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EFFECT OF ORGANIC AND FINE DISPERSER ADDITIONS ON RHEOLOGICAL PROPERTIES OF MINERAL SUSPENSIONS

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In this study, the effect of mineral and organic additives on the properties of mineral suspensions was studied. Disperse mineral additives are used in cement systems to increase the amount of rheological matrix and ensure high fluidity. Due to the high dispersion of mineral additives, high-efficiency plasticizers were used to regulate the rheotechnological properties of cement-based mixtures. The effect of sulfonaphthalene-formaldehyde oligomer and polycarboxylate-based hyperplasticizers on the rheological properties of cement systems as a plasticizer was evaluated according to the methodology proposed by prof. V.I.Kalashnikov. Based on the results obtained, it was determined that limestone powder is more effective than other stone powders. As a result of the research, the optimal amounts of mineral additives and plasticizers were determined and the possibility of obtaining efficient, high-strength cement stone on their basis confirmed.

Keywords: *mineral additive, cement suspension, stone powder, hyperplasticizers, rheological matrix, dispersion aggregate*
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Introduction

Recently, extensive research has been conducted on the acquisition and application of new mineral and organic modifiers that regulate the rheology of cement systems and improve their properties [1-3]. It is known that the amount of rheological matrix in self-leveling concrete mixes must be sufficient to ensure the free movement of large and small aggregates in the mix. To increase the volume of the rheological matrix, the amount of finely dispersed components such as cement or rock powder in the mixture should be increased [4, 5]. However, the addition of disped additives worsens the rheological properties of cement systems. Therefore, high-efficiency plasticizers are used to regulate the rheotechnological properties of cement systems, taking into account the high dispersion of mineral additives used in the preparation of various types of mortars and concrete mixtures. The most effective of these plasticizers are hyperplasticizers based on polycarboxylates [6-10].

Materials and research methods

In the present study, powders obtained from the grinding of mineral rocks in a laboratory ball mill were used as a disperse additive. The following mountain rocks are used as local raw materials for the purchase of fine dispersed powders:

- limestone of Garadagh deposit
- marble of Dashkesan deposit
- a granite of Zurnabad bed of Khanlar region.

In the research, Glenium SKY 500, Glenium 313 hyperplasticizers and Rheobuild 878 superplasticizer derived from BASF were used as a plasticizer addition. Hyperplasticizer Glenium SKY 500 is aqueous solutions with different degrees of polymerization based on Glenium 313 polycarboxylate esters. Superplasticizer Rheobuild 878 naphthalene is an anionic surface-active agent consisting of a mixture of oligomer and polymer compounds obtained due to the condensation of sulfonate with formaldehyde.

The CERM I - 52,5N Portland cement of the Holcim cement plant, such as cement, was used.

Rheological characteristics were evaluated by the V. Kalashnikov method [11]. According to this method, the modified Suttard viscosimeter was used. The viscosimeter is a stainless steel cylinder with an internal diameter of 25 mm and a height of 50 mm. The change in water demand and fluidity is estimated by the spread of water-mineral mixture in the gravitational flow of the dough. In this case, the flow rate is calculated by the following formula:

$$\tau_0 = hd^2r/ kD^2$$

Where t_0 is the flow rate of the paste, Pa; h and d height and diameter of the viscometer, m; ρ - density of dough, kg / m^3; k - coefficient that takes into account the distribution of stresses in the viscoplastic mass and is taken equal to 2; D- dough diameter, m.

The method includes the following steps: under 180 x 180 mm size glass, the circular scales are placed on paper; then the cylinder and the glass are moistened. A sample of material is taken, completely filling the cylinder. Upon completion, the cylinder is removed and the diameter of the dough is measured. The density of the dough taken from each measurement is indicated. According to the results of measurements, the plastic effect is determined, in particular by water reducing index characterizing the reduction of water consumption in the isoreological system:

$$W_{red} = (Water/Solid)n/(Water/Solid)pl$$

Where (Water/Solid) n and (Water/Solid) pl - is a water/solid ratio of normal and plasticized paste.

On the basis of cement paste, 5 cm cube samples were kept in normal conditions.

Results and discussion

At the initial stage of the research, reotechnological properties and sedimentation effects of mineral suspensions (cement, limestone, marble and granite powder) were studied (Table 1). Three different plasticizers were used in the research. The results show that plasticizers reduce the water / solid ratio from 0.5 to 0.32 in suspension, from 0.44 to 0.11 in marble suspension, from 0.4 to 0.26 in granite and from 0.42 to 0.12 in limestone.

