Modification of fine-grained polymer concrete with microsilica

Vadim Balabanov[1], and *Ksenia* Putsenko[1,*]

[1]Irkutsk National Research Technical University, 664074, Lermontova str., 83, Irkutsk, Russia

Abstract. At present, one of the most promising areas in construction is the modification of concrete by means of a complex of modifying additives and production wastes that will allow to obtain concrete with improved technical and operational characteristics and solve a number of problems: import substitution and nanotechnology. The aim of scientific research is the development of new technologies for obtaining concrete with enhanced performance characteristics, provided that raw materials, energy and labor costs are minimized. The article presents the results of research work on the development of fine-grained polymer concrete, modified with microsilica. In the framework of the study, a literature review for the last 68 years has been conducted, devoted to the experience of using microsilica and polymers in concrete construction as a modifier for building materials. The main characteristics of the starting materials and modifying additives are determined. A study was conducted to determine the effect of various modifying additives on the physicomechanical characteristics of fine-grained concrete. The main rheological properties and strength characteristics of the entire spectrum of the investigated compositions are determined. A microscopic study of the structure was carried out. The result of scientific research is the establishment of an optimal combination of additives, the development of cement concrete with the use of microsilica and acrylic dispersion and the determination of the effect of additives on the physical and mechanical properties.

1 Introduction

In a modern and ever-evolving world in which increasing demands for building materials are proportional to the growth of scientific and technological progress, there is an urgent need to modify concrete, for the purpose of using them in the construction of buildings and structures, bridges of viaducts, overpasses, highways and other critical structures, to which, at the present time, are subject to increased demands due to the increasing transport load of the massiveness of the erected structures, where it is necessary to take into account the load from direct facilities, etc. In this regard, the actual task of building materials science is the development of new technologies for the production of concrete with enhanced performance characteristics, subject to minimization of raw materials, energy and labor costs.

[*]Corresponding author: putsenko_kseniya@mail.ru

The relevance of this paper is that:

1. At present, there is an urgent need to develop new technologies for the production of high-quality and durable cement-concretes in conditions of minimizing material, energy and labor costs.

2. The cost of cement concrete is determined by the cost of the binder. Due to the fact that the binder is more expensive than other constituent components of the cement concrete compound, it becomes necessary to search for materials that have similar properties and are able to replace some of the binder without losing the mechanical characteristics of products or structures.

At present, the method of modifying cement-concretes by means of a complex of modifying additives is gaining increasing popularity, which allows us to eventually obtain a building material with improved technical and operational characteristics. Some of these additives are microsilica and acrylic dispersions.

Microsilica is a by-product of silicon production, formed as a result of oxidation in the gas phase of SiO, which is formed during smelting of silicon-containing alloys in electric arc furnaces, by condensation of SiO_2 microparticles from the gas phase and their extraction from furnace gases. After oxidation and condensation, some of the SiO_2 forms small spherical particles with an increased content of amorphous silica [1-5].

Microsilica (MK) is widely used in the production of concrete, reinforced concrete structures and products, by adding it to the mixture, in order to replace some of the cementitious cement. Since 1950, intensive work has begun to develop and install systems that capture microsilica. Since 1950, the first tests have begun to add microsilica to concrete. The result of these research works is the adoption of standards for microsilicon in cements and concretes. In 1990, the world community recognized microsilicon as an effective additive in concretes, and in 2000, microsilica became widespread in all European countries [6-9].

With the use of microsilica, such structures as high-rise buildings in Chicago, the Tunnel under the English Channel, a bridge across the Northumberland Strait in Canada, Norwegian offshore drilling platforms in the North Sea, etc. were built. A few decades later, the first attempts to introduce microsilica into concrete mixtures began in Russia. A few years later, the following facilities were built: transport tunnels on Kutuzovsky, Leninsky, Nakhimovsky avenues, bridge in Bratislavskaya street, overpass on Oleny Val street, gravity-type oil platforms for the Sakhalin-2 project, etc.

