Application features of additives based on metakaolin in concrete

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Abstract. The present paper is devoted to the influence of additives based on metakaolin (U-YF, UM-YF and YF-UMD) on speed concrete strength development in the early stages of concrete hardening, as well as the strength increase in 28 days. The authors have proved that metakaolin gauging in concrete should not exceed 3%. Introduction of 5% of metakaolin or more entails the fault in concrete strength in the later stages of concrete hardening and decreases its resistance to the influence of sulfate and frosty environments. The most effective of the developed additives are UM-YF and UMD-YF which provide high sulfate and frost resistance to the concrete (up to 800…1000 cycles). The above mentioned influence of additives on concrete properties is connected with an intended formation of structure of the cement matrix of concrete that is resistant to various aggressive environments.

1. Introduction

For highly efficient construction materials active mineral additives are widely used including granulated blast slag, silica fume, rice hull ash, and other additives; metakaolin is of particular interest lately.

Metakaolin (MTK) is a metastable reaction product of dehydroxylated kaolin at the temperature of 650 – 850 °C. The research on the influence of additives on the properties of MTK cement compositions was initiated in the middle of the twentieth century, but until now various issues on its application are still unclear. Disagreement among researchers relates to the formation of various compositions of hydrate neoplasms. Taking into account the defect structure and the weak link of the aluminum ions in the lattice, we can assume that in the presence of water MTK dissociates into aluminate and silicate parts, wherein there is a great probability of recovery of the lattice with the addition of different elements to form compositions characteristic of the “Al₂O₃–SiO₂–CaO–H₂O” system. Thus, F.L. Glekel in his work has noted that calcium hydroaluminates of various basicity and composition, gidrogelenit, calcium hydrosilicates, which are developed in dependence on the concentration of calcium ions in the liquid phase, may be the pozzolanic reaction products in the presence of MTK [1]. According to [2,3] and other researchers the Al(OH)₃ gel may occur in the system “Al₂O₃–CaO–H₂O” at an early stage of interaction which thereafter crystallizes in highly hydroaluminates of calcium, hydrogarnets, hydrogelenits, and calcium hydrosilicates (depending on the acidity and other factors). It is not feasible to identify patterns in the formation of the phasic composition of cement matrix in the presence of addition of MTK because the “Al₂O₃-CaO-SiO₂–H₂O” system is quite complex and the formation of connections is determined by the conditions of the reaction, as well as the quality of ingredients and manufacturing technology. Besides the phasic
composition, there are disputable differences in MTK gauging. Great number of researchers indicate the MTK dosage as about 10 \([4, 3]\), 20 \([5]\), or even 30\% \([6]\) of the mass of cement which they believe will improve the instant and final strength of cement formations. In addition, S.A. Zakharov \([4]\) noted that MTK gauging 1.5 ... 2\% of the whole weight of cement is sufficient to improve the water resistance cement compositions. Moreover, statements of different researchers on the impact of addition of MTK on resistance to aggressive environments are ambiguous. Metakaolin is an aluminosilicate additive which includes \(\text{Al}_2\text{O}_3 : \text{SiO}_2 \approx 1:2\), while the state standards of Russia 55224-2012 and 22266-94 strictly regulate limit of C3A content in cement – not more than 7\%, in sulphate-resistant cements – not more than 5\%. Limitation of the amount of aluminate in cement is determined by the lower opportunity to form metastable hydroaluminates of calcium in the cement matrix \([2, 7]\). As a conclusion, the researchers note that MTK reduces the consumption of cement in concrete, accelerates the hydration and hardening of cement compositions resulting in a high, early, and final strength of concrete and reveals the increased water requirement, so that it should be used in conjunction with water-reducing admixtures.

The aim of the current study is to investigate the possibility of obtaining cement compositions with high strength and sulphate and frost resistance by modifying the complex additives based on MTK.

2. Materials and methods

Complex additives previously developed on the basis of MTK - U-YF (1.5-3.5\% of MTK, 0.6\% of SP-1), UM-YF (1.5-3.5\% of MTK, 5\% of SF, 1.2\% of SP-1) and the UMD-YF (1.5-3.5\% of MTK, 10\% of SF, 1.2\% of SP-1) were used. For the purpose of research the authors used MTK produced by ‘Plast-Refey’ in accordance with the specification TU 5729-095-51460677-2009, silica fume (SF) of Novokuznetsk factory (TU 5743-048-02495332-96) and superplasticizer SP-1 produced by "Polylayer" Novomoskovsk (TU 5870-005-58042865-2005). Moreover, the authors used the cement CEMI 42.5 produced by "Nevyanskiy cementnik"; quartz sand from Belonosovsky field by the state standard of Russia 8736-93 and gravel of 5-20 mm fraction in accordance with the state standard of Russia 8269.0-93. The authors carried out the testing of the strength characteristics of the cement and concrete in accordance with the state standard of Russia 310.4-81 and 10180-2012; specific surface area of cement matrix was evaluated by the BET method; the porosity was determined according to the state standard of Russia 12730.4-78; frost resistance was assessed by the third accelerated method by repeated freezing and defrosting in accordance with the state standard of Russia 10060.2-95. To study the water and frost resistance in accordance with the state standard of Russia 24211-2008 the authors developed heavy concrete samples. To study the structure of cement matrix the authors used the scanning electronic microscope JeolJSM-700 1F. The sulphate resistance was tested in accordance with the state standard. The solution concentration is determined at 1000 mg/l = 10 g/l. Water resistance is determined by the accelerated method according to the state standard of Russia 12730.5-84.