The results obtained show that the used plastifiers indicate the ratio of water/solids content of 0.5 to cement suspension is 0.32, water/solids ratio is 0.44 in marble suspension, 0.4 in granite and 0.42 in limestone 0.11, 0.26 and 0.12 respectively. The water reducing effect of hyperplastifers is 1.56 in cement suspension, 1.54 in granite, 3.5-4 in marble and lime stone.

Table 1. Impact of mineral suspensions on water / solids ratio of plasticizers

№	Materials	SP type	Water/sol	Spread, D,sm	Water reducing index
1	2	3	4	5	6
1	Cement	-	0.5	9	
		Glenium SKY500	0.32	9	1.56
		Glenium 313	0.34	9	1.47
		Rheobuild 878	0.38	8.8	1.32
2	Marble	-	0.44	9	
		Glenium SKY500	0.11	9	4
		Glenium 313	0.14	9	3.14
		Rheobuild 878	0.19	9.2	2.31
3	Granite	-	0.4	9	
		Glenium SKY500	0.26	9	1.54
		Glenium 313	0.26	9	1.54

		Rheobuild 878	0.3	9.1	1.33
4	Limestone	-	0.42	9	
		Glenium SKY500	0.12	9	3.5
		Glenium 313	0.14	9	3.0
		Rheobuild 878	0.19	9.2	2.2

Results of studies into the effect of plastifiers on the dissolution and flow of mineral suspensions (Table 2) show that the use of 1% of additives significantly increases the diffusion diameter of the mixture in all constituents and decreases the flow rate accordingly.

Table 2. Impact of plastifiers (1%) on the spread of mineral suspensions

№	Materials	SP type	Water/sol	Spread, D, sm	τ, Pa
1	2	3	4	5	6
1	Cement	-	0.5	9	34.60
		Glenium SKY500	0.5	17	9.70
		Glenium 313	0.5	17	9.70
		Rheobuild 878	0.5	13	16.90
2	Marble	-	0.4	9	33.00
		Glenium SKY500	0.4	20	7.20
		Glenium 313	0.4	19	7.93
		Rheobuild 878	0.4	16.5	12.50
3	Granite	-	0.4	9	35.40
		Glenium SKY500	0.4	17.5	9.90
		Glenium 313	0.4	15	12.20
		Rheobuild 878	0.4	14	14.00
4	Limestone	-	0.42	9	30.20
		Glenium SKY500	0.42	21.7	6.08
		Glenium 313	0.42	19.7	7.22
		Rheobuild 878	0.42	18	10.70

The maximum flow rate characterizing the diffusion of gravitational flow at the lime suspension is observed during the use of the Glenium SKY500 plasticizer (6.08 Pa). Under the influence of the hyperplasticizer, mineral suspensions behave like Newtonian fluids and flow like water.

At the next stage of the research, the effects of mineral supplements (limestone, marble and granite powder) on rheotechnological properties of cement suspensions, first of all, on the flow rate were studied with both plastifers and without plasticizers (Fig. 1-3). It can be seen from the curves that with an increase in the amount of mineral additives, the flow limit decreases, and the solution dissipates well. When using plasticizers as compared with pure cement, the flow rate of mineral additives decreases to 26-37%. As the particles of the finely dispersed filler are positively charged as cement, the electrostatic and steric effecting mechanisms contribute to the adsorption of the plasticizer, with the flow of binary mineral suspensions decreased to the minimum. In this case, binary mineral suspensions begin to flow like new tonic fluids, not as fluid-structured liquid.

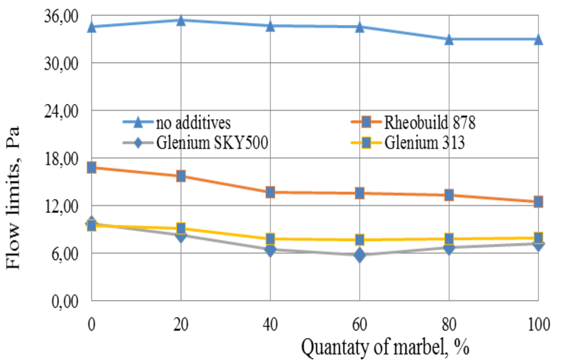


Figure 1. The effect of plasticizers on the flow rate of cement-marble solution on the amount of marble

