DOI 10.52209/1609-1825_2024_3_211 UDC 691.32:620

Corrosion Resistance of Reinforcement in Reinforced Concrete Products

[1]**AKMALAIULY Kenzhebek,** *Dr. of Tech. Sci., Professor, kakmalaev@mail.ru,*
[1]***TOLEGENOVA Aigerim,** *Doctoral Student, aigerim.tolegenova.94@mail.ru,*
[2]**KOSHKOMBAYEVA Guldana,** *Senior Technologist, guldana-kk@mail.ru,*
[1]NCJSC «Kazakh National Research Technical University named after K.I. Satpayev», Satpayev Street, 22a, Almaty, Kazakhstan,
[2]LLC «ISKER Company», Bolashak Street, 7, Kaskelen, Kazakhstan,
**corresponding author.*

Abstract. *The compositions of modified concrete and grease for metal molds have been developed, which can be recommended for wide implementation in production to increase the corrosion resistance of reinforcement. Therefore, the purpose of the study is to protect the reinforcement from corrosion in the specified period (corrosion of reinforcement begins after 15 min) is an important problem in increasing the durability of reinforced concrete products. Methods of research of reinforced concrete products show that for several technological reasons prepared for molding products form with installed and – fixed reinforcement is in the unfilled concrete state from 30 to 60 minutes and more. Steel reinforcement in the concrete, during the manufacture of which the molds were lubricated with the lubricant developed by us, is in an even more favorable (passive) state. Even after 10 min of measurements, the potential of steel, also polarized to +600 mV, did not reach its stationary value and was at the level of +90 mV values.*

Keywords: *concrete, reinforcement, corrosion, admixtures, freezing-thawing resistance, corrosion inhibitors, micro silica.*

Introduction. Reinforced concrete products for high-strength structures are subject to complex requirements for strength, crack resistance, hydrophysical properties and corrosion resistance. Modern methods of designing heavy concrete for reinforced concrete products do not consider the conditions of operation in extremely cold climates, the impact of groundwater and highly mineralized soils. In order to improve the performance characteristics of concrete, fly ash, meta kaolin, blast furnace slag, amorphous micro silica and other types of pozzolanic additives are introduced into the concrete mixture.

The solution to the problem of obtaining effective heavy concrete for reinforced concrete products of high-speed highways with improved performance indicators of strength, crack resistance, hydrophysical properties and corrosion resistance, can be achieved by densification and strengthening of the structure of the cement matrix due to the joint influence of stabilized suspension of activated micro silica, plasticizing additive and basalt fiber.

Material and labor costs caused to the national economy by corrosion of concrete and reinforced concrete are very significant. Their values are in inverse dependence on the service life of products and structures. The estimated service life of reinforced concrete lining of subways is about 40-50 years and reinforced concrete products – are not less than 20 years and require constant monitoring of their corrosion state.

The service life of these products depends on several technological and operational characteristics, which include technological defects occurring during the manufacture of prestressed reinforced concrete structures. These are longitudinal cracks in the zone of location of prestressed reinforcement caused by its slippage in concrete as a result of insufficient anchorage. Such defects occur in case of improper design of concrete composition, its compaction, hardening, and improper tempering of tensioned reinforcement, e.g. in prestressed reinforced concrete products. The defects arising due to operational reasons include cracks in the zone of reinforcement location, which arise as a result of damage to the reinforcement under the influence of water filtration through the concrete of the subway lining. Such a circumstance leads to corrosion of concrete of type I classification. As a result of such processes (water filtration), the alkalinity of the liquid phase of concrete decreases below the critical values set and equal to pH = 11.8, and consequently, the passivating effect of concrete about steel reinforcement. Corrosion of steel reinforcement in concrete also occurs due to the leakage of currents from electrification transport (stray currents, which will be discussed further).

The analysis of technical literature has shown that a significant extension of the service life of prestressed reinforced concrete products can be achieved through the use of chemical additives in concrete. Such additives should densify the concrete structure and passivate the surface of steel reinforcement [1]. At present, in many industrialized countries, the share of concrete placed with the use of chemical modifier additives has amounted to more than 50% of the volume, in some countries of the world 80-90 and even 100% of concrete is produced with additives [2].

Positive results in the field of obtaining modified concretes, achieved as a result of numerous and long-term tests, allowed us to recommend such concretes for manufacturing reinforced concrete structures used in subway construction [3].

