Dissertation

Master in Civil Engineering – Building Construction

Corrosion resistance of cement composites modified with polymeric additives

Anastasiya Lastouskaya

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Leiria, *November of 2019*

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RESUME

ABSTRACT

Ensuring the durability of buildings and structures is of great importance in the construction industry. Degradation of building structures has significant economical impacts and requires a lot of resources. Despite a large number of works devoted to the corrosion resistance, the question still relevant today.

Common strategies for increasing the corrosion resistance of concrete in an aggressive environment is the use of products to slow the diffusion or penetration depth of contaminants in the cement matrix [1].Corrosion resistance in a cement based matrix can be increased, through judicious selection of binders and the use of polymer additives which react with the cement matrix creating various mechanisms that reduces or eliminates the conduction contact area for corrosive components of the environment [1]. The effect of additives on the properties of polymer composites of cement due to their chemical composition and curing conditions is known. Polymer additives, depending on the dosage may either increase or decrease the strength characteristics.

The emergence in the construction industry of the Republic of Belarus of new types of polymer additives justifies the current research on their use and their impact on the physical and mechanical properties of cement-based products, including their corrosion resistance.

The current study focuses on polymers based on both vinyl acetate-ethylene copolymer and acrylic emulsion polymer as a modifier for cement based composites

Keywords: aggressive environment, sodium sulfate, sulfate corrosion, polymer additives, methods for determining the durability of concrete.

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1. INTRODUCTION

1.1 Preface

The durability of concrete and reinforced concrete depends on a large number of factors that affect the operation, type and composition of concrete, as well as the degree of aggressiveness of groundwater. In fresh water bodies, the sulfate content is 60 mg / l, in mineralized groundwater – 200 - 400 mg / l, and in seawater – 2500 - 2700 mg / l [2]. Sulfates located in an aggressive environment in contact with cement stone can significantly increase the solubility of the components of the cement stone and cause the development of exchange reactions with the substitution of the cation in the sulfate for calcium ion from cement stone (second type corrosion). At the same time, the effect of sulfates can cause the development of corrosion processes of the third type [3]. In connection with this study of the effect of polymer additives based on vinyl acetate-copolymer of ethylene and acrylic, Dow Chemical Company trademarks, the resistance of cement stone to sulfate corrosion is an obvious factor.

1.2 Objectives

The aim of the master's thesis is to study the effect of polymer additives on the physic-mechanical characteristics of cement composites and to determine the sulfate resistance of cement composites modified with polymer additives.

To achieve this goal, the following tasks solved:

1. The analysis of modern ideas about the use of polymer additives in concrete;
2. The effect of polymer additives based on vinyl acetate-ethylene acrylate copolymer on the mobility of cement paste, the density and strength of cement stone and cement-sand mortar was research;
3. The effect of heat treatment has been research and effective hardening modes have been determined using polymer additives;
4. The sulfate resistance of cement stone modified with polymer additives investigated.
5. Work done to study the effect of a polymer additive based on a vinyl acetate copolymer on the density and strength of concrete.

1.3 Structure

Present research work consists of 5 chapters. Chapter 1 contains the introduction, objectives and structure of the work done.

Chapter 2 presents an analysis of the global practice of using polymer additives in cement composites. Studying the effect of heat treatment on the strength characteristics of modified cement stone, as well as methods for studying sulfate corrosion of cement concrete.

Chapter 3 describes the main materials, techniques and equipment used in research work.

The main experimental work is set forth in Chapter 4. This chapter presents the results: The results of a study of the effect of polymer additives based on vinyl acetate-ethylene copolymer of the Dow Chemical Company trademark on the mobility of cement paste, the density and strength of cement stone and cement-sand mortar; Experimental data on the influence of temperature and hardening modes on the strength of modified composites; The results of studies of the sulfate resistance of cement stone modified with polymer additives based on vinyl acetate-ethylene-acrylic copolymer; The results of a study of the effect of the polymer additive DLP2141 on the strength characteristics of concrete.

Chapter 5 outlines the conclusions on the work done and the results.

2. MODERN PRESENTATIONS ABOUT APPLICATION OF POLYMERIC ADDITIVES

2.1 The use of polymer additives in the composition of cement composites

Polymeric materials due to their properties are widely used in the construction: as an additive in concrete or mortar mix as an additional binder component for impregnating concrete products, for the production of dry mortars. Recently, it increased significantly application of polymers as additives Cement concretes and mortars.

Polymer concrete (or PC) is a composite material consisting of aggregate, filler and polymeric binder, by replacing conventional hydraulic cement by polymeric resins. Polymer concrete has many advantages compared with Portland cement concrete, such as rapid curing, high mechanical strength, high resistance to chemicals etc. [4,5].Concrete-polymer composites can be classified into polymer concrete, polymer cement concrete and polymer modified concrete, resin impregnated, among which the polymer concrete is well known for its versatile design using [6-9].

The authors [10] examined the state of polymer and its use as a sustainable building material. The analysis of the use of polymer additives and their advantages over conventional compositions cement composites. Obtained indicators such as high mechanical properties, rapid curing, durability and resistance to chemical and biological attack.

Strength characteristics of polymer concrete depends on the quality of materials, their proportions, and space and exposure conditions. Quality of raw materials used in clinker production, firing conditions, fineness and particle size of cement, water cement ratio, all these variables have significant influence on the physicochemical characteristics of the cement paste. Also, the type of cement, the nature of the aggregates, water, mixing temperature, additives and curing conditions determine the mechanical properties and durability of concrete [11].

Concrete based on Portland cement is the main material supporting and enclosing structures used in modern industrial and civil construction. The complex of adverse effects: alternating moistening - drying, freeze - thawing, exposure to active corrosion relative to the cement stone materials, concrete leads to corrosion manifests itself in the reduction of material strength and deterioration in performance of this product [12-14].

Defined [14] that the corrosion resistance of the concrete is determined by two major parameters - permeability to aggressive environment and ability of cement paste and aggregate chemically to react with the components of corrosive environment. Studies [12, 13] have shown the relation between the mass transfer in the material structure and the processes of cement stone degradation. The lower the rate of mass transfer, the higher the corrosion resistance of cement matrix.

Major disadvantages of polymer concrete are related with their fragility, pronounced creep, and shrinkage, low thermal resistance. To reduce the brittleness of polymer concrete are used in their formulation fibers of asbestos, glass and others. To regulate viability in the polymer concrete mixture based on urea resins is suggested [15] the inclusion of ferric chloride and a mineral filler (porcelain flour, silica sand). Reduced combustibility while maintaining the values of physical and mechanical properties at elevated temperatures are achieved using a composition of polymer concrete based on a low molecular weight polybutadiene of sulfur, thiuram, captax, zinc oxide, calcium oxide, silica sand, crushed granite, and flame retardant - aluminum hydroxide [16].

A separate group are concretepolimery. Concretepolimery - a cement concrete, impregnated after curing by low viscosity monomers or oligomers, liquid, for example, styrene, and methyl methacrylate. After the heat treatment, these monomers proceeds in polymers, filling the pores and other defects of the concrete by solid polystyrene or polymethyl methacrylate. This treatment promotes a drastic increase in strength (100 MPa), cold resistance, durability, hardly permeable [17].

Currently, much attention is given to the polymers that are produced in the regional chemical enterprises. For example, low molecular weight polyethylene is a byproduct of the synthesis of large-tonnage production of high-pressure polyethylene. In [18] performed a study on the development ofpolymeric additives based on aqueous dispersions of (meth) acrylic polymers - polymethacrylates (PMA), polyacrylates (PA), thermal decomposition products of the polyamide-6 in the medium oils and low molecular weight polyethylene (NMPE). The resulting mixture of low molecular weight polyamides (NMPA) with an average molecular weight of 3400 ... 8600 was used as independent and in the complex additive for concrete. Based on data obtained during the study [18], it was established that the polymeric additives are plasticizing additives, they slow down the curing of concrete mixtures and reduce the water-cement ratio of from 6,5% - to 19,4%. Additives in an amount of 0,5 ... to 0,7% increases the strength of the concrete samples V22,5 for 28 days under the conditions of air-dry hardening compared with the standard to 28,2%. Polymer additives increase the water-resistance of concrete V 22,5 compared to standard up to 195 times. Optimal complex additive that increases the time cement slurry setting, water resistance and compressive strength of concrete is the composition of a mixture of polyacrylates and polymethacrylates (PA and PMA), thermal decomposition products of the polyamide-6 (NMPA) and low molecular weight polyethylene (NMPE) in the ratio 1: 1 : 0,5 (wt.) [18].

In [19] as a fine concrete additive is proposed to use an acrylic dispersion grade VDSM-KI-02-04, intended for the paint industry, which is a styrene polymer and acrylic monomers, the resulting emulsion method. Acrylic dispersion is applied as a film former. Well it combined with many modern polymers, additives and ingredients.

Using additives in cement composites can be adjusted basic construction and technical properties and give a new quality of the material. By varying, the composition of the material with the help of additives may be: increase the plasticity, increased strength, improved water resistance, to accelerate or retard setting time, etc.

When administered polymer additives significantly reduced water-cement ratio, which was found in [20, 21].

Dosages polymeric additive for mortars on mineral binders, usually in the range of 1-5%. The optimum dosage is established based on the need to achieve the maximum values of useful properties (or set of core properties) at minimum cost [22, 23].

Polymer-cement mixture due to the presence of surfactants typically is good foaming agents, characterized by the ability to entrain air into the mortar mix. The air stored in the mortar in the form of tiny bubbles, and its volume may reach 30% of the solution volume.

The results of studies of the effect of additives on polymer complex hydration processes are reflected in [24-27] have shown that the additives do not affect the hydration process.

In [28] found that in the polymer-cement slurries of polymers or the polymerization process occurs before the cement hydration or hydration process in parallel. In comparison with conventional solutions, polymer-cement mortars are more resistant to the effects of the dynamic forces are capable of conversion and dissipation of energy, are very large values of compressive strength, flexural, tensile, higher adhesion and low water resistance. Using such compositions, as a rule, for the construction of staircases, roads, floors, repair of concrete building of the new to the old, to eliminate the cracks, strengthening floors, anti-corrosion protection.

The established method of localization (distribution) polymer films and bonds for stone that quality does not depend on the dosage of re-dispersible powder (PSC) and the nature of the considered polymer-based and does not change with an increase in dosage over rational values. It is revealed that a portion of the water-soluble polymer is concentrated at the interface "entrained air - solution" and in most cases leads to increased local shrinkage strain [29]

2.2 Conditions of curing cement paste with polymer additives

Under normal conditions the film formation process in the cement stone - the polymeric composition finishes within 48 hours curing systems [30].

Contrary to popular belief that the process of film formation does not occur at temperatures below the film-forming temperature in the course of [30], it was found that the film still is formed as indicated and indexes changes deformation values and strength of the samples as polymers and cement - polymer compositions. Reducing mother strength occurs because of significant deceleration cement hydration process, and improving deformability characteristic values corresponds to a deeper penetration of the polymer matrix in the form of a film in a matrix of the mineral binder.

The physico-mechanical characteristics of cement compositions, the modified polymers are affected by numerous factors. In [30-32], the results on the effect of curing conditions on the strength of the cement-polymer compositions. It is found that at high temperatures the polymer with a high film formation temperature increases the strength characteristics of the cement-polymer compositions, but reduces deformation characteristics. Under normal conditions, the process of film formation in a polymer-cement stone finishes within 48h curing system.

Defined [33] that the compressive strength of the cement composite decreases with increasing amounts of polymer so as polymers retard the cement hydration. Established [22, 34], that the part of the water-soluble polymer can be concentrated at the interface "entrained air - solution" phases. The fine, uniformly distributed air exerts a plasticizing effect on the cement paste, resulting in increasing their diameter face breaking. Results [35, 36], the interaction of polymer additives with other raw materials, can lead to the capture of a significant amount of air during mixing.

2.3 Sulfate resistance of cement stone

The durability of concrete and reinforced concrete depends on many factors, the main of which are the operating conditions, the type and composition of the concrete, as well as the degree of aggressiveness of groundwater to which the structures are subjected. As is well known [37], the main cause of destruction of concrete arrays in contact with groundwater zone is the corrosion of cement concrete matrix. Greatest destructive effect on the concrete regardless of the composition and structure of concrete, type of construction, nature and amount of the workload, conditions of service provides sulfate corrosion.

Formation and destruction of calcium hydrogen-aluminate is an important chemical process. The study of the mineralogical composition of cement stone samples stored in a sulfate environment, showed that the cement stone binds a significant amount of SO_4 [38]. The more cement tricalcium aluminate (C_3A), the more ions SO_4^- bound, ie. e. absorption is sulfoaluminate character [39].

The corrosion resistance of concrete is determined by two major parameters - permeability to aggressive media and ability of cement paste and aggregate chemically react with the components of corrosive media. Low permeability concrete is provided a complex of events: applying hydrophobic and water-reducing additives, the purpose of particle size distribution of aggregates and mineral additives provides a concrete structure with a minimum volume and minimum pore sizes and capillaries; effective compaction of concrete mix, the optimum modes hardening.

Transferring concrete in aggressive media porous body is carried out by the mechanism of viscous flow under pressure gradient and capillary forces and diffusion transfer mechanism, in the presence of a gradient of concentration of the aggressive matter.

The essence of the corrosion processes occurring in the concrete in sulfate environment, is to form a structure of concrete and gypsum gidrosulfoalyuminatov with increasing volume of hard phases, which causes the appearance of internal stresses exceeding the strength of the concrete and concrete-destroying. Sulfate corrosion occurs when subjected sulfate solution [40].

Effective measure of protection from sulfate corrosion is to reduce the permeability of the concrete for the SO_4 ions$^-$Coming from the aggressive environment. Introducing additives into the concrete complexes, including effective water reducing and mineral, achieve this. In recent decades, the attention of researchers have drawn two destructive process - after the formation of ettringite and $3CaO\text{-}Al_2O_3\text{-}3CaSO_4\text{-}32H_2O$ taumasita CA_6 $[Si\ (OH)_6]_2$ $(SO_4)_2$ $(CO_3)_2\text{-}24H_2O$. Review of domestic and foreign works on education and ettringite taumasita given in [41,42].

Shown [41,42] that the interaction of components of cement concrete matrix with an aggressive environment formed colmatant two types: 1st consists of silica gel, which is formed by reaction of cement stone silicate component with an aggressive environment; type 2 is formed by the chemical reaction of components aggressive environment with the main parts of cement paste containing calcium ions $CaCO_3$, Mg $(OH)_2$, etc.

One effective way to reduce the intensity of mass transfer and, accordingly, for obtaining concrete high resistance to corrosion is the use of polymers in cement concretes. The polymers may partially or fully replace mineral binder (polymer concrete) impregnated concrete after curing (concrete polymer) or polymer emulsions are used as additives in concrete. A detailed analysis of structure and properties of polymer concretes made Paturoev V.V. [33].

2.4 Test methods for sulfate resistance

Currently practiced methods of reducing the corrosion resistance tests are often strongly distort the physic-chemical processes occurring in the interaction of components of the materials with the dirty environment and can give unreliable results, which should be considered when choosing methods. To comply with the laws of similarity and dimensions when the latter is recommended to use dimensionless selection criteria reflecting geometric similarity, the time factor, the diffusion characteristics of the material, etc.

The corrosion test lasts a very long time, hence the understandable desire of researchers to find such methods to obtain reliable results in the shortest possible time. To test for resistance to cement chemical aggression samples of cement composites is usually used which are placed in the proper aggressive environment. Then follow the change in appearance of the samples are tested for their flexural strength and compression, expansion determined value of dynamic modulus of elasticity, etc.

Designed V.V. Kindy method of small samples [13] is a variation of the method of Koch and Shteynegger [43]. The samples he applied prism dimensions 1x1x3 cm, as a filler - sand, a larger than usual (Wolski with Mcr = 2.4-2.5), to give samples of a porous structure. With this aggressive solutions are easier to penetrate into the sample and quickly destroy it, allowing for faster test times.

Anstett [44] proposed a test method for cement sulfate, based on the measurement of the expansion cylinder-pressed samples of crushed hardened cement stone supplemented with 50% (wt.) Of gypsum dihydrate placed in wet conditions. Sulfate was estimated to expand the diameter of the test sample, which should not exceed 1.25%.

Miller [45] turned again to the measuring method of expansion of samples in sulfate environment, with dimensions 5x10 cm cylinders. It is found that the elongation of samples of 0.25 mm per 10 cm of length corresponds to a loss of strength

50-70%. On resistance of samples can also be judged by how much time is required to expand them in the sulfate solution at 0.25 mm. Later, however, Miller [46] concluded that a lack of reliability of their early experiments.

Torvaldson, Larm and Vigfusson [47] as a measure of aggression received value swelling samples in sulfate solutions, and they were compared between a flexural strength of cement mortar samples of 1: 3 after storage in water and sodium sulfate, and expanding prisms of the same composition.

Merriman [48] developed and applied the accelerated sulfate resistance test method. He made plate samples measuring 5x10x10,6 cm from pure cement dough and, after daily storage in molds in a moist chamber, placed in a 10% solution of sodium sulfate. Merriman considered the absence of cracks and distortions in the samples after 28-day storage as a sign of sulfate resistance.

2.5 Chapter summary

1. With the help of polymer additives, it is possible to regulate the physic-mechanical characteristics of cement composites. It is recommended to use them in an amount of 1% to 15%.
2. During the heat treatment of cement composites with polymer additives, the strength characteristics increase by two times. To accelerate the polymerization process, curing modes with a temperature higher than the film-forming temperature of polymer additives are used.
3. Polymer additives improve the sulfate resistance of cement composites. Polymer additives in the composition of cement composites slow down the corrosion process in the structure of cement composites. To determine sulfate resistance, methods of the accelerated process are used to obtain results in the shortest possible time.

3. Characteristics of the materials used and methods of research

3.1 Characteristics of the materials used in the studies

For research use of cements of "Belarusian Cement Plant", satisfying the requirements of GOST 31108-2003 [49].

The physic-mechanical characteristics shown in table 3.1.

Table 3.1 – Physical and mechanical properties of cement

Cement type and name of the manufacturer	Density, kg / m^3	NGTST %	Setting time, hr-m		Activit, MPa
			Start	end	
Portland cement CEM I, (42,5N) Kostyukovichi	3200	25,0	3-10	4-50	45

As a fine aggregate used sand, quarry "Borovoe" satisfying the requirements of GOST 8736-2014 [50], whose characteristics are listed in table 3.2.

Table 3.2 – Characteristics of sand

Bulk density, kg / m^3	Density grains kg / m^3	Content silty and clay particles,%	Emptiness, %	Humidity, %
1567	2650	2,5	39,2	5,26

Sand quality assessed according to GOST 8735-88[51]. Determination results of size distribution shown in table 3.3.

Table 3.3 – Grain size distribution of sand

Dimensions sieve holes, mm	2,5	1,25	0,63	0,315	0,16	m. 0,16
Private residues %	5,5	8,5	21,5	34,0	28,5	2,0
Full residues %	5,5	14,0	35,5	69,5	98,0	100

According to test results the sand belongs to the group of middle-class II module size $M_{fineness}$ = 2.23.

