Investigation of Mechanism of Action of Modifying Admixtures Based on Products of Petrochemical Synthesis on Concrete Structure

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Abstract. The creation of composite materials for generating structural elements with the desired properties has always been and still remains relevant. The basis of a modern concrete technology is the creation of a high-quality artificial stone characterized by low defectiveness and structure stability. Improving the quality of concrete compositions can be achieved by using chemical admixtures from local raw materials which is a very promising task of modern materials’ science for creation of a new generation of concretes. The new generation concretes are high-tech, high-quality, multicomponent concrete mixes and compositions with admixtures that preserve the required properties in service under all operating conditions. The growing complexity of concrete caused by systemic effects that allow you to control the structure formation at all stages of the technology ensures the obtaining of composites with "directional" quality, compositions, structure and properties. The possibility to use the organic fraction of oil refining as a multifunctional hydrophobic-plasticizing admixture in the effective cement concrete is examined.

1. Introduction

Currently the use of advances of basic science in the field of modifications of concrete becomes a strategic line of development of the applied building science. Analysis of publications and materials of conferences held in Russia and abroad, on issues of practical application of complex admixtures in construction in recent years have shown that great attention is paid to the use of the products and industrial wastes in the production of building materials, including modified concrete and mortar. The use of modifiers allows you to create concrete and mortars of various functional purposes with a wide range of desired properties [1-5].

Construction, including production of construction materials, can obtain greater benefits from the use of complex admixtures which give special properties to concrete. Concrete is basically a complex structure partially located on the nanoscale level, including a hydrate phase of the cement with a particle size of 1-100 nm, the grain of the original cement 10-100 nm, additives and fillers are ideal candidates for management of their properties. Notice that the programmable use of chemicals in the concrete can ensure maximum efficiency of the used binder from the viewpoint of preventing the occurrence of cracks and for providing the strength enhancement. Overcoming of internal structural defects is the path to radical improvement of the quality of material.
When it comes to the production technology of modified concrete we mean such a "thin" technology which renders possible to control the processes of receipt of material at atomic-molecular level, i.e. using the atomic-molecular effects. This means that we may talk of "aimed" material science, including construction material science [6-10].

2. Relevance and scientific merit of the subject
The most effective way of improving the concrete quality and improving its performance characteristic which requires no capital expenditure is its modification by the chemical and mineralogical admixtures. All scientists in all countries are handling a problem of development and search of new efficient admixtures. Construction practice proves tangible technical and economic effect and increasing of durability of concrete and reinforced concrete structures, and engineering structures made of precast and mix-in-situ concrete due to the use of admixtures as modifiers of concrete. Complex admixtures that combine several types of effects on the concrete mix are the best solution to develop effective new generation concretes with high strength, low permeability and high durability, as mono-admixes along with the positive effect often have negative effect on properties of concrete, which reduces its effectiveness [11-15].

Often wastes of various industries and its by-products are used as admixtures-modifiers. Their effectiveness should be assessed carefully and empirically, considering both positive and possible negative effects. Such admixtures may be products of natural origin (volcanic ash), by-products from the combustion of fuel (fly ash), by-products of metallurgical industry (silica dust, microsilica), as well as a variety of products and wastes of petrochemical production [16-19].

The concept of construction industry development is based on significant expansion in the production of concrete mixtures using effective multifunctional admixtures, given that the modification was and remains the most universal, affordable and flexible method of managing the technology of manufacturing concrete and the regulation of its properties. The developments of new modifying admixtures allowing for densifying the gel structure of the concrete matrix at the nanoscale level are of considerable interest.

The idea of using anthropogenic industrial wastes and products as highly efficient and multifunctional additives of complex action has always been and is still essential. Maximum technical effect of such admixtures is manifested individually, and the analysis of the mechanism of complex action should be considered in each particular case [20-23].

3. Research objective and theoretical part
Admixtures are multifunctional component of modern concrete which properties are not limited to, for example, only high strength. Chemical reaction of cement hydration and corrosion of concrete, colloidal-chemical surface phenomena at the interfaces of disperse systems: adsorption, wetting, sedimentation, contraction, adhesion, heat and mass transfer are typical spontaneous processes [24-26].

Modifiers change the speed and completeness of the flow of spontaneous chemical reactions by reducing the excess energy of a highly developed concrete surface without energy supply from outside. Therefore, one of the main tasks of the concrete sciences is the coordination of speeds of spontaneous and planned processes of hardening of cement compositions at the expense of prescription-technological solutions. Such solutions may include: water-reducing, plastification, coherence, air entrainment, acceleration and retardation of setting and hardening. However this is not a complete list of effects of supplements.

In modern practice various chemicals of domestic and foreign production are used [17,19,23,27,28]. The most common are silicone monomeric and polymeric waters, surfactants, and complex admixtures based on superplasticizers. The use of surface-active substances (surfactants) gives an opportunity to save cement which is one of the important ways to solving the general problem of rational and economical use of material resources in construction. Small amounts of surfactants
(tenths and hundredths of a percent by weight of cement) not only plasticize freshly mixed concrete, but hydrophobizate concrete compositions or mortar products.

Surfactants obtained from products of the petrochemical synthesis and substances formed during the refining of oil, are cheap and available. Hence, the analysis of possibility of using by-products from processing oil is of concern. By-products of selective oil refining are represented by extracts containing low-index polycyclic aromatic hydrocarbons and resinacious compounds. Chemical composition of hydrocarbon groups in distillate extract (OFN) is shown in figure 1.

