политехнического университета, ведущий научный сотрудник АО «НЦ ВостНИИ» (650000, Российская Федерация, г. Кемерово, ул. Весенняя, 28), SPIN-код, ScopusID, fomin-ai@kuzbasscot.ru

**Анатолий Александрович Трубицын,** доктор технических наук, профессор кафедры аэрологии, охраны труда и природы Кузбасского политехнического университета (650000, Российская Федерация, г. Кемерово, ул. Весенняя, 28), <u>SPIN-код</u>, <u>ScopusID</u>, <u>atrubitsyn@rambler.ru</u>

**Нэля Вадимовна Трубицына,** доктор технических наук, доцент кафедры аэрологии, охраны труда и природы Кузбасского политехнического университета (650000, Российская Федерация, г. Кемерово, ул. Весенняя, 28), SPIN-код, ScopusID, ntrubitsyna@rambler.ru

**Дмитрий Александрович Бесперстов,** кандидат технических наук, доцент кафедры техносферной безопасности Кемеровского государственного университета (650056, Российская Федерация, г. Кемерово, Бульвар Строителей, 47), <u>SPIN-код</u>, <u>gpnbesperstov@yandex.ru</u>

**Екатерина Андреевна Попова,** доцент кафедры техносферной безопасности Кемеровского государственного университета (650056, Российская Федерация, г. Кемерово, Бульвар Строителей, 47), <u>SPIN-код, popovakatalpa@gmail.com</u>

**Валерия Андреевна Петрова,** студент кафедры техносферной безопасности Кемеровского государственного университета (650056, Российская Федерация, г. Кемерово, Бульвар Строителей, 47), ORCID, valera petrova@inbox.ru

### Заявленный вклад авторов:

- А.И. Фомин: контроль, лидерство и наставничество в процессе планирования и проведения исследования.
- А.А. Трубицын: создание и подготовка рукописи, визуализация результатов исследования и полученных данных.
- **Н.В. Трубицына:** применение статистических, математических, вычислительных методов для анализа или синтеза данных исследования.
  - Д.А. Бесперстов: осуществление научно-исследовательского процесса, включая сбор данных.
  - Е.А. Попова: разработка методологии исследования.
  - В.А. Петрова: создание и подготовка рукописи, написание черновика, включая его перевод на иностранный язык.

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Green Roofs in Infill Development to Improve the Environmental Safety of Urban Areas

Svetlana E. Manzhilevskaya De, Aleksandr I. Evtushenko ,

Dmitrii R. Mailyan

Don State Technical University, Rostov-on-Don, Russian Federation



#### Abstract

Introduction. When designing construction projects in urban areas, it is essential to protect the environment from dust pollution. This is particularly challenging in densely populated areas where the construction site is often surrounded by existing buildings and infrastructure. Successful implementation of such projects requires a thorough analysis of many factors, including weather conditions, environmental risks, and limited space for maneuvering. A crucial aspect of this process is the development of measures to control dust emissions during construction. Therefore, technological innovations in the field of eco-friendly roofing systems are becoming a key element of modern urban planning. As scientific research in recent years has shown, eco-friendly structures contribute to the rational use of urban space and significantly improve the environment. However, the results of these studies lack data on the effectiveness of green roof structures and vegetation on them in reducing dust pollution in residential areas. They are adjacent to already populated objects and the lack of space makes it impossible to completely protect urban residents from dust exposure. The aim of this work is to evaluate the effectiveness of green roofs to control the spread of dust in areas with active infill development and to develop our own green roof designs. The introduction of green roofs into residential construction not only improves the architectural appearance of neighborhoods, but also enhances the quality of the urban environment. The use of eco-friendly solutions in construction contributes to the modernization of the industry, making it safer for the environment and more comfortable for residents.

Materials and Methods. An environmental experiment was conducted as part of the large-scale construction of the Krasny Aksai residential complex in Rostov-on-Don. In March 2020, in the construction area and outside the site, employees of the contractor planted herbaceous plants of six species typical of the Rostov region. Each plant species occupied an area of six square meters, creating a total experimental area of 36 square meters. The methodology for determining the volume of dust deposits trapped by plants included sampling dust particles from the surface of plant leaves with a brush, which was performed twice a week from May to October 2020, during the active construction of a multi-storey residential building. Air samples were taken to measure dust concentrations using an electric aspirator PU-3E/12 and filters made from perchlorvinyl fiber AFA-VP10.

Results. The research showed that during the construction period with an easterly wind of 3–5 meters per second and humidity of 40%, the planted vegetation had a significant impact on air quality. There was a decrease in the concentration of PM10 dust particles above the green area by 10%, and at a distance of 10 meters from the vegetation cover, compared to the adjacent construction area, by 15%. Measurements of dust deposits over the growing season (May–October) revealed a significant dynamics: if at the beginning of the season (May–June) the amount of dust deposits on plants was a maximum of 0.42 mg/cm², then in the midst of the warm season (July–October) it reached 1.81 mg/cm². Financial calculations showed that traditional and green roofs were equally cost-effective over the long term (up to 40 years). To achieve this research goal, the authors have developed and implemented two types of constructive solutions for green roofs for public and residential buildings.

**Discussion and Conclusion.** Green roof structures can act as an effective barrier against the spread of dust in the air, especially in areas near infill development where there is a high concentration of suspended solids. To reduce this concentration in residential areas near infill development, it is recommended to install green roofs on terraces, rooftops, and substructures of buildings with windows and entrances located near the construction site. In order to curb the spread of suspended particles, it is also suggested that green roof installation be considered for low-rise buildings such as kindergartens, schools, and shopping malls. The decision on where to install these structures should depend on the overall urban development plan for the area or specific territory.

Keywords: green roofs, dust distribution, environmental safety of urban areas, fine dust, dust pollution

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Оригинальное эмпирическое исследование

### Применение зеленых крыш в точечном строительстве для повышения экологической безопасности городских территорий

С.Е. Манжилевская 🕒 🖂 , А.И. Евтушенко 🕩 , Д.Р. Маилян 🕩

Донской государственный технический университет, г. Ростов-на-Дону, Российская Федерация ⊠ smanzhilevskaya@yandex.ru

### Аннотация

Введение. При проектировании строительных работ в условиях городской застройки важнейшим аспектом является защита окружающей среды от пылевого загрязнения. Особую сложность представляет организация работ в густонаселенных районах, где строительная площадка бывает зажата существующими зданиями и инфраструктурой. Успешная реализация подобных проектов требует тщательного анализа множества факторов: погодных условий, экологических рисков и ограниченного пространства для маневра. Принципиальное значение имеет разработка комплекса мер по контролю пылевых выбросов, возникающих в ходе строительных операций. Поэтому технологические инновации в области экологичных кровельных систем становятся ключевым элементом современного градостроительства. Как показывают научные изыскания последних лет, экологичные конструкции способствуют рациональному использованию городского пространства и заметно улучшают состояние окружающей среды, но при этом в результатах таких исследований отсутствуют данные, которые бы подтверждали, что конструкции зеленой кровли и растительный покров на них эффективны для снижения пылевого загрязнения в условиях точечной застройки, где источники пылевого загрязнения — строительные площадки — соседствуют с уже заселенными объектами и стесненность пространства не дает возможности полностью оградить жителей городов от пылевого воздействия. Цель данной работы — дать оценку эффективности использования зеленых крыш для борьбы с распространением пыли в районах активного точечного строительства, а также разработать собственные конструкции зеленой кровли. Внедрение зеленых крыш в точечное строительство не только преображает архитектурный облик городских кварталов, но и существенно улучшает качество городской среды. Применение подобных экологичных решений способствует общей модернизации строительной отрасли, делает её более безопасной для окружающей среды и комфортной для жителей.

Материалы и методы. В рамках масштабного строительства жилого комплекса «Красный Аксай» в Ростовена-Дону был проведен экологический эксперимент. В зоне ведения строительных работ и за пределами ограждающих конструкций строительной площадки в марте 2020 года сотрудники подрядной организации высадили травянистые растения шести разновидностей, типичные для Ростовской области. Каждый вид растений занимал площадь в шесть квадратных метров, формируя общую экспериментальную зону в 36 квадратных метров. Методология определения объема пылевых отложений, улавливаемых растениями, включала в себя отбор при помощи кисти проб пылевых частицы с поверхности листьев растений, который производился два раза в неделю с мая по октябрь 2020 года, в период активного строительства многоэтажного дома точечной застройки. Отбор проб воздуха для определения концентрации в нем пыли производился с использованием электрического аспиратора ПУ-3Е/12 и фильтров из перхлорвиниловых волокон АФА-ВП10.

**Резульмамы** исследования. Исследования показали, что в условиях преобладающего восточного ветра (3–5 м/с) и влажности в 40 % в период производства строительных работ высаженная растительность значительно влияла на качество воздуха. Над озелененной зоной наблюдалось снижение концентрации пылевых частиц РМ10 на 10 %, на расстоянии 10 метров от растительного покрова, по сравнению с прилегающей строительной зоной, — на 15 %. Замеры количества пылевого осадка в вегетационный период (май—октябрь) выявили существенную динамику: если в начале сезона (май—июнь) количество пылевых отложений на растениях составляло максимум 0,42 мг/см², то в

разгар теплого сезона (июль-октябрь) оно достигало 1,81 мг/см². Финансовые расчеты показали, что при долгосрочной эксплуатации (до 40 лет) традиционные и озелененные крыши имеют одинаковую стоимость. Для достижения поставленной цели исследования авторами были разработаны и применены на практике два типа конструктивных решений зеленой кровли для общественных и жилых зданий.

Обсуждение и заключение. Конструкции зеленой кровли могут служить эффективной преградой для распространения пыли в воздушной среде, что особенно актуально для районов, расположенных вблизи точечных застроек, где отмечается значительная концентрация взвешенных веществ в воздухе. Для снижения концентрации взвешенных веществ в жилой зоне рядом с точечной застройкой монтаж конструкций зеленой кровли необходимо осуществлять на террасах, крышах, стилобатной части зданий, где окна и входные группы расположены рядом со строительной площадкой. В целях сдерживания распространения взвешенных частиц монтаж зеленой кровли должен быть осуществлен на малоэтажных зданиях, например, детских садах, школах, торговых павильонах — в зависимости от общей концепции градостроительного плана застройки района или конкретной территории.

**Ключевые слова:** зеленые крыши, распространение пыли, экологическая безопасность городских территорий, мелкодисперсная пыль, пылевое загрязнение

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**Introduction.** Modern cities are actively integrating new environmental solutions into their infrastructure, and green roofs have already become a traditional element of urban planning [1]. Recent studies have demonstrated that these structures significantly contribute to the efficient use of urban space and significantly improve the environment [2, 3]. The effectiveness of plant coatings in neutralizing pollutants, including PM0.5-PM10 has been confirmed by numerous studies [4, 5]. Today, green roofs are not considered as an innovative concept, but rather as a crucial part of strategies to improve urban ecosystems. Experts and the public are increasingly recognizing their contribution to enhancing the quality of life for citizens and restoring natural balance in urban areas [6].

Studies have shown that residential buildings significantly worsen the quality of air in cities, releasing harmful PM0.5-PM10 particles, which negatively affect the health of residents [7]. Therefore, architects and developers should consider green roofs as a standard element of construction projects [8]. The introduction of such eco-friendly solutions into everyday practice is becoming a key factor in ensuring the environmental sustainability and safety of modern urban planning [9].

The limited availability of natural resources in cramped urban spaces requires their rational use and functional expansion, which is especially important in the case of residential development and reconstruction of outdated buildings [10]. The strategy of replenishing such dwindling resources is the introduction of environmentally friendly and economically cost-effective architectural concepts, including green roofs [11]. These solutions minimize dust pollution in residential areas, have a beneficial effect on the quality of life of urban residents, and contribute to more efficient environmental management [12].

In an urban environment where space is limited, the transformation of standard roofing structures into ecological oases seems to be a perfect solution for the restoration of natural cover. This is particularly true when there are no other land use options available. A green roof is a multi-level structure that sits on the top of buildings [13]. It includes a base and a variety of intermediate elements, from waterproofing barriers to vegetation cover. All these layers function as a single mechanism that ensures the vital activity of flora on the roof and effectively replenishes the green areas lost during the construction process. The implementation of such projects requires detailed design and analysis of weight characteristics to ensure the reliability and stability of these innovative systems.

The research focus in the area of green roof systems is primarily on their ability to clean the air of such pollutants as SO<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub> and PM10 [14, 15]. Vegetation on roofs, like other urban landscaping elements, shows significant potential in reducing atmospheric pollution and harmful emissions by up to 35–100%. This has been demonstrated through research, and these environmental benefits have led to an increasing interest in green roofs worldwide.

The aim of this research is to evaluate the effectiveness of green roofs in reducing the spread of dust in urban environments, which is particularly important for areas with active infill development. To accomplish this goal, we have solved the task of identifying vegetation types that effectively collect dust, and developed designs for green roof systems that were suitable for installation in residential areas. Such environmental solutions contribute to the overall modernization of the construction industry, making it safer for the environment and more comfortable for residents.

Technosphere Safety

Materials and Methods. The choice of an optimal location plays a key role in maximizing the benefits of green roof structures in the fight against PM2.5 and PM10 pollutants, given the difficulties with their installation. For Russian cities, there are specific parameters for determining the priority areas for the installation of these environmental structures. One of the most important factors is the location in a certain climatic zone according to the zoning scheme (Fig. 1) [16]. It is the correct location of green roofs that determines their effectiveness in reducing the concentration of harmful particles in the atmosphere.

Modern urban trends require a systematic approach to creating eco-friendly spaces in an urban environment. This task can be solved by developing affordable, cost-effective and technologically uncomplicated solutions. The criteria for implementation include location in urban centers with a population of more than 250,000 people, as well as the prerequisite that green areas make up at least 40% of the total area of the block [17].



Fig. 1. Map of the territorial delimitation of Russia for optimal use of green roofs in various climatic conditions

During the construction of the Krasny Aksai residential complex in Rostov-on-Don, herbaceous plants of six varieties typical of the Rostov region were planted in March 2020 in the construction area and outside the site (Fig. 2). From May to September, during the construction of the monolithic frame of the building and the stone-installation works, 10 air samples were taken twice a week for 120 minutes at three control points according to the standard RD 52.04.893–2020<sup>1</sup> method — at the border of the construction site at 117 b, Beregovaya St., b. 5 (point A in Fig. 2), above the vegetation zone (point B in Fig. 2) and at a distance of 10 meters from the green zone, in the residential area of the Krasny Aksai residential complex (point C in Fig. 2). During the entire observation period, atmospheric parameters fluctuated: the air warmed up from +14 to +25°C, the wind reached 3–5 meters per second, and the relative humidity was from 30 up to 60%.



