The Structure and Properties of Hardened Cement Paste with Modifiers

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Abstract. Currently, the durability of concrete is normalized by indirect indicators - the quality of the materials used, reinforcement and additives, the properties of the concrete mixture and its degree of compaction when molding reinforced concrete structures, the duration and parameters of concrete care. Regulatory documents, depending on the operating environment, regulate the maximum allowable value of W/C, the minimum allowable consumption of cement and the class of concrete for compressive strength. The main structural element of concrete is cement stone, the products of cement hydration provide its adhesive and cohesive properties and form a concrete conglomerate. Low basic calcium hydroxides form a cement gel - the densest and most durable component of cement stone. Modification of cement stone with water-reducing additives and microsilicon contributes to the formation of hydrosilicate phases in the form of an uncrystallized gel, a weakly crystallized gel-like C-S-H (I) phase with a ratio of C/S=1,1-1,3, and individual inclusions of calcium hydroxide are observed.

1. Introduction

At present, heavy concrete is the most produced building material in terms of volume. It has gained such popularity due to its ability to preserve its qualities, being under the influence of chemical environments and physical exertion. In turn, the composition and structure of artificial stone make up its future range of properties.

Currently, the development of concrete technology and the problems of improving the quality, durability, and efficiency of concrete are solved by using various types of chemical additives. The introduction of organic and inorganic compounds in the composition of concrete allows a wide range to change its physical and mechanical properties, composition and structure, and also has a positive effect on the durability of concrete and reinforced concrete structures.

The main quality criteria of high-functional concrete are high strength, frost resistance, water resistance, chemical resistance, low diffusion permeability, etc. The directed formation of the structure of the hydrate phases of cement stone by the introduction of modifier additives increases the content of cement gel in concrete, and the joint introduction of water-reducing additives and effective pozzolana increases the stability of the cement gel under cyclic influences [1-4].

Durability – the ability of a construction object to maintain the strength, physical and other properties that are established during design and ensure its normal operation during the design life with proper maintenance [5].

The main factors influencing the durability of concrete are:

- the quality of raw materials, type and amount of introduced additives, the chemical composition of water used to temper and pour concrete;
- the W/C value as a means of controlling the density, durability, and strength of concrete;
• the aggressiveness of the operating environment, which causes chemical degeneration of the structural elements of hardened cement paste, as well as the loss of the protective properties of concrete with respect to steel reinforcement;
• the structure of hardened cement paste, which forms the properties of concrete, and its stability in the actual operating conditions of concrete and reinforced concrete structures.

Of the factors that affect the durability of concrete, first of all, the role of the materials used should be noted. In addition to the requirements for cement, the content of harmful impurities contained in aggregates is standardized.

The content of dusty and clay particles, clay in lumps that increase the water demand of the concrete mixture, shrinkage and creep of concrete is limited, which negatively affects its durability. The content of plate-like and needle-like shaped grains, the content of weak rock grains, frost resistance, and resistance to disintegration are additionally regulated for coarse aggregates.

Water resistance of cement concretes is formed as a result of cement hydration and depends mainly on the W/C and the degree of cement hydration. The permeability of hardened cement paste is 20-100 times higher than that of the gel, and grows with an increase in the W/C due to an increase in the volume of the macrocapillary pores. The higher the W/C, the longer the concrete curing time; if the W/C exceeds 0.6, the macrocapillary porosity of concrete cannot be eliminated, even if the curing time is more than 1 year. The introduction of active mineral additives allows us to reduce the coefficient of water filtration through concrete by up to 1000 times.

To increase the durability of concrete, it is necessary to strive to obtain a finely dispersed structure of the hydrated phases of the cement stone and to increase the gel porosity. In a number of publications mention the role of increased dispersion of hydrate phases of cement stone on the properties of concrete [6-8].

Some publication note the possibility of aging in cement gel connected with the following factors:
• concrete hardening conditions - steam and autoclave treatments contribute to the formation of the coarsely-dispersed structure of hardened cement paste with reduced resistance and durability;
• cyclic freeze-thaw of concrete according to the standard procedure also intensifies ageing of the hardened cement paste structure;
• pozzolanic stabilization of the structure of the hydrated phases of hardened cement paste during cyclic freezing, which contributes to the improvement of frost resistance and durability of concrete.

According to [9], additives which increase water resistance and frost resistance of concrete, strengthening its bioreistance and protecting steel against corrosion, are used to ensure durability.

The amorphous structure of ordinary concrete is preserved while reducing the content of free Ca(OH)2 due to pozzolanication and the use of an effective plasticizer.