For all its positive qualities, concretes without the use of additives acquire a number of drawbacks: long setting times, low values in bending and compression tests, low chemical resistance and crack resistance. To prevent the appearance of the above listed deficiencies, it is recommended to use additives that modify concrete and give it special properties [10-12]. Required indicators are concrete, modified with polymers. In this regard, such concrete was called - polymer cement concrete. One of the most common polymers is acrylic dispersion (latex). Acrylic dispersion - a polymer consisting of the smallest polymer particles (0.05-5 microns), which are dispersed in water by polymerization of emulsions.

In 1923, Cresson [13] received the first patent for polymer cement, which included acrylic dispersion. In 1924 Lefebre patented the idea of modifying solutions and concretes by means of natural rubber latex, and in 1925 Kirpatrik presented his idea of modifying with latex. In general, the whole period of 1920 - 1930 can be characterized as a large-scale application of latex in concrete technologies. This technology was widely used in Great Britain: British builders erected such important structures as airfields, various facilities for storing water, etc. In 1932 Bond was granted a patent. His idea was to use synthetic rubber latex. In 1933, Rodwell patented the idea of using latex synthetic resins. In 1940, several patents were published on the modification of synthetic latexes - polychloroprene rubber latexes and polyacrylate ether latexes.

A new type of concrete has become actively used in shipbuilding, bridge construction and simply as anticorrosive coatings. At the same time, two British, Griffiths and Stevenson, are conducting research on the use of natural rubber.

In 1953, Gaste and other researchers presented the results of his research on polyvinyl acetate solutions. 1960s are characterized by active study of modification of concrete by means of polyethylene vinyl acetate and its copolymers, polyacrylic ether, methylcellulose, polyvinyl chloride and various types of synthetic rubber.

The popularity of the use of polymers in the USSR fell on 50-70 years. This period is characterized by the active use of polyvinyl acetate dispersion and synthetic latex. The peak of popularity has since declined, but despite this, research is currently being carried out on the use of latex in modern building materials, taking into account the newly emerging requirements for them.

In view of the foregoing, the research problem is:

1. Saving the binder by replacing its part with a similar material,
2. Intensification of hydration of binder,
3. Russia has large volumes of silicon waste products that are not used anywhere, while abroad they have been successfully used for 68 years.

The solution to these problems can be:

1. Modification of the structure of cement stone by means of microsilica and acrylic dispersion,
2. Development of technology for obtaining fine-grained polymer concrete,

The purpose of the research work is the development of technology for the production of cement concrete using acrylic dispersion.

To achieve the goal, the following tasks were set:

- to study the effect of microsilica and acrylic dispersion on the structure of cement stone;
- Investigate the physicochemical processes of interaction of microsilica and acrylic dispersion with the main components of cement concrete;
- determine the properties of modified cement concrete;
- Develop a technology for the production of cement concrete with improved technical and operational characteristics;

The scientific novelty of the work is as follows:

1. The combined use of microsilica and acrylic dispersion is proposed for the first time;
2. The developed cement concrete will refer to concrete with special properties (polymer cement concrete);
3. It is possible to expand the use of the developed technology for other types of concrete.

2 Materials and methods

The aim of the studies was to obtain reliable results based on the conducted experiments to determine the degree of influence of modifiers on the technical and operational characteristics, structure and properties of concrete.

To study the characteristics and properties of the raw materials, test methods were used, regulated by normative and technical documents.

To obtain reliability of the results, a comprehensive approach to the study and determination of the technical and operational properties of concrete was used, namely, the composition and structure of the cement stone and the properties of concrete mixtures. In addition to standard techniques, a study was carried out using an electron microscope.