Fig. 2. Construction site of an infill development: 1, 2 — planting sites; A, B, C — control points for measuring the PM10 concentration

<sup>&</sup>lt;sup>1</sup> RD 52.04.893–2020. Mass concentration of suspended solids in atmospheric air samples. Method of gravimetric measurements. Electronic Fund of Legal. and Regulatory and Technical Documents. (In Russ.) URL: <a href="https://files.stroyinf.ru/Data2/1/4293720/4293720281.pdf">https://files.stroyinf.ru/Data2/1/4293720/4293720281.pdf</a> (accessed: 10.03.2025).

Each plant species planted in the area of the site occupied an area of six square meters, forming a total experimental area of 36 square meters. All the selected plants had a high dust absorption capacity, which was a key criterion in their selection for this study (Fig. 3) [18, 19].

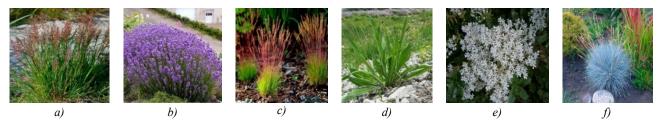


Fig. 3. Herbaceous plants characterized by high efficiency of dust deposition: a — Agrostis stolonifera; b — Lavandula angustifolia; c — Festuca rubra; d — Plantago lanceolata; e — Sedum album; f — Festuca festina

The methodology for determining the amount of dust deposited on plants involved taking 50 measurements twice a week in the morning. Dust particles were collected from the surface of plant leaves using a brush. The process took place during the period of active construction of a multi-storey residential building, that is, from May to September 2020. The collected material was carefully transferred into a pre-weighed container for further evaporation and weighing. After collecting samples from each plant species, laboratory treatment was performed: the liquid was evaporated and the sediment was dried until the mass stabilized. Using these recorded indicators, we were able to calculate the specific dust concentration — the number of milligrams of dust collected per square centimeter of plant leaf surface. The results of particle deposition on the leaves of the studied plants can be seen in Figure 4.

Air sampling to determine dust concentration in it was carried out using an electric aspirator PU-3E/12, which was tested, and filters made of PVC fibers AFA-VP10. Preliminary tests of this measuring equipment in a wind tunnel showed that the measurement error during a one-time experiment did not exceed 12%, which met the requirements of RD 52.04.893-2020.

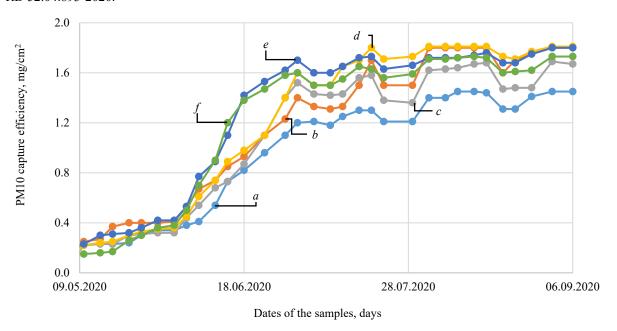


Fig. 4. Density of PM10 dust deposition on plants in the zone of infill development: a — Agrostis stolonifera; b — Lavandula angustifolia; c — Festuca rubra; d — Plantago lanceolata; e — Sedum album; f — Festuca festina

**Results.** The analysis of measurements showed that in conditions of prevailing easterly wind (3–5 m/s) and an air humidity of 30–60% during the period of work, the planted vegetation significantly affected the air quality. Above the landscaped area, there was a decrease in the concentration of PM10 dust particles from construction work from an average of 10 (humidity — 30–35%) to 20% (humidity — 35–60%), and at a distance of 10 meters from the vegetation cover, compared with the adjacent construction area, from an average of 15 (humidity — 30–35%) up to 30% (humidity — 35–60%).

Technosphere Safety

Measurements of the amount of dust deposition during the growing season (May–September) revealed the following dynamics: if at the beginning of the season (May–June) the amount of dust deposition on plants was a maximum of 0.42 mg/cm², then at the height of the warm season (July–September) it reached 1.81 mg/cm². The dynamics of changes in the amount of dust deposition on plants was explained by the fact that during the measurement period, plants grew at the beginning of the growing season, then the area of vegetation increased, but at the same time, the dust deposition formed on the leaves could be blown into the air by the wind at a speed of 3.5 m/s and higher. In the period from July to September, the vegetation surface area was already at its maximum. The process of active dust deposition was also influenced by the fact that dew formed on plants in the first half of the day, and the volume of green mass of plants, which allowed dust deposits to accumulate on the leaves, prevented external sources of exposure (wind, precipitation) from sweeping the dust deposits onto the ground or into the air. Figure 5 shows the dynamics of changes in the PM10 concentration during the study period at three control points for measurements (construction site, vegetation area, residential area).

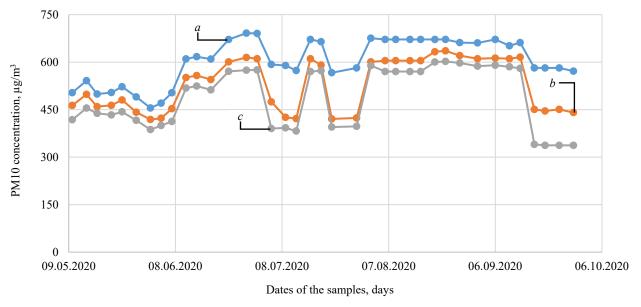
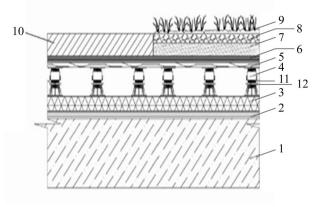


Fig. 5. Dynamics of changes in the PM10 concentration during the construction period: a — point A, construction site; b — point B, vegetation area; c — point B, residential area

To achieve the aim of this research, the authors have developed innovative, resource-efficient and practical green roof designs that can be incorporated into the planning stage of residential developments. These designs can easily serve as a tool for reducing the negative impact of dust emissions during construction, whether it is the construction of new buildings or the renovation of the existing structures for various purposes.

The first mobile green roof structure was developed with the possibility of its dismantling for the winter period. Patent No. 191863U1 was registered for this type of roof [20]. The structural elements of such a roof were a combination of reinforced concrete slab, durable anti-rot roofing felt, adjustable Forest Style supports made of high-strength propylene (with the possibility of building up due to an additional nozzle of 60 mm), as well as Ondulin double-layer asphalt concrete coating. Figure 6 provides the structural scheme of the green roof and the implementation of this structure at the facility after reconstruction in Rostov-on-Don.



Green roof design for installation on public buildings

- 1 Reinforced concrete floor slab;
- 2 Covering layer of roofing felt;
- 3 Thermal insulation layer;
- 4 Adjustable supports;
- 5 Ondulin lining layer;
- 6 Waterproofing layer;
- 7 Drainage layer;
- 8 Ground;
- 9 Green spaces;
- 10 Decking;
- 11 Galvanized studs;
- 12 Locking nut

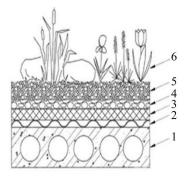




Fig. 6. Design solutions of green roof for public buildings: *a* — design scheme; *b* — object for the green roof structure implementation — business center "League of Nations" (91, Suvorova St., Rostov-on-Don; *c* — implemented green roof design solutions

The second type of structure is intended for residential buildings, winter gardens and terraces. This system is characterized by simple dwsign, cost-effectiveness, high thermal insulation, and moisture protection. Patent No. 163334U1 [21] was registered for the utility model. The vegetation layer is planted in the final stage of the project. It is placed along the perimeter of the green areas of the structure. The installation of this type of roof involves the use of two types of coatings: one for the side section, which allows for year-round use of the green roof, and the other for the central area, where a swimming pool or café can be located, for example.

Figure 7 shows the developed design of the second type of green roof, which consists of a reinforced concrete floor slab, filter and vegetation layers. Ondulin is used as a protective element. The structure is additionally equipped with a layer of anchors in the ground. The implementation of this design solution at an urban development facility is also presented.



### Green roof design for residential buildings

- 1 Reinforced concrete slab;
- 2 Ondulin protective layer;
- 3 Thermal insulation layer made of expanded polystyrene;
- 4 Filter layer made of peat and/or gravel;
- 5 Fixing soil mixture;
- 6 Plant layer containing a substrate with plants





Fig. 7. Green roof design solutions for residential buildings: *a* — design scheme; *b* — object for the implementation of a green roof structure in design solutions (Zhemchuzhina Dona residential complex; 240, Maxim Gorky Str., Rostov-on-Don); *c* — implemented green roof design solutions

The cost of these green roof structures starts from 4,200 rubles per square meter. Financial calculations show that with long-term operation (up to 40 years), traditional and green roofs have approximately the same cost. At the same time, investments in the installation of green roof systems for the League of Nations business center amounted to only 1.3% of the total reconstruction budget. In the case of the Zhemchuzhina Dona multi-apartment high-rise residential complex, the share of costs for the development of design solutions, installation and landscaping of the roof amounted to 4% of the total construction costs of the facility.

**Discussion and Conclusion.** The research conducted by the authors proves that the creation of vegetation cover is a fairly effective barrier to the spread of dust pollution from infill construction. The efficiency of dust collection can reach an average of 10 to 20%, depending on the air humidity level. At the same time, it is important to choose the right plants for the green roof and arrange it well in order to maximize the effect of dust suppression, which will significantly increase the environmental safety of residential areas in residential buildings. The two types of constructive green roof solutions developed by the authors, which are applicable for the reconstruction of buildings and the construction of new facilities, make it possible to create a comprehensive protection of the urban area from one of the most harmful sources of dust emissions in the urban environment — the construction site. Although the introduction of such technologies requires additional financial investments, they are offset by a decrease in the incidence of workers from harmful effects of dust by about 15%. This leads to a corresponding reduction in the cost of construction work and labor savings, while providing a higher level of protection for both workers on the construction site and residents of nearby areas.

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#### About the Authors:

Svetlana E. Manzhilevskaya, Cand. Sci. (Eng.), Associate Professor of the Department of Construction Organization, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344001, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:ORCID">ORCID</a>, <a href="mailto:ScopusID">ScopusID</a>, <a href="mailto:smanzhilevskaya@yandex.ru">smanzhilevskaya@yandex.ru</a>

Aleksandr I. Evtushenko, Dr. Sci. (Eng.), Dean of the Faculty of Industrial and Civil Engineering, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344001, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:ORCID">ORCID</a>, <a href="mailto:ScopusID">ScopusID</a>, <a href="mailto:a.evtushenko@mail.ru">a.evtushenko@mail.ru</a>

**Dmitrii R. Mailyan,** Dr. Sci. (Eng.), Head of the Department of Reinforced Concrete and Stone Structures, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344001, Russian Federation), <a href="mailyan868@mail.ru">SPIN-code</a>, <a href="mailyan868@mail.ru">ORCID</a>, <a href="mailyan868@mail.ru">ScopusID</a>, <a href="mailyan868@mail.ru">dmailyan868@mail.ru</a>

### Claimed Contributorship:

**SE Manzhilevskaya:** formulation of the main concept, goals and objectives of the research, carrying out calculations, preparing the text, drawing the conclusions.

AI Evtushenko: carrying out calculations, design of a scientific article.

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### Об авторах:

**Светлана Евгеньевна Манжилевская,** кандидат технических наук, доцент кафедры организации строительства Донского государственного технического университета (344001, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), <u>SPIN-код</u>, <u>ORCID</u>, <u>ScopusID</u>, <u>smanzhilevskaya@yandex.ru</u>

**Александр Иванович Евтушенко,** доктор технических наук, декан факультета промышленного и гражданского строительства Донского государственного технического университета (344001, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), <u>SPIN-код</u>, <u>ORCID</u>, <u>ScopusID</u>, <u>a.evtushenko@mail.ru</u>

Дмитрий Рафаэлович Маилян, доктор технических наук, заведующий кафедрой железобетонных и каменных конструкций Донского государственного технического университета (344001, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), SPIN-код, ORCID, ScopusID, dmailyan868@mail.ru

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## MACHINE BUILDING MAШИНОСТРОЕНИЕ





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### Probability Grid Method for Fisher-Tippett Law

Anatoly A. Kotesov

Don State Technical University, Rostov-on-Don, Russian Federation

⊠ a.kotesov@yandex.ru



### **Abstract**

Introduction. Estimation of the parameters of probability distribution laws using probability grids is widely used in practice, particularly in modern software systems. This approach is actively employed for statistical analysis, where the calculation results are presented as a probability graph. This allows for the assessment of the correspondence between a given data set and a proposed probability model, as well as the identification of outliers. In the context of probabilistic assessment of the loading of machine elements and structures, some authors suggest applying the Fisher–Tippett law. This law is characterized by a distribution function with three parameters and is oriented to the maximum. This provides flexibility in the description of statistical data and enables the estimation of the maximum value in the context of loading. Nevertheless, the existing literature has not sufficiently substantiated the graphical representation of calculation results and the method of parameter estimation, including the use of the probability grid method, which limits the practical application of the Fisher–Tippett law. Therefore, the aim of this study is to justify and develop a methodology for estimating parameters of the Fisher–Tippett law using the probability grid method.

Materials and Methods. The principles and theoretical foundations of constructing probability grids, the preliminary grouping of data, and a ranking method for estimating the empirical distribution were considered as the materials for the study. Analytical dependencies for constructing a probability grid and estimating the parameters of the Fisher–Tippett law were justified. The method of mathematical modeling and comparative analysis were employed. The Matlab 8.6 software package was utilized for modeling. The data were summarized in a tabular format and visualized in the form of graphs.

**Results.** The method of constructing a probabilistic graph and the method of graphical estimation of the parameters of the Fisher–Tippett law were justified and demonstrated by example. A graph of the empirical distribution function and a probability plot with a description of the locations were presented. A method for constructing a special scale for estimating the shape parameter centered on the origin was proposed. A comparative analysis of parameter estimates obtained using graphical and analytical methods was performed. Estimates of the scale, shape, and shift parameters were compared. The relative error in estimates using the probability grid method was not more than 2%. The indicator for the scale parameter was 1.83%; for the shape parameter was it 0.67%, and for the shift parameter it was 0.45%. Corresponding results of the analytical assessment were 4.4%, 9.33% and 2.13%. In this case, the error was higher, but it did not mean that the analytical method was less accurate.