The additives used in the polymer additive based on acrylic Primal SM330 and polymeric additives an ethylene vinyl acetate copolymer DLP2141 and DLP2000 trademark Dow Chemical Company. Polymer additive Primal SM330 is lactic, white liquid, specific gravity 1.06 g / cm^3 dry residue was 46,5-47,5%, pH -. 9,5-10,5, MFFT t = 10 ^{0}C. Polymer additiveDLP2141 - white free flowing powder based on a vinyl acetate-ethylene copolymer, the residual humidity max. 2%, the bulk density of 0,400-0,550 g/ml, zolnost10-14%, pH-7,5 , MFFT t= 3^{0}C. DLP2000 is a white free flowing powder based on a vinyl acetate-ethylene copolymer, the residual humidity max. 2 %, the bulk density of 0,375-0,525 ml /g, ash content of 10-14%, pH-6 MFFT t= 3 ^{0}C.

To mix the cement paste and mortar, tap water used, which corresponded to the requirements of STB 1114-98 [52].

3.2 The methodology of the research

Studies conducted using standardized techniques. Cements tested in accordance with GOST 31108-2003 [49]. Sand quality assessed according to GOST 8735-88. [51]

To determine the strength of the cement stone produced samples cubes with an edge of 20 mm. Compressive strength was determined by a modified stone aged 7 days and 28 days of hardening under various conditions.

Determination of strength of cement-sand mortar carried out according to the procedure STB EN 196-1 / PR [53]. Summary technique is to compare the compressive strength and bending strength of mortars produced from Portland cement (the control composition) with compressive strength and bending strength of mortars produced from Portland cement modified with polymer additives. For the test, samples were made ravine-size 40x40x160 mm. Thermal treatment of the samples was carried out in an oven SNOL 120/300 (Figure 3.1.).

Figure 3.1. - Drying chamber SNOL 120/300

Determination of concrete mix mobility performed according GOST 10181-2014 [54]. Strength of the concrete determined by GOST 10180-2012[55]. Determination of strength was carried out on a test press PGM 1000MG4 (Figure 3.2.).

Figure 3.2. - Test press PGM 1000MG4

3.3 The method for determining sulfate corrosion

It is known that corrosion processes of materials are slow, therefore the study of these processes, the researchers give preference methods, which allow obtaining reliable results in a short time.

To determine the sulfate corrosion of cement paste with the additives Primal SM 330, DLP2141 and DLP2000, the basis of technique, rapid determination of Sulfate concrete presented in the manual [56] adopted. This method based on a comparison of the absorption rate of aggressive ions SO_4^{2-} test cement stone. To determine sulfate conventional Portland cement concrete samples made cubes measuring 50×50×50 mm cubes hardening should be conducted by mode corresponding to the heat treatment regime for specific structural elements.

Concrete composition are selected to provide brand waterproofing least V8. For each test made on six twin samples from one batch. Samples placed in a desiccator and pour a solution of sodium sulfate in an amount of 5 l prepared based 2.8 g of anhydrous sodium sulfate (Na_2SO_4) in 1 l of distilled water. If test samples give different compositions of concrete, sodium sulfate solution should be prepare directly on the workload.

After installation of the samples in an aggressive solution, at a time corresponding to 1, 3, 6, 9 and 12 weeks of each desiccator pipetted sample solution to determine the aggressive ions SO_4^{2-} in an amount of 100 ml. The content of SO_4^{2-} ions in each sample is determined and aggressive initial solution prepared for the test cubes. To determine the content of sulfate ions in solution in the test solution sampled in an amount of 100 ml is added 1 ml of concentrated HCl was heated on a hot plate almost to boiling. In 25 ml of a 2.5% solution of BaCl solution warmed to reflux, was added with stirring the test solution and allowed to warm hot plate for 3 h, covered with a glass with a watch glass test solution, cooling the solution to room temperature, it was filtered through a dense filter (blue ribbon). The precipitate was quantitatively transferred to a filter and washed with warm water until the washing waters in response to the chloride ion (as silver nitrate). Filter the precipitate was transferred to a crucible and dried in an oven and calcined at a temperature of 800 - 900 ° C to constant weight. The content of sulfate ions SO_4^{2-} in a solution Q_{SO4} p, mg / l.

Based on a review of methods for determining the resistance to sulfate corrosion given in section 1.4, and accelerated method of determining sulfate-cement composites was performed by following the procedure described above.

Previously, it has been found that the dosage of the test polymer additives should not exceed 3% by weight of cement, and the most favorable temperature mode is a processing mode with the temperature t = 60^0C for 2 hours.

At a given dosage and solidification mode were prepared samples cubes with an edge of 20 mm. At the age of 7 days, when the cement stone gaining 70% strength, moisture was determined using samples of moisture MG4B, weighed on scales VK-300 and determined by their geometrical characteristics, then immersed in a corrosive solution.

To prepare 2% solution was used Sodium sulfate decahydrate $Na_2SO_4 \cdot 10H_2O$. Sodium sulfate crystallises from aqueous solutions with ten water molecules ($Na_2SO_4 \times 10H_2O$), and as such is called Glauber's salt. Physical properties of sodium sulfate are presented in table 3.4.

Table 3.4 – Basic the physical properties of sodium sulfate

Molecular formula	Na_2SO_4
Molar mass	142
Density (20^0C) g / cm^3	2,68
Melting point, ° C	883

Solubility in water (20^{0}C), g / 100 ml	19,2

Determination salt mass and weight of the solution determined by the following method:

Molar mass Na_2SO_4= 142,04 g / mol

Molecular mass Na_2SO_4 = 142,04 + 10 × 18 = 322,19 g / mol

For one liter of distilled water, count the number of moles:

$0.02 = \frac{142n}{1000+322n}$ => n = 0,1475 moles

Determine the weight of Glauber's salt:

m ($Na_2SO_4 \cdot 10H_2O$) = 0,1475 × 322 = 47,5g.

Upon reaching 28 and 60 days of finding modified cement paste in a corrosive environment, the samples were removed from the solution, dried to a constant weight, then were tested for compressive strength at press PGM-500MG4A also determined sample weight were measured geometric features and fixed external changes specimens -Threefold.

Test specimens for compression and bending carried out in accordance with GOST 10180-2012 [55] on a test press PGM-500MG4A (Figure 3.3), which provides a fully automatic operation.

The dimensions of the finished samples checked using a type I digital caliper. Ranges 0-150 mm, measurement speed - not more than 1,5 m / s. Caliper complies with GOST 166-89 [57].

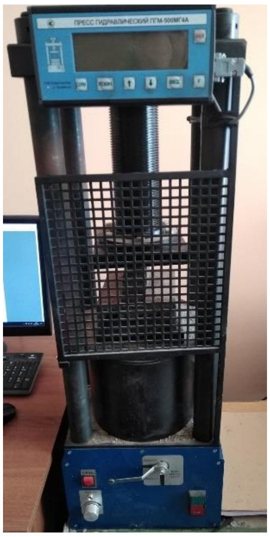

Figure 3.3. - Test press PGM-500MG4A

Humidity samples was determined hygrometer MG4B (Figure.3.4.).

Figure 3.4. - Moisture MG4B

Weight samples was determined using an electronic balance VC-300 (Figure 3.5.). Laboratory scales VC-300 used for accurate mass measurement. This type of electronic scales used in industrial laboratories where increased accuracy is required. Electronic balance laboratory VC-300 Class II production precision "Weight-to" may operate with multiple units of weight and measure different weighting modes.

Figure 3.5. - Libra VC-300

3.4 Chapter summary

1. Physic-mechanical characteristics of cement. Characterization of sand and its particle size distribution. The chemical composition of polymer additives DLP2141, DLP2000 and Primal SM330.
2. Standardized test methods. Methods for determining the strength of cement stone, mortar, concrete.
3. An accelerated method for the determination of sulfate corrosion on small samples of cement stone in an aggressive environment. Preparation of 2% sodium sulfate solution for use as an aggressive medium.

4. Physical and mechanical characteristics cement composites modified with polymer additives

4.1 The effect of polymer additives on the mobility of cement pasted with polymer additives

The introduction of polymer additives in cement affects the mobility of cement paste, cement stone strength and a number of other indicators. Established [22, 34], that the part of the water-soluble polymer can be concentrated at the interface "entrained air - solution" phases. The fine, uniformly distributed air exerts a plasticizing effect on the cement paste, resulting in increasing their diameter face breaking.

It is found that the dosage of polymer additives using mineral binding agents are usually in the range of 1-5% [22]. The optimum dosage is established based on the need to achieve maximum values at the maximum strength values of the mobility of the cement paste.

In the first stage of the study investigated the effect of polymer additives Primal SM300, DLP2141, DLP2000 the mobility of the cement paste. Samples- cubes with an edge of 20 mm were investigated at two modes hardening: normal-humidity environment (DDP) and heat treatment t = 60℃ for 2 hours.

To determine the effect of additives on the mobility of the polymer cement paste polymeric additives introduced in an amount of 1%, 3%, 5% by weight of cement on dry matter. Water-cement ratio of 0,5 accepted. Determination of the cement paste is performed for the mobility procedure NIIZhB [58], a mini cone. Flat-cone height of 3 cm filled with cement paste with the polymer additive after raising mini cone cement paste melt, cone face breaking value determined in 2 directions metal ruler with a scale division of 1 mm (Figure 4.1).

Figure 4.1. - Definition of face breaking cement slurry with polymer additive DLP2000

Cement paste broke without polymeric additive was 6 cm. The results of the influence of polymer addition on the mobility of cement slurry shown in table 4.1 and figure 4.2.

Table 4.1 – Effect of Polymer Additives on the mobility of the cement paste

Name of polymer additives	Mobility cm of cement paste, the introduction of the additive in% of cement weight		
	1	3	5
Primal SM330	8	8,75	8,9
DLP2141	4,8	5,2	5,8
DLP2000	7,7	8,8	9,5

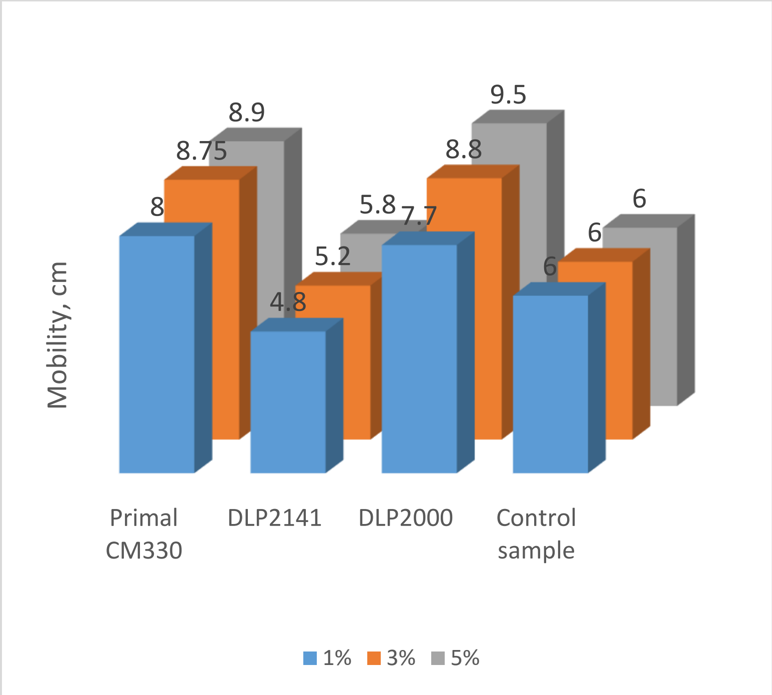

Figure 4.2. - Effect of Polymer Additives on the mobility of the cement paste at a dosage of 1%, 3%, 5% by weight of cement.

The study showed that the polymer additive DLP2141 1,2 times reduces the mobility of cement paste. Introduction DLP2000 polymeric additive increases fluidity of the cement paste in 1,45 times. By increasing the polymer dosage DLP2000 additives mobility increases. The addition of Primal SM330 increases the mobility of cement paste 1,42 times, but does not occur with increasing dosage to further increase mobility.

4.2 Effect of additives on polymer density and strength cement stone

Further study on the cement paste strength with polymer additives DLP2000, DLP2141, Primal SM300 1,3,5 conducted under dosage% by weight of cement. To determine the strength of the cement paste samples - cubes with 20 mm edge (figure

4.3). After molding, the samples hardened for 24 hours in air-dry conditions at a temperature t = 18-20° C, further for 2 hours the samples were heat-treated at 60° C, and then continued to harden in air-dry conditions at a temperature t = 18- 20°C. Before testing, the samples weighed and their geometric characteristics determined. The strength of the samples was determined on a press PGM-500MG4A aged 7 days and 28 days (Figure 4.4).

Figure 4.3. - Samples of cement stone with polymer additive
DLP 2141 (I- 1%, III-3%, V-5%)

Figure 4.4. - Samples after the test at the age of 7 days
(3% polymer additive Primal CM330)

Determination results of the strength and density of the cement stone with polymer additives Primal SM 330, DLP2141 DLP2000 and shown in table 4.2. and in figure 4.5.

Table 4.2 – Strength of the cement stone with polymer additives

Designation Polymer Additives	The amount of additive,% of the cement paste	Durability compression channel R, MPa (% R com) aged 7 days	Durability compression channel R, MPa (% R com) aged 28 days	Density, kg / m^3 aged 7 days	Density, kg / m^3 28 days
Primal SM 330	1	9,48 (62,02)	9,64 (70,49)	1508,75	1573,53
	3	14,81 (40,67)	21,49 (34,22)	1577,71	1668,45
	5	18,36 (36,44)	26,32 (19,44)	1597,50	1663,10
DLP2141	1	38,23 (53,17)	34,81 (6,64)	1820,63	1804,81
	3	34,59 (38,58)	31,41 (3,86)	1804,17	1871,66
	5	24,89 (0,28)	35,68 (9,21)	1776,25	1899,73
DLP2000	1	19,28 (22,77)	36,57 (1,93)	1697,92	1832,89
	3	21,3 (14,66)	34,31 (5,02)	1700,21	1778,07
	5	21,91 (12,22)	33,31 (1,96)	1724,58	1818,18

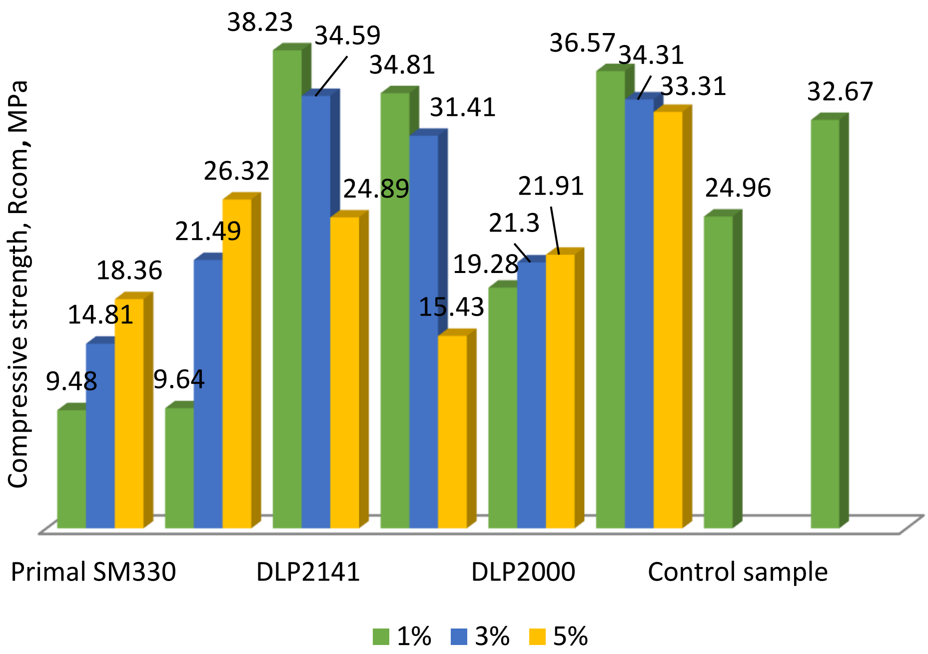

Figure 4.5. - Effect of Polymer Additives on the strength of the cement stone at 7 and 28 days

Density control sample without polymeric additive aged 7 days was 1670,31 kg/m^3, compressive strength $R_{com}^{control.}$= 24,96 MPa, aged 28 days, the density was 1757,75kg / m^3, compressive strength—32,67 MPa.

The study found that increasing the dosage of polymer additive Primal SM 330 with 1% to 5% by weight of cement, leads to increased strength of the cement stone at the age of 7 days. Thus, strength at a dosage of 1% of 9,48 MPa; at a dosage of 3% -14,81 MPa; at a dosage of 5% -18,36MPa, representing 73,6% of the strength of the control sample without additive. Cement stone modified polymeric additive Primal SM 330 in an amount of 1%, and after 28 days, compressive strength is 3 times less than the strength of the cement stone without modifications.

The polymeric additive DLP2000 causes a slight deceleration of set cement matrix strength to age 7 days strength reaches 83,45% of control values. Increased dosage has no significant effect on the rate of strength development. The greatest effect on the rate of curing had DLP2141 additive. At a dosage of 1% by weight of cement strength at 7 days reached 153,16% of the strength of a control sample; at a dosage of 3% -138,58%; at dozirovke5% -99,72%. Cement stone, modified by the addition DLP2141, has a denser structure compared to the cement matrix without the additive.

Thus, when using a polymeric additive based on vinyl acetate-ethylene copolymer DLP2141, the compressive strength of the cement stone at 7 day strength of cement stone above modified polymer additives Primal SM330 on the basis of acrylic and DLP2000. Polymeric additives lead to slower set cement paste strength process.

At the age of 28 days compressive strength of cement paste with additive DLP2000 above control values at 2% at a dosage of 1% by weight of cement; with the addition of DLP2141 at 7% at a dosage of 1%; strength cement paste with additive Primal SM 330 does not reach the reference value.

It found that the polymer additive based on DLP2141 ethylene vinyl acetate copolymer accelerates the set cement stone at an early age strength and promotes formation of a dense structure of cement stone. Dosage polymeric additiveDLP2141 should not exceed 3% by weight of cement.

Studies have shown that at a dose of additive DLP2141v amount up to 3% by weight of cement on dry matter there is no decrease in the strength after 28 days compared to the control sample without additive.

4.3 The effect of heat treatment on the strength cement stone

The next stage of the research is to study the effect of temperature on the modified cement stone. After molding, the samples hardened in two modes: a first mode (I) -to per 7 days air-dry conditions at a temperature t = 18-20°C, humidity of 60%; the second mode (II) in -24 hours air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t =

60°C in SNOL 120/300 chamber and subsequent hardening in for 6 days in an air-dry conditions at a temperature t = 18-20°C, humidity 60%.
Before testing the samples were weighed and measured their geometric characteristics. The strength of the samples was determined at 7 and 28 days in the press-SGP 500G4A. The nature of the destruction of the samples in determining the compressive strength (Figure 4.6.).

Figure 4.6. - Character fracture cement paste with a polymeric additive under compression DLP2141

Results of the study of cement paste strength with polymer additives Primal SM 330, DLP2141 DLP2000 and under various conditions of hardening shown in table 4.3.