To determine the properties of the starting materials, the following methods were used:

1. Determination of the ultimate strength of cement for bending and compression [14],
2. Determination of the normal density and timing of setting to confirm the factory characteristics of cement [15],
3. Determination of the characteristics of quartz sand [16],
4. Determination of the properties of the concrete mixture [17],
5. Methods for determining the density of concrete [18],
6. Methods for determining the strength of concrete from control samples [19],

In order to determine the most effective amount of the modifying additive, it is necessary to study the complex interaction and the effect of these additives on the properties of cement paste and cement stone. For this, it is necessary to study the influence of microsilica, the plasticizing additive SP-1 and latex. The choice of these modifying additives is explained by the fact that they have a positive effect on the physical and mechanical properties of cements [20].

One of the most important properties of a concrete mix is its workability. The formation of a mass of a homogeneous consistency is facilitated by the amount of water, astringent and specialized additives. The index of workability is characterized by mobility, stiffness and connectivity of the mixture, and is an indicator of the rheological characteristics of mixtures.

The rheology of concrete mixtures is related to the process of structure formation. Special influence on rheological properties is exerted by such factors as:

- concentration dependence,
- grading,
- structure and texture of the aggregate,
- dynamic load,
- distribution of particles,
- thixotropy of the mixture
- time factor, etc.

To assess the rheological properties of the concrete mixture, the following characteristics are evaluated: cohesion (which depends on two parameters - cement activity and B / C, which are quantitative parameters of the strength of the CC), viscosity, internal friction. In the framework of this research work, two indicators of the rheological properties of the cement test were evaluated: the normal density of the cement test and the setting time, taking into account the additives used: acrylic dispersion, microsilica, polyplastic SP-1.

Normal density is characterized by the amount of water, which is expressed as a percentage of the mass of the cement. The indicator of the normal density of the cement paste was determined experimentally according to GOST 310.3-81 [15].

The following compositions were tested:

1. Control sample (KO) + latex (1.0 - 5.5%)
2. Control sample + microsilica (10.0 - 30.0%)
3. Control sample + SP-1 (0.5-1.0%)
4. (Control sample + microsilica) + SP-1 (1.0-1.6%)
5. Control sample + microsilica + latex (1.5-4.5%)
6. (Control sample + microsilica) + (SP-1 + latex) (3.0 / 1.0%)

Based on the data obtained as a result of studies to determine the index of the normal density of the cement test, the following conclusions can be drawn:

- with the maximum amount of latex, the water demand is reduced by 12% compared to the water requirement of KO. With a minimum amount of latex, the water demand rises by 2.67%. This suggests that the increase in water demand is inversely related to the amount of latex;

- with the maximum number of MK-95 water demand increased by 22.23% compared to the water demand of KO. With a minimum number of MK-95, water demand increased by 13.24%. When microsilica is added in an amount of 15-20%, the smallest amount of water necessary to achieve the required normal density;
- with the maximum number of SP-1 water demand is reduced by 13.33%. With a minimum amount of SP-1, water demand is reduced by 8.88%. This suggests that the reduction in water demand is in inverse proportion to the amount of added SP-1;
- with the maximum number of SP-1 and (MK-95 + KO), water demand is reduced by 4.44%. With a minimum number of SP-1 and (MK-95 + KO), water demand is also reduced, but by a higher value - by 15.11%;
- with the maximum amount of latex and (KO + MK-95), water demand is increased by 7.12%. With a minimum amount of latex (KO + MK-95), water demand is increased by 13.34%. This suggests that the increase in water demand is inversely related to the amount of latex;
- at 3,0% of the amount of latex and 1,0% of the amount of SP-1 in (KO + MK-95), water demand is increased by 8.89%. The increase in water demand is due to the joint use of the additive SP-1 and latex.

Determination of the setting time is one of the indicators of the rheological properties of the mixtures. Determination of the setting time is carried out in accordance with GOST 310.3-76 [15].

Based on the data obtained as a result of tests to determine the effect of additives on the setting time, it can be concluded that the simultaneous introduction of MC and latex had a significant effect on the timing of the seizure of the prototypes. Absolute values of all prototypes with latex in (KO + MK-95) are in the interval -45 / + 55 minutes compared to the values of the control sample. The introduction of latex in an amount of 3.0% or more in (KO + MK-95) shortens the beginning of the setting time by 10+ minutes and the end - for 25+ minutes. The control time for the end of the setting time for samples with a latex content of 3.0% or more decreases from 275 to 265 minutes.

