

THE MECHANISM OF ACTION OF PLASTICIZING ADDITIVES OF VARIOUS MODIFICATIONS ON THE STRENGTH OF CEMENT STONE

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Annotation: The article presents the mechanism of action of plasticizing additives of various modifications of foreign and local production on the strength of cement stone, the technology of introducing into the concrete mixture, as well as the classification of super plasticizers of different nature.

Keywords: Superplasticizer, thinner, formaldehyde, polycarboxylate, neoplasms, adsorption, concrete, mortar mixture, additive, modification, adsorption layer, hydration, crystallization.

Introduction

Superplasticizers and highly plasticizing additives, discovered in the 30s of the last century, have taken a special place in the modification of concrete and mortar mixtures. Being thinners and highly effective plasticizers of concrete and mortar mixtures, they allow, *ceteris paribus*, increasing their mobility several times against the original one, without causing a decrease in the compressive strength of concrete or mortar.

The plasticizing effect is also determined by the change in the water of the solvate shells of the particles of new cement formations. During the adsorption of surfactants on the surface of the solid phase, the amount of water in the solvate shells decreases, while the amount of free water increases. This leads to an improvement in the rheological characteristics of the mixture, but somewhat slows down the processes of structure formation and cement hardening.

Main part

By their nature, superplasticizers are divided into four groups: I - sulfonated melamine-formaldehyde resins, II - condensation products of naphthalenesulfonic acid and formaldehyde, III - modified (purified and practically sugar-free) lignosulfonates, IV - additives based on polycarboxylates and some others (Table 1). Along with domestic additives, the table also includes foreign-made superplasticizers, which are widely represented on the construction market and are successfully used both for concrete and for dry building mixtures.

Table 1. Classification of superplasticizers

Opening year	Group	Type of	Water content reduction , %	Name
1960	I	sulfomelamin formaldehyde MSFDVERTISING	15-30	NIL-10, 10-03, Melment , Konplast , Zikament-FF
1932	II	sulfonaphthalene formaldehyde NSF	15-25	C-3, 40-03, Dophen , Mighty , Cormix , Criso Fluid
1939	III	modified lignosulfonates LS	5-15	LSTM, HDSK-1, Plastiment BV40
1993	IV	polycarboxylate RA	20-30	Melflux 1641F
1997		polycarboxylic ether new RAE	25-40	Zika Viscocrete-20SE
1997		acrylic copolymer StrAU	25-40	Flux 1

Superplasticizers are anionic organic substances of colloidal size with a large number of polar groups in the chain. The effectiveness of superplasticizers depends on the structure, presence and type of functionally active groups, their location in molecules, the length and shape of chains, molecular weight. Additives-thinners, being in a state adsorbed on cement grains and neoplasms, create a “ steric ” repulsion effect. This effect, due to the shapes of the chains and the nature of the charges on the surface of the grains of cement and hydrates, is the reason for the long-term preservation of the viability of concrete and mortar mixtures. Such a mechanical action of superplasticizers increases the mobility of the concrete mixture by 3...4 times.

The action of superplasticizers is limited to 2-3 hours from the moment of their introduction, and after the initial slowdown in the processes of hydration and the formation of a coagulation structure, the acceleration of concrete hardening occurs. This is explained by the fact that the adsorption layer of the additive on the surface of cement grains is permeable to water, and the deflocculating effect of surfactants increases the contact surface of cement and water, which leads to an increase in the number of hydrate formations.

Superplasticizers are introduced into concrete mixtures in the form of aqueous solutions of working or increased concentration based on the content of the additive in the range of 0.7..1.5% of the mass of cement. At the same time, the dose of superplasticizer should be higher for high-aluminate cements. The intensity of the decrease in the mobility of the concrete mixture over time also depends on the aluminosity of the cement.

Superplasticizers are mainly synthetic polymeric substances, therefore they are very expensive, and their use in concrete and mortar mixtures must be technically and economically justified. But despite the increased cost, concretes modified with such surfactants are effective, since cement savings in them can reach 50 kg/m³ or more. In addition, the use of superplasticizers makes it possible to use cast concrete mixtures, which leads to a reduction in labor costs and an improvement in working conditions in production.

Medium plasticizing additives are substances of the hydrophilic type, which include such widely used organic products as lignosulfonates, some ethers and other substances, each molecule of which

contains a significant number of functional groups of different polarity, interspersed with non-polar radicals.

When adsorbed on cement particles, not all polar groups of such surfactants are turned towards the solid phase, some of the least "philic" of them, like non-polar organic radicals, are turned outward. Such an adsorption coating primarily affects the initial phase—cement grains. Although the film itself can be mono- or bimolecular (depending on the dosage of the plasticizer), but due to long-range van der Waals forces, it retains a fairly thick layer of water near it. For this reason, a hydrodynamic lubricant is created between the solid particles, which reduce the coefficient of internal friction. At the same time, due to physical adsorption at the mouths of microcracks and microcracks of the clinker part of the cement, the roughness of the grain microrelief is smoothed out, which also contributes to the plasticization of the concrete mixture.

A very important feature of hydrophilic surfactants is their peptizing (dispersing) action. Peptization consists in the separation of aggregates into primary particles under the influence of the expanding action of the active surface of cement particles in the process of hydration and hydrolysis, which in turn accelerates the interaction of cement with water and reduces the amount of unreacted clinker material.

