

Application of the Effect of Ultra-low Concentration in Concrete Technology

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Received: 22 Jul 2020

Accepted: 28 August 2020



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ABSTRACT: The results of studies of the influence of nano-modifiers on the appearance of dimmers of colloidal surfactants on the compressive strength of concrete and the rate of its formation are presented. It has been shown that colloidal aliphatic surfactant increases the strength of concrete. Moreover, the joint introduction of a colloidal aliphatic surfactant and traditional hydrophilic surfactants leads to an even greater increase in the strength of concrete. A significant increase in concrete strength occurs at an early age in concrete.

KEYWORDS: Concrete, Strength, Surfactants, Nanomodifier, Cement, Concrete, Water.

The Essence of The Applied Scientific Problem

The essence of the applied scientific problem, which is considered in the paper, is to develop the scientific basis of nanomodification of fine-grained concretes by introducing into their composition filled micelles of colloidal hydrophobic aliphatic surfactants in low concentrations.

Actuality of Theme

Certain types of concrete and reinforced concrete materials, products and structures, namely construction solutions for surface decoration and repair of building structures, thin-walled and thin-walled products, reinforced concrete, including monolithic, building structures, it is advisable to make of fine-grained concrete.

Every year in the world practice of concrete and reinforced concrete production the production of high-quality concretes of fine-grained concretes is growing rapidly and has become an objective reality, caused by considerable savings of material and energy resources. Significant scientific advances in the creation of superplasticized binders, micro-disperse mixtures with reactive powders from high-strength rocks have allowed water-reducing effects to be reduced to 60% by the use of superplasticizers of oligomeric composition and hyperplasticizers of polymeric composition.

Typical nanowires in Portland cement systems are SiO₂ micro- and silica nanocrystals, TiO₂, Al₂O₃, Fe₂O₃, CaCO₃,

shungite, taurite and carbon nanomaterials (carbon nanotubes and nanofibers) [1,2].

Research Tolmachev and Belichenko [3] showed that with the introduction of a small amount of carbon nanotubes (CNTs) (0.0045% and 0.0225%), the compressive and flexural strength increases by 1.2 and 1.5 times, respectively.

In the writings of Suhanevich [4] showed that the introduction of multilayer carbon nanotubes together with plasticizer C-3 in cement mortar leads to increased flexural strength and reduced porosity. Moreover, the pore distribution becomes more uniform [5].

In the implementation of complex modification of the superplasticizer and active silicon dioxide is achieved by providing water-reducing properties and is the binding of calcium hydroxide with hydrosilicates, and the process occurs without increasing the solid phase, ie without the formation of internal stresses. The overall porosity of the structure is reduced by the replacement of the mechanically weak calcium hydroxide phase by the stronger hydrosilicate phase [5].

These concretes, regardless of their scope, must have certain general properties. Namely, sufficient durability and high speed of formation of its structure that will shorten the time of production of such concrete products and structures or shorten the construction time.

One of the disadvantages of many cement-water systems is their relatively low rate of structure formation and, therefore, its basic properties. Yes, for the reaction of hydration of cement minerals, the usual conversion time is several weeks or even months, so finding effective methods of accelerating these reactions is an urgent task.

In addition, the use of some surfactants may make them incompatible with cement [6]. Therefore, studying the effects of chemicals in low doses is of great interest [7,8].

At this time, a steady trend has been the use of various types of catalysis to accelerate virtually all reactions used in organic chemistry. Even those transformations that were previously carried out without the use of any catalysts are now involved in a range of catalytic processes, reflecting the general general direction [9,10]. The interest in solutions of colloidal surfactants arises from their general ability to structure water molecules, and to promote peptization of binder particles, that is, to act as a catalyst in chemical reactions [11,12]. These substances activate the water, which eliminates their negative impact on the processes of hydration of cement. Therefore, determining the effect of low dose surfactants is relevant.

The novelty of the work is to summarize the experience of using filled micelles in concrete technology and to determine that their most rational creation on the basis of colloidal surfactants of aliphatic type at low concentrations.

Materials Used in the Research and Methods of Their Implementation

The investigated design projects were best performed by Portland Cement 42.5 of Private joint stock company (PJSC) Heidelberg Cement. (Kryvyi Rih, Ukraine). River sand was used as a small concrete filler. As the surfactant forming the hydrophobic micelles (MPAR) used sodium oleate, as plasticizers used: superplasticizer Master Silk, as well as hyperplasticizer company Srase "Adva 151". The plasticizers were dissolved in water to a concentration of 0.001. The plasticizer aqueous solution in the amount calculated according to the design of the experiment was added to the container with a metered amount of water for mixing the concrete. The compositions of the tested concrete mixtures were determined in accordance with the requirements of the rules.