![Figure 1. Chemical composition of hydrocarbon groups in the distillate extract: 1 - wax 6-8 %; 2 - naphthanoic 40-45%; flavor - 45-50%; resins and asphaltenes - 3-5%](image)

Extracts for refineries are commercial products and used as raw materials for the bitumen production, gear oil, form coating grease for concrete goods, concrete plasticizers of rubbers in the rubber-processing and tire industry. This study gives the possibility of expanding the use of distillate extract for oil products reforming, in particular, in construction industry [23].

A product in the form of the organic fraction of oil refining (OFN) considered in this paper is worth exploring for its complex action in the compositions of the concretes as a modifying admixture, and to determine the mechanism of influence of OFN on the processes of cement hydration.

4. Results obtained in experimental studies

OFN contains aromatic hydrocarbons and resin-asphaltene compounds, so the system can be considered as disperse. OFN being a multicomponent mixture is subject to physical aggregation on the surface of cement grains. Intercommunion at the border of the cement grains is due to adsorption forces and is based on the processes related to the surface tension and the wetting. Such hydrophobic-plasticizing effect is manifested while introduction of this admixture because it belongs to the category of surface-active substances (surfactants) which allows to form adsorption monomolecular shells on the surfaces of cement particles, which reduce internal friction in the concrete composition. In addition, there is the effect of peptization of binder - splitting of units encountered in the coagulation of disperse systems, which counteracts the creation of flocculus from cement particles in the process of the mechanism of hydration. The phenomenon of peptization, increasing the specific surface of the cement particles, also has a positive effect on the intensity of the processes of hydration and structure formation of cement stone.

Plasticizing effect of OFN is due to the layered structure of thin oriented films of this surfactant, which are the slide planes formed by the methyl groups. Slide planes are formed of OFN molecules oriented in a certain way that have the ability to come into the easy glide relative to each other, while putting up a strain resistance in all other directions. A silicone fluid GasLiquid-10 is classified as hydrophobic-plasticizing admixture. The mechanism of action of such modifier as GasLiquid-10 in concrete compositions is well known. Therefore, to evaluate the hydrophobic and plasticizing effect of the action of OFN we used silicone fluid GasLiquid-10 as the comparison object [29,30]. Hydrophobic effect of modifiers was assessed by the change in limiting wetting angle and surface tension of the mortar part in relation to the amount of admixtures. Graphical interpretation of the obtained results is shown in figure. 2, figure. 3.
Figure 2. Change in limiting wetting angle in relation to the amount and type of admixture.

Figure 3. Change in surface tension in relation to the amount and type of admixture.

With the increase in the percentage of complex admixture in composition, the limiting wetting angle decreases which is characteristic of surfactant molecules. The result of the action of OFN molecules and GasLiquid-10 is to reduce the surface tension at the interface "liquid - solid". But, at the same time, it is believed that most surfactants reduce the surface tension at the interface "gas - liquid". This circumstance fully explains the low air entrainment in the concrete mixture in the presence of the plasticizer, the molecules of which have a dispersing effect on the particles of the cement binder [31].

Admixtures OFN and GasLiquid-10 adsorbed on the interface, form monomolecular layers that modify the balance of forces in the system of the composite, and reduce the surface energy of the binder which is a necessary condition for the wetting according to Young equation.
Upon contact with hydration products of cement admixtures are settled out in the form of fine droplets on the walls of small pores and capillaries forming a hydrophobic coating. The surface tension at the interface "liquid-air" with increasing OFN concentration in composition of the binder is reduced. Silicone fluid GasLiquid–10, introduced in composition of the binder also reduces its surface tension. Thus, with increasing OFN concentration in composition of the binder there is a decrease in surface tension. So when the concentration of admixtures (0,5%) for GasLiquid-10, the surface tension respectively equal 72,69 mJ/m², for OFN admixture this value is 70,62 mJ/m², which is 3.1% less than the surface tension of the clear mortar; at the same concentration of GasLiquid-10 a reduction of surface tension was 1.4 %. This trend also appears while increasing content of admixtures. The effectiveness of the admixtures depends on the type of water repellent sealer, and its use in each case is justified by feasibility study.

Comparing concepts of the processes of action of OFN and GasLiquid-10 admixtures we can see both similarity and the possibility of development and additions to existing concepts of complex behavior of OFN in cement systems. The complexity of the processes increases with the use of hydrophobic plasticizer multi-component admixtures, such as OFN. Along with common features with GasLiquid-10, admixture OFN has its own specifics and requires an individual approach in the preparation and application for concrete technology [20,23].

5. Conclusions

The directional formation of the structure of new materials, optimization of physicochemical principles of production and design process require general evidence-based approach and detailed study of the regularities of structure formation of disperse systems during their processing and use.

Thus, modification of concrete provides a means of management of individual technological processes with the aim of obtaining the desired nano-structure of a material with defined properties, which greatly improves the quality of building constructions and products, creating compositions for production of reliable and durable building materials.

The application of modified concretes opens up opportunities for builders allowing through the use of various complexes of modifying admixtures getting concretes with a wide range of desired properties. In turn, the use of refinery waste as a hydrophobic plasticizer modifier allows us to extend the range of admixtures of complex action which is important for the production of efficient concrete with improved quality.

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