Table 4.3 – Strength of the cement stone with polymeric additives for different modes of hardening

Designation Polymer Additives	Compressive strength Rszh, MPa (% of Rkontr) at curing conditions				Density, kg / m^3, with curing modes			
	I		II		I		II	
	aged				aged			
	7days	28days	7days	28days	7days	28days	7days	28days
Check sample (without additives)	26.6 (100)	27.8 (100)	24.96 (100)	28.6 (100)	1715.2	1590.42	1670.3	1638.13
Primal SM 330 (based acrylic)	14.62 (55.0)	22.02 (79.2)	14.81 (40.7)	20.3 (70.9)	1517.4	1415.83	1577.7	1642.98
DLP2141 (Based on ethylene-vinyl acetate copolymer)	28.26 (106.2)	28.13 (101.18)	34.59 (138.6)	29.7 (103.9)	1702.8	1497.1	1804.2	1902.19
DLP2000 (Based on ethylene-vinyl acetate copolymer)	27.57 (103.6)	29.7 (106.8)	21.3 (85.3)	32.42 (113.4)	1684.4	1508.13	1700.2	1756.8

Research has shown that when both the curing conditions there is a significant reduction in strength of cement paste with a polymeric additive Primal SM 330:

hardening in air-dry condition (mode I) by 45%, with an additional heat treatment for 2 hours at 60°C (mode II) 59,3%. Note also decrease the density values of a cement stone that explained air-entraining additives ability. Strength reduction can be due to significant adsorption of the polymer particles on the surface of cement particles hydrating, which further prevents the cement hydration process.

Test modes curing had a positive influence on the strength of the set cement matrix with polymeric additive DLP2141. Both modes hardening provided to increase the compression strength, compared with a control sample no additives: hardening in air-dry condition (mode I) of 6,2 %, with an additional heat treatment for 2 hours at 60°C(II mode) 38,6%. DLP2141 polymeric additive does not retard the cement hydration process and aging the samples for 2 hours at a temperature 60°C contributes to an active film formation and deep penetration of the polymer matrix in the mineral binder matrix, as evidenced by an increase in sample density.

Air-dry hardening conditions (mode I) had no significant effect on the strength of the cement stone with a polymeric additive DLP2141, aged 7 days compressive strength amounted to 103,6%. Processing temperature 60°C after days of hardening inair-dry conditions led to a decrease in strength by 14,7%. This fact can be explained by the fact that at the time of film formation cementitious matrix does not have sufficient strength, resulting in penetration of the polymeric matrix lead to the appearance of structural defects.

4.4 Effect of temperature and humidity conditions of hardening the strength of the modified cement stone

Hardening models affect the strength characteristics of cement composites. To determine the most effective temperature and humidity curing hardening taken five modes: a first mode (I) -to per 7 days air-dry conditions at a temperature t = 18-20°C, humidity of 60%; the second mode (II) - 24 hours air-dry conditions at a temperature t =18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60° C in SNOL 120/300 chamber and subsequent hardening in for 6 days in an air dry conditions at a temperature t = 18-20°C, humidity of 60%; the third mode (III)) -24 hours air-dry conditions at a temperature t = 18-20° C, 60% humidity, further for 4 hours treatment temperature t =60°C. SNOL 120/300 chamber and subsequent hardening for 6 days in an air-dry conditions at a temperature t = 18-20° C, humidity of 60%, a fourth (IV) mode - 24 hours of air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at a temperature t =40° C. SNOL 120/300 chamber and subsequent hardening for 6 days in an air- dry conditions at a temperature t = 18-20° C, humidity of 60%; a fifth mode (V) - during 2 hours of air-dry conditions at a temperature t = 18-20°C, humidity of 60%, followed within 2-hours heat treatment at a temperature t = 60° C. SNOL 120/300 chamber and subsequent hardening for 6 days in an air-dry conditions at a temperature t = 18-20°C, humidity 60%.

Samples of cubes with an edge of 20 mm, the modified polymeric additives Primal SM 330, DLP2141 and 2000 and DLP samples without polymer additives given in terms of hardening then aged 7 days and 28 days were tested for compressive strength at press PGM-500MG4A.

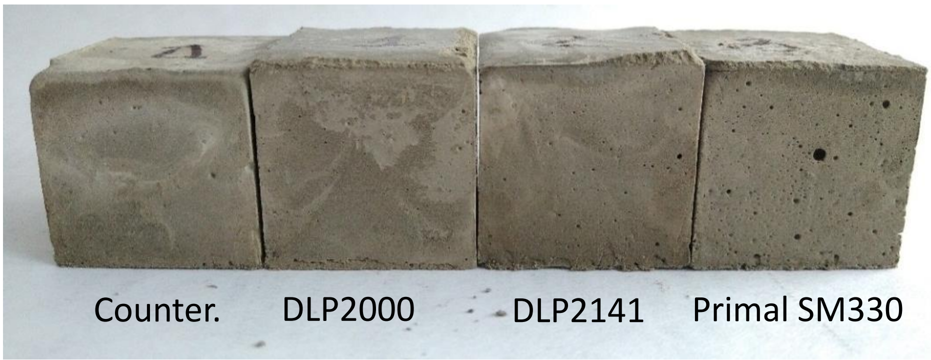

Figure 4.7. - Samples after heat treatment
(III solidification mode)

Before the test, the cement stone at the press, weighed, and samples determined by their geometric characteristics then calculated density samples. The test results of compressive strength shown in table 4.4.

Table 4.4 – Influence of the temperature and humidity conditions on the strength of the modified cement stone

Designation Polymer Additives	The amount of additive,% of the cement paste	I		II		III		IV		V	
		Strength R c, MPa (% R com) 7 days	Rszh Strength, MPa (% R com) 28 days	Durability compression channel R, MPa (% R com) 7	Durability compression channel R, MPa (% R com) 28	Durability compression channel R, MPa (% R com) 7	Durability compression channel R, MPa (% R com) 28	Strength R SJ, MPa (% R com) 7 days	Durability compression channel R, MPa (% R com) 28	Durability compression channel R, MPa (% R com) 7 days	Durability compression channel R, MPa (% R com)
Sample without additive	-	23.63 (100)	29.6 (100)	19.135 (100)	30,09 (100)	13.84 (100)	15.27 (100)	13.96 (100)	14.61 (100)	15.49 (100)	13.49 (100)
DLP2141	3	23.87 (101.01)	30.54 (103.18)	29.57 (154.53)	32.16 (106.88)	13.09 (94.58)	16.45 (107.73)	12.85 (92.05)	12.41 (84.94)	9.82 (63.4)	10.15 (75.24)
DLP2000	3	21.54 (91.15)	25.57 (86.39)	23.271 (121.62)	27.86 (92.59)	18.81 (135.9)	21.54 (141.06)	22.53 (161.039)	18.67 (127.79)	12.32 (79.53)	11.22 (85.06)
Primal SM 330	3	20.07 (84.93)	21.25 (71.79)	26.059 (136.19)	20.23 (67.23)	13.63 (98.48)	14.02 (91.81)	17.77 (127.29)	16.9 (115.67)	5.99 (38.67)	4.79 (33.28)

Depending on the choice of the temperature - humidity conditions can be obtain by different strength characteristics of materials. If the mode II, the compressive strength is increased by 5% with the use of additives DLP2141. With increasing time of heat treatment, a modified stone strength decreases by 26% compared to the compressive strength when set in the normal strength-dry conditions. The sharp decrease in strength occurs when the temperature-humidity conditions in which the initial extract samples in dry conditions normally lasted for 2 hours, after which the samples were subjected to heat treatment t = 60̊ C for 2 hours. With increasing temperature decreases from t = 60̊ to t = 40̊, modified stone strength decreases by 32%. The most efficient temperature and humidity conditions for the modified stone.

4.5 Effect of Polymer Additives on the strength characteristics of the cement-sand mortar

Determination of the influence of polymer additives on the strength characteristics of the cement-sand mortar carried out according to the procedure STB EN 196-1 / PR [59]. Samples ravine, size 40x40 mm h160 (figure 4.8.) Made of cement-sand mortar with addition of polymer additives in an amount of 3% by weight of cement. After forming, the samples hardened in two modes: a first mode (I) - in 24 hours of air-dry conditions at a temperature t = 18-20̊ C, 60% humidity and then placed in a container of water prior to the tests; the second mode (II) - 24 hours air-dry conditions at a temperature t = 18-20̊ C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60̊ C. SNOL 120/300 chamber and subsequent hardening in container with water.

Strength tests were performed on press - GMP 500MG4A. Determination results of flexural strength and compression cement-sand mortar presented in table 4.5.

Figure 4.8. - Samples before demoulding with 3% polymer additive DLP2000, without heat treatment

Table 4.5 – Flexural strength and compressive grout represented at 28 and 60 days

Designation Polymer Additives	The amount of additive,% of the cement paste	Curing condition					
		I			II		
		Durability R mfd. , MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 60 days	Durability R mfd. , MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 60 days
Sample without additive	-	6,078 (100)	2,532 (100)	3,384 (100)	6,15 (100)	2,25 (100)	3,707 (100)
DLP2141	3	5,633 (92,68)	2,151 (84,95)	2,948 (87,12)	6,84 (111,2)	2,421 (107,6)	3,204 (82,43)
DLP2000	3	5,453 (89,71)	2,001 (79,03)	3,141 (92,82)	6,31 (102,6)	2,265 (100,6)	3,427 (92,45)

According to the test results show that the flexural strength increased by the heat treatment of the modified cement-sand mortar. In the first mode, adding polymeric additive DLP2141 DLP2000 and a cement-sand mortar, the flexural strength is less than the reference value by 8 and 11%, respectively. Flexural strength of samples subjected to heat treatment at 2 and 3% above control values. Thus, the bending strength of the modified cement-sand mortar above the recruitment strength in terms II-th mode.

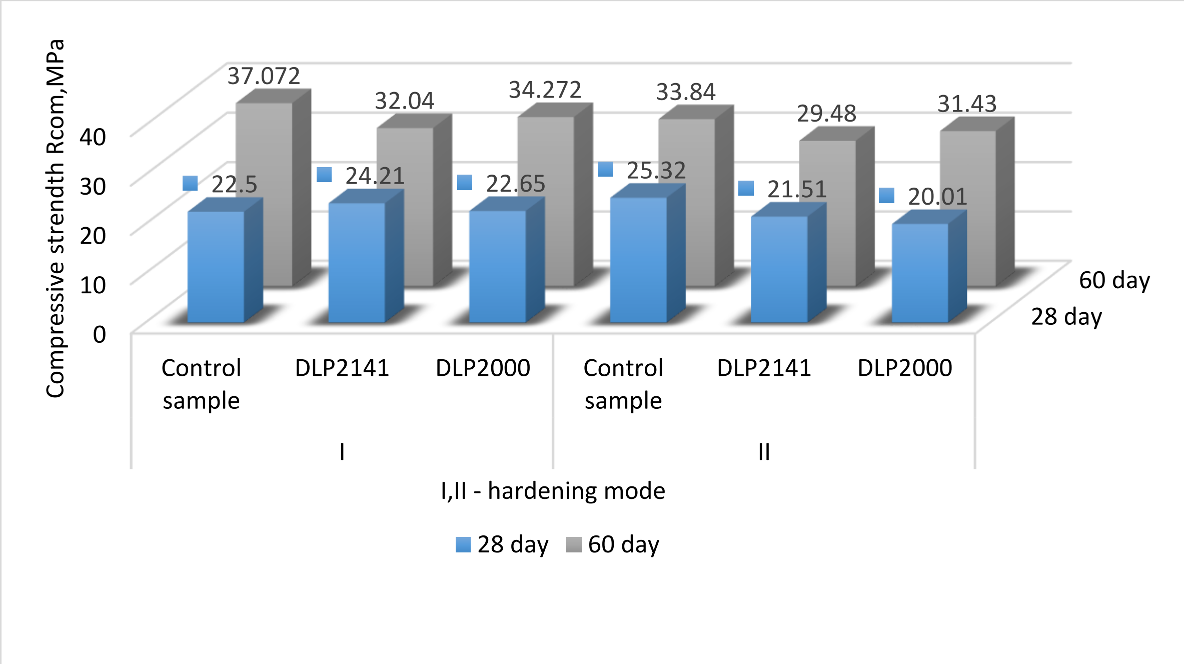

Figure 4.9. - Effect of Polymer Additives on the strength of the cement-sand mortar after 28 and 60 days.

The compressive strength of the modified cement stone above the reference values at a set of strength of cement-sand mortar under I-th mode to the age of 28 days. When added to a cement-sand additive solution based on vinyl acetate-copolymer of the compressive strength with time (from 28 to 60 days) increased by 35%. The compressive strength of the cement-sand mortar with addition of polymer additives do not reach the control values after 28 days in the I-st and the II-nd during curing modes.

4.6 Effect of polymeric additives on the strength characteristics of concrete

To determine the strength characteristics of concrete samples made with 100 mm cubes face (Figure 4.10.). During curing hardened samples at three curing modes: I - an air-dry conditions at a temperature t = 18-20°C, humidity of 60%; II - 24 hours air-dry conditions at a temperature t = 18-20°C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60̊ C in SNOL 120/300 chamber and subsequent hardening for 6 days in dry air at the temperature t = 18-20̊ C, humidity of 60%; control samples hardened in a normal-humidity mode (III), at a temperature t = 18 ° C, humidity 80%.

Determination of concrete mix mobility determined by [55], it mixes two compounds: 1 The control composition (no polymer additive); 2- modified concrete mix DLP2141 polymeric additive in an amount of 3% by weight of cement. Formulations of concrete mixes presented in table 4.6. The results of the concrete mix mobility listed in table 4.7.

Table 4.6 – Formulations of concrete mixes.

Room composition	Consumption				
	kg per 1 m^3 of concrete				% Of the binder weight
	Cement (U)	Sand (P)	crushed stone (U)	Water (AT)	DLP2141
1	500	570	1075	210	-
2	500	570	1075	210	0,105

Table 4.7 – Effect of polymeric additives on the mobility of the concrete mix.

Number of staff	Water-binder ratio	Mobility	
		OK, see	Mark on mobility
1	0.42	5	P2
2	0.42	6	P2

Figure 4.10. - The appearance of the concrete specimen

At 7, 14 and 28 days was determined by compression strength of concrete on the press PGM 1000MG4 (Figure 4.11.). Before the test, on the press, samples were weighed, determined by their geometric characteristics and the calculated density of the concrete (Figure 4.12.). Compressive strength results in table 4.8. and figure 4.14.

Figure 4.11. - Sample cube after testing on the press PGM 1000MG4

Table 4.8– Effect of polymer additives on the strength and density of the concrete.

Name of compositions	Curing condition	Density, kg / m^3			Compressive strength R_{com}, MPa (% of $R_{control}$) aged 7,14,28 days		
		7days	14 days	28 days	7 days	14 days	28 days
1	III	2434	2461	2441	38.6 (100)	42.81 (100)	43.53 (100)
2	I	2305	2312	2320	30.105 (77.99)	34.17 (79.82)	35.13 (80.15)
	II	2290	2326	2381	35.23 (91.27)	38.37 (89.63)	39.96 (91.79)

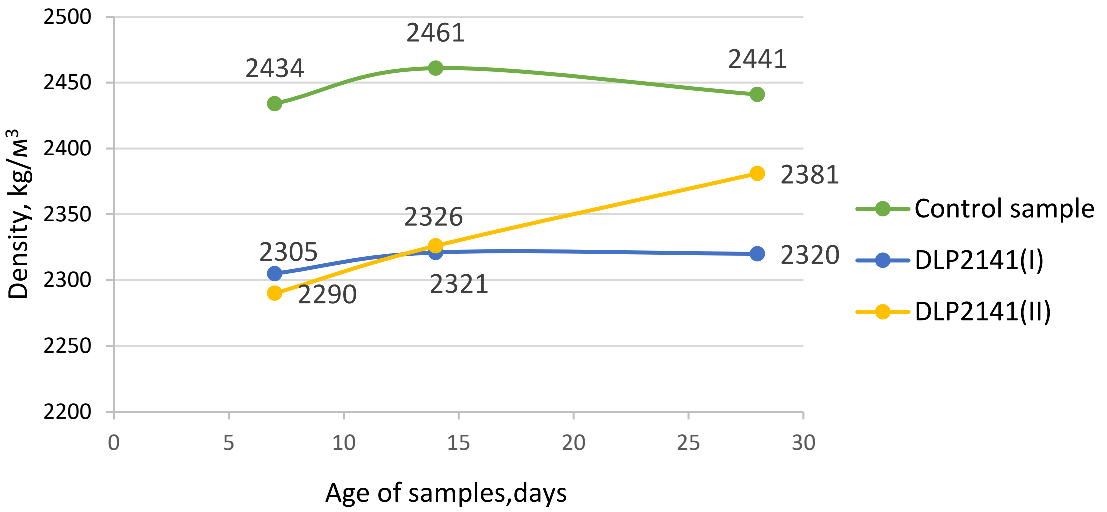

Figure 4.12. - Effect of additive on the polymer DLP2141 concrete density

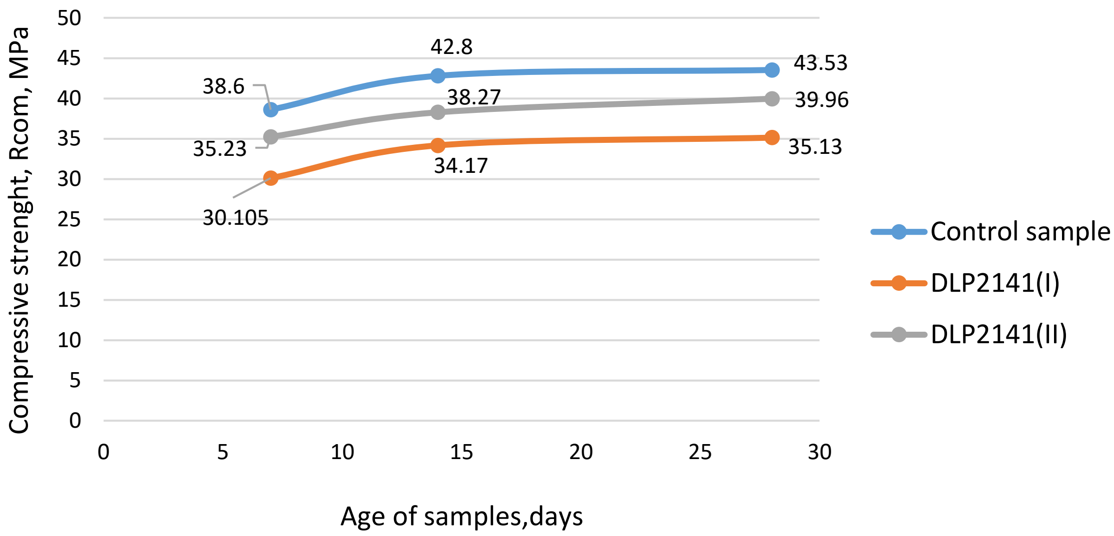

Figure 4.13. - Effect of additive on DLP2141 polymer concrete strength

According to the test results, it can be conclude that the addition DLP2141 polymeric additive in an amount of 3% by weight of cement in the concrete mix, the concrete density reduced by 4% compared with the control sample.

The density of the modified sample with a mode II hardening time is increased by 4%, and the density of a modified stone during mode I is increased by only 1%. It can be concluded that the solidification mode II, specimen concrete strength will be higher than the strength of the concrete hardening in the I mode.

