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J.A. Turgaev

Karakalpak State University named after Berdakh
t.f.f.d. (PhD), docent

Z.M. Niyazova

Karakalpak State University named after Berdakh
magistrant

A.S. Mambetaliev

Karakalpak State University named after Berdakh
magistrant

EFFECT OF HYDROPHOBIC ADMIXTURE ON CEMENT STONE STRUCTURE

Abstract: In the article the results of studies on the effect of various additives on cement paste were presented, optimization was carried out, optimal values of additives were found and technological processes were developed to obtain a modified hydrophobizer. According to the results of the research, it was found that the received mineral filler hydrophobizer molecules actively influence the adsorption processes and are reflected in the spatial composition of this cement stone. In this case, the level of their effect on the cement binder is correlated to the proposed indicator of the hydration activity of fillers P_{pga} , which confirms the feasibility of using this criterion in evaluating the adsorption activity of the hydrophobizing additive.

Key words: cement, microsilica, polycarboxylate, super plasticizer, water repellent, cement stone, modifying water repellent, concrete, technological scheme.

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Introduction

The waterproofing additive for concrete gives the final product water-repellent and waterproof properties, which extends the life of the entire structure. Additives of this type make concrete stronger, reduce porosity, protect reinforcement and steel elements in contact with the structure from corrosion.

From the physico-chemical point of view, the cement paste to which water has been added should be considered as a concentrated suspension. One of its most important technical characteristics is the persistence of staying in a plastic state, which is determined by the sticking times of normal dry cement paste.

However, the standard definition of cement paste adhesion time is largely dependent on conditions and does not provide an idea of the rate of reduction of the mobility of the paste. The method of determining the plastic strength with a conical plastometer was used to study the structure formation process of the cement paste with silicon-organic compound additives from the time of adding water to cement stone.

The initial kinetics of cement paste structure formation largely depends on the mixing time, which we assumed to be constant (5 minutes).

During the interaction of cement with water, the processes of coagulation and crystallization structure formation take place in parallel at the same time. However, it can be seen from the analysis of the curves obtained regarding the kinetics of the increase

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in plastic strength of cement paste with different amounts of methylsiliconate additive that the processes leading to the formation of a coagulation structure in the cement paste during the first hours of water addition consist of a relatively coarse dispersed suspension. The degree of plastic strength is very low at this stage. The higher the concentration of the methylsiliconate additive, the more it prolongs the induction period of the coagulation structure.

However, in the process of hydration and subsequent development of pentization, cement grains are adsorbed and do not affect the ongoing processes. As a result, there is a moment in which the entire plasticizer binds, and it is insufficient to stabilize the resulting particles. This moment corresponds to a sharp increase in structural strength, that is, cement adhesion. The higher the concentration of the plasticizer in the system, the later this increase in strength occurs and the formation of the crystallization structure is explained by the priority of this stage.

Crystallization structures occur during the formation of a new phase or when many small crystals

of new hydrate derivatives and a dense crystal growth are added and merged from a supersaturated mixture.

A completely different picture is observed when the addition of sodium ethylsilicopate is added to the cement paste. In this case, with an increase in the amount of additives the induction period is lengthened only up to a certain level (0.5% in our experiments), after which increasing the amount of additives leads to a rapid increase in plastic strength. After 2% addition of cement by weight the system can be seen to be fully set after one hour. This very interesting phenomenon is explained by the priority of the pentization effect in large doses of the additive, which is expressed in the increase in the strength of the coagulation structure which helps to create a fast-hardening system. The results of studies on the kinetics of structure formation, obtained using a cone plastometer are fully consistent with the data on the determination of the start and end periods of adhesion obtained by the standard method (table 1).

Table 1. Effect of organic silica hydrophobic fluid additives on cement paste normal density and setting times.

Portland cement produced in factories	Methylsiliconate				Ethylsiliconate			
	The amount of additives is % cement by weight	Normal density %	Adhesion time s-min		Additive amount % by weight of cement	Normal density %	Adhesion time s-min	
			start	ending			start	ending
Karakalpak	-	25,5	2-25	4-00	-	25,5	2-25	4-00
	0,05	25,5	5-07	10-06	0,05	25,25	2-35	10-14
	0,1	25,5	5-12	10-21	0,1	24,5	1-21	12-02
	0,5	25,65	6-46	12-12	0,3	23,5	0-33	10-25
	0,6	25,75	6-52	12-16	0,5	23,2	0-21	7-55
					1	22,7	0-48	6-36
Titanium	-	22,75	2-00	4-20	-	22,75	2-00	4-20
	0,01	22,5	5-43	8-46	0,03	22,75	3-47	6-38
	0,03	22,5	6-19	12-04	0,07	22,75	2-21	10-10
	0,07	22,5	6-15	13-20	0,1	22,75	0-46	11-25
	0,1	22,5	6-05	13-05	0,15	22	0-24	11-26
	0,15	22,35	7-06	13-21	0,2	21,8	0-23	11-10
	0,2	22,35	7-05	14-51	0,3	20,75	0-10	8-48
	0,3	22,25	8-04	15-04	-	-	-	-

