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RESEARCH ARTICLE

CORROSION RESISTANCE OF CONCRETE IN AGGRESSIVE MEDIA

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Abstract. *Sulfate corrosion of concrete is the most common type of corrosion in Kazakhstan and is a complex physical and chemical process depending on many factors. Therefore, we studied the processes of cement and concrete corrosion in sulfate corrosive media. Methods of corrosion resistance assessment were developed taking into account the basic provisions of the theory of heterogeneous chemical processes occurring in cement stone or concrete under the action of various aggressive media. When studying the behavior of cement stone (concrete) in aggressive solutions, researchers use different criteria to evaluate corrosion resistance. In some cases, the criterion is based on the comparative change in the chemical composition of cement stone before and after exposure to aggressive solution, in others - on the change in the mechanical characteristics of concrete, and thirdly, on the magnitude of their volumetric deformations. Analysis of the study of the microstructure of cement stone of three compositions, showed the presence of clusters of elongated tubular crystals in the form of "needles", which are characteristic of the morphology of ettringite, formed in the zone of micropore formation. It was found that in the crystals of the modified cement stone their size decreases from 80 to 110 nm, which is significantly lower than in the control composition - from 200 to 300 nm and from 100 to 200 nm. Research on the strength of concrete with micro silica consumption from 10 to 15%, the results of which showed an accelerated process of hydration.*

Keywords: *concrete, aggressive environment, corrosion, sulfate, resistance, cement stone, micro silica.*

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ҒЫЛЫМИ МАҚАЛА

АГРЕССИВТІ ОРТАДАҒЫ БЕТОННЫҢ КОРРОЗИЯҒА ТӨЗІМДІЛІГІ

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Аңдатпа. *Бетонның сульфатты коррозиясы Қазақстанда коррозияның ең көп таралған түрі болып табылады және көптеген факторларға байланысты күрделі физика-химиялық процесс болып табылады. Сондықтан біз сульфатты коррозиялық ортадағы цемент пен бетонның коррозия процестерін зерттедік. Коррозияға төзімділікті бағалау әдістері әртүрлі агрессивті орталардың әсерінен цемент таста немесе бетонда жүретін гетерогенді химиялық процестер теориясының негізгі ережелерін ескере отырып жасалған. Коррозиялық ерітінділердегі цемент тасының (бетонның) мінез-құлқын зерттеу кезінде зерттеушілер коррозияға төзімділікті бағалау үшін әртүрлі критерийлерді пайдаланады. Кейбір жағдайларда критерий агрессивті ерітіндінің әсеріне дейін және одан кейін цемент тасының химиялық құрамының салыстырмалы өзгеруіне, басқаларында бетонның механикалық сипаттамаларының өзгеруіне, үшіншіден, олардың көлемдік деформацияларының мөлшеріне негізделген. Үш құрамды цемент тасының микроқұрылымын зерттеу кезінде жүргізілген талдау микропоралардың пайда болу аймағында пайда болатын эттрингит морфологиясына тән "инелер" түріндегі ұзартылған құбырлы кристалдардың шоғырларының болуын көрсетті. Модификацияланған цемент тастарының кристалдарында олардың мөлшері 80 - ден 110 нм-ге дейін азаятыны анықталды, бұл бақылау құрамынан едәуір төмен-сәйкесінше 200-ден 300 нм-ге дейін және 100-ден 200 нм-ге дейін. Микрокремнезем шығыны 10-нан 15% - ға дейінгі бетонның беріктігі бойынша зерттеулер жүргізілді, оның нәтижелері гидратацияның жеделдетілген процесін көрсетті.*

Түйін сөздер: *бетон, коррозиялық орта, коррозия, сульфат, төзімділік, цемент тасы, микро кремний диоксиді.*