The modifying action of surfactants leads to a slowdown in the growth of crystalline nuclei of neoplasms as a result of the formation of adsorption layers on their surface. The slowdown in the growth of individual nuclei causes an increase in their total number, i.e., the dispersion of crystalline products of cement hydrolysis and hydration increases significantly, which can have a positive effect on the density of the emerging structure, the deformability of the cement stone and the ultimate tensile strength of concrete.

When adsorbed Surfactants on the centers of crystallization of aluminum -containing phases are stabilized, which consists in a decrease in the growth rate and the accumulation of a large number of tiny particles of neoplasms (often X-ray amorphous or poorly crystallized), i.e., the dispersion of the resulting hardening structures increases with the introduction of increased concentrations of surfactants. This applies both to the size of the solid phase and to the average effective diameter of pores and capillaries.

Thus, surfactant additives, introduced in small amounts - 0.2 ... 0.25%, slow down the processes of hydration and hardening of cement, primarily due to screening of its grains by adsorption layers.

It should be taken into account that at high dosages of additives, the viscosity of the medium increases, as well as the adsorption of surfactants on hydrates neoplasms, leading to a significant slowdown in the hardening of concrete. With an overdose of hydrophilizing Surfactants may involve air bubbles in the concrete mixture, but they are isolated and easily removed from the mixture during mixing.

Studies have shown that the effect of plasticizing additives is different for individual cement clinker minerals. When introducing additives, one should take into account their compatibility with cements (due to the content of C_3A and gypsum in them), mineral dispersed components and between additives when they are combined. Plasticizers of hydrophilizing action (type L C T) are adsorbed according to the scheme: $C_3A > C_4AF > C_3S > C_2S$, therefore, their use is most effective in "fat" concrete mixtures on high-aluminate cement.

The mechanism of action of weakly plasticizing **additives** (plasticizing-air-entraining), which are substances of a hydrophobic type, is to involve the smallest air bubbles in the concrete mixture and the formation of thin (monomolecular) hydrophobic films on the surface of cement grains. Such an action of additives sharply reduces the wetting of cement grains with water, which leads to a slowdown in the reactions of hydration and hydrolysis of clinker minerals and, consequently, to the preservation of the initial viscosity of the binder dough for some time.

The amount of entrained air can reach ~ 5% of the volume of the mixture. As a result, the volume of cement paste, which plays the role of lubrication of the solid components of the mixture, increases, and the effect of plasticization is achieved. This indicates that the use of hydrophobic type plasticizers is most effective in "lean" blends.

In the process of mixing the concrete mixture, the films of surfactant molecules adsorbed on the cement grains are mechanically torn off, which ensures the interaction of water with cement and does not disturb the course of hydration processes. Weakly plasticizing additives, as well as hydrophilizing additives, prolong the period of the initial stage of structure formation, slow down the growth of the plastic strength of concrete over time.

A system of evenly distributed pores with a hydrophobized surface in hardened concrete reduces the capillary suction of moisture and, thereby, reduces the permeability of concrete. In the process of freezing, the formed pores are similar to contraction act as dampers: reduce stresses and deformations, providing increased frost resistance of the material. Therefore, the main economic effect of the use of weakly plasticizing additives, in addition to reducing the water demand of concrete mixtures and reducing cement consumption, is to increase the durability of reinforced concrete structures .

It should be taken into account that hydrophobizing additives (such as GKZH-10, GKZH-11), in contrast to hydrophilic ones, are well adsorbed on silicate cement minerals according to the scheme: $C_3S > C_2S > C_4AF$ and are practically not adsorbed on C_3S . Therefore, slightly plasticizing additives are more effective when using low-aluminate cements with a high content of calcium silicates.

Main problems in the application of traditional superplasticizers MSD and NSF , which manufacturers have encountered in practice, are associated with the dependence of their effectiveness on the type and quality of cement, the rapid loss of mobility by the concrete mix and its insufficient resistance to delamination, high sensitivity to overdose, as well as certain limitations in the compatibility of these products with other additives. The solution of these problems is very important for the further development of technology.

The mechanism of action of a new class of additives - polycarboxylates is due not to electrostatic repulsion, but to a strong steric hindrance of the interaction of hydrated cement particles due to bulky side chains of polymer molecules adsorbed on them. This contributes to the long-term preservation of the viability of concrete mixtures [3,4,6,7,8,9].

These supplements are referred to as "new generation supplements". In the synthesis of such products, a unique opportunity arises for directed control of the properties of modifier additives.

The possibilities of modifying polycarboxylane are practically unlimited. When creating highly effective water- soluble carbon -chain superplasticizers , the molecular design was based on such a chemical modification of carboxyl-containing polymers that made it possible to introduce long side oligoalkylene oxide chains into these macromolecules through the formation of the corresponding ester or amide groups.

Intensive research in the field of chemistry and technology of polycarboxylate superplasticizers , as well as their use in concrete, are carried out by many foreign companies, such as: BASF (Germany), Kao soap Co. and Takemoto Oil & Fat Co. (Japan), Grace (USA), Mapei S. _ p . A. (Italy) and a number of other countries [1]. The disadvantage of these additives is their too high cost. The use of these additives in the production of reinforced concrete structures must be justified by a technical and economic calculation [2].

In recent years, the development of new formulations of complex concrete modifiers has also been very actively carried out in our country. The superplasticizer obtained on the basis of polycarboxylate ether has already gained wide popularity, i.e. superplasticizer POLIMIX. It represents a wide range of

additives based on polycarboxylates , i.e. belong to the 4th group (RA) [2].

In the technology of non- heating and low- heating concretes, SP should not only extremely thin concrete mixes, but also simultaneously serve as an accelerator of the process of initial and subsequent hardening [5].

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