It is known from Table 1 that when ethylsiliconate additives are added in the amount of 0,3% of the cement weight and more (in all studied batches), it was found that the beginning and end of the adhesion process of cement paste is much faster.

Adding smaller amounts of additives will slightly speed up the onset of adhesion and slow down the end by about half.

The amount of active hydrogen in polyhydrosiloxane emulsions has a significant effect on the structure formation process of cement paste.

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They are similar to each other in terms of their structure and character and consist of four distinct periods. In the initial period is characterized by a small heat release it is not observed as soon as water is added, because the cement particles are covered with gel-like products of hydration and the hydration process slow down dramatically. With the addition of active hydrogen the induction period is significantly extended. This conclusion is consistent with the data obtained using a conical plastomer.

The third period of hydration of cement paste is distinguished by the release of a large amount of heat and the maximum temperature of the cement paste. It is at this time that gel-like products of hydration accumulate, they turn into new crystalline products and begin to recrystallize. As the amount of active hydrogen in the additive increases the temperature of the cement paste begins to decrease. In the curves the maximum falls and shifts to the right, which indicates the slowing down of the hydration and structure formation processes.

By the fourth period, the amount of released heat decreases. Temperature curves decrease evenly and approach the horizontal axis. It is possible to think about the structure formation process of cement stone depending on the character of the heat release curves and change in strength.

According to the temperature curves the change of heat release rates and curves of the cement paste with the same additives were constructed. These curves clearly demonstrate that the hydration process of cement has a step-like appearance, which is also confirmed by the data provided by A.E.Sheikin [10]. As the amount of active hydrogen in the admixture increases the maximum of the heat release rate in the curves also change as the temperature curves decrease and shift to the right as the cement paste hydrates and forms a structure without the admixture.

This organosilicon additives slow down the hydration process (the curve in the graph pays off). This is explained on the one hand by the presence of free hydrogen in the cement paste, which surrounds cement particles and prevents their hydration and on the other hand, by the accumulation of derivatives of the interaction of additives with cement constituents in the system. In this case, the type of radical in the Si-C bond also has a certain effect.

Accordingly, there is a need to modify the silicon-organic hydrophobizer.

Previous studies have allowed us to assume that it is possible to find a solution to these problems related to the extension of the service life of concrete structures using silicon-organic hydrophobizers [7- 9]. However, the shortcomings identified in connection

with the use of this hydrophobizer indicate the need to continue these studies. According to the research results it was found that the use of the additive has a negative effect not only on the early formation of the structure, but also on the subsequent hardening process of cements. However, the difference in the strength of the samples decreases slightly of the 28th day of cement hardening, but it still remains significant. In this regard, it can be said that finding a solution to this problem is of both scientific and practical importance.

In order to eliminate the negative effect of hydrophobizing additives in the initial stages of solidification it is suggested to carry out their initial adsorption on a finely dispersed carrier [4-6]. The main problem with slow band times and low initial strength is that the hydrophobizer molecules are adsorbed on the cement grains, preventing their further hydration. It is assumed that initial adsorption of molecules on the carrier allows coordination of adhesion periods due to the fact that the desorption process of hydrophobizing molecules on the surface of the carrier occurs later.

According to scientific work [2, 6], the adsorption of molecules of silicon-organic hydrophobizer with mineral filler takes place according to the mechanism of acid-base interaction. In this case, the greater the number of active centers, the higher the adsorption capacity of the selected carrier.

[1-3] the criterion of "indicated hydration activity index" proposed by the authors of the work allows to more accurately determine the progress of mineral interactions and transformation processes, as well as the contribution of hydrophobizer molecules to the adsorption capacity of these carriers.