**Discussion and Conclusion.** The adequacy of the proposed method of graphical estimation of the parameters of the Fisher–Tippett law by the probabilistic grid method has been demonstrated. This method can be applied, for example, within software packages or user applications. A special scale for graphically estimating the shape parameter can also be used to estimate the shape parameter of the Weibull law. The obtained analytical dependencies, the provisions of the methodology and the graphical materials can be used in the development of the corresponding national standard.

**Keywords:** probability grid, probability graph, distribution parameter estimation, reliability analysis, Weibull law, Fisher-Tippett law

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Оригинальное теоретическое исследование

### Метод вероятностной сетки для закона Фишера – Типпета

А.А. Котесов

#### Аннотация

Введение. Оценка параметров вероятностных законов распределения с использованием вероятностных сеток находит широкое применение на практике, особенно в современных программных комплексах. Такой подход активно используется для статистического анализа, где результаты вычислений представляются в виде вероятностного графика, что даёт возможность оценить соответствие набора данных предполагаемой вероятностной модели и выявить выбросы. В контексте вероятностной оценки нагруженности элементов машин и конструкций некоторые авторы предлагают применять закон Фишера – Типпета. Этот закон характеризуется функцией распределения, которая содержит три параметра и ориентирована на максимум, что обеспечивает гибкость в описании статистических данных и позволяет получать оценку максимального значения в контексте нагруженности. Тем не менее, в существующей литературе недостаточно обоснованы графическое представление результатов вычислений и методика оценки параметров, в том числе и с использованием метода вероятностной сетки, что ограничивает практическое применение закона Фишера – Типпета. Таким образом, основная цель данного исследования заключается в обосновании и разработке методики оценки параметров закона Фишера – Типпета с использованием метода вероятностной сетки.

*Материалы и методы.* В качестве материалов рассматривались принципы и теоретические основы построения вероятностных сеток, предварительная группировка данных и ранговый метод оценки эмпирической функции распределения. Обосновывались аналитические зависимости для построения вероятностной сетки и оценки параметров закона Фишера — Типпета. Использовались метод математического моделирования и сравнительный анализ. Для моделирования задействовали программный комплекс «Матлаб 8.6». Данные обобщали в табличном формате и визуализировали в виде графиков.

**Результаты исследования.** Обоснована и показана на примере методика построения вероятностного графика и методика графической оценки параметров закона Фишера – Типпета. Представлены график эмпирической функции распределения и вероятностный график с описанием позиций. Предложена методика построения специальной шкалы для оценки параметра формы, ориентированной на точку отсчета в начале координат. Выполнен сравнительный анализ оценок параметров, полученных графическим и аналитическим методами. Сопоставлялись оценки параметров масштаба, формы и сдвига. Относительная погрешность оценок методом вероятностной сетки не превышает 2 %. Показатель для параметра масштаба — 1,83 %; формы — 0,67 %, сдвига — 0,45 %. Соответствующие итоги аналитической оценки: 4,4, 9,3 %3 % и 2,13 %. В данном случае погрешность выше, однако это не значит, что аналитический метод менее точен.

Обсуждение и заключение. Показана адекватность предложенной методики графической оценки параметров закона Фишера – Типпета методом вероятностной сетки. Ее можно применять, например, в программных комплексах или пользовательских приложениях. Специальная шкала для графической оценки параметра формы также подходит для оценки параметра формы закона Вейбулла. Полученные аналитические зависимости, положения методики и графический материал можно использовать при разработке соответствующего национального стандарта.

**Ключевые слова:** вероятностная сетка, вероятностный график, оценка параметров распределения, анализ надежности, закон Вейбулла, закон Фишера – Типпета

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**Introduction.** Graphical representation of statistical analysis results in the form of probability graphs is widely used in modern software systems, particularly in the analysis of reliability or survival. This allows for the estimation of distribution law parameters and the identification of outliers<sup>1</sup>. Estimation of parameters using probability grids is used alongside other well-known methods and in some cases may be preferable. Probabilistic graphs are employed in the processing of resource test results<sup>2</sup> and the creation of control maps in quality management systems<sup>3</sup>. The probability grid method enables a visual assessment of the correspondence between a data set and an assumed model for a random variable, as described in the works of M.A. Deryabin [1], S.A. Dobrotin [2], V.L. Shper [3], Ya.I. Bulanov [4], K.S. Ablazova [5], N.P. Velikanova [6], G.Sh. Khazanovich [7] and other modern scientists.

V.E. Kasyanov [8] and A.A. Kotesov [9] propose using one of the forms of generalized distribution of extreme values [10] with a certain type of parameterization, which they propose to call the Fisher–Tippett law, for probabilistic assessment of machine element and structure loading, but differs in that it focuses on maximum values. The Fisher–Tippett law is suitable for estimating reliability indicators in combination with the Weibull law, for example, when applying the load–strength failure model [11].

The graphical representation of the calculation results and the method used to estimate the parameters for the Fisher–Tippett law are not well justified. The scientific literature and regulatory and technical documents do not provide a specific method for estimating these parameters using a probability grid, which limits the practical application of this law. Therefore, the aim of this study is to develop and substantiate a methodology for estimating Fisher–Tippett law using the probability grid method.

Materials and Methods. Estimation of distribution parameters using probability graphs is based on grouping data by intervals and constructing an interval empirical distribution regardless of the assumed theoretical distribution. Therefore, such methods are often called nonparametric or rank-based. A probability grid is constructed for a specific probability distribution law in order to get a linear relationship between variables<sup>4</sup>. Plotting involves linear approximation of an array of empirical points on a probability grid. Therefore, this approach may be considered crude, but it is often used along with others. The probability grid method can be decisive in the case when other methods are untenable. For example, when estimating parameters using the maximum likelihood method, the likelihood function may contain several local maximas. In this case, parameter estimates can be very inaccurate [12].

To justify the probability grid, we need to reduce the probability distribution function to a linear form. The Fisher–Tippett distribution function is defined by the following expression:

$$F(x) = \begin{cases} 1 - e^{-\left(\frac{c - x}{a}\right)^b}, & x \le c, \\ 0, & x > c, \end{cases}$$
 (1)

where x — value of a random variable; a, b, c — scale, shape, and shift parameters of the distribution, respectively.

We transform distribution function (1) by taking the logarithm of both the left and right sides. Provided that c > x, we get:

$$-ln(1-F(x)) = \left(\frac{c-x}{a}\right)^b,$$

$$ln(-ln(1-F(x))) = b ln(c-x) - b ln(a).$$
(2)

Obviously, expression (2) is a linear function of the form:

$$y = qx + m, (3)$$

where x — function variable; q and m — constants.

Comparing (2) and (3), we get:

$$\underbrace{ln(-ln(1-F(x)))}_{v} = \underbrace{b\,ln(c-x)-b\,ln(a)}_{qx+m}.$$

Expression (2) differs from a similar sound to the Weibull distribution with three parameters in that only the right side is different:

$$\overbrace{b \ln(x-c) - b \ln(a)}^{\text{Weibull law}} \quad \overbrace{b \ln(c-x) - b \ln(a)}^{\text{Fisher}}.$$

<sup>&</sup>lt;sup>1</sup> GOST R ISO 16269–4–2017. Statistical methods. Statistical data presentation. Part 4. Detection and treatment of outliers. Electronic Fund of Legal and Regulatory and Technical Documents (In Russ.) URL: <a href="https://docs.cntd.ru/document/1200146680">https://docs.cntd.ru/document/1200146680</a> (accessed: 15.01.2025).

<sup>&</sup>lt;sup>2</sup> GOST R 50779.27–2017. Statistical methods. Weibull distribution. Data analysis. Electronic Fund of Legal and Regulatory and Technical Documents. (In Russ.) URL: <a href="https://docs.cntd.ru/document/1200146523">https://docs.cntd.ru/document/1200146523</a> (accessed: 15.01.2025).

<sup>&</sup>lt;sup>3</sup> GOST ISO 7870–1–2022. Statistical methods. Control charts. Part 1. General guidelines. Electronic Fund of Legal and Regulatory and Technical Documents. (In Russ.) URL: <a href="https://docs.cntd.ru/document/1200192703">https://docs.cntd.ru/document/1200192703</a> (accessed: 15.01.2025).

<sup>&</sup>lt;sup>4</sup> GOST 11.008–75. Applied statisticas. Graphic methods of data processing. Use of probability papers. (In Russ.) URL: <a href="https://meganorm.ru/Data2/1/4294753/4294753131.pdf">https://meganorm.ru/Data2/1/4294753/4294753131.pdf</a> (accessed: 15.01.2025).

Therefore, to construct a probability graph of the Fisher–Tippett law, it is advisable to use the basic provisions of GOST 11.008 and GOST 50779.27. According to these standards, statistical data are plotted on a probability grid during graphical analysis, and then the distribution parameters are estimated. Let us note that the probability grid method is implemented both graphoanalytically and completely analytically. Therefore, to eliminate possible ambiguity, we will call the estimation of parameters using the probability grid method graphical, and the estimation by the maximum likelihood method analytical.

The left side of expression (2) allows us to determine the ordinate of the probability scale for estimating the scale parameter. Let us assume that c - x = a. By substituting this value in (2), we get:

$$ln(-ln(1-F(x))) = b \ln(a) - b \ln(a),$$

$$ln(-ln(1-F(x))) = 0,$$

$$e^{\ln(-ln(1-F(x)))} = e^{0},$$

$$-ln(1-F(x)) = 1,$$

$$e^{-ln(1-F(x))} = e^{1},$$

$$\frac{1}{1-F(x)} = e,$$

$$F(x) \approx 0.6321.$$
(4)

Result (4) allows us to conclude that the abscissa of the point approximating the line with zero ordinate will be an estimate of the scale parameter.

The decimal logarithm can be used along the abscissa axis of the probability graph. In this case, dependency (2) will take the form:

$$ln(-ln(1-F(x))) = \frac{1}{lg(e)}(blg(c-x)-blg(a)).$$

An important aspect of implementing the probability grid method is the initial processing of statistical data, specifically, obtaining an interval series of variations and estimating the empirical distribution function values. To obtain an empirical distribution function, a ranking method is typically used, which involves estimating the position of a distribution based on ordered data, considering the characteristics of the variation series (mean, median, mode, etc.). Therefore, various dependencies are used to determine the ordinates of points, including expressions for approximate estimation [13]. In this case, the choice will be determined by the amount of empirical data, the expected theoretical distribution, and the type of probability graph. This takes into account the need for an adequate description of the extreme members of the variation series [14].

It should be noted that some previous approaches to estimating the empirical distribution function have been criticized, and this may be the subject of a separate discussion [15].

**Results.** The inverse function method is used to model a set of random data without a specific physical meaning, distributed according to the Fisher–Tippett law.

The inverse distribution function is obtained analytically from expression (1):

$$F(x) = 1 - e^{-\left(\frac{c - x}{a}\right)^{b}},$$

$$-ln(1 - F(x)) = \left(\frac{c - x}{a}\right)^{b},$$

$$\frac{c - x}{a} = \left(-ln(1 - F(x))\right)^{\frac{1}{b}},$$

$$x = c - a\left(-ln(1 - F(x))\right)^{\frac{1}{b}},$$

$$F^{-1}(x) = c - a\sqrt[b]{-ln(1 - F(x))}.$$
(5)

https://bps-journal.ru

a' 104.40

The simulation was conducted using the Matlab 8.6 software package, (Fig. 1), according to the specified parameters a, b, and c. The initial data used for the modeling are presented in Table 1.

Initial data for modeling

	111	itiai data ioi modeniig	
Paramete	ers of the Fisher-Tip	ppett law	Number of values
	b	c	n
	3.00	250.00	100

```
fisher_tippet.m* × +
        '@Исходные
 2 -
       а = 100; '/параметр масштаба';
 3 -
       b = 3;
                '/параметр формы';
 4 -
        с = 250; '/параметр сдвига';
        '@Генерация массива случайных числел в интервале [0;1] с помощью команды rand():';
        gamma = rand(100,1);
         «Вычисление значений обратной фукнкции закона фишера-Типпета и получение случайной выборки в виде массива data:';
        data = c-a*((-log(1-gamma)).^(1/b));
10
11 -
        ' «Оценка параметров распределения по ранее полученной случайной выборке методом максимального правдоподобия:';
12 -
        '@Функция плотности распределения закона:';
13 -
        custompdf = @(x,a,b,c) (c>x).*(b/a).*(((c-x)/a).^(b-1)).*exp(-((c-x)/a).^b);
14 -
        '@Точность и количество итераций: ';
15 -
        opt = statset('MaxIter',le5,'MaxFunEvals',le5,'FunValCheck','off');
16 -
        '@Оценка параметров распределения с помощью команды mle()';
       params = mle(data,'pdf',custompdf,'start',[100 3 250],'Options',opt,'UpperBound',[0 0 -Inf],'UpperBound',[max(data) Inf Inf]);
```

Fig. 1. Modeling a set of random data in Matlab 8.6

The simulation results in the form of a set of random data  $x_i$  are presented in Table 2.

a 100.00

A set of random data with no definite physical meaning

Table 3

Table 1

No.					х	i				
1	201.98	222.87	182.26	183.98	133.30	114.41	204.15	157.16	169.63	217.17
2	124.97	100.63	138.10	112.03	185.71	160.66	169.88	123.02	192.45	179.76
3	143.79	97.90	118.26	208.58	152.80	95.93	179.54	214.92	155.05	132.63
4	140.21	199.05	140.76	179.14	200.77	189.65	178.47	117.03	152.32	174.79
5	148.32	164.27	169.47	153.61	160.16	200.97	201.86	198.03	187.74	205.69
6	160.11	147.75	109.29	188.97	127.93	179.33	153.42	128.49	159.80	160.55
7	176.62	180.02	183.43	149.66	113.64	170.37	180.74	132.75	84.58	172.97
8	147.27	138.01	158.67	133.01	161.65	168.27	194.75	114.29	162.36	139.61
9	199.99	156.53	104.26	161.36	181.23	178.00	241.30	197.14	144.12	159.39
10	195.72	167.66	182.20	148.29	148.13	144.22	180.65	161.10	169.07	132.26

An analytical assessment of the scale, shape, and shift parameters has been conducted. The estimates are indicated respectively — a', b', c' (Table 3).

Results of the analytical evaluation of the parameters

Estimates	of the parameters of the Fisher-T	Tippett law
	b'	c'
	3.28	255.32

The Fisher-Tippett law, unlike the Weibull law, has a restriction on the right and sets the maximum value for a random variable. Therefore, to obtain a series of variations, it is necessary to order the values in the dataset (sample) from maximum to minimum.

If the sample size is  $n \le 30$ , then it is not advisable to group the data by intervals. In such cases, each variant should be assigned a rank of j, and an approximation for the median position of these ranks can be used to estimate the values of the empirical distribution function [16]:

$$F(x_i) = \frac{j - 0.3}{n + 0.4} (j = 1, 2...n),$$
(6)

where  $x_i$  — value of the sample variants ordered from maximum to minimum, corresponding to the *j*-th rank; *j* — ordinal number of the rank; *n* — sample size.