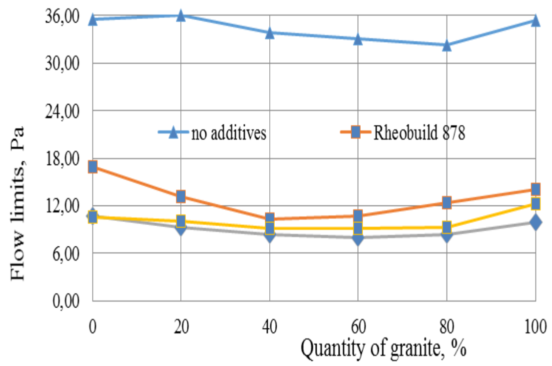


Figure 2. The effect of plasticizers on the flow rate of the cement-granite solution on the granite content

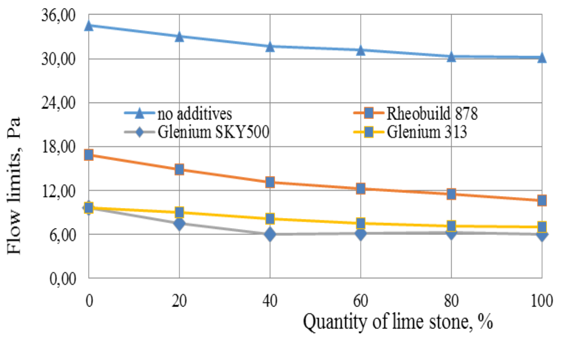


Figure 3. The effect of plasticizers on the flow rate of cement-limestone solution on the amount of limestone

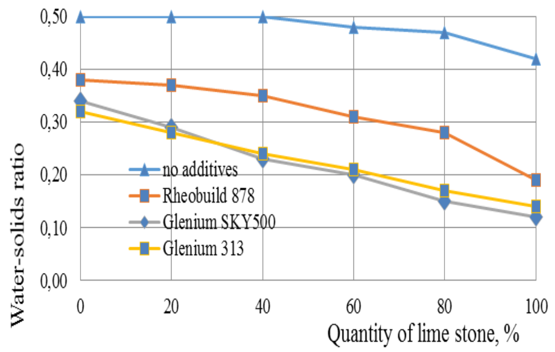


Figure 4. Dependence of the effect of the cement-limestone solution on the water-solids ratio of the plasticizers to the amount of limestone

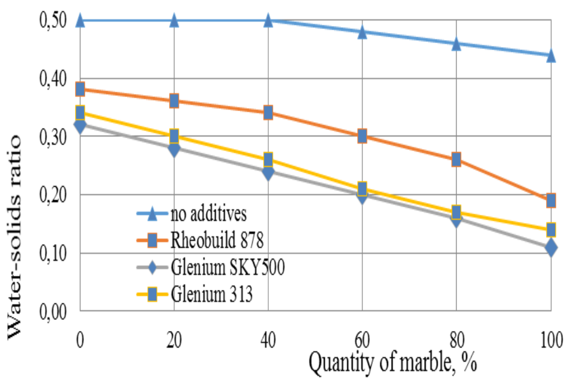


Figure 5. Dependence of cement-marble mortar on the solids content of the plasticizers depends on the amount of marble

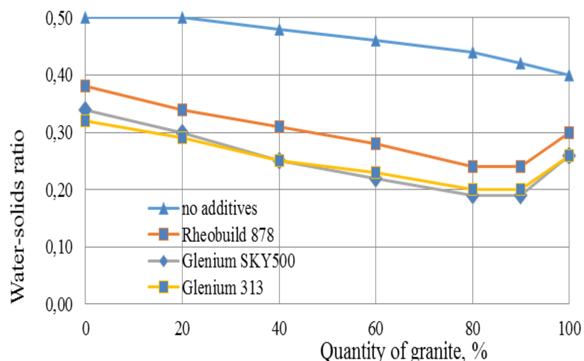


Figure 6. Dependence of the effect of the cement-granite solution on the solid substance ratio of the plasticizers to the amount of granite

The influence of plasticizers on water/solid matter ratio was studied in the research process depending on the quantity of mineral supplements. The results show that the ratio of water/solids in respect to cement decreases in cement-limestone (Fig. 4) and cement-marble (Fig. 5), in proportion to the increase in mineral supplements.