The proposed indicator is denoted by the symbol-Prga and is found according to the following formula:

$$P_{\text{pga}} = R_{\text{kv}} + R_{\text{kl}} + 0.33P_{\text{ol}} - 0.1P_{\text{ob}}, \text{ in this } (1)$$

$R_{\text{kv}}, R_{\text{kl}}, P_{\text{ol}}, P_{\text{ob}} - \text{bu } 0 < rKa < 7; rKa > 13, 0; -4 < rKa < 0; 7 < rKa < 13, 0$ the number of adsorption center on the spheres respectively at 10^{-3} mg-eq/g.

This criterion, which describes the acid-base properties of the surface of mineral fillers, allows to scientifically classify mineral fillers according to the degree of their influence on cement system and adsorption capabilities. In general it is proposed to classify mineral fillers according to the indicator of hydration activity based on- P_{pga} (Table 2).

Table 2 presents the calculation of this criterion, that is, the indicated indicator of hydration activity, for mineral fillers selected for the purpose of research.

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Table 2. Classification of mineral fillers according to the indicated indicator of hydration activity P_{pga} .

No o/n	Type of mineral filler	P_{pga} criterion values	Potential efficiency in cement systems, cement savings, in %
1.	Less active	From 0 < to <10	up to 10%
2.	Moderately active	From 10 < to <25	10-20%
3.	Strong active	From 25 < to <50	20-30%
4.	Super active	More than >50	up to 50%

The comparative analysis of mineral fillers according to the P_{pga} criterion allows to predict their effective adsorption capacity, which makes it possible to scientifically select an adsorbent for hydrophobizing molecules.

In order to test the previously proposed theory, we chose a micro silica filler. The experiment is carried out by soaking mineral fillers in water-

repellent liquid (at 25% concentration) for 24 hours. After that it is dried to a constant mass at a temperature of 60-80°C and crushed. The modified filler was placed in the ratio of 0,01-0,1% of the binder mass, and after mixing, water was added to it. A technological scheme for obtaining a modified hydrophobizer was developed (Fig.1)

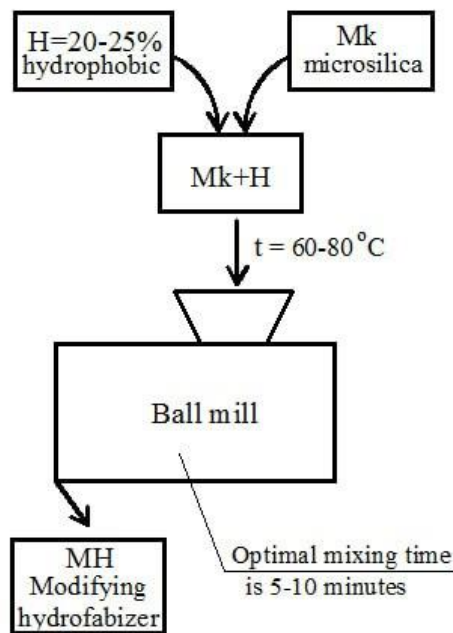


Figure 1. A technological scheme for obtaining a modified hydrophobizer.

The results of the kinetics of increasing the plastic strength of the modified cement binder are presented in Figure 2,3.

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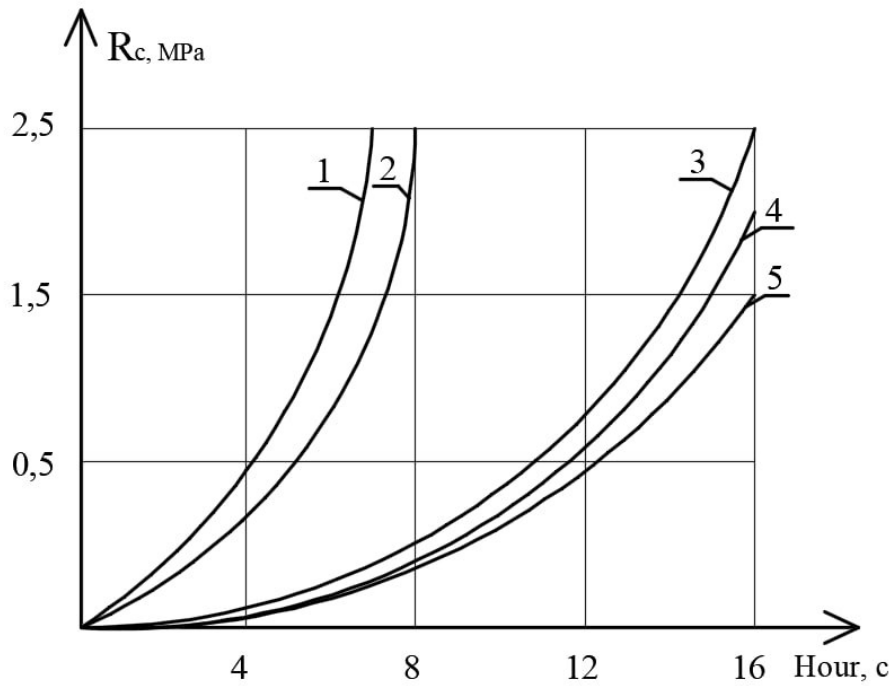