Otherwise, for n > 30 it is necessary to group the data by intervals in accordance with the absolute sample size. At the same time, it is recommended to take the number of interval k in the range of  $7 \le k \le 40$  depending on sample size n. To group the data, it is necessary to determine the boundaries of the interval by selecting the values  $X' \le x_{\min}$  and  $X'' \ge x_{\max}$ , and divide the resulting interval [X'; X''] into the intervals of equal length h:

$$h = \frac{X'' - X'}{k} \,. \tag{7}$$

Then, an interval variation series should be obtained by determining the number of sample values  $n_i$ , that fall within each interval. Each interval is described by abscissa  $X_i$ , which defines the position of the ordered data distribution. For the middle position, the empirical distribution function is estimated using the expression:

$$F(X_i) = \sum_{i=1}^k \frac{n_i}{n+1} (i = 1, 2...k),$$
(8)

where  $X_i$  — middle of the i-th interval;  $n_i$  — number of sample members that fell into the i-th interval; k — number of intervals; n — sample size.

As an example, the values of the empirical distribution function were grouped and calculated (Fig. 2) for the data set from Table 3.

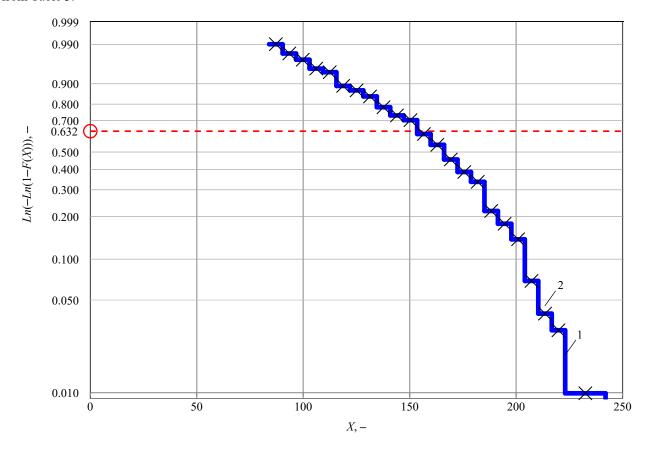


Fig. 2. Empirical distribution function: 1 — function; 2 — middle of the interval

Figure 2 shows the probability value along the ordinate axis; and the values of the dataset (sample) without a specific physical meaning are shown along the abscissa axis.

For data grouping, we assume k = 25, X' = 84, X'' = 242 and determined value h = 6.32. One sample value falls into the first three intervals, so they are combined. The total number of intervals — k = 23. Table 4 provides the calculation results.

Calculation results

i	Rank i	nterval	$n_{\mathrm{i}}$	$X_i$	$F(X_i)$	$F(X_i)$ + $F(X_{i+1})$	$Lg(X_i)$	$Ln(-Ln(1-(F(X_i)+F(X_{i+1}))))$	$C-X_i$	$Lg(C' eg X_j)$
ı	beginning	end	$n_1$	$A_l$	$\Gamma(\Lambda_l)$	$F(X_i)$ +,	T81	Ln(-Ln(1-(F(	<i>C.</i> -	Lg(C)
1	2	3	4	5	6	7	8	9	10	11
1*	223.04*	242.00*	1	232.52	0.0099	0.0099	2.3665	-4.6101	22.68	1.3555
2	216.72	223.04	2	219.88	0.0198	0.0297	2.3422	-3.5015	29.00	1.4623
3	210.40	216.72	1	213.56	0.0099	0.0396	2.3295	-3.2087	35.32	1.5480
4	204.08	210.40	3	207.24	0.0297	0.0693	2.3165	-2.6335	41.64	1.6195
5	197.76	204.08	7	200.92	0.0693	0.1386	2.3030	-1.9024	47.96	1.6808
6	191.44	197.76	4	194.60	0.0396	0.1782	2.2891	-1.6282	54.28	1.7346
7	185.12	191.44	4	188.28	0.0396	0.2178	2.2748	-1.4038	60.60	1.7824
8	178.80	185.12	12	181.96	0.1188	0.3366	2.2600	-0.8906	66.92	1.8255
9	172.48	178.80	5	175.64	0.0495	0.3861	2.2446	-0.7175	73.24	1.8647
10	166.16	172.48	7	169.32	0.0693	0.4554	2.2287	-0.4979	79.56	1.9007
11	159.84	166.16	9	163.00	0.0891	0.5446	2.2122	-0.2402	85.88	1.9339
12	153.52	159.84	7	156.68	0.0693	0.6139	2.1950	-0.0497	92.20	1.9647
13	147.20	153.52	9	150.36	0.0891	0.7030	2.1771	0.1939	98.52	1.9935
14	140.88	147.20	3	144.04	0.0297	0.7327	2.1585	0.2771	104.84	2.0205
15	134.56	140.88	5	137.72	0.0495	0.7822	2.1390	0.4214	111.16	2.0459
16	128.24	134.56	6	131.40	0.0594	0.8416	2.1186	0.6111	117.48	2.0699
17	121.92	128.24	3	125.08	0.0297	0.8713	2.0972	0.7179	123.80	2.0927
18	115.60	121.92	2	118.76	0.0198	0.8911	2.0747	0.7963	130.12	2.1143
19	109.28	115.60	5	112.44	0.0495	0.9406	2.0509	1.0379	136.44	2.1349
20	102.96	109.28	1	106.12	0.0099	0.9505	2.0258	1.1005	142.76	2.1546
21	96.64	102.96	2	99.80	0.0198	0.9703	1.9991	1.2575	149.08	2.1734
22	90.32	96.64	1	93.48	0.0099	0.9802	1.9707	-4.6101	155.40	2.1914
23	84.00	90.32	1	87.16	0.0099	0.9901	1.9403	-3.5015	161.72	2.2088

where \* — Correction when combining intervals 1-3 into one interval [223,04; 242,00]

On the x-axis of the probability graph, we use a scale with decimal logarithms. The calculation results from columns 8 and 9 of Table 4 determine the coordinates of the points for plotting  $\{Lg(X_i); Ln(-Ln(1-(F(X_i)+F(X_{i+1}))))\}$ .

At the next stage, the shift parameter is evaluated. To do this, a smooth curve (rather than a straight line) (Fig. 3, pos. 2) should be drawn through the array of points (Fig. 3, pos. 1).

At the point where the straight line intersects the zero ordinate (Fig. 3, pos. 7), graphical estimation of scale parameter A' is made.

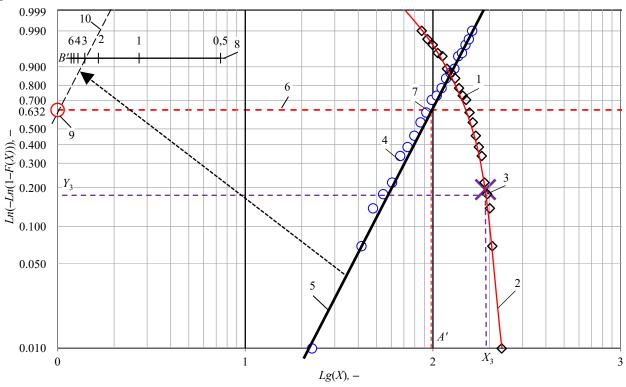


Fig. 3. Graphical estimation of the Fisher–Tippett law parameters: 1 — points with coordinates  $\{Lg(X_i); Ln(-Ln(1-(F(X_i)+F(X_{i+1}))))\}$ ; 2 — line for estimating abscissa  $X_3$  along ordinate  $Y_3$ ; 3 — point with coordinates  $\{Y_3; X_3\}$ ; 4 — points with coordinates  $\{Lg(C'-X_i); Ln(-Ln(1-(F(X_i)+F(X_{i+1}))))\}$ ; 5 — straight line approximating points 4; 6 — line for estimating the scale parameter; 7 — intersection point of lines 5 and 6, advising the estimation of scale parameter A'; 8 — scale for estimating shape parameter B'; 9 — point with coordinates  $\{0; 0\}$ ; 10 — straight line drawn through point 9 parallel to straight line 5, to evaluate shape parameter B' on scale 8

Figure 3 shows the probability value along the ordinate axis, and the abscissa axis shows the values of a data set (sample) without a specific physical meaning.

The coordinates of the points of the extreme members of the variation series are denoted by  $\{X_1; Y_1\}$  and  $\{X_2; Y_2\}$ , and  $Y_3$  coordinate is estimated:

$$Y_3 = \frac{Y_1 + Y_2}{2} \,. \tag{9}$$

Using ordinate  $Y_3$  on the previously indicated curve, abscissa  $X_3$  can be determined (Fig. 3, pos. 3). Then shift parameter C' is estimated:

$$C' = \frac{X_1 \cdot X_2 - X_3^2}{X_1 + X_2 - 2X_3} \,. \tag{10}$$

In the example presented, the extreme terms of the variation series are the midpoints of intervals i = 1 and i = 23 with coordinates  $\{Lg(X_l); Ln(-Ln(1-(F(X_l)))\}$  and  $\{Lg(X_{23}); Ln(-Ln(1-(F(X_{22})+F(X_{23})))\}$ . Accordingly,  $Y_1 = Ln(-Ln(1-(F(X_l))), Y_2 = Ln(-Ln(1-(F(X_{22})+F(X_{23}))), X_1 = Lg(X_1); X_2 = Lg(X_{23})$ . As a result, a graphical estimate of shift parameter C' = 248.88. We use it to adjust the abscissa of all points, determining values  $(C'-X_l)$ , and plot the points with the corresponding coordinates on the graph (Fig. 3, pos. 4). As you can see, after the correction, the points lined up "more evenly", which allows us to draw a straight line through them (Fig. 3, pos. 5).

The estimate of the shape parameter corresponds to the angle of inclination of the approximating straight line (Fig. 3, pos. 5) to the abscissa axis. To graphically evaluate the parameter, you can use the coordinates of the points or a special scale (if available). When estimating the shape parameter by coordinates, it is necessary to express the values along the abscissa axis on the scale of the natural logarithm, i.e. use the value Ln(X) instead of Lg(X).

The considered example shows a scale for graphical evaluation of shape parameter B' (Fig. 3, pos. 8). To construct the scale, the coordinates of points  $\{Lg(X); Ln(Y)\}$  were calculated based on the set values of the shape parameter (Table 5). The scale is oriented to the reference point with coordinates  $\{0; 0\}$  (Fig. 3, pos. 9). To estimate the shape parameter, it is necessary to draw a straight line parallel to the approximating line through the reference point (Fig. 3, pos. 10).

Table 6

Building a scale for graphical evaluation of the shape parameter

B'	0.5000	1.0000	2.0000	3.0000	4.0000	5.0000	6.0000
Ln(Y)	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Ln(X)	2.0000	1.0000	0.5000	0.3333	0.2500	0.2000	0.1667
Lg(X)	0.8686	0.4343	0.2171	0.1448	0.1086	0.0869	0.0724

As a result of data processing, graphical estimates of the parameters of the Fisher–Tippett law were obtained (Table 6).

Results of graphical parameter estimation

Estimates of the parameters of the Fisher–Tippett law A' B' C' 98.17 2.98 248.87

After evaluating the parameters, we need to perform a check using inverse function (5) with the specified probability values:

$$F^{-1}(x) = C' - A' \left( -\ln(1 - F(x)) \right)^{\frac{1}{B'}}.$$
 (11)

By calculating the values of inverse distribution function (11) and connecting the resulting points on the graph, you can visually assess the quality of the model. As you can see, the graph of the inverse function (Fig. 4) smoothly describes the array of initial points (Fig. 4, pos. 1 and 2). This suggests that the model is able to accurately describe the data, and the parameter estimation has been performed correctly.

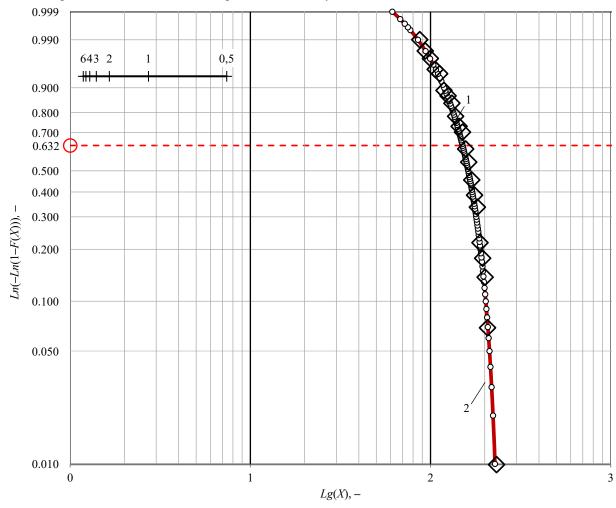


Fig. 4. Checking the model after graphical evaluation of the parameters 1 — starting points with coordinates  $\{Lg(X_i); Ln(-Ln(1-(F(X_i)+F(X_{i+1}))))\};$ 

<sup>2 —</sup> graph of inverse distribution function  $F^{-1}(x)$  with parameters A', B', C'

Figure 4 shows the probability value along the ordinate axis, and the abscissa axis shows the values of the data set (sample) without a specific physical meaning.

The results of the verification calculations are presented in Table 7.

The results of the model's testing

Table 7

F(x)	$F^{-1}(x)$	$Lg(F^{-1}(x))$	Ln(-Ln(1-(F(x))
0.0010	239.1548	2.3787	-6.9073
0.0050	232.2033	2.3576	-5.2958
0.0100	227.8309	2.3068	-4.6001
0.0500	212.5564	2.2775	-2.9702
0.1000	202.6589	2.2537	-2.2504
0.2000	189.4586	2.2317	-1.4999
0.3000	179.3564	2.2096	-1.0309
0.4000	170.4725	2.1862	-0.6717
0.5000	162.0373	2.1596	-0.3665
0.6000	153.5320	2.1263	-0.0874
0.7000	144.4053	2.0758	0.1856
0.8000	133.7435	2.0299	0.4759
0.9000	119.0766	1.9303	0.8340
0.9900	85.1730	1.8882	1.5272
0.9990	61.3715	1.7880	1.9326

As it can be seen, the graphical and analytical estimates of the parameters are close to the parameters set during the modeling of the dataset (a, b, c).

It is not entirely correct to compare the estimates obtained with respect to the specified parameters, however, such a comparison is justified if the specified parameters are taken as the true parameters of the general population, and the set of random data  $x_i$  is considered a representative sample. A comparative analysis of graphical and analytical estimates is presented in Table 8.