In cement-granite suspension (Fig. 6), the results are somewhat different. The ratio of water / solid to a substance is reduced by 80%, and then begins to increase. None of the selected plastids after this range affect the spread of cement-granulose suspension.

This can be explained by the weak absorption of the superplasticizer in the aqueous suspensions into the surface of granite particles which is due with their negative charge.

It is enough to add a small amount of cement (up to 5-10% of the mineral component) to mineral suspension to re-fill the granite particles and enhance the plasticizer effect of superplasticizers and hyperplasticizers.

It looks like that curves fitted to the values of the effectiveness of cement-limestone and cement-marble binary systems are closely related to each other. This is explained as being due to the fact that both of these marble and lime stones are composed of $CaCO_3$ and its effect is similar when used with cement and plasticizer. Therefore, when choosing a dispersed filler for cement-mineral powder systems, it is advisable to give preference not to marble, the resources of which are limited in Azerbaijan, but to limestone, which has rather large deposits on the Absheron Peninsula. Thus, the use of limestone beds for the acquisition of rheological-active stone powder is more promising together with subsequent phases of research being carried out with cement-limestone systems.

An important criterion for the selection of powders is the compatibility of cement with chemical and mineral supplements.

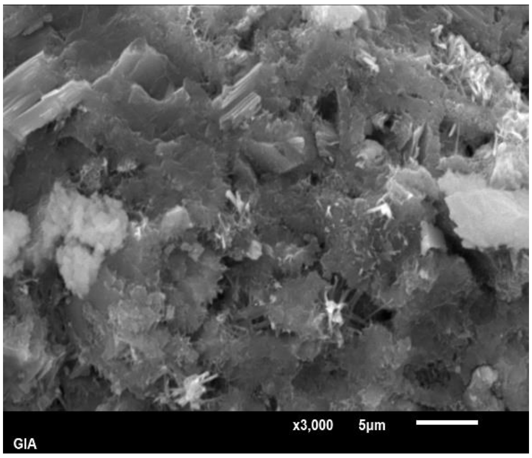
It should be noted that the study into self-settling mixtures was carried out with the application of stone powder based on dense limestone. The cost of concrete was significantly lower due to the use of limestone powder as a finely dispersed additive in the preparation of these mixtures. In this study, Glenium SKY 500 was used as a hyperplasticizer and Garadagh limestone was used as a carbonate powder as a dispersed mineral additive to increase the viscosity of the cement mortar (Table 3).

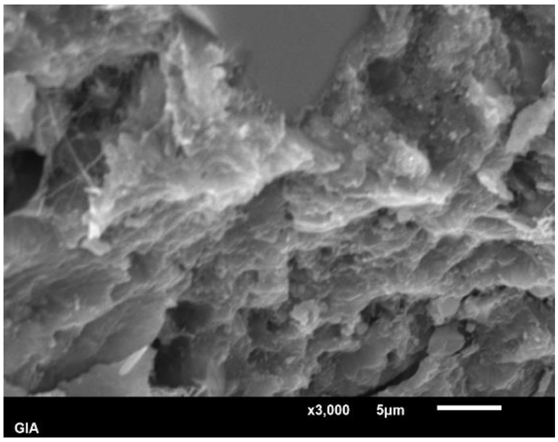
Table 3. Effects of lime powder on properties of the cement mortar

N	Composition of cement mix, kg / m^3				slump, sm	Compressive strength, MPa (day)	
	cement	carbonate powder	Glenium SKY500	Water		7	28
1	440	44	6.78	140	14	53.5	71.23
2	440	88	8.45	140	14	55.41	73.56
3	440	132	9.15	142	14	60.56	81.30
4	440	176	9.86	142	14	58.67	79.02

When applying lime stone powder, the effectiveness of the cement mix increases. Its particles are distributed between cement particles to form a three-dimensional spatial carcass with larger particles. This carcass consists of chains and aggregates caused by numerous coagulant connections. As a result of an increase in viscosity, plastic strength, cohesion and thixotropy from the mixture, the segregation process in the mixture is eliminated, and the system becomes self-settling without stratification. Studies have shown that without the addition of limestone powder, the spread of the cone increases to 14 cm, as a result of which a sharp separation of the cement mortar occurs and the mixture cannot be molded in its previous state.