The main and main mechanical characteristic is the bending and compression strength index. To determine this characteristic, GOST 310.4-81 was used [14]. Tests to determine the strength characteristics were carried out using all additives. Based on the data obtained as a result of studies to determine the flexural and compressive strength, the following conclusions can be drawn:

- with the addition of 1.0% to 3.5% of the cement mass, the maximum increase in strength relative to the strength of the KO was 10.15%;
- when adding 10.0 to 20.0% of the cement mass, the maximum increase in strength relative to the strength of the KO was 47.25%;
- the increase in strength indicators when using SP-1 is observed;
- with the addition of SP-1 in the amount of 1.0% of the mass of cement in (KO + MK-95), an increase in strength relative to the strength of KO by 80.44%.

Based on the data obtained, the compositions were prepared and samples were made. Determination of the compressive strength was carried out at the age of 28 days. The data are presented in Figure 1.

Analyzing the dynamics of the strength composition of the composition of KO + MK + latex in wet and air-dry conditions of hardening, it was revealed that when the samples are hardened in air-dry conditions that are identical in composition with the samples that are hardened in water, the strength set is faster and the strength values on compression at the age of 28 days higher. Based on this, we can draw conclusions:

- in air-dry conditions, hardening is more preferable for hardening;
- with the addition of latex in an amount of up to 2.5% of the mass of cement in (KO + MK-95 under wet conditions of hardening), an increase in strength relative to the strength of KOs by 74.24%;
- when latex is added in an amount up to 2.5% of the mass of cement in (KO + MK-95 under dry conditions of hardening), the strength relative to the strength of KO is increased by 105.43%;
- when combined (latex + SP-1) in (KO + MK-95) in the amount (3.0 / 1.0) of the cement mass, the effect is not observed.

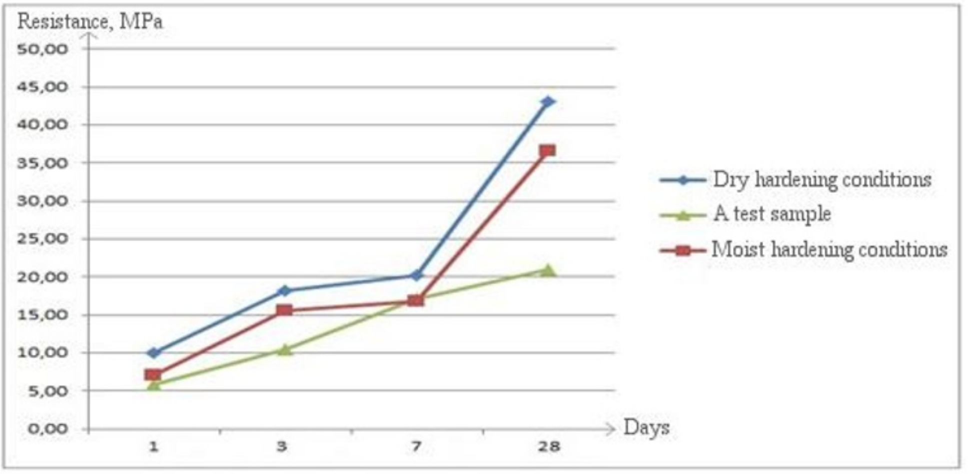


Fig. 1. Graph comparing the dynamics of the strength set of the composition of KO + MK + latex (wet and air-dry conditions of hardening).

Concrete mixture is a multicomponent system that includes binder (cement), coarse and fine aggregate (sand, gravel), water, aggregates and additives. During the preparation of the mixture, air is drawn into it, thereby increasing the porosity and aggregate volume of the mixture. Due to the fact that the mixture contains air, it becomes a multiphase medium, which is located between viscous liquids and granular media [21-22].

Particular influence on the properties of concrete is due to the dimensions of structural elements, such as: the dimensions of grains, pores, voids, etc. In this regard, there are such two concepts as macro- and microstructure [21].