In determining the compressive strength of concrete samples aged 7,14,28 days data were obtained on the basis of which to conclude that the compressive strength of concrete with a modified curing mode II 12% higher durability of concrete with the modified mode I. hardening concrete compressive strength without the polymer additive is 8% higher than the modified concrete hardening regime II.

In determining the grade of concrete strength were determined: M400 - concrete without polymer additive; M350 - concrete with a polymer additive DLP2141 during curing mode (I); M400 - concrete with a polymer additive DLP2141 during curing mode (II). Concrete DLP2141 modified polymer additive and curing mode (II), corresponds to the same brand of concrete, and that no additional concrete.

Concrete with DLP2141 polymeric additive in an amount of 3% by weight of cement and 24 hour hardening time of air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60° C , can be used in building constructions.

M400 concrete that meets the requirements of GOST, used for the construction of facilities, the operation of which involves significant exposure to a mechanical load, causing significant stress formed in the concrete body.

These objects include: bridges with rail tracks, trestles for road transport, viaducts, viaduct line, and so on. etc.; bank vault - for their arrangement used concrete M400 f150; load - bearing structures in the form of columns, beams, connectors and so on. etc.; concrete class B30 M400 is indispensable for the construction of a hydraulic nature; monolithic high-rise buildings.

4.7 Resistance modified cement stone to sulfate corrosion

Corrosion resistance of the samples determined by three parameters: mass, density and strength.

The samples of cement stone, modified in an amount of 3%, were placed in a corrosive solution, then aged 28, 60 and 120 days was evaluated in corrosion performance.

Upon reaching 28, 60, 120 days finding modified stone in a corrosive environment, the samples removed from solution, and their mass was determined, and then measured and the geometric characteristics determined external changes cubes samples. Specimens mass changes results presented in table 4.9. and figure 4.15. The results of the change in density in figure 4.15. and table 4.10.

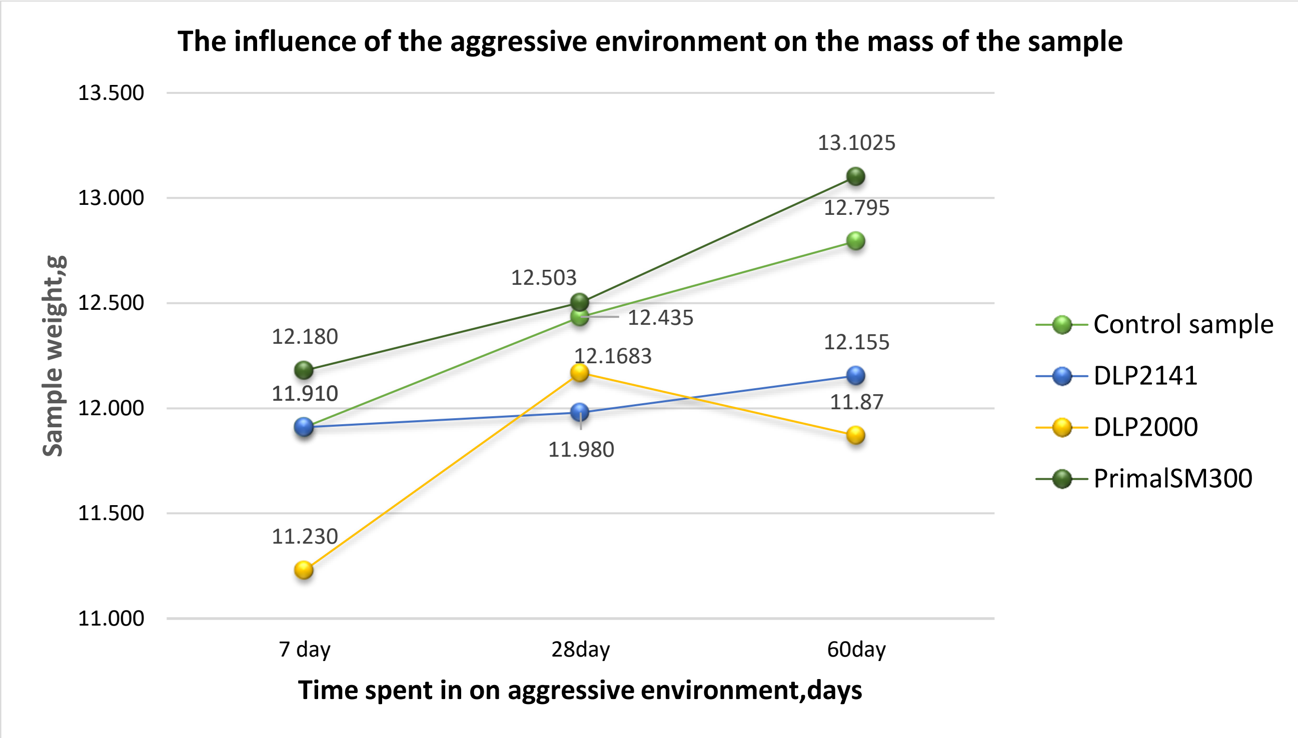

Figure 4.14.-Effect aggressive environment in weight of samples

Table 4.9 – Effect of aggressive environment in weight of samples

Designation Polymer Additives	7 days before the dive		28 days in solution		7 days before the dive		60 days in solution		7 days before the dive		120 days in solution	
	The surface moisture of the samples before immersion in the aggressive environment, W (%)	Weight before immersion in the aggressive solution, m (g)	Weight after extraction from aggressive environments, m (r)	Weight after drying, m (g)	The surface moisture of the samples before immersion in the aggressive environment, W (%)	Weight before immersion in the aggressive solution, m (g)	Weight after removal from the corrosive environment, m (r)	Weight after drying, m (g)	The surface moisture of the samples before immersion in the aggressive environment, W (%)	Weight before immersion in the aggressive solution, m	Weight after removal from the corrosive environment, m (r)	Weight after drying, m (g)
Check sample	14,7	12.210 (100)	14.825 (121.42)	12.435 (101.84)	14,5	12.535 (100)	15.335 (122.3)	12.795 (102.07)	14,6	12.58 (100)	15,45 (123.1)	13.55 (107.71)
DLP2141	13,8	11.910 (100)	14.105 (118.43)	11.980 (100.59)	13,4	12.070 (100)	14,497 (120.1)	12.155 (103.98)	13,7	11.95 (100)	14.35 (120.1)	12.36 (103.43)
DLP2000	15,5	11.230 (100)	14.465 (128.81)	12.1683 (108.36)	15,1	11.540 (100)	14,102 (122.2)	11.87 (102.86)	15,4	11.96 (100)	14.67 (122.76)	12.53 (104.76)
Primal SM330	13,2	12.180 (100)	14.925 (122.54)	12.503 (102.65)	13,4	12.535 (100)	15.612 (124.6)	13.1025 (104.53)	13,3	12.04 (100)	15.19 (126.16)	13.71 (113.8)

According to the results it is evident that samples of the modified polymeric additives based on vinyl acetate copolymer, gaining weight rapidly just prior to 28 days of being in an aggressive environment. After 28 days this process is inhibited, it is explained that the polymer additives do not allow the deposition of sparingly soluble substances, contained in an aggressive solution. In [60], these processes due to the fact that the interaction of the modified cement paste with aggressive environment formed with the maximum number colmatant highest specific diffusion resistance, which makes the process self-locking corrosion.

As is known, the contact area between matrix cement of conventional composition is a channel through which penetrate deep into products aggressive agents: gases, SO_4 ions -, Mg, Cl-, etc. To strengthen the adhesion can be achiev by providing the chemical and physical coalescence of the surface layers of cement matrices. It can be concluded that, to ensure adhesion between the cement matrix must be used, such additives as a DLP2141, DLP2000.

The results of the study of the influence of aggressive environment on cement paste density shown in table 4.10. and figure 4.15.

Table 4.10–Effect on the aggressive environment of the cement stone density.

Designation Polymer Additives	The density of the modified cement paste, kg / m3						
	The density before immersion in the aggressive environment, kg / m^3	Density after removal from the solution, kg / m^3	The density of the samples after drying, kg / m^3	Density after removal from the solution, kg / m^3	The density of the samples after drying, kg / m^3	Density after removal from the solution, kg / m^3	The density of the samples after drying, kg / m^3
	7 days before the dive	28 days in solution		60 days in solution		120 days in solution	
Check sample	1695.83	2059.03	1727.08	2129.86	1896.08	1931.2	1693.75
DLP2141	1654.17	1959.03	1663.89	2013.54	1688.19	1931.33	1545.3
DLP2000	1559.72	2009.03	1690.04	1958.68	1648.61	1833.75	1566.25
PrimalSM330	1691.67	2072.92	1736.53	2168.40	1819.79	1898.75	1713.75

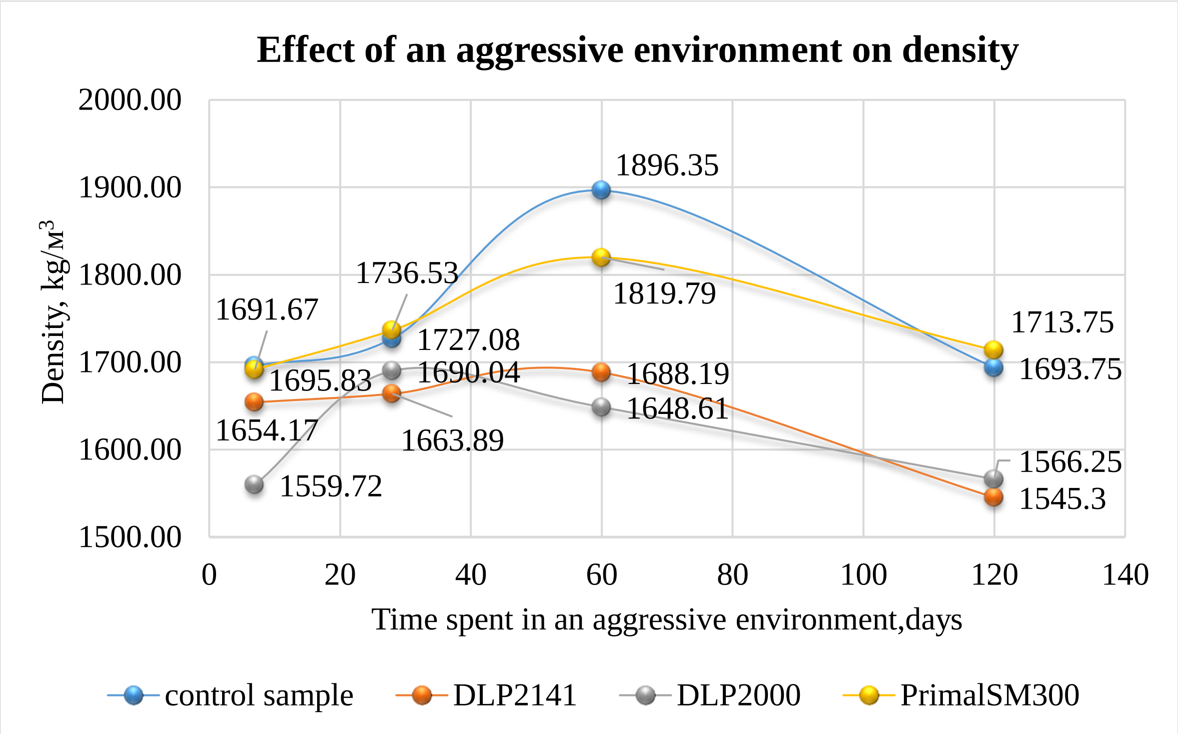

Figure 4.15.-Effect on the aggressive medium density samples

The density of the cement stone with polymer additives and without any additives increases with time. Which means that the cement stone absorbs not only water but also salt are in an aggressive solution, which over time will increase in volume and destroying cement matrix structure due to internal stresses.

After 60 days of being in an aggressive environment, the control sample continues to increase its density.

In cement paste samples with polymer additives, DLP2141 andDLP2000 density growth is less active compared to without additives samples, indicating that, hat the corrosion process slowed down.

Thus, to increase the sulfate cement stone can be recommend use additives based on vinyl acetate-ethylene copolymer.

Determination results of the compressive strength cubes samples aged 7 days (before immersion in the aggressive solution) and after 28 and 60 days of being in aggressive environments is presented in Table 4.11. and figure 4.16.

Table 4.11 – The compressive strength of the test samples on sulfate corrosion resistance of cement matrix

Name polymer additives	Durability compression channel R, MPa (% R czh, RA), at curing conditions			
	DDP	Aggressive environment		
	Aged			
	7 days	28 days	60 days	120 days
Check sample	13.47 (100)	51.09 (379.28)	28.69 (212.99)	33.42 (248.11)
DLP2141	19.65 (100)	34.396 (175.04)	31,12 (158.37)	43.74 (222.57)
DLP2000	21.214 (100)	44.64 (210.46)	42.32 (199.53)	48.39 (228.126)
PrimalSM300	13.91 (100)	44,56 (320.35)	32.79 (235.73)	38.3158 (275.45)

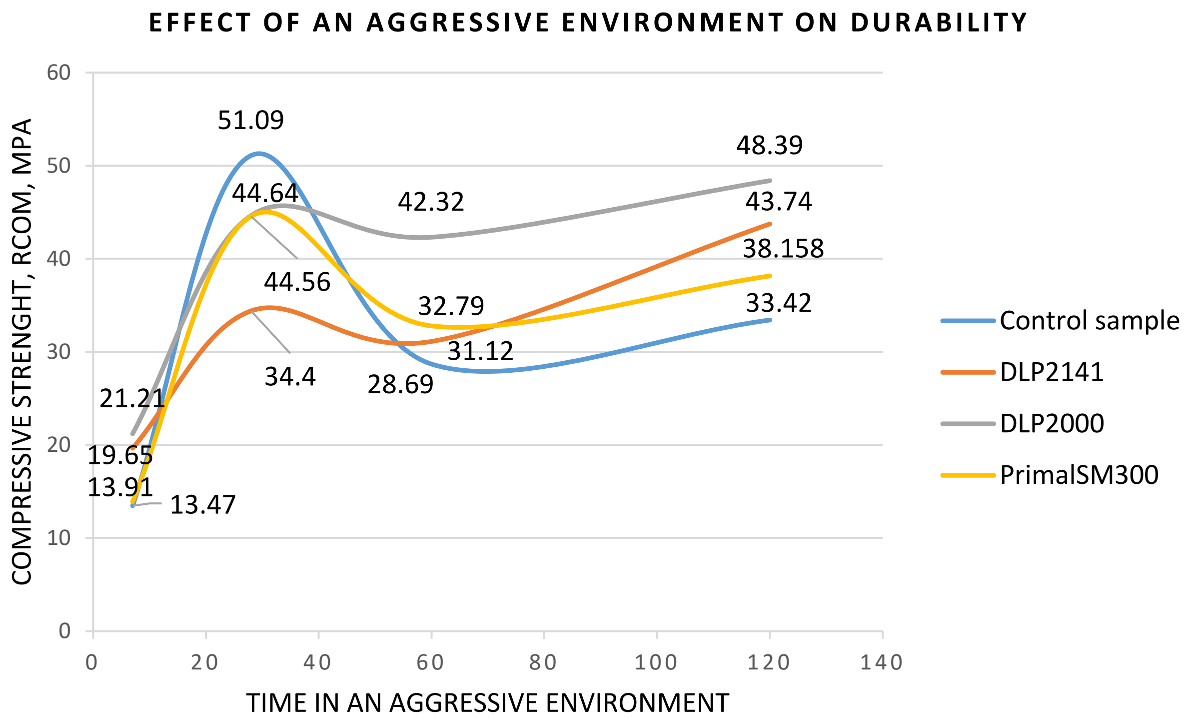

Figure 4.16. - Effect on the aggressive environment strength cement stone

A control sample, while in the aggressive environment of 28 days gaining strength better than the modified samples. The reason is that in order to ensure favorable conditions for the hydration of cement paste needed to ensure high humidity. For modified cement paste, specimen's high humidity adversely affects the strength development and course of the polymerization process.

The samples were aged for 28 days is rapidly gaining strength, but after 60 days of being in an aggressive environment, the strength has fallen sharply from a control sample, which suggests that calcium ions, increasing in volume, destroying the structure of cement stone.

The compressive strength of the cement stone with a polymeric additive DLP2141 28 days increased by 75% compared to the strength at 7 days. Compressive strength at 60 days of finding decreased by 17% in the aggressive environment.

Modified stone with DLP2000 additive also increased its compressive strength after 28 days of being in the aggressive environment by 2 times compared to the strength before the immersion of samples in an aggressive environment. After finding a corrosive environment of 60 days, the compressive strength decreased by 11%.

The compressive strength of the cement stone PrimalSM330 additive as well as the cement stone without drastically gaining strength additives, and then sharply decreases it. After 28 day, strength increased by three times, but after 60 days of being in an aggressive environment has decreased by 85% compared to the strength before immersion in the aggressive environment.

Thus, it found that polymeric additives and DLP2141 DLP2000 composed improve sulfate cement stone cement stone. Moreover, to ensure sulfate recommended supplements based on ethylene vinyl acetate copolymer in an amount of 3% by weight of cement.

4.8 Chapter summery

1. Supplementation additives based on ethylene vinyl acetate copolymer in the cement composites in an amount of 3% by weight of cement increases the strength characteristics of the cement stone.

2. Temperature-humidity mode, which provides the initial exposure composites in dry-air conditions for 24 hours, the subsequent heat treatment t = 60^0C for 2 hours, provides acceleration of the polymerization of polymer additives which positively affects the strength characteristics of the cement stone.

3. Established that modified cement-sandy solutions continue to gain strength after 28 days 30% more than the cement-sand mortar without polymer additives.

4. The polymer additive DLP2141 corresponds to the grade for strength M400.

5. Polymer additives an ethylene vinyl acetate copolymer DLP2141, DLP2000, improve the corrosion resistance of cement matrix.

5. CONCLUSIONS AND FUTURE DEVELOPMENTS

5.1 Conclusions

1. The influence of the polymeric additives on the mobility, density and strength of the cement composites. Polymer Additives Primal SM330 DLP2000 and increase the mobility of 1.42 times. Additive DLP2141v 1.2 times reduces the mobility of cement paste. It found that the polymer additive DLP2141 based on vinyl acetate-ethylene copolymer accelerates the set of strength of cement stone at an early age contributes to the formation of a denser structure of cement stone. Dosage polymeric additiveDLP2141 should not exceed 3% by weight of cement. Studies have shown that at a dose of additive DLP2141v amount up to 3% by weight of cement on dry matter there is no decrease in the strength after 28 days compared to the control sample without additive.

2. Normal air-dry hardening conditions do not significantly affect the strength of the cement stone with a polymeric additive DLP2141, aged 7 days compressive strength amounted to 103.6% of the control values.

3. The most effective temperature and humidity conditions for a modified stone is 24-hour mode of air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60° C in chamber SNOL 120/300 and subsequent hardening for 6 days in an air dry conditions at a temperature t = 18-20° C, humidity 60%.

4. DLP2141 polymeric additive in an amount of 3% when curing mode II-24 hours air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60° C in SNOL 120/300 chamber and subsequent hardening for 6 days in the air dry conditions at a temperature t = 18-20° C, humidity 60%, no mark on reduces M400 concrete strength.