Comparison of graphical and analytical estimates of parameters

Table 8

Indicator	Scale parameter	Value	δ, %	Shape parameter	Value	δ, %	Shift parameter	Value	δ, %
Preset parameters	а	100.00	-	b	3.00	_	С	250.00	_
Analytical estimation of parameters	a'	104.40	4.40	b'	3.28	9.33	c'	255.32	2.13
Graphical estimation of parameters	A'	98.17	1.83	В'	2.98	0.67	C'	248.87	0.45

Comparative analysis has shown that the relative error of graphical estimates does not exceed 2% ( $\delta$  < 2%). The error of the analytical estimates in this example turned out to be higher, but this does not mean that the analytical method is less accurate.

**Discussion and Conclusion.** The presented probability grid method for the Fisher-Tippett law is adequate and suitable for practical application. For example, it can be used in software packages or when creating custom applications for graphical representation of statistical analysis results. It opens up the possibility to perform model fitting together with other known methods, even if they are untenable. The proposed method of constructing a scale for graphically estimating the shape parameter can be used to evaluate the shape parameter of the Weibull's law. The obtained analytical dependencies, the provisions of the methodology and the graphic material can be useful in the development of an appropriate national standard.

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#### About the Author:

Anatoly A. Kotesov, Cand.Sci. (Eng.), Associate Professor of the Department of Transport Systems and Logistics, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344003, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:ORCID">ORCID</a>, <a href="mailto:ScopusID">ScopusID</a>, <a href="mailto:ResearcherID">ResearcherID</a>, <a href="mailto:a.kotesov@yandex.ru">a.kotesov@yandex.ru</a>

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The author has read and approved the final version of manuscript.

#### Об авторе:

**Анатолий Анатольевич Котесов**, кандидат технических наук, доцент кафедры эксплуатации транспортных систем и логистики Донского государственного технического университета (344003, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), SPIN-код, ORCID, ScopusID, ResearcherID, a.kotesov@yandex.ru

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#### Methodology for Determining the Classification Group of Jib Cranes of Foreign Companies when Assessing Their Technical Condition during Current Sanctions

Dmitry N. Simonov<sup>2</sup>, Roman V. Khvan<sup>1</sup> ⋈, Elvira A. Panfilova ,



- <sup>1</sup> Don State Technical University, Rostov-on-Don, Russian Federation
- <sup>2</sup> "Mysl" Engineering and Consulting Center, Novocherkassk, Russian Federation

⊠ khvanroman@yandex.ru



*Introduction.* Currently, more than 7,000 legal entities and individual entrepreneurs in the Russian Federation operate hazardous production facilities (HPFs) and over 90,000 lifting facilities, including cranes, hoists, and elevators. Periodically, serious accidents leading to injuries and deaths are recorded at these facilities, emphasizing the importance of ensuring safety on lifting cranes. However, sanctions against imported cranes installed in ports make it difficult to ensure their safe operation, as many of these cranes exceed or approach the end of their service life. According to the regulatory legal acts of the Russian Federation, an industrial safety inspection is required for further operation of these cranes. The existing studies on the assessment of technical condition of lifting machines primarily focus on issues related to residual life. However, the analysis reveals that the features of evaluating the condition of cranes manufactured by foreign companies, in particular, their actual loads as determined by FEM<sup>1</sup>, have not been thoroughly investigated. This discrepancy between actual and specified loading leads to increased risk of accidents. The aim of this research is to develop a methodology for determining the actual classification group of jib cranes produced by foreign companies, which will allow for an objective assessment of their technical condition during the industrial safety inspections, as well as verifying the developed methodology through a specific example.

Materials and Methods. The assessment was based on statistical data collected over the past 27 years. The study was conducted through a systematization of typical damages to cranes identified during industrial safety inspections. Statistical data on the number of cranes and accidents were collected from open sources. During the observation period, there were 254,250 cranes, and the average number of accidents was 42.29, which allowed us to calculate a background probability of accidents of  $1.66 \cdot 10^{-4}$ . This allowed us to identify an excess in the permissible destruction probability, which was  $2 \times 10^{-3}$ , compared to the established regulatory level of 10<sup>-4</sup>. Based on this, we analyzed the technical condition of cranes and refined the risk assessment methodology. The direct analysis of the technical condition of cranes was based on the study of loading functions, which depended on the weight of the load and the boom outreach, considered as random variables. For this purpose, we collected and processed primary information in the form of histograms of the distribution of transported cargo masses and boom outreach of the tested cranes. We used these data to calculate the remaining fatigue life of the resource-determining component of the metal structure and the probability of structural failure. Statistical data processing techniques were used to formalize conclusions about the risk level of crane operation based on specific numerical values of accident and damage probabilities, taking into account economic and social factors.

Results. To assess the technical condition of jib cranes manufactured by foreign companies, a methodology was developed to determine the actual classification group. The methodology included calculating the load distribution coefficient (Kp) through load moments, estimating the residual resource by a characteristic number, calculating fatigue stresses for a resource-determining unit, determining the probability of structural failure, and assessing the risk of an

<sup>&</sup>lt;sup>1</sup> F.E.M. 1.001–1998. Rules for the Design of Hoisting Appliances. VBOOK.PUB. URL: <a href="https://vbook.pub/documents/fem-1001-3-edition-revised-">https://vbook.pub/documents/fem-1001-3-edition-revised-</a> 19981041-rules-for-the-design-of-hoisting-appliances-5wglvlzj78o7 (accessed: 24.02.2025).

accident. The article provides an example of the application of this technique to a specific jib crane. For a crane with design  $K_p = 0.30$  (group A6) and a standard characteristic number of 125,000, the actual characteristic number was 179,323, indicating that service life had been exhausted. Verification calculation of fatigue stresses in the reference contour showed close proximity to the ultimate strength. The value of the probability of destruction, considering the statistical data on the crane load, exceeded the permissible value.

**Discussion and Conclusion.** The analysis of the results, using a specific example, showed that exceeding the passport classification of the crane's operating mode, and as a result, exceeding the assigned resources of its structural components, led to a significant increase in the risk of accidents. Based on the examination, it was found that the actual classification group of the crane's operating mode exceeded the passport value and amounts to A6 instead of A5. The developed methodology for assessing the actual classification group of the operating mode of jib cranes from foreign manufacturers allows for a significant reduction in the likelihood of structural failure and accident rate during industrial safety inspections. At the same time, it is recommended to use the background probability of a lifting crane accident of  $1.66 \cdot 10^{-4}$  and the average value of material damage of 73.2 million rubles in calculations.

Keywords: jib cranes, industrial safety inspection, probability of destruction, classification group, service life

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Оригинальное эмпирическое исследование

#### Методика определения группы классификации стреловых кранов зарубежных фирм при оценке их технического состояния в период действующих санкций

Д.Н. Симонов<sup>2</sup>, Р.В. Хван<sup>1</sup> См., Э.А. Панфилова См., Л.А. Терновской См.

⊠ khvanroman@yandex.ru

#### Аннотация

Введение. На текущий момент в Российской Федерации более 7 000 юридических лиц и индивидуальных предпринимателей эксплуатируют опасные производственные объекты (ОПО) и свыше 90 тысяч подъемных сооружений, включая грузоподъемные краны, подъемники и лифты. Периодически на этих сооружениях регистрируются серьезные аварии, приводящие к несчастным случаям и гибели людей, что подчеркивает значимость вопроса обеспечения безопасности на грузоподъемных кранах. При этом санкции, введенные зарубежными компаниями — производителями импортных кранов, установленных в портах, усложняют их дальнейшую безопасную эксплуатацию, поскольку многие из них превышают или приближаются к предельному сроку службы. В соответствии с нормативными правовыми актами Российской Федерации, для их дальнейшей эксплуатации необходимо проведение экспертизы промышленной безопасности. Существующие исследования, посвященные оценке технического состояния грузоподъемных машин, в основном затрагивают вопросы остаточного ресурса. Однако анализ показывает, что особенности оценки состояния кранов зарубежных производителей, включая их фактические нагрузки в соответствии с FEM<sup>2</sup>, остаются недостаточно исследованы. Это приводит к несоответствию фактической и паспортной загрузки, что создает повышенные риски аварийных ситуаций. Цель данного исследования заключается в разработке методики определения фактической группы классификации (режима) стреловых кранов зарубежных компаний. Эта методика позволит произвести объективную оценку технического состояния кранов в процессе экспертизы промышленной безопасности. Также в рамках работы будет проведена проверка разработанной методики на конкретном примере. *Материалы и методы*. Оценка базировалась на статистических данных, собранных последние 27 лет. Ис-

материалы и метооы. Оценка оазировалась на статистических данных, сооранных последние 27 лет. Исследование проводилось на основе систематизации типовых повреждений кранов, выявленных в ходе экспертизы промышленной безопасности. Использовались статистические данные о количестве кранов и авариях, собранные из открытых источников. Количество кранов за период наблюдения составило 254 250 единиц, а среднее число аварий — 42,29. Это дало возможность рассчитать фоновую вероятность аварий, равную

<sup>&</sup>lt;sup>1</sup> Донской государственный технический университет, г. Ростов-на-Дону, Российская Федерация

<sup>&</sup>lt;sup>2</sup> ООО ИКЦ «Мысль» НГТУ, г. Новочеркасск, Российская Федерация

<sup>&</sup>lt;sup>2</sup> F.E.M. 1.001–1998. *Правила проектирования подъёмных устройств*. VBOOK.PUB. URL: <a href="https://vbook.pub/documents/fem-1001-3-edition-revised-1998101-rules-for-the-design-of-hoisting-appliances-5wglvlzj7807">https://vbook.pub/documents/fem-1001-3-edition-revised-1998101-rules-for-the-design-of-hoisting-appliances-5wglvlzj7807</a> (дата обращения: 24.02.2025).

 $1,66\cdot10^{-4}$ , что позволило выявить превышение допустимого значения вероятности разрушения, которое составило  $2\cdot10^{-3}$  против установленного нормативного уровня  $10^{-4}$ . Данные результаты стали основанием для проведения анализа технического состояния кранов и доработки методики оценки рисков. Непосредственно анализ технического состояния кранов основывался на исследовании функций загрузки, которые зависят от массы груза и вылета стрелы, рассматриваемых как случайные величины. Для этого был произведен сбор и обработка первичной информации в форме гистограмм распределения перемещаемых масс грузов и вылетов стрелы испытуемых кранов. Эти данные использовались для расчета остаточного ресурса по наработке на усталость ресурсоопределяющего узла металлоконструкции и вероятности разрушения конструкции. При статистической обработке данных применялись методики, позволяющие формализовать выводы об уровне риска эксплуатации кранов, основанные на конкретных численных значениях вероятности аварий и величины ущерба, учитывающие экономические и социальные аспекты.

**Результаты** исследования. Для оценки технического состояния стреловых кранов зарубежных фирм разработана методика, позволяющая определить фактическую группу классификации (режим). Методика включает расчет коэффициента распределения нагрузок ( $K_p$ ) через грузовые моменты, оценку остаточного ресурса по характеристическому числу, расчет напряжений на усталость для ресурсоопределяющего узла, определение вероятности разрушения конструкции, а также оценку уровня риска аварии. В статье представлен пример применения данной методики на конкретном стреловом кране. Для крана с расчетным  $K_p = 0.30$  (группа A6) и нормативным характеристическим числом равным 125 000, фактическое характеристическое число составляет 179 323, что указывает на исчерпание ресурса. Проверочный расчет напряжений на усталость опорного контура показал близость к пределу прочности. Значение вероятности разрушения с учетом статистических данных о загруженности крана превысило допустимое значение.

Обсуждение и заключение. Анализ результатов на конкретном примере показал, что превышение паспортной группы классификации режима работы крана и, как следствие, превышение назначенного ресурса его конструктивных элементов приводит к значительному увеличению риска аварий. В результате экспертизы установлено, что фактическая группа классификации режима работы крана превышает паспортное значение и составляет А6 вместо А5. Разработанная методика оценки фактической группы классификации режима работы стреловых кранов зарубежных производителей позволит существенно снизить вероятность разрушения конструкций и уровень аварийности в процессе экспертизы промышленной безопасности. При этом рекомендуется при расчетах использовать фоновое значение вероятности аварии грузоподъемного крана 1,66·10<sup>-4</sup> и среднее значение материального ущерба 73,2 млн рублей.

**Ключевые слова:** стреловые краны, экспертиза промышленной безопасности, вероятность разрушения, группа классификации, ресурс

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**Introduction.** Currently, there are 51,670 hazardous production facilities registered in the Russian Federation that operate more than 284,000 lifting devices, including 224,363 cranes. It's worth noting that 51.2% of these lifting devices have already reached the end of their standard service life.

In 2023, there were 30 recorded accidents at lifting facilities. The analysis of causes of accidents over the past few years has revealed that the main contributing factors are: poor production control [1], operation of faulty lifting structures, and inadequate organization of inspections, maintenance, and scheduled repairs for lifting structures [2].

The sanctions imposed by producing countries have affected foreign lifting cranes that are mainly used in sea and river ports. For many imported lifting cranes, their service life has reached a critical point or exceeded the established standard [3]. To ensure the safe operation of these devices in accordance with the regulatory legal acts of the Russian Federation, an industrial safety inspection is required. This mandatory step ensures the reliability and safety of crane operation and compliance with applicable standards and regulations. The classification groups, classes of use, and loading modes for these cranes are based on the international European standard FEM 1.001-1998<sup>3</sup> "Rules for the

<sup>&</sup>lt;sup>3</sup> F.E.M. 1.001–1998. Rules for the Design of Hoisting Appliances. VBOOK.PUB. URL: <a href="https://vbook.pub/documents/fem-1001-3-edition-revised-1998101-rules-for-the-design-of-hoisting-appliances-5wglvlzj7807">https://vbook.pub/documents/fem-1001-3-edition-revised-1998101-rules-for-the-design-of-hoisting-appliances-5wglvlzj7807</a> (accessed: 24.02.2025).

Design of Hoisting Appliances", which is equivalent to the Russian standard GOST 34-017-2016<sup>4</sup>. A comparative analysis of these regulatory documents has shown that, according to FEM<sup>5</sup>, the crane loading is indicated as Q2 in the certificate, while the actual load corresponds to Q3. This results in an excess of the classification group value and increased risk of accidents.

The main challenge of operating such cranes in the context of sanctions imposed by manufacturing countries is the termination or severe restriction of the supply of equipment, spare parts, and assemblies for these cranes, as well as disruption of contact for consulting services related to their operation. Additionally, there has been a cessation of equipment maintenance by specialists from supplier companies, as well as remote monitoring of equipment status and updates to software products that ensure the safe operation of the cranes.