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НАУЧНАЯ СТАТЬЯ

КОРРОЗИОННАЯ СТОЙКОСТЬ БЕТОНА В АГРЕССИВНЫХ СРЕДАХ

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Аннотация. *Сульфатная коррозия бетона является наиболее распространенным видом коррозии в Казахстане и представляет собой сложный физико-химический процесс, зависящий от многих факторов. Поэтому мы изучили процессы коррозии цемента и бетона в сульфатно-агрессивных средах. Методы оценки коррозионной стойкости были разработаны с учетом основных положений теории гетерогенных химических процессов, протекающих в цементном камне или бетоне под действием различных агрессивных сред. При изучении поведения цементного камня (бетона) в агрессивных растворах исследователи используют различные критерии для оценки коррозионной стойкости. В одних случаях критерий основан на сравнительном изменении химического состава цементного камня до и после воздействия агрессивного раствора, в других - на изменении механических характеристик бетона, и, в-третьих, на величине их объемных деформаций. Анализ, проведенный при изучении микроструктуры цементного камня трех составов, показал наличие скоплений удлиненных трубчатых кристаллов в виде "игл", которые характерны для морфологии эттрингита, образующихся в зоне образования микропор. Было обнаружено, что в кристаллах модифицированного цементного камня их размер уменьшается с 80 до 110 нм, что значительно ниже, чем в контрольном составе - с 200 до 300 нм и со 100 до 200 нм соответственно. Проведены исследования прочности бетона с расходом микрокремнезема от 10 до 15%, результаты которых показали ускоренный процесс гидратации.*

Ключевые слова: *бетон, агрессивная среда, коррозия, сульфат, стойкость, цементный камень, микрокремнезем.*

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CONFLICT OF INTEREST

The authors state that there is no conflict of interest.

АЛҒЫС / ҚАРЖЫЛАНДЫРУ КӨЗІ

Зерттеу жеке қаржыландыру көздерін пайдалана отырып жүргізілді.

МҮДДЕЛЕР ҚАҚТЫҒЫСЫ

Авторлар мүдделер қақтығысы жоқ деп мәлімдейді.

БЛАГОДАРНОСТИ / ИСТОЧНИК ФИНАНСИРОВАНИЯ

Исследование проводилось с использованием частных источников финансирования.

КОНФЛИКТ ИНТЕРЕСОВ

Авторы заявляют, что конфликта интересов нет.

1 INTRODUCTION

In connection with the wide application of concrete and reinforced concrete structures and the development of new areas in the Republic of Kazakhstan with aggressive external environments (mineralized soils and groundwater) one of the main tasks of construction is to ensure the durability of concrete under the action of various external aggressive environments. For this purpose it is necessary to know not only the essence of corrosion, i.e. the changes that occurred in cement stone or concrete under the action of aggressive media, but also the speed of these processes.

To estimate the corrosion rate, it is necessary to use specially developed methods taking into account the main provisions of the theory of heterogeneous chemical processes occurring in cement stone or concrete under the action of various aggressive media.

Sulfate corrosion of concrete is the most common type of corrosion in Kazakhstan and is a complex physical and chemical process depending on many factors. Therefore, we studied the processes of cement and concrete corrosion in sulfate corrosive media. At the same time, the assessment of corrosion resistance of concrete by a single has an important scientific and practical significance. It should be noted that in recent years there have been many publications on this issue, but the results of these studies are not comparable and builders cannot get an unambiguous answer about the resistance of a particular material.

The variety of research methods leads to the fact that the results of determining the corrosion resistance of cements are not comparable.

2 LITERATURE REVIEW

A review of the information available in the literature shows that the methods of determining the sulfate resistance of cements (concretes) can be divided into four groups: the visual method of assessment, which records changes in the appearance of samples, such as the appearance of cracks and distortion of the sample (**Fedosov S.V., 2003; Sheinfeld A.V., 2014; Brykov A.S., 2014**).

This method has significant disadvantages: evaluation of cement durability is subjective and is not expressed quantitatively. Moreover, the determination of durability based on external signs of fracture may lead to incorrect results, since concrete fracture often occurs uniformly throughout the entire volume, without the formation of noticeable cracks, and at the same time the strength of the specimen is almost zero, its shape may still be well preserved. If the specimens are placed in an aggressive solution after long storage in water, a protective crust of calcium carbonate is usually formed on their surface, and then destruction will occur only inside, where there are free lime, not converted to $CaCO_3$; the external shape of the specimen may remain unchanged (**Glass G.K., Buenfeld N., 2000; Stroganov V.F., 2014**).

Therefore, qualitative visual inspection of the specimens is necessary as an additional way to confirm the quantitative characteristics obtained by other methods to evaluate the corrosion resistance of concrete. Some authors (**Alekseev S.N., et al., 1990; Rozental N.K., 2006**) consider the method of measuring the deformations of the specimens to be reliable when evaluating the sulfate corrosion of concrete. The increase in the size of cement-sand and concrete specimens stored for a long time in an aggressive environment occurs as a result of crystallization of corrosion products - gypsum and calcium hydrosulfoaluminate, occupying a larger volume than the original substances. In some countries, the strain method is proposed as a standard method (**Pullar-Strecker P., 1988; Bazhenov Y. M., 2002; Rahman M., et al., 2012**) to evaluate the sulfate resistance of cements and concretes.