5. It is found that the polymeric additive and DLP2141, DLP2000 composed improve sulfate cement stone cement stone. In addition, to ensure sulfate recommended using them in an amount of 3% additive based on ethylene vinyl acetate copolymer.

5.2 Future developments

For further research, we offer a number of accelerated methods for studying sulfate corrosion. It is also possible to investigate the effect of polymer additives DLP2141, DLP2000, Primal SM330 on cement composites in the composition of which cement made by foreign manufacturers is used as a binder.

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1. INTRODUCTION

1.1 Preface

The durability of concrete and reinforced concrete depends on a large number of factors that affect the operation, type and composition of concrete, as well as the degree of aggressiveness of groundwater. In fresh water bodies, the sulfate content is 60 mg / l, in mineralized groundwater – 200 - 400 mg / l, and in seawater – 2500 - 2700 mg / l [2]. Sulfates located in an aggressive environment in contact with cement stone can significantly increase the solubility of the components of the cement stone and cause the development of exchange reactions with the substitution of the cation in the sulfate for calcium ion from cement stone (second type corrosion). At the same time, the effect of sulfates can cause the development of corrosion processes of the third type [3]. In connection with this study of the effect of polymer additives based on vinyl acetate-copolymer of ethylene and acrylic, Dow Chemical Company trademarks, the resistance of cement stone to sulfate corrosion is an obvious factor.

1.2 Objectives

The aim of the master's thesis is to study the effect of polymer additives on the physic-mechanical characteristics of cement composites and to determine the sulfate resistance of cement composites modified with polymer additives.

To achieve this goal, the following tasks solved:

1. The analysis of modern ideas about the use of polymer additives in concrete;
2. The effect of polymer additives based on vinyl acetate-ethylene acrylate copolymer on the mobility of cement paste, the density and strength of cement stone and cement-sand mortar was research;
3. The effect of heat treatment has been research and effective hardening modes have been determined using polymer additives;
4. The sulfate resistance of cement stone modified with polymer additives investigated.
5. Work done to study the effect of a polymer additive based on a vinyl acetate copolymer on the density and strength of concrete.

1.3 Structure

Present research work consists of 5 chapters. Chapter 1 contains the introduction, objectives and structure of the work done.

Chapter 2 presents an analysis of the global practice of using polymer additives in cement composites. Studying the effect of heat treatment on the strength characteristics of modified cement stone, as well as methods for studying sulfate corrosion of cement concrete.

Chapter 3 describes the main materials, techniques and equipment used in research work.

The main experimental work is set forth in Chapter 4. This chapter presents the results: The results of a study of the effect of polymer additives based on vinyl acetate-ethylene copolymer of the Dow Chemical Company trademark on the mobility of cement paste, the density and strength of cement stone and cement-sand mortar; Experimental data on the influence of temperature and hardening modes on the strength of modified composites; The results of studies of the sulfate resistance of cement stone modified with polymer additives based on vinyl acetate-ethylene-acrylic copolymer; The results of a study of the effect of the polymer additive DLP2141 on the strength characteristics of concrete.

Chapter 5 outlines the conclusions on the work done and the results.

2. MODERN PRESENTATIONS ABOUT APPLICATION OF POLYMERIC ADDITIVES

2.1 The use of polymer additives in the composition of cement composites

Polymeric materials due to their properties are widely used in the construction: as an additive in concrete or mortar mix as an additional binder component for impregnating concrete products, for the production of dry mortars. Recently, it increased significantly application of polymers as additives Cement concretes and mortars.

Polymer concrete (or PC) is a composite material consisting of aggregate, filler and polymeric binder, by replacing conventional hydraulic cement by polymeric resins. Polymer concrete has many advantages compared with Portland cement concrete, such as rapid curing, high mechanical strength, high resistance to chemicals etc. [4,5].Concrete-polymer composites can be classified into polymer concrete, polymer cement concrete and polymer modified concrete, resin impregnated, among which the polymer concrete is well known for its versatile design using [6-9].

The authors [10] examined the state of polymer and its use as a sustainable building material. The analysis of the use of polymer additives and their advantages over conventional compositions cement composites. Obtained indicators such as high mechanical properties, rapid curing, durability and resistance to chemical and biological attack.

Strength characteristics of polymer concrete depends on the quality of materials, their proportions, and space and exposure conditions. Quality of raw materials used in clinker production, firing conditions, fineness and particle size of cement, water cement ratio, all these variables have significant influence on the physicochemical characteristics of the cement paste. Also, the type of cement, the nature of the aggregates, water, mixing temperature, additives and curing conditions determine the mechanical properties and durability of concrete [11].

Concrete based on Portland cement is the main material supporting and enclosing structures used in modern industrial and civil construction. The complex of adverse effects: alternating moistening - drying, freeze - thawing, exposure to active corrosion relative to the cement stone materials, concrete leads to corrosion manifests itself in the reduction of material strength and deterioration in performance of this product [12-14].

Defined [14] that the corrosion resistance of the concrete is determined by two major parameters - permeability to aggressive environment and ability of cement paste and aggregate chemically to react with the components of corrosive environment. Studies [12, 13] have shown the relation between the mass transfer in the material structure and the processes of cement stone degradation. The lower the rate of mass transfer, the higher the corrosion resistance of cement matrix.

Major disadvantages of polymer concrete are related with their fragility, pronounced creep, and shrinkage, low thermal resistance. To reduce the brittleness of polymer concrete are used in their formulation fibers of asbestos, glass and others. To regulate viability in the polymer concrete mixture based on urea resins is suggested [15] the inclusion of ferric chloride and a mineral filler (porcelain flour, silica sand). Reduced combustibility while maintaining the values of physical and mechanical properties at elevated temperatures are achieved using a composition of polymer concrete based on a low molecular weight polybutadiene of sulfur, thiuram, captax, zinc oxide, calcium oxide, silica sand, crushed granite, and flame retardant - aluminum hydroxide [16].

A separate group are concretepolimery. Concretepolimery - a cement concrete, impregnated after curing by low viscosity monomers or oligomers, liquid, for example, styrene, and methyl methacrylate. After the heat treatment, these monomers proceeds in polymers, filling the pores and other defects of the concrete by solid polystyrene or polymethyl methacrylate. This treatment promotes a drastic increase in strength (100 MPa), cold resistance, durability, hardly permeable [17].

Currently, much attention is given to the polymers that are produced in the regional chemical enterprises. For example, low molecular weight polyethylene is a byproduct of the synthesis of large-tonnage production of high-pressure polyethylene. In [18] performed a study on the development ofpolymeric additives based on aqueous dispersions of (meth) acrylic polymers - polymethacrylates (PMA), polyacrylates (PA), thermal decomposition products of the polyamide-6 in the medium oils and low molecular weight polyethylene (NMPE). The resulting mixture of low molecular weight polyamides (NMPA) with an average molecular weight of 3400 ... 8600 was used as independent and in the complex additive for concrete. Based on data obtained during the study [18], it was established that the polymeric additives are plasticizing additives, they slow down the curing of concrete mixtures and reduce the water-cement ratio of from 6,5% - to 19,4%. Additives in an amount of 0,5 ... to 0,7% increases the strength of the concrete samples V22,5 for 28 days under the conditions of air-dry hardening compared with the standard to 28,2%. Polymer additives increase the water-resistance of concrete V 22,5 compared to standard up to 195 times. Optimal complex additive that increases the time cement slurry setting, water resistance and compressive strength of concrete is the composition of a mixture of polyacrylates and polymethacrylates (PA and PMA), thermal decomposition products of the polyamide-6 (NMPA) and low molecular weight polyethylene (NMPE) in the ratio 1: 1 : 0,5 (wt.) [18].

In [19] as a fine concrete additive is proposed to use an acrylic dispersion grade VDSM-KI-02-04, intended for the paint industry, which is a styrene polymer and acrylic monomers, the resulting emulsion method. Acrylic dispersion is applied as a film former. Well it combined with many modern polymers, additives and ingredients.

Using additives in cement composites can be adjusted basic construction and technical properties and give a new quality of the material. By varying, the composition of the material with the help of additives may be: increase the plasticity, increased strength, improved water resistance, to accelerate or retard setting time, etc.

When administered polymer additives significantly reduced water-cement ratio, which was found in [20, 21].

Dosages polymeric additive for mortars on mineral binders, usually in the range of 1-5%. The optimum dosage is established based on the need to achieve the maximum values of useful properties (or set of core properties) at minimum cost [22, 23].

Polymer-cement mixture due to the presence of surfactants typically is good foaming agents, characterized by the ability to entrain air into the mortar mix. The air stored in the mortar in the form of tiny bubbles, and its volume may reach 30% of the solution volume.

The results of studies of the effect of additives on polymer complex hydration processes are reflected in [24-27] have shown that the additives do not affect the hydration process.

In [28] found that in the polymer-cement slurries of polymers or the polymerization process occurs before the cement hydration or hydration process in parallel. In comparison with conventional solutions, polymer-cement mortars are more resistant to the effects of the dynamic forces are capable of conversion and dissipation of energy, are very large values of compressive strength, flexural, tensile, higher adhesion and low water resistance. Using such compositions, as a rule, for the construction of staircases, roads, floors, repair of concrete building of the new to the old, to eliminate the cracks, strengthening floors, anti-corrosion protection.

The established method of localization (distribution) polymer films and bonds for stone that quality does not depend on the dosage of re-dispersible powder (PSC) and the nature of the considered polymer-based and does not change with an increase in dosage over rational values. It is revealed that a portion of the water-soluble polymer is concentrated at the interface "entrained air - solution" and in most cases leads to increased local shrinkage strain [29]

2.2 Conditions of curing cement paste with polymer additives

Under normal conditions the film formation process in the cement stone - the polymeric composition finishes within 48 hours curing systems [30].

Contrary to popular belief that the process of film formation does not occur at temperatures below the film-forming temperature in the course of [30], it was found that the film still is formed as indicated and indexes changes deformation values and strength of the samples as polymers and cement - polymer compositions. Reducing mother strength occurs because of significant deceleration cement hydration process, and improving deformability characteristic values corresponds to a deeper penetration of the polymer matrix in the form of a film in a matrix of the mineral binder.

The physico-mechanical characteristics of cement compositions, the modified polymers are affected by numerous factors. In [30-32], the results on the effect of curing conditions on the strength of the cement-polymer compositions. It is found that at high temperatures the polymer with a high film formation temperature increases the strength characteristics of the cement-polymer compositions, but reduces deformation characteristics. Under normal conditions, the process of film formation in a polymer-cement stone finishes within 48h curing system.

Defined [33] that the compressive strength of the cement composite decreases with increasing amounts of polymer so as polymers retard the cement hydration. Established [22, 34], that the part of the water-soluble polymer can be concentrated at the interface "entrained air - solution" phases. The fine, uniformly distributed air exerts a plasticizing effect on the cement paste, resulting in increasing their diameter face breaking. Results [35, 36], the interaction of polymer additives with other raw materials, can lead to the capture of a significant amount of air during mixing.

2.3 Sulfate resistance of cement stone

The durability of concrete and reinforced concrete depends on many factors, the main of which are the operating conditions, the type and composition of the concrete, as well as the degree of aggressiveness of groundwater to which the structures are subjected. As is well known [37], the main cause of destruction of concrete arrays in contact with groundwater zone is the corrosion of cement concrete matrix. Greatest destructive effect on the concrete regardless of the composition and structure of concrete, type of construction, nature and amount of the workload, conditions of service provides sulfate corrosion.

Formation and destruction of calcium hydrogen-aluminate is an important chemical process. The study of the mineralogical composition of cement stone samples stored in a sulfate environment, showed that the cement stone binds a significant amount of SO_4 [38]. The more cement tricalcium aluminate (C_3A), the more ions SO_4^- bound, ie. e. absorption is sulfoaluminate character [39].

The corrosion resistance of concrete is determined by two major parameters - permeability to aggressive media and ability of cement paste and aggregate chemically react with the components of corrosive media. Low permeability concrete is provided a complex of events: applying hydrophobic and water-reducing additives, the purpose of particle size distribution of aggregates and mineral additives provides a concrete structure with a minimum volume and minimum pore sizes and capillaries; effective compaction of concrete mix, the optimum modes hardening.

Transferring concrete in aggressive media porous body is carried out by the mechanism of viscous flow under pressure gradient and capillary forces and diffusion transfer mechanism, in the presence of a gradient of concentration of the aggressive matter.

The essence of the corrosion processes occurring in the concrete in sulfate environment, is to form a structure of concrete and gypsum gidrosulfoalyuminatov with increasing volume of hard phases, which causes the appearance of internal stresses exceeding the strength of the concrete and concrete-destroying. Sulfate corrosion occurs when subjected sulfate solution [40].

Effective measure of protection from sulfate corrosion is to reduce the permeability of the concrete for the SO_4 ions$^-$Coming from the aggressive environment. Introducing additives into the concrete complexes, including effective water reducing and mineral, achieve this. In recent decades, the attention of researchers have drawn two destructive process - after the formation of ettringite and $3CaO\text{-}Al_2O_3\text{-}3CaSO_4\text{-}32H_2O$ taumasita CA_6 [Si $(OH)_6]_2$ $(SO_4)_2$ $(CO_3)_2\text{-}24H_2O$. Review of domestic and foreign works on education and ettringite taumasita given in [41,42].

Shown [41,42] that the interaction of components of cement concrete matrix with an aggressive environment formed colmatant two types: 1st consists of silica gel, which is formed by reaction of cement stone silicate component with an aggressive environment; type 2 is formed by the chemical reaction of components aggressive environment with the main parts of cement paste containing calcium ions $CaCO_3$, Mg $(OH)_2$, etc.

One effective way to reduce the intensity of mass transfer and, accordingly, for obtaining concrete high resistance to corrosion is the use of polymers in cement concretes. The polymers may partially or fully replace mineral binder (polymer concrete) impregnated concrete after curing (concrete polymer) or polymer emulsions are used as additives in concrete. A detailed analysis of structure and properties of polymer concretes made Paturoev V.V. [33].

2.4 Test methods for sulfate resistance

Currently practiced methods of reducing the corrosion resistance tests are often strongly distort the physic-chemical processes occurring in the interaction of components of the materials with the dirty environment and can give unreliable results, which should be considered when choosing methods. To comply with the laws of similarity and dimensions when the latter is recommended to use dimensionless selection criteria reflecting geometric similarity, the time factor, the diffusion characteristics of the material, etc.

The corrosion test lasts a very long time, hence the understandable desire of researchers to find such methods to obtain reliable results in the shortest possible time. To test for resistance to cement chemical aggression samples of cement composites is usually used which are placed in the proper aggressive environment. Then follow the change in appearance of the samples are tested for their flexural strength and compression, expansion determined value of dynamic modulus of elasticity, etc.

Designed V.V. Kindy method of small samples [13] is a variation of the method of Koch and Shteynegger [43]. The samples he applied prism dimensions 1x1x3 cm, as a filler - sand, a larger than usual (Wolski with Mcr = 2.4-2.5), to give samples of a porous structure. With this aggressive solutions are easier to penetrate into the sample and quickly destroy it, allowing for faster test times.

Anstett [44] proposed a test method for cement sulfate, based on the measurement of the expansion cylinder-pressed samples of crushed hardened cement stone supplemented with 50% (wt.) Of gypsum dihydrate placed in wet conditions. Sulfate was estimated to expand the diameter of the test sample, which should not exceed 1.25%.

Miller [45] turned again to the measuring method of expansion of samples in sulfate environment, with dimensions 5x10 cm cylinders. It is found that the elongation of samples of 0.25 mm per 10 cm of length corresponds to a loss of strength

50-70%. On resistance of samples can also be judged by how much time is required to expand them in the sulfate solution at 0.25 mm. Later, however, Miller [46] concluded that a lack of reliability of their early experiments.

Torvaldson, Larm and Vigfusson [47] as a measure of aggression received value swelling samples in sulfate solutions, and they were compared between a flexural strength of cement mortar samples of 1: 3 after storage in water and sodium sulfate, and expanding prisms of the same composition.

Merriman [48] developed and applied the accelerated sulfate resistance test method. He made plate samples measuring 5x10x10,6 cm from pure cement dough and, after daily storage in molds in a moist chamber, placed in a 10% solution of sodium sulfate. Merriman considered the absence of cracks and distortions in the samples after 28-day storage as a sign of sulfate resistance.

2.5 Chapter summary

1. With the help of polymer additives, it is possible to regulate the physic-mechanical characteristics of cement composites. It is recommended to use them in an amount of 1% to 15%.
2. During the heat treatment of cement composites with polymer additives, the strength characteristics increase by two times. To accelerate the polymerization process, curing modes with a temperature higher than the film-forming temperature of polymer additives are used.
3. Polymer additives improve the sulfate resistance of cement composites. Polymer additives in the composition of cement composites slow down the corrosion process in the structure of cement composites. To determine sulfate resistance, methods of the accelerated process are used to obtain results in the shortest possible time.

3. Characteristics of the materials used and methods of research

3.1 Characteristics of the materials used in the studies

For research use of cements of "Belarusian Cement Plant", satisfying the requirements of GOST 31108-2003 [49].

The physic-mechanical characteristics shown in table 3.1.

Table 3.1 – Physical and mechanical properties of cement

Cement type and name of the manufacturer	Density, kg / m^3	NGTST %	Setting time, hr-m		Activit, MPa
			Start	end	
Portland cement CEM I, (42,5N) Kostyukovichi	3200	25,0	3-10	4-50	45

As a fine aggregate used sand, quarry "Borovoe" satisfying the requirements of GOST 8736-2014 [50], whose characteristics are listed in table 3.2.

Table 3.2 – Characteristics of sand

Bulk density, kg / m^3	Density grains kg / m^3	Content silty and clay particles,%	Emptiness, %	Humidity, %
1567	2650	2,5	39,2	5,26

Sand quality assessed according to GOST 8735-88[51]. Determination results of size distribution shown in table 3.3.

Table 3.3 – Grain size distribution of sand

Dimensions sieve holes, mm	2,5	1,25	0,63	0,315	0,16	m. 0,16
Private residues %	5,5	8,5	21,5	34,0	28,5	2,0
Full residues %	5,5	14,0	35,5	69,5	98,0	100

According to test results the sand belongs to the group of middle-class II module size $M_{fineness}$ = 2.23.

The additives used in the polymer additive based on acrylic Primal SM330 and polymeric additives an ethylene vinyl acetate copolymer DLP2141 and DLP2000 trademark Dow Chemical Company. Polymer additive Primal SM330 is lactic, white liquid, specific gravity 1.06 g / cm^3 dry residue was 46,5-47,5%, pH -. 9,5-10,5, MFFT t = 10 ^{0}C. Polymer additiveDLP2141 - white free flowing powder based on a vinyl acetate-ethylene copolymer, the residual humidity max. 2%, the bulk density of 0,400-0,550 g/ml, zolnost10-14%, pH-7,5 , MFFT t= 3^{0}C. DLP2000 is a white free flowing powder based on a vinyl acetate-ethylene copolymer, the residual humidity max. 2 %, the bulk density of 0,375-0,525 ml /g, ash content of 10-14%, pH-6 MFFT t= 3 ^{0}C.

To mix the cement paste and mortar, tap water used, which corresponded to the requirements of STB 1114-98 [52].