Research Results

Due to the fact that a special role in the problems of forming the optimal structure of cement composites is given to mixing water with cement, as the main component. Water nanostructuring, which leads to changes in its parameters, is a way to improve the rheological characteristics of cement dough and the physical and mechanical properties of nanomodified cement stone and concrete made on its basis. This occurs through the activation of the liquid phase and the physicochemical processes that form the structures of the composites. Well-known experimental data indicate that aqueous systems in which solutes are in low (picomolar) and ultra-low (phentomolar) concentrations have a number of special unclear properties. One of the features

observed in the field of low or ultra-low concentrations of soluble substances is the nonlinear dependence of the physicochemical properties of the solution on the concentration.

Indirect characteristics of the degree of structuring of water, namely the size of the solvation shell around nano-modifiers—MPARs, may be electrical conductivity, pH of the suspension and change of the meniscus in the capillary. Measurement of these indicators allows us to judge the comparative size of the solvation shell and, accordingly, the size of these molecules that are adsorbed on it.

These data allow to state that the introduction of nano-modifier—surfactant forming the hydrophobic micelles (MPAR) dimers in water leads to the formation of a volumetric fractal grid due to changes in the water's own structure, which are manifested in changes in its physicochemical properties.

Based on the study of the physicochemical properties of aqueous suspensions with different concentrations of dimers, the interval of a nanomodifier in which a volumetric fractal mesh arises that is capable of altering the electrochemical properties of miscible water is determined. As a result of researches the mechanism of nanostructuring of water is formulated by sorption of hydroxyl groups by the surface of the nanomodifier. This revealed a poly-extreme relationship between the concentration of the MPAR nano-modifier dimers and the properties of the suspension. The results of complex studies revealed that the optimum concentration of nanomodulator dimers—MPAR in mixing water is in the range of $10^{-3}\%$ – $10^{-6}\%$. In the case of mixing water structured with nano-modifiers—MPAR dimers, the dispersion system "Portland cement-water" should demonstrate the properties of water as a structured system, namely: providing a high degree and speed of hydration of dry matter (rapid dissolution of inorganic salts) at a deeper and more uniform the bonding of the filler particles with cement. The electrokinetic potential of molded surfaces and bulk agglomerates of hydrate complexes of solids charge increases. The degree of topography of the active centers of the surface of the particles of the dispersed phase increases.

According to the results of the integrated analysis of dispersed components (Portland cement), which was carried out by sieve analysis, it was found that there was a significant reduction in the particle size of Portland cement in the dispersion system "Portland cement—water—MPAR" due to the action of water structured by MPAR dimers. This is indicated by the increase in dissolution of Portland cement particles when mixed with water, structured with MPAR dimers. The results of the experiments showed that the introduction of a low concentration of MPAR in the cement-water dispersion system under the experimental conditions leads to an increase in the amount of bound water in concrete and a significant increase in the rate of formation of its structure throughout the study period.

At a certain interval of change of concentration of MPAR ($10^{-3}\%$ – $10^{-6}\%$) the specific electrical conductivity of the system practically does not change (Figure 1).

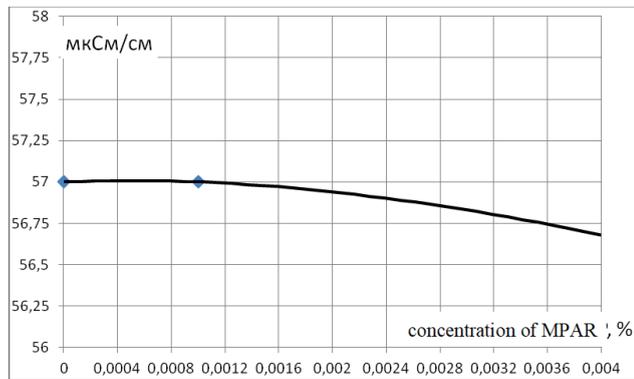


Figure 1. The dependence of the electrical conductivity on the concentration of MPAR.

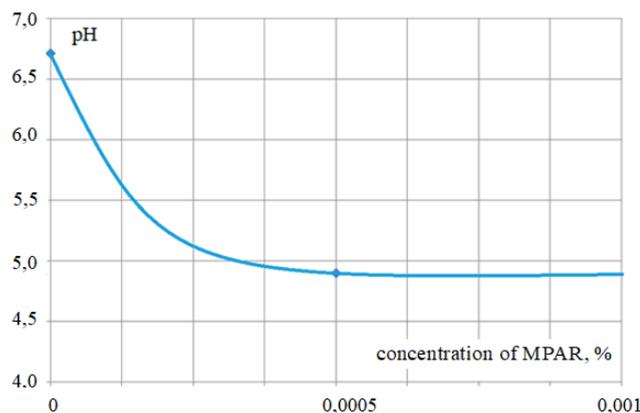


Figure 2. Changing the pH of the system depending on the concentration of MPAR.

This indicates a change in the ionic strength of the water caused by the sorption of hydroxyl groups on the surface of the dimmers introduced into the liquid.