The main disadvantage of the strain measurement method is that its accuracy depends on the accuracy of the instrument recording the elongation of the specimens. In addition, it must be taken into account that the magnitude of expansion does not increase in direct proportion with the rate of corrosion, but usually increases very rapidly just before the process of concrete decomposition, that is, a false impression of well-being is created, which can lead to accident and destruction of buildings and structures. Therefore, the deformation method as well as the visual method for assessing the sulphate resistance of cements can be used as a supplementary method.

3 MATERIALS AND METHODS

Recently, various physicochemical methods of corrosion process investigation have become widespread. This group includes non-destructive methods of control, such as determining the concentration of hydrogen ions (pH) in the liquid phase of concrete and concrete samples stored in aggressive liquids or determining the amount of calcium ions transferred into solution from the samples. These methods are very effective in studying the causes of the nature of corrosion and can be used, as well as the first two groups of methods as additional to confirm the quantitative characteristics obtained by the main method.

The most widespread among the accelerated methods for determining sulfate resistance is the method that determines changes in the strength characteristics of samples stored in aggressive sulfate media of high concentration (**Erofeev V.T., et al., 2020; Mahmoodian, M. & Li, C.Q., 2011**).

Neither deformations, nor external signs of deterioration, nor changes in the chemical composition of cement stone unambiguously determine the condition of concrete structures operating in aggressive environments; their load-bearing capacity and service life can be assessed by changes in strength properties. It should be noted that the current GOST defines the corrosion resistance of cements by their strength properties. The change in strength properties of concrete can be monitored by three indicators: compressive, tensile and flexural strength.

In the process of exposure of concentrated sulfate solutions on concrete in the pores of cement stone will be released in the solid phase of new formations, which in the initial period compact and harden the concrete. The process of filling the pores and voids with the neoplasms leads to an increase in the compression resistance of the specimens and can create the perception that there are no destructive processes. In addition, pores and capillaries close during load application in compressive testing of concrete, which leads to an overestimation of the compressive strength.

At the same time, when concrete pores are filled with gypsum formed in the process of concrete corrosion, the process of bending resistance reduction is observed (**Alekseev S.I.,& Ivanov F.M., 2000**).

Considering the above, it is reasonable to choose the strength characteristic, namely the flexural strength, as a criterion of concrete corrosion resistance, because the results of determining the compressive strength are overestimated due to objective reasons, and the bending tensile test is difficult (**Stepanova V.F., 2016; Glass G.K., Buenfeld N., 2000**).

The flexural strength is a direct quantitative characteristic of the condition of the structure in an aggressive environment; the flexural test is easy to perform, and based on the study of literature data and laboratory studies can be recommended as a criterion for the corrosion resistance of cement and concrete.

Therefore, we evaluated the corrosion resistance of samples by their bending test. In this case, the dimensions of the tested specimens should be such that the ratio between the span of the supports and the height of the specimens - beams, i.e. its cross-section was not less than 4, because at its smaller value in the bending test may occur failure not from bending tension, but from folding stresses (**Fedosov S. V., & Bazanov S. M., 2003**). The distance from the supports to the edge of the specimen should be at least 1cm. Beam specimens with a cross section of 10x10 mm and length of 6 cm meet the above requirements (for the evaluation of corrosion resistance of cements.) Corrosion resistance of concrete was determined on beam specimens with a cross section of 100x100 mm and length of 400 mm where the distance between the supports was 300 mm.

Observance of the above conditions and methods of testing cements and concretes for sulfate resistance will allow to objectively assess their true resistance and obtain reliable results regardless of the regional location of testing laboratories. This will allow manufacturers to reasonably approach the choice of cements for concrete and reinforced concrete structures operating in aggressive sulfate environments.

4 RESULTS AND DISCUSSION

The composition of cement-sand samples should be 1:3 (Cement : Volsky sand), and the water-cement ratio is 0.6. The mobility of the mortar is 75-80 mm of immersion of the cone "StroiTsNIILa".