Figure 2. 1- PS M400 (Karakalpak), 2- PS M400 (Titanium), 3- S (Q) +H 0,01%, 4- S (Q)+H 0,05%, 5- S (Q)+H 0,1%.

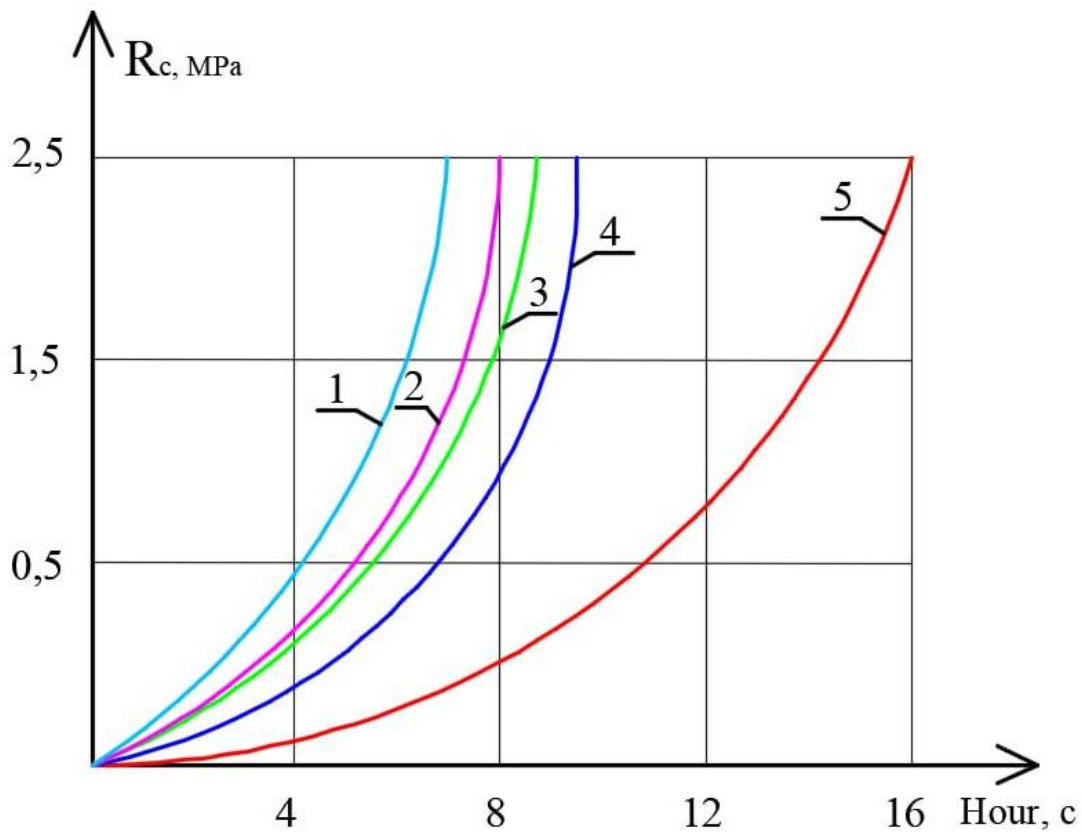


Figure 3. 1- PS M400 (Karakalpak), 2- PS M400 (Titanium), 3- S (Q) +MH 0,01%, 4- S (Q)+MH 0,05%, 5- S (Q)+MH 0,1%.

According to the results of the research, it was found that the hydrophobizing molecules of the received mineral filler have an active effect on the adsorption processes and are reflected in the phase

structure of this cement stone. In this case, the level of their effect on the cement binder is correlated to the proposed index of the given hydration activity of fillers Ppga, which confirms the feasibility of using

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this criterion in evaluating the adsorption activity of the hydrophobizing additive.

It was found that the optimal amount of modified hydrophobizer is about 0,05% of the cement mass.

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