Materials and methods of research. The essence of the test method by GOST 27677-88 consists of the comparative analysis of the obtained results of the investigated samples placed in a non-aggressive medium with the values of indicators of samples of the same composition placed in an aggressive medium. For each composition 3 control and 3 basic samples were prepared for each investigated aggressive medium. The sizes were established based on the largest aggregate coarseness and set as recommended with the dimensions of the ribs 100×100×100 mm. Studies were carried out on sample cubes at the age of 28 days of normal curing in aqueous solutions of 5% sodium sulfate (Na_2SO_4), 3% sodium chloride (NaCl), distilled water, and 0,01 M hydrochloric acid (HCl) solution. As a non-aggressive medium, bottled drinking water meets the requirements of GOST 32220-2013 «Drinking water packed in containers. General technical conditions». Before the research, the samples were dried and weighed. At the next stage, three control samples were tested in bending tension and compression. Three specimen prisms of each composition were placed in the above-mentioned aggressive media, ensuring uniform access to the sample from all sides, with the duration of the study of 6 months.

To conduct frost resistance tests, the first basic method was used according to the requirements of GOST for repeated freezing and thawing in a water-saturated state in accordance with the methodology in which the test conditions were established: water for saturation and thawing with a temperature of 20±2°C and with a freezing temperature of minus 18±2°C. The determination of the frost resistance grade of concrete was carried out on samples with ribs 100×100×100 mm at the age of 28 days.

As part of the research on this topic, an X-ray phase analysis of the structure of the samples was carried out. The objective of the research was to identify possible neoplasms in the cement stone of concrete. The method of X-ray diffractometry makes it possible to qualitatively assess the mineral composition of cement and its hydration products by the intensity of diffraction reflections on the X-ray image. X-ray studies were carried out on the DRON-2.0 device in SoKα radiation at an accelerating voltage U = 20 kV, a current strength of 1 = 20 mA, and a counter rotation speed of 2 degrees/min.

The powder method was used during the study.

This method consists in taking X-ray images using monochromatic ray emission cameras and multicrystalline samples from a powder cylindrical column (diameter usually 0,45-0,85 mm, height 4-7 mm), you can also use a flat strip or powder that is glued to a substrate. The radiation is recorded on a narrow strip of photographic film, which is rolled into a cylinder. X-rays are reflected from a polycrystalline sample, the crystals of which are randomly arranged.

To determine the corrosion resistance by the requirements of GOST 31383-2008 12 samples of cylindrical shape, height 50 mm and diameter 50 mm, with maximum grain size of coarse aggregate not more than 10 mm were prepared for each investigated composition. The specimens were examined at the age of 28 days of normal curing with preliminary preparation of side surfaces and application of coatings: a primer in the form of a solution of epoxy glue and acetone with a ratio of components 1:1; putty consisting of epoxy glue and Portland cement with a ratio of 1:25; two layers of epoxy glue with a total thickness of 0,4 mm.

The working surfaces were then stripped of the cement film and layers of protective coatings. The required solution was poured into the exicators and the samples were immersed with a maintained distance of 40 mm from its walls and the surface of the solution. At the same time, the volume of the aggressive medium to the working surface of the investigated samples was strictly maintained in the ratio 50:1.

The acid concentration was kept constant and determined by acid-base titration method using 0,01M sodium hydroxide (NaOH) and phenolphthalein.

Experiments were conducted based on the joint-stock company «BENT», where a pilot batch of pre-stressed products for the railroad gauge 1520 mm type ShS-1u, made with the use of cement of 400 DO grade with additives of modifiers «Biotech-NM» and latex SKS-65GP was produced. Washed crushed stone of Koturbulak deposits of 5-10 and 10-20 mm fractions were used as aggregates. The fine aggregate was sand of Alexeevskoye deposit of medium size. For reinforcement, we used a periodic profile wire of class BpII with increased plastic properties with a diameter of 3 mm, according to TU 14-4-716-76. The number of reinforcing wires in the product is 44.

Reinforcement packages with clamps at the ends were assembled at a separate installation and then transferred and installed in the grips of the stands. Tensioning of the reinforcement package consisting of 44 wires was carried out in one go using a powerful hydraulic jack. The total tension force of the reinforcement wires in the package was 36,42 tf. The average tension force of one wire was 827 kgf, and the deviations of the tension force of individual wires did not differ from the average value by more than 8%.

Before filling with concrete mixture having mobility P-2, the molds were lubricated with a special grease for metal molds [4]. The use of this grease containing a «volatile» steel corrosion inhibitor is justified by the fact that during the manufacture of reinforcing strings of packages, the wire is coiled and passed through the correct braking and cutting devices. In this case, a spiral-shaped notch is formed on the wire along its entire length, and the natural oxide layer formed by the rolling scale is destroyed.