A promising way to improve the quality of knitting without significant changes in production technology is to introduce various finely dispersed additives that actively influence the formation of the structure and properties of cement stone in the process of cement hydration [10]. Thanks to the use of micro-fillers, it is possible to save cement and improve the exploitative of concrete.

Active mineral additives bind calcium hydroxide and form a hardened cement paste structure with a high content of gel-like low-basic calcium hydrosilicates, which favorably influences the density and resistance of concrete to various types of corrosion [11,12].

Microsilica (MC) is a by-product of metallurgical production in the smelting of ferrosilicon and its alloys, formed as a result of the reduction of silica in electric furnaces. In the process of smelting silicon alloys, some silicon monoxide SiO goes into a gaseous state and, subject to oxidation and condensation, forms an extremely small product in the form of spherical particles with a high content of amorphous silica [13].

Microsilica as the active mineral additive in concrete exhibits two major effects: [14].
• micro filling
• pozzolanic
Due to pozzolanization, large crystals of portlandite disappear and voids between cement grains are filled with cement gel, which reduces the permeability of cement stone to liquid and gaseous media [15].

In modern construction, chemical additives are full effective components of cement systems of varying degrees of complexity, allowing them to purposefully control their properties both at the stage of preparation and use, and for the long-term operation of the obtained stone materials.

The key elements of high-quality concrete technology are the use of MC and superplasticizers (SP) [16,17].

MC has a high specific surface area and low bulk density, its use provides an increase in the strength characteristics of concrete, but leads to an increase in the water demand of the concrete mix. Therefore, the use of MC is advisable in combination with water-reducing additives such as superplasticizers [18-20].

Introduction of MC both with SP and without them significantly increases the heat flow and accelerates the hydration processes. It is known that the silica fume reacts in a pozzolanic reaction with Ca(OH)2 and forms a low-basic hydrosilicates of calcium [21].

2. Materials
Portland cement CEM I 42.5N manufactured by Dückerhoff Korkino Cement, SP-1 naphthalene-maldehyde superplasticizer manufactured by Polyplast UralSib LLC, meeting the requirements of technical conditions 5870-005-58042865-05; active mineral additive - microsilica (MS), Novokuznetsk, corresponding to technical conditions 5743-048-02495332-96.

Since MS possesses pozzolanic properties and interacts with calcium hydroxide released during hydrolysis of C3S, we took it as a binder component and evaluated the water demand not by the water-cement ratio, but by the water-binding ratio.

3. Results and discussion
According to the data obtained, the compression strength of cement stone mainly depends on the W/B. The introduction MC modifies the products of hydration and contributes to improved strength, but this effect is manifested only with increasing age.

General X-ray phase analysis of the additive-free hardened cement paste aged 28 days (Figure 1) showed that its structure is a slightly-crystallized CSH(I) hydrosilicate with d/n=11, 5.6, 3.07, 2.8, 1.83 Å and C-S-H(II) d/n=9.8, 3.07, 2.85, 2.8, 2.4, 1.83, 1.56 Å, Ca(OH)2 d/n=4.93, 3.11, 2.63, 1.93, 1.79, 1.485 Å and residues of unreacted source minerals.

![Figure 1. X-ray of cement stone without additives at the age of 28 days.](image-url)
Electron microscopy confirms this data (Figure 2). According to a local X-ray analysis, well-formed Ca(OH)2 crystals, weakly-crystalized masses of hydrosilicates with an increased basicity of C-S-H(II) type and silica gel sections are visible on the cleavage surface.

The cement stone modified with MS has a dense surface with a shell-like, splintery fracture and mainly consists of low-basic C-S-H(I) phases interspersed with calcium hydroxide.

According to the obtained data, the SP-1 additive does not influence the phase composition, but when used together with MS, a predominantly-amorphized structure of low-basic hydrosilicates C-S-H(I) phases is formed (Figure 3).

From the given data of x-ray phase analysis and electron microscopy, it follows that with the introduction of additives SP-1 and MK, the structure of the cement stone is represented by more crystallized phases.

4. Conclusions
The complex naphthalene formaldehyde superplasticizer SP-1 and MK increases the strength and provides a sharp reduction in capillary porosity, which is responsible for the density, permeability, resistance, and therefore the durability of concrete. This complex additive makes it possible to obtain cement stone mainly from weakly crystallized (amorphized) low-basic calcium hydrosilicates, which are more resistant to various cyclic influences, such as freezing and thawing, moistening and drying, as well as variable mechanical stresses.

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