The compressive strength of the cement stone obtained by using limestone powder is in the range of 71.23-81.30 MPa. When the amount of lime powder rises from 10% to 40%, the cement density based on the same fluidized cement solution increases by 10MPa. The microstructure of the samples without additives and with the addition of 30% limestone powder was analyzed under an electron microscope after 28 days of curing under normal conditions. (Fig. 7).





a) **b)**

Fig. 7. Microstructure of cement stone (3, 000 times increase)
a- cement stone without additive; b- cement stone with limestone powder.

As can be seen, the structure of the cement stone without an additive is not homogeneous (Fig.7a). Its structure is grouped as portlandite crystals and described as a weak crystallization layer with high content of calcium hydrocrystals. When limestone powder is added to fine particles, a homogeneous structure of the cement stone is formed (Fig. 7b). Thin crystals of portlandite are observed in closed pores only, crystallization of which occurs after the formation of the basic structure of cement.

Results

1. The surveys found that the rheological activity of the stone powders used are close to the rheological activity of cement while the flow rate of the cement suspension when using the Glenium SKY500 plasticizer is 9.7 Pa and 6.08 Pa in the lime suspension.
2. When we used 10-40% limestone powder as rheological active additive, the strength of cement stone was 71.23-81.30 MPa.
3. Following the results of electron microscopic analysis, an increase in strength with the addition of limestone powder occurs due to the formation of a dense, homogeneous structure of a cement stone due to finely dispersed particles.

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ÜZVİ VƏ NARINDİSPERS ƏLAVƏLƏRİN MİNERAL SUSPENZİYALARIN REOLOJİ XASSƏLƏRİNƏ TƏSİRİ

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Hazırkı işdə mineral və üzvi əlavələrin mineral suspenziyalarının xüsusiyyətlərinə təsiri öyrənilmişdir. Reoloji matrisanın miqdarını artırmaq və yüksək axıcılığı təmin etmək üçün sement sistemlərində dispers mineral əlavələrdən istifadə edilmişdir. Mineral əlavələrin yüksək dispersliyini nəzərə alaraq sement əsaslı qarışıqların reotexnoloji xüsusiyyətlərini nizamlamaq üçün yüksək səmərəli plastifikatorlardan istifadə olunmuşdur. Plastikləşdirici əlavə kimi sulfonaftalin-formaldehid oliqomerinin və polikarboksilat əsasında olan hiperplastifikatorların sement sistemlərinin reoloji xassələrinə təsiri Prof. V.İ.Kalaşnikov tərəfindən təklif edilmiş metodika üzrə qiymətləndirilmişdir. Alınmış nəticələr əsasında digər daş tozları ilə müqayisədə əhəng daşı tozunun daha səmərəli olduğu müəyyən edilmişdir. Aparılmış tədqiqatlar nəticəsində mineral əlavələrin və plastifikatorların optimal miqdarları müəyyənləşdirilmiş və onlar əsasında səmərəli, yüksək mohkəmlikli sement daşının alınmasının mümkünlüyü təsdiq edilmişdir.

Açar sözlər: *mineral əlavə, sement suspenziyası, daş tozu, hiperplastifikatorlar, reoloji matrisa, dispers doldurucu*

ВЛИЯНИЕ ОРГАНИЧЕСКИХ И ТОНКОДИСПЕРСНЫХ ДОБАВОК НА РЕОЛОГИЧЕСКИЕ СВОЙСТВА МИНЕРАЛЬНЫХ СУСПЕНЗИЙ

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В работе изучено влияние минеральных и органических добавок на свойства минеральных суспензий. Дисперсные минеральные добавки используются в цементных системах для увеличения количества реологической матрицы и обеспечения высокой текучести. Из-за высокой дисперсности минеральных добавок для регулирования реотехнологических свойств смесей на основе цемента использовались высокоэффективные пластификаторы. Влияние сульфонафталинформальдегидного олигомера и гиперпластификаторов на основе поликарбоксилатов на реологические свойства цементных систем в качестве пластификатора оценивалось по методике, предложенной проф. V.I.Калашниковым. На основании полученных результатов было определено, что порошок известняка более эффективен, чем другие каменные порошки. В результате исследований определены оптимальные количества минеральных добавок и пластификаторов и подтверждена возможность получения на их основе эффективного высокопрочного цементного камня.

***Ключевые слова**: минеральная добавка, цементная суспензия, каменный порошок, гиперпластификаторы, реологическая матрица, дисперсный заполнитель.*