Thus, in the case of nanostructured water modification, an orientation interaction of its molecules with dimmers occurs, which translates the system into an activated state.

In an aqueous medium containing dimmers, a new structure is formed, which depends on the interaction of the interfaces, significantly distorting its own structure of pure water, while the spatial hydrogen grid is not destroyed and its stability is not broken. Dimmers (nanomodifiers) act as stabilizers of the self-organization processes of the water system. The development of this process leads to the emergence of a secondary nanostructure—the fractal grid.

The obtained research results indicate the presence of a concentration interval of nanomodifiers—dimmers ($10^{-3}\%$ – $10^{-6}\%$), where the pH of the suspension decreases (Figure 2). The explained effect can be considered only in view of the change in the ionic production of water caused by the sorption on the surface of nanoparticles—dimmers of hydroxyl groups MPAR.

In the course of research, it was found that when using a superplasticizer in the amount of 0.17% with a content of sodium oleate 0.00024% concrete strength was 150% of the

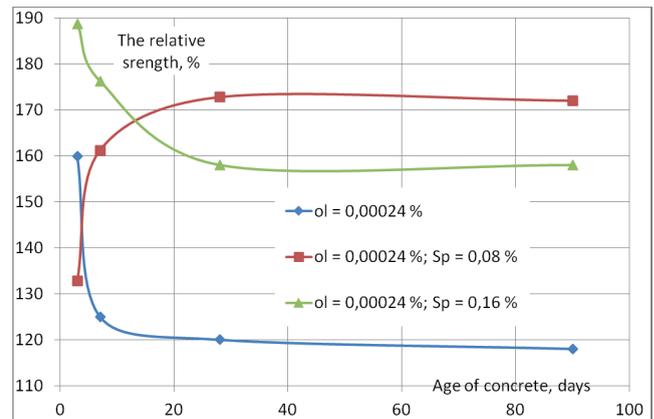


Figure 3. Influence of MPAR on the formation of concrete strength when using superplasticizer (Sp) and sodium oleate (ol).

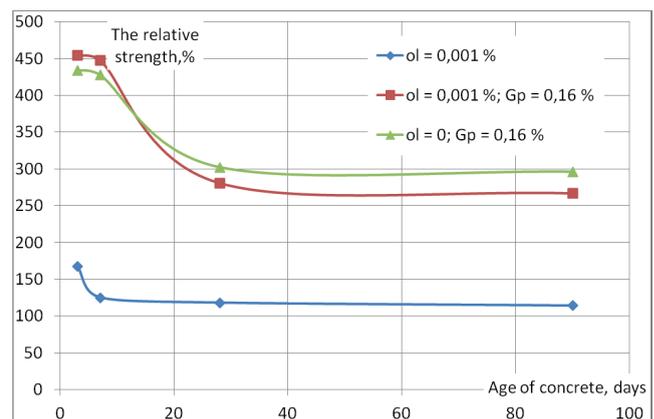


Figure 4. Influence of MPAR on the formation of concrete strength when using hyperplasticizer (Gp) and sodium oleate (ol).

strength of concrete without additives, and in the absence of sodium oleate was 121% (Figure 3).

When using a hyperplasticizer (Gp) in the amount of 0.17% with a content of sodium oleate (ol) 0.0003% the strength of concrete was 240% of the strength of concrete without additives. In the absence of sodium oleate, the strength of concrete containing 0.17% of hyperplasticizer was 260% of the strength of concrete without additives (Figure 4).

When using filled oleate-based micelles in the amount of 0.0004% the strength of sodium concrete was 198% the strength of concrete without additives.

Conclusions

The results of the studies allow us to draw the following conclusions:

- the influence of surfactants on the formation of compressive strength of concrete exceeds the influence of solid nanomodifiers, in particular carbon nanotubes, silicon microxide and others;
- the use of aliphatic hydrophobic surfactants capable of forming micelles, most effectively as nanomodifiers of concrete;

- when using aliphatic hydrophobic surfactants, which are capable of forming micelles as separate modifiers of concrete, their costs are $10^{-4}\%$ – $10^{-6}\%$ By weight of cement. The increase in the strength of concrete at an early age reaches 90%, and at the age of 28 days—40%. The mechanism of action of modifiers of this type and application is to structure the water due to hydrophobic hydration and the « effect of ultra-low concentration »;
 - when using aliphatic hydrophobic surfactants capable of forming micelles as filled micelles, their costs are 10^{-4} – 10^{-6} wt.% the weight of cement (when filled with polymers). The strength of concrete at the age of 28 days reaches—100%–200%. The mechanism of action of modifiers of this type and application is consistent with the mechanism of micellar catalysis and the “low concentration effect”;
 - it is advisable to use aliphatic hydrophobic surfactants to enhance the strength of concrete at an early age. To increase the strength of concrete in older age, it is advisable to use micelles derived from aliphatic hydrophobic surfactants.
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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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