The prepared mortar is transferred to a pre-wiped wet cloth stirrer bowl stirred in it for 2.5 minutes (20 revolutions of the stirrer bowl)

The samples are compacted on a shaking table (30 blows for 30+5 s).

After manufacturing, the samples are stored in the molds for 24 +2 hours in a bath with a hydrovlichicheskom shutter. Then the samples are unmolded and placed in tubs with drinking water in a horizontal position so that they do not touch each other. The water should cover the specimens by at least 20 mm. The distance between the samples must also be at least 20 mm.

After 28 days from the date of their manufacture, the samples are removed from water and placed in Na_2SO_4 solution. The amount of corrosive solution should be not less than 100 ml for each specimen. Control specimens are left to harden in water until the moment of testing. The change of solution is made when the concentration of sulfate ion in the test solution decreases by no more than 10%, which is established by determining the concentration of the initial solution. It is not allowed to restore the initial concentration of aggressive solutions by adding salt or concentrated solutions.

Concentration control of working aggressive solutions during their preparation is carried out by the density of solutions, which is controlled by measuring their density using areometers at a given temperature, at a temperature of 20+2 ^{0}C. Determination of flexural strength of specimens is carried out after 56 days, 6 and 12 months. The number of specimens for one test period should be at least 10. It is recommended to make control long-term tests in terms of 1, 2 and 3 years. The test shall be performed not later than 1 hour after the specimens have been removed from the solution. The specimens shall be wiped dry before testing.

Concrete specimens are stored in sulphate mortar for the same period as cement-sand specimens, with the only difference being that the amount of aggressive mortar must be such that it covers the specimen on all sides by at least 20 mm.

A quantitative characteristic of cement durability is the durability coefficient (K_{st}), which is calculated as the ratio of the flexural strength of samples tested in Na_2SO_4 solution to the strength of control samples cured in water.

We tested concrete made on Portland cement of 400 DO grade. As a coarse aggregate we used crushed stone of Koturbulak deposit of 5-20 mm fraction, fine aggregate was sand with a coarseness modulus of 2.2.

The data analysis showed that when cement is mixed with a suspension of activated micro silica, it leads to intensification of the hydration process and binding of formed calcium hydroxide ($Ca(OH)_2$) by micro silica to the formation of low basic calcium hydrosilicates, which causes its reduction by more than 23% relative to pure cement stone, reduction of the intensity of analytical lines (C_3S), and, accordingly, compaction and strengthening of the cement stone structure.

The strength of concrete with complex additives was studied on different concretes. In all cases, equilibrated mixtures with stiffness of 20-21 s were used, which were obtained by reducing the water content. The results obtained are presented in Table 1.

Table 1
Effect of complex chemical admixtures on concrete strength

№	Additive content, %			Concrete density, kg/m³	Compressive strength, MPa, at the age of		
	Master Air 200	Master Rheobuild 1000	C-3		7 days heat and humidity treatments	28 days heat and humidity treatments	28 days of curing under normal conditions
1	0	0	0	2385	30,8	41.4	41.8
2	0.6	0	0	2400	36.1	53.7	53.0
3	0.6	1.0	0	2400	37.4	55.5	54.2
4	0.6	1.0	0.16	2380	39.1	58.8	57.2
5	0	0	0	1930	23.8	32.0	34.6
6	0.6	0	0	1940	26.8	39.6	40.1
7	0.6	1.0	0	1940	28.8	39.9	41.0
8	0.6	1.0	0.16	1935	27.0	38.9	39.6

From the obtained results it follows that at introduction of Master Air 200 the strength of heavy concrete at the age of 12 hours after heat and humidity treatment increases by 17%, and in 28-day curing by 30%; after 28 days of curing in normal conditions by 27%. At introduction of complex admixture Master Air 200+Master Rheobuild 1000 the strength of heavy concrete at the age of 12 hours after heat and humidity treatment increases by 20%, and in 28-day curing by 34%; after 28 days of curing in normal conditions by 30%. At introduction of complex admixture Master Air 200+Master Rheobuild 1000+C-3 the strength of heavy concrete at the age of 12 hours after heat and humidity treatments increases by 27%, and in 28-day by 42%; after 28 days of curing in normal conditions by 37%.

