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Д.В. Сокольский атындағы
«Жанармай, катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Химия және технология сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество в глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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**INCREASING THE RESISTANCE OF CONCRETE AGAINST
SULFATE CORROSION**

Abstract. The article presents the results of a study on the effect of sulfate corrosion on the physical and mechanical properties of concrete. When concrete is exposed to aqueous media, concrete destruction may occur because of corrosion. Sulfate attack occurs when sulfates react with compounds in the cement paste such as monosulfate, portlandite, and C–S–H gel. The reaction products may include ettringite, gypsum, and thaumasite. As a result of the insufficient durability of concrete, structures are destroyed. During the design of the structure, it is necessary to consider various factors, such as the constituents of the aggressive environment, the service conditions of the structure. A correct and careful selection of raw materials is required, as well as the appointment of the specified physical and mechanical characteristics of concrete, to ensure the required durability of the structure. The corrosion rate of concrete in seawater is difficult to predict for two reasons: firstly, this environment contains many chemical elements, and therefore many reactions will occur in concrete at once, both parallel and one after another; secondly, some of the reactions lead to destructive processes, while others lead to constructive ones. The issue of the safety of reinforcement in reinforced concrete structures has a decisive role.

Key words: construction, construction, concrete, modifiers, structure, climatic effects, corrosion, aggressive effects.

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БЕТОННЫҢ СУЛЬФАТТЫ КОРРОЗИЯҒА ТӨЗІМДІЛІГІН АРТТЫРУ

Аннотация. Бұл мақалада бетонның физика-механикалық қасиеттеріне сульфатты коррозияның тигізетін әсерін зерттеу нәтижелері көрсетілген. Бетон су ортасына түскен кезде коррозия салдарынан бетонның бастапқы қалпы өзгеріске ұшырауы мүмкін. Сульфаттың әсері сульфаттар цемент массасындағы моносульфат, портландит және С–S–Н гелі сияқты қосылыстармен әрекеттескенде пайда болады. Реакция өнімдеріне этtringит, гипс және таумазит кіруі мүмкін. Сулы ортаның әсерінен коррозияға ұшыраған бетон жойылуы мүмкін. Бетонның жеткіліксіз төзімділігі нәтижесінде құрылымдар бұзылады. Құрылымды жобалау кезінде әртүрлі факторларды ескеру қажет, мысалы, агрессивті ортаның құрамдас бөліктері, құрылымның қызмет көрсету жағдайлары. Құрылымның қажетті ұзақ мерзімділігін қамтамасыз ету үшін шикізатты дұрыс және мұқият таңдау, сондай-ақ бетонның көрсетілген физикалық-механикалық сипаттамаларын тағайындау қажет. Теңіз суындағы бетонның коррозияға ұшырау жылдамдығын екі себеп бойынша болжау қиын: біріншіден, бұл ортада көптеген химиялық элементтер бар, сондықтан бетонда бірден параллель және бірінен соң бірі көптеген реакциялар жүреді; екіншіден, реакциялардың бір бөлігі деструктивті процестерге, ал басқалары конструктивті процестерге әкеледі. Осыған орай темірбетон конструкцияларындағы арматураның қауіпсіздік мәселесі шешуші рөл атқарады.

Түйін сөздер: құрылыс, құрама, бетон, модификаторлар, құрылым, климаттық әсерлер, коррозия, агрессивті әсерлер.

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ПОВЫШЕНИЕ УСТОЙЧИВОСТИ БЕТОНА К СУЛЬФАТНОЙ КОРРОЗИИ

Аннотация. В статье представлены результаты исследования влияния сульфатной коррозии на физико-механические свойства бетона. Когда бетон подвергается воздействию водных сред, из-за коррозии может произойти разрушение бетона. Сульфатная атака возникает, когда сульфаты вступают в реакцию с соединениями в цементной массе, такими как моносульфат, портландит и гель C–S–H. Продукты реакции могут включать этtringит, гипс и таумазит. Во время воздействия на бетон водных сред может происходить разрушение бетона в результате коррозии. В результате недостаточной стойкости бетона при этом происходит разрушение конструкций. Во время проектирования сооружения необходимо учитывать различные факторы, такие как составляющие агрессивной среды, условия службы сооружения. Необходим верный и тщательный подбор сырьевых материалов, а также назначение заданных физико-механических характеристик бетона, для обеспечения необходимой долговечности конструкции. Скорость коррозии бетона в морской воде сложно прогнозировать по двум причинам: во-первых, в этой среде содержится множество химических элементов, и поэтому в бетоне будет происходить сразу множество реакций, как параллельных, так и идущих друг за другом; во-вторых, одни из реакций приводят к деструктивным процессам, а другие - к конструктивным. Вопрос сохранности арматуры в железобетонных конструкциях имеет определяющую роль.

Ключевые слова: строительство, конструкция, бетон, модификатор, структура, климатические воздействия, коррозия, агрессивная среда.

Introduction. During the construction of hydraulic structures in various regions, it is often necessary to encounter aggregates containing reactive soluble silica, which, reacting with cement alkalis causes internal alkaline corrosion of concrete and can lead to premature destruction of concrete structures.

Structures of hydraulic facilities have direct contact with water, and commonly the affected waters are aggressive towards the concrete. The most common are aggressive sulfate-containing waters, which, penetrating the capillary-porous structure of concrete, cause sulfate corrosion, which leads to a decrease in the durability of structures. The operating conditions of reinforced concrete structures are complicated by climatic influences: these are alternating temperature loads in the zones of above-water and variable water levels; waterjet abrasion, which introduces additional difficulties in the selection of materials and the development of concrete (Bazhenov, 2002; Romain et.al, 2021; Ruijun et.al, 2022).

Currently, multicomponent concretes are actively used in various construction industries. Previously, their widespread use was impossible due to some features of the properties and structure. The use of concrete structure modifiers has significantly improved the performance characteristics of such concretes. Now, this has become possible thanks to the transition to multicomponent concrete with various additives, such as superplasticizers and fine mineral additives of different types (Cyrill et.al, 2018).

Denser materials have greater strength than materials with a coarse-grained structure. Denser materials have less permeability than materials with a cellular structure, which, in turn, have less permeability. The materials with a coarse-grained structure have the greatest water absorption.

The dimensions of the structural elements of concrete influence the properties of the materials. Depending on the size, the macro-and microstructure is distinguished in concrete. A structure visible to the naked eye or at a small magnification is a macrostructure. A structure that can be seen at high magnification with a microscope is a microstructure. The most important for the properties of concrete is the microstructure of cement stone, which consists of hydrate neoplasms and micropores of various sizes. It also contains inclusions of unreacted cement grains (Walid et.al, 2021).

Common problems in the construction of reinforced concrete structures of hydraulic structures are unfavorable climatic conditions, aggressive environments, and the lack of high-quality materials. They can expose the risk of various types of corrosion and premature destruction of concrete structures.

When constructing hydraulic structures in various regions, it is supposed that economically feasible to use geographically available building materials, such as aggregates for concrete, cement, active mineral, chemical additives, etc. In practice, local building materials do not always meet the regulatory requirements of standards. Generally, we must deal with aggregates containing reactive soluble silica (SiO_2), which can cause an alkali-silicate reaction of aggregates and lead to internal corrosion of concrete (Tang et.al, 2015).

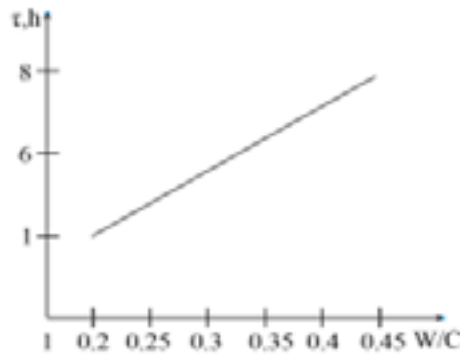


Figure 1. Dependence of the period of formation of the cement stone structure (setting time) on the W/C.

The time interval from the moment of sealing the binder with water to the beginning of the rapid strength gain of the resulting cement stone is the period of structure formation. The duration of this period is the setting time of the concrete mixture. The setting time directly depends on the concentration of the binder, that is, on the water-cement ratio (Fig. 1). The lower the W/C, the shorter the setting time of the cement dough. The ratio of the dense and porous component of the cement stone to the end of the setting also depends on the concentration of the binder. This structure, consisting of primary neoplasms resulting from the hydration of cement, is an “initial matrix” by which one can judge the future structure of concrete (Chang et.al, 2021).

Besides, a crucial role in the formation of the concrete structure is played by the phenomenon of shrinkage or contraction. Studies show that the volume of laid concrete is noticeably reduced in the initial setting and hardening periods. The shrinkage of concrete can be explained by the fact that during the interaction of the two main components of concrete, cement, and water, the total volume of the cement + water system becomes smaller. During a few hours from the moment of closure due to shrinkage, the geometric volume of the concrete structure decreases by about 2%, while the absolute volume decreases to 95-96% of the initial volume of the laid concrete mixture.

Material and Methods. Sulfate attack is the most common form of a chemical attack that the concrete is subjected to. Sulfates are commonly found in soil, aggregates, seawater, and cement. The chemical consequences of sulfate attacks on concrete components are detailed below (Daman, 2019).

1. The formation of ettringite (calcium aluminate trisulfate), increasing in solid volume, leading to expansion and cracking;
2. The formation of gypsum (calcium sulfate dihydrate), leading to softening and loss of concrete strength.

- The sulfate attack on concrete might show itself in different forms depending on:
- when the chemical form of the sulphate;
 - the atmospheric environment in which the concrete is exposed.

Protection against sulfate attack can be achieved by using concrete with low [P NO 247] permeability, using cement with a low C_3A content and blends of Portland cement with pozzolans (thus reducing the available $Ca(OH)_2$). Proper placement, compaction, finishing, and curing of concrete are essential to minimize the ingress and movement of water, which is the carrier of the aggressive salts.

The study notes that the strength of cement stone was provided by forces of polycondensation origin, which was based on covalent bonds of the Si-O-Si type, hydrogen bonds, as well as bonds of donor-acceptor origin, based on the strength of the interaction of water molecules with surface calcium ions and other positive ions (Ragoug et.al, 2019; Xiong et.al, 2014).

Complete interactions of Ca_2^+ cations with oxygen atoms of water molecules ensure the unification of Tobermory-like C-S-H crystals into a single polycrystalline neoplasm. Molecules of water can enter the coordinate sphere of calcium cations, because of which, when interacting inside C-S-H crystals, an O-Ca-O bond is formed, and a Ca-O bond is formed on the crystal surface. In the first variant, individual layers of crystals merge, and the second variant, because of the unsaturation of bonds, leads to the unification of crystals at their contact points and the formation of large polycrystalline splices. If there is no direct contact between individual C-S-H crystals, the formation of O-Ca-H₂O-Ca-O bonds occurs when interacting with sorption moisture. These compounds, in turn, also have an impact on the physical and mechanical characteristics of a polycrystalline compound, since they can perceive certain mechanical stresses. This type of bond is formed only if the distance between the surfaces of neighboring crystals is no more than 1.3 nm. However, that the interlayer bonds increase and the crystals become wider due to an increase in the coordination number of calcium ions, if the number of water molecules in the price increases, even more, the distance between the crystals will increase dramatically, which will eventually lead to the formation of microcracks, and consequently, to a drop-in strength (Roziere et.al, 2011). This means that with an increase in the number of bulls in the cement system, its strength decreases.

Conducting an experiment. By creating optimal hardening conditions by introducing chemical additives, it is possible to significantly reduce the structural porosity of cement stone and achieve a significant increase in its bending strength. Directional structure formation during the hardening of cement stone with mineral additives can significantly improve such operational properties of concrete as permeability, frost resistance, resistance to aggressive environments, crack resistance, resistance to compressive, tensile, bending loads, etc.

Chemical phenomena that determine the curing of binders occur on the initial surface of solid particles, and then continue at the interface and in the volume of the hydrating system. The observed effect of reducing the strength of contacts between cement particles in the presence of an additive with a diphilic structure is mainly due to the layer directly connected to the hydrating surface. The strength characteristics of the adsorption layers of the diphilic structure on solid surfaces detected during boundary friction depend both on the nature of the polar group and on the length and branching of the hydrocarbon chain. For example, the antifriction effect of adsorption layers increases in the homologous series from the lowest homologue to the highest as a result of increased interaction of hydrocarbon “tails” with an increase in the number of methylene links of the hydrocarbon chain in a series of additives with different functional groups with an increase in adsorption capacity. the binding energy of the polar group with a hydrophilic surface.

By changing the dispersion of germinal crystals through adsorption modification, stopping their further growth, blocking with adsorption layers, as well as changing the conditions for further crystal growth and clogging of the frame, it is possible to control the stage of appearance and development of a new phase during the induction period of structure formation, and consequently, the strength of induction structures, i.e. to approach the solution of the main problem of concrete technology – obtaining materials with a given structure and properties.

In the observed cases, the destruction of building structures occurs, on the one hand, due to the effect of salt crystallization pressure in the pores of the material, and on the other hand, due to the formation of salt crystallohydrates or the transition of the latter into crystallohydrates with a high content of water hydrate and an increase in the volume of the solid phase in the pores compared to the initial volume of the system.

Crystal growth is usually accompanied by their creep. The determining factor in its occurrence is the tendency of dissolved crystalline substances to wet the solid surfaces over which the film spreads, while capillaries significantly contribute to the development of creep of salt solutions. A reliable means of preventing this phenomenon is the creation of hydrophobic surfaces.

To obtain concretes with high corrosion resistance under the influence of high concentration salt solutions in the presence of an evaporating surface, concrete modification should be used by hydrophobizing the inner surface of pores and capillaries in combination with the creation of a favorable cement stone structure. It was this circumstance that decisively influenced the increase in corrosion resistance of concretes modified with such oligomers as polyhydrosiloxanes, sodium silicone and, especially, alkoxysiloxanes, which have high hydrophobic properties.

In a highly aggressive environment, according to, it is not recommended to use concretes of normal density ($W/C = 0.6$). The average degree of aggressive action of the aqueous medium for concretes of normal density in the presence of an evaporating surface ensures the content of various salts in the range of 16...20g / l, for particularly dense concretes – 30 ...50g / l.

Concretes modified with complex modifiers are also characterized by high hydrophobicity and, accordingly, corrosion resistance. Experiments on the modification of concrete with hydrophobic oligomers and, especially, hydrophobic-gas-separating action, have shown an increase in the sulfate resistance of concrete under conditions of gypsum and sulfoaluminate corrosion, which fully corresponds to the idea of the possibility of creating the most favorable, from the point of view of concrete resistance, structure due to mosaic hydrophobization of the inner surface of pores and capillaries of cement stone and concrete in combination with thin, evenly distributed pore system. Modification of concretes on high-layer Portland cement allows to increase their sulfate resistance to the level of compositions on low-layer cements.

Results and discussions. Concrete and reinforced concrete structures for civil, industrial, and hydraulic purposes have a destructive effect on various aggressive environments. Moreover, the corrosion resistance of concrete, as well as the degree of reinforcement protection determine the durability of structures. The presence and concentration of aggressive components in liquid media determine the degree of their aggressive effect on concrete and reinforced concrete structures. In addition, the degree of aggressive influence of the medium depends on the temperature, pressure, or fluid flow rate over the surface of the structure. If we talk about gaseous media, the degree of their aggressiveness depends on the type and concentration of gas, their solubility in water, temperature, and humidity of the medium. For solid dispersed substances (dust, aerosols, salts), aggressiveness is determined by solubility in water, dispersion, temperature, and humidity of the environment. The degree of aggressive impact of various media on concrete is regulated by the state standards of anticorrosive protection of building structures. Depending on the depth of destruction of the structure, 4 degrees of aggressiveness of the medium are distinguished: non-aggressive, weak, medium, and highly aggressive media (Table 1).

The volume of entrained air increases during the transition to the structure of the second type, and the nature of the porosity of concrete also changes. This can be determined by the pore saturation coefficient. If in the structure of the first type, it is equal to 0.7- 0.75, then in the structure of the second type it is already equal to 0.6-0.65, which may indicate the presence in the system of conditionally closed pores (Beddoe et.al, 2005). A significant increase in the relative volume of entrained air with conditionally closed pores up to 5-6% provides special

hydraulic engineering, as well as concrete for road and airfield coatings with increased frost resistance and durability. It assumed that the size of the air pores should be within certain limits, which is considered the most effective. In various studies, different pore sizes indicated, which is considered the most effective for increasing frost resistance. The optimal pore size ranges from 20 to 500 microns, which means that the most effective pore sizes range from 1...2 to 300...500 microns.

Table 1. Acceptable depth (cm) of concrete destruction over 50 years of operation.

The degree of aggressiveness of the water-medium	Type of structures	
	reinforced concrete	concrete
Non - aggressive	1	2
Mildly aggressive	1...2	2...4
Medium aggressive	2...4	4...6
Highly aggressive	more 4	more 6

During exposure to water, media on concrete, concrete may be destroyed because of corrosion. Because of insufficient resistance of concrete, structures are destroyed. During the design of the structure, it is necessary to consider various factors, such as the components of the aggressive environment, the service conditions of the structure. The correct and careful selection of raw materials, as well as the assignment of the specified physical and mechanical characteristics of concrete, is necessary to ensure the necessary durability of the structure.

Figure 2 illustrates the effects of corrosion, due to the leaching of $\text{Ca}(\text{OH})_2$, from concrete during water filtration through concrete.



Figure 2. Leaching of $\text{Ca}(\text{OH})_2$ from concrete as a result of water filtration.

Corrosion combines destructive processes occurring in concrete under the action of media that contain chemicals that interact with the components of cement stone. In this case, the reaction products either become easily soluble and are carried away by water, or remain in concrete, representing an amorphous mass that does not have astringent properties. This type includes corrosion processes that occur when exposed to aqueous solutions of acids, as well as magnesium salts.

Although it is noted that the introduction of pozzolana additives is ineffective in carbonate-alkaline types of reactions. Some studies say that volumetric expansions can be reduced by introducing lithium-containing additives in an amount of 1% (Xiong et.al, 2011). In addition, barium salts (Cefis et.al, 2017), phosphates (Vollertsen et.al, 2008), and some other substances also have a beneficial effect (Santhanam et.al, 2003).

Conclusion. Concrete and reinforced concrete structures of civil, industrial, and hydraulic engineering have a destructive effect on various aggressive environments. Moreover, the corrosion resistance of concrete, as well as the degree of protection of reinforcement determine the durability of structures. The presence and concentration of aggressive components in liquid media determine the degree of their aggressive effect on concrete and reinforced concrete structures. Also, the degree of aggressive influence of the medium depends on the temperature, the pressure value, or the velocity of the liquid flow over the surface of the structure.

The effects of the developed complex additive on the corrosion resistance of concrete in sulfate-containing media have been revealed. It has revealed that the coefficients of resistance in terms of compressive and bending strength of concrete samples with the developed complex additive, both when using sulfate-resistant and ordinary Portland cement in aggressive sulfate and neutral water, are close to one. From this, it is concluded that during the test period of 12 months, the expected phase of concrete strength progression in an aggressive sulfate-containing medium due to increased density in the pores with the formation of calcium hydrosulfoaluminate did not occur, which proves the high resistance of the studied concrete in aggressive sulfate-containing media.

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ПАМЯТИ УЧЕНЫХ



ПАМЯТИ ЛЕПЕСОВА КАМБАРА КАЗЫМОВИЧА

Безвременно ушел из жизни известный ученый-электрохимик, кандидат химических наук, профессор Лепесов Камбар Казымович. Большая часть его научной деятельности прошла в стенах Института органического катализа и электрохимии им. Д.В. Сокольского.

Камбар Казымович родился в 1947 г. в Актюбинской области. В 1971 г., после окончания инженерно-физико-химического факультета Московского химико-технологического института им. Д.И. Менделеева, поступил в аспирантуру Института органического катализа и электрохимии АН КазССР по специальности «теоретическая электрохимия». В 1975 г. защитил кандидатскую диссертацию по теме «Исследование кинетики и механизма ионизации висмута, меди и индия на вращающемся дисковом электроде с кольцом». С 1974 по 1987 г.г. работал в ИОКЭ АН КазССР в должности младшего, затем старшего научного сотрудника. С 1987 по 2007 г.г. – заведующий лабораторией защиты металлов от коррозии ИОКЭ им. Д.В. Сокольского (в 2001 г. переименована в лабораторию прикладной электрохимии и коррозии).

Результаты исследований К.К. Лепесова в области электрохимии металлов, полученные методом дискового электрода с кольцом, классической и

нестационарной вольтамперметрии, позволили выявить основные закономерности образования промежуточных продуктов – ионов металлов низшей валентности в процессах разряда-ионизации поливалентных металлов и установить протекание стадийных электродных реакций с участием ионов металлов промежуточной и необычной валентности в химических реакциях диспропорционирования и репропорционирования, комплексообразования в зависимости от природы металла и анионов раствора, активности воды в электролите.

Им впервые было показано и обосновано применение метода дискового электрода с кольцом для исследования комплексообразования ионов металлов промежуточной и высшей валентности в растворах.

К.К. Лепесов являлся высококвалифицированным специалистом в области исследования кинетики и механизма электрохимических и коррозионных процессов металлов и разработки методов защиты от коррозии. Он был ответственным исполнителем программы «Разработать композиционные ферритные антикоррозионные материалы на основе продукции и вторичных ресурсов предприятий Казахстана» 2003-2005 г.г., инновационной программы «Организация опытного производства импорт-замещающих средств электрохимической защиты стальных конструкций от коррозии» 2003-2005 г.г., ряда хоздоговорных работ по коррозии.

По результатам исследований разработаны антикоррозионные составы лакокрасочных материалов с различными добавками, повышающие коррозионную стойкость покрытий в водно-солевых и кислых средах, которые нашли применение при защите водоводов в различных регионах.

Лепесов К.К. – автор более 300 научных публикаций, 1 монографии и 28 патентов на изобретения. Среди его учеников 8 кандидатов наук и 1 PhD.

Прирожденный талант исследователя в сочетании с неисчерпаемой творческой энергией и глубокой эрудицией определили его большой вклад в развитие химической науки.

Он всегда останется для нас талантливым ученым, мудрым учителем и хорошим другом.

Коллектив АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского» выражает глубокое соболезнование родным и близким.

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