Jib cranes, in accordance with the legislation of the Russian Federation No. 116 FZ<sup>6</sup>, belong to potentially dangerous objects of hazard class IV, and must comply with standard safety requirements, such as reliability, durability, maintainability, and safety [4, 5].

During the scheduled expert inspections of cranes, the presence of separate resource-determining (resource-limiting) components and elements of metal structures was established [6]. Damage (resource depletion) of such components can lead to the complete destruction of the structure. For example, there have been accidents related to: the destruction of the rail attachment unit of the boom outreach mechanism for an Albatross type portal jib crane (Fig. 1), the destruction of the outrigger attachment unit for a tower crane (Fig. 2), the destruction of the lifting mechanism for a portal jib crane (Fig. 3).





Fig. 1. Accident of an Albatross type portal jib crane due to the destruction of the rail attachment unit of the boom departure: a — general view; b — place of destruction

<sup>&</sup>lt;sup>4</sup> GOST 34 017–2016. Cranes. Classification of operating modes. Electronic Fund of Legal and Regulatory and Technical Documents. URL: <a href="https://docs.cntd.ru/document/1200144610?ysclid=mb95dc232z408543082">https://docs.cntd.ru/document/1200144610?ysclid=mb95dc232z408543082</a> (In Russ.) (accessed: 24.02.2025).

<sup>&</sup>lt;sup>6</sup> On Industrial Safety of Hazardous Production Facilities. Federal Law No. 116 FZ dated 21 July, 1997. Electronic Fund of Legal and Regulatory and Technical Documents. (In Russ.) URL: <a href="https://docs.cntd.ru/document/9046058?ysclid=mb95ftxllk548884359">https://docs.cntd.ru/document/9046058?ysclid=mb95ftxllk548884359</a> (accessed: 24.02.2025).





Fig. 2. Accident of a tower crane due to the destruction of the attachment point of the outriggers of the carriage frame: a — general view; b — place of destruction





Fig. 3. An accident of a portal jib crane due to the destruction of the lifting mechanism: a — before the accident; b — after the accident

The described accidents have a common cause, which is exceeding the crane's classification group (mode) of the specified value in the passport, which in turn leads to exceeding the service life for the crane as a whole and the resource-determining components of the crane specifically.

The task of conducting an objective assessment of the technical condition of jib cranes during the process of industrial safety inspection is essential. Therefore, the aim of this work was to develop a methodology for determining the actual classification group (mode) of jib cranes of foreign companies and to test the developed methodology using a specific example.

**Materials and Methods.** Gottwald type cranes have an A5 or A6 crane operating mode classification group with recommended parameters according to International European standards FEM 1.001–1998<sup>7</sup> [8]:

- crane classification group A;
- mechanism classification group M;
- other components classification group E;
- usage class U for each group;
- loading mode Q for each group.

With these parameters, the expected lifetime of the components and mechanisms [9] of the crane must be achieved, expressed in operating hours (Table 1).

F.E.M. 1.001–1998. Rules for the Design of Hoisting Appliances. VBOOK.PUB. URL: <a href="https://vbook.pub/documents/fem-1001-3-edition-revised-1998101-rules-for-the-design-of-hoisting-appliances-5wglvlzj7807">https://vbook.pub/documents/fem-1001-3-edition-revised-1998101-rules-for-the-design-of-hoisting-appliances-5wglvlzj7807</a> (accessed: 24.02.2025).

Table 1

	Serv	ice life	e diagran	n for HM	K, HSK t	ype crane	es.			
Components Hours in service Service life of components										
Components	Hours in service	5,000	10,000	15,000	20,000	25,000	30,000	40,000 Q2	45,000	50,000 Q3
Metal structure	Check every 5000 hours									
	Overhaul									
Diesel unit	Generator									
	Clutch									
	Reduction unit									
	Engine									
Swing mechanism	Rotation crown									
	gear									
	Brake									
Axes	Axis									
TINOS	Brake									
Undercarriage	Hydraulic motors Valves									
II	Pump									
Hydraulic system	Seals									
E1()	Drive									
Electrical system	Control system									
	Reduction unit									
	Brake									
I iftim a maahaniam	Blocks									
Lifting mechanism	Engine									
	Ropes 6000 hours									
Outrigger support system	Cylinders									
Derricking mechanism	Cylinders									
Undercarriage on rails										
	Axis									
Undercarriage on	Engine									
tires	Brake									
	Reduction unit									

This table determines the recommended service life in operating hours for the bearing metal structures of cranes, as well as for the main components of the crane — lifting, rotating, chassis, electrical, and hydraulic equipment — under a specific loading mode Q. For instance, the service life of a crane's metal structure under loading mode Q2 was 40,000 operating hours.

15,000

20,000

25,000

30,000

40,000

45,000

50,000

5,000 10,000

Hours in service

Components

According to FEM8, Q2 load mode is recommended for imported cranes. However, when we analyzed the actual load on several cranes that were surveyed, we found that the current load mode corresponded to Q3 level, which exceeded the passport values for the crane's classification group [10].

<sup>&</sup>lt;sup>8</sup> F.E.M. 1.001-1998. Rules for the Design of Hoisting Appliances. VBOOK.PUB. URL: https://vbook.pub/documents/fem-1001-3-edition-revised-1998101-rules-for-the-design-of-hoisting-appliances-5wglvlzj78o7 (accessed: 24.02.2025).

When conducting an industrial safety inspection, it is essential to collect data on the actual loading of the crane [11]. However, it is not always possible to use parameter recorders, as they may not be operational. Therefore, in such situations, it was decided to use statistical data on the actual loading of cranes.

Loading of jib cranes is a function of at least two parameters — the load weight and the boom outreach, the product of which determines the load moment. In general, these parameters can be random values [12]; they should be taken into account when determining the crane load.

Therefore, the key task of determining the classification group (mode) of the crane is to gather initial data and construct histograms of the distribution of transported cargo masses and boom outreach of the crane under test. The distribution of random variables (the mass of the transported goods and the boom outreach of the crane) is characterized by such quantities as the average value (mathematical expectation) and the standard deviation (variance).

Let us take the random values distribution law (the mass of the transported goods and the boom outreach of the crane) as normal, which will greatly simplify calculations in the future [13]. The accepted assumptions are supported by studies of the boom outreach and angle of inclination of portal jib crane presented in [7, 8].

**Results.** In order to obtain more objective information to make an informed decision on further operation of jib cranes of foreign companies, a methodology has been developed for assessing the actual classification group (mode) for conducting an industrial safety inspection. The process included several stages. The first step was to determine the actual value of the load distribution coefficient  $K_p$  through the load moments and compare it with the passport value. The second stage included an assessment of the remaining operating life and its comparison with the standard value. Then, the maximum fatigue stresses of the resource-determining unit of the metal structure were calculated, followed by a comparison of the obtained value with the limit value. The probability of structural failure was also calculated and compared with the acceptable value. An important element of the assessment was the analysis of the accident risk level.

As an example, we considered a specific case where the actual classification group (mode) of a jib crane was determined and it was recommended for decommissioning. At the first stage, the load distribution coefficient  $K_p$  was determined in terms of load moments from the expression:

$$K_{p} = \sum_{i} \left[ \frac{C_{i}}{C_{T}} \right] \left( \frac{M_{(xy)}}{M_{n}} \right)^{3}, \tag{1}$$

where  $C_i/C_T$  — ratio of the number of operating cycles of a crane with an average load torque to the total number of cycles (we assumed 1 in calculations);  $M_{(xy)}$  — mathematical expectation of the load moment;  $M_n$  — maximum load moment of the crane specified in its certificate;  $M_{xy} = 28 \times 40 = 1,120 \text{ t·m}$ ;  $M_n = 33.4 \times 50 = 1,670 \text{ t·m}$  (40 and 50 — average and highest outreach value in the hook mode; 28.0 and 33.4 — average and highest lifting capacity of the crane in the hook mode according to cargo characteristics).

$$K_p = 1 \cdot \left(\frac{1120}{1670}\right)^3 \cdot 3 = 0.30.$$
 (2)

According to [5, 6, 9], the crane classification group (mode) is generally determined depending on the class of use (U0 - U9), characterized by the maximum number of cycles per service life, and the loading mode (Q1-Q4). Calculated value of the load distribution coefficient Kp = 0.30 corresponded to A6 classification group (mode) of the crane as a whole, but was higher than A5 nominal value [14].

At the second stage, the residual life of the crane was estimated based on the current value of the characteristic number, which was a measure of the crane's life, and was determined taking into account the load distribution coefficient of the crane for the corresponding loading mode and the number of operating cycles [15].

The limiting condition of the crane in terms of operating time occurred if the current characteristic number was equal or higher than the standard value. The residual life was calculated using the following equation:

$$C_{\text{oct}} = \left(N_{H} - N_{T}\right) \cdot \left(\frac{M_{n}}{M_{xy}}\right)^{3},\tag{3}$$

where  $N_H$  — standard value of the characteristic number, which was determined by the crane's classification group and operating mode according to [9, 10];  $N_T$  — current value of the characteristic number.

$$N_T = C \cdot \left(\frac{M_{xy}}{M_n}\right)^3. \tag{4}$$

For the example discussed earlier, the additional conditions were as follows:

N<sub>H</sub> = 125,000 — standard value of the characteristic number for A5 crane classification group (mode);

C = 596,228 — estimated number of working cycles;

Then the current value of the characteristic number was:

 $N_T = 596,228 \times 0.67^3 = 179,323;$ 

179,323 > 125,000;

 $N_T > N_H$ .

Conclusion: the resource was exhausted.

At the next stage, a verification calculation of the resource-determining assembly of the metal structure [11] for fatigue resistance was performed according to the formula.

$$\sigma_{max} = \alpha_V \cdot R_v \cdot \gamma_v \cdot \gamma_c, \tag{5}$$

where  $\sigma_{max}$  — maximum stress;  $\alpha_{\nu}$  — coefficient of the operating mode of the element;  $R_{\nu}$  — calculated fatigue resistance calculated considering time resistance, steel, and the group of elements' joints, taking into account the degree of stress concentration;  $\gamma_{\nu}$  — coefficient that took into account the type of stress state and the asymmetry of operating stresses;

 $\gamma_c$  — coefficient of operating conditions.

The value of operating mode coefficient  $\alpha_v$  was determined based on the crane's operating mode group and the level of stress concentration. The value  $\gamma_v$  was calculated based on the type of stress state and the stress asymmetry coefficient:

$$\rho = \frac{\sigma_{max}}{\sigma_{min}},\tag{6}$$

where  $\sigma_{min}$  and  $\sigma_{max}$  — maximum and minimum absolute stresses in the calculated element.

As an example, we calculated the reference contour of the rotary device on a portal jib crane. The results of this calculation can be found in Table 5, which shows the fatigue resistance.

Fatigue resistance calculation results

Table 5

Parameter	Value
Maximum compressive stress, $\sigma_{max}$	65 MPa
Maximum tensile stress, $\sigma_{min}$	55 MPa
Coefficient of the operating mode of the element $\alpha_{\nu}$	1.5
Calculated $R_{\nu}$ fatigue resistance for the 6th group of elements in terms of stress concentration	60 MPa
	1.5
Coefficient of the operating mode of the element, $\alpha_{\nu}$	1.3
Coefficient that takes into account the type of stress state and the asymmetry of the acting stresses, $\gamma_{\nu}$	1.08
Coefficient of operation conditions, $\gamma_c$	0.7
Fatigue resistance strength condition	65 MPa not more than 68 MPa

The verification calculation of the reference contour of the portal jib crane's rotary device for fatigue resistance indicated that the maximum stress values calculated were close to the limiting value.

Based on the statistical data on the load of the jib crane, we could determine the probability of destruction of the resource-determining element of the metal structure using the following expression:

$$P_{\text{pasp}} = \left[\frac{1}{2} - \Phi\left(\frac{\sigma_{\text{K}} - \sigma_{\text{vep}}}{\sigma_{\text{H}}}\right)\right] \left[\frac{1}{2} + \Phi\left(\frac{\sigma_{\text{K}} - \sigma_{\text{\Picp}}}{\sigma_{\text{H}}}\right)\right],\tag{7}$$

where  $\Phi(x)$  — Laplace function;  $\sigma_H$  — average square deviation of stresses in the distribution of the load factor;  $\sigma_{\pi}$  — average square deviation of stresses in the distribution of the strength factor;  $\sigma_{vep}$  — average calculated stress in the structure;  $\sigma_{nep}$  — average value of the fatigue limit of the structural material, taking into account the cycle asymmetry;  $\sigma_{\kappa}$  — calculated stress value at the intersection point of the alternating stresses distribution of and the distribution of fatigue limits, which could be obtained from solving the equality of load and strength distribution equations. Table 6 provides the calculation results.

Table 7

The results of calculating the probability of destruction of the resource-determining element of a metal structure

Parameter	Value
$\sigma_{ m vcp}$	58 MPa
$\sigma_{\scriptscriptstyle H}$	2.5 MPa
Х(н)	1.6
Ф(н)	0.4452
Опер	68 MPa
$\sigma_{\pi}$	3.3 MPa
$\sigma_{\scriptscriptstyle K}$	62 MPa
Х(п)	1.81
Ф(п)	0.4649
Estimated value of the probability of destruction	2×10 <sup>-3</sup>
$P = (0.5 - 0.4452) \times (0.5 - 0.4649) = 0.0548 \times 0.0351$	2^10
Acceptable probability value	1.0 – 0.9999=0.0001 (10 <sup>-4</sup> )

The safety condition was not fulfilled, because the calculated value of the probability of destruction equal to  $2 \times 10^{-3}$  exceeded the permissible value of  $10^{-4}$ .

For comparison, Table 7 shows the failure probabilities of jib-type crane elements.

Probability of failure of jib-type crane elements

Name	Event	Probability
Brake	Failure	$3.5 \times 10^{-5} - 3.3 \times 10^{-7}$
Rope	Wire breakage Wear and tear	3.6×10 <sup>-4</sup> 3.8×10 <sup>-5</sup>
Blocks	Failure	$2.7 \times 10^{-3} - 5.6 \times 10^{-4}$
Engine	Failure	$1.28 \times 10^{-4} - 6.2 \times 10^{-7}$
Metal structure	Damage	2.5×10 <sup>-5</sup>
Starting-and-control devices	Failure	9.5×10 <sup>-4</sup>
Running wheels	Wear and tear	9.9×10 <sup>-6</sup>
Electrical wiring	Failure	1.9×10 <sup>-4</sup>
Reducer	Failure	8.7×10 <sup>-6</sup>

At the final stage, based on regulatory and technical documentation, a risk assessment was conducted to determine the level of safety for further operation of the jib crane. The background risk of accidents for lifting cranes was calculated using statistical data from the last 27 years:

- average number of cranes during the observation period—254,250 units;

Economic damage, rub.