The grease was prepared by mixing the above components in a rotary pulsation apparatus (RPA). The grease obtained in this way is ready for use and has high stability (does not delaminate during 6 months). It has high dispersibility due to the presence of an oil-soluble inhibitor (dicyclohexylammonium nitrate), which combines well with oils and disperses them. The grease is easily applied with a spray gun, does not clog main pipelines and hoses, and does not soften the rubber of hoses [5].

Before molding the products, the power molds lubricated with the given compositions of greases, with the reinforcing strings fixed in them, were covered with polyethylene films. The curing time of the concrete mixture before placement in both cases was 30 min. The ambient air temperature in the shop was within 22-25°C [6].

The corrosion state of steel reinforcement in heat and moisture-treated concrete was evaluated by the method of reinforcement polarizability and rate of potential drop. This method is based on the relationship between the corrosion state of the reinforcement, the nature and rate of decline of the steel potential to the initial value of the stationary potential after its anodic polarization from an external current source. Anodic polarization is carried out for 1 min, then the current is switched off, and after 0,5, 1,0, 2,0, and 3.0 min the potential value is measured. If for 1 minute the potential drops to no more than zero volts, the steel reinforcement in concrete is in a passive state, if the potential drops faster, the steel is active and its corrosion damage is possible [7].

Results and discussion

The analysis of X-ray phase analysis data has shown that cement mixing with micro silica-activated suspension leads to an intensification of hydration process and binding of formed calcium hydroxide $Ca(OH)_2$ by micro silica to formation of low basic calcium hydrosilicates, which causes its reduction by more than 23% relative to pure cement stone, reduction of intensity of analytical lines (C_3S) and, accordingly, densification and hardening of cement stone structure.

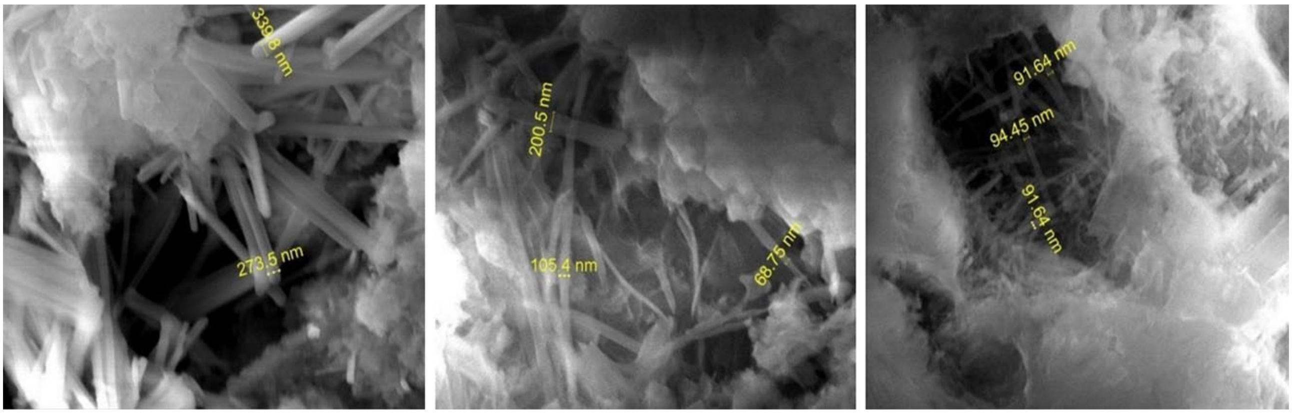
It was found that in the crystals of the modified cement stone their size decreases – from 80 to 110 nm (Figure c), which is significantly lower than in the control composition – from 200 to 300 nm (Figure a) and composition (Portland cement + micro silica) – from 100 to 200 nm (Figure b). The established changes are associated with the formation of additional amounts of low-base calcium hydro silicates due to alkaline excitation of silica-containing particles.

For frost resistance tests the first basic method according to GOST requirements was used at repeated freezing and thawing in a water-saturated state by the methodology, in which the test conditions were established: water for saturation and thawing with the temperature of 20±2°C and freezing temperature of minus 18±2°C. Determination of concrete frost resistance grade was carried out on specimens with ribs 100×100×100 mm at the age of 28 days.

The results of frost resistance tests of the investigated concrete are shown in Table.