3.2 The methodology of the research

Studies conducted using standardized techniques. Cements tested in accordance with GOST 31108-2003 [49]. Sand quality assessed according to GOST 8735-88. [51]

To determine the strength of the cement stone produced samples cubes with an edge of 20 mm. Compressive strength was determined by a modified stone aged 7 days and 28 days of hardening under various conditions.

Determination of strength of cement-sand mortar carried out according to the procedure STB EN 196-1 / PR [53]. Summary technique is to compare the compressive strength and bending strength of mortars produced from Portland cement (the control composition) with compressive strength and bending strength of mortars produced from Portland cement modified with polymer additives. For the test, samples were made ravine-size 40x40x160 mm. Thermal treatment of the samples was carried out in an oven SNOL 120/300 (Figure 3.1.).

Figure 3.1. - Drying chamber SNOL 120/300

Determination of concrete mix mobility performed according GOST 10181-2014 [54]. Strength of the concrete determined by GOST 10180-2012[55]. Determination of strength was carried out on a test press PGM 1000MG4 (Figure 3.2.).

Figure 3.2. - Test press PGM 1000MG4

3.3 The method for determining sulfate corrosion

It is known that corrosion processes of materials are slow, therefore the study of these processes, the researchers give preference methods, which allow obtaining reliable results in a short time.

To determine the sulfate corrosion of cement paste with the additives Primal SM 330, DLP2141 and DLP2000, the basis of technique, rapid determination of Sulfate concrete presented in the manual [56] adopted. This method based on a comparison of the absorption rate of aggressive ions SO_4^{2-} test cement stone. To determine sulfate conventional Portland cement concrete samples made cubes measuring 50×50×50 mm cubes hardening should be conducted by mode corresponding to the heat treatment regime for specific structural elements.

Concrete composition are selected to provide brand waterproofing least V8. For each test made on six twin samples from one batch. Samples placed in a desiccator and pour a solution of sodium sulfate in an amount of 5 l prepared based 2.8 g of anhydrous sodium sulfate (Na_2SO_4) in 1 l of distilled water. If test samples give different compositions of concrete, sodium sulfate solution should be prepare directly on the workload.

After installation of the samples in an aggressive solution, at a time corresponding to 1, 3, 6, 9 and 12 weeks of each desiccator pipetted sample solution to determine the aggressive ions SO_4^{2-} in an amount of 100 ml. The content of SO_4^{2-} ions in each sample is determined and aggressive initial solution prepared for the test cubes. To determine the content of sulfate ions in solution in the test solution sampled in an amount of 100 ml is added 1 ml of concentrated HCl was heated on a hot plate almost to boiling. In 25 ml of a 2.5% solution of BaCl solution warmed to reflux, was added with stirring the test solution and allowed to warm hot plate for 3 h, covered with a glass with a watch glass test solution, cooling the solution to room temperature, it was filtered through a dense filter (blue ribbon). The precipitate was quantitatively transferred to a filter and washed with warm water until the washing waters in response to the chloride ion (as silver nitrate). Filter the precipitate was transferred to a crucible and dried in an oven and calcined at a temperature of 800 - 900 ° C to constant weight. The content of sulfate ions SO_4^{2-} in a solution Q_{SO4} p, mg / l.

Based on a review of methods for determining the resistance to sulfate corrosion given in section 1.4, and accelerated method of determining sulfate-cement composites was performed by following the procedure described above.

Previously, it has been found that the dosage of the test polymer additives should not exceed 3% by weight of cement, and the most favorable temperature mode is a processing mode with the temperature t = 60^0C for 2 hours.

At a given dosage and solidification mode were prepared samples cubes with an edge of 20 mm. At the age of 7 days, when the cement stone gaining 70% strength, moisture was determined using samples of moisture MG4B, weighed on scales VK-300 and determined by their geometrical characteristics, then immersed in a corrosive solution.

To prepare 2% solution was used Sodium sulfate decahydrate $Na_2SO_4 \cdot 10H_2O$. Sodium sulfate crystallises from aqueous solutions with ten water molecules ($Na_2SO_4 \times 10H_2O$), and as such is called Glauber's salt. Physical properties of sodium sulfate are presented in table 3.4.

Table 3.4 – Basic the physical properties of sodium sulfate

Molecular formula	Na_2SO_4
Molar mass	142
Density (20^0C) g / cm^3	2,68
Melting point, ° C	883

Solubility in water (20^0C), g / 100 ml	19,2

Determination salt mass and weight of the solution determined by the following method:

Molar mass Na_2SO_4= 142,04 g / mol

Molecular mass Na_2SO_4 = 142,04 + 10 × 18 = 322,19 g / mol

For one liter of distilled water, count the number of moles:

$0.02 = \frac{142n}{1000+322n}$ => n = 0,1475 moles

Determine the weight of Glauber's salt:

m ($Na_2SO_4 \cdot 10H_2O$) = 0,1475 × 322 = 47,5g.

Upon reaching 28 and 60 days of finding modified cement paste in a corrosive environment, the samples were removed from the solution, dried to a constant weight, then were tested for compressive strength at press PGM-500MG4A also determined sample weight were measured geometric features and fixed external changes specimens -Threefold.

Test specimens for compression and bending carried out in accordance with GOST 10180-2012 [55] on a test press PGM-500MG4A (Figure 3.3), which provides a fully automatic operation.

The dimensions of the finished samples checked using a type I digital caliper. Ranges 0-150 mm, measurement speed - not more than 1,5 m / s. Caliper complies with GOST 166-89 [57].

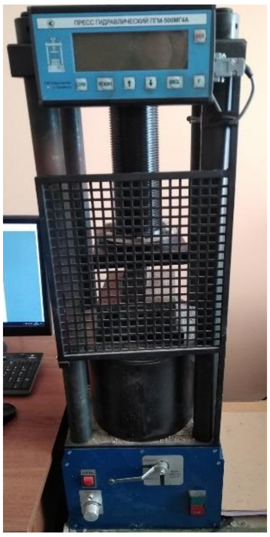

Figure 3.3. - Test press PGM-500MG4A

Humidity samples was determined hygrometer MG4B (Figure.3.4.).

Figure 3.4. - Moisture MG4B

Weight samples was determined using an electronic balance VC-300 (Figure 3.5.). Laboratory scales VC-300 used for accurate mass measurement. This type of electronic scales used in industrial laboratories where increased accuracy is required. Electronic balance laboratory VC-300 Class II production precision "Weight-to" may operate with multiple units of weight and measure different weighting modes.

Figure 3.5. - Libra VC-300

3.4 Chapter summary

1. Physic-mechanical characteristics of cement. Characterization of sand and its particle size distribution. The chemical composition of polymer additives DLP2141, DLP2000 and Primal SM330.
2. Standardized test methods. Methods for determining the strength of cement stone, mortar, concrete.
3. An accelerated method for the determination of sulfate corrosion on small samples of cement stone in an aggressive environment. Preparation of 2% sodium sulfate solution for use as an aggressive medium.

4. Physical and mechanical characteristics cement composites modified with polymer additives

4.1 The effect of polymer additives on the mobility of cement pasted with polymer additives

The introduction of polymer additives in cement affects the mobility of cement paste, cement stone strength and a number of other indicators. Established [22, 34], that the part of the water-soluble polymer can be concentrated at the interface "entrained air - solution" phases. The fine, uniformly distributed air exerts a plasticizing effect on the cement paste, resulting in increasing their diameter face breaking.

It is found that the dosage of polymer additives using mineral binding agents are usually in the range of 1-5% [22]. The optimum dosage is established based on the need to achieve maximum values at the maximum strength values of the mobility of the cement paste.

In the first stage of the study investigated the effect of polymer additives Primal SM300, DLP2141, DLP2000 the mobility of the cement paste. Samples- cubes with an edge of 20 mm were investigated at two modes hardening: normal-humidity environment (DDP) and heat treatment t = 60℃ for 2 hours.

To determine the effect of additives on the mobility of the polymer cement paste polymeric additives introduced in an amount of 1%, 3%, 5% by weight of cement on dry matter. Water-cement ratio of 0,5 accepted. Determination of the cement paste is performed for the mobility procedure NIIZhB [58], a mini cone. Flat-cone height of 3 cm filled with cement paste with the polymer additive after raising mini cone cement paste melt, cone face breaking value determined in 2 directions metal ruler with a scale division of 1 mm (Figure 4.1).

Figure 4.1. - Definition of face breaking cement slurry with polymer additive DLP2000

Cement paste broke without polymeric additive was 6 cm. The results of the influence of polymer addition on the mobility of cement slurry shown in table 4.1 and figure 4.2.

Table 4.1 – Effect of Polymer Additives on the mobility of the cement paste

Name of polymer additives	Mobility cm of cement paste, the introduction of the additive in% of cement weight		
	1	3	5
Primal SM330	8	8,75	8,9
DLP2141	4,8	5,2	5,8
DLP2000	7,7	8,8	9,5

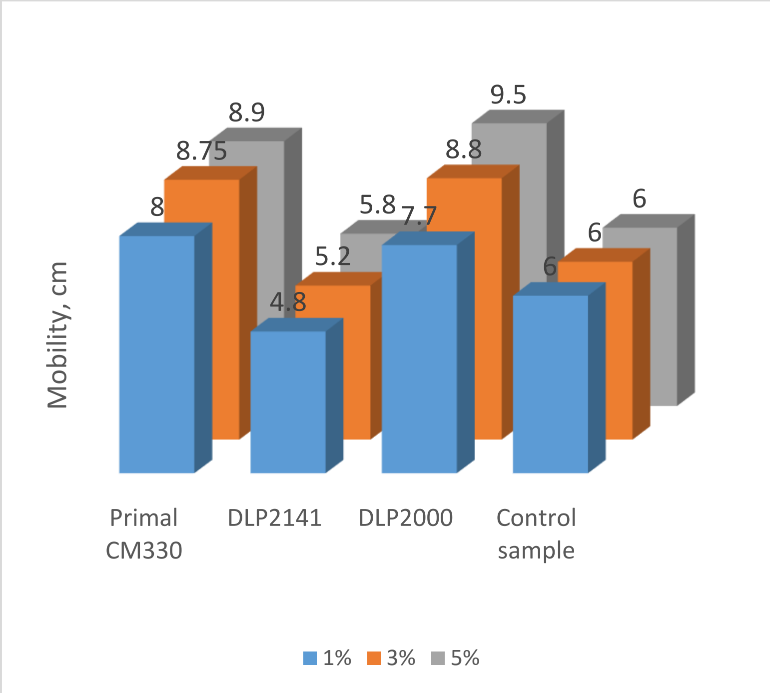

Figure 4.2. - Effect of Polymer Additives on the mobility of the cement paste at a dosage of 1%, 3%, 5% by weight of cement.

The study showed that the polymer additive DLP2141 1,2 times reduces the mobility of cement paste. Introduction DLP2000 polymeric additive increases fluidity of the cement paste in 1,45 times. By increasing the polymer dosage DLP2000 additives mobility increases. The addition of Primal SM330 increases the mobility of cement paste 1,42 times, but does not occur with increasing dosage to further increase mobility.

4.2 Effect of additives on polymer density and strength cement stone

Further study on the cement paste strength with polymer additives DLP2000, DLP2141, Primal SM300 1,3,5 conducted under dosage% by weight of cement. To determine the strength of the cement paste samples - cubes with 20 mm edge (figure

4.3). After molding, the samples hardened for 24 hours in air-dry conditions at a temperature t = 18-20° C, further for 2 hours the samples were heat-treated at 60° C, and then continued to harden in air-dry conditions at a temperature t = 18- 20°C. Before testing, the samples weighed and their geometric characteristics determined. The strength of the samples was determined on a press PGM-500MG4A aged 7 days and 28 days (Figure 4.4).

Figure 4.3. - Samples of cement stone with polymer additive DLP 2141 (I- 1%, III-3%, V-5%)

Figure 4.4. - Samples after the test at the age of 7 days (3% polymer additive Primal CM330)

Determination results of the strength and density of the cement stone with polymer additives Primal SM 330, DLP2141 DLP2000 and shown in table 4.2. and in figure 4.5.

Table 4.2 – Strength of the cement stone with polymer additives

Designation Polymer Additives	The amount of additive,% of the cement paste	Durability compression channel R, MPa (% R com) aged 7 days	Durability compression channel R, MPa (% R com) aged 28 days	Density, kg / m^3 aged 7 days	Density, kg / m^3 28 days
Primal SM 330	1	9,48 (62,02)	9,64 (70,49)	1508,75	1573,53
	3	14,81 (40,67)	21,49 (34,22)	1577,71	1668,45
	5	18,36 (36,44)	26,32 (19,44)	1597,50	1663,10
DLP2141	1	38,23 (53,17)	34,81 (6,64)	1820,63	1804,81
	3	34,59 (38,58)	31,41 (3,86)	1804,17	1871,66
	5	24,89 (0,28)	35,68 (9,21)	1776,25	1899,73
DLP2000	1	19,28 (22,77)	36,57 (1,93)	1697,92	1832,89
	3	21,3 (14,66)	34,31 (5,02)	1700,21	1778,07
	5	21,91 (12,22)	33,31 (1,96)	1724,58	1818,18

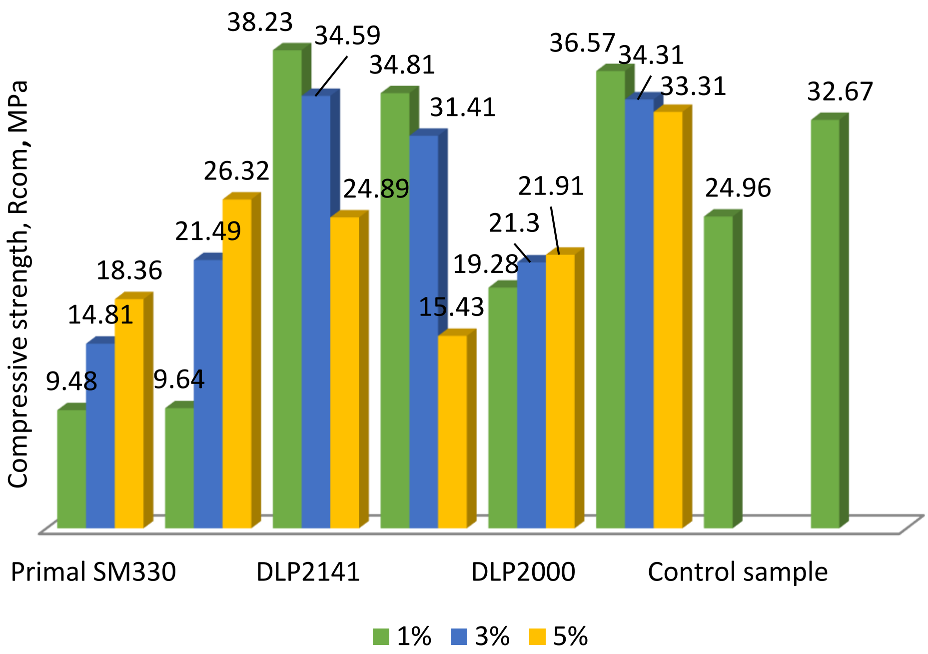

Figure 4.5. - Effect of Polymer Additives on the strength of the cement stone at 7 and 28 days

Density control sample without polymeric additive aged 7 days was 1670,31 kg/m^3, compressive strength $R_{com}^{control.}$= 24,96 MPa, aged 28 days, the density was 1757,75kg / m^3, compressive strength–32,67 MPa.

The study found that increasing the dosage of polymer additive Primal SM 330 with 1% to 5% by weight of cement, leads to increased strength of the cement stone at the age of 7 days. Thus, strength at a dosage of 1% of 9,48 MPa; at a dosage of 3% -14,81 MPa; at a dosage of 5% -18,36MPa, representing 73,6% of the strength of the control sample without additive. Cement stone modified polymeric additive Primal SM 330 in an amount of 1%, and after 28 days, compressive strength is 3 times less than the strength of the cement stone without modifications.

The polymeric additive DLP2000 causes a slight deceleration of set cement matrix strength to age 7 days strength reaches 83,45% of control values. Increased dosage has no significant effect on the rate of strength development. The greatest effect on the rate of curing had DLP2141 additive. At a dosage of 1% by weight of cement strength at 7 days reached 153,16% of the strength of a control sample; at a dosage of 3% -138,58%; at dozirovke5% -99,72%. Cement stone, modified by the addition DLP2141, has a denser structure compared to the cement matrix without the additive.

Thus, when using a polymeric additive based on vinyl acetate-ethylene copolymer DLP2141, the compressive strength of the cement stone at 7 day strength of cement stone above modified polymer additives Primal SM330 on the basis of acrylic and DLP2000. Polymeric additives lead to slower set cement paste strength process.

At the age of 28 days compressive strength of cement paste with additive DLP2000 above control values at 2% at a dosage of 1% by weight of cement; with the addition of DLP2141 at 7% at a dosage of 1%; strength cement paste with additive Primal SM 330 does not reach the reference value.

It found that the polymer additive based on DLP2141 ethylene vinyl acetate copolymer accelerates the set cement stone at an early age strength and promotes formation of a dense structure of cement stone. Dosage polymeric additiveDLP2141 should not exceed 3% by weight of cement.

Studies have shown that at a dose of additive DLP2141v amount up to 3% by weight of cement on dry matter there is no decrease in the strength after 28 days compared to the control sample without additive.

4.3 The effect of heat treatment on the strength cement stone

The next stage of the research is to study the effect of temperature on the modified cement stone. After molding, the samples hardened in two modes: a first mode (I) -to per 7 days air-dry conditions at a temperature t = 18-20°C, humidity of 60%; the second mode (II) in -24 hours air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t =

60°C in SNOL 120/300 chamber and subsequent hardening in for 6 days in an air-dry conditions at a temperature t = 18-20°C, humidity 60%.

Before testing the samples were weighed and measured their geometric characteristics. The strength of the samples was determined at 7 and 28 days in the press-SGP 500G4A. The nature of the destruction of the samples in determining the compressive strength (Figure 4.6.).

Figure 4.6. - Character fracture cement paste with a polymeric additive under compression DLP2141

Results of the study of cement paste strength with polymer additives Primal SM 330, DLP2141 DLP2000 and under various conditions of hardening shown in table 4.3.

Table 4.3 – Strength of the cement stone with polymeric additives for different modes of hardening

Designation Polymer Additives	Compressive strength Rszh, MPa (% of Rkontr) at curing conditions				Density, kg / m^3, with curing modes			
	I		II		I		II	
	aged				aged			
	7days	28days	7days	28days	7days	28days	7days	28days
Check sample (without additives)	26.6 (100)	27.8 (100)	24.96 (100)	28.6 (100)	1715.2	1590.42	1670.3	1638.13
Primal SM 330 (based acrylic)	14.62 (55.0)	22.02 (79.2)	14.81 (40.7)	20.3 (70.9)	1517.4	1415.83	1577.7	1642.98
DLP2141 (Based on ethylene-vinyl acetate copolymer)	28.26 (106.2)	28.13 (101.18)	34.59 (138.6)	29.7 (103.9)	1702.8	1497.1	1804.2	1902.19
DLP2000 (Based on ethylene-vinyl acetate copolymer)	27.57 (103.6)	29.7 (106.8)	21.3 (85.3)	32.42 (113.4)	1684.4	1508.13	1700.2	1756.8

Research has shown that when both the curing conditions there is a significant reduction in strength of cement paste with a polymeric additive Primal SM 330:

hardening in air-dry condition (mode I) by 45%, with an additional heat treatment for 2 hours at 60̊ C (mode II) 59,3%. Note also decrease the density values of a cement stone that explained air-entraining additives ability. Strength reduction can be due to significant adsorption of the polymer particles on the surface of cement particles hydrating, which further prevents the cement hydration process.