16,000,000

8,000,000

- average number of accidents 42.29;
- background probability of an accident  $42.29/254,250 = 0.000166 = 1.66 \cdot 10^{-4}$

Table 8 presents the damage from accidents at hazardous production facilities with lifting cranes, including direct losses, costs for localizing and mitigating the consequences, and economic losses based on statistical data from open press sources.

Economic damage from accidents

Year

2014

2015

rub.	

Economic damage,

50,000,000

78,000,000

Table 8

 2005
 60,000,000
 2021
 150,000,000

 2008
 165,000,000
 2022
 73,778,191

 2009
 62,000,000
 2023
 70,648,042

For comparison, Table 9 provides information on the probability of events with other types of equipment operated at hazardous production facilities.

Year

2003

2004

Probabilities of events for various types of equipment

Type of equipment	Event	Probability
Pressure vessels	Depressurization	$4.0 \times 10^{-5} - 6.2 \times 10^{-6}$
Fressure vessels	Total destruction	3.0×10 <sup>-7</sup>
Tanks for flammable liquids	Total destruction	5.0×10 <sup>-6</sup>
Fixed-roof tanks	Fire	9.0×10 <sup>-5</sup>
Industrial pipeline	Break	$1.4 \times 10^{-6} - 6.4 \times 10^{-9}$
Metallurgical workshop	Fire	1.9×10 <sup>-5</sup>
Road transport (USA)	Accident	3×10 <sup>-4</sup>
Road transport (Russian Federation)	Accident	2.7×10 <sup>-4</sup>
Water, air transport (USA)	Accident	9×10 <sup>-6</sup>
Water transport (Russia)	Accident	2.2×10 <sup>-7</sup>
Air transport (Russian Federation)	Accident	3.4×10 <sup>-7</sup>
Railway transport (USA)	Accident	4×10 <sup>-6</sup>
Railway transport (Russian Federation)	Accident	2×10 <sup>-8</sup>

**Discussion and Conclusion.** Using a specific example, the results showed that exceeding the crane's classification group (mode) and the assigned crane resources as a whole, including structural elements that determine the resource, will inevitably increase the risk of accidents involving jib cranes. Therefore, it was determined that the actual classification group of the crane was A6, which exceeds the passport value A5.

The developed methodology for assessing the actual classification group (mode) of jib cranes of foreign companies will significantly reduce the likelihood of structural failure of jib cranes and the level of accidents during industrial safety inspections. Currently, in Russia, the acceptable level of risk is determined qualitatively without specific numerical values for the probability of accidents or the amount of damage. The numerical values of the probability of accidents and the amount of damage are determined based on the economic and social development of society and may vary depending on the industry. Therefore, it is recommended to use the background probability of a lifting crane accident of  $1.66 \cdot 10^{-4}$  and an average material damage value of 73.2 million rubles in calculations.

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#### About the Authors:

**Dmitry N. Simonov**, Chief Designer, "Mysl" Engineering and Consulting Center OOO NGTU (88, Troitskaya St., Novocherkassk, 346428, Russian Federation)

Roman V. Khvan, Cand. Sci. (Eng.), Associate Professor of the Department of Transport Systems and Logistics, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344003, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:ORCID">ORCID</a>, <a href="mailto:ResearcherID">ResearcherID</a>, <a href="mailto:ScopusID">ScopusID</a>, <a href="mailto:khvanroman@yandex.ru">khvanroman@yandex.ru</a>

Elvira A. Panfilova, Cand. Sci. (Philosophy), Associate Professor of the Department of Transport Systems and Logistics, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344003, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, ORCID, korotkaya elvira@mail.ru

**Leonid A. Ternovskoi**, Postgraduate Student of the Department of Transport Systems and Logistics, Don State Technical University (1, Gagarin Sq., Rostov-on-Don, 344003, Russian Federation), ORCID

#### Claimed Contributorship:

DN Simonov: concept development, academic advising, methodology development.

**RV Khvan:** administrative management of a research project, conducting research, writing a manuscript — reviewing and editing.

EA Panfilova: visualization, formal analysis, validation of the results.

LA Ternovskoi: data curation, writing a draft manuscript.

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#### Об авторах:

**Дмитрий Николаевич Симонов,** главный конструктор ООО ИКЦ «Мысль» НГТУ (346428, Российская Федерация, г. Новочеркасск, ул. Троицкая,88)

**Роман Владимирович Хван,** кандидат технических наук, доцент кафедры эксплуатации транспортных систем и логистики Донского государственного технического университета (344003, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), <u>SPIN-код</u>, <u>ORCID</u>, <u>ResearcherID</u>, <u>ScopusID</u>, <u>khvanroman@yandex.ru</u>

**Эльвира Анатольевна Панфилова,** кандидат филосовских наук, доцент кафедры эксплуатации транспортных систем и логистики Донского государственного технического университета (344003, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), <u>SPIN-код</u>, <u>ORCID</u>, <u>korotkaya\_elvira@mail.ru</u>

**Леонид Александрович Терновской,** аспирант кафедры эксплуатации транспортных систем и логистики Донского государственного технического университета (344003, Российская Федерация, г. Ростов-на-Дону, пл. Гагарина, 1), <u>ORCID</u>

#### Заявленный вклад авторов:

- Д.Н. Симонов: разработка концепции, научное руководство, разработка методологии.
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  - Э.А. Панфилова: визуализация, формальный анализ, валидация результатов.
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# CHEMICAL TECHNOLOGIES, MATERIALS SCIENCES, METALLURGY XИМИЧЕСКИЕ ТЕХНОЛОГИИ, НАУКИ О МАТЕРИАЛАХ, МЕТАЛЛУРГИЯ



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Original Empirical Research

Influence of Pre-Carburization on the Structure and Properties of Chromium Coatings on Steels Formed by Diffusion Alloying in Liquid Metal Media Solutions

Lev I. Svistun, Eduard E. Bobylyov, Aslan D. Nirov, Ivan D. Storozhenko, Roman A. Popov

Kuban State Technological University, Krasnodar, Russian Federation

⊠ ebobylev@mail.ru



#### **Abstract**

Introduction. Diffusion alloying from the medium of low-melting liquid metal solutions (DALMMS) allows us to form coatings for metal products. At the same time, the carbon content in the alloy is reduced under the carbide coating layer, which negatively affects the operation of products under contact stresses. To neutralize decarburization, as well as to obtain deep hardened layers, a complex chemical-thermal treatment (CCTT) is proposed. It means pre-carburization and subsequent DALMMS with chromium. It is important to compare the characteristics of coatings on metal samples that have undergone and have not undergone carburization. The results of such studies have not been published before. The aim of the work is to analyze the effect of pre-carburization on chromium-based diffusion coatings and the structure of the coated sample.

*Materials and Methods.* The coatings were obtained by immersing St3 and 40X steel samples in a PbLi reaction transport medium with the addition of chromium. Some of the samples were previously subjected to vacuum carburization. The coating thickness and structure of the coated sample were determined using a universal microscope NU-2E (Carl Zeiss Jena). Electron microprobe analysis was performed on a Tescan Lyra 3 electron microscope with the Oxford Ultim MAX PCMA system. Microhardness was determined by the Dura Scan Falcon 500 microhardness tester. X-ray phase analysis (XPA) was performed on a Bruker D8 Advance Eco X-ray diffractometer.

**Results.** Without carburization, a coating with a thickness of 12 μm was formed on the St3 steel sample, while with carburization it was 22 μm. The difference was 1.83 times. The chromium diffusion depth in the sample without carburization was 18 μm. In the sample with pre-carburization it was 34 μm. Carburization provided a significant increase in the depth of the hardened layer. Without pre-treatment, the microhardness values of the coating were recorded after DALMMS: 1400 HV0.02 for Ct3 and 1650 HV0.02 for 40X. After CCTT: 1500 HV0.02 for Ct3 and 1800 HV0.0 for 40X. However, at a depth of 10 μm, the microhardness (160 HV0.02) was lower than that of the coated material for both samples. After CCTT, the areas with reduced microhardness disappeared, and the depth of the hardened layer was 1.5 mm for Ct3 and 2 mm for 40X.

**Discussion and Conclusion.** Pre-carburization helps to avoid the formation of a softened sublayer between the coating and the coated material, which is important for the performance of products under contact stresses. Consequently, chrome-coated structural steel parts can be used after carburization in conditions of abrasive corrosion and high mechanical loads. Examples of these applications include compressor equipment and oil and gas equipment.

**Keywords:** chemical-thermal strengthening methods, diffusion metallization, pre-carburization, diffusion alloying with chromium, decarburized ferrite sublayer

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Оригинальное эмпирическое исследование

### Влияние предварительной цементации на структуру и свойства диффузионных покрытий на основе хрома на сталях, полученных в среде легкоплавких жидкометаллических растворов

Л.И. Свистун , Э.Э. Бобылёв , А.Д. Ниров , И.Д. Стороженко , Р.А. Попов Кубанский государственный технологический университет, г. Краснодар, Российская Федерация ebobylev@mail.ru

#### Аннотация

Введение. Диффузионная металлизация из среды легкоплавких жидкометаллических растворов (ДМЛЖР) позволяет формировать покрытия для изделий из металла. При этом под слоем карбидного покрытия сокращается содержание углерода в сплаве, что негативно сказывается на работе изделий в условиях контактных напряжений. Для нейтрализации обезуглероживания, а также получения глубоких упрочненных слоев предложена комплексная химико-термическая обработка (КХТО) — это предварительная цементация и последующая ДМЛЖР хромом. Важно сопоставить особенности покрытий на металлических образцах, прошедших и не прошедших цементацию. Результаты таких исследований ранее не публиковались. Цель работы — анализ влияния предварительной цементации на хромовые диффузионные покрытия и структуру покрываемого образца.

*Материалы и методы.* Покрытия получены путем погружения образцов из сталей Ст3 и 40X в реакционнотранспортную среду PbLi с добавлением хрома. Часть образцов предварительно прошла вакуумную цементацию. На универсальном микроскопе NU-2E Carl Zeiss Jena («Карл Цейс Джина» (англ.)) определялись толщина покрытия и структура образца. Микроренттеноспектральный анализ (MPCA) проводился на электронном микроскопе Tescan Lyra 3 («Тискан Лира 3» (англ.)) с системой PCMA Oxford Ultim MAX («Пи-си-эм-эй Оксфорд Ультим MAKC» (англ.)). Микротвердость определял микротвердомер Dura Scan Falcon 500 («Дюра Скан Фалькон 500» (англ.)). Рентгенофазовый анализ (РФА) проводили на рентгеновском дифрактометре Bruker D8 Advance Eco («Брюкер Ди-8 Эдванс Эко» (англ.)).

Результаты исследования. Без цементации на образце из стали Ст3 сформировалось покрытие толщиной 12 мкм, с цементацией — 22 мкм. Разница — в 1,83 раза. Глубина диффузии хрома в образце без цементации составила 18 мкм, в образце с предварительной цементацией — 34 мкм. Цементация обеспечила значительное увеличение глубины упрочненного слоя. Без предварительной обработки после ДМЛЖР фиксировались показатели микротвердости покрытия: 1400 HV0,02 для Ст3 и 1650 HV0,02 для 40Х. После КХТО: 1500 HV0,02 для Ст3 и 1800 HV0,0 для 40Х. Однако на глубине 10 мкм микротвердость (160 HV0,02) оказалась ниже показателя покрываемого материала для обоих образцов. После КХТО исчезают зоны с пониженной микротвердостью, глубина упрочненного слоя — 1,5 мм для Ст3 и 2 мм для 40Х.

Обсуждение и заключение. Предварительная цементация позволяет избежать формирования разупрочненного подслоя между покрытием и покрываемым материалом, что важно для эксплуатации изделий при контактных напряжениях. Следовательно, детали из конструкционных сталей с хромовым покрытием после цементации можно использовать в условиях абразивно-коррозионного воздействия и высоких механических нагрузок. Примеры такой эксплуатации — компрессорная техника и нефтегазовое оборудование.

**Ключевые слова:** химико-термические методы упрочнения, диффузионная металлизация, предварительная цементация, диффузионное легирование хромом, обезуглероженный ферритный подслой

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**Introduction.** In modern mechanical engineering, surface hardening of parts is a widely used technique [1]. Known technologies make it possible to obtain products with different properties and structures [2] by changing the properties and structure of the surface layer [3]. Special attention should be paid to chemical and thermal hardening methods. They are characterized by simplicity [4], provide high-quality hardened surfaces [5], as well as a smooth change in structure and properties from coating to coated material [6]. The technology of diffusion alloying from the medium of low-melting liquid metal solutions (DALMMS) refers to the technologies of chemical and thermal treatment (CCTT) and is promising from the point of view of obtaining functional coatings [6]. This technology is used to form coatings based on Cr, Ti, W, Mo, Ni, Cu, etc. on the surface of products made of steels [6], hard alloys [7], and cast iron [8].

Chromium is one of the elements that is often used as a basis for functional coatings [9]. These coatings increase wear resistance of parts [10] and corrosion resistance in aggressive environments [11]. Chrome coatings can also improve resistance to simultaneous complex effects of mechanical and corrosive wear [12]. The high resistance to wear and corrosion is due to the fact that the coatings are based on carbides [13]. During the formation of these carbides, carbon diffuses from the coated material. As a result, the carbon content in the alloy under the coating decreases, leading to the formation of decarbonization zones. This causes the carbide layer to press onto the coated part during operation [14]. To counteract the effect of decarburization and further harden the coated material, complex chemical and thermal treatment (CCTT) can be employed. It means the pre-carburization and diffusion alloying of samples with chromium in the medium of low-melting liquid metal solutions [15].

The aim of this research was to analyze the effect of pre-carburization on the formation of chromium-based diffusion coatings and the structure of the coated sample.

**Materials and Methods.** CCTT and DALMMS were performed on cylindrical samples with a diameter of 20 mm and a length of 30 mm. The samples were made of St3 and 40X steel (Table 1).

Chemical composition of the studied materials

Table 1

Steel grade	Element content, weight %									
	С	Si	Mn	Ni	S	P	Cr	Cu		
St3	0.14-0.22	0.15-0.3	0.4-0.65	up to 0.3	up to 0.05	up to 0.04	up to 0.3	up to 0.3		
40X	0.36-0.44	0.17-0.37	0.5-0.8	up to 0.3	up to 0.035	up to 0.035	0.8–1.1	up to 0.3		

Chrome coatings were obtained through the process of diffusion alloying of samples in low-melting liquid metal solutions. To do this, we used the DALMMS setup [16]. The reaction transport medium was a PbLi eutectic melt, into which 10% chromium powder was added. The coating was applied by immersing and then isothermally exposing the samples in the melt at 1050°C for 8 hours, with argon filling the space above the melt. This process also involved solid-phase diffusion, leading to the formation of solid solutions and chemical compounds.