A macrostructure is a structure that is visible to the eye or with a slight increase. Studying the macrostructure, you can see the filler, cement stone and pores [21, 23].

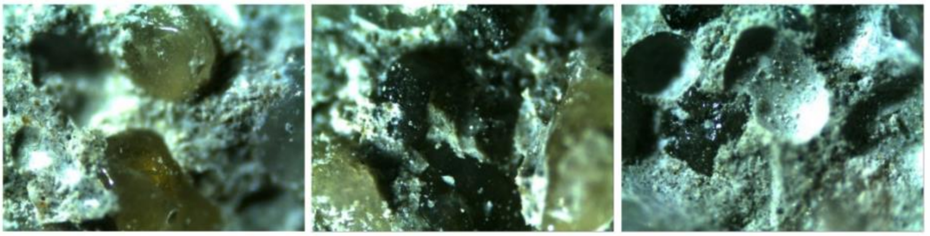
A microstructure is something that can be seen under a microscope at high magnification. When studying the microstructure of concrete, special attention should be paid to grains of cement and voids [21].

Summarizing the studied material on the structure of concrete, it can be concluded that:

1. The structure of concrete is heterogeneous - it is a spatial lattice of cement stone, which is filled with grains of coarse and fine aggregates of different fractional composition;
2. The structure of concrete also includes micropores and capillaries, which contain chemically unconnected water, water vapor and air;
3. Concrete - a capillary-porous material with broken mass continuity;
4. The cement stone is characterized by a heterogeneous structure, consisting of crystalline growth and cement gel;
5. Macrostructure can be seen without using special equipment, and microstructure - only with the help of a microscope;

6. Different microstructures can be obtained by adjusting the mineralogical composition of the binder and the hardening conditions;
7. Microstructure has a more significant effect on the strength of concrete, so it must be carefully studied under a microscope with subsequent evaluation of the results.

Microscopic examination was carried out using a polarizing microscope. The receipt of the photograph was to be described from the point of view of the microstructure (Fig. 1). The structure should be described by the content of cement stone in it and its placement in concrete.



а) б) в)

Fig. 1. The structure of the control samples (a), the structure of the samples with (MK + latex), gaining strength in moist (b) and dry conditions (c).

The structure of the control sample can be characterized as a homogeneous, type I (dense) type. An increased volume of cement stone is also observed. There is a small amount of pores.

The structure of samples with 1.5 - 2.5% latex content, which gained strength in wet conditions, can be characterized as a homogeneous, type I (dense) type. An increased volume of cement stone is also observed. There are fewer pores, compared to control samples.

The structure of samples with 1.5 and 2.5% latex content, which gained strength in air-dry conditions, can be characterized as a homogeneous, type I (dense) type. An increased volume of cement stone is also observed. There is a much larger number of pores, compared to control samples and samples that are hardened in wet conditions.

3 Results

Based on the results of the studies, the following results were achieved:

1. The influence on the rheological properties of the cement test and the strength of the cement stone additives of latex, microsilica, SP-1 separately and when combined into the mixture.
2. The study of the physico-mechanical characteristics of modified cement shows that the additives that have the most vivid effect are the combination (MC-95 + latex). The optimum content of these additives is 10.0 - 20.0% MC and up to 2.5% latex. The increase in strength relative to the strength of the RO is:

- when hardened in air-dry conditions - 43.08 MPa (ie an increase of 22.11 MPa),
- when hardened under humid conditions - 36.54 MPa (ie an increase of 15.57MPa).

3. The conducted study to determine the timing of setting and strength characteristics of cement stone modified with latex, and MC shows that the absolute values of all prototypes with latex in (KO + MC-95) are in the interval -45 / +55 minutes compared to the values of the control sample. The introduction of latex in an amount of 3.0% or more in (KO + MC-95) shortens the beginning of the setting time by 10+ minutes and the end - for 25+ minutes. The control time for the end of the setting time for samples with a latex content of 3.0% or more decreases from 275 to 265 minutes.