3. Results

Study of strength characteristics of cement matrix (Figure 1) revealed that the introduction of additives of U -YF leads to an increase in its strength for 2 days of hardening in 2 times compared to no additives composition. By the 28 days of hardening with the use of complex additive of U -YF strength cement matrix above 80\% compared to non-additive composition. UM-YF and UMD-YF modifiers slightly underestimate the strength development in 7 days compared to the addition of U -YF, but by 28 days the strength of concrete with the abovementioned additives is increased by 10\%. Application of 5\% of MTK is accompanied with the loss of strength of cement in the later stages of hardening which is associated with recrystallization aluminate metastable phases in a stable one and is consistent with Kuznetsova’s data \([2]\). Application of designed complexes reduces open porosity of cement matrix (Figure 2), increases the specific surface area of hydrated phases and creates a more dense packing. This is due to the filling of intergranular space of highly dispersed mineral supplements and decrease the W/C ratio, as well as due to the formation of hydrated phases in the form of a tightly
welded plates, hexagonal and cubic hydroaluminates, hydroaluminosilicates and that is confirmed by electron microscopy analysis (Figure 3).

Study the effect of supplementation with MTK possible to establish the following. Application of MTK at 2 ... 3% by weight of cement does not lead to a decrease in sulfate-resistant cement and has level similar to one without additives.

Introduction of additives 5% by weight of cement MTK (Figure 4) causes a decrease in cement matrix sulphate resistance Kh.s. <0.9 after 1 month of testing, sulphate corrosion due to the interaction of sulfate ions with aluminate phases and calcium hydroxide cement matrix to form ettringite and gypsum.

With the addition of 5% in the MTK structure of cement is constant recrystallization aluminate phases under the influence of sulfates, which leads to disruption of contacts in the cement matrix and strength to discharges [8]. Introduction of additives to complex "MTK + SP-1" promotes the formation of cement matrix and stable hydroaluminates hydrogarnets but this creates a more dense structure of cement matrix (Figure 3, d) due to active hydration, all this leads to a reduction in permeability and increased resistance to sulphate corrosion (Figure 4). The study revealed a significant waterproofing concrete complex additives influence on its seal, by accelerating the hydration of cement hydrate phases and increase in cement matrix. This effectively resulted in a decline of porosity and water
resistant concretes provided when administered supplements U-YF brand W18, using complexes UM-YF and UMD-YF over W20, whereas no additives and composition with 5% MTK brand waterproofing had no more than W8.

Application of MTK without 5% super plasticizer increases frost concrete brand (F 300) in comparison with non-additive composition (F 200), which is associated with accelerated cement hydration process and therefore a seal structure.

Developed complex additives - modifiers can significantly improve the frost resistance of concrete. Since the introduction of additives have U-YF hardness increases by three times (F 600) for cement compared with non-additive composition, the use of additives UM-YF and UMD-YF improves frost resistance of concrete to F800-1000. All this testifies to the active influence of additives included in the complex formation of frost on concrete structure which is due to compaction and reduction of open porosity, and due to the formation of hydrated phases presented as hydro silicates calcium (GSK), resistant to cyclical changes in the acidity of the medium pore space reduction leaching of portlandite under cyclic temperature changes and facilitate stress relaxation during thermal cycling.

4. Conclusions
1. MTK dosage must be strictly limited to the production of concrete with high demands on performance hardness and resistance to sulphate corrosion. MTK should be administered no more than 3%;
2. Developed additives are effective accelerators providing increased strength at 2nd day of curing over 50% compared to the strength at 28 days with no additives composition.
3. The most effective of the developed additives that provide high resistance to frost and sulfate resistance of concrete are UM-YF and UMD-YF, allowing to get the hardness of F800…1000 which is connected with the peculiarities of formation structure of concrete.
4. U-YF, UM-YF and UMD-YF additives can be used for fast setting and high-strength concrete with ordinary cement at normal hardening in the field or in the factory without heat-moisture treatment or with low-temperature heat treatment to 50 °C.
5. Complex supplements of UM-YF, UMD-YF allow producing effective concretes with high strength and durability and can be used in the production of concrete for hydraulic structures, road construction, bridge construction and in the construction of other important structures.

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