Prior to the start of DALMMS, in order to saturate the surface layers of steels with carbon, vacuum carburization was performed in a propane-butane mixture at a temperature of 950°C for 8 hours.

The structure of the coated material and the thickness of the coating were studied using a NU-2E universal optical microscope (Carl Zeiss Jena). The microhardness of the samples after DALMMS and CCTT was studied on a Dura Scan Falcon 500 microhardness tester. Electron microprobe analysis was performed on a Tescan Lyra 3 scanning electron microscope with the Oxford Ultim MAX PCMA system. An X-ray diffractometer Bruker D8 Advance Eco (Bruker AXS GmbH) with a  $\theta$ - $\theta$  vertical goniometer was used for X-ray phase analysis (XPA). The samples were etched in a 4% alcohol solution of HNO<sub>3</sub>.

**Results.** Figure 1 shows micrographs of St3 steel samples after DALMMS and CCTT.

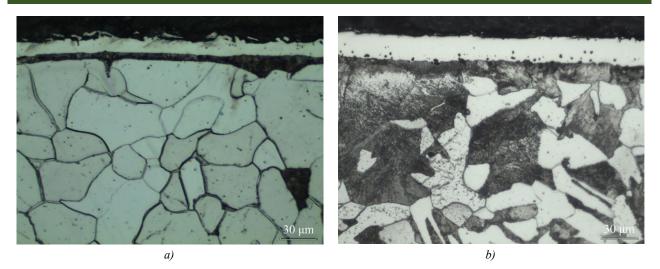


Fig. 1. Surface layers of St3 steel after 8-hour DALMMS at 1050°C: a — without pre-carburization; b — with pre-carburization

Thus, pre-carburization affected both the steel and coating structure after DALMMS. Without pre-carburization, carbon diffused into the area under the coating, forming a pearlitic layer and a decarbonized ferritic layer in which there were no pearlitic grains. If pre-carburization was performed, the structure of the coated material changed. After CCTT, there was no decarbonized ferritic sublayer in it, even when low-carbon St3 steel was saturated. The structure of the material was perlite with ferrite inclusions (Fig. 1b).

Several zones could be distinguished that formed the surface layers of the material after CCTT:

- coating,
- transition zone between the coating and the material to be coated,
- carburization zone,
- transition carburization zone base.

Figure 2 shows the structure of a 40X steel sample after CCTT.

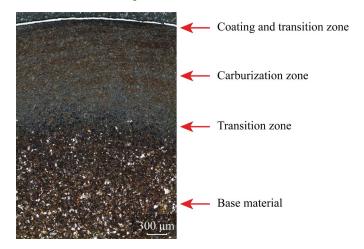
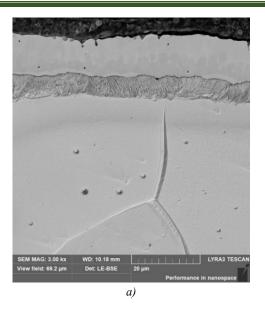


Fig. 2. Sample structure after CCTT

In case of DALMMS without pre-carburization, a zone of lamellar perlite alloyed with chromium was formed under the coating, followed by a soft ferritic layer. There was no decarbonized layer in the pretreated samples. Without carburization, a coating with a thickness of  $12~\mu m$  was formed on the St3 steel sample; with carburization it was  $22~\mu m$ . Thus, pre-carburization helped to increase the coating thickness by 1.83 times. There was a physical explanation for this result. Pre-carburization increased the intensity of carbon diffusion from the sample to the adsorbed chromium. Carbon heterodiffusion was recorded under the influence of high temperatures characteristic of DALMMS. This helped to equalize the carbon content and eliminate decarbonized zones that could occur as a result of the formation of carbides. Figure 3 shows micrographs of 40X steel after DALMMS and CCTT. On the sample after CCTT, the perlite structure was thinner, and there was no decarbonized zone.



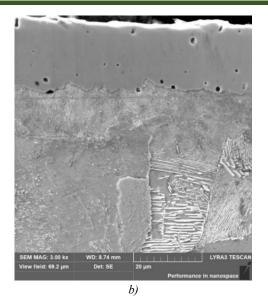
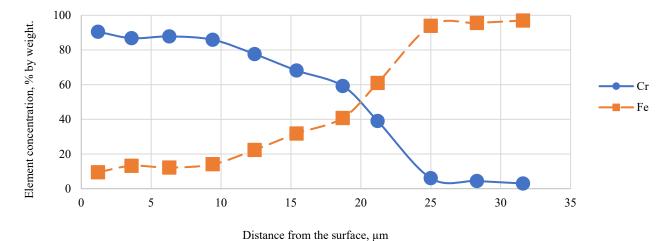


Fig. 3. The structure of the 40X steel surface layer after an 8-hour DALMMS at 1050°C: a — DALMMS; b — CCTT

Carburization did not significantly affect the chemical and phase composition. In both cases, the chromium content on the surface was 90% (wt.). However, the depth of chromium diffusion in the sample without carburization was 18  $\mu$ m. In the sample with pre-carburization it was 34  $\mu$ m, that is, twice as much. The results of electron microprobe analysis of the samples are shown in Figure 4.



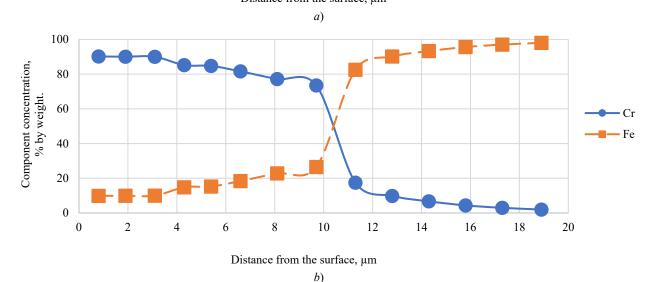


Fig. 4. The results of electron microprobe analysis of coatings after an 8-hour DALMMS at 1050°C: a — without pre-carburization; b — with pre-carburization

Phase composition of the coatings was represented by chromium carbides  $M_{23}C_6$  and  $M_7C_3$ . In the sample without pre-carburization, there was a slight iron content in chromium carbide  $M_{23}C_6$  (Fig. 5).

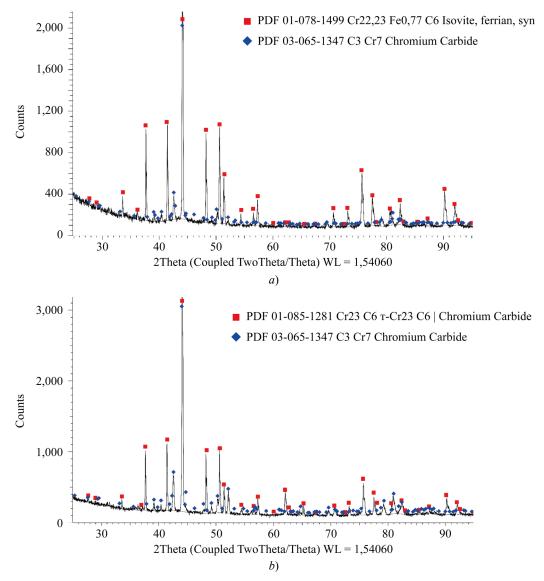


Fig. 5. The results of X-ray phase analysis of the coatings after 8-hour DALMMS at 1,050°C: a — without pre-carburization; b — with pre-carburization

Pre-carburization provided a significant increase in the depth of the hardened layer (Fig. 6).

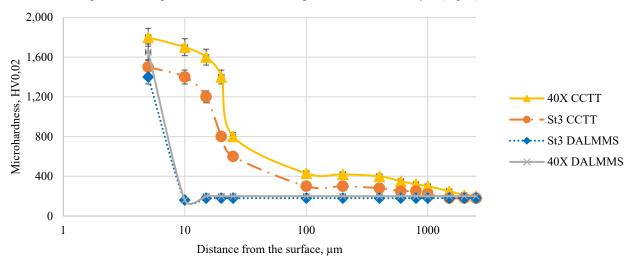


Fig. 6. Distribution of microhardness in samples after 8-hour DALMMS at 1050°C

According to Figure 6, on samples without pre-carburization, the microhardness index of the coating after DALMMS for St3 steel was  $1400~HV_{0,02}$ ,  $40X - 1650~HV_{0,02}$ . After CCTT, the microhardness of the St3 steel coating was  $1500~HV_{0,02}$ ,  $40X - 1800~HV_{0,0}$ . However, at a depth of  $10~\mu m$ , the microhardness was  $160~HV_{0,02}$ . This was lower than the microhardness of the coated material in both cases (i.e. for St3 and 40X samples). After CCTT, the microhardness distribution had a different character:

- there were no zones with reduced microhardness,
- the depth of the hardened layer was 1.5 mm for St3 steel and 2 mm for 40X steel.

**Discussion and Conclusion.** Thus, under the conditions considered, the main effect of carburization was manifested in the intensification of coating growth and the exclusion of the formation of a soft ferritic layer between the coating and the coated material. The composition of the coating and the chromium content did not depend on carburization. In any case, the coatings consisted of chromium carbides such as  $M_{23}C_6$  and  $M_7C_3$ , the chromium content on the surface reached 90%.

CCTT affected the structure of the layer between the coating and the base material. In case of DALMMS, the layer under the coating had a pearlitic structure, turning into a ferritic one and further into the structure of the coated material. Pre-carburization made the transition zone more uniform. Here, a pearlitic structure was formed with a gradual change in chromium concentration — from 10% at the boundary of the coating and the pearlitic zone to 0.3% at a depth of  $35~\mu m$ .

Thus, the positive results of pre-carburization have been proven. Firstly, the carbon content in the surface layers of the product increased, and this made it possible to intensify carburization.

Secondly, it became possible to obtain a carbon-saturated layer between the coating and the base material, which also strengthened the structure of the coated material. Therefore, it can be argued that pre-carburization is promising in terms of expanding the scope of application of parts with diffusion coatings based on chromium carbide. It eliminates the penetration of the layer under the coating and its subsequent destruction. The parts after CCTT are capable of operating at high contact stresses without chipping the functional layer.

Thirdly, the formation of a diffusion coating is accelerated. In addition, it will be thicker. As part of this study, the indicator was 1.83. The coating obtained after carburization was that much thicker (compared with the technology without pre- carburization). This indicates the significant role of carbon in the mechanism of coating creation.

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#### About the Authors:

**Lev I. Svistun,** Dr.Sci (Eng.), Professor of the Department of Engineering of Control Systems, Materials and Technologies in Mechanical Engineering, Kuban State Technological University (2, Moskovskaya Str., Krasnodar, 350072, Russian Federation), SPIN-code, ORCID, saas25@mail.ru

**Eduard E. Bobylyov**, Cand.Sci. (Eng.), Associate Professor of the Department of Engineering of Control Systems, Materials and Technologies in Mechanical Engineering, Kuban State Technological University (2, Moskovskaya Str., Krasnodar, 350072, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:ORCID">ORCID</a>, <a href="mailto:Scopus">Scopus</a>, <a href="mailto:ebobylev@mail.ru">ebobylev@mail.ru</a>

Aslan D. Nirov, Cand.Sci. (Eng.), Associate Professor of the Department of Transport Processes and Technological Complexes, Kuban State Technological University (2, Moskovskaya Str., Krasnodar, 350072, Russian Federation) <a href="mailto:SPIN-code">SPIN-code</a>, ORCID, <a href="mailto:nirovaslan@list.ru">nirovaslan@list.ru</a>

**Ivan D. Storozhenko**, Senior Lecturer of the Department of Mechanical Engineering, Armavir Institute of Mechanics and Technology, Kuban State Technological University (2, Moskovskaya Str., Krasnodar, 350072, Russian Federation), <a href="mailto:SPIN-code">SPIN-code</a>, <a href="mailto:ORCID">ORCID</a>, <a href="mailto:storojenko">storojenko</a> <a href="mailto:armv@mail.ru">armv@mail.ru</a>

**Roman A. Popov,** Postgraduate Student of the Department of Engineering of Control Systems, Materials and Technologies in Mechanical Engineering, Kuban State Technological University (350072, Russian Federation, Krasnodar Territory, Krasnodar, Moskovskaya str., 2), <u>SPIN-code</u>

#### Claimed Contributorship:

LI Svistun: concept development.

**EE Bobylyov:** reviewing and editing the manuscript.

AD Nirov: writing a draft of the manuscript.

**ID Storojenko:** conducting research. **RA Popov:** conducting research.

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All authors have read and approved the final manuscript.

#### Об авторах:

**Лев Иванович Свистун,** доктор технических наук, профессор кафедры инженерии систем управления, материалов и технологий в машиностроении Кубанского государственного технологического университета (350072, Российская Федерация, г. Краснодар, ул. Московская, 2), <u>SPIN-код, ORCID</u>, <u>saas25@mail.ru</u>

https://bps-journal.ru

Эдуард Эдуардович Бобылёв, кандидат технических наук, доцент кафедры инженерии систем управления, материалов и технологий в машиностроении Кубанского государственного технологического университета (350072, Российская Федерация, г. Краснодар, ул. Московская, 2) <u>SPIN-код</u>, <u>ORCID</u>, <u>Scopus</u>, <u>ebobylev@mail.ru</u>

**Аслан Дантесович Ниров,** кандидат технических наук, доцент кафедры транспортных процессов и технологических комплексов Кубанского государственного технологического университета (350072, Российская Федерация, г. Краснодар, ул. Московская, 2) <u>SPIN-код, ORCID</u>, <u>nirovaslan@list.ru</u>

**Иван Дмитриевич Стороженко,** старший преподаватель кафедры машиностроения Армавирского механико-технологического института (филиала) Кубанского государственного технологического университета (350072, Российская Федерация, г. Краснодар, ул. Московская, 2) <u>SPIN-код, ORCID, storojenko armv@mail.ru</u>

**Роман Андреевич Попов,** аспирант кафедры инженерии систем управления, материалов и технологий в машиностроении Кубанского государственного технологического университета (350072, Российская Федерация, г. Краснодар, ул. Московская, 2), <u>SPIN-код</u>

#### Заявленный вклад авторов:

Л.И. Свистун: разработка концепции.

Э.Э. Бобылёв: рецензирование и редактирование рукописи.

**А.Д. Ниров:** написание черновика рукописи. **И.Д.** Стороженко: проведение исследования.

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