Test modes curing had a positive influence on the strength of the set cement matrix with polymeric additive DLP2141. Both modes hardening provided to increase the compression strength, compared with a control sample no additives: hardening in air-dry condition (mode I) of 6,2 %, with an additional heat treatment for 2 hours at 60°C(II mode) 38,6%. DLP2141 polymeric additive does not retard the cement hydration process and aging the samples for 2 hours at a temperature 60°C contributes to an active film formation and deep penetration of the polymer matrix in the mineral binder matrix, as evidenced by an increase in sample density.

Air-dry hardening conditions (mode I) had no significant effect on the strength of the cement stone with a polymeric additive DLP2141, aged 7 days compressive strength amounted to 103,6%. Processing temperature 60°C after days of hardening inair-dry conditions led to a decrease in strength by 14,7%. This fact can be explained by the fact that at the time of film formation cementitious matrix does not have sufficient strength, resulting in penetration of the polymeric matrix lead to the appearance of structural defects.

4.4 Effect of temperature and humidity conditions of hardening the strength of the modified cement stone

Hardening models affect the strength characteristics of cement composites. To determine the most effective temperature and humidity curing hardening taken five modes: a first mode (I) -to per 7 days air-dry conditions at a temperature t = 18-20̊ C, humidity of 60%; the second mode (II) - 24 hours air-dry conditions at a temperature t =18-20̊ C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60̊ C in SNOL 120/300 chamber and subsequent hardening in for 6 days in an air dry conditions at a temperature t = 18-20̊ C, humidity of 60%; the third mode (III)) -24 hours air-dry conditions at a temperature t = 18-20̊ C, 60% humidity, further for 4 hours treatment temperature t =60̊C. SNOL 120/300 chamber and subsequent hardening for 6 days in an air-dry conditions at a temperature t = 18-20̊ C, humidity of 60%, a fourth (IV) mode - 24 hours of air-dry conditions at a temperature t = 18-20̊ C, humidity of 60%, followed within 2 hours of heat treatment at a temperature t =40̊ C. SNOL 120/300 chamber and subsequent hardening for 6 days in an air- dry conditions at a temperature t = 18-20̊ C, humidity of 60%; a fifth mode (V) - during 2 hours of air-dry conditions at a temperature t = 18-20°C, humidity of 60%, followed within 2-hours heat treatment at a temperature t = 60°C. SNOL 120/300 chamber and subsequent hardening for 6 days in an air-dry conditions at a temperature t = 18-20°C, humidity 60%.

Samples of cubes with an edge of 20 mm, the modified polymeric additives Primal SM 330, DLP2141 and 2000 and DLP samples without polymer additives given in terms of hardening then aged 7 days and 28 days were tested for compressive strength at press PGM-500MG4A.

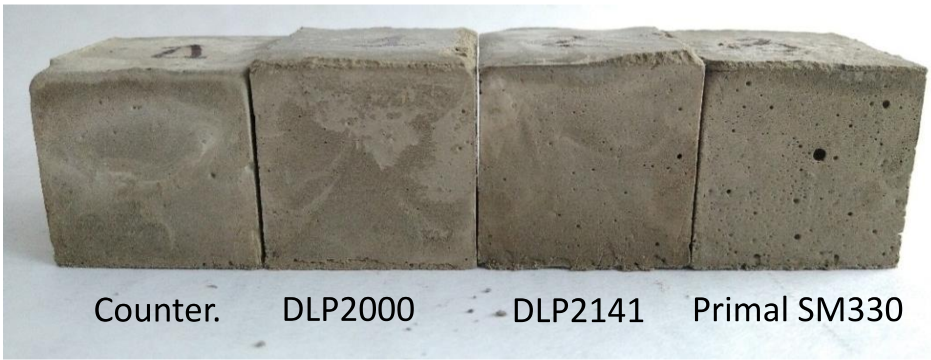

Figure 4.7. - Samples after heat treatment
(III solidification mode)

Before the test, the cement stone at the press, weighed, and samples determined by their geometric characteristics then calculated density samples. The test results of compressive strength shown in table 4.4.

Table 4.4 – Influence of the temperature and humidity conditions on the strength of the modified cement stone

Designation Polymer Additives	The amount of additive,% of the cement paste	I		II		III		IV		V	
		Strength R c, MPa (% R com) 7 days	Rszh Strength, MPa (% R com) 28 days	Durability compression channel R, MPa (% R com) 7	Durability compression channel R, MPa (% R com) 28	Durability compression channel R, MPa (% R com) 7	Durability compression channel R, MPa (% R com) 28	Strength R SJ, MPa (% R com) 7 days	Durability compression channel R, MPa (% R com) 28	Durability compression channel R, MPa (% R com) 7 days	Durability compression channel R, MPa (% R com)
Sample without additive	-	23.63 (100)	29.6 (100)	19.135 (100)	30,09 (100)	13.84 (100)	15.27 (100)	13.96 (100)	14.61 (100)	15.49 (100)	13.49 (100)
DLP2141	3	23.87 (101.01)	30.54 (103.18)	29.57 (154.53)	32.16 (106.88)	13.09 (94.58)	16.45 (107.73)	12.85 (92.05)	12.41 (84.94)	9.82 (63.4)	10.15 (75.24)
DLP2000	3	21.54 (91.15)	25.57 (86.39)	23.271 (121.62)	27.86 (92.59)	18.81 (135.9)	21.54 (141.06)	22.53 (161.039)	18.67 (127.79)	12.32 (79.53)	11.22 (85.06)
Primal SM 330	3	20.07 (84.93)	21.25 (71.79)	26.059 (136.19)	20.23 (67.23)	13.63 (98.48)	14.02 (91.81)	17.77 (127.29)	16.9 (115.67)	5.99 (38.67)	4.79 (33.28)

Depending on the choice of the temperature - humidity conditions can be obtain by different strength characteristics of materials. If the mode II, the compressive strength is increased by 5% with the use of additives DLP2141. With increasing time of heat treatment, a modified stone strength decreases by 26% compared to the compressive strength when set in the normal strength-dry conditions. The sharp decrease in strength occurs when the temperature-humidity conditions in which the initial extract samples in dry conditions normally lasted for 2 hours, after which the samples were subjected to heat treatment t = 60° C for 2 hours. With increasing temperature decreases from t = 60° to t = 40°, modified stone strength decreases by 32%. The most efficient temperature and humidity conditions for the modified stone.

4.5 Effect of Polymer Additives on the strength characteristics of the cement-sand mortar

Determination of the influence of polymer additives on the strength characteristics of the cement-sand mortar carried out according to the procedure STB EN 196-1 / PR [59]. Samples ravine, size 40x40 mm h160 (figure 4.8.) Made of cement-sand mortar with addition of polymer additives in an amount of 3% by weight of cement. After forming, the samples hardened in two modes: a first mode (I) - in 24 hours of air-dry conditions at a temperature t = 18-20° C, 60% humidity and then placed in a container of water prior to the tests; the second mode (II) - 24 hours air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60° C. SNOL 120/300 chamber and subsequent hardening in container with water.

Strength tests were performed on press - GMP 500MG4A. Determination results of flexural strength and compression cement-sand mortar presented in table 4.5.

Figure 4.8. - Samples before demoulding with 3% polymer additive DLP2000, without heat treatment

Table 4.5 – Flexural strength and compressive grout represented at 28 and 60 days

Designation Polymer Additives	The amount of additive,% of the cement paste	Curing condition					
		I			II		
		Durability R mfd. , MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 60 days	Durability R mfd. , MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 28 days	Durability compression channel R, MPa (% R_{com}) 60 days
Sample without additive	-	6,078 (100)	2,532 (100)	3,384 (100)	6,15 (100)	2,25 (100)	3,707 (100)
DLP2141	3	5,633 (92,68)	2,151 (84,95)	2,948 (87,12)	6,84 (111,2)	2,421 (107,6)	3,204 (82,43)
DLP2000	3	5,453 (89,71)	2,001 (79,03)	3,141 (92,82)	6,31 (102,6)	2,265 (100,6)	3,427 (92,45)

According to the test results show that the flexural strength increased by the heat treatment of the modified cement-sand mortar. In the first mode, adding polymeric additive DLP2141 DLP2000 and a cement-sand mortar, the flexural strength is less than the reference value by 8 and 11%, respectively. Flexural strength of samples subjected to heat treatment at 2 and 3% above control values. Thus, the bending strength of the modified cement-sand mortar above the recruitment strength in terms II-th mode.

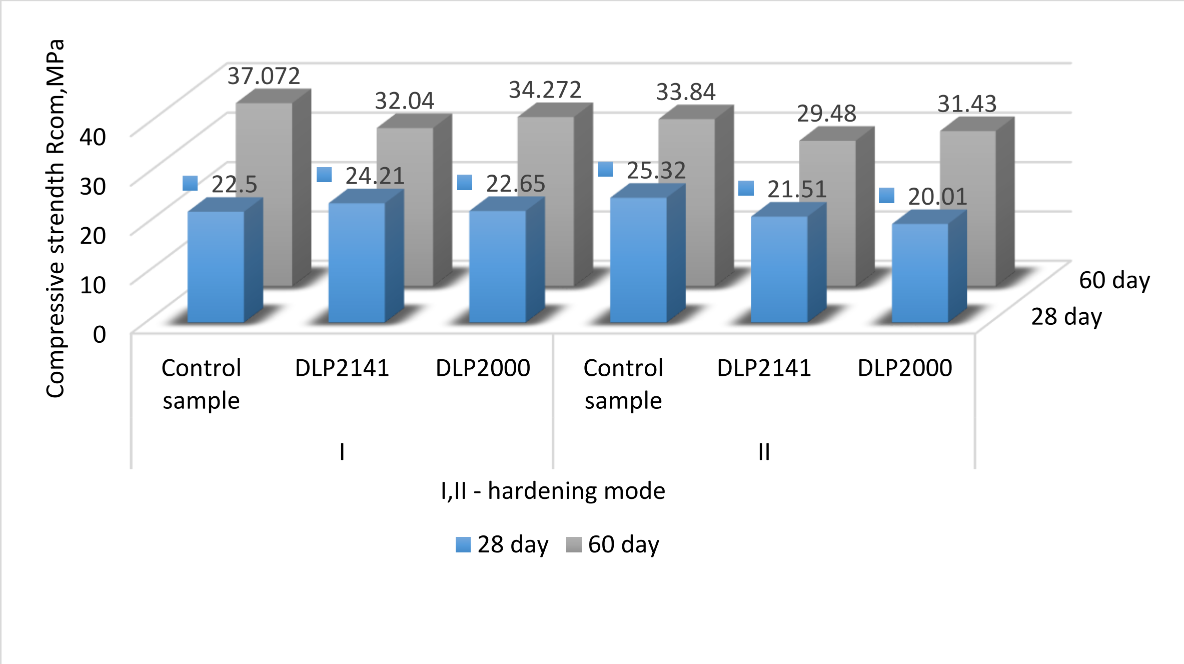

Figure 4.9. - Effect of Polymer Additives on the strength of the cement-sand mortar after 28 and 60 days.

The compressive strength of the modified cement stone above the reference values at a set of strength of cement-sand mortar under I-th mode to the age of 28 days. When added to a cement-sand additive solution based on vinyl acetate-copolymer of the compressive strength with time (from 28 to 60 days) increased by 35%. The compressive strength of the cement-sand mortar with addition of polymer additives do not reach the control values after 28 days in the I-st and the II-nd during curing modes.

4.6 Effect of polymeric additives on the strength characteristics of concrete

To determine the strength characteristics of concrete samples made with 100 mm cubes face (Figure 4.10.). During curing hardened samples at three curing modes: I - an air-dry conditions at a temperature t = 18-20°C, humidity of 60%; II - 24 hours air-dry conditions at a temperature t = 18-20°C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60° C in SNOL 120/300 chamber and subsequent hardening for 6 days in dry air at the temperature t = 18-20° C, humidity of 60%; control samples hardened in a normal-humidity mode (III), at a temperature t = 18 ° C, humidity 80%.

Determination of concrete mix mobility determined by [55], it mixes two compounds: 1 The control composition (no polymer additive); 2- modified concrete mix DLP2141 polymeric additive in an amount of 3% by weight of cement. Formulations of concrete mixes presented in table 4.6. The results of the concrete mix mobility listed in table 4.7.

Table 4.6 – Formulations of concrete mixes.

Room composition	Consumption				
	kg per 1 m^3 of concrete				% Of the binder weight
	Cement (U)	Sand (P)	crushed stone (U)	Water (AT)	DLP2141
1	500	570	1075	210	-
2	500	570	1075	210	0,105

Table 4.7 – Effect of polymeric additives on the mobility of the concrete mix.

Number of staff	Water-binder ratio	Mobility	
		OK, see	Mark on mobility
1	0.42	5	P2
2	0.42	6	P2

Figure 4.10. - The appearance of the concrete specimen

At 7, 14 and 28 days was determined by compression strength of concrete on the press PGM 1000MG4 (Figure 4.11.). Before the test, on the press, samples were weighed, determined by their geometric characteristics and the calculated density of the concrete (Figure 4.12.). Compressive strength results in table 4.8. and figure 4.14.

Figure 4.11. - Sample cube after testing on the press PGM 1000MG4

Table 4.8– Effect of polymer additives on the strength and density of the concrete.

Name of compositions	Curing condition	Density, kg / m^3			Compressive strength R_{com}, MPa (% of $R_{control}$) aged 7,14,28 days		
		7days	14 days	28 days	7 days	14 days	28 days
1	III	2434	2461	2441	38.6 (100)	42.81 (100)	43.53 (100)
2	I	2305	2312	2320	30.105 (77.99)	34.17 (79.82)	35.13 (80.15)
	II	2290	2326	2381	35.23 (91.27)	38.37 (89.63)	39.96 (91.79)

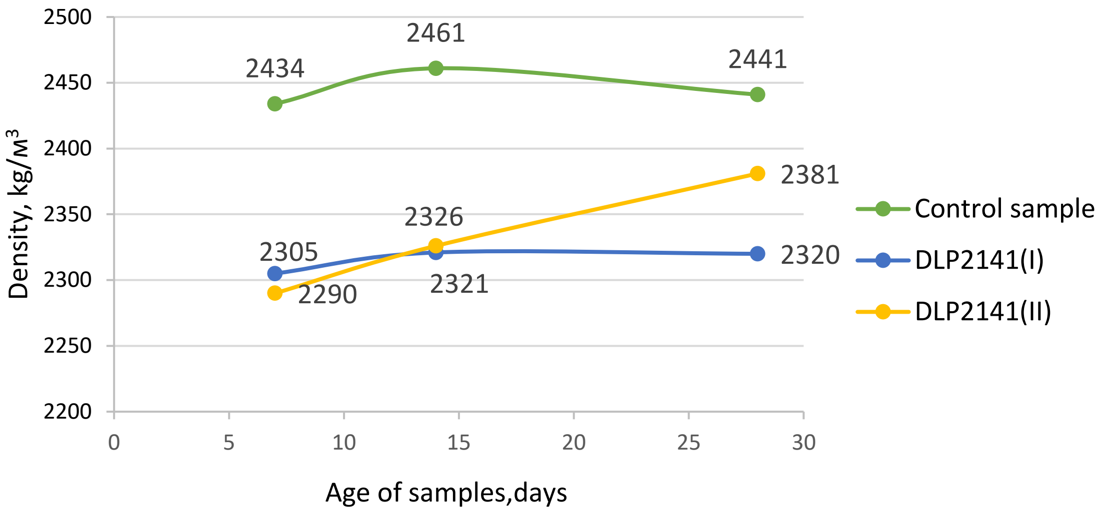

Figure 4.12. - Effect of additive on the polymer DLP2141 concrete density

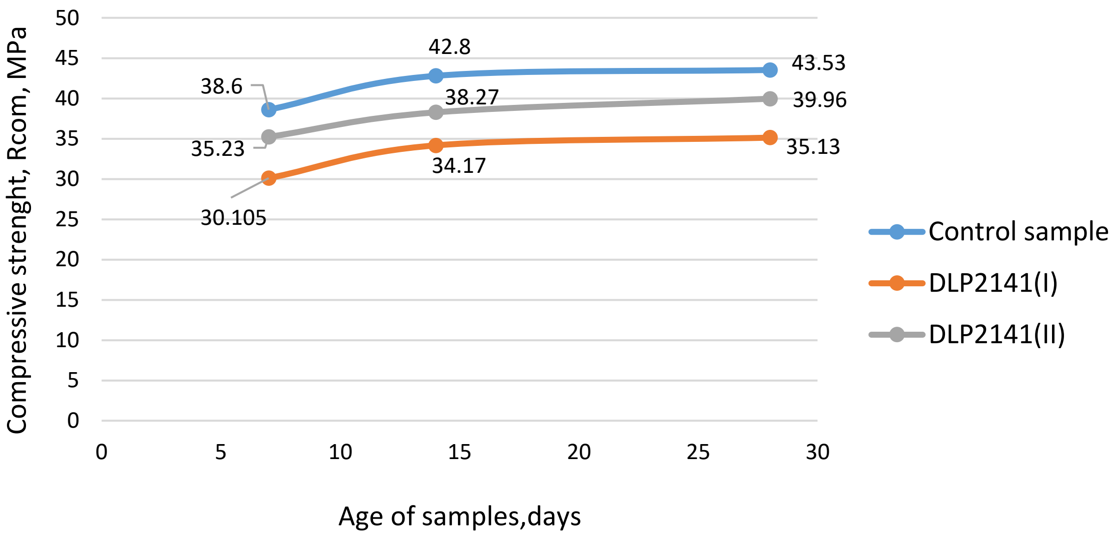

Figure 4.13. - Effect of additive on DLP2141 polymer concrete strength

According to the test results, it can be conclude that the addition DLP2141 polymeric additive in an amount of 3% by weight of cement in the concrete mix, the concrete density reduced by 4% compared with the control sample.

The density of the modified sample with a mode II hardening time is increased by 4%, and the density of a modified stone during mode I is increased by only 1%. It can be concluded that the solidification mode II, specimen concrete strength will be higher than the strength of the concrete hardening in the I mode.

In determining the compressive strength of concrete samples aged 7,14,28 days data were obtained on the basis of which to conclude that the compressive strength of concrete with a modified curing mode II 12% higher durability of concrete with the modified mode I. hardening concrete compressive strength without the polymer additive is 8% higher than the modified concrete hardening regime II.

In determining the grade of concrete strength were determined: M400 - concrete without polymer additive; M350 - concrete with a polymer additive DLP2141 during curing mode (I); M400 - concrete with a polymer additive DLP2141 during curing mode (II). Concrete DLP2141 modified polymer additive and curing mode (II), corresponds to the same brand of concrete, and that no additional concrete.

Concrete with DLP2141 polymeric additive in an amount of 3% by weight of cement and 24 hour hardening time of air-dry conditions at a temperature t = 18-20° C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60° C , can be used in building constructions.

M400 concrete that meets the requirements of GOST, used for the construction of facilities, the operation of which involves significant exposure to a mechanical load, causing significant stress formed in the concrete body.

These objects include: bridges with rail tracks, trestles for road transport, viaducts, viaduct line, and so on. etc.; bank vault - for their arrangement used concrete M400 f150; load - bearing structures in the form of columns, beams, connectors and so on. etc.; concrete class B30 M400 is indispensable for the construction of a hydraulic nature; monolithic high-rise buildings.

4.7 Resistance modified cement stone to sulfate corrosion

Corrosion resistance of the samples determined by three parameters: mass, density and strength.

The samples of cement stone, modified in an amount of 3%, were placed in a corrosive solution, then aged 28, 60 and 120 days was evaluated in corrosion performance.

Upon reaching 28, 60, 120 days finding modified stone in a corrosive environment, the samples removed from solution, and their mass was determined, and then measured and the geometric characteristics determined external changes cubes samples. Specimens mass changes results presented in table 4.9. and figure 4.15. The results of the change in density in figure 4.15. and table 4.10.

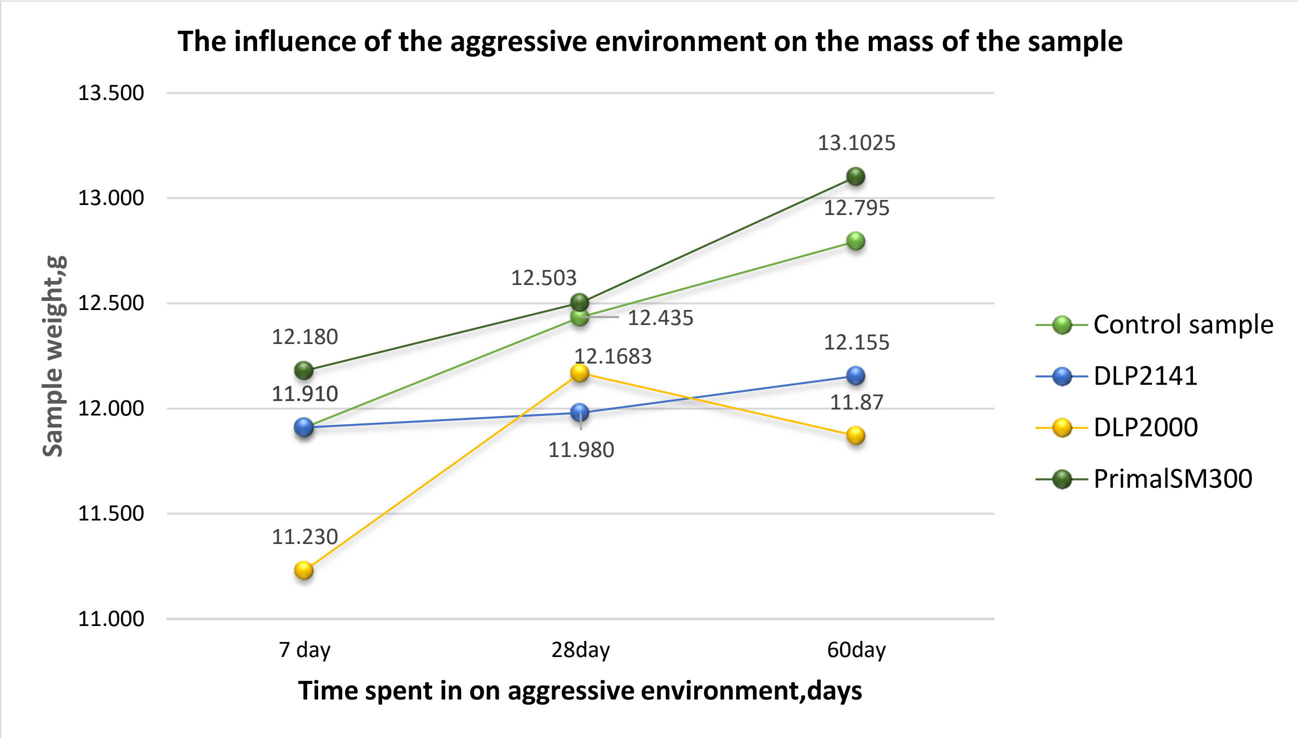

Figure 4.14.-Effect aggressive environment in weight of samples

Table 4.9 – Effect of aggressive environment in weight of samples

Designation Polymer Additives	7 days before the dive		28 days in solution		7 days before the dive		60 days in solution		7 days before the dive		120 days in solution	
	The surface moisture of the samples before immersion in the aggressive environment, W (%)	Weight before immersion in the aggressive solution, m (g)	Weight after extraction from aggressive environments, m (r)	Weight after drying, m (g)	The surface moisture of the samples before immersion in the aggressive environment, W (%)	Weight before immersion in the aggressive solution, m (g)	Weight after removal from the corrosive environment, m (r)	Weight after drying, m (g)	The surface moisture of the samples before immersion in the aggressive environment, W (%)	Weight before immersion in the aggressive solution, m	Weight after removal from the corrosive environment, m (r)	Weight after drying, m (g)
Check sample	14,7	12.210 (100)	14.825 (121.42)	12.435 (101.84)	14,5	12.535 (100)	15.335 (122.3)	12.795 (102.07)	14,6	12.58 (100)	15,45 (123.1)	13.55 (107.71)
DLP2141	13,8	11.910 (100)	14.105 (118.43)	11.980 (100.59)	13,4	12.070 (100)	14,497 (120.1)	12.155 (103.98)	13,7	11.95 (100)	14.35 (120.1)	12.36 (103.43)
DLP2000	15,5	11.230 (100)	14.465 (128.81)	12.1683 (108.36)	15,1	11.540 (100)	14,102 (122.2)	11.87 (102.86)	15,4	11.96 (100)	14.67 (122.76)	12.53 (104.76)
Primal SM330	13,2	12.180 (100)	14.925 (122.54)	12.503 (102.65)	13,4	12.535 (100)	15.612 (124.6)	13.1025 (104.53)	13,3	12.04 (100)	15.19 (126.16)	13.71 (113.8)

According to the results it is evident that samples of the modified polymeric additives based on vinyl acetate copolymer, gaining weight rapidly just prior to 28 days of being in an aggressive environment. After 28 days this process is inhibited, it is explained that the polymer additives do not allow the deposition of sparingly soluble substances, contained in an aggressive solution. In [60], these processes due to the fact that the interaction of the modified cement paste with aggressive environment formed with the maximum number colmatant highest specific diffusion resistance, which makes the process self-locking corrosion.

As is known, the contact area between matrix cement of conventional composition is a channel through which penetrate deep into products aggressive agents: gases, SO_4 ions -, Mg, Cl-, etc. To strengthen the adhesion can be achiev by providing the chemical and physical coalescence of the surface layers of cement matrices. It can be concluded that, to ensure adhesion between the cement matrix must be used, such additives as a DLP2141, DLP2000.

The results of the study of the influence of aggressive environment on cement paste density shown in table 4.10. and figure 4.15.

Table 4.10–Effect on the aggressive environment of the cement stone density.

Designation Polymer Additives	The density of the modified cement paste, kg / m3							
	The density before immersion in the aggressive environment, kg / m^3	Density after removal from the solution, kg / m^3	The density of the samples after drying, kg / m^3	Density after removal from the solution, kg / m^3	The density of the samples after drying, kg / m^3	Density after removal from the solution, kg / m^3	The density of the samples after drying, kg / m^3
	7 days before the dive	28 days in solution		60 days in solution		120 days in solution	
Check sample	1695.83	2059.03	1727.08	2129.86	1896.08	1931.2	1693.75
DLP2141	1654.17	1959.03	1663.89	2013.54	1688.19	1931.33	1545.3
DLP2000	1559.72	2009.03	1690.04	1958.68	1648.61	1833.75	1566.25
PrimalSM330	1691.67	2072.92	1736.53	2168.40	1819.79	1898.75	1713.75

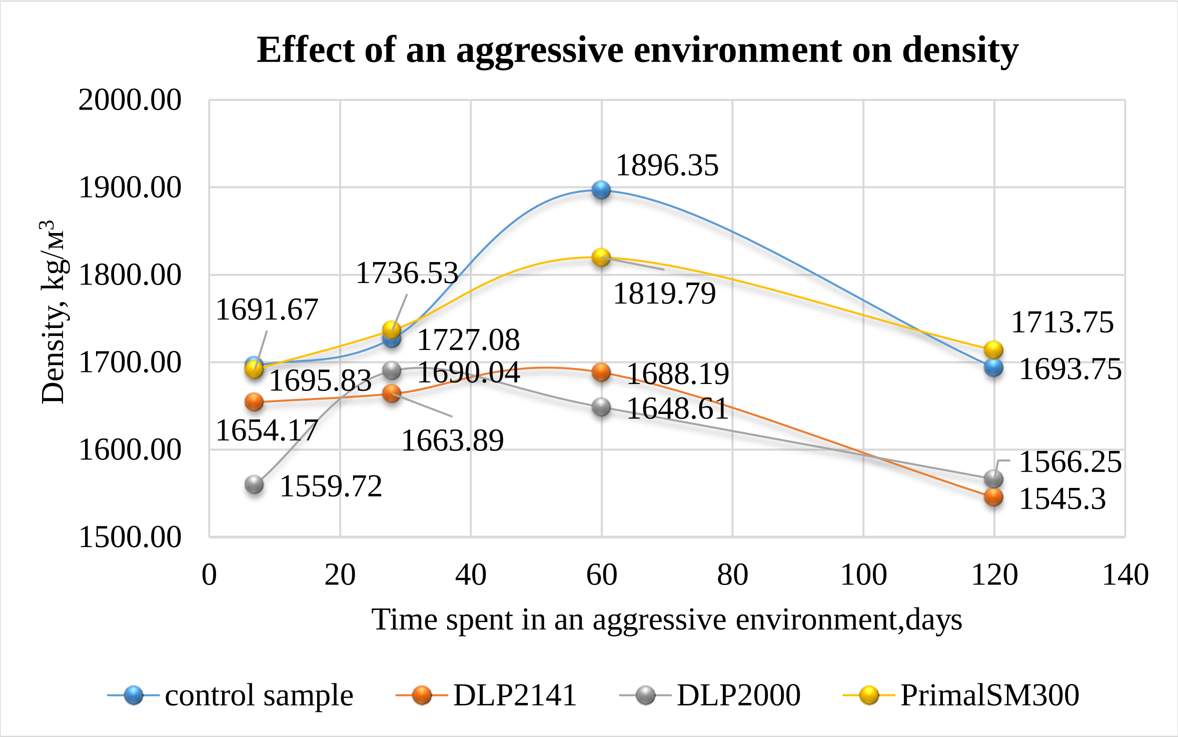

Figure 4.15.-Effect on the aggressive medium density samples

The density of the cement stone with polymer additives and without any additives increases with time. Which means that the cement stone absorbs not only water but also salt are in an aggressive solution, which over time will increase in volume and destroying cement matrix structure due to internal stresses.

After 60 days of being in an aggressive environment, the control sample continues to increase its density.

In cement paste samples with polymer additives, DLP2141 andDLP2000 density growth is less active compared to without additives samples, indicating that, hat the corrosion process slowed down.

Thus, to increase the sulfate cement stone can be recommend use additives based on vinyl acetate-ethylene copolymer.

Determination results of the compressive strength cubes samples aged 7 days (before immersion in the aggressive solution) and after 28 and 60 days of being in aggressive environments is presented in Table 4.11. and figure 4.16.

Table 4.11 – The compressive strength of the test samples on sulfate corrosion resistance of cement matrix

Name polymer additives	Durability compression channel R, MPa (% R czh, RA), at curing conditions			
	DDP	Aggressive environment		
	Aged			
	7 days	28 days	60 days	120 days
Check sample	13.47 (100)	51.09 (379.28)	28.69 (212.99)	33.42 (248.11)
DLP2141	19.65 (100)	34.396 (175.04)	31,12 (158.37)	43.74 (222.57)
DLP2000	21.214 (100)	44.64 (210.46)	42.32 (199.53)	48.39 (228.126)
PrimalSM300	13.91 (100)	44,56 (320.35)	32.79 (235.73)	38.3158 (275.45)

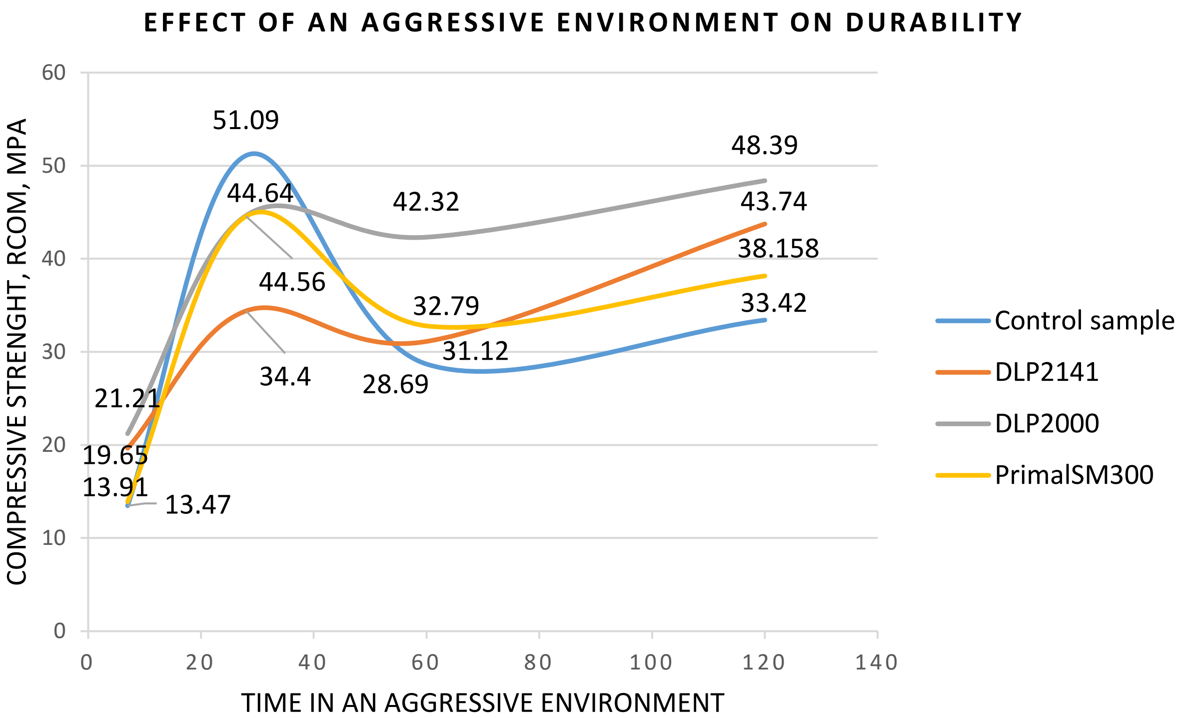

Figure 4.16. - Effect on the aggressive environment strength cement stone

A control sample, while in the aggressive environment of 28 days gaining strength better than the modified samples. The reason is that in order to ensure favorable conditions for the hydration of cement paste needed to ensure high humidity. For modified cement paste, specimen’s high humidity adversely affects the strength development and course of the polymerization process.

The samples were aged for 28 days is rapidly gaining strength, but after 60 days of being in an aggressive environment, the strength has fallen sharply from a control sample, which suggests that calcium ions, increasing in volume, destroying the structure of cement stone.

The compressive strength of the cement stone with a polymeric additive DLP2141 28 days increased by 75% compared to the strength at 7 days. Compressive strength at 60 days of finding decreased by 17% in the aggressive environment.

Modified stone with DLP2000 additive also increased its compressive strength after 28 days of being in the aggressive environment by 2 times compared to the strength before the immersion of samples in an aggressive environment. After finding a corrosive environment of 60 days, the compressive strength decreased by 11%.

The compressive strength of the cement stone PrimalSM330 additive as well as the cement stone without drastically gaining strength additives, and then sharply decreases it. After 28 day, strength increased by three times, but after 60 days of being in an aggressive environment has decreased by 85% compared to the strength before immersion in the aggressive environment.

Thus, it found that polymeric additives and DLP2141 DLP2000 composed improve sulfate cement stone cement stone. Moreover, to ensure sulfate recommended supplements based on ethylene vinyl acetate copolymer in an amount of 3% by weight of cement.

4.8 Chapter summery

1. Supplementation additives based on ethylene vinyl acetate copolymer in the cement composites in an amount of 3% by weight of cement increases the strength characteristics of the cement stone.

2. Temperature-humidity mode, which provides the initial exposure composites in dry-air conditions for 24 hours, the subsequent heat treatment t = 60^0C for 2 hours, provides acceleration of the polymerization of polymer additives which positively affects the strength characteristics of the cement stone.

3. Established that modified cement-sandy solutions continue to gain strength after 28 days 30% more than the cement-sand mortar without polymer additives.

4. The polymer additive DLP2141 corresponds to the grade for strength M400.

5. Polymer additives an ethylene vinyl acetate copolymer DLP2141, DLP2000, improve the corrosion resistance of cement matrix.

5. CONCLUSIONS AND FUTURE DEVELOPMENTS

5.1 Conclusions

1. The influence of the polymeric additives on the mobility, density and strength of the cement composites. Polymer Additives Primal SM330 DLP2000 and increase the mobility of 1.42 times. Additive DLP2141v 1.2 times reduces the mobility of cement paste. It found that the polymer additive DLP2141 based on vinyl acetate-ethylene copolymer accelerates the set of strength of cement stone at an early age contributes to the formation of a denser structure of cement stone. Dosage polymeric additiveDLP2141 should not exceed 3% by weight of cement. Studies have shown that at a dose of additive DLP2141v amount up to 3% by weight of cement on dry matter there is no decrease in the strength after 28 days compared to the control sample without additive.

2. Normal air-dry hardening conditions do not significantly affect the strength of the cement stone with a polymeric additive DLP2141, aged 7 days compressive strength amounted to 103.6% of the control values.

3. The most effective temperature and humidity conditions for a modified stone is 24-hour mode of air-dry conditions at a temperature t = 18-20̊ C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60̊ C in chamber SNOL 120/300 and subsequent hardening for 6 days in an air dry conditions at a temperature t = 18-20̊ C, humidity 60%.

4. DLP2141 polymeric additive in an amount of 3% when curing mode II-24 hours air-dry conditions at a temperature t = 18-20̊ C, humidity of 60%, followed within 2 hours of heat treatment at the temperature t = 60̊ C in SNOL 120/300 chamber and subsequent hardening for 6 days in the air dry conditions at a temperature t = 18-20̊ C, humidity 60%, no mark on reduces M400 concrete strength.

5. It is found that the polymeric additive and DLP2141, DLP2000 composed improve sulfate cement stone cement stone. In addition, to ensure sulfate recommended using them in an amount of 3% additive based on ethylene vinyl acetate copolymer.

5.2 Future developments

For further research, we offer a number of accelerated methods for studying sulfate corrosion. It is also possible to investigate the effect of polymer additives DLP2141, DLP2000, Primal SM330 on cement composites in the composition of which cement made by foreign manufacturers is used as a binder.

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