At introduction of Master Air 200 the strength of concrete at the age of 12 hours after heat and humidity treatment increases by 13%, and in 28-day curing by 24%; after 28 days of curing in normal conditions by 16%. At introduction of complex admixture Master Air 200+Master Rheobuild 1000 the strength of concrete at the age of 12 hours after heat and humidity treatment increases by 21%, and in 28-day by 25%; after 28 days of curing in normal conditions by 19%. At introduction of complex admixture Master Air 200+Master Rheobuild 1000+C-3 the strength of concrete at the age of 12 hours after heat and humidity treatment increases by 14%, and in 23-day by 22%; after 28 days of curing in normal conditions by 14%.

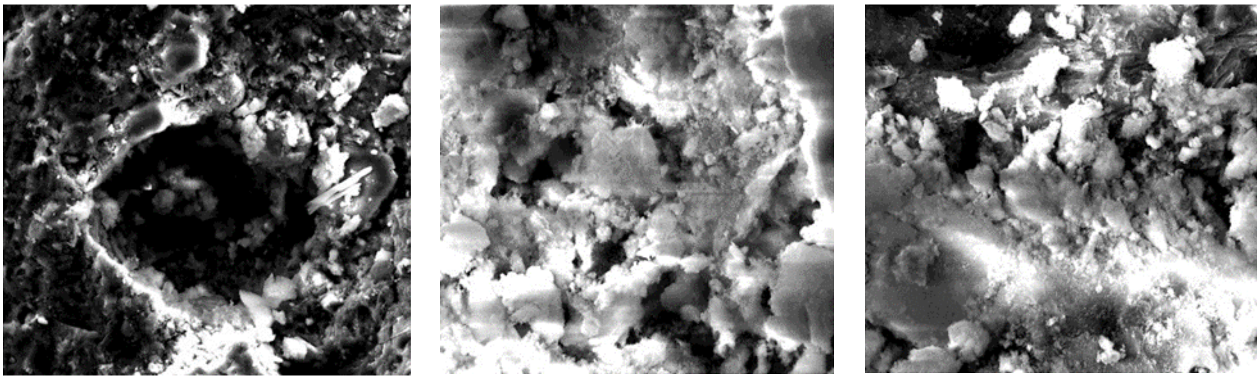
From the analysis of the obtained results it follows that when Master Air 200 or Master Air 200+Master Rheobuild 1000 additives are introduced, the strength of lightened heavy concrete increases more intensively in all cases. When the complex admixture Master Air 200+Master Rheobuild 1000+C-3 is introduced, the strength of the concrete decreases by 3-7% and the strength of the concrete increases by 6 - 8%. It follows that the technological effects achieved by the introduction of Master Air 200 and Master Air 200+Master Rheobuild 1000 additives into concrete are equivalent. The use of Master Air 200+Master Rheobuild 1000+C-3 complex admixture in concrete is more effective than in other admixtures.

Analysis of the study of the microstructure of cement stone of three compositions, showed the presence of clusters of elongated tubular crystals in the form of "needles", which are characteristic of the morphology of ettringite, formed in the zone of micropore formation.

It is established that in the crystals of the modified cement stone their size decreases from 80 to 110 nm, which is much lower than in the control composition - from 200 to 300 nm and from 100 to 200 nm. The established changes are connected with formation of additional amount of low-base calcium hydrosilicates due to alkaline excitation of silica-containing particles.

The cement stone was found to have a denser and more homogeneous fine porous structure with micropore sizes ranging from 0.1 to 1 μm Figure 1 (c) in the composition (Portland cement +

micro silica + Master Air 200), the main range was from 2 to 5 μm **Figure 1(b)** in the control sample, from 2 to 10 μm **Figure 1 (a)** with the presence of pores up to 100 μm.



(a) **(b)** **(c)**

Figure 1 – Microstructure of cement stone: (a) control sample; (b) portland cement + micro silica; (c) portland cement + micro silica + Master Air 200

The obtained positive results of cement stone modification formed the basis for the development of concrete composition with a given complex of operational properties.

5 CONCLUSIONS

Tests of concrete samples after 6 months of exposure in Master Air 200 solution of 5% concentration showed that the flexural strength of concrete increased compared to the initial one by about 5-7%. This can be explained by the fact that probably the process of cement hydration is still ongoing (due to the presence of sufficient clinker stock) and the absence of calcium hydroxide binding components in the concrete. In addition, the introduction of Master Air 200 into the concrete mix compacted the concrete structure due to its polymerization in the pores and capillaries, which increased the water resistance of concrete W12. It should be noted that similar effect on the influence on technological parameters of concrete mix and concrete.

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