4. Investigation of the microstructure allows us to conclude that, depending on the composition and hardening conditions, the microstructure of the concrete will also change. Analyzing all the data, it was revealed that the structure of the samples obtained on the basis of the developed formulation is homogeneous, belonging to type I (dense). This structure is characterized by a tight contact between the binder and the filler, which is achieved by adding some MC. This allows the activation of hydration processes and the formation of crystallization centers of calcium hydrosilicates, thereby contributing to the compaction of the cement matrix structure that binds the constituent components of concrete into a conglomerate with increased physicomechanical properties. There was also an increase in the volume of cement stone. A much larger number of pores are present in the sample, compared to control samples and samples that are hardened in wet conditions.

5. The increase in strength of fine-grained polymer concrete due to the use of microsilica and acrylic emulsion is substantiated. The joint use of these additives helps to increase the degree of hydration of cement.

6. The technology of increasing the operational properties of concrete by adding microsilica in the amount of 10% to 20% and up to 2.5% of acrylic emulsion from the mass of cement was developed. The optimum mode of hardening of concrete is determined - air-dry mode.

7. The class and brand of the developed formulation increased from B15 (M200) to B30 (M400).

4 Conclusion

Summarizing the results obtained, it can be concluded that the combined use of microsilica and acrylic dispersion is very effective from the point of view of increasing the strength characteristics of fine-grained concrete. Microsilica is a waste of silicon production. Therefore, its use in the production of concrete solves three more important tasks - import substitution, waste utilization through their use in the production of building materials and the application of environmentally friendly waste products.

References

1. K. Iler Ralph, The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica (P 1), **896** (1979)
2. Electronic Magazine “Construction” (St. Petersburgr, http://library.stroit.ru/articles/kremzem/index.html, 2018)
3. ASTM International, *Official website* (https://www.astm.org/cis/ru/index.html, 2018)
4. T. C. Holland, Silica Fume User's Manual: Technical Report No FHWA-IF-05-016, **193** (2005)
5. H. E Bergna, The Colloid Chemistry of Silica. Am. Chem. Soc., **718** (1994)
6. European Silica Fume Committee, *History & manufacturing process* (http://www.microsilicafume.eu/web/history%20and%20manufacturing%20process/1011306087/list1187970101/f1.html, 2018)
7. Silica Fume Association, *What is silica fume?* (http://www.silicafume.org/general-silicafume.html, 2017)
8. The Silica Fume Association, *Silica fume in concrete* (http://www.silicafume.org/general-concrete.html, 2018)
9. S. Bhanja, B. Sengupta, ACI Materials Journal, 407-712 (2003)

10. G. D. Fedorova, Building Materials, **4**, 70-71 (2014)
11. G. I. Berdov, Building Materials, **9**, 79-83 (2012)
12. V. R. Falikman, O. O Kalashnikov, Concrete and Reinforced Concrete, **1**, 2-9 (2015)
13. *Isotex (insulating technology)* (http://www.izoteh-spb.ru/services/floors/poli-cement-poli/4)
14. GOST 310.4-81, **11** (2015)
15. GOST 310.3-81, **6** (2015)
16. GOST 8735 -88, **25** (2015)
17. GOST 10181-2014, **24** (2015)
18. GOST 12730.1-78, **4** (2015)
19. GOST 10180-2012, **32** (2015)
20. Yu. M. Bazhenov, L. A. Alimov, V. V. Voronin, Structure and properties of concretes with nanomodifiers based on man-made waste, **204** (2013)
21. Yu. M. Bazhenov, Technology of Concrete, **500** (2003)
22. V. S. Ramachandran, Concrete Admixtures Handbook: Properties, Science and Technology, **1183** (1996)
23. L. N. Thyui Zang, N. A. Epishkin, V. B. Balabanov, V. P. Baryshok, Proceedings of Universities. Investment. Construction. Real Estate, **4(23)**, 155-161 (2017)