Analysis of the data on frost resistance allowed us to draw the following conclusions:

- the obtained test results of the control (composition 1) concrete showed that starting from 250-300 cycles in the samples there was a decrease in mass by up to 3,2% and cubic strength by 9%.



a) 30000x b) 30000x c) 30000x

Microstructure of cement stone: a) control sample; b) Portland cement + micro silica; c) Portland cement + micro silica + superplasticizer

Results of concrete testing for frost resistance

Labeling sample	Weight loss of the sample, %, after cycles					Coefficient of frost resistance after cycles				
	200	300	400	500	550	200	300	400	500	550
Composition 1 control	1,16	3,20	6,34	-	-	0,97	0,91	0,69	-	-
Composition 2 15% amorphous micro silica	0,52	1,15	2,0	3,4	5,32	1,05	0,96	0,93	0,90	0,72
Composition 3 15% micro silica active	0,47	0,96	1,62	2,8	4,96	1,06	1,02	0,95	0,91	0,74
Composition 4 15% micro silica active + 0.75% basalt fiber	0,12	0,34	0,68	1,37	2,81	1,10	1,07	1,02	0,96	0,92
Composition 5 15% active micro silica + 0.75% polypropylene fiber	0,24	0,53	1,11	2,23	3,95	1,09	1,05	0,99	0,93	0,89

Fiber and activated micro silica (composition 5) became critical, which reduced the strength characteristics by more than 7%, and the weight loss reached 3,95%.

High frost resistance with optimal consumption of activated micro silica of MKU-95 grade with consumption of 15% and basalt fiber 0,75% is characterized by mass loss up to 1,37% and strength by 4,0% at 500 test cycles, which is due to the creation of a closed fine porous structure of cement stone and its high-water impermeability. The obtained results indicate that the proposed composition has a reserve after 500 test cycles for mass loss and strength, which significantly exceeds the required index of frost resistance of concrete F=200, which is regulated by the interstate standard.

Measurements are usually carried out using high-impedance voltmeters with an input resistance of at least 10 ohms. We used a voltmeter VK-2-16 with an input resistance of more than 103 Ohm since this voltmeter allows us to carry out electrochemical measurements of the potential of steel reinforcement in reinforced concrete structures with any degree of concrete moistening [8].

Electrochemical measurements were carried out in both the compressed (upper reinforcement wire) and tensile (lower reinforcement wire) zones. The reference electrode was a non-polarizing copper-sulfate electrode, which was moved along the reinforcement with a step of 20-25 cm to obtain 5-6 potential values. The steel armature was polarized by anodic current from a 9-12 V battery to a potential of +600 mV.

The experiments showed that the potential drop on the reinforcement in concrete, during the production of which the molds were lubricated with the previously used lubricant, reaches its stationary value only after 5 min. This indicates a high protective ability of the developed concretes with the additives of modifiers Biotech-NM, latex SKS 65GP, and corrosion inhibitor NNK about the stressed steel reinforcement.

Conclusion. Thus, the conducted studies of the corrosion resistance of steel reinforcement in steel concrete with additives of modifiers allow us to conclude that the developed compositions of modified concretes can be recommended for widespread introduction into production.

Corrosion resistance estimates have been developed taking into account the main provisions of the theory of heterogeneous chemical processes occurring in cement stone or concrete under the influence of various aggressive media. When studying the behavior of cement stone (concrete) in aggressive solutions, researchers use various criteria to assess corrosion resistance. In some cases, the criterion is based on a comparative change in the chemical composition of cement stone before and after exposure to an aggressive solution, in others – on a change in the mechanical characteristics of concrete, and, thirdly, on the magnitude of their volumetric deformations.

The analysis of the X-ray phase analysis data showed that when cement is sealed with a suspension, it leads to an intensification of the hydration process and the binding of the formed calcium hydroxide ($Ca(OH)_2$) before the formation of low-base calcium hydrosilicates, which causes a decrease of more than 23% relative to pure cement stone, a decrease in the intensity of analytical lines (C_3S), and, accordingly, a compaction and strengthening of the cement stone structure.

According to frost resistance, the following conclusions were made: the test results of the control concrete showed that starting from 250-300 cycles, the samples showed a decrease in weight to 3.8% and cubic strength by 10%. It is characterized by a loss of mass up to 1.4% and strength by 4.5% at 500 test cycles, due to the creation of a closed fine-porous structure of cement stone and its high water resistance. The results obtained indicate that it has a margin after 500 cycles of weight and strength loss tests, which significantly exceeds the required frost resistance index of concrete, which is regulated by the interstate standard.

This, in turn, eliminated the condition of corrosion of steel reinforcement during the period when the mold is not yet filled with a concrete mixture. After filling the mold with a concrete mixture, the reinforcement is in even more favorable conditions, since the concrete mixture contains an inorganic corrosion inhibitor NNA, which simultaneously seals the concrete structure. The combination of volatile and inorganic inhibitors in the composition of the developed concrete mixture irreversibly changed the properties of the metal and led to complete passivation of the stressed reinforcement. The obtained data confirmed the experimental data, as well as the high efficiency of the concrete mix compositions developed by us.

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Темірбетон бұйымдарындағы арматураның коррозияға төзімділігі

[1]***АҚМАЛАЙҰЛЫ Кенжебек,*** *т.ғ.д., профессор, kakmalaev@mail.ru,*
[1]****ТОЛЕГЕНОВА Айгерим Кайратовна,*** *докторант, aigerim.tolegenova.94@mail.ru,*
[2]***КОШКОМБАЕВА Гулдана,*** *бас технолог, guldana-kk@mail.ru,*
[1]*«Қ.И. Сәтбаев атындағы Қазақ ұлттық техникалық зерттеу университеті» КеАҚ, Сәтбаев көшесі, 22а, Алматы, Қазақстан,*
[2]*«ISKER Company» ЖШС, Болашақ көшесі, 7, Қаскелең, Қазақстан,*
**автор-корреспондент.*

Аңдатпа. *Арматураның коррозияға төзімділігін арттыру мақсатында өндіріске кеңінен енгізу үшін ұсынылуы мүмкін металл қалыптарға арналған модификацияланған бетондар мен майлағыштардың құрамы әзірленді. Сондықтан зерттеудің мақсаты арматураны көрсетілген кезеңде коррозиядан қорғау (арматураның коррозиясы 15 минуттан кейін басталады) темірбетон бұйымдарының беріктігін арттырудың маңызды мәселесі болып табылады. Темірбетон бұйымдарын зерттеу әдістері бірқатар технологиялық себептерге байланысты бұйымдарды қалыптауға дайындалған, орнатылған және бекітілген арматурасы бар қалып бетонмен толтырылмаған күйде 30-дан 60 минутқа дейін және одан да көп болатындығын көрсетеді. Бетондағы болат арматура, оның өндірісінде біз жасаған майлаумен майланған, одан да қолайлы (пассивті) күйде. 10 минуттық өлшеулерден кейін де +600 мВ-қа дейін поляризацияланған болаттың потенциалы өзінің стационарлық мәніне жете алмады және +90 мВ деңгейінде болды.*

Кілт сөздер: *бетон, арматура, коррозия, қоспалар, аязға төзімділік, коррозия ингибиторлары, микрокремний диоксиді.*

Коррозионная стойкость арматуры в железобетонных изделиях

[1]***АКМАЛАЙУЛЫ Кенжебек,*** *д.т.н., профессор, kakmalaev@mail.ru,*
[1]****ТОЛЕГЕНОВА Айгерим Кайратовна,*** *докторант, aigerim.tolegenova.94@mail.ru,*
[2]***КОШКОМБАЕВА Гулдана,*** *главный технолог, guldana-kk@mail.ru,*
[1]*НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева», ул. Сатпаева, 22а, Алматы, Казахстан,*
[2]*ТОО «ISKER Company», ул. Болашак, 7, Каскелен, Казахстан,*
**автор-корреспондент.*

Аннотация. *Разработаны составы модифицированных бетонов и смазки для металлических форм, которые могут быть рекомендованы для широкого внедрения в производство с целью повышения коррозионной стойкости арматуры. Поэтому цель исследования – предохранение арматуры от коррозии в указанный период (коррозия арматуры начинается уже через 15 мин) – является важной проблемой повышения долговечности железобетонных изделий. Методы исследования железобетонных изделий показывают, что по ряду технологических причин подготовленная к формованию изделий форма с установленной и зафиксированной на ней арматурой находится в незаполненном бетоном состоянии от 30 до 60 мин и более. Стальная арматура в бетоне, при изготовлении которого формы были смазаны разработанной нами смазкой, находится в еще более благоприятном (пассивном) состоянии. Даже через 10 мин измерений потенциал стали, также поляризованной до +600 мВ, не достиг своего стационарного значения и находился на уровне значений +90 мВ.*

Ключевые слова: *бетон, арматура, коррозия, добавок, морозостойкость, ингибиторы коррозии